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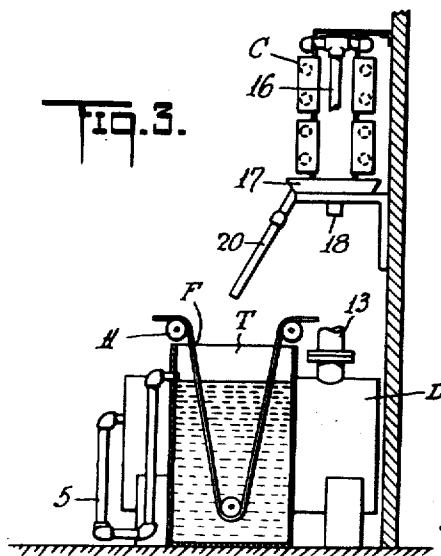
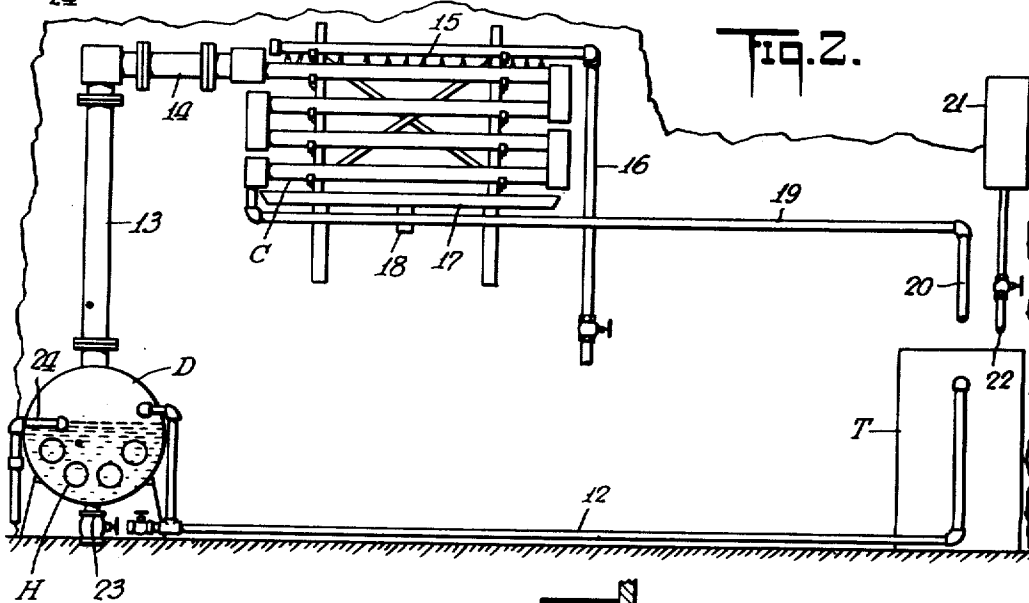
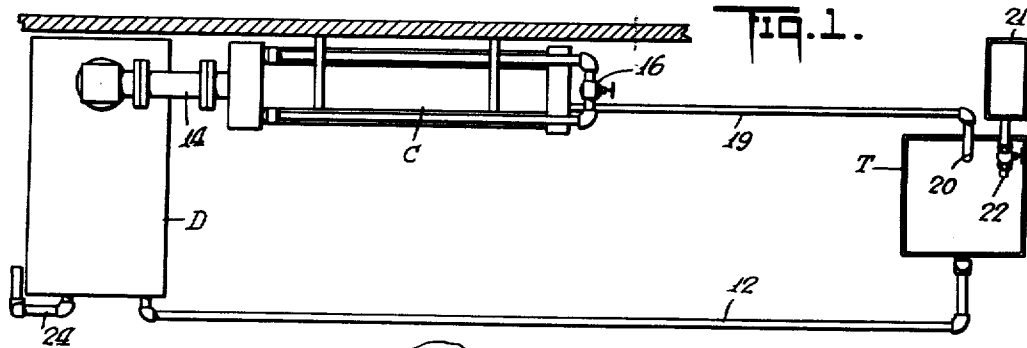
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2,378,052

ETCHING PROCESS

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2 Sheets-Sheet 1



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2,378,052

ETCHING PROCESS

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5 Claims. (Cl. 41-42)

While the present invention is useful for the reclaiming of etching reagent in the continuous etching of aluminum foil for use in electrolytic condensers, the invention in some aspects has wider applicability in other etching procedures.

The prior application of George F. Coggins, Serial No. 364,625, filed November 7, 1940, sets forth and claims the optimum controls of the etching liquor for attaining the desired high gain in capacitance per unit area of aluminum foil used in the manufacture of electrolytic condensers. The present invention is more especially concerned with a process and equipment for automatically precluding variation in the selected composition of the etching liquor. Such constancy of composition is important, for as the etching operation proceeds, the active reagent in the etching liquor is consumed and its concentration reduced and the product of reaction is increased, so that the gain in capacitance per unit area of foil being treated in such deteriorating etching liquor drops progressively and the economy effected in condenser manufacture is lost, since more foil and more materials generally are required, as the high capacity gain per unit of foil area is not assured for all of the foil being etched.

Among the objects of the invention are to provide a process by which etching may not only be performed uniformly and reliably throughout, but by which considerable economy is effected in the re-use of otherwise waste reagent, and in which such re-use may be effected by a substantially continuous and self-controlling action which requires no elaborate apparatus or skilled supervision.

Where the composition of the etching liquor is kept substantially constant, not only in the concentration of the etching reagent therein, but in the proportion of contaminating salt and product of the reaction as well, practically complete recovery of the etching reagent from the contaminated etching liquor may be continuously effected by the present invention, provided the salts forming in the liquor during etching operation have a much lower volatility than the reagent itself. To this end etching liquor is constantly withdrawn from the etching tank at such rate that salt reaction product is removed there-with at substantially the same rate as fresh salt is formed in the tank as the etching proceeds. The withdrawn liquor is collected in a distillation kettle that is maintained at constant temperature well above that at which the etching reagent will begin to vaporize. By reason of the

distillation thus occurring in the process, the kettle contents do not become diluted and the distillate will be inherently of substantially the concentration of the original etching liquor, and the undesirable salt products of reaction will be removed therefrom. The composition of the etching liquor is readily kept constant by supplying thereto in addition to the distillate from the still, additional reagent and water at the rate at which such liquids are consumed in the etching process.

While the invention is not limited in its application to the etching of any particular metal, or the use of any particular reagent, it is particularly useful in the etching of aluminum foil with acid solutions, for instance, hydrochloric acid in any desired concentration, depending upon the characteristics of the foil to be etched and the degree of etch desired.

In the accompanying drawings, in which is illustrated the application of the invention in its preferred field of use

Fig. 1 is a plan view of an installation in which the process may be carried out,

Fig. 2 is a side elevation thereof,

Fig. 3 is an end elevation thereof,

Fig. 4 is a graph illustrating the relationship of temperature to recovery of distillate from the still for an illustrative sample of etching reagent, and

Fig. 5 is a graph illustrating the percentage of recovery of hydrochloric acid at various still temperatures for an illustrative feed to the still.

In Figs. 1 to 3 of the drawings, is shown more or less diagrammatically a specific installation, wherein the etching process is carried on in a tank T containing an aqueous solution of reagent through which foil F is continuously conveyed for etching purposes. Desirably the strip aluminum from a reel (not shown) is passed through tank T over a series of rollers 11 to a second reel (not shown). The overflow from the tank passes through pipe 12 into kettle D in the interior of which are a plurality of heaters H near the bottom thereof, which maintain the tank contents at a predetermined temperature. From the kettle D a riser 13 leads to a horizontal pipe 14 communicating with a condenser C wherein the vapors from kettle D are condensed. This condenser may be of more or less conventional construction. Cooling water is passed over the condenser from a perforated pipe 15 in turn supplied through a riser 16, the water being collected in a pan 17 under the condenser from which it is drawn off through drain 18. The distillate from the still is passed through pipe 19, whence by means of hose

20. it passes into the tank T for re-use in the etching process. The tank T also has connected thereto a vessel 21 containing a fresh supply of reagent and the outlet 22 of which is adjusted to feed such fresh reagent at compensating rate, that is at rate corresponding to that at which reagent is depleted in the entire process. Water is also added at a replenishing rate through a spigot (not shown). The concentrated salt liquor forming as an end product in kettle D may be drawn off through drain valve 23 in the bottom of said kettle.

Liquor from the etching tank T, illustratively comprising an aqueous solution or dispersion of hydrochloric acid and aluminum chloride, is passed into the kettle D which is kept filled to a predetermined level, determined by the location of siphon 24. The composition of the residue in the kettle will, of course, depend upon the temperature at which said kettle is maintained. The relationship of still liquor and distillate compositions at various still temperatures is illustratively indicated in the graph of Fig. 4 when an etching solution of 84.4 grams per liter of hydrochloric acid and 36.5 grams per liter of aluminum chloride is fed to the kettle. As shown in the graph, the higher the temperature maintained in the kettle, the less its percentage of hydrochloric acid and the greater its percentage of aluminum chloride. For instance, if the kettle be kept at a temperature of 247 degrees F., the concentration of hydrochloric acid therein will be much less than in the etching tank, i. e. about 4 grams per liter, while the aluminum chloride will have risen to 390 grams per liter and the recovered hydrochloric acid in the distillate will have a concentration of 93 grams per liter.

While the etching liquor with a relatively high concentration of the end product of reaction, in this instance aluminum chloride, would have poor etching efficacy, a concentration of aluminum chloride in the etching liquor of between 35 and 40 grams per liter is used because it is practical and does not involve the high operating cost of keeping the aluminum chloride at a much lower concentration.

From the graph of Fig. 5 it appears that where the liquor in the kettle is kept at 240 degrees F. about 98 per cent of the total hydrochloric acid in the feed is recovered. At 242.5 degrees F. 99 per cent is recovered and at 250 degrees F. recovery thereof is substantially 100 per cent.

The graphs show the operation with substantially a nine per cent aqueous solution of hydrochloric acid (84.4 grams per liter) containing 36.5 grams per liter of aluminum chloride, which is practical for many purposes, but similar graphs may be prepared to serve for carrying on the process with any other concentration of acid and salt.

Thus, in practice, the etching may be conducted at any suitable temperature, and the composition of liquor in the etching tank is kept substantially constant. The collected volume of liquor in the kettle is kept at the economical operating temperature and the distillate therefrom is returned to the etching tank. That distillate remains uniform in composition as does also the concentration of aluminum chloride in the kettle, the excess of which is drained off continuously, the level of liquor in the kettle being maintained constant.

It will thus be seen that in actual operation, the process can be carried out with a minimum of technical supervision. The foil being passed

at uniform temperature conditions through the etching tank, the composition in the tank remains substantially constant, since the overflow causes withdrawal of the aluminum chloride at substantially the same rate as it is formed in the continued etching operation. Water and hydrochloric acid are returned to the etching tank after the distillation and only sufficient adjustment with fresh material is required to make up for consumption and losses in the entire process.

In the kettle D the fairly concentrated liquor with its high content of aluminum chloride is not diluted by the addition thereto of liquor from the etching tank because such liquor, except for the equilibrium residue of aluminum chloride, is vaporized almost instantly by its contact with the hot concentrated liquor.

Inasmuch as the distillation of etching liquid produces a distillate of exceptional purity, it is possible to operate the etching process with make-up acid that is relatively impure. Such make-up acid, even though containing considerable amounts of deleterious impurity, will have its harmful effects reduced by its mixture with the much larger quantity of high purity distillate. Should make-up acid be so impure as to seriously impair the efficacy of the etching bath, then it should be introduced into the process in the tank overflow or directly into the still kettle.

As many changes could be made in the above process and installation, and many apparently widely different embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. The etching process which comprises treating the substance to be etched with etching liquid that has in solution any given percentage of etching reagent and any given percentage of the reaction product of said reagent, and maintaining substantial constancy of composition of said etching solution throughout the etching procedure by withdrawing contaminated etching liquid therefrom to remove products of reaction entrained therewith at substantially the rate at which the latter are formed in the etching process, adding such withdrawn reagent to a body of liquid consisting of an aqueous solution containing a lesser proportion of etching reagent and a greater proportion of products of reaction than the etching liquid, while maintaining said body of liquid at a substantially constant elevated temperature for practically instantaneous and continuous distillation of the vaporizable component of said added contaminated etching liquid, while discharging by overflow from said body the undistilled residue of said liquid, thereby to maintain the volume of said body substantially constant, returning the resultant distillate for further etching use, while adjusting the etching bath with fresh material at rate corresponding to that of depletion in the entire process.

2. The process of recovering etching reagent from solution, which consists in continuously withdrawing spent liquor from the etching process, delivering the liquor into a volume of liquid that has an aqueous solution of substantially the ingredients of the etching liquor but a much lower etching reagent content and a much higher content of reaction product, maintaining said volume

of liquid at a temperature sufficiently high for substantially instant distillation therefrom of the vaporizing constituent of the spent liquor as it is supplied thereto, and maintaining said volume substantially constant by continuously drawing off by overflow the residual liquid fraction of such spent liquor, and continuously returning the distillate for re-use in the etching reaction, while adjusting the etching bath with fresh material at rate corresponding to that of depletion in the entire process.

3. The process of continuously recovering hydrochloric acid in the etching of aluminum, which consists in drawing off the contaminated etching liquor at a constant rate, delivering the same to a body of liquid that has substantially the ingredients of the etching liquor including an aqueous solution of hydrochloric acid and aluminum chloride, but a much lower proportion of the former and a much higher proportion of the latter, maintaining the volume of said body of liquid constant by withdrawal therefrom in two fractions, a vapor fraction and a liquid fraction, conjointly at substantially the same rate at which etching liquor is supplied thereto, said fractionation and withdrawal being accomplished by maintaining said volume of liquid at a temperature sufficiently high for substantially instant distillation of the more vaporizable component of said liquor as it is supplied to the volume, and discharging by overflow from a given level of said body of liquid the residual less vaporizable liquid fraction from the spent liquor, condensing the distillate and returning the same for re-use in the etching process, while replenishing the etching liquor with fresh material equivalent to that combined with the aluminum as well as other losses in the entire process.

4. The combination recited in claim 3 in which the aluminum chloride content in the etching tank is maintained in the range of 35 to 40 grams per liter and in which the volume of liquid to which spent etching liquor is delivered has an aluminum chloride content in the order of 400 grams per liter and the hydrochloric acid content is in the order of 4 grams per liter, and in which said volume is kept at a temperature in the order of 250 degrees F.

5. The process of treating etching liquor throughout etching operation in order to maintain uniformity of etching efficacy and to reclaim etching reagent therefrom, which consists in maintaining the etching reagent and the products of etching reaction, each of predetermined concentration within the etching liquor, by drawing off etching liquor throughout the etching operation to remove reaction products at substantially the same rate at which they are formed, conveying the withdrawn etching liquor to a body of liquid of substantially fixed volume that has an aqueous solution of substantially the ingredients of the etching liquor but a much lower etching reagent content and a much higher content of reaction product, maintaining said body at a temperature sufficiently high to effect distillation of the vaporizing constituents of said withdrawn liquor at substantially the rate it is added to the collected volume, continuously removing the residual liquid fraction of the added liquor by overflow, condensing the distillate and returning the condensed distillate for re-use in the etching process.

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