METHOD FOR CHEMICALLY POLISHING COPPER OR COPPER ALLOY

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ABSTRACT OF THE DISCLOSURE

This invention relates to a method for polishing copper or copper alloys so as to obtain lustrous surfaces which involves treating copper or copper alloy articles with a mixture of an aqueous solution of hydrogen peroxide, an acid, and a saturated aliphatic alcohol to form thereby an oxide film on the surface of said article, and thereafter removing the film by chemical dissolution.

The foregoing "Abstract of the Disclosure" is solely for the purpose of enabling the Patent Office and the public generally to determine quickly from a cursory inspection the nature and gist of the technical disclosure, and the abstract shall not be used for interpreting the scope of the claims.

The present invention relates to a convenient and safe method for chemically polishing copper and copper alloys, to obtain a smooth surface with uniform lustre. More particularly, the present invention relates to a method for chemically polishing the surface of copper or copper alloy articles by treating the material to be polished with an aqueous solution comprising hydrogen peroxide, an acid or acids, and a saturated aliphatic alcohol, thereby to produce a film of an oxide or oxides on said surface, and thereafter removing said film by dissolving it with acids, alkali or other chemicals.

The conventional methods employed for polishing the surface of copper or copper alloys have included both mechanical and chemical techniques. Mechanical methods such as buff-polishing or barrel-polishing have the disadvantage of requiring a number of steps and a fair degree of experience. Furthermore, using such methods it is difficult to obtain a uniform, lusted surface, and in many cases, depending on the size or the form of the articles to be treated, polishing is difficult or even impossible.

On the other hand, chemical polishing methods, such as those wherein a mixture of acids, composed of for example, sulfuric, nitric, and a small amount of hydrochloric acid, is employed, have similarly not been entirely satisfactory. Not only is experience required in carrying out the operation, using such a mixture, but the operation itself is hazardous due to the evolution of poisonous nitrous acid gas during the process of polishing. This is considered to be a serious drawback of this conventional method.

Additionally, when this method is employed, pitting, irregularity of colour, change of colour after polishing and the like, are likely to occur. At the same time the method requires the use of a concentrated mixture of nitric and sulfuric acids, and the danger accompanying such use is apparent.

In order to overcome the above mentioned disadvantages of conventional methods, the present invention contemplates the use of hydrogen peroxide and acid, together with a saturated aliphatic alcohol as hereinafter described.

In view of the properties of hydrogen peroxide, the invention provides a means for polishing copper and copper alloys using a system which is easily handled.

Conventional methods according to which hydrogen peroxide and an acid or acids are used, are greatly restricted in regard to the temperature, the concentration of hydrogen peroxide and the concentration of acids to be employed in order to obtain a sufficient polishing effect. Furthermore, an important disadvantage of the above-mentioned conventional method is that the stability of the hydrogen peroxide markedly deteriorates after copper is dissolved to some extent into the solution during the polishing operation. The useful life of the polishing solution is therefore remarkably short. It is thought that the reason for this is that heavy metal ions seriously affect the stability of hydrogen peroxide. Because of these disadvantages, a practical method for chemical polishing the surface of copper and copper alloys by using hydrogen peroxide has not been available.

We have now found that when a saturated aliphatic alcohol or alcohols is added to the aqueous solution of hydrogen peroxide and an acid or acids, and the solution obtained thereby is employed, it is possible to produce a sufficient film on the surface of copper or copper alloys within a wider range of molar ratio of acid to hydrogen peroxide when compared with the case wherein hydrogen peroxide and an acid or acids are used alone. At the same time the stability of hydrogen peroxide is much improved over the case where an alcohol is not added.

Accordingly, the present invention comprises treating copper or copper alloys with an aqueous solution containing hydrogen peroxide and a mineral acid or acids such as sulfuric acid, hydrofluoric acid, nitric acid or the like, and a saturated aliphatic alcohol or alcohols, to produce a film of oxide or oxides on said surface, and thereafter removing said film by dissolving it chemically with such chemicals as dilute acid, ammonia, sodium cyanide, or a chelating agent in order to obtain a lustrous surface.

In the present invention, as the acid employed in the hydrogen peroxide containing solution, there may be mentioned inorganic acids such as sulfuric acid, hydrofluoric acid, nitric acid, hydrochloric acid or phosphoric acid and organic acids such as formic acid, acetic acid, citric acid or gluconic acid and mixtures of such inorganic and/or organic acid or acids. Among the acids employable, sulfuric acid, hydrofluoric acid, nitric acid or a mixture of nitric acid with another acid or acids is most preferable.

In accordance with the method of the present invention, the molar ratio of acid to hydrogen peroxide is below 0.23 and preferably from 0.05 to 0.15, when sulfuric acid or hydrofluoric acid is used. When nitric acid or a mixture of nitric acid and other acids is used, the molar ratio thereof to hydrogen peroxide is below 0.95 and preferably from 0.05 to 0.6. When the molar ratio of acid goes above these levels, the production of the oxide film is not sufficient. A higher molar ratio of nitric acid is used over that employed when other acids are used, since it is thought that the oxidizing power of nitric acid is additive to the oxidizing power of hydrogen peroxide and thus, proportionately less hydrogen peroxide is required, to produce a sufficient oxide film.

When alcohols are not added, the molar ratio of acid to hydrogen peroxide at which a sufficient film of oxide is produced is below 0.1, thus requiring a proportionately larger amount of hydrogen peroxide when compared with the method of the present invention.

In addition, in polishing baths in which alcohols are not added, a rapid decrease in hydrogen peroxide concentration is brought about after copper has been dissolved and the molar ratio of acid to hydrogen peroxide increases beyond the range in which preferred film production is achieved. In the method of the present invention, however, the treatment is carried out under addition of an alcohol or alcohols and the decomposition of hydrogen peroxide...
in the polishing solution is remarkably controlled, making it possible to produce the uniform film of oxide.

One of the examples showing the control of the decomposition of hydrogen peroxide when an alcohol is added in accordance with the method of the present invention is given below.

\[
\begin{align*}
\text{H}_2\text{O}_2 & \quad \text{Mol/L} \quad 1.5 \\
\text{H}_2\text{SO}_4 & \quad \text{Mol/L} \quad 0.005 \\
\text{CuSO}_4 & \quad \text{Mol/L} \quad 0.05
\end{align*}
\]

The decomposition rate constant of hydrogen peroxide was \(8 \times 10^{-2} \text{ min}^{-1}\) at a temperature of 70°C, and when 0.5 vol percent of methanol was added thereto, the decomposition rate constant became 1.1 \times 10^{-2}, which shows that the decomposition velocity was suppressed up to about 1/8. This tendency was almost the same at temperatures of 50°C and 30°C.

In accordance with the present invention, water soluble mono- or polyhydric alcohols are employed. Typical of these are methanol, ethanol, propanol or butanol, and ethylene glycol, propylene glycol or glycerine and the like. Polyhydric alcohols exert an excellent stabilizing effect when used at lower temperatures, however they are not as effective at higher temperatures, while the monohydric alcohols are remarkably effective throughout the whole temperature range employed in the present invention.

When a monohydric alcohol is employed, the decomposition of hydrogen peroxide decreases with the increase of the carbon number in the alcohol. As to the concentration of the alcohol from 0.1% to the solubilities of the alcohols employed may be used, but from 0.1 to 10% is practical.

In regard to the concentration of hydrogen peroxide in the present invention, concentrations as low as 0.1% or as high as 50% may be used, but a concentration from 5 to 15% is practical and a concentration around 7-8% is most preferable. In regard to the reaction temperature, it is preferable to employ a temperature up to 70°C at most. In other words, hydrogen peroxide is quickly decomposed as the temperature is elevated, and therefore in order to control the decomposition of hydrogen peroxide and to prevent the evaporation of alcohols, the above mentioned range of reaction temperatures is practical.

In carrying out the present invention 0.1 to 0.2% of a nonionic surface active agent may be added to the polishing solution to aid in producing the uniform film on the surface of the copper or copper alloy and also to prevent the evaporation of the polishing solution.

In regard to the method for removing the oxide film after it is produced, it is possible to use various kinds of materials if they can dissolve the film. As examples of the material used for removing the film, acids, alkalis, or complex salt producing materials may be mentioned. Preferred materials are sulfuric acid, nitric acid, ammonium, sodium cyanide, ethylene diamine tetraacetic acid, and the salts thereof, nitrito triacetic acid, diethylene triamine pentaaacetic acid, and the salts thereof and such like chelating agents. The temperature for dissolving and removing the film of oxide is not critical, room temperature being suitable and preferred. The practical value and the advantages of the present invention will be made further apparent from the following examples in which the percent values are percent by weight unless otherwise specified.

**EXAMPLE 1**

A part of a musical instrument made of brass containing 65% of Cu and 35% of Zn, was dipped into an aqueous solution containing 15% of \(\text{H}_2\text{O}_2\), 9.95% of \(\text{H}_2\text{SO}_4\), and 5% of \(\text{C}_2\text{H}_5\text{OH}\), and 0.1% of nonionic surface active agent at a temperature of 50°C for 30 seconds. The part was washed with 5% \(\text{H}_2\text{SO}_4\), and then with water, and a lustrous surface was obtained.

**EXAMPLE 2**

A brass stick used for antennae, composed of 65% of Cu and 35% of Zn, was dipped into an aqueous solution containing 3.5% of \(\text{H}_2\text{SO}_4\), 17.5% of \(\text{H}_2\text{O}_2\), and 0.1% of an alkyl phenol type nonionic surface active agent at a temperature of 40°C for about one minute. It was then washed with water, and thereafter washed with 3% \(\text{H}_2\text{SO}_4\). It was again washed with water, and a lustrous surface was obtained. A nickel plating process and chrome plating process were respectively carried out on said antenna stick, and a lustrous smooth finish was produced.

**EXAMPLE 3**

An iron plate having copper plating thereon was dipped into an aqueous solution containing 0.5 w/v percent of \(\text{H}_2\text{SO}_4\), and 7.1 w/v percent of \(\text{C}_2\text{H}_5\text{OH}\), 3% of \(\text{H}_2\text{O}_2\), 0.1% of an alkyl phenol type nonionic surface active agent at a temperature of 30°C. An iron plate having copper plating thereon was dipped into an aqueous solution containing 3% \(\text{H}_2\text{SO}_4\). A lustrous copper surface was obtained.

**EXAMPLE 4**

Part of an electric instrument made of iron having copper plating thereon was dipped into an aqueous solution containing 1% of \(\text{H}_2\text{SO}_4\), 8% of \(\text{H}_2\text{O}_2\), 1% of \(\text{C}_2\text{H}_5\text{OH}\), 5% of \(\text{CH}_3\text{OH}\), and 0.1% of nonionic surface active agent at a temperature of 50°C for about 3 minutes. It was then washed with water, and then with 2% \(\text{NH}_3\text{OH}\). Thereafter it was again washed with water and a lustrous surface was obtained. A nickel plating process and chrome plating process were carried out respectively on said part, and a lustrous mirror-like surface was obtained without carrying out the conventional copper buff-polishing treatment.

**EXAMPLE 5**

A furniture piece which is composed of brass, was dipped into an aqueous solution containing 0.5% of \(\text{H}_2\text{SO}_4\), 8% of \(\text{H}_2\text{O}_2\), and 1% of \(\text{C}_2\text{H}_5\text{OH}\), and 5% of \(\text{CH}_3\text{OH}\), and 0.1% of nonionic surface active agent at a temperature of 50°C for about 3 minutes, and then washed with water. It was then treated by using 3% \(\text{NaCN}\), and a lustrous surface was obtained. No smut caused by polishing was observed.

**EXAMPLE 6**

A brass plate composed of 70% of Cu and 30% of Zn was dipped into an aqueous solution composed of 0.3% of \(\text{H}_2\text{SO}_4\), 5% of \(\text{H}_2\text{O}_2\), and 5% of \(\text{C}_2\text{H}_5\text{OH}\), 5% of \(\text{CH}_3\text{OH}\), and 0.1% of surface active agent, and then washed with water. It was then treated with 2% \(\text{NaCN}\), and thereafter washed with water. Non-electro-plating was carried out in the presence of \(\text{KAg(CN)}_2\) and a lustrous surface was obtained.

**EXAMPLE 7**

An article made of iron having copper plating thereon was dipped into an aqueous solution containing 1% of \(\text{H}_2\text{SO}_4\), 7% of \(\text{H}_2\text{O}_2\), 1% of \(\text{C}_2\text{H}_5\text{OH}\), 1% of \(\text{C}_2\text{H}_3\text{OH}\), and 0.1% of surface active agent at room temperature for three minutes, and then washed with water. It was then dipped into an aqueous solution of 2% EDTA for 5 minutes, and then washed with water. A chrome plating process was carried out on the article, and a lustrous surface was obtained.

**EXAMPLE 8**

A roller bearing retainer composed of Phosphor bronze was dipped into an aqueous solution containing 1% of \(\text{HF}\), 7.5% of \(\text{H}_2\text{O}_2\), 5% of \(\text{C}_2\text{H}_3\text{OH}\), and 0.1% of nonionic surface active agent at a temperature of 48°C for about 5 minutes, and then washed with water. It was next washed by using 3% \(\text{H}_2\text{SO}_4\), washed again with water, and then dried. A lustrous surface was obtained.

**EXAMPLE 9**

An electric contact composed of Phosphor bronze was dipped into an aqueous solution containing 0.8% of \(\text{HF}\), 0.2% of formic acid, 7.5% of \(\text{H}_2\text{O}_2\), 5% of \(\text{C}_2\text{H}_3\text{OH}\), 1% of \(\text{C}_2\text{H}_5\text{OH}\), and 0.1% of a surface active agent, at a
temperature of 45° C. for about 3 minutes. It was next washed with water, then with 3% NaCN, and again with water and dried. It was thereby possible to obtain a lustrous surface.

**EXAMPLE 10**

A part of a cosmetic container composed of brass containing 60% of Cu and 40% of Zn was dipped into an aqueous solution containing 7.5% of H$_2$O$_2$, 13.0% of HNO$_3$, 5% of CH$_3$-CH$_2$OH—OH and 0.1% of nonionic surface active agent at a temperature of 60° C. for about one minute and thirty seconds. It was then treated with a solution of 3% NaCN and then washed with water. A lustrous surface was obtained. An alkaline type silver plating process was carried out on the part and a lustrous surface was obtained.

**EXAMPLE 11**

A part of an electric instrument composed of pure copper was dipped into an aqueous solution containing 15% of H$_2$O$_2$, 2% of HNO$_3$, 5% of C$_2$H$_5$OH, and 0.1% of nonionic surface active agent at a temperature of 70° C. for one minute. It was then washed with 3% H$_2$SO$_4$, and thereafter with water. A lustrous surface was obtained.

**EXAMPLE 12**

A brass plate composed of 60% of Cu and 40% of Zn was dipped into an aqueous solution containing 3% of HNO$_3$, 8% of H$_2$O$_2$, 1% of C$_2$H$_5$OH, and 0.3% of CH$_3$OH, and 0.1% of a surface active agent at room temperature for one minute. It was then treated with 3% H$_2$SO$_4$, and then washed with water. A lustrous surface was obtained.

**EXAMPLE 13**

An alloy plate of nickel and copper was dipped into an aqueous solution containing 0.5% of HF, 0.2% of HNO$_3$, 3% of H$_2$SO$_4$, 7.5% of H$_2$O$_2$, 3% of C$_2$H$_5$OH, 1% of CH$_3$OH, and 0.1% of surface active agent at a temperature of 50° C. for one minute, washed with water and then treated with 3% H$_2$SO$_4$ to yield a lustrous surface.

What is claimed is:

1. A method for chemically polishing copper or copper alloy which comprises treating at a temperature of less than 70° C., copper or a copper alloy to be polished with an aqueous solution comprising from 5 to 17.5% by weight hydrogen peroxide, from 0.1 to 10% by weight of at least one water soluble saturated aliphatic alcohol and sufficient of at least one acid selected from the group consisting of sulfuric, hydrofluoric, nitric, hydrochloric, phosphoric, formic, acetic, citric and gluconic acids to provide a mole ratio of acid to peroxide of from .02 to less than 0.95 to produce thereby a film of oxide on said copper or alloy, and thereafter removing the film of oxide by dissolving it chemically.

2. A process according to claim 1, wherein said acid is at least one of sulfuric and hydrofluoric acids and the mole ratio of said acid to peroxide is from .02 to less than .23.

3. A process according to claim 1, wherein said acid comprises nitric acid and the mole ratio of acid to peroxide is from .03 to below .95.

4. A method according to claim 7, wherein the film of oxide is dissolved by using at least one material of the class consisting of sulfuric acid, nitric acid, ammonia, sodium cyanide, ethylene diamine tetra acetate acid, nitrite trinicotet acid, diethylene triamine penta acetate acid and the salts thereof.

5. The method according to claim 1 wherein said alcohol is methanol, ethanol, propanol, butanol or mixtures thereof.

6. The method according to claim 1 wherein the concentration of hydrogen peroxide is from 5 to 15 percent.

7. The method according to claim 1 wherein the film of oxide is dissolved by using acid, alkali, or a complex salt producing substance.

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