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

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PROVISIONAL SPECIFICATION

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

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 is 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 percentage 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 invloves the same period for annealing as we require for eaching 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% greater than the value obtained by conventional etching procedure irrespective of the electrolyte used for etching.

To these ends, 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/cs 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 0.4A/sq. cm for 70 seconds. It is then formed at 30 volts in 0.25% 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 120 ohms. A plain aluminium foil is treated with 10% NaOH solution kept at 40°C for two minutes and washed with tape 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 and formed under identical condition without impressing ultrasonic vibrations	12
Etch ratio of the etched foil in ultrasonic vibration	15

Example 2

Electrolyte for etching :

200 gms of AR BDH grade sodium chloride plus 140 gms of chromium trioxide 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 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 ratio of the foil etched and formed under identical condition without impressing ultrasonic vibrations	22-23
Etch ratio of the etched foil in the ultrasonic vibration	30-31

Price : TWO RUPEES.

Example 3

Electrolyte for etching :

300 grams of AR BDH grade sodium chloride plus 240 gms 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.

Etch ratio of the foil etched and formed under identical conditions without impressing ultrasonic vibrations	24-26
Etch ratio of the etched foil in ultrasonic vibration	30-32

Example 4

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.

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 field. 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 altrasonic etching is treated in 1% phosphoric acid at 80°C for 5 minutes. After this treatment the foil is subjected to heat treatment at 600°C for 1½ to 2 hours in the presence of air and gradually cooled to room temperature. Forming and measuring are carried out as stated in Example I.

Etch ratio of the foil etched and formed under identical conditions without impressing ultrasonic vibrations	22-23
Etch ratio of the foil etched under identical conditions in the ultrasonic vibration and annealing and then forming under identical condition	40-45

The following are the main advantages of the invention :

1. It is possible to obtain etch ratio of 30-32 by adopting ultrasonic etching.

2. The ultrasonic etched foil is susceptible for further increase in etch ratio to 40-45 using the process of annealing and thereby reduction in the volume/size of the capacitor is achieved which is the main trend in the miniaturisation of electronic components.

Dated this 6th day of September, 1971.

(Sd.)
(R. BHASKAR PAI)
PATENTS OFFICER,
Council of Scientific and Industrial Research.

COMPLETE SPECIFICATION

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

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)

THIS IS AN INVENTION BY BALKUNJE ANANTHA SHENOI, SCIENTIST, VENKATASUBRAMANIAN LAKSHAMINARASIMHAN, SENIOR SCIENTIFIC ASSISTANT AND DEVARAJ KANAGARAJ, JUNIOR SCIENTIFIC ASSISTANT, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-623003, INDIA, ALL INDIAN CITIZENS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates more particularly to a new method of etching of super pure aluminium of purity 99.99% for use as anode in electrolytic capacitor industry.

Hitherto it has been proposed to treat the aluminium foil anodically in a soluble 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 objection in that etching in conventional sodium chloride electrolyte using pure direct current does not give etch ratio of more than 12 at 30V. Superimposition of alternating current over direct current requires an alternating current source to deliver high current output at 130 HZ. The equipment also requires suitable chokes and filters. Similarly, special type of equipment are required for producing pulsating direct current. Such equipment are costly and probably have to be imported if indigenous sources are not available. Etching in special electrolytes described in our earlier patent also do not give an etch ratio more than 20-22 at 30V.

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. Careful design of the continuos annealing unit for maintaining the uniform optimum temperature throughout the furnace is essential. The continuous annealing furnace may cost over two lakhs of rupees and it requires 350 KW electric power for the operation.

The object of this invention is to get high etch ratio values by etching aluminium or its alloys in an etching electrolyte which is subjected to ultrasonic vibration.

The main finding in this invention is that etching of super pure aluminium foil of purity 99.99% in an etching electrolyte which is subjected to ultrasonic vibration increases the etch ratio by 35 to 50% of its original value whatever may be the electrolyte used for etching.

The present invention consists of 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 0.16A to 0.64 A/Cm^2 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.

By adopting the method described in this invention, the heat treatment step after etching process can be dispensed with by subjecting the etching electrolyte to ultrasonic vibration during etching process.

The investigation is carried out as follows :

1"×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 70-95 seconds depending on the nature of the electrolyte.

The etched foil is formed to 30 volts in a forming electrolyte containing 0.1% dihydrogen ammonium orthophosphate at 85°C till a minimum leakage current of 100-125 μA sq. in. for super pure aluminium (99.99%) is obtained.

The capacitance is measure in a capacitance bridge by appling 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/cm^2 by means of ammonia. The etch 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

Etching electrolyte . .	200 grams of Analytical Reagent Sodium Chloride dissolved in 2 litres.
Temeprature of etching electrolyte.	98°-100°C
Anode	Super pure aluminium (99·99%) foil.
Cathode	Stainless steel.
Current density . . .	0·4 A/cm^2
Duration	70 seconds.
Ultrasonic frequency . .	200 kilocycles per second.
Etch ratio of the foil etched without impressing ultrasonic vibrations . . .	12
Etch ratio of the etched foil in u trasonic vibrations . . .	15

Example 2

Etching electrolyte . :	200 grams of Analytical Reagent grade Sodium Chloride plus 140 grams of chromium trioxide dissolved in 2 litres of water.
Etching conditions :	
Temperature of etching electrolyte . . :	98°-100°C
Anode . . . :	Super purity aluminium (99·99%) foil.
Cathode . . . :	Stainlesssteel
Current density . . :	0·4 A/sq. cm.
Duration . . . :	70 seconds.
Ultrasonic frequency .	200 kilocycles/second
Etch ratio of the foil etched without impressing ultrasonic vibration . . .	20-23
Etch ratio of the etched foil in the ultrasonic vibration . .	30-31

Example 3

Etching electrolyte .	300 grams of Analytical Reagent grade sodium chloride plus 240 grams of ammonium persulphate dissolved in 2 litres of water.
Etching conditions .	
Temperature of etching electrolyte . .	98°-100°C
Anode . . .	Super purity aluminium (99·99%) foil.
Cathode . . .	Stainless steel
Current density . .	0·4 A/sq.cm.
Duration . . .	95 seconds
Ultrasonic frequency .	200 kilocycles/second
Etch ratio of the foil etched without impressing ultrasonic vibrations . . .	22-23
Etch ratio of the etched foil in ultrasonic vibration: . . .	31-32

Example 4

Electrolyte for etching :

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

Etching condition : .	
Temperature of etching electrolyte : . .	98°-100°C
Anode . . .	Super purity aluminium (99·99%) foil.
Cathode . . .	Stainlesssteel
Current density . .	0·4 A/sq.cm.
Duration . . .	95 seconds
Ultrasonic frequency .	45 kilocylces/second
Etch ratio of the foil etched without impressing ultrasonic vibration . .	22-23
Etch ratio of the etched foil in the ultrasonic vibration. . .	25-26

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/cm^2 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 10th day of August 1972.

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