

PATENT SPECIFICATION

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(72) Inventors HENLEY FRANK STERLING
ERIC LANGLEY BUSH and
STEPHEN JOHN McMANUS



(54) ELECTROLYTIC CAPACITOR

(71) We, STANDARD TELE-
PHONES AND CABLES LIMITED, a
British Company, of 190 Strand, London,
W.C.2, England, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be
particularly described in and by the
following statement:—

This invention relates to electrolytic
capacitors.

Electrolytic capacitors may have anodes
manufactured from a valve metal powder
by suitable compaction thereof to form a
coherent porous body which is
subsequently processed to produce the
dielectric of the capacitor, by anodising the
valve metal, and to introduce into or cause
formation within the anodised, porous body
an appropriate electrolyte liquid or solid
respectively.

Since a considerable proportion of the
valve metal does not play an active part in
the capacity forming mechanism, there has
been used a valve metal coated powder to
form the porous anode, again using suitable
compaction techniques. This approach,
which reduces the amount of valve metal
required, is particularly attractive from a
cost-saving point of view when the valve
metal employed is relatively expensive, e.g.
tantalum, niobium, or tantalum/niobium
alloys.

The core material of the valve metal
coated powder may be electrically
conducting, as described for example in our
Patent Specification No. 1,298,928 but
there are disadvantages in employing
certain categories of electrically
conducting core material, particularly if it
is of a metal or alloy which is not a valve
metal, in that compaction of the coated
powder may cause the core material to be
exposed through the valve metal coating.

Alternatively, the core material may be
electrically insulating, typically a ceramic.
So far as is known to the Applicants, all
anode compaction processes for producing
capacitor anodes from valve metal coated

ceramic powder have involved a two-stage
process in which the powder is first pressed
and then sintered, the sintering
temperature being at least 1600°C. for
tantalum coated alumina powder.

It is an object of the present invention to
eliminate the sintering stage, whereby
production costs are reduced.

According to the invention there is
provided an electrolytic capacitor having
an anode comprising a pressure compacted,
non-sintered, porous body of valve metal
coated particles whose core material is
electrically insulating and is significantly
harder than the valve metal coating.

According to the invention there is also
provided a method of manufacturing an
electrolytic capacitor which includes the
steps of pressure compacting valve metal
coated particles whose core material is
electrically insulating and is significantly
harder than the valve metal coating to form
a coherent porous anode body, and,
without sintering the body, anodising the
valve metal to form the dielectric of the
capacitor.

The invention may be more clearly
understood from the following description
taken in conjunction with the
accompanying drawings, in which:—

Fig. 1 is a graph showing % theoretical
density of tantalum powder and tantalum
coated alumina powder vs. compaction
pressure, and

Figs. 2 to 8 show diagrammatically the
successive structural build-up of an
electrolytic capacitor having a tantalum
coated powder anode.

The ability to produce satisfactory
anodes from valve metal coated insulating
particles compacted solely by pressure is
dependent on a number of factors.

1. The compaction pressure.
2. The expansion coefficient of the
core material.
3. The size of the particles of core
material.
4. The mechanical and physical
characteristics of the core material.

5. The thickness of the valve metal coating.

The compaction pressure is in the range 25 to 40 tons per square inch whatever the valve metal coating used.

In Fig. 1, curve A is for all-tantalum powder, which can be compacted to virtually 100% theoretical density ($d=16.6$), i.e. substantially no porosity, at a pressure below 20 tons per square inch. Accordingly, to achieve a lesser % theoretical density, i.e. to have porosity, the compaction pressure would not exceed at most 10 tons per square inch.

With valve metal coated insulating particles substantially harder than the coating, there is a form of automatic density determining mechanism on compaction, in that the applied pressure squeezes the coated particles together until the cores contact one another. Clearly the valve metal coating thickness determines the final % theoretical density, because for a given core size, a relatively thick coating gives a higher density than a relatively thin coating.

The thickness of the valve metal coating is preferably less than $1\text{ }\mu\text{m}$ so that, as more fully described in our copending Application No. 27378/74, upon anodisation of the anode at a voltage determined by the required voltage code of the capacitor the average thickness of the unanodised valve coating does not exceed $0.5\text{ }\mu\text{m}$.

The core size is typically in the range of $9\text{--}13\text{ }\mu\text{m}$, and curve B of Fig. 1 shows the % theoretical density (around 57%) for tantalum coated powder with alumina cores in this range with a tantalum coating of about $0.3\text{ }\mu\text{m}$. The same curve B would be obtained with the same thickness of tantalum coating on cores with a size in the range of $13\text{--}17\text{ }\mu\text{m}$, or $17\text{--}21\text{ }\mu\text{m}$.

Higher density may be obtained by extending the range of core size, and curve C is for a range of $9\text{--}17\text{ }\mu\text{m}$, achieving around 70% theoretical density. This higher figure is because the smaller cores in the range pack into the interstices between the larger cores.

The expansion coefficient of the core material should be comparable with that of the valve metal coating.

As regards physical and chemical characteristics, hardness and electrically insulating have already been mentioned. The core material should not degrade either in its own right or by reaction with the deposited valve metal coating. The core material may be crystalline or amorphous.

For tantalum, alumina is the preferred core material. Other ceramic core materials include silicon carbide and titania.

The core material may alternatively

be of silica or a suitable glass. Ready availability in a particle size graded form is clearly another factor.

The valve metal coating may consist exclusively of the particular valve metal, or alloy of valve metals, or additionally may contain a small amount (typically up to 1% by weight) of doping elements such as Mo as it has been found to improve the electrical characteristics of the finished capacitor.

Compaction of the valve metal coated powder is carried out either by using conventional hard dies and punches, with a binder incorporated into the powder and subsequently removed prior to subsequent capacitor forming stages. Isostatic compaction is an alternative method, using a polyurethane sack for the material containment and to act as a "tooling". A binder does not have to be used with isostatic compaction and the powder can be dry pressed using this latter method.

Referring now to Figs. 2 to 8, these show successive stages in the manufacture of a tantalum coated powder capacitor.

There are five stages of production.

1. Tantalum coating the core material.
2. Production of anodes from tantalum coated powder.
3. Anodising coated powder anodes.
4. Manganising coated powder anodes.
5. Finishing the capacitor unit.

1. (Figs. 2 and 3). The tantalum coating 2 on crystalline alumina core material 1, coating thickness typically $0.3\text{ }\mu\text{m}$ on cores in the range $9\text{--}13\text{ }\mu\text{m}$, is produced by reducing tantalum pentachloride, with an atmosphere of hydrogen, in the presence of alumina powder at a temperature of about 1000°C . Practically this is achieved in a fluid bed type reactor where the alumina powder is held in suspension by a gas stream containing a mixture of argon and hydrogen. Tantalum pentachloride held in a separate container is vaporised, then carried in either argon or hydrogen into the fluid bed reactor.

During the reaction tantalum metal is deposited on the surface of the alumina and hydrogen chloride is liberated. The liberated gas is processed to prevent atmospheric pollution.

2. (Fig. 4). The tantalum coated alumina is mixed with 10 to 15% by weight of camphor, by dissolving the camphor in a quantity of ethyl ether or Arcton (Registered Trade Mark), adding this mixture to the powder and finally evaporating the solvent in an atmosphere of dry inert gas, e.g. argon or nitrogen.

Inert gas is used to prevent atmospheric moisture being condensed on the powder, due to the reduction in temperature during evaporation. Moisture in the powder mix

tends to make it sticky and difficult to handle.

After sieving, the camphored powder is pressed into a compact of a pre-determined weight and diameter, e.g. 0.046 grams and $\frac{1}{4}$ inch respectively for a 10 μ F.15 V working capacitor, by one of the two methods previously mentioned. During compaction a tantalum lead wire 3 is introduced into the compact. For a capacitor as just quoted, the compaction pressure is 25 tons per square inch. This ensures a strong compact which does not need sintering.

Following compaction the anodes are welded by the tantalum lead wires to frames for processing and then (if they have been camphored) the camphor is removed by placing the anodes in an oven with a temperature set at $145^{\circ} \pm 5^{\circ}\text{C}$. for a minimum of 1 hour. Times vary with anode size.

To remove any residues of camphor and to prepare the anodes for anodising, the anodes are boiled in demineralised water to which has been added a small quantity of a wetting agent, for example Tee-pol (Registered Trade Mark) (Shell).

3. (Fig. 5). To form the tantalum pentoxide dielectric layer 4, the boiled anodes are suspended in a bath of 0.1% phosphoric acid solution at a temperature of 50°C . The bath is made of stainless steel and is connected as cathode to a power supply which can act in both constant current and constant voltage modes. The anodes are connected via their frame to the positive output of the power supply.

A constant current of 60 mA per gram of tantalum coated powder is applied until a predetermined voltage has been reached (60 V for 10 μ F.15 V capacitors). This voltage is then held for 3 hours on the constant voltage mode.

On completion of the anodising process, the anodes are removed from the bath and boiled in demineralised water until the phosphoric acid has been removed. The water is then removed by oven drying at 200°C . for 30 minutes.

4. (Fig. 6). The manganising process to form the manganese dioxide 5 is divided into three stages.

a. Primary dips. These are to fill the porous interior of the anodes and a fairly dilute solution of manganese nitrate of specific gravity 1.45 is used. Typical small anodes might need 5 cycles of primary manganising and large anodes 8 to 10. The anodes are dipped in the solution for 15 minutes and then transferred to a drying oven at 85°C . for 1 hour. After drying the anodes are placed in a decomposition oven at 200°C . for 1 hour.

b. Secondary dips. Similar to primary

dips except that a more concentrated manganese nitrate solution is used of specific gravity 1.74. The secondary dips build up an outer coating of manganese dioxide on the anode. The coating is soft in nature, but thick. Typically 2 to 4 of these dips are used depending on anode size.

c. Rapid dips. Used to build up a hard impervious layer on the outside of the secondary dips. Same dip time and specific gravity as the secondary dips, but no drying cycle and a rapid decomposition of 15 minutes. During decomposition water is injected into the oven to provide a humid atmosphere. Between 3 and 5 of these rapid dips are used depending on anode size.

After every two dips throughout the whole manganising process, a reform cycle is interposed. This is similar to anodising, but using phosphoric acid of 0.01% concentration. A power supply generates a voltage ramp rising to a preset voltage (30 V for 10 μ F.15 V capacitors) over 40 minutes. This voltage is held for 5 minutes. The manganised anodes are boiled in demineralised water after each reform cycle.

5. (Figs. 7 and 8). After manganising, the capacitors consist of a tantalum layer 2, on the alumina 1, acting as anode, tantalum pentoxide 4 as a dielectric, and manganese dioxide 5 as the cathode. The final stages of processing consist of making good electrical contact to the manganese dioxide, and encapsulation.

Two coatings are added to the outside of the manganese dioxide, firstly graphite 6 to give a low resistance cover, and then silver loaded resin 7 to give a base for soldering the unit into a can 8 for encapsulation.

An extension lead wire of solder coated nickel is welded to the tantalum anode wire after removal of the anode from the process frame. The anode is soldered into its can and the can sealed by a glass/metal seal.

It is to be understood that the foregoing description of specific examples of this invention is made by way of example only and is not to be considered as a limitation on its scope.

WHAT WE CLAIM IS:—

1. An electrolytic capacitor having an anode comprising a pressure compacted, non-sintered, porous body of valve metal coated particles whose core material is electrically insulating and is significantly harder than the valve metal coating.
2. A capacitor as claimed in claim 1 in which the initial thickness of the valve metal coating is less than 1 micrometre.
3. A capacitor as claimed in claim 1 or 2 in which the core material is a ceramic.
4. A capacitor as claimed in claim 3 in which the ceramic is alumina.

tends to make it sticky and difficult to handle.

After sieving, the camphored powder is pressed into a compact of a pre-determined weight and diameter, e.g. 0.046 grams and $\frac{1}{4}$ inch respectively for a 10 μ F.15 V working capacitor, by one of the two methods previously mentioned. During compaction a tantalum lead wire 3 is introduced into the compact. For a capacitor as just quoted, the compaction pressure is 25 tons per square inch. This ensures a strong compact which does not need sintering.

Following compaction the anodes are welded by the tantalum lead wires to frames for processing and then (if they have been camphored) the camphor is removed by placing the anodes in an oven with a temperature set at $145^{\circ}\pm 5^{\circ}\text{C}$. for a minimum of 1 hour. Times vary with anode size.

To remove any residues of camphor and to prepare the anodes for anodising, the anodes are boiled in demineralised water to which has been added a small quantity of a wetting agent, for example Tee-pol (Registered Trade Mark) (Shell).

3. (Fig. 5). To form the tantalum pentoxide dielectric layer 4, the boiled anodes are suspended in a bath of 0.1% phosphoric acid solution at a temperature of 50°C . The bath is made of stainless steel and is connected as cathode to a power supply which can act in both constant current and constant voltage modes. The anodes are connected via their frame to the positive output of the power supply.

A constant current of 60 mA per gram of tantalum coated powder is applied until a predetermined voltage has been reached (60 V for 10 μ F.15 V capacitors). This voltage is then held for 3 hours on the constant voltage mode.

On completion of the anodising process, the anodes are removed from the bath and boiled in demineralised water until the phosphoric acid has been removed. The water is then removed by oven drying at 200°C . for 30 minutes.

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After every two dips throughout the whole manganising process, a reform cycle is interposed. This is similar to anodising, but using phosphoric acid of 0.01% concentration. A power supply generates a voltage ramp rising to a preset voltage (30 V for 10 μ F.15 V capacitors) over 40 minutes. This voltage is held for 5 minutes. The manganised anodes are boiled in demineralised water after each reform cycle.

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Two coatings are added to the outside of the manganese dioxide, firstly graphite 6 to give a low resistance cover, and then silver loaded resin 7 to give a base for soldering the unit into a can 8 for encapsulation.

An extension lead wire of solder coated nickel is welded to the tantalum anode wire after removal of the anode from the process frame. The anode is soldered into its can and the can sealed by a glass/metal seal.

It is to be understood that the foregoing description of specific examples of this invention is made by way of example only and is not to be considered as a limitation on its scope.

WHAT WE CLAIM IS:—

1. An electrolytic capacitor having an anode comprising a pressure compacted, non-sintered, porous body of valve metal coated particles whose core material is electrically insulating and is significantly harder than the valve metal coating.

2. A capacitor as claimed in claim 1 in which the initial thickness of the valve metal coating is less than 1 micrometre.

3. A capacitor as claimed in claim 1 or 2 in which the core material is a ceramic.

4. A capacitor as claimed in claim 3 in which the ceramic is alumina.



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5. A capacitor as claimed in claim 1 or 2 in which the core material is silica.
6. A capacitor as claimed in claim 1 or 2 in which the core material is a glass.
- 5 7. A capacitor as claimed in any one of claims 1 to 6 in which the size of the cores is between 9 and 21 micrometres.
8. A capacitor as claimed in any one of claims 1 to 7 in which the valve metal is tantalum, niobium or a tantalum/niobium alloy.
- 10 9. A capacitor as claimed in any one of claims 1 to 8 in which the metal coating includes a small proportion of a doping element.
- 15 10. A capacitor as claimed in any one of claims 1 to 9 in which the anode is produced by compaction of the valve metal coated powder at a pressure of between 25 to 40 tons per square inch.
- 20 11. An electrolytic capacitor substantially as described and as shown in Figs. 7 and 8 of the accompanying drawings.
- 25 12. A method of manufacturing an electrolytic capacitor which includes the steps of pressure compacting valve metal coated particles whose core material is electrically insulating and is significantly harder than the valve metal coating to form a coherent porous anode body, and, without sintering the body, anodising the valve metal to form the dielectric of the capacitor.
- 30 13. A method as claimed in claim 12 in which the initial thickness of the valve metal coating is less than 1 micrometre.
- 35 14. A method as claimed in claim 12 or 13 in which the core material is a ceramic.
15. A method as claimed in claim 12 in which the ceramic is alumina. 40
16. A method as claimed in Claim 12 or 13 in which the core material is silica.
17. A method as claimed in claim 12 or 13 in which the core material is a glass. 45
18. A method as claimed in any one of claims 12 to 17 in which the size of the cores is between 9 and 21 micrometres.
19. A method as claimed in any one of claims 12 to 17 in which the valve metal is tantalum, niobium, or a tantalum/niobium alloy. 50
20. A method as claimed in any one of claims 12 to 19 in which the metal coating includes a small proportion of a doping element. 55
21. A method as claimed in any one of claims 12 to 20 in which the anode is produced by compaction of the valve metal coated powder at a pressure of between 25 and 40 tons per square inch. 60
22. A method as claimed in claim 21 in which the compaction is isostatic.
23. A method of manufacturing an electrolytic capacitor substantially as described with reference to the accompanying drawings. 65
24. An electrolytic capacitor manufactured by the method claimed in any one of claims 12 to 23. 70
- S. R. CAPSEY,
Chartered Patent Agent,
For the Applicants.

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