United States Patent

Gulla

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[54] **ELECTROLESS COPPER PLATING**

[72] Inventor: **Michael Gulla, Newton, Mass.**

[73] Assignee: **Shipley Company, Inc., Newton, Mass.**

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[52] U.S. Cl..............................**106/1**, 117/47 A, 117/130 E,
117/160 R
[51] Int. Cl...**C23c 3/02**
[58] Field of Search ....**106/1; 117/47 A, 130, 130 E,**
117/160 R

[56] **References Cited**

UNITED STATES PATENTS

3,457,089	7/1969	Shipley et al.	.............................106/1
3,472,664	10/1969	Bastenbeck et al.	........................106/1

Primary Examiner—Lorenzo B. Hayes
Attorney—Dike Bronstein and Roberts and Cushman

[57] **ABSTRACT**

The invention is directed to an electroless copper solution characterized by inclusion of a polyether adduct of an alkine alcohol and an alkylene oxide for improved solution stability and deposit appearance.

27 Claims, No Drawings

ELECTROLESS COPPER PLATING

BACKGROUND OF THE INVENTION

1. Introduction

This invention relates to autocatalytic deposition of copper and has for its principle object, the provision of an improved copper plating solution and decomposition methods embodying the same.

2. Description of the Prior Art

Electroless copper deposition refers to the chemical plating of copper over active surfaces in the absence of an external electric current. Such processes and compositions useful therefor are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example, U.S. Pat. No. 3,011,920 and 3,457,089.

Known electroless copper deposition solutions comprise four ingredients dissolved in water. These are (1) a source of cupric ions, usually copper sulphate, (2) formaldehyde as reducing agent therefor, (3) alkali, generally an alkali metal hydroxide and usually sodium hydroxide, sufficient to provide the required alkaline solution in which said compositions are effective, and (4) a complexing agent for the copper sufficient to prevent its precipitation in alkaline solution. A large number of suitable complexing agents are known and are described for example in the above cited patents and also in U.S. Pat. Nos. 2,874,072; 3,075,856; 3,119,709 and 3,075,855.

The above compositions containing both an oxidizing and a reducing agent present in the same solution, have limited stability and tend to trigger (spontaneously decompose) with reduction of substantially all of the copper in the solution not only on the part to be plated, but on the walls of containers, stirring elements and the like. Consequently, it is customary to include stabilizers in the composition which provide resistance against triggering and which increase the range of useable concentration and temperature without destroying the capacity of the solutions to deposit copper by reduction at catalytic surfaces in contact therewith.

In U.S. Pat. No. 3,457,089, referenced above, there is disclosed and claimed improved copper plating baths containing as stabilizer, a soluble lower molecular weight alkine alcohol where the acetylenic group, particularly such group containing an active hydrogen atom, is believed to be the effective portion. The stabilizer is generally added in amounts varying between about 2.5 and 2000 parts per million parts of total solution dependent upon the molecular weight of the alcohol, the higher molecular weight alcohols being less soluble in solution than the lower molecular weight alcohols.

SUMMARY OF THE INVENTION

In accordance with the subject invention, it has been found that improved stabilization as well as improved deposit appearance is achieved when the stabilizer used for the electroless copper depositing solution is a polyether adduct of an alkine alcohol and an alkylene oxide. The alkine alcohols contemplated for formation of the adduct are those of the above mentioned U.S. Pat. No: 3,457,089 as well as higher molecular weight homologues thereof and aryl substituted alkine alcohols. It has been found that the adducts have greater solubility in solution than alkine alcohols from which they are formed and therefore, higher molecular weight alcohols can be used. This is believed to be responsible for increased stabilization. Improved deposit appearance is believed to be due to the surfactant affect of the non-ionic hydrophobes of the polyether resulting from the epoxidation of the alkylene oxide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The components of the polymeric adduct in accordance with the invention comprise an alkine alcohol and an alkylene oxide. The alkine alcohols useful in forming the adduct correspond to one of the following formulas:

$$HC \equiv C - R - OH \text{ or } HO - R' - C \leq R'' - OH$$
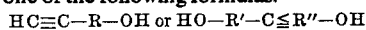
where each of R, R' and R'' individually are divalent alkylene, cycloalkylene, alkylene ether, and arylene radicals, said radicals having from one to 12 carbon atoms. Useful examples of alkine alcohols corresponding to the above formulas include the following:

(1) Ethynl cyclohexanol

$$
\begin{array}{c}
CH_2-CH_2 \quad C\equiv CH \\
CH_2 \qquad\qquad C \\
CH_2-CH_2 \quad OH
\end{array}
$$

(2) Methyl butynol

$$
\begin{array}{c}
CH_3 \\
CH_3-C\equiv CH \\
OH
\end{array}
$$

(3) Methyl pentynol

$$
\begin{array}{c}
CH_3 \\
CH_3-CH_2-C-C\equiv CH \\
OH
\end{array}
$$

(4) Dimethyl hexynol

$$
\begin{array}{c}
CH_3 \qquad\quad CH_3 \\
CH_3-CH-CH_2-C-C\equiv CH \\
OH
\end{array}
$$

(5) 2-butyne-1,4-diol

$$
\begin{array}{c}
C-CH_2-OH \\
\| \\
C-CH_2-OH
\end{array}
$$

(6) Dimethyl hexynediol

$$
\begin{array}{c}
CH_3 \qquad\quad CH_3 \\
CH_3-C-C\equiv C-C-CH_3 \\
OH \qquad\quad OH
\end{array}
$$

(7) Propargyl alcohol

$$HC\equiv C-CH_2-OH$$

(8) Bis-hydroxyethyl butynediol ether

$$HO-CH_2-CH_2-O-CH_2-C\equiv C-CH_2-O-CH_2-CH_2OH$$

(9) Hexynol

$$
\begin{array}{c}
CH_2-CH_2-CH_2-CH-C\equiv CH \\
OH
\end{array}
$$

10. Ethyl octynol

$$
\begin{array}{c}
CH_2-CH_3 \\
CH_3-CH_2-CH_2-CH_2-CH-CH-C\equiv H \\
OH
\end{array}
$$

In the above examples, it should be understood that there may be further substitution with water solubilizing groups on the radicals represented by R, R' and R''. For example, each can be substituted with a member selected from the group of — NH_2, $-SO_3OH$, $-COOH$, $-NO_3$, $-Cl$, $-I$, $-Br$, $-F$ and the like.

Lower molecular weight alkylene oxides having from two to five carbon atoms are contemplated for formation of the adducts. Examples of such oxides include ethylene oxide, propylene oxide, isobutylene oxide and 1,2-epoxy butane. The adducts are formed by an epoxidation reaction with cleavage of the epoxide group of the alkylene oxide by the —OH group of the alcohol to form the polyether. The adducts can be represented by the following formulas:

I and

$$HC\equiv C-R-\left[O-A\right]_n-OH$$

II

$$OH-\left[A-O\right]_n-R'-C\equiv C-R''-\left[O-A\right]_n-OH$$
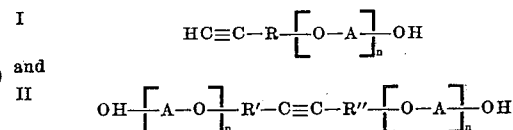
where R, R' and R'' are as stated above, A is an alkylene radical having from two to five carbon atoms, and n is a whole in-
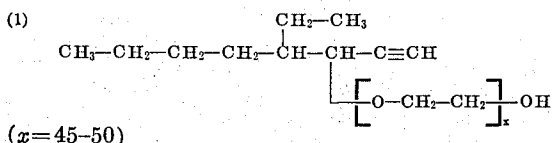
teger ranging from 1 to 100 and preferably from 5 to 50. These adducts are believed to be new compounds. The compounds represented by Formula II above are less preferred as they are less than one-half as effective as stabilizers than the compounds represented by Formula I above.

The adducts are formed using conventional epoxidation reactions for alcohols and alkylene oxides. Generally, elevated temperatures, e.g., 50° to 150° C, and elevated pressures, e.g., in excess of 1 and preferably above 2 atmospheres, are used. Typically, an epoxidation catalyst such as BCl_3 or a tertiary amine is also used. The ratio of the alkylene oxide to the alcohol is dependent upon the number of —OH groups on the alcohol and the desired chain length of the polyether in accordance with art recognized procedure. Details for formation of polyether adducts of alcohols and alkylene oxides can be found in Jelinek, C.F. and May hew, R.L., *Industrial Engineering Chemistry*, 46, 1954, incorporated herein by reference. In considering the above formulas, it should be understood that these adducts are not single compounds, but the reaction products represent mixtures approximating Poisson distribution.

The above polyether adducts are used in quantities which are effective to improve stability and deposit appearance or otherwise improve the performance of the solution, but in quantities that are not so great as to prevent deposition. Generally, useful quantities are between 2.0 and 2000 parts per million parts of solution by weight though the preferred range is from about 25 to 200 parts per million parts. The maximum quantity of any given adduct that can be put into solution is dependent upon the degree of ethoxylation—i.e., the chain length of the polyether. Generally, the higher the degree of ethoxylation, the larger the quantity of adduct that can be dissolved in solution.

EXAMPLE 1

Copper sulphate pentahydrate	7.5 grams
sodium hydroxide	5.0 grams
formaldehyde	2.5 grams
Rochelle salts	12.0 grams
adduct [1]	50 p.p.m.
water	to 1 liter

(1)

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}\overset{\displaystyle CH_2{-}CH_3}{CH}{-}CH{-}C{\equiv}CH$$

$$\left[O{-}CH_2{-}CH_2\right]_x{-}OH$$

$(x = 45{-}50)$

The stability of the above solution was determined using the palladium chloride drop test which comprises addition of 50 drops of a 0.5 percent by weight palladium chloride solution to a 30 ml sample of the formulation. The 50 drops are added at the rate of 10 drops per 30 seconds with constant stirring to prevent localized triggering or decomposition. The time for spontaneous decomposition is determined starting from the time that the addition of palladium chloride is completed. With reference to the above formulation, triggering did not occur within 48 hours.

Example 1 was repeated without the addition of the adduct. Triggering occurred within 1 hour.

The procedure of example 1 was repeated, but ethyloctynol was substituted for the adduct. A maximum of about 25 ppm of the ethyloctynol went into solution due to limited solubility. The remainder formed an insoluble phase in the solution. The solution triggered in about 18 hours following the palladium chloride drop test, possibly due to the lower quantity of the stabilizer in solution.

A phenolic substrate was prepared for plating using the conventional pre-treatment steps of cleaning, conditioning and catalyzing with Cuposit 6F, a one step palladium-stannic acid catalyst. The part was plated by immersion in the formulation

of Example 1. The part so plated had a bright surface appearance.

A phenolic part was plated with the formulation of Example 1 where ethyloctynol was substituted for the adduct and a shiny deposit was obtained, though the deposit was not as bright as that obtained from the solution containing the adduct.
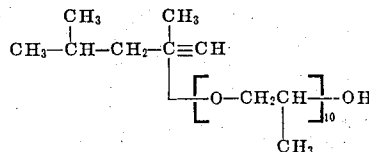
EXAMPLE 2

The procedure of Example 1 was repeated substituting for the adduct of Example 1, the following compound in an amount of 100 parts per million parts of solution:

$$CH_3{-}\overset{\displaystyle CH_3}{\underset{}{C}}{-}C{\equiv}CH$$

$$\left[O{-}CH_2{-}CH_2\right]_2{-}OH$$
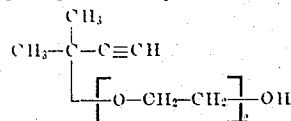
Using the palladium drop test, the bath did not trigger within 30 hours.

EXAMPLE 3

Using the formulation and procedure of Example 1, the adduct of Example 1 was substituted with the following compound in an amount of 75 parts per million parts of solution:

$$CH_3{-}\overset{\displaystyle CH_3}{\underset{}{CH}}{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{}{C}}{\equiv}CH$$

$$\left[O{-}CH_2CH\right]_{10}{-}OH$$
$$\underset{\displaystyle CH_3}{}$$

With the palladium drop test, the bath did not trigger within 36 hours.

In the above examples, other well known complexing agents and sources of cupric ion may be substituted for those listed. For example, those disclosed in the above cited patents provide useful solutions.

The concentrations of the above ingredients are not critical and are generally in the ranges previously known to be useful in electroless coppering solutions. Sufficient copper must be employed to provide a useful deposit and sufficient alkali to provide the high pH required, generally from 10 to 14. Sufficient formaldehyde must be employed to serve as a reducing agent for the copper in the presence of a catalytic surface and sufficient complexing agent used to prevent precipitation of copper in the alkali solution during storage and use. Generally, the known concentrations most useful for these materials are given in the following table:

CONCENTRATIONS

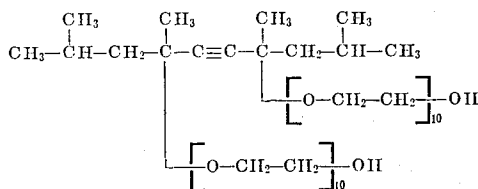| Cu^{++} | 0.02–0.12 | mols/liter |
Alkali	0.17–1.15	mols/liter
HCHO	2 to 20	mols/liter Cu^{++}
Complexer	1.1 to 5	mols/liter Cu^{++}

The use of the adducts herein described is believed to be effective through the acetylnic group to hold impurities such as cuprous materials in the activated form. The ethoxylation of the alkine alcohol is believed to be the improvement as it renders higher molecular weight alkine alcohols soluble in solution, which higher molecular weight alcohols seem to be more effective as stabilizers for the electroless solution. Also, the polyether so formed acts as a surfactant in the solution which is believed to be related to the improvement in surface appearance.

Of the adducts disclosed herein, those possessing the —C ≡ CH group are at least twice as effective as those containing the —C ≡ C— group and consequently comprise a preferred embodiment of this invention. This is believed to be due to the higher reactivity of the —C ≡ CH grouping. This is illustrated in the following example.

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EXAMPLE 4

The formulation of Example 1 was used substituting for the adduct of Example 1, the following:

$$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-\underset{\underset{\left[O-CH_2-CH_2\right]_{10}-OH}{|}}{C}-C\equiv C-\underset{\underset{CH_3}{|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_3$$

A solution containing the above compound in an amount of 75 ppm triggered in about 8 hours following the palladium drop test, substituting the diol for the adduct, 15 ppm went into solution and triggering occurred in about 3 hours. The solution free of stabilizer triggered in slightly less than 1 hour.

Because the polyether adducts of this invention are considered to be new compounds, an example is set forth below illustrating a process for their synthesis.

EXAMPLE 5

Charge 2 moles of ethyl octynol and a tertiary amine catalyst into a stainless steel pressure vessel equipped with agitator, temperature gauge, inlet tubes for ethylene oxide and nitrogen, and connection for a vacuum system. Flush with nitrogen until all oxygen has been removed from the system. Pull 28 inch vacuum and then start addition of 20 moles of ethylene oxide while maintaining the temperature in the system within the range of 50°–120° C. The vessel is maintained at a pressure of 20 to 40 psi. The ethylene oxide is added over a period of 10 hours. Thereafter, the system is cooled to 40° C, flushed with nitrogen and the product is discharged from the vessel. The yield is about 98 percent.

I claim:

1. In an aqueous, alkaline electroless copper plating solution comprising a source of cupric ions, formaldehyde as a reducing agent, a complexing agent to maintain said cupric ions in solution and hydroxide to provide required solution pH, the improvement comprising an polyether stabilizer selected from the group of

$$HC\equiv C-R-\left[O-A\right]_n-OH$$

and

$$HO-\left[A-O\right]_n-R''-C\equiv C-R''-\left[O-A\right]_n-OH$$
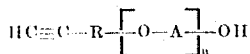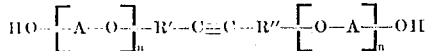
where each of R, R' and R'' are individually selected from the group of divalent alkylene, cycloalkylene, alkylene ether and arylene radicals, said radicals having from one to 12 carbon atoms, A is an alkylene radical having from two to five carbon atoms and n is a whole integer ranging between 1 and 100.

2. The solution of claim 1 where the polyether is the reaction product of an alkine alcohol and an alkylene oxide.

3. The solution of claim 2 where the alkylene oxide is selected from the group of ethylene oxide, propylene oxide, isobutylene oxide and 1,2-epoxy butane.

4. The solution of claim 2 where the alkylene oxide is ethylene oxide.

5. The solution of claim 1 where R, R' and R'' are individually alkylene radicals.

6. The solution of claim 1 where R, R' and/or R'' are substituted with a polar group.

7. The solution of claim 6 where the polar group is selected from the group of —NH$_2$, —SO$_3$OH, —COOH, —NO$_3$, —Cl, —Br, —I, and —F.
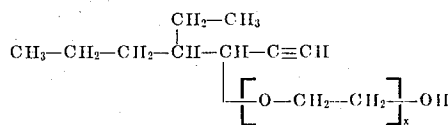
8. The solution of claim 1 where n varies between 5 and 50.

9. The solution of claim 1 containing said polyether in an amount of from 2 to 2,000 parts per million parts of solution.

10. The solution of claim 1 containing said polyether in an amount of from 25 to 200 parts per million parts of solution.

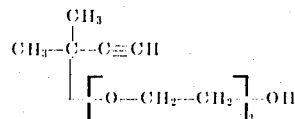11. The solution of claim 1 where the polyether has the formula

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$$CH_3-CH_2-CH_2-\underset{\underset{\left[O-CH_2-CH_2\right]_x-OH}{|}}{C}H-\underset{\underset{CH_2-CH_3}{|}}{C}H-C\equiv CH$$

where x varies between about 45 and 50.

12. The solution of claim 1 where the polyether has the formula

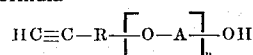$$CH_3-\underset{\underset{\left[O-CH_2-CH_2\right]_?-OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH$$

13. In an aqueous, alkaline electroless copper plating solution comprising a source of cupric ions, formaldehyde as a reducing agent, a complexing agent to maintain said cupric ions in solution and hydroxide to provide required solution pH, the improvement comprising a stabilizing quantity of a polyether of the formula

$$HC\equiv C-R-\left[O-A\right]_n-OH$$

where R is selected from the group of divalent alkylene, cycloalkylene, alkylene ether and arylene radicals, said radicals having from one–12 carbon atoms. A is an alkylene radical having from two–five carbon atoms and n is a whole integer ranging between 1 and 100.

14. The composition of claim 13 where R is alkylene and A is ethylene.

15. The composition of claim 14 wherein A varies between five and 50 and the polyether is contained in solution in an amount of from 25 and 200 parts per million parts of solution.

16. A method for stabilizing an electroless copper plating solution comprising a source of cupric ions, formaldehyde as a reducing agent, a complexing agent to maintain said cupric ions in solution and hydroxide to provide required solution pH, said method comprising addition to said solution of a stabilizing quantity of a polyether adduct corresponding to the formula

$$HC\equiv C-R[-O-A]_nOH$$

and

$$HO-\left[A-O\right]_n-R'-C\equiv C-R''-\left[O-A\right]_n-OH$$
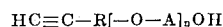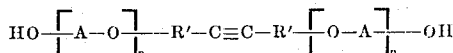
where each R,R' and R'' are individually selected from the group of divalent alkylene, cycloalkylene, alkylene ether and arylene radicals, said radicals having from one to 12 carbon atoms, A is an alkylene radical having from two to five carbon atoms and n is a whole integer ranging between 1 and 100.

17. The method of claim 16 where the polyether adduct conforms to the formula

$$HC\equiv C-R-\left[O-A\right]_n-OH$$
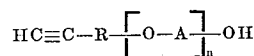
18. The method of claim 17 where the polyether is the reaction product of an alkylene oxide and an alkine alcohol.

19. The method of claim 18 where the alkylene oxide is selected from the group of ethylene oxide, propylene oxide, isobutylene oxide and 1,2-epoxy butane.

20. The method of claim 18 where the alkylene oxide is ethylene oxide.

21. The method of claim 17 where R is an alkylene radical.

22. The method of claim 17 where R is substituted with a polar group.

23. The method of claim 22 where the polar group is selected from the group of —NH$_2$, —SO$_3$OH, —COOH, —NO$_3$, —Cl, —Br, —I and —F.

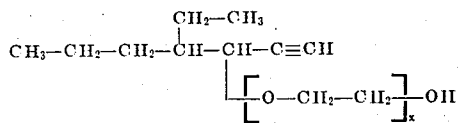24. The method of claim 17 where from 2 to 2000 parts of polyether adduct per million parts of solution are added.

25. The method of claim 17 where from 25 to 2000 parts of polyether adduct per million parts of solution are added.

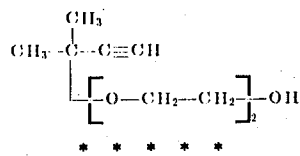26. The method of claim 17 where the polyether has the formula

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$$CH_3-CH_2-CH_2-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH-C\equiv CH$$

$$\underset{\overset{|}{\left[O-CH_2-CH_2\right]_x}-OH}{}$$

where x varies between about 45 and 50.

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27. The method of claim 17 where the polyether has the formula

$$CH_3-\underset{\underset{CH_3}{|}}{C}-C\equiv CH$$

$$\left[O-CH_2-CH_2\right]_2-OH$$

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