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(54) **METHOD FOR PREPARING AN ELECTROPLATED PRODUCT BY DEPOSITING AN UNDERLAYER, DIFFUSION BARRIER LAYER AND TOP LAYER ON THE SURFACE OF A SUBSTRATE AND SUCH PREPARED ELECTROPLATED PRODUCT**

(57) The present invention refers to a method for preparing an electroplated product by depositing an underlayer, a barrier diffusion layer and a top layer on a surface of a substrate comprising or consisting of copper or a copper or copper alloy layer wherein the underlayer comprises or consists of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof and the top layer comprises or consists of a pre-

cious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof. The underlayer and the top layer are separated by a barrier diffusion layer comprising or consisting of Indium or an alloy of Indium. This barrier layer prevents the interdiffusion between the underlayer and the top layer. Moreover, the present invention also refers to an electroplated product obtainable by such a method.

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Description

[0001] The present invention refers to a method for preparing an electroplated product by depositing an underlayer, a barrier diffusion layer and a top layer on a surface of a substrate comprising or consisting of copper or a copper or copper alloy layer wherein the underlayer comprises or consists of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof and the top layer comprises or consists of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof. The underlayer and the top layer are separated by a barrier diffusion layer comprising or consisting of Indium or an alloy of Indium. This barrier layer prevents the interdiffusion between the underlayer and the top layer. Moreover, the present invention also refers to an electroplated product obtainable by such a method.

[0002] In the field of electroplating of decorative articles like custom jewellery, the common electroplating sequence comprises a deposition of an underlayer of acid copper on the surface of the substrate to ensure a proper levelling of the substrate roughness followed subsequently by a white bronze layer of 2 to 5 μm and a thin palladium based layer of a thickness from 0.2 to 0.5 μm to stop the diffusion of the top precious metal layer, mainly gold or a gold alloy, into the copper or copper alloy underlayer, and most importantly to prevent the diffusion of copper into the precious metal layer.

[0003] This type of sequence is now preferred as a substitute to nickel underlayers because the use of nickel in articles in direct and prolonged contact with the human skin has been prohibited according to the REACH directive. An alternative would be a palladium layer. However, the use of palladium is problematic as its price has increased considerably due to its wide use in other applications.

[0004] The present bronze technology mainly uses cyanide as a complexing agent to enable the co-deposition of a ternary alloy of copper, tin and zinc, which is also efficient as a copper diffusion barrier.

[0005] The deposition of indium on copper can lead to two different problems based on the thickness of the deposit. If the deposit has a low thickness, it could raise doubts for the operator about the presence of the deposit on the surface because of his 'translucid' aspect. A higher thickness could lead to many defects on the deposit, up to obtaining a dull deposit which is unacceptable for aesthetic reasons.

[0006] EP^{3°540°097°A1} discloses electroplated products having a combination of layers used to provide a diffusion barrier layer under a precious metal top layer on a substrate comprising a copper-based material and/or a copper-based underlayer, such that the layer or combination of layers prevents or retards the migration of copper into the precious metal layer or the opposite. The diffusion barrier layer comprises indium or an indium alloy.

[0007] EP^{2°139°012°A1} discloses a silver-coated material for a movable contact component includes an electrically conductive base member that is comprised of copper or a copper alloy; an underlayer that is comprised of nickel or a nickel alloy to coat on the electrically conductive base member; an intermediate layer that is comprised of palladium, or a palladium alloy, or a silver tin alloy, to coat on the underlayer; and an outermost surface layer that is comprised of silver or a silver alloy, and that is formed on the intermediate layer.

[0008] US^{2013/0224515°A1} discloses a thin indium metal layer that is electroplated onto silver to prevent silver tarnishing. The indium and silver composite has high electrical conductivity.

[0009] EP^{3°359°710°A1} discloses a process for deposition of indium or indium alloys and an article obtained by the process, wherein the process comprises the steps:

- i. providing a substrate having at least one metal or metal alloy surface;
- ii. depositing a first indium or indium alloy layer on at least one portion of said surface whereby a composed phase layer is formed of a part of the metal or metal alloy surface and a part of the first indium or indium alloy layer;
- iii. removing partially or wholly the part of the first indium or indium alloy layer which has not been formed into the composed phase layer;
- iv. depositing a second indium or indium alloy layer on the at least one portion of the surface obtained in step iii.

[0010] None of those prior art documents has disclosed a diffusion barrier comprising indium between two layer comprising a precious metal. Those prior art that disclose a indium barrier do not mention that is often complicated to obtain a high thickness for this barrier combined with a good brightness that is necessary for a product in the field of precious metal.

[0011] It was therefore an object of the present invention to provide an electroplated product having an improved aesthetic stability by avoiding or substantially reducing the diffusion of copper into the precious metal top layer.

[0012] This problem is solved by the method for preparing an electroplated product with the features of claim 1 and the electroplated product with the features of claim 8. The further dependent claims mention preferred embodiments.

[0013] According to the present invention for preparing an electroplated product by electroplating of a substrate comprising the following steps:

- a) Depositing an underlayer comprising or consisting of a precious metal selected from the group consisting of Au,

Ag, Pd, Rh, Ru, Pt and its alloys from an electrolyte comprising at least one source of a precious metal ion and at least one conductive salt on a surface comprising copper or having a copper coating,

b) Depositing a diffusion barrier layer on the underlayer with an aqueous bath comprising at least one source of indium ions and at least one conductive salt, wherein the diffusion barrier layer prevents the interdiffusion between the substrate and the top layer and

c) Depositing a top layer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and its alloys on the diffusion barrier layer with an electrolyte comprising at least one source of a precious metal ion and at least one conductive salt.

[0014] Surprisingly, it has been found that the plating of indium on a precious metal lead to a bright lucid and white deposit. It was further found that this underlayer permits to increase the thickness of the indium barrier while maintaining the brightness. Furthermore, the bath can be operated more easily due to the fact that the electroplating bath is less sensible to parameter variations. It was found out that by using a precious metal underlayer under an indium diffusion barrier layer the barrier properties of the indium diffusion layer can be improved significantly.

[0015] In a preferred embodiment, the electroplating bath of step b) has a pH in the range of 1 to 14, preferably from 2 to 11, and more preferably from 4 to 10.

[0016] In a preferred embodiment, in the electroplating bath of step b) the at least one source of indium ions is selected from the group consisting of indium sulfate, indium chloride, indium acetate, indium sulfamate and combinations or mixtures thereof.

[0017] In the following, all concentrations is the mass concentration which refers to the mass of the ingredient in 1 L of the electroplating bath.

[0018] In a preferred embodiment, the concentration of the at least one source of indium ions of the electroplating bath of step b) is from 0,1 to 20 g/L, preferably from 0,2 to 15 g/L, more preferably from 0,3 to 10 g/L, and even more preferably from 0,5 to 10 g/L.

[0019] In a more preferred embodiment, the electroplating bath of step b) contains conductive salts in order to spread the indium distribution throughout the required current density range. The conductive salts are selected and balanced to not only act as a conductive salt but also as a buffering agent. The conductive salts/buffering agents are preferably selected from the group consisting of citrates (e.g. sodium or potassium citrate or their corresponding acidic version), formates (e.g. sodium formate or the corresponding acidic version), pyrophosphates (e.g. tetrapotassium pyrophosphate) and gluconates (e.g. sodium or potassium gluconate), nitrate, carbonate, borate and combinations or mixtures thereof.

[0020] It is preferred that the electroplating bath of step b) comprises 30 to 600 g/L, more preferably 40 to 500 g/L, and most preferably 100 to 400 g/L of the at least one conductive salt. 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.

[0021] The brightness of the indium deposit is preferably controlled by adding a surfactant to the electroplating bath of step b). The surfactant acts as a wetting agent and reduces the surface tension to allow indium deposition. The surfactants may belong to the amphoteric family and are selected from the group consisting of propionic amino acids, propionic imino acids, quaternary alkyl betaines or sulfo-betains. The surfactant is preferably selected from the group consisting of betain, aminobetain, imidazoline, cocoamidopropyl betaine, N,N-dimethyl-N-(3-cocoamidopropyl)-N-(2-hydroxy-3-sulfopropyl) ammonium betain, N,N-dimethyl-N-octadecyl-N-(3-sulfopropyl)ammonium betaine, N,N-dimethyl-N-dodecyl-N-(3-sulfopropyl)ammonium betaine and combinations or mixtures thereof.

[0022] The electroplating bath in step b) comprises preferably from 0.01 to 5 g/L, more preferably from 0.01 to 1.5 g/L of the surfactant.

[0023] In order to increase the solubility or to improve the electrodeposition in step b), the indium ions may be complexed in solution by a complexing agent. The complexing agent is preferably selected from the group consisting of carbohydrates, amino acids, imino acids, sulfur compounds, sugar alcohols, and combinations or mixtures thereof. More preferably, the complexing agent is selected from the group consisting of sorbitol, mannitol, gluconate, erythritol, xylitol, nitrilotriacetic acid, cysteine, iminodiacetic acid, triethanolamine and combinations or mixtures thereof. Said complexing agents were found to be perfectly suited for complexing indium ions.

[0024] The electroplating bath of step b) comprises preferably from 0.5 to 100 g/L, preferably from 1 to 75 g/L, most preferably from 2.5 to 50 g/L, and in particular from 5 to 35 g/L of the complexing agent. A concentration in these ranges is sufficient for complexing the indium ions which are comprised in the inventive electroplating solution. A concentration of complexing agent under 0.5 g/L was found to be detrimental and not able to stabilize the bath at the required pH.

[0025] Importantly, it has surprisingly found that electroplating baths with non-complexed indium show a lack of stability at pH above 2 and that the stability is considerably improved with the use of appropriated complexing agents.

[0026] In a preferred embodiment, the sequence of steps a) to c) is not interrupted by any further deposition steps with the consequence that the layers electroplated in step a) to c) abut to each other.

[0027] In a preferred embodiment, the at least one source of the precious metal ion in the electroplating bath of step a) is at least one source of Au and/or Ag ion.

[0028] In a preferred embodiment, the at least one source of the precious metal ion in the electroplating bath of step c) is selected from the group consisting of at least one source of Au, Ag, Pd, Pt ions or combinations thereof, preferably of Au and/or Ag ions.

[0029] In a preferred embodiment, in a further step d) directly following deposition step c), a passivation or a lacquer or a finishing agent layer is deposited on the top layer.

[0030] In a more preferred embodiment, the step d) comprises dipping the product obtained in step c) in a chemical solution.

[0031] Moreover, also an electroplated product is provided comprising a substrate comprising copper or having a copper coating on which with an underlayer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof and a top layer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof is deposited. The underlayer and the top layer are separated by a barrier diffusion layer comprising or consisting of Indium or an alloy of Indium with the material of the top layer which prevents the interdiffusion between the underlayer and the top layer.

[0032] In a preferred embodiment, the underlayer has a thickness of 10 to 500 nm, preferably 25 to 400 nm and more preferably 40 to 300 nm.

[0033] In a preferred embodiment, the diffusion barrier layer has a thickness of 1 to 500 nm, preferably 25 to 300 nm and more preferably 50 to 250 nm.

[0034] In a preferred embodiment, the top layer has a thickness of 1 to 500 nm, preferably 3 to 400 nm and more preferably 5 to 300 nm.

[0035] In a preferred embodiment, the top layer consists of a precious metal selected from the group consisting of Au, Ag, Pd, Pt and its alloys, preferably of Au, Ag and its alloys.

[0036] In a more preferred embodiment, the first layer consists of gold or gold alloy.

[0037] In a preferred embodiment, there is a passivation or a lacquer or a finishing agent layer on the top layer.

[0038] With reference to the following figures and examples, the subject-matter according to the present invention is intended to be explained in more detail without wishing to restrict said subject-matter to the specific embodiments shown herein.

Fig.1 shows the GDOES spectra of example 1 without (on the left) and with thermal treatment (on the right).

Fig.2 shows the GDOES spectra of example 2 without (on the left) and with thermal treatment (on the right).

Fig.3 shows the GDOES spectra of example 3 without (on the left) and with thermal treatment (on the right).

Fig.4 shows the GDOES spectra of example 4 without (on the left) and with thermal treatment (on the right).

Fig.5 shows the GDOES spectra of example 5 without (on the left) and with thermal treatment (on the right).

Fig.6 shows the GDOES spectra of example 6 without (on the left) and with thermal treatment (on the right).

Fig.7 shows the GDOES spectra of example 7 without (on the left) and with thermal treatment (on the right).

Fig.8 shows the GDOES spectra of example 8 without (on the left) and with thermal treatment (on the right).

Fig.9 shows the GDOES spectra of example 9 without (on the left) and with thermal treatment (on the right).

Fig.10 shows the GDOES spectra of example 10 without (on the left) and with thermal treatment (on the right).

Fig.11 shows the GDOES spectra of example 11 without (on the left) and with thermal treatment (on the right).

Fig.12 shows the GDOES spectra of example 12 without (on the left) and with thermal treatment (on the right).

Examples

[0039] The experiments were conducted 5 on flat brass items with a surface of 0.22 dm². The flat brass items were submitted to the preparation sequence as described below:

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- Alkaline cathodic cleaner (PRESOL 1540 - 4V - room temperature - 110 seconds)
- Acidic activation (H₂SO₄ 2% - room temperature - 1 minute)

[0040] CIE Lab measurement were performed with Minolta CM-503i spectrophotometer. Illuminant used was Daylight D65 (6500K) with reflective component included (sci). Observer was set at standard (10°) and the measurements were performed in the Color space CIE L*a*b*.

[0041] The GDOES values were measured on a GD-Profilier 2 from Horiba using the software QUANTUM V2.08. The Pressure was set at 650 Pa, Power at 35 W, without Pulse, the Module Voltage 6V and the Phase Voltage 5V.

Electroplating with gold:

Formulation Copper plating bath

[0042]

- COVENTYA process CUBRAC 440
- 20°C - 3 A/dm²
- time of deposition: 15 minutes to reach 15 µm

Formulation Indium plating bath (Formulation A)

[0043]

- Sodium gluconate 100 g/L
- Sodium formate 100 g/L
- In 2 g/L (from indium sulphate 100 g/L); precomplexed with sorbitol (molar ratio indium : sorbitol = 1 :4)

Operating conditions:

[0044] Temperature 25°C, Current density: 1 A/dm², pH 10, time :4 min

Formulation Indium plating bath (Formulation B)

[0045]

- Sodium formate 250 g/L
- Citric Acid 100 g/L
- In 4 g/L (from indium sulphate solution 100 g/L)
- cocoamidopropyl betaine 15 ppm

Operating conditions:

[0046] Temperature 50°C, Current density: 2 A/dm², time: 2 min, pH 4.5

Formulation Gold plating bath

[0047]

- COVENTYA process AURANE 793
- 40°C - 2 A/dm²
- time of deposition: 3 minutes to reach 0.5 µm

[0048] For our purposes, the aesthetic aspect is not the only requirement. We must verify that indium works as copper migration barrier also in this sequence.

[0049] In order to study this property, we prepare many couples of panels with different sequences. For each couple, one panel was put in oven at 180°C for 24h for thermal treatment. After a subsequent aesthetic evaluation, we performed GDOES analysis on every panel to investigate the relative position of each metal composing every sequence.

[0050] In the following table 1, the GDOES analysis graphs and the colour coordinates of the samples are shown (as

far as measurable).

Table 1 Examples with Gold

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Layer 1	Copper	Copper	Copper	Copper	Copper	Copper
	10 - 15 μm	10 - 15 μm	10 - 15 μm	10 - 15 μm	10 - 15 μm	10 - 15 μm
Layer 2	Gold	Indium	Indium	Gold	Gold	Gold
	0.25 μm	75 nm	75 nm	50 nm	50 nm	0.1 μm
Layer 3			Gold	Indium	Indium	Indium
			0.25 μm	0.1 μm	0.1 μm	0.15 μm
Layer 4					Gold	Gold
					0.25 μm	0.25 μm
ΔL^*	-25	1	-2	2	-2	-1
Δa^*	17	4	0	2	1	0
Δb^*	35	7	-1	23	1	-1

[0051] The aspect of the panel from Example 1 after thermal treatment is very dark and irregular. Fig.1 confirms that after heating treatment, the copper diffuses in gold reaching the surface.

[0052] In Fig.3, a barrier effect can be observed, but with the plate that was obtained it is obvious that the brightness of the gold layer is not optimal.

[0053] In Fig.4, a particular behaviour can be observed. After heat treatment, gold diffusion into indium reaching the top, as can be seen from the colour coordinates, and copper remains blocked. This confirms the affinity between gold and indium and that the barrier to the copper migration is the indium-gold alloy.

[0054] In Fig. 5, the two panels show very little differences, also observing the colour coordinates. GDOES analysis confirmed the property as copper diffusion barrier of indium in this new sequence.

[0055] With Fig.6, we verify that the thickness of gold underlayer does not influence the property of copper diffusion barrier of indium. The results are the same of example 5.

Electroplating with silver:

Formulation Copper plating bath

[0056]

- COVENTYA process CUBRAC 440
- 20°C - 3 A/dm²
- time of deposition: 15 minutes to reach 15 μm

Formulation Indium plating bath (Formulation A)

[0057]

- Sodium gluconate 100 g/L
- Sodium formate 100 g/L
- In 2 g/L (from indium sulphate 100 g/L); precomplexed with sorbitol (molar ratio indium : sorbitol = 1 :4)

Operating conditions:

[0058] Temperature 25°C, Current density: 1 A/dm², pH 10, time :4 min

Formulation Indium plating bath (Formulation B)**[0059]**

- Sodium formate 250 g/L
- Citric Acid 100 g/L
- In 4 g/L (from indium sulphate solution 100 g/L)
- cocoamidopropyl betaine 15 ppm

Operating conditions:

T 50°C, Current density: 2 A/dm², time: 2 min, pH 4.5

Formulation Gold Plating bath**[0061]**

- COVENTYA process AURANE 793
- 40°C - 2 A/dm²
- time of deposition: 2 minutes to reach 0.25 µm

Formulation Silver Plating bath**[0062]**

- COVENTYA process SILVIUM 100
- 20°C- 0.5 A/dm²
- time of deposition: 1 minutes to reach 0.25 µm

Table 2: Examples with Silver

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Layer 1	Copper	Copper	Copper	Copper	Copper	Copper
	10 - 15 µm	10 - 15 µm	10 - 15 µm	10 - 15 µm	10 - 15 µm	10 - 15 µm
Layer 2	Silver	Silver	Silver	Silver	Indium	Gold
	0.25 µm	0.25 µm	0.25 µm	0.25 µm	0.075 µm	0.1 µm
Layer 3		Indium	Indium	Indium		Indium
		0.1 µm	0.1 µm	0.1 µm		0.1 µm
Layer 4			Silver	Gold		Silver
			0.25 µm	0.25 µm		0.25 µm
ΔL*	-25	-49	-55	-20	-9	-2
Δa*	17	-4	-5	0	1	0
Δb*	35	1	-25	-3	9	3

[0063] A comparison of Fig. 7, 8 and 9 comes to the conclusion, that the indium layer has a barrier effect but not as

strong compared to a gold underlayer.

[0064] Fig.10 evidences that by choosing a gold top layer the barrier effect can be improved.

5 Claims

1. Method for preparing an electroplated product by depositing an underlayer, a diffusion barrier layer and a top layer on the surface of a substrate comprising the following steps:
 - a) Depositing an underlayer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and its alloys from an electrolyte comprising at least one source of a precious metal ion and at least one conductive salt on a surface comprising copper or having a copper coating,
 - b) Depositing a diffusion barrier layer on the underlayer with an aqueous bath comprising at least one source of indium ions and at least one conductive salt, wherein the diffusion barrier layer prevents the interdiffusion between the substrate and the top layer
 - c) Depositing a top layer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and its alloys on the diffusion barrier layer with an electrolyte comprising at least one source of a precious metal ion and at least one conductive salt.
2. Method for preparing an electroplated product of claim 1, **characterised in that** the electroplating bath in step b) has a pH in the range of 1 to 14, preferably from 2 to 11, and more preferably from 4 to 10.
3. Method for preparing an electroplated product of claim 1 or 2, **characterised in that** the at least one source of indium ions in the electroplating bath of step b) is selected from the group consisting of indium sulfate, indium chloride, indium acetate, indium sulfamate and combinations or mixtures thereof.
4. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the concentration of the at least one source of indium ions in the electroplating bath is preferably from 0,1 to 20 g/L, more preferably from 0,2 to 15 g/L, even more preferably from 0,3 to 10 g/L, and most preferably from 0,5 to 10 g/L.
5. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the sequence of steps a) to c) is not interrupted by further deposition steps with the consequence that the layers deposited in step a) to c) abut to each other.
6. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the at least one source of the precious metal ion in the electroplating bath of step a) is at least one source of Au, Ag ions and combinations thereof.
7. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** at least one source of the precious metal ion in the electroplating bath of step c) is selected from the group consisting of at least one ion source of Au, Ag, Pd, Pt and combinations thereof, preferably of Au, Ag and its alloys.
8. Electroplated product comprising a substrate comprising copper or having a copper coating on which an underlayer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof and a top layer comprising or consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof is deposited, **characterised in that** the underlayer and the top layer are separated by a barrier diffusion layer comprising or consisting of Indium or an alloy of Indium with the material of the top layer which prevents the interdiffusion between the underlayer and the top layer.
9. Electroplated product of claim 8, **characterised in that** the diffusion barrier layer has a thickness of 1 to 500 nm, preferably 25 to 300 nm and more preferably 50 to 250 nm.
10. Electroplated product of claim 8 or 9, **characterised in that** the underlayer has a thickness of 10 to 500 nm, preferably 25 to 400 nm and more preferably

40 to 300 nm.

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11. Electroplated product of any of the preceding claims, **characterised in that** the top layer has a thickness of 1 to 500 nm, preferably 3 to 400 nm and more preferably 5 to 300 nm.
12. Electroplated product of any of the preceding claims, **characterised in that** the top layer comprises or consists of a precious metal selected from the group consisting of Au, Ag, Pd, Pt and its alloys, preferably of Au, Ag and its alloys.
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13. Electroplated product of any of the preceding claims **characterised in that** the underlayer comprises or consists of gold or a gold alloy.

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Fig. 1

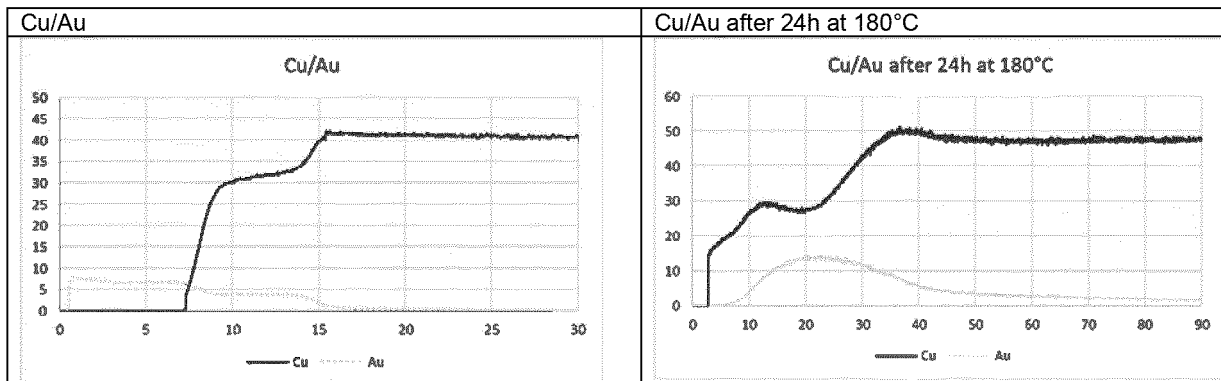


Fig. 2

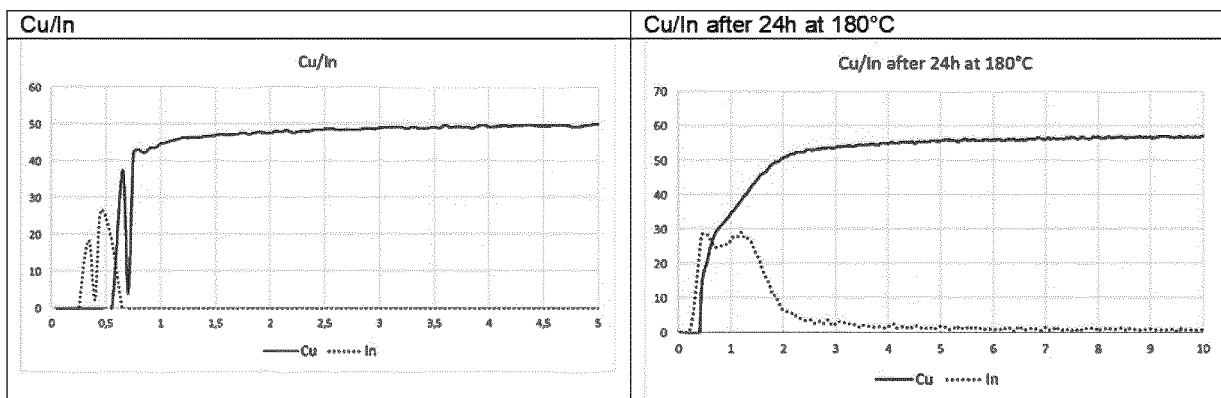


Fig. 3

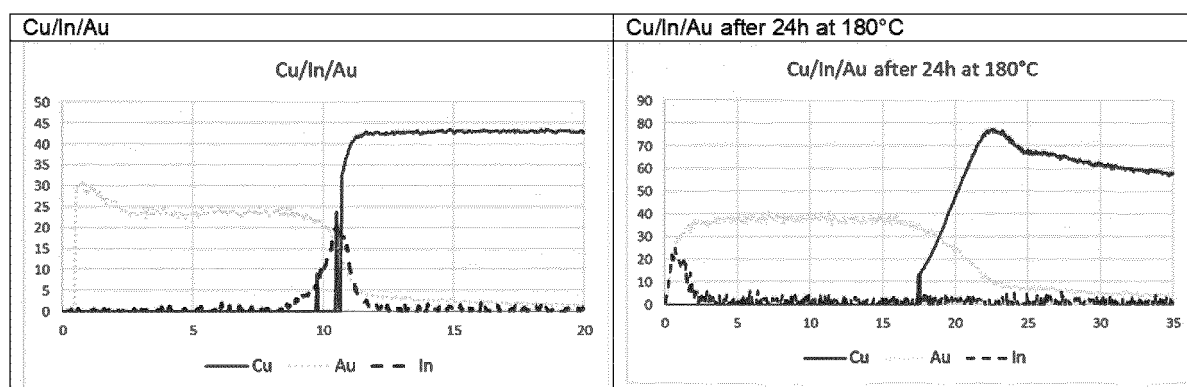


Fig. 4

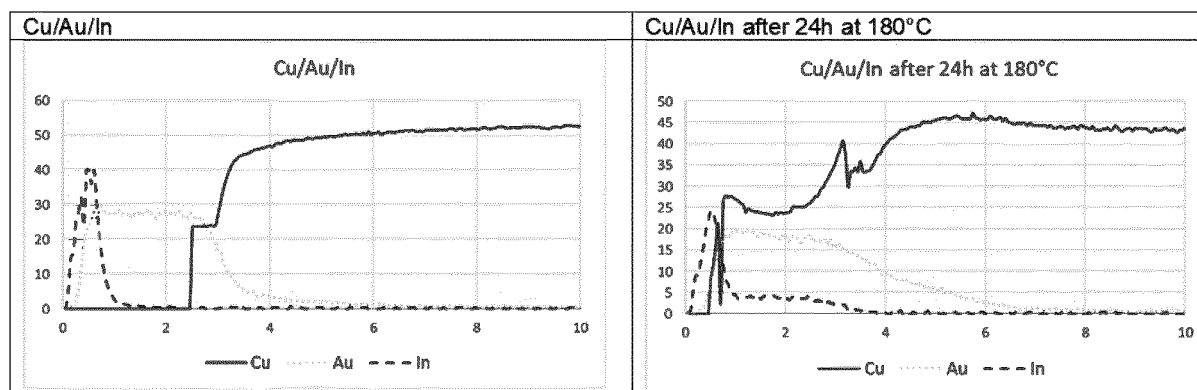


Fig. 5

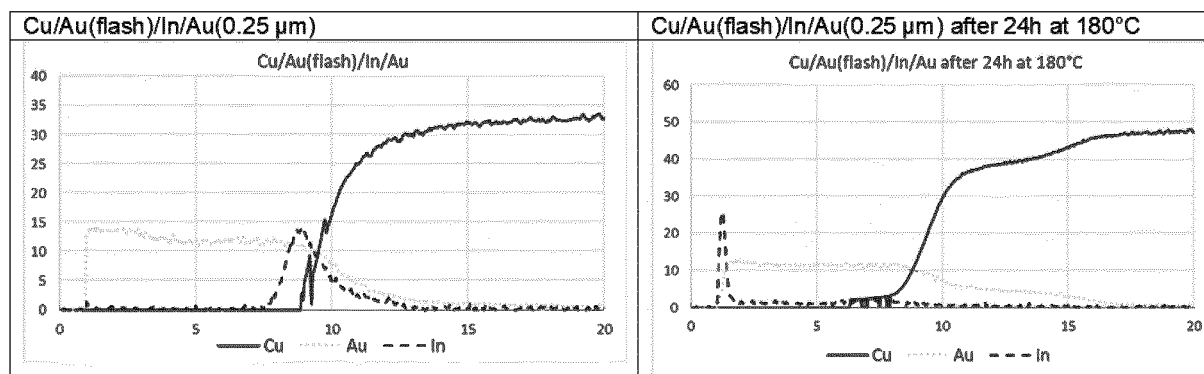


Fig. 6

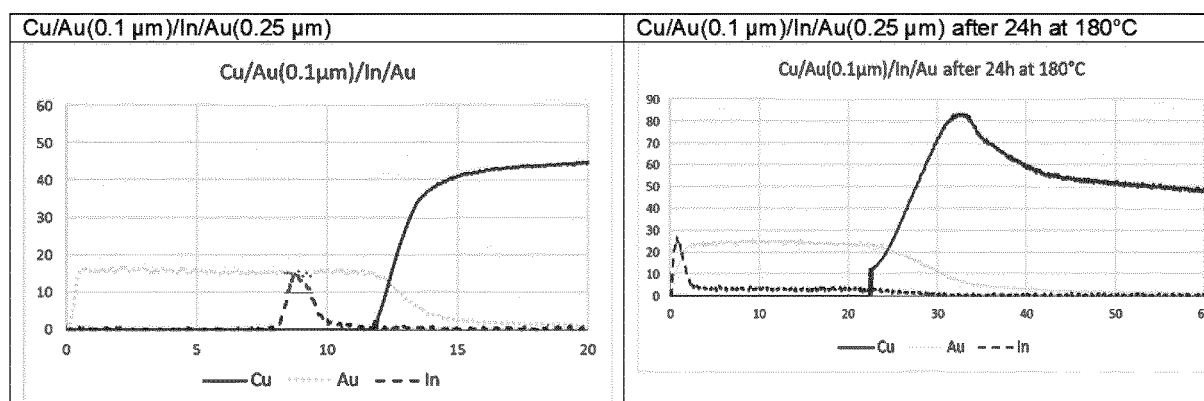


Fig. 7

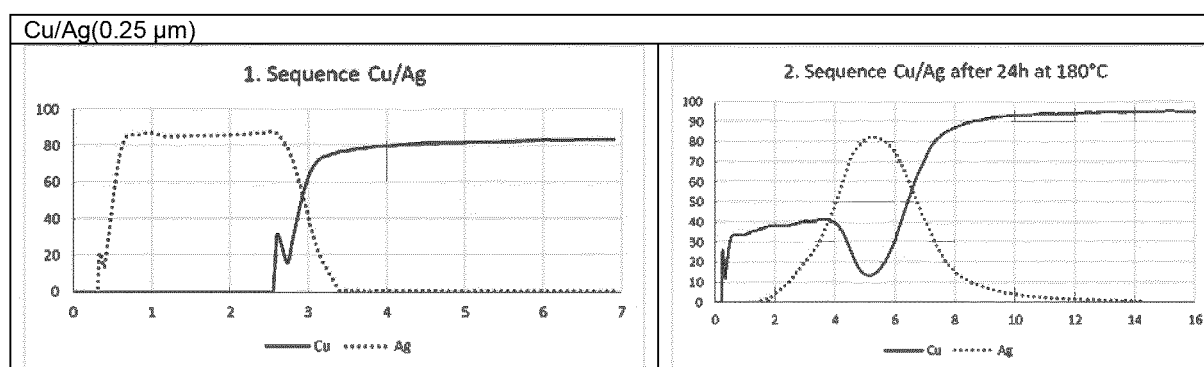


Fig. 8

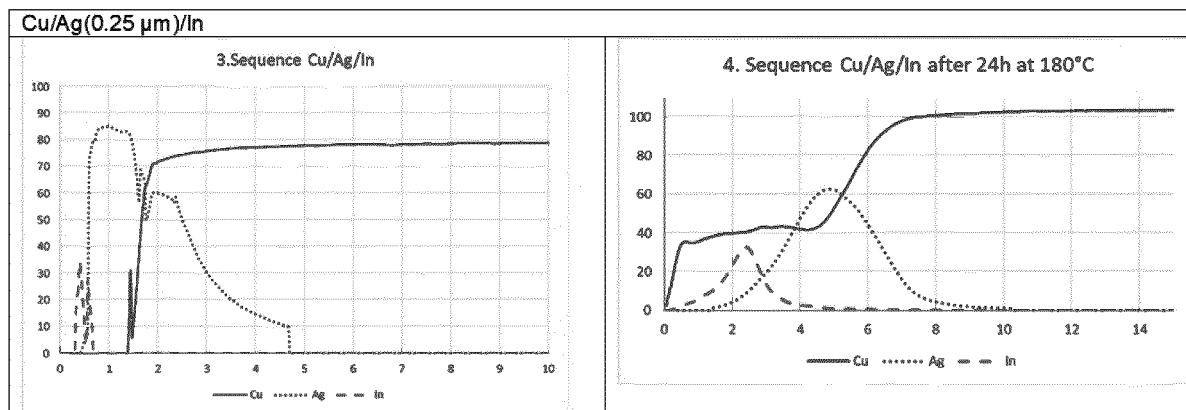


Fig. 9

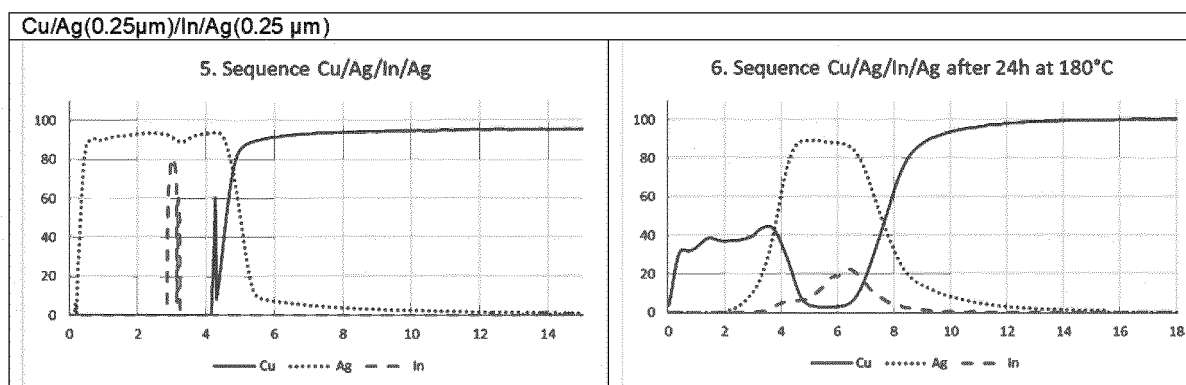


Fig. 10

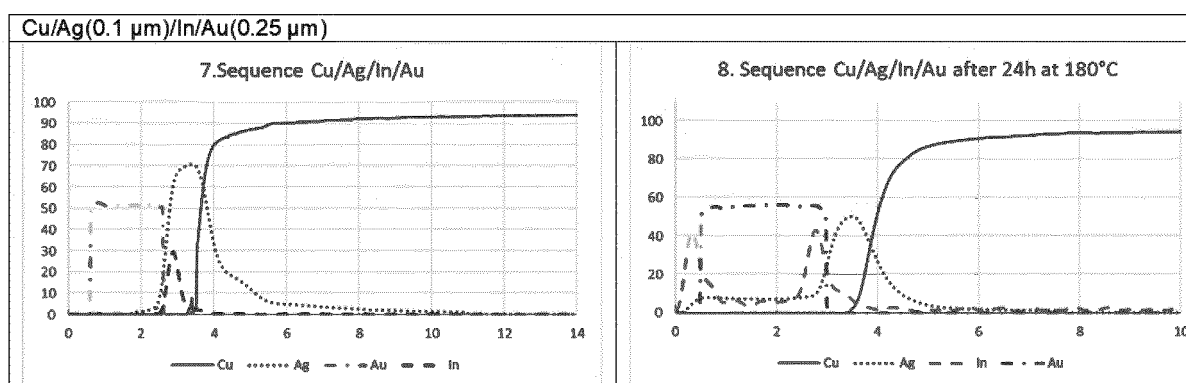


Fig. 11

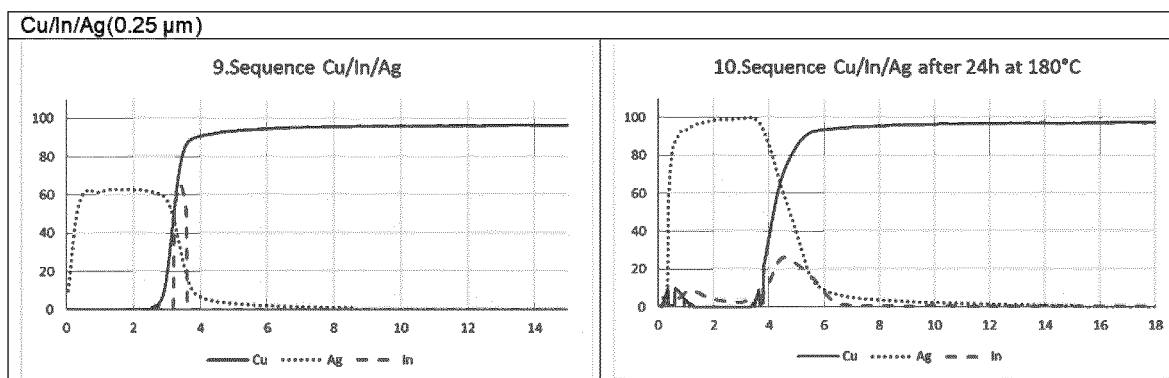
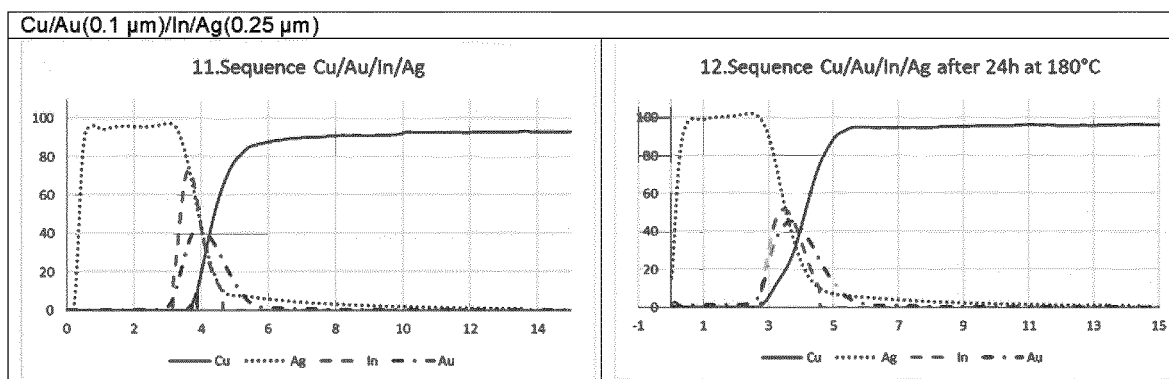


Fig. 12





EUROPEAN SEARCH REPORT

 Application Number
 EP 20 20 7754

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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)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 9 April 2021	Examiner Lange, Ronny
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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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 20 20 7754

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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