

1

3,782,978

ELECTROLESS NICKEL PLATING

Joseph Francis Souza, Everett, Mass., assignor to Shipley Company, Inc., Newton, Mass.

No Drawing. Filed July 6, 1971, Ser. No. 160,087

Int. Cl. C23c 3/02

U.S. Cl. 106—1

24 Claims

ABSTRACT OF THE DISCLOSURE

The subject matter of this invention is an electroless nickel plating solution especially formulated for nickel plating aluminum alloys. Aluminum is a difficult metal to plate from an electroless bath because aluminum is active and deposition over aluminum takes place at a rapid rate. As a result, there is excessive gassing at the aluminum interface resulting in migration of smut particles from the aluminum surface into the plating bath. These particles act as nuclei for deposition of nickel resulting in spontaneous decomposition (triggering) of the bath and loss thereof, as well as plate-out on walls of the plating tank, racks and the like. The invention overcomes these difficulties by addition of an unsaturated carboxylic acid to the solution alone or preferably in combination with a second stabilizer. The acid acts to suppress the rate of deposition over aluminum decreasing gas evolution and migration of smut into the solution. As a result, triggering of the solution is retarded.

BACKGROUND OF THE INVENTION

(1) Introduction

This invention relates to a metal-depositing composition and more particularly, to an electroless nickel plating solution especially formulated for nickel plating aluminum which composition is characterized by the addition of an unsaturated carboxylic acid suppressant preferably in combination with a stabilizer for said electroless nickel composition.

(2) Description of the prior art

Electroless metal deposition refers to the chemical plating of a metal over an active surface by chemical reduction in the absence of an external electric current. Processes and compositions useful therefor are known, are in substantial commercial use, and are described in numerous publications. For example, compositions for depositing electroless nickel are described in U.S. Pats. Nos. 2,690,401; 2,690,402; 2,762,723; 2,935,424; 2,929,742; and 3,338,726. These patents are included herein by reference.

Known electroless nickel deposition solutions generally comprise at least four ingredients dissolved in a solvent, typically water. They are (1) a source of nickel ions, (2) a reducing agent such as hypophosphite, (3) an acid or hydroxide pH adjustor to provide required pH, and (4) a complexing agent for the nickel ions sufficient to prevent precipitation in solution. A large number of suitable complexing agents for electroless nickel solutions are described in the aforesaid U.S. patents. In some formulations, the complexing agent is helpful, but not a necessity.

Although electroless nickel solutions have been known for many years, the commonly used solutions have not been fully satisfactory for plating aluminum. Aluminum is a highly active metal. Exposure to air results in rapid formation of a thin, tenacious film of aluminum oxide which must be removed as a step in preparing the metal for plating. The process of removing the oxide usually involves etching where the aluminum is contacted with a suitable etchant for a time sufficient to remove all of the oxide film. During the etching process, a smut usually

2

forms on the surface of the aluminum. This smut consists of some aluminum and insoluble or partially soluble alloy residue, especially silicon. The smut is normally frangible and non-adherent. In some plating operations, plating takes place directly over the smut. In others, much of the smut is removed prior to plating by contact with a solution of a desmuter such as an aqueous nitric acid solution. Regardless of the nature of the plating operation, some smut is usually retained on the surface of the aluminum substrate to be plated, though the amount may vary.

Upon contact of an aluminum part prepared for plating with an electroless nickel solution, because of the high activity of the aluminum, plating takes place at a rapid rate resulting in considerable gassing over the entire surface of the part. This gassing is believed to break smut particles off the surface and carry the particles into the electroless solution. These act as nucleating centres in solution for deposition of electroless nickel with the result that the electroless nickel solution triggers or spontaneously decomposes. Thus, the solution is lost and plating takes place over anything in contact with the solution such as plating racks, walls of the plating tank and the like.

It is known in the art that certain additives or inhibitors added to an electroless solution in properly controlled quantities act to stabilize the solution and prolong the time to trigger. In general, these additives, or stabilizers as they are referred to in the art, are catalytic poisons. The concentration of such stabilizers is usually critical. Trace quantities typically in the range of a few parts per million parts of solution provide stability. An excess of stabilizer will partially or totally stop deposition of the electroless metal. As of the present time, even under conditions of careful control and use of such stabilizers, it is believed that stabilizers which effectively prevent or retard triggering of electroless nickel solutions are relatively ineffective when the bath is used to plate aluminum.

STATEMENT OF THE INVENTION

The present invention is predicated in part upon the discovery that the addition of an unsaturated carboxylic acid to substantially any electroless nickel hypophosphite plating solution results in suppression of the plating rate and decreased gassing. Consequently, introduction of smut particles into the electroless plating solution as a consequence of excessive gassing is minimized and the useful life of the solution is prolonged.

Though the nature of the invention is not fully understood, it is postulated that in addition to preventing excessive gassing, the unsaturated carboxylic acid might also coordinate with aluminum introduced into the solution both from the smut and from free aluminum ions migrating into solution as a result of initial displacement plating of nickel for aluminum. Since aluminum ions in solution might accelerate triggering, coordination of the ions could also act to increase the useful life of the solution.

There are secondary advantages to this invention. For example, it has been found that the unsaturated carboxylic acid improves the effectiveness of prior art stabilizers, whether the solutions are used to plate aluminum or other materials. Moreover, the deposits seem to have unique properties. For example, at substantially any deposit thickness, the deposit has a bright, shiny surface appearance. By way of contrast, deposits from prior art nickel solutions can be made to have a bright, shiny appearance in relatively thick sections, i.e., 1/2 mil or more, but generally have a matted appearance when thin. Also, prior art electroless nickel over aluminum, when rinsed with water, frequently stains. The electroless nickel

of this invention over aluminum does not stain when rinsed.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As noted above, the electroless nickel solutions of this invention are especially useful for plating aluminum due to the unsaturated carboxylic acid alone and preferably in combination with a stabilizer. The unsaturated carboxylic acid contemplated is that soluble in solution and containing one or more double or triple bonds. In this respect, low molecular weight aliphatic mono- and polycarboxylic acids, i.e. having from 2 to 6 carbon atoms in the chain are more soluble than aromatic and higher molecular weight aliphatic carboxylic acids and are therefore preferred. Examples of such carboxylic acids include acrylic acid, maleic acid, propiolic acid, acetylene dicarboxylic acid, cotonic acid, vinyl acetic acid, tetraloic acid, glutaconic acid, itaconic acid, mesaconic acid, allyl acetic acid, ethylacrylic acid, vinyl acrylic acid, muconic acid, tiglic acid, sorbic acid and fumaric acid.

The above carboxylic acids can be substituted with various substituents such as alkyl groups, hydroxyl groups, nitro groups, amino groups, halo groups, sulfonic acid groups and the like. Examples of substituted unsaturated carboxylic acids include by way of examples, bromocrotonic acid, bromomaleic acid, chloroacrylic acid, chloromaleic acid, dibromomaleic acid, dimethylacrylic acid, ethylcrotonic acid, nitro glutaconic acid, methylfumaric acid, mucobromic acid, mucochloric acid, and teraconic acid. Acids of this nature constitute a lesser preferred embodiment of this invention, though are still considered suitable for purposes set forth herein.

Other unsaturated carboxylic acids that are insoluble or partially soluble in the electroless nickel solution may be made more soluble by substitution onto the compound of a solubilizing group such as a halo group, nitro group, sulfo group, hydroxyl group, amino group and the like. By such substitution, some aromatic carboxylic acids that might otherwise be unsuitable or provide limited improvement may be made soluble and thus fulfill the objects of this invention. Typical examples of such materials include bromo cinnamic acid, coumaric acid, dihydroxycinnamic acid, nitrocinnamic acid, phenyl angelic acid, and the like. The aromatic unsaturated carboxylic acids are least preferred.

The amount of carboxylic acid added to solution is not critical, small amounts providing some benefit and larger amounts providing greater benefit until a practical maximum is reached. In general, the amount of unsaturated carboxylic acid is that amount that at least doubles the life of the electroless nickel solution in contact with the aluminum part to be plated. More specifically, it is preferred that the carboxylic acid range from about 0.001 mole per liter of solution to saturation and most preferably, from about 0.01 to 0.20 mole per liter of solution.

As earlier stated, the principal function of the unsaturated carboxylic acid in solution is to prevent triggering of the electroless nickel solution in contact with an aluminum substrate. It is believed that triggering is caused by smut and possibly, aluminum ions entering the solution by virtue of excessive gassing during plating with respect to the smut and by displacement plating of nickel for aluminum with respect to the aluminum ions at least during the initial phase of plating. The unsaturated carboxylic acid appears to suppress gas formation on the surface of the aluminum during plating thus preventing much of the smut from breaking off the surface and entering the solution. Since the unsaturated carboxylic acid suppresses gas evolution, it will be referred to at times throughout the remainder of this specification as a "suppressant." It is also conceivable that triggering is prevented by the unsaturated carboxylic acid coordinating with the aluminum and further by dissolving at least in part, any smut that does enter the solution.

In a preferred embodiment of this invention, the unsaturated carboxylic acid is used in conjunction with an electroless nickel solution stabilizer because the combination provides baths of substantially enhanced stability when used to plate aluminum. In this respect, the combination provides, in many cases, a synergistic improvement.

Illustrative of stabilizers used for electroless nickel solutions are the divalent sulphur containing compounds many of which are disclosed in U.S. Pat. No. 3,361,540 incorporated herein by reference. Representative examples of such sulphur compounds are the inorganic sulfides such as potassium sulfide, sodium sulfide, sodium polysulfide, and potassium polysulfide; organic and inorganic thiocyanates such as sodium thiocyanate, potassium thiocyanate, potassium dithionate, sodium thiosulfate, and potassium thiosulfate; and organic sulphur containing compounds such as thiourea, 2-mercaptobenzothiazole, 1,2-ethanedithiol, 1,2-benziosothiazine, methionine, 2,2-thioethanol, dithioglycol and thioglycolic acid. Also useful for the stabilization of nickel solutions are iodate compounds, such as potassium and sodium iodate, sources of Pb^{++} such as lead acetate, and sources of mercury ions such as mercuric acetate. These latter compounds are used in solution in amounts sufficient to provide typically less than 100 parts stabilizing ions per million parts of solution.

An additional class of stabilizers are acetylinic compounds corresponding to one of the following formulas:



where each of R, R' and R'' are selected from the class of lower monovalent hydroxyalkyl, cyclohydroxyalkyl, and hydroxyalkyl ether. Examples include ethynyl cyclohexanol, methyl butynol, methyl pentynol, dimethyl hexynol, 2-butyne-1, 4-diol, dimethyl hexynediol, propargyl alcohol, hexynol and ethyl actynol. For purposes of convenience, the stabilizers will be referred to as "solution soluble acetylenic compounds." Further examples of such compounds are set forth in U.S. Pat. No. 3,457,089.

The particular electroless nickel solution to which the unsaturated carboxylic acid is added is not critical. Thus, the electroless nickel solution in accordance with the invention will comprise a source of nickel ions, a reducing agent for the nickel ions such as a hypophosphite, a complexing agent to maintain the nickel ions in solution and a stabilizer for the solution. Examples of suitable sources of nickel ions, complexing agents, stabilizers, and the like as well as the relative amounts of each are well known in the art and illustrated in the above referenced patents.

There are secondary advantages to the use of the suppressants of this invention. One such advantage is that the electroless nickel deposits from the solutions of this invention are bright regardless of thickness whereas prior art deposits may be bright in relatively thick sections, but in thin deposits, typically are matted. A further advantage is that the deposits of the invention over aluminum do not stain when rinsed in water whereas deposits from prior art solutions are prone to staining.

In addition to aluminum, the electroless plating solutions of the invention may be used to deposit nickel over substantially any substrate in the same manner as any prior art electroless nickel solution. In this respect, the surface of the part to be plated should be free of grease and contaminating material. Where a non-metallic surface is to be plated, the surface area to receive the deposit must be sensitized to render it catalytic to the reception of the electroless nickel as by the well known treatment with an acidic aqueous solution of stannous chloride followed by treatment with a dilute aqueous solution of palladium chloride. Alternatively, extremely good sensitization of non-metallic surfaces is achieved by contact with a colloid of a precious metal having a protective stannic acid colloid and formed by the admixture of stannous chloride and a precious metal chloride, preferably palladium chlo-

ride, the stannous chloride being present in stoichiometric excess based upon the amount of precious metal chloride.

When using the electroless nickel solutions of this invention to plate aluminum, the aluminum must be prepared by removing the oxide film. In this respect, the aluminum is first preferably degreased such as by contact with an organic solvent. It is thereafter etched with an acid such as hydrochloric acid of alkali such as potassium carbonate to remove the oxide coating. If the etching is too extensive and a heavy smut forms on the surface, the

sodium hypophosphite and water to 1 liter of solution. In some of the examples, for purposes of illustration, no maleic acid is used. In others, maleic acid alone is used. In still other examples, maleic acid is used in combination with prior art stabilizers. Where maleic acid is used, it is added in an amount of 2½ grams per liter of solution.

The following table illustrates the results obtained wherein the complexing agent used, the prior art stabilizer used, number of parts processed, time to trigger and solution activity is set forth.

TABLE 1

Example number	Complexing agent (amount, gm./liter)	Maleic acid ¹	Secondary stabilizer (amount, p.p.m./liter)	Number of parts ²	Time to trigger ³	Solution activity ⁴
1.....	Hydroxyacetic acid (20).....			1	2	Very heavy.
2.....	do.....	X		1	10	Heavy.
3.....	do.....	X	Potassium iodate (20).....	3	40	Moderate.
4.....	do.....	X	Mercuric acetate (10).....	3	35	Do.
5.....	do.....	X	Methylbutynoxyethanol (40).....	4	56	Light.
6.....	do.....	X	Thiourea (3).....	5	71	Do.
7.....	Citric acid (10).....		Lead acetate (5).....	1	2	Very heavy.
8.....	do.....	X		1	9	Heavy.
9.....	do.....	X	Potassium iodate (20).....	2	21	Moderate.
10.....	do.....	X	Mercuric acetate (10).....	1	15	Do.
11.....	do.....	X	Methylbutynoxyethanol (40).....	3	41	Light.
12.....	do.....	X	Thiourea.....	4	56	Do.
13.....	Oxydiacetic acid (15).....		Lead acetate (5).....	1	3	Very heavy.
14.....	do.....	X		1	9	Heavy.
15.....	do.....	X	Potassium iodate (20).....	4	50	Light.
16.....	do.....	X	Thiourea (3).....	5	65	Do.
17.....	do.....	X	Lead acetate (5).....	5	70	Do.
18.....	Lactic acid (20).....			1	4	Very heavy.
19.....	do.....	X		1	11	Heavy.
20.....	do.....	X	Potassium iodate (20).....	2	21	Moderate.
21.....	do.....	X	Thiourea (3).....	4	48	Light.
22.....	do.....	X	Lead acetate (5).....	4	49	Do.
23.....	Levulinic acid (20).....			1	1	Very heavy.
24.....	do.....	X		1	6	Heavy.
25.....	do.....	X	Potassium iodate (20).....	3	38	Moderate.
26.....	do.....	X	Thiourea (3).....	5	75+	Light.
27.....	do.....	X	Lead acetate (5).....	5	75+	Do.
28.....	Amino acetic acid (15).....			1	3	Very heavy.
29.....	do.....	X		2	30	Moderate.
30.....	do.....	X	Potassium iodate (20).....	5	75+	Light.
31.....	do.....	X	Thiourea (3).....	5	75+	Do.
32.....	do.....	X	Lead acetate (5).....	5	75+	Do.

¹ In the column entitled Maleic acid where there is an entry of an X, this indicates that maleic acid was added to the formulation in an amount of 2½ grams per liter.

² In the column entitled number of parts, the numeral indicates the number of parts plated sequentially until triggering occurred. Each part was plated 15 minutes. If triggering occurred during plating of a part, it was included.

³ In the column entitled Time to trigger, the entry in the column indicates the number of actual plating minutes prior to triggering.

⁴ Solution activity is a subjective observation of the amount of gassing at the surface being plated.

aluminum part may be contacted with a desmutter such as a mixture of nitric acid and hydrofluoric acid.

The invention will be better understood by reference to the following examples wherein in all examples, the aluminum alloy used was a number 6061 alloy which was cut to a size measuring 2½ x 3 inches. In all examples, parts were prepared by etching in a 40% hydrochloric acid solution maintained at 70° F. for a period of four minutes. This provides an even gray-black coating over the aluminum. The parts were then rinsed for two minutes with water in an overflow rinse tank with water temperature at 60° F. In all examples, a first part was plated in an electroless nickel solution for 15 minutes, removed and saved. If the solution did not trigger during this period, the procedure was repeated by plating a second part for a period of 15 minutes in the same solution. This procedure was continuously repeated until the solution triggered. The total number of parts plated and the total effective plating time of the solution were recorded. All electroless nickel solutions were used at a temperature between 195 and 200° F. unless otherwise indicated.

EXAMPLES 1 TO 32

These examples illustrate how maleic acid, as one example of a preferred unsaturated carboxylic acid, suppresses the rate of electroless nickel deposition over aluminum and thereby retards triggering of the electroless nickel solution. In the examples, various electroless nickel solutions are used where the variation within the solution is change of complexing agent. The base electroless solution comprises 30 grams of nickel sulphate, 40 grams of

From the above table, it can be seen that the maleic acid alone provides some benefit, but major benefit is realized when the maleic acid is used in conjunction with a prior art stabilizer. It can also be seen from the table that the maleic acid alone and in combination with the prior art stabilizer provides effective results regardless of the complexing agent used in the solution.

EXAMPLES 33 AND 34

For purposes of comparison, Examples 4 and 25 were repeated without the addition of maleic acid. With respect to Example 4, without the maleic acid, the bath triggered in five minutes and there was heavy gassing at the aluminum surface. With respect to Example 25, without maleic acid, the bath triggered in 8 minutes, again with heavy gassing. These examples illustrate the synergistic effect of combining a prior art stabilizer with a suppressant in accordance with the invention.

EXAMPLES 35 TO 47

Bath formulation

	Grams
Nickel sulphate	30
Sodium hypophosphite	40
Lactic acid	20
Water to 1 liter.	

Using the above formulation, various unsaturated carboxylic acid suppressants are added alone or in com-

bination with prior art stabilizers. The additives, their amounts and results are set forth in the following table:

Ex. No.	Suppressant (amount, gm.)	Stabilizer (amount, p.p.m.)	Number of parts	Time to trigger (min.)	Solution activity
35	-----	-----	1	3	Very heavy.
36	Fumaric acid (3)	-----	1	11	Moderate.
37	do	Potassium iodate (20)	3	34	Do.
38	do	Thiourea (3)	4	52	Light.
39	Itaconic (3)	-----	1	8	Heavy.
40	do	Potassium iodate (2)	3	31	Moderate.
41	do	Thiourea (3)	3	38	Do.
42	Cinnamic acid (3)	-----	1	7	Heavy.
43	do	Potassium iodate (20)	4	48	Light.
44	do	Thiourea (3)	5	75+	Do.
45	Acetylene dicarboxylic acid (3)	-----	3	45	Do.
46	do	Potassium iodate (20)	5	75+	Do.
47	do	Thiourea (3)	5	75+	Do.

From the above results, it can be seen that there is substantial improvement when combining a suppressant with a stabilizer for an electroless nickel solution.

EXAMPLES 48 TO 52

Bath formulation

	Grams
Nickel sulphate -----	30
Sodium hypophosphite -----	40
Lactic acid -----	20
Potassium iodate: 20 p.p.m.	
Water: to 1 liter.	

Cinnamic acid was added to the above formulation in amounts varying from no addition to 7½ grams per liter to show the effect of concentration on a suppressant activity. The amounts used and the results are set forth in the following table:

Example number:	Suppressant (amount, gm.)	Number of parts	Time to trigger	Solution activity
48	0	1	2	Very heavy.
49	1	2	19	Moderate.
50	2	2	19	Do.
51	3	4	48	Light.
52	7½	5	75+	Do.

From the above, it can be seen that increasing concentration of suppressant results in increased stability. It should be noted that though there appears to be a continuing improvement with increasing amount to a maximum of 7½ grams, with maleic acid, a maximum is reached at 5 grams per liter of solution and increasing amounts beyond 5 grams per liter result in a slight decrease indicating that the results are not the same for all suppressants within the scope of the invention. For maleic acid at least, the beneficial results maximize at a level less than 10 grams per liter and then decrease.

EXAMPLES 53 TO 57

Bath formulation

	Grams
Nickel sulphate -----	30
Sodium hypophosphite -----	40
Levulinic acid -----	20
Maleic acid -----	2½
Potassium iodate: 20 p.p.m.	
Water: to 1 liter.	

The pH of the above solution was varied from about 4.3 to 9.0 using sulfuric acid or ammonium hydroxide in an effort to determine effect of pH on suppressant activity. The results obtained are set forth in the following table:

Example number:	pH	Number of parts	Time to trigger (min.)	Solution activity
53	4.3	2	22	Moderate.
54	4.9	3	38	Light.
55	5.6	2	18	Moderate.
56	6.6	2	17	Do.
57	9.0	1	14	Do.

From the above, it can be seen that though pH is a factor, the improvement is realized regardless of pH.

EXAMPLES 58 TO 60

Examples 3, 10 and 16 were repeated though the formulations of said examples were used to plate a phenolic panel rather than aluminum. The panel was prepared by abrading and sensitizing with a catalyst identified as Cuposit Catalyst 6F. In all cases, nickel deposited over the phenolic board and triggering did not occur within a period of 75 minutes.

In all of the above examples, it can be seen that the carboxylic acid suppressant was used in an amount less than the amount of complexing agent since it does not function by itself as the complexing agent for the solution.

What is claimed is:

1. In an aqueous electroless nickel plating solution comprising a source of nickel ions in an amount sufficient to provide a useful deposit, hypophosphite as a reducing agent for said nickel ions and complexing agent to maintain said nickel ions in solution, the improvement comprising the addition to the solution of at least 0.001 mole per liter of solution of a solution soluble aliphatic, unsaturated carboxylic acid as a suppressant, said carboxylic acid is selected from the group of acrylic acid, maleic acid, propiolic acid, acetylene dicarboxylic acid, crotonic acid, vinyl acetic acid, tetraloic acid, glutaric acid, itaconic acid, mesaconic acid, alkyl acetic acid, ethylacrylic acid, vinyl acrylic acid, muconic acid, sorbic acid, fumaric acid and cinnamic acid and being present in an amount less than the amount of complexing agent.

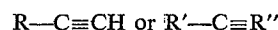
2. The nickel plating solution of claim 1 where the concentration of the carboxylic acid ranges between about 0.01 and 0.20 mole per liter of solution.

3. The nickel plating solution of claim 1 where the unsaturated carboxylic acid suppressant is maleic acid.

4. The nickel plating solution of claim 1 containing a stabilizing agent.

5. The nickel plating solution of claim 4 where the stabilizer is selected from the group consisting of divalent sulphur compounds, lead ions, iodate compounds and solution soluble acetylinic compounds.

6. The nickel plating solution of claim 4 where the stabilizer is a solution soluble acetylinic compound corresponding to one of the following formulas:



where R, R' and R'' are radicals selected from the group of monovalent hydroxyalkyl, cyclohydroxyalkyl and hydroxyalkyl ether.

7. The nickel plating solution of claim 4 where the stabilizer is a source of lead ions.

8. The nickel plating solution of claim 4 where the stabilizer is a thio compound.

9. The nickel plating solution of claim 8 where the thio compound is thiourea.

10. The nickel plating solution of claim 4 where the stabilizer is an iodate compound.

11. The nickel plating solution of claim 4 where the stabilizer comprises a maximum of 100 parts per million parts of solution.

9

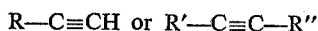
12. In an aqueous electroless plating solution for plating over aluminum comprising a source of nickel ions in an amount sufficient to provide a useful deposit, hypophosphite as a reducing agent for said nickel ions, a complexing agent to maintain said nickel ions in solution and a stabilizing agent for said solution, the improvement comprising the addition to the solution of at least 0.001 mole of an aluminum complexing agent that is an unsaturated aliphatic carboxylic acid in an amount sufficient to suppress evolution of gas from said aluminum surface, said carboxylic acid is selected from the group of acrylic acid, maleic acid, propiolic acid, acetylene dicarboxylic acid, crotonic acid, vinyl acetic acid, tetraloic acid, glutaric acid, taconic acid, mesaconic acid, alkyl acetic acid, ethylacrylic acid, vinyl acrylic acid, muconic acid, sorbic acid, fumaric acid and cinnamic acid and being present in an amount less than the amount of said complexing agent for maintaining nickel ions in solution.

13. The nickel plating solution of claim 12 where the concentration of the carboxylic acid ranges between about 0.01 and 0.20 mole per liter of solution.

14. The nickel plating solution of claim 12 where the unsaturated carboxylic acid suppressant is maleic acid.

15. The nickel plating solution of claim 12 where the stabilizer is selected from the group consisting of divalent sulphur compounds, lead ions, iodate compounds and solution soluble acetylinic compounds.

16. The nickel plating solution of claim 15 where the stabilizer is a solution soluble acetylinic compound corresponding to one of the following formulas:



where R, R' and R'' are radicals selected from the group of monovalent hydroxyalkyl, cyclohydroxyalkyl and hydroxyalkyl ether.

10

17. The nickel plating solution of claim 15 where the stabilizer is a source of lead ions.

18. The nickel plating solution of claim 15 where the stabilizer is a thio compound.

19. The nickel plating solution of claim 18 where the thio compound is thiourea.

20. The nickel plating solution of claim 15 where the stabilizer is an iodate compound.

21. A method for electroless nickel plating of aluminum comprising contact of an aluminum part with the electroless nickel plating solution of claim 1.

22. A method for electroless nickel plating of aluminum comprising contact of an aluminum part with the electroless nickel plating solution of claim 12.

23. An article of manufacture comprising a substrate coated with electroless nickel from the bath of claim 1.

24. An article of manufacture comprising aluminum coated with an electroless nickel deposit from the bath of claim 12.

References Cited

UNITED STATES PATENTS

3,148,072	9/1964	West et al.	106—1
3,515,564	6/1970	Mallory et al.	106—1
3,597,267	8/1971	Mallory et al.	106—1 X
3,370,074	2/1968	Hepfer	106—1 X

FOREIGN PATENTS

1,131,483	6/1962	Germany	117—130 E
-----------	--------	---------------	-----------

LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

117—130 E