

PATENT SPECIFICATION (11)

1 494 955

1 494 955

- (21) Application No. 37664/75 (22) Filed 12 Sept. 1975 (19)
 (31) Convention Application No. 540 481 (32) Filed 13 Jan. 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 14 Dec. 1977
 (51) INT. CL.³ G02F 1/17
 (52) Index at acceptance
 G2F 21C 23E 25A 25C 28M CE



(54) ELECTROCHROMIC DISPLAY

(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 generally to electro-optical displays of the type using electrochromic material which undergoes reversible colour changes upon the application of an electric field. More particularly, the invention relates to an improved sandwich construction for an electrochromic display.

It is known that some materials exhibit the property of existing in more than one oxide state wherein the material in one state exhibits different optical properties from the material in another state. Examples of such materials are disclosed in United States Patents No. 2,319,765 and 3,521,941. It is also known that a reversible electric field applied to electrochromic materials may be used selectively to produce visible images and to erase such images as described in United States Patents Nos. 1,068,774 and 3,521,941 supra.

Various systems have been used in an electrooptic display, such as liquid systems with a colouring material as the electrolyte — United States Patent No. 3,283,656; solid state systems with no electrolyte — United States Patent No. 3,560,078; or systems employing a gelled electrolyte — United States Patent No. 3,704,057.

In some cases it is preferred to employ a liquid electrolyte for an ion transfer between spaced electrochromic layers. This gives rise to problems of sealing the display against leakage and providing for changes in thermal expansion of the electrolyte which can require a flexible seal. However, if very close spacing is employed, which would also reduce temperature effects and allow lower operating voltage, there is a problem of hiding the counter-electrode so as to get good contrast between the electrochromic ma-

terial on the image segments and the background around the segments.

It has been suggested in United States Patent No. 3,807,832 that an electrochromic mirror, having no discrete display characters, can employ a metallic reflecting surface having pores to allow a liquid electrolyte to permeate the reflective layer. However, in an image display device, it is preferably desired to have a contrasting, but not necessarily reflective, background for the optical characters of electrochromic material, dependent on the optical characteristics of the electrochromic material.

Accordingly, one object of the present invention is to provide an improved electrochromic display of the type using liquid electrolyte which provides improved resistance to the effects of temperature change.

Another object of the invention is to provide an improved electrochromic image display with improved means for providing contrasting background for the images.

Still another object of the invention is an improved electrochromic display which allows closer spacing between spaced substrates using a liquid electrolyte between electrochromic layers.

According to the invention there is provided an electrochromic display comprising a first substrate having thereon selectively actuatable transparent electrodes, each electrode being coated with an electrochromic layer, a second substrate having thereon a counter-electrode coated with an electrochromic layer, a porous separator uniformly and closely spacing said first and second substrates, the pores of said separator being filled with liquid electrolyte, and pigmentation held by said separator and selected to provide contrast with said electrochromic layers on the selectively actuatable electrodes and disposed to hide said electrochromic layer on the counter-electrode.

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

Figure 1 is an exploded perspective view

55

60

65

70

75

80

85

90

95

100

of a preferred embodiment of electrochromic display according to the present invention, and

5 Figure 2 is an enlarged horizontal cross-section taken through an assembled display according to Figure 1.

Referring now to Figure 1 of the drawings, the electrochromic display is a sandwich construction of a first transparent substrate 1 and a second spaced substrate 2, which need not be transparent. Substrate 1 has a conductive pattern of transparent electrodes on the underside thereof such as segments 3, 4 of a pattern which 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 and removing the conductive coating except for electrodes 3, 4. (The word "NESA" is a registered Trade Mark).

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

Coated on the transparent electrode segments 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 segments 3 and 4 respectively are applied by suitable masking techniques to cover a smaller area than the electrodes so as to give good edge definition.

Many electrochromic materials which change colour according to the oxide state are well known in the art and are documented, for example, in the prior Patents referred to above. The preferred electrochromic material used in the present invention is tungsten oxide. Preferably the tungsten oxide is deposited by vacuum evaporation, although other processes such as sputtering, electrochemical deposition, spray or silk screening may be used.

In accordance with the present invention, a porous separator 15 is utilized between the substrates. Although separator 15 is shown in Figure 1 as a separate pre-cut element, it may optionally be applied as a layer, either to substrate 1 or to substrate 2, over the electrodes and electrochromic layers thereof, as desired, by dip coating, spraying, knife blading or other methods. Optionally, the separator 15 may be a separate pre-cut film or membrane which is dropped into place.

The porous separator should be very thin and uniform, of the order of 25 microns in thickness. The preferred material for sep-

arator 15 is porous polypropylene, although porous polytetrafluoroethylene, porous polyethylene, nitrocellulose and cellulose nitrate have also been used with success. The separator 15 preferably has pores of a size not exceeding 25 microns, more preferably in the range of 0.1 to 5 microns. Its porosity should be such that of the order of 50 per cent or less of its total volume is composed of solid material, although this is not a critical amount.

A commercially available material suitable for separator 15 is "Celgard" microporous polypropylene manufactured by Celanese Corp. (The word "CELGARD" is a registered Trade Mark). Another suitable material is Chemplast porous polytetrafluoroethylene, manufactured by Chemplast, Inc.

Contrast-enhancing pigmentation is associated with the very thin separator, preferably employing a suitable pigment as a filler for the separator. Premixed in with the porous separator material is a pigment selected to provide the best contrast for the electrochromic layers 11, 12 and for hiding layer 13. One such suitable pigment is titanium dioxide which is white in colour, provides good contrast with the upper layers 11, 12 of tungsten oxide electrochromic material and also hides the counter-electrode with electrochromic layer 13 beneath the pigmented separator.

An alternative approach for associating the pigment with the separator is to deposit a layer of contrast-enhancing pigment flakes or powder on either the electrochromic layers 11, 12 or on the layer 13. The layer of pigment can be deposited by spraying, painting, dip-coating and so forth. The separator, which may now be transparent, is pressed or positioned on top of the pigment layer holding the powder or flakes stationary in the presence of an electrolyte. For this purpose titanium dioxide powder may be used. However, an important consideration is that the particle size of the pigment must be larger than the hole size of the porous separator, otherwise the particles may migrate through the separator pores and impair effectiveness of the display. As an example, 5 micron particles of titanium dioxide would be associated with a separator having holes of the order of 1 micron.

Other suitable pigments include mica flakes coated with a layer of high refractive index thereby imparting to the porous separator optical interference colours. Such flakes are produced by the Mearl Corp., and are known as mearlin Luster pigments.

Figure 2 of the drawings shows the assembled display. The two substrates 1, 2 are attached to one another by an adhesive 16, such as epoxy resin, the display is filled with electrolyte and then sealed with adhesive around the remaining sides. The pre-

12

ferred electrolyte is dilute sulphuric acid or silicotungstic acid solution saturated with tungstic acid.

5 Suitable well known means for actuating the display elements include means for applying an electric field from a battery 17 to a selected segment 4 via a terminal 8 and the counter-electrode via a terminal 10. Means for reversing the polarity of the applied voltage to erase the image is indicated symbolically in Figure 1 by a two-pole double-throw switch 18.

15 The porous separator 15 has several significant functions. First, it serves as a spacer to provide very close uniform spacing between substrates 1, 2 and hence the electrochromic layers. Secondly, it serves as a carrier for the liquid electrolyte, obviating the need of gelling substances. Thirdly, the separator structure serves to carry or to hold in place the pigmentation so as to provide a contrast-enhancing background for the electrochromic layers 11, 12 on the upper image segments, while also hiding the electrochromic layer 13 on the counter-electrode.

25 Since the electrochromic layers are closely and uniformly spaced, significantly lower operating voltages may be used. The thermal expansion of the very thin film of liquid electrolyte is minimized, eliminating the previously required flexible seal.

WHAT WE CLAIM IS:—

35 1. An electrochromic display comprising a first substrate having thereon selectively actuatable transparent electrodes, each electrode being coated with an electrochromic layer, a second substrate having thereon a counter-electrode coated with an electrochromic layer, a porous separator uniformly and closely spacing said first and second substrates, the pores of said separator being filled with liquid electrolyte, and pigmentation held by said separator and selected to provide contrast with said electrochromic layers on the selectively actuatable electrodes and disposed to hide said electrochromic layer on the counter-electrode.

2. A display according to Claim 1, wherein said separator is a layer having a thickness of the order of 25 microns and applied to the first substrate.

3. A display according to Claim 1, wherein said porous separator is a layer having a thickness of the order of 25 microns and applied to said second substrate.

4. A display according to Claim 1, wherein said porous separator is a pre-cut membrane having a thickness of the order of 25 microns.

5. A display according to any one of Claims 1 to 4, wherein said porous separator comprises porous polypropylene.

6. A display according to any one of Claims 1 to 5, wherein said electrolyte comprises dilute sulphuric acid.

7. A display according to any one of Claims 1 to 6, wherein said pigmentation is premixed in said separator.

8. A display according to any one of Claims 1 to 6, wherein said pigmentation is a layer of powder on the electrochromic layers on the selectively actuatable electrodes or on the electrochromic layer on the counter-electrode and held in place by said separator, the separator having pores smaller than the particle size of said powder.

9. A display according to any one of Claims 1 to 8, wherein said pores are of a size in the range between 0.1 and 25 microns.

10. A display according to Claim 9, wherein said pores are of a size in the range of 0.1 to 5 microns.

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

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5, Quality Court,
Chancery Lane,
London, WC2A 1HZ.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No. 1,356,120.

ferred electrolyte is dilute sulphuric acid or silicotungstic acid solution saturated with tungstic acid.

Suitable well known means for actuating the display elements include means for applying an electric field from a battery 17 to a selected segment 4 via a terminal 8 and the counter-electrode via a terminal 10. Means for reversing the polarity of the applied voltage to erase the image is indicated symbolically in Figure 1 by a two-pole double-throw switch 18.

The porous separator 15 has several significant functions. First, it serves as a spacer to provide very close uniform spacing between substrates 1, 2 and hence the electrochromic layers. Secondly, it serves as a carrier for the liquid electrolyte, obviating the need of gelling substances. Thirdly, the separator structure serves to carry or to hold in place the pigmentation so as to provide a contrast-enhancing background for the electrochromic layers 11, 12 on the upper image segments, while also hiding the electrochromic layer 13 on the counter-electrode.

Since the electrochromic layers are closely and uniformly spaced, significantly lower operating voltages may be used. The thermal expansion of the very thin film of liquid electrolyte is minimized, eliminating the previously required flexible seal.

WHAT WE CLAIM IS:—

1. An electrochromic display comprising a first substrate having thereon selectively actuatable transparent electrodes, each electrode being coated with an electrochromic layer, a second substrate having thereon a counter-electrode coated with an electrochromic layer, a porous separator uniformly and closely spacing said first and second substrates, the pores of said separator being filled with liquid electrolyte, and pigmentation held by said separator and selected to provide contrast with said electrochromic layers on the selectively actuatable electrodes and disposed to hide said electrochromic layer on the counter-electrode.

2. A display according to Claim 1, wherein said separator is a layer having a thickness of the order of 25 microns and applied to the first substrate.

3. A display according to Claim 1, wherein said porous separator is a layer having a thickness of the order of 25 microns and applied to said second substrate.

4. A display according to Claim 1, wherein said porous separator is a pre-cut membrane having a thickness of the order of 25 microns.

5. A display according to any one of Claims 1 to 4, wherein said porous separator comprises porous polypropylene.

6. A display according to any one of Claims 1 to 5, wherein said electrolyte comprises dilute sulphuric acid.

7. A display according to any one of Claims 1 to 6, wherein said pigmentation is premixed in said separator.

8. A display according to any one of Claims 1 to 6, wherein said pigmentation is a layer of powder on the electrochromic layers on the selectively actuatable electrodes or on the electrochromic layer on the counter-electrode and held in place by said separator, the separator having pores smaller than the particle size of said powder.

9. A display according to any one of Claims 1 to 8, wherein said pores are of a size in the range between 0.1 and 25 microns.

10. A display according to Claim 9, wherein said pores are of a size in the range of 0.1 to 5 microns.

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

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5, Quality Court,
Chancery Lane,
London, WC2A 1HZ.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No. 1,356,120.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1977.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

