

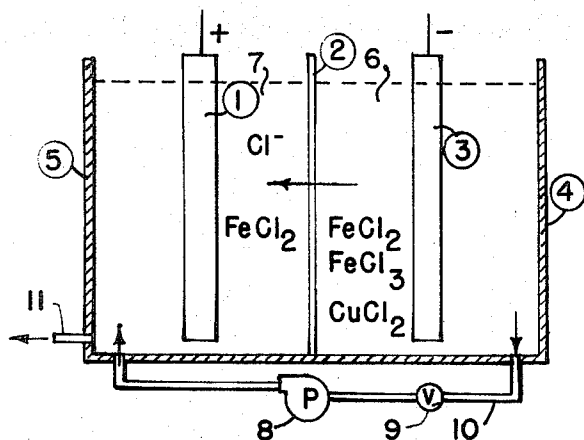
Sept. 25, 1973

C. E. TIRRELL
PROCESS FOR THE ELECTROLYTIC RECLAMATION
OF SPENT ETCHING FLUIDS

3,761,369

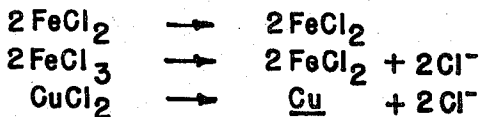
Filed Oct. 18, 1971

2 Sheets-Sheet 1



- ① GRAPHITE ANODE
- ② ANION EXCHANGE MEMBRANE
- ③ TITANIUM CATHODE
- ④ CATHODE CHAMBER
- ⑤ ANODE CHAMBER

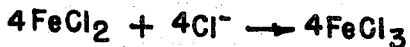
CATHODE REACTIONS



MEMBRANE



ANODE



OVERALL REACTIONS

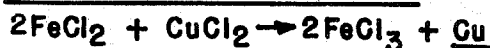
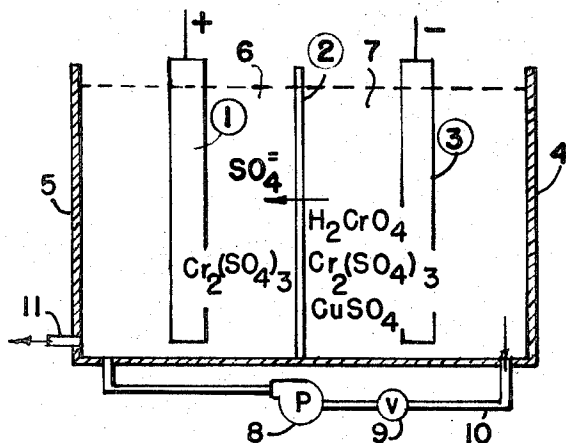


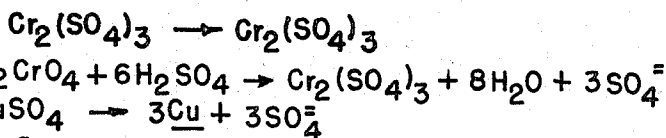
FIG. 1



- ① LEAD OR LEAD ALLOY ANODE
- ② ANION EXCHANGE MEMBRANE
- ③ TITANIUM CATHODE

FIG. 2

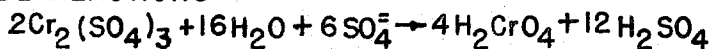
CATHODE REACTIONS



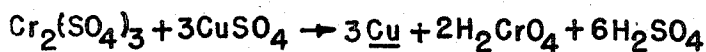
MEMBRANE



ANODE REACTIONS



OVERALL REACTIONS



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2 Sheets-Sheet 2

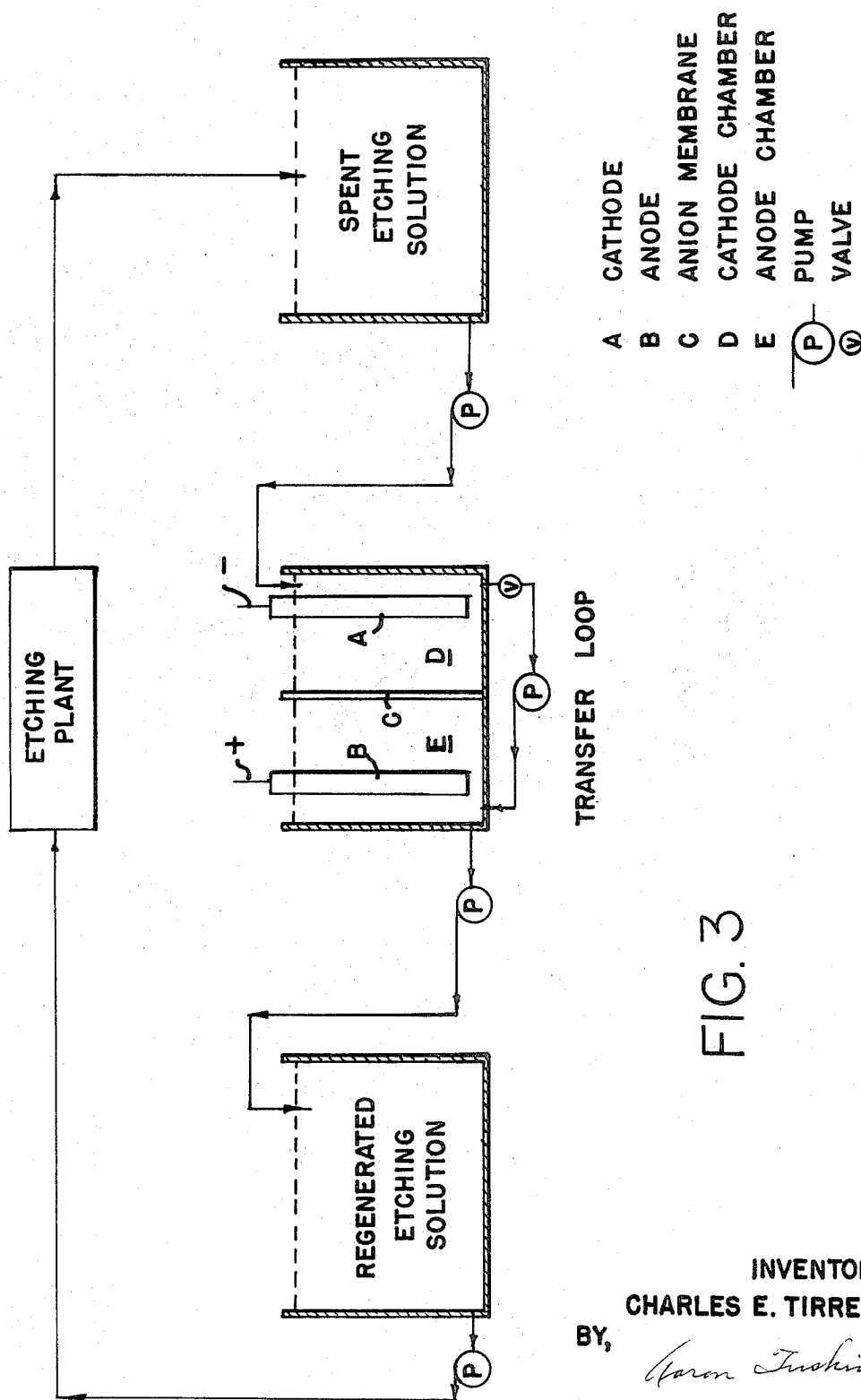


FIG. 3

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3,761,369

PROCESS FOR THE ELECTROLYTIC RECLAMATION OF SPENT ETCHING FLUIDS

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Int. Cl. B01d 13/02; C02c 5/12

U.S. Cl. 204—151

7 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to the method and apparatus for the electrolytic reclamation of spent copper etching fluids, and also to overcoming the problem of waste discharge stream pollution of aqueous solutions of iron and chromium metal, by passing the spent etchant, as the catholyte, into the cathode chamber of a two chamber electrolytic cell having an anion permselective ion exchange membrane separating said cathode chamber from the anode chamber. The chemically reduced spent etchant of a previous batch comprises the anolyte. When a direct electric current is passed through the cell, copper is reduced and deposited on the cathode, and the chemically reduced spent etching fluid is oxidized in the anode chamber to comprise the reclaimed etching fluid for further use. This invention is also directed to the electrolytic cell and the system of carrying out the invention as noted above.

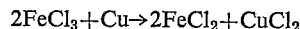
This invention relates to a process and apparatus for regenerating chemical etching solution. Specifically this invention relates to the batch electrolytic recovery of metals from spent etching solutions containing the same and simultaneously the regeneration of the spent etchant to its approximate original composition for further use. More particularly, the invention relates to the improved recovery of the metal copper from both ferric chloride and chromic acid-sulfuric acid etching solutions used in the manufacture of copper clad printed circuit boards, and the reclamation of the spent etching solution for further use as an etchant.

In the manufacture of printed circuit boards, the starting material is usually a copper clad plastic. If the finished product is to be a single sided board (circuitry on one side) the starting material has a layer of copper on one side of the plastic. For a two sided board (circuitry on both sides) the starting material is a sandwich (laminated) comprising a layer of copper on each side of a plastic layer. A common material is $\frac{1}{16}$ " thick total. The copper thickness is designated in ounces per square inch. The most common copper layers are one ounce and two ounce copper, that is, one ounce or two ounces of copper per square foot per side. One ounce per square foot is approximately 0.014" thick, two ounce copper approximately 0.028" thick. In the manufacture of such circuit boards, common practice is to "silk screen" the board image on the laminate or to apply a photo sensitive resist (such as Kodak Photo Resist) and apply the image photographically by direct contact with a photographic negative or positive. After the resist is applied, the laminate is subjected to an etchant such as ferric chloride, chromic acid-sulfuric acid, etc. Other etchants are known to effect the etching of copper, such as cupric chloride, ammonium persulfate, etc. However, the present invention is restricted to the use of ferric chloride and chromic acid-sulfuric acid containing the transitory metals necessary for chemically reduction and oxidation as will be described in detail hereinafter. It will be understood that transitory metals are of that class having more than one valence so that said chemical reduction and oxidation reactions in an electrolytic cell are effected. The etchant dissolves all the copper except that which is protected by

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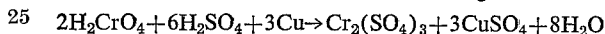
the resist. After etching, the resist is removed by an appropriate solvent such as trichloroethylene for screened resist or methylene chloride for photo resist. The result is a plastic sheet with the desired circuitry of copper.

Etching is usually performed in a batch process. The etcher, is filled with the etchant and the process is operated until the etchant is spent. The etching machine is then emptied, refilled with new etchant and the process continued. In etching with the ferric chloride, a solution of ferric chloride is used ranging from 30° Baumé (2.1 N FeCl_3) to 42° Baumé (3.4 N FeCl_3). One gallon of 42° Baumé ferric chloride will dissolve 8 to 10 ounces of copper according to the following reaction:



After 8 to 10 ounces of copper has been dissolved, only 55% to 70% of the ferric chloride has been consumed. However, the reaction rate is uneconomically slow and the etching fluid must be replaced.

In etching copper with chromic acid-sulfuric acid etching fluid, a solution of 12 % chromic acid (3.69 N H_2CrO_4) and 19% sulfuric acid (4.9 N H_2SO_4) has been employed. One gallon of this etchant will dissolve approximately 8 ounces of copper, according to the following reaction:



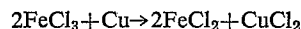
After 8 ounces of copper has been dissolved, the chromic acid has been 50%–55% consumed. However, the etching reaction has become uneconomically slow and the etchant must be replaced.

Disposal of spent etchant is difficult and the usual procedure is to haul and dump it in an area where restrictions are minimal. With present day anti-pollution laws in effect, the spent baths cannot be emptied into sewage systems or surface waters without violating such laws. Spent etching solutions of the character indicated herein, even when greatly diluted, are detrimental to marine growth and their high content of dissolved metals interferes with bacterial action used in most sewage disposal plants. Accordingly, sewerage spent etchants is prohibited in most sewage areas. Building deep dry wells for disposal is very limited and offers no lasting solution to the problem.

The prior art has recognized the problem resulting in the attempt to regenerate spent etching solutions as noted by the U.S. Pat. to Eisler No. 2,748,071. This patent disclosure is directed to a continuous steady-state process wherein the spent etching solution is electrolytically treated in a cell which has a porous partition separating the cathode and anode chambers, and wherein a continuously moving cathode carries deposited copper from the cell through squeeze rollers and scraper blades for removing the deposited copper metal therefrom.

In the form of the cell described in column 2, lines 31 to 45 of the above patent, the spent etchant is introduced into the cathode chamber and flows through a porous separator into the anode chamber. Only a small fraction of the copper is removed because of conditions existing in the cathode compartment. They are:

(1) The bulk of the remaining ferric ions are not reduced to ferrous ions and thus, any copper plated may be re-dissolved according to the reaction:



(2) As the moving cathode moves up through the catholyte in the cathode chamber, the ferric ions in contact with the cathode are reduced to ferrous ions and cupric ions then plate as copper in a very thin layer which is removed from the catholyte before it can be dissolved by ferric ions.

This method removes only a small amount of the cupric ions present since the bulk of the catholyte never

contacts the cathode and only the cupric ions which directly contact the cathode can be plated.

(3) Ferric ions generated in the anode chamber will transfer through the porous separator to the cathode chamber where they re-dissolve plated copper and are thereby reduced to ferrous ions.

The net result of these conditions is that only a small amount of the copper is removed from the spent etching fluid since most of the current is expended in reducing ferric ions which back migrate from the anode to the cathode chamber.

In the form of the cell described in column 2, line 46 through column 3, line 6, in said patent, the spent etching fluid is introduced into the anode chamber. Although there is not necessarily a flow through the separator between the anode and cathode chambers, the existing conditions prevent the removal of most of the copper. These conditions are:

(1) Since the spent etching fluid is introduced into the anode chamber, the cupric ions must migrate through the separator to the cathode chamber. Not only cupric ions but ferric and ferrous ions also migrate to the cathode chamber and ferric and ferrous ions are present in two to three times the concentration of cupric ions, more ferrous and ferric ions migrate to the cathode chamber than cupric ions. Thus, most of the cupric ions remain in the effluent from the anode chamber.

(2) Most of the current passed from the cathode to the anode is used to reduce ferric ions migrated from the anode chamber and the bulk of the copper never reaches the cathode chamber where it can be plated and removed.

The advantages of the present inventions are:

(1) The anion selective membrane prevents passage of the ferric ions from the anode to cathode chamber and prevents migration of cupric ions from the cathode to the anode chamber.

(2) Since all the ferric ions in the cathode chamber are first reduced at the cathode to ferrous ions the copper then plated out cannot redissolve and essentially all the cupric ions can be removed from the spent etching solution.

(3) Since ferric and ferrous ions cannot migrate through the anion exchange membrane from the anode to the cathode chamber, essentially all the ferrous and ferric ions remain in the anode chamber until all ferrous ions have been oxidized to ferric ions and recovery of the etching fluid is virtually 100%.

It is an object of the present invention to provide a process and apparatus for batchwise regeneration of the etchant of a spent etching solution of the character noted hereinabove in a most efficient and economical manner.

It is a further object of the present invention to recover the copper as metallic copper to the extent of over 90% and regenerate the etching solution for further reuse.

A further object of this invention is to meet the requirements of the pollution laws and overcome the objections and problems so critically raised at the present time to ordinary disposal by dumping into rivers, lakes, etc. corrosion of metallic drain pipes, etc.

Many other objects, advantages and features of invention reside in the construction, arrangement and combination of parts involved in the invention and its practice as will be understood from the following description and accompanying drawing wherein:

FIG. 1 is a schematic diagram of an electrolytic ferric chloride etching fluid regeneration cell with the chemical reactions taking place therein.

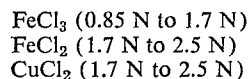
FIG. 2 is a schematic diagram of an electrolytic chromic acid-sulfuric acid etching fluid regeneration cell with the chemical reactions taking place therein.

FIG. 3 is a schematic diagram of the entire system involved in the regeneration of the etching fluid showing the overall flow of the spent etchant and the regenerated etching solution through the system.

Regeneration of both spent ferric chloride and spent chromic acid-sulfuric acid etching fluids are achieved in electrochemical cells shown in FIGS. 1 and 2.

In the regeneration of spent ferric chloride, a two-chambered cell is used such as shown in FIG. 1. The cathode chamber (4) and the anode chamber (5) are separated by an anion permselective ion exchange membrane (2) and regeneration is effected batchwise.

Spent 42° Baumé ferric chloride (6) contains the following chemical species:



Regeneration is performed in two phases. In the first phase the spent etching fluid (6) is placed in the cathode chamber (4) and the chemically reduced spent fluid (7) obtained from the cathode chamber at the end of a previous batch run, is placed in the anode chamber (5) and a direct current is passed through the cell through electrodes (1) and (3), accompanied preferably but not necessarily with agitation. Substantially all the remaining ferric ions (Fe^{+3}) in the spent fluid (6) in the cathode chamber (4) are first reduced to ferrous ions (Fe^{+2}). Following reductions of ferric ions, cupric ions (Cu^{+2}) are only then reduced to copper and plated on the cathode (3). Following reduction of the cupric ions, hydrogen gas is only then evolved from the cathode (3) which is an indication that the ferric and cupric ions have been completely reduced and the catholyte in chamber (4) then contains only ferrous chloride (FeCl_2) which will form the starting anolyte in the anode chamber (7) in a subsequent batch operation of the cell. The surplus chloride ions (Cl^-) released in chamber (4) from the reduction of both FeCl_3 and CuCl_2 pass through the anion permselective membrane (2) into the anode chamber (5) where oxidation of the FeCl_2 to FeCl_3 takes place at the anode in accordance with the chemical reactions noted in FIG. 1. It is to be noted that the chemically reduced spent etchant in the cathode chamber (4) at the end of the run is transferred through line (10) through valve (9) by pump (8) into anode chamber (5) as the anolyte electrolyte of a subsequent batch operation. The regenerated etchant is removed from anode chamber (5) through outlet (11).

The reactions above occur in the sequence stated because of the electrochemical reduction potentials which are as follows, as shown in Lang's Handbook of Chemistry, revised 10th edition, 1967—McGraw-Hill Book Company.

Electrode reaction:	E° red (volts)
$\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$ -----	0.77
$\text{Cu}^{++} + 2e \rightarrow \text{Cu}$ -----	0.34
$2\text{H}^+ + 2e \rightarrow \text{H}_2$ -----	0.00

Following reduction of ferric ions and removal of copper by plating on the cathode, the resulting ferrous chloride (FeCl_2) solution in the cathode chamber (4) is the electrolyte of the anode chamber (5) in a subsequent batch operation. A direct current is passed through the cell and the following reaction occurs at the anode.

Electrode reaction:	E° ox (volts)
$\text{Fe}^{++} \rightarrow \text{Fe}^{+++} + e$ -----	-0.77

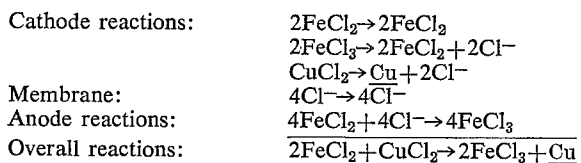
Following complete oxidation of ferrous ions (Fe^{+2}) to ferric ions (Fe^{+3}) in the anode chamber (5) the next reaction that will occur is oxidation of chloride ions to chlorine gas, an indication that all ferrous ions have been oxidized. Chlorine evolution occurs at the following potential.

Electrode reaction:	E° ox (volts)
$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e$ -----	-1.36

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Thus, while a batch of spent etching fluid is being treated in the cathode chamber (4) to reduce ferric ions and remove copper, leaving only ferrous chloride, a previously treated batch transferred to the anode chamber (5) is being oxidized to ferric chloride.

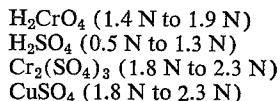
The cell reactions for regeneration of 50% spent ferric chloride etching fluid are as follows:



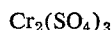
The plated copper is physically removed from the cathode (3) and the regenerated ferric chloride in chamber (5) is ready for reuse as an etchant. In this cell the composition of the anode is preferably graphite and the cathode, titanium. The perm-selective anion exchange membrane (2) is one of the many well known in the art, as for example, those described in the Clarke, U.S. Pat. Nos. 2,730,768 and 2,731,411 of Jan. 17, 1956, and others manufactured by Ionics, Incorporated, of Watertown, Mass., and to be further noted hereinafter.

In the regeneration of spent chromic acid-sulfuric acid etching fluid, a two chamber cell is used such as shown in FIG. 2, like numerals being used for like parts in FIG. 1. The cathode chamber (4) and the anode chamber (5) are separated by an anion selective ion exchange membrane (2) and regeneration is performed by a batch method.

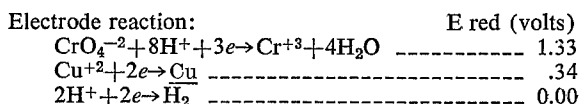
Spent chromic acid etching fluid contains the following species:



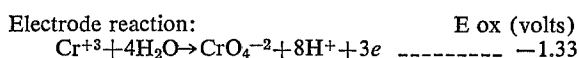
Regeneration is performed in two phases. In the first phase, the spent etching fluid is placed in the cathode chamber (4) a chemically reduced spent etching fluid from the cathode chamber of a previously run batch is placed in the anode chamber (5), and a direct current is passed through the cell through electrodes (1) and (2). The remaining Cr^{+6} is reduced to Cr^{+3} . Following reduction of Cr^{+6} , Cu^{+2} is reduced to Cu and plated on the cathode. Following the reduction of all the cupric ions, hydrogen is then evolved at the cathode which is an indication that all the Cr^{+6} and Cu^{+2} have been reduced and that the catholyte contains only a solution of



The above reactions occur in the sequence stated because of the electrochemical reduction potentials which are as follows.



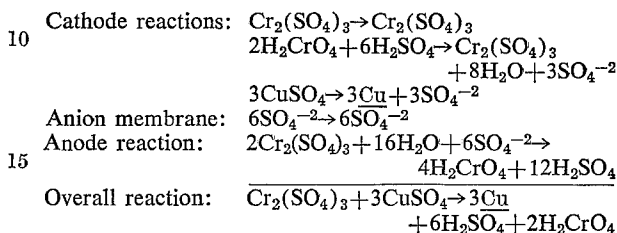
Following reduction of Cr^{+6} and removal of copper by plating on the cathode (3), the resulting $\text{Cr}_2(\text{SO}_4)_3$ solution is transferred to the anode chamber (5), the cathode chamber is filled with spent etching fluid and a direct current is passed through the cell. The following reaction occurs at the anode.



Since the oxidation potential for evolution of oxygen is lower than the above potential for oxidation of Cr^{+3} to Cr^{+6} , an anode material having a high oxygen overvoltage is preferable. Lead and lead alloys of tin, bismuth and antimony have proven to be satisfactory.

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Thus, while a batch of spent etching fluid is being treated in the cathode chamber to reduce Cr^{+6} and remove copper by plating it on the cathode, a batch previously so treated in the cathode chamber and which had been transferred to the anode chamber is being oxidized to chromic acid at the anode (1) in the anode chamber (5). The cell reactions for regeneration of 50% spent chromic acid-sulfuric acid etching fluid are as follows:



The plated copper is easily physically stripped from the cathode and the regenerated chromic acid is ready for reuse as an etchant.

FIG. 3 is a schematic representation of the entire system and is self-explanatory. The important novel features here are:

(1) The use of an anion permselective ion exchange membrane C to define the anode chamber E and cathode chamber D.

(2) The means, termed a transfer loop, whereby the chemically reduced spent etchant of the cathode chamber D may be pumped, when valve X is in its open position, into anode chamber E after the oxidized contents of the anode chamber E (regenerated etching fluid) has been removed by a pump (P) to the regenerated etching solution tank. It is to be noted that while the batch operation of the system may be by manual attendance, the operation could very well be maintained by well known automatic electronically controlled pumps, valves, etc.

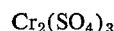
The following examples will serve to further illustrate the invention:

EXAMPLE I

220 ml. of spent chromic acid-sulfuric acid etching solution was placed in the cathode chamber of a two chamber cell. The composition of the spent etchant was 2.38 N H_2CrO_4 , 2.24 N H_2SO_4 , 1.36 N $\text{Cr}_2(\text{SO}_4)_3$ and 1.36 N CuSO_4 . 210 ml. of 3.40 N H_2SO_4 was placed in the anode chamber of the cell. The sulfuric acid used as an anolyte solution does not represent chemically reduced spent etching fluid but was used as a starting solution in order to prepare the first batch of chemically reduced spent etching solution which was then transferred to the anode chamber after all Cr^{+6} had been reduced to Cr^{+3} and the Cu^{+2} has been removed by plating to Cu on the cathode. After all Cr^{+6} and Cu^{+2} was reduced, the sulfuric acid anolyte was discarded. The anode was composed of lead and the cathode was commercially pure titanium.

The membrane separating the two chambers was an anion selective ion exchange membrane supplied by Ionics, Inc. and designated 111BZL183 (see Ionics, Inc. Bulletin No. AR111.0-C) which is essentially a polymer of vinyl compounds containing quaternary ammonium groups and tertiary amine groups. The membrane area and electrode areas were each 4 square inches. A direct current of 2.4 amps was passed for 450 minutes preferably with agitation in the cathode chamber, at which time hydrogen gas began to evolve from the cathode. The current flow was terminated and samples analyzed.

The catholyte contained 208 ml. of solution having a composition of 2.80 N $\text{Cr}_2(\text{SO}_4)_3$, 0.01 N H_2SO_4 and 0.05 N CuSO_4 . This solution was then ready to be transferred to the anode chamber for oxidation of the



to H_2CrO_4 . The sulfuric acid anolyte used as a starting solution was discarded. 9 grams of copper metal were

recovered from the cathode. The original catholyte contained 9.5 grams of dissolved copper. Thus, 95% of the copper was recovered as copper metal. The current efficiency was calculated for the catholyte. 2.4 amps was passed for 450 minutes for a total of 1080 amp minutes or 0.67 Faraday. A total of 0.58 chemical equivalents of Cr^{+6} and Cu^{+2} was reduced in the cathode chamber at a current efficiency of 87%. The above catholyte was transferred to the anode chamber of the cell and the cathode chamber was filled with 220 ml. of spent etching fluid. The composition of the spent etchant was 2.38 N H_2CrO_4 2.24 N H_2SO_4 , 1.36 N $\text{Cr}_2(\text{SO}_4)_3$ and 1.36 N CuSO_4 . A direct current of 4.2 amps was passed for 405 minutes at which time hydrogen gas began to evolve from the cathode. The current flow was terminated and samples analyzed. The composition of the catholyte was 3.10 N $\text{Cr}_2(\text{SO}_4)_3$ 0.10 N H_2SO_4 and 0.04 N CuSO_4 . This solution was then ready to be subsequently transferred to the anode chamber for oxidation of the $\text{Cr}_2(\text{SO}_4)_3$ to H_2CrO_4 .

The composition of the anolyte was 3.20 N H_2CrO_4 , 3.95 N H_2SO_4 0.01 N $\text{Cr}_2(\text{SO}_4)_3$ and 0.12 N CuSO_4 . This solution was then ready for reuse as an etchant. 9.1 grams of copper metal were recovered from the cathode. The original catholyte contained 9.9 grams of dissolved copper. Thus 92% of the copper was recovered as copper metal.

The current efficiency was calculated for both the anolyte and catholyte. 4.2 amps was passed for 405 minutes a total of 1700 amp minutes or 1.05 Faradays. A total of 0.63 chemical equivalents of $\text{Cr}_2(\text{SO}_4)_3$ was oxidized at the anode to H_2CrO_4 at a current efficiency of 60%. A total of 0.60 equivalents of H_2CrO_4 and CuSO_4 were reduced at the cathode to $\text{Cr}_2(\text{SO}_4)_3$ and Cu respectively at a current efficiency of 57%.

EXAMPLE 2

1600 ml. of a spent 42° Bé. ferric chloride etching fluid was put in the cathode chamber of a two compartment cell as described above. The composition of the spent etchant was 1.79 N FeCl_2 , 1.47 N FeCl_3 and 1.79 N CuCl_2 .

1600 ml. of a previously reduced spent etchant, from which the copper had been substantially removed following the reduction of ferric ions to ferrous ions, was placed in the anode chamber of the cell. The composition of this solution was 3.30 N FeCl_2 and 0.04 N CuCl_2 . No FeCl_3 was present. The anode was composed of AGR-58 graphite supplied by National Carbon Company. The cathode was made of commercially pure titanium.

The membrane separating the two chambers was an anion selective ion exchange membrane supplied by Ionics, Inc. and designated 111BZL183, noted above. The membrane area and electrode areas were each 48 square inches. A direct current of 96 amps was passed for 84 minutes at which time hydrogen gas began to evolve from the cathode. The current flow was terminated and samples analyzed.

The composition of the anolyte was 2.96 N FeCl_3 and 0.15 CuCl_2 . No FeCl_2 was present. This solution was then ready for reuse as an etchant.

The composition of the catholyte was 2.91 N FeCl_2 , 0.05 N FeCl_3 and 0.05 N CuCl_2 . This solution was then ready to be subsequently transferred to the anode chamber for oxidation of the FeCl_2 to FeCl_3 .

90 grams of copper was recovered from the cathode. The original catholyte contained 97 grams of dissolved copper. Thus, 93% of the copper was recovered as copper metal. The current efficiency was calculated for both

catholyte and anolyte. 96 amps was passed for 84 minutes, a total of 8064 amp minutes or 5.00 Faradays (1608 amp minutes/Faraday). A total of 4.65 chemical equivalents of cupric and ferric ion were reduced in the cathode chamber at a current efficiency of 93%. A total of 4.74 chemical equivalents of ferric ion were oxidized at the anode at a current efficiency of 95%.

It will accordingly be apparent that in addition to the substantial economic advantages obtained by the extremely high recovery values and reuse of recovered etchant solutions, and a very important consideration of eliminating the pollution problem involved in discharging large quantities of metal containing spent etching plant sewage effluents, are effectively overcome by the present invention.

I claim:

1. The method for the reclamation of spent copper etching fluid comprising: introducing said spent etching fluid into the cathode chamber of an electrolytic cell, said cell having a cathode chamber and an anode chamber defined by an anion permselective ion exchange membrane disposed therebetween and having a cathode and an anode in their respective chambers, introducing an electrolyte into said anode chamber, passing a direct electric current through said cell causing the chemical reduction in said cathode chamber of unspent etchant followed by the plating of copper metal from said spent copper etching fluid on said cathode, said anode electrolyte being the electrolytically chemically reduced fluid obtained from said cathode chamber of a previous run, separately removing the plated copper metal from said cathode and the oxidized fluid electrolyte from said anode chamber as the reclaimed spent etching fluid products.

2. The method of claim 1 wherein said method is carried out batchwise.

3. The method of claim 1 wherein the etching fluid comprises an aqueous solution of a metal compound of the transitory group consisting of iron and chromium.

4. The method of claim 1 wherein the etching fluid is an aqueous solution of ferric chloride.

5. The method of claim 1 wherein the etching fluid is an aqueous solution of chromic acid and sulfuric acid.

6. The method of claim 1 wherein the unspent etching fluid comprises substantially a solution of ferric chloride and the spent etchant comprises a solution of ferrous, ferric, and cupric chlorides.

7. The method of claim 1 wherein the unspent etching fluid comprises substantially a sulfuric acid solution of chromic acid and the spent etchant comprises substantially a sulfuric acid solution of chromic acid, copper sulfate, and chromic sulfate.

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