



US 20070221503A1

(19) **United States**

(12) **Patent Application Publication**
Larson et al.

(10) **Pub. No.: US 2007/0221503 A1**

(43) **Pub. Date: Sep. 27, 2007**

(54) **PRECOAT COMPOSITION FOR ORGANIC
SOLDERABILITY PRESERVATIVE**

Publication Classification

(51) **Int. Cl.**

C25D 5/54 (2006.01)

(52) **U.S. Cl.** **205/85**

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(57) **ABSTRACT**

An improved method of enhancing the solderability of a copper surface comprising the steps of contacting one or more copper surfaces with a pretreatment composition comprising a dilute solution of an aliphatic carboxylic acid and an additive selected from the group consisting of amines and ammonia and thereafter contacting the one or more surfaces with an organic solderability preservative composition. The improved organic solderability preservative process of the invention forms a more uniform coating that has a better appearance and color.

(21) Appl. No.: **11/386,901**

(22) Filed: **Mar. 22, 2006**

PRECOAT COMPOSITION FOR ORGANIC SOLDERABILITY PRESERVATIVE

FIELD OF THE INVENTION

[0001] The present invention is directed to an organic solderability preservative process for coating copper circuitry during printed wiring board manufacture. The improved process of the invention comprises the use of a pre-coat coating prior to the main organic solderability preservative bath to enhance solderability of the copper surfaces.

BACKGROUND OF THE INVENTION

[0002] In the manufacture of printed wiring boards (PWB) having metal containing components which are to be soldered, it is necessary to protect the metal from oxidation to enhance its solderability. Typically, many such electronic components have copper circuitry thereon and may also have gold leads or other electrical connections which are generally used to connect the electronic component to other electronic components.

[0003] Processes currently used to protect copper prior to soldering typically employ a protective coating deposited on the copper. Prior art processes include hot air solder leveling (HASL), organic solderability preservatives (OSP) and other metallic printed circuit board surface finishes. The protective coating provides protection against copper solderability degradation caused by various process steps in the fabrication process.

[0004] Copper protective coating systems utilize a number of steps including cleaning, microetching and acid rinsing followed by the formation of a protective coating on the copper using a solution containing a protective forming agent.

[0005] In general, the surface of the copper or copper alloy is first cleaned by immersion of the board in a cleaner and then preferably etched to increase the adhesion of the copper. The copper is then immersed in a solution containing an organic solderability preservative material such as triazole, imidazole, benzimidazole or derivatives thereof. Spraying or other forms of coating may also be used.

[0006] Cleaning of the PWB may be performed using any number of cleaners including alkaline, acid or neutral cleaners and is preferably an acidic cleaner comprising sulfuric acid, hydrochloric acid or citric acid. The PWB is typically contacted with the cleaner for up to about 5 minutes at a temperature of 80° to 120° F.

[0007] An etchant is preferably used to microetch the surface of the copper. Etchants such as an acidified persulfate salt such as sodium persulfate or sulfuric/peroxide type material at 70°-100° F. for about 1 min. are typically employed.

[0008] All the steps in the conventional OSP process are followed by rinsing the substrate typically with deionized water. Rinsing is usually performed at an ambient temperature.

[0009] Organic solderability protective coatings typically comprise a material such as a triazole, an imidazole or benzimidazole, or a derivative thereof. The substrate is treated with the OSP solution to form a protective layer on

the copper metallurgy. This is usually performed at a temperature of 95° to 115° F., preferably about 105° to 110° F. for about 15 seconds to 1 minute.

[0010] A number of patents have been issued for OSP coatings with an objective of providing protective coatings that are more uniform and have a better appearance, and with the goal of also improving solderability.

[0011] U.S. Pat. No. 5,658,611 to Ishiko et al., the subject matter of which is herein incorporated by reference in its entirety, provides an aqueous surface protection composition for PWB's containing a benzimidazole derivative that is adjusted to a pH of 1-5 with a salt forming acid of a heavy metal such as copper, manganese and zinc in an amount of less than 50 ppm.

[0012] U.S. Pat. No. 5,173,130 to Kinoshita et al., the subject matter of which is herein incorporated by reference in its entirety, describes a process for the surface treatment of copper which comprises immersing the surface of the copper in an aqueous solution containing a benzimidazole compound having an alkyl group of at least three carbon atoms at the 2-position and an organic acid. Similarly, in U.S. Pat. Nos. 5,498,301 and 5,560,785 to Hirao et al., the subject matter of each of which is herein incorporated by reference in its entirety, describe a water-based surface treatment agent used to protect copper on a printed wiring board with excellent heat-resistance and moisture-resistance which uses a 2-arylimidazole compound as an active ingredient.

[0013] U.S. Pat. No. 5,362,334 to Adams et al., the subject matter of which is herein incorporated by reference in its entirety, describes a composition and process for the surface treatment of metallic surfaces such as copper circuitry on printed circuit boards which comprises treating the surface with an aqueous solution comprising a benzimidazole compound having either a halogenated phenyl group, a halogenated benzyl group or a halogenated ethyl phenyl group in the 2-position.

[0014] U.S. Pat. No. 5,376,189 to Kukanskis, the subject matter of which is herein incorporated by reference in its entirety, describes a composition and process for the treatment of metallic surfaces such as copper on printed circuit boards which comprises treating the surface with an aqueous solution comprising a benzimidazole compound which has at least one carboxylic or sulfonic acid group directly or indirectly attached to the benzimidazole compound. The carboxylic acid or sulfonic acid group was believed to increase the solubility of the benzimidazole which provides for longer bath life and ease of operation.

[0015] U.S. Pat. No. 6,635,123 to Cavallotti et al., the subject matter of which is herein incorporated by reference in its entirety, provides for the addition of zinc salts in the OSP solution to improve copper surface characteristics. The addition of the zinc salts causes surface oxidation to decrease, both during soldering and during exposure to the atmosphere, and improves the wettability of the copper surface, even after extended periods at elevated temperatures. In addition, the addition of the zinc salts improves the adhesion of the tin solder alloy to the surface.

[0016] Other prior art processes have suggested forming a precoat layer on the copper surface prior to applying the final protective coating. For example, U.S. Pat. No. 4,373,

656 to Parker, Jr. et al., the subject matter of which is herein incorporated by reference in its entirety, describes a method for treating bare copper printed circuit boards comprising first subjecting the copper surfaces to a mild etch solution, stabilizing the surfaces by treatment with an aqueous solution of phosphoric acid in combination with a glycol and subsequently treating the surface with an azole (e.g., imidazole).

[0017] U.S. Pat. No. 6,524,644 to Wengenroth, the subject matter of which is herein incorporated by reference in its entirety, provides a pre-treatment step before the OSP coating to provide an enhanced final protective coating, comprising a benzimidazole compound and an alkanolamine. The pretreatment coating described by Wengenroth is believed to preserve the solderability of the copper surface while substantially excluding gold surfaces from attracting the OSP coating, which could cause cosmetic defects in the form of staining and possibly reduce the conductivity of the gold contact surface.

[0018] The inventors of the present invention have determined that additional improvements to the OSP coating process can be made that produce a more uniform coating having a better appearance and color. To that end, the inventors of the present invention have developed a novel pretreatment composition comprising an aliphatic carboxylic acid and preferably an amine. Once a substrate has been coated with the novel precoat composition of the invention, the substrate can be processed in the normal manner (i.e., coated with an OSP comprising an azole compound).

SUMMARY OF THE INVENTION

[0019] It is an object of the present invention to provide an improved OSP coating process that uses a pretreatment composition prior to the OSP coating.

[0020] It is another object of the present invention to use the improved OSP coating process of the invention to prepare electronic components such as printed wiring boards.

[0021] To that end, the present invention is directed to a method of enhancing the solderability of a copper surface comprising the steps of:

[0022] a) contacting one or more copper surfaces with a pretreatment composition comprising a solution of an aliphatic carboxylic acid and preferably an additive selected from the group consisting of amines and ammonia; and thereafter

[0023] b) contacting the one or more surfaces with an organic solderability preservative composition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] The present invention is directed to an improved protective coating system for coating copper metallurgy on printed wiring boards (PWB's) including copper pads and through holes.

[0025] In the present invention, a conventional azole-based OSP coating is improved by using a pre-treatment step, wherein the copper surfaces are contacted with a pre-treatment solution comprising an aliphatic carboxylic acid and preferably an amine before the OSP treatment. The

inventors of the present invention have found that the use of the pretreatment composition of the invention enhances the final protective coating on the copper surfaces and provides a more uniform coating that also has a better appearance and color.

[0026] More particularly, the present invention is directed to a method of enhancing the solderability of a copper surface comprising the steps of:

[0027] a) contacting one or more copper surfaces with a pretreatment composition comprising a dilute solution of an aliphatic carboxylic acid and preferably an additive selected from the group consisting of amines and ammonia; and thereafter

[0028] b) contacting the one or more surfaces with an organic solderability preservative composition.

[0029] The improved pretreatment layer of the invention is preferably a dilute mixture of an aliphatic carboxylic acid and an additive selected from amines and ammonia, although amines are generally most preferred. The aliphatic carboxylic acid is preferably of the C5-C9 chain length, including pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, and nonanoic acid. In a preferred embodiment, the aliphatic carboxylic acid is heptanoic acid. If used, the amine is typically selected from the group consisting of triethanolamine, dimethylamine, dipropylamine, diethanolamine, ammonia, and ethanolamine. In a preferred embodiment, the amine is triethanolamine or a similar compound.

[0030] One example of a solution that is usable in the practice of the invention is a dilute solution of heptanoic acid and triethanolamine at approximately 1 g/l each. Such solution is preferably approximately equimolar, i.e., contains about the same number of molecules of each component, and can be viewed as a solution of a salt between the triethanolamine and the heptanoic acid, with a pH of approximately 6. Preferably the concentration of the aliphatic carboxylic acid and the amine in the solution can be varied between about 1 g/l to about 10 g/l for each ingredient, preferably from about 1 g/l to about 5 g/l for each ingredient. Varying the ratio of acid and amine, and thus modifying the pH between about 4.5 and 9.5 is practical in the practice of this invention. A copper surface of a PCB leaving the precoat is hydrophobic, indicating the formation of a film. This film may be thinned, modified or desorbed during rinsing as evidenced by loss of hydrophobicity of the copper surface.

[0031] The pretreatment composition of the invention can be used at room temperature or higher. Preferably, the step of contacting the electronic component with the pretreatment composition comprises immersing the electronic component in the pretreatment composition. In this case, the dwell time of the electronic component in the solution can be between 1 and 5 minutes, preferably about 1 to 2 minutes.

[0032] A rinsing step may also be performed between the pretreatment step and the organic solderability preservative step to remove excess pretreatment solution.

[0033] A number of OSP solutions have been developed which may be used to form the OSP coating, examples of several of which have been cited herein. However, any suitable OSP solution described in the prior art may be used to provide the final coating on the substrate metallurgy.

Preferably, the organic solderability preservative comprises at least one azole, and more preferably, the azole is an imidazole.

[0034] The pretreatment composition and step of this invention is followed, preferably after rinsing, with the application of an organic solderability preservative. The organic solderability preservative is preferably an aqueous solution of a substituted or unsubstituted triazole, substituted or unsubstituted imidazole, substituted or unsubstituted benzimidazole, substituted or unsubstituted benzotriazole and/or substituted or unsubstituted azole. The inventors have found that imidazoles or benzimidazoles substituted with an alkyl group in the 2-position or the 5-position are most beneficial. 5-methyl Benzimidazole is particularly preferred. The concentration of the foregoing azoles in the aqueous OSP solution is preferably from 0.5 to 50 g/l and the pH is preferably from about 3 to 11. The copper surface is contacted with the OSP solution by immersion, spray or flood at from room temperature to about 180° F.

[0035] The benefit of using the precoat of the invention is a better organic solderability preservative coating, which provides a more uniform coating and that also has a better appearance. As a result, solderability is also better.

[0036] After the OSP treatment, the substrate is rinsed and typically dried by dry forced air. The substrate may then be soldered and is protected against oxidation until the soldering step is performed.

[0037] It can thus be seen that the present invention provides an improved solderable copper surface by using a novel precoat composition prior to an organic solderability preservative.

What is claimed is:

1. A method of enhancing the solderability of a copper surface comprising the steps of:

- a) contacting the copper surface with a pretreatment composition comprising a solution of an aliphatic carboxylic acid and optionally, but preferably, an additive selected from the group consisting of amines and ammonia; and thereafter
- b) contacting the one or more surfaces with an organic solderability preservative composition.

2. A method according to claim 1 wherein the organic solderability preservative composition comprises an aqueous solution of one or more materials selected from the group consisting of substituted or unsubstituted triazoles, substituted or unsubstituted imidazoles, substituted or unsubstituted benzimidazoles, substituted or unsubstituted benzotriazoles, and substituted or unsubstituted azoles.

3. The method according to claim 2, wherein the aliphatic carboxylic acid is selected from the group consisting of carboxylic acids with from 5 to 9 carbons.

4. The method according to claim 3, wherein the aliphatic carboxylic acid comprises heptanoic acid.

5. The method according to claim 2, wherein the additive is used and comprises an amine which is selected from the group consisting of triethanolamine, dimethylamine, dipropylamine, diethanolamine, ammonia, and ethanolamine.

6. The method according to claim 5, wherein the amine is triethanolamine.

7. The method according to claim 5, wherein the aliphatic carboxylic acid and the amine are each present in the pretreatment composition at a concentration between about 1 to about 10 g/l.

8. The method according to claim 2, wherein the pH of the pretreatment solution is between about 4.5 and about 9.5.

9. The method according to claim 8, wherein the pH of the pretreatment solution is about 6.0.

10. The method according to claim 2, wherein the pretreatment composition comprises the additive.

11. The method according to claim 2, wherein a rinsing step is performed between the pretreatment step and the organic solderability preservative step.

12. The method according to claim 2, wherein said step of contacting the electronic component with the pretreatment composition comprises immersing the electronic component in the pretreatment composition.

13. The method according to claim 12, wherein the electronic component is immersed in the pretreatment composition for about 1 to about 5 minutes.

14. The method according to claim 1, wherein the organic solderability preservative composition comprises at least one azole.

15. The method according to claim 14, wherein the at least one azole is an imidazole.

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