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(54) **CYANIDE-FREE ELECTROPLATING BATHS FOR WHITE BRONZE BASED ON COPPER (I) IONS**

(57) Copper alloy electroplating baths include one or more sources of copper (I) ions and one or more sources of tin ions to electroplate copper/tin alloys of mirror bright white bronze. The copper alloys may also include one or

more sources of silver ions to electroplate ternary alloys of bright white bronze containing copper/tin/silver. The copper alloy electroplating baths are cyanide-free.

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Description

Field of the Invention

[0001] The present invention is directed to cyanide-free electroplating baths for white bronze based on copper (I) ions. More specifically, the present invention is directed to cyanide-free electroplating baths for white bronze based on copper (I) ions which are stable and electroplate bright white bronze deposits.

Background of the Invention

[0002] White bronze is commonly used in decorative and sanitary industries as material for nickel replacement. In general, bronze is 40% to 70% by weight copper with the remainder tin or tin and silver or tin and zinc. It is hard enough, provides adequate wear and corrosion resistance such that it may be substituted for nickel in both decorative and sanitary functions. Presently, most industrial white bronze is not only toxic due to cyanide content but also has a relatively slow plating speed of 0.1 ASD to around 2 ASD with a low current efficiency ranging from 50% to 80%.

[0003] U.S. 7,780,839 to Egli et al. is a cyanide-free white bronze which may be used as an alternative to conventional cyanide containing white bronze electroplating baths. Although the plating speed of this electrolyte is significantly improved over many conventional white bronze electroplating baths, the white bronze deposit may be slightly brittle and unable to pass abrasion tests. It may also be difficult to plate finishing top layers such as gold, chrome (III) or (VI), palladium or silver on white bronze. In top coating of articles for decorative and sanitary applications, the general process involves degreasing the article using a conventional degreasing formulation, rinsing with water followed by a thick copper plate for leveling purposes and then electroplating white bronze from a cyanide containing bath, rinsing with water, then plating a gold, chrome (III) or (VI), palladium or silver finish on the white bronze. When a cyanide-free white bronze electroplating bath is used as in U.S. 7,780,839, an extra step is typically needed prior to plating the finishing layer. An organic film of unknown composition may form on the white bronze after electroplating diminishing the surface appearance of the white bronze. An ultrasonic rinse or cathodic degreasing step is then included in the process to remove the film prior to plating the finishing layer. This extra step reduces the efficiency and increases the cost of the overall process because ultrasonic equipment must be installed or in the case of cathodic degreasing separate tanks with current suppliers is needed. Accordingly, there is still a need for an improved white bronze electroplating bath and process.

Summary of the Invention

[0004] An electroplating bath includes one or more sources of copper (I) ions, one or more sources of alloying tin ions, optionally one or more sources of alloying silver ions, one or more compounds having a formula:



wherein X and Y may be the same or different and may be substituted or unsubstituted phenol groups, HO-R- or -R'S-R"-OH wherein R, R' and R" may be the same or different and are linear or branched alkylene radicals having 1 to 20 carbon atoms; and one or more tetrazoles wherein a mole ratio of the one or more tetrazoles to the copper (I) ions in the electroplating bath is ≥ 1 and a mole ratio of the one or more tetrazoles to the one or more compounds of formula (I) is 0.05 to 4, the electroplating bath is cyanide-free.

[0005] A method of electroplating includes contacting a substrate with an electroplating bath comprising one or more sources of copper (I) ions, one or more sources of alloying tin ions, optionally one or more sources of alloying silver ions, one or more compounds having a formula:



wherein X and Y may be the same or different and may be substituted or unsubstituted phenol group, HO-R- or -R'S-R"-OH wherein R, R' and R" may be the same or different and may be linear or branched alkylene radicals having 1 to 20 carbon atoms; and one or more tetrazoles, wherein a mole ratio of the one or more tetrazoles to the copper (I) ions in the electroplating bath is ≥ 1 and a mole ratio of the one or more tetrazoles to the one or more compounds of formula (I) is 0.05 to 4, the electroplating bath is cyanide-free; and electroplating a copper/tin alloy or a copper/tin/silver alloy on the substrate.

[0006] The cyanide-free copper alloy electroplating baths deposit a bright, white bronze copper/tin alloy or copper/tin/silver alloy. The copper alloy electroplating baths are stable over prolonged periods of time and deposit copper/tin alloys and copper/tin/silver alloys with high current efficiencies and high plating speeds in contrast to many conventional copper alloy baths which electroplate white bronze. The copper/tin alloys and copper/tin/silver alloys electroplated from the

baths have good ductility, thermal stability and abrasion resistance. The copper/alloys may be directly plated with gold, chrome (III) or (VI), palladium and silver finishing layers without many of the conventional post-treatment steps of conventional processes such as ultrasonic rinse or cathodic degreasing. Therefore, the cyanide-free copper alloy electroplating bath enables more efficient processes than many conventional cyanide-free white bronze processes and may be used for nickel replacement.

Brief Description of the Drawings

[0007]

Figure 1 is a graph of % Current Efficiency v. Bath Age of a cyanide-free copper/tin/silver alloy electroplating bath. Figure 2 is a photograph of a chrome layer over a white bronze deposit electroplated from a cyanide-free copper (I) containing electroplating bath after one month at room temperature.

Figure 3 is a photograph of a chrome layer over a cyanide-free white bronze deposit electroplated from a copper (II) containing electroplating bath after one month at room temperature.

Detailed Description of the Invention

[0008] As used throughout the specification, the following abbreviations have the following meanings, unless the context clearly indicates otherwise: °C = degrees Centigrade; g = gram; cm = centimeters; mL = milliliter; L = liter; mg = milligrams; ppm = parts per million = mg/L; DI = de-ionized; μm = microns; mol = mole; wt% = percent by weight; A = amps; A/dm^2 and ASD = amps per square decimeter; Ah = ampere hours; %CE = percent current efficiency; rpm = revolutions per minute; IEC = International Electrochemical Commission; XRF = X-ray fluorescence; and ASTM = American standard testing method. Electroplating potentials are provided with respect to a hydrogen reference electrode. Relating to the electroplating process, the terms "depositing", "coating", "electroplating" and "plating" are used interchangeably throughout this specification. "Halide" refers to fluoride, chloride, bromide and iodide. All percentages are by weight, unless otherwise noted. All numerical ranges are inclusive and combinable in any order, except where it is logical that such numerical ranges are construed to add up to 100%.

[0009] The copper (I), silver, tin, and copper (I) and tin alloy electroplating baths are substantially free of cyanide. Cyanide is primarily avoided by not employing any silver or tin salts or other compounds in the baths which include the CN^- anion. The copper (I), silver, tin and copper (I) and tin alloy electroplating baths are also substantially free of copper (II) ions to enable the copper alloy electroplating baths to plate a bright white bronze deposit.

[0010] Sources of copper (I) ions include, but are not limited to cuprous salts such as cuprous oxide, cuprous chloride, cuprous bromide, cuprous iodide and cuprous ammonium salts such as cuprous ammonium chloride. The copper (I) salts are generally commercially available or may be prepared by methods described in the literature. When cuprous oxide is used, alkane or aryl sulfonic acids or mixtures thereof are preferably included in the bath. Sufficient amounts of one or more copper (I) salts are included in the baths such that the amount of copper (I) ions may range from 0.5 g/L to 150 g/L, preferably 10 g/L to 50 g/L.

[0011] Sources of tin ions include, but are not limited to salts, such as tin halides, tin sulfates, tin alkane sulfonates, tin alkanol sulfonates, and acids. When tin halide is used, it is typical that the halide is chloride. The tin compound is preferably tin sulfate, tin chloride or a tin alkane sulfonate, and more preferably tin sulfate or tin methane sulfonate. The tin compounds are generally commercially available or may be prepared by methods known in the literature. Preferably the tin salts are readily water-soluble. The amount of tin salts used in the bath depends on the desired composition of the alloy to be deposited and operating conditions. Sufficient amounts of tin salts are included in the baths to provide tin ions which may range from 1 g/L to 100 g/L, preferably from 5 g/L to 50 g/L.

[0012] Sources of silver ions include, but are not limited to silver halides, silver gluconate, silver citrate, silver lactate, silver nitrate, silver sulfates, silver alkane sulfonates and silver alkanol sulfonates. When a silver halide is used, it is preferable that the halide is chloride. Preferably the silver salts are silver sulfate, a silver alkane sulfonate or mixtures thereof. The silver salts are generally commercially available or may be prepared by methods described in the literature. Preferably the silver salts are readily water-soluble. The amounts of the one or more silver salts used in the baths depend, for example, on the desired alloy composition to be deposited and operating conditions. Sufficient amounts of silver salts are included in the baths to provide silver ions which may range from 0.01 g/L to 100 g/L, preferably from 0.5 g/L to 50 g/L.

[0013] The copper (I) alloy electroplating baths include one or more sulfur compounds having formula:

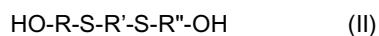


where X and Y may be substituted or unsubstituted phenol groups, HO-R- or -R'-S-R"-OH where R, R' and R" are the same or different and are linear or branched alkylene radicals having 1 to 20 carbon atoms. Substituent groups on the

phenol include, but are not limited to linear or branched (C₁-C₅)alkyl. Such compounds may function as complexing agents for copper (I) ions.

[0014] Examples of such compounds where X and Y are the same are 4,4'-thiodiphenol, 4,4'-thiobis(2-methyl-6-tert-butylphenol) and thiodiethanol.

[0015] When X and Y are different, the compounds preferably have the following general formula:



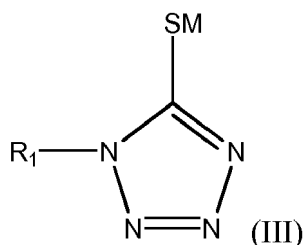
wherein R, R' and R'' are the same or different and are linear or branched alkylene radicals having from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, more preferably R and R'' have 2 to 10 carbon atoms and R' has 2 carbon atoms. Such compounds are known as dihydroxy bis-sulfide compounds. Preferably the dihydroxy bis-sulfide compounds are included in the alloy baths over the phenol containing compounds.

[0016] Examples of such dihydroxy bis-sulfide compounds are 2,4-dithia-1,5-pentanediol, 2,5-dithia-1,6-hexanediol, 2,6-dithia-1,7-heptanediol, 2,7-dithia-1,8-octanediol, 2,8-dithia-1,9-nonanediol, 2,9-dithia-1,10-decanediol, 2,11-dithia-1,12-dodecanediol, 5,8-dithia-1,12-dodecanediol, 2,15-dithia-1,16-hexadecanediol, 2,21-dithia-1,22-doeicasanediol, 3,5-dithia-1,7-heptanediol, 3,6-dithia-1,8-octanediol, 3,8-dithia-1,10-decanediol, 3,10-dithia-1,8-dodecanediol, 3,13-dithia-1,15-pentadecanediol, 3,18-dithia-1,20-eicosanediol, 4,6-dithia-1,9-nonanediol, 4,7-dithia-1,10-decanediol, 4,11-dithia-1,14-tetradecanediol, 4,15-dithia-1,18-octadecanediol, 4,19-dithia-1,22-dodeicosanediol, 5,7-dithia-1,11-undecanediol, 5,9-dithia-1,13-tridecanediol, 5,13-dithia-1,17-heptadecanediol, 5,17-dithia-1,21-uneicosanediol and 1,8-dimethyl-3,6-dithia-1,8-octanediol.

[0017] The copper (I) alloy baths also include one or more tetrazoles as complexing agents for the copper (I) ions. Such tetrazoles are heterocyclic nitrogen compounds having five membered rings and at least one sulfur substituent on the ring. While not being bound by theory, the tetrazoles along with the compounds of formula (I) and (II) inhibit the copper (I) ions from oxidizing to copper (II) ions and stabilize the bath. Inhibiting of the oxidation of the copper (I) ions to copper (II) ions assists in enabling the formation of a copper/tin/silver or copper/tin alloy. Tetrazoles are included in the bath such that the mole ratio of the tetrazoles to the copper (I) ions in the bath are ≥ 1 , preferably > 1 , more preferably > 1 to 10, even more preferably > 1 to 6 and most preferably 1.1 to 4. In general, the amount of tetrazoles included in the bath may range from 0.5 g/L to 500 g/L.

[0018] Compounds of formula (I) and (II) are included in the baths such that the mole ratio of the one or more tetrazoles to the compounds of formula (I) or (II) is from 0.05-4, preferably from 0.1-3.

[0019] Preferably the tetrazoles are mercaptotetrazole compounds having the following formula:



where M is hydrogen, NH₄, sodium or potassium and R₁ is substituted or unsubstituted, linear or branched (C₂-C₂₀)alkyl, substituted or unsubstituted (C₆-C₁₀)aryl, preferably substituted or unsubstituted, linear or branched (C₂-C₁₀)alkyl and substituted or unsubstituted (C₆)aryl, more preferably substituted or unsubstituted, linear or branched (C₂-C₁₀)alkyl. Substituents include, but are not limited to alkoxy, phenoxy, halogen, nitro, amino, substituted amino, sulfo, sulfamyl, substituted sulfamyl, sulfonylphenyl, sulfonyl-alkyl, fluorosulfonyl, sulfoamidophenyl, sulfonamide-alkyl, carboxy, carboxylate, ureido carbamyl, carbamyl-phenyl, carbamylalkyl, carbonylalkyl and carbonylphenyl. Preferred substituents include amino and substituted amino groups. Examples of mercaptotetrazoles are 1-(2-diethylaminoethyl)-5-mercapto-1,2,3,4-tetrazole, 1-(3-ureidophenyl)-5-mercaptotetrazole, 1-((3-N-ethyl oxalamido)phenyl)-5-mercaptotetrazole, 1-(4-acetamidophenyl)-5-mercapto-tetrazole and 1-(4-carboxyphenyl)-5-mercaptotetrazole.

[0020] The combination of one or more tetrazoles with compounds of formulae (I) or (II) provides stability to the alloy baths during storage or during electroplating as well as stable alloy compositions over the applicable current density range such that hard bright copper/tin/silver or copper/tin alloys may be deposited as a replacement for nickel in decorative or sanitary articles.

[0021] Any aqueous soluble acid which does not otherwise adversely affect the bath may be used. Suitable acids include, but are not limited to, arylsulfonic acids, alkanesulfonic acids, such as methanesulfonic acid, ethanesulfonic acid and propanesulfonic acid, aryl sulfonic acids such as phenylsulfonic acid and tolylsulfonic acid, and inorganic acids such as sulfuric acid, sulfamic acid, hydrochloric acid, hydrobromic acid and fluoroboric acid. Typically, the acids are

alkane sulfonic acids and aryl sulfonic acids. Although a mixture of acids may be used, it is typical that a single acid is used. The acids are generally commercially available or may be prepared by methods known in the literature.

[0022] While depending on the desired alloy composition and operating conditions, the amount of acid in the plating compositions may be in the range of 0.01 to 500 g/L or such as from 10 to 400 g/L. When the silver ions and tin ions are from metal halides, use of the corresponding acid may be desired. For example, when one or more of tin chloride or silver chloride are used, use of hydrochloric acid as the acid component may be desired. Mixtures of acids also may be used.

[0023] Optionally, one or more suppressors may be included in the baths. Typically they are used in amounts of 0.5 to 15 g/L or such as from 1 to 10 g/L. Such suppressors include, but are not limited to alkanol amines, polyethyleneimines and alkoxyated aromatic alcohols. Suitable alkanol amines include, but are not limited to, substituted or unsubstituted methoxylated, ethoxylated, and propoxylated amines, for example, tetra (2-hydroxypropyl)ethylenediamine, 2-[[2-(dimethylamino)ethyl]-methylamino]ethanol, N,N'-bis(2-hydroxyethyl)-ethylenediamine, 2-(2-aminoethyl-amine)-ethanol, and combinations thereof.

[0024] Suitable polyethyleneimines include, but are not limited to, substituted or unsubstituted linear or branched chain polyethyleneimines or mixtures thereof having a molecular weight of from 800-750,000. Suitable substituents include, for example, carboxyalkyl, for example, carboxymethyl, carboxyethyl.

[0025] Useful alkoxyated aromatic alcohols include, but are not limited to ethoxylated bis phenol, ethoxylated phenol, ethoxylated beta naphthol, and ethoxylated nonyl phenol.

[0026] Optionally one or more reducing agents can be added to the baths to assist in keeping the tin in a soluble, divalent state. Suitable reducing agents include, but are not limited to hydroquinone, hydroquinone sulfonic acid, potassium salt and hydroxylated aromatic compounds, such as resorcinol and catechol. Such reducing agents when used in the compositions are present in an amount of 0.01 to 20 g/L or such as from 0.1 to 5 g/L.

[0027] For applications requiring good wetting capabilities, one or more conventional surfactants may be included in the baths. Surfactants include, but are not limited to ethylene oxide and/or propylene oxide derivatives of aliphatic alcohols containing one or more alkyl group or ethylene oxide and or propylene oxide derivatives of aromatic alcohols. The aliphatic alcohols may be saturated or unsaturated. Such aliphatic and aromatic alcohols may be further substituted, for example, with sulfate or sulfonate groups. Surfactants may be included in conventional amounts. In general, surfactants may be included in amounts of 0.1 g/L to 50 g/L.

[0028] Other optional compounds may be added to the baths to provide further grain refinement. Such compounds include, but are not limited to alkoxyates, such as the polyethoxylated amines JEFFAMINE T-403 or TRITON RW, or sulfated alkyl ethoxyates, such as TRITON QS-15, and gelatin or gelatin derivatives. Alkoxyated amine oxides also may be included. Conventional amounts of such grain refiners may be used. Typically they are included in the baths in amounts of 0.5 g/l to 20 g/L.

[0029] Other grain refiners include, but are not limited to phenanthroline compounds such as 1,10-phenanthroline monohydrate, bismuth salts such as bismuth nitrate, bismuth acetate, bismuth tartrate and bismuth alkane sulfonates. Indium salts such as indium chloride, indium sulfate and indium alkane sulfonates. Antimony salts such as antimony lactate, antimony potassium tartrate. Selenium and tellurium may be added as dioxides. Iron salts such ferric bromide and anhydrous ferric chloride. Cobalt salts such as cobaltous nitrate, cobaltous bromide and chloride. Zinc salts such as zinc lactate and zinc nitrate. Chromium salts such as chromous chloride and chromous formate. Such grain refiners are included in conventional amounts. In general such grain refiners are included in amounts of 5ppm to 1000 ppm.

[0030] The electroplating baths are typically prepared by adding to a vessel one or more of the acids, one or more of the compounds of formula (I) and one or more tetrazoles followed by one or more of the solution soluble copper (I), silver and tin compounds, one or more optional additives, and the balance water. Preferably the compounds of formula (II) and the tetrazoles are added to the vessel followed by copper (I) compounds and acid before silver and tin compounds. Once the aqueous bath is prepared, undesired material can be removed, such as by filtration and then water is typically added to adjust the final volume of the bath. The bath may be agitated by any known means, such as stirring, pumping, or recirculating, for increased plating speed. The baths are acidic having a pH of less than 7, preferably less than 3.

[0031] Current density used to plate the copper alloys depends on the particular plating method. Generally, the current density is 0.01 ASD or more, preferably from 0.1 ASD to 10 ASD, more preferably from 1 ASD to 6 ASD.

[0032] The copper/tin/silver and copper/tin alloys may be electroplated at room temperature to 60° C, preferably from 30° C to 50° C. More preferably electroplating is done at temperatures of 30° C to 45° C.

[0033] The baths may be used to deposit copper/tin/silver and copper/tin alloys of various compositions. In general, the copper content of the copper/tin/silver alloys ranges from 40% to 60% by weight with tin in amounts of 15% to 50% by weight with the remainder silver. The copper content of the copper/tin alloys ranges from 40% to 70% by weight with the remainder tin. Such weights are based on measurements taken by either atomic adsorption spectroscopy ("AAS"), X-ray fluorescence ("XRF"), inductively coupled plasma ("ICP") or differential scanning calorimetry ("DSC").

[0034] In addition to providing a bright white bronze deposit, the copper alloys also accept finishing layers of gold, silver, palladium and chromium. After the white bronze is plated on a substrate, a finishing layer of gold, silver, palladium

or chromium (III) or (VI) may be directly plated on the bright white bronze without any preparatory or other intervening steps such as ultrasonic rinse or cathodic degreasing. Conventional gold, silver, palladium or chromium plating baths may be used along with conventional plating parameters. Such finishing layers may range in thickness of 0.05 μm to 10 μm .

[0035] The copper alloy electroplating baths are stable over prolonged periods of time and deposit copper/tin alloys and copper/tin/silver alloys with high current efficiencies and high plating speeds in contrast to many conventional copper alloy baths which electroplate white bronze. Current efficiencies range from 90% to as high as 100% with a mean value of 95%. The copper/tin alloys and copper/tin/silver alloys electroplated from the baths have good ductility, thermal stability and abrasion resistance. The copper/alloys may be directly plated with gold, chrome (III) or (VI), palladium and silver finishing layers without many of the conventional post-treatment steps of conventional processes such as ultrasonic rinse or cathodic degreasing. Therefore, the cyanide-free copper alloy electroplating baths enable a more efficient process than many conventional cyanide-free white bronze processes and are suitable for nickel replacement such as for decorative and sanitary articles.

[0036] The following examples are intended to further illustrate the invention, but are not intended to limit the scope of the invention.

Example 1

Ternary White Bronze of Copper/Tin/Silver

[0037] The following aqueous acid white bronze electroplating bath was prepared:

Table 1

COMPOUND	CONCENTRATION (g/L)
Copper (I) ions as copper oxide	30
Tin (II) ions as tin methane sulfonate	12
Silver (I) ions as silver methane sulfonate	5
1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole	96
3,6-dithia-1,8-octanediol	75
Methane sulfonic acid (70%)	150 g/L
Antimony as potassium antimony tartrate	0.16
Nonionic phenol ethoxylate ¹	0.8
Hydroquinone monosulfonic acid	1 g/L
¹ Adeka Tol PC-8: non-ionic surfactant, available from Adeka Corporation.	

[0038] The pH of the bath was less than 1 as measured using a KNICK Instruments conventional laboratory pH meter. The molar mass of the tetrazole compound, 3,6-dithia-1,8-octanediol and copper (I) ions was 173.24, 182.30 and 63.55 g/mol, respectively. The mole ratio of the tetrazole to the copper (I) ions in the bath was 1.2:1 and the mole ratio of the tetrazole to the 3,6-dithia-1,8-octanediol was 1.3:1.

[0039] A brass panel having dimensions 10 x 7.5 x 0.025 cm was degreased cathodically at 4 ASD for 1 minute by using RONACLEAN™ DLF cleaner solution (available from Dow Electronic Materials) and activated by immersing the substrate for 20 seconds in RONASALT™ 369 solution (available from Dow electronic Materials). The panel was then placed in a Hull cell containing 250 mL of the white bronze bath. A platinized titanium electrode was used as anode material. The working bath temperature ranged from 35° C to 45° C with optimum panel brightness at around 40° C over a broad current density range. The panel was electroplated with the white bronze bath at 0.5 A for 5 minutes. After the electroplating was complete the panels were removed from the plating cells and rinsed with DI water. The deposit on the panel was bright at all of the following current densities of the Hull cell test: 0.05 ASD, 0.2 ASD, 0.5 ASD, 0.73 ASD, 1 ASD, 2 ASD and 2.5 ASD.

[0040] Two brass panels having the above dimensions were placed in a plating bath containing 2 liters of the white bronze bath in Table 1 with two bronze anodes. A current density of 1 ASD was applied to one panel for 15 minutes and 2 ASD was applied to the second panel for 10 minutes. The thickness of the white bronze on each panel was 10 μm . The plating was done until a bath life of 15 Ah/L was reached. Throughout electroplating there was no observable

decomposition of bath components, observable abnormal precipitation or loss of plating performance. After the electroplating was complete the panels were removed from the plating cells, rinsed with DI water and their appearance was observed with the naked eye. All of the panels appeared bright. The plating baths of this example were still stable after idling for a month.

Example 2

Binary White Bronze of Copper/Tin

[0041] The following aqueous acid white bronze electroplating bath was prepared:

Table 2

COMPOUND	CONCENTRATION (g/L)
Copper (I) ions as copper oxide	14
Tin (II) ions as tin methane sulfonate	8
1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole	42
Thiodiethanol	80
Hydroquinone monosulfonic acid	1.6 g/L
Methane sulfonic acid (70%)	90 g/L
Bismuth methane sulfonate	0.02
1,10-Phenanthroline mono hydrate	0.01
Nonionic phenol ethoxylate ²	0.8
² Adeka Tol PC-8: non-ionic surfactant, available from Adeka Corporation.	

[0042] The pH of the bath was less than 1 as measured using a KNICK Instruments conventional laboratory pH meter. The mole ratio of the tetrazole to the copper (I) ions in the bath was 1.1:1 and the mole ratio of the tetrazole to the thiodiethanol was 0.4:1.

[0043] A brass panel having dimensions 10 x 7.5 x 0.025 cm was degreased cathodically at 4 ASD for 1 minute using RONACLEAN™ DLF solution and activated by immersing the substrate for 20 seconds in RONASALT™ 369 solution. The panel was then placed in a Hull cell containing 250 mL of the white bronze bath. A platinized titanium electrode was used as anode material. The working bath temperature ranged from 30° C to 40° C with an optimum at around 35° C. The panel was electroplated with the white bronze bath at 0.5 A for 5 minutes. The baths appeared stable throughout electroplating and the deposits appeared bright at the following current densities of the Hull cell test: 0.05 ASD, 0.2 ASD, 0.5 ASD, 0.73 ASD, 1 ASD, 2 ASD and 2.5 ASD.

[0044] Two brass panels having the above dimensions were placed in a plating bath containing 2 liters of the white bronze bath in Table 2 with two bronze anodes. A current density of 1 ASD was applied to one panel for 15 minutes and 2 ASD was applied to the second panel for 10 minutes. The thickness of the white bronze on each panel was 10 μm. The plating was until a bath life of 15 Ah/L was reached. Throughout electroplating there was no observable decomposition of bath components, observable abnormal precipitation or loss of plating performance. After the electroplating was complete the panels were removed from the plating cells, rinsed with DI water and their appearance was observed with the naked eye. All of the panels appeared bright. The plating baths of this example were still stable after idling for a month.

Example 3

Tetrazole/3,6-Dithia-1,8-Octanediol Mole Ratio in a Copper/Tin/silver Electroplating Bath

[0045] The white bronze copper/tin/silver alloy electroplating bath was prepared as described in Example 1 with the exception that the amount of 3,6-dithia-1,8-octanediol was varied as shown in Table 3 below. The mole ratio of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole to 3,6-dithia-1,8-octanediol was as shown in Table 3.

[0046] A plurality of brass panels having dimensions 10 x 7.5 x 0.025 cm was degreased and activated as described in Example 1 above. Each panel was then placed in separate Hull cells containing 250 mL of the white bronze bath. The pH of the bath was less than 1. A platinized titanium or bronze electrode was used as anode material. The working bath

temperature ranged from 35° C to 45° C. The panels were electroplated with the white bronze bath at 1 A for 3 minutes. Throughout electroplating all of the baths appeared stable.

[0047] After electroplating the panels were removed from the Hull cells, rinsed with DI water and their appearance was observed with the naked eye. As disclosed in Table 3 below, the copper/tin/silver electroplating bath which did not include the combination of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole and 3,6-dithia-1,8-octanediol all showed undesirable matte deposits at all of the current densities.

Table 3

Octanediol (g/L)	Mole Ratio	Deposit Appearance at 0.1 ASD	Deposit Appearance at 1 ASD	Deposit Appearance at 3 ASD	Deposit Appearance at 5 ASD
0	-----	Matte	Matte	Matte	Matte
30	3.35	Bright	Bright	Matte	Matte
50	2	Bright	Bright	Bright	Matte
70	1.43	Bright	Bright	Bright	Bright
90	1.11	Bright	Bright	Bright	Bright
110	0.91	Bright	Bright	Bright	Bright

[0048] Although there were panels plated with the formulation which included the combination of the tetrazole and the octanediol which had matte deposits in some of the higher current densities, the majority of the deposits were bright.

Example 4

Tetrazole/Thiodiethanol Mole Ratio in a Copper/Tin Electroplating Bath

[0049] The white bronze copper/tin alloy electroplating bath was prepared as described in Example 2 with the exception that the amount of thiodiethanol was varied as shown in Table 4 below. The mole ratio of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole to thiodiethanol was as shown in Table 4.

[0050] A plurality of brass panels having dimensions 10 x 7.5 x 0.025 cm was degreased and activated as described in Example 2. Each panel was then placed in separate Hull cells containing 250 mL of the white bronze bath. A platinized titanium or bronze electrode was used as anode material. The working bath temperature ranged from 30° C to 40° C. The panels were electroplated with the white bronze bath at 1 A for 3 minutes. Throughout electroplating all of the baths appeared stable.

[0051] After electroplating the panels were removed from the Hull cells, rinsed with DI water and their appearance was observed with the naked eye. As disclosed in Table 4 below, the copper/tin electroplating bath which did not include the combination of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole and thiodiethanol showed undesirable matte deposits at all of the current densities. While the panel that was electroplated with the bath which included the combination of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole and thiodiethanol at a mole ratio of 2.96 had bright deposits at the lower current density ranges, and the bath which had the mole ratio of 1.14 had bright deposits at the higher current densities, the baths which had mole ratios below 1.14 had significant bright deposits at all of the current densities.

Table 4

Thio-diethanol (g/L)	Mole Ratio	Deposit Appearance at 0.1 ASD	Deposit Appearance at 1 ASD	Deposit Appearance at 2 ASD	Deposit Appearance at 3 ASD	Deposit Appearance at 5 ASD
0	-----	Matte	Matte	Matte	Matte	Matte
10	2.96	Bright	Bright	Matte	Matte	Matte
26	1.14	Matte	Matte	Matte	Bright	Bright
38	0.78	light Matte	light Matte	Bright	Bright	Bright

(continued)

Thio-diethanol (g/L)	Mole Ratio	Deposit Appearance at 0.1 ASD	Deposit Appearance at 1 ASD	Deposit Appearance at 2 ASD	Deposit Appearance at 3 ASD	Deposit Appearance at 5 ASD
61	0.49	Bright	Bright with small Matte line	Bright	Bright	Bright
90	0.33	Bright	Bright	Bright	Bright	Bright with small Matte line
120	0.25	Bright	Bright	Bright	Bright	Bright with small Matte line
150	0.2	Bright	Bright	Bright	Bright	Bright with small Matte line

Example 5 (Comparative)

Copper (II) Bronze Formulations

[0052] Three copper (II) bronze electroplating baths were prepared as shown in Table 5 below.

Table 5

Component	Comparative Bath 1 (g/L)	Comparative Bath 2 (g/L)	Comparative Bath 3 (g/L)
Copper (II) ions as copper methane sulfonate	14	10	14
Tin (II) ions as tin methane sulfonate	10	12	8
Methane sulfonic acid (70%)	90 g/L	90 g/L	90 g/L
1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole	6	12	42
Thiodiethanol	5	20	80
Phenanthroline	0.01	0	0.01
Hydroquinone monosulfonic acid	2 g/L	2g/L	1.6 g/L
Bismuth methane sulfonate	0	0	0.02
Nonionic phenol ethoxylate ³	0.6	0.6	0.8
³ Adeka Tol PC-8: non-ionic surfactant, available from Adeka Corporation.			

[0053] The mole ratio of 1-(2-dimethylamino-ethyl)-5-mercapto-1,2,3,4-tetrazole to copper (II) ions was 0.15:1 in Comparative Bath 1, was 0.4:1 in Comparative Bath 2 and 1.1:1 in Comparative Bath 3.

[0054] A plurality of brass panels having dimensions 10 x 7.5 x 0.025 cm was degreased and activated. Each panel was then placed in separate Hull cells containing 250 mL of one of the three copper/tin electroplating baths. The pH of the baths was less than 1. A platinized titanium or bronze electrode was used as anode material. The working baths were maintained at 35° C during plating. The panels were electroplated with the copper/tin bronze baths at 1 A for 3 minutes. After the panels were electroplated they were rinsed with deionized water and observed with the naked eye for their appearance. The results for each bath are shown in Table 5a.

Table 5a

Comparative Bath	Mole Ratio of Tetrazole:Thiodiethanol	0.05 ASD Deposit	0.5 ASD Deposit	1 ASD Deposit	2 ASD Deposit	4 ASD Deposit
1	0.84	Bright	Bright	Bright	Bright	Bright
2	0.42	Bright	Bright	Bright	Bright	Bright
3	0.37	Very thin Yellow bronze	Very thin Yellow bronze	Thin Yellow bronze	Thin Yellow bronze	Thin Yellow bronze

[0055] While Comparative Baths 1 and 2 had good bright deposits for all current densities, Comparative Bath 3 had undesirable yellow bronze deposits due to greater than 70% copper content and a very low current efficiency of less than 30% as indicated by a thin deposit.

[0056] Comparative Baths 1 and 2 were allowed to idle 24 hours. A new set of panels were then electroplated with the Comparative Baths 1 and 2. Because of the poor results obtained from Comparative Bath 3, its plating performance was not tested for performance after 24 hours idling time. The results of Comparative Baths 1 and 2 are shown in Table 5b.

Table 5b

Comparative Bath	Mole Ratio of Tetrazole:Thiodiethanol	0.05 ASD Deposit	0.5 ASD Deposit	1 ASD Deposit	2 ASD Deposit	4 ASD Deposit
1	0.84	Bright	Matte	Matte	Matte	Matte
2	0.42	Matte	Matte	Matte	Matte	Matte

[0057] The matte bronze deposits plated after the 24 hour idling time indicated that the baths were unstable. By adding additional amounts of tin (II) ions in amounts of half the original concentration to the baths, the brightness was re-established; however, the tin (II) rapidly oxidized to tin (IV) as indicated by the orange color of the baths.

Example 6

Hull Cell Test for Alloy Composition of Copper/Tin/Silver

[0058] A steel panel 10 x 7.5 x 0.025 cm was immersed for one minute in 40% hydrochloric acid solution to remove the protective zinc layer on its surface. The panel was degreased anodically at 3 ASD for one minute in RONACLEAN™ DLF cleaning solution. The panel was activated by immersion in RONASALT™ 369 solution, rinsed with DI water and placed in a Hull cell containing 250 ml of a white bronze bath as described in Example 1 above. A platinized titanium electrode was used as an anode. The mole ratio of the tetrazole to the copper (I) ions in the bath was 1.2:1 and the mole ratio of the tetrazole to the 3,6-dithia-1,8-octandiol was 1.3:1.

[0059] The alloy composition was measured on steel Hull cells plated at a current of 0.5 A for 5 minutes at different current densities as shown in Table 6 below. Metal content was measured by XRF using a FISCHERSCOPE X-Ray model XDV-SD from Helmut Fischer AG. This measurement was repeated on three different steel panels coated with the white bronze. The average metal content at each current density is shown in Table 6.

Table 6

Metal	0.05 ASD	0.1 ASD	0.5 ASD	1 ASD	1.5 ASD	2 ASD	2.5 ASD
% Copper	50	49	48	48	48	48	49
% Tin	34	36	38	40	41	42	43
% Silver	16	15	14	12	11	10	8

All of the alloys had a bright appearance upon observation with the naked eye.

Example 7

Plating Speed of Copper (I) Copper/Tin/silver Alloy Electroplating Bath vs. Copper (II)

Copper/Tin Alloy Electroplating Bath

[0060] One liter of the white bronze bath of Example 1 was introduced in a glass cell. Two platinized titanium anodes were placed in the cell. A steel cylindrical ring of 12 mm in diameter and 7 mm high was mounted on a rotating axis of an electrical motor. The rotation speed of the axis was fixed at 1000 rpm. The axis was immersed in the bath and electrical contact established between the electrodes. The current density was varied and the plating speeds were measured for a new electroplating bath as well as the same electroplating bath at different bath ages as shown in Table 7a. At each current density, the thickness of the bronze coating was measured by using XRF. The plating rate was calculated at each current density as the thickness in microns of white bronze plated divided by the plating time in minutes. The results in microns per minute are displayed in the table.

Table 7a

Bath Age	0.05 ASD	0.25 ASD	0.5 ASD	1 ASD	1.5 ASD	2 ASD	2.5 ASD
0 Ah/L	0.1	0.2	0.4	0.6	0.9	1.1	1.3
5 Ah/L	0.1	0.2	0.4	0.6	0.8	1.1	1.3
10 Ah/L	0.1	0.2	0.3	0.6	0.8	1	1.2
15 Ah/L	0.1	0.2	0.4	0.6	0.8	1	1.3

[0061] As indicated by the results in Table 7a the plating speed increased with the increase in the current density and remained substantially the same at each current density regardless of the age of the bath. This indicated that the electroplating bath was stable and its performance was reliable as it aged. There was no need to dispose of the original electroplating bath and use a new bath to complete the plating process.

[0062] The process was repeated at bath ages of 0 Ah/L and 10 Ah/L with the copper (II) Comparative Bath in Table 7b below. The results are in Table 7c.

Table 7b

COMPONENT	AMOUNT
Tin (II) ions as tin sulfate	5 g/L
Copper (II) ions as copper sulfate	5 g/L
Sulfuric acid (50% v/v)	180 ml/L
Hydro quinone	1.5 g/L
Benzylidene acetone	0.01 g/L
Methacrylic acid	0.5 g/L
Imidazole/epichlorohydrin polymer ³	0.5 ml/L
Ethylene oxide/propylene oxide copolymer ⁴	5 g/L
1-(2-Dimethylethylamino)-5-mercapto-1,2,3,4-tetrazole	2 g/L
S,S-ethylenediamine-disuccinic acid (EDDS)	100 g/L
³ LUGALVAN® IZE (available from BASF)	
⁴ PLURONIC® PE 6400 (available from BASF)	

Table 7c

Bath Age	0.05 ASD	0.25 ASD	0.5 ASD	1 ASD	1.5 ASD	2 ASD	2.5 ASD
0 Ah/L	---	0.16	0.3	0.42	0.6	0.69	0.75

(continued)

Bath Age	0.05 ASD	0.25 ASD	0.5 ASD	1 ASD	1.5 ASD	2 ASD	2.5 ASD
10 Ah/L	---	0.17	0.3	0.4	0.57	0.7	0.76

[0063] The plating speed was substantially stable with the bath age; however, the speed at most of the current densities was lower compared to the results in Table 7a. This showed that the current efficiency in the copper (II) Comparative Bath was lower than the bath of Example 1.

Example 8

Current Efficiency of Copper/Tin/Silver Alloy Bath

[0064] The current efficiency of the white bronze electroplating bath of Example 1 was estimated as the experimental mass of the deposit divided by the theoretical mass all multiplied by 100. The experimental mass was determined by measuring the weight difference of a brass panel 5 x 7.5 x 0.025 cm before and after white bronze plating. The theoretical mass of the deposit was calculated based on the Faraday law and by taking into consideration the alloy composition. This method is described in "Frederick Adolph Lowenheim, Electroplating (1978) page 377; Library of Congress Cataloging, McGraw-Hill Book Company: ISBN 0-07-038836-9".

[0065] The current efficiency was determined at a high current density of 2 ASD over a bath age of 0 Ah/L to 15 Ah/L. Multiple estimations were made over the life of the bath as shown in the graph of Figure 1 of % CE v. Bath age. The current efficiency ranged from 90% to 100% with an average of about 95%. Values above 100% were due to possible experimental error. The sustained high and stable current efficiency over the life of the bath indicated a very stable electroplating bath where undesired hydrogen evolution was insignificant.

Example 9

Ductility Measurement of White Bronze from a Copper (I) Copper/Tin/Silver Bath v. Copper (II) Copper/Tin Bath

[0066] Three brass panels 2 x 10 x 0.025 cm were electroplated with the white bronze electroplating bath of Example 1 and another three were electroplated with the copper (II) copper/tin bronze alloy bath of Table 8 below. Two liters of each bronze bath were added into separate electrochemical cells. Two white bronze anodes were also placed in the cells. An electric current density of 1 ASD was applied between the anodes and the brass cathodes for 5 minutes to plate a 3 μ m thick layer on each brass panel. The plating time was 7 minutes for the formulation in Table 8. The deposits appeared bright.

Table 8

COMPONENT	AMOUNT
Tin (II) ions as tin sulfate	5 g/L
Copper (II) ions as copper sulfate	5 g/L
Sulfuric acid (50% v/v)	180 ml/L
Hydro quinone	1.5 g/L
Benzylidene acetone	0.01 g/L
Methacrylic acid	0.5 g/L
Imidazole/epichlorohydrin polymer	0.5 ml/L
Ethylene oxide/propylene oxide copolymer ⁴	5 g/L
1-(2-Dimethylethylamino)-5-mercapto-1,2,3,4-tetrazole	2 g/L
S,S-ethylenediamine-disuccinic acid (EDDS)	100 g/L
³ LUGALVAN® IZE (available from BASF)	
⁴ PLURONIC® PE 6400 (available from BASF)	

[0067] The ductility of each plated brass panel was tested using a Bend-tester from SHEEN INSTRUMENTS Ltd. according to ASTM standard B 489-85. The average ductility for each set of three panels was determined. The average ductility for the white bronze of the bath from Example 1 was 1.2 % elongation. Above this value cracks were observed in the deposit. Cracks were observed at an elongation of 0.8% for the deposits from the formulation in Table 8. 0.8% is the lower scale for the ductility test when using the above instrument. The test was repeated except that the amount of white bronze electroplated on the brass panels was 6 μm . The average elongation for the bath from Example 1 was again 1.2% and cracks were observed at 0.8% from the sample plated from the bath of Table 8. The white bronze deposit from Example 1 showed improved ductility in contrast to the bath from Table 8.

Example 10

Thermal Stability of White Bronze

[0068] Six brass panels 2 x 10 x 0.025 cm were electroplated with the white bronze electroplating bath of Example 1 and another three were electroplated with the copper (II) copper/tin bronze alloy bath of Table 8 from Example 9. Two liters of each bronze bath were added into separate electrochemical cells. Two white bronze anodes were also placed in the cells. An electric current density of 1 ASD was applied between the anodes and the brass cathodes for 4 minutes to plate a 3 μm thick layer on each brass panel. Two panels plated with the bath containing the formulation of Example 1 and two panels plated with the formulation of Table 8 were introduced in a conventional laboratory oven from BINDER™ Inc. for 24 hours at 150 °C. The remaining plated brass panels were not annealed and kept at room temperature as controls. After 24 hours the brass panels were removed from the oven and visually examined along with the panels which were not annealed. The panels plated with the white bronze bath from Example 1 and those that were left at room temperature were bright; however, the panels that were plated with the bath from Table 8 and annealed had an undesired blue appearance.

[0069] The test was repeated at 200 °C for 2 hours. The panels electroplated with the white bronze bath of Example 1 were once again bright as well as the control panels. In contrast, the panels that were electroplated with the bath from Table 8 and annealed had an intensive dark color. The white bronze electroplated from the bath of Example 1 showed improved heat resistance over the conventional bath of Table 8.

Example 11

Top Layer Deposition on White Bronze of Copper/Tin/Silver Alloy

[0070] Three brass panels 2 x 10 x 0.025 cm were electroplated with the white bronze electroplating bath of Example 1 and another three were electroplated with the copper (II) copper/tin bronze alloy bath of Example 9. Two liters of each bronze bath were added into separate electrochemical cells. Two white bronze anodes were also placed in the cells. An electric current density of 1 ASD was applied between the anodes and the brass cathodes for 5 minutes to plate a 3 μm thick layer on each brass panel. The deposits appeared bright.

[0071] RONAFLASH™ P pure gold electroplating bath, available from Dow Electronic Materials, was placed in a separate electrochemical cell. The white bronze plated brass panels were rinsed with DI water and introduced in the gold bath. The panels were then electroplated with the gold without any further surface treatment or preparation before gold plating. A current density of 1 ASD was applied for 40 seconds between the bronze coated brass panels and platinized titanium anode. The panels were removed, rinsed with DI water and dried with pressurized air. All of the deposits had a shiny gold color appearance. The panels were kept at room temperature in the open air for one month. The samples plated with the bath of Example 1 were still shiny. In contrast, the panels which were electroplated with the bath of Example 9 appeared stained with several dull areas present on the surface.

[0072] The process described above was repeated except instead of plating pure gold on the panels the panels were plated with chrome using CHROME GLEAM™ 3C chrome (III) electroplating bath available from Dow electronic Materials. The current density was 10 ASD and plating was done for 3 minutes. A shiny chrome color was deposited on the white bronze of each panel. The panels were exposed to the open air at room temperature for one month. No stains were observed on the panels which included the white bronze plated from the formulation of Example 1. Figure 2 is a photograph taken with an OLYMPUS BX60M optical microscope of one of the panels. The chrome deposit was unstained. In contrast, the panels which were plated with the bath from Example 9 all had unsightly stains. Figure 3 is a photograph of one of the panels which was plated with the bath from Example 9 taken with the OLYMPUS BX60M optical microscope. Severe surface staining of the chrome deposit is apparent. The panels electroplated with the white bronze bath of Example 1 showed significant improvement in the ability to resist staining in contrast to the conventional bronze bath.

Claims

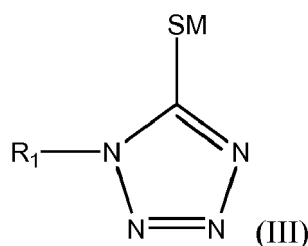
1. An electroplating bath comprising one or more sources of copper (I) ions, one or more sources of alloying tin ions, optionally one or more sources of alloying silver ions, one or more compounds having a formula:



wherein X and Y may be the same or different and may be substituted or unsubstituted phenol groups, HO-R- or -R'S-R"-OH wherein R, R' and R" may be the same or different and are linear or branched alkylene radicals having 1 to 20 carbon atoms; and one or more tetrazoles wherein a mole ratio of the one or more tetrazoles to the copper (I) ions in the electroplating bath is ≥ 1 and a mole ratio of the one or more tetrazoles to the one or more compounds of formula (I) is 0.05 to 4, the electroplating bath is cyanide-free.

2. The electroplating bath of claim 1, wherein X and Y are different and are HO-R- or -R'S-R"-OH, and R, R' and R" may be the same or different.

3. The electroplating bath of claim 1, wherein the one or more tetrazoles have a formula:



wherein M is hydrogen, NH₄, sodium or potassium and R₁ is substituted or unsubstituted, linear or branched (C₂-C₂₀)alkyl, or substituted or unsubstituted (C₆-C₁₀)aryl.

4. A method of electroplating comprising:

a) contacting a substrate with an electroplating bath comprising one or more sources of copper (I) ions, one or more sources of alloying tin ions, optionally one or more sources of alloying silver ions, one or more compounds having a formula:

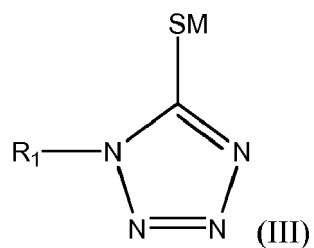


wherein X and Y may be the same or different and may be substituted or unsubstituted phenol group, HO-R- or -R'S-R"-OH wherein R, R' and R" may be the same or different and may be linear or branched alkylene radicals having 1 to 20 carbon atoms; and one or more tetrazoles, wherein a mole ratio of the one or more tetrazoles to the copper (I) ions in the electroplating bath is ≥ 1 and a mole ratio of the one or more tetrazoles to the one or more compounds of formula (I) is 0.05 to 4, the electroplating bath is cyanide-free; and

b) electroplating a copper/tin alloy or optionally a copper/tin/silver alloy on the substrate.

5. The method of claim 4, wherein X and Y are different and are HO-R- or -R'S-R"-OH, and R, R' and R" may be the same or different.

6. The method of claim 4, wherein the one or more tetrazoles have a formula:



wherein M is hydrogen, NH₄, sodium or potassium and R₁ is substituted or unsubstituted, linear or branched (C₂-C₂₀)alkyl, or substituted or unsubstituted (C₆-C₁₀)aryl.

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7. The method of claim 4, further comprising electroplating a finishing layer of silver, gold, palladium or chromium on the copper/tin alloy or the copper/tin/silver alloy.

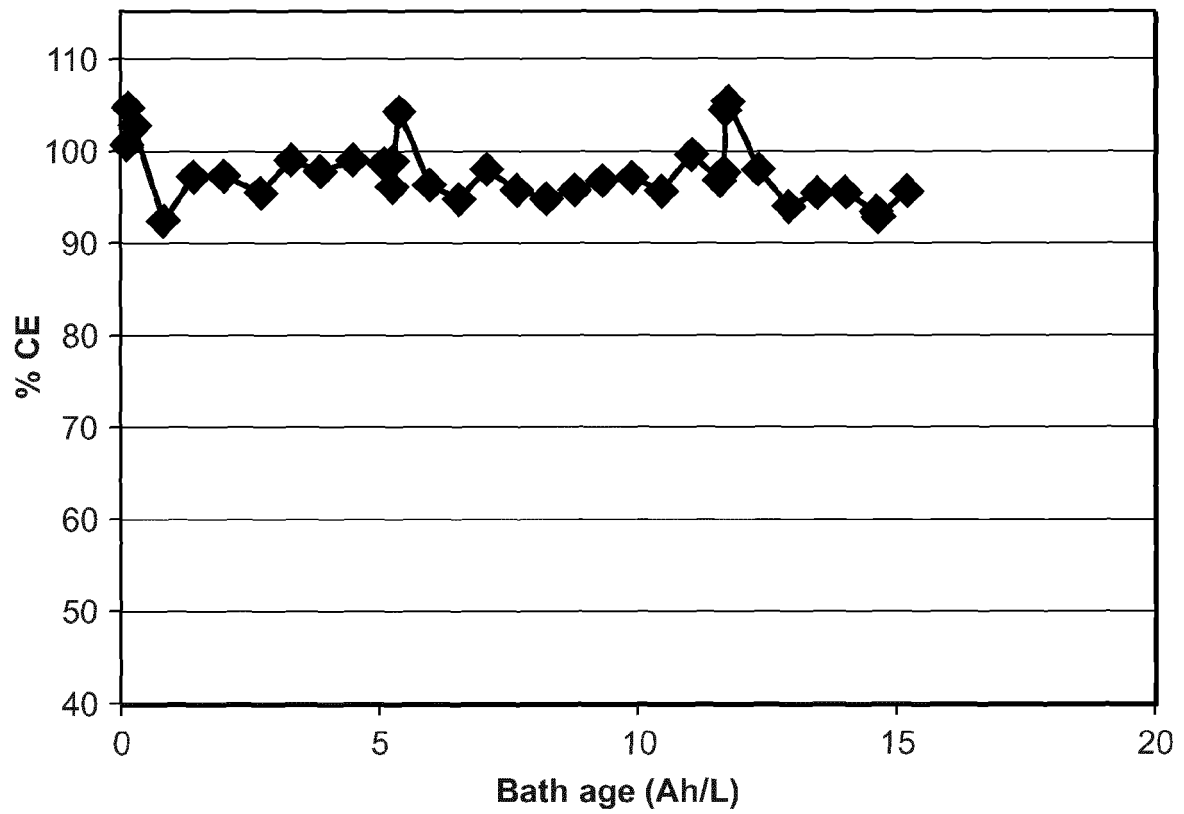


FIG. 1

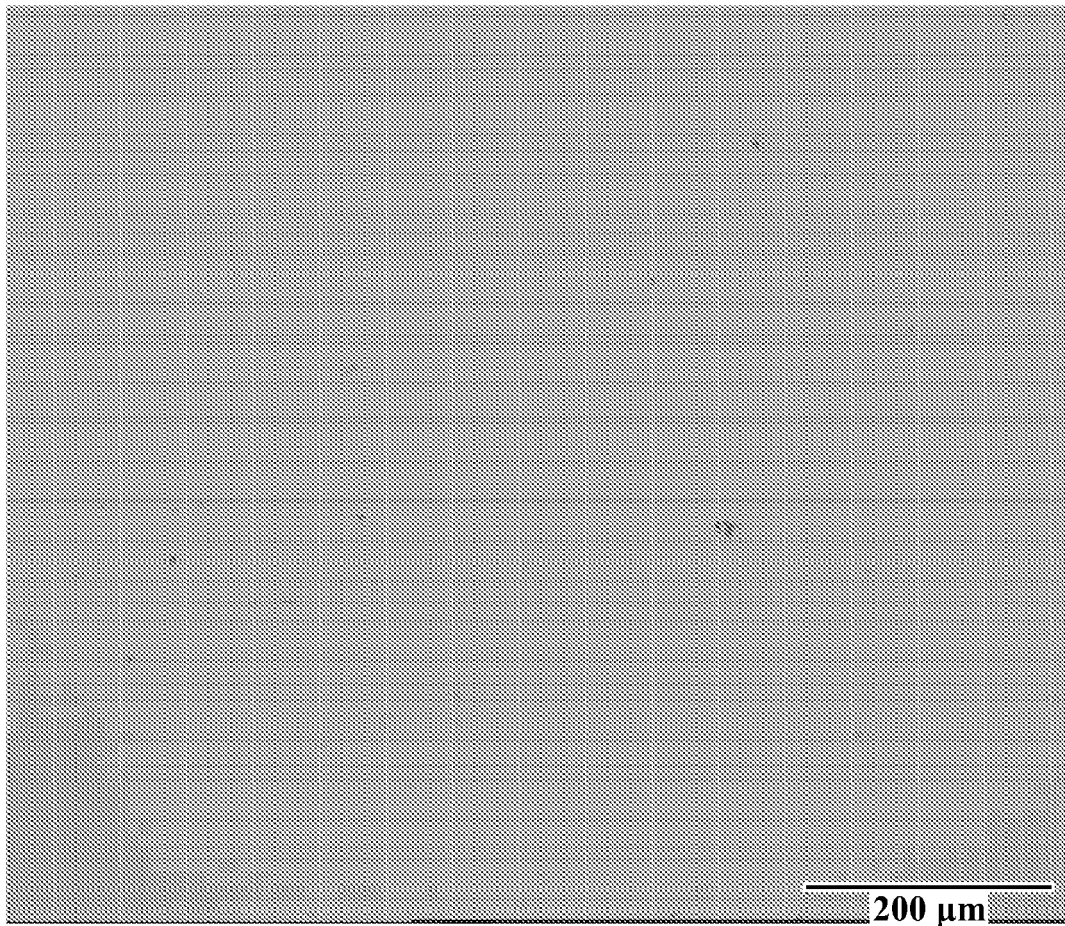


FIG. 2

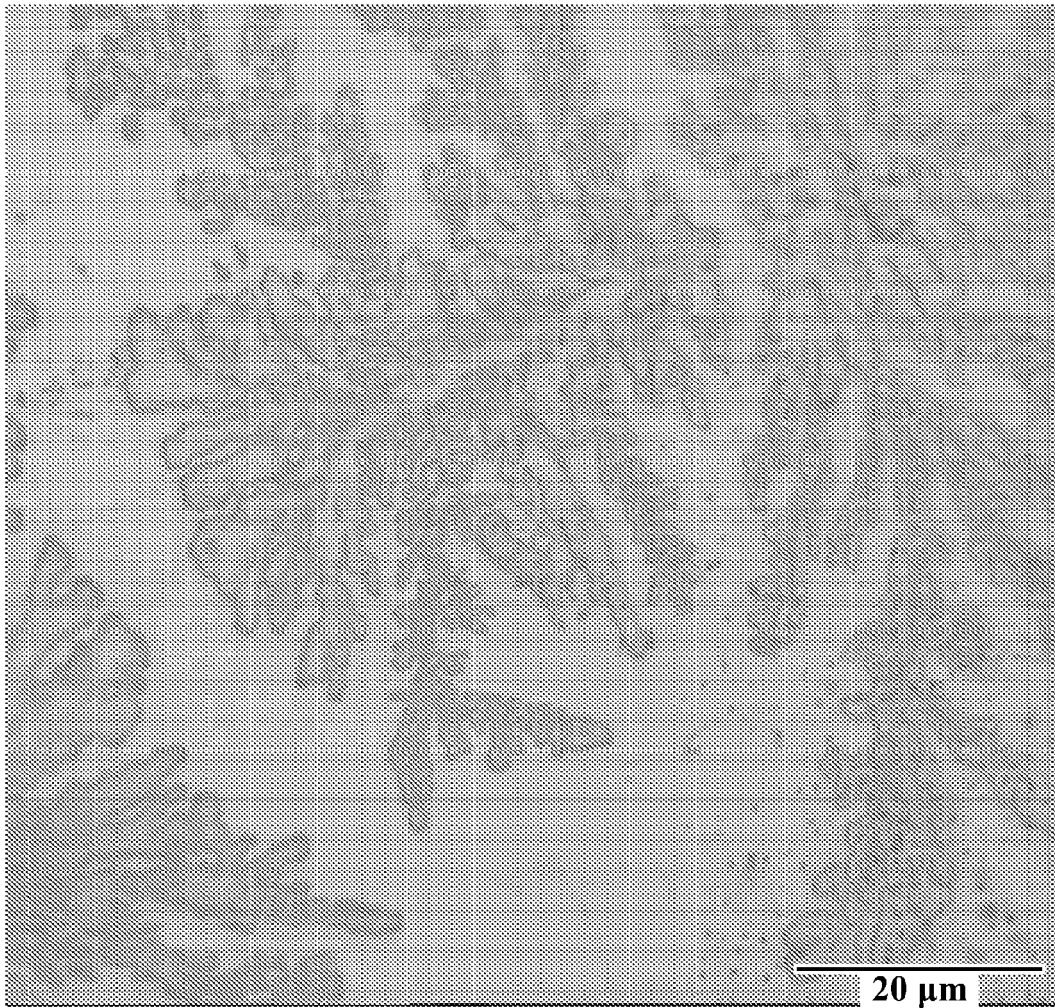


FIG. 3



EUROPEAN SEARCH REPORT

Application Number
EP 15 18 5289

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Place of search The Hague		Date of completion of the search 12 February 2016	Examiner Lange, Ronny
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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