

March 19, 1946.

G. F. COGGINS

2,396,685

ART OF ALUMINUM ETCHING

Filed Nov. 7, 1940

3 Sheets-Sheet 1

FIG. 1.

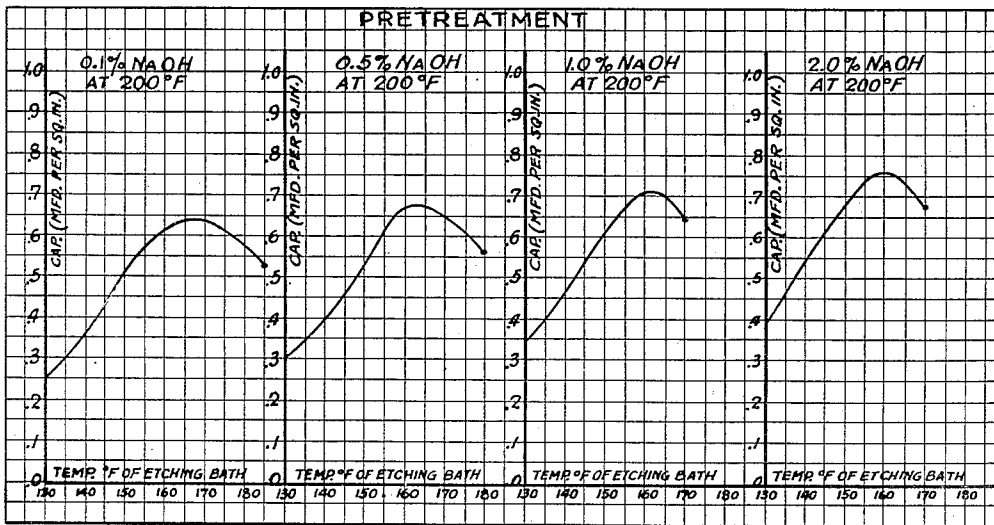
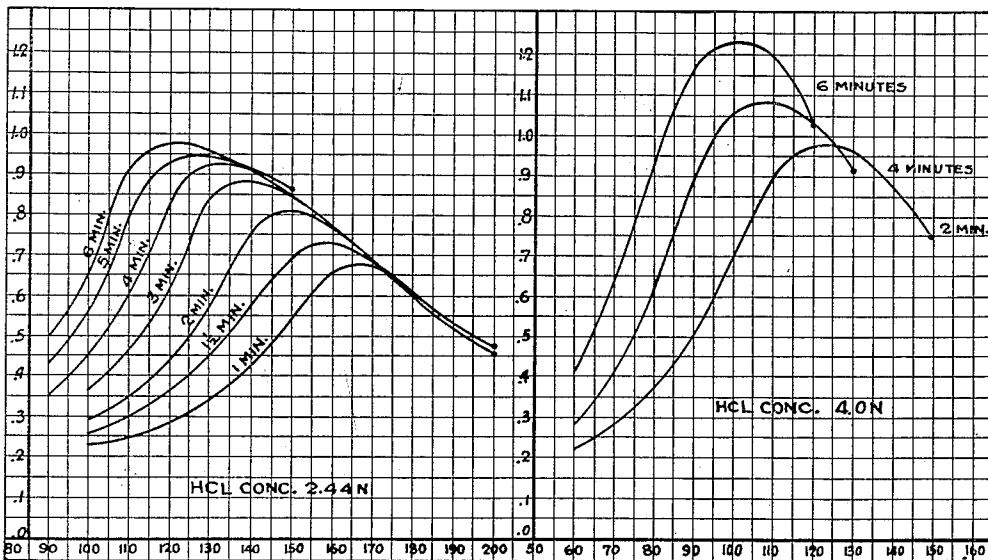


FIG. 2.



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40-134

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3 Sheets-Sheet 2

FIG. 3.

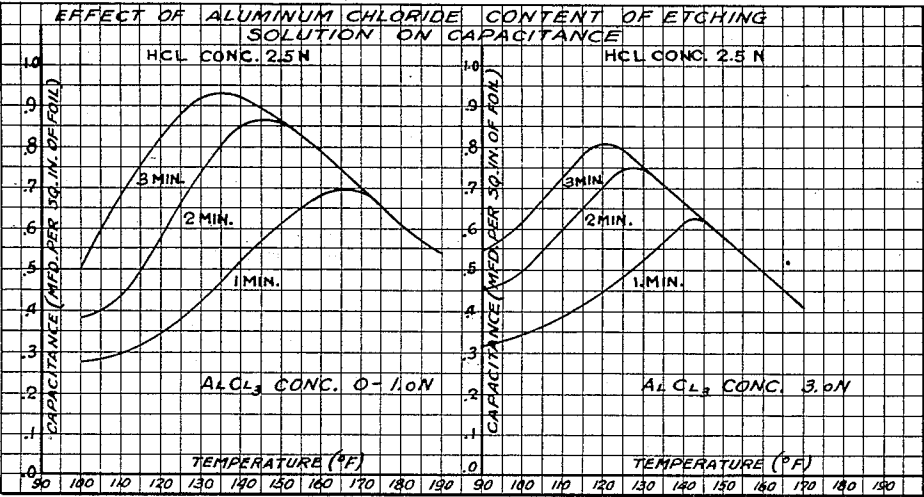
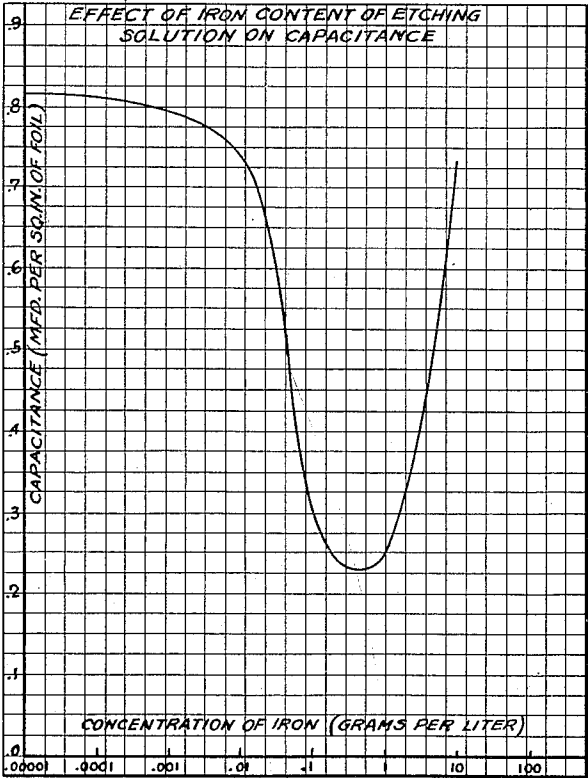


FIG. 4.



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3 Sheets-Sheet 3

FIG. 5.

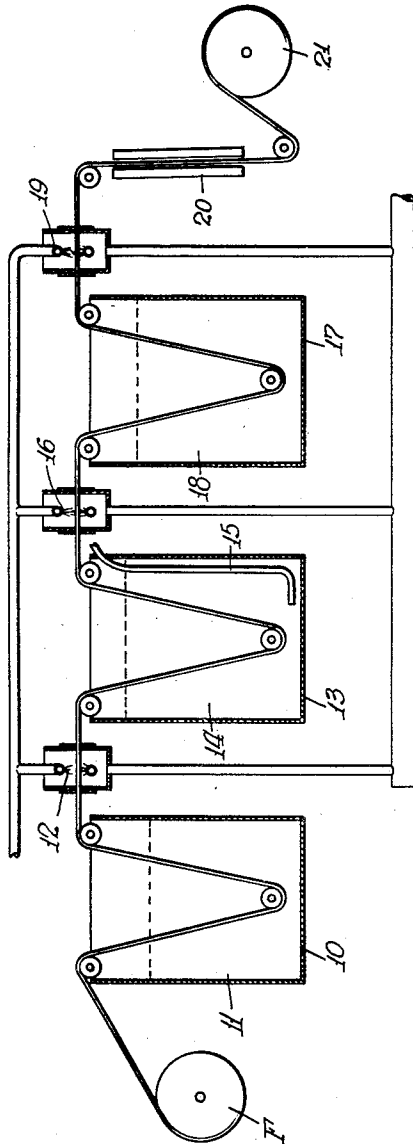
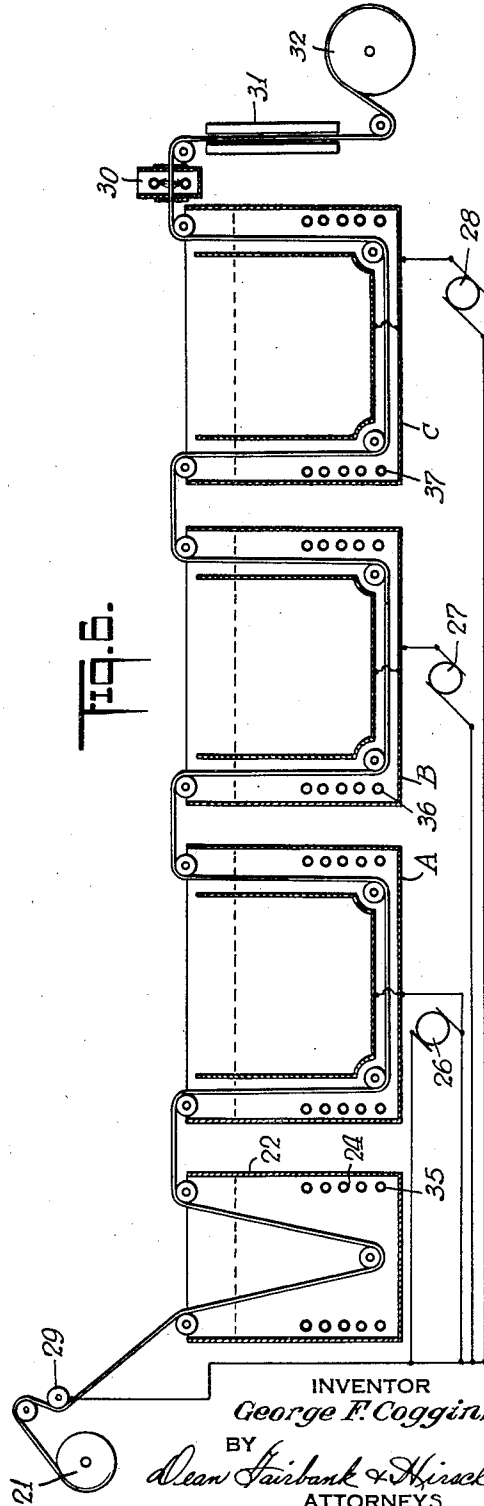


FIG. 6.



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2,396,685

ART OF ALUMINUM ETCHING

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Application November 7, 1940, Serial No. 364,625

15 Claims. (Cl. 41—42)

The present invention is particularly concerned with the etching of aluminum plates or foils.

An object of the invention is to provide an etching process by which aluminum foil or plates may be etched in large scale quantity production with uniformity within relatively close tolerances as to surface gain attained, all by simple procedure, with simple equipment and at low cost.

The etching process while useful in preparing a roughened surface for aluminum foil or plates in a variety of other arts, has especial utility in the preparation of electrodes for electrolytic condensers, in which application great economy is attained in the electrode material required for any given capacitance at any given voltage.

As conducive to a clear understanding of the invention, it is noted that where the etching of aluminum plates or foils is practiced without the particular controls of the present invention, the gain attained in surface area of foil may vary widely from section to section of one and the same lot or batch of aluminum. The length of foil area needed to assure at least a given effective surface area would have to be considerably greater than where the controls of the present invention are utilized on the etching process, since the latter brings about a greatly reduced range of variation in the high surface gain attained.

The present invention results from my discovery that the efficacy and uniformity of the etching with hydrochloric acid for high surface gain depends upon the control of a number of factors that heretofore were not suspected to have any bearing upon the etching efficacy, and would be expected by those skilled in the art to have no bearing whatsoever upon etching efficacy. Among these factors are an optimum temperature for an etching bath of any given concentration; the concentration of the caustic solution with which the foil as it comes from the mill must be treated prior to etching; the concentration within the etching liquid of the aluminum salts that pass into solution as the etching proceeds, and the iron content of the etching solution and of the sheet stock to be etched. Failure to control any of these factors results in reduction in the etching gain attained, regardless how closely the other factors above-mentioned may be controlled.

While the desired uniformity of surface gain of the aluminum foil may be attained by controlling the various variables referred to, I have made extensive tests to determine not only the

conditions for uniformity of surface gain, but also those for such gain of optimum magnitude. The results of these tests are shown in the graphs on the drawings and are set forth in the specification.

By effecting the control in the manner herein-after set forth, I have succeeded in producing aluminum foil with substantially uniform gain in surface area in predetermined fixed ratio selected anywhere from four to ten times the area of the plain foil and kept within tolerances of about plus or minus ten per cent. This result, while useful in other relations, spells tremendous economy in the manufacture of electrolytic condensers. For a 450 volt working, 525 volt peak electrolytic condenser for instance, an area of 1.5 square inches (and when desired, as little as 0.8 square inch) per microfarad has been attained in the finished condenser.

In the accompanying drawings in which are diagrammatically shown the graphs indicating the process in its general application and one important specific application thereof,

Fig. 1 is a set of graphs indicating the variations in the gain attained in capacitance per unit area, where the subsequent etching process is performed after pre-treatment of the foil with different concentrations of caustic solution,

Fig. 2 is a set of graphs indicating the relationship of the capacitance per unit area attained at various temperatures of given concentrations of hydrochloric acid when treated for various lengths of time and indicating the existence of points of optimum working conditions for each concentration used,

Fig. 3 is a pair of graphs indicating the effect upon the resultant capacitance per unit of area of change in concentration of the aluminum chloride produced in the etching bath,

Fig. 4 is a graph indicating the capacitance attained per unit area with varying concentrations of iron in the etching solution,

Fig. 5 is a diagrammatic view illustrating the pre-treating and etching set up, and

Fig. 6 is a diagrammatic view illustrating the forming procedure in electrode manufacture.

The procedure and control method will first be described under title headings in its general application and then the particular application to electrolytic condensers will be set forth.

In the graphs, the ordinates show microfarads per square inch of the plate or foil when formed after etching, it being understood that such capacitance is a measure of the surface gain attained under the conditions indicated, when com-

pared with the capacitance with identical un-etched foil subjected to like forming treatment, which yields a capacitance of but 0.18 microfarad per square inch.

Aluminum plates or foil

The foil or plate is preferably in rolls that must be continuous and free from patches or splices. When unwrapped the foil must not stick so as to become torn or marred and should present no substantial camber. The surface should be substantially free from lubricants or any such foreign material as is not readily removable in the caustic treatment to which the foil is subjected prior to etching.

Where foil is used that has been annealed for about two days at about 900 degrees F. and where the rate of cooling is slow and closely controlled the gain in area due to etching may be maintained at a uniform value, up to in the order of 40 per cent greater than where unannealed foil is used. On the other hand, where the foil has been annealed for a long time at high temperatures, and with uncontrolled cooling the efficacy of the etching again falls off materially from the optimum value.

The foil should be in the order of 99.8, preferably 99.82 to 99.85 per cent pure. In the less than two-tenth per cent impurity, there will ordinarily be present small proportions of copper, silicon and iron. The copper content should be kept down to little more than a trace, the iron to about .08-.12 per cent and the silicon to about .06 per cent.

In practice a small test sample of each batch of foil delivered from the foil manufacturer is subjected to the pre-treating and etching procedure hereinafter set forth. The test sample is then formed with a dielectric film and its capacitance is measured to make sure that the foil is of character such as to attain the desired gain in surface area. In practice but an occasional batch of foil ordered from the manufacturer has to be rejected.

Treatment prior to etching

The set of graphs shown in Fig. 1 indicates the relation of the concentration of the caustic bath at a given temperature to the capacitance per unit area attained as a result of subsequently etching in a definite solution of hydrochloric acid under various temperature conditions. This capacitance per unit area is substantially a measure of the surface area attained by the etching and the graphs are applicable therefore, to determine the control required, whether the desired gain in area is required for electrolytic condenser or for other purposes.

As will be seen from the graphs, the gain in surface area attained in the etching procedure rises with the concentration of the caustic kept at uniform temperature in the pre-treating tank. Pre-treatment with a caustic concentration of two per cent results in a better surface gain in the subsequent etching operation than with a lower concentration of caustic. With the particular foil used no advantage is however gained by resort to a caustic pre-treating solution of concentration greater than two per cent.

The caustic treatment of the foil as it comes from the rolling mill apparently results in dissolving off the oxide film left on the foil upon exposure to atmosphere after annealing and rolling. This treatment also results in saponifying and thus removing any traces of oil remaining on the foil. By immersing the aluminum in the two

per cent caustic solution at 200 degrees F. for one-half minute, the removal of oxide and oil is complete for all practical purposes and thorough, while the attack by the caustic upon the metallic aluminum surface is kept at a minimum. While the graphs of Fig. 1 are based on the use of hydrochloric acid of 2.2 N concentration in the etching, the relationship shown in the graphs would be similar for etching baths of other concentrations.

Just why the concentration of the caustic treatment step affects the ratio of surface gain in the subsequent etching step is not known or understood. Evidently, aside from the removal of oxide and oil as above set forth, this step results in some important modification, not visible to the eye, in the surface structure of the aluminum, and it certainly levels out to a considerable degree the variations in the surface of the aluminum as it is delivered from the rolling mill. Since therefore the caustic bath does something more than to clean the foil, I designate the bath as a pre-treatment rather than merely as a cleaning bath.

It has been found that the accumulation of aluminum compounds in the caustic solution due to the slight attack of the metal thereby has no deleterious effect upon the efficacy of the caustic treatment. Desirably however, the concentration of aluminum compounds is not allowed to reach a value so high as to come out of solution and to form a cake on the tank. With that one qualification, it is the concentration of the caustic which alone is important at this stage of the process.

To guard against the considerable falling off in efficacy of the subsequent etching step as the caustic solution changes in concentration, it is therefore important to adjust that concentration at frequent intervals to maintain approximate constancy.

For practical purposes substantial constancy in concentration of caustic may be attained by testing and adjusting the caustic bath at intervals, desirably of about one-half hour. The adjustment is effected by the addition of caustic or water to the bath as the case may be or preferably by continuous addition of liquid caustic and water through separate faucets at the required rate. Such aluminum hydroxide as is formed by attack of the foil by the caustic reacts with the titrating hydrochloric acid in the same way as does the sodium hydroxide, but does not contribute to the pre-treatment of the foil. For correct measurement of the caustic concentration a double titration is therefore resorted to.

One desirable titration method is the following: To a given portion of the caustic tank solution add a predetermined amount of normal hydrochloric acid solution. Add a drop of Metanil Yellow indicator and titrate with a normal solution of sodium hydroxide to a yellow color. Then add three drops of phenolphthalein indicator and titrate with normal solution of sodium hydroxide to a pink color. From the two end points a calculation of the aluminum and sodium hydroxide concentration is readily made.

After pre-treatment has been completed the foil is washed with cold tap water and then subjected to the etching which will now be set forth.

Etching

When foil previously subjected to the caustic treatment above described, is etched in hydro-

chloric acid, the conditions governing the gain in surface area are pictured in the graph shown in Fig. 2. For a given concentration of hydrochloric acid, shown in the graph at the left in the drawing as 2.44 N, there is a temperature of etching at which the optimum gain in superficial area is attained for any given time of etching, the gain dropping off sharply when a temperature is used that is more than five degrees either lower or higher than such optimum. In substantially the five degree range to either side of the optimum temperature, approximate maximum etching ratio is maintained.

As appears from Fig. 2, the temperature of the etching bath of 2.44 N to attain maximum surface gain in one and one-half minutes of immersion is 155 degrees F. but if the temperature is lowered to 125 degrees F. the surface gain attained is reduced by about fifty per cent.

As moreover appears from such graph, if the period during which the etching is conducted is increased, not only is there added gain in surface area as might be expected, but the temperature of the etching bath at which optimum effectiveness of surface gain occurs is decreased as shown. It is noted that if the temperature of the etching bath is well above that for optimum results the reduced efficacy is nearly uniform regardless of the time during which the etching is conducted.

A family of curves similar to those shown at the left of Fig. 2 might be prepared for each concentration of the etching bath. For instance, as shown in the curve at the right of Fig. 2 where a 4 N solution of hydrochloric acid is employed, the maxima of surface area gain are somewhat higher than with the 2.44 N solution, and the temperatures of treatment at which such maxima occur are lower than with the more dilute solution.

Thus, depending upon the surface gain desired, etching solution would be selected of concentration, and the etching would be conducted for the period of time indicated by the maximum on the graph. For instance, where, as is ordinarily sufficient, it is desired to produce a condenser having 1.5 square inches of electrode area per microfarad at 450 volts working, 525 volts peak, the foil of the specifications noted when immersed for one and one-half minutes in the hydrochloric etching bath of between 2.3 and 2.5 N will present the desired surface gain. Where, however, it is desired to produce foil requiring but 1.0 square inch per microfarad for a condenser of the same voltage, it would be desirable to immerse the same in 4.0 N etching solution for a period of four and one-half minutes at 100 degrees F., as best indicated in the graph at the right of Fig. 2.

While the presence of aluminum salts in solution in the caustic bath has been found to have no effect upon the efficacy of cleansing and upon the gain in effective area attained in the subsequent etching process, the presence of such aluminum salts in the etching bath has been found to have a decidedly harmful effect upon the efficacy of the etching.

In Fig. 3 appears at the left, a series of graphs showing the gain in surface area attained in etching solution of a concentration of 2.5 N containing aluminum chloride in solution therein at a concentration of 1.0 N. It will be found by comparison with the graph at the left of Fig. 2 that the presence of the aluminum chloride up to that concentration has practically no effect upon the efficacy of performance.

Under the same conditions and with aluminum chloride of 3.0 N, as appears at the graph at the right, there has been a sharp drop in the efficacy of performance, a sharp lowering in the temperature at which such maximum as is attainable under these adverse conditions is reached and that maximum is at a sharp peak, so that control becomes difficult in that a small departure from optimum temperature results in a considerable loss in etching efficacy. In the etching process it is therefore important, not only that the concentration of the etching acid be kept nearly constant, but also that the concentration of the aluminum chloride dissolved therein be not permitted to exceed 1 N, and preferably not 0.8 N.

Desirably the etching solution is subjected to a continuous distillation process to reclaim the acid for re-use freed of the aluminum salts. This process may be conducted according to the procedure set forth in the allowed application of Herbert Waterman Serial No. 191,887 for Art of reclaiming reagent and filed February 23, 1938, on which Patent No. 2,235,658 has since issued on March 18, 1941.

After accounting for and correcting variations in the efficacy of surface gain in etched aluminum, that are due to variations in the raw stock, in the concentration of the caustic solution, in the concentration of the etching solution of hydrochloric acid and the concentration of aluminum salts therein, further sharp and fortuitous reduction in the surface gain were incurred which for a long time remained unremedied.

These variations were finally ascribed to the presence of minor amounts of iron salts in the etching solution. As appears from the graph in Fig. 4 in which the abscissa is shown on an exponential scale, where the concentration of iron is as little as .001 gram (1 milligram) per liter, the reduction in the gain of surface area otherwise attainable in the etching process is as much as six per cent. Where, however, the iron concentration in the etching fluid is one-tenth gram per liter, the reduction in the effective gain of surface area is to well below one-half of its optimum value. When the iron content in the etching solution reaches .5 gram per liter, the reduction in etching gain is so serious as to render inadvisable the further use of the solution unless the excess iron is first removed therefrom. The graph of Fig. 4 is based on the use of hydrochloric acid of 2.2 N concentration, in a bath kept at 155° F., the foil being etched for one and one-half minutes, but the graph is of substantially the same shape for other concentrations, temperatures and durations of etching.

The technical grades of hydrochloric acid, while sufficiently pure for most chemical processes have been found to contain minor proportions of iron chloride which vary from lot to lot and which lead to the difficulty just set forth. Moreover any small proportion of iron on the surface of the foil that would pass off into the etching solution would as it accumulates therein, also lead to the sharp drop from the desired surface gain.

That the difficulty was in fact due to the iron salts as set forth, was corroborated by the complete elimination of the disturbing reduction in surface gain of the etched foil when so-called chemically pure hydrochloric acid was used, which has at most minor traces of iron therein.

It will be understood that while it is preferred to perform the process by operating under the optimum conditions revealed in the graphs in

the caustic pre-treatment, in the concentration and temperature of etching bath and in the content of iron and of aluminum salts in said bath, it is within the scope of the invention to maintain substantial constancy of surface gain less than the maximum, by operating as to some or all of these factors at a predetermined value or range below the optimum.

In a typical specification, foil of the purity previously noted and of the thickness of .00325 inch may in conformity with the graph of Fig. 2 be etched for one and one-half minutes at a temperature of 155 degrees F. plus or minus 2 degrees in chemically pure hydrochloric acid of concentration between 2.3 N and 2.5 N. Equivalent results may be obtained by decreasing the concentration of acid and increasing the temperature or time of etching, or increasing the concentration and decreasing the temperature or time of etching in manner clear from the graphs of Fig. 2. In general, higher concentrations of hydrochloric acid such as 6 N or even up to 10 N may be used, but only with thicker foil, because holes would otherwise etch therethrough. With concentrations above 10 N the etching efficacy is sharply reduced. Throughout the etching operation the etching liquor should be continuously stirred, desirably by passing compressed air thereinto.

While minor quantities of aluminum salts that pass into the liquor in the etching operation are not prejudicial, a concentration of aluminum salts therein in excess of 1 N or preferably of 0.8 N as above pointed out is to be avoided. Tests and adjustments to this end are made, desirably every fifteen minutes and this by a double titration similar to that used for testing and adjusting the caustic solution.

After etching, the foil is washed with cold tap water, desirably for about 45 seconds, to remove the acid. To remove any iron particles that remain on the surface of the etched foil as well as copper and any loose aluminum particles thereon, the foil is then desirably treated in a dilute solution of nitric acid. A two per cent solution is suitable at 200 degrees F. and this treatment also may be conducted for 45 seconds. The nitric acid treatment is especially important when it is desirable to remove the last traces of iron from the surface of the foil, which said removal appears to be desirable for completely satisfactory dielectric film formation when the foil is to be used as the electrode of a dielectric condenser.

The nitric acid treatment appears also to condition the surface for better formation characteristics as well as to contribute somewhat to the etching. This appears to be demonstrated by the fact that the capacitance of condensers prepared from the foil is about five per cent lower if the said nitric acid treatment is omitted and better reforming characteristics are evident with nitric acid washed foil.

While the plate or foil processed as above set forth may be used for other purposes, the further treatment thereof in a special application to electrolytic condensers will now be set forth.

Dielectric film formation in production

Foil treated and etched as above set forth is conditioned prior to film formation by treatment in boiling water for a period of preferably not less than one-half minute, although beneficial results are obtained if the treatment in boiling water is conducted for as little as 10 or 15 seconds or for as much as one minute or more. The boil-

ing water treatment in some way not understood by me, unlike cold water or even hot water at temperature below the boiling point, conditions the surface of the foil to promote the subsequent film forming procedure. Where the hot water treatment is omitted, in the order of forty per cent more amperage is needed for formation of the film upon the foil for any given voltage, a circumstance which enhances the cost not only for power but also for equipment, wiring and the like.

The formation is conducted preferably in a sequence of forming tanks, each containing a suitable electrolyte. An illustrative film forming treatment for producing electrodes suitable for condensers of 450 volt working voltage includes a sequence of three tanks which in a practical embodiment have the electrolytes and applied voltages as set forth in the following tabulations:

Tank A.—120 gallons of electrolyte made up of 150 pounds of boric acid in aqueous solution is kept at a temperature of 190 degrees F. to 210 degrees F. and the applied voltage may be 520 volts. Since the initial formation activity in this tank is vigorous and the liquid becomes agitated, it is desirable to cool the contents of the tank by appropriate cooling coils therein which prevent the temperature from rising excessively.

Tank B.—120 gallons of electrolyte made up of 100 pounds of boric acid and 35 grams of borax in aqueous solution is kept at a temperature of 190 degrees F. to 210 degrees F. and the applied voltage may be 520 volts. Heating coils are provided to bring the temperature to the operating point, and sometimes to maintain the temperature.

Tank C.—In this case the solution of 120 gallons includes 100 pounds of boric acid and 25 grams of borax and is maintained at a temperature of 190 degrees F. to 210 degrees F. and the applied voltage may be 620 volts. The activity in this tank is but low and the same is ordinarily heated to the desired temperature as for instance by a heating coil to maintain the efficacy of formation.

For production of electrodes suitable for low voltage condensers, there need be no graduation of the voltage applied in each forming tank, but that voltage in every case should be higher than the rated voltage of the condenser. For instance for a 110 volt A. C. condenser the formation is desirably 180 volts in each tank.

The solutions in the tanks are tested and re-adjusted from time to time to maintain constancy of operation.

After the condenser sections have been built according to conventional practice from foil with both electrodes, or only the anode in the case of direct current condensers, made of the processed foil as above described, the sections are aged by applying thereto desirably a series of progressively higher voltages. For a 450 volt working voltage condenser for instance, the voltage may be applied in four steps of 200, 300, 400 and 500 volts, the last say for one hour. Thereupon the sections are tempered in an oven at about 160 degrees F. for from two to four hours. The latter operation enables the units to withstand higher temperature in use and brings about a lower leakage and faster formation at room temperature.

By the process set forth, a gain in capacity per unit of area is attained in the order of 400 to 1000 per cent as contrasted with foil prepared without the etching and the various procedural steps

set forth. The accuracy and uniformity of the formation leads to variations in the capacity of the completed condenser of only ten per cent from rated reading. Accordingly the present process eliminates the need for the great excess of foil length required in the case of foil treating processes that lead to much wider variations in capacity of the completed condenser.

In the diagram of Fig. 5, is shown an installation for pre-treating and etching the aluminum foil for condenser electrode or other use.

Foil from the spool F is passed through tank 10 which is charged with the caustic solution 11. The foil after it leaves the solution is washed by the cold water spray delivered through pipes 12. The foil then passes into the tank 13 containing the hydrochloric acid etching solution 14 which is maintained stirred or agitated by compressed air admitted through pipe 15. Thence the foil passes a spray of water delivered through pipes 16 and passes into and through a tank 17 charged at 18 with the dilute nitric acid. The nitric acid is washed off the foil by a spray of water from pipe 19, whence the foil passes through an electric dryer 20 and the clean etched foil is rolled upon reel 21.

In the preparation of electrodes for electrolytic condensers, the caustic and etching baths would be controlled as previously set forth. In an advantageous commercial application, each area of foil remains immersed in the caustic bath 11 for about one-half minute. It is washed with water at 12 for about ten seconds before entering the etching bath 14, in which latter it remains for about 1½ minutes. The foil is washed for about 45 seconds at 16 after leaving the etching bath and is submerged for 45 seconds in the nitric acid bath 18, the final water wash at 19 is also about 45 seconds, and the traverse through the drying heater takes 20 seconds.

In the diagram of Fig. 6 is shown an installation for further treatment of the foil to produce formed electrodes. The foil from reel 21 is passed through a tank 22 charged at 23 with water maintained at boiling temperature by coil 24. Thence the foil is fed in succession through the three forming tanks A, B and C charged with the electrolytes previously described. Current is passed to the tanks at the respective voltages by motor generators 26, 27 and 28 respectively, the circuit to the foil being completed at metal roller 29. Distilled water for washing the foil after it leaves the tank C is shown passed through pipe 30. The washed foil is dried by electric dryer 31 and collected upon roll 32.

Motor starting condensers

In preparing the foil, the caustic pre-treating operation and the etching operation may be the same as those previously described but the forming operation is modified.

The formation in the first tank A is conducted in an electrolyte composed of an aqueous solution with a low concentration of borax therein, desirably three pounds of borax in 100 pounds of water maintained at about 200 degrees F. during formation. Borax in the initial tank is greatly superior to boric acid for the production of condensers of low power factor. A high concentration of borax in the initial tank has however been found to attack the foil and reduce the etching ratio.

In the second and third tanks (B and C), 120 gallons of electrolyte contains about 750 grams of borax and 60 pounds of boric acid.

In order to maintain the desired low power factor of the motor starting condensers, the pre-treatment in boiling water is omitted and the forming electrolyte should be frequently replaced, because substantial quantities of aluminum oxide and hydroxide in the electrolyte impair the power factor. After the formation, the foil is washed as previously described.

As many changes could be made in the above method 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 my invention, what I claim as new and desire to secure by Letters Patent is:

1. The processing of aluminum sheet material to attain a substantially uniformly large gain in surface area thereof, which consists in pre-treating the same in a caustic bath, while maintaining the concentration and temperature of the latter within a limited range of variation and then treating the sheet material for a predetermined period of time in an etching acid bath maintained within a limited range of variation of concentration and at a predetermined temperature that affords substantially the optimum of etching efficacy for said conditions as indicated by the maximum point on each of the family of curves of Fig. 2 of the drawings.

2. The processing of aluminum sheet material to attain a substantially uniformly large gain in surface area thereof, which consists in pre-treating the same in caustic solution maintained at a temperature of approximately 200 degrees F. and of concentration within a limited range of variation and after washing the foil treating the same for a predetermined period of time in an etching bath of hydrochloric acid maintained within a limited range of variation in concentration and at a predetermined temperature that affords substantially the optimum of etching efficacy for said conditions as indicated by the maximum at each of the family of curves of Fig. 2 of the drawings.

3. The processing of clean aluminum sheet material in the order of 99.8 per cent pure to attain a substantially uniform gain in surface area thereof, which consists in treating the same for a predetermined period of time in a bath of hydrochloric acid solution within a limited range of variation in concentration and at a temperature that affords substantially the optimum of etching efficacy for said conditions as indicated by the maximum at each of the family of curves of Fig. 2 of the drawings.

4. The processing of aluminum sheet material in the order of 99.82 to 99.85 per cent pure to attain a substantially uniform high gain in surface area thereof, which consists in treating the same in a bath of sodium hydroxide of approximately two per cent concentration and at a temperature of approximately 200 degrees F. for about one-half minute and then treating the foil in a bath of hydrochloric acid solution of 2.3 to 2.5 N at a temperature of about 155 degrees F. for a period of about one and one-half minutes.

5. The processing of aluminum foil for a substantially predetermined gain in surface area, which consists in passing the foil through a caustic solution held to close limits of concen-

tration and at a temperature in the order of 200 degrees F. and then treating the foil in a solution of hydrochloric acid at substantially a given concentration and temperature, while controlling the etching liquid to maintain below 1 N the concentration of aluminum salts dissolved therein.

6. In the process of etching aluminum foil for substantially a predetermined surface gain, the step of passing the foil through a bath of hydrochloric acid maintained substantially at constant concentration below 10 N, and at substantially constant temperature and with the iron impurity content of said etching bath maintained at all times at less than .005 gram per liter.

7. In the process of etching aluminum sheet material for substantially a predetermined surface gain, the step of passing the material through a bath of hydrochloric acid maintained substantially at constant concentration below 10 N, and at substantially constant temperature and with the iron impurity content of said etching bath maintained at all times at less than .005 gram per liter, and having aluminum salt dissolved therein not exceeding a concentration of 1 N.

8. The processing of aluminum sheet material for substantially constant gain in surface area, which consists in pre-treating the material in a bath of sodium hydroxide, maintaining said bath at substantially constant concentration and temperature, then passing the material through a bath of hydrochloric acid solution maintained at nearly constant temperature below 6 N while maintaining the iron impurity content of said etching bath below .005 gram per liter.

9. The processing of aluminum sheet material for substantially constant gain in surface area, which consists in pre-treating the material in a bath of sodium hydroxide, maintaining said bath at substantially constant concentration and temperature, then passing the material through a bath of hydrochloric acid solution at concentration below 6 N, maintained at nearly constant temperature, while maintaining the iron impurity content of said etching bath below .005 gram per liter, with the aluminum salt concentration not exceeding 1 N.

10. The processing of aluminum sheet material 99.82 to 99.85 per cent pure with iron content of between .08 and .12 per cent and silicon content of about .06 per cent, and of the degree of hardness attained by annealing the same for two days at 900 degrees F. followed by a slow cooling, which consists in passing the same through a bath of sodium hydroxide of concentration of substantially two per cent and temperature of approximately 200 degrees F., washing the foil and then passing it through a bath of hydrochloric acid substantially devoid of iron, maintained at a substantially constant concentration in the order of 2 to 4 N, and at a sub-

stantially fixed temperature, while maintaining the concentration of aluminum salts in the etching bath at a value not exceeding 1 N.

11. The process which consists of the steps of etching clean aluminum sheet material in a solution of hydrochloric acid, washing the same with cold tap water for less than one minute to remove acid, and removing any iron, copper and loose particles of aluminum and conditioning the surface for better film formation characteristics by treatment in a two per cent solution of nitric acid at about 200 degrees F. for less than one minute.

12. The processing of clean aluminum foil in preparation for film formation of electrolytic condensers, which consists in etching the foil in a dilute hydrochloric acid bath, while agitating the bath and removing therefrom aluminum salts in excess of a concentration of about 1 N, and then treating the foil with boiling water for about one-half minute.

13. The processing of clean aluminum foil in preparation for film formation of electrolytic condenser, which consists in etching the foil in hydrochloric acid of high purity and substantially devoid of iron content and in concentration of between 2.3 and 2.5 N at a temperature of about 155 degrees F. and for a period of about one and one-half minutes, washing the etched foil with cold water and, thereupon washing it with a dilute solution of nitric acid followed by treatment with boiling water for a period of between ten seconds and one minute.

14. The processing of clean aluminum foil approximately 99.8% pure in preparation for film formation of electrolytic condensers which consists in etching the same in a dilute bath of hydrochloric acid substantially devoid of iron, washing the etched foil with cold water, thereupon washing it with a two per cent solution of nitric acid at 200 degrees F. and then rinsing the film with water and promptly drying the same, and conditioning the film by treatment in boiling water for a period not less than one-half minute.

15. The processing of clean aluminum foil that is at least 99.8% pure in preparation for film formation of electrolytic condensers which consists in first treating the surface of the foil with caustic at controlled temperature and concentration, washing the foil thus treated, etching the clean foil in a bath of dilute hydrochloric acid substantially free from iron, removing acid from the etched foil by washing in water, removing any impurities of iron, copper or loose particles of aluminum and conditioning the surface for better film formation characteristics by washing in dilute nitric acid, rinsing off the nitric acid with water and promptly drying the foil and thereupon treating the dried foil in boiling water for a period of about one-half minute.

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