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(54) **Plating bath composition for immersion plating of gold**

Plattierungsbadzusammensetzung für die Tauchplattierung von Gold

Composition de bain de placage pour dépôt par immersion de l'or

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**EP-A2- 1 201 789 JP-A- 2000 192 248**  
**US-A1- 2006 269 761**

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**Description****Field of the Invention**

5 [0001] The present invention relates to aqueous plating bath compositions for immersion plating of gold layers onto a substrate. The plating bath is particularly suitable in the manufacture of printed circuit boards, IC substrates, semiconducting devices, interposers made of glass and the like.

**Background of the Invention**

10 [0002] Immersion-type plating is an established method to deposit a layer of gold onto a metal substrate. Gold ions present in such plating bath compositions are reduced to metallic gold when in contact with a metal present on the substrate surface which is less noble than gold. Thereby, the metal from the substrate surface is oxidised and transferred to the gold plating bath. Such plating bath compositions do not contain a strong reducing agent such as hypophosphite ions or formaldehyde which is common in plating baths for electroless deposition of e.g., nickel alloys and copper.

15 [0003] Immersion plated gold layers are frequently used as solderable and/or wire bondable surfaces in the manufacture of printed circuit boards, IC substrates, semiconducting devices and the like. Gold layers are usually deposited by immersion-type plating onto a barrier layer such as a nickel phosphorous alloy or onto an intermediate layer such as a palladium or palladium alloy layer.

20 [0004] An important property of the deposited gold layer is a sufficient wettability of a molten solder material which is usually a tin based alloy on the surface of the gold or gold alloy layer. Furthermore, the gold layer should be applicable for wire bonding with e.g. aluminium, copper and gold wires.

[0005] Another desired property of the gold layer is the optical appearance: a discoloration of the gold layer is not acceptable.

25 [0006] Furthermore, toxic ingredients such as cyanide ions or heavy metal ions as stabilising agents commonly used in such immersion type plating baths need to be replaced by less or non toxic raw materials.

[0007] A cyanide-free immersion type plating bath comprising a source for gold ions, a sulfite salt, complexing agents, a heavy metal ion stabiliser (antimony or bismuth) and a quaternary ammonium salt type polymer is disclosed in JP 2004-250765 A.

30 [0008] EP 1 201 789 A2 discloses an aqueous plating bath for electrodeposition of tin-zinc alloys comprising at least one bath-soluble stannous salt, at least one bath soluble zinc salt, and a quaternary ammonium polymer selected from a ureylene quaternary ammonium polymer, an iminoureylene quaternary ammonium polymer or a thioureylene quaternary ammonium polymer. The plating baths also may contain one or more of the following additives: hydroxy polycarboxylic acids or salts thereof such as citric acid; ammonium salts; conducting salts; aromatic carbonyl-containing compounds; polymers of aliphatic amines such as a poly(alkyleneimine); and hydroxyalkyl substituted diamines as metal complexing agents. The plating baths of this invention deposit a bright and level deposit, and they can be adapted to provide plated alloys having high tin concentration over a wide current density range.

35 [0009] JP 2000 192248 A discloses a plating bath containing a soluble gold salt, a complexing agent consisting of sulfite and thiosulfite, a concealing complexing agent consisting of oxycarboxylic acid, such as tartaric acid, an amine compound, such as aminoacetic acid or ethylene diamine and an ammonium compound., a pH control agent, an amphoteric surfactant or a mixture composed of the amphoteric surfactant and a nonionic surfactant. The plating bath is characterized in that the sulfite and the thiosulfite are combined as the complexing agent, that the concealing complexing agent is used and that the kind of the surfactant is limited to the mixture of the amphoteric or amphoteric and nonionic system. The stabilization of the gold ions in the plating bath and the suppression of the plating spreading at the time of gold plating may be simultaneously achieved by the synergistic effect based on the constitution.

40 [0010] A cyanide-free immersion type plating bath comprising gold ions, a pyrosulfurous acid compound, a thiosulfuric acid compound, a sulfurous acid compound and an aminocarboxylic acid is disclosed in US 2006/0269761 A1.

**Objective of the Invention**

50 [0011] It is the objective of the present invention to provide an aqueous immersion-type gold plating bath composition which is free of cyanide ions and from which gold layers can be deposited having an improved wettability for tin-based solder materials and showing no discoloration.

**Summary of the Invention**

55 [0012] This objective is solved by an aqueous immersion type plating bath composition which is free of cyanide ions, the plating bath composition comprising

(i) a source of gold ions,

(ii) at least one complexing agent selected from the group consisting of carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and salts of the aforementioned,

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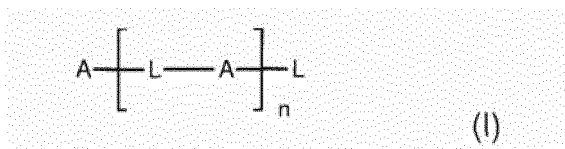
(iii) sulfite ions,

(iv) thiosulfate ions, and

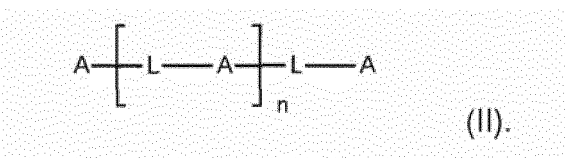
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(v) at least one ureylene polymer additive represented by formulae (I) and (II):

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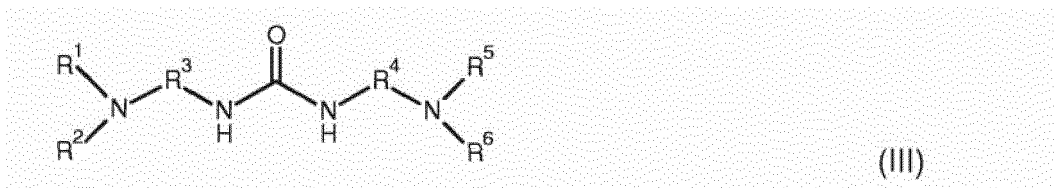
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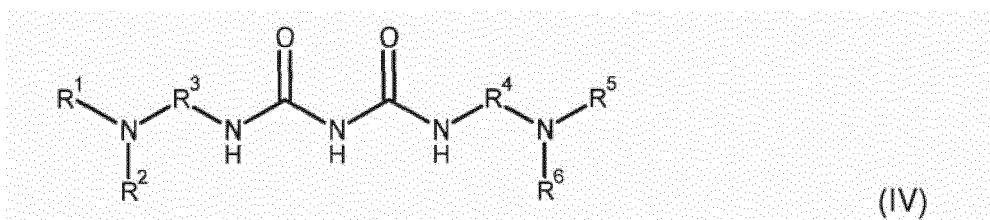
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wherein n is an integer and ranges from 1 to 40, preferably from 3 to 30 and more preferably from 5 to 20. Monomer A is derived from a diamino compound represented by compounds according to formulae (III) to (V) :

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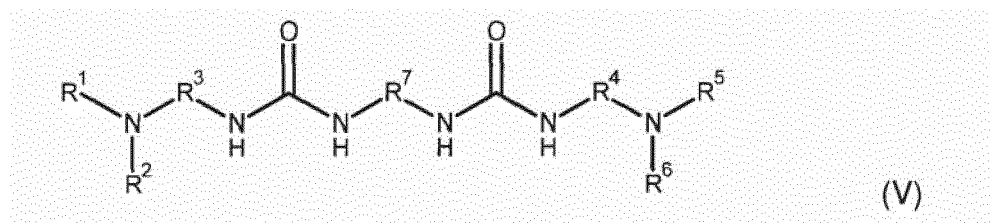


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wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, and R<sup>6</sup> are independently selected from the group consisting of a substituted or unsubstituted hydrocarbon residue with 1 to 10 carbon atoms, preferably methyl, ethyl, hydroxyethyl or -CH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>y</sub>-OH, wherein y is between 0 and 4, and R<sup>3</sup>, R<sup>4</sup> and R<sup>7</sup> are independently selected from the group consisting of (CH<sub>2</sub>)<sub>p</sub>, wherein p stands for an integer of 2 to 12, preferably for an ethylene or propylene group, or for a -[CH<sub>2</sub>CH<sub>2</sub>O]<sub>m</sub>-CH<sub>2</sub>CH<sub>2</sub>- group, wherein m is

between 1 and 40, preferably for a  $-(\text{CH}_2)_2\text{-O-(CH}_2)_2-$  or  $-(\text{CH}_2)_2\text{-O-(CH}_2)_2\text{-O-(CH}_2)_2-$  group, and wherein L stands for a divalent residue, which is selected from the group consisting of  $-(\text{CH}_2)_p-$ , wherein p is an integer between 1 and 12, preferably between 1 and 6, and most preferably between 2 and 4,  $-\text{CH}_2\text{-CH(OH)-CH}_2-$ ,  $-\text{[CH}_2\text{O]}_q\text{-CH}_2\text{CH}_2-$  and  $-\text{[CH}_2\text{CH}_2\text{O]}_q\text{-CH}_2\text{CH}_2-$ , wherein q is an integer between 1 and 40, preferably  $-(\text{CH}_2)\text{-O-(CH}_2)_2-$ ,  $-(\text{CH}_2)_2\text{-O-(CH}_2)_2-$  or  $-(\text{CH}_2)_2\text{-O-(CH}_2)_2\text{-O-(CH}_2)_2-$ , and  $-\text{CH}_2\text{-CH(OH)-CH}_2-$ .

and wherein the ureylene polymer additive according to formulae (I) and (II) are obtained by reacting one or more diamino compounds of formulae (III) to (V) with one or more compounds of the following formula (VI)



wherein L has the same meaning as in formulae (I) and (II) and wherein P and Q are each the same or different and selected from the group consisting of Cl, Br, I, mesylate, triflate, nonaflate, methanesulfonate, or tosylate.

**[0013]** Gold layers having a sufficient wettability to tin based solder materials and the desired lemon-yellow colour are obtained by the aqueous immersion-type plating bath composition according to the present invention. Furthermore, in case the gold layer is deposited onto a nickel or nickel alloy layer, a reduced corrosive attack of the underlying nickel or nickel alloy layer is observed when plating a gold layer from the aqueous plating bath according to the present invention.

## Detailed Description of the Invention

**[0014]** The aqueous immersion-type plating bath according to the present invention comprises gold ions in either  $\text{Au}^+$ ,  $\text{Au}^{3+}$  or both oxidation states. The source of gold ions is a water soluble salt such as trisodium gold disulfite, tripotassium gold disulfite and triammonium gold disulfite, gold thiosulfate, gold thiocyanide, gold sulfate, gold chloride, and gold bromide. Preferably, the source of gold ions is added to the aqueous plating bath in the form of a gold sulfite solution. The concentration of gold ions in the aqueous plating bath preferably ranges from 0.1 to 10 g/l, more preferably from 0.3 to 6 g/l.

**[0015]** The at least one complexing agent present in the aqueous plating bath is selected from the group comprising carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids or a salt of the aforementioned and serves as a complexing agent for gold ions as well as for metal ions dissolved from the substrate during plating, e.g., nickel ions. A preferred carboxylic acid is for example oxalic acid or a salt thereof. Preferred hydroxycarboxylic acids are for example tartaric acid, citric acid, lactic acid, malic acid, gluconic acid and salts of the aforementioned. Preferred aminocarboxylic acids are for example glycine, cysteine, methionine and salts of the aforementioned. In all cases also the sodium, potassium and ammonium salts of said compounds are also suitable. The concentration of the at least one complexing agent preferably ranges from 0.1 to 25 g/l, more preferably from 0.5 to 10 g/l.

**[0016]** More preferably, the aqueous plating bath comprises two different complexing agents and/or salts thereof, such as a hydroxycarboxylic acid or salt thereof and an aminocarboxylic acid or salt thereof.

**[0017]** Most preferably, the aqueous plating bath comprises three different complexing agents such as two different hydroxycarboxylic acids or salts thereof and one aminocarboxylic acid or salt thereof.

**[0018]** The aqueous plating bath according to the present invention further comprises sulfite ions which also serve as a complexing agent for gold ions. Sulfite ions are added to the aqueous plating bath in form of a water soluble sulfite salt such as sodium sulfite, potassium sulfite and ammonium sulfite or together with gold ions as trisodium gold sulfite, tripotassium gold sulfite and ammonium gold sulfite. The concentration of sulfite ions in the aqueous plating bath preferably ranges from 0.05 to 20 g/l, more preferably from 0.1 to 10 g/l.

**[0019]** The aqueous plating bath according to the present invention further comprises thiosulfate ions which also serve as a complexing agent for gold ions. Suitable sources for thiosulfate ions are water soluble salts of thiosulfate such as sodium thiosulfate, potassium thiosulfate and ammonium thiosulfate. The concentration of thiosulfate ions in the plating bath preferably ranges from 0.1 to 20 g/l, more preferably from 0.5 to 10 g/l.

**[0020]** The aqueous plating bath according to the present invention further comprises at least one ureylene polymer additive which enhances the wettability of the tin based solder materials on the gold layer.

**[0021]** Preferably, monomer A is selected from compounds according to formula (III). The concentration of the at least one ureylene polymer additive according to formulae (I) and (II) in the aqueous plating bath preferably ranges from 0.005 to 10 g/l, more preferably from 0.01 to 5 g/l.

**[0022]** The term "polymer" has to be understood in a broad sense in connection with the present invention. It comprises any compound which has been formed by reaction of at least two monomer molecules A and one divalent residue L. The term "polymer" does comprise, in particular, compounds which are typically designated as oligomers. The term "polymer" is, in connection with the present invention also applied to compounds, which are formed by a poly "condensation" reaction.

[0023] According to claim 1 the ureylene polymer additive according to formulae (I) and (II) are obtained by reacting one or more diamino compounds of formulae (III) to (V) with one or more compounds of the following formula (VI)



wherein L has the same meaning as in formulae (I) and (II) and wherein P and Q may each be the same or different and represent halogens such as Cl, Br and I or pseudohalogens such as mesylate, triflate, nonaflate, methanesulfonate, or tosylate. The compounds of the formula (VI) are organic di(pseudo)halogen compounds.

[0024] In case of ureylene polymer additives according to formula (I), the molar ratio ( $n_A : n_B$ ) of the total amount of substance used of the compound(s) of formulae (III) to (V) ( $n_A$ ) to the total amount of substance of the compound(s) of formula (VI) ( $n_B$ ) is 1 : 1.

[0025] In case of ureylene polymer additives according to formula (II), the molar ratio ( $n_A : n_B$ ) of the total amount of substance used of the compound(s) of formulae (III) to (V) ( $n_A$ ) to the total amount of substance of the compound(s) of formula (VI) ( $n_B$ ) is preferably at least 1.1 : 1, more preferably at least 1.3 : 1, and most preferably at least 1.5 : 1.

[0026] This means that in the preparation of ureylene polymer additives according to formula (II), the di(pseudo)halogen compound of the formula (VI) is used in a substoichiometric amount with respect to component(s) of the formulae (III) to (V). Thus, it is effected that the chain of the ureylene polymer additive according to formula (II) has units A having amino groups at both ends. These terminal amino groups are at first tertiary (as in the compounds of formulae (III) to (V)), but may be quaternized. In acidic solution, the amino groups exist in completely or partially protonated form.

[0027] The linkages between units A and residues L occur via quaternary ammonium groups, which are formed by substitution of groups P and Q in the compounds of formula (VI) by the tertiary amino groups of the compounds of the formulae (III) to (V).

[0028] These terminal tertiary amino groups may be quaternized in accordance with the desired properties by using an organic monohalide, such as benzyl chloride, allyl chloride, alkyl chloride, such as 1-chloro-hexane or their corresponding bromides, or by using an appropriate mineral acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid or sulfuric acid.

[0029] The ureylene polymer additives according to formulae (I) and (II) preferably have a weight average molecular mass  $M_W$  of 1000 to 25000 Da, more preferably of 2000 to 20000 Da.

[0030] The reaction of diamino compounds of the formulae (III) to (V) with the compounds of the formula (VI) may preferably be carried out in aqueous or aqueous-alcoholic solutions or solvent-free substances at temperatures of preferably 20 to 100°C.

[0031] The ureylene polymer additives according to formula (II) do not contain any organically bound (pseudo-)halogen, such as a covalent C-Cl moiety.

[0032] In another embodiment of the present invention, halide ions serving as the counter ions of the positively charged ureylene polymer additives according to formulae (I) and (II) are replaced after preparation of the polymer by anions such as hydroxide, sulfate, hydrogensulfate, carbonate, hydrogencarbonate, alkylsulfonate such as methane sulfonate, alkaryl-sulfonate, arylsulfonate, alkyl-carboxylate, alkarylcarboxylate, arylcarboxylate, phosphate, hydrogenphosphate, dihydrogenphosphate, and phosphonate. The halide ions can be for example replaced by ion exchange over a suitable ion exchange resin. The most suitable ion exchange resins are basic ion exchange resins such as Amberlyst® A21. Halide ions can then be replaced by adding an inorganic acid and/or an organic acid containing the desired anions to the ion exchange resin.

[0033] The aqueous plating bath according to the present invention may further comprise sulfate ions. Suitable sources for optional sulfate ions are water soluble salts of sulfate ions such as sodium sulfate, potassium sulfate, and ammonium sulfate. The concentration of the optional sulfate ions preferably ranges from 0.05 to 20 g/l, more preferably from 0.1 to 10 g/l.

[0034] The aqueous plating bath according to the present invention is prepared by adding the ingredients to water. In one embodiment of the present invention, concentrates of the aqueous plating bath are prepared and further diluted with water prior to use of the plating bath.

[0035] Preferably, the cyanide-free aqueous immersion-type bath according to the present invention is free of antimony or bismuth ions.

[0036] In one embodiment of the present invention, a kit comprising two different aqueous solutions is provided. The first solution contains at least one complexing agent selected from the group consisting of carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and salts of the aforementioned, thiosulfate ions and the at least one ureylene polymer additive according to formulae (I) and/or (II). The second solution contains gold ions and sulfite ions. Prior to use of the immersion-type plating bath, the first solution and the second solution of the kit are mixed to obtain the immersion-type plating bath according to the present invention.

[0037] The pH of the aqueous plating bath according to the present invention preferably ranges from 5 to 8, more preferably from 5.5 to 7.5. The target pH value can be adjusted using for example sulfuric acid or sodium hydroxide.

**[0038]** The substrate to be plated with gold or a gold alloy has a surface area consisting of a metal or metal alloy less noble than gold and is contacted with the aqueous plating bath according to the present invention by either dipping the substrate into the plating bath or by spraying the plating bath onto the substrate.

**[0039]** Gold or a gold alloy is then deposited onto the surface area consisting of a metal or metal alloy less noble than gold, selected from the group comprising nickel, nickel alloys such as nickel phosphorous alloys, nickel boron alloys, cobalt, cobalt alloys such as cobalt phosphorous alloys, cobalt molybdenum phosphorous alloys, cobalt molybdenum boron alloys, cobalt molybdenum boron phosphorous alloys, cobalt tungsten phosphorous alloys, cobalt tungsten boron alloys, cobalt tungsten boron phosphorous alloys, palladium, palladium alloys such as palladium phosphorous alloys, palladium boron alloys, copper and copper alloys.

**[0040]** The temperature of the aqueous plating bath is preferably in the range of 30 to 70 °C, more preferably from 40 to 60 °C during plating. The plating time is preferably in the range of 40 to 60 min, more preferably in the range of 5 to 30 min.

**[0041]** The immersion-type plating bath according to the present invention may be used with horizontal, vertical and spray plating equipment.

**[0042]** The following non-limiting examples further illustrate the present invention.

## Examples

### General Procedures

**[0043]** The weight average molecular mass  $M_w$  of the ureylene polymer additives according to formulae (I) and (II) was determined by gel permeation chromatography (GPC) using a GPC apparatus from WGE-Dr. Bures equipped with a molecular weight analyzer BI-MwA from Brookhaven, a TSK Oligo +3000 column, and Pullulan and PEG standards with  $M_w = 400$  to 22000 g/mol. The solvent used was Millipore water with 0.5 % acetic acid and 0.1 M  $\text{Na}_2\text{SO}_4$ .

**[0044]** Substrates (length: 27.5 mm, width: 12.5 mm) containing 40 plated through-holes (0.8 mm diameter, 1.5 mm land size, and a surface consisting of a plated nickel phosphorous alloy) were used throughout all examples. Gold was deposited onto the plated through-holes.

**[0045]** Test C1, a solder float test with lead-free solder according to IPC J-STD-003B (March 2007) was applied to all gold plated samples in order to assess the solder wettability of the gold layers. A SnAg3.0Cu0.5 solder bath was used. Next, three reflow cycles in air atmosphere were applied to each sample prior to inspection. The samples are evaluated after the test with an optical microscope (magnification: 10 x). A sufficient wetting of the gold layer with solder material is achieved when at least 95 % of the gold surfaces being tested exhibit good wetting.

**[0046]** An aqueous immersion type gold plating bath stock solution comprising

1.5 g/l	trisodium gold sulfite
3.72 g/l	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
1 g/l	oxalic acid
3.1 g/l	trisodium citrate dihydrate
5 g/l	methionine

was used throughout all examples. Further additives added to the stock solution are indicated in the respective example.

**[0047]** The plating bath pH was 6.

**[0048]** The plating bath temperature during plating was 50 °C and the plating time was 15 min. The thickness of the deposited gold layers ranged between 60 and 80 nm.

### Comparative Example 1

**[0049]** No ureylene polymer additive according to formulae (I) or (II) was added to the aqueous immersion-type gold plating bath stock solution.

**[0050]** The gold layer obtained has a green colour which is not desired.

**[0051]** A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was only achieved for 5 % of the gold plated area. Accordingly, the gold layer failed the solder float test.

### Example 1

**[0052]** 0.1 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $(\text{CH})_2\text{O}(\text{CH}_2)_2$  was added to the aqueous immersion-type gold plating bath stock solution. The polymer additive according to formula

(II) was obtained according to preparation example 12 in WO 2011/029781 A1 and comprises chloride ions as counter ions. The weight average molecular mass  $M_W$  of the ureylene polymer additive obtained was 5380 Da.

**[0053]** The gold layer obtained has the desired lemon-yellow colour.

**[0054]** A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 98 % of the gold plated area.

#### Example 2

**[0055]** 0.3 ml/l of a solution comprising 25 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $(CH_2)_2O(CH_2)_2$  was added to the aqueous immersion-type gold plating bath stock solution.

**[0056]** The ureylene polymer additive was prepared by reacting 20 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 22.77 g oxybis-(ethane-2,1-diyl)-methanesulfonate (monomer L) in a molar ratio of 4 : 3 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises methanesulfonate as counter ions and has a weight average molecular mass  $M_W$  of 5677 Da.

**[0057]** The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 96 % of the gold plated area.

#### Example 3

**[0058]** 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (I) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $(CH_2)_2O(CH_2)_2$  was added to the aqueous immersion-type gold plating bath stock solution.

**[0059]** The polymer additive according to formula (I) was prepared by reacting 20 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 22.7 g oxybis-(ethane-2,1-diyl)-methanesulfonate (monomer L) in a molar ratio of 1 : 1 for 20 h at a temperature of 80 °C. The ureylene polymer additive according to formula (I) comprises methanesulfonate as counter ions and has a weight average molecular mass  $M_W$  of 17260 Da.

**[0060]** The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 98 % of the gold plated area.

#### Example 4

**[0061]** 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $(CH_2)_2O(CH_2)_2O(CH_2)_2$  was added to the aqueous immersion-type gold plating bath stock solution.

**[0062]** The polymer additive according to formula (II) was prepared by reacting 25 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 24.94 g ethane-1,2-diyl-bis(oxy)-bis(ethane-3,1-diyl)-dimethanesulfonate (monomer L) in a molar ratio of 3 : 2 for 24 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises methanesulfonate as counter ions and has a weight average molecular mass  $M_W$  of 7299 Da.

**[0063]** The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 100 % of the gold plated area.

#### Example 5

**[0064]** 0.3 ml/l of a solution comprising 20 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $CH_2-CH(OH)-CH_2$  was added to the aqueous immersion-type gold plating bath stock solution.

**[0065]** The polymer additive according to formula (II) was prepared by reacting 15 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 6.43 g 1,3-dichloropropane-2-ol (monomer L) in a molar ratio of 4 : 3 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises chloride as counter ions and has a weight average molecular mass  $M_W$  of 5202 Da.

**[0066]** The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 97 % of the gold plated area.

#### Example 6

**[0067]** 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L =  $(CH_2)_3$

was added to the aqueous immersion-type gold plating bath stock solution.

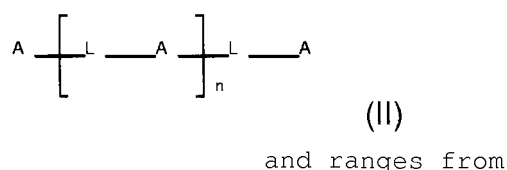
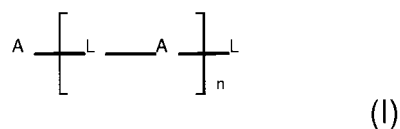
**[0068]** The polymer additive according to formula (II) was prepared by reacting the 45 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 18.6 g 1-bromo-3-chloro-propane in a molar ratio of 3 : 2 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises bromide and chloride as counter ions and has a weight average molecular mass  $M_w$  of 5016 Da.

**[0069]** The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 99 % of the gold plated area.

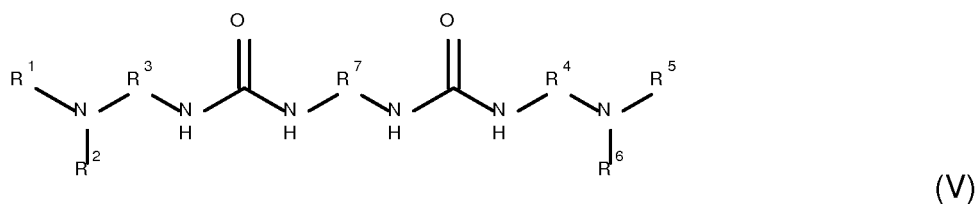
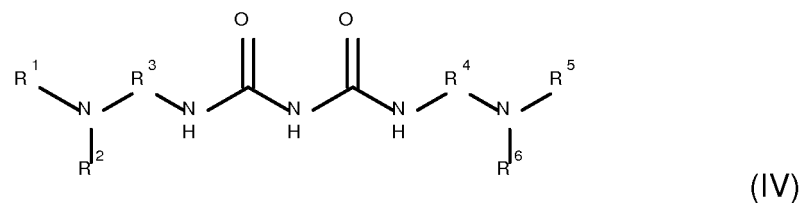
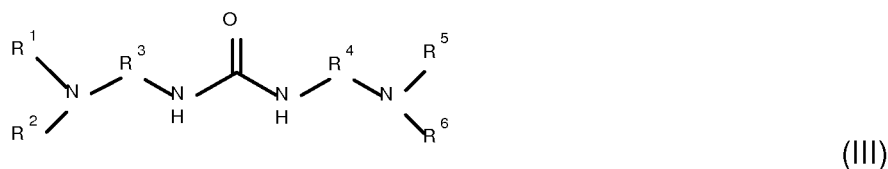
**Claims**

1. A cyanide-free aqueous immersion-type plating bath for deposition of gold, comprising

- (i) a source of gold ions,
- (ii) at least one complexing agent selected from the group consisting of carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and salts of the aforementioned,
- (iii) sulfite ions,
- (iv) thiosulfate ions, and
- (v) at least one ureylene polymer additive selected from polymers according to formulae (I) and (II):



wherein n is an integer 1 and 40,  
 wherein monomer A is selected from compounds according to formulae (III) to (V)



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wherein  $R^1$ ,  $R^2$ ,  $R^5$ , and  $R^6$  are independently selected from the group consisting of a substituted or unsubstituted hydrocarbon residue with 1 to 10 carbon atoms,

$R^3$ ,  $R^4$  and  $R^7$  are independently selected from the group consisting of  $(CH_2)_p$ , wherein  $p$  stands for an integer of 2 to 12,  $-[CH_2CH_2O]_m-CH_2CH_2-$  group, wherein  $m$  is between 1 and 40,

and wherein

$L$  stands for a divalent residue, which is selected from the group consisting of  $-(CH_2)_p-$ , wherein  $p$  is an integer between 1 and 12,  $-CH_2-CH(OH)-CH_2-$ ,  $-[CH_2O]_q-CH_2CH_2-$  and  $-[CH_2CH_2O]_q-CH_2CH_2-$ , wherein  $q$  is an integer between 1 and 40

and wherein the ureylene polymer additive according to formulae (I) and (II) are obtained by reacting one or more diamino compounds of formulae (III) to (V) with one or more compounds of the formula (VI)



wherein  $L$  has the same meaning as in formulae (I) and (II) and wherein  $P$  and  $Q$  are the same or different and selected from the group consisting of Cl, Br, I, mesylate, triflate nonaflate, methansulfonate and tosylate.

2. The cyanide-free aqueous immersion-type plating bath according to claim 1 wherein the concentration of gold ions ranges from 0.1 to 10 g/l.
3. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the at least one complexing agent comprises a hydroxycarboxylic acid selected from the group consisting of tartaric acid, citric acid, lactic acid, malic acid, gluconic acid or a salt of the aforementioned.
4. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the at least one complexing agent consisting of an aminocarboxylic acid selected from the group comprising glycine, cysteine, methionine or a salt of the aforementioned.
5. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of the at least one complexing agent ranges from 0.1 to 25 g/l.
6. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of sulfite ions ranges from 0.05 to 10 g/l.
7. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of thiosulfate ions ranges from 0.1 to 20 g/l.
8. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein monomer A is selected from compounds according to formula (III).
9. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein  $R^1$ ,  $R^2$ ,  $R^5$ , and  $R^6$  are independently selected from the group consisting of methyl, ethyl, hydroxyethyl and  $-CH_2CH_2(OCH_2C_2H_5)_y-OH$ , wherein  $y$  is between 0 and 4.
10. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein  $R^3$ ,  $R^4$  and  $R^7$  are independently selected from the group consisting of  $-(CH_2)_p-$ , wherein  $p$  is 2,  $-(CH_2)_2-O-(CH_2)_2-$  and  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ .
11. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the monomer  $L$  is selected from the group consisting of  $-(CH_2)_p-$ , wherein  $p$  is an integer between 1 and 6,  $-(CH_2)-O-(CH_2)_2-$ ,  $-(CH_2)_2-O-(CH_2)_2-$ ,  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$  and  $-CH_2-CH(OH)-CH_2-$ .
12. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of the at least one ureylene polymer ranges from 0.005 to 10 g/l.
13. The cyanide-free aqueous immersion-type bath according to any of the foregoing claims which is free of antimony or bismuth ions.
14. A kit comprising a first solution which contains at least one complexing agent selected from the group consisting of

carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and salts of the aforementioned, thiosulfate ions and at least one ureylene polymer additive according to formulae (I) and/or (II) according to step v) of claim 1 and wherein the ureylene polymer additive according to formulae (I) and (II) are obtained by reacting one or more diamino compounds of formulae (III) to (V) with one or more compounds of the formula (VI) and a second solution which contains a source of gold ions and sulfite ions.

15. A method for depositing a gold layer onto a substrate, comprising, in this order, the steps

- (i) providing a substrate having a surface area consisting of a metal or metal alloy less noble than gold
- (ii) contacting the substrate with a cyanide-free aqueous immersion-type plating bath according to claims 1 to 13

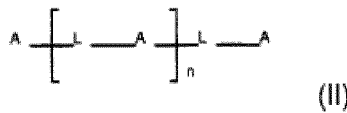
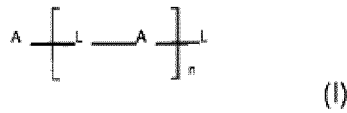
and thereby depositing a gold layer onto the surface area consisting of a metal or metal alloy less noble than gold.

16. The method for depositing a gold or gold alloy layer onto a substrate according to claim 15 wherein the metal or metal alloy less noble than gold is selected from the group consisting of nickel, nickel alloys, cobalt, cobalt alloys, palladium, palladium alloys, copper and copper alloys.

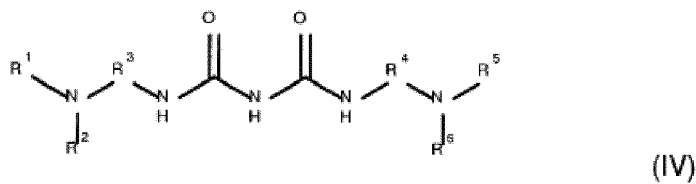
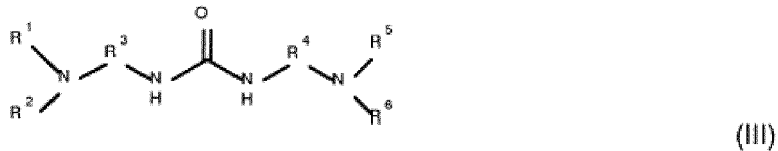
**Patentansprüche**

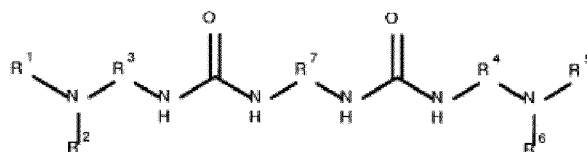
1. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp für das Abscheiden von Gold, umfassend

- (i) eine Quelle von Goldionen,
- (ii) mindestens einen Komplexbildner ausgewählt aus der Gruppe bestehend aus Carbonsäuren, Hydroxycarbonsäuren, Aminocarbonsäuren und Salzen der zuvor erwähnten,
- (iii) Sulfitionen,
- (iv) Thiosulfationen und
- (v) mindestens ein Ureylenepolymerzusatzmittel ausgewählt unter Polymeren den Formeln (I) und (II) entsprechend:



wobei n eine ganze Zahl von 1 bis 40 ist,  
wobei das Monomer A unter Verbindungen den Formeln (III) bis (V) entsprechend ausgewählt wird





(V)

wobei  $R^1$ ,  $R^2$ ,  $R^5$  und  $R^6$  unabhängig aus der Gruppe ausgewählt werden bestehend aus einem substituierten oder unsubstituierten Kohlenwasserstoffrest mit 1 bis 10 Kohlenstoffatomen,

$R^3$ ,  $R^4$  and  $R^7$  unabhängig aus der Gruppe ausgewählt werden bestehend aus  $(CH_2)_p$ , -wobei  $p$  für eine ganze Zahl von 2 bis 12,  $-[CH_2CH_2O]_m-CH_2CH_2-$  Gruppe steht, wobei  $m$  zwischen 1 und 40 liegt, und wobei

$L$  für einen zweiwertigen Rest steht, der aus der Gruppe ausgewählt ist bestehend aus  $-(CH_2)_p-$ , wobei  $p$  eine ganze Zahl zwischen 1 und 12,  $-CH_2-CH(OH)-CH_2-$ ,  $-[CH_2O]_q-CH_2CH_2-$  und  $-[CH_2CH_2O]_q-CH_2CH_2-$  ist, wobei  $q$  eine ganze Zahl zwischen 1 und 40 ist

und wobei das Ureylenpolymerzusatzmittel den Formeln (I) und (II) entsprechend durch Reagieren einer oder mehrerer Diaminverbindungen der Formeln (III) bis (V) mit einer oder mehreren Verbindungen der Formel (VI)



erhalten werden,

wobei  $L$  dieselbe Bedeutung wie in den Formeln (I) und (II) aufweist und wobei  $P$  und  $Q$  gleich oder verschieden und aus der Gruppe ausgewählt sind bestehend aus  $Cl$ ,  $Br$ ,  $I$ , Mesylat, Triflat, Nonafat, Methansulfonat und Tosylat.

2. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach Anspruch 1, wobei die Konzentration von Goldionen im Bereich von 0,1 bis 10 g/l liegt.
3. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei der mindestens eine Komplexbildner eine Hydroxycarbonsäure umfasst ausgewählt aus der Gruppe bestehend aus Weinsäure, Zitronensäure, Milchsäure, Apfelsäure, Gluconsäure oder einem Salz der vorgenannten.
4. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei der mindestens eine Komplexbildner aus einer Aminocarbonsäure besteht ausgewählt aus der Gruppe bestehend aus Glycin, Cystein, Methionin oder einem Salz der vorgenannten.
5. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei die Konzentration des mindestens einen Komplexbildners im Bereich von 0,1 bis 25 g/l liegt.
6. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei die Konzentration von Sulfitionen im Bereich von 0,05 bis 10 g/l liegt.
7. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei die Konzentration von Thiosulfationen im Bereich von 0,1 bis 20 g/l liegt.
8. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei das Monomer A unter Verbindungen der Formel (III) entsprechend ausgewählt wird.
9. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei  $R^1$ ,  $R^2$ ,  $R^5$  und  $R^6$  unabhängig aus der Gruppe ausgewählt werden bestehend aus Methyl, Ethyl, Hydroxyethyl und  $-CH_2-CH_2(OCH_2CH_2)_y-OH$ , wobei  $y$  zwischen 0 und 4 liegt.
10. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei  $R^3$ ,  $R^4$  and  $R^7$  unabhängig aus der Gruppe ausgewählt werden bestehend aus  $-(CH_2)_p-$ , wobei  $p$  2 ist  $-(CH_2)_2-O-(CH_2)_2-$  und  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ .
11. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei

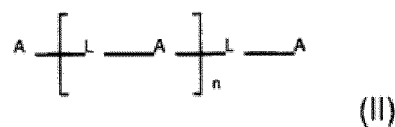
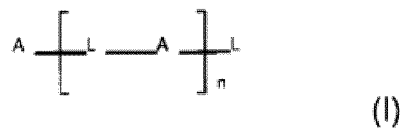
das Monomer L aus der Gruppe ausgewählt ist bestehend aus  $-(CH_2)_p-$ , wobei p eine ganze Zahl zwischen 1 und 6 ist,  $-(CH_2)-O-(CH_2)_2-$ ,  $-(CH_2)_2-O-(CH_2)_2-$ ,  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$  und  $-CH_2-CH(OH)-CH_2-$ .

- 5 12. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, wobei die Konzentration des mindestens einen Ureylenpolymers im Bereich von 0,005 bis 10 g/l liegt.
13. Cyanidfreies wässriges Plattierungsbad vom Tauchtyp nach irgendeinem der vorhergehenden Ansprüche, das frei von Antimon- oder Wismutionen ist.
- 10 14. Kit umfassend eine erste Lösung, die mindestens einen Komplexbildner enthält ausgewählt aus der Gruppe bestehend aus Carbonsäuren, Hydroxycarbonsäuren, Aminocarbonsäuren und Salzen der zuvor erwähnten, Thiosulfationen und mindestens ein Ureylenpolymerzusatzmittel entsprechend den Formeln (I) und/oder (II) entsprechend Schritt v) von Anspruch 1 und wobei das Ureylenpolymerzusatzmittel entsprechend den Formeln (I) und (II) durch Reagieren einer oder mehrerer Diaminverbindungen der Formeln (III) bis (V) mit einer oder mehreren Verbindungen der Formel (VI) erhalten werden
- 15 und eine zweite Lösung, die eine Quelle von Goldionen und Sulfitionen enthält.
15. Verfahren zum Abscheiden einer Goldschicht auf ein Substrat, umfassend, in dieser Reihenfolge, die Schritte
- 20 (i) Bereitstellen eines Substrats, das einen Oberflächenbereich aufweist, der aus einem Metall oder einer Metalllegierung, die weniger edel als Gold ist, besteht  
(ii) Kontaktieren des Substrats mit einem cyanidfreien wässrigen Plattierungsbad vom Tauchtyp nach den Ansprüchen 1 bis 13
- 25 und dadurch Abscheiden einer Goldschicht auf den Oberflächenbereich bestehend aus Metall oder Metalllegierung, das/die weniger edel als Gold ist.
16. Verfahren zum Abscheiden einer Gold- oder Goldlegierungsschicht auf ein Substrat nach Anspruch 15, wobei das Metall oder die Metalllegierung, das/die weniger edel als Gold ist, aus der Gruppe ausgewählt wird bestehend aus
- 30 Nickel, Nickellegierungen, Kobalt, Kobaltlegierungen, Palladium, Palladiumlegierungen, Kupfer und Kupferlegierungen.

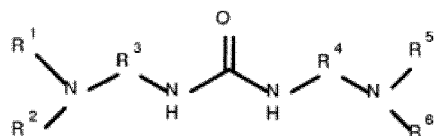
35 **Revendications**

1. Bain aqueux de placage de type immersion sans cyanure pour le dépôt d'or, comprenant :

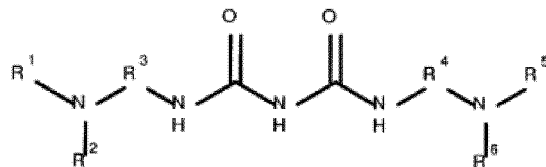
- (i) une source d'ions or,  
(ii) au moins un agent complexant choisi dans le groupe constitué par les acides carboxyliques, les acides hydroxycarboxyliques, les acides aminocarboxyliques et les sels des composés susmentionnés,  
40 (iii) des ions sulfite,  
(iv) des ions thiosulfate, et  
(v) au moins un additif polymère d'uréylène choisi parmi les polymères répondant aux formules (I) et (II) :



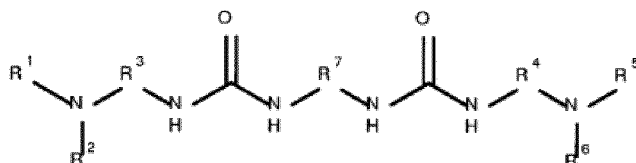
dans lesquelles n est un entier et va de 1 à 40,  
dans lesquelles le monomère A est choisi parmi les composés répondant aux formules (III) à (V)



(III)



(IV)



(V)

dans lesquelles R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup> et R<sup>6</sup> sont indépendamment choisis dans le groupe constitué par un résidu hydrocarboné substitué ou non substitué avec 1 à 10 atomes de carbone, R<sup>3</sup>, R<sup>4</sup> et R<sup>7</sup> sont indépendamment choisis dans le groupe constitué par les groupes (CH<sub>2</sub>)<sub>p</sub>, où p représente un entier de 2 à 12, et -[CH<sub>2</sub>CH<sub>2</sub>O]<sub>m</sub>-CH<sub>2</sub>CH<sub>2</sub>-, où m vaut entre 1 et 40, et dans lesquelles

L représente un résidu divalent, qui est choisi dans le groupe constitué par les groupes -(CH<sub>2</sub>)<sub>p</sub>-, où p est un entier entre 1 à 12, -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-, -[CH<sub>2</sub>O]<sub>q</sub>-CH<sub>2</sub>CH<sub>2</sub>- et -[CH<sub>2</sub>CH<sub>2</sub>O]<sub>q</sub>-CH<sub>2</sub>CH<sub>2</sub>-, où q est un entier entre 1 et 40

et dans lequel l'additif polymère d'uréylène répondant aux formules (I) et (II) sont obtenus par réaction d'un ou plusieurs composés diamminés des formules (III) à (V) avec un ou plusieurs composés de la formule (VI)



dans laquelle L a la même signification que dans les formules (I) et (II) et dans laquelle P et Q sont identiques ou différents et choisis dans le groupe constitué par Cl, Br, I, le mésylate, le triflate, le nonaflate, le méthanesulfonate et le tosylate.

2. Bain aqueux de placage de type immersion sans cyanure selon la revendication 1 dans lequel la concentration d'ions or va de 0,1 à 10 g/l.
3. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel l'au moins un agent complexant comprend un acide hydroxycarboxylique choisi dans le groupe constitué par l'acide tartrique, l'acide citrique, l'acide lactique, l'acide malique, l'acide gluconique ou un sel des composés susmentionnés.
4. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel l'au moins un agent complexant consiste en un acide aminocarboxylique choisi dans le groupe comprenant la glycine, la cystéine, la méthionine ou un sel des composés susmentionnés.
5. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel la concentration de l'au moins un agent complexant va de 0,1 à 25 g/l.
6. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel la concentration d'ions sulfite va de 0,05 à 10 g/l.

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7. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel la concentration d'ions thiosulfate va de 0,1 à 20 g/l.
- 5 8. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel le monomère A est choisi parmi les composés répondant à la formule (III).
- 10 9. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup> et R<sup>6</sup> sont indépendamment choisis dans le groupe constitué par les groupes méthyle, éthyle, hydroxyéthyle et -CH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>y</sub>-OH, où y vaut entre 0 et 4.
- 15 10. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel R<sup>3</sup>, R<sup>4</sup> et R<sup>7</sup> sont indépendamment choisis dans le groupe constitué par les groupes -(CH<sub>2</sub>)<sub>p</sub>-, où p vaut 2, -(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>- et -(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-.
- 20 11. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel le monomère L est choisi dans le groupe constitué par les groupes -(CH<sub>2</sub>)<sub>p</sub>-, où p est un entier entre 1 et 6, -(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-, -(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-, -(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>2</sub>- et -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-.
- 25 12. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes dans lequel la concentration de l'au moins un polymère d'uréylène va de 0,005 à 10 g/l.
- 30 13. Bain aqueux de placage de type immersion sans cyanure selon l'une quelconque des revendications précédentes qui est dépourvu d'ions antimoine ou bismuth.
- 35 14. Kit comprenant une première solution qui contient au moins un agent complexant choisi dans le groupe constitué par les acides carboxyliques, les acides hydroxycarboxyliques, les acides aminocarboxyliques et les sels des composés susmentionnés, des ions thiosulfate et au moins un additif polymère d'uréylène répondant aux formules (I) et/ou (II) selon le point v) de la revendication 1 et dans lequel l'additif polymère d'uréylène répondant aux formules (I) et (II) sont obtenus par réaction d'un ou plusieurs composés diamminés des formules (III) à (V) avec un ou plusieurs composés de la formule (VI), et une deuxième solution qui contient une source d'ions or et des ions sulfite.
- 40 15. Procédé de dépôt d'une couche d'or sur un substrat comprenant, dans cet ordre, les étapes suivantes :
- 45 (i) se procurer un substrat ayant une zone de surface consistant en un métal ou un alliage métallique moins noble que l'or,
- (ii) mettre le substrat en contact avec un bain aqueux de placage de type immersion sans cyanure selon les revendications 1 à 13
- 50 et déposer ainsi une couche d'or sur la zone de surface consistant en un métal ou un alliage métallique moins noble que l'or.
- 55 16. Procédé de dépôt d'une couche d'or ou d'alliage d'or sur un substrat selon la revendication 15 dans lequel le métal ou l'alliage métallique moins noble que l'or est choisi dans le groupe constitué par le nickel, les alliages de nickel, le cobalt, les alliages de cobalt, le palladium, les alliages de palladium, le cuivre et les alliages de cuivre.

**REFERENCES CITED IN THE DESCRIPTION**

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[0057] [0060] [0063] [0066] [0069]