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2,955,992

BRIGHT COPPER PLATING PROCESS

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10 Claims. (Cl. 204—52)

This invention relates to the electroplating of bright copper from copper cyanide solutions. More specifically it relates to a new and improved process for plating from a bath containing a particular brightening agent with the use of a modified current.

In recent years selenium brighteners have been introduced into bright copper plating since they permit operation over a wide range of current densities, and the low valence selenium compounds are especially efficient brighteners, being active at very small concentrations in the plating bath. However, at concentrations capable of producing good brightness in the plated product at low and high current densities, these brighteners cause the plating to be dull within a narrow medium current density range. Accordingly, in order to produce uniform brightness over a wide current density range secondary brighteners have been added to the bath, which may consist generally of metals, such as antimony or lead. However, the use of a secondary brightener complicates the process since the bath now becomes critical, it being difficult to maintain the two brighteners in proper balance. Furthermore, these secondary brighteners produce considerable surface irregularity or roughness in the plated copper.

In bright plating it is generally accepted that the application of periodically reversed current to the cell gives smoother and more uniform deposits than uninterrupted direct current. This general proposition does not hold in the case of copper cyanide baths containing low valence selenium brighteners either alone or in combination with secondary brighteners. For example, a typical decorative cycle of 15 seconds plate and 3 seconds reversed current definitely increases the medium current density dullness, while longer and more sacrificial cycles are still worse. The prior art indicates that the quantity of reversed current should equal more than at least 10% of the coulombs of the plating phase, and in the above example the quantity of reversed current was 20% of of that of the plating current.

It is an object of the present invention to provide a broad current density range bright copper plating process which requires only one brightener, while using either interrupted current or periodically reversed current. It is a further object of the present invention to provide a more economical plating process and one which is simpler to control. It is a further object to provide a plating process which permits high plating speeds and in which the resulting copper plate is bright, ductile and adherent over a wide range of plating thicknesses. It is a still further object of the present invention to provide a process which considerably reduces the roughness of the copper plate, and also to provide a process which has improved tolerances toward impurities, especially sulfur.

In accordance with the present invention I have discovered that surprisingly in baths containing just one low valence selenium brightener the medium current density dullness is eliminated if too high polarization

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on the work is prevented by interrupting the plating current, either by periodic current interruption or by periodic current reversal, with reverse phases so short that they merely eliminate polarization. I have also found that by so operating, the troublesome secondary metallic brighteners, with their inherent control and product quality problems, are unnecessary.

The preferred brighteners in accordance with the present process are those selenosulfates (SeSO_3)= and selenocyanates (SeCN)= soluble in the copper plating bath, and preferably the alkali metal salts of these materials. Both the selenosulfates and selenocyanates are stable in dilute solutions and are preferably added to the bath from solutions of suitable concentration, which makes for easy dosage and good distribution of the brightener throughout the bath.

In addition to the selenosulfates and selenocyanates, many other selenium compounds soluble in the copper cyanide bath give similar effects. The selenium compounds within the scope of the present invention may be either organic or inorganic, but they will all contain selenium with a valence lower than +4, which are referred to herein as low valence selenium compounds. In the selenides for example selenium has a valence of -2. In other cases covalent bonds seem to be involved and the question of valence cannot be answered simply. Examples of such compounds are the selenosulfates, selenocyanates, polyselenides, and selenium compounds corresponding to the dithionites and dithionates. For the purposes of the present invention the designation "selenium compounds with selenium valencies lower than +4" is sufficient since the compounds in this class have been found to behave relatively similarly. However, unfavorable qualitative and quantitative differences were observed where selenium compounds of valence +4 and higher, for example the selenites and selenates, were employed. The present invention also contemplates the use of finely divided metallic selenium, which I believe forms low valency selenium compounds in the bath.

Extensive tests have shown that the brightening agents of the present invention give excellent results at extremely low concentrations in the plating bath. Furthermore, limitation of polarization by the methods set forth hereinafter not only produces a uniform brightness over the whole plating current density range, but also by so operating the brightener concentration is much less critical than it is with uninterrupted direct current. The present process gives a bright plate of excellent uniformity with selenium concentrations equivalent to 0.00008 to 0.0032 gram of selenium per liter. The activity of the brighteners actually begins about at 0.00008 gram per liter, and with some of the organic compounds as much as 0.05 gram per liter is required.

It is believed that the current cycles of the present process have the effect of preventing too high cathodic polarization. If interrupted current is used, the plating phase should not be too long, preferably shorter than 60 seconds. The shortest phases possible with mechanical switches, which generally will be about 1 second, work quite well. In this connection it has been found that unfiltered half wave current from a rectifier, which produces a cycle of $\frac{1}{120}$ second plate: $\frac{1}{120}$ second interruption, does not produce the desired effect. Thus the plating phase should not be less than about 1 second. The length of the interruption phase must be sufficient to permit a considerable decrease of cathodic polarization. If, on the other hand, this phase is made exceedingly long, plating speed is of course reduced unnecessarily. The optimum length of interruption depends on various conditions, such as temperature and degree of agitation. It has been found that interruption times amounting to from 10 to 100% of the plating time are satisfactory,

Such cycles as 5:1 seconds or 10:4 produce very satisfactory plates as do cycles like 15:3 and 40:16.

When the current is periodically reversed, the reversed phase must be of a duration giving satisfactory decrease of polarization without leading to substantial deplating action. In other words, operating conditions of the present process with periodically reversed current are outside the operating conditions of normal periodically reversed plating. In accordance with the present invention, I have found that the reversed phase must apply less than 10% of the coulombs of the plating phase, and under these conditions undesirable reactions at the work are avoided. Generally, for convenience sake the reversed current is applied at the same current density as the plating current. Cycles such as 15:½ seconds or 20:1 are preferred, but 40:2 still produces satisfactory plate. The times above mentioned apply to the current on the work, and if the switching devices used work with considerable delay this time lag should be taken into consideration.

The process of the present invention is effective with any of the basic copper alkali metal cyanide solutions as used in commercial and conventional copper plating. Examples of such basic copper plating baths are given in "Modern Electroplating," 1953 Ed., pages 194-225 inc. As is well known, the concentration of the basic chemicals used in such baths and the operating conditions thereof such as current density, temperature, agitation, etc. are mutually interdependent.

The following non-limiting examples illustrate the present process as applied to copper cyanide plating baths to which the selenium brighteners aforementioned have been added. In each of the following examples the temperature was about 150° F. and a works agitation of about 3 feet per minute was applied to a Hull cell panel.

Example I

Copper was electrodeposited from the following aqueous bath:

	G./l.
CuCN	45
"Free" KCN	11
KOH	8
Se (from K_2SeSO_3)	0.0004

The selenosulfate was added in the form of a suitably diluted aqueous solution of good stability, such as described in my co-pending application Serial No. 572,797, filed March 21, 1956, now abandoned.

When in this bath periodically interrupted current of a cycle 15:3 (seconds) was applied, a deposit of good brightness and uniformity was obtained in the current density range of about 1 to 40 a.s.f. (amperes per square foot). It is understood that these current densities refer to the plating phase of the above cycle.

Example II

Copper was plated from the following bath:

	G./l.
CuCN	45
"Free" KCN	11
KOH	8
Se (from K_2Se_x)	0.0032

The polyselenide was prepared according to "Organic Synthesis," vol. 18, page 27.

In this bath a periodically interrupted current of cycle 10:4 produced a deposit of good brightness and excellent uniformity over a current density range of about 1 to 45 a.s.f.

Example III

A copper plating bath was prepared as follows:

	G./l.
CuCN	65
"Free" KCN	15
KOH	9
Se (elemental)	0.0016

Finely powdered selenium was added to the hot bath and the solution was agitated for about 2 hours, when dissolution resulted.

Periodically interrupted current of a cycle 5:1 gave a deposit of good brightness and uniformity over a current density range of about 1 to 75 a.s.f.

Example IV

Copper was deposited from the following bath:

	G./l.
CuCN	45
"Free" KCN	11
KOH	8
Potassium tartrate	45
Se (from K SeCN)	0.0008

The selenocyanate was added in the form of a suitably diluted solution.

Application of periodically interrupted current of a cycle 20:4 produced a deposit of good brightness and uniformity over a current density range of about 1 to 40 a.s.f.

Example V

Periodically interrupted current of a cycle 10:4 was applied to a bath of the following composition:

	G./l.
CuCN	45
"Free" KCN	11
KOH	8
Se (from C_6H_5SeH)	0.05

C_6H_5SeH was prepared according to "Organic Synthesis," vol. 24, pages 89-93. Good brightness and excellent uniformity were produced over a current density range of about 1 to 45 a.s.f.

Example VI

Copper was deposited from the following bath:

	G./l.
CuCN	65
"Free" KCN	15
KOH	9
Potassium gluconate	12
Se (from $HOC_6H_4SeC_6H_4OH$)	.012

This organic selenide was made as described in "Chemical Abstracts," vol. 22 (1928), 3400.

Applying a periodically interrupted current of 40:16 gave a deposit of good brightness and uniformity over a current density range of about 1 to 55 a.s.f.

Example VII

A plating bath was prepared as follows:

	G./l.
CuCN	45
"Free" KCN	11
KOH	8
Se (from K_2SeSO_3)	0.0008

In this bath periodically reversed current of a cycle 20 seconds plate:1 second reversed current was applied. Copper of good brightness and uniformity was obtained over a current density range of about 1 to 45 a.s.f. In this case the current densities apply to both the plating and the reversed current phase.

This application is a continuation-in-part of my co-pending application Serial No. 572,797, filed March 21, 1956, and now abandoned.

What is claimed is:

1. A process for producing decorative or protective uniform bright copper-plate in a current density range of 1 to 75 a.s.f., which consists essentially of electroplating copper at a current density of 1 to 75 a.s.f. from a copper cyanide plating solution containing as the only compound which has a brightening effect upon the copper plate within said current density range and inorganic selenium compound in which selenium has a valence of less than

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+4, in amount equivalent to 0.00008 to 0.0032 gram per liter of selenium, while applying interrupted current, where the plating phases are longer than 1 second and shorter than about 60 seconds and the interruption phases reduce polarization with removal of less than 10% of the deposit of the plating phases.

2. A process as set forth in claim 1 wherein the interruption phases employ a current density of from zero to 100% of that of the plating phases.

3. A process for producing decorative or protective uniform bright copper plate in a current density range of 1 to 75 a.s.f., which consists essentially of electro-plating copper at a current density of 1 to 75 a.s.f. from a copper cyanide plating solution containing as the only compound which has a brightening effect upon the copper plate within said current density range an inorganic selenium compound in which selenium has a valence of less than +4, in amount equivalent to 0.00008 to 0.0032 gram per liter of selenium, while applying periodically interrupted current where the plating phases are longer than about 1 second and shorter than about 60 seconds and where the interruption phases amount to at least 10% of the plating phase time.

4. A process as set forth in claim 3 wherein the inorganic selenium compound is an alkali metal selenocyanate.

5. A process as set forth in claim 3 wherein the inorganic selenium compound is an alkali metal selenosulfate.

6. A process as set forth in claim 3 wherein the inorganic selenium compound is an alkali metal selenide.

7. A process for producing decorative or protective uniform bright copper plate in a current density range

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of 1 to 75 a.s.f., which consists essentially of electro-plating copper at a current density of 1 to 75 a.s.f. from a copper cyanide plating solution containing as the only compound which has a brightening effect upon the copper plate within said current density range an inorganic selenium compound in which selenium has a valence of less than +4, in amount equivalent to 0.00008 to 0.0032 gram per liter of selenium, while applying a periodically reversed current where the plating phases are longer than about 1 second and shorter than about 60 seconds, and where the reversed phase employs less than 10% of the coulombs of the plating phase.

8. A process as set forth in claim 7 wherein the inorganic selenium compound is an alkali metal selenocyanate.

9. A process as set forth in claim 7 wherein the inorganic selenium compound is an alkali metal selenosulfate.

10. A process as set forth in claim 7 wherein the inorganic selenium compound is an alkali metal selenide.

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