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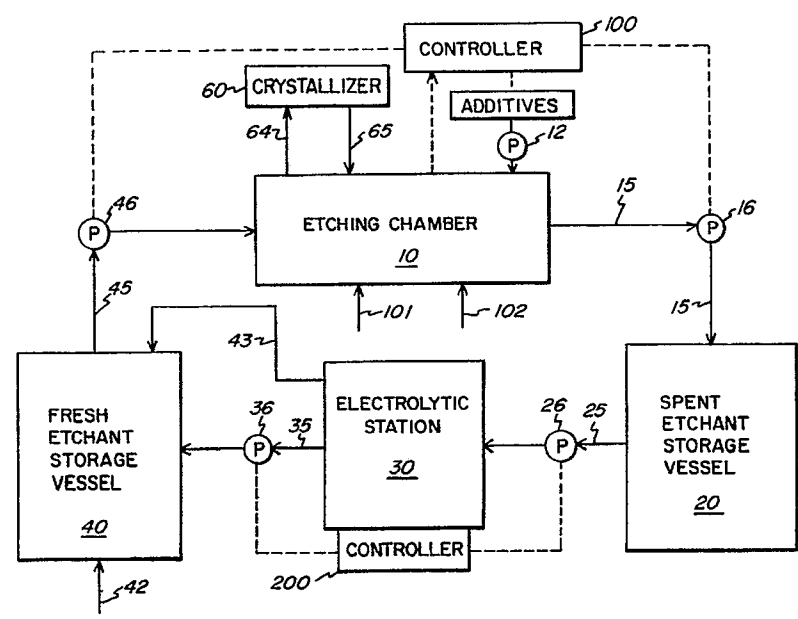
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System and process for etching with, and regenerating, alkaline ammoniacal etchant solution.

A process and related system is disclosed for etching copper with, and regenerating, a working alkaline ammoniacal etchant solution, the regeneration involving withdrawal of a portion of the working solution as spent etchant solution (15) and electrolytic removal (30) therefrom of at least a portion of the etched copper therein so as to produce a fresh

etchant (45) solution which is returned to the working solution (10) accumulation vessels upstream (20) and downstream (40) of the electrolytic process; and supply to the working solution and/or the fresh etchant solution of sufficient oxygen and ammonia to maintain the desired cupric ion content and pH in the working solution.



EP 0 448 870 A1

The present invention relates to etchant baths for dissolution of metals and, more particularly, to a system and process for regenerating alkaline ammoniacal etchant solutions which have reached a degree of reduced etching ability, particularly as a consequence of increased concentration therein of etched metals.

Solutions for etching away metals from substrate surfaces find widespread use in a variety of technologies. Most notable among these technologies is the manufacture of printed circuits, where copper-clad non-conductive substrates are patterned with an etch-resistant material to protect selected portions of the underlying copper metal, and then contacted (e.g., by immersion or spraying) with a copper etchant solution to selectively remove copper from the unprotected areas.

A wide variety of etchants for copper are potentially useful in processes of this type, but considerations of undesired aggressiveness toward other metals and materials, and desired high copper etch rates, greatly narrow the range of commercially practical etchant solutions. One class of etchant solutions which have of late been a subject of interest are alkaline ammoniacal etchant solutions, typically aqueous solutions of cupric sulfate, ammonium sulfate or like non-halogen ammonium salts, and sufficient ammonium hydroxide to adjust the pH of the solution to a value in the range of from about 8.0 to 10.0, preferably about 8.5 to 9.5. Solutions of this type have the advantage of not producing significant quantities of difficult to treat waste products, in contrast to cupric chloride alkaline ammoniacal etchants which are widely used commercially. Disadvantageously, these cupric sulfate-containing solutions offer copper dissolution rates of only about one-third those found with cupric chloride containing solutions, but this problem has since been overcome through the improvement set forth in U.S. Patent No. 4,784,785, incorporated herein by reference, describing additives which greatly increase the etching rate without compromising the other advantages of the etchant solution.

During the course of the etching operation using these solutions, the solution becomes progressively less efficient as its active components are consumed or altered (e.g., $\text{Cu}^{+2} \rightarrow \text{Cu}^{+1}$) and as the concentration of etched metals therein increases. It has been proposed that these solutions can be regenerated by electrolytic removal therefrom of etched metals and oxidation of the resultant solution (e.g., with air or oxygen gas). See, e.g., U.S. Patent Nos. 4,557,811 and 4,564,428, both incorporated herein by reference. In practice, however, it has been found that the systems and processes proposed in this regard are inadequate in a number of respects, particularly in failing to

achieve a steady-state level of consistent etching efficiency throughout the entirety of the process.

According to the present invention there is provided a process for etching copper metal with, and regenerating, a working alkaline ammoniacal etchant solution comprising non-halogen cupric and ammonium salts and having a pH in the range of from about 8.0 to about 10.0, said process comprising:

- (a) etching copper metal with said working alkaline ammoniacal etchant solution in an etching chamber;
- (b) withdrawing at least a portion of said working alkaline ammoniacal etchant solution from said etching chamber, as spent etchant solution having a decreased etching ability and an increased concentration of etched copper relative to the desired etching ability and concentrations in a working etchant solution, and transferring said spent etchant solution to a collection vessel for accumulation of said spent etchant solution;
- (c) withdrawing at least a portion of spent etchant solution from said spent etchant collection vessel and transferring it to an electrolytic cell having anode and cathode elements, and there subjecting said spent etchant solution to electrolysis to decrease the concentration of etched copper therein by deposition of etched copper, as copper metal, on said cathode element;
- (d) withdrawing spent etchant treated in step (c), as fresh etchant having a decreased concentration of etched copper relative to that in said spent etchant, and transferring it to a collection vessel for accumulation of fresh etchant therein;
- (e) transferring at least a portion of said fresh etchant solution to said etching chamber as working alkaline ammoniacal etchant solution; and
- (f) supplying to said fresh etchant solution and/or to said working alkaline ammoniacal etchant solution sufficient oxygen to maintain a desired level of cupric ion in said working alkaline ammoniacal etchant solution and sufficient ammonia to maintain the pH of said working alkaline ammoniacal etchant solution in the range of from about 8 to about 10.

In accordance with the present invention, working alkaline ammoniacal etchant solution which has been employed in the etching of copper in a suitable etching chamber is drawn off from the etching chamber as "spent etchant" and transferred to a spent etchant collection or storage vessel; spent etchant from the spent etchant storage vessel is drawn off therefrom to an electrolytic treatment vessel in which the spent etchant is electrolyzed to remove therefrom, in the form of elemental metal deposited on the cathode, at least a portion of the etched metals (e.g., copper) contained in the spent

etchant as a consequence of its etching of copper; the so-treated spent etchant of reduced etched metal content is drawn off from the electrolytic treatment vessel as "fresh etchant" and transferred to a fresh etchant collection or storage vessel; and fresh etchant is withdrawn from the fresh etchant storage vessel and transferred to the etching chamber for admixture with the working alkaline ammoniacal etchant solution there present.

As part of the regeneration process, an oxygen-containing gas is employed to effect oxidation of cuprous ion to cupric ion, and ammonia is employed to maintain the appropriate pH in the working etchant solution. These regenerating additions can be employed at any one or more stages of the overall etching and regenerating system. In a preferred embodiment of the invention, for example, oxygen and ammonia are at least periodically fed to the etching chamber containing the working alkaline ammoniacal etchant solution such that the appropriate pH is maintained therein and such that the cuprous species generated during the etching (i.e., by the reaction of the cupric species of the working solution with the metallic copper to be etched, in which the metal is oxidized ($\text{Cu}^0 \rightarrow \text{Cu}^{+1}$) and the cupric species is correspondingly reduced ($\text{Cu}^{+2} \rightarrow \text{Cu}^{+1}$)) are oxidized back to the cupric (Cu^{+2}) state. As a portion of this working solution is drawn off as spent etchant (having reduced etching ability because of the build-up therein of oxidized copper), it is then processed in the electrolytic treatment vessel to decrease its copper ion content (by reduction to copper metal at, and plating out onto, the cathode). In this electrolytic treatment, oxygen and ammonia are also liberated and the electrolyzed solution also may still have present cuprous ions. From this point, the electrolyzed solution can be transferred to the fresh etchant storage vessel, and from there to the etching chamber, without additions of ammonia and/or oxygen, relying on the fact that in the etching chamber, required additions of these gases to the entire working solution will in any event be made as needed. Alternatively, however, additions of oxygen and/or ammonia could also be made to the electrolyzed solution before it is transferred to the etching chamber, e.g., in the fresh etchant storage vessel and/or at points between transfer into or out of that storage vessel.

In this most preferred embodiment, at least a portion of the oxygen and/or ammonia additions made anywhere in the process can utilize as their source the gases liberated during electrolyzing.

Additives which are employed in the alkaline ammoniacal etchant solution as etch rate increasers, e.g., small amounts of ammonium halide, water-soluble salts of anions containing sulfur or selenium or tellurium, organic thio compounds and,

optionally, water-soluble salts of noble metals, as described in the earlier-mentioned U.S. Patent No. 4,784,785, generally are not regenerated as such in the process, and thus are periodically or continuously metered directly to the working etchant solution used in the etching chamber and/or to fresh etchant before it is transferred to the etching chamber.

In the course of the process, nitrates may form during the electrolytic treatment, particularly when chloride-containing rate-increasing additives have been employed in the alkaline ammoniacal etchant solution. These nitrates generally have limited solubility in the alkaline ammoniacal etchant solution and, because of the closed nature of the overall etching and regenerating system, the nitrates will precipitate and progressively build up in the system as the overall process continues through etching and regeneration steps, unless the nitrates are maintained at appropriate low levels (i.e., below saturation levels at the temperatures of interest). In the preferred embodiment of the present invention, steps are taken to at least periodically remove a sufficient portion of these nitrates from the system by drawing off solution from any appropriate stage in the overall process (e.g., from the etching chamber or spent etchant storage vessel or fresh etchant storage vessel, etc.), treating the drawn off portion to eliminate or at least reduce the nitrate content thereof (e.g., by crystallization), and then returning the so-treated solution back to an appropriate step in the overall system. In the preferred embodiment, this nitrate reduction, to the extent needed, is effected by at least periodic treatment of a portion of the working alkaline ammoniacal etchant solution drawn off from the etch chamber.

The system and process according to the invention are designed ultimately to maintain the alkaline ammoniacal etchant solution at an essentially constant composition, and preferably one which ensures efficient and rapid etching. In this way, a high degree of dependable consistency becomes inherent in the process as it is used in the etching of a large quantity of copper-coated substrates. Thus, residence times established for particular substrates having generally uniform amounts of copper thereon to be etched can be dependably adhered to over the course of etching a large number of such substrates without undue concern for compositional changes in the etchant which might lead to insufficient etching in the predetermined residence time. At the same time, of course, efficient regeneration of the etchant leads to greatly improved process economics.

In the known regeneration processes, the limited capacity of particular treatment operations relative to the amount of solution to be treated, and/or the time necessary to complete such treatments,

often leads to wide swings in the composition of the working etchant solution, and hence in its etching rate, at any given time over the course of the overall process. In the present invention, the system steps are designed and arranged such that draw off from the etchant solution for regeneration and replenishment thereof can occur at regulated periodic intervals or continuously, thereby maintaining an essentially constant etching composition. So too, the use of storage vessels for spent etchant and for fresh etchant permits these solutions to be accumulated and, thus, enables regeneration to be conducted essentially independent of the etching process.

The system and process of the present invention preferably is operated in conjunction with sensors or meters for on-stream measuring of relevant parameters of the system (e.g., pH, dissolved oxygen, specific gravity, level sensors and the like) and associated controls responsive as necessary to those measured characteristics of the system.

As earlier noted, the system and process of the invention have particular reference to alkaline ammoniacal etchant solutions used in copper etching, and particularly such solutions whose fundamental components are non-halogen cupric and ammonium salts having oxygen in their anion, such as cupric sulfate and ammonium sulfate, and most particularly those solutions containing the rate-increasing additives as set forth in U.S. Patent No. 4,784,785.

Reference is made herein to "spent" etchant, and to the regeneration of spent etchant, with the understanding that the solutions are generally not truly "spent" in the sense of having lost all ability to etch copper. Rather, the terminology is employed for ease of reference in describing alkaline ammoniacal etchant solutions which, as a consequence of their use in etching copper, experience diminished concentration of active etching components and increased concentration of metal (in the form of copper salts).

The present invention will now be described further by way of example only, with reference to the sole figure of the accompanying drawing which is a schematic illustration of a preferred system and process of the present invention.

Referring to the sole figure of the drawing, working alkaline ammoniacal etchant solution is contacted with the substrates to be etched at etching chamber 10. The etching process can be an immersion etching process, in which case substrates are immersed in the working etchant bath in a suitable vessel, or alternatively a spray etching process, in which case the etchant is supplied to a suitable spraying apparatus (not shown) contained in an appropriately-sized vessel for spraying onto the substrate and for collecting the run-off of the

spraying process. Provision can be made for recirculation of run-off etchant back to the spraying apparatus within the etching chamber 10.

Typically, the etching process will be carried out at working bath temperatures in the range of from room temperature to about 130° F.

A predetermined portion of the working etchant solution in etching chamber 10 is drawn off therefrom as spent etchant through line 15 (e.g., by pump 16) and into spent etchant storage vessel 20 in which it can be accumulated and then drawn off for further processing (regeneration) as needed. Thus, a portion of spent etchant from spent etchant storage vessel 20 is drawn off therefrom, through line 25 (e.g., via pump 26), to electrolytic processing station 30. The electrolyzing station 30 can be any suitable vessel or parallel sets of vessels containing appropriate anode and cathode elements connected to a rectifier and operated at current densities effective to plate out in metallic form, onto the cathode, at least a portion of the etched metals (copper) contained in the spent etchant solution. During the electrolyzing process, gaseous oxygen and ammonia will be produced and liberated and, as described hereinafter, can be vented off and used at other stages in the process for oxidizing cuprous ions to cupric ions and for maintaining suitable operating pH (e.g., between about 8 to 10) in the working etchant bath.

Also, as previously noted, possibility exists that nitrates also will form in the electrolytic process, particularly if chloride-containing rate-enhancing additives have been employed in the working etchant bath, and such nitrates are dealt with as hereinafter described.

The fresh etchant from electrolyzing station 30, now of reduced etched metal content, is drawn off at line 35 (e.g., via pump 36) to fresh etchant storage vessel 40, where it can be accumulated until needed.

From the fresh etchant storage vessel 40, fresh etchant is drawn off through line 45 (e.g., via pump 46) to etching chamber 10 for admixture there with working alkaline ammoniacal etchant solution.

In the etching and regeneration process, it is necessary to employ oxygen (per se or an oxygen-containing gas) to oxidize cuprous ions to the cupric ions needed in the working alkaline ammoniacal solution, and to employ ammonia for maintaining the pH of the working bath. In the system shown in the accompanying drawing, there exist a number of choices where these additions can be made. As shown in the accompanying drawing, oxygen and ammonia are added directly to the working etchant solution in etching chamber 10, as for example through porous diaphragm tubes or pipes arranged therein or at inlets thereto, fed by source lines 101 and 102, respectively. In this

manner, the cuprous ions formed in the oxidation of the copper metal being etched and in the corresponding reduction of the cupric ions in the working solution, are wholly or partially oxidized to the desired Cu^{+2} state, and the appropriate operating pH is maintained in the working solution. As an alternative, or in addition to, these feeds of oxygen and ammonia directly to the solution in etching chamber 10, a portion of the working solution (distinct from that portion drawn off as spent etchant) can at least periodically be drawn off from etching chamber 10, treated in a separate draw-off vessel with oxygen and/or ammonia as necessary, and then returned to the working bath in the etching chamber 10.

When the system is operated in the foregoing manner, spent etchant drawn off from the etching chamber 10 -- for processing through spent etchant storage vessel 20, electrolytic treatment station 30 and fresh etchant storage vessel 40 for return to the etching chamber 10 -- need not necessarily be treated with oxygen or ammonia before return to the etching chamber 10, i.e., any cuprous ions present in the so-processed spent etchant and/or any ammonia deficiency can be handled simply in the course of the treatment of the working etchant solution of which the processed spent etchant becomes a part. Nevertheless, it may still be desirable to treat the spent etchant, after it has been electrolyzed, with oxygen and/or ammonia, at a point prior to its return to the etching chamber 10 for admixture with working etchant solution. To this end, one convenient place for such treatment is in fresh etchant storage vessel 40, where the fresh etchant therein can be admixed with ammonia and/or oxygen as necessary (shown generally as 42). Indeed, one convenient means for effecting these additions is to vent the gases formed in the electrolysis (oxygen, ammonia) directly to the fresh etchant contained in fresh etchant storage vessel 40 (e.g., via line 43), either in lieu of or in addition to adds of oxygen and/or ammonia to the fresh etchant storage vessel 40 by other distinct means (e.g., porous tubes or pipes 42).

Alternatively or in addition, fresh etchant from the electrolyzing step can be treated with oxygen and/or ammonia at a separate station either before being fed to, or after leaving, the fresh etchant vessel 40. In either case, but particularly if performed after the fresh etchant leaves its storage vessel, provision can be made for using that same station for delivering oxygen and/or ammonia to portions of working solution drawn off from etching chamber 10 for treatment and return to the etching chamber, as previously described.

Also as earlier noted, all or a portion of the mixed gases liberated in the electrolyzing step can instead be vented directly to the etching chamber

10 for supplying oxygen and ammonia to the working etchant solution therein.

Also as noted previously, copper and/or ammonium nitrates or complexes thereof may form as a consequence of electrolytic treatment of the spent etchant, a tendency which appears more pronounced when chloride-containing rate-enhancing additives are used in the working alkaline ammoniacal solution. If permitted to build up as the overall process continues in its etching and regeneration steps, and given the fact that the overall system is essentially a closed one, these nitrates eventually will exceed saturation levels in etcher 10 (or in other equipment) and form precipitates therein causing problems of interference with and/or clogging of apparatus associated with the etcher, as well as the general problem of solids build-up requiring interruption of the process to effect removal. In the preferred embodiment of the invention, means are provided for eliminating or at least reducing the content of these nitrates at any one or more appropriate stages in the overall system.

Preferably, the means for effecting removal of these nitrates is by crystallization and still further by crystallization treatment of a portion of working etchant solution at least periodically drawn off from the etching chamber 10. To this end, crystallization unit 60 is employed to cool portions of working etchant solution, drawn off from etching chamber 10 via line 64, to temperatures at which nitrate solubility is reduced as compared to that in the working etchant solution, thereby encouraging and effecting precipitation of at least a portion of the nitrates as solids in the crystallization unit. The so-treated etchant solution, now of reduced nitrate concentration, is returned as working etchant solution to etching chamber 10 via line 65 where it intermixes with solution having an elevated temperature relative to the crystallization unit, and thus an increased capacity for solubilizing nitrates, thereby substantially eliminating precipitation of nitrates in etching chamber 10. The crystallization unit 60 can be of any appropriate type or construction, so long as its capacity, efficiency and cooling coil area are sufficient to effect the required temperature drop for the amount of etchant solution required to be drawn off from the etching chamber 10 so as to maintain nitrates at below saturation levels.

As an alternative to the foregoing, or in addition thereto, the removal of nitrates can be conducted by treatment of other solutions in the process, e.g., spent etchant or fresh etchant drawn off from their respective storage vessels for such treatment.

At steady-state operation, the system is designed to maintain a relatively constant volume of working etchant solution, of relatively constant composition, in etching chamber 10, and can be

readily automated to achieve those ends. Thus, suitable control/logic circuits which measure and are operable in response to particular process and composition parameters can be employed. As shown in the preferred embodiment of the accompanying drawing, a control unit 100 is used primarily to assimilate information regarding the specific gravity of the working etchant bath in etching chamber 10 as a measure of the amount of copper etched and the corresponding depletion of active components in the working bath. Optionally, the control unit 100 can assimilate information regarding the quantity and specific gravity of spent etchant solution drawn off from etching chamber 10 via line 15 as additional data for use in indicating the amount of copper etched by the working solution and the depletion of active compounds.

For non-regeneratable additives, the information obtained at control unit 100 can be used to activate, as necessary, transfer means (shown as pump 12 in the accompanying drawing) for delivering to etcher 10 appropriate quantities of fresh additives. With regard to the major regeneratable active components of the system, control unit 100 is used to activate transfer (e.g., via pump 46) of an appropriate quantity of fresh etchant from fresh etch storage vessel 40 for delivery to etching chamber 10 to replenish the working etchant solution therein. At the same time, a substantially equal volume of the working etchant solution (as spent etchant) is drawn off from etching chamber 10, via overflow or pumping (e.g., pump 16), to spent etchant storage vessel 20.

Spent etchant in vessel 20 can be accumulated (and, if necessary heated) until such time as it is necessary to deliver a portion thereof to the electrolyzing unit 30 and thereafter to fresh etchant storage vessel 40. Spent etchant in the electrolyzer 30 can be monitored by specific gravity and/or amp-hours and/or residence time therein, to determine when a sufficient quantity of etched copper has been removed therefrom in the form of metallic copper deposited on the cathode. The information is assimilated by controller 200 which responsively actuates transfer (via pump 36) of the so-processed solution to the fresh etchant storage vessel 40 and refilling of the electrolytic cell with a quantity of spent etchant from spent etchant storage vessel 20 (via pump 26).

Additional controls can be employed in the system, most notably those assimilating information from meters reading pH and dissolved oxygen, for responsively actuating and regulating ammonia (e.g., anhydrous ammonia) and oxygen additions.

Also, of course, the various storage vessels (e.g., for spent etchant and/or for fresh etchant) can be provided with agitation means if desired or necessary, and/or can be provided with means for

withdrawing and recirculating solution therein as a means for agitation and for keeping solutions moving as may be desired.

Generally speaking, the system of the invention is best operated as a feed and bleed type system where additions of replenished working etchant solution from fresh etchant storage vessel 40 trigger corresponding draw off of spent etchant and regeneration of spent etchant. An important feature of the invention, however, is that regeneration can be carried out and continued independent of the etching process, so that fresh etchant can be built up for reserve in its storage vessel 40 and spent etchant can correspondingly be depleted from its vessel 20. By virtue of the utilization of storage vessels for both the spent etchant and fresh etchant, the system is arranged to be responsive even to substantial periodic replenishment and draw-off demands without being restricted in this regard by capacity- and/or rate-limiting steps (e.g., electrolysis of spent etchant).

Claims

1. A process for etching copper metal with, and regenerating, a working alkaline ammoniacal etchant solution comprising non-halogen cupric and ammonium salts and having a pH in the range of from about 8.0 to about 10.0, said process comprising:
 - (a) etching copper metal with said working alkaline ammoniacal etchant solution in an etching chamber;
 - (b) withdrawing at least a portion of said working alkaline ammoniacal etchant solution from said etching chamber, as spent etchant solution having a decreased etching ability and an increased concentration of etched copper relative to the desired etching ability and concentrations in a working etchant solution, and transferring said spent etchant solution to a collection vessel for accumulation of said spent etchant solution;
 - (c) withdrawing at least a portion of spent etchant solution from said spent etchant collection vessel and transferring it to an electrolytic cell having anode and cathode elements, and there subjecting said spent etchant solution to electrolysis to decrease the concentration of etched copper therein by deposition of etched copper, as copper metal, on said cathode element;
 - (d) withdrawing spent etchant treated in step (c), as fresh etchant having a decreased concentration of etched copper relative to that in said spent etchant, and transferring it to a collection vessel for accumulation of fresh etchant therein;

- (e) transferring at least a portion of said fresh etchant solution to said etching chamber as working alkaline ammoniacal etchant solution; and
- (f) supplying to said fresh etchant solution and/or to said working alkaline ammoniacal etchant solution sufficient oxygen to maintain a desired level of cupric ion in said working alkaline ammoniacal etchant solution and sufficient ammonia to maintain the pH of said working alkaline ammoniacal etchant solution in the range of from about 8 to about 10.
2. A process according to claim 1, wherein the supplying of oxygen and ammonia of step (e) is solely to said working alkaline ammoniacal etchant solution.
 3. A process according to claim 1, wherein the supplying of oxygen and ammonia of step (e) is to both said fresh etchant solution and said working alkaline ammoniacal etchant solution.
 4. A process according to claim 1, 2 or 3, wherein the supplying of oxygen and ammonia of step (e) employs, at least in part, oxygen and ammonia liberated in the electrolysis of step (c).
 5. A process according to any one of the preceding claims, wherein nitrates are formed during the electrolysis of step (c) and wherein at least a portion of the nitrates are at least periodically removed from the working alkaline ammoniacal etchant solution and/or the fresh etchant solution and/or the spent etchant solution.
 6. A process according to claim 5, wherein the nitrates are removed by crystallization and precipitation of the nitrates from said solution.
 7. A process according to claim 6, wherein the nitrates are removed from the working alkaline ammoniacal etchant solution by withdrawing a portion of the working solution, distinct from a portion withdrawn as spent etchant solution, from the etching chamber, and said distinct withdrawn portion is subjected to reduced temperature treatment to crystallize and precipitate nitrates therein, the precipitated nitrates are separated from said distinct withdrawn portion, and the separated distinct withdrawn portion is returned to the etching chamber.
 8. A process according to any one of the preceding claims, in which the volumetric portion of the working alkaline ammoniacal etchant solution withdrawn from the etching chamber as spent etchant solution substantially corresponds to the volumetric portion of the fresh etchant solution transferred to the etching chamber as working alkaline ammoniacal etchant solution.
 9. A process according to claim 8, wherein the withdrawing of a portion of working etchant solution from the etching chamber as spent etchant, and the transfer of fresh etchant solution to the etching chamber as working alkaline solution, are intermittent.
 10. A system for etching copper metal with, and regenerating, a working alkaline ammoniacal etchant solution comprising non-halogen cupric and ammonium salts and having a pH in the range of from about 8.0 to about 10.0, said system comprising:
 - (a) an etching chamber adapted for etching copper-containing substrates with a working alkaline ammoniacal etchant solution;
 - (b) a collection vessel for accumulating spent etchant solution having a decreased etching ability and an increased concentration of etched copper as compared to desired etching ability and concentrations in said working etchant solution;
 - (c) means for withdrawing at least a portion of working etchant solution, as spent etchant solution, to said spent etchant collection vessel;
 - (d) an electrolytic cell comprising anode and cathode elements and adapted to remove at least a portion of etched copper from spent etchant solution by deposit thereof, in metallic form, on said cathode;
 - (e) means for withdrawing at least a portion of spent etchant solution from said spent etchant collection vessel to said electrolytic cell;
 - (f) a collection vessel for accumulating fresh etchant having a decreased concentration of etched copper as compared to that in said spent etchant;
 - (g) means for withdrawing at least a portion of spent etchant solution from said electrolytic cell, as fresh etchant, to said fresh etchant collection vessel;
 - (h) means for transferring fresh etchant to said etching chamber as working etchant solution; and
 - (i) means for supplying to at least one of said fresh etchant or working etchant solution oxygen and ammonia in amounts sufficient to maintain in said working etchant solution a desired concentration of cupric

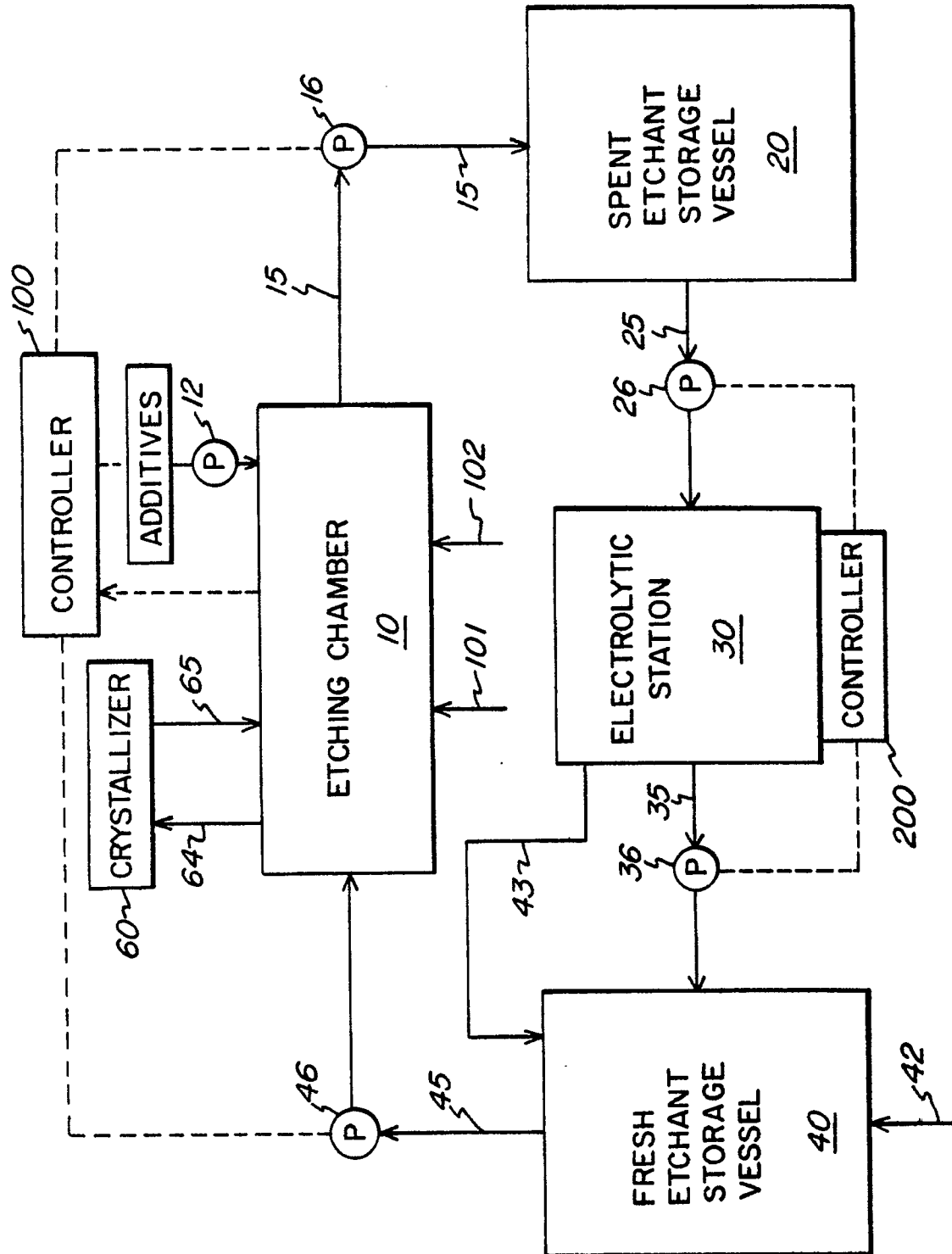
ions and a pH in the range of from about 8 to about 10.

11. A system according to claim 10, further comprising means for introducing into the working etchant solution etch rate-increasing additives to replace those consumed in the etching process. 5
12. A system according to claim 10 or 11, further comprising means for treating at least a portion of one or more of the working etchant solution, spent etchant solution and fresh etchant solution to remove at least a portion of precipitable nitrates therein. 10 15
13. A system according to claim 12, wherein the treating means for removing at least a portion of the precipitable nitrates comprises crystallization means. 20
14. A system according to any one of claims 10 to 13, further comprising control means for sensing a predetermined increased concentration of etched copper in the working etchant solution and for actuating the means for transferring fresh etchant solution to the etching chamber as working etchant solution and the means for withdrawing at least a portion of working etchant solution, as spent etchant, from the etching chamber. 25 30
15. A system according to any one of claims 10 to 14, further comprising control means for sensing a predetermined decrease in etched copper in the spent etchant in the electrolytic cell, and for actuating the means for withdrawing at least a portion of spent etchant from said cell as fresh etchant, and means for withdrawing at least a portion of spent etchant from said spent etchant collection vessel to the electrolytic cell. 35 40

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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 3186

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 117 068 (THE ELECTRICITY COUNCIL) * Claims 1,6-9,10,12,17-20; figure 1 *	1,2,8,9, 10,11,14	C 23 F 1/46
Y	-----	3,4	
Y	DE-A-3 738 022 (W. HOLZER) * Claims 1,2 *	3,4	

A	EP-A-0 144 742 (KERNFORSCHUNGSANLAGE JÜLICH GmbH)		

A	DE-A-3 608 516 (M.M. BRINGHAM) -----		
The present search report has been drawn up for all claims			
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 23 F
Place of search		Date of completion of search	Examiner
The Hague		26 June 91	TORFS F.M.G.
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