

PATENT SPECIFICATION

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(54) ELECTRO-OPTIC LIGHT VALVE

(71) We, RCA CORPORATION (formerly Radio Corporation of America), a corporation organised under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, 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:—

Nematic liquid crystal light valves and display devices, and nematic liquid crystal compounds useful therein have been described in U.S. Patent 3,322,485. Such light valves are controlled by an electric field and operate when the liquid crystal material is in its mesomorphic state. Generally, with no electric field applied to the nematic liquid crystal material the device containing a thin layer of this material is relatively transparent to light. When an electric field is applied to the liquid crystal material above a threshold value, which value depends upon the particular liquid crystal composition, the device appears to darken in the region of the field. This darkening is due to the scattering of light by domains of the liquid crystal molecules which align themselves in the field. In the liquid crystals described herein the change in optical properties is believed to be due to the alignment of domains or swarms of birefringent liquid crystal molecules in the electric field.

The electro-optical effect due to alignment of domains of the nematic liquid crystal molecules in an electric field may be employed in transmissive, reflective, or absorptive type flat panel displays in light shutters and other applications. Prior art liquid crystals of this type have relatively high crystal-nematic transition temperatures. That is, the temperature at which the material enters its nematic mesomorphic state is relatively high. Since the nematic liquid crystal composition

must be operated while in its nematic mesomorphic state, it is therefore desirable to use compositions which have a low crystal-nematic transition temperature. It is also desirable to use materials that are highly polar so that the time required to align the domains in an electric field will be relatively short.

According to the invention we provide a liquid crystal light valve comprising a composition including at least one member of the group of nematic liquid crystals consisting of *p*-*n*-butoxybenzylidene-*p*'-aminobenzonitrile, *p*-*n*-octoxybenzylidene-*p*'-aminobenzonitrile and *p*-ethoxybenzylidene-*p*'-aminobenzonitrile, and means for applying an electric field to said composition.

Figure 1 is a schematic showing of nematic liquid crystal in its normal state without an electric field applied thereto.

Figure 2 is a schematic showing of the novel nematic liquid crystal composition in its electric field induced, aligned state.

Figure 3 is a perspective partly cut away view of an electro-optic device embodying the invention.

Figure 4 is a schematic view of the electro-optic device of Figure 3 showing its operation between cross polarizers.

In the absence of an electric field, a nematic liquid crystal composition of the type described herein is believed to have its molecules arranged in small randomly oriented domains, as shown in Figure 1, when in its mesomorphic state. Upon the application of a sufficiently high electric field to the liquid crystal composition it is believed that the domains tend to align themselves, as shown in Figure 2, so that a substantial proportion of the domains and hence a substantial proportion of the liquid crystal molecules are aligned essentially parallel to the direction of the applied field. The degree of alignment is a function of the strength of the field.

In practice, the liquid crystal display in-

cludes two planar elements with a thin liquid crystal film between them. One of the elements is transparent while the other may be transparent, reflective or absorptive depending upon the desired mode of operation of the device. Row conductors and column conductors, which may be transparent conductors may be applied to a surface of each of the planar elements for applying an electric field to selected areas of the liquid crystal film. All of this is discussed and shown in the prior art patent. One specific embodiment of this type of light valve is shown with reference to Figure 3. The device 30 consists of back and front transparent support plates 31 and 32, respectively. The support plates 31 and 32 are parallel and are spaced apart by a distance of about one-half mil. On the inner face 33 of the back plate 31 is an array of parallel spaced transparent conductive back electrode strips 35. On the inner surface 34 of the front plate 32 is an array of parallel, spaced transparent conductive strips 36. The conductive strips 35 are mutually perpendicular to the strips 36.

In the device the space between the front and back plates 31 and 32 is filled with a liquid crystal mixture 37 comprising equal weight proportions of *p*-ethoxybenzylidene-*p'*-aminobenzonitrile and *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile. The mixture may be sealed in the device 30 by using an epoxy cement around the edges of the device. In operation in the transmissive mode a light source is on the same side as the front face of the device 30 and the observer is on the same side as the back face of the device 30. With no field applied to the device 30, the device 30 appears uniformly bright to the observer. When a D.C. or A.C. field of, for example, about 10 volts is applied to any portion of the liquid crystal composition, that portion appears relatively brighter than the remainder of the device. This mode is preferred because of the higher contrast ratios obtained as compared to other modes. When the device is operated in a reflective or absorptive mode both light source and observer are on the same side as the front plate 32 of the device 30 and the back plate is made reflective or absorbing respectively.

In order to increase the contrast ratio in the preferred transmissive mode of the device 30, it is preferred to use the device 30 between crossed polarizers 41 and 42, as shown in Figure 4. When used in this manner, the device takes advantage of the birefringent properties of the nematic liquid crystal composition which causes rotation of the plane of polarization (or more precisely causes a change of state) of polarized light incident thereon. In operation light 43 from a light source 44 is polarized when passed through the first polarizer 41. The polarized light is transmitted through the device 30 and when no field is applied to the device 30 a substantial portion

of this light passes through the second polarizer 42. Hence with no field applied, the device appears uniformly bright to an observer 45. This is due to the random orientation of the domains which causes rotation of some of the polarized light which rotated light is then able to pass through the second polarizer 42. When an electric field is applied across the device 30, the domains of the liquid crystal composition align such that the liquid crystal molecules are parallel to the direction of the incident light. When this occurs, the plane of polarization is not rotated and hence the second polarizer 42 which is crossed with relation to the first polarizer 41 impedes the passage of light therethrough and the device in the region of the applied field appears dark to the observer 45. When the device 30 is operated in combination with crossed polarizers, contrast ratios of about 10 to 1 have been observed. A gray scale is possible since the degree of domain rotation is dependent upon the field strength of the applied electric field.

Using the same principal, the device can be operated in a reflective mode with just one polarizer.

Another mode of operation of the device is in combination with pleochroic dyes. In this configuration a pleochroic dye is mixed with the nematic liquid crystal composition and rotation and alignment of the liquid crystal molecules causes rotation and alignment of the dye molecules. This effect thereby changes the absorption characteristics of the device when viewed in the transmission mode with polarized light. An example of a useful dye material is methyl red.

The liquid crystal compounds useful in the disclosed device are *p*-ethoxybenzylidene-*p'*-aminobenzonitrile; *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile; and *p*-*n*-octoxybenzylidene-*p'*-aminobenzonitrile. Although these materials can be used separately, it is preferred to use mixtures of *p*-ethoxybenzylidene-*p'*-aminobenzonitrile with either *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile or *p*-*n*-octoxybenzylidene-*p'*-aminobenzonitrile or mixtures of all three compounds. In order to substantially lower the crystal-nematic transition temperature, mixtures of from 10 to 90 weight percent of *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile with *p*-ethoxybenzylidene-*p'*-aminobenzonitrile or mixtures containing of from 15 to 70 weight percent of each of the three compounds are preferred. The lowest crystal-nematic transition temperatures have been found with a mixture comprised of equal weights of *p*-ethoxybenzylidene-*p'*-aminobenzonitrile and *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile or a mixture comprised of equal weights of *p*-ethoxybenzylidene-*p'*-aminobenzonitrile, *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile, and *p*-*n*-octoxybenzylidene-*p'*-aminobenzonitrile. The

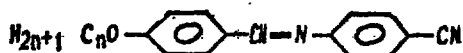
following Table shows the comparison between crystal-nematic transition temperatures and the nematic-isotropic transition temperatures of some of the particular prior art compounds

and that of the *p-n*-alkoxybenzylidene-*p'*-aminobenzonitrile compounds and the mixtures thereof.

Composition	Crystal-Nematic Transition Temperature (°C.)	Nematic-Isotropic Transition Temperature (°C.)
<i>p</i> -azoxyanisole	116	135
4,4'-diethoxyazoxybenzene	137	167
4,4'-di- <i>n</i> -pentoxyazoxybenzene	79	121
<i>p</i> -ethoxybenzylidene- <i>p'</i> -aminobenzonitrile	105	130
<i>p-n</i> -butoxybenzylidene- <i>p'</i> -aminobenzonitrile	63	106
<i>p-n</i> -octoxybenzylidene- <i>p'</i> -aminobenzonitrile	79	94.5
<i>p</i> -ethoxybenzylidene- <i>p'</i> -aminobenzonitrile and <i>p-n</i> -butoxybenzylidene- <i>p'</i> -aminobenzonitrile (equal weights)	41	109
<i>p</i> -ethoxybenzylidene- <i>p'</i> -aminobenzonitrile <i>p-n</i> -butoxybenzylidene- <i>p'</i> -aminobenzonitrile <i>p-n</i> -octyloxybenzylidene- <i>p'</i> -aminobenzonitrile (equal weights)	50	91

Threshold voltages for a one-half mil thick cell containing the mixtures are approximately 10 volts A.C. or D.C. Switching time for switching of a one-half mil cell at 100 volts D.C. is in the order of 10 milliseconds for the rise time and about 30 to 100 milliseconds for the decay time. By rise time, it is meant the time necessary to align the domains. By decay time, it is meant the time it takes after the removal of the applied field for the liquid crystals to return to its random state.

The mixtures are comprised of anils having the structural formula



Generally, these materials can be prepared by the condensation of *p*-aminobenzonitrile with the appropriate *p*-alkoxybenzaldehyde in a refluxing benzene solution with benzenesulfonic acid as a catalyst and azeotropic removal of water. Purification of the compound is generally accomplished by repeated recrystallization from hexane solution to a constant nematic-isotropic transition temperature.

For example, the compound *p*-ethoxybenzylidene-*p'*-aminobenzonitrile can be prepared in the following manner: A solution

of 0.10 moles of *p*-aminobenzonitrile, 0.10 moles of *p*-ethoxybenzaldehyde, 0.1 grams of benzene sulfonic acid in 500 millimeters of benzene is refluxed for about three hours. A Dean-Stark trap is used to collect the water which is azeotropically removed. After refluxing, the solvent is removed by evaporation under reduced pressure in a rotating film evaporator. The residue is collected and recrystallized several times from hexane.

The *p-n*-butoxybenzylidene-*p'*-aminobenzonitrile compound is prepared in a similar manner except that *p*-butoxybenzaldehyde is used rather than the ethoxybenzaldehyde stated above. In a like manner, *p-n*-octoxybenzylidene-*p'*-aminobenzonitrile is prepared by substituting *p*-octoxybenzaldehyde for ethoxybenzaldehyde in the above example.

In order to prepare the mixtures, the pure crystalline compounds are weighed into a vial into the desired weight proportion and the mixture heated to the isotropic melting point so as to form an isotropic solution. The isotropic solution is allowed to cool to zero degrees centigrade and becomes solidified during this cooling. The resulting solid mass can be broken off into small pieces and can be placed in a capillary tube or on a glass slide for melting point determination. The mixtures may be inserted in the liquid crystal

- device by having the planar supporting elements either separated by means of a shim or by sealing three sides together with an epoxy cement leaving a space between the elements.
- 5 The liquid crystal composition is then heated to a temperature greater than its crystal-nematic transition temperature and injected into the space between the planar elements, for example, by means of a syringe.
- 10 **WHAT WE CLAIM IS:—**
1. A liquid crystal light valve comprising a composition including at least one member of the group of nematic liquid crystals consisting of *p* - *n* - butoxybenzylidene - *p'* -
- 15 aminobenzonitrile, *p* - *n* - octoxybenzylidene - *p'* - aminobenzonitrile, and *p* - ethoxybenzylidene - *p'* - aminobenzonitrile, and means for applying an electric field to said composition.
- 20 2. A liquid crystal light valve as claimed in claim 1, wherein said mixture of nematic liquid crystals consists essentially of 10 to 90 weight percent of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile with the remainder *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile.
- 25 3. A liquid crystal light valve as claimed in claim 2, wherein said mixture of nematic liquid crystals consists of equal weight proportions of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile and *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile.
- 30 4. A liquid crystal light valve as claimed in claim 1, wherein the nematic liquid crystal mixture is comprised of from 15 to 70 weight percent of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile, from 15 to 70 weight percent of *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile, and from 15 to 70 weight per cent of *p* - *n* - octoxybenzylidene - *p'* - aminobenzonitrile.
5. A liquid crystal light valve as claimed in claim 4, wherein the nematic liquid crystal mixture is comprised of approximately equal weights of each component, said mixture located between crossed polarizers.
6. A liquid crystal light valve as claimed in claim 1, wherein the composition is in the form of a thin layer.
7. A liquid crystal light valve described in any one of the preceding claims, said light valve including a pleochroic dye in solution with said nematic liquid crystal mixture.
8. A liquid crystal light valve substantially as described with reference to the accompanying drawing.

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- device by having the planar supporting elements either separated by means of a shim or by sealing three sides together with an epoxy cement leaving a space between the elements.
- 5 The liquid crystal composition is then heated to a temperature greater than its crystal-nematic transition temperature and injected into the space between the planar elements, for example, by means of a syringe.
- 10 **WHAT WE CLAIM IS:—**
1. A liquid crystal light valve comprising a composition including at least one member of the group of nematic liquid crystals consisting of *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile, *p* - *n* - octoxybenzylidene - *p'* - aminobenzonitrile, and *p* - ethoxybenzylidene - *p'* - aminobenzonitrile, and means for applying an electric field to said composition.
- 15 2. A liquid crystal light valve as claimed in claim 1, wherein said mixture of nematic liquid crystals consists essentially of 10 to 90 weight percent of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile with the remainder *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile.
- 20 3. A liquid crystal light valve as claimed in claim 2, wherein said mixture of nematic liquid crystals consists of equal weight proportions of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile and *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile.
- 30 4. A liquid crystal light valve as claimed in claim 1, wherein the nematic liquid crystal mixture is comprised of from 15 to 70 weight percent of *p* - ethoxybenzylidene - *p'* - aminobenzonitrile, from 15 to 70 weight percent of *p* - *n* - butoxybenzylidene - *p'* - aminobenzonitrile, and from 15 to 70 weight per cent of *p* - *n* - octoxybenzylidene - *p'* - aminobenzonitrile.
5. A liquid crystal light valve as claimed in claim 4, wherein the nematic liquid crystal mixture is comprised of approximately equal weights of each component, said mixture located between crossed polarizers.
- 40 6. A liquid crystal light valve as claimed in claim 1, wherein the composition is in the form of a thin layer.
7. A liquid crystal light valve described in any one of the preceding claims, said light valve including a pleochroic dye in solution with said nematic liquid crystal mixture.
- 50 8. A liquid crystal light valve substantially as described with reference to the accompanying drawing.

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