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(54) ELECTROLESS NICKEL PLATING BATHS COMPRISING AMINONITRILES AND A METHOD FOR DEPOSITION OF NICKEL AND NICKEL ALLOYS

(57) Aqueous electroless nickel plating baths comprising at least one source of nickel ions are characterised in that they comprise aminopropanenitrile and/or at least one aminopropanenitrile derivative thereof. Such aqueous electroless nickel plating baths are useful for the deposition of nickel and nickel alloy. The deposited nickel or nickel alloy layers are advantageously corrosion resistant due to their high compressive stress. Also, the aqueous electroless nickel plating bath comprising said compounds are very stable and show improved resistance to plate-out.

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Description

Field of the Invention

[0001] The present invention relates to aqueous electroless nickel plating bath. The present invention relates further to a method for depositing of nickel and nickel alloys utilizing the aqueous electroless nickel plating bath. The aqueous electroless nickel plating baths have high stability against undesired decomposition.

[0002] Such coatings are suitable as a functional coating in aerospace, automotive, electronics and chemical industries. The metal layers deposited from such aqueous electroless nickel plating baths are also useful as barrier and cap layers in semiconducting devices, printed circuit boards, IC substrates and the like. The metal layers deposited are also suitable as overcoat for hard disks or rigid memory disks (RMD).

Background of the Invention

[0003] Barrier layers are used in electronic devices such as semiconducting devices, printed circuit boards, IC substrates and the like to separate layers of different composition, e.g. substrate layers and further layers, and thereby prevent undesired diffusion between such layers of different compositions.

[0004] Another application of barrier layer materials in electronic devices is as a cap layer which is e.g. deposited onto copper to prevent corrosion of copper.

[0005] Rigid memory disks are used as magnetic data storage media in hard disk drives. The disks are basically composed of a substrate, made of aluminium, glass or ceramics. An overcoat is deposited onto the substrate by a vacuum deposition process or an electroless metal plating process. The overcoat may consist of various metallic, mostly non-magnetic, alloys one of which may be a nickel phosphorus alloy layer. The overcoat provides e.g. a smooth surface onto which the magnetic recording layers are deposited. Further protective layers are coated onto the recording layers. Another application of nickel and nickel alloy deposits is corrosion protection for various substrates.

[0006] Typical stabilising agents are heavy metal ions such as lead. However, due to environmental requirements such heavy metal ions have to be avoided wherever possible. Heavy metal ion free stabilisers are therefore required.

[0007] Aqueous electroless nickel plating bath for applying nickel coatings are well known in the art and plating processes and plating baths are described in numerous publications such as U.S. Patents Nos. 2,935,425; 3,338,726; 3,597,266; 3,915,716 and 4,780,342. Electroless plating generally describes methods without using external current sources for reduction of metal ions. Plating processes using external current sources are commonly described as electrolytic or galvanic plating methods. In the electroless plating solutions chemical reducing agents like hypophosphite, boranes or formaldehyde are used to reduce the metal ions to their metallic form and thereby forming a deposit on the substrate.

[0008] One commonly used nickel alloy deposit is nickel phosphorus (NiP) alloy. In general, NiP deposition solutions comprise at least three ingredients dissolved in a solvent, typically water. They are (1) a source of the nickel ions, (2) a reducing agent and (3) a complexing agent for metal ions sufficient to prevent their precipitation in solution. A large number of suitable complexing agents for NiP solutions are described in the above noted publications. If hypophosphite is used as the reducing agent, the deposit will contain nickel and phosphorous. Similarly, if an aminoborane is employed, the deposit will contain nickel and boron as shown in U.S. Pat. No. 3,953,654.

[0009] Alkyl isonitriles are known to be stabilizers for electroless nickel phosphorous plating baths from S. Watanabe, Journal of the Surface Finishing Society Japan 2012, 63, 369. However, this document also teaches that alkyl nitriles such as pentyl nitrile and pivaloyl nitrile do not have any stabilising effect on electroless nickel plating baths (see *inter alia* table 4 and figure 4 therein).

Objective of the present Invention

[0010] It is the objective of the present invention to provide an electroless plating bath for deposition of nickel and nickel alloys which has a high stability against undesired decomposition such as plate-out. It is a further objective of the present invention to provide electroless nickel and nickel alloy plating baths having high stability during use and during storage. Furthermore, it is an objective of the present invention to provide an electroless plating bath for deposition of nickel and nickel alloys which has a good plating performance and generates coatings of good quality.

Summary of the Invention

[0011] These objectives are solved by the aqueous electroless nickel plating bath according to the invention which comprises at least one source of nickel ions and which is characterised in that it comprises aminopropanenitrile and/or at least one aminopropanenitrile derivative.

[0012] These objectives are further solved by the inventive method for electroless deposition of nickel and nickel alloys comprising the steps of

(A) providing a substrate,
(B) contacting the substrate with the aqueous electroless nickel plating bath according to the invention,

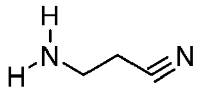
and thereby depositing a nickel or nickel alloy onto the substrate.

[0013] The nickel and nickel alloy coatings obtained by the invention show high corrosion resistance and adhesion to the subjacent substrate.

Detailed Description of the Invention

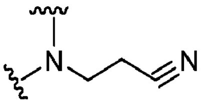
[0014] Percentages throughout this specification are weight-percentages (wt.-%) unless stated otherwise. One exception thereof are yields which are given as percentage of the theoretical yield. Concentrations given in this specification refer to the volume of the entire solutions unless stated otherwise.

[0015] Aminopropanenitrile (more precisely the typically used regiosiomer 3-aminopropanenitrile) is represented by formula (I)



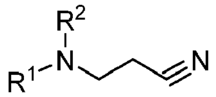
(I).

[0016] Aminopropanenitrile derivatives comprise other molecular structures which are bound to the nitrogen atom of the amino moiety instead of one or two hydrogen atoms depicted in formula (I). Said molecular structures include *inter alia* alkyl, aryl, alkaryl which may comprise cyclic ring systems optionally incorporating the nitrogen atom(s) of the amino group(s). The aminopropanenitrile derivatives optionally comprise more than one 3-aminopropanenitrile moiety as depicted in formula (Ia) wherein the bonding to said moiety is highlighted (as commonly done so in the art) by wavy lines ("〰 ").



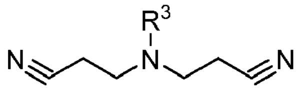
(Ia).

[0017] The aqueous electroless nickel plating bath preferably comprises at least one aminopropanenitrile derivative chosen from any one of formulae (II) to (VII)



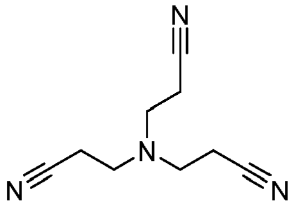
(II)

wherein R^1 and R^2 are independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl with the proviso that at least one of said residues is other than hydrogen;

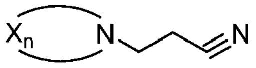


(III)

wherein R^3 is selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl;

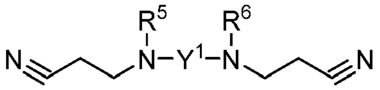


(IV),



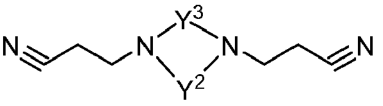
(V)

wherein n is an integer ranging from 4 to 7 and each X is independently from each other selected from the group consisting of $-CH_2-$, -O-, $-N(R^4)-$ with each R^4 being independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl;



(VI)

wherein Y^1 is a C1-C8-alkylene group, R^5 and R^6 are independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl; and



(VII)

wherein each Y^2 and Y^3 are independently from each other selected to be C1-C8-alkylenes.

[0018] The aminopropanenitrile derivatives according formulae (II) to (VII) improve the stability of the aqueous electroless nickel plating bath and compressive stress of the nickel or nickel alloy deposits formed with said aqueous electroless nickel plating bath (also compared to one aqueous electroless nickel plating bath containing only 3-aminopropanenitrile as stabiliser).

[0019] The aminopropanenitrile derivatives according formulae (II) to (VII) all comprise at least one moiety according to formula (Ia), bearing residues at the nitrogen atom of the amino group.

[0020] The amino group of the at least one aminopropanenitrile moiety (according to formula (Ia)) of the aminopropanenitrile derivatives is preferably not permanently quaternized. If more than one 3-aminopropanenitrile moiety is comprised in the aminopropanenitrile derivative, none of said amino groups is preferably permanently quaternized. A permanently quarternised amino group bears four permanently attached residues other than hydrogen like e.g. alkyl, aryl or alkaryl. In cases where said additives with permanently quaternized amino group are used in aqueous electroless nickel plating baths, the stability of such aqueous electroless nickel plating bath is inferior compared to those aqueous electroless nickel plating baths which contain aminopropanenitrile derivatives without permanently quaternized amino groups.

[0021] Preferably, R^1 is selected from the group consisting of non-cyclic, unfunctionalised alkyl and non-cyclic, functionalised alkyl wherein said functionalisation is one or more of hydroxyl and carboxyl and R^2 is selected from hydrogen, alkyl, aryl, and alkaryl.

[0022] The aminopropanenitrile derivatives according to formula (III) comprises R^3 which is preferably selected from the group consisting of non-cyclic alkyl and alkaryl.

[0023] The aminopropanenitrile derivative according to formula (V) comprises a ring-shaped moiety (including the nitrogen atom of the aminopropanenitrile moiety depicted by formula (Ia)) wherein n is an integer ranging from 4 to 7 (thus forming 5 to 8 membered rings), preferably n ranges from 4 to 5 (thus forming 5 to 6 membered rings), and each X are independently from each other selected from the group consisting of $-CH_2-$, -O-, $-N(R^4)-$ with each R^4 being independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl.

[0024] Preferably, at least half of X in the aminopropanenitriles derivative according to formula (V) are selected to be $-CH_2-$. More preferably, the ring-shaped moiety is selected from the group consisting of $1\lambda^2$-pyrrolidine, $2\lambda^2$-pyrazolidine, $3\lambda^2$-imidazolidine, $2\lambda^2$-isoxazolidine, $3\lambda^2$-oxazolidine, $1\lambda^2$-piperidine, tetrahydro-1*H*-$2\lambda^2$-pyridazine, tetrahydro-2*H*-$3\lambda^2$-pyrimidine, $4\lambda^2$-piperazine, 1,$2\lambda^2$-oxazinane, 1,$3\lambda^2$-oxazinane, $4\lambda^2$-morpholine and derivatives thereof. Derivatives in this context shall mean the hydroxyl and/or carboxyl derivatives and alkyl derivatives of the named ring shaped moieties.

[0025] Preferably, Y^1 in aminopropanenitriles derivative according to formula (VI) is an unfunctionalised, unbranched, non-cyclic C1-C6-alkylene rendering said aminopropanenitriles derivative more hydrophilic, more preferably an unfunctionalised, unbranched, non-cyclic C2-C4-alkylene. Preferably, at least one of residues R^5 and R^6 is selected to be different from hydrogen as this improves the stability of the aqueous electroless nickel plating bath, such that one of said residues is selected from the group consisting of alkyl, aryl, and alkaryl while the other residue is selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl. More preferably, R^5 and/or R^6 are selected to be non-cyclic C1-C4-alkyl.

[0026] As stated above, in the aminopropanenitriles derivative according to formula (VII) each bridging moiety Y^2 and Y^3 is independently from each other selected to be C1-C8-alkylenes, preferably C1-C6-alkylenes, more preferably C2-C4-alkylenes rendering molecules according to formula (VII) less hydrophobic with the advantages outlined below. Preferably, both bridging moieties Y^2 and Y^3 are selected to be the same for the ease of synthesis.

[0027] It is possible within the scope of the present invention that the aqueous electroless nickel plating bath according to the invention comprises more than one of said aminopropanenitrile derivatives. Also, two or more of said aminopropanenitrile derivatives of the same or different formulae may suitably be used.

[0028] The aqueous electroless nickel plating bath according to the invention comprises more preferably at least one aminopropanenitrile derivative according to any one of formulae (II) or (VII). The aminopropanenitrile derivatives according to formulae (II) or (VII) show even more pronounced improvements of the stability of aqueous electroless nickel plating bath and the nickel or nickel alloy layers formed with an aqueous electroless nickel plating bath containing said aminopropanenitrile derivatives according to formulae (II) or (VII) show an enhanced compressive stress. In one more preferred embodiment, the aqueous electroless nickel plating bath according to the invention comprises at least one aminopropanenitrile derivative according to formula (VII).The use of at least one aminopropanenitrile derivative according to formula (VII) is even more preferred as these derivatives allow for outstanding compressive stress of such deposited nickel or nickel alloy layers to be obtained (see Application Examples 1j-1l and 2). In another more preferred embodiment, the aqueous electroless nickel plating bath according to the invention comprises at least one aminopropanenitrile derivative according to formula (II) as said aminopropanenitrile derivatives enhance the plating bath's stability decisively (see Application Example 2).

[0029] The preparation of the aminopropanenitriles derivatives is known in the art. Exemplarily but not limiting, they may be synthesized by a Michael type addition of suitable amines to acrylonitrile (see Preparation Examples). The aminopropanenitriles derivatives may be used as received or purified prior to use. Useful purification methods include chromatography such as column chromatography, recrystallization and distillation depending on the physical properties of the individual aminopropanenitriles derivatives.

[0030] The term "alkyl" according to the present invention comprises branched or unbranched alkyl groups comprising cyclic and/or non-cyclic structural elements, wherein cyclic structural elements of the alkyl groups naturally require at least 3 carbon atoms. The term "C1-CX-alkyl group" according to the present invention refers to alkyl groups having 1 to X carbon atoms. Unless stated otherwise, alkyl groups herein have 1 to 8 carbon atoms and are thus C1-C8-alkyl groups. Preferably, C1-C6 alkyl groups, more preferably C2-C4-alkyl groups are used in the context of the present invention for their reduced hydrophobicity. C1-C8-alkyl for example includes, among others, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *sec*-butyl, *tert*-butyl, *n*-pentyl, *iso*pentyl, *sec*-pentyl, *tert*-pentyl, *neo*-pentyl, hexyl, heptyl and octyl. Alkyl groups may be functionalised (also referred to as substituted) and are (theoretically) obtained by replacing at least one hydrogen by a functional group preferably selected from amino, hydroxyl, thiol, halides such as fluorine, chlorine, bromine, iodine, carbonyl, carboxyl, carboxylic acid esters, sulphonyl ($-SO_3H$). More preferably, this at least one functionalisation is selected from the group consisting of hydroxyl and carboxyl, as these groups improve the hydrophilicity of such functionalised molecules resulting in improved properties of formed nickel or nickel alloy layers, particularly in improved compressive stress of such deposited nickel or nickel alloy layers.

[0031] Alkylene are respective derivatives of alkyl having with two free bonding sites. They may be functionalised as described for alkyl using the same functional groups. They may be branched or unbranched. The term "C1-CX-alkylene" according to the present invention refers to alkylene groups having 1 to X carbon atoms.

[0032] In so far as the term "aryl" is used in this description and in the claims, it refers to ring-shaped aromatic hydrocarbon residue, for example phenyl or naphtyl, where individual ring carbon atoms can be replaced by N, O and/or S, for example benzothiazolyl. Furthermore, aryl residues can be functionalised by (theoretically) replacing a hydrogen in each case by a functional group, preferably selected from amino, hydroxyl, thiol, halides such as fluorine, chlorine, bromine, iodine, carbonyl, carboxyl, carboxylic acid esters, more preferably selected from the group consisting of hydroxyl and carboxyl for the same reasons outlined above.

[0033] In so far as the term "aralkyl" is used in this description and in the claims, it refers to a hydrocarbon residue consisting of at least one alkyl and at least one aryl group such as benzyl and tolyl.

[0034] The aminopropanenitrile derivatives can be used as stabilising agents in aqueous electroless nickel plating baths.

[0035] The aqueous electroless nickel plating bath according to the invention comprises aminopropanenitrile and/or at least one aminopropanenitrile derivative in a total concentration of 1 to 10000 μmol/l, preferably in a total concentration of 50 to 5000 μmol/l. Total concentration in this aspect means that if more than one of said compounds is comprised in the aqueous electroless nickel plating bath, the sum of concentrations of all aminopropanenitrile derivatives and aminopropanenitrile shall be in above-defined range. Concentration below said ranges may not be sufficient in order to stabilise the aqueous electroless nickel plating bath according to the invention. Concentration above said range may not allow for high enough plating rates.

[0036] The aqueous electroless nickel plating bath according to the invention is an aqueous solution. The term "aqueous solution" means that the prevailing liquid medium, which is the solvent in the solution, is water. Further liquids, that are miscible with water, as for example alcohols and other polar organic liquids, that are miscible with water, may be added. It is preferred that at least 95 wt.-%, more preferably 99 wt.-%, of all solvents used is water because of its ecologically benign character.

[0037] The aqueous electroless nickel plating bath according to the invention may be prepared by dissolving all components in aqueous liquid medium, preferably in water.

[0038] The aqueous electroless nickel plating bath according to the invention comprises at least one source of nickel ions. The at least one source of nickel ions can be provided by any water-soluble salt or any water-soluble nickel complex. Preferably, nickel ions are provided by any one of nickel sulphate, nickel chloride, nickel acetate, nickel methyl sulphonate, nickel sulphamate and mixtures thereof. The concentration of the nickel ions in the aqueous electroless nickel plating bath may vary widely and preferably ranges from 0.01 mol/l to 1 mol/l, more preferably from 0.03 mol/l to 0.8 mol/l, even more preferably from 0.06 mol/l to 0.3 mol/l.

[0039] The aqueous electroless nickel plating bath according to the invention further comprises at least one reducing agent. The at least one reducing agent is preferably a chemical reducing agent. Reducing agents provide the electrons needed to reduce metal ions to their metallic form and thereby form a metal deposit on a substrate. Thus, the at least one reducing agent is suitable to reduce nickel ions. Preferably, the at least one reducing agent is selected from the group consisting of hypophosphite compounds such as hypophosphite salts or hypophosphorous acid, aminoboranes, borohydrides, hydrazine and derivatives thereof and formaldehyde. The at least one reducing agent is more preferably a hypophosphite salt or hypophosphorous acid, even more preferably a hypophosphite salt. The hypophosphite salt is supplied to the aqueous electroless nickel plating bath by any suitable source such as sodium, potassium, ammonium and nickel hypophosphite. Two or more reducing agents may be employed as a mixture in the aqueous electroless nickel plating bath. The concentration of the at least one reducing agent is generally in molar excess of the amount sufficient to reduce the nickel ions in the aqueous electroless nickel plating bath. The concentration of the reducing agent preferably ranges from 0.01 mol/l to 3.0 mol/l, more preferably from 0.1 mol/l to 1 mol/l.

[0040] In case a hypophosphite compound is used as the reducing agent, a Ni-P alloy deposit is obtained. Such reducing agents provide the source of phosphorous in the deposited alloy. A borane-based compound as reducing agent leads to a Ni-B alloy deposit and a mixture of hypophosphite compounds and borane-based compounds as the reducing agents leads to a ternary Ni-B-P alloy deposit. A nitrogen-based reducing agent such as hydrazine and derivatives thereof as well as formaldehyde as reducing agent provide nickel deposits.

[0041] The aqueous electroless nickel plating bath according to the invention may be acidic, neutral or alkaline. An acidic or an alkaline pH adjustor may be selected from a wide range of materials such as ammonium hydroxide, sodium hydroxide, hydrochloric acid, sulfuric acid and the like. The pH of the aqueous electroless nickel plating bath according to the invention may range from about 2 to 12. In one embodiment, the aqueous electroless nickel plating bath according to the invention is preferably acidic. More preferably, the pH of the acidic aqueous electroless nickel plating bath according to the invention ranges from 3.5 to 7, even more preferably from 3.5 to 6.5, most preferably from 3.5 to 5.5. In another embodiment, the aqueous electroless nickel plating bath according to the invention is preferably alkaline. More preferably, the pH of the alkaline aqueous electroless nickel plating bath according to the invention ranges from 7.5 to 12, even more preferably from 8 to 10, most preferably from 8 to 9.

[0042] The aqueous electroless nickel plating bath according to the invention further comprises at least one complexing agent. A complexing agent (sometimes also referred to as chelating agent) or mixture of complexing agents is included in the aqueous electroless nickel plating bath. A complexing agent keeps metal ions dissolved and prevents their undesired precipitation in solution. The at least one complexing agent is preferably selected from complexing agents for nickel ions and optionally, complexing agents for alloying metal ions, more preferably from complexing agents for nickel ions.

[0043] The at least one complexing agent is preferably selected from the group consisting of alkyl amines, ammonia, carboxylic acids, hydroxylcarboxylic acids, aminocarboxylic acids, salts of the aforementioned and mixtures thereof.

[0044] In one embodiment, carboxylic acids, hydroxylcarboxylic acids, aminocarboxylic acids and salts of the aforementioned or mixtures thereof may be employed as the at least one complexing agent. Useful carboxylic acids include the mono-, di-, tri- and tetra-carboxylic acids. The carboxylic acids may be substituted with various substituent moieties such as hydroxyl or amino groups and the acids may be introduced into the aqueous electroless nickel plating bath as their sodium, potassium or ammonium salts. Some complexing agents such as acetic acid, for example, may also act as a pH buffering agent, and the appropriate concentration of such additive components can be optimised for any aqueous electroless nickel plating bath in consideration of their dual functionality.

[0045] Examples of such carboxylic acids which are useful as complexing or chelating agents in the aqueous electroless nickel plating bath of the present invention include: iminosuccinic acid, iminodisuccinic acid, derivatives thereof and salts thereof as disclosed in WO 2013/113810, monocarboxylic acids such as acetic acid, hydroxylacetic acid (glycolic acid), aminoacetic acid (glycine), propanoic acid, 2-amino propanoic acid (alanine); 2-hydroxyl propanoic acid (lactic acid); dicarboxylic acids such as succinic acid, amino succinic acid (aspartic acid), hydroxyl succinic acid (malic acid), propanedioic acid (malo-nic acid), tartaric acid, hexane-1,6-dicarboxylic acid (adipic acid); tricarboxylic acids such as 2-hydroxyl-1,2,3-propane tricarboxylic acid (citric acid); and tetracarboxylic acids such as ethylene diamine tetra acetic acid (EDTA). Preferred carboxylic acids are acetic acid, aminoacetic acid, propanoic acid, 2-hydroxyl propanoic acid, succinic acid, hydroxyl succinic acid, adipic acid or 2-hydroxyl-1,2,3-propane-tricarboxylic acid. In one embodiment, mixtures of two or more of the above complexing agents are utilised in the aqueous electroless nickel plating bath according to the invention.

[0046] Alkyl amines may also be used as the at least one complexing agent, for example mono-, di- and trialkylamines. (Functionalised) C1-C3-alkyl amines, for example triethanol-amine are preferred. Ammonia may also be used as the at least one complexing agent.

[0047] The concentration of the at least one complexing agent or, in case more than one complexing agent is used, the concentration of all complexing agents in total preferably ranges from 0.01 mol/l to 3.0 mol/l, more preferably from 0.1 mol/l to 1.0 mol/l and even more preferably from 0.2 mol/l to 0.6 mol/l.

[0048] The aqueous electroless nickel plating bath according to the invention optionally comprises at least one further stabilising agent. Such optional stabilising agent may further improve the bath lifetime, a reasonable plating rate and to control the phosphorous content in the as deposited nickel phosphorous alloy. Since the aminopropanenitrile derivatives act as stabilising agents, a further stabilising agent is not necessary. Suitable optional stabilising agents are, without limitation, heavy metal ions such cadmium, thallium, bismuth, lead and antimony ions, iodine containing compounds such as iodide and iodate, sulphur containing compounds such as thiocyanate, thiourea and mercaptoalkanesulphonic acids like 3-mercaptopropanesulphonic acid or the respective disulphides derived therefrom as disclosed in WO 2013/013941 and unsaturated organic acids such as maleic acid and itaconic acid or suitably substituted alkynes as those taught by EP 2 671 969 A1. It is also within the scope of the present invention to use combinations of stabilising agents such as bismuth ions and mercaptobenzoic acids, mercaptocarboxylic acids and/or mercaptosulphonic acids as taught by WO 2013/113810.

[0049] The concentration of the at least one optional stabilising agent in the inventive electroless nickel plating bath ranges from 0.1 to 100 mg/l, preferably from 0.5 to 30 mg/l.

[0050] Other materials may be included in the aqueous electroless nickel plating bath according to the invention such as pH buffers, wetting agents, accelerators, brighteners, additional stabilising agents, plating rate modifiers such as those disclosed in European patent application no. 14198380.9, etc.

[0051] The aqueous electroless nickel plating bath according to the invention optionally contains further metal stabilising agents such as copper, selenium, tin, bismuth, antimony ions. The concentration of the metal ions can vary and e.g. range from 0.1 to 100 mg/l, preferably from 0.1 to 50 mg/l, more preferably from 0.1 to 10 mg/l. In one embodiment, the aqueous electroless nickel plating bath according to the invention does not contain toxic heavy metals. In this embodiment, the aqueous electroless nickel plating bath according to the invention does preferably not contain lead, cadmium, antimony, bismuth, arsenic or mercury (disregarding trace residues commonly present in technical raw materials which are herein defined to be 0.1 mg/l or less).

[0052] In case a hypophosphite compound is used as the reducing agent for nickel, nickel and phosphorous containing alloy deposits are obtained. The amount of phosphorous in said alloy deposit depends *inter alia* on the concentration of hypophosphite and nickel ions in the inventive aqueous electroless nickel plating bath and the optional stabilising agent. The aqueous electroless nickel plating bath according to the invention and the method of the present invention are suitable to provide nickel phosphorous alloy coatings with a wide range of P content of between 1 to 15 wt.-% P. Preferably, the amount of phosphorous in said alloy deposit ranges from 5 to 15 wt.-% with the balance being nickel, more preferred it ranges from 10.5 to 15 wt.-% with the balance being nickel as these so-called high-phosphorous (high NiP) coatings are paramagnetic.

[0053] In case a boron-based reducing agent is used as the reducing agent for nickel, nickel and boron containing alloy deposits are obtained. The amount of boron in said alloy deposit depends *inter alia* on the concentration of boron-based reducing agent and nickel ions in the inventive aqueous electroless nickel plating bath and the optional stabilising agent. Preferably, the amount of boron in said alloy deposit ranges from 1 to 20 wt.-% with the balance being nickel. In case one or more of hydrazine or formaldehyde are used as the reducing agents for nickel, pure nickel deposits are obtained.

[0054] The aqueous electroless nickel plating bath according to the invention optionally further comprises at least one alloying element. In this embodiment, nickel alloy layers containing the alloying element are deposited from the aqueous electroless nickel plating bath according to the invention. The at least one alloying element may be selected from phosphorus, boron, and a further source of metal ions which is not a source of nickel ions.

[0055] The alloying elements phosphorus or boron may be comprised in the aqueous electroless nickel plating bath in the form of a hypophosphite salt, hypophosphorous acid or a borane-based compound, such as aminoboranes or borohydrides, as mentioned above as reducing agents.

[0056] The at least one source of metal ions which is not a source of nickel ions may be comprised in the aqueous electroless nickel plating bath in the form of a water-soluble metal salt containing the ions of the alloying metal M. The optional at least one alloying metal M is preferably selected from the group consisting titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminium, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, gallium, indium, tin, and thallium. More preferably, the optional alloying metal M is selected from the group consisting of molybdenum, tungsten, copper, silver, gold, aluminium, zinc and tin.

[0057] The concentration of the optional at least one alloying metal M preferably ranges from 10^{-5} to 0.2 mol/l, more preferably from 10^{-4} to 0.2 mol/l, even more preferably from 10^{-2} to 0.1 mol/l.

[0058] In case additional metal salts or metal ions are present in the aqueous electroless nickel plating bath, the respective nickel alloy is obtained as deposit. When adding an alloying metal M to the aqueous electroless nickel plating bath (depending on the kind of reducing agent present) ternary or quaternary alloys Ni-M-P, Ni-M-B, and Ni-M-B-P are deposited.

[0059] Optionally, a water-soluble salt of an alloying metal M and a water-soluble salt of a second alloying metal M^* are added to the aqueous electroless nickel plating bath according to the invention. In this case, nickel alloy deposits comprising alloying metals M and M* are obtained.

[0060] The present invention further relates to a method for electroless deposition of nickel and nickel alloys by contacting the substrate to be plated with the above described aqueous electroless nickel plating bath.

[0061] The deposition method comprises the steps of

(A) providing a substrate,
(B) contacting the substrate with the aqueous electroless nickel plating bath according to the invention as described above, and thereby depositing a nickel or nickel alloy onto the substrate.

[0062] The substrate to be nickel or nickel alloy plated may be plated to the desired thickness and deposit quantity by contacting the substrate with the aqueous electroless nickel plating bath according to the invention. The inventive aqueous electroless nickel plating bath may be maintained over a temperature range of 20 °C to 100 °C, preferably 70 °C to 95 °C, more preferably 85 °C to 90 °C or 95 °C during deposition.

[0063] A deposit thickness of up to 100 μm, or higher may be employed. Preferably, the thickness of the nickel or nickel phosphorus (NiP) deposits varies between 1 - 60 μm. The thickness depends on the technical application and can be higher or lower for some applications. For example, if the nickel or NiP layer is deposited to provide a corrosion resistant coating, a thickness of between 30 - 60 μm is desired, while for electronics applications a thickness of between 1 - 15 μm is applied. In the technical area of rigid memory disks, the thickness of the nickel or nickel-phosphorus deposits preferably ranges from 9 to 13 μm. In the technical area of semi-conductors, the thickness of the nickel or nickel-phosphorus deposits preferably ranges from 1 to 5 μm. Thicknesses of nickel or nickel alloy layers may be measured with x-ray fluorescence (XRF) which is known in the art.

[0064] The aqueous electroless nickel plating bath for electroless deposition of nickel and nickel alloys and the methods of the present invention are suitable to provide nickel and nickel alloy coatings having an attractive bright or semi-bright appearance.

[0065] In contrast to stabilising agents known in the art, the aminopropanenitrile derivatives of the present invention do not shift the internal stress to neutral or tensile stress. To the contrary, the aminopropanenitrile derivatives of the present invention shift the stress to higher compressive stress values which is advantageous (see e.g. Application Example 1). The advantages of nickel or nickel alloy layers having compressive stress are high corrosion resistance and good adhesion to the substrate surface.

[0066] The use of aminopropanenitrile derivatives according to the present invention does not change the phosphorous content of the deposited nickel alloy layers compared (significantly) to electroless nickel-phosphorus baths containing no such additive. Thus, the use of aminopropanenitrile derivatives according to the present invention has no negative effect on the bath performance and no negative effect on the coating quality. On the contrary, the stability of aqueous electroless nickel plating baths comprising the inventive aminopropanenitrile derivatives improve is significantly enhanced (see Application Example 2).

[0067] The above parameters of the aqueous electroless nickel plating bath and methods of the present invention are only provided to give general guidance for practicing the invention.

[0068] The phosphorus content of nickel alloy layers and the thickness of nickel or nickel alloy layers were measured by x-ray fluorescence (XRF) which is well known to persons skilled in the art. The XRF measurements make use of the characteristic fluorescence radiation emitted from a sample (substrate, deposit) being excited with x-rays. By evaluating the wavelength and intensities and assuming a layered structure of the sample, phosphorus content and layer thicknesses can be calculated.

[0069] High NiP alloys obtained by the aqueous electroless nickel plating bath according to the present invention contribute to generating alloys having high compressive stress. The stress values for example range between 0 to -70 N/mm^2, preferably between 0 to -50 N/mm^2, more preferably between - 30 to -50 N/mm^2. Such deposits show high corrosion resistance and excellent adhesion to the underlying substrate they are plated on.

[0070] Various kinds of substrates can be metal plated with the aqueous electroless nickel plating bath according to the invention and the method according to the invention. The substrates to be metal plated are preferably selected from the group consisting of electrical non-conductive substrates, electrical conductive substrates, and electrical semi-conductive substrates.

[0071] The electrical non-conductive substrates to be metal plated can be selected from the group consisting of glass, ceramics, and plastics. Electrical nonconductive substrates may have to be made receptive for the deposition of nickel or nickel alloys. This is referred to as activation in the art. The activation can be accomplished for example by depositing a catalytic layer of palladium or another noble metal on said substrate which renders in nonconductive substrate suitable for nickel or nickel alloy deposition.

[0072] Plastics can be selected from acrylnitrile-butadiene-styrol-copolymer (ABS copolymer); polyamide; a mixture of an ABS copolymer and at least one other polymer which is different to the ABS copolymer; polycarbonate (PC); ABS/PC blends; epoxy resin; bismaleimide-triazine resin (BT); cyanate ester resin; polyimide; polyethylene terephthalate (PET); polybutylene terephthalate (PBT); polylactic acid (PLA); polypropylene (PP); and polyester.

[0073] The electrical conductive substrates to be metal plated can be selected from metallic substrates, and conductive metal oxides.

[0074] The metallic substrates to be metal plated are preferably selected from the group consisting of copper, zinc, silver, gold, platinum, palladium, iron, iridium, tin, aluminium and nickel.

[0075] The conductive metal oxides to be metal plated can be selected from indium tin oxide (ITO), antimony tin oxide (ATO), aluminium doped zinc oxide (AZO), fluorine doped tin oxide, magnesium doped zinc oxide, and chromium doped titanium oxide; preferably, they are selected from indium tin oxide, antimony tin oxide and aluminium doped zinc oxide.

[0076] The electrical semi-conductive substrates to be metal plated can be selected from the group consisting of silicon, germanium, gallium, arsenic, silicon nitride and silicon carbide.

[0077] Without limiting the scope of the present invention, the substrates are typically used in the electronics industry, for example for the manufacturing of printed circuit boards, IC substrates, semiconductor wafers, chip carriers, touch screens and so forth.

[0078] Substrates are optionally pretreated prior to step (ii). Such pretreatment is known in the art. Typical pretreatments include etching, cleaning and activation steps. Useful pretreatments may improve the plating results by removing undesired dirt or oxides from the surface of the substrate. Pretreatments may vary widely depending on the substrate provided. Some guidance can exemplarily be found in WO2015/161959 A1 (page 13, line 11 to page 15, line 30).

[0079] The method according to the invention optionally comprises rinsing steps, preferably with water, and/or drying steps.

Examples

[0080] The following non-limiting examples further illustrate the present invention.

Substrates

[0081] Steel plates (provided by Q-Lab Deutschland GmbH, type QD-2-3.5, size 51x89 mm, thickness 0.51 mm) were used as substrates. They were pretreated prior to NiP deposition as described in Table I. Products which were used in this pretreatment (Uniclean® 155 and Nonacid® 701) were supplied by Atotech Deutschland GmbH. Deionised water was used.

Table I: Pretreatment procedure.

Pre-treatment step	Product	Concentration	Temp. (°C)	Time
Soak cleaner	Uniclean 155	60 g/l	70	5 min
Rinse	Water	-	-	30 s

(continued)

Electro-cleaner	Nonacid 701	150 g/l	50°C, 10 A/dm^2	1 min
Rinse	Water	-	-	30 s
Activate	HCl (37% solution)	1/1 (v/v)	RT	30 s
Rinse	Water	-	-	30 s

Determination of thickness of the metal or metal alloy deposits and plating rate

[0082] The phosphorus content and deposit thickness were measured at 5 points of each substrate by XRF using the XRF instrument Fischerscope XDV-SDD (Helmut Fischer GmbH, Germany). By assuming a layered structure of the deposit the layer thickness can be calculated from such XRF data. The plating rate was calculated by dividing the obtained layer thickness by the time necessary to obtain said layer thickness.

Determination of stress

[0083] Stress in the nickel-phosphorus coating was measured using a stress-strip finger. The test strips were made of copper and had spring-like properties. After plating, the test strip was mounted on the Testing Stand (Deposit stress analyzer Model No. 683 of Specialty Testing & Development Co., York, PA, USA) which measured the distance which the test strip legs had spread after plating. The distance U is included in the following formula which allows for the deposit stress to be calculated.

$$Stress = U / 3 * T * K$$

[0084] U is the number of increments spread, T is the deposit thickness and K is the strip calibration constant. Each lot of test strips manufactured will respond with slight differences when used for deposit stress test. This degree of difference was determined by the supplier when each lot of test strips was calibrated. The value for K was supplied with each lot of test strips provided by Specialty Testing & Development Co. Stress was also determined to be of compressive or tensile nature. If the test strip legs were spread outward on the side that has been plated, the deposit stress was tensile in nature. If the test strip legs were spread inward on the side that has been plated, the deposit stress was compressive in nature.

Analytical data

[0085] Purification by column chromatography was done with an *Interchim* PuriFlash 450 on silica gel (25 μm) using dichloromethane and methanol as eluents. Mass-spectra were obtained with a *Waters* GC TOF (EI) and a *Bruker* ESI-Q-TOFmicro. Fusion points were determined in open glass capillaries on a *Büchi* M-560. NMR spectra were obtained on a *Varian* VNMRS 500. IR spectra were recorded with the FT-IR spectrometer Spectrum One by *Perkin Elmer* using a Germanium-ATR unit and are reported in wave numbers (cm^{-1}).

Preparation Example 1: 3,3'-(Piperazin-1,4-diyl)dipropannitril

[0086] A 100 ml reaction flask equipped with thermometer and magnetic stirring bar was charged with piperazine (10.0 g, 116 mmol) in 60 mL water. The solution was adjusted to 25°C and acrylonitrile (18.5 g, 348 mmol) was added. The reaction mixture was stirred overnight and the reaction was monitored by thin layer chromatography. After 15 hours of total reaction time, the volatile compounds of the reaction mixture were removed under reduced pressure. Then, the remaining residue was extracted three times with 100 mL ethyl acetate and the combined organic phases were dried over magnesium sulphate. After removal of the solvent under reduced pressure, 21.5 g of yellowish solid were obtained which was recrystallized from 100 mm diethyl ether and 50 mL ethyl acetate yielding 5.3 g of the desired product as wide solid. The volatile components of the supernatant liquid were removed under reduced pressure and the resulting oily residue was added drop-wise into diethyl ether (0°C) whereupon the desired product crystallised as white solid. In total, 18.2 g (95 mmol, 82% yield) of the desired product were obtained.

[0087] Analytical data: F_P: 63°C; ^{1}H-NMR (500 MHz, methanol-d_4, ppm): δ 2.57 (s, 8H), 2.60-2.72 (m, 8H); ^{13}C-NMR (125 MHz, methanol-d_4, ppm): δ 15.9, 53.4, 54.3, 120.2; IR: 2950, 2930, 2878, 2832, 2809, 2243, 1471, 1449, 1434, 1402, 1377, 1353, 1344, 1300, 1272, 1162, 1134, 1024, 1001, 943, 905, 772, 612; HRMS (EI): calculated for $C_{10}H_{16}N_4$

$[M]^+$: 192.1375, found: 192.1369.

Preparation Example 2: 3-Morpholinopropannitrile (alternative purification method)

[0088] Following the procedure given for Preparation Example 1, morpholine (10.0 g, 115 mmol) was reacted with acrylonitrile (9.14 g, 172 mmol). After one hour of total reaction time, the solvents were removed under reduced pressure and the oily residue was purified by column chromatography (dichloromethane/methanol 20/1 (v/v) to 5/1 (v/v)). The desired product was obtained as yellowish oil (15.2 g, 109 mmol, 95% yield).

[0089] Analytical data: ^{1}H-NMR (500 MHz, D_2O, ppm): δ 2.59-2.65 (m, 4H), 2.70-2.83 (m, 4H), 3.75-3.81 (m, 4H); ^{13}C-NMR (125 MHz, D_2O, ppm): δ 14.0, 52.0, 52.5, 65.9, 120.2; IR: 2954, 2855, 2815, 2248, 1458, 1448, 1359, 1292, 1274, 1142, 1114, 1069, 1018, 1008, 919, 904, 866, 855, 763, 611; HRMS (ESI): calculated for $C_7H_{13}N_2O$ $[M+H]^+$: 141.1022, found: 141.1021.

Application Example 1: Nickel bath

[0090] Substrates as described above were used for deposition of nickel-phosphorus alloy layers. The substrates were immersed in aqueous electroless nickel plating bath comprising the following components:

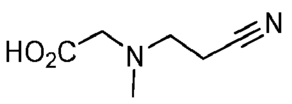
$NiSO_4 \cdot 6\ H_2O$	0.1 mol/l
succinic acid	0.055 mol/l
malic acid	0.1 mol/l
lactic acid	0.1 mol/l
sodium hypophosphite monohydrate	0.3 mol/l

[0091] The aqueous electroless nickel plating bath further comprised additives as given in Table II. The pH value of the aqueous electroless nickel plating bath was 4.8. Deposition was carried out in 1l-beakers. Each beaker was placed on a heater and temperature was maintained at 89.0 °C. Agitation was done by air injection. Bath loading was 0.9 dm^2/l corresponding to one steel panel per bath volume. Deposition time was 120 min.

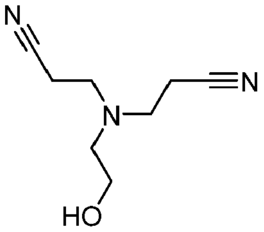
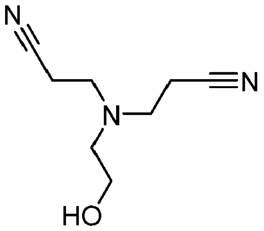
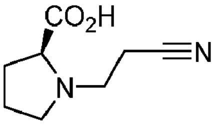
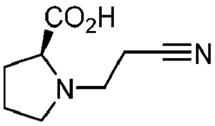
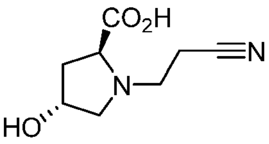
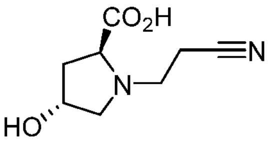
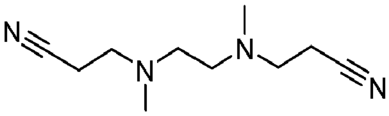
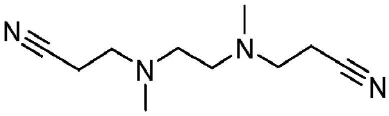
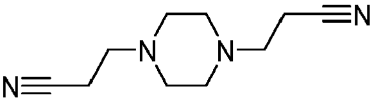
[0092] Application Example 1a (comparative example) contained no further additives.

[0093] Application Example 1b (according to the present invention) comprised an aminopropanenitrile according to formula (II) wherein R^1 was selected to be methyl ($-CH_3$) and R^2 was $-CH_2-CO_2H$. Application Example 1c and 1d (according to the present invention) comprised an aminopropanenitrile according to formula (III) wherein R^3 was selected to be 2-hydroxyleth-1-yl ($-CH_2-CH_2-OH$). Application Example 1e and 1f (according to the present invention) comprised aminopropanenitriles according to formula (V) with n equalling 4 and all X were to be $-CH_2-$ wherein one carbon atom (in α-position to the nitrogen atom of the aminopropanenitrile moiety) bore a carboxyl moiety. Application Example 1g and 1h (according to the present invention) comprised aminopropanenitriles according to formula (V) with n equalling 4 and all X were selected to be $-CH_2-$ wherein one carbon atom (in α-position to the nitrogen atom of the aminopropanenitrile moiety) bore a carboxyl moiety and another carbon atom bore an additional hydroxyl moiety (in β-position of both the nitrogen atom of the aminopropanenitrile moiety and the carboxyl moiety bearing carbon atom). Application Example 1i and 1j (according to the present invention) comprised an aminopropanenitrile according to formula (VI) wherein Y^1 was selected to be ethylene ($-CH_2-CH_2-$) and R^5 as well as R^6 were both selected to be methyl ($-CH_3$). Application Example 1 k and 1l (according to the present invention) comprised an aminopropanenitrile according to formula (VII) wherein both Y^2 and Y^3 were selected to be ethylene ($-CH_2-CH_2-$).

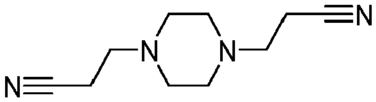
Table II: Plating results.

	Additive	C	Plating rate	Stress	Phosphorous content
		[μmol/l]	[μm/h]	[N/mm^2]	[wt.-%]
1a	No additive (comparative)	-	14.2	-16	10.8
1b		100	11	-21	11.1

(continued)

	Additive	C	Plating rate	Stress	Phosphorous content
		[μmol/l]	[μm/h]	[N/mm^2]	[wt.-%]
1c		100	11	-13	10.6
1d		1000	8	-25	11.1
1e		100	13	-16	10.6
1f		1000	11	-21	10.7
1g		100	11	-21	10.5
1h		1000	11	-17	10.2
1i		100	10.5	-19	11.2
1j		1000	6	-31	11.1
1k		100	11	-23	10.7

(continued)

	Additive	C	Plating rate	Stress	Phosphorous content
		[μmol/l]	[μm/h]	[N/mm²]	[wt.-%]
1l		1000	6	-39	11.0

[0094] The deposited nickel-phosphorus alloy layers of the inventive examples completely covered the substrate surface; no skip plating was obtained contrary to the comparative example which showed substantial skip plating. The deposited nickel phosphorous alloy layers were of uniform thickness, adhered well to the substrate surface and had a good appearance with technical brightness and a typical grey colour.

[0095] The plating rate of all inventive examples was decreased compared to the comparative example. Also, the stress of the nickel phosphorous alloy layers formed from the inventive examples was more compressive compared to the nickel phosphorus alloy layers obtained from the comparative examples.

[0096] A further advantage of the inventive examples was that no nickel phosphorous alloy was deposited on surfaces of the beaker or other surfaces than the substrate surface.

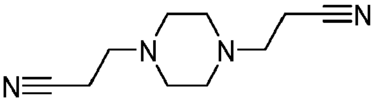
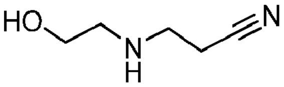
Application example 2: stability of aqueous electroless nickel plating baths

[0097] Aqueous electroless nickel plating baths comprising the following components were used to plate onto Q panels and onto test strips and the stability was monitored over time. The plating was run in a 1 L beaker at 88°C; the pH of the aqueous electroless nickel plating bath was 4.8.

$NiSO_4 \cdot 6\ H_2O$	0.1 mol/l
complexing agent	0.255 mol/l
sodium hypophosphite monohydrate	0.3 mol/l

[0098] The results of the stability monitoring summarised the following table.

Table III: Stability tests.

	Additive	Concentration [mmol/l]	First signs [min]	Plate-out [min]	Stress
2a	No additive (comparative)	-	0	2	compressive
2b		0.1	3	5	compressive
2c		1.0	3	5	compressive

[0099] The comparative plating bath comprising no additives other than those described above should little stability and started to deteriorate directly after the beginning of the plating. Plate-out was complete after two minutes.

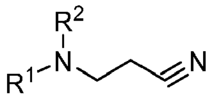
[0100] The inventive examples 2b and 2c enhanced the stability of the plating bath significantly. Both aminopropanenitrile derivatives improved the time until plate-out of the aqueous electroless nickel plating bath by factor 2.5.

[0101] Other embodiments of the present invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope of the invention being defined by the following claims only.

Claims

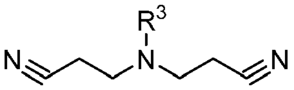
1. An aqueous electroless nickel plating bath comprising at least one source of nickel ions **characterised in that** it comprises aminopropanenitrile and/or at least one aminopropanenitrile derivative.

2. The aqueous electroless nickel plating bath according to claim 1 **characterised in that** it comprises at least one aminopropanenitrile derivative according to any one of formulae (II) to (VII)



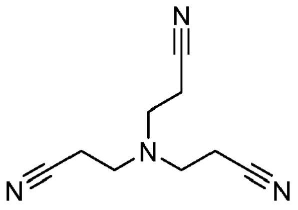
(II)

wherein R^1 and R^2 are independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl with the proviso that at least one of said residues is other than hydrogen;

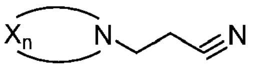


(III)

wherein R^3 is selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl,

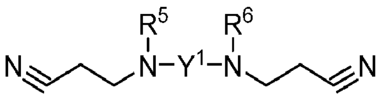


(IV),



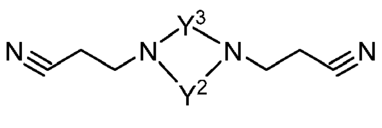
(V)

wherein n is an integer ranging from 4 to 7 and each X are independently from each other selected from the group consisting of $-CH_2-$, -O-, $-N(R^4)-$ with each R^4 being independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl,



(VI)

wherein Y^1 is a C1-C8-alkylene group, R^5 and R^6 are independently from each other selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl; and



(VII)

wherein each Y^2 and Y^3 are independently from each other selected to be C1-C8-alkylenes.

3. The aqueous electroless nickel plating bath according to claim 2 **characterised in that** it comprises at least one aminopropanenitrile derivative according to any one of formulae (II) or (VII).

4. The aqueous electroless nickel plating bath according to claim 3 **characterised in that** it comprises at least one

aminopropanenitrile derivative according to formula (II).

5. The aqueous electroless nickel plating bath according to claim 4 **characterised in that** it R^1 is selected from the group consisting of non-cyclic, unfunctionalised alkyl and non-cyclic, functionalised alkyl wherein said functionalisation is one or more of hydroxyl and carboxyl.

6. The aqueous electroless nickel plating bath according to claim 3 **characterised in that** it comprises at least one aminopropanenitrile derivative according to formula (VII).

7. The aqueous electroless nickel plating bath according to claim 6 **characterised in that** it comprises at least one aminopropanenitrile derivative according to formula (VII) and both bridging moieties Y^2 and Y^3 are selected to be C2-C4-alkylenes and are selected to be the same.

8. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** the amino group of the at least one aminopropanenitrile moiety of the aminopropanenitrile derivatives is not permanently quaternized.

9. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** it comprises aminopropanenitrile and/or at least one aminopropanenitrile derivative in a total concentration of 1 to 10000 μmol/l.

10. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** it comprises at least one reducing agent suitable to reduce nickel ions.

11. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** it comprises at least one complexing agent for nickel ions.

12. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** it does not contain lead, cadmium, antimony, bismuth, arsenic or mercury.

13. The aqueous electroless nickel plating bath according to any one of the preceding claims **characterised in that** it comprises at least one further source of metal ions selected from the group consisting titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminium, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, gallium, indium, tin, and thallium.

14. A method for electroless deposition of nickel and nickel alloys comprising the steps of

    (A) providing a substrate,
    (B) contacting the substrate with the aqueous electroless nickel plating bath according to any of claims 1 to 13,

    and thereby depositing a nickel or nickel alloy onto the substrate.

15. The method for electroless deposition of nickel and nickel alloys according to claim 14 **characterised in that** the substrates are selected from the group consisting of electrical non-conductive substrates, electrical conductive substrates, and electrical semi-conductive substrates.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 15 0307

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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	18 July 2016	Suárez Ramón, C

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