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BRIGHT COPPER PLATING BATH

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The present invention is directed to electro-plating baths and more particularly to an improved bath for plating a bright copper deposit which is ductile, soft and easily buffable, highly adherent and mirror bright for all thicknesses of plate.

It has been considered desirable in this art to provide plated articles in which the surface is highly polished or bright. Up to the present time this has been accomplished usually by a mechanical operation such as by buffing with the ordinary buffing wheel. Although this method produced the desired results, it required extra operations and thus added to the cost of production.

In order to overcome this disadvantage it has been proposed to add compounds to the plating bath for the purpose of producing a brighter plated surface. Among such compounds were those of lead, which acted to brighten the plated surface, but they had the serious disadvantage that the deposited metal was hard and brittle and the plating bath was difficult to control. It had also been proposed to add to the bath certain wetting agents of the betaine type which, while having some effect in brightening the surface, was disadvantageous in various respects in that the rinsing quality of the solution was poor and the deposit was not brilliant. Another material has been proposed which is capable of producing bright plating but only at low current densities, rendering control quite difficult.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior bath compositions, it being among the objects of the present invention to modify the ordinary copper plating baths by addition of suitable substances, whereby a brilliant and highly reflective surface is produced during the plating operation.

It is also among the objects of the present invention to provide a plating bath of the character described, which is operable over a wide range of current densities and temperatures, with excellent results.

It is further among the objects of the present invention to provide a bath which is adapted to produce a brilliant surface for all thicknesses of plate, wherein the plate is ductile and adherent.

In practicing the present invention, there is provided a copper plating bath which is an alkaline solution in water, containing copper cyanide and free alkali metal cyanide as the essential constituents. There is added to the bath a primary brightener that is a compound of selenium, which is soluble in the plating solution. A bath of this character gives excellent results in producing brilliant deposits where high current densities are used. In some cases, where a low current density is employed or the article being plated has low current areas, it has been found advantageous to add a secondary brightener. The latter substances are certain condensation products which act in conjunction with the primary brighteners to give bright deposits over a very wide range of current densities.

The selenium compounds consituting the primary brighteners may be organic or inorganic and they are added to the bath in relatively small amounts. The selenium in these compounds has a valence of minus 2 and the effectiveness thereof continues in the bath over long periods of time, whereas those compounds in which the selenium has a valence of plus 4 or 6 are either ineffective or lose their effectiveness in the bath after a short time. The invention includes particularly organic compounds having a valence of minus 2, such as selenocyanates. Other types of organic selenium compounds are also applicable, such as the seleno-phenols or derivatives thereof, such as alkyl substituted phenols, including cresols and others. Specific compounds of this characters are ΦSeH, NH_2ΦSeH and ΦSeO_2H.

The baths used may be any one of those which are standard in the art, as for example, a bath of the following compositions:

	Ounces per gallon
CuCN	6–8
Free KCN	.5 to 2.0
$K_2C_4H_4O_6$	6–8
KOH	2–4

Such a bath is normally operated at a pH of 12 to 13.5 and the temperature of operation is generally between 140° and 170° F. Another alkaline bath of similar character has the following composition:

	Grams per liter
CuCN	45–60
Free NaCN	3.75–7.5
Rochelle salts	45
KOH	15

The tartrates in either or both of the above solutions may be omitted in some instances while obtaining good results.

In accordance with the present invention, such baths may be modified as follows:

Example 1

The following composition is provided in water solution:

	Ounces per gallon
CuCN	8
Free NaCN	.5
Rochelle salts	6
KOH	2
NH_2ΦSeH	.2

The bath is operated at a current density of 10 to 60 amperes per square foot at a range of temperature of 140° to 170° F. The deposit is extremely smooth and has a high degree of brightness for all thicknesses of plate.

Secondary brighteners contemplated by the present invention consists of condensation products of certain nitrogen compounds containing amino and cyano groups, including nitriles, having not over 8 carbon atoms. These compounds are reacted with unsaturated esters and aldehydes and acylketones, such as acetonylacetone, and having up to 10 carbon atoms. The following are examples of such condensation products.

Example 2

A mixture is made of the following constituents:

	Cubic centimeters
Vinyl acetate	15
Tetraethylenepentamine	10
Water	75

The mixture is agitated and warmed in order to start reaction which is exothermic. When all of the vinyl acetate has been solubilized and has blended into the product, the mixture is heated to boiling and the temperature maintained for a few minutes to complete the reaction.

The exact nature of the constituents of the condensation product are not fully known. The product may be added to the composition of Example 1 in an amount equal to 4 cc. per liter. The resulting bath gives excellent brightness in plated products at low current densities.

Example 3

A mixture is made of the following composition:

	Cubic centimeters
Aldol	15
Ethylenediamine	8
Water	75

The reaction is conducted as set forth in Example 2. The resulting product is added to the composition of Example 1 in the amount of .5 oz. per gallon. Excellent brightness is obtained on the plated product at low current densities.

Example 4

A mixture is made of the following compostion:

	Grams
Vinyl acetate	10
KOH	10
Potassium cyanide	8
Water	20

The reaction is conducted as set forth in Example 2 and 2 cc. of the product is added to the standard copper plating bath.

Although the invention has been described setting forth several specific embodiments of the invention, the examples are intended to illustrate the invention and not to limit it as many variations in the details may be made within the spirit thereof. For instance, other copper plating baths of suitable character, such as are known in the art, may be used and the conditions of operation, such as temperatures and current densities, may be varied greatly. The proportions of the constituents of the bath may be altered and usually the amount of the primary brightener for good results is about 1 gram per liter of solution. A greater amount may be used and about 4.0 grams per liter appears to be the maximum. Smaller amounts may be used and substantial brightening has been obtained with as little as .005 gram per liter.

The amount of secondary brightener may range from .01 cc. per liter up to as high as 20 cc. per liter. In usual operations, about 4.0 cc. per liter has been found excellent. Other compounds than those specifically mentioned in the examples may be used in making the condensation products, such as aldehydes, including aldol, glyoxal, various ketones and substituted ketones, all such compounds having from 1 to 7 carbon atoms. Among the nitrogen containing compounds condensed with the above, such amines as ethanolamine, triethylene tetramine, alkali metal cyanides and the like may be used.

These and other changes in the details of the invention may be made within the spirit thereof and the invention is, therefore, to be broadly construed and not to be limited except by the character of the claims appended hereto.

This application is a continuation-in-part of my abandoned application, Serial No. 6,354, filed February 4, 1948, and entitled "Electro Deposition of a Bright Copper."

I claim:

1. A bright copper plating bath consisting essentially of an alkaline aqueous copper cyanide solution containing at least .005 gram per liter of selenium in the form of a soluble selenophenol wherein the valence of the selenium is minus 2.

2. A bright copper plating bath consisting essentially of an alkaline aqueous copper cyanide solution containing at least .005 gram per liter of selenium in the form of a soluble selenium compound wherein the valence of the selenium is minus 2 and taken from the class consisting of selenophenols and selenocyanates, and at least .01 cc. per liter of the condensation product of a substance taken from the class consisting of aldehydes and ketones having 1 to 7 carbon atoms and vinyl acetate with an aliphatic polyamine having from 2 to 8 carbon atoms and from 2 to 5 amino groups.

3. A bright copper plating bath consisting essentially of an alkaline aqueous copper cyanide solution containing at least .005 gram per liter of selenium in the form of a soluble selenium compound wherein the valence of the selenium is minus 2 and taken from the class consisting of selenophenols and selenocyanides, and at least .01 cc. per liter of the condensation product of a substance taken from the class consisting of aldol, glyoxal and acetonylacetone with an aliphatic polyamine having from 2 to 8 carbon atoms and from 2 to 5 amino groups.

4. A bright copper plating bath consisting essentially of an alkaline aqueous copper cyanide solution containing at least .005 gram per liter of selenium in the form of a soluble selenium compound wherein the valence of the selenium is minus 2 and taken from the class consisting of selenophenols and selenocyanates, and at least .01 cc. per liter of the condensation product of a substance taken from the class consisting of aldehydes and ketones having 1 to 7 carbon atoms and vinyl acetate with an aliphatic polyamine taken from the class consisting of tetraethylene-pentamine, ethylenediamine and triethylene-tetramine.

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