

PATENT SPECIFICATION

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(54) ELECTROCHROMIC DEVICE WITH CATIONIC ION EXCHANGE RESIN SEPARATOR

(71) We, TIMEX CORPORATION, a Corporation organized under the Laws of the State of Delaware, United States of America, of Waterbury, Connecticut 06720, United States America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to electrochromic display devices and more particularly to electrochromic display devices having an electrolyte for ion transfer disposed between a display electrode and a counter electrode, and

15 a layer of electrochromic material on one or on both of the conductive electrodes. An electrochromic display device which is described in United States Patent No. 3,827,784 has a sandwich structure comprising a substrate

20 having deposited thereon a conductive electrode in segmented form which can be selectively activated to form displays, a layer of persistent electrochromic material on top of the conductive electrode, an electrolyte compartment containing either a separator saturated with electrolyte or an electrolyte gel, and

25 another layer of persistent electrochromic material of the same general type as the first-mentioned layer which is applied over a counter electrode which in turn is carried on a second substrate.

30 Prior art devices, because they utilize concentrated sulphuric or other acids as electrolytes in liquid or gel form or impregnated in the separator show many drawbacks caused by the deterioration of the electrochromic layer by the electrolyte and also the migration of anions from the counter electrode to the display electrode. Prior art devices also encounter

35 sealing problems because of the utilization of relatively high amounts of concentrated acid as electrolyte.

40 It is the purpose of the present invention to provide an electrochromic display device where in the electrochromic material is significantly

less subject to degradation than in prior devices, improved sealing of the display sandwich is obtained, and which has improved ionic transfer between the electrode layers due to the mobility of hydrated hydrogen ions.

50 According to the invention there is provided an electrochromic display device comprising in layered form:

a first transparent substrate with a pattern of selectively actuatable transparent first electrodes thereon and a first electrochromic layer on said transparent first electrodes,

55 a second substrate with a second, counter-electrode, and

a solid electrolyte-separator layer between first and said second electrodes, said electrolyte-separator layer being composed of a chemically wetted cationic ion exchange resin in acid form.

60 Electrochromic display devices of the type described according to the present invention may, and preferably do, include a second electrochromic layer disposed on the second electrode and composed of substantially the same electrochromic material as said first electrochromic layer. By utilizing a cationic ion exchange resin as the electrolyte-separator layer, the function of the electrolyte can be accomplished without any or with very little free acid being present in the display device as is required in conventional display devices which

65 utilize electrolytes.

70 The electrolyte-separator layer of the present invention may be formed from pre-formed membranes by casting, or gently packing the powdered form of the cationic ion exchange resin in the space between the electrochromic layers. The cationic ion exchange resin provides the necessary conductivity for operation of the display, it is believed, by enhancing the mobility of hydrated hydrogens through the resin layer. Acid groups which are normally free when a liquid sulphuric acid is employed do not move, and it is therefore believed that the corrosive and degradative effects on the electrochromic material at the interface with

75 80 85 90

the electrolyte which are normally encountered are eliminated or at least vastly minimized with display devices according to the present invention.

5 Greater contrast of the display can be effected if opaque pigments are incorporated into the separator or if a pigment is held in place by the separator between the electrochromic layer and separator.

10 The above and other advantages of the invention will be further understood from the following description, taken in connection with the accompanying drawings in which:—

Figure 1 is an exploded perspective view of a preferred electrochromic display device embodying the present invention, and

Figure 2 is an enlarged cross-sectional view taken through an assembled display device according to Figure 1.

20 Referring now to Figure 1 of the drawings, the electrochromic display device is shown as a sandwich construction comprising a first transparent substrate 2 and a second spaced substrate 4, which need not be transparent, and a separator-electrolyte layer 28 between the substrates 2 and 4.

As indicated above, the present invention is concerned primarily with this separator-electrolyte layer and the improved displays resulting when the separator-electrolyte layer—which is described in detail below—is employed in existing electrochromic display devices of the type described.

30 Substrate 2 has a conductive pattern of transparent electrodes on the underside thereof. The electrodes forming the pattern such as electrodes 6 and 8 can be selectively actuated to form digits or other optical patterns via conductive leads 10 12 leading to terminals 14, 16.

Substrate 2 may be of transparent glass or plastics with the transparent electrodes thereon formed of a clear, conductive material such as tin oxide, applied using known methods.

45 The pattern for example may be etched on the substrate by using a commercially available material such as "NESA" glass (the word "NESA" is a registered Trade Mark) and then removing the conductive coating except where it is to form the electrodes.

50 The second substrate 4 has a conductive counter-electrode 18 thereon connected to a terminal 20. Substrate 4 may be of glass, ceramic or plastics coated with a suitable conductive layer to form counter-electrode 18.

55 Coated on the transparent electrodes 6, 8 and also on the counter-electrode 18 are layers of electrochromic material indicated as 22, 24, 26. The electrochromic layers 22, 24 on electrodes, 6, 8 are applied by suitable masking techniques to cover a smaller area than the electrodes so as to give good edge definition.

60 There are many suitable electrochromic materials which change their colour according to the particular oxide state. The materials

are well known to those skilled in the art and there is no need to list in detail the many materials which we can use. Merely by way of example, a large number of conventional materials used are referred to in United States Patent No. 3,521,941. We prefer to employ tungsten oxide as the electrochromic material. Tungsten oxide is preferably deposited on glass substrates by vacuum evaporation, but many other processes can be utilized to form the electrodes 6, 8 and the counter-electrode layer 18.

Referring to Figure 2 of the drawings, an assembled display device according to the present invention is shown in cross-section. The substrates 2 and 4 are bound to one another by an adhesive 30 such as epoxy resin which serves to hold the assembly together and to seal the inner layers around the periphery of the sandwich structure between the substrates 2 and 4.

80 Illustrated in the drawing are a conventional schematic circuit and conductors for actuating the display device by applying an electric charge from a battery 32 to, for example, a selected electrode via a terminal 14, 16 and to the counter-electrode 18 at terminal 20. The polarity of the applied voltage may be reversed to erase the image formed by the actuation of the two-pole double-throw switch 34.

90 The electrochromic material of layers 22, 24 and 26 may range in thickness from 0.1 to 100 microns; however a thickness of approximately 1 to 10 microns is preferred.

100 The separator 28 which serves as the solid electrolyte for the display device is usually on the order of 25 microns in thickness. The solid electrolyte utilized in this invention thus is a selectively permeable cationic ion exchange resin. It has a high degree of preferential transportability for cations as opposed to anions, and also for hydrogen ions as opposed to other cations. Optionally, a contrast enhancing opaque pigment, such as titanium dioxide, can be incorporated in the separator-electrolyte material. The separator 28 may comprise a sheet membrane or powdered cationic ion exchange resin particles with or without a suitable binder.

115 As indicated, the resin may be in the form of a solid membrane layer or powdered cation ion exchange resin in the hydrogen form. Preferred cationic ion exchange resins are familiar to those skilled in the art and particularly preferred are Rohm & Haas "Amberlite" IR-20 and CG-50 (the word "Amberlite" is a registered Trade Mark) and most especially preferred is duPont Nafion perfluorosulphonic acid resin because of its great inertness at processing temperatures. Other suitable resin membranes are Fisher Scientific's Rexsyn sulphonated polystyrene in hydrogenated form.

120 The cationic exchange resins in powder form can be used by themselves or with opaque 130

pigments and other additives and/or in admixture with various binders by simply filling the space between the two conductive electrochromic layers 22, 24 and 26 with the finely powdered cationic resin particles and enclosing the periphery of the display device sandwich with adhesive 30.

The utilization of a cationic ion exchange resin as the electrolyte in electrochromic display devices according to the present invention minimizes the need for the presence of significant amounts of sulphuric or other acids which previously were utilized as electrolytes. This minimizes the difficulties of sealing the display initially and of deterioration of the seal and degradation of the electrochromic material over a period of time. It especially prevents or greatly minimizes the migration of anions from the counter-electrode material through the electrolyte to the display electrode and thus the deterioration of the electrochromic material of the display.

In order to activate the electrolyte-separator layer, it should, before or after assembly, be chemically wetted with water or a dilute acid such as dilute sulphuric acid, for example by dipping it. For best results in the form of stability of the electrochromic layers, no liquid excess moisture should be present, i.e. the layers should only be chemically wet and no more. It is not necessary nor desirable that flowable liquid be present in the membrane or resin powder.

The Nafion membrane is especially preferred because it is very selectively permeable to positively charged ions and impermeable to negatively charged ions and extremely inert, being composed of a fluoro-carbon polymer chain, having attached thereto negatively charged and substantially immobile sulphonic acid groups. Nafion polymer combines extremely good ionic selectivity with low resistance to cationic flow and high physical strength.

Thus the electrolyte-separator 28 is composed of a membrane or powder of cationic ion exchange resin which is permeable to positively charged ions (cations) but substantially impermeable to negatively charged ions (anions).

In the case of the Nafion which is a preferred membrane for use in this invention, perfluorocarbon sulphonyl fluoride copolymer chains have negatively charged but substantially immobile sulphonic acid groups which are clustered with associated cations. Thus, the positive ions are clustered with the negatively charged sulphonic groups which are distributed in voids between polymer chains through which the cations pass. The Nafion cationic ion exchange resin membrane is formed by reaction of SO_3 and tetrafluoroethylene to form a cyclic sultone which is rearranged to a linear form and reacted with hexafluoropropylene epoxide to yield a sulphonyl fluoride vinyl ether which in turn is polymerized with tetrafluoroethylene

to give the perfluorocarbon sulphonyl fluoride copolymer, that is saponified with caustic and then treated with nitric acid to yield the acid (hydrogen form).

The cationic resin allows preferential migration of hydrated hydrogen ions and prevents electrophoretic diffusion of colloidal particles from the rear electrode to the front electrode.

It is not necessary to the functioning of the electrochromic display that the counter-electrode 18 be coated with electrochromic material as are the display electrodes, 6, 8. It is preferred, however, that the counter-electrode be coated with the same or substantially the same electrochromic material as is utilized on the display electrodes, so that any ions migrating between electrodes are of the same nature to further serve to eliminate contamination of the display electrode electrochromic material due to ion migration.

WHAT WE CLAIM IS:-

1. An electrochromic display device comprising in layered form:

a first transparent substrate with a pattern of selectively actuatable transparent first electrodes thereon and a first electrochromic layer on said transparent first electrodes,

a second substrate with a second, counter-electrode, and

a solid electrolyte-separator layer between said first and said second electrodes, said electrolyte-separator layer being composed of a chemically wetted cationic ion exchange resin in acid form.

2. A device as claimed in claim 1, wherein a second electrochromic layer is disposed on the second electrode and is composed of substantially the same electrochromic material as said first electrochromic layer.

3. A device as claimed in claim 1 or claim 2 wherein said electrolyte-separator layer is composed of a perfluorosulphonic acid polymer membrane.

4. A device as claimed in any one of claims 1 to 3 wherein said electrolyte-separator layer is wetted with water.

5. A device as claimed in any one of claims 1 to 3 wherein said electrolyte-separator layer is wetted with a dilute acid.

6. A device as claimed in claim 5, wherein said electrolyte-separator layer is wetted with dilute sulphuric acid.

7. A device as claimed in any one of claims 1 to 6, wherein said electrolyte-separator layer has incorporated therein an opaque pigment.

8. A device as claimed in claim 1 wherein said electrolyte-separator layer is composed of a finely powdered cationic ion exchange resin in the hydrogen ion form.

9. A device as claimed in claim 3 wherein said first or said first and said second electrochromic layers are tungsten oxide, and wherein said electrolyte-separator layer is wetted with dilute sulphuric acid.

pigments and other additives and/or in admixture with various binders by simply filling the space between the two conductive electrochromic layers 22, 24 and 26 with the finely powdered cationic resin particles and enclosing the periphery of the display device sandwich with adhesive 30.

The utilization of a cationic ion exchange resin as the electrolyte in electrochromic display devices according to the present invention minimizes the need for the presence of significant amounts of sulphuric or other acids which previously were utilized as electrolytes. This minimizes the difficulties of sealing the display initially and of deterioration of the seal and degradation of the electrochromic material over a period of time. It especially prevents or greatly minimizes the migration of anions from the counter-electrode material through the electrolyte to the display electrode and thus the deterioration of the electrochromic material of the display.

In order to activate the electrolyte-separator layer, it should, before or after assembly, be chemically wetted with water or a dilute acid such as dilute sulphuric acid, for example by dipping it. For best results in the form of stability of the electrochromic layers, no liquid excess moisture should be present, i.e. the layers should only be chemically wet and no more. It is not necessary nor desirable that flowable liquid be present in the membrane or resin powder.

The Nafion membrane is especially preferred because it is very selectively permeable to positively charged ions and impermeable to negatively charged ions and extremely inert, being composed of a fluoro-carbon polymer chain, having attached thereto negatively charged and substantially immobile sulphononic acid groups. Nafion polymer combines extremely good ionic selectivity with low resistance to cationic flow and high physical strength.

Thus the electrolyte-separator 28 is composed of a membrane or powder of cationic ion exchange resin which is permeable to positively charged ions (cations) but substantially impermeable to negatively charged ions (anions).

In the case of the Nafion which is a preferred membrane for use in this invention, perfluorocarbon sulphonyl fluoride copolymer chains have negatively charged but substantially immobile sulphononic acid groups which are clustered with associated cations. Thus, the positive ions are clustered with the negatively charged sulphononic groups which are distributed in voids between polymer chains through which the cations pass. The Nafion cationic ion exchange resin membrane is formed by reaction of SO_3 and tetrafluoroethylene to form a cyclic sultone which is rearranged to a linear form and reacted with hexafluoropropylene epoxide to yield a sulphonyl fluoride vinyl ether which in turn is polymerized with tetrafluoroethylene

to give the perfluorocarbon sulphonyl fluoride copolymer, that is saponified with caustic and then treated with nitric acid to yield the acid (hydrogen form).

The cationic resin allows preferential migration of hydrated hydrogen ions and prevents electrophoretic diffusion of colloidal particles from the rear electrode to the front electrode.

It is not necessary to the functioning of the electrochromic display that the counter-electrode 18 be coated with electrochromic material as are the display electrodes, 6, 8. It is preferred, however, that the counter-electrode be coated with the same or substantially the same electrochromic material as is utilized on the display electrodes, so that any ions migrating between electrodes are of the same nature to further serve to eliminate contamination of the display electrode electrochromic material due to ion migration.

WHAT WE CLAIM IS:—

1. An electrochromic display device comprising in layered form:
 - a first transparent substrate with a pattern of selectively actuatable transparent first electrodes thereon and a first electrochromic layer on said transparent first electrodes,
 - a second substrate with a second, counter-electrode, and
 - a solid electrolyte-separator layer between said first and said second electrodes, said electrolyte-separator layer being composed of a chemically wetted cationic ion exchange resin in acid form.
2. A device as claimed in claim 1, wherein a second electrochromic layer is disposed on the second electrode and is composed of substantially the same electrochromic material as said first electrochromic layer.
3. A device as claimed in claim 1 or claim 2 wherein said electrolyte-separator layer is composed of a perfluorosulphonic acid polymer membrane.
4. A device as claimed in any one of claims 1 to 3 wherein said electrolyte-separator layer is wetted with water.
5. A device as claimed in any one of claims 1 to 3 wherein said electrolyte-separator layer is wetted with a dilute acid.
6. A device as claimed in claim 5, wherein said electrolyte-separator layer is wetted with dilute sulphuric acid.
7. A device as claimed in any one of claims 1 to 6, wherein said electrolyte-separator layer has incorporated therein an opaque pigment.
8. A device as claimed in claim 1 wherein said electrolyte-separator layer is composed of a finely powdered cationic ion exchange resin in the hydrogen ion form.
9. A device as claimed in claim 3 wherein said first or said first and said second electrochromic layers are tungsten oxide, and wherein said electrolyte-separator layer is wetted with dilute sulphuric acid.



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10. A device as claimed in claim 9 wherein said separator layer holds an opaque pigment.
11. An electrochromic display device substantially as hereinbefore described with reference to the accompanying drawings.

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