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(54) **ELECTROPLATING BATH FOR ELECTROCHEMICAL DEPOSITION OF A CU-SN-ZN-PD ALLOY, METHOD FOR ELECTROCHEMICAL DEPOSITION OF SAID ALLOY, SUBSTRATE COMPRISING SAID ALLOY AND USES OF THE SUBSTRATE**

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CU-SN-ZN-PD-LEGIERUNG, VERFAHREN ZUR ELEKTROCHEMISCHEN ABSCHIEDUNG VON  
DIESER LEGIERUNG, SUBSTRAT MIT DIESER LEGIERUNG UND VERWENDUNG DES  
SUBSTRATS

BAIN D'ÉLECTRODÉPOSITION POUR LE DÉPÔT ÉLECTROCHIMIQUE D'UN ALLIAGE  
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**EP 3 356 579 B1**

## Description

**[0001]** The invention provides an electroplating bath for electrochemical deposition of a novel Cu-Sn-Zn-Pd alloy on a substrate. The novel alloy is characterized by exceptional corrosion resistance. The commonly used precious metal intermediate layer (e.g. a Pd-layer) between the substrate and the finishing layer is no longer necessary which allows a substantial reduction of the production costs of the plated substrates. Moreover, the novel alloy can be provided free of toxic metals (e.g. free of nickel) which makes it hypoallergenic and not prone to cause skin irritation. Finally, the plating of the inventive alloy between a substrate and its finishing layer prevents discolouration or colour fading of the finishing layer over time. All these advantages render the novel alloy particularly suitable for plating it on items of the fashion industry.

**[0002]** Nickel has been highlighted as an allergenic metal and its use in consumer products is strongly restricted. Prior to these restrictions, a decorative galvanic layer sequence comprised a nickel layer to reach the bright aspect of the final article, but also to optimize the corrosion resistance properties and to function as a copper diffusion barrier. A high robustness is required for the final object in order to resist the aggressive media created by environmental pollution. A specific nickel-phosphorus alloy was also proposed in order to protect articles produced for the Asian market, where the atmosphere tends to contain high nitrogen and sulphur oxide concentrations.

**[0003]** In a large number of research projects it is presently attempted to substitute nickel by non-allergenic alternatives. As one of the results, the introduction of ternary bronze alloys (copper-tin-zinc) for replacing the nickel layer has been proposed to producers and has become the currently most common solution to the technical problem.

**[0004]** Unfortunately, however, bronze as a protective under-layer does not provide the provision of a corrosion resistance like the one previously achieved with nickel. These copper alloys are also less efficient as copper diffusion barriers. In order to improve the performance of the galvanic sequence of layers by substituting a nickel layer with a bronze layer, most variants require the use of a precious metal under-layer like palladium which is commonly applied between the bronze layer and the final decorative finishing layer. This additional under-layer considerably increases the production costs and can lead to a lack of adhesion of the finishing layer due to palladium passivity.

**[0005]** Tin and other tin alloys as barrier layers with high tin content have also been developed, but are not really efficient regarding the high brightness required by the fashion market or the high resistance necessary to pass pertinent corrosion tests.

**[0006]** EP 1930 478 B1 presents a quaternary bronze alloy where the fourth metal is gallium, indium or thallium. Thallium was introduced into the decorative market as a grain refining agent to substitute lead previously present in typical cyanide bronze electrolytes. However, the use of thallium does not raise the bronzes corrosion resistance i.e. the alloy is still highly sensitive to acidity generated by nitrogen and sulphur oxides present ubiquitously in polluted atmospheres. In addition, thallium is highly toxic. Gallium and indium alloys have the disadvantage that they are poorly resistant to aggressive media such as synthetic sweat or saline humidity.

**[0007]** EP 2 035 602 B1 proposes the introduction of a palladium, ruthenium, rhodium or cobalt layer between the copper-tin layer and the finishing layer. These metals raise considerably the production costs of the final article. Moreover, the passivity of these electroplated layers results in poor adhesion of the final layer and in poor performance regarding corrosion resistance.

**[0008]** EP 2 757 180 A1 recommends the use of tin alloys with a precious metal, ruthenium in this particular case. The ruthenium content needs to be high and this does not allow reducing the production costs due to the high price of ruthenium. Moreover, the process does not yield products with the bright aspect required by the decorative and fashion industries.

**[0009]** CN 1175 287 A discloses the deposition of white ornamental surfaces built on a base material covered with copper with a thickness of 1 micron as an under-layer. Said layer is followed by a layer of a Sn-Cu-Pd alloy in a thickness of 0.2 microns or higher, comprising 10-20 wt.-% Sn, 10-80 wt.-% Cu and 10-50 wt.-% Pd as the essential components. Owing to the lack of zinc in this alloy, it does not give the required performance regarding the efficiency as a copper migration barrier. This ternary copper-tin-palladium alloy is not suitable as a nickel substitute since the deposit is not bright and shows only poor corrosion resistance.

**[0010]** JP 2 977503 B2 discloses an alkaline copper-palladium alloy plating liquid comprising a soluble zinc compound, an alkaline salt, a soluble copper compound, a soluble palladium component and a soluble stannic alkaline compound, wherein the concentration of the palladium component is 5 to 20 g/L.

**[0011]** WO 2017/021916 A2 with publication date 09-02-2017, discloses an electroplating bath for electrochemical deposition of a Cu-Sn-Zn-Pd alloy on a substrate, comprising water, a source of copper ions, a source of tin ions, a source of zinc ions and a palladium complex.

**[0012]** To date, the prior art does not provide a suitable unique under-layer to substitute nickel for its specific applications regarding brightness, corrosion-resistance and metal diffusion barrier.

**[0013]** It is therefore the objective of the present invention to substitute nickel by providing an under-layer with outstanding corrosion resistance in an economic way, wherein the under-layer is supposed to form an efficient metal

migration barrier.

**[0014]** The problem is solved by the electroplating bath according to claim 1, the method according to claim 4, the substrate according to claim 9 and the use of the substrate according to claim 13.

**[0015]** According to the invention, an electroplating bath for electrochemical deposition of a Cu-Sn-Zn-Pd alloy (preferably a quaternary Cu-Sn-Zn-Pd alloy) on a substrate is provided, the bath comprising or consisting of

- a) water;
- b) a source of copper ions;
- c) a source of tin ions;
- d) a source of zinc ions; and
- e) a palladium salt and/or a palladium complex;
- f) an inorganic brightening agent selected from the group consisting of bismuth nitrate, bismuth acetate, bismuth citrate, bismuth chloride, potassium antimony hexahydroxide, antimony chloride, antimony nitrates, sodium selenite, selenium dioxide, selenium tetrachloride, selenium sulphide and mixtures thereof;

wherein the electroplating bath has an alkaline pH, and wherein the concentration of copper in the electroplating bath is between 2.5 g/L and 25 g/L; and tin in the electroplating bath is between 5 g/L to 35 g/L; and zinc in the electroplating bath is between 0.25 g/L to 5 g/L; and the palladium as palladium salt and/or palladium complex in the electroplating bath is between 5 and 200 mg/L.

**[0016]** The inventive electroplating bath allows the provision of a substrate having an alloy layer which comprises the precious metal palladium. The novel alloy resists aggressive atmospheric and other environmental conditions and considerably increases the shelf and usage life of substrates (plated articles). Even without an intermediate precious metal under-layer (e.g. a palladium under-layer) between the substrate and the finishing layer, excellent corrosion protection is provided (pertinent standardized corrosion tests are successfully passed). Furthermore, without disadvantages related to corrosion protection, the use of the inventive alloy allows a substantial reduction of the production costs compared to the use of a pure precious metal underlayer. In addition, the final article can be provided free of toxic metals (e.g. free of nickel) which renders it hypoallergenic and not prone to cause skin irritation. Finally, the new alloy provides a smooth coating to the article and prevents diffusion of metallic components from the lower layers to the finishing layer and vice versa. Thus, a colour fading or discolouration of the final aspect is prevented.

**[0017]** In summary, the new bronze alloy layer has lower production costs, very high brightness, very high corrosion resistance and excellent ageing behaviour.

**[0018]** By adjusting the copper and/or tin content, the final colour (yellow or white bronze) may be adjusted. For efficient copper migration barrier properties, it has been discovered that a concentration range of 1 to 20 % wt.-% zinc in the final alloy is sufficient. The palladium content of  $\geq 0.25$  wt.-% in the alloy was found sufficient for providing the required corrosion resistance. Production costs can be minimized by keeping the palladium concentration  $\leq 5$  wt.-% in the final alloy while corrosion protection performance is maintained. It was found that a palladium content higher than 5 wt.-% in the alloy considerably raises the production costs without significantly improving corrosion resistance.

**[0019]** In the inventive electroplating bath, the concentration of

- a) copper in the electroplating bath is between 2.5 g/L and 25 g/L, preferably 3.5 g/L to 20 g/L; and/or
- b) tin in the electroplating bath is between 5 g/L to 35 g/L, preferably 9.75 g/L to 26.25 g/L; and/or
- c) zinc in the electroplating bath is between 0.25 g/L to 5 g/L; and/or
- d) palladium as palladium salt and/or palladium complex in the electroplating bath is between 5 to 200 mg/L.

**[0020]** In a preferred embodiment of the invention,

- a) the source of copper ions is selected from the group consisting of copper sulphate, copper oxide, copper hydroxide, copper chloride, copper nitrate, copper acetate, copper carbonate and copper cyanide, or a mixture thereof, preferably copper cyanide; and/or
- b) the source of tin ions is a tin(II) and/or tin(IV) compound, preferably a tin(IV) salt, more preferably potassium stannate; and/or
- c) the source of zinc ions is zinc acetate, zinc chloride, zinc cyanide, zinc sulphate and/or an alkali zincate; and/or
- d) the palladium salt and/or palladium complex is selected from the group consisting of palladium chloride, palladium bromide, palladium cyanide, palladium nitrite, palladium nitrate, palladium sulphate, palladium thiosulphate, palladium acetate, palladium hydrogencarbonate, palladium hydroxide and palladium oxide, with or without ligands selected from the group of ammonia and amines, most preferably complexes selected from the group consisting of palladium diamino dichloride, palladium diamino sulphate, palladium diamino dinitrate, tetramine palladium chloride, tetramine palladium sulphate, tetramine palladium nitrate, tetramine palladium hydrogencarbonate, palladium eth-

ylenediamine chloride, palladium ethylenediamine sulphate, palladium potassium thiosulphate, and mixtures thereof.

**[0021]** In a further preferred embodiment, the electroplating bath does not comprise a source of nickel ions, preferably no source of nickel and silver ions, optionally no source of nickel, silver and indium ions.

**[0022]** The electroplating bath may further comprise

- a) a complexing agent, preferably potassium cyanide and/or sodium cyanide, preferably at a concentration of 20 to 80 g/L, more preferably, 25 to 60 g/L; and/or
- b) a base, preferably potassium hydroxide and/or sodium hydroxide, preferably at a concentration of 1 to 60 g/L, more preferably 2 to 40 g/L; and/or
- c) a conductive salt, preferably Rochelle salt, potassium carbonate and/or sodium carbonate, preferably at a concentration of 10-100 g/L; and/or
- d) a surfactant, preferably an amphoteric, anionic and/or non-ionic surfactant, more preferably selected from the group consisting of betaines, sulfobetaines, alkyl sulphates, alkyl ether sulphates, alkyl ether phosphates, alkyl sulfonates, alkyl sulfosuccinates, alkyl benzene sulfonates, alcohol polyglycol ethers, polyethylene glycols, and mixtures thereof, wherein the surfactant concentration is preferably 0.05 g/L to 1 g/L, more preferably 0.15 g/L to 0.5 g/L.

**[0023]** According to the invention, the electroplating bath comprises an inorganic brightening agent selected from the group consisting of bismuth nitrate, bismuth acetate, bismuth citrate, bismuth chloride, potassium antimony hexahydroxide, antimony chloride, antimony nitrates, sodium selenite, selenium dioxide, selenium tetrachloride, selenium sulphide and mixtures thereof.

**[0024]** Furthermore, a method for the electrochemical deposition of a Cu-Sn-Zn-Pd alloy on a substrate is provided, the method comprising the steps

- a) forming an electrical contact between a substrate and a negative electrode of a power source;
- b) contacting the substrate with the inventive electroplating bath;
- c) contacting at least a part of a positive electrode of the power source with the inventive electroplating bath; and
- d) applying a voltage between the positive and negative electrode of the power source until a deposit of a Cu-Sn-Zn-Pd alloy has formed on the substrate.

**[0025]** The method may be characterized in that a substrate is used that comprises or consists of a metal or an alloy selected from the group consisting of bronze, brass, Zamack, alpaca, copper alloy, tin alloy, steel and mixtures thereof and/or the substrate used is a metal-plated object of plastic and/or an alloy-plated object of plastic.

**[0026]** In a preferred embodiment, a positive electrode may be used that comprises or consists of an insoluble anode material, preferably graphite, mixed metal oxides, platinated titanium and/or stainless steel.

**[0027]** In a further preferred embodiment, the applied voltage is adjusted to provide a current density of 0.05 to 5 A/dm<sup>2</sup>, preferably 0.2 to 3 A/dm<sup>2</sup>.

**[0028]** The temperature of the electroplating bath may be kept at between 20 and 80 °C, preferably at between 40 to 70 °C. At temperatures below 20 °C, the coating is less bright, not homogeneous and not uniform in its colour. Above 80 °C, the electroplating results in too many break-down products which results in a quick build-up of potassium carbonate as well as a rapid ageing of the electrolyte. The optimum temperature range was discovered to be between 40 to 70°C.

**[0029]** Moreover, according to the invention, a substrate comprising an electrochemically deposited Cu-Sn-Zn-Pd alloy layer is provided, the alloy layer comprising or consisting of

- a) 30 to 90 % wt.-% of copper;
- b) 5 to 60 % wt.-% of tin;
- c) 1 to 20 wt.-% of zinc; and
- d)  $\geq 0.25$  to  $\leq 5$  wt.-% palladium,

characterized in that the substrate is producible with the method according to the invention, and wherein the substrate has additionally an electrochemically deposited layer comprising or consisting of copper, wherein said layer has a thickness of 1 nm to 1 mm.

**[0030]** The Cu-Sn-Zn-Pd alloy layer electrochemically deposited on the inventive substrate is free of cracks, bright and provides the substrate with excellent corrosion resistance. Moreover, the inventive substrate is characterized by an excellent ageing behaviour i.e. it does not show discolouration or colour fading over time.

**[0031]** In a preferred embodiment of the invention, the alloy comprises

- a) 40 to 85 % wt.-% of copper, optionally 45 to 80 wt.-%; and/or  
 b) 10 to 50 % wt.-% of tin, optionally 15 to 45 wt.-%; and/or  
 c) 2 to 15 wt.-% of zinc, optionally 3 to 10 wt.-%; no silver; and/or  
 d) no indium; and/or  
 e) no nickel; and/or  
 f) no mercury.

**[0032]** A concentration of zinc between 2 and 15% wt.-% in the alloy was discovered to give the most effective copper diffusion barrier.

**[0033]** In a preferred embodiment, the alloy layer is free of nickel, preferably free of nickel and silver, optionally free of nickel, silver and indium or free of nickel, silver, indium and mercury.

**[0034]** The thickness of the electrochemically deposited Cu-Sn-Zn-Pd alloy layer may be 1 nm to 25  $\mu\text{m}$ , preferably 10 nm to 20  $\mu\text{m}$ , more preferably 0.1  $\mu\text{m}$  to 15  $\mu\text{m}$ , even more preferably 1  $\mu\text{m}$  to 10  $\mu\text{m}$ , most preferably 2  $\mu\text{m}$  to 5  $\mu\text{m}$ .

**[0035]** The inventive substrate may be characterized in that it comprises additionally

a) an electrochemically deposited finishing layer comprising or consisting of a noble metal, wherein the electrochemically deposited Cu-Sn-Zn-Pd alloy layer is located between the substrate and the electrochemically deposited finishing layer.

**[0036]** According to the invention, the inventive substrate is characterized in that it comprises additionally an electrochemically deposited layer comprising or consisting of copper. The electrochemically deposited layer comprising or consisting of copper is preferably located between the substrate and the electrochemically deposited Cu-Sn-Zn-Pd alloy layer.

**[0037]** According to the invention, the electrochemically deposited layer comprising or consisting of copper has a thickness of 1 nm to 1 mm, preferably 10 nm to 500  $\mu\text{m}$ , more preferably 0.1  $\mu\text{m}$  to 100  $\mu\text{m}$ , even more preferably 1  $\mu\text{m}$  to 50  $\mu\text{m}$ , most preferably 5  $\mu\text{m}$  to 20  $\mu\text{m}$  or even 10  $\mu\text{m}$  to 15  $\mu\text{m}$ .

**[0038]** The electrochemically deposited finishing layer may optionally have a thickness of 0.01  $\mu\text{m}$  to 20  $\mu\text{m}$ , preferably 0.02 to 10  $\mu\text{m}$ , more preferably 0.05 to 5  $\mu\text{m}$ , most preferably 0.1  $\mu\text{m}$  to 3.0  $\mu\text{m}$  or even 0.2  $\mu\text{m}$  to 0.5  $\mu\text{m}$ .

**[0039]** According to the invention, the substrate is producible with the inventive method.

**[0040]** Finally, the use of the inventive substrate as fashion item is suggested, preferably as an article selected from the group consisting of jewellery, fashion, leather article, watch, eyewear, trinket, lock and/or perfume packaging application. In fact, the inventive substrate fulfils all requirements of the fashion industry (especially the one for jewellery and leather goods articles), namely:

- no alterations by long synthetic sweat contact (standard NFS-80772 - from 12 to 24 hours);
- resistance to interactions with leather under severe conditions for 96 hours (standard ISO-4611 in humid heat atmosphere);
- resistance to aqueous nitric acid simulating the atmosphere polluted with nitrogen oxides; and
- stability to exposure to an atmosphere containing both nitrogen and sulphur oxides simulating common atmospheric pollution (not standardized).

**[0041]** With reference to the following 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.

**[0042]** In all examples, the electroplating method for depositing an alloy on a substrate (brass or Zamack) comprised the following plating sequence:

- copper layer on substrate: 10 - 15 microns layer thickness
- bronze layer on copper layer:  $\geq 2$  microns layer thickness
- gold finishing layer on bronze layer: 0.2 - 0.5 microns layer thickness

#### **Example 1 (not according to the invention): Electrodeposition of a quaternary white bronze Cu-Sn-Zn-Pd deposit**

**[0043]** The deposit was obtained using the following electrolyte solution:

- copper as CuCN: 6 g/L
- tin as  $\text{K}_2\text{SnO}_3$ : 30 g/L
- zinc as  $\text{Zn}(\text{CN})_2$ : 1 g/L

(continued)

- palladium as  $\text{Pd}(\text{NH}_3)_4\text{SO}_4$ : 50 mg/L
- free potassium cyanide: 50 g/L
- free potassium hydroxide: 25 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 3 mL/L

**[0044]** The electrodeposition was performed at 60 °C since this temperature turned out to be the best compromise for spreading the (white) brightness range to its maximum and obtaining a homogeneous alloy throughout the current density range. The copper plated substrate is introduced into the electrolyte after proper cleaning and activation, with a current density of 1 A/dm<sup>2</sup> applied for 20 minutes in order to raise the Cu-Sn-Zn-Pd bronze layer thickness to 5 microns.

**[0045]** The final aspect of the ternary Cu-Sn-Zn-Pd bronze layer is bright and presents a white colour.

**Example 2 (not according to the invention): Electrodeposition of a quaternary yellow bronze Cu-Sn-Zn-Pd deposit**

**[0046]** The deposit was obtained using the following electrolyte solution:

- copper as CuCN: 15 g/L
- tin as  $\text{K}_2\text{SnO}_3$ : 12 g/L
- palladium as  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ : 30 mg/L
- zinc as  $\text{Zn}(\text{CN})_2$ : 1 g/L
- free potassium cyanide: 35 g/L
- free potassium hydroxide: 15 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 5 mL/L

**[0047]** The electrodeposition was performed at 50°C since this temperature turned out to be the best compromise for spreading the (yellow) brightness range at its maximum and obtain a homogeneous alloy through the current density range. The copper plated substrate is introduced into the electrolyte after proper cleaning and activation with a current density at 1.5 A/dm<sup>2</sup> applied for 15 minutes in order to raise the Cu-Sn-Zn-Pd bronze layer thickness to 5 microns.

**[0048]** The final aspect of the quaternary Cu-Sn-Zn-Pd bronze layer is bright and presents a pale yellow colour.

**Example 3 (not according to the invention): Electrodeposition of quaternary white bronze Cu-Sn-Zn-Pd deposit with claimed Zinc content (1 - 20 wt.-%)**

**[0049]** The deposit was obtained using the following electrolyte solution:

- copper as CuCN: 6 g/L
- tin as  $\text{K}_2\text{SnO}_3$ : 30 g/L
- zinc as  $\text{ZnCN}_2$ : 2 g/L
- palladium as  $\text{Pd}(\text{NH}_3)_4\text{SO}_4$ : 50 mg/L
- free Potassium Cyanide: 50 g/L
- free Potassium Hydroxide: 25 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 3 mL/L

**[0050]** The quaternary bronze alloy electrodeposition is performed at 60°C, since this temperature turned out to be the best compromise to obtain a bright and homogeneous alloy on the whole range of current density. The copper plated substrate is introduced into the electrolyte after proper cleaning and activation, current density was fixed at 1 A/dm<sup>2</sup> and applied for 15 minutes in order to obtain a bronze layer thickness of 3 microns.

**[0051]** The final aspect of the quaternary Cu-Sn-Zn-Pd bronze layer is bright and presents a white colour.

**Reference example 1: Electrodeposition of a ternary white bronze Cu-Sn-Zn deposit**

**[0052]** A deposit was obtained using the following electrolyte solution:

5	- copper as CuCN:	6 g/L
	- tin as $K_2SnO_3$ :	30 g/L
	- zinc as $Zn(CN)_2$ :	1 g/L
	- free potassium cyanide:	50 g/L
10	-free potassium hydroxide:	25 g/L
	- surfactant solution:	3 mL/L
	-brightening agent solution:	3 mL/L

**[0053]** The electrodeposition is performed using the same conditions as in Example 1.

**[0054]** The final aspect of the ternary Cu-Sn-Zn bronze layer is bright and presents a white colour.

**Reference example 2: Electrodeposition of a ternary white bronze Cu-Sn-Pd deposit**

**[0055]** The deposit was obtained using the following electrolyte solution:

20	- copper as CuCN:	6 g/L
	- tin as $K_2SnO_3$ :	30 g/L
	- palladium as $Pd(NH_3)_4SO_4$ :	50 mg/L
25	- free potassium cyanide:	50 g/L
	- free potassium hydroxide:	25 g/L
	- surfactant solution:	3 mL/L
	- brightening agent solution:	3 mL/L

**[0056]** The electrodeposition is performed using same conditions as in Example 1.

**[0057]** The final aspect of the ternary Cu-Sn-Pd bronze layer is hazy and presents a grey colour. The aspect of the deposit is not homogeneous.

**Reference Example 3: Electrodeposition of a ternary yellow bronze Cu-Sn-Zn deposit**

**[0058]** The deposit was obtained using the following electrolyte solution:

40	- copper as CuCN:	15 g/L
	- tin as $K_2SnO_3$ :	12 g/L
	- zinc as $Zn(CN)_2$ :	1 g/L
	- free potassium cyanide:	35 g/L
	- free potassium hydroxide:	15 g/L
45	- surfactant solution:	3 mL/L
	-brightening agent solution 2:	5 mL/L

**[0059]** The electrodeposition is performed using the same conditions as in Example 2.

**[0060]** The final aspect of the ternary Cu-Sn-Zn bronze layer is bright and presents a pale yellow colour.

**Reference Example 4: Electrodeposition of a ternary yellow bronze Cu-Sn-Pd deposit**

**[0061]** The deposit was obtained using the following electrolyte solution:

55	- copper as CuCN:	15 g/L
	- tin as $K_2SnO_3$ :	12 g/L
	- palladium as $Pd(NH_3)_4Cl_2$ :	30 mg/L
	- free potassium cyanide:	35 g/L

(continued)

- free potassium hydroxide: 15 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 5 mL/L

[0062] The electrodeposition is performed using the same conditions as in Example 2.

[0063] The final aspect of the ternary Cu-Sn-Pd bronze layer is bright and presents a yellow colour.

#### Reference Example 5: Electrodeposition of a nickel and nickel phosphorus layer sequence

[0064] This nickel layer sequence is used as a reference to highlight the comparable behaviour of the new quaternary Cu-Sn-Zn-Pd alloy regarding corrosion resistance of final articles.

- substrate: copper alloys (brass or Zamack)
- copper: 15 microns
- bright nickel: 10 microns
- nickel phosphorus: 3 microns
- finishing: gold

#### Reference Example 6: Electrodeposition of a white ternary Cu-Sn-Zn alloy and a precious metal underlayer sequence

[0065] The layer of ternary bronze and palladium as underlayer sequence is used as a reference to highlight the advantages of the nickel-free quaternary Cu-Sn-Zn-Pd alloy regarding corrosion resistance and the savings in production costs in comparison of the actual hypoallergenic solution.

- substrate: copper alloys (brass or Zamack)
- copper: 15 microns
- ternary Cu-Sn-Zn alloy: 5 microns
- palladium alloy: 0.3 microns
- gold finishing: 0.5 microns

#### Reference Example 7: Electrodeposition of quaternary white bronze Cu-Sn-Zn-Pd deposit with low Zinc content (0.5 wt.-%)

[0066] The deposit was obtained using the following electrolyte solution:

- copper as CuCN: 8 g/L
- tin as  $K_2SnO_3$ : 25 g/L
- zinc as  $ZnCN_2$ : 0.5 g/L
- palladium as  $Pd(NH_3)_4SO_4$ : 50 mg/L
- free Potassium Cyanide: 45 g/L
- free Potassium Hydroxide: 8 g/L
- surfactant solution: 3 mL/L
- brightening agent solution: 3 mL/L

[0067] The quaternary bronze alloy electrodeposition is performed at 60°C, since this temperature turned out to be the best compromise to obtain a bright and homogeneous alloy on the whole range of current density. The copper plated substrate is introduced into the electrolyte after proper cleaning and activation, current density was fixed at 1 A/dm<sup>2</sup> and applied for 15 minutes in order to obtain a bronze layer thickness of 3 microns.

[0068] The final aspect of the quaternary Cu-Sn-Zn-Pd bronze layer is slightly hazy and presents a white colour.



**Reference Example 8: Electrodeposition of quaternary white bronze Cu-Sn-Pd deposit with high Zinc content (> 25 wt.-%)**

**[0069]** The deposit was obtained using the following electrolyte solution:

- copper as CuCN:	9 g/L
- tin as $K_2SnO_3$ :	16 g/L
- zinc as $ZnCN_2$ :	6 g/L
- palladium as $Pd(NH_3)_4SO_4$ :	100 mg/L
- free Potassium Cyanide:	45 g/L
- free Potassium Hydroxide:	6 g/L
- surfactant solution:	3 mL/L
- brightening agent solution:	3 mL/L

**[0070]** The quaternary bronze alloy electrodeposition is performed at 60°C, since this temperature turned out to be the best compromise to obtain a bright and homogeneous alloy on the whole range of current density. The copper plated substrate is introduced into the electrolyte after proper cleaning and activation, current density was fixed at 1 A/dm<sup>2</sup> and applied for 15 minutes in order to obtain a bronze layer thickness of 3 microns.

**[0071]** The final aspect of the quaternary Cu-Sn-Zn-Pd bronze layer is slightly hazy and presents white colour.

**Example 3 - Evaluation of the electroplated products****Table 1: EDS analysis for determination of alloy composition**

**[0072]** The electroplated products obtained in Examples 1 to 3 and Reference Examples 1 to 4, 7 and 8 were subjected to EDS analysis to obtain the alloy compositions. The result expressed as weight percentage is shown in Table 1.

Table 1

	Copper content	Tin content	Zinc content	Palladium content
<b>Example 1:</b> White Cu-Sn-Zn-Pd alloy	49%	42%	7%	2%
<b>Example 2:</b> Yellow Cu-Sn-Zn-Pd alloy	79%	16%	4.5%	0.5%
Example 3: White Cu-Sn-Zn-Pd alloy	49%	42%	7%	2%
Ref. Example 1: White Cu-Sn-Zn alloy	44%	46%	9%	-
Ref. Example 2: White Cu-Sn-Pd alloy	48%	49%	-	3%
Ref. Example 3: Yellow Cu-Sn-Zn alloy	78%	18%	4%	-
Ref. Example 4: Yellow Cu-Sn-Pd alloy	80%	19%	-	1%
Ref. Example 7: White Cu-Sn-Zn-Pd alloy (low Zn content)	48%	49%	0.4%	2.6%
Ref. Example 8: White Cu-Sn-Zn-Pd alloy (high Zn content)	32%	40%	26%	2%

**Table 2: Performance tests of electroplated layers**

**[0073]** The electroplated products obtained in Examples 1 to 3 and Reference Examples 1 to 8 were subjected to corrosion resistance tests. Salt spray tests were performed according to the ISO 9227 standard. Synthetic sweat resistance tests were conducted following NFS 80722 requirements, and leather interaction resistance was evaluated in accordance with ISO 4611 testing conditions. The resistance to a SO<sub>2</sub>/NO<sub>x</sub> atmosphere was tested in a close container with high SO<sub>2</sub> and NO<sub>x</sub> gas concentrations. The results are shown in Table 2.

Table 2 (n/a: data not available)

	Salt Spray-96h	Synthetic sweat 24h	Leather interaction 48h	SO <sub>2</sub> /NO <sub>x</sub> exposition 2h
<b>Example 1:</b> WHITE Cu-Sn-Zn-Pd alloy 5 µm Gold finishing 0.5 µm	No oxidation at 96h	No alteration after 48h (upper than required)	Similar aspect after 96h (upper than required)	No pitting
<b>Example 2:</b> YELLOW Cu-Sn-Zn-Pd alloy 5 µm Gold finishing 0.5 µm	Oxidation visible at 72h	Slight oxidation at 24h	No oxidation at 48h Slight oxidation at 96h	No pitting
<b>Example 3:</b> WHITE Cu-Sn-Zn-Pd alloy 3 µm Gold finishing 0.2 µm	n/a	No sign of oxidation or change of colour	n/a	n/a
Ref. Example 1: WHITE Cu-Sn-Zn alloy 5 µm Gold finishing 0.5 µm	Oxidation visible after 48h	Corrosion product after 12h	Slight alteration after 48h	Pitting
Ref. Example 2: WHITE Cu-Sn-Pd alloy 5 µm Gold finishing 0.5 µm	Corrosion products visible after 24h	Oxidation visible after 6h	Alteration starts at 24h	Strong pitting
Ref. Example 3: YELLOW Cu-Sn-Zn alloy 5 µm Gold finishing 0.5 µm	Oxidation visible after 24h	Corrosion product after 6h	Alteration after 48h	Pitting
Ref. Example 4: YELLOW Cu-Sn-Pd alloy 5 µm Gold finishing 0.5 µm	Oxidation visible after 48h	Corrosion product after 12h	Alteration after 48h	Slight pitting
Ref. Example 5: Nickel + Nickel Phosphorus (15 microns in total) Gold finishing 0.5 µm	No oxidation at 96h	No alteration after 48h (upper than required)	Similar aspect after 96h (upper than required)	No pitting
Ref. Example 6: WHITE Cu-Sn-Zn alloy 5 µm Palladium alloy 0.3 Gold finishing 0.5 µm	Oxidation visible at 72h	Slight oxidation at 24h	No oxidation at 48h Slight oxidation at 96h	Slight pitting
Ref. Example 7: WHITE Cu-Sn-Zn-Pd alloy 3 µm Gold finishing 0.2 µm (low Zn content)	n/a	Evolution of the general aspect: red deviation of the colour	n/a	n/a
Ref. Example 7: WHITE Cu-Sn-Zn-Pd alloy 3 µm Gold finishing 0.2 µm (high Zn content)	n/a	Presence of white rust at low current density areas	n/a	n/a

**[0074]** A comparison of the results of the corrosion tests of the selected embodiments and of the Reference Examples demonstrates the improvements reached with the quaternary Cu-Sn-Zn-Pd alloy.

**[0075]** Regarding Example 3 and Reference Examples 7 and 8, an additional synthetic sweat resistance tests has been performed, namely an ageing with TURBULA for 3 minutes has been performed. After said ageing, Example 3 still shows no sign of oxidation or change of colour. On the contrary, in Reference Example 7, green salt and exfoliations from the copper layer were observed and in Reference Example 8, white rust and exfoliations from the copper layer were observed. The comparison of the data obtained with Example 3 with the data obtained with Reference Examples 7 and 8 demonstrates that the zinc content in the alloy is important to ensure a sufficient corrosion protection. Indeed, it has become evident that if the final alloy comprises zinc below or above the range of 1 to 20 wt.-%, the corrosion resistance is lost.

### Table 3: Evaluation of the copper migration barrier properties

**[0076]** The electroplated products obtained in Examples 1 to 3 and Reference Examples 1 to 8 were subjected to

copper diffusion tests. The copper migration barrier properties are evaluated by heating the final articles for 48 h at 180°C. Under these conditions, the precious metal layer aspect must not be altered. The results are shown in Table 3.

Table 3

	Original aspect	Aspect after 48 hours
<b>Example 1:</b> WHITE Cu-Sn-Zn-Pd alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Bright Without alteration
<b>Example 2:</b> YELLOW Cu-Sn-Zn-Pd alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Bright Without alteration
<b>Example 3:</b> WHITE Cu-Sn-Zn-Pd alloy 3 $\mu\text{m}$ Gold finishing 0.2 $\mu\text{m}$	Bright Without alteration	Bright Without alteration
Ref. Example 1: WHITE Cu-Sn-Zn alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Gold and white bronze layer mixed (white aspect)
Ref. Example 2: WHITE Cu-Sn-Pd alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Hazy Without alteration	Under-plated copper is migrating to the top of the final articles
Ref. Example 3: YELLOW Cu-Sn-Zn alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Spots due to copper migration
Ref. Example 4: YELLOW Cu-Sn-Pd alloy 5 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Under-plated copper is migrating to the top of the final articles
Ref. Example 5: Nickel + Nickel Phosphorus (15 microns in total) Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Bright Without alteration
Ref. Example 6: WHITE Cu-Sn-Zn alloy 5 $\mu\text{m}$ Palladium alloy 0.3 $\mu\text{m}$ Gold finishing 0.5 $\mu\text{m}$	Bright Without alteration	Bright Without alteration
Ref. Example 7: WHITE Cu-Sn-Zn-Pd alloy 3 $\mu\text{m}$ Gold finishing 0.2 $\mu\text{m}$	Slightly hazy aspect without alteration	Copper underlayer migrates to the surface and the item presents pink colour
Ref. Example 8: WHITE Cu-Sn-Zn-Pd alloy 3 $\mu\text{m}$ Gold finishing 0.2 $\mu\text{m}$	Slightly Hazy aspect without alteration	Copper underlayer migrates to the surface and visual alteration is observed

**[0077]** A comparison of the results of the copper migration tests for the selected embodiments and for the Reference Examples demonstrates the improvements reached with the quaternary Cu-Sn-Zn-Pd alloy.

**[0078]** The copper diffusion tests results regarding Example 3 and Reference Examples 7 and 8 highlight the importance of zinc content in the electroplated alloy to ensure a copper diffusion barrier. Indeed, it has become clear that if the final alloy comprises zinc below or above the range of 1 to 20 wt.-%, the copper migration barrier property is lost.

#### Table 4: Nitric acid resistance tests

**[0079]** The nitric acid resistance tests are conducted by dipping the plated article into a 65 % aqueous solution of  $\text{HNO}_3$ . The results are shown in Table 4.

Table 4

	Nitric acid resistance
<b>Example 1:</b> WHITE Cu-Sn-Zn-Pd alloy 5 $\mu\text{m}$	Cu-Sn-Zn-Pd is not altered by nitric acid
<b>Example 2:</b> YELLOW Cu-Sn-Zn-Pd alloy 5 $\mu\text{m}$	Nitric acid dissolves 25% of the alloy
Ref. Example 1: WHITE Cu-Sn-Zn alloy 5 $\mu\text{m}$	Cu-Sn-Zn alloy is dissolved
Ref. Example 2: WHITE Cu-Sn-Pd alloy 5 $\mu\text{m}$	Cu-Sn-Pd alloy is dissolved
Ref. Example 3: YELLOW Cu-Sn-Zn alloy 5 $\mu\text{m}$	Cu-Sn-Zn alloy is dissolved
Ref. Example 4: YELLOW Cu-Sn-Pd alloy 5 $\mu\text{m}$	Cu-Sn-Pd alloy is dissolved
Ref. Example 5: Nickel + Nickel Phosphorus (15 microns in total)	Nickel phosphorus is not altered by nitric acid

**[0080]** A comparison of the results of the nitric acid resistance tests demonstrates the improvements reached with the quaternary Cu-Sn-Zn-Pd alloy.

## Claims

1. Electroplating bath for electrochemical deposition of a Cu-Sn-Zn-Pd alloy on a substrate, comprising or consisting of

- a) water;
- b) a source of copper ions;
- c) a source of tin ions;
- d) a source of zinc ions;
- e) a palladium salt and/or a palladium complex; and
- f) an inorganic brightening agent selected from the group consisting of bismuth nitrate, bismuth acetate, bismuth citrate, bismuth chloride, potassium antimony hexahydroxide, antimony chloride, antimony nitrates, sodium selenite, selenium dioxide, selenium tetrachloride, selenium sulphide and mixtures thereof;

wherein the electroplating bath has an alkaline pH, and

wherein the concentration of

copper in the electroplating bath is between 2.5 g/L and 25 g/L; and tin in the electroplating bath is between 5 g/L to 35 g/L; and

zinc in the electroplating bath is between 0.25 g/L to 5 g/L; and

the palladium as palladium salt and/or palladium complex in the electroplating bath is between 5 and 200 mg/L.

2. Electroplating bath according to the preceding claim, **characterized in that**

a) the source of copper ions is selected from the group consisting of copper sulphate, copper oxide, copper hydroxide, copper chloride, copper nitrate, copper acetate, copper carbonate and copper cyanide, or a mixture thereof, preferably copper cyanide; and/or

b) the source of tin ions is a tin(II) and/or tin(IV) compound, preferably a tin(IV) salt, more preferably potassium stannate; and/or

c) the source of zinc ions is zinc acetate, zinc chloride, zinc cyanide, zinc sulphate and/or an alkali zincate; and/or

d) the palladium salt and/or palladium complex is selected from the group consisting of palladium chloride, palladium bromide, palladium cyanide, palladium nitrite, palladium nitrate, palladium sulphate, palladium thio-sulphate, palladium acetate, palladium hydrogencarbonate, palladium hydroxide and palladium oxide, with or without ligands selected from the group of ammonia and amines, most preferably complexes selected from the group consisting of palladium diamino dichloride, palladium diamino sulphate, palladium diamino dinitrate, tetramine palladium chloride, tetramine palladium sulphate, tetramine palladium nitrate, tetramine palladium hydrogencarbonate, palladium ethylenediamine chloride, palladium ethylenediamine sulphate, palladium potassium thiosulphate, and mixtures thereof.

3. Electroplating bath according to one of the preceding claims, **characterized in that** the electroplating bath further comprises

a) a complexing agent, preferably potassium cyanide and/or sodium cyanide, preferably at a concentration of 20 to 80 g/L, more preferably 25 to 60 g/L; and/or

b) a base, preferably potassium hydroxide and/or sodium hydroxide, preferably at a concentration of 1 to 60 g/L, more preferably 2 to 40 g/L; and/or

c) a conductive salt, preferably Rochelle salt, potassium carbonate and/or sodium carbonate, preferably at a concentration of 10-100 g/L; and/or

d) a surfactant, preferably an amphoteric, anionic and/or non-ionic surfactant, more preferably selected from the group consisting of betaines, sulfobetaines, alkyl sulphates, alkyl ether sulphates, alkyl ether phosphates, alkyl sulfonates, alkyl sulfosuccinates, alkyl benzene sulfonates, alcohol polyglycol ethers, polyethylene glycols, and mixtures thereof, wherein the surfactant concentration is preferably 0.05 g/L to 1 g/L, more preferably 0.15 g/L to 0.5 g/L.

4. Method for the electrochemical deposition of a Cu-Sn-Zn-Pd alloy on a substrate, comprising the steps

- a) forming an electrical contact between a substrate and a negative electrode of a power source;
- b) contacting the substrate with an electroplating bath according to one of the claims 1 to 3;
- c) contacting at least a part of a positive electrode of the power source with the electroplating bath according to one of claims 1 to 3; and
- d) applying a voltage between the positive and negative electrode of the power source until a deposit of a Cu-Sn-Zn-Pd alloy has formed on the substrate.

5. Method according to claim 4, **characterized in that** a substrate is used that comprises or consists of a metal or an alloy selected from the group consisting of bronze, brass, Zamack, alpaca, copper alloy, tin alloy, steel and mixtures thereof and/or the substrate used is a metal-plated object of plastic and/or an alloy-plated object of plastic.

6. Method according to one of claims 4 or 5, **characterized in that** a positive electrode is used that comprises or consists of an insoluble anode material, preferably graphite, mixed metal oxides, platinated titanium and/or stainless steel.

7. Method according to one of claims 4 to 6, **characterized in that** the applied voltage is adjusted to provide a current density of 0.05 to 5 A/dm<sup>2</sup>, preferably 0.2 to 3 A/dm<sup>2</sup>.

8. Method according to one of claims 4 to 7, **characterized in that** the temperature of the electroplating bath is kept at between 20 and 80 °C, preferably at between 40 to 70 °C.

9. Substrate comprising an electrochemically deposited Cu-Sn-Zn-Pd alloy layer, the alloy layer comprising or consisting of

- a) 30 to 90 % wt.-% of copper;
- b) 5 to 60 % wt.-% of tin;
- c) 1 to 20 wt.-% of zinc; and
- d)  $\geq 0.25$  to  $\leq 5$  wt.-% palladium,

**characterized in that** the substrate is producible with the method according to one of claims 4 to 8, wherein the substrate has additionally an electrochemically deposited layer comprising or consisting of copper, wherein said layer has a thickness of 1 nm to 1 mm.

10. Substrate according to claim 9, **characterized in that** the alloy comprises

- a) 40 to 85 % wt.-% of copper, optionally 45 to 80 wt.-%; and/or
- b) 10 to 50 % wt.-% of tin, optionally 15 to 45 wt.-%; and/or
- c) 2 to 15 wt.-% of zinc, optionally 3 to 10 wt.-%; and/or
- d) no silver; and/or
- e) no indium; and/or
- f) no nickel; and/or
- g) no mercury.

11. Substrate according to one of the claims 9 or 10, **characterized in that** the thickness of the electrochemically deposited Cu-Sn-Zn-Pd alloy layer is 1 nm to 25  $\mu\text{m}$ , preferably 10 nm to 20  $\mu\text{m}$ , more preferably 0.1  $\mu\text{m}$  to 15  $\mu\text{m}$ , even more preferably 1  $\mu\text{m}$  to 10  $\mu\text{m}$ , most preferably 2  $\mu\text{m}$  to 5  $\mu\text{m}$ .

12. Substrate according to one of the claims 9 to 11, **characterized in that** the

- a) electrochemically deposited layer comprising or consisting of copper has a thickness of 10 nm to 500  $\mu\text{m}$ , more preferably 0.1  $\mu\text{m}$  to 100  $\mu\text{m}$ , even more preferably 1  $\mu\text{m}$  to 50  $\mu\text{m}$ , most preferably 5  $\mu\text{m}$  to 20  $\mu\text{m}$ , and wherein said layer is preferably located between the substrate and the electrochemically deposited Cu-Sn-Zn-Pd alloy layer; and/or
- b) substrate has additionally an electrochemically deposited finishing layer comprising or consisting of a noble metal, wherein said finishing layer has optionally a thickness of 0.01  $\mu\text{m}$  to 100  $\mu\text{m}$ , preferably 0.02 to 50  $\mu\text{m}$ , more preferably 0.05 to 5  $\mu\text{m}$ , most preferably 0.1  $\mu\text{m}$  to 3  $\mu\text{m}$ , and wherein the electrochemically deposited Cu-Sn-Zn-Pd alloy layer is located between the substrate and the finishing layer.

13. Use of the substrate according to one of claims 9 to 12 as fashion item, preferably as an article selected from the group consisting of jewelry, fashion, leather article, watch, eyewear, trinket, lock and/or perfume packaging application.

## Patentansprüche

1. Galvanisierungsbad zur elektrochemischen Abscheidung einer Cu-Sn-Zn-Pd Legierung auf einem Substrat, enthaltend oder bestehend aus

- a) Wasser;
- b) einer Quelle für Kupferionen;
- c) einer Quelle für Zinnionen;
- d) einer Quelle für Zinkionen;
- e) einem Palladiumsalz und/oder einem Palladiumkomplex; und
- f) einen anorganischen Glanzbildner ausgewählt aus der Gruppe bestehend aus einem Salz von Bismut, Antimon und/oder Selen, vorzugsweise Bismutnitrat, Bismutacetat, Bismutcitrat, Bismutchlorid, Kaliumantimonhexahydrid, Antimonchlorid, Antimonnitrat, Natriumselenit, Selendioxid, Seleniumtetrachlorid, Selenisulfid und/oder Mischungen davon;

wobei das Galvanisierungsbad einen alkalischen pH-Wert aufweist, und  
wobei die Konzentration von  
Kupfer im Galvanisierungsbad zwischen 2,5 g/L und 25 g/L liegt; und die Konzentration von  
Zinn im Galvanisierungsbad zwischen 5 g/L und 35 g/L liegt; und die Konzentration von  
Zinkionen im Galvanisierungsbad zwischen 0,25 g/L und 5 g/L liegt; und  
das Palladium als Palladiumsalz und/oder Palladiumkomplex im Galvanisierungsbad zwischen 5 und 200 mg/L liegt.

2. Galvanisierungsbad nach dem vorstehenden Anspruch, **dadurch gekennzeichnet, dass**

- a) die Quelle für Kupferionen ausgewählt ist aus der Gruppe bestehend aus Kupfersulfat, Kupferoxid, Kupferhydroxid, Kupferchlorid, Kupfernitrat, Kupferacetat, Kupfercarbonat und Kupfercyanid oder einem Gemisch davon, vorzugsweise Kupfercyanid; und/oder
- b) die Quelle der Zinnionen eine Zinn(II)- und/oder Zinn(IV)-Verbindung ist, bevorzugt ein Zinn(IV)-Salz, besonders bevorzugt Kaliumstannat; und/oder
- c) die Quelle der Zinkionen Zinkacetat, Zinkchlorid, Zinkcyanid, Zinksulfat und/oder ein Alkalizinkat ist; und/oder
- d) das Palladiumsalz und/oder der Palladiumkomplex ausgewählt ist aus der Gruppe bestehend aus Palladiumchlorid, Palladiumbromid, Palladiumcyanid, Palladiumnitri, Palladiumnitrat, Palladiumsulfat, Palladiumthiosulfat, Palladiumacetat, Palladiumhydrogencarbonat, Palladiumhydroxid und Palladiumoxid, mit oder ohne Liganden ausgewählt aus der Gruppe Ammoniak und Amine, bevorzugt Komplexe ausgewählt aus der Gruppe bestehend aus Palladiumdiammindichlorid, Palladiumdiamminsulfat, Palladiumdiammindinitrat, Tetraamminpalladiumchlorid, Tetraamminpalladiumsulfat, Tetraamminpalladinnitrat, Tetraamminpalladiumhydrogencarbonat, Palladiummethyldiaminchlorid, Palladiummethyldiaminsulfat, Palladiummethyldiaminsulfat, Palladiumkaliumthiosulfat und Mischungen davon.

3. Galvanisierungsbad nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Galvanisierungsbad weiterhin enthält

- a) einen Komplexbildner, vorzugsweise Kaliumcyanid und/oder Natriumcyanid, bevorzugt in einer Konzentration von 20 bis 80 g/L, besonders bevorzugt 25 bis 60 g/L; und/oder
- b) eine Base, vorzugsweise Kaliumhydroxid und/oder Natriumhydroxid, bevorzugt in einer Konzentration von 1 bis 60 g/L, besonders bevorzugt 2 bis 40 g/L; und/oder
- c) ein Leitsalz, vorzugsweise Rochellesalz, Kaliumcarbonat und/oder Natriumcarbonat, bevorzugt in einer Konzentration von 10 bis 100 g/L; und/oder
- d) ein Tensid, vorzugsweise ein amphoter, anionisches und/oder nichtionisches Tensid, das bevorzugt ausgewählt ist aus der Gruppe bestehend aus Betainen, Sulfobetainen, Alkylsulfaten, Alkylethersulfaten, Alkyletherphosphaten, Alkylsulfonaten, Alkylsulfosuccinaten, Alkylbenzolsulfonaten, Alkoholpolyglykolethern, Polyethylenglykolen und Mischungen davon, wobei die Tensidkonzentration bevorzugt 0,05 g/L bis 1 g/L, besonders bevorzugt 0,15 g/L bis 0,5 g/L beträgt.

4. Verfahren zur elektrochemischen Abscheidung einer Cu-Sn-Zn-Pd-Legierung auf einem Substrat, umfassend die Schritte

- a) Bilden eines elektrischen Kontaktes zwischen einem Substrat und der negativen Elektrode einer Stromquelle;
- b) Kontaktieren des Substrates mit einem Galvanisierungsbad nach einem der Ansprüche 1 bis 3;
- c) Kontaktieren der positiven Elektrode der Stromquelle mit dem Galvanisierungsbad nach einem der Ansprüche 1 bis 3; und
- d) Anlegen einer Spannung zwischen der positiven und negativen Elektrode der Stromquelle, bis sich auf dem Substrat eine Abscheidung einer Cu-Sn-Zn-Pd-Legierung gebildet hat.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet, dass** ein Substrat verwendet wird, das ein Metall oder eine Legierung ausgewählt aus der Gruppe bestehend aus Bronze, Messing, Zamak, Alpaka, Kupferlegierung, Zinn-Al-Legierung, Stahl und Mischungen daraus umfasst oder daraus besteht und/oder das verwendete Substrat ein metallplattierter Gegenstand aus Kunststoff und/oder Legierungs-beschichteter Gegenstand aus Kunststoff ist.

6. Verfahren nach einem der Ansprüche 4 oder 5, **dadurch gekennzeichnet, dass** eine positive Elektrode verwendet wird, die ein unlösliches Anodenmaterial, vorzugsweise Graphit, Mischmetalloxide, platinisiertes Titan und/oder Edelstahl, enthält oder daraus besteht.

7. Verfahren nach einem der Ansprüche 4 bis 6, **dadurch gekennzeichnet, dass** die angelegte Spannung so eingestellt wird, dass eine Stromdichte auf der Substratoberfläche von 0,05 bis 5 A/dm<sup>2</sup>, vorzugsweise 0,2 bis 3 A/dm<sup>2</sup> bereitgestellt wird.

8. Verfahren nach einem der Ansprüche 4 bis 7, **dadurch gekennzeichnet, dass** die Temperatur des Galvanisierungsbad zwischen 20 und 80 °C, vorzugsweise zwischen 40 und 70 °C, gehalten wird.

9. Substrat, enthaltend eine elektrochemisch abgeschiedene Cu-Sn-Zn-Pd Legierungsschicht, wobei die Legierungsschicht

- a) 30 bis 90 Gew.-% Kupfer;
- b) 5 bis 60 Gew.-% Zinn;
- c) 1 bis 20 Gew.-% Zink; und
- d)  $\geq 0,25$  bis  $\leq 5$  Gew.-% Palladium,

enthält oder daraus besteht, wobei das Substrat mit dem Verfahren nach einem der Ansprüche 4 bis 8 herstellbar ist, und wobei das Substrat zusätzlich eine elektrochemisch abgeschiedene Oberflächenschicht aufweist, die Kupfer enthält oder aus Kupfer besteht, wobei die Schicht eine Dicke von 1 nm bis 1 mm aufweist.

10. Substrat nach Anspruch 9, **dadurch gekennzeichnet, dass** die Legierung

- a) 40 bis 85 Gew.-% Kupfer, optional 45 bis 80 Gew.-%; und/oder
- b) 10 bis 50 Gew.-% Zinn, gegebenenfalls 15 bis 45 Gew.-%; und/oder
- c) 2 bis 15 Gew.-% Zink, optional 3 bis 10 Gew.-%; und/oder
- d) kein Silber; und/oder
- e) kein Indium; und/oder
- f) kein Nickel; und/oder
- g) kein Quecksilber

enthält.

11. Substrat nach einem der Ansprüche 9 oder 10, **dadurch gekennzeichnet, dass** die Dicke der elektrochemisch abgeschiedenen Cu-Sn-Zn-Pd Legierungsschicht 1 nm bis 25  $\mu\text{m}$ , vorzugsweise 10 nm bis 20  $\mu\text{m}$ , bevorzugt 0,1  $\mu\text{m}$  bis 15  $\mu\text{m}$ , besonders bevorzugt 1  $\mu\text{m}$  bis 10  $\mu\text{m}$ , am bevorzugtesten 2  $\mu\text{m}$  bis 5  $\mu\text{m}$  beträgt.

12. Substrat nach einem der Ansprüche 9 bis 11, **dadurch gekennzeichnet, dass**

- a) die elektrochemisch abgeschiedene Schicht, enthaltend oder bestehend aus Kupfer eine Dicke von 10 nm

bis 500  $\mu\text{m}$ , bevorzugt 0,1  $\mu\text{m}$  bis 100  $\mu\text{m}$ , besonders bevorzugt 1  $\mu\text{m}$  bis 50  $\mu\text{m}$ , am bevorzugtesten 5  $\mu\text{m}$  bis 20  $\mu\text{m}$  aufweist, und wobei sich die Schicht zwischen dem Substrat und der elektrochemisch abgeschiedenen Cu-Sn-Zn-Pd-Legierungsschicht befindet; und/oder

b) das Substrat zusätzlich eine elektrochemisch abgeschiedene Oberflächenschicht aufweist, die ein Edelmetall enthält oder aus einem Edelmetall besteht, eine Dicke von 0,01  $\mu\text{m}$  bis 100  $\mu\text{m}$ , vorzugsweise 0,02 bis 50  $\mu\text{m}$ , bevorzugt 0,05 bis 5  $\mu\text{m}$ , besonders bevorzugt 0,1  $\mu\text{m}$  bis 3  $\mu\text{m}$  aufweist, und wobei sich die elektrochemisch abgeschiedene Cu-Sn-Zn-Pd-Legierungsschicht unterhalb der Endbeschichtung befindet.

13. Verwendung des Substrates nach einem der Ansprüche 9 bis 12 als Modeartikel, vorzugsweise als Artikel ausgewählt aus der Gruppe bestehend aus Schmuck, Mode, Lederartikel, Uhr, Brille, Verschluss und/oder Parfümverpackung.

## Revendications

1. Bain de galvanoplastie pour le dépôt électrochimique d'un alliage Cu-Sn-Zn-Pd sur un substrat, comprenant ou consistant de

a) l'eau;

b) une source d'ions cuivre;

c) une source d'ions étain;

d) une source d'ions zinc;

e) un sel de palladium et/ou un complexe de palladium; et

f) un brillanteur inorganique choisi dans le groupe constitué par le nitrate de bismuth, l'acétate de bismuth, le citrate de bismuth, le chlorure de bismuth, l'hexahydroxyde de potassium et d'antimoine, le chlorure d'antimoine, les nitrates antimonieux, le sélénite de sodium, le dioxyde de sélénium, le tetrachlorure de sélénium et le sulfure de sélénium ainsi que leurs mélanges;

dans laquelle le bain de galvanoplastie a un pH alcalin, et

dans laquelle la concentration

du cuivre dans le bain de galvanoplastie se situe entre 2,5 g/L et 25 g/L ; et

de l'étain dans le bain de galvanoplastie se situe entre 5 g/L et 35 g/L ; et

des ions zinc dans le bain de galvanoplastie se situe entre 0,25 g/L et 5 g/L ; et

du palladium sous forme de sel de palladium et/ou de complexe de palladium dans le bain d'électrodéposition se situe entre 5 et 200 mg/L.

2. Bain de galvanoplastie selon la revendication précédente, **caractérisé en ce que**

a) la source d'ions cuivre est choisie dans le groupe constitué par le sulfate de cuivre, l'oxyde de cuivre, l'hydroxyde de cuivre, le chlorure de cuivre, le nitrate de cuivre, l'acétate de cuivre, le carbonate de cuivre et le cyanure de cuivre, ou un mélange de ceux-ci, de préférence du cyanure de cuivre ; et/ou

b) la source d'ions étain est un composé d'étain(II) et/ou d'étain(IV), de préférence un sel d'étain(IV), plus préférentiellement du stannate de potassium ; et/ou

c) la source d'ions zinc est l'acétate de zinc, le chlorure de zinc, le cyanure de zinc, le sulfate de zinc et/ou un zincate alcalin ; et/ou

d) le sel de palladium et/ou le complexe de palladium est choisi dans le groupe constitué par le chlorure de palladium, le bromure de palladium, le cyanure de palladium, le nitrite de palladium, le nitrate de palladium, le sulfate de palladium, le thiosulfate de palladium, l'acétate de palladium, le carbonate de palladium hydrogencarbonate, l'hydroxyde de palladium et l'oxyde de palladium avec ou sans ligands sélectionnés dans le groupe par ammoniacs et amines, le plus préférentiellement des complexes choisis dans le groupe comprenant le di-chlorure de palladium diamino, le sulfate de palladium diamino, le dinitrate de palladium diamino, le chlorure de tétrammine palladium, le sulfate de tétrammine palladium, le nitrate de palladium tétra-mine, le carbonate de palladium hydrogéné, le chlorure de palladium éthylène-diamine, le sulfate de palladium éthylène diamino, le potassium thiosulfate, et leurs mélanges.

3. Bain de galvanoplastie selon l'une des revendications précédentes, **caractérisé en ce que** le bain de galvanoplastie comprend en outre

a) un complexant, de préférence du cyanure de potassium et/ou du cyanure de sodium, de préférence à une



concentration de 20 à 80 g/L, de préférence de 25 à 60 g/L; et/ou

b) une base, de préférence de l'hydroxyde de potassium et/ou de l'hydroxyde de sodium, de préférence à une concentration de 1 à 60 g/L, de préférence de 2 à 40 g/L; et/ou

c) un sel conducteur, de préférence du sel de Rochelle, du carbonate de potassium et/ou du carbonate de sodium, de préférence à une concentration de 10-100 g/L; et/ou

d) un tensioactif, de préférence un tensioactif amphotère, anionique et/ou non ionique, plus préférentiellement choisi dans le groupe constitué des bétaines, sulfobétaines, alkylsulfates, alkyléthersulfates, alkyléthersulfates, alkyléthersulfonates, alkylsulfonates, alkylsulfosuccinates, alkylbenzènesulfonates, alcool polyglycol éthers, polyéthylène glycols et leurs mélanges, où la concentration en tensioactif est, avant la prise, 0,05 g/l à 1 g/l et plus préférentiellement 0,15 g/l à 0,5 g/L.

4. Procédé de dépôt électrochimique d'un alliage Cu-Sn-Zn-Pd sur un substrat, comprenant les étapes suivantes

a) la formation d'un contact électrique entre un substrat et une électrode négative d'une source d'énergie ;

b) la mise en contact du substrat avec un bain de galvanoplastie selon l'une des revendications 1 à 3 ;

c) la mise en contact d'au moins une partie d'une électrode positive de la source d'alimentation avec le bain galvanique selon l'une des revendications 1 à 3 ; et

d) l'application d'une tension entre les électrodes positive et négative de la source d'alimentation jusqu'à ce qu'un dépôt d'un alliage Cu-Sn-Zn-Pd se soit formé sur le substrat.

5. Procédé selon la revendication 4, **caractérisé en ce qu'on** utilise un substrat qui comprend un métal ou un alliage choisi dans le groupe constitué par le bronze, le laiton, le Zamack, l'alpaga, l'alliage de cuivre, l'alliage d'étain, l'acier et leurs mélanges et/ou le substrat utilisé est un objet métallique en plastique et/ou un objet en plastique plaqué alliage.

6. Procédé selon l'une des revendications 4 ou 5, **caractérisé en ce qu'on** utilise une électrode positive qui comprend ou consiste en un matériau anodique insoluble, de préférence du graphite, des oxydes métalliques mixtes, du titane platiné et/ou de l'acier inoxydable.

7. Procédé selon l'une des revendications 4 à 6, **caractérisé en ce que** la tension appliquée est ajustée pour fournir une densité de courant de 0,05 à 5 A/dm<sup>2</sup>, de préférence 0,2 à 3 A/dm<sup>2</sup>.

8. Procédé selon l'une des revendications 4 à 7, **caractérisé en ce que** la température du bain galvanique est maintenue entre 20 et 80 °C, de préférence entre 40 et 70 °C.

9. Substrat comprenant une couche d'alliage Cu-Sn-Zn-Pd déposée par voie électrochimique, la couche d'alliage comprenant ou consistant en

a) 30 à 90 % en poids de cuivre ;

b) 5 à 60 % en poids d'étain ;

c) 1 à 20 % en poids de zinc ; et

d)  $\geq 0,25$  à  $\leq 5$  % en poids de palladium,

dans laquelle le substrat peut être produit avec le procédé selon l'une des revendications 4 à 8, et

dans laquelle le substrat a en outre une couche de finition déposée par voie électrochimique comprenant du cuivre ou consistant en cuivre, ladite couche ayant une épaisseur de 1 nm à 1 mm.

10. Substrat selon la revendication 9, **caractérisé en ce que** l'alliage se compose de

a) 40 à 85 % en poids de cuivre, éventuellement 45 à 80 % en poids ; et/ou

b) 10 à 50 % en poids d'étain, éventuellement 15 à 45 % en poids ; et/ou

c) 2 à 15 % en poids de zinc, éventuellement 3 à 10 % en poids ; et/ou

d) pas d'argent ; et/ou

e) pas d'indium ; et/ou

f) pas de nickel ; et/ou

g) pas de mercure.

11. Substrat selon l'une des revendications 9 ou 10, **caractérisé en ce que** l'épaisseur de la couche d'alliage Cu-Sn-

Zn-Pd déposée par voie électrochimique est de 1 nm à 25  $\mu\text{m}$ , de préférence de 10 nm à 20  $\mu\text{m}$ , de préférence de 0,1  $\mu\text{m}$  à 15  $\mu\text{m}$ , encore plus de 1  $\mu\text{m}$  à 10  $\mu\text{m}$ , de préférence de 2  $\mu\text{m}$  à 5  $\mu\text{m}$ .

**12. Substrat selon l'une des revendications 9 à 11, caractérisé en ce que**

- a) la couche déposée par voie électrochimique comprenant du cuivre ou consistant en cuivre, dans laquelle ladite couche a éventuellement une épaisseur de 10 nm à 500  $\mu\text{m}$ , plus préféablement de 0,1  $\mu\text{m}$  à 100  $\mu\text{m}$ , encore plus préféablement de 1  $\mu\text{m}$  à 50  $\mu\text{m}$ , plus préféablement de 5  $\mu\text{m}$  à 20  $\mu\text{m}$ , et dans laquelle ladite couche est située entre le substrat et la couche déposée par voie électrochimique en alliage Cu-Sn-Zn-Pd ; et/ou
- b) le substrat comporte en outre une couche de finition déposée par voie électrochimique comprenant un métal noble ou consistant en un métal noble a une épaisseur de 0,01  $\mu\text{m}$  à 100  $\mu\text{m}$ , de préférence de 0,02 à 50  $\mu\text{m}$ , plus préféablement de 0,05 à 5  $\mu\text{m}$ , plus préféablement de 0,1  $\mu\text{m}$  à 3  $\mu\text{m}$ , et où la couche d'alliage Cu-Sn-Zn-Pd déposée par voie électrochimique est située entre le substrat et la couche de finition.

**13. Utilisation du substrat selon l'une des revendications 9 à 12 en tant qu'article de mode, de préférence en tant qu'article choisi dans le groupe constitué par les bijoux, la mode, les articles en cuir, les montres, les lunettes, les bibelots, les serrures et/ou les emballages pour parfums.**

**REFERENCES CITED IN THE DESCRIPTION**

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