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PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) LIQUID CRYSTAL DISPLAY ELEMENT HAVING STORAGE

(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:—

This invention relates to an electro-optical element.

According to the invention we provide an electro-optical element comprising a substantially transparent liquid mixture and means for applying a voltage for causing said mixture to form a highly light scattering emulsion-like state, said mixture being capable of remaining in said highly light scattering emulsion-like state upon the removal of the voltage causing it to enter said state.

The mixture includes cholesterol, a cholesterol derivative or a cholesteric liquid crystal compound with a nematic liquid crystal of the type that exhibits non-destructive turbulent motion when an electric current of sufficient magnitude is passed therethrough.

In the accompanying drawings:

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;

FIGURE 3 is a perspective, partially cut away view of an electro-optical device embodying the invention;

FIGURE 4 is a graph, showing the rate of decay of brightness due to scattering, of a liquid crystal element embodying the invention.

As shown in the drawings, liquid crystal molecules 11 are arranged in the manner shown in FIGURE 1 when in their mesomorphic state. As contrasted to ordinary liquids wherein the molecules assume essentially completely random orientations, small groups of the molecules may be in align-

ment with one another. These groups may be termed domains. The orientations of the domains relative to one another is random and in view of the fact that the number of molecules in each domain is relatively small, the liquid crystal appears to be relatively transparent. This is termed their unexcited state.

In the use of a nematic liquid crystal in display and other applications, the crystal is located between two conducting elements, shown schematically at 10 and 12 in FIGURE 2, and a current is injected into the liquid crystal at a field greater than the dynamic scattering threshold electric field of the crystal. This applied electric field causes a number of the domains of FIGURE 1 to become aligned so that each domain becomes relatively large. While it may appear that the electric field also should align the relatively large domains with one another, it has been discovered that when the liquid crystal is operated in this manner, the domains exhibit turbulent motion, as indicated schematically by the arrows such as 14 and 15. This is termed their excited state. The effect on the eye of such movement is that of scattering light which is incident on the liquid crystal. Contrast ratios due to such scattering of more than 10 to 1 have been observed. In other words, the brightness of scattered light from a thin film of liquid crystal in the presence of incident light (this normally is unpolarized light) may be more than 10 times greater during the time the domains are in a turbulent state as shown in FIGURE 2 than during the time the liquid crystal is in an unexcited state as shown in FIGURE 1. Generally, the liquid crystals relax to their unexcited state within about 100 milliseconds after the removal of the exciting electric field.

In practice, a liquid crystal display includes two planar elements with a thin liquid film between them. One of the elements may be transparent and the other reflective. Row and column conductors, which may be transparent conductors, may be in contact with the

liquid crystal for exciting selected areas of the liquid crystal. Reflective displays as well as displays modulating the transmission or absorption of light can be produced.

5 It has now been discovered that by providing a mixture comprised of at least one nematic liquid crystal of the type which exhibits turbulent motion as described above with either cholesterol and/or cholesterol derivatives and/or cholesteric liquid crystals, 10 the time required for the liquid crystal mixture to return to its transparent state can be extended to as much as several weeks. This can be employed to give displays having 15 storage. It has additionally been discovered that the mixture can be returned to its transparent state in a matter of milliseconds by the application of a relatively high frequency A.C. field to the liquid crystal mixture. This 20 return to the transparent state is termed erasure.

It is believed that in its quiescent or un-excited state the liquid crystal mixture consists of an essentially single phase homogeneous molecular solution of guest molecules of a cholesteric liquid crystal, cholesterol or cholesterol derivatives in a host nematic liquid crystal. This single phase molecular solution is essentially transparent. When a 25 D.C. or a low frequency A.C. field which causes an electric current in the mixture is applied thereto the nematic liquid crystals go into turbulent motion as previously described in connection with FIGURE 2. It is 30 hypothesized that when this happens the single phase molecular solution of the guest molecules in the nematic host separates into two separate phases, a nematic host phase and a cholesterol or cholesteric guest phase, and 35 the mixture resembles an emulsion. Light scattering at this instant in time is believed to be due to the combined effect of the turbulent motion of the nematic liquid crystal phase and to the passage of incident light 40 through many interfaces of the two separate phases which possess different indices of refraction. When the exciting field is removed the turbulent motion of the nematic crystals ceases but the mixture remains in a two 45 phase emulsion-like state for a period of time which depends on the particular mixture. The retention of this state results in the continued light scattering after removal of the exciting field. This state is termed 50 the storage state. It is further hypothesized that the application of a relatively high frequency field to the mixture in the storage state breaks down the emulsion and causes the mixture to reform an essentially single 55 phase substantially transparent solution. This explains the erasure feature of the device. 60

grid optical display device 30. The device 65 consists of back and front transparent support plates 31 and 32, respectively. The plates 31 and 32 are parallel and are separated by a distance of about 1/4 mil. On the inner 70 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 75 front and back conductive strips 35 and 36 are mutually perpendicular.

The space between the front and back plates 31 and 32 is filled with a liquid mixture 37 comprising 80 weight percent of a nematic liquid crystal composition and 20 80 weight percent of cholesterol derivatives. The nematic composition consists mainly of an equal weight ratio of anisylidene - *p* - amino phenylacetate, *p* - *n* - butoxybenzylidene - *p* - aminophenylacetate and anisylidene - *p* - 85 aminophenylbutyrate. The cholesterol derivatives consist mainly of 23 weight percent of cholesteryl chloride and 77 weight percent of cholesteryl oleate i.e. approximately in the ratio of 1:3. The mixture may be sealed 90 in the device 30 by using epoxy cement around the edges of the device 30.

Also shown in FIGURE 3 is a schematic representation of a selection circuit which 95 may be used for operating the device. The selection circuit for purposes of this application is illustrated as a group of mechanical switches the details of which is given below. As appreciated by those skilled in the art, 100 in practice, electronic switches such as transistors, diodes, or the like, may be used instead. Such circuits are in themselves well known and are therefore not illustrated herein.

The circuit shown includes a back electrode strip commutator switch 41 having its 105 common contact connected to one central terminal of a double pole double throw switch 42 and to ground 43. The commutator contacts of the commutator switch 41 are connected to each of the back electrode strips 35 through connecting leads 44, as shown. A 110 front electrode strip commutator switch 45 is provided which has its commutator contacts connected to the front electrode strips 36 through connecting leads 46, and has its common contact 47 connected to a second 115 central terminal of the double pole double throw switch 42. One set of poles of the double pole double throw switch 42 is connected to a D.C. or a low frequency A.C. 120 power supply 48 used for writing information onto the device 30. The other set of poles of the double pole double throw switch 42 is connected to a high frequency A.C. 125 power supply 49 used for erasing the previously written information. Hence, the power supplies 48 and 49, for writing and erasing, are alternatively serially connected to the dis-

EXAMPLE 1

FIGURE 3 is an example of a preferred liquid crystal element in the form of a crossed

play device 30 by the double pole double throw switch 42 through the commutator switches 41 and 45 so as to activate or erase one element at a time of the device 30 depending upon the position of the commutator contacts.

In operation, the device 30 is normally substantially transparent to light incident upon it. By applying a D.C. voltage, of for example 50—100 volts, or a low frequency A.C. voltage, of for example 50—100 volts at 30—120 Hertz, across the intersection of any of the conductive strips 35 and 36, the region of the liquid mixture 37 in this intersection will scatter light incident upon it. Upon removal of the voltage, light will still be scattered in this region until the mixture thermally relaxes and returns to its unexcited state or until a high frequency A.C. voltage of for example 100 volts at 1200 to 2000 Hertz is applied to the intersection whereupon the mixture 37 returns to its transparent unexcited state within the order of about 10 milliseconds. Complete thermal relaxation to the transparent state may take several weeks or longer at room temperature. This relaxation time is substantially decreased at increased operating temperatures. After three days at room temperature the contrast ratio of this cell was reduced by about 25 percent.

EXAMPLE 2

In this example, the device 30 or a similar device is comprised of a mixture of the same compounds as described in Example 1 except that the nematic liquid crystal composition comprises 90 weight percent of the total mixture and the cholesterol derivatives comprise 10 weight percent of the mixture. With this mixture, scattering can be produced with only 35 volts D.C. or 60—110 volts A.C. at 30 Hertz. Erasure of the light scat-

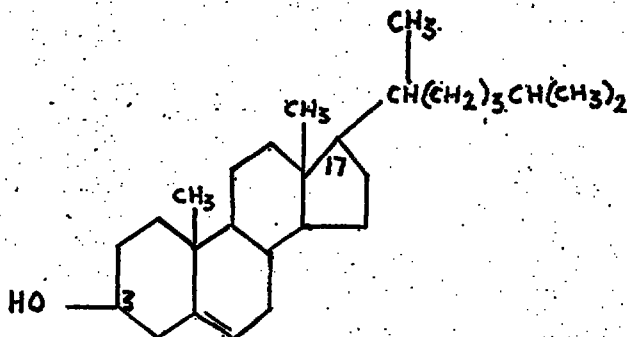
tering can be accomplished with from 60—100 volts A.C. at about 600 Hertz. The contrast ratios between the light scattering region and an adjacent transmitting region is in the order of about 6:1. This value depends on the particular mixture being used and the voltage and temperatures to which it is subjected. The configuration given by way of example is not meant to be limiting and any electro-optic light valve comprising a liquid mixture as taught herein are included in this invention.

Generally any liquid mixture characterized in that the mixture is normally in a substantially transparent single phase which can be converted to a light scattering multiphase mixture upon the application of an electric field can be employed in the device.

Mixtures found useful in the practice of this invention include a nematic liquid crystal composition of the type that exhibits turbulent motion when an above threshold electric current is passed therethrough.

Examples of these materials are alkoxy benzylidene - *p* - aminophenylesters such as *p* ethoxybenzylidene - *p* aminophenylacetate and aminophenylalkoxy - *p* - benzylidene esters such as *p* aminophenylmethoxy - *p* - benzylidenepropionate, and mixtures thereof. Further examples of useful nematic compositions can be found with reference to Table 1. The useful mixtures also include either cholesterol, cholesterol derivatives or cholesteric liquid crystals or mixtures thereof. Any cholesterol derivative and/or any cholesteric liquid crystal can be used. It is preferred that the nematic composition comprise at least 50 weight percent of the total mixture and more preferably from about 75 to 95 weight percent of the mixture.

Cholesterol is represented by the structural formula:



The preferred cholesterol derivatives are those wherein substitutions are made at the 3 and 17 positions. For example, substitution for the OH by; saturated or unsaturated, aliphatic or aromatic esters or ethers, halogens,

nitrate, sulfonate, and cinnamate, or substitution of the hydrocarbon chain at the 17 position by modifications in the chain and/or chain length result in preferred cholesterol derivatives. Still other examples of cholesterol

derivatives useful herein are cholest - 4 - en - 3 - one, cholestanylbenzoate and stigmasterol derivatives. Examples of useful cholesteric liquid crystals are *p* - (4 - cyano - benzylamino) - cinnamic acid active amyl ester, and *p* - (4 - methoxybenzylamino) - cinnamic acid active amyl ester. Further and more specific examples of cholesterol derivatives and cholesteric liquid crystals useful in the device are listed in Table 1.

TABLE 1
Compounds Useful in the Device

	Nematic Liquid Crystals
15	<i>p</i> - <i>n</i> - anisylidene - <i>p'</i> - aminophenylacetate
	<i>p</i> - <i>n</i> - butoxybenzoic acid dimer
	<i>p</i> - <i>n</i> - butoxybenzylidene - <i>p'</i> - amino - phenylacetate
	<i>p</i> - <i>n</i> - octoxybenzylidene - <i>p'</i> - amino - phenylacetate
20	<i>p</i> - <i>n</i> - benzylideneacetate - <i>p'</i> - amino - phenylethoxide
	<i>p</i> - <i>n</i> - anisylidene - <i>p'</i> - aminophenyl - butyrate
25	<i>p</i> - <i>n</i> - butoxybenzylidene - <i>p'</i> - amino - phenylpentoate
	<i>p</i> - <i>n</i> - hexoxybenzylidene - <i>p'</i> - amino - phenylacetate
	<i>p</i> - iso - pentoxybenzylidene - <i>p'</i> - amino - phenylacetate
30	<i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylmethoxide
	<i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylhexoxide
35	<i>p</i> - <i>n</i> - nonoxybenzylidene - <i>p'</i> - amino - phenylacetate
	<i>p</i> - <i>n</i> - anisylidene - <i>p'</i> - aminophenyl - pentoate
	<i>p</i> - <i>n</i> - propoxybenzylidene - <i>p'</i> - amino - phenylacetate
40	<i>p</i> - <i>n</i> - propoxybenzylidene - <i>p'</i> - amino - phenylbutyrate
	<i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylpropoxide
45	<i>p</i> - <i>n</i> - benzylideneacetate - <i>p'</i> - amino - phenylmethoxide
	Cholesterol Derivatives and Cholesteric Liquid Crystals
	Stigmasterol
50	Cholesteryl Palmitate
	Cholesteryl Decanoate
	Cholesteryl Laurate
	Cholesteryl Propionate
	Cholesteryl Heptafluorobutyrate
55	Cholesteryl 2-Furoate
	Cholesteryl Cinnamate
	Cholesteryl Cyclohexanecarboxylate
	Cholesteryl Anisoate
	Dicholesteryl Phthalate
	Cholesteryl <i>p</i> -Nitrobenzoate
60	Cholesteryl <i>p</i> -Phenylazobenzoate
	Cholesteryl 3, 5 - Dinitrobenzoate

	Cholesteryl 2 - (Ethoxyethoxy)ethyl Carbonate
65	Cholesteryl 2 - (2 - Methoxyethoxy)ethyl Carbonate
	Cholesteryl Geranyl Carbonate
	Cholesteryl Octadecyl Carbonate
	Cholesteryl 2 - Propyn - 1 - yl Carbonate
70	Cholesteryl 2 - Methyl - 2 - propene - 1 - yl Carbonate
	Allyl Cholesteryl Carbonate
	Cholesteryl 2, 2, 2 - Trifluoroethyl Carbonate
	Cholesteryl Methyl Carbonate
	Cholesteryl Cinnamyl Carbonate
75	Cholesteryl <i>p</i> - Menth - 1 - en - 8 - yl Carbonate
	Cholesteryl Nitrate
	Cholestanyl Propynyl Carbonate
80	3 β - Chlorocholest - 5 - ene
	Cholesteryl Methanesulfonate
	5 α - Cholestan - 3 β - yl Chloroformate
	Cholesteryl Chloroformate
	5 α - Cholestan - 3 β - ol

FIGURE 4 is a graph showing the thermal decay of scattering as a function of time after the removal of the voltage which initiated the scattering effect. Brightness due to scattering is plotted as the ordinate in arbitrary units and time in minutes is plotted on the abscissa. A test cell was comprised of parallel glass plates separated by a 1/2 mil thick layer of a mixture of 10 weight percent cholesteryl nitrate, 30 weight percent anisylidene - *p* - aminophenylacetate, 30 weight percent panisylidene - *p* - amino - phenylbutyrate and 30 weight percent *p* - *n* - butoxybenzylidene - *p* - aminophenylacetate. These nematic materials comprise between 80 to 90 percent of the total weight of the mixture. The inner face of one glass plate was coated with aluminum and the inner face of the other glass plate was coated with conductive transparent tin oxide. These coatings served as conductive contacts. The cell, maintained at 28° C. was excited to its light scattering state by a D.C. voltage. The voltage was removed shortly thereafter and the brightness of scattered light from the cell was measured as a function of time. The brightness of this particular mixture at 28° C. is shown to be reduced by about 75 percent of its initial brightness in about 10 minutes. If one compares this to the relaxation rate of the mixture of Example 1, it can be seen that the relaxation rate and hence the storage time is greatly dependent upon the particular composition of the mixture.

WHAT WE CLAIM IS:—

1. An electro-optical element comprising a substantially transparent liquid mixture and means for applying a voltage for causing said mixture to form a highly light scattering emulsion-like state, said mixing being capable of remaining in said highly light scatter-



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derivatives useful herein are cholest - 4 - en - 3 - one, cholestanylbenzoate and stigmasterol derivatives. Examples of useful cholesteric liquid crystals are *p* - (4 - cyano - benzalamino) - cinnamic acid active amyl ester, and *p* - (4 - methoxybenzylamino) - cinnamic acid active amyl ester. Further and more specific examples of cholesterol derivatives and cholesteric liquid crystals useful in the device are listed in Table 1.

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	Nematic Liquid Crystals
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20	<i>p</i> - <i>n</i> - benzylideneacetate - <i>p'</i> - amino - phenylethoxide <i>p</i> - <i>n</i> - anisylidene - <i>p'</i> - aminophenyl - butyrate <i>p</i> - <i>n</i> - butoxybenzylidene - <i>p'</i> - amino - phenylpentoate <i>p</i> - <i>n</i> - hexoxybenzylidene - <i>p'</i> - amino - phenylacetate <i>p</i> - iso - pentoxybenzylidene - <i>p'</i> - amino - phenylacetate
30	<i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylmethoxide <i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylhexoxide <i>p</i> - <i>n</i> - nonoxybenzylidene - <i>p'</i> - amino - phenylacetate <i>p</i> - <i>n</i> - anisylidene - <i>p'</i> - aminophenyl - pentoate <i>p</i> - <i>n</i> - propoxybenzylidene - <i>p'</i> - amino - phenylacetate
40	<i>p</i> - <i>n</i> - propoxybenzylidene - <i>p'</i> - amino - phenylbutyrate <i>p</i> - <i>n</i> - benzylidenebutyrate - <i>p'</i> - amino - phenylpropoxide <i>p</i> - <i>n</i> - benzylideneacetate - <i>p'</i> - amino - phenylmethoxide
45	
	Cholesterol Derivatives and Cholesteric Liquid Crystals
50	Stigmasterol Cholesteryl Palmitate Cholesteryl Decanoate Cholesteryl Laurate Cholesteryl Propionate Cholesteryl Heptafluorobutyrate Cholesteryl 2-Furoate
55	Cholesteryl Cinnamate Cholesteryl Cyclohexanecarboxylate Cholesteryl Anisoate Dicholesteryl Phthalate Cholesteryl <i>p</i> -Nitrobenzoate
60	Cholesteryl <i>p</i> -Phenylazobenzoate Cholesteryl 3, 5 - Dinitrobenzoate

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Cholesteryl 2 - Propyn - 1 - yl Carbonate	
Cholesteryl 2 - Methyl - 2 - propene - 1 - yl Carbonate	70
Allyl Cholesteryl Carbonate	
Cholesteryl 2, 2, 2 - Trifluoroethyl Carbonate	
Cholesteryl Methyl Carbonate	
Cholesteryl Cinnamyl Carbonate	
Cholesteryl <i>p</i> - Menth - 1 - en - 8 - yl Carbonate	75
Cholesteryl Nitrate	
Cholestanyl Propynyl Carbonate	
3 β - Chlorocholest - 5 - ene	
Cholesteryl Methanesulfonate	80
5 α - Cholestan - 3 β - yl Chloroformate	
Cholesteryl Chloroformate	
5 α - Cholestan - 3 β - ol	

FIGURE 4 is a graph showing the thermal decay of scattering as a function of time after the removal of the voltage which initiated the scattering effect. Brightness due to scattering is plotted as the ordinate in arbitrary units and time in minutes is plotted on the abscissa. A test cell was comprised of parallel glass plates separated by a 1/2 mil thick layer of a mixture of 10 weight percent cholesteryl nitrate, 30 weight percent anisylidene - *p* - aminophenylacetate, 30 weight percent *p* - anisylidene - *p* - aminophenylbutyrate and 30 weight percent *p* - *n* - butoxybenzylidene - *p* - aminophenylacetate. These nematic materials comprise between 80 to 90 percent of the total weight of the mixture. The inner face of one glass plate was coated with aluminum and the inner face of the other glass plate was coated with conductive transparent tin oxide. These coatings served as conductive contacts. The cell, maintained at 28° C. was excited to its light scattering state by a D.C. voltage. The voltage was removed shortly thereafter and the brightness of scattered light from the cell was measured as a function of time. The brightness of this particular mixture at 28° C. is shown to be reduced by about 75 percent of its initial brightness in about 10 minutes. If one compares this to the relaxation rate of the mixture of Example 1, it can be seen that the relaxation rate and hence the storage time is greatly dependent upon the particular composition of the mixture.

WHAT WE CLAIM IS:—

1. An electro-optical element comprising a substantially transparent liquid mixture and means for applying a voltage for causing said mixture to form a highly light scattering emulsion-like state, said mixing being capable of remaining in said highly light scatter-



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ing emulsion-like state upon removal of the voltage causing it to enter said state.

2. An electro-optical element as claimed in claim 1, wherein the mixture comprises a nematic liquid crystal composition of the type that exhibits turbulent motions upon passage of an electric current therein.

3. An electro-optical element as claimed in claim 2, wherein the mixture includes at least one member of the group consisting of cholesterol, cholesterol derivatives, and cholesteric liquid crystals.

4. An electro-optical element as claimed in claim 2, wherein the nematic liquid crystal portion of said mixture comprises at least one member of the group consisting of anisylidene - *p* - aminophenylacetate, *p* - *n* - butoxybenzylidene - *p* - aminophenylacetate and anisylidene - *p* - aminophenylbutyrate.

5. An electro-optical element as claimed in claim 4, wherein the mixture includes a cholesterol derivative comprising cholesteryl oleate and cholesteryl chloride.

6. An electro-optical element as claimed in claim 4, wherein the nematic liquid crystals, anisylidene - *p* - aminophenylacetate, *p* - *n* - butoxybenzylidene - *p* - amino - phenylacetate and anisylidene - *p* - amino - phenylbutyrate are in equal proportions by weight and wherein these nematic materials

comprise between 80 to 90 percent of the total weight of the mixture.

7. An electro-optical element as claimed in claim 6 wherein the mixture includes a cholesterol derivative comprising cholesteryl chloride and cholesteryl oleate in a weight ratio of cholesteryl chloride to cholesteryl oleate of approximately 1:3.

8. An electro-optical element as claimed in any one of the preceding claims including high frequency A.C. voltage means coupled thereto for erasing images formed on said element.

9. An electro-optical element as claimed in claim 1 wherein said means for applying a voltage for causing light scattering in said liquid is D.C. or low-frequency A.C., means being provided for applying a high frequency electric field to said composition for erasing said light-scattering.

10. An electro-optical element substantially as in any of the examples hereinbefore described.

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