

Surface Treatment Liquid for Copper-Containing Metal

The present invention relates to a surface treatment liquid for a copper-containing metal. Particularly, the present invention relates to an aqueous liquid composition for chemically polishing or cleaning a surface of a copper-containing metal material.

It is well known that copper-containing metal materials, namely copper materials or copper alloy materials, have an excellent electrical conductivity and an economical advantage and are thus widely utilized as materials for electric and electronic parts. However, when a copper-containing metal material is processed into a product, a various works, for example, rolling and punching, are applied to the metal applied, and various problems, for example, flash formation and surface-discoloration of the metal material, occur. These problems affect any the surface finish process, for example, a plating process, of the copper-containing metal products and thus the copper-containing metal product is generally surface-treated with a surface treatment liquid to solve the above-mentioned problems.

As a conventional surface treatment liquid for the copper-containing material, a mixed acid consisting of sulfuric acid, nitric acid and hydrochloric acid or a chromate-containing aqueous solution is used. The mixed acid has a disadvantage in that a harmful NO_x gas is generated during the treatment therewith. Also, the chromate-containing solution contains hexavalent chromium ions, and thus the waste solution therefrom must be treated to make it harmless. Namely, the conventional surface treatment liquids are not preferable from the point of view of environment protection.

To avoid the above-mentioned disadvantages, currently, a surface treatment liquid containing hydrogen peroxide and a mineral acid, for example, sulfuric acid, which does not generate an environmental problem, is utilized.

When the surface treatment liquid comprising hydrogen peroxide and the mineral acid is used, the treatment results of the copper-containing metal depend heavily on the dissolution rate of the copper-containing metal in the surface treatment solution. Generally, when the dissolution rate is too high, the resultant surface of the copper-containing metal exhibits a reduced smoothness. Also, the treating capacity of the surface treatment liquid is variable in response to the concentrations of the effective components. To enhance the treating capacity, the concentration of the effective components must be increased. However, an increase in the concentrations of the effective components causes the dissolution rate of the copper-containing metal with the surface treatment liquid to increase and thus affects the surface conditions and appearance of the resultant finished product.

Namely, the conventional surface treatment liquid comprising hydrogen peroxide and a mineral acid is disadvantageous in that when a surface treatment liquid having an increased treatment capacity, namely, an increased concentrations of the effective components, is used, the resultant finished products exhibit an unsatisfactory surface condition and appearance.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a surface treatment liquid, for a copper-containing metal, having a satisfactory treatment capacity and dissolution rate and an enhanced stability of the dissolution rate.

Another object of the present invention is to provide a surface treatment liquid, for a copper-containing metal, capable of imparting a satisfactory

surface condition and appearance to the treated copper-containing metal.

The above-mentioned objects can be attained by the surface treatment liquid of the present invention for copper-containing metal, which comprises:

(A) an aqueous acid solution comprising hydrogen peroxide, a mineral acid and a stabilizer for hydrogen peroxide; and

(B) a metal dissolution rate regulator comprising at least one member selected from the group consisting of amino-phenolsulfonic acid and benzamide.

In the surface treatment liquid of the present invention, the metal dissolution rate regulator can be protected from degradation during the storage and transportation thereof before employment or during employment under severe conditions by optionally adding sulfanilic acid to the surface treatment liquid.

Also, an optional addition of ammonium hydrogenfluoride to the surface treatment liquid is contributory to enhancing the smoothness and gloss of the copper-containing metal surface.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph showing a relationship between the amount of a dissolved copper alloy and the dissolution rate of the copper alloy when the copper alloy is surface-treated with a surface treatment liquid of the present invention or with a comparative surface treatment liquid.

BEST MODE OF CARRYING OUT THE INVENTION

The surface treatment liquid of the present invention for a copper-containing metal, comprises a metal dissolution rate regulator (B) comprising at least one member selected from the group consisting of aminophenolsulfonic acid and benzamide, in addition to an aqueous acid solution (A) comprising hydrogen peroxide, a mineral acid and a hydrogen peroxide-stabilizer.

The metal dissolution rate regulator (B) of the

present invention is contributory to minimizing a change in the dissolution rate of the copper-containing metal in the surface treatment liquid in response to the concentration of the dissolved metal.

The surface treatment liquid of the present invention optionally contains sulfanilic acid which is contributory to minimizing a change in the dissolution rate of the copper-containing metal in the surface treatment liquid, in response to the lapse of time.

The surface treatment liquid of the present invention optionally contains ammonium hydrogenfluoride which contributes to enhancing the smoothness and gloss of the treated copper-containing metal surface.

The surface treatment liquid of the present invention is useful for the surface treatment of copper-containing metals, namely metallic copper and copper alloys, for example, copper-tin alloys, copper-tin-chromium alloys, copper-tin-silicon-nickel alloys, and copper-nickel-silicon-magnesium alloys, which are merely representative and do not limit the scope of the copper alloys to which the surface treatment liquid of the present invention can be applied, in any way.

In the surface treatment liquid of the present invention, the concentrations of hydrogen peroxide and the mineral acid are variable depending on the desired dissolution rate and the amount of the copper-containing metal material to be surface-treated. Preferably the surface treatment liquid of the present invention contains hydrogen peroxide in a concentration of 10 to 150 g/liter, more preferably 20 to 50 g/liter, and the mineral acid in a concentration of 10 to 300 g/liter, more preferably 50 to 200 g/liter.

If the concentrations of hydrogen peroxide and/or the mineral acid are less than 10 g/liter, the resultant surface treatment liquid may exhibit an unsatisfactory metal-dissolution effect. Also, if the concentrations of hydrogen peroxide and/or the mineral acid are more than

150 g/liter and 300 g/liter, respectively, the resultant surface treatment liquid may exhibit too high a dissolution rate and a reduced surface gloss.

The mineral acid usable for the present invention includes preferably sulfuric acid, nitric acid and phosphoric acid and, more preferably, consists essentially of sulfuric acid.

The aqueous acid solution (A) contains a stabilizer in addition to hydrogen peroxide and the mineral acid. The stabilizer can restrict a wasteful decomposition of hydrogen peroxide even at a high concentration of the metal dissolved in the surface treatment liquid, and thus is contributory to improving the smoothness, gloss and uniformity of the resultant surface-treated copper-containing metal surface.

The stabilizer comprises at least one member selected, preferably, from alcohols, amines, ethers and carboxylic acids, more preferably from alcohols, and still more preferably from aliphatic alcohols.

The aliphatic alcohols usable as a stabilizer include ethyl alcohol, propyl alcohols, ethylene glycol, diethylene glycol and triethylene glycol. The amines include monobutylamine, dibutylamine, tributylamine and isomers thereof. The ethers include polyoxyethyleneglycolether, polyoxyethylene nonylphenylether and polyoxyethyleneoctylphenylether. The carboxylic acids include benzoic acid, salicylic acid and dipicolinic acid.

The stabilizer is contained preferably in a concentration of 0.1 to 30 g/liter, more preferably 1 to 10 g/liter, in the surface treatment liquid of the present invention.

If the concentration of the stabilizer is less than 1 g/liter, the resultant stabilizing effect on hydrogen peroxide may be insufficient. Also, if the concentration is more than 10 g/liter, the resultant surface treatment liquid may exhibit an undesirably decreased metal

dissolution rate and may degrade the surface conditions.

The metal dissolution rate regulator comprising aminophenolsulfonic acid and/or benzamide is contained preferably in a concentration of 0.1 to 10 g/liter, more preferably 1 to 5 g/liter, in the surface treatment liquid of the present invention. The concentration of the metal dissolution rate regulator is variable dependent on the initial concentrations of hydrogen peroxide and/or the mineral acid and the desired metal dissolution rate.

If the concentration of the metal dissolution rate regulator is 0.1 g/liter, the resultant surface treatment liquid may exhibit an unsatisfactory stability in the metal dissolution rate. Also, if the concentration is more than 10 g/liter, the resultant surface treatment liquid may be disadvantageous in that the metal dissolution rate significantly decreases and thus the treatment becomes difficult to effect.

Where sulfanilic acid is added to the surface treatment liquid of the present invention, the concentration of sulfanilic acid is established in consideration of the initial concentrations of hydrogen peroxide and the mineral acid and the desired metal dissolution rate, and is preferably in the range of from 0.1 to 20 g/liter, more preferably 1 to 10 g/liter.

When sulfanilic acid is used together with the metal dissolution rate regulator, since not only the change in the metal dissolution rate with the change in the concentration of the dissolved metal can be restricted, but also the change in the metal dissolution rate with the lapse of time can be restricted, and therefore, the change in the metal dissolution rate throughout the surface treatment can be minimized and the smoothness and appearance of the treated copper-containing metal surface can be improved.

If the concentration of sulfanilic acid is less than 0.1 g/liter, the resultant surface treatment liquid may

exhibit an unsatisfactory prevention effect on the change in the metal dissolution rate with time. If the concentration is more than 20 g/liter, the resultant surface treatment liquid may be disadvantageous in that, since the solubility of sulfanilic acid is low, the sulfanilic acid therein crystallizes and deposits.

The surface treatment liquid of the present invention is optionally supplied with ammonium hydrogenfluoride which is contributory to enhancing the gloss of the treated copper-containing metal surface. There is no strict limitation to the concentration of ammonium hydrogenfluoride. Preferably, ammonium hydrogenfluoride is used in a concentration of 0.1 to 100 g/liter, more preferably 1 to 50 g/liter. If the concentration of ammonium hydrogenfluoride is less than 0.1, the resultant gloss-enhancing effect may be insufficient. Also, if the concentration is more than 100 g/liter, the resultant surface treatment liquid may be disadvantageous in that the metal dissolution rate significantly increases and thus the surface treatment becomes difficult to control.

The surface treatment of the copper-containing metal with the surface treatment liquid of the present invention is carried out preferably at a temperature of 10 to 60°C, more preferably 20 to 50°C for a treatment time of from 10 seconds to 10 minutes, more preferably from 20 seconds to 5 minutes. The surface treatment is carried out by immersing a copper-containing metal article in the surface treatment liquid. The treated metal article is then removed from the surface treatment liquid, rinsed with water and dried.

EXAMPLES

The present invention will be further explained by the following examples.

Examples 1 to 7

In each of Examples 1 to 7, a surface treatment liquid was prepared by mixing an aqueous solution of

30 g/liter of hydrogen peroxide, 150 g/liter of sulfuric acid and 1 g/liter of ethylene-glycol with the compound or compounds as shown in Table 1 in the concentration or concentrations as shown in Table 1.

A lead frame consisting of a copper-tin (Cu/Sn) alloy was immersed in the surface treatment liquid at a temperature of 40°C for one minute, rinsed with water and dried.

The dissolution rate of the copper-tin alloy in the surface treatment liquid was determined in accordance with the following equation:

$$D_r (\%) = \frac{W_0 - W_1}{W_0} \times 100$$

wherein D_r represents the metal dissolution rate (%), W_0 represents a weight of the copper-tin alloy before the surface treatment and W_1 represents a weight of the copper-tin alloy after the surface treatment at 40°C for one minute.

The measurement of the metal dissolution rate (D_r) was carried out at the following stages.

Stage A-①: A stage immediately after preparation of the surface treatment liquid which had a concentration of the dissolved Cu/Sn alloy of zero

Stage A-②: A stage at which the concentration of the dissolved Cu/Sn alloy reached 10 g/liter

Stage A-③: A stage at which the concentration of the dissolved Cu/Sn alloy reached 20 g/liter

Stage B-①: A stage immediately after storage of a fresh surface treatment liquid at a temperature of 50°C for 14 days

Stage B-②: A stage immediately after storage of the fresh surface treatment liquid at a

temperature of 50°C for 30 days

Stage B-③: A stage immediately after storage of the fresh surface treatment liquid at a temperature of 50°C for 60 days

Further, the surface conditions of the treated Cu/Sn alloy were checked by the naked eye and at the above-mentioned stage A-① to B-③, and evaluated as follows.

Class	Surface conditions
4	Excellent in uniformity, smoothness and gloss
3	Satisfactory in uniformity, smoothness and gloss
2	Partially uneven in smoothness and gloss
1	Entirely uneven in smoothness and gloss

The test results are shown in Tables 1 and 2.

Fig. 1 shows a relationship between the dissolved metal concentration and the metal dissolution rate of Example 3.

Comparative Example 1

The same procedures as in Example 3 were carried out except that 2-aminophenyl-4-sulfonic acid and sulfanilic acid were not employed. The test results are shown in Tables 1 and 2.

Fig. 1 shows a relationship between the dissolved metal concentration and the metal dissolution rate of Comparative Example 1.

Fig. 1 shows that in Example 1, the initial metal dissolution rate of the surface treatment liquid is significantly reduced in comparison with that of Comparative Example 1, and the metal dissolution rate in Example 1 decreased very gradually with increase in metal concentration whereas in Comparative Example 1, the metal dissolution rate decreased rapidly with increase in metal

concentration.

Table 1

Item Example No.	Metal dissolution rate-regulator and additive (g/liter)	Metal dissolution rate (%)					
		Stage			Stage		
		A-①	A-②	A-③	B-①	B-②	B-③
Comparative Example 1	None	4.16	2.38	0.59	-	-	-
1	Benzamide (1.0)	0.93	0.60	0.30	1.58	2.58	3.76
2	2-Aminophenol-4- sulfonic acid (1.0)	1.20	0.69	0.21	1.58	2.61	3.85
3	2-Aminophenol-4- sulfonic acid (1.0) Sulfanilic acid (5.0)	1.20	0.69	0.21	1.15	1.20	1.33
4	Benzamide (1.0) Sulfanilic acid (5.0)	1.31	0.73	0.23	1.20	1.30	1.35
5	2-Aminophenol-4- sulfonic acid (1.0) Ammonium hydrogenfluoride (5.0)	1.22	0.71	0.20	1.60	2.60	3.96
6	2-Aminophenol-4- sulfonic acid (1.0) Sulfanilic acid (5.0) Ammonium hydrogenfluoride (5.0)	1.21	0.74	0.30	1.22	1.28	1.30
7	2-Aminophenol-4- sulfonic acid (1.0) Benzamide (1.0) Sulfanilic acid (5.0)	1.01	0.52	0.18	1.10	1.22	1.29

Table 2

Item Example No.	Metal dissolution rate-regulator and additive (g/liter)	Finished surface condition						
		Stage			Stage			
		A-①	A-②	A-③	B-①	B-②	B-③	
Comparative Example 1	None	1	1	1	-	-	-	
1	Benzamide (1.0)	3	3	3	2	1	1	
2	2-Aminophenol-4-sulfonic acid (1.0)	3	3	3	2	1	1	
3	2-Aminophenol-4-sulfonic acid (1.0) Sulfanilic acid (5.0)	3	3	3	3	3	3	
4	Benzamide (1.0) Sulfanilic acid (5.0)	3	3	3	3	3	3	
5	2-Aminophenol-4-sulfonic acid (1.0) Ammonium hydrogenfluoride (5.0)	4	4	4	4	4	4	
6	2-Aminophenol-4-sulfonic acid (1.0) Sulfanilic acid (5.0) Ammonium hydrogenfluoride (5.0)	4	4	4	4	4	4	
7	2-Aminophenol-4-sulfonic acid (1.0) Benzamide (1.0) Sulfanilic acid (5.0)	3	3	3	3	3	3	

Tables 1 and 2 shows that the metal dissolution rate regulator of the present invention effectively restricts the change in the metal dissolution rate due to the increase in the concentration of metal dissolved in the surface treatment liquid, the addition of sulfanilic acid effectively restricts the change in the metal dissolution rate with the time lapse, and the addition of ammonium hydrogenfluoride advantageously improves the surface condition of the treated copper-containing metal.

Comparative Example 2

A surface treatment liquid was prepared by the same procedures as in Example 3 except that 2-aminophenol sulfonic acid and sulfanilic acid were not employed, and an aqueous solution of 7 g/liter of hydrogen peroxide, 150 g/liter of sulfuric acid and 1 g/liter of ethylene glycol was used as a comparative surface treatment liquid which exhibited an initial dissolution rate (about 1.3%) of the Cu/Sn alloy similar to that of Example 3. The Cu/Sn alloy lead frame was treated by the comparative surface treatment liquid by the same procedures as in Example 3.

It was found that when the concentration of the Cu/Sn alloy dissolved in the comparative surface treatment liquid reached 7 g/liter, the dissolution of the Cu/Sn alloy was stopped.

Although the initial metal dissolution rate of the surface treatment liquid of Comparative Example 2 was approximately the same as that of Example 3, the treatment capacity of the surface treatment liquid of Comparative Example 2 was about one third of that of Example 3.

The present invention is contributory to obtaining a surface treatment liquid capable of surface treating a copper-containing metal with a small change in the metal dissolution rate due to increase in the dissolved metal concentration, and of providing a treated surface with an enhanced uniformity, smoothness and gloss. Therefore,

the surface treating liquid of the present invention has a significantly enhanced treatment capacity and stability with respect to storage, transportation and use under severe conditions.

Also, in the present invention, the addition of sulfanilic acid effectively restricts the change in the metal dissolution rate with the time lapse, and the addition of ammonium hydrogenfluoride effectively enhance the surface conditions, for example, uniformity, smoothness and gloss of the treated copper-containing metal surface.



CLAIMS

1. A surface treatment liquid for copper-containing metal, comprising

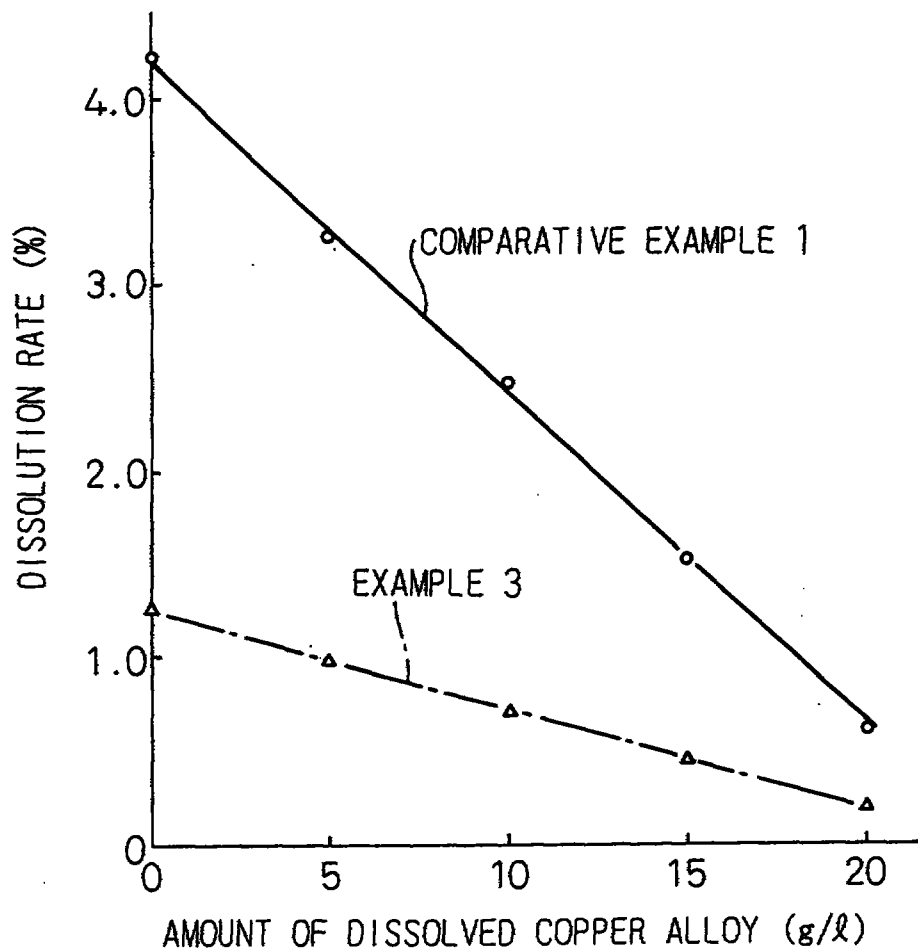
(A) an aqueous acid solution comprising hydrogen peroxide, a mineral acid and a stabilizer for hydrogen peroxide; and

(B) a metal dissolution rate regulator comprising at least one member selected from the group consisting of amino-phenolsulfonic acid and benzamide.

2. The surface treatment liquid as claimed in claim 1, further comprising sulfanilic acid.

3. The surface treatment liquid as claimed in claim 1 or 2, further comprising ammonium hydrogenfluoride.

Fig. 1



ABSTRACT

SURFACE TREATMENT LIQUID FOR COPPER-CONTAINING METAL

A surface treatment liquid for copper-containing metal, having a high treatment capacity and a capability of forming a smooth surface, includes (A) an aqueous acid solution including hydrogen peroxide, a mineral acid and a H_2O_2 stabilizer, (B) a metal dissolution rate-regulator including aminophenolsulfonic acid and/or benzamide and optionally an additive such as sulfanilic acid, as an agent for preventing change in metal dissolution rate with the lapse of time, and/or ammonium hydrogenfluoride as a surface-smoothing agent.

(Figure 1)

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