

United States Patent

[15] **3,668,131**

Banush et al.

[45] ***June 6, 1972**

[54] **DISSOLUTION OF METAL WITH ACIDIFIED HYDROGEN PEROXIDE SOLUTIONS**

2,894,986	7/1959	Bearer et al.....	260/553 C
3,148,100	9/1964	Elston.....	156/14
3,188,312	6/1965	Gundel et al.	252/149
3,407,141	10/1968	Banush et al.	252/79.4
3,074,825	1/1963	Gardner.....	252/149

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FOREIGN PATENTS OR APPLICATIONS

[73] Assignee: **Allied Chemical Corporation**, New York, N.Y.

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[*] Notice: The portion of the term of this patent subsequent to Oct. 25, 1985, has been disclaimed.

OTHER PUBLICATIONS

Desi et al., "Thiourea and Its Derivatives as Corrosion Inhibitors" Published in *Anti-Corrosion*, July 1968, pp. 12, 13, 14 and 15 and 16 cited

[22] Filed: **Aug. 9, 1968**

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[21] Appl. No.: **751,388**

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[52] U.S. Cl.....**252/79.4**, 156/3, 156/18, 252/98, 252/148

[57] **ABSTRACT**

[51] Int. Cl.....**C09k 3/00**, C23f 1/04

Invention relates to the treatment of metal with hydrogen peroxide, and particularly to urea and thiourea catalyzed acid-hydrogen peroxide solutions as etchants for copper in the manufacture of printed circuits.

[58] Field of Search156/3, 14, 18; 252/79.4, 148, 252/149, 98; 134/3, 28, 41

[56] **References Cited**

21 Claims, No Drawings

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DISSOLUTION OF METAL WITH ACIDIFIED HYDROGEN PEROXIDE SOLUTIONS

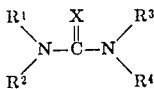
Dissolution or etching of metals in the manufacture of printed circuits is not a simple matter and involves several considerations if it is to be a practical success. Among the more important considerations are rate of attack of the etchant, control of the etchant, stability and efficiency of the etchant, time and temperature conditions, effect of the etchant on the materials forming the printed circuit board, and effect on the equipment and masking material employed in the etching process. In order to be practical a chemical etchant must have capacity to etch a relatively large amount of metal before the etch rate is slowed to an impractical level by the effective exhaustion of the etchant. Each increment in the amount of metal etched represents a significant increase in efficiency and a substantial reduction in the cost per weight unit of metal etched.

Etching of metals, such as copper, has been carried out with an aqueous ferric chloride solution which has been satisfactory at least in its ability to efficiently etch copper without material adverse side effects. However, in more recent times, the disposition of the spent ferric chloride etchant solution containing both iron and copper has become a problem, largely because of the disposal of the waste liquor and difficulty in recovering copper therefrom which is, of course, desirable from a cost standpoint. Other copper etchants have therefore been sought with the result that aqueous solutions of ammonium persulfate have been adopted by some users. This etchant permits electrolytic recovery of copper from the spent etchant solution and eliminates the problem of disposing of metal containing waste liquors. However, ammonium persulfate as an etchant is a premium material because of its low etching capacity and is subject to other drawbacks which have left considerable room for improvement in the provision of an etchant for copper.

As an etchant for copper, aqueous hydrogen peroxide is very attractive because of its relatively low cost and ability to recover copper electrolytically from a spent peroxide etchant solution. However, the utilization of hydrogen peroxide for a constructive purpose in metal etching is subject to numerous problems and pitfalls. Basically, potentially useful solutions combining hydrogen peroxide and acid were found subject to great deficiencies by way of etch rates and capacity. Recently, acidified hydrogen peroxide solutions have been developed whereby metal may be dissolved or etched for constructive purposes in a practical manner and at considerable savings over conventional etching solutions. Such solutions may contain additives such as phenacetin, sulfathiazole and silver ions, water soluble salts and mixtures thereof and satisfy all requirements necessary to constitute new and improved etchants for even copper metal, including unexpectedly fast etch rates and high capacity. See U.S. Pat. No. 3,293,093. In practical use these etchants are designed to be prepared from concentrates and after preparation are subject to a loss of maximum effectiveness with the passage of time, typically a depreciation of 10 percent over a period of 12-36 hours. Etchants of improved capability of storage for extended periods of time after preparation without substantial depreciation and capable of dissolving large amounts of metal at fast rates are disclosed in our U.S. Pat. No. 3,407,141. The acidified hydrogen peroxide solution of that application is catalyzed with an additive selected from phenylurea, diphenylurea, benzoic acid, hydroxy benzoic acid and salts and mixtures thereof.

It has now been found that acidified hydrogen peroxide solutions having high capacity and capable of etching metals at fast rates are provided by incorporating in such solutions a small amount of thiourea compounds and urea compounds other than those covered in our co-pending application.

The urea and thiourea compounds which have been found to increase the capacity and rate of etching of acidified hydrogen peroxide solutions are the substituted urea and thiourea compounds of the formula:



wherein X is a member selected from oxygen and sulfur and each of R¹R², R³ and R⁴ is a radical which may be selected from hydrogen and a hydrocarbon radical (aliphatic, straight or branched, cyclic or aromatic, saturated or unsaturated, substituted or unsubstituted) containing up to about 18 carbon atoms, preferably up to about 12 carbon atoms. Those urea and thiourea compounds suitable for use in the acidified hydrogen peroxide solutions of the present invention should be soluble in the solution to an extent of at least about 20, preferably at least about 50, parts per million. Substituted hydrocarbon radicals may be employed so long as the substituent group does not adversely affect the etch rate or the capacity of the etchant solutions.

Included in the definition of each of the R groups are, for instance, an alkyl radical, e.g., methyl, ethyl, propyl, isopropyl, butyl, tertiary-butyl, hexyl and octyl; an alkenyl radical, e.g., ethenyl (vinyl), allyl, 1-propenyl, 3-hexenyl and 4-octenyl; a cycloalkyl radical, e.g., cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and 4-methylcyclohexyl; and aryl radical, e.g., phenyl, p-tolyl, xylyl (dimethylphenyl), chlorophenyl, alkoxypheyl, naphthyl; an aralkyl radical, e.g., benzyl, phenylethyl and phenyl-propyl; and acyl radicals, e.g., acetyl and benzoyl. Since our aforementioned U.S. Pat. No. 3,407,141 discloses and claims the use of phenylurea and diphenylurea as catalytic additives to acidified hydrogen peroxide etchant solution, these additives are excluded from coverage from this application. Thus, when X is oxygen and one or two of the radicals, R, is an unsubstituted phenyl group, then at least one of the remaining radicals is a substituent other than hydrogen. For instance, when two of the substituent radicals are unsubstituted phenyl groups, then at least one of the remaining radicals is a different substituent radical, such as an alkyl group or an aryl group.

Exemplary of urea and thiourea compounds which may be employed as additives in the acidified hydrogen peroxide etchant solutions of the present invention include: methylurea, ethylurea, butylurea, cyclohexylurea, dimethylurea, diethylurea, trimethylurea, tetramethylurea, allylurea, malonylurea (together R¹ and R³ or R² and R⁴ with the nitrogen atoms form barbituric acid), acetylurea, diacetylurea, benzoylurea, N-acetyl-N¹-methyl urea, acetonylurea, triphenylurea, tetraphenylurea, tolylurea, chlorophenylurea, phenetylurea (ethoxyphenylurea), benzylurea, dibenzylurea, N-alkyl-N¹-phenylurea, N-ethyl-N¹-phenylurea, carbanilide, N,N'-dimethylcarbanilide, N,N'-diethylcarbanilide, methylthiourea, diethylthiourea, acetylthiourea, allylthiourea, phenylthiourea, diphenylthiourea, ditolylthiourea, benzylthiourea, N-methyl-ditolylthiourea, and naphthylthiourea.

Solutions containing such additives not only etch metals including copper at high rates and with high capacity but also exhibit good storage life without substantial deterioration after preparation over periods of 4-10 days, or even greater. It has been also found that acidified hydrogen peroxide solutions having further and markedly improved etch rates and capacity are provided by incorporating therein a combination of one or more of the above-indicated additives with a small amount of at least one additive selected from the group consisting of sulfathiazole, phenacetin and silver ions. The acidified peroxide solutions of the present invention are effective in dissolving copper, and may be employed in accurate, controlled and highly efficient etching of copper-clad laminates as in the manufacture of printed circuit boards.

The additives may be employed in relatively small amounts, thus as little as 20 parts per million is capable of providing an etchant of improved capacity etch rate. However, increasing the amount of additive will further increase etch rate and capacity of the solution. Thus, about 50-2,000 parts of an additive is preferred, with about 100 to 1,000 parts per million being especially preferred. The upper limit is not critical and is primarily a matter of economics. Generally, amounts of additive above about 5,000 parts per million offer no added advantage and are less desirable from a process and economic standpoint.

As previously stated- the etchant may also contain one or more additives from the group of sulfathiazole, phenacetin, and silver ions. In the solutions containing these additives as little as 20 parts per million of such additive may be employed, and smaller amounts of free silver ion are useful, particularly in immersion etching procedures where as little as about 10 parts per million would be effective. The preferred total amount of additives is between about 100 to 150-1,500 parts per million, with between about 50-500 parts per million of each being employed.

As disclosed in U.S. Pat. No. 3,269,881 acidified hydrogen peroxide solutions for etching copper should contain less than 2 parts per million total free chloride and bromide ions, preferably less than 1 part per million. For example, deionized water may be used to make up an etchant containing less than 2 parts per million of chloride and bromide ions. Or, if desired, ordinary water may be employed in make up to the etchant solution if accompanied by addition of suitable material capable of removing free chloride and bromide ions. For example, a small amount of water-soluble silver salt, preferably silver nitrate, may be added to effect the removal of chloride and bromide ion. The precipitated silver halide matter may remain in the acid-peroxide solution since it does not interfere with the etching process. The addition of excess soluble silver salt will furnish free silver ions in the etchant and have a highly beneficial and catalytic effect upon etch rate and capacity.

When sulfathiazole is employed in the etchant the presence of chloride and bromide ions is less deleterious, and no special precautions to remove them need be taken. While the reason for this is uncertain, it is evident that sulfathiazole functions not only to increase the etching capacity of peroxide solutions, but also to negate the adverse repressive effect of the chloride and bromide ion concentration on etch rate and capacity. Hence, the addition of sulfathiazole may permit use of ordinary tap water in preparation of the etchants. Salts yielding sulfathiazole may also be employed and are generally preferred because such compounds are more easily dissolved in the acid-peroxide solution. The sodium salt of sulfathiazole is an example of preferred salt which may be added to the solutions. When employing sulfathiazole for this purpose in etchants prepared from ordinary tap water between about 150 and 250 parts per million is usually required to negate the adverse effects of the free chloride and bromide ions in the water. The capacity of sulfathiazole in overcoming the adverse effect of chloride and bromide ion is apparently not unlimited. Solutions containing the higher concentrations of these ions, say above about 20-30 parts per million, will require additional treatment to negate this effect of such ions, e.g. deionization or addition of a soluble silver salt.

The hydrogen peroxide concentration may vary over a fairly wide range. Etching of metal is desirably carried out in acidified peroxide solutions having a hydrogen peroxide concentration between about 2-12 percent. At solution concentrations less than about 2 percent by weight etch rates are impractically low and etching unsatisfactory. At concentrations above 12 percent by weight, it has been found that copper metal may be etched, but the dissolution of the etched copper ions in the etchant causes decomposition of the peroxide with the result that etching at such high concentrations is less economical. The best results are obtained in solutions having a peroxide concentration between about 2-10 percent.

During the etching process, hydrogen peroxide is consumed as more and more amounts of metal are treated. In order to be practical it is necessary that a single etchant dissolve a substantial amount of metal before the solution becomes exhausted to the extent that a particular workpiece cannot be etched within a reasonable time, e.g. 1-2 hours. The hydrogen peroxide solutions employed in the invention should therefore have an initial hydrogen peroxide concentration of at least about 4 percent in order to dissolve sufficient metal to be practical from an economic standpoint. Desirably, the etchant

solution has initially a hydrogen peroxide concentration within the range of about 5-10 percent by weight. Such hydrogen peroxide solutions are useful in etching a single large metal piece or a series of workpieces containing limited amounts of metal. The etchant is capable of operating effectively at good etch rates after partial exhaustion and at high dissolved concentrations of metals including copper in amounts equivalent to at least 9 ounces of copper per gallon and even substantially higher.

The acid concentration may also vary considerably, and it is desirable that the etchant solution have a hydrogen ion concentration from about 0.45 to about 5.5 grams per liter, preferably between about 0.65-4.5 grams per liter. Below a hydrogen ion concentration of about 0.45 grams per liter, the etch rate is slow and peroxide decomposition high, particularly after partial exhaustion of the peroxide bath. The desired upper limit of the hydrogen ion concentration may depend on several factors including the particular acid employed. A hydrogen ion concentration above about 5.5 grams per liter is generally less economical and tends to slow down rather than increase the etch rate. Inorganic acids and even the stronger organic acids, such as acetic acid, may be used to supply the hydrogen ion concentration in the etchant solution. Examples of the acids which are the more suitable include sulfuric acid, nitric acid, and fluoboric acid, preferably sulfuric acid. The amount of sulfuric acid in the hydrogen peroxide etchant is between about 2-23 percent by weight, preferably between about 3-20 percent by weight. Sulfuric acid concentrations above about 23 percent are less desirable in copper etching as they tend to result in less uniform dissolution, apparently caused by the formation of a protective coating on substantial portions of the exposed copper surface which is thereby made resistant to etching.

The influence of the acid concentration on the copper etch rate has been found of interest. When the acidified hydrogen peroxide etchant solution contains only minor amounts of dissolved copper the effect of acid concentration on etch rate is negligible and the full range of hydrogen ion concentrations between about 0.45 to 5.5 grams per liter results in little variance in etch rate. As the peroxide bath becomes more exhausted and dissolved copper concentration increases, the influence of the acid concentration increases markedly. At the higher dissolved copper concentrations both the lower and higher acid concentrations result in longer etch times. An optimum etch rate has been found to be reached at an intermediate hydrogen ion concentration between about 0.9 to 1.4 grams per liter (about 4-6 percent by weight sulfuric acid). In the etching of metals, such as copper, the hydrogen peroxide and acid are theoretically consumed at a rate equivalent to a mol ratio of hydrogen peroxide. Thus, according to the etching reaction one mol of sulfuric acid is consumed for each mol of peroxide and the acid concentration slowly decreases as the dissolved copper concentration increases.

As the acid concentration does not have a substantial effect on etch rate at low dissolved copper concentrations, it will be noted that the hydrogen peroxide etchant may contain initially a high hydrogen ion concentration with relatively little sacrifice of etch rate after partial exhaustion and increase of the dissolved copper concentration. In situations where it is desired to optimize etch rates and employ lower acid concentrations the etchant solution may be advantageously made up to contain initially a low or intermediate hydrogen ion concentration, of the order of about 0.45-3.4 grams per liter (about 2-15 percent by weight sulfuric acid), preferably between about 1.1-2.6 grams per liter (about 5-12 percent by weight sulfuric acid). Then, as the etchant is consumed causing reduction of the hydrogen ion concentration additional acid is added to regulate the hydrogen ion concentration within the optimum range of about 0.9-1.4 grams per liter (about 4-6 percent by weight sulfuric acid). Addition of the acid may take place either continuously or intermittently and either immediately after the start of the etching or after significant exhaustion of the etchant solution. When the initial hydrogen

ion concentration is low, say of the order of about 0.45–1.1 grams per liter (and 2–5 percent by weight sulfuric acid), the addition of the acid preferably takes place substantially immediately after etching commences and is desirably more or less continuous until the hydrogen ion concentration is increased to well within the range of about 0.9–1.4 grams per liter. When the initial hydrogen ion concentration is greater than about 1.1 grams per liter the addition of acid to maintain the optimum concentration preferably takes place from time to time and after the etchant solution has been exhausted to the extent that the hydrogen ion concentration is below about 1.1 grams per liter, usually just after the concentration is reduced below about 0.9 grams per liter.

In the etchant solution the ratio of hydrogen peroxide to acid is less important than the concentration of the acid. As the chemical reaction or mechanism by which copper is etched consumes one mol of peroxide and 2 mols of acid hydrogen a mol ratio of 1 to 2 is indicated, i.e. a H_2O_2/H^+ ratio of 1 to 2. Peroxide to hydrogen ion mol ratios of less than 1 to 2 are therefore generally unnecessary and may tend to slow the etch rate, particularly at the higher reagent concentrations. In practice, the amount of hydrogen peroxide actually consumed seldom will exceed about 75 percent so that the inclusion of just slightly more than about 1.5 mols of hydrogen ion per mol of peroxide will be adequate to supply sufficient acid for complete utilization of the particular etchant solution. As some peroxide is also not utilized because of decomposition, the etchants made up to include sufficient acid for complete utilization without addition of more acid preferably have a hydrogen peroxide to hydrogen ion mol ratio of not less than about 1.0 to 1.6, and desirably in the range of about 1.0:1.6 to 1.0 to 1.0. When acid is to be later added and the etchant solution contains initially a low or intermediate acid concentration, the mol ratio of peroxide to acid hydrogen may, of course, be initially somewhat greater, preferably between about 1.0:0.2 to 1.0:1.0. As hydrogen peroxide is consumed and more acid added, the mol ratio of peroxide to acid will be reduced and eventually become similar to the mol ratios preferably employed in the solutions made up to contain the complete acid requirement. Again, because peroxide utilization seldom exceeds 75 percent, it is desirable from a practical viewpoint not to add an amount of acid sufficient to reduce the mol ratio of peroxide to acid hydrogen below about 1.0 to 1.6.

The temperature of the acidified-hydrogen peroxide solution is another important factor in etching copper. As a practical matter, copper metal is not etched at room temperatures or below. The nature of the attack of the acid hydrogen peroxide solution on copper at such temperatures is more of a polishing, oxidizing or brightening effect. In order to efficiently etch copper the hydrogen peroxide solution should have a temperature of at least about 40° C. when in contact with the metal. The solution temperature has a strong effect on etch rates and increasing the temperature to a preferred range between about 50°–62° C. will substantially increase the rate of etching to a level significantly greater than heretofore realized with ammonium persulfate etchants at recommended optimum temperatures. At hydrogen peroxide solution temperatures above about 65° C. little further increase in etch rate is realized and such temperatures are undesirable since they result in an impractically high rate of peroxide decomposition. As with acid concentration the influence of temperature on etch rate has been found to be greatest after partial exhaustion of the etchant and increase of the dissolved copper concentration. If desired, etching may be commenced at the lower temperatures, for example, between about 40° C. to 55° C., and temperature of the solution then gradually increased up to a higher temperature of approximately 55°–62° C. as the solution is further exhausted. Some increase in the temperature of the etchant solution is caused by the moderately exothermic etching reaction itself. Increasing the temperature of the etchant may be used to advantage to regulate etch rates at a more or less constant value when a number of pieces are to be

etched in the same solution, for example, when employing automatic systems used in the manufacture of printed circuits.

Generally, the etchant compositions of the invention may be prepared by simple mixing of the required components. They are most conveniently and readily prepared from an aqueous hydrogen peroxide concentrate containing between about 20–70 percent, preferably between 30–60 percent by weight hydrogen peroxide and between about 200–20,000 parts per million, preferably between 500–5,000 parts per million of the desired additive. Such concentrates may also contain silver ions in an amount between about 200–5,000 parts per million, preferably between about 500–2,500 parts per million silver ions. The silver ions are preferably furnished by addition of silver nitrate in an amount between about 300–7,000 parts per million, more usually between 750–3,500 parts per million. The etchant solutions are readily prepared from the concentrates by addition of acid and water and, preferably, other desired additives such as sulfathiazole. The hydrogen peroxide concentrate may be easily and safely shipped and has the further advantage of being storable for extended periods of time at room temperatures and above without depreciation.

The acid-hydrogen peroxide solutions of the present invention are eminently suited for etching of copper or other metal and they may be applied generally in other conventional chemical dissolving operations such as chemical milling, graining and bright dipping or polishing. In such application the temperature of the acid-peroxide solution may be varied, if desired, outside of the range prescribed for the etching of copper. For example, bright dipping operations may be carried effectively at room temperature or slightly above. The additives provided by the invention are beneficially effective not only in the presence of copper but also other metal ions. Thus, the acid solutions containing the additives may be employed in the dissolution of other metals such as iron, nickel, cadmium, zinc, germanium, lead, steel, aluminum and alloys containing a major portion of such metals. Aluminum metal is more effectively dissolved when the acid employed is nitric acid or fluoboric acid, particularly fluoboric acid. The solutions are however, less effective on certain other metals such as gold, tin, chromium, stainless steel and titanium.

The following examples in which parts and percentages are by weight unless otherwise noted demonstrate the practice and advantages of the present invention.

The copper-clad laminates employed in the following examples were cut into specimens having dimensions of $2\frac{1}{4}$ inch \times $4\frac{1}{2}$ inch. Each specimen had 2.7 mil thick copper (2 ounces per square foot) laminated to a plastic base. Etch time was determined with a stopwatch and etch rate calculated after weighing each specimen before and after treatment.

EXAMPLE I

A series of immersion etchants were prepared containing approximately 2,000 parts per million of a test compound in acidified hydrogen peroxide solutions having an analysis of 8 percent H_2O_2 , 17 percent H_2SO_4 and 267 parts per million $AgNO_3$.

A stock etch solution was prepared by first mixing approximately 335 cc of 50 percent H_2O_2 with about 250 cc of H_2SO_4 (93 percent electrolyte grade) and about 1,635 cc of tap water. To 500 gm. of this stock solution (445 ml.) were added approximately 1.0 gram of test compound resulting in an additive content of about 2,000 parts per million. The 2-ounce copper laminated boards were etched 1 at a time. The copper capacity (ounces of copper dissolved per gallon of etchant) at a terminating etch time of 10 minutes was determined at an etching temperature of 60° C. The results are presented in Table I.

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TABLE I

Additive	Conc. (parts per million)	Copper Conc. (oz. of copper dissolved/gal. of etchant)
None	- 6.4-6.7	
Methylurea	2000	9.4
Ethylurea	2000	9.0
Sym-N, N'-diethylurea	2000	9.0
Butylurea	2000	9.5
Allylurea	2000	9.8
1,3 Dimethylurea	2000	9.3
Acetylurea	2000	9.2
1-Acetyl-3-methylurea	2000	9.2

EXAMPLE II

A second series of runs were made employing a etchant solution similar in composition to the one used in Example I, except that deionized water was employed. The etchant contained 8 percent H₂O₂, 17 percent H₂SO₄ and 267 parts per million AgNO₃. Approximately ½ grams of additive compound was added to about 500 grams (445 ml) of the stock etchant solution, which when dissolved provided a concentration of about 1,000 parts per million. Some of the additives tested did not completely dissolve. In these instances the solution was stirred hot for at least about 15 minutes and filtered. The copper content of each of the etchant baths was determined at a terminating etch time of 10 minutes for 2 ounces of copper. Additionally, the percent of the original hydrogen peroxide decomposed in the etchant while etching 9 ½ to 10 ounces of copper was determined. Etching was carried out at 60° C. These data are presented in Table II, below.

TABLE II

Additive	Copper Conc. of etchant (oz. of copper dissolved/gal. of etchant)	Percent H ₂ O ₂ Decomposed
None	9.0	21
p-chlorophenylurea	12.8	6
m-tolylurea	12.0	5
p-phenetylurea	13.5	5
1,1-diphenyl-2-thiourea	13.0	8
1-(1-naphthyl)-2-thiourea	11.9	9
1-Phenyl-2-thiourea	12.5	10
N,N'-diethyl carbanilide	12.5	—
N,N' dimethyl carbanilide	13.0	13
Benzoylurea	11.8	14
benzylurea	11.8	16
3,3' Dimethyl carbanilide	11.8	17
2,2' Dimethyl carbanilide	11.6	18
1,3-dicyclohexylurea	9.8	18

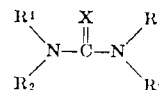
All the test runs found in Table II, above, exceeded the common point of etching 9 ½ to 10 oz. of copper. At this point some 40 percent of the original H₂O₂ had been utilized to etch the copper, approximately 40 to 55 percent remained for etching additional copper, with the remaining unaccounted for H₂O₂ being lost to decomposition. As can be observed from the data in Table II, the decomposition of the H₂O₂ in the control etch solution amounted to 21 percent while having a capacity of 9.0 ounces of copper. The reduced decomposition of the H₂O₂, as exhibited by the etch solutions containing additive of the present invention can increase the useful etchant life up to about 30 percent or an additional 2 to 3 ounces of copper per gallon of etchant during a given period of time.

Although certain preferred embodiments of the invention have been disclosed for purposes of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

We claim:

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1. The method for dissolution of a metal selected from the group consisting of copper, iron, nickel, cadmium, zinc, steel, aluminum and alloys thereof which comprises contacting the metal at a temperature within the range from about 40° C. up to about 65° C. with an acidified aqueous hydrogen peroxide solution having incorporated therein at least about 2 weight percent hydrogen peroxide, about 0.45 to 5.5 grams per liter hydrogen ion and a catalytic amount of at least about 20 parts per million of an additive having the structure:



- 15 wherein X is a member selected from the group consisting of oxygen and sulfur; and each of R¹, R², R³ and R⁴ is a radical selected from the group consisting of hydrogen, a non-aromatic hydrocarbon radical; acyl; and mono- and di-nuclear aromatic hydrocarbon radicals wherein the aromatic ring may be bonded to the nitrogen atom through an alkylene or carbonyl group; said hydrocarbon radicals containing from 1 up to about 18 carbon atoms; provided that at least one of R¹, R², R³ and R⁴ is a radical other than hydrogen and provided further that when X is oxygen and up to two of R¹, R², R³ and R⁴ is an unsubstituted phenyl, then at least one of said remaining R groups is a radical other than hydrogen.

2. The method according to claim 1 in which the solution has incorporated therein about 2 to 12 percent by weight hydrogen peroxide.

3. The method according to claim 1 in which the solution has incorporated therein about 2 to 23 percent by weight sulfuric acid.

4. The method of claim 1 wherein the additive is present in an amount between 20 to 5,000 parts per million.

5. The method of claim 1 in which the amount of additive incorporated in the solution is between about 50 to 2,000 parts per million.

6. The method of claim 1 in which the solution also has incorporated therein as catalyst an additive selected from the group consisting of sulfathiazole, phenacetin, silver ions and water-soluble salts and mixtures thereof.

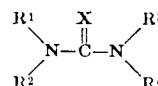
7. The method of claim 1 wherein the additive is selected from the group consisting of p-chlorophenyl urea, tolyurea, phenetylurea, N,N'-diethylcarbanilide, N,N'-dimethylcarbanilide, benzoylurea, dibenzylurea.

8. The method of claim 1 wherein the additive is selected from the group consisting of phenylthiourea, diphenylthiourea, and naphthylthiourea.

9. The method of claim 1 wherein each of R¹, R², R³ and R⁴ is a radical selected from the group consisting of hydrogen, a non-aromatic hydrocarbon containing from 1 to 12 carbon atoms and acyl derivatives of said hydrocarbons.

10. The method of claim 1 wherein the aqueous solution has a total free chloride and bromide ion content of not more than 2 parts per million.

11. A composition for metal dissolution consisting essentially of an acidified aqueous hydrogen peroxide solution having incorporated therein at least about 2 weight percent hydrogen peroxide and a catalytic amount of at least about 20 parts per million of an additive having the structure:



- wherein X is a member selected from the group consisting of oxygen and sulfur; and each of R¹, R², R³ and R⁴ is a radical selected from the group consisting of hydrogen, a non-aromatic hydrocarbon radical; acyl; and mono- and di-nuclear aromatic hydrocarbon radicals wherein the aromatic ring may be bonded to the nitrogen atom through an alkylene or carbonyl group; said hydrocarbon radicals containing from 1 up to about 18 carbon atoms; provided that at least one of R¹, R²,

R³ and R⁴ is a radical other than hydrogen and provided further that when X is oxygen and up to two of R¹, R², R³ and R⁴ is an unsubstituted phenyl, then at least one of said remaining R groups is a radical other than hydrogen.

12. The composition of claim 11 in which the amount of additive incorporated therein is between about 50 to 2,000 parts per million.

13. The composition of claim 11 in which there is also incorporated as catalyst an additive selected from the group consisting of sulfathiazole, phenacetin, silver ions and water-soluble salts and mixtures thereof.

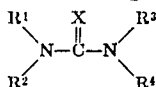
14. The composition according to claim 11 in which the solution has incorporated therein about 2 to 12 percent by weight hydrogen peroxide and about 0.45 to 5.5 grams per liter hydrogen ion.

15. The composition according to claim 11 in which the solution has incorporated therein between about 2 to 23 percent by weight sulfuric acid.

16. A composition according to claim 11 in which the total chloride and bromide ion content does not exceed 2 parts per million.

17. The composition of claim 11 wherein the additive is present in an amount between 20 and 5,000 parts per million.

18. A composition suitable for conversion to an acidified-hydrogen peroxide etchant containing 2-12 percent by weight hydrogen peroxide and a catalytic amount of at least about 20 parts per million of an additive having the structure:



wherein X is a member selected from the group consisting of oxygen and sulfur; and each of R¹, R², R³ and R⁴ is a radical selected from the group consisting of hydrogen, a non-aromatic hydrocarbon radical; acyl; and mono- and di-nuclear aromatic hydrocarbon radicals wherein the aromatic ring may be bonded to the nitrogen atom through an alkylene or carbonyl group; said hydrocarbon radicals containing from 1 up to 18 carbon atoms; provided that at least one of R¹, R², R³ and R⁴ is a radical other than hydrogen and provided further that when X is oxygen and up to two of R¹, R², R³ and R⁴ is an unsubstituted phenyl, at least one of said remaining R groups is a radical other than hydrogen; said composition consisting essentially of a concentrated aqueous solution containing 20-70 percent hydrogen peroxide and at least one of said additives in a total amount between about 200-20,000 parts per million.

19. A composition in accordance with claim 18 in which said concentrated aqueous solution has incorporated therein 30-60 percent hydrogen peroxide, and between about 500-5,000 parts per million of the additive.

20. The composition of claim 18 which additionally has incorporated therein a compound selected from the group consisting of sulfathiazole, phenacetin, silver ions, and water-soluble salts and mixtures thereof.

21. The composition of claim 18 which additionally has incorporated therein about 200 to 5,000 parts per million silver ions.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,668,131 Dated June 6, 1972

Inventor(s) Russell S. Banush and Donald P. Hagerty

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 53 - "deterioration" should be -- depreciation -- ;

Col. 7, Table I, First line under second heading "-6.4-6.7"
should read -- - --
First line under third heading should read
-- 6.4-6.7;

Col. 7, Table II, Eighth line under third heading " - "
should read -- 13 --;

Col. 10, line 8 - "to 18 carbon" should read -- to about 18
carbon --;

Col. 10, line 11 - ", at least" should read -- , then at least --

Signed and sealed this 16th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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