

PATENT SPECIFICATION

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(54) PASSIVE-TYPE DISPLAY DEVICE

(71) We, KABUSHIKI KAISHA SUWA SEIKOSHA, a Japanese company, of 3-4, 4-chome, Ginza, Chuo-ku, Tokyo, Japan, 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 passive-type display devices.

In recent times, a demand has developed, especially in the field of electronic desk calculators and electronic wrist watches, for a digital display device which has a relatively low power consumption. At the present time, this demand is satisfied to some extent by liquid crystal display devices. However, a field effect type liquid crystal display device, which is driven by a relatively low voltage, requires a polarizing system to produce the display and is unsatisfactory because it is difficult to produce a clearly visible display on a light coloured substrate due to light absorption by the polarizing system. Further, because the liquid crystal material is orientated in a given manner, the display is not visible from all possible directions. On the other hand, electrochromic display devices, which produce a display by utilizing an oxidation-reduction reaction undergone by an electrochromic material, have the advantage that they can be energised by an extremely low voltage, e.g. 1 volt, have an inherent memory making it possible to maintain a display without maintaining energisation, have an average power consumption which is relatively low even though the reduction current has a relatively large current density, do not require a polarizing system, and produce a display which is visible from all directions. However, electrochromic display devices are not, as yet, in practical use because the life thereof is uncertain.

This invention seeks to provide a passive-type display device with an anode electrode which has a longer life than the anode electrode of conventional passive-type display devices. In the case where a passive-type display device has an aqueous electrochromic electrolyte solution between an anode electrode and a cathode electrode, electrolysis of the electrolyte solution is an important factor influencing the life of the display device especially since the electrolysis is irreversible. From a detailed analysis of such a display device, most of the voltage applied between the anode electrode and the cathode electrode, in effect appears across electric double layers at the interfaces between respective electrodes and the electrolytic solution. The voltage drop through the electrolytic solution, due to ohmic resistance, is, therefore, relatively small.

According to the present invention there is provided a passive-type display device comprising a metallic first electrode, a second electrode and an electrochromic electrolyte solution therebetween, the first electrode having, on a surface which is in contact with the electrolyte solution, a solid layer composed of the metal oxide of the metal of which the first electrode is made.

The first electrode may be made of any one of silver, antimony, tungsten, germanium and bismuth.

The electrolyte solution is preferably aqueous. Thus the electrolyte solution may include viologen bromide as an electrochromic material.

The invention is illustrated, merely by way of example, in the accompanying drawings, in which:—

Figure 1 illustrates schematically the operation of a passive-type display device according to the present invention; and

Figure 2 illustrates one embodiment of a passive-type display device according to the present invention.

Figure 1 illustrates, in particular, the potential distribution in a passive-type display device according to the present invention. The display device has a first electrode

1 which is made of, for example, gold or silver, and a transparent second electrode 2 composed of 95% indium oxide (In_2O_3) and 5% tin oxide (SnO_2). An aqueous electrolyte solution 3 is disposed between the first electrode and the second electrode. The electrolyte solution may consist of 0.3 mol/l of a viologen bromide having the formula:



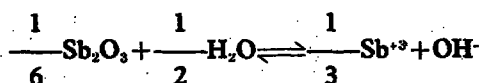
the pH thereof being adjusted using sodium acetate, and subsequently a sodium acetate buffer solution is added. The electrolyte solution uses water deoxygenated by passing nitrogen gas for one hour through ion-exchanged water, the nitrogen gas having first been passed through a boiling alkaline solution of pyrogallol.

The potential distribution just before the viologen bromide changes colour on the surface of the second electrode 2 is shown in Figure 1. In the case where the first electrode 1 is silver, a voltage V_3 is applied from a power source 4 and adjacent the surface of the first electrode in the electrolyte solution 3, the voltage is V_2 , whereas adjacent the surface of the second electrode 2, the voltage is V_1 . In the case where the first electrode 1 is of gold, a voltage V_3' is required from the power source 4 to make the voltage adjacent the surface of the first electrode in the electrolyte solution equivalent to V_2 , where $V_3' > V_3$.

The bigger the value of $(V_3 - V_2)$ the greater the risk of an electrolytic decomposition reaction at the surface of the first electrode 1 so that in the above example a first electrode made of silver is preferable to a first electrode made of gold to make it possible to write and erase displays over a relatively long period of time.

It is necessary that the reaction at the first electrode is such that the first electrode reversibly reacts with the negative ions in the electrolyte solution. Thus it is desirable that an anion either of high mobility or having high specific conductivity is produced by the reaction at the first electrode to increase the speed of writing and erasing a display. Since the electrolyte solution 3 is aqueous, the reaction at the first electrode may produce OH^- ions which are highly mobile.

The first electrode 1 is, therefore, made of a metal on the surface of which is a solid layer composed of the metal oxide of the metal of which the first electrode 1 is made. Thus in the embodiment described with reference to Figure 1, the first electrode 1 of silver has, on its surface, silver oxide. The first electrode may also be made of any one of the following metals, antimony, tungsten, germanium and bismuth on which there is a coating of antimony oxide, tungsten oxide, germanium oxide and bismuth oxide. With a first electrode made of antimony with antimony oxide on its surface, the following reversible reaction is presumed to occur:



A seven segment/digital display device according to the present invention is shown in Figure 2. A first electrode 6 made of antimony is evaporated by a sputtering technique, in the shape of a frame on a ceramic substrate 5 together with an electrical lead wire 15. A segment pattern as shown in Figure 2(b) is formed from a transparent NESA (Trade Mark) second electrode 9 deposited on a transparent glass plate 10. The plate 10 is spaced from the substrate 5 by spacers 7. A plurality of electrical lead wires 14 extend from the segments of the electrode 9.

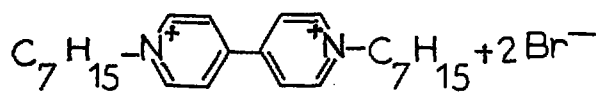
An electrolyte solution 13 such as that described in relation to Figure 1 is injected into the space between the plate 10 and the substrate 5 through one of two apertures 12 which are then filled with antimony balls 11 and sealed with a bonding agent 12. The electrical lead wires 14, 15 are electrically connected to a decoder/driver terminal of circuitry of a quartz crystal wrist watch so as to display a time indication. The display appears reddish-purple in colour against the background of the substrate 5 which, in this case, is white. The display is very clear and a display device of this type has functioned for one month without trouble.

WHAT WE CLAIM IS:—

1. A passive-type display device comprising a metallic first electrode, a second electrode and an electrochromic electrolyte solution therebetween, the first electrode

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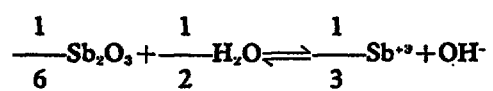
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The potential distribution just before the viologen bromide changes colour on the surface of the second electrode 2 is shown in Figure 1. In the case where the first electrode 1 is silver, a voltage V₃ is applied from a power source 4 and adjacent the surface of the first electrode in the electrolyte solution 3, the voltage is V₂, whereas adjacent the surface of the second electrode 2, the voltage is V₁. In the case where the first electrode 1 is of gold, a voltage V₃' is required from the power source 4 to make the voltage adjacent the surface of the first electrode in the electrolyte solution equivalent to V₂, where V₃' > V₃.

The bigger the value of (V₃ - V₂) the greater the risk of an electrolytic decomposition reaction at the surface of the first electrode 1 so that in the above example a first electrode made of silver is preferable to a first electrode made of gold to make it possible to write and erase displays over a relatively long period of time.

It is necessary that the reaction at the first electrode is such that the first electrode reversibly reacts with the negative ions in the electrolyte solution. Thus it is desirable that an anion either of high mobility or having high specific conductivity is produced by the reaction at the first electrode to increase the speed of writing and erasing a display. Since the electrolyte solution 3 is aqueous, the reaction at the first electrode may produce OH⁻ ions which are highly mobile.

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An electrolyte solution 13 such as that described in relation to Figure 1 is injected into the space between the plate 10 and the substrate 5 through one of two apertures 12 which are then filled with antimony balls 11 and sealed with a bonding agent 12. The electrical lead wires 14, 15 are electrically connected to a decoder/driver terminal of circuitry of a quartz crystal wrist watch so as to display a time indication. The display appears reddish-purple in colour against the background of the substrate 5 which, in this case, is white. The display is very clear and a display device of this type has functioned for one month without trouble.

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having, on a surface which is in contact with the electrolyte solution, a solid layer composed of the metal oxide of the metal of which the first electrode is made.

2. A display device as claimed in claim 1 in which the first electrode is made of any one of silver, antimony, tungsten, germanium and bismuth.

3. A display device as claimed in claim 1 or 2 in which the electrolyte solution is aqueous.

4. A display device as claimed in claim 3 in which the electrolyte solution includes viologen bromide as an electrochromic material.

5. A passive-type display device substantially as herein described with reference to and as shown in the accompanying drawings.

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