Title: WATER SOLUBLE AND AIR STABLE PHOSPHAADAMANTANES AS STABILIZERS FOR ELECTROLESS METAL DEPOSITION

Abstract: The present invention relates to the use of water soluble and air stable phosphaadamantanes as stabilizers for electroless metal deposition. An electrolyte, as well as a method for the electroless deposition of metals is disclosed. The plated metal layers can comprise nickel, copper, cobalt, boron, silver, palladium or gold, as well as alloys comprising at least one of the aforementioned metals as an alloying metal. The present invention further relates to an organic stabilizer for electroless plating processes, and an electrolyte for the electroless deposition of a metal layer on a substrate, comprising a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, a stabilizer and preferably an accelerator. A method for the electroless deposition of a metal layer on a surface from an electrolyte according to the invention is also disclosed.
Water Soluble and Air Stable Phosphaadamantanes as Stabilizers for Electroless Metal Deposition

FIELD OF THE INVENTION

The present invention relates to the use of water soluble and air stable phosphaadamantanes as stabilizers in electrolytes for electroless metal deposition. The invention provides an electrolyte, as well as a method, for the electroless deposition of metals.

The present invention further relates to an organic stabilizer for an electroless plating method, and an electrolyte for the electroless deposition of a metal layer on a substrate.

BACKGROUND OF THE INVENTION

Electroless plating methods have long been known from the state of the art in the metal plating industry. By electroless plating, also known as chemical plating, the coating of almost every metal and a huge number of non-conductive substrate surfaces is possible. Electrolessly deposited metal layers differ from galvanically deposited metal layers, i.e. those layers deposited by the use of an external current, in physical as well as mechanical aspects. Often, metal alloy layers with non-metal elements, like cobalt/phosphorus, nickel/phosphorus, nickel/boron or boron carbide are deposited by means of electroless deposition methods. In this respect, electrolessly deposited layers in many cases differ in their chemical nature from the galvanically deposited layers.

One major advantage of the electroless deposited metal layer is the outline accuracy of the layer thickness of the deposited layer independent from the substrate geometry.

Electroless plating methods are also used for the coating of other non-conductive substrates, like plastic substrates, to render the surface of such substrates conductive and/or to change the aesthetic appearance of the substrate. The material properties of the coated substrate can be improved or amended with electroless plating. Specifically, the corrosion
resistance or the hardness of the surface and/or the wear resistance of the substrate can be improved, e.g. for gas and/or oil industry applications.

Electroless plating methods are based on an autocatalytic process, in which process the metal ions comprised in the electrolytes are reduced to the elemental metal by a reducing agent which is oxidized during this redox reaction.

Sodium hypophosphite is a commonly used reducing agent in the field of electroless deposition of metals on substrate surfaces. Other reducing agents are also used in dependency of the metals to be deposited.

In known electroplating baths, it is necessary to use a stabilizer to avoid the uncontrolled plate-out (wild deposition) of the electrolyte, which means the unregulated wild deposition of metal on the substrate surface and tank walls. Heavy metals like lead, bismuth, zinc or tin have commonly been used as stabilizers. According to common environmental regulations [ROHS (Restriction of the use of certain hazardous substances), WEEE (Waste electrical and electronic equipment), ELV (End of lifetime of vehicles)] prior to the disposal of expended electrolytes and the co-deposition of heavy metals, such heavy metals have to be removed from the electrolyte solution in an adequate treatment step. When the heavy metals are present in the electrolyte only in small amounts, such a treatment causes additional expenses for the disposal. Therefore, the use of heavy metal in electrolytes for the deposition of metal layers has to be avoided. In some other types of electrolytes, like electrolytes for the electroless deposition of copper, cyanides are used as stabilizers. Like heavy metal ions, cyanides are subject to environmental regulations. The same is true for selenium compounds, which are also commonly used as stabilizers. In addition, some heavy metal stabilizers are difficult to analyze. Since analyzing of concentration of said heavy metal stabilizers is mandatory but difficult, bath control can also be difficult.

U.S. Pat. No. 6,146,702 discloses an electroless nickel cobalt phosphorus composition and plating process. The process provides for enhancing the wear resistance of aluminium and other materials by depositing a nickel, cobalt, phosphorus alloy coating on the substrate.
using an electroless plating bath to provide a plated alloy having a cobalt content of at least about 20% by weight and a % Co / % P weight ratio of at least about 5.

European patent application EP 1 413 646 A2 discloses an electrolyte for the electroless deposition of nickel layers having internal compressive stress. The electrolyte disclosed in the application comprises a metal salt of the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer. The accelerator is used to increase the deposition rate of the metal on the substrate surface.

JP 2009-149965A discloses a silver-plating method, which does not need to form an unnecessary layer of a nickel layer in between a substrate, which is difficult to be plated, and a silver-plated film. The silver-plated film has sufficient adhesiveness directly on the substrate, which is difficult to be plated, with the use of a halide-free plating bath under a satisfactory working environment. The silver-plating method disclosed is used for forming the silver-plated film on the substrate on which an oxide film is easily formed and the oxide film hinders the adhesiveness of a plated film, and comprises at least the steps of: (A) degreasing the substrate; (B) removing the oxide film with a strongly acidic solution; and then, (C) plating the substrate with silver by using a phosphine-containing acidic silver-plating bath which essentially does not contain a halide ion and a cyanide ion while skipping the step of nickel strike plating or nickel-alloy strike plating.

JP 2005-290415A discloses a stabilizing agent for electroless copper-plating electrolytes, which imparts adequate stability to an electroless copper-plating solution without lowering characteristics of an electroless copper-plated film. The stabilizing agent is made of a highly safe material. The electroless copper-plating solution includes a phosphine compound expressed by the following general Formula, as the stabilizing agent:

\[
\text{R}_1 \text{P-R}_2
\]

\[
\text{R}_3
\]
wherein R1, R2 and R3, are each the same or different, and represent a monovalent aliphatic hydrocarbon group which may have a substituent group, an aryl group which may have a substituent group, or a heterocyclic group which may have a substituent group.

CN 101348927A discloses a cyanogen-free preplated copper solution. The solution comprises a nontoxic organic phosphine compound to replace cyanide as a complexing agent for the preplated copper. This is particularly suitable for preplated copper used to electroplate steel, aluminum, magnesium, zinc, titanium and titanium alloy. The cyanogen-free preplated copper solution has the following main technical characteristic that the solution comprises: (a) one sort of copper sulphate, basic cupric carbonate or copper nitrate with the volume concentration of between 30 and 60 g/L; (b) one sort or two sorts of compounds selected from methylene diphosphonic acid, 1-hydroxyethylidene 1,1-diphosphonic acid and 1-hydroxybutyleneidene 1,1-diphosphonic acid with the volume concentration of between 120 and 160 g/L; (c) one sort or two sorts of compounds selected from methylamino dimethylene diphosphonic acid, hexamethylene diamine tetramethylene phosphonic acid and ethylenediamine tetramethylene phosphonic acid, with the volume concentration of between 2 and 5 g/L; (d) one sort of potassium citrate, amine citrate or seignette salt, with the volume concentration of between 6 and 12 g/L, and (e) polyethyleneimine alkyl slat or aliphatic amine ethoxy sulfonated substance (AESS), with the volume concentration of between 0.02 and 0.05 g/L. The cyanogen-free preplated copper solution has the characteristics of stable service performance, simple solution compositions, convenient maintenance, high safety, environmental protection, reliable plating binding coatings and the like.

Furthermore, there is an interest in the art of metal plating to avoid sulfur compounds that comprise sulfur in an oxidation state between -2 and +5, since the compounds are also subject to environmental regulations. However, such compounds are often needed in the electrolytes to gain good plating results. Especially for so called "high phos" electroless nickel electrolytes. The use of sulfur compounds is critical, since such compounds may negatively affect the corrosion resistance of the plated nickel layer.
SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved formulation for electroless plating that is stabilized against uncontrolled plate-out of the metal to be deposited.

It is a more particular object of various preferred embodiments of the pending application to provide an electrolyte for electroless deposition which is free of heavy metal stabilizers, cyanides, selenium compounds, and/or sulfur compounds comprising sulfur in an oxidation state between -2 and +5.

This object is solved by an aqueous electrolyte for the electroless deposition of a metal layer on a substrate, comprising a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer, characterized in that the electrolyte comprises a phosphaadamantane, as a stabilizer, according to the general Formula I,

![Phosphaadamantane](attachment:image.png)

(Formula I)

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, an alcohol group having 1 to 6 carbon atoms.

It is a further object of the present invention to provide an improved stabilizer for electroless plating processes, a new electrolyte, and a method for the electroless deposition of a metal layer having improved properties.
The invention is summarized as being an aqueous electrolyte composition for the electroless deposition of a metal layer on a substrate, comprising:

- a metal ion source of the metal to be deposited;
- a reducing agent;
- a complexing agent;
- an accelerator; and
- a stabilizer, characterized in that the stabilizer is a phosphaadamantane according to the general Formula 1:

\[
\text{N} \quad \text{N} \\
\text{N} \quad \text{P} \\
\text{N} \quad \text{N}
\]

(Formula 1)

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms.

The inventive method is summarized as a method for the electroless deposition of a metal layer on a substrate comprising the steps of:

- contacting the substrate to be plated with an electrolyte comprising:
    - a metal ion source of the metal to be deposited;
    - a reducing agent;
    - a complexing agent;
    - an accelerator; and
    - a stabilizer, characterized in that the electrolyte comprises phosphaadamantane, as a stabilizer, according to the general Formula 1:
wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Surprisingly, it was found that phosphaadamantanes, according to the general Formula I, are capable of completely replacing heavy metal stabilizers, cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between -2 and +5 in electrolytes for the electroless deposition of metal layers.

While not being bound to this theory, the applicant believes that the phosphaadamantanes, according to general Formula I, due to their indirectly tertiary amino groups, as well as their tertiary phosphorus group are capable to at least temporarily jam the active centers on the substrate surface, which are responsible for the uncontrolled deposition. Wild deposition of the metals can now therefore be avoided. Additionally, the foreign ions present in the electrolyte, which are responsible for the wild deposition, are inactivated by the phosphaadamantanes.

A further benefit of the inventive electrolyte is that an effect known as edge weakness can be avoided. When using electrolytes that comprise heavy metal ions as stabilizers for the electroless deposition of metal layers which at high convection of the electrolyte, a decreased deposition of metal at the edges of the substrate occurs. This is deemed to be related to an increased assembly of the heavy metal ions used as stabilizers in these areas. This effect
deteriorates the outline accuracy of the plating. Surprisingly, by the use of phosphaadamantanes, according to general Formula I, as stabilizers in electroless plating methods, this edge weakening effect can be avoided. Using phosphaadamantanes as stabilizers significantly increases the overall outline accuracy of the plating, especially when plating large substrates.

Furthermore, the use of a phosphaadamantane as a stabilizer, according to general Formula I, results in a more even deposit with less nodules.

The use of phosphaadamantanes, according to general Formula I, as stabilizers results in improved deposition and a significant reduction of discard, especially on alumina or zincate substrates.

A further benefit of the inventive electrolyte is that a significant reduction of deposition on components of the plating equipment, especially on the heating systems used in the plating baths, occurs. This significantly reduces equipment maintenance, which in turn results in a notable economic benefit to the plating shops due to less down time.

An electrolytic bath, with a single class of metal, containing the stabilizer of the present invention, leads to deposited metal layers, having properties like an amorphous metal. These properties are, for example, that these layers have no edge weakness effect; they are very passive; have a good resistance against corrosion; wear-resistance; and good compressive stress properties.

Further benefits of the stabilizer according to the present invention are: that it is metal free; provides a deposit having significantly better corrosion resistance including excellent resistance vs. nitric acid; it is environmental friendly (non-toxic additive); has a higher phosphorus concentration at given pH level; and lower plating temperatures can be used to achieve the same plating speed and phosphorus content.

Surprisingly, it was found that by the use of phosphaadamantanes, according to the general Formula I, plating electrolytes for the electroless deposition become less sensitive to
foreign metal carry-over, like e.g. palladium ions resulting from the activation pretreatment of the substrate to be plated. This is especially relevant when non-conductive substrates, like e.g. plastics, are intended to be plated by direct plating processes using noble metal colloids for seeding the surfaces. While the known plating electrolytes turned out to be quite sensitive to foreign metals and therefore required intensive rinse steps after the activation, the inventive plating electrolytes do not show any significant deterioration even at Pd-concentrations > 2mg/L.

In particular, phosphaadamantanes, according to general Formula I, having no substituted hydrogens, are found to be very effective as stabilizers in electroless plating electrolytes. Hence, 1,3,5-triaza-7-phosphaadamantane (PTA) is a preferred embodiment of the phosphaadamantanes according to general Formula I. Beneficially, PTA has a sufficiently high solubility in aqueous systems and has a high oxidation stability.

The phosphaadamantanes according to general Formula I can be comprised in the inventive electrolyte within a range of >0.05 mg/L and ≤ 100 mg/L, preferably between >0.1 mg/L and ≤ 25 mg/L, most preferably between >0.5 mg/L and ≤ 10 mg/L.

According to an embodiment of the invention the electrolyte comprises at least one reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes. The reducing agent may be present in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. Preferably, the electrolyte may comprises e.g. sodium hypophosphite (mono hydrate) with a concentration of 10 to 40 g/L and even more preferably with a concentration of 12 to 30 g/L.

A metal ion source in the inventive electrolyte can be selected from the group consisting of metal chlorides, metal sulfates, metal acetates, metal nitrates, metal propionates, metal formates, metal oxalates, metal citrates, metal ascorbinates, and mixtures thereof. The source of cations of the metal to be deposited may comprise the counter anion of any of such salts. Metal compounds having volatile ions, like metal acetates, metal nitrates, metal propionates, and metal formates are preferred because the volatile character of the anions leak
out from the electrolyte in gaseous form which enables a reduction in the amount of anions in
the electrolyte. This significantly extends the lifetime of the electrolyte, which under normal
conditions, is only limited. By using volatile anions, even at 22 metal turnovers, the metal
layers deposited have internal compressive stress. Volatile ions, in the sense of this invention,
are ions which form together with counter ion moieties, which are volatile at the temperature
the electrolyte is commonly used at. An example of such a volatile ion is acetate, which
forms under the plating conditions acetic acid. Since acetic acid has a vapor pressure of
16 hPa at 20 °C, it will evaporate from the electrolyte under the plating conditions, and can be
recovered from the exhaust air system.

According to an embodiment of the invention, the inventive electrolyte comprises a
compound a complexing agent selected from the group consisting of 2-hydroxy propionic
acid, propanedioic acid (malonic acid), EDTA, and amino acetic acid. The complexing agent
may be in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably
between 0.2 mol/L and 0.4 mol/L.

The inventive electrolyte comprises an accelerator, which preferably is selected from
the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The
accelerator can be in the electrolyte in a concentration of between 0.05 mmol/L and 0.1
mol/L, preferably between 0.005 mol/L and 0.025 mol/L.

The metal to be deposited by the inventive electrolyte can be selected from the group
consisting of nickel, copper, cobalt, boron, silver, palladium and gold. The metal to be
deposited may also be alloys such as nickel/cobalt, nickel/phosphorus, cobalt/phosphorus,
nickel/boron or the like. The deposition of nickel/PTFE-layers or nickel/boron
carbide/graphite-layers from dispersion baths is also possible using the inventive electrolyte.

The inventive electrolyte can have a pH-value within a range of between pH 4 and pH
7, preferably within pH 4 and pH 6. It is preferred that the inventive electrolyte is slightly
acidic. The electrolyte may comprise pH adjusting compounds, like acids, bases, and/or
buffers to control the pH of the electrolyte.
The electrolyte may comprise organic and inorganic acids. Examples of these acids are sulfuric acid, acetic acid, lactic acid, citric acid, hypophosphorus acid, sulfonic acids or combinations of these. The electrolyte may also comprise bases such as sodium carbonate, ammonium hydroxide, sodium hydroxide, potassium hydroxide, lithium hydroxide, or combinations thereof. The electrolyte may comprise an acetic acid/acetate buffer, or a citric acid/citrate buffer.

According to another embodiment of the invention, the electrolyte may comprise as an additional stabilizer, a β-amino acid. Preferably useful are, β-amino acids having a pKₐ value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, 3-amino propionic acid (β-alanin), 3-aminobutyric acid, 3-amino-4-methylI valeric acid and 2-aminoethane-sulfonic acid (Taurin) are useful as additional stabilizers. The β-amino acid may be used in the inventive electrolyte within a range of 1 mg/L to 5 g/L, preferably 100 mg/L to 2 g/L, and even more preferred 200 mg/L to 1.5 g/L.

The electrolyte of the invention may comprise an organic stabilizer comprising an organic molecule, which is the condensation product (adduct) of at least one β-amino acid and at least one carboxyl component. This may be introduced into the aqueous medium as the free carboxylic acid or a salt thereof. The condensation product of the β-amino acid (e.g. β-alanine) and a carboxylic functional group derived from the carboxylic acid or its salt, is a β-amide. The condensation product is a monomeric, oligomeric and/or polymeric form, i.e., as the N-terminal amide of a β-amino acid monomer, dimer, trimer, oligopeptide or polypeptide. The condensation product of the β-amino acid can be present in the inventive electrolyte within a range of 1 mg/L to 5 g/L, preferably 100 mg/L to 2 g/L, and even more preferred 200 mg/L to 1.5 g/L.

The addition of a pre mixture of a β-amino acid in the inventive electrolyte, e.g. β-alanine, with a carboxylic acid, e.g. lactic acid, glycine, or malic acid, increases the stabilizing effect and can be beneficially used as a second stabilizer. It has been discovered that the carboxylic acid reacts with β-amino acids to form amide structures, which is deemed to be the reason for the enhanced stabilizing effect.
In preferred embodiments of the invention, the carboxylic acid may be a compound selected from the group consisting of acrylic acids, aromatic carboxylic acids, fatty acids, aliphatic carboxylic acids, keto acids, dicarboxylic acids, tricarboxylic acids, straight chain carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, and alpha-hydroxy acids. It is also possible to use other organic compounds having a carboxylic functional group. In particular, the salts of carboxylic acids (carboxylate anion -\( \text{RCO}_2^- \)) can be used.

The electrolyte according to this invention may additionally comprise an inorganic stabilizer, preferably antimony. Such an inorganic stabilizer can be present in a concentration of between 0.05 mg/L and 0.5 g/L, preferably between 0.5 mg/L and 0.1 g/L.

Yet in another embodiment of the invention the electrolyte may comprise three different stabilizers, one being a phosphine according to the general Formula I (e.g. PTA), a second one being a β-amino acid, and a third one being an inorganic stabilizer (e.g. antimony).

The inventive electrolyte deposits a metal layer on a surface of a substrate, wherein the phosphorous content of the metal layer is 2-6%, 6-10% or >10.5%. The amount of phosphorous in the deposit has a considerable effect on the properties of the metal layer. A high phosphorous content of the metal layer leads to improved properties, for example improved corrosion resistance. A lower phosphorous content in the metal layer has, for example, improved hardness.

A further property of a metal layer, according to the present invention, is that it is very passive. Another further advantage is that the metal layers have good residual compressive stress.

It is possible to yield metal layers having various phosphorus content by using a stabilizer according to the present invention: low phosphorus, 3-5% (crystalline); middle phosphorus, 5-7 (up to 9) % (partially crystalline); high phosphorus, >10% (amorphous).
According to another embodiment of the invention, the electrolyte may comprise an alkali metal halogenide and/or an alkali metal halogenate, i.e. a salt of an alkali metal with a halogen or a conjugated base of a halogen acid, wherein the halogen has an oxidation state of +5. Such halogen and/or halogen oxygen compounds may be present in the inventive electrolyte in a concentration of between ≥ 0.05 g/L and ≤ 5 g/L, preferably between ≥ 0.1 g/L and ≤ 2 g/L. While not being bound to this theory, it is assumed that these compounds act as thermal stabilizers, by which deposition of nickel on the heating elements or areas of local overheating is avoided. Examples of alkali metal halogenides and/or an alkali metal halogenates are potassium iodite, potassium iodate, sodium iodite, sodium iodate, potassium chloride, potassium chlorate, sodium bromide, lithium chloride, lithium iodate, lithium chlorate, or mixtures thereof.

The inventive method for the electroless deposition of a metal layer on a substrate comprises the steps of: contacting the substrate to be plated with an electrolyte comprising: a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer; characterized in that the electrolyte comprises phosphaadamantane, as a stabilizer, according to the general Formula I:

\[
\text{\textbf{(Formula I)}}
\]

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms.

According to an embodiment of the inventive method, the substrate is contacted with the electrolyte at a temperature within the range of between >20 °C and ≤ 100 °C, preferably between >25 °C and ≤ 95 °C, e.g. between >70 °C and ≤ 91 °C.
According to another embodiment of the inventive method, the substrate is contacted with the electrolyte for a time between $\geq 1$ s and $\leq 480$ min, preferably between $\geq 10$ s and $\leq 240$ min.

The inventive electrolyte, as well as the inventive method, for the electroless deposition of metal layers on substrates is explained in terms of examples in the following, while the electrolyte and the method cannot be restricted to only these embodiments.

In preferred embodiments, the electrolyte of the invention contains ions of at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. Sources for these metal ions are salts of the metals, which are present in the electrolyte as metal chlorides, metal sulfates, metal acetates, metal nitrates, metal propionates, metal formates, metal oxalates, metal citrates, and metal ascorbinates of the respective metals. The metal ions are present in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. The electrolyte comprises at least one reducing agent from the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, other organic boranes, or mixtures thereof. The reducing agent may be present in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. The electrolyte comprises a complexing agent that is selected from the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, amino acetic acid, and mixtures thereof. The complexing agent is present in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably between 0.2 mol/L and 0.4 mol/L. The electrolyte comprises an accelerator selected from the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator is present in the electrolyte in a concentration of between 0.05 mmol/L and 0.1 mol/L, preferably, between 5 mmol/L and 0.25 mol/L. The electrolyte comprises at least a phosphaadamantane, as a stabilizer, according to general Formula I:
wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms. The phosphaadamantane is present within a range of $>$0.05 mg/L and $\leq 100$ mg/L, preferably between $>$0.1 mg/L and $\leq 25$ mg/L, most preferably between $>$0.5 mg/L and $\leq 10$ mg/L. The use of a phosphaadamantane, according to general Formula I, as stabilizer results in a more even deposition, having less nodules.

According to another embodiment, the electrolyte of the invention contains ions of at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. Sources for these metal ions are salts of the metals, which are present in the electrolyte as metal chlorides, metal sulfates, metal acetates, metal nitrates, metal propionates, metal formates, metal oxalates, metal citrates, and metal ascorbinates of the respective metals. The metal ions are present in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. The electrolyte comprises at least one reducing agent from the group consisting of sodium hypophosphate, formaldehyde, dimethylaminoborane, aminoborane, other organic boranes, or mixtures thereof. The reducing agent may be present in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. The electrolyte comprises a complexing agent that is selected from the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, amino acetic acid, and mixtures thereof. The complexing agent is present in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably between 0.2 mol/L and 0.4 mol/L. The electrolyte comprises an accelerator selected from the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator is present in the electrolyte in a concentration of...
between 0.05 mmol/L and 0.1 mol/L, preferably, between 5 mmol/L and 0.25 mol/L. The electrolyte comprises at least a phosphaadamantane, as a stabilizer, according to general Formula I:

![Phosphaadamantane](image)

(Formula I)

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms. The phosphaadamantane is present within a range of >0.05 mg/L and ≤100 mg/L, preferably between >0.1 mg/L and ≤25 mg/L, most preferably between >0.5 mg/L and ≤10 mg/L. As an additional stabilizer, the electrolyte comprises at least one β-amino acid having a pK\textsubscript{a}-value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, the electrolyte comprises at least one β-amino acid of the group consisting of 3-amino propionic acid (β-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin). The β-amino acid is present in this embodiment of the inventive electrolyte within a range of 1 mg/L to 2 g/l, preferably 100 mg/L to 1 g/l, and even more preferred 200 mg/L to 400 mg/L. The use of a combination of two stabilizers beneficially results in reduction of nodules in the plated deposit.

In another preferred embodiment the electrolyte of the invention contains ions of at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. Sources for these metal ions are salts of the metals, which are present in the electrolyte as metal chlorides, metal sulfates, metal acetates, metal nitrates, metal propionates, metal formates, metal oxalates, metal citrates, and metal ascorbinates of the respective metals. The metal ions are present in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. The electrolyte
comprises at least one reducing agent from the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, other organic boranes, or mixtures thereof. The reducing agent may be present in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. The electrolyte comprises a complexing agent that is selected from the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, amino acetic acid, and mixtures thereof. The complexing agent is present in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably between 0.2 mol/L and 0.4 mol/L. The electrolyte comprises an accelerator selected from the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator is present in the electrolyte in a concentration of between 0.05 mmol/L and 0.1 mol/L, preferably, between 5 mmol/L and 0.25 mol/L. The electrolyte comprises at least a phosphaadamantane, as a stabilizer, according to general Formula 1:

(Formula I)

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms. The phosphaadamantane is present within a range of >0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between >0.5 mg/L and ≤ 10 mg/L. As an additional stabilizer, the electrolyte comprises antimony, an inorganic stabilizer. Antimony is present in a concentration of between 0.05 mg/L and 0.5 g/l, preferably 0.5 mg/L and 0.1 g/l. The antimony is added to the electrolyte as water soluble salt, preferably as chloride, sulfate, acetate, nitrate, propionate, formate, oxalate, citrate, ascorbate, or a mixture of these.
In a preferred embodiment of the invention, the electrolyte contains ions of at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. Sources for these metal ions are salts of the metals, which are present in the electrolyte as metal chlorides, metal sulfates, metal acetates, metal nitrates, metal propionates, metal formates, metal oxalates, metal citrates, and metal ascorbinates of the respective metals. The metal ions are present in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. The electrolyte comprises at least one reducing agent from the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, other organic boranes, or mixtures thereof. The reducing agent may be present in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. The electrolyte comprises a complexing agent that is selected from the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, amino acetic acid, and mixtures thereof. The complexing agent is present in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably between 0.2 mol/L and 0.4 mol/L. The electrolyte comprises an accelerator selected from the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator is present in the electrolyte in a concentration of between 0.05 mmol/L and 0.1 mol/L, preferably, between 5 mmol/L and 0.25 mol/L. The electrolyte comprises at least a phosphaadamantane, as a stabilizer, according to general Formula 1:

\[
\begin{align*}
&N_1N_2N_3N_4 \quad \text{(Formula I)} \\
&\text{wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms. The phosphaadamantane is present within a range of } >0.05 \text{ mg/L and } \leq
\end{align*}
\]
100 mg/L, preferably between \( \geq 0.1 \) mg/L and \( \leq 25 \) mg/L, most preferably between \( >0.5 \) mg/L and \( < 10 \) mg/L. As an additional stabilizer, the electrolyte comprises at least one \( \beta \)-amino acid having a \( pK_a \)-value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, the electrolyte comprises at least one \( \beta \)-amino acid selected from the group consisting of 3-amino propionic acid (\( \beta \)-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin). The \( \beta \)-amino acid is present in this embodiment of the inventive electrolyte within a range of 1 mg/L to 2 g/l, preferably from 100 mg/L to 1 g/l, and even more preferred from 200 mg/L to 400 mg/L. As a third stabilizer, the electrolyte comprises antimony as an inorganic stabilizer. Antimony is present in a concentration of between 0.05 mg/L and 0.5 g/l, preferably between 0.5 mg/L and 0.1 g/l. The antimony is added as a water soluble salt, preferably as a chloride, sulfate, acetate, nitrate, propionate, formate, oxalate, citrate, ascorbinate, or a mixture of these.

In preferred embodiments, the electrolyte contains a carboxyl component. For example, the electrolyte formulation may contain a monocarboxylic, dicarboxylic, or tricarboxylic organic acid. This component can comprise an aryl carboxylic acid, an aliphatic carboxylic acid, or a heterocyclic carboxylic acid. Among suitable aliphatic carboxylic acids are fatty acids, \( \alpha \)-hydroxycarboxylic acids, including \( \alpha \)-hydroxy dicarboxylic acids, particularly \( C_1 \) to \( C_4 \), \( \alpha \beta \)-unsaturated carboxylic acids, particularly \( C_1 \) to \( C_4 \) and especially acrylic.

The inventive the electrolyte is essentially free of inorganic stabilizers, lead, bismuth, zinc and/or tin. The electrolyte composition is also essentially free of cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between -2 and +5. Essentially free means that these compounds cannot be detected by common and readily available analytical techniques used for electrolyte analysis.

**EXAMPLE 1:**

In a preferred embodiment of the invention, the electrolyte according to the present invention comprises:

- 13.03 g/l nickel sulfate;
- 1.925 mg/L potassium iodide;
17.27 g/l lactic acid;
5.94 g/l malic acid;
40.2 g/l sodium hypophosphite;
9.81 g/l sodium hydroxide; and
1.00 mg/L PTA;
wherein the pH is in a range of pH 4 to pH 7.

EXAMPLE 2:
A substrate (steel sheet) was brought into contact with an electrolyte, at a temperature between 80 °C and 94 °C, comprising:

8.8 g/l nickel acetate tertahydrate;
0.2 g/L potassium iodide;
30 g/L lactic acid;
2.5 g/L saccharine, sodium salt;
16 g/l sodium hydroxide solution, 33 % by weight;
30 g/L sodium acetate;
35 g/L sodium hypophosphite dihydrate;
2.0 mg/L PTA;

wherein the pH is in a range of pH 4 to pH 5, at a temperature between 80 and 94°C.

An aluminum panel was plated in an electrolyte with the above mentioned composition. The aluminum was treated according to the standard pre-treatment cycle before plating in the electroless nickel bath. A glossy nickel deposit, without nodules, was plated from this electrolyte with a plating speed of 6 - 8 μm/h, with a composition of 88 - 89 % by weight nickel, and 11 - 12 % by weight of phosphorous.

EXAMPLE 3:
In another preferred embodiment of the invention, the electrolyte according to the present invention comprises:

8.8 g/L nickel acetate tertahydrate;
0.2 g/L potassium iodide;
30 g/L lactic acid;
2.5 g/L saccharine, sodium salt;
16 g/L sodium hydroxide solution, 33 % by weight;
35 g/L sodium hypophosphite dihydrate;
0.5 mg/L PTA;
15 mg/L potassium antimony tartrate;
wherein the pH is in a range of pH 4.0 to pH 5 at a temperature between 80 °C and 94°C. A steel panel was plated in an electrolyte with the above mentioned composition. A glossy nickel deposit was plated from this electrolyte with a plating speed of $8 - 10 \, \mu\text{m}/\text{h}$, with a composition of 88 - 89 % by weight nickel, and 10 - 11.5 % by weight of phosphorous.

EXAMPLE 4:

In another preferred embodiment of the invention, the electrolyte according to the present invention comprises:

8.8 g/L nickel sulfate;
0.1 mg/L potassium iodate;
25 g/L lactic acid;
1.0 g/L saccharine
2 g/L B-alanine;
15.5 g/L sodium hydroxide solution, 33 % by weight;
20 g/L sodium acetate;
35 g/L sodium hypophosphite dihydrate;
0.5 mg/L PTA;
18 mg/L potassium antimony tartrate;
wherein the pH is in a range of pH 4.0 to pH 5, at a temperature between 80 °C and 94 °C. An ABS plaque was plated in an electrolyte with the above mentioned composition. The ABS plaque was pre-treated in a standard POP (plating-on-plastic) pretreatment cycle before plating. A glossy nickel deposit was plated from this electrolyte with a plating speed of $8 - 10 \, \mu\text{m}/\text{h}$, with a composition of 90 - 91 % by weight nickel, and 9 - 10 % by weight of phosphorous.
IN THE CLAIMS:

1. An aqueous electrolyte composition for the electroless deposition of a metal layer on a substrate, comprising:
   a metal ion source of the metal to be deposited;
   a reducing agent;
   a complexing agent;
   an accelerator; and
   a stabilizer, characterized in that the stabilizer is a phosphaadamantane according to the general Formula I:

![Formula I]

(Formula I)

wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms.

2. The aqueous electrolyte composition according to claim 1, wherein the phosphaadamantane is present in a concentration between >0.05 mg/L and ≤ 100 mg/L.

3. The aqueous electrolyte composition according to claim 2, wherein the phosphaadamantane is present in a concentration between >0.1 mg/L and ≤ 25 mg/L.

4. The aqueous electrolyte composition according to claim 3, wherein the phosphaadamantane is present in a concentration between >0.5 mg/L and ≤ 10 mg/L.
5. The aqueous electrolyte composition according to claim 1, wherein the metal to be deposited is at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, and gold.

6. The aqueous electrolyte composition according to claim 1, wherein the accelerator is selected from the group consisting of saccharine, hydantoin, rhodanine, carbamide, carbamide derivates and mixtures thereof.

7. The aqueous electrolyte composition according to claim 1, wherein the electrolyte is essentially free of inorganic stabilizers, lead, bismuth, zinc and/or tin.

8. The aqueous electrolyte composition according to claim 1, wherein the composition is essentially free of cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between -2 and +5.

9. The aqueous electrolyte composition according to claim 1, further comprising at least one additional carboxylic acid and/or at least one salt of a carboxylic acid.

10. The aqueous electrolyte composition according to claim 9, wherein the carboxylic acid is selected from the group consisting of acrylic acids, aromatic carboxylic acids, fatty acids, aliphatic carboxylic acids, keto acids, dicarboxylic acids, tricarboxylic acids, straight chained carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, ct-hydroxy acids, and mixtures thereof.

11. The aqueous electrolyte composition according to claim 1, wherein the pH-value of the composition is in the range of between pH 4 and pH 7.

12. The aqueous electrolyte composition according to claim 1, wherein the reducing agent is selected from the group consisting of sodium hypophosphite, formaldehyde, dimethyl aminoborane, amino borane, other organic boranes, and mixtures thereof.

13. The aqueous electrolyte composition according to claim 1, wherein the complexing agent is selected from the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA and amino acetic acid.
14. A method for the electroless deposition of a metal layer on a substrate comprising the steps of:
   contacting the substrate to be plated with an electrolyte comprising:
   a metal ion source of the metal to be deposited;
   a reducing agent;
   a complexing agent;
   an accelerator; and
   a stabilizer, characterized in that the electrolyte comprises phosphaadamantane, as a stabilizer, according to the general Formula I:

   \[
   \begin{align*}
   &N \quad 3 \\
   &\text{P} \quad 2 \\
   &4 \quad 1 \\
   &5 \\
   &6
   \end{align*}
   \]

   \text{(Formula I)}

   wherein the hydrogen atoms on carbon atoms 1 to 6 may independently from each other be substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atoms.

15. The method according to claim 14, wherein the substrate is contacted with the electrolyte at a temperature within the range of between >20 °C and ≤ 85 °C.

16. The method according to claim 15, wherein the substrate is contacted with the electrolyte at a temperature within the range of between ≥ 25 °C and ≤ 70 °C.

17. The method according to claim 14, wherein the substrate is contacted with the electrolyte for a time between ≥ 1s and ≤ 180 min.
18. The method according to claim 17, wherein the substrate is contacted with the electrolyte for a time preferably between \( \geq 10 \text{s} \) and \( \leq 60 \text{ min} \).

19. The method according to claim 14, wherein the stabilizer in the electrolyte composition is 1,3,5-triaza-7-phosphatricyclo[3,3,1,1]decane (F\( \text{T} \)A).
INTERNATIONAL SEARCH REPORT
PCT/US16/55655

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) C23C 18/34, 18/40, 18/44 (2016.01)
CPC C23C 18/34, 18/40, 18/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C23C 18/34, 18/40, 18/44 (2016.01)
CPC: C23C 18/34, 18/40, 18/44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US 2015/0167175  A1 (ENTHONE INC.)  18 June 2015; abstract; paragraphs [0016], [0024], [0036], [0157]; claims 7-13, 16-17</td>
<td>1-19</td>
</tr>
<tr>
<td>Y</td>
<td>MOHR, F et al. Organometalic Gold(I) and Gold(III) Complexes Containing 1,3,5-Triaza-7-phosphaadamantane (TPA): Examples of Water-Soluble Organometalic Gold Compounds. Organometallics, Vol. 25, 2006, pp. 644-648; page 644, column 2, paragraph 1; page 645, scheme 1</td>
<td>1-19</td>
</tr>
</tbody>
</table>

* Further documents are listed in the continuation of Box C. See patent family annex.

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