United States Patent [19]

Fong et al.

[11] **3,887,405**

[45] **June 3, 1975**

[54] **METHOD AND COMPOSITION FOR CLEANING COPPER SURFACES**

[75] Inventors: **Jaan-Jiue Fong,** Tolland; **Merton M. Beckwith,** Rockville, both of Conn.

[73] Assignee: **Minnesota Mining and Manufacturing Company,** St. Paul, Minn.

[22] Filed: **May 10, 1974**

[21] Appl. No.: **468,645**

[52] **U.S. Cl.** **156/18;** 134/3; 134/41; 252/79.2

[51] **Int. Cl.** **C23f 1/00**

[58] **Field of Search** 134/3, 41; 156/3, 8, 14, 156/18, 19; 252/79.1, 79.2; 117/49, 50

[56] **References Cited**

UNITED STATES PATENTS

2,291,202	7/1942	Bassett et al.	156/18 X
3,216,873	11/1965	Jones	156/14

Primary Examiner—William A. Powell
Attorney, Agent, or Firm—Peter L. Costas

[57] **ABSTRACT**

The surfaces of copper workpieces are mildly etched by an aqueous composition containing potassium monopersulfate, a water-soluble chloride and sulfuric acid sufficient to provide a pH of 0.2–1.8. An alkali metal sulfate is an optional additive, and the bath is operated at a temperature of 10°–70° Centigrade and preferably about 20°–35° Centigrade.

12 Claims, No Drawings

METHOD AND COMPOSITION FOR CLEANING COPPER SURFACES

BACKGROUND OF THE INVENTION

Occasionally, it is desirable to treat the surfaces of copper workpieces to provide a uniform surface finish and to prepare those surfaces for further finishing operations. Such pretreatment is particularly desirable in the instance of copper surfaces which are to be electroplated to form printed circuits or other electrical components since such pretreatment can materially improve the adhesion of the deposit and the uniformity of the deposit.

Among the various compositions which have been used for the purpose are conventional ammonium persulfate solutions which tend to rapidly deteriorate and which exhibit an undesirable characteristic in the tendency of the dissolved copper to deposit from the solution on the surface of the workpiece as the copper condensation increases. This redeposition characteristic is particularly undersirable because it materially affects adhesion of the subsequent metal deposit and it also undesirably affects solderability.

A number of etchants have been proposed which will rapidly attack and dissolve the copper but excessive attack is undesirable where only pretreatment is sought. Rendering dilute the solutions of the more active etchants does not necessarily achieve the desired result of uniform, controlled mild etching of the surface as is desired for the pretreatment of the copper surface.

Accordingly, it is an object of the present invention to provide an aqueous composition which will mildly etch the surface of copper workpieces and which will provide uniform etching action over extended periods of use.

It is also an object to provide such a composition which demonstrates long life and resistance to redeposition of dissolved copper even when the copper concentration approaches the working limit for the solution.

Another object is to provide a simply and highly effective method for mildly etching the surfaces of copper workpieces and which method does not require highly controlled operation or critical immersion times.

SUMMARY OF THE INVENTION

It has now been found that the foregoing and related objections may be readily attained by a mild etchant for copper workpieces consisting essentially of an aqueous solution of 60–240 grams per liter of an alkali metal monopersulfate, 15–500 parts per million of a water-soluble inorganic chloride compound, sulfuric acid in an amount sufficient to provide a pH of 0.2–1.8, and up to 10 grams per liter of an alkali metal sulfate.

In the preferred compositions, the alkali metal monopersulfate is potassium monopersulfate and is present in an amount of 90–200 grams per liter. The water-soluble inorganic chloride is present in an amount of less than 300 parts per million, and the alkali metal sulfate is present in an amount of 0.5–4 grams per liter. The etchants are desirably operated at a pH of 0.8–1.5 through adjustment with the sulfuric acid and the most desirable compositions contain the chloride in an amount of 30–60 parts per million.

In the method of etching, the solution is prepared and maintained at a temperature of 10°–70° Centigrade. The workpiece having a copper surface is immersed in the solution for a period of time sufficient to produce the desired uniform etching action upon the surface of the workpiece. The bath is preferably operated at a temperature of 20°–35° Centigrade and at a pH of 0.8–1.5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As has been previously indicated, the compositions of the present invention necessarily contain alkali metal monopersulfate, water-soluble inorganic chloride compound and sulfuric acid. Alkali metal sulfate is an optional though desirable additive as will be explained hereinafter.

Although sodium and lithium monopersulfates do provide the necessary monopersulfate radical, potassium monopersulfate has been found highly advantageous and is more readily available commercially. Ammonium monopersulfate is undesirable because of the tendency of the ammonium ion to complex the dissolved copper and to cause problems both in bath operation and in subsequent waste treatment. As indicated hereinbefore, the monopersulfate many range from as little as 60 grams per liter to as much as 240 grams per liter, but the rate of etching tends to decrease as the concentration exceeds about 200 grams per liter. Thus, the preferred compositions contain the monopersulfate salt in the range of 90–200 grams per liter and most desirably about 100–140 grams per liter.

The chloride ion is extremely advantageous and produces a fine grain, unstained surface finish. It is effective for this purpose in very small amounts ranging from as low as 15 parts per million. The amount of chloride compound may range as high as 500 parts per million but there is a tendency for chloride fumes to emanate from the bath as the concentration exceeds 300 parts per million. Thus, the most desirable range of operation is about 30–60 parts per million. The chloride compound can be any water-soluble noninterfering salt and the alkali metal chlorides have proven particularly advantageous.

As indicated hereinbefore, the bath is intended to be operated at a pH of 0.2–1.8 and preferably in the range of 0.8–1.5. As a result, sulfuric acid is added to the bath in an amount sufficient to adjust the pH to the desired operating point.

The alkali metal sulfate is not an essential component of the bath but it is desirably employed as a means for blending the alkali metal or other inorganic chloride salt with the monopersulfate salt. A preblend of alkali metal sulfate and chloride compound is formed and then this preblend is admixed with the monopersulfate to produce the desired powder composition. The preferred alkali metal sulfate is sodium sulfate, although potassium sulfate may also be employed advantageously and avoids the introduction of another cation. The amount of sulfate salt may range as high as 10 grams per liter but is preferably maintained at an amount of less than 4 grams since it is effectively only a diluent.

As indicated hereinbefore, the bath may be operated over a fairly wide range of 10°–70° Centigrade but is preferably maintained at a range of about 20°–35° Centigrade. The time of immersion of the workpiece in the bath will vary with the operating conditions selected and the concentration of the several components. Generally, the time of immersion for a given workpiece is

best determined empirically by visual observation of the surface effects produced with immersion times of as little as one minute producing desirable results in many instances.

In formulating the compositions, the dry powder components are first blended to provide a powder additive which is then admixed with water and sulfuric acid. Alternatively, the several components can be individually added to water to produce the desired bath.

Because of the highly corrosive nature of the solution, it is desirably maintained in tanks of synthetic resin such as polyvinyl chloride or polypropylene or metal tanks lined with synthetic resin or rubber. Pipes and other fluid handling materials should be selected to resist the corrosive action.

The solution is particularly advantageously employed upon copper intended for printed circuit board applications where it is desired to achieve both a uniform surface and good adhesion of the subsequent metal deposit whether produced by electrolytic or electroless techniques. The resulting uniform surface characteristics significantly improve the appearance and condition of the metal deposit thereon. The solution may be used as an immersion dip to remove tarnish and similar films from copper surfaces which are otherwise free from soil or surface aberration.

After the solution is spent, copper can be readily recovered therefrom by adjusting the pH to 10.0 or above and heating the solution to at least 70° Centigrade for two hours or more. Upon cooling of the solution, a copper oxide precipitate will form and precipitation can be enhanced by adding small quantities of a polyelectrolyte.

Illustrative of the efficacy of the present invention are the following specific examples wherein all parts are parts by weight unless otherwise indicated.

EXAMPLE ONE

A dry powder concentrate is prepared containing 98 parts potassium monopersulfate, 1.94 parts sodium sulfate and 0.06 part sodium chloride. This concentrate is added to water in an amount sufficient to provide 120 grams per liter thereof and 1 percent by volume sulfuric acid (66° Baumé) is added to adjust the pH to 1.30. The bath is maintained at a temperature of 21° Centigrade.

Copper surfaced workpieces are immersed therein for varying periods of time and the etching rate (the rate of dissolution of copper) is determined to be 1.95 mils copper per hour. The surface of the copper workpieces is found to be uniform in character, clean and free from streaking.

EXAMPLE TWO

To determine the effect of variation of concentration of the composition, the amount of powder concentrate added to water is varied and the etching rate at the various concentrations measured.

Powder Concentrate Grams per Liter	Etching Rate Mils per Hour
20	0.39
60	0.93
120	1.95
200	1.68
268	0.33

As can be seen, the etching rate reaches an optimum level at about 120 grams per liter of the powder concentrate and then begins to decrease. At the higher cencentration levels, i.e., those approaching 268 grams per liter or saturation, there is a tendency for the salt to deposit upon the surface of the copper workpieces and this in turn inhibits etching action.

EXAMPLE THREE

To determine the effect of temperature variations, a bath produced in accordance with Example One is operated at several different temperatures and the etching rate is measured at each of the temperatures.

Temperature, ° Centigrade	Etching Rate Mils Per Hour
4	0.57
24	2.40
71	5.73

As the temperature is increased above 70° Centigrade, there appears to be definite instability of the bath, possibly resulting from decomposition of the potassium monopersulfate.

EXAMPLE FOUR

To determine the effect of variation in the pH of the solution, the composition of Example One is prepared except that the amount of sulfuric acid is varied. In addition, the temperature in this particular set of experiments is maintained at 24° Centigrade.

Sulfuric Acid % By Volume	pH	Etching Rate Mils Per Hour
0	1.80	1.42
0.5	1.40	1.96
1.0	1.30	2.76
2.0	0.95	2.96
4.0	0.76	2.02

As can be seen, adjusting the pH into the preferred range significantly improves the etching rate. Efforts to use hydrochloric acid or nitric acid for such pH adjustment produces excessive fuming.

EXAMPLE FIVE

To determine the effect of the chloride salt, a series of formulations is prepared each containing 120 grams per liter potassium monopersulfate and 1 percent by volume sulfuric acid. The amount of sodium chloride added is varied, the temperature is maintained at 21° Centigrade, and the etching rate upon the copper specimens is determined.

Sodium Chloride Parts per Million	Etching Rate Mils per Hour
0	2.37
50	2.37
100	2.40
500	2.19
1000	2.16

The specimens treated in the bath which did not contain chloride ion evidenced streaking and staining and a coarser grain surface. As the chloride ion was increased to 100 parts per million, the etching rate was slightly improved, streaking was eliminated and a fine grain finish was obtained. As the chloride concentration approached 500 parts per million, the etching rate was reduced and some detrimental effect on quality of the finish was observed.

As can be seen from the foregoing detailed specification and examples, the compositions of the present invention provide a novel and highly effective bath for mildly etching the surfaces of copper workpieces so as to produce a uniform, fine grain surface finish which is free from staining and which functions as a useful base for the subsequent deposition of other metals. The compositions may be operated from ambient through moderately elevated temperatures and are capable of retaining in solution a large amount of dissolved copper without any significant tendency for redeposition upon the copper workpieces.

Having thus described the invention, we claim:

1. A mild etchant for copper workpieces consisting essentially of an aqueous solution of 60–240 grams per liter of an alkali metal monopersulfate, 15–500 parts per million of a water-soluble inorganic chloride compound, sulfuric acid in an amount sufficient to provide a pH of 0.2–1.8, and up to 10 grams per liter of an alkali metal sulfate.

2. The etchant in accordance with claim **1** wherein said alkali metal monopersulfate is potassium monopersulfate.

3. The etchant in accordance with claim **1** wherein said alkali metal sulfate is present in an amount of 0.5–4 grams per liter.

4. The etchant in accordance with claim **1** wherein said water-soluble inorganic chloride compound is an alkali metal chloride and is present in an amount of less than 300 parts per million.

5. The etchant in accordance with claim **1** wherein the said alkali metal monopersulfate is potassium monopersulfate in an amount of 90–200 grams per liter, wherein said water soluble chloride compound is an alkali metal chloride and is present in an amount of 30–60 parts per million, and wherein said sulfuric acid is present in an amount sufficient to provide a pH of 0.8–1.5.

6. The etchant in accordance with claim **5** wherein said alkali metal sulfate is present in an amount of 0.5–4 grams per liter.

7. A method for mildly etching the surfaces of copper workpieces comprising preparing an aqueous solution consisting essentially of 60–240 grams per liter of an alkali metal monopersulfate, 15–500 parts per million of a water-soluble inorganic chloride compound, sulfuric acid in an amount sufficient to provide a pH of 0.2–1.8 and up to 10 grams per liter of an alkali metal sulfate; maintaining said aqueous solution at a temperature of 10°–70° Centigrade; and immersing a workpiece having a copper surface in said solution for a period of time sufficient to produce the desired uniform etching action upon the surface of the workpiece.

8. The method in accordance with claim **7** wherein said solution is maintained at a termperature of 20°–35° Centigrade and wherein the sulfuric acid provides a pH of 0.8–1.5.

9. The method in accordance with claim **7** wherein said alkali metal monopersulfate is potassium monopersulfate.

10. The method in accordance with claim **7** wherein said alkali metal sulfate is present in an amount of 0.5–4 grams per liter.

11. The method in accordance with claim **7** wherein said water-soluble inorganic chloride compound is an alkali metal chloride and is present in an amount of less than 300 parts per million.

12. The method in accordance with claim **7** wherein the said alkali metal monopersulfate is potassium monopersulfate in an amount of 90–200 grams per liter, wherein said water soluble chloride compound is an alkali metal chloride and is present in an amount of 30–60 parts per million, and wherein said sulfuric acid is present in an amount sufficient to provide a pH of 0.8–1.5.

* * * * *