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

Complete Specification No. 131900. Application and Provisional Specification filed on 29th June, 1971. Complete Specification filed on 28th March, 1972. (Acceptance advertised on 16th March, 1974.)

Index at acceptance—31A [LVIII(2)]

PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO HEAT TREATMENT OF ETCHED ALUMINIUM AND ITS ALLOY 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 IS AN INVENTION BY SHRI BALKUNJE ANANTHA SHENOI, SCIENTIST, SHRI KANDADAI RAJA GOPALACHARI NARASIMHAN, SCIENTIST, SHRI VENKATASUBRAMANIAN LAKSHMINARASIMHAN, SENIOR SCIENTIFIC ASSISTANT AND DEVARAJ KANAGARAJ, JUNIOR SCIENTIFIC ASSISTANT, ALL ARE INDIAN NATIONALS AND ALL ARE EMPLOYED IN CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, TAMIL NADU, INDIA.

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

The modern trend in electronic industry is miniaturisation. The recent developments in solid state physics have made it possible to replace almost all components in an electronic gadget by tiny ones. Electrolytic capacitor is another component which is used in large numbers in any electronic equipment and miniaturisation in this field has been achieved by newer developments in the etching technique. Etching aluminium foil is carried out electrolytically to increase the surface area and thereby reduce the over-all size of the capacitors. 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 (unetched) 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. Now with developments in the rolling and etching technique, it is possible to obtain etch ratio of 25—30.

Hitherto it has been proposed to treat the foil anodically in soluble chloride solution using either pure DC or AC super-imposed DC.

This is open to the objection that the use of DC with known formulations does not give etch ratio more than 12 at 25 volts. AC superimposed DC source is used for etching aluminium foil to produce high etch ratio. But special generators for the AC source as well as suitable filters like choke etc. are needed which are very costly.

Annealing the foil during the rolling process to the desired thinner gauges is said to improve the etch ratio and here again, the etch ratio reported is also not above 15 or 16.

In our earlier patent (Provisional Specification No.) we have claimed that it is possible to increase the etch ratio from 12 to values near about 22 by the use of suitable electrolyte composition. We have now found that it possible to increase etch ratio claimed in the above stated patent by another 30 to 40% i.e. from 22 to 30 by suitable heat treatment of the etched foil before forming.

In the course of our investigation, we find that the heat treatment of the etched foil increases the etch ratio by 30 to 50% of its original value whatever may be the electrolyte used for etching such as sodium chloride etc.

To these ends, the invention broadly consists in etching the aluminium foil by the conditions described in our earlier two patents (No. 100313 dated 29-6-1965 and the patent sent for filing in February 1971) and then annealing the etched foil at suitable temperatures 450° to 600°C in presence of air or oxygen or any inert gases like nitrogen or hydrogen for periods ranging from 20 minutes to 2 hours.

The following examples are given to illustrate the invention:

Example 1

Electrolyte for etching

200 gms of AR sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water.

Temperature of the electrolyte: 98 to 100°C

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 72 seconds. The foil is then washed and kept at 550°C for one and half hours for annealing in the presence of air and gradually cooled to room temperature. It is then formed at 30 volts in 0.1% dihydrogen ammonium orthophosphate solution and then measured in an electrolyte containing 12 gm/litre of ammonium pentaborate adjusting the resistance by the addition of NH_3 to 120 ohms. The aluminium foil is treated with 10% NaOH solution kept at 40°C for two minutes and washed with tap water and then with dcionized water. The above treated foil is used as the cathode for measuring the capacitance of the annealed and formed foil.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated above)	21.4
After annealing (fresh foils etched as described above are annealed and then formed as described above and measured)	28.0

Price: TWO RUPEES.

Example 2

Electrolyte for etching

200 grams of AR grade sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water.

Temperature of the electrolyte: 98 to 100°C

Etching of the super purity foil is carried out as described under Example 1. The foil is then washed and kept at 600°C for one and half hours in the presence of air and then gradually cooled to room temperature. Forming and measuring are carried out as stated in Example 1.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated above)	22
After annealing (fresh foils etched as described above are annealed and then formed as described above and measured)	30.3

Example 3

Electrolyte for etching: 200 grams of AR sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water. Temperature of the electrolyte: 98° to 100°C.

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 72 seconds. The foil is then washed and kept at 600°C for 2 hours for annealing in the presence of oxygen and gradually cooled to room temperature. Forming and measuring are carried out as stated in Example 1.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated above)	22
After annealing (fresh foils etched as described above are annealed and then formed as described above and measured)	31

Example 4

Electrolyte for etching

200 grams of AR grade sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water.

Temperature of the electrolyte: 98° to 100°C

Etching of the aluminium alloy containing not less than 99.5% aluminium suitable for use as cathode in electrolytic capacitor is carried out as described under Example 1. The foil is then washed and kept at 600°C for one and half to two hours in the presence of air and cooled gradually cooled to room temperature. Forming and measuring are carried out as stated in Example 1.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated above)	31.0
After annealing (fresh foils etched as described above are annealed and then formed as described above and measured)	43.0

Example 5

Electrolyte for etching

200 grams of AR grade sodium chloride dissolved in 2 litres of water.

Temperature of the electrolyte: 98° to 100°C.

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 72 seconds. The foil is then washed and kept at 60°C for 2 hours for annealing in the presence of air and gradually cooled to room temperature. Forming and measuring are carried out as stated in the Example 1.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated before)	13.5
After annealing (fresh foils etched as described above are annealled and then formed as described above and measured)	19.0

Example 6

Electrolyte for etching

200 grams of AR grade sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water.

Temperature of the electrolyte: 98° to 100°C.

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 72 seconds. The foil is then washed and kept at 600°C for 2 hours for annealing in the presence of hydrogen and gradually cooled to room temperature. Forming and measuring are carried out as stated in Example 1.

Etch ratio of the etched foil before annealing (the etched foil is formed at 30V and measured as stated before	21.0
After annealing (fresh foils etched as described above are annealed and then formed as described above and measured)	26.00

The following is the main advantage of the invention:

It is possible to obtain each ratio of 28—30 by adopting the correct condition 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 21st day of June, 1971.

Sd./-

PATENTS OFFICER,
Council of Scientific & Industrial Research.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO HEAT TREATMENT OF ETCHED ALUMINIUM AND ITS ALLOY FOR USE AS ELECTRODES IN ELECROLYTIC 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 particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

THIS IS AN INVENTION BY BALKUNJE ANANTHA SHENOI, SCIENTIST, KANDADAI RAJAGOPALACHARI NARASIMHAN, SCIENTIST, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, SENIOR SCIENTIFIC ASSISTANT AND DEVARAJ KANAGARAJ, JUNIOR SCIENTIFIC ASSISTANT, ALL ARE INDIAN NATIONALS AND ARE EMPLOYED IN CENTRAL ELECRTOCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, TAMIL NADU, INDIA.

This invention relates to the improvements in or relating to heat treatment of etched aluminium foil of purity 99.99% for use as anode or its alloys purity of 99.4% to 99.98% for use as cathode in electrolytic capacitor industry.

Hitherto it has been proposed to heat treat the plain aluminium foil or its alloys at 350 to 600°C for 15 minutes to 24 hours before etching operation.

This is open to the objection in that heat treatment of aluminium foils before etching operation does not give an etch ratio of more than 8 to 12 at 100 volts. The increase in surface area of the foil after etching operation is expressed in terms of etch ratio. Etch ratio is defined as ratio of capacitance of the etched foil to that of the plain foil of same geometrical area when formed and measured under indentical conditions.

The main object of this invention is to increase the etch ratio of the etched aluminium or its alloys by heat treatment process.

The main finding in this investigation is that the heat treatment of etched aluminium or its alloys increases the etch ratio by 35 to 50% of its original value whatever may be electrolyte used for etching aluminium or its alloys. Etching the aluminium or its alloys followed by heat treatment of these etched foils at 400 to 600°C in the presence of air or oxygen for half an hour to 2½ hours increases the etch ratio of the foil by 35 to 50% of its initial value i.e. from 30 to 42 at 30V.

According to the present invention, there is provided a process for the heat treatment of aluminium or its alloys for use as electrodes in electrolytic capacitors by heating aluminium foil or its alloys up to 600°C characterised in that the heat treatment is imparted to etched foil (instead of the conventional heat treatment on plain foil before etching) further characterised in that the heating of the etched foil is done at 400 to 600°C in the presence of air or other gases for a period ranging from half an hour to 2½ hours whereby etch ratio of the etched foil is increased by 35 to 50%.

Air or a gas like oxygen or hydrogen or nitrogen is circulated during heat treatment.

Etched super pure aluminium foil of purity 99.99% or its alloy of purity 99.4% to 99.98% may be used for heat treatment.

The process comprises heat treatment of aluminium or its alloys in the form of a thin foil of thickness in the range between 25 and 250 micron wherein the etched aluminium or its alloy is kept at 400 to 600°C in the presence of air or oxygen or gases like nitrogen or hydrogen for a period ranging from half an hour to 2½ hours to increase the etch ratio by 35 to 50% of its initial value.

The invention is carried out as follows:

Super pure aluminium of purity 99.99% or its alloy of purity 99.5% in the form of a thin foil of size 1"×4" is anodically etched in two litres of etching solution using stainless steel as cathode. The foils are etched according to the conditions described in our earlier patents. The foil after etching is washed with tap water and then with deionised water.

The foil is heat-treated in a suitable oven provided with automatic temperature control at 400 to 600°C in the presence of air or oxygen for a period ranging from half an hour to 2½ hours. The foil is removed from the oven and cooled to room temperature.

The heat-treated foil is then anodically oxidised at 30 volts to form the dielectric oxide layer in a forming electrolyte containing 0.25% dihydrogen ammonium orthophosphate at 85°C till a minimum leakage current of 100 to 125 μ A/in^2 for super pure aluminium foil and 600—700 μ A/in^2 for commercial grade aluminium foil is obtained.

The capacitance is measured in a capacitance bridge at 25V in a measuring electrolyte containing 12 g/l of ammonium pentaborate at room temperature whose resistance is adjusted to 120 ohms with ammonia. The aluminium foil used as cathode for measurement is treated with 10% sodium hydroxide solution kept at 40°C for two minutes and washed with tap water and then with deionised water.

The etch ratio values stated in this invention are calculated by dividing the capacitance of etched and heat treated foil with the capacitance of plain foil of the same geometrical area.

The following typical examples are given to illustrate the invention:

Example 1

Etching condition: 200 grams of sodium chloride plus 200 grams of tartaric acid dissolved in 2 litres of water.

Temperature	98—100°C
Anode	Super pure aluminium (99·99%)
Cathode	Stainless steel
Current density	0·39 A/sq. cm
Duration	100 seconds

The foil is heat treated for 1½ hours in the presence of air at 550°C. It is then cooled to room temperature.

Etch ratio of the etched foil at 30V (without heat treatment).	21·4
Etch ratio of the etched and then heat treated foil at 30V.	28·0

Example 2

Etching is carried out with super pure aluminium foil as described in Example 1.

The foil is then heat treated at 600°C in the presence of oxygen for a period of two hours and then cooled to room temperature.

Etch ratio of the etched foil at 30V (without heat treatment)	22.0
Etched ratio of etched and then heat treated foil at 30V.	31·2

Example 3

Etching is carried out with super purity aluminium foil as described in Example 1.

The foil is then heat treated in the presence of hydrogen at 580°C for 1½ hours and then gradually cooled to room temperature.

Etch ratio of the etched foil at 30V . . .	21·0
Etch ratio of the etched and heat treated foil at 30V.	26·0

Example 4

Etching condition: 200 grams of AR sodium chloride dissolved in 2 litres of water.

Temperature . .	98—100°C
Anode . . .	Super pure aluminuum 99·99%
Cathode . . .	Stainless steel
Current density . .	0·48 A/cm²
Duration . . .	75 seconds

The foil is heat treated in the presence of air for two hours at 600°C and gradually cooled to room temperature.

Etch ratio of the etched foil at 30V . .	13·5
Etch ratio of the etched and heat treated foil at 30V.	19·0

Example 5

Etching condition: 200 grams of sodium chloride plus 140 grams of chromic acid dissolved in 2 litres of water.

Temperature . .	98—100°C
Anode . . .	Suder pure aluminum (99·99%)
Catnode . . .	Stainless steel
Current density . .	0·48 A/cm²
Duration . . .	86 seconds

The foil is heat treated for one hour in the presence of air at 550°C and then gradually cooled to room temperature.

Etch ratio of etched foil at 30V . . .	19·3
Etch ratio of etched and heat treated foil at 30V	28·2

Example 6

Etching is carried out with super pure aluminium foil as described in Example 5 in ultrasonic medium.

The foil is then heat treated in the presence of air for one hour at 550°C.

Etch ratio of etched foil at 30V . . .	28·4
Etch ratio of etched and heat-treated foil at 30V	41·8

Example 7

Etching is carried out with commercial purity aluminium foil of purity 99.5% as described in Example 4.

The foil is then heat treated at 500°C for one and a half hours in the presence of air and then it is cooled gradually to room temperature.

Etch ratio of etched foil at 30V . . .	11
Etch ratio of etched and then heated foil at 30V	17

Example 8

Etching condition: 200 grams of sodium chloride plus 140 grams of chromic acid dissolved in 2 litres of water.

Temperature . .	98—100°C
Anode . . .	Super pure aluminium (99·99%)
Cathode . . .	Stainless steel
Current density . .	0·48 A/cm²
Duration . . .	86 seconds

The foil is heat treated for one and half hours in the presence of nitrogen at 550°C and then gradually cooled to room temperature.

Etch ratio of etched foil at 30V . . .	19·3
Etch ratio of etched and heat-treated foil at 30V	26·4

The main advantage of the invention is that the heat-treatment of etched aluminium or its alloys in the form of thin foil increases the etch ratio by 35 to 50% of its original value irrespective of the electrolyte used for etching the foil.

Etching aluminium foil is carried out to increase the surface area and thereby reduce the overall size of the capacitor. Since the surface area of the etched aluminium foils determines the ultimate size of the finished capacitors, newer technique has been developed in the field of electrolytic etching of aluminium foil to get very high etch ratio. Such foils are required for making miniaturised electrolytic capacitor. We have developed a heat treatment technique increasing the etch ratio of the etched foil by 35 to 50% of its initial value. Both super pure aluminium 99.99% or its alloy 99.4% to 99.98% can be processed by placing the etched foil inside a suitable stainless steel chamber and heating it to 400 to 600°C furnace. The rate of flow of air of other gases is not very critical.

WE CLAIM:

1. A process for the heat treatment of aluminium or its alloys for use as electrodes in electrolytic capacitors by heating aluminium foil or its alloys upto 600°C characterised in that the heat treatment is imparted to etched foil (instead of the conventional heat treatment of plain foil before etching) further characterised in that the heating of the etched foil is done at 400 to 600°C in the presence of air or other gases for a period ranging from half an hour to 2½ hours whereby etch ratio of the etched foil is increased by 35 to 50%.

2. A process as claimed in claim 1 wherein air or a gas like oxygen or hydrogen or nitrogen is circulated during heat treatment.

3. A process as claimed in claim 1 or 2 wherein etched super pure aluminium foil of purity 99.99% or its alloy of purity 99.4% to 99.98% is used for heat treatment.

Dated this 25th day of March, 1972.

(Sd/-)

PATENTS OFFICER,

Council of Scientific & Industrial Research.

GIPN—S3—6 (2) C P & D Cal/74—1-11 75—150