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COPPER ELECTROPLATING AND COMPOSITIONS THEREFOR

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This invention relates to new and useful electroplating compositions, and to a new and improved method for the electrodeposition of copper.

One of the objects of the invention is to prepare new and useful cyanide copper plating baths.

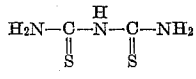
Another object of the invention is to prepare new and useful cyanide copper plating baths which produce improved brightening effects.

Still another object of the invention is to provide a method of electroplating copper whereby a bright copper plate is obtained on polished steel over which chromium can be plated without buffing the copper.

Another object of the invention is to provide a method of electrodepositing copper which operates efficiently in temperature ranges that are lower than those used in most cyanide copper plating baths. Other objects will appear hereinafter.

These objects are accomplished in accordance with this invention by preparing an alkaline aqueous cyanide copper electroplating bath containing dithiobiuret and electrodepositing copper therefrom.

Dithiobiuret has the following formula



The dithiobiuret is employed in an amount which is sufficient to enhance the brightness of the electrodeposited copper plate.

The invention will be further illustrated by the following example:

Example

An electrolyte was prepared by mixing the following ingredients:

9 ounces sodium cyanide
7 ounces copper cyanide
3–4 ounces sodium hydroxide
0.4 gram dithiobiuret
4 cc. Antarox B–201 (polyethylene glycol esterether)
Water sufficient to make a gallon of solution.

Polished steel sheets were plated in this electrolyte at a temperature of 130° F. and at a current density of 20 amperes per square foot.

An extremely bright copper plate was produced over which chromium could be plated without buffing the copper.

Other cyanide copper plating baths can be

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used in the practice of the invention. For example, any of the copper cyanide plating baths described in "Metal Finishing," 1949 edition, page 229 can be employed by substituting dithiobiuret for the brightener addition agents used in said baths. The same plating conditions can also be used.

In the foregoing example the Antarox B–201 is a non-ionic wetting agent. The wetting agent functions in the electroplating bath to prevent pitting due to hydrogen bubbles that stick to the surface of the plate unless made more readily removable by agitation or lower surface tension resulting from the use of a wetting agent. It will be understood that any bath stable wetting agent can be used and even such use is optional.

The quantity of the dithiobiuret added to the copper plating bath may be varied. However, an increase in the quantity over that given in the illustrated example does not substantially increase the brightness of the resultant plate and a decrease in the quantity tends to reduce the brightness of the plate. In general it is preferable to employ a quantity of dithiobiuret within the range of about 0.4 to 1 gram per gallon of a cyanide copper plating bath.

The current densities employed in plating copper from electroplating baths prepared in accordance with the invention and the temperatures used may be substantially the same as those now employed in the art for plating copper from alkaline cyanide solutions. Most copper plating baths are operated at current densities of 15 to 20 amperes per square foot. In some instances the current densities can be as low as 5 amperes per square foot and higher current densities above 20 amperes per square foot can also be employed. The temperature used is preferably within the range of 120° to 140° F., the optimum temperature being around 130° F., whereas the temperatures customarily employed in the art for most bright copper cyanide plating baths are at least 140° F. and usually somewhat higher.

The quantity of copper in the copper plating bath described in the example is around 5 ounces of copper per gallon of bath. In general, it is preferable that the bath contain 3 to 8 ounces of copper in dissolved form per gallon of bath where direct current is used. Where pulsating direct current is used the bath can contain higher concentrations of copper as, for example, around 12 ounces of copper per gallon of bath. A concentration of copper around 5 ounces per gallon of plating solution is preferred.

Although the invention does not reside in the

specific proportions of cyanide and free hydroxide present in the bath, it is preferable that the electroplating bath contain 0.5 to 1.75 ounces per gallon of free sodium cyanide over and above the amount required to form the complex sodium copper cyanide $Na_2Cu(CN)_3$. The quantity of free alkali usually corresponds to 1 to 7 ounces of alkali metal hydroxide, preferably 3 to 4 ounces of sodium hydroxide. Sodium carbonate may be present in the bath either as an impurity or as a makeup agent.

An ordinary alkaline cyanide copper bath containing 5 ounces per gallon of copper gives a frosty or burned copper plate when copper is electrodeposited therefrom at a temperature of 130° F. at a current density of 20 amperes per square foot. The same bath containing a small quantity of dithiobiuret when electroplated under the same conditions gives a brilliant copper plate so bright that it can be electrodeposited on polished steel and chromium can be plated thereover without buffing the copper. It will therefore be apparent that the present invention provides a new and useful contribution to the art of bright copper plating. The electrolytes provided in accordance with the invention also have excellent throwing power even in the lower temperature ranges of 120° to 140° F.

The invention is hereby claimed as follows:

1. An alkaline copper cyanide plating bath comprising copper in a soluble form dissolved in an alkaline cyanide aqueous liquid containing dithiobiuret dissolved in said bath, the quantity of dithiobiuret being sufficient to produce a bright plate when copper is electrodeposited from said bath.

2. An alkaline cyanide copper plating bath comprising essentially 3 to 8 ounces per gallon of metallic copper dissolved in the form of a complex alkaline copper cyanide salt in water containing 0.4 to 1 ounce per gallon of dithiobiuret.

3. An alkaline copper cyanide plating bath comprising essentially copper in the form of the complex salt $Na_2Cu(CN)_3$ dissolved in water in

proportions such that the quantity of copper is within the range of 3 to 12 ounces per gallon, free cyanide in proportions within the range of 0.5 to 1.75 ounces per gallon, free sodium hydroxide in proportions within the range of 1 to 7 ounces per gallon and dithiobiuret in proportions within the range of 0.4 to 1 gram per gallon together with sufficient water to make a gallon of electrolyte.

4. A method of copper plating which comprises electrodepositing copper from an alkaline aqueous cyanide bath containing copper in a soluble form in proportions within the range of 3 to 8 ounces of copper as metal per gallon of bath and a sufficient quantity of dithiobiuret to brighten the resultant copper plate.

5. A method of copper plating which comprises electrodepositing copper at a temperature within the range from 120° to 140° F. from an alkaline aqueous cyanide plating bath containing copper in a soluble form in proportions within the range of about 3 ounces to 8 ounces of copper as metal per gallon of bath and dithiobiuret in proportions within the range of about 0.4 to 1 gram per gallon of bath.

6. A method of copper plating which comprises electrodepositing copper from an alkailne aqueous cyanide plating bath onto polished steel, said bath containing 3 ounces to 8 ounces per gallon of copper as metal dissolved in the form of a complex sodium copper cyanide, 0.5 ounces to 1.75 ounces per gallon of cyanide, as NaCN, 3 to 4 ounces per gallon of NaOH and sufficient dithiobiuret to increase the brightness of the copper electrodeposited from said bath.

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