



- (51) **International Patent Classification:**  
*H01G 9/22* (2006.01)
- (21) **International Application Number:**  
PCT/EP2012/001094
- (22) **International Filing Date:**  
12 March 2012 (12.03.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
10 2011 016 493.6 8 April 2011 (08.04.2011) DE  
61/476,554 18 April 2011 (18.04.2011) US
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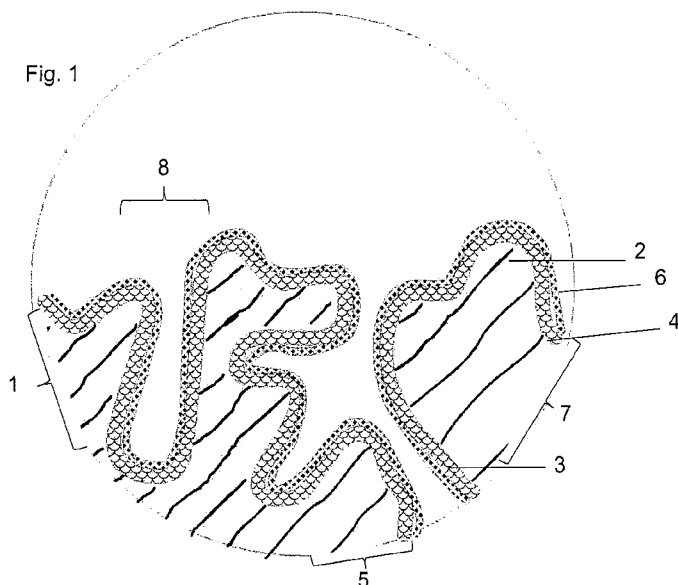
(81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LI, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))

(54) **Title:** PROCESS FOR IMPROVING THE ELECTRICAL PARAMETERS IN CAPACITORS COMPRISING PEDOT/PSS AS SOLID ELECTROLYTE, BY MEANS OF ADDITIVES



(57) **Abstract:** The present invention relates to a process for the production of a capacitor, comprising the process steps: a) the provision of an electrode body (1) from an electrode material (2), wherein a dielectric (3) at least partially covers a surface (4) of this electrode material (2) to form an anode body (5); b) the introduction of a dispersion comprising a conductive polymer, a dispersing agent and an additive with the general structural formula (I) Ar-X-Y Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl group; X stands for a connector selected from the group consisting of O, OCR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group; Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl; into at least part of the anode body (5); the at least partial removal of the dispersing agent to obtain a capacitor body (7); The invention also relates to a capacitor obtainable by this process, the use of the capacitor, electronic circuits as well as the use of a dispersion.



through chemical modification. Examples of known  $\pi$ -conjugated polymers are polypyrroles, polythiophenes, polyanilines, polyacetylenes, polyphenylenes and poly(p-phenylenevinylene), one particularly important and technically used polythiophene being poly(3,4-ethylenedioxythiophene) (PEDOT), since it exhibits a  
5 very high conductivity in the oxidised form.

The application of the electrolyte based on conductive polymers to the oxide layer can be accomplished in a variety of ways. EP-A-0 340 512, for example, describes the production of a solid electrolyte from 3,4-ethylenedioxythiophene and its use  
10 in electrolyte capacitors. As instructed by this publication, 3,4-ethylenedioxythiophene is polymerised *in situ* on the oxide layer. After the deposition of the solid electrolyte, the oxide layer must normally be reformed to achieve low residual currents as is described, for example, in EP-A-0 899 757. For that purpose the capacitor is soaked in an electrolyte and exposed to a voltage not  
15 exceeding the anodising voltage of the oxide layer.

The disadvantage of producing solid electrolyte capacitors using *in situ* polymerisation is, however, amongst other things, the complexity of the process. As such, the polymerisation process, each time involving the process steps of soaking,  
20 polymerisation and washing, generally takes several hours. Possibly, explosive or toxic solvents may be required. A further disadvantage of the *in situ* process for the production of solid electrolyte capacitors is that, generally, anions of the oxidation agent, or perhaps other monomeric anions, serve as counter ion for the conductive polymer. Owing to their small size, however, these are not bound to  
25 the polymer with sufficient stability. This can lead to diffusion of the counter ions and thus to an increase in the equivalent series resistance (ESR) of the capacitor, especially at high operating temperatures of the capacitor. The alternative use of high molecular polymeric counter ions in the chemical *in situ*-polymerisation does not lead to sufficiently conductive layers and thus does not lead to low enough  
30 ESR values.

In the state of the art, alternative processes for the production of conductive polymer based solid electrolytes in capacitors have therefore been developed. DE-A-10 2005 043828, for example, describes a process for the production of solid electrolytes in capacitors, wherein a dispersion comprising the already polymerised thiophene, for example the PEDOT/PSS dispersion known from the state of the art, is applied to the oxide layer and thereafter the dispersing agent is removed by evaporation. However, solid electrolytes obtained from such dispersions are often characterised by improvable parameters, in particular improvable capacitances and equivalent series resistances.

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One approach to the improvement of the equivalent series resistance of solid electrolytes obtained using PEDOT/PSS dispersions is described in JP 2010-129651, wherein in an aluminium wound capacitor a solid electrolyte obtained using a PEDOT/PSS dispersion is additionally impregnated with a solution comprising conductive monomers and oxidation agents, in order to cause a chemical polymerisation of the monomers in the solid electrolyte layer. This approach to improvement of the equivalent series resistance is also comparatively costly because it requires an additional process step.

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The object of the present invention is to overcome the disadvantages resulting in the state of the art in connection with capacitors, particularly in connection with solid electrolyte capacitors, especially preferably in connection with aluminium capacitors known from the state of the art, particularly with aluminium wound capacitors.

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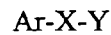
In particular, the object of the present invention is to provide a process for the production of a capacitor, particularly an aluminium wound capacitor, by which capacitors can be produced which exhibit as low an equivalent series resistance as possible together with as high a capacitance as possible. This improvement in the equivalent series resistance and the capacitance of the capacitor should be achieved using as technically simple a means as possible, and in particular should required no additional process steps.

30

A contribution to the solution of the abovementioned objects is achieved by a process for the production of a capacitor, particularly of an electrolyte capacitor, comprising the following process steps:

5

- a) the provision of an electrode body from an electrode material, wherein a dielectric at least partially covers a surface of this electrode material to form an anode body;
- 10 b) the introduction of a dispersion comprising a conductive polymer, a dispersing agent and an additive with the general structural formula (I)



(I)

15

in which

20 Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl radical;

25 X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;

30 Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl, wherein the substituents of the aromates can be, for example, halogen atoms, hydroxyl groups, carboxyl groups or alkyl groups as well as additional -X-Y groups;

into at least part of the anode body;

c) the at least partial removal of the dispersing agent to form a capacitor body.

In process step a) of the process according to the invention, an electrode body is  
5 firstly prepared from an electrode material, wherein a dielectric at least partially  
covers a surface of this electrode material to form an anode body.

In principle the electrode body can be produced by pressing and sintering a valve  
metal powder to give a mostly porous electrode body. Hereby a contact wire,  
10 preferably made of a valve metal e.g. Tantalum, is pressed therewith into the elec-  
trode body. The electrode body is then coated with a dielectric, for example  
through electrochemical oxidation. Alternatively, metal foils can be etched and  
coated with a dielectric by means of electrochemical oxidation in order to obtain  
an anode foil with a porous area. In wound capacitors an anode foil with a porous  
15 area forming the electrode body and a cathode foil are separated by separators and  
wound.

In the context of the invention, valve metal is to be understood as meaning those  
metals of which the oxide layers do not render possible current flow equally in  
20 both directions. In the case of an anodically applied voltage, the oxide layers of  
the valve metals block the current flow, while in the case of a cathodically applied  
voltage large currents occur, which may destroy the oxide layer. The valve metals  
include Be, Mg, Al, Ge, Si, Sn, Sb, Bi, Ti, Zr, Hf, V, Nb, Ta and W and an alloy  
or compound of at least one of these metals with other elements. The best known  
25 representatives of the valve metals are Al, Ta and Nb. Compounds with electrical  
properties comparable to a valve metal are those with metallic conductivity, which  
can be oxidized and of which the oxide layers have the properties described  
above. For example, NbO has metallic conductivity, but in general is not regarded  
as a valve metal. Layers of oxidized NbO have, however, the typical properties of  
30 valve metal oxide layers, so that NbO or an alloy or compound of NbO with other  
elements are typical examples of such compounds with electrical properties com-  
parable to a valve metal. Electrode materials of tantalum, aluminium and those

electrode materials based on niobium or niobium oxide are preferred. Aluminium is particularly preferred as the electrode material.

5 For production of the electrode body often with a porous region, the valve metals can be sintered, for example in powder form, to give a usually porous electrode body, or a porous structure is stamped on a metallic body. The latter can be carried out e.g. by etching a foil.

10 For simplicity, bodies with a porous region are also called "porous" in the following. Thus, for example, electrode bodies with a porous region are also called porous electrode bodies. On the one hand, the porous bodies can be permeated by a plurality of channels and therefore be sponge-like. This is often the case if tantalum is used for the production of capacitors. Furthermore, it is possible for only the surface to have pores and for the region following under the surface pores to be solid in construction. Such a situation is often observed if aluminium is used  
15 for the production of capacitors.

The often porous electrode bodies produced in this manner are then oxidized, for example, in a suitable electrolyte, such as e.g. phosphoric acid or an aqueous solution of ammonium adipate, by application of a voltage, in order to form the dielectric. The level of this forming voltage depends on the oxide layer thickness to be achieved or the later use voltage of the capacitor. Preferred forming voltages are in a range of from 1 to 2,000 V.  
20

25 In one particular embodiment of the capacitor according to the invention, the capacitor is an aluminium capacitor, particularly preferably an aluminium wound capacitor.

30 In process step b) of the process according to the invention, a dispersion which comprises a conductive polymer and a dispersing agent, preferably particles of a conductive polymer and a dispersing agent, is introduced into the porous region of the anode body. The dispersion is introduced into the porous region using known

processes, e.g. impregnation, dipping, pouring, dripping on, injection, spraying, knife coating, brushing or printing, for example ink-jet printing, screen printing, or tampon printing. It is preferable for this introduction to be made by dipping the anode body provided in process step a) into the dispersion so that it becomes im-  
5 pregnated with this dispersion. The dipping in and impregnation with the dispersing agent are preferably carried out for a period in a range from 1 second to 120 minutes, particularly preferably in a range from 10 seconds to 60 minutes and most preferably in a range from 30 seconds to 15 minutes. The introduction of the dispersion into the anode body can be facilitated, for example with excess pres-  
10 sure, negative pressure, vibration, ultrasound or heat.

The introduction of the dispersion can be achieved directly or using a binding agent, for example a silane, e.g. organofunctional silanes or their hydrolysates, e.g. 3-glycidoxypropyltrialkoxysilane, 3-aminopropyltriethoxysilane, 3-mercapto-  
15 propyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, vinyltrimethoxysilane or octyltriethoxysilane, and/or one or more other functional layers in the anode body.

It is preferable for the introduction to cause at least partial coating of the cavity  
20 surfaces, rather than covering of the pores with a surface. In this way the particles present in the dispersion not only form a layer covering the pore openings, but also cover at least part, and often all, of the surface area of the pores with a layer of the dispersion particles.

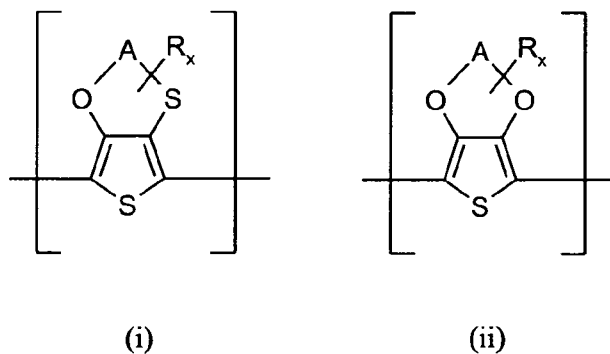
25 The term "polymer", as used in the context of the present invention, as defined in relation to the invention, includes all compounds with more than one identical or different recurring unit.

The electrically conductive polymer in the dispersion preferably comprises at least  
30 one polythiophene, polypyrrole or polyaniline, which are optionally substituted.



Here in particular, "*conductive polymers*" are understood as meaning the compound class of  $\pi$ -conjugated polymers which have an electrical conductivity after oxidation or reduction. Preferably, conductive polymers are understood as meaning those  $\pi$ -conjugated polymers which, after oxidation, have an electrical conductivity of the order of at least  $0.1 \text{ S cm}^{-1}$ . According to a particularly preferred embodiment according to the invention, the conductive polymer comprises an anion, preferably a polyanion. Anions and cations are then present in the conductive polymer. The two components together then form the conductive polymer.

In this connection, it is particularly preferable for the conductive polymer to comprise a polythiophene, particularly preferably a polythiophene with recurring units of the general formula (i) or (ii) or a combination of units of the general formulae (i) and (ii), preferably a polythiophene with recurring units of the general formula (ii)



wherein

A represents an optionally substituted  $\text{C}_1$ - $\text{C}_5$ -alkylene radical,

R represents a linear or branched, optionally substituted  $\text{C}_1$ - $\text{C}_{18}$ -alkyl radical, an optionally substituted  $\text{C}_5$ - $\text{C}_{12}$ -cycloalkyl radical, an optionally substituted  $\text{C}_6$ - $\text{C}_{14}$ -aryl radical, an optionally substituted  $\text{C}_7$ - $\text{C}_{18}$ -aralkyl radical, an optionally substituted  $\text{C}_1$ - $\text{C}_4$ -hydroxyalkyl radical or a hydroxyl radical,

x represents an integer from 0 to 8 and

in the case where several radicals R are bonded to A, these can be the same or different.

- 5 The general formulae (i) and (ii) are to be understood as meaning that x substituents R can be bonded to the alkylene radical A.

Polythiophenes with recurring units of the general formula (ii) wherein A represents an optionally substituted C<sub>2</sub>-C<sub>3</sub>-alkylene radical and x represents 0 or 1 are particularly preferred. Poly(3,4-ethylenedioxythiophene), which is optionally substituted, is very particularly preferred as the conductive polymer of the solid electrolyte.

In the context of the invention, the prefix poly- is to be understood as meaning that the polymer or polythiophene contains more than one identical or different recurring units of the general formulae (i) and (ii), respectively. In addition to the recurring units of the general formula (i) and/or (ii), the polythiophenes can optionally also comprise other recurring units, but it is preferable for at least 50 %, particularly preferably at least 75 % and most preferably at least 95 % of all recurring units of the polythiophene to have the general formula (i) and/or (ii), preferably the general formula (ii). The polythiophenes contain n recurring units of the general formula (i) and/or (ii), preferably the general formula (ii), in total, wherein n is an integer from 2 to 2,000, preferably 2 to 100. The recurring units of the general formula (i) and/or (ii), preferably of the general formula (ii), can in each case be identical or different within a polythiophene. Polythiophenes with in each case identical recurring units of the general formula (ii) are preferred.

The polythiophenes preferably in each case carry H on the end groups.

- 30 In the context of the invention, C<sub>1</sub>-C<sub>5</sub>-alkylene radicals A are preferably methylene, ethylene, n-propylene, n-butylene or n-pentylene. C<sub>1</sub>-C<sub>18</sub>-alkyl radicals R preferably represent linear or branched C<sub>1</sub>-C<sub>18</sub>-alkyl radicals, such as methyl,

ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl, C<sub>5</sub>-C<sub>12</sub>-cycloalkyl radicals R represent, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclodecyl, C<sub>5</sub>-C<sub>14</sub>-aryl radicals R represent, for example, phenyl or naphthyl, and C<sub>7</sub>-C<sub>18</sub>-aralkyl radicals R represent, for example, benzyl, o-, m-, p-tolyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylyl or mesityl. The preceding list serves to illustrate the invention by way of example and is not to be considered conclusive.

In the context of the invention, numerous organic groups are possible optional further substituents of the radicals A and/or of the radicals R, for example alkyl, cycloalkyl, aryl, aralkyl, alkoxy, halogen, ether, thioether, disulphide, sulphoxide, sulphone, sulphonate, amino, aldehyde, keto, carboxylic acid ester, carboxylic acid, carbonate, carboxylate, cyano, alkylsilane and alkoxy silane groups and carboxamide groups.

The polythiophenes contained in the conductive polymer can be neutral or cationic. In preferred embodiments they are cationic, "cationic" relating only to the charges on the polythiophene main chain. The polythiophenes can carry positive and negative charges in the structural unit, depending on the substituent on the radicals R, the positive charges being on the polythiophene main chain and the negative charges optionally being on the radicals R substituted by sulphonate or carboxylate groups. In this context, the positive charges of the polythiophene main chain can be partly or completely satisfied by the anionic groups optionally present on the radicals R. Overall, in these cases the polythiophenes can be cationic, neutral or even anionic. Nevertheless, in the context of the invention they are all regarded as cationic polythiophenes, since the positive charges on the polythiophene main chain are the deciding factor. The positive charges are not shown in the formulae, since their precise number and position cannot be determined absolutely. However, the number of positive charges is at least 1 and at most n, where-

in n is the total number of all recurring units (identical or different) within the polythiophene.

To compensate the positive charge, if this is not already done by the optionally  
5 sulphonate- or carboxylate-substituted and therefore negatively charged radicals R, the cationic polythiophenes require anions as counter-ions, it being possible for the counter-ions to be monomeric or polymeric anions. Polymeric anions are also called polyanions in the following. In the case where polyanions are employed, it is particularly preferable for the conductive polymer to comprise complexes of  
10 polythiophenes and polyanions, very particularly preferably complexes of poly(3,4-ethylenedioxythiophene) and polystyrenesulphonic acid.

Polyanions are preferable to monomeric anions, since they contribute towards film formation and because of their size lead to electrically conductive films  
15 which are more stable to heat. Polyanions here can be, for example, anions of polymeric carboxylic acids, such as polyacrylic acids, polymethacrylic acid or polymaleic acids, or of polymeric sulphonic acids, such as polystyrenesulphonic acids and polyvinylsulphonic acids. These polycarboxylic and -sulphonic acids can also be copolymers of vinylcarboxylic and vinylsulphonic acids with other polymeriz-  
20 able monomers, such as acrylic acid esters and styrene. Particularly preferably, the solid electrolyte contains an anion of a polymeric carboxylic or sulphonic acid for compensation of the positive charge of the polythiophene.

The anion of polystyrenesulphonic acid (PSS), which, if a polythiophene is used, in particular poly(3,4-ethylenedioxythiophene), is preferably present bonded as a  
25 complex in the form of the PEDOT/PSS complexes known from the prior art, is particularly preferred as the polyanion. Such complexes are obtainable by polymerizing the thiophene monomers, preferably 3,4-ethylenedioxythiophene, oxidatively in aqueous solution in the presence of polystyrenesulphonic acid.

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The molecular weight of the polyacids which supply the polyanions is preferably 1,000 to 2,000,000, particularly preferably 2,000 to 500,000. The polyacids or

their alkali metal salts are commercially obtainable, e.g. polystyrenesulphonic acids and polyacrylic acids, or can be prepared by known processes (see e.g. Houben Weyl, Methoden der organischen Chemie, vol. E 20 Makromolekulare Stoffe, part 2, (1987), p. 1141 et seq.).

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Polyanions and polythiophenes, in particular polystyrenesulphonic acid and poly(3,4-ethylenedioxythiophene) can be present in the conductive polymer and also in the solid electrolyte in a weight ratio of from 0.5:1 to 50:1, preferably from 1:1 to 30:1, particularly preferably 2:1 to 20:1. The weight of the electrically conducting polymers here corresponds to the weight of the monomers employed for the preparation of the conductive polymers, assuming that complete conversion takes place during the polymerization. According to a particular embodiment of the capacitor according to the invention, the polystyrenesulphonic acid is present in an excess by weight compared with the polythiophene, in particular poly(3,4-ethylenedioxythiophene).

15

Monomeric anions which are used are, for example, those of C<sub>1</sub>-C<sub>20</sub>-alkanesulphonic acids, such as methane-, ethane-, propane-, butanesulphonic acid or higher sulphonic acids, such as dodecanesulphonic acid, of aliphatic perfluoro-sulphonic acids, such as trifluoromethanesulphonic acid, perfluorobutanesulphonic acid or perfluorooctanesulphonic, of aliphatic C<sub>1</sub>-C<sub>20</sub>-carboxylic acids, such as 2-ethylhexylcarboxylic acid, of aliphatic perfluorocarboxylic acids, such as trifluoroacetic acid or perfluorooctanoic acid, and of aromatic sulphonic acids optionally substituted by C<sub>1</sub>-C<sub>20</sub>-alkyl groups, such as benzenesulphonic acid, o-toluenesulphonic acid, p-toluenesulphonic acid or dodecylbenzenesulphonic acid, and of cycloalkanesulphonic acids, such as camphorsulphonic acid, or tetrafluoroborates, hexafluorophosphates, perchlorates, hexafluoroantimonates, hexafluoroarsenates or hexachloroantimonates.

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Preferred as monomeric anions are the anions of the p-toluenesulphonic acid, methanesulphonic acid or camphorsulphonic acid.

30

The particles of the dispersion, in particular the particles of the conductive polymer, have a specific electrical conductivity of greater than 100 S/cm. The specific electrical conductivity of the particles is thereby the specific electrical conductivity of the film in the dry state, which upon drying of the dispersion is composed of the particles. It is preferable to use dispersions whose particles have a specific electrical conductivity of greater than 150 S/cm, more preferably greater than 250 S/cm, more preferably greater than 400 S/cm and yet more preferably greater than 750 S/cm. In some cases particles with a specific conductivity of up to 5,000 S/cm are used.

10

According to the invention, the particles of the conductive polymer in the dispersion preferably have a diameter  $d_{50}$  in a range from 1 to 70 nm, preferably in a range from 1 to below 40 nm, more preferably in a range from 1 to 35 nm, more preferably in a range from 1 to 30 nm, more preferably in a range from 5 to 25 nm.

15

The dispersion preferably contains a purity with respect to metals and transition metals as described in WO2010/003874A2 on page 6 lines 10-29. The low concentrations of metals in the dispersions have the advantage that the dielectric is not damaged during formation of the solid electrolyte and in the later operation of the capacitor.

20

The dispersions contain one or more dispersing agents, where water, organic solvents or mixtures of organic solvents and water are preferred dispersing agents. Examples of solvents employed as dispersing agent include: aliphatic alcohols such as methanol, ethanol, i-propanol and butanol, aliphatic ketones such as acetone and methylethylketone, aliphatic carboxylic acid esters such as ethylacetate and butylacetate; aromatic hydrocarbons such as toluene and xylene; aliphatic hydrocarbons such as hexane, heptane and cyclohexane; chlorohydrocarbons such as dichloromethane and dichloroethane; aliphatic nitriles such as acetonitrile, aliphatic sulphoxides and sulphones such as dimethylsulphoxide and sulfolane; aliphatic carboxamides such as methylacetamide, dimethylacetamide and dime-

30

thylformamide; aliphatic and araliphatic ethers such as diethylether and anisole. Furthermore, water or a mixture of water and the abovementioned organic solvents can be used as dispersing agent.

- 5 Preferred dispersing agents are water or other protic solvents such as alcohol, e.g. methanol, ethanol, i-propanol and butanol, as well as mixtures of water with these alcohols. Water is particularly preferred as dispersing agent.

The dispersion can, in addition to the conductive polymer, the dispersing agent,  
10 and the additive with the general formula (I) described below, comprise further additive materials, such as surface active substances, e.g. anionic surfactants, such as e.g. alkylphenylsulphonic acids and salts, parafinsulphonates, alcoholsulphonates, ethersulphonates, sulphosuccinates, phosphateesters, alkylethercarboxylic acids or carboxylates, cationic surfactants, e.g. quaternary alkylammonium salts,  
15 non-ionic surfactants, e.g. linear alcoholethoxylates, oxoalcoholethoxylates, alkylphenolethoxylate or alkylpolyglucosides, or can contain binding agents such as e.g. organofunctional silanes or their hydrolysates, e.g. 3-glycidoxypropyltrialkoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-metacryloxypropyltrimethoxysilane, vinyltrimethoxysilane or octyltriethoxysilane,  
20 cross linking agents such as melamine compounds, blocked isocyanates, functional silanes - e.g. tetraethoxysilane, alkoxy silane hydrolysate, e.g. based on tetraethoxysilane, epoxysilanes such as 3-glycidoxypropyltrialkoxysilane, polyurethanes, polyacrylates or polyolefin dispersions.

- 25 It is preferable for the conductive polymer comprising dispersions to contain further additive materials which increase the conductivity, e.g. ether group containing compounds, e.g. tetrahydrofurane, lactone group containing compounds such as  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone, amide or lactam group containing compounds such as caprolactam, N-methylcaprolactam, N,N-dimethylacetamide, N-methylacetamide, N,N-dimethylformamide (DMF), N-methylformamide, N-methylformanilide,  
30 N-methylpyrrolidone (NMP), N-octylpyrrolidone, pyrrolidone, sulphones and sulphoxides, e.g. sulpholane (tetramethylenesulphone), dime-

thylsulphoxide (DMSO), sugars or sugar derivatives, e.g. saccharose, glucose, fructose, lactose, sugar alcohols e.g. sorbitol, mannitol, furan derivatives, e.g. 2-furancarboxylic acid, 3-furancarboxylic acid, glycerine, diglycerine, triglycerine or tetraglycerine.

5

Alkylene glycols, dialkylene glycols, trialkylene glycols, polyalkylene glycols composed of more than three alkylene units or mixtures of these compounds can also be contained in the dispersion as the conductivity increasing additive.

10 As alkylene glycol, ethylene glycol and propylene glycol are particularly preferred.

Particularly preferred dialkylene glycols, trialkylene glycols or polyalkylene glycols are those based on ethylene and propylene glycols or statistical copolymers of  
15 both. Particularly preferred are diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, polyethylene glycol or polypropylene glycol. The polyalkylene glycols can also be branched. Furthermore, polyalkylene glycols can have the end groups unsubstituted, i.e. they can carry two free hydroxyl groups, or alternatively can have the end groups singly or doubly functionalised. The poly-  
20 alkylene glycol or polyalkylene glycol derivative preferably exhibits a molecular weight, as determined by gel permeation chromatography, in a range from 100 to 100,000 g/mol, particularly preferably in a range from 200 to 50,000 g/mol and most preferably in a range from 200 to 5,000 g/mol. Polyethylene glycols are particularly preferred as polyalkylene glycols. Particularly suitable are those polyeth-  
25 ylene glycols known as „PEG 300“, „PEG 400“, „PEG 1000“, „PEG 2000“ or „PEG 4000“. PEG 400 is particularly preferred.

In this connection it is furthermore preferred, for the dispersion to contain a quantity of the alkylene glycol, the polyalkylene glycol or the mixture of an alkylene  
30 glycol and a polyalkylene glycol in a range from 1 to 25 % by weight, particularly preferably in a range from 2 to 20 % by weight and most preferably from 3 to



15 % by weight, in each case based on the total weight of the dispersion employed in process step b).

The conductive polymer comprising dispersions can additionally contain as additive one or more organic binding agents which are soluble in organic solvents as described in WO 2009/141209 A1 on page 12 lines 16-34. The dispersions can have a pH value from 1 to 14, preferably a pH value from 1 to 8. For dielectrics sensitive to corrosion, for example aluminium oxide or niobium oxide, dispersions with a pH value from 2.5 to 8 are preferred in order not to damage the dielectric.

10

In order to adjust the pH value of the conductive polymer comprising dispersions, bases or acids as described in WO 2010/003874 A2 on page 4 lines 13-32 can be added as additives. Preferred are those additives which do not interfere with the film formation of the dispersion and which are not volatile at high temperatures, e.g. soldering temperatures, rather remain in the solid electrolyte under these condition, such as e.g. the bases 2-dimethylaminoethanol, 2,2'-iminodiethanol or 2,2',2''-nitrilotriethanol and the acid polystyrenesulphonic acid.

15

The viscosity (measured with a rheometer at 20°C and at a shear rate of 100 s<sup>-1</sup>) of the conductive polymer comprising dispersion can be between 0.1 and 1,000 mPa·s depending on the manner of application. The viscosity is preferably from 1 to 500 mPa·s, particularly preferably between 10 and 250 mPa·s, especially preferred 40 to 200 mPa·s.

20

The solid content of conductive polymer, preferably PEDOT/PSS, of the conductive polymer comprising dispersion preferably lies in a range from 0.1 to 20 % by weight, particularly preferably in a range from 0.5 to 10 % by weight and most preferably in a range from 1 to 5 % by weight, in each case based on the total weight of the conductive polymer comprising dispersion. The solid content of conductive polymer, preferably PEDOT/PSS (without additive and additional materials) is determined upon drying of the dispersion at a temperature which is suf-

30

ficiently high to remove the dispersing agent but not so high as to decompose the solid.

The dispersion employed in process step b) is characterised in that, in addition to  
5 the conductive polymer, the dispersing agent and optionally one or more of the above described additional materials, it comprises an additive of the general structural formula (I):



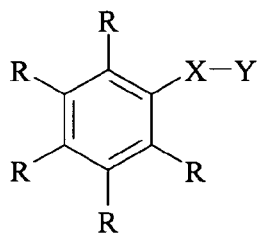
wherein

15 Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl group, a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl radical;

20 X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> in each case stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;

25 Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl, wherein substituents of the aromates can be, for example, halogen atoms, hydroxyl groups, carboxyl groups or alkyl groups as well as further -X-Y groups.

It is particularly preferable according to the invention for the compound to exhibit the general structural formula (II)



(II)

in which X and Y have the meaning given above and

5

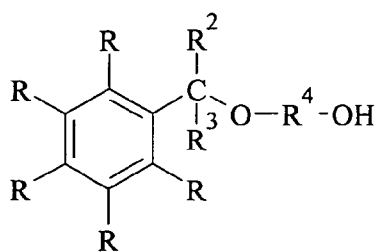
R stands for an H atom, a halogen atom, an amino group, a hydroxyl group, a carboxyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group or a C<sub>1</sub>-C<sub>10</sub>-alkyl group and where the R groups within the general structural formula can be the same or different.

10

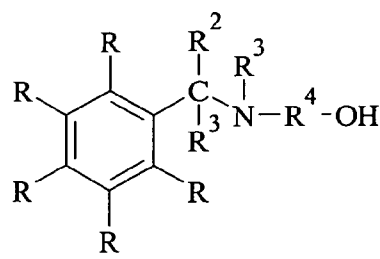
It is preferable for this additive to be an aryloxy derivative with the general structural formula (I), an arylamide derivative with the general structural formula (I), a benzoyloxy derivative with the general structural formula (I), a benzyloxy derivative with the general structural formula (I), a benzylamide derivative with the general structural formula (I) or a mixture of at least two of these compounds.

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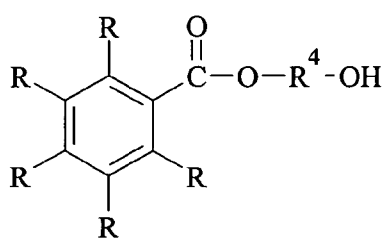
In this connection, additives exhibiting one of the following structural formulae (III) to (VI) are preferred:



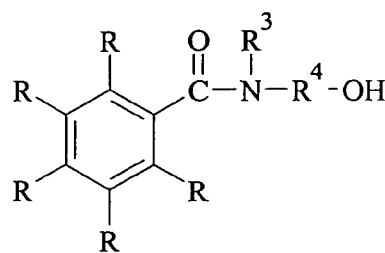
(III)



(IV)



(V)



(VI)

in which  $R^1$ ,  $R^2$  and  $R^3$  have the meaning already stated, however preferably stand for a hydrogen atom;

5

$R^4$  stands for a straight chain or branched  $C_1$ - $C_{10}$ -alkylene group, which can optionally carry one or more OH groups, preferably a methylene group, an ethylene group or an isopropylene group, or for an oxyalkylene group, a di(oxyalkylene) group, or a tri(oxyalkylene) group, preferably for an oxyethylene group, a di(oxyethylene) group or a tri(oxyethylene) group;

10

R stands for an H atom, a halogen atom, an amino group, a hydroxyl group or a  $C_1$ - $C_{10}$ -alkyl group wherein the R groups within the general structural formula can be the same or different.

15

Examples of specifically suitable additives from the aryloxy derivative group are in particular 2-phenoxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)-phenol, di(ethyleneglycol)phenylether, tri(ethyleneglycol)phenylether, tetra(ethyleneglycol)phenylether, poly(ethyleneglycol)phenylether, guaiacolglycerylether, 3-phenoxy-1,2-propanediol, bis(2-hydroxyethyl)terephthalate, phenoxyacetic acid, 2-phenoxypropionic acid, (4-hydroxyphenoxy)acetic acid, 4-carboxy-

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phenoxyacetic acid, 2-[4-(2-hydroxyethoxy)phenoxy]ethanol, 2-(2-naphthyloxy)ethanol, 2-[3-(2-hydroxy)phenoxy]ethanol, 2-(4-methoxyphenoxy)ethanol, 2-[2-(2-hydroxyethoxy)phenoxy]ethanol, 2-(4-phenoxyphenoxy)ethanol, [2-(carboxymethoxy)phenoxy]acetic acid, (2-methylphenoxy)acetic acid, (4-tert.-butylphenoxy)acetic acid, 2-(pentafluorophenoxy)ethanol, 2-(4-chlorophenoxy)-2-methylpropanoic acid and mixtures of at least two of those named.

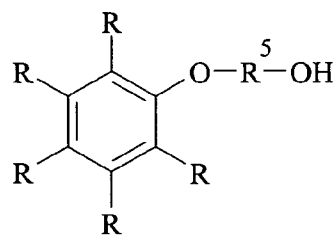
Examples of specifically suitable additives of the arylamine derivative group are in particular N-(2-hydroxyethyl)aniline, 2-(4-(ethylamino)anilin)ethanol, 2-(1-naphthylamino)ethanol, 2-(methylphenylamino)ethanol, N-phenylglycine, N-phenyldiethanolamine, 2-(N-ethylanilino)ethanol, 2,2'-(4-methylphenylimino)diethanol, (2-fluoroanilino)acetic acid, 4-[bis(2-hydroxyethyl)amino]benzaldehyde, 4-chloro-N-(2-hydroxyethyl)-2-nitroanilin, 2-(2-hydroxyethylamino)-5-nitrobenzotrile, (iso-propylanilino)oxoacetic acid, N-(2-ethyl-6-methylphenyl)-2-hydroxyacetamide, 4-(2,2-dicyanovinyl)-N-bis(hydroxyethyl)aniline and mixtures of at least two of those named.

Examples of specifically suitable additives of the benzyloxy derivative group are in particular 2-(benzyloxy)ethanol, di(ethyleneglycol)benzylether, poly(ethyleneglycol)benzylether, ethyleneglycolmonosalicylate, bis(2-hydroxyethyl)terephthalate, 1-benzyloxy-2-propanol, 2-benzyloxy-1,3-propandiol, 1-benzyloxy-2-propanol, 1-(benzyloxymethyl)tri(ethyleneglycol), 3-(benzyloxy)-1,2-propandiol, (2,3)-3-(benzyloxy)-1,2,4-butantriol, [(2S,3S)-3-phenyl-2-oxiranyl]methanol, 2-phenyl-1,3-dioxan-5-ol, 1,3-dibenzyloxy-2-propanol, mono(benzalpentarythritol), 1-benzyloxy-3-(p-tosyloxy)-2-propanol, benzylglycolate and mixtures of at least two of those named.

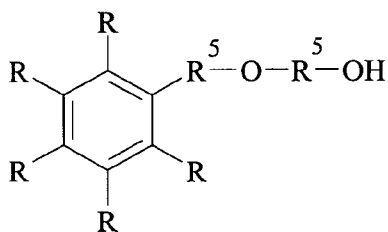
Examples of specifically suitable additives of the benzylamine derivative group are in particular 2-(benzylamino)ethanol, 2-(benzylamino)-1-propanol, 2-[benzyl(methyl)amino]ethanol, 2,2'-(benzylimino)diethanol, N-(2-hydroxyethyl)phthalimide, N-phthaloylglycine, 2-(dibenzylamino)ethanol, N-benzylimino-

diacetic acid, (benzoylamino)acetic acid and mixtures of at least two of those named.

According to a particularly preferred embodiment of the present invention the additive exhibits the general structural formula (VII) or (VIII)



(VII)



(VIII)

10

in which

15 R stands for an H atom, an OH group, a C<sub>1</sub>-C<sub>10</sub>-alkyl group or a C<sub>1</sub>-C<sub>10</sub>-alkoxy group wherein the R groups within the general structural formula can be the same or different;

20 R<sup>5</sup> stands for a straight chain or branched alkylene group, which can optionally carry further OH groups, wherein the R<sup>5</sup> group in the phenyl group in the structural formula (X) is preferably a methylene group.

Alkylene group R<sup>5</sup> can be, for example, an ethylene group, an n-propylene group or an iso-propylene group. Examples of especially preferred additives are phe-

noxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)phenol, 3-phenoxy-1,2-propandiol, di(ethyleneglycol)benzylether or a mixture of at least two of these compounds.

5 In this connection it is particularly preferred, according to the invention, if the dispersion comprises 0.1 to 25 % by weight, particularly preferred 0.25 to 10 % by weight and most preferred 0.5 to 5 % by weight of the above described additive, in each case based on the total weight of the dispersion employed in process step b).

10

After the anode bodies have been impregnated with the above described dispersion, the dispersing agent contained in the dispersion is at least partially removed or cured in process step c), so that a solid electrolyte, which covers the dielectric wholly or partially, thusly forms a capacitor body. In this connection it is preferred that the coating of the dielectric with the solid electrolyte amount to at least 15 50 %, particularly preferably at least 70 % and most preferably at least 80 %, where this can be determined by measurement of the capacitance of the capacitor in the dry and in the damp state at 120°C, as described in DE-A-10 2005 043 828.

20 The removal or curing is preferably effected by removing the electrode body from the dispersion and drying it, this drying preferably being carried out in a temperature range from 20°C to 230°C, particularly preferably in a range from 50°C to 220°C and most preferably in a range from 80°C to 200°C. The process steps b) and c) can also be repeated once or several times in order to adjust as required the 25 thickness of the layer of the solid electrolyte deposited on the dielectric or the filling degree of the sold electrolyte in the electrode body.

After the capacitor bodies have been produced in this way, they can be modified in the manner know to the person skilled in the art. In the case of a tantalum electrolyte capacitor, the capacitor bodies can be covered, for example, with a graphite 30 layer and a silver layer, as is known from DE-A-10 2005 043 828, while in the case of an aluminium wound capacitor, in accordance with the teaching of

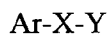
US 7,497,879 B2, the capacitor body is incorporated in an aluminium beaker, provided with a sealing inspection glass and firmly closed mechanically by crimping. The capacitor can then be freed from defects in the dielectric in a known manner by ageing.

5

A contribution towards achieving the abovementioned objects is also made by a capacitor obtainable by the process according to the invention. This capacitor is preferably an aluminium capacitor, particularly preferably an aluminium wound capacitor.

10

A contribution towards achieving the abovementioned objects is made particularly by a capacitor comprising an electrode body made of an electrode material, wherein a dielectric at least partially covers the surface area of this electrode material and forms an anode body, wherein the anode body is at least partially coated with a solid electrolyte which comprises a conductive polymer and wherein the solid electrolyte comprises an additive with the general structural formula (I),



(I)

20

in which

Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a hydroxyl terminal group;

25

X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;

30

Ar stands for an optionally substituted aromate selected from the group of phenyl and naphthyl, wherein the substituents of the aromates can be, for ex-



ample, halogen atoms, hydroxyl groups, carboxyl groups or alkyl groups as well as additional -X-Y groups.

Such a capacitor is obtainable, for example, using the process according to the invention as described at the beginning. Preferred additives in this connection are those which have already been mentioned in connection with the process according to the invention. Especially preferred are additives with the structural formulae (II), (III), (IV), (V), (VI), (VII) or (VIII), most preferred being those additives selected from the group consisting of phenoxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)phenol, 3-phenoxy-1,2-propandiol, di(ethyleneglycol)benzyl-ether or a mixture of at least two of these compounds.

A further contribution towards achieving the abovementioned objects is also made by an electronic circuit comprising a capacitor according to the invention or a capacitor obtainable by the process according to the invention. In this connection there are to be mentioned, for example, electronic circuits such as are found, for example, in computers (desktop, laptop, server), in computer peripherals (e.g. PC cards), in portable electronic equipment, such as e.g. mobile telephones, digital cameras or electronic entertainment systems, in devices for electronic entertainment systems, such as e.g. in CD/DVD players and computer games consoles, in navigation systems, in telecommunications installations, in domestic appliances, in medical technology, e.g. for defibrillators. According to the invention the capacitors can also be used in electronic circuits in hybrid or electric propulsion means for an automobile. Here the capacitors can serve in particular as intermediate capacitors (DC link capacitors).

A contribution towards achieving the abovementioned objects is also made by the use of a capacitor obtainable by the process according to the invention in electronic circuits, for example as intermediate capacitors in an electrical circuit in hybrid or electro car engines.

A contribution towards achieving the abovementioned objects is also made by the use of a dispersion comprising a conductive polymer, a dispersing agent and an additive with the general structural formula



in which

Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a hydroxyl terminal group;

X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;

Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl, wherein the substituents of the aromates can be, for example, halogen atoms, hydroxyl groups, carboxyl groups or alkyl groups as well as additional -X-Y groups.

Here also, preferred additives are those additives which have already been mentioned at the beginning as preferred additives in connection with the process according to the invention. Especially preferred are additives with the structural formulae (II), (III), (IV), (V), (VI), (VII) or (VIII), the most preferred additives being selected from the group consisting of phenoxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)phenol, 3-phenoxy-1,2-propandiol, di(ethylene-glycol)benzylether or a mixture of at least two of these compounds.

30

The invention will now be further explained with the help of non limiting figures and examples.

Figure 1 is a schematic cross sectional depiction through part of capacitor obtain-  
able by the process according to the invention. This shows an electrode body 1,  
usually of a porous electrode material 2 such as aluminium. On the surface 4 of  
5 the electrode material 2 is a dielectric 3 developed as a thin layer, thus resulting in  
a yet more porous anode body 5, comprising the electrode body 1 made of the  
electrode material 2 and the dielectric 3. Onto the dielectric 3, optionally after  
further layers, follows a layer of a solid electrolyte 6 (e.g. comprising  
PEDOT/PSS particles), such that a capacitor body 7 results which comprises the  
10 electrode body 1 made of the electrode material 2, the dielectric 3 and the solid  
electrolyte 6.

#### METHODS OF MEASUREMENT

##### 15 Equivalent Series Resistance

The equivalent series resistance (in  $m\Omega$ ) was determined at 20°C at 100 kHz us-  
ing an LCR meter (Agilent 4284A).

##### 20 Capacitance

The capacitance (in micro Farad) was determined at 20°C at 120 Hz using an LCR  
meter (Agilent 4284A).

#### 25 EXAMPLES

##### Example 1 (Production of a dispersion of conductive polymers)

868 g of deionised water, 330 g of an aqueous solution of polystyrenesulphonic  
30 acid with an average molecular weight of 70,000 and a 3.8 % solid content by  
weight were placed in a 2 l three necked flask with stirrer and internal thermome-  
ter. The reaction temperature was maintained between 20 and 25°C. 5.1 g of 3,4-

ethylenedioxythiophene was added under stirring. The solution was stirred for 30 minutes. Subsequently 0.03 g of iron(III) sulphate and 9.5 g of sodium persulphate were added and the solution stirred for a further 24 hours. After completion of the reaction 100 ml of a strongly acidic cation exchanger and 250 ml of a weakly basic anion exchanger were added and the solution stirred for a further 2 hours to remove inorganic salts. The ion exchanger was filtered out. The poly(3,4-ethylenedioxythiophene)/polystyrenesulphonate dispersion was homogenised ten times with a high pressure homogeniser at a pressure of 700 bar. Then the dispersion was concentrated to a 2.5 % solid content and then homogenised a further five times at a pressure of 1500 bar.

The dispersion was diluted to a concentration of 2.2 % by addition of deionised water and then adjusted to a pH value of 3 with ammonia water.

## 15 Example 2 (Production of an aluminium wound capacitor)

### 2.1 Production of an oxidised electrode body

A porous aluminium foil formed at 92 V with dimensions 630 mm × 8 mm (anode foil) and a porous aluminium foil with dimension 660 mm × 8 mm (cathode foil) were each furnished with a contact wire, then wound up together with two cellulose separator papers and fixed with sticky tape. 10 of these oxidised electrode bodies were produced. The separator paper of the oxidised electrode bodies was subsequently carbonised in an oven at 300°C.

25

### 2.2 Production of the solid electrolyte

The oxidised electrode bodies from 2.1 were soaked in PEDOT dispersions in a vacuum for 15 minutes. Thereafter drying at 150°C was carried out for 30 min. Soaking and drying were carried out two further times.

30

## Example 3 (Production of a PEDOT/PSS dispersion with additive)

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol.

Example 4 (Production of a PEDOT/PSS dispersion with additive)

5

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 1 g phenoxyethanol.

Example 5 (Production of a PEDOT/PSS dispersion with additive)

10

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 1 g phenoxy-1,2-propandiol.

Example 6 (Production of a PEDOT/PSS dispersion with additive)

15

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 1 g 1-phenoxy-2-propanol.

Example 7 (Production of a PEDOT/PSS dispersion with additive)

20

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 1 g 2-(2-hydroxyethoxy)phenol.

Example 8 (Production of a PEDOT/PSS dispersion with additive)

25

100 g of the dispersion from example 1 were stirred with 10 g ethylene glycol and 1 g di(ethyleneglycol)benzylether.

Comparative example 1 (Production of a PEDOT/PSS dispersion without additive)

100 g of the dispersion from example 1 was stirred with 7.5 g of ethylene glycol  
5 and 2.5 g of polyethylene glycol (PEG400).

Example 9 (Production of a PEDOT/PSS dispersion with additive)

100 g of the dispersion from example 1 was stirred with 7.5 g of ethylene glycol,  
10 2.5 g polyethylene glycol (PEG400) and 1 g phenoxyethanol.

Example 10 (Production of an aluminium wound capacitor)

Capacitors were produced and measured analogously to example 2:

15

10.1: The electrode bodies were soaked in the dispersion described in the example 3 and dried;

10.2: The electrode bodies were soaked in the dispersion described in the example 4 and dried;  
20

10.3: The electrode bodies were soaked in the dispersion described in the example 5 and dried;

10.4: The electrode bodies were soaked in the dispersion described in the example 6 and dried;  
25

10.5: The electrode bodies were soaked in the dispersion described in the example 7 and dried;  
30

10.6: The electrode bodies were soaked in the dispersion described in the comparative example 1 and dried;

10.7: The electrode bodies were soaked in the dispersion described in the example 9 and dried;

- 5 The average electrical values of the so produced capacitors can be taken from table 1.

Table 1

	Capacitance [ $\mu$ F] at 20°C	Series Resistance [m $\Omega$ ] at 20°C
Example 10.1 (not according to the invention)	459.1	35
Example 10.2 (according to the invention)	462.5	20
Example 10.3 (according to the invention)	453.8	22
Example 10.4 (according to the invention)	462.5	19
Example 10.5 (according to the invention)	464.2	23
Example 10.6 (not according to the invention)	500.2	28
Example 10.7 (according to the invention)	483.1	20

- 10 The capacitors from examples 10.1 and 10.6 exhibit a high series resistance. The capacitors produced according to the invention from examples 10.2 to 10.5 and 10.7 exhibit clearly lower series resistances and at the same time show a capacitance which is comparable with the capacitance of the capacitors from examples 10.1 and 10.6.

15

Example 11 (Production of a PEDOT/PSS dispersion with additive)

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 0.5 g phenoxyethanol.

5 Example 12 (Production of a PEDOT/PSS dispersion with additive)

100 g of the dispersion from example 1 was stirred with 10 g ethylene glycol and 2 g phenoxyethanol.

10 Example 13 (Production of an aluminium wound capacitor)

Capacitors were produced and measured analogously to example 2:

15 13.1: The electrode bodies were soaked in the dispersion described in example 11 and dried;

13.2: The electrode bodies were soaked in the dispersion described in example 12 and dried;

20 The average electric values of the so produced capacitors can be taken from table 2.

Table 2

	Capacitance [ $\mu$ F] at 20°C	Series Resistance [m $\Omega$ ] at 20°C
Example 13.1 (according to the invention)	462.4	24.1
Example 13.2 (according to the invention)	419.9	15.8

25 A relationship between the series resistance and the concentration of the phenoxyethanol can be seen.

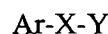


REFERENCE LIST

- 1 electrode body
- 5 2 electrode material
- 3 dielectric
- 4 surface
- 5 anode body
- 6 solid electrolyte
- 10 7 capacitor body
- 8 pores

## PATENT CLAIMS

1. A process for the production of a capacitor, comprising the process steps:
- 5 a) the provision of a an electrode body (1) from an electrode material (2), wherein a dielectric (3) at least partially covers a surface (4) of this electrode material (2) to form an anode body (5);
- b) the introduction of a dispersion comprising a conductive polymer, a dispersing agent, and an additive with the general structural formula (I)
- 10

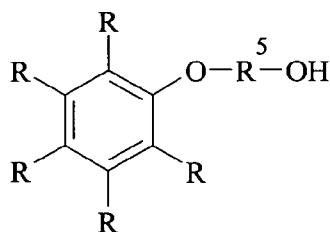


(I)

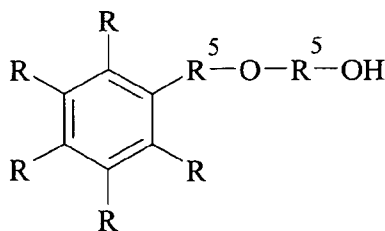
- 15 in which
- Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl radical;
- X stands for a connector selected from the group consisting of
- 20 O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;
- Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and natphtyl;
- 25 into at least a part of the anode body (5);
- c) the at least partial removal of the dispersing agent to obtain a capacitor body (7).
2. The process according to claim 1, wherein the conductive polymer comprises a polythiophene.
- 30



7. The process according to claim 5 or 6, wherein the conductive polymer comprises a complex of poly(3,4-ethylenedioxythiophene) and polystyrenesulphonic acid.
- 5 8. The process according to one of the preceding claims, wherein the additive is selected from the group consisting of aryloxy derivatives with the general structural formula (I), arylamide derivatives with the general structural formula (I), benzoyloxy derivatives with the general structural formula (I), benzyloxy derivatives with the general structural formula (I) and benzylamide derivatives with the general structural formula (I).
- 10
9. The process according to the one of the preceding claims, wherein the additive exhibits the general structural formula (VII) or (VIII)



(VII)



(VIII)

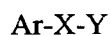
20

in which

R stands for an H atom, for an OH group, for a C<sub>1</sub>-C<sub>10</sub>-alkyl group or for a C<sub>1</sub>-C<sub>10</sub>-alkoxy group and wherein the groups R within the general structural formula can be the same or different;

R<sup>5</sup> stands for a straight chain or branched alkylene group, which can optionally carry further OH groups.

10. The process according to the one of the preceding claims, wherein the additive is selected from the group consisting of phenoxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)phenol, 3-phenoxy-1,2-propandiol, di(ethyleneglycol)benzylether or a mixture of at least two of these compounds.
11. The process according to the one of the preceding claims, wherein the dispersion comprises 0.1 to 25 % by weight of the additive based on the total weight of the dispersion employed in process step b).
12. A capacitor obtainable by a process according to one of the claims 1 to 11.
13. A capacitor comprising an electrode body (1) of an electrode material (2), wherein a dielectric (3) at least partially covers the surface (4) of this electrode material (2) forming an anode body (5), wherein the anode body (5) is at least partially coated with a solid electrolyte (6) which comprises a conductive polymer and wherein the solid electrolyte comprises an additive with the general structural formula (I)



(I)

in which

Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical, for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl group;

X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in

which  $R^1$ ,  $R^2$  and  $R^3$  each stand for a hydrogen atom or a  $C_1$ - $C_{10}$ -alkyl group;

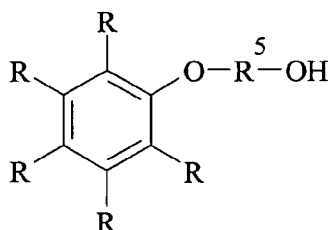
Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl.

5

14. Capacitor according to claim 13, wherein the additive is selected from the group consisting of aryloxy derivatives with the general structural formula (I), arylamide derivatives with the general structural formula (I), benzoyloxy derivatives with the general structural formula (I) and benzylamide derivatives with the general structural formula (I).

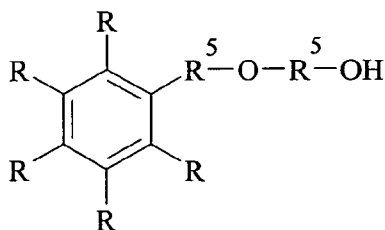
10

15. Capacitor according to claim 13 or 14, wherein the additive exhibits the structural formula (VII) or (VIII)



15

(VII)



(VIII)

20

in which

R stands for an H atom, for an OH group, for a  $C_1$ - $C_{10}$  alkyl group or for a  $C_1$ - $C_{10}$ -alkoxy group, wherein the groups R within the general structural formula can be the same or different;

R<sup>5</sup> stands for a straight chain or branched alkylene group, which can optionally carry further OH groups.

16. Capacitor according to one of the claims 13 to 15, wherein the additive is  
5 selected from the group consisting of phenoxyethanol, 1-phenoxy-2-propanol, 2-(2-hydroxyethoxy)phenol, 3-phenoxy-1,2-propandiol, di(ethyleneglycol)benzylether and a mixture of at least two of these compounds.
- 10 17. The capacitor according to one of the claims 13 to 16, wherein the capacitor is an aluminium capacitor.
18. The capacitor according to claim 17, wherein the capacitor is an aluminium wound capacitor.
- 15 19. The use of capacitors according to one of the claims 13 to 18 in electronic circuits.
20. An electrical circuit, comprising a capacitor according to one of the  
20 claims 13 to 18.
21. Use of a dispersion comprising a conductive polymer, a dispersing agent and an additive with the general structural formula (I)

25

Ar-X-Y

(I)

in which

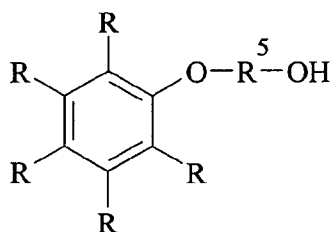
- Y stands for a C<sub>1</sub>-C<sub>18</sub>-alkyl group with at least one hydroxyl radical,  
30 for a C<sub>1</sub>-C<sub>18</sub>-alkylcarboxylic acid or for a polyalkyleneoxy radical with a terminal hydroxyl group;

X stands for a connector selected from the group consisting of O, O-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>O, NR<sup>3</sup>-CR<sup>1</sup>R<sup>2</sup>, CR<sup>1</sup>R<sup>2</sup>-NR<sup>3</sup>, COO and CONR<sup>3</sup>, in which R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each stand for a hydrogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group;

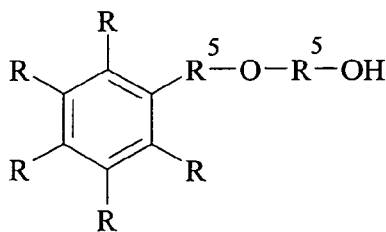
5 Ar stands for an optionally substituted aromate selected from the group consisting of phenyl and naphthyl;

for the production of a solid electrolyte in a capacitor.

22. The use according to claim 21, wherein the additive exhibits the general  
10 structural formula (VII) or (VIII)



(VII)



(VIII)

15

in which

R stands for an H atom, an OH group, a C<sub>1</sub>-C<sub>10</sub>-alkyl group or a C<sub>1</sub>-  
20 C<sub>10</sub>-alkyl group and wherein the groups R within the structural formula can be the same or different;

R<sup>5</sup> stands for a straight chain or branched alkylene group, which can optionally carry further OH groups.



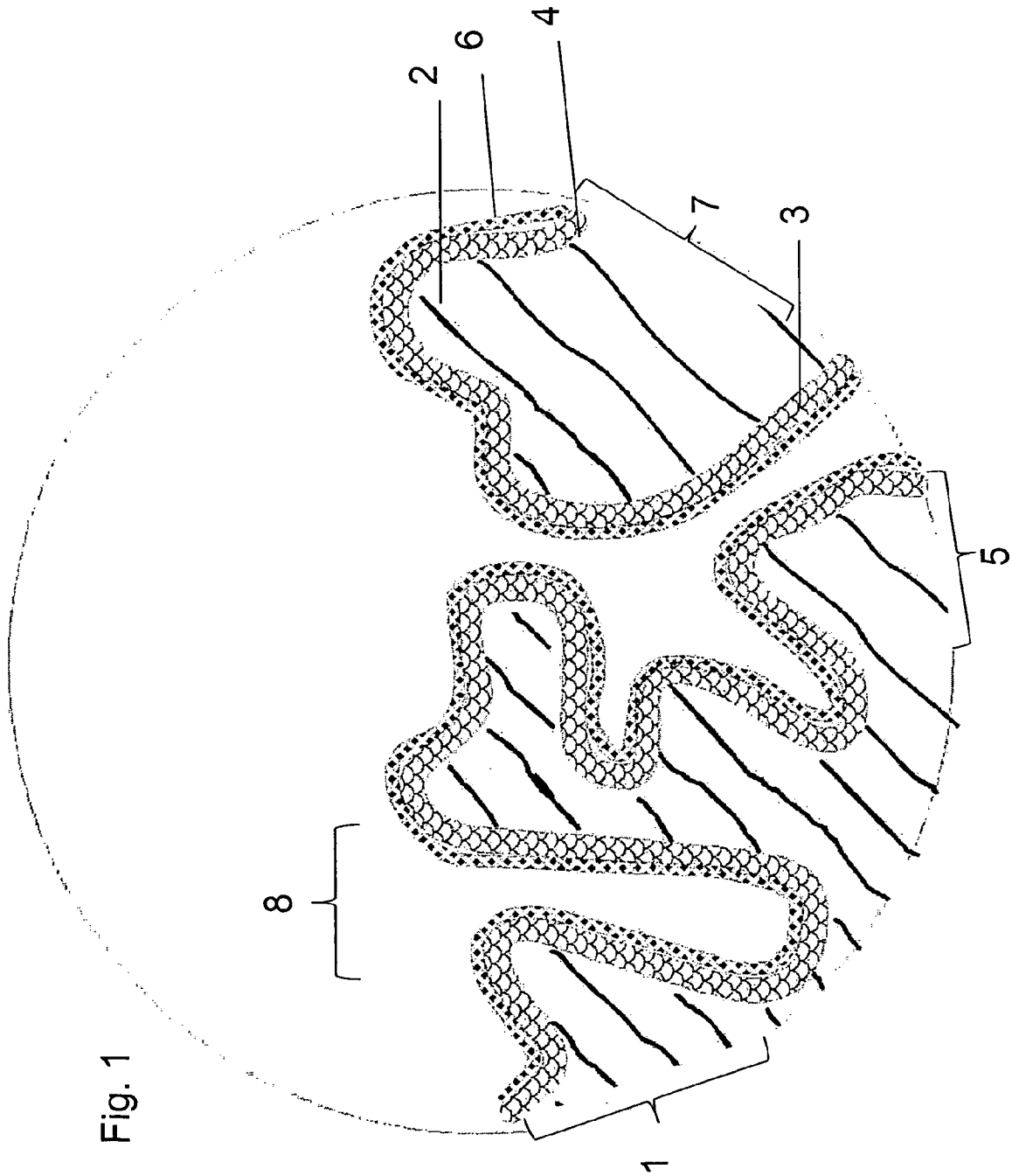


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/001094

A. CLASSIFICATION OF SUBJECT MATTER  
INV. H01G9/22  
ADD.  
  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101 486 839 A (ZHENGZHOU TAIDA ELECTRONIC MAT [CN] ZHENGZHOU TAIDA ELECTRONIC MATERIA) 22 July 2009 (2009-07-22) the whole document	1-22
X	JP 11 102844 A (MATSUSHITA ELECTRIC IND CO LTD) 13 April 1999 (1999-04-13) paragraph [0004] paragraph [0013] - paragraph [0019] paragraph [0025] - paragraph [0040]	1,13,21
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search  5 July 2012	Date of mailing of the international search report  12/07/2012
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Korb, Wolfgang
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/001094

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	EP 1 988 128 A1 (SHINETSU POLYMER CO [JP]) 5 November 2008 (2008-11-05) the whole document -----	1-22
A	EP 0 440 957 A2 (BAYER AG [DE]) 14 August 1991 (1991-08-14) the whole document -----	1-22

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International application No PCT/EP2012/001094
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