

NEMATIC LIQUID CRYSTAL MATERIALS FOR DISPLAY DEVICES"

1 This invention relates to a nematic liquid
crystal composition used for display devices, particu-
larly those of a multiplexing drive system.

Twisted nematic type (TN type) liquid crystal
5 display elements which belong to field-effect type
liquid crystal display elements and have a structure as
shown in the attached Fig. 1 are widely used now.
The liquid crystal display element shown in Fig. 1
comprises a first substrate 1 and a second substrate 2
10 both of which are made of transparent glass or other
like material and arranged substantially parallel to
each other with a predetermined spacing, for example
5 to 15 μm , and sealed at the periphery with a sealant
3 such as glass frit or an organic adhesive, and a
15 nematic liquid crystal 4 encapsulated therein. The
predetermined spacing may be provided by placing a
spacer 5 made of fiber glass, glass powder or such.
The sealant 3 may be so designed as to double as
spacer.

20 Electrodes 6 of a predetermined pattern are
formed on the internal opposing sides of said first and
second substrates 1 and 2, and the faces contacted with
the liquid crystal are worked into liquid crystal
controlling planes 7 and 8 where the liquid crystal
25 molecules in the vicinity of these planes are oriented

50

1 in a given direction. Such orientation controlling
planes can be formed by coating the electrode-carrying
side of each substrate with an oblique vacuum vaporiza-
tion film of SiO or with an organic high-molecular film
5 or a film of an inorganic material, and rubbing the
coated surface in a given direction with cotton or other
means.

The liquid crystal orientation controlling
planes 7 and 8 of the first and second substrates 1 and
10 2 are differentiated in the liquid crystal orienting
direction so that the molecules of the nematic liquid
crystal 4 disposed between said both substrates 1 and 2
will be oriented twistedly from one direction (first
direction on the controlling plane 7) to the other
15 direction (second direction on the controlling plane
8). The angle made by the first and second directions,
namely, the angle of twist of the liquid crystal
molecules may be suitably selected, but usually such
angle is defined to be about 90° as shown in Fig. 2.

20 A first polarizer 9 and a second polarizer
10 are disposed on the outside of the substrates 1 and
2, respectively. These two polarizers 9, 10 are
usually arranged such that the angle made by their
respective axes of polarization will be equal to the
25 twist angle of the liquid crystal molecules (the
angle made by said first and second orientation direc-
tions) or will be zero (in this case the respective
axes of polarization are parallel to each other), and

- 1 that the axis of polarization of each polarizer will be parallel to or cross at right angles with the liquid crystal orienting plane of the associated substrate.

Such display element is widely utilized as
5 a reflection type display element by providing a reflector 11 on the back side of the second polarizer 9 for effectuating normal display as seen from the first substrate side, or as a night-time display element by further incorporating a photoconductor made of an
10 acrylic resin, glass or the like with a suitable thickness between the second polarizer 9 and reflector 11 and placing a light source on a suitable location on a side of said photoconductor.

Here, the operational principle of a reflection type liquid crystal display element arranged with
15 90° twist angle and 90° polarization axes crossing angle is described.

In case no electric field is present in the liquid crystal layer, the incoming light (ambient
20 light incident upon the first polarizer 9 of the liquid crystal display element) is transmitted through the first polarizer 9 to become rectilinear polarized light running along the axis of polarization and enters the liquid crystal layer, but since the liquid crystal
25 molecules are twisted 90° in said layer, the plane of polarization of the polarized light is optically rotated by 90° upon passage of the light through the liquid crystal layer, and then the polarized light passes the

1 second polarizer 10. This polarized light is then
reflected on the reflector 11 and transmitted reversely
through the second polarizer 10, liquid crystal layer
4 and first polarizer 9 in that order and finally
5 emanated out of the liquid crystal display element.
Thus, the observer can see the polarized light which
has entered the liquid crystal display element and
again comes out of said element after reflected by the
reflector.

10 On the other hand, when a predetermined
voltage is applied to a certain selected electrode 6
to give an electric field in a certain area of the
liquid crystal layer in said display element, the
liquid crystal molecules in that area are oriented in
15 the direction of the electric field, and as a result,
such area of the liquid crystal layer is deprived of
its optical rotating capacity for the polarization
plane and hence the plane of polarization in said area
undergoes no optical rotation, so that the light
20 polarized by the first polarizer 9 is intercepted by
the second polarizer 10 and therefore that area looks
dark to the observer. It is thus possible to effect
desired display by applying an electric voltage to a
pertinent electrode.

25 It is said that most desirable ones of the
liquid crystal materials (including compounds and
compositions) used for field-effect type liquid crystal
display elements mentioned above are those which meet

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- 5 -

1 the following three requirements:

First requirement: good adaptability to the orientation controlling section.

5 Second requirement: operability over a wide temperature range.

Third requirement: good responsiveness over a wide temperature range, particularly at low temperatures.

Regarding the first requirement, it is of
10 paramount importance for the structure of the display element to control the molecular arrangement such that the molecules of the liquid crystal compound 4 will be oriented parallel to each other and in one direction at the interfaces of the upper and lower plates which
15 hold the molecules. Such control has been accomplished heretofore by forming a SiO film at the interface by oblique vacuum vaporization, or by rubbing techniques.

As for the second requirement, it is the minimum requirement that the material is liquid crystal
20 at around normal temperature (25°C), but practically it is required that the material presents a liquid crystal condition in the temperature range of -10°C to about +60°C or higher.

In this invention, the transition temperature
25 of a solid ↔ a liquid crystal (or a smectic liquid crystal ↔ a nematic liquid crystal) is decided and defined according to the results of the following measurements. There are many occasions where the

1 individual single liquid crystal compounds or mixed
compositions thereof undergo over-cooling. In such a
case, the compound (or composition) is cooled to a
sufficiently low temperature (for example -40°C) and
5 then the transition temperature in the rising trend of
temperature is measured by a micro melting-point
measuring apparatus, and the thus measured temperature
is given as transition temperature of the solid $\leftrightarrow$
liquid crystal compounds (or the smectic liquid
10 crystal $\leftrightarrow$ the nematic liquid crystal). This second
requirement is of great significance not only for
ordinary static driving but also for driving by a
so-called multiplexing drive system. The multiplexing
drive system according to, for example, the voltage-
15 averaging method is now predominantly employed in the
liquid crystal display devices, particularly those
requiring voluminous informations, such as for example
table-type electronic computers or matrix displays.
Low voltage driving is desirable for the table-type
20 electronic computers or the like, and usually there is
employed a 4.5 V driving system (using three 1.5 V
cells) or 3 V driving system (using two 1.5 V cells)
where the cells are connected in series to effect direct
driving. This low voltage driving requires no boosting
25 circuit since the cells are connected in series, and
also the cell life can be prolonged to 500 to 2,000
hours by combination with C-MOS.

However, such multiplexing drive system is

1 subject, in principle, to certain operational restric-
tions which are not seen in the static driving system.
In the multiplexing drive display devices, it is
required to prevent cross-talks in the picture element
5 at each half-selection or non-selection point, and the
voltage-averaging method is most popularly used for
prevention of such cross-talks. This method was
designed for expanding the operational margin by averag-
ing the cross-talk voltages to enlarge the difference
10 from the selection voltage. This method is explained
below by citing a typical case of application.

Described here is a case of application of
the voltage-averaging method where the cross-talk
voltages are averaged down to $1/3$ of the selection
15 voltage and the driving wave form is made alternating.
The driving wave form of this system is shown in Fig.
3 in which V_x is selection voltage, V_y is signal
voltage, and $V_x - V_y$ is applied voltage. In Fig. 3, a
voltage of $\pm V_o$ is applied to the liquid crystal in the
20 selected condition while a voltage of $\pm (1/3)V_o$ is
applied to the liquid crystal in the half-selected or
non-selected condition. In this case, the effective
voltage v_{sl} applied to the display point (the point at
which the liquid crystal is brought into a displaying
25 condition) is given by the following formula:

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$$\begin{aligned}
 v_{s1} &= \sqrt{\frac{1}{N} \{ V_o^2 + (N - 1) \frac{1}{9} V_o^2 \}} \\
 &= \frac{1}{3} V_o \sqrt{1 + \frac{8}{N}}
 \end{aligned} \tag{1}$$

1 wherein N: duty number

On the other hand, effective voltage v_{s2} applied to the non-display point is given by:

$$v_{s2} = \frac{1}{3} V_o \tag{2}$$

Here, in order to evolve a displaying mode at the
 5 display point, effective voltage v_{s1} must be greater than or equal to threshold voltage V_{th} of the liquid crystal ($v_{s1} \geq V_{th}$), and in order to prevent cross-talks from being produced at the non-display point, effective voltage v_{s2} must be smaller than or equal to
 10 V_{th} ($v_{s2} \leq V_{th}$). In other words, the following condition must be met for providing a cross-talk-free display according to this driving system:

$$v_{s2} \leq V_{th} \leq v_{s1} \tag{3}$$

Introducing the formulae (1) and (2) into the formula (3), V_o is defined as follows:

$$3 V_{th} \sqrt{\frac{N}{N+8}} \leq V_o \leq 3 V_{th} \tag{4}$$

- 1 Measuring brightness at the display and non-display
points by varying V_o , there are obtained the results
such as shown in Fig. 8. At the display and non-
display points exist the liquid crystal threshold
5 voltages V_{th1} and V_{th2} as converted to the V_o basis,
and when the following condition is met:

$$V_{th1} \leq V_o \leq V_{th2} \quad (5)$$

cross-talk-free display is made possible. From the
formula (4), V_{th1} and V_{th2} can be given as follows:

$$V_{th1} = 3 V_{th} \sqrt{\frac{N}{N+8}} \quad (6)$$

$$V_{th2} = 3 V_{th} \quad (7)$$

- To be more exact concerning the formula (5), the lower
10 threshold value of voltage that allows display is not
 V_{th1} but should rather be the saturation voltage V_{sat1}
shown in Fig. 8. In other words, the voltage range
that allows cross-talk-free display is given by the
following formula:

$$V_{sat1} \leq V_o \leq V_{th2} \quad (8)$$

- 15 It may be said that the greater the range of fluctua-
tion of V_o in the above-formula (8), the broader is
the operational margin (M) of the display device.

1 In the above-described derivation of formulae, v_{s1} and
 v_{s2} and hence V_{th1} , V_{th2} , and V_{sat1} are all considered
as constant, but these values are actually variable
depending on the ambient temperature (T), viewing
5 angles to the element (θ , ϕ) and other factors (Fig. 4).
In the above explanations for the formula (1) through
formula (8), viewing angle θ defined in Fig. 4 is
supposed to be 0, but actually such viewing angle may
take a value within a limited range.

10 As viewed above, there are various factors
that decide the operational margin (M). These factors
are explained in due order hereinbelow, but it will be
convenient for understanding such factors and the
essence of the problem to give particular considerations
15 to the following three essential elements:

(i) variation of threshold voltage with change of
temperature

(ii) variation of threshold voltage with change of
angle

20 (iii) sharpness of voltage-brightness characteristic.
The relation between (i) - (iii) and operational margin
(M) will be clarified quantitatively by means of actual
measurements.

The electro-optical characteristics of the
25 multiplexing drive system are determined by the method
illustrated in Fig. 5. A liquid crystal display element
51 is placed in a constant-temperature tank 53 with an
inclination between 10° and 40° to the luminometer 52,

1 and light is applied to said display element 51 through
a heat-absorbing glass filter 55 from a tungsten lamp
54 disposed with an angle of 30° to the luminometer 52,
and the brightness of said element 51 is measured by
5 the luminometer 52.

The driving wave forms in the case of $1/3$
bias, $1/3$ duty and $1/2$ bias, $1/2$ duty multiplexing
drive as measured by the above-said method are as shown
in Figs. 6 and 7. Fig. 8 shows the voltage-brightness
10 characteristics as determined from these wave forms.
In Fig. 8, region I is the area where the display is
not lighted, and region II is the area where the
display is lighted only at the selected segments.
Desired display of figures, letters, etc., can be made
15 in the region II. Region III is the area where all
the segments are lighted and no display function is
performed, that is, cross-talk occurs. In the drawing,
 V_{th1} is voltage at selected segment (ON mode) of 10%
brightness, V_{th2} is voltage at non-selected segment
20 (OFF mode) of 10% brightness, V_{sat1} is 50% brightness
selected segment voltage, and V_{sat2} is 50% brightness
non-selected segment voltage.

The operational margin (M) is defined by the
following formula:

$$M(\%) = \frac{\{V_{th2}(T=40, \theta=40^\circ, f=100) - V_{sat1}(T=0, \theta=10^\circ, f=550)\}}{\{V_{th2}(T=40, \theta=40^\circ, f=100) + V_{sat1}(T=0, \theta=10^\circ, f=550)\}} \times 100 \quad (9)$$

- 1 wherein T = temperature ($^\circ\text{C}$) 0 - 40°C
 θ = viewing angle ($^\circ$) 10 - 40°
 f = frequency (Hz) 100 - 550 Hz

Therefore, "broad operational margin" is synonymous
 5 with "broad region II". Thus, the multiplexing drive system must be driven in a certain range of voltage margin.

Further analysis of the operational margin (M) given by the formula (9) shows that M is decided
 10 by the afore-said three factors (i) - (iii), and these factors are quantitatively defined by the following formulae:

(1) Temperature characteristic ΔT of V_{th} :

$$\Delta T = \frac{V_{th2}(T=0^\circ\text{C}) - V_{th2}(T=40^\circ\text{C})}{V_{th2}(T=0^\circ\text{C}) + V_{th2}(T=40^\circ\text{C})} \times 100 (\%) \quad (10)$$

The definition is made under the following
 15 conditions: T = 0 - 40°C , $\theta = 40^\circ$, f = 100 Hz.

- 1 (ii) Angle dependency $\Delta\theta$ of V_{th} :

$$\Delta\theta = \frac{V_{th2}(\theta = 40^\circ)}{V_{th2}(\theta = 10^\circ)} \quad (11)$$

at $T = 40^\circ\text{C}$, $f = 100 \text{ Hz}$.

- (iii) Sharpness γ of voltage-brightness characteristic:

$$\gamma = \frac{V_{sat1}}{V_{th1}} \quad (12)$$

- Although these three factors (i) - (iii) are the
5 principal elements, usually frequency characteristic
 Δf should be also taken into consideration as additional factor.

$$\Delta f = \frac{V_{th1}(f = 550)}{V_{th1}(f = 100)} \quad (13)$$

Δf was defined under the conditions of $T = 40^\circ\text{C}$ and
 $\theta = 40^\circ$.

- 10 The margin α of the voltage-averaging method
is defined as follows for convenience of derivation of
formulae:

$$\alpha = \frac{V_{th2}}{V_{th1}} \quad (14)$$

- 1 Substituting the formulae (10) - (14) for the formula (9), operational margin M is given as:

$$M = \frac{1 - \left(\frac{\gamma}{\Delta\theta}\right) \frac{\Delta f}{\alpha \cdot A}}{1 + \left(\frac{\gamma}{\Delta\theta}\right) \frac{\Delta f}{\alpha \cdot A}} \quad (15)$$

wherein $A = \frac{1 - \Delta T}{1 + \Delta T}$

Generally, γ , $\Delta\theta$, ΔT and Δf may be defined as follows:

- 5 $\gamma \geq 1$, $\Delta\theta \leq 1$, $\Delta T \geq 0$ and $\Delta f \leq 1$.

The hereabove defined operational margin may vary over a wide range depending on the liquid crystal compound used, but it is noticed that the compound capable of giving a greater margin is suited for

- 10 multiplexing drive. As apparent from the formula (15), it is required for enlarging the operational margin M to make temperature characteristic ΔT approach zero as much as possible and to make the angle dependency $\Delta\theta$, voltage-brightness sharpness and frequency characteris-
- 15 tic Δf approach as close to 1 as possible. In some cases, the effect of the temperature characteristic may be made almost ignorable in enlarging the operational margin by incorporating a temperature compensation circuit in the device. However, provision of such
- 20 temperature compensation circuit necessarily leads to an elevated manufacturing cost of the device, so that it is desirable to employ the parts (elements) which

1 can provide a wide operational margin with no extra condition such as provision of a compensation circuit, particularly in the case of the popularly used devices such as table-type electronic computers.

5 As for the third requirement, namely, good responsiveness over a wide temperature range, particularly at low temperatures, the following consideration will be instructive. Generally, responsiveness in the twisted nematic mode for multiplexing drive is given by
10 the following formulae:

$$t_{\text{rise}} = \frac{1}{\left(\frac{8}{N} + 1\right)} \cdot \frac{\eta \cdot d^2}{K} \quad (16)$$

$$t_{\text{fall}} = d^2 \eta / K \quad (17)$$

η : viscosity

K : elastic constant (refer to formula (43)"
shown later)

d : liquid crystal layer thickness

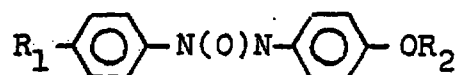
15 It is noticed from the above formulae that liquid crystal responsiveness is decided mostly by viscosity of the liquid crystal material. It is said that these theoretical formulae well agree with actual measurements, and it is apparent to those skilled in the art
20 that improvement of responsiveness can be attained by properly adjusting the viscosity of the liquid crystal compound used.

Thus, fulfillment of the third requirement

1 depends on whether a liquid crystal compound having a
low viscosity (and of course meeting the first and
second requirements) can be found or not.

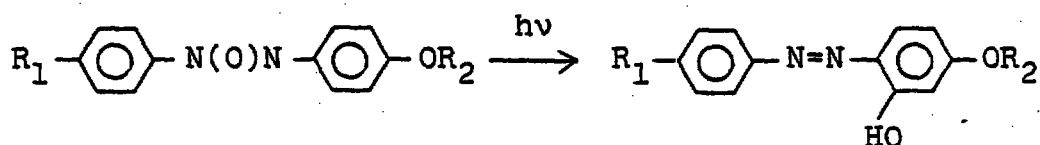
As for the third requirement, there has been
5 studied to find out liquid crystal materials having a
low viscosity as well as satisfying the first and
second requirements mentioned above.

On one hand, various types of liquid crystal
materials for display elements, particularly those of
10 a multiplexing drive system, such as Schiff base type,
ester type, biphenyl type, azoxy type, etc., have been
proposed to date. The azoxy type liquid crystal
materials have excellent temperature characteristics
(small in ΔT), that is, they are very limited in
15 variation of threshold voltage with change of temper-
ature and, as explained later, they provide an operatio-
nal margin M of greater than 10% under the 1/3 bias and
1/3 duty multiplexing drive conditions. The azoxy
liquid crystal materials are represented by the
20 following general formula:



They possess per se weakly negative dielectric aniso-
tropy and are usually used as a mixed system with a
nematic liquid crystal compound having positive
dielectric anisotropy (N_p). But these azoxy type
25 liquid crystal materials are colored (in yellow) as

- 1 they absorb a part of visible light. Also, they show the maximum light absorption at 350 nm and undergo the following photochemical reaction owing to the wavelength around such level:



- 5 A non-liquid crystal compound is produced by such photochemical reaction and this new product changes the color of the liquid crystal from yellow into red. Usually, electric resistance of the liquid crystal is also sharply lowered. Therefore, in actual use of such
- 10 azoxy type nematic liquid crystals, it needs to adapt a 500 nm cut filter in the device (element) so as to avoid photo-deterioration that might be caused by the sunlight or fluorescent light. This naturally complicates the mechanism of the device (element).

- 15 Other types of liquid crystals which are resistant to such photo-deterioration, such as Schiff base type, biphenyl type, ester type, etc., have been noticed for their availability as white display material and their adaptation to the display devices
- 20 has been debated.

The biphenyl type liquid crystals are credited with high chemical stability as they are highly resistant to light, water and oxygen. However, most of the known biphenyl type materials which form

1 liquid crystal at room temperature are the ones having
positive dielectric anisotropy, and a few are known of
the negative equivalents which are liquid crystal at
room temperature and practically useful. Therefore,
5 there are only a few kinds of liquid crystal compounds
which can form a mixed system with biphenyl type alone.
Also, because of not so high value of positive dielec-
tric anisotropy, wide range adjustment of threshold
value is hardly possible with these materials, and
10 further, such threshold voltage has high temperature
dependency (large in ΔT), so that these materials are
generally considered unsuited for multiplexing drive.

The ester type liquid crystal compounds have
relatively good chemical stability and there are known
15 many kinds of single liquid crystal compounds of posi-
tive or negative dielectric anisotropy. However,
threshold voltage of these compounds has relatively
high temperature dependency and their viscosity is also
considerably high, so that generally these compounds
20 can hardly meet the afore-said second and third
requirements.

The Schiff base type liquid crystal compounds
have better properties than the ester type, but because
of strong hydrolytic disposition, matching with the
25 packing portion of the display element is often required
for their use.

Individual liquid crystal materials are
disclosed in, for example, U.S. Patent Nos. 4,137,192.

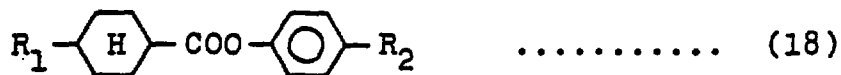
1 and 4,147,651, Molecular Crystals and Liquid Crystals
22, 285-299 (1973), J. Org. Chem. 38, 3160-3164 (1973),
East German Patent No. 105,701, etc., but their special
combinations are not known yet.

5 The present inventors have found that a system
using a nematic liquid crystal with negative dielectric
anisotropy (Nn type liquid crystal) as matrix and also
incorporating a proper quantity of a nematic liquid
10 liquid crystal) and/or its analogue (a substance
analogous to the positive nematic liquid crystal in
molecular structure, hereinafter referred to as Np
type liquid crystal analogue) can meet the second and
third of the aforesaid three requirements and that such
15 system can exist in the Schiff base type liquid crystal
systems or cyclohexanecarboxylic acid-trans-4'-alkoxy-
phenyl ester type liquid crystal systems.

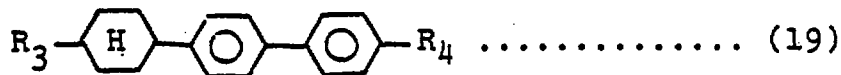
According to this invention, therefore, the
said defects of the conventional liquid crystal
20 materials are desirably eliminated, in other words, there
is provided a liquid crystal composition which is
capable of stable orientation in a wide temperature
range, permits setting of the threshold voltage value
over a wide range, is minimized in both temperature
25 dependency and viewing angle dependency of such thresh-
hold value and also has high responsiveness.

The present invention provides a liquid
crystal composition for display devices comprising at

- 1 least one compound represented by the following general formula:



- wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$,
 R_2 is $n\text{-C}_q\text{H}_{2q+1}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$, and m and
 5 q are each an integer of 1 to 10, and at least one compound represented by the general formula:



- wherein R_3 is $n\text{-C}_r\text{H}_{2r+1}$ or $n\text{-C}_r\text{H}_{2r+1}\text{-O}$, R_4 is
 $n\text{-C}_s\text{H}_{2s+1}$ or $n\text{-C}_s\text{H}_{2s+1}\text{-O}$, and r and s are each
 an integer of 1 to 10. In the above definitions,
 10 n is a symbol denoting that carbon is straight-chain, and this denotation applies throughout this specification. Also, in the above-shown compounds, linkage of cyclohexane ring carbon to carboxyl group carbon and that of cyclohexane ring carbon to benzene
 15 group are supposed to be an equatorial bond.

The present invention also provides a liquid crystal composition best suited for multiplexing drive by combining said matrix mixture system and a nematic liquid crystal with positive dielectric anisotropy
 20 (Np).

This invention further provides a liquid crystal composition capable of improving the various properties required for multiplexing drive by adding

1 an Nn type liquid crystal to the
mixture system consisting of an Nn type mixture system
comprising the compounds of the above-shown formulae
(18) and (19) and an Np type liquid crystal obtained
5 from the above-said researches.

In the accompanying drawings, Fig. 1 is a
sectional view showing an example of liquid crystal
display element; Fig. 2 is a structural diagram showing
a pattern of orientation of the liquid crystal molecu-
10 les; Fig. 3 is a diagram exemplifying the multiplexing
drive waveforms according to the voltage-averaging
method (1/3 bias); Fig. 4 is a drawing illustrating
the definition of viewing angle; Fig. 5 is a schematic
illustration of an electro-optical properties measuring
15 device; Fig. 6 shows the 1/3 bias and 1/3 duty driving
waveforms; Fig. 7 shows the 1/2 bias and 1/2 duty
driving waveforms; Fig. 7 is a graphic representation
of the brightness-voltage characteristics in multiplex-
ing drive; Fig. 9 is a characteristic diagram showing
20 the relationship between Np/Nn mixing ratio and V_{th} ;
and Figs. 10 to 13 are characteristic diagrams of
viscosity as observed when the compounds of the general
formula:

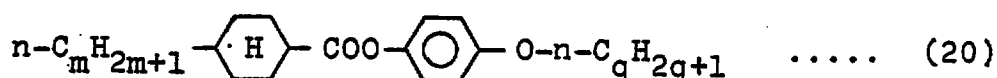


were added to various matrix liquid crystals.

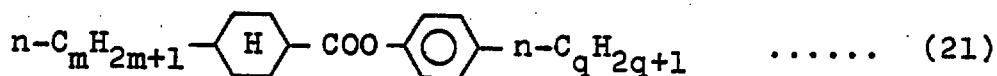
25 The invention is described in further detail

1 hereinbelow while showing the preferred embodiments thereof.

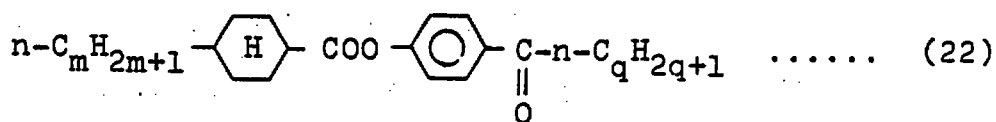
Regarding first the compositions constituted by the respective liquid crystal compounds having the
5 chemical structure shown by the formula (18), the most preferred constituent compounds are those of the formula:



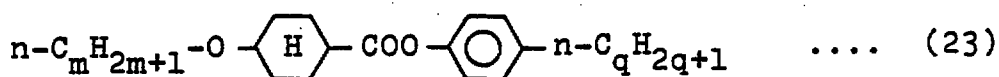
wherein m and q are each an integer of 1 to 10, and the preferred combinations of (m and q) in the above formula
10 (20) are: (3 and 5), (4 and 5), (5 and 5), (6 and 5), (4 and 6), (3 and 1), (3 and 2), (3 and 3), (3 and 4), (3 and 9), (4 and 1), (4 and 2), (4 and 3), (4 and 4), (4 and 6), (4 and 8), (5 and 1), (5 and 2), (5 and 3), (5 and 4), (5 and 6), and (5 and 7). In the case of
15 the compounds of the formula:



wherein m and q are each an integer of 1 to 10, the (m and q) combinations of (5 and 2), (5 and 3) and (5 and 5) are preferred. As for the compounds of the formula:



- 1 wherein m and q are each an integer of 1 to 10, the combinations of (3 and 4), (4 and 4), (4 and 1), (5 and 4) and (5 and 9) are preferred, and for the compounds of the formula:



- 5 wherein m and q are each an integer of 1 to 10, the combinations of (5 and 3) and (5 and 5) are recommended. As regards the compounds represented by the formula (19), the following types are most preferred: ($R_3 = C_2H_5$ and $R_4 = CH_3$), ($R_3 = C_2H_5$ and $R_4 = n-C_4H_9$),
- 10 ($R_3 = n-C_3H_7$ and $R_4 = n-C_5H_{11}$), ($R_3 = n-C_4H_9$ and $R_4 = n-C_4H_9$), ($R_3 = n-C_5H_{11}$ and $R_4 = n-C_5H_{11}$), ($R_3 = n-C_7H_{15}$ and $R_4 = n-C_5H_{11}$), ($R_3 = CH_3$ and $R_4 = C_2H_5O$), ($R_3 = CH_3$ and $R_4 = n-C_8H_{17}O$), ($R_3 = C_2H_5$ and $R_4 = CH_3O$), ($R_3 = n-C_4H_9$ and $R_4 = CH_3O$), ($R_3 = n-C_4H_9$ and $R_4 =$
- 15 C_2H_5O), ($R_3 = n-C_4H_9$ and $R_4 = n-C_6H_{13}O$), ($R_3 = n-C_5H_{11}$ and $R_4 = n-C_8H_{17}O$), ($R_3 = n-C_6H_{13}$ and $R_4 = n-C_6H_{13}O$), ($R_3 = CH_3O$ and $R_4 = C_2H_5$), ($R_3 = CH_3O$ and $R_4 = n-C_3H_7$), ($R_3 = n-C_5H_{11}O$ and $R_4 = n-C_3H_7$), ($R_3 = CH_3O$ and $R_4 = n-C_4H_9$), ($R_3 = C_2H_5O$ and $R_4 = n-C_4H_9$), ($R_3 = n-C_{10}H_{21}O$
- 20 and $R_4 = n-C_4H_9$), ($R_3 = n-C_4H_9$ and $R_4 = n-C_5H_{11}$), ($R_3 = n-C_5H_{11}O$ and $R_4 = n-C_5H_{11}$) and ($R_3 = CH_3O$ and $R_4 = n-C_8H_{17}$).

In the mixed system of at least one compound of the formula (18) and at least one compound of the formula (19), it is desirable that the respective

25

1 compounds of the formulae (18) and (19) have per se a wide mesomorphic range (MR) so as to be a matrix system satisfying not only the first requirement but also the second and third requirements as well.

5 Table 1 below shows mesomorphic ranges (MR) of principal Nn type 4-n-alkyl-cyclohexanecarboxylic acid-trans-4'-alkoxyphenyl esters.

Table 1

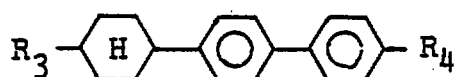
$R_1 - \text{C}_6\text{H}_{10} - \text{COO} - \text{C}_6\text{H}_4 - \text{OR}_2$ (4-n-alkyl-cyclohexane-carboxylic acid-trans-4'-alkoxyphenyl esters)			
Symbol	R ₁	R ₂	MR (°C)
A	C ₃ H ₇	C ₅ H ₁₁	37 to 67
B	C ₄ H ₉	C ₅ H ₁₁	26 to 67
C	C ₅ H ₁₁	C ₅ H ₁₁	31 to 77
D	C ₆ H ₁₃	C ₅ H ₁₁	44 to 52
E	C ₄ H ₉	C ₆ H ₁₃	25 to 69
F	C ₃ H ₇	CH ₃	55 to 64
G	C ₃ H ₇	C ₃ H ₇	54 to 65
H	C ₄ H ₉	CH ₃	42 to 61
I	C ₄ H ₉	C ₂ H ₅	36 to 74
J	C ₄ H ₉	C ₆ H ₁₃	26 to 70
K	C ₅ H ₁₁	C ₂ H ₅	56 to 86
L	C ₅ H ₁₁	C ₄ H ₉	48 to 80

- 1 Proper mixing of these compounds gives mixed systems having fairly wide MR as shown in Table 2 below.

Table 2

No.	Symbol	Nn liquid crystals (figures in parentheses show % by weight)	MR (°C)
1	1-1	A(50) + C(50)	13 to 70
2	1-2	C(50) + E(50)	17 to 71
3	1-3	A(50) + E(50)	12 to 65
4	1-4	A(50) + C(25) + E(25)	9 to 69.5
5	1-5	A(33.3) + C(33.3) + E(33.3)	11 to 70
6	1-6	A(33.3) + B(33.3) + C(33.3)	15 to 69
7	1-7	D(50) + K(50)	13 to 81
8	1-8	B(50) + K(50)	15 to 78
9	1-9	B(50) + D(50)	21 to 69
10	1-10	A(50) + K(50)	21 to 77
11	1-11	C(50) + K(50)	15 to 81

- 5 Table 3 shows mesomorphic ranges (MR) of typical examples of the compounds represented by the general formula:

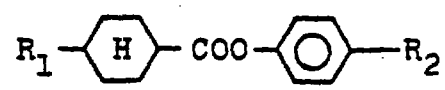


(see formula (19)).

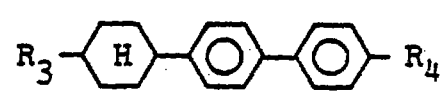
Table 3

$R_3 - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - R_4$				
Symbol	R_3	R_4	Crystal-smectic transition temp. ($^{\circ}\text{C}$)	MR ($^{\circ}\text{C}$)
3-1	$n\text{-C}_5\text{H}_{11}\text{-}$	$\text{C}_2\text{H}_5\text{-}$	143	146 to 163
3-2	$n\text{-C}_5\text{H}_{11}\text{-}$	$n\text{-C}_4\text{H}_9\text{-}$	143	160 to 168

1 Table 4 shows the mesomorphic ranges (MR) of mixed systems of the compounds represented by the general formula:



and mixed systems of the compounds represented by the
5 general formula:



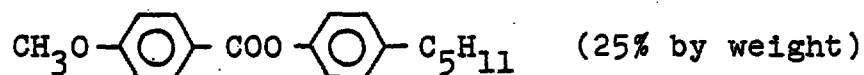
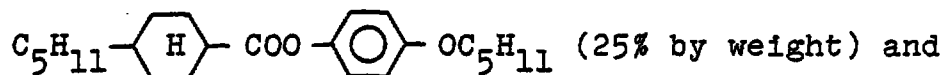
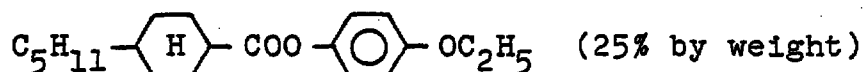
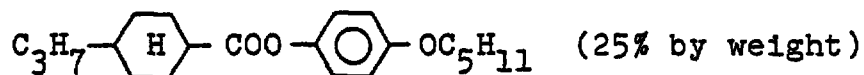
76

- 27 -
Table 4

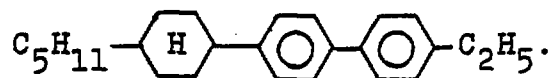
Symbol	A (wt%)	B (wt%)	MR (°C)
4-1	100	0	4 to 62
4-2	95	5	-15 to 66
4-3	90	10	-13 to 71
4-4	85	15	-10 to 75

1

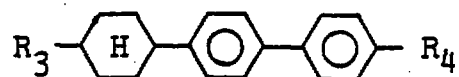
In the above table, A is composed of:



and B is composed of:



As is clear from the above-shown tables, the upper limit of the mesomorphic range (MR) rises as a compound of the formula:



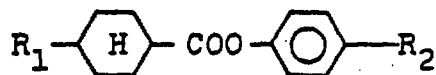
1 is added. Also, as shown in Table 3, some of the compounds of the formula:



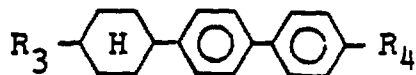
have a smectic phase in a relatively high mesomorphic range, but when they are mixed in the matrix systems principally composed of the liquid crystals represented by the formula (18), the result is that either the smectic phase appears in a low temperature range alone or it does not appear at all.

In case these mixed system liquid crystals are used in the twisted nematic field-effect type liquid crystal display elements, it is essential that the mixed system liquid crystals used have positive dielectric anisotropy, that is, $\epsilon_{||} - \epsilon_{\perp} (= \Delta\epsilon)$ is positive.

It is very easy to impart positive dielectric anisotropy to said mixed liquid crystal systems by modifying the their quality. To be more definitely, although the mixed system of the liquid crystals of the formulae:

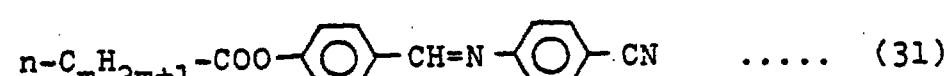
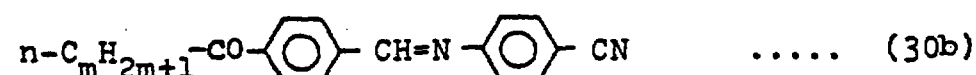
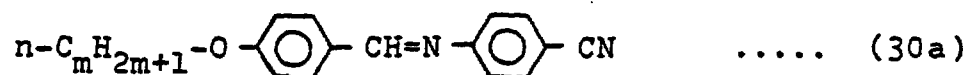
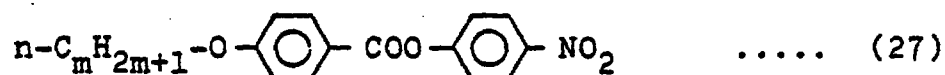
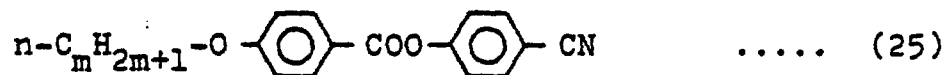


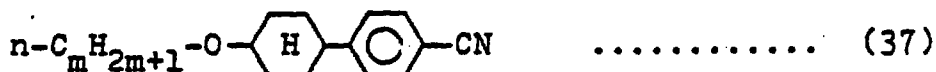
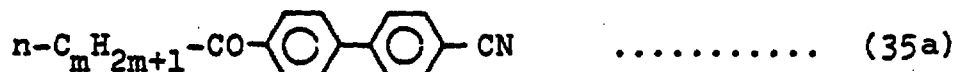
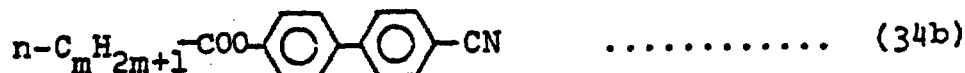
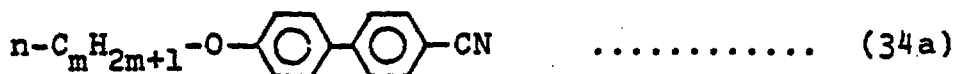
20 and



1 according to this invention has negative or very weakly
positive dielectric anisotropy, such mode of dielectric
anisotropy can be changed to positive by adding a
relatively small quantity of one or more nematic liquid
5 crystals having strongly positive dielectric anisotropy
(Np) without inducing any notice-
able change in the desirable properties possessed by
said mixed system such as, for example, wide mesomorphic
range and low viscosity.

10 The present inventors have also discovered the
substances of the following formulae, especially at least
two such substances, as preferred Np type liquid crystals
for use in the mixed system of this invention:



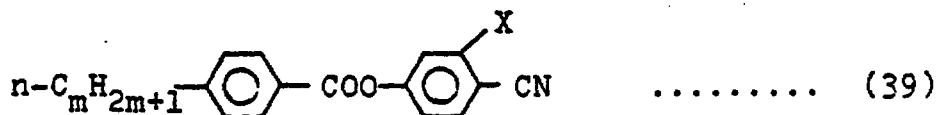


1 In the above formulae (24) to (37), m is an integer of 1 to 10. Among the above-specified substances, those of the formulae (24) to (37) are preferred.

5 Favorable results are also obtained by adding the substances of the following formulae to the matrix system:

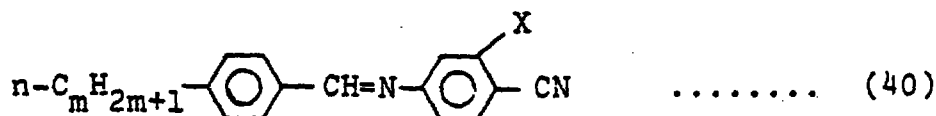


m: an integer of 1 to 8



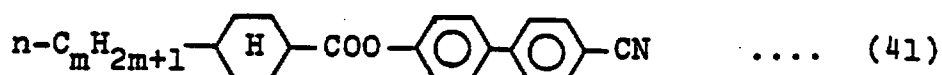
m: an integer of 1 to 8

X: F, Br, Cl or I (halogen)

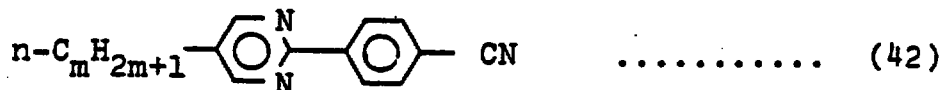


m: an integer of 1 to 10 (especially 1 to 8)

X: F, Br, Cl or I (halogen)



m: an integer of 1 to 10



m: an integer of 1 to 10

- 1 In case of adding the substances of the above-shown formulae (24) to (42) or their optional mixed systems as the third component, the following general facts or rules will serve as the guiding
- 5 principle for deciding the amount of such third component to be added although in general they are used in an amount of 2 to 50% by weight of the whole composition. The amount of the Np type liquid crystal to be mixed with the matrix Nn type liquid crystal is decided by the working
- 10 threshold voltage required by the mixed system, but the relation between said amount to be mixed and working threshold voltage is determined substantially according to the following conceptions. The threshold voltage (Vth) of the twisted nematic liquid crystal element is
- 15 given by the following formula:

$$(4\pi)^{-1}(\epsilon_{\parallel} - \epsilon_{\perp})V_{th}^2 = \pi^3 \cdot K_{11} + (K_{33} - 2K_{22})\phi^2 \quad \dots (43)$$

wherein ϕ is twist angle which is usually $\pi/2$, and K_{11} , K_{22} and K_{33} are elastic constants of splay, twist and bend, respectively. The above formula (43) may be

1 simplified as:

$$V_{th} = 2\pi^{\frac{3}{2}} \cdot \left(\frac{K}{\Delta\epsilon}\right)^{\frac{1}{2}} \dots\dots\dots (43)'$$

wherein $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$.

$$K = K_{11} + \frac{1}{4}(K_{33} - 2K_{22}) \dots\dots\dots (43)''$$

It is possible, in principle, to obtain a liquid crystal with any desired value of $\Delta\epsilon$ by mixing
5 the liquid crystals with different values of $\Delta\epsilon$.
Assuming here that dielectric constants of the two different kinds of liquid crystals A and B are $\epsilon_{||}^A$ and $\epsilon_{\perp}$, respectively, and their mixing ratio A/B = X/(1 - X) and further supposing that additivity of the dielectric
10 constants applies here, then $\Delta\epsilon$ of the mixed system is given as follows:

$$\Delta\epsilon = X\Delta\epsilon^A + (1 - X)\Delta\epsilon^B = X(\Delta\epsilon^A - \Delta\epsilon^B) + \Delta\epsilon^B \dots\dots\dots (44)$$

Also assuming that same additivity applies for K, too, then K of the mixed liquid crystal is given by the following formula:

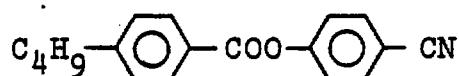
$$K = XK^A + (1 - X)K^B = X(K^A - K^B) + K^B \dots\dots\dots (45)$$

- 1 Substituting the formulae (44) and (45) for the formula (43)',

$$V_{th} = \frac{2\pi^{\frac{3}{2}} \sqrt{X(K^A - K^B) + K^B}}{\sqrt{X(\Delta\epsilon^A - \Delta\epsilon^B)\Delta\epsilon^B}} \dots\dots (46)$$

The threshold voltage may be calculated in the following way by giving the definite figures to the respective constants.

Assuming that $\Delta\epsilon^B$ of the Nn type liquid crystal is -0.3 and $\Delta\epsilon^A$ of the Np type liquid crystal of the formula:



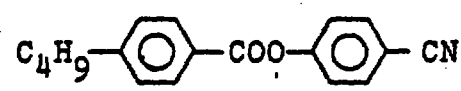
is 25 and further supposing $K^B = 4 \times 10^{-7}$ dyne and $K^A = 17 \times 10^{-17}$ dyne, then the formula (46) gives:

$$V_{th} = \frac{2\pi^{\frac{3}{2}} \sqrt{(13 \times 4)10^{-7}}}{\sqrt{25.3X - 0.3}} \dots\dots\dots (46)'$$

It will suggest itself to those skilled in the art that above assignment of figures to $\Delta\epsilon^A$, $\Delta\epsilon^B$, K^A and K^B is not arbitrary but well conforms to the actual properties of the liquid crystals.

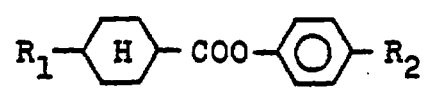
15 Fig. 9 shows the relationship between the mixing ratio and the value of V_{th} (static drive) when

- 1 the Np and Nn type liquid crystals are mixed by using a substance of the formula:

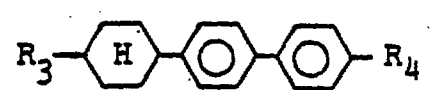


- as Np type liquid crystal and the matrix 1-4 shown in Table 2 as Nn type liquid crystal. The experimental results well agree with the product of the theoretical formula (calculation formula) (46) or (46)'.

To the above three-component compositions, that is, the combination of the substances of the formulae:



- 10 and

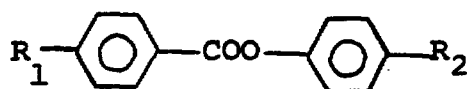


- and an Np type liquid crystal, depending on the properties desired, it may be desirable to add an Nn type, particularly polar Nn type substance (a polar Nn type liquid crystal) as the fourth component. The amount of such substance to be added may be properly selected in conformity to the amount of the Np type liquid crystal. This will be exemplified by the embodiments shown later.

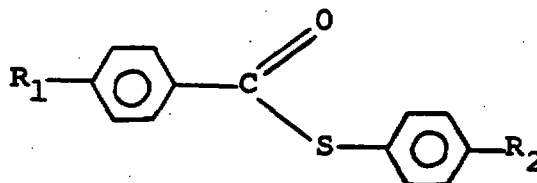
- In order to enhance compatability of the non-polar Nn type matrix liquid crystals with the polar

Np type liquid crystals and to also obtain a wide MR,
it is recommended to add as the fourth component an Nn
type liquid crystal system of the type other than the
Nn type matrix mixed systems represented by the above-
5 shown formula (18). The nematic liquid crystals or
analogues thereof having electric polarity in their
molecules and also having negative dielectric anisotropy
are preferred for use as the fourth component since they
are capable of providing said favourable properties,
10 namely, increased compatibility of the mixed system and
wide MR.

Examples of such Nn type liquid crystals to be
used as the fourth component are compounds of the formula:

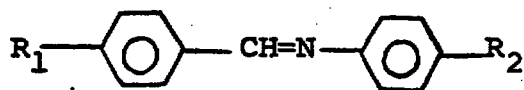


15 wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$, $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$,
 $n\text{-C}_m\text{H}_{2m+1}\text{-COO}$ or $\text{-C}_m\text{H}_{2m+1}\text{-O-COO}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$,
 $n\text{-C}_q\text{H}_{2q+1}\text{-O}$, $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$, $n\text{-C}_q\text{H}_{2q+1}\text{-COO}$ or
 $n\text{-C}_q\text{H}_{2q+1}\text{-O-COO}$; and m and q are each an integer of 1
to 10; or of the formula:



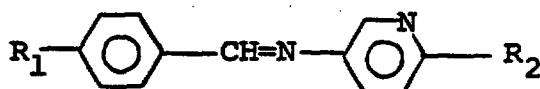
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wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O}$;
 R_2 is $n\text{-C}_q\text{H}_{2q+1}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-O}$; and m and q are each an
integer of 1 to 10; or of the formula:



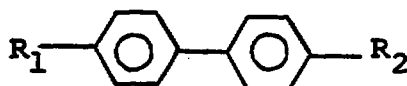
wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O-CO}$;
 R_2 is $n\text{-C}_q\text{H}_{2q+1}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O}$, $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O-CO}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-O-COO}$; and m and q are each an

5 integer of 1 to 10; or of the formula:



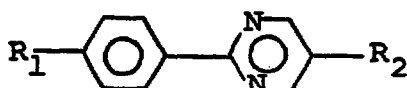
wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}\text{-O}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-COO}$; R_2 is
 $n\text{-C}_q\text{H}_{2q+1}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-O}$; and m and q are each an integer
of 1 to 10; or of the formula:

10

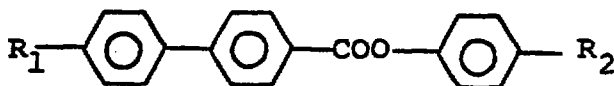


wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$;
 R_2 is $n\text{-C}_q\text{H}_{2q+1}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O}$, $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$ or
 $n\text{-C}_q\text{H}_{2q+1}\text{-COO}$; and m and q are each an integer of 1 to
10; or of the formula:

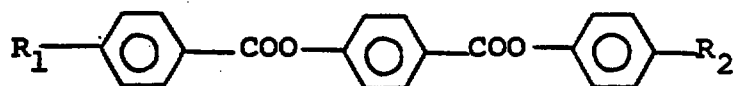
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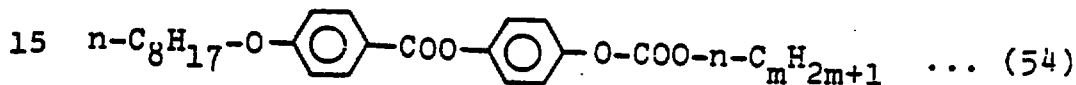
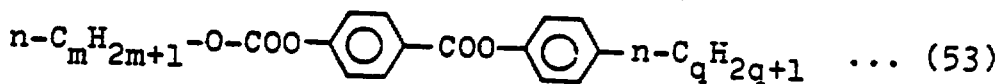
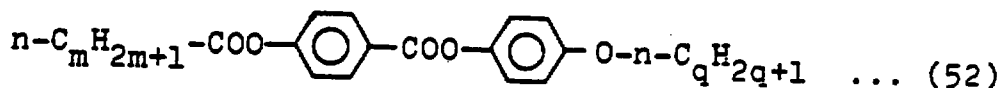
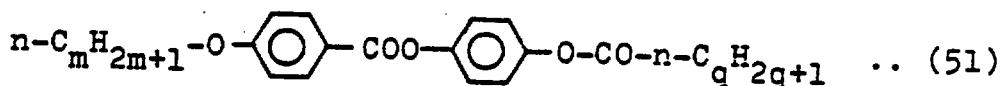
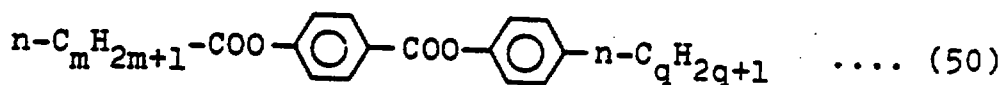
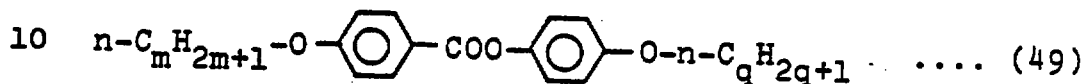
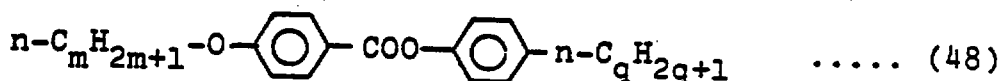
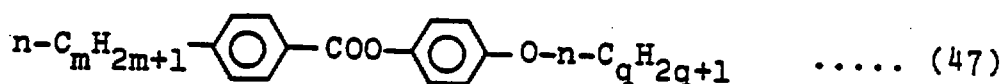
wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}\text{-O}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$; and m and
 q are each an integer of 1 to 10; or of the formula:

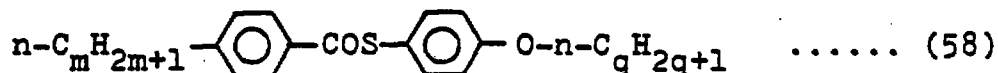
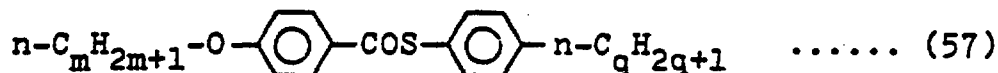
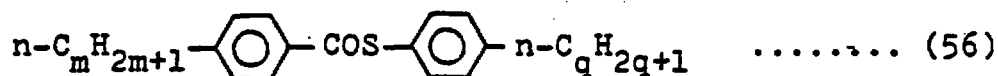
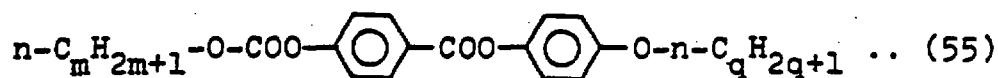


wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$; and m and q
20 are each an integer of 3 to 8; or of the formula:

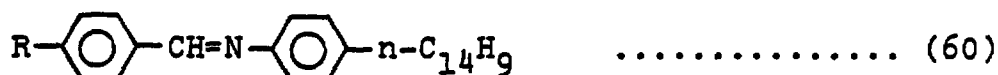


wherein R_1 is $n\text{-C}_r\text{H}_{2r+1}$ or $n\text{-C}_r\text{H}_{2r+1}\text{-O}$; R_2 is $n\text{-C}_s\text{H}_{2s+1}$ or $n\text{-C}_s\text{H}_{2s+1}\text{-O}$; and r and s are each an integer of 1 to 10. Preferably the fourth component comprises at least two such substances. Preferred examples of such Nn type liquid crystals to be used as the fourth component are listed below:

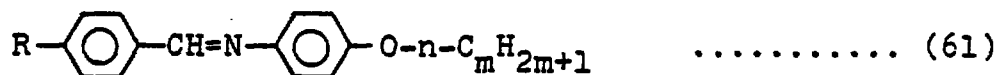




1 In the foregoing formulae (47) to (59), m and q are each an integer of 1 to 10.

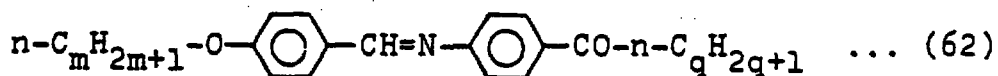


R: $\text{CH}_2\text{-O-CH}_2\text{CH}_2$ or $\text{CH}_3\text{-O-(CH}_2)_3\text{-O}$

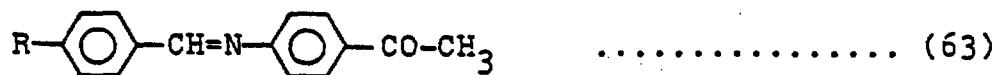


m: an integer of 1 to 9

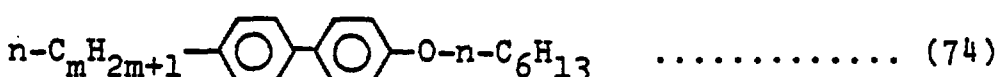
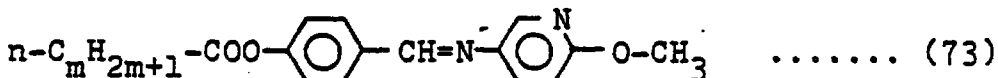
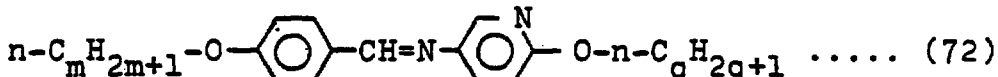
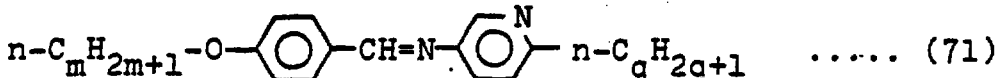
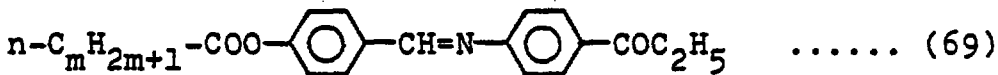
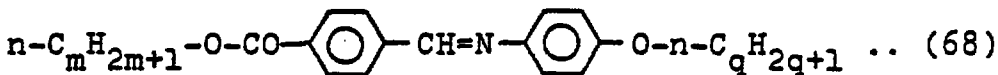
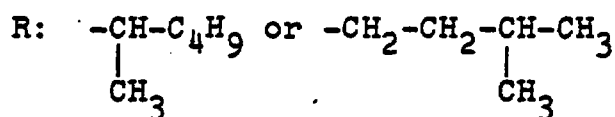
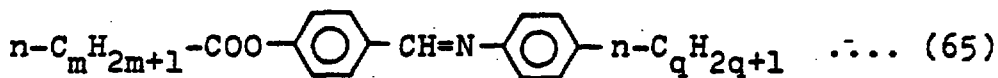
R: $(\text{CH}_2)_2\text{-CH-O}$ or $(\text{CH}_2)_2\text{-CH(CH}_2)_2\text{-O}$



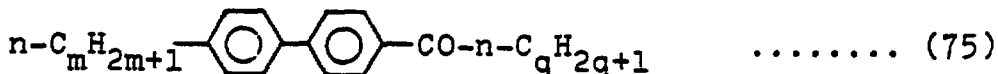
m and q: each an integer of 1 to 10



R: $\text{CH}_3\text{-O-CH}_2\text{-O}$, $\text{CH}_3\text{-O-(CH}_2)_2\text{-O}$,
 $\text{C}_2\text{H}_5\text{-O-(CH}_2)_2\text{-O}$, $\text{CH}_3\text{-O-(CH}_2)_3\text{-O}$,
 $\text{C}_3\text{H}_7\text{-O-(CH}_2)_2\text{-O}$ or $\text{C}_2\text{H}_5\text{-O-(CH}_2)_3\text{-O}$

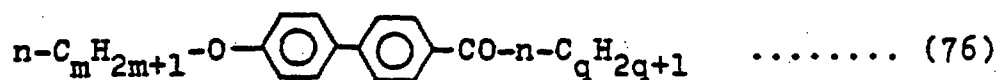


1 In the foregoing formulae (64) to (74), m and q are each an integer of 1 to 10.



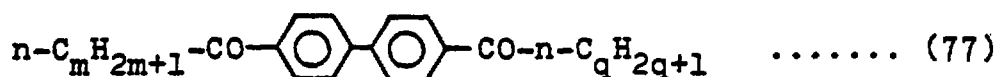
m: an integer of 1 to 10

q: an integer of 1 to 8

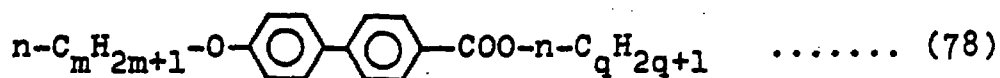


m: an integer of 1 to 12

q: an integer of 1 to 10

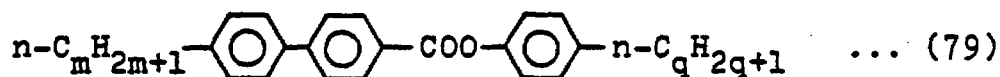


m, q: each an integer of 1 to 10

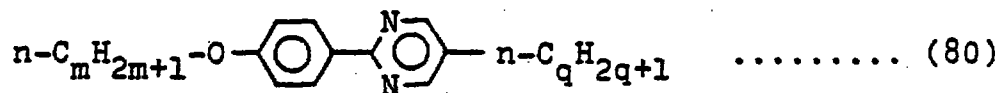


m: an integer of 1 to 18

q: an integer of 1 to 6

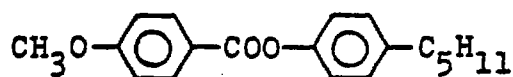


m, q: each an integer of 3 to 8



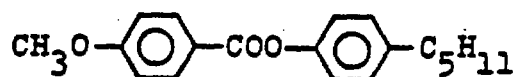
m, q: each an integer of 1 to 10

- 1 Shown here as an example using an Nn type liquid crystal is a mixed liquid crystal indicated by A in Table 4. This is a system prepared by adding a substance of the formula:



- 5 to a matrix liquid crystal of the formula (18), and this system has wide MR of from 4° to 62°C and is

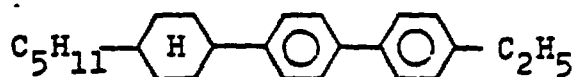
1 applicable to practical use. In comparison with this,
MR of the system not added with an Nn type liquid
crystal of the formula:



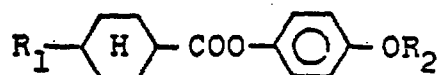
is in a higher temperature region, i.e., 13-70°C, as
5 noted from Example 1 shown in Table 2.

Therefore, use of an Nn liquid crystal as the
fourth component in an amount of 50% or less,
by weight of the whole composition gives a favourable
result. A particularly good result is obtained when
10 said Nn liquid crystal as the fourth component is
added in an amount of 2-40%, especially 30±10%, by weight
of the whole Nn liquid crystal system.

The examples indicated by 4-2, 4-3 and 4-4
in Table 4 are the systems formulated by adding the
15 liquid crystal B composed of a compound of the formula:

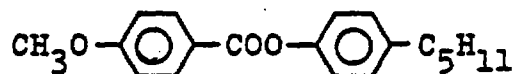


in an amount of 5 to 15% by weight to an Nn type mixed
liquid crystal A principally composed of a compound of
the formula:

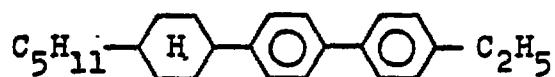


according to this invention. It will be seen that these

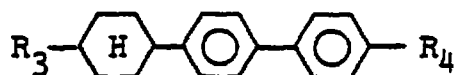
- 1 systems have very wide MR and hence high practical utility. It was also found that the mixed system consisting of an Nn matrix liquid crystal given by removing the compound of the formula:



- 5 from A and a compound of the formula:



which constitutes the liquid crystal B, is inferior in MR to the mixed system of A and B. It was thus clarified that the compounds of the formula:



- are well miscible with the Nn matrix liquid crystals
10 mainly composed of the compounds of the formula (18) and give a wide MR.

Another significant fact concerning the effective properties derived from addition of a substance of the formula:

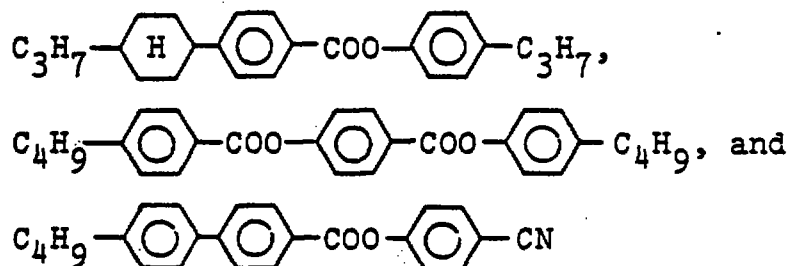


- 15 is that when this substance is added to an Nn matrix principally composed of a compound of the formula (18)

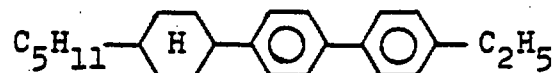
- 1 or to such matrix system further added with an Np type
liquid crystal, the whole system is appreciably
suppressed in rise of viscosity. For example, when the
system (B-1) formulated by adding a substance of the
5 formula:



- to the mixed system of a matrix liquid crystal C
represented by the formula (18) and a phenylcyclohexane
Np type mixed liquid crystal D was compared with the
liquid crystal systems 5-2, 5-3 and 5-4 formulated by
10 adding said substance to the other systems effective
for expanding MR, i.e., the systems of the formulae:

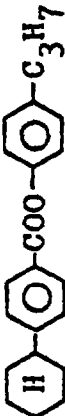
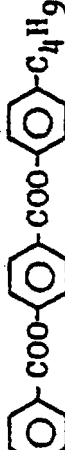
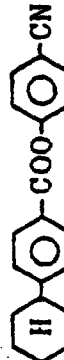


respectively, the results showed that the rise of
viscosity by 10% addition of the substance of the
formula:



- 15 to the C + D mixed matrix system (having a viscosity of
23 CP at 25°C) was only 2 CP as shown in Table 5. Other
addition systems caused a sharp rise of viscosity.

Table 5

Symbol	Composition (Figures in parentheses are % by weight)	Driving conditions: 1/3 bias, 1/3 duty			ΔT (%)	γ	$\Delta\theta$
		Margin M (%)	Central voltage (V)				
5-1	C + D + C ₅ H ₁₁ (45)(45)	9.32	3.38		7.51	1.13	0.874
5-2	C + D + C ₃ H ₇ (45)(45)	6.94	3.24		8.80	1.13	0.830
5-3	C + D + C ₄ H ₉ (45)(45)	6.80	3.09		9.15	1.16	0.850
5-4	C + D + C ₄ H ₉ (45)(45)	5.56	3.06		8.35	1.16	0.833

- Cont'd -

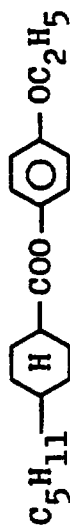
Table 5 (cont'd)

t_r (ms) 25°C	t_f (ms) 25°C	Viscosity η (cp) 25°C	Mesomorphic range MR(°C)
140	80	25	-11 to 65.6
155	90	28	-25 to 67.2
160	105	30	-21 to 66.0
160	110	33	-18 to 70.5

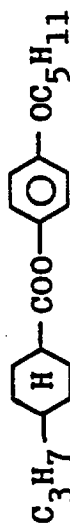
In the above table:



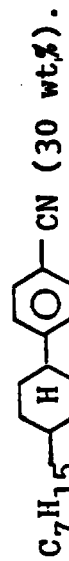
(40 wt%),



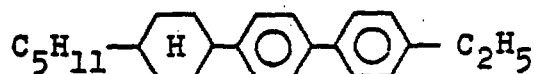
(20 wt%) and



(40 wt%).



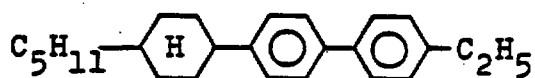
1 Generally speaking, to obtain a mixed system
 which is capable of expanding the mesomorphic range
 (MR) while suppressing the rise of viscosity (η) means
 to obtain a liquid crystal system for multiplexing drive
 5 with excellent responsiveness and high working margin
 (M), and usually it is possible to reduce the temper-
 ature dependency (ΔT , see formula (10)) of the threshold
 value of MR by bringing the upper limit of MR to a
 higher temperature region in a mixed system. Thus, as
 10 apparent from the comparison with other addition systems
 5-2, 5-3 and 5-4, the system 5-1 added with a substance
 of the formula:



is excellent in both responsiveness and working margin
 (M) as seen in Table 5. It is to be noted that the
 15 factor which causes rise of viscosity when adding a
 compound of the formula:



to other matrix liquid crystals does not originate in
 the intrinsic properties of the compound of said
 formula. As a result of minute studies on viscosity
 20 of the whole systems in case of adding a compound of
 the formula:



1 to other various mixed liquid crystal systems such as, for example, a biphenyl type liquid crystal (trade name: E-7):

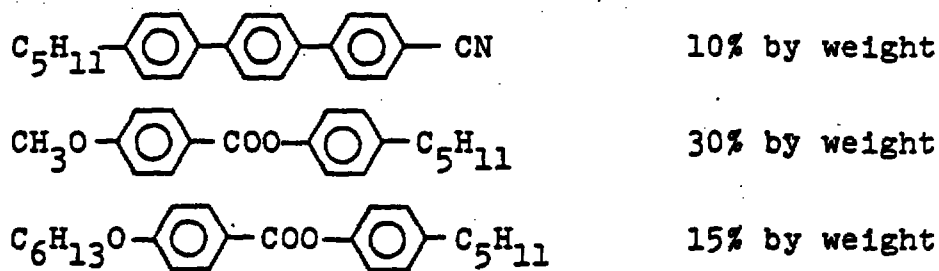
$\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	50.5% by weight
$\text{C}_7\text{H}_{15}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	27.5% by weight
$\text{C}_8\text{H}_{17}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	14.6% by weight
$\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	7.4% by weight

5 a phenylcyclohexane type liquid crystal (trade name, ZLI-1083):

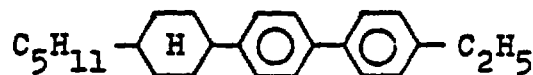
$\text{C}_3\text{H}_7-\text{H}-\text{C}_6\text{H}_4-\text{CN}$	36.6% by weight
$\text{C}_5\text{H}_{11}-\text{H}-\text{C}_6\text{H}_4-\text{CN}$	36.4% by weight
$\text{C}_7\text{H}_{15}-\text{H}-\text{C}_6\text{H}_4-\text{CN}$	27.0% by weight

a mixed system of an Nn type ester and biphenyl (trade name, SP-21):

$\text{C}_7\text{H}_{15}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	15% by weight
$\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	2% by weight
$\text{C}_6\text{H}_{13}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	10% by weight



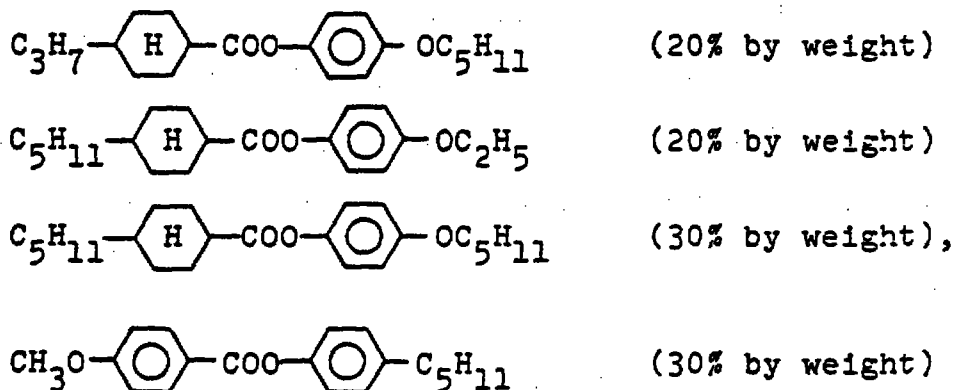
1 etc., the fact was disclosed that it is not that addition of these mixed liquid crystal systems does not cause rise of viscosity for any matrix. More definitely, when the compound of the formula:



5 among the compounds represented by the general formula:



was added to a matrix liquid crystal of the following composition:



which constitutes the principal component of the
10 liquid crystal mixture of this invention and which is

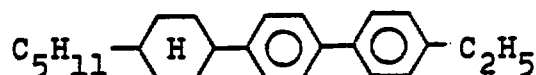
1 represented by the formula (18), and to a mixed liquid
crystal system of the following composition:



and

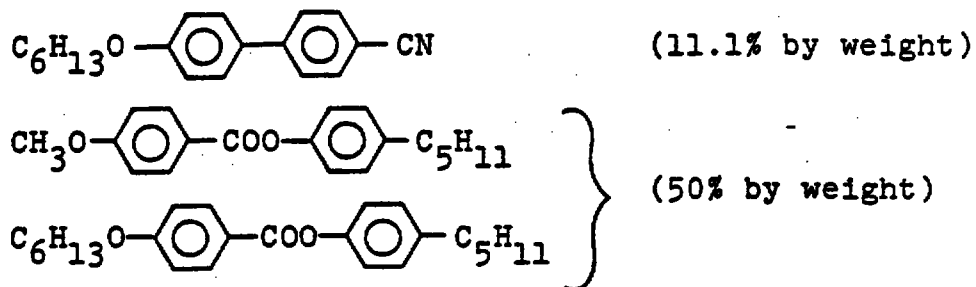


which is principally composed of a phenylcyclohexane
5 type liquid crystal, the resulting rise of viscosity at
25°C was very slight in both cases as shown in Fig. 10
and Fig. 11, respectively. On the other hand, it was
clarified that when the said compound of the formula:



is added to the biphenyl type liquid crystal (trade
10 name: E-7) and to the mixed system of an Nn type
ester and biphenyl (trade name: SP-21), there takes
place a sharp rise of viscosity at 25°C as shown in
Fig. 12 and Fig. 13, respectively. Said mixed liquid
crystal system of an Nn type ester and biphenyl has the
15 following composition:



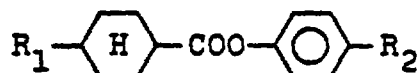


- 1 As described above, the nematic liquid crystal compositions for display devices according to this invention have high margin and fast responsiveness, so that they are best suited for use as a material for the
- 5 multiplexing drive systems. Also, the liquid crystal compositions of this invention are chemically stable and have high reliability as a liquid crystal material, so that they can find best application for the liquid crystal display devices.



CLAIMS

1. A nematic liquid crystal composition for display devices comprising at least one compound of the formula:

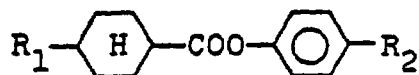


wherein R_1 is $n-C_mH_{2m+1}$, $n-C_mH_{2m+1}-O$ or $n-C_mH_{2m+1}-CO$; R_2 is $n-C_qH_{2q+1}$, $n-C_qH_{2q+1}-O$ or $n-C_qH_{2q+1}-CO$; and m and q are each an integer of 1 to 10, and at least one compound of the formula:



wherein R_3 is $n-C_rH_{2r+1}$ or $n-C_rH_{2r+1}-O$; R_4 is $n-C_sH_{2s+1}$ or $n-C_sH_{2s+1}-O$; and r and s are each an integer of 1 to 10.

2. A nematic liquid crystal composition for display devices comprising a mixed liquid crystal system of at least one compound of the formula:



wherein R_1 is $n-C_mH_{2m+1}$, $n-C_mH_{2m+1}-O$ or $n-C_mH_{2m+1}-CO$; R_2 is $n-C_qH_{2q+1}$, $n-C_qH_{2q+1}-O$ or $n-C_qH_{2q+1}-CO$; and m and q are each an integer of 1 to 10, and at least one compound of the formula:



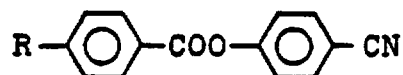


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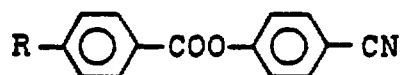
wherein R_3 is $n-C_rH_{2r+1}$ or $n-C_rH_{2r+1}-O$; R_4 is $n-C_sH_{2s+1}$ or $n-C_sH_{2s+1}-O$; and r and s are each an integer of 1 to 10, said mixed liquid crystal system being further mixed with at least one nematic liquid crystal having positive dielectric anisotropy in an amount of 2% by weight or more based on the weight of the whole composition.

3. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n-C_mH_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

4. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



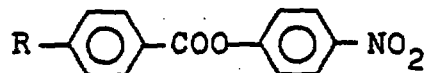
wherein R is $n-C_mH_{2m+1}-O$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

5. A nematic liquid crystal composition for

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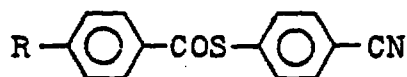


display devices according to Claim 2, wherein at least one compound of the formula:



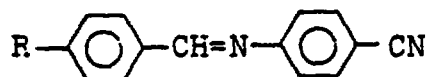
wherein R is $n\text{-C}_m\text{H}_{2m+1}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

6. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

7. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



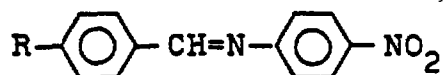
wherein R is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$, $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-COO}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.



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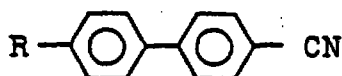
- 54 -

8. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



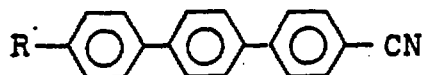
wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

9. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$, $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-COO}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

10. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one of the compounds of the formula:



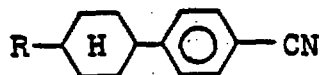
wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

(10.3)



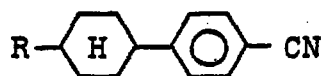
- 55 -

11. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



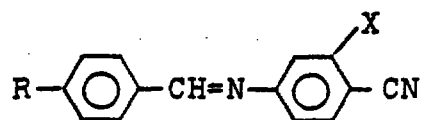
wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

12. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}\text{-O}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

13. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



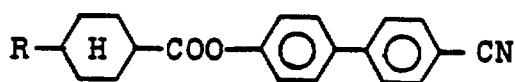
wherein R is $n\text{-C}_m\text{H}_{2m+1}$; m is an integer of 1 to 8; and X is a halogen selected from F, Cl, Br and I, is used as said nematic liquid crystal having positive dielectric anisotropy.



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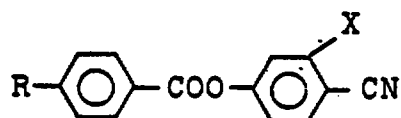
- 56 -

14. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



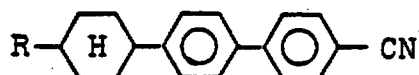
wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

15. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}$; m is an integer of 1 to 8; and X is a halogen selected from F, Cl, Br and I, is used as said nematic liquid crystal having positive dielectric anisotropy.

16. A nematic liquid crystal composition for display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 8, is used as said nematic liquid crystal having positive dielectric anisotropy.

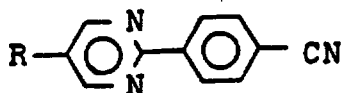
17. A nematic liquid crystal composition for

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display devices according to Claim 2, wherein at least one compound of the formula:



wherein R is $n\text{-C}_m\text{H}_{2m+1}$; and m is an integer of 1 to 10, is used as said nematic liquid crystal having positive dielectric anisotropy.

18. A nematic liquid crystal composition for display devices according to Claim 2, wherein a mixture comprising at least two of the compounds set forth in any of Claims 3 to 17 is used as said nematic liquid crystal having positive dielectric anisotropy.

19. A nematic liquid crystal composition for display devices according to any of Claims 2 to 18, containing at least one nematic liquid crystal having positive dielectric anisotropy in an amount of 2 to 50% by weight based on the weight of the whole composition.

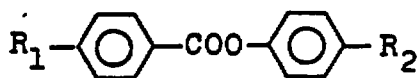
20. A nematic liquid crystal composition for display devices according to any one of claims 2-19 additionally comprising at least one nematic liquid crystal having negative dielectric anisotropy.



(106)

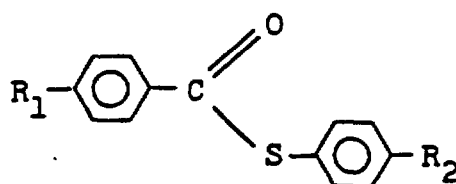
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21. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:



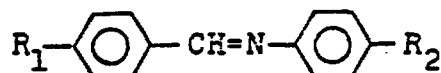
wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$, $n\text{-C}_m\text{H}_{2m+1}\text{-CO}$, $n\text{-C}_m\text{H}_{2m+1}\text{-COO}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O-COO}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O}$, $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$, $n\text{-C}_q\text{H}_{2q+1}\text{-COO}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-O-COO}$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

22. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:



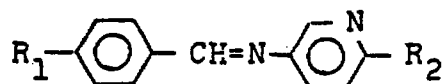
wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-O}$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

23. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:



wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$, $n\text{-C}_m\text{H}_{2m+1}\text{-O}$ or $n\text{-C}_m\text{H}_{2m+1}\text{-O-CO}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O}$, $n\text{-C}_q\text{H}_{2q+1}\text{-CO}$, $n\text{-C}_q\text{H}_{2q+1}\text{-O-CO}$ or $n\text{-C}_q\text{H}_{2q+1}\text{-C-COO}$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

24. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:

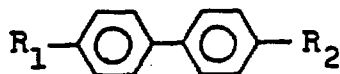




(102)

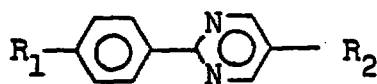
wherein R_1 is $n-C_mH_{2m+1}-O$ or $n-C_mH_{2m+1}-COO$; R_2 is $n-C_qH_{2q+1}$ or $n-C_qH_{2q+1}-O$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

25. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:



wherein R_1 is $n-C_mH_{2m+1}$, $n-C_mH_{2m+1}-O$ or $n-C_mH_{2m+1}-CO$; R_2 is $n-C_qH_{2q+1}$, $n-C_qH_{2q+1}-O$, $n-C_qH_{2q+1}-CO$ or $n-C_qH_{2q+1}-COO$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

26. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:

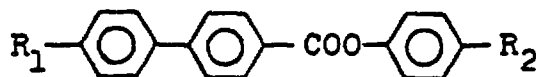


wherein R_1 is $n-C_mH_{2m+1}-O$; R_2 is $n-C_qH_{2q+1}$; and m and q are each an integer of 1 to 10, is used as said nematic liquid crystal having negative dielectric anisotropy.

27. A nematic liquid crystal composition for



display devices according to Claim 20, wherein at least one compound of the formula:



wherein R_1 is $n\text{-C}_m\text{H}_{2m+1}$; R_2 is $n\text{-C}_q\text{H}_{2q+1}$; and m and q are each an integer of 3 to 8, is used as said nematic liquid crystal having negative dielectric anisotropy.

28. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least one compound of the formula:



wherein R_1 is $n\text{-C}_r\text{H}_{2r+1}$ or $n\text{-C}_r\text{H}_{2r+1}\text{-O}$; R_2 is $n\text{-C}_s\text{H}_{2s+1}$ or $n\text{-C}_s\text{H}_{2s+1}\text{-O}$; and r and s are each an integer of 1 to 10 is used as said nematic liquid crystal having negative dielectric anisotropy.

29. A nematic liquid crystal composition for display devices according to Claim 20, wherein at least two of the substances set forth in Claims 21 to 28 are used as said nematic liquid crystal having negative dielectric anisotropy.

30. A nematic liquid crystal composition for display devices according to any of Claims 20 to 29, wherein the ratio of said nematic liquid crystal having



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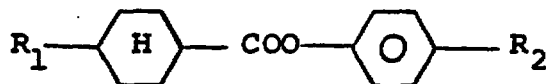
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negative dielectric anisotropy to the whole composition is 50% by weight or less.

31. A composition according to any one of claims 20-30 wherein the nematic liquid crystal having negative dielectric anisotropy is at least one of the compounds 47-80 hereinbefore specifically mentioned for this purpose.

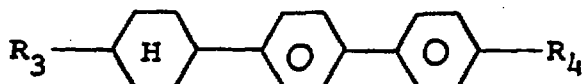
32. A composition according to any one of claims 2-31 wherein the nematic liquid crystal having positive dielectric anisotropy is at least one of the compounds 24-42 hereinbefore specifically mentioned for this purpose.

33. A composition according to any one of the preceding claims wherein the compound of formula



is one of those hereinbefore specifically mentioned.

34. A composition according to any one of the preceding claims wherein the compound of formula



is one of those hereinbefore specifically mentioned.

35. A composition according to claim 1 substantially as hereinbefore described.



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36. A composition according to claim 2 substantially as hereinbefore described.

37. A composition according to claim 20 substantially as hereinbefore described.
