

Bistable ferroelectric liquid crystal display

The invention relates to a liquid crystal display cell having a chiral ferroelectric smectic liquid crystal layer consisting of an achiral S_c host mixture consisting of at least two liquid crystal components, at least one of which has a tilted smectic phase (e.g. S_c), and one or more chiral dopants which individually or together induce a helical pitch $p < 1\mu m$ in the mixture, with a spontaneous polarisability $P > 10$ nC/cm² and an S_c tilting angle of $\theta > 10^\circ$, and the structure of which can be so influenced by the action of an electric field that its optical anisotropy changes, a pair of transparent plates enclosing the liquid crystal and comprising electrodes for generating an electric field therein, at least one plate having a surface structure which aligns the molecules of the liquid crystal, and two crossed polarisers, one disposed in front of and one behind the liquid crystal cell.

Liquid crystal cells of the aforementioned kind, depending on the nature of the liquid crystal, react in various ways when a strong electric field (e.g. 10 V/ μ) is switched on or off. In most cases, switching-on results in an approximately homogenous structure (possibly with a number of dislocations) whereas switching-off may result in a helix, as is the case in DHF cells, the basics of which are described in B. I. Ostrovski, *Advances in Liquid Crystal Research and Applications*, Oxford/Budapest, 1980, pages 469 ff. A DHF cell usable in practice was described for the first time in EP-A-309 774. It comprises a layer of high-

twist ferroelectric liquid crystal with the helix axis parallel to the defining plates. Application of a voltage between the plates so deforms the helix that the transmission changes in combination with the polarisers disposed in front of and behind the liquid crystal layer.

The known Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) effect of Lagerwall and Clark is different in nature, its main characteristic being that the helix which normally forms in the liquid crystals is suppressed by interaction with the surface. In order for the suppression to occur, the pitch of the helix must be considerably longer than the thickness of the display. This effect is described in Mol. Cryst. Liq. Cryst. 94 (1983), 213-134 and 114 (1984), 151-187.

European patent application EP-A-0 283 916 (No. 88104176.8) describes another liquid crystal display which also uses liquid crystals having a small pitch. In this device, the structure of the liquid crystal in the cell comprises homogeneously oriented boundary layers (as in SSF-LCDs) and a helix structure in the interior of the cell.

The disadvantages of the known cells is that the critical wall orientation causes difficulties. Also, the "memory switching angles" are considerably smaller than the optimum of 45°. The aim of the invention is to eliminate these disadvantages.

According to the invention, this is achieved by a cell of the initially-described kind, characterised by the features disclosed in claim 1.

It has surprisingly been found that if the liquid crystal has the right composition the helix does not form or its formation is greatly delayed (for seconds to hours) and the homogeneous structure is maintained in that it is stabilised by a network of parallel dislocations visible as dark lines under crossed polarisers. If a field is briefly applied in the opposite direction, a homogeneous structure again forms but its optical axis is rotated from the first direction through the "bistable switching angle". This can be used for bistable switching between two stable or quasi-stable positions of the director.

This effect is also observable in thick cells (e.g. 25 μ). This is in contrast to the SSFLC effect.

The cell according to the invention has a number of important advantages.

It has great brightness. In contrast to SSF-LCDs, the "memory switching angle" is almost the same as the switching angle on saturation, i.e. the bistable structure is efficiently stabilised even at zero voltage. As a result, optimum memory switching angles (45°) are obtainable.

The cell has short switching times. It is because the LC mixtures have high spontaneous polarisation, that

the switching times are correspondingly short. There are no problems of 'pitch compensation' or the like.

The choice of cell thickness is relatively unrestricted. The bistability is not due to a surface effect, and consequently there is no restriction in the choice of cell thickness. However, thin cells are best ($\Delta n \cdot d = \lambda/2$ with λ = wavelength (0.55 μ)).

Finally, the wall orientation is less critical than in the prior art. The bistable structure of the liquid crystal layer is substantially determined by the applied field, and the surface is not responsible for bistability but only for the alignment of the smectic planes on transition to the S_c^* phase.

Exemplified embodiments of the invention will now be described with reference to the accompanying drawings, in which:

Fig. 1 is a diagrammatic perspective view of a small portion of a liquid crystal cell according to a preferred embodiment of the invention;

Fig. 2 shows the texture of the cell in a preferred embodiment of the invention;

Fig. 3 shows the texture of a prior-art DHF cell;

Fig. 4 shows part of a pulse sequence for actuating the cell in Fig. 1, and

Fig. 5 shows the transmittance of a 1.8μ thick cell, in the case of the pulse sequence shown in Fig. 4.

As Fig. 1 shows, the liquid crystal cell comprises a liquid crystal layer 1 disposed between two substantially plane-parallel glass plates 2, 3. Instead of glass, the plates can be made from another transparent material such as acrylic glass or plastic sheets. The spacing between the plates is obtained in known manner, using polymer balls having a diameter of 2μ . The plates are thus spaced apart by $d = 1.8\mu$. A polariser 4 is disposed in front of the front plate 2 and connected thereto e.g. by sticking. A polariser 5 is similarly associated with the rear plate 3.

The surfaces of plates 2, 3 facing the liquid crystal have the conventional electrode coatings, which are segmented to represent characters or image dots. The portion of a cell shown in the drawing comprises only a single electrode segment 6 on plate 2 and a facing electrode segment 7 on the rear plate 3.

The surfaces of the glass plates facing the liquid crystal, i.e. the inner surfaces, are also treated so that they exert a directional effect on the adjacent liquid-crystal molecules and thus determine the direction of the director. In the present description, the result of this treatment is called "surface orientation".

One known method of surface orientation is to provide the inner surfaces of the glass plates with a PVA layer which is rubbed in one direction. The directions in

which the two plates are rubbed are approximately parallel.

Measurements on cells in which only one plate was rubbed, have shown that the initially-mentioned dislocation lines are rotated through an angle α of about 4 to 8° relatively to the direction of rubbing. In a given liquid crystal mixture the rotation is always in the same direction relative to the direction of the normal to the liquid crystal layer. It is therefore particularly advantageous to rub the two plates so that the dislocation lines near the plates are parallel, i.e. one plate is rubbed after being rotated through an angle 2α relatively to the other plate. This avoids disturbances to the parallelism of the dislocation lines, which would occur if the two plates were exactly parallel when rubbed.

Another possible method of obtaining optimum parallelism of the dislocation lines, is to rub only one of the two plates.

In general, it is assumed that the two bistable states become more stable when the parallelism of the dislocation lines is improved.

Another known method of surface orientation is oblique vacuum metallising of orienting layers, etc.

Surface orientation occurs mainly in the S_A phase above the S_C^* phase, the result being that the smectic planes are disposed perpendicularly to the direction of rubbing (the "bookshelf" structure). The surface

orientation on the two plates in the S_A phase is shown by the short arrows. The direction of the lines of intersection between the smectic planes and the glass plate is denoted by an arrow 8. On transition to the S_C^* phase there is no change in the direction of the planes, or at least in the direction of the straight lines of intersection between the smectic planes and the electrode surfaces. The director itself can rotate away from the direction of rubbing.

The polariser 4 belonging to the front plate is disposed at an angle β to the axis of the helix or the direction of the dislocation lines. The polariser belonging to the rear plate is rotated through an angle of 90° relatively to the front polariser. The directions of polarisation are shown by the long arrows in Fig. 1. This arrangement of polarisers is a preferred exemplified embodiment. Other arrangements are possible and likewise give good results. The suitable polariser arrangements can be determined without difficulty by simple adjustment.

The liquid crystal 1 is a chiral smectic ferroelectric crystal, frequently described as smectic C (S_C) in the literature. Liquid crystals of this kind are known from the literature. They are characterised by the fact that their molecules are disposed not at right angles to the smectic planes but at a certain angle, the smectic tilt angle θ_0 . The chirality is due to the fact that, unless influenced by walls or electric fields, the directions of the molecules are not parallel in all the layers, but are turned in different

directions in different layers, resulting in an overall helical twist.

The liquid crystal is preferably a mixture of an achiral S_c host mixture comprising at least two LC components, at least one containing a tilted smectic phase (e.g. S_c), and one or more chiral dopants which individually or together induce a helical pitch $p < 1\mu m$; the spontaneous polarisability of the total mixture being $P > 10 \text{ nC/cm}^2$ and the S_c tilt angle of the final mixture being $\theta > 10^\circ$. The following values are particularly preferred: $p < 0.8\mu m$, $P > 20 \text{ nC/cm}^2$ and $\theta > 17^\circ$.

Mixtures of the following components have been found particularly suitable:

1. 5 - 30 wt.% of a phenyl benzoate comprising a cyclohexyl radical bonded via a flexible group.

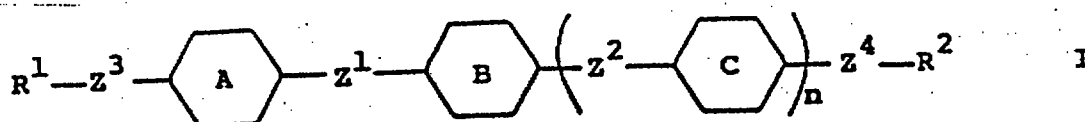
Such substances are described e.g. in EP-A-0 269 963 (formula IX).

2. 30 - 85 wt.% of other S_c materials as described in the aforementioned EP-A-0 269 963, e.g. esters (formula VI), phenyl pyrimidines (formula VII), phenyl pyridines (formula VIII), alkenyl-substituted compounds (formula X), tricyclic pyrimidines (formula XI) and dioxan derivatives (formula I).

3. 10 - 40 wt.% of chiral dopants with two terminal chiral groups as described in European patent

application EP-A-0 339 414 (No. 89106808.2) (formula I)
or in EP-A-0 213 841 and WO 87/05017.

Preferred chiral dopants include optically active
compounds having the general formula:



where n stands for the number 0 or 1; the rings A, B
and C independently denote 1,4-phenylene, unsubstituted
or substituted by halogen, cyano, methyl and/or methoxy
and in which 1 or 2 CH groups are replaced by nitrogen
if required, or one of the rings A, B and C also
denotes trans-1,4-cyclohexylene; Z¹ and Z²
independently denote a single covalent bond, -CH₂CH₂-,
-OCH₂-, -CH₂O-, -COO- or -OOC-; Z³ and Z⁴ independently
denote a single covalent bond, oxygen, -COO- or -OOC-;
R¹ and R² independently denote the radical of an
optically active terpene alcohol after splitting off
the hydroxy group or a chiral group -C*HX¹-R³,
-CH₂-C*HX¹-R³, -C*H(CH₃)-COOR³, -C*HR⁴COOR³,
-C*H(CH₃)-CH₂OR³, -C*H(CH₃)-CH₂COOR³ or
-C*H(CH₃)-CH₂CH₂OR³; C* denotes a chiral carbon atom;
X¹ denotes fluorine, chlorine, cyano, methyl, hydroxy,
methoxy or methoxycarbonyl; R³ denotes alkyl or alkenyl
and R⁴ denotes phenyl.

In the above formula I, Z¹ and Z² preferably each
denote a single covalent bond. Preferably also, all
the rings A, B and C are aromatic, more particularly

1,4-phenylene, Z^3 preferably stands for $-OOC-$ and Z^4 stands for $-COO-$.

One preferred group of chiral dopants comprises those optically active compounds of formula I in which n stands for the number 1; the rings A, B and C independently denote 1,4-phenylene unsubstituted or substituted with halogen, cyano, methyl and/or methoxy, and in which 1 or 2 CH groups are replaced by nitrogen if required. Z^1 and Z^2 each denote a single covalent bond; Z^3 denotes $-OOC-$ and Z^4 denotes $-COO-$; R^1 and R^2 independently denote the radical of an optically active terpene alcohol after splitting off the hydroxy group or a chiral group $-CH^*X^1R^3$ or $-CH_2-C^*HX^1-R_3$; C^* denotes a chiral carbon atom, X^1 denotes fluorine, chlorine, cyano, methyl or methoxy, and R^3 denotes alkyl or alkenyl.

The expression "1,4-phenylene unsubstituted or substituted with halogen, cyano, methyl and/or methoxy, in which 1 or 2 CH groups are replaced by nitrogen if required", according to the invention, comprises groups such as 1,4-phenylene, fluoro-1,4-phenylene, chloro-1,4-phenylene, cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, methyl-1,4-phenylene, methoxy-1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, pyrazine-2,5-diyl, pyridazine-3,6-diyl and the like.

The term "halogen" comprises fluorine, chlorine, bromine and iodine, preferably fluorine and chlorine.

The expression "radical of an optically active terpene alcohol after splitting off the hydroxy group" denotes

the group T of an optically active terpene alcohol having the formula TOH. The term "terpene alcohol" is well known to the skilled addressee, e.g. from Römpps Chemie-Lexikon, Volume 6 (1977), and denotes alcohols derived from monoterpenes. The term "monoterpene" includes terpene hydrocarbon $C_{10}H_{16}$ and hydrogenation and dehydrogenation derivatives thereof. The following are examples of preferred optically active terpene alcohols: (1R,2S,5R)-(-)-menthol, (1S,2R,5R)-(+)-isomenthol, (1S,2S,3S,5R)-(+)-isopinocampheol, (1S)-(-)-borneol, (1R)-(-)-myrtenol, (1S,2S,5R)-(+)-neomenthol, (-)-carveol, (+)=dihydrocarveol (+)-terpinene-4-ol, (+)- α -terpineol and the like.

The terms "alkyl" and "alkenyl" include straight-chain and branched radicals, preferably with not more than 15 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, vinyl, 1-propenyl, 1-butenyl, 1-pentenyl, allyl, 2-butenyl, 2-pentenyl, 3-butenyl, 3-pentenyl, 4-pentenyl, 5-hexenyl, 6-heptenyl and the like.

Production of chiral dopants is described in the cited references or can be carried out by similar methods.

The following compounds are examples of particularly preferred chiral dopants (C denotes a crystalline phase, S_c^* denotes a chiral smectic C phase, S_A denotes a smectic phase A, Ch denotes a cholesteric phase and I denotes the isotropic phase, the spontaneous polarisation P_s was measured for a mixture of 5 wt.% of the dopant and 95 wt.% of 4-octyloxybenzoic acid-4-

hexyloxyphenyl ester, and P_s^e is the extrapolated value of the spontaneous polarisation):

4,4"-di-[2(R)-cyano-1-propyloxycarbonyl]-p-terphenyl,
m.p. 179, 2°C, $P_s = 5.53\text{nC/cm}^2$, $P_s^e = 111\text{nC/cm}^2$;

4,4"-di-[2(S)-chloro-2-pentyloxycarbonyl]-p-terphenyl,
m.p. (C-S_c*) 106°C, S_c*-S_A 110,2°C, S_A-CH 140°C, clar.
temp. (CH.I) 141°C, $P_s = 6.8\text{nC/cm}^2$, $P_s^e = 136\text{nC/cm}^2$;

4,4"-di-[2(R)-chloro-4-methyl-1-pentyloxycarbonyl]-p-
terpyhenyl, m.p. 169,4-170,0°C, $P_s = 9\text{nC/cm}^2$, $P_s^e = 180\text{nC/cm}^2$;

4,4"-di-[2(S)-cyano-4-methyl-1-pentyloxycarbonyl]-p-
terphenyl, m.p. 129-131°C, $P_s = 20\text{nC/cm}^2$, $P_s^e = 400\text{nC/cm}^2$;

4,4"-di-[1(R),2(S),5(R)-menthyloxycarbonyl]-p-
terphenyl, m.p. 168-169°C, $P_s = 11\text{nC/cm}^2$, $P_s^e = 220\text{nC/cm}^2$;

4,4"-di-[2(R)-cyano-2-pentyloxycarbonyl]-p-terphenyl,
 $P_s = 20\text{nC/cm}^2$, $P_s^e = 400\text{nC/cm}^2$;

4,4"-di-[2(S)-chloro-1-butyloxycarbonyl]-p-terphenyl,
m.p. (C-S_A) 137.3°C, S_A-CH 139.3°C, clar. temp. (Ch-I)
153°C, $P_s = 3.4\text{nC/cm}^2$, $P_s^e = 68\text{nC/cm}^2$;

4,4"-di-[2(R)-cyanol-1-butyloxycarbonyl]-p-terpyhenyl,
m.p. 129.9°C, $P_s = 12.5\text{nC/cm}^2$, $P_s^e = 250\text{nC/cm}^2$;

4,4"-di-[2(R)-cyano-1-hexyloxycarbonyl]-p-terphenyl,
 $P_s = 23\text{nC/cm}^2$, $P_s^e = 460\text{nC/cm}^2$;

4,4"-di-[2(S)-chloro-3-methyl-2-butyloxycarbonyl]-p-
terphenyl, m.p. 171.1°C, $P_s = 8.0\text{nC/cm}^2$, $P_s^e = 160\text{nC/cm}^2$;

4,4"-di-[2(R)-cyano-3-methyl-1-butyloxycarbonyl]-p-
terphenyl, m.p. 132.9°C, $P_s = 11.2\text{nC/cm}^2$, $P_s^e = 224\text{nC/cm}^2$;

4,4"-di-[1(S)-(methoxycarbonyl)ethoxy]-p-terphenyl,
m.p. 142.6°C, $P_{\pi} = 15.4\text{nC/cm}^2$; $P_{\pi}^{\circ} = 308\text{nC/cm}^2$;
4,4"-di-[1(S)-(ethoxycarbonyl)ethoxy]-p-terphenyl, m.p.
91.3°C, $P_{\pi} = 13.75\text{nC/cm}^2$; $P_{\pi}^{\circ} = 275\text{nC/cm}^2$;
4,4"-di-[1(S))-methyl-2-2(ethoxycarbonyl)ethoxy]-p-
terphenyl, $P_{\pi} = 3.75\text{nC/cm}^2$; $P_{\pi}^{\circ} = 75\text{nC/cm}^2$.

The phenyl pyrimidines having the formula VII given in
EP-A-0 269 963 are particularly suitable compounds for
the aforementioned S_{π} materials. Preferably, the S_{π}
material or the achiral S_{π} host mixture contains at
least about 50 wt.% of the aforementioned compounds.

A particularly preferred mixture consists of

10 wt.% 4-decyloxy-2,3-difluorobenzoic acid-4-(2-trans-
4-heptyl cyclohexyl)ethyl]phenyl ester,

21 wt.% 5-octyl-2-(4-octyloxyphenyl)pyrimidine,

21 wt.% 5-octyl-2-(4-nonyloxyphenyl)pyrimidine,

21 wt.% 5-octyl-2-(4-decyloxyphenyl)pyrimidine,

27 wt.% 4,4"-di-[2(S)-octyloxycarbonyl]-p-terphenyl.

The exact configuration of the liquid crystal layer,
however, is not known. It is assumed that twists and
the like also occur inside the layers but are not at
present measurable. Also, the liquid crystal is in a
dynamic equilibrium, i.e. the structures are subject to
continuous changes. For this reason, no molecular
arrangement is shown in the drawings.

On the other hand, the texture of the liquid crystal in the cell is characteristic and distinguishable from other textures known in the prior art. As shown in Fig. 2, the texture recorded in a cell according to the invention with a 2 μ thick layer without an applied voltage and between crossed polarisers, is characterised by substantially parallel dislocation lines. Only one plate has a surface orientation produced by rubbing.

The texture shown for comparison in Fig. 3 was recorded in a DHF cell of similar structure, except that the two plates were rubbed parallel to one another. As can be seen, this structure has a lack of directional arrangement and thus differs greatly from the texture in Fig. 2.

The liquid crystal mixture is filled between the plates when hot, i.e. by capillary action when in the isotropic state, and is cooled to room temperature at an applied a.c. voltage of 30 V, 10 kHz.

If a voltage is applied to electrodes 6 and 7, an electric field is produced in the liquid crystal and re-orientes the molecules. In practice, the symbolically-indicated voltage source 10 delivers periodic signals or actuating pulses which can have opposite polarity in the present cell, as explained in detail hereinafter.

When the cell has been shaped by an electric field, i.e. the helix has been wound, the director, when no field is applied, is in one of two bistable positions.

If a suitably polarised voltage is applied, it can be flipped into the other stable position, thus altering the light-transmitting capacity of the cell. The optical contrast is greatest if firstly the angle β is chosen so that the light-transmitting capacity is at a minimum in one stable position, and if secondly the switching angle (the angle between the projections of the director on to the plane of the electrodes in the two stable positions) is substantially equal to 45° .

Test measurements were made on a cell having the aforementioned construction. A pulse sequence, part of which is shown in Fig. 4, was applied to the cell. The sequence increases linearly from zero to 26 V. The last pair of pulses is shown. The left bipolar pulse switches the cell from light to dark whereas the right-hand pulse switches from dark to light. The width of each positive and negative pulse is 40 μ sec. An important feature of this actuation is that the average value of the applied voltage is zero, preventing electrochemical decomposition of the liquid crystal.

As long as the pulse amplitude is below the switching time for this pulse length, there is practically no change in light-transmitting capacity, whereas complete switching occurs above this amplitude. This property is important for multiplexing. Fig. 5 shows the corresponding transmission curve for the top liquid-crystal mixture in a 1.8 μ thick cell and with the pulse sequence shown in Fig. 4 at 25°C .



C L A I M S

1. A liquid crystal display cell having a chiral ferroelectric smectic liquid crystal layer (1) consisting of an achiral S_c host mixture consisting of at least two liquid crystal components, at least one of which has a tilted smectic phase, and one or more chiral dopants which individually or together induce a helical pitch $p < 1\mu m$ in the mixture, with a spontaneous polarisability $P > 10 \text{ nC/cm}^2$ and an S_c tilting angle of $\theta > 10^\circ$, and the structure of which can be so influenced by the action of an electric field that its optical anisotropy changes in bistable manner,

a pair of transparent plates (2, 3) enclosing the liquid crystal and comprising electrodes (6, 7) for generating an electric field therein, at least one plate having a surface structure which aligns the molecules of the liquid crystal,

and two crossed polarisers (4, 5), one disposed in front of and one behind the liquid crystal cell,

characterised in that the liquid crystal composition is so selected and shaped, by application of an electric alternating field to the electrodes until the mesophase is reached, that the layer has a non-homogeneous structure having a texture of light and dark parallel strips between the crossed polarisers.



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2. A liquid crystal cell according to claim 1, characterised in that both plates (2, 3) are provided with the said surface structure and the directions of orientation are offset by 8 to 16° relatively to one another.