GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

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**Index at acceptance—31A [LVIII(2)], 70C5 [LVIII(5)].**

## PROVISIONAL SPECIFICATION.

### IMPROVEMENTS IN OR RELATING TO ETCHING OF TANTALUM FOR USE IN ELECTROLYTIC CAPACITORS.

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).

*The following specification describes the nature of this invention.*

THIS IS AN INVENTION BY BALKUNJI ANANTHA SHENOI, SCIENTIST, KANDADAI RAJAGOPALACHARI NARASIMHAN, SENIOR SCIENTIFIC ASSISTANT, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, JUNIOR SCIENTIFIC ASSISTANT, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, ALL INDIAN CITIZENS.

This invention relates to improvements in or relating to etching of tantalum for use as anodes in electrolytic capacitors.

Hitherto it has been proposed to use direct current or a.c. superimposed d.c. (Indian Patent No. 95423, dated 31-8-1964) for etching tantalum anodes for capacitors.

This is open to objection that the use of d.c. gives rather a low etch ratio whereas the superimposed current gives high etch ratio. But the equipment is comparatively costly.

The objective of this invention is to obviate these disadvantages by using interrupted or continuous unidirectional pulsed currents for etching tantalum and thereby obtain a high etch ratio.

To these, ends, the invention broadly consists in etching of tantalum and tantalum alloys electrolytically in a non-aqueous electrolyte using pulsed currents.

The following are the typical examples:

Tantalum foils of size 3 cm×2 cm×.0075 cm is etched in a non-aqueous electrolyte of the following composition :

Electrolyte: 12.0 gms. of ammonium bromide plus one litre of A.R. Methanol plus 4.0 ml. of water.

The average current density while using pulsed current of 50 cycles frequency is 5.8 ams/sq.dm. The temperature of the bath is maintained at 30 to 33° C. during the etching time of ten minutes. The etched foil is washed well and then formed in 1 per cent. sodium sulphate solution at room temperature. The etch ratio is in the order of 10 to 12.

EXAMPLE.

Tantalum of size 3 cm×2 cm×0.0075 cm. is etched in a non-aqueous electrolyte of the following composition:

Electrolyte: 12.0 gms. of ammonium chloride plus one litre of A.R. Methanol. This may contain water in the range of 4 to 10 ml.

The average current density is 5.8 amps/dm², and the foil is etched for 10 minutes maintaining the bath temperature between 30 to 33° C. The etched foils are formed in 1 per cent. sodium sulphate solution at room temperature at 30 volts. The etch ratio obtained is in the order of 10 to 12.

The following are the main advantages :

1 The high etch ratio makes possible the use of smaller size foils to get the desired capacitance rating.

2 The equipment for the production of pulsed currents may be made cheaper by proper selection of the type of current form required.

R. BHASKAR PAI,

*Patents Officer,*

*Council of Scientific and Industrial Research.*

*Dated this 10th day of February 1966.*

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## COMPLETE SPECIFICATION.

### IMPROVEMENTS IN OR RELATING TO ETCHING OF TANTALUM FOR USE IN ELECTROLYTIC CAPACITORS.

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).

*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 BALKUNJI ANANTHA SHENOI, SCIENTIST, KANDADAI RAJAGOPALACHARI NARASIMHAN, SENIOR SCIENTIFIC ASSISTANT, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, JUNIOR SCIENTIFIC ASSISTANT, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, ALL INDIAN CITIZENS.

This invention relates to improvements in or relating to etching of tantalum for use as anodes in electrolytic capacitors.

Tantalum electrolytic capacitors are known for their excellent electrical performance and long shelf life. Since the metal is imported from foreign countries, it is desirable to have maximum surface area per unit weight of the metal.

Several foreign patents are available on etching tantalum for use as capacitor anode; but the method claimed in this patent gives very high etch ratio and has not been hitherto reported in literature.

Etching materially increases the effective surface area of the capacitor anode and thereby correspondingly increases the electrical capacity per unit of projected area or the capacity value for a given electrode side. The term '*etch ratio*' which will be used, in this connection, is defined as the ratio of capacity of the etched foil and plain foil of the same dimension, when formed to the same voltage under identical conditions.

Hitherto it has been proposed to use direct current for etching tantalum anodes for capacitors.

This is open to the objection that the use of DC gives rather a low etch ratio.

The object of this invention is to obviate this disadvantage by using pulsating direct current for etching tantalum and thereby obtain a high etch ratio.

According to the present invention, the process of electrolytically etching tantalum to get a high etch ratio in the order of 10-12 (the term "etch ratio" is defined as the ratio of the capacity of the etched foil and the plain foil of similar dimension when formed at the same voltage under identical conditions), consists in making tantalum as anode in an electrolyte

using methanol-water mixture as solvents and inorganic soluble salt as the solutions in pulsating direct current as the source.

Tantalum forms its oxide film in most of the aqueous electrolyies and it is essential that the etchant should be non-film forming in nature. Methanol has wide solubility range for inorganic substances like halides, thiocyanates of sodium, potassium and ammonium. Therefore, suitable concentration of any one of them or a mixture of them in methanol can be employed as an etchant.

The water content should be kept at an optimum range in the etchant for getting satisfactory results.

Using pulsating direct current while one can get very high etch ratio, the etched foil to be used subsequently in rolling operations during fabrication of capacitors should retain sufficient mechanical strength. This maximum etch ratio without loss in mechanical strength can be obtained with pulsating direct current in an electrolyte containing the required range of water concentration.

As the etch ratio decreases with forming voltage, etch ratio of more than 5 can be obtianed using 200 volts as forming voltage.

The following examples illustrate the invention:

EXAMPLE 1.

Tantalum foils of the size 3 cm×2 cm×0.0075 cm is etched in one litre of methanol containing 12.5 gms. of ammonium bromide and 5 ml. of water. Foils are etched for ten minutes at a current density of 5 A/dm$^2$ and at the temperature between 30-33° C. The etched foils are washed well and formed at 30 volts in a solution of 1 per cent. sodium sulphate at room temperature. Etch ratio of 9 to 13 can be obtained using pulsating direct current density of 4.2 to 7.5 A/dm.$^2$ Further increase in current density leads to loss of mechanical strength as also evidenced by the increase in weight loss of more than 20 per cent.

EXAMPLE 2.

Tantalum of size 3 cm×2 cm×0.0075 cm is etched in an electrolyte containing 12.0 gms. of ammonium chloride present in 1 litre of AR methanol and water in the range of 4 to 10 ml. The average current density is 5.8 A/dm$^2$ and the foil is etched for 10 minutes maintaining the bath temperature between 30 and 33° C. The etched foils are formed in 1 per cent. sodium sulphates solution at room temperature at 30 volts. The etch ratio obtained is in the order of 10 to 12.

Table 1 gives the variation of etch ratio and pulsating direct current of 50 pulses/sec. The advantages of DC using pulsating direct current over DC can be seen from the table.

Since the range of concentration of water in etching solution giving high etch ratio is fairly wide, it may not be essential to use AR methanol for this work. Distilled methanol with known amount of water may be efficient for the etching.

The equipment for the production of pulsed currents may be made cheaper by proper selection of the type of current form required.

*TABLE 1.*

| DC from battery | | Pulsating direct current | |
|---|---|---|---|
| Water concentration ml/1 | Etch ratio | Water concentration ml/1 | Etch ratio |
| 0 | 2.5 | 0 | 1.4 |
| 1.5 | 3.1 | 2.0 | 8.0 |
| 2.5 | 2.4 | 5.5 | 11.3 |
| 4.0 | 1.6 | 10.0 | 11.6 |
| 6.0 | 1.3 | 12.5 | 12.2 |
| 7.5 | 1.2 | 30.0 | 10.2 |
| 10.0 | 1.1 | 50.0 | 8.0 |

We claim:

1. A process of electrolytically etching tantalum to get a high etch ratio in the order of 10-12 (the term "etch ratio" is defined as the ratio of the capacity of the etched foil and the plain foil of similar dimension when formed at the same voltage under identical conditions), which consist in making tantalum as anode in an electrolyte using methanol-water mixture as solvents and inorganic soluble salt as the solutions in pulsating direct current as the source.

2. A process as claimed in Claim 1, wherein the current density of the pulsating direct current is in the range of 4 to 8 A/dm$^2$.

3. A process as claimed in Claim 1 or 2, wherein the electrolyte is a solution of methanol containing an inorganic soluble salt and water in the range of 1-10 ml. per litre.

4. A process as claimed in Claim 3, wherein an inorganic soluble salt such as bromide or chloride of sodium or ammonium is dissolved in the above-mentioned electrolyte in the range of 1 to 5 per cent. by weight.

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*Dated this 16th day of November 1966.*

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