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ELECTROLYTICALLY ETCHED CONDENSER ELECTRODE

Filed July 25, 1951

2 Sheets-Sheet 1

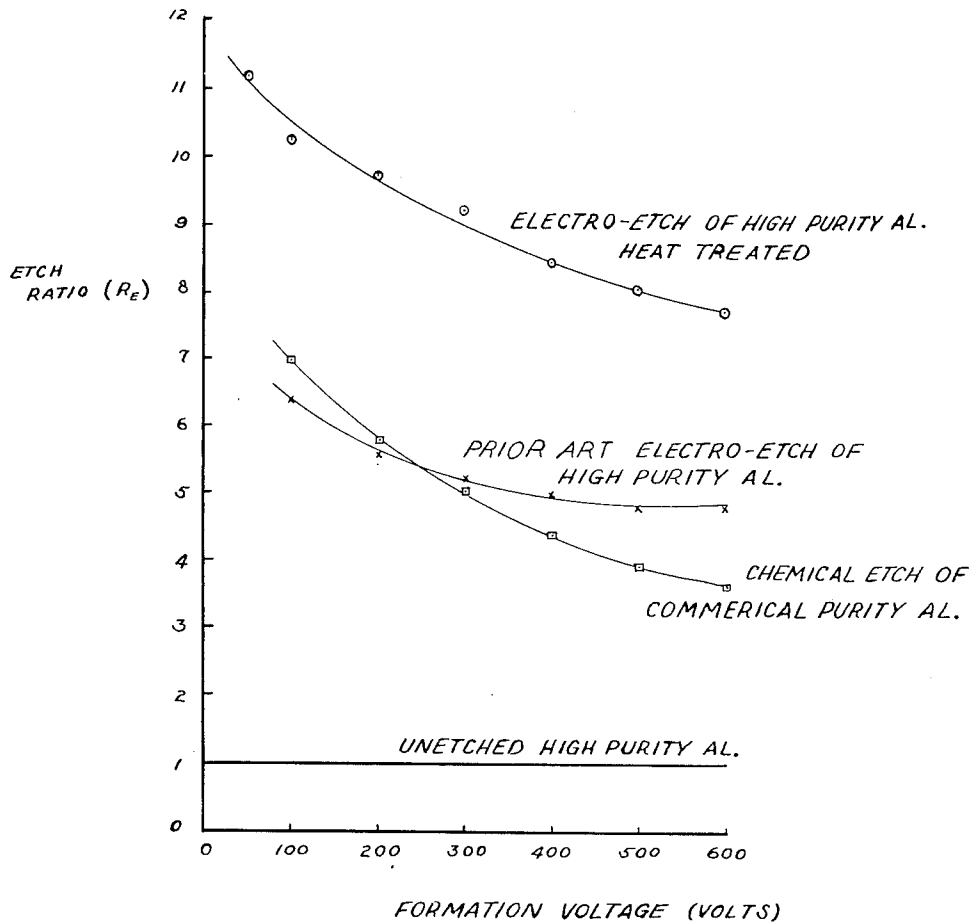


Fig. 1

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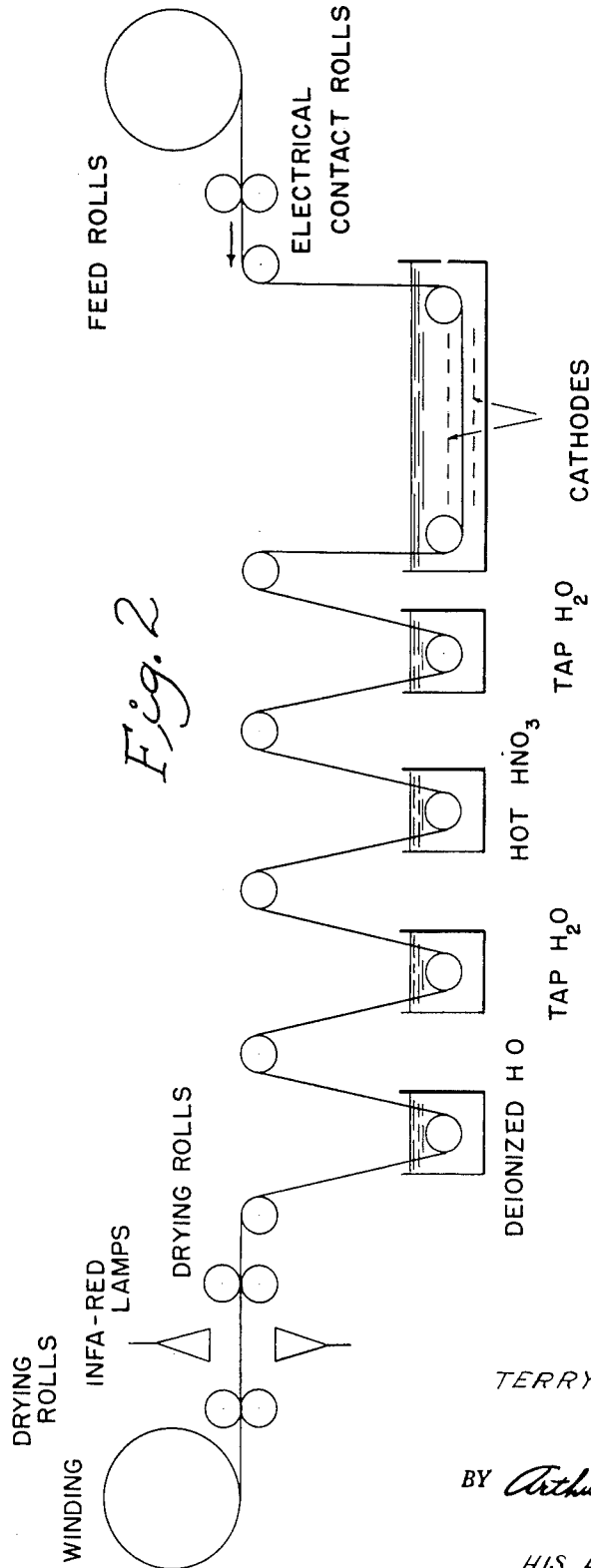
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ELECTROLYTICALLY ETCHED CONDENSER
ELECTRODE

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8 Claims. (Cl. 204—33)

This invention relates to the electrolytic etching of aluminum, and in particular to the formation of etched aluminum anodes for electrolytic capacitors.

It is customary to etch the aluminum anodes used in electrolytic capacitors in order to eat indentations into and thereby increase the effective surface area so that a higher electrical capacity can be obtained from electrodes of the same marginal dimensions. The term "etch ratio" is used in the art to effectively designate the success of this etching operation. The etch ratio of a metal foil is defined by the expression:

$$Re = \frac{\text{Capacitance per unit area of etched foil}}{\text{Capacitance per unit area of plain (unetched) foil}}$$

where Re stands for the etch ratio, the etched and unetched foils are subsequently coated with oxide under the same conditions and the measured capacitances are those of the oxide coating.

A majority of electrolytic condenser electrodes manufactured today are formed of commercial purity aluminum, which has been chemically but non-electrolytically etched. As later will be shown, etch ratios of from $3\frac{1}{2}$ to approximately 7, as the formation voltage of the oxide film is varied, are possible with this type of anode. Prior types of electrolytic etching have not found too wide an acceptance because they are not as simple as the chemical process. High purity aluminum cannot be satisfactorily etched by these chemical methods.

One of the objects of this invention is to provide a method whereby foil may be electrolytically etched so as to provide materially higher etch ratios than are obtained with prior art processes. A further object of this invention is to provide aluminum electrolytic capacitor anodes which have an extremely large effective surface area as compared to the known aluminum anodes. A still further object is to provide a method whereby high purity aluminum foil can be satisfactorily etched. These and other objects of the inventive concept will appear from the following description and claims, considered with the accompanying drawings wherein:

Fig. 1 is a graphical illustration of the improvements provided by the present invention; and

Fig. 2 is a schematic showing of how the process of the present invention can be carried out.

According to this invention these objects are obtained by heating aluminum sheets or foils to give the aluminum a crystal orientation such that the 200 planes (Miller indices of crystal construction) are parallel to the surface of the aluminum, and to relieve strains within the aluminum, and to place the impurities present in it in solid solution and then electrolytically etching this sheet in an aqueous solution of a metal halide. It is to be understood that this reorientation can be measured. It is not known why the heat treatment is effective in enabling higher than normal etch ratios to be obtained, but it is observed that after the heat treatment the etching eats deeper indentations leaving cube-like undissolved columns of aluminum between them.

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The crystal reorientation step with the aluminum is preferably carried out by heating in a furnace at from 500° to just below the melting point (660° C.) for a period of from 15 minutes to 24 hours. Any type of furnace, including an induction furnace may be used. A great deal of latitude is permissible within this step, depending upon the final crystalline orientation which is to be obtained. Any treatment within these limits, however, provides a crystal orientation in which the 200 planes of the aluminum crystals in a rolled aluminum foil or sheet are parallel to the surface.

After an aluminum foil has been heat treated as indicated, it is next electrolytically etched in an aqueous metal halide solution. Any of the soluble halides are satisfactory for this step. The etching is preferably carried out during a period of from 2 to 20 minutes with a current density from $\frac{1}{2}$ to 5 amperes per square inch of anode surface at temperatures ranging from the freezing to the boiling points of the electrolyte used. The temperature of the electrolyte directly affects the size of the etched cubes obtained on the aluminum surface. In general the lower the temperature of the electrolyte, the larger the etched cubes obtained. Higher etching temperatures around 100° C. appear to be most satisfactory when high formation voltages of 300 or more volts are to be used in electrolytically producing an oxide film on the etched aluminum electrode. The lower etching temperatures (50 to 90° C.) are particularly suited for low purity aluminum.

Aluminum foils that have been heat treated and etched in accordance with the present invention may be anodically coated with oxide films according to the known methods presently used in the art at formation voltages of from 50 to 600 volts. In general it is preferred to use as an oxidizing electrolyte an aqueous or non-aqueous solution of ammonia and boric acid, as shown for example in the U. S. Patent No. 2,444,725 to Burnham.

The results obtained with a two hour heat treatment at 600° C. in accordance with the present invention are illustrated in Fig. 1 which also compares the invention with the prior art over the usual range of oxide forming voltages. The term "commercial purity aluminum" as used in connection with this figure, means aluminum which is either 99.88% or 99.80% pure; and the term "high purity aluminum" means aluminum which is 99.99% pure. It is readily seen that electrolytically etched high purity aluminum foil, which has been treated in accordance with this invention, is much more desirable for use in electrolytic condensers than is etched high purity foil which has not been treated. Increased etch ratios are obtained with aluminum of commercial purity. Etch ratios of at least 7.5 have become practical.

In a preferred embodiment of the invention aluminum foil is etched on an apparatus of the type indicated in Fig. 2. As will be seen from this figure, a sheet of heat treated aluminum foil is passed through an electro etching tank between perforated cathodes; is next rinsed in tap water; then rinsed in hot dilute nitric acid; and then again rinsed in tap water; and finally is rinsed with deionized water before being passed through heated drying rolls and past infra-red lamps. A great many modifications of the apparatus pictured in Fig. 2 can be made as will be evident to those skilled in the art. With the illustrated apparatus it is preferable to etch aluminum foil 99.99% pure in an aqueous electrolytic bath containing 1 to 15% NaCl held at 100° C. using an etching period of approximately 10 minutes and a current density of .8 of an ampere per square inch. Aluminum foils as thin as 3 mils have been very successfully etched using this apparatus. The invention is applicable to any foil thickness equal to or greater than two mils.

While it is preferred to carry out the etching operation with a direct current, direct currents with alternating current ripples, half-wave rectified currents, and currents using square, saw-tooth, or other special wave forms may be employed with this invention. Sodium chloride is preferred as an electrolyte because of its low cost and outstanding performance, but soluble bromides, iodides, fluorides, and chlorides of any of the alkali or alkali earth metals may be satisfactorily employed. If desired, wetting agents can be added to the electrolytic etching bath. Pre-cleaning of the aluminum is not necessary with this invention in order to obtain satisfactory results. The heat treated aluminum should not be exposed more than about one to two hours to temperatures below 500° C. before the etching.

The etched and oxide-coated aluminum can be fashioned into electrolytic capacitors in any desired manner with a suitable electrolyte and opposing electrode. One effective technique is described in the above-mentioned Burnham patent.

The unoxidized, etched aluminum foil obtained by this invention is quite pretty and can be advantageously used for decorative effects.

Those skilled in the art will realize that by virtue of the process set forth herein, electrolytic condensers of smaller size per unit of capacity may be readily formed. It will also be realized that the invention herein involved is not to be limited specifically to electrolytic condenser electrodes, but may be employed wherever a large amount of oxide coating or active surface per unit of area is desired, so long as these applications come within the scope of the appended claims.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. The process of electro-etching aluminum foil so as to obtain a greater effective surface area than the marginal dimensions of the surface which process comprises heating an aluminum foil having a purity of at least 99.88% at a temperature of from 500° C. to just below its melting point for from 15 minutes to 24 hours to orient the 200 planes of the metal crystals parallel to the foil surface, and after less than 2 hours exposure to lower temperatures, electrolytically etching said treated foil in an aqueous solution of a halide.

2. The process as defined in claim 1 in which the halide is sodium chloride.

3. An electrolytic condenser electrode comprising an etched aluminum foil of about 99.99% purity in which the 200 planes of the aluminum crystal are parallel to the foil surface and having an etch ratio greater than about 7.5 when formed at 600 volts the foil surface having deep indentations with cube-like columns of aluminum between them.

4. The method of forming an electrolytic condenser electrode which comprises heating an aluminum foil of about 99.88% purity to a temperature between 500 and 660° C. for from 15 minutes to 24 hours so as to orient the 200 planes of the crystalline structure of said foil parallel to its surface, after less than one hour's exposure of the heated foil to temperatures below 500° C. electrolytically etching said surface of the foil in an aqueous solution of a halide, and anodically oxidizing said etched surface to aluminum oxide.

5. The process of claim 1 in which said electrolytic etching is effected by a direct current having alternating current ripples.

6. The process of preparing an etched aluminum foil, which process comprises the steps of heating an aluminum foil of at least 99.88% purity at a temperature of about 600° C. for from 15 minutes to 24 hours, and before the heat treated foil is exposed to temperatures below 500° C. for one hour, anodically etching it in an aqueous solution of a halide selected from alkali metal and alkaline earth halides.

7. The process of claim 6 in which the etching is effected with half-wave rectified alternating current.

8. An electrolytic condenser electrode comprising an etched foil of aluminum having a purity of at least 99.88% the 200 planes of the aluminum crystals in said foil being parallel to the foil surface, the etched aluminum surface having deep indentations with cube-like columns of aluminum the foil being formed and having an etch ratio greater than about 7.5 when formed at 600 volts.

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