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UNITED STATES PATENT OFFICE

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BRIGHT COPPER PLATING FROM CYANIDE BATHS

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4 Claims. (Cl. 204—52)

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This invention relates to cyanide baths for electroplating copper, and to processes of electrodepositing smooth and bright copper therefrom, and provides improvements therein. Advantages of the bath and process according to the present invention are:

1. Wide limits of the free cyanide without detriment to smooth and bright deposits, and to cathode current efficiency;
2. High current efficiency, with bright and smooth deposits obtainable at 90 to 100% cathode current efficiency;
3. Pitting of the electrodeposit is avoided;
4. Free rinsing properties of the electrodeposits, making unnecessary a special cleaning cycle after copper plating and prior to bright nickel plating;
5. Low concentration and stability of the brighteners used, making the bath economical to operate;
6. Wide latitude in the operating temperature range; and
7. Softness and easy flow of the copper electrodeposite on buffing.

An example of a bath composition, together with ranges for the constituents is given below.

Bath composition

	g./l.	Range
CuCN	63.5	30 to 75.
Total KCN	100.	50 to 125.
KOH	15.	7.5 to 30.
Rhodanine (brightener addition)	0.05	0.005 to 1.

Analytical values

	g./l.	Range
Cu	45	20 to 55.
Free KCN	11.2	5 to 13.
KOH	15	7.5 to 30.

pH approximately 12.5 to 13.5.

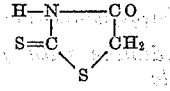
Sodium salts are equivalents of the potassium salts.

The novel constituent is the substance rhodanine, or substituted rhodanines, or condensation products of rhodanine, or of a substituted rhodanine, with compounds containing an active carbonyl (CO) group such as aromatic or aliphatic aldehydes or aldehydic acids. The particular brightener additive that is chosen should have a solubility in the bath of at least 0.005 gram per liter.

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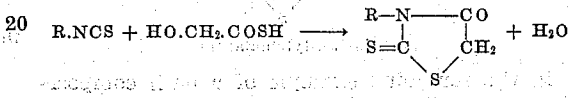
"Anti-pit" agents are not required in the bath when rhodanine, substituted rhodanine, or a condensation product of rhodanine, is present.

Rhodanine (2-mercaptothiazolidone-4) has the following structural formula



I have discovered that it exerts a powerful brightening effect when added to the cyanide copper bath.

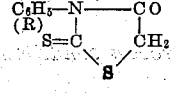
I have also discovered that the addition of substituted rhodanines, i. e., compounds formed by the interaction of aliphatic or aromatic isothiocyanates with thioglycollic acid according to the following general reaction, also produces a powerful brightening effect.



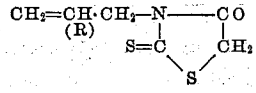
R stands for an aliphatic or substituted aliphatic group, or an aromatic or substituted aromatic group.

Examples of specific substituted rhodanines are the following:

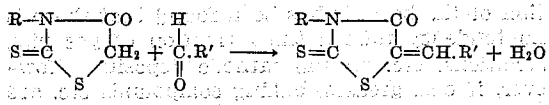
1. N-phenylrhodanine R-phenyl (C_6H_5—)



2. N-allylrhodanine R-allyl (CH_2=$CH.CH_2$—)



I have also discovered that the addition of condensation products of rhodanine, and of substituted rhodanines, with compounds containing an active carbonyl (CO) group, such as aliphatic or aromatic aldehydes, or aldehydic acids, also exerts a powerful brightening effect. The general reaction whereby such condensation products are formed is the following:

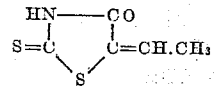


R stands for H, an aliphatic or substituted aliphatic group, or an aromatic or substituted aromatic group. R′ stands for an aliphatic or substituted aliphatic group, an aromatic or substituted aromatic group, a carboxyl group (COOH),

or an aliphatic or aromatic group containing a carboxyl group.

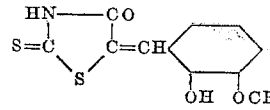
Examples of such condensation products of rhodanine and substituted rhodanines are the following:

1. *Rhodanine with acetaldehyde*



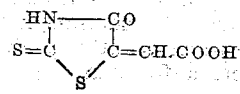
acetald-rhodanine

2. *Rhodanine with O-hydroxy-m-methoxy-benzaldehyde*



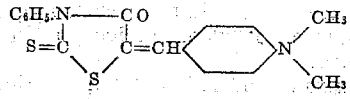
O-hydroxy-m-methoxy-benzalrhodanine

3. *Rhodanine with glyoxalic acid*



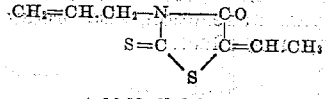
glyoxylal-rhodanine

4. *N-phenyl rhodanine with p-dimethylamino-benzaldehyde*



p-dimethylamino benzal-N-phenylrhodanine

5. *N-allylrhodanine with acetaldehyde*



acetald-N-allylrhodanine

In the foregoing example of a bath composition, a substituted rhodanine, or a rhodanine or substituted rhodanine condensation product can be used in place of rhodanine, and the amount of the substituted rhodanine or the rhodanine or substituted rhodanine condensation product, when used in place of rhodanine, is substantially the same amount and range given in the aforesaid example.

Process conditions

		Range
Bath-as above:		
Cathode current density	8-25 a. p. s. f.	5 to 35.
Temperature	170° F.	140° to 180° F.
Cathode Bar Agitation	15 ft./min.	5 to 20.

Efficiency (anode and cathode) approximately 100%.

Note: The bath will give bright deposits at current densities in the low part of the range without agitation. The higher current densities require agitation.

It is desirable to continuously filter the bath.

If ordinary precautions are taken in the operation of the bath, it has been found that there is no tendency toward the formation of gas pits, striations, etc. on the cathode deposits. However, if oils, greases, buffing compounds etc. are introduced into the bath in appreciable quantities, some pitting may occur in the cathode deposits. In such cases, it has been found advantageous to add to the bath small quantities of compatible wetting or anti-pitting agents. Examples of wetting agents which were found to have been effective are proprietary substances known as "Cerfak Liquid" (a sodium salt of a sulfated fatty acid amide) and "Tergitol 08" (a sodium salt of sulfater 2-ethylhexanol).

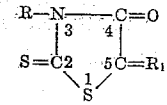
Brighteners have heretofore been used in cyanide copper baths, and some of these brighteners (thio-cyanates, for example) have been found to be of such a nature as to cause pitting, striation, etc. in the copper cathode deposits even though the bath may not be contaminated with foreign matters such as oils, greases, etc. In the case of such brighteners, it is necessary to use wetting agents to counteract pitting, striations, etc. Brighteners according to the present invention do not of themselves cause copper electrodeposits to be pitted or striated, wetting agents in the present bath being added only to counteract the effect of impurities and contaminants introduced into the bath through careless and faulty operation practice.

What is claimed is:

1. An aqueous cyanide type of bath for electroplating copper having as its essential constituents Cu 20 to 55 grams per liter, free KCN 5 to 13 g./l., KOH 7.5 to 30 g./l. and 0.005 to 1 g./l. rhodanine as a brightener addition.

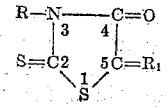
2. The method of electroplating smooth and bright copper consisting in immersing a cathode aritcle in an aqueous cyanide type of bath consisting essentially of Cu 20 to 55 grams per liter, free KCN 5 to 13 g./l., KOH 7.5 to 30 g./l., 0.005 to 1 g./l. rhodanine as a brightener addition and passing current to the cathode article at a current density between 5 amperes per square foot and 35 amperes per square foot, with the bath at a temperature between 140° F. and 180° F.

3. An aqueous cyanide type of bath for electroplating copper having as its essential constituents Cu—20 to 55 grams per liter, free KCN—5 to 13 grams per liter, KOH—7.5 to 30 grams per liter, and 0.005 to 1 gram per liter of a brightener addition having the general formula



in which R is a substituent selected from the class consisting of hydrogen, aliphatic, and aromatic substituents, and in which R_1 is a substituent selected from the class consisting of (1) hydrogen sufficient to saturate the number five carbon atom to which said R_1 is attached, (2) an aliphatic substituent connected to said number five carbon atom through a double bond, and (3) an aromatic substituent connected to said number five carbon atom through a double bond.

4. A method of electroplating smooth and bright copper consisting of immersing a cathode article in an aqueous cyanide type of bath consisting essentially of Cu—20 to 55 grams per liter, free KCN—5 to 13 grams per liter, KOH—7.5 to 30 grams per liter, and 0.005 to 1 gram per liter of a brightener addition having the general formula



in which R is a substituent selected from the class consisting of hydrogen, aliphatic, and aromatic substituents, and in which R_1 is a sub-

stituent selected from the class consisting of (1) hydrogen sufficient to saturate the number five carbon atom to which said R_1 is attached, (2) an aliphatic substituent connected to said number five carbon atom through a double bond, and (3) an aromatic substituent connected to said number five carbon atom through a double bond, and passing current to the cathode article at a current density between 5 amperes per square foot and 35 amperes per square foot, with the bath at a temperature between 140° F. and 180° F.

FRANK PASSAL.

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The following references are of record in the file of this patent:

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