WETTING AGENTS FOR ELECTROLEPLATING BATHS

This invention relates to additives for electroplating baths and to a process and a bath for electroplating making use of such additives. It more specifically relates to the addition of organic phosphoric acid ester derivatives to electroplating baths as wetting and porosity preventing agents.

It is known to add wetting agents to electroplating baths for the production of nickel, copper or zinc electroplates. These additives have the effect that the hydrogen which forms at the cathode during the electroplating process is released rapidly and as completely as possible. If the hydrogen remains on the cathode material for longer periods of time it causes an undesirable pore formation in the metal electroplates.

The prevention of pore formation is of great importance in the electroplating art in view of the desired corrosion resistance of the metal electroplates. Another task of the wetting agents is to prevent the electrophoretic deposition of small particles of impurities on the metal surfaces, because the corrosion resistance also suffers from the inclusion of foreign bodies in the electrodeposit.

Wetting agents have recently also been used in chromium baths. The effect achieved thereby is that the quantities of oxygen and hydrogen released in the chromium baths due to the poor current output do not escape in the form of fogs, but that instead a fog cover forms on the bath liquid. This measure prevents considerable losses in relatively expensive chromium bath liquid due to continuous removal of the fog by suction, so that in many instances the suction removal of the bath fog can be completely omitted.

Despite the great number of known wetting agents the selection of operative substances is relatively small. Thus, alkylsulphonates, alkylsulphates and alkyloxyalkylsulphonates or sulphonates are preferably used in nickel electrolyzing baths, while in the field of acid and cyanide preliminary copper-plating alkylpolyglycol ethers are employed. Perfluoro-alkylsulphonates are known to be stable wetting agents for chromium baths.

It is an object of this invention to provide wetting agent additive compounds for electroplating baths which have a high degree of stability.

It is a further object to provide additive compounds which prevent vaporization and loss of the electroplating bath solution.

It is a further object to provide wetting agents which may be used in acid, alkaline or cyanide electroplating baths to produce deposits of the well known plating metals.

Another object is to provide electroplating processes and baths wherein electrodeposits may be obtained which are free from pores and inorganic impurities. These and other objects of our invention will become apparent as the description thereof proceeds.

We have now found that acid alkyl- and aralkyl-phosphoric acid esters as well as alkylpolyglycol ether-phosphoric acid esters or their salts may be used with advantage in a variety of electroplating baths. In addition to their good wetting properties, these compounds have the advantage over the corresponding sulphonates or sulphonates that they are considerably more stable in the baths. Further, they have the advantage over the alkylpolyglycol ethers that they do not have a turbidity point and are not salted out even in hot cyanide copper-plating baths. The phosphoric acid esters even have brightening properties in the electrolyzing baths. In chromium-plating baths, especially the alkylphosphates exhibit excellent stability properties, so that they may be used in place of the expensive and difficult-to-prepare perfluorinated organic sulfuric acids.

Examples of compounds of the claimed type are the acid mono- or diphasosphoric acid esters of octyl, decyl, dodecyl, octadecyl or undecane decyl alcohol, or of hexyl, octyl or dodecyl phenol and their water-soluble salts, as well as the phosphoric acid esters of alkylpolyglycol ethers having the general structural formula

\[ C_{2n+1}O(CH_2CH_2O)_nCH_2CH_2PO_3X \]

wherein \( n = 8 \) to 20 and \( m = 0 \) to 50, and \( X \) is hydrogen or an inorganic or organic base.

The wetting agents may be used in acid, cyanide or alkaline baths for the production of copper, nickel, chromium, zinc, cadmium, tin, brass, bronze, gold and silver electroplates. They are added to the baths preferably in amounts from 0.01 to 5 g./liter. The electroplating bath is carried out at bath temperatures from room temperature to 60° C., and up to 90° C. for alkaline baths; and at current density ranges from 0.5 amp./dm.² to 16 amp./dm.², and up to 40 amp./dm.² for alkaline baths.

The following examples have been set forth to enable persons skilled in the art to better understand and practice our invention. However, it will be understood that there is no intention on our part of limiting our invention to these examples.

**Example I**

When 0.01 to 0.2 g./liter dodecyl-phosphoric acid ester was dissolved in a cyanide copper bath containing 105 g./liter copper cyanide, 128 g./liter sodium cyanide and 30 g./liter sodium hydroxide, and objects made of iron or steel were electroplated therein between 60° and 80° C. in a current density range of about 1 to 6 amp./dm.², pore-free copper electroplates were obtained. These electroplates are characterized over those which were obtained without the alkylphosphate additive and under otherwise identical conditions by a distinctly finer grain structure.

**Example II**

0.02 to 0.1 g./liter octyl-phosphoric acid ester was dissolved in a bright chromium-plating bath containing 290 g./liter CrO₃. When bright nickel-plated objects were chromium-plated in this bath at current densities of 10 to 20 amp./dm.² and 35 to 45° C., a foam cover of a thickness of about 1 to 2 cm. formed on the bath, which completely prevented the occurrence of chromic acid fogs. The chromium electroplates turned out full-bright.

**Example III**

When an acid copper bath, which contained 0.25 g./liter N,N-diethyl-dithiocarbamic acid-n-propyl ester sodium sulphate and 2 g./liter 1-diethylamino-3-chloropropan-2-ol as brightening agents in addition to 200 g./liter CuSO₄·5H₂O and 60 g./liter H₂SO₄, was modified with 0.01 to 0.3 g./liter of the compound C₉H₁₈O(CH₂CH₂O)₇CH₂CH₂PO₃Na₂, and iron or brass objects were electroplated in this bath within a current density range of 0.5 to 7.5 amp./dm.², full-bright copper electroplates completely free from pores were obtained.

While we have disclosed certain specific embodiments and preferred modes of practice of our invention, it will be understood that we do not intend to be limited thereby and various changes and modifications may be made with-
out departing from the spirit of the disclosure and the scope of the appended claims.

We claim:
1. An electroplating bath for producing electrodeposits of metals capable of being electrodeposited comprising an aqueous solution of an inorganic salt of the metal to be deposited and 0.01 to 5 gm./liter of an additive compound comprising a phosphoric acid ester having a structural formula selected from the group consisting of:

\[ \text{Z} - \text{O} - \text{PO}_2\text{X} \]

wherein Z is a radical having at least eight carbon atoms selected from the group consisting of alkyl, alkyaryl and polyglycolether radicals and X is selected from the group consisting of hydrogen and cations capable of rendering the phosphoric acid ester water soluble.

2. The bath of claim 1 wherein the additive compound is dodecyl phosphoric acid ester.

3. The bath of claim 1 wherein the additive compound is octyl phosphoric acid ester.

4. The bath of claim 1 wherein the additive compound is a compound having the formula:

\[ \text{C}_{13}\text{H}_{25}\text{O}((\text{CH}_{2}\text{CH}_{2}\text{O})_7\text{CH}_{2}\text{CH}_2\text{OPO}_3\text{Na}_2} \]

5. A process for producing smooth, pore free metal electrodeposits of metals capable of being electrodeposited which comprises depositing the metal from a bath containing the metal in the form of an aqueous solution of an inorganic salt thereof, in the presence of 0.01 to 5 gm./liter of an additive compound comprising a phosphoric acid ester having a structural formula selected from the group consisting of:

\[ \text{Z} - \text{O} - \text{PO}_2\text{X} \]

wherein Z is a radical having at least eight carbon atoms selected from the group consisting of alkyl, alkyaryl and polyglycolether radicals and X is selected from the group consisting of hydrogen and cations capable of rendering the phosphoric acid ester water soluble.

6. The process of claim 5 wherein the additive compound is dodecyl phosphoric acid ester.

7. The process of claim 5 wherein the additive compound is octyl phosphoric acid ester.

8. The process of claim 5 wherein the additive compound is a compound having the formula:

\[ \text{C}_{13}\text{H}_{25}\text{O}((\text{CH}_{2}\text{CH}_{2}\text{O})_7\text{CH}_{2}\text{CH}_2\text{OPo}_3\text{Na}_2} \]

9. A method for preventing vapor losses of the bath solution in the operation of electroplating baths which comprises adding to said bath 0.01 to 5 gm./liter of an additive compound comprising a phosphoric acid ester having a structural formula selected from the group consisting of:

\[ \text{Z} - \text{O} - \text{PO}_2\text{X} \]

10. A method for preventing vapor losses of bath solution in the operation of chromium electroplating baths which comprises adding to said bath 0.01 to 5 gm./liter of an additive compound comprising a phosphoric acid ester having a structural formula selected from the group consisting of:

\[ \text{Z} - \text{O} - \text{PO}_2\text{X} \]

wherein Z is a radical having at least 8 carbon atoms selected from the group consisting of alkyl, alkyaryl and polyglycolether radicals and X is selected from the group consisting of hydrogen and cations capable of rendering the phosphoric acid ester water soluble.

References Cited in the file of this patent

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