

The present invention relates to the manufacture of electrolytic capacitors and more particularly to the manufacture of electrolytic capacitors taking the form of components which can be transferred flat onto a substrate entering into the design of an electronic assembly. These components are generated designated under the Anglo-Saxon name of chips.

Various types of electrolytic capacitors are known. The internal structure of such a component is variable in accordance with the nature of the filmogenic metal used. Thus, it can be a matter of a porous mass which is well defined geometrically when the metal used is tantalum or niobium. On the other hand, when the metal lends itself only with difficulty to obtaining a porous mass, the capacitive element is then realised in the form of a surface, etched or not, suitably oxidized and coiled on itself. Complementary elements, cathode and electrolyte carrier, are generally incorporated in the element.

The processes for making these coils are well known. They lead to capacitive elements which lend themselves with difficulty to obtaining a component of the chip type. This is due to reasons ascribable to the cylindrical geometry of the capacitive elements and to the more or less liquid nature of the electrolyte used.

In order to obviate these disadvantages, the invention proposes an electrolytic capacitor taking the form of a sandwich structure and allowing a chip to be obtained. This capacitor can be obtained by a process of realisation which is well suited to mass production at low cost and which comprises the winding of anode foil, electrolyte carrier and cathode foil onto a wheel of large diameter.

The invention therefore has as its object a process for making electrolytic capacitors, characterised in that the

process comprises at least the following steps:

- a) obtaining at least one capacitance tape by winding an anode foil, a cathode foil and an electrolyte carrier onto a wheel,
- b) scooping coating the lateral faces of the tape in order to produce anode and cathode plates,
- c) dismantling the capacitance tape from the wheel,
- d) delimitation of capacitor sections by means of cuts made in the tape,
- e) impregnation of the said carrier with an electrolyte,
- f) mounting the capacitor sections on connecting means intended to form the electrodes of the capacitors,
- g) coating sections with a protective material in such a way as to allow portions of the connecting means to project,
- h) shaping said portions in order to constitute the electrodes of the capacitors.

The process makes it possible to obtain advantageously capacitors in the form of chips by realising the coating of each capacitor section in the form of a parallelepiped and by bending the electrodes onto two opposite faces of the parallelepiped.

The invention also has as its object the capacitors obtained by this manufacturing process.

The invention will be better understood and other advantages will become apparent by means of the following description and of the accompanying figures, in which:

- figures 1 and 2 are views of a stack constituting a capacitance tape,
- figure 3 is an explanatory diagram of a method of making a capacitance tape by winding,
- figure 4 is a top view of a partially sectioned capacitance tape,
- figure 5 illustrates an operation for restoring the anode dielectric,
- figure 6 shows a capacitor section mounted on its

connecting member,

- figure 7 is a sectional view of the final component obtained.

The manufacture of stacked capacitors from plastic dielectric is known. This manufacture consists in winding films of metallised plastic dielectric onto a wheel of large diameter in accordance with a number of determined revolutions. The capacitance tape realised in this way constitutes a mother capacitor. An insert wider than the plastic films is then wound for one wheel revolution. A superposition of a certain number of capacitance tapes can be realised which is limited only by the risks of collapse of the stack. Schoop coating and cutting operations are then carried out until a parellelepiped is obtained which, after moulding, will constitute the chip. The schoop coating operation consists in obtaining, by projection of metal, a mechanical connection and an electrical connection between the metallised foils constituting the electrodes of the capacitors.

The invention proposes to adapt and to improve this process in order to realise electrolytic capacitors having stacked metallised foils. In a general manner, the process commences by the simultaneous winding, onto a wheel of large diameter, of an anode foil, an electrolyte carrier and a cathode foil. Each revolution of the wheel gives rise to the creation of an elementary sandwich. The consecutive winding of n elementary sandwiches makes it possible to obtain a capacitance tape of a value corresponding to the connection in parallel of these n layers. This winding is then interrupted in order to position an insert intended to separate the first capacitance tape from the next one. This operation will be repeated so as to realise a stack of tapes the number of which will be limited by the height beyond which there is the risk of collapse of the assembly. This assembly will be covered, on its lateral faces, with a conductive material compatible with the electro-chemical

requirements of the capacitor. There is placing in parallel of the plates of the same sign within the capacitance tape. These tapes are then cut in order to break the circumference, separated from one another and capacitance tapes of a length of 1 to 3 metres are obtained. The next phase consists in sectioning the tapes perpendicularly in relation to their longitudinal axis in order to obtain sections the electrical capacitance of which will depend upon the basic characteristics of the anode foil, on the number of elementary sandwiches placed in parallel and on the length separating the cuts.

The cutting of the tapes into sections causes in practice damage to the anode portions laid bare. This damage consists in a partial disappearance of the layer of dielectric which covers the anode foil. It is then necessary to proceed to an anodic oxidation in order to reconstitute the layer of dielectric. This reconstitution operation is effected from an electrolyte bath. Preferably an electrolyte will be used which, once the reconstitution operation is concluded, can easily be eliminated by drying. The next operation will consist of the impregnation of the electrolyte carriers contained in the section with an electrolyte intended to remain in the capacitor.

The sections prepared in this way will receive conductive connection elements. It is advantageous to place these sections in connection elements which have a double role: to contribute weldable metallic tongues in order to render the chips functional and to ensure the intermediate role of joint plane upon the operation of moulding by injection or transfer when it is wished to mould the bare section.

The various operations mentioned will be detailed below within the framework of the realisation, given by way of a non-restrictive example, of electrolytic capacitors in aluminium. This realisation is capable of several variants, some of which will be described at greater length.

The anode foil can be made up of an etched and oxidized aluminium foil. The anodic oxidation voltage can be of the order of 35V. For example, the width of the anode foil will be 4.5 mm and its thickness 90 μm . The cathode foil can be easily etched, have the same width and a thickness of 30 μm . Such foils are easily available commercially. The electrolyte carrier will be chosen from a certain number of materials. Its choice is determined by the nature of the electrolyte adopted, by the value of the series resistances and by the desired behaviour under voltage. To these considerations relating to the internal structure of the capacitor it is advisable to add those of a mechanical order encountered during the winding operations. Among the materials capable of being adopted, mention can be made of paper, porous or microporous plastics materials on the basis of polypropylene, polybutylene, polyethylene as well as their derivatives. Fine meshed structures of polytetrafluoroethylene or of glass fibres, etc., can also be used.

These three foils are, for example, wound simultaneously onto a wheel of large diameter (from 80 to 100 cm). The winding is effected so that the anode and cathode foils are superposed with a slight lateral displacement and so that they are separated one from the other by the electrolyte carrier. Figure 1 is a sectional view showing the manner of stacking the various foils and the electrolyte carrier. The anode foil 1 is shown with its purely metallic portion 2 made of aluminium and the dielectric layer 3 constituted of oxide Al_2O_3 . The cathode foil 4 is displaced in relation to the anode foil by about 0.1 to 0.3 mm. The electrolyte carrier 5 is advantageously arranged so as to project slightly on one side of the anode foil and on the opposite side of the cathode foil. This allows a better electrical insulation between anode and cathode.

It can be advantageous to turn the outer edges of the anode and cathode foils down by an angle close to 90° as

shown in figure 2. In this figure it can be seen that the anode foils are turned down on the side where they project from the stack, likewise for the cathode foils. These projections can be realised thanks to serrated rollers placed perpendicularly to the anode and cathode foils. This flanging has a certain benefit upon the schoop coating operation since it makes it possible to ensure a better mechanical and electrical connection between the anode foils on the one hand and the cathode foils on the other hand.

When the wheel has accomplished one revolution, an elementary capacitive sandwich is obtained. It is sufficient to realise several wheel revolutions in order to obtain a stack of n elementary sandwiches which will later be assembled in parallel to form a capacitance tape. Figure 3 illustrates the way of proceeding to the winding. The rotation of the wheel 6 makes it possible to realise the stacking of the elementary sandwiches from four reels. It is necessary to have at least four reels available: one reel 7 for the cathode foil, one reel 8 for the anode foil and two reels 9 and 10 for the electrolyte carrier. It is in fact necessary to have two reels 9 and 10 available, otherwise, at the end of one wheel revolution, the anode and cathode foils would be put into contact. In this way stacks are realised: cathode foil - electrolyte carrier - anode foil - electrolyte carrier - cathode foil - etc.

Once the stacking of n elementary sandwiches, that is to say the capacitance tape, has been realised, an insert is wound over one wheel revolution. It is imperative that the nature of the insert be such that it ensures poor adhesion between this latter and the metal used for the schoop coating. In the case of anode and cathode foils made of aluminium, the schoop coating can be realised by projection of aluminium. The inserts will then advantageously be chosen made of steel. An insert width of 6 to 7 mm is satisfactory in the case of a foil width of 4.5 mm.

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The operation of winding the capacitance tapes is continued in accordance with the same process, the number of superposed tapes being limited only by the risk of collapse of the stack. In the example described it is possible to realise the stacking of 25 tapes, which represents a thickness of 40 mm. The stack is then bound thanks to a device for controlled tying-up, for compaction purposes.

According to the nature of the electrolyte carrier used, it can be of interest to realise, at this stage of manufacture, a thermal treatment assisting the welding or the adhesion of the various layers of electrolyte carrier onto the anode or cathode foils. This operation gives greater rigidity to the whole. The temperature at which the thermal treatment is effected can be comprised between 125 and 140°C and the operation can last up to 8 hours.

The next step consists in connecting the various foils of the same polarity to one another. In order to do this, use will preferably be made of pure aluminium which will be deposited by schoop coating. The schoop coating will be able to be carried out alternately on one face then on the other, but it is preferable to carry it out symmetrically and simultaneously so as to reduce the deformations of the capacitance tape. This also makes it possible to reduce the cost of the operation.

The various capacitance tapes are then separated from the supporting wheel by sectioning at one or two locations on the circumference in accordance with the thickness of each of the tapes. As the case may be, the length of these tapes goes from 1 to 3 metres. When they are detached from the wheel, their shape is that of an arc of large radius. It is a matter then of proceeding to the cutting-up of the tapes at the pitch intended for obtaining the capacitor sections.

Several cutting processes can be used. Techniques of sawing, milling, grinding at faster or slower speed with or

- 0 -

without the supplying of lubricant can be employed. A technique of laser cutting or of cutting by high-pressure liquid jet can even be employed. This latter technique can use as liquid the electrolyte which will be used in the next step. Whatever the technique used, the cutting causes damage to the anode foils at the section. This damage consists in the local disappearance of the anode dielectric. The surface areas affected by this damage are not very large, but it is necessary to restore them.

The cutting in itself can be carried out in two different ways. According to a first variant, the capacitance tapes are going to be cut at the intended pitch but the cut will be incomplete, so as not to breach the end of the positive plate. Figure 4 is a partial top view of the capacitance tape cut up in this way. In this way a sort of comb is obtained, the teeth of which are constituted by the sections 11 with their negative plate. The sections will therefore be retained by the positive plate 13 which remains continuous.

The restoration of the dielectric can be effected by electrolysis, by immersing the capacitance tape in an electrolytic bath whilst keeping the positive plate out of the bath. The electrolytic bath is, for example, made up of an aqueous solution of boric acid at 7%. The direct current applied will be of the order of 0.4 mA per cm² of anode surface, until a voltage is obtained which is equivalent to the oxidation voltage of the anode foil (35 V in the example chosen). The duration of the operation is rapid and does not exceed a few minutes. Figure 5 describes the operation of restoring the dielectric. The capacitance tape is viewed in accordance with one of its sectioned ends. The destroyed portions of the dielectric 3 have been shown. Its sectioned negative plate 12 is placed on a porous insulating support 14 resting on the bottom of a tank 15 made of material which conducts electricity. The level of the electrolytic bath 16 is such that it does not reach the positive plate 13. The

direct-current generator 17 allowing the electrolysis is connected between the positive plate 13 and the tank 15.

One then proceeds to the elimination of the electrolyte by washing and drying. The tape sectioned in comb-shaped manner is then ready to receive its final electrolyte.

In accordance with a second variant, the capacitance tapes are completely sectioned. The capacitor sections are grouped into a work unit by transfer into an electrolysis tank. They are placed as previously on a porous insulating support and their positive electrodes emerge from the electrolytic bath. The sections are arranged so that the positive plates can easily be connected to the voltage generator. For example, the sections are aligned and a contact bar is placed on the positive plates. The anodic oxidation operations can be realised as previously.

It is a matter then of realising the impregnation of the electrolyte carriers. Several electrolytes can be employed, for example manganese dioxide MnO_2 or solid organic electrolytes. According to the choice made, the process of this operation can be very different.

It is known that the thermal decomposition of a solution of manganese nitrate gives the oxide MnO_2 . It is therefore sufficient to impregnate the electrolyte carriers contained in each of the sections in order then to proceed to the controlled pyrolysis of the manganese nitrate and to obtain the manganese dioxide. It is then advantageous to choose as electrolyte carrier a grid made of tetrafluoroethylene better known under the registered trade-mark "teflon", or made of glass fabric. The impregnation will be effected by absorption after a possible passage under vacuum. The pyrolysis has to be controlled with precision so as to avoid as far as possible the corrosion of the dielectric layers by the nitrogen oxides stemming from the pyrolysis. It is also known that it is necessary to proceed to several pyrolysis

operations in order to obtain a layer of oxide of sufficient thickness. The low corrosion suffered by the dielectric layer can be repaired by the customary methods of reformation. These operations are equally applicable to the partially or completely sectioned tapes.

The impregnation can also be realised by a solid organic electrolyte (electro-active polymer). There are a certain number of organic semiconductors capable of advantageously replacing the manganese dioxide. The best known of these products are the complex salts of 7-7-8-8 tetracyanoquinodimethane designated more simply under the expression TCNQ. The pyropyroles can also be used as well as tetrathiofulvalene (TTF). The use of these products is effected from solutions in suitable solvents, from crystalline suspensions or from the molten product. The advantage of these products is that of contributing a great improvement in the behaviour at high frequencies as well as a low level of leakage current. The impregnation is effected in accordance with a technology adapted to the product chosen. It is in any case much simpler to apply than that relating to manganese dioxide.

After the impregnation operation, the sectioning of the tapes is, as the case may be, continued to obtain individual sections.

The following operations will consist of the shaping of the sections in order to obtain components which can be transferred flat.

The sections take the form of parallelepipeds and have to be given connections in the form of flat tongues. These tongues must be able to be welded. A protection of the sections is also necessary and this protection has to take account of the thermal stresses given rise to upon the welding of the components obtained onto a substrate.

The sections can be transferred automatically onto a connecting member which has a double role: to contribute the tongues necessary for the connection and to ensure the role of joint plane upon the moulding of the section. The moulding can be realised either with the aid of resins which can be injected under pressure, or with the aid of resins which can be utilised by the process of transfer moulding, or by casting. Figure 6 is an example of a connecting member which can be used. This connecting member is constituted by a foil 23 of a material which can be welded onto the anode 21 and cathode 22 schoop coatings of the capacitor sections 20. Cutouts 24 in the form of an H are made in the foil 23 in order to realise tongues 25 which are folded vertically so as to hold the sections in position by a slight spring action and to ensure the electrical contact with the schoop coatings. The welding of the tongues on the schoop coatings can be realised by various techniques.

After the moulding operation consisting in coating each section with resin, the foil 23 is cut up in accordance with the dotted lines 26 and the tongues 25 are folded and crimped around the coating 27 as shown by figure 7.

It is advantageous to provide on each tongue 25 bosses realised so as to hold the capacitor sections 20 in position in accordance with very reduced surfaces. This will have the advantage of ensuring a good mechanical retention of the sections. To allow the capacitive element to retain its properties, it is necessary for it to be able to withstand without damage the thermal stresses of the transfer flat. A reduction in cross-section of the fixing tabs makes it possible to create a thermal resistance between the schoop coated faces and the future electrodes. The restriction of cross-section will preferably be realised over a small length in order not to increase too much the series resistance of the connection and consequently the losses of the capacitor. The restricted cross-section can be obtained by holes pierced in the fixing tabs.

The example of a connecting member shown in figure is not the only one possible. Other configurations are possible. The cutouts effected in the foil 23 can have a different shape than the one shown. The capacitor sections can be deposited flat or edgewise. In particular, the folds can be provided so as to support the sections in a stable manner prior to the welding. According to the shape which will be given to the cutout, the external electrodes of the coated component will be able to be situated in planes perpendicular to the schoop coated faces.

Within the framework of an automated manufacture, the connecting member foil will take the form of a band possessing uniformly spaced cutouts in order to receive the capacitor sections. The drive of the band can be obtained through the medium of lateral holes and of a suitable device in accordance with known techniques.

The final component obtained then takes a form which can be transferred flat. It remains to mark the anode and cathode electrodes and to effect the inscribing of the component. This inscribing can be realised by laser marking or by any other method.

In the example of application quoted above, six wheel revolutions and a cutout into sections in accordance with the dimensions: thickness 1.5 mm, width of the tape 4.5 mm and length of cut 3.2 mm, lead to chips with a capacitance of 18 microfarads and with a nominal operating voltage of 25 V.

- 13 -

CLAIMS

1. Process for manufacturing electrolytic capacitors, characterised in that the process comprises at least the following steps:

- a) obtaining at least one capacitance tape by winding an anode foil (1), a cathode foil (4) and an electrolyte carrier (5) onto a wheel,
- b) scooping coating the lateral faces of the tape in order to produce anode (13) and cathode (12) plates,
- c) dismounting the capacitance tape from the wheel,
- d) delimitation of capacitor sections (11) by means of cuts made in the tape,
- e) impregnation of the carrier (5) with an electrolyte,
- f) mounting the capacitor sections on connecting means (23) intended to form the electrodes of the capacitors,
- g) coating the sections (20) with a protective material (27) in such a way as to allow portions of the connecting means to project,
- h) shaping said portions in order to constitute the electrodes (25) of the capacitors.

2. Process according to claim 1, characterised in that the coating of each section takes the shape of a parallelepiped, and that the electrodes are bent onto two opposite faces of the parallelepiped so that the capacitor obtained takes the form of a chip.

3. Process of realisation according to one of claims 1 or 2, characterised in that the winding of step a) is followed by a binding step adapted to ensure a controlled tying-up of the anode (1) and cathode (4) foils and of the electrolyte carrier (5).

4. Manufacturing process according to any one of claims 1 to 3, characterised in that prior to step b) the tape is subjected to a thermal treatment to assist the welding or



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- 17 -

adhesion of the electrolyte carrier (5) onto the anode (1) and cathode (4) foils.

5. Manufacturing process according to any one of claims 1 to 4, characterised in that the cuts made in step d) consist of a partial sectioning of the tape which leaves the anode plate (13) intact.

6. Manufacturing process according to any one of claims 1 to 4, characterised in that the cuts made in step (d) consist of a complete sectioning of the capacitor tape.

7. Manufacturing process according to any one of claims 1 to 6, characterised in that the capacitor sections (11) are subjected to an anodic oxidation intended to restore the dielectric (3) of the anode foils (1) after step (d).

8. Manufacturing process according to any one of claims 1 to 7, characterised in that the impregnating electrolyte is manganese dioxide.

9. Manufacturing process according to any one of claims 1 to 7, characterised in that the impregnating electrolyte is a solid organic material.

10. Electrolytic capacitor, characterised in that it is obtained via the manufacturing process according to any one of claims 1 to 9.

11. Capacitor according to claim 10, characterised in that the anode (1) and cathode (4) foils consist of aluminium.

12. Capacitor according to claim 11, characterised in that the anode foil (1) is etched and oxidized.

