



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
09.07.2008 Bulletin 2008/28

(51) Int Cl.:
C23C 18/28 (2006.01)

(21) Application number: **06077232.4**

(22) Date of filing: **18.12.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

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(30) Priority: **08.12.2006 CN 200610165903**

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(54) **Pre-treatment solution and method of forming a layer of a coating metal on a plastics surface containing substrate**

(57) For the purpose of forming a layer of a coating metal on a substrate, more specifically on a plastics surface, the metal layer firmly adhering to the plastics surface, the method being easy and low effort and hence performed at low cost, environmentally acceptable and acceptable with respect to health, i.e., with respect to

toxicity of the chemical species used, a pre-treatment solution and method of forming a layer of a coating metal on such substrate are provided, the pre-treatment solution containing at least one organic solvent, at least one noble metal in ionic form being capable of reducing coating metal ions to elemental coating metal and at least one acid.

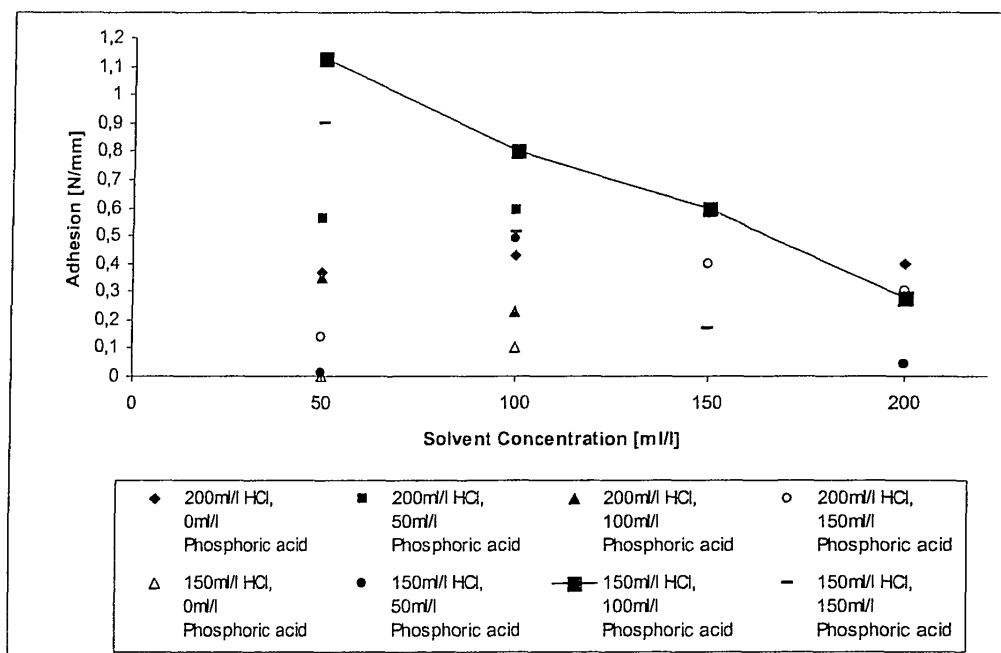


Fig. 1

Description

Field of Invention:

5 **[0001]** The present invention relates to a pre-treatment solution and to a method of forming a layer of a coating metal on a substrate, said substrate having a plastics surface, more specifically to a method of forming a layer of a coating metal on at least one of a polyamide and a polyoxymethylene plastics part. Such solutions and methods are applied to plating polyamide or polyoxymethylene plastics substrates especially in decorative plating industry.

10 Background Art:

[0002] Polyamide plastics parts have been electroplated for many years. Nevertheless, little research effort has been made in this field because electroplating polyamide plastics parts has ever been an application having a narrow application range due to the limited market thereof. A first method has been described in a publication on the 65th Conference of the American Electroplating Society (AES) in Washington (1978) which achieved a peel strength of the metal layer to the plastics part higher than about 1 N/mm. However, no indication was made as to specific details of this method, except for that no chromic acid was used. The influence of the surface texture obtained after the first method step on the adhesion strength was described to be similar to that of acrylonitrile-butadiene-styrene-copolymer (ABS) plastics parts. With ABS plastics parts a clear correlation proves to exist between the microscopic surface texture and adhesion strength.

20 **[0003]** Nowadays two main alternatives are available as to the first method step in pre-treating polyamide plastics parts, these alternatives comprising pre-treating the parts with a solution containing chromium(VI), on the one hand, and pre-treating the parts using a solvent and an acid, on the other hand. Pre-treatment using chromium(VI) has the main disadvantage of being dangerous to health and to environment, therefore its use is limited. Further, in contrast to ABS plastics, polyamide plastics exhibit a relatively open structure of the polymer, thus having a considerable water uptake of up to 6 %. This property will bring also about considerable uptake of chromium(VI) into the polymer, which cannot be easily removed by rinsing and other chemical treatment.

[0004] Therefore the other alternative method mentioned comprising pre-treating polyamide plastics parts with an aqueous solution containing mineral acid in combination with a solvent, mostly a glycol ether, has seemed to be advantageous. In this method, after pre-treatment has been performed, the plastics part is catalyzed, this method step being comprised of two or three method steps: A first optional step comprises immersing the plastics part into a solution of a polar polymer thus providing the surface of the part with a very thin layer of this polymer. This polymer serves to bond the catalyst more strongly, and at a higher concentration, to the surface of the polyamide plastics part. Thus consumption of the expensive catalyst will be reduced and further catalyzation of the part will be more reliable. After rinsing off adhering solution from the plastics part, the part is usually catalyzed by contacting same with a - solution containing colloidal palladium. Such solutions are acidic and contain tin chloride and are perfectly well suited to catalyze nonpolar olefinic polymers like ABS or polycarbonate. Such solutions are also described to be used for the catalyzation of polyamide plastics parts (EP 0 406 859 B1).

[0005] However, it has proved not to be necessary to use these complicated and expensive catalysts for the treatment of the microporous polyamide plastics parts. Solutions containing ionic palladium also prove suitable, such solutions being much easier to prepare and being less expensive. Depending on the type of the catalyzation method, after treatment with the catalyst, the plastics parts are further treated in a specific solution. If, for example a colloidal palladium catalyst has been used, the plastics part is contacted with a so-called accelerator, which is to remove a tin sheath surrounding the colloidal particles. All solutions which are capable of solubilizing tin(II) may serve this purpose, such as diluted hydrochloric acid, sulphuric acid, sodium hydroxide and organic acids. Ionic palladium being adsorbed to the plastics parts used will instead be reduced to the elemental palladium metal by means of reducing agents, such as by boranates (dimethylaminoborane and alkali metal borohydrides) and hypophosphites.

[0006] Nowadays, most applied methods comprise treating a polyamide plastics part using a swelling and cleansing solution, said solution containing a glycol ether, a mineral acid and a surface active agent. Residues of this solution adhering to the plastics part will be rinsed off thoroughly after it has been treated in this solution for the treatment time required. Thereafter the part is treated in a suitable conditioner and finally catalyzed in an acidic palladium salt solution. After having been exposed to a reduction solution the part is nickel plated in an electroless nickel solution, then electroplated with copper and finally electroplated with a metal desired to be the final finish, mostly nickel or chromium.

[0007] Further DE 31 37 587 C2 discloses pre-treatment of polyamide plastics parts for decorative applications with a solution containing an organic solvent, a glycol ether, for example, and an acid, such as hydrochloric acid. Subsequently, the parts are plated by electroless metal coating, the metal adhering well to the parts.

[0008] Further, EP 0 406 859 B1 and EP 0 604 131 B1 disclose pre-treating polyamide plastics parts with oxidizing acids, such as chromic acid/sulfuric acid for example. In addition EP 0 604 131 B1 discloses etching the polyamide plastics part with mineral acids including hydrochloric acid, sulfuric acid, phosphoric acid, chromic acid, formic acid and

acetic acid. The method of both documents further comprises contacting polyamide plastics parts with a solution containing colloidal palladium and tin (II) the tin (II) being removed after the treatment by acceleration. In addition EP 0 604 131 B1 discloses treating the polyamide plastics parts applying a sensitizer-activator method or soaking the parts in a palladium solution-reduction solution.

[0009] Considering that three rinse steps are in general required between each of the steps of this method described above, the overall sequence, up to the electroless nickel plating step, involves 16 method steps. "Kunststoffmetallisierung - Handbuch für Theorie und Praxis" ("Plastics Metallization - Handbook for the Theory and Practice"), Eugen G. Leuze Verlag, Saulgau, Germany, 1991, pages 47 and 141-156, mentions another treatment method for polyamide plastics parts involving catalyzing same with a palladium catalyst which comprises palladium complex compounds comprising organic ligands. Such organic ligands provide the complex compounds with a specific affinity to the polyamide surface, which are said to influence adhesion of the metal layer formed thereafter on the plastics part. This document further mentions, that slight swelling or "roughening" of the polyamide plastics surface would be advantageous. Treatment with chromic acid, as well as with acids, and caustic, would not be applicable since these agents would damage the plastics parts irreversibly. More specifically, the method comprises contacting the polyamide plastics part with an organic palladium complex first, then intermediate treatment of the part, comprising swelling the amorphous surface of the part, using an etchant, which contains salts of calcium und aluminium, and finally electroless nickel plating the part.

[0010] The aforementioned methods prove to be lengthy and complicated. In order to reliably metal-plate a polyamide plastics substrate with as little effort as possible, a method will have to be provided which requires considerably less method steps while achieving metal coatings on the polyamide plastics substrate having strong adhesion to the surface thereof.

[0011] A method of forming a metal layer on the surface of polyamide plastics parts is described in U.S. Patent No. 5,296,020, the method comprising treating the polyamide plastics part with an activator formulation consisting of organic noble metal, fillers, organic solvent and an aqueous dispersion of a polyurethane polymer. More specifically, the organic noble metals are provided by organometallic compounds of palladium with olefins, with α,β -unsaturated carbonyl compounds, with crown ethers and with nitriles. The activator compounds are then reduced to metallic form, or are complexed by means of complexing agents and introduced into the aqueous dispersion of the polyurethane polymer. The solvent may be glycol ethers, for example ethylene glycol monomethyl ether, diglyme or propylene glycol monomethyl ether acetate and simply serves to dissolve the organic Pd compound. Therefore, such solvent may be employed in a small amount. Metallization of the plastics part, once pre-treated in this formulation, by dipping for example, will be performed by electroless metal plating, such as by electroless nickel plating. Ionic palladium may be reduced in the electroless metal plating solution directly with no further method step being required.

[0012] Further, U.S. Patent No. 5,300,140 discloses a hydroprimer for metallizing substrate surfaces, polyamide surfaces for example. This hydroprimer is used to be applied to the substrate surfaces by application of a thin layer thereof to the substrate surfaces for subsequent electroless metal plating, nickel plating for example. The hydroprimer contains, in addition to water, a water-dispersible polymer selected from the group consisting of water-dispersible polyacrylates, polybutadienes, polyesters, melamine resins, polyurethanes and polyurethane-ureas, further an ionic noble metal, a colloidal noble metal or a covalent or complex compound of a noble metal as metallization catalyst and a filler. Possible activators are organometallic complex compounds of palladium with olefins, with α,β -unsaturated carbonyl compounds, with crown ethers, with nitriles and with diketones. Ionic metals in the form of salts, such as halides, may likewise be used. The noble metal may be reduced in the electroless metal plating solution directly.

[0013] The aforementioned methods are said to yield metal layers coating the substrate surfaces at high adhesion. The catalyst formulations, however, have been shown not to be very reliable in terms of metal plating capability (uniformity of metal plating) and adhesion of a metal layer deposited.

[0014] Another method of electroless plating a polyamide plastics part is disclosed in U.S. Patent No. 4,554,183. This method comprises pre-treating the polyamide plastics part with a solution of a mixture of halides of elements of the 1st and 2nd main groups of the Periodic Table of Elements with salts of weak inorganic bases and strong inorganic acids in a non-etching organic swelling agent or solvent for polyamides and treating the plastics part with a metal-organic complex compound of palladium, for example. Coordination complexes of olefins with palladium, which contain functional groups, as indicated in this document, are used as the metal-organic complex compounds. The metal-organic complex compounds are advantageously employed in the form of the dispersions thereof, and in particular, the solutions thereof in suitable organic solvents, these solvents being water-immiscible. Examples are given which exclusively describe solutions comprising a coordination complex of an olefin with palladium in an organic solvent. Reduction of the coordination complex compound may be performed in an electroless nickel plating bath directly.

[0015] The method described in U.S. Patent No. 4,554,183 suffers from the disadvantage that the solutions contained therein do not contain water at all and instead contain pure organic solvent. In practice, such solutions may not be used due to the requirement to reduce total oxygen concentration (TOC). Moreover, the solution will have to fulfil the requirements, that it shall not have any detrimental environmental impact, not contain solvents having any halogens being bonded to carbon, be water-based and, if organic solvents are used, these solvents not being easily volatile, having a

high ignition point and not being toxic, like mutagenic or teratogenic. Thus the solutions disclosed in this document cannot be used in industrial practice.

[0016] It is therefore an object of the present invention to provide a method of forming a layer of a coating metal on a substrate.

[0017] More specifically, it is an object of the present invention to provide a method of forming a layer of a coating metal on a plastics surface, more specifically on at least one of a polyamide and a polyoxymethylene plastics surface.

[0018] It is still another object of the present invention to provide a method of forming a layer of a coating metal on a polyamide or polyoxymethylene plastics surface, this metal layer firmly adhering to the plastics surface.

[0019] It is still another object of the present invention to provide a method of forming a layer of a coating metal on a polyamide or polyoxymethylene plastics surface, the method being easy and low effort and hence performed at low cost.

[0020] It is still another object of the present invention to provide a method of forming a layer of a coating metal on a polyamide or polyoxymethylene plastics surface, the method being environmentally acceptable, and acceptable with respect to health, *i.e.*, with respect to toxicity of the chemical species used.

[0021] It is still another object of the present invention to provide a pre-treatment solution to be used in a method of forming a layer of a coating metal on a substrate surface, more specifically on a polyamide or polyoxymethylene plastics surface.

[0022] It is still another object of the present invention to provide a pre-treatment solution to be used in a method of forming a layer of a coating metal on a polyamide or polyoxymethylene surface, the solution being cost-effective.

Description of the Invention:

[0023] The aforementioned objects are achieved by the pre-treatment solution of claim 1 and by the method of claim 17. Preferred embodiments of the invention are recited in the subordinate claims.

[0024] In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be understood, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail, in order not to unnecessarily obscure the present invention.

[0025] As referred to herein, the term "inorganic ligands" means any neutral or ionic inorganic chemical species which is arranged at a central atom or ion and the number of which depends on the coordination number of the central atom or ion. In contrast to organic ligands, the inorganic ligands comprise those species which do not contain C-H-bonds.

[0026] As referred to herein, the term "halogen acids" means hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid.

[0027] As referred to herein, the term "pKs" means the negative Brigg's logarithm of Ks, Ks being the dissociation constant of the acid in an aqueous solution, producing hydronium (H_3O^+) ions.

[0028] As referred to herein, the term "electroless metal plating solution" means a metal plating solution which contains a chemical species capable of reducing coating metal ions to elemental coating metal. For example, an electroless nickel plating solution may contain hypophosphite salts, hypophosphoric acid or dimethyl amine borane as the reducing agents.

[0029] As referred to herein, the term "substrate" means any workpiece which may be coated with a metal layer, such as a plate, other moulded device or powder.

[0030] As referred to herein, the term "wt-%" means a fraction of components contained in a mixture, the term indicating this fraction as parts of the component by weight per 100 parts of the mixture by weight.

[0031] As referred to herein, the term "alkyl" means a chemical species with the general chemical formula C_nH_{2n+1} , with n being an integer > 0 and more specifically being an integer from 1 to 8, more specifically from 1 to 6 and most specifically from 1 to 4. Alkyl species may be branched or unbranched and may preferably be methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl and tert-butyl.

[0032] As referred to herein, the term "etching of plastics surface" means the roughening and modifying of a plastics surface using chemical species, more specifically solutions into which the plastics substrates may be immersed. Due to this treatment the bonds of the polymers treated are either broken and/or oxidized and/or certain chemical functional groups are modified. Concurrently with chemically modifying the plastics surface it will also be hydrophilized. Such effects have not only been found out with polyamide and with polyoxymethylene substrates but also with ABS substrates. If ABS substrates are treated using a chromic acid etch, carboxylic acid, keto and aldehyde groups are formed from the polybutadiene moiety of the polymer whereas, in the case of polyamide and polyoxymethylene substrates, the condensation reaction performed to form the polyamide or polyoxymethylene polymer is reversed by the action of strong acids, such as sulfuric acid, hydrochloric acid, phosphoric acid, acetic acid or formic acid. The amino groups formed due to this reaction in polyamide plastics are believed to cause hydrophilicity of the polyamide surface. The hydroxyl groups formed due to this reaction in polyoxymethylene plastics are believed to cause hydrophilicity of this plastics material.

[0033] As referred to herein, the term "swelling of plastics surface" means swelling such surfaces with polar organic species, which are believed to be incorporated into the polymer matrix, thus expanding same and slightly softening the

surface thereof. Very strong polar solvents are capable of completely dissolving the polymer. Such dissolution will damage the plastics surface considerably. Therefore, for the treatment of polyamide and polyoxymethylene substrates only organic solvents may be used which cause slight swelling thereof, glycol ethers for example, or strong solvents the impact thereof being reduced if they are mixed with water (propylencarbonate, γ -butyrolactone for example).

[0034] As referred to herein, the term "conditioner" (agent promoting adsorption of noble metal catalyst nuclei to the polyamide or polyoxymethylene surface) means chemical species which are capable of influencing the surface properties of plastics substrates for the metal plating of such substrates. Predominantly the conditioners are organic molecules which adsorb at the plastics surface and enhance hydrophilicity of the substrate due to a plurality of identical functional groups, -OH groups or -NH groups for example. The conditioner may comprise positively or negatively charged groups.

[0035] As referred to herein, the term "activating" means a preparation of the plastics surface for the subsequent electroless metal plating method step, comprising depositing a noble metal, being in ionic form or in colloidal form, to the plastics surface. If the noble metal is in ionic form such noble metal ions are subsequently reduced to elemental noble metal using a reducing solution, the elemental noble metal forming noble metal catalyst nuclei. If the noble metal is in colloidal form such colloidal metal serves the starting catalyst nuclei. In general, any protective colloid surrounding the colloid particles must be removed after deposition of the particles (acceleration). In any case electroless metal plating will thereafter be initiated from a solution containing coating metal salt and reducing agent. In general gold, palladium and platinum as well as iridium and rhenium can be employed as the noble metal catalyst used for the oxidation of phosphite or formaldehyde reducing agents (for silver depositing for example). This can concurrently initiate autocatalytic reduction of metals like nickel, copper, iron and cobalt.

[0036] The pre-treatment solution and the method serve the formation of a layer of a coating metal on a substrate, the substrate preferably having at least one of a polyamide and a polyoxymethylene surface, the substrate more specifically being a polyamide or polyoxymethylene plastics substrate. Such solution and method may accordingly be used to plate polyamide or polyoxymethylene plastics substrates for decorative purpose, for example for sanitary appliances, in automotive industry, as furniture fittings, for jewelry and for other applications, wherein a polyamide or polyoxymethylene plastics substrate, which is mainly used because of its mechanical, chemical, processing or thermal properties, is metal-plated.

[0037] The polyamide plastics substrate may be a polyamide 6, polyamide 6.6, polyamide 11 and polyamide 12 plastics substrate, but may likewise be any other polyamide plastics substrate. Further, both polyamide or polyoxymethylene plastics material being provided with filler material (for example mineral powder such as kaolin or glass fibers), and polyamide or polyoxymethylene plastics material not being provided with filler material may be treated in accordance with the method of the invention. It has been found out that polyamide 11 and polyamide 12 plastics substrates cannot be metal plated using prior art methods. Polyamide and polyoxymethylene plastics substrates are injection molded to give them a specific shape depending on their intended use.

[0038] The pre-treatment solution of the invention contains at least one organic solvent, at least one noble metal in ionic form being capable of reducing coating metal ions to elemental coating metal and at least one acid. The method of the invention comprises: a) providing the substrate; b) contacting the substrate with the pre-treatment solution; and c) forming the layer of coating metal on the substrate by contacting the substrate with an electroless metal plating solution.

[0039] By using the pre-treatment solution and the method of the invention the problems encountered with the prior art solutions and methods will be overcome:

[0040] Due to the fact that the solution contains an acid, adhesion of the coating metal applied to the polyamide or polyoxymethylene plastics substrate will be optimized without being urged to use those organic solvents in the pre-treatment solution, which are problematic, with regard to toxicity, environmental impact, water-miscibility, volatility, ignition point, stability against decomposition by acid attack, cost and the necessity of having halogens bonded to carbon.

[0041] Further, as adhesion of the coating metal to the polyamide or polyoxymethylene plastics substrate will be achieved without any problem, the solution of the invention may also be aqueous, such that the content of any organic solvent contained therein may be minimized. Therefore, TOC will be minimized, too.

[0042] Further, due to the fact that only four method steps, including three rinse steps, are required for pre-treatment prior to metal plating the plastics substrate, the method of the invention can be easily performed with low effort. This again will also assure application of the method at low cost.

[0043] Further, due to the fact that no film of a polymer is formed on the plastics substrate, if a pre-treatment solution is used which contains a binder, in which method the catalyst metal would be incorporated in such film, metal plating may be effected without any problem at all surface sites on the plastics substrate, even if catalyst metal is used at a low concentration. As concentration of the expensive catalyst metal may be low therefore, the pre-treatment solution may likewise be cost-effective.

[0044] The at least one acid may preferably have a pKs at or below 5, more preferred at or below 3 and most preferred at or below 2. The at least one acid is able to attack the surface of the polyamide or polyoxymethylene plastics material, thereby rendering same wettable by further treatment agents on the one side and imparts a certain roughening to the surface thereof on the other side, because acids are in general capable of dissolving polyamide and polyoxymethylene

plastics material. Unlike with pre-treatment of ABS substrates, roughening of the plastics surface will, however, not be required to achieve sufficient adhesion of a metal layer formed on the plastics surface and will be minimized to avoid too much damage of the surface. It seems that surface texture does not significantly influence adhesion of the metal layer formed. It is rather believed that the acid contained in the pre-treatment solution dissolves a thin surface film of the polyamide or polyoxymethylene plastics material, thus creating a clean and polar surface. However, acid attack was not observed to dissolve a considerable amount of polyamide or polyoxymethylene plastics material. The impact of the acid may therefore be based on another mechanism. Though not bound to any theory, the inventors assume that the acid breaks hydrogen bonds present at the plastics surface. This would be in contrast to the breakdown (etching) mechanism of chromic acid which seems to involve breaking carbon-carbon bonds, thus chemically modifying the plastics surface.

[0045] It has been known that the history of the substrate to be treated will have considerable influence on the final product being metal plated. This will, in particular, be true for polyamide and polyoxymethylene plastics substrates. In this respect an important parameter is the temperature of the moulding tool applied during the moulding process and which is used to form a plastics part. In general, moulding temperature is not controlled. If polyamide or polyoxymethylene plastics material is processed, however, a low tool temperature will be responsible for a slightly corrugated surface being formed. However, adhesion of the metal layer deposited on the plastics surface will be very high. For this reason as low a tool temperature as possible, of 25 to 35°C for example, will be favourable. If a higher tool temperature of, for example, above 60°C is applied, surface quality will be better. However, adhesion will then be lower. Such lower adhesion values may be compensated for, to a certain extent, by using in the pre-treatment solution a suitable acid at a suitable concentration. For example hydrochloric acid proves to be favourable at a concentration of up to about 200 ml/l (37 wt.-% hydrochloric acid solution), whereas sulfuric acid, phosphoric acid (without hydrochloric acid) or methane sulfonic acid were not suitable. C₁- to C₄-carboxylic acids, such as formic acid and acetic acid, formic acid being preferred, likewise cause considerable adhesion of the metal layer to the plastics surface. Optimum concentration of these other acids is 200 - 250 g/l. It has to be taken into consideration, however, that formic acid may reduce noble metal, more specifically Pd²⁺, to elemental noble metal, more specifically palladium.

[0046] However, rendering the surface wettable by contacting it with the at least one acid is believed to be due to a chemical functionalization of the surface: Polyamide plastics contain amide functional groups which will be broken with the aid of the acid, thereby forming carboxylic acid groups and amine groups. These functional groups render the plastics substrate hydrophilic and thus wettable by aqueous solutions. Similar mechanisms provide for wettability of polyoxymethylene plastics surfaces.

[0047] As indicated before, the at least one acid is even more preferably selected from the group comprising halogen acids, formic acid, acetic acid and lactic acid. Most preferably the halogen acid is hydrochloric acid. Using these acids a very good adhesion of the metal layer formed on the surface of the polyamide or polyoxymethylene plastics substrate may be achieved.

[0048] Particularly good adhesion of the metal layer formed on the polyamide or polyoxymethylene plastics surface was found to be realized, if the pre-treatment solution contains phosphoric acid in addition to another strong acid such as hydrochloric acid. Most preferably the pre-treatment solution contains in one litre about 150 ml of an aqueous solution of 37 wt.-% hydrochloric acid, about 100 ml phosphoric acid and about 50 ml organic solvent. Best adhesion values are obtained if the concentration of hydrochloric acid in the pre-treatment solution is 150 ml/l.

[0049] The at least one organic solvent contained in the pre-treatment solution may preferably be selected from the group comprising glycol ethers, more specifically glycol ethers having chemical formula R₁-O-gly_x-R₂, wherein R₁ is C₁- to C₆-alkyl, gly is -CH₂-CH₂-O- or -CH₂-CH(CH₃)-O-, wherein further x is 1, 2, 3 or 4 and wherein R₂ is H, C₁- to C₆-alkyl or R₃-CO-, with R₃ being C₁- to C₆-alkyl. More preferably the organic solvent is selected from the group comprising diethylene glycol monoethyl ether and diethylene glycol monoethyl ether acetate. The concentration thereof in the pre-treatment solution may be in the range of from 1 to 990 ml/l, preferably from 15 ml/l to 150 ml/l. If concentration of the organic solvent is in a concentration range of from 50 to 200 ml/l adhesion of a metal layer on the polyamide or polyoxymethylene plastics surface drops if the acids are a mixture of hydrochloric and phosphoric acid.

[0050] The organic solvent proves to significantly influence the adhesion of a metal layer formed on the polyamide or polyoxymethylene plastics surface. Glycol ethers have been found out to be particularly suitable. The compounds mentioned explicitly prove to fulfil the requirements of not having any detrimental environmental impact, not comprising any halogens being bonded to carbon, being water-miscible, not being easily volatile, not having a low ignition point, being stable against decomposition by acid attack, having low cost and not being toxic, like mutagenic or teratogenic.

[0051] Both, the at least one acid and the at least one organic solvent further serve the wetting of the plastics surface in order to assure complete and reliable contacting of the plastics surface with the treatment liquids. Further, the plastics surface must be pre-treated prior to metal plating such that no contamination thereof may interfere with the electroless metal plating method. As pre-treatment according to the invention only comprises one method step and in addition three rinse steps, such pre-treatment step must be able to remove all contaminants in addition to wet (hydrophilize) the surface and allow the catalyst to sufficiently adsorb to the plastics surface. Experiments have shown that some cleansing effect

takes place if the pre-treatment solution of the invention is used. However, severe impurities adsorbed at the plastics surfaces as well as finger prints have to be avoided thoroughly.

[0052] In a preferred embodiment the noble metal is palladium. Such metal proves to have superior catalyst properties, once it has been reduced to metallic nuclei. Its concentration in the pre-treatment solution may be in the range of from 10 mg/l to 2000 mg/l, preferably from 20 mg/l to 100 mg/l.

[0053] The noble metal being in ionic form may in a preferred embodiment be formed not to comprise any ligand or to exclusively comprise inorganic ligands, such as halide ligands, more specifically chloride ligands, hence not comprising any organic ligand. Most preferably the noble metal in ionic form is Pd^{2+} . If nickel is subsequently electroless plated, any other metal, having an electrochemical standard potential of a few hundred mV more negative than nickel, may be used and will hence be able to initiate nickel deposition, such as iron or nickel. In an aqueous solution palladium ions will have water molecules be coordinated to the central ion. Pd^{2+} may be used in the form of palladium chloride, palladium nitrate or palladium sulfate. The concentration thereof will, in general, not be critical as to the ability of the activated plastics substrate to be metal plated. Neither too high a concentration thereof, nor too low a concentration thereof has revealed any negative effects. The noble metal concentration may be selected to be at or below 100 mg/l, more specifically at or below 80 mg/l, even more specifically at or below 60 mg/l, even more preferably at or below 40 mg/l and most preferably from 20 to 40 mg/l (or at about 30 mg/l). Of course, if noble metal concentration is reduced more and more, initiation of electroless metal deposition will be delayed more and more. However, such delay does not have any detrimental implication, all the more electroless metal plating is more slowly during the first plating period than in subsequent periods.

[0054] Most preferably, the pre-treatment solution is an aqueous solution. Again, such embodiment fulfils the requirement that the pre-treatment solution shall have reduced TOC and no detrimental environmental impact.

[0055] Further the pre-treatment solution may advantageously be free of any binder. In contrast to the embodiments disclosed in U.S. Patents No. 5,296,020 and 5,300,140, the present invention will preferably do without such binder, such that no film will be formed on the surface of the polyamide or polyoxymethylene plastics substrate, such film incorporating the catalyst nuclei required for initiating electroless metal plating. Thus, such films would require much more catalyst metal to initiate electroless metal plating than the present method, because many catalyst nuclei in the film would be sheathed from the electroless plating solution.

[0056] A very favourable embodiment of the present invention comprises using an agent promoting adsorption of noble metal catalyst nuclei to the polyamide or polyoxymethylene surface (conditioner). Such agent will preferably be contained in the pre-treatment solution. More specifically, the agent promoting adsorption of noble metal catalyst nuclei to the polyamide or polyoxymethylene surface may be a water-soluble polymer having polar groups, for example positively or negatively charged groups, such that they are able to mediate adhesion between the plastics surface and chemical species contained in the solution. It may, for example, be a polyelectrolyte compound. In one most preferred embodiment such polyelectrolyte compound may be a polyimidazolium compound, such as polyimidazolium methosulfate. Using the adsorption promoting agent, adsorption of a metal layer formed on the polyamide or polyoxymethylene plastics surface will be considerably enhanced. Concentration of this agent in the pre-treatment solution may be in the range of from 1 mg/l to 5000 mg/l, preferably from 10 mg/l to 100 mg/l.

[0057] The agent promoting adsorption promotes adsorption of the noble metal catalyst nuclei to the plastics substrate but also promotes adsorption of the catalyst to any holding elements for plastics parts, a rack, for example. This adsorption will increase noble metal consumption on the one hand and further initiate coating metal deposition on the holding elements on the other hand. Thus coating metal must be stripped off either frequently. However, as the agent promoting adsorption of the noble metal catalyst nuclei will enhance adsorption of the noble metal, the concentration thereof may be minimized, to 20 mg Pd^{2+} per litre pre-treatment solution for example. In addition, if the agent promoting adsorption of the noble metal catalyst nuclei is used, a couple of polyamide or polyoxymethylene plastics substrates may be metal plated, which would otherwise not be accessible to plating.

[0058] In addition the agent promoting adsorption of the noble metal catalyst seems to some extent enhance adhesion of a metal layer deposited on the plastics substrate if no phosphoric acid is used in the pre-treatment solution but only hydrochloric acid.

[0059] Further the pre-treatment solution of the invention may contain a surface active agent. This agent will reduce surface tension of the solution such that the plastics substrate may be more easily wetted. No requirements are posed to its chemical structure and identity. Apart from an as low as possible surface tension of the pre-treatment solution to be achieved, this agent will preferably simply be easily rinsed off and be harmless, especially with respect to animals. For this reason nonylphenol derivatives are not preferred.

[0060] For forming an electrically conductive layer on the polyamide or polyoxymethylene plastics substrate any electroless metal plating solution may be employed. In a preferred embodiment of the invention the coating metal is nickel. Therefore, to deposit the first metal layer an electroless nickel plating solution may be used, since electroless nickel plating is cost-effective and offers the advantage of easily being performed because the nickel plating solution is essentially stable to decomposition. Further, use of any noxious compounds such as formaldehyde may be dispensed

with.

[0061] In general an electroless metal plating solution, more specifically an electroless nickel plating solution, contains at least one metal ion source, more specifically at least one nickel ion source, such as nickel sulfate or nickel chloride, further a reducing agent, such as at least one hypophosphite salt, hypophosphoric acid, a borane compound, such as dimethyl amine borane or sodium borohydride or, if copper is to be deposited, formaldehyde, further at least one complexing agent, such as carboxylic acids, like succinic acid, citric acid, lactic acid, malic acid, ethylene tetraacetic acid as well as the salts thereof, at least one buffer or other pH adjusting agent, like acetic acid/acetate salt or sodium hydroxide. Hypophosphite salts and hypophosphoric acid are preferred over the other reducing agents due to the cost thereof. In addition, the plating solution may contain additives which act as a stabilizer to prevent spontaneous decomposition of the solution.

[0062] The method of the invention makes use of the fact that the reducing agent of the metal plating solution may also be employed to reduce palladium or other noble metal ions to elemental palladium or another elemental noble metal. As the same reducing agent may be used both for the reduction of the noble metal ions and for the deposition of the coating metal, the noble metal ions may be reduced using the reducing agent contained in the electroless metal plating solution. Thus the method may in one embodiment comprise only four method steps (pre-treatment step and three rinse steps) prior to electroless metal plating the plastics substrate. Hypophosphite salts and hypophosphoric acid prove to react spontaneously with Pd^{2+} ions adsorbed to the polyamide or polyoxymethylene plastics surface, forming palladium catalyst nuclei which may be large enough to store hydrogen atoms to initiate nickel plating. If the temperature of the electroless nickel plating solution is about 50°C reduction of Pd^{2+} is complete after less than 30 seconds. Surprisingly, there is practically no delay in reduction of Pd^{2+} , compared with methods, in which Pd^{2+} is reduced in a separate method step. In general, electroless nickel plating takes about 6 to 12 minutes; therefore any minor delay in nickel plating initiation cannot be detected. Electroless nickel plating proves to be reliable irrespective of which electroless nickel plating solution is employed.

[0063] The method of the invention comprising reducing the noble metal ions in the electroless metal plating solution, has been found out to be reliable as to metal plating capability (uniform metal plating), though treatment of the pre-treated plastics substrate with the electroless metal plating solution was assumed to strip off, by rinsing, at least partly, the noble metal ions adsorbed to the plastics surface before reduction can take place. In such event part of the noble metal adsorbed could not serve initiation of electroless metal plating, but would render the electroless coating metal plating solution unstable, since coating metal would be deposited at the stripped off noble metal. Such assumption did not turn out to take place, however. Otherwise noble metal being stripped off the plastics surface would have tended to destabilize the metal plating solution. However, such behaviour could not be verified and, likewise, increased consumption of the reducing agent contained in the metal plating solution could not be observed.

[0064] Preliminary tests have shown that the previously separately applied method steps of etching, conditioning and activating, can be merged in one method step (organic solvent, acid, conditioner and catalyst contained in pre-treatment solution) and that the previous method steps of reducing the activator species and electroless metal plating may be merged into another method step, three rinse steps being performed in between. No precipitation or not negative interference occurs when the pre-treatment solution of the invention is formulated. Further, the conditioner species is not stripped off the plastics surface due to the action of the pre-treatment chemicals. Moreover, simultaneous etching and activating of the plastics surface does not result in uneven coverage of the surface with noble metal nuclei.

[0065] In another embodiment of the present invention, the substrate may be contacted additionally with a reducing solution, after method step b), and prior to method step c). Such reducing solution preferably contains at least one reducing agent capable of reducing the at least one noble metal in ionic form to elemental noble metal. The reducing agent may preferably be selected from the group comprising hypophosphite salts and hypophosphoric acid. By additionally contacting the polyamide or polyoxymethylene plastics substrates with the reducing solution metal plating may be even more reliable in that metal plating may, at a given noble metal concentration in the pre-treatment solution, be performed to yield quicker metal coverage of the surface of the plastics substrates or the noble metal concentration may even be reduced to a very low value, 20 mg palladium per litre solution for example. Thus, the method may be rendered very economic since consumption of noble metal may be minimized due to less loss of noble metal as a consequence of drag-out of the pre-treatment solution from the pre-treatment bath. Furthermore, the electroless metal plating solution will be protected by removing any species from the pre-treatment solution, eventually adhering to the plastics surface from dragging same into the electroless metal plating solution.

[0066] If such separate reducing solution is used for initiating electroless nickel plating from Pd^{2+} activation the reducing solution will preferably be operated at a pH not below 3. Further, the temperature of this solution is preferably not below 35°C. The concentration of hypophosphite salt in this solution is recommended to be below 30 g/l, about 20 g/l being sufficient (sodium hypophosphite; other salts or hypophosphoric acid being at the same molar concentration).

[0067] Rinsing between the pre-treatment step and the electroless metal plating step proves not to be critical as to metal-plastics adhesion, uniform metal plating and other requirements. However, the period of time used between the pre-treatment and the first rinse step has to be as short as possible, to prevent formation of draining structures on the

plastics surface. The first rinse should take at least 1 minute and should be performed with efficient agitation of the plastics substrate in the rinse, in order to remove any organic solvent from the substrate matrix.

[0068] Experiments have shown that adhesion seems to significantly depend on the extent water is absorbed into a polyamide plastics part and also being adsorbed on the surface thereof. Such assumption may, for example, be derived from the fact that caustic will not be able to pre-treat the surface of the polyamide or polyoxymethylene plastics substrate such that sufficient adhesion of a metal layer thereon will be attained. Caustic is assumed to break the amide bonds or polyamide plastics material, too, but it will also introduce much water into the polymer matrix due to its strong hydrophilization properties and thus impedes sufficient adhesion of the metal layer. Similar effects will be brought about with polyoxymethylene. For this reason, using aqueous solutions to process the polyamide or polyoxymethylene plastics substrates seems to be of major disadvantage. However, since the method consists of but four method steps prior to metal plating the plastics substrate, and the first metal layer will then seal the plastics surface, thus preventing any further contact of the surface with water, excessive water uptake is avoided. It moreover proves advantageous to store a metal plated plastics part in order to enhance adhesion of the metal layer. In general, such increase in adhesion will be complete after about 3 days at room temperature, but may be complete after only a few hours if the storage temperature is raised to 60°C for example.

[0069] Adhesion of the metal layer to the polyamide or polyoxymethylene plastics substrate may be higher than a metal layer to an ABS substrate, though roughness of the polyamide and polyoxymethylene plastics surfaces is much lower than that of an ordinarily pre-treated ABS plastics surface. This observation may be attributed to electrostatic interactions between the metal layer and the polyamide or polyoxymethylene plastics surface, which is more polar than the ABS plastics surface. Such higher adhesion will be obtained with polyamide or polyoxymethylene plastics surfaces after any water being adsorbed to the interface between the metal layer and the plastics surface and absorbed into the plastics material has been distributed all over the plastics material. Such distribution may be brought forward by the porosity of the polyamide and polyoxymethylene plastics material.

[0070] To treat the plastics substrates in accordance with the invention they are brought into contact with the pre-treatment solution, optionally the reducing solution, the electroless metal plating solution and the rinse liquids by immersing them into these liquids or by spraying or splashing the solutions to the plastics substrate surfaces. For this purpose, the plastics parts may either be secured to racks, or contained in a drum, or be conveyed through a treatment apparatus, which may for holding the parts be equipped with baskets on which the parts are deposited.

[0071] The invention will be described more clearly with reference to the following Figure and Examples. The embodiments shown in the Figures and Examples are not intended to limit the scope of the invention.

Fig. 1 shows a graph of adhesion of a nickel/copper layer on a polyamide plastics strip using different acids and acid combinations at different organic solvent concentrations in the pre-treatment solution.

Example 1:

[0072] To prepare a pre-treatment solution, to 1 litre of an aqueous solution containing 200 ml/l diethylene glycol monomethyl ether and 40 ml/l 37 wt.-% hydrochloric acid 250 µl of a solution of palladium dichloride, which contained the palladium salt at a concentration of 10 wt.-%, referring to the palladium content, 0.5 ml of a 30 wt.-% solution of the conditioner Lugalvan® (trade mark of BASF, Germany) PVI and 0.1 g sodium lauryl sulfonate were added. Thus, the concentration of Pd²⁺ was 25 mg/l in the pre-treatment solution. The pre-treatment solution formed was clear and slightly yellowish. This solution was heated and held at a temperature of 40°C.

[0073] 3 mm thick plates made from Durethan® (trade mark of Lanxess, Germany) BM240 (polyamide 6, filler: kaoline) which had a width of 5 cm and a length of 7 cm were treated in the pre-treatment solution for 10 minutes while slightly agitating the plate in the solution. Thereafter the plate was rinsed with cold tap water and afterwards held in the water for another 2 minutes while slightly agitating same. Then the plate was nickel-plated for 10 minutes at a temperature of 45°C in a commercial electroless nickel-plating bath which contained 3 g/l nickel and 20 g/l sodium hypophosphite. The nickel layer deposited was subsequently copper electroplated (Cupracid® (trade mark of Atotech, Germany) Ultra), with 2.5 A/dm² cathodic current density, until a metal layer thickness of about 30 µm was attained. After rinsing, the plate was stored for 1 hour at 70°C. Then a stripe having a width of 1 cm was cut from each plate and copper peeled off the strip using a tensile testing machine (Instron® (trade mark of Instron Corp., USA)). The adhesion of metal to the polyamide plastics part was measured to be 1.10 N/mm.

Example 1.1:

[0074] Repeating Example 1, the concentration of Pd²⁺ in the pre-treatment solution was varied and the amount of Pd [mg/m²] measured depending on the Pd²⁺ concentration (dissolution of Pd from a plate having a defined surface area using nitric acid and determination of Pd amount in the nitric acid solution by AAS (atomic absorption spectrometry)).

The amount of Pd adsorbed on the polyamide plastics parts is given in Table 1.

Table 1: Amount of Pd on polyamide plastics plates		
	Palladium Concentration [mg/l]	Palladium Amount Adsorbed [mg/m ²]
5	40	12.7
	60	18.0
	80	23.2
	100	25.2
10	120	30.7

Example 1.2:

[0075] Further experiments have been performed to evaluate maximum temperature of the pre-treatment solution. For this purpose Example 1 was repeated. An upper temperature of 40°C was considered appropriate to assure that no streaks formed if the polyamide plastics parts treated were transferred from a container containing the pre-treatment solution to a first rinse tank. If temperature was selected to be higher than 40°C too much solvent proved to be evaporated during the transfer so that the components of the pre-treatment solution contained in the liquid film adhering to the plastics surface concentrated, further reacted with the plastics surface and thus uneven conditions occurred at the plastics surface (formation of relief-like structure).

Example 2:

[0076] The procedure of Example 1 was repeated. Instead of hydrochloric acid 40 ml/l formic acid (about 98 wt.-%) were used. After copper electroplating adhesion of the metal layer on the plastics strip was found to amount to 1.85 N/mm.

Example 3:

[0077] The procedure of Example 1 was repeated. Instead of Durethan® BM240 Minlon® (trade mark of E.I. Du Pont de Nemours, USA) 73M40 (polyamide 6.6) was used. The dimensions of the plastics part were the same as before. Adhesion of the metal layer to the plastics surface was determined to be 0.97 N/mm.

Example 4:

[0078] An interior door handle as typically used in automotive industry and made from Durethan® BM240, which had been moulded into a mould having a tool temperature of 40°C, was treated according to the method described in Example 2. After a storage time period of 3 days adhesion could no longer be measured because it was so high that either the metal strip ruptured or the plastics material ruptured; no separation at the interface between the metal layer and the plastics surface could be attained during the peel testing.

Example 5:

[0079] To prepare a pre-treatment solution, to 1 litre of an aqueous solution containing 150 ml/l diethylene glycol monoethyl ether acetate and 100 ml/l 98 wt.-% formic acid 0.50 ml of a palladium sulfate solution, which contained the palladium salt at a concentration of 4 wt.-%, referring to the palladium content, and 0.1 g sodium lauryl sulfonate were added. Thus concentration of Pd²⁺ was 20 mg/l in the pre-treatment solution. The pre-treatment solution formed was heated and held at a temperature of 40°C.

[0080] A 3 mm thick plate made from Durethan® BM 420 which had a width of 5 cm and a length of 7 cm was treated in the pre-treatment solution for 10 minutes while slightly agitating the plate in the solution. Thereafter, the plate was rinsed with cold tap water and afterwards held in the water for another 2 minutes while slightly agitating same. Then the plate was nickel-plated for 10 minutes at a temperature of 45°C in a commercial electroless nickel-plating bath which contained 3 g/l nickel and 20 g/l sodium hypophosphite. The nickel layer deposited was subsequently copper electroplated. After rinsing, the plate was stored for 1 hour at 70°C. As described previously, adhesion between the plastics surface and the metal layer was tested and measured to be 1.64 N/mm.

Example 6:

[0081] Example 1 was repeated with the palladium ion concentration in the pre-treatment solution being, in this case, 50 mg/l, different acids and acid combinations as well as the organic solvent (diethylene glycol monoethyl ether) being used at different concentrations. The temperature of the pre-treatment solution was 30°C. Duration of treatment in the pre-treatment solution was 6 minutes. Adhesion values measured are shown in a graph in Fig. 1.

[0082] Fig. 1 shows that best results with respect to adhesion of the nickel/copper layer on the polyamide strip were obtained using 150 ml/l hydrochloric acid (37 wt.-%) and 100 ml/l phosphoric acid. Best adhesion was achieved if the organic solvent concentration was set to a relatively low value (50 ml/l for example). Further, if the concentration of the acids used is rather low, concentration of the solvent has preferably to be increased to a concentration higher than 50 ml/l. Some difference in adhesion values was in fact observed on either side of the plates. This was attributed to different moulding conditions on the two sides of the plate.

Claims

1. Pre-treatment solution, containing at least one organic solvent, at least one noble metal in ionic form being capable of reducing coating metal ions to elemental coating metal and at least one acid.
2. Pre-treatment solution according to claim 1, wherein the at least one acid has a pKs at or below 5.
3. Pre-treatment solution according to any one of the preceding claims, wherein the at least one acid is selected from the group comprising halogen acids, formic acid, acetic acid and lactic acid.
4. Pre-treatment solution according to claim 3, wherein the halogen acid is hydrochloric acid.
5. Pre-treatment solution according to any one of the preceding claims, wherein one of the at least one acid is phosphoric acid.
6. **Pre-treatment solution according to any one of the preceding claims**, wherein the pre-treatment solution contains in one litre about 150 ml of an aqueous solution of 37 wt.-% hydrochloric acid, about 100 ml phosphoric acid and about 50 ml organic solvent.
7. Pre-treatment solution according to any one of the preceding claims, wherein the noble metal is palladium.
8. Pre-treatment solution according to any one of the preceding claims, wherein the noble metal in ionic form does not comprise any ligand or exclusively comprises inorganic ligands.
9. Pre-treatment solution according to any one of the preceding claims, wherein the noble metal in ionic form is Pd²⁺.
10. Pre-treatment solution according to any one of the preceding claims, wherein the at least one organic solvent is selected from the group comprising glycol ethers having chemical formula R₁-O-gly_x-R₂, wherein R₁ is C₁- to C₆-alkyl, gly is -CH₂-CH₂-O- or -CH₂CH(CH₃)-O-, wherein further x is 1, 2, 3 or 4 and wherein R₂ is H, C₁- to C₆-alkyl or R₃-CO-, with R₃ being C₁- to C₆-alkyl.
11. Pre-treatment solution according to any one of the preceding claims, wherein the organic solvent is selected from the group comprising diethylene glycol monoethyl ether and diethylene glycol monoethyl ether acetate.
12. Pre-treatment solution according to any one of the preceding claims, wherein the pre-treatment solution is an aqueous solution.
13. Pre-treatment solution according to any one of the preceding claims, wherein the pre-treatment solution is free of any binder.
14. Pre-treatment solution according to any one of the preceding claims, wherein the pre-treatment solution further contains an agent promoting adsorption of noble metal catalyst nuclei to a plastics surface.
15. Pre-treatment solution according to claim 14, wherein the agent promoting adsorption of noble metal catalyst nuclei

to the plastics surface is a polyelectrolyte compound.

16. Pre-treatment solution according to claim 15, wherein the polyelectrolyte compound is a polyimidazolium compound.

5 **17.** Method of forming a layer of a coating metal on a substrate, the substrate having a plastics surface, the method comprising:

a) providing the substrate;

b) contacting the substrate with the pre-treatment solution according to any one of claims 1 to 16;

10 c) forming the layer of coating metal on the substrate by contacting the substrate with an electroless metal plating solution.

18. Method according to any one of the preceding claims, wherein the substrate is contacted with a reducing solution after method step b) and prior to method step c), said reducing solution containing at least one reducing agent capable of reducing the at least one noble metal in ionic form to elemental coating metal.

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19. Method according to claim 18, wherein the at least one noble metal is palladium and the at least one reducing agent is selected from the group comprising hypophosphite salts and hypophosphoric acid.

20 **20.** Method according to any one of claims 17 to 19, wherein the coating metal is nickel.

21. Method according to any one of claims 17 to 20, wherein the electroless metal plating solution is an electroless nickel solution.

25 **22.** Method according to any one of claims 17 to 21, wherein the plastics surface is at least one of a polyamide and a polyoxymethylene surface.

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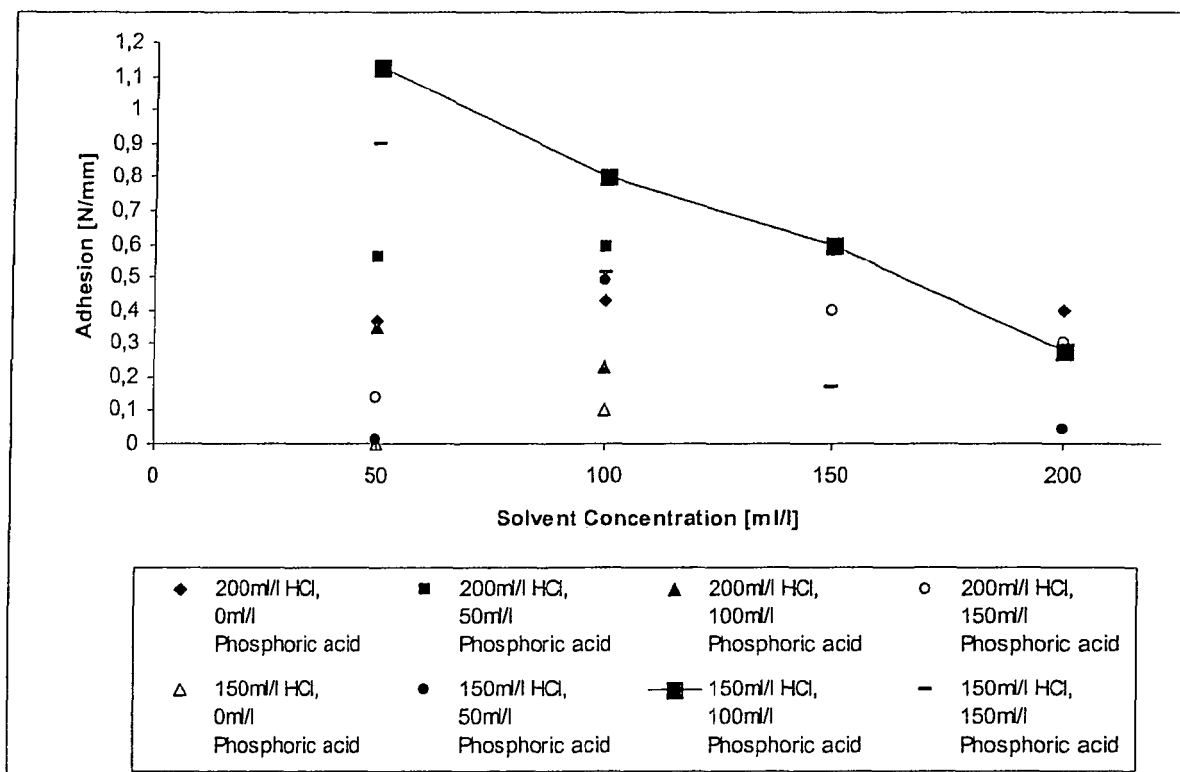


Fig. 1



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 06 07 7232

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