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## METHOD OF MANUFACTURING SOLID ELECTROLYTIC CAPACITORS

### FIELD OF THE INVENTION

The present invention relates to the field of method of manufacturing a solid electrolytic capacitor that employ a valve metal on which an anodized film is formed as an anode.

### BACKGROUND OF THE INVENTION

In conventional methods of manufacturing solid electrolytic capacitors (hereafter referred to as "solid capacitors"), an anodized film, base layer, conductive polymer layer, and cathode conductor layer are successively formed on the surface of a foil or fine powder sintered body of valve metal which becomes an anode (positive electrode). After lead wires are connected to a capacitor element, it is molded with a packaging resin to complete the solid capacitor. In general, a  $\text{MnO}_2$  layer is used as a base layer in this series of manufacturing processes. As the  $\text{MnO}_2$  layer is usually formed by thermally decomposing manganese nitrate, the anodized film is significantly damaged when aluminum is used as the anode, causing large leak current in the completed solid capacitors.

For solving the above problem, the Japanese Laid-open Patent No. S63-181310 and H2-260516 disclose re-anodization in electrolytic solution after forming the conductive polymer layer. Japanese Laid-open Patent No. H3-178117 also discloses a method of forming a conductive polymer layer on the  $\text{MnO}_2$  layer after

adhering an insulating resist tape on the anodized film to separate a cathode (negative electrode) and anode, and then forming the  $\text{MnO}_2$  layer by means of thermal decomposition.

These conventional methods disclosed in Japanese Laid-open Patent Nos. S63-181310 and H2-260516 involve re-anodization after forming a conductive polymer layer in the electrolytic solution. The electrolytic solution is thus difficult to be sufficiently provided on the anodized film, making this process insufficient for fully repairing any damage to the anodized film. In addition, the conductive polymer layer sometimes degrade under some anodizing conditions, resulting in unsatisfactory impedance characteristics.

The conventional method disclosed in the Japanese Laid-open Patent No. H3-178117 requires re-anodization after formation of the  $\text{MnO}_2$  layer by thermal decomposition. Otherwise, the significantly damaged anodized film permits the flow of large leak current. In addition, even if re-anodization is implemented, adhesives on the resist tape seeps out and interferes with the repairability of defective portions of the anodized film near the resist tape.

## SUMMARY OF THE INVENTION

The present invention aims to address the above disadvantages of conventional methods, and provides a method of manufacturing solid electrolytic capacitors with less leak current and good impedance characteristics.

The method of manufacturing solid capacitors of the present invention comprises:

forming an anodized film on the surface of an anode body made of a valve metal;

separating a cathode part and anode part on the anodized film;

forming a base layer for a solid electrolyte layer on the anodized film;

immersing a capacitor element on which the base layer is formed into an organic polar solvent or its solution;

removing the capacitor element from the organic polar solvent or its solution and immersing it in electrolytic solution before the solvent or its solution dries up, for re-anodization; and

forming a solid electrolyte layer and cathode conductor layer on the base layer.

Furthermore, the method of manufacturing solid capacitors of the present invention comprises:

forming an anodized film on the surface of the anode made of a valve metal;

adhering an insulating resist tape for separating cathode part and anode part on the anodized film;

immersing a capacitor element on which the insulating resist tape is adhered into a solution containing dissolved manganese salts;

removing the capacitor element from the solution and forming a  $MnO_2$  layer by thermally decomposing attached manganese salts;

immersing the capacitor element in an organic polar solvent or its solution;

removing it from the organic polar solvent or its solution and immersing it in the electrolytic solution, before the solvent or solution dries up, for re-anodization;

and

forming a solid electrolyte layer and cathode conductor layer on the base layer.

Accordingly, wettability of the cathode in the re-anodization process improves, and small defects on the anodized film can be repaired. The present invention thus offers solid capacitors with less leak current.

### **DESCRIPTION OF THE PREFERRED EMBODIMENT**

Exemplary embodiments of the present invention are described below. However, it is apparent that the present invention is not limited to these exemplary embodiments.

#### **First exemplary embodiment**

An insulating resist tape is adhered on an aluminum foil to separate cathode part and anode part after electrolytic etching of the aluminum foil. The effective area of the anode body of a capacitor element are set to 3.0 mm x 4.0 mm, and this is immersed in a solution containing 5 weight percent of ammonium adipate at a liquid temperature of 70 °C. A 12 V DC voltage is then applied for 20 minutes to form an anodized film. This anode body is then immersed in manganese nitrate solution, and attached manganese salts are thermally decomposed at 300 °C for 5 minutes to form a MnO<sub>2</sub> layer on the surface of the anode body.

The anode body is then immersed in a aqueous solution containing 6 weight percent of 1-butanol. Before the solution dries, the anode body is immersed in a

aqueous solution containing 5 weight percent of ammonium adipate at 70°C liquid temperature, and a 10 V DC voltage is applied for 10 minutes for re-anodization. After these processes are complete, a conductive polymer layer made of a polypyrrole film is formed on the  $\text{MnO}_2$  layer using the electrolytic polymerization method. Graphite paste (aqueous suspension) and silver paste are subsequently applied to this conductive polymer layer to form a cathode conductor layer. After connecting lead wires to this anode body, the capacitor element is molded in packaging resin to complete a solid capacitor.

#### Second exemplary embodiment

A second exemplary embodiment employs a solution containing 25 weight percent of isopropyl alcohol aqueous solution instead of the 1-butanol aqueous solution described in the first exemplary embodiment. Other methods are the same as those in the first exemplary embodiment for manufacturing a solid capacitor.

#### Third exemplary embodiment

In a third exemplary embodiment, the anode body was immersed in the isopropyl alcohol aqueous solution for 5 seconds. Other methods are the same as those in the second exemplary embodiment for manufacturing a solid capacitor.

#### Fourth exemplary embodiment

A fourth exemplary embodiment employs a solution containing 25 weight percent of acetonitril aqueous solution instead of the 1-buthanol solution in the first exemplary embodiment. Other methods are the same as those in the first exemplary embodiment for manufacturing a solid capacitor.

### Comparative example

A comparative solid capacitor was manufactured using the same steps as the first exemplary embodiment but without the step of immersing the anode body in the 1-butanol aqueous solution after thermal decomposition.

Table 1 shows the initial characteristics of the solid capacitor in accordance with the first to fourth exemplary embodiments and comparative example. The characteristics of the capacitor were measured at 25 to 30 °C, the capacity and  $\tan \delta$  (delta) at 120 Hz, and impedance at 400 kHz. Leak current was measured 30 seconds after applying 6.3 V DC. Table 1 shows the mean value of  $n = 30$  test pieces.

Table 1

|                        | Capacitance | $\tan \delta$ | Impedance<br>(milliohms) | Leak current<br>(nA) |
|------------------------|-------------|---------------|--------------------------|----------------------|
| First embodiment       | 1 2 . 3     | 1 . 0         | 5 8                      | 1 7 7                |
| Second embodiment      | 1 2 . 4     | 0 . 8         | 6 1                      | 1 6 5                |
| Third embodiment       | 1 2 . 4     | 0 . 9         | 5 7                      | 1 3 2                |
| Fourth embodiment      | 1 2 . 5     | 0 . 9         | 6 3                      | 1 5 1                |
| Comparative<br>example | 1 2 . 1     | 1 . 2         | 6 9                      | 8 9 0                |

Table 2 shows the mean value of five solid electrolytic capacitors each from the first to the fourth exemplary embodiments and comparative example 1. The initial leak current and leak current after keeping the test pieces under high temperature and high humidity conditions of 85 °C and 85% RH for 500 hours without load were measured. Leak current was measured at 25 to 30 °C thirty seconds after applying a 6.3 V DC voltage.

Table 2

|                     | Leak current (nA) |            |
|---------------------|-------------------|------------|
|                     | Initial value     | after test |
| First embodiment    | 1 8 3             | 7 0 4      |
| Second embodiment   | 1 5 0             | 6 4 0      |
| Third embodiment    | 1 2 5             | 5 1 1      |
| Fourth embodiment   | 1 5 6             | 5 8 5      |
| Comparative example | 1 0 0 2           | 1 1 2 0 8  |

It is apparent from Tables 1 and 2 that the manufacturing method of solid capacitors described in the first to fourth exemplary embodiments has better capability to suppress an increase in leak current during production, compared to that of the comparative example 1.

In addition, solid capacitors manufactured according to the method described in the first to fourth exemplary embodiments show less increase in leak current after being left in unloaded condition in a high temperature and high humidity environment.

More specifically, the solid capacitors of the present invention are manufactured by immersing a capacitor element onto which a  $\text{MnO}_2$  layer has been formed into an organic polar solvent or its solution, immersing the capacitor element in electrolytic solution before the organic polar solvent or its solution dries for re-anodization, and then forming electrolyte on the  $\text{MnO}_2$  layer. This reduces the detrimental effect on wettability of a portion of the cathode due to seepage of adhesives from the resist tape during the thermal decomposition of manganese salts.

Furthermore, electrolytic solution is uniformly supplied to the entire cathode during re-anodization, and fine defects may thus be repaired, forming a high quality anodized film. Accordingly, the present invention enables the suppression of an increase in leak current during production, as well as the reduction of an increase in leak current as a result of the solid capacitor kept at high temperature and high humidity without load.

As described above, the manufacturing method of the present invention suppresses an increase in leak current during the manufacture of solid capacitors. In addition, the present invention reduces an increase in leak current when the solid capacitor is kept at high temperature and high humidity without load. The manufacturing method of the present invention forms the  $\text{MnO}_2$  layer on every portion of the anodized film, enabling the production of solid capacitors with low impedance at high frequencies.

The exemplary embodiments also describe the case of forming the  $\text{MnO}_2$  layer as a base layer for the conductive polymer layer. However, other than  $\text{MnO}_2$ , conductive or semiconductive metal oxides including tin, zinc, tungsten, nickel, and vanadium may be used independently or as composite oxides for the base layer. If a non-aqueous solvent is used, a highly conductive metal oxide such as ruthenium oxide may also be used.

The exemplary embodiments also describe the case of using aluminum as a valve metal. Other than aluminum, titanium, tantalum, and other valve metals are naturally applicable to the manufacturing method of the present invention.

Still more, the exemplary embodiments describe the case of employing the aluminum foil. However, other than the foil, the present invention is also applicable to capacitor elements made such as of fine powder sintered body.

**What is claimed is:**

1. A method of manufacturing solid electrolytic capacitors, said method comprising:
  - forming an anodized film on a surface of an anode made of a valve metal;
  - forming a capacitor element by adhering an insulating resist tape for separating cathode and anode on said anodized film;
  - forming a  $\text{MnO}_2$  layer by immersing said capacitor element in a solution containing dissolved manganese salts, removing said capacitor element from said solution, and thermally decomposing attached manganese salts;
  - immersing said capacitor element on which said  $\text{MnO}_2$  layer is formed in at least one of organic polar solvents or their aqueous solutions;
  - re-anodizing said capacitor element by immersing said capacitor element in electrolytic solution before one of said organic polar solvents or their solutions dries; and
  - forming a solid electrolyte layer and cathode conductor layer on said  $\text{MnO}_2$  layer.
2. The method of manufacturing solid electrolytic capacitors as defined in Claim 1, wherein said organic polar solvent is soluble in water.

