

March 26, 1963

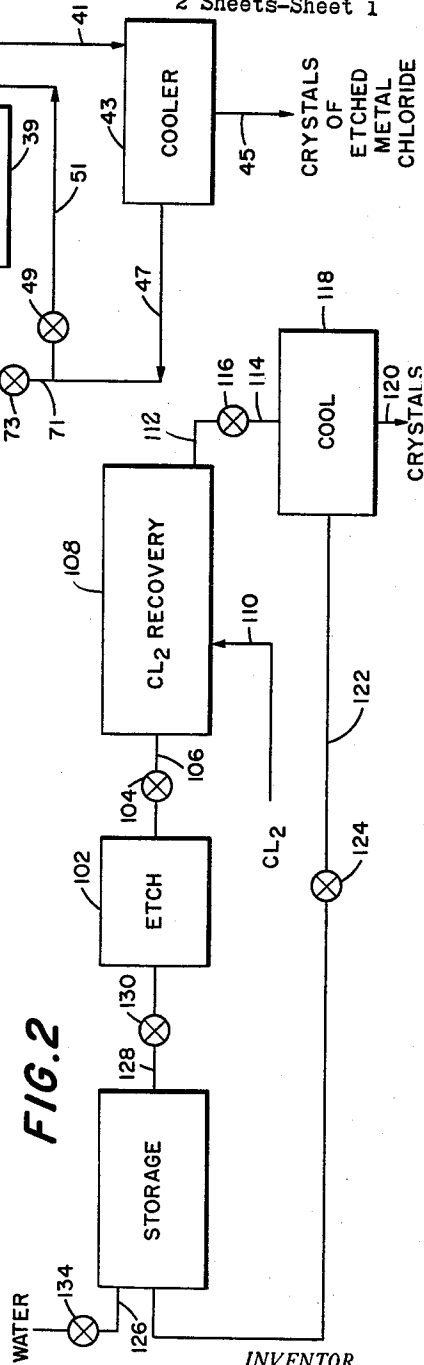
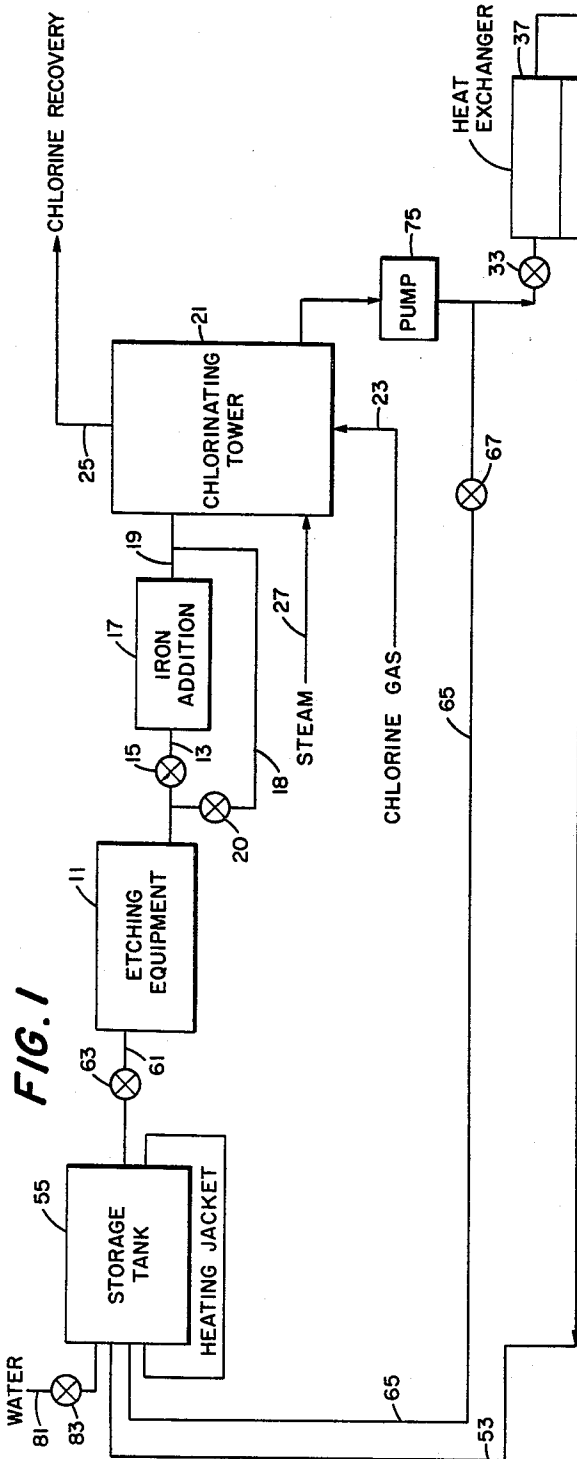
A. JONES ET AL

3,083,129

METHOD OF ETCHING COPPER WITH REJUVENATION AND RECYCLING

Filed Oct. 1, 1958

2 Sheets-Sheet 1



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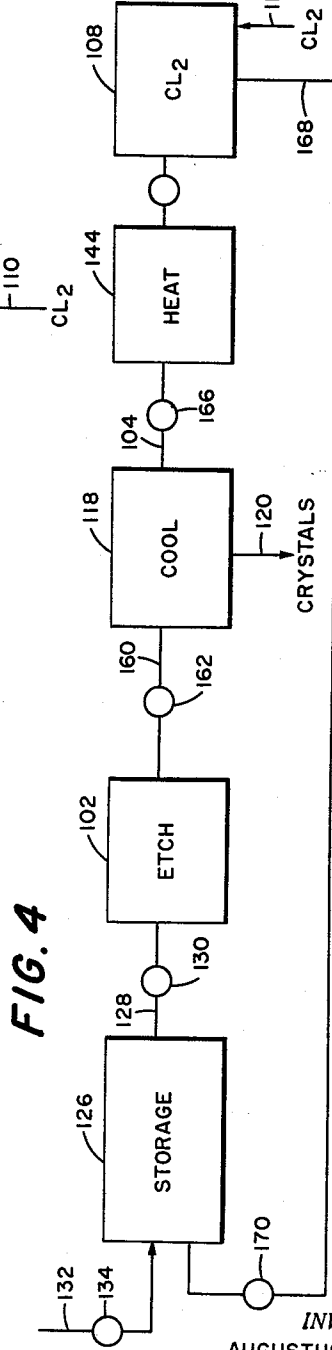
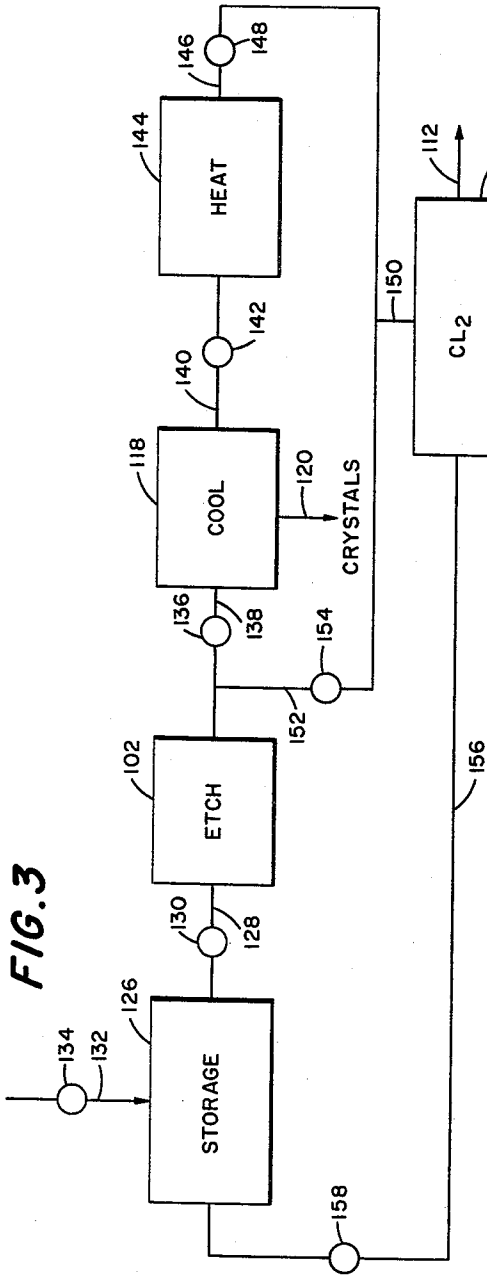
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METHOD OF ETCHING COPPER WITH REJUVENATION AND RECYCLING

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9 Claims. (Cl. 156-19)

The present invention relates to etching baths, and more particularly to a process for regenerating an etching bath in a manner to retain its activity.

The present application is a continuation-in-part of application Serial No. 589,532, filed June 5, 1956, now Patent 2,886,420, issued May 12, 1959, the entire disclosure of which is hereby incorporated by reference. In our parent application there is described a process of etching a metal, more particularly copper, with a ferric chloride bath in which process the ferric chloride is reduced to ferrous chloride and the spent mixture is rejuvenated by converting the ferrous chloride to ferric chloride with the aid of chlorine, a substantial proportion of the copper chloride is removed and thereafter the rejuvenated mixture is returned to the etching bath.

Surprisingly, it has been found that the rejuvenated bath is a better etchant than the fresh ferric chloride etching solution. Apparently, the cause of the improved etching properties is due to the presence of cupric chloride formed as the result of the etching and chlorination process. While a portion of the cupric chloride is removed by precipitation, the remainder passes into the etching bath in an amount up to the solubility of cupric chloride in the aqueous mixture at the precipitation temperature.

It is an object of the present invention to provide a generally improved and more satisfactory etching bath process.

Another object is to provide an improved and more satisfactory etching bath process for etching copper.

A more specific object is to provide an improved and more satisfactory cupric chloride etching bath for etching copper.

A further object is to provide a simple and inexpensive process for maintaining the activity of a bath for etching copper.

An additional object is the provision of a process for the recovery of cuprous chloride as a valuable by-product produced in the etching of copper by cupric chloride.

Yet another object is to recover cupric chloride formed as a valuable by-product produced in the etching of copper by cupric chloride followed by subsequent chlorination.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained in a preferred aspect of the invention by etching copper with cupric chloride at a relatively high temperature and

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then either (1) chlorinating to oxidize the cuprous chloride formed to cupric chloride and then cooling to crystallize out cupric chloride, heating and returning the solution now only partially saturated with cupric chloride to the etching bath, or (2) dividing the spent etching solution into two portions, cooling one portion to crystallize out cuprous chloride, heating the solution remaining after crystallization and combining it with the other portion from which no cuprous chloride has been removed, and then chlorinating the combined solution to restore it to its original composition with respect to cupric and cuprous copper and returning this solution to the etching bath, or (3) cooling the spent etching bath to crystallize out cuprous chloride in an amount equivalent to the amount of copper dissolved, heating this solution from which the cuprous chloride has been crystallized, and then chlorinating this solution to restore it to its original composition with respect to cupric and cuprous copper and returning this solution to the etching bath, or (4) removing etching bath when the amount of cuprous chloride formed is twice the amount which will crystallize out at the temperature to which the used etching solution will be cooled, cooling the used etching to crystallize out an amount of cuprous chloride equivalent to the amount of copper dissolved, chlorinating to completion the solution remaining and returning this solution to the etching bath.

It will be observed that by procedure (1) cupric chloride is recovered as the by-product, while by procedures (2), (3) and (4) cuprous chloride is recovered. Both cuprous and cupric chloride are valuable chemicals and can be sold as such to reduce the overall cost of the etching process. Since no additives are employed, there are no impurities to contaminate the copper chloride by-product.

While the above general description refers to the use of cupric chloride solution as the etchant, there can be used in place thereof cupric bromide. In the latter case, the by-products recovered in the process will be cupric bromide or cuprous bromide.

The etching of copper by cupric chloride or cupric bromide goes somewhat slowly. The reaction speed can be increased by adding a water-soluble chloride or bromide as an accelerant. Among such accelerants, there may be mentioned hydrochloric acid, hydrobromic acid, sodium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride, ammonium bromide, calcium chloride, calcium bromide, barium chloride, barium bromide, aluminum chloride, aluminum bromide, zinc chloride, zinc bromide, titanium tetrachloride, titanium tetrabromide, magnesium chloride and magnesium bromide. The accelerant can be used in any amount up to its solubility limit.

Ferric chloride (or ferric bromide) can also be employed as an accelerant. It has the advantage of being one of the most effective accelerants. However, when ferric chloride or ferric bromide is employed, some iron impurities occur in the cuprous or cupric chloride or bromide and, hence, it is frequently preferred to utilize other accelerants which do not add the difficulty of removing impurities. Ferrous chloride can be utilized as an initial accelerant, although in the chlorination stage it will be converted to ferric chloride and, hence, on recycling the end result will be that ferric chloride is the primary accelerant.

A solution containing cupric chloride, preferably with an accelerant, will etch not only copper but also iron, tin, nickel, cobalt, cadmium, zinc, aluminum, magnesium and their alloys, e.g., stainless steel.

It has been observed that not only is titanium tetrachloride an accelerant for cupric chloride in etching copper, but that it can etch copper at a fast rate by itself even when cupric chloride is omitted.

Unless otherwise stated, all parts and percentages are by weight.

When utilizing ferric chloride, titanium tetrachloride or other materials which not only accelerate the action of cupric chloride as an etchant of copper but also act as etchants in their own right, it sometimes is more convenient to merely add the ferric chloride or titanium chloride to water to form the initial etching solution and allow the etching solution to build up gradually to the saturation point of cupric chloride at the temperature at which it is separated out in the cooling step.

In general, the higher the temperature, the higher the rate of etching. Therefore, the temperature of the etching bath is desirably the highest which can be used without damage to the work being processed or to the equipment. When etching a metal laminate on a phenol-formaldehyde base the limiting factor with respect to the temperature is usually the danger of injury to the phenol-formaldehyde sheet or to the bond between the metal and the phenol-formaldehyde sheet. Therefore, the working temperature is kept at about 120° F. when etching a

the bath eats away those portions of the copper which are not covered by the resist layer, leaving intact those portions which are covered by the resist layer.

The cooling in order to precipitate out cuprous or cupric chloride or bromide can be done at any temperature below the temperature of the etching bath. Generally, the greater the difference in temperature between the etching bath and the crystallization chamber, the more copper chloride will be removed by the crystallization. Also, the greater the temperature difference, the greater the etching rate at a given etching bath temperature because the etching bath contains less of the products of the etching reaction. Temperatures from just above the freezing point of the solution to 80° F. have proven very satisfactory when an etching bath temperature of 120° F. is employed.

The chlorinating or brominating tower is operated by allowing the cuprous chloride or bromide solution to enter the tower near the top and fall by gravity flow to the bottom of the tower. The chlorine or bromine enters the tower at the bottom and passes by countercurrent flow to the top.

The process of the invention can be carried out either continuously or semi-continuously. In the latter case, while the etching procedure is continuous, the crystallization and/or the chlorination need only be done intermittently.

The rate of attack of various aqueous solutions on metallic copper are set forth in Table I.

TABLE I

Solution	Grams per mil								Mils of Copper etched in 10 minutes	
	FeCl ₃	CuCl ₂	Cu ₂ Cl ₂	NaCl	TiCl ₄	FeCl ₂	CuBr ₂	NaBr	at 79° F.	at 120° F.
1	0.529	¹ 0.145							0.34	0.67
2	0.485	¹ 0.187							0.35	0.67
3	0.436	¹ 0.203							0.40	0.68
4	0.384	¹ 0.272							0.39	0.60
5	0.351	¹ 0.304							0.37	0.64
6	0.302	¹ 0.321							0.33	0.65
7		0.269		¹ 0.234					0.44	0.78
8		¹ 0.56		¹ 0.234					0.21	0.44
9	0.212	0.089							0.49	
10		0.27								0.20
11		0.27				0.25				0.31
12						0.25				0.02
13	0.20	0.27								0.70
14	0.213	¹ 0.44							0.32	0.53
15					0.47					0.70
16					0.38					0.61
17					0.28					0.24
18					0.19					0.05
19		¹ 0.19			0.46					0.62
20		0.39								0.25
21				¹ 0.234	0.33					0.53
22							0.45	0.41		0.75
23		0.54	0.029	¹ 0.234						0.49

¹ Solubility limit or saturation amount at 79° F.

metal laminate on such a phenolic sheet. If a base sheet and bond of greater resistance to heat are used, the working temperature can be raised to a value not exceeding the safe temperature for such materials. When etching an article made entirely of copper or a copper alloy, no part of which is damaged by a higher working temperature, the temperature can be raised substantially to the boiling point of the etching solution if the equipment such as tanks, pipes, valves, etc. is made of material designed to stand this temperature. A temperature as low as room temperature or even lower can be used so long as the low rate of etching associated with such low temperatures is acceptable. In the specific examples the etching was carried out on copper laminate plates of the kind known in the electronics industry as "printed circuit" plates. These are thin sheets of copper laminated to a base sheet of electric insulating material, e.g., phenol-formaldehyde sheet in the specific examples, certain portions of the copper being covered, before the etching process begins, by a "resist" layer of known form. When the copper laminate sheet is immersed in the etching bath,

In the drawings:

FIGURE 1 is a flow sheet of a ferric chloride etching process;

FIGURE 2 is a flow sheet of a cupric chloride etching process wherein cupric chloride is also recovered as a by-product;

FIGURE 3 is a flow sheet of a cupric chloride etching process wherein cuprous chloride is recovered as a by-product; and

FIGURE 4 is a flow sheet of an alternative cupric chloride etching process wherein cuprous chloride is recovered as a by-product.

Example 1

An aqueous mixture containing 560 grams of cupric chloride and 230 grams of sodium chloride per liter formed the initial bath in etching tank 102 at a temperature of 120° F. When the etching had proceeded to the extent that 29 grams per liter of cuprous chloride was formed, valve 104 was opened and the partially spent etching bath drawn off through conduit 105 to the top

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of chlorinating tower 108. The tower was filled with ceramic packing and the solution trickled to the bottom of the tower, while in contact with an upward or counter-flow of chlorine gas introduced at the bottom of the tower at 110. The flow of chlorine gas is sufficient to convert all of the cuprous chloride to cupric chloride. Chlorine gas reaching the top of the tower is drawn off at 112 to the chlorine recovery apparatus for reuse. The concentrated solution of cupric chloride (also containing sodium chloride) is withdrawn from the bottom of the tower by conduit 114 via control valve 116 to crystallizer 118. Crystallizer 118 is maintained at 80° F. Cupric chloride crystallizes out as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and is removed at 120. An analysis of the crystals showed no cuprous chloride was present as an impurity. The solution, now saturated with cupric chloride and also containing sodium chloride, passes via line 122 and valve 124 to storage tank 126 where it is reheated to 120° F. The solution then is led via conduit 128 and valve 130 back to etching tank 102. Make-up water can be added to storage tank 126 as needed via line 132 and valve 134. Make-up sodium chloride solution can also be added through line 132 to replace that lost with the wet cupric chloride crystals. The cupric chloride crystals can be washed with distilled water to remove the cupric chloride and sodium chloride containing solution which clings to the crystals.

To avoid precipitation of sodium chloride with the cupric chloride, it is advantageous to utilize slightly less sodium chloride than that which will saturate the cooled solution in crystallizer 118. This minimizes the chance of introducing sodium chloride as an impurity in the cupric chloride crystals.

By cooling to a temperature below 80° F. the amount of crystallized cupric chloride recovered will be increased, and the amount of cupric chloride returned to the etching bath will be decreased. This is advantageous since, as shown in Table I, the etching process is more efficient utilizing 269 grams per liter of cupric chloride with a saturated sodium chloride solution rather than utilizing a solution saturated with both cupric chloride and sodium chloride. However, for convenience, cooling is normally done with water from the main and, hence, the temperature of cooling will usually be that of the outside water supply.

Example 2

Example 1 was repeated but instead of utilizing 560 grams of cupric chloride and 230 grams of sodium chloride per liter in the starting etching composition, there were employed 100 grams of cupric chloride and 220 grams of sodium chloride. During the etching and regeneration process the cupric chloride content gradually built up to the solubility limit at 80° F., after which cupric chloride crystallized out in crystallizer 118. The sodium chloride content remained at 220 grams per liter which is below the solubility limit for sodium chloride at 80° F. in the solution.

The process can also be carried out as described in Examples 1 and 2 by replacing the starting etching mixture of the examples with any one of solutions 1-6, 9-11, 13, 14, 19 or 20 of Table I, and the cupric chloride above its solubility in the solution at 80° F. recovered from crystallizer 118.

Example 3

The process of Example 1 was repeated but the starting etching solution was solution 15 of Table I. The cupric chloride content of the solution gradually built up upon recycling and eventually the solution became saturated at 80° F. and cupric chloride crystallized out in crystallizer 118.

The same results were obtained when solutions 16, 17 and 21 of Table I were utilized in place of solution 15 in this example.

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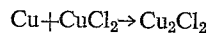
Example 4

Example 1 was repeated utilizing as the starting etching solution an aqueous mixture containing 450 grams per liter of cupric bromide and 410 grams per liter of sodium bromide. In place of chlorine in tower 108 there was introduced bromine. Also, the tower was heated to 140° F. so that the bromine was in the gaseous state. Cupric bromide crystals were recovered from crystallizer 118 at 80° F. A mixture of cupric bromide and cupric chloride would be obtained in the crystallizer if sodium chloride were employed rather than sodium bromide.

Example 5

Example 1 was repeated but the temperature in crystallizer 118 was maintained at 50° F.

The following examples are directed to processes wherein instead of recovering cupric chloride by crystallization, there is recovered cuprous chloride. The etching solution dissolves cuprous chloride formed by the reaction of copper and cupric chloride according to the equation:



The recovery depends on the difference in solubility of cuprous chloride at the elevated temperature used in dissolving copper and at the lower temperature to which the solution is cooled before regenerating it by chlorination. This procedure is applicable, of course, to the formation of cuprous bromide. This method also is operative if other chlorides, such as ferric chloride, titanium chloride, sodium chloride, calcium chloride or aluminum chloride, for example, are present in the etching solution in addition to the cupric chloride. The etching solution is used to dissolve copper at an elevated temperature until it contains more cuprous copper in solution at this elevated temperature than is soluble at the lower temperature to which it is cooled. Cooling the solution to the lower temperature causes cuprous chloride to crystallize out. Then the solution is regenerated with chlorine.

Since the copper is recovered in this method as Cu_2Cl_2 rather than as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, the copper removed from the solution as Cu_2Cl_2 can be twice as much as is dissolved. Unless the proper procedures, as outlined hereinafter, are followed, the etching solution will be depleted with respect to copper to a greater extent than desired.

While the cupric chloride content of the etching bath can be any amount up to saturation when the copper is recovered as cuprous chloride, preferably it is that which gives the best etching rate. Thus, when utilizing a mixture of cupric chloride and sodium chloride in the etching bath, there is preferably employed 269 grams per liter of cupric chloride with the solution being slightly less than saturated with sodium chloride, e.g., 220 grams per liter of sodium chloride.

Example 6

An etching bath containing 269 grams per liter of cupric chloride and 220 grams per liter of sodium chloride was placed in tank 102 of FIGURE 3 of the drawing. A printed copper circuit was etched in the tank at 120° F. As a result, the amount of cuprous copper increased by twice the amount of copper dissolved. Reaction was continued until the solution was saturated with cuprous chloride, and at the elevated temperature the solution was then divided into two equal parts. One part flowed via valve 136 and conduit 138 to cooler 118 maintained at room temperature (70° F.). Cuprous chloride crystallized out and was separated from the solution at 120. The solution from which the cuprous chloride had crystallized was led via conduit 140 and valve 142 to heater 144 where it was heated to 120° F. The solution then passed via conduit 146 and valve 148 to line 150 where it joined the other equal part of the solution which had bypassed crystallizer 118 via conduit 152 and valve 154. The combined solutions then went to chlorinator 108

where the chlorination was controlled to reduce the cuprous chloride content of the solution to just that amount which was soluble in the solution at 70° F. The solution then passed via line 156 and valve 158 to storage tank 126 and thence back to etching tank 102.

While equal parts of the solution were sent to the crystallizer 118 and the by-pass line 152, it is possible to send more than half of the solution to the crystallizing tank providing that there is enough cuprous chloride retained in the solution going to line 152 together with the unprecipitated cuprous chloride emerging through line 140 to restore the cupric chloride to its initial concentration. Likewise, the amount of solution sent to the crystallizing tank can be less than half the amount of total solution providing the chlorination is sufficient to insure no precipitation of cuprous chloride when the combined solution is returned at 120° F. to the etching tank. In this latter alternative, however, sufficient solution must go to crystallizer 118 to insure that the amount of cupric chloride leaving chlorinator 108 is not so great that after the etching in tank 102 sufficient cupric chloride will remain to crystallize out at 70° F. in crystallizer 118. While chlorination was carried out at 120° F. in the example, it can be done at higher or lower temperatures. In general, the higher the temperature, the more rapid the chlorination. However, it is more difficult to control the reaction with increase in temperature.

Example 7

An etching bath containing 269 grams per liter of cupric chloride and 220 grams per liter of sodium chloride was placed in tank 102 of FIGURE 4 of the drawings. A printed copper circuit was etched in the tank at 120° F. As a result, the amount of cuprous copper was increased by twice the amount which was dissolved. The reaction was continued until the solution contained 40 grams per liter of cuprous chloride. The solution was then passed via line 160 and valve 162 to crystallizing tank 118 where the solution was cooled to a temperature at which the amount of cuprous chloride precipitated contained the same amount of copper as the amount of copper dissolved in the etching bath. The solution from which the cuprous chloride had crystallized was passed via line 164 and valve 166 to heater 144 where it was heated to 120° F. The hot solution then passed to chlorinator 108. Excess chlorine was passed in counter-current flow to the solution to insure complete oxidation of the cuprous chloride in solution. The solution thus having its cupric chloride content restored to its original value was returned via conduit 168 and valve 170 to storage tank 126 and eventually to etching tank 102.

The procedure of this example can also be carried out in a manner which does not require as careful a temperature control on the chlorination step. Thus, instead of cooling to the temperature where exactly half the cuprous chloride will precipitate from the spent etching bath, the cooling can be to a lesser extent. In such event, rather than using excess chlorine, the amount of chlorine added is restricted so that only that amount of cuprous chloride remaining in solution which corresponds to the cupric chloride which had been reduced in the etching process is reoxidized. Then the rejuvenated solution which also contains the balance of the cuprous chloride in solution is returned to the etching bath.

In the event that it is desired to vary the amount of cupric chloride in the etching bath, this can be done either by varying the amount of controlled partial chlorination or by varying the temperature in the crystallizer. In general, the lower the temperature in the crystallizer, the smaller will be the copper concentration when the rejuvenated solution is returned to the etching bath.

The chlorination can be controlled either manually or automatically. Thus, the potential of the cell, Pt/Etching Solution//Reference Half Cell, can be used to in-

dicating and to control the etching process and, in turn, the chlorination.

As described in parent application Serial No. 589,532, the ferric chloride etching procedure is applicable to etching many metals, e.g., lead, tin, nickel, iron, cobalt, chromium, zinc, aluminum, magnesium, cadmium, etc. or alloys of such metals. While copper is referred to in the subsequent description, any other metal capable of being etched by ferric chloride can be utilized.

Referring now to FIGURE 1 of the drawing, the etching equipment 11 is of conventional kind, usually embodying a tank for containing the etching bath of ferric chloride, provided with suitable racks or hangers for supporting the work to be etched. The work may be bathed with ferric chloride either by immersing the work in the solution or by spraying with the solution. Since this etching bath is highly corrosive to iron and various other metals, the tank or container 11 has a lining of glass or ceramic material or hard rubber or other suitable lining material which resists the corrosive action of the etching bath. The same is true of all of the other containers, conduits, valves, pumps, and other pieces of equipment which come into contact with the etching solution.

According to the present invention, when etching metallic articles in a bath of ferric chloride, the bath in the tank 11 is initially composed essentially of ferric chloride having, at the start, a specific gravity in the neighborhood of 42° Baumé, corresponding to 39 percent ferric chloride, when the articles being etched are composed of copper or of nickel or cobalt or other metals which are attacked by the ferric chloride at about the same rate as copper, or having a somewhat lower specific gravity when the articles are of metal attacked more rapidly by ferric chloride, such as aluminum or magnesium. Such etching is continued, by successive removal of finished work and insertion of fresh work to be etched. As etching continues, there is a drop in the concentration of the ferric chloride etching solution, this drop in concentration being caused by the reaction of the bath with the metal being etched, which converts part of the ferric chloride into ferrous chloride, accompanied by the formation of a chloride of the metal being etched (e.g., copper chloride when copper is being etched).

According to the present invention, the bath is preferably not discarded in toto, but rather is treated (preferably in a continuous manner) both to regenerate the bath and to recover the chlorides of the etched metal, which constitute valuable and saleable by-products. To accomplish this, the present invention provides a flow (preferably continuous, but it may be intermittent if desired) of active etching solution into the container 11 and of partially spent solution out of the container. The entering bath is of ferric chloride (carrying in solution a minor amount of chlorides of the metal being etched, after the process has been in operation for some time, as explained below) at a specific gravity of about 42° Baumé or close to it for example when etching copper or other metals having similar etching characteristics, but lower when etching aluminum, magnesium or other fast-reacting metals, and at a working temperature as high as can safely be used without damage to the work being processed or to the equipment.

In the etching bath, ferric chloride is converted to ferrous chloride and (when copper is the metal being etched) copper chloride is formed from the copper eaten away. But the concentration of the bath is not allowed to go lower than about 24% ferric chloride. The partially spent etching bath is drawn off through a conduit 13 and metering valve 15, to iron addition apparatus 17 comprising, for example, a liquid container having a few iron plates immersed therein so that the bath may react with the iron plates to pick up enough iron to compensate for the iron dragged out of the etching bath by loss of that part of the bath which clings to the work when the finished etched work is withdrawn from the container 11.

A by-pass 18, valved at 20, extends around the iron addition apparatus.

From the iron addition apparatus 17, the liquid passes through a conduit 19 to the top of a chlorinating tower 21, while in contact with an upward or counter-flow of chlorine gas introduced at the bottom of the tower at 23, which gas reacts with the ferrous chloride in the descending liquid and converts at least a major part of it and preferably all of it to ferric chloride. Any chlorine gas reaching the top of the tower is drawn off at 25 to chlorine recovery apparatus for reuse.

The liquid reaching the bottom of the tower consists essentially of a mixture of chloride of the metal being etched and ferric chloride, with possibly a small amount of unregenerated ferrous chloride, but in relatively minor quantity, if any. The rate of outflow of the liquid from the etching bath 11 is so regulated with respect to the amount of work being etched in the bath, that this liquid withdrawn from the bath and reaching the tower will contain chloride of the metal being etched in a concentration close to but slightly below its saturation point in a solution of ferric-ferrous chloride, at the particular working temperature of the bath. The reaction in the tower produces heat, thus raising the temperature of the liquid in the tower somewhat, so that there is no danger of premature crystallization in the reaction tower of the chloride of the metal being etched. Moreover, steam is preferably added to the tower at 27 to raise the temperature of the regenerated solution to 212° F., to free the solution of chlorine gas.

This liquid at the bottom of the tower, consisting essentially of ferric chloride carrying in solution a high concentration (but less than saturation) of chloride of the metal being etched, and possibly minor quantities of ferrous chloride, is withdrawn from the bottom of the tower through a conduit 31 valved at 33, to a heat interchanger 35, and passes through the cooling portion 37 thereof which is in heat exchanging relation with a heating portion 39. After being partially cooled in the heat interchanger, the liquid passes through a conduit 41 to a cooler 43 where it is cooled to an extent sufficient to crystallize out in the form of a crude or unrefined form of such chloride. The exact temperature to which the liquid is cooled in the cooler 43 is not critical, so long as it is low enough to crystallize out most of the metallic chloride (other than the more soluble ferric-ferrous chloride) and the exact temperature will depend on the available supply of cooling water flowing through a cooling coil or other suitable cooling means associated with the cooler 43. In most localities, cooling water is available at temperatures not above about 65° F., and cooling is usually carried to about this temperature.

The crystals of metallic chloride are removed from the cooler 43 at 45 and are further treated in any suitable manner. For example, they may be dried in a centrifuge dryer, washed with water, dried again, and packaged for sale. The liquid from the cooler 43, after separation of the etched metal chloride crystals therefrom, is drawn off through the conduit 47, and now consists of a relatively cold liquid solution of ferric chloride, with a minor amount of etched metal chloride in solution therein and possibly a small amount of ferrous chloride. The etched metal chloride will be in saturated solution, but its quantity will be relatively small because of the low temperature of the solution. This cold solution is passed through the control valve 49 and conduit 51 to the heating portion 39 of the heat interchanger 35, to be partially warmed by heat extracted during the passage of the warm solution through the cooling portion 37.

After this partial heating in the interchanger 35, the liquid flows through the conduit 53 to a storage tank 55 in which it is heated by any suitable means such as the heating jacket 57, back to the desired working temperature of the etching bath, which, as above explained, is governed by the ability of the equipment and the work

being etched to withstand high temperatures, and which may ordinarily be in the neighborhood of 120° F., when etching laminated printed circuit plates, for example. The heating of the liquid raised the solubility of the contained etched metal chloride, so that the latter is now way below the saturation point. From this storage tank containing the now regenerated bath at the proper temperature, the liquid is fed through the conduit 61 and regulating valve 63 into the etching container 11, where it again comes into contact with the work to be etched. This cycle is repeated indefinitely.

The description thus far has proceeded on the assumption that the etching process had been operating for some time before any regeneration or crystallization, so that the etching process had before regeneration and crystallization decreased the concentration of the ferric chloride down to below substantially 27% and had built up a relatively high concentration of etched metal chloride in the etching bath, approaching the saturation point thereof at the working temperature of the bath. When this is not the case (i.e., when simultaneously starting both the regenerating-crystallization and etching processes) it may be desired to regenerate the ferrous chloride to ferric chloride to keep the concentration and activity of the ferric chloride up to a desired high level, even though the process has not yet produced enough etched metal chloride to be crystallized out economically. When this is the case, the flow may be diverted through the conduit 65 and control valve 67, to by-pass the heat interchanger 35 and cooler 43, thus returning the regenerated liquid from the chlorinating tower 21 directly to the storage tank 55 without the recovery of crystals. Also, there may be times when it is desired to transfer liquid from the cooler 43 direct to the storage tank 55 without sending it through the heat interchanger 35, and this may be accomplished by a by-pass conduit 71 valved at 73.

One or more pumps are provided wherever necessary to insure flow through the various conduits. As an example, one pump has been indicated at 75 in the conduit 31 leading from the bottom of the chlorinating tower 21 to the heat interchanger 35. Water is added at any desired point in the flow circuit, to make up for the water taken out as water of crystallization in the crystallized etched metal chloride. For example, the make-up water may be added to the storage tank 55 through a conduit 81 valved at 83.

A number of variations are possible without departing from the invention. For example, the iron addition apparatus is not necessarily located between the etching container 11 and the chlorinating tower 21, but may be placed at any other desired point in the path of flow; or instead of using separate iron addition apparatus, the iron plates may be physically placed in the chlorinating tower near the top thereof, so that as the ferric chloride in the mixture entering the tower passes over the iron plates, it will react therewith to pick up iron and form a fresh supply of ferrous chloride, which then is converted to ferric chloride as it flows down through the chlorinating tower.

Again, it is not necessary that the regenerating or chlorinating step precede the cooling step to crystallize out the etched metal chloride. The flow may extend direct from the etching equipment 11 to the heat interchanger 35 and crystallizing cooler 43, and then the regenerating or chlorinating step may take place in the course of the flow from the cooler 43 to the storage tank 55. This has the advantage that the heat produced by the reaction in the chlorinating tower is added after the cooling and crystallization step, and so does not have to be absorbed or dissipated later, when cooling for crystallization purposes. However, it is normally preferred to chlorinate before crystallizing out the etched metal chloride, especially as the chlorinating or regenerating step converts the less soluble ferrous chloride to the more soluble ferric chloride, thereby eliminating danger of undesired crystalliza-

tion of some of the ferrous chloride if it were present in high concentration during the cooling step to crystallize the etched metal chloride.

It is seen that in the preferred form of the invention, the etching process can be carried on continuously in a very satisfactory, efficient, and economical manner. To recapitulate briefly, the work to be etched, in the form of articles wholly or partly of metal, is inserted in and removed from the etching container 11 from time to time. Through the conduit 61, there is a constant inflow into the etching container 11 of replenishment liquid consisting essentially of ferric chloride as its active ingredient, at a relatively high concentration of, say, 39%, and at a temperature of, say, 120° F., which replenishment liquid contains a relatively low concentration of chloride of the metal being etched, far below the saturation concentration thereof at this working temperature. There is a continuous outflow (in the preferred continuous process) of liquid from the etching container 11 through the conduit 13, the outflowing liquid consisting essentially of a mixture of ferric chloride and ferrous chloride at a considerably reduced concentration of ferric chloride and carrying in solution with it, etched metal chloride at a relatively high concentration of the solution at this particular temperature, which temperature is still close to if not the same as the initial working temperature in the etching equipment 11.

This liquid mixture of ferric chloride, ferrous chloride, and etched metal chloride is then regenerated in the chlorinating tower. The regenerating reaction or activity raises the temperature of the regenerated solution, and it is preferably further raised by addition of steam to clear the solution of chlorine gas, so that there is no danger of premature crystallization of the etched metal chloride at this stage. The liquid, now consisting of ferric chloride carrying a high concentration of etched metal chloride in solution (with possibly some small amount of ferrous chloride, although usually all of the ferrous chloride will have been regenerated or converted to ferric chloride) is then partially cooled in the interchanger 35 and further cooled in the cooler 43 to crystallize out the etched metal chloride, the crystals of which may carry with them water of crystallization, whereupon the cooled mixture, now consisting essentially of ferric chloride with a relatively minor amount of etched metal chloride, goes either directly or through the interchanger 35 to the storage tank 55 to be heated to the working temperature (e.g., 120° F.) and thence to flow back into the etching container 11 for reuse.

This process, in its preferred form, greatly reduces the cost of etching as compared with the prior practice of using batches of ferric chloride which have heretofore been discarded and wasted when no longer fit for use. The cost of the chlorine gas required for regenerating the ferrous chloride to ferric chloride is usually considerably less than the cost of an equivalent amount of a new or fresh batch of ferric chloride purchased as such, in addition to which there may be a substantial market value for the recovered etched metal chloride crystals (particularly if the metal being etched is copper) so that there is a double saving in cost, both from the regeneration step and the metallic chloride recovery step.

It may be mentioned here that the valves 15 and 20 are adjusted to such extent as necessary to pick up enough iron from the iron addition apparatus so that the solution in the storage tank 55 is kept at a specific gravity of about 42° Baumé (when copper and similarly reacting metals are to be etched), which specific gravity corresponds to a concentration of about 39% ferric chloride by weight, in water. If the concentration rises above this, the valve 15 is closed down somewhat and the valve 20 is opened somewhat, or vice versa if the concentration falls.

The liquid entering the cooler 43 through the conduit 41 will usually be at a temperature above 120° F.,

but contains only the amount of etched metal chloride which is soluble at 120° F., assuming that this is the temperature in the etching tank 11 where the solution was formed. If the cooling water supply has a temperature of 65° or cooler, the solution is preferably cooled in the cooler 43 to a temperature of about 75° F. Assuming that copper is the metal being etched, the copper chloride formed in the etching process will have a solubility of about 6.41 moles per 1000 grams of water at the formation temperature of 120° F., and about 5.69 moles per 1000 grams of water at the crystallization temperature of 75° F., so that about 0.72 mole per 1000 grams of water will crystallize out. When etching other metals rather than copper, the amount crystallizing out will be different, but in each case it will be the result of difference in solubility of the chloride of the etched metal, at the higher temperature in the bath 11 as compared with the lower temperature in the cooler 43, it thus being advisable to operate the process with the bath 11 as hot as is reasonably possible under all the circumstances, and the cooler 43 as cold as is reasonably possible in view of the availability of cheap cooling water.

Iron was mentioned above, among the metals which could be etched by the ferric chloride. However, when etching iron, the iron cannot be recovered by crystallization or precipitation. Therefore, when using the present invention in etching iron, the regenerating or chlorinating part of the process (tower 21, etc.) is employed just as when etching other metals, e.g., copper, except that one starts with a relatively weak etching solution of ferric chloride, e.g., about 27° Baumé, corresponding to about 24% ferric chloride. After leaving the chlorinating tower, the solution is sent back to the storage tank 55 through the by-pass 65, omitting the cooling and crystallizing step entirely, except as needed to place the solution entering the tank 55 at the proper temperature. The solution will gradually become more and more concentrated as the process continues. When the concentration finally reaches the highest limit which may be safely used as a practical matter, a portion of this concentrated ferric chloride solution is withdrawn. Then, the remaining solution is restored to its original concentration and volume by the addition of water. The withdrawn concentrated ferric chloride solution may be sold.

Also, where the solubility of the chloride of the metal being etched is very high (as is the case, e.g., with aluminum chloride and zinc chloride) there may not be enough difference in solubility at the etching bath temperature and at the cooling temperature to make it practical to crystallize out the chloride. In such cases, it may be more practical and economical to omit the cooling step (except as may be needed to bring the temperature down from the tower exit temperature of about 212° F. to the storage tank temperature of about 120° F.) and to run the process until a highly concentrated solution of the etched metal chloride is produced, then discard the solution and start again with a fresh batch. But in either case, the regenerating or chlorinating step of the present invention is employed, and constitutes a substantial improvement over the prior art even when the cooling and crystal recovery step is not employed. Of course when etching metals whose chlorides have substantially different solubility at the different working temperatures, such as copper, nickel, and cobalt, both the regenerating step and the crystallizing-out step are employed in combination with each other, and this constitutes the preferred form of the invention in its full fruition.

It will be apparent from the foregoing that by the proper choice of the relative capacities of the etching equipment as compared to the regenerating tower the solution in the etching bath may be kept at or nearly at the same concentration of ferric chloride as the new solution was, assuming drag out iron and evaporated water have been replaced. This is possible by selecting a tower having a capacity sufficiently large so that it will

always be able to regenerate all the ferrous chloride that would be generated by the maximum capacity of the etching equipment. It is also obvious that as the capacity of the etching equipment is increased the capacity of the crystallizing equipment would also have to be increased in order to handle the increased volume of metallic salts to be precipitated. At this point, we would like to emphasize that the exact means to etch the metal by the etchant forms no part of this invention. The term "placing metal to be etched in an etching bath" as used in the claims is intended to cover not only bathing by immersion, using either air or mechanical agitation, but also spraying, splashing the etching solution on the work, or by still immersion whereby the etchant is brought in contact with the work.

What is claimed is:

1. In the process of etching copper with an etching bath of a copper halide of the group consisting of cupric chloride and cupric bromide, the improvement comprising removing a portion of the copper halide as cuprous halide from the spent etching mixture and rejuvenating the spent etching mixture with the aid of a member of the group consisting of bromine and chlorine.

2. A process according to claim 1 wherein there is present an accelerant selected from the group consisting of hydrochloric acid, hydrobromic acid, alkali metal chlorides, ammonium chloride, ammonium bromide, alkaline earth metal chlorides, alkaline earth metal bromides, zinc bromide, zinc chloride, aluminum chloride, aluminum bromide, titanium tetrachloride and titanium tetrabromide.

3. A process according to claim 2 wherein the accelerant is sodium chloride.

4. A process according to claim 2 wherein the accelerant is titanium tetrachloride.

5. In the process of etching copper with a chloride etching bath and wherein cuprous chloride is formed in the etching process, the improvement comprising withdrawing a portion of the bath from the copper being etched, separating the withdrawn portion into two parts, cooling one of said parts to below the temperature of

the etching bath to precipitate out at least a portion of the cuprous chloride therein, then combining said one part with the other part and rejuvenating the combined parts with the aid of chlorine to convert at least a portion of the cuprous chloride to cupric chloride and then returning the rejuvenated mixture to the etching bath.

6. A process according to claim 5 wherein the parts are substantially equal.

7. In the process of etching copper with a cupric chloride etching bath and wherein cuprous chloride is formed in the etching process, the improvement comprising withdrawing a portion of the bath from the copper being etched, cooling the withdrawn portion to below the temperature of the etching bath to precipitate at least a portion of the cuprous chloride therein, then rejuvenating the withdrawn portion with the aid of chlorine to convert at least a portion of the cuprous chloride to cupric chloride and then returning the rejuvenated mixture to the etching bath.

8. A process according to claim 7 wherein the temperature during the precipitation is controlled so that less than 50% of the cuprous chloride is precipitated and the amount of chlorination is controlled so that the rejuvenated mixture contains approximately the same amount of cupric chloride as that in the etching bath.

9. A process according to claim 7 wherein the cooling is done at a temperature wherein about 50% of the cuprous chloride in the spent bath is precipitated and the chlorination is carried out to oxidize substantially all the remaining cuprous chloride to cupric chloride.

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