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IMPROVEMENTS IN ~~THE~~ OR RELATING TO ETCHING OF ALUMINIUM OR ITS ALLOY FOR USE AS ELECTRODE IN ALUMINIUM ELECTROLYTIC CAPACITOR.

COUNCIL OF SCIENTIFIC AND 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 KANDADAI RAJAGOPALACHARI NARASIMHAN, Scientist, BALKUNJE ANANTHA SHENOI, Scientist, HANDADY VENKATAKRISHNA UDUPA, Director, VENKATASUBRAMANIAN LAKSHMI-NARASIMHAN, Senior Scientific Assistant, DEVARAJ KANAGARAJ, Junior Scientific Assistant, Mrs. VIJAYALAKSHMI RAMAKRISHNAN, Senior Laboratory Assistant, ANGUSWAMY PERUMAL, Senior Laboratory Assistant, all are Indian Nationals and all are employed in Central Electrochemical Research Institute, Karaikudi-623003, Tamil Nadu, India.

The following specification describes the nature of this invention.

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This invention relates to improvements in or relating to etching of aluminium or its alloys for use as electrodes (anode or cathode) in aluminium electrolytic capacitors.

Electrolytic capacitors are used in large numbers in any electronic equipment and the recent trend in the electronic industry is to reduce the size of these capacitors. This is done by using high gain etched foils for the fabrication of the electrolytic capacitors. High gain etched foils are made by electrolytic method.

The degree of etching of 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. Now with the recent developments in the rolling and etching technique, it is possible to obtain etch ratio of over 40 when formed at 30 volts.

Hitherto it has been proposed to treat the foil anodically in soluble chloride solution using d.c. or a.c. superimposed d.c. or square wave or d.c. with various percentages of pulsation.

This is open to objection in that the conventional sodium chloride electrolyte with pure d.c. gives etch ratio of only 15 at 30 volts forming. Other electrolytes with sodium chloride as the principal constituent have been developed but all of them give maximum etch ratio of 40 only, including the process patented by this Institute. The etching process using different forms of current involves the import of special generators as well as suitable filters and chokes.

So, the object of the present invention is to obviate these disadvantages by an electrochemical etching process employing suitable formulation and d.c. and adopting proper post treatment procedures in order to obtain high etch ratio between 40 and 55 at 30 volts forming.

To these ends, the invention broadly consists in an electrochemical process of etching aluminium using d.c. in a suitable bath formulations as mentioned below and adopting a special posttreatment procedure to inhibit the reaction between aluminium and water during the subsequent washing process for removing the last traces of chloride over the etched foil.

The main constituent of the bath consists of soluble chloride either alone or as mixture in sufficiently high concentration (1 to 5 molar concentrations). To this, one or more of the substances selected from the following list of substances given under the three sub-divisions indicated below are added so as to adjust the pH in the range of 1 to 5.5 :

- (i) Soluble salt of (a) of organic acids of mono, di, tri, or hydroxy aliphatic acids or (b) of inorganic acids like sulphuric, chromic or boric acid.
- (ii) The corresponding acid of the soluble salt added under (i) mentioned above or boric acid and (iii)
- (iii) a dihydroxy acid (aliphatic or aromatic) aliphatic amino alcohol, polyhydric alcohol, mono saccharide, disaccharide or products of hydrolysis of a disaccharide like sugar or polysaccharide like starch.

By soluble chloride or soluble salt, we mean the chloride or salt of sodium, potassium, ammonia, calcium or magnesium.

During the post-treatment of the etched foil for removing the chlorides, the reaction between aluminium and water may be inhibited by using solutions containing inorganic substances like phosphate, dichromate, silicate, periodate or surface active compounds of anionic type containing a strongly inhibiting inorganic group attached to the hydrocarbon.

The investigation is carried out as follows:

10 cm x 2.5 cm super pure aluminium foil of purity 99.99% or its alloy of purity 99.5% is anodically etched in two litres of the etching solution using stainless steel as cathode. A current density in the range of 0.2 A/sq.cm to 0.75 A/sq.cm is applied from a three-phase rectifier for a period of 80 to 120 seconds depending on the nature of the electrolyte and thickness of the foil. After etching, the foil is washed well with tap water and then it is immersed for 1 to 5 minutes in a special treatment solution kept at 75 to 90°C. The foil is washed well with deionised water kept at 90-95°C.

The etched foil is formed to 30 volts DC in a forming electrolyte containing 0.1% dihydrogen ammonium orthophosphate at 85°C.

The capacitance is measured in a capacitance bridge by applying four-fifth of the forming voltage in a measuring electrolyte containing 5% boric acid at 30°C whose resistivity is adjusted to 100 ohm/cm 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 typical examples are given to illustrate the invention:

EXAMPLE 1

(a) Etching electrolyte:

200 grams of commercial sodium chloride and 100 grams of sodium citrate are dissolved in one litre of water. The pH of the resulting solution is 4.

(b) Etching condition:

Anode: 100 micron thick aluminium foil of purity 99.99%

Cathode: Stainless steel

Current density: 0.7 A/cm²

Duration: 90 seconds.

Temperature: 100 - 102°C

(c) Post-treatment:

The etched foil is immersed in 0,1% ammonium dihydrogen orthophosphate solution at 5.4 pH for 2 minutes kept at 80°C. The foil is immersed in hot deionised water kept at 95°C for two minutes. The foil is formed at 30V.

(d) Etch ratio:

An etch ratio of 48 is obtained at 30V forming.

EXAMPLE 2

(a) Etching electrolyte:

200 grams of commercial sodium chloride, 75 grams of commercial sodium sulphate and 40 grams of boric acid are dissolved in one litre of water. The pH of the resulting solution is 4.3.

(b) Etching condition:

Same as given in Example 1.

(c) Post-treatment:

The etched foil is immersed in 0.1% dihydrogen ammonium orthophosphate solution for two minutes kept at 90°C. Then the foil is immersed in hot deionised water at 95°C for two minutes. The foil is formed to 30V.

(d) An etch ratio of 47 is achieved at 30 V forming.

EXAMPLE 3

(a) Etching electrolyte:

250 grams of commercial sodium chloride, 70 grams of sodium sulphate, 40 grams of boric acid and 100 grams of mannitol are dissolved in one litre of water. The pH of the resulting solution is 4.3.

(b) Etching condition:

Anode: 90 micron thick super pure aluminium foil of purity 99.99%

Cathode: Stainless steel

Current density: 0.65 A/cm²

Duration: 100 seconds

Temperature: 102°C

(c) Post-treatment:

Same as given in Example 1.

(d) An etch ratio of 43 is obtained at 30V forming.

EXAMPLE 4

(a) Etching electrolyte:

225 grams of commercial sodium chloride, 90 grams of commercial sodium sulphate, 40 grams of commercial boric acid are dissolved in 600 ml water. To 100 grams of sugar in 200 ml water is added 1:1 hydrochloric acid to adjust the pH to 1.8 and then boiled for half an hour. The solution is cooled and the pH is adjusted to 5.0 by adding dilute alkali. The sugar solution so hydrolysed is added to the mixture of chloride, sulphate and boric acid. The total volume is made upto 1000 ml. The pH of the resulting solution is 4.6.

(b)&(B) Etching condition and post-treatment are same as given in Example 1.

(d) Etch ratio:

An etch ratio of 54 is achieved at 30V forming.

EXAMPLE 5

(a) Etching electrolyte:

225 grams of commercial sodium chloride, 70 grams of sodium citrate are dissolved in 900 ml of water. To this, 100 ml of ethylene glycol is added. The pH of the resulting solution is adjusted to 4.5 with citric acid.

(b) & (c) Etching condition and post-treatment are the same as given in Example 2.

(d) Etch ratio:

An etch ratio of 54 is obtained at 30V forming.

EXAMPLE 6

(a) Etching electrolyte:

Same as given in Example 5.

(b) Etching condition:

Anode: 76 micron thick commercial aluminium foil of purity 99.5% is used.

Cathode: Stainless steel

Current density: 0.5 A/cm²
Duration: 60 seconds
Temperature: 100°C

(c) Post-treatment

Same as given in Example 2.

For the cathode foil the usual practice is to give the capacitance as $\mu\text{F}/\text{dm}^2$ at 0 volts. The following procedure is employed for measuring the capacitance at 0 volts.

Two test pieces of size 5 cm x 2.5 cm are cut out of the etched foils. Tabs of size 2 mm x 5 cm are attached to both the pieces. The two foils are then wound together with electrolytic tissue paper and immersed in an electrolyte containing 5% A.R. boric acid having a resistivity of 50 ohm-cm (adjusted by adding ammonium hydroxide). The tabs are connected to the capacitance measuring bridge and the capacitance value was read.


The capacitance value obtained with foils etched by the process mentioned above was 27,000 $\mu\text{F}/\text{dm}^2$.

The value that can be obtained with other electrolyte is usually less than 20,000 $\mu\text{F}/\text{dm}^2$ at 0 volts.

The following are among the main advantages of the invention:

1. It is possible to obtain high etch ratio (40-50 at 30V forming) by adopting a suitable process using d.c. suitable etching electrolyte formulation, etching conditions and post-treatment procedures for the etched foil and thereby effect considerable reduction in the volume/size of the capacitor which is the main trend in the miniaturisation of the electronic industry.
2. Likewise, ^{by this process} it is possible to get high capacitance value 15,000-25,000 $\mu\text{F}/\text{dm}^2$ ^{at 0 volts for the cathode foil using} for the commercial purity foils when etched by the new process.

Dated this 21st day of February, 1974.


ASST. PATENTS OFFICER,
Council of Scientific and Industrial Research.

INDIAN PATENTS ACT 1970

COMPLETE SPECIFICATION

SECTION 10

IMPROVEMENTS IN OR RELATING TO ETCHING OF ALUMINIUM OR ITS ALLOY FOR USE AS ELECTRODE 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 particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by KANDADAI RAJAGOPALACHARI NARASIMHAN, Scientist, BARKUNJE ANANTHA SHENCI, Scientist, HANDADY VENKATAKRISHNA UDUPA, Director, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, ~~Scientist~~ *Senior Scientific Assistant*, DEVARAJ KANAGARAJ, Junior Scientific Assistant, Mrs. VIJAYALAKSHMI RAMAKRISHNAN, Senior Laboratory Assistant, ANGUSAMY PERUMAL, Senior Laboratory Assistant, all are Indian Nationals and all are employed in Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

This invention relates to improvements in or relating to etching of aluminium or its alloys for use as electrodes (anode or cathode) in aluminium electrolytic capacitors.

Electrolytic capacitors are used in large numbers in any electronic equipment and the recent trend in the electronic industry is to reduce the size of these capacitors. This is done by using high gain etched foils for the fabrication of the electrolytic capacitors. High gain etched foils are made by electrolytic method.

The degree of etching of 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. Now with the recent developments in the rolling and etching techniques, it is possible to obtain etch ratio of over 40 when formed at 30 volts.

Hitherto it has been proposed to treat the foil anodically in soluble chloride solution using direct current or alternating current superimposed on direct current or square wave or direct current with various percentages of pulsation.

This is open to objection in that the conventional sodium chloride electrolyte with pure direct current gives an etch ratio of only 15 at 30 volts forming. Some of the other electrolytes

developed with sodium chloride as the principal constituent including the processes patented by us earlier (Indian Patent Number 100313 and 130553) did not include any post-treatment procedure to inhibit the reaction between the etched aluminium foil and water with the result they gave an etch ratio of only 40 at 30 volts forming. A few other processes using different forms of current involve the import of special generators as well as suitable filters and chokes.

So, the object of the present invention is to obviate these disadvantages by an electrolytic etching process employing suitable formulation and direct current and adopting proper post-treatment procedures in order to obtain high gain etch foil with suitable electrical characteristics and having the minimum chloride content.

To these ends, the invention broadly consists in electrolytic etching of aluminium foil which comprises subjecting the foil to an anodic treatment in an aqueous solution consisting of (i) a soluble chloride 15-30%, (ii) a soluble salt of sulphuric acid, aliphatic hydroxy (mono or di or tri) carboxylic acid 1-8% (iii) aliphatic hydroxy (mono, di or tri) carboxylic acid or boric acid 1.0 to 20% and (iv) one or more of the substances like tartaric acid, polyhydric alcohol, products of hydrolysis of sugar, inorganic acids like hydrochloric acid or sulphuric acid so as to adjust the pH between 1.0 and 4.5, the said anodic treatment being carried out at a current density of 0.48 to 1.24 amps/cm² for 48 coulomb to 125 coulomb per sq. cm of the foil surface, at a temperature of 98-105°C wherein the etched foil is subjected to a post-treatment in a hot solution containing one or more of the inorganic substances like, phosphate, silicate, periodate and boric acid in order to achieve high gain etched foil with an etch ratio of 40 and above at 30 volts forming.

By soluble chloride or soluble salt, we mean the chloride or salt of sodium, potassium, ammonium, calcium or magnesium.

During the post-treatment of the etched foil for removing the chlorides, the reaction between aluminium and hot water may be inhibited by using solutions containing inorganic substances like phosphate, dichromate, silicate, periodate and boric acid. This treatment enables us to obtain foils having low chloride content and having good electrical characteristics.

The investigation is carried out as follows:

10 cm x 2.5 cm super pure aluminium foil of purity 99.99% or its alloy of purity 99.5-99.8% is anodically etched in two litres of the etching solution using stainless steels, carbon or nickel as cathode. A current density in the range of 0.48 to 1.24 A/cm² is applied from a three phase rectifier for 0.8 to 1.4 ampere minutes per square centimeter of the foil depending on the nature of the electrolyte and the thickness of the foil. After etching, the foil is washed well with tap water and then it is immersed for 1 to 5 minutes in a special treatment solution kept at 80-90°C. The foil is washed well with deionised water kept at 85-90°C.

The etched foil is formed at 30 volts using direct current in a forming electrolyte containing 0.1% dihydrogen ammonium orthophosphate at 85°C.

The capacitance is measured in a capacitance bridge by applying four-fifth of forming voltage in a measuring electrolyte containing 5% boric acid at 30°C whose resistivity is adjusted to 100 ohm-cm with 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 typical examples are given to illustrate the invention:

EXAMPLE 1

(a) Electrolyte composition:

Sodium chloride:	20%
Sodium citrate:	10%
Citric acid:	1.0%
Hydrochloric acid:	to adjust the pH to 3.0

(b) Etching condition:

Anode:	100 micron thick foil of purity 99.99%
Cathode:	Stainless steel
Current density:	0.7 A/cm ²
Duration:	90 seconds
Temperature:	102°C

(c) Post-treatment:

The etched foil is immersed in 0.1% ammonium dihydrogen orthophosphate solution at pH 5.4 for 2 minutes maintained at 80°C. The foil is immersed in hot deionised water for 2 minutes and formed at 30 volts.

(d) Etch ratio: Etch ratio obtained is 48 at 30 volts forming.

EXAMPLE 2

(a) Electrolyte composition:

Sodium chloride:	20%
Sodium sulphate:	7.5%
Boric acid:	4.0%
Hydrochloric acid	to adjust the pH to 2.4

(b) Etching conditions:

Same as given in Example 1

(c) Post-treatment:

The etched foil is immersed in a solution containing 0.1% dihydrogen ammonium orthophosphate and 0.01% disodium hydrogen phosphate at pH 5.5 for 2 minutes. Then the foil is immersed in hot deionised water at 90°C for 2 minutes. The foil is then formed at 30 volts.

(d) Etch ratio:

An etch ratio of 47 is achieved at 30 volts.

EXAMPLE 3

(a) Electrolyte composition:

Sodium chloride:	25%
Sodium sulphate:	7.5%
Boric acid:	4.0%
Mannitol	To adjust the pH to 4.3

(b) Etching conditions:

Anode:	90 micron thick super pure aluminium foil of purity 99.99%
Cathode:	Carbon plate
Current density:	0.65 A/cm ²
Duration:	100 seconds
Temperature:	102°C

(c) Post-treatment:

Same as given in Example 1

(d) Etch ratio:

An etch ratio of 43 is obtained at 30 volts forming.

EXAMPLE 4

(a) Electrolyte composition:

Sodium chloride:	22.5%
Sodium sulphate:	8%
Boric acid:	4%

To this, the following solution is added and the pH of the resulting solution is 4.5. 100 grams of sugar is added to 200 ml of 1N hydrochloric acid solution and the pH is adjusted to 1.5 and then boiled for half an hour. The solution is then

pH is adjusted to 5.0 by adding dilute alkali. The sugar solution then hydrolysed is added to the solution containing sodium chloride.

(b) & (c) The etching condition and Post-treatment are same as given in Example 1.

(d) Etch ratio:

An etch ratio of 54 is achieved at 30 volts forming.

EXAMPLE 5

(a) Electrolyte composition:

Sodium chloride:	22.5%
Sodium citrate:	7.0%
Citric acid:	1.0%

100 ml ethylene glycol is added and the pH of the resulting solution is 4.5.

(b) and (c) Etching condition and Post-treatment are the same as given in Example 2.

(d) Etch ratio:

Etch ratio obtained is 54 at 30 volts forming.

EXAMPLE 6

(a) Etching electrolyte:

Same as given in Example 5.

(b) Etching conditions:

Anode:	76 micron thick commercial purity aluminium containing 99.5% aluminium
Current density:	0.5 A/cm ²
Duration:	60 seconds
Temperature:	100°C

(c) Post-treatment:

The etched foil is treated in 0.1% periodate solution at 80°C for 2 minutes and then in hot water at 85°C for 2 minutes.

(d) Etch ratio:

For the cathode foil, the usual practice is to give the capacitance as $\mu\text{F}/\text{cm}^2$ at 0 volt. The following procedure is employed for measuring the capacitance at 0 volt:

The sample is cut into two pieces of size 5 cm x 2.5 cm and tabs of size 2 mm x 5 cm are attached to both the pieces. The two foils are then wound together with electrolytic tissue paper and immersed in an electrolyte containing 5% AR boric acid having a resistivity of 50 ohm-cm (adjusted by adding ammonium hydroxide). The tabs are connected to the capacitance measuring bridge and the capacitance was read.

The capacitance value obtained with foils etched by the process mentioned above was $27,000 \mu\text{F}/\text{dm}^2$.

The value that can be obtained with other electrolyte is usually less than $20,000 \mu\text{F}/\text{dm}^2$ at 0 volt.

EXAMPLE 1

Electrolyte composition:

(a) Sodium chloride:	15%
Sodium sulphate:	3%
Boric acid:	10%
Tartaric acid:	to adjust the pH to 2.9

(b) Etching conditions:

Anode:	100 micron thick super pure aluminium foil
Cathode:	Stainless steel
Current density:	$1.0 \text{ A}/\text{cm}^2$
Duration:	80 seconds
Temperature:	102°C

(c) Post-treatment:

The foil is immersed in 2.5% boric acid solution at 80°C for 2 minutes and then in hot deionised water solution at 88°C for 2 minutes and then formed at 30 volts.

(d) Etch ratio:

An etch ratio of 41 is obtained at 30 volts.

EXAMPLE 2

(a) Electrolyte composition:

Sodium chloride:	15%
Sodium sulphate:	6%
Boric acid:	4%
Ethylene glycol and Sulphuric acid	to adjust the pH to 2.4

(b) Etching conditions:

Anode:	100 micron thick super pure aluminium foil
Cathode:	Stainless steel
Current density:	$1.0 \text{ A}/\text{cm}^2$
Duration:	80 seconds
Temperature:	104°C

(c) Post-treatment:

Same as given in example 1

(d) Etch ratio:

An etch ratio of 43 is obtained at 30 volts forming.

The following are among the main advantages of the invention:

1. It is possible to obtain high etch ratio (40-50 at 30 volts forming) by adopting a suitable process using direct current suitable etching electrolyte formulation, etching conditions and post-treatment procedures for the etched foil and thereby effect considerable reduction in the volume/size of the capacitor which is the main trend in the miniaturisation of the electronic industry.
2. Likewise, by this process it is possible to get high capacitance value of 15,000-25,000 $\mu\text{F}/\text{dm}^2$ at 0 volt for the cathode foil using commercial purity foil.

WE CLAIM

1. A process for electrolytically etching aluminium foil which comprises subjecting the aluminium foil to an anodic treatment in an aqueous solution consisting of (i) a soluble chloride 15-30% (ii) a soluble salt of sulphuric acid, aliphatic hydroxy (mono, di or tri) carboxylic acid 1-8% (iii) aliphatic hydroxy (mono, di or tri) carboxylic acid or boric acid 1.0 to 20% and (iv) one or more of the substances like tartaric acid, polyhydric alcohol, products of hydrolysis of sugar, inorganic acids like hydrochloric acid or sulphuric acid so as to adjust the pH between 1 and 4.5, the said anodic treatment being carried out at a current density of 0.48 to 1.24 amps/cm^2 for 48 coulomb to 125 coulomb per sq.cm. of the foil surface, at a temperature of 98-105°C wherein the etched foil is subjected to post-treatment in a hot solution containing one or more of the inorganic substances like, phosphate, silicate, periodate and boric acid in order to achieve high gain etched foil with an etch ratio of at least 40 and above at 30 volts forming.
2. A process for electrolytic etching as claimed in 1 in which the aluminium foil is subjected to an anodic current density of 0.48 to 1.24 A/cm^2 and for 48 coulomb to 125 coulomb per sq.cm of the foil.
3. A process for electrolytic etching as claimed in claims 1 and 2 wherein the foil is subjected to a post-treatment in a hot solution containing inorganic substances like phosphate, dichromate, silicate, periodate and boric acid maintained at 80-90°C for a duration of 2 to 5 minutes during the continuous processing.
4. A process for electrolytic etching as claimed in claim 3 wherein the post-treatment aqueous solution is kept at a pH of 5 to 6.5.

Dated this 4th day of February 1975.

R. Bhaskar Bai

PATENTS OFFICER
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