

PATENT SPECIFICATION

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(54) IMPROVED ELECTROCHROMIC DISPLAY DEVICE

(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 particularly to an electrochromic display device having an improved electrolyte.

Various electrochromic materials which may exist in more than one oxide state which each exhibit different optical properties are known. Typical materials are set forth in United States Patent Nos. 2,319,765 and 3,521,941.

The use of electrochromic materials in various electro-optical displays is referred to in United States Patent Nos. 3,283,656 (use of a colouring material as the electrolyte) and 3,704,057 (use of a gelled electrolyte), 3,451,741 and 3,807,832.

Further patents of interest include United States Patent No. 3,827,784 which discloses an electrochromic device including an improved bonded graphite counter electrode which is deposited from a sample solution or suspension under ambient conditions, and 3,840,287 which describes an electrochromic cell having a colour promoting agent located between first and second layers of electrochromic material and provides an unbalanced arrangement wherein one of the electrochromic layers is initially in its coloured state so that current can readily flow through the coloured layer.

Our co-pending Application No. 37664/75 (Serial No. 1,494,955) relates to an electrochromic display wherein a liquid electrolyte is used for ion transfer between

spaced electrochromic layers.

An object of this invention is to provide an improved electrochromic display device of this general type and a method of making said display device.

Another object of this invention is to reduce the degradation of the electrochromic layers in an electrochromic display device by providing an improved electrolyte.

In the case where a particular oxide state of the electrochromic material is soluble in the electrolyte, there will be degradation of the electrochromic layers with time and temperature. The degree of solubility may differ with each oxidation state through which the electrochromic material passes. It would be desirable to provide an improved electrolyte which reduces the degradation of the more soluble oxidation states of the electrochromic layers and hence improves the life and visibility of the overall display.

A more specific object of this invention is thus to provide an improved electrochromic display device having an improved electrolyte which compensates for the solubility of the more soluble oxide states of electrochromic layers in the electrolyte thereby prolonging the life of the display.

United States Patent No. 3,819,252 discusses electrochromic devices wherein a conductive electrolyte is saturated with the same compounds as those used in the imaging layer, alleged to result in faster switching time. However, the additive compounds suggested do not correspond with those associated with the greatest degradation of the image layers.

According to the present invention there is provided an electrochromic display device comprising first and second parallel spaced substrates, selectively actuatable spaced electrodes on said first substrate and a counter-electrode on said second

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substrate, said spaced electrodes and said counter-electrode each having thereon a respective layer of electrochromic material capable of existing in different oxidation states, said states having different optical, electrical, and solubility properties, and an electrolyte between the first and second substrates, wherein the electrolyte is saturated at the expected operating temperature of the device with at least two of the more soluble states of said electrochromic material, so as to reduce the degradation of the electrochromic layers with time and temperature.

In one example the electrolyte is saturated by the addition of three different materials representing three different states in which the electrochromic material may exist during operation of the display device, i.e., tungsten dioxide, tungsten trioxide, and hydrogen tungsten oxide are all added to the electrolyte.

The invention further provides the method of making an electrochromic display device of the type comprising first and second parallel spaced substrates, selectively actuatable spaced electrodes on said first substrate and a counter-electrode on said second substrate, said spaced electrodes and said counter-electrode each having thereon a respective layer of electrochromic material capable of existing in different oxidation states, said states having different optical, electrical, and solubility properties, and an electrolyte between the first and second substrates, in which electrolyte at least two of said states are soluble, the method comprising: adding to the electrolyte an amount of at least two of the more soluble states of the same electrochromic material, which amount is sufficient to saturate the electrolyte at the expected operating temperature of the device, heating said electrolyte above the expected operating temperature of said display device to dissolve the excess of said material therein, permitting said electrolyte to cool down to an ambient temperature to produce a saturated electrolyte, and filling the space between said substrates with said saturated electrolyte during assembly of the display device, in order to reduce degradation of the electrochromic layers with time and temperature.

Preferably a porous separator is also employed in the display device to prevent migration of electrically conductive material.

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

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.

Referring now to Figure 1 of the drawings, the electrochromic display device is a sandwich construction of a first transparent substrate 1 and a second parallel spaced substrate 2, which need not be transparent, and a separator 15 therebetween. Substrate 1 has a conductive pattern of spaced transparent electrodes on the underside thereof. The electrodes such as 3, 4 of the pattern can be selectively actuated to form digits or other optical patterns via conductive leads 5, 6 leading to terminals 7, 8. Substrate 1 may be of transparent glass or plastics with a selected pattern of transparent electrodes 3, 4 thereon of a material such as tin oxide. The pattern may be etched on the substrate by using a commercially available material known as "NESA" glass (the word "NESA" is a registered Trade Mark) and removing the conductive coating except for the electrodes.

The second substrate 2 has a conductive counter-electrode 9 thereon connected to a terminal 10. Substrate 2 may be of glass, ceramic or plastics coated with a suitable conductive layer to form counter-electrode 9.

Coated on the transparent electrodes 3, 4 and also on the counter-electrode 9 are layers of electrochromic material indicated as 11, 12 and 13. The electrochromic layers 11 and 12 on electrodes 3 and 4 respectively are applied by suitable masking techniques to cover a smaller area than the electrodes so as to give a good edge definition.

The separator 15 may be a porous separator as disclosed in co-pending Application No. 37664/75 (Serial No. 1 494 955) of a material such as porous polypropylene. A pigment may be mixed in with the porous separator material to provide contrast for the electrochromic layers 11, 12 and to hide layer 13. One suitable pigment material is titanium oxide which is white in colour and provides the desired contrast with the upper layers 11, 12 of electrochromic material and also hides the counter-electrode layer beneath the pigmented separator 15. The separator 15 serves other important functions; that of a spacer to provide very close uniform spacing between substrates 1, 2 and secondly, that of a carrier for the liquid electrolyte, obviating the need for gelling substrates. In the present invention it also serves to isolate and prevent migration of any conductive particles which might come out of solution and cause electrical shorts between the front and back electrodes.

Many electrochromic materials exist which change colour according to the oxide state. These materials are well known in the art and to a great extent are disclosed in the prior patents cited above. The preferred electrochromic material used in the present invention for the electrode layers is an oxide of tungsten such as tungsten trioxide. The tungsten trioxide is deposited by vacuum evaporation or some other suitable process on the electrodes 3, 4 and the back electrode 9.

In the process of changing colour the electrochromic material passes through various intermediate valence states or oxide states where it can exist as non-stoichiometric compounds with intermediate valence states. In the present case, it passes in turn from tungsten trioxide, through various non-stoichiometric valence states of tungsten oxide (also known as hydrogen tungsten oxide) and may approach a state very close to tungsten dioxide and then back again. Each of these compounds has different optical, electrical, and solubility properties. For example, tungsten dioxide is the most soluble state; non-stoichiometric tungsten oxides are the most electrically conductive states; and tungsten trioxide is the most transparent but the least conductive and least soluble state, and so forth.

Reference to Figure 2 of the drawing shows the assembled display device. The two substrates 1 and 2 are partly attached to one another by an adhesive 16, such as epoxy resin, the display device is filled with electrolyte and then sealed with adhesive. The preferred electrolyte is dilute sulphuric acid saturated with materials in accordance with the process to be described, for example with tungsten dioxide and hydrogen tungsten oxide, or with tungsten dioxide, hydrogen tungsten oxide, and tungsten trioxide. Other suitable electrolytes are tungsto-silicic acid or phosphoric acid, or a mixture of dilute sulphuric acid and titanium dioxide.

Suitable well known means for actuating the display include means for applying an electric field from a battery 17 to a selected electrode 4 via a terminal 8 and the counter-electrode 9 via the terminal 10. Means for reversing the polarity of the applied voltage to erase the image is indicated symbolically by a two-pole double-throw switch 18.

In accordance with the present invention, the electrolyte is saturated at its expected operating temperature with electrochromic material in at least two of its more soluble oxide states, preferably the most soluble states, and in the preferred case, in several or all of its oxide states. This will prevent degradation with time and temperature of

the electrochromic material deposited on the electrodes as it passes through various states in operation at normal temperatures.

EXAMPLE

A typical method of preparing the saturated electrolyte is as follows:—

To one hundred milliliters of an electrolyte of dilute sulphuric acid is added 1 gram or more of tungsten dioxide, 1 gram or more of tungsten trioxide, and 1 gram or more of hydrogen tungsten oxide. The slurry thus formed is heated and stirred constantly for several hours at 70°C or more to dissolve the oxides therein and is then allowed to cool down to ambient temperature. The saturated electrolyte thus formed is used to fill the electrochromic display device.

The tungsten dioxide and tungsten trioxide powders are obtained from commercial sources. The hydrogen tungsten oxide is prepared by either passing hydrogen gas across tungsten oxide or by placing tungsten oxide in contact with a metal powder such as zinc in a dilute acid solution, and filtering and drying the hydrogen tungsten oxide thus formed.

The resultant display device is thus similar in construction to prior art display devices but includes a saturated electrolyte. The saturated electrolyte minimizes or substantially eliminates the solubility of all of the various oxidation states of the electrochromic material therein. This factor prolongs display life and improves display visibility and performance.

WHAT WE CLAIM IS:—

1. An electrochromic display device comprising first and second parallel spaced substrates, selectively actuatable spaced electrodes on said first substrate and a counter-electrode on said second substrate, said spaced electrodes and said counter-electrode each having thereon a respective layer of electrochromic material capable of existing in different oxidation states, said states having different optical, electrical, and solubility properties, and an electrolyte between the first and second substrates, wherein the electrolyte is saturated at the expected operating temperature of the device with at least two of the more soluble states of said electrochromic material, so as to reduce the degradation of the electrochromic layers with time and temperature.

2. The display device according to Claim 1, wherein said electrochromic layers are selected to undergo transition into states of at least tungsten trioxide and hydrogen tungsten oxide.

3. The display device according to Claim 2, wherein the electrolyte is saturated with tungsten dioxide and hydrogen tungsten oxide.

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Suitable well known means for actuating the display include means for applying an electric field from a battery 17 to a selected electrode 4 via a terminal 8 and the counter-electrode 9 via the terminal 10. Means for reversing the polarity of the applied voltage to erase the image is indicated symbolically by a two-pole double-throw switch 18.

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The tungsten dioxide and tungsten trioxide powders are obtained from commercial sources. The hydrogen tungsten oxide is prepared by either passing hydrogen gas across tungsten oxide or by placing tungsten oxide in contact with a metal powder such as zinc in a dilute acid solution, and filtering and drying the hydrogen tungsten oxide thus formed.

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2. The display device according to Claim 1, wherein said electrochromic layers are selected to undergo transition into states of at least tungsten trioxide and hydrogen tungsten oxide.

3. The display device according to Claim 2, wherein the electrolyte is saturated with tungsten dioxide and hydrogen tungsten oxide.



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4. The display device according to Claim 2, wherein the electrolyte is saturated with tungsten dioxide, hydrogen tungsten oxide, and tungsten trioxide.
5. The display device according to Claim 2 or Claim 4, wherein the electrolyte is a mixture of dilute sulphuric acid and titanium dioxide.
6. The display device according to any one of Claims 1 to 5, wherein the electrolyte is carried in a porous separator positioned between the substrates.
7. A method of making an electrochromic display device of the type comprising first and second parallel spaced substrates, selectively actuatable spaced electrodes on said first substrate and a counter-electrode on said second substrate, said spaced electrodes and said counter-electrode each having thereon a respective layer of electrochromic material capable of existing in different oxidation states, said states having different optical, electrical, and solubility properties, and an electrolyte between the first and second substrates, in which electrolyte at least two of said states are soluble, the method comprising: adding to the electrolyte an amount of at least two of the more soluble states of the same electrochromic material, which amount is sufficient to saturate the electrolyte at the expected operating temperature of the device, heating said electrolyte above the expected operating temperature of said display device to dissolve the excess of said material therein, permitting said electrolyte to cool down to an ambient temperature to produce a saturated electrolyte, and filling the space between said substrates with said saturated electrolyte during assembly of the display device, in order to reduce degradation of the electrochromic layers with time and temperature.
8. The method according to Claim 7, wherein one added state of electrochromic material comprises tungsten dioxide and wherein the electrolyte is heated to a temperature of 70°C.
9. The method according to Claim 7, wherein an amount of tungsten trioxide, hydrogen tungsten oxide, and tungsten dioxide is added to an electrolyte of dilute sulphuric acid and the electrolyte is heated to a temperature of 70°C.
10. An electrochromic display device substantially as hereinbefore described with reference to the accompanying drawings.
11. A method of making an electrochromic display device, substantially as hereinbefore described and in accordance with reference to the accompanying drawings.
11. A method of making an electrochromic display device, substantially as hereinbefore described and in accordance with the Example.

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Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patents No'd 1,414,036 and 1,356,120.

