

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 of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrochromic display devices, and more particularly to such display devices having an ion-conducting medium for ion transfer disposed between spaced layers of electrochromic material.

The term "electrochromic material" as used herein is defined in the literature, and is understood in the art to mean or to refer to a material responsive to the application of an electric field of a given polarity to change from a first stable persistent state in which it is essentially non-absorptive of electromagnetic radiation in a given wave length region, and hence is clear or substantially colourless, to a second stable persistent state in which it is absorptive of electromagnetic radiation in the given wave length region, and hence coloured. Once in said second stable state, it is responsive to the re-application of an electric field of the opposite polarity to return to the first stable state. As is well known in this art, the phenomenon is evidenced by a change in colour, for example, the change in colour from essentially clear to blue, and back to clear, obtained by electrically reducing thin films of tungsten (VI) oxides in a sulphuric acid electrolyte, as described in *Journal of the American Chemical Society* (Vol. 73, pp. 5427-5732, Nov. 1951) at p. 5429 in an article by Brimm *et al.*, entitled "Sodium Potassium Tungsten Bronzes".

Prior art display devices which incorporate a crystalline or solid state ion conducting medium exhibit switching speeds from clear

to coloured to clear states, which are too slow for many display applications, for example, timepiece displays. Moreover, prior art devices which utilize concentrated acids in liquid or semi-solid form, for example, sulphuric acid, also exhibit the same defects, and as well additional defects in that (1) the concentrated acid promotes the migration of anion from one layer of electrochromic material to another, and (2) the concentrated acid attacks, and ultimately destroys, conventional seals of the device.

It is suggested in our copending Patent Application No. 18504/76, Serial No. 1,533,639 to use a cationic ion exchange resin as an ion conductive material between two layers of solid electrochromic materials. However, proper operation of the display requires continual uniform contact between both layers of electrochromic material and the cationic ion exchange resin. The cationic ion exchange resins which are disclosed and claimed are in Application No. 18504/76, Serial No. 1,533,639, for example in the form of sheets or powders, and are all insoluble. The sheet form is thick, and ultimately exhibits discontinuities in contact between two solid layers of electrochromic material, as well as expanding significantly in volume when chemically wetted, causing physical separation of the substrates of the fabricated device, and consequent leakage of fluids contained therein. Resins fabricated in powder form are difficult to work with from a manufacturing standpoint, since the insoluble powder must first be dispersed in a binder before being placed between two layers of electrochromic material.

It is, therefore, an object of the present invention to provide a display device, incorporating spaced layers of solid electrochromic material, which is significantly less subject to degradation than prior devices, because no liquid electrolyte is employed, thereby obtaining improved sealing of the

display construction, and having improved ionic transfer between the electrochromic layers due to the mobility of hydrated hydrogen ions and having improved switching speeds due to the blocking of passage of anions through the ion transferring medium.

According to the present 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, a counter-electrode having a second electrochromic layer thereon, and an electrolyte-separator layer between said electrochromic layers, wherein the electrolyte-separator layer comprises a solid membrane composed of a soluble polymer cationic ion exchange resin in the acid form, chemically wetted.

The electrolyte-separator layer may be a membrane of the acid form of a soluble polystyrene sulphonic acid polymer, or a membrane of the acid form of a soluble perfluorosulphonic acid polymer. Preferably also one of the electrochromic layers of the display device, is an electro-reactive layer comprising a coating of electrochromic material containing hydrogen adsorbed or chemically reacted therein as disclosed and claimed in our copending Patent Application No. 37304/76, Serial No. 1,503,630. By utilizing the soluble cationic ion exchange resin as the electrolyte-separator layer, the function of the electrolyte can be accomplished without any free acid being present in the display as is required in present displays which utilize acid electrolytes.

The electrolyte-separator layer used in the present invention may be formed directly on one of the solid electrochromic material layers by casting or spraying. The soluble cationic ion exchange resin provides the necessary conductivity for operation of the display, it is believed, by enhancing the mobility of hydrated hydrogen ions through the resin layer. Acid groups, which are normally free when a liquid sulphuric acid is employed, do not move; it is therefore believed that the corrosive and degradative effects on the display's seal and switching speed, which are normally encountered, are eliminated or at least vastly minimized with displays according to the present invention.

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 one electrochromic layer and the separator.

Preferred soluble polystyrene sulphonic acid polymer cationic ion exchange resins are known to those skilled in the art, and particularly preferred are the family of soluble polystyrene sulphonates marketed by National Starch and Chemical Corporation

under the U.S. Registered trademark VERSA-TL, e.g. VERSA-TL 71, VERSA-TL 20 series, VERSA-TL 70 series, VERSA-TL 400 series, VERSA-TL 500 series and VERSA-TL 700 series.

The utilization of a soluble acid polymer cationic ion exchange resin, e.g. soluble polystyrene sulphonic acid polymer cationic ion exchange resin, as the electrolyte-separator in display devices according to the present invention eliminates the presence of a liquid or semi-solid acid electrolyte and thus the need for the presence of significant amounts of sulphuric or other strong acids, which previously were utilized as electrolytes. This minimizes the difficulties of sealing the display initially and of deterioration of the seal over a period of time. It especially prevents or greatly minimizes the passage of anions from the counter-electrode electrochromic material through the electrolyte-separator to the display electrode electrochromic material, thereby, dramatically improving the display's switching speed.

While the present invention eliminates the presence of electrolyte in liquid form, in order to activate the electrolyte-separator member, it must be "chemically wetted" with water or an aqueous solution of the soluble resin. It is not necessary nor desirable that flowable liquid be present in the membrane after chemically wetting it.

The soluble polystyrene sulphonic acid polymer membrane is especially preferred because it is very selectively permeable to positively charged ions and impermeable to negatively charged ions, and extremely inert, being comprised of a polymer chain, having attached thereto negatively charged and essentially immobile sulphonic acid groups. Such polymer combines extremely good ionic selectivity with low resistance to cationic flow, ease of application, and high physical strength.

Thus the electrolyte-separator of the present invention is comprised of a membrane of a soluble acid polymer cationic ion exchange resin, e.g. a soluble polystyrene sulphonic acid polymer cationic resin exchange resin, which is permeable to positively charged ions or cations, but essentially impermeable to negatively charged ions or anions.

This cationic ion exchange resin allows preferential migration of hydrated hydrogen ions and prevents electrochromic diffusion of colloidal particles from the electrochromic counter-electrode to the electrochromic display electrode.

The invention will be further understood from the following description of a preferred embodiment, taken in conjunction with the accompanying drawings in which:—

Figure 1 is an exploded perspective view of a typical 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.

5 Referring now to Figure 1 of the drawings, the 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
10 separator-electrolyte layer 28 between the elements 2 and 4.

As depicted in Figure 1, substrate 2 has a conductive pattern of transparent electrodes on the underside thereof. The electrodes
15 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 plastic with the transparent electrodes thereon formed of a clear, conductive material such as tin oxide, applied using known methods.

The pattern, for example, may be etched
25 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.
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The second section 4 has a conductive counter-electrode 18 thereon connected to a terminal 20. Section 4 may be of glass, ceramic or plastics, coated with a conductive
35 layer to form the counter-electrode 18.

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

There are many suitable solid electrochromic materials which change their colours according to the particular oxide state, for, example, tungsten (VI) oxide, disclosed by Brimm *et al. op.cit.* The materials are well known to those skilled in the art and there
50 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, which can be used, are identified in U.S. Patents 2,173,141; 2,281,013 and
55 2,319,765. We prefer to employ tungsten (VI) oxide as the electrochromic material for layers 22, 24. Tungsten (VI) oxide is preferably deposited on segments 6, 8 by vacuum evaporation, or other conventional processes.

60 The electrochromic counter-electrode layer 26 in the embodiment being described is, however, formed in accordance with the process described and claimed in our co-pending Application No. 37304/76, Serial
65 No. 1,503,630, and comprises tungsten oxide

heat treated in a hydrogen or forming gas atmosphere, or tungsten surface oxidised and then heat treated "in situ" in a hydrogen or forming gas atmosphere. The electrochromic material 26 formed thereby is brown in colour, is stable in air, and contains substantially more capacity to colour the front electrochromic layers 22, 24 than the blue counter-electrode disclosed in U.S. Patent 3,840,287, or than the partially electrically charged or partially "blued" counter-electrode disclosed in U.S. Patent No. 3,973,829.

Referring to Figure 2 of the drawings, an assembled display device according to the
80 present invention is shown in cross-section. The elements 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
85 the periphery of the sandwich structure between the elements 2 and 4.

Illustrated in the drawings are a conventional schematic circuit and conductors for actuating the display device for applying an electric charge from the 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
95 formed, by the actuation of the two-pole double-throw switch 34.

The electrochromic material of layers 22 and 24 may range in thickness from 0.1 to 100 microns, however, a thickness of approximately 1 to 10 microns or less is preferred. The preferred thickness of the electrochromic material layer 26 is about 25 microns. Suitably the thickness of the electrochromic layer 22, 24 and the electrochromic
105 layer 26 are in the ratio of at least 1:5.

The separator layer 28 which serves as the solid electrolyte for the display device is usually on the order of 25 to 75 microns in thickness.

The present invention is concerned primarily with this separator-electrolyte layer 28 and the improved displays resulting therefrom, especially in combination with the electrochromic counter-electrode layer disclosed in Application No. 37304/76, Serial No. 1,503,630, although when the separator-electrolyte layer — which is described below — is employed in existing display devices of the kind described the operation and life
120 of such other displays are improved.

The solid electrolyte-separator layer 28 utilized in this invention is a soluble, selectively permeable acid polymer cationic ion exchange resin made, for example, from a soluble polystyrene sulphonic acid polymer. It has a high degree of preferential transportability for cations as opposed to anions, and also for hydrogen ions as opposed to other cations. An opacifier or a contrast
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enhancing opaque pigment, such as titanium dioxide, can be incorporated in the separator-electrolyte material to conceal the counter-electrode 18 from the field of view of the optical patterns formed by segments 6, 8, the separator 28 preferably comprises a membrane formed directly on the electrochromic layers 22, 24 or 26 by spraying or casting.

- 10 Before or after assembly, the separator-electrolyte is chemically wetted with water, or a water solution of the soluble acid polymer cationic ion exchange resin incorporated in the separator e.g. a water solution of polystyrene sulphonate acid polymer. For best results in the form of stability of the electrochromic layers, no liquid excess moisture should be present, namely the cationic ion exchange resin layer should only be chemically wetted and no more.

WHAT WE CLAIM IS:-

1. An electrochromic display device comprising in layered form, a first transparent substrate with a pattern of selectively actuable transport first electrodes thereon and a first electrochromic layer on said transparent first electrode a counter-electrode having a second electrochromic layer thereon, and an electrolyte-separator layer between said electrochromic layers, wherein the electrolyte-separator layer comprises a solid member composed of a soluble polymer cationic ion exchange resin in the acid form, chemically wetted.

2. An electrochromic display device in accordance with Claim 1, wherein said resin is a soluble polystyrene sulphonate acid polymer cationic ion exchange resin.

3. An electrochromic display device in accordance with Claim 1, wherein said resin

is a soluble perfluorosulphonic acid polymer cationic ion exchange resin.

4. An electrochromic display device in accordance with Claim 2 or Claim 3, wherein said first electrochromic layer comprises tungsten (VI) oxide, and said second electrochromic layer comprises tungsten oxide heat treated in a hydrogen or forming gas atmosphere.

5. An electrochromic display device in accordance with Claim 2 or Claim 3, wherein said first electrochromic layer comprises tungsten (VI) oxide and said second electrochromic layer comprises tungsten surface oxidized and heat treated in a hydrogen or forming gas atmosphere.

6. An electrochromic display device in accordance with Claim 4 or Claim 5, wherein the thicknesses of said first electrochromic layer and said second electrochromic layer are in the ratio of at least 1:5.

7. An electrochromic display device in accordance with any one of the preceding claims, wherein said electrolyte-separator layer has an opacifying agent incorporated therein, and is chemically wetted with water.

8. An electrochromic display device in accordance with any one of Claims 2 to 6, wherein said electrolyte-separator layer has an opacifying agent incorporated therein, and is chemically wetted with an aqueous solution of said soluble polymer resin.

9. An electrochromic display device substantially as hereinbefore described with reference to the accompanying drawings.

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