Electroplating of Copper and Its Alloys


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This invention relates to a method and bath for electroplating copper and its alloys and has for its object the provision of an improved electroplating method and bath for this class of alloys.

Another object is to provide an electroplating method and bath for producing a corrosion-resistant electroplated surface on copper and its alloys.

A further object is to provide a simple and effective electroplating method and bath for electroplating the surface of copper and its alloys and imparting thereto a corrosion-resistant surface which subsequently may be surfaced with other metals by electro-plating.

Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects, we have discovered that articles comprised of copper and its alloys may be electro-plated to a bright, clean, corrosion-resistant surface by immersing the article as the anode electrode in an aqueous solution containing an alkali metal salt of an alkylene polyamine carboxylic acid, an inorganic acid in an amount sufficient to produce a pH of about 4, and a sufficient amount of a non-electrolyte to increase the specific resistance of the solution and passing an electric current (D. C.) between the anode and cathode at such a current density for such a time as will produce the desired electro-plating result on the article at the temperature of the bath.

By the term "copper and its alloys" we mean to identify copper and copper-based alloys such as one of the plurality of alloys known as brasses and bronzes.

By the term "corrosion resistant" we mean the alteration of a metallic surface to the extent that a continuous thin film of metallic oxide becomes bonded to the electroplated surface of the metal, thereby preventing further oxidation or reaction to other chemicals or chemical gases, for example, hydrogen sulfide.

By the term "increase the specific resistance of the solution" we mean that a diluent of non-electrolyte should be present to limit the current flowing in the bath to a value such that the electrolysis current component may be held to a minimum. This provides for the most efficient use of the current and prevents gassing problems.

By the term "alkylene polyamine carboxylic acids" we mean to identify that class of alkylene amino acids that contain at least two amino nitrogen groups that are spaced apart by an alkylene group either ethylene or propylene and wherein at least one of the amino hydrogens have been displaced by a carboxylic acid group consisting of an acetic acid or homologous acid group, and having the generic structure:

\[
\begin{align*}
\text{N-alkylene-} & \quad \text{N} \\
\text{R} & \quad \text{R'} \\
\text{X} & \quad \text{Y}
\end{align*}
\]

wherein "alkylene" consists of one of the groups \(\text{CH}_2-\text{CH}_2-\) (ethylene);

\[
\begin{align*}
\text{CH}_2-\text{CH}_2- & \quad \text{(isopropylene)} \\
\end{align*}
\]

and \(\text{CH}_2-\text{CH}-\text{CH}_2-\) (propylene); \(R\) and \(R'\) consists of one of the groups \(\text{CH}_2-\text{COOH}\), an aliphatic radical of short carbon chain (below 7) and by preference one ending in hydroxyl group; \(X\) and \(Y\) consists of \(\text{CH}_2-\text{COOH}\) or a homologue thereof. While the ethylene diamine and/or propylene and trimethylene analogue amino acids are entirely satisfactory, we prefer to employ, however, those amino acids of this type which do not exhibit an isoelectric point (i.e., the point of precipitation or crystallization) at the pH of the solutions employed in this invention.

Of this broad class of alkylene polyamine carboxylic acids, the species acids known chemically as ethylene diamine mono to tetra acetic acid are the most readily obtainable and for the purposes of the present invention are the most economically practical acids to employ in the practice of the present invention and for purposes of illustration but not by way of limitation the invention will be hereinafter described as it has been adopted for use with the above mentioned species alkylene polyamine acids.

In the commercial adaptation of this invention on any given article comprised of copper or one of its brass or bronze alloys, the bath composition may be widely varied without essential departure from the invention as will hereinafter be apparent, to obtain the desired electroplating result.

In our experiments the electroplating of copper, brass and bronze articles is most effectively obtained in a bath containing ethylene diamine tetraacetic acid when the bath pH is brought to a pH of about 4 (±.5) by appropriate additions of phosphoric acid (H_3PO_4) to neutralize the alkalinity of the solution and where the concentration of the amino acid salt is within the range 20% to 34%, at a temperature of 60° C. and at a current density relative to the size of the article, spacing between electrodes, temperature, time and voltage that is effective to accomplish the desired electroplating result. The addition of a non-electrolyte such as glycol to the bath solution has the effect of increasing the specific resistivity of the solution and permitting the use of lower current densities to obtain equivalent electroplating results.

As one specific embodiment of this specific example of electroplating bath, but not by way of limitation thereof, an electroplating bath consisting of an aqueous solution containing 20% ethylene diamine tetraacetic acid as the tetra sodium salt, 3% glycol, and sufficient H_3PO_4 to lower the pH of the solution to pH 4, produced a corrosion-resistant electropolish surface on standard brass 30-06 cartridge cases at a current density of 5/8 amperes per square inch and an electrode spacing of 1 1/4 inches and a bath temperature of 60° C. within a time interval of 30 seconds.

The current density may be widely varied without departure from the invention, as one skilled in the art will recognize, the general effect being to decrease the time of immersion. However, there are certain practical limits which in the specific embodiment given restricts the current density range to 800 to 3000 amperes, per square foot.

In the electroplating of copper and its alloys by the method and bath of the present invention, precautions should be taken to inhibit premature surface polarization of the anode-article by the formation of a polarizing oxy-
gen film layer thereon. This is most conveniently accomplished by vigorous agitation of the bath and circulating the bath over the surface of the article.

In general, the formation of a relatively thin polarizing oxide film over the polished metal surface is a desirable end result of the present invention as such a film imparts corrosion resistance to the polished surface. The thickness of the film, however, should be the minimum thickness to impart such corrosion resistance.

In the specific embodiment given we have increased the concentration of the ethylene diamine tetracetic acid salt from the 20% amount given to as high as 34% without detrimental results, however, we find that as the concentration increases the tendency of the amino acid to precipitate out of solution on long standing increases and therefore prefer to maintain the concentration on the low side of this range.

In substitution for ethylene diamine tetra acetic acid we have successfully employed the di- and tri-acetic acid compounds of ethylene diamine and a large number of substituted ethylene diamine poly acetic acid compounds wherein one of the amino hydrogens of one or each of the amino nitrogen has been displaced by a solubilizing group, such as ethanol, isopropanol, C₂H₂O₃ hydroxyethoxyethyl i.e. (HO-CH₂-CH₂-OCH₂-CH₂—) and propionic acid with excellent results. Our observations, however, lead us to conclude that those alkylene poly amine carboxylic acids in which there are at least one acetic group and one amino nitrogen group are the most effective for the purposes of the present invention, particularly where at least one of the remaining amino hydrogens of the compound has been displaced by a solubilizing group, such as ethanol, in which case the other amino hydrogens may be retained or may be displaced by an acetic acid group without much effect on the efficiency of the compound.

In this specific embodiment, phosphoric acid may be displaced in part or in whole by other inorganic acids with varying results. Hydrochloric acid (HCl), for example, tends to impart a coppery appearance to brass articles which increases with increase in HCl substitution. Sulfuric acid, nitric acid, and other acids also vary the electro-polishing results characteristically. For best electropolishing results, however, phosphoric acid is preferred.

In place of glycol in the above specific example, isopropanol, glycerine and water-soluble cellulose may be employed as non-electrolyte additions to increase the specific resistivity of the bath.

In general, we have found that while higher voltages and higher bath temperatures have the effect of increasing the rate at which the metal surfaces are electropolished, the polarization difficulties are increased and the surface of the article is likely to be covered with an oxide film layer that dulls the brightness of the polished surface. It is preferred, therefore, to hold the bath temperature at about 60° C. and to employ the minimum voltage necessary at this temperature to obtain the desired polished surface and the minimum thickness oxide film over the polished surface effective to impart corrosion resistance without dullying the polished surface.

In view of the above disclosure and specific examples given it is believed apparent the invention may be widely varied without essential departure therefrom and all such modifications and departures are contemplated as may fall within the scope of the following claims wherein the term “alkylene poly amine mono and poly carboxylic acids” is intended to define ethylene diamine mono to tetracetic acid, its homologue and equivalent amino acids and the various substituted compounds hereinabove described, the term “non-electrolyte” is meant to define glycol and one of its identified equivalents, and the term “organic acid” is meant to define phosphoric acid and one of its identified equivalent acids.

What we claim is:

1. The method of electropolishing the surfaces of articles composed of copper and copper base alloys, which comprises making the article an anode in an aqueous electrolytic bath consisting essentially of an alkali metal salt of an alkylene polyamine carboxylic acid, an inorganic acid in an amount establishing a pH of about 4 in the said aqueous solution, and a non-electrolyte, and passing an electric current through the solution under such conditions of current density, solution temperature, time and agitation, as to clean and polish the said surface electrolytically and to cover the polished surface with a thin polarizing oxide film layer to impart corrosion resistance to the polished surface.

2. The method of electropolishing the surfaces of articles formed of copper and copper base alloys, which comprises making the article an anode in an aqueous electrolytic bath consisting essentially of from 20 percent to 34 percent of an alkali metal salt of a compound selected from the group consisting of mono-, di-, tri- and tetracetic acid derivatives of ethylenediamine, with an amount of phosphoric acid sufficient to produce a pH of about 4 in the said solution, and a proportion of a non-electrolyte sufficient to increase the specific resistivity of the anode and passing an electric current to the said article through the solution for the time interval sufficient to clean and polish the surface of the article while maintaining the temperature of the solution at about 60° C., and agitating the bath sufficiently to maintain a substantially constant composition therein and to inhibit the formation of a thicker polarizing oxide film layer over the surface of said article.

3. The method in accordance with claim 2 wherein the said alkali metal salt is the tetra-sodium salt of ethylene diamine tetracetic acid.

4. The method in accordance with claim 2 wherein the said alkali metal salt is the tri-sodium salt of monoethylenediaminetetraacetic acid.

5. The method in accordance with claim 2 wherein said electrolytic bath consists of 20 percent to 34 percent of ethylenediaminetetraacetic acid, its homologue and equivalent amino acids and a mineral acid salt selected from the group consisting of hydrochloric and phosphoric acids.

6. An electrolytic bath composition for the electropolishing of copper and copper base alloys, said bath consisting of an aqueous solution containing a non-electrolyte and from about 20 percent to 34 percent of an alkali metal salt of an ethylene polyamine polyacarboxylic acid and a mineral acid selected from the group consisting of hydrochloric and phosphoric acids.

7. An electrolytic bath in accordance with claim 6 wherein said alkali metal salt is the disodium salt of diethylenetriaminediacetic acid.

8. An electrolytic bath in accordance with claim 6 wherein said alkali metal salt is the tetrasodium salt of ethylenediaminetetraacetic acid.

9. An electrolytic bath in accordance with claim 6 wherein said alkali metal salt is the trisodium salt of monoethylenediaminetetraacetic acid.

10. An electrolytic bath for electropolishing copper and its alloys, said bath consisting of an acid aqueous solution containing from 20 percent to 34 percent of the tetrasodium salt of ethylene diamine tetracetic acid, phosphoric acid in an amount providing a pH of about 4 of the solution, and about 5 percent glycol.

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