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ELECTROLYTIC DESILVERING AGENTS AND
ELECTROLYTIC DESILVERING METHOD



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FIELD OF THE INVENTION

This invention relates to a electrolytic desilvering agents and electrolytic desilvering method using the same, and more specifically to electrolytic desilvering agents and desilvering method suitable for electrolytically removing or peeling off unwanted silver plated portions from silver plated surface. The term "desilver" is herein used to mean removing or peeling off from silver plated surface unwanted silver plated portion(s).

This invention also relates to electrolytic desilvering agents and desilvering method which permit the prevention of tarnishing or corrosion during storage of desilvered parts or workpieces based on copper, copper alloy, or the like.

The electrolytic desilvering agents and the method using the same of this invention do not adversely affect the bondability of the desilvered parts in the bonding step known as die bonding and wire bonding.

BACKGROUND OF THE INVENTION

Electronic parts and devices, such as lead frames and connector pins, are often partially plated with silver. The surface portions not to be silver-plated are masked or otherwise shielded, and yet the silver plated film

occasionally extends over base surface portions where such silver plating does not to be made. When this happens, the excess silver plated film must be taken away. A method known in the art for removing the unwanted silver film is termed electrolytic desilvering. The electrolytic desilvering method comprises immersing the excessively silver plated workpieces into a bath of desilvering agent (desilvering solution) and carrying out electrolysis using the objects as anodes, thereby removing the unnecessary silver film portions.

Electrolytic desilvering agents that have hitherto been used include concentrated sulfuric acid mixed with sodium nitrate, one containing a cyanogen compound, and ones based on sodium thiosulfate. They have presented problems of attacking even necessary silver plated portions while etching the base (copper or copper alloy) or needing care in handling because of the high toxicity of cyanogen compound.

In view of these, desilvering agents that do not use the dangerous concentrated sulfuric acid and highly toxic cyanogen compound but are composed mainly of a cyclic acid imide that contains one nitrogen atom in the molecule have been developed. Among them are agents based on succinimide or phthalimide and an alkali metal hydroxide (Japanese Patent Application Kokai No. 2-104699 (Kokoku No. 5-87598) and those containing 2-pyrrolidone-5-carboxylic acid with or without the addition of a saccharide (Patent Application Kokai No. 6-41800). Patent Application Kokai No. 2-175825 discloses five- and six-membered ring compounds having -NH-, such as

barbituric acid, uracil, and glutarimide. Patent Application Kokai No. 7-243100 proposes the use of a hydantoin compound as a complexing agent.

The desilvering agents of compounds based on cyclic acid imides containing one nitrogen atom in the molecule have many drawbacks. They tend to be hydrolyzed with alkalies, and accumulation of the decomposition products can undesirably affect to the necessary silver plated surface such as passivation, tarnishing, lack of uniformity and others of the silver plated surface. They also result in excessive consumption of the main constituent with short bath life. Another problem is the tendency that desilvering under high current density condition causes unwanted passivation or irregular desilvering of the surface.

Manufacture of semiconductor devices involves bonding steps, known as die bonding and wire bonding. Die bonding is a step in which a semiconductor chip is attached to a lead frame with epoxy resin. If epoxy bleedout occurs during the process, the die pad will be contaminated with organic matter to cause inferior ground bonding and make conduction to the outside impossible. Wire bonding is a step for attaching fine wire of Au, Al, etc. to semiconductor chips and frame inner leads to interconnect them. Here again any contamination of the Ag surface of the inner leads or a very rough surface condition will not permit conduction to the outside. It is thus important for a desilvering agent to have no adverse effect upon the bondability of the desilvered surface. The

above-mentioned agents of the prior art are unable to meet these requirements.

OBJECT OF THE INVENTION

It is therefore an object of this invention to develop agents and a method for electrolytic desilvering that permit removal of silver at a high current density while ensuring long bath life with little hydrolysis of the principal constituent and further without any deleterious effect upon the bondability of the desilvered surface.

A problem common to the desilvering agents of the prior art has been that, when the base is copper, copper alloy, or the like, desilvering induces some dissolving of the base material and activation of the surface. This in turn tends to cause surface tarnishing or corrosion of the desilvered parts during storage. Thus it is another object of this invention to develop electrolytic desilvering agents and desilvering method which, when the parts to be processed are based on copper, copper alloy, or the like, render it possible to prevent the tarnishing or corrosion of the desilvered surface during storage.

SUMMARY OF THE INVENTION

After our intensive investigations to realize the objects it has now been found that specified nitrogen cyclic compounds or their derivatives having two or more N atoms in the ring show electron polarized states unlike those with a single N

atom and that they hardly undergo hydrolysis and thereby extend the bath life, permit desilvering at high current density, and, with the addition of a boric acid compound, preclude adverse effects upon the bondability of desilvered surfaces.

On the basis of this discovery, the present invention provides an electrolytic desilvering agents comprising a desilvering component selected from the group consisting of hydantoin, 5,5-dimethyl-hydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin as a principal constituent and a boric acid compound as an accessory constituent. A surfactant may be added to the agents.

It has also been found that the addition of a certain copper inhibitor to the electrolytic desilvering agent allows it to be adsorbed by the base surface, making it possible to prevent tarnishing or corrosion of the desilvered surface during storage.

Based on this finding, this invention provides electrolytic desilvering agents of the above compositions further containing one or more of the compounds selected from the group consisting of benzotriazole, benzimidazole, thiouracil, thiobarbituric acid, benzothiazole, benzoxazole, indazole, indole, imidazole, imidazoline, and their derivatives as a copper inhibitor and inhibitors.

This invention further provides an electrolytic desilvering method characterized by immersing of an

excessively silver plated copper or copper alloy object in a solution of one of the above mentioned electrolytic desilvering agents and carrying out the electrolysis using said object as an anode. The electrolytic desilvering is desirably performed with stirring under the conditions of: pH of the agent: 7 to 14; bath current density: 0.1 to 50 A/dm²; and bath temperature: 10 to 60°C .

Under this invention the main constituent of the desilvering agent, which has two or more N atoms in the ring, shows an electron polarized state different from that with a single N atom and seldom undergoes hydrolysis. That presumably accounts for extended bath life and the possibility of desilvering at high current density. It is also presumed that, according to this invention, the adsorption of a copper inhibitor on a copper or copper alloy base surface controls the activation of the base surface, even though it may accompany some dissolution of the base, and prevents the desilvered surface from tarnishing or corroding while being stored.

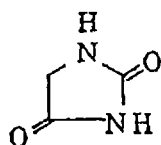
DETAILED DESCRIPTION OF THE INVENTION

The principal constituent of the desilvering agent of the invention is a specified nitrogen cyclic compound or its derivative having two or more N atoms in the ring. It is selected from the group consisting of hydantoin, 5,5-dimethyl-hydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin. The chemical formulas of these

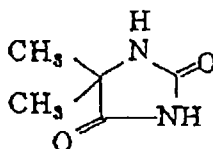
principal constituents are given below for reference.

[Chemical Formulas 1]

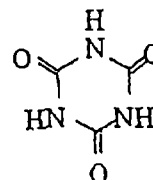
Hydantoin



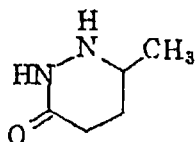
5,5-dimethyl
hydantoin



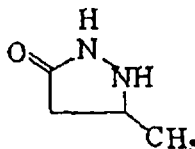
Cyanuric
acid



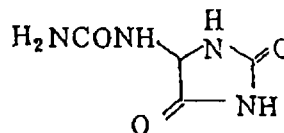
6-Methyl-3-
pyridazone



3-Methyl-5-
pyrazolone



Allantoin



The concentration of such a principal constituent in a bath ranges from 5 to 200 g/ℓ , preferably from 15 to 100 g/ℓ . A too low concentration tends to cause silver passivation, while a too high concentration is undesirable because it can pose a problem of the desilvering agent (solution) being wastefully carried out.

As an accessory constituent, basically as a pH buffering agent, a boric acid compound such as potassium tetraborate, (ortho)boric acid, potassium diborate, sodium borate, sodium pentaborate, or other borate, diborate, tetraborate, or pentaborate is added. The concentration of the boric acid compound is in the range of 5 to 100 g/ℓ , preferably 10 to 50 g/ℓ . If the concentration is too low the pH buffering

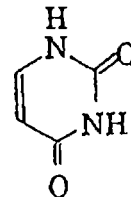
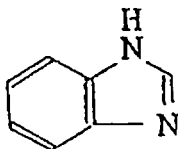
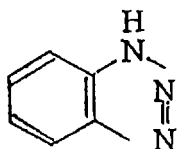
action is limited, but if the concentration is too high the effect is more than saturated to no avail. This accessory constituent contributes greatly to the bondability of the desilvered surface.

Further, where necessary, a surfactant is added. An anionic, cationic, or nonionic type or their mixture may be used. The concentration range of the surfactant is between $0.1 \mu\text{g}/\ell$ and $10 \text{g}/\ell$, preferably between $10 \mu\text{g}/\ell$ and $1 \text{g}/\ell$. Inadequate concentration does not produce a surfactant effect whereas excessive concentration wastefully saturates its effect.

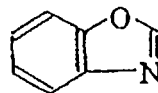
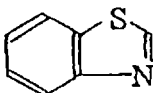
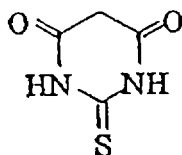
As a copper inhibitor, any one or more selected from the group consisting of benzotriazole, benzimidazole, thiouracil, thiobarbituric acid, benzothiazole, benzoxazole, indazole, indole, imidazone, imidazoline, and their derivatives may be used. The concentration of the copper inhibitor ranges from 1 to 1000 mg/ℓ , preferably from 5 to 500 mg/ℓ . Too low a concentration is not effective in preventing tarnishing while too high a concentration is no more effective beyond saturation. The above-mentioned copper inhibitors have the following structural formulas:

[Chemical Formulas 2]

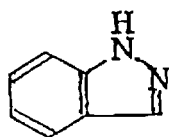
Benzotriazole Benzimidazole Thiouracil



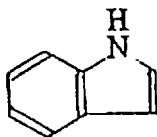
Thiobarbituric a. Benzothiazole Benzoxazole



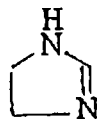
Indazole



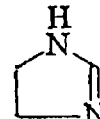
Indole



Imidazole



Imidazoline



Using such a desilvering agent, desilvering is carried out under predetermined conditions. The desilvering agent is adjusted with a pH adjuster such as sodium hydroxide or other alkali metal hydroxide or alkaline earth metal hydroxide to pH 7 to 14, preferably pH 7 to 12. If the pH is below the range the desilvering rate is so low that the silver surface tends to become uneven, and poor selective desilvering results. On the other hand, a pH above the range brings no merit.

The objects to be processed in accordance with this

invention are those consisting of a base of copper, copper alloy, iron-nickel alloy such as 42 alloy, stainless steel, nickel alloy, or other metal, formed with a silver coating film on the surface by silver plating, silver soldering, etc.

An object having a silver coating film thus formed on the surface is immersed into a bath of the electrolytic desilvering agent prepared as above, and electrolysis is conducted making the object an anode. The material of the cathode is not specially limited but stainless steel is usually used. The current density is between 0.1 and 50 A/d m², preferably between 0.5 and 10 A/m², with respect to the area of the silver plated surface to be removed. A too low current density slows down the desilvering process while a too high current density can frequently cause passivation of silver. The bath temperature for electrolysis ranges from 10 to 60°C, preferably from 15 to 40°C. Too low and too high bath temperatures are undesirable because they retard desilvering and make the bath unstable, respectively. Agitation of the bath during electrolysis is advisable and in order to avoid passivation especially when the current density is high, the faster the agitation the better.

When the object to be desilver consists of a base of copper or a copper alloy having a silver coating film formed by silver plating, silver soldering, or the like, it is immersed in a bath which further contains a copper inhibitor and is electrolyzed as an anode under the above-mentioned conditions. Alternatively, the same effect is attained by

dipping the object in a copper inhibitor solution before or after the electrolytic desilvering. Dipping for at least one second in the solution proves effective for protecting copper against tarnishing.

When the silver coating film of an object is to be partly removed by a desilvering bath, it is possible to either mask the silver plated surface portions to be retained or locally immerse the portions to be desilvered into the bath. If the silver film in the portions to be retained is thick enough to survive the desilvering of the unwanted portions, the whole object may be immersed in the bath. In the case of a lead frame, the silver coating film in its pad and other necessary portions usually becomes a low current density region during electrolytic desilvering while the silver film in the surrounding unnecessary portions becomes a high current density region. Thus, the object can be directly desilvered electrolytically without masking the necessary silver plated portions and only the unnecessary silver plated film portions are selectively removed.

EXAMPLES

The invention will now be described in further details in connection with its working examples, reference examples, and comparative examples.

Example Series I

Desilvering baths of different compositions were prepared

as represented by Example Nos. 1~6 in Table 1.

Copper lead frames, with their pads partly silver plated to a thickness of 5 μ m each (the portions around the pad being likewise silver plated unnecessarily), were used as test specimens. They were immersed into the desilvering baths and were electrolytically desilvered under the conditions given also in Table 1. That is, the unnecessary portions were removed by an electrolysis performed at pH 8~11, current density of 3.0~5.0 A/d m², bath temperature of 25 °C, and stirring rate of 1.0 m/sec for 30 seconds.

The desilvered specimens were evaluated by observation under a microscope (x100) of the outward appearances of the silver plated and base surfaces and also of the appearances of the bases after boiling. At the same time, the desilvered film thicknesses were determined by fluorescent X-ray analysis. Both die bonding and wire bonding were done, and the specimens were inspected for any trace of epoxy bleedout after the former and for the wire bond conditions after the latter.

The same electrolytic desilvering was repeated 42 days after the preparation of the baths, and the results were evaluated in the same manner.

The outward appearances of the silver and base surfaces were all good. Boiling caused some tarnishing of the bases but not to the extent that the bases were unusable. The desilvered film thicknesses were 0.9~1.6 μ m, indicating adequate desilvering performance. Bondability ratings were

high too. Exactly the same results were obtained in the tests conducted 42 days after the preparation of the baths. This signifies that the baths had outlived the tests.

Reference Examples

As Reference Example Nos. 1 and 2 in Table 1 shows, similar electrolytic desilvering tests were conducted using a bath of hydantoin alone and a bath of hydantoin and potassium pyrophosphate, in place of a boric acid compound, as the pH buffering agent of accessory constituent.

With the bath of hydantoin alone, the outward appearances of both silver and base surfaces were good but the base appearance changed due to tarnishing on boiling. The bath of hydantoin and potassium pyrophosphate as the pH buffering agent deteriorated the both appearances of silver and base surfaces, impairing the bondability of the desilvered surface either. This means the importance of the combination of the desilvering agent such as hydantoin and a boric acid compound according to this invention. Tests conducted 42 days after the preparation of the bath gave exactly the same results.

Comparative Examples

A desilvering bath composed mainly of succinimide, a conventional desilvering agent and another bath of succinimide plus potassium tetraborate were prepared, as represented by Comparative Example Nos. 1 and 2 in Table 1. In the manner described in Examples, lead frames of copper whose pad

portions had been partly silver plated to a thickness of $5\mu\text{ m}$ were used as test specimens and they were immersed in the above baths for electrolytic desilvering under the conditions shown in Table 1. That is, silver was removed from unwanted portions by electrolysis at pH 9, current density of 3.0 A/d m^2 , bath temperature of 25°C , and stirring rate of 1.0 m/sec for 30 seconds.

The desilvered specimens were evaluated in the same way as above. Tests with freshly prepared baths showed that both the silver and base surfaces of the specimens had good outward appearances. The base surface tarnished upon boiling. The desilvered film thickness was $0.8\mu\text{ m}$. Tests with the baths 42 days after their preparation gave the silver and base surfaces uneven and poor outward appearances. The specimens showed poor bondabilities too. The desilvered film thickness sharply decreased to $0.4\mu\text{ m}$ indicating that the bath life had already expired.

TABLE I

	Specimen No.	Example						Reference Example		Comparative Example	
		1	2	3	4	5	6	1	2	1	2
Bath composition	principal constituent	hydantoin 50 g/l	5,5-dimethyl hydantoin 50 g/l	cyanuric acid 50 g/l	6-methyl-3-pyridazone 25 g/l	3-methyl-5-pyridazone 50 g/l	allantoin 50 g/l	hydantoin 50 g/l	hydantoin 50 g/l	succinimide 50 g/l	succinimide
	accessory constituent	(ortho)-boric acid 30 g/l	potassium tetraborate 30 g/l	potassium tetraborate 30 g/l	sodium tetraborate 30 g/l	(ortho)-boric acid 30 g/l	(ortho)-boric acid 30 g/l	-	potassium pyrophosphate 30 g/l	-	potassium tetraborate 30 g/l
	surfactant	-	-	polyoxy-ethylene nonylphenyl ether 10 mg/l	-	-	lauryl betaine 10 mg/l	-	-	-	-
Desilvering condition	pH (adj. w/NaOH)	10.0	10.0	8.0	10.0	9.0	11.0	12.0	10.0	9.0	9.0
	cur dens (A/dm ²)	5.0	5.0	3.0	4.0	5.0	5.0	5.0	5.0	3.0	3.0
	bath temp (°C)	25	25	25	25	25	25	25	25	25	25
	stir rate (m/s)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	time (s)	30	30	30	30	30	30	30	30	30	30
Initial	silver surface appearance	good	good	good	good	good	good	good	poor	good	good
	base appearance	good	good	good	good	good	good	good	poor	good	good
	base appearance after boiling	some tarnish	some tarnish	some tarnish	some tarnish	some tarnish	some tarnish	tarnish	tarnish	tarnish	tarnish
	desilvered film thickness (μm)	1.6	1.6	0.9	1.3	1.5	1.5	1.6	1.6	0.8	0.8
Results of evaluation	epoxy bleedout	no	no	no	no	no	no	yes	yes	no	no
	wire bonding	good	good	good	good	good	good	poor	poor	good	good
	silver surface appearance	good	good	good	good	good	good	good	poor	poor	poor
	base appearance	good	good	good	good	good	good	good	poor	poor	poor
42 days later	base appearance	some tarnish	some tarnish	some tarnish	some tarnish	some tarnish	some tarnish	tarnish	tarnish	tarnish	tarnish
	after boiling	tarnish	tarnish	tarnish	tarnish	tarnish	tarnish	tarnish	tarnish	tarnish	tarnish
	desilvered film thickness (μm)	1.6	1.6	0.9	1.3	1.5	1.5	1.6	1.6	0.4	0.4
	epoxy bleedout	no	no	no	no	no	no	yes	yes	yes	yes
	wire bonding	good	good	good	good	good	good	poor	poor	poor	poor

Example Series II

This series used copper inhibitors. Baths of compositions represented by Example Nos. 1~7 in Table 2 were prepared. Copper lead frames, with their pads partly silver plated to a thickness of $5\mu\text{m}$ each (the portions around the pad being likewise silver plated unnecessarily), were used as test specimens. They were immersed into the desilvering baths and were electrolytically desilvered under the conditions given in Table 2. That is, the unnecessary silver plated portions were removed by an electrolysis performed at pH 8 ~ 12, current density of $3.0\sim 5.0\text{ A/dm}^2$, bath temperature of 25°C , and stirring rate of 1.0 m/sec for 30 seconds. The desilvered specimens were evaluated in the manner described in Example Series I.

The silver and base surfaces of the specimens after the electrolysis looked fine. The desilvering performance was satisfactory with the desilvered film thickness ranging from 0.9 to $1.6\mu\text{m}$. The desilvered specimens, even after 10 minutes of immersion in boiling pure water, showed good silver and base appearances. Their bondabilities were favorable too. Tests conducted 42 days after the preparation of the baths gave quite the same results. This meant that the baths still had service life after the tests.

Reference Examples

Electrolytic desilvering was carried out in the same manner as above with the exception that a bath of hydantoin

alone and a bath of hydantoin, potassium pyrophosphate as an accessory constituent as a pH buffering agent, and benzotriazole as a copper inhibitor were used instead, as Reference Example Nos. 1 and 2 in Table 2.

As stated already, the bath of hydantoin alone gave both good silver and base surface appearances but the base tarnished upon boiling. With the bath of hydantoin, potassium pyrophosphate as an accessory constituent as a pH buffering agent, and benzotriazole as a copper inhibitor, the appearances of the silver and base surfaces were poor. The bondability too was undesirable. These demonstrate the importance of the combination of the desilvering constituent such as hydantoin, a boric acid compound, and a copper inhibitor as taught by this invention. Tests repeated 42 days after the preparation of the baths gave just the same results.

Comparative Examples

A desilvering bath containing succinimide as a principal constituent and a bath containing succinimide, potassium tetraborate as a pH buffering agent, and benzotriazole as a copper inhibitor were prepared, as shown in Comparative Example Nos. 1 and 2 in Table 2. In the manner described in Examples, lead frames of copper whose pad portions had been partly silver plated to a thickness of $5\mu\text{m}$ were used as test specimens and they were immersed in the above baths for electrolytic desilvering under the conditions shown in Table 2. That is, silver was removed from unwanted portions by

electrolysis at pH 9, current density of 3.0 A/dm², bath temperature of 25 °C, and stirring rate of 1.0 m/sec for 30 seconds.

The desilvered specimens were likewise evaluated. Tests with freshly prepared baths showed that both the silver and base surfaces of the specimens had good outward appearances. Boiling tarnished the base in the desilvering bath of succinimide as a chief constituent, but the base surface looked good in the bath of succinimide that contained also potassium tetraborate and benzotriazole. The desilvered film thickness was 0.8 μ m. Tests with the baths 42 days after their preparation gave the silver and base surfaces uneven and poor outward appearances. The specimens showed poor bondabilities too. The desilvered film thickness sharply decreased to 0.4 μ m, indicating that the baths had no longer be useful.

ADVANTAGE OF THE INVENTION

This invention can prolong the life of an electrolytic desilvering agent markedly compared with the spans of existing agents. It permits desilvering at high current density. Also it has no adverse effect upon the bondability of the workpieces. This invention renders it possible to protect workpieces of copper, copper alloy, or the like from tarnishing or corrosion during storage after their electrolytic desilvering. Thus, the life of the electrolytic desilvering agent is by far the longer than those of conventional agents, and tarnishing or corrosion of copper, copper alloy, or other similar base can be prevented while performing desilvering at greater current density.

What is claimed is:

1. An electrolytic desilvering agent comprising:

- (a) at least one desilvering constituent selected from the group consisting of hydantoin, 5,5-dimethylhydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin, as a principal constituent; and
- (b) a boric acid compound as an accessory constituent.

2. An electrolytic desilvering agent comprising:

- (a) at least one desilvering constituent selected from the group consisting of hydantoin, 5,5-dimethylhydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin, as a principal constituent;
- (b) a boric acid compound as an accessory constituent; and
- (c) a surfactant.

3. An electrolytic desilvering agent comprising:

- (a) at least one desilvering constituent selected from the group consisting of hydantoin, 5,5-dimethylhydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin, as a principal constituent;
- (b) a boric acid compound as an accessory constituent; and
- (c) at least one selected from the group consisting of benzotriazole, benzimidazole, thiouracil, thiobarbituric acid, benzothiazole, benzoxazole, indazole, indole, imidazole, imidazoline, and their derivatives, as a copper

inhibitor or inhibitors.

4. An electrolytic desilvering agent comprising:

(a) at least one desilvering constituent selected from the group consisting of hydantoin, 5,5-dimethylhydantoin, cyanuric acid, 6-methyl-3-pyridazone, 3-methyl-5-pyrazolone, and allantoin, as a principal constituent;

(b) a boric acid compound as an accessory constituent;

(c) a surfactant; and

(d) at least one selected from the group consisting of benzotriazole, benzimidazole, thiouracil, thiobarbituric acid, benzothiazole, benzoxazole, indazole, indole, imidazole, imidazoline, and their derivatives, as a copper inhibitor or inhibitors.

5. An agent according to claim 4 wherein the desilvering constituent as a principal constituent is used in a bath at a concentration of from 5 to 200 g/ℓ, the boric acid compound as an accessory constituent at a concentration of from 5 to 100 g/ℓ, the surfactant at a concentration of from 0.1 μg to 10 g/ℓ, and the copper inhibitor or inhibitors at a concentration of from 1 to 1000 mg/ℓ.

6. An electrolytic desilvering method which comprises immersing a workpiece of copper or a copper alloy silvered on the surface into a bath of an electrolytic desilvering agent according to any of claims 1 to 5 and thereby carrying out

electrolysis using the workpiece as an anode.

7. A method according to claim 6 wherein the electrolytic desilvering is performed with stirring under the conditions of pH: 7 to 14; bath current density: 0.1 to 50 A/d m²; and bath temperature: 10 to 60°C .