GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.


Index at acceptance—70C5(L/V/II(5))

PROVISIONAL SPECIFICATION

"INVENTION RELATING TO A NEW METHOD OF ETCHING OF SUPER PURITY ALUMINIUM FOR USE AS ELECTRODES IN ALUMINIUM ELECTROLYTIC CAPACITORS".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI 1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification describes the nature of this invention.

This invention relates to improvements in or relating to etching of super purity aluminium for use as electrodes in aluminium electrolytic capacitors.

Miniaturisation of electronic components is the modern trend in electronic industries. Since electrolytic capacitor is one of the important components, used in large numbers in electronic equipment, miniaturisation in this field has been achieved by newer developments in the etching technique. The degree of etching of the aluminium foil determines the ultimate size of the capacitor and is expressed as etch ratio. It is the ratio of the capacitance of an etched and formed foil to the capacitance of the plain foil of similar area and also formed at the same voltage. Till a few years ago, it was felt that it was not possible to go beyond an etch ratio of 10-14.

Hitherto it has been proposed to treat the foil anodically in a chloride solution using pure direct current or alternating current superimposed on direct current or square wave or direct current with various percentages of pulsation. Heat treatment of the etched foil or etching with special electrolytes have also been proposed.

This is open to the objection that direct current with known formulations does not give etch ratio more than 12 at 15 volts.

Though AC superimposed DC is used for etching aluminium foil to get high etch ratio, it requires special generators for the AC source and suitable filters which are very costly. AC to be superimposed is of special frequency.

In the case of heat treatment of the etched foil before forming to get high etch ratio, it requires a separate continuous annealing unit after etching. Furthermore, it involves the same period for annealing as we require for etching which ultimately affects the rate of production of the etched foil. Moreover, the careful design of the continuous annealing unit for maintaining the uniform optimum temperature throughout the furnace is essential. The equipment is also very costly.

The object of this invention is to obviate the disadvantages by using ultrasonic technique for etching aluminium foils to obtain desired high etch ratio and further improvement in the etch ratio can be obtained by using the process of annealing of the ultrasonically etched foil. In the course of our investigation, we find that ultrasonic etching gives an etch ratio of 30 to 50 times greater than the value obtained by conventional etching procedure irrespective of the electrolyte used for etching.

To this end, the invention broadly consists of etching aluminium foil in a suitable etching electrolyte using ultrasonic sound waves of frequencies of the order of 200 k/cps per second.

The following examples are given to illustrate the invention.

Example 1

Electrolyte for etching:

200 gms of Analytical Reagent BDH sodium chloride dissolved in 2 litres of water.

Temperature of the electrolyte 98 to 100°C.

Ultrasonic frequency: 200 kilocycles per second.

Etching is carried out using super purity aluminium as anode and stainless steel cathode at a current density of 0.4 A/sq. cm for 70 seconds. It is then formed at 30 volts in 0.5% dihydrogen ammonium orthophosphate solution and then measured in an electrolyte containing 12 gms/litre of ammonium pentaborate adjusting the resistance by addition of ammonia to 129 ohms. A plain aluminium foil is treated with 10% NaOH solution kept at 40°C for two minutes and washed with tap water and then with deionised water. The above plain foil is used as the cathode for measuring the capacitance.

| Etch ratio of the foil etched in ultrasonic vibration | 12 |

Example 2

Electrolyte for etching:

200 gms of AR BDH grade sodium chloride plus 140 gms of chromium trichloride dissolved in 2 litres of water.

Temperature of the electrolyte: 98 to 100°C

Ultrasonic frequency: 200 kilocycles per second.

Etching is carried out using super purity aluminium as anode and stainless steel cathode at a current density of 0.29 A/sq. cm for 70 seconds in the ultrasonic medium. Since forming the etched foil after treating it in diluted nitric acid and washing with tap water and subsequently with deionised water, is rather difficult, the foil after ultrasonic etching is treated in 1% phosphoric acid at 80°C for five minutes. After this treatment, the usual method of washing is carried out. Forming and measuring are carried out as stated in Example 1.

| Etch rate of the foil etched and formed under identical condition without imparting ultrasonic vibrations | 22-23 |

| Etch rate of the foil etched in the ultrasonic vibration | 30-31 |

Price: TWO RUPEES.
Example 3

Electrolyte for etching:

300 grams of AR BDH grade sodium chloride plus 240 grams of ammonium persulphate dissolved in 2 litres of water.

Temperature of the electrolyte: 98 to 100°C.

Ultrasonic frequency: 200 kilocycles per second.

Etching is carried out using super purity aluminium as anode and stainless steel cathode at a current density of 0.39 A/sq. cm for 95 seconds in the ultrasonic medium. The foil is treated in diluted nitric acid for 2 minutes washed with tap water and finally with distilled water. Forming and measuring are carried out as stated in Example No 1.

Electrolyte for etching:

200 grams of AR BDH grade sodium chloride plus 140 grams of chromium trioxide dissolved in 2 litres of water.

Temperature of the electrolyte: 98 to 100°C.

Ultrasonic frequency: 200 kilocycles per second.
The investigation is carried out as follows:

1" x 4" super pure aluminium foil of purity 99.99% is anodically etched in two litres of the etching solution using stainless steel as cathode. The solution is agitated using an ultrasonic unit. A current density in the range of 0.3 A/sq. cm. to 0.6 A/sq. cm. is applied from a three-phase rectifier for a period of 70.55 seconds depending on the nature of the electrolyte.

The etched foil is formed to 30 volts in a forming electrolyte containing 0.1% dihydroxy ammonium orthophosphate at 80°C till a minimum leakage current of 100-125 μA/sq. in. for super pure aluminium (99.99%) is obtained.

The capacitance is measured in a capacitance bridge by applying 4/5th of its forming voltage in a measuring electrolyte containing 5% boric acid at room temperature whose resistivity is adjusted to 100 ohm cm/cm² by means of ammonia. The ech ratio values stated in the examples are calculated by dividing the capacitance of the etched foil with the capacitance of the plain foil of the same geometrical area when both the foils are formed and measured under identical conditions.

The following examples are given to illustrate the invention:

**Example 1**

<table>
<thead>
<tr>
<th>Etching electrolyte</th>
<th>200 grams of Analytical Reagent grade sodium chloride dissolved in 2 litres.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of etching electrolyte</td>
<td>95°C - 100°C</td>
</tr>
<tr>
<td>Anode</td>
<td>Stainless steel (99-99%) foil</td>
</tr>
<tr>
<td>Cathode</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Current density</td>
<td>0.4 A/sq.cm</td>
</tr>
<tr>
<td>Duration</td>
<td>70 seconds</td>
</tr>
<tr>
<td>Ultrasonic frequency</td>
<td>200 kilocycles per second</td>
</tr>
<tr>
<td>Ech ratio of the foil etched without using ultrasonic vibrations</td>
<td>12</td>
</tr>
<tr>
<td>Ech ratio of the etched foil in ultrasonic vibrations</td>
<td>15</td>
</tr>
</tbody>
</table>

**Example 2**

<table>
<thead>
<tr>
<th>Etching electrolyte</th>
<th>200 grams of Analytical Reagent grade Sodium Chloride plus 140 grams ofchromium trioxide dissolved in 2 litres of water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching conditions</td>
<td>38°C - 100°C</td>
</tr>
<tr>
<td>Anode</td>
<td>Super pure aluminium (99-99%) foil</td>
</tr>
<tr>
<td>Cathode</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Current density</td>
<td>0.4 A/sq.cm</td>
</tr>
<tr>
<td>Duration</td>
<td>70 seconds</td>
</tr>
<tr>
<td>Ultrasonic frequency</td>
<td>200 kilocycles per second</td>
</tr>
<tr>
<td>Ech ratio of the foil etched without using ultrasonic vibration</td>
<td>20-23</td>
</tr>
<tr>
<td>Ech ratio of the etched foil in ultrasonic vibration</td>
<td>20-23</td>
</tr>
</tbody>
</table>

**Example 3**

- Etching electrolyte: 500 grams of Analytical Reagent grade sodium chloride plus 240 grams of ammonium persulphate dissolved in 2 litres of water.
- Ech ratio of the foil etched without using ultrasonic vibrations: 22-23
- Ech ratio of the etched foil in ultrasonic vibration: 31-32

**Example 4**

Electrolyte for etching:

- 300 grams of Analytical Reagent BDPS sodium chloride plus 240 grams of ammonium persulphate dissolved in 2 litres of water.
- Ech ratio of the foil etched without using ultrasonic vibrations: 22-23
- Ech ratio of the etched foil in ultrasonic vibration: 22-26

Following are the main advantages of this invention:

It is possible to obtain an etch ratio of 30-32 at 30V by etching in ultrasonic medium. Moreover, a 2 kw ultrasonic generator is sufficient for continuous production of etched aluminium foil.

WE CLAIM:

1. A process for etching of super pure aluminium foil of 99.99% purity using an etching electrolyte containing an aqueous solution of soluble chloride and one or more film forming compound at a temperature of 98 to 100°C and at a current density of 0.16 to 0.64 A/cm² wherein an ultrasonic vibration of frequencies ranging from 40 to 200 KHz is passed to increase the etch ratio by 35 to 50% of its original value.

2. A process for etching of super pure aluminium as claimed in Claim 1 wherein etching is carried out with aluminium foil of thickness 25 microns to 200 microns.

Dated this 16th day of August 1972.

(R. BHASKAR PAI)

PATENTS OFFICER,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.