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(54) Electroless nickel plating.

(57) Nickel-phosphorus deposits are electrolessly coated onto substrates at a commercially acceptable rate of deposition in a manner that enhances corrosion resistance and reduces the internal tensile stress of the electroless deposit on the substrate. This is done by plating from a bath that is sulfur-free (or free of sulfur except at its highest oxidation state) and that includes an unsaturated carboxylic acid of the formula $R(\text{COOH})_n$ wherein R is an unsaturated alkyl group of at least 2 carbon atoms and n is at least 1, or a derivative thereof. Such compounds include aconitic, citraconic, fumaric, itaconic and maleic acids. The reducing agent of the bath may also be its phosphorus source e.g. an alkali metal hypophosphite.

ELECTROLESS NICKEL PLATING

The present invention relates to electroless nickel plating onto substrates.

5 Electroless deposition of nickel onto metal substrates has long been known to impart to the substrate enhanced corrosion resistance, hardness and similar properties. When electroless nickel deposits are made onto various substrates, there tends to develop cracking,
10 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
15 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
20 adverse conditions. It is, therefore, generally observed that great advantages can be realized by electrolessly plating _____

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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 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 tensile stress reduction agent that is
5 a bath soluble unsaturated carboxylic acid $R(\text{COOH})_n$ (wherein R is an unsaturated alkyl and n is at least one) and/or derivative thereof, the baths also including an electroless bath reducing agent and a nickel source. The products of
10 this invention exhibit reduced tensile stress when compared with products plated from baths that are not in accordance with this invention.

It is accordingly a general object of this invention to improve electroless nickel plating by enabling the
15 plating of products to have reduced tensile or contractile stress, 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
20 enhancing the stress properties and therefore the corrosion resistance of circuit boards having an electroless nickel deposit thereon.

Maximum phosphorus contents may also be achieved at relatively high pH values.

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

5 In the stress-reducing agent the group R preferably has less than 20 carbon atoms, more preferably 6 or less, 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
10 interfere with the stress reduction properties of the bath. Typically, 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
15 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

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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
5 or in the form of a bath soluble derivative thereof, the carbon chain length typically being no greater than 20, preferably no greater than 10, and most preferably no greater than 6, and n is preferably 2 or more, most preferably 2. Exemplary unsaturated acid tensile stress
10 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 gm/l, with the upper limit being a matter of
15 economics and bath solubility. There reaches a point, typically at no more than 10 gm/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
20 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
25 by the tensile stress reduction agent. Baths 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-
30 free baths of this invention do not include divalent sulfur

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containing compounds such as the organic sulfur-containing compounds, the organic and inorganic thiocompounds, and the inorganic sulfides.

Organic sulfur-containing compounds include thiourea
5 and its derivatives, dithioglycol, thioglycolic acid,
2,2-thiodiethanol, 1,2-ethanedithiol, 2-mercaptobenzothiazole,
1,2-benziosothiazine, methionine, and the like. Thiocompounds
include the thiocyanate salts and the thiosulfate salts such
as sodium thiocyanate, potassium thiocyanate, potassium
10 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 typically included within baths
15 according to this invention. Such buffers provide the proper
environment for the tensile stress reduction agent. While
traditional monocarboxylic acid derived buffering systems may
be incorporated in baths according to this invention, such as
acetic acid-sodium acetate systems, boric acid-borate systems,
20 and propionic acid-propionate systems, maximum efficiency
of these baths, especially in connection with the enhancement
of phosphorus deposition percentages without adversely
affecting the plating rate, is attained when the buffer is a
saturated alkyl or aromatic polycarboxylic acid and/or bath
25 soluble derivative thereof, which may be exemplified by 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
30 than 10 carbon atoms, more preferably of not more than 6 carbon

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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 gm/l the concentration being varied according to needs for maintaining pH control, which concentration will usually be no more than about 40 gm/l and often not more than about 20 gm/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 about 14, and preferably not greater than about 6, especially preferred compounds having an R'' chain length of not more than 4; and s may be between 1 and 4. The

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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

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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 prepared according to this invention has a pH above 4.0, which is the pH to which known baths are often adjusted in order to lay down an electroless nickel deposit having a high phosphorus content. A typical pH value according to this invention is at least about 4.5, usually on the order of 5.0, including a pH of

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5.0 $\pm$ 0.5, preferably a pH of 5.0 $\pm$ 0.3, and most preferably a pH of 5.0 $\pm$ 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
5 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
10 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,
15 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 on the order of 4.0 will provide nickel deposits having high phosphorus contents in excess of 10 weight per cent, the plating rate
20 thereof is on the order of 0.2 mil/hr, while baths according to this invention, which have a pH on the order of 5.0, attain plating rates more on the order of 0.4 through 0.8 mil/hr while providing a nickel deposit having the same high phosphorus content as such a conventional bath. Accordingly, the method
25 according to this invention has 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 0.25 and 1.0 square foot per gallon.

30 Products produced according to this invention have

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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.

- 5 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
- 10 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
- 15 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
- 20 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,
- 25 beryllium and its alloys, especially beryllium-nickel alloys, cast iron, magnesium and non-conductive materials.

- Product having the nickel-phosphorus deposits onto these substrates preferably have a phosphorus content of at least 10 per cent, with the maximum phosphorus content being
- 30 limited only by the maximum phosphorus deposition capabilities

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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
5 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 VHN₁₀₀ and between 800 and 950 VHN₁₀₀ after heat treatment at 400°C for one
10 hour.

The following examples are offered to illustrate the present invention.

EXAMPLE 1

Various sulfur-free baths were formulated in
15 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
20 between about 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
25 value indicating internal compressive stress.

Unsaturated Polycarboxylic Acid	Acid Concentration (In Bath)	Stress
-	-	13,200 psi
Aconitic Acid	2 gm/l	6,400 psi
30 Aconitic Acid	5 gm/l	3,800 psi

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	Aconitic Acid	10 gm/l	3,900 psi
	Citraconic Acid	5 gm/l	6,600 psi
	Citraconic Acid	10 gm/l	4,600 psi
	Citraconic Acid	15 gm/l	1,500 psi
5	Itaconic Acid	5 gm/l	5,400 psi
	Itaconic Acid	10 gm/l	-4,100 psi
	Itaconic Acid	15 gm/l	-7,800 psi
	Maleic Acid	1 gm/l	11,000 psi
	Maleic Acid	5 gm/l	-4,500 psi

10 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
15 range, which enhanced the fatigue resistance of these panels.

EXAMPLE II

Sulfur-free baths were prepared to include 27 gm/l of malic acid, 9 gm/l of citric acid, a total of 9 gm/l saturated alkyl dicarboxylic acid buffers, 6 gm/l of aconitic
20 acid, 37 gm/l of sodium hypophosphite, 27 gm/l of sodium hydroxide, and enough nickel salt to provide 6 gm/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 0.5 mil, three to a
25 plating thickness of 1 mil, and three were immersed in the bath until the plating thickness was 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
30 panel. The testing chamber was open at 24 hour intervals on

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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 III

A sulfur-free bath including 30 gm/l lactic acid, 10 gm/l succinic acid buffer, a 15 gm/l acetic acid and 15 gm/l sodium acetate buffer system, 5 gm/l aconitic acid, 30 gm/l sodium hypophosphite and enough liquid nickel sulfate to provide 6 gm/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 0.5 mil, 1.0 mil and 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 II, and all nine of these panels passed the salt spray test.

EXAMPLE IV

Sulfur-free baths generally in accordance with Example II 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 0.4 and 0.5 mil per hour at a tank loading of about 0.25 square foot per gallon and at a temperature between about 190 and 195°F. The deposit appearance was hazy bright. A brightener

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was added to some of the baths, and deposit brightness was found to be enhanced.

EXAMPLE V

A sulfur-free bath was prepared to include about
5 36 gm/l of a combination of citric acid and malic acid
complexing agent, 36 gm/l of sodium hypophosphite, 10 gm/l
of a blend of saturated alkyl dicarboxylic acids, 5 gm/l of
aconitic acid, and enough nickel salt to provide 6 gm/l of
nickel as nickel metal. This bath had a pH of 4.9, the
10 temperature was maintained between 190 and 195°F, and its
plating rate was estimated at 0.33 mil/hr when plating
steel panels. Panels having a plating thickness of 0.5
and 0.6 mil were tested according to ASTM B-117 for one
thousand hours of 5% salt spray, after which no spots were
15 observed. Another panel plated in this bath to 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
0.5 mil deposit from this bath were subjected to heat treat-
ment at 260°C for either 4 or 12 hours, and again no spots
20 were observed after one thousand hours of salt spray.
Another panel having a 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
25 after 168 hours. Two panels having a 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.
30 This bath was also used to plate a 1 mil nickel

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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
5 that was not heat treated exhibited no spots after one thousand hours of salt spray testing according to ASTM B-117.

EXAMPLE VI

A deposit of 89% nickel and 11% phosphorus was plated at a rate of deposition of 0.6 mil/hr, the deposit
10 having an internal stress of 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 gm/l lactic acid, 10 gm/l succinic acid, 5 gm/l aconitic acid, 30 gm/l sodium hypophosphite and 6 gm/l of nickel.

15

EXAMPLE VII

A sulfur-free bath was prepared to include 3 gm/l of aconitic acid, 9 gm/l of citric acid, 27 gm/l of malic acid, 36 gm/l of sodium hypophosphite, 10 gm/l of a mixed dicarboxylic acids buffer system, and enough liquid nickel
20 sulfate to provide 6 gm/l of nickel as nickel metal. This bath had a pH of 4.8 and a rate of deposition of 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.

25

EXAMPLE VIII

A sulfur-free bath having a pH of 4.8 was prepared to include 5 gm/l of aconitic acid, with the rest of the bath being substantially identical with the bath of Example VII. The nickel phosphorus deposit included about 11.5% phosphorus,
30 and the plated product had an internal stress of 3,000 psi

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in the negative or compressive range.

EXAMPLE IX

Another sulfur-free bath similar to Example VII was prepared, except this one included about 7 gm/l of aconitic acid and deposited 12% phosphorus to provide a plated steel product having an internal stress of 3,000 psi, compressive.

EXAMPLE X

A sulfur-free bath similar to that of Example VI, but having a pH of 5, was found to have a plating rate of 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 XI

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 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 6,000 psi in the tensile, or positive, range; that is, the sulfur-containing bath had an internal tensile stress that was 8,000 psi greater than the sulfur-free bath.

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While in the foregoing specification certain
embodiments and examples of this invention have been described
in detail, it will be appreciated that modifications and
variations therefrom will be apparent to those skilled in
5 this art.

CLAIMS:

1. An electroless nickel bath comprising:
 - (a) a bath-soluble tensile stress reduction
5 agent that is an unsaturated carboxylic acid of the formula $R(\text{COOH})_n$ or a bath-soluble derivative thereof, wherein R is an unsaturated alkyl chain having at least 2 carbon atoms, and wherein n is at least 1;
 - (b) a bath-soluble reducing agent; and
 - 10 (c) a bath-soluble source of nickel, wherein said bath is free of sulfur (or free of sulfur which is at an oxidation state lower than the highest oxidation state of sulfur).
- 15 2. A bath according to claim 1, wherein R has a carbon chain of not greater than 20 carbon atoms, and n is at least 2.
3. A bath according to claim 1 or claim 2, further
20 including a bath-soluble buffer that is a saturated alkyl or aryl polycarboxylic acid of the formula $R'(\text{COOH})_p$ or a bath-soluble derivative thereof, wherein R' is a saturated alkyl or aromatic carbon chain having from 0 to 20 carbon atoms, and wherein p is at least 2.
- 25 4. A bath according to claim 3, wherein each of said unsaturated carboxylic acid tensile stress reduction agent and said saturated polycarboxylic acid buffer are present within the bath at a concentration of at least about 1 gm/l.
- 30 5. A bath according to claim 3 or claim 4, wherein R' has a carbon chain of not greater than 10 carbon atoms, and p is 2.
- 35 6. A bath according to claim 3, claim 4 or claim 5

wherein said buffer is adipic acid, glutaric acid, isophthalic acid, malonic acid, oxalic acid, succinic acid, a salt, ester or anhydride thereof, or a mixture of any of these.

5

7. A bath 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 about 1 and 14, and s is between about 1 and 4.

10 8. A bath according to claim 7, wherein said substituted carboxylic acid complexing agent is present within the bath at a concentration of at least about 1 gm/l.

9. A bath according to claim 7 or claim 8, wherein R'' has a carbon chain length of not greater than 6 carbon atoms, and s is not greater than 2.

10. A bath according to claim 7, claim 8 or claim 9, wherein said complexing agent is α -alanine, aspartic acid, citric acid, glutamic acid, glycine, glycolic acid, iminoacetic acid, iminodiacetic acid, lactic acid, malic acid, a bath-soluble derivative thereof, or a mixture of any of these.

30 11. A bath according to claim 7, claim 8, claim 9 or claim 10, wherein X is in the alpha position relative to at least one of the COOH groups, and R'' has a carbon chain length equal to or less than 6 carbon atoms.

35 12. A bath according to any one of the preceding claims

which is operated at a temperature of between about 160 and 212°F.

13. A bath according to any one of the preceding claims
5 which has a pH numerically greater than 4.0.

14. A bath according to any one of the preceding claims
which has a pH of at least about 4.5 and deposits at least
about 10 per cent phosphorus onto a substrate.

10

15. A bath according to any one of the preceding claims
wherein said reducing agent is alkali metal hypophosphite.

16. A bath according to any one of the preceding claims
15 wherein said tensile stress reduction agent is aconitic
acid, citraconic acid, fumaric acid, itaconic acid, maleic
acid, a bath-soluble derivative thereof, or a mixture of
any of these.

20 17. The bath of claim 1, wherein R has a carbon chain of
equal to or less than 6 carbon atoms and n is 2.

18. A method of depositing onto a substrate with reduced
stress in the deposit, comprising electrolessly forming a
25 nickel phosphorus deposit onto a substrate from a sulfur-
free bath according to any one of the preceding claims.

19. A method according to claim 18 which includes
preparing the bath to have a pH between about 4.5 and about
30 5.5, preferably about 5.0.

20. A method according to claim 19 wherein said method
includes preparing the bath to have a pH of about 5.0.

35 21. A method according to claim 18, claim 19 or claim 20

wherein the process of electrolessly forming a nickel phosphorus deposit is at a plating rate greater than about 0.3 mil per hour, and the deposit formed has a phosphorus content of at least about 10 per cent.

5

22. A method according to claim 18, claim 19, claim 20 or claim 21 wherein the substrate is a ferrous metal or alloy, titanium, copper or copper alloy, beryllium or beryllium alloy, aluminium or aluminium alloy, or magnesium.

10

23. A method according to any one of claims 18 to 22 wherein the substrate is a printed circuit board.

24. An electroless nickel deposit on a substrate, said
15 deposit having been produced by immersing the substrate into a sulfur-free electroless nickel bath according to any one of claims 1 to 17.



European Patent
Office

EUROPEAN SEARCH REPORT

0071436

Application number

EP 82 30 3913

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	FR-A-2 144 782 (SHIPLEY) *Page 3, lines 25-28; page 5, lines 33-35; page 7, line 9; page 8, table 1; pages 9-10; examples 33-34, 35-47; page 11, examples 53-57*	1, 2, 7, 8, 9, 10, 12-22, 24	C 23 C 3/02
A	US-A-2 935 425 (GUTZEIT)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 23 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-11-1982	Examiner NGUYEN THE NGHIEP
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	