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AN IMPROVED PROCESS FOR THE REMOVAL OF CHLORIDE IONS  
FROM AN ETCHED ALUMINIUM FOIL FOR USE IN ALUMINIUM  
ELECTROLYTIC CAPACITOR.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH  
Rafi Marg, New Delhi- 110001, Indian, an Indian  
registered body incorporated under the Registration  
of Societies Act ( Act XXI of 1860 )

The following specification describes the nature of this invention.

PRICE : TWO RUPEES .

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This is an invention by Shri BALKUNJE ANANTHA SHENOI, Scientist, Shri KANDADAI RAJAGOPALACHARI NARASIMHAN, Scientist, VENKATASUBRAMANIAN LAKSEMI NARASIMHAN, Scientist, Shri DEVARAJ KANAGARAJ, Senior Scientific Assistant and Shri ANGUSAMY PERUMAL, Senior Laboratory Assistant all are Indian nationals and all are employed in Central Electrochemical Research Institute, Karaikudi-6, India.

This invention relates to improvement in or relating to post treatment process for the removal of chlorides from etched aluminium foil for use in aluminium electrolytic capacitor.

Hitherto it has been prepared to remove the chloride in etched aluminium foil after etching operation by rinsing the etched foil in running tap water or by treating the foil in acid such as hydrochloric acid or nitric acid or by treating the foil as cathode in running distilled water.

This is open to the objection due to the following reasons:  
(i) The chloride present in the etched foil appears to be present as basic aluminium chloride. Treatment in 0.5 N HCl acid is given to convert the basic chloride to form more soluble form of chloride. In the above process the treatment time is 5 to 10 minutes and the chloride is not completely removed in subsequent washing with water. (ii) The foil is treated as cathode in running water at 400 V.D.C. The application of high D.C. Voltage requires proper insulation and safety devices to switch off the source instantaneously.

The object of this invention is to obviate these disadvantages by treating the etched Aluminium foil chemically in a acid mixture containing either 5 to 10%  $\text{HNO}_3$  and 1 to 5% nitric acid and 1 to 5% phosphoric acid followed by cathodic treatment in a solution containing 0.2 to 3%  $\text{NH}_4 \text{B}_5\text{O}_8$  and 0.1 to 1.0%  $\text{H}_3\text{BO}_3$  at 30V for a period ranging between 6 to 120 seconds.

To these ends, the invention broadly consists in post treatment process for removal of chlorides in etched aluminium foil. After etching operation the foil is washed in running

tap water followed by treatment in a mixture of 5 to 10%  $\text{HNO}_3$  and 1 to 5%  $\text{HCl}$  for 60 to 100 secs. After jet washing in tap water, it is electrochemically treated in a solution containing 0.2% to 3%  $(\text{NH}_4)_2\text{B}_5\text{O}_{10}$  and 0.1 to 1.0%  $\text{H}_3\text{BO}_3$  at 30V at a temperature of  $50 \pm 2^\circ\text{C}$  for a period from 60 to 120 secs. Then the foil is treated in a special treatment solution to preserve the capacitance on storage followed by the treatment in boiling deionized water as described in our Indian Patent No. 141250, and then in boiling deionized water.

The following examples are given to illustrate the invention :

#### EXAMPLE-1

The aluminium foil is etched in an electrolyte described in our Indian Patent No. 141250 is treated in a solution containing 10%  $\text{HCl}$  + 5%  $\text{HNO}_3$  at  $55^\circ\text{C}$  for 120 seconds. Subsequently the foil is washed with jet water and then in running tap water. The chloride content in the etched foil is estimated as per the procedure given hereinafter. The chloride content after chemical treatment and washing is 3 mg per active square meter. Then the foil is subjected to electrochemical treatment in an electrolyte containing 1.0% ammonium pentaborate and 0.1% boric acid to adjust the pH from 7 to 9. The foil is treated as cathode using stainless steel as anodes at 30V for 2 min. at  $55^\circ\text{C}$ . It is followed by special treatment in a solution as described in our Indian Patent No. 141250. The chloride content of the etched foil after electrochemical treatment followed by special treatment and in boiling deionized water treatment is estimated. The chloride content in the etched foil after giving all the post treatment is 0.5 mg per active sq. meter.

#### EXAMPLE-2

The aluminium foil etched in an electrolyte described in our Indian Patent No. 139702 is treated in an acid mixture containing 3%  $\text{H}_3\text{PO}_4$  + 5%  $\text{HNO}_3$  at room temperature for 120 secs. The etched foil after jet washing and washing in running tap water is given all the treatments as in Example No. 1

The chloride content in the etched foil after chemical treatment followed by jet and running tap water is found to be 2.5 mg per active square meter.

The chloride content in the etched foil after electro-chemical treatment and post treatments is found to be 0.5 mg per active square meter.

The following is the main advantages of the invention:

The removal of chloride present in the etched foil is brought down to 0.5 mg/m<sup>2</sup> by adopting this process which prevents the contamination of the costly forming bath thereby increases the life of the forming electrolyte. The low chloride content in the etched foil will reduce the forming time and attain very low leakage current.

Procedure for estimating chloride content in etched foil.

The chloride in the etched foil is estimated as follows :

800 cm<sup>2</sup> (26.7 cm x 15 cm) area of etched foil treated as stated above is taken and suitably cut into three equal portions. 200 ml. of deionized water is heated to 100°C in a beaker and the foils are boiled for three minutes and the extract is then cooled to laboratory temperature. 20 ml. of the extracted solution is pipetted out into 50 ml. graduated measuring cylinder, 10 drops of 65% nitric acid is added to the above extract. 1.25 ml. of 15% solution of silver nitrate is added. The resulting solution is made upto 50ml. 1000 ppm of sodium chloride is prepared by dissolving 1.650 gms of AR Sodium chloride in one litre deionized water. From the mother solution containing 1000 ppm of it ion 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 ml. of the solution is pipetted out and again made up to one litre using deionized water. Now the standard solution prepared as stated above contains 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 ppm of solutions. To 20 ccs from each of the standard solution 10 drops of 65% HNO<sub>3</sub> and 1.25 ml. of 15% solution of silver nitrate are added and made into 50ml. using deionized water. The turbidity is compared with the standard solution. If it is comparable with 2.0 mg/l standard solution, the chloride content present in 1 sq.m. of the etched foil is calculated

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as follows :

$$\frac{2.0 \text{ mg/l} \times 0.2 \text{ l}}{\times 0.08 \text{ m}^2} = 5.0 \text{ mg/m}^2$$

( 1 m<sup>2</sup> = 100 cm x 50 cm of etched foil )

Dated this 18th day of August, 1977

*W. M. M. M. M.*

ASSISTANT PATENTS OFFICER  
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

**COMPLETE SPECIFICATION**

( Section—10 )

" AN IMPROVED PROCESS FOR THE REMOVAL OF CHLORIDE IONS FROM AN ETCHED ALUMINIUM FOIL FOR USE IN ALUMINIUM ELECTROLYTIC CAPACITOR. "

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH,  
Rafi Marg, New Delhi- 110001, India, an Indian  
Registered body incorporated under the Registration  
of Societies Act ( Act XXI of 1960 )

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, Scientist, DEVARAJ KANAGARAJ, Senior Scientific Assistant and ANGUSAMY PERUMAL, Senior Laboratory Assistant all are Indian citizens and are employed in the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

This invention relates to an improved process for the removal of chloride ions from etched aluminium foil for use in aluminium electrolytic capacitor.

Hitherto it has been proposed to remove the chloride ions in etched aluminium foil after etching operation by rinsing the foil in running tap water or by treating in hydrochloric acid or nitric acid or by treating the foil as cathode in running distilled water. .

This is open to the objection due to the following reasons: (i) washing the foil in running tap water is not an effective method for removing the chloride ion from the deep etch pits (ii) The treatment in acid solution convert the basic aluminium chloride into a more soluble form of chloride. The soluble chloride is washed in running tap water. This subsequent washing step is not adequate to remove chloride ion right down to 0.5 mg/meter square of the etched foil (iii) The foil is treated as cathode in running water at 400V D.C. which requires proper insulation and safety devices to switch off the devices instantaneously.

Removal of chloride ion from etched foil is difficult if the etch pits are narrow and deep as in the case of low voltage etched anode foils. By treating with acid such as hydrochloric or nitric acid followed by washing with jet water or in running tap water, the chloride ion in the deep etch pits is not completely removed. During subsequent forming operation the

chloride ion prevents the complete formation of oxide film and reduces the life of the costly forming bath. Capacitors fabricated with high chloride ion content etched foils give less reliability and low electrical performance.

The main object of the invention is to obviate these disadvantages and to effect removal of chloride ions content from the etched aluminium foil to less than 0.5 mg/active meter square. The foils thus prepared according to this invention produce capacitors with excellent performance in the way of very low current leakage better shelf life and more reliability, by treating the etched aluminium foil in a acid mixture containing 5 to 10% V/V of nitric acid and 1 to 5% V/V of hydrochloric or phosphoric acid, washing with jet water by means of a series of jets, followed by cathodic treatment in a solution containing 0.5 to 5% W/V ammonium pentaborate and 0.5 to 2.0% W/V boric acid at a temperature of 35 to 50°C for a period ranging between 60 and 120 secs. A current density of 0.4 to 1 A/dm<sup>2</sup> is applied to the foil from a rectifier. The etched foil after cathodic cleaning is treated in a solution containing phosphate ions and then in boiling water as described in our earlier Indian Patent No. 141260.

Accordingly this invention provides improved process for the removal of chloride ions from an etched aluminium foil for use in aluminium electrolytic capacitor <sup>which</sup> comprises treating the etched foil in acid mixture and washing the same with water <sup>and</sup> which is characterised in that the etched foil is then further treated electrochemically in a solution of ammonium pentaborate and boric acid.

The invention further provides that the electrochemical treatment of the etched foil consists in making the foil as cathode using as electrolyte a solution of 0.5 to 5 W/V% of ammonium pentaborate and 0.5 to 2 W/V% of boric acid and a stainless steel anode.

According to another feature of the invention, the



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electrochemical treatment is carried at 25° to 50° C for a period of 60 to 120 secs. using a current density of 0.4 to 1 A/dm<sup>2</sup>.

According to yet another feature of the invention the electrochemically treated foil is further treated in a solution containing phosphate ions and then washed with boiling deionised water.

The process for removal of chloride ion from the etched aluminium foil thus comprises i) treating the etched aluminium foil in an acid mixture containing 5 to 10% V/V of nitric acid plus 1 to 5% V/V phosphoric acid or hydrochloric acid ii) washing the foil by means of a series of jets fixed on either side of the path of the foil iii) cleaning the foil by making it as cathode in a solution containing 0.5 to 5% W/V of ammonium pentaborate plus 0.5 to 2% W/V of boric acid kept at 35 to 50° for a period of 60 to 120 secs. and a current density of 0.4 to 1 A/dm<sup>2</sup> being applied to the foil from a rectifier iv) treating the foil in a solution containing phosphate ion and then in boiling deionized water wherein the chloride ion content in the etched foil is reduced to less than 0.5 mg per active metre square.

The following examples are given to illustrate the invention:

#### EXAMPLE 1

The foil etched in an electrolyte as per process described in our Indian Patent No. 141250 is treated in a solution containing 10% HNO<sub>3</sub> + 5% HCl at 25° for 120 secs. Subsequently the foil is washed with jet water. The chloride in the etched foil is estimated as follows : 800 cm<sup>2</sup> (26.7 cm x 15 cm) areas of etched foil treated as stated above is taken and suitably cut into three equal portions. 200 ccs of deionized water is heated to 100°C in a beaker and the foils are boiled for three minutes and the extract is then cooled to laboratory temperature. 20 ccs of the extracted solution is pipetted out into 50 cc graduated measuring cylinder, 10 drops of 65%

nitric acid is added to the above extract. 1.25 ccs of 15% solution of silver nitrate is added. The resulting solution is made up to 50 ccs. 1000 ppm of sodium chloride is prepared by dissolving 1.650 gms of AR sodium chloride in one litre deionised water. From the mother solution containing 1000 ppm of chloride ion 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 ccs of the solution is pipetted out and again made up to one litre using deionised water. Now the standard solutions prepared as stated above contains 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 ppm of chloride ion in the solutions. To 20ccs from each of the standard solutions 10 drops of 65%  $\text{HNO}_3$  and 1.25 ccs of 15% solution of silver nitrate are added and made into 50 ccs using deionised water. The turbidity is compared with the standard solution. If it is comparable with 2 mg/l standard solution, the chloride content present in 1 sq.m. of the etched foil is calculated as follows:

$$\frac{2 \text{ mg} \quad 1 \quad \times \quad 0.2 \quad 1}{\times \quad 0.08 \text{ m}^2} = 5 \text{ mg/m}^2$$

( 1 m<sup>2</sup> = 100 cm x 50 cm of etched foil )

The chloride content in the etched foil after chemical treatment is 5 mg/m<sup>2</sup>.

After washing in running tap water and jet water, the foil is subjected to electrochemical treatment in an electrolyte containing 4.0% W/V ammonium pentaborate and 1.0% W/V Boric acid for adjusting the pH from 7 to 9. The foil is treated as cathode at a current density of 0.6 amp. per dm<sup>2</sup> for 2 minutes at 35° C using stainless steel as anodes. It is followed by further treatment in a solution as described in our Indian Patent No. 141250 and then in boiling deionized water. The chloride content of the etched foil after the chemical and electrochemical treatment followed by special treatment and in boiling deionized water treatment is estimated as described

above. The chloride content in the etched foil after giving all the post treatment is 0.5 mg per active sq. metre.

#### EXAMPLE 2

The foil etched in an electrolyte as per process described in our Indian Patent No. 139702 is treated in acid mixture containing 3%  $H_3PO_4$  + 5%  $HNO_3$  at room temperature for 120 secs. Then it is cleaned with jet water. The estimation of chloride is carried out as stated in Example No. 1. The chloride content in the etched foil after the chemical treatment and jet washing is found to be 3 mg/m<sup>2</sup>.

The etched foil after the treatment in the phosphoric acid, nitric acid mixture, is washed with running tap water. This again is washed with jet water. Then the foil is electrochemically cleaned and given subsequent treatments as in Example number 1.

The chloride content of the etched foil after completing all the post treatments as described in Example No. 1 is estimated. The amount of chloride present in etched foil is 0.5 mg/active square metre of the etched foil.

Treating the etched foil in an acid mixture followed by cathodic cleaning the chloride content in the etched foil is brought down to less than 0.5 mg per active meter square.

#### We Claim:

1. An improved process for the removal of chloride ions from an etched aluminium foil for use in aluminium electrolytic capacitor comprising treating the etched foil in an acid mixture and washing the same with water characterised in that the etched foil is then further treated electrochemically in a solution of ammonium pentaborate and boric acid.

2. The process as claimed in claim I wherein the electrochemical treatment of the etched foil comprises making the foil as cathode using as electrolyte a solution containing

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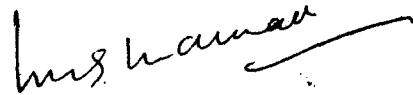
0.5 to 5 W/V% of ammonium pentaborate acid 0.5 to 2 W/V% of boric acid using a stainless steel anode.

3. The process as claimed in claim 1 and 2 wherein the electrochemical treatment is carried out at 35 to 50°C for a period of 60 to 120 seconds using a current density of 0.4 to 1 A/dm<sup>2</sup>.

4. The process as claimed in any of the preceding claims wherein the electrochemically treated etched foil is further treated in a solution containing phosphate ions and then washed with boiling deionised water.

5. An improved process for the removal of chloride ions from an etched aluminium foil for use in aluminium capacitor substantially as have described and illustrated in examples.

Dated 15th day of Nov., 1978.



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