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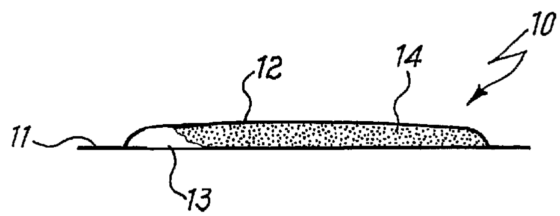
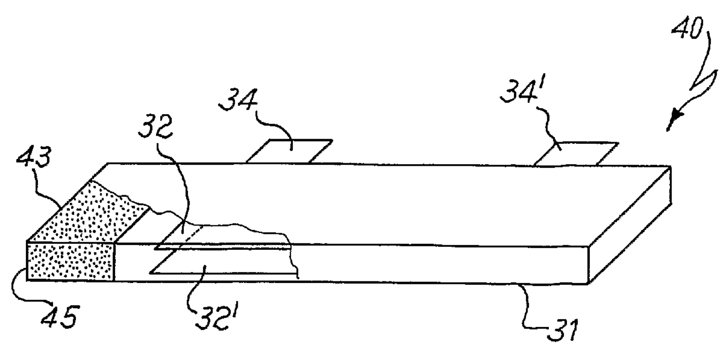
(54) Title: ELECTROLYTIC CAPACITOR COMPRISING MEANS FOR THE SORPTION OF HARMFUL SUBSTANCES





(57) Abstract: An electrolytic capacitor is described, comprising an airtight casing, electrodes immersed in an electrolytic solution, electrical contacts connected to the electrodes and a means (10, 43) for the sorption of harmful substances comprised of a polymeric housing (11, 12), permeable to said harmful substances but impermeable to the electrolyte, containing one or more getter materials (14, 45) for the sorption of said harmful substances.

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"ELECTROLYTIC CAPACITOR COMPRISING MEANS FOR THE SORPTION OF HARMFUL SUBSTANCES"

The present invention relates to electrolytic capacitors containing means able to sorb the harmful substances created by such capacitors during their operation.

Known electrolytic capacitors, e.g. EDLC (Electrochemical Double Layer Capacitor) supercapacitors, are essentially comprised of an airtight casing, wherein electrodes typically formed of metal sheets are arranged, the electrodes being immersed in particular electrolytic solutions. The casing also contains elements having a gettering action for the sorption of harmful substances, and electrical contacts communicating said electrodes with the outside of the capacitor.

As to the electrolytic solutions, they are typically formed of a solvent and an ionic salt. In the case of EDLCs, for example, acetonitrile and propylene carbonate are often used as solvents, while tetraethyl-ammonium-tetrafluoborate is often used as a salt.

During the operation of the capacitor, these solutions can create harmful substances, often in gaseous form, which can damage the capacitors even in an unrepairable manner; another possible source of harmful gases can be due to the desorption of some materials used inside the capacitor.

Carbon dioxide, carbon oxide and hydrogen are among the most harmful gaseous species; while water, which is another species being particularly harmful, is typically present in liquid form inside the electrolytic solution.

The problem of the sorption of harmful species inside the capacitors can be tackled by adding one or more sorbing elements mixed in the electrolytic solution, or by means of non-mixed sorbing systems. The use of materials with a gettering action being mixed in the electrolyte can be accomplished by liquid sorbers: such a type of solution is disclosed in patent application PCT/IT2006/000349 in the applicant's name. A second embodiment prescribes the use of solid sorbers being added to the electrolyte, as described in JP 03-292712, wherein an additive including a particulate of platinum, palladium or alloys thereof is applied onto the sheets after these have been impregnated with the electrolytic solution; however, these sheets may have a very small thickness, in particular lower than 10 micrometers (μm), whereby they may be damaged by the particles contained in such a particulate due to their relatively large diameter, resulting in the risk of accidental short-circuits within the capacitor.

A system employing gas sorbers placed in delimited regions of the capacitor is described in patent application JP 2003-197487. In this case the sorbing material is used in the form of sheets made of a polymeric material, such as polypropylene, supporting the sorbing material, such sheets being directly in contact with the electrolytic solution.

These types of solution are limited by the fact that the sorbing material, in addition to have the function of sorbing the harmful substances produced within the capacitor, must be compatible with the electrolyte, i.e. it must be completely inert with respect thereto, in order to prevent its sorbing properties from being jeopardized, or, even worse, that chemical species harmful for the correct operation of the capacitor are released as an effect of the reaction with the electrolyte; for instance, the possible decomposition of the gas sorber could vary the electric conductivity of the electrolyte. Such a chemical compatibility must be ensured by the sorber even after the sorber has carried out its function by binding with the harmful species.

In a first aspect thereof, the present invention relates to an electrolytic capacitor being able to overcome the problems still present in the prior art, and particularly consists in an electrolytic capacitor comprising an airtight casing containing an electrolytic solution wherein electrodes are immersed, electrical contacts connected to the electrodes, and in said casing a means for the sorption of harmful substances is present, characterized in that said means for the sorption of harmful substances is comprised of a polymeric housing being permeable to said harmful substances but impermeable to the electrolyte, containing one or more getter materials for the sorption of said harmful substances.

The invention will be illustrated with reference to the following figures, in which:

- Figure 1 shows in cross-section a means for the sorption of harmful substances in electrolytic capacitors according to the present invention;
- Figure 2 shows another embodiment of a means for the sorption of harmful substances in electrolytic capacitors of the invention;
- Figure 3 shows a cross-sectional view of an electrolytic capacitor comprising a permeable polymeric housing containing getter materials;

- Figure 4 shows an alternative embodiment of the electrolytic capacitor shown in Fig. 3;
- Figure 5 shows a cross-sectional view of an electrolytic capacitor having a different geometry, comprising a permeable polymeric housing containing getter materials; and
- Figure 6 shows a cross-sectional view of a preferred embodiment of the electrolytic capacitor shown in Fig. 5.

The size and size ratios of the various elements shown in the drawings are not correct, having been altered in order to facilitate the understanding of the same drawings.

Figure 1 shows in cross-section a means 10 for the sorption of harmful substances, the means comprising two polymeric sheets 11 and 12 welded to each other at their periphery, thus defining a cavity 13 containing powders 14 of one or more getter materials. At least one and preferably both the materials forming the polymeric sheets 11 and 12 are permeable to harmful substances but impermeable to the electrolyte, thus exerting a protective action with respect to the getter material; this allows a free choice of getter material, regardless of the type of electrolyte used inside the capacitor.

The thickness of the polymeric sheets 11 and 12 is a very important parameter for the invention, as it is necessary that these sheets are thin in order to allow an effective permeation of the harmful substances, but at the same time they must be thick enough to avoid breaking and the consequent leakage of the getter material. As a result of these opposing requests, it has been found that the thickness of the polymeric sheets is suitably comprised between 2 and 50 μm, and preferably between 5 and 15 μm; in a preferred embodiment the two polymeric sheets have the same thickness.

Of course, means for the sorption of harmful substances with a structure equivalent to what described with reference to Figure 1 could as well be obtained by using a single polymeric sheet, folded over itself along one line to form one side of the means and welded along the other edge or edges to form a closed cavity analogous to cavity 13; this arrangement also satisfies the preferred choices above described, that the sheets 11 and 12 have the same thickness and characteristics of permeability.

In the case in which the getter system is installed along one of the internal walls of the electrolytic capacitor, it is possible to use a greater thickness for the sheet contacting such a wall, as along the contact surface between the getter system and the capacitor wall there is no permeation of harmful substances.

The getter materials contained in the polymeric housing are preferably in the form of powders, with grain size comprised lower than 60 μm; it is also possible that the getter material is used in the form of pills made of compressed powders only. Such a solution is useful when a greater amount of getter material must be introduced into the electrolytic capacitor.

Fig. 2 shows a system 20 for the sorption of harmful substances, wherein two different getter materials, 22 and 22', are introduced in the form of pills enclosed in a cylindrical housing 21 made of polymeric material permeable to harmful substances.

Getter materials in permeable polymeric housings used in other applications and in other fields are known and described, for example, in patents US 4,830,643, US 5,743,942 and US 6,428,612.

As to the materials forming the permeable polymeric housing, the inventors have found that polytetrafluoroethylene (PTFE) and polyolefins are suitable materials for the accomplishment of the invention. As to polyolefins, preferred is polyethylene, particularly low-density polyethylene (LDPE).

The getter materials used in the means according to the invention are of various kinds, depending on the harmful substances to be removed from the inside of the capacitor; the nature of these substances may be ascertained, for any kind of capacitor, by means of preliminary tests carried out analyzing the gas developed during operation by different types of capacitors without any means for removing gases.

When the harmful substance is hydrogen, it is possible to use non-evaporable getter alloys, particularly the zirconium-vanadium-iron alloys described in patent US 4,312,669 and sold by the applicant under the name St 707, or the zirconium-cobalt-Rare Earths alloys described in patent US 5,961,750 and sold by the applicant under the name St 787; it is also possible to use unsaturated organic compounds (possibly along with hydrogenation catalysts), zeolites with a silver deposit or carbon nanotubes; finally, it is possible to use materials that react with hydrogen forming water, such as palladium oxide (PdO) or cobalt(II,III) oxide (Co_3O_4), in combination with H_2O sorbers.

In case the harmful substance is H_2O, as getter material is possible to use alkaline earth metals oxides (preferred is calcium oxide), boron oxide or zeolites.

In case the harmful substance is carbon dioxide, CO_2, suitable getter materials are lithium hydroxide, alkaline-earth metals hydroxides, or lithium salts such as $LiXO_y$, where X is chosen among zirconium, iron, nickel, titanium and silicon and y is comprised between 2 and 4.

In case the harmful substance is carbon monoxide, CO, it is possible to use the cobalt(II,III)oxide (Co_3O_4), copper(II) oxide (CuO), or potassium permanganate ($KMnO_4$), preferably along with a CO_2 sorber.

The means for the sorption of harmful substances for use in the electrolytic capacitors of the present invention may also include more than one getter material, depending on the harmful substances needed to be removed from the capacitor. For example, in capacitors where the solvent is acetonitrile, hydrogen production mainly occurs, whereby it is advisable to use a composition with more getter material for such a gas, whereas in the case where the solvent is propylene carbonate, a larger amount of powder must be used to sorb CO and CO_2.

The electrolytic capacitors of the present invention can be manufactured by placing the permeable housing containing the getter material along one side of the electrolytic capacitor, in a region of the capacitor free from electrodes, as shown, for example, in Fig. 3. In this case the structure of the electrolytic capacitor 30 comprises a plurality of planar electrodes (only the outermost two, 32 and 32', are shown in the drawing in order not to jeopardize its readability) in the form of parallel metal plates immersed in the electrolytic solution (not shown). The permeable polymeric housing 33, containing the getter material for the sorption of harmful gases, is arranged on one side of this capacitor. The electrical contacts 34 and 34' communicate the electrodes with the outside of the airtight casing 31 of the electrolytic capacitor.

Fig. 3 shows a preferred embodiment for an electrolytic capacitor 30; alternative and completely equivalent embodiments prescribe the use of one or more permeable polymeric housings arranged along portions of the internal walls of the airtight casing of the electrolytic capacitor.

Figure 4 shows an electrolytic capacitor 40 similar to the one described with reference to Figure 3 (elements in Figure 4 having the same numerals of Figure 3 are the same as described above), but wherein a portion 43 is added to the capacitor structure with the aim of containing the getter means 45 for the sorption of harmful substances. Actually, portion 43 containing said getter means, forms a portion of the airtight casing of the electrolytic capacitor free from its elements (electrodes, contacts), but communicating along one side with the inside of the electrolytic capacitor. If the permeable polymeric housing does not occupy the whole available volume of the portion 43, a part of this volume is filled with the electrolyte.

Alternatively, the permeable housing containing the getter material may be inserted into the central portion of the electrolytic capacitor, as shown, for instance, in Figure 5. In this case the capacitor 50 has a cylindrical geometry and an axial cross-sectional view thereof is shown. The capacitor comprises an airtight casing 51 containing the electrodes 52 in form of thin sheets coiled to form a spiral, the cross-sectional view of which is represented by parallel lines vertically close to each other, immersed in a liquid electrolyte (not shown); electrical contacts 54, 54' communicate the electrodes with the outside of the airtight casing (in figure 5, for clarity reasons, the contacts have been drawn as separate elements with respect to the electrodes). The means for sorption of harmful substances 55, consisting in a permeable polymeric housing containing the getter material, is located in the central portion of this capacitor.

Another preferred embodiment of the invention is shown in Fig. 6. In this case the electrolytic capacitor, 60, still has a cylindrical geometry and contains electrodes in the form of spiral coil 62. The airtight casing 61 has a portion 63 in its lower part that serves to host the means 65 for sorption of harmful substances, again in the form of a permeable polymeric housing containing the getter material. Such an embodiment is particularly advantageous as there are no particular geometric constraints due to the proximity of the means for the sorption of harmful substances to the electrical contacts.

In the embodiments shown in Figures 4 and 6, it is advisable to add a separation grid (not shown) between the region hosting the permeable polymeric housing and the electrodes, in order to prevent these latter from damaging the polymeric housing, that could cause the leakage of the getter material contained therein. Such a grid must be electrically insulating, as being in contact with the different electrodes it must not result in short-circuits among the same.

CLAIMS

1. Electrolytic capacitor (30; 40; 50; 60) comprising an airtight casing (31; 51; 61), electrodes (32, 32'; 52; 62) immersed in an electrolytic solution, electrical contacts (34, 34'; 54, 54') connected to the electrodes and a means (10; 20; 33; 45; 55; 65) for the sorption of harmful substances, characterized in that said means for the sorption of harmful substances is comprised of a polymeric housing (21) permeable to said harmful substances but impermeable to the electrolyte, containing one or more getter materials (14; 22, 22') for the sorption of said harmful substances.

2. Electrolytic capacitor according to claim 1, wherein said permeable polymeric housing is comprised of two welded polymeric sheets (11, 12).

3. Electrolytic capacitor according to claim 1, wherein said permeable polymeric housing is comprised of one polymeric sheet, folded over itself along one line to form one side of the means and welded along the other edge or edges to form a closed cavity.

4. Electrolytic capacitor according to claim 2 or 3, wherein the thickness of said polymeric sheets is comprised between 2 and 50 μm.

5. Electrolytic capacitor according to claim 4, wherein said thickness is comprised between 5 and 15 μm.

6. Electrolytic capacitor according to claim 2, wherein said polymeric sheets have the same thickness.

7. Electrolytic capacitor according to claim 1, wherein said getter materials are in the form of powders having grain size lower than 60 μm.

8. Electrolytic capacitor according to claim 7, wherein said powders are compressed to form pills.

9. Electrolytic capacitor according to claim 1, wherein said polymeric housing (21) has a cylindrical shape.

10. Electrolytic capacitor according to claim 1, wherein said permeable polymeric housing is made of a polyolefin.

11. Electrolytic capacitor according to claim 10, wherein said polyolefin is low-density polyethylene (LDPE).

12. Electrolytic capacitor according to claim 1, wherein said permeable polymeric housing is made of polytetrafluoroethylene (PTFE).

13. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise hydrogen and said getter material comprises non-evaporable getter alloys.

14. Electrolytic capacitor according to claim 13, wherein said non-evaporable getter alloys comprise zirconium-vanadium-iron alloys or zirconium-cobalt-Rare Earth alloys.

15. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise hydrogen and said getter material comprises unsaturated organic compounds.

16. Electrolytic capacitor according to claim 15, further comprising a hydrogenation catalyst.

17. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise hydrogen and said getter material comprises carbon nanotubes or zeolites with a silver deposit.

18. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise hydrogen and said getter material comprises one or more compounds between palladium oxide or cobalt(II,III) oxide.

19. Electrolytic capacitor according to claim 18, wherein said getter material is used together with a getter material for the removal of H_2O.

20. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise H_2O and said getter material comprises one or more among the following compounds: alkaline-earth metals oxides, boron oxide or zeolites.

21. Electrolytic capacitor according to claim 20, wherein said alkaline-earth metals oxide is calcium oxide.

22. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise CO_2 and said getter material comprises one or more among the following compounds: lithium hydroxide, alkaline-earth metals hydroxides, or lithium salts of formula $LiXO_y$, where X is chosen among zirconium, iron, nickel, titanium and silicon and y is comprised between 2 and 4.

23. Electrolytic capacitor according to claim 1, wherein said harmful substances comprise CO and said getter material comprises one or more among the following

compounds: cobalt(II,III) oxide, copper(II) oxide, potassium permanganate.

24. Electrolytic capacitor according to claim 23, wherein said getter material is used together with a getter material for the removal of CO_2.

25. Electrolytic capacitor according to claim 1, comprising one or more polymeric housings containing getter materials and said polymeric housings are arranged along one or more portions of the inner walls of the airtight casing.

26. Electrolytic capacitor according to claim 1, wherein a portion of the airtight casing is devoted to hosting said polymeric housing comprising the getter material.

27. Electrolytic capacitor according to claim 26, wherein said portion for hosting the polymeric housing comprising the getter material is separated from the residual portion of the electrolytic capacitor by an electrically insulating grid.

Fig.1

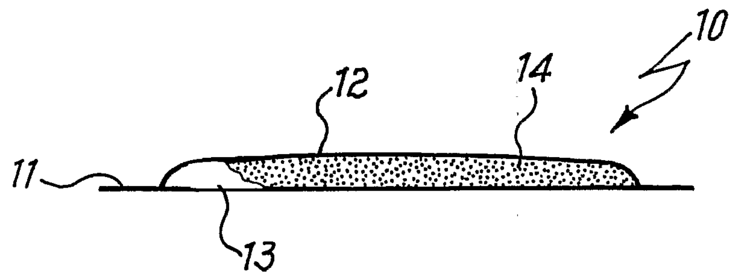

Fig.2

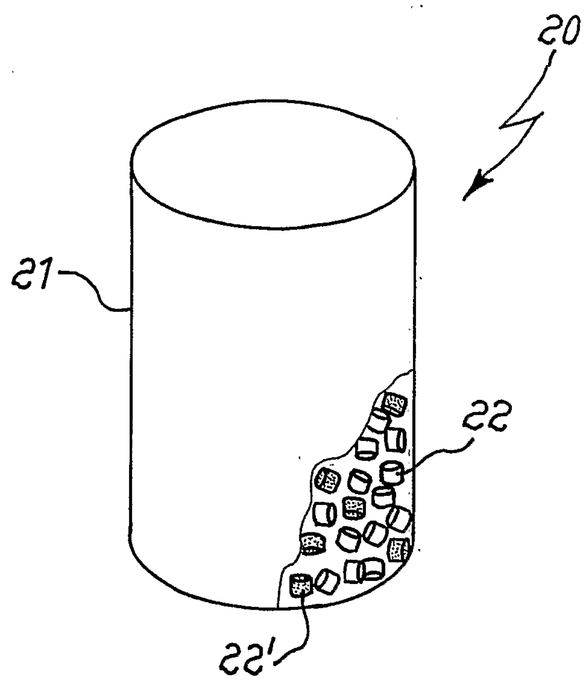

Fig.3

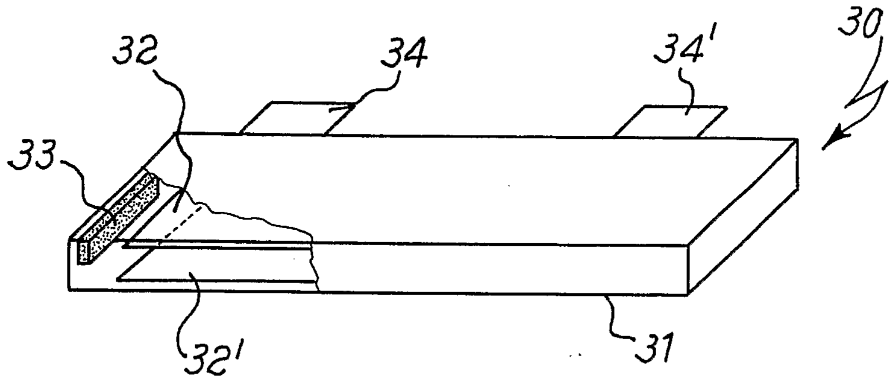

Fig.4

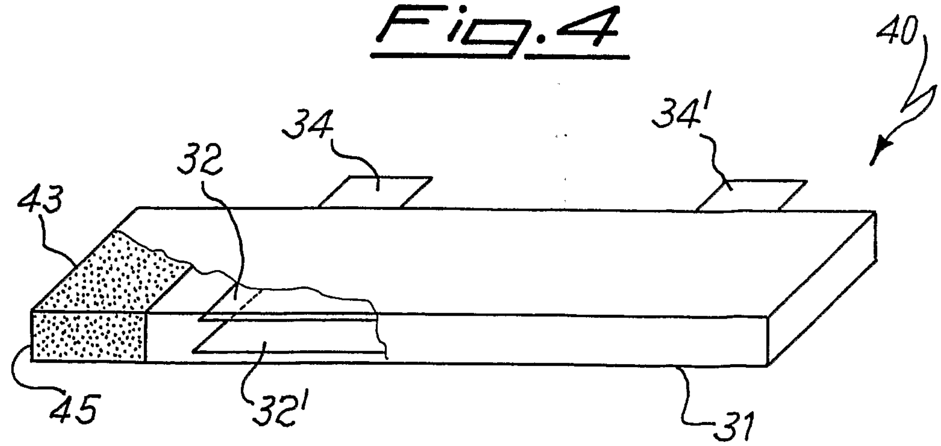

Fig. 5

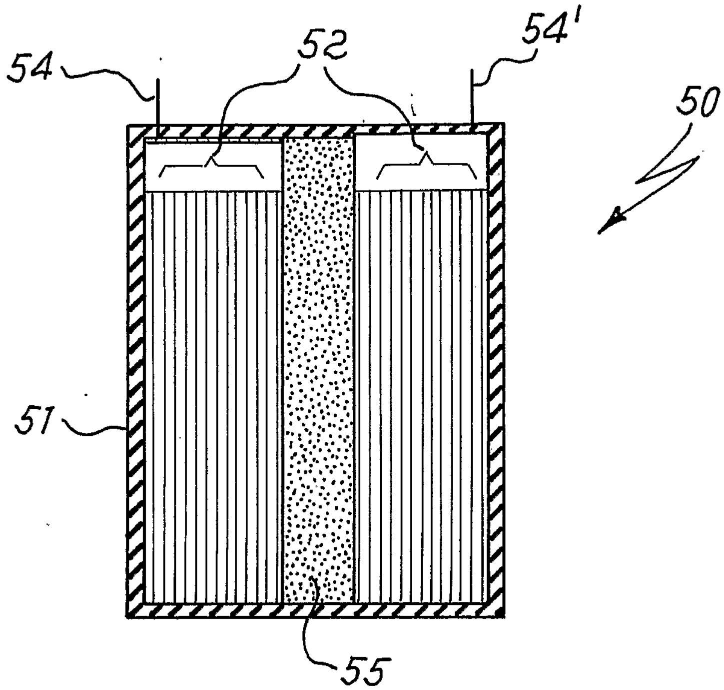

Fig. 6