

(19)



(11)

EP 1 930 478 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

11.06.2008 Bulletin 2008/24

(51) Int Cl.:

C25D 3/56 (2006.01)

C25D 3/58 (2006.01)

(21) Application number: **06025184.0**

(22) Date of filing: **06.12.2006**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK RS

(71) Applicant: **Enthone, Inc.**

West Haven, CT 06516 (US)

(72) Inventor: **Lalanne, Pierre**

01170 Echenevex (FR)

(74) Representative: **Stenger, Watzke & Ring**

Intellectual Property

Am Seestern 8

40547 Düsseldorf (DE)

(54) **Electrolyte composition and method for the deposition of quaternary copper alloys**

(57) The present invention relates to an electrolyte composition as well as a method for the deposition of a quaternary copper alloy on a substrate. The electrolyte composition according to the invention comprises besides the alloying metals copper, tin and zinc, at least one metal from the group consisting of indium, gallium

and thallium. The electrolyte composition according to the invention enables to deposit white bronze layers which present a high corrosion resistance and hardness and are free of noxious heavy metals.

EP 1 930 478 A1

Description

[0001] The present invention relates to an electrolyte composition as well as a method for the deposition of quaternary copper alloys. In particular, the present invention relates to an electrolyte composition as well as a method for the deposition of bronze alloys which comprise copper, tin and zinc and a fourth alloying metal.

[0002] The deposition of metal or alloy layers on substrates is widely used in many technical fields. Substrate surfaces can be coated with corresponding metal or alloy layers for decorative or functional reasons. Thus, it is for example possible to increase the corrosion resistance of surfaces by applying corresponding corrosion resistant metal or alloy layers, to improve the abrasion resistance of the surfaces or to give them a more decorative design. Accordingly, electroplating surface coatings are used in very different fields such as for example the automobile industry, the fittings industry or the manufacture of jewellery.

[0003] In particular where the corresponding surfaces are in direct contact with a body, such as for example in the case of jewellery or also in the case of medical instruments, it has been endeavoured for a long time to design surfaces such that eventual irritations caused by for example allergies or heavy metal intoxications are avoided.

[0004] In particular bronzes comprise a non negligible portion of heavy metals, such as for example lead, and they can also comprise portions of nickel which is suspected of provoking allergies if it is in direct contact with the skin.

[0005] Furthermore, substrates are often provided with nickel and/or chromium layers for decorative purposes. Since these substances are suspected of provoking allergies, it is endeavoured, in particular in the field of the jewellery industry, to replace such coatings with harmless coatings that present the same or better properties.

[0006] It is thus the object of the present invention to provide an electrolyte composition for the deposition of quaternary copper alloy layers on substrates, which is free of noxious heavy metals. Furthermore, it is the object of the present invention to provide a corresponding method for the deposition of such alloy layers.

[0007] Concerning the electrolyte composition, this aim is achieved by an electrolyte composition for the deposition of a quaternary copper alloy on a substrate, comprising at least copper, tin and zinc in form of the ions thereof as well as ions of a metal that is selected from the group consisting of indium, gallium and thallium. Thallium is proved to be a brightener (grain refiner) in the electrodeposition of bronze alloys. With a concentration of 0.05 g/l in the electrolyte, the deposit can contain up to 1 % of this elements.

[0008] Surprisingly it has been found that the addition of a metal selected from the group consisting of indium, gallium and thallium, to bronzes comprising copper, tin and zinc clearly improves the surface properties of the

deposited layers with regard to hardness and corrosion resistance. Hereby, the thus deposited bronze alloys can be very well used in the field of decorative coatings as well as electronics.

5 **[0009]** The addition of an alloying metal selected from the group consisting of indium, gallium and thallium, makes it possible to deposit white, brilliant bronze alloy layers which do not release any noxious metals. Hereby, the thus deposited copper alloy layers can also be used as an alternative of nickel or chromium coatings.

10 **[0010]** The white metals such as tin, zinc as well as the metals from the group consisting of indium, gallium and thallium, can be widely varied in the electrolyte composition according to the invention, whereby copper alloy layers having surface properties that can be widely adjusted can be deposited. The addition of a fourth alloying metal of the described type to bronze alloys on the base of copper, tin and zinc permits to clearly increase the corrosion resistance of the deposited layers against aggressive environmental influences such as for example salt water or human sweat. Furthermore, the hardness of the deposited alloy layers is significantly increased by the addition of the fourth alloying metal.

15 **[0011]** The electrolyte compositions according to the invention comprise cyanide besides the mentioned alloying metals. Herein, the cyanide concentration can vary in a range comprised between 1 and 100 g/l according to the invention, wherein as cyanide source not only alkali-cyanides but also the alloying metals of the electrolyte composition in form of cyanide complexes, such as for example copper cyanide or zinc cyanide, can be added.

20 **[0012]** Furthermore, the alloying metals of the electrolyte composition can be added in form of the soluble oxides, sulphates thereof or other suitable soluble compounds.

25 **[0013]** Besides the mentioned alloying metals, the electrolyte composition according to the invention comprises complexing agents for the complexation of the metals present in the electrolyte composition. Herein, suitable complexing agents are for example nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), phosphonates such as for example the phosphonate that is distributed by the company Monsanto under the name "Dequest", derivatives or salts of the D-gluconic acid as well as alkali hydroxides. Depending on the alloying metal concentrations, such complexing agents can be contained in the electrolyte composition according to the invention singly or in a suitable mixture.

30 **[0014]** Furthermore, the electrolyte compositions according to the invention can comprise alkali salts of phosphonic acids, such as for example ethylenediaminetetra(methylphosphonic acid) (EDTMPA) or 1-hydroxyethylenediphosphonic acid (HEDP or etidronic acid).

35 **[0015]** The function of these compounds is to maintain indium, gallium and thallium in solution by forming soluble complexes which are strong enough in order to regulate

their co-deposition with copper, tin and zinc.

[0016] Without being limited to this theory it appears that zinc deposition is more relied to these complexing agents, than to the cyanide complex $K_2Zn(CN)_4$.

[0017] Furthermore, the electrolyte composition according to the invention can content Rochelle salt (Sodiumpotassiumtartrat), and (or) glycolic acid, for example in form of alkali salts thereof. These salts function as conductive salts and as pH buffers to the electrolyte. Besides the above mentioned constituents, the electrolyte compositions according to the invention advantageously comprise surface-active agents, such as for example the additive distributed by the company Enthone under the name Brightener SW or also the betaine derivate distributed under the name ATC Solution No. 10.

[0018] The copper content of the electrolyte compositions can be comprised between 1 and 30 g/l. Advantageously, the cyanide-copper-ratio is comprised between 1 : 1 and 10 : 1, calculated on the base of potassium cyanide.

[0019] The tin concentration of the electrolyte composition according to the invention can vary in a range comprised between 1 and 40 g/l, wherein it advantageously comprises a hydroxide-tin-ratio comprised between 1 : 1 and 5 : 1, calculated on the base of potassium hydroxide. The tin concentration of the electrolyte composition according to the invention can vary between 0.4 and 20 g/l.

[0020] The concentration of the fourth alloying metal selected from the group consisting of indium, gallium and thallium, can vary between 0.1 and 10 g/l, depending on the selected complexing agent. Herein, it is the object of the complexing agent to stabilize the alloying metals present in the electrolyte composition in alkaline solution, in order to avoid the precipitation of corresponding metal hydroxides.

[0021] Concerning the method, the aim of the invention is achieved by a method for the deposition of a quaternary copper alloy on a substrate comprising the process steps:

contacting the substrate with an electrolyte composition that at least comprises copper, tin and zinc in form of the ions thereof as well as ions of a metal selected from the group consisting of indium, gallium and thallium.

applying a voltage between the substrate and a counter-electrode for the electroplating deposition of a quaternary alloy layer on the substrate.

[0022] Advantageously, the set current density of the method according to the invention for the deposition of a corresponding quaternary copper alloy layer on the substrate is comprised between 0.05 and 5 A/dm², preferably between 0.1 and 3 A/dm².

[0023] The temperature during the step of contacting the substrate to be coated with the electrolyte composition according to the invention can vary between 20 and 80°C, preferably between 50 and 70°C. Below 50°C, the deposit is less bright, not homogeneous, colour is not

uniform and corrosion resistance is less good. Above 70°C, the electrolyte generates too much break-down products and consumes more energy, more potassium hydroxide and more potassium cyanide. The consequence is a quick build-up of potassium carbonate, as also a rapid ageing of the electrolyte.

[0024] Using the electrolyte composition according to the invention as well as the coating method according to the invention, quaternary copper alloys having a layer thickness of up to 20 µm can be deposited, which are free of fissures and brilliant.

[0025] The deposited layers are uniform and present a high corrosion resistance.

[0026] The corrosion resistance to Neutral Salt Spray (according to the standard ISO 9227) for the same thickness of this deposit, plated on the same substrate, is minimum twice better than for the white ternary alloy copper/tin/zinc. Corrosion resistance to artificial sweat (according to the standard ISO 3160-2) is also twice better than for the white ternary alloy copper/tin/zinc. For example, a deposit of 3 µm of copper/tin/zinc/indium according to the invention, plated on brass substrate resists more than 300 hours in the neutral salt spray test. The comparative ternary white alloy copper/tin/zinc resists less than 120 hours.

[0027] In artificial sweat test, the quaternary alloy resists 7 days, and the ternary alloy resists maximum 36 hours. The hardness of the alloy deposited according to the invention, with the following composition: 53% Cu; 29% Sn; 7% Zn; 11 % In, has been measured at 500 to 520 Hv 0.05.

[0028] The alloying metals can vary within the deposited alloy layers depending on the set electrolyte composition. Herein, the copper content of the deposited layers can vary between 52 and 55 % by mass, the tin content can vary between 23 and 35 % by mass and the zinc content can vary between 5 and 13 % by mass. The content of the fourth alloying metal selected from the group consisting of indium, gallium and thallium, can vary between 0.5 and 17 % by mass in the alloy layers deposited according to the invention, with a preferred content of 4 to 12% by mass in the alloy for optimum performances.

[0029] The following exemplary embodiments represent examples of the electrolyte composition according to the invention, which however cannot be limited to the concrete exemplary embodiments.

Example 1

Aqueous electrolyte composition comprising

[0030]

12 g/l	copper as copper cyanide
12 g/l	tin as potassium or sodium stannate
2.5 g/l	zinc as $Zn(CN)_2$ or ZnO
3 g/l	In as $In_2(SO_4)_3$
25 g/l	ethylenediaminetetra(methylphosphonic ac-

id) as sodium or potassium salt
 10 ml/l 1-hydroxyethylidenediphosphonic acid as sodium or potassium salt
 50 ml/l glycolic acid (as sodium or potassium salt)
 45 g/l KCN
 14 g/l KOH
 2 ml/l Brightener SW (brightener of Enthone Inc.)
 1 ml/l ATC solution no. 10 (surface-active agent on the base of betaine derivatives)

Example 2

[0031] A temperature of 62°C and a current density of 1.0 A/dm², from this aqueous electrolyte at in 20 minutes a 5 µm thick, white, fully bright and levelling deposits which contained 52.1 % copper, 27.6% tin, 7.7% zinc and 12.6% indium were obtained. The deposit was corrosion and tarnish resistant, with a hardness of 510 HV_{0.05}.

Example 3

[0032] From the aqueous electrolyte described in example 1, at a temperature of 62°C, a current density of 1.7 A/dm², in 44 minutes a 12.4 µm thick, white, fully bright and levelling deposits which contained 56.2% copper, 25.1 % tin, 7.3% zinc and 11.4% indium were obtained.

Example 4

[0033] A plating barrel is filled with small pieces made of brass. Rotation speed of the barrel is adjusted at 8 rotations per minute. From the aqueous electrolyte described in example 1, at a temperature of 62°C, a current density of 0.15 A/dm², in 120 minutes a 4 µm thick, white, fully bright and levelling deposits which contained 53.3% copper, 26.7% tin, 8.2% zinc and 11.7% indium were obtained.

Example 5

Aqueous electrolyte composition comprising

[0034]

13 g/l copper as copper cyanide
 13 g/l tin as potassium or sodium stannate
 2.5 g/l zinc as Zn(CN)₂ or ZnO
 2 g/l Gallium as Ga₂O₃
 25 g/l ethylenediaminetetra(methylphosphonic acid) as sodium or potassium salt
 10 ml/l 1-hydroxyethylidenediphosphonic acid as sodium or potassium salt
 50 ml/l glycolic acid (as sodium or potassium salt)
 45 g/l KCN
 14 g/l KOH
 2 ml/l Brightener SW (brightener of Enthone Inc.)

1 ml/l ATC solution no. 10 (surface-active agent on the base of betaine derivatives)

Example 6

5

[0035] From the aqueous electrolyte described in example 5, at a temperature of 62°C, a current density of 1.0 A/dm², in 20 minutes a 4.5 µm thick, white, fully bright and slightly levelling deposits which contained 52.8% copper, 38.1 % tin, 5.6% zinc and 3.5% gallium were obtained.

10

Example 7

15

Aqueous electrolyte composition comprising

[0036]

14 g/l copper as copper cyanide
 20 7 g/l tin as potassium or sodium stannate
 2.5 g/l zinc as Zn(CN)₂ or ZnO
 0.02 g/l thallium as thallium sulphate
 10 ml/l 1-hydroxyethylidenediphosphonic acid as sodium or potassium salt
 25 50 ml/l glycolic acid (as sodium or potassium salt)
 70 g/l KCN
 10 g/l KOH
 1 ml/l ATC solution no. 10 (surface-active agent on the base of betaine derivatives)

30

Example 8

[0037] From the aqueous electrolyte described in example 7, at a temperature of 55°C, a current density of 0.5 A/dm², in 20 minutes a 2.5 µm thick, white, fully bright deposits which contained 58% copper, 34% tin, 7.4% zinc, and 0.6% thallium were obtained. In this example, thallium functions as metallic brightener.

35

40

Claims

1. An electrolyte composition for the deposition of a quaternary copper alloy on a substrate, comprising at least copper, tin and zinc in form of the ions thereof as well as ions of a metal that is selected from the group consisting of indium and gallium.
2. An electrolyte composition according to claim 1, comprising 1 to 30 g/l copper.
3. An electrolyte composition according to one of the preceding claims, comprising 0.4 to 20 g/l zinc.
4. An electrolyte composition according to one of the preceding claims, comprising 1 to 40 g/l tin.
5. An electrolyte composition according to one of the

45

50

55

preceding claims, comprising a metal of the group consisting of indium, gallium and thallium, in a concentration comprised between 0.1 and 10 g/l.

6. An electrolyte composition according to one of the preceding claims, furthermore comprising cyanide in a concentration comprised between 1 and 100 g/l. 5
7. An electrolyte composition according to one of the preceding claims, at least comprising a complexing agent for the metals contained in the electrolyte composition. 10
8. An electrolyte composition according to claim 7, wherein the complexing agent is selected from the group consisting of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), Dequest®, a derivative or salt of the D-gluconic acid or mixtures thereof. 15
20
9. An electrolyte composition according to one of the preceding claims, comprising an alkali hydroxide or ammonium hydroxide.
10. An electrolyte composition according to one of the preceding claims, furthermore comprising a compound of the group consisting of ethylenediaminetetra(methylphosphonic acid) (EDTMPA), 1-hydroxyethylidenediphosphonic acid (etidronic acid, HEDP) or salts thereof. 25
30
11. An electrolyte composition according to one of the preceding claims, furthermore comprising glycolic acid. 35
12. An electrolyte composition according to one of the preceding claims, comprising a surface-active agent.
13. A method for the deposition of a quaternary copper alloy on a substrate, comprising the process steps: 40
 - contacting the substrate with an electrolyte composition that at least comprises copper, tin and zinc in form of the ions thereof as well as ions of a metal selected from the group consisting of indium, gallium and thallium; 45
 - applying a voltage between the substrate and a counter-electrode for the electroplating deposition of a quaternary alloy layer on the substrate. 50
14. A method according to claim 13, wherein for the deposition of the alloy layer a current density between 0.05 and 5 A/dm² is set. 55
15. A quaternary copper alloy layer deposited by electroplating and comprising copper, tin, zinc as well as

a metal of the group consisting of indium, gallium and thallium.

16. A quaternary copper alloy layer deposited by electroplating, wherein the alloy comprises 52 to 55 % by mass copper, 23 to 35% by mass tin, 5 to 13% by mass zinc as well as 4 to 12% by mass of a metal selected from the group consisting of indium, gallium and thallium.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 02 5184

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	US 4 389 286 A (MCCOY EWALD H) 21 June 1983 (1983-06-21) * abstract * * column 2, lines 44-55 * * column 5, lines 9-22 * * column 5, lines 50-60 * * column 6, lines 22-51 * -----	1,2,4,7, 9,13,15	INV. C25D3/56 C25D3/58
Y	GB 2 071 697 A (ALIPRANDINDI P) 23 September 1981 (1981-09-23) * abstract * * page 1, lines 15-46 * -----	1-4,6, 13-15	
Y	EP 1 091 023 A (SHIPLEY CO LLC [US]) 11 April 2001 (2001-04-11) * abstract * * paragraphs [0010], [0021] - [0023], [0032], [0041], [0042], [0044], [0049] * -----	1-4,6, 13-15	
Y	WO 2005/031812 A (ROCKWELL SCIENT LICENSING LLC [US]) 7 April 2005 (2005-04-07) * claims 1,2,6,7,15 * * page 12, lines 5-17 * * page 19, line 27 - page 20, line 19 * -----	1,2, 6-10, 13-15	TECHNICAL FIELDS SEARCHED (IPC) C25D
Y	WO 2006/032933 A (MIDDLESEX SILVER CO LTD [GB]; JOHNS PETER GAMON [GB]) 30 March 2006 (2006-03-30) * abstract * * page 2, lines 5-10 * * page 10, lines 14-22 * * page 11, line 15 - page 12, line 18 * ----- -/--	1,2, 6-10, 13-15	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 July 2007	Examiner Haering, Christian
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			

2

EPO FORM 1503 03.82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 02 5184

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	WO 2006/120291 A (LUVATA OY [FI]; SOMERKOSKI JUKKA [FI]) 16 November 2006 (2006-11-16) * page 3 * * claims 15,17,19,20,24-26,29,30 * * page 4, lines 9-12 * -----	1,13,15	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 July 2007	Examiner Haering, Christian
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			

2
EPO FORM 1503 03.82 (P04C01)

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

EP 06 02 5184

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-07-2007

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4389286	A	21-06-1983	NONE	

GB 2071697	A	23-09-1981	CH 626657 A5	30-11-1981
			DE 3020987 A1	24-09-1981
			FR 2478133 A1	18-09-1981
			IT 1128925 B	04-06-1986
			US 4364804 A	21-12-1982

EP 1091023	A	11-04-2001	JP 2001158990 A	12-06-2001
			KR 20010040038 A	15-05-2001
			SG 83221 A1	18-09-2001
			TW 573071 B	21-01-2004

WO 2005031812	A	07-04-2005	CA 2539481 A1	07-04-2005
			CN 1882719 A	20-12-2006
			EP 1665345 A2	07-06-2006
			KR 20060061395 A	07-06-2006
			US 2005067297 A1	31-03-2005

WO 2006032933	A	30-03-2006	AU 2005286209 A1	30-03-2006
			CA 2580960 A1	30-03-2006
			EP 1794335 A1	13-06-2007

WO 2006120291	A	16-11-2006	NONE	
