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" IMPROVED PROCESS FOR THE PRODUCTION OF DIELECTRIC OXIDE FILM COATED ETCHED ALUMINIUM FOIL FOR USE AS ANODE IN HIGH VOLTAGE ELECTROLYTIC CAPACITOR."

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi- 110001, 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, SRI VENKATASUBRAMANIAN LAKSHMINARASIMHAN, Scientist, SRI DEVARAJ KANAGARAJ, Senior Scientific Assistant and Sri Angusamy Perumal, Senior Laboratory Assistant all are Indian Nationals employed in the Central Electrochemical Research Institute, Karaikudi-6, India.

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

This invention relates to improvements in or relating to a formation which consists of formation, stripping and reformation steps for producing high quality dielectric oxide film that can be used in intermediate and high voltage electrolytic capacitors.

Hitherto it has been proposed in the Aluminium electrolytic capacitor art to use preboiled Aluminium etched foil in the formation process to produce efficient formation due to its lesser consumption of electrical energy. The preboiled foil even after formation contains some excess Pseudobochmite hydrous aluminium oxide film. This causes a sharp decrease upto 15% in the capacitance and undesirable increase in the dissipation factor of the finished electrolytic capacitor. This excess of hydrous oxide is stripped away in a solution containing H_3PO_4 and CrO_3 mixture and again anodically reformed in non-borate electrolyte systems to form stable, efficient oxide film used for high voltage capacitors. The reforming step heals any flaws or defects brought about by the stripping process.

This is open to the objection that the H_3PO_4 and CrO_3 stripping solution used in the prior art, if not thoroughly washed, remains in the crevices of the oxide film. This will readily attack the film formed in borate electrolyte during the reforming steps. So non-borate electrolyte like Sodium benzoate are to be used for forming. Non-borate electrolytes used in the prior art can be used to reform only upto 350volts. Reforming above 350 volts is the difficulty met with the prior art.

By reforming the foil, after striping hydrous oxide layer a decrease in capacitance upto 4% is reported in hither to known process.

The object of the present invention is to obviate these disadvantages by using a stripping solution containing phosphoric acid and any one of the acids like boric acid, acetic acid or Nitric acid instead of CrO_3 to remove the excess hydrous oxide film which is not converted into barrier oxide during the formation process. After stripping, the foil is washed with deionised water and reformed in boric acid electrolyte to the voltage previously formed to attain minimum leakage current. The new stripping solutions not only prevent the usage of non-borate electrolyte for reforming but also obviate the difficulty met with the prior art of reforming above 350 volts. By using any one of the stripping solutions, the foil can be reformed in boric acid electrolyte upto 600V. It was also observed that by the reforming in the boric acid electrolyte the capacitance value increases by 3 to 10% and the dissipation factor decreases by 10 to 16% compared to the value obtained before striping the formed foil.

To these ends, the invention broadly consists of stripping the formed foil in the stripping solutions with phosphoric acid based electrolyte containing Nitric acid, acetic acid, boric acid and again reformed in boric acid electrolyte to the previously formed voltage thereby increases the capacitance value and decreases the dissipation factor of the formed foil for use in intermediate and high voltage aluminium electrolytic capacitor.

The following typical examples are given to illustrate the inventions:

EXAMPLE-I

Electrolyte for forming:

A.R.Boric acid	:	100 gm/litre
Temperature of the bath	:	90 ± 2°C
Anode	:	Preboiled etched superpure aluminium foil
Area	:	25 cm^2
Cathode	:	Degreased plain aluminium foil
Duration	:	30 minutes
Current density	:	10 mA/sq.cm
Forming voltage	:	550 volts D.C.
Measuring voltage	:	400 volts D.C.

Preboiled etched foil is made as anode in 10% boric acid solution at 550 volts. The current for forming is kept at 10mA/Sq.cm. till 550 volts is reached and thereafter maintained at 550V till the current falls to 0.6 mA/sq.cm. Normally it takes 30-40 minutes for complete formation. It is then washed and the capacitance is measured at 400 volts in a measuring electrolyte containing 3% boric acid at room temperature whose resistivity has been adjusted to 100 ohm/cm with NH_3. The capacitance and tanδ values obtained are measured in a capacitance bridge.

The value obtained were :

Capacitance : 5.0 MFD

Tan δ : 3.2%

The above formed foil is then stripped in a solution containing 4% H_3PO_4 + 3% boric acid for 120 ± 10 secs. at 85 ± 2°C. The foil after washing in deionised water at room temperature is again reformed in the above mentioned Boric acid electrolyte to 550V for 120 ± 10 secs. to cure any defects or flaws in the barrier oxide layer caused by stripping process. The value measured at 400V, is

Capacitance : 5.3 MFD

Tan δ : 2.5%

EXAMPLE-II

The preboiled super pure etched aluminium foil is formed and measured as stated in Example No.1. The value measured at 400V before stripping operation is

Capacitance : 4.95 MFD

Tan δ : 3%

The formed foil is then stripped in a solution containing 5% H_3PO_4 + 4% acetic acid at 75 ± 2°C for 90 ± 10 secs. After washing in deionised water at room temperature, again reformed as stated in Example No. 1 for 180 ± 10 secs. Thevalue measuredat 400 volts is

Capacitance : 5.4 MFD

Tan δ : 1.5%

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EXAMPLE-III

The preboiled superpure etched Aluminium foil is formed and measured as stated in Example No.I. The value obtained before stripping operation is

Capacitance : 6 MFD

Tan δ : 3%

The above formed foil is then stripped in a solution containing 4% H_3PO_4 + 5% HNO_3 (conc.) for 150 ± 10 secs. at 85 ± 2°C and that washed with deionised water. The foil is again reformed in boric acid electrolyte to 550V for 90 secs. to heal any defects or flaws caused by the stripping step.

The value measured at 400V is

Capacitance : 6.2 MFD

Tan δ : 1.5%

The following are among the main advantages of the invention:

It is possible to obtain high capacitance and low dissipation factor of high voltage capacitor anode foil by adopting the stripping of amorphous hydrous oxide film after forming and again reforming in the conventional electrolyte.

Dated this 9th day of August, 1977.

Asstt. Patents Officer,
Council of Scientific & Industrial Research

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

IMPROVED PROCESS FOR THE PRODUCTION OF DIELECTRIC OXIDE FILM COATED ETCHED ALUMINIUM FOIL FOR USE AS ANODES IN HIGH VOLTAGE ELECTROLYTIC CAPACITOR.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi- 110001, 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 Shri Balakunje Mantha Shenoi, Scientist, Shri Kandadai Rajagopalchari Narasimhan, Scientist, Shri Venkateswaramanian Lakshminarasimhan, Scientist, Shri Devaraj Kanagaraj, Senior Scientific Assistant and Shri Angusamy Perumal, Senior Laboratory Assistant, all are Indian nationals and are employed in the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

This invention relates to the field of capacitor industry which involves formation, stripping and reformation steps to produce high quality dielectric oxide film on etched aluminium foil that can be used in intermediate and high voltage aluminium electrolytic capacitors. The improved process of the invention is for the production of dielectric oxide film coated etched aluminium foil for use as anode in high voltage aluminium electrolytic capacitors.

Hitherto it has been proposed to use preboiled etched aluminium foil which contains pseudoboehmite hydrous aluminium oxide film, for efficient formation of dielectric oxide film as it consumes lesser energy for forming. During the formation process, the hydrous oxide film is converted into barrier layer oxide film. Even after complete formation of the barrier film, some excess hydrous oxide film remains unconverted. This causes a sharp decrease upto 15% in the capacitance and undesirable increase in the dissipation factor of the finished electrolytic capacitor. This excess hydrous oxide is stripped away in a solution containing a mixture of H_3PO_4 and CrO_3 acids and again anodically reformed in non-borate electrolyte systems. By adopting this method, a stable efficient oxide film can be formed. The reforming step heals any flaws or defects brought about by the stripping step.

This process is open to the objection in that, the H_3PO_4 and CrO_3 stripping solution used in the prior art, if not thoroughly washed, remains in the crevices of the oxide film and readily attacks the film reformed in the borate electrolyte. To overcome this difficulty

non-borate electrolyte sucha as sodium benzoate is used for forming. Again reforming with non-borate electrolyte above 350 volts is not possible.

By reforming the foil, after stripping the excess hydrous oxide layer, a decrease in capacitance upto 4% is reported in the hitherto known process.

The object of the present invention is to obviate these disadvantages by using a stripping solution containing phosphoric acid and any one of the acids like boric acid, acetic acid or nitric acid instead of H_3PO_4 to remove the excess unconverted hydrous oxide film and also to eliminate the non-borate electrolyte systems which can be used to reform only upto 350 volts.

The other objections of the invention are that the reforming can be carried out to a voltage of 550V in boric acid electrolyte itself. and that an increase in capacitance value by 5 to 10% and decrease in dissipation factor by 10 to 30% can be achieved, compared to the value obtained before stripping.

The main finding underlying the invention consists of removing the excess hydrous oxide film present even after complete formation in boric acid electrolyte in a stripping solution containing phosphoric acid in the concentration range between 3 and 5% and any one of the acids such as acetic acid, boric acid and nitric acid in the concentration range between 3 and 5% for a period of 90 to 160 secs. at a temperature of 75 to 87°C. This is followed by thorough washing in deionised water at room temperature and then reformed in boric acid electrolyte to the voltage previously formed to attain minimum leakage current.

By using any one of the stripping solutions mentioned above, the foil can be reformed in boric acid electrolyte itself to the already predetermined voltage instead of sodium benzoate electrolyte. An increase in the capacitance value by 5 to 10% and decrease in the

dissipation factor by 10 to 30% can be achieved by this method.

The present invention accordingly consists of an improved process for the production of dielectric oxide film coated etched aluminium foil for use as anodes in high voltage aluminium electrolytic capacitor which comprises forming preboiled etched aluminium foil, stripping the excess hydrous oxide film and reforming the oxide layer in sodium benzoate electrolyte and is characterised in that the stripping of the coated oxide film on the foil is carried out in a solution containing phosphoric acid and acetic acid, nitric acid or boric acid in a ratio to effect the stripping and that the reforming is carried out in boric acid at 80° to 90°C.

The formed aluminium foil is stripped in a solution containing 3 to 5% V/V of phosphoric acid and 3 to 5% V/V of any one of the acids such as acetic acid, boric acid, nitric acid maintained at 75 to 87°C for a period of 90 to 160 secs, followed by washing in deionized water and reforming the aluminium foil in 10 W/V of boric acid kept at 80 to 90°C for a period of 90 to 160 secs. to the original predetermined forming voltage of upto 550V whereby the capacitance of the aluminium foil is increased by 5 to 10% and the dissipation factor is decreased by 10 to 30% of the value obtained before stripping.

The following typical examples are given to illustrate the process invention :

Example-1

Electrolyte for forming :		
A.R.Boric acid	:	100 gm/litre
Temperature of the bath	:	90 ± 2°C
Anode	:	Preboiled etched superpure aluminium foil
Area	:	25 Cm^2
Cathode	:	Degreased plain aluminium foil
Duration	:	30 minutes
Current density	:	10 mA/sq.cm.
Forming voltage	:	550 Volts D.C.
Measuring voltage	:	400 volts D.C.

Preboiled etched foil is made as anode in 10% boric acid solution at 550 volts. The current for forming is kept at 10 mA/sq.cm. till 550 volts is reached and thereafter maintained at 550V till the current falls to 0.6 mA/sq.cm. Normally it takes 30-40 minutes for complete formation. It is then washed and the capacitance is measured at 400 volts in a measuring electrolyte containing 5% boric acid at room temperature whose resistivity has been adjusted to 100 ohm/cm with NH_3. The capacitance and tan δ values obtained are measured in a capacitance bridge. The value obtained is

Capacitance	:	5.0 MFD
Tan δ	:	3.25%

The above formed foil is then stripped in a solution containing 4% H_3PO_4 + 5% boric acid for 120 + 10 secs at 85 + 2° C. The foil after washing in deionised water at room temperature is again reformed in the above mentioned boric acid electrolyte to 550V for 120 + 10 secs. to cure any defects or flaws in the barrier oxide layer caused by stripping process. The value measured at 400 V is

Capacitance	:	5.3 MFD
Tan δ	:	2.5%

Example - II

The preboiled super pure etched aluminium foil is formed and measured as stated in Example No.1. The value measured at 400V before stripping operation is

Capacitance	:	4.95 MFD
Tan δ	:	3%

The formed foil is then stripped in a solution containing 5% H_3PO_4 + 4% acetic acid at 75 + 2°C for 90 + 10 secs. After washing in deionized water at room temperature, again reformed as stated in Example No. 1 for 150 + 10 secs. The value measured at 400 Volts is

Capacitance	:	5.4 MFD
Tan δ	:	2.1%

Example-III

The preboiled superpure etched aluminium foil is formed and measured as stated in Example No. 1. The value obtained before stripping operation is :

Capacitance	:	6 MFD
Tan δ	:	3%

The above formed foil is then stripped in a solution containing 4% H_3PO_4 +5%HNO_3 (Conc.) for 150 + 10 secs. at 85 + 2°C and that washed with deionized water. The foil is again reformed in boric acid electrolyte to 550 V for 90 secs., to heal any defects of flaws caused by the stripping step.

The value measured at 400V is

Capacitance	:	6.2 MFD
Tan δ	:	2.2%

We Claim :

1. Improved process for the production of dielectric oxide film coated etched aluminium foil for use as anodes in high voltage aluminium electrolytic capacitor comprising forming preboiled etched aluminium foil, stripping the excess hydrous oxide film and reforming the oxide layer in sodium benzoate electrolyte characterised in that the stripping of the coated oxide film on the foil is carried out in a solution containing phosphoric acid and acetic acid, nitric acid or boric acid in a ratio to effect the stripping and the reforming is carried out in boric acid at 80° to 90°C.

2. Process as claimed in claim 1 wherein the formed aluminium foil is treated in a stripping solution containing 3 to 5% V/V of phosphoric acid and 3 to 5% V/V of acetic acid or nitric acid or boric acid at a temperature of 75° to 87°C for a period of 90 to 160 secs.

3. Process as claimed in claim 1 or 2 wherein the formed and stripped aluminium foil is reformed by treatment with 10% W/V of boric acid at 80°C to 90°C for a period of 90 to 160 seconds to a voltage between 350 V and 550 volts.

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4. Improved process for the production of dielectric oxide film coated etched aluminium foil for use as anodes in high voltage aluminium electrolytic capacitor substantially as herein described and illustrated.

Dated this 8th day of November, 1978

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