

United States Patent

[11] 3,607,352

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[54] **ELECTROLESS METAL PLATING**
23 Claims, No Drawings
 [52] U.S. Cl. 117/47,
 117/212, 117/213, 106/1
 [51] Int. Cl. C23c 17/00
 [50] Field of Search 117/47, 50,
 212, 213; 106/1

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ABSTRACT: Sensitizer solutions and sensitizer concentrates for use in forming the sensitizer solutions, utilizable in chemical reduction metal plating. The sensitizer solution comprises an acid aqueous solution containing stannous chloride, HCl, and one or more of an alpha hydroxy dicarboxylic acid and water-soluble, solution-compatible salts thereof, for example tartaric acid, present in effective amount sufficient to inhibit formation of tin oxychloride. The sensitizer solution preferably also contains nickel and/or cobalt ions as an accelerator for the reduction and deposition of the catalytic noble metal during the activating of the surface to be electrolessly plated, and a buffering agent.

ELECTROLESS METAL PLATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to electroless metal plating and more particularly to new and improved sensitizer solutions and sensitizer concentrates for use in forming such sensitizer solutions, utilizable in chemical reduction metal plating, and to a method for the electroless metal plating involving the use of such sensitizer solution. 2. Description of the Prior Art

The chemical reduction metal plating of nonmetallic or electrically nonconductive surfaces, for instance plastic surfaces, in the past has involved cleaning when required of the nonconductive surface, conditioning the surface, sensitizing the surface, activating the surface to render it catalytic, and then contacting the activated surface with, usually by immersing the surface in, a chemical reduction metal plating solution until the surface is electrically conductive. The conductive surface could then be electroplated.

The sensitizing has usually been effected heretofore with sensitizer solutions containing stannous chloride, HCl and water. One problem encountered heretofore with the use of such sensitizer solutions has been the formation of tin oxychloride, which appears as a white dispersion or precipitate in the sensitizer solution. The tin of the tin oxychloride is unavailable for reducing the ionic noble metal to catalytic metal in the activating step and the tin oxychloride formation tends to result in insufficient stannous ions being absorbed on the nonmetallic surface. The tin of the tin oxychloride is non-recoverable. To overcome this problem of tin oxychloride formation, the prior art employed a large excess of HCl over that required for dissolving the stannous chloride, typically about 50 percent by weight of HCl (37 percent concentration) in the sensitizer concentrate which was diluted usually in a ratio of 1:15 of concentrate to water respectively to form the sensitizer solution. Although the use of the large excess of HCl prevented the tin oxychloride from forming, the use of the large excess of HCl suffers in that the excess HCl too tightly complexes the stannous ions with the result there is not a maximum enrichment of the substrate or surface to be plated with stannous tin. And the too tightly complexed stannous ions which are withheld from the substrate or surface to be plated are unavailable for reducing the noble metal ions to catalytic metal during the activating step. On the other hand, when the large excess of HCl is avoided and too little HCl utilized, the undesirable formation of tin oxychloride occurs.

Another difficulty encountered heretofore with use of the sensitizer solutions containing stannous chloride, HCl and water is the formation of a precipitate of a tin-hydroxyl complex. The tin-hydroxyl complex gets on the vinyl plastisol rack and is very difficult to remove from the rack.

SUMMARY OF THE INVENTION

In accordance with the present invention, we have found that the tin oxychloride formation is inhibited without the requirement of utilizing the aforementioned large excess of HCl in the sensitizer solution with the attendant disadvantages results by having present as an ingredient of the aqueous sensitizer solution, in addition to the stannous chloride and HCl, one or more of an alpha hydroxy dicarboxylic acid and sensitizer-solution-compatible, water-soluble salts thereof, for example tartaric acid. The new and improved sensitizer solutions herein, in addition to inhibiting the undesirable stannous oxychloride formation by the aforementioned alpha hydroxy-substituted carboxylic acid or soluble, compatible salt thereof with resultant considerably longer life of the sensitizer solution, result in maximum enrichment of the nonmetallic surface with stannous tin or in considerable larger amounts of stannous tin being absorbed or deposited on the nonmetallic surface to be plated and with more uniform deposition of the tin on the nonmetallic surface. Consequently the stannous tin-enriched surface consistently results in the reduction and deposition of considerably larger amounts of

catalytic noble metal on the surface during the activation, and hence a more uniform deposition of metal on the substrate during the chemical reduction metal plating and with elimination or substantial elimination of skip plating of the surface.

Further, the formation of the tin-hydroxyl complex, which is removable from the vinyl plastisol rack with considerable difficulty, is inhibited by the new sensitizer solutions herein. The considerable improvement provided by the alpha hydroxy dicarboxylic acid of this invention in inhibiting the stannous oxychloride formation was unexpected and surprising.

Sensitizer concentrates adapted to be mixed together with an aqueous liquid, usually water, to yield sensitizer solutions, are also provided by the present invention. The sensitizer concentrate comprises an acid aqueous solution containing stannous chloride, HCl and one or more of the alpha hydroxy dicarboxylic acid and the water soluble, solution-compatible salts thereof. The ingredients of the concentrate are of course present therein in considerably larger proportions than in the ready-to-use sensitizer solution.

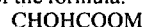
The alpha mono-and/or di-hydroxy dicarboxylic acids and their salts of this invention correspond to the following formula:



wherein R is -H or -OH and M is -H or a sensitizer solution-compatible, hydrophilic, i.e. water loving or water-solubilizing, cation. Exemplary of the hydrophilic cation M is an alkali metal cation, e.g. Na and K cations, and the ammonium, i.e. NH_4 , cation. Such compounds are exemplified by tartaric acid and malic acid, and their salts.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred hydroxy dicarboxylic acid and salts herein is of the formula:



wherein M has the meaning previously set forth herein. Tartaric acid is especially preferred among such compounds for use herein.

The sensitizer solution preferably has a pH in the range of about 0.45 to about 1.00, inasmuch as at a pH of the solution much above 1.00 the stannous oxychloride (white precipitate) forms in the solution. At a pH much below 0.45, the solution does not function as effectively to sensitize the surface. An especially preferred pH of the sensitizer solution is a pH within the range of about 0.45 to about 0.75.

A buffering agent is preferably employed in the sensitizer solution and sensitizer concentrate herein in amount sufficient to maintain the pH of the sensitizer solution within the preferred pH range of about 0.45 to about 1.00 or, if desired, within the especially preferred range of about 0.45 to about 0.75. Exemplary of such buffering agent is a weak acid, for example an aliphatic hydrocarbon monocarboxylic acid having 2-4 carbon atoms per molecule, e.g. acetic acid, propionic acid and butyric acid, with or without their salts, e.g. alkali metal salts thereof, for example sodium or potassium salts thereof. A preferred buffering agent herein is glacial acetic acid in the presence or absence of sodium acetate.

Ions of nickel and/or cobalt are also preferably an ingredient of the sensitizer solution and concentrates herein, and function as an accelerator to speed up the reduction and deposition of the catalytic noble metal during the activating. The nickel ions are the preferred accelerator. The ionic nickel also results in a denser, more uniform noble metal catalyst film or deposit on the surface to be plated whereby the likelihood of "skip" plating during the electroless metal plating is significantly reduced. The nickel and/or cobalt ions are preferably supplied to the sensitizer solution and concentrate as a water-soluble, readily ionizable salt of nickel and/or cobalt, e.g. nickel sulfate, cobalt sulfate, or a halide of nickel and/or cobalt, e.g. nickel chloride, cobalt chloride, nickel bromide, cobalt bromide, nickel iodide and cobalt iodide.

The alpha hydroxy-substituted dicarboxylic acid and/or its soluble, compatible salt or salts is utilized in the sensitizer solution of this invention in an effective amount sufficient to inhibit formation of the tin oxychloride therein. Preferred amounts of the alpha hydroxy-substituted carboxylic acid and/or the soluble, compatible salt thereof in the sensitizer solution are a minor amount in the range from about 1-20 g/l, i.e. grams per liter.

The nickel and/or cobalt ions are utilized in the sensitizer solution in an effective or minor amount sufficient to accelerate appreciably the deposition of the catalytic noble metal on the surface during the subsequent activating step.

A preferred sensitizer aqueous solution herein contains the following ingredients within the proportions hereafter specified:

	Grams per liter of sensitizer aqueous solution
Stannous Chloride	from about 36-45
HCl (37% concentration)	from about 5-30
Tartaric Acid	from about 1-20

An especially preferred sensitizer aqueous solution herein contains the following ingredients within the proportions hereafter specified.

	Grams per liter of sensitizer aqueous solution
Stannous Chloride	from about 36-40
HCl (37% concentration)	from about 20-30
Tartaric Acid	from about 3-8
NiCl ₂ ·6H ₂ O	from about 0.36-36
Glacial Acetic Acid	from about 1.8-98

The ingredients of the sensitizer concentrates of this invention herein are not especially critical and can be varied over wide limits.

A preferred sensitizer aqueous concentrate herein contains the following ingredients within the proportions hereafter specified:

	Grams per liter of sensitizer aqueous concentrate
Stannous Chloride	from about 592-672
HCl (37% concentration)	from about 384-448
Tartaric acid	from about 64-128

An especially preferred sensitizer aqueous concentrate herein contains the following ingredients within the proportions hereafter specified:

sensitizer aqueous	Grams per liter of concentrate
Stannous Chloride	from about 592-672
HCl (37% concentration)	from about 384-448
Tartaric Acid	from about 64-128
NiCl ₂ ·6H ₂ O	from about 27-128
Glacial Acetic Acid	from about 32-128

The sensitizer concentrates of this invention are preferably diluted or mixed together with an aqueous liquid, usually

water, to form the ready-to-use sensitizer solution in a concentrate to aqueous liquid weight ratio in the range of about 1:10 to about 1:60 respectively, more preferably a weight ratio of about 1:15 respectively. The surfaces of the object or article which are electrolessly metal plated in accordance with the plating method herein are nonmetallic surfaces. Exemplary of such nonmetallic surfaces are plastic surfaces, e.g. acrylonitrile-butadiene-styrene terpolymer and epoxy resin surfaces.

Prior to electrolessly plating the nonmetallic surfaces such as the plastic surfaces, such surfaces if not already clean are cleaned by immersion in a conventional nonsilicated mild alkaline cleaner solution. The plastic surface or surfaces destined to be electrolessly metal plated are then converted from a hydrophobic state to a hydrophilic state wherein the surfaces are readily receptive to the aqueous solutions of the chemical reduction metal plating process or cycle. The conversion of the hydrophobic plastic surfaces is preferably effected by contacting the hydrophobic surface with, usually by immersing such surface in, a chromic acid - and sulfuric acid - containing aqueous conditioning solution at a solution temperature of typically 140° F. and which may also contain phosphate ions. A typical conditioning solution contains, by weight, 27.5 percent of 66 Be'H₂SO₄, 27.5 percent of CrO₃ and 45 percent of H₂. The conversion of the hydrophobic plastic surfaces to hydrophilic surfaces can also be effected mechanically by roughening or deglazing the plastic surface, for instance by sanding, abrading or sand blasting the hydrophobic plastic surface. When such a mechanical conversion is employed, the prior chemical cleaning of dirty plastic surfaces may be omitted as the mechanical roughening or deglazing itself effects a cleaning of the plastic surface.

The conditioned nonmetallic surfaces are then sensitized by contacting the plastic surfaces or surface with, usually by immersing the surface in, the sensitizer solution of this invention, at typically room temperature of the solution and for one minute. After removal from the sensitizer solution, the plastic surface is water rinsed.

The sensitized plastic surface is then contacted with, usually by immersing the sensitized surface in, an activator solution containing a noble metal salt, HCl and water, preferably PdCl₂, HCl and water, at typically room temperature of the solution and for one minute. An especially preferred activator aqueous solution contains, per liter of activator aqueous solution, 0.26 grams of PdCl₂, 0.35 grams of HCl (37 percent concentration) 0.24 grams of NiCl₂·6H₂O and 0.16 grams of sodium acetate. The resulting redox reaction causes the noble metal ions of the activator solution to be reduced to the zero valent metallic state and the catalytic noble metal deposited on the nonmetallic surface.

The activated nonmetallic surface is then electrolessly metal plated by contact with, usually by immersing the surface in, a chemical reduction metal plating solution, e.g. a chemical reduction aqueous nickel plating solution or a chemical reduction aqueous copper plating solution. The chemical reduction nickel plating solution comprises an aqueous alkaline solution of a water-soluble nickel salt, e.g. nickel chloride or nickel sulfate, and a hypophosphite as reducing agent, the solution having a pH preferably in the range of 8 to 10 inclusive. A preferred low or room temperature chemical reduction nickel plating solution herein has the following composition:

	Grams/Liter
NiSO ₄ ·6H ₂ O	21
Sodium Hypophosphite	40
Citric Acid	10
NH ₄ OH	9
NH ₄ Cl	30

The chemical reduction nickel plating is continued until the plastic surface becomes electrically conductive by deposition of a thin continuous nickel layer thereon. The chemical reduction copper plating solution comprises an aqueous alkaline solution of copper ions supplied as a water-soluble copper salt, a complexing agent for the ionic copper, e.g. Rochelle salt, and a reducing agent for the ionic copper, usually formaldehyde, the solution preferably having a pH in the range of pH 10-13 inclusive. A typical chemical reduction copper plating solution is the following:

	Grams/Liter
CuSO ₄ ·5H ₂ O	23
Rochelle Salt	55
HCHO (37% concentration)	124
NaOH	16
Na ₂ CO ₃	5

The chemical reduction copper plating solution is at a temperature of typically room temperature to about 85° F. during the plating, and the plating is continued until the plastic surface or surfaces become electrically conductive with a thin continuous copper layer.

The metal plated plastic surface is then withdrawn from the chemical reduction metal plating solution and water rinsed.

The metal plated surface can then be electroplated with, for example, acid copper or low stress nickel, followed by electroplating with a decorative or finish metal layer, for example of chrome, gold or silver over the previously mentioned electroplated layer.

The following examples of sensitizer solutions herein further illustrate the invention:

Example 1	Grams per Liter
Stannous Chloride	40
Tartaric Acid	5
HCl (37% Concentration)	28

Example 2	Grams per Liter
Stannous Chloride	38
Tartaric Acid	8
HCl (37% Concentration)	26
NiCl ₂ ·6H ₂ O	4
Glacial Acetic Acid	2

The following examples of sensitizer concentrates herein also further illustrate the invention:

Example 3	Grams per Liter
Stannous Chloride	640
Tartaric Acid	80
HCl (37% Concentration)	448

Example 4	Grams per Liter
Stannous Chloride	608
Tartaric Acid	128
HCl (37% Concentration)	416
NiCl ₂ ·6H ₂ O	64
Glacial Acetic Acid	32

Tests carried out employing a hydroxy tricarboxylic acid salt, viz sodium citrate, as inhibitor or stabilizer in the SnCl₂- and HCl-containing aqueous sensitizer solution showed the sodium citrate to be unsatisfactory, as the sensitizer solution containing 5-25 grams per liter of sodium citrate actually

decomposed faster and with the formation of the white tin oxychloride precipitate than did such sensitizer solutions without any citrate ion.

Test work conducted utilizing a monocarboxylic acid and its salt, viz acetic acid and sodium acetate, as inhibitor or stabilizer in the SnCl₂- and HCl-containing aqueous sensitizer solution also evidenced the acetic acid and sodium acetate to be unsatisfactory, as a very unstable sensitizer solution having a white precipitate of tin oxychloride therein resulted shortly after preparation of such sensitizer solution. Thus a sensitizer solution formed by diluting one part of a sensitizer concentrate containing, by weight, 41.2% SnCl₂, 6.2% HCl (37%), 3.3% sodium acetate trihydrate, 3.7% acetic acid, 1.8% NiCl₂·6H₂O and 45.3% H₂O with 15 parts of water formed a white tin oxychloride precipitate in about 5 minutes after its formation. However, the addition of two grams per liter of tartaric acid to the water diluent portion before diluting the sensitizer concentrate of the same composition as that set forth immediately above therewith resulted in a sensitizer solution which was stable and showed no white tin oxychloride precipitate for in excess of 2 1/2 days after its formation.

A plurality of panels of acrylonitrile-butadiene-styrene terpolymer, i.e. ABS terpolymer, were processed through an electroless nickel plating cycle involving (1) conditioning of the panels in a conventional chromic acid- and sulfuric acid-containing aqueous conditioning solution at a solution temperature of 140° F. for 5-8 minutes; (2) immersion of the thus-conditioned panels in an acid solution; (3) sensitizing the panels separately in one of the Sensitizer Solutions A, B, C and D having the composition hereinafter set forth; (4) activating the thus-sensitized panels in a conventional activator solution containing PdCl₂, HCl and water; (5) immersing the thus-activated panels in acid solution; and (6) electrolessly nickel plating the activated panels in a conventional chemical reduction nickel plating bath. The compositions of Sensitizer Solutions A, B, C and D follows:

Sensitizer Solution A	
HCl (37.5%)	50g/l
SnCl ₂	41g/l
Tartaric Acid	5g/l
H ₂ O	To 1 liter

Sensitizer Solution B	
HCl (37.5%)	50g/l
SnCl ₂	41g/l
Tartaric Acid	5g/l
Ni ⁺⁺ (as NiCl ₂ ·6H ₂ O)	2×10 ⁻⁴ M
H ₂ O	To 1 liter

Sensitizer Solution C	
HCl (37.5%)	50g/l
SnCl ₂	41g/l
Tartaric Acid	5g/l
Ni ⁺⁺ (as NiCl ₂ ·6H ₂ O)	2×10 ⁻⁴ M
H ₂ O	To 1 liter

Sensitizer Solution D	
HCl (37.5%)	50g/l
SnCl ₂	41g/l
Tartaric Acid	5g/l
Ni ⁺⁺ (as NiCl ₂ ·6H ₂ O)	2×10 ⁻⁴ M
H ₂ O	To 1 liter

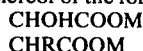
Sensitizer Solutions A, B, C and D were stable after 7 days and showed no white precipitate of tin oxychloride. The tests also showed a significant improvement in extent of coverage of electroless nickel on the ABS panel surfaces as the amount of

Ni⁺⁺ increased in the sensitizer solutions. Use of the control Sensitizer Solution A not containing Ni ions resulted in considerable skip plating of the ABS surfaces, i.e. unplated areas as well as plated areas, in the electroless nickel plating step. However, use of the Sensitizer Solution B containing Ni ions resulted in materially less skip plating of the ABS surfaces in the electroless nickel plating; use of the Sensitizer Solution C containing more ionic Ni than in Sensitizer Solution B resulted in appreciably less skip plating of the ABS surfaces in the electroless nickel plating step than with use of Sensitizer Solution B; and use of the Sensitizer Solution D resulted in no skip plating of the ABS surfaces in the electroless nickel plating step.

Although the invention has been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example only and is not taken by way of limitation, the spirit and scope of this invention being limited only by the terms of the appended claims.

What is claimed is:

1. An acid aqueous sensitizer solution comprising stannous chloride, HCl, and a minor amount, sufficient to inhibit tin oxychloride formation therein, of at least one material selected from the group consisting of an alpha hydroxy dicarboxylic acid and soluble, sensitizer solution-compatible salts thereof of the formula:

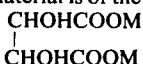


wherein R is -H or -OH and M is -H or a solution-compatible, hydrophilic cation.

2. The sensitizer solution of claim 1 also containing a minor amount, sufficient to accelerate deposition of a catalytic noble metal on a surface to be electrolessly metal plated during a subsequent activating step, of ions of a metal from the group consisting of nickel and cobalt.

3. The sensitizer solution of claim 2 also containing a buffering agent in amount sufficient to maintain the pH of the solution within the pH range of about 0.45 to about 1.00.

4. The sensitizer solution of claim 1 wherein the selected material is of the formula:



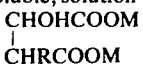
wherein M is -H or a solution-compatible, hydrophilic cation.

5. The sensitizer solution of claim 4 wherein the selected material is tartaric acid.

6. The sensitizer solution of claim 2 wherein the metal ions are divalent nickel ions.

7. The sensitizer solution of claim 3 wherein the buffering agent is glacial acetic acid.

8. A sensitizer concentrate adapted to be mixed together with an aqueous liquid to form a ready-to-use sensitizer solution comprising an acid aqueous solution containing stannous chloride, HCl, and at least one material selected from the group consisting of an alpha hydroxy dicarboxylic acid and soluble, solution-compatible salts thereof of the formula:

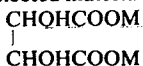


wherein R is -H or -OH and M is -H or a solution-compatible, hydrophilic cation.

9. The sensitizer concentrate of claim 8 also containing a soluble, ionizable salt of a metal from the group consisting of nickel and cobalt.

10. The sensitizer concentrate of claim 9 also containing a buffering agent.

11. The sensitizer concentrate of claim 8 wherein the selected material is of the formula:



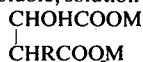
M is -H or a solution-compatible, hydrophilic cation.

12. The sensitizer concentrate of claim 11 wherein the selected material is tartaric acid.

13. The sensitizer concentrate of claim 9 wherein the soluble ionizable metal salt is a divalent nickel salt.

14. The sensitizer concentrate of claim 10 wherein the buffering agent is glacial acetic acid.

15. A method for electrolessly metal plating an electrically nonconductive surface of an object which comprises sensitizing the nonconductive surface by contacting the surface with an acid aqueous sensitizer solution comprising stannous chloride, HCl, and a minor amount, sufficient to inhibit tin oxychloride formation, of at least one material selected from the group consisting of an alpha hydroxy dicarboxylic acid and soluble, solution-compatible salts thereof of the formula:

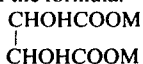


wherein R is -H or -OH and M is -H or a solution-compatible, hydrophilic cation, activating the sensitized surface, and electrolessly metal plating the activated surface by contacting the surface with a chemical reduction metal plating solution until the surface is electrically conductive.

16. The plating method of claim 15 wherein the sensitizer solution contains as an additional ingredient a minor amount, sufficient to accelerate the deposition of a catalytic noble metal on the surface during the subsequent activating step, of ions of a metal from the group consisting of nickel and cobalt.

17. The plating method of claim 16 wherein the sensitizer solution also contains a buffering agent in amount sufficient to maintain the pH of the solution within the pH range of about 0.45 to about 1.00.

18. The method of claim 15 wherein the selected material is of the formula:



wherein M is -H or a solution-compatible, hydrophilic cation.

19. The plating method of claim 18 wherein the selected material is tartaric acid.

20. The plating method of claim 16 wherein the metal ions are divalent nickel ions.

21. The plating method of claim 17 wherein the buffering agent is glacial acetic acid.

22. The sensitizer solution of claim 5 wherein the following ingredients are present in proportions within the proportion ranges hereafter specified:

Grams per liter

Stannous chloride	from about 36-45
HCl (37% concentration)	from about 5-30
Tartaric acid	from about 1-20

23. The sensitizer concentrate of claim 12 wherein the following ingredients are present in proportions within the proportion ranges hereafter specified:

Grams per liter

Stannous chloride	from about 592-672
HCl (37% concentration)	from about 384-448
Tartaric acid	from about 64-128

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607, 352 Dated September 21, 1971

Inventor(s) Earl J. Fadgen, Jr. and Gary Leibowitz

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

Column 3, line 64, "sensitizer aqueous" should be read in line 64 but directly below and immediately after "Grams per liter of ". Column 4, line 48, " $\text{NiCl}_2 \cdot 6\text{H}_2$ " should read " $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ". Column 6, line 52, " $2 \times 10^{16}\text{M}$ " should read " $2 \times 10^{-6}\text{M}$ "; line 60, " $2 \times 10^{14}\text{M}$ " should read " $2 \times 10^{-4}\text{M}$ "; line 68, " 2×10 " should read " $2 \times 10^{-2}\text{M}$ "; line 69, " 12M " should be deleted. Column 7, line 45, "irons" should read "--ions--".

Signed and sealed this 28th day of March 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents