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SOLUTION AND METHOD FOR DISSOLVING COPPER

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ABSTRACT OF THE DISCLOSURE

Etchant solution for dissolving copper of the "non-metallic" aqueous alkaline ammoniacal chlorite type reinforced by inclusion of ammonium chloride or nitrate in full or partial substitution of ammonium bicarbonate used in a prior system, resulting in substantially improved operating results.

This application is a continuation-in-part of my prior application Ser. No. 620,682, filed Mar. 6, 1967, now abandoned.

This invention is directed to etchant solutions for dissolving copper and to methods of using such solutions; still more particularly it is directed to solutions and methods for dissolving copper coating or cladding from various substrates, both metallic and non-metallic.

The etchant solution here disclosed is of the so-called "non-metallic" type, i.e. one which does not itself contain metal ions (apart from dissolved copper) to effect the etching process. Many etchant solutions contain metal ions, for example iron or chromium ions, which introduce problems of waste disposal in handling the spent solution. Etchant solutions of the "non-metallic" type have been heretofore disclosed and used. In the patent to Eric Laue No. 3,231,503, for example, there is disclosed an ammoniacal chloride solution used in the alkaline range of pH 8–13 for dissolving copper. As that patent points out, such an etchant system possesses advantages of avoiding waste disposal problems attending the use of the chromate or ferric chloride systems commonly used on copper. The patent further recommends inclusion of ammonium bicarbonate specifically in the chlorite system to serve as a buffer in reducing attack on steel substrates coated or clad with copper and mentions that other ammonium salts might be used in place of the bicarbonate.

It has now been discovered that ammoniacal chlorite solutions in the alkaline range containing ammonium chloride or ammonium nitrate in place of all or at least part of the carbonate produce substantial and quite unexpected improvement in copper dissolution capabilities that is unique to the ammonium chloride or nitrate inclusion. The solution is particularly suited to use in preparing printed circuit boards. Such modified solutions possess up to 50% faster etching rate, practical copper dissolution capacities up to 28% greater per gallon of solution, and significantly improved stability or life, especially with pH control, than heretofore possible with the prior patent system. These chloride/nitrate solutions also provide higher solubility limits for the components, permitting use of solutions of higher concentration, resulting in higher dissolution capacity and more economical operation.

While substitution of ammonium chloride or nitrate (or mixtures) for all of the ammonium bicarbonate of the prior etchant system results in maximum etching rates and copper dissolution capacity, such system has two shortcomings for certain applications. The first of these is a tendency to darken solder. Since solder is often present as a resist or for other purpose in composite printed circuit boards to be etched, and since darkening or discoloration of the solder would interfere with subsequent solderability, such a condition is to be avoided if possible where solderability is important. The all-chloride/nitrate substitution for ammonium bicarbonate also has the effect of substantially eliminating the buffering capacity of the system. If the solution is consumed in a day's operation, as is the usual case in industrial circuit board spray etching practice, no problem of pH stability arises; but if the solution is kept over any length of time, lack of buffering in the solution may be a handicap. For either of these reasons therefore it is sometimes advisable to employ a solution in which a part only of the ammonium bicarbonate is replaced by ammonium chloride or nitrate or mixture of these. Accordingly the present invention further contemplates such partial substitution of the bicarbonate.

Each of the bicarbonate-chloride-nitrate systems of the invention herein disclosed permits operation to extend its useful life upon exhaustion of the primary oxidant, i.e. the chlorite, first by increasing the 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. And secondly, prolongation of the useful life of the system can be effected by aeration at the elevated temperature just prior to or during the terminal portion of the etchant bath life. Oxygen in the air of course serves as the oxidant under this condition of operation. No advantage accrues from aeration prior to exhaustion of the primary (chlorite) oxidant, and preferably aeration is withheld until substantial depletion occurs of the secondary (cupric copper) oxidant. This condition is indicated by a reduction in the etch rate obtained and serves as a guide in determining when to employ aeration.

The three stages of copper etching reaction involved in the foregoing are represented by the following expressions:

$$(a)\quad 2Cu+NaClO_2+2NH_4Cl+4NH_4OH \rightarrow 2Cu(NH_3)_4Cl_2+NaCl+6H_2O$$

$$(b)\quad Cu+Cu(NH_3)_4Cl_2 \rightarrow 2Cu(NH_3)_2Cl$$

$$(c)\quad 2Cu(NH_3)_2Cl+2O_2+2NH_4Cl+2NH_4OH \rightarrow 2Cu(NH_3)_4Cl_2+3H_2O$$

The divalent copper in the complex formed according to Equation (*a*) is thus available for further oxidation of metallic copper according to Equation (*b*) to form the monovalent (cuprous) complex which latter is then oxidized according to (*c*) by aeration. Obviously the same conditions hold whether ammonium nitrate is employed in place of or in conjunction with the chloride and/or the bicarbonate. Conversion of most if not all of the copper to the cupric state, plus increasing concentration of copper in solution to a point where reaction (etching) rates are too slow to be commercially practical, dictate the point at which the solution must be replaced.

The improvement over the prior system of Patent No. 3,231,503 is best illustrated by a comparison of

results obtained using that system and those of the present invention, as set out in Table I below.

TABLE I

No.	$NaClO_2$, mol/l.	NH_4OH, mol/l.	NH_4HCO_3, mol/l.	NH_4Cl, NH_4NO_3 or mixture, mol/l.	Temp., °C.	Cu etch rate, in./min.	Cu capacity before dumping, oz./gal.	Percent theoretical capacity
1	0.375	3.0	1.5	0	25	0.00013	10.9	85.8
2	0.375	3.0	0.75	1.0	25	0.00018	12.5	98.4
3	0.375	3.0	0	1.5	25	0.00021	12.5	98.4
4	0.375	3.0	1.5	0	40	0.00026	10.9	85.8
5	0.375	3.0	0.75	1.0	40	0.00036	12.5	98.4
6	0.375	3.0	0	1.5	40	0.00039	12.5	98.4
7	0.375	3.0	1.5	0	55	0.00032	10.9	85.8
8	0.375	3.0	0.75	1.0	55	0.00043	12.5	98.4
9	0.375	3.0	0	1.5	55	0.00046	12.5	98.4

The figures given in Table I are without aeration, the effect of which will be described presently.

Examples 1, 4 and 7 in the foregoing table represent the experience of the known system of Patent No. 3,231,-503 referred to above. The remaining examples in the table illustrate the significantly improved etching rate and total copper capacity of systems of the present invention.

In using the solutions of the invention, the copper clad printed circuit boards or other substrates are contracted with the etchant solution, by immersion in a tank or bath or by spriying onto the surface of the substrates. Initially the solution is maintained at room temperature, but as the amount of dissolved copper in solution increases, the etching rate will decrease and it is desirable accordingly to compensate by progressively increasing the temperature of the solution. As a general rule it is recommended that the temperature be elevated whenever the time required to remove all the copper from a standard 2 ounce copper clad panel approaches 30 minutes. Temperature increases can be made up to a maximum of about 55° C. Because of the high loss rate of ammonia from the system at temperatures above this, this is considered a practical upper limit.

In order to maintain an effective rate of etching it is also desirable periodically to add ammonium hydroxide so that the solution pH does not drop substantially below 9.0, and preferably not below 9.8.

When the amount of copper in solution exceeds about 11 ounces per gallon, it is generally advisable to dump the solution and start over, although with aeration this limit can be increased to about 14 oz./gal. as explained later. The dissolved copper in the spent solution is readily precipitated by reducing the solution to substantially neutral condition, either by addition of excess water or by addition of dilute sulfuric to a pH of about 6.0. Upon standing, the copper hydroxide will settle out of solution and the recovery is generally at least 99%. The supernatant solution may be readily decanted and discharged without danger of pollution, the copper values remaining as a sludge in the settling tank which may be recovered and processed for recovery of the metal.

The system is exceedingly stable, particularly when good pH control is maintained at or above about 9.0, so that no precipitation or settling occurs in the etching tanks. This is true, even though the solution may stand for some time between operating periods, particularly if the temperature of the solution, if initially above around 35° C., is promptly cooled below that point when the period of nonuse exceeds about 3 hours.

The solution is not critical as to oxidant concentration since as little as 0.1 mol per liter of sodium chlorite will provide some stripping action, although obviously the rate is low. At the other extreme, the concentration may be anything up to the saturation limit of the chlorite in the solution. It is preferred to operate at a concentration range of about 0.375 mol per liter. The ammonium ion concentration should always exceed that of the copper

dissolved in the solution and generally the preference is for an excess over the copper in a mol ratio of at least 2:1. This is supplied, of course, by the ammonium hydroxide as well as ammonium chloride, nitrate, and bicarbonate used. Since the amount of ammonium hydroxide required is determined largely by the requirement for maintaining a solution pH of at least 9.0, it is generally recommended to employ about 3 mols per liter of the base. The ammonium chloride, nitrate, bicarbonate concentration in such system should be at least 0.2 mol per liter and is preferably 2.0 mol per liter for achieving maximum etch rate and copper capacity. A practical upper limit for the ammonium chloride, or nitrate, and bicarbonate if present, is generally about 4.0 mol per liter. Ammonium chloride is preferred over the nitrate simply because of the hazzard involved in storing dry ammonium nitrate. The effectiveness of the nitrate in the etchant solution, however, is fully as good as that of the chloride, and the storage problem with the nitrate can be mitigated of course by using a concentrated solution rather than the dry salt.

When the solution has been at least partially exhausted, i.e. to the point where the primary oxidant is consumed and the dissolved copper concentration is in excess of about 6 ozs. per gallon, continued operation is greatly improved by introducing air agitation while maintaining the temperature at 55° C. This is illustrated in Table II below using a solution having the composition of Example No. 8 in Table I.

TABLE II

Ounces of Cu/gal. in solution	Etch rate before aeration, inches per minute	Etch rate after aeration, inches per minute
6	0.00015	0.00017
8	0.00011	0.00021
10	0.00008	0.00015

Although the etch rate at 6 ozs./gal. in the above table shows some improvement with aeration, the difference here is believed to be due primarily to experimental error as the rates should theoretically be identical since all of the copper would probably be in divalent form at this level of concentration. At the two higher levels of exhaustion that condition no longer obtains and it will be noted that the etch rate is nearly doubled.

The copper dissolution capacity of solutions under aerating conditions as described above is no longer limited by the initial chlorite concentration since a further oxidant, namely the air, has been introduced. Under such condition, the ammonia content will be controlling and in the examples given above, the theoretical capacity of the solutions will be about 19 ozs./gal. However, solubility problems will limit the practical capacity in normal operations to about 14 ozs./gal. Although the increase in capacity thus effected is not too great, the increased etchant speeds effected is of real importance, more especially in automated processing operations.

What is claimed is:

1. A copper etchant solution consisting essentially of water, sodium chlorite, ammonium hydroxide and an ammonium salt selected from the group consisting of

ammonium chloride, ammonium nitrate, ammonium bicarbonate and mixture thereof wherein at least one of said nitrate and chloride salts is always present, and wherein the chlorite concentration is from about 0.1 mol per liter to saturation, the ammonium salt concentration is from about 0.2 molar to saturation, and ammonium hydroxide is present in amount to produce a minimum pH of about 9.0 in the solution.

2. A copper etchant solution as defined in claim 1, wherein the sodium chlorite is 0.375 molar, the ammonium salt is 1.5 molar in a member selected from the group consisting of ammonium chloride, ammoniu nitrate and mixtures thereof, and the ammonium hydroxide is 3.0 molar.

3. A copper etchant solution as defined in claim 1, wherein the sodium chlorite is 0.375 molar, the ammonium salt is 0.75 molar ammonium bicarbonate and 1.0 molar in a member selected from the group consisting of ammonium chloride, ammonium nitrate and mixtures thereof.

4. A process of dissolving copper from a copper substrate, which comprises:

(a) providing an etchant solution of the composition defined in claim 1, said solution being initially at approximately room temperature;

(b) contacting the copper bearing substrate to be etched with said etchant solution for a period sufficient to dissolve the desired amount of copper therefrom;

(c) progressively increasing the solution temperature to not over 55° C. as the amount of dissolved copper in the etchant solution increases and the etching rate thereof decreases;

(d) periodically adding ammonium hydroxide to the solution to maintain the pH at not lower than about 9.0.

5. A process of dissolving copper as defined in claim 4, which further includes the step of aerating the solution after the dissolved copper content exceeds about 6 ozs./gal.

References Cited

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