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Liquid-crystalline mixture

5 The present invention relates to a liquid-crystalline mixture of low birefringence, and to the use thereof for electrooptical purposes.

10 Liquid crystals are used, in particular, as dielectrics in display devices since the optical properties of such substances can be affected by an applied voltage. Electrooptical devices based on liquid crystals are extremely well known to those skilled in the art and may be based on various effects. Devices of this type are, for example, cells having dynamic scattering, DAP (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (supertwisted nematic) cells, SBE (super-birefringence effect) cells and OMI (optical mode interference) cells. The most common display devices are based on the Schadt-Helfrich effect and have a twisted nematic structure.

20 The liquid-crystal materials must have good chemical and thermal stability and good stability toward electrical fields and electromagnetic radiation, especially in the visible and ultraviolet spectral range. Furthermore, the liquid-crystal materials should have low viscosity and give short addressing times, low threshold voltages, high contrast in the cells and at the same time a wide viewing angle. This wide viewing angle results from the so-called first "minimum" condition (U.S. Patent No. 4,398,803). The optical path difference, i.e. the product of cell thickness and birefringence is to be
25 adjusted to about 0.4-0.5 μm . Therefore for cell thickness of about 2.5-4 μm liquid-crystalline mixtures with birefringence of about 0.12 to 0.19 are required. Furthermore, they should
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have a suitable mesophase, for example, for the above mentioned cells, a nematic or cholesteric mesophase, at customary operating temperatures, i.e. generally in the broadest possible range above and below room temperature: Since liquid
5 crystals are generally used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as electrical conductivity, dielectric anisotropy and optical anisotropy, must meet various requirements depending on the
10 cell type and the area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

15 For display devices addressed with low multiplex ratios (common use displays), which are the preferred subject-matter of the present invention, nematic mixtures having clearing points above 55° (preferably above 65°), birefringence in the range from 0.185 to 0.130 (preferably 0.12 to 0.19) and
20 dielectric anisotropy in the range from 1.5 to 39 (preferably from 4 to 19) are desired.

A known mixture from the prior art is E7 (BDH, Poole, Great Britain), which contains cyanobiphenyls and has the following
25 parameters:

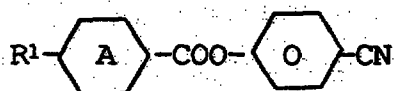
$T_{N,I}$	=	60.5°
Δn	=	0.225
η_{20}	=	39 cSt
30 V_{10} (TN)	=	1.5 volts

For many applications, however, mixtures of this type have undesired high birefringence and/or excessively low dielectric anisotropy, which results in undesirably small view angle or excessive threshold voltages.

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The invention relates to a liquid-crystalline mixture consisting essentially of two or more compounds of the general formula I,

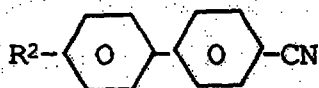
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I

in which R¹ is straight-chain alkyl having 2 to 12 carbon atoms in which, in addition, one CH₂ group may be replaced by -O- or -CH=CH-, the ring A is 1,4-phenylene or trans-1,4-cyclohexylene, one or more compounds of the general formula II,

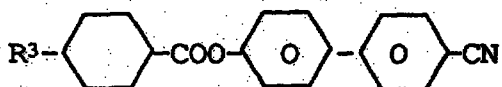
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II

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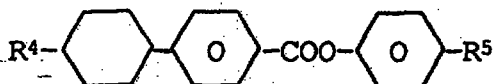
in which R² has one of the meanings indicated for R¹, one or more compounds of the general formula III,



III

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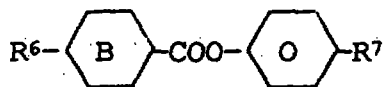
in which R³ has one of the meanings indicated for R¹, one or more compounds of the general formula IV,



IV

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in which R⁴ and R⁵ each independently have one of the meanings indicated for R¹ and one or more compounds of the formula V



V

in which R^6 and R^7 each independently have one of the meanings of R^1 and the ring B is 1,4-phenylene or trans-1,4-cyclohexylene.

It has been found that even a relatively small proportion of compounds of the formula II, III, IV or V results in a considerable improvement in the addressing times and in the low threshold voltages. The compounds of the formula II have high optical anisotropy. However, the optical anisotropy of the mixture in the mixing range indicated is increased only relatively little by the compounds of the formula II, while the threshold voltage is significantly improved. Larger amounts of a compound of the formula II generally only cause a slight improvement in the threshold voltage, but a comparatively large increase in the viscosity. The invention thus facilitates liquid-crystal mixtures of low viscosity and short switching times.

The term straight-chain alkyl having 2 to 12 carbon atoms covers the straight-chain groups ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. Groups having 2-7 carbon atoms are generally preferred.

Preferred radicals R^1 to R^7 in which a CH_2 group in the alkyl ethers has been replaced by $-\text{O}-$ or $-\text{CH}=\text{CH}-$ are indicated below:

Alkoxy groups having 1-11 carbon atoms, in particular the straight-chain groups methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, nonoxy and decoxy. Groups having 1-7 carbon atoms are generally preferred.

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Alkenyl groups having 3-13 carbon atoms, in particular the straight-chain groups C_3 - C_{12} -7-alkenyl, in particular C_4 - C_{12} -3E-alkenyl, C_5 - C_{12} -4-alkenyl, C_6 - C_{12} -5-alkenyl, C_7 - C_{12} -6-alkenyl and C_8 - C_{12} -7-alkenyl, in particular C_2 - C_{12} -1E-alkenyl, C_4 - C_{12} -3E-alkenyl and C_5 - C_{12} -4-alkenyl. Examples of preferred alkenyl groups are 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 1E-octenyl, 1E-nonenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-octenyl, 3E-nonenyl, 4-pentenyl, 4Z-hexenyl, 4Z-heptenyl, 4Z-octenyl, 4Z-nonenyl, 5-hexenyl, 6-heptenyl, 7-octenyl and the like. Groups having up to 7 carbon atoms are generally preferred.

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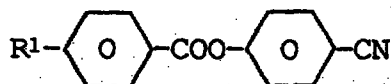
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The compounds of the formulae I to V are known or analogs of known compounds. Suitable methods for the preparation of these compounds are known to a person skilled in the art.

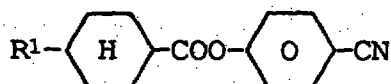
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Formula I covers the highly polar compounds of the general formulae

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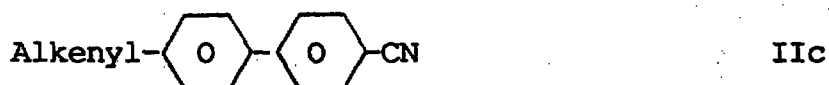
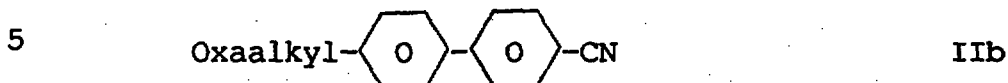
Ia



Ib

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Formula II covers the highly polar compounds of the formulae



10 of which IIa and IIb are particularly preferred for achieving particularly low threshold voltages.

Through a suitable choice of the meanings of R^1 to R^7 and the ring A, the addressing times, the threshold voltage, the steepness of the transmission characteristic lines, etc., can be modified in the desired manner. For example, 1E-alkenyl radicals, 3E-alkenyl radicals and the like generally result in shorter addressing times, improved nematic phase ranges and a higher ratio between the elastic constants k_{33} (bend) and k_{11} (splay) compared with alkyl or alkoxy radicals. 4-Alk- enyl radicals, 3-alkenyloxy radicals and the like generally give lower threshold voltages and smaller values of k_{33}/k_{11} compared with alkyl and alkoxy radicals.

25 The optimum mixing ratio of the compounds of the formula I to V depends substantially on the desired properties, on the choice of the components of the formula I to V and on the choice of any other components which may be present. Suitable mixing ratios within the above mentioned range can easily be determined from case to case. In general, a ratio between the

total weight of compounds of the formula I and the total weight of compounds of the formula II of from about 3:1 to 10:1 is preferred.

5 The total amount of compounds of the formulae I to V in the mixtures according to the invention is not crucial. The mixtures can therefore contain one or more further components in order to optimize various properties. However, the
10 observed effect on the addressing times and the threshold voltage is generally the greater, the higher the total concentration of the compounds of the formula I to III.

Preferred mixtures according to the invention are therefore those in which the proportion of compounds of the formulae I
15 to III together in the total mixture is at least 35-80 % by weight, and in particular those in which the proportion of compounds of the formula I is at least 15 % by weight. It goes without saying that the proportion may also be up to 100 % by weight.

20 Preferred concentration ranges for the compounds of the formulae I to V arise from the indicated weight ratios and the preferred total amounts. Particular preference is given to mixtures in which the proportion of one or more compounds
25 of the formula II in the total mixture is 10-40 % by weight, in particular 10-30 % by weight. Further more, particularly preferred mixtures are those in which the proportion of one or more compounds of the formula III in the total mixture is at least 10 % by weight, in particular at least 15 % by
30 weight.

Particular preference is given to mixtures in which the proportion of one or more compounds of the formula IV in the total mixture is 5-40 % by weight, in particular 7.5-30 % by weight.

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Particular preference is given to mixtures in which the proportion of one or more compounds of the formula V in the total mixture is 10-50 % by weight, in particular 10-40 % by weight. Furthermore, particularly preferred mixtures are those in which the proportion of one or more compounds of the formula I in the total mixture is at least 15 % by weight, in particular at least 30 % by weight.

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The mixtures according to the invention preferably contain one or more compounds of the formula Ia, wherein  is 1,4-phenylene and one or more compounds of the formula Ib, wherein  is 1,4-cyclohexylene.

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The total amount of any compounds of the formula Ib which may be present in the mixture is preferably at least 5 % by weight, particularly preferably at least 10 % by weight. If the mixture according to the invention contains one or more compounds of the formula Ia and one or more compounds of the formula Ib the weight ratio between the compounds of the formula Ia and the compounds of the formula Ib is preferably at least 1:1.

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Liquid-crystalline mixtures according to the invention consists of

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15-50 % by weight of two or more compounds of formula I,
15-50 % by weight of one or more compounds of formula II,
5-20 % by weight of one or more compounds of formula III,
5-25 % by weight of one or more compounds of formula IV

5 and

15-50 % by weight of two or more compounds of formula V,

in particular, wherein R¹ to R⁷ of the compounds of the formulae I to V are each n-alkyl having 2 to 7 carbon atoms, in particular n-alkyl having 2, 3, 4 or 5 C atoms.

Particular preference is given to consisting of liquid-crystalline mixtures of the compounds of the formulae I to V wherein

15 R¹ is n-alkyl with 3 or 5 C atoms,
R² is n-alkyl with 3 or 5 C atoms,
R³ is n-alkyl with 2, 3 or 5 C atoms,
R⁴ is n-alkyl with 3 or 5 C atoms,
20 R⁵ is n-alkyl with 3 or 5 C atoms,
R⁶ is n-alkyl with 3 or 5 C atoms,
R⁷ is n-alkyl with 3 or 5 C atoms,

in particular wherein,

25 R¹ is n-alkyl with 5 C atoms,
R² is n-alkyl with 5 C atoms,
R³ is n-alkyl with 2 C atoms,
R⁴ is n-alkyl with 3 C atoms,
30 R⁵ is n-alkyl with 5 C atoms,
R⁶ is n-alkyl with 5 C atoms,
R⁷ is n-alkyl with 5 C atoms.

The mixtures according to the invention are particularly suitable for nematic and cholesteric applications. The mixture of the compounds of the formulae I, II, III and/or V can be used as such or mixed with further liquid-crystalline and/or non-liquid-crystalline components. Suitable further components are known to a person skilled in the art and some are commercially available, such as, for example, nematic or nematogenic (monotropic or isotropic) 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 cyclohexanecarboxylic 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'-biscyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, 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 most important compounds suitable as further constituents of media according to the invention can be characterized by the formulae 1, 2, 3, 4 and 5:

- (1) $R'-L-E-R''$
- (2) $R'-L-COO-E-R''$
- (3) $R'-L-OOC-E-R''$
- (4) $R'-L-CH_2CH_2-E-R''$
- (5) $R'-L-C\equiv C-E-R''$

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 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-Cycl (sic). The media 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 a preferred sub-group of the compounds of the formulae 1, 2, 3, 4 and 5, R' and R'' are in each case, independently of one another, alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms (group 1). In most of these compounds, R' and R'' are different from one another, one of these radicals usually being alkyl or alkenyl. In a further preferred sub-group of the compounds of the formulae 1, 2, 3, 4 and 5, R'' is -CN, -CF₃, F, Cl or -NCS; in this case, R has the meaning given for the compounds of group 1 and is preferably alkyl or alkenyl (group 2). However, other variants of the proposed substituents in the compounds of the formulae 1, 2, 3, 4 and 5 are common. Many such substances or alternatively mixtures thereof are commercially available. All these substances can be obtained by methods which are known from the literature or analogously thereto.

Besides components from group 1, the mixtures according to the invention preferably also contain components from group 2, whose proportions are preferably as follows:

group 1: 20 to 90 %, in particular 30 to 90 %,
group 2: 10 to 80 %, in particular 10 to 50 %,

the sum of the proportions of the compounds of the formulae I, II, III, IV and V of the compounds from groups 1 and 2 adding up to 100 %.

The mixtures according to the invention preferably contain 1 to 40 %, in particular preferably 5 to 30 %, of compounds according to the invention. Further preferred media are those

which contain more than 40 %, in particular 45 to 90 %, of compounds according to the invention. The media preferably contain three, four or five compounds according to the invention.

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Besides one or more compounds of the formulae I, II, III, IV and/or V the liquid-crystalline mixtures according to the invention preferably contain, as further constituents, 2 to 40, in particular 4 to 30, components. These mixtures very particularly preferably contain 7 to 25 components in addition to one or more compounds of the formulae I, II, III, IV and/or V.

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The mixtures according to the invention may also contain one or more optically active compounds. Examples of suitable optically active compounds are the cholesteryl derivatives (for example cholesteryl chloride or cholesteryl nonanoate), and the optically active compounds of the formulae I-V with a chiral side chain [for example optically active 4-(2-methylbutyl or 2-methylbutoxy)-4-biphenylcarbonitrile]. The mixtures according to the invention may furthermore contain one or more dichroic dyes (for example azo, azoxy and/or anthraquinone dyes). The proportion of optically active compounds and/or dyes is determined by the solubility, the desired pithc, color, extinction and the like. In general, the proportion of optically active compounds with dichroic dyes is at most in each case about 10 % by weight in the total mixture.

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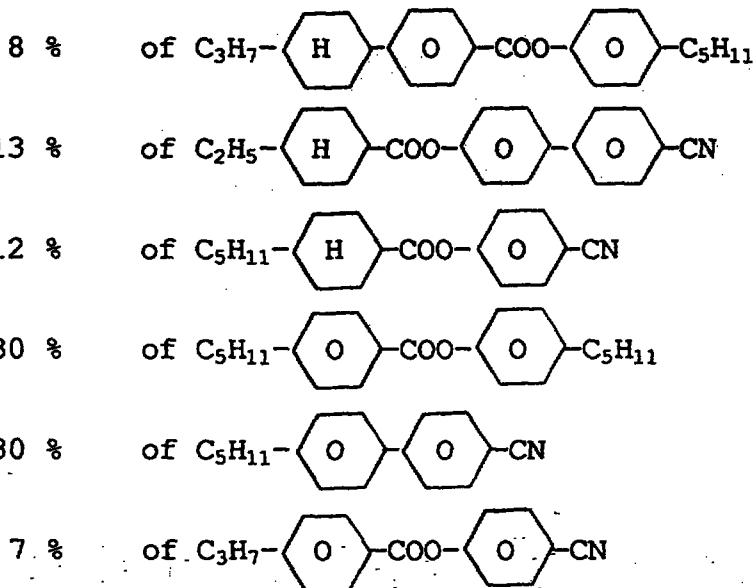
The mixtures according to the invention and the electrooptical devices which contain this mixture as liquid-crystalline dielectric can be produced by methods known per se.

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The invention is illustrated further by the examples below. C denotes a crystalline phase, S a smectic phase, S_B a smectic B phase, N a nematic phase and I the isotropic phase. V_{10} denotes the voltage for 10 % transmission (view angle perpendicular to the plate surface). t_{on} denotes the switch-on time and t_{off} the switch-off time at an operating voltage corresponding to 2.5 times the value of V_{10} . Δn denotes the optical anisotropy and n_o the refractive index for the NaD (sic) line, unless otherwise stated. $\Delta \epsilon$ denotes the dielectric anisotropy $\Delta \epsilon = \epsilon - \epsilon_{\perp}$, where $\epsilon_{||}$ denotes the dielectric constant parallel to the longitudinal molecular axes and $\epsilon_{\perp}$ denotes the dielectric constant perpendicular thereto. The electrooptical data were measured at 20 °C in a TN cell at a plate separation matched to the optical delay desired, unless expressly stated otherwise. The optical data were measured at 20 °C, unless expressly stated otherwise.

Example 1

A mixture comprising



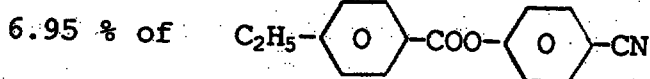
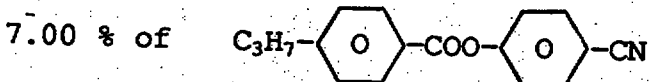
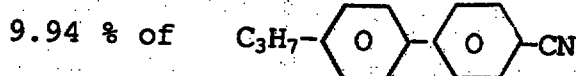
has a viscosity of 57 cSt at 20 °C, N 68.1 I, $V_{10} = 2.37$ volts and Δn 0.1818.

Example 2

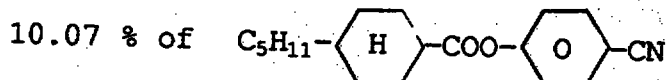
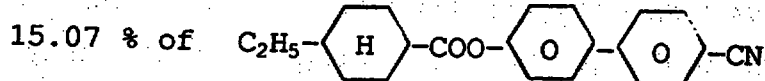
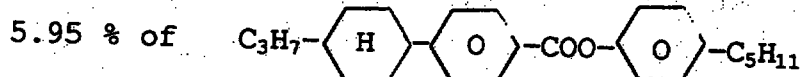
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A mixture comprising

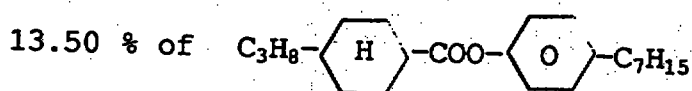
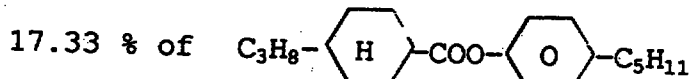
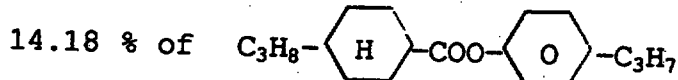
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has a viscosity of 38 cSt at 20 °C, N 69.8 I, $V_{10} = 1.93$ volts and Δn 0.1317.

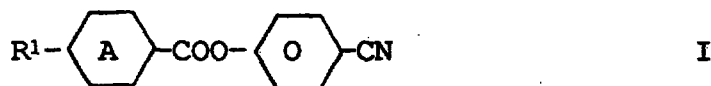
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Patent Claims

1. Liquid-crystalline mixture consisting essentially of two or more compounds of the general formula I,

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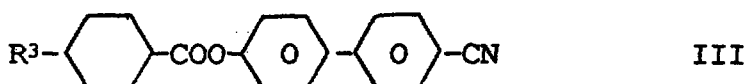
in which R^1 is straight-chain alkyl having 2 to 12 carbon atoms in which, in addition, one CH_2 group may be replaced by $-\text{O}-$ or $-\text{CH}=\text{CH}-$, the ring A is 1,4-phenylene or trans-1,4-cyclohexylene, one or more compounds of the general formula II,

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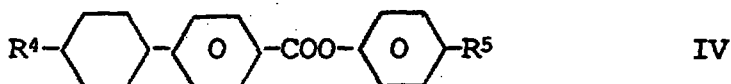
in which R^2 has one of the meanings indicated for R^1 , one or more compounds of the general formula III,

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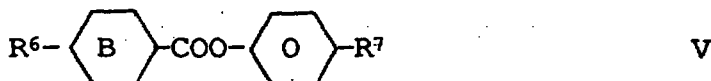
in which R^3 has one of the meanings indicated for R^1 , one or more compounds of the general formula IV,

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in which R^4 and R^5 each independently have one of the meanings indicated for R^1 and one or more compounds of the formula V

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in which R⁶ and R⁷ each independently have one of the meanings of R¹ and the ring B is 1,4-phenylene or trans-1,4-cyclohexylene.

5 2. Liquid-crystalline mixture according to Claim 1, characterized in that it contains one or more compounds of the formula I wherein  is 1,4-phenylene and one or more compounds of the formula I wherein  is 1,4-cyclohexylene.

10 3. Liquid-crystalline mixture according to Claim 1 or 2, characterized in that  is .

15 4. Liquid-crystalline mixture according one of the Claims 1 to 3, characterized in that the proportion of compounds of the formulae I, II and III in the total mixture is 35-80 % by weight.

20 5. Liquid-crystalline mixture according to one of Claims 1 to 4, characterized in that the proportion of compounds of the formula I in the total mixture is at least 15 % by weight.

25 6. Liquid-crystalline mixture according to one of Claims 1 to 5, characterized in that it consists of

15-50 % by weight of two or more compounds of formula I,
15-50 % by weight of one or more compounds of formula II,
5-20 % by weight of one or more compounds of formula III,
30 5-25 % by weight of one or more compounds of formula IV
and
15-50 % by weight of two or more compounds of formula V.



7. Liquid-crystalline mixture according to one of Claims 1 to 6, characterized in that R¹ to R⁷ are each n-alkyl having 2 to 7 carbon atoms.
- 5 8. Liquid-crystalline mixture according to Claim 7, characterized in that R¹ to R⁷ are each independently n-alkyl having 2, 3, 4 or 5 C atoms.
- 10 9. Liquid-crystalline mixture according to Claim 8, characterized in that
- 15 R¹ is n-alkyl with 3 or 5 C atoms,
R² is n-alkyl with 3 or 5 C atoms,
R³ is n-alkyl with 2, 3 or 5 C atoms,
R⁴ is n-alkyl with 3 or 5 C atoms,
R⁵ is n-alkyl with 3 or 5 C atoms,
R⁶ is n-alkyl with 3 or 5 C atoms,
R⁷ is n-alkyl with 3 or 5 C atoms.
- 20 10. Liquid-crystalline mixture according to Claim 9, characterized in that
- 25 R¹ is n-alkyl with 5 C atoms,
R² is n-alkyl with 5 C atoms,
R³ is n-alkyl with 2 C atoms,
R⁴ is n-alkyl with 3 C atoms,
R⁵ is n-alkyl with 5 C atoms,
R⁶ is n-alkyl with 5 C atoms,
R⁷ is n-alkyl with 5 C atoms.