

(4)

PATENT SPECIFICATION

(11) 1 556 311

1 556 311

- (21) Application No. 36777/77 (22) Filed 2 Sept. 1977
(31) Convention Application No. 51/106 394
(32) Filed 6 Sept. 1976
(31) Convention Application No. 51/108 366
(32) Filed 9 Sept. 1976
(31) Convention Application No. 51/117 399
(32) Filed 30 Sept. 1976 in
(33) Japan (JP)
(44) Complete Specification published 21 Nov. 1979
(51) INT CL² C09K 3/34//G02F 1/13
(52) Index at acceptance C4X 12



(54) A LIQUID CRYSTAL COMPOSITION

(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 liquid crystal display devices.

Two types of nematic liquid crystal display devices are in current use:

(1) In a dynamic scattering mode (DSM) display device an ionic material is added to a nematic liquid crystal material of negative dielectric anisotropy, and light scattering phenomena resulting from an applied electric field is used to produce display.

(2) In a field effect mode (FEM) display device a nematic liquid crystal material of positive dielectric anisotropy has its molecular axes orientated in a given manner, e.g. helically, between electrode plates. By employing two polarization filters, a display can be produced by controlling the optical activity of the liquid crystal material when an electric field is applied.

FEM display devices are now mainly used because they have lower consumption than DSM display devices. However, FEM display devices have a basic defect in that the polarization filters darken the display produced. There is no problem in a transparent or "see through" type of FEM display device but is fairly disadvantageous in a reflection-type FEM display device having a low power consumption such as that used for a wristwatch or a portable computer.

A DSM display device of the reflection type needs a specular surface and this restricts the range of viewing angles and increases power consumption and reduces contrast.

According to one aspect of the present invention there is provided a liquid crystal composition for use in a liquid crystal display device comprising a non-steriodal cholesteric liquid crystal material having positive dielectric anisotropy consisting of at least one optically active liquid crystal compound with relatively weak negative dielectric anisotropy, at least one optically active compound with relatively strong positive dielectric anisotropy and a dyestuff whose absorption spectrum for light is different in the direction of the long molecular axis from that in the direction of the short molecular axis.

The dyestuff may be any one or more of methyl red, Sudan black B, indole blue and the compounds specified in Table III.

The liquid crystal material may comprise any one or more of the compounds specified in Table I.

According to a further aspect of the present invention there is provided a liquid crystal display comprising a liquid crystal composition as recited above sandwiched between a pair of plates carrying electrodes which are in contact with the liquid crystal composition. Preferably one of the electrodes is made of a highly reflective material. The highly reflective material may be aluminium, silver or gold.

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

Figures 1 to 3 illustrate the principle of a liquid crystal display device according to the present invention; and

Figure 4 is a schematic diagram of a liquid crystal display device according to the present invention.

The principle of a liquid crystal display device according to the present invention is illustrated in Figure 1. A non-steroidal cholesteric liquid crystal material 1 of positive dielectric anisotropy assumes a structure with a spatial period or half pitch 2 when in contact with a substrate. When a multicolor dyestuff 5 is added to the nematic liquid crystal material 1 to form a non-steroidal liquid crystal composition 6 (Figure 2), the molecules of the dyestuff 5 enter into the structure as shown in Figure 2, the liquid crystal composition being disposed between electrodes 3, 4. Therefore, compared to the case where the molecules of the dyestuff are randomly mixed with nematic liquid crystal material, the efficiency of absorption of color at the same concentration is enhanced.

With an electric field larger than a certain threshold value depending upon the liquid crystal composition is applied, the structure of the molecules 11 of the liquid crystal composition is destroyed and the molecules become aligned with the direction of the electric field as shown in Figure 3. Figure 3 shows the electrodes 3, 4 in greater detail consisting of flat transparent plates 7, 9, with respective conductive films 8, 10 thereon. When an electric field is impressed between the conductive films 8, 10 by an electric power source 13, the molecules 11 of the liquid crystal composition 6 and the molecules 12 of the dyestuff 5 become orientated with the electric field.

The absorption spectrum for light of the molecules of the dyestuff for the long axis is different from that for the short axis. Thus if the molecules of the dyestuff are seen from the direction of the long axis they appear coloured and if they are seen from the direction of the short axis they appear to be of a different colour or clear. Thus a color display is produced on a colourless or differently coloured background.

To increase contrast, a highly reflective substance such as aluminium, silver, or gold is used in one embodiment of a liquid crystal display device according to the present invention to enhance clearness of the display. This form of liquid crystal display device is shown in Figure 4. On the inner surface of a flat plate 15 made of transparent material, such as glass, there is formed a transparent conductive film 16 along the inner surface of a flat plate 18 there is formed an aluminium thin film 19 having slight convexity or concavity. A liquid crystal composition 20 according to the present invention is sealed, by means of a spacer 17, of, for example, glass frit, polyester etc between the plates 15, 18. Electrical lead wires are taken from the films 16, 19 and connected to an electric power source 21 and a switch 22.

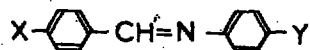
This liquid crystal display device produces a clear display in which numerals and letters of pure white color are produced upon a coloured background. If the film 19 is of gold having slight convexity or concavity a gold-coloured display is produced upon a coloured background. Since the film 19 is formed by an evaporation technique, plating technique or other means it is exceedingly bright thus producing the white display in the case where the film 19 is made of aluminium or silver.

Since the liquid crystal display device is of the type where there is a phase shift from the cholesteric phase to the nematic phase under the influence of an electric field, the response time, voltage-contrast characteristics, etc., are suitable for multiframe time division driving.

A liquid crystal composition according to the present invention includes at least one optically active liquid crystal compound with relatively weak negative dielectric anisotropy, examples of which are given in Table I.

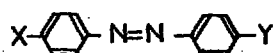
TABLE I

(1) Schiff compounds



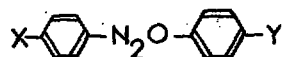
	X	Y	Temperature range of liquid crystal phase
1	CH ₃ O	$-\text{CH}_2-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_2\text{H}_5$	23 (°C) (monotropic)
2	C ₂ H ₅ O	„	25 ~ 58 (°C)
3	C ₃ H ₇ O	„	31 ~ 41 (°C)
4	C ₄ H ₉ O	„	30 ~ 56 (°C)

(2) Azo compounds



	X	Y	Range of temperature of liquid crystal phase
5	C ₂ H ₅ O	$-\text{CH}_2-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_2\text{H}_5$	47 ~ 65 (°C)
6	C ₃ H ₇ O	„	34 ~ 42 (°C)
7	C ₄ H ₉ O	„	36 ~ 59 (°C)
8	C ₅ H ₁₁ O	„	34 ~ 50 (°C)
9	C ₆ H ₁₃ O	„	37 ~ 59 (°C)

(3) Azoxy compounds



	X	Y	Range of temperature of liquid crystal phase
10	CH ₃ O	$-\text{CH}_2-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_2\text{H}_5$	41 ~ 53 (°C)
11	C ₂ H ₅ O	„	4 ~ 76 (°C)
12	C ₃ H ₇ O	„	33 ~ 59 (°C)
13	C ₄ H ₉ O	„	46 ~ 73 (°C)
14	C ₆ H ₁₃ O	„	52 ~ 73 (°C)

10

4

1,556,311

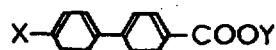
4

(4) Ester compounds



	X	Y	Range of temperature of liquid crystal phase
15	$\text{C}_2\text{H}_5-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\text{O}-$	OCH_3	$24 \sim 30 (^{\circ}\text{C})$

(5) Biphenyl compounds



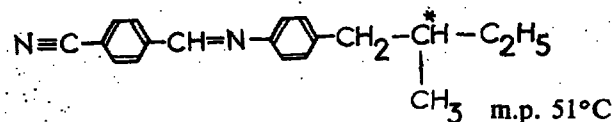
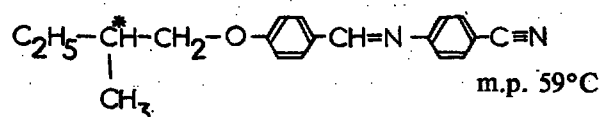
	X	Y	Range of temperature of liquid crystal phase
16	$\text{C}_6\text{H}_{11}\text{O}$	$\text{C}_2\text{H}_5-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-$	$58 \sim 64 (^{\circ}\text{C})$
17	$\text{C}_7\text{H}_{15}\text{O}$	„	$44 \sim 64 (^{\circ}\text{C})$

It is advantageous to use in a liquid crystal composition according to the present invention optically active compounds with relatively weak negative dielectric anisotropy. For example, if equal amounts of Nos. 2 and 3 are mixed, a non-steroidal liquid crystal material having a liquid crystal phase between 5°C and 50°C is obtained. Similarly, by mixing 70% of No. 11 and 30% of No. 15 a non-steroidal liquid crystal material having a liquid crystal phase between -10°C and 65°C is obtained.

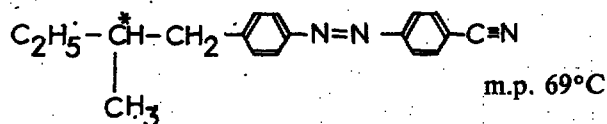
A liquid crystal composition according to the present invention also includes at least one optically active compound with relatively strong positive dielectric anisotropy, such as those specified in Table II.

TABLE II

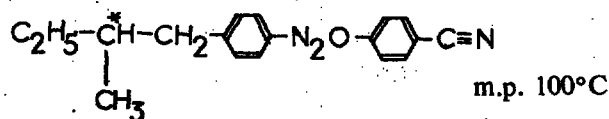
(1) Schiff compounds



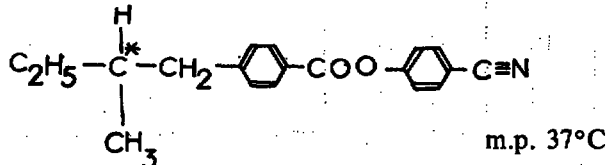
(2) Azo compounds



(3) Azoxy compounds



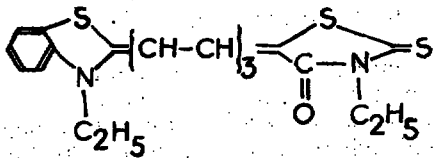
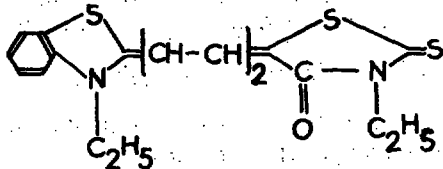
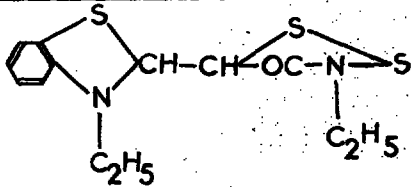
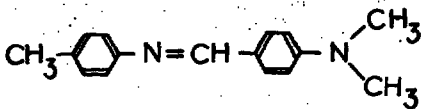
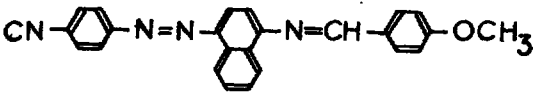
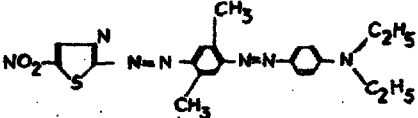
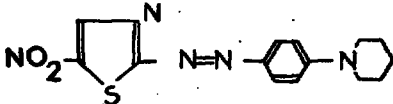
(4) Ester compounds



By mixing 5% to 40% by weight of one or more of these compounds having relatively strong positive dielectric anisotropy with one or more compounds having relatively weak negative dielectric anisotropy, a non-steroidal cholesteric liquid crystal composition with a threshold voltage of 3V to 15V is obtained.

A liquid crystal composition according to the present invention also includes a dyestuff whose absorption spectrum for light is different in the direction of the long molecular axis from that in the direction of the short molecular axis. As such dyestuffs there may be used methyl red, but other dyestuffs such as Sudan black B, indole blue and those listed in the Table III may be used.

TABLE III

Multicolour dyestuff	maximum absorption wavelength
	640 nm
	610 nm
	580 nm
	415 nm
	450 nm
	595 nm
	595 nm

A liquid crystal composition according to the present invention comprises a non-steroidal cholesteric liquid crystal material, such as those described above in admixture with a multicolour dyestuff and is sandwiched between two electrodes one of which at least has a transparent conductive film thereon. When an electric field is applied to the composition a coloured display due to the multicolour dyestuff is produced. A liquid crystal display device according to the present invention may be made to have a response time of several tens of milliseconds

which is considerably quicker than conventional liquid crystal display devices. Moreover, because of the steep rise in the voltage contrast characteristics curve, it is adaptable to multifigure time division driving (dynamic driving). A liquid crystal display device according to the present invention is most suitable for use in portable computers, wristwatches and as a simple alphanumeric display in information terminal devices.

WHAT WE CLAIM IS:—

1. A liquid crystal composition for use in a liquid crystal display device comprising a non-steroidal cholesteric liquid crystal material having positive dielectric anisotropy consisting of at least one optically active liquid crystal compound with relatively weak negative dielectric anisotropy, at least one optically active compound with relatively strong positive dielectric anisotropy and a dyestuff whose absorption spectrum for light is different in the direction of the long molecular axis from that in the direction of the short molecular axis.

2. A composition as claimed in claim 1 in which the dyestuff is any one or more of methyl red, Sudan black B, indole blue and the compounds specified in Table III.

3. A composition as claimed in claim 1 or 2 in which the liquid crystal material comprises one or more of the compounds specified in Table I.

4. A liquid crystal display device comprising a liquid crystal composition as claimed in any preceding claim sandwiched between a pair of plates carrying electrodes which are in contact with the liquid crystal composition.

5. A display device as claimed in claim 4 in which one of the electrodes is made of a highly effective material.

6. A display device as claimed in claim 5 in which the highly reflective material is aluminium, silver or gold.

7. A liquid crystal display device substantially as herein described with reference to and as shown in Figure 4 of the accompanying drawings.

J. MILLER & CO.,
Chartered Patent Agents,
Agents for the Applicants,
Lincoln House,
296—302 High Holborn,
London WC1V 7JH.



12
6

1,556,311

6

5 which is considerably quicker than conventional liquid crystal display devices. Moreover, because of the steep rise in the voltage contrast characteristics curve, it is adaptable to multifigure time division driving (dynamic driving). A liquid crystal display device according to the present invention is most suitable for use in portable computers, wristwatches and as a simple alphanumeric display in information terminal devices. 5

WHAT WE CLAIM IS:—

- 10 1. A liquid crystal composition for use in a liquid crystal display device comprising a non-steroidal cholesteric liquid crystal material having positive dielectric anisotropy consisting of at least one optically active liquid crystal compound with relatively weak negative dielectric anisotropy, at least one optically active compound with relatively strong positive dielectric anisotropy and a dyestuff whose absorption spectrum for light is different in the direction of the long molecular axis from that in the direction of the short molecular axis. 10
- 15 2. A composition as claimed in claim 1 in which the dyestuff is any one or more of methyl red, Sudan black B, indole blue and the compounds specified in Table III. 15
- 20 3. A composition as claimed in claim 1 or 2 in which the liquid crystal material comprises one or more of the compounds specified in Table I. 20
4. A liquid crystal display device comprising a liquid crystal composition as claimed in any preceding claim sandwiched between a pair of plates carrying electrodes which are in contact with the liquid crystal composition.
- 25 5. A display device as claimed in claim 4 in which one of the electrodes is made of a highly effective material. 25
6. A display device as claimed in claim 5 in which the highly reflective material is aluminium, silver or gold.
7. A liquid crystal display device substantially as herein described with reference to and as shown in Figure 4 of the accompanying drawings.

**J. MILLER & CO.,
Chartered Patent Agents,
Agents for the Applicants,
Lincoln House,
296—302 High Holborn,
London WC1V 7JH.**

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.