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PATENT SPECIFICATION

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(54) ELECTROCHROMIC DISPLAY ELEMENT AND PROCESS

(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 electrochromic display which includes an improved rear electrode with a specific electro-reactive layer and to a process for making such an improved electrochromic display.

United States Patent No. 3,840,287 describes a typical electrochromic cell having a symmetrical type structure. The cell has a colour promoting agent such as a palladium layer having hydrogen associated therewith located between a first and second layer of electrochromic material and respective electrode layers which are on the outside of said electrochromic layers. The cell arrangement disclosed can be represented as follows: $\text{SnO}_2/\text{WO}_3/\text{Color Assisting Agent}/\text{WO}_3/\text{SnO}_2$; wherein SnO_2 represents a conductive tin oxide layer and WO_3 represents an electrochromatic tungsten oxide layer. The feature of the cell is the unbalanced arrangement wherein one of the electrochromic layers is initially in its coloured state so that current can readily flow through this layer. Thus, one of the electrochromic layers is coloured after the cell is completed by exposure to ultra-violet radiation or another suitable process.

United States Patent No. 3,827,784 discloses an electrooptical data display formed by a sandwich arrangement of an imaging area and a counter electrode area with a suitable ion conducting layer therebetween. The counter electrode comprises a bonded graphite tungsten oxide

mixture which improves the electrochromic reversibility, speed, and cell life under prolonged colouration and erase cycles.

A serious problem in existing electrochromic displays is the difficulty in achieving a hermetic seal to prevent air from leaking into the display. In the prior art one of the electrochromic layers serves as a source of hydrogen ions which travel from the rear to the front electrode by ionic conduction through the electrolyte to provide colour in the front layers of electrochromic material. If the seal leaks and air enters the cell, the hydrogen will combine with oxygen in the air and become depleted. It is necessary to provide sufficient hydrogen to provide the colour changes for display purposes and to respond to an applied voltage. Attempts have been made to solve this problem by generating hydrogen during cell usage but such an arrangement requires a rather high voltage. Another solution has been to import molybdenum into the tungsten oxide to make it photosensitive and then expose the material to light to produce a blue hydrogen-rich layer. This arrangement, however, generally requires three separate voltages, one to turn on the display, a second to turn off the display and a third to maintain it off.

Accordingly, an object of this invention is to provide an improved electrochromic display having a treated electroreactive layer which improves the operating and life characteristics of the display.

Another object of this invention is to provide an improved electroreactive layer for an electrochromic display which can also serve as rear electrode.

Another object of this invention is to provide a process for producing an improved electroreactive electrode for an electrochromic display.

The present invention provides an electrochromic display comprising first and second parallel spaced substrates, said first substrate having a plurality of transparent front electrodes with a layer of electro-

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chromic material thereon which assumes colouration when supplied with hydrogen, said second substrate having means providing a rear electrode, an electrolyte hermetically sealed between the first and second substrates, and an electroreactive layer associated with said rear electrode means, said layer comprising a coating of electrochromic material containing hydrogen in said coating.

The present invention also provides a process of making an electrochromic display which comprises the steps of: providing a first substrate having transparent front electrodes and an electrochromic layer thereon, providing a second substrate having a rear electrode, providing an electroreactive layer for the rear electrode by:

a) heating an electrochromic material to a temperature ranging from 250° to 1,000°C.

b) passing hydrogen or forming gas as herein defined over the surface of the electrochromic material to impart hydrogen into the material, filling the space between the substrates with an electrolyte, and sealing the first and second substrates together with an adhesive.

A 'forming-gas' is defined as a mixture of free hydrogen and an inert diluent gas, typically nitrogen, whereby the mixture minimizes the hazards present when one uses pure hydrogen.

A preferred embodiment of the invention comprises an electrochromic display including a first substrate with transparent front electrodes and electrochromic layers thereon, an intermediate electrolyte and a second substrate with a rear electroreactive coated electrode. The rear electrode layer is first surface oxidized and then heat treated in a hydrogen or forming gas atmosphere to impart an excess of hydrogen to the layer. The layer is treated in the aforementioned hydrogen atmosphere until an electrically conductive oxide coating is formed on the surface, termed herein an electroreactive layer. The layer prolongs cell life and improves the operating characteristics of the display by providing an electrocatalytic hydrogen-donating layer to serve as a "getter" for any oxygen entering the cell.

An advantage of this invention is that the display operates at a lower voltage than prior art displays since it is not necessary to generate hydrogen from the electrolyte. Having a lower operating voltage also prolongs cell life since operating at higher voltages over a prolonged period tends to destroy the display.

The rear electroreactive layer may be oxidized and heat treated "in situ" to provide a display having a lower operating voltage and increased display life. Alternatively a conventional rear electrode

coated with electrochromic material may be integrated into a single layer construction.

The above and other features and 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 preferred embodiment of electrochromic display according to the invention, and

Figure 2 is an enlarged partial cross-section of an assembled display according to Figure 1.

Referring now to the drawings, the electrochromic display 10 is a sandwich type construction wherein the display elements are contained between an outer transparent glass or plastics substrate 11 and an inner substrate 12 which need not be transparent. Substrate 11 has a conductive pattern of transparent electrodes 13 on the underside thereof, the pattern providing segments 14 and 15 which can be selectively actuated via conductive leads 16 and 17 which lead to terminals 18 and 19 to form digits or other optical patterns. The electrodes 13 may be a tin oxide coating which is etched onto the substrate 11 in a pattern 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 electrode segments.

The display may also include a pigmented porous membrane 20 carrying an electrolyte 21 mounted between the substrates 11 and 12 to prevent viewing through to the rear of the display 10, or alternatively the electrolyte 21 between the substrates 11 and 12 may be pigmented and the membrane 20 omitted entirely. The rear substrate 12 may be a glass or ceramic material and has a rear common electrode layer 22 coated thereon leading to terminal 28.

A layer of electrochromic material, indicated as 23 is coated by a process such as vacuum deposition on the front electrode segments 14 and 15. The rear electrode 22 is also coated with suitable material and then surface oxidized and heat treated under exposure to hydrogen gas to form a conductive electroreactive coating 24 on the electrode surface. The preferred material used in the present invention is tungsten oxide.

More specifically, in accordance with one form of the present invention, the rear coating layer 24 may be a tungsten oxide or a tungsten oxide-tungstate mixture which has been oxidized and then heat treated under hydrogen or forming gas prior to deposition on the rear electrode 22. The tungsten oxide or tungsten oxide-tungstate mixture may be in the form of a powder which can be

deposited by standard means such as painting, spraying or dip coating onto the rear electrode 22 of the electrochromic display. The mixture can be deposited by itself or with a binder such as cellulose. The rear electrode 22 may be a separate layer of conductive metal or metallized ceramic material. In another form of the invention, the electroreactive layer 24 may be formed "in situ" on the rear electrode 22 and may even become one single layer of electroreactive material serving the functions of the rear electrode, i.e., to act as an electrically conductive member facilitating current flow into the electrolyte. In this form, a tungsten metal film, comparable to layer 22, is applied as a metallized layer on a ceramic base, comparable to substrate 12. The tungsten then is oxidized into a non-conductive tungsten trioxide layer and subsequently reduced to a brown conductive tungsten oxide layer (tungsten bronze) by passing hydrogen or forming gas over the surface.

The following examples further illustrate the invention.

Example No. 1

On the glass substrate, a conductive film of gold was coated with a mixture of tungsten trioxide and sodium tungstate by spraying. The coated substrate was placed in a tube furnace and heated at a temperature between 250° and 1,000°C while forming gas was passed through the furnace until the surface coating was converted into a brown conductive film.

Example No. 2.

A ceramic base was metallized with a layer of tungsten, and "in situ" oxidation of the tungsten layer was followed by treating the surface oxidized tungsten layer in a hydrogen atmosphere. The metallized base was placed in a tube furnace, heated to a temperature between 250°—1,000°C, and sufficient air bled in to oxidize the surface. (The surface may also be oxidized by bubbling water into the furnace). Hydrogen was then passed over the surface until a brown conductive oxide layer formed on the surface.

In both of the above Examples the exposure of the surface coating to the hydrogen or forming gas was continued until the surface-oxidized coating had taken up as much hydrogen as is necessary to form the desired electrically conductive oxide coating. The exact nature of the mechanism involved is uncertain, whether the hydrogen is chemically reacted or absorbed or both, but the results obtained show that the treatment is able to convert the coating into a material able to impart colouration to the electrochromic material on the front

electrode namely there is a surplus of a thermally stable material which serves as a source of hydrogen for the display.

Assembly of the Display

The rear unit or plate 25 comprising substrate or base 12, electrode 22 and the electroreactive layer 24 treated or prepared as above is then attached to a second plate 26 including conductive glass 11 onto which the desired display pattern has been etched and onto which a tungsten oxide layer 23 has been deposited. A space left between the plates 25 and 26 is filled with a conventional electrolyte. The plates are then hermetically sealed together by adhesive 27. If desired, a pigment can be dispersed in the electrolyte 21 or can be deposited on either of the display elements to improve contrast. Another alternative, as mentioned previously, is to use a pigmented porous membrane 20.

The treatment process imparts a surplus amount of absorbed or chemically reacted hydrogen to the layer 24 which converts the layer into an electroreactive material. The electroreactive layer therefore serves as a source of hydrogen ions for colouration in relatively large amounts, so that even if air leaks into the cell and removes some hydrogen, there will still remain sufficient hydrogen for the cell to function over an extended period of time. In fact, the layer 24 may have so much surplus hydrogen that the material in the rear of the layer does not change colour, even when the front portion does.

As a further advantage, the tungsten oxide-hydrogen layer 24 is very electrically conductive. Therefore it serves the function of the rear electrode 22 depicted in the drawings, which may be omitted in certain designs. Also, the display operates at a lower voltage since it is not necessary to generate hydrogen from the electrolyte. A typical operating voltage would be in the order of 0.4 volts. This lower voltage also increases cell life since operating at higher voltages tends to destroy the NESA electrodes 13 over a period of time.

WHAT WE CLAIM IS:—

1. An electrochromic display comprising first and second parallel spaced substrates, said first substrate having a plurality of transparent front electrodes with a layer of electrochromic material thereon which assumes colouration when supplied with hydrogen, said second substrate having means providing a rear electrode, an electrolyte hermetically sealed between the first and second substrates, and an electroreactive layer associated with said rear electrode means, said layer comprising a coating of electrochromic material con-



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deposited by standard means such as painting, spraying or dip coating onto the rear electrode 22 of the electrochromic display. The mixture can be deposited by itself or with a binder such as cellulose. The rear electrode 22 may be a separate layer of conductive metal or metallized ceramic material. In another form of the invention, the electroreactive layer 24 may be formed "in situ" on the rear electrode 22 and may even become one single layer of electro-reactive material serving the functions of the rear electrode, i.e., to act as an electrically conductive member facilitating current flow into the electrolyte. In this form, a tungsten metal film, comparable to layer 22, is applied as a metallized layer on a ceramic base, comparable to substrate 12. The tungsten then is oxidized into a non-conductive tungsten trioxide layer and subsequently reduced to a brown conductive tungsten oxide layer (tungsten bronze) by passing hydrogen or forming gas over the surface.

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electrode namely there is a surplus of a thermally stable material which serves as a source of hydrogen for the display.

Assembly of the Display

The rear unit or plate 25 comprising substrate or base 12, electrode 22 and the electroreactive layer 24 treated or prepared as above is then attached to a second plate 26 including conductive glass 11 onto which the desired display pattern has been etched and onto which a tungsten oxide layer 23 has been deposited. A space left between the plates 25 and 26 is filled with a conventional electrolyte. The plates are then hermetically sealed together by adhesive 27. If desired, a pigment can be dispersed in the electrolyte 21 or can be deposited on either of the display elements to improve contrast. Another alternative, as mentioned previously, is to use a pigmented porous membrane 20.

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WHAT WE CLAIM IS:—

1. An electrochromic display comprising first and second parallel spaced substrates, said first substrate having a plurality of transparent front electrodes with a layer of electrochromic material thereon which assumes colouration when supplied with hydrogen, said second substrate having means providing a rear electrode, an electrolyte hermetically sealed between the first and second substrates, and an electro-reactive layer associated with said rear electrode means, said layer comprising a coating of electrochromic material con-

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- taining hydrogen absorbed or chemically reacted in said coating.
2. A display according to Claim 1, wherein the hydrogen is present in said coating in an amount substantially in excess of the amount needed to impart colouration to the electrochromic material on the front electrodes.
3. A display according to Claim 1 or Claim 2, wherein the electroreactive layer comprises a tungsten oxide-tungstate mixture heated in the presence of hydrogen and applied to said rear electrode means.
4. A display according to Claim 1 or Claim 2, wherein the rear electrode means comprises a tungsten layer and said electroreactive layer comprises conductive tungsten oxide formed by "in situ" surface oxidation of said rear electrode means.
5. A display according to Claim 4, wherein the rear electrode means and the electroreactive layer are provided by a single layer of conductive tungsten oxide.
6. A process of making an electrochromic display which comprises the steps of providing a first substrate having transparent front electrodes and an electrochromic layer thereon, providing a second substrate having a rear electrode, providing an electroreactive layer for the rear electrode by,
- (a) heating an electrochromic material to a temperature ranging from 250° to 1,000°C,
- (b) passing hydrogen or a forming gas as herein defined over the surface of the electrochromic material to impart hydrogen into the material, filling the space between the substrates with an electrolyte, and sealing the first and second substrates together with an adhesive.
7. A process according to Claim 6, wherein the rear electrode is a layer of metallized tungsten and is first surface oxidized and then subjected to hydrogen or forming gas "in situ" in a furnace to provide said electroreactive layer.
8. An electrochromic display substantially as hereinbefore described with reference to the accompanying drawings.
9. A process according to Claim 6 of making an electrochromic display and substantially as hereinbefore described.
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