Dissolution of Metal with Acidified Hydrogen Peroxide Solutions

21 Claims. (Cl. 252—79.4)

Abstract of the Disclosure

Relates to acidified hydrogen peroxide solutions and method for dissolving metals, particularly useful in the manufacture of printed circuit boards, wherein said acidified hydrogen peroxide solutions contain an additive selected from the group consisting of phenylurea, diphenylurea, benzoic acid, hydroxy benzoic acid and salts and mixtures thereof.

Dissolution or etching of metals for a constructive purpose as 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, ourselves and our associates have participated in the development of acidified hydrogen peroxide solutions and conditions of use thereof 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 and satisfy all requirements necessary to constitute new and improved etchants for even copper metal, including unexpectedly fast etch rates and high capacity. 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% over a period of 12–36 hours. Etchants of improved capability of storage without substantial depreciation are desirable for convenience of the user in permitting greater flexibility in preparation of the solutions and avoiding loss of effectiveness during extended periods of shutdown of operations.

An object of the present invention is to provide a new and improved etchant based on hydrogen peroxide.

Another object is to provide new acidified peroxide etchants especially having improved capacity for standing for extended periods of time after preparation without substantial loss of effectiveness.

Another object is to provide new and improved hydrogen peroxide etchants capable of dissolving large amounts of metal at fast rates.

A further object is to provide new and improved acid-peroxide solutions for etching copper for a constructive purpose as in the manufacture of printed circuits.

A still further object is to provide hydrogen peroxide etchants adapted for efficient use particularly in various conventional etching apparatus and procedures including both immersion and spray etching operations.

Other objects and advantages will be evident from the following description of the invention.

In accordance with the present invention it has been found that acid-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 one or more additives selected from the group consisting of phenylurea, diphenylurea, benzoic acid and hydroxy benzoic acid. Solutions containing such additives not only etch metals including copper at high rates and with high capacity but also exhibit exceptionally good storage life without substantial depreciation after preparation over periods of 4–10 days, or even greater. It has been also found that acidified hydrogen peroxide solutions having further and more particularly 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 particularly preferred solutions provided by the present invention contain a combination of phenylurea and sulfathiazole and are characterized by ability to etch large amount of metal at very fast rates and also ability to be stored or permitted to stand over extended time periods after preparation without substantial loss of maximum effectiveness. All the acidified peroxide solutions provided by the invention are effective in dissolving copper metal and may be employed in accurate, controlled and highly efficient etching of copper-Clad laminates as in the manufacture of printed circuit boards.

Phenylenes, diphenylurea, benzoic acid and hydroxy benzoic acid are all highly effective in improving the etch rate and capacity of acid-peroxide solutions. Salts yielding these additives in the acid-peroxide solution may also be employed. For example, the sodium salt of benzoic acid and hydroxy benzoic acid may be added to the solution. The preferred additive is phenylurea. In preparation of the acidified peroxide solutions of the invention, only a small amount of the above-mentioned additive is required to have the desired catalytic affect on etch rate and capacity. The phenylenes and benzoic acid compounds may be added in an amount as little as 30 parts per million to provide an etchant of improved capacity etch rate. Increasing the amount of additive will further increase etch rate and
capacity. About 100—1000 parts per million of the phenylurea and benzoic acid additives is preferred. The upper limit of the amount of additive is not critical and mostly a matter of economics. Generally, an amount of additive in excess of about 5,000 parts per million offers no added advantage and is less desirable from a process and economic standpoint.

Acid-hydrogen peroxide solutions of exceptionally fast etch rates are also provided by the invention by incorporating the solutions a combination of additives involving one or more of phenylurea and benzoic acid compounds with one or more additives from the group of sulfathiazole, phenacetin and silver ions. In the solutions containing such combinations as little as 20 parts per million of each additive may be employed. Sometimes, the etchant solutions which contain silver ions may be employed, particularly in immersion etching procedures where as little as about 10 parts per million would be effective. The particularly preferred additive combination is phenylurea and sulfathiazole with the phenylurea preferred over di-phenylurea in such combination by reason of difference between cost of the compounds. Silver ions may also be incorporated in the phenylurea-sulfathiazole combination to further improve the etch rate performance of the solution. Combination of benzoic acid compounds and silver ions are also effective in producing etchants having fast etch rates and high capacity substantially improved over benzoic acid alone. The preferred total amount of additives in the combination systems is between about 150—1500 parts per million with between about 50—500 parts per million of each being employed. Hence, the particularly preferred solutions have incorporated therein between about 50—500 parts per million phenylurea and between 50—500 parts per million sulfathiazole. Another preferred solution contains benzoic acid and sulfathiazole each in an amount of 50—500 parts per million.

In preparation of acid-hydrogen peroxide solutions for treatment of copper metal special consideration must be given to provide solutions which 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 of the etchant solution if accompanied by additions 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 ions. The precipitated silver halide matter is allowed to remain in the solution and 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 each rate and capacity. When sulfathiazole is employed in the etchant it has been found that special consideration may be dispensed with. While the explanation for this result 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 etchant. Small yields sulfathiazole may also be employed and are generally preferred because such compounds are more easily dissolved in the acid-peroxide solutions. The sodium salt of sulfathiazole is an example of preferred salt which may be added to the solutions. Sulfathiazole for this purpose in etchants prepared from ordinary tap water between about 150 to 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 limited. 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. denitration or addition of a soluble silver salt.

In the dissolution of metal by the invention the hydrogen peroxide and acid solutions offer a fairly wide range. Etching of metal is desiredly carried out in acidified solutions having a hydrogen peroxide concentration between about 2—12%. At solution concentrations less than about 2% by weight etch rates are impractically low and etching unsatisfactory. At concentrations about above 12% 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%. 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 must therefore have an initial hydrogen peroxide concentration of at least about 4% 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%. The hydrogen peroxide solutions having the indicated initial hydrogen peroxide concentrations 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 8 ounces of copper per gallon and even substantially higher.

The acid concentration may also vary considerably. In etching 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% by weight, preferably between about 3—20% by weight. Sulfuric acid concentrations about above 23% are less desirable in copper etching as tendency to result in less uniform dissolution. This effect is 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 is of limited interest. When the acidified hydrogen peroxide etchant solution contains only minor amounts of dissolved copper and 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% by weight sulfuric acid). In the etching of metals such as copper the hydrogen peroxide and acid are theoretically assumed to be 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 maintain the etchant solution the enthan 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% by weight sulfuric acid), preferably between about 1.1-2.6 grams per liter (about 5-12% 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% 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% 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 gram 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 $\text{H}_2\text{O}_2/\text{H}^+$ ratio of 1 to 2. Peroxide to hydrogen ion mol ratios 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% 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 1.0:1.6 to 1.0:1.0. 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 1.0:2.0 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%, 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.

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 on copper by 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 must have a temperature of at least about 40° C. at time of contact with the metal. Solution temperature has a strong effect on etch rates and, therefore, to a preferred range between about 50-60° C. will substantially increase the rate of etching to a level significantly greater than heretofore realized with ammonium persulfate etchants recommended optimum temperatures. At hydrogen peroxide solution temperatures above about 65° C. little further increase in etch rate is realized and such temperatures have been found particularly undesirable as resulting in an impractically high rate of peroxide decomposition. As is the case 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 55-65° C. as the solution is further exhausted and the temperature of the etchant solution is aided by the etching reaction itself which is moderately exothermic. 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 such as, 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. The etchants are most conveniently and readily prepared from an aqueous hydrogen peroxide concentrate containing between about 20-70%, preferably between 30-60%, by weight hydrogen peroxide and between about 200-20,000 parts per million, preferably between 500-5,000 parts per million of phenylene, diphenylene, benzoic acid, hydroxy benzoic acid, or mixtures thereof, desirably phenylene. Such concentrates may be prepared by the addition of 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 sulfathiozole. 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 deprecia-
cadium, 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 fluoroboric acid, particularly fluoroboric 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 supplied by General Electric Company under trademark "Textolite" (No. 11571). In the examples the copper laminates were cut into board specimens having dimensions of 9 x 9 x 1/8 inch. Each specimen had 2.7 mil thick copper (2 ounces per square foot) laminated to a plastic base. Each of these specimens was spray etched using a Model 600 Spray Etcher manufactured by the Chemcut Division of Centre Circuits Company (U.S.A.). The reservoir of the spray etcher was charged with about 3 gallons of etchant solution and the spray etcher set to apply about 5 gallons per minute to each specimen. Etch time was determined with a stopwatch and etch rate calculated after weighing each specimen before and after treatment.

Examples 1–8

Employing the spray etching apparatus referred to above, eight different etchant solutions were evaluated by etching a series of the copper-clad specimens with each solution. All solutions tested (Baths A–H) contained 6% by weight hydrogen peroxide and 13.0% by weight sulfuric acid such that the mol ratio of peroxide to acid was about 1 to 0.75. All etchants were prepared with deionized water and contained not more than 1 part per million total free chloride and bromide ions. Baths A and B were evaluated for purposes of comparison. Bath A contained 300 parts per million phenacetin while Bath B contained a combination of 400 parts per million phenacetin and 400 parts per million sulfathiazole. Bath C contained 150 parts per million of phenylurea and Bath D contained both 150 parts per million of phenylurea and sulfathiazole in an amount of 250 parts per million. To Bath E there was added 150 parts per million of phenylurea and about 150 parts per million silver nitrate. Bath F contained 150 parts per million of diphenylurea while Bath G contained 500 parts per million of sodium benzoate. Bath H had incorporated therein a combination of 500 parts per million sodium benzoate and 250 parts per million sulfathiazole. The acid-hydrogen peroxide baths were regulated at a temperature of about 60°C, during etching. Results summarizing Examples 1–8 are given in Table 1.

Table 2 shows that Bath I containing the combination of diphenylurea and sodium sulfathiazole exhibits substantially the same high capacity and fast etch rates as the combination of phenylurea with sulfathiazole as employed in Bath D, as reported in Table 1. The results obtained with Bath J demonstrate that the combination of hydroxybenzoic acid and silver ions results in exceptionally fast rates and high capacity almost equivalent to preferred combination of phenylurea and sulfathiazole in Bath D of Table 1.

Table 1 shows the etch rate and capacity of the acid-hydrogen peroxide baths of the invention to be generally very high and at least approximately equivalent or superior to those of the previously developed additive systems based on phenacetin. Bath C shows that solutions containing only 150 parts per million of phenylurea are clearly superior in both etch rate and capacity to solutions containing 300 parts per million of phenacetin, as employed in Bath A. Bath D shows that the combination of phenylurea and sulfathiazole results in exceptionally fast etch rates and high capacity markedly superior to Baths A and C containing respectively phenacetin and phenylurea, and to Bath B in which there was incorporated a combination of both phenacetin and sulfathiazole. Bath E shows similarly excellent results when combining phenylurea and silver ions. Bath F demonstrates that diphenylurea is substantially as equally as effective phenacetin. Bath G shows that 500 parts per million sodium benzoate (benzoic acid) is highly effective in providing solutions of fast etch rate and high capacity superior to Bath C containing phenylurea alone. Bath H shows further improvement in the benzoic acid system upon combination with sulfathiazole although the resulting bath fall short of achieving of unusually excellent etch rates and capacity exhibited by Bath D containing less total amounts of the preferred combination of phenylurea and sulfathiazole.

Examples 9–10

Two additional etchant solutions were prepared and evaluated in spray etching of copper the same as in the preceding examples. Bath I contained as additives the combination of 100 parts per million diphenylurea and 250 parts per million sodium sulfathiazole. Bath J contained 2,000 parts per million para hydroxy benzoic acid and 200 parts per million silver nitrate. Results are summarized below in Table 2.

Table 2 shows that Bath I containing the combination of diphenylurea and sodium sulfathiazole exhibits substantially the same high capacity and fast etch rates as the combination of phenylurea with sulfathiazole as employed in Bath D, as reported in Table 1. The results obtained with Bath J demonstrate that the combination of hydroxybenzoic acid and silver ions results in exceptionally fast rates and high capacity almost equivalent to preferred combination of phenylurea and sulfathiazole in Bath D of Table 1.

Table 1

<table>
<thead>
<tr>
<th>Concentration—Ounces Copper Dissolves per Ounce of Etchant</th>
<th>Bath A</th>
<th>Bath B</th>
<th>Bath C</th>
<th>Bath D</th>
<th>Bath E</th>
<th>Bath F</th>
<th>Bath G</th>
<th>Bath H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Peroxide: 200 p.p.m. Phenacetin</td>
<td>1.0</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Acid Peroxide: 200 p.p.m. Sulfathiazole, 400 p.p.m. Phenacetin</td>
<td>2.0</td>
<td>2.5</td>
<td>3.5</td>
<td>2.0</td>
<td>3.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Concentration—Ounces Copper Dissolves per Ounce of Etchant</th>
<th>Bath I</th>
<th>Bath J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rate</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>2 ounces</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>4 ounces</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>6 ounces</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>8 ounces</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 1 shows the etch rate and capacity of the acid-hydrogen peroxide baths of the invention to be generally very high and at least approximately equivalent or superior to those of the previously developed additive systems based on phenacetin. Bath C shows that solutions containing only 150 parts per million of phenylurea are clearly superior in both etch rate and capacity to solutions containing 300 parts per million of phenacetin, as employed in Bath A. Bath D shows that the combination of phenylurea and sulfathiazole results in exceptionally fast etch rates and high capacity markedly superior to Baths A and C containing respectively phenacetin and phenylurea, and to Bath B in which there was incorporated a combination of both phenacetin and sulfathiazole. Bath E shows similarly excellent results when combining phenylurea and silver ions. Bath F demonstrates that diphenylurea is substantially as equally as effective phenacetin. Bath G shows that 500 parts per million sodium benzoate (benzoic acid) is highly effective in providing solutions of fast etch rate and high capacity superior to Bath C containing phenylurea alone. Bath H shows further improvement in the benzoic acid system upon combination with sulfathiazole although the resulting bath fall short of achieving of unusually excellent etch rates and capacity exhibited by Bath D containing less total amounts of the preferred combination of phenylurea and sulfathiazole.

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Table 2 shows that Bath I containing the combination of diphenylurea and sodium sulfathiazole exhibits substantially the same high capacity and fast etch rates as the combination of phenylurea with sulfathiazole as employed in Bath D, as reported in Table 1. The results obtained with Bath J demonstrate that the combination of hydroxybenzoic acid and silver ions results in exceptionally fast rates and high capacity almost equivalent to preferred combination of phenylurea and sulfathiazole in Bath D of Table 1.
ing of copper according to the procedures and conditions described in the preceding examples. Results given below in Table 3 are measured in terms of loss or reduction of etch rate of the stored solutions compared with the freshly prepared solution as determined at 6 ounces of dissolved copper.

<table>
<thead>
<tr>
<th>Bath and Additives</th>
<th>Storage Period in weeks</th>
<th>Percent of Maximum Effectiveness After Storage Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath A—Phenacetin</td>
<td>1</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Bath B—Phenacetin</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Bath C—Phenylurea</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Bath D—Phenylurea Sulphate</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Bath F—Diphenylurea</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Bath G—Sodium benzoate</td>
<td>4</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3 shows that Baths A and B containing phenacetin with or without sulfathiazole are less than 90% of maximum effectiveness after 1 week storage while Baths C, D and F containing benzoic acid and the phenylureas with or without sulfathiazole surprisingly retain substantially 100% of maximum effectiveness after storage for as much as 4 weeks time.

Examples 17–19

Three bath-holding tests were made employing Baths B, D and H. In these tests the freshly prepared solutions were employed in spray etching as in the preceding examples up to the point where the baths contained 6 ounces per gallon of dissolved copper. Etching was then stopped and the solutions held in the etcher over various periods of time after which etching was again commenced and loss or reduction of maximum effectiveness after the holding period was determined. In these tests Baths B and H containing phenacetin and benzoic acid, respectively, showed a reduction to less than 90% of maximum effectiveness after 48 hours while the preferred Bath D containing phenylurea showed remarkable superiority with a retention of better than 90% of maximum effectiveness on resumption of etching after a 1 week holding period.

Although certain preferred embodiments of the invention have been disclosed for purpose 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:

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. to about 65° C. with an acidified aqueous hydrogen peroxide solution having incorporated therein about 0.45 to 5.5 grams per liter hydrogen ion and a catalytic amount of an additive selected from the group consisting of phenylurea, diphenylurea, benzoic acid, hydroxy benzoic acid and salts and mixtures thereof, said aqueous solution having a total free chloride and bromide ion content of not more than 2 p.p.m.

2. The method of claim 1 in which the amount of additive incorporated in the solution is between about 100 to 1,000 parts per million.

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

4. The method of claim 1 wherein the additive is phenylurea.

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

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

7. The method of claim 1 wherein the additive is present in an amount between 20 to 5000 p.p.m.

8. A composition for metal dissolution consisting essentially of an acidified aqueous hydrogen peroxide solution having incorporated therein a catalytic amount of an additive selected from the group consisting of phenylurea, diphenylurea, benzoic acid, hydroxy benzoic acid, and salts and mixtures thereof.

9. The composition of claim 8 in which the amount of additive incorporated therein is between about 100 to 1,000 parts per million.

10. The composition of claim 8 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.

11. The composition of claim 8 having incorporated therein between about 50 to 1500 parts per million phenylurea or diphenylurea and between about 20 to 1500 parts per million sulfathiazole or salt thereof.

12. The composition of claim 8 having incorporated therein between about 50 to 1500 parts per million phenylurea or diphenylurea and between about 10 to 1500 parts per million silver ions.

13. The composition according to claim 8 in which the solution has incorporated therein about 2 to 12% by weight hydrogen peroxide and about 0.45 to 5.5 grams per liter hydrogen ion.

14. The composition according to claim 8 in which the solution has incorporated therein between about 2 to 23% by weight sulfuric acid.

15. A composition according to claim 8 in which the total chloride and bromide ion content does not exceed 2 p.p.m.

16. The composition of claim 8 wherein the additive is present in an amount between 20 and 5000 p.p.m.

17. The composition of claim 8 in which the additive is phenylurea.

18. A composition suitable for conversion to an acidified-hydrogen peroxide etchant containing 2–12% by weight hydrogen peroxide and a catalytic amount of an additive selected from the group consisting of phenylurea, diphenylurea, benzoic acid, hydroxy benzoic acid and salts and mixtures thereof, said composition consisting essentially of a concentrated aqueous solution containing 20–70% 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% hydrogen peroxide and between about 500–5000 parts per million phenylurea.

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 5000 p.p.m. silver ions.

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