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(54) **Process for applying a metal coating to a non-conductive substrate**

(57) Described is a new process for applying a metal coating to a non-conductive substrate comprising the steps of (a) contacting the substrate with an activator comprising a noble metal/group IVA metal sol to obtain a treated substrate, (b) contacting said treated substrate with a composition comprising a solution of: (i) a Cu(II), Ag, Au or Ni soluble metal salt or mixtures thereof, (ii) 0.05 to 5 mol/l of a group IA metal hydroxide and (iii) a

complexing agent for an ion of the metal of said metal salt comprising an organic material having a cumulative formation constant log K of from about 0.73 to about 21.95 for an ion of the metal of said metal salt, **characterised in that** the composition according to step (b) is treated with an electrical current for a period of time prior to and / or during contacting said solution with the substrate.

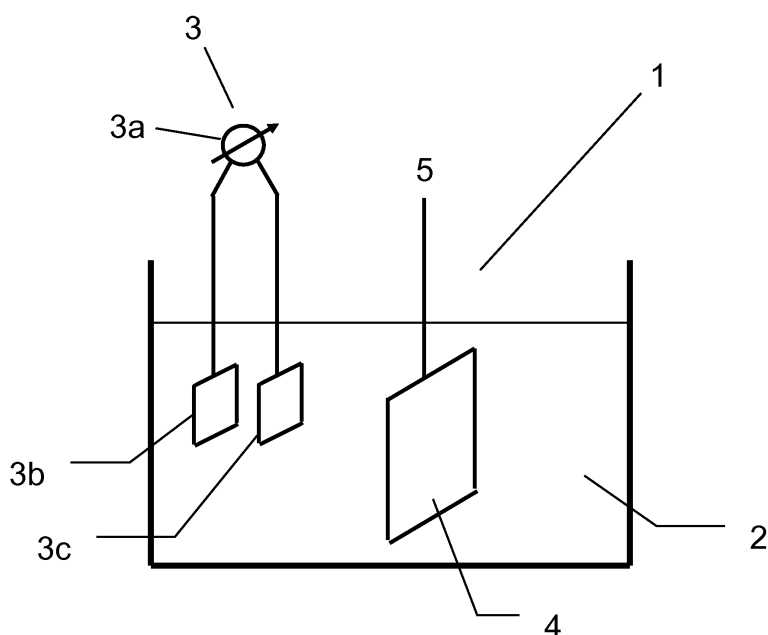


Fig. 1

Description**Field of the Disclosure**

5 **[0001]** The invention relates to a process for applying a metal coating to a non-conductive substrate and to a composition used in this process which is electrically treated to enhance its performance.

Background of the Invention

10 **[0002]** Various methods are known of coating non-conductive surfaces. In wet chemical methods, the surfaces to be metallised are, after an appropriate preliminary treatment, either firstly catalysed and then metallised in an electroless manner and thereafter, if necessary, metallised electrolytically, or are directly electrolytically metallised.

15 **[0003]** Methods according to the first variant with electroless metallisation have, however, proved disadvantageous, as process management of the electroless metallising bath is difficult, treatment of the waste water from this bath is complex and expensive, and the process is lengthy and thus likewise expensive due to the low deposition speed of the metallising bath.

20 **[0004]** Especially for metal coating of plastic parts, for example for sanitary fittings and for the automobile industry, and of parts which are used as casings for electrical appliances which are screened against electromagnetic radiation, the electroless metallising methods are problematic. In treatment of such moulded parts, generally relatively large volumes of the treatment solutions are carried over from one treatment bath into the next, as these have a shape by means of which the treatment solution is transported out of the baths when the parts are lifted out. As electroless metallising baths normally contain considerable quantities of toxic formaldehyde and complex formers which are only removable with difficulty, in their treatment large quantities of these baths are lost and must be disposed of in a complicated manner.

25 **[0005]** For this reason a series of metallising methods was developed, by means of which the non-conductive surfaces could be directly coated with metal without electroless metallisation (see, for example, EP 0 298 298 A2, US 4,919,768, EP 0 320 601 A2, US 3,984,290, EP 0 456 982 A1 and WO 89/08375 A1).

30 **[0006]** In EP 0 616 053 A1 there is disclosed a method for direct metallisation of non-conductive surfaces, in which the surfaces are firstly treated with a cleaner/conditioner solution, thereafter with an activator solution, for example a palladium colloidal solution, stabilised with tin compounds, and are then treated with a solution which contains compounds of a metal which is more noble than tin, as well as an alkali hydroxide and a complex former. Thereafter the surfaces can be treated in a solution containing a reducing agent, and can finally be electrolytically metallised.

35 **[0007]** WO 96/29452 concerns a process for the selective or partial electrolytic metallisation of surfaces of substrates made from electrically non-conducting materials which for the purpose of the coating process are secured to plastic-coated holding elements. The proposed process involves the following steps: a) preliminary treatment of the surfaces with an etching solution containing chromium (VI) oxide; followed immediately by b) treatment of the surfaces with a colloidal acidic solution of palladium-/tin compounds, care being taken to prevent prior contact with adsorption-promoting solutions; c) treatment of the surfaces with a solution containing a soluble metal compound capable of being reduced by tin (II) compounds, an alkali or alkaline earth metal hydroxide, and a complex forming agent for the metal in a quantity sufficient at least to prevent precipitation of metal hydroxides; d) treatment of the surfaces with an electrolytic metallisation solution.

40 **[0008]** The processes described in EP 0 616 053 A1 and WO 96/29452 are disadvantageous in that they require the use of high amounts of a noble metal such as palladium which is a very expensive metal. If the palladium amount in the activation step is reduced, the plating results are unsatisfactory.

45 **[0009]** Hence, it is the object underlying the present invention to provide a process requiring a reduced amount of a noble metal such as palladium to activate the surface of the non-conductive substrate to be metal-coated and to achieve high quality and reliable plating performance also for substrates having a complex geometrical form.

Summary of the Disclosure

50 **[0010]** This object is achieved by a process for applying a metal coating to a non-conductive substrate comprising the steps of

(a) contacting the substrate with an activator comprising a noble metal/group IVA metal sol to obtain a treated substrate,

55 (b) contacting said treated substrate with a composition comprising a solution of:

(i) a Cu(II), Ag, Au or Ni soluble metal salt or mixtures thereof,

(ii) a source of hydroxide ions,

(iii) a complexing agent for an ion of the metal of said metal salt comprising an organic material having a cumulative formation constant $\log K$ of from about 0.73 to about 21.95 for an ion of the metal of said metal salt,

characterised in that the composition according to step (b) is treated with an electrical current for a period of time prior to or during contacting said solution with the substrate.

Brief Description of the Figure

[0011]

Figure 1 shows a typical set up of a system according to the present invention having a current source to provide an electrical current to compositions according to step (b) for treatment of substrates.

Detailed Description of the Invention

[0012] It has been found that applying an electrical current to compositions according to step (b) for a period of time prior to or during contacting said solution with the substrate significantly improves the plating results and process reliability. The amount of noble metal like palladium required in the preceding activation step (a) to obtain a good surface finish can be greatly reduced when applying the method according to the present invention.

[0013] When applying the electrical current to the composition according to step (b), the current density preferably ranges between 0.01 and 10 A/dm² as measured on the cathode, more preferred between 0.05 and 1 A/dm² and even more preferred between 0.1 and 0.5 A/dm².

[0014] The electrical current can be applied continuously while contacting the substrate with a solution according to step (b). Alternatively, the electrical current can be applied prior to contacting the substrate with a solution according to step (b) and be stopped during immersion of the substrate.

[0015] In a third alternative the electrical current can be applied prior to contacting the substrate with a solution according to step (b) and additionally during immersion of the substrate.

[0016] For prior treatment of the solution according to step (b) the electrical current is usually applied for a time between 30 s and 120 minutes, more preferred between 10 and 60 minutes and even more preferred between 20 - 40 minutes. The electrical current can be applied once to an activator solution as described herein and thereafter several substrates may be treated in such treated solution. Alternatively, the electrical current may be applied before each treatment in the activator solution.

[0017] When the electrical current is applied continuously while contacting the substrate with a solution according to step (b) this can preferably be done during the entire immersion of the substrate into the solution. Alternatively, the current may be discontinued at some point during the immersion of the substrate.

[0018] The anode material used preferably is stainless steel, copper, a copper alloy like brass, titanium, platinized titanium, graphite, iridium or rhodium. The cathode material can be the same or different as the anode material. Preferably used is stainless steel, copper, a copper alloy like brass, titanium, platinized titanium, graphite, iridium or rhodium.

[0019] The dimensions of the anode and cathode may vary according to the current applied, geometry of the work pieces, concentrations of compounds in a solution according to step (b), temperature of the solution etc. For example, for a treatment tank containing a solution according to step (b) having the dimensions of 0.90 m x 0.96 m x 3.16m and an approximate volume of 2700 l of treatment liquid the anode and cathode can have dimensions from 90 cm x 300 cm to 10 cm x 10 cm, preferred from 90 cm x 30 cm to 30 cm x 30cm. The dimensions of the anode and the cathode can be the same or different. This depends on the tank size and the facility limitation e.g. maximum current which can be applied. Optimum dimensions of cathode and anode can be determined in routine experiments.

[0020] A typical set up of a system (1) according to the present invention is shown in Figure 1. The treatment liquid (2) is a solution according to step (b) as described above. A substrate (4) is immersed into such treatment liquid using a holding device (5). A set up for supplying an electrical current (3) comprises a source of an electrical current (3a), an anode (3b) and a cathode (3c).

[0021] The anode treatment of the activator solution results in reduced chemical consumption, less drag-out of precious metals and higher production reliability.

[0022] The non-conductive substrates to be coated according to the process of the present invention are not particularly limited. These substrates include plastic parts which are intensely structured, such for example as combs or articles designed with a substantial extension in the third dimension, e.g. coffee pots, telephone handsets, water pipe fittings, etc. However, also other non-conductive substrates such as ceramic substrates or other metal oxide non-conductive substrates can be coated according to the present invention. In addition, small surfaces such as through-hole walls of

printed circuit boards can be coated.

[0023] The non-conductive substrates can be a polymer, selected from the group consisting of polyolefins like polystyrene, polystyrene copolymers such as poly(styrene-butadiene-styrene, SBS), polypropylene, polyethylene; polyamides; copolymers of acrylonitrile and methyl acrylate, acrylonitrile and methylmethacrylate, vinyl chloride and styrene (SAN), butadiene and styrene (ABS), butadiene, styrene (ABS) and polycarbonate (PC); polyimides, polyesters, phenolic resins, and epoxides. Also the non-conductive substrate can be a glass substrate.

[0024] The substrate may then optionally be micro-etched with a chemical etchant, where the substrate comprises a non-conductive material having a metal layer on it such as a copper-clad substrate which is employed in the manufacture of circuit boards. An example of such a chemical etchant includes standard etching agents containing a mixture of chromic and sulphuric acid. The microetching step is employed in order to prepare the metal layer such as the copper layer portion of the substrate for subsequent electroplating. Acid dips and water rinses may be included after etching.

[0025] Prior to treating the substrate with an activator, it may be immersed in a commercial pre-dip containing NaCl, SnCl_2 and HCl, the pH of which is below about 0.5.

[0026] The substrate is then treated with an activator comprising a noble metal/Group IVA metal sol. Noble metals comprise Ag or Au or Group VIII noble metals including Ru, Rh, Pd, Os, Ir, Pt, or various mixtures of such noble metals. The preferred noble metals are the Group VIII noble metals and especially palladium.

[0027] The activator of the present invention is prepared in such a fashion that there is excess Group IVA metal compound reducing agent present, i.e., a stoichiometric excess of reducing agent (e.g., divalent tin) compared to the noble metal compound (e.g., divalent Pd) from which the activator is made. In this way the activator such as the Pd/Sn sol has residual divalent Sn that can function as a reducing agent.

[0028] The Group IVA metals that may be employed include, for example, Ge, Sn and Pb, or mixtures thereof Sn being preferred.

[0029] The activator preferably will contain a stoichiometric excess of the Group IVA metal as compared to the noble metal. The Group IVA metal is substantially in its lowest oxidation state so that it will be available to reduce the more noble metal salts that are employed in forming the activator. Because it is also employed in a stoichiometric excess based on the salts of the noble metal that are employed to form the activator, the excess of the Group IVA metal in combination with the activator will also be substantially in its lowest oxidation state. The activator thus prepared with the excess of the Group IVA metal in its lowest oxidation state will also be available to reduce the Group IB or other more noble metal salts that are subsequently brought into contact with the activator, such as the salts of copper as described herein. The Group IVA metal is preferably employed as a salt, such as a halide and especially a chloride, but in any event, will be present in an amount so that the molar ratio of the Group IVA metal to the noble metal of the activator is from 4:1 to 95:1, especially 10:1 to 55:1 and preferably from 15:1 to 50:1. Some specific Group IVA metal salts that may be used in this regard comprise PbCl_2 , SnCl_2 or a mixture of GeCl_2 and GeCl_4 dissolved in dilute hydrochloric acid. The preferred Group IVA metal comprises tin and especially tin in the form of stannous chloride.

[0030] The preparation of the activator is conventional and is disclosed in United States Patent No. 3,011,920 and United States Patent No. 3,682,671.

[0031] The treated substrate, after the activator solution has been applied, is rinsed and then treated with the above mentioned composition comprising the Cu(II), Ag, Au or Ni soluble metal salt, the group IA metal hydroxide and the iminosuccinic acid (derivative) as a complexing agent for the ions of the metal of the aforementioned metal salts, comprising Ag^+ , Ag^{2+} , Au^+ , Au^{2+} and Ni^{2+} salts. Preferably, the metal salt is a Cu(II) salt.

[0032] Anywhere from 0.0002 to 0.2 mol/l and especially from 0.004 to 0.01 mol/l of the said metal salt may be employed in the bath where the solvent preferably comprises water.

[0033] The bath includes a source of hydroxide ions. Preferably, the source of hydroxide ions is a Group IA metal hydroxide in an amount from 0.05 to 5 mol/l, preferably 1 to 3 mol/l and most preferred 1.5 to 2 mol/l. The Group IA metals in this regard comprise Li, Na, K, Rb, Cs or mixtures thereof, especially Li, Na, K and mixtures thereof and preferably a metal comprising Li.

[0034] The complexing agent is employed in an amount sufficient for the bath to form a thin, dense metal-rich catalytic film on the substrate with sufficient electrical conductivity for subsequent electroplating and at the same time produce relatively clean metal surfaces. In general, the complexing agent is used in an amount of 0.005 to 1.5 mol/l, preferably 0.05 to 1 mol/l and most preferably 0.2 to 0.5 mol/l.

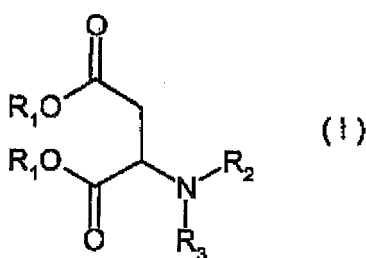
[0035] Suitable complexing agents include complexing agents selected from the group consisting of acetate, acetylacetone, citric acid, 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, dimethylglyoxime (50% dioxane), 2,2'-dipyridyl, ethanolamine, ethylenediamine, ethylenediamine N,N,N',N'-tetraacetic acid, glycine, N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid, 8-hydroxy-2-methylquinoline (50% dioxane), 8-hydroxyquinoline-5-sulfonic acid, lactic acid, nitrilotriacetic acid, 1-nitroso-2-naphthol (75% dioxane), oxalate, 1,10-phenanthroline, phthalic acid, piperidine, propylene-1,2-diamine, pyridine, pyridine-2,6-dicarboxylic acid, 1-(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo)resorcinol (PAR), pyrocatechol-3,5-disulfonate, 8-quinolinol, salicylic acid, succinic acid, 5-sulfosalicylic acid, tartaric acid, thioglycolic acid, thiourea, triethanolamine, triethylenetetramine (trien), 1,1,1-trifluoro-3,3'-thenoylacetone (TTA).

[0036] The preferred additional complexing agent for copper ions is an alkanolamine comprising for example monoethanolamine. Alkanolamines in addition to monoethanolamine that may be employed in this regard include the following lower alkanolamines: diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, mono-*sec*-butanolamine, di-*sec*-butanolamine, 2-amino-2-methyl-1-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2-dimethylamino-2-methyl-1-propanol, tris(hydroxymethyl)aminomethane, and various mixtures of the alkanolamines.

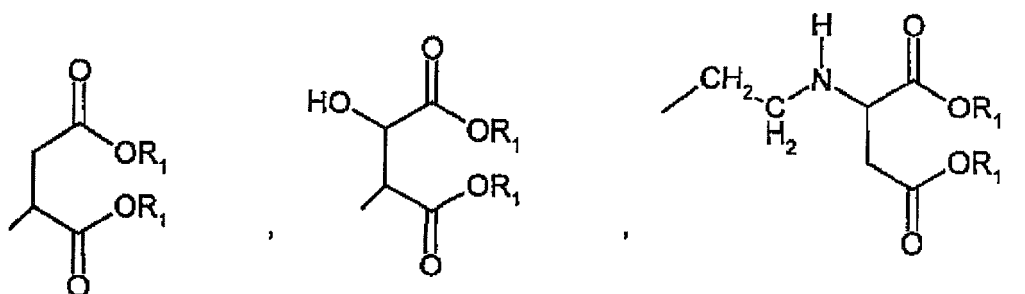
[0037] Other weak complexing agents can be used such as other amines, including aliphatic and cyclic, e.g., aromatic amines having up to 10 carbon atoms all of which are described in Kirk-Othmer, Encyclopedia of Chemical Technology under "Amines". Additionally, mono and poly carboxylic acids having up to 8 carbon atoms and their salts can be used and include amino acids. These acids are also defined in Kirk-Othmer, Id. under "Carboxylic Acids" and "Amino Acids". The preferred acids in this regard include gluconic acid, lactic acid, acetic acid and tartaric acid.

[0038] Also preferred is iminosuccinic acid or a derivative thereof. This group of complexing agents further helps to reduce the amount of noble metal such as palladium in the activator.

[0039] Suitable iminosuccinic acid derivatives for use in the present invention include those having the formula (I) shown below:



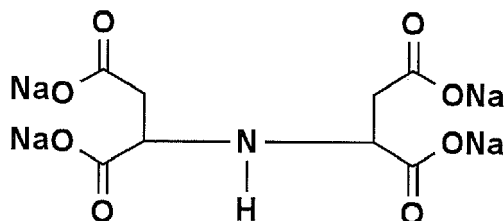
wherein R_1 is selected from the group consisting of H, Na, K, NH_4 , Ca, Mg, Li and Fe, R_2 is selected from the group consisting of



$-CH_2-COOR_1$, $-CH_2-CH_2-COOR_1$, $-CH_2-CH_2-OH$, $-CH_2-CHOH-CH_3$ and $-CH_2-CHOH-CH_2OH$, and R_3 is selected from the group consisting of H, $-CH_2-COOR_1$, $-CH_2-CH_2-COOR_1$, $-CH_2-CH_2-OH$, $-CH_2-CHOH-CH_3$ and $-CH_2-CHOH-CH_2OH$.

[0040] The above mentioned compounds are described in DE 198 50 359 A1 and its application in methods for direct metallisation in WO 2008/135179. WO 00/26398 describes a method of producing compounds of formula (I) and their mixtures on the basis of carbohydrates by fermentation in the presence of microorganisms.

[0041] Preferably, the iminosuccinic acid derivative is the iminosuccinic acid sodium salt having the following structural formula:



[0042] The various anions of the above mentioned water-soluble metal salts include inorganic acid anions or mixtures thereof such as the halogen anions, i.e., F⁻, Cl⁻, Br⁻ or I⁻; Cl⁻ being especially preferred, sulfate or carbonate anions, lower molecular weight organic acid anions such as formate or acetate anions or salicylate anions and the like. Additionally, mixtures of the foregoing anions can be employed as well as salt-like anions such as CuCl₂·2KCl·2H₂O, CuCl₂·2NaCl·2H₂O and the various art known equivalents thereof.

[0043] According to the present invention, the activator comprises at least 10 mg/l of palladium and usually not more than 400 mg/l ppm as noble metal. Preferred is a range between preferably 30 - 130 mg/l. The higher the palladium concentration the higher the palladium drag out, which is disadvantageous. Therefore, it is an aim to reduce the palladium concentration in the activator. If the palladium concentration is too small, though, subsequent metallisation of the activated substrate remains incomplete.

[0044] After contacting the substrate with the activator, the substrates are treated with the composition comprising a solution of the Cu(II), Ag, Au or Ni soluble metal salts or mixtures thereof, the group IA metal hydroxide and the complexing agent, for example, about 10 minutes with the temperature above 60°C. Bath temperature may vary from 40°C to 85°C. Treatment time ranges from 4 to 12 minutes or more which is typical for production purposes, however, may vary out of this range depending on the temperature and condition of the bath. The time used is actually the time necessary to provide the best metal coverage for the formation of the conductive film or to provide minimum required coverage. The conductive film is then electrolytically coated by methods well known in the art.

[0045] Subsequent electroplating is best achieved if the coating is microetched in an acidic oxidising medium so that the adhesion and morphology of the electrolytically applied metal coating (e.g. copper) is optimised. Microetching is effected by an acidic oxidising agent which is conventional in the art, however, it has been found that even short exposures (e.g. about one-half minute) to the microetch solution causes a loss in conductivity and if microetching is carried out over a period of time for about two minutes the coating loses substantially all of its conductivity which indicates it is most likely entirely removed from the substrate.

[0046] Accordingly, after the substrate has been treated with the copper bath, for example, it is then preferably rinsed with water and subjected to a neutralisation and reducing bath to eliminate this problem. The neutralisation and reducing bath neutralises the residual alkali on the treated surfaces and also improves the resistance of the conductive film to oxidising chemical micro-etchants.

[0047] The neutralisation and reducing steps may be conducted separately, i.e., in separate steps employing a first acid neutralisation bath and a second reducing bath.

[0048] Reducing agents that may be employed in this regard are generally disclosed in United States Patent No. 4,005,051 and EP-A-0 616 053.

[0049] The treated substrate may then be coated electrolytically with a further or a final metal coating. In other words, the application of the composition as described above to the substrates as defined herein comprises the first step (in a two-step process) for the application of a metal coating to a non-metallic substrate. In this first step, a coating is obtained on the surface of the substrate which significantly lowers the resistivity of the substrate as compared to the conductivity of the substrate prior to the application of the composition according to the present invention. Thus, the present invention is directed to a two-step process wherein the conductivity is increased initially by applying a very thin metal coating.

[0050] The present invention is further illustrated by the following examples.

Example 1

[0051] Two compositions (A) and (B) were prepared as shown below:

Composition (A):

[0052]

(A1) according to Table 1 below,

(A2) about 4.0% by weight $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,

(A3) potassium sodium tetrates, 0.12 mol/l,

the remainder being water.

Composition (B):

[0053]

(B1) 6.0% by weight sodium hydroxide,

(B2) 9.0% by weight lithium hydroxide,

the remainder being water.

[0054] The pH of composition (A) was 4.1. The pH of composition (B) was 13.

[0055] 90 ml/l of composition (A) and 13 ml/l of composition (B) were mixed to obtain a bath comprising the above mentioned components and ingredients.

[0056] Two plates made of ABS-PC (8 x 10 cm) were treated with an etching solution containing chrome (VI) oxide for 10 minutes at a temperature of 70°C. After a rinsing treatment, chrome (VI) compounds adhering to the substrate surfaces were reduced to chrome (III) compounds by treating the substrate with a reducing agent for one minute at room temperature.

[0057] After a further rinsing treatment, the substrates were treated in a solution for four minutes at 40°C, the solution being composed as follows: Activator: Colloidal solution containing 120 ppm palladium as palladium chloride, 35 g/l stannous chloride (18.5 g/l Sn) and 350 ml/l hydrochloric acid with a pH of 1 or less for 4 minutes.

[0058] After the activator treatment, the substrates were again rinsed.

[0059] After the rinsing treatment, the substrate was immersed into the bath obtained from compositions (A) and (B) described. The temperature applied was 60°C, treatment time was 3 minutes.

[0060] Substrate Sample 2 (Table 1): No electrical current was applied either prior or during immersion of the substrate.

[0061] Substrate Sample 2 (Table 1): An electrical current of 0.2 A/dm² was applied (as measured on the cathode) to such composition during immersion of the substrate. The anode material used was copper, the cathode material brass. The treatment tank containing a solution according to step (b) had the dimensions of 20cm x 20cm x 20cm and a volume of 8 l of treatment liquid. The anode and cathode can had dimensions of 10cm x 19cm.

[0062] The results obtained in Example 1 are summarised in Table 1 below.

[0063] As can be seen from Table 1 the amount of palladium absorbed on the surface of the treated substrates is about the same for Sample 1 (0.35 mg/dm²) and Sample 2 (0.36 mg/dm²) since the same solution is used for activation. However, when applying an electrical current to the mixture of compositions (A) and (B) as described above the amount of copper deposited is much higher: for Sample 1 0.2335 mg/dm² and Sample 2 3.082 mg/dm². Generally, the higher the amount of copper, the better is the conductivity of such treated surface. This is confirmed by the ohmic resistance measurements shown in Table 1. The resistance of Sample 1 is 400 kΩ and thus the conductivity far smaller than for Sample 2 (60 kΩ, electrical treatment of the solution).

[0064] The conductivity affects the final plating result as is shown in Example 2.

Table 1: Results of adsorption measurements on surfaces

Sample		Pd {mg/dm ² }	Sn {mg/dm ² }	Cu {mg/dm ² }
1	No electrical treatment	0.35	<0.05	0.2335
2	Electrical treatment, 0.2 A/dm ² ,	0.36	<0.05	3.082
Sample		Ratio Pd:Cu	Surface ohmic resistance / kΩ	Surface appearance
1	No electrical treatment	6:4	400	Non uniform
2	Electrical treatment, 0.2 A/dm ²	1:9	60	uniform

Example 2: Electrolytic Copper Plating of Pretreated Samples 1 and 2

[0065] The following experiment was performed to show the superior metallisation results:

5 The substrates treated according to Example 1 were washed with water and then subjected to a subsequent copper electroplating step. A commercially available copper electroplating bath Cupracid® Ultra (Atotech Deutschland GmbH) was used, which contains 250 g/l copper sulfate, 50 g/l sulphuric acid, 50 ppm chloride ions and a brightening agent.

10 The electroplating operation was performed at a plating solution temperature of 25°C and a current density of 3 A/dm² for 5 min.

Metallisation result:

15 **[0066]** Sample 1 (no electrical treatment): incomplete metal coverage of the surface, voids remaining.

[0067] Sample 2 (electrical treatment): complete metal coverage of the surface, no voids remaining, very good plating result.

[0068] The higher amount of metallic Cu (0) absorbed on the substrate surface results in an excellent final metal coating deposited thereon. A treatment not applying an electrical current does not result in a completely metallised surface of the non-conductive surface.

Claims

25 **1.** A process for applying a metal coating to a non-conductive substrate comprising the steps of

(a) contacting the substrate with an activator comprising a noble metal/group IVA metal sol to obtain a treated substrate,

30 (b) contacting said treated substrate with a composition comprising a solution of:

(i) a Cu(II), Ag, Au or Ni soluble metal salt or mixtures thereof,

(ii) a source of hydroxide ions and

(iii) a complexing agent for an ion of the metal of said metal salt comprising an organic material having a cumulative formation constant log K of from about 0.73 to about 21.95 for an ion of the metal of said metal salt,

35 **characterised in that** the composition according to step (b) is treated with an electrical current for a period of time prior to and / or during contacting said solution with the substrate.

40 **2.** The process according to claim 1 wherein the electrical current is applied during contacting said solution with the substrate.

3. The process according to any of the foregoing claims wherein the electrical current ranges between 0.05 and 1 A/dm².

45 **4.** The process according to any of the foregoing claims wherein the anode to provide the electrical current is a stainless steel, a copper, a copper alloy, a titanium, a platinized titanium, a graphite, an iridium or a rhodium anode.

5. The process according to any of the foregoing claims wherein the cathode is a stainless steel, a copper, a titanium, a platinized titanium, a graphite, an iridium or a rhodium cathode.

50 **6.** The process according to any of the foregoing claims wherein the noble metal in the solution 1 (a) is palladium and the group IVA metal is tin.

7. The process according to any of the foregoing claims wherein the salt in the solution 1 (b) (i) is a copper (II) salt.

55 **8.** The process according to any of the foregoing claims wherein the concentration of hydroxide ions in the solution 1 (b) (ii) is between 0.05 to 5 mol/l.

9. The process according to any of the foregoing claims wherein the source of hydroxide ions in the solution 1 (b) (ii)

is a group IA metal hydroxide.

10. The process according to any of the foregoing claims wherein the complexing agent is used in an amount of 0.005 to 1 mol/l.

11. The process according to any of the foregoing claims wherein the complexing agent is selected from the group consisting of iminosuccinic acid, gluconic acid, lactic acid, acetic acid, tartaric acid and salts thereof.

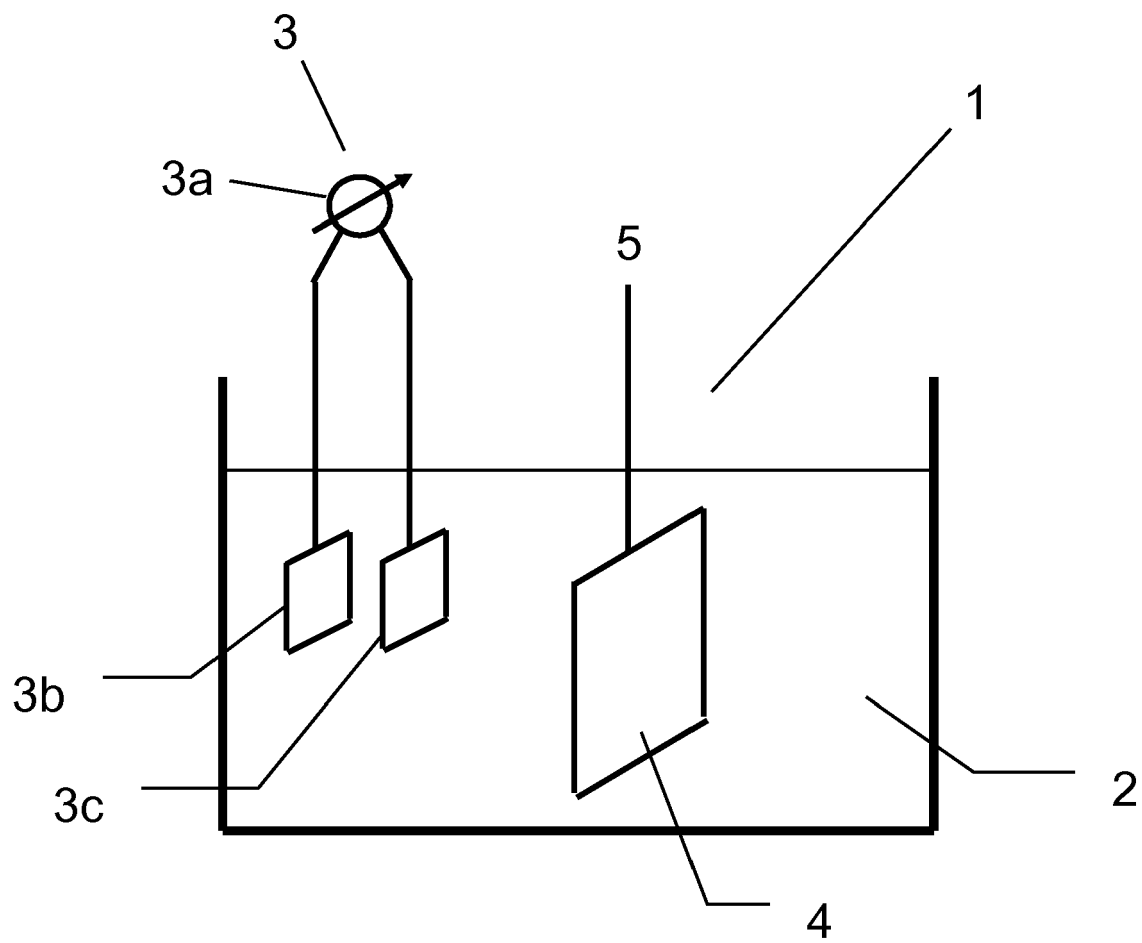


Fig. 1



EUROPEAN SEARCH REPORT

Application Number
EP 09 17 1442

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 4 938 853 A (RETALLICK RICHARD C [US] ET AL) 3 July 1990 (1990-07-03) * column 2, lines 36-41 * * column 4, line 46 - column 6, line 8; claims 1,3,8,9; example 1 *	1-11	INV. C23C18/31 C23C18/40 C23C18/54
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