An electrolytic plating composition and related plating process where the composition comprises chromium ions, a mineral acid, halogen oxoanion, alkylsulfonic acid, and a source of sulfosuccinic acid for electrolytically coating a surface of a substrate with a chromium layer or a chromium alloy layer.
PROCESS FOR DEPOSITION OF CRACK-FREE AND CORROSION-RESISTANT HARD CHROMIUM AND CHROMIUM ALLOY LAYERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to DE patent application 102005059367.4, filed Dec. 13, 2005.

BACKGROUND OF THE INVENTION

[0002] This invention relates to a process for the deposition of crack free and corrosion resistant hard chromium and chromium alloy layers and an electrolytic chromium plating composition for depositing chromium and chromium alloy layers.

[0003] Surfaces are coated through electrolytic plating for a variety of reasons such as improving the surface properties in terms of hardness, abrasivity, and corrosion resistance. Additionally, surfaces can be coated for purely aesthetic reasons, such as in decorative coating.

[0004] Chromium is a typical decorative and functional coating layer deposited by electrolytic plating methods. Adjusting the components and their concentrations in the electrolytic plating composition can affect chromium layer properties such as hardness, corrosion resistance, and brightness.

[0005] Electrolytic chromium plating compositions typically comprise a source of hexavalent chromium and sulfuric acid for depositing chromium over a base metal surface. The deposition temperature is typically between 50°C and 70°C, with current densities in the range of 30 A/dm² to 50 A/dm². Under these conditions, current efficiencies are typically between 12% and 16%. German Patent Application DE 4302564 discloses that the addition of fluoride ions and alkylsulfonic acids can increase the current efficiency up to 26%.

[0006] Besides adjusting the composition chemistry to affect the properties of the chromium deposit, it is also possible to affect the properties by adjusting the plating conditions. For example, bright chromium layers are deposited at current densities between 2 A/dm² and 8 A/dm² and at a composition temperature of about 30°C, or at current densities between 3 A/dm² and 18 A/dm² and at a composition temperature of about 50°C, or at current densities between 6 A/dm² and 28 A/dm² and at a composition temperature of about 50°C. Matte layers are deposited at current densities below 2 A/dm² and at a composition temperature of about 30°C. It is possible to deposit matte layer at current densities up to about 6 A/dm² by controlling the composition temperature.

[0007] A hot chrome process available from Enthone Inc. under the trade name ANKORO 1141 can be used to plate a chromium layer having a hardness of 700 HV 0.1. This process achieves current efficiencies of about 10% at a composition temperature of 70°C. Higher current efficiencies result in a layer which cracks during mechanical processing.

[0008] European patent application EP 0073568 discloses an electrolytic chromium plating composition capable of current efficiencies of about 30% by adding a carboxylate to a chromium composition also comprising potassium iodate as a halogen source.

SUMMARY OF THE INVENTION

[0009] Among the various aspects of the invention may be noted an electrolytic chromium plating composition and method for plating a chromium layer or chromium alloy layer which is corrosion resistant, crack free, and hard. The plating method is capable of plating with a high current efficiency.

[0010] Briefly, therefore, the invention is directed to a process for electrolytically coating a surface of a substrate with a chromium-based layer, the process comprising contacting the surface of the substrate with an electrolytic plating composition comprising a source of chromium ions, a mineral acid, a source of halogen oxoanion, an alkylsulfonic acid, and a source of sulfonic acid selected from the group consisting of sulfonic acid, a sulfonic acid salt, a sulfonic acid ester, a sulfonic acid anhydride, and a reactant which generates sulfonic acid; and supplying an external source of electrons to electrolytically deposit the chromium-based layer onto the surface of the substrate.

[0011] In another aspect the invention is directed to an electrolytic plating composition for electrolytically coating a surface of a substrate with a chromium layer or a chromium alloy layer, the composition comprising a source of chromium ions; a mineral acid; a source of halogen oxoanion; a source of alkylsulfonic acid; and a source of sulfonic acid selected from the group consisting of sulfonic acid, a sulfonic acid salt, a sulfonic acid ester, a sulfonic acid anhydride, and a reactant which generates sulfonic acid.

[0012] Other objects and features of the invention will be in part apparent and in part pointed out hereinafter.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0013] This application claims priority to DE patent application 102005059367.4, filed Dec. 13, 2005, the entire disclosure of which is incorporated by reference.

[0014] The electrolytic chromium plating composition and method of the present invention is capable of plating a chromium layer or chromium alloy layer which is corrosion resistant, crack free, and hard. The plating method is capable of plating with a high current efficiency, with current efficiencies greater than 30% typically achieved.

[0015] The electrolytic chromium plating composition which can plate a corrosion resistant, crack free, hard chromium layer at high current efficiencies comprises a source of chromium ions, a mineral acid, a source of halogen oxoanion, an alkylsulfonic acid, and a source of sulfonic acid selected from the group consisting of sulfonic acid, sulfonic acid salts, sulfonic acid esters, sulfonic acid anhydride, and reactants which generate sulfonic acid. When it is desirable to plate a chromium alloy layer, the electrolytic chromium plating composition can comprise a source of alloying metal ions, such as poly-anion forming metals, including molybdenum, tungsten, vanadium.

[0016] The source of chromium ions provides hexavalent chromium (chromium(VI) ions) to the electrolytic chro-
mium plating composition. Sources of hexavalent chromium include chromium(VI) oxide (CrO$_3$O$_2$, commonly referred to as the anhydride of chromic acid); chromate (CrO$_4^{2-}$) salts of sodium, potassium, and ammonium; and dichromate (CrO$_7^{2-}$) salts of sodium, potassium, and ammonium. A preferred source of hexavalent chromium is CrO$_3$ because CrO$_3$ avoids introducing other metal ions and cations in the plating bath, which may limit the conductivity of the plating bath. The source of chromium ions can provide hexavalent chromium into the electrolytic plating composition in an initial concentration of at least about 0.5M. Preferably, the source of chromium ions can provide hexavalent chromium into the electrolytic plating composition in a concentration of at least about 1M, more preferably at least about 2M. The concentration is preferably at least about 0.5M to avoid loss conductivity in the plating bath, necessitating a high plating voltage. The source of chromium ions can provide hexavalent chromium into the electrolytic plating composition in an initial concentration no greater than about 5M, preferably no greater than about 4M, more preferably no greater than about 3M. At higher concentrations than 5M, their may be disadvantages related to high drag out rate from the plating bath and increased cost. Accordingly, the source of chromium ions can provide hexavalent chromium into the electrolytic plating composition in a concentration between about 0.5M and about 5M, preferably between about 1M and about 4M, even more preferably between about 2M and about 3M. When CrO$_3$ (M.W. 99.99 g/mol) is the source of hexavalent chromium, these molar concentrations correspond to concentrations of about 50 g/L to about 500 g/L, preferably about 100 g/L to about 400 g/L, even more preferably about 200 g/L to about 300 g/L in the electrolytic plating composition.

[0017] A mineral acid can be added for pH adjustment. Preferably, the pH of the electrolytic chromium plating composition is no greater than about 1. In one embodiment a mineral acid suitable for lowering the composition pH is preferably sulfuric acid.

[0018] A source of halogen oxoanion can be added to the electrolytic chromium plating composition to increase the current efficiency and improve the chromium layer properties. Although the mechanism is not fully understood, it has been observed that the absence of the halogen oxoanion results in significantly lower current efficiency. The present invention is directed to a combination of such anions that provide improved efficiency and crack free deposits. The discovered catalyst and bath formulation provides a desirable combination of deposit properties such as relatively high hardness, crack free deposit, and improved corrosion resistance. Sources of halogen oxoanion include bromo-oxy compounds and iodo-oxy compounds. Exemplary bromo-oxy compounds include bromate (BrO$_5^{2-}$) and perbromate (BrO$_7^{2-}$) salts. The compounds can include bromate and perbromate alkali metal and alkaline earth metal salts such as the salts of sodium, potassium, magnesium, calcium, and barium. The compounds may also include bromate and perbromate salts of ammonium and amines. Bromate and perbromate may also be provided as acids. Exemplary iodo-oxy compounds include iodate (IO$_5^{2-}$) and periodate (IO$_7^{2-}$) salts. The compounds can include iodate and periodate alkali metal and alkaline earth metal salts such as the salts of lithium, sodium, potassium, magnesium, calcium, and barium. The compounds may also include iodate and periodate salts of ammonium and amines. Iodate and periodate may also be provided as acids. The source of halogen oxoanion be a bromide salt, bromine, an iodide salt, or iodine, which could be oxidized in the electrolytic chromium plating bath to the halogen oxoanion. Chlorine oxoanions are also applicable, such as chlorates, chlorites, perchlorates, hypochlorites, as well as chlorine and chlorides which may be oxidized in the electrolytic chromium plating bath to a chloro-oxoanion.

[0019] A preferred source of halogen oxoanion is potassium iodate. Of the applicable halogen oxoanion, potassium iodate results in the highest plating bath efficiency. The source of halogen oxoanion can be added to the electrolytic chromium plating bath in an initial concentration of at least about 0.001M, preferably at least about 0.005M, even more preferably at least about 0.007M. The source of halogen oxoanion can be added to the electrolytic chromium plating bath in an initial concentration of no greater than about 0.1M, preferably no greater than about 0.08M, even more preferably no greater than about 0.05M. Accordingly, the source of halogen oxoanion can be added to the electrolytic chromium plating bath in an initial concentration between about 0.001M and about 0.1 M, preferably between about 0.005M and about 0.08M, even more preferably between about 0.007M and about 0.03M. At concentrations outside the range of between about 0.001M and about 0.1 M, the bath experiences a loss of plating efficiency. At concentrations higher than about 0.1M, there is the additional disadvantage of poor adhesion of the chromium layer on the substrate. When potassium iodate (KIO$_3$, M.W. 210.00 g/mol) is the source of the halogen oxoanion, these molar concentrations correspond to concentrations of about 0.23 g/L to about 23 g/L, preferably about 1.15 g/L to about 18.4 g/L, even more preferably about 1.61 g/L to about 6.9 g/L in the electrolytic plating composition.

[0020] The alkylsulfonic acid can be added to the electrolytic chromium plating composition because its inclusion results in an increase in the hardness of the deposited chromium layer without impairing the current efficiency or deposition speed. The effect of the alkylsulfonic acids on the plating mechanism is not fully understood. It is thought that alkylsulfonic acids increase the percentage of (100) oriented crystallites, providing higher hardness than other crystal orientations. Alkylsulfonic acids for use in the electrolytic plating compositions of the invention typically have alkyl groups from one to four carbons, more typically from one to two carbons. Alkylsulfonic acids can have from one to four sulfonate groups, preferably from one to two sulfonate groups. Exemplary alkylsulfonic acids include methylsulfonic acid, methanedisulfonic acid, ethylsulfonic acid, and propylsulfonic acid. Preferably, the alkylsulfonic acid is methylosulfonic acid. The alkylsulfonic acid may be added to the electrolytic chromium plating bath as a salt, typically, the sodium, potassium, or ammonium salt. The alkylsulfonic acid can be added to the electrolytic chromium plating bath in an initial concentration of at least about 0.01 M, preferably at least about 0.015 M, even more preferably at least about 0.02 M. At concentrations lower than about 0.01M, the plated chromium layer may be less hard than desirable. The alkylsulfonic acid can be added to the electrolytic chromium plating bath in an initial concentration no greater than about 0.1 M, preferably no greater than about 0.06 M, even more preferably no greater than about 0.04 M. At concentrations greater than about 0.1M, the plating bath experiences a loss of plating efficiency, and cracks may
develop in the plated chromium layer. Accordingly, the alkylsulfonic acid can be added to the electrolytic chromium plating bath in an initial concentration between about 0.01 M and about 0.1 M, preferably between about 0.015 M and about 0.06 M, even more preferably between about 0.02 M and about 0.04 M.

[0021] The source of sulfocacetic acid can be added to increase the current efficiency of the plating bath. The source of sulfocacetic acid can be selected from sulfocacetic acid, sulfonate salts, sulfonate esters, and sulfonate anhydride. Additionally, the source of sulfocacete can be a reactant which generates sulfocacete. Exemplary reactants which generate sulfocacete in the electrolytic chromium plating bath include 3-hydroxypropene-1-sulfonic acid, hydroxymethanesulfonic acid, or aldhydeomethanesulfonic acid. When these sources are used, sulfocacetic acid is a degradation product of an oxidation process of chromic acid. Preferably, the source of sulfocacetic acid is sulfocacetic acid in its pure form. The source of sulfocacetic acid can be added to the electrolytic chromium plating bath in an initial concentration of at least about 0.03 M, preferably at least about 0.05M, more preferably at least about 0.06 M. At concentrations lower than about 0.03M, the current efficiency in the plating bath decreases. The source of sulfocacetic acid can be added to the electrolytic chromium plating bath in an initial concentration no greater than about 0.3 M, preferably no greater than about 0.15 M, more preferably no greater than about 0.12 M. At concentrations higher than about 0.3M, the chromon layer may develop cracks and adhesion of the chromon layer to the substrate suffers. Accordingly, the source of sulfocacetic acid can be added to the electrolytic chromium plating bath in an initial concentration between about 0.03 M and about 0.3 M, preferably between about 0.05 M and about 0.15 M, more preferably between about 0.06 M and about 0.12 M.

[0022] The method of the present invention may also be used to plate chromium alloys. Typically, chromium may be plated in an alloy with poly-anion forming metals, such as molybdenum, tungsten, and vanadium. The concentration of the alloying metal may be added to yield a chromium alloy layer having between about 0.1% and about 5%.

[0023] The invention further proposes a method for electrolytic chromium plating, in which an electrolytic chromium plating composition comprising the above mentioned components is used. Substrates applicable for plating a hard chromium layer with the compositions of the present invention include parts such as pistons, cylinders, shocks, struts, and hydraulic shafts. Substrates for decorative chromium plating include electrical appliances and exterior car parts such as door handles, hub caps, and bumpers. The base metal over which the chromium layer or chromium alloy layer can be plated can be any conductive metal substrate, but is typically steel, iron, copper, aluminum based alloys, and stainless steel including casted metals. A particularly preferred substrate is CK45 steel.

[0024] The cathode substrate, i.e., the part upon which the chromium layer is deposited, and anode are electrically connected by wiring and, respectively, to a rectifier (power supply). The cathode substrate for direct or pulse current has a net negative charge so that chromium(VI) ions in the electrolytic plating composition are reduced at the cathode substrate forming plated chromium metal on the cathode surface. An oxidation reaction takes place at the anode. The cathode and anode may be horizontally or vertically disposed in the plating tank.

[0025] During operation of the electrolytic plating system, chromium metal is plated on the surface of a cathode substrate when the rectifier is energized. A pulse current, direct current, reverse periodic current, or other suitable current may be employed. Preferably, plating is carried out by means of direct current. The temperature of the electrolytic solution may be maintained using a heater/coolor whereby electrolytic solution is removed from the holding tank and flows through the heater/cooler and then is recycled to the holding tank.

[0026] The electrolytic plating bath can be operated at any temperature from about 20°C to about 90°C, preferably from 45°C to about 65°C. The electrical current density is typically up to about 20 A/dm² and about 500 A/dm², more typically between about 20 A/dm² and about 150 A/dm². The deposition speed may vary between about 0.2 μm/min and about 60 μm/min depending on current densities applied, which is faster than conventional methods. At a current density of about 50 A/dm² and 55°C C, the deposition speed is typically greater than about 1.3 μm/min. Current efficiencies typically between about 25% and about 40%, with current efficiencies exceeding about 30% routinely achieved. In a typical industrial application, the chromium layer may be deposited to a thickness between about 2 μm and about 200μm.

[0027] The electrolytic chromium plating composition and electrolytic plating method are capable of depositing hard chromium layers. The Vickers Hardness values of the chromium layers are typically between about 650 HV 0.1 and about 1100 HV 0.1, with layers having hardness values exceeding about 800 HV 0.1 routinely achieved. Moreover, the deposited chromium layers exhibit excellent corrosion resistance. The corrosion resistance of a chromium layer having a thickness of 25 μm typically exceeds 200 hours under the DIN 50021 SS standard test.

[0028] The following examples further illustrate the present invention.

EXAMPLES 1-10

Electrolytic Chromium Plating Compositions

[0029] Ten electrolytic chromium plating compositions were prepared including the additives of the present invention. Each composition was used to plate an alloy layer over an inductively hardened CK45 steel substrate. The base electrolytic composition (included in all 10 compositions) contained chromium(VI) oxide (Cr₂O₃) in a concentration of 280 g/L, and sulfuric acid (H₂SO₄) in a concentration of 2.8 g/L. The steel substrates were plated at current of either 10A or 14A for 30 minutes, and the performance of the electrolytic plating compositions were measured in terms of current efficiency and deposition rate. The results are shown in the following table.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Deposition Rate (μm/min)</th>
<th>Current Efficiency (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>70</td>
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<tr>
<td>2</td>
<td>0.6</td>
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</table>
### Table

<table>
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<tr>
<th>No.</th>
<th>3-hydroxy propane-1-sulfonic acid (mL/L)</th>
<th>Halogen oxoanion concentration (g/L)</th>
<th>Sulfonic acid (g/L)</th>
<th>Current (A)</th>
<th>Current Density (A/dm²)</th>
<th>Current Efficiency (%)</th>
<th>Deposition Rate (μm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>n.d.</td>
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</table>

### Text

n.d.—not determined

All deposited layers from Example Compositions 1-10 had hardness greater than 800 HV 0.1, and a corrosion resistance according to DIN 5002165 of more than 200 hours.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

When introducing elements of the present invention of the preferred embodiment(s) thereof, the articles “a”, “an”, “the” and “said” are intended to mean that there are one or more of the elements. The terms “comprising”, “including” and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements.

As various changes could be made in the above without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for electrolytically coating a surface of a substrate with a chromium-based layer, the process comprising:

   contacting the surface of the substrate with an electrolytic plating composition comprising a source of chromium ions, a mineral acid, a source of halogen oxoanion, an alkylsulfonic acid, and a source of sulfonic acid selected from the group consisting of sulfonic acid, a sulfonate salt, a sulfonate ester, a sulfonate anhydride, and a reactant which generates sulfonic acid; and

   supplying an external source of electrons to electrolytically deposit the chromium-based layer onto the surface of the substrate.

2. The process of claim 1 wherein the halogen oxoanion is an alkali metal salt or alkaline earth metal salt of the halogen oxoanion, and the composition has an initial concentration of halogen oxoanion between about 0.001 M and about 0.1 M.

3. The process of claim 2 wherein the salt of the halogen oxoanion is selected from the group consisting of an iodate salt, a periodate salt, a chlorate salt, a chlorite salt, a perchlorate salt, a hypochlorite salt, a bromate salt, and combinations thereof, and the composition has an initial concentration of halogen oxoanion between about 0.001 M and about 0.1 M.

4. The process of claim 1 wherein:

   the source of chromium ions is selected from the group consisting of chromium(VI) oxide; chromate (CrO₄²⁻) salts of sodium, potassium, and ammonium; dichromate (Cr₂O₇²⁻) salts of sodium, potassium, and ammonium; and combinations thereof; and the composition has an initial concentration of chromium ions between about 0.5 M and about 5 M;

   the source of halogen oxoanion is a salt selected from the group consisting of an iodate salt, a periodate salt, a chlorate salt, a chlorite salt, a perchlorate salt, a hypochlorite salt, a bromate salt, and combinations thereof; and the composition has an initial concentration of halogen oxoanion between about 0.001 M and about 0.1 M;

   the source of alkylsulfonic acid is selected from the group consisting of methanesulfonic acid, methanedisulfonic acid, ethylsulfonic acid, propylsulfonic acid, salts thereof, and combinations thereof; and the composition has an initial concentration of the alkylsulfonic acid of between about 0.01 and 0.1 M;

   the composition has an initial concentration of sulfonic acid in the range of about 0.03 and about 0.3 M; and

   the composition has a pH of less than 1.

5. The process of claim 1 wherein:

   the source of chromium ions is selected from the group consisting of chromium(VI) oxide; chromate (CrO₄²⁻) salts of sodium, potassium, and ammonium; dichromate (Cr₂O₇²⁻) salts of sodium, potassium, and ammonium; and combinations thereof; and the composition has an initial concentration of chromium ions between about 2 M and about 3 M;

   the source of halogen oxoanion is a salt selected from the group consisting of an iodate salt, a periodate salt, a chlorate salt, a chlorite salt, a perchlorate salt, a hypochlorite salt, a bromate salt, and combinations thereof; and the composition has an initial concentration of halogen oxoanion between about 0.007 M and about 0.03 M;

   the source of alkylsulfonic acid is selected from the group consisting of methanesulfonic acid, methanedisulfonic acid, ethylsulfonic acid, propylsulfonic acid, salts thereof, and combinations thereof; and the composition has an initial concentration of the alkylsulfonic acid of between about 0.01 and 0.1 M; and

   the composition has a pH of less than 1.
acid, ethylsulfonic acid, propylsulfonic acid, salts thereof, and combinations thereof, and the composition has an initial concentration of the alkylsulfonic acid of between about 0.02 and 0.04 M; and the composition has an initial concentration of sulfocetic acid in the range of about 0.06 and about 0.12 M; and the composition has a pH of less than 1.

6. The process of claim 1 wherein the external source of electrons provides a current density between about 20 A/dm² and about 150 A/dm².

7. The process of claim 1 wherein the electrolytic plating composition has a temperature between about 20° C. and about 90° C.

8. The process of claim 1 wherein the chromium-based layer has a hardness of more than 800 HV 0.1.

9. The process of claim 1 wherein the chromium-based layer has a corrosion resistance of greater than 200 hours when tested according to DIN 50021 SS.

10. An electrolytic plating composition for electrolytically coating a surface of a substrate with a chromium layer or a chromium alloy layer, the composition comprising:
    a source of chromium ions;
    a mineral acid;
    a source of halogen oxoanion;
    a source of alkylsulfonic acid; and
    a source of sulfocetic acid selected from the group consisting of sulfocetic acid, a sulfocetate salt, a sulfocetate ester, a sulfocetate anhydride, and a reactant which generates sulfocetic acid.

11. The electrolytic plating composition of claim 10 wherein the source of chromium ions is selected from the group consisting of chromium(VI) oxide; chromate (CrO₄²⁻) salts of sodium, potassium, and ammonium; dichromate (Cr₂O₇²⁻) salts of sodium, potassium, and ammonium; and combinations thereof.

12. The electrolytic plating composition of claim 10 wherein the source of chromium ions has an initial concentration of chromium ions between about 1M and about 4M.

13. The electrolytic plating composition of claim 10 wherein the source of chromium ions is added to yield an initial concentration of chromium ions between about 2 M and about 3 M.

14. The electrolytic plating composition of claim 10 wherein the composition has an initial pH less than about 1.

15. The electrolytic plating composition of claim 10 wherein the source of halogen oxoanion is an alkali metal salt or alkaline earth metal salt of the halogen oxoanion.

16. The electrolytic plating composition of claim 15 wherein the salt is selected from the group consisting of an iodate salt, a periodate salt, a chlorate salt, a chloride salt, a perchlorate salt, a hypochlorite salt, a bromate salt, and combinations thereof.

17. The electrolytic plating composition of claim 16 having an initial concentration of halogen oxoanion between about 0.001 M and about 0.1 M.

18. The electrolytic plating composition of claim 16 having an initial concentration of halogen oxoanion between about 0.005 M and about 0.08 M.

19. The electrolytic plating composition of claim 16 having an initial concentration of halogen oxoanion between about 0.007 M and about 0.03 M.

20. The electrolytic plating composition of claim 10 wherein the source of alkylsulfonic acid is selected from the group consisting of methanesulfonic acid, methanedisulfonic acid, ethylsulfonic acid, propylsulfonic acid, salts thereof, and combinations thereof.

21. The electrolytic plating composition of claim 20 wherein the source of alkylsulfonic acid is added in an initial concentration between about 0.015 M and about 0.06 M.

22. The electrolytic plating composition of claim 20 having an initial concentration of sulfocetic acid between about 0.03 M and about 0.3 M.