PROCESS FOR THE PRODUCTION OF METAL ELECTRODEPOSITS

Wennesmar Strauss, Dusseldorf-Benrath, Alfred Kirsch, Dusseldorf, and Wolf-Dieter Willmund, Dusseldorf-Holthausen, Germany, assignors to Dehnydag, Deutsche Hydrierwerke GmbH., Dusseldorf, Germany, a corporation of Germany

No Drawing. Application September 28, 1954
Serial No. 458,985

Claims priority, application Germany April 22, 1954
11 Claims. (Cl. 204—52)

This invention relates to a process for producing bright metal electrodeposits, and more particularly to electroplating solutions containing additives which eliminate the adverse effects of impurities in such solutions upon the electrodeposits produced therefrom.

It is well known in the electroplating art that the brightening effect of brightening agents added to electroplating solutions is seriously impaired by certain impurities contained in such solutions. Impurities which have such an impairing effect upon electrodeposits include those substances which cause the hardness of water as well as impurities which occur in technical grade metal salts employed to prepare electroplating baths, particularly copper-plating baths.

The obvious solution to this problem is to employ distilled water and chemically pure metal salts for the preparation of electroplating baths intended to be used in conjunction with brightening agents. However, it is evident that the use of such chemically pure components would not only be very impractical but also render the cost of electroplating objects so high as to make bright plated articles too costly.

It is, therefore, an object of the present invention to provide a method of electroplating objects in electroplating baths containing brightening agents which makes it possible to produce bright electrodeposits despite the presence of interfering impurities in the electroplating bath.

Another object of this invention is to provide additives for electroplating baths containing brightening agents which will render impurities present in the bath impotent as interfering substances in the production of bright electrodeposits.

Other objects and advantages will become apparent as the description of our invention proceeds. We have found that the interfering effect of impurities in electroplating baths containing brightening agents can be eliminated by adding to such electroplating baths tertiary amino compounds, free from carboxyl groups, having the general structural formula

\[ \text{G} \text{R} \text{N} \text{R} \text{G} \]

wherein \text{G} is selected from the group consisting of halogen, cyano, thiocyanato and nitro, \text{R} is selected from the group consisting of lower alkylene, monohydroxy lower alkylene, phenyl, and \text{R} \text{a} and \text{R} \text{b} are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and heterocyclic radicals which include the nitrogen atom selected from the group consisting of morpholino and piperidino, the radical \text{G} and the nitrogen atom being attached to carbon atoms of radical \text{R}.

Examples of compounds which are suitable for modifi- ing electroplating baths containing brightening agents in accordance with our invention are the following:

- \((\text{C}_2\text{H}_4)_2\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- 1-dioxyethylamino-ethylchloride-2
- \((\text{HOCH}_2\text{CH}_2)_2\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- 1-dioxyethylamino-ethylchloride-2
- \((\text{C}_2\text{H}_5)_2\text{N}—\text{CH}_2—\text{CHOHCH}_2\text{Cl}\)
- 1-dioxyethylamino-3-chloropropanol-2
- \((\text{HOCH}_2\text{CH}_2)_2\text{N}—\text{CH}_2—\text{CHOHCH}_2\text{Cl}\)
- 1-dioxyethylamino-3-chloropropanol-2
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N-(2-chloroethyl)-N-ethyl-aniline
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N-(3-chloro-2-oxypropy)-N-methyl-aniline
- \(\text{N}—\text{CH}_2\text{CHOHCH}_2\text{Cl}\)
- N-(3-chloro-2-oxypropy)-N-methyl-cyclohexylamine
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dicyclohexyl-2-chloro-ethylamine
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dicyclohexyl-2-chloroethyl-amine
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dimethyl-4-bromoaniline
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dimethyl-4-chloroaniline
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dimethyl-2-chloroaniline
- \(\text{N}—\text{CH}_2\text{CH}_2\text{Cl}\)
- N,N-dimethyl-3-nitroaniline
Tertiary amino compounds of this type may also be employed in the form of their salts of inorganic and organic acids, or in the form of the corresponding quaternary ammonium compounds.

In order to obtain the desired result the additives in accordance with our invention are added to electroplating baths, modified with brightening agents, in amounts ranging from 0.01 g./liter and 20 g./liter of bath, preferably from 2 to 8 g./liter of bath. The particular amount required varies from one specific compound to the other and also depends upon the nature of the brightening agents employed as well as upon the type and amount of impurities present. In general, objects are electroplated in a bath modified in accordance with our invention at a temperature ranging between 30° and 60° C. with a current density between 0.5 and 15 amp./dm².

Electroplating baths containing brightening agents and modified in the above manner in accordance with our invention will produce bright and lustrous electrodeposits over the entire effective range of current densities despite the presence of impurities of the above-described nature in the bath. Moreover, the additives in accordance with our invention have the further advantage that they increase the ductility of the electrodeposits produced from electroplating baths modified with such additives.

The additives of our invention are effective in all those electroplating baths which contain magnesium and calcium ions due to the use of hard tap water, and ferric ions introduced by the use of technically pure metal salts in the preparation of the electroplating solution. However, it has been found that they do not act as water-softening agents in the usual sense, and that they cannot be replaced by the typical water-softening agents such as sequestering agents or detergents. Nevertheless, these additives are capable of completely eliminating the adverse effect of the above-described impurities upon the brightness of electrodeposits produced from baths containing such impurities and brightening agents.

Although the exact theoretical reason for their action is not fully understood, it is believed that their effect comes into play at the surface of the metal object, which is indicated by the high concentrations in which these substances must be used in some instances to produce the desired effect.

The use of the additives in accordance with our invention does not require any changes in the conditions under which objects are usually electroplated in metal salt baths, particularly with respect to temperature and current densities. As amines, they are soluble in acid metal salt solutions, particularly in electroplating baths made from copper salts, and they are not decomposed by the action of heat or electric current during the plating process.

The additives of our invention can be employed to modify all types of electroplating baths containing brightening agents and in which the qualities of electrodeposits produced therefrom are adversely affected by the presence of impurities of the type described above. Thus, the additives may be used in electroplating baths for electrodepositing zinc, nickel, chromium, precious metals, and particularly copper, if such baths contain brightening agents.

The following examples will enable persons skilled in the art to understand our invention more completely.

Example I

A copper-plating bath was prepared which contained distilled water, 200 g./liter crystalline chemically pure copper sulfate and 60 g./liter chemically pure sulfuric acid. The bath was then modified with 0.75 g./liter N,N-dipropyl-dithiocarbamic acid-n-butylester-w-sodium sulfonate as a brightening agent. Iron objects were then electroplated in the modified bath using a current density range of 0.5–8 amp./dm². The copper deposits produced thereby were bright and lustrous.

As a comparison, a copper-plating bath having the same composition was prepared by using hard tap water instead of the distilled water, and technical grade copper sulfate rather than chemically pure copper sulfate. This bath was then modified with a brightening agent as above. Iron objects copper-plated in such a bath were provided with a copper deposit which was not as bright and lustrous as when distilled water and chemically pure copper sulfate were used to make up the copper-plating solution.

Example II

A copper-plating bath was prepared from hard tap water, 200 g./liter technical grade copper sulfate and 60 g./liter sulfuric acid. This bath was then modified by adding 0.75 g./liter N,N-dipropyl-dithiocarbamic acid-n-butylester-w-sodium sulfonate. Thereafter, 2.5 g./liter 2-dithiylamino-ethylchloride-1 were added. Iron objects were then electroplated in this bath within a current density range of 0.5–8 amp./dm². The copper deposits produced thereby were bright and lustrous, as well as being highly ductile.

Example III

A copper electroplating bath, prepared as described in Example II, where added 0.5 g./liter N,N-diethyl-dithiocarbamic-n-propelyester-w-sodium sulfonate as brightening agent together with 4 g./liter N-2-chloro-ethyl-piperidine. Iron objects were then electroplated in this bath within a current density range of 0.5–8 amp./dm². The copper deposits produced thereby were bright and lustrous, as well as being highly ductile.

Example IV

A copper electroplating bath, prepared as described in Example II, were added 0.5 g./liter N,N-diethyl-dithiocarbamic-n-propelyester-w-sodium sulfonate and thereafter 2 g./liter of the quaternary compound, prepared by mixing together morpholine with epichlorohydrin. Iron objects were then electroplated in this bath within a current density range of 0.5–8 amp./dm². The copper deposits produced thereby were bright and lustrous, as well as being highly ductile.

Example V

A copper electroplating bath of the same composition as described in Example II was modified by adding 0.5 g./liter N,N-diethyl-dithiocarbamic-n-propelyester-w-sodium sulfonate and 2.5 g./liter of the reaction product from diethylamine with epichlorohydrin. Iron objects were then electroplated in this bath within a current density range of 0.5–8 amp./dm². The copper deposits produced thereby were bright and lustrous, as well as being highly ductile.

While we have illustrated certain specific embodiments of our invention, we wish it to be understood that various changes and alterations can be made without departing...
from the spirit of our invention or the scope of the appended claims.

We claim:

1. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of an N-substituted monoamino compound, free from carboxyl groups, selected from the group consisting of compounds having the structural formula

\[
O-R-N^+R_2
\]

wherein R is selected from the group consisting of lower alkylene, monohydroxy lower alkylene and phenyl, G is a halogen atom, and R₁ and R₂ are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and heterocyclic radicals which include the nitrogen atom selected from the group consisting of morpholino and piperidino, the radical G and the nitrogen atom being attached to carbon atoms of radical R, their salts and their quaternary ammonium compounds formed with chlorohydric acid, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

2. In the process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of a quaternary ammonium compound formed by reacting with chlorohydric acid an N-substituted monoamino compound, free from carboxyl groups, having the structural formula

\[
O-R-N^+R_2
\]

wherein R is selected from the group consisting of lower alkylene, monohydroxy lower alkylene and phenyl, G is a halogen atom, and R₁ and R₂ are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and heterocyclic radicals which include the nitrogen atom selected from the group consisting of morpholino and piperidino, the radical G and the nitrogen atom being attached to carbon atoms of radical R, their salts and their quaternary ammonium compounds formed with chlorohydric acid, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the brightening agent.

3. In the process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of a compound, free from carboxyl groups having the structural formula

\[
O-R-N^+R_2
\]

wherein R is selected from the group consisting of lower alkylene, monohydroxy lower alkylene and phenyl, G is selected from the group consisting of halogen, cyano, thiocyanato and nitro, and R₁ and R₂ are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and heterocyclic radicals which include the nitrogen atom selected from the group consisting of morpholino and piperidino, the radical G and the nitrogen atom being attached to carbon atoms of radical R, their salts and their quaternary ammonium compounds formed with chlorohydric acid, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

4. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of a sulfonic acid brightening agent, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

5. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and N,N-diethyl-dithiocarbamic acid-n-butyl ester-sodium sulfonate as a brightening agent, the steps which comprise adding to said electroplating baths from 0.01 to 20 gm./liter of a sulfonic acid brightening agent, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

6. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of N,N-dimethylamino-ethylchloride-1, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

7. The process according to claim 6, wherein said brightening agent is N,N-diethyl-dithiocarbamic acid-n- propyl ester-sodium sulfonate.

8. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of a sulfonic acid brightening agent, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

9. The process according to claim 8, wherein the brightening agent is N,N-diethyl-dithiocarbamic acid-n-propyl ester-sodium sulfonate.

10. In a process of producing bright copper electrodeposits from acid copper electroplating baths comprising hard water, technical grade copper salts and a sulfonic acid brightening agent, the steps which comprise adding to said acidic copper electroplating baths from 0.01 to 20 gm./liter of a sulfonic acid brightening agent, and electrodepositing copper from said baths, whereby the impurities contained in said water and technical grade copper salts are prevented from interfering with the brightening action of the sulfonic acid brightening agent.

11. The process according to claim 10, wherein the brightening agent is N,N-diethyl-dithiocarbamic acid-n-propyl ester-sodium sulfonate.

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