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(54) **Alkaline, cyanide-free solution for electroplating of gold alloys, a method for electroplating and a substrate comprising a bright, corrosion-free deposit of a gold alloy**

(57) The present invention relates to an electroplating solution which is free of cyanides and toxic compounds for the electrodeposition of bright deposits of gold-copper alloys. Thus, substrates are provided which comprise a bright gold-copper alloy deposit which is corrosion resistant according to NFS 80772, ISO 4538 and/or ISO 9227 and has 14 to 22 karats of gold in the alloy. Remarkably, the inventive electroplating solution

allows electroplating of gold-copper alloy deposits which have a color matching the Swiss standard ISO 8654 from 0.5 N to 5 N. Furthermore, the invention provides a method for electroplating a gold-copper alloy deposit on a substrate. The inventive electroplating solution may be used for electroplating a substrate selected from the group consisting of decorative substrates, jewelry, watches and eyeglass trade.

Figure 1

Example	alloying metal	complexing agent	molar ratio of alloy metal : complexing agent	alloy metal concentration	aspect of the deposit	color of the deposit
6	indium	NTA	1:2	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	indium	Sorbitol	1:5	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	indium	Cysteine	1:4	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	iron	Sorbitol	1:3	50 – 200 mg/L	Bright	From pink to 0.5 N color as iron content increases

Description

[0001] The present invention relates to an electroplating solution which is free of cyanides and toxic compounds for the electrodeposition of bright deposits of gold-copper alloys. Thus, substrates are provided which comprise a bright gold-copper alloy deposit which is corrosion resistant according to NFS 80772, ISO 4538 and/or ISO 9227 and has 14 to 22 karats of gold in the alloy. Remarkably, the inventive electroplating solution allows electroplating of gold-copper alloy deposits which have a color matching the Swiss standard ISO 8654 from 0.5 N to 5 N. Furthermore, the invention provides a method for electroplating a gold-copper alloy deposit on a substrate. The inventive electroplating solution may be used for electroplating a substrate selected from the group consisting of decorative substrates, jewelry, watches and eyeglass trade.

[0002] Currently, cyanide processes are used for most decorative applications, but in order to reduce environmental risks and ensure manipulator safety, the demand of non-toxic and especially non-cyanide processes rose suddenly. Therefore, various kinds of non-cyanide gold plating baths have been developed in order to generate cyanide-free gold depositions.

[0003] For example, many non-cyanide gold plating solutions use $\text{Na}_3\text{Au}(\text{SO}_3)_2$ as gold salt. However, in a gold plating bath using $\text{Na}_3\text{Au}(\text{SO}_3)_2$ sulfite ions in the solution are unstable and easily oxidized. Consequently, the stability of complexes of gold in the gold plating solution becomes lower and gold may precipitate.

[0004] Japanese Patent publication No. 2005-256072 discloses a different complex discovered few years ago, using hydantoin compounds as chelating agent and starting from trivalent gold compounds e.g. gold hydroxide salt or chloroaurate gold. However, this gold complex was found to be unstable regarding the electroless deposit that occurs after a month when complexed gold and conductive salts were in the same bath.

[0005] In fact, the prior art fails to provide a cyanide-free and toxic compounds free-solution for electroplating of a gold alloy with the following required characteristics:

- The deposit must be bright so that no further polishing is required after plating.
- The deposit must have the desired color, as required. Usually, these colors are matching the Swiss standard (ISO 8654) from 0.5 N to 5 N.
- The karat of the deposit should be as required by its industrial application, generally ranging from about 14 to 22.
- The deposit should be corrosion resistant, according to classical requirements of the luxury industry such as NFS 80772, ISO 4538 or ISO 9227.

[0006] Thus, the object of the present invention was to provide a cyanide-free and toxic compounds free solution for electroplating of a gold-copper alloy which meets the characteristics cited above.

[0007] The solution to the problem is provided with the alkaline, cyanide-free solution for electroplating of a gold-copper alloy according to claim 1, the method for electroplating a gold-copper alloy deposit on a substrate according to claim 11, the substrate comprising a bright, electroplated deposit of a gold-copper alloy according to claim 12 and the use according to claim 15. The dependent claims show advantageous embodiments.

[0008] The present invention provides an alkaline, cyanide-free electroplating solution for electroplating a gold-copper alloy, comprising

- a) 0.5 to 10 g/L of gold ions;
- b) 1.0 to 40 g/L of hydantoin, a salt or a derivative thereof;
- c) 60 to 200 g/L of a sulfite salt;
- d) 0.1 to 8 g/L of copper ions; and
- e) 0 to 3 g/L of zinc, iron and/or indium ions;
- f) 0 to 75 g/L of a complexing agent which is different from hydantoin, a salt or a derivative thereof.

[0009] The inventive electroplating solution is suitable for electroplating a gold-copper alloy deposit on a substrate, wherein the deposit has the following characteristics:

- The deposit is bright.
- The deposit may have a large panel of colors, as required. Importantly, the colors of the deposit are matching the Swiss standard (ISO 8654) from 0.5 N to 5 N.
- The karat of the deposit is comprised between 14 and 22 kts.
- The deposit is corrosion resistant according to classical requirements of the luxury industry (NFS 80772, ISO 4538 and/or ISO 9227).

[0010] It was discovered that the inventive alkaline, cyanide-free electroplating solution must comprise a sulfite salt concentration of at least 60 g/L, preferably in the range of 60 to 200 g/L. At this concentration, the sulfite salt may prevent deposit of gold on tank walls over time. The concentration of the sulfite salt may be 65 to 160 g/L, preferably 70 to 120 g/L, more preferably 75 to 100 g/L. Especially at concentrations ≥ 70 g/L, it was discovered that the stability of the electroplating solution over time is significantly improved.

[0011] Sulfite salts which may be comprised in the inventive solution are sodium sulfite and/or potassium sulfite.

[0012] In a preferred embodiment of the invention, the gold ions in the inventive solution are at least partially complexed by hydantoin or its derivatives.

[0013] In a further preferred embodiment, the molar ratio between gold ions and hydantoin, a salt or a derivative thereof, is 1:2 to 1:6, preferably 1:2.5 to 1:5, more preferably 1:3 to 1:4. A ratio in this range is favorable for complexing gold ions by hydantoin and thus increasing the stability of the electroplating solution.

[0014] The concentration of the copper ions may be 0.2 to 10 g/L more preferably 0.5 to 7.5 g/L and most preferably 1 to 5 g/L.

[0015] The electroplating solution according to the present invention may further comprise ions of metals which can improve the final characteristics of the plated gold-copper alloy deposit. For example, it was discovered that if zinc, iron and/or indium ions are comprised in the inventive alkaline plating solution, the final gold-copper alloy deposit has an improved brightness. Furthermore, the addition of said metal ions allows to selectively regulate the color of the deposit which is produced after electroplating.

[0016] In this regard, a suitable concentration range of the zinc, iron and/or indium ions is 10 mg/L to 3 g/L, preferably 20 mg/L to 1 g/L, more preferably 50 mg/L to 500 mg/L. As a matter of fact, the brightness of the electrode or substrate which is electroplated with the inventive solution can be further improved if all three metal ions i.e. zinc, iron as well as indium ions are comprised in the solution.

[0017] In a further preferred embodiment of the invention, the electroplating solution comprises a brightening agent. Suitable brightening agents increase the codeposition of zinc, iron and/or indium metal in the deposit. For example, the addition of a brightening agent allows obtaining a 1 N color when zinc ions are comprised in the inventive solution. Examples for brightening agents according to the invention are pyridine sulfonic acid, trans pyridyl acrylic acid, nicotinic acid and/or antimony. Antimony may be in the form of KSb(OH)_6 . Antimony was found to be suitable for significantly improving the brightness of the deposit.

[0018] The concentration of the brightening agent will be comprised between 0.01 to 1 g/L more preferably between 10 and 500 mg/L.

[0019] In order to increase the solubility or improve the electrodeposition of the alloy metals, the copper ions or the zinc, iron and/or indium ions may be complexed in solution by a complexing agent. According to the invention, the complexing agent may be selected from the group consisting of carbohydrates, amino acids, sulfur compounds and sugar alcohols, preferably selected from the group consisting of sorbitol, mannitol, gluconate, erythritol, xylitol, nitritol-riacetic acid, cysteine. Said complexing agents were found to be perfectly suited for complexing e.g. copper, zinc, iron and/or indium ions.

[0020] The complexing agent may have a concentration of 0.1 to 60 g/L, preferably 0.5 to 40 g/L, more preferably 1 to 20 g/L, most preferably 1.5 to 10 g/L. A concentration in these ranges is sufficient for complexing the copper ions which are comprised in the inventive alkaline electroplating solution as well as optionally zinc, iron and/or indium ions. A concentration of complexing agent above 75 g/L was found to be detrimental for some type of metal ions. For example, for copper ions, a concentration of a chelating agent above 75 g/L will lead to the reduction of copper (II) into copper (0) and lead to the formation of a brick-red copper precipitate.

[0021] In a further preferred embodiment, the concentration of the complexing agent is dependent on the concentration of the copper ions or optionally the zinc, iron and/or indium ions. Preferably, the ratio of the chelating agent concentration to the concentration of alloy metal ions (e.g. copper ions) ranges from 1 : 0.25 to 1:1. This range was found to be sufficient for suitable complexation of the alloy metal ions.

[0022] The electroplating solution according to the present invention may further comprise a buffering agent, preferably a buffering agent which is selected from the group consisting of phosphate (e.g. K_3PO_4 , HK_2PO_4 , H_2KPO_4 , or the corresponding sodium phosphate salt), formiate (e.g. sodium formiate), pyrophosphate (e.g. tetrapotassium pyrophosphate) and citrate (e.g. sodium citrate). The advantage of citrate as a buffering agent is that citrate not only acts as a buffering agent, but also as a complexing agent for many metal ions. Phosphate as buffering agent has the advantage

that it acts both as buffering agent and as conductive agent.

[0023] The buffering agent may have a concentration of 30 to 300 g/L, preferably 40 to 200 g/L, more preferably 50 to 100 g/L. A concentration in this range is suitable for keeping the pH of the inventive electroplating solution constant for many turnovers (TOs) of the electroplating solution.

[0024] The pH of the alkaline electroplating solution may be pH 10 to 14, preferably pH 11 to 13, more preferably pH 12 to 13. It was discovered that a pH in this range was found to improve the bath stability and brightness of the deposits. This is especially true for a pH above pH 11. Importantly, it was discovered that the copper complex in the electroplating solution becomes unstable at a pH < 11. In terms of long term stability of components which contact the inventive solution, a pH lower or equal to 13 is beneficial compared to a pH which is higher than pH 13 since the corrosive potential (concentration of the OH⁻ ions) of the solution is higher at pH > 13 and the aspect of the deposit becomes drabber.

[0025] The electroplating solution may be at a temperature of 20 to 80 °C, preferably 30 to 70 °C, more preferably 40 to 60 °C. This temperature range was found to be the best compromise between bath stability and process efficiency during electroplating. This is especially true for a temperature in the range of 40 to 60 °C,

[0026] The inventive electroplating solution can further comprise a wetting agent. The advantage of a wetting agent in the electroplating solution is that hydrogen formation during electroplating is reduced. Preferred wetting agents are selected from the group consisting of cocamido propyl betaine, ethoxy ester phosphate and sodium lauryl ether sulfate.

[0027] The invention further provides a method for electroplating a gold alloy deposit on an electrode or substrate, the method comprising electroplating the electrode or substrate with the inventive electroplating solution for 5 to 30 minutes at a current density of 0.1 to 4 A/dm², characterized in that the electroplating solution is kept at a constant temperature of 20 to 80 °C.

[0028] The current density preferably ranges from 0.8 A/dm² to 2.2 A/dm², more preferably 1.0 A/dm² to 2.0 A/dm². It was discovered that a current density lower than 1 A/dm² leads to a satin aspect and with more than 2 A/dm², the deposit is burned.

[0029] In a preferred embodiment of the inventive method, the electroplating solution is kept at a constant temperature of 30 to 70 °C, more preferably at a temperature of 40 to 60 °C.

[0030] Furthermore, an electrode or substrate comprising a bright, electroplated deposit of a gold-copper alloy is provided, characterized in that the deposit has 14 to 22 karats of gold in the alloy and is corrosion resistant according to NFS 80772, ISO 4538 and/or ISO 9227.

[0031] Preferably, the electrode or substrate has a color matching the Swiss standard ISO 8654 from 0.5 N to 5 N and/or has excellent stability. The color of the electrode or substrate matching the Swiss standard ISO 8654 may be regulated by varying the ratio of alloy metal ions to gold ions in the inventive solution and may e.g. be 0.5 N, 1 N, 1.5 N, 2 N, 2.5 N, 3 N, 3.5 N, 4 N, 4.5 N or 5 N, or any value in between said values. Stability of the color is excellent i.e. the color is stable for at least 6 months without modification of the Lab color coordinates.

[0032] In a preferred embodiment, the inventive electrode or substrate is producible by the inventive method.

[0033] The inventive electroplating solution may be used for electroplating an electrode or substrate selected from the group consisting of decorative substrates, jewelry, watches and eyeglass frame.

[0034] With reference to the following figures and examples, the subject according to the present invention is intended to be explained in more detail without wishing to restrict said subject to the special embodiments shown here.

Example 1

Production of the gold stock solution

[0035] First of all, a complex of gold and hydantoin is obtained after a reaction between trivalent gold coming from HAuCl₄ and an hydantoin-based compound, preferably 5,5 dimethylhydantoin. Finally, the complex is stabilized by adding a sulfite salt to the solution, preferably Na₂SO₃ or K₂SO₃. The solution is kept between pH 12 and 13.

[0036] Additional sulfite is only added after the formation of the gold complex. It was discovered that it is beneficial to separate the sulfite addition from the gold complexation, because otherwise a substantial extra time will be needed to obtain a bright deposit; this waiting period is not suitable for an industrial application and is avoided by adding directly the sufficient amount of sulfite compound to the already complexed gold solution with at least a 1:1 molar ratio.

Example 2

Production of the copper stock solution

[0037] First of all, a complex of copper ions with a complexing agent is to be produced. The copper ions remain equimolar or in a molar excess to the sugar alcohol, preferably equimolar to a 4-fold molar excess. To promote complex formation, a base (e.g. NaOH) is added to the solution to generate an alkaline pH (pH ≈ 14). Consequently, at least a

certain part of the copper ions forms a complex with the sugar alcohol molecules.

[0038] This copper complex solution is then mixed with the solution obtained in Example 1 to produce an alkaline, cyanide-free solution for electroplating of a gold-copper alloy.

Example 3

Production of zinc, iron and indium stock solutions

[0039] It was discovered that if the cyanide-free solution comprises up to 3 g/L of zinc, iron and/or indium ions, the brightness and the color tone of the gold alloy deposit obtained with the present invention is improved. If desired, the amount or type of chelating agent in the cyanide-free solution may be adjusted. In order to achieve excellent brightness and color tone, certain molar ratios or molarities of chelating agents dependent on the type of ions [Fe^{3+} , Zn^{2+} or In^{3+}] were found to be beneficial (see Tables 1 and 2).

Table 1

Iron as Fe^{3+}	Stable in alkali media with a solubility bottom limit for the molar ratio between Fe : chelating compound* = 1:3
Zinc as Zn^{2+}	Stable in alkali media with a solubility bottom limit for the molar ratio between Zn : chelating compound = 2:1
Zinc as $[\text{ZnOH}_4]^{2-}$	<i>not complexed</i>
Indium as In^{3+}	Stable in alkali media with a solubility bottom limit for the molar ratio between In : chelating compound = 1:5
* The chelating compound may e.g. be a sugar alcohol	

Table 2

	chelating compound		
	sugar-alcohol	amino acid	sulfur compound
Iron as Fe^{3+}	0.55 - 55 g/L	0.025 g/L - 2.5 g/L	<i>Harmful for Fe deposition</i>
Zinc as Zn^{2+}	0.730 g/L - 73 g/L	0.017 g/L - 1.7 g/L	<i>Harmful for Zn deposition</i>
Zinc as $[\text{ZnOH}_4]^{2-}$	<i>Doesn't need to be complexed</i>		
Indium as In^{3+}	0.38 g/L - 38 g/L	0.16 g/L - 16 g/L	0.057 g/L - 5.68 g/L

Example 4

Production of a coating of a gold-copper-zinc alloy on a brass substrate, bronze substrate and nickel substrate

[0040] First of all, the conductive substrate to be treated, in the first case a substrate made of brass, was prepared using the Coventya S.A.S. brass substrate preparation product PRESOL 7073 as cleaner and PICKLANE 33 as activator of the surface.

[0041] The electroplating was performed with the following alkaline, cyanide-free electroplating solution:

- Gold (as $\text{Au}(5,5\text{-dimethylhydantoin})_3$): 3 g/L
 - Copper (as $\text{Cu}_2(\text{sorbitol})$): 2 g/L
 - Zinc (as $\text{Zn}_2(\text{sorbitol})$): 50 mg/L
 - Potassium or Sodium Phosphate tri basic: 100 g/L
 - Sodium sulfite: 75 g/L
- (Comprising ca. 9.75 g/L from the gold stock solution) pH is adjusted to pH 12 (with phosphoric acid)

[0042] The gold complex comes from the gold stock solution prepared as described in example 1, the copper complex comes from the copper stock solution prepared as described in example 2 and the zinc complex comes from the zinc

stock solution prepared as described in example 3, table 1.

[0043] The electroplating was performed at 50 °C, since this temperature turned out to be the best compromise between the electrolyte efficiency and the zinc deposition which is disturbed by high temperature.

[0044] After plating for at a current density of 1 A/dm² for 10 min., an 18 karat gold-copper-zinc alloy deposit was obtained on the brass electrode.

[0045] After the first deposition on a brass substrate, the same electrolyte solution was employed for electroplating a brass substrate having a white bronze under layer and a brass substrate having a nickel under layer. The same electroplating parameters were used (1 A/dm² for 10 min.).

[0046] In both cases, the deposit produced was very bright, with a 5 N color (regarding the ISO 8654 standard) and an excellent resistance to tarnishing. Yet, the tarnishing resistance was better with a white under layer. Furthermore, the deposits were free of any faults such as pitting or stress cracking and demonstrated an excellent resistance to corrosion.

[0047] The following parameters of the electroplating bath containing the alkaline, cyanide-free solution were found to be beneficial for the properties of the resulting deposit:

- > Incubating the bath for at least 12 hours, preferably 24 hours, before electroplating to reach perfect stability;
- > Agitating the bath by stirring the electroplating solution, for example with a magnetic stirrer. Stirring of the bath is beneficial compared to moving the parts since the deposit is disturbed if parts are in motion.

Example 5

Production of a coating of a gold-copper-zinc alloy on a brass substrate and nickel substrate

[0048] First of all, the conductive substrate to be treated, in the first case a substrate made of brass, was prepared using the Coventya S.A.S. brass substrate preparation product PRESOL 7073 as cleaner and PICKLANE 33 as activator of the surface.

[0049] The electroplating was performed with the following alkaline, cyanide-free electroplating solution:

- Gold (as Au(5,5-dimethylhydantoin) ₃):	3 g/L
- Copper (as Cu ₂ (sorbitol)):	2 g/L
- Zinc (as Zn ₂ (sorbitol)):	350 mg/L
- Antimony (as KSb(OH) ₆):	500 mg/L
- Potassium or Sodium Phosphate tri basic:	100 g/L
- Sodium sulfite:	75 g/L
(Comprising ca. 9.75 g/L from the gold stock solution) pH is adjusted to pH 12 (with phosphoric acid)	

[0050] The gold complex comes from the gold stock solution prepared as described in example 1, the copper complex comes from the copper stock solution prepared as described in example 2 and the zinc complex comes from the zinc stock solution prepared as described in example 3, table 1.

[0051] The electroplating was performed at 50 °C, since this temperature turned out to be the best compromise between the electrolyte efficiency and the zinc deposition which is disturbed by high temperature.

[0052] After plating at a current density of 1 A/dm² for 10 min., a 18 karat gold-copper-zinc alloy deposit was obtained on the brass electrode.

[0053] After the first deposition on a brass substrate, the same electrolyte solution was employed for electroplating a brass substrate having a white bronze under layer and a brass substrate having a nickel under layer. The same electroplating parameters were used (1 A/dm² for 10 min.).

[0054] In both cases, the deposit produced was very bright, with a 1 N color (regarding the ISO 8654 standard) and an excellent resistance to tarnishing. Furthermore, the deposits were free of any faults such as pitting or stress cracking and demonstrated an excellent resistance to corrosion.

Example 6

Production of a coating of a gold-copper alloy on a brass substrate having or not white under layer

[0055] The same electrolyte and same operating conditions were used as in examples 3 and 4, but without the zinc (as Zn₂(sorbitol)).

[0056] The results were deposits having a hazy aspect and burning problems.

Example 7

Production of a coating of an alloy comprising gold, copper and either iron or indium on a brass substrate

[0057] The conductive substrates to be treated were brass hull cells. The brass hull cells were prepared using the Coventya S.A.S. brass substrate preparation product PRESOL 7073 as cleaner and PICKLANE 33 as activator of the surface.

[0058] The electroplating was performed with the following alkaline, cyanide-free electroplating solutions, comprising different alloy metals and complexing agents, respectively (see Figure 1):

- Gold (as Au(5,5-dimethylhydantoin)₃): 3 g/L
 - Copper (as Cu₂(sorbitol)): 2 g/L
 - Alloy metal type and concentration: 50 - 200 mg/L
 - Complexing agent type and concentration: see Table 4
 - Potassium or Sodium Phosphate tri-basic: 100 g/L
 - Sodium sulfite: 75 g/L
- (Comprising ca. 9.75 g/L from the gold stock solution) pH is adjusted to pH 12 (with phosphoric acid)

[0059] The gold complex comes from the gold stock solution prepared as described in example 1 and the copper complex comes from the copper stock solution prepared as described in example 2.

[0060] Plating was performed with a current density of 1 A/dm² for 10 minutes. Characteristics of the deposits after electroplating are highlighted in Figure 1.

Example 8

Production of a gold-copper alloy on a brass substrate having different karats of gold in the alloy

[0061] The conductive substrate to be treated was brass hull cells. The brass hull cells were prepared using the Coventya S.A.S. brass substrate preparation product PRESOL 7073 as cleaner and PICKLANE 33 as activator of the surface.

[0062] The electroplating was performed with the following alkaline, cyanide-free electroplating solutions comprising different amounts of copper as alloy metal:

- Gold (as Au(5,5-dimethylhydantoin)₃): 3 g/L
 - Copper (as Cu₂(sorbitol)): 1-4 g/L
 - Zinc (as Zn₂(sorbitol)): 25 - 150 mg/L
 - Potassium or Sodium Phosphate tri-basic: 100 g/L
 - Sodium sulfite: 75 g/L
- (Comprising ca. 9.75 g/L from the gold stock solution) pH is adjusted to pH 12 (with phosphoric acid)

[0063] The gold complex comes from the gold stock solution prepared as described in example 1, the copper complex comes from the copper stock solution prepared as described in example 2 and the zinc complex comes from the zinc stock solution prepared as described in example 3, table 1.

[0064] Plating was performed with a current density of 1 A/dm² for 10 minutes. The relationship between copper concentration in the electrolyte and the karat of the deposit is highlighted in Table 3:

Table 3

Cu content	1 g/L	2 g/L	3 g/L	4 g/L
Zn content	25 mg/L	50 mg/L	75 mg/L	100 mg/L
Karats	20 KT	18 KT	16 KT	14 KT

[0065] Table 4 shows the dependency of the aspect and color of a deposit produced with variants of the inventive electroplating solutions. In particular, it can be seen that all deposits are bright if indium, iron or zinc ions were comprised in the inventive electroplating solution. Furthermore, it is evident that the color of the deposit can be selectively regulated by the type of alloy ions (e.g. zinc, indium or iron) which are comprised in the electroplating solution.

Table 4

Example	alloying metal	complexing agent	molar ratio of alloy metal : complexing agent	alloy metal concentration	aspect of the deposit	color of the deposit
7	indium	NTA	1:2	50 - 200 mg/L	Bright	From pink to grey as indium content increases
7	indium	Sorbitol	1:5	50 - 200 mg/L	Bright	From pink to grey as indium content increases
7	indium	Cysteine	1:4	50 - 200 mg/L	Bright	From pink to grey as indium content increases
7	iron	Sorbitol	1:3	50 - 200 mg/L	Bright	From pink to 0.5 N color as iron content increases

Claims

- Alkaline, cyanide-free electroplating solution for electroplating of a gold-copper alloy, comprising
 - 0.5 to 10 g/L of gold ions;
 - 1.0 to 40 g/L of hydantoin, a salt or a derivative thereof;
 - 60 to 200 g/L of a sulfite salt;
 - 0.1 to 8 g/L of copper ions; and
 - 0 to 3 g/L of zinc, iron and/or indium ions;
 - 0 to 75 g/L of a complexing agent which is different from hydantoin, a salt or a derivative thereof.
- Electroplating solution according to the preceding claim, **characterized in that** the gold ions are at least partially complexed by hydantoin or its derivatives.
- Electroplating solution according to one of the preceding claims, **characterized in that** the concentration of the sulfite salt is 65 to 160 g/L, preferably 70 to 120 g/L, more preferably 75 to 100 g/L.
- Electroplating solution according to one of the preceding claims, **characterized in that** the molar ratio between gold ions and hydantoin, a salt or a derivative thereof, is 1:2 to 1:6, preferably 1:2.5 to 1:5, more preferably 1:3 to 1:4.
- Electroplating solution according to one of the preceding claims, **characterized in that** the concentration of the copper ions is 0.2 to 10 g/L, preferably 0.5 to 7.5 g/L, more preferably 1 to 5 g/L.
- Electroplating solution according to one of the preceding claims, **characterized in that** the concentration of zinc, iron and/or indium ions is 10 mg/L to 3 g/L, preferably 20 mg/L to 1 g/L, more preferably 50 mg/L to 500 mg/L.
- Electroplating solution according to one of the preceding claims, **characterized in that** the complexing agent is selected from the group consisting of carbohydrates, amino acids, sulfur compounds and sugar alcohols, preferably selected from the group consisting of sorbitol, mannitol, gluconate, erythritol, xylitol, nitrilotriacetic acid and cysteine.
- Electroplating solution according to one of the preceding claims, **characterized in that** the complexing agent has a concentration 0.1 to 60 g/L, preferably 0.5 to 40 g/L, more preferably 1 to 20 g/L, most preferably 1.5 to 10 g/L.

9. Electroplating solution according to one of the preceding claims, **characterized in that** the electroplating solution further comprises a buffering agent, preferably a buffering agent which is selected from the group consisting of phosphate, formate, pyrophosphate and citrate.
- 5 10. Electroplating solution according to one of the preceding claims, **characterized in that** the pH of the solution is pH 10 to 14, preferably pH 11 to 13, more preferably pH 12 to 13.
11. Method for electroplating a gold-copper alloy deposit on a substrate, the method comprising electroplating the electrode with an electroplating solution according to one of claims 1 to 10 for 5 to 30 minutes at a current density of 0.1 to 4 A/dm², **characterized in that** the electroplating bath is kept at a constant temperature of 20 to 80 °C.
- 10 12. Substrate comprising a bright, electroplated deposit of a gold-copper alloy, **characterized in that** the karat of the deposit is comprised between 14 and 22 kts and the deposit is corrosion resistant according to NFS 80772, ISO 4538 and/or ISO 9227.
- 15 13. Substrate according to claim 12, **characterized in that** it has a colour matching the Swiss standard ISO 8654 from 0.5 N to 5 N and/or has a stability for at least 6 months without modification of the Lab colour coordinates.
- 20 14. Substrate according to one of claims 12 or 13, **characterized in that** it is producible by the method according to claim 11.
- 15 15. Use of the electroplating solution according to one of claims 1 to 10 for electroplating a gold-copper alloy on a substrate selected from the group consisting of decorative substrates, jewelry, watches and eyeglass frame.

Figure 1

Example	alloying metal	complexing agent	molar ratio of alloy metal : complexing agent	alloy metal concentration	aspect of the deposit	color of the deposit
6	indium	NTA	1:2	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	indium	Sorbitol	1:5	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	indium	Cysteine	1:4	50 – 200 mg/L	Bright	From pink to grey as indium content increases
6	iron	Sorbitol	1:3	50 – 200 mg/L	Bright	From pink to 0.5 N color as iron content increases



EUROPEAN SEARCH REPORT

Application Number
EP 12 19 2458

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Y	* claims 1,9,10; example 3 * * page 2, paragraphs 2,8 * * page 3, paragraphs 14,20 * * page 7, paragraph 51 *	1-11,15	
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Y	US 5 750 018 A (BRASCH WILLIAM R [US]) 12 May 1998 (1998-05-12) * claim 1; examples 1,5,6 * * column 3, lines 29-32 *	1-3,5, 7-11,15	
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Place of search The Hague		Date of completion of the search 10 March 2014	Examiner Gault, Nathalie
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