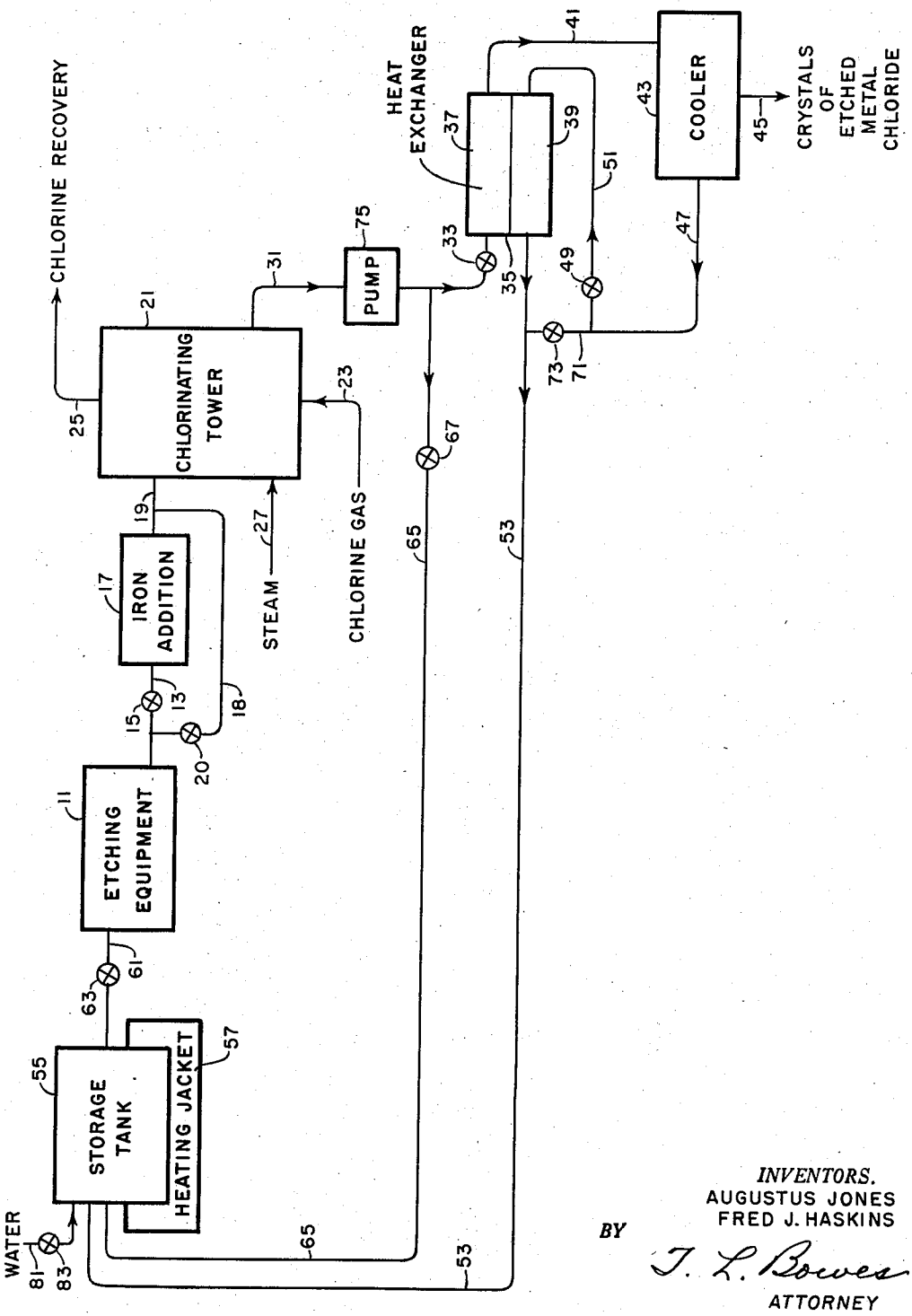
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ETCHING PROCESS

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ETCHING PROCESS

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

An object of the present invention is the provision of a generally improved and more satisfactory etching bath process.

Another object is the provision of a process and apparatus for maintaining the activity of an etching bath, which are simple and relatively inexpensive.

Still another object is the provision of a bath regenerating process which is particularly adapted and suitable for use with etching baths of ferric chloride.

A further object is the provision of both a process and an apparatus for the recovery of metal chloride as a valuable by-product produced in the etching of a metal by a ferric chloride etching bath.

A still further object is the provision of a process and apparatus adapted especially but not exclusively for the etching of copper by a ferric chloride solution and for the recovery of copper chloride as a valuable by-product.

These and other desirable objects may be attained in the manner disclosed as an illustrative example of the invention in the following description and in the accompanying drawing forming a part hereof, which drawing constitutes both a flow sheet illustrating a preferred example of the process of the invention and a diagrammatic illustration of a preferred form of apparatus in accordance with the invention.

In certain types of etching operations, as for example when etching metals such as copper, tin, aluminum, zinc, and many others, and their alloys, it is desirable to use an etching bath of ferric chloride, because it is relatively active for the intended purpose and relatively safe with respect to the operating personnel. However, the activity of the etching bath decreases with a decrease in the amount of ferric chloride in the bath (the ferric chloride being converted to ferrous chloride during the etching reaction) and with an increase in the amount of metal or alloy etched away from the article being etched. As the concentration of chlorides of the etched metal or metals in the bath increases, and the concentration of ferric chloride decreases, a point is eventually reached at which the activity of the bath is so reduced that the use of the bath is no longer commercially economical.

Also, in many cases it is not commercially economical to discard the bath when it reaches this point of exhaustion, and substitute a new or fresh bath, because the ferric chloride is relatively expensive (whether purchased either as crystals or as a previously prepared solution) so that the substitution of a new and fresh bath or even the addition of more ferric chloride to the old bath would involve undesirable expense of considerable amount. Moreover, there is the further factor that by the time the etching bath has been used long enough to reduce its activity to a relatively low level, it may contain valuable metallic salts, which should not be discarded if an inexpensive way to recover them can be found.

The present invention serves not only to replenish or

rejuvenate the activity of the etching bath, but also to recover the metallic salts in a commercially economical manner.

As a convenient illustrative example, the invention will be described with reference to the etching of 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 or panel of electrical insulating material (e.g., a phenolic sheet such as "Bakelite"), 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, 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 etching of printed circuit plates furnishes a good example to form a basis for describing the invention, because it illustrates that certain factors, e.g., the temperature of the etching bath, may be limited by or be dependent upon the characteristics of the insulating sheet or the characteristics of the bond between the copper sheet and the insulating sheet. The choice of this illustrative example also enables the inclusion of the step of recovery of a valuable by-product, since the copper chloride formed during the etching reaction can be recovered and sold to advantage. But it must be clearly borne in mind that copper printed circuit plates, or indeed copper in any shape or form, is but an example and is not intended as a limitation upon the scope or usefulness of the invention. The invention is applicable equally well to the etching of any of the many metals which are capable of being attacked or etched by ferric chloride, e.g., lead, tin, nickel, iron, cobalt, cadmium, chromium, zinc, aluminum, magnesium, or alloys of any such metals. The term "metal" as hereafter used in this application is intended, unless otherwise plainly indicated, to include alloys as well as pure or relatively pure metals. And where copper happens to be mentioned, as the description proceeds, it will be understood that this metal is named only for the sake of giving the desired specific example, and that any other metal (including alloys) capable of being etched by ferric chloride could be substituted, except as otherwise plainly indicated, without departing from the invention.

Referring now to 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. As already mentioned, the etching bath used in accordance with the present invention is ferric chloride, known per se as an etching bath for various metals. 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). In the prior practice, when the concentration of the bath is lowered to approximately 24 percent ferric chloride (in the case of etching of copper) it is found that the use of the bath is no longer economical, because the required etching time becomes too great, and the bath is then discarded and replaced by a fresh bath.

According to the present invention, as distinguished from the above mentioned prior practice, 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. When etching copper laminate on a phenolic base, the limiting factor in the working temperature of the etching bath is usually the danger of injury to the phenolic sheet or to the bond between the copper and the insulating sheet, and the working temperature is preferably kept at about 120° F. If a base sheet and bond having higher heat resistance are used, the working temperature can be correspondingly raised, so long as it does not exceed the safe temperature with respect to the lining or other delicate parts of the apparatus. When etching an article entirely of metal, or a laminated article in which neither the base sheet nor the bond constitutes a limiting factor, the temperature may be raised substantially to the boiling point of the etching solution, if the tanks, conduits, valves, etc., will safely stand this temperature.

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 percent 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**, which may be in the form of a conventional chemical reaction tower filled with ceramic packing of conventional kind, down which the solution trickles 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 **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 chlorinating tower has no effect upon the chloride of the metal being etched, which was included along with ferric chloride and ferrous chloride in the liquid entering the top of the tower. Therefore, 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 the major part of the chloride of the metal being etched, which crystallizes 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 percent 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 crystallization 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 percent, 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 heat 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 percent 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 percent 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° to the storage tank temperature of about 120°) 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.

It is seen from the foregoing disclosure that the above mentioned objects of the invention are well fulfilled. It is to be understood that the foregoing disclosure is given by way of illustrative example only, rather than by way of limitation, and that without departing from the invention, the details may be varied within the scope of the appended claims.

What is claimed is:

1. The continuous process of etching metal with ferric chloride which comprises the steps of bringing metal to be etched into contact with a liquid etching bath the active ingredient of which is ferric chloride, to form in said bath a liquid mixture of ferric chloride, ferrous chloride, and chloride of the etched metal, continuing the etching until the concentration of etched metal chloride in said bath approaches the saturation point at the working temperature of the bath, continuously withdrawing from the bath a quantity of said liquid containing said concentration of etched metal chloride, subjecting the withdrawn liquid to reaction with chlorine gas to convert at least a substantial part of the ferrous chloride therein to ferric chloride, cooling the withdrawn liquid to crystallize out a substantial part of the etched metal chloride, removing the etched metal chloride crystals from the cooled liquid, reheating the cooled liquid to the working temperature of the etching bath, and returning the regenerated liquid to the etching bath.

2. The continuous process of etching copper with ferric chloride which comprises the steps of bringing copper to be etched into contact with a liquid etching bath, the active ingredient of which is ferric chloride at a temperature of substantially 120° F. and at a concentration of substantially 39 percent, to form in said bath a liquid mixture of ferric chloride, ferrous chloride, and cupric chloride, continuing the etching until the concentration of the bath drops below substantially 27 percent and the concentration of cupric chloride in the bath approaches the saturation point at the working temperature of the bath, continuously withdrawing from the bath a quantity of said liquid, subjecting the withdrawn liquid to reaction with chlorine gas to convert at least the major part of the ferrous chloride therein to ferric chloride, cooling the withdrawn liquid to approximately 65° F. to crystallize out a substantial part of the cupric chloride, removing the cupric chloride crystals from the cooled liquid, reheating the cooled liquid to substantially 120° F., and feeding the regenerated and reheated liquid continuously to the etching bath.

3. The process which comprises the steps of placing metal to be etched in an etching bath composed essentially of ferric chloride and a relatively low concentration of chloride of the metal being etched, to form in said bath ferrous chloride and a relatively high concentration of chloride of the metal being etched, withdrawing a portion of said bath from the presence of the metal being etched, regenerating the withdrawn portion by reaction with chlorine to convert the ferrous chloride therein to ferric chloride, cooling the withdrawn portion to crystallize out a part of the etched metal chloride, separating the crystallized chloride from the cooled portion of the bath, reheating the cooled portion to the working

temperature of the etching bath, and returning the regenerated and reheated portion to the etching bath.

4. The process as defined in claim 3, further including the step of adding iron to the withdrawn portion of the bath to replace iron lost in the form of iron chloride clinging to an article which has been etched when such article is removed from the etching bath.

5. The process which comprises the steps of placing metal to be etched in an etching bath composed essentially of ferric chloride and a relatively low concentration of chloride of the metal to be etched, to form in said bath ferrous chloride and a relatively high concentration of etched metal chloride, withdrawing a portion of said bath from the presence of the metal being etched, regenerating the withdrawn portion by reaction with chlorine to convert the ferrous chloride therein to ferric chloride, and returning the regenerated portion to the etching bath.

6. The continuous etching process which comprises the steps of providing an etching bath of liquid for contact with a metal article to be etched, continuously feeding to said bath a liquid solution of ferric chloride containing a relatively low concentration of chloride of the metal to be etched, and continuously withdrawing from said bath a liquid solution of a mixture of ferric chloride and ferrous chloride containing a relatively high concentration of chloride of the metal to be etched, reacting said mixture of ferric chloride and ferrous chloride with chlorine gas to convert the ferrous chloride therein to ferric chloride, then cooling to remove a substantial part of the etched metal chloride by crystallization and thereafter recycling the liquid solution containing ferric chloride to said bath.

7. A process according to claim 1 wherein the metal to be etched is copper.

8. In the process of etching a metal with a ferric chloride etching bath in which process the ferric chloride is reduced to ferrous chloride, the improvement comprising rejuvenating the spent mixture by converting the ferrous chloride to ferric chloride with the aid of chlorine, removing a substantial proportion of the chloride of the etched metal and thereafter returning the rejuvenated mixture to the etching bath.

9. A process according to claim 8 wherein the metal is copper.

10. A process according to claim 8 wherein prior to rejuvenation at least a portion of the spent mixture is passed over iron to replace the iron lost during removal of the etched chloride.

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