United States Patent Office 2,732,336 Patented Jan. 24, 1956

2,732,336

ELECTROPLATING COMPOSITION FOR COPPER

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No Drawing. Application April 20, 1953, Serial No. 349,935

5 Claims. (Cl. 204—52)

This invention relates to electroplating from cyanide baths, more particularly to a bath composition which is particularly adapted to produce bright coatings of soft, ductile electroplates of copper. The present application is a continuation-in-part of my co-pending application Serial No. 242,041, filed August 15, 1951, entitled "Electrolytic Bath for Copper and Silver," and now abandoned and is also a continuation-in-part of copending application Serial No. 126,679, now Patent No. 2,694,677, dated November 16, 1954.

Numerous attempts to obtain such bright coatings have been made. For instance, it has been proposed to use alkali metal selenite as an addition agent to an electrolytic bath in relatively large amounts. Such baths had a number of disadvantages in that the selenites tended to break down with a resultant adverse effect on the bright plating range. During the electrolysis the anodes became blackened, forming insoluble selenium compounds which were loosened from the anodes and tended to co-deposit with the desired metal, resulting in rough deposits which were commercially unusable. Also in commercial operation, due to the resulting very narrow bright plating range, non-uniform appearance of the deposits resulted, and the platings were in many cases insufficiently bright so that buffing was necessary.

It has also been proposed to provide a bath composition containing as one of the plating metals antimony or the like, as for example, in providing a plated alloy of copper, zinc and antimony. However, such coatings were not at all bright and required further operations in order to obtain a bright surface. The addition of lead or antimony in soluble form to copper plating baths resulted in hard and brittle deposits.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior baths of the type described, it being among the objects of the present invention to provide a bath composition into which a relatively small amount of addition agents is introduced and which results in greatly increased brightness of the plated surface, with a wider, more uniform and bright plating range.

It is also among the objects of the present invention to provide a bath composition which results in a plate which is brilliant, soft and ductile and which may be readily buffed if desired to cause the coating to flow, as for example, on steel.

The invention is based on the discovery that the addition to a copper cyanide bath of very small amounts of selenium in soluble form together with small amounts of lead or antimony in soluble form, gives a plate which is bright and does not require buffing. It is the cooperative action of the additives which is necessary to obtain the full benefits of the invention.

In practicing the present invention there is provided an alkaline cyanide bath composition which is usually of the ordinary type and containing cyanides of copper. There is added thereto a selenium compound which may be a metal selenide or an organic selenium compound or

mixtures thereof. The amounts so added are extremely small, being from .0001 to .01 gram per liter. It is highly desirable to have present together with the selenium, a small amount of a metal in the form of its water soluble salts, the metal being lead or antimony. The amounts thereof may vary considerably and usually there is present an amount of lead equal to about .001 to 1.0 gram per liter, the antimony being used in greater amounts, usually from about .01 to 5.0 grams per liter.

The active brightening agents in the present high speed copper cyanide plating baths are controlled quantities of organic selenium compounds or selenides which are converted into organic form in the bath. Less effective, but useable, are the soluble selenites and selenates. Care must be taken to maintain a small and less than critical amount of such selenium compounds in the bath, as otherwise the bright plating range will be reduced. Such selenium compounds are effective in the presence of lead or antimony salts. Preferably, those soluble selenium compounds having a valence of —2 are used.

The following are specific examples of the operation of the present invention. In said examples the stated amounts are in grams per liter and water.

Example 1

The composition is as follows:

CuCN	45.0
Total KCN	72.0
Free KCN	9–12
Dipotassium tartrate	45.0
KOH	15.0
Na_2Se	.002
Pb (as nitrate)	.001

The article is plated at a temperature of 140° to 170° F. with a current density of 10 to 60 amperes per square foot. During the plating the bath is continuously agitated. The resulting coating is smooth, brilliant and ductile.

Example 2

The following composition is provided:

CuCN	60.0
Total KCN	84.0
KOH	30.0
Free KCN	10–15
KCNSe	.001
Pb (as tartrate)	.002

The plating is conducted at 140°–180° F. with a current density of 20 to 50 amperes per square foot with continuous agitation.

Example 3

The following composition is provided:

CuCN	75.0
Total NaCN	90.0
Rochelle salts	45.0
KOH	15.0
Free NaCN	7.5
Selenophenol	.005
Sb (as tartrate)	.003
Pb (as tartrate)	.001

The plating is accomplished at about 175° F. with a current of 60 amperes per square foot and continuous agitation.

The selenides used are the ordinary alkali metal compounds or such other salts of selenium as are soluble in the bath. The organic selenium compounds may be the alkali metal selenocyanates or other soluble compounds. Also selenoureas or selenophenols may be used. In addition, compounds having the formula RSeH which are analogous to the mercaptans are suitable for the present purpose. R represents aryl or alkyl, the aryl groups be-

ing mono or polynuclear and the alkyl groups having 1 to 6 carbon atoms.

Also suitable for the purpose are the water soluble selenites and selenates although they are considerably inferior to the above named compounds and relatively large amounts thereof are necessary. Such selenites and selenates when added to the bath in the absence of lead or antimony in the form of their salts, break down during the plating operation and fail to give bright deposits over a wide range of current densities. However, in combination with soluble compounds of lead or antimony, or both, satisfactory results in plating are obtained. However, relatively large amounts of the selenites or selenates are used up to, say, 5 grams of selenium per litre. When the selenites or selenates are used, larger amounts of the lead or antimony salts are added to the bath than when selenium compounds having a valence of —2 are used. Also, baths containing selenites or selenates which have broken down, may be made operable by the addition of relatively large amounts of lead or antimony salts; for instance, more than .01 gram per liter of lead salts. The following are specific examples of such baths.

Example 4

The following bath is prepared:

CuCN	45 gm. per liter.
Free KCN	9.5 gm. per liter.
$K_2C_4H_4O_6$	45 gm. per liter.
KOH	15 gm. per liter.
K_2SeO_3	1 gm. per liter.
Pb (as acetate)	0.002 gm. per liter.

The bath is maintained at a temperature of about 150° F. and a current density of 35 to 40 amperes per square foot is used. A bright deposit not requiring buffing is obtained.

Example 5

The following bath is prepared:

CuCN	8 oz. per gal.
Free NaCN	.5 oz. per gal.
Rochelle salts	6 oz. per gal.
KOH	2 oz. per gal.
K_2SeO_4	1 gm. per liter.
Pb (as chloride)	0.002 gm. per liter.

The bath is maintained at 160° to 170° F. with a current density of about 35 amperes per square foot. The plating is a satisfactorily bright plate.

The lead and antimony are used in the form of soluble salts either organic or inorganic, such as the tartrate, nitrate or chloride. While these metals would ordinarily render the coating brittle, in the presence of said selenium compounds the deposits are not only ductile but also more uniform and brilliant. These effects are obtained over all current densities ordinarily used in the plating of copper, thereby insuring uniform brightness over the entire plated area.

Example 6

Selenium in the form of organic substances having a valence of —2 and in the form of selenides, also having a valence of —2, are capable of giving bright deposits in small quantities in copper and silver cyanide baths. A bath having the following composition in grams per litre of solution is typical:

	G.
Copper cyanide	45
Total KCN	72
Free KCN	9–12
KOH	15
Rochelle salts	45
KCNSe	.002

Plating is conducted at 140° to 170° F. with a current density of 10 to 60 amperes per square foot. The cathode is agitated and the deposit is bright and ductile. While the deposit is not as brilliant as those of Examples 1 and 2, it is sufficiently bright for an undercoat for bright nickel deposits. The bath is somewhat less tolerant to inorganic impurities than those of Examples 1, 2 and 3 but is sufficiently tolerant for commercial use.

The effectiveness of this bath continues over long periods of time, in contrast to baths containing the selenium having valences of +4 or +6, such as selenites or selenates, which are either ineffective or lose their effectiveness in the bath after a short time; they are unstable compounds which form dark deposits on the anode, cause the cathode to become dull, have a narrow bright range and give rough deposits, whereas those selenium compounds having a valence of —2 do not show such defects.

Although the invention has been described setting forth several specific examples of the operation thereof, the invention is not to be limited thereto as many changes may be made in the details thereof. For instance, the composition of the baths may be considerably altered and other substances may be added thereto, such as alkyl polyamines, including ethylene diamine, diethylene triamine, triethylene tetramine, and others up to alkyl groups having 5 carbon atoms, the number of amino groups being from 2 to 5, in amounts of about .25 to 50 grams per litre, although preferably smaller amounts up to 10.0 are used.

In place of the polyethylene compound set forth in Example 5, substances such as the polyglycols and esters thereof may be used, for instance, nonyl phenol polyethylene glycol, wherein the polyethylene radical has a molecular weight of at least 400. The tartrate of Examples 4 and 5 is usually represented by the formula $K(SbO)C_4H_4O_6$. The selenophenols include compounds of the type RSeH, wherein R is mono- or poly-nuclear aryl and alkyl having 2 to 12 carbon atoms. The conditions of operation may be varied within usual practice.

Larger amounts of the additives may be used, even above the maxima stated herein. However, such excess does not usually give beneficial effects, and too much excess may even be detrimental. This applies particularly to large amounts of selenium having a valence of +4, namely, the selenites.

These and other variations are possible within the spirit of the invention, which is to be broadly construed and not to be limited except by the claims appended hereto.

I claim:

1. An electrolytic bath comprising an aqueous alkaline solution of a cyanide of copper, a soluble selenium compound taken from the class consisting of selenides, selenoureas, selenocyanates, selenites, selenates, and compounds of the formula RSeH wherein R is an organic radical taken from the class consisting of alkyl radicals of 1 to 6 carbon atoms and aryl radicals of 6 to 12 carbon atoms said selenium compound being present in an amount from .0001 to 5 grams per liter, together with a soluble compound of a metal taken from the class consisting of lead and antimony in which the metal is present in an amount from .001 to 5 grams per liter.

2. An electrolytic bath according to claim 1 in which there is present an alkyl polyamine in the amount of .25 to 50 grams per liter.

3. An electrolytic bath according to claim 1 in which there is present an alkyl polyamine in the amount of .25 to 50 grams per liter, the alkyl group having from 2 to 5 carbon atoms.

4. An electrolytic bath according to claim 1 in which there is present an alkyl polyamine in the amount of .25 to 50 grams per liter, the number of amino groups being from 2 to 5.

5. An electrolytic bath comprising an aqueous alkaline solution of a cyanide of copper, a soluble selenite in an amount from 1 to 5 grams per liter, together with a soluble compound of a metal taken from the class consisting

of lead in an amount from .001 to .018 gram per liter and antimony in an amount from .01 to .2 gram per liter.

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