United States Patent Office 2,905,602
Patented Sept. 22, 1959



2,905,602

# PRODUCTION OF METAL ELECTRODEPOSITS

Alfred Kirstahler, Dusseldorf, and Wolf-Dieter Willmund and Wennemar Strauss, Dusseldorf-Holthausen, Germany, assignors to Dehydag, Deutsche Hydrierwerke G.m.b.H., Dusseldorf, Germany, a corporation of Germany

No Drawing. Application November 2, 1955
Serial No. 544,586
Claims priority, application Germany November 5, 1954
7 Claims. (Cl. 204—46)

This invention relates to a process for the production of bright metal electrodeposits, and more particularly to electroplating solutions having quaternary ammonium compounds dissolved therein which eliminate the adverse effects of impurities in such solutions upon the brightness of the electrodeposits produced therefrom.

It is well known in the electroplating art that the brightening effect of brightners added to electroplating solutions is impaired by certain inorganic impurities contained in such solutions. Impurities which usually have such an impairing effect upon metal electrodeposits are those substances which cause the hardness of water and impurities which occur in technical grade metal salts employed to prepare electroplating baths, particularly in inorganic copper salts used to compound acid copper-plating baths.

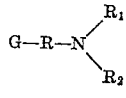
The obvious solution to this problem would be to employ distilled water and chemically pure metal salts in the preparation of electroplating baths intended to be modified with brighteners. However, it is evident that the use of such chemically pure components would not only be very impractical, but would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

It is an object of the present invention to provide a method of electroplating objects in plating baths containing brightening agents, whereby bright metal electrodeposits are produced despite the presence of interfering impurities in the electroplating bath.

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

Other objects and advantages of our invention will become apparent as the description thereof proceeds.

We have found that the interfering effects of impurities in electroplating baths containing brighteners can be readily eliminated by adding to such electroplating baths quaternary ammonium compounds which are formed by internal rearrangement of the molecular structure of halogen-substituted tertiary amines having the general formula

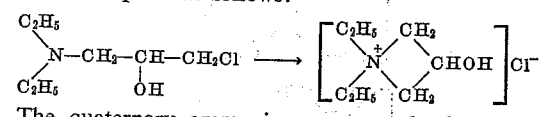


wherein G is a halogen atom, R, $R_1$ and $R_2$ are cyclic or acyclic hydrocarbon radicals which may carry further substituents, such as alkyl radicals, OH-groups or halogen atoms, or may be interrupted by heteroatoms, i.e. sulfur, oxygen and nitrogen atoms. $R_1$ and $R_2$ may also be replaced by a heterocyclic ring system which includes the nitrogen atom.

The production of such quaternary ammonium compounds by internal rearrangement of the molecule of halogenated tertiary amines is well known. The internal rearrangement takes place when the tertiary amines are



allowed to stand for extended periods of time, or are slightly heated. In either case, the transformation will take place when the tertiary amines are kept for some time or warmed as such or in solution respectively. According to Rothstein and Binovic, Comptes Rendus, 236, pp. 1050–1052 (1953), for example the transformation of N,N-diethylamino-3-chloro-propanol-2 is said to take place as follows:



The quaternary ammonium compounds thus formed need not be isolated or specially purified prior to their use as additives for electroplating baths in accordance with the present invention.

Specific examples of halogenated tertiary amines which may be transformed into quaternary ammonium compounds suitable for use as electroplating bath additives according to our invention are the following:

1-diethylamino-ethylchloride-2
1-dioxyethylamino-ethylchloride-2
1-diethylamino-3-chloropropanol-2
1-dioxyethylamino-3-chloropropanol-2
N-(2-chloroethyl)-N-ethyl-aniline
N-(3-chloro-2-oxy-propyl)-N-methyl-aniline
N-(3-chloro-2-oxy-propyl)-N-methyl-cyclohexylamine
N,N-dicyclohexyl-N-2-chloroethyl-amine
N-2-chloroethyl-piperidine
N-(3-chloro-2-oxy-propyl)-morpholine
Bis-(2-bromoethyl)-benzylamine, and the like.

In order to obtain the desired result, the quaternary ammonium compounds are added to the electroplating bath in amounts ranging from 0.01 gm./liter and 20 gm./liter of bath, preferably from 2 to 8 gm./liter of bath. The particular amount required varies from one specific quaternary ammonium compound to the other, and also depends upon the nature of the brightening agent employed as well as upon the type and amount of impurities present in the bath.

In general, objects are electroplated in a bath modified in accordance with our invention at temperatures ranging from 30 to 60° C. and at current densities between 0.5 and 15 amp./dm.$^2$.

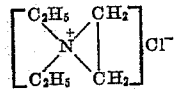
Electroplating baths containing brightening agents and modified in the above manner in accordance with our invention will produce bright and lustrous electrodeposits over the entire effective range of current densities, despite the presence of impurities of the above-described nature in the bath. Moreover,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

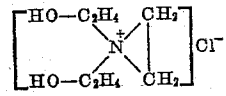
The quaternary ammonium compounds are effective in the manner described in all those electroplating baths which contain magnesium and calcium ions introduced by the use of hard tap water, and ferric ions introduced by the use of metal salts of technical purity in the preparation of the electroplating solution. We have found, however, that they do not act as water-softening agents in the usual sense, and that they can not be replaced by the typical water-softening agents, such as sequestering agents and detergents. Nevertheless, these quaternary ammonium additives are capable of completely eliminating the adverse effects of the above-described impurities upon the brightness of electrodeposits produced from baths containing such impurities and brighteners.

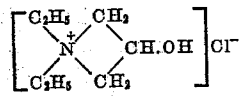
Although the exact theoretical reason for the beneficial action of these quaternary ammonium compounds is not fully understood, it is believed that their effect comes into play at the surface of the metal object being electroplated,

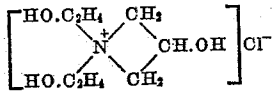
which is indicated by the high concentrations in which these substances must in some instances be used to produce the desired effect.

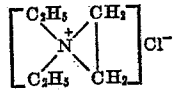
Some examples for the quaternary ammonium compounds which may be used according to the described invention are:

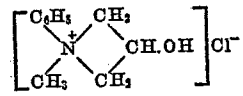
(1) 

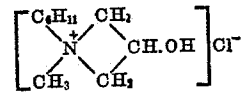
(2) 

(3) 

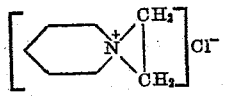
(4) 

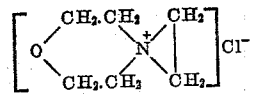
(5) 

(6) 

(7) 

(8) 

(9) 

(10) 

The employment of the quaternary ammonium compounds in the manner above set forth does not necessitate any changes in the conditions under which objects are usually electroplated in metal salt baths, particularly with respect to temperatures and current densities. The quaternary ammonium additives 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 described above can be successfully employed to modify all types of electroplating baths in which the presence of impurities of the type mentioned previously adversely affects the qualities of electrodeposits produced therefrom. Thus, the quaternary ammonium additives may be used in electroplating baths for electrodepositing zinc, nickel, chromium, precious metals, and particularly copper.

The following example will further illustrate our invention and enable others skilled in the art to understand it more completely. It is understood, however, we do not intend to limit the invention to this example.

*Example*

0.75 gm./liter N,N-dipropyl-dithiocarbamic acid-n-butylester-ω-sodium sulfonate was added as brightening agent to an acid copper plating bath prepared with distilled water, 200 gm./liter crystalline chemically pure copper sulfate and 60 gm./liter chemically pure sulfuric acid.

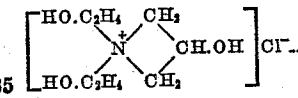
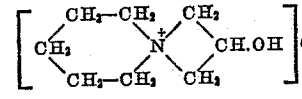
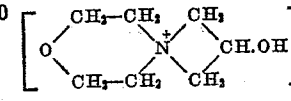


Iron objects were then electroplated in this bath at a current density between 0.5 and 8 amp./dm.$^2$. The copper electrodeposits produced thereby were bright and lustrous.

As a comparison, other iron objects were electroplated under the same conditions in a bath composed of the same quantities of water, copper sulfate and brightening agent as above, except that the water was hard tap water and the copper sulfate was technically pure instead of chemically pure. The copper electrodeposits produced thereby were not nearly as bright and lustrous as those produced from the bath composed of distilled water and chemically pure copper sulfate.

Thereafter, 2.5 gm./liter of the quaternary ammonium compound formed by internal rearrangement of 3-diethylamino-1-chloropropanol-2 to this electroplating bath are added to eliminate the adverse effects of the inorganic impurities introduced by the tap water and the technical grade copper sulfate. Iron objects electroplated in this modified bath were provided with very bright and exceptionally ductile copper electroplate.

The same advantageous results were obtained by substituting for the quaternary ammonium compound described above the indicated quantities of the following quaternary ammonium compounds:

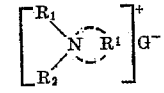
| Quaternary ammonium compound | Amount of quaternary ammonium compound added to bath, gm./liter |
|---|---|
|  | 4-6 |
|  | 1-6 |
|  | 2 |

Similarly, the quaternary ammonium additives may be used in conjunction with other brightening agents whose brightening power is adversely affected by the presence of impurities in the electroplating bath, such as N,N-diethyldithiocarbamic-acid-n-propylester-ω-sodium sulfonate and the like.

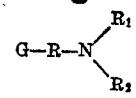
While we have illustrated our invention by certain specific embodiments, it will be obvious to persons skilled in the art that various changes and modifications may be made therein without departing from the spirit of the present invention or the scope of the appended claims.

We claim:

1. In a process of producing bright metal electrodeposits of metals selected from the group consisting of copper, zinc, nickel, chromium and precious metals from acidic electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step which comprises adding to such electroplating baths 0.01 to 20 gm. per liter of a quaternary ammonium compound having the general structural formula

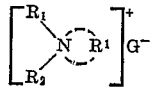


formed by the internal rearrangement of tertiary amines, free from carboxyl groups, having the general structural formula

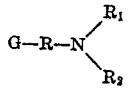


wherein G is a halogen atom, R is selected from the group consisting of lower alkylene and monohydroxy lower alkylene, and $R_1$ and $R_2$ are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and a heterocyclic radical, which includes the nitrogen atom and the $R_1$ and $R_2$ groups, selected from the group consisting of morpholino and piperidino radicals, and $R^1$ represents the internally rearranged R radical.

2. In a process of producing bright metal electrodeposits of metals selected from the group consisting of copper, zinc, nickel, chromium and precious metals from acidic electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step which comprises adding to such electroplating baths 0.01 to 20 gm. per liter of a quaternary ammonium compound having the general structural formula

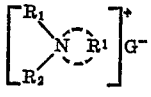


formed by the internal rearrangement of tertiary amines, free from carboxyl groups, having the general structural formula

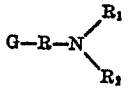


wherein G is a halogen atom, R is selected from the group consisting of lower alkylene and monohydroxy lower alkylene, and $R_1$ and $R_2$, together with the N atom represent a heterocyclic radical selected from the group consisting of morpholino and piperidino radicals, and $R^1$ represents the internally rearranged R radical.

3. In a process of producing bright metal electrodeposits of metals selected from the group consisting of copper, zinc, nickel, chromium and precious metals from acidic electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step which comprises adding to such electroplating baths 0.01 to 20 gm. per liter of a quaternary ammonium compound having the structural formula

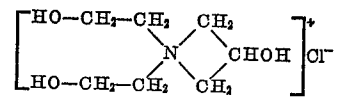


formed by the internal rearrangement of tertiary amines, free from carboxyl groups, having the general structural formula



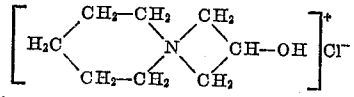
wherein G is a halogen atom, R is a hydroxy propyl and $R_1$ and $R_2$ are selected from the group consisting of lower alkyl, monohydroxy lower alkyl, phenyl, cyclohexyl and a heterocyclic radical, which includes the nitrogen atom and the $R_1$ and $R_2$ groups, selected from the group consisting of morpholino and piperidino radicals, and $R^1$ represents the internally rearranged R radical.

4. In a process of producing bright electrodeposits of metals selected from the group consisting of copper, zinc, nickel, chromium and precious metals, from acidic electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step which comprises adding to said baths 4 to 6 gm./liter of the quaternary ammonium compound having the general structural formula:



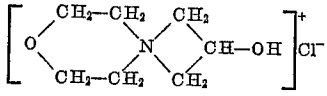
formed by internal rearrangement of 1-dioxyethylamino-3-chloropropanol-2, whereby said impurities are prevented from interfering with the production of bright metal deposits.

5. In a process of producing bright copper electrodeposits from acidic copper electroplating baths containing impurities found in hard water and in technical grade copper salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step which comprises adding to said baths 1 to 6 gm./liter of the quaternary ammonium compound having the general structural formula:



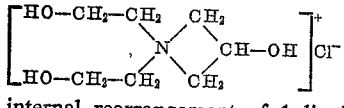
formed by internal rearrangement of N-3-chloro-propanol-2-piperidine, whereby said impurities are prevented from interfering with the production of bright copper deposits.

6. In a process of producing bright copper electrodeposits from acidic copper electroplating baths containing impurities found in hard water and in technical grade copper salts, and containing a brightening agent whose brightening power is adversely affected by the presence of such impurities, the step of adding to said baths 2 gm./liter of the quaternary ammonium compound having the general structural formula.:



formed by internal rearrangement of N-(3-chloro-2-oxypropyl)-morpholine, whereby said impurities are prevented from interfering with the production of bright copper deposits.

7. In a process of producing bright metal electrodeposits of metals selected from the group consisting of copper, zinc, nickel, chromium and precious metals, from acidic electroplating baths containing said metals wherein said baths contain impurities found in hard water and in technical grade metal salts, and a brightening agent whose brightening power is adversely affected by the presence of such impurities, the steps which comprise adding to said baths 2 to 8 gm. per liter of the quaternary ammonium compound having the general structural formula:



formed by internal rearrangement of 1-di-ethylamino-3-chloro-propanol-2, whereby said impurities are prevented from interfering with the production of bright deposits of said metals.


**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,663,684 | Pierce | Dec. 22, 1953 |
| 2,707,166 | Brown et al. | Apr. 26, 1955 |