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(54) **Solution and method for electrochemically depositing a metal on a substrate**

(57) To electroplate a metal layer which has silica particles dispersed therein, a solution and a method for electrochemically depositing a metal on a substrate are provided, wherein the solution contains ions of the metal to be deposited and silica particles, wherein at least one silicon containing organic moiety is provided to said silica

particles, said silicon containing organic moiety comprising at least one functional group selected from the group comprising amino, quaternized ammonium, quaternized phosphonium and quaternized arsonium which imparts the silica particles a positive electric charge while being in contact with the solution.

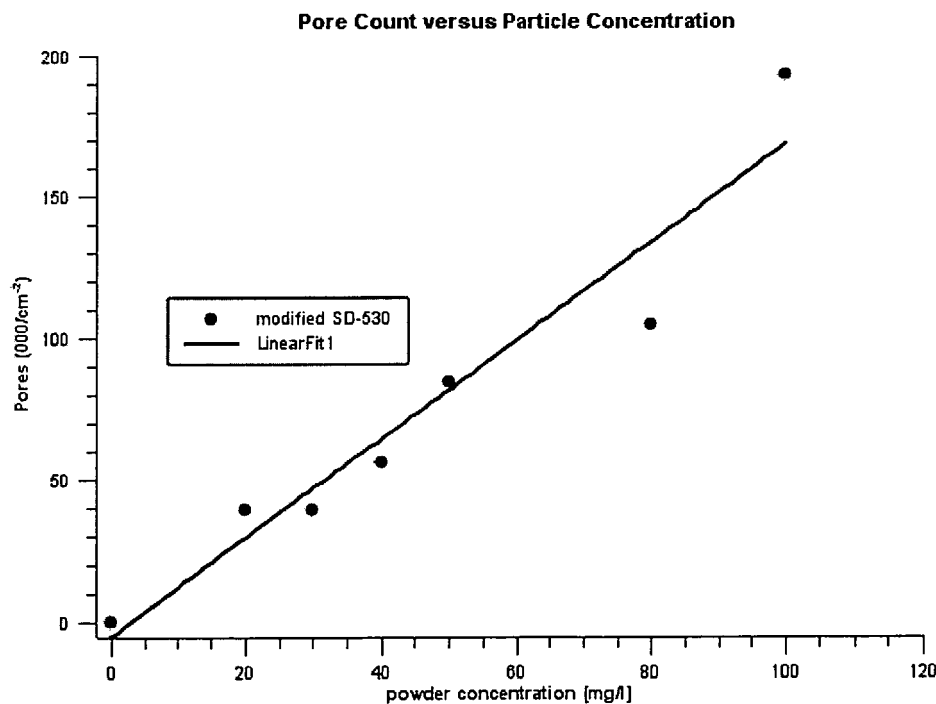


Fig. 2

EP 2 145 986 A1

DescriptionField of the Invention:

[0001] The present invention relates to a solution and a method for electrochemically depositing a metal on a substrate and a method of forming a corrosion-resistant nickel multilayer on a substrate. Such corrosion-resistant nickel multilayer systems are used, e.g., in automotive industry, sanitary industry, furniture fitting industry, spectacles industry and for jewelry.

Background Art:

[0002] It is meanwhile state of the art to achieve corrosion resistance of plated articles mainly for the automotive industry by plating a multilayer nickel system on a substrate followed by a thin chromium layer. The last nickel layer in such a system produces tiny (micro-) pores in the chromium layer which are invisible for the bare eye but which are able to distribute a corrosive attack.

[0003] The nickel multilayer normally consists of two or three nickel layers: an optional first layer having a rather noble (positive) electric potential, a second nickel layer which is a bright nickel layer and which is less noble than the first nickel layer and a third nickel layer which is plated on top of the second (bright) nickel layer. The second nickel layer may also be split into two nickel layers: a high sulfur nickel layer, which is very active and which is deposited on the first nickel layer and a further active, high leveling and bright nickel layer. Plating of the uppermost (third) nickel layer is performed while co-depositing particles which are incorporated into this third nickel layer. Finally a chromium layer is plated on top of the third nickel layer. The chromium layer contains holes (pores) due to the particles being incorporated into the third nickel layer. Any corrosive attack takes place through these holes and will first cause dissolution of the less noble second (bright) nickel layer. As long as the (top) third nickel layer and the chromium layer do not collapse, corrosion remains invisible. Corrosion stops at the first more noble nickel layer which protects the base material against any corrosion, and proceeds laterally until all less noble nickel in the second (bright) nickel layer is dissolved.

[0004] The described system works on plated plastic articles where the metal layer plated first normally is copper as well as on steel parts. Its performance is checked by the CASS test (ASTM B368: Copper-Accelerated Acetic Acid-Salt Spray Testing). The result of this test is given as a rank between 1 and 10 where '10' means: no visible change compared to a surface without any corrosive attack and '1' denotes a destroyed surface. The test furthermore distinguishes between the appearance of a surface after prolonged corrosion, and the base material corrosion. It therefore gives a pair of numbers, e.g., 10/9 which means: no attack of the base material but some minor change of appearance of a surface. After 48 hours CASS testing only, a properly adjusted nickel and chromium multilayer system should be able to completely protect a surface, leading to a 10/10 result. CASS testing correlates with the number of pores being produced in the chromium layer which are in turn due to the incorporation of inert particles into the third nickel layer (E.P.Harbulak et al., "Chromium Microporosity and Active Sites", Plating and Surface Finishing, (1989) 58-61).

[0005] Corrosion gets visible when the produced holes are growing bigger, or when the protective action of the third nickel and chromium layers collapse if there is no supporting bright nickel anymore.

[0006] Several parameters influence the multilayer nickel system. These are mainly the thickness of the metal layers, their individual relative electric potentials and the pores produced in the chromium top layer. Because the second (bright) nickel layer sacrifices itself, a thicker layer might help to withstand longer attacks. Very low thickness of the third nickel layer or of the chromium layer let the protecting layers collapse earlier. One main influence consists in the different electric potentials of the nickel layers. Organic additives comprising double bonds or containing chloride might make the electro-deposited nickel more noble. Well known additives suitable for this purpose for instance are vinylsulfonic acid, allylsulfonic acid and chloralhydrate. Other organic additives which increase the sulfur content entrapped in a nickel layer make it less noble. One member of this group is saccharine. Normally, by using suitable additives, the electric potential difference established between the first (semi-bright) nickel layer and the second (bright) nickel layer is adjusted to be in a range of from 90 mV to 140 mV. The electric potential and the resulting potential difference are determined using the STEP test (ASTM B764: "Simultaneous Thickness and Electrochemical Potential Determination of Individual Layers in Multilayer Nickel Deposit"). Like the first nickel layer, the third nickel layer must be more noble than the second nickel layer, as the third nickel layer with its tiny pores has to cover the second (bright) nickel layer without experiencing any dissolution once corrosion takes place. In order to achieve this, a potential difference between the third nickel layer and the second nickel layer in a range of from 20 mV to 60 mV normally is adjusted.

[0007] Without ensuring that the tiny pores in the last two metal layers are uniformly distributed, corrosion takes place less uniformly, rather soon producing only few but big holes easily visible with bare eyes which soon are able to even destroy the semi-bright nickel layer and attack the base material. The corrosive attack therefore should be uniformly distributed (M. Hap et al.: "DUR-NI 4000 - Verbesserte Korrosionsschutz mit größerer Prozesssicherheit", Galvanotechnik, (2004) 894-897). This is achieved by the use of non-conductive material being contained in the plating solution

for the third nickel layer. The non-conductive material causes said tiny pores ("microporous" surface). The third (discontinuous) nickel layer is therefore referred to as "microporous nickel". Particles of aluminium oxide, titanium oxide, filtering earth, iron oxide, chromium oxide and molybdenum oxide are indicated in US Patent No 3,449,223 to be suitable for this purpose.

[0008] Many attempts have been made to achieve a uniform distribution of pores and a reliable pore count. It is believed that the number of pores should be greater than $10,000 \text{ cm}^{-2}$ (E.P.Harbulak et al., *ibid.*). The number of pores is counted after plating a specimen with copper in an acidic copper electrolyte which will not deposit copper over chromium but only on nickel (Dubpernell-Test, ASTM B604, B456). Normally inorganic material is added to the third nickel electrolyte solution to produce the pores. Such material might be silica (US Patent No. 3,825,478, in combination with Al^{+++} ions [Ex. I]), titanium oxide (EP 0 431 228 A1, in combination with Ca^{++}), titanium oxide coated with Al_2O_3 or SiO_2 (JP 04371597 A) or an insoluble reaction product, for example a nickel compound being insoluble in the bath solution (US Patent No. 3,736,108). Electrically non-conductive organic fibers have been used as well to be incorporated into a nickel layer (GB Patent No. 1,118,167).

[0009] There are substantial disadvantages of the inorganic particles used to be incorporated into the third nickel layer: Particles from finely ground inorganic material have a greater specific density than water or than the nickel electrolyte and therefore have a strong tendency to sediment at the bottom of a plating tank. To avoid sedimentation, strong air agitation is used which in turn is disadvantageous as all particles coming into contact with the surface of the part to be plated are immediately blown away though they should remain there in order to be incorporated into the nickel layer. A disadvantage of SiO_2 particles has been established of having the risk of clogging the anode bags. This is believed to be due to the SiO_2 particles presumably having a negative net charge when being in a nickel electroplating bath. G. Vldrich et al., "Dispersion Behavior of Al_2O_3 and SiO_2 Nanoparticles in Nickel Sulfamate Plating Baths of Different Composition", J. Electrochem. Soc., 152(5), C294-C297 (2005), reports on the co-deposition of metal ions and dispersed particles of Al_2O_3 and SiO_2 . They argue that one reason for the lack of rare investigations on the plating of SiO_2 -nickel matrix material would be due to the often-observed negative net charge of the SiO_2 even at low ion concentrations in aqueous solution in pH ranges larger than 3 or 4.

[0010] In order to reverse the surface charge of silica, C. J. Brinker, G. W. Scherrer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing", 1st. Ed., Academic Press, 1990, pp. 410-415 report absorbing positively charged material on the surface thereof without, however, referring to nickel electroplating. Charged material suitable to reverse the charge of silica to the positive are indicated to be, e.g., tri- and tetravalent metals such as Al, Cr, Ga, Ti and Zr. Also polyvalent organic cations may be absorbed to the silica instead of these metals. In an alternative WO 2005/106106 A1 discloses an aqueous dispersion for the use as a finishing agent for textiles, wherein the dispersion contains a pyrogenically produced, aggregated dioxide powder and a cationic polymer which is soluble in the dispersion. Further EP 1 894 888 A1 1 discloses an aqueous silica dispersion which is cationically stabilized. Such dispersion is mentioned to be used as a paint to be applied on paper, foils and onto other printing media, as a coating on a substrate like wood, plastics, metal, textiles and foils for improving the mechanical and optical properties thereof, as a coating on foils for improving the separation of two foils from each other and in grinding and polishing agents.

[0011] In addition, DE 24 32 724 A1 refers to a nickel deposition solution comprising alkali metal silicates and kaolin to form particles in the deposited nickel layer. The alkali metal silicates are reported to change the charge of the kaolin particles in order to make the incorporation thereof into the nickel deposit possible.

Object of the Present Invention:

[0012] In view of the foregoing an object of the present invention is to provide a solution for electrochemically depositing a metal on a substrate. Another object of the present invention is to provide a method of electrochemically depositing a metal on a substrate. An even further object of the present invention is to provide a method of forming a corrosion-resistant nickel multilayer on a substrate. An even further object of the present invention is to provide means to improve uniformity of resistance to corrosion attack to the surface of a metallic coating, in particular of a nickel coating, even more particularly of a nickel coating coated with a chromium coating. More specifically, a further object of the present invention is to provide means to improve uniformity of pores formed in the chromium coating and in particular to provide means to improve uniformity of distribution of non-conductive particles incorporated into a nickel layer which is deposited directly underneath the chromium coating. Most specifically an object of the present invention is to provide a solution and a method for electrochemically depositing a metal, more specifically nickel, on a substrate which contains silica particles which are co-deposited with nickel.

Definitions:

[0013] For the purposes of this disclosure the following definitions apply:

[0014] "Alkyl" means any saturated or unsaturated monovalent or divalent radical exhibiting a hydrocarbon chain.

Accordingly, alkyl may be a monovalent saturated hydrocarbon chain which, when being unsubstituted, has general chemical Formula C_nH_{2n+1} , wherein n is an integer, which is greater than zero, like methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, tert-pentyl, neo-pentyl, hexyl, heptyl, octyl and the like, most preferably methyl, or a divalent saturated alkyl chain which, when being unsubstituted, has general chemical Formula C_nH_{2n} , wherein n is an integer, which is greater than zero, like methylen ($-CH_2-$), ethylen ($-CH_2-CH_2-$), n-propylene ($-CH_2-CH_2-CH_2-$), iso-propylene ($-CH(CH_3)-CH_2-$) and the like. Further alkyl may be a monovalent unsaturated hydrocarbon chain, *i.e.*, a hydrocarbon chain which has at least one double bond or at least one triple bond or both, at least one double bond and at least one triple bond. Monovalent hydrocarbon chains having at least one double bond have, when being unsubstituted, general chemical Formula C_nH_{2n-1} , wherein n is an integer, which is greater than zero, like ethenyl ($-CH=CH_2$) and propenyl ($-CH=CH-CH_3$, $-CH_2-CH=CH_2$). Divalent hydrocarbon chains having at least one double bond have, when being unsubstituted, general chemical Formula C_nH_{2n-2} , like ethenylene ($-CH=CH-$). Monovalent hydrocarbon chains having at least one triple bond have, when being unsubstituted, general chemical Formula C_nH_{2n-3} , wherein n is an integer, which is greater than zero, like ethynyl ($-C\equiv CH$). Divalent hydrocarbon chains having at least one triple bond have, when being unsubstituted, general chemical Formula C_nH_{2n-4} , like ethynylene ($-C\equiv C-$). In the above definitions n may be an integer from 1 to 16, more preferably from 1 to 12, even more preferably from 1 to 10, even more preferably from 1 to 6, even more preferably from 1 to 5 and most preferably from 1 to 4. Referring to these definitions, n may be in an alternative embodiment at least 2 or at least 3. Hence, alkyl may be C_1-C_6 alkyl or C_1-C_5 alkyl or C_1-C_4 alkyl.

[0015] Alkyl may be substituted, wherein at least one hydrogen atom thereof is substituted by any radical group like aryl, heteroaryl, OR, $NR'R''$, COOR, $CONR'R''$, wherein R, R' and R'' are independently selected from hydrogen, alkyl, aryl and heteroaryl.

[0016] "Aryl" means an aromatic C_5-C_{12} hydrocarbon moiety which may be substituted or unsubstituted. In substituted aryl, at least one hydrogen atom thereof is substituted by any radical group like, alkyl, aryl, heteroaryl, OR, $NR'R''$, COOR, $CONR'R''$, wherein R, R', R'' are independently selected from hydrogen, alkyl, aryl and heteroaryl. Most preferably aryl is phenyl.

[0017] "Heteroaryl" means an aromatic moiety having 5 to 12 ring members and having as the ring members, in addition to carbon atoms, at least one of N, S and O atoms. Heteroaryl moieties may be unsubstituted or substituted. In substituted heteroaryl, at least one hydrogen atom is substituted by any functional group like alkyl, aryl, heteroaryl, OR, $NR'R''$, COOR, $CONR'R''$, wherein R, R', R'' are independently selected from hydrogen, alkyl, aryl and heteroaryl. Most preferably heteroaryl is pyridyl, pyrrol, thiophenyl, furanyl, pyrazoyl and the like.

[0018] "Amino" means the moiety $-NR'R''$, wherein R' and R'' are independently selected from the group comprising hydrogen, alkyl, aryl, heteroaryl or, alternatively, may form one single divalent group to be with the N atom a ring moiety.

[0019] "Imino" means the moiety $-NR-$ or $=NR$, wherein R is hydrogen, alkyl, aryl, heteroaryl, and may form two bonds to two other atoms ($-NR-$) or a double bond to one other atom ($=NR$).

[0020] "Silica" roughly is silicon dioxide. Silica particles may vary, depending on the method of production thereof, in terms of particles' size, degree of agglomeration, degree of crystallinity, specific surface area thereof, porosity and the like. "Silica" in accordance with the present invention may also be understood as a material which consists of particles of any other material like alumina, wherein these particles of the other material are completely covered with the silica material, such that the particles' surface predominately behaves like a silica surface. Silica is commercially available under trade names like Aerosil® (Evonik Degussa), HDK® (Wacker Chemie) and Cab-O-Sil® (Cabot). Silica may be crystalline or amorphous. Silica may also be provided as a colloid.

Description of the Present Invention:

[0021] The aforementioned objects are achieved by the solution for electrochemically depositing a metal on a substrate according to claim 1, by the method of electrochemically depositing a metal on a substrate according to claim 7 and by the method of forming a corrosion-resistant nickel multilayer on a substrate according to claim 8. Preferred embodiments of the invention are indicated in the sub-claims.

[0022] It has now been discovered that uniform distribution of pores in an outer chromium layer may easily be achieved if a metal layer, in particular a nickel layer, is deposited with silica particles being co-deposited wherein the silica particles are conferred a sufficiently large positive electric charge to ensure that these particles are effectively transferred to the workpiece surface. Thus, the invention makes use of particles having an improved performance regarding their behavior in metal electrolytes, preferably nickel electrolytes and in an electric field. The particles allow the creation of high pore counts and a wide range of pore sizes. The positive electric charge on the silica particles is imparted to the silica particles by providing same with at least one silicon containing organic moiety thus giving the silica particles this positive electric charge while being in contact with the solution.

[0023] One aspect of the present invention is therefore to provide a solution for electrochemically depositing a metal on a substrate, said solution containing ions of the metal to be deposited, and silica particles, wherein at least one silicon

containing organic moiety is provided which imparts the silica particles a positive electric charge while being in contact with the solution. Said at least one silicon containing organic moiety comprises at least one functional group selected from the group comprising amino, quaternized ammonium, quaternized phosphonium and quaternized arsonium and is preferably bonded to the silica particles. The at least one functional group imparts the silica particles the positive electric charge as required while being in contact with said solution.

[0024] Another aspect of the present invention is to provide a method of electrochemically depositing a metal on a substrate, said method comprising the following method steps: (a) contacting the substrate and at least one anode with the solution for electrochemically depositing a metal according to the present invention and (b) applying an electric current to flow through the substrate and the at least one anode so that metal is deposited on the substrate.

[0025] A nickel layer produced in accordance with the method of the present invention and by using the solution of the present invention is deposited as a part of a nickel multilayer structure, e.g., a two-, three or four layered nickel multilayer structure, which is preferably superposed by a chromium layer.

[0026] Accordingly, a further aspect of the present invention is to provide a method of forming a corrosion-resistant nickel multilayer on a substrate, wherein the method comprises the following method steps: (a) depositing a first nickel layer having a first electric potential, (b) depositing a second nickel layer having a second electric potential which is more negative than the first electric potential (i.e., the second nickel layer is less noble than the first nickel layer) over the first nickel layer, and (c) depositing a third nickel layer using the solution for electrochemically depositing a metal of the invention over the second nickel layer.

[0027] In water, silica will normally develop a negative net charge, and therefore will not be transferred to the cathode where it is intended to produce pores. Instead it will be transferred to the anode and at elevated concentrations might even block the anode bags. By providing at least one organic moiety which imparts the silica particles a positive electric charge when being in contact with the solution, a uniform high pore count in the chromium layer is achieved. Such advantage is combined with silica having other advantages over other material particles to be incorporated into the third nickel layer, these other advantages being that silica is highly porous and that it exhibits a hydrophilic surface. Porous hydrophilic silica (or glass particles) (which are commercially available in almost any size or porosity) is chosen instead of ground alumina or minerals like talc, because it is easily dispersible in water or electrolyte for a long time. High porosity of the silica particles offers the additional benefit of attributing the particles a low specific gravity which in turn causes more uniform distribution thereof in the plating solution because of a lower tendency to sediment. This in turn makes sophisticated and complicated air injection into the bath solution unnecessary which would otherwise be required to keep the particles suspended.

[0028] The silica particles are not prone to precipitation in water. For this reason silica particles can be applied to an electrolyte solution as suspension which makes replenishment very simple and reliable. While other inorganic material, especially talc, at slightly elevated pore concentration (e.g., $> 20,000 \text{ cm}^{-2}$) causes a hazy chromium deposit, the newly invented powder does not produce any visible haze even at a pore count which is much higher than $100,000 \text{ cm}^{-2}$.

[0029] A further great advantage of the present invention is the commercial availability of a huge number of different types of silica. Silica particles having a porosity and size in a wide range are available and can easily be provided with the silicon containing organic moieties as desired. Because the particles after modification with the organic moieties have a defined positive electric charge, the pore count may simply be adjusted by setting the current density and by adjusting the concentration of the modified silica particles in the metal electrolyte, in particular nickel electrolyte. There is no requirement to provide a sophisticated and complicated architecture of air agitation which would lead to unpredictable results.

[0030] Alumina coated silica particles for instance exhibit a positive net charge at the pH where the nickel electrolyte is operated (pH = 3.5 to 5.5) to ensure that these particles are transferred to the workpiece. Furthermore, such coated particles are more hydrophilic than solid alumina and become more easily wetted and dispersed in the electrolyte solution than solid alumina particles. However, these particles do not exhibit the same surface charge amount as the silica particles which are obtained by providing same with the organic moiety according to the present invention.

[0031] The organic moieties are silicon containing organic moieties. Silanes and siloxanes or the like as silicon containing organic compounds are easily reacted to form the silicon containing organic moieties attached, preferably covalently bonded, to the surface of the silica particles.

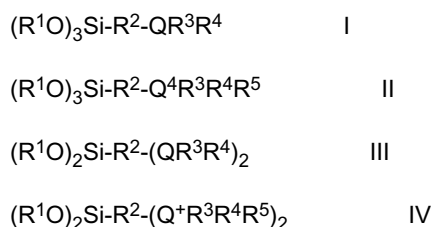
[0032] In accordance with a preferred embodiment of the present invention, the at least one organic moiety is bound to the silica particles. This means, that a chemical (covalent) bond is formed between corresponding reactive centers on the organic moiety on the one hand and the silica surface on the other hand. Chemical bonding ensures that the moieties imparting the silica particles the positive charge are not desorbed or otherwise peeled away from the silica particles. Thus, the positive charge delivered to the silica particles by the organic moieties is constant and does not depend from any surface effects like an equilibrium which forms in the electrolyte deposition solution.

[0033] In order to impart the silica particles a positive electric charge the organic moieties have a positive electric charge on at least one of the atoms thereof, i.e., on a nitrogen or phosphorus or arsenic atom. The positive electric charge may be provided by a chemical radical which is part of the organic moiety which forms or has a positive electric

charge. The latter embodiment of chemical radicals possess a permanent positive electric charge, *i.e.*, ammonium, phosphonium and arsonium radicals. Chemical radicals form such positive electric charge only under the conditions of metal plating, *i.e.*, due to the pH conditions present in the metal plating solution. Chemical radicals which form such positive electric charge are for example amine radicals. Thus, such positive electric charge is formed or provided by at least one functional group selected from the group comprising amino, quaternized ammonium, quaternized phosphonium and quaternized arsonium. Whereas quaternized ammonium, quaternized phosphonium and quaternized arsonium feature a permanent positive electric charge, amino features a positive electric charge only if the pH of the metal deposition solution is below a certain threshold value, which may be defined to be pH about 7, more preferably pH about 6, even more preferably pH about 5.5, even more preferably pH about 5 and most preferably pH about 4.5. Hence, if the pH is below any one of the upper limits given herein above, amino will be protonized to form ammonium ions and will accordingly impart the silica particles a positive electric charge. The lower limit of the pH of the metal deposition solution will depend on the type of the metal deposition solution and will be pH about 0, more preferably pH about 1, even more preferably pH about 2, even more preferably pH about 3, even more preferably pH about 3.5 and most preferably pH about 4.

[0034] In a more preferred embodiment of the present invention positive charges are introduced into silica particles by bonding a silane, an aminosilane for example, to the silica particles' surface. Alternatively, a silane may be bonded to the silica particles' surface which has at least one of ammonium, phosphonium and arsonium groups or which does not have such groups when the silane is bonded to the silica particles' surface, but wherein such onium groups are formed thereafter, *i.e.*, when the silanes have already been bonded to the silica particles' surface.

[0035] Even more preferably, the at least one organic moiety is formed by a reaction of the silica particles with a reagent, wherein the reagent has general chemical Formula I, II, III or IV:



wherein

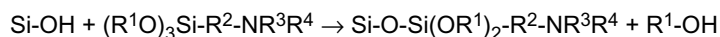
Q is N (nitrogen), P (phosphorus) or As (arsenic), Q is preferably N;

R¹ and R², independently from each other, are unsubstituted or substituted alkyl or unsubstituted or substituted aryl, preferably unsubstituted or substituted alkyl, wherein R¹ is more preferably C₁-C₅ alkyl and R² is more preferably C₁-C₆ alkyl, R¹ may also be hydrogen;

R³, R⁴ and R⁵ are hydrogen, unsubstituted or substituted alkyl, unsubstituted or substituted aryl, wherein R³, R⁴ and R⁵ may, independently from each other, further contain at least one functional radical comprising amino and imino moieties.

[0036] The silica particles provided with the organic moiety show an overwhelming effect: Only 50 mg/l of silica modified with this material may produce more than 100,000 pores per square centimeter when being co-deposited into a nickel layer. While other material particles require a concentration of > 300 mg/l and a careful air distribution in the electrolyte, porous silica provided with the organic moiety does not need any care for the air agitation or the air distribution.

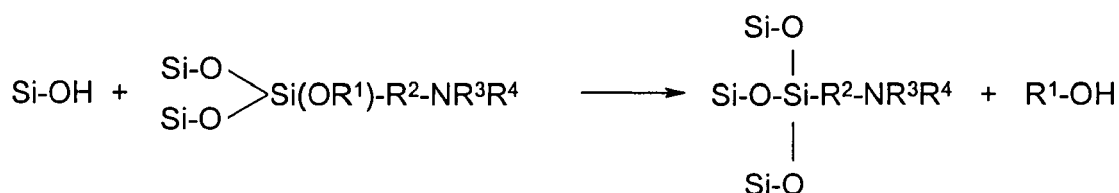
[0037] More specifically the at least one organic moiety is formed by a reaction of the silica particles with (3-aminopropyl) triethoxysilane. Such reaction is believed to be a condensation reaction at the silica particles' surface which normally has, due to hydrolysis, Si-OH group which are exposed at the surface thereof. Such condensation reaction of the compound having general chemical Formula I with the silica particles' surface Si-OH groups may be as follows:



[0038] It is believed that further reaction steps may take place at further surface Si-OH groups as follows:



and:



[0039] The silica particles provided with the organic moiety may be produced by reacting the silica particles with a silane compound by mixing same in a non-aqueous solvent, like acetone or chloroform and left to react the reaction mixture for a short time period, one hour for example. Then a precipitate formed in the reaction mixture can be separated, by filtration for example. Alternatively, a silane is mixed with an acid in an aqueous medium. Then silica is dispersed in this reaction mixture, while preferably stirring the reaction mixture. More elaborate and diverse embodiments and examples of preparing the silica particles modified by bonding one or a plurality of different aminosilanes to the surface thereof are disclosed in EP 1 894 888 A1, wherein the type of diverse silica sources and types, the solvent used to react the silica particles with the aminosilanes, the acid used in the reaction mixture as well as the pH prevailing during the reaction step, the type of aminosilane compounds ($\text{R}_a\text{SiX}_{(4-a)}$), wherein one or a plurality of such aminosilanes are used to be bonded to the silica particles' surface, the concentration and ratio of concentrations of silica and aminosilanes, the operations for reacting the silica particles with the aminosilanes (mixing, stirring), the concentration of the silica particles suspended in the reaction mixture, the type of additives added to the product being obtained and the like from EP 1 894 888 A1 are referred to be incorporated into the description of the present application.

[0040] The silica particles used in accordance with the present invention preferably have a specific surface area of up to $300 \text{ m}^2/\text{g}$. The lower limit of the specific surface area preferably is $40 \text{ m}^2/\text{g}$. More preferably the upper limit is $250 \text{ m}^2/\text{g}$ and the lower limit is $140 \text{ m}^2/\text{g}$. The upper and lower limit of the ranges given herein above may be combined to give any range. The above values for the specific surface area are chosen to give an optimum positive surface charge once the silica particles have been reacted to have the organic moiety be bonded to the surface thereof. The specific surface area is determined using the BET method.

[0041] Furthermore, the silica particles preferably have a mean diameter in a range of from $0.3 \mu\text{m}$ to $15 \mu\text{m}$, more preferably of from $0.6 \mu\text{m}$ to $12 \mu\text{m}$ and most preferably of from $0.6 \mu\text{m}$ to $5 \mu\text{m}$. The expression "mean diameter" is defined here as the d_{50} value of the particle size distribution obtained by, e.g., dynamic laser scattering measurement. Such methods for determination of particle size distributions are known to the person skilled in the art. Accordingly, the lower limit of the mean diameter is preferably $0.3 \mu\text{m}$ and more preferably $0.6 \mu\text{m}$. The upper limit is preferably $15 \mu\text{m}$, more preferably 12 and most preferably $5 \mu\text{m}$. The upper and lower limit of the mean diameter may be combined to give any range having these limits. The above mean values for the mean diameter are chosen to give an optimum dispersibility (uniform distribution) in the dispersant (metal deposition bath).

[0042] Silica may be contained in the electrolyte solution of the invention at a concentration of from 2 mg/l to 10 g/l , more preferably from 10 mg/l to 1 g/l , even more preferably from 20 to 500 mg/l and most preferably from 35 to 100 mg/l . Thus, the lower limit of this concentration may be 2 mg/l , more preferably 10 mg/l , even more preferably 20 mg/l and most preferably 35 mg/l and the upper limit of this concentration may be 10 g/l , more preferably 1 g/l , even more preferably 500 mg/l and most preferably 100 mg/l . The lower and upper limit values may be combined in any way to give a preferred concentration range. Concentration of silica in the electrolyte solution may be about 50 mg/l .

[0043] Metal may be deposited onto the substrate using direct current or pulsed current, including unipolar or bipolar pulsed current. Alternatively, metal may be deposited using a sequence of time periods wherein direct current time periods alternate with pulsed current time periods. Plating may furthermore be performed in a conventional plant using dip tanks and racks holding the articles to be plated and dipping same into the electrolyte solution of the invention contained in such tanks with anodes facing the articles to be plated. The articles may also be contained in drums which are dipped into the plating solution. Alternatively, the articles to be plated may be placed and treated in a conveyORIZED plating plant which uses trays to accommodate the articles. The anodes may be placed at one or, preferably, at both sides of the articles to be plated and may be soluble anodes, i.e., anodes which dissolve due to the electroplating operation because they are made substantially from the same metal as the metal being deposited. Or the anodes are made from a material which does not dissolve during the electroplating operation, i.e., is inert against the solution and under the plating conditions. Plating is performed using more or less vigorous agitation of the solution, including air injection.

[0044] The substrate may be any work piece suitable to plate a metal layer, e.g., a work piece made of metal or a work piece made of plastics material or of any other non-conductive material. A nonconducting substrate may first be

plated with any ground metal plating with or without applying electric current, *i.e.*, by immersion plating or electroless plating. Thereafter, the metal layer is plated using the solution according to the invention. And finally, other metal layers may be plated on top of the metal layer plated with the solution of the invention.

[0045] Further, in addition to the ions of the metal to be deposited and the silica particles modified with the silicon containing organic moieties, the plating solution preferably contains a pH adjusting agent, like an acid or a buffer.

[0046] In a more preferred embodiment of the present invention the metal to be deposited is nickel. Nickel may be provided to the metal deposition solution as a nickel ion source, more specifically as a nickel salt and most preferably as nickel sulfate, nickel chloride, nickel carbonate, nickel acetate, nickel borate, nickel sulfamate, nickel methane sulfonate.

[0047] The metal, preferably nickel, deposition solution may further contain at least one acid, preferably an inorganic acid and most preferably an acid which has a counter anion which is common with the counter anion of the nickel salt, for example sulfuric acid, sulfamic acid, methane sulfonic acid, boric acid and acetic acid. Most preferably the metal, preferably nickel, deposition solution of the invention contains boric acid as the acid or pH adjusting agent.

[0048] The acid can furthermore be understood to be identical with the pH adjusting agent or be part of the pH adjusting agent, wherein the latter may be a buffer mixture.

[0049] Further, the metal, preferably nickel, deposition solution contains additives which serve the control of the metal deposition bath, like organic compounds which influence metal deposit properties, like brightness, leveling, corrosion behavior (electric potential of corrosion) and the like. Such compounds may be unsaturated compounds like vinyl sulfonic acid, allylsulfonic acid, further chloralhydrate and organic compounds having sulfur atoms in a low oxidation state, like saccharine.

[0050] A nickel multilayer may be deposited onto a substrate surface. Optionally a chromium layer may be deposited on top of the nickel multilayer. Such nickel multilayer and chromium layer are well-known in the art to be largely corrosion-resistant. The nickel multilayer generally consists of two or three nickel layers: an optional first nickel layer having a rather noble (positive) electric potential, a second nickel layer which is a bright nickel layer and which is less noble than the first nickel layer and a third nickel layer which is plated on top of the second (bright) nickel layer. On top of the third nickel layer with co-deposited silica particles contained therein, a chromium layer may be deposited. Corrosion attack will take place through the plurality of pores created in the chromium layer and third nickel layer and will first proceed in the less noble second (bright) nickel layer. Therefore, no visible change of the metal coating will take place. The first nickel layer may be deposited using a so-called Watts electrolyte which contains nickel chloride, nickel sulfate and boric acid, for example about 60 g $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, 270 g $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and 45 g boric acid per liter plating solution. This bath typically contains besides salicylic acid ethyne derivatives like hexynediol or butynediol or propargyl alcohol derivatives as additives or a mixture of a plurality of additives. The second nickel layer may be deposited using a Watts electrolyte which differs from the electrolyte used to deposit the first nickel layer by using typically sulfur containing compounds like toluene sulfonic acid or propargylsulfonates and in addition saccharine instead of salicylic acid as the additive or a mixture of a plurality of additives. The third nickel layer may be deposited using a Watts nickel electrolyte as in the case of depositing the first and second nickel layers, but additionally contains saccharine or a salt thereof and chloralhydrate as a mixture of additives and further silica as described to form the pores. All the electrolyte solutions mentioned may additionally contain further additives, like a brightener or a wetting agent like ethylhexylsulfate. pH of the electrolyte solution may be from 2.5 - 6, more preferably from 3 - 4.5 and most preferably 4.0. Temperature of the electrolyte during the nickel electroplating operation may be elevated, such as 40 - 70 °C, more specifically 50 - 60 °C and most preferably 55 °C.

[0051] Hereinafter the invention will be described more clearly with reference to the following Examples. The embodiments shown in the Figures and Examples are not intended to limit the scope of the invention.

Fig. 1 shows the relationship obtained of the pore count vs. current density for the electrolyte solution according to the invention (P305b) and for a prior art electrolyte solution containing alumina and silica particles which are not modified with an organic moiety (GZZ);

Fig. 2 shows the ratio of pore count vs. particle concentration of the powder using modified silica particles;

Fig. 3 shows a schematic drawing of a bent panel used to investigate pore distribution;

Fig. 4 shows a schematic drawing of a bent steel plate used to investigate pore distribution;

Fig. 5 shows a part plated according to the invention.

Example 1 (Preparation of silica particles modified by bonding an aminosilane to the surface thereof and use thereof in a nickel electroplating bath):

[0052] 3.0 ml (3-aminopropyl)triethoxysilane were dissolved in 200 ml of dry acetone. The solution was poured over 15 g SD-530 powder (porous silica of Hang Tian SaiDe / Beijing, P.R. China, peak volume of 26.2 % at 5 μm particles size). The mixture was allowed to react at room temperature for one hour. The powder was then washed with acetone

and was allowed to dry at room temperature until a constant weight was reached.

[0053] A rectangular PVC tank equipped with two nickel anodes at opposite sides was filled with 2 l of a Watts nickel electrolyte (60 g/l $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, 270 g/l $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, 45 g/l boric acid). The electrolyte was heated to 55°C. It was then adjusted by the addition of 0.2 ml/l of a solution of a wetting agent based on ethylhexylsulfate, 0.7 g/l sodium saccharate, 50 mg/l chloralhydrate and a brightener. The pH of the electrolyte after all additions was found to be pH = 4.0. To the 2 l electrolyte, 100 mg of the modified silica were added. The solution remained clear without any noticeable turbidity. The agitation of the solution was achieved by only slight moderate air agitation.

[0054] Rectangular steel panels were pretreated properly and plated with approximately 10 μm semi-bright nickel and approximately 10 μm bright nickel. Such prepared panels were then plated in the above described electrolyte at a current density of 3 A/dm² for three minutes and afterwards for three minutes in a conventionally available chromium electrolyte (Unichrome® 843 of Atotech).

[0055] Average thickness of the chromium layer was found to be 0.23 μm on the edges of the panels and 0.16 μm in the middle of the panels. Total thickness of all nickel layers was 17 μm / 25 μm .

[0056] The electric potential between the semi-bright nickel layer and the bright nickel layer was in the range of from 121 mV to 135 mV, and the potential between the last two nickel layers (between second and third nickel layer) was in a range of from 28 mV to 35 mV. The average pore count was 55,000 cm⁻². After 198 hours CASS testing the ranking (average of five independent inspectors) for appearance was 9.33 and for protection was 9.72.

Example 2 (Preparation of silica particles modified by bonding an aminosilane to the surface thereof):

[0057] Syloid 244FP (Grace, peak volume 15.2% at 3.3 μm) was dried at 110°C in an oven for two hours. The silica powder lost 4.2 % weight. 5.0 ml (3-aminopropyl)triethoxysilane were dissolved in 100 ml chloroform (HPLC grade, water < 0.001 %) and poured over 15 g of the silica powder in a PP bottle which then was tightly closed. The opaque gel after short reaction time turned to a slurry. After one hour, the suspension was poured over a filter paper in a Büchner funnel, the chloroform was sucked off by vacuum and the remaining material was carefully washed with chloroform. The resulting material was again dried at 110°C until its weight did not change anymore. The weight gain after the reaction was 9.5 %.

Example 2.1:

[0058] The trial of example 2 was repeated with SD-530.

Initial weight [g]	Oven temperature [°C]	Drying duration [min]	Weight loss [%]
20.3000	110	60	4.88
23.6294	110	90	5.40

Initial weight [g]	Reaction duration [min]	Weight gain [%]
14.6948	240	8.17
16.3673	30	6.90

[0059] At different concentrations of the aminosilane, the weight gain obtained was only slightly different:

Amount of silane [ml]	Weight gain [%]
1.00	4.06
2.00	5.51
3.00	6.90

Example 3 (Preparation of silica particles modified by bonding an aminosilane to the surface thereof and use thereof in a nickel electroplating bath):

[0060] Two kinds of particles were compared: a modified SD-530 as described in example 1 - but with 5 ml aminosilane

for 15 g powder, and a commercially used alumina-modified silica. From a stock of 5 l Watts nickel electrolyte, one liter was adjusted with saccharine, surfactant and brightener as is already described in example 1. In a 250 ml Hull cell, the adjusted electrolyte was used to plate micro-porous nickel within three minutes at 2 A cell current. The amount of pores versus current was then calculated. Fig. 1 shows the relationship obtained of the pore count vs. current density for the electrolyte solution according to the invention (A) and for a prior art electrolyte solution containing alumina and silica particles which are not modified with an organic moiety according to the invention. While pore count made by the alumina-containing material could not follow an increasing current density, the pore count / current density behavior of the amino-group modified material is linear. Therefore, the pore count can be influenced to attain as high pore count values as desired if the current density is increased. For example, whereas the pore count for conventional silica particles in the nickel electroplating bath is about 27,000 cm⁻² at a current density of 5 A/dm², the pore obtained with silica particles modified with the silicon containing organic moieties according to the invention is about 50,000 cm⁻² at the same current density.

Example 4 (Use of the modified silica in a nickel electroplating bath):

[0061] A rectangular tank filled with 2 liter nickel electrolyte as described in Example 1 was used to plate a micro-discontinuous nickel layer over panels previously plated with approximately 10 μm of bright nickel at different concentrations of powder SD-530 modified with aminosilane as was described in Example 1. A ratio of pore count vs. concentration of the powder as shown in Fig. 2 was obtained. This ratio is linear up to high values of powder concentration and pore count, respectively. Pore count has been found to rise to about 200,000 cm⁻² if a powder concentration of 100 mg/l is used and is expected to even rise further if the concentration is increased.

Comparative Example 5 (Use of unmodified silica in a nickel electroplating bath):

[0062] A nickel electrolyte was prepared as described in Example 1. The plating was repeated in the same plating tank. This time SD-530 powder was used without silane-modification. The electrolyte contained 2 g/l powder. The pore count was found to be only 2,300 cm⁻².

Example 6 (Use of the modified silica in a nickel electroplating bath):

[0063] A 250 l tank was filled with a Watts nickel solution (concentrations of main components, NiCl₂, NiSO₄, boric acid, as in Example 1). The solution was heated to 55°C and adjusted as described in Example 1 with organic additives like surfactant, saccharine and brightener. After adjusting the pH to 4.2 and after addition of 50 mg/l of modified silica powder, a bent panel (Fig. 3) was fixed in the middle of the tank parallel to the anodes and plating was started at a current density of 5 A/dm². Plating took place for three minutes. The panel then was rinsed and chromium plated. Afterwards, the panel was cut into pieces and the pores in the chromium surface were counted after copper plating (Dubpernell-Test). Pore counts according to the Table 1 were obtained.

Example 7 (Use of the modified silica in a nickel electroplating bath):

[0064] A nickel multilayer and chromium layer on top of the nickel multilayer was deposited on a bent steel plate (as shown in Fig. 4). Experiments were performed in 100 l tanks.

[0065] In a first nickel plating step an about 16 μm thick semi-bright nickel layer was deposited (20 min @ 4 A/dm²) on the steel plate from a commercially available semi-bright nickel plating bath (Duplalux® Step, Atotech). Thereafter, an about 8 μm thick bright nickel layer was deposited (10 min @ 4 A/dm²) on top of the first nickel layer from a commercially available bright nickel plating bath (Makrolux® NF, Atotech). The electric potential of this second nickel layer was determined to be 140 mV with respect to the first nickel layer. Thereafter, an about 2 μm thick nickel layer was deposited (4 min @ 3 A/dm²) on top of the bright nickel layer while silica was incorporated into this third nickel layer. The solution to deposit this nickel layer was the same as that of Example 1, but instead of ethylhexylsulfate, sodium saccharate and chloralhydrate as the additives an unsaturated carboxylic acid (allyl carboxylic acid, vinyl carboxylic acid), saccharine and a brightener (Makrolux®, Atotech) were contained in the plating solution. Different silica types were used in this case as given in Table 2. The electric potential of this third nickel layer was determined to be 30 mV with respect to the second nickel layer. The anodes used in all nickel plating steps were nickel pieces containing sulfur which were held in baskets. Finally, an about 0.4 μm thick chromium layer was deposited (4 min @ 10 A/dm²) on top of the third nickel layer from a commercially available chromium plating bath (Glanzchrombad Cr 843, Atotech).

[0066] For determining the pore counts the Fuhrmann-Tester automatic program was used (program: 30 s @ 1.0 V; 30 s @ 0 V; 30 s @ -0.4 V; pores > 4 μm, 50 x; Markus Häp *et al.*, *ibid.*). The results of the pore counts found in the chromium layer are shown in Table 3.

[0067] From Table 3 it will be evident that the number of pore counts is much larger in the case of the solution of the invention than in the case of the prior art solutions. Further, the variation of pore counts is much larger in the case of the prior art solutions than in the case of the solution of the invention. Therefore, a much more consistent result in terms of pore count distribution on the bent steel plate are obtained with the solution of the invention than with the prior art compositions.

Example 8 (Use of the modified silica in a nickel electroplating bath):

[0068] A further experiment was conducted in a larger production plant having 1400 l tanks. The parts to be plated are shown in Fig. 5. The procedure of depositing the first (semi-bright), second (bright), third nickel layers and the chromium layer were as described in Example 7. For depositing the third nickel layer containing particles the composition was as described in Example 7, too. The particles used in this case were as shown in Table 4.

[0069] For determining the pore counts the Fuhrmann-Tester automatic program was used (program: 30 s @ 1.0 V; 30 s @ 0 V; 30 s @ -0.4 V; pores > 4 μm , 50 x; Markus Hap *et al.*, *ibid.*). The results of the pore counts found in the chromium layer are shown in Table 5.

[0070] From Table 5 it will be evident that the number of pore counts is much larger in the case of the solution of the invention than in the case of the prior art solutions. Further, the variation of pore counts is much larger in the case of the prior art solution than in the case of the solution of the invention. Therefore, a much more consistent result in terms of pore count distribution on the plated article are obtained with the solution of the invention than with the prior art compositions.

Table 1 (Pore counts in bent panel from Example 6):

Area	Pore count [cm^{-2}]
A	57,000
B	27,000
C	43,000
D	47,000
E	42,000

Table 2 (Particle types from Example 7):

Experiment	Particles used
Experiment a) (Invention)	Silica modified with an aminosilane (according to EP 1 894 888 A1)
Experiment b) (Prior Art)	Mixture of talc and silica particles which not have been modified
Experiment c) (Prior Art)	Mixture of alumina and silica particles which have not been modified
Experiment d) (Prior Art)	Mixture of alumina and silica particles which have not been modified

Table 3 (Pore counts [cm^{-2}] from Example 7):

Particle Type	Point 1 *)	Point 2 *)	Point 3 *)	Point 4 *)	Point 5 *)	Mean Value	Standard Deviation
a) Invention	11,400	16,700	30,700	42,700	26,400	25,580	12,247
b) Prior Art	2,400	4,400	59,300	900	600	13,520	25,636
c) Prior Art	3,200	8,900	43,800	2,900	3,900	12,540	17,644

(continued)

Particle Type	Point 1 *)	Point 2 *)	Point 3 *)	Point 4 *)	Point 5 *)	Mean Value	Standard Deviation
d) Prior Art	1,800	4,500	77,000	4,800	500	17,720	33,188
*) Points on the bent steel plated indicated in Fig. 4							

Table 4 (Particle types from Example 8):

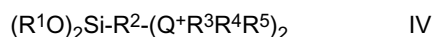
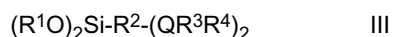
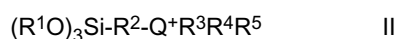
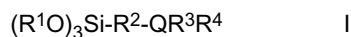
Experiment	Particles used
Experiment e) (Invention)	Silica modified with (3-aminopropyl)triethoxysilane
Experiment f) (Prior Art)	talc particles non-modified

Table 5 (pore counts [cm⁻²] from Example 8):

Particle Type	Point 1 *)	Point 2 *)	Point 3 *)	Point 4 *)	Point 5 *)	Point 6 *)	Point 7 *)	Point 8 *)	Mean Value	Standard Deviation
e) Invention	4,700	6,600	17,500	18,600	11,400	9,200	15,200	29,300	13,083	7,928
f) Prior Art	1,900	4,700	5,600	5,700	3,800	8,800	7,500	46,700	6,017	14,745
*) Points on the bent steel plated indicated in Fig. 4										

Claims

1. A solution for electrochemically depositing a metal on a substrate, said solution containing ions of the metal to be deposited and silica particles, **characterized in that** at least one silicon containing organic moiety is provided to said silica particles, said silicon containing organic moiety comprising at least one functional group selected from the group comprising amino, quaternized ammonium, quaternized phosphonium and quaternized arsonium which imparts the silica particles a positive electric charge while being in contact with said solution.
2. The solution for electrochemically depositing a metal on a substrate according to claim 1, **characterized in that** the at least one organic moiety is formed by a reaction of the silica particles with a reagent, wherein the reagent has general chemical Formula I, II, III or IV:



wherein

Q is N (nitrogen), P (phosphorus) or As (arsenic)

R¹ and R², independently from each other, are unsubstituted or substituted alkyl,

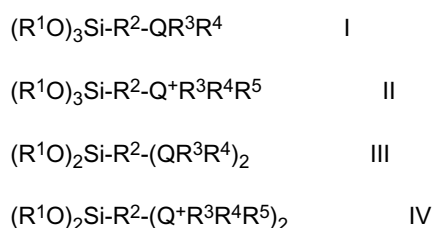
R³, R⁴ and R⁵ are hydrogen, unsubstituted or substituted alkyl, unsubstituted or substituted aryl, wherein R³, R⁴ and R⁵ may, independently from each other, further contain at least one functional radical comprising amino and imino moieties.

3. The solution for electrochemically depositing a metal on a substrate according to any one of the preceding claims, **characterized in that** the at least one organic moiety is formed by a reaction of the silica particles with (3-amino-propyl)triethoxysilane.
- 5 4. The solution for electrochemically depositing a metal on a substrate according to any one of the preceding claims, **characterized in that** the silica particles have a specific surface area of up to 300 m²/g.
5. The solution for electrochemically depositing a metal on a substrate according to any one of the preceding claims, **characterized in that** the silica particles have a mean diameter in a range of from 0.3 μm to 15 μm.
- 10 6. The solution for electrochemically depositing a metal on a substrate according to any one of the preceding claims, **characterized in that** the metal is nickel.
- 15 7. A method of electrochemically depositing a metal on a substrate, **characterized in that** the method comprises the following method steps: (a) contacting the substrate and at least one anode with the solution for electrochemically depositing a metal on the substrate according to any one of claims 1 - 6 and (b) applying an electric current to flow through the substrate and the at least one anode so that metal is deposited on the substrate.
- 20 8. A method of forming a corrosion-resistant nickel multilayer on a substrate, **characterized in that** the method comprises the following method steps: (a) depositing a first nickel layer having a first electric potential, (b) depositing a second nickel layer having a second electric potential which is more negative than the first electric potential over the first nickel layer and (c) depositing a third nickel layer using the solution for electrochemically depositing a metal according to any one of claims 1-6 over the second nickel layer.

Amended claims in accordance with Rule 137(2) EPC.

1. A method of forming a corrosion-resistant nickel multilayer on a substrate, wherein the method comprises the following method steps: (a) depositing a first nickel layer having a first electric potential, (b) depositing a second nickel layer having a second electric potential which is more negative than the first electric potential over the first nickel layer and (c) depositing a third nickel layer over the second nickel layer using a solution for electrochemically depositing a metal on a substrate, said solution containing ions of the metal to be deposited and silica particles, wherein at least one silicon containing organic moiety is provided to said silica particles, said silicon containing organic moiety comprising at least one functional group selected from the group comprising amino, quaternized ammonium, quaternized phosphonium and quaternized arsonium which imparts the silica particles a positive electric charge while being in contact with said solution.

2. The method of forming a corrosion-resistant nickel multilayer on a substrate according to claim 1, **characterized in that** the at least one organic moiety is formed by a reaction of the silica particles with a reagent, wherein the reagent has general chemical Formula I, II, III or IV:



wherein

Q is N (nitrogen), P (phosphorus) or As (arsenic)
R¹ and R², independently from each other, are unsubstituted or substituted alkyl,
R³, R⁴ and R⁵ are hydrogen, unsubstituted or substituted alkyl, unsubstituted or substituted aryl, wherein R³,
R⁴ and R⁵ may, independently from each other, further contain at least one functional radical comprising amino and imino moieties.

3. The method of forming a corrosion-resistant nickel multilayer on a substrate according to any one of the preceding

claims, **characterized in that** the at least one organic moiety is formed by a reaction of the silica particles with (3-aminopropyl)triethoxysilane.

5 **4.** The method of forming a corrosion-resistant nickel multilayer on a substrate according to any one of the preceding claims, **characterized in that** the silica particles have a specific surface area of up to 300 m²/g.

5. The method of forming a corrosion-resistant nickel multilayer on a substrate according to any one of the preceding claims, **characterized in that** the silica particles have a mean diameter in a range of from 0.3 μm to 15 μm.

10 **6.** The method of forming a corrosion-resistant nickel multilayer on a substrate according to any one of the preceding claims, **characterized in that** the metal is nickel.

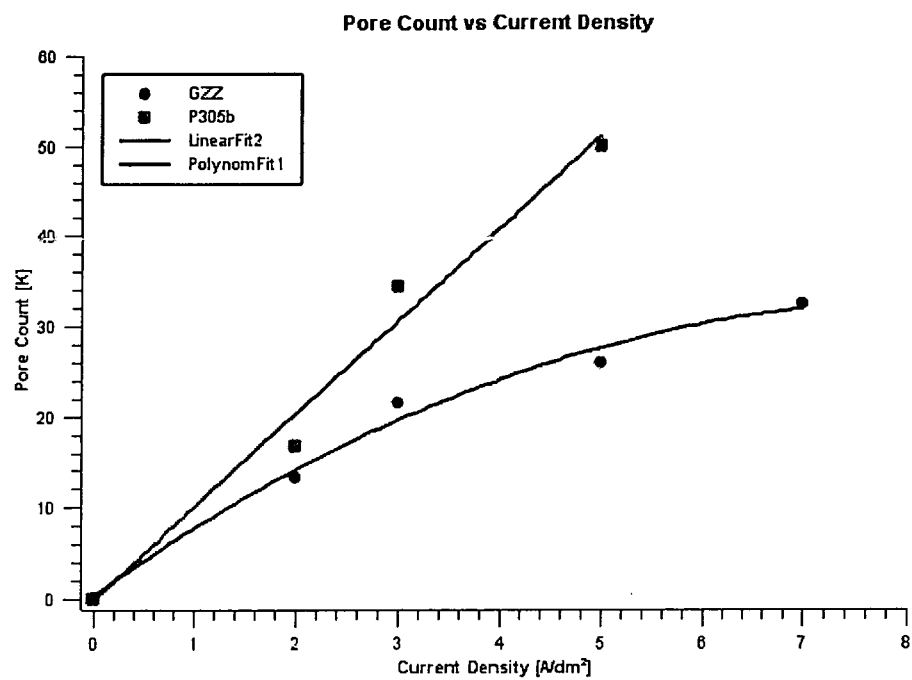


Fig. 1

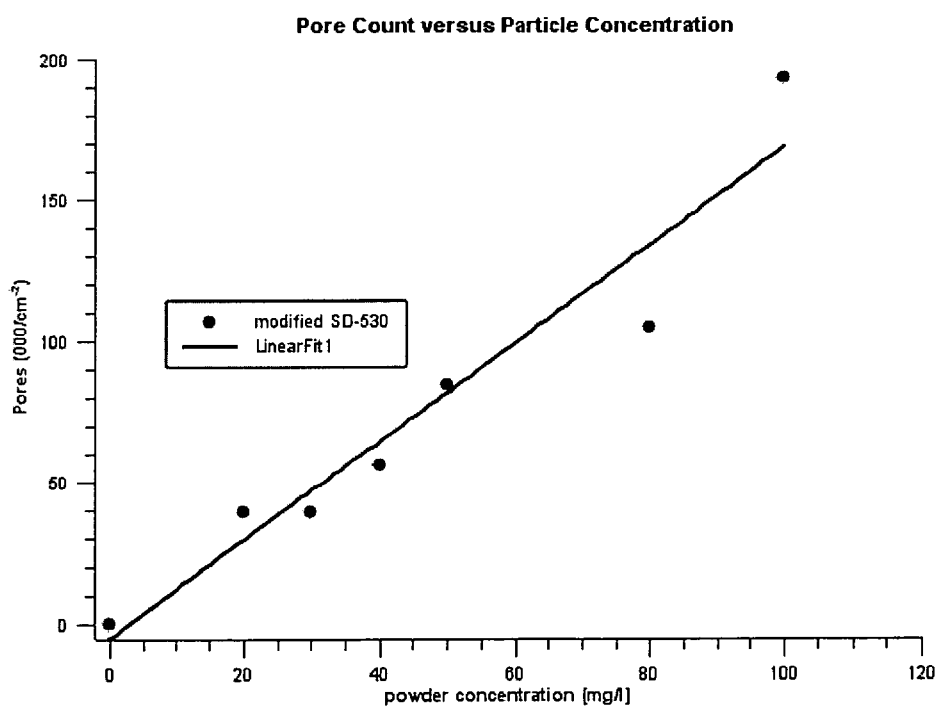


Fig. 2

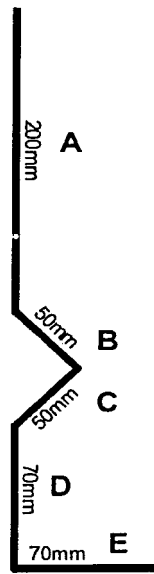


Fig. 3

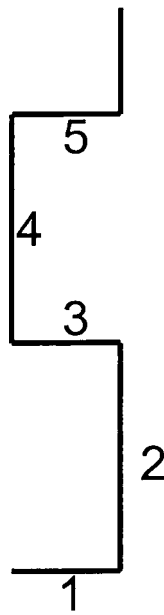


Fig. 4

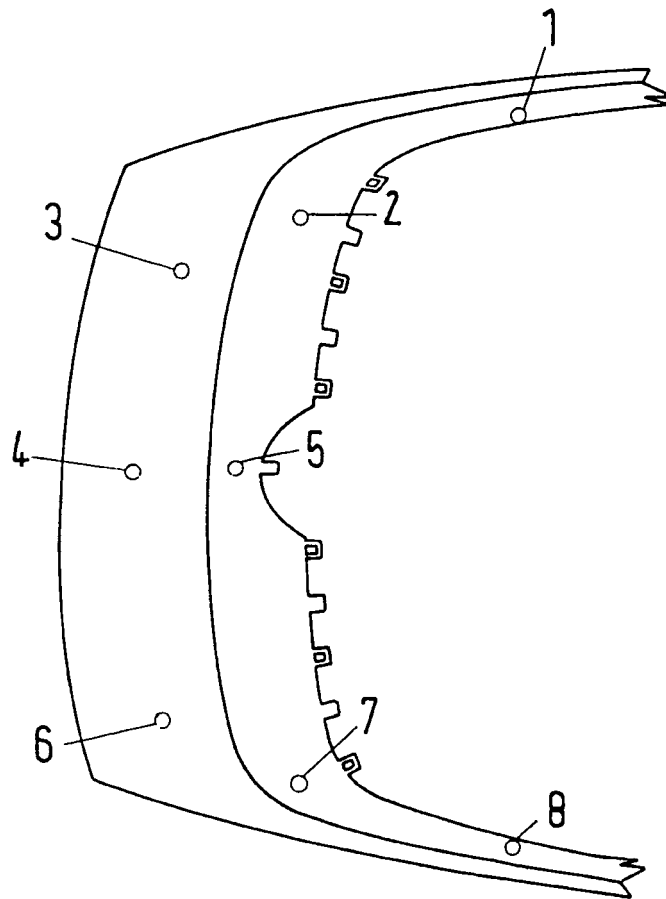


Fig.5



EUROPEAN SEARCH REPORT

 Application Number
 EP 08 07 5637

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Place of search Munich		Date of completion of the search 26 November 2008	Examiner Haering, Christian
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 07 5637

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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