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Description

The present invention relates to electroless nickel plating onto substrates.

Electroless deposition of nickel onto metal substrates has long been known to impart to the substrate ephanced corrosion resistance, hardness and similar properties. When electroless nickel deposits are made onto various substrates, there tends to develop cracking, blistering, surface distortion and adhesion failure of the electroless deposit. It is generally accepted that these undesirable properties are the result of deposits that exhibit a high tensile stress and that these problems can be substantially reduced by laying down a deposit that is of exceedingly low tensile stress or that has a compressive internal stress, the latter typically being particularly effective for maintaining the integrity of the electroless nickel deposit onto the substrate for especially long time periods and/or under exceptionally adverse conditions. It is, therefore, generally observed that great advantages can be realized by electrolessly plating from a bath that lays down a deposit having reduced tensile stress, it being understood that when used herein, the term "reduced tensile stress" includes both lowering the tensile stress (also known as positive or contractile stress) to as low as zero and also reducing the tensile stress to such an extent that the stress becomes compressive (also known as negative or expansive stress). Tensile stress is sometimes referred to as concave internal stress, while compressive stress is correspondingly referred to as convex internal stress.

It is generally believed that the tenacity of the electroless nickel deposit and the advantageous protective properties thereof with respect to substrates, especially metal substrates, are enhanced and that the tensile stress is decreased as the percentage of phosphorus in the electroless nickel deposit is increased. Heretofore, in order to reduce the internal tensile stress, it has been necessary to increase the phosphorus content of an electroless nickel deposit by reducing the pH of the bath to a level at which the rate of deposition is severely slowed with the result that an electroless nickel deposit having especially high resistance to failure and low tensile stress had to be a deposit having an exceptionally high phosphorus content such as can be plated from a low pH bath exhibiting a slow rate of deposition. It is of course desirable to form a nickel-phosphorus deposit having reduced tensile stress and enhanced deposit integrity within a bath that has a high deposition rate, that is, does not have to be carried out under conditions traditionally recognized as needed for reduced tensile stress with increased phosphorus content of the deposit.

Baths used in the method according to this invention accomplish these desirable results; such baths are sulfur-free (in the sense that if any sulfur is present it is in its highest oxidation state) and include a bath soluble unsaturated carboxylic acid $R(COOH)_n$, (wherein R is an unsaturated alkyl and n is at least one) and/or derivative thereof, the baths also including a saturated carboxylic acid (or derivative thereof) of formula $R^1(COOH)_p$ (wherein R^1 is absent or is a saturated alkyl or aromatic group having 1 to 20 carbon atoms and p is at least 2), an electroless bath reducing agent, a nickel source and a phosphorus source which may be the said reducing agent. The products of these baths exhibit reduced tensile stress when compared with products plated from baths that are not in accordance with this invention.

Various ingredients of these baths have been proposed in the prior art. For example, FR-A-2144782 and Velemitzina "Electroless nickel plating as a method of protecting and strengthening parts of power engineering equipment" include baths with a nickel source, a reducing agent such as sodium hypophosphite, and an unsaturated carboxylic acid as a "stabilizer". Some of these baths did not have any addition of sulfur. At least in the case of Velemitzina, specific after-treatments were needed to relieve tensile stress in the deposit. Gawrilov, "Chemische (stromlose) Vernicklung" 1974 shows saturated acids in baths which may either contain an unsaturated acid or sulfur as stabilizer.

In US-A-2935425 saturated polycarboxylic acids including specifically succinic and glutaric acids were used in electroless nickel baths as "exalting agents" to increase hydrogen gas evolution.

It is accordingly a general object of this invention to improve electroless nickel plating by a method which enables the plating of products to have reduced tensile or contractile stress and which may be done onto metallic surfaces which characteristically bring about high internal stresses such as high-strength steel, without sacrificing the plating rate of the electroless bath. The invention also permits enhancing the stress properties and therefore the corrosion resistance of circuit boards having an electroless nickel deposit thereon.

The features of the method according to the present invention are defined in claim 1. Preferred features are defined in the dependent claims.

Maximum phosphorus contents in the deposit are achieved at relatively high pH values of the bath. namely at least about 10% by weight at a pH of at least 4.5, at good plating rates. The good plating rates obtained are greater than about 0.0075 mm (0.3 mil) per hour.

Indeed, the products of the present invention may have a residual internal stress that has a negative value, that is, compressive or expansive.

In the stress-reducing agent the group R has 6 or less carbon atoms, and aconitic acid (or derivatives thereof) may be particularly mentioned. The reducing agent may also be the phosphorus source. As stated, the bath is sulfur-free; that is, it does not contain sulfur in a form or state that will interfere with the stress reduction properties of the bath, i.e. the bath will be free of sulfur except for sulfur in its highest oxidation state, for example sulfur may be present as nickel sulfate to supply the nickel to be plated by the bath. Other typical electroless nickel bath additives may also be included, provided they are also sulfur-free and do not otherwise adversely affect the advantageous properties of the bath.

With more particular reference to the tensile stress reduction agent in accordance with this invention, R represents an unsaturated alkyl group having a carbon chain length short enough to obtain bath solubility when the tensile stress reduction agent is either in its acid form or in the form of a bath soluble derivative thereof, the carbon chain length being no greater than 6, and n is preferably 2 or more, most preferably 2. Exemplary unsaturated acid tensile stress reduction agents include aconitic acid, citraconic acid, fumaric acid, itaconic acid, maleic acid, and their bath soluble derivatives, which will preferably be present within the electroless nickel bath at a concentration of at least about 1 g/l, with the upper limit being a matter of economics and bath solubility. There reaches a point, typically at no more than 10 g/l, based on the total bath, at which added stabilizer no longer increases the percentage of phosphorus deposition.

Referring more particularly to the sulfur-free characteristic or condition of these baths, it has been discovered that the inclusion in these baths of sulfur that is in an oxidation state lower than its highest oxidation state, such as that of the sulfate group, will substantially offset the stress reduction properties imparted to the bath by the tensile stress reduction agent. Baths used in the method according to this invention avoid the sulfur-containing condition of many electroless nickel baths that often include sulfur-containing compounds, either as bath impurities or as an added constituent for bath stabilization or some other function. The sulfur-free baths used in the method according to this invention do not include divalent sulfur containing compounds such as the organic sulfur-containing compounds, the organic and inorganic thiocompounds, and the inorganic sulfides.

Organic sulfur-containing compounds include thiourea and its derivatives, dithioglycol, thioglycolic acid, 2,2-thiodiethanol, 1,2-ethanedithiol, 2-mercaptobenzothiazole, 1,2-benzisothioazine, methionine, and the like. Thiocompounds include the thiocyanate salts and the thiosulfate salts such as sodium thiocyanate, potassium thiocyanate, potassium dithionate, sodium thiosulfate, potassium thiosulfate, and the like. Included within the organic sulfides are sodium sulfide, potassium sulfide, sodium polysulfide, potassium polysulfide, and the like.

A buffer is included within baths according to this invention. Such buffers provide the proper environment for the tensile stress reduction agent. Maximum efficiency of these baths, especially in connection with the enhancement of phosphorus deposition percentages without adversely affecting the plating rate, is attained with the buffer according to the present invention which is a saturated alkyl or aromatic polycarboxylic acid and/or bath soluble derivative thereof, having the formula: $R'(COOH)_p$, wherein R' is a saturated carbon chain of from 0 to 20 carbon atoms or an aromatic ring containing a chain of not more than 20 carbon atoms, and p is at least 2, preferably 2. Preferably R' is a carbon chain of not more than 10 carbon atoms, more preferably of not more than 6 carbon atoms. Especially preferred buffers are those defined when R' is between 2 and 4 and when p is 2, and combinations of such buffers.

As is typically the case for buffering systems, these buffers may be provided as acids in combination with salts or esters thereof. Exemplary buffers in accordance with this invention include the acid and salt or ester forms of adipic acid, glutaric acid, isophthalic acid, malonic acid, oxalic acid, and succinic acid. These buffers are included within the electroless nickel baths at a total concentration of at least about 1 g/l the concentration being varied according to needs for maintaining pH control, which concentration will usually be no more than about 40 g/l and often not more than about 20 g/l.

It is also preferred within the baths utilized and prepared according to this invention to include within the bath, in combination with the unsaturated carboxylic acid tensile stress reduction agent, and preferably in further combination with the saturated alkyl or aromatic carboxylic buffer systems, a hydroxy and/or amino substituted carboxylic acid complexing agent having the general formula $XR''(COOH)_s$, wherein X is either or both a hydroxy group or an amino group, including OH, NH, NH_2, ^+NH, $^+NH_2$, $^+NH_3$, it being especially preferred that the X group is in the alpha position relative to at least one of the carboxylic groups; R" is saturated alkyl, heterocyclic, or alkylaryl, and may be substituted or unsubstituted, the carbon chain length being between 1 and 14, and preferably not greater than 6, especially preferred compounds having an R" chain length of not more than 4; and s may be between 1 and 4. The carboxylic acid group may be in the acid, anhydride, salt or ester form, provided it is bath soluble.

Exemplary complexing agents include the amino acids such as α-alanine, aspartic acid, glutamic acid, glycine, and the like, as well as citric acid, glycolic acid (hydroxyacetic acid), iminoacetic acid, iminodiacetic acid, lactic acid and malic acid. When lactic acid is incorporated into the bath, the plating rate tends to be enhanced when compared with that achieved in baths using other complexing agents, and citric acid has been found to be especially useful in enhancing the highest possible percentage of phosphorus deposit. These complexing agents are included within the baths at a concentration of at least about 1 gm/l, with the upper limit being dictated by economic considerations and bath solubility limitations, with a typical upper limit being no more than about 100 gm/l, and most often no more than about 50 gm/l.

The bath must also contain a reducing agent and a source of phosphorus, and the well-established manner of accomplishing same is to utilize a reducing agent that is also a source of phosphorus ions, such as the widely used reducing agent sodium hypophosphite. The bath also, of course, includes a source of nickel, which may be added as a bath-soluble salt, such as the sulfates, chlorides, sulfamates, or other anions compatible with these electroless systems. Typically the baths will be operated at a temperature of between about 160 and 212°F (about 71 to 100°C).

Deposition baths prepared with formulations according to this invention may, if desired, also contain conventional bath additives that are commonly employed in electroless nickel deposition baths. Included are traditional buffers such as acetic acid/sodium acetate, other complexing agents and stabilizers, and the like, except for those that add sulfur to the bath in a form other than the highest oxidation state of sulfur, which is necessary in order that the bath will be a sulfur-free bath.

In proceeding with the method according to this invention, an electroless deposition bath is prepared to include an unsaturated carboxylic acid compound $R(COOH)_n$ as the tensile stress reduction agent previously defined herein, a source of nickel, a reducing agent and a source of phosphorus, said bath being a sulfur-free bath. Also typically included is a saturated or aromatic polycarboxylic acid compound $R'(COOH)_p$ as the buffer previously defined herein, usually in combination with a hydroxy and/or amino substituted carboxylic acid complexing agent of the formula XR"(COOH)s as previously defined herein. The bath lays down a deposit that is lower in tensile stress than those laid down by baths which are not sulfur-free and/or do not include the tensile stress reduction agent, which deposition according to this invention lays down a nickel deposit having a high phosphorus content while avoiding a substantial slowing of the deposition rate by maintaining the pH at as high a value as can be attained by the combination of bath ingredients. More particularly, the bath used in the method according to this invention has a pH of at least about 4.5, usually of the order of 5.0, including a pH of 5.0±0.5, preferably a pH of 5.0±0.3, and most preferably a pH of 5.0±0.2.

With the bath thus prepared, a substrate is immersed therein to form a deposit of nickel and phosphorus having an especially low tensile stress condition for a bath at such a relatively high pH and that exhibits a rate of deposition that is rapid for a bath that lays down a deposit having a high phosphorus content. The method is most advantageously employed when the substrate upon which the deposit is made is one that results in a nickel phosphorus deposit onto the substrate that has a high tensile stress condition when plating from a bath that is not in accordance with this invention. The method according to this invention results in a deposit having a low internal tensile stress, which includes substantially zero internal stress as well as an internal stress in the compressive or negative range.

Although a conventional bath at a pH of the order of 4.0 will provide nickel deposits having high phosphorus contents in excess of 10 weight per cent, the plating rate thereof is on the order of 0.005 mm/h (0.2 mil/h), while baths according to this invention, which have a pH of the order of 5.0, attain plating rates more of the order of 0.01 to 0.02 mm/h (0.4 to 0.8 mil/h) while providing a nickel deposit having the same high phosphorus content as such a conventional bath. Accordingly, the method according to this invention may have a plating rate from 2 to 4 times faster than that of conventional baths which form nickel phosphorus deposits having a high phosphorus content. Loadings of baths according to this invention are between about 0.087 and 0.35 m^2/l (about 0.25 and 1.0 square foot per US gallon) preferably.

Products produced according to this invention have a low tensile stress nickel phosphorus deposit over a substrate, including substrates that are known to be characterized by having nickel phosphorus deposits thereon which exhibit a high internal tensile stress condition. Products according to this invention have deposits of a low tensile stress to thereby enhance the integrity of the plating onto the metal substrate in order to increase the useful life of the product and to reduce the susceptibility of the product to exhibit metal fatigue leading to catastrophic metal failure. Such products also resist cracking, blistering, surface distortion and adhesion failure while providing substantial corrosion protection of the underlying metal substrate.

The invention finds special application for products of nickel plated high strength steel that are utilized in highly fatigue inducing situations such as aircraft parts, turbine blades and the like as well as for nickel plated circuit boards and the like. The advantageous reduced tensile stress condition of the products according to this invention typically has the greatest advantage when the substrate of the product is titanium or a ferrous alloy such as nickel alloy steels, nickel-cobalt alloy steel, stainless steel, or the like. Other substrates that may be advantageously included within these products are copper, copper alloys, beryllium and its alloys, especially beryllium-nickel alloys, cast iron, magnesium and non-conductive materials.

Products having the nickel-phosphorus deposits onto these substrates have a phosphorus content of at least 10 per cent, with the maximum phosphorus content being limited only by the maximum phosphorus deposition capabilities of the total bath, such maximum amount typically approaching not more than about 15 per cent phosphorus. The thickness or the quantity of the nickel phosphorus deposit varies, of course, with the plating rate and the length of time that the metal substrate is immersed within the bath, varying anywhere between a flash deposit and a heavily built-up plating of several mils. Typical hardness values for the deposits are between 500 and 600 VHN_{100} and between 800 and 950 VHN_{100} after heat treatment at 400°C for one hour.

The following test and examples are offered to illustrate the present invention.

Test

Various sulfur-free baths were formulated in accordance with this invention, and steel panels were electrolessly plated, after which the plated steel panels were subjected to internal stress measurements made with a Spiral Contractometer. The bath pH was between 4.8 and 5.0 for these several baths, which were maintained at temperatures between about 87.8 and 90.6°C (190 and 195°F). Various unsaturated polycarboxylic acid tensile stress reduction agents were added at varying concentrations, and the results of the stress measurements were as follows, a positive stress value indicating internal tensile stress, and a negative stress value indicating internal compressive stress.

Unsaturated polycarboxylic acid	Acid concentration (in bath)	Stress
—	—	91.1×10^6 Pa (13,200 psi)
Aconitic acid	2 g/l	44.2×10^6 Pa (6,400 psi)
Aconitic acid	5 g/l	26.2×10^6 Pa (3,800 psi)
Aconitic acid	10 g/l	26.4×10^6 Pa (3,900 psi)
Citraconic acid	5 g/l	45.6×10^6 Pa (6,600 psi)
Citraconic acid	10 g/l	31.75×10^6 Pa (4,600 psi)
Citraconic acid	15 g/l	10.35×10^6 Pa (1,500 psi)
Itaconic acid	5 g/l	37.3×10^6 Pa (5,400 psi)
Itaconic acid	10 g/l	-28.3×10^6 Pa (−4,100 psi)
Itaconic acid	15 g/l	-53.8×10^6 Pa (−7,800 psi)
Maleic acid	1 g/l	75.9×10^6 Pa (11,000 psi)
Maleic acid	5 g/l	-31.1×10^6 Pa (−4,500 psi)

It is observed that the addition of the unsaturated polycarboxylic acids substantially lowered the tensile stress of the plated panels even to the extent that, with respect to certain of the panels, the tensile stress was removed completely, and the stress was moved into the compressive range, which enhanced the fatigue resistance of these panels.

Example I

Sulfur-free baths were prepared to include 27 g/l of malic acid, 9 g/l of citric acid, a total of 9 g/l saturated alkyl dicarboxylic acid buffers, 6 g/l of aconitic acid, 37 g/l of sodium hypophosphite, 27 g/l of sodium hydroxide, and enough nickel salt to provide 6 g/l of nickel as nickel metal. Nine 1010 steel Q panels were electrolessly nickel phosphorus plated in the bath, three of the panels having been plated to a thickness of 0.0125 mm (0.5 mil), three to a plating thickness of 0.025 mm (1 mil), and three were immersed in the bath until the plating thickness was 0.05 mm (2 mils). All nine of the samples were exposed to salt spray, 5%, for one thousand hours in accordance with ASTM B-117 wherein failure was defined as pitting and/or red rust in three or more locations on the panel. The testing chamber was open at 24 hour intervals on weekdays, and each panel was examined after the first 360 hours of exposure, after which the panels were examined after 72 hour intervals on weekdays. All nine of the panels passed the tests in that there was no pitting or rusting except for minor occurrences originating at panel edges, and there was some tarnish on most panels. The internal stress of the panels was slightly compressive, and they passed the 180° bend adhesion test.

Example II

A sulfur-free bath including 30 g/l lactic acid, 10 g/l succinic acid buffer, a 15 g/l acetic acid and 15 g/l sodium acetate buffer system, 5 g/l aconitic acid, 30 g/l sodium hypophosphite and enough liquid nickel sulfate to provide 6 g/l of nickel as nickel metal, balance being deionized water, the pH of this system being 5.2.

High strength steel panels were plated in this bath to thicknesses of 0.0125 mm (0.5 mil), 0.025 mm (1.0 mil) and 0.05 mm (2.0 mils), after which they were subjected to salt spray for one thousand hours under the conditions specified in ASTM B-117. These panels were inspected at the same intervals and to the same extent as those of Example I, and all nine of these panels passed the salt spray test.

Example III

Sulfur-free baths generally in accordance with Example I were prepared and successfully plated onto steel panels. These baths, which had pH values of 4.7, 4.6, 4.8, 5.0, 4.9, 4.9 and 5.0, had plating rates between about 0.01 and 0.015 mm (0.4 and 0.5 mil) per hour at a tank loading of about 0.25 square foot per gallon and at a temperature between about 87.8 and 90.6°C (190 and 195°F). The deposit appearance was hazy bright. A brightener was added to some of the baths, and deposit brightness was found to be enhanced.

Example IV

A sulfur-free bath was prepared to include about 36 g/l of a combination of citric acid and malic acid complexing agent, 36 g/l of sodium hypophosphite, 10g/l of a blend of saturated alkyl dicarboxylic acids, 5 g/l of aconitic acid, and enough nickel salt to provide 6 g/l of nickel as nickel metal. This bath had a pH of 4.9, the temperature was maintained between 87.8 and 90.6°C (190 and 195°F), and its plating rate was estimated at 0.008 mm/h (0.33 mil/hr) when plating steel panels. Panels having a plating thickness of 0.0125 mm (0.5 mil) and 0.015 mm (0.6 mil) were tested according to ASTM B-117 for one thousand hours of 5% salt spray, after which no spots were observed. Another panel plated in this bath to 0.0125 mm (0.5 mil) was subjected to heat treatment at 200°C for two hours, and again no spots were observed. Four other panels having a 0.0125 mm (0.5 mil) deposit from this bath were subjected to heat treatment at 260°C for either 4 or 12 hours, and again no spots were observed after one thousand hours of salt spray. Another panel having a 0.0125 mm (0.5 mil) deposit laid down by this bath was subjected to heat treatment at 400°C for one hour, and six spots were observed after one thousand hours of salt spray, while another substantially identical panel failed after 168 hours. Two panels having a 0.0125 mm (0.5 mil) deposit from this bath were subjected to two hours of heat treatment at 600°C; six small spots appeared after one thousand hours of salt spray on one of them and the other exhibited some blistering and nine small spots after one thousand hours.

This bath was also used to plate a 0.025 mm (1 mil) nickel phosphorus electroless deposit onto zincate pretreated aluminum panels. One of them, which was subjected to heat treatment at 200°C for two hours, developed blistering after 88 hours of salt spray testing while the other one that was not heat treated exhibited no spots after one thousand hours of salt spray testing according to ASTM B-117.

Example V

A deposit of 89% nickel and 11% phosphorus was plated at a rate of deposition of 0.015 mm (0.6 mil)/hr, the deposit having an internal stress of 6.9×10^6 Pa (1,000 psi), compressive, this deposit having been on high strength steel from a sulfur-free bath at a pH of 5.2 including 30 g/l lactic acid, 10 g/l succinic acid, 5 g/l aconitic acid, 30 g/l sodium hypophosphite and 6 g/l of nickel.

Example VI

A sulfur-free bath was prepared to include 3 g/l of aconitic acid, 9 g/l of citric acid, 27 g/l of malic acid, 36 g/l of sodium hypophosphite, 10 g/l of a mixed dicarboxylic acids buffer system, and enough liquid nickel sulfate to provide 6 g/l of nickel as nickel metal. This bath had a pH of 4.8 and a rate of deposition of 0.01 mm (0.4 mil)/hr and plated a nickel phosphorus deposit having 10.5% phosphorus. Analysis on a Spiral Contractometer showed an internal stress of zero.

Example VII

A sulfur-free bath having a pH of 4.8 was prepared to include 5 g/l of aconitic acid, with the rest of the bath being substantially identical with the bath of Example VI. The nickel phosphorus deposit included about 11.5% phosphorus, and the plated product had an internal stress of 20.7×10^6 Pa (3,000 psi) in the negative or compressive range.

Example VIII

Another sulfur-free bath similar to Example VI was prepared, except this one included about 7 g/l of aconitic acid and deposited 12% phosphorus to provide a plated steel product having an internal stress of 20.7×10^6 Pa (3,000 psi), compressive.

Example IX

A sulfur-free bath similar to that of Example V, but having a pH of 5, was found to have a plating rate of 0.02 mm (0.8 mil)/hr onto steel plates to form deposits thereon exhibiting low tensile stress and good corrosion resistance. The plated product, when observed in photomicrographs, was found to have a particularly homogeneous appearance.

Example X

A sulfur-free bath including aconitic acid as the tensile stress reduction agent, citric acid and malic acid complexing agents, and saturated dicarboxylic acid buffers according to this invention, together with sodium hypophosphite reducing agent and an appropriate source of nickel provided a nickel phosphorus deposit of 11% phosphorus to form a plated product having an internal compressive, or negative stress of 13.8×10^6 Pa (2,000 psi). When substantially the same bath was modified to be sulfur-containing rather than sulfur-free by adding a thiourea stabilizer thereto, this bath still formed a deposit having 11% phosphorus, but the internal stress of the plated product was 41.4×10^6 Pa (6,000 psi) in the tensile, or positive, range; that is, the sulfur-containing bath had an internal tensile stress that was 55.2×10^6 Pa (8,000 psi) greater than the sulfur-free bath.

Claims

1. A method of electrolessly depositing a nickel phosphorus deposit onto a substrate with reduced stress in the deposit from a bath having a pH of at least about 4.5 and comprising
   (a) a bath soluble unsaturated carboxylic acid of the formula $R(COOH)_n$ or bath-soluble derivative thereof wherein R is an unsaturated alkyl group with at least 2 and not more than 6 carbon atoms and n is at least 1; and
   (b) a bath-soluble reducing agent; and
   (c) a bath-soluble source of nickel,
   (d) a bath-soluble saturated alkyl or aryl polycarboxylic acid of the formula $R^1(COOH)_p$ or a bath-soluble salt ester or anhydride thereof, wherein R^1 is absent or is a saturated alkyl or aromatic group having from 1 to 20 carbon atoms and p is at least 2;
   (e) any sulfur if present being exclusively in the highest oxidation state of sulfur; and
   (f) a bath-soluble phosphorus source which may be the said reducing agent; the deposit formed having a phosphorus content of at least about 10 per cent by weight.

2. A method according to claim 1, wherein n is 2.

3. A method according to claim 1 or 2 wherein the bath has a pH between 4.5 and 5.5

4. A method according to claim 3 wherein said bath has a pH of about 5.0.

5. A method according to any one of the preceding claims wherein said unsaturated acid is aconitic acid, citraconic acid, fumaric acid, itaconic acid, maleic acid, a bath-soluble derivative thereof, or a mixture of any of these.

6. A method according to any one of the preceding claims wherein each of said unsaturated carboxylic acid and said saturated polycarboxylic acid are present within the bath at a concentration of at least about 1 gm/l.

7. A method according to claim 6, wherein R^1 has a carbon chain of not greater than 10 carbon atoms, and p is 2.

8. A method according to claim 6 or claim 7 wherein said saturated acid is adipic acid, gluraric acid, isophthalic acid, malonic acid, oxalic acid, succinic acid, a salt, ester or anhydride thereof, or a mixture of any of these.

9. A method according to any one of the preceding claims, further including a bath-soluble complexing agent that is a substituted carboxylic acid of the formula $XR''(COOH)_s$ or bath-soluble derivative thereof, wherein x is a hydroxy group, an amino group or a combination thereof, R" is saturated alkyl, heterocyclic or alkylaryl having a carbon chain length of between 1 and 14, and s is between 1 and 4.

10. A method according to claim 9, wherein said substituted carboxylic acid complexing agent is present within the bath at a concentration of at least about 1 gm/l.

11. A method according to claim 9 or claim 10 wherein R" has a carbon chain length of not greater than 6 carbon atoms, and s is not greater than 2.

12. A method according to claim 9 or claim 10 wherein X is in the alpha-position relative to at least one of the COOH groups.

13. A method according to any one of the preceding claims wherein the substrate is a printed circuit board.

Patentansprüche

1. Ein Verfahren zum chemischen Abscheiden einer Nickel-Phosphor-Beschichtung auf ein Substrat, mit verringerter Spannung in der Beschichtung, aus einem Bad mit einem pH-Wert von wenigstens 4,5 und umfassend
   a) eine badlösliche, ungesättigte Carbonsäure der Formel $R(COOH)_n$ oder ein badlösliches Derivat derselben, worin R eine ungesättigte Alkyigruppe mit wenigstens 2 und nicht mehr als 6 C-Atomen ist und n wenigstens 1 bedeutet; und
   b) ein badlösliches Reduktionsmittel; und
   c) eine badlösliche Nickelquelle,
   d) eine badlösliche, gesättigte Alkyl- oder Arylpolycarbonsäure der Formel $R^1(COOH)_p$ oder ein im Bad lösliches Salz oder ein solcher Ester oder ein solches Anhydrid derselben, worin R^1 abwesend ist oder für eine gesättigte Alkyl- oder aromatische Gruppe mit 1 - 20 C-Atomen steht und p wenigstens 2 bedeutet;
   e) sämtlichen gegebenenfalls vorhandenen Schwefel im höchsten Oxydationszustand; und
   f) eine im Bad lösliche Phosphorquelle, die das genannte Reduktionsmittel sein kann, wobei die gebildete Abscheidung einen Phosphorgehalt von wenigstens etwa 10 Gew.-% aufweist.

2. Ein Verfahren nach Anspruch 1, worin n für 2 steht.

3. Ein Verfahren nach Anspruch 1 oder 2, worin das Bad einen pH-Wert zwischen 4,5 und 5,5 aufweist.

4. Ein Verfahren nach Anspruch 3, worin das Bad einen pH-Wert von etwa 5,0 aufweist.

5. Ein Verfahren nach einem der vorhergehenden Ansprüche, worin die ungesättigte Säure Akonitinsäure, Citrakonsäure, Fumarsäure, Itakonsäure, Maleinsäure, ein badlösliches Derivat derselben oder ein Gemisch von beliebigen dieser Stoffe ist.

6. Ein Verfahren nach einem der vorhergehenden Ansprüche, worin jede der ungesättigten Carbonsäuren und die gesättigte Polycarbonsäure im Bad in einer Konzentration von wenigstens 1 g/l vorliegt.

7. Ein Verfahren nach Anspruch 6, worin R^1 eine Kohlenstoffkette von nicht mehr als 10 C-Atomen aufweist und p für 2 steht.

8. Ein Verfahren nach Anspruch 6 oder 7, worin die gesättigte Säure Adipinsäure, Glutarsäure, Isophthalsäure, Malonsäure, Oxalsäure, Succinsäure, ein Salz, ein Ester oder ein Anhydrid derselben oder eine Mischung von beliebigen dieser Stoffe ist.

9. Ein Verfahren nach einem der vorhergehenden Ansprüchen, weiters umfassend einen im Bad löslichen Komplexbildner in Form einer substituierten Carbonsäure der Formel $XR''(COOH)_s$ oder ein badlösliches Derivat derselben, worin x eine Hydroxygruppe, eine Aminogruppe oder eine Kombination derselben ist, R” ein gesättigtes Alkyl, einen Heterocyclus oder ein Aralkyl mit einer Kohlenstoffkettenlänge zwischen 1 und 14 bedeutet und s zwischen 1 und 4 ist.

10. Ein Verfahren nach Anspruch 9, worin der Komplexbildner in Form der substituierten Carbonsäure innerhalb des Bades in einer Konzentration von wenigstens 1 g/l vorliegt.

11. Ein Verfahren nach Anspruch 9 oder 10, worin R” eine Kohlenstoffkettenlänge von nicht mehr als 6 C-Atomen aufweist und s nicht mehr als 2 bedeutet.

12. Ein Verfahren nach Anspruch 9 oder 10, worin sich x in Alpha-Stellung in bezug auf wenigstens eine der COOH-Gruppen befindet.

13. Ein Verfahren nach einem der vorhergehenden Ansprüche, worin das Substrat eine gedruckte Schaltung ist.

Revendications

1. Procédé pour déposer non électrolytiquement un dépôt de nickel phosphore sur un substrat qui réduit la contrainte dans le dépôt d’un bain ayant un pH d’au moins environ 4,5 et comprenant :
   (a) un acide carboxylique insaturé soluble dans le bain de formule $R(COOH)_n$ ou son dérivé soluble dans le bain où R est un groupe alcoyle insaturé avec au moins 2 et pas plus de 6 atomes de carbone et n est au moins 1; et
   (b) un agent réducteur soluble dans le bain; et
   (c) une source de nickel soluble dans le bain,
   (d) un acide alkyl ou aryl polycarboxylique saturé soluble dans le bain de formule $R^1(COOH)_p$ ou son ester d’un sel ou anhydride soluble dans le bain, où R’ est absent ou est un groupe alcoyle saturé ou aromatique ayant de 1 à 20 atomes de carbone et p est au moins 2;
   (e) tout soufre, s’il y en a, étant exclusivement à l’état d’oxydation supérieure du soufre; et
   (f) une source de phosphore soluble dans le bain qui peut être ledit agent réducteur; le dépôt formé ayant une teneur en phosphore d’au moins environ 10 pour cent en poids.

2. Procédé selon la revendication 1 où n est 2.

3. Procédé selon la revendication 1 ou 2 où le bain a un pH compris entre 4,5 et 5,5.

4. Procédé selon la revendication 3 où ledit bain a un pH d’environ 5,0.

5. Procédé selon l’une quelconque des revendications précédentes où ledit acide insaturé est l’acide aconitique, l’acide citraconique, l’acide fumarique, l’acide itaconique, l’acide maléique, un dérivé soluble dans le bain ou un mélange de ceux-ci.

6. Procédé selon l’une quelconque des revendications précédentes où chacun dudit acide carboxylique insaturé et dudit acide polycarboxylique saturé sont présents dans le bain à une concentration d’au moins environ 1 g/l.

7. Procédé selon la revendication 6 où R^1 a une chaîne de carbone ne dépassant pas 10 atomes de carbone,

et p est 2.

8. Procédé selon la revendication 6 ou la revendication 7 où ledit acide saturé est l'acide adipique, l'acide glutarique, l'acide isophtalique, l'acide malonique, l'acide oxalique, l'acide succinique, un sel, ester ou anhydride, ou un mélange de ceux-ci.

9. Procédé selon l'une quelconque des revendications précédentes, contenant de plus un agent complexant soluble dans le bain qui est un acide carboxylique substitué de formule $XR''(COOH)_s$ ou son dérivé soluble dans le bain, où x est un groupe hydroxy, un groupe amino ou une combinaison, R" est un alcoyle saturé, hétérocyclique ou alkylaryle ayant une longueur de chaîne de carbone comprise entre 1 et 14, et s est compris entre 1 et 4.

10. Procédé selon la revendication 9 où ledit agent complexant d'acide carboxylique substitué est present dans le bain à une concentration d'au moins environ 1 g/l.

11. Procédé selon la revendication 9 ou la revendication 10 où R" a une longueur de chaîne de carbone ne dépassant pas 6 atomes de carbone, et s ne dépasse pas 2.

12. Procédé selon la revendication 9 ou la revendication 10 où X est à la position alpha relativement à au moins l'un des groupes COOH.

13. Procédé selon l'une quelconque des revendications précédentes où le substrat est une planche de circuit imprimé.