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DISSOLUTION OF COPPER

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This invention relates to the dissolution of copper and particularly to a method of dissolving metallic copper in an aqueous persulfate (peroxydisulfate) solution.

There are many applications in which it is desirable to dissolve metallic copper. One of such applications for dissolving or etching copper is in the production of copper printing plates by photoengraving. In this process the copper plate is covered with a mask and then exposed to the copper-etching solution. By dissolving the copper in areas not covered by the masking material, a plate having the desired pattern and suitable for printing can be produced.

Heretofore, the agents most often used to dissolve copper have been strong mineral acids, e.g., nitric or sulfuric acids, or ferric chloride solutions. These agents all have disadvantages. In the case of the strong acids, their highly corrosive nature requires the use of special process equipment. Additionally, these acids generate noxious fumes and, in general, are difficult to work with. With respect to the ferric chloride solutions, this agent similarly is quite corrosive so that special equipment is required. Further, it gives rise to noxious fumes. Additionally, ferric chloride solutions must be used at high ferric chloride concentrations, with the result that solid reaction products readily form in them if they become loaded with dissolved copper. This can seriously reduce the precision of etchings. Further, disposal of the exhausted solution presents a serious problem because of the toxicity of the iron contained therein. Additionally, copper recovery from ferric chloride is not feasible, although economically desirable.

Solutions of persulfate also dissolve copper, but they do not share these heretofore described disadvantages with either acid or ferric chloride solutions. In contrast, they are only mildly acidic, do not generate noxious fumes, produce only soluble-reaction products, and can be disposed of readily following a simple removal of dissolved copper.

The one major drawback of persulfate solutions is that they dissolve copper at a slow rate. While this disadvantage has been overcome by catalyzing the dissolution reaction by the addition of certain catalysts, for example, mercury (as described in copending patent application Serial No. 633,547, filed January 11, 1957), the resultant solutions are not desirable for etching printing plates, since mercury would be constantly removed with the body of the copper plate and would interfere with subsequent printing operations. Additionally, mercury on the surface of the plates constitutes a health hazard in the printing plate industry.

Another method for overcoming the slow copper dissolution rate of aqueous persulfate solutions is described in copending patent application Serial No. 723,973, filed March 26, 1958. In this method it was found that the rate of dissolution of copper by the aqueous persulfate solution could be substantially increased by working at higher temperatures, without decomposing material quantities of the persulfate. This method has not met with widespread acceptance in the printing plate industry because the existing equipment employed is not designed for operation at these higher temperatures. Accordingly, only by expensive modification of existing equipment can this heating technique be effectively employed.

It is a feature of this invention to provide a method for rapidly dissolving metallic copper with mildly acidic, noncorrosive aqueous persulfate solutions.

These and other objects will be apparent from the following disclosure.

It has now been determined that the dissolution rate of copper in persulfate solutions, containing 10 to 45% of a persulfate, may be increased, in far greater measure than would be expected, by applying an electric potential to the copper higher than the polarizing potential of copper in a persulfate solution but below the deposition potential of copper (i.e., about 1.2 volts). The copper serves as the anode, the persulfate solution serves as the electrolyte, and an inert conductor serves as the cathode.

The aqueous persulfate solution employed herein contains about 10 to 50 parts by weight of a dipersulfate and, preferably, about 20 to 30 parts by weight of this ingredient. It is preferred, for present purposes, to employ ammonium persulfate by reason of its ready and high degree of solubility in water, although other persulfate, for example, sodium persulfate or mixtures of persulfate, having the requisite solubility, can be employed.

There is no critical temperature of operation for dissolving copper by the present process. It is preferred to operate at, or about, room temperature as this eliminates the need for special heating or cooling apparatus. It has been found, however, that heated (e.g., about 100° F. or higher) aqueous persulfate solutions dissolve copper somewhat more rapidly than do solutions at room temperature.

In the process of the present invention, the copper engraving plates are contacted by the persulfate solution and become the anode of an electrolytic cell. An inert material is employed as the cathode, and similarly contacts the persulfate solution. A small electric potential is then applied to the cell. The amount of the electric potential applied must be greater than the polarization potential of copper in the persulfate solution being employed as the etchant; that is, the applied potential must be sufficient to allow a current to be passed through the cell. When this current flows, it synergistically activates the dissolution of the anodic copper. It has been determined, for example, that applied potentials of 0.1 volt which passed as little as 40 milliamps were sufficient to activate copper dissolution.

The maximum electrical potential to be applied should be below the deposition potential of copper in the persulfate solution being employed as etchant, this value being about 1.2 volts. Above this value, the applied potential no longer merely acts as an activating means for dissolving copper but is sufficiently high to dissolve copper at the anode and physically plate it out at the cathode. This type of operation is not desired because, in addition to copper plating out at the cathode, persulfate solution is simultaneously reduced at the cathode and converted to the corresponding sulfate with the serious loss of active oxygen. As a result, increased use of electricity and excess loss of persulfate result when the applied potential is above the deposition potential of copper in persulfate.

In contrast, operation at below the deposition potential uses relatively minimal amounts of current, the exact amount depending upon the internal resistance of the system. Further, at these potentials there is almost no appreciable loss of persulfate due to electrolytic reduction at the cathode. The efficiency of the instant process, in terms of the utilization of persulfate, is about 90%. This is comparable to the efficiency obtained in commercial use without any substantial reduction in efficiency due to the loss of persulfate by virtue of the applied current. This is illustrated in Example 3, hereinafter described.

When these small electric potentials are applied to the cell, the dissolution rate of copper increases, but in far greater degree than would be expected due to the electrolytic dissolution of copper. The expected effect is found to be only a small percentage of the over-all increase in the dissolution rate. The increased dissolution rate is so much greater than the sum of the chemical dissolution rate due to the effect of the persulfate on the copper, plus the electrolytic dissolution rate caused by the electrical current, that it can only be described as synergistic. This synergistic dissolution effect appears to reach its peak when the voltage is about 60% of the deposition potential of copper. The preferred range of operation for the present process is between about 25% to about 85% of the deposition potential of copper in the persulfate solution (i.e., about 0.3 to 1.0 volt).

The instant process increases the dissolution rate of copper to a point where it is comparable to that obtained when mercury ions are employed as catalysts in the persulfate solutions. This rate is of the same order of magnitude as that obtained with commercial ferric chloride solutions. Therefore by means of this electrolytic activation, the present process can dissolve copper at substantially the same rate as ferric chloride solutions but with none of their disadvantages.

The present process works exceptionally well with photoengraving copper which generally contains minor amounts of silver, of the order of 1%, as an alloying constituent. The present process is also applicable to the etching of pure copper. However, the synergistic effect obtained by activating the dissolution of copper with a small electric potential is not as great when pure copper is used as compared with the alloyed copper employed for photoengraving purposes.

The following examples are given by way of illustration only and are not intended to limit the operating procedures or materials employed in carrying out the present process.

EXAMPLE 1

Pure copper panels, 2" x 1" x ¼", were separately immersed in an ammonium persulfate solution having a concentration of 25% by weight. The panels were agitated in the solution by being rotated at 250 r.p.m. Electrical contact to a panel was made by use of a mercury seal and current was supplied by a 5-volt rectifier. Various amperages were supplied to the test panels during the copper dissolution and are reported in Table I. The panels were etched in this manner for a 2-minute interval after which the panels were rinsed, dried and weighed. This procedure was repeated two additional times until the total time of immersion was six minutes. Thereafter, the panels were again etched in this same manner for a 4-minute interval after which the panels were rinsed, dried and weighed. This latter procedure was repeated three more times, so that the copper panels had a total etching period of twenty-two minutes.

The milliamps and the voltage readings employed during the dissolution were recorded. Solution temperature during the dissolution reaction was maintained between 105° and 110° F. by a constant temperature water bath. The dissolution rates are reported in Table I and are an average of the seven readings made above. A control panel was employed in one of the runs in which no current was used to activate the dissolution rate. This control run was performed under the same conditions in the same bath and for the same duration of time as the other "activated" runs.

An additional panel, identical in size and composition to those heretofore employed, was tested in a persulfate bath having the same concentration and temperature as the previously recited bath. The sample was tested in the same manner as previously carried out except that no potential was applied, and the ammonium persulfate solution contained 5 ppm. of mercury ion as the activator. The result obtained is reported in Table I and is an average of the seven readings made above.

Table I

DISSOLUTION RATE OF AMMONIUM PERSULFATE ON PURE COPPER

Activation:	Dissolution rate, mg./sq. in./min.
None	31.7
500 milliamps, 0.8 volt	46.5
Mercury ion, 5 p.p.m	54.1

It is known that 1-amp hour of current will deposit, and cause dissolution of, 1,186 grams of copper. This corresponds to a dissolution rate, at 500 milliamps and under the conditions of the experiment, of

$$\overset{\text{Weight of copper}}{1186\ \text{Mg}} \times \overset{\text{Amperage}}{\frac{500\ \text{milliamps}}{1000\ \text{milliamps}}} \times \overset{\text{Time}}{\frac{1}{60\ \text{secs}}} \times \overset{\text{Surface area}}{\frac{1}{4.35\ \text{sq. in.}}}$$

$$=2.3\ \text{mg./sq. in./min}$$

Thus, the maximum rate due to the additive chemical and electrolytic dissolution should have been 34.0 whereas the actual dissolution rate obtained was 46.5, clearly indicating a synergistic effect.

EXAMPLE 2

Photoengraving copper panels, containing about 1% silver, 2" x 1" x ¼", were separately immersed in an ammonium persulfate solution having a concentration of 25%. The panels were agitated in the solution by being rotated at 250 r.p.m. Electrical contact to a panel was made by use of a mercury seal and current was supplied by a 5-volt rectifier. Various amperages were supplied to the panels during the copper dissolution and are reported in Table II. The panels were etched in this manner for a 2-minute interval after which the panels were rinsed, dried and weighed. This procedure was repeated two additional times until the total time of immersion was six minutes. Thereafter, the panels were again etched in this same manner for a 4-minute interval after which the panels were rinsed, dried and weighed. This latter procedure was repeated three more times, so that the copper panels had a total etching period of twenty-two minutes.

The milliamps and the voltage readings employed during the dissolution were recorded. Solution temperature during the dissolution reaction was maintained between 105° and 110° F. by a constant temperature water bath. The dissolution rates are reported in Table II and are an average of the seven readings made above. A control panel was employed in one of the runs in which no current was used to activate the dissolution rate. This control run was performed under the same conditions, in the same bath, and for the same duration of time as the other "activated" runs.

An additional panel, identical in size and composition to those heretofore employed, was tested in a persulfate bath having the same concentration and temperature as the previously recited bath. The sample was tested in the same manner as previously carried out except that no potential was applied, and the ammonium persulfate solution contained 5 p.p.m. of mercury ion as the activator. The result obtained is reported in Table II and is an average of the seven readings made above.

Table II

DISSOLUTION RATE OF AMMONIUM PERSULFATE ON PHOTOENGRAVING COPPER

Activation:	Dissolution rate, mg./sq. in./min.
None	44.4
40 milliamps, 0.1 volt	49.5
50 milliamps, 0.3 volt	58.3
100 milliamps, 0.4 volt	56.3
200 milliamps, 0.7 volt	64.9
500 milliamps, 1.0 volt	62.8
1.0 amps,[1] 1.2 volts	57.3
Mercury ion, 5 p.p.m.	61.3

[1] Copper plates out.

The dissolution rate due to the electrolytic dissolution, using 500 milliamps and under the conditions of the experiment, is 2.3 mg./sq. in./min. Therefore the maximum rate due to the additive chemical and electrolytic dissolution should have been 46.7 whereas the actual dissolution rate obtained was 62.8, clearly indicating a synergistic effect.

EXAMPLE 3

Ammonium persulfate baths, similar to those employed in Example 1, were tested ceriometrically for their ammonium persulfate concentration. This was found to be 19.04%. Using a carbon anode and a stainless steel cathode, 300 milliamps of D.-C. current were passed through this solution for 66 minutes. The resultant persulfate concentration was again ceriometrically determined and found to be 18.59%.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A method for dissolving copper which comprises contacting the copper with an aqueous solution consisting essentially of about 10 to about 45% of a persulfate while simultaneously applying an electric potential between said copper and an inert conductor, said copper serving as an anode, said persulfate serving as the electrolyte, and said inert conductor serving as the cathode, said electric potential being above the polarizing potential of copper in said persulfate solution and sufficient to permit a substantial current flow through said cell, but below the deposition potential of copper in said persulfate solution.

2. The method of claim 1, wherein the applied electric potential is maintained between about 25% to about 85% of the deposition potential of the copper in said persulfate solution.

3. A method for etching photoengraving copper which comprises contacting the photoengraving copper plate with an aqueous solution consisting essentially of about 10 to about 45% of a persulfate while simultaneously applying an electric potential between said photoengraving copper and an inert conductor, said photoengraving copper serving as an anode, said persulfate serving as the electrolyte, and said inert conductor serving as the cathode, said electric potential being above the polarizing potential of photoengraving copper in said persulfate solution and sufficient to permit a substantial current flow through said cell, but below the deposition potential of photoengraving copper in said persulfate solution.

4. The method of claim 3, wherein the applied electric potential is maintained between about 25% to about 85% of the deposition potential of the photoengraving copper in said persulfate solution.

References Cited in the file of this patent

UNITED STATES PATENTS

1,082,596	Kitsee	Dec. 30, 1913
2,196,133	Webb	Apr. 2, 1940
2,361,680	Enrhardt	Oct. 31, 1944
2,558,504	Aller	June 26, 1951
2,596,307	Stuffer	May 13, 1952
2,647,864	Goffredo	Aug. 4, 1953
2,843,538	Haugen	July 15, 1958

OTHER REFERENCES

Mohler: "Plating," October 1948, pp. 1013 and 1014.

Mathers et al.: "Monthly Report of A.E.S.," July 1945, pp. 672–676.

Davis: Metals Handbook, pages 1471–1472, 1939 Edition.

Gwathmey et al.: Journal of Electrochemical Society, vol. 77, April 1940, pages 211–222.

Williams et al.: Journal of Electrochemical Society, vol. 77, April 1940, pages 261–265.