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(54) **ELECTROPLATED PRODUCTS AND ELECTROPLATING BATH FOR PROVIDING SUCH PRODUCTS**

(57) The present invention relates to 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. Moreover, the present invention refers a method for preparing such an electroplated product.

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Description

[0001] The present invention relates to 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. Moreover, the present invention refers a method for preparing such an electroplated product.

[0002] In the field of electroplating of decorative articles like custom jewellery, the common electroplating sequence comprises electroplating on the substrate a first layer of acid copper to ensure a proper levelling of the substrate roughness followed by a white bronze layer of 2 to 5 μm and by 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] WO2016/166330 A1 describes an electroplated product with a precious metal finishing layer that has an improved corrosion and abrasion resistance. The electroplated product comprises two electroplated copper alloy layers having a different copper concentration (e.g. white bronze and yellow bronze). Another advantage of the electroplated product is that the use of allergenic nickel or expensive palladium intermediate layers against copper migration can be dispensed with.

[0006] WO2017/055553 A1 describes an electroplating bath for electrochemical deposition of a novel Cu-Sn-Zn-Pd alloy on a substrate. The novel alloy is characterized by improved corrosion resistance but is based on cyanide media.

[0007] The metal indium is nowadays used mainly for photovoltaic applications due to its high thermal conductivity ($\sim 82 \text{ W/mK}$). It also has other unique physical properties which make it very useful in numerous industries. For example, it is sufficiently soft such that it is readily deformed and fills microstructures between two mating parts, has a low melting temperature (156°C). Such properties recommend indium for various uses in the electronics and related industries.

[0008] The use of indium in electroplating has already been tested as a constituent of bronze layers. WO2015/000010 A1 describes a bath for the cathodic deposition of ternary bronze alloys. In addition to copper and tin, the electrolyte composition comprises indium as a third metallic alloying constituent. A ternary copper-tin-indium alloy is deposited directly on an optional copper layer.

[0009] EP 1 930 478 A1 teaches an electrolyte composition as well as a method for the deposition of another quaternary copper alloy on a substrate. The electrolyte composition comprises besides the alloying metals copper, tin and zinc, at least one metal from the group consisting of indium and gallium providing white bronze layers free of noxious heavy metals. However, the previously mentioned documents are based on baths containing cyanide. Cyanide based solutions have several disadvantages associated with the high toxicity of the electrolyte, difficulties associated with storage and transportation of the cyanide salts and solutions, and costs associated with the wastewater treatments. Several attempts have been made to formulate cyanide free ternary bronze to substitute the dangerous complexing agent but none of them fulfils the market requirements to prevent the gold and copper inter diffusion as well as to maintain a bright and shiny aspect of the electroplated layers.

[0010] WO2004/035875 A3 refers to a method for bronze galvanic coating which consists of metallizing a substrate to be coated by its immersion into an acidic electrolyte which contains at least tin and copper ions. The acidic electrolyte used for bronze coating is also disclosed.

[0011] WO2013/092314 cites an aqueous alkaline electrolyte, which is cyanide-free, pyrophosphate-free and phosphonic acid-free for depositing a ternary alloy comprising copper and tin present in dissolved form and zinc present as a zinc salt.

[0012] Additionally, KR1168215 B1 teaches a copper-tin alloy plating film, a non-cyanide-based copper-tin alloy plating bath, and a plating method using the same. However, the deposit was not a barrier to copper diffusion.

[0013] In the prior art up to the present, there is no suitable solution to significantly reduce the copper diffusion into the gold layer to substitute the actual cyanide ternary or quaternary bronzes or the common use of the toxic nickel or the expensive palladium intermediate layer.

[0014] The US 2,458,839 A teaches a bath which comprises at least 20 g/L of indium. However, with such high concentrations that no thin bright layers can be provided.

[0015] On the other hand, WO2009/097360 A1 describes an electroplating solution for the deposition of a pure indium film on a conductive surface useful in fabricating electronic devices. The indium electroplating solutions are used to deposit indium films which are compositionally pure, uniform, substantially free of defects and smooth. Such films can

be plated with almost 100% plating efficiency. In this document, sub-micron thick indium layers are described. Such indium layers are used in fabrication of electronic devices such as thin film solar cells.

[0016] EP 2 123 799 B1 teaches a method to prevent silver from tarnishing by electroplating a thin indium metal layer onto a silver substrate. The indium and silver composite has high electrical conductivity.

[0017] WO2017/060216 A1 teaches a process for indium or indium alloy deposition and for the formation of very smooth and glossy indium or indium alloy layers and their use in electronic and semiconductor devices, in particular interconnections used in electronic and semiconductor industries such as flip chips, tape automated bonding and the like.

[0018] It was therefore the object of the present invention to provide electroplated products with a sequence of layers which avoid the migration of metals between the different layers and to substitute nickel or palladium as an underlayer. Moreover, for the preparation of such products an electroplating bath is required which is free of toxic substances, mainly nickel and cyanides.

[0019] These objectives are achieved by the method for preparing an electroplated product and the electroplated product of claim 9. The further dependent claims mention preferred embodiments.

[0020] According to the present invention a method for preparing an electroplated product by electroplating a substrate comprising the following steps:

a) Electroplating a substrate with an underlayer consisting of copper or a copper alloy with an electrolyte comprising at least one source of copper ions, at least one conductive salt, and, optionally, at least one ion source of an alloy former for copper,

b) Electroplating of a barrier layer on the underlayer with an aqueous bath comprising at least one source of indium ions and at least one conductive salt,

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

[0021] Surprisingly, indium has been found to be an efficient copper diffusion barrier, able with very low thickness to prevent copper migration to the top gold layer and thus preventing the article from undesirable change of colour.

[0022] The indium in the diffusion barrier layer which is deposited between the copper or copper alloy underlayer and the precious metal or precious metal alloy top layer, can migrate into the precious metal top layer, but prevents the interdiffusion between the underlayer and the top layer.

[0023] According to the present invention, an underlayer consisting of copper or a copper alloy is obtained by electrodeposition from a copper electroplating solution. This copper electroplating solution is generally very acidic as it contains up to 60 g/L of 98% sulfuric acid. It produces a bright deposit with high levelling characteristics. The deposits are free of pits even at high thicknesses. The electroplated copper thicknesses can vary from 5 to 60 μm depending on the substrate and the targeted properties.

[0024] The function of the top layer consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and its alloys is highly decorative, it must be of a constant colour and give a very uniform and generally bright aspect to the final item. The thickness is generally low due to the cost of the precious metals used. It typically varies between 0.05 μm up to 5 μm preferably between 0.1 and 1 μm . It is absolutely necessary that the top layer colour and aspects are not affected by the copper underlayer. In the absence of a proper diffusion barrier, the interdiffusion of the copper or copper rich underlayer and the top finishing layer will lead to a non-acceptable finish of the part upon ageing or storage. That is why it is so important to provide an intermediate layer that prevents the interdiffusion of the copper rich underlayer and the precious metal top layer.

[0025] The electroplating bath of step b) preferably has a pH in the range of 1 to 14, more preferably of 2 to 11, and most preferably of 4 to 10.

[0026] The at least one source of indium ion in the electroplating bath of step b) is preferably selected from the group consisting of indium sulfate, indium chloride, indium acetate, indium sulfamate and its combinations or mixtures. Considering the cost of this valuable metal, the source of indium ion should be affordable.

[0027] It is preferred that the bath has a concentration of indium as a metal of 0.1 to 20 g/L, preferably 0.2 to 15 g/L, more preferably 0.3 to 10 g/L, most preferably 0.5 to 7 g/L. A concentration in these ranges is sufficient to obtain the suitable aspect of the indium thin layer. A concentration of indium above 20 g/L was found to be detrimental to maintain brightness and thickness distribution.

[0028] According to the invention, the electroplating bath 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), formiates (e.g.

sodium formiate or the corresponding acidic version), pyrophosphates (e.g. tetrapotassium pyrophosphate) and gluconates (e.g. sodium or potassium gluconate) and combinations or mixtures thereof.

[0029] It is preferred that the at least one conductive salt has a concentration of 30 to 500 g/L, more preferably 50 to 300 g/L, and most preferably 100 to 200 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.

[0030] The brightness of the indium deposit is controlled by the introduction of a surfactant. The surfactant acts as a wetting agent and reduces the surface tension to allow indium electroplating. 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 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.

[0031] The surfactant concentration according to the invention is preferably from 0.1 to 5 g/L, more preferably from 0.5 to 1.5 g/L.

[0032] In order to increase the solubility or improve the electrodeposition, 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.

[0033] The concentration of the complexing agent in the bath is 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. 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.

[0034] Importantly, it was discovered that baths with uncomplexed indium show lack of stability at pH above 2, and that the stability is considerably improved with the use of appropriated complexing agents.

[0035] According to another preferred embodiment of the present invention the diffusion barrier layer consists of an alloy of indium with the material of the top layer, which is preferably gold. Such a diffusion barrier layer of gold and indium allows to strongly reduce copper migration.

[0036] For such a gold-indium alloy layer the electroplating bath comprises at least one source of gold ions, preferably selected from the group consisting of potassium gold (I) cyanide, sodium gold(I) sulphite, potassium gold(III) cyanide, gold (III) chloride and tetrachloroaurates(III), gold(I) thioglycerol and gold(I) and gold(III) hydantoin complexes, and combinations or mixtures thereof.

[0037] The concentration of the at least one source of gold is preferably from 0.5 to 10 g/L, more preferably from 1 to 5 g/L and most preferably from 2.5 to 3.5 g/L. On the other hand the concentration of indium in the electroplating bath is preferably from 0.1 to 20 g/L, more preferably from 0.2 to 15 g/L and most preferably from 0.25 to 0.75 g/L.

[0038] It is preferred that the sequence of steps a) to c) is not interrupted by further deposition steps with the consequence that the layers electroplated in step a) to c) abut to each other.

[0039] Moreover, according to the present invention an electroplated product is provided which comprises a substrate which is coated with an underlayer consisting of copper or a copper alloy and a top layer consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof.

[0040] It is essential for the inventive coating that the underlayer and the top layer are separated by a diffusion barrier layer consisting of indium or an alloy of indium with the material of the top layer

[0041] The diffusion barrier layer has preferably a thickness of 10 to 200 nm, more preferably 25 to 150 nm and most preferably 50 to 100 nm. It has been determined that a thickness of the indium intermediate layer of less than 50 nm does not prevent the diffusion of copper into the gold. A thickness above 200 nm leads to poor brightness and presents a powdering aspect.

[0042] It is preferred that the diffusion barrier layer comprises an gold indium alloy, preferably with 90 to 95 % by weight of gold and 5 to 10 % by weight of indium.

[0043] The electroplated products are preferably selected from the group consisting of jewelry, leather goods, spectacle frame, fashion, watch, trinkets and/or lock industry.

[0044] 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.

[0045] The experiments were conducted on flat brass items with a surface of 0.22 dm². The flat brass items were submitted to the preparation sequence as described below:

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

[0046] The panels were then plated with an acidic copper electrolyte CUBRAC 440 from the company COVENTYA using the following parameters :

- 3 A/dm² at room temperature
- Time to reach sufficient copper thickness (around 15 - 20 μm)

[0047] The copper plated panels were then plated with various subsequent layers using different electrolytes.

1) Bronze electrolyte cyanide based (example 2)

[0048]

- copper as CuCN: 6 g/L
- tin as K₂SnO₃: 30 g/L
- zinc as Zn(CN)₂: 1 g/L
- free potassium cyanide: 50 g/L
- free potassium hydroxide: 25 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 3 mL/L

[0049] The operating conditions to obtain the bronze layer were:

- current density 1 A/dm²
- temperature 60°C
- time of deposition: 10 minutes to reach 2 μm

2) Indium electrolyte 1 (example 3)

[0050]

- [indium] = 5 g/L (as indium sulfate 100 g/L)
- [formic acid 85%] = 50 g/L
- [sodium formate] = 100 g/L
- [potassium citrate] = 50 g/L
- [citric acid] = 50 g/L
- [N-dodecyl N,N-dimethyl 3-ammonium propane sulfonate - 10 g/L] = 20 mL/L (0.1 g/L of active surfactant)

[0051] The operating conditions to obtain a thin layer of indium were:

- pH 4
- current density 1 A/dm²
- 25°C
- time of deposition: 2 minutes to reach 0.1 μm

3) Indium electrolyte 2 (example 4)

[0052]

- [indium] = 2 g/L (as indium sulfate 100 g/L), pre-complexed with sorbitol (molar ratio indium : sorbitol = 1 : 4)
- [sodium formate] = 100 g/L
- [potassium citrate] = 100 g/L

[0053] The operating conditions to obtain a thin layer of indium were:

- pH 10
- current density 1 A/dm²
- Temperature : 25°C
- time of deposition: 4 minutes

4) Gold electrolyte (example 1 to 4)**[0054]**

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

5) Gold indium electrolyte (example 5 and 6)**[0055]**

- [gold] = 2 g/L (as Gold-Thioglycerol)
- [indium] = 0.1 g/L (as indium thioglycerol), to obtain 5% of indium into the alloy
- [indium] = 0.2g/L (as indium thioglycerol), to obtain 10% of indium into the alloy
- [sodium formate] = 100 g/L

[0056] The operating conditions to obtain a thin layer of gold/indium alloy with 95% wt of gold and 5% wt of indium were:

- pH 11
- 50°C
- Current density : 1.5 A/dm²
- time of deposition: 5 minutes to reach 0.5 µm

[0057] The thus prepared samples were submitted to a thermal treatment during 24 hours at 180°C. This heat treatment accelerates any interdiffusion of the elements.

[0058] The samples were analysed via GDOES measurement in order to evaluate the diffusion of the various elements into the combination of layers. It has to be noted that the GDOES measurements here reported are only qualitative and should only be used in a comparative mode.

[0059] Internal studies showed that indium as a thin layer is highly efficient to prevent copper migration. The experimental copper diffusion test was conducted with different indium thicknesses showing better results for layers with lower thicknesses

The required thickness of indium has been evaluated using CIE Lab measurements before and after thermal treatment. It was desired to have no colour variation induced by thermal treatment for 24 hours at 180°C. CIE Lab measurement results*:

*measured 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 done in the Color space CIE L*a*b*.

[0060] The tested samples are described below:

- The following sequences were used on the reference brass panels
- Copper underlayer: 15 µm obtained via the method here above described
- indium intermediate layer: from 0 to 3 µm obtained via the method here above described (electrolyte 1)
- Gold top layer: 0.5 µm (obtained via the method here above described)

The table below resume the colorimetric coordinates variations between original value and after thermal treatment. We are looking for the smallest variation which would indicate minimal cooper migration through thermal treatment:

Table 1: Determination of optimum thickness to obtain copper migration barrier

Indium thickness	0 µm	0.05 µm	0.1 µm	0.25 µm	0.5 µm	1 µm	3 µm
Gold thickness	0.5 µm	0.5 µm	0.5 µm	0.5 µm	0.5 µm	0.5 µm	0.5 µm
ΔL*	-44	-2,7	-1,5	-2,8	-2,9	0	-4,8
Δa*	6,1	0,7	-2,3	-7,8	-9,6	-9,8	-10,7
Δb*	-38,2	1,4	3,8	-19,1	-22,1	-25,1	-26,4

[0061] Each sample was submitted to thermal treatment (180°C - 24 hours) and we recorded the values on the following

figures:

- Fig. 1: L^* evolution over thermal treatment depending on indium thickness
- Fig. 2: a^* evolution over thermal treatment depending on indium thickness
- Fig. 3: b^* evolution over thermal treatment depending on indium thickness

[0062] Figs. 1, 2 and 3 show that for example 1 where gold is plated directly on copper, there is a strong evolution of the Lab value after heat treatment indicating a reorganization of the two elements upon heating:

$\Delta L^* = - 17.5$ points / $\Delta a^* = - 7$ points / $\Delta b^* = - 40$ points

[0063] In Fig. 1 to 3, we encircled the targeted areas, showing the low variations before and after thermal treatment. We then notice that the indium layer thickness has to be in the range between 0.05 and 0.1 μm to maintain the aesthetical aspect of the object:

- Fig. 1 shows that from 0.05 μm to 2 μm of indium between copper and gold, the L^* value does not change after heating at 180°C
- Fig. 2 and 3 show the evolution of a^* and b^* values versus thickness of the indium layer. In this case, the range of thicknesses where the evolution of a^* and b^* values are acceptable is comprised between 0.05 and 0.1 μm .

[0064] The results obtained by colorimetric measurements have been confirmed by GDOES analysis in order to support the observed phenomena.

[0065] GDOES measurements:

GDOES (glow discharge optical emission spectrometry) principle

[0066] The sample forms the cathode and a thin (4 mm diameter) copper tube forms the anode. A small O-ring separates the anode from the cathode. High-purity argon is pumped into the anode chamber. A high voltage (DC or RF) between sample and anode ionizes the argon to produce a glow discharge plasma. The excited argon ions bombard the electroplated product sample and cause uniform sputtering of the sample surface. Atoms ejected are then excited by the argon plasma, and finally relax to their fundamental energy level, emitting a characteristic X-ray photon.

[0067] Emitted photons, whose energy is characteristic of the energy level of a chemical element, are then collected by photomultipliers. The intensity of each emission depends on the concentration of the element in the sample. The recorded signals are processed to obtain the distribution of the elements according to the erosion time. GDOES provides a depth profiling analysis of solids like metals, powders, polymers, glasses and ceramics (in the present case: depth profiling of electroplated substrates).

[0068] The advantages of GDOES are its rapid, multi-elemental acquisition, a simple implementation (no ultra-high vacuum) and the high sensitivity of detection for light elements, (like e.g. C, N and O).

GDOES analysis

[0069] The following parameters were used for the GDOES analysis:

- GD Profiler, HORIBA, Jobin Yvon
- detection of elements: Au, In, Cu
- diameter of the anode: 4 mm
- analyses of samples without and with heat treatment: Au, In and Cu, additionally Sn, Zn for example 2
- power: 25 W
- pressure: 620 Pa
- wavelengths of the spectral lines used (in nm):
- Au 242,8 ; Cu 224, 7; Zn 481; Sn 317,5; Ni 341,5 ; In 451,1 nm

[0070] The analysis was performed before and after heat treatment for 24 hours at 180°C

[0071] A low power was retained to decrease the speed of abrasion of the deposits with low thickness and to obtain maximum information at the interfaces. Quantified compositional results were evaluated automatically utilizing the standard Jobin Yvon Quantum Intelligent Quantification software. The instrument was calibrated with standards of known composition. Depths were calculated using relative sputtering rates, obtained from the sputtering yields of each major element with corrections for composition and discharge conditions.

[0072] The spectrum obtained represents the qualitative intensity of the metallic signal variation depending on time of sputtering in s.

[0073] Figs. 4 to 9 give the GDOES depth profiles for the different electroplated products of Examples 1 to 6 before and after the heat treatment at 180°C for 24 hours. The concentration of each chemical element Au, Cu, In and optionally

Sn and Zn for reference is shown (y-axis for intensity) as a function of the distance from the surface of the finishing layer towards the base material of the electroplated product (x-axis for erosion time).

Table 2: Samples analyzed by GDOES analysis

Copper thickness	15 μm	15 μm	15 μm	15 μm	15 μm	15 μm
Layer 1	GOLD	White bronze	Indium	Indium	Gold-Indium alloy %Au 95 %In 5	Gold-Indium alloy %Au 90 %In 10
Thickness layer 1	0,5 μm	3 μm	100 nm	100 nm	0,5 μm	0,5 μm
Layer 2	-	GOLD	GOLD	GOLD	-	-
Thickness layer 2	-	0,5 μm	0,5 μm	0,5 μm	-	-
REF example	Comparative EX 1	Comparative EX 2	EX 3	EX 4	EX 5	EX 6
REF Figure (without thermal treatment)	4a	5a	6a	7a	8a	9a
REF Figure (with thermal treatment)	4b	5b	6b	7b	8b	9b

[0074] The same panels were then analyzed by GDOES in order to assess the diffusion of the various metallic elements after heat treatment for 24 h at 180°C.

Comparative Example 1

[0075] In this comparative example the following sequence was used on the reference brass panels:

- Substrate = brass (copper - zinc alloy)
- Acid copper = 15 μm (CUBRAC 440)
- Gold layer = 0.5 μm (AURANE 793)

[0076] The reported thicknesses in table 2 were measured by X ray diffraction using a Fischerscope XAN 222

[0077] The GDOES profile reported on Fig. 4a before heat treatment shows a clear differentiation between gold and copper layers. For comparison, GDOES reference experiments have shown that an analogous heat treatment of a Au-Cu double layer not separated by an In layer (on a substrate) leads to an extensive redistribution with the elements Au - Cu being mixed (alloyed) by counter directional diffusion as reported on Fig. 4b. The exchange is also visible from the color changes of the surface.

Comparative Example 2

[0078] In comparative example 2, a white bronze layer between copper and gold was deposited. In this comparative example the following sequence was used on the reference brass panels:

- Substrate = brass (copper-zinc alloy)
- Acid copper = 15 μm (CUBRAC 440)
- White bronze - cyanide medium = 3 μm (AURALLOY 450 LF)
- Gold layer = 0.5 μm (AURANE 793)

[0079] Fig. 5a is the profile of a sample reported in Example 2 before heat treatment. We can see that each layer is well-defined, and no copper is present in the gold layer.

[0080] After heat treatment (Fig. 5b), tin, and zinc have diffused into the gold layer until reaching the surface of the sample, while copper migrated to a lesser extent. Simultaneously gold diffused into the white bronze. So we can deduce that white bronze alone is efficient enough to slow down the copper diffusion, but that gold still diffuses into the white bronze.

Example 3 (according to the invention)

[0081] In Example 3 according to the present invention the following sequence was used on the reference brass panels:

- Substrate = brass (copper-zinc alloy)
- Acid copper = 15 μm (CUBRAC 440)
- Indium = 100 nm - obtained from ELECTROLYTE 1
- Gold layer = 0.5 μm (AURANE 793)

[0082] Copper, indium and gold were electrodeposited on a substrate. For this Au-In-Cu (substrate) three-layer system it has been demonstrated by GDOES measurements (Fig 6b) that heat treatment (180 °C, 24 h) leads to a redistribution of In into Au, but not - or to a much lesser extent - of Cu into In or vice versa. This result was confirmed by a colour stability ($L^*a^*b^*$ measurement) of the surface over the heating period (Fig. 1 to 3).

[0083] From Example 3 according to the invention, it can be seen from Fig. 6a that the thin intermediate layer of indium is located between the copper and the top gold top layer.

[0084] After heat treatment for 24 hours at 180°C (Fig 6b), one can clearly observe that indium has migrated into the gold layer thus preventing the copper to migrate up to the surface.

[0085] The resulting top layer is an alloy of gold and indium that contains only very little if any copper. Obviously, copper migration to the surface was inhibited. After the heat treatment, the top layer is composed of an Au-In alloy as a cover layer for the Cu under layer (and the substrate). It appears, therefore, that In can be employed as a copper diffusion barrier between a copper or copper alloy substrate and a gold surface layer in a way similar to the action of a nickel or palladium barrier commonly used until recently.

Example 4 (according to the invention)

[0086] In example 4 according to the present invention the following sequence was used on the reference brass panels:

- Substrate = brass (copper - zinc alloy)
- Acid copper = 15 μm (CUBRAC 440)
- Indium = 100 nm - obtained from ELECTROLYTE 2
- Gold layer = 0.5 μm (AURANE 793)

[0087] It can be seen from example 4 that the surprising effect is independent of the type of bath (alkaline or acidic). The GDOES profile on Fig. 7a before heat treatment shows a peak of indium at the interface between indium and gold. After heat treatment (Fig. 7b) indium diffused into the gold thus preventing to a great extent the diffusion of copper into the top layer.

Example 5 (according to the invention)

[0088] In Example 5 according to the present invention the following sequence was used on the reference brass panels:

- Substrate = brass (copper - zinc alloy)
- Copper underlayer: 15 μm obtained via the method here above described
- Gold indium alloy top layer (95% Au - 5% In): 0.5 μm (obtained via the method here above described on page 10 paragraph 5)

Example 6 (according to the invention)

[0089] In Example 5 according to the present invention the following sequence was used on the reference brass panels:

- Substrate = brass (copper - zinc alloy)
- Copper underlayer: 15 μm obtained via the method here above described
- Gold indium alloy top layer (90% Au - 10% In): 0.5 μm (obtained via the method described before (s. Point 5) : Gold indium electrolyte)

[0090] From examples 5 and 6, it can be seen on the GDOES profiles presented on Fig. 8a and Fig. 8b and Fig. 9a and Fig. 9b that the gold-indium alloy (Au 90-95 % : In 5-10 %) layer can strongly reduce the copper migration during the thermal treatment procedure. The interface between the copper layer and the gold-indium alloys is well defined in

both cases and no copper migration is observed from the bottom copper layer.

Claims

1. Method for preparing an electroplated product by electroplating a substrate comprising the following steps:

- a) Electroplating a substrate with an underlayer consisting of copper or a copper alloy with an electrolyte comprising at least one source of copper ions, at least one conductive salt, and, optionally, at least one ion source of an alloy former for copper,
- b) Electroplating of a barrier layer on the underlayer with an aqueous bath comprising at least one source of indium ions and at least one conductive salt,
- c) Electroplating of a top layer consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and its alloys with an electrolyte comprising at least one ion source for the precious metal 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** 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, wherein the concentration of indium 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 7 g/L.

4. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** for the electroplating bath of step b) the at least one conductive salt is selected from the group consisting of citrates, formiates, pyro-phosphates, gluconates, and combinations or mixtures thereof, preferably selected from the group consisting of sodium citrate, sodium formiate, tetrapotassium pyrophosphate, sodium gluconate, potassium gluconate, and combinations or mixtures thereof, wherein the concentration of the at least one conductive salt is preferably from 30 to 500 g/L, more preferably from 50 to 300 g/L, and most preferably from 100 to 200 g/L.

5. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the electroplating bath of step b) comprises at least one surfactant, preferably selected from the group consisting of propionic amino acids, propionic imino acids, quaternary alkyl betaines or sulfo-betaines, more preferably selected from the group of betaine, aminobetaine, imidazoline Cocamidopropyl betaine, N,N-Dimethyl-N-(3-cocoamidopropyl)-N-(2-hydroxy-3-sulfopropyl) ammonium betaine, 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, wherein the concentration of the at least one surfactant is preferably from 0,1 to 5 g/L, more preferably from 0,5 to 1,5 g/L.

6. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the electroplating bath of step b) comprises at least one complexing agent consisting of carbohydrates, amino acids, imino acids, sulfur compounds, sugar alcohols, and combinations or mixtures thereof, preferably selected from the group consisting of sorbitol, mannitol, gluconate, erythritol, xylitol, nitrilotriacetic acid, cysteine, iminodiacetic acid, triethanolamines, and combinations or mixtures thereof, wherein the concentration of the at least one complexing agent is preferably from 0,5 to 100 g/L, more preferably from 1 to 75 g/L, even more preferably from 2,5 to 50 g/L, and most preferably from 5 to 35 g/L.

7. Method for preparing an electroplated product of any of the preceding claims, **characterised in that** the electroplating bath of step b) comprises at least one source of gold ions, preferably selected from the group consisting of potassium gold (I) cyanide, potassium gold(III) cyanide, sodium gold(I) sulphite, potassium gold(I) sulfite, gold (III) chloride and tetrachloroaurates(III), gold(I) thioglycerol and gold(I) and gold(III) hydantoin complexes, and combinations or mixtures thereof, wherein the concentration of the at least one source of gold ions is preferably from 0,5 to 10 g/L, more preferably from 1 to 5 g/L and most preferably from 2,5 to 3,5 g/L.

8. 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 electroplated in step a) to c) abut to each other.

9. Electroplated product comprising a substrate which is coated with an underlayer consisting of copper or a copper alloy and a top layer consisting of a precious metal selected from the group consisting of Au, Ag, Pd, Rh, Ru, Pt and alloys thereof,
characterised in that the underlayer and the top layer are separated by a diffusion barrier layer consisting of Indium or an alloy of Indium with the material of the top layer.

10. Electroplated product of claim 9
characterised in that the diffusion barrier layer has a thickness of 10 to 200 nm, more preferably 25 to 150 nm and most preferably 50 to 100 nm.

11. Electroplated product of claim 9 or 10,
characterised in that the diffusion barrier layer comprises an gold indium alloy, preferably with 90 to 95 % by weight of gold and 5 to 10 % by weight of indium.

12. Electroplated product of any of claims 9 to 11,
characterised in that the diffusion barrier layer abuts to the underlayer and, on the opposite side, to the top layer.

13. Electroplated product of any of claims 9 to 12,
characterised in that the electroplated product is selected from the group consisting of jewelry, leather goods, spectacle frame, fashion, watch, trinkets and/or lock industry.

14. Electroplated product of any of claims 9 to 13 producible with the method of any of claims 1 to 8.

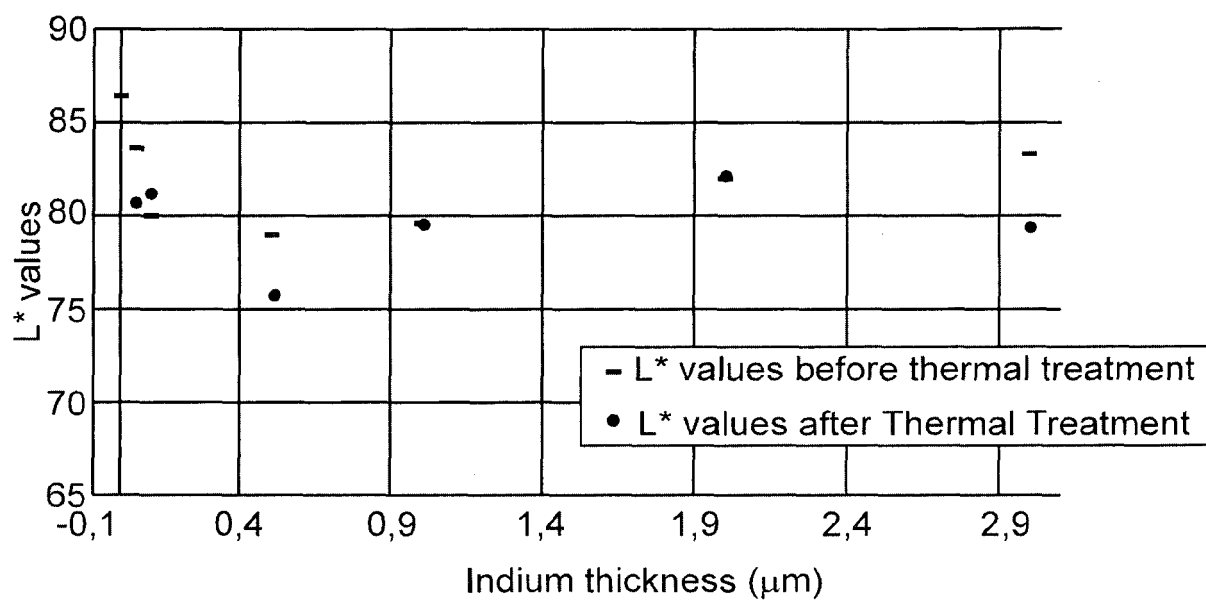


Fig. 1

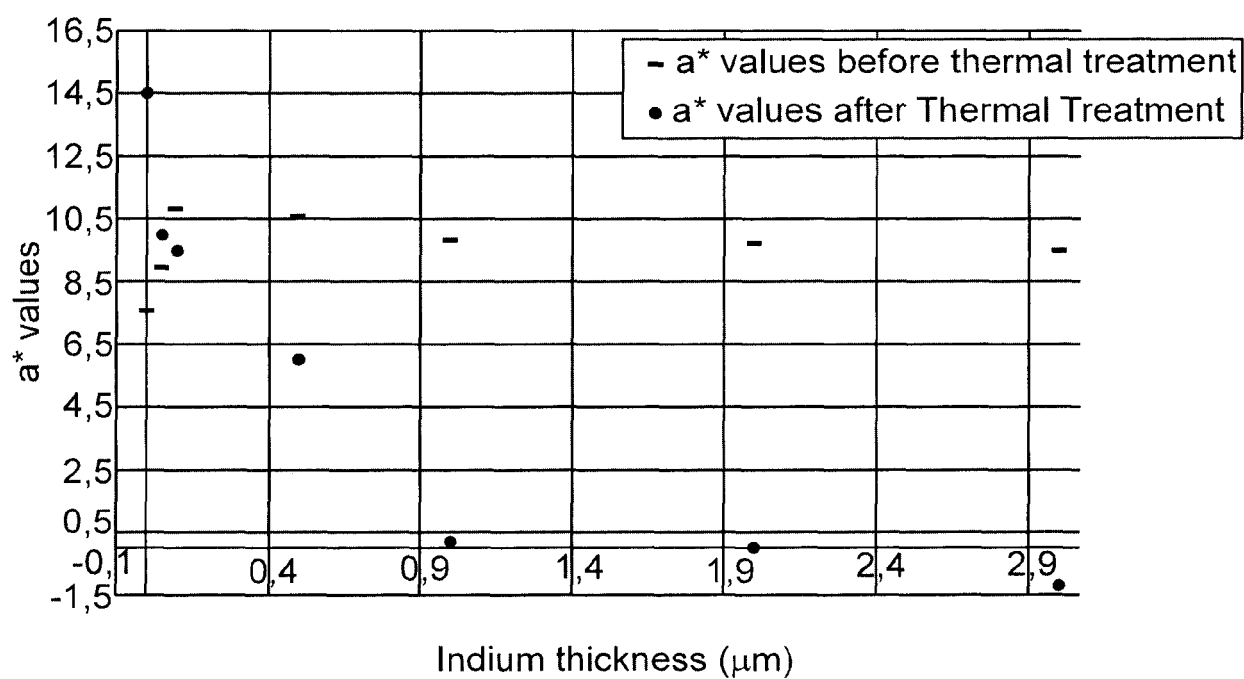


Fig. 2

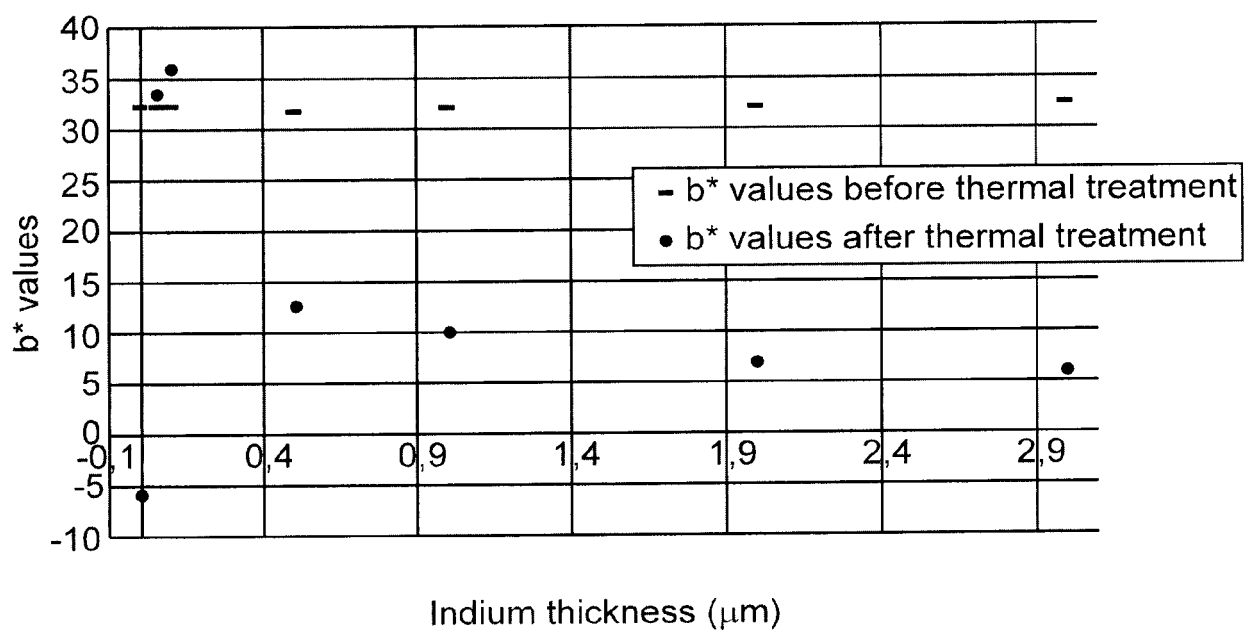
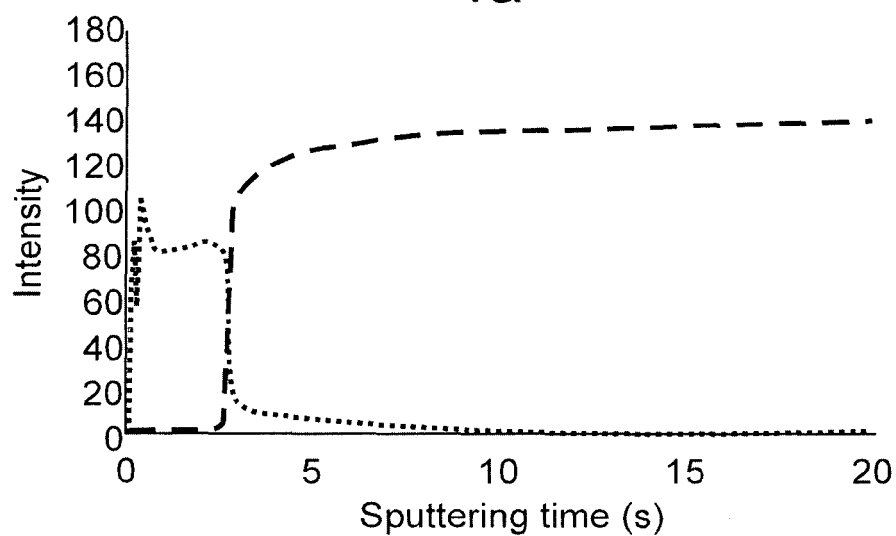


Fig. 3

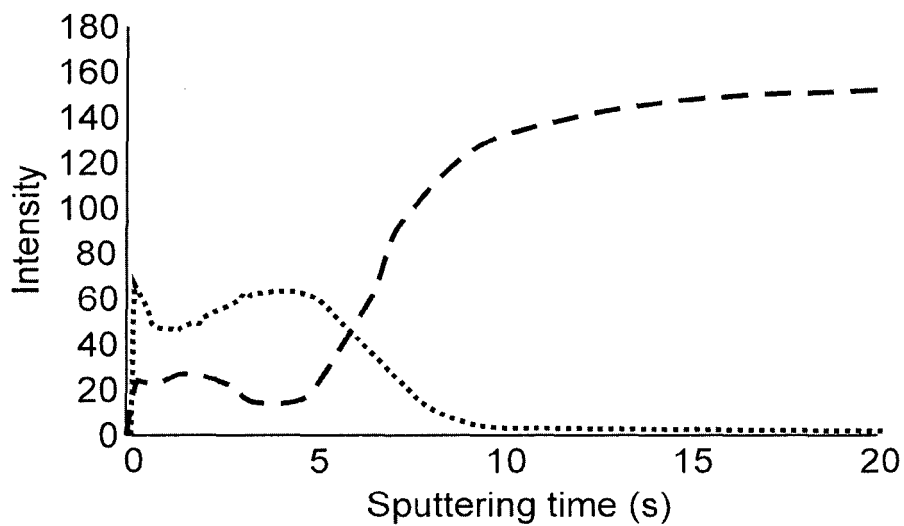
4a



..... Au*5 - - Cu/3

GD OES profiles of Cu / Au before thermal treatment

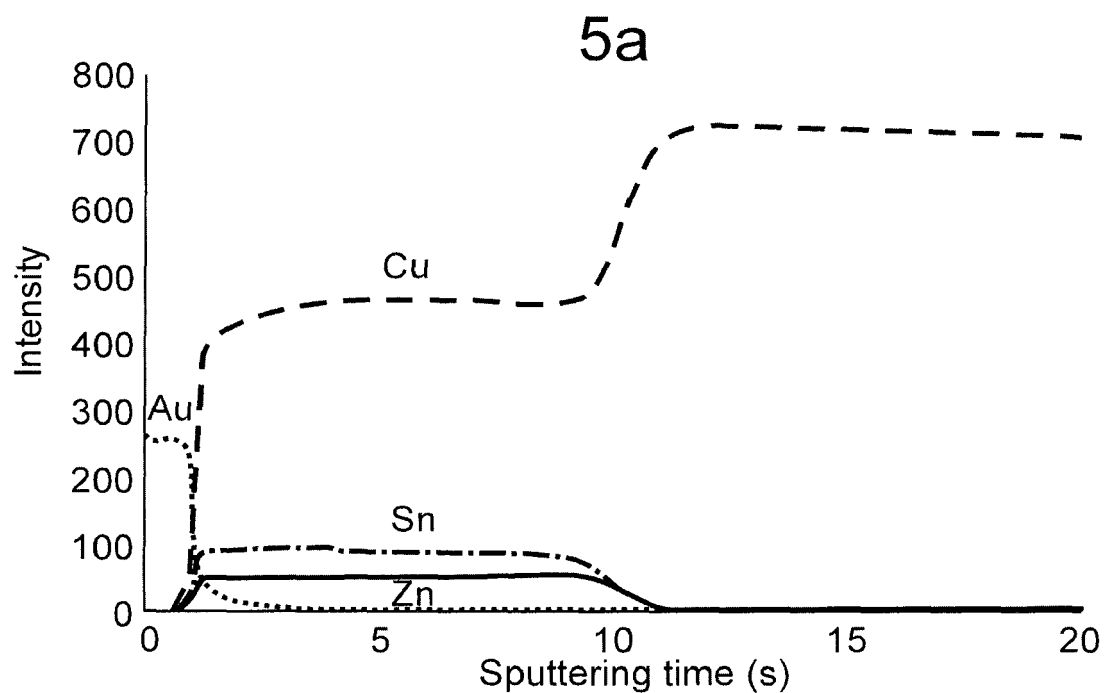
4b



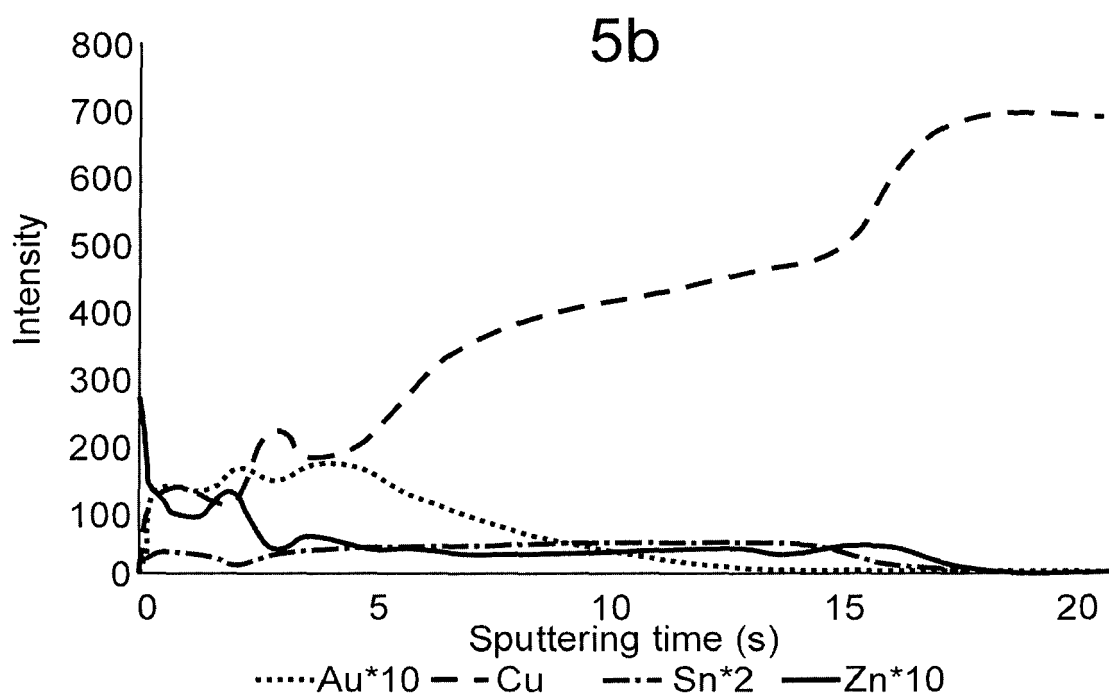
..... Au*5 - - Cu/3

GD OES profiles of Cu / Au after 24 hours-180°C

Fig. 4



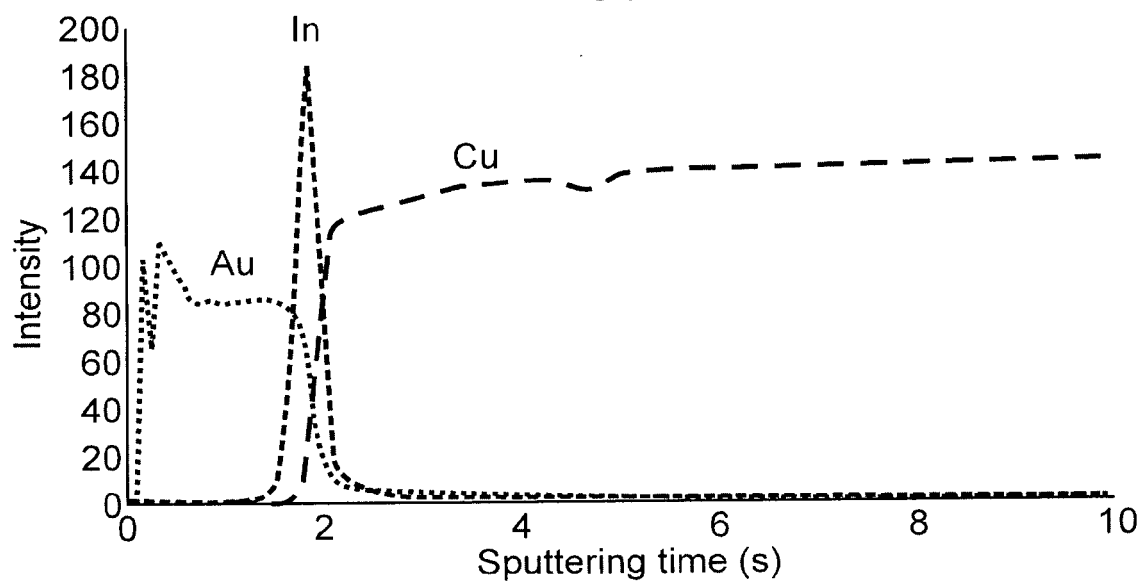
GD OES profiles of Cu/White bronze/Au without heat treatment



GD OES profiles of Cu/White bronze/Au after heat treatment

Fig. 5

6a

GDOES profile of Cu/**INDIUM**/Au without heat treatment

6b

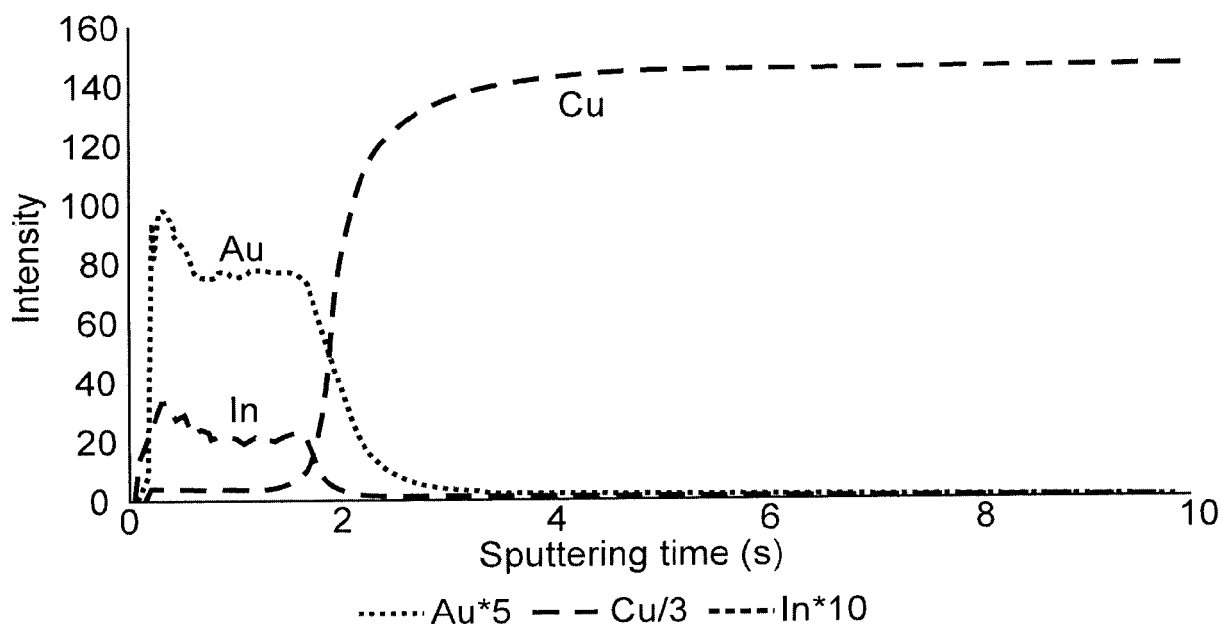
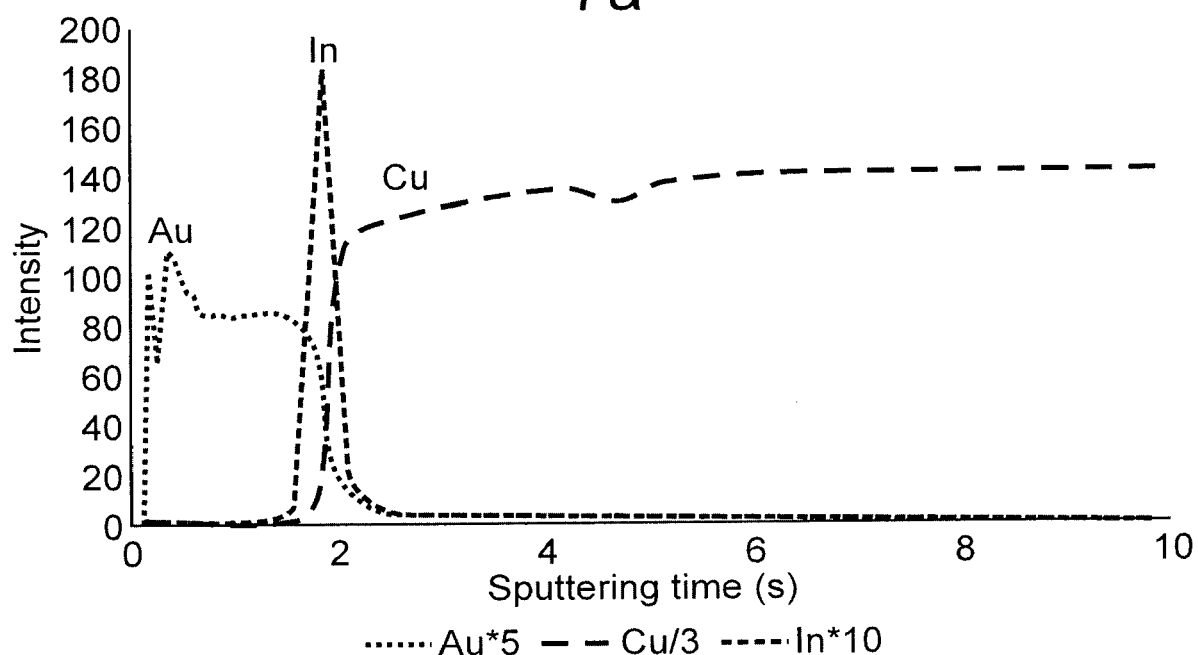
GDOES profile of Cu/**INDIUM**/Au after heat treatment 24 hours at 180°C

Fig. 6

7a

GDOES profile of Cu/**INDIUM**/Au without heat treatment

7b

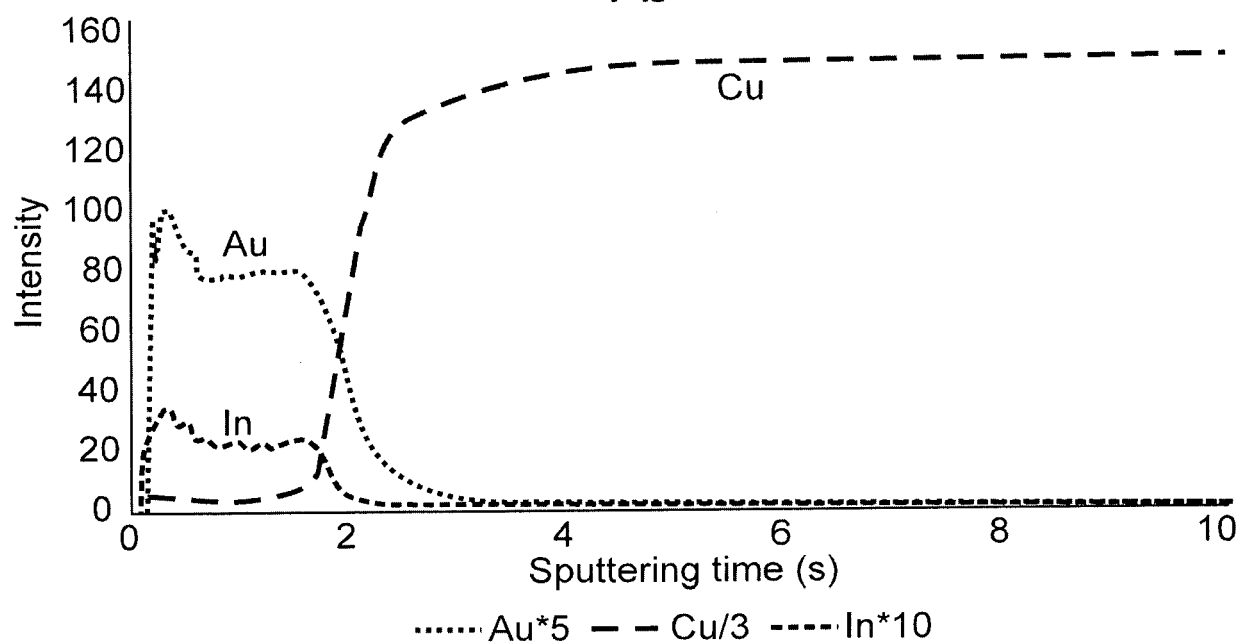
GDOES profile of Cu/**INDIUM**/Au after heat treatment 24 hours at 180°C

Fig. 7

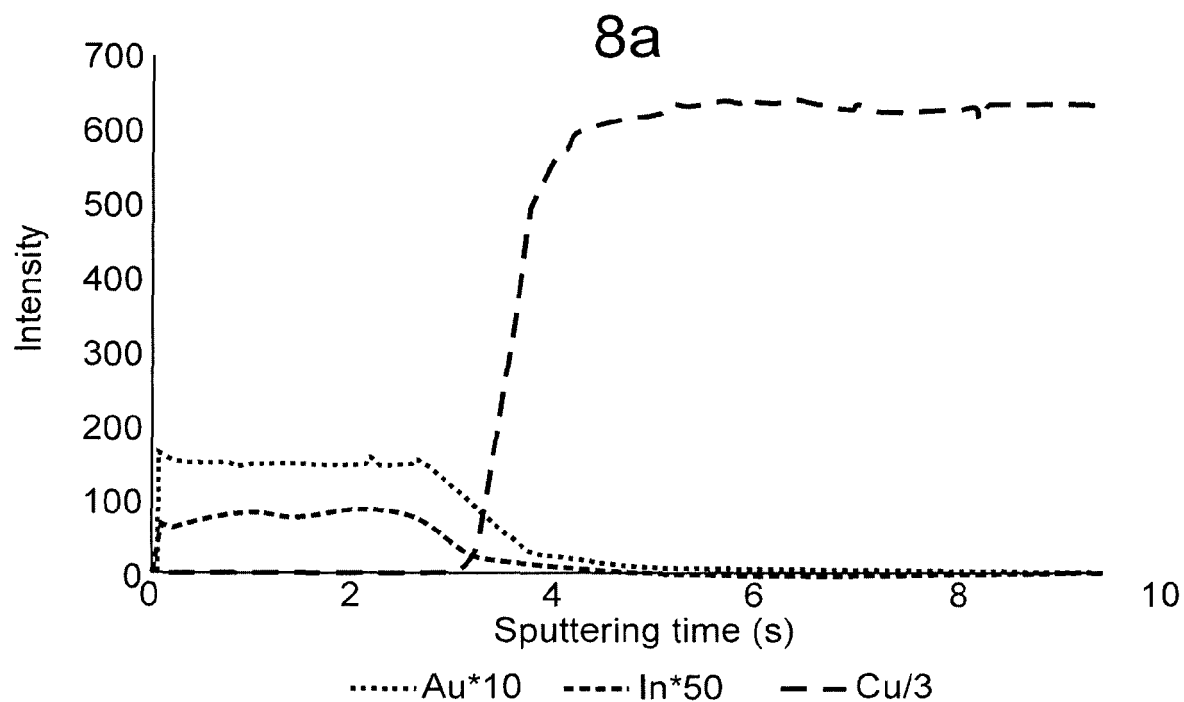
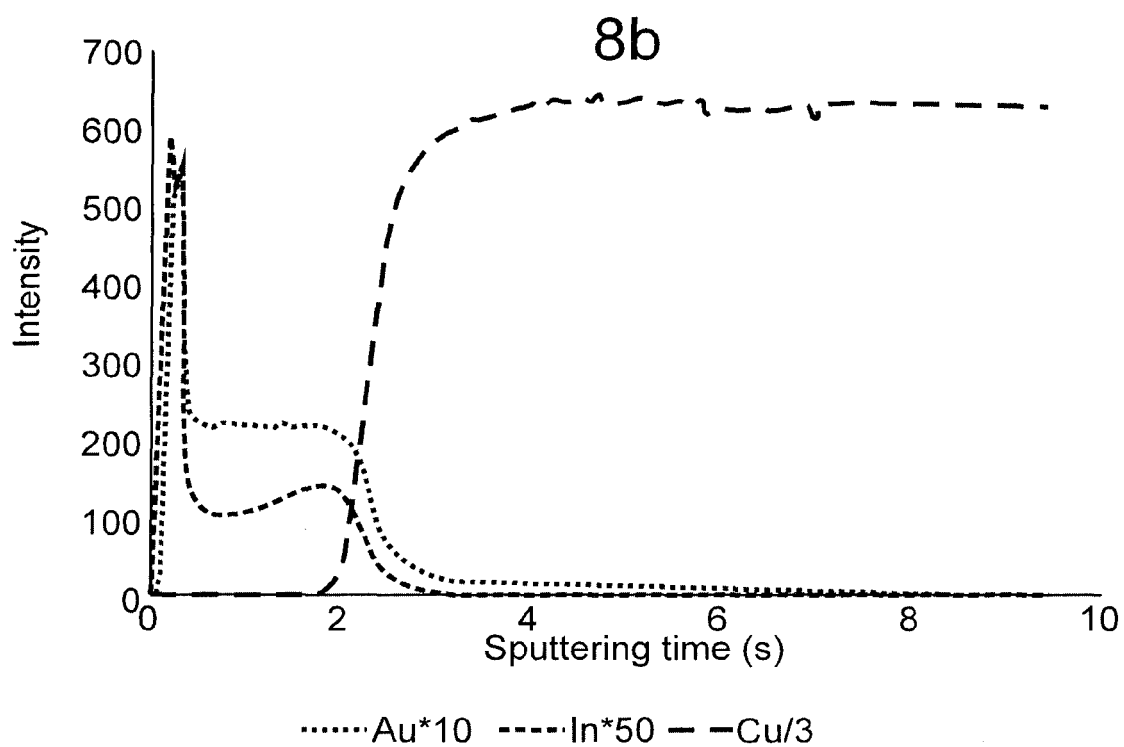
GDOES profile of Cu/**Au95In5** alloy without heat treatmentGDOES profile of Cu/**Au95In5** alloy after heat treatment 24 hours at 180°C

Fig. 8

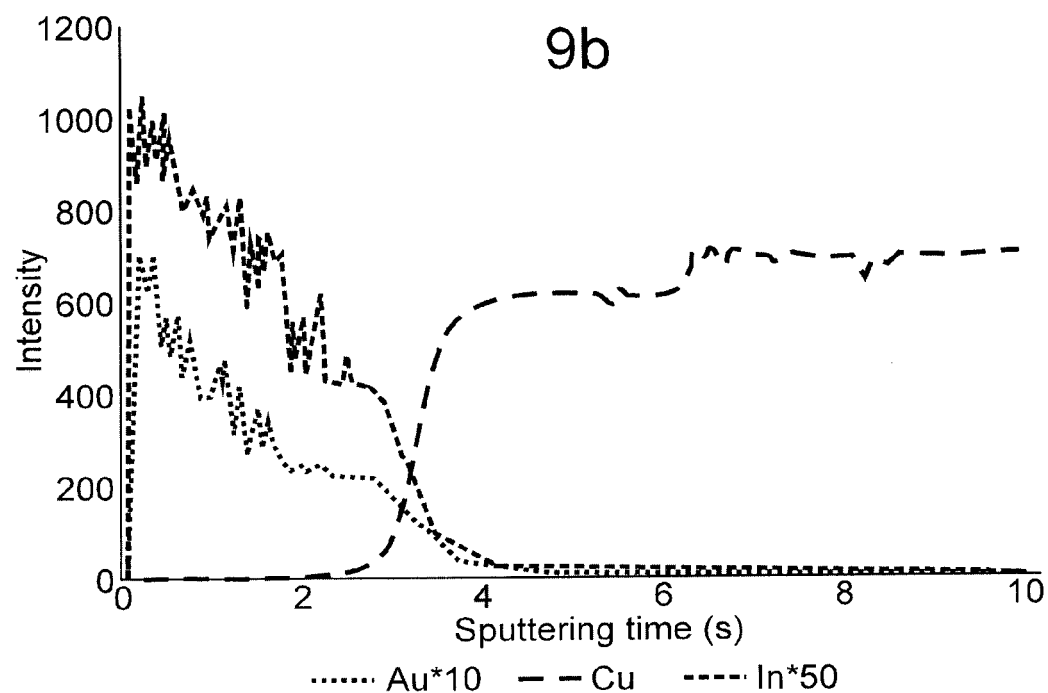
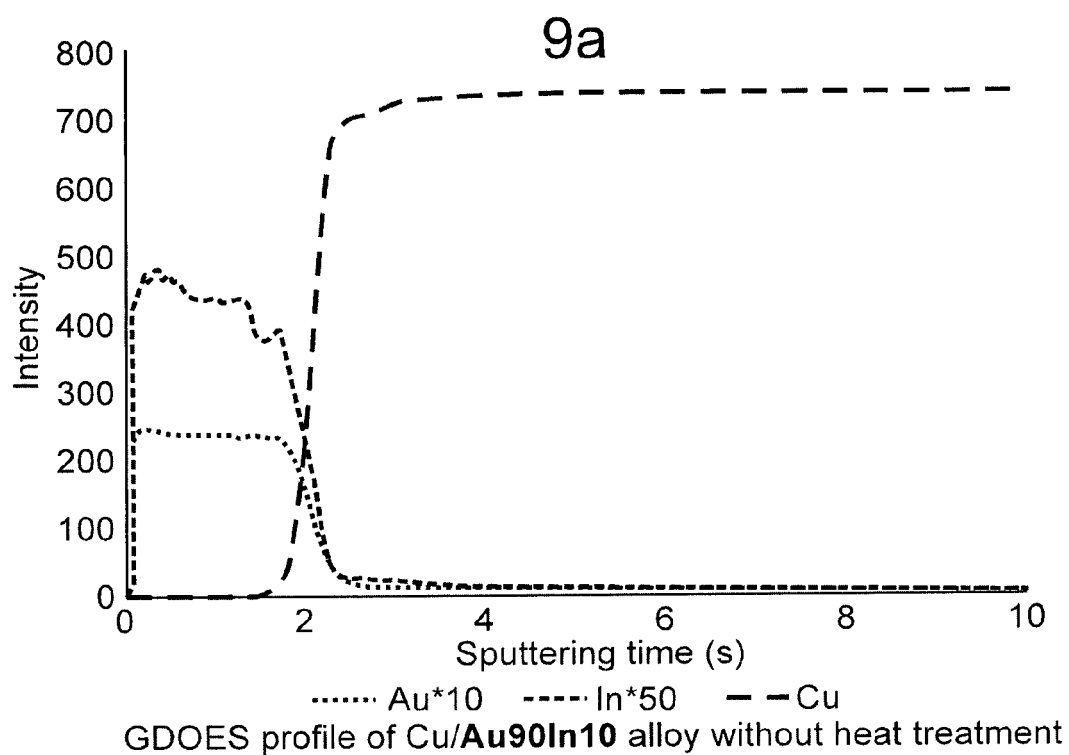


Fig. 9



EUROPEAN SEARCH REPORT

 Application Number
 EP 18 16 1575

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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 A	EP 2 139 012 A1 (FURUKAWA ELECTRIC CO LTD [JP]) 30 December 2009 (2009-12-30) * paragraphs [0009] - [0015] * * paragraphs [0023] - [0025] * * claims 1-5; figure 1 *	1,8,9, 12-14 7,11	INV. C25D7/00 C25D3/54 C25D3/56 C25D3/62 C25D5/10
X A	JP 2015 045045 A (JX NIPPON MINING & METALS CORP) 12 March 2015 (2015-03-12) * paragraphs [0012] - [0015] * * paragraph [0033] * * paragraphs [0026] - [0029] * * paragraphs [0033] - [0034] * * paragraphs [0040] - [0041] *	1,9,10, 12-14 7,11	
X,D	WO 2015/000010 A1 (W GARHÖFER GES M B H ING [AT]) 8 January 2015 (2015-01-08) * page 7, line 18 - page 8, line 34; examples 1-4 *	1-6,8	
X	US 3 367 754 A (DUGAN WILLIAM P ET AL) 6 February 1968 (1968-02-06) * column 4, line 55 - column 5, line 20 * * column 5, line 65 - column 6, line 75 * * column 7, line 27 - column 8, line 26 *	1,2,9, 13,14	TECHNICAL FIELDS SEARCHED (IPC) C25D
X	US 2011/259753 A1 (GROSSENBACHER PASCAL [CH] ET AL) 27 October 2011 (2011-10-27) * paragraphs [0029] - [0048] *	9,10, 12-14	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 4 September 2018	Examiner Crottaz, Olivier
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.**

EP 18 16 1575

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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04-09-2018

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15

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25

30

35

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45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2139012 A1	30-12-2009	CN 101681728 A	24-03-2010
		EP 2139012 A1	30-12-2009
		JP 4834022 B2	07-12-2011
		JP 2008270192 A	06-11-2008
		KR 20090127405 A	11-12-2009
		TW 200842212 A	01-11-2008
		US 2010186993 A1	29-07-2010
		WO 2008123259 A1	16-10-2008

JP 2015045045 A	12-03-2015	NONE	

WO 2015000010 A1	08-01-2015	AT 514427 A4	15-01-2015
		WO 2015000010 A1	08-01-2015

US 3367754 A	06-02-1968	NONE	

US 2011259753 A1	27-10-2011	CN 102233702 A	09-11-2011
		CN 105272379 A	27-01-2016
		EP 2380864 A1	26-10-2011
		EP 2383244 A1	02-11-2011
		HK 1220682 A1	12-05-2017
		JP 5385333 B2	08-01-2014
		JP 2011230506 A	17-11-2011
		KR 20110118569 A	31-10-2011
		KR 20130038895 A	18-04-2013
		US 2011259753 A1	27-10-2011

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2016166330 A1 [0005]
- WO 2017055553 A1 [0006]
- WO 2015000010 A1 [0008]
- EP 1930478 A1 [0009]
- WO 2004035875 A3 [0010]
- WO 2013092314 A [0011]
- KR 1168215 B1 [0012]
- US 2458839 A [0014]
- WO 2009097360 A1 [0015]
- EP 2123799 B1 [0016]
- WO 2017060216 A1 [0017]