

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) LIQUID CRYSTAL ELECTRO-OPTIC DEVICE

(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 are light valves which are controlled by an electric field. They operate when the liquid crystal material is in its mesomorphic state. Generally, with no electric field applied to the nematic liquid crystal material, the material is slightly turbid in appearance and scatters light to some extent. However, a thin layer of such a material is relatively transparent to light incident thereon. When an electric field above a threshold value, which value depends upon the particular liquid crystal composition, is applied to the layer of liquid crystal material, there is a change in appearance of the layer in the region of the applied field. The layer may appear either brighter or darker to a viewer observing light transmitted through the layer, depending upon the direction of alignment of the liquid crystal molecules in the field with respect to their molecular axes. If the liquid crystal molecules align essentially perpendicular to the direction of the incident light, then additional scattering occurs and that region of the device appears darker to a viewer on the side of the device opposite the source of incident light. If the liquid crystal molecules align with their molecular axes essentially parallel to the direction of the incident light, then there is less scattering of the incident light, and that region appears brighter to the viewer. The direction of alignment of the liquid crystal molecules (which in the absence of an electric field exist in ran-

domly oriented domains), in an electric field depends upon the direction of the dipole moment of the molecules with respect to its molecular axis.

The electro-optical effect due to alignment 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 in other applications.

Since the nematic liquid crystal composition of these devices must be operated while in its nematic mesomorphic state, it is therefore desirable to use compositions which have a lower crystal-nematic transition temperature than prior art compositions. It is also desirable to use compositions wherein the contrast ratio between an excited or aligned region of the composition and an unexcited or unaligned region of the composition is greater than that achieved in prior art devices.

An electro-optic device herein comprises a mixture comprised of a nematic liquid crystal composition of the type whose molecules align in an electric field with at least one member of the group consisting of cholesterol, a cholesterol derivative and a cholesteric liquid crystal. The device includes means for applying an electric field to this mixture.

FIGURE 1 is a schematic showing of a liquid crystal in its unexcited state;

FIGURE 2 is a schematic showing of a liquid crystal in its excited state; and

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

In the absence of an electric field, a nematic liquid crystal composition of the preferred type described herein has its dipole moment essentially parallel to its molecular axis and 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 field strength.

In practice, the liquid crystal display includes 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.

It has been found that by mixing cholesterol, and/or a cholesterol derivative, and/or a cholesteric liquid crystal with a nematic liquid crystal composition of the type whose molecules align in an electric field, one achieves a mixture which is highly light scattering. The mixture also results in depression of the crystal-nematic transition temperature of the nematic liquid crystals. When an electric field is applied to such a mixture, so as to align the nematic liquid crystal molecules of the mixture with their axes substantially parallel to the direction of the incident light, the mixture essentially no longer scatters the light as it would in its unexcited state and becomes transparent to the incident light. This discovery makes possible light valves and display devices having improved contrast ratios as compared to prior art liquid devices of the type which depend upon alignment of nematic liquid crystal molecules in an electric field.

A preferred embodiment of a liquid crystal element is shown in FIGURE 3 in the form of a crossed grid reflective electro-optic display device 30. The device 30 consists of a back and a front transparent support plate 31 and 32, respectively. The support plates 31 and 32 are parallel and are separated by a distance of about one-half mil. On the inner surface 33 of the back plate 31 is an array of parallel spaced conductive back electrode strips 35. On the inner surface 34 of the front plate 32 is an array of parallel spaced transparent conductive front electrode strips 36. The front conductive strips 36 are perpendicular to the back conductive strips 35. The outer surface 37 of the back plate 31 is coated with a reflective material 38, such as aluminum.

In the device 30, the space between the front and back plates 31 and 32 is filled with a mixture 39 comprising 80 weight percent of a nematic liquid crystal composition and 20 weight percent of cholesterol derivatives. The nematic composition consists essentially of equal weights of p - ethoxybenzylidene - p' - aminobenzonitrile and p - n - butoxy -

benzylidene - p' - aminobenzonitrile. The cholesterol derivatives consist essentially of 23 weight percent of cholesteryl chloride and 77 weight percent of cholesteryl oleate. The mixture may be sealed in the device 30 by using epoxy cement around the edges of the device 30. The nematic composition by itself has a crystal-nematic transition temperature of about 41°C. However, this transition temperature is reduced to about room temperature when mixed with the cholesteryl compounds.

In operation, in its reflective mode, a light source 40 and an observer 41 are both on the same side of the device as the front support plate 32. With no field applied to the device 30, the device 30 appears uniformly bright to the observer 41. When a dc or ac field of, for example, about 10 volts is applied to any portion of the liquid crystal composition, that portion appears darker than the remainder of the device. Desired or specific portions of the device can be darkened by applying proper voltages to particular pairs of front and back electrode strips.

The device 30 can operate in a light transmitting mode when there is no reflective coating 39 on the back plate 31 and when the back electrode strips 35 are transparent. In this mode, an observer is on the side of the device opposite a light source, and will observe transmitted light rather than reflected light. In this mode of operation, the device appears brighter to the observer in the region of an applied electric field when the incident light is essentially parallel to the direction of the field. This effect is due to the reduction of scattered light upon the application of the electric field and the direction passage of the light to the observer.

As previously stated, the mixtures useful in the practice of this invention include a nematic liquid crystal portion and a portion comprised of either cholesterol, or at least one cholesterol derivative, or at least one cholesteric liquid crystal, or combinations of these materials. An example of nematic liquid crystal materials of the type in which the molecules align in the direction parallel to the direction of an applied electric field are the family of compounds which may be described as p - n - alkoxybenzylidene - p' - amino - benzonitriles. Mixtures of the compounds p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile and p - n - octoxybenzylidene - p' - aminobenzonitrile have been found especially useful in combination with cholesterol, cholesterol derivatives or cholesteric liquid crystals. Mixtures of these compounds combine fast response times due to the large dipole moment of the nematic liquid crystal molecule and also provide reduced crystal - nematic transition temperatures. With the reduced transition temperatures achieved, devices can be operated at lower temperatures than prior art devices.

The of and The by the self ture em- nure nds. ight on sup- the mly ac- lled osi- re- cific by airs	70	5	Preferred weight percent ranges of the compounds comprising the nematic liquid crystal portion of the overall mixture are from 10 to 90 weight percent of p - ethoxybenzylidene - p' - aminobenzonitrile with 10 to 90 weight percent of p - n - butoxybenzylidene - p' - aminobenzonitrile or nematic liquid crystal compositions containing from 15 to 70 weight percent of each of the three compounds referred to above. The lowest crystal nematic transition temperatures have been found with mixtures comprised of equal weights of p - ethoxybenzylidene - p' - aminobenzonitrile and p - n - butoxybenzylidene - p' - amino - benzonitrile or mixtures comprised of equal weights of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxy - benzylidene - p' - aminobenzonitrile. The former composition has a crystal - nematic transition temperature of about 41°C, and the latter composition has a crystal - nematic transition temperature of about 50°C. Both these transition temperatures are depressed to even lower temperatures upon the addition of the cholesteric material to the nematic composition. The mixture may include from 5 to 30 weight percent of the combination of cholesteryl oleate and cholesteryl chloride.	65	combination with the nematic liquid crystal compositions as described above.
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seful de a rtion least one is of liquid the o the e the ribed ino - s p - itrile, enzo- p' - cially holes- tals. t res- ent of also sition tem- rated vices.	85	15			
	90	20			
	95	25			
	100	30			
	105	35			
	110	40			
	115	45			
	120	50			
	125	55			
	130	60			

TABLE I

Cholesterol	Derivatives and Liquid Crystals	Cholesteric
Cholesteryl Oleate (Pract.)		70
Cholesteryl Palmitate		
Cholesteryl Decanoate		
Cholesteryl Laurate		
Cholesteryl Propionate		
Cholesteryl Heptafluorobutyrate		75
Cholesteryl 2 - Furoate		
Cholesteryl Cinnamate		
Cholesteryl Cyclohexanecarboxylate		
Cholesteryl Anisoate		
Dicholesteryl Phthalate		80
Cholesteryl p - Nitrobenzoate		
Cholesteryl p - Phenylazobenzoate		
Cholesteryl 3,5 - Dinitrobenzoate		
Cholesteryl 2 - (2 - Ethoxyethyl)ethyl Carbonate		85
Cholesteryl 2 - (2 - Methoxyethyl)ethyl Carbonate		
Cholesteryl Geranyl Carbonate		
Cholesteryl Octadecyl Carbonate		
Cholesteryl 2 - Propyn - 1 - yl Carbonate		90
Cholesteryl 2 - Methyl - 2 - propene - 1 - yl Carbonate		
Allyl Cholesteryl Carbonate		
Cholesteryl 2,2,2 - Trifluoroethyl Carbonate		95
Cholesteryl Methyl Carbonate		
Cholesteryl Cinnamyl Carbonate		
Cholesteryl p - Menth - 1 - en - 8 - yl Carbonate		100
Cholesteryl Nitrate		
Cholestanyl Propynyl Carbonate		
3β - Chlorocholest - 5 - ene		
Cholesteryl Methanesulfonate		
5α - Cholestan - 3β - yl Chloroformate		105
Cholesteryl Chloroformate		
5α - Cholestan - 3β - ol		
Cholesterol		
Stigmasterol		

It is preferred that the nematic liquid crystal portion of the overall mixture comprise at least 50 weight percent of the total mixture, and preferably from about 75 to 95 weight percent of the overall mixture. However, it is possible to use mixtures containing as little as 5% nematic liquid crystals and up to 95% of cholesteric material.

The mixtures can be prepared by placing the desired proportions of the pure compounds in a vial and heating these compounds until a uniform isotropic liquid solution is formed. Generally, heating to a temperature of about 100°C. is sufficient. This isotropic liquid is then allowed to cool slowly to room temperature. During cooling the mixture enters its mesomorphic state and, depending upon the particular mixture, may solidify. The mix-

tures can be incorporated into the device by, for example, placing some of the mixture in its mesomorphic state on one support plate and carefully placing the other support plate over the first so that the mixture spreads to form a uniform film between them. Another technique is to have the spaced supports separated by shims and/or sealed on three sides and injecting the mixture into the space with a syringe.

WHAT WE CLAIM IS:—

1. An electro-optic device characterized by comprising: a mixture comprised of a nematic liquid crystal composition of the type whose molecules align in an electric field with at least one member of the group consisting of cholesterol, a cholesterol derivative, and a cholesteric liquid crystal, and means for applying an electric field to said mixture.

2. An electro-optic device as claimed in claim 1, further characterized by comprising: spaced plates at least one of which is transparent to light, said mixture being placed in the space between said plates.

3. A device as claimed in claim 1, wherein said mixture comprises at least one nematic liquid crystal compound selected from the group consisting of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxybenzylidene - p' - aminobenzonitrile.

4. A device as claimed in claim 3, wherein said nematic liquid crystal portion of said mixture comprises between 10 and 90 weight percent of p - ethoxybenzylidene - p' - aminobenzonitrile, and p - n - butoxybenzylidene - p' - aminobenzonitrile.

5. A device as claimed in claim 3, wherein said nematic liquid crystal portion of said mixture comprises between 15 and 75 weight percent of each of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxybenzylidene - p' - aminobenzonitrile.

6. A device as claimed in claim 4, wherein said nematic liquid crystal compound in said mixture comprises equal weights of p -

ethoxybenzylidene - p' - aminobenzonitrile and p - n - butoxybenzylidene - p' - aminobenzonitrile.

7. A device as claimed in claim 5, wherein said nematic liquid crystal compounds in said mixture comprises equal weights of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxybenzylidene - p' - aminobenzonitrile.

8. A device as claimed in claim 1, wherein the mixture consists of essentially from 5 to 95 weight percent of nematic liquid crystals and from 5 to 95 weight percent of cholesteric material.

9. A device as claimed in claim 1, wherein the nematic liquid crystal portion of the mixture comprises from about 75 to 95 weight percent of the mixture.

10. A device as claimed in claim 3, wherein the mixture includes from 5 to 30 weight percent of the combination of cholesteryl oleate and cholesteryl chloride.

11. An electro-optic device as claimed in claim 1, further including a transparent front support plate, a specularly reflective back support plate spaced from and parallel to said front support plate, a plurality of parallel transparent conductive strips on said front support plate, a plurality of parallel conductive strips on said back support plate running in a direction essentially perpendicular to said transparent conductive strips on said front support plate and wherein said mixture fills the space between said support.

12. A device as claimed in claim 9, wherein said mixture includes at least one nematic liquid crystal compound chosen from the group known as p - n - alkoxybenzylidene - p' - aminobenzonitriles.

13. An electro-optic device substantially as described with reference to the accompanying drawings.

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tures can be incorporated into the device by, for example, placing some of the mixture in its mesomorphic state on one support plate and carefully placing the other support plate over the first so that the mixture spreads to form a uniform film between them. Another technique is to have the spaced supports separated by shims and/or sealed on three sides and injecting the mixture into the space with a syringe.

WHAT WE CLAIM IS:—

1. An electro-optic device characterized by comprising: a mixture comprised of a nematic liquid crystal composition of the type whose molecules align in an electric field with at least one member of the group consisting of cholesterol, a cholesterol derivative, and a cholesteric liquid crystal, and means for applying an electric field to said mixture.

2. An electro-optic device as claimed in claim 1, further characterized by comprising: spaced plates at least one of which is transparent to light, said mixture being placed in the space between said plates.

3. A device as claimed in claim 1, wherein said mixture comprises at least one nematic liquid crystal compound selected from the group consisting of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxybenzylidene - p' - aminobenzonitrile.

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ethoxybenzylidene - p' - aminobenzonitrile and p - n - butoxybenzylidene - p' - aminobenzonitrile.

7. A device as claimed in claim 5, wherein said mixture comprises equal weights of p - ethoxybenzylidene - p' - aminobenzonitrile, p - n - butoxybenzylidene - p' - aminobenzonitrile, and p - n - octoxybenzylidene - p' - aminobenzonitrile.

8. A device as claimed in claim 1, wherein the mixture consists of essentially from 5 to 95 weight percent of nematic liquid crystals and from 5 to 95 weight percent of cholesteric material.

9. A device as claimed in claim 1, wherein the nematic liquid crystal portion of the mixture comprises from about 75 to 95 weight percent of the mixture.

10. A device as claimed in claim 3, wherein the mixture includes from 5 to 30 weight percent of the combination of cholesteryl oleate and cholesteryl chloride.

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