(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 875 168 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
20.12.2017 Bulletin 2017/51

(21) Application number: **13820572.9**

(22) Date of filing: **17.07.2013**

(51) Int Cl.:
C23C 18/16 *(2006.01)* ***C23C 18/32*** *(2006.01)*
C23C 18/36 *(2006.01)* ***C23C 18/54*** *(2006.01)*

(86) International application number:
PCT/US2013/050932

(87) International publication number:
WO 2014/015063 (23.01.2014 Gazette 2014/04)

(54) **ELECTROLESS NICKEL COATINGS AND COMPOSITIONS AND METHODS FOR FORMING THE COATINGS**

CHEMISCHE VERNICKELUNGSBESCHICHTUNGEN SOWIE ZUSAMMENSETZUNGEN UND VERFAHREN ZUR BILDUNG DERSELBEN

REVÊTEMENTS AUTOCATALYTIQUES DE NICKEL ET COMPOSITIONS ET PROCÉDÉS DE FORMATION DESDITS REVÊTEMENTS

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **17.07.2012 US 201261672584 P**

(43) Date of publication of application:
27.05.2015 Bulletin 2015/22

(73) Proprietor: **Coventya, Inc.**
Brooklyn Heights, OH 44131-1049 (US)

(72) Inventors:
- **WOJCIK, Matthew, Joseph**
  Marcy, NY 13403 (US)
- **SCHAFFER, Ambrose**
  Canajoharie, NY 13317 (US)
- **LAPLANTE, Jean, M.**
  Oriskany, NY 13424 (US)

(74) Representative: **Maiwald Patentanwalts GmbH**
Elisenhof
Elisenstrasse 3
80335 München (DE)

(56) References cited:
JP-A- 2005 290 400
JP-A- 2007 154 223
KR-A- 20120 066 303
US-A- 4 483 711
US-A- 4 511 614
US-B2- 7 846 503

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 875 168 B1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] This application relates to electroless nickel coatings, methods for forming the electroless nickel coating, and electroless nickel baths for forming the electroless nickel coatings.

BACKGROUND

[0002] Electroless nickel plating is a widely utilized plating process, which provides a continuous deposit of a nickel metal or nickel/alloy coating on metallic or non-metallic substrates without the need for external electric plating current. Electroless plating has been described as a controlled autocatalytic chemical reduction process for depositing metals. The process involves a continuous buildup of a nickel coating on a substrate by immersion of the substrate in a nickel plating bath under appropriate electroless plating conditions. The plating baths generally comprise an electroless nickel salt and a reducing agent. Some electroless nickel baths use hypophosphite ions as a reducing agent, and during the process, the hypophosphite ions are oxidized to orthophosphite ions, and the nickel cations in the plating bath are reduced to form a nickel phosphorous alloy as a deposit on the desired substrate surface. As the reaction proceeds, the level of orthophosphite ions in the bath increases, and the orthophosphite ions often are precipitated from the plating solutions as insoluble metal orthophosphites. Typically, the source of nickel ions in the electroless plating baths described in the prior art has included nickel chloride, nickel sulfate, nickel bromide, nickel fluoroborate, nickel sulfonate, nickel sulfamate, and nickel alkyl sulfonates.

[0003] In order to have a continuous and consistent electroless plating process, the reactants must be replenished. The frequency at which additions of the reactants are made to the bath depends on how far the concentrations of the reacting species can be allowed to vary from their optimum concentrations without adversely affecting the plating process, or concurrently the deposit. The electroless plating reaction not only yields a nickel alloy deposit; it also generates by-products, which accumulate in solution. As the concentration of the by-products increase, their influence on the plating reaction also increases.

[0004] Electroless nickel-phosphorous coatings can be chemically treated, e.g., etched, to produce black coatings (Ni-P black). These black electroless nickel coatings can act as efficient absorbers and be used as very low reflectance coatings in optical instruments and sensors. Chemical etching of electroless nickel-phosphorous coatings typically involves acid etching of low (1-3% phosphorous) or medium-low (3-6% phosphorous) nickel phosphorous alloys. Higher phosphorous content alloys are not suitable because they are too corrosion resistant to blacken as result of acid etching.

[0005] Japanese patent application JP 2007/7154223 A provides an electroless nickel-plating liquid containing no lead, and a plating method using the same.

[0006] US patent application US 2004/0144285 A1 discloses an electrolyte for electroless deposition of metal layers with internal compressive stresses containing a metal base salt, a reducing agent, a complexing agent, an accelerator and a stabilizer, where preferably nickel, copper, silver or gold, especially preferably nickel is used as metal.

[0007] Japanese patent application JP 2005/ 290400 A provides an electroless nickel (alloy) plating bath capable of achieving satisfactory formation of plating film and satisfactory continuous use of the plating bath without substantially incorporating lead etc. which are hazardous substances therein. The electroless nickel plating bath contains a water-soluble nickel salt, a reducing agent, molybdenum, and bismuth and the electroless nickel (alloy) plating bath contains further an alloying metal salt in addition thereto.

[0008] US patent 4,511,614 discloses a process for producing an optically black coating having high absorptivity and emissivity values utilizing an electroless nickel plating process, and to a substrate provided with said black coating.

SUMMARY

[0009] The present invention is directed to a method for forming a multilayer electroless metal coating on a substrate, the method comprising:

i. contacting the substrate with a first electroless nickel plating bath to form a first eletroless nickel coating on the substrate, the first electroless nickel coating having a phosphorus content of 7% to 13% by weight

ii. contacting the substrate coated with the first electroless coating with a second aqueous electroless nickel plating bath to form a second electroless nickel coating over the first electroless coating, the second electroless coating having a phosphorous content of 8% to 11%, the second bath including nickel, a hypophosphorous reducing agent, 40 ppm to 100 ppm zinc, at least one of a complexing agent, chelating agent, and/or pH buffer, and 5 ppm to 30 ppm bismuth stabilizer, wherein the bath is free of an organic sulfur compound;

iii. etching the second electroless nickel coating with an etchant agent to provide the coated substrate with a black

surface or contacting the substrate coated with the first and second electroless nickel coatings with an electroless copper plating bath to provide a copper top coat.

[0010] In a preferred embodiment of the method of the present invention, the hypophosphorous reducing agent is selected from the group consisting of sodium hypophosphite, potassium hypophosphite, ammonium hypophosphite, and combinations thereof.

[0011] In a preferred embodiment of the method of the present invention, the second electroless nickel plating bath includes at least one pH buffer, complexing agent, or chelating agent selected from the group consisting of acetic acid, formic acid, succinic acid, malonic acid, an ammonium salt, lactic acid, malic acid, citric acid, glycine, alanine, glycolic acid, lysine, aspartic acid, ethylene diamine tetraacetic acid (EDTA), and combinations thereof.

[0012] In a preferred embodiment of the method of the present invention, the method comprises at least two of a pH buffer, complexing agent, and/or chelating agent.

[0013] In a preferred embodiment of the method of the present invention, the nickel is provided in the second electroless plating bath in the form of a water soluble nickel salt.

[0014] In a preferred embodiment of the method of the present invention, the nickel salt is selected from the group consisting of nickel chloride, nickel bromide, nickel iodide, nickel acetate, nickel malate, and nickel hypophosphite.

[0015] In a preferred embodiment of the method of the present invention, the pH of the second electroless nickel plating bath is maintained at 4.5 to 5.0 and the temperature at 79°C to 93°C.

[0016] In a preferred embodiment of the method of the present invention, the second electroless nickel plating bath comprises 2 g/l to 10 g/l nickel, 20 g/l to 35 g/l of the hypophosphorous reducing agent, 1 g/l to 75 g/l each of the complexing agent, chelating agent, and/or pH buffer.

[0017] In a preferred embodiment of the method of the present invention, the second electroless nickel plating bath comprises lactic acid, acetic acid, malic acid, succinic acid, sodium hypophosphite, ammonium hydroxide, nickel, zinc, and ethylenediamine tetraacetic acid.

[0018] In a preferred embodiment of the method of the present invention, the etchant agent comprises an iron blackening agent and an acid, preferably, the etchant agent comprises ferric sulfate and hydrochloric acid.

[0019] In a preferred embodiment of the method of the present invention, the substrate coated with the first and second electroless nickel coatings is contacted with an acid solution prior to contacting the substrate with the electroless copper plating bath.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

Fig. 1 illustrates a flow diagram showing a black electroless nickel plating process in accordance with an embodiment.

Fig. 2 illustrates a flow diagram showing an electroless copper-nickel plating process in accordance with another embodiment.

Fig. 3 illustrates a graph comparing the rates of deposition per metal turnover (MTO) of electroless nickel coatings formed using an electroless nickel plating bath in accordance with an embodiment of the application and using a commercially available electroless nickel plating bath.

Fig. 4 illustrates a graph showing the percent phosphorous content per metal turnover (MTO) of electroless nickel deposits formed using an electroless nickel plating bath in accordance with an embodiment of the application.

Fig. 5 illustrates a photograph comparing black electroless nickel coatings subjected to neutral salt spray formed using an electroless nickel plating bath in accordance with an embodiment of the application and using a commercially available electroless nickel plating bath.

Fig. 6 illustrates a photograph showing an electroless copper-nickel multilayer coating prepared in accordance with an embodiment.

Fig. 7 illustrates a photograph comparing various electroless nickel deposits coated with an electroless copper coating.

DETAILED DESCRIPTION

[0021] In the specification and the claims, which follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

[0022] The singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

[0023] "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

[0024] As used herein, the term "solvent" can refer to a single solvent or a mixture of solvents.

[0025] It is also understood that terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms. Furthermore, whenever a particular feature of the invention is said to comprise or consist of at least one of a number of elements of a group and combinations thereof, it is understood that the feature may comprise or consist of any of the elements of the group, either individually or in combination with any of the other elements of that group.

[0026] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about", is not to be limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value.

[0027] Embodiments described herein relate to methods of forming multilayer electroless nickel coatings on a substrate.

[0028] The electroless nickel plating bath used to form the electroless nickel coatings, multilayer electroless nickel coatings, and/or black electroless nickel coatings described herein is free of sulfur compounds, such as organic sulfur compounds, and can form a sulfur-free electroless nickel coatings, which can be uniformly etched or blackened to provide a black electroless nickel coating. The electroless nickel plating bath replaces sulfur compounds, which have been typically employed in solutions for forming black electroless nickel coatings, with metallic containing compounds, such as zinc and bismuth. Replacement of the sulfur compounds with the metallic containing compound allows for improvements in operability, stability, and uniformity over current black electroless nickel plating methods.

[0029] Sulfur containing electroless nickel plating baths used to form black electroless nickel coatings require the addition of spent components (e.g., nickel) at precise moments (e.g., additions made at last 5-10 minutes of plating to insure sulfur codeposition) in order to achieve a repeatable coloring effect. If the timing is not precise, the resulting effect will alter the black coloring to the point of possibly failing to produce the desired color. The proposed compositions, baths, and methods require no such addition, besides the normal addition to replenish spent components, as per the normal operation of an electroless nickel plating bath.

[0030] Electroless nickel plating baths having a sulfur based chemistry also rely on the codeposition of the sulfur directly into the electroless nickel deposit. The result is often an uneven distribution of the sulfur across the substrate surface, resulting in a streaky, nonuniform coloring. The electroless nickel plating baths described herein do not rely on the presence of sulfur for co-deposition, and instead rely on the concentration of the available bismuth to allow for blackening of the electroless nickel plating deposit when exposed to an etchant. The presence of organic-sulfur compounds can cause decomposition of the sulfur compound at cathode surfaces forming very small particles of nickel sulfide which in turn adversely affects ductility, internal stress, electrical conductivity and corrosion resistance of the deposit. The breakdown of the organic-sulfur compounds can result in byproducts that accumulate within the electroless nickel plating bath, which interferes with the deposition of the sulfur. This limits the potential age of the bath to 2 metal turnovers (MTOs) before issues begin to arise. The sulfur-free or non-sulfur containing electroless nickel plating baths have no such limitation, and can be plated out for at least 4 MTOs. During this time, there is no loss of uniformity or depth of color from makeup of electroless nickel deposit formed on a substrate from the electroless nickel plating bath.

[0031] Advantageously the inclusion of zinc in the electroless nickel plating bath causes electroless nickel deposit to be formed with an increased phosphorous content. Electroless nickel plating baths that include zinc can plate at a slower rate. Plating at a slower rate causes a black electroless nickel deposit to be formed with an increased overall phosphorous content (*e.g.*, at least 5% increase) compared to electroless nickel deposits formed using typical sulfur based black electroless nickel chemistry, which contains on average 1-5% phosphorous. Black electroless nickel deposits with an increased phosphorous content prepared using the sulfur-free electroless nickel plating baths described herein are more corrosion resistant than electroless nickel deposits of other available sulfur based chemistry.

[0032] In some embodiments, the electroless nickel plating bath used to form the electroless nickel coating, multilayer coating, or black coating is free of a sulfur compound and can include an aqueous solution of nickel, a hypophosphorous reducing agent, zinc, at least of one of a complexing agent, chelating agent, and/or pH buffer, and a bismuth stabilizer.

[0033] The nickel can be provided in the bath in the form of a water soluble nickel salt. The water-soluble nickel salts can include those which are soluble in the plating bath and which can yield an aqueous solution of a predetermined concentration. The nickel salt can be selected from the group consisting of nickel chloride, nickel bromide, nickel iodide, nickel acetate, nickel malate, a nickel hypophosphite and combinations thereof. The water-soluble nickel salts may be used alone or as a mixture.

[0034] In some embodiments, the concentration of nickel in the electroless nickel plating bath can be from about 1 g/L to 70 g/L. In other embodiments, the concentration of nickel in the electroless nickel plating bath can be about 4 g/L to about 6g/L. Electroless nickel coatings formed from sulfur-free electroless nickel baths that include about 4 g/l showed decrease in blackening; whereas electroless nickel coatings formed from sulfur-free electroless nickel baths with 8 g/l showed no increase in the resulting black deposit.

[0035] The hypophosphorous reducing agent used in the bath can include any of a variety of hypophosphorous reducing agents used in known types of the electroless nickel plating baths. In some embodiments, the hypophosphorous reducing

agent is selected from the group consisting of sodium hypophosphite, potassium hypophosphite, ammonium hypophosphite, and combinations thereof.

[0036] The concentration of the hypophosphorous reducing agent in the electroless nickel plating can differ with the respective types of hypophosphorous reducing agent and can be adjusted to vary the concentration of the phosphorous in the electroless nickel coating that is formed using the bath. In some embodiments, the concentration of the hypophosphorous reducing agent in the electroless nickel plating bath can be about 15 g/L to about 40 g/L. In other embodiments, the concentration of the hypophosphorous reducing agent in the electroless nickel plating bath can be about 20 to about 35 g/L. A decrease in concentration of the hypophosphorous reducing agent from about 30 g/l to about 25 g/l can result in a decrease in phosphorous in the electroless nickel coating so formed by 2%. This decrease in phosphorous content can result in a deeper black being produced upon blackening of the coating.

[0037] The zinc or zinc ions can be incorporated into the electroless nickel plating bath by introducing a zinc compound into the bath. Examples of the zinc compound are zinc carbonate, zinc oxide, zinc chloride, zinc benzoate, zinc nitrate, zinc phosphate, zinc stearate, and zinc salicylate.

[0038] The concentration of zinc in the electroless nickel plating bath is about 40 ppm to about 100 ppm. A concentration of zinc in the electroless nickel plating bath below 40 ppm can result in a loss of color of the electroless nickel coating formed from the bath. A concentration of zinc in the electroless nickel plating bath above 100 ppm did not adversely affect color of the electroless nickel coating formed from the bath, but the plating rate substantially decreased.

[0039] The bismuth stabilizer can be incorporated into the electroless nickel plating bath by introducing a bismuth salt into the bath, such as bismuth trichloride or bismuth nitrate. The concentration of the bismuth stabilizer in the electroless nickel plating bath is about 5 ppm to about 30 ppm. The higher the concentration of bismuth stabilizer provided in the electroless nickel plating bath the deeper the black color that can be produced from an electroless nickel coating formed from the bath. At concentration of the bismuth stabilizer over about 30 ppm, the bath can become over-stabilized and further plating is inhibited.

[0040] A complexing agent or a mixture of complexing agents is included in the electroless nickel plating bath. Complexing agents as used herein can also include chelating agents. The complexing agents and/or chelating agents generally retard the precipitation of nickel ions from the plating solution as insoluble salts, such as phosphites, by forming a more stable nickel complex with the nickel ions and provide for a moderate rate of the reaction of nickel precipitation.

[0041] The complexing agents and/or chelating agents can be included in the plating bath in amounts sufficient to complex the nickel ions present in the bath and to further solubilize the hypophosphite degradation products formed during the plating process. Generally complexing agents and/or chelating agents are employed in amounts of up to about 200 g/l with amounts of about 1 to about 75 g/l being more typical. In other embodiments, the complexing agents and/or chelating agents are provided in the electroless nickel plating bath at amounts from about 20 to about 40 g/l.

[0042] A variety of complexing agents, used in known electroless nickel plating solutions, may be used. Specific examples of the complexing agents may include monocarboxylic acids, such as glycolic acid, lactic acid, gluconic acid or propionic acid, dicarboxylic acids, such as malic acid, malonic acid, succinic acid, tartaric acid, oxalic acid or adipic acid, aminocarboxylic acids, such as glycine or alanine, ethylene diamine derivatives, such as ethylenediamine tetraacetate, versenol (N-hydroxyethyl ethylenediamine-N,N',N'-triacetic acid) or quadrol (N,N,N', N'-tetrahydroxyethyl ethylene diamine), phosphnic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, ethylene diamine tetramethylene phosphonic acid and water-soluble salts thereof. The complexing agents may be used either alone or in combination.

[0043] Some complexing agents, such as acetic acid or succinic, for example, may also act as a pH buffering agent, and the appropriate concentration of such additive components can be optimized for any plating bath after consideration of their dual functionality.

[0044] In some embodiments, at least one pH buffer, complexing agent, or chelating agent can be selected from the group consisting of an acetic acid, formic acid, succinic acid, malonic acid, an ammonium salt, lactic acid, malic acid, citric acid, glycine, alanine, glycolic acid, lysine, aspartic acid, ethylene diamine tetraacetic acid (EDTA), and combinations thereof. In some embodiments, mixtures of 2 or more of the above pH buffers, complexing agents, and/or chelating agents can be used in the electroless nickel plating bath described herein, with each pH buffer, complexing agent, and/or chelating agent being provided at a concentration of about of about 1 to about 75 g/l.

[0045] The plating bath may also contain, in addition to the above components, additives with various kinds of purposes so long as the properties of the plating bath are not deteriorated.

[0046] The aqueous electroless nickel plating baths can be operated or maintained at a pH of about 4.5 to about 5.0 during electroless nickel plating of the substrate. With this range of pH, the reducing reaction by the hypophosphorous reducing agent is allowed to occur efficiently to prevent decomposition of the hypophosphorous reducing agent as well as to prevent the performance of precipitation for plating from being deteriorated and to prevent the plating bath from being decomposed. Moreover, with this range of pH, it is possible to prevent the plating bath from being lowered in stability as a result of the excessively high reducing potential of the reducing agent.

[0047] At least one pH adjustment agent can be used to adjust the pH to the above range. When the pH of the bath is too high, it can be adjusted by adding, for example, an acid. When the pH of the bath is too low, it can be adjusted by

adding, for example, ammonium hydroxide.

[0048] The stability of the operating pH of the plating bath can be controlled by the addition of various buffer compounds such as acetic acid, propionic acid, boric acid, or the like, in amounts up to about 30 g/l with amounts of from about 2 to about 30 g/l being typical. As noted above, some of the buffering compounds such as acetic acid and succinic acid may also function as complexing agents.

[0049] In accordance with the methods described herein, a substrate can be plated with the electroless nickel plating bath to provide an electroless nickel deposit or coating on the substrate. The substrate can be any substrate capable of supporting the electroless nickel coating but is typically a material for which the electroless nickel coating displays sufficient affinity to form a stable coating thereupon. Substrates may be inorganic materials, such as metals, or organic materials such as plastics, or composite materials, for example, organic polymer comprising inorganic filler. In one embodiment, the substrate is a metal substrate. Non-limiting examples of metal substrates include iron, chromium, nickel, cobalt, copper, aluminum, titanium, and the like. In another embodiment, the substrate comprises steel. In one embodiment, the substrate comprises low alloy steel, for example low alloy carbon steel.

[0050] The substrate can be plated by contacting the substrate with or immersing the substrate in the plating bath for a duration time effective to form an electroless nickel coating or deposit on a desired surface of the substrate. In some embodiment, the substrate can be cleaned or pre-processed prior to plating. During plating, the bath can be maintained at a bath temperature about 175°F to about 200°F. The duration of contact of the electroless nickel plating bath with the substrate being plated will determine the thickness of the electroless nickel coating. Typically, a contact time can range from as little as about one minute to several hours or even several days.

[0051] During the deposition of the electroless nickel deposit or coating, mild agitation can be employed. The mild agitation can be, for example, a mild air agitation, mechanical agitation, bath circulation by pumping, rotation of a barrel for barrel plating, etc. The electroless nickel plating bath also may be subjected to a periodic or continuous filtration treatment to reduce the level of contaminants therein. Replenishment of the constituents of the bath may also be performed, in some embodiments, on a periodic or continuous basis to maintain the concentration of constituents, and in particular, the concentration of nickel ions and hypophosphite ions, as well as the pH level within the desired limits.

[0052] The electroless nickel coated substrate so formed can be removed from the electroless nickel plating bath and rinsed, for example, with deionized water.

[0053] The electroless nickel coating formed on a surface of the substrate using the electroless nickel plating bath can have of relatively uniform thickness. In one embodiment, the electroless nickel coating can have an average thickness in a range from about 1 micron to about 250 microns. In another embodiment, the electroless nickel coating can have an average thickness in a range from about 1 micron to about 100 microns. In yet another embodiment, the electroless nickel coating can have an average thickness in a range from about 1 micron to about 10 microns. The electroless nickel coating can also have a phosphorous content of about 8% to about 11%.

[0054] In some embodiments, the electroless nickel coating can be a top coating that is plated over a mid-phosphorous (e.g., about 7% to about 9% phosphorous) or a high phosphorous (about 9% to about 13% phosphorous) electroless nickel under coating to form a duplex or multilayer electroless nickel deposit or coating. The duplex or multilayer electroless nickel coating can advantageously be blackened to form a black electroless nickel coating.

[0055] Fig. 1 illustrates a flow diagram showing a method 10 of preparing a black electroless nickel coating on a substrate. In the method 10, at step 12 a substrate can be contacted with a first electroless nickel plating bath, by, for example, immersing the substrate in the first electroless nickel plating bath, to form a first electroless nickel coating on the substrate. The first electroless nickel plating bath can include nickel, a hypophosphorous reducing agent, at least one of a complexing agent, chelating agent, or pH buffer, and optionally a sulfur compound, such as thiosulfates, thionic acid, or thiourea to provide a mid-phosphorous or high-phosphorous under coating.

[0056] An example of an electroless nickel plating bath that can be used to produce a high phosphorous electroless nickel coating can include about 6 g/l nickel, about 36 g/l sodium hypophosphite, about 20 g/l malic acid, about 15 g/l lactic acid, about 5 g/l succinic acid, and about 0.4 ppm lead.

[0057] An example of an electroless nickel plating bath that can be used to produce a mid phosphorous electroless nickel coating can include about 6 g/l nickel, about 30 g/l sodium hypophosphite, about 12 g/l malic acid, about 18 g/l lactic acid, about 14 g/l acetic acid, 1.0 ppm thiourea, and about 1.0 ppm lead.

[0058] The electroless nickel coating formed on a surface of the substrate using the first electroless nickel plating bath can have of relatively uniform thickness. In one embodiment, the electroless nickel under coating can have an average thickness in a range from about 5 micron to about 250 microns, or about 5 microns to about 100 microns. In some embodiments, the thickness of the electroless nickel under coating be at least two times, three times, four times, or five times greater than the thickness of the top coat. In yet another embodiment, the electroless nickel under coating can have an average thickness in a range from about 5 micron to about 15 microns. The electroless nickel coating has a phosphorous content of about 7% to about 13%.

[0059] After formation of the first electroless nickel under coating on the surface of the substrate, at step 14, the coated substrate can be removed from the first electroless nickel plating bath, optionally rinsed, and then contacted with the

second electroless nickel plating bath to form a second electroless nickel coating over the first electroless coating. The coated substrate can be contacted with the second electroplating bath by, for example, immersing the coated substrate in the second electroless nickel plating bath for a duration a time effective to form the second electroless nickel coating or top coating.

[0060] The second electroless nickel plating bath is different that the first electroless nickel plating bath and be formulated such that it is free of a sulfur compound as described above. In some embodiments, the second electroless nickel plating bath includes nickel, a hypophosphorous reducing agent, zinc, a bismuth stabilizer, and at least one of a complexing agent, chelating agent, or pH buffer, and is free of a sulfur compound. In other embodiments, the electroless nickel plating bath can include lactic acid, acetic acid, malic acid, succinic acid, sodium hypophosphite, ammonium hydroxide, nickel, zinc, and ethylenediamine tetraacetic acid. In still other embodiments, the electroless nickel plating bath can include about 2 g/l to about 10 g/l nickel, about 20 g/l to about 35 g/l of a hypophosphorous reducing agent, about 1 g/l to about 75 g/l each of the complexing agent, chelating agent, and/or pH buffer, about 40 ppm to about 120 ppm zinc, and about 5 ppm to about 30 ppm of a bismuth stabilizer.

[0061] The second electroless nickel coating formed on first electroless nickel coating using the second electroless nickel plating bath can have of relatively uniform thickness and an average thickness in a range from about 1 micron to about 100 microns. In some embodiments, the average thickness can be less than the thickness of the first electroless nickel coating and be in a range from about 1 micron to about 10 microns. The second electroless nickel coating can also have a phosphorous content of about 8% to about 11%.

[0062] Following formation of the second electroless nickel top coating over the first electroless nickel coating, at step 16, the multilayer or duplex coated substrate can be removed from the second electroless nickel plating bath, optionally rinsed, and then etched with an etching agent to provide the coated substrate with a black surface. The etchant agent can include an aqueous solution of an iron blackening agent and an acid. In some embodiments, the etchant agent can include an aqueous solution of ferric sulfate and hydrochloric acid. In still other embodiments, the etchant agent can include ferric sulfate, hydrochloric acid, and reaction enhancer, such as potassium iodate. The temperature of the etchant agent can be about 70°F to 90°F and the coated substrate can be immersed in the etchant agent for a duration of time effective to blacken the coating, for example, for about 1 minute to about 3 minutes.

[0063] On removal black electroless nickel coated substrate from the etchant agent, the substrate can be rinsed and dried. The black electroless coating so formed has a consistent uniform deposit of black electroless nickel with a uniform thickness and black coloring, which is streakless.

[0064] In other embodiments, the duplex or multilayer electroless nickel coating can advantageously be further plated with another material to modify the coating. Fig. 2 illustrates a flow diagram showing a method 20 of preparing an electroless copper-nickel coating on a substrate. In the method 20, at step 22 a substrate can be contacted with a first electroless nickel plating bath, by, for example, immersing the substrate in the first electroless nickel plating bath, to form a first electroless nickel coating on the substrate. The first electroless nickel plating bath can include nickel, a hypophosphorous reducing agent, at least one of a complexing agent, chelating agent, or pH buffer, and optionally a sulfur compound, such as thiosulfates, thionic acid, or thiourea to provide a mid-phosphorous or high-phosphorous under coating.

[0065] The electroless nickel coating formed on a surface of the substrate using the first electroless nickel plating bath can have of relatively uniform thickness. In one embodiment, the electroless nickel under coating can have an average thickness in a range from about 5 micron to about 250 microns, or about 5 microns to about 100 microns. In some embodiments, the thickness of the electroless nickel under coating be at least two times, three times, four times, or more greater that the thickness of the top coat. In yet another embodiment, the electroless nickel under coating can have an average thickness in a range from about 5 micron to about 15 microns. The electroless nickel coating has a phosphorous content of about 7% to about 13%.

[0066] After formation of the first electroless nickel under coating on the surface of the substrate, at step 24, the coated substrate can be removed from the first electroless nickel plating bath, optionally rinsed, and then contacted with the second electroless nickel plating bath to form a second electroless nickel coating over the first electroless coating. The coated substrate can be contacted with the second electroplating bath by, for example, immersing the coated substrate in the second electroless nickel plating bath for a duration a time effective to form the second electroless nickel coating or top coating.

[0067] The second electroless nickel plating bath is different that the first electroless nickel plating bath and be formulated such that it is free of a sulfur compound as described above. In some embodiments, the second electroless nickel plating bath is includes nickel, a hypophosphorous reducing agent, zinc, a bismuth stabilizer, and at least one of a complexing agent, chelating agent, or pH buffer, and is free of a sulfur compound. In other embodiments, the electroless nickel plating bath can include lactic acid, acetic acid, malic acid, succinic acid, sodium hypophosphite, ammonium hydroxide, nickel, zinc, and ethylenediamine tetraacetic acid. In still other embodiments, the electroless nickel plating bath can include about 2 g/l to about 10 g/l of nickel, about 20 g/l to about 35 g/l hypophosphorous reducing agent, about 1 g/l to about 75 g/l each of the complexing agent, chelating agent, and/or pH buffer, about 40 ppm to about 120 ppm

zinc, and about 5 ppm to about 30 ppm bismuth stabilizer.

[0068] The second electroless nickel coating formed on first electroless nickel coating using the second electroless nickel plating bath can have of relatively uniform thickness and an average thickness in a range from about 1 micron to about 100 microns. In some embodiments, the average thickness can be less than the thickness of the first electroless nickel coating and be in a range from about 1 micron to about 10 microns. The second electroless nickel coating has a phosphorous content of about 8% to about 11%.

[0069] Following formation of the second electroless nickel top coating over the first electroless nickel coating, at step 26, the multilayer or duplex coated substrate can be removed from the second electroless nickel plating bath, optionally rinsed, and then immersed in an acid solution, such as a hydrochloric acid solution, to reactivate the surface of the coating. Reactivation of the surface using an acid solution was found to advantageously enhance copper deposition in the subsequent copper coating step.

[0070] Following reactivation of the duplex coating, at step 28, the multilayer or duplex coated substrate can be removed from the acidic solution, optionally rinsed, and then contacted with an electroless copper plating bath by, for example, immersing the duplex coated substrate in the electroless copper plating bath. The electroless copper plating bath can include an aqueous solution of copper sulfate pentahydrate and sulfuric acid. The coated substrate can be immersed in the electroless copper plating bath for a duration of time effective to form a copper coating, for example, for about 1 minute to about 3 minutes.

[0071] On removal electroless copper-nickel coated substrate from the electroless copper plating bath, the substrate can be rinsed and dried. The electroless copper-nickel coating so formed had a consistent uniform deposit with a uniform thickness and copper coloring.

[0072] The following examples illustrate the electroless nickel plating solutions of the invention. Unless otherwise indicated in the following examples, in the written description and in the claims, all parts and percentages are by weight, temperatures are in degrees centigrade and pressure is at or near atmospheric pressure.

Example 1

[0073] A black electroless coating was prepared using a high phosphorous nickel undercoating, a sulfur free electroless nickel top coating, and an acidic iron sulfate etchant.

[0074] The high-phosphorous electroless nickel plating bath was prepared with the following formulation:

High Phosphorus electroless nickel plating bath	
Nickel Metal	6 g/l
Sodium Hypophosphite	36 g/l
Malic Acid	20 g/l
Lactic Acid	15 g/l
Succinic Acid	5 g/l
Lead	0.4 ppm
pH	4.6 -4.8
Temperature	190°F

[0075] The sulfur-free electroless nickel plating bath was prepared with the following formulation.

Sulfur-free electroless nickel plating bath	
Lactic Acid	20 g/l
Acetic Acid	28 g/l
Malic Acid	3 g/l
Succinic Acid	8 g/l
Sodium Hypophosphite	25 g/l
Ammonium Hydroxide	34 g/l
Nickel	6 g/l

(continued)

Sulfur-free electroless nickel plating bath	
Zinc	100 ppm
Bismuth Trichloride	15 ppm
EDTA	100 ppm
Temperature (EN Bath) = 192°F	
pH= 4.8	

[0076] The etchant agent for blackening the sulfur-free electroless nickel plating bath was prepared with the following formulation.

Etchant agent	
50% Ferric Sulfate	50% of total volume of
12M Hydrochloride Acid	2.5% of total Volume of
Potassium Iodate	50 ppm
Temperature (Blackening Agent) = 70°F	

[0077] An undercoat of the high phosphorous electroless nickel was plated on a steel substrate for a time of about 1 hour, to provide a high phosphorous electroless nickel coating having a thickness of about 0.50 mils. The steel substrate was then rinsed and placed in the sulfur-free electroless nickel plating bath for 30 minutes, to provide an electroless nickel top coat with a thickness of about 0.15 mils. The steel substrate was then removed from the sulfur-free electroless nickel bath, rinsed for 30 seconds, then submerged in the etchant solution for about 1 minute. The steel substrate was again removed, rinsed, and allowed to set for 24 hours for maximum hardness. The chemistry of the process allowed the electroless nickel coated steel substrate to be stored following the application of the undercoating for a later date, if the user desires. If this is the case, the electroless nickel coated steel substrate would need to be electrocleaned and reactivated in 50% HCl acid before the steel substrate can be submerged

[0078] A summary of the black electroless nickel plating process is shown below. Process:

1.) Appropriate clean cycle for substrate being plated.
2.) EN High Phosphorous bath - 60 mins.
3.) Rinse- 30 secs
4.) Electroclean-2 mins*
5.) Activation- 10 secs*
6.) Proposed Sulfur-free EN Bath- 30 mins
7.) Rinse- 30 secs
8.) Ferric Sulfate Solution-1 min
9.) Rinse 30 secs
10.) Blow dry parts

* These steps only need to be done if part is allowed to set for 1 hour or more before top coat is applied.

Example 2

[0079] Each component of the electroless solution was modified in an attempt to increase the black produced.

Lactic Acid

[0080] 20% increase showed no benefit, while a 20% decrease seemed to result in slight increase in black. Further removal of the Lactic acid, 40% and 60% decrease, resulted in no increase of the depth of the black, but the bath began to display stability issues.

Acetic Acid

[0081] 20% decreased had no effect on the final product. 20% increase caused slight increase in black. Further increase of Acetic Acid showed no benefit in overall deposit quality.

Malic Acid

[0082] Any increase of in Malic resulted in a decrease in the black coloring. When complete removal was trialed, the result was the best produce black coloring, but stability issues were seen when the levels dropped to under 3 g/l.

Glycine

[0083] Showed no effect on the black when the levels were increased or decreased. For this reason, Glycine was removed completely from the formula to lower potential cost.

Sodium Hypophosphite

[0084] Tested reduction in solution in an attempt to reduce the %P in the deposit. From the initial amount, the concentration was reduced to 25 g/l from 30 g/l, which resulted a drop in percent phosphorous by 2% in the final product. This drop resulted in a deeper black being produced.

Ammonium hydroxide

[0085] The concentration was adjusted in order to compensate for the increased Acetic Acid in solution. Trials to judge the effect that ammonia played in the solution, resulted in attempting to produce an ammonia-free chemistry, but the resulting solution would not blacken.

Nickel

[0086] Trials at 4 g/l showed decrease in blacking, where as a solution with 8 g/l showed no increase in the resulting black deposit

Succinic Acid

[0087] The Succinic acid was added to assist in controlling the phosphorus content and deepening the final color. Trialed concentrations that went up to 12 g/l. The result was a darker overall deposit up to 8 g/l, which gradually decrease as the concentrations exceed this amount.

EDTA

[0088] Increasing or decreasing the amount in solution showed no final effect on the black color. Amounts were left at initial level to ensure proper chelation of addition metals.

Zinc

[0089] When trials dropped this amount below 40 ppm, the result was a loss of color. Trials in which the amount was increased above 100 ppm, there was no effect on the black produced, but the plating rate drops sharply.

Bismuth Trichloride

[0090] Trials showed that higher the concentration that can be maintain, deeper the black that is produced. Although if you exceed 30ppm, the bath would become over-stabilized and further plating would be impossible. 15 ppm would allow for 1 hour of plating without any replenishment before an effect in the black color can be observed.

Example 3

[0091] Initial Testing on the life of the bath, showed that the bath is able to age out to at least 4 metal turnovers (MTOs) with no loss in color or uniformity compared to conventional electroless nickel baths, such as a sulfur-compound con-

taining, mid-phosphorous electroless nickel plating bath. The rate of deposition per metal turnover (MTO) of electroless nickel coatings formed using the sulfur-free electroless nickel plating bath was compared with the rate of deposition per metal turnover (MTO) using a commercially available electroless nickel plating bath. (Fig. 3) The test was repeated in triplicate to validate this information. Solutions were also tested for percent Phosphorous at 0 and 4 MTOs. The result showed that their respective phosphorous concentrations were 10.8% and 8.5% respectively. (Fig. 4) Intrinsic Stress was also measured at 0 and 4 MTOs to determine the effect the higher levels of Bismuth would have on the bath. The values were measured to be 1500 PSI compressive in both cases. Further testing was also performed to determine proper adhesion. In this case, the deposit at 0 and 4 MTOs were subjected to the Quench Test (the rapid heating then cooling of the deposit), bend test (the deposit was bent to 90° and examined to look for poor adhesion for deposit to substrate), and the Scribe test (In which the deposit's surface is marred and then examined for cracks due to stress). The proposed chemistry passed all the tests. When deposit is allowed 24 hrs to set, the color passes the Eraser test (>10 swipes of an eraser across the surface and examined for abrasion). Moreover, compared to black, electroless nickel coatings prepared using commercially available black electroless plating processes, a black electroless nickel coating prepared by the process described herein when subjected 116 hours of neutral salt spray exposure maintains a higher level of black (Fig. 5).

Example 4

[0092] The duplex coated substrate with the sulfur-free electroless nickel top coating prepared by process described above (ebENi process) was further studied by subjecting the duplex coating to a copper immersion process for bare steel surfaces. The duplex coated steel substrate described above was immersed in an electroless copper bath having the following formulation.

Electroless copper plating bath
10 g/L Copper Sulfate Pentahydrate
5 mL/L Sulfuric Acid

[0093] A summary of electroless copper plating process is shown below:

1. Panel was plated to a thickness of 0.4 mils in EN High Phosphorous bath
2. Rinse: 1 min
3. Panel was plated in proposed Sulfur-free EN Bath to a thickness of 0.2 mils
4. Rinse: 30 secs
5. 50% HCl: 20 secs
6. Rinse: 30 secs
7. Electroless CuSO4 solution 2 mins
8. Rinse 30 secs
9. Dried

[0094] An example of the deposit so formed is illustrated in Fig. 6. Testing showed than an intermediate step is need to reactivate the surface before exposure to the electroless copper plating bath.

[0095] In order to fully assess the deposit, the immersion properties needed to be compared against the traditional EN processes.

[0096] Four EN baths were plated then exposed to a cycle in an attempt to facilitate copper immersion over the EN deposit:

En Chemistry:

1. Traditional low phosphorous electroless nickel plating bath

[0097] 60 mL/L 6% LNS
150 mL/L Enova EF-163B
Temperature: 190°F
pH: 4.9

2. Traditional mid phosphorous electroless nickel plating bath

[0098] 60 mL/L 6% LNS
150 mL/L Enova MS-9
Temperature: 190°F
pH :4.9

3. Traditional high phosphorous electroless nickel plating, bath 60 mL/L 6% LNS

[0099] 150 mL/L Enova EF-949B.
Temperature: 190°F
pH :4.8

4. Proposed ebENi process:

[0100] 60 mL/L Enova 949
150 mL/L proposed Sulfur-free EN Bath
Temperature: 190°F
pH :4.9

Plating Cycle

[0101] Cycle for Low, Mid, and High Phos system:

1. Panel was plated to a thickness of 0.4 mils
2. Rinse: 30 secs
3. 50% HCl: 20 secs
4. Rinse: 30 secs
5. $CuSO_4$ solution: 2 mins
6. Rinse: 30 secs
7. Dried

Cycle for ebENi system:

[0102]

1. Panel was plated to a thickness of 0.4 mils in Enova 949
2. Rinse: 1 min
3. Panel was plated in ebENi to a thickness of 0.2 mils
4. Rinse: 30 sec
5. 50% HCl 20 secs
6. Rinse: 30 secs
7. $CusO_4$ solution 2 mins
8. Rinse: 30 secs
9. Dried

[0103] As illustrated in Fig. 6, all three traditional processes show the copper did not fully cover the panel. The ebENi system shows complete, uniform coverage of copper over the top of the EN deposit.

Claims

1. A method of forming a multilayer electroless metal coating on a substrate, the method comprising:

i. contacting the substrate with a first electroless nickel plating bath to form a first eletroless nickel coating on the substrate, the first electroless nickel coating having a phosphorus content of 7% to 13% by weight
ii. contacting the substrate coated with the first electroless coating with a second aqueous electroless nickel plating bath to form a second electroless nickel coating over the first electroless coating, the second electroless

coating having a phosphorous content of 8% to 11%, the second bath including nickel, a hypophosphorous reducing agent, 40 ppm to 100 ppm zinc, at least one of a complexing agent, chelating agent, and/or pH buffer, and 5 ppm to 30 ppm bismuth stabilizer, wherein the bath is free of an organic sulfur compound;
iii. etching the second electroless nickel coating with an etchant agent to provide the coated substrate with a black surface or contacting the substrate coated with the first and second electroless nickel coatings with an electroless copper plating bath to provide a copper top coat.

2. The method of claim 1, wherein hypophosphorous reducing agent is selected from the group consisting of sodium hypophosphite, potassium hypophosphite, ammonium hypophosphite, and combinations thereof.

3. The method of claim 1, wherein the second electroless nickel plating bath includes at least one pH buffer, complexing agent, or chelating agent is selected from the group consisting of acetic acid, formic acid, succinic acid, malonic acid, an ammonium salt, lactic acid, malic acid, citric acid, glycine, alanine, glycolic acid, lysine, aspartic acid, ethylene diamine tetraacetic acid (EDTA), and combinations thereof.

4. The method of claim 3, comprising at least two of a pH buffer, complexing agent, and/or chelating agent.

5. The method of claim 1, wherein the nickel is provided in the second electroless plating bath in the form of a water soluble nickel salt.

6. The method of claim 5, the nickel salt being selected from the group consisting of nickel chloride, nickel bromide, nickel iodide, nickel acetate, nickel malate, and nickel hypophosphite.

7. The method of claim 1, wherein the pH of the second electroless nickel plating bath is maintained at 4.5 to 5.0 and the temperature at 79°C to 93°C.

8. The method of claim 1, the second electroless nickel plating bath comprising 2 g/l to 10 g/l nickel, 20 g/l to 35 g/l of the hypophosphorous reducing agent, 1 g/l to 75 g/l each of the complexing agent, chelating agent, and/or pH buffer.

9. The method of claim 1, the second electroless nickel plating bath comprising lactic acid, acetic acid, malic acid, succinic acid, sodium hypophosphite, ammonium hydroxide, nickel, zinc, and ethylenediamine tetraacetic acid.

10. The method of claim 1, the etchant agent comprising an iron blackening agent and an acid, preferably, the etchant agent comprising ferric sulfate and hydrochloric acid.

11. The method of claim 1, contacting the substrate coated with the first and second electroless nickel coatings with an acid solution prior to contacting the substrate with the electroless copper plating bath.

Patentansprüche

1. Verfahren zum Bilden einer stromlosen Mehrschicht-Metall-Beschichtung auf einem Substrat, wobei das Verfahren umfasst:

i. Kontaktieren des Substrats mit einem ersten stromlosen Nickel-Plattierungs-Bad zum Bilden einer ersten stromlosen Nickel-Beschichtung auf dem Substrat, wobei die erste stromlose Nickel-Beschichtung einen Phosphor-Gehalt von 7 % bis 13 Gew.-% aufweist,
ii. Kontaktieren des mit der ersten stromlosen Beschichtung beschichteten Substrats mit einem zweiten wässrigen stromlosen Nickel-Plattierungs-Bad zum Bilden einer zweiten stromlosen Nickel-Beschichtung über der ersten stromlosen Beschichtung, wobei die zweite stromlose Beschichtung einen Phosphor-Gehalt von 8 % bis 11 % aufweist, das zweite Bad Nickel, ein unterphosphoriges Reduktions-Mittel, 40 ppm bis 100 ppm Zink, mindestens eines von einem Komplexierungs-Mittel, Chelatisierungs-Mittel und/oder pH-Puffer und 5 ppm bis 30 ppm Wismut-Stabilisator enthält, wobei das Bad frei von einer organischen Schwefel-Verbindung ist;
iii. Ätzen der zweiten stromlosen Nickel-Beschichtung mit einem Ätz-Mittel zum Versehen des beschichteten Substrats mit einer schwarzen Oberfläche oder Kontaktieren des mit den ersten und zweiten stromlosen Nickel-Beschichtungen beschichteten Substrats mit einem stromlosen Kupfer-Plattierungs-Bad zum Bereitstellen einer Kupfer-Deck-Schicht.

2. Verfahren nach Anspruch 1, wobei das unterphosphorige Reduktions-Mittel aus der Gruppe, bestehend aus Natriumhypophosphit, Kaliumhypophosphit, Ammoniumhypophosphit und Kombinationen davon, ausgewählt ist.

3. Verfahren nach Anspruch 1, wobei das zweite stromlose Nickel-Plattierungs-Bad, das mindestens einen pH-Puffer, Komplexierungs-Mittel oder Chelatisierungs-Mittel enthält, aus der Gruppe, bestehend aus Essigsäure, Ameisensäure, Bernsteinsäure, Malonsäure, einem Ammoniumsalz, Milchsäure, Äpfelsäure, Zitronensäure, Glycin, Alanin, Glycolsäure, Lysin, Asparaginsäure, Ethylendiamintetraessigsäure (EDTA) und Kombinationen davon, ausgewählt ist.

4. Verfahren nach Anspruch 3, umfassend mindestens zwei von einem pH-Puffer, Komplexierungs-Mittel und/oder Chelatisierungs-Mittel.

5. Verfahren nach Anspruch 1, wobei das Nickel in dem zweiten stromlosen Plattierungs-Bad in Form von einem in Wasser löslichen Nickel-Salz bereitgestellt wird.

6. Verfahren nach Anspruch 5, wobei das Nickel-Salz aus der Gruppe, bestehend aus Nickelchlorid, Nickelbromid, Nickeliodid, Nickelacetat, Nickelmalat und Nickelhypophosphit, ausgewählt ist.

7. Verfahren nach Anspruch 1, wobei der pH von dem zweiten stromlosen Nickel-Plattierungs-Bad bei 4,5 bis 5,0 und die Temperatur bei 79°C bis 93°C gehalten wird.

8. Verfahren nach Anspruch 1, wobei das zweite stromlose Nickel-Plattierungs-Bad 2 g/l bis 10 g/l Nickel, 20 g/l bis 35 g/l von dem unterphosphorigen Reduktions-Mittel, 1 g/l bis 75 g/l von jedem von dem Komplexierungs-Mittel, Chelatisierungs-Mittel und/oder pH-Puffer umfasst.

9. Verfahren nach Anspruch 1, wobei das zweite stromlose Nickel-Plattierungs-Bad Milchsäure, Essigsäure, Äpfelsäure, Bernsteinsäure, Natriumhypophosphit, Ammoniumhydroxid, Nickel, Zink und Ethylendiamintetraessigsäure umfasst.

10. Verfahren nach Anspruch 1, wobei das Ätz-Mittel ein Eisen schwärzendes Mittel und eine Säure umfasst, vorzugsweise wobei das Ätz-Mittel Eisen(III)sulfat und unterchlorige Säure umfasst.

11. Verfahren nach Anspruch 1, wobei das mit den ersten und zweiten stromlosen Nickel-Beschichtungen beschichtete Substrat mit einer sauren Lösung vor dem Kontaktieren des Substrats mit dem stromlosen Kupfer-Plattierungs-Bad kontaktiert wird.

Revendications

1. Procédé de formation d'un revêtement métallique autocatalytique multicouche sur un substrat, le procédé comprenant :

   i. la mise en contact du substrat avec un premier bain de placage au nickel autocatalytique pour former un premier revêtement de nickel autocatalytique sur le substrat, le premier revêtement de nickel autocatalytique présentant une teneur en phosphore de 7 % à 13 % en poids ;
   ii. la mise en contact du substrat revêtu du premier revêtement autocatalytique avec un deuxième bain de placage aqueux au nickel autocatalytique pour former un deuxième revêtement de nickel autocatalytique au-dessus du premier revêtement autocatalytique, le deuxième revêtement autocatalytique présentant une teneur en phosphore de 8 % à 11 %, le deuxième bain contenant du nickel, un agent réducteur hypophosphoreux, 40 ppm à 100 ppm de zinc, au moins l'un parmi un agent complexant, un agent chélatant, et/ou un tampon de pH, et 5 ppm à 30 ppm d'un stabilisant au bismuth, lequel bain étant exempt de composé soufré organique ;
   iii. la gravure du deuxième revêtement de nickel autocatalytique avec un agent de gravure pour que le substrat revêtu soit doté d'une surface noire, ou la mise en contact du substrat revêtu des premier et deuxième revêtements de nickel autocatalytiques avec un bain de placage au cuivre autocatalytique pour former une couche de finition en cuivre.

2. Procédé selon la revendication 1, dans lequel l'agent réducteur hypophosphoreux est choisi dans l'ensemble constitué par l'hypophosphite de sodium, l'hypophosphite de potassium, l'hypophosphite d'ammonium, et leurs combi-

naisons.

3. Procédé selon la revendication 1, dans lequel le deuxième bain de placage au nickel autocatalytique contient au moins un tampon de pH, un agent complexant ou un agent chélatant qui est choisi dans l'ensemble constitué par l'acide acétique, l'acide formique, l'acide succinique, l'acide malonique, un sel d'ammonium, l'acide lactique, l'acide malique, l'acide citrique, la glycine, l'alanine, l'acide glycolique, la lysine, l'acide aspartique, l'acide éthylènediaminetétraacétique (EDTA), et leurs combinaisons.

4. Procédé selon la revendication 3, comprenant au moins deux parmi un tampon de pH, un agent complexant, et/ou un agent chélatant.

5. Procédé selon la revendication 1, dans lequel le nickel est fourni dans le deuxième bain de plage autocatalytique sous la forme d'un sel de nickel soluble dans l'eau.

6. Procédé selon la revendication 5, dans lequel le sel de nickel est choisi dans l'ensemble constitué par le chlorure de nickel, le bromure de nickel, l'iodure de nickel, l'acétate de nickel, le malate de nickel, et l'hypophosphite de nickel.

7. Procédé selon la revendication 1, dans lequel le pH du deuxième bain de placage au nickel autocatalytique est maintenu à une valeur de 4,5 à 5,0 et la température est maintenue à une valeur de 79°C à 93°C.

8. Procédé selon la revendication 1, dans lequel le deuxième bain de placage au nickel autocatalytique comprend 2 g/l à 10 g/l de nickel, 20 g/l à 35 g/l de l'agent réducteur hypophosphoreux, 1 g/l à 75 g/l de chacun parmi l'agent complexant, l'agent chélatant, et/ou le tampon de pH.

9. Procédé selon la revendication 1, dans lequel le deuxième bain de placage au nickel autocatalytique comprend de l'acide lactique, de l'acide acétique, de l'acide malique, de l'acide succinique, de l'hypophosphite de sodium, de l'hydroxyde d'ammonium, du nickel, du zinc, et de l'acide éthylènediaminetétraacétique.

10. Procédé selon la revendication 1, dans lequel l'agent de gravure comprend un agent noircisseur au fer et un acide, de préférence l'agent de gravure comprend du sulfate ferrique et de l'acide chlorhydrique.

11. Procédé selon la revendication 1, comprenant la mise en contact du substrat revêtu des premier et deuxième revêtements de nickel autocatalytiques avec une solution acide avant la mise en contact du substrat avec le bain de placage au cuivre autocatalytique.

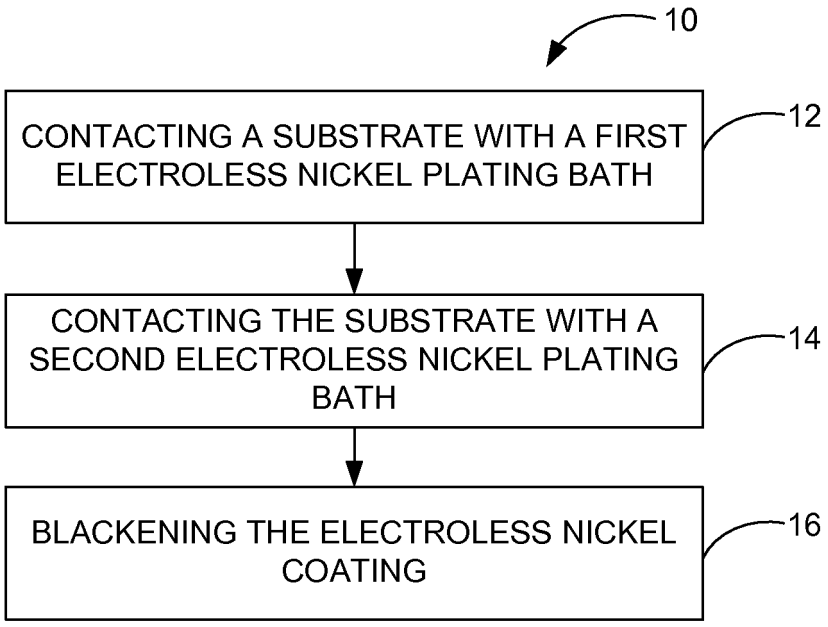

10
CONTACTING A SUBSTRATE WITH A FIRST ELECTROLESS NICKEL PLATING BATH
12
CONTACTING THE SUBSTRATE WITH A SECOND ELECTROLESS NICKEL PLATING BATH
14
BLACKENING THE ELECTROLESS NICKEL COATING
16

Fig. 1

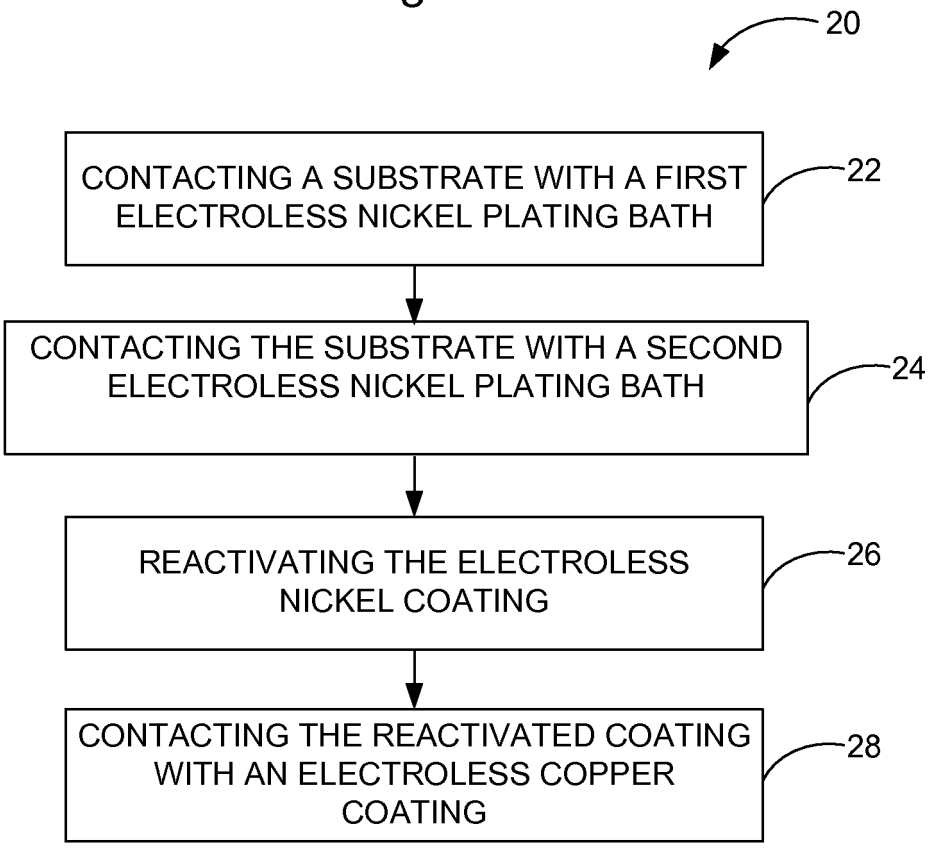

20
CONTACTING A SUBSTRATE WITH A FIRST ELECTROLESS NICKEL PLATING BATH
22
CONTACTING THE SUBSTRATE WITH A SECOND ELECTROLESS NICKEL PLATING BATH
24
REACTIVATING THE ELECTROLESS NICKEL COATING
26
CONTACTING THE REACTIVATED COATING WITH AN ELECTROLESS COPPER COATING
28

Fig. 2

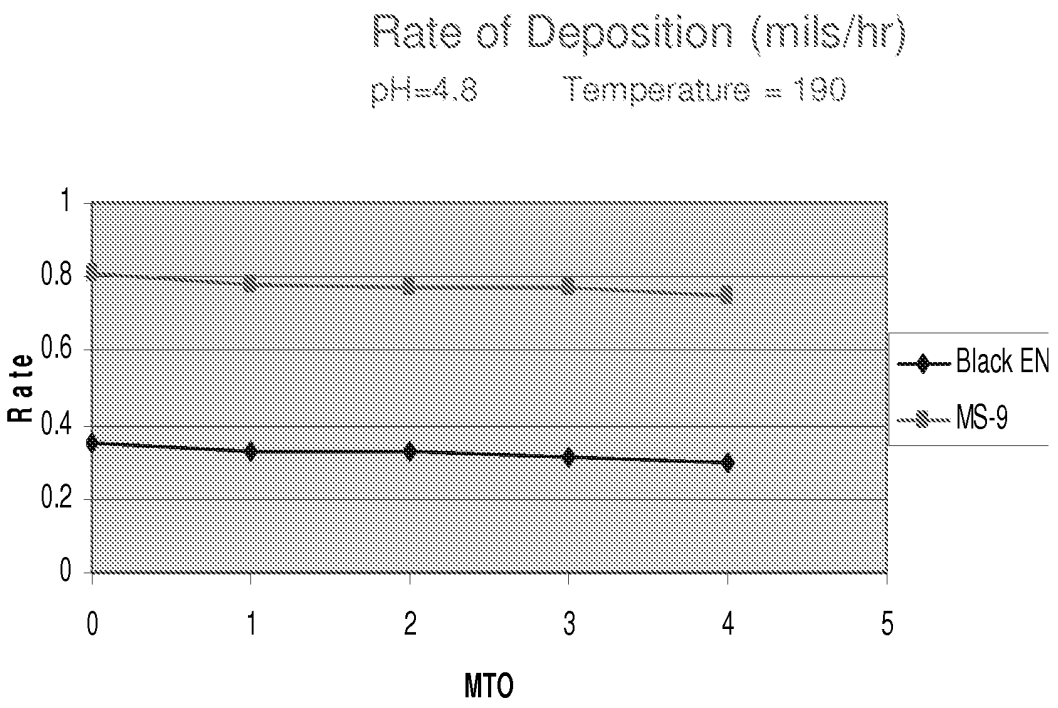

Rate of Deposition (mils/hr)
pH=4.8 Temperature = 190
Rate
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
MTO
Black EN
MS-9

Fig. 3

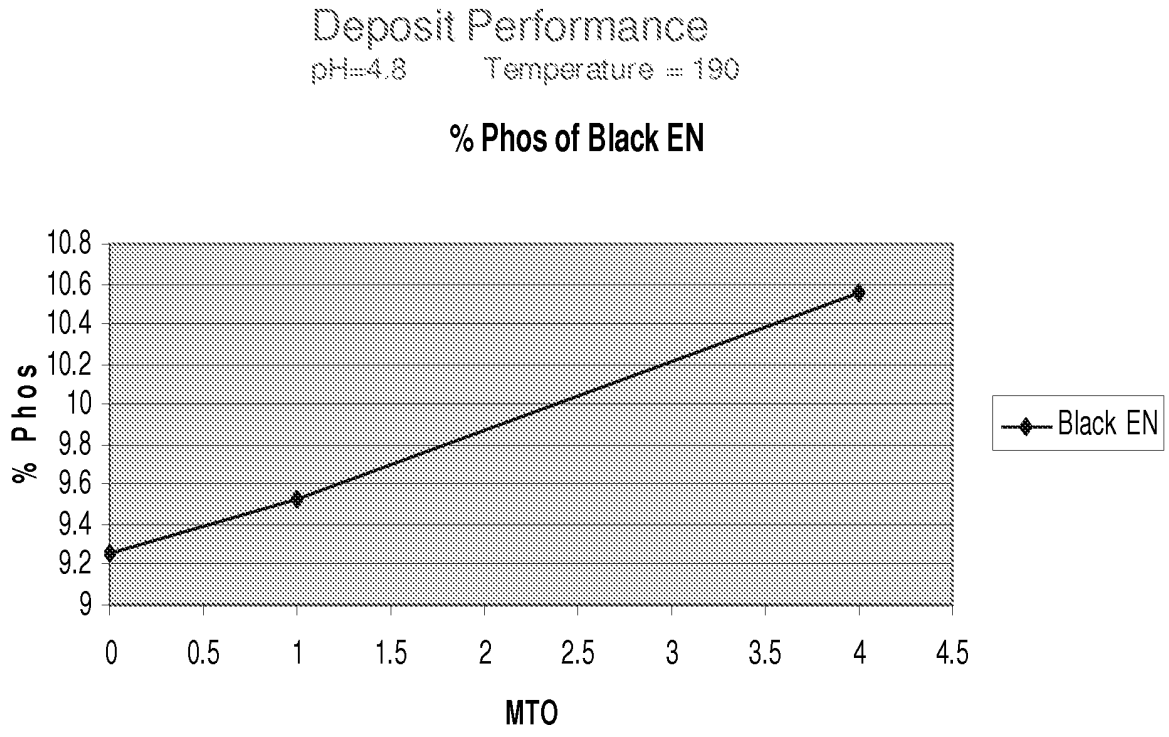

Deposit Performance
pH=4.8 Temperature = 190
% Phos of Black EN
% Phos
10.8
10.6
10.4
10.2
10
9.8
9.6
9.4
9.2
9
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
MTO
Black EN

Fig. 4

NSS Performance

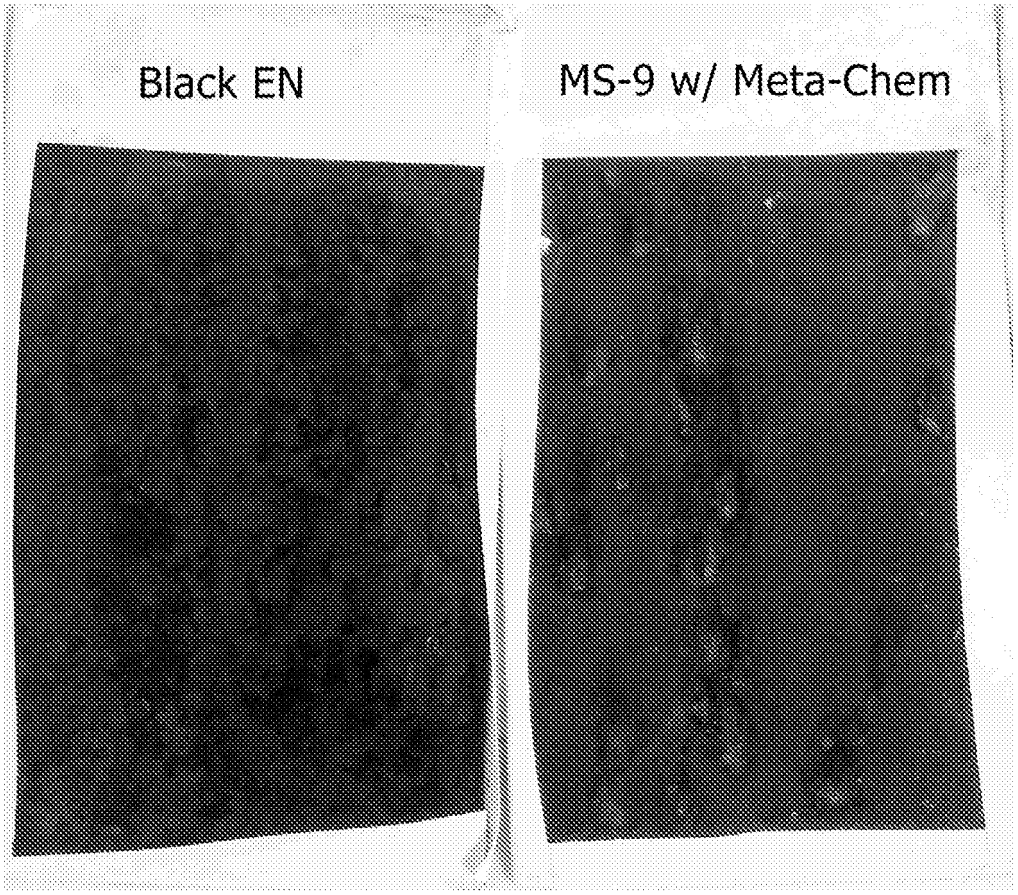


Fig. 5

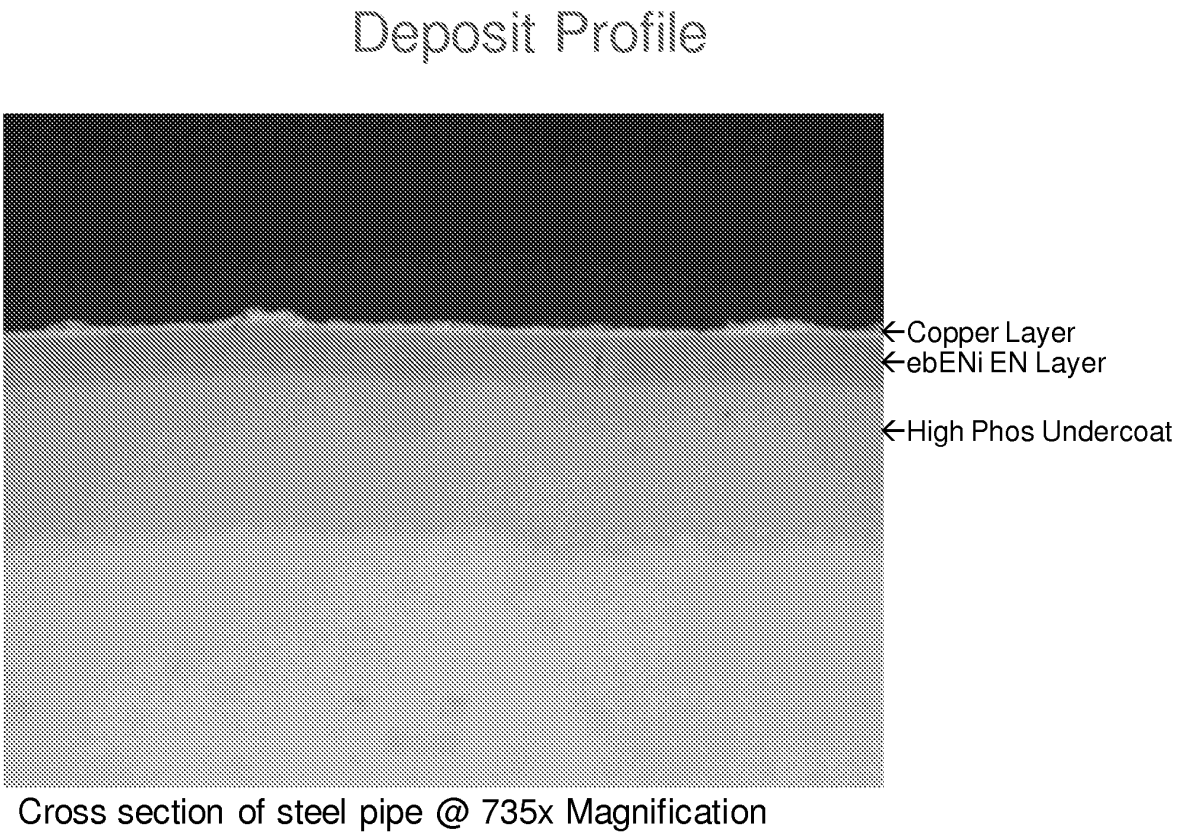

Deposit Profile
←Copper Layer
←ebENi EN Layer
←High Phos Undercoat
Cross section of steel pipe @ 735x Magnification

Fig. 6

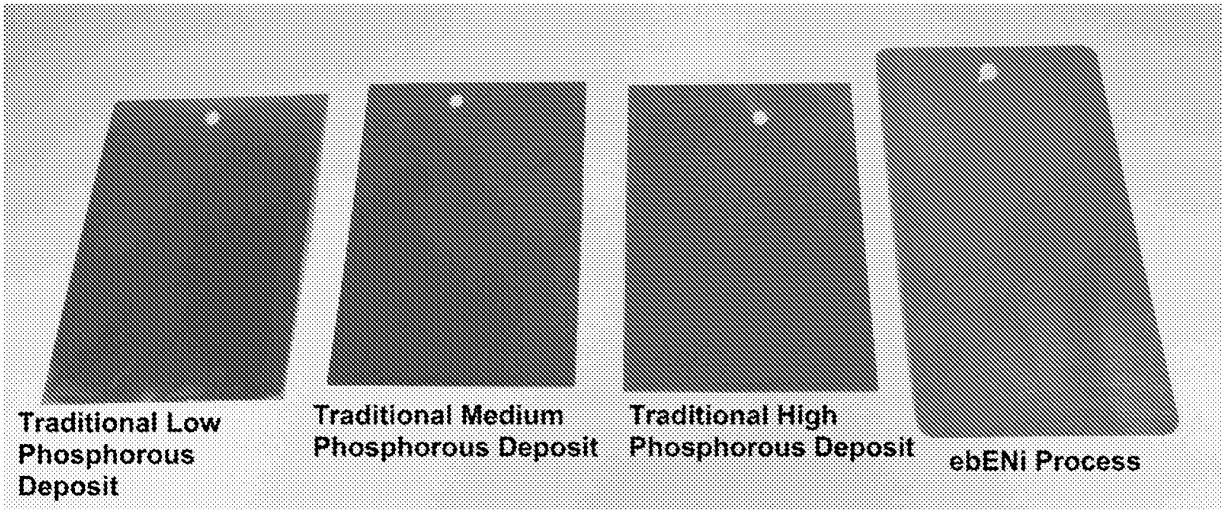

Traditional Low Phosphorous Deposit
Traditional Medium Phosphorous Deposit
Traditional High Phosphorous Deposit
ebENi Process

Fig. 7

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 20077154223 A **[0005]**
- US 20040144285 A1 **[0006]**
- JP 2005290400 A **[0007]**
- US 4511614 A **[0008]**