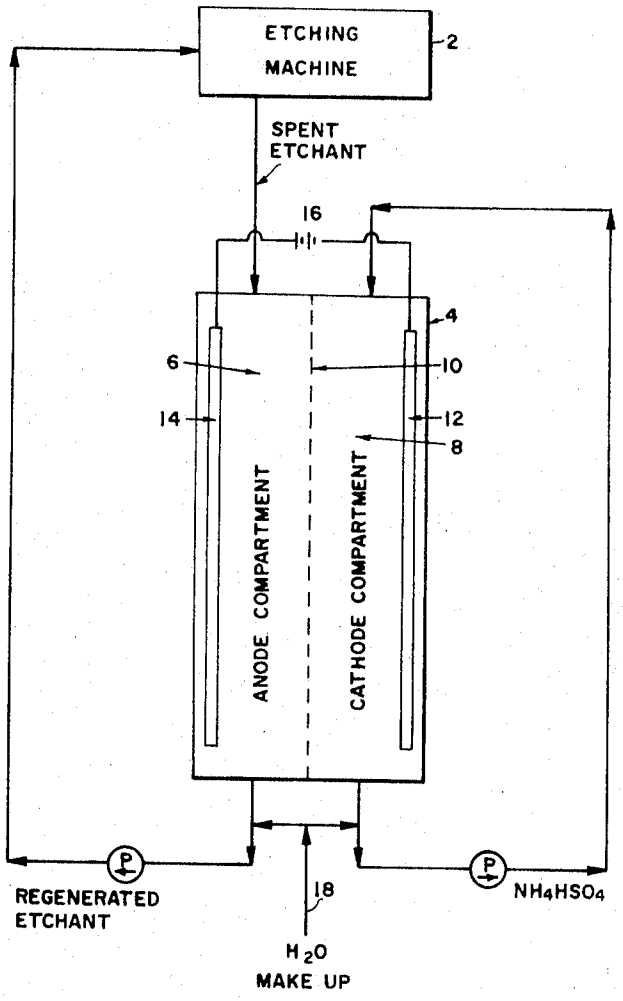
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ELECTROLYTIC REGENERATION OF SPENT AMMONIUM PERSULFATE ETCHANTS

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INVENTOR
KENNETH J. RADIMER

BY Frank J. Jones
Eugene Keeney
Milton Zucker

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ELECTROLYTIC REGENERATION OF SPENT AMMONIUM PERSULFATE ETCHANTS

Kenneth J. Radimer, Little Falls, N.J., assignor to FMC Corporation, New York, N.Y., a corporation of Delaware

Continuation-in-part of application Ser. No. 495,374, Oct. 1, 1965, now Patent No. 3,406,108, dated Oct. 15, 1968. This application June 30, 1967, Ser. No. 650,484

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U.S. Cl. 156—19 9 Claims

ABSTRACT OF THE DISCLOSURE

A spent ammonium persulfate etching solution is regenerated, without loss of residual persulfate values, by electrolysis of the etching solution in an electrolytic cell having a cation exchange separator; the solution serves as the anolyte, and sulfate values therein are converted to persulfate values at the anode while dissolved metal ions are removed at the cathode.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of patent application Ser. No. 495,374, filed Oct. 1, 1965, now U.S. Patent 3,406,108, in the names of Kenneth J. Radimer and Frank E. Caropreso.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the regeneration of spent ammonium persulfate solutions, and further, to the recovery of the unused persulfate values in said spent etching solutions.

Description of the prior art

Solutions of peroxygen chemicals such as ammonium persulfate are commonly used to dissolve metals such as copper, cobalt, iron, nickel, zinc and alloys thereof. This is desirable, for example, in place of ordinary machining in order to remove specified amounts of these metals from surfaces of fragile or peculiarly shaped objects. A more widespread application of this technique is the production of printed electrical circuits. In this application a resist or mask in the form of the desired circuit is placed over the surface of a copper film laminated to a base, and the partially masked copper film is treated with the etchant. The copper area not covered by the resist is dissolved, while the copper covered by the resist remains to form the desired circuit.

Ammonium persulfate solutions are desirable in such applications because they do not generate obnoxious fumes, are easy to work with, and are relatively noncorrosive to certain common materials of construction, such as stainless steels. In use, the metal, e.g., copper, is dissolved in the nonmasked areas by the persulfate solution until the dissolution rate is below commercially acceptable rates. The resulting spent etchant must be treated to remove the dissolved metal, e.g., copper, before it is sewered.

One serious problem that has arisen in using this process is that substantial amounts of persulfate are discarded in the spent etchant. It has not been possible to recover or make use of these remaining persulfate values in the spent etchant on a commercial scale; the mere addition of fresh ammonium persulfate to a spent etching solution to restore the original persulfate concentration

does not yield an acceptable etching solution because such solutions give inferior and erratic etching.

A second problem is that the treatment of spent persulfate solutions to remove metal values, e.g., copper, entails an additional process step which adds to the expense of disposing of these solutions. Copper must be removed from the persulfate solutions before they are sewered because of the toxicity of the copper values.

One method for regenerating spent ammonium persulfate etching solutions, thereby eliminating the expense of disposing of the solutions, is set forth in our parent application, Ser. No. 495,374, filed Oct. 1, 1965. In this application a process is disclosed whereby the spent etching solutions are cooled to a temperature sufficient to crystallize copper sulfate values and ammonium sulfate values from the spent solution without crystallizing substantial ammonium persulfate. The persulfate-free crystalized solids are then used in the make up of a catholyte, while the remaining solution containing sulfate values and all of the remaining persulfate values, is passed into the anode section of an electrolytic cell for use as an anolyte. The cathode and anode sections of this electrolytic cell are separated by a means (generally a membrane) which prevents substantial amounts of persulfate values present in the anolyte from mixing with the catholyte, but permitting the free passage of current between the solution by the passage of ions, and in particular, hydrogen ions, through the separation means. An electric current is then passed through the cell and the copper ions present in the catholyte are reduced to copper while the sulfate ions present in the anolyte are converted to persulfate values.

While the above process is effective in regenerating spent ammonium sulfate etching solutions, it requires two stages to be effective; a first stage in which the copper values are separated from the remaining spent solution (containing residual persulfate) and a second electrolytic stage in which the separated copper is converted to elemental copper, while sulfate values remaining in the spent etchant are converted to persulfate values. As a result, there is a need for a simple and economic method of treating spent ammonium persulfate etching solutions, on a commercially acceptable basis, to recover residual persulfate values and to regenerate additional persulfate values.

SUMMARY OF THE INVENTION

We have now found that a spent aqueous ammonium persulfate etching solution which has been used to dissolve a metal such as copper, cobalt, iron, nickel, zinc or alloys thereof, and which contains the corresponding metal sulfate, ammonium sulfate and residual ammonium persulfate values can be regenerated without substantial loss of ammonium persulfate values by introducing the above spent solution as the anolyte of an electrolytic cell, introducing an electrolyte (preferably an acidic sulfate or a bisulfate containing electrolyte) as the catholyte of said electrolytic cell, the cathode and anode sections of said electrolytic cell being separated by a cation exchange separator (preferably a cation exchange membrane) which permits the dissolved metal ions to pass from the anolyte into the catholyte but which prevents any substantial amounts of persulfate in the anolyte from mixing with the catholyte, passing an electric current through the catholyte and anolyte by means of a cahtode in the catholyte and an anode in the anolyte, removing the dissolved metal from solution at the cathode, converting sulfate values to persulfate values at the anode, and recovering an anolyte solution having increased persulfate values and a decreased dissolved metal concentration so that it is suitable as an etching solution.

It has further been found that regeneration of per-

sulfate values at the anode is facilitated by carrying out the regeneration in the presence of urea or ammonium thiocyanate (NH_4CNS) in the anolyte.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing, a diagrammatical flow sheet is shown of the electrolytic cell containing a cation exchange membrane, in combination with an etching machine that supplies the spent etchant.

DESCRIPTION OF THE INVENTION AND THE PREFERRED EMBODIMENTS

In the following detailed description of the invention, the process will be described with reference to regenerating ammonium persulfate solutions which have been used to etch copper. However, it should be understood that copper is only illustrative of one embodiment and that substantially similar effects can be obtained with cobalt, iron, nickel or zinc.

An initial, conventional etching is first carried out with a fresh aqueous 0.75 to 1.25 molar (M) ammonium persulfate etching solution (containing from about 171 g. to 285 g. of ammonium persulfate per liter of solution) at temperatures of from about 35 to 46° C. This etching solution can be used to etch unmasked portions of copper either by conventional immersion etching or spray etching. In the immersion etching process the masked copper workpiece is immersed in the solution for the amount of time required to etch the exposed copper surface. In the spray etching technique the persulfate solution is discharged from a spray nozzle under pressure, and the spray impinges on the masked copper workpiece.

In practice, the spray etching technique is preferred because it permits shorter etching times and results in a better quality etch. This is due in large measure to constant replacement of the copper-rich layer of etchant that is in immediate contact with the workpiece with fresh etchant.

Etching can be continued until the solution has been depleted of persulfate values to a concentration of about 0.45 M ammonium persulfate. At this point, the solution is capable of further etching, but the etch rate and quality of etch diminishes, and such solutions are normally discarded as "spent" solutions.

This "spent" solution, which contains dissolved copper, ammonium, and "sulfate values" as well as residual persulfate values, is passed into the anode section of an electrolytic cell for use as an anolyte. The term "sulfate values" as used in the specification and claims refers to both sulfate and bisulfate water-soluble compounds. The catholyte section of the above cell is filled with an aqueous, persulfate-free electrolyte, preferably one that is acidic and contains "sulfate values" having about the same concentration as the "sulfate values" in the "spent" solution in the anolyte. While it is possible to use alkaline electrolytes as catholytes when regenerating an alkaline persulfate etching solution, these electrolytes are not as desirable, since ammonium persulfate solutions are more stable in the presence of neutral, and preferably, acidic solutions.

The anolyte and catholyte solutions must be separated in a manner to prevent any substantial amounts of persulfate values in the anolyte from mixing with the catholyte, but without preventing the flow of copper ions from the anolyte to the catholyte. This can best be achieved by placing a cation exchange membrane or any other suitable cation exchange separator between the two solutions. The cation exchange membrane permits the flow of electric current between the anolyte and catholyte, but prevents substantial amounts of persulfate in the anolyte from diffusing into the catholyte. The flow of current between the anolyte and catholyte takes place by passing cations, especially copper ions and some hydrogen ions, through the membrane and is a necessary part of the electric circuit of the cell. The cation exchange membrane in the electrolytic cell can be any type of cation selective membrane, e.g., homogeneous films of sulfonated copolymers of vinyl compounds on fiber glass or synthetic cloth backing. For example, cation exchange membranes CR60 and CR61 manufactured by Ionic's Inc., Watertown, Massachusetts, have been found suitable.

To complete the electrolytic cells an electrode is immersed in each of the catholyte and anolyte solutions. These electrodes can be any material which can conduct an electric current and which does not react with the solutions of the cell during the electrolysis. Generally, noble metals such as platinum or gold are preferred, as the anode, and copper or stainless steel is preferred as the cathode, since copper plates out on the cathode in the ensuing reaction. The copper can readily be stripped, mechanically or otherwise, from a stainless steel cathode. An electric potential is placed across the electrodes (the anode and cathode) by means of a battery, rectifier, or other source of direct current to complete the electrolytic cell.

The electric potential which is applied across the electrodes must be sufficient to cause a positive electrical current to flow outside the cell from cathode to anode. When this occurs, copper flows from the anolyte through the cation exchange membrane to the catholyte and is plated out as elemental copper at the cathode while sulfate values in the anolyte are converted to persulfate at the anode. Normally, an EMF of as litlte as about 4 volts has been found operable with from about 4.5 to 9 volts being preferred. The electrolytic regeneration normally is conducted at a temperature of from about 2 to about 45° C. with temperatures of from about 15 to 35° C. being preferred. The EMF and current density which are used in operating the cell must be such that persulfate is produced at the anode and the dissolved metal is removed at the cathode and can be adjusted, depending upon the rate of regeneration which is desired.

The regeneration has been found to proceed with greater efficiency in the conversion of sulfate values to persulfate when urea or ammonium thiocyanate (NH_4CNS) is present in the anolyte in concentrations of up to about 0.2%. The presence of urea or NH_4CNS in amounts of about 0.005% has been found most effective in increasing anode efficiency for conversion of sulfate values to persulfate by 50 to 100%. The presence of urea or NH_4CNS in the catholyte does not interfere in any manner with the regeneration or operation of the electrolytic cell, nor does it interfere with the use of the regenerated etchant for etching copper.

In general, a cathode having a large surface area is used to facilitate copper deposition while the anode can have a much smaller surface area. Thus, in typical operations, current densities from 25 to 80 amps./sq. ft. at the cathode and 1200 amps./sq. ft. at the anode have been used with good effect.

The desired half-reactions for each of the half cells are as follows:

At the cathode:

$$Cu^{++} + 2 \text{ electrons} \rightarrow Cu^{\circ}$$

At the anode:

$$2SO_4^{--} \rightarrow S_2O_8^{--} + 2 \text{ electrons}$$

The desired overall reaction of the electrolytic cell is:

$$2SO_4^{--} + Cu^{++} \rightarrow Cu^{\circ} \rightarrow S_2O_8^{--}$$

In the above described regeneration, copper ions must pass through the cation exchange membrane into the catholyte before they can be plated out as metallic copper on the cathode. This transfer of copper ions is also accompanied by the transfer of some hydrogen ions through the cation exchange membrane.

In the preferred embodiments a solution of ammonium sulfate and sulfuric acid or of ammonium bisulfate is used initially as the catholyte in order to bring the sulfate

values of the anolyte and catholyte into equilibrium. This minimized undesired diffusion of sulfate values through the cation exchange membrane. An acid catholyte is desired to prevent any possible decomposition of persulfate values in the anolyte, since persulfates are less stable when in contact with alkaline solutions.

In general, one continues electrolysis until the persulfate concentration has been increased to the desired level. During this reaction copper in the anolyte will be substantially decreased by migrating through the cation exchange membrane and plating out at the cathode. It generally is not necessary to remove all of the copper in the anolyte, since good etching can be achieved with the anolyte solution even though it contains some copper.

The electrolytic regeneration can be conducted batchwise or continuously. In a continuous operation, for reasons of efficiency, electrolytic cells should be used in which the electrolytes are introduced at one end of the cell and flow along the membrane until they are removed from the cell of the opposite end. During this flow an increase in the persulfate concentration and a reduction in the copper concentration in the anolyte occur. The catholyte solution does not appreciably change. The solutions can be introduced in other such cells in cascade, if desired. The catholyte solution is then returned to the cell in a continuous, cyclic system, while untreated "spent" etchant is introduced into the anode compartment.

When the regeneration has been completed, the persulfate-rich anolyte is passed to the etching machine and the catholyte is recycled back to the cathode chamber. In the course of the electrolysis the persulfate concentration of the anolyte can be raised to any extent desired from about 0.5 molar up to about 1.0 molar; concentrations of about 0.7 to 1.0 molar are more desirable for faster etching but longer regeneration periods are required to reach these concentrations.

Ideally, it is desired to operate the electrolytic cell such that an amount of persulfate, equivalent to the amount of plated copper, is produced with the theoretical equivalent of current. However, this is seldom achieved due to inefficiency in electrode reactions. In electrochemical processes, usually it is easier to obtain high cathode efficiencies for copper plating vis-a-vis anode efficiencies. In the present cell the reverse is true, and the higher anode efficiency obtained during early stages of operation is believed due in some measure to the lack of complete mobility of the copper ion in passing from the anolyte, through the cation exchange membrane, to the catholyte to be plated out on the cathode. Despite this, however, there is substantial lowering of the copper concentration of the anolyte sufficient to regenerate the etching solution which is present as the anolyte.

One embodiment of the invention that is contemplated to enable an ammonium persulfate solution to be used indefinitely for etching is carried out by continuously removing a portion of the etching solution, continuously adding the removed portion of etching solution to the anode compartment of an electrolytic cell, adding an acidic catholyte solution containing sulfate values to the cathode compartment of the electrolytic cell and passing a current through the electrolytic cell. The resulting electrolytic regeneration increases the persulfate values in the anode compartment while copper ions in the anode compartment pass through the cation exchange membranes, separating the catholyte from the anolyte, and plate out on the cathode. The regenerated anolyte, enriched in persulfate values and decreased in copper values is removed from the cell and recycled back to the main body of etching solution continously. The exit catholyte, which is substantially unchanged in concentration and composition, is recycled back to the cathode compartment of the cell.

The resulting etching solution in such a process thus can be used continuously with a cyclic electrolytic regeneration procedure unless or until foreign impurities, which may be introduced inadvertently or build up in the solution, reach a point where the quality of etch is affected. Such a process obviates the need for replacing etching solution and for disposing of the spent solutions or other waste materials.

Generally, the quality of etchant obtained by using regenerated persulfate solution is about the same as that obtained with fresh ammonium persulfate solution. Thus, the electrolytic regeneration technique described above does not entail any reduction in the high quality of etch obtained when using ammonium persulfate etchants.

The present invention will now be described by reference to the drawing which is a diagrammatical flow sheet of the process.

In the drawing, an ammonium persulfate etching solution is heated in an etching machine **2** and used to etch copper-containing printed circuit panels until the rate and quality of etch are no longer commercially acceptable. The spent solution is then withdrawn from the etching machine **2** and transferred to the anode compartment **6** of a diaphragm cell **4**. The diaphragm cell **4** is made up on an anode compartment **6** and a cathode compartment **8** separated by a cation exchange diaphragm **10** through which cations, and particularly copper ions, can pass, but which prevents any substantial diffusion of anions from one side of the diaphragm to the other. The diaphragm **10** must prevent substantial amounts of persulfate ions from diffusing from the anode compartment to the cathode compartment. Where desired, the free surface of the catholyte in the cathode compartment **8** can be maintained slightly higher than that of the anolyte in the anode compartment **6** to diminish such diffusion. The anolyte and catholyte are electrolyzed by passing a direct current through the anode **14** immersed in the anolyte and through the cathode **12** immersed in the catholyte. Direct current is supplied by battery **16** or other equivalent source of direct current. Within the cell, electric current is carried between the anode and the cathode by the cations, particularly the copper ions which diffuse through the diaphragm **10**.

During electrolysis, copper ions in the anolyte pass through the cation exchange diaphragm **10** and are plated out on the cathode **12**. Sulfate values in the anolyte simultaneously are converted at the anode **14** into persulfate ions. Residual persulfate values present in the anolyte are not affected in any way during the electrolysis reactions. Most desirably, the diaphragm cell **10** operates so that the quantity of copper plated out at the cathode **12** is approximately equivalent, chemically, to the amount of persulfate produced at the anode **14**. However, due to the competing electrolysis of water, the rates of metallic deposition and persulfate production will become equal only after the entire system has reached a state of dynamic equilibrium. In the early stages of operation of the instant cell **4**, the efficiency of the copper electrolysis may be lower than that of the persulfate electrolysis.

Electrolysis is continued until the persulfate concentration in the anolyte has reached the desired level. During this period substantial amounts of copper which have diffused from the anolyte to the catholyte will have been plated out at the cathode **12**. The exit anolyte, rich in persulfate and depleted of its copper, is recycled back to the etching machine **2** for further etching. The exit catholyte from cathode compartment **8**, which is substantially unchanged, is recycled back to the cathode compartment **8**. In some cases additional water is added to the catholyte, and/or anolyte, through line **18** as make-up to offset water losses in the system. If desired, filter means, not shown, can also be inserted in the recycle stream of the catholyte and the anolyte to remove undesired impurities which may build up in the system.

In the above illustrated process no chemicals need be added to the system after it has been put into operation except for small operating losses, e.g. such as losses of chemicals in solution adhering to the etched printed circuit. Further, no by-products or waste materials are produced. The net effect of this system's operation is solely

the movement of copper metal on the printed circuit board onto the copper cathode. All other chemicals remain in balance and the applied electrical current merely reconverts sulfate values to persulfate values, and dissolved copper to copper metal.

In the embodiment of the above illustrated process which is described in Example 1, the process has been carried out by etching batch-wise with a quantity of etchant until all of the etchant is spent and then treating the entire etchant in each of the unit operations in sequence, until the etchant is finally regenerated. However, it is within the contemplated scope of this invention to withdraw continously only a portion of the etching solution in a constant stream and to regenerate this stream of withdrawn etchant constantly by continuous treatment in the electrolytic cell. The regenerated stream of withdrawn etchant is then recycled continually to the etching machine.

Operation in such a completely continuous manner has the advantage that both the electrolytic cell and the etching machine would be in continuous operation, and the concentration of solutes in the etchant would be maintained constant. This would result in highly desirable, constant, etching rates and reduce the amount of maintenance required to keep the etching precise and within commercial tolerances. The system would also lend itself to automation most readily, since it is a balanced system in which the chemical solutions would be recycled throughout the units without varying in solute concentrations at any point in the system.

The following examples are given to illustrate the present invention and are not deemed to be limiting thereof.

EXAMPLE 1

A process for regenerating an etching solution was carried out as follows: An aqueous ammonium persulfate etchant containing 5 p.p.m. of dissolved mercury as an etching catalyst was used to etch photoresisted, single-sided printed circuit test panels, the copper foil of which weighed 1 oz./sq. ft The etching was conducted by immersing test panels in the air-agitated etchant at a temperature of 35–39° C. After continuous etching the quality and rate of etch gradually diminished until the etchant was considered to be spent. At this point one liter of the etchant contained:

	Mole
Persulfate values	.44
Dissolved copper	.49
Sulfate values	.98

The etchant was placed into the anode compartment of an electrolytic cell along with .02% by weight urea. A platinum wire was suspended in the anode compartment to serve as an anode, while a 316 stainless steel sheet was used as a cathode in the cathode compartment of a cell. The anolyte and catholyte compartments were separated by a homogeneous cation exchange membrane. The cathode compartment of the electrolytic cell contained a solution of 0.5 M $(NH_4)_2SO_4$ and 0.5 M H_2SO_4. The anode and cathode were connected to a rectifier, and electrolysis was conducted for about 90 minutes using a current of about 10 amps. The current density was about 813 amps./sq. ft at the anode and about 58 amps./sq. ft at the cathode. The temperature of the anolyte and catholyte was about 25 to 30° C. during electrolysis. After electrolysis the anolyte was analyzed with the following results:

	Moles
Persulfate	.50
Dissolved copper	.43
Sulfate values	.86

The ammonium persulfate contents of the anolyte solutions both prior to and subsequent to regeneration were determined by addition of a known excess of standard ferrous ammonium sulfate and back titration with standard potassium permanganate. The composition of the catholyte did not substantially alter during electrolysis. In the cathode compartment copper was deposited on the cathode.

The recovered anolyte was used for etching a printed circuit test panel as described above; increased etch rates and quality of etch was obtained compared with the spent etchant.

The initial anolyte and the final anolyte solution are reported in Table I, as Run 1.

EXAMPLE 2

A series of additional runs were made using the same technique as Example 1. The initial and final anolyte solutions as well as the electrolysis time and amperage are set forth in Table I as Runs 2–4.

EXAMPLE 3

A series of runs were made in substantially the same manner as set forth in Example 1 except that in place of copper the spent etchant contained either cobalt, iron, nickel or zinc dissolved in the etchant. The spent etchants containing the ingredients in concentration levels set forth in Table II were used as anolytes of an electrolytic cell having a homogeneous cation exchange membrane as set forth in Example 1. The cathode compartment of the electrolytic cell in all runs contained a solution of 0.5 M $(NH_4)_2SO_4$ and 0.5 M H_2SO_4. In each run electrolysis was conducted for about 16 minutes using a current of 10 amps. The current densities at the anode and cathode and the temperature of the electrolysis were identical to those set forth in Example 1. After operation of the electrolytic cell the anolytes were analyzed to determine if there was an increase in persulfate concentration, while the cathode was examined to determine if the etchant metal plated out on the cathode. The results are given in Table II.

TABLE I

Run		Anolyte composition (molar concentration) Initial	Final	Amps	Electrolysis time (min.)	Current density (amps/sq. ft.) Anode	Cathode	Cathode deposit
1 [1]	Persulfate	.44	.50	10	90	813	58	Copper.
	Copper	.49	.43					
	Sulfate	.98	.86					
2 [1]	Persulfate	.43	.50	10	120	813	58	Do.
	Copper	.51	.42					
	Sulfate	1.02	.88					
3a [1] [2]	Persulfate	.45	.48	10	60	813	58	Do.
	Copper	0.5	----					
	Sulfate	1.0	.94					
3b [1]	Persulfate	.48	.57	15	75	1220	88	Do.
	Copper	----	.43					
	Sulfate	.94	.76					
4 [3]	Persulfate	.60	.72	15	120	1220	88	Do.
	Copper	.40	.36					
	Sulfate	.80	.56					

[1] Catholyte contained 0.5 M $(NH_4)_2SO_4$ and 0.5 M H_2SO_4.
[2] Run 3a continued as 3b when current was increased.
[3] Catholyte contained 0.5 M $(NH_4)_2SO_4$ and 1.0 M H_2SO_4.

TABLE II

Run	Metal etched	Spent etchant composition (molar concentration) Persulfate	Sulfate	Metal	Electrolyzed Solutions Cathode	Anode
1	Cobalt	0.4	0.9	0.5 cobalt	Cobalt metal deposited.	Persulfate values increased in concentration.
2	Iron	0.4	0.9	0.5 iron	Iron metal deposited.	Do.
3	Nickel	0.2	0.4	0.2 nickel	nickel metal deposited.	Do.
4	Zinc	0.4	0.9	0.4 zinc	Zinc metal deposited.	Do.

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 process for regenerating an aqueous ammonium persulfate etching solution which has been used to dissolve a metal selected from the group consisting of copper, cobalt, iron, nickel, zinc and alloys thereof and which contains the corresponding metal sulfate, ammonium sulfate and residual persulfate values, which comprises introducing said etching solution into the anode section of an electrolytic cell for use as the anolyte, introducing an aqueous electrolyte substantially free of persulfate values as the catholyte of said electrolytic cell, the cathode and anode sections of said electrolytic cell being separated by a cation exhange diaphragm which permits the dissolved metal ions to pass from said anolyte into said catholyte but which prevents any substantial amount of persulfate in the anolyte from mixing with the catholyte, passing an electric current through said catholyte and said anolyte by means of a cathode in said catholyte and an anode in said anolyte, removing the dissolved metal at said cathode, converting sulfate values to persulfate values at said anode, and recovering an anolyte solution having increased persulfate values and a decreased dissolved metal concentration and which is suitable as an etching solution.

2. The process of claim 1 wherein the dissolved metal is copper.

3. The process of claim 1 wherein the dissolved metal is zinc.

4. The process of claim 1 wherein the dissolved metal is iron.

5. Process of claim 1 wherein urea in amounts of from about 0.005% to 0.20% is added to said anolyte.

6. Process of claim 1 wherein the electrolyte of said catholyte is a mixture of ammonium sulfate and sulfuric acid.

7. A process for continuous etching and regeneration of an ammonium persulfate etching solution comprising etching a metal selected from the group consisting of cooper, cobalt, iron, nickel, zinc and alloys thereof with an aqueous ammonium persulfate etching solution, continuously removing a portion of said etching solution containing the corresponding metal sulfate, ammonium sulfate, and residual persulfate values, introducing said portion of etching solution into the anode section of an electrolytic cell for use as the anolyte, introducing an aqueous electrolyte substantially free of persulfate values as the catholyte of said electrolytic cell, the cathode and anode sections of said electrolytic cell being separated by a cation exchange diaphragm which permits the dissolved metal ions to pass from said anolyte into said catholyte but which prevents any substantial amount of persulfate in the anolyte from mixing with the catholyte, passing an electric current through said catholyte and said anolyte by means of a cathode in said catholyte and an anode in said anolyte, removing the dissolved metal at said cathode, converting sulfate values to persulfate values at said anode, continuously recycling said anolyte solution having increased persulfate values and a decreased dissolved metal concentration back to the main body of said etching solution and continuously dissolving additional amounts of said metal with the increased persulfate values produced in the anode compartment of said electrolytic cell.

8. Process of claim 7 wherein the dissolved metal is copper.

9. Process of claim 7 wherein the electrolyte of said catholyte is a mixture of ammonium sulfate and sulfuric acid.

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JACOB H. STEINBERG, Primary Examiner

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