United States Patent [19]

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[11] **3,715,289**

[45] **Feb. 6, 1973**

[54] **BRIGHTENER COMPOSITION FOR ACID COPPER ELECTROPLATING BATHS**

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[22] Filed: **Feb. 8, 1971**

[21] Appl. No.: **113,602**

[52] **U.S. Cl.** .....**204/52 R**, 204/DIG. 2

[51] **Int. Cl.** **C23b 5/18**

[58] **Field of Search** .....204/52 R, DIG. 2

[56] **References Cited**

UNITED STATES PATENTS

3,267,010	8/1966	Creutz et al.	204/52 R
3,269,925	8/1966	Du Rose	204/32
3,328,273	6/1967	Creutz et al.	204/52 R
3,542,655	11/1970	Kardos et al.	20/52 R

FOREIGN PATENTS OR APPLICATIONS

1,521,021	8/1969	Germany	204/52 R

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Attorney—Daniel S. Ortiz, Robert C. Sullivan, John L. Callahan, Paul J. Jeuttner and Rocco S. Barrese

[57] **ABSTRACT**

There is disclosed a novel brightener composition for aqueous, acid copper electroplating baths comprising a combination of an ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol; disodium 2,7-dihydroxy-4,5-dithiaoctane-1,8-disulfonate monohydrate; and, 2-mercaptopyridine. The use of this brightener composition if found to provide bright, leveled ductile copper deposits from an acid copper electrolyte.

4 Claims, No Drawings

BRIGHTENER COMPOSITION FOR ACID COPPER ELECTROPLATING BATHS

BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, it is often necessary or desirable to plate base metals with copper before they are plated with other metals so as to be able to attain a metal coating or finish having certain desired characteristics. However, in order to obtain a satisfactory coating of the subsequently applied metal, it is necessary that the initial copper plating should display certain properties. Thus, it is required that the copper plating should be smooth and uniform, i.e., it should be leveled; it should be bright and resist tarnishing rather than dull and readily tarnishable; it should have a small rather than a large grain size; and, it should have adequate ductility.

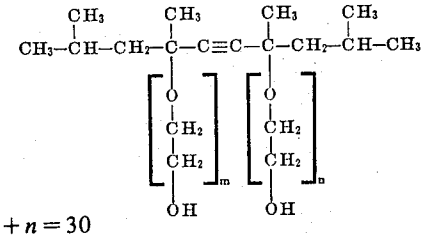
In an effort to achieve these necessary properties, and particularly brightness and leveling, in copper deposits derived from acidic plating baths, the use of a wide variety of additives has been resorted to. Thus, among the different materials which have been used in this manner are casein, animal glue, sugar, urea and thiourea and their derivatives and polyvinyl alcohol. However, while the use of many of these additives, either alone or in combination, has led to some improvement in certain of these desired characteristics, their presence often leads to various defects such, for example, as brittleness and lack of uniformity and also makes it more difficult to readily control such important process variables as the current density and the plating temperature.

Thus, it is the prime object of this invention to provide a novel plating bath additive which produces bright, leveled and ductile copper deposits from an acid copper electrolyte over a wide range of current densities. Various other objects and advantages of this invention will be apparent from the disclosure which follows hereinafter.

TECHNICAL DISCLOSURE OF THE INVENTION

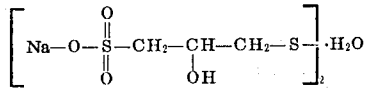
It has now been found that excellent copper deposits can be electrodeposited from an aqueous, acid copper electrolyte by the incorporation, therein of an additive which comprises a mixture of:

1. A polyether comprising the ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol, said polyether corresponding to the formula:



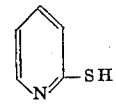
where $m + n = 30$

2. Disodium 2,7-dihydroxy-4,5-dithiaoctane-1,8-disulfonate monohydrate;



and,

3. 2-mercaptopyridine, i.e.,



More particularly, the use of the above described additive mixture in acid copper plating baths is found to provide coppee deposits which are characterized by their excellent brightness, levelling and ductility along with a desirably small grain size. And, of great significance is the fact that the novel additive of this invention produces these high quality results over a very broad current range.

It is interesting to note that the prior art discloses a number of acid copper plating bath additives which contain the individual components of the novel additive of this invention either alone or, in some cases, in combinations which contain two out of its three required ingredients or of compounds which are closely related to these ingredients. For example, German Pat. No. 1,521,021 discloses the use of 2-mercaptopyridine; U.S. Pat. Nos. 3,328,273 and 3,267,010 each disclose the use of a combination of compounds related to the disulfonate and the polyether components of the additive mixture of this invention; and, Netherlands patent application No. 69–06599, which cliams priority on application Ser. No. 725,209 filed in the U.S. Patent Office on Apr. 29, 1968, now U.S. Pat. No. 3,542,655, discloses an additive containing the specific disulfonate and polyether ingredients used in the additive mixture of this invention.

The novel additive mixture of this invention may be incorporated into any of the standard aqueous acid copper plating baths such, for example, as the copper sulfate-sulfuric acid and copper fluoborate-fluoboric acid systems as well as those systems containing such copper salts as copper sulfonate, copper methane sulfonates, copper ethane sulfonates and copper propane sulfonates wherein excess acidity is supplied by the respective free sulfonic acids.

With respect to proportions, the ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol (i.e., the polyether) component of the additive should be present in the plating bath in a concentration of from about 0.03 to 1.66 grams/liter with the use of a concentration of about 0.16 grams/liter being preferred; the disodium 2,7-dihydroxy-4,5-dithiaoctane-1,8-disulfonate monohydrate (i.e. the disulfonate) component of the additive should be present in a concentration of from about 0.005

to 0.0266 grams/liter with the use of a concentration of about 0.018 grams/liter being preferred; and, the 2-mercaptopyridine should be present in a concentration of from about 0.0005 to 0.014 gams/liter with the use of a concentration of about 0.006 grams/liter being preferred.

In conducting the actual electroplating operation, current densities of from about 1.5 to 120, and preferably about 25 to 45 amperes per square feet (ASF) may be utilized. The bath temperature may be in the range of from about 70° to 105°, and preferably from about 70° to 80°F. Moreover, the use of air agitation, is desirable for high speed plating and optimum results.

If desired, the acid copper plating baths containing the novel additive mixture of this invention may also contain one or more of the various materials heretofore used as additives in such baths. These optional additives include copolymers of ethylene oxide and propylene oxide having a molecular weight in the range of from about 950–1,750 with the use of a copolymer containing 10–30 percent of ethylene oxide moieties in a concentration of from about 0.05–0.1 grams/liter being preferred.

The following examples will further illustrate the embodiment of this invention. In these examples all parts given are by weight unless otherwise noted.

EXAMPLE I

This example illustrates the electrodeposition of copper from an acid copper plating bath containing the novel additive mixture of this invention. It also illustrates the need for having all three of the required components of the additive mixture present within the bath. Part A—A bath containing the following ingredients is prepared:

$CuSO_4 \cdot H_2O$	29.0 oz/gal
H_2SO_4 (97%)	7.93 oz/gal
HCl (37%)	90 cc/1,000 gal

A 300 ml sample of this solution is placed in a Hull Cell and the following additions are made:

0.004 g of the above described disulfonate

0.3 g of the above described ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

The chloride content of the solution is adjusted by adding the equivalent of 100 cc HCl(37%)/1,000 gal. and a 3 ampere brass Hull Cell panel is run in this solution for 5 minutes with air agitation. The plated panel is found to be dull in the range of from 0–18 ASF and bright in the range of from 18 ASF to the upper edge of the panel.

Part B—The equivalent of 75 cc HCl (37%)/1,000 gal. and 0.000375 g of 2-mercaptopyridine is then added to another portion of the Hull Cell solution described in Part A, hereinabove, and a 3 ampere brass Hull Cell panel is plated for 5 minutes with air agitation. The plated panel is found to be full bright and ductile and appears to be highly leveled.

EXAMPLE II

This example illustrates the criticality inherent in the use of 2-mercaptopyridine in the additive system of this invention.

A bath containing the following ingredients is prepared:

$CuSO_4 \cdot H_2O$	27.9 oz/gal
H_2SO_4 (97%)	7.6 oz/gal
HCl (37%)	95 cc/1,000 gal

The equivalent of 175 cc HCl(37%)/1,000 gal. is added with the electrolyte in a 300 ml Hull Cell and the following additions are then made:

0.004 g of the above described disulfonate

0.3 g of the above described ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol

0.000375 g of 4-methyl-2-mercaptopyridine

A brass Hull Cell panel is plated from this solution at 3 amperes for 5 minutes with air agitation. The plated panel has the following appearance:

Bright	0 – 3 ASF
Hazy Bright	3 – 30 ASF

Thus, upon comparing these results with the results obtain in Part B of Example I, it is seen that the effect of the 2-mercaptopyridine is highly specific in being able to produce full bright deposits with the additive system of this invention.

EXAMPLE III

This example again illustrates the operation of the process of this invention.

To a 2 liter beaker containing phosphorized copper anodes and an air agitator, there is added 1.8 liter of an acid copper solution similar to that used in Example II. The chloride content of this bath is adjusted to the equivalent of 340 cc HCl (37%)/1,000 gal. and the following additions are made:

0.0067 g/l of the above described disulfonate

0.90 g/l of the above described ethylene oxide adduct

0.001 g/l of 2-mercaptopyridine

A number of 1 × 4 inch bent brass cathode panels are plated from this bath for a period of 30 minutes at 2 amperes while fresh additions of 2-mercaptopyridine and the disulfonate are periodically added in order to maintain full bright deposits. No adverse effects on the brightness of the resulting deposits is found to occur with the bath being used in this manner for 75 ampere-hours of plating. The consumption rate of the disulfonate and of the 2-mercaptopyridine necessary to maintain full brightness in this bath over the period of the test is calculated as follows:

For the disulfonate = 5.09 g/10,000 ampere-hours

For the 2-mercaptopyridine = 1.27 g/10,000 ampere-hours

EXAMPLE IV

This example illustrates the excellent leveling obtained with the novel additive system of this invention.

To a 5 gallon tank containing an electrolyte similar to that of Part B of Example I there is added:

The above described ethylene oxide adduct — 1.84 g/l

2-mercaptopyridine — 0.008 g/l

The above described disulfonate — 0.0266 g/l

The chlorides in this tank are adjusted to the equivalent of 400 cc HCl (37%)/1,000 gal. A number of 1¼ × 4½ inch belt sanded, steel panels are then bent at a 90° angle thus forming a ¾ inch shelf. These panels are cleaned and given a 2 minute copper strike at 2 amperes in a cyanide copper strike. The panels are then plated at 3 amperes for 25 minutes in the above described electrolyte solution. Periodic additions of the disulfonate, 2-mercaptopyridine and of the ethylene oxide adduct are made to the bath in order to maintain full bright leveled deposits after 200 ampere hours of plating from this tank. Leveling measurements are taken on the deposits using a Model 150 "Surfanalyzer' ' sold by the Clevite Corporation. These measurements are taken on the top of the shelf as well as the front and

back of the panel. The following table gives the results of these measurements:

Average current density (ASF)	Shelf			Front			Back		
	Roughness [1]			Roughness [1]			Roughness [1]		
	Before plating [2]	After plating [2]	Percent leveling [3]	Before plating [2]	After plating [2]	Percent leveling [3]	Before plating [2]	After plating [2]	Percent leveling [3]
25	4.2	1.7	59.5	4.4	1.5	65.9	6.0	1.4	76.7
29	5.7	2.1	63.2	5.0	1.6	68.0	3.8	1.8	52.6
32	4.3	1.9	55.8	4.3	1.8	58.1	6.0	1.8	70.0
35	5.1	1.6	68.6	5.1	1.7	66.7	6.2	1.6	74.2
38	4.8	1.5	68.8	5.0	1.6	68.0	5.4	0.8	85.2
42½	5.6	2.1	62.5	5.6	1.5	73.2	4.1	1.8	56.1

[1] Results are an arithmetic average.
[2] Data are in microinches, i.e., 1×10^{-6} inches.
[3] Percent leveling $=\frac{\text{Roughness before plating}-\text{roughness after plating}}{\text{Roughness Before Plating}}\times100$

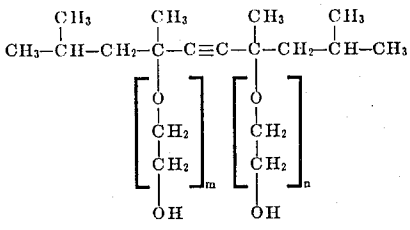
From the data in the above table, the mean percent leveling is calculated to be 66.3 percent which indicates that the additive system of this invention provides copper plating exhibiting very good leveling.

Variations may be made in proportions, procedures and materials without departing from the scope of this invention as defined in the following claims.

What is claimed is:

1. In an aqueous acid copper bath for the electrodeposition of copper, the improvement which comprises having dissolved in said bath an additive mixture comprising:

1. from about 0.03 to 1.66 grams/liter of an ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol corresponding to the formula:



where $m+n=30$;

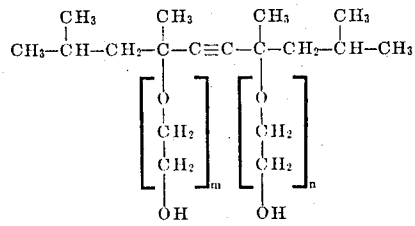
2. from about 0.005 to 0.0266 grams/liter of disodium 2,7-dihydroxy-4,5dithiaoctane-1,8-disulfonate, monohydrate;

3. from about 0.005 to 0.14 grams/liter of 2-mercaptopyridine.

2. The bath of claim **1**, wherein said ethylene oxide adduct is present in a concentration of about 0.16 grams/liter, said disodium 2,7-dihydroxy-4,5-dithiaoctane-1,8-disulfonate monohydrate is present in a concentration of about 0.018 grams/liter and said 2-mercaptopyridine is present in a concentration of about 0.006 grams per liter.

3. In the process of electrodepositing copper from an aqueous, acid copper plating bath, the improvement which comprises the dissolution in said bath of an additive mixture comprising

1. from about 0.03 to 1.66 grams/liter of ethylene oxide adduct of 2,4,7,9-tetramethyl-5-decyne-4,7-diol corresponding to the formula:



where m + n =30;

2. from about 0.005 to 0.0266 grams/liter of disodium 2,7-dihydroxy-4,5-dithiaoctane-1,8-disulfonate monohydrate; and,

3. from about 0.005 to 0.14 grams/liter of 2-mercaptopyridine.

4. The process of claim **3**, wherein said ethylene oxide adduct is present in a concentration of about 0.16 grams/liter, said disodium 2,7-dihydroxy-4,5-5-dithiaoctane-1,8-disulfonate monohydrate is present in a concentration of about 0.018 grams/liter and said 2-mercaptopyridine is present in a concentration of about 0.006 grams per liter.

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