Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
The present invention relates to a tin plating solution and an electrolytic tin plating method; and in further detail relates to an electrolytic tin plating solution and plating method for plating chip components such as ceramic capacitors.

Chip components are metal plated with tin, copper, silver, gold, nickel, palladium, or an alloy thereof, or the like, using a plating method such as barrel plating, plating with a flow-through plater, or the like, depending on the shape of the chip and the construction of the regions to be plated. The purpose for tin plating is to provide solderability to the electrode parts of the chip component.

However, with tin plating, and particularly barrel plating, there is a problem where the chip components will stick to each other (hereinafter also referred to as aggregation, sticking, and coupling). Chips that stick together become defective products, and reduce the yield of the product. The ratio of chip components that stick together from the total number of chip components is referred to as the coupling rate, and in severe cases, the coupling rate can exceed 90%.

Coupling is known to occur when chip components are plated in a barrel using a conventional plating bath with a sulfuric acid or methanesulfonic acid as a base. In order to resolve this problem, Japanese unexamined patent application 2003-82492 discloses a method of forming an electrode on chip-type ceramic electronic components using a tin electroplating bath containing stannous sulfonate as a stannous salt, a complexing agent such as citric acid, gluconic acid, or pyrophosphoric acid, or the like, and a glossing agent.

However, with the plating solution of Japanese unexamined patent application 2003-82492, a complexing agent is included, so wastewater processing of the plating solution and wash water is difficult. Therefore, a low pH tin plating bath that does not contain a complexing agent is preferable from the perspective of protecting the environment.

Furthermore, a tin plating bath with excellent solder wetting properties is important for tin plating to provide solderability to the chip components, or the like. The present inventors have previously improved on this point, and have discovered that specific naphthol compounds are useful as an additive for electrolytic tin plating that can form a tin film with uniform appearance, and the deposited tin film will have favorable solder wetting properties, and have also discovered that the solderability can be improved using specific naphthol compounds.

Therefore, an objective present invention is to provide a plating solution for chip components and a plating method for chip components, which does not use a complexing agent, and which provides favorable solder wetting properties and an extremely low coupling rate when electrolytic tin plating is performed, and particularly when electrolytic tin plating is performed using a barrel plating method.

As a result of diligent research to achieve the aforementioned objectives, the present inventors have discovered that a smooth tin plating film with higher film surface hardness than a conventional film and which can minimize sticking between plated substrates can be achieved by using specific compounds in a strongly acidic (pH of 1 or lower) tin plating bath, and particularly in a barrel tin plating bath that does not contain a complexing agent.

In other words, one aspect of the present invention provides an electrolytic tin plating solution for chip components, comprising (A) stannous ions; (B) acid; (C) N,N-dipolyoxyalkylene-N-alkyl amine, amine oxide, or blend thereof; (D) an anti-sticking agent; (E) a plating uniformity Improver; (F) an acrylic acid or acrylic acid derivative; and (G) an antioxidant, wherein the pH is 1 or lower.

The acrylic acid or acrylic acid derivative is compound expressed by the following General Formula (1)

\[ RH = \frac{\text{CH}_2 \cdot \text{COOH}}{\text{R}} \]

In the above formula, \( R \) represents a hydrogen atom or an alkyl group containing between 1 and 3 carbon atoms.

The aforementioned N,N-dipolyoxyalkylene-N-alkyl amine is one or more compounds expressed by the following General Formula (2).

\[ \text{RN}[(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_w(\text{CH}_2\text{CH}_2\text{O})_y][\text{CH}_2\text{CH}_2\text{O})_x\text{H}][\text{CH}_2\text{CH}_2\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_w\text{H}] \]

In the above formula, \( R \) represents an alkyl group with between 6 and 28 carbon atoms, and \( w, x, y, \) and \( z \) each represent an integer between 0 and 30. However, the sum of \( w, x, y, \) and \( z \) is not 0.

Furthermore, one aspect of the present invention provides an electrolytic tin plating solution for chip components, wherein the aforementioned amine oxide is one or more compound expressed by the following General Formula (3).
In the above formula, R represents an alkyl group, cycloalkyl group, or aryl group, and R' represents a hydrogen atom, alkyl group, or cycloalkyl group.

The aforementioned (D) anti-sticking agent is one or more compound selected from a group consisting of aromatic aldehydes and aromatic ketones.

Furthermore, one aspect of the present invention provides a method of plating chip components, comprising electrolytically tin plating chip components using an electrolytic tin plating solution comprising (A) stannous ions; (B) acid; (C) N,N-dipolyoxyalkylene-N-alkyl amine, amine oxide, or blend thereof; (D) an anti-sticking agent; (E) a plating uniformity improver; (F) an acrylic acid or acrylic acid derivative; and (G) an antioxidant, wherein the pH is 1 or lower.

The plating solution of the present invention is very effective at preventing substrates from sticking together and can minimize plating defects so the product yield increases when a plurality of substrates such as chip components, or the like, are electrolytically tin plated, and particularly when electrolytically tin plated using a barrel plating method. In other words, making the tin plating film smooth can reduce the sticking phenomenon that occurs when substrates come in contact with each other, where substrates lock together and physically cannot be peeled apart, similar to mat plating. Furthermore, increasing the film surface hardness can prevent tin plating films from deforming when substrates come in mutual contact, caused by the film surface being soft such as with mat plating, and can minimize the occurrence of tin plating films sticking together. Furthermore, the plating solution of the present invention does not include a complexing agent, so wastewater treatment is easier than with a convention plating solution for barrel plating.

The abbreviations used in this specification have the following meanings unless otherwise noted.

g = grams; mg = milligrams; °C = degrees Celsius; min = minutes; m = meters; cm = centimeters; L = liters; mL = milliliters; A = amperes; and dm² = square decimeters. All of the number ranges include the boundary points, and can be combined in any arbitrary order. The terms "plating solution" and "plating bath" used in this specification have exactly the same meaning and are used interchangeably.

The electrolytic tin plating solution of the present invention is an electrolytic tin plating solution for chip components, containing: (A) stannous ions, (B) acid, (C) N,N-dipolyoxyalkylene-N-alkyl amine, amine oxide, or blend thereof, (D) an anti-sticking agent, (E) a plating uniformity improver, (F) an acrylic acid or acrylic acid derivative, and (G) an antioxidant; wherein the pH is 1 or lower. The components are described below in order.

(A) Stannous ion

The plating bath of the present invention contains stannous ions as an essential component. Stannous ions are bivalent tin ions. Any compound that can provide stannous ions to the plating bath can be used. Generally, the tin salt of an inorganic acid or an organic acid is preferable. Examples of tin salts of inorganic acids include the stannous salt of sulfuric acid or hydrochloric acid; and examples of tin salts of organic acids include the stannous salt of substituted or unsubstituted alkanesulfonic acids or alkanolsulfonic acids, such as methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, 2-hydroxyethane-1-sulfonic acid, 2-hydroxypropane-1-sulfonic acid, and 1-hydroxypropane-2-sulfonic acid, and the like. Particularly preferable sources of stannous ions are stannous sulfate for salts of inorganic acids and stannous methanesulfonate for salts of organic acids. The compounds which can provide these ions can be used individually, or as a blend of 2 or more types.

The amount of stannous ion added to the plating bath is, for example, between 1 g/L and 150 g/L, preferably between 5 g/L and 50 g/L, and more preferably between 8 g/L and 20 g/L.

(B) Acid

The acid can be any arbitrary acid that can adjust the pH to 1 or lower and can provide conductivity to the plating bath. The acid can be any inorganic or organic acid. Examples of organic acids include substituted or unsubstituted alkanesulfonic acids or alkanolsulfonic acids, such as methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, 2-hydroxyethane-1-sulfonic acid, 2-hydroxypropane-1-sulfonic acid, and 1-hydroxypropane-2-sulfonic acid. Methanesulfonic acid is preferable. Examples of inorganic acids include sulfuric acid and hydrochloric acid, and sulfuric acid is preferable. These acids that can adjust the pH to 1 or lower and can provide conductivity to the plating bath can be used individually, or as a blend of 2 or more types.

The amount of acid in the plating bath solution is preferably at least stoichiometrically equivalent to the amount of bivalent tin ions in the plating bath. The amount of free acid in the plating bath is, for example, between 10 g/L and
500 g/L, preferably between 30 g/L and 300 g/L, and more preferably between 50 g/L and 200 g/L.

(C) N,N-dipolyoxyalkylene-N-alkyl amine or amine oxide

[0025] The plating bath of the present invention contains N,N-dipolyoxyalkylene-N-alkyl amine, amine oxide, or blend thereof as an essential component. The present inventors have evaluated various nonionic surfactants, and have discovered that uniform plating at the required plating film thickness can be achieved by using N,N-dipolyoxyalkylene-N-alkyl amine or amine oxides which are specific anionic surfactants.

[0026] N,N-dipolyoxyalkylene-N-alkyl amine is a polyoxypropylene polyoxyethylenealkylamine expressed by the following General Formula (2).

\[
RN[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_yH][(CH_2CH_2CH_2O)_zH] (2)
\]

[0027] In the aforementioned formula, R represents a straight or branched alkyl group with between 6 and 26 carbon atoms, \( w, x, y, \) and \( z \) each represent an integer between 0 and 30. However, the sum of \( w, x, y, \) and \( z \) is not 0. Preferably, \( R \) represents a straight chain alkyl group with between 8 and 18 carbon atoms, and the sum of \( w, x, y, \) and \( z \) is between 10 and 20.

[0028] The amine oxide is one or more compound expressed by the following General Formula (4).

\[
\begin{array}{c}
R^1 \\
\downarrow \\
N \rightarrow O
\end{array} \quad \begin{array}{c}
R^2 \\
R^3
\end{array} \quad \begin{array}{c}
\text{General Formula (4)}
\end{array}
\]

[0029] In the aforementioned formula, \( R^1, R^2, \) and \( R^3 \) each represent an alkyl group, a cycloalkyl group, or an aryl group, which may have a substitution group. Examples include a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, phenyl group, tolyl group, xylyl group, and naphthyl group, and the like.

[0030] In particular, the amine oxide of the present invention is preferably one or more amine oxides with a structure as expressed by General Formula (3).

\[
\begin{array}{c}
H \\
\downarrow
\end{array} \quad \begin{array}{c}
\text{General Formula (3)}
\end{array}
\]

[0031] In the aforementioned formula, \( R \) represents an alkyl group, cycloalkyl group or aryl group, and \( R' \) represents an alkyl group or a cycloalkyl group.

[0032] N,N-dipolyoxyalkylene-N-alkyl amine or amine oxide can act as a film modifying agent in the plating bath of the present invention. In other words, smoothing the plating film with N,N-dipolyoxyalkylene-N-alkyl amine or amine oxide can minimize the sticking phenomenon where substrates lock together and physically cannot be peeled apart, similar to mat plating, which occurs when substrates come in contact with each other.

[0033] The concentration of N,N-dipolyoxyalkylene-N-alkyl amine or amine oxide in the plating bath is suitably between 0.01 g/L and 100 g/L, preferably between 0.1 g/L and 50 g/L, and more preferably between 1 g/L and 25 g/L.

(D) Anti-sticking agent

[0034] The plating bath of the present invention contains an anti-sticking agent as an essential component. The anti-sticking agent acts to prevent the plated chip components from agglomerating (sticking) together in the plating bath of the present invention. The anti-sticking agent is useful for preventing the chip components from agglomerating together, or in other words, preventing the chip components from sticking together, particularly during barrel plating. The anti-sticking agent is selected from aromatic aldehydes and aromatic ketones. Examples of preferable anti-sticking agents include benzaldehyde and benzylidene acetone. These compounds act to increase the film surface hardness in particular. In other words, increasing the film surface hardness can prevent tin plating films from deforming when substrates come in mutual contact, which is caused by the film surface being soft such as with mat plating, and can minimize the occurrence of tin plating films sticking together.

[0035] The aforementioned preferable anti-sticking agents are particular effective when used in combination with the aforementioned (C) N,N-dipolyoxyalkylene-N-alkyl amine or amine oxide. The concentration of anti-sticking agent in the
plating bath is suitably between 1 mg/L and 50 g/L, preferably between 5 mg/L and 10 g/L, and more preferably between 10 mg/L and 5 g/L.

(E) Plating Uniformity Improver

[0036] The plating bath of the present invention contains a plating uniformity improver. The plating uniformity improver of the present invention is a compound that improves the plating uniformity particularly in areas of low current density. With barrel plating in particular, the object to be plated is placed in a barrel and electroplating is performed while rotating the barrel with the parts immersed in the plating solution, and therefore variation in the current density will occur, the current density range of the object to be plated will vary widely from a high current density region to a low current density region, and in the low current density region, there will be problems with lower plating uniformity, and therefore the plating film will have variation. By adding a plating uniformity improver, the plating can be uniformly performed even in the low current density regions.

[0037] The plating uniformity improver is 2-naphthol-7-sulfonic acid, which can be either in the form of a free acid or as a salt. Suitable salts of 2-naphthol-7-sulfonic acid include water soluble salts such as potassium, sodium, ammonium, and tin, or the like, but potassium and sodium salts are preferable, and sodium 2-naphthol-7-sulfonate is even more preferable. These salts can be used individually, or as a blend of two or more types. As shown in patent document 2, specific naphtholsulfonic acids where a sulfonic acid group is bonded to a hydroxyl group in specific positions on a naphthalene ring, and specifically 2-naphthol-7-sulfonic acid or alkali salt thereof is remarkably more effective than other naphtholsulfonic acids or salts thereof. Other positional isomers such as 2-naphthol-6-sulfonic acid and 1-naphthol-4-sulfonic acid have almost no effect, and are not preferable.

[0038] The amount of 2-naphthol-7-sulfonic acid or salt thereof added to the plating bath is between 0.01 g/L and 20 g/L, preferably between 0.1 g/L and 10 g/L, and more preferably between 0.2 g/L and 5 g/L.

(F) Acrylic acid or acrylic acid derivative

[0039] The plating bath of the present invention contains one or more acrylic acid or acrylic acid derivative expressed by the following General Formula (1). In particular, acrylic acid and methacrylic acid are preferable.

\[
CH_2 = \text{C} - \text{COOH} \quad (1)
\]

[0040] In the formula, R represents a hydrogen atom or an alkyl group containing between 1 and 3 carbon atoms. The methacrylic acid or acrylic acid is preferably added to the plating solution of the present invention as an auxiliary anti-sticking agent that supports the aforementioned (D) anti-sticking agent. The methacrylic acid or acrylic acid can further increase the component anti-sticking effect of the (D) anti-sticking agent, and in particular has the effect of increasing the film surface hardness, and can increase the sustainability of the anti-sticking effect, by being used in combination with the (D) anti-sticking agent.

[0041] The amount of acrylic acid or acrylic acid derivative expressed by the aforementioned General Formula (1) in the plating solution is suitably such that the concentration is between 0.1 g/L and 100 g/L, preferably between 0.1 g/L and 50 g/L, more preferably between 0.5 g/L and 10 g/L.

(G) Antioxidant

[0042] An antioxidant is used in the plating solution of the present invention. The antioxidant is used to prevent oxidation of the bivalent tin ions to tetravalent tin ions, and examples include hydroquinone, catechol, resorcin, phloroglucin, pyrogallol, hydroquinonesulfonic acid, and salts thereof.

[0043] The concentration of antioxidant in the plating bath is suitably between 10 mg/L and 100 g/L, preferably between 100 mg/L and 50 g/L, more preferably between 0.5 g/L and 5 g/L.

[0044] Furthermore, other commonly known additives can be added to the plating bath of the present invention, if necessary, such as glossing agents, smoothing agents, conductivity agents, and anode dissolving agents, and the like.

[0045] The order when adding the various components when making the plating bath is not restricted in particular, but from the perspective of safety, the acid is added after adding the water, and after sufficiently mixing, the tin salt is added, and after sufficiently mixing, the other required chemicals are added in order.

[0046] Examples of the chip components that can be plated using the plating solution of the present invention include electronic components such as resistors, capacitors, inductors, variable resistors, variable capacitors, and other passive components, quartz oscillator, LC filter, ceramic filter, delay lines, SAW filters, and other functional components, switches,
connectors, relay fuses, optical components, and other contact components.

**Plating method**

[0047] The electroplating method that is used with the plating solution of the present invention can be a commonly known plating method such as barrel plating, and plating using a flow-through plater, or the like. The concentration of the various components (A) through (G) in the plating solution can be arbitrarily selected based on the foregoing descriptions for each of the components.

[0048] The electroplating method that is used with the plating solution of the present invention can be performed at a bath temperature between 10°C and 50°C, preferably between 15°C and 30°C.

[0049] Furthermore, the cathode current density is suitably selected within a range between 0.01 and 5 A/dm², preferably between 0.05 and 3 A/dm².

[0050] During the plating process, the plating bath may be left without stirring, or can be stirred using a stirrer, or the like, or re-circulated using a pump, or the like.

**Example 1**

[0051] A bath was formed using the tin plating solution with the following composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Stannous methanesulfonate (as tin ion):</td>
<td>12 g/L</td>
</tr>
<tr>
<td>(B) Methanesulfonic acid (as free acid):</td>
<td>50 g/L</td>
</tr>
<tr>
<td>(C) Amine oxide: oxirane, methyl-, polymer with oxirane, ether with 2,2′-(oxidoimino)bis[ethanol] (2:1)</td>
<td>10 g/L</td>
</tr>
<tr>
<td>N-[3-(C9-11-isoalkyloxy)propyl] derives</td>
<td></td>
</tr>
<tr>
<td>(D) Benzylidene acetone:</td>
<td>0.4 g/L</td>
</tr>
<tr>
<td>(E) Methacrylic acid:</td>
<td>2 g/L</td>
</tr>
<tr>
<td>(F) Sodium 2-naphthol-7-sulfonate:</td>
<td>0.5 g/L</td>
</tr>
<tr>
<td>(G) Potassium hydroquinonesulfonate:</td>
<td>2 g/L</td>
</tr>
<tr>
<td>(H) Distilled water:</td>
<td>balance</td>
</tr>
</tbody>
</table>

[0052] Barrel tin plating was performed on chip resistors that had been nickel plated using a 1 L tin plating solution at the conditions shown below, and then various evaluations were performed. The results are shown in Table 1.

**Barrel plating**

[0053]

Object for plating: chip resistor, barrel: Yamamoto minibarrel (volume: 140 mL)
Rotational speed: 20 rpm
Nickel plating: 2.4 A- 60 minutes
Tin plating: 2 A- 90 minutes
Chip R resistor (size 1608): 4.7 kΩ 15 mL/barrel
Steel ball: 1 mm ø 30 mL/barrel

**Evaluation items**

Plating thickness

[0054] After barrel plating, the plating thickness on the front surface, back surface, and on the left and right sides was measured using a fluorescent light x-ray film thickness meter, and the thickness and the plating thickness various between each point were evaluated.

Coupling rate

[0055] The barrel-plated chip components were sorted into chips which were stuck together and chips that were not stuck together, and the coupling rate was calculated as a ratio (%) with the weight of chips that stuck together in the numerator and the weight of all of the chips in the denominator (stuck chips/(stuck chips + unstuck chips) x 100).
Solder wetting test

[0056] One liter of each of the plating solutions of the embodiments and comparative examples were prepared, and tin electroplating was performed for 90 minutes at a current of 2 A and a bath temperature of 20°C. Each of the tin plated films obtained was subjected to humidity resistance testing at 105°C and 100% RH, for 8 hours, and then the solder wetting properties of the humidity resistance tested plated films were evaluated by measuring the zero cross time ("ZCT") using the solder paste equilibrium method using a Multi Solderability Tester SWET-2100 manufacturer by TARUTIN. The measurement conditions were as shown below.

Zero cross time measurement conditions

[0057]

- Solder paste: Sn: Ag: Bi:Cu = 96:2.5:1:0.5
- Bath temperature: 245°C
- Immersion depth: 0.25 mm
- Immersion speed: 2 mm/sec
- Immersion time: 8 sec

[0058] The zero cross time was measured and a value of 3.0 seconds or less was considered a PASS. The pass rate was calculated as a percentage using the number of samples with a zero cross time of 3 seconds or less in the numerator, and the total number of samples measured (10 samples) in the denominator.

Examples 2 through 11 and Comparative Examples 1 through 7

[0059] Tin plating baths were created at the ratios shown in Table 1 and Table 2 in a similar manner to Example 1, and the various tests were performed similar to Example 1. The results are also shown in Table 1 and Table 2. Note, the symbols related to the evaluation of the plating thickness are as shown below.

[0060] Plating thickness is uniform on the front surface, back surface, and on the left and right sides: O

- Plating is not uniform: △
- Plating is not formed: X
Table 1 (Values in the table are express in g/L. However values for compound (I) are expressed as mg/L)

<table>
<thead>
<tr>
<th></th>
<th>Embodiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td><strong>Tin salt</strong></td>
<td></td>
</tr>
<tr>
<td>Tin methanesulfonate (as tin)</td>
<td>12</td>
</tr>
<tr>
<td>Stannous sulfate (as tin)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Acid</strong></td>
<td></td>
</tr>
<tr>
<td>Methanesulfonic acid</td>
<td>50</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>0</td>
</tr>
<tr>
<td><strong>Surfactant</strong></td>
<td></td>
</tr>
<tr>
<td>Amine oxide</td>
<td>10</td>
</tr>
<tr>
<td>N,N-dipolyoxyalkylene- N-alkyl amine Note 1)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Anti-sticking agent</strong></td>
<td></td>
</tr>
<tr>
<td>Benzyldene acetone</td>
<td>0.4</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
</tr>
<tr>
<td><strong>Auxiliary anti-sticking agent</strong></td>
<td></td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>0</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>2</td>
</tr>
<tr>
<td><strong>Plating uniformity improver</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium 2-naphthol-7-sulfonate</td>
<td>0.5</td>
</tr>
<tr>
<td>Compound (I)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Antioxidant</strong></td>
<td></td>
</tr>
<tr>
<td>Potassium hydroquinone sulfonate</td>
<td>2</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>1 or lower</td>
</tr>
<tr>
<td><strong>Plating thickness</strong></td>
<td>O</td>
</tr>
<tr>
<td><strong>Coupling rate</strong></td>
<td>0</td>
</tr>
<tr>
<td><strong>ZCT (average)</strong></td>
<td>2.5 sec</td>
</tr>
<tr>
<td><strong>Pass rate</strong></td>
<td>100</td>
</tr>
</tbody>
</table>

Note 1) N,N-dipolyoxyalkylene-N-alkyl amine is expressed by the following structural formula (2), and in the formula, w + x + y + z = 16.
(2) 

$\text{(CH}_3\text{HCH}_2\text{O)}_n\text{(CH}_2\text{CH}_2\text{O)}_m\text{H}$
Table 2 (In the table, values are expressed as g/L)

<table>
<thead>
<tr>
<th></th>
<th>Comparative Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Tin salt</td>
<td></td>
</tr>
<tr>
<td>Tin methanesulfonate (as tin)</td>
<td>12</td>
</tr>
<tr>
<td>Stannous sulfate (as tin)</td>
<td>0</td>
</tr>
<tr>
<td>Acid</td>
<td></td>
</tr>
<tr>
<td>Methanesulfonic acid</td>
<td>50</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>0</td>
</tr>
<tr>
<td>Surfactant</td>
<td></td>
</tr>
<tr>
<td>Amine oxide</td>
<td>0</td>
</tr>
<tr>
<td>Surfactant 1 Note 1</td>
<td>10</td>
</tr>
<tr>
<td>Surfactant 2 Note 2</td>
<td>0</td>
</tr>
<tr>
<td>Surfactant 3 Note 3</td>
<td>0</td>
</tr>
<tr>
<td>Surfactant 4 Note 4</td>
<td>0</td>
</tr>
<tr>
<td>Anti-sticking agent</td>
<td></td>
</tr>
<tr>
<td>Benzyldiene acetone</td>
<td>0.4</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>0</td>
</tr>
<tr>
<td>Auxiliary anti-sticking agent</td>
<td>2</td>
</tr>
<tr>
<td>Plating uniformity improver</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium 2-naphthol-7-sulfonate</td>
<td>0</td>
</tr>
<tr>
<td>Compound (I)</td>
<td>0</td>
</tr>
<tr>
<td>Sodium 1-naphthol-6-sulfonate</td>
<td>0</td>
</tr>
<tr>
<td>Antioxidant</td>
<td></td>
</tr>
<tr>
<td>Potassium hydroquinonesulfonate</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>1 or lower</td>
<td>X</td>
</tr>
<tr>
<td>Plating thickness</td>
<td></td>
</tr>
<tr>
<td>Coupling rate (%)</td>
<td>0</td>
</tr>
<tr>
<td>ZCT (average)</td>
<td>5 sec or more</td>
</tr>
</tbody>
</table>
### Comparative Examples

<table>
<thead>
<tr>
<th>Pass rate (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Note 1) Surfactant 1 is: In the formula, XI through X^{III} are approximately 13, Y^{I} through Y^{III} are approximately 11, and the molecular weight is approximately 800.

Note 2) Surfactant 2 is:

\[
\begin{aligned}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_2\text{N} & \quad \text{R} \\
\text{NH}_2 & \quad \text{CH}_3
\end{aligned}
\]

R: polyoxalkene

Note 3) Surfactant 3: polyoxyethylene allyl phenyl ether

Note 4) Surfactant 4: lauryl dimethyl betaine
Claims

1. An electrolytic tin plating solution for chip components, comprising:
   (A) stannous ions;
   (B) acid;
   (C) one or more compounds expressed by the following General Formula:

\[
RN[(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}_2\text{CH}_2\text{O})_z\text{H}][(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_w\text{H}],
\]

wherein \( R \) represents an alkyl group with between 6 and 28 carbon atoms, and \( w, x, y, \) and \( z \) each represent an integer between 0 and 30, however, the sum of \( w, x, y, \) and \( z \) is not 0, an amine oxide, or a blend thereof; and
   (D) an anti-sticking agent selected from a group consisting of aromatic aldehydes and aromatic ketones;
   (E) 2-naphthol-7-sulfonic acid or alkali salt thereof;
   (F) one or more acrylic acid or acrylic acid derivative as expressed by the following General Formula (1):

\[
\text{CH}_2 = \text{C} - \text{COOH}
\]

where \( R \) represents hydrogen or an alkyl group containing between 1 and 3 carbon atoms; and
   (G) an antioxidant;
wherein the pH is 1 or lower.

2. The electrolytic tin plating solution for chip components according to Claim 1, wherein the aforementioned amine oxide is one or more compounds expressed by the following General Formula (3):

\[
\text{CH}_2\text{CH} = \text{O}
\]

where \( R \) represents an alkyl group, cycloalkyl group, or aryl group, and \( R' \) represents a hydrogen atom, alkyl group, or cycloalkyl group.

3. The electrolytic tin plating solution for chip components according to Claim 1, wherein the anti-sticking agent is selected from benzaldehyde and benzylidene acetone.

4. A method of plating chip components, comprising electrolytically tin plating chip components using an electrolytic tin plating solution comprising:
   (A) stannous ions;
   (B) acid;
   (C) one or more compounds expressed by the following General Formula:

\[
RN[(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}_2\text{CH}_2\text{O})_z\text{H}][(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_w\text{H}],
\]

wherein \( R \) represents an alkyl group with between 6 and 28 carbon atoms, and \( w, x, y, \) and \( z \) each represent an integer between 0 and 30, however, the sum of \( w, x, y, \) and \( z \) is not 0, an amine oxide, or a blend thereof;
   (D) an anti-sticking agent selected from a group consisting of aromatic aldehydes and aromatic ketones;
   (E) 2-naphthol-7-sulfonic acid or alkali salt thereof;
   (F) one or more acrylic acid or acrylic acid derivative as expressed by the following General Formula (1):
where R represents hydrogen or an alkyl group containing between 1 and 3 carbon atoms; and
(G) an antioxidant;
wherein the pH is 1 or less.

**Patentansprüche**

1. Eine elektrolytische Zinnplattierungslösung für Chipkomponenten, die Folgendes beinhaltet:

   (A) Zinn-(II)-Ionen;
   (B) Säure;
   (C) eine oder mehrere Verbindungen, ausgedrückt durch die folgende allgemeine Formel:

   \[
   RN[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_zH][(CH_2CH_2CH_2O)_y(CH_2CH_2O)_wH],
   \]

   wobei R eine Alkylgruppe mit zwischen 6 und 28 Kohlenstoffatomen darstellt und w, x, y und z jeweils eine ganze Zahl zwischen 0 und 30 darstellen, wobei die Summe von w, x, y und z allerdings nicht 0, ein Aminoxid oder eine Mischung davon ist; und
   (D) ein Antihaftmittel, das ausgewählt ist aus der Gruppe, bestehend aus aromatischen Aldehyden und aromatischen Ketonen;
   (E) 2-Naphthol-7-sulfonsäure oder ein Alkalisalz davon;
   (F) eine oder mehrere Acrylsäuren oder ein oder mehrere Acrylsäurederivate, wie durch die folgende allgemeine Formel (1) ausgedrückt:

   \[
   CH_2 = C - COOH
   \]

   wobei R Wasserstoff oder eine Alkylgruppe, die zwischen 1 und 3 Kohlenstoffatome enthält, darstellt; und
   (G) ein Antioxidationsmittel;
   wobei der pH-Wert 1 oder niedriger ist.

2. Elektrolytische Zinnplattierungslösung für Chipkomponenten gemäß Anspruch 1, wobei das oben erwähnte Aminoxid eine oder mehrere Verbindungen, ausgedrückt durch die folgende allgemeine Formel (3), ist:

   \[
   \text{CH}_3\text{C} = \text{C} - \text{COOH}
   \]

   wobei R eine Alkylgruppe, Cycloalkylgruppe oder Arylgruppe darstellt und R' ein Wasserstoffatom, eine Alkylgruppe oder eine Cycloalkylgruppe darstellt.

3. Elektrolytische Zinnplattierungslösung für Chipkomponenten gemäß Anspruch 1, wobei das Antihaftmittel aus Benzaldehyde und Benzylidenacetan ausgewählt ist.

4. Ein Verfahren zum Plattieren von Chipkomponenten, beinhaltend das elektrolytische Zinnplattieren von Chipkomponenten unter Verwendung einer elektrolytischen Zinnplattierungslösung, welche Folgendes beinhaltet:

   (A) Zinn-(II)-Ionen;
(B) Säure;
(C) eine oder mehrere Verbindungen, ausgedrückt durch die folgende allgemeine Formel:

\[
RN\left[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_zH\right]\left[(CH_2CH_2CH_2O)_y(CH_2CH_2O)_wH\right],
\]

wobei \(R\) eine Alkylgruppe mit zwischen 6 und 28 Kohlenstoffatomen darstellt und \(w, x, y, und z\) jeweils eine ganze Zahl zwischen 0 und 30 darstellen, wobei die Summe von \(w, x, y, and z\) allerdings nicht 0, Aminoxid oder eine Mischung davon ist;

(D) ein Antihaftmittel, das ausgewählt ist aus der Gruppe, bestehend aus aromatischen Aldehyden und aromatischen Ketonen;

(E) 2-Naphthol-7-sulfonsäure oder ein Alkalisalz davon;

(F) eine oder mehrere Acrylsäuren oder ein oder mehrere Acrylsäurederviate, wie durch die folgende allgemeine Formel (1) ausgedrückt:

\[
\begin{align*}
CH_2 & = C - COOH \\
& \overset{\text{R}}{\text{R}}
\end{align*}
\]

Revendications

1. Une solution de placage d’étain électrolytique pour des composants de puce, comprenant:

(A) des ions stanneux ;
(B) de l’acide ;
(C) un ou plusieurs composés exprimés par la formule générale suivante :

\[
RN\left[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_zH\right]\left[(CH_2CH_2CH_2O)_y(CH_2CH_2O)_wH\right],
\]

dans laquelle \(R\) représente un groupe alkyle avec entre 6 et 28 atomes de carbone, et \(w, x, y, \text{et} z\) représentent chacun un nombre entier compris entre 0 et 30, cependant la somme de \(w, x, y, \text{et} z\) ne fait pas 0, un oxyde d’amine, ou un mélange homogène de ceux-ci ; et

(D) un agent anticollant sélectionné dans un groupe constitué d’aldéhydes aromatiques et de cétones aromatiques ;

(E) de l’acide 2-naphtol-7 sulfonique ou un sel alcalin de celui-ci ;

(F) un acide acrylique ou dérivé d’acide acrylique ou plus tel qu’exprimé par la formule générale (1) suivante :

\[
\begin{align*}
CH_2 & = C - COOH \\
& \overset{\text{R}}{\text{R}}
\end{align*}
\]

où \(R\) représente un hydrogène ou un groupe alkyle contenant entre 1 et 3 atomes de carbone ; et

(G) un antioxydant ;

dans laquelle le pH est de 1 ou en deçà.

2. La solution de placage d’étain électrolytique pour des composants de puce selon la revendication 1, dans laquelle l’oxyde d’amine susmentionnée est un ou plusieurs composés exprimés par la formule générale (3) suivante :

\[
RN\left[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_zH\right]\left[(CH_2CH_2CH_2O)_y(CH_2CH_2O)_wH\right],
\]
où R représente un groupe alkyle, un groupe cycloalkyle, ou un groupe aryle, et R' représente un atome d’hydrogène, un groupe alkyle, ou un groupe cycloalkyle.

3. La solution de placage d'étain électrolytique pour des composants de puce selon la revendication 1, dans laquelle l'agent anticollant est sélectionné parmi du benzaldéhyde et de l'acétone benzylidine.

4. Une méthode de placage de composants de puce, comprenant le placage à l'étain de façon électrolytique de composants de puce en utilisant une solution de placage d'étain électrolytique comprenant :

(A) des ions stanneux ;
(B) de l'acide ;
(C) un ou plusieurs composés exprimés par la formule générale suivante :

$$RN[(CH_2CH_2CH_2O)_x(CH_2CH_2O)_yH][(CH_2CH_2CH_2O)_z(CH_2CH_2O)_wH],$$
dans laquelle R représente un groupe alkyle avec entre 6 et 28 atomes de carbone, et w, x, y, et z représentent chacun un nombre entier compris entre 0 et 30, cependant la somme de w, x, y, et z ne fait pas 0, un oxyde d’amine, ou un mélange homogène de ceux-ci ;
(D) un agent anticollant sélectionné dans un groupe constitué d’aldéhydes aromatiques et de cétones aromatiques ;
(E) de l’acide 2-naphtol-7 sulfonique ou un sel alcalin de celui-ci ;
(F) un acide acrylique ou dérivé d’acide acrylique ou plus tel qu’exprimé par la formule générale (1) suivante :

$$CH_2 \equiv C - \overset{-C-}{\text{H}} - \overset{-R-}{\text{R}}$$

(1)
où R représente un hydrogène ou un groupe alkyle contenant entre 1 et 3 atomes de carbone ; et
(G) un antioxydant ;
dans laquelle le pH est de 1 ou moins.
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

• JP 2003082492 A [0004] [0005]