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Maguire

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[54] **PROCESS FOR ELECTROLESS PLATING**

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[21] Appl. No.: **320,688**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 224,228, Feb. 7, 1972, abandoned, which is a continuation-in-part of Ser. No. 65,685, Aug. 20, 1970, abandoned.

[52] **U.S. Cl.** ..... **106/1,** 117/47 A, 117/130 E

[51] **Int. Cl.** **C23c 3/02**

[58] **Field of Search** 106/1; 117/130 E, 47 A, 160 R

[56] **References Cited**

UNITED STATES PATENTS

2,938,805	5/1960	Agens	106/1
3,310,430	3/1967	Schneble et al.	106/1
3,454,416	7/1969	Heyman et al.	106/1

Primary Examiner—Lorenzo B. Hayes

Attorney, Agent, or Firm—Christie, Parker & Hale

[57] **ABSTRACT**

Organo-nitrogen compounds containing at least two nitrogen atoms separated by no more than one carbon atom stabilize electroless plating solutions against plating of the metal on passivated stainless steel and solution decomposition as caused by the presence of impurities such as palladium ion.

10 Claims, No Drawings

PROCESS FOR ELECTROLESS PLATING

BACKGROUND OF THE INVENTION

This is a continuation-in-part of our application Ser. No. 224,228, filed Feb. 7, 1972, which in turn is a continuation-in-part of our application Ser. No. 65,685, filed Aug. 20, 1970, both now abandoned.

The present invention relates to the electroless plating of catalyzed resin surfaces with metals and more particularly to the stabilizing of an electroless plating bath against plating on metal surfaces and solution decomposition, due to the presence of impurities such as palladium ion.

Considerable demand has developed for metal plated non-conductive articles, particularly plastic articles. In the finished product, the desirable characteristics of both the plastic and the metal are combined to offer thereby the technical and aesthetic advantages of each.

Although most resins are electrically non-conductive, a metal bond to the surface of the resin can be established by initial plating operation known as "electroless plating". This is typically accomplished by conditioning the surface of the resin for plating by contact with a strong oxidizing acid, seeding the conditioned surface by contact with a noble metal salt, e.g., a palladium chloride solution, then immersing the seeded surface in an auto-catalytic electroless plating solution wherein an initial coating of a conductive metal is established by chemical deposition. The metal coating formed acts as a buss and allows a thicker metal coating to be built up electrolytically. For most resins, contact with the oxidizing acid is often preceded by a chemical etch to improve the bond strength of the copper plate.

A typical formulation for an electroless plating solution may be exemplified by an electroless copper plating solution which consists essentially of a soluble cupric salt, such as copper sulfate; a complexing agent for the cupric ion, such as Rochelle salt; an alkali hydroxide for adjusting pH; a carbonate radical as a buffer; and a reducing agent for the cupric ion such as formaldehyde.

The mechanism by which polymeric objects having surfaces catalyzed by palladium metal may be plated autocatalytically has been well described in literature, such as, for example, U. S. Pat. No. 2,874,052.

Electroless plating solutions as described above are, however, subject to decomposition. For copper plating solutions, for example, the cupric ion inherently tends to reduce to the insoluble cuprous form. This may be overcome, in part, by the use of stabilizers, or by air agitation which serves to oxidize cuprous ion back to the cupric state.

Secondary sources of contamination, however, also materially contribute to decomposition. When the catalyzed plastic article is withdrawn from the noble metal salt bath, it too often carries with it, as "drag-out", substances including copper, nickel, iron, palladium, gold, silver and even dust particles, which are catalytic toward solution deoomposition. Palladium ion (Pd^{++}) is notorious in that if stainless steel tanks or equipment are in contact with electroless (copper) bath even a minute amount of palladium ion will initiate plating of the copper onto steel. In addition, concentrations as low as one part per million will cause spontaneous decomposition of the solution with attendant precipitation and loss of copper.

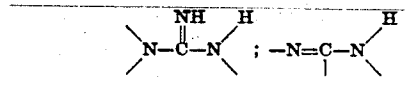
It has been proposed to use plastic lined tanks for electroless plating baths to avoid the problem of plating on the stainless steel tanks. Even in plastic lined tanks, however, inevitable scratches in the lining result in initiation of decomposition because the scratches provide recesses within which hydrogen produced during the plating reaction is concentrated.

Attempts have also been made to stabilize electroless plating baths to minimize decomposition. However, most compounds which have been proposed as stabilizers retard the rate of electroless plating. While heating may be employed to increase the rate of deposition, it has not been generally used because heating also promotes decomposition.

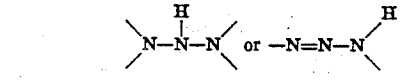
We have employed an alternate route to minimize loss of valuable chemicals through decomposition of the plating solutions. This involves the use of two plating baths. One is a strike bath in which a noble catalyzed surface is initially plated in a bath essentially free of inhibitors. The other is a plating bath in which the surface plated article is further electrolessly plated and which is inhibited to the extent that if the article having the catalytic noble metal surface were passed directly into the bath without first passing through the strike bath, no plating metal would be deposited on the article. In this system, the plating bath remains stable while the strike bath continuously decomposes. The volume of the strike bath, however, is low with respect to the volume in the plating bath and losses have been minimized.

SUMMARY OF THE INVENTION

It has now been found that organo-nitrogen compounds containing the radicals or groups:



and



serve as effective stabilizers to prevent contaminant decomposition of electroless plating solutions. Their presence in the solution remarkably increases solution tolerance for palladium and other impurities which normally causes solution decomposition or plating of the metal on the stainless steel surfaces. The compounds embraced are those which are soluble in water or a dilute base in quantities sufficient to complex with palladium ion.

When used alone or in conjunction with other stabilizers or a source of oxygen to oxidize cuprous ions in an electroless copper plating solution back to the cupric state, the organonitrogen compounds of this invention will stabilize electroless copper plating solutions for long periods of time. In use, amounts which will permit deposition of a plate onto the surface of a suitably catalyzed article within 30 seconds after immersion, will stabilize electroless copper plating solutions in the presence of palladium ions at concentrations well in excess of that which could be reasonably expected to be "dragged-in" in 48 hours provided a source of oxygen is present. When some of the stabilizer is consumed in

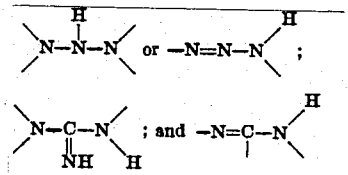
coping with contaminants, additional quantities can be added without retarding deposition rate.

While useful for any electroless plating solution the stabilizers of this invention are preferably used as stabilizers for the strike bath of a two-bath system wherein a thin film of plating metal is deposited in a strike bath, followed by additional plating in a plating bath inhibited to the extent that if non-conductive articles having a catalytic noble metal film were immersed in the solution no plating would occur.

DESCRIPTION

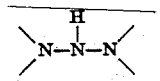
According to the present invention, there is provided organo-nitrogen stabilizers for electroless plating solutions which materially increase the tolerance of the electroless plating solutions for metallic ions and other impurities which normally cause solution decomposition.

The organo-nitrogen compounds which are used to stabilize electroless plating solutions according to the practice of this invention are compounds which contain at least two nitrogen atoms separated by no more than one carbon atom and in particular radicals or groups:

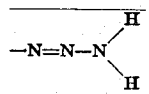


The organo nitrogen compounds containing the above radicals which are useful in accordance with this invention are those which are soluble in water or a dilute base in quantities sufficient to complex with palladium ion and still permit deposition of a plate of copper onto a noble metal catalyzed surface.

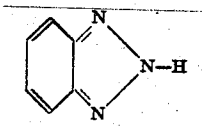
Illustrative of the organo-nitrogen compounds containing the radical



or its tautomeric form

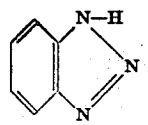


there may be mentioned benzotriazole; which exists as:



(I)

or its tautomeric form:

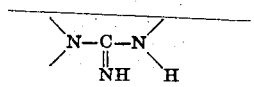


(II)

benzotriazole; 4 amido-1(nitrosamino amidino)-1-tetrazene; 5-methylbenzotriazole; guanazolo; 1,2,3-triazole; tetrazole; 4,5-triazole carboxylic acid; 5-aminotetrazole and the like.

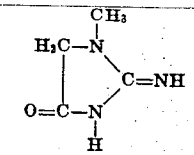
The above organo nitrogen compounds may be classified generally as 1,2,3 triazoles and tetrazoles and in most instances are part of a ring structure.

Of the organo nitrogen containing the group:



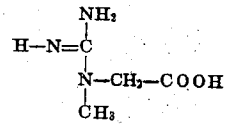
which may be classified as amidines there may be mentioned:

creatinine



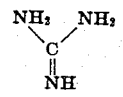
(III)

creatine



(IV)

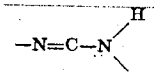
guanidine



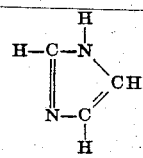
(V)

aminoguanidine; diphenylguanidine; 1,1,3,3 tetramethyl guanidine; guanine, guanilic acid, phenylbiguanidine, guanosine, streptidine and the like. Of these guanidine and aminoguanidine are normally provided in a salt form, in particular, as the carbonate salt, but the salt group has no influence on their functionality.

Of the organo nitrogen compounds containing the group



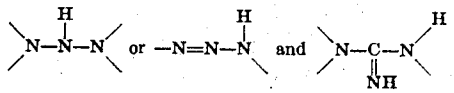
which may typically be 1,2,4 triazoles, diazoles and pyrimidines there may be mentioned imidazole;



(VI)

xanthine; 3-amino -(1H)-1,2,4-triazole; 2-aminopyrimidine; melamine; benzoguanamine; phenazopyridine; folic acid; 2-amino-4(3H)-pyrimidone; 1,2,4 triazole; 2-aminopyridine; 2-amino-4-methylpyrimidine; and the like.

Of these, compounds containing the groups:



have been found to be the most effective and are preferred.

Benzotriazole which has been found to stabilize electroless plating solutions at Pd^{++} concentrations of 100 ppm or more when present in an amount of only about 0.005 grams per liter of solution is most preferred.

While no wise bound by theory, it is believed that the free electrons available from the closely associated tri-

valent nitrogen atoms in the organo-nitrogen stabilizers of this invention in some way complex, possibly as a chelate, with divalent palladium ions as well as other foreign metallic ions which may be introduced in the electroless plating solutions in the "drag-out". They also have been found to complex or chelate cuprous ions.

The organo-nitrogen stabilizers of this invention do not, however, appear to stabilize against the normal solution decomposition as, for example, the natural reduction of cupric ion to the cuprous state, but as indicated, do chelate them. Accordingly, for long solution stability and conservation of the organo nitrogen compounds to cope with palladium ions they should be used with another system which prevents normal reduction of the plating metal ions. For electroless copper solutions, the presence of another stabilizer and/or source of oxygen to oxidize cuprous ions back to the cupric state is suggested. The stabilizers of this invention may, for instance, be conveniently used in conjunction with air-agitated solutions wherein air is drawn into the solution by mere agitation or bubbled through the solution to stabilize cupric ion against reduction to the cuprous state. Equally convenient is to introduce oxygen through oxidizing compounds such as sodium peroxide, hydrogen peroxide, chromic acid, sodium bromate, potassium bromate, sodium perborate, potassium perborate, sodium chlorate, potassium chlorate and the like.

While the organo-nitrogen compounds of this invention do stabilize electroless plating solutions against decomposition due to the presence of foreign substance, they do not hinder deposition onto a suitably catalyzed plastic substrate. At the concentrations shown in Table I, for instance, a uniform deposition of a copper plate onto a catalyzed plastic substrate will begin within 30 seconds after immersion. Yet, the solutions will remain stable at the palladium ions concentration shown for at least 24 hours at room temperature in that decomposition or plating on steel will not occur provided there is present a source of oxygen to prevent normal reduction of cupric ions to the cuprous state.

In the absence of a source of oxygen, stabilization time will be reduced since some of the organo-nitrogen compounds present will be consumed in coupling cuprous ions formed by the natural reduction of cupric ions.

TABLE I

Stabilizer	Conc. g/liter	Pd^{++}(ppm)
Benzotriazole	0.005	110
Creatinine	0.009	85
Creatine	0.3	80
Guanidine Carbonate	0.02	100
Imidazole	0.1	45

While the organo-nitrogen stabilizers of this invention are preferably used in the strike bath of a two-bath plating system as hereinafter described, they may also be used in single bath plating systems given consideration to the following general observations regarding electroless copper plating.

Benzotriazole results in the formation of dark brown copper deposits which cannot be brightened. Creatinine, creatine and quanidine also give dark brown deposits but can be brighted by wash in dilute sulfuric acid. Imidazole gives reddish deposits which can also be brightened by an acid wash. The shade of the latter group also darkens as stabilizer concentration increases and may, at certain concentration, terminate copper deposition after an initial plate, possibly due to the formation of film. This film, however, can be easily removed in an acid wash for additional electroless plating in another bath or in an electrolytic plating bath.

As will be appreciated by one skilled in the art, the amount of inhibitor to be incorporated in a bath may be broadly varied. Electroless plating baths are generally continuously replenished as the metals are consumed as a consequence of plating. Accordingly, the solution need only be stabilized against the estimated amount of foreign materials which will be brought into the solution between periods of addition of replenishing solutions and fresh stabilizers.

As indicated, although the inhibitors of this invention may be used in conventional single bath copper and nickel plating systems, when the metal is at least copper we prefer to use them in the strike bath of a two-bath plating system hereinafter described.

Generally, the two-bath plating process involves forming an initial copper plate on the catalyzed surface of a suitably conditioned plastic article in strike bath inhibited with the organo-nitrogen stabilizers of this invention followed by a buildup of electroless plated copper in a highly inhibited plating bath.

As indicated, the organo-nitrogen stabilizers of this invention are at least used in the strike bath. The strike bath serves to provide an initial plate. The article is then passed into a highly stabilized plating bath. The concentration of inhibitor in the plating bath being such that, if the article having a catalytic noble metallic surface were passed directly into the plating bath without first passing through the strike bath, no plating metal would be deposited on the article.

Using the organo-nitrogen inhibitors of this invention, the composition of the strike bath may be any of those conventionally employed for electroless deposition of copper on a non-conductive article. Formulations of room temperature electroless copper plating baths include, for example, the following general composition for an aqueous solution:

INGREDIENT	MOLAR CONCENTRATION
Soluble Cupric Salt	0.02–0.15
Complexing Agent	0.03–0.75
Reducing Agent	0.05–1.50
pH Adjustor	Sufficient to give pH from about 11.5 to 14

The concentrations of complexing agent and reducing agent are somewhat related to the concentrations of cupric ion in solution.

As the water soluble cupric salt there may be employed copper sulfate, cupric halides, cupric nitrates, cupric acetates, and other inorganic and organic cupric salts. Copper sulfate and cupric chloride are preferred.

As complexing agents for the cupric ion there may be employed Rochelle salts, the mono-, di-, tri-, and tetrasodium salts of ethylenediaminetetracetic acid; the ethanolamines, such as triethanolamine; nitrilotriacetic acid and its alkali metal salts; gluconic acid; gluconates; glucono-γ-lactone; N-hydroxyethylene ethylenediaminetriacetate; hydroxyalkyl substituted dialkylene triamines, such as pentahydroxypropyl diethylenetriamine; the salicilates; citrates; lactones, and other complexing agents well known in the art.

As reducing agents there may be employed formaldehyde and its precursors or derivatives such as paraformaldehyde; glyoxyl; borohydrides, such as alkali

metal borohydrides and substituted alkali metal borohydrides and the like. Formaldehyde is particularly preferred.

There may also be employed buffering agents such as sodium bicarbonate.

With this fundamental system, the plating bath can be operated at an elevated temperature without significant decomposition. Accordingly, the high plating rates are obtained by the use of both baths without attendant loss of valuable chemicals and production problems.

More specifically, a detailed description of the two-bath process solution utilizing the organo-nitrogen stabilizers of this invention may be made in terms of the history of the electroless copper plating of a molded plastic article such as an ABS article.

The molded plastic article is normally cleaned, pre-etched with an organic chemical solvent, if required, and then etched in an etching chemical bath such as a mixture of chromic and sulfuric acids. After cleaning of the etched article, including rinsing in an alkaline cleaner, the article is sensitized in a stannous chloride-hydrochloric acid bath and then activated in a bath of a noble salt, such as palladium chloride, to provide a catalytic noble metal on the surface of the plastic. Following rinsing to remove excess palladium from the surface of the article, it is passed into the stabilized strike bath.

The organo-nitrogen stabilized strike bath can be an electroless copper plating solution having a formulation such as the following:

INGREDIENT	CONCENTRATION
Rochelle Salt	34 grams/liter
Caustic Soda	12 grams/liter
Copper Sulphate	7 grams/liter
Sodium Carbonate	6 grams/liter
Formaldehyde (Formalin)	25 cc./liter
Organo-nitrogen Stabilizer	Sufficient to stabilize against 20–80 ppm Pd^{++}
Water	Sufficent to make 1 liter

The strike bath is typically maintained at room temperature. The plastic article with palladium metal on its surface is immersed in the strike bath for from about 30 seconds to about 3 minutes and then removed. This is a sufficient period of immersion to enable deposition of a thin copper film over the entire surface of the article. The strike bath, in addition to preparing the article for deposition in the electroless plating bath, also serves as a collector for the bulk of the metallic contaminants which otherwise would pass directly into the plating bath, these contaminants being complexed by the organo-nitrogen stabilizers.

Upon removal from the strike bath, the plastic article having a thin copper deposit is passed directly into the electroless plating bath. In order to increase the rate of plating as described above, this bath is maintained at an elevated temperature, preferably a temperature somewhere in the range from 90° to 140°F. An example of a formulation for the preferred plating bath is as follows:

INGREDIENT	MOLAR CONCENTRATION
Copper Sulfate	0.036
Rochelle Salt	0.138
Sodium Bicarbonate	0.11
Formaldehyde	0.11
Free Sodium Hydroxide	0.125
Potassium Cyanide	0.006
Water	Sufficient to make 1 liter

The free sodium hydroxide referred to above is that quantity which is in addition to the amount required to form the chelate and to convert the sodium bicarbonate in the solution to sodium carbonate.

The plastic article is retained in the electroless plating bath for a period of from 3 to 6 minutes. During this period of time, additional thicknesses of copper sufficient to permit subsequent electrolytic metallic plating are deposited. After removal from the electroless plating bath, the article is rinsed and soaked, and, if electrolytic plating is required, is passed to the electroplating process.

Through the use of the organo-nitrogen stabilizers of this invention, a highly stabilized, nonsensitive formulation can be used in both the strike and plating baths without significant decomposition over its service life. Further, as indicated, solutions can be used in stainless steel tanks with stainless steel heaters and filters. As a result of the stability imparted to both baths, roughness or so-called "bumps" in the plating deposit are avoided and the plating bath can be operated at elevated temperatures with attendant improvements in production rate economies.

EXAMPLE 1

To a series of electroless copper solutions having the formulation:

$CuSO_4 \cdot 2H_2O$	7.5 gr.
Rochelle Salt	29.0 gr.
NaOH (free)	12.0 gr.
$NaHCO_3$	9.4 gr.
Formaldehyde	10.75 gr.
Water	Sufficient to make 1 liter

there was added organo-nitrogen compounds in concentrations which would permit copper deposition onto an immersed catalyzed substrate within 30 seconds at room temperature.

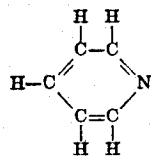
A stainless steel plate (type 304) was immersed in each bath. Palladium as Pd^{++} was added in increasing amounts until deposition on the stainless steel was initialed or decomposition occurred. For compounds which behaved as stabilizers, the palladium ion concentration which could be stabilized for at least 24 hours at room temperature was then determined. The results are shown in Table II.

TABLE II

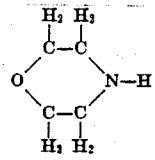
Compound	Conc. gr/l	Pd^{++} ppm	Remarks
Benzotriazole	0.005	110	—
Creatinine	0.009	85	—
Imidazole	0.1	45	developed white ppt
Creatine	0.3	80	—
Guanadine carbonate	0.02	100	—

A solution under the same conditions without the stabilizers began to plate on the stainless steel upon introduction of Pd^{++} and spontaneously decomposed at Pd^{++} concentrations of less than 1 ppm.

Under identical conditions, plating on the steel began at 8 ppm Pd^{++} when pyridine

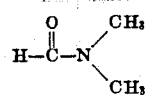


was present in a concentration of 0.5 gr/l. and at a Pd^{++} concentration of 1 ppm when morpholine

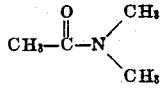


was present at a concentration of 1.0 gr/l.

Decomposition occurred at a Pd^{++} concentration of 1 ppm when dimethyl formamide



and dimethylacetamide



were present in quantities of 1 cc/l.

EXAMPLE 2

Tests were performed to compare the stabilizing activity of the organo-nitrogen compounds of the invention alone and in conjunction with other known stabilizers.

The base plating solution employed in each test had the following composition:

Copper Sulfate ($CuSO_4 \cdot 5H_2O$)	7.5 gr/l
Sodium Bicarbonate	9.4 gr/l
Rochelle Salt	28.0 gr/l
Formaldehyde (Formalin)	26.0 cc/l
Free Sodium Hydroxide	12.0 gr/l
Balance	Water plus stabilizers

In each instance 10 ppm palladium chloride was added to the solution with stirring. No further agitation was employed.

In each instance a suitably catalyzed ABS resin plaque was electrolessly plated by immersion in the solution for 5 minutes at a temperature of 70°F – 75°F.

It will be appreciated if free ionic palladium is present in an electroless copper solution, it will be reduced by the reducing agent present in bath to Pd° which will result in solution decomposition. The reduction of palladium will be hastened by the hydrogen generated in the plating reaction.

After plating, the plaque was removed. The solutions were observed for stability over a 4-hour period, this being regarded as an indication of a highly stable solution.

As alternate stabilizers there was tested potassium antimony tartrate in a concentration of 0.03 gr/l as taught by U.S. Pat. No. 3,310,430 and 2'2' biquinoline in a concentration of 0.01 gr/l as taught by U.S. Pat. No. 3,377,174.

The organo nitrogen stabilizers employed were benzotriazole in a concentration of 0.005 gr/l and creatinine in a concentration of 0.01 gr/l.

The results are shown in Table III.

TABLE III

Stabilizer System	Decomposition Time
Potassium Antimony Tartrate	40 min.
2'2'-biquinoline	27 min.
Benzotriazole	4 hr.
Benzotriazole+Potassium Antimony Tartrate	4 hr.
Benzotriazole+2'2'-biquinoline	4 hr.
Creatinine	165 min.
Creatinine+Potassium Antimony Tartrate	200 min.
Creatinine+2'2'-biquinoline	2 hr.

CONTROL I

To establish the uniqueness of the organo nitrogen compounds of this invention to cooperate with a source of oxygen to induce maximum bath stability, 2'2'-biquinoline and potassium antimony tartrate were tested under conditions as set forth in Example 1.

In these tests there was initially added 2 ppm Pd^{++} as palladium chloride and if no solution breakdown occurred an additional part per million Pd^{++} was added about every 15 minutes.

For 2'2'-biquinoline at a solution concentration of 0.01 gr/l the solution in the presence of air agitation and type 304 stainless steel decomposed upon the addition of 2 ppm palladium ion.

For potassium antimony tartrate at a solution concentration of 0.03 gr/liter, upon the addition of 15 ppm Pd^{++} solution breakdown occurred. The period of time involved was slightly in excess of 3 hours.

CONTROL II

To further evaluate potassium antimony tartrate it was determined the maximum amount which would permit a complete deposit of copper on a plaque of a catalyzed ABS resin within 30 seconds at room temperature from a solution prepared according to Example 1 in which it was used as the stabilizer. This concentration was determined to be again 0.03 gr/l.

Employing the conditions of Example 1, various quantities of Pd^{++} were added to samples. While maintaining air agitation the solutions were allowed to stand for 7 hours. The results are shown in Table IV.

TABLE IV

Sample	Pd^{++} Added ppm	Stable[1]
A	5	Yes
B	10	No
C	12.5	No
D	17.5	No
E	20.0	No

[1]The sample was judged not stable when plating of copper on stainless steel occurred.

These tests establish that the electroless copper plating solution containing potassium antimony tartrate has tolerance for less than 10 ppm Pd^{++} in the presence of stainless steel even when aided by air agitation.

EXAMPLE 3

Using the base copper plating solution described in Example 2 a number of organo nitrogen stabilizers were tested for their ability to cope with palladium ion. In each instance the concentration of palladium ion (Pd^{++}) was 25 ppm. Employing air agitation, the solutions containing the organo-nitrogen compounds at the concentrations set forth below were allowed to stand for 2hours. In each instance the solutions remained clear which was indicative of the inability of palladium ion to cause solution decomposition because of the presence of the organo nitrogen compounds.

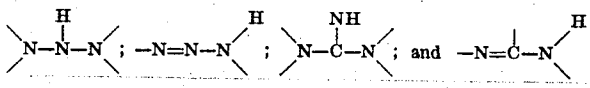
TABLE V

Organo Nitrogen Compound	Conc. gr./l.
Benzotriazine	0.006
Amminoguanidine (bicarbonate)	0.02
3 amino-(1H)-1,2,4 triazole	0.02
diphenylguanidine	0.02
Melamine	0.007
Benzoguanamine	0.02

In each instance the prepared solution permitted copper decomposition onto an immersed catalyzed substrate in about 30 seconds. However the total immersion time in each instance was about 1.5 minutes. In each instance a uniform plate of copper was deposited.

What is claimed is:

1. In a process for electroless copper plating which comprises immersing a surface which is receptive to electroless deposition of copper in an alkaline aqueous bath containing a water soluble cupric salt; a complexing agent for cupric ions; an alkali metal hydroxide for maintaining solution pH between about 11.5 and 14, and a reducing agent for cupric ions the improvement which comprises the use of stabilizing amount of at least one organo-nitrogen compound containing a group selected from the groups consisting of



the organo-nitrogen compound being present in an amount sufficient to stabilize the bath against decomposition due to the presence of at least palladium ion but insufficient to terminate copper deposition.

2. A process as claimed in claim **1** in which another stabilizer is present.

3. A process as claimed in claim **1** in which an oxidizing agent for cuprous ion is present.

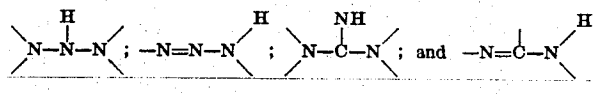
4. A process as claimed in claim **2** in which the oxidizing agent is oxygen.

5. In a process for electroless copper plating which comprises immersing a surface which is receptive of electroless deposition of copper in an alkaline aqueous bath containing a water soluble cupric salt, a complexing agent for cupric ions, an alkaline metal hydroxide for maintaining solution pH between about 11.5 and 14, and a reducing agent for cupric ions, the improvement which comprises the use of a stabilizing amount of at least one organo-nitrogen compound selected from the group consisting of benzotriazole, creatinine, creatine, guanidine, imidazole, benzotriazine, aminoguanidine, 3 amino-(1H)-1,2,4 triazole, diphenyl guanidine, melamine and benzoguanamine, the organo-nitrogen compound being present in an amount sufficient to stabilize the bath against decomposition due to the presence of at least palladium ion but insufficient to terminate copper deposition.

6. A process as claimed in claim **5** in which an oxidizing agent for cuprous ion is present.

7. A process as claimed in claim **6** in which the oxidizing agent is oxygen.

8. In an aqueous alkaline electroless copper plating solution comprising a soluble cupric salt, a complexing agent for cupric ion; an alkali metal hydroxide to maintain solution pH between about 11.5 and 14, a reducing agent for cupric ion and a source of oxygen to oxidize cuprous ions back to the cupric state, improvement comprising at least one organo-nitrogen compound containing a group selected from the groups consisting of



said organo nitrogen compound being present in solution in an amount sufficient to stabilize the solution against decomposition due to the presence of at least palladium ion but insufficient to prevent copper deposition onto a surface receptive to copper deposition.

9. In an alkaline electroless copper plating solution comprising a soluble cupric salt; a complexing agent for cupric ions; an alkali metal hydroxide for pH control and a reducing agent for cupric ions, the improvement comprising an amount of benzotriazole sufficient to stabilize the solution against decomposition due to the presence of at least palladium ion but insufficient to terminate copper deposition onto a surface receptive to copper deposition.

10. In an aqueous alkaline electroless copper plating solution consisting of water, a soluble cupric salt, a complexing agent for cupric ion, an alkali metal hydroxide to maintain solution pH between about 11.5 and 14, a reducing agent for cupric ion and a source of oxygen to oxidize cupric ions back to the cupric state, the improvement comprising at least one stabilizer selected from the group consisting of benzotriazole, creatinine, creatine, guanidine, imidazole, benzotriazine, aminoguanidine, 3 amino-(1H)-1,2,4 triazole, diphenylguanidine, melamine and benzoguanamine present in solution in an amount sufficient to stabilize the solution against decomposition due to the presence of at least palladium ion but insufficient to prevent deposition of copper onto a surface receptive to copper deposition.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,793,038 Dated February 19, 1974

Inventor(s) Leon A. Kadison and Eileen Maguire

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Inventor reads as "Eileen Maguire", should read as -- Leon A. Kadison and Eileen Maguire --.

Column 1, line 62, "deoomposition" should be -- decomposition --.

Column 7, line 38, "25 cc./liter" should be -- 25 ccs/liter --.

Column 11, line 14, "2hours" should be -- 24 hours --.

Signed and sealed this 10th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents