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PATENT SPECIFICATION

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(54) SOLID ELECTROLYTIC CAPACITOR

(71) We, SPRAGUE ELECTRIC COMPANY, a Corporation organised and existing under the laws of the State of Massachusetts, United States of America, of North Adams, Massachusetts, United States of America, 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 a solid electrolytic capacitor.

The present invention in one aspect provides a solid electrolytic capacitor including an electrode comprising a porous valve-metal body, a dielectric film covering the body, a solid electrolyte covering of manganese dioxide overlying said dielectric film, an outer layer of graphite overlying said electrolyte covering, an inner layer of graphite disposed within said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, said sandwiched portion containing graphite particles to reduce the electrical impedance between said inner and outer graphite layers, and a conductive counterelectrode overlying said outer graphite layer.

In a further aspect the invention provides a method of making a solid electrolytic capacitor including the steps of providing a porous valve-metal body as an electrode of the capacitor, covering said body with a dielectric film, forming on said dielectric film a solid electrolyte covering of manganese dioxide, the electrolyte covering having disposed within the covering an inner layer of graphite, forming an outer layer of graphite over said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, and forming a conductive counterelectrode over said outer graphite layer.

The invention makes possible a low cost solid valve-metal capacitor which offers

superior performance characteristics especially after exposure to elevated temperatures, and which is capable of being exposed to soldering processes at temperatures as high as 360°C for several minutes without degradation.

Features and advantages of the invention will also appear from the following description of a preferred embodiment thereof, given by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a longitudinal sectional view of a preferred embodiment of a capacitor according to the invention; and

Figure 2 is a magnified detail of Figure 1.

In one typical known method of making a solid electrolytic valve-metal capacitor a sintered porous tantalum body is anodised to form a film of tantalum oxide over all the exposed surfaces of the tantalum. Several coatings, typically about eight, of a manganous nitrate solution are applied over the tantalum oxide including regions in the pores of the tantalum body. Each coating is fired at a temperature of about 400°C, pyrolysing and transforming the manganous nitrate to a semiconductor, namely manganese dioxide (MnO₂). The composite coating of pyrolysed MnO₂ is then coated with a layer of graphite from an aqueous suspension, a layer of silver from a paint suspension, a layer of solder, and a metallic conductor. The body of the unit can then be encapsulated, for example, in an epoxy resin.

Electronic components including solid electrolyte capacitors are frequently required to withstand elevated temperatures, for example up to 360°C, for several minutes, while they are being solder connected to printed circuit boards or other circuit assemblies. Capacitors constructed in the manner described often fail at 360°C due to inadequacies in the silver, the solder, and the encapsulating resin. For example, the organic binder in the silver may be subject to degradation and the resulting organic vapours then cause reduction of MnO₂ to a species of lower

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conductivity; the silver metal may also be leached by the covering layer of solder. The solder is applied with the aid of a flux which is usually another source of organic vapours liable to cause reduction of the MnO_2 . The solder of the capacitor itself will also tend to melt at $360^\circ C$ which is clearly an undesirable feature, though we have found the most severe problem to be caused by the vapour from the encapsulating resin. Encapsulation intensifies the problem due to reaction of any vapour from the binder or flux due to entrapment of the vapour in the capacitor structure.

Various attempts have been made to overcome this problem with only limited degrees of success but we have been able to obtain improved results with the present invention.

The solid electrolytic capacitor of this preferred embodiment of the invention has a porous valve-metal body, an oxide film of the valve-metal covering the surfaces of the porous body, and a solid electrolyte coating of manganese dioxide overlying the oxide film. On the outer surface of the manganese dioxide coating is a layer of graphite that is in turn covered by a conductive counterelectrode. Buried within the manganese dioxide coating is one or more graphite layers. The adjacent graphite layers, including the outer layer, have a layer portion of the manganese dioxide coating sandwiched between them. The sandwiched manganese dioxide contains graphite particles that electrically connect the adjacent graphite layers.

The preferred capacitor additionally has a housing or protective outer encapsulation containing or consisting of an organic material. When such a capacitor is soldered into a circuit involving subjection to temperatures as high as $360^\circ C$ for several minutes, organic vapours are generated that permeate an outer portion of the manganese dioxide coating that is sandwiched between graphite layers with the result that some or all of this sandwiched manganese dioxide is reduced. Nevertheless, although the sandwiched manganese dioxide becomes reduced and highly resistive, the high conductivity of the manganese dioxide lying between the innermost buried graphite layer and the dielectric oxide film remains unchanged and the innermost buried graphite layer continues to present a path of graphite of low electrical impedance extending to the counterelectrode.

In addition it appears likely that the selective reduction of only the sandwiched manganese dioxide layers, near the outer surface and closer to the source of the reducing organic vapours, is enhanced by

the absorption and exhaustion of the vapours in the outer sandwiched layers.

By such means we have found it possible to make a capacitor, using in its construction organic materials that give rise to organic vapours during manufacture, and to expose the capacitor to high soldering temperatures without substantial degradation of the series impedance presented by the capacitor.

The structural features of the capacitor are shown in Figure 1, which is a cross-sectional view. A rectangular porous tantalum body 10 has a tantalum riser wire 11 partially embedded therein. The tantalum body 10 serves as the anode of the capacitor, but capacitors can be made using other porous valve-metal bodies, including tantalum, aluminium, titanium and niobium. The tantalum is covered with a tantalum oxide dielectric film 12 grown over the surfaces of the body 10, including surfaces within the pores. In the drawing the oxide 12 is represented diagrammatically as lying over the outer surface portions of the body 10.

A covering 13 of manganese dioxide lies over and adjacent the oxide film 12. This covering 13 is formed by first applying a dilute solution of manganous nitrate within the pores and over the oxide film that conforms to all body surfaces. By subjecting the body to about 300° in steam, the manganous salt is pyrolytically converted to a solid semiconducting manganese dioxide (MnO_2). Pyrolysis can also be accomplished by heating the body in a dry atmosphere at about $400^\circ C$. A second application of the manganous salt is again pyrolysed as before, and yet a third and so on until a sufficiently thick covering 13 of manganese dioxide is formed over the body.

Next a layer of graphite 14 is applied over the MnO_2 covering 13 and another coating or layer of MnO_2 15 is applied over the graphite layer 14. Another outer layer of graphite 16 is then formed over the outer MnO_2 coating 15. Thus, the outer coating 15 of MnO_2 is positioned between the two graphite layers 14 and 16. It will be understood that the two graphite layers are not sharply defined and separate, as is indicated in the detail of Figure 2 and as will be explained.

Over the outer layer 16 of graphite there is provided a relatively heavy coat 19 of a metal-bearing material that serves as cathode or the counterelectrode of the capacitor. Such material is a silicone resin containing particles of silver, copper or nickel. A metal cathode lead 23 is electrically and physically attached to the counterelectrode 19 by means of a conductive silicone resin 22 being bonded

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to the two parts. The anode riser wire 11 is welded or otherwise attached to a metal anode lead terminal 24. A silicone resin or other suitable organic material is used to form a housing encapsulant 20 encompassing the body and a portion of the terminal leads 23 and 24.

An example of a preferred method for making the capacitor described is as follows:

A porous tantalum body was anodized in known manner to form an oxide coating. This was then coated with MnO_2 by pyrolytic decomposition of manganous nitrate using the technique of first applying dilute solutions to penetrate and coat the whole surface of the body, followed by more concentrated solutions to achieve the required build up of MnO_2 on the outside of the body. The body was repeatedly dipped in a concentrated solution of 1.78 specific gravity manganous nitrate; the number of coatings applied was determined by the desired build up but 5 to 10 coatings were suitable; a greater number of top coats could be employed. After about the fourth or fifth top coat, however, the capacitor was coated with material available as Aquadag (R.T.M.), which is a commercial colloidal graphite suspension. The Aquadag coating was then dried at a suitable temperature, such as $150^\circ C$, for ten minutes. The Aquadag was applied as an aqueous solution of about 2 to 4% solids concentration.

After forming this first graphite layer, one or more further coats of MnO_2 were pyrolytically deposited, and then another layer of graphite was formed. At this stage the capacitor section could be completed by applying a metallic coating to form the counterelectrode and cathode connection, and it was found that in the presence of organic material the capacitor showed good impedance stability when exposed to a temperature of $300^\circ C$.

Moreover, even greater stability could be achieved by applying further alternate coats of MnO_2 and graphite. The number of such coats which could be applied was limited only by the dimension to which the final capacitor had to conform. A graphite layer, eventually to be covered, is layer 14 shown in Figure 1. From one to four applications of Aquadag (R.T.M.) are preferably employed to form each such buried layer.

It has been found that the later layers of a series of pyrolysed MnO_2 layers are porous and friable compared with the earlier relatively dense and non-porous underlying layers of MnO_2 . It is postulated that such porous layers become permeated by a subsequently applied manganous nitrate solution as well as covered by a layer of this

solution, such that upon a subsequent pyrolysis step a new porous MnO_2 layer is formed over said last layer and said last layer is filled and no longer porous. Microscopic examination of cross-sections of typical MnO_2 layers of partially completed capacitors support this hypothesis.

In a capacitor made as described with a layer of MnO_2 positioned between graphite layers, the layer of MnO_2 contains enough graphite particles 16a effectively to provide an electrical short circuit of the MnO_2 layer. Thus, the metal counterelectrode that lies over and electrically contacts the outer graphite layer is always in good electrical connection with the buried graphite layer without dependence upon the intervening MnO_2 for this purpose. Therefore, when or if the intervening MnO_2 is reduced and made highly resistive, for example by the action of organic vapour, the electrical connection existing between the metal-bearing counterelectrode and the dense MnO_2 coating under the buried graphite layer, is not impaired.

The point at which the first coat of graphite can be applied is determined by the desirability of keeping the highly conductive carbon from contacting the tantalum oxide surface or from penetrating the MnO_2 structure to any point at which it might cause an increase in leakage current. The graphite can be deposited following the first top coat of MnO_2 and following each subsequent top coat. However, unless this coat is adequately thick, such a procedure may lead to impaired operation due to excessive leakage current. It is therefore desirable that sufficient MnO_2 be applied before depositing the graphite to prevent such high leakage current.

The number of MnO_2 layers required prior to the application of the first graphite layer will depend on the method used to deposit the MnO_2 layer. Thus, in a method in which heavy layers of MnO_2 are deposited by dipping in a slurry of MnO_2 particles and manganous nitrate, only one such layer might be required. Other methods of forming a thick layer of MnO_2 are described in U.S. 3,481,029 and 3,241,008. Using a method in which MnO_2 is built up by dipping in the concentrated manganous nitrate solution having a specific gravity of about 1.78 g/cc as described, three to five layers give an adequate thickness of MnO_2 on which the first layer of graphite can be deposited. This foundation layer of MnO_2 is thus preferably thicker than about 0.002 inches regardless of the manner of its production.

Following pyrolysis of the last MnO_2 coat, a final outer layer of graphite was applied, suitably by applying one or more

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coats of the graphite suspension. The oxide film could be reformed after pyrolysis, and good results have been obtained by depositing the graphite either immediately prior to or immediately after this reformation. Alternatively, only one coat need be applied, either before or after reformation.

The capacitor is coated with a conducting layer such as a silver paint or a sprayed metal, after which it can be attached by a conducting medium to a solderable metal lead. Many such methods of terminating may be used provided they will withstand exposure soldering temperature such as 360°C. In the preferred embodiment the unit is coated with a conducting paint such as Eccobond 59C, made by Emerson and Cumming Inc., Canton, Mass., U.S.A. which is a silicone resin containing silver particles, and then cured for 30 minutes at 200°C. Another coat of the Eccobond 59C paint is then applied to an area of the capacitor section

and to this is cemented a suitable termination in place. Such termination may typically be a metal can in which the capacitor is contained or a metal lead frame strip or a wire. After thoroughly baking at about 250°C to cure and to remove the most volatile organic vapours from the conducting compounds, the capacitor can be hermetically sealed in a metal can, or can be encapsulated in a suitable resin.

To illustrate the practical results which can be obtained, Table I presents impedance values of experimental solid electrolyte tantalum capacitors having different numbers of buried graphite layers. The impedance of each is given for before and after heating at 360°C for three minutes and again after six minutes. The capacitors are nominal 22 μ f, 10 V tantalum capacitors having a counterelectrode of Eccobond 59C silver paint and being moulded in a silicone resin, specifically resin part number 306 made by Dow Corning Corp., Midland, Michigan, U.S.A.

TABLE I

Sample No.	No. of MnO ₂ layers prior to first graphite	Total No. of graphite layers	Impedance (Ohms)		
			Initial	After 360°C/ 3 min.	After 360°C/ 6 min.
1	5	3	0.14	0.24	0.44
2	5	4	0.14	0.22	0.34
3	5	5	0.14	0.23	0.32
4	6	2	0.14	0.28	0.60
5	6	3	0.15	0.23	0.35
6	6	4	0.15	0.23	0.32
7	6	1	0.15	4.2	—
8	6	1	0.15	20.4	—

The experimental capacitors of Samples 1 to 6 show useful characteristics; by contrast, data from a capacitor which was constructed in exactly the same manner except that only one layer of graphite was applied, namely after completion of pyrolysis, is included as Sample 7.

Further by way of contrast, data from an experimental capacitor, Sample 8, constructed with only a single layer of graphite after completion of pyrolysis and with an epoxy case, gave the results shown. It is to be concluded that a silicone resin encapsulation is preferable to an epoxy material and that generally only one buried or intermediate graphite layer is required

for a silicone resin encapsulated capacitor.

Although in making the preferred arrangement described, graphite particles are introduced into the sandwiched MnO₂ coating by applying Aquadag (R.T.M.) over the porous MnO₂ that lies over a graphite layer, a variety of other methods can be used to accomplish the same purpose. For example, the manganous nitrate, applied over a graphite layer can itself contain graphite particles. As a further example, instead of introducing the graphite by means of a suspension as has previously been described it may be introduced as a dry powder; the units can be coated with a liquid to which the graphite will adhere

when it is either sprayed at the units or they are immersed in the powder as for example in a fluidised bed.

WHAT WE CLAIM IS:—

1. A solid electrolytic capacitor including an electrode comprising a porous valve-metal body, a dielectric film covering the body, a solid electrolyte covering of manganese dioxide overlying said dielectric film, an outer layer of graphite overlying said electrolyte covering, an inner layer of graphite disposed within said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, said sandwiched portion containing graphite particles to reduce the electrical impedance between said inner and outer graphite layers, and a conductive counterelectrode overlying said outer graphite layer.
2. A capacitor according to Claim 1 including a metal terminal lead having one end thereof connected to said counterelectrode.
3. A capacitor according to Claim 2, wherein connection between said counterelectrode and said terminal lead is effected by a resin layer containing metal particles and which is electrically conductive.
4. A capacitor according to Claim 3, wherein said resin is silicone resin.
5. A capacitor according to any preceding claim including a wire extending from said body, and a metal terminal lead connected to said wire.
6. A capacitor according to any of the preceding claims, including an organic encapsulant encompassing said counterelectrode, and serving as a protective covering for the capacitor.
7. A capacitor according to Claim 6, wherein said encapsulant is of silicone resin.
8. A capacitor as claimed in any preceding claim, wherein said counterelectrode comprises metal particles bonded by an organic bonding agent.
9. A capacitor according to Claim 8, wherein said metal particles of said counterelectrode comprise silver copper or nickel.

10. A capacitor according to Claim 9, wherein said bonding agent is a silicone resin.

11. A capacitor according to any of the preceding claims, wherein said electrolyte covering of manganese oxide has a thickness in excess of 0.002 inch between said inner graphite layer and said body.

12. A solid electrolytic capacitor substantially as described with reference to the accompanying drawing.

13. A method of making a solid electrolytic capacitor including the steps of providing a porous valve-metal body as an electrode of the capacitor, covering said body with a dielectric film, forming on said dielectric film a solid electrolyte covering of manganese dioxide, the electrolyte covering having disposed within the covering an inner layer of graphite, forming an outer layer of graphite over said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, and forming a conductive counterelectrode over said outer graphite layer.

14. A method as claimed in Claim 13, wherein said electrolyte covering of manganese dioxide is formed by applying and pyrolysing successive layers of a manganese salt to said body, said inner graphite layer being formed by depositing graphite over said succession of layers, and thereafter applying and pyrolysing more successive layers of said manganese salt to complete said electrolyte covering.

15. A method as claimed in Claim 14, including forming more than one inner graphite layer by depositing successive layers of graphite, spaced from one another by layers of said pyrolysed manganese salt.

16. A method as claimed in Claim 13 or 14, wherein said outer graphite layer is formed by applying and thereafter drying a dilute colloidal graphite solution to said electrolytic covering.

17. A method as claimed in Claim 13 and substantially as described herein.

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when it is either sprayed at the units or they are immersed in the powder as for example in a fluidised bed.

WHAT WE CLAIM IS:—

- 5 1. A solid electrolytic capacitor including an electrode comprising a porous valve-metal body, a dielectric film covering the body, a solid electrolyte covering of manganese dioxide overlying said dielectric film, an outer layer of graphite overlying said electrolyte covering, an inner layer of graphite disposed within said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, said sandwiched portion containing graphite particles to reduce the electrical impedance between said inner and outer graphite layers, and a conductive counterelectrode overlying said outer graphite layer.
- 10 2. A capacitor according to Claim 1 including a metal terminal lead having one end thereof connected to said counterelectrode.
- 15 3. A capacitor according to Claim 2, wherein connection between said counterelectrode and said terminal lead is effected by a resin layer containing metal particles and which is electrically conductive.
- 20 4. A capacitor according to Claim 3, wherein said resin is silicone resin.
- 25 5. A capacitor according to any preceding claim including a wire extending from said body, and a metal terminal lead connected to said wire.
- 30 6. A capacitor according to any of the preceding claims, including an organic encapsulant encompassing said counterelectrode, and serving as a protective covering for the capacitor.
- 35 7. A capacitor according to Claim 6, wherein said encapsulant is of silicone resin.
- 40 8. A capacitor as claimed in any preceding claim, wherein said counterelectrode comprises metal particles bonded by an organic bonding agent.
- 45 9. A capacitor according to Claim 8, wherein said metal particles of said counterelectrode comprise silver copper or nickel.
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10. A capacitor according to Claim 9, wherein said bonding agent is a silicone resin.

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11. A capacitor according to any of the preceding claims, wherein said electrolyte covering of manganese oxide has a thickness in excess of 0.002 inch between said inner graphite layer and said body.

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12. A solid electrolytic capacitor substantially as described with reference to the accompanying drawing.

13. A method of making a solid electrolytic capacitor including the steps of providing a porous valve-metal body as an electrode of the capacitor, covering said body with a dielectric film, forming on said dielectric film a solid electrolyte covering of manganese dioxide, the electrolyte covering having disposed within the covering an inner layer of graphite, forming an outer layer of graphite over said electrolyte covering whereby to provide a layer of said electrolyte covering sandwiched between said inner and outer graphite layers, and forming a conductive counterelectrode over said outer graphite layer.

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14. A method as claimed in Claim 13, wherein said electrolyte covering of manganese dioxide is formed by applying and pyrolysing successive layers of a manganese salt to said body, said inner graphite layer being formed by depositing graphite over said succession of layers, and thereafter applying and pyrolysing more successive layers of said manganese salt to complete said electrolyte covering.

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15. A method as claimed in Claim 14, including forming more than one inner graphite layer by depositing successive layers of graphite, spaced from one another by layers of said pyrolysed manganese salt.

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16. A method as claimed in Claim 13 or 14, wherein said outer graphite layer is formed by applying and thereafter drying a dilute colloidal graphite solution to said electrolytic covering.

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17. A method as claimed in Claim 13 and substantially as described herein.

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