

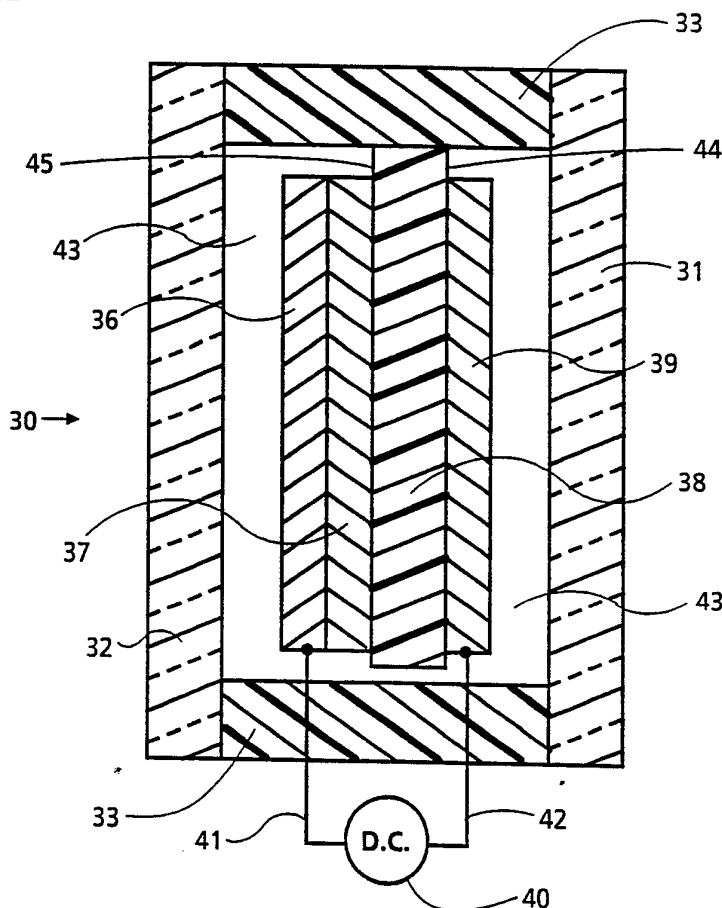


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(21) International Application Number: PCT/US91/01506 (22) International Filing Date: 5 March 1991 (05.03.91) (30) Priority data: 488,907 6 March 1990 (06.03.90) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: SHABRANG, Mani ; 1515 Dilloway, Midland, MI 48640 (US). (74) Agent: JUHL, Nis, H.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), SU. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: SEALED ELECTROCHROMIC DEVICE**(57) Abstract**

An electrochromic device (30) including an electronic conductor (36) such as gold, an electrochromic material (37) such as tungsten oxide, an ion conducting layer (38) such as a sulfonated polymer, and a counter electrode (39) such as gold, characterized by the feature that the electronic conductor (36), the ion conducting layer (38), the electrochromic material (37) and the counter electrode (39) are positioned in a space (43) consisting essentially of a mixture of an inert gas such as nitrogen and the vapor of a high dielectric constant material such as water.



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SEALED ELECTROCHROMIC DEVICE

Modern electrochromic devices generally comprise a number of layers such as is shown in Figure 1 of United States Patent 4,193,670. One example of such a device is: a backing of a pane of glass first coated with an electronic conductor such as a thin transparent layer of indium/tin oxide to form what some call a front electrode or a working electrode; then the working electrode is coated with a thin transparent layer of tungsten oxide to form an electrochromic layer; then the electrochromic layer is coated with a thin transparent layer of an ion conducting polymer (see United States Patent 4,231,641) such as NAFION perfluorosulfonate polymer (from E. I. du Pont de Nemours and Company, Wilmington DE) to form an ion conducting layer; and finally the ion conducting layer is coated with a thin transparent coating of gold to form a counter electrode. The completed device usually has the appearance of lightly tinted transparent glass. The device can be made to transmit substantially less light by applying an electrical potential between the working electrode and the counter electrode. This effect can be reversed by reversing the electrical potential to take the device through one cycle of operation. The theory of operation of such a device is: (1) that hydrogen ions and

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electrons are forced from the ion conducting layer into the electrochromic layer by the electrical potential and form a highly colored hydrogen/tungsten oxide bronze in the electrochromic layer; and (2) when the electrical potential is reversed, the hydrogen ions of the
5 hydrogen/tungsten oxide bronze in the electrochromic layer and electrons are forced out of the electrochromic layer into the ion conducting layer converting the highly colored hydrogen/tungsten oxide bronze back into
10 the essentially colorless tungsten oxide.

Several problems remain with such electrochromic devices. One problem is a deterioration of the device after it has been cycled several hundred
15 times. United States Patent 4,193,670 addressed this problem by placing a transparent electrically insulating but ionically conducting inorganic compound, such as a thin layer of silicon oxide, between the ion conducting layer and the electrochromic layer and between the
20 working electrode layer and the electrochromic layer. The devices of United States Patent 4,193,670 have a reported life of 5,000 to 7,000 cycles or 5 to 6 years of estimated service at 3 cycles per day. This level of
25 performance is short of the desired minimum of 11,000 cycles that would provide a 10 year estimated service at 3 cycles per day.

One important benefit of the present invention is increased cycle life. The invention is an
30 electrochromic device including a plurality of layers on one side of a backing, the layers including an electronically conducting layer, an electrochromic layer, an ion conducting layer and a counter electrode layer, characterized by the additional following features: (a) a panel, the panel juxtaposed

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substantially biplanar and spaced away from the one side of the backing and the layers thereon leaving a space volume between the panel and the layers; (b) means for sealing the panel with the backing so that at least a portion of the space volume is sealed between the panel and the backing to form a sealed space volume; and (c) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the sealed space volume.

10 The invention is also a sealed double pane window including a first pane of glass peripherally sealed with a second juxtaposed spaced apart substantially biplanar pane of glass so that a space volume is sealed between the first pane of glass and the second pane of glass, the first pane of glass having a first side and a second side, the second side being exposed to the sealed space volume, characterized by the additional following features: (a) a multi-layer electrochromic system coated on the second side of the first pane of glass, the electrochromic system comprising an electronically conducting layer, an electrochromic layer, an ion conducting layer and a counter electrode layer; and (b) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the sealed space volume.

30 The invention is also a sealed double pane window including a first pane of glass peripherally sealed with a juxtaposed spaced apart second substantially biplanar pane of glass so that a given space volume is sealed between the first pane of glass and the second pane of glass, characterized by the following additional features: (a) a multi-layer electrochromic system of a given solid volume, the

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electrochromic system positioned in the sealed space volume, the volume of the electrochromic system being less than the sealed space volume so that there is a remaining sealed space volume, the electrochromic system comprising an electronically conducting layer, an
5 electrochromic layer, an ion conducting layer and a counter electrode layer; and (b) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the remaining sealed space volume.

10 Thus, in a general sense the invention is an electrochromic device including an electronic conductor, an electrochromic material, an ion conducting layer, and a counter electrode, characterized by the following
15 additional feature: positioning the electronic conductor, the ion conducting layer, the electrochromic material and the counter electrode in a space consisting substantially of a mixture of an inert gas and the vapor of a high dielectric constant material.

20 Figure 1 is a cross-sectional side view of a double pane window embodiment of the present invention showing a multiple layer electrochromic device formed on one of the interior surfaces of the window; and

25 Figure 2 is a crosssectional view of a double pane window embodiment of the present invention showing an electrochromic device within the sealed space of the window.

30 Referring now to Figure 1, therein is shown a sealed electrochromic double pane window 10. The window 10 includes a backing of a first pane of glass 11 and a panel of a second substantially biplanar spaced apart pane of glass 12. The periphery of the pane of glass 11

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is sealed with the periphery of the pane of glass 12 by a seal means 13 of epoxy cement. The first pane of glass 11 has a first side 15 and a second side 14. The first side 15 is coated with a thin transparent electronically conductive layer of tin dipped indium oxide 16. Glass coated with tin dipped indium oxide (indium/tin oxide or ITO) is commercially available, e.g., from the Donnelly Corp., Holland MI, as ITO glass PD5002. An electrochromic layer 17 of tungsten oxide (WO₃) is deposited on the electrically conducting layer 16, see for example United States Patents 4,193,670, 3,971,624, 4,231,641 and 4,338,000. An ion conducting layer 18 of a copolymer of tetrafluoroethylene and 1,1,2,2-tetrafluoro-2-((trifluoroethenyl)oxy)ethane sulfonic acid having an equivalent weight of 780 is formed on the electrochromic layer 17 by a dipping process to be described below. It should be understood that this dipping process is not critical in the present invention and that the ion conducting layer can be formed as desired. A counter electrode layer 19 of gold is deposited on the ion conducting layer 18, see for example United States Patents 4,338,000 and 3,971,624 for a procedure for depositing gold layers. A direct current power supply 20 is connected to the electrically conducting layer 16 and the counter electrode layer 19 via a wire 21 and a wire 22. The pane of glass 11, the pane of glass 12 and the seal means 13 define a sealed space volume 23. The sealed space volume 23 is filled with a mixture of an inert gas and the vapor of a high dielectric constant material. It should be understood that the space volume 23 can be small in the present invention, such as when the pane of glass 12 is positioned immediately adjacent the layer 19.

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Referring now to Figure 2, therein is shown another sealed electrochromic double pane window embodiment 30 of the present invention. The window 30 includes a first pane of glass 31 and a second substantially biplanar spaced apart juxtaposed pane of glass 32. The periphery of the pane of glass 31 is sealed with the periphery of the pane of glass 32 by a seal means 33 of epoxy cement. The pane of glass 31, the pane of glass 32 and the seal means 33 define a sealed space volume. An ion conducting layer 38 of a copolymer of tetrafluoroethylene and 1,1,2,2-tetrafluoro-2-((trifluoroethenyl)oxy)ethane sulfonic acid having an equivalent weight of 780 is eventually suspended in the sealed space volume. The ion conducting layer 38 has a first side 44 and a second side 45. An electrochromic layer 37 of tungsten oxide (WO_3) is deposited on the ion conducting layer 38, see for example United States Patents 4,193,670, 3,971,624, 4,231,641 and 4,338,000. The electrochromic layer 37 is coated with a thin transparent electronically conductive layer of gold 36, see for example United States Patents 4,338,000 and 3,971,624 for a procedure for depositing gold layers. A counter electrode layer 39 of gold is deposited on the first side 44 of the ion conducting layer 38, see for example United States Patents 4,338,000 and 3,971,624 for a procedure for depositing gold layers. A direct current power supply 40 is connected to the electronically conducting layer 36 and the counter electrode layer 39 via a wire 41 and a wire 42. The layers 36, 37, 38, and 39 define an electrochromic system having a given solid volume that is less than the sealed space volume so that there is a remaining sealed space volume 43. The remaining sealed space volume 43

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is filled with a mixture of an inert gas and the vapor of a high dielectric constant material.

The specific material used for the electronic conductor, e.g., the layer 16 of Figure 1 and the layer 36 of Figure 2, is not critical in the present invention and can include gold and other metals or nonmetals although tin-doped indium oxide (indium/tin oxide) is preferred for a device as shown in Figure 1 whereas gold is preferred for the device shown in Figure 2. The specific electrochromic material used in the present invention, e.g., the layer 17 in Figure 1 and the layer 37 in Figure 2, is not critical in the present invention and can include molybdenum oxide, and other materials that are colored by the simultaneous injection of protons (or other cations) and electrons, although tungsten oxide is preferred, as well as other types of electrochromic materials that are anodically transformed, such as nickel oxide. The specific material used for the counter electrode, e.g., the layer 19 in Figure 1 and the layer 39 in Figure 2, is not critical in the present invention. It is not critical in the present invention that the above layers contact each other as shown in Figure 1 and Figure 2. For example, the use of interposed silicon oxide and nucleating layers (to increase cycle life time) as taught in United States Patent 4,193,670 is specifically contemplated in the present invention. The use of a metal grid (to overcome the IR drop of large areas of transparent working electrodes) as taught in United States Patent 4,768,865 is specifically contemplated in the present invention. Thus, the present invention is an improvement upon any electrochromic device that incorporates an electronic conductor, an ion conducting

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layer, an electrochromic material and a counter electrode by positioning them in a space consisting essentially of a mixture of an inert gas and the vapor of a high dielectric constant material (or materials) if so doing increases the cycle life of the device by more
5 than 30 percent relative to operating a like device in ordinary air.

An inert gas in the present invention is a gas or mixture of gases that do not chemically react with
10 the electronic conductor, the ion conducting layer, the electrochromic material or the counter electrode to substantially reduce the cycle life of the device, i.e., more than thirty percent. Oxygen, for example, is not
15 usually an inert gas in the present invention when it is present above a level that substantially reduces the cycle life of the device, e.g. above about ten percent oxygen. Inert gasses in the preferred embodiment of the present invention include nitrogen, and the nobel gases.
20 Argon, and sulfur hexafluoride are sealed in commercially available double pane windows because argon and sulfur hexafluoride are relatively good thermal insulators. Argon should be an excellent inert gas in the present invention. Sulfur hexafluoride should be an
25 excellent inert gas in the present invention. Nitrogen is an excellent inert gas in the present invention.

A high dielectric constant material in the present invention is a material that has a dielectric
30 constant of greater than about 10. Preferably the dielectric constant of the high dielectric constant material of the present invention is greater than about 25. More preferably the dielectric constant of the high dielectric constant material of the present invention is greater than about 50. Even more preferably the

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dielectric constant of the high dielectric constant material of the present invention is greater than about 70. The most preferred high dielectric constant material of the present invention is water. Most preferably, the relative humidity of the inert gas of the present invention using the preferred perfluorosulfonate polymer ion conductor described below is between 25 and 35 percent. A relative humidity of above 35 percent, e.g., 50 percent, 60 percent, 75 percent, 80 percent, and even 100 percent, results in a workable device but also in a shorter cycle lifetime for the device, especially at higher temperature, e.g., at 50°C. A relative humidity of below 25 percent, e.g., 20 percent, 15 percent, 10 percent, or even 5 percent, can result in progressively slower response time for such a device. A humidistat means would be beneficial in the embodiments of the present invention wherein the inert gas is sealed in a device to correct the relative humidity of the inert gas for shifts in temperature of the device. In the embodiments of the present invention where the inert gas is not sealed in the device, the relative humidity of the inert gas can be controlled as desired, of course, i.e., the present invention does not require a sealed space for the humidified inert gas.

The seal means of the present invention, e.g., the epoxy cement 13 of Figure 1 and the epoxy cement 33 of Figure 2, should be selected to inhibit long term permeation of atmospheric oxygen into the inert gas. The best seal means in this regard, thus, would be welded glass. However, it is possible for water to be electrolyzed in an electrochromic device to generate

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oxygen and hydrogen. This electrolysis can be controlled by limiting the voltage applied to the device, e.g., by limiting the voltage to 2.1 volts in the preferred embodiment of the present invention. However, large surface area devices having significant IR drops in the working and/or counterelectrodes, without more, are believed to probably require higher applied voltages so that the device colors evenly across its area. The grid of United States Patent 4,768,865 is one solution to this problem. In the sealed embodiments of the present invention the inert gas can, thus, become contaminated with oxygen which is believed to shorten the cycle life of the device. One solution to this problem is to occasionally flush the sealed space with fresh humidified inert gas.

The specific material used in the ion conducting layer is not believed to be critical in the present invention. For example, many polymeric electrolytes have been shown to be useful as ion conducting layers in electrochromic devices. United States Patents 4,231,641, 3,971,624, 4,116,545, 4,750,817, 4,361,385, and 4,715,691, 4,193,670, 4,338,000. Nafion brand perfluorosulfonate polymer from DuPont was recognized as an ideal material. United States Patent 4,231,641. A preferred material in this regard is a polymer having a substantially fluorinated backbone which has recurring pendant groups attached thereto represented by the formula $-O-(CFR'_f)_b-(CFR_f)_a-SO_3^-$, where $a=0-3$, $b=0-3$, $a+b=at least 1$, and R_f and R'_f are independently selected from the group consisting of a halogen and a substantially fluorinated alkyl group having one or more carbon atoms. A specific example is the copolymer of FFC=CFF and FRC=CFF having an

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equivalent weight of 780, where R is -O-CFF-CFF-SO₃H⁺. This material has been shown to allow a higher temperature of operation than Nafion brand perfluorosulfonate polymer.

5 A preferred method of preparing a dispersion of the preferred perfluorosulfonate polymer of the present invention will now be described. Referring to United States Patent 4,358,545, the sulfonyl fluoride form of the polymer is synthesized, using as the monomers
10 tetrafluoroethylene (FFC=CFF) and 1,1,2,2-tetrafluoro-2-((trifluoroethenyl)oxy) ethane sulfonyl fluoride (FRC=CFF, where R is -O-CFF-CFF-SO₂F, see United States Patent 3,560,568) to produce a polymer having an
15 equivalent weight of 780. The polymer is then hot pressed into a film 1 to 20 thousands of an inch thick at a temperature no hotter than 20°F above its softening point. This helps to prevent the formation of a brown to gray color in the polymer. This film is cut into
20 strips and the sulfonyl fluoride groups of the polymer are then converted to sulfonate groups by immersing the strips in 25 percent sodium hydroxide at 70°C to 80°C for 12 hours. The polymer strips are then boiled repeatedly in deionized water to remove the excess sodium
25 hydroxide. Infrared spectroscopy can be used to confirm conversion of the polymer to the sodium sulfonate form.

 The polymer is then converted to the sulfonic acid form by twice immersing the strips in 6N
30 hydrochloric acid at 70°C to 90°C, four hours each time. The polymer is then washed repeatedly in 70°C deionized water to remove the excess hydrochloric acid and finally air dried.

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A near colorless dispersion of the sulfonic acid form of the polymer in ethanol/water is then prepared. The percentage of polymer to be added to the ethanol/water is determined by the equivalent weight and molecular weight of the polymer. Low equivalent weight polymers may be made up to give a higher weight percent solution than required and then diluted with additional quantities of ethanol and water to provide more solution. Typically an 800 equivalent weight polymer is made up at 5 to 10 percent by weight. High equivalent weight polymers having high melt viscosities are typically made up at 2 percent by weight.

It is very important in preventing the formation of color in the dispersion to use ethanol which does not contain ketones or other color forming impurities. Ethanol denatured with methanol or isopropanol has been found to be acceptable. The dried polymer strips are immersed in a 50/50 weight percent ethanol/water mixture and heated in a pressure reactor at 240°C for one to twelve hours to form the dispersion, a longer time being needed for the higher molecular weight/equivalent weight polymers. **WARNING, diethyl ether can be produced as a byproduct during this reaction.** The reactor is cooled and opened in a hood. The dispersion is then filtered by passing it through a coarse glass frit to remove any gels or undissolved material.

A portion of the electrochromic device shown in Figure 1 can now be prepared using the above described dispersion. A 1X2 inch indium/tin oxide (ITO) coated glass slide (PD5002, Donnelly Corp., Holland MI) is soaked in a 50 percent sodium hydroxide solution for 10 to 15 minutes and then washed thoroughly with deionized

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water to clean it. A small peripheral area of the ITO layer is coated with silver paint to facilitate an electrical connection to the ITO layer. A 3,000 to 4,000 Angstrom thick layer of tungsten oxide is deposited on the remaining ITO layer in a deposition chamber operated at a base oxygen pressure of 2×10^{-5} torr and a substrate temperature of 50°C to 70°C . The slide is then dipped in the above described dispersion for a few seconds, removed and then the inactive side of the slide is wiped clean. The slide is then placed in an oven at 85°C to 90°C for two hours to form the ion conducting layer on the tungsten oxide layer. Then, a 200 to 300 Angstrom thick layer of gold is deposited on a 1X3 centimeter central area of the ion conducting layer in a deposition chamber operated at base pressure of 1×10^{-5} torr. A 600 to 1000 Angstrom thick additional gold layer is made on a small peripheral portion the gold layer to provide a thicker more rugged electrical connection to the gold layer. A 2.5 volt direct current (D.C.) power source is connected to the device (+ to the gold layer, - to the ITO layer) to darken it. The device remains darkened for an hour even when the potential is removed. Reversing the potential lightens the device. The device is tested in air to determine its cycle life. The cycle life of the device is 10,000 cycles. Please note that a device of the type shown in Figure 2, although not the subject of this paragraph, can be made by treating the polymer film as above but not cutting it into strips and not forming a dispersion of it. The various layers can then be deposited on the converted film and then it can be sealed in a double pane window.

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The device shown in Figure 1 can now be completed. The procedure of the immediately preceding paragraph is repeated to obtain a new electrochromic device. Four lengths of one eighth inch diameter glass tubing are laid on the periphery of this device with one
5 end of each length of tubing overhanging the periphery of the glass slide about one half inch. A 1X3 inch glass slide is laid on the glass tubing so that it is juxtaposed and biplanar with the glass slide of the electrochromic device. Epoxy cement is then applied to
10 the peripheral one eighth inch gap between the two glass slides as a sealing means. When the epoxy cement has hardened, the two lengths of tubing overhanging the long ends of the slide are fused shut at their overhanging
15 tips with a flame. Nitrogen having a relative humidity of 30 percent is then flowed into one of the glass tubes overhanging the short ends of the slide, flowed between the two glass slides to the other end of the device and then flowed out of the remaining glass tube. The flow
20 of nitrogen is then stopped and the tips of these tubes are then also fused shut with a flame to seal the humidified nitrogen in the space between the glass slides. The device is tested to determine its cycle
25 life. The cycle life of the device is 14,000 cycles. It is believed that if the voltage applied to the device were closer to 2.1 volts, then the device of this example would have had an even longer cycle life.

30 A new device of the immediately preceding paragraph is made except that the flow of humidified nitrogen is continued through the device. The device is tested to determine its cycle life. The cycle life of the device is 30,000 cycles.

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CLAIMS

1. An electrochromic device including a plurality of layers on one side of a backing, the layers including an electronically conducting layer, an electrochromic layer, an ion conducting layer and a counter electrode layer, characterized by the additional following features:

5 (a) a panel, the panel juxtaposed substantially biplanar and spaced away from the one side of the backing and the layers thereon leaving a space volume between the panel and the layers;

10 (b) means for sealing the panel with the backing so that at least a portion of the space volume is sealed between the panel and the backing to form a sealed space volume; and

15 (c) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the sealed space volume.

2. A sealed double pane window including a
20 first pane of glass peripherally sealed with a second juxtaposed spaced apart substantially biplanar pane of glass so that a space volume is sealed between the first pane of glass and the second pane of glass, the first
25 pane of glass having a first side and a second side, the

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second side being exposed to the sealed space volume, characterized by the additional following features:

(a) a multi-layer electrochromic system coated on the second side of the first pane of glass, the electrochromic system comprising an electronically
5 conducting layer, an electrochromic layer, an ion conducting layer and a counter electrode layer; and

(b) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the
10 sealed space volume.

3. A sealed double pane window including a first pane of glass peripherally sealed with a juxtaposed spaced apart second substantially biplanar
15 pane of glass so that a given space volume is sealed between the first pane of glass and the second pane of glass, characterized by the following additional features:

(a) a multi-layer electrochromic system of a given solid volume, the electrochromic system positioned in the sealed space volume, the volume of the electrochromic system being less than the sealed space
20 volume so that there is a remaining sealed space volume, the electrochromic system comprising an electronically conducting layer, an electrochromic layer, an ion conducting layer and a counter electrode layer; and

(b) a mixture of an inert gas and the vapor of a high dielectric constant material positioned in the
30 remaining sealed space volume.

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4. An electrochromic device including an electronic conductor, an electrochromic material, an ion conducting layer, and a counter electrode, characterized by the following additional feature: positioning the electronic conductor, the ion conducting layer, the electrochromic material and the counter electrode in a space consisting substantially of a mixture of an inert gas and the vapor of a high dielectric constant material.

5. The device of Claims 1-4, wherein the high dielectric constant material has a dielectric constant of greater than about 25.

6. The device of Claim 5, wherein the high dielectric constant material has a dielectric constant of greater than about 50.

7. The device of Claim 6, wherein the high dielectric constant material has a dielectric constant of greater than about 70.

8. The device of Claim 7, wherein the high dielectric constant material is water.

9. The device of Claims 1-8, wherein the ion conducting layer is substantially a polymer having a substantially fluorinated backbone which has recurring pendant groups attached thereto represented by the formula $-O-(CFR'_f)_b-(CFR_f)_a-SO_3^-$, where $a=0-3$, $b=0-3$, $a+b=$ at least 1, and R_f and R'_f are independently selected from a halogen and a substantially fluorinated alkyl group having one or more carbon atoms.

10. The device of Claim 9, wherein the formula is $-O-(CFR'_f)_b-(CFR_f)_a-SO_3^-H^+$, where $a=0-3$, $b=0-$

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3, a+b=at least 1, R_f and R'_f are independently selected from a halogen and a substantially fluorinated alkyl group having one or more carbon atoms.

5 11. The device of Claim 10, wherein the ion conducting layer comprises a copolymer of FFC=CFF and FRC=CFF, and wherein R is -O-CFF-CFF-SOOO-H⁺.

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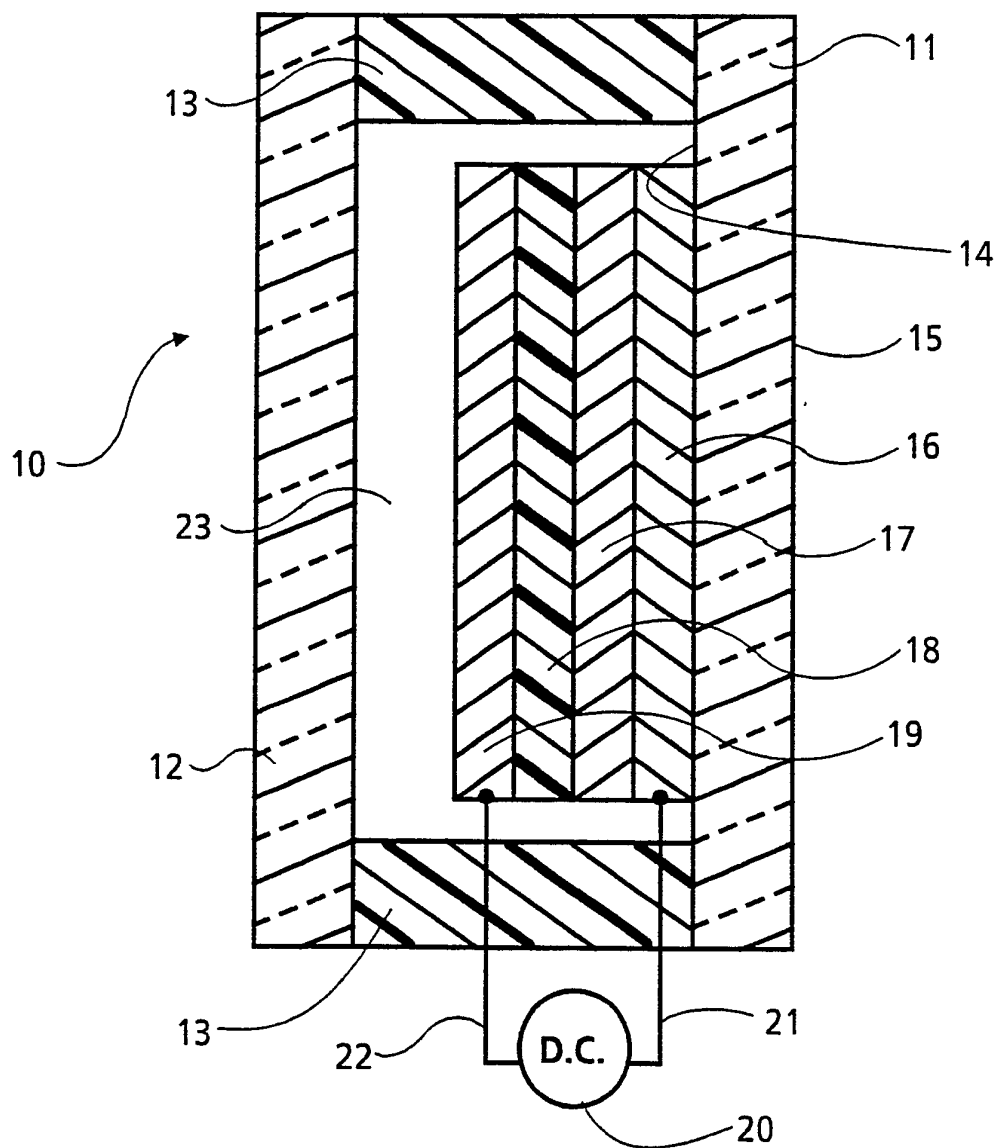
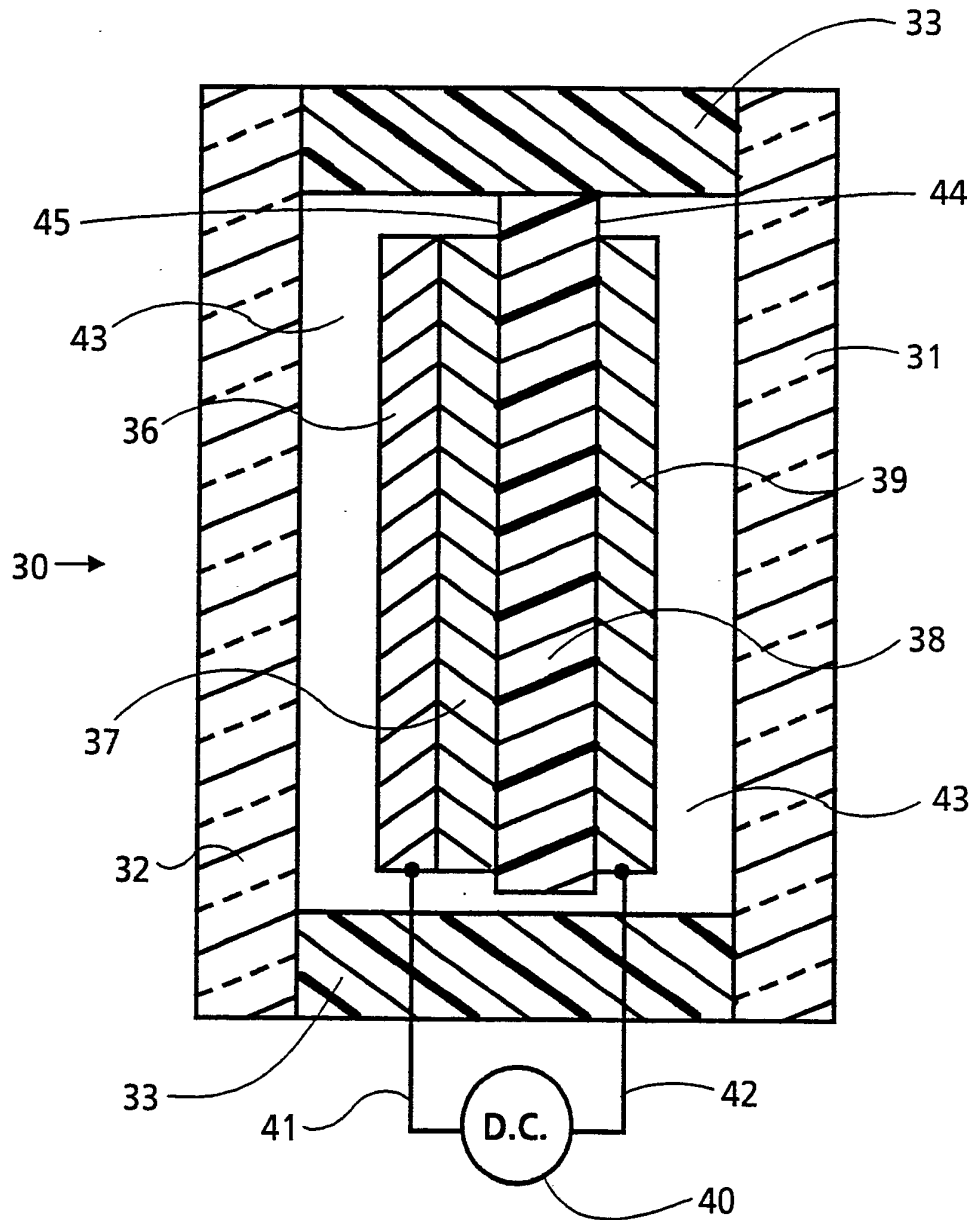
FIG. 1

FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US91/01506

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): G02F 1/00, 1/01 US CL.: 350/357 252/583		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
US	350/357 252/583	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	JP, A, 62-177529 (CANON) 04 August 1987 See figure 2 for panel 1,9.	1-8
Y	US, A, 4,231,641 (RANDIN) 04 November 1980 Note the polymer NAFION, column 7, line 15.	9-11
A	US, A, 4,264,150 (YANO ET AL.) 28 April 1981	1-8
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12 JUNE 1991		12 JUL 1991
International Searching Authority		Signature of Authorized Officer
ISA/US		NGUYEN HO INTERNATIONAL DIVISION ROBERT LIMANEK

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-8 drawn to an electrochromic device with a panel.
- II. Claims 9-11 drawn to an ion conducting layer composition.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☒ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.