

- [54] CONTINUOUS ETCHING PROCESS
- [75] Inventor: Charles R. Shipley, Newton, Mass.
- [73] Assignee: Shipley Company, Inc., Newton, Mass.
- [22] Filed: Mar. 16, 1972
- [21] Appl. No.: 235,176

**Related U.S. Application Data**

- [63] Continuation-in-part of Ser. No. 58,170, July 24, 1970, Pat. No. 3,650,958.
- [52] U.S. Cl. .... 156/19, 156/3, 156/8
- [51] Int. Cl. .... C23f 1/00
- [58] Field of Search ..... 156/3, 8, 18, 19, 156/345; 96/36.2; 252/79, 1; 134/13

**References Cited**

**UNITED STATES PATENTS**

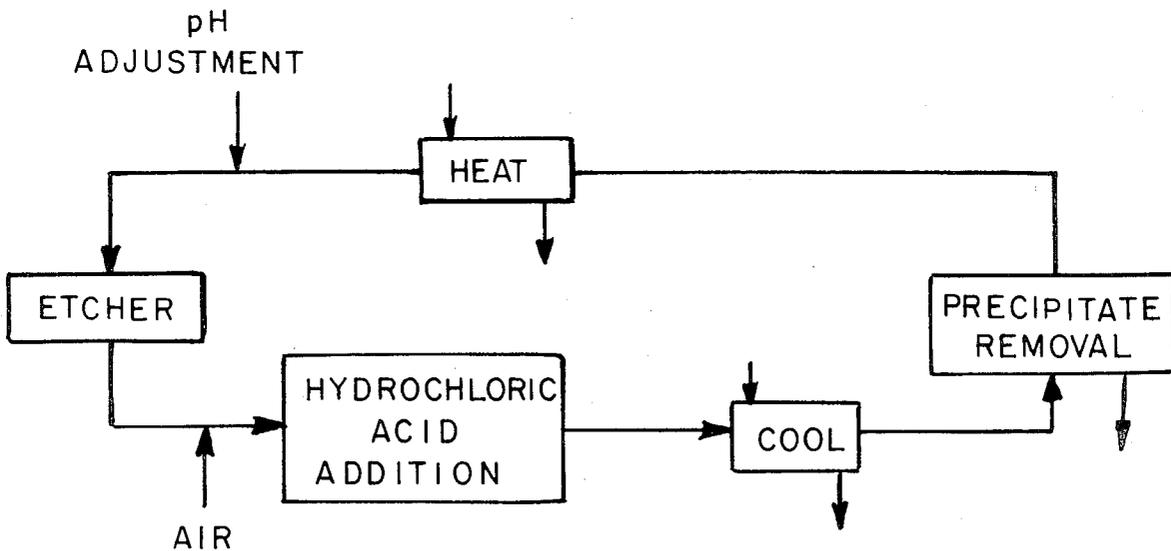
- 3,083,129 3/1963 Jones et al. .... 156/19

Primary Examiner—William A. Powell  
Attorney—Sewall P. Bronstein et al.

[57] **ABSTRACT**

This invention relates to a continuous process for etching cuprous metal which process comprises etching copper with the etchants of the invention, precipitation and removal of the copper from the etchant and regeneration of the etchant making the same available for further use. The etchant used comprises complexed cupric ions as an oxidant. In practice, the etchant is used to etch copper until the dissolved copper concentration reaches a predetermined point, typically from 10 to 24 ounces per gallon of solution. At this point, the etchant is circulated in a loop where it is treated to precipitate dissolved copper, the precipitate is removed and the etchant is returned to the etching apparatus for further use.

27 Claims, 3 Drawing Figures



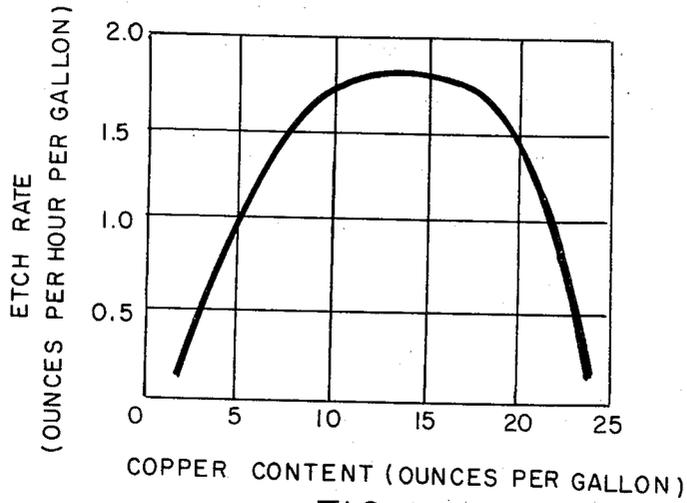


FIG. 1

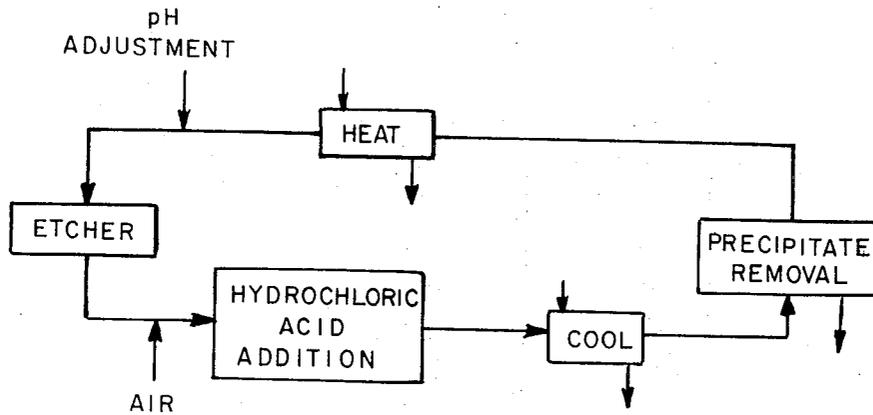


FIG. 2

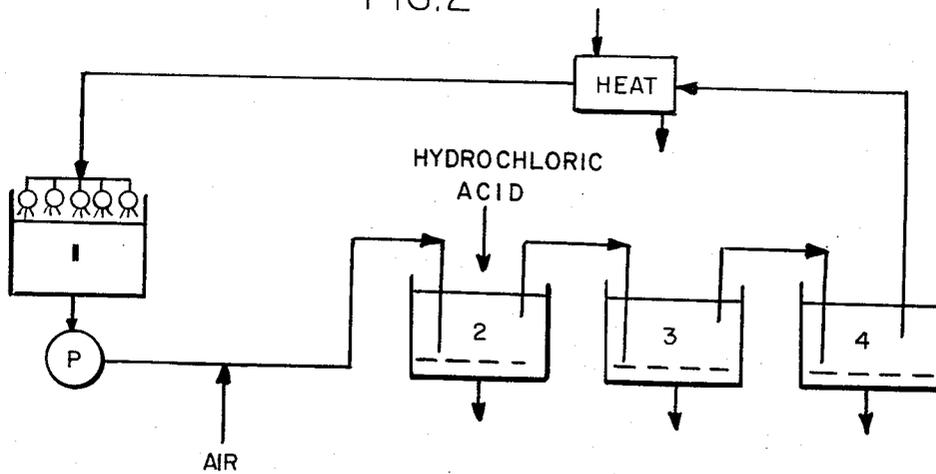


FIG. 3

# CONTINUOUS ETCHING PROCESS

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending U.S. Pat. application Ser. No. 58,170 filed July 24, 1970, now U.S. Pat. No. 3,650,958 in the name of Charles R. Shipley, Jr.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to a process for continuously etching cupreous metal using an etchant containing complexed cupric ions as an oxidant.

#### 2. Description of the Prior Art

Solutions of cupric ions and complexing agents have been used to dissolve metal, especially copper and copper alloys. 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 wide spread application of this technique is the production of electrical printed circuits. In this application, a resist or mask in the form of the desired circuit is placed over a copper film laminated to a base, and the partially masked copper film is placed in contact with an etchant. The copper surface not covered by the resist is dissolved while the copper covered by the resist remains to form the desired circuit pattern.

One such cupric etchant is the well known, highly acidic cupric chloride etchant dissolved in hydrochloric acid. Another such etching solution is disclosed as a secondary etchant in U.S. Pat. No. 3,231,503. This patent teaches a primary etchant solution of a chlorite such as sodium chlorite in an alkaline solution containing an ammonium salt as a complexing agent for the metal stripped. The etchant is used at a pH of from 8 to 13, preferably above pH 9. It is disclosed in said patent that the useful life of the etchant can be extended upon exhaustion of the primary oxidant; i.e., the chlorite by increasing temperature to utilize dissolved copper in the cupric state as a secondary oxidant for further dissolution of copper converting the cupric copper to the cuprous form in the process. Consequently, at this stage of the etching operation, the etchant solution is a cupric ion-ammoniacal etchant as it comprises an ammonium chloride solution of cupric ions as the oxidant having a pH between about 9 and 13. The ammonia is the complexing agent holding copper in solution.

An improved cupric ion type etchant is disclosed in co-pending U.S. Pat. application Ser. No. 58,170 filed July 24, 1970, now U.S. Pat. No. 3,650,958 in the name of Charles R. Shipley, Jr. This etchant essentially comprises cupric ions and a non-fuming complexing agent to maintain said cupric ions and dissolved copper in solution, preferably an amine complexing agent capable of forming a solution soluble copper (II) complex, and preferably, a source of chloride or bromide ions. Though capable of operating within a broad range of pH dependent upon the selection of the complexing agent, the etchant is preferably an essentially neutral etchant operating within a pH range of 7 to 8. The etchants treated herein are believed to be an improvement over those of the aforesaid U.S. Pat. No. 3,231,503 because they are non-fuming, thereby avoiding noxious fumes and in addition, have the capacity of operating within the preferred pH range of 7 to 8 within which

range, they do not attack materials used in the manufacture of printed circuit boards such as resists and the like.

In use of the aforesaid etchants, the metal e.g., copper is dissolved by one mole of the cupric ion oxidizing one mole of elemental copper to form two moles of cuprous ion. This continues until the rate of dissolution decreases to an unacceptable commercial level due to saturation with dissolved copper. As a result of high concentration of copper, the etching rate is substantially decreased and copper begins to precipitate from solution in a form believed to be either the oxide or hydroxide of copper. If left in the etchant, etching would stop because of saturation of the solution and the etching equipment would become clogged by the heavy, somewhat gelatinous precipitate.

The spent etchant as described above, cannot be readily discarded because of strict code regulations prohibiting the dumping of materials which adversely effect the ecology. The dumping of copper, as an example, is generally prohibited. Moreover, dumping of the spent etchant is also economically undesirable because the etchant contains materials that have intrinsic value. For example, copper dissolved in solution has value as scrap metal or as a raw material for preparation of fresh etchant. The complexing agent for the copper is also of value and it would be highly desirable to recover and/or re-use this material. Various methods have been proposed for treatment of spent etchant. For example, it has been proposed to vaporize the water and collect the solids. However, this method is uneconomical and the recovered solids have to be further treated to recover their components in useful form. A further method proposed in the prior art for treating spent etchant of the ammonium persulphate type rather than the type treated by the process disclosed herein, comprises electroplating all copper from solution. This method is generally unacceptable because it has for an object removal of all copper to permit dumping. The cost of removing the last remaining parts of copper from solution is expensive and time consuming. Furthermore, the remaining persulphate may be destroyed to a degree by the process, thereby preventing full utilization of the remaining oxidant.

### SUMMARY OF THE INVENTION

The subject invention provides a process for etching copper utilizing the aforesaid etchants comprising complexed cupric ions which process is continuous, regenerates and re-uses spent etchant thereby avoiding the problem of dumping spent etchant and the cost of providing fresh etchant, and permits recovery of dissolved copper in a commercially useable form.

The etchants contemplated by the subject invention are those comprising complexed cupric ions as an oxidant, preferably using an amine complexing agent, and also containing ammonium and chloride or bromide ions. The preferred etchants are those defined in the aforesaid U.S. Pat. application Ser. No. 58,170.

In practice, the aforesaid etchants are used to etch copper until the concentration of dissolved copper in solution reaches a predetermined point, which concentration may be the saturation point of the copper in solution, the point where the etching rate decreases due to the presence of dissolved copper, or any other convenient point, but preferably a concentration range of from 10 to 24 ounces of dissolved copper per gallon of

solution. The etchant containing dissolved copper in this predetermined concentration range is preferably circulated in a closed loop wherein copper is precipitated, the precipitate is removed by any convenient means such as by filtration and the etchant is returned to the etching apparatus in a form suitable for further use with minor replenishment as necessary.

#### DESCRIPTION OF THE DRAWINGS

In the drawings:

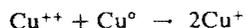
FIG. 1 represents graphically the relationship between dissolved copper content and etch rate for a preferred etchant formulation;

FIG. 2 represents a schematic form, a preferred process in accordance with the invention; and

FIG. 3 is a schematic representation of apparatus suitable for performing the process of the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred etchants treated in accordance with this invention are those defined in the aforesaid U.S. Pat. application Ser. No. 58,170 which etch in accordance with the following two reactions:



As presented above, one mole of the divalent copper oxidizes one mole of metallic copper to two moles of monovalent copper dissolved in solution. The monovalent copper is continuously converted to the divalent form by aeration such as by bubbling air through the solution or by use of a spray etcher. Thus, there is always sufficient divalent copper available in solution for continuous etching. The process continues until the total concentration of copper in solution exceeds that which can be solubilized in solution resulting in a slowdown of etching and precipitation of a copper salt. The relationship between etch rate and copper concentration in the etchant can be seen from reference to FIG. 1 of the drawings where as represented, etch rate peaks at between about 10 and 18 ounces of dissolved copper per gallon of solution and then rapidly drops off as concentration increases. The graphical representation typifies the etchants generally treated in accordance with the invention but specifically represents the etch characteristics of the etchant of Example 1 below.

To make the etchant, substantially any cupric salt may be used as a source of the cupric ion. Typical cupric salts include, by way of example, cupric sulphate, cupric chloride, cupric nitrate, cupric acetate and the like. The amount of cupric ion initially in solution is not critical, may vary within broad limits, and to some extent, is dependent upon the quantity of complexing agent used. A preferred range comprises from about 4 to 6 ounces as cupric ion per gallon of solution.

A complexing agent is preferably used in the makeup of the etchant and serves two important functions. It solubilizes sufficient cupric ion to permit etching and further it holds dissolved copper in solution. As copper is etched, its concentration builds in solution to the point where the capacity of the complexing agent to hold additional copper is used up and should begin to precipitate from solution. In this respect, it should be noted that within the pH range of 4 to 13, cupric salts are fairly insoluble and insufficient cupric ion could be held in solution to provide a satisfactory etch rate with-

out the complexing agent. Thus, increasing the concentration of the cupric ion beyond its normal solubility limit by means of the addition of the complexing agent permits addition of sufficient cupric ion to provide a satisfactory etch rate which is defined for purposes of commercial use as at least 0.1 mils copper per minute with solution agitation.

The selection of the complexing agent is not critical. One complexing agent used in the prior art is ammonium hydroxide which forms a soluble complex with the copper at pH of about at least 8.2. However, the use of ammonium hydroxide as the complexing agent is least preferred because of the liberation of noxious ammonia fumes during etching, the resultant loss of this agent by fuming and the inability to form a copper complex at pH below about 8.2.

Preferably, the complexing agent used is one that is non-fuming so that it will not liberate appreciable ammonia fumes during the etching operation. Also, it should form the copper (II) complex with the cupric ion at the solution pH at which it is desired to use the etching solution. The complex formed with the cupric ion should dissociate in solution to an extent that permits etching of copper at a minimum rate of 0.1 mils per hour. In this respect, it should be readily apparent that the extent of dissociation of a complex is dependent upon numerous factors such as solution pH, solution temperature, concentration of various additives and the like. Thus, though a particular copper (II) complex may not dissociate to a sufficient extent under one set of operating conditions, it may dissociate sufficiently under a different set of operating conditions to provide a satisfactory etch rate. As a guideline only, the log of the stability constant ( $K_1$ ) for a particular copper (II) complex should not exceed 18 and preferably should not exceed 12 at 25° C. Stability constants for a great number of copper (II) complexes are set forth in Martell, *Stability Constants of Metal-Ion Complexes*, Special Publication Number 17, Section II, The Chemical Society, London, 1964, incorporated herein by reference.

Preferred complexing agents heretofore used with cupric ion to form an etchant include alkanolamines such as monoethanolamine, diethanolamine, monoisopropanolamine, and diisopropanolamine.

The amount of complexing agent used is in excess of that amount necessary to complex all of the cupric ion initially in solution, generally at least 1.5 times the amount necessary to complex all of the cupric ion and preferably, at least that amount capable of complexing 15 ounces of copper per gallon of solution. The excess is desirable so as to hold dissolved copper in solution after it is etched and then oxidized by air to the cupric form.

Ammonium ion in addition to the complexing agent is not required for the etchants to be operable, but for purposes of this invention, is desirable as it acts as an exaltant for the etching rate solubilizing the cuprous ion and is replenished by the process of the invention. Typical ammonium salts that may be used include ammonium carbonate, ammonium sulphate, ammonium chloride and the like. The amount of ammonium salt is not critical and may vary broadly from no addition to less than that amount which causes appreciable fuming during the etching operation. The preferred range comprises between 0.5 moles per liter to 5 moles per liter

of solution and more preferably, from about 1 to 2 moles per liter of solution.

Chloride and/or bromide ions may be added to the preferred etchants either in the form of cupric or ammonium chloride or bromide or in any other convenient form as would be obvious to those skilled in the art such as sodium chloride or bromide. The function of this ion is not fully understood, but is believed to increase the etching rate, possibly by acting as a solubilizer for cuprous copper formed on the surface of a copper part being etched. The chloride or bromide ion may be present in minor amounts, the actual concentration not being critical. Preferably, it is present in solution in an amount of at least 0.1 moles per liter and more preferably in an amount of from 0.2 to 3.0 moles per liter. It appears that there may be a synergism between the ammonium and halide ions resulting in a substantially increased etching rate.

The preferred etchants may be used over a wide range of pH, typically from about 3 to 13. However, in the preferred embodiments, the etchants are used within the relatively neutral pH range of from 4 to 10 and most preferably from about 7 to 8. The essentially neutral range is preferred to substantially reduce volatilization of ammonia gas; because of the lack of attack on substrate materials, photo-masks, photoresists and the like; ease of handling; and safety.

With reference to FIG. 2 of the drawings, there is shown in schematic form the process of this invention. The etchant is used to etch the cuprous metal in the etcher until the concentration of the dissolved copper in the solution reaches a predetermined point, which concentration may be the saturation point of the copper in solution, the point where the etching rate decreases due to the presence of dissolved copper or any other convenient point, but preferably a concentration range of from 10 to 24 ounces of dissolved copper per gallon of solution and most preferably, from 14 to 20 ounces of dissolved copper per gallon of solution. When the predetermined amount of copper is dissolved in the etchant, preferably the etchant is circulated through the loop illustrated in FIG. 2.

At this point in the operation, the etch probably contains some precipitate due to saturation of the solution. However, in order to increase the etching capacity of the etchant, it is desirable to precipitate additional copper from solution in the form of a salt. This can be accomplished by any one of a number of different ways. For example, the etchant can be cooled to decrease the solubility of the copper salt in solution. Alternatively, the copper may be "salted out" of solution by the addition of a precipitant such as hydrochloric or hydrobromic acid which acid will form the corresponding halide salt of copper. These two methods may be combined. The step of precipitating additional copper from the etchant is preferably carried out externally of the etcher. For example, with reference to FIG. 2, there is represented both the addition of the hydrohalide acid and the cooling of the etchant external to the etcher.

When using a hydrohalide acid to precipitate copper from solution, preferably, the halide ion should be common to the halide ion contained in the etchant. For example, if the halide ion is chloride, hydrochloric acid should be added to the etchant. In addition, the hydrochloric acid may contain other additives for replenishment of the etchant such as inhibitors, other complexing agents that might be lost through "drag-out" and

the like. Though the etchants of the invention do not require substantial replenishment since active ingredients are not consumed, some minor replenishment might be required to compensate for this drag-out.

Further, with use of a hydrohalide acid to salt out the copper, the amount of hydrohalide added is dependent upon the amount of copper to be removed from the etchant. Normally, under steady state operating conditions, the amount of copper to be removed should essentially equal the amount of copper dissolved during the etching operation. For example, if the etch rate is about one ounce of copper per hour per gallon of solution, the rate of copper removal should also equal about one ounce of copper per hour per gallon of solution. In general, approximately one and one half moles of the hydrohalide acid precipitates about one mole of copper (in a form believed to be the copper halide salt). However, this ratio is dependent upon numerous factors such as operating temperature of the etchant and the complexing system used. Thus, in general, the amount of hydrohalide acid added may vary between about 1 and 3 moles per mole of copper to be removed and preferably, about one to two moles per mole of copper.

At some point in the loop, such as illustrated in FIG. 2 of the drawings, in advance of the hydrohalide acid addition, air is preferably introduced into the line to aerate the etchant and thus convert cuprous copper to cupric form as it is the cupric form that is the oxidant in the etching operation. This step is optional, especially in a spray etching operation as sufficient aeration takes place in the spray etcher.

At the next stage of the operation, the etchant may be cooled to facilitate precipitation of the copper from solution. A substantial decrease in temperature is not required and further, would be uneconomical. A temperature drop of 25° F is possible though from 5° to 10° F would be preferred.

The precipitate formed by the above operation is somewhat gelatinous and though it can be removed by as simple an operation as filtering, somewhat more complex procedures are preferred as the precipitate clogs the filter medium rather rapidly. FIG. 2 merely represents the step of removal broadly, though more specific procedures will be described in greater detail below.

Following removal of the precipitate from the etchant, it is returned to the etcher, preferably through an external heat exchanger to bring the etchant back to operating temperature. Alternatively, the etcher may contain heating means. If a salting out step is used, pH adjustment at this point may be necessary.

Following temperature and pH adjustment, the etchant has had copper removed so that it has an increased capacity for further etching of copper, has had all of the cuprous ions converted to the cupric form so as to be available for further etching, has had replenishment to the extent necessary and is otherwise suitable for further use. Thus, there is no material to dump nor is there any substantial new chemical costs associated with the process. The copper salt recovered from the process is of commercial value as a raw material. Consequently, there is no dumping problems associated with this material.

The above process can be performed in a batch operation wherein the etchant is used to etch copper until the predetermined concentration is reached and then

cycled to remove the copper halide salt or alternatively, can be operated on a continuous basis where the etchant is continuously passed through the above described loop and copper is etched at about the same rate as it is removed from solution. Finally, a combination of the batch and continuous processes may be used where copper is etched continuously with some precipitate removed continuously, and the bulk of the precipitate being removed during a shut-down period such as during the night.

#### EXAMPLE

Cupric chloride dihydrate <sup>(1)</sup>	0.8 pounds per gallon
monoethanolamine	1.3 pounds per gallon
ammonium salts <sup>(2)</sup>	2.2 pounds per gallon
ammonium hydroxide	0.2 pounds per gallon
water	to 1 gallon

(1) Equivalent to 4.8 ounces of cupric ion per gallon of solution.

(2) A combination of ammonium salts including ammonium chloride and ammonium nitrate.

Approximately 300 gallons of the above etchant are used to fill a spray etching apparatus having a 75 gallon capacity and three sedimentation tanks external to the spray etching apparatus but connected thereto by the necessary piping, pumps and the like as to form a closed loop such as that illustrated in FIG. 3 of the drawings. The spray etching apparatus (1) is filled throughout this run, with a succession of copper clad boards ("1 ounce" copper laminated epoxy panels having a copper laminate thickness of 0.0013 inches) which are continuously conveyed and sprayed with the etchant.

The solution in the etching apparatus (1) is heated to and maintained at between 120° and 130° F with pH maintained between about 7.2 and 7.8.

Prior to start-up, or even during the etching operation, the etchant is passed through the loop represented in FIG. 3 at a rate of about 300 gallons per hour so that every hour, all of the etchant has passed through the loop as shown in FIG. 3. The etchant passes from the etching apparatus (1) to and through a series of sedimentation tanks (2), (3) and (4), through a heat exchanger (5) and back to etching apparatus (1).

Etching is started and initially, the etch rate is about 1 ounce of copper per gallon of solution per hour or about 75 ounces of copper per hour as there are 75 gallons of etchant in the etchant apparatus (1) in contact with the copper. Preferably, etching is continued for about 4 to 5 hours without addition of hydrochloric acid during which period of time, the etch rate increases due to increased dissolved copper content. After 5 hours of etching, the dissolved copper content will be about 12.5 ounces per gallon of solution and the etch rate will be at its maximum of about 1.8 ounces per hour per gallon of solution. At this point in the process, in this particular example, hydrochloric acid addition should begin with sufficient hydrochloric acid added so that copper will be removed at substantially the same rate as it is dissolved. In this respect, it takes about 1.5 moles of hydrochloric acid to precipitate about one mole of the copper. Therefore, the hydrochloric acid is added in an amount of about 4.2 ounces per hour per gallon or about 20 pounds per hour.

The precipitate is preferably collected in overflow type sedimentation tanks (2), (3) and (4) as illustrated in FIG. 3 of the drawings. As a practical matter, the precipitate may not form immediately upon contact of the hydrochloric acid with the etchant and there might

be a continued increase in dissolved copper content in the etchant until "steady state" conditions are reached. At the end of an 8 hour shift, the system is typically closed down and allowed to stand over night. During this period, substantially all precipitate will settle out of solution.

Following the sedimentation tanks, the etchant is passed through the heat exchanger whereby it is heated to operating temperature of about 120° to 130° F. Typically, in this loop with the addition of hydrochloric acid at room temperature and passage through the sedimentation tanks, the etchant would have dropped about 10° in temperature. This is desirable as it enhances precipitation of the copper salt from solution. Following return to operating temperature, there is addition of preferably a hydroxide to increase the pH to the operating pH, for this etchant, pH of about 7.5. Ammonium hydroxide and sodium hydroxide are both satisfactory for this purpose, ammonium hydroxide being preferred.

In the above example, other recovery means may be substituted for the sedimentation tanks. For example, a centrifuge may be used or conventional filter means. Difficulty filter been experienced with use of a filter as the precipitate is in gelatinous form and quickly clogs most filter materials.

I claim:

1. A process for continuously etching copper comprising dissolving copper in an etchant and removing formed copper precipitate in an amount sufficient to prevent saturation of the etchant with said precipitate, said etchant comprising a source of cupric ions as an oxidant for copper and at least one non-fuming complexing agent for said cupric ions, said complexing agent being capable of forming a solution soluble copper (II) complex at solution pH and said copper (II) complex being capable of sufficient dissociation in solution under operating conditions to permit etching of copper at a rate of at least 0.1 mils per minute, said etching solution having pH of from about 4 to 13.

2. The process of claim 1 containing as an exaltant for said etchant at least one member selected from the group of chloride ions, bromide ions and ammonium ions.

3. The process of claim 2 where the etchant has a pH varying between about 6 and 8.

4. The process of claim 2 where the etchant has a pH varying between about 7 and 7.8.

5. The process of claim 3 where the etchant contains cupric ions present initially in an amount of from 0.1 to 1.2 moles per liter and complexing agent present in an amount sufficient to at least complex with all of said cupric ions.

6. The process of claim 3 where the etchant contains chloride or bromide ions in an amount of from 0.2 to 2.0 moles per liter of solution.

7. The process of claim 3 where the etchant also contains ammonium ions in an amount of from 0.5 to 5.0 moles per liter of solution.

8. The process of claim 3 where the etchant contains chloride ions in an amount of from 0.2 to 2.0 moles per liter of solution and ammonium ions in an amount of from 0.5 to 5.0 moles per liter of solution.

9. The process of claim 8 where in the etchant, the log of the stability constant ( $K_1$ ) of the copper (II) complex does not exceed about 18 at 25° C.

10. The process of claim 8 where the etchant contains an amine complexing agent.

11. The process of claim 8 where the etchant contains as a complexing agent an alkanolamine.

12. The process of claim 3 comprising continuously etching copper with said etchant, enhancing the precipitation of dissolved copper from solution by at least one of the steps of cooling said etchant and lowering the pH of said etchant, removing precipitate from said etchant, replenishing said etchant including adjustment of pH to the extent necessary, etching additional copper with said etchant and repeating said process.

13. The process of claim 12 where the etchant contains from about 10 to 24 ounces of dissolved copper per gallon of solution prior to the step of enhancing the precipitation of dissolved copper.

14. The process of claim 12 where the etchant contains from about 14 to 20 ounces of dissolved copper per gallon of solution prior to the step of enhancing the precipitation of dissolved copper from solution.

15. The process of claim 12 where copper is precipitated by cooling the etchant and the addition of hydrochloric acid.

16. The process of claim 15 where the etchant is cooled to a maximum of 25° F.

17. The process of claim 15 where the etchant is cooled between 5° and 10° F.

18. The process of claim 15 where the acid is added in an amount of from 1 to 3 moles per mole of copper to be removed.

19. The process of claim 15 where the acid is added

in an amount of from 1 to 2 moles per mole of copper to be removed.

20. The process of claim 15 where the dissolved copper content in the etchant is reduced to no less than 4 ounces of copper per gallon of etchant.

21. The process of claim 15 where the etchant is heated back to operating temperature and the etchant is aerated to convert cuprous ions to cupric form.

22. The process of claim 15 where replenishers are added to the etchant to replace those additives lost through drag-out prior to repeating the etching process.

23. The process of claim 15 where the copper is etched, the etchant is passed out of a spray etcher containing said etchant to remove said precipitate, and recycled back to said etcher.

24. The process of claim 15 where the etchant is passed continuously from an etcher containing said etchant to means to remove precipitate and back to said etcher and where copper is dissolved at about the same rate as it is removed as a precipitate.

25. The process of claim 24 where copper is removed in sedimentation tanks.

26. The process of claim 24 where copper is removed by centrifugation.

27. The process of claim 24 where copper is removed by filtration.

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