

LIQUID-CRYSTAL MIXTURES AND DISPLAYS

5 The invention relates to a liquid-crystal mixture based on medium-polarity compounds of the superfluorinated liquid-crystal material (SFM) type and to a liquid-crystal display based on a twisted nematic cell and having

- two substrates provided with electrode layers and alignment layers thereon and, with a frame, forming a cell,
- 10 - a nematic liquid-crystal mixture, based on medium-polarity compounds of the SFM type and having positive dielectric anisotropy present in the cell, and
- a twist angle of the liquid-crystal layer in the cell with a value of between 0° and 600° from alignment layer to alignment layer.

15 The term twisted nematic cell is broadly drawn here and includes cells having a dielectrically positive, twisted nematic liquid-crystal layer having a twist angle of $0 < \theta \leq 600^\circ$. Liquid-crystal cells having twist angles θ of between about 80° and 100° are usually known as TN
20 (twisted nematic) cells; the structure of such cells is described, for example, in Thermotropic Liquid Crystals, G.W. Gray [ed.], pp. 77 ff. Liquid-crystal cells having twist angles $\theta > 100^\circ$ are generally called STN (super-twisted nematic) cells, while the term LTN (low-twisted
25 nematic) cell has been proposed in P 40 10 503 for cells where $\theta < 80^\circ$. A short description of STN displays is given, for example, in B.S. Scheuble, Liquid Crystal Displays with High Information Content, Kontakte 1/89, pp. 34-38, Darmstadt.

30 The nematic liquid-crystal mixture is positioned between 2 substrates provided with electrode layers and alignment layers thereon and, with a frame, forming a cell. The term nematic is broadly drawn here and also

includes nematic-cholesteric liquid-crystal mixtures.

The liquid-crystal displays according to the invention can be addressed statically. In this case, one of the two electrode layers is usually segmented, each segment being provided with a separate supply line, while the other electrode is generally in the form of a large-area counterelectrode.

Due to the large number of supply lines necessary, static addressing is generally less preferred, and multiplex addressing has generally become established, in particular in the case of displays having a relatively high or high information content. In the case of passive multiplex addressing, a matrix comprising $p \times q$ pixels is defined by p segment leads on one electrode and q backplane leads on the other electrode. This matrix is addressed by applying generally complex voltage programs to segment and backplane leads, as described, for example, in E. Kaneko, Liquid Crystal Displays, KTK Scientific Publishers, Tokyo, 1978, chapter 4.

By contrast, if an active matrix is used the individual pixel is switched by nonlinear addressing elements integrated into the pixel. The nonlinear elements used to produce the active matrix may have 2 or 3 connections. The elements having 2 connections are, for example, varistors or diodes (for example MIM = metal-insulator-metal, MSI = metal/silicon nitride/indium-tin oxide), while the nonlinear elements having 3 connections are generally thin-film transistors (TFTs), of which several types are discussed, differing through the semiconductor material used.

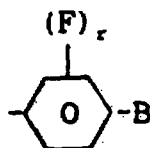
When nonlinear elements having 3 connections are used, only one connection is generally necessary for the counterelectrode, while the counterelectrode is usually also scanned in the case of active matrix addressing based on elements having 2 connections.

Further details on the addressing of liquid-crystal displays by an active matrix of nonlinear elements is given, for example, in A.H. Firester, SID, 1987, Society for Information Display Seminar 5: Active

Matrices for Liquid Crystals, further in E. Kaneko, Liquid Crystals Displays, KTK Scientific Publishers, Tokyo, Japan, 1987, chapters 6 and 7 or P.M. Knoll, Displays, Heidelberg, 1986, pp. 216 ff.

5 The liquid crystals used in twisted nematic cells must, in addition to a broad mesogenic range, a high clearing point and favourable values for the optical anisotropy, in particular also have high specific resistance and high UV and heat stability of the specific
10 resistance. This is, in particular, of crucial importance for cells addressed by means of an active matrix, which is associated with the fact that each pixel, with respect to the active nonlinear element in each case, represents a capacitive load which is charged in the rhythm of the
15 addressing cycle. The blocking resistance of these elemental capacitors must be as high as possible so that the voltage applied to an addressed pixel only drops a little before the pixel is recharged in the next addressing cycle. A quantitative measure of the drop in voltage
20 applied to a pixel is the so-called holding ratio (HR), which is defined as the ratio between the drop in voltage over a pixel in the unaddressed state and the applied voltage; a method for determining the HR is indicated, for example, in Rieger, B. et al., Conference Proceedings
25 of the Freiburg Conference on Liquid Crystals, Freiburg 1990.

It has been shown that liquid-crystal compounds of the SFM type (superfluorinated liquid-crystal materials, see, for example, H.J. Plach et al., Eurodisplay
30 90) generally satisfy the requirement for high specific resistance and for high heat and UV stability of the specific resistance to a particular extent, while liquid-crystal compounds containing a terminal cyano group have significantly poorer heat and UV stability. SFM compounds
35 contain a terminal group



in which B is, for example, F, Cl, OCF₃, OCHF₂, CF₃, C₂F₅

or OC_2F_5 , and the 1,4-phenylene ring may be monofluorinated or polyfluorinated ($r = 0-4$).

Although liquid-crystal mixtures based on SFM compounds were originally developed for active matrix applications, the use of such materials has in the meantime also been discussed for passively multiplexed TN, LTN and STN systems due to their excellent stability.

However, it is disadvantageous that liquid-crystal compounds of the SFM type generally have only moderate polarity, resulting in relatively high threshold voltages. Since considerable simplification and reduction in costs for the driving electronics can frequently be achieved by reducing the threshold voltage, twisted nematic cells which have a low threshold voltage and high UV and heat stability are highly desirable from both technological and economical points of view.

A further important requirement of liquid-crystal mixtures used in twisted nematic cells is that they must have low viscosity values in order to achieve short response times.

The object of the present invention was to provide nematic liquid-crystal mixtures which are characterised, in particular, by advantageous viscosity values in addition to high stability, a large mesogenic range, a high clearing point and advantageous values for the optical anisotropy, and, when used in a twisted nematic cell, are characterised by advantageous values for the threshold voltage and the response times.

This object is achieved by the liquid-crystal mixtures and the liquid-crystal displays according to the invention.

According to a first aspect of the invention, there is provided a nematic liquid-crystal mixture based on medium-polarity compounds of the SFM type, which are selected so that the mixture has a viscosity at 20°C of less than $30 \text{ mm}^2 \text{ s}^{-1}$ and has a value of

$$\frac{\bar{K}}{\Delta\epsilon} \leq 1.5$$

for the quotient of the Frank constant $\bar{K}$

$$\bar{K} = K_{11} + \left(\frac{\vartheta}{\pi} \right)^2 [K_{33} - 2 K_{22} (1 - \frac{2\pi d}{p \vartheta})]$$

and the dielectric anisotropy $\Delta\epsilon$

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

when used in a TN cell. ($\vartheta = \frac{\pi}{2}$ $d/p \ll 1$)

$$\frac{\bar{K}}{\Delta\epsilon} \leq 1.5$$

where ϑ is the twist angle in rad, d is the layer thickness in μm , p is the pitch length in μm and K_{11} , K_{22} and K_{33} are the elastic constants for splay, twist and bend in 10^{-12} N.

The invention also relates to a liquid-crystal display based on a twisted nematic cell and having

- two substrates provided with electrode layers and alignment layers thereon and, with a frame, forming a cell,
- 5 - a nematic liquid-crystal mixture having positive dielectric anisotropy present in the cell, and
- a twist angle of the liquid-crystal layer in the cell with a value of between 0° and 600°
- 10 from alignment layer to alignment layer,

characterized in that the nematic liquid-crystal mixture is a nematic liquid-crystal mixture in accordance with the first aspect of the invention, or

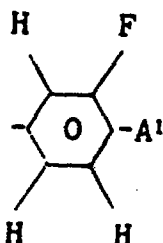
15 any of its embodiments as hereinafter disclosed.

The invention is based on the knowledge that, in order to achieve a low threshold voltage, the liquid-crystal compounds must be selected to that the elastic

20 constants and the dielectric anisotropy of the liquid-crystal mixture are optimized.

A parameter which takes into account both the elastic properties and the dielectric properties of the medium is the quotient $K/\Delta\epsilon$ formed from the Frank constant K and the dielectric anisotropy $\Delta\epsilon$ of the medium. The elastic constants K_{11} , K_{22} and K_{33} are preferably measured by the method described in A. Beyer, U. Finkenzeller, Physical Properties of Liquid Crystals, VI: Elastic Constants, The Merck Group Liquid Crystal Newsletter No. 7, February 91, Darmstadt.

It has been found that SFM compounds which contain a terminal group of the formula (G1)



(G1)

in which A^1 is $-OCF_2$ or $-CF_2$,

frequently have relatively high values for the elastic constants, in particular for K_{11} and K_{33} . Thus, for example, the following elastic constants have been measured (at $T_{red} = 0.715$) for

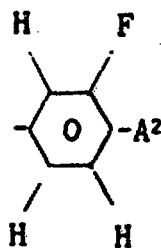


$$\begin{aligned} K_{11} &= 20.9 \cdot 10^{-12} \text{ N} \\ K_{22} &= 11.0 \cdot 10^{-12} \text{ N} \\ K_{33} &= 33.7 \cdot 10^{-12} \text{ N} \end{aligned}$$

It is frequently not possible to adequately compensate these relatively high values for elastic constants through the values for $\Delta\epsilon$, which are frequently also relatively high, so that the proportion of compounds containing a terminal group (G1) in the liquid-crystal mixtures according to the invention is preferably not too high and in particular is less than 5 %. The dielectric anisotropy for the abovementioned compound is $\Delta\epsilon = 8.1$.

By contrast, SFM compounds containing a terminal group (G2)

- 7 -



(G2)

in which A² is Cl, F, CF₃ or OCF₃, in particular Cl or F, are frequently characterised by favourable values for the elastic constants.

5 A homolog mixture comprising

60.0 % of H₅C₂-Cyc-Cyc-Phe.3F-F

20.0 % of H₇C₃-Cyc-Cyc-Phe.3F-F

20.0 % of H₉C₄-Cyc-Cyc-Phe.3F-F

has, for example, the following physical parameters:

10

$$\begin{aligned} \Delta \epsilon &= 3.6 \\ K_{11} &= 5.4 \cdot 10^{-12} \text{ N} \\ K_{22} &= 3.9 \cdot 10^{-12} \text{ N} \\ K_{33} &= 8.6 \cdot 10^{-12} \text{ N} \end{aligned} \quad (T_{\text{red}} = 0.950)$$

For a TN cell filled with this mixture

$$\left(\theta = \frac{\pi d}{2 p} \ll 1 \right)$$

15 this gives a value of $\frac{\bar{K}}{\Delta \epsilon} = 1.6$.

SFM compounds which contain a structural element of the formula (G2) frequently have relatively low values for $\Delta \epsilon$ in addition to the favourable values for the elastic constants. The proportion of such compounds in mixtures according to the invention is therefore preferably not too high and is in particular not greater than 65 % and very particularly not greater than 50 %. Thus, Use Example 2 of EP 0 387 032 describes a liquid-crystal mixture obtained by adding

25 15.0 % of H₇C₃-Cyc-Cyc-Phe.3F5F-F

to a base mixture comprising

33.3 % of H_5C_2 -Cyc-Cyc-Phe.3F5F-F

33.3 % of H_7C_3 -Cyc-Cyc-Phe.3F5F-F

33.3 % of $H_{11}C_5$ -Cyc-Cyc-Phe.3F5F-F.

5 The threshold voltage, measured in a TN cell, of the mixture obtained by adding H_7C_3 -Cyc-Cyc-Phe.3F5F-F to the base mixture is 2.32 V. This high value for the threshold voltage is attributable to the fact that the proportion by weight of compounds containing the structural elements (G2) in this mixture is 85 % and is thus too high.

10 Particularly preferred constituents of liquid-crystal mixtures according to the invention are SFM compounds which contain a terminal group (G3)



15 in which T^1 and T^2 , independently of one another, are H or F, and A^3 is F, Cl, CF_3 , OCF_3 , C_2F_5 , or OC_2F_5 .

Particular preference is given to liquid-crystal mixtures containing one or more compounds which contain a polar group of the formula (G3) where $A^3 = F$. Thus, the following homolog mixture, comprising

20 33.7 % of H_7C_3 -Cyc-Phe-Phe.3F5F-F

66.3 % of $H_{11}C_5$ -Cyc-Phe-Phe.3F5F-F

has the following physical parameters:

25 $\Delta \epsilon = 7.4$
 $K_{11} = 4.1 \cdot 10^{-12} \text{ N}$
 $K_{22} = 2.6 \cdot 10^{-12} \text{ N}$
 $K_{33} = 4.9 \cdot 10^{-12} \text{ N}$
 $\frac{K}{\Delta \epsilon} = 0.54$
 30 Melting point $T_m = -7^\circ \text{C}$

($T_{red} = 0.950$)

If 3,4,5-trifluorophenyl compounds are used, a particularly high proportion by weight of these compounds in the liquid-crystal mixtures according to the invention of greater than 15 %, in particular greater than 20 %, is preferred, and liquid-crystal mixtures which contain more than 25 % by weight of 3,4,5-trifluorophenyl compounds are particularly preferred. Liquid-crystal mixtures which contain at least one bicyclic and one tricyclic 3,4,5-trifluorobenzene derivative are distinguished by favourable dielectric and elastic constants and by advantageous viscosity values.

The proportion by weight of 3,4,5-trifluorobenzene derivatives in the liquid-crystal mixture may frequently also be greater than 30 %, and in some cases liquid-crystal mixtures which comprise more than 50 % or even more than 60 % of 3,4,5-trifluorobenzene derivatives are particularly preferred.

If 3,5-difluoro-4-chlorobenzene derivatives and 3,5-difluoro-4-trifluoromethoxybenzene derivatives are used, the proportion by weight of these compounds in the liquid-crystal mixtures according to the invention is generally less crucial, and a significant improvement in the properties of the starting mixture is frequently observed even when less than 15 % of these compounds are added. However, liquid-crystal mixtures according to the invention which contain more than 15 %, in particular more than 20 %, very particularly more than 25 %, of 3,5-difluoro-4-chlorobenzene derivatives and/or 3,5-difluoro-4-trifluoromethoxybenzene derivatives are very particularly preferred here too.

Mixtures containing very high proportions by weight of these compounds of more than 40 % are frequently particularly preferred. An example which may be mentioned is the following homolog mixture, comprising

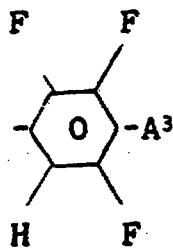
41.0 % of H_7C_3 -Cyc-Phe-Phe.3F5F-Cl
66.3 % of $H_{11}C_3$ -Cyc-Phe-Phe.3F5F-Cl

which has the following properties:

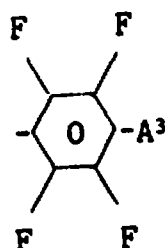
$$\begin{aligned}\Delta\epsilon &= 6.0 \\ K_{11} &= 3.8 \cdot 10^{-12} \text{ N} \\ K_{22} &= 3.8 \cdot 10^{-12} \text{ N} \\ K_{33} &= 7.4 \cdot 10^{-12} \text{ N} \quad (T_{\text{red}} = 0.950) \\ \text{Clearing point } T_c &= 98.7^\circ\text{C} \\ R/\Delta\epsilon &= 0.63.\end{aligned}$$

It has furthermore been found that 3,5-difluoro-4-trifluoromethoxy derivatives are characterised by particularly favourable values for the dielectric anisotropy and the viscosity, while these compounds frequently have somewhat less favourable values for the elastic constants compared with 3,4,5-trifluorobenzene derivatives, 3,5-difluoro-5-chlorobenzene derivatives and 3,5-difluoro-4-trifluoromethyl derivatives. The proportion by weight of 3,5-difluoro-4-trifluoromethoxybenzene derivatives in the liquid-crystal mixture is preferably not too high and is in particular less than 30 %, very particularly not greater than 20 %. Particular preference is given to liquid-crystal mixtures containing between 5 % and 15 % of 3,5-difluoro-4-trifluoromethoxy compounds for improving the viscosity and between 5 % and 45 % of one or more compounds containing a structural element (G3) in which A³ is F, Cl, CF₃, C₂F₅ or OC₂F₅ for optimising the dielectric and elastic properties.

Particularly preferred constituents of the liquid-crystal mixtures according to the invention are furthermore SFM compounds which contain one of the following terminal groups



(G3-3)

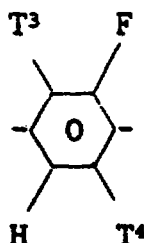


(G3-4)

where A³ is as defined above.

Surprisingly, it has been found that the threshold voltage of the liquid-crystal displays according to the invention can frequently be significantly improved merely on addition of relatively small amounts of greater than 5 % and in particular greater than 10 % of one or more compounds containing one of the structural elements (G3-3) or (G3-4). However, the proportion by weight of these compounds in the liquid-crystal mixtures according to the invention is preferably greater than 12 %, in particular greater than 15 %, very particularly not less than 20 %.

Particularly preferred constituents of the liquid-crystal mixtures according to the invention are furthermore SFM compounds which contain a non-terminal group of the formula (G4)



(G4)

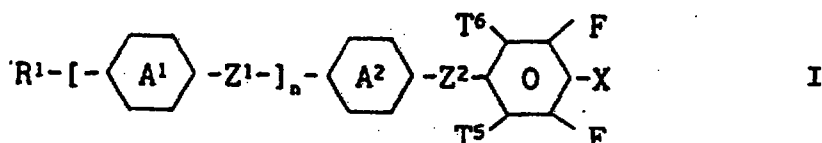
where at least one of the radicals T³ and T⁴ is F and the other radical is H or F.

Particular preference is given to the liquid-crystal mixtures which contain 5-50 % of one or more compounds containing a structural element (G2) and simultaneously 5-65 % of one or more compounds containing a structural element (G3).

Liquid-crystal mixtures which contain one or more compounds selected from the group comprising SFM compounds containing the structural features (G1)-(G4) and in particular (G2)-(G4) and which have a value for $\bar{K}/\Delta\epsilon$

which is less than 1.5 and in particular less than 1.3 are preferred. Particular preference is given to liquid-crystal mixtures where $K/\Delta\epsilon$ is < 1.2 , in particular where $K/\Delta\epsilon$ is < 1.1 , and very particularly where $K/\Delta\epsilon$ is < 1.0 .

5 Very particular preference is furthermore given to liquid-crystal mixtures based on compounds of the formula I



in which

10 R^1 is an alkyl, alkoxy, oxaalkyl or alkenyl radical having 1-10 carbon atoms which is unsubstituted or at least monosubstituted by halogen,

n is 0 or 1,

15 Z^1 and Z^2 , independently of one another, are $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$, $-\text{OCO}-$ or a single bond,

T^5 and T^6 , independently of one another, are H or F,

20 $-\text{A}^1-$ and $-\text{A}^2-$, independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene, and one of $-\text{A}^1-$ and $-\text{A}^2-$ is alternatively pyridine-2,5-diyl, pyrimidine-2,5-diyl or trans-1,3-dioxane-2,5-diyl, and

25 X is F, Cl, OCF_3 or CF_3 ,

and which have a value for $K/\Delta\epsilon$ of less than 1.3 and in particular less than 1.2.

For reasons of simplicity below, Phe is 1,4-

phenylene, Phe.2F is 2-fluoro-1,4-phenylene, Phe.3F is 3-fluoro-1,4-phenylene, Cyc is trans-1,4-cyclohexylene, Dio is trans-1,5-dioxane-2,5-diyl, Pyr is pyrimidine-2,5-diyl and Pyd is pyridine-2,5-diyl, the two abbreviations Pyr and Pyd each covering the two possible positional isomers. Furthermore, Phe.(F) denotes a 1,4-phenylene group which is unsubstituted or 2- or 3-monofluorinated. Phe.3F is a 3-monofluorinated 1,4-phenylene group, and Phe.2F and Phe.5F have corresponding meanings; Phe.3F5F denotes a 3,5-disubstituted 1,4-phenylene group, while Phe.F₂ is a 2,3-difluorinated 1,4-phenylene group. Phe.2F3F5F is a 2,3,5-trifluorinated 1,4-phenylene group, and the meanings of Phe.2F3F6F and Phe.2F3F5F6F are corresponding.

Liquid-crystal mixtures containing one or more bicyclic compounds of the formulae I2-1 - I2-9 are preferred:

R-Cyc-Phe.3F5F-X	I2-1
R-Cyc-CH ₂ CH ₂ -Phe.3F5F-X	I2-2
R-Phe-Phe.3F5F-X	I2-3
R-Phe.3F-Phe.3F5F-X	I2-4
R-Phe.(F)-COO-Phe.3F5F-X	I2-5
R-Pyr-Phe.3F5F-X	I2-6
R-Pyd-Phe.3F5F-X	I2-7
R-Dio-Phe.3F5F-X	I2-8
R-Phe.(F)-CH ₂ CH ₂ -Phe.3F5F-X	I2-9

In the compounds of the formulae I2-1 - I2-9, X is F, Cl, OCF₃ or CF₃, in particular Cl or CF₃. In the case where X = F, the proportion by weight of the compounds of the formulae I2-1 - I2-9 in the liquid-crystal mixture is preferably at least 15 %, in particular not less than 20 %.

Preference is furthermore given to liquid-crystal mixtures which contain one or more tricyclic compounds of the formulae I3-1 - I3-25:

R-Cyc-Cyc-Phe. 3F5F-X	I3-1
R-Cyc-Cyc-CH ₂ CH ₂ -Phe. 3F5F-X	I3-2
R-Cyc-Cyc-COO-Phe. 3F5F-X	I3-3
R-Cyc-Phe-Phe. 3F5F-X	I3-4
R-Cyc-CH ₂ CH ₂ -Phe. (F)-Phe. 3F5F-X	I3-5
R-Cyc-COO-Phe. (F)-Phe. 3F5F-X	I3-6
R-Cyc-Phe. 3F-Phe. 3F5F-X	I3-7
R-Cyc-Phe. 2F-Phe. 3F5F-X	I3-8
R-Cyc-Phe. 3F5F-Phe. 3F5F-X	I3-9
R-Phe. (F)-Phe. (F)-Phe. 3F5F-X	I3-10
R-Phe-CH ₂ CH ₂ -Phe. (F)-Phe. 3F5F-X	I3-11
R-Phe-COO-Phe. (F)-Phe. 3F5F-X	I3-12
R-Phe-Phe. (F)-CH ₂ CH ₂ -Phe. 3F5F-X	I3-13
R-Cyc-Phe-CH ₂ CH ₂ -Phe. 3F5F-X	I3-14
R-Cyc-Phe. 3F-CH ₂ CH ₂ -Phe. 3F5F-X	I3-15
R-Cyc-Phe. 3F5F-CH ₂ CH ₂ -Phe. 3F5F-X	I3-16
R-Cyc-Phe-COO-Phe. 3F5F-X	I3-17
R-Cyc-Phe. 3F-COO-Phe. 3F5F-X	I3-18
R-Cyc-Phe. 2F-COO-Phe. 3F5F-X	I3-19
R-Cyc-Phe. 3F5F-COO-Phe. 3F5F-X	I3-20
R-Pyd-Phe. (F)-Phe. 3F5F-X	I3-21
R-Pyr-Phe. (F)-Phe. 3F5F-X	I3-22
R-Dio-Cyc-Phe. 3F5F-X	I3-23
R-Dio-Cyc-CH ₂ CH ₂ -Phe. 3F5F-X	I3-24
R-Dio-Cyc-COO-Phe. 3F5F-X	I3-25

5 In compounds of the formulae I3-1 - I3-25, R is preferably n-alkyl or n-alkoxy having 1-10 carbon atoms, or alternatively n-alkoxymethyl or n-alkoxyethyl having 1-8 carbon atoms. Very particular preference is given to compounds of the formulae I3-1 - I3-25 in which R is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, 10 octyl, nonyl, decyl, methoxy, ethoxy, propoxy, butoxy,

5 pentoxy, hexoxy, heptoxy, octoxy, methoxymethyl, ethoxy-
methyl, propoxymethyl, butoxymethyl, methoxyethyl,
ethoxyethyl or propoxyethyl. Compounds which, in addition
to the terminals 3,5-difluoro-4-X-phenyl group, contain
one trans-1,4-cyclohexylene group or a further fluorin-
ated 1,4-phenylene group have particularly favourable
elastic properties. In the compounds of the formulae I3-1
- I3-25, X is F, Cl, CF₃ or OCF₃, and in particular F, Cl
or CF₃, the proportion by weight of the compounds of the
10 formulae I3-1 - I3-25 in the liquid-crystal mixture
according to the invention preferably being greater than
15 %, in particular not less than 20 %.

Preference is furthermore given to liquid-crystal
mixtures which contain one or more tetracyclic compounds
15 of the formulae I4-1 - I4-9:

R-Phe-Phe. (F) -Phe. (F) -Phe. 3F5F-X	I4-1
R-Cyc-Phe. (F) -Phe. (F) -Phe. 3F5F-X	I4-2
R-Dio-Phe. (F) -Phe. (F) -Phe. 3F5F-X	I4-3
R-Cyc-Cyc-Phe. (F) -Phe. 3F5F-X	I4-4
R-Cyc-Cyc-CH ₂ CH ₂ -Phe. (F) -Phe. 3F5F-X	I4-5
R-Cyc-Cyc-COO-Phe. (F) -Phe. 3F5F-X	I4-6
R-Cyc-Cyc-Cyc-Phe. 3F5F-X	I4-7
R-Cyc-Cyc-Cyc-CH ₂ CH ₂ -Phe. 3F5F-X	I4-8
R-Cyc-Cyc-Cyc-COO-Phe. 3F5F-X	I4-9

20 Compounds of the formula I4 and in particular of
the formulae I4-1 - I4-9 have a high clearing point and
favourable dielectric properties and, in spite of the
relatively great molecular extension, are characterised
by favourable values for the viscosity and the elastic
properties. Compounds of the formula I4 and in particular
of the formulae I4-1 - I4-9 are therefore used for fine
25 adjustment for optimisation of certain properties, such
as, for example, clearing points or values of the meso-
genic range, of liquid-crystal mixtures which are based
on bicyclic and/or tricyclic compounds of the formulae I2

and I3 without the dielectric and in particular the elastic properties of these mixtures being excessively impaired.

5 The proportion by weight of the compounds of the formula I4 and in particular of the formulae I4-1 - I4-9 in the liquid-crystal mixtures according to the invention is preferably not too high, in particular is less than 20 % and very particularly not more than 10 %.

10 The compounds of the formula I are known per se, and processes for their preparation are indicated, for example, in P 39 29 525 and P 40 24 760. Compound classes or compounds not mentioned therein can be prepared by analogous processes or by further known methods, as described in the literature (see, for example, in 15 Houben/Weyl, Methoden der organischen Chemie).

SFM compounds selected from the group of compounds containing at least one structural element of the formulae (G1)-(G4) and/or characterised by the formula I are highly suitable as a constituent of liquid-crystal 20 mixtures having optimised values for the dielectric anisotropy, viscosity and elastic constants, it having been shown that the proportion by weight of these compounds in the liquid-crystal mixtures according to the invention must generally not be too low and is preferably 25 greater than 10 %, in particular greater than 15 % and very particularly greater than 20 %.

The properties of the liquid-crystal mixtures according to the invention can frequently be improved if the starting mixtures to which compounds are added which 30 contain at least one structural element (G1)-(G4) and/or are characterised by the formula I are designed carefully and already have relatively favourable values for the elastic constants, the dielectric anisotropy and the viscosity.

35 The starting mixture preferably contains dielectrically neutral or dielectrically positive, bicyclic compounds of the formula II, particular preference being given to the relatively small group of compounds of the formulae II-1 - II-52 listed below:

R^2 -Cyc-Phe- R^2	II-1
R^2 -Cyc-Phe. (F) -F	II-2
R^2 -Cyc-Phe. (F) -Cl	II-3
R^2 -Cyc-Phe. (F) -CF ₃	II-4
R^2 -Cyc-Phe. (F) -OCF ₃	II-5
R^2 -Cyc-Phe. (F) -C ₂ F ₅	II-6
R^2 -Cyc-CH ₂ CH ₂ -Phe. (F) - R^2	II-7
R^2 -Cyc-CH ₂ CH ₂ -Phe. (F) -Cl	II-8
R^2 -Cyc-CH ₂ CH ₂ -Phe. (F) -F	II-9
R^2 -Cyc-CH ₂ CH ₂ -Phe. (F) -CF ₃	II-10
R^2 -Cyc-CH ₂ CH ₂ -Phe. (F) -OCF ₃	II-11
R-Cyc-COO-Phe. (F) - R^2	II-12
R-Cyc-COO-Phe. (F) -Cl	II-13
R-Cyc-COO-Phe. (F) -F	II-14
R-Cyc-COO-Phe. (F) -CF ₃	II-15
R-Cyc-COO-Phe. (F) -OCF ₃	II-16
R-Phe. (F) -Phe. (F) - R^2	II-17
R-Phe. (F) -Phe. (F) -F	II-18
R-Phe. (F) -Phe. (F) -Cl	II-19
R-Phe. (F) -Phe. (F) -CF ₃	II-20
R-Phe. (F) -Phe. (F) -OCF ₃	II-21
R-Phe. (F) -COO-Phe. (F) - R^2	II-22
R-Phe. (F) -COO-Phe. (F) -F	II-23
R-Phe. (F) -COO-Phe. (F) -Cl	II-24
R-Phe. (F) -COO-Phe. (F) -CF ₃	II-25
R-Phe. (F) -COO-Phe. (F) -OCF ₃	II-26
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) - R^2	II-27
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) -F	II-28
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) -Cl	II-29
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) -CF ₃	II-30
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) -OCF ₃	II-31
R-Phe. (F) -CH ₂ CH ₂ -Phe. (F) -OC ₂ F ₅	II-32
R-Dio-Cyc- R^2	II-33

R-Cyc-Cyc-R ²	II-34
R-Pyr-Phe. (F) -R ²	II-35
R-Pyr-Phe. (F) -F	II-36
R-Pyr-Phe. (F) -Cl	II-37
R-Pyr-Phe. (F) -CF ₃	II-38
R-Pyr-Phe. (F) -OCF ₃	II-39
R-Pyr-Phe. (F) -OCHF ₂	II-40
R-Pyr-Phe. (F) -C ₂ F ₅	II-41
R-Pyd-Phe. (F) -R ²	II-42
R-Pyd-Phe. (F) -F	II-43
R-Pyd-Phe. (F) -Cl	II-44
R-Pyd-Phe. (F) -OCF ₃	II-45
R-Pyd-Phe. (F) -OCHF ₂	II-46
R-Pyd-Phe. (F) -C ₂ F ₅	II-47
R-Dio-Phe. (F) -R ²	II-48
R-Dio-Phe. (F) -F	II-49
R-Dio-Phe. (F) -Cl	II-50
R-Dio-Phe. (F) -OCF ₃	II-51
R-Dio-Phe. (F) -C ₂ F ₅	II-52

In the compounds of the formulae II 1 - II 52, R is n-alkyl, n-alkoxy or n-alkenyl having 1-9 carbon atoms, in particular 1-8 carbon atoms, in particular methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, prop-2-enyl, but-2-enyl, but-3-enyl, pent-2-enyl, pent-3-enyl, pent-4-enyl, hex-3-enyl, hex-4-enyl, hex-5-enyl or hex-6-enyl.

Particular preference is given to liquid-crystal mixtures according to the invention which contain at least 10 %, in particular more than 15 %, of compounds of the formula II and simultaneously more than 15 %, in particular more than 20 %, of compounds selected from the group of compounds which contain at least one structural element (G1)-(G4) and/or are characterised by the formula I. Very particular preference is furthermore given to liquid-crystal mixtures which are based on bicyclic compounds of the formula II and tricyclic compounds

containing at least one structural element (G1)-(G4) and/or of the formula I. The component of liquid-crystal mixtures according to the invention which comprises compounds of the formula II preferably contains between 0 and 60 % of dielectrically neutral compounds where $Y = R^2$ and between 40 % and 100 % of dielectrically positive compounds where $Y = F, Cl, CF_3, OCF_3$ or OCF_2H .

Liquid-crystal mixtures according to the invention which contain at least one compound of the formula II frequently have particularly favourable viscosity values. Liquid-crystal mixtures which have a viscosity at 20°C of not more than $25 \text{ mm}^2 \cdot \text{s}^{-1}$, in particular less than $20 \text{ mm}^2 \cdot \text{s}^{-1}$, very particularly less than $16 \text{ mm}^2 \cdot \text{s}^{-1}$, are particularly preferred.

The starting mixture furthermore preferably contains dielectrically neutral compounds of the formula III containing 3 or 4 rings.

Particular preference is given to the following smaller group of compounds of the formulae III3-1 - III3-12 and III4-1 - III4-5:

$R^3\text{-Cyc-Phe. (F) -CH}_2\text{CH}_2\text{-Phe-R}^4$	III3-1
$R^3\text{-Cyc-Phe-CH}_2\text{CH}_2\text{-Cyc-R}^4$	III3-2
$R^3\text{-Cyc-Cyc-CH}_2\text{CH}_2\text{-Phe-R}^4$	III3-3
$R^3\text{-Cyc-CH}_2\text{CH}_2\text{-Cyc-Phe-R}^4$	III3-4
$R^3\text{-Cyc-Cyc-Phe. (F) -R}^4$	III3-5
$R^3\text{-Cyc-Phe-Cyc-R}^4$	III3-6
$R^3\text{-Cyc-Cyc-COO-Cyc-R}^4$	III3-7
$R^3\text{-Cyc-COO-Cyc-Phe-R}^4$	III3-8
$R^3\text{-Cyc-Cyc-COO-Phe. (F) -R}^4$	III3-9
$R^3\text{-Cyc-Phe. (F) -Phe-R}^4$	III3-10
$R^3\text{-Phe-Phe-Phe-R}^4$	III3-11
$R^3\text{-Cyc-CH}_2\text{CH}_2\text{-Phe. (F) -Phe-R}^4$	III3-12
$R^3\text{-Cyc-Phe. (F) -Phe-Cyc-R}^4$	III4-1
$R^3\text{-Cyc-CH}_2\text{CH}_2\text{-Phe-Phe-Cyc-R}^4$	III4-2
$R^3\text{-Cyc-Cyc-Phe-Cyc-R}^4$	III4-3
$R^3\text{-Cyc-Cyc-CH}_2\text{CH}_2\text{-Phe. (F) -Cyc-R}^4$	III4-4
$R^3\text{-Cyc-Cyc-Cyc-Phe. (F) -R}^4$	III4-5

In the compounds of the formulae III3-1 - III3-12 and III4-1 - III4-5, R³ and R⁴ are preferably, independently of one another, n-alkyl or n-alkoxy having 1-8 carbon atoms or (trans)-n-alkenyl having 3-7 carbon atoms. The proportion of compounds III3-1 - III3-12 and III4-1 - III4-5 in the liquid-crystal mixtures according to the invention is preferably between 1 % and 20 %, in particular between 2 % and 15 %. Particular preference is given to liquid-crystal mixtures according to the invention which contain one or more compounds containing at least one structural element (G1)-(G4) and/or of the formula I in a proportion by weight of 15 % - 75 %, in particular 20 % - 70 %, one or more compounds of the formula II in a proportion by weight of 2 % - 70 %, in particular 5 % - 60 %, and furthermore one or more compounds of the formula III in a proportion by weight of between 0 % and 20 %, in particular between 1 % and 15 %.

The liquid-crystal displays filled with liquid-crystal mixtures according to the invention are distinguished by a low threshold voltage, high stability and favourable response times.

The liquid-crystal mixtures according to the invention may, in addition to one or more compounds selected from a group of compounds containing at least one structural element (G1)-(G4) and/or of the formula I and if desired of the formulae II and III, also contain further compounds. Thus, the liquid-crystal compounds according to the invention may contain, for example, nitrile compounds of the formulae IV-VIII

30	$\bar{R}$ -P-Phe.(F)-CN	IV
	$\bar{R}$ -P-Cyc-CN	V
	$\bar{R}$ -P-Phe-V-Phe.(F)-CN	VI
	W-Pyd-Phe.(F)-CN	VII
	W-Pyr-Phe.(F)-CN	VIII

35 in which

$\bar{R}$ are each, independently of one another, an alkyl

group having 1-15 carbon atoms in which, in addition, one or two non-adjacent CH_2 groups may be replaced by $-\text{O}-$, $-\text{CO}-$ and/or $-\text{CH}=\text{CH}-$,

V is a single bond, $-\text{COO}-$ or $-\text{OOC}-$,

5 P is $-\text{Phe}-\text{V}$ or $\text{Cyc}-\text{V}$, and

W is $\bar{\text{R}}$, $\bar{\text{R}}-\text{Phe}(\text{F})$ or $\bar{\text{R}}-\text{Cyc}$.

10 However, it has been found that systems according to the invention whose liquid-crystal mixture contains more than 15 % of nitrile compounds frequently have inadequate stability, which is undesired, in particular, when the liquid-crystal mixture is used in active matrix displays.

15 The proportion by weight of nitrile compounds in the liquid-crystal mixture is preferably small and is in particular not greater than 10 %, very particularly not greater than 7.5 %. Systems according to the invention whose liquid-crystal mixtures contain no nitrile compounds are particularly preferred for active matrix applications.

5 The liquid-crystal mixtures used according to the invention may contain further constituents, preferably selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the classes of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of benzoic acid, of cyclohexanecarboxylic acid and of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyl-

dioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)-ethanes, 1-cyclohexyl-2-biphenylethanes, 1-phenyl-2-cyclohexylphenylethanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acids. The 1,4-phenylene groups in these compounds may also be fluorinated.

The liquid-crystal mixtures used in the electro-optical systems according to the invention preferably also contain one or more dielectrically neutral compounds of the formulae 1-5:

	$R''-L-E-R'''$	1
	$R''-L-COO-E-R'''$	2
15	$R''-L-OOC-E-R'''$	3
	$R''-L-CH_2CH_2-E-R'''$	4
	$R''-L-C=C-E-R'''$	5

In the formulae 1, 2, 3, 4 and 5, L and E, which may be identical or different, are in each case, independently of one another, a bivalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -G-Phe- and -G-Cyc- and their mirror images, where Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and G is 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

One of the radicals L and E is preferably Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. The liquid crystals according to the invention preferably contain one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which L and E are selected from the group comprising Cyc, Phe and Pyr and simultaneously one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which one of the radicals L and E is selected from the group

comprising Cyc, Phe and Pyr and the other radical is selected from the group comprising -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-, and optionally one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which the radicals L and E are selected from the group comprising -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

In the compounds of the sub-formulae 1a, 2a, 3a, 4a and 5a, R" and R''' are in each case, independently of one another, preferably alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms. In most of these compounds, R" and R''' are different from one another, one of these radicals being, in particular, alkyl, alkoxy or alkenyl.

The proportion by weight of the compounds of the formulae 1-5 in the liquid crystals used according to the invention is preferably 0-50 %, in particular 0-40 %.

The examples below are intended to illustrate the invention, without representing a limitation.

Above and below, percentages are always percent by weight and temperatures are given in °C.

Example 1

A liquid-crystal mixture comprising

25.0 % of H_7C_3 -Cyc-Cyc-Phe.3F5F-F
15.0 % of $H_{11}C_3$ -Cyc-Cyc-Phe.3F5F-F
20.0 % of H_7C_3 -Cyc-Phe-Phe.3F5F-F
40.0 % of $H_{11}C_3$ -Cyc-Phe-Phe.3F5F-F

has the following parameters:

$\Delta\epsilon$ = 9.4
 K_{11} = $5.3 \cdot 10^{-12}$ N
 K_{22} = $3.6 \cdot 10^{-12}$ N
 K_{33} = $8.4 \cdot 10^{-12}$ N
 $\bar{K}/\Delta\epsilon$ = 0.60

A TN cell having $\phi = 90^\circ$ filled with this liquid-crystal



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CLAIMS

1. A nematic liquid-crystal mixture based on medium-polarity compounds of the SFM type, wherein said compounds are selected so that the mixture has a viscosity at 20°C of less than $30 \text{ mm}^2 \text{ s}^{-1}$ and has a value of

$$\frac{\bar{K}}{\Delta\epsilon} \leq 1.5$$

for the quotient of the Frank constant $\bar{K}$

$$\bar{K} = K_{11} + \left(\frac{\vartheta}{\pi} \right)^2 [K_{33} - 2 K_{22} \left(1 - \frac{2\pi d}{p \cdot \vartheta} \right)]$$

and the dielectric anisotropy $\Delta\epsilon$

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

when used in a TN cell $\left(\vartheta = \frac{\pi}{2} \right)$, $d/p \ll 1$

$$\frac{\bar{K}}{\Delta\epsilon} \leq 1.5$$



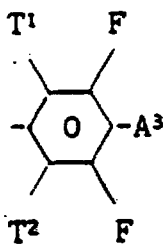
26

where θ is the twist angle in rad, d is the layer thickness in μm , p is the pitch length in μm and K_{11} , K_{22} and K_{33} are the elastic constants for splay, twist and bend in 10^{-12}N .

5

2. A liquid-crystal mixture as claimed in claim 1, comprising at least one compound of the SFM type which includes a terminal group (G3):

10



(G3)

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in which T^1 and T^2 , independently of one another, are H or F, and A^3 is F, Cl, CF_3 , OCF_3 , C_2F_5 or OC_2F_5 .

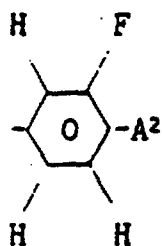
3. A liquid-crystal mixture as claimed in claim 2, wherein $A^3 = \text{F}$.



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4. A liquid-crystal mixture as claimed in claim 2 or claim 3, comprising 5-50% of one or more compounds containing a structural element of the formula (G2):

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(G2)

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in which A^2 is Cl, F, CF_3 or OCF_3 and, preferably, Cl or F, and 5-65% of the compound or compounds including the terminal group (G3).

5. A liquid-crystal mixture as claimed in any of the preceding claims, wherein the value of

15

$$\frac{\bar{K}}{\Delta \epsilon} < 1.2$$

6. A liquid-crystal display based on a twisted nematic cell and having

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- two substrates provided with electrode layers and alignment layers thereon and, with a frame, forming a cell,



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- a nematic liquid-crystal mixture having positive dielectric anisotropy present in the cell, and
- a twist angle of the liquid-crystal layer in the cell with a value of between 0° and 600° from alignment layer to alignment layer,

5

characterised in that the nematic liquid-crystal mixture is a nematic liquid-crystal mixture as claimed in any of claims 1-6.

10

7. A display as claimed in claim 6, characterised in that one of the electrode layers is in the form of an active matrix having nonlinear addressing elements integrated into the pixel, while the other electrode layer forms the counterelectrode.

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8. Use of a liquid-crystal mixture as claimed in any of claims 1-5 in an electro-optical system.
