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# METHOD OF PRODUCING A SOLID ELECTROLYTIC CAPACITOR

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The present invention relates to a method of producing a solid electrolytic capacitor.

As it is well known, capacitors of this kind comprise a sintered body consisting of the metals tantalum or niobium serving as the anode. On a dielectric layer of this metal there is provided a semiconducting layer consisting of manganese dioxide serving to act as a "solid electrolyte" for carrying the metallic cathode layer. These capacitors have already proved to be satisfactory.

Capacitors with a sintered body of titanium, however, have not yet been manufactured in this form. The reason for this is presumably to be seen in the fact that the metal of titanium cannot be produced with the necessary purity and, on the other hand, in the fact that the titanium oxides TiO or $Ti_2O_3$ respectively, are conductive and, therefore, disturb the construction of a suitable blocking layer (barrier layer) when employing the conventional forming methods. Finally, objections were also raised against the use of titanium because this metal is very soft, thus rendering the production of a sintered body rather difficult.

The phesent invention provides a way of producing a solid electrolytic titanium capacitor.

The invention itself is based on the application of a suitable temperature treatment, forming and contacting process in order to build up the necessary stacking structure on a sintered body of titanium powder.

In carrying out the inventive method one may start with titanium powder having a purity degree of only 99.4%, although an increased purity degree will also improve the electrical properties.

According to the invention there is preferably used a flat pressed plate shaped sintered body, because it has proved that the best electrical results are obtained with such an embodiment.

Further details of the invention will be seen from the following description of the individual steps of the process:

The sintering of the titanium powder is appropriately carried out in a high vacuum, at a temperature ranging between 1200 and 1400° C. Preferably the titanium powder shall have a grain size of 10–100$\mu$. A very suitable sintering temperature is considered to be at 1300° C., with a sintering period of about 30 to 60 minutes. The values of both the capacitances and the residual current may be changed by varying the sintering time.

As a material for the lead-in wire extending to the sintered body, it is proposed to use titanium of a purity as high as possible. It has proved favorable to sinter the titanium wire into the body when producing the sintered body, so that the freely projecting end can be used as the lead-in wire.

Upon completion of the sintering process there is first of all removed the superficial oxide film which would otherwise have a disturbing effect during the further process. This can be accomplished by etching the sintered body, e.g., with the aid of a diluted solution of hydrofluoric acid. The removal of the oxide film can be regarded as being completed as soon as there appears a strong formation of gas bubbles indicating that now the titanium metal itself is being attacked. The etching of



the titanium not only causes an enlargement of the capacitance of the sintered body, but also cleans or purifies the surface thereof. The success of the etching process can be proved in particular when comparing the residual current measurements of etched and unetched sintered bodies.

Subsequent to the etching process the sintered body must be carefully washed, in order to remove all traces of fluor. The use or employment of an ultrasonic cleansing has proved to be very useful in this respect. A good result, however, is also obtainable when subjecting the sintered body to a repeated boiling in purest water. In no case is the wash-water allowed to have a milky opacity.

The etched and washed sintered bodies are dried and put for sometime, at least for several hours, into an aqueous oxidizing solution at room temperature. A mixture of e.g. one part concentrated nitric acid and one part of a 30% hydrogen peroxide has proved to be favorable. The oxidizing treatment serves the purpose of converting conductive foreign metal particles in the sintered body, such as particles of iron or silicon, into non-conducting oxides. This leads to a reduction of the residual current of the future capacitor.

Thereupon there is carried out an oxidizing temperature treatment at a temperature of about 400–500° C., which in air must last for several hours. Preferably, however, there is used pure oxygen if the time of treatment is to be reduced to about 15–30 minutes, and if there is to be avoided the formation of conductive titanium nitrides. By this step of the process the sintered body which hitherto had a metallically grey appearance, is provided with a tarnish decolorization quite depending on the kind and duration of treatment. At a temperature of 300° C. the sintered body will have a yellow appearance, at a higher temperature a brown appearance, and thereafter a bluish-violet appearance, then grey, and finally a white appearance. The bluish-violet color is to be preferred.

The thus pre-treated sintered bodies are now subjected to various forming processes under electric voltages. First of all there is carried out a forming in the solution of an aqueous electrolyte having a good conductivity, e.g., an acid solution, at about 20° C., to about 20 volts or higher. Subsequently to the washing (rinsing) and drying there is carried out the second forming process in a mixture of several salts at a temperature of about 350° C. Preferably, and in accordance with the invention, there is used a salt melt consisting of sodium, potassium, and lithium salts. As particularly favorable the following composition was used:

| | G. |
|---|---|
| Sodium nitrite | 138 |
| Potassium nitrate | 101 |
| Lithium nitrate | 101 |

Upon termination of the forming process, and with voltage still applied, there is effected a cooling down to a temperature of about 125° C., and the sintered body is brought out of the melt and into boiling water for removing the remainders of the salt melt. Thereupon the drying and, subsequently thereto, a third forming process is carried out in an electrolyte which substantially consists of an organic solution containing small amounts of water, such as "glycol," to which, preferably for the purpose of increasing the conductivity, there are added several ionogenes, such as borates. This third forming process is carried out at a temperature ranging between 120 and 150° C. Finally, there is performed a cooling down to room temperature under electric voltage.

As may be taken from the above, there is thus carried out a temperature uninterrupted transition between the individual steps of the forming process, in other words; there is in no case effected a sudden variation of the temperature of treatment between the individual steps.

Now the sintered body is ready for a layer of semiconducting material to be deposited on the thus produced dielectric layer.

To this end the sintered body, in vacuo, is saturated, e.g., with a mixture consisting of a manganese nitrate solution and manganese hydroxide. Such a mixture will be obtained when adding or mixing an aqueous acid manganese-nitrate solution to or with a solution of ammonia until a sufficient amount of manganese hydroxide exists in the solution.

Subsequently thereto a temperature treatment in air is carried out at a temperature ranging from about 150 to 250° C. with a view of forming manganese dioxide. The following reaction takes place:

$$Mn(NO_3)_2 + 2Mn(OH)_2 + O_2 \longrightarrow 3MnO_2 + 2\uparrow NO_2 + 2\uparrow H_2O$$

A temperature of 200° C. has proved to be most favorable.

By the formation of $MnO_2$ cracks are easily caused to appear in the oxide layer, which have to be healed. According to the invention this may be accomplished by the action of an alkaline reacting aqueous electrolyte.

According to the invention, the semiconducting layer, consequently the $MnO_2$-layer, is preferably produced in partial layers, and each time between the formation of two such layers there is carried out a heating of the defects by subjecting them to a forming process in the above-mentioned electrolyte.

The secured capacitance of a cylindric sintered body such as described above with a diameter of 3.2 millimeters and a length of 11 millimeters containing 0.2 gram of titanium is 30 microfarads after forming treatment at 40 volts. The maximum working voltage is 35 volts.

The electrode system produced in this way is now provided with a graphite coating serving as the base or support for a solderable metal coating to which a lead-in wire may be soldered.

We claim:

**1.** A process for manufacturing a capacitor having a titanium body as one electrode, comprising the steps of:

removing any titanium oxide film from the surface of said body;

heating said body in an oxidizing atmosphere at a temperature between 300 and 500° C. until a bluish-violet colored film of titanium oxide becomes visible;

electrolytically forming an additional titanium oxide film on said colored film; and

depositing a counterelectrode on said additional film.



**2.** A process according to claim **1** further comprising the step of converting any foreign metal particles present on the surface of said body into non-conducting oxides before performing said heating step.

**3.** A process according to claim **1**, wherein said additional film is formed by the steps of:

immersing said body in an aqueous electrolyte of good conductivity at ambient temperature, and applying a potential of at least 20 volts between said body and said electrolyte;

immersing said body in an electrolyte comprising a mixture of fused salts at a temperature between 300 and 400° C. while applying a potential between said body and said fused salt electrolyte; and

immersing said body in an organic electrolyte at a temperature between 120 and 150° C. while applying a potential between said body and said electrolyte.

**4.** A process according to claim **3** wherein said fused salt mixture comprises sodium nitrite, potassium nitrate, and lithium nitrate, in the relative proportions of approximately 138:101:101 by weight.

**5.** A process according to claim **4**, wherein said counterelectrode is deposited by the steps of:

saturating the surface of said body with a mixture of manganese nitrate solution and manganese hydroxide;

heating said saturated body at a temperature between 150 and 250° C. to pyrolytically form a layer of manganese dioxide from said mixture;

reforming said additional film by immersing said body in an aqueous electrolyte while applying a potential between said body and said electrolyte below the potential applied therebetween during the steps of forming said additional film; and

depositing a conductive layer on said manganese dioxide layer.


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