United States Patent Office 3,288,690 Patented Nov. 29, 1966

3,288,690

ELECTRODEPOSITION OF COPPER FROM ACIDIC BATHS

Hans-Gerhard Creutz, Wayne, and Henry Brown, Huntington Woods, Mich., assignors to The Udylite Corporation, Warren, Mich., a corporation of Delaware

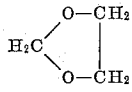
No Drawing. Filed Mar. 11, 1966, Ser. No. 533,434
10 Claims. (Cl. 204—52)

This application is a continuation-in-part of our co-pending application Serial No. 187,930, filed April 16, 1962, now abandoned.

This invention relates to the electrodeposition of copper from aqueous acid baths, especially from acidic copper sulfate and fluoborate baths. More particularly it relates to the use of certain organic compounds in the baths which make possible bright, highly ductile, low stress, good leveling copper deposits.

While a rather large number of organic compounds have been proposed and used to decrease the grain size and increase the luster of the copper deposits from acidic baths, nevertheless, much remains to be desired from the standpoint of obtaining lustrous leveling copper plate without striations and ribbing and without substantially decreasing the very high ductility of the copper plate from the acidic baths.

It has now been found that bath-soluble homo-polymers of 1,3-dioxolane,



which have molecular weights greater than 296 and at least up to about 30,000, when used in acidic copper sulfate or acidic copper fluoborate baths, make possible smooth, low stress, ductile semi-bright copper plate that is free from striations. For example, if about 0.1 gram/liter of a poly-1,3-dioxolane of average molecular weight of about 5,000 is added to an acid copper bath made up of 150 to 275 grams/liter of blue vitriol and containing about 3 to 70 grams/liter of sulfuric acid, a very smooth semi-bright copper plate is obtained within a current density range from the very lowest to the burning point or limiting current density, which with ordinary agitation is around 10 to 15 amps./sq. dm., but is higher with very rapid solution agitation. In the acidic fluoborate bath containing about 150 to at least 450 grams/liter of copper fluoborate and about 0.5 to at least 30 grams/liter of fluoboric acid, even higher current densities can be used at the same bath temperatures and the same excellent copper plate can be obtained with the addition of about 0.1 gram/liter of the poly-dioxolane of average molecular weight of about 5,000. With lower molecular weight polymers, for example about 400 to 1,000, larger concentrations up to at least 5 grams/liter should be used. With the higher molecular weight polymers, i.e., about 5,000 and higher, concentrations as low as about 0.01 gram/liter can be used with good results, especially when used in conjunction with other organic additives.

In contrast with other high molecular weight polyethers, no striations or ribbing of the plate occurs from the use of these polydioxolanes, and it is not essential to have present in the bath concentrations of chloride or bromide ion of at least about 0.02 to 0.1 gram/liter.

The 1,3-dioxolane though a 5-membered ring, can be converted into high molecular weight homo-polymers in accordance with well-known polymerization procedures,

namely by heating the dioxolane in the presence of an acidic catalyst until a polymer of the desired molecular weight has been obtained, which for this application is about 5,000. The best acidic catalyst for the polymerization of the dioxolane is the boron trifluoride type. The polymers of 1,3-dioxolane are polyethers consisting of alternating methylene and ethylene groups interrupted by oxygen atoms. The homo-polymer of 1,3-dioxolane can be reacted with other compounds to introduce other groups such as halogen, amino, sulfonic, sulfate, phosphate, phosphonic, etc. into the molecule.

When acid copper baths are used for plating steel or ferrous articles, such as automobile bumper bars, hub caps, printing rollers, etc., a preliminary copper or brass strike from a cyanide bath or a nickel strike from an acidic, pH of about 0.5 to 5, nickel plating bath, is first used to avoid poorly adherent immersion deposits. The acidic nickel strike (low chloride, high sulfate type to minimize drag-in of chloride ions into the copper bath) is often preferred because it is easier to control and easier to rinse and easier for waste disposal. The inorganic composition of the acid copper plating baths such as the acidic sulfate or acidic fluoborate may vary over rather wide limits, and actually much lower acid content may be used with the unique combination of additives of this invention than is present in the usual standard compositions. However, when very low acid contents are used, higher tank voltages are needed. In the examples listed below as illustrations of lustrous copper plating baths, the standard types of acidic copper sulfate and fluoborate baths are used for the inorganic compositions. However, other acidic copper plating baths such as copper sulfamate, copper methane sulfonates, copper ethane sulfonates, and copper propane sulfonates with excess acidity supplied by the free sulfonic acids, can be used.

Many inorganic cations which do not plate out from the normal acidic copper plating baths, may be present in concentrations as high as at least 25 grams/liter without detrimental effects, for example, ferrous, nickel, cobalt, zinc and cadmium cations. Chloride and/or bromide anions should in general be kept below about 0.1 gram/liter, and preferably below about 0.02 gram/liter. Air agitation or cathode-rod agitation, or solution agitation and cathode-rod agitation is desirable for highest speed plating and optimum results. The best bath temperatures are 25–35° C., though lower or higher (even up to 50° C. in some cases) temperatures can be used.

It is preferred not to use surface-active agents, even though such anionic types as sodium octyl sulfate, sulfonated non-ionic types such as Triton 720 (U.S. Patent 2,489,538, November 29, 1949), and similar materials, or polyoxy non-ionic wetting agents, have often been previously used in acidic copper plating baths with good results, they are not needed in the present type baths.

Also, the polydioxolanes cooperate with other acidic copper bath brighteners to make possible copper plates of increased luster. For example, the polydioxolanes cooperate with one or more of the following classes of acidic copper plating brighteners to give improved luster, phenazine dyes, phenazine dyes containing azo and diazo linkages, dicyandiamide and other bath soluble derivatives of cyanamide, thiourea, and bath soluble derivatives of thiourea and isothiourea, dextrins, molasses, and mixtures of these various additives.

Below is a list of acid copper plating baths for producing highly ductile, fine-grained copper deposits. It is preferred for most applications to use phosphorized copper anodes in the acidic baths employing the polymers

of 1,3-dioxolane. The plate has more luster when phosphorized copper anodes are use, and phosphorus is also found in the plate. Of course, where phosphorus in the copper plate is not desired as for highest electrical conductivity or high temperature uses, then phosphorus-free copper anodes should be used.

EXAMPLE A

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–225
H_2SO_4	30–75
1,3-dioxolane polymer av. mol. wt. 5,000	0.05–0.15

Temp. 20–35° C.
Average cathode current density 5 amps./sq. dm.

EXAMPLE B

	Concentration, grams/liter
$Cu(BF_4)_2$	150–425
HBF_4	10–30
H_3BO_3	0–30
1,3-dioxolane polymer av. mol. wt. 1,000	0.01–1

Temp. 20–35° C.
Av. cathode current density 8 amps./sq. dm.

EXAMPLE C

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–225
H_2SO_4	30–75
1,3-dioxolane polymer av. mol. wt. 5,000	0.1–0.15
Diethyl Safranine azo dimethyl aniline (Janus Green–B)	0.001–0.01

Temp. 25–30° C.
Av. cathode current density 5 amps./sq. dm.

EXAMPLE D

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–250
H_2SO_4	30–75
1,3-dioxolane polymer av. mol. wt. 296	0.05–0.15
Dimethyl Safranine azo dimethyl aniline	0.001–0.02

Temp. 20–35° C.
Av. cathode current density 5 amps./sq. dm.

EXAMPLE E

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–250
H_2SO_4	30–75
1,3-dioxolane polymer av. mol. wt. 10,000	0.005–0.2
Dicyandiamide	0.001–0.1
Dimethyl Safranine azo dimethyl aniline	0.001–0.01

Temp. 20–35° C.
Av. cathode current density 5 amps./sq. dm.

EXAMPLE F

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–250
H_2SO_4	30–60
1,3-dioxolane polymer av. mol. wt. 30,000	0.05–0.3
Trifluoroacetyl thiourea	0.001–0.01
Janus Green B	0.001–0.01

Temp. 25–30° C.
Av. cathode current density 5 amps./sq. dm.

EXAMPLE G

	Concentration, grams/liter
$CuSO_4 \cdot 5H_2O$	150–250
H_2SO_4	30–60
Reaction product of 1,3-dioxolane and 1-thiosorbitol (mol. wt. 525)	0.02–0.4
1,3-dioxolane polymer av. mol. wt. 5,000	0.05–0.15
Janus Green B or Janus Black R	0.001–0.01

Temp. 25–30° C.
Av. cathode current density 5 amps./sq. dm.

What is claimed is:

1. A bath for electrodepositing fine-grained ductile copper, comprising an aqueous acidic copper plating bath containing a homo-polymer of 1,3-dioxolane of molecular weight greater than 296, in a concentration range of about 0.01 to at least 5 grams per liter.

2. A bath as claimed in claim **1** wherein said polymer of 1,3-dioxolane has an average molecular weight of about 5,000.

3. A bath as claimed in claim **1** wherein said polymer of 1,3-dioxolane has an average molecular weight of about 10,000.

4. A bath as claimed in claim **1** wherein said acidic copper bath also contains a phenazine dye in a concentration of about 0.001 to about 0.02 gram per liter.

5. A bath as claimed in claim **1** wherein said acidic copper plating bath contains at least one copper salt selected from the group consisting of copper sulfate, copper fluoborate, copper sulfamate, copper methane sulfonate, copper ethane sulfonate, and copper propane sulfonate.

6. A method for electrodepositing fine-grained ductile copper comprising the step of electrodepositing copper from an aqueous acidic copper plating bath containing dissolved therein a homo-polymer of 1,3-dioxolane of molecular weight greater than 296, in a concentration range of about 0.01 to at least 5 grams per liter.

7. A method as claimed in claim **6** wherein said polymer of 1,3-dioxolane in the said acidic copper bath has an average molecular weight of about 5,000.

8. A method as claimed in claim **6** wherein said polymer of 1,3-dioxolane in the said acidic copper bath has an average molecular weight of about 10,000.

9. A method as claimed in claim **6** wherein said acidic copper plating bath also contains a phenazine dye dissolved therein in a concentration range of about 0.001 to about 0.02 gram per liter.

10. A method as claimed in claim **6** wherein said acidic copper plating bath contains at least one copper salt selected from the group consisting of copper sulfate, copper fluoborate, copper sulfamate, copper methane sulfonate, copper ethane sulfonate, and copper propane sulfonate.

References Cited by the Examiner

UNITED STATES PATENTS

2,366,737	1/1945	Loder et al.	204—45 X
2,707,166	4/1955	Brown et al.	204—52
2,707,167	4/1955	Hoover	204—52
2,738,318	3/1956	Fellows et al.	204—52
2,882,209	4/1959	Brown et al.	204—52
3,075,898	1/1963	Brown et al.	204—49

JOHN H. MACK, *Primary Examiner.*
G. KAPLAN, *Assistant Examiner.*