

DESCRIPTION

ELECTROLYTIC STRIPPING AGENT FOR SILVER

TECHNICAL FIELD

[0001] The present invention relates to an electrolytic stripping agent for silver, and more particularly to an electrolytic stripping agent for silver, which is suitable for electrolytically stripping the unnecessary portion of silver plating films.

BACKGROUND ART

[0002] Succinimides or phthalimides (for example, Japanese Patent Publication No. 2-104699A), 5,6-membered ring compounds having a group of -NH- (for example, Japanese Patent Publication No. 2-175825A), 2-pyrrolidone-5-carboxylic acids (for example, Japanese Patent Publication No. 6-41800A), and hydantoin compounds (for example, Japanese Patent Publication No. 7-243100A) have been disclosed as cyan-free stripping agents for silver. However, the drawbacks of the agents of the first three groups is that the stripping bath decomposes intensively, the consumption of the agents is high, and the bath life is short. On the other hand, hydantoin compounds demonstrate small bath decomposition, which provides for a low agent consumption and a long bath life. However, the problem associated with those compounds was that if silver stripping was conducted at a high current density to increase productivity, unevenness appeared on the silver surface formed on the necessary portions or the gloss of the silver surface easily increased.

[0003] In order to resolve this problem, Japanese Patent Publication No. 9-49100A (Japanese Patent No. 293181) disclosed a method ensuring a long service life and preventing the

unevenness of the silver surface at a high current density by using a hydantoin compound and cyanuric acid as the main components and adding a boron compound as an auxiliary component thereto.

DISCLOSURE OF THE INVENTION

[0004] However, in applications of silver stripping solutions to lead frames and the like, it has recently become necessary to increase the silver stripping capacity on unnecessary portions formed by silver leaking to the side surfaces of lead frames and to suppress the increase in gloss on the silver surface on the necessary portions after the unnecessary portions were treated with a silver stripping agent. Silver that leaked to the side surface is considered a cause for migration as the size of lead frames is decreased. Furthermore, if the gloss is too high, it is said to produce an adverse effect on image recognition in wire bonding.

[0005] The present invention provides an electrolytic stripping agent for silver that meets the aforesaid needs, and it is an object of the present invention to provide a cyan-free electrolytic stripping agent for silver that has a long service life and a high stripping capacity on side surface and prevents the appearance of unevenness on the silver surface on the necessary portions after silver stripping and the increase in gloss on the silver surface.

[0006] Based on the results of a comprehensive study, the inventors have discovered that the aforesaid problems can be resolved with the below-described composition of an electrolytic solution for silver. Thus, the present invention provides:

[0007] (1) An electrolytic stripping agent for silver, comprising a hydantoin compound and an aminocarboxylic acid or a salt thereof as the main components, excluding pyridines and cyclic polyamine compounds.

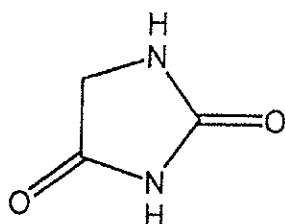
[0008] (2) The electrolytic stripping agent for silver, according to (1) above, wherein the aminocarboxylic acid is a monoaminodicarboxylic acid.

[0009] (3) The electrolytic stripping agent for silver, according to (1) or (2) above, which comprises, as the main components, hydantoin, 5,5-dimethylhydantoin, 5,5-dimethylhydantoin-3-hydroxymethyl, alantoin or salts thereof as the aforesaid hydantoin compound, and asparagic acid, glutamic acid or salts thereof as the aforesaid aminocarboxylic acid or salt thereof.

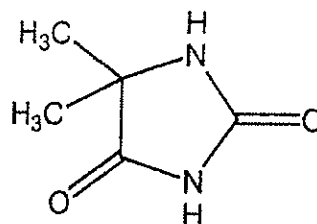
[0010] The electrolytic stripping solution for silver in accordance with the present invention comprises a hydantoin compound and an aminocarboxylic acid or salt thereof as the main components. Using the hydantoin compound was found to extend the bath life and using the aminocarboxylic acid or salt thereof could increase stripping capacity for a silver plating on the unnecessary portions. Further, it was also found that the occurrence of unevenness and increase in gloss of the silver plating surface on the necessary portions after the silver plating of the unnecessary portions has been stripped could be suppressed.

BEST MODE FOR CARRYING OUT THE INVENTION

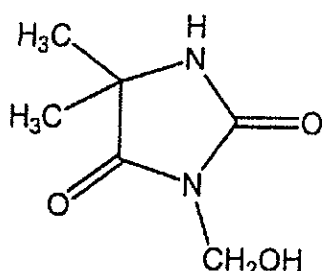
[0011] The preferred examples of the hydantoin compound which is one of the main components of the electrolytic stripping agent for silver in accordance with the present invention include hydantoin, 5,5-dimethylhydantoin, 5,5-dimethylhydantoin-3-hydroxymethyl, and alantoin which are represented by the following chemical formulas, or their salts. The preferred salts are sodium salts and potassium salts.



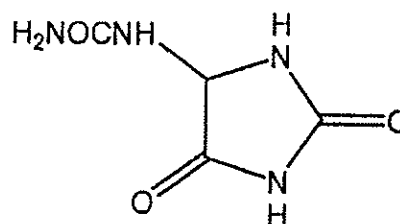
Hydantoin



5,5-Dimethylhydantoin



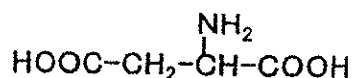
5,5-Dimethylhydantoin-3-hydroxymethyl



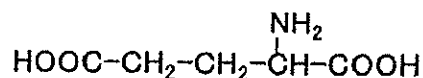
Alantoin

[0012] The concentration range thereof in the bath is 1 to 500 g/L, preferably, 5 to 200 g/L. It is undesirable that the concentration be too low, because the passivation of silver easily occurs. On the other hand, if the concentration is too high, then oozing of the stripping agent (stripping solution) becomes a problem.

[0013] The preferred examples of the aminocarboxylic acid which is one of the main components of the electrolytic stripping agent for silver in accordance with the present invention include monoaminodicarboxylic acids, and asparagic acid, glutamic acid or salts thereof are especially preferred. Chemical formulas of asparagic acid and glutamic acid are shown below. The preferred salts are sodium salts and potassium salts.



Asparagic acid



Glutamic acid

[0014] The concentration range thereof in the bath is 1 to 500 g/L, preferably, 5 to 200 g/L. If the concentration is too low, the stripping capacity on the side surface and the effect of suppressing the gloss increase and unevenness of the silver surface of the necessary portions are low. Too high a concentration also undesirable because the effect reaches saturation.

[0015] Further, if necessary, a pH buffer, a surfactant, a copper discoloration preventing agent, an epoxy bleed-out preventing agent, and the like, may be also added to the electrolytic stripping agent for silver in accordance with the present invention. Any of the well-known pH buffers, surfactants, copper discoloration preventing agents, and epoxy bleed-out preventing agents can be used.

[0016] Electrolytic stripping of silver is conducted by using the aforesaid stripping agent under the prescribed conditions. The pH of the stripping agent is adjusted with a pH buffer, for example, an alkali metal hydroxide such as sodium hydroxide or an alkaline earth metal hydroxide, so that the pH becomes no less than 7, preferably between 9 to 12. If the pH is too low, the stripping rate is low and the surface of silver on the necessary portions after the silver on the unnecessary portions have been stripped off easily becomes uneven and a selective stripping ability is poor. On the other hand, no merits are gained by employing too high a pH.

[0017] The stripping objects for the application of the present invention include silver films obtained by silver plating or soldering on a variety of metal base substrates such as copper, copper alloys, iron-nickel alloys such as 42 alloy, stainless steel, and nickel alloys.

[0018] The treatment object having a silver film formed on the surface thereof is immersed in a bath of the electrolytic stripping agent prepared in the above-described manner and

electrolysis is conducted by using the treatment object as an anode. No specific limitation is placed on the cathode, but stainless steel is typically used. The current density is 0.1 to 50 A/dm², preferably 0.5 to 20 A/dm², based on the surface area of silver which is to be stripped. It is undesirable that the current density be too low, because the stripping rate becomes low. On the other hand, if the current density is too high, the passivation of silver easily occurs. Furthermore, the electrolysis is conducted at a bath temperature of 5°C or higher, preferably 10 to 60°C. It is undesirable that the bath temperature be too low, because the stripping rate becomes too low. On the other hand, if the bath temperature is too high, the bath becomes unstable. Further, it is desirable that the bath be stirred during the electrolysis. In particular, when the current density is high, it is preferred that the stirring rate be high to prevent the occurrence of passivation.

[0019] When part of the silver plating film, which is the treatment object, is stripped with the stripping agent bath, the silver plating film on the necessary portions that should not be stripped is masked or a method of locally immersing only the portions which are to be stripped can be used. Furthermore, when the silver plating film on the necessary portions is sufficiently thick and may be stripped to the same degree as the unnecessary portions that are to be stripped, the entire treatment object may be immersed. Furthermore, when a lead frame is the treatment object, the necessary portions such as pads and leads have a large thickness of the silver plating film, whereas the unnecessary portions such as lead side surface have a small thickness of the silver plating film. Therefore, only the silver film plated on the unnecessary portions can be stripped even if the electrolytic stripping is conducted directly without masking the silver film plated on the necessary portions.

EXAMPLES

[0020] The present invention will be described below in greater detail based on the examples thereof.

Examples 1 through 8 and Comparative Examples 1 through 3

[0021] Stripping baths with compositions shown in Tables 1-1, 1-2, and 1-3 were prepared. 28-pin SOP-type lead frames in which a copper alloy substrate was plated over the entire surface with copper by strike plating to a thickness of 0.05 μm and spot plated with silver to a thickness of 5 μm was used as samples. The samples were immersed in the aforesaid stripping baths and electrolytic stripping was conducted under the stripping conditions shown in Tables 1-1, 1-2, and 1-3.

[0022] The samples after stripping were evaluated as follows.

Silver surface appearance and substrate surface appearance

[0023] Unevenness and defects were observed visually and via a microscope (x50). The samples without unevenness and defects were considered as good.

Silver surface gloss

[0024] Measurements were conducted with a gloss meter (Dainippon Screen, DM-400). The larger is the numerical value, the higher is the gloss. The gloss of the silver surface before the stripping was 0.40.

Silver stripping rate

[0025] The thickness of the silver plating film before and after silver stripping was measured with a fluorescent X-ray coating thickness gauge (Seiko Instruments Inc., SFT-3200) and the silver stripping rate was calculated.

Side surface stripping capacity

[0026] The silver stripping state on the side surface was observed under a microscope (x50). Samples in which silver was stripped from the side surface were considered good.

The evaluation results are shown in Tables 1-1, 1-2, and 1-3.

Table 1-1

		Examples			
		1	2	3	4
Bath composition	Main component 1	Hydantoin	5,5-Dimethyl hydantoin	5,5-Dimethyl hydantoin-3-hydroxymethyl 30 g/L	Alantoin
	Main component 2	50 g/L Sodium aspartate 50 g/L	40 g/L Sodium aspartate 60 g/L	70 g/L Sodium aspartate	20 g/L Sodium aspartate 80 g/L
	pH buffer	-	-	-	Boric acid 15 g/L
	Surfactant	-	-	-	Polyoxyethylene nonylphenyl ether 10 mg/L
	Copper discoloration preventing agent	-	-	-	1,2,3-Benzotriazole 50 mg/L
	Epoxy bleed-out preventing agent	-	-	-	Hexadecyl mercaptan 50 mg/L
Stripping conditions	pH	10.5	10.5	10.5	10.5
	Current density (A/dm ²)	10.0	10.0	10.0	10.0
	Bath temperature (°C)	25	25	25	25
	Stirring rate (m/s)	0.5	0.5	0.5	0.5
	Time (s)	30	30	30	30
Evaluation results	Silver surface appearance	Good	Good	Good	Good
	Silver surface gloss	0.41	0.38	0.36	0.34
	Substrate appearance	Good	Good	Good	Good
	Silver stripping rate (μm/min)	1.8	1.9	1.7	1.6
	Side surface stripping capacity	Good	Good	Good	Good

Silver surface gloss prior to silver stripping is 0.40 (the higher is the numerical value, the higher is the gloss).

Table 1-2

		Examples			
		5	6	7	8
Bath composition	Main component 1	Hydantoin	5,5-Dimethyl hydantoin	5,5-Dimethyl hydantoin-3-hydroxymethyl	Alantoin
		50 g/L	40 g/L	30 g/L	20 g/L
	Main component 2	Sodium glutamate	Sodium glutamate	Sodium glutamate	Sodium glutamate
		50 g/L	60 g/L	70 g/L	80 g/L
	pH buffer	-	-	-	Boric acid
		-	-	-	15 g/L
	Surfactant	-	-	-	Polyoxyethylene nonylphenyl ether
		-	-	-	10 mg/L
	Copper discoloration preventing agent	-	-	-	1,2,3-Benzotriazole
	Epoxy bleed-out preventing agent	-	-	-	50 mg/L
Stripping conditions	pH	10.5	10.5	10.5	Lauric acid
					50 mg/L
	Current density (A/dm ²)	10.0	10.0	10.0	10.5
	Bath temperature (°C)	25	25	25	10.0
	Stirring rate (m/s)	0.5	0.5	0.5	25
	Time (s)	30	30	30	0.5
Evaluation results	Silver surface appearance	Good	Good	Good	30
	Silver surface gloss	0.42	0.38	0.37	Good
	Substrate surface appearance	Good	Good	Good	0.35
	Silver stripping rate (μm/min)	1.8	1.9	1.7	Good
	Side surface stripping capacity	Good	Good	Good	1.6
					Good

Silver surface gloss prior to silver stripping is 0.40 (the higher is the numerical value, the higher is the gloss).

Table 1-3

		Comparative Examples		
		1	2	3
Bath composition	Main component 1	Succinimide 100 g/L	5,5-Dimethyl hydantoin 100 g/L	Sodium glutamate 100 g/L
	Main component 2	-	-	-
	pH buffer	-	-	-
	Surfactant	-	-	-
	Copper discoloration preventing agent	-	-	-
	Epoxy bleed-out preventing agent	-	-	-
	pH	9.0	10.5	10.5
	Current density (A/dm ²)	10.0	10.0	10.0
	Bath temperature (°C)	25	25	25
	Stirring rate (m/s)	0.5	0.5	0.5
Stripping conditions	Time (s)	30	30	30
	Silver surface appearance	Uneven	Uneven	Good
	Silver surface gloss	0.45	0.66	0.44
	Substrate appearance	Good	Good	Poor
Evaluation results	Silver stripping rate (μm/min)	1.7	1.9	0.4
	Side surface stripping capacity	Poor	Poor	Poor

Silver surface gloss prior to silver stripping is 0.40 (the higher is the numerical value, the higher is the gloss).

[0027] The electrolytic stripping agent for silver in accordance with the present invention, which comprises a hydantoin compound and an aminocarboxylic acid or a salt thereof as the main components has a long service life and high side surface stripping capacity and makes it possible to suppress the occurrence of unevenness or gloss increase on the silver surface of the necessary portions after silver stripping.

CLAIMS

1. An electrolytic stripping agent for silver, comprising a hydantoin compound and an aminocarboxylic acid or a salt thereof as the main components, excluding pyridines and cyclic polyamine compounds.
2. The electrolytic stripping agent for silver, according to claim 1, wherein the aminocarboxylic acid is a monoaminodicarboxylic acid.
3. The electrolytic stripping agent for silver, according to claim 1 or 2, which comprises, as the main components, hydantoin, 5,5-dimethylhydantoin, 5,5-dimethylhydantoin-3-hydroxymethyl, alantoin or salts thereof as the hydantoin compound, and asparagic acid, glutamic acid or salts thereof as the aminocarboxylic acid or salt thereof.