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TAKESHI NAMIKATA ET AL

3,477,929

METHOD OF ETCHING ALUMINUM FOIL IN THE MANUFACTURING
OF ALUMINUM ELECTROLYTIC CONDENSERS

Filed April 14, 1967

2 Sheets-Sheet 1

FIG. 1

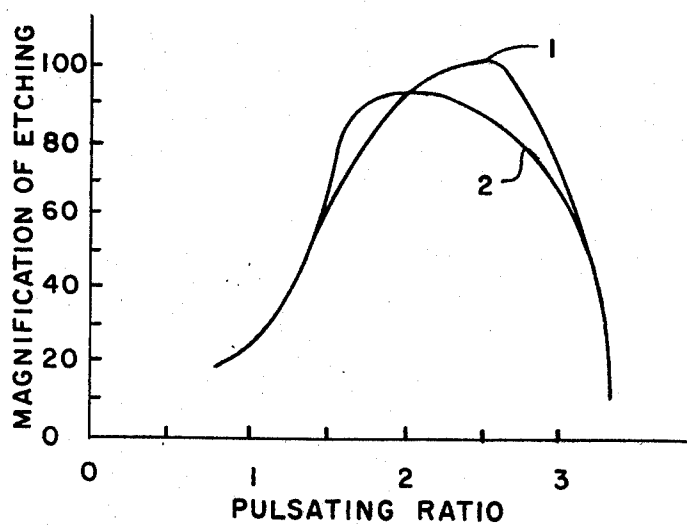
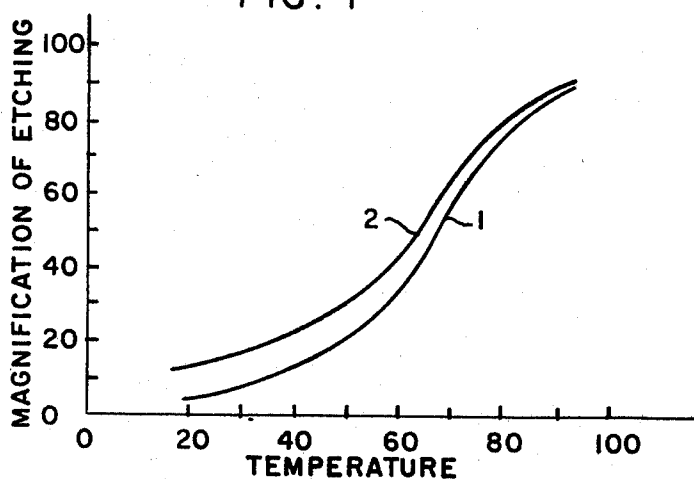


FIG. 2

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FIG. 3

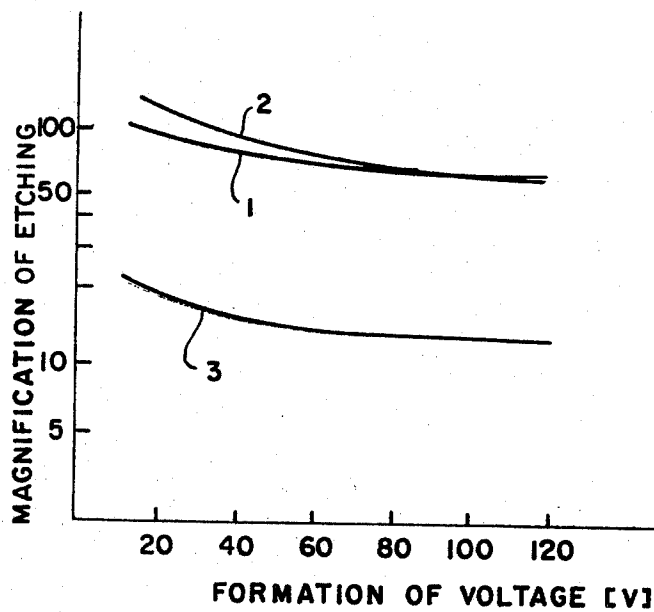
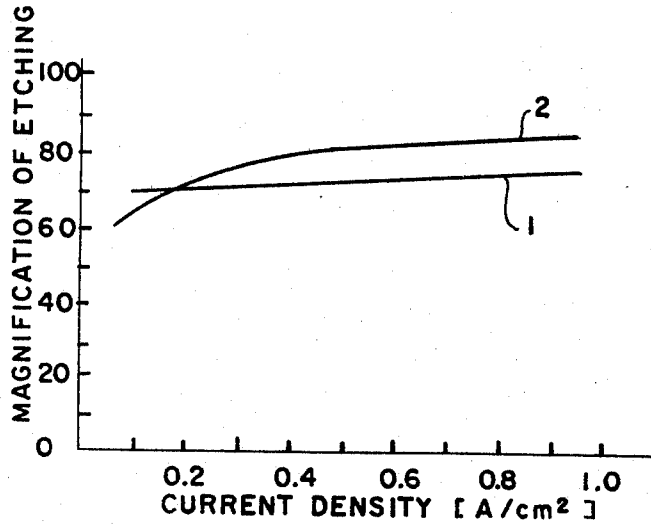


FIG. 4

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METHOD OF ETCHING ALUMINUM FOIL IN THE MANUFACTURING OF ALUMINUM ELECTROLYTIC CONDENSERS

Takeshi Namikata and Kazuo Kubo, Kawasaki-shi, Japan, assignors to Fujitsu Limited, Kawasaki, Japan, a corporation of Japan

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8 Claims

ABSTRACT OF THE DISCLOSURE

Method of etching an aluminum electrode required in the manufacturing process of the electrolytic condenser by applying a pulsating direct current to the aluminum electrode immersed in an aqueous solution made up essentially of Cl^- of 0.02–0.2 mol/l. and CrO_4^{2-} of 0.02–0.1 mol/l.

Our invention relates to a method of manufacturing aluminum electrolytic condensers. In the manufacture of an aluminum electrolytic condenser, the aluminum anode element is etched to increase the effective surface area of the aluminum anode element thus increasing the capacity of the condenser.

In the conventional method, the aluminum anode element is etched electrolytically in a liquid including a large amount of halogen ion. For example, the aluminum anode element is etched electrolytically in an etchant comprising a 16% aqueous solution of HCl using a steady (non-pulsating) direct current at a temperature of about 70°C . for several minutes. However, since a relatively high halogen concentration is present, the entire surface can only be etched to a depth of less than 20μ . It is, therefore, impossible to make the surface area broader than a certain value. Furthermore, since the etching liquid is a weak acid, the pH gradually increases as the etching proceeds and aluminum hydroxide precipitate (or settlings) is produced. These settlings lower the conductivity of the liquid and raise the bath voltage as they are precipitated on the electrode.

Our invention has as an object the obviating of the above-mentioned defects and increasing the effective surface area of the aluminum anode element and inhibiting the settlings of aluminum hydroxide. Our invention makes the aluminum anode element porous by etching. We add corrosion inhibitors, such as chromic acid and chromate, to a solution including halogen ion. The chromic acid simultaneously inhibits the settlings of aluminum hydroxide. We have also found that in the etching of the anode element to make it porous, the etching effectivity can be increased by properly selecting the wave form of the current used and the temperature of the liquid. A pulsating current with a pulsating ratio of voltage [(the maximum value of a voltage—the minimum value of voltage)/the average value of voltage] of 1.5–3 is well suited as the current wave form and $65\text{--}85^\circ\text{C}$. is the optimum temperature. Moreover, in order to further inhibit the settlings of aluminum hydroxide, we lower the pH by adding inorganic acids such as HNO_3 , H_3PO_4 and H_2SO_4 in an amount that the etching form may not be affected.

In the drawings, FIGS. 1, 2, 3 and 4 respectively show variations of magnification (increase) of etching on the ordinate versus, respectively, temperature, pulsating ratio, current density and voltage.

Characteristic features of our etching method:

(1) The etching phenomenon cannot occur if the Cl^-

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concentration is too low, and the etching proceeds uniformly if the Cl^- concentration is too high. In order to etch the anode element to make it porous, the Cl^- concentration should be 0.02–0.2 mol/l. with 0.1 mol/l. the optimum value.

(2) If the CrO_4^{2-} concentration is too much lower than the Cl^- concentration, only the effect of Cl^- appears. It thus becomes difficult to make the anode element porous. On the other hand, if the CrO_4^{2-} concentration is too high, the etching or eroding property of Cl^- is inhibited and a thick film is formed on the surface of the element by the protective property of CrO_4^{2-} thus preventing etching of the element. When the CrO_4^{2-} concentration is 0.02–0.1 mol for a Cl^- concentration of 0.02–0.2 mol/l. and particularly when the CrO_4^{2-} concentration is 0.05 mol/l. for a Cl^- concentration of 0.1 mol/l., the anode element can be made properly porous and the effect of increasing the surface becomes maximized.

(3) The concentration of the inorganic acid added to prevent the precipitation of aluminum hydroxide during the etching, should preferably be higher from the viewpoint of lowering the pH, but it has a certain upper limit since the etching of the anode element to make it porous by the above-mentioned liquid must not be affected. The upper limit of the amount of nitric acid and sulfuric acid that can be added to a liquid of which the Cl^- concentration is 0.1 mol/l. and the CrO_4^{2-} concentration is 0.05 mol/l. is 0.2, mol/l., and the upper limit of phosphoric acid is 0.4 mol/l. Also, the upper limit of the amount of nitric acid and sulfuric acid that can be added to a liquid of which the Cl^- concentration is 0.2 mol/l. is 0.8 mol/l. and the upper limit of phosphoric acid in this case is 0.8 mol/l.

(4) The higher the etching temperature, the greater the surface increase (magnification of etching), but $65\text{--}85^\circ\text{C}$. is the optimum temperature from the practical viewpoint.

(5) Greater effect can be achieved by using the etching method of this invention in combination with the conventional etching method.

(6) As described above, this invention exhibits a particularly valuable effect in the etching of a thick aluminum plate.

The drawings will now be described in greater detail.

FIG. 1 shows the effect on increase of porosity (magnification) in a 50 v. formation when the temperature of the liquid is varied in the examples of this invention. Curve 1 corresponds to Example 1 and curve 2 corresponds to Example 3.

FIG. 2 shows the effect on magnification in a 50 v. formation when the pulsation factor of the etching voltage is varied according to the examples. Curve 1 corresponds to Example 1 and curve 2 corresponds to Example 3. It can be seen from this figure that 1.5–3 is the optimum pulsation factor.

FIG. 3 shows the variation of magnification in a 50 v. formation when the current density is varied according to the examples. Curve 1 corresponds to Example 1 and curve 2 corresponds to Example 3. It can be seen from the figure that the influence of current density is not great.

FIG. 4 shows the relation between the formation voltage and the magnification of etching. Curve 1 corresponds to Example 1 and curve 2 corresponds to Example 3 with curve 3 corresponding to the conventional etching method.

EXAMPLES

Example 1: A smooth aluminum plate of a purity of 99.99% and a thickness of 1 mm. was etched electrolytically for 10 minutes in an aqueous solution of HCl of 0.1 mol/l. and CrO_3 of 0.05 mol/l., at 80°C ., using a pulsating current of single phase full wave (pulsation factor 1.6) with a current density of 0.6 a./cm^2 . This was formed at 50 v. and then the electrostatic capacity on both sur-

faces of 1 cm.² was 19 μ f. This is 79 times as great as the case of the smooth surface.

Example 2: An aluminum plate of a thickness of 1 mm. was etched electrolytically for 10 minutes in an aqueous solution containing 0.1 mol/l. of HCl, 0.05 mol/l. of CrO₃ and 0.1 mol/l. of HNO₃, at 80° C., by the use of a pulsating current of single phase full wave of a current density of 0.6 a./cm.². The same magnification as in Example 1 was obtained. Furthermore, settlings of aluminum hydroxide were precipitated when a current of 10 a.h. was flowed per 1 liter of the liquid of Example 1 including no HNO₃, but in the case of the liquid of this example including HNO₃, the settlings of aluminum hydroxide did not precipitate until the current was increased to 35 a.h. per liter of the liquid. The increase of the bath voltage was also slight making it possible to continue etching under a stable condition.

Example 3: A smooth aluminum plate of a purity of 99.99% and of a thickness of 1 mm. was first etched electrolytically, weakly for 60 seconds in an aqueous 16% solution of HCl at 70° C. by a direct current of a current density of 0.7 a./cm.² including no ripple and was then etched deeply by the method of Example 2. This was formed at 50 v. The electrostatic capacity on both surfaces of 1 cm.² was 21 μ f. and the magnification of etching (surface increase) as against the smooth surface was 87 times.

Example 4: An aluminum plate was etched electrolytically in an aqueous solution including 0.2 mol/l. H₃PO₄ instead of HNO₃ in Example 2 and by the same method as the case of Example 2. The same magnification and stability as in Example 2 were obtained.

Example 5: An aluminum plate was etched electrolytically in an aqueous solution including 0.1 mol/l. H₂SO₄ instead of HNO₃ in Example 2 and by the same method as the case of Example 2. The same magnification and stability as in Example 2 were obtained.

Example 6: A smooth aluminum plate of a purity of 99.99% and a thickness of 1 mm. was dipped for 90 seconds in an aqueous solution containing 5% HCl and 0.3% CuSO₄ at a bath temperature of 65° C. The copper precipitated on the aluminum plate was resolved (dissolved) and removed by dipping the plate in a cold concentrated nitric acid. The thus etched aluminum plate was then etched deeply by the method of Example 2. The porous aluminum plate thus obtained was formed at 50 v. and then the electrostatic capacity amounted to 90 times that of the smooth surface.

Example 7: An aluminum wire of a purity of 99.99%

and a diameter of 3 mm. was etched electrolytically and was made porous by the same method as Example 4. This was formed at 50 v. and then the electrostatic capacity per 1 cm. of the wire was 8 μ f. This is 70 times as great as the electrostatic capacity of the wire the surface of which is left smooth.

When a red ink is dropped onto the surfaces of the aluminum anode elements obtained by the methods of the above-mentioned examples, the reverse surfaces turned red. Thus it is shown that the etched holes penetrate through the elements.

We claim:

1. A method of manufacturing aluminum electrolytic condensers, which comprises electrolytically etching the aluminum as the anode using a pulsating current with a pulsation factor of 1.5-3 in an aqueous solution consisting essentially of 0.02-0.2 mol/l. Cl⁻ and 0.02-0.1 mol/l. CrO₄²⁻ in a pH range at which the precipitation of aluminum hydroxides is minimized.

2. The method of claim 1, wherein the etching bath is at a temperature of 65-85° C.

3. The method of claim 1, wherein 0.05-0.4 mol/l. HNO₃ is added to maintain the pH within said range.

4. The method of claim 3, wherein the aqueous solution is at a temperature of 65-85° C.

5. The method of claim 1, wherein 0.05-0.8 mol/l. H₃PO₄ is added to maintain the pH within said range.

6. The method of claim 5, wherein the aqueous solution is at a temperature of 65-85° C.

7. The method of claim 1, wherein 0.05-0.4 mol/l. H₂SO₄ is added to maintain the pH within said range.

8. The method of claim 7, wherein the aqueous solution is at a temperature of 65-85° C.

References Cited

UNITED STATES PATENTS

2,721,835	10/1955	Axtell	204-141
2,755,238	7/1956	Turner	204-141
2,930,741	3/1960	Burger et al.	204-141
3,035,990	5/1962	Davis et al.	204-33
3,085,950	4/1963	Thomas et al.	204-141
3,249,523	5/1966	Post et al.	204-141
3,321,389	5/1967	Anderson	204-141

ROBERT K. MIHALEK, Primary Examiner

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