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(71) Applicant: **Enthone, Inc.**
West Haven, CT 06516 (US)

(72) Inventor: **Desthomas, Guy**
74140 Veigy (FR)

(74) Representative: **Michalski Hüttermann & Partner**
Patentanwälte mbB
Speditionstraße 21
40221 Düsseldorf (DE)

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(54) **ELECTROLYTE AND METHOD FOR ELECTROLYTIC DEPOSITION OF GOLD-COPPER
ALLOYS**

(57) This invention relates to an electrolyte as well
as a method for the deposition of a gold-copper alloy on
a substrate surface. With the electrolyte and method dis-
closed, deposition of gold-copper alloys with a value of
carat in the range of 12 to 19 kt is possible. Beneath a
source of gold and copper, the inventive electrolyte com-
prises potassium cyanate (KCN) in a concentration ca-
pable to maintain a copper to KCN ratio in the range of
3 to 7, and at least one complexing agent of the group

consisting of ethylenediamine tetraacetic acid, diethyl-
enetriamine pentaacetic acid, nitrilo-triacetic acid, ethyl-
enediamine tetraacetic acid [EDTA], diethylenetriamine
pentaacetic acid and nitrilotriacetic acid [NTA] Hydrox-
yethyl imino diacetic acid [HEIDA], nitrilo propionic diace-
tic acid [NPDA], imino diacetic acid [IDA], nitrilo trimeth-
ylphosphoric acid [NTMA, Dequest 2000], triethanol
amine [TEA].

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Description

[0001] This invention relates to an electrolyte as well as a method for the electrolytic deposition of a gold-copper alloy on a substrate surface.

[0002] It is a well-known technique in the art to plate the surfaces of articles with alloys of gold for decorative or functional purposes. Especially for application in jewellery or in the field of electro-technical devices, there is a need for alloy layers which can be varied in respect of their physical properties like brightness, hardness, wear resistance or colour. These properties are influenced by the composites of the alloys, e. g. the metals co-plated, as well as by the composition of the bath used for the deposition of the alloy, e. g. the electrolyte. Further, also the method and the plating parameters like temperature and current density are influencing the plating result in important ways.

[0003] In the state of the art, there has been a number of proposals to deposit alloy layers of gold-copper alloys.

[0004] For example, U.S. patent 5,006,208 discloses a galvanic gold alloying bath which contains beneath gold and copper in form of cyanide compounds a selenium compound. The deposit achieved from this galvanic bath is soft, light yellow and matt. The gold-alloy containing is constituted by 14 - 18 carat.

[0005] European patent EP 0 384 679 B1 discloses a bath for the electrolytic deposition of gold-copper alloy as well as a method for electroplating articles using such a bath. An electrolyte is disclosed which contains gold in form of a cyanide compound, copper in the form of a cyanide compound as well as tellurium or bismuth in the form of water soluble compounds.

[0006] Also, European patent application 0 566 054 A1 discloses a solution for electroplating gold-copper alloys. Here, an electrolyte is disclosed comprising a soluble gold compound present as a gold cyanide complex, a soluble copper compound present as a copper cyanide complex as well as a soluble divalent sulfur compound in an amount sufficient to brighten the alloys. The brightening additive may be a thiocyanate, thiomalic acid, imidazolidinethione, a sulfite or thiobarbituric acid.

[0007] All of these have drawbacks when the deposition of a thick deposit is needed. So, Au/Cu/Ag-processes can produce thick deposits as a coat but the deposition of silver creates a strong nodulation not acceptable for thick deposits. Further, some of these processes known from the state of the art comprise cadmium, which is deemed to be toxic and may be banned for application.

[0008] It is therefore an object of the invention to provide an improved electrolyte as well as an improved method for the electrolytic deposition of gold-copper alloy.

[0009] In view of the electrolyte, this object is solved by an electrolyte for the electrolytic deposition of a gold-copper alloy on a substrate surface, wherein the electrolyte comprises beneath a source of gold and copper potassium cyanide (KCN) in a concentration capable to maintain a copper to KCN ratio in the range of 3 to 7, and at least one complexing agent of the group consisting of ethylenediamine tetraacetic acid [EDTA], diethylenetriamine pentaacetic acid and nitrilotriacetic acid [NTA] hydroxyethyl imino diacetic acid [HEIDA], nitrilo propionic diacetic acid [NPDA], imino diacetic acid [IDA], nitrilo trimethylphosphoric acid [NTMA, Dequest 2000], triethanol amine [TEA].

[0010] The electrolyte according to the invention can comprise gold in a concentration between 2 to 20 g/l and copper in a concentration between 10 to 50 g/l. The at least one complexing agent of the group mentioned above is comprised in the inventive electrolyte in a concentration between 0,05 to 0,6 mol/l. It is believed that the strong chelating agents beneath functioning as complexing agent will contribute to the conductivity of the electrolyte.

[0011] The inventive electrolyte may further comprise one of at least one metal of the group consisting of Sb, Se, Ag, Pt, Ni and Zn.

[0012] Those metals will influence the physical properties of the alloy deposit. For example, selenium functions as brightener for the deposit. The same is true for tellurium and antimony.

[0013] Platinum is believed to result in better homogeneity of the alloy for high carat and thickness.

[0014] Zinc and nickel can function as grain refiner as well as stabilizer to the free KCN.

[0015] Gold is believed to function as efficiency booster to yield in higher plating velocity and carat.

[0016] The metals mentioned above can be comprised in the inventive electrolyte in an amount between 0,1 mg/l and 10 g/l. It is within the scope of the invention that the electrolyte can comprise further additive metals to influence the physical properties of the deposit.

[0017] The inventive electrolyte can further comprise a surface active agent or wetting agent which will function as brightener. A capable surface active agent which can be comprised in the electrolyte is for example sodium-lauryl-etherphosphate. Further, commercially available products known by name of nonionic, cationic, or amphoteric surfactants can be employed single or in combinations.

[0018] The amount of the surface active agent in the inventive electrolyte may vary in a range of 0,1 to 5 ml/l.

[0019] It is further within the scope of the invention that the electrolyte can comprise secondary brightener and/or stabilizing agents. Examples for such a secondary brightener and/or stabilizing agents are pyridin sulfonic acid and ammonium hydrogen difluoride. The amount of these secondary brightener and/or stabilizing agents may vary in a range between 0,1 g/l to 10 g/l.

[0020] The pH-value of the inventive electrolyte may vary in a range of pH 8 to pH 13, with a preferred pH-value of about 11. To influence the pH-value, the inventive electrolyte may comprise alkaline hydroxide or alkaline earth hydroxide.

[0021] Beneath the inventive electrolyte, with this invention a method for depositing a gold-copper alloy layer on a substrate surface is provided, wherein the method comprises the steps:

pretreating the substrate surface to be plated;

contacting the substrate surface to be plated with the inventive electrolyte;

and

conducting a current between the substrate and an anode.

[0022] According to the inventive method, the current density conducted between the substrate and the anode may vary in a range of 0,2 to 2 A/dm².

[0023] According to the inventive method, during contacting the substrate surface with the inventive electrolyte and applying a current the temperature of the electrolyte is in the range of 70° C to 90° C.

[0024] Surprisingly, it was found that there is a relationship between temperature and current density applied to the substrate as following:

Temperature increases: efficiency increases (and opposite)

Current density increases: efficiency decreases (and opposite).

[0025] It is a main advantage of the invention to offer the possibility of thick and bight gold alloy layers on substrate surfaces without addition of toxic metal like cadmium. The inventive electrolyte together with the inventive method permits to produce a large range of carat suitable for plating and electroforming producing accurate value of carat between 18 and 14. Surprisingly, it was found that the value of carat can be controlled by measurement of efficiency in Mg/A.nm. According to the relationship of temperature and current density disclosed above, the right efficiency for an adequate value of carat is obtained by tuning the current density and temperature respectively.

[0026] To control the plating process it is within the scope of the invention that all operating conditions are controlled by an adequate computer system to get an adequate value of carat.

[0027] Surprisingly, it was found that a further advantage of the deposits resulting from the inventive- electrolyte and the inventive method showing a good resistance to nitric acid stripping even with a carat value of 14. This is especially useful for electroforming processes in jewellery when nitric acid stripping is necessary to clean the inside of pieces.

[0028] A further advantage of the deposit yield by the inventive electrolyte and the inventive method is the possibility to heat-treat the deposited alloys in order to get an optimum ductility for a gold alloy. This is advantageously for both decorative and functional applications. By heat-treating the alloys deposited, a relatively high hardness is achieved. Relatively high in these terms means higher than that of the metallurgical alloy.

[0029] For example, after a heat-treatment at 500° C for 10 minutes under controlled atmosphere nitrogen or cracking ammonia, the hardness rises from 280 HV to 380 HV while the aspect of surface isn't changed by oxidation.

[0030] A further advantage of the deposits obtained from the inventive electrolyte is the good solder ability of the alloys. This characteristic is especially important in electroforming when it is necessary to close holes done to empty the mandrels and for further artistic work.

[0031] Due to the strong complexing power of the complexing agent used according to this invention, the electrolyte is relatively none-sensitive to possible contaminations from various metals like Sn, Zn, Ag, Ni or Cr coming from different sources like drag ins from pre-treatment, mandrels composition or replenishment products. Generally, such types of contamination create an instability of the relation between current density and efficiency which may cause problems during electroforming processes. So, the non-sensivity of the electrolyte to this contaminations is a further advance of this invention.

[0032] By the inventive electrolyte as well as the inventive method gold-copper alloy deposits on substrate surfaces are obtainable showing a thickness of > 20 microns and a carat in the range of 12 to 19 carat. By the invention, also electroforming at a thickness of 200 microns and more is possible.

[0033] Furthermore, the inventive electrolyte is also of high economic interest since it shows a minimum turn-over of 0,25 kg/l.

[0034] The following embodiments are describing the invention in terms of examples, while the invention is not limited to this embodiments.

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Examples:

[0035] The following electrolytes for gold-copper-alloy deposition are embodiments for the invention

Au/Cu alloys					
Bath no	1	2	3	4	5
Gold	4	8	6	6	5
Copper	20	10	20	30	20
Free KCN	5	2	10	10	7
Ratio Cu/KCN	4	5	2	3	3
Potassium carbonate		10			
Potassium sodium tart rate			10		
Di Potassium hydrogen phosphate	10				
EDTA	5			5	
HEIDA		5			
NTA	10			50	
NPDA					5
IDA			20		
NTMP					50
TEA	10	50			
PSA			2		2
Ammonium Hydrogen difluoride				5	2
Sb mg/l				2	
Zn g/l				0.5	
Pt g/l		0.5			1
Ag mg/l			10		
Wetting agent	0.1 to 5 g/l or ml/l				
KOH	to adjust ph to 10/12				

Pre-treatment						
	Product	Temperature	Time	CD	Brass	Stainless Steel
Electroless cleaner	Enprep 100	60°C	2 mn		x	x
Rince water					x	x
Electrolytic cleaner	Enprep 285	40°C	1 mn	3 A/dm ²	x	x
Rince water					x	x
Neutralisation	actane 345	room	30 sec		x	x
Rince water					x	x
Gold flash	Aurobond XDA	40°C	2 mn	4 A/dm ²		x
Rince water						x
Gold flash	Aurobond TN	50°C	30 sec	1 A/dm ²	x	x
Rince water					x	x
Acide gold	Karatclad Omega	30°C	10 mn	1 A/dm ²	x	x

Claims

1. An electrolyte for the electrolytic deposition of a gold-copper alloy on a substrate surface, wherein the electrolyte

comprises beneath a source of gold and copper potassium cyanide (KCN) in a concentration capable to maintain a copper to KCN ratio in the range of 3 to 7, and at least one complexing agent of the group consisting of ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid, nitrilo-triacetic acid, ethylenediamine tetraacetic acid [EDTA], diethylenetriamine pentaacetic acid and nitrilo-triacetic acid [NTA] Hydroxyethyl imino diacetic acid [HEIDA], nitrilo propionic diacetic acid [NPDA], imino diacetic acid [IDA], nitrilo trimethylphosphoric acid [NTMA, Dequest 2000], triethanol amine [TEA].

2. The electrolyte according to claim 1, comprising gold in a concentration between 2 to 20 g/l and copper in a concentration between 10 to 50 g/l.

3. An electrolyte according to one of the claims 1 or 2, wherein the at least one complexing agent of the group consisting of ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid, nitrilo-triacetic acid, ethylenediamine tetraacetic acid [EDTA], diethylenetriamine pentaacetic acid and nitrilo-triacetic acid [NTA] Hydroxyethyl imino diacetic acid [HEIDA], nitrilo propionic diacetic acid [NPDA], imino diacetic acid [IDA], nitrilo trimethylphosphoric acid [NTMA, Dequest 2000], triethanol amine [TEA] comprised in a concentration between 0,05 to 0,6 mol/l.

4. An electrolyte according to one of the claims 1 to 3, further comprising ions of at least one metal of the group consisting of Te, Sb, Se, Ag, Pt, Ni and Zn.

5. An electrolyte according to claim 4, comprising the ions of at least one metal of the group consisting of Sb, Se, Ag, Pt, Ni and Zn in an amount between 0,1 mg/l and 10 g/l.

6. An electrolyte according to one of the claims 1 to 5, further comprising a surface active agent.

7. An electrolyte according to claim 6, wherein the surface active agent is a sodium-lauryl-etherphosphate.

8. An electrolyte according to claim 7, comprising the surface active agent in an amount of 0,1 to 5 ml/l.

9. An electrolyte according to one of the claims 1 to 8, further comprising secondary brightener and/or stabilising agents.

10. An electrolyte according to one of the claims 1 to 4, wherein the pH-value of the electrolyte is in the range of 8 to 13.

11. A method for depositing a gold-copper-alloy layer on a substrate surface, wherein the method comprises the steps:

- pretreating the substrate surface to be plated;
- contacting the substrate surface to be plated with an electrolyte according to one of the claims 1 to 10; and
- conducting a current between the substrate and an anode.

12. The method according to claim 11, wherein the current density conducted between the substrate and the anode is in the range of 0,2 to 2 A/dm².

13. A method according to claim 11 or 12, wherein the temperature of the electrolyte is in the range of 70°C to 90°C.

14. A gold-copper alloy deposit on a substrate surface, wherein the thickness of the deposit is >20 microns and the carat is in the range of 12 to 19kt.



EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 193 848 A1 (EMMENEGGER HEINZ) 10 September 1986 (1986-09-10)	14	INV. C25D3/58 C25D3/62
Y	* claims 4,5,7,9,12-14 * * Formulation B1-B5 of; example 3; table 1 * * column 5, lines 52-61 * * column 6, lines 59-62 *	1-13	
X	GB 1 375 611 A (LEA RONAL INC [US]) 27 November 1974 (1974-11-27)	14	
Y	* claims 1-7; examples 1,3,4 * * page 1, lines 17-23 * * page 2, lines 31-35 * * page 3, lines 4-12,62-65 * * page 5, lines 33-35 * * page 6, lines 66-81 *	1-13	
X	GB 2 053 276 A (ALIPRANDINI P) 4 February 1981 (1981-02-04)	14	
Y	* claims 1-5,7; example 2 * -----	1-13	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			C25D C23C
Place of search		Date of completion of the search	Examiner
The Hague		12 April 2017	Gault, Nathalie
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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12-04-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0193848 A1	10-09-1986	CH 662583 A5	15-10-1987
		DE 193848 T1	18-12-1986
		DE 3665078 D1	21-09-1989
		EP 0193848 A1	10-09-1986
		US 4687557 A	18-08-1987

GB 1375611 A	27-11-1974	NONE	

GB 2053276 A	04-02-1981	CA 1159006 A	20-12-1983
		CH 632533 A5	15-10-1982
		DE 3022370 A1	22-01-1981
		FR 2459299 A1	09-01-1981
		GB 2053276 A	04-02-1981
		IT 1129220 B	04-06-1986
		US 4309256 A	05-01-1982

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 5006208 A [0004]
- EP 0384679 B1 [0005]
- EP 0566054 A1 [0006]