NON-CYANIDE SILVER PLATING BATH COMPOSITION

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ABSTRACT

Disclosed is an electroplating solution for the deposition of silver; said solution containing silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound; said solution also containing an excess of the hydantoin or substituted hydantoin compound employed, together with an effective quantity of a nonprecipitating electrolyte salt, and also an effective quantity of 2,2’ dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit.
NON-CYANIDE SILVER PLATING BATH COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION


BACKGROUND OF THE INVENTION

[0002] Numerous non-cyanide silver plating processes have been attempted (See Citation No. 1). Of these, the only ones to have achieved commercial success have been those employing succinimide, either as a premanufactured silver complex (See Citation Nos. 2 and 3), or as a reagent. Succinimide undergoes hydrolysis at pH values above neutrality, which in turn causes the pH of the plating solution, normally in the range of 8 to 9 or so, to become unstable; and also to require frequent replenishment of the succinimide.

[0003] Hydantoin (CAS Number 461-72-3) is a cyclic diimide possessing structural features similar to succinimide, and similarly effective as a complexing agent for silver. A series of substituted hydantoins exist, of which the most commonly available commercially is 5,5-dimethylhydantoin (CAS No. 77-71-4). As a class, the hydantoins are soluble in moderate-to-strongly alkaline (pH 12 to 14) solutions, are capable of forming complexes with silver and other metals, and are more resistant to hydrolysis than succinimide.

[0004] Nishihama et al., (JP 411302893A or JP ’893) discusses the use of 5,5-dimethylhydantoin as a bath constituent in Examples 2, 4, 7, 8, 9, and 10. Calculating from an atomic weight of 107.87 for silver and molecular weights of 123.11 for nicotinic acid and 128.13 for 5,5-dimethylhydantoin, one sees that Examples 2, 9, and 10 do not include sufficient 5,5-dimethylhydantoin to form the silver bis (5,5-dimethylhydantoin) complex.

[0005] In all of the Examples of JP ’893 in which 5,5-dimethylhydantoin is included it is accompanied by a large stoichiometric excess of nicotinic acid, which is one of the class of pyridine compounds which the authors consider to be the active complexing agents for silver. In half of those Examples, insufficient 5,5-dimethylhydantoin is included to form the silver-hydantoin complex at all.

[0006] In coordinate complexes with organic ligands, monovalent silver displays a coordination number of two. Thus complexes of silver (I) with pyridine, say, include two pyridine moieties bound to each silver (I) ion. The same is true of nicotinic acid or of 5,5-dimethylhydantoin. In performing a chemical reaction it is common practice to employ a slight excess of one reagent in order to ensure completion of the reaction. Large excesses of a complexing agent, however, are not incorporated into the reaction product, but remain unreacted in the reaction mixture, where they compete with and act to prevent complexation by any other reagent which may be introduced. This is the case in the electroplating solutions described in the Examples given in JP ’893.

[0007] In Examples 4, 7, and 8 of JP ’893, the ratio of 5,5-dimethylhydantoin to silver is 2.208 to one, which is sufficient to form the silver bis (5,5-dimethylhydantoin) complex. This, however, is accompanied by an excess of nicotinic acid amounting to 9.201 times, on a molecular equivalent basis, the amount of silver present. Assuming that the stability constants of the 5,5-dimethylhydantoin and nicotinic acid complexes of silver are even within an order of magnitude of each other, it is clear that the claimed silver bis (5,5-dimethylhydantoin) complex of the present invention cannot be effectively formed in any of the Examples of JP ’893.

[0008] The present inventor submits that the silver-hydantoin compounds recited in the claims would not have formed in the electroplating solution disclosed in JP ’893. This is true for a number of reasons, most particularly so because in all of the Examples of JP ’893 in which 5,5-dimethylhydantoin is included it is accompanied by a large stoichiometric excess of nicotinic acid, which is one of the class of pyridine compounds which the authors consider to be the active complexing agents for silver. In half of those Examples, insufficient 5,5-dimethylhydantoin is included to form the silver-hydantoin complex at all.

[0009] Asakawa, in U.S. Pat. No. 5,601,606, discloses a non-cyanide plating solutions for silver in which silver salts are added together with a hydantoin compound and an inorganic or organic acid salt for the purpose of providing electrical conductivity. Asakawa also teaches the use of various sulfur-containing compounds as gloss-controlling agents for the deposits from the plating solutions of his invention, and states that with the use of such additives deposit appearance suitable for decorative applications can be obtained. There is no mention of mirror-bright appearance, however, and the Examples provided do not appear to indicate that mirror-bright deposits would be obtained. In particular, all of the Examples cited include significant quantities of chloride ion, which is a known precipitant for silver and highly likely to form insulating films at the anodes.

[0010] Other background references (Citation Nos. 1-5) of interest include the following, which are hereby incorporated herein by reference:

[0012] 2. Hradil, et al., U.S. Pat. No. 4,126,524;
[0014] 4. Soutar, et al., U.S. Pat. No. 5,955,141; and

[0016] Since much commercial silver plating is for the purpose of obtaining mirror-bright to brilliant deposits, it would clearly be desirable to electroplate such deposits from a non-cyanide plating solution, thus saving the costs of cyanide waste treatment, and also of subsequent polishing and buffing.

SUMMARY OF THE INVENTION

[0017] Accordingly, it is an object of this invention to provide a non-cyanide plating solution for the deposition of silver, said solution being capable of yielding mirror-bright to brilliant deposits. It is a further object that the plating
Thus, one embodiment of the present invention is an electroplating solution for the deposition of silver, said solution consisting essentially of:

(a) a premade aqueous solution of silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound wherein said solution includes an excess molar ratio of the hydantoin or substituted hydantoin compound;

(b) a premade aqueous solution of a conducting electrolyte comprising an effective quantity of a nonprecipitating electrolyte salt, and the hydantoin or the a substituted hydantoin compound employed in part (a); and

(c) an effective quantity of 2,2'-dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit; said plating solution having a pH of from about 9 to about 13.

Preferably, the electroplating solution includes an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained.

Preferably, the electroplating solution also includes an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

Advantageously, in the electroplating solution of the present invention, the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

Advantageously, in the electroplating solution of the present invention, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts.

Advantageously, in the electroplating solution of the present invention, the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

Preferably, in the electroplating solution of the present invention, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

Another embodiment of the present invention is a process for the formation of a mirror-bright to brilliant electrodeposited silver on a substrate comprising the step of:

(a) electroplating said substrate in an electroplating solution, said solution consisting essentially of:

(a) a premade aqueous solution of silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound wherein said solution includes an excess molar ratio of the hydantoin or substituted hydantoin compound;

(b) a premade aqueous solution of a conducting electrolyte comprising an effective quantity of a nonprecipitating electrolyte salt, and the hydantoin or the substituted hydantoin compound employed in part (a); and

(c) an effective quantity of 2,2'-dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit; said plating solution having a pH of from about 9 to about 13.

Preferably, in the process of the present invention, the electroplating solution also includes an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained.

Preferably, in the process of the present invention, the electroplating solution also includes an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

Advantageously, in the process of the present invention, the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

Advantageously, in the process of the present invention, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts.

Preferably, in the process of the present invention, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

Preferably, in the process of the present invention, the pH of the electroplating solution is from about 10 to 11.

Preferably, in the process of the present invention, the substituted hydantoin compound is 5,5-dimethylhydantoin.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

One preferred embodiment of the present invention is an electroplating solution for the deposition of silver; said solution comprising silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound; said solution also comprising an excess (i.e., more than a stoichiometric amount based on the silver) of the hydantoin or substituted hydantoin compound, together with an effective quantity of a nonprecipitating electrolyte salt, and also an effective quantity of 2,2'-dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit. An excess amount of the hydantoin or substituted hydantoin compound ensures the complete (or nearly complete) complexation of the silver.

Preferably, the electroplating solution further comprises an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained. Advantageously, the electroplating solution further comprises an effective quan-
tity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

[0042] In certain preferred embodiments the surface-active material is selected from the group of commercial products known as Hamposyl C (also known generically as—cocoyl sarcosine), Hamposyl L (also known generically as—lauryl sarcosine), Hamposyl O (also generically known as—oleoyl sarcosine), Blancol (also known generically as—the sodium salt of a sulfonated naphthalene condensate), Blancol N (also known generically as—the sodium salt of a sulfonated naphthalene-formaldehyde condensate), Rhodacal (also known generically as—the alkylamine salt of alkylbenzene sulfonic acid), and Rhodacal N (also known generically as—the sodium salt of a sulfonated naphthalene-formaldehyde condensate). These surfactants are collectively classified as follows; substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

[0043] In certain preferred embodiments, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. In certain preferred embodiments, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

[0044] Thus, in accordance with the present invention, the electroplating solution is made by mixing the following premade solutions:

[0045] (a) a premade aqueous solution of silver in the form of a complex with hydantoin or a substituted hydantoin compound wherein said solution includes an excess molar ratio of the hydantoin or substituted hydantoin compound;

[0046] (b) a premade aqueous solution of a conducting electrolyte comprising an effective quantity of a nonprecipitating electrolyte salt, and the hydantoin or the substituted hydantoin compound employed in part (a); and

[0047] (c) an effective quantity of 2,2'-dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit.

[0048] Another preferred embodiment of the present invention is a process for the formation of a mirror-bright to brilliant electrodeposit of silver on a substrate comprising the step of:

[0049] electroplating said substrate in an electroplating solution formed as above;

[0050] said solution comprising silver in the form of a complex with hydantoin or a substituted hydantoin compound;

[0051] said solution also comprising an excess of the hydantoin or substituted hydantoin compound, together with an effective quantity of a nonprecipitating electrolyte salt, and an effective quantity of 2,2'-dipyridyl for the formation of a mirror-bright to brilliant deposit.

[0052] Preferably, the electroplating solution used in the process of the invention further comprises an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained. Advantageously, the electroplating solution used in the process of the invention further comprises an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained. In certain preferred embodiments the surface-active material is selected from the group consisting of Hamposyl C, Hamposyl L, Hamposyl O, Blancol, Blancol N, Rhodacal, and Rhodacal N. In certain preferred embodiments, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. In certain preferred embodiments, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

[0053] It has been found that in moderately alkaline (pH ≥9) plating solutions containing silver in the form of a complex formed with hydantoin or a substituted hydantoin, together with a nonprecipitating electrolyte salt, addition of 2,2'-dipyridyl (CAS No. 566-18-7), either alone or in conjunction with other substituted pyridines and/or surfactants, produces mirror-bright to brilliant deposits.

[0054] As used herein, the terms “nonprecipitating electrolyte salts” refer to salts of acids the silver salts of which are soluble. Examples of such nonprecipitating electrolyte salts would include the sodium, potassium, or ammonium salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic and lactic acids. Such materials do not cause film formation at the anodes, and in some cases promote anode corrosion. Additionally, the silver-hydantoin complexes of this invention are premanufactured in that form to the plating solution, together with an excess of the hydantoin and the nonprecipitating electrolyte salt.

[0055] Addition of 2,2'-dipyridyl to the plating solutions of this invention, usually in amounts in the range of about 0.1 to 10 grams per liter, produces bright deposits over a current density range from about 5-20 mA/cm² for solutions operated at room temperature. Addition of further quantities of various substituted pyridine compounds, usually in amounts greater than that of the 2,2'-dipyridyl itself, expands the range of usable current density from about 1 to 30 mA/cm², and improves the uniformity and whiteness of the entire deposit. Preferred substituted pyridine compounds for the purposes of this invention include nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. These are added in amounts from about 2.5 to 100 grams per liter, depending on other parameters of the plating solution. It should be pointed out that in the absence of 2,2'-dipyridyl, addition of substituted pyridine compounds is generally ineffective for the purposes of this invention. It should also be pointed out that additions of 4,4'-dipyridyl and 1,10-phenanthroline are likewise ineffective for the purposes of this invention.

[0056] Finally, it has been discovered that the addition of a suitable surfactant to the plating solutions of this invention containing both 2,2'-dipyridyl and a substituted pyridine compound, produces an overall improvement of deposit brightness from mirror-bright to brilliant. Surfactants suitable for the purposes of this invention include the class of substituted glycine derivatives known commercially as
Hamposyls, and also the sulfonated naphthalene-formaldehyde condensate known commercially as Blancol N or Rhodacal N and their aqueous solutions. Both of these classes of surfactants have been used previously for conventional (cyanide based) silver plating.

[0057] The plating solutions of this invention produce mirror-bright to brilliant deposits over a range of pH from about 9 to about 13. Certain practical considerations act to limit this range somewhat. The corrosivity of the solutions toward silver anodes increases generally with increasing pH from about pH 9.5 to about pH 13. It also happens that 2,2'-dipyridyl is subject to hydrolysis at pH values above about 10.5, the rate of hydrolysis increasing with increasing pH. In order to obtain adequate replenishment of silver from the anodes and to preserve the useful life of the brightener chemicals, an optimum pH range of about 10-11 is arrived at.

[0058] Some Examples of plating solutions of this invention are given as follows. In each of the Examples, silver is added as a preformed complex formed by the reaction of silver oxide with hydantoin, or with a substituted hydantoin, such as 5,5-dimethyl-hydantoin, as appropriate. No foreign ions are thus introduced. Other substituted hydantoin compounds can likewise be employed. Methyl-hydantoin, other alkyl-hydantoins, other dialkyl-hydantoins, and the like are useful herein. See the hydantoin compounds of U.S. Pat. No. 5,750,018 for additional examples. This patent is hereby incorporated herein by reference.

**EXAMPLE 1**

Sufficient water was used to form one liter of a solution containing the following:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydroxide</td>
<td>60 grams</td>
</tr>
<tr>
<td>Sulfamic Acid</td>
<td>52.5 grams</td>
</tr>
<tr>
<td>5,5-dimethylhydantoin</td>
<td>60 grams</td>
</tr>
<tr>
<td>Silver as complex with</td>
<td>25 grams Ag</td>
</tr>
<tr>
<td>5,5-dimethylhydantoin</td>
<td></td>
</tr>
<tr>
<td>2,2'-dipyridyl</td>
<td>0.8 grams</td>
</tr>
</tbody>
</table>

The final solution pH was approximately 11.0. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was white and mirror-bright at indicated current densities from about 12.5 mA/cm².

**EXAMPLE 2**

Sufficient water was used to form one liter of a solution containing the following:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydroxide</td>
<td>45 grams</td>
</tr>
<tr>
<td>Sulfamic Acid</td>
<td>45 grams</td>
</tr>
<tr>
<td>Hydantoin</td>
<td>45 grams</td>
</tr>
<tr>
<td>Silver as complex with</td>
<td>25 grams Ag</td>
</tr>
<tr>
<td>with hydantoin</td>
<td></td>
</tr>
<tr>
<td>2,2'-dipyridyl</td>
<td>2.64 grams</td>
</tr>
</tbody>
</table>

The final solution pH was approximately 11.0. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature, with moving-vane agitation. The deposit obtained was white and mirror-bright at indicated current densities from about 5 mA/cm².
EXAMPLE 8

[0069] A plating solution was made up as in Example 7 except additionally containing 26.4 grams of nicotinamide. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was white and mirror-bright at current densities from near zero to greater than 20 mA/cm².

EXAMPLE 9

[0070] A plating solution was made up as in Example 8 except additionally containing 0.16 grams of Hampspots L in the form of an aqueous solution solubilized with potassium hydroxide. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to 20 mA/cm².

[0071] It will be apparent to those skilled in the art that the Examples provided herein are illustrative of the present invention, but do not represent the totality of the useful embodiments thereof.

What is claimed is:

1. An electroplating solution for the deposition of silver; said solution consisting essentially of:
   (a) a premade aqueous solution of silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound wherein said solution includes an excess molar ratio of the hydantoin or substituted hydantoin compound;
   (b) a premade aqueous solution of a conducting electrolyte comprising an effective quantity of a nonprecipitating electrolyte salt, and the hydantoin or the substituted hydantoin compound employed in part (a); and
   (c) an effective quantity of 2,2′ dipyridyldi for the purpose of obtaining a mirror-bright to brilliant deposit;

said plating solution having a pH of from about 9 to about 13.

2. The electroplating solution of claim 1, including an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained.

3. The electroplating solution of claim 1 or 2, including an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

4. The electroplating solution of claim 3, wherein the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

5. The electroplating solution of claim 2, wherein the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts.

6. The electroplating solution of claim 5, wherein the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

7. The electroplating solution of claim 1 or 2, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

8. The electroplating solution of claim 3, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

9. The electroplating solution of claim 4, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

10. The electroplating solution of claim 5, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

11. The electroplating solution of claim 6, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoroboric, glycolic, and lactic acids.

12. A process for the formation of a mirror-bright to brilliant electrodeposition of silver on a substrate comprising the step of:

   electroplating said substrate in an electroplating solution, said solution consisting essentially of:
   (a) a premade aqueous solution of silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound wherein said solution includes an excess molar ratio of the hydantoin or substituted hydantoin compound;
   (b) a premade aqueous solution of a conducting electrolyte comprising an effective quantity of a nonprecipitating electrolyte salt, and the hydantoin or the substituted hydantoin compound employed in part (a); and
   (c) an effective quantity of 2,2′ dipyridyldi for the purpose of obtaining a mirror-bright to brilliant deposit;

said plating solution having a pH of from about 9 to about 13.

13. The process of claim 12, wherein the electroplating solution also includes an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained.

14. The process of claim 12 or 13, wherein the electroplating solution also includes an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

15. The process of claim 14, wherein the surface-active material is selected from the group of surfactants consisting of substituted glycine derivatives, sulfonated naphthalene-formaldehyde condensates, and aqueous solutions thereof.

16. The process of claim 15, wherein the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts.

17. The process of claim 12 or 13, wherein the nonprecipitating electrolyte salt is selected from the group consisting
of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

18. The process of claim 14, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

19. The electroplating solution of claim 15, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

20. The electroplating solution of claim 16, wherein the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

21. The electroplating solution of claim 3, wherein the pH is from about 10 to 11.

22. The electroplating solution of claim 3, wherein the substituted hydantoin compound is 5,5-dimethylhydantoin.