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(54) Title: IMPROVED LIQUID CRYSTAL MIXTURE

(57) Abstract

The invention relates to a twisted nematic liquid crystal display device operating in the high multiplex mode and having a high contrast, the improvement wherein the liquid crystal mixture has a ratio of the elastic constants $K_5/K_1$ as small as possible but not more than 0.9 and a ratio of $\Delta e/\epsilon_0$ of at most +0.5.
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Improved Liquid Crystal Mixture

The invention relates to the improvement of a twisted nematic liquid crystal display device operating in the high multiplex mode with a very high contrast and with a particularly steep electro-optical characteristic. The device is operating in the first Gooch and Tarry transmission minimum. The invention furthermore relates to new liquid crystal mixtures which are most suited for use of matrix type liquid crystal display devices driven by time sharing and which have a ratio of the elastic constants $K_3/K_1$ as small as possible but not more than 0.9 and a ratio of $\Delta e/e$ of at most 0.3. Such dielectrics are used in the matrix type liquid crystal display devices driven by time sharing according to the invention.

The properties of nematic or nematic-cholesteric liquid-crystalline materials are utilized for liquid-crystal display elements in order to effect significant changes in their optical properties, such as light transmission, light scattering, birefringence, reflectance or color, under the influence of electric fields. The functioning of display elements of this type is based here, for example, on the phenomena of dynamic scattering, the deformation of aligned phases or the Schadt-Helfrich effect in the twisted cell.

Among these usual types of liquid-crystal display elements, especially those based on the twisted nematic cell (TN cell) have gained particular importance recently, because they can be operated with relatively low control voltages which can be readily made available even by small batteries. Moreover, these display elements have hitherto been the best which can be constructed as matrix display elements which allow the presentation of a high information density without an intolerably large number of control lines, lead-ins and lead-outs.
When used in practice, however, the TN cell, in particular in the form of matrix display elements, still raises considerable difficulties. These include above all the more or less pronounced dependence of the contrast on the angle of observation and the restricted multiplexing capacity.

Conventional dielectrics for TN cells have a ratio of the elastic constants $K_3/K_1$ of approximately 1.2-1.3 and $\Delta \varepsilon/\varepsilon$ above 1.0. Such conventional liquid crystal compositions are widely used in commercial twisted nematic display devices and disclosed in many references, e.g. Published Unexamined Japanese Patent Applications No. 56-105 510 and 56-105 511 and U.S. Patent 4,285,829. In these compositions, design is made based on the concept that the proportion of liquid crystal compounds having a distinct positive dielectric anisotropy generally is 30 % or more. These compositions are characterized in that the threshold voltages are in the range of 1 to 2 volts in most cases.

Operation margin and contrast of liquid crystal elements are determined by voltage-luminance property. Namely, as the change in transmittance to the change in intensity of electric field applied to liquid crystal is sharp, allowance for the operation margin can be large and contrast can be enhanced. Sharpness in voltage-luminance property is expressed by ratio $\gamma$ of voltage $V_{50}$ in which transmittance becomes 50 % to threshold voltage $V_C$. As the $\gamma$ value approximates to 1, the aforesaid change in transmittance is sharp so that operation margin can be broadened and contrast can be increased.
Further visual angle property depends on the product $\Delta n \cdot d$ of layer thickness $d$ of liquid crystal and refractive index anisotropy $\Delta n$ of liquid crystal. That is, in case that $\Delta n \cdot d$ is large, an apparent rate of change in $\Delta n \cdot d$ is large when viewed from the oblique direction of liquid crystal so that visual characteristic is poor; when $\Delta n \cdot d$ is small, visual characteristic is good.

Furthermore, time sharing-driven liquid crystal elements have an increased time sharing number and one selection period becomes short so that it is required that a response speed be fast. This response speed depends most greatly on the intensity of an electric field applied to liquid crystal. Namely, a thin layer thickness $d$ of liquid crystal provides an intense intensity of electric field so that liquid crystal molecules behave at a high speed.

As has been described above, matrix type liquid crystal display devices which are driven by high time sharing require that:

1. The $\gamma$ property should approximate to 1.
2. Visual angle should be broad.
3. Response speed should be fast.

Research on the properties such as $\gamma$ value or the like in liquid crystal display elements has been made by M. Schadt et al. According to the research, it is known that sharpness $\gamma$ in voltage-luminance property is expressed by equation (1) described below well complies with the property shown by actual elements.
\[ \gamma = \frac{V_{50}}{V_C} = (2.04 - \frac{1.044}{1 + \frac{K_{33}}{K_{11}}}) \]

\[ \cdot \left[ 1 + 0.123 \left( \frac{\Delta \varepsilon}{\varepsilon_\parallel} \right)^{0.6} - 1 \right] \]

\[ \cdot \left[ 1 + 0.1321n \left( \frac{\Delta n \cdot d}{2\lambda} \right) \right] \]

...(1)

wherein:  

- \( V_{50} \): voltage applied when transmittance becomes 50%  
- \( V_C \): threshold voltage  
- \( K_{33}/K_{11} \): elasticity constant ratio of liquid crystal  
- \( \Delta \varepsilon \): anisotropy in dielectric constant of liquid crystal  
- \( \varepsilon_\parallel \): dielectric constant in the direction perpendicular to the molecular axis of liquid crystal  
- \( \Delta n \): anisotropy in refractive index of liquid crystal  
- \( d \): layer thickness of liquid crystal

According to the equation (1), it is clear that for approximating \( \gamma \) to 1, the first, second and third members of the equation should approximate to 1, respectively. Accordingly, conventional time sharing-driven liquid crystal devices were designed to satisfy the following requirements simultaneously:

(a) \( K_{33}/K_{11} \) should be small.
(b) \( \Delta \varepsilon/\varepsilon_\parallel \) should be small.
(c) The value of \( \Delta n \cdot d \) should be 1.1 (\( \mu \)m) when wavelength of an incident light is 550 nm.
In this case, influence by Δn.d appears most significantly so that the value of Δn.d is most predominantly determined. In order to make Δε/ε_∥ small, Δε must be made small. However, liquid crystal having small Δε has a slow response speed. Therefore, Δε cannot be made small.

From the foregoing circumstances, with respect to conventional liquid crystal compositions, merely those having \( \frac{K_{33}}{K_{11}} \) above 1.2-1.3 and \( \Delta \varepsilon / \varepsilon_\parallel \) above 1.0 are used. Conventional liquid crystal compositions are widely used in commercial TN liquid crystal elements and, for example, Published Unexamined Japanese Patent Application Nos. 56-105510 and 56-105511 and U.S. Patent No. 4,285,829. In these compositions, design is made based on the concept that the proportion of liquid crystal compounds having a distinct positive dielectric anisotropy generally is 30% or more. As a result, these compositions are characterized in that the threshold voltages are in the range of 1 to 2 volts in most cases.

In operating the conventional liquid crystal compositions described above in time sharing-driven devices, the γ property is not so improved since values of \( \frac{K_{33}}{K_{11}} \) and \( \Delta \varepsilon / \varepsilon_\parallel \) are not small. Further due to large Δn.d, visual angle property is also poor. In case that values of \( \frac{K_{33}}{K_{11}} \) and \( \Delta \varepsilon / \varepsilon_\parallel \) are increased, liquid crystal compounds having a small \( \frac{K_{33}}{K_{11}} \) value generally have a high viscosity and a tendency to form smectic phases so that their response speed decreases. Further liquid crystal compositions having a small \( \Delta \varepsilon / \varepsilon_\parallel \) value involve problems that their response speed becomes slow due to a small Δε and a high voltage is required for operation.
In view of the foregoing circumstances, an object of the present invention is to provide liquid crystal compositions for time sharing drive having small $K_{33}/K_{11}$ and small $\Delta \varepsilon/\varepsilon_\parallel$, in order to improve response speed, $\gamma$ property and visual angle property in time sharing-driven liquid crystal display devices.

It has now been surprisingly found that when values of $\Delta \varepsilon/\varepsilon_\parallel$ and $K_{33}/K_{11}$ of liquid crystal dielectrics become extremely small in time sharing-driven liquid crystal display devices, response speed and $\gamma$ property (the sharpness in voltage-luminance property) are markedly improved in such a range of $d\Delta n$ that does meet the requirements for the first Gooch and Tarry minimum. The liquid crystal dielectrics are most suited for use in liquid crystal display devices operating in the high multiplex mode and having a surprisingly improved contrast.

The present invention has been made based on a new finding that when values of $\Delta \varepsilon/\varepsilon_\parallel$ and $K_{33}/K_{11}$ of liquid crystal compositions become extremely small in time sharing-driven liquid crystal display devices, response speed and $\gamma$ property are markedly improved in such a range of $d\Delta n$ that does not meet the equation (1) described above and in this case, the liquid crystal compositions are most suited for use in time sharing-driven liquid crystal display devices.

It is an object of the invention to provide improved display devices, in which both a markedly improved contrast, and, simultaneously, also a high response speed are ensured by operating the display elements in the first transmission minimum according to Gooch and Tarry.
Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

It has now been found that, with a suitable choice of the liquid crystal parameters, it is possible, surprisingly, to obtain the desired properties by operating the display elements in the first transmission minimum.

A subject of the invention, therefore, is the improvement of a twisted nematic liquid crystal display device operating in the high multiplex mode and having a high contrast, wherein the liquid crystal mixture has a ratio of the elastic constants $K_3/K_1$ as small as possible but not more than 0.9 and a ratio of $\Delta \varepsilon /\varepsilon_\parallel$ of at most 0.3. In many cases the electro-optical characteristic curve in the first transmission minimum is at least as steep or even steeper as that curve in the second such transmission minimum. The steepness in the second transmission minimum is measured in a display device which is identical to that operated in the first minimum except that the layer thickness is enlarged, in an appropriate manner for operation in the second minimum.

A further subject of the invention is a method of simultaneously minimizing the dependence of contrast on the angle of observation of an electro-optical display element based on a liquid crystal mixture and of maximizing its multiplexing capacity by maximizing its steepness of its characteristic curve, comprising operating the element in the first Gooch and Tarry transmission minimum, selecting a mixture having a $K_3/K_1$ ratio as small as possible but not more than 0.9 and a ratio of $\Delta \varepsilon /\varepsilon_\parallel$ of at most 0.3.
The construction of the liquid crystal display element according to the invention from polarizers, electrode base plates and electrodes with such a surface treatment that the preferential orientation of the particular adjoining liquid crystal molecules is usually twisted by 90° from one electrode to the other, corresponds to the type of construction conventional for such display elements. The concept of the conventional type of construction is here taken in a very wide sense and also comprises all the variations and modifications, known from the literature, of the twisted nematic cell, and in particular also matrix display elements. An essential difference between the display elements according to the invention and those hitherto conventional and based on the twisted nematic cell is, however, the choice of the liquid crystal parameters in the liquid crystal layer. Whereas, for example, the $K_3/K_1$ ratio in the conventional liquid-crystalline phases for display elements of this type is at least $> 0.8$ and the $\Delta \varepsilon/\varepsilon_\| \, \text{ ratio is normally between 1.2 and } 1.7$, the $K_3/K_1$ ratio in the display elements according to the invention is $\leq 0.9$ and $\Delta \varepsilon/\varepsilon_\|$ is $\leq 0.3$. The $K_3/K_1$ ratio in the display elements according to the invention preferably is 0.4 to 0.9 and $\Delta \varepsilon/\varepsilon_\|$ preferably is 0.04 to 0.3. Particularly preferred dielectrics are those, wherein $K_3/K_1$ is 0.2 to 0.75 and $\Delta \varepsilon/\varepsilon_\|$ is 0.1 to 0.3.

The parameters used to define the invention are fully known to skilled workers. The contemplated definitions are to be found in many publications, e.g. W.H. De Jeu, Physical Properties of Liquid Crystal Materials, Gordon and Breach 1980 and the brochure "Liquid Crystals, Measurement of the Physical Properties" of E. Merck, whose disclosures are incorporated by reference herein.
The thickness of a liquid crystal layer of the display element according to the invention and/or the optical anisotropy \( \Delta n \) of the liquid crystal material are chosen such that

\[
d \cdot \Delta n = \frac{\lambda}{2} \cdot \sqrt{3}
\]

the value of 550 nm, normally used for the maximum sensitivity of the human eye, being taken for the wavelength \( \lambda \).

The layer thicknesses of the display elements according to the invention can, for example, be within the range from 2 to 10 \( \mu \)m. Preferably, the smallest possible layer thicknesses are chosen, the lower limit of \( d \) being determined by the quality standards required for mass production. A particularly preferred range of \( d \) is thus 3 to 8 \( \mu \)m, in particular 4 to 7 \( \mu \)m.

Liquid-crystalline dielectrics, the material parameters of which are within the ranges according to the invention, can be prepared from conventional liquid-crystalline base materials. Numerous such materials are known from the literature. Preferably, the dielectrics according to the invention comprise at least five components. Advantageously, the dielectrics used for the display elements according to the invention comprise

(a) at least 10 wt% of a first liquid crystal material comprising at least one of liquid crystal compounds represented by general formula:

\[
R^1\left(N\bigg(\begin{array}{cc}
O & N
\end{array}\bigg)\right)\left(N\bigg(\begin{array}{cc}
A & \end{array}\bigg)\right)\left(Z^1-Q^1\right)_{m-R^2}
\]

(I)
wherein $R_1$ represents a group $R$; and $R_2$ represents $R$ or $OR$; $R$ being in each case independently a straight chain alkyl group having up to 12 carbon atoms wherein one or two non-adjacent CH$_2$ groups may be replaced by -O- and/or -CH=CH-, two oxygen atoms not being directly attached to one another, $A$ is 1,4-phenylene or trans-1,4-cyclohexylene, $Z^1$ is -CO-O-, -O-CO-, -CH$_2$-O-, -OCH$_2$-, -CH$_2$CH$_2$- or a single bond, $Q^1$ is 1,4-phenylene or trans-1,4-cyclohexylene, and $m$ is 0, 1 or 2.

(b) less than 10 wt% of a second liquid crystal material comprising one or more liquid crystal compounds having a distinct positive dielectric anisotropy ($\Delta\varepsilon \geq +3$); and,

(c) less than 90 wt% of a third liquid crystal material comprising at least one liquid crystal compound having a negative or substantially 0 dielectric anisotropy.

Under this aspect of the invention, the liquid crystal composition is composed of a liquid crystal compound of pyrimidine type, as a main component, having formulated therein a small quantity of a liquid crystal compound having a distinct positive $\Delta\varepsilon$ value. The liquid crystal composition of the present invention can also be obtained by formulating a liquid crystal compound having a negative or substantially 0$\Delta\varepsilon$ value, in addition to the liquid crystal mixture described above. In the thus formulated liquid crystal composition, values of $K_{33}/K_{11}$
and \( \Delta \varepsilon / \varepsilon \downarrow \) are reduced by the use of a liquid crystal
having particularly large \( K_{11} \) in large quantities and
a liquid crystal having large \( \varepsilon \downarrow \) in large quantities
and, the liquid crystal composition has a positive
\( \Delta \varepsilon \) as a whole.

The second liquid crystal material can be absent if the
first and third liquid crystal material is selected in
such a manner that the resulting mixture has a slightly
positive \( \Delta \varepsilon \) and a \( \Delta \varepsilon \) in the range of 0.04 to 0.3.

The liquid crystal compounds of pyrimidine type de-
scribed above are preferably represented by general
formula (Ia) described below.

\[
\begin{align*}
R_1 \left( \begin{array}{c}
\text{O} \\
\text{N}
\end{array} \right) - \left( \begin{array}{c}
\text{O} \\
\text{N}
\end{array} \right) - R_2
\end{align*}
\]  ... (Ia)

wherein \( R_1 \) represents \( R \) and \( R_2 \) represents \( R \) or \( OR \),
\( R \) being in each case independently a straight chain
alkyl group having 1 to 12 carbon atoms wherein one
or two nonadjacent \( \text{CH}_2 \) group may be replaced by \(-O-\)
or \(-\text{CH}=\text{CH}-\), with two oxygen atoms not being directly
attached to each other.

The liquid crystal compounds of pyrimidine type de-
scribed above have a small \( K_{33} / K_{11} \) value of approxi-
mately 0.55, and \( K_{11} \) is as large as about \( 1.8 \times 10^{-2} \).

Further \( \Delta \varepsilon \) is in a range of approximately +0.9 to +2.5.

In the liquid crystal compounds represented by general
formula (Ia), \( R_1 \) preferably is \( n \)-alkyl having 3 to 9
carbon atoms. \( R^2 \) preferably is ethyl, \( n \)-propyl or
\( n \)-alkoxy having 5 to 9 carbon atoms.

In addition pyrimidines of formula Ia are preferred
wherein \( R^2 \) is methoxy. Components of formula (Ia)
wherein \( R_1 \) is \( n \)-alkyl of 6 to 9 carbon atoms and
\( R^2 \) is \( n \)-alkoxy of 5 to 9 carbon atoms are pre-
ferably selected as components of the mixtures according to this invention. Especially preferred are components wherein $R^1$ is $n$-hexyl or $n$-heptyl and $R^2$ is $n$-pentyloxy, $n$-heptyloxy or $n$-nonyloxy.

As these liquid crystal compounds of pyrimidine type, preferably liquid crystal compounds shown in Table 1 are used. Their physical properties are also shown in the same table. Among the liquid crystal compounds exemplified in Table 1, preferably at least one of them is formulated to make the first liquid crystal material.

As the aforesaid liquid crystal compound having a distinct positive $\varepsilon$ value, there can be used for example liquid crystal compounds of dioxane type, phenycyclohexane type, biphenyl type or pyrimidine type, which are used to render the $\varepsilon$ value of the liquid crystal composition positive. The preferred liquid crystal compounds are represented by general formulas (II), (III), (IV), (V), etc.

\[
\begin{align*}
R_3 & = \begin{array}{c}
\text{-CN} \\
\text{O} \\
\text{O}
\end{array} \quad \ldots \quad (II) \\
R_4 & = \begin{array}{c}
\text{CN} \\
\text{O} \\
\text{H}
\end{array} \quad \ldots \quad (III) \\
R_5 & = \begin{array}{c}
\text{CN} \\
\text{O} \\
\text{O}
\end{array} \quad \ldots \quad (IV) \\
R_6 & = \begin{array}{c}
\text{CN} \\
\text{O} \\
\text{N}
\end{array} \quad \ldots \quad (V)
\end{align*}
\]

wherein $R_3$, $R_4$, $R_5$ and $R_6$ independently represent a straight chain alkyl group having 1 to 12 carbon atoms wherein one or two nonadjacent $\text{CH}_2$ group may be replaced by $-\text{O}$- or $-\text{CH}=\text{CH}$-, with two oxygen atoms not being directly attached to each other.
Table 1

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<td>n-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>0.14</td>
<td></td>
<td>37</td>
<td>-20</td>
</tr>
<tr>
<td>n-C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.17</td>
<td></td>
<td>21</td>
<td>-70</td>
</tr>
<tr>
<td>n-C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>-O-CH&lt;sub&gt;2&lt;/sub&gt;-CH=CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.4</td>
<td>0.18</td>
<td>44</td>
<td>40</td>
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Table 2

<table>
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<tr>
<th>Chemical Formula</th>
<th>$\Delta \varepsilon / \varepsilon_\perp$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_5H_{11}$-</td>
<td>2.7</td>
<td>0.14</td>
<td>57°C</td>
<td>48°C</td>
</tr>
<tr>
<td>$n-C_5H_{11}$-</td>
<td>2.7</td>
<td>0.11</td>
<td>31</td>
<td>50</td>
</tr>
<tr>
<td>$n-C_5H_{11}$-</td>
<td>2.9</td>
<td>0.20</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>$n-C_7H_{15}$-</td>
<td>3.3</td>
<td>0.22</td>
<td>43</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$-CH=CH-C$_2$H$_4$-</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>74</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$-</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>20</td>
</tr>
</tbody>
</table>
Under another aspect of the invention the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae II\text{f} to II\text{h}:

\[ R-\begin{array}{c} A^1 \\ X \end{array} -Z^2 -O -F \quad \text{II\text{f}} \]

\[ R-\begin{array}{c} A^2 \\ F \end{array} -Z^3 -O -CN \quad \text{II\text{g}} \]

\[ R-\begin{array}{c} A^3 \\ X \end{array} -Z^4 -O -CN \quad \text{II\text{h}} \]

wherein

\[ A^1 \text{ is } \begin{array}{c} -H -, -O -, -O -O -, \\ -H -H -, -O -O -, \\ -N -N -, -N -O -O -, -O -N \end{array} \]

\[ A^2 \text{ and } A^3 \text{ are in each case } \begin{array}{c} -H -, -O - \\ -H -O -, -H -H - \text{ or } \end{array} \]

\[ -O -O - \]

\[ Z^2 \text{ is } -CO -O -, -O -CO -, -CH_2 CH_2 - \text{ or a single bond,} \]

\[ X \text{ is } \text{hydrogen or fluorine,} \]
\( Z^3 \) is \(-\text{CO-O-}, -\text{O-CO-}, -\text{CH}_2\text{O-}, -\text{CH}_2\text{CH}_2-\) or a single bond,

\( Z^4 \) is \(-\text{CO-O-}, -\text{O-CO-} \) or \(-\text{CH}_2\text{CH}_2-\), and

\( R \) being in each case independently a straight chain alkyl group having up to 12 carbon atoms, wherein one or two non-adjacent \( \text{CH}_2 \) groups may be replaced by \(-\text{O-} \) or \(-\text{CH=CH-} \), two oxygen atoms not being directly attached to each other.

Preferred components of this type or those liquid crystal compounds represented by the general formulae

\[
\begin{align*}
R &\rightarrow \text{H} \rightarrow \text{H} \rightarrow \text{CH}_2\text{CH}_2 \rightarrow \text{O} \rightarrow \text{F} \\
&\rightarrow \text{O} \rightarrow \text{COO} \rightarrow \text{O} \rightarrow \text{CN} \\
&\rightarrow \text{F} \\
&\rightarrow \text{H} \rightarrow \text{O} \rightarrow \text{COO} \rightarrow \text{O} \rightarrow \text{CN} \\
&\rightarrow \text{F} \\
&\rightarrow \text{H} \rightarrow \text{H} \rightarrow \text{O} \rightarrow \text{CN} \\
&\rightarrow \text{O} \rightarrow \text{CH}_2\text{CH}_2 \rightarrow \text{O} \rightarrow \text{CN} \\
&\rightarrow \text{H} \rightarrow \text{CH}_2\text{CH}_2 \rightarrow \text{O} \rightarrow \text{CN}
\end{align*}
\]

wherein \( R \) has the meaning given above for formulae III, g and h and \( x \) is hydrogen or fluorine.
The liquid crystal compounds have the dielectric anisotropy $\Delta \varepsilon$ value is +3 or more; it is particularly desired that the $\Delta \varepsilon$ value be in a range of +12 to +40 and viscosity $\eta$ value be 20 to 60 cp.

Liquid crystal compounds as shown in Table 2 can be used among others. Among the liquid crystal compounds exemplified in Table 2, preferably at least one compound is formulated to make the second liquid crystal material.

As the liquid crystal compound having a negative or substantially 0 $\Delta \varepsilon$ value, there can be used liquid crystal compounds of phenylcyclohexane type (German Patent 26 36 684), phenyl cyclohexane carboxylates (German Patent 24 29 093), cyclohexyl cyclohexanes (USP 4,622,164), biphenylcyclohexanes (Japanese Patent 1,311,608), phenyl cyclohexylcyclohexane carboxylates (Japanese Patent 1,297,121), 1-phenyl-2-cyclohexylcyclohexylethanes (USP 4,606,845), cyclohexyl cyclohexylcyclohexane carboxylates (Japanese Patent 1,297,121), 4,4'-biscyclohexylbiphenyls (USP 4,331,552) and 4,4'-biscyclohexyl-2-fluorobiphenyls (USP 4,419,264). These liquid crystal compounds are low viscosity liquid crystal compounds for controlling viscosity, high temperature liquid crystal for raising N-I point and liquid crystals for suppressing smectic phases. As low viscosity liquid crystal compounds, there can be used liquid crystal compounds shown in Table 3 which show $\eta$ of approximately 6 to 20 mPa.s.

As high temperature liquid crystals, there can be used liquid crystal compounds shown in Table 4 having N-I point of approximately 130 to 330 °C. $\eta$ is approximately 13 to 65 mPa.s.
In all components of the liquid crystal compositions according to this invention R is preferable alkyl of 1 to 10 carbon atoms. A particularly preferred range is 1 to 5 carbon atoms.

The third liquid crystal material comprises preferably liquid crystal compounds having a dielectric anisotropy of -1 to +1. These liquid crystal compounds are represented by general formulas described below:

\[
\begin{align*}
R_7 & - \text{H} - \text{O} - R_8 \\
R_9 & - \text{H} - \text{COO} - \text{O} - R_{10} \\
R_{11} & - \text{H} - \text{H} - R_{12} \\
R_{13} & - \text{H} - \text{O} - \text{O} - R_{14} \\
R_{15} & - \text{H} - \text{H} - \text{COO} - \text{O} - R_{16} \\
R_{17} & - \text{H} - \text{H} - \text{CH}_2\text{CH}_2\text{O} - R_{18} \\
R_{19} & - \text{H} - \text{H} - \text{COO} - \text{H} - R_{20} \\
R_{21} & - \text{H} - \text{O} - \text{O} - \text{H} - R_{22} \\
R_{23} & - \text{H} - \text{O} - \text{O} - \text{H} - R_{24}
\end{align*}
\]

wherein \( R_7, R_9, R_{11} \) to \( R_{24} \) represents R; and \( R_8, R_{10}, R_{12} \) represents R or OR, R being in each case independently a straight chain alkyl group having 1 to 12 carbon atoms wherein one or two oxygen atoms not being directly attached to each other.
Table 3

<table>
<thead>
<tr>
<th>R&lt;sup&gt;7&lt;/sup&gt;</th>
<th>R&lt;sup&gt;8&lt;/sup&gt;</th>
<th>Δε / ε&lt;sub&gt;⊥&lt;/sub&gt;</th>
<th>Δn</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>+ 0.1</td>
<td>0.08</td>
<td>-8°C</td>
<td>-13°C</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.09</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>OC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.09</td>
<td>41</td>
<td>37</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>n − OCH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.09</td>
<td>36</td>
<td>32</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>n − OC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.08</td>
<td>40</td>
<td>27</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>n − OC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.08</td>
<td>42</td>
<td>30</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>n − OC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.08</td>
<td>36</td>
<td>40</td>
</tr>
<tr>
<td>n − C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>n − OC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;</td>
<td>- 0.2</td>
<td>0.09</td>
<td>39</td>
<td>47</td>
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Table 4

<table>
<thead>
<tr>
<th>$R_9$</th>
<th>$R_{10}$</th>
<th>$\Delta \varepsilon / \varepsilon \perp$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-$C_5H_{11}$</td>
<td>$n$-$C_5H_{11}$</td>
<td>-0.1</td>
<td>0.08</td>
<td>37°C</td>
<td>47°C</td>
</tr>
<tr>
<td>$n$-$C_3H_7$</td>
<td>OCH$_3$</td>
<td>-0.3</td>
<td>0.09</td>
<td>57</td>
<td>60</td>
</tr>
<tr>
<td>$n$-$C_3H_7$</td>
<td>n-OC$_2$H$_5$</td>
<td>-0.3</td>
<td>0.09</td>
<td>48</td>
<td>78</td>
</tr>
<tr>
<td>$n$-$C_3H_7$</td>
<td>n-OC$_4$H$_9$</td>
<td>-0.3</td>
<td>0.09</td>
<td>43</td>
<td>70</td>
</tr>
<tr>
<td>$n$-$C_4H_9$</td>
<td>OCH$_3$</td>
<td>-0.3</td>
<td>0.09</td>
<td>43</td>
<td>58</td>
</tr>
<tr>
<td>$n$-$C_4H_9$</td>
<td>OC$_2$H$_5$</td>
<td>-0.3</td>
<td>0.09</td>
<td>37</td>
<td>75</td>
</tr>
<tr>
<td>$n$-$C_5H_7$</td>
<td>OCH$_3$</td>
<td>-0.3</td>
<td>0.09</td>
<td>40</td>
<td>71</td>
</tr>
</tbody>
</table>
### Table 5

<table>
<thead>
<tr>
<th>$R_{11}$</th>
<th>$R_{12}$</th>
<th>$\Delta \varepsilon / \varepsilon_\perp$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_6H_7$</td>
<td>OCH$_3$</td>
<td>-0.1</td>
<td>0.04</td>
<td>9 $^\circ$C</td>
<td>10 $^\circ$C</td>
</tr>
<tr>
<td>$n-C_6H_7$</td>
<td>OC$_2$H$_5$</td>
<td>-0.2</td>
<td>0.03</td>
<td>49</td>
<td>30</td>
</tr>
<tr>
<td>$n-C_6H_7$</td>
<td>n-OC$_2$H$_7$</td>
<td>-0.2</td>
<td>0.04</td>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>$n-C_8H_{11}$</td>
<td>OC$_2$H$_5$</td>
<td>-0.1</td>
<td>0.04</td>
<td>35</td>
<td>40</td>
</tr>
</tbody>
</table>
These liquid crystal compounds are composed of low viscosity liquid crystal compounds for controlling viscosity and high temperature liquid crystal compounds for raising N-I point. By selectively formulating these liquid crystal compounds, a tendency that smectic phases appear is suppressed.

As low viscosity liquid crystal compounds, there can be used liquid crystal compounds of general formulas (VI), (VII) and (VIII) shown in Tables 3, 4 and 5, respectively, which show η of approximately 6 to 20 cp.

As high temperature liquid crystals, there can be used liquid crystal compounds of general formulas (IX), (X), (XI), (XII), (XIII) and (XIV) described above and shown in Tables 6, 7, 8, 9, 10 and 11, respectively. These high temperature liquid crystal compounds have a clearing point (N-I point) of approximately 130 °C to 330 °C.

Among these liquid crystal compounds, the liquid crystal compound represented by general formula (XI) has a viscosity of 13 to 19 mPa.s and is used to increase splay elasticity constant K_{11}.

Among the liquid crystal compounds represented by general formula (VI) to (XIV), it is desired as the liquid crystal compounds used in the liquid crystal composition of the present invention that R be an alkyl group having 1 to 10 carbon atoms. In particular, it is desired that R be an alkyl group having 1 to 5 carbon atoms.

At least one of the liquid crystal compounds shown in these Tables 6 to 11 is formulated to make the third liquid crystal material.
### Table 6

<table>
<thead>
<tr>
<th>R₁₃</th>
<th>R₁₄</th>
<th>Δε / ε⊥</th>
<th>Δn</th>
<th>mp</th>
<th>cp</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₃H₇</td>
<td>C₂H₅</td>
<td>0.1</td>
<td>0.18</td>
<td>66℃</td>
<td>166℃</td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>C₂H₅</td>
<td>0.1</td>
<td>0.18</td>
<td>34</td>
<td>164</td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>n-C₅H₁₁</td>
<td>0.1</td>
<td>0.16</td>
<td>15</td>
<td>159</td>
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</table>

### Table 7

<table>
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<tr>
<th>R₁₅</th>
<th>R₁₆</th>
<th>Δn</th>
<th>mp</th>
<th>cp</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₃H₇</td>
<td>n-C₃H₇</td>
<td>0.11</td>
<td>64℃</td>
<td>190℃</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>n-C₅H₁₁</td>
<td>0.11</td>
<td>31</td>
<td>180</td>
</tr>
<tr>
<td>n-C₅H₇</td>
<td>n-C₅H₇</td>
<td>0.10</td>
<td>18</td>
<td>190</td>
</tr>
<tr>
<td>n-C₅H₇</td>
<td>n-C₅H₁₁</td>
<td>0.10</td>
<td>7</td>
<td>180</td>
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</tbody>
</table>
Table 8

<table>
<thead>
<tr>
<th>$R_{17}$</th>
<th>$R_{18}$</th>
<th>$\Delta \varepsilon / \varepsilon_{\perp}$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_3H_7$</td>
<td>CH$_3$</td>
<td>0.1</td>
<td>0.11</td>
<td>45$^\circ$C</td>
<td>130$^\circ$C</td>
</tr>
<tr>
<td>$n-C_3H_7$</td>
<td>C$_2$H$_5$</td>
<td>0.1</td>
<td>0.11</td>
<td>13</td>
<td>130</td>
</tr>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_3H_7$</td>
<td>0.1</td>
<td>0.12</td>
<td>-19</td>
<td>130</td>
</tr>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_5H_{11}$</td>
<td>0.1</td>
<td>0.10</td>
<td>-2</td>
<td>140</td>
</tr>
<tr>
<td>$n-C_5H_{11}$</td>
<td>$n-C_5H_{11}$</td>
<td>0.1</td>
<td>0.10</td>
<td>8</td>
<td>150</td>
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Table 9

<table>
<thead>
<tr>
<th>$R_{19}$</th>
<th>$R_{20}$</th>
<th>$\Delta \varepsilon / \varepsilon_{\perp}$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_3H_7$</td>
<td>-0.3</td>
<td>0.06</td>
<td>58$^\circ$C</td>
<td>189$^\circ$C</td>
</tr>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_5H_{11}$</td>
<td>-0.3</td>
<td>0.06</td>
<td>53</td>
<td>188</td>
</tr>
<tr>
<td>$n-C_4H_7$</td>
<td>$n-C_3H_7$</td>
<td>-0.3</td>
<td>0.05</td>
<td>59</td>
<td>184</td>
</tr>
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<td>$n-C_4H_7$</td>
<td>$n-C_5H_{11}$</td>
<td>-0.3</td>
<td>0.05</td>
<td>38</td>
<td>186</td>
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</table>
Table 10

<table>
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<tr>
<th>$R_{z1}$</th>
<th>$R_{z2}$</th>
<th>$\Delta \varepsilon / \varepsilon_\perp$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_3H_7$</td>
<td>0.1</td>
<td>0.16</td>
<td>109 °C</td>
<td>324 °C</td>
</tr>
<tr>
<td>$n-C_5H_{11}$</td>
<td>$n-C_3H_7$</td>
<td>0.1</td>
<td>0.19</td>
<td>55</td>
<td>310</td>
</tr>
<tr>
<td>$n-C_5H_{11}$</td>
<td>$n-C_5H_{11}$</td>
<td>0.1</td>
<td>0.17</td>
<td>75</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 11

<table>
<thead>
<tr>
<th>$R_{z3}$</th>
<th>$R_{z4}$</th>
<th>$\Delta \varepsilon / \varepsilon_\perp$</th>
<th>$\Delta n$</th>
<th>mp.</th>
<th>cp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n-C_3H_7$</td>
<td>$n-C_3H_7$</td>
<td>-0.1</td>
<td>0.16</td>
<td>131 °C</td>
<td>296 °C</td>
</tr>
<tr>
<td>$n-C_5H_{11}$</td>
<td>$n-C_3H_7$</td>
<td>-0.04</td>
<td>0.16</td>
<td>82</td>
<td>290</td>
</tr>
<tr>
<td>$n-C_5H_{11}$</td>
<td>$n-C_5H_{11}$</td>
<td>-0.1</td>
<td>0.17</td>
<td>80</td>
<td>278</td>
</tr>
</tbody>
</table>
At least one of the liquid crystal compounds shown in these Tables 3, 4 and 5 and at least one of the compounds shown in Tables 6 to 11 may be used for said third liquid crystal material.

Preferred devices according to the invention are those, wherein the liquid crystal dielectric comprises at least five components.

Among the first to third liquid crystal materials described above, at least the first liquid crystal material and the second liquid crystal material are formulated in the composition. In this case, the first liquid crystal material is formulated so as not to exceed 90 wt% and the second liquid crystal material is formulated in a rate of less than 10 wt% so that the $\Delta \varepsilon$ value does not become excessively large. Further in case that the first, second and third liquid crystal materials are formulated, respectively, the first liquid crystal material is formulated in an amount of 10 wt% or more as the minimum formulation ratio that is necessary for exhibiting an effect of lowering the $K_{33}/K_{11}$ value. The second liquid crystal material is formulated in an amount of less than 10 wt% in such a manner that the $\Delta \varepsilon$ value does not increase unnecessarily; and the third liquid crystal material is formulated in an amount of less than 90 wt%.

Particularly in the liquid crystal composition using a low viscosity liquid crystal as the third liquid crystal material, high speed response can be achieved and such a composition is suited for television display.
It is desired that the first, second and third liquid crystal materials be formulated in amounts of 30 wt% or more, less than 10 wt% and less than 70 wt%, respectively. It is more preferred that the first, second and third liquid crystal materials be formulated in amounts of 30 to 65 wt%, less than 5 wt% and 35 to 70 wt%, respectively.

Particularly preferred are mixtures of this type wherein said second liquid crystal material comprises one or more liquid crystal materials represented by general formula (II):

\[
R_3 - \begin{array}{c}
\text{O} \\
\text{O}
\end{array} - \begin{array}{c}
\text{O} \\
\text{O}
\end{array} - \text{CN} \tag{II}
\]

wherein \( R_3 \) represents a straight chain alkyl group having 1 to 12 carbon atoms, and said third liquid crystal material comprises liquid crystal compounds represented by general formulae:

\[
R_7 - \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{O} \\
\text{O}
\end{array} - R_8 \tag{VI}
\]

\[
R_{17} - \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_2\text{CH}_2
\end{array} - \begin{array}{c}
\text{O} \\
\text{O}
\end{array} - R_{18} \tag{XI}
\]

wherein \( R_7, R_{17} \) and \( R_{18} \) independently represent a straight chain alkyl group having 1 to 12 carbon atoms, \( R_8 \) represents a straight chain alkyl group a straight chain alkoxy group or a straight chain alkanoyloxy group having 1 to 12 carbon atoms,
and comprises 5 to 25 wt% of liquid crystal compounds represented by general formula (VI), 20 to 35 wt% of liquid crystal compounds represented by general formula (XI).

5 Preferably these mixtures additionally comprise 2 to 10 wt% of liquid crystal compounds represented by general formula (IX):

$$R_{13} \left( \begin{array} {c} H \\ H \end{array} \right) \bigcirc \bigcirc \bigcirc - R_{14}$$  \hspace{1cm} (IX)

wherein $R_{13}$ and $R_{14}$ independently represent a straight chain alkyl group having 1 to 12 carbon atoms.

Furthermore preferred are mixtures of this type wherein said second liquid crystal material comprises one or more liquid crystal compounds represented by the formula (II) below:

$$R_{3} \left( \begin{array} {c} O \\ O \\ O \end{array} \right) - \text{CN}$$  \hspace{1cm} (II)

wherein $R_{3}$ represents a straight chain alkyl group having 1 to 12 carbon atoms, and said third liquid crystal material comprises 5 to 45 wt% of liquid crystal compounds represented by the formulae (VI) and (VII) below, and optionally 5 to 25 wt%, 10 to 25 wt%, and 20 to 25 wt%, respectively, of liquid crystal compounds represented by the formulae (IX), (X), and (XI) below:
wherein \( R_7 \), \( R_9 \) and \( R_{13} \) to \( R_{18} \) independently represent a straight chain alkyl group having 1 to 12 carbon atoms. \( R_{10} \) represents a straight chain alkyl group or straight chain alkoxy group having 1 to 12 carbon atoms, and \( R_8 \) represents a straight chain alkyl group, a straight chain alkoxy group or a straight chain alkanoyloxy group having 1 to 12 carbon atoms.

Preferably these mixtures comprise as said third liquid crystal material 10 to 40 wt% of liquid crystal compounds represented by the formulae (VI) and (VII).

Furthermore preferred are mixtures of this type wherein said second liquid crystal material comprises one or more liquid crystal compounds represented by the formula (II) below:

\[
R_3 - \begin{array}{c}
O \\
O
\end{array} \text{CN} \quad (II)
\]
wherein \( R_3 \) represents a straight chain alkyl group having 1 to 12 carbon atoms, and said third liquid crystal material comprises 15 to 30 wt%, less than 10 wt%, and 20 to 40 wt%, respectively, of liquid crystal compounds represented by the formulae (VI), (IX) and (X) below, and optionally 5 to 45 wt% of liquid crystal compounds represented by the formula (VII) below:

\[
\begin{align*}
R_7 & - \begin{array}{c} H \end{array} - \begin{array}{c} O \end{array} - R_8 & \text{(VI)} \\
R_9 & - \begin{array}{c} H \end{array} - \text{COO} - \begin{array}{c} O \end{array} - R_{10} & \text{(VII)} \\
R_ {13} & - \begin{array}{c} H \end{array} - \begin{array}{c} O \end{array} - \begin{array}{c} O \end{array} - R_{14} & \text{(IX)} \\
R_ {15} & - \begin{array}{c} H \end{array} - \begin{array}{c} H \end{array} - \text{COO} - \begin{array}{c} O \end{array} - R_{16} & \text{(X)}
\end{align*}
\]

wherein \( R_7 \), \( R_9 \) and \( R_{13} \) to \( R_{16} \) independently represent a straight chain alkyl group having 1 to 12 carbon atoms, \( R_{10} \) represents a straight chain alkyl group or straight chain alkoxy group having 1 to 12 carbon atoms, and \( R_8 \) represents a straight chain alkyl group, a straight chain alkoxy group or a straight chain alkanoyloxy group having 1 to 12 carbon atoms.

Preferably these mixtures comprise less than 42.6 wt% of liquid crystal compounds represented by the general formula (VII).

Furthermore preferred are mixtures wherein said third liquid crystal material comprises one or more liquid crystal compounds represented by the formulae (XV) and (XVI) below:
$R_{25}-\overset{\text{O}}{\text{C}}=\overset{\text{O}}{\text{C}}-R_{26}$  \hspace{1cm} \text{(XV)}$

$R_{27}-\overset{\text{H}}{\text{C}}=\overset{\text{O}}{\text{C}}=\overset{\text{O}}{\text{C}}-R_{28}$  \hspace{1cm} \text{(XVI)}$

wherein $R_{25}$ and $R_{27}$ each represent $R$; and $R_{26}$ and $R_{28}$ each represent $R$ or $OR$; $R$ being in each case independently a straight chain alkyl group having up to 12 carbon atoms wherein one or two non-adjacent $CH_2$ groups may be replaced by $-O-$ or $-CH=CH-$, two oxygen atoms not being directly attached to each other.

Said compounds of formulae (XV) and (XVI) are preferably present in an amount of 5 to 15 wt%.

It is desired to use the liquid crystal compound represented by general formula (II) having particularly large dielectric anisotropy $\Delta \varepsilon$ and a small $\Delta \varepsilon/\varepsilon_l$ value as the second liquid crystal material. In this case, it is desired that the liquid crystal material represented by general formula (II) be formulated in a proportion of 10 wt% or less, most desirably 5 wt% or less.

In the third liquid crystal material, at least one of low viscosity liquid crystal compounds represented by general formulas (VI), (VII) and (VIII) or, in addition to the low viscosity liquid crystal compounds, at least one of high temperature liquid crystals represented by general formulas (IX), (X), (XI), (XII), (XIII) and (XIV) are formulated. As the low viscosity liquid crystal compounds, at least one of or both of the liquid crystal compound represented by general formula (VI) and the liquid crystal compound represented by general formula (VII) is/are formulated. In case that the liquid crystal compound represented by general formula (VI) is formulated as the low viscosity liquid crystal compound, it is desired to
formulate the liquid crystal compound represented by
general formula (IX) as the high temperature liquid crystal
and selectively the liquid crystal compound represented by
general formula (XI). In this case, it is desired to
5 formulate the liquid crystal compounds represented by
general formulas (VI), (IX) and (XI) in proportions
of 15 to 45 wt%, 2 to 10 wt% and 20 to 35 wt%, respecti-
vely. Particularly in the case of formulating the liquid
crystal compounds represented by general formulas
10 (VI) and (XI), the most preferred proportions to be
formulated are 17 to 31 wt% and 24 to 33 wt%, respecti-
vely. Further in the case of formulating the liquid
crystal compounds represented by general formulas (VI),
(IX) and (XI), preferred proportions to be formulated
15 are 15 to 30 wt%, 10 wt% or less and 20 to 40 wt%,
respectively, most preferably 17 or 27 wt%, 2 to 10 wt%
and 23 to 30 wt%, respectively.

In the case that the liquid crystal compounds represented
by general formulas (VI) and (VII) as the low viscosity
20 liquid crystal compounds, it is desired to selectively
formulate the liquid crystal compounds represented by
general formulas (IX), (X) and (XI) as the high tempera-
ture liquid crystal materials. In this case, it is desired
to formulate the liquid crystal compounds represented by
general formulas (VI) and (VII) in proportions of 10 to
25 40 wt% and 5 to 45 wt%, respectively and to formulate
the liquid crystal compounds represented by general
formulas (IX), (X) and (XI) in proportions of 5 to 25 wt%,
10 to 25 wt% and 20 to 25 wt%, respectively. In particular,
30 it is desired that the liquid crystal compound represented
by general formula (VII) be formulated in a proportion of
5 to 42.6 wt%.
In the liquid crystal composition of the present invention, the second liquid crystal material can also be formulated with pyrimidine type liquid crystal compounds. In this case, liquid crystal compounds represented by general formula (V) are used as the second liquid crystal material, in which at least one of the liquid crystal compound, represented by general formula (IX), (X) and (XI) is formulated.

Thus, the liquid crystal composition of the present invention is formulated in such that the $\Delta \varepsilon /\varepsilon_j$ value ranges from 0.12 to 0.58 and the $K_{33}/K_{11}$ value is 0.88 or less.

Preferred dielectrics are those, wherein the formulation ratios of said first liquid crystal material, said second liquid crystal material and said third liquid crystal material are at least 30 wt%, less than 10 wt% and less than 70 wt%, respectively.

Particularly preferred dielectrics are those, wherein the formulation ratios of said first liquid crystal material, said second liquid crystal material and said third liquid crystal material are 30 to 65 wt%, less than 5 wt% and 35 to 70 wt%, respectively.

Such dielectrics can additionally contain dyes and/or doping substances in the usual quantities, unless the liquid crystal parameters are thus taken out of the ranges according to the invention.
Mixing of the liquid crystalline components to achieve the parameters discussed above can be routinely accomplished by the usual preliminary orientation experiments taking into account the usual considerations. Some of the many publications, whose disclosures are incorporated by reference herein, disclosing details of suitable materials include German Offenlegungsschrift 2,257,588; 2,306,738; 2,017,727; 2,321,632; European Published Application 0,126,883; USP 3,997,536; 4,062,798; 4,462,923; 4,389,329; 4,364,838; 4,066,570; 4,452,718; 4,419,262; 4,510,069; Japanese Published Applications 144,770/84; 144,771/84; 144,772/84 43,961/83; D. Demus et al., Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974 and D. Demus et al., Flüssige Kristalle in Tabellen II, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1984.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting of the remainder of the disclosure in any way whatsoever. In the tables 1-4 above and the following examples, all temperatures are set forth uncorrected in degrees Celsius; unless otherwise indicated, all parts and percentages are by weight.

These liquid crystal compositions are sealed between base plates facing to each other in which electrodes are formed, so as to twist-orient the liquid crystal molecules to almost 90° and, a voltage for time sharing drive is applied to a large number of facing electrodes. In this case, the layer thickness of liquid crystal in liquid crystal elements is set to 7.0 μm or less.
With respect to the liquid crystal composition of the present invention, concrete examples are explained below. Respective proportions of the liquid crystal compositions of the present invention are shown in Tables 12 through 14, wherein formulation proportions are by wt%.

Formulation proportions of Examples 1 through 48 using the dioxane liquid crystal compounds represented by general formula (II) as the second liquid crystal material are shown in Tables 12 and 13. In Table 13, Example 1 indicates a composition in which the first liquid crystal material is formulated in a proportion of 30 wt%; Example 2 indicates a liquid crystal composition in which the first liquid crystal material is formulated in the smallest proportion; and Examples 3 and 4 indicate liquid crystal compositions in which the second liquid crystal material is formulated in the largest proportion. In Example 5, only the liquid crystal compound represented by general formula (VII) is formulated as the low viscosity liquid crystal compound. In Examples 6 through 25, only the liquid crystal compound represented by general formula (VI) is used as the low viscosity liquid crystal compound; in this case, the liquid crystal compound represented by general formula (IX), (X), (XI) or (XIII) is selectively formulated as the high temperature liquid crystal compound.

Table 13 shows liquid crystal compositions using the liquid crystal compounds represented by general formulas (VI) and (VII) as the third liquid crystal material. In Example 26, the low viscosity liquid crystal compound represented by general formula (VIII) is additionally
formulated to provide a liquid crystal composition having an extremely low viscosity. Examples 27 through 48 shown in Table 13 indicate liquid crystal compositions in which the liquid crystal compounds represented by general formulas (IX), (X), (XI), (XII) and (XIII) are selectively formulated.

Examples of the liquid crystal compositions in accordance with the present invention using the liquid crystal compound represented by general formula (IV) or (V) as the second liquid crystal material are shown in Table 14. In Examples 49 through 53, the liquid crystal compound represented by general formula (VI) is formulated as the third liquid crystal material and the liquid crystal compounds represented by general formulas (VII) to (IX) are selectively formulated.

Of major liquid crystal compositions in Examples 1 through 53 described above, physical properties are shown in Table 15. As is clear from Table 15, in the liquid crystal compositions of the present invention, temperatures at S-N point (smectic phase - nematic phase transition point) are 0°C or lower and temperatures at N-I point (nematic phase - isotropic phase transition point) are 55°C or higher; anisotropy in refractive index Δn is 0.14 or less; and viscosity is 38 cp. or less. The value of dielectric anisotropy Δε is as relatively small as +2 or less but the value of a ratio of dielectric anisotropy Δε to a dielectric constant in the direction perpendicular to the molecular axis of liquid crystal, Δε/ε⊥, is as extremely small as 0.6 or less.
Further in the examples described above, measurement values of elasticity constant ratio $K_{33}/K_{11}$ are shown in Table 16, with respect to major liquid crystal compositions. As shown in Table 16, in the liquid crystal compositions of the present invention, liquid crystal compounds having a small elasticity constant ratio $K_{33}/K_{11}$ value and liquid crystal compounds having a particularly large spray elasticity constant $K_{11}$ are formulated so that the elasticity constant ratio $K_{33}/K_{11}$ value of the liquid crystal compositions is as extremely small as 0.88 or less.

The aforesaid equation (1) which agrees with found values when applied to conventional liquid crystal display elements is inapplicable to the liquid crystal display elements using small values in elasticity constant ratio $K_{33}/K_{11}$ and in $\Delta \varepsilon/\varepsilon_0$. Namely, in the liquid crystal display element using the liquid crystal composition of the present invention, the $\gamma$ property becomes the best when the product of anisotropy in refractive index of the liquid crystal composition, $\Delta n$, and layer thickness of liquid crystal, $d$, i.e., the $\Delta n\cdot d$ value is smaller than 1.1 ($\mu m$) even in the case of wavelength of a light being 550 nm. Accordingly, $\Delta n\cdot d$ becomes small so that visual angle properties are improved; further the layer thickness $d$ of liquid crystal can be reduced so that a decrease in response speed is relatively small.

Here, as the response speed of liquid crystal element has been studied by M. Schadt et al, rise time $t_{ON}$ and trailing time $t_{OFF}$ are expressed by:
\[ t_{ON} = \frac{\eta}{\varepsilon_0 \Delta \varepsilon E^2 - Kq^2} \] \hspace{1cm} \text{(2)}

\[ t_{OFF} = \frac{\eta}{Kq^2} \] \hspace{1cm} \text{(3)}

wherein \( q = \pi/d \), \( \eta \): viscosity, \( E \): electric field

\[
K = K_{11} + \frac{K_{33} - 2K_{22}}{4}
\]

Further the equation (2) for \( t_{ON} \) is modified as:

\[
\eta = \gamma_1 \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}}
\]

\[ V_C = \pi \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}} \] \hspace{1cm} \text{(4)}

to become:

\[
t_{ON} = \frac{\gamma_1 d^2}{2 \pi K (V/V_C - 1)}
\] \hspace{1cm} \text{(5)}

As is clear from the equations (3) and (5) described above, the liquid crystal composition of the present invention has small \( t_{ON} \) and \( t_{OFF} \) and response speed is fast because the \( K_{33}/K_{11} \) value is rendered small by increasing the \( K_{11} \) value. Further by increasing \( \varepsilon_\perp \), teh \( \Delta \varepsilon/\varepsilon_\perp \) value reduced so that there is no necessity to reduce the \( \Delta \varepsilon \) value excessively and, \( \Delta \varepsilon \) value is relatively large though the \( \Delta \varepsilon/\varepsilon_\perp \) value is small. Therefore, increase of \( V_C \) can be relatively reduced, as shown by the equation (4). Accordingly, rise in operation voltage is small.
As has been described hereinabove, the liquid crystal display element using the liquid crystal composition of the present invention provides the best γ property when the Δn.d value is in a small range, rapid visual angle properties and response speed and, high contrast, whereby operation margin can be broadened.

Therefore, the liquid crystal composition of the present invention is most suited for liquid crystal display elements for high time share driving.

Hereafter electro-optical properties will be explained when a liquid crystal display element for time share driving using the liquid crystal composition of the present invention is driven by a time share driving signal of 1/64 duty. Table 17 indicates constitutional factors of the liquid crystal display element and electro-optical properties thereof. The numbering of liquid crystal element corresponds to the number of composition in the liquid crystal composition used.

Herein, anisotropy in refractive index, Δn, indicates a value measured at λ = 589 nm; and contrast is the maximum value of a value (Y_{ON}/Y_{OFF}) obtained by dividing a value of transmittance Y_{ON} when the signal is on in each direction of visual angles by a value of transmittance when it is off, when driven by a driving signal of 1/64 duty.

Threshold voltage V_{th} is a voltage applied when the contrast shows the maximum.

Further the response speed is defined to be value of (Tr + Tp)/2, when rise time is Tr until luminance reaches from 10 % to 90 % and trailing time is Tp until reaches from 90 % to 10 %.
As is clear from this Table 17, the $\Delta n.d$ value is in a range sufficiently smaller than 1.1, contrast is high and the $\gamma$ property is also good. As such, in order to obtain high contrast and good $\gamma$ property with the $\Delta n.d$ value being in the range smaller than 1.1, the elasticity constant ratio $K_{33}/K_{11}$ value is 0.88 or less and the $\Delta\varepsilon/\varepsilon_1$ value is 0.6 or less.

With respect to major liquid crystal display elements out of these elements, visual angle properties thereof are shown in Table 18. Herein, the visual angle property is defined by a value of $V_{th} (\theta = 10^\circ)$ at a temperature of 25°C when a threshold voltage is made $V_{th} (\theta = 10^\circ)$ when observed from direction $P$ inclined from the Z-axis perpendicular to the base plate surface of the liquid crystal display element toward the visual angle direction by 10°; a threshold voltage is made $V_{th} (\theta = 30^\circ)$ when observed from direction $Q$ inclined from the Z-axis toward the visual angle direction by 30° and a threshold voltage is made $V_{th} (\theta = -10^\circ)$ when observed from direction $Q$ inclined from the Z-axis toward the reversed direction to the visual angle direction by 10°. This visual angle property is good, namely, indicates that visual angle is widened, as the value approximates to 1.

As shown in Table 18, the liquid crystal display element using the liquid crystal composition of the present invention is excellent also in visual angle properties. That is, the liquid crystal display elements using the liquid crystal compositions in the aforesaid examples show excellent properties in contrast, operational margin and visual angle properties and can respond at a sufficiently high speed, using driving signals of a voltage obtained by ordinary driving circuits using integral circuits.
Liquid crystal display elements for displaying animations such as television images, etc. require high speed response of 30 msec or more; in this case, when the Δn.d value of the liquid crystal display elements is large, the visual angle properties are worsened and its response speed becomes slow and further when the Δn.d value is small, contrast decreases so that the Δn.d value is desirably in a range of 0.55 to 0.70. Further when the anisotropy in refractive index Δn of the liquid crystal composition is large, the visual angle properties are worsened so that the Δn value is desirably 0.14 or less. Furthermore, when the layer thickness d value of liquid crystal becomes large, a response speed becomes slow so that the layer thickness d value of liquid crystal is desirably 0.7 μm or less.

The liquid crystal compositions for obtaining such liquid crystal display elements for displaying animations have their elasticity constant ratio K_{33}/K_{11} value of 0.8 or less and their Δε/ε value of 0.5 or less. The smaller these values, the more are the electro-optical properties of the liquid crystal display elements improved.

As described above, the liquid crystal composition of the present invention is suited for highly time share-driven liquid crystal display elements and, in particular, most suited for use in liquid crystal display elements requiring high contrast, high speed response and wide visual angle as in television receivers.
In the liquid crystal compositions of the present invention, $K_{11}$ can be increased thereby to decrease $K_{33}/K_{11}$, by formulating pyrimidine type liquid crystal compounds therein as main components. Further liquid crystal compounds having a negative or almost null dielectric anisotropy are mainly formulated and a small amount of liquid crystal compounds having a positive dielectric anisotropy is formulated therein so that $\varepsilon_{\perp}$ can be increased thereby to reduce the $\Delta\varepsilon/\varepsilon_{\perp}$ value. Accordingly, the liquid crystal compositions enable to operation of time sharing-driven liquid crystal display devices at high contrast and high speed and also enable to broadening visual angle.
### Table 12

<table>
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Second Liquid Crystal Material

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Table 15 (continued)

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<td>Electro-optical property:</td>
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</tr>
<tr>
<td>Vth (V)</td>
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<tr>
<td>Response speed (ns)</td>
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<td>34.0 (d-5.3)</td>
<td>39 (d-5.8)</td>
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### Table 18

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<td>34.2</td>
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### Table 18 (continued)

<table>
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<tr>
<th>Liquid Crystal Element No.</th>
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<td><strong>Electro-optical</strong></td>
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<tr>
<td><strong>property:</strong></td>
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<tr>
<td>$Y_{on}/Y_{off}$</td>
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<td>$V_{th} (V)$</td>
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<td>$Y_{on}/Y_{off}$</td>
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<td>$V_{th} (V)$</td>
<td>25.1</td>
<td>34.0</td>
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<td>25.2</td>
</tr>
<tr>
<td><strong>Visual angle</strong></td>
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<td><strong>property</strong></td>
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<td>0.951</td>
<td>0.971</td>
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</table>
Further examples of liquid crystal compositions according to this invention are given below:

Example 54

A liquid crystalline composition consisting of

5  3 % 2-p-cyanophenyl-5-pentyl-1,3-dioxane,
10 % trans-1-p-propylphenyl-4-pentylcyclohexane,
9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
10  6 % 2-p-ethylphenyl-5-heptylpyrimidine,
5  5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyoxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyoxyphenyl-5-heptylpyrimidine,
15  5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-methylphenyl)-ethane,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
20  9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
3 % trans-4-(trans-4-propylcyclohexyl)-methylcyclo-
hexane

and

25  3 % trans-4-(trans-4-propylcyclohexyl)-ethylcyclo-
hexane

has a clearing point of 47.0°, Δε = 1.2 and Δn = 0.125.
Example 55

A liquid crystalline composition consisting of

3 % 2-p-cyanophenyl-5-pentyl-1,3-dioxane,
10 % trans-1-p-propylphenyl-4-pentylcyclohexane,
5 9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,
5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
10 5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
15 2-(p-methylphenyl)-ethane,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentyloxyphenyl)-ethane,
20 and
3 % trans-4-(trans-4-propylcyclohexyl)-ethoxymethylene-
cyclohexane

has a clearing point of 47.0°, Δε = 1.2 and Δn = 0.124.
Example 56

A liquid crystalline composition consisting of

10 % trans-1-p-propylphenyl-4-pentylcyclohexane,
10 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,

5  7 % 2-p-ethylphenyl-5-propylpyrimidine,
  7 % 2-p-propylphenyl-5-propylpyrimidine,
  6 % 2-p-ethylphenyl-5-heptylpyrimidine,

5  5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
  5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
10  5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
  5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
  5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
  2-(p-methylphenyl)-ethane,
15  9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
  2-(p-propylphenyl)-ethane,
  9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
  2-(p-pentyloxyphenyl)-ethane,
  4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
  2-(p-fluorophenyl)-ethane and
  4 % 1-[trans-4-(trans-4-pentyloxyphenyl)-cyclohexyl]-
  2-(p-fluorophenyl)-ethane

has a clearing point of 64°, Δε = 1.0 and Δn = 0.123.

Example 57

A liquid crystalline composition consisting of

10 % trans-1-p-propylphenyl-4-pentylcyclohexane,
  9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine, 
7 % 2-p-propylphenyl-5-propylpyrimidine, 
6 % 2-p-ethylphenyl-5-heptylpyrimidine, 
5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine, 
5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine, 
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine, 
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine, 
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine, 
11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane, 
11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane, 
11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentyloxyphenyl)-ethane and 
15 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 65°, Δε = 1.4 and Δn = 0.124.

Example 58

A liquid crystalline composition consisting of

10 % trans-1-p-ethylphenyl-4-propylcyclohexane, 
8 % trans-1-p-ethoxycyclohexyl-4-propylcyclohexane, 
6 % 2-p-ethylphenyl-5-propylpyrimidine, 
6 % 2-p-propylphenyl-5-propylpyrimidine, 
6 % 2-p-ethylphenyl-5-heptylpyrimidine, 
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine, 
5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine, 
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine, 
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine, 
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[(trans-4)-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
9 % 1-[(trans-4)-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
5  9 % 1-[(trans-4)-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
9 % 1-[(trans-4)-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
3  10 % 1-[(trans-4)-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 68°, Δε = 0.46 and Δn = 0.121.

Example 59

A liquid crystalline composition consisting of

10 % trans-1-p-butanoyloxyphenyl-4-propylcyclohexane,
15  9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,

5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
20  5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
5 9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
3 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 70°, Δe = 1.3 and Δn = 0.127.

Example 60

A liquid crystalline composition consisting of

10 % trans-1-p-propylphenyl-4-pentylocyclohexane,
15 8 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,

7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,

5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
20 5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-(p-methylphenyl)ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-(p-propylphenyl)ethane,
5 8 % 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-(p-pentylphenyl)ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-(p-ethylphenyl)ethane and .
4 % 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-
10 2-(p-cyanophenyl)ethane

has a clearing point of 67°, Δε = 0.55 and Δn = 0.124.

Example 61

A liquid crystalline composition consisting of

12 % trans-1-p-ethylphenyl-4-propylcyclohexane,
15 15 % trans-1-p-methoxyphenyl-4-propylcyclohexane,

5 % 4-butyln-4'-propyl-tolane,
4 % 4-pentyl-4'-propyl-tolane,
4 % 4-butyln-4'-pentyl-tolane,

5 % 2-p-phenylxyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptoxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptoxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
25 2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
8 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
8 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
3 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 60°, Δε = 0.78 and Δn = 0.119.

**Example 62**

A liquid crystalline composition consisting of

9 \% trans-1-p-ethylphenyl-4-propylcyclohexane,
9 \% trans-1-p-ethoxyphenyl-4-propylcyclohexane,

7 \% 2-p-ethylphenyl-5-propylpyrimidine,
7 \% 2-p-propylphenyl-5-propylpyrimidine,
6 \% 2-p-ethylphenyl-5-heptylpyrimidine,

5 \% 2-p-pentyloxyphenyl-5-hexylpyrimidine,
5 \% 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 \% 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 \% 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 \% 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
8 \% 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,

has a clearing point of 65°, Δε = 1.4 and Δn = 0.123.
Example 63

A liquid crystalline composition consisting of

\[ \begin{align*}
6 \% & \text{ trans-1-p-ethylphenyl-4-propylcyclohexane}, \\
5 \% & \text{ trans-1-p-ethoxyphenyl-4-propylcyclohexane}, \\
9 \% & \text{ trans-1-p-butanoyloxyphenyl-4-propylcyclohexane}, \\
6 \% & \text{ 2-p-ethylphenyl-5-propylpyrimidine}, \\
6 \% & \text{ 2-p-propylphenyl-5-propylpyrimidine}, \\
6 \% & \text{ 2-p-ethylphenyl-5-heptylpyrimidine}, \\
5 \% & \text{ 2-p-pentyloxyphenyl-5-hexylpyrimidine}, \\
10 \% & \text{ 2-p-heptyloxyphenyl-5-hexylpyrimidine}, \\
5 \% & \text{ 2-p-nonyloxyphenyl-5-hexylpyrimidine}, \\
5 \% & \text{ 2-p-heptyloxyphenyl-5-heptylpyrimidine}, \\
5 \% & \text{ 2-p-nonyloxyphenyl-5-heptylpyrimidine}, \\
8 \% & \text{ 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane}, \\
15 \% & \text{ 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane}, \\
9 \% & \text{ 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentyloxyphenyl)-ethane and} \\
20 \% & \text{ 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane}
\end{align*} \]

has a clearing point of 67°, \( \Delta \varepsilon = 1.4 \) and \( \Delta n = 0.123 \).

Example 64

A liquid crystalline composition consisting of

\[ \begin{align*}
11 \% & \text{ trans-1-p-ethylphenyl-4-propylcyclohexane}, \\
9 \% & \text{ trans-1-p-butanoyloxyphenyl-4-propylcyclohexane},
\end{align*} \]
6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,
5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
15 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-pentyloxyphenyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 63°, Δε = 1.3 and Δn = 0.119.

Example 65

A liquid crystalline composition consisting of

6 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
9 % trans-1-p-butanoyloxyphenyl-4-propylcyclohexane,

25 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,
5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,  
5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,  
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,  
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,  
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,  

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,  
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,  
10 9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane and  
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane

has a clearing point of 68°, Δε = 1.5 and Δn = 0.123.

15 Example 66

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,  
9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,  

7 % 2-p-ethylphenyl-5-propylpyrimidine,  
7 % 2-p-propylphenyl-5-propylpyrimidine,  
6 % 2-p-ethylphenyl-5-heptylpyrimidine,  

5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,  
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,  
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,  

25 5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,  
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-methylphenyl)-ethane,
8 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-propylphenyl)-ethane,
5 8 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-pentylphenyl)-ethane,
8 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-ethylphenyl)-ethane and
4 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-cyanophenyl)-ethane

has a clearing point of 66°, Δε = 1.5 and Δn = 0.123,
K₃/K₁ = 0.74 and V(10,0,20) = 4.19 Volt.

Example 67

A liquid crystalline composition consisting of

15 9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,

7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,

20 5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

25 9 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-methylphenyl)-ethane,
8 % 1-[(trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
5  4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 66°, Δε = 1.5 and Δn = 0.123.

Example 68

A liquid crystalline composition consisting of
10  2 % 2-p-cyanophenyl-5-pentyl-1,3-dioxane,
   6 % trans-1-p-propylphenyl-4-pentylcyclohexane,
   9 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
   6 % 4-butyl-4'-propyl-tolane,
   6 % 4-pentyl-4'-propyl-tolane,
15  5 % 4-butyl-4'-pentyl-tolane,

7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,

5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
20  5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
25  8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane and
3 % 1-[trans-4-(trans-4-propylcyclohexyl)-4'-methoxy-tolane

has a clearing point of 55°, Δε = 1.2 and Δn = 0.146.
Example 69

A liquid crystalline composition consisting of

10 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
7 % 4-butyl-4'-propyl-tolane,
5 7 % 4-pentyl-4'-propyl-tolane,
7 % 4-butyl-4'-pentyl-tolane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
5 % 2-p-pentyloxyphenyl-5-hexylpyrimidine,
10 5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
15 2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
20 7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-cyanophenyl)-ethane

has a clearing point of 63°, Δε = 1.3 and Δn = 0.151.

Example 70

A liquid crystalline composition consisting of

6 % trans-1-p-propylphenyl-4-pentylcyclohexane,
10 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
5 % 4-butyl-4'-propyl-tolane,
5 % 4-pentyl-4'-propyl-tolane,
5 % 4-butyl-4'-penty1-tolane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propy1phenyl-5-propylpyrimidine,

5 % 2-p-penty1oxyphenyl-5-hexylpyrimidine,
5 % 2-p-hepty1oxyphenyl-5-hexylpyrimidine,
5 % 2-p-nonylx0xyphenyl-5-hexylpyrimidine,
5 % 2-p-hepty1oxyphenyl-5-heptylpyrimidine,

10 5 % 2-p-nonx0xyphenyl-5-heptylpyrimidine,

7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,

15 7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane and

4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-cyanophenyl)-ethane

has a clearing point of 63°, Δε = 1.3 and Δn = 0.139.

Example 71

A liquid crystalline composition consisting of

6 % trans-1-p-propy1phenyl-4-pentylcyclohexane,
25 10 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
5 % 4-butyl-4'-propyl-tolane,
5 % 4-pentyl-4'-propyl-tolane,
5 % 4-butyl-4'-penty1-tolane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
30 6 % 2-p-propy1phenyl-5-propylpyrimidine,
5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,

5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
10 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 64°, Δε = 1.3 and Δn = 0.140.

Example 72

A liquid crystalline composition consisting of

6 % trans-1-p-propylphenyl-4-pentylcyclohexane,
20 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
8 % 4-pentyl-4'-propyl-tolane,
7 % 4-butyl-4'-pentyll-tolane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,

25 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 65°, Δε = 1.4 and Δn = 0.140.

Example 73

A liquid crystalline composition consisting of

6 % trans-1-p-propylphenyl-4-pentylcyclohexane,
15 11.6 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
6.8 % 4-pentyl-4'-propyl-tolane,
6.2 % 4-butyl-4'-pentyl-tolane,
1.2 % 4-ethoxy-4'-methyl-tolane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
20 6 % 2-p-propylphenyl-5-propylpyrimidine,

5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
25 5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
6.6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
7.0 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane and
6.6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane

has a clearing point of 63°, Δε = 1.2 and Δn = 0.139.

Example 74

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans,trans-4-propyl-4'-proproxy-cyclohexylcyclohexane,

7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,

5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane

has a clearing point of 69°, Δε = 1.4 and Δn = 0.119.
Example 75
A liquid crystalline composition consisting of

9.4 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9.4 % trans,trans-4-propyl-4'-propoxy-cyclohexyl-
5
cyclohexane,

7.3 % 2-p-ethylphenyl-5-propylpyrimidine,
7.3 % 2-p-propylphenyl-5-propylpyrimidine,
6.3 % 2-p-ethylphenyl-5-heptylpyrimidine,

5.2 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
10 5.2 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5.2 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5.2 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5.2 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9.4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
15 2-(p-methylphenyl)-ethane,
8.3 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
8.3 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
20 2-(p-pentylphenyl)-ethane and
8.3 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane

has a clearing point of 62°, Δε = 0.8 and Δn = 0.118.

Example 76
A liquid crystalline composition consisting of

25 16 % trans-1-p-ethylphenyl-4-propylcyclohexane,
5 % trans-1-p-methoxyphenyl-4-propylcyclohexane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
5 % 2-p-ethylphenyl-5-heptylpyrimidine,
4 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
10 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane and
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-fluorophenyl)-ethane

has a clearing point of 62°, Δε = 1.2 and Δn = 0.111.

Example 77

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
20 % trans, trans-4-propoxy-4′-propyl-cyclohexylcyclohexane,
4 % 1-(p-cyanophenyl)-2-(trans-4-propylcyclohexyl)-ethane

7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
25 % 2-p-ethylphenyl-5-heptylpyrimidine,

5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
30 % 5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane and
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane

has a clearing point of 62°, δε = 1.4 and Δn = 0.117.

Example 78

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans,trans-4-propoxy-4-propyl-cyclohexylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
7 % 2-p-ethylphenyl-5-heptylpyrimidine,
7 % 2-p-propylphenyl-5-pentylpyrimidine,
3 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
25 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane and
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane
has a clearing point of 63°, Δε = 1.6 and Δn = 0.119.

Example 79

A liquid crystalline composition consisting of
12 % trans-1-p-ethylphenyl-4-propylcyclohexane,
6 % trans-1-p-methoxyphenyl-4-propylcyclohexane,
10 % trans,trans-4-propoxy-4-propylcyclohexylcyclohexane,
8 % 2-p-ethylphenyl-5-propylpyrimidine,
5 % 2-p-propylphenyl-5-propylpyrimidine,
5 % 2-p-hexyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-hexylpyrimidine,
15 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methyphenyl)-ethane,
6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-cyanophenyl)-ethane
has a clearing point of 60°, Δε = 1.2 and Δn = 0.114.
Example 80

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans,trans-4-propoxy-4'-propyl-cyclohexylcyclohexane,
5  7 % 2-p-ethylphenyl-5-propylpyrimidine,
    7 % 2-p-propylphenyl-5-propylpyrimidine,
    7 % 2-p-ethylphenyl-5-heptylpyrimidine,
    7 % 2-p-propylphenyl-5-pentylpyrimidine,
3  2-p-hexyloxyphenyl-5-nonylpyrimidine,
10  3 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
    4 % 2-p-nonyloxyphenyl-5-hexyloxyphenyl-5-heptylpyrimidine,
    4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
    3 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
15  8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-methylphenyl)-ethane,
    7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-propylphenyl)-ethane,
    7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-pentylphenyl)-ethane,
20  7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-ethylphenyl)-ethane and
    8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-cyanophenyl)-ethane

has a clearing point of 65°, Δε = 2.1 and Δn = 0.120.
Example 81

A liquid crystalline composition consisting of

17 % trans-1-p-ethylphenyl-4-propylcyclohexane,
5 % trans-1-p-methoxyphenyl-4-propylcyclohexane,

5 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
6 % 2-p-ethylphenyl-5-heptylpyrimidine,

4 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
10 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-methylphenyl)-ethane,
15 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane and
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-cyanophenyl)-ethane

has a clearing point of 62°, Δε = 1.9 and Δn = 0.113.

Example 82

A liquid crystalline composition consisting of

9 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans,trans-4-methoxy-4'-propyl-cyclohexylcyclohexane,
7 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
7 % 2-p-ethylphenyl-5-heptylpyrimidine,
7 % 2-p-propylphenyl-5-pentylpyrimidine,

5 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

10 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-propylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-pentylphenyl)-ethane,
15 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-ethylphenyl)-ethane and
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
    2-(p-cyanophenyl)-ethane

has a clearing point of 63°, Δɛ = 2.2 and Δn = 0.118.

Example 83

A liquid crystalline composition consisting of

5 % trans-1-p-ethylphenyl-4-propylcyclohexane,
9 % trans,trans-4-methoxy-4'-propylcyclohexylcyclohexane,

25 % 2-p-ethylphenyl-5-propylpyrimidine,
7 % 2-p-propylphenyl-5-propylpyrimidine,
10 % 2-p-ethylphenyl-5-heptylpyrimidine,
9 % 2-p-propylphenyl-5-pentylpyrimidine,
3 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
4 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
4 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-propylphenyl)-ethane,
10 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-pentylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-cyanophenyl)-ethane

has a clearing point of 62°, Δε = 1.7 and Δn = 0.123.

Example 84

A liquid crystalline composition consisting of

3 % trans-1-p-ethylphenyl-4-propylcyclohexane,
20 % trans,trans-4-methoxy-4′-propyl-cyclohexylcyclohexane,

8 % 2-p-ethylphenyl-5-propylpyrimidine,
8 % 2-p-propylphenyl-5-propylpyrimidine,
12 % 2-p-ethylphenyl-5-heptylpyrimidine,
10 % 2-p-propylphenyl-5-pentylpyrimidine,

25 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
3 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
3 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9% 1-[(trans-4-)(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-methylphenyl)-ethane,
9% 1-[(trans-4-)(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-propylphenyl)-ethane,
8% 1-[(trans-4-)(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-pentylphenyl)-ethane,
9% 1-[(trans-4-)(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-ethylphenyl)-ethane and
4% 1-[(trans-4-)(trans-4-propylcyclohexyl)-cyclohexyl]-
2-(p-cyanophenyl)-ethane

has a clearing point of 65°, Δε = 1.7 and Δn = 0.125.

Example 85

A liquid crystalline composition consisting of

10% trans-1-p-propylphenyl-4-pentylcyclohexane,
6% trans-1-p-ethoxyphenyl-4-propylcyclohexane,
1% 4-pentyl-4’-cyanobiphenyl,

8% 2-p-ethylphenyl-5-propylpyrimidine,
8% 2-p-propylphenyl-5-propylpyrimidine,
7% 2-p-ethylphenyl-5-heptylpyrimidine,

20% 7% 2-p-methoxyphenyl-5-heptylpyrimidine,
5% 2-p-heptyloxyphenyl-5-hexylpyrimidine,
5% 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5% 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5% 2-p-nonyloxyphenyl-5-heptylpyrimidine,
11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane and
5 11 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane
has a clearing point of 60°, Δε = 1.1 and Δn = 0.128.

Example 86
A liquid crystalline composition consisting of
10 10 % trans-1-p-propylphenyl-4-pentylcyclohexane,
6 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
1 % 4-pentyl-4'-cyanobiphenyl,
6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,
15 5 % 2-p-ethylphenyl-5-heptylpyrimidine,
6 % 2-p-propylphenyl-5-pentylpyrimidine,
7 % 2-p-methoxyphenyl-5-heptylpyrimidine,
5 % 2-p-heptyloxycyclohexyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
20 5 % 2-p-heptyloxycyclohexyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,
9 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-methylphenyl)-ethane,
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-propylphenyl)-ethane,
25 8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-pentylphenyl)-ethane and
8 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-(p-ethylphenyl)-ethane
has a clearing point of 61°, Δε = 1.2 and Δn = 0.129.
Example 87

A liquid crystalline composition consisting of

6 % trans-1-p-propylphenyl-4-pentylcyclohexane,
14 % trans-1-p-ethoxyphenyl-4-propylcyclohexane,
5 % 4-pentyl-4'-propyl-tolane,
5 % 4-butyl-4'-pentyl-tolane,
3 % 4-ethoxy-4'-methyl-tolane,

6 % 2-p-ethylphenyl-5-propylpyrimidine,
6 % 2-p-propylphenyl-5-propylpyrimidine,

10 % 2-p-hexyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-nonylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-hexylpyrimidine,
5 % 2-p-heptyloxyphenyl-5-heptylpyrimidine,
5 % 2-p-nonyloxyphenyl-5-heptylpyrimidine,

15 % 6-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-methylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-propylphenyl)-ethane,
7 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-pentylphenyl)-ethane,
6 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-ethylphenyl)-ethane and
4 % 1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-
   2-(p-cyanophenyl)-ethane

has a clearing point of 64°, Δε = 1.3 and Δn = 0.140.
CLAIMS:

1. In a twisted nematic liquid crystal display device operating in the high multiplex mode and having a high contrast, the improvement wherein the liquid crystal mixture has a ratio of the elastic constants $K_3/K_1$ as small as possible but not more than 0.9 and a ratio of $\Delta\varepsilon/\varepsilon_\parallel$ of at most 0.3.

2. An improved liquid crystal mixture according to claim 1 in a device operating in the first Gooch and Tarry transmission minimum.

3. An improved liquid crystal mixture according to claim 2 in a device, wherein the electro-optical characteristic curve is at least as steep as that curve in the second such transmission minimum.

4. An improved liquid crystal mixture according to claim 3 in a device, wherein the steepness of the characteristic curve in the first minimum is greater than that in the second minimum.

5. An improved liquid crystal mixture according to claim 1 in a device, wherein $K_3/K_1$ is 0.4 to 0.9 and $\Delta\varepsilon/\varepsilon_\parallel$ is 0.04 to 0.3.
6. An improved liquid crystal mixture according to claim 1 in a device, wherein $K_2/K_1$ is 0.2 to 0.75 and $\Delta \varepsilon/\varepsilon_1$ is 0.1 to 0.3.

7. An improved liquid crystal mixture according to claim 1 which comprises at least five components.

8. An improved liquid crystal mixture according to claim 1 which comprises

(a) at least 10 wt% of a first liquid crystal material comprising at least one of liquid crystal compounds represented by general formula:

$$R_1 - O - N - A - (Z^1 - Q^1)_m - R_2$$  \hspace{1cm} (I)

wherein $R_1$ represents a group $R$; and $R_2$ represents $R$ or $OR$; $R$ being in each case independently a straight chain alkyl group having up to 12 carbon atoms, wherein one or two non-adjacent CH$_2$ groups may be replaced by -O- and/or -CH=CH-, two oxygen atoms not being directly attached to each other,

$A$ is 1,4-phenylene or trans-1,4-cyclohexylene,

$Z^1$ is -CO-O-, -O-CO-, -CH$_2$-O-, -OCH$_2$-, -CH$_2$CH$_2$- or a single bond,

$Q^1$ is 1,4-phenylene or trans-1,4-cyclohexylene, and $m$ is 0, 1 or 2,
(b) less than 10 wt% of a second liquid crystal material comprising one or more liquid crystal compounds having a distinct positive dielectric anisotropy ($\Delta \varepsilon \geq +3$); and,

(c) less than 90 wt% of a third liquid crystal material comprising at least one liquid crystal compound having a negative or substantially neutral dielectric anisotropy.

9. An improved liquid crystal mixture according to claim 8, wherein the first liquid crystal material comprises at least one of liquid crystal compounds represented by the general formula Ia

$$\begin{array}{c}
\text{II} \\
R_3 \\
\text{III} \\
R_4 \\
\end{array}$$

wherein $R_1$ and $R_2$ have the meaning given in claim 8.

10. An improved liquid crystal mixture according to claim 8, wherein the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae II to V:
wherein R₃, R₄, R₅ and R₆ independently represent a straight chain alkyl group having up to 12 carbon atoms, wherein one or two non-adjacent CH₂ groups may be replaced by -O- or -CH=CH-, two oxygen atoms not being directly attached to each other.

11. An improved liquid crystal mixture according to claim 8, wherein the third liquid crystal material comprises liquid crystal compounds having a dielectric anisotropy of -1 to +1.

12. An improved liquid crystal mixture according to claim 8, wherein the third liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae VI to VIII;

wherein R₇ represents R; and R₈ represents R or OR,
wherein R₉ represents R; and R₁₀ represents R or OR,

\[ \text{VIII} \]

wherein R₁₁ represents R; and R₁₂ represents R or OR.

R being in each case independently a straight chain alkyl group having up to 12 carbon atoms wherein one or two non-adjacent CH₂ groups may be replaced by -O- or -CH=CH-, two oxygen atoms not being directly attached to each other.

13. An improved liquid crystal mixture according to claim 8 or 12, wherein the third liquid crystal material further comprises at least one of liquid crystal compounds represented by general formulae IX to XIV:

\[ \text{IX} \]

wherein R₁₃ and R₁₄ represent independently from each other R

\[ \text{X} \]

wherein R₁₅ and R₁₆ represent independently from each other R;

\[ \text{XI} \]
wherein \( R_{17} \) and \( R_{18} \) represent independently from each other \( R \);

\[ R_{19} - \text{H} - \text{H} - \text{COO} - \text{H} - R_{26} \quad \text{XII} \]

wherein \( R_{19} \) and \( R_{20} \) represent independently from each other \( R \);

\[ R_{21} - \text{H} - \text{O} - \text{O} - \text{H} - R_{22} \quad \text{XIII} \]

wherein \( R_{21} \) and \( R_{22} \) represent independently from each other \( R \);

\[ R_{23} - \text{H} - \text{O} - \text{O} - \text{H} - R_{24} \quad \text{XIV} \]

wherein \( R_{23} \) and \( R_{24} \) represent independently from each other \( R \);

\( R \) being in each case independently a straight chain alkyl group having up to 12 carbon atoms, wherein one or two non-adjacent \( \text{CH}_2 \) groups may be replaced by \(-\text{O}-\) or \(-\text{CH}=\text{CH}-\), two oxygen atoms not being directly attached to each other.
14. An improved liquid crystal mixture according to claim 8, wherein the formulation ratios of said first liquid crystal material, said second liquid crystal material and said third liquid crystal material are at least 30 wt%, less than 10 wt% and less than 70 wt%, respectively.

15. An improved liquid crystal mixture according to claim 8, wherein the formulation ratios of said first liquid crystal material, said second liquid crystal material and said third liquid crystal material are 30 to 65 wt%, less than 5 wt% and 35 to 70 wt%, respectively.

16. An improved liquid crystal mixture according to claim 8, wherein the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae II\(\text{f}\) to II\(\text{h}\):

\[
\begin{align*}
\text{II}\text{f} & : R-A^1Z^2O-F \\
\text{II}\text{g} & : R-A^2Z^3O-CN \\
\text{II}\text{h} & : R-A^3Z^4O-CN
\end{align*}
\]
wherein

$A^1$ is

\[
\begin{align*}
&-H\cdot -O-, \\
&-H\cdot -H-, \\
&-N\cdot -N-, \\
&-O\cdot -O-, \\
&-O\cdot -N-, \\
&or -O\cdot -O-, \\
\end{align*}
\]

$Z^2$ is

- CO-O-, -O-CO-, -CH$_2$CH$_2$- or a single bond,

$X$ is hydrogen or fluorine,

$A^2$ and $A^3$ are in each case

\[
\begin{align*}
&-H\cdot -O-, \\
&-H\cdot -H-, \\
&-O\cdot -O-, \\
&or -O\cdot -H-, \\
\end{align*}
\]

$Z^3$ is

- CO-O-, -O-CO-, -CH$_2$O-, -CH$_2$CH$_2$- or a single bond,

$Z^4$ is

- CO-O-, -O-CO- or -CH$_2$CH$_2$-, and

$R$ being in each case independently a straight chain alkyl group having up to 12 carbon atoms, wherein one or two non-adjacent CH$_2$ groups may be replaced by -O- or -CH=CH-, two oxygen atoms not being directly attached to each other.
17. An improved liquid crystal mixture according to claim 16, wherein the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formula

\[ R-\begin{array}{c}
\text{H} \\
\text{H}
\end{array}-\begin{array}{c}
\text{CH}_{2}\text{CH}_{2}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{F}
\end{array} \]

wherein \( R \) and \( X \) have the meaning given in claim 16.

18. An improved liquid crystal mixture according to claim 16, wherein the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae

\[ R-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{COO}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{CN}
\end{array} \]

\[ R-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{COO}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{CN}
\end{array} \]

\[ R-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{CN}
\end{array} \]

wherein \( R \) has the meaning given in claim 16.

19. An improved liquid crystal mixture according to claim 16, wherein the second liquid crystal material comprises at least one of liquid crystal compounds represented by the general formulae

\[ R-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{CH}_{2}\text{CH}_{2}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{CN}
\end{array} \]

\[ R-\begin{array}{c}
\text{H}
\end{array}-\begin{array}{c}
\text{CH}_{2}\text{CH}_{2}
\end{array}-\begin{array}{c}
\text{O}
\end{array}-\begin{array}{c}
\text{CN}
\end{array} \]

wherein \( R \) has the meaning given in claim 16.
20. An improved liquid crystal mixture according to
claim 15, wherein said second liquid crystal material
comprises one or more liquid crystal materials rep-resented by general formula (II):

\[ R_3 \begin{array}{c}
\text{O} \\
\text{O} \\
\text{CN}
\end{array} \]  

(II)

wherein \( R_3 \) represents a straight chain alkyl group
having 1 to 12 carbon atoms, and said third liquid
crystal material comprises liquid crystal compounds
represented by general formulae:

\[ R_7 \begin{array}{c}
\text{H} \\
\text{O} \\
\text{R_8}
\end{array} \]  

(VI)

\[ R_{17} \begin{array}{c}
\text{H} \\
\text{H} \\
\text{CH}_2\text{CH}_2 \\
\text{O} \\
\text{R_{18}}
\end{array} \]  

(XI)

wherein \( R_7, R_{17} \) and \( R_{18} \) independently represent a
straight chain alkyl group having 1 to 12 carbon
atoms, \( R_8 \) represents a straight chain alkyl group,
a straight chain alkoxy group or a straight chain
alkanoyloxy group having 1 to 12 carbon atoms,

and comprises 5 to 25 wt% of liquid crystal com-
pounds represented by general formula (VI), 20 to
35 wt% of liquid crystal compounds represented by
general formula (XI).
21. An improved liquid crystal mixture according to claim 20, wherein said second liquid crystal material additionally comprises 2 to 10 wt% of liquid crystal compounds represented by general formula (IX):

\[
R_{13}-\overset{\text{H}}{\text{H}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-R_{14}
\]  

(IX)

wherein \(R_{13}\) and \(R_{14}\) independently represent a straight chain alkyl group having 1 to 12 carbon atoms.

22. An improved liquid crystal mixture according to claim 15, wherein said second liquid crystal material comprises one or more liquid crystal compounds represented by the formula (II) below:

\[
R_{3}\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\text{CN}
\]  

(II)

wherein \(R_{3}\) represents a straight chain alkyl group having 1 to 12 carbon atoms, and said third liquid crystal material comprises 5 to 45 wt% of liquid crystal compounds represented by the formulae (VI) and (VII) below, and optionally 5 to 25 wt%, 10 to 25 wt%, and 20 to 25 wt%, respectively, of liquid crystal compounds represented by the formulae (IX), (X), and (XI) below:
wherein $R_7$, $R_9$ and $R_{13}$ to $R_{18}$ independently represent a straight chain alkyl group having 1 to 12 carbon atoms, $R_{10}$ represents a straight chain alkyl group or straight chain alkoxy group having 1 to 12 carbon atoms, and $R_8$ represents a straight chain alkyl group, a straight chain alkoxy group or a straight chain alkanoyloxy group having 1 to 12 carbon atoms.

23. An improved liquid crystal mixture according to claim 22, wherein said third liquid crystal material comprises 10 to 40 wt% of liquid crystal compounds represented by the formulae (VI) and (VII).
24. An improved liquid crystal mixture according to claim 15, wherein said second liquid crystal material comprises one or more liquid crystal compounds represented by the formula (II) below:

\[ R_3 - \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ 

wherein \( R_3 \) represents a straight chain alkyl group having 1 to 12 carbon atoms, and said third liquid crystal material comprises 15 to 30 wt%, less than 10 wt%, and 20 to 40 wt%, respectively, of liquid crystal compounds represented by the formulae (VI), (IX), and (X) below, and optionally 5 to 45 wt% of liquid crystal compounds represented by the formula (VII) below:

\[
\begin{align*}
R_7 \text{--} & \text{H} \text{--} \text{O} \text{--} R_8 \\
R_9 \text{--} & \text{H} \text{--} \text{COO} \text{--} \text{O} \text{--} R_{10} \\
R_{12} \text{--} & \text{H} \text{--} \text{O} \text{--} \text{O} \text{--} R_{14} \\
R_{15} \text{--} & \text{H} \text{--} \text{H} \text{--} \text{COO} \text{--} \text{O} \text{--} R_{16}
\end{align*}
\]

wherein \( R_7, R_9 \) and \( R_{12} \) to \( R_{16} \) independently represent a straight chain alkyl group having 1 to 12 carbon atoms, \( R_{10} \) represents a straight chain alkyl group or straight chain alkoxy group having 1 to 12 carbon atoms, and \( R_8 \) represents a straight chain alkyl group, a straight chain alkoxy group or a straight chain alkanoyloxy group having 1 to 12 carbon atoms.
25. An improved liquid crystal mixture according to
claim 24, wherein said third liquid crystal material
comprises less than 42.6 wt\% of liquid crystal com-
ounds represented by the general formula (VII).

5 26. An improved liquid crystal mixture according to one
of claims 1 to 20, wherein said third liquid crystal
material comprises one or more liquid crystal com-
ounds represented by the formulae (XV) and (XVI)
below:

10 \[ R_{25} - \begin{array}{ccc}
\backslash\backslash & \backslash\backslash \\
\circ & C & C \end{array} - R_{26} \] (XV)

\[ R_{27} - \begin{array}{ccc}
\backslash\backslash & \backslash\backslash \\
H & C & C \end{array} - R_{28} \] (XVI)

wherein \( R_{25} \) and \( R_{27} \) each represent \( R \); and \( R_{26} \) and \( R_{28} \)
each represent \( R \) or \( OR \); \( R \) being in each case indepen-
dently a straight chain alkyl group having up to 12
carbon atoms wherein one or two non-adjacent \( CH_2 \)
groups may be replaced by \(-O-\) or \(-CH=CH-\) two oxygen
atoms not being directly attached to each other.

27. An improved liquid crystal mixture according to
claim 26, which comprises 5 to 25 wt\% of said
compounds of formulae (XV) and (XVI).

28. A method of simultaneously minimizing the dependence
of contrast on the angle of observation of an elec-
trooptical display element based on a liquid crystal
mixture and of maximizing its multiplexing capacity
by maximizing its steepness of its characteristic
curve, comprising operating the element in the first
Gooch and Tarry transmission minimum, selecting a
mixture having a \( K_3/K_1 \) ratio as small as possible
but not more than 0.9 and a ratio of \( \Delta\varepsilon/\varepsilon_\perp \) of at
most 0.3.
# INTERNATIONAL SEARCH REPORT

**International Application No**: PCT/EP 88/00928

## I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

- **IPC**: C 09 K 19/02; C 09 K 19/42; G 02 F 1/137

## II. FIELDS SEARCHED

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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<td>X</td>
<td>EP, A, 0174541 (MERCK) 19 March 1986 see page 4, lines 17-32; page 5, lines 1-2,15-36; page 6, lines 1-25; claims 1-4; examples 1,2</td>
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<td>EP, A, 0151446 (MERCK) 14 August 1985 see page 1, lines 1-11; page 3, lines 17-36; examples 1-4; claims 1-4</td>
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<td>WO, A, 87/05714 (MERCK) 24 September 1987 see page 3, lines 10-21; page 4, lines 1-34; page 7, lines 4-11, 20-26; page 8, lines 13-30; pages 16-18; claim 1</td>
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### Special categories of cited documents:

- **A** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier document but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed
- **T** later document published after the international filing date or priority date and not in conflict with the invention cited to understand the principle or theory underlying the invention
- **X** document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- **Y** document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- **Z** document member of the same patent family

## IV. CERTIFICATION

- **Date of the Actual Completion of the International Search**: 31st January 1989
- **Date of Mailing of this International Search Report**: 22 FEB 1989

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: [Signature]

Form PCT/ISA/210 (second sheet) (January 1988)
FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND incompletely searchable

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers *, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   *8,16-27

Claims not fully supported by the description. Search limited to compositions for which examples have been given.

3. Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This international searching authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the international searching authority did not invite payment of any additional fee.

Remarks on protest:

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (supplemental sheet (2)) (January 1985)
ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 8800928
SA 24930

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/02/89. The European Patent Office is in no way liable for those particulars which are merely given for the purpose of information.

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82.