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3,309,293

COPPER CYANIDE ELECTROPLATING BATH

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This application is a continuation-in-part of co-pending application Ser. No. 636,862 filed Jan. 29, 1957, now abandoned, for "Copper Bath With Alkylene Oxide Derivatives," which is a continuation-in-part of Ser. No. 478,908 filed Dec. 30, 1954, now abandoned, for "Copper Plating Composition."

The present invention is directed to electroplating, more particularly to an improvement in a copper cyanide plating bath whereby higher efficiency is obtained.

The addition of surface active agents to cyanide copper baths has been proposed frequently in the past to increase the tolerance of the baths toward organic addition agents and these agents were required to be present in comparatively large concentrations. For example, the use of alkyl betaines has been suggested. In order to overcome the adverse effects of water breaks inherent in these materials, cationic quaternary ammonium chloride compounds were incorporated therewith.

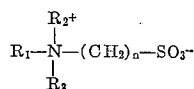
The concentration of betaine to be effective was comparatively high, the minimum being .075 gram per liter. The tolerance thereof to organic compounds was low, and the rinsability of the coating was far from that desired. Also, the brightening effect was only moderate.

The present invention is intended to overcome the deficiencies of the prior art, it being among the objects thereof to provide an additive to a cyanide copper plating bath which will not only impart improved brightness thereto, but will also be effective in the low current density areas.

It is also among the objects of the invention to introduce such an additive which will give better rinsability with little or no tendency for water breaking, have greater tolerance to organic contamination, and be compatible with other bath additives.

It is further among the objects to provide a substance which will act as an improved hydrotrope when used in conjunction with other wetting agents and will show synergistic effects.

In practicing the invention, there is added to the bath a compound of the following general formula, that is a sulfobetaine:



wherein R_1 is $CH_3(CH_2)_y$ and the CH_2 chain may have some unsaturated radicals, having y carbon atoms, and y is 5 to 25. R_2 and R_3 are the same or different radicals taken from the class of H and alkyl and hydroxy alkyl having 1 to 4 carbon atoms, n is 1 to 6. The components include the anhydrides wherein S is linked to N through oxygen. Examples of such radicals are oleyl, myristyl, methyl, octyl, hydroxy propyl, and the like.

Such components are very active surface active wetting agents when used alone. They also improve the characteristics of other known wetting agents, including those described below.

In conjunction with such brightening agents, such as the ethylene oxide adducts, the sulfobetaines show synergistic effects. For instance, many such adducts exhibit reduced solubility in the bath and cause cloudiness at increased temperatures. Such cloudiness is greatly reduced and even completely eliminated when the sulfobetaines are added to the bath.

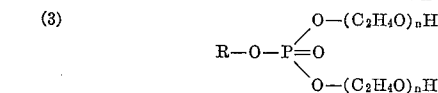
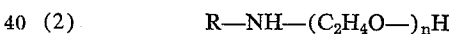
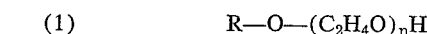
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Cyanide copper plating baths, particularly the high efficiency baths, operating with a low free cyanide content, are desirable for improved and broader bright current density range and higher efficiency. However, such baths are highly sensitive to skip plating and they exhibit dullness in the low current density range when contaminated with organic substances. The prior carboxy betaines and carboxy acids do not improve the brightness in the low current density areas to any such extent as the sulfobetaines under equivalent conditions.

In cyanide copper plating, numerous metallic addition agents are used to help brighten the deposit. Some of the metallics which have been proposed are the soluble salts of lead, antimony, bismuth, thallium and arsenic. Lead, antimony and thallium have been used in conjunction with sulfur compounds such as thiocyanate or with selenium compounds. They, however, have the undesirable characteristic of occasionally causing rough deposits. Also, when the plating bath was idle, they tended to deposit on the anode by immersion and were thus removed from solution. This deposition necessitated the use of excessively large amounts of these metallics and required a period of initial electrolysis to dissolve the deposited metallic brighteners from the anodes in order to make them effective in the bath.

It has been found that certain surface active wetting agents when used in cyanide copper electrolytes in conjunction with certain metallic addition agents, prevent the metallics from depositing on the copper anode by immersion when the bath is idle. They thus reduce the necessity of requiring higher concentrations of these metallics in order to be effective and hence reduce or eliminate the tendency to cause roughness of the deposit. These wetting agents are also beneficial when used alone or in combination with each other as herein subsequently described.

The aforementioned addition agents are compounds having the following formulas wherein n is 2 to 100:



R is aryl or alkyl containing from 6 to 20 carbon atoms. R' is $(CH_2)_yCOOH$ where y is 1 to 6.

Of these agents, nitrogen containing compounds are preferred to the others, although a beneficial effect upon the bath is produced by the use of any one or more.

Many of the aforementioned compounds can be used in small concentrations, for example .001 to .01 gram per liter, and still remain effective. It is true, however, that under certain conditions higher concentrations may be required or desired and are not harmful. These concentrations may go up to the limit of solubility of the particular compound used. Since these materials have the characteristic of increasing the tolerance of the cyanide copper bath to organic contamination, they may also be used in higher concentrations to overcome the effect of organic contamination in addition to having the beneficial effect referred to above on the heavy metals. However, with very high concentrations, many of these ethylene oxide condensates tend to cloud or even salt out under the operating conditions of the cyanide copper baths and thus

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tend to limit the concentration which can effectively remain in solution.

It has been found that by incorporating with these ethylene oxide compounds small amounts of ampholytic surface active agents or anionic wetting agents, a reduction in the clouding tendency is obtained, permitting the use of larger amounts of these condensates. By ampholytic compounds is meant those compounds which have the property of dissociation in either acid or basic media. The ampholytic compounds which have been found satisfactory for the use described in the foregoing paragraphs are as follows:

(8) RNHR'

R is aryl or alkyl containing from 6 to 20 carbon atoms. R' is $(CH_2)_ySO_3H$, wherein y is 1 to 6.

It is also possible using the modified ethylene oxide compound 7 to provide additives which do not readily cloud when used in high concentrations in the bath without impairing the beneficial effect thereof on the heavy metal addition agents.

These modified compounds have an improved cloud point, impart brightness to the cyanide copper baths and still maintain the desirable property of reacting with heavy metal addition agents. These ethylene oxide-carboxy acid ampholytes of Example 7 and the sulfonic ampholytes of Example 8 are also effective brighteners in the cyanide copper baths and are completely stable under all normal conditions of operation.

In view of the disadvantages inherent in prior art additives, the present invention overcomes practically all of the defects above noted. Applicants have obtained superior brightening of the deposits and particularly so in the low current density areas. They obtain better rinsability of the work, and have eliminated the tendency to water breaking. The additives produce greater tolerance to the presence of contaminants of organic nature. When used in conjunction with other wetting agents they act as improved hydrotropes. Our baths are notably effective to give excellent results in low free cyanide baths. The baths are not subject to skip plating.

The following examples will serve to further illustrate this invention, the conditions of operation being the same as for the standard cyanide copper bath, the amounts being grams per liter (g./l.). The conditions of operation are those ordinarily used in Hull cell operation. A temperature of about 140° to 180° F. is used with a current density of about 10 to 60 amperes per square foot. Plating is conducted for 10 minutes with continuous agitation:

Example 1

CuCN	60
KCN	90
KOH	30
Rochelle salts	45
TI as a soluble salt	.007
Se as K_2Se	.004
Lauryl amine of polyethylene glycol 660	.02
Sodium ethyl taurate of lauryl amine	.08

Example 2

CuCN	60.0
KCN	95.0
KOH	30.0
Rochelle salts	25.0
$C_{12}H_{25}OPO_3(C_2H_4O)_{20}H$	0.15
Se as K_2SeO_3	0.3
Lauryl sulfobetaine	0.2

Example 3

CuCN	45.0
KCN	83.0
KOH	30.0
Decylamine sodium ethyltaurate	0.25

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Example 4

CuCN	60
KCN	95
KOH	15
5 Rochelle salts	25
Sodium acetate of lauryl amine polyethylene glycol 660 $(C_{12}H_{24}-N-(C_2H_4O)_{15}H)CH_3COONa$	0.25

Example 5

CuCN	60
10 KCN	95
KOH	30
KCNS	15
Sb as tartrate	.008
Lauryl diethylenetriamine of polyethylene glycol 800	0.1
15 Lauryl dimethyl sulfobetaine	0.5

Example 6

CuCN	60
KCN	95
20 KOH	30
KCNS	15
Sb as tartrate	.008
Lauryl thioether of polypropylene glycol 1000	.05
25 Lauryl amine sulfoacetate	0.4

Example 7

Copper cyanide	60.0
Free KCN	12.0
KOH	45.0
30 NaCNS	15.0
KSb Tartrate	0.02
Cetyltrimethyl sulfobetaine	0.3

Example 8

35 Copper Cyanide	45.0
Free KCN	10.0
K Tartrate	45.0
Selenourea	.003
Pb acetate	.004
40 Nonyl ether of polyethylene glycol 2000	0.20
Oleyldimethyl sulfobetaine	0.1

Example 9

CuCN	60
45 KCN	95
KOH	25
Rochelle salts	30
Se as selenourea	.003
Methyl, hydroxyethyl, cetyl sulfobetaine	1.0

Example 10

CuCN	45
KCN	70
KOH	15
55 Rochelle salts	30
Se as potassium selenosulfite	.005
Sodium methyl taurate of decylamine	0.2

Example 11

CuCN	60
60 KCN	100
KOH	30
Potassium citrate	30
Dimethyl, lauryl sulfobetaine	.03

While only a certain number of specific embodiments of this invention have been described, nevertheless this invention is not limited thereto and such changes as may be apparent to one skilled in the art may be made without departing from the spirit thereof. Furthermore, this specification is to be broadly construed and not to be limited except by the character of the claims appended hereto.

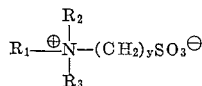
In the claims there are listed a number of sulfonic acids. These may be introduced or used in the form of the soluble salts thereof. Such salts are formed in the alkaline baths when the free acids are added.

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What is claimed is:

1. In an aqueous alkaline cyanide copper plating bath, the improvement which comprises the addition to said bath of $\text{RNH}(\text{CH}_2)_y\text{SO}_3\text{X}$; in the amount of 0.001 g/l. to the limit of solubility and wherein R is a radical selected from the group consisting of alkyl radicals having 6 to 20 carbon atoms, X is H or alkali metal, and y is 1 to 6.

2. In an aqueous alkaline cyanide copper plating bath, the improvement which comprises the addition to said bath of at least one compound selected from the group consisting of



wherein y is 1 to 6; R_1 is a radical selected from the group consisting of aliphatic chains having 6 to 20 carbon atoms; and R_2 and R_3 are radicals selected from the group consisting of alkyl having 1 to 4 carbon atoms; the amount of said additive being from 0.001 g/l. to the limit of solubility.

3. An alkaline cyanide copper bath according to claim 2, characterized in that it contains polyglycol ethers hav-

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ing surface activity, said ethers having 2 to 100 ethoxy groups.

4. An alkaline cyanide copper bath according to claim 1, characterized in that there is also present an agent which is selected from the group consisting of an ethoxylated alcohol amine and thio-alcohol.

References Cited by the Examiner

UNITED STATES PATENTS

10	2,255,057	9/1941	Holt	204—52
	2,541,700	2/1951	Holt	204—52
	2,765,269	10/1956	Ostrow et al.	204—46
	2,817,627	12/1957	Ostrow et al.	204—44
15	2,828,252	3/1958	Fischer	204—49
	2,848,394	8/1958	Foulke et al.	204—52
	2,873,234	2/1959	Passal	204—52
	2,873,235	2/1959	Passal	204—52
	3,111,465	11/1963	Passal	204—44

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