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ELECTROPLATING COPPER

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4 Claims. (Cl. 204—52)

This invention relates to electroplating copper and more particularly to the electroplating of copper from cyanide solutions.

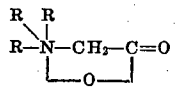
Excellent, adherent, dense coatings of copper are advantageously electroplated from cyanide copper solutions. Such solutions contain the double cyanide of copper and an alkali metal, for example copper sodium cyanide, with or without other salts and with or without an excess of free cyanide. An excellent type of copper plating bath contains the double copper alkali metal cyanide in high concentration (e. g. 12 to 20 oz. per gallon of CuCN), with little or no free cyanide and a high concentration of alkali metal hydroxide. Ordinarily, electrodeposits from cyanide copper plating baths are dull and buffing is required to obtain a bright, smooth finish. However, methods have been developed for directly electroplating bright, smooth copper deposits, for example by the method described in the copending application Serial No. 206,002, filed May 4, 1938 by Christian J. Wernlund, Harry L. Benner and Robert R. Bair.

A difficulty sometimes experienced in electroplating copper cyanide solutions is the formation of pits in the electroplated surface. This is particularly troublesome when a bright copper plating process is utilized. The formation of pits is especially apparent when a process is utilized for electroplating smooth, bright copper deposits. Also, it has been observed that pitting generally is most likely to occur in baths having relatively high concentrations of copper cyanide.

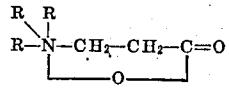
An object of the present invention is an improved method for electroplating smooth bright copper deposits. Another object is to provide means for the prevention of pitting in cyanide copper plating baths. A further object is to provide for cyanide copper plating baths certain addition agents which will prevent pitting and act as brighteners. Other objects will be hereinafter apparent.

The above objects may be attained in accordance with the present invention by adding small amounts of certain betaine-type organic compounds to cyanide copper plating baths. These materials, which are more fully described hereinafter, have been found to inhibit or completely prevent the formation of pits in plating from copper cyanide baths and further, they usually have more or less of a brightening effect. The extent of the brightening effect will depend upon the particular betaine material used, the particular type of composition of electroplating solution utilized and plating conditions such as current density and bath temperature. The antipitting effect is substantially independent of such conditions.

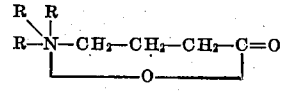
The addition agents used in practicing my invention are derivatives of the simple alpha, beta and gamma betaines, which have the following structural formulae, wherein R stands for an alkyl radical, e. g. methyl, ethyl, etc. or a modified alkyl radical, e. g., hydroxyethyl and the like.



Alpha betaine

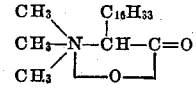


Beta betaine

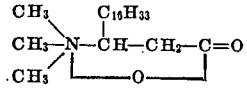


Gamma betaine

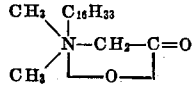
The above simple betaines are not all suitable as addition agents for my method. My addition agents are betaines which have at least one non-cyclic hydrocarbon radical containing from 10 to 20 carbon atoms. The non-cyclic hydrocarbon radical may be a straight chain or a branched chain and it may be either saturated or unsaturated. It may or may not be modified by the inclusion therein of radicals or groups such as hydroxyl, amino and the like. These hydrocarbon radicals are substituted either for one of the alkyl groups on the nitrogen atom of the betaine or for one of the hydrogen atoms on the alkylene group in the betaine or both. For example, trimethyl-C-cetyl alpha betaine which is a suitable addition agent, has the following formula:



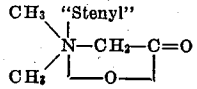
Similarly, the formula of trimethyl-C-cetyl beta betaine is as follows:



The other type of betaine utilized in my invention is one in which the long chain hydrocarbon radical is substituted on the nitrogen atom as exemplified by the following:



Dimethyl-N-cetyl alpha betaine



Dimethyl-N-"stenyl" alpha betaine

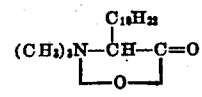
In the N-"stenyl" betaine shown above the term "stenyl" is used to designate a mixture of essentially C_{16} and C_{18} carbon length chains with some C_{12}, C_{14} and C_{20} carbon length chains also present. Thus, the N-"stenyl" betaine is a mixture of betaines having substituted hydrocarbons of the nature indicated by the above definition of the term "stenyl." The preparation of the above

N-stenyl betaine and similar betaines is described in U. S. Patent 2,129,264, Downing et al. It is understood that in the various betaines utilized in this invention the metal groups attached to the nitrogen atom in the above formulations may be replaced by other alkyl groups which may contain more or less than 12 carbon atoms. For example, in the N-"stenyl" betaine shown above, the two methyl groups may be replaced by other alkyl or modified alkyl groups such as ethyl, propyl, hydroxyethyl and the like.

Various of the betaines which may be used to practice my invention are listed below by way of illustration:

Trimethyl-C-decyl alpha betaine
Trimethyl-C-cetyl alpha betaine
Trimethyl-C-cetyl gamma betaine
Dimethyl, beta-hydroxyethyl-C-cetyl alpha betaine
Methyl, di(beta-hydroxyethyl)-C-cethyl alpha betaine
Trimethyl-C-lauryl alpha betaine
Trimethyl-C-lauryl gamma betaine
Trimethyl-C-stearyl alpha betaine
Dimethyl-N-stenyl alpha betaine
Dimethyl-N-stenyl-C-methyl alpha betaine
Methyl-N-distenyl alpha betaine
Dimethyl-N-stenyl-C-cetyl beta betaine
Dimethyl-N-decyl, beta-hydroxy gamma betaine
Dimethyl-N-heptadecyl alpha betaine
Dimethyl-N-octadecyl-C-methyl alpha betaine
Dimethyl-N-octadecyl beta betaine
Dimethyl-N-octadecyl, beta-hydroxy gamma betaine

Of the various betaines which may be utilized in practicing my invention I prefer to use trimethyl-C-cetyl alpha betaine, dimethyl-N-stenyl alpha betaine and trimethyl-C-decyl alpha betaine. The latter betaine has the formula:



Trimethyl-C-decyl alpha betaine

The following examples further illustrate my invention:

EXAMPLE No. 1

Plating bath

NaCN	17 oz./gal.
CuCn	16 oz./gal.
NaOH	4 oz./gal.
NaCNS	2 oz./gal.
Trimethyl-C-cetyl alpha betaine	1 to 20 cc./gal. (25% H_2O soln.)
Temperature	75–80° C.
Anodes	Electrolytic cathode copper
Ratio anode to cathode surface	3:1

Betaine concentration	Current density	Plate thickness	Results
	Amps./sq. ft.		
1 cc./gal	45	0.001" Cu.	Bright—no pits.
2 cc./gal	45	0.001" Cu.	Do.
4 cc./gal	45	0.001" Cu.	Do.
10 cc./gal	45	0.001" Cu.	Do.
20 cc./gal	45	0.001" Cu.	Do.

No pitting could be produced in these solutions at 15 to 45 amps. per sq. ft.

EXAMPLE No. 2

Plating bath

NaCN	18 oz./gal.
CuCN	16 oz./gal.
NaOH	4 oz./gal.
NaCNS	2 oz./gal.
Trimethyl-C-decyl alpha betaine	2 & 4 cc./gal. (25% H_2O soln.)

Operating conditions as in Example No. 1.

A. Betaine concentration, 2 cc. per gal.

Current density	Time	Results
	Min.	
20 amps./sq. ft.	20	Bright—no pits.
30 amps./sq. ft.	15	Do.
40 amps./sq. ft.	15	Do.

B. Betaine concentration, 4 cc. per gal.

Current density	Time	Results
	Min.	
20 amps./sq. ft.	20	Not bright—no pits.
40 amps./sq. ft.	15	Bright—no pits.

EXAMPLE No. 3

Plating bath

NaCN	17.5 oz./gal.
CuCN	16 oz./gal.
NaOH	4 oz./gal.
NaCNS	2 oz./gal.
*Dimethyl - N - stenyl alpha betaine	0.2 to 10 gms./gal.
Operating conditions	Same as in Example No. 1
Current density	45 amps./sq. ft.

Run	Betaine concentration	Plate thickness	Results
	Gms./gal.		
A	0.2	0.001" Cu.	Bright but hazy.
B	1	0.0007" Cu.	Brighter than A.
C	2	0.0008" Cu.	Bright—no pitting.
D	10	0.0008" Cu.	Very bright—no pitting.

* The betaine was added as a 10% water solution.

The amounts of the betaines required in the copper plating solution are small and usually will not exceed about one ounce per gallon. Generally, the betaines are effective as anti-pitting agents in amounts as low as 0.01 oz. per gallon. The optimum amount will vary, depending upon the betaine used and the composition of the copper plating bath. For electroplating copper from a copper plating bath containing 8 or more ounces per gallon of copper cyanide and sufficient alkali metal cyanide to form the copper double salt, I prefer to use from about 0.02 to 0.2 ounce per gallon of trimethyl-C-cetyl alpha betaine, trimethyl-N-stenyl alpha betaine, or trimethyl-C-decyl alpha betaine.

I have found the betaines to be substantially chemically stable in the copper cyanide electroplating solutions, even when the electroplating operation is carried out at elevated temperatures of 60 to 80° C. in baths of low or high alkalinity. It is therefore only necessary to add sufficient of the betaine from time to time to replace that lost by adherence to the work removed from the plating bath. Other addition agents or brightening agents may be added to the bath in addition to the betaine, for example, the brightening agents specified in the aforesaid patent application, Serial No. 206,002. The betaines are chem-

ically compatible with the various addition agents commonly used in copper plating.

I claim:

1. A copper plating process which comprises electrolyzing a copper alkali metal cyanide solution to which has been added from 0.01 to not more than 1 ounce per gallon of a betaine having at least one non-cyclic hydrocarbon radical which contains 10 to 20 carbon atoms.

2. A copper plating process which comprises electrolyzing a copper sodium cyanide solution to which has been added 0.02 to 0.2 ounce per gallon of trimethyl-C-cetyl alpha betaine.

3. A copper plating process which comprises electrolyzing a copper sodium cyanide solution to which has been added 0.02 to 0.2 ounce per gallon of trimethyl-C-decyl alpha betaine.

4. A copper plating process which comprises electrolyzing a copper sodium cyanide solution to which has been added 0.02 to 0.2 ounce per gallon of dimethyl-N-stenyl alpha betaine.

DONALD A. HOLT.