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# (54) TIN ALLOY ELECTROPLATING BATH AND PLATING METHOD USING SAME

(57) A tin alloy electroplating bath, wherein the tin alloy electroplating bath includes (A) a soluble tin salt, (B) a soluble nickel salt and/or a soluble cobalt salt, (C) an oxycarboxylic acid or a salt thereof, (D) a nitrogen-containing heterocyclic unsaturated compound, and (E) a surfactant, and the pH of the tin alloy electroplating bath is 3 to 7.

EP 3 842 572 A1

## Description

### Technical Field

**[0001]** The present invention relates to a tin alloy electroplating bath and a plating method using the same.

### Background Art

**[0002]** Electroplating of tin alloys such as tin-nickel and tin-cobalt has been used in the fields such as tin alloy electroplated coatings for soldering electronic parts and chip-type ceramic electronic parts.

**[0003]** Various types of baths such as a fluoride bath, a pyrophosphoric acid bath, and an organic acid bath have been conventionally developed as baths for plating of a tin-nickel alloy or a tin-cobalt alloy by means of electrolysis. In a situation where the fluoride bath is used, work environment is poor and deterioration of facilities is significant because fluorides are discharge regulated substances and are hazardous. In the pyrophosphoric acid bath (Japanese Patent Application Publication No. S60-29482), a supply source of tin is tetravalent ions due to an alkaline PH, and the deposition rate of the pyrophosphoric acid bath is 50% lower than that of an acidic to neutral bath in which the supply source is divalent ions. Moreover, the pyrophosphoric acid bath has a working current density range of about 1 A/dm$^2$ at maximum and thus has poor productivity. As the organic acid bath, there has been developed, for example, an acidic tin-cobalt alloy electroplating bath (Japanese Patent Application Publication No. 2006-9039) containing methanesulfonic acid. As an neutral bath of an organic acid bath, a tin-nickel alloy electroplating bath (Japanese Patent Application Publication No. 2013-44001) having a pH of 4.0 and containing phenanthrolinedione as a burning prevention agent and as an essential component has been developed. Since phenanthrolinedione exhibits its effects in a very trace amount, management of the bath is difficult. Moreover, a tin-cobalt alloy electroplating bath (Japanese Patent Application Publication No. H09-241885) with a pH of 6.5 to 10 that uses a stannate alkali substance and that essentially includes one of ethylenediamine and amino carboxylic acid has been also developed. The essential components of this bath are a stannate alkali substance and one of ethylenediamine and amino carboxylic acid whose bath management is industrially difficult.

**[0004]** In the case of such tin alloy electroplating, for example, a high-speed electroplating apparatus is used. In such an apparatus, a plating bath needs to allow deposition of a coating with a desired alloy ratio in a wide range of current density corresponding to demanded high speed. The deposited coating needs to be even, have excellent adhesion to a base material, and have a desired external appearance. Moreover, the plating bath needs to be stable against oxidation due to agitation and air contact, and the like and has to maintain clearness and absence of turbidity.

**[0005]** However, in conventionally known tin alloy electroplating baths, particularly in tin alloy electroplating baths with high Sn ratios, these properties are not satisfactory and there is a demand for further improvements.

### Summary of Invention

**[0006]** An object of the present invention is to provide tin-nickel and tin-cobalt alloy electroplating baths and a plating method using the same which allow deposition of a coating with a desired alloy ratio and in which a deposited coating has excellent adhesion to a base material and an even external appearance and a plating solution is stable against oxidation due to agitation and air contact, and the like and can maintain clearness and absence of turbidity.

**[0007]** As a result of earnest studies, the present inventors found that a tin alloy electroplating bath solving the aforementioned problems can be obtained when the tin alloy electroplating bath uses an oxycarboxylic acid or a salt thereof as a complexing agent and contains a nitrogen-containing unsaturated heterocyclic compound and a surfactant. Specifically, the present invention provides a tin alloy electroplating bath comprising: (A) a soluble tin salt; (B) at least one of soluble nickel salts and soluble cobalt salts; (C) an oxycarboxylic acid or a salt thereof; (D) a nitrogen-containing unsaturated heterocyclic compound; and (E) a surfactant, wherein a pH of the tin alloy electroplating bath is 3 to 7.

**[0008]** Moreover, the present invention provides a method of electroplating an object with a tin alloy, comprising applying a DC current or a pulse current at a current density of 1 to 30 A/dm$^2$ to the object in the tin alloy electroplating bath.

**[0009]** The tin alloy electroplating baths of the present invention are tin-nickel and tin-cobalt alloy electroplating baths: which allow deposition of a coating with a desired alloy ratio; in which a deposited coating has excellent adhesion to a base material and an even external appearance and a plating solution is stable against oxidation due to agitation and air contact, and the like and can maintain clearness and absence of turbidity; which is mild acidic or neutral with a pH of 3 to 7; and which use no glossing agent such as an amine compound or an amino carboxylic acid compound and enable easy bath management.

Description of Embodiment

**[0010]** A tin alloy electroplating bath of the present invention includes (A) a soluble tin salt, (B) at least one of soluble nickel salts and soluble cobalt salts, (C) an oxycarboxylic acid or a salt thereof, (D) a nitrogen-containing unsaturated heterocyclic compound, and (E) a surfactant.

**[0011]** (A) The soluble tin salt is basically an organic or inorganic tin salt that generates $Sn^{2+}$ in water and specifically includes, for example, salts of organic sulfonic acids such as methanesulfonic acid and 2-propanolsulfonate, tin pyrophosphate, tin sulfamate, stannous sulfate, stannous oxide, stannous chloride, stannous fluoborate, and the like. Among these substances, the inorganic tin salts are preferable.

**[0012]** One of the aforementioned soluble tin salts may be used alone or two or more of the soluble tin salts may be used in combination.

**[0013]** The concentration of tin ions in the tin alloy electroplating bath is preferably 1 to 100 g/L, more preferably 5 to 80 g/L, and even more preferably 30 to 80 g/L in total.

**[0014]** (B) The soluble nickel salts are organic or inorganic nickel salts and specifically include, for example, nickel chloride, nickel nitrate, nickel sulfate, nickel bromide, nickel hypophosphite, nickel phosphate, nickel ammonium chloride, nickel ammonium sulfate, potassium nickel sulfate, nickel sulfamate, nickel acetate, nickel carbonate, nickel acetylacetonate, nickel formate, nickel iodide, nickel oxalate, nickel stearate, nickel citrate, nickel tartrate, nickel lactate, and the like. Among these substances, the inorganic nickel salts are preferable.

**[0015]** One of the aforementioned soluble nickel salt may be used alone or two or more of the soluble nickel salts may be used in combination.

**[0016]** The concentration of nickel ions in the tin alloy electroplating bath is preferably 0.05 to 20 g/L, and more preferably 0.1 to 10 g/L in total.

**[0017]** (B) The soluble cobalt salts are organic or inorganic cobalt salts and specifically include, for example, cobalt sulfate, cobalt chloride, cobalt nitrate, cobalt bromide, cobalt iodide, cobalt hypophosphite, cobalt phosphate, cobalt ammonium sulfate, cobalt ammonium chloride, potassium cobalt sulfate, cobalt sulfamate, cobalt acetate, cobalt carbonate, cobalt acetylacetonate, cobalt formate, cobalt oxalate, cobalt stearate, cobalt citrate, cobalt tartrate, cobalt lactate, and the like. Among these substances, the inorganic nickel salts are preferable.

**[0018]** One of the aforementioned soluble cobalt salt may be used alone or two or more of the soluble cobalt salts may be used in combination.

**[0019]** The concentration of cobalt ions in the tin alloy electroplating bath is preferably 0.05 to 20 g/L, and more preferably 0.1 to 10 g/L in total.

**[0020]** Moreover, the total concentration of the nickel ions and the cobalt ions contained in the tin alloy electroplating bath is preferably 0.05 to 20 g/L, and more preferably 0.1 to 10 g/L.

**[0021]** (C) The oxycarboxylic acid or the salt thereof is preferably an aliphatic oxycarboxylic acid, particularly an open-chain saturated aliphatic oxycarboxylic acid or a salt thereof. The oxycarboxylic acid specifically includes, for example, gluconic acid, tartaric acid, citric acid, glycolic acid, glucoheptonic acid, lactic acid, malic acid, and salicylic acid. The salt of the oxycarboxylic acid includes ammonium salts, alkali metal salts such as potassium salts and sodium salts, and similar salts of the aforementioned oxycarboxylic acids. In the present invention, one of the aforementioned oxycarboxylic acid and the salt thereof may be used alone or two or more of the aforementioned oxycarboxylic acids and the salts thereof may be used in combination.

**[0022]** The concentration of the oxycarboxylic acid and the salt thereof in the tin alloy electroplating bath is preferably 50 to 500 g/L, and more preferably 100 to 300 g/L in total. When the concentration of the oxycarboxylic acid and the salt thereof is too low, the tin ions become unstable and tin hydroxide tends to be formed. On the other hand, when the concentration of the oxycarboxylic acid and the salt thereof is too high, the oxycarboxylic acid and the salt thereof cannot dissolve into the tin alloy electroplating bath in some cases.

**[0023]** (D) The nitrogen-containing unsaturated heterocyclic compound is preferably a nitrogen-containing six-membered unsaturated heterocyclic compound or a nitrogen-containing five-membered unsaturated heterocyclic compound. Specific examples of the nitrogen-containing six-membered unsaturated heterocyclic compound are pyridines such as pyridine, picolinic acid, 2,2'-bipyridyl, 4-methoxypyridine, nicotinamide, 3-pyridinol, 2-mercaptopyridine, 3-acetoxypyridine, quinoline, isoquinoline, and acridine acid, derivatives of these pyridines, pyrazines such as pyrazine, pyridazine, pyrimidine, quinoxaline, pyrazinecarboxylic acid, 2-acetylpyrazine, quinazoline, derivatives of these pyrazines, and the like. The nitrogen-containing five-membered unsaturated heterocyclic compounds include pyrroles such as pyrrole and indole, derivatives of these pyrroles, imidazoles such as imidazole and pyrazole, derivatives of these imidazoles, triazole, derivatives of triazole, and the like. In the present invention, one of the aforementioned nitrogen-containing unsaturated heterocyclic compounds may be used alone or two or more of the nitrogen-containing unsaturated heterocyclic compounds may be used in combination.

**[0024]** The concentration of the nitrogen-containing unsaturated heterocyclic compound in the tin alloy electroplating bath is preferably 0.01 to 5 g/L, more preferably, 0.02 to 3 g/L, and most preferably 0.03 to 1 g/L in total.

**[0025]** As (E) the surfactant, various types of surfactants such as general anionic, cationic, nonionic, and amphoteric surfactants can be used for the purpose of improving the external appearance, denseness, smoothness, adhesion, and the like of a plated coating.

**[0026]** The anionic surfactants include alkyl sulfate, polyoxyethylene alkyl ether sulfate, polyoxyethylene alkyl phenyl ether sulfate, alkylbenzene sulfonete, alkylnaphthalene sulfonate, and the like. The cationic surfactants include mono- to tri-alkylamine salts, dimethyl dialkyl ammonium salt, trimethyl alkyl ammonium salt, and the like. The nonionic surfactants include condensation products obtained by adding 2 to 300 mols of ethylene oxide (EO) and/or propylene oxide (PO) to $C_1$ to $C_{20}$ alkanols, phenol, naphthol, bisphenols, $C_1$ to $C_{25}$ alkylphenols, arylalkylphenol, $C_1$ to $C_{25}$ alkylnaphthols, $C_1$ to $C_{25}$ alkoxyl phosphoric acids (salts), sorbitan ester, polyalkylene glycol, or $C_1$ to $C_{22}$ aliphatic amides, and the like. The amphoteric surfactants include carboxybetaine, imidazoline betaine, amino carboxylic acid, and the like. One of the aforementioned surfactants may be used alone or two or more of the surfactants may be used in combination.

**[0027]** In the present invention, the surfactant is preferably an amphoteric or nonionic surfactant, particularly, for example, an alkylamidobetaine type amphoteric surfactant such as coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine or, for example, a polyoxyethylene alkylamine type nonionic surfactant such as polyoxyethylene tallow alkylamine. The tin alloy electroplating bath containing any of these surfactants enables deposition of a fine alloy in a high-speed plating apparatus.

**[0028]** The concentration of the surfactant in the tin alloy electroplating bath is preferably 0.1 to 50 g/L, and more preferably 0.5 to 10 g/L in total. When the concentration of the surfactant is too low, an effect of deposition suppression cannot be achieved and a deposit cannot form a smooth coating. Meanwhile, when the concentration is too high, the deposition suppression effect is too high and a sufficient deposition amount cannot be achieved.

**[0029]** The tin alloy electroplating bath of the present invention may contain any of sulfuric acid, hydrochloric acid, sulfonic acid, sulfamic acid, pyrophosphoric acid, alkali metal salts (sodium, potassium, and lithium salts) of these acids, alkali earth metal salts (magnesium, calcium, and barium salts, and the like) of these acids, ammonium salts of these acids, organic amine salts (monomethylamine, dimethylamine, trimethylamine, ethylamine, isopropylamine, ethylenediamine, diethylenetriamine, and the like) of these acids, and the like to improve electric conductivity in plating. Specific components thereof include methanesulfonic acid, ammonium sulfate, ammonium chloride, sodium pyrophosphate, monomethyl sulfamate, and the like. The content of these compounds is 10 to 500 g/L, and preferably 30 to 400 g/L.

**[0030]** In addition to the components described above, other publicly-known additives such as, for example, a leveling agent and an anti-foaming agent may be added as necessary to the tin alloy electroplating bath of the present invention. Meanwhile, a brightener does not have to be added to the tin alloy electroplating bath of the present invention.

**[0031]** The aforementioned leveling agent includes peptone, gelatin, or the like. An amount of the leveling agent or the like used is 0.1 to 20 g/L, and preferably 0.5 to 10 g/L and even and fine plating can be obtained by the addition of the leveling agent.

**[0032]** The pH of the tin alloy electroplating bath in the present invention is 3 to 7, and preferably 4 to 6. In this pH range, the bath has good stability and the plated coating has excellent evenness. The pH may be adjusted by using inorganic acid such as sulfuric acid, hydrochloric acid, or acetic acid, hydroxide alkali such as sodium hydroxide, or the like as necessary. The remaining portion other than the aforementioned components in the tin alloy electroplating bath of the present invention is water.

**[0033]** An electroplating method of the present invention is performed by applying a current to an object in the tin alloy electroplating bath. A DC direct current or a pulse current can be used to perform the electroplating and the pulse current is particularly preferable. In the case of using the pulse current, a duty ratio (ON/OFF ratio) is preferably 0.1 to 0.9 and more preferably 0.5 to 0.8. Using the pulse current under conditions of ON time of 5 to 500 ms and OFF time of 5 to 500 ms is preferable because fine and smooth particles are electrically deposited. Bath temperature is generally within a range of 25 to 120 °C, and preferably in a range of 50 to 100°C. A current density is generally within a range of 0.1 to 30 $A/dm^2$, and preferably 1 to 20 $A/dm^2$. The electroplating may be performed by preferably using any of various types of publicly known high-speed plating apparatuses.

**[0034]** It is desirable to agitate the tin alloy electroplating bath and/or shake an object to be plated.

**[0035]** For example, use of jet flow, ultrasonic agitation, and the like enables an increase of the current density. Moreover, the object to be plated for which the electroplating method of the present is used is any of copper, iron, nickel, and alloys thereof. The present invention is particularly effective when a composite of a metal and an insulating material such as ceramic, crystal glass, plastic, or ferrite is used. In the electroplating method of the present invention, the object to be plated is used as a cathode. For example, any of conductive objects including, but not limited to, electronic parts such as a printed circuit board, a lead frame, a resistor, a capacitor, a thermistor, a LED, a crystal oscillator, and a lead line can be used as the cathode. Any of tin metal, zinc metal, copper metal, lead metal, bismuth metal, indium metal, and alloys of these metals is used as an anode. In some cases, an insoluble anode such as a titanium plate, a carbon plate, or the like plated with platinum may be used as the anode.

**[0036]** In the plating, the object to be plated is subjected to pretreatment in a normal method and then subjected to a plating step.

**[0037]** In the pretreatment step, at least one of operations of immersion degreasing, pickling, and electrolytic cleaning and activation of the anode is performed. Water washing is performed between the operations. After the plating, the obtained coating only needs to be simply washed and dried. Moreover, discoloration prevention treatment (immersion treatment into trisodium phosphate and the like) after tin plating or tin-alloy plating may be performed.

**[0038]** An alloy ratio of a tin alloy deposition coating obtained from the plating solution of the present invention by the electroplating method can be adjusted to any ratio. In a low-speed plating apparatus, Ni (Ni/(Sn+Ni)) or Co (Co/(Sn+Co)) in the deposition alloy is preferably within a range of 5 to 50 wt, more preferably 10 to 40 mass%, and most preferably 10 to 30 mass%. In a high-speed plating apparatus, Ni or Co in the deposition alloy is preferably within a range of 0.01 to 20 mass%, more preferably 0.02 to 10 mass%, even more preferably 0.03 to 7 mass%, and most preferably 0.05 to 3 mass%. The tin alloy electroplating bath of the present invention is particularly preferable in the case where a Sn-Ni or Sn-Co coating having a low alloy ratio in which the deposition ratio of Ni or Co is about 0.01 to 20 mass% is deposited at a desired alloy ratio by a high-speed plating apparatus.

**[0039]** Next, the present invention is described by demonstrating examples and comparative examples.

Examples

(Example 1)

[Plating Solution]

**[0040]** Ammonium citrate (150 g/L), ammonium sulfate (170 g/L), stannous sulfate (80 g/L), nickel sulfate hexahydrate (5 g/L), coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine (1.5 g/L), and picolinic acid (0.2 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 6.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a green external appearance.

[Plating Method]

**[0041]** A tough pitch copper flat plate with a size of 1.0 cm by 3.0 cm was subjected to cathode electrolytic degreasing (electrolytic degreasing-cleaning agent NC-20 manufactured by Dipsol Chemicals Co. Ltd. was used), washed with water, subjected to acid activation treatment (10% sulfuric acid), washed with water again, and then immersed in the aforementioned plating solution. Using the tough pitch copper flat plate as the cathode and a tin plate with a purity of 99.99% as the anode, a current was applied for 100 seconds at a current density of 15 $A/dm^2$ by using a DC power supply device at a liquid temperature of 50°C in an environment involving liquid flow and cathode shaking. The copper flat plate was immediately taken out after the current application and sufficiently washed with water and the water was then completely removed by air blowing.

[Result]

**[0042]** The obtained deposit was visually observed. The deposit had an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. After the observation of the external appearance, the deposit was put into a 100 mL beaker and 20 mL of 6 mol/L hydrochloric acid and 0.4 mL of 35% hydrogen peroxide solution were added thereto. The deposit was removed until the base copper was completely exposed. The obtained solution was diluted to an appropriate amount and concentrations of tin and nickel were measured by using an atomic absorption spectrophotometer (AA-6300 manufactured by Shimadzu Corporation) to check deposition amounts. A co-deposition ratio of nickel was calculated by using a formula of nickel deposition amount ÷ (tin deposition amount + nickel deposition amount) and the deposit was confirmed to contain 1.55 mass% of nickel. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 2)

[Plating Solution]

**[0043]** Ammonium citrate (150 g/L), ammonium sulfate (170 g/L), stannous sulfate (80 g/L), nickel sulfate hexahydrate (5 g/L), coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine (1.5 g/L), polyoxyethylene tallow alkylamine (0.5 g/L), and picolinic acid (0.1 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 6.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a green external ap-

pearance.

[Plating Method]

**[0044]** The same operations as those in Example 1 were performed except that the power supply device was changed to a pulse power supply. The ON time and OFF time of the pulse power supply were set to 0.4 seconds and 0.1 seconds, respectively, to achieve a duty ratio of 0.8.

[Result]

**[0045]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and the deposit was confirmed to contain 2.40 mass% of nickel. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 3)

[Plating Solution]

**[0046]** Ammonium citrate (150 g/L), ammonium sulfate (170 g/L), stannous sulfate (80 g/L), cobalt sulfate heptahydrate (15 g/L), coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine (1.5 g/L), polyoxyethylene tallow alkylamine (0.5 g/L), and picolinic acid (0.1 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 6.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a purple external appearance.

[Plating Method]

**[0047]** The same operations as those in Example 1 were performed except that the current density was changed to 5 $A/dm^2$.

[Result]

**[0048]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. A co-deposition ratio of cobalt was checked in the same procedure as in Example 1 except that the nickel in Example 1 was changed to cobalt. The deposit was confirmed to contain 1.07 mass% of cobalt. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 4)

[Plating Solution]

**[0049]** Ammonium citrate (150 g/L), ammonium sulfate (170 g/L), stannous sulfate (80 g/L), cobalt sulfate heptahydrate (15 g/L), coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine (1.5 g/L), polyoxyethylene tallow alkylamine (0.5 g/L), and picolinic acid (0.1 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 6.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a purple external appearance.

[Plating Method]

**[0050]** The same operations as those in Example 1 were performed except that the current density was changed to 10 $A/dm^2$ and the power supply device was changed to a pulse power supply. The ON time and OFF time of the pulse power supply were set to 0.4 seconds and 0.1 seconds, respectively, to achieve a duty ratio of 0.8.

[Result]

**[0051]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. A co-deposition ratio of cobalt was checked in the same procedure as in Example 1 except that the nickel in Example 1 was changed to cobalt. The deposit was confirmed to contain 1.46 mass% of cobalt. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 5)

[Plating Solution]

**[0052]** Gluconic acid (190 g/L), methanesulfonic acid (350 g/L), stannous oxide (62 g/L), nickel chloride hexahydrate (10 g/L), polyoxyethylene bisphenol A ether (1.0 g/L), and pyrazine (0.2 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 5.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a yellowish green external appearance.

[Plating Method]

**[0053]** The same operations as those in Example 1 were performed except that the current density was changed 1 to 10 $A/dm^2$.

[Result]

**[0054]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and the deposit was confirmed to contain 0.40 mass% of nickel. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 6)

[Plating Solution]

**[0055]** Gluconic acid (190 g/L), methanesulfonic acid (350 g/L), stannous oxide (62 g/L), nickel chloride hexahydrate (10 g/L), polyoxyethylene β-naphthol ether (1.0 g/L), and pyrazine (0.2 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 5.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a yellowish green external appearance.

[Plating Method]

**[0056]** The same operations as those in Example 1 were performed except that the current density was changed from that in Example 1 to 20 $A/dm^2$ and the power supply device was changed from that in Example 1 to a pulse power supply. The ON time and OFF time of the pulse power supply were set to 0.4 seconds and 0.1 seconds, respectively, to achieve a duty ratio of 0.8.

[Result]

**[0057]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and the deposit was confirmed to contain 1.05 mass% of nickel. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 7)

[Plating Solution]

**[0058]** Gluconic acid (190 g/L), methanesulfonic acid (350 g/L), stannous oxide (62 g/L), cobalt chloride hexahydrate (20 g/L), polyoxyethylene β-naphthol sulfuric acid ether (4.0 g/L), and pyrazine (0.2 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 5.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a purple external appearance.

[Plating Method]

**[0059]** Treatment was performed in the same conditions as those in Example 1.

[Result]

**[0060]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. A co-deposition ratio of cobalt was checked in the same procedure as in Example 1 except that the nickel in Example 1 was changed to cobalt. The deposit was confirmed to contain 1.92 mass% of cobalt. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 8)

[Plating Solution]

**[0061]** Malic acid (220 g/L), ammonium sulfate (170 g/L), stannous sulfate (60 g/L), nickel sulfate hexahydrate (10 g/L), coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine (0.3 g/L), polyoxyethylene tallow alkylamine (0.2 g/L), and 2,2'-bipyridyl (0.05 g/L) were dissolved into ion-exchange water and the pH thereof was adjusted to 5.0 by adding an appropriate amount of ammonia water. The plating solution after the preparation had a green external appearance.

[Plating Method]

**[0062]** The same operations as those in Example 1 were performed except that the current density was changed to 10 $A/dm^2$.

[Result]

**[0063]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and the deposit was confirmed to contain 0.11 mass% of nickel. The external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 9)

[Plating Solution]

**[0064]** A plating solution was prepared as in Example 1 except that the concentration of the nickel sulfate hexahydrate was changed from 5 g/L to 10 g/L. The plating solution after the preparation had a green external appearance.

[Plating Method]

**[0065]** Treatment was performed in the same conditions as those in Example 1.

[Result]

**[0066]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and the deposit was confirmed to contain 2.80 mass% of nickel. In comparison with the result of Example 1, it can be determined that any nickel co-deposition ratio can be obtained by changing the concentration of the nickel salt in the plating bath. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Example 10)

[Plating Solution]

**[0067]** A plating solution was prepared as in Example 4 except that the concentration of the cobalt sulfate heptahydrate was changed from 15 g/L to 10 g/L. The plating solution after the preparation had a purple external appearance.

[Plating Method]

**[0068]** Treatment was performed in the same conditions as those in Example 4.

[Result]

**[0069]** The deposit was visually observed as in Example 1 and was confirmed to have an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of cobalt was checked in the same procedure as that in Example 4 and the deposit was confirmed to contain 1.07 mass% of cobalt. Judging from this result in view of the result of Example 4, it can be determined that any cobalt co-deposition ratio can be obtained by changing the concentration of the cobalt salt in the plating bath. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 1)

**[0070]** A plating solution was prepared by using the liquid composition of Example 1 excluding the picolinic acid and the same operations as those in Example 1 were performed under the same plating conditions. The plating solution after the preparation had a green external appearance. The obtained deposit was visually observed as in Example 1 and was confirmed to have unevenness formed therein and therefore have an external appearance with poor evenness. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 2)

**[0071]** A plating solution was prepared by using the liquid composition of Example 3 excluding the coconut oil fatty acid-amidopropyl dimethyl-amino acetic acid betaine and the polyoxyethylene tallow alkylamine and the same operations as those in Example 3 were performed under the same plating conditions. The plating solution after the preparation had a purple external appearance. As a result of visual observation in the same way as in Example 1, the obtained deposit was black and dull and was easily peeled off from the base. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 3)

**[0072]** A plating solution was prepared by using the liquid composition of Example 5 excluding the gluconic acid without performing the pH adjustment (the obtained pH was 1.0) and the same operations as those in Example 5 were performed under the same plating conditions. The plating solution after the preparation had a green external appearance. As a result of visual observation in the same way as in Example 1, the obtained deposit had a dark gray external appearance and was coarse. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity

or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 4)

**[0073]** In the plating solution of Comparative Example 3, an amount of polyoxyethylene bisphenol A ether added was increased to 5.0 g/L and the same operations as those in Example 5 were performed under the same plating conditions. The plating solution after the preparation had a green external appearance. As a result of visual observation in the same way as in Example 1, the obtained deposit had an even, grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of nickel was checked in the same procedure as that in Example 1 and no deposition of nickel was recognized. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 5)

**[0074]** A plating solution was prepared by using the liquid composition of Example 7 excluding the gluconic acid and by adding triethylenetetramine hexaacetic acid (250 g/L), and the same operations as those in Example 5 were performed under the same plating conditions. The plating solution after the preparation had a purple external appearance. As a result of visual observation in the same way as in Example 1, the obtained deposit had a grayish white, dull external appearance. A cellotape (registered trademark) (CT-18 manufactured by Nichiban Co., Ltd.) was attached to a surface of the deposit and removed. No adherence of the deposit to the tape was observed and thus the deposit demonstrated good adhesion. The co-deposition ratio of cobalt was checked in the same procedure as that in Example 7 and no deposition of cobalt was recognized. Moreover, the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 6)

**[0075]** A plating solution was prepared by using the liquid composition of Example 2 excluding the picolinic acid and by adding pyrrolidine (0.1 g/L) instead, and the same operations as those in Example 2 were performed under the same plating conditions. The plating solution after the preparation had a green external appearance. As a result of visual observation in the same way as in Example 1, the obtained deposit, the obtained deposition had a dark gray external appearance, was coarse, and easily peeled off. Moreover the external appearance of the plating solution after the plating was checked. No turbidity or precipitation was recognized and no change in color tone was confirmed.

(Comparative Example 7)

**[0076]** A plating solution was attempted to be prepared by using the liquid composition of Example 8 excluding the malic acid and by adding ethylenediamine tetra(methylene phosphonic acid) (220 g/L) instead. When ammonium water was added, a white precipitation was formed and the plating solution failed to be obtained.

**[0077]** Results of Examples 1 to 10 and Comparative Examples 1 to 7 are summarized in Table 1 presented below.

[Table 1]

| | Plating solution external appearance | | Plated coating external appearance | Adhesion | Co-deposition ratio |
|---|---|---|---|---|---|
| | After preparation | After plating | | | |
| Example 1 | Green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 1.55 mass% |
| Example 2 | Green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 2.40 mass% |
| Example 3 | Purple | No turbidity or discoloration | Grayish white, dull, even | Good | Co 1.07 mass% |
| Example 4 | Purple | No turbidity or discoloration | Grayish white, dull, even | Good | Co 1.46 mass% |

(continued)

| | Plating solution external appearance | | Plated coating external appearance | Adhesion | Co-deposition ratio |
|---|---|---|---|---|---|
| | After preparation | After plating | | | |
| Example 5 | Yellowish green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 0.40 mass% |
| Example 6 | Yellowish green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 1.05 mass% |
| Example 7 | Purple | No turbidity or discoloration | Grayish white, dull, even | Good | Co 1.92 mass% |
| Example 8 | Green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 0.11 mass% |
| Example 9 | Green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 2.80 mass% |
| Example 10 | Purple | No turbidity or discoloration | Grayish white, dull, even | Good | Co 1.07 mass% |
| Comparative Example 1 | Green | No turbidity or discoloration | Uneven | - | - |
| Comparative Example 2 | Purple | No turbidity or discoloration | Black, dull | - | - |
| Comparative Example 3 | Green | No turbidity or discoloration | Dark gray external appearance | - | - |
| Comparative Example 4 | Green | No turbidity or discoloration | Grayish white, dull, even | Good | Ni 0 mass% |
| Comparative Example 5 | Purple | No turbidity or discoloration | Gray | Good | Co 0 mass% |
| Comparative Example 6 | Green | No turbidity or discoloration | Dark gray | - | - |
| Comparative Example 7 | White turbid | - | - | - | - |

## Claims

**1.** A tin alloy electroplating bath comprising:

(A) a soluble tin salt;
(B) at least one of soluble nickel salts and soluble cobalt salts;
(C) an oxycarboxylic acid or a salt thereof;
(D) a nitrogen-containing unsaturated heterocyclic compound; and
(E) a surfactant, wherein

a pH of the tin alloy electroplating bath is 3 to 7.

**2.** The tin alloy electroplating bath according to claim 1, wherein the nitrogen-containing unsaturated heterocyclic compound is a nitrogen-containing six-membered unsaturated heterocyclic compound or a nitrogen-containing five-membered unsaturated heterocyclic compound.

**3.** The tin alloy electroplating bath according to claim 1, wherein the nitrogen-containing unsaturated heterocyclic

compound includes at least one nitrogen-containing six-membered unsaturated heterocyclic compound selected from the group consisting of pyridines, derivatives of pyridines, pyrazines, and derivatives of pyrazines.

4. The tin alloy electroplating bath according to any one of claims 1 to 3, wherein the surfactant is selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and combinations of these surfactants.

5. A method of electroplating an object with a tin alloy, comprising
applying a DC current or a pulse current at a current density of 0.1 to 30 A/$dm^2$ to the object in the tin alloy electroplating bath according to any one of claims 1 to 4.

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2019/027743

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C25D3/60(2006.01)i, C25D5/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl. C25D3/60, C25D5/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2019
Registered utility model specifications of Japan 1996-2019
Published registered utility model applications of Japan 1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 2010-265491 A (ISHIHARA CHEMICAL CO., LTD.) 25 November 2010, entire text (Family: none) | 1-5 |
| A | JP 2017-31447 A (ISHIHARA CHEMICAL CO., LTD.) 09 February 2017, entire text (Family: none) | 1-5 |
| A | JP 2004-244719 A (ISHIHARA CHEMICAL CO., LTD.) 02 September 2004, entire text & WO 2004/065663 A1 & US 2006/0113006 A1 & EP 1591563 A1 & KR 10-1045189 B1 & TW 200422439 A & KR 10-2005-0092132 A & CN 1742118 A | 1-5 |

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 05.08.2019 | 13.08.2019 |
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### Patent documents cited in the description


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- JP H09241885 B **[0003]**