## (19) World Intellectual Property Organization

International Bureau





(10) International Publication Number WO 2013/124040 A1

- (43) International Publication Date 29 August 2013 (29.08.2013)
- (51) International Patent Classification:

  C09K 19/44 (2006.01) C09K 19/54 (2006.01)

  C09K 19/04 (2006.01)
- (21) International Application Number:

PCT/EP2013/000407

(22) International Filing Date:

12 February 2013 (12.02.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12001174.7 22 February 2012 (22.02.2012)

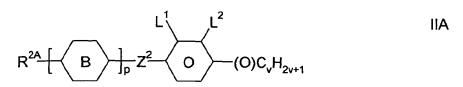
EP

- (71) Applicant: MERCK PATENT GMBH [DE/DE]; Frankfurter Strasse 250, 64293 Darmstadt (DE).
- (72) Inventors: JEONG, Ji-Won; Woojangsan Lotte Castle Apt. 104-1101, Hwagok 6-dong, Gangseo-gu, Seoul 157-734 (KR). YUN, Yong-Kuk; Posco the Sharp 318-1102, Bansong-dong, Hwaseong-Shi, Gyeonggi-do, Hwaseong 445-724 (KR). SONG, Dong-Mee; 313-202, Im-kwang, APT, Wow-ri, Bongdam-eub, HwaSung-Shi, Gyeonggi-do, Hwasung 445-737 (KR). LEE, Jung-Min; #1008 Hae-Joo Tower, 870-1 Jungang-dong, Gwanak-gu, Seoul 151-060 (KR).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Published:

— with international search report (Art. 21(3))

(54) Title: LIQUID CRYSTALLINE MEDIUM



$$R^{2B} \underbrace{ \left( \begin{array}{c} L^{2} \\ H \end{array} \right)}_{q} \underbrace{ \left( \begin{array}{c} L^{2} \\ O \end{array}$$

(57) Abstract: The invention relates to a liquid-crystalline medium which contains at least two polymerisable compounds or reactive mesogens (RM) and at least one compound selected from the group of compounds of the formula IIA, IIB and IIC, in which  $R^{2A}$ ,  $R^{2B}$ ,  $R^{2C}$ ,  $L^{1-6}$ , ring B,  $Z^2$ ,  $Z^2$ , p, q and v have the meanings indicated in Claim 1, and to the use thereof for an active-matrix display, in particular based on the VA, PSA, PS-VA, PALC, FFS, PS-FFS, IPS or PS-IPS effect, especially for the use in LC displays of the PS (polymer stabilised) or PSA (polymer sustained alignment) type.



10

15

## Liquid crystalline medium

The invention relates to a liquid crystalline medium which contains at least two polymerisable compounds and at least one compound with a negative dielectric anisotropy.

Media of this type can be used, in particular, for electro-optical displays having active-matrix addressing based on the ECB effect and for IPS (in-plane switching) displays or FFS (fringe field switching) displays.

The principle of electrically controlled birefringence, the ECB effect or also DAP (deformation of aligned phases) effect, was described for the first time in 1971 (M.F. Schieckel and K. Fahrenschon, "Deformation of nematic liquid crystals with vertical orientation in electrical fields", Appl. Phys. Lett. 19 (1971), 3912). This was followed by papers by J.F. Kahn (Appl. Phys. Lett. 20 (1972), 1193) and G. Labrunie and J. Robert (J. Appl. Phys. 44 (1973), 4869).

The papers by J. Robert and F. Clerc (SID 80 Digest Techn. Papers (1980), 30), J. Duchene (Displays 7 (1986), 3) and H. Schad (SID 82 Digest Techn. Papers (1982), 244) showed that liquid-crystalline phases must have high values for the ratio of the elastic constants K<sub>3</sub>/K<sub>1</sub>, high values for the optical anisotropy Δn and values for the dielectric anisotropy of Δε ≤ -0.5 in order to be suitable for use in high-information display elements based on the ECB effect. Electro-optical display elements based on the ECB effect have a homeotropic edge alignment (VA technology = vertically aligned). Dielectrically negative liquid-crystal media can also be used in displays which use the so-called IPS or FFS effect.

30

35

Displays which use the ECB effect, as so-called VAN (vertically aligned nematic) displays, for example in the MVA (multi-domain vertical alignment, for example: Yoshide, H. et al., paper 3.1: "MVA LCD for Notebook or Mobile PCs ...", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book I, pp. 6 to 9, and Liu, C.T. et al., paper 15.1: "A 46-inch TFT-LCD HDTV Technology ...", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book II, pp. 750 to 753), PVA

WO 2013/124040 PCT/EP2013/000407

5

10

15

20

25

30

35

(patterned vertical alignment, for example: Kim, Sang Soo, paper 15.4: "Super PVA Sets New State-of-the-Art for LCD-TV", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book II, pp. 760 to 763), ASV (advanced super view, for example: Shigeta, Mitzuhiro and Fukuoka, Hirofumi, paper 15.2: "Development of High Quality LCDTV", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book II, pp. 754 to 757) modes, have established themselves as one of the three more recent types of liquid-crystal display that are currently the most important. in particular for television applications, besides IPS (in-plane switching) displays (for example: Yeo, S.D., paper 15.3: "An LC Display for the TV Application", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book II, pp. 758 & 759) and the long-known TN (twisted nematic) displays. The technologies are compared in general form, for example, in Souk, Jun, SID Seminar 2004, seminar M-6: "Recent Advances in LCD Technology", Seminar Lecture Notes, M-6/1 to M-6/26. and Miller, Ian, SID Seminar 2004, seminar M-7: "LCD-Television", Seminar Lecture Notes, M-7/1 to M-7/32. Although the response times of modern ECB displays have already been significantly improved by addressing methods with overdrive, for example: Kim, Hyeon Kyeong et al., paper 9.1: "A 57-in. Wide UXGA TFT-LCD for HDTV Application", SID 2004 International Symposium, Digest of Technical Papers, XXXV, Book I, pp. 106 to 109, the achievement of video-compatible response times, in particular on switching of grey shades, is still a problem which has not yet been satisfactorily solved.

Industrial application of this effect in electro-optical display elements requires LC phases, which have to satisfy a multiplicity of requirements. Particularly important here are chemical resistance to moisture, air and physical influences, such as heat, infrared, visible and ultraviolet radiation and direct and alternating electric fields.

Furthermore, industrially usable LC phases are required to have a liquidcrystalline mesophase in a suitable temperature range and low viscosity.

None of the hitherto-disclosed series of compounds having a liquid-crystalline mesophase includes a single compound which meets all these require-

15

20

25

30

35

ments. Mixtures of two to 25, preferably three to 18, compounds are therefore generally prepared in order to obtain substances which can be used as LC phases. However, it has not been possible to prepare optimum phases easily in this way since no liquid-crystal materials having significantly negative dielectric anisotropy and adequate long-term stability were hitherto available.

Matrix liquid-crystal displays (MLC displays) are known. Non-linear ele-10 ments which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). The term "active matrix" is then used, where a distinction can be made between two types:

- 1. MOS (metal oxide semiconductor) transistors on a silicon wafer as substrate
- 2. thin-film transistors (TFTs) on a glass plate as substrate.

In the case of type 1, the electro-optical effect used is usually dynamic scattering or the guest-host effect. The use of single-crystal silicon as substrate material restricts the display size, since even modular assembly of various part-displays results in problems at the joints.

In the case of the more promising type 2, which is preferred, the electrooptical effect used is usually the TN effect.

A distinction is made between two technologies: TFTs containing compound semiconductors, such as, for example, CdSe, or TFTs based on polycrystalline or amorphous silicon. The latter technology is being worked on intensively worldwide.

The TFT matrix is applied to the inside of one glass plate of the display. while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be extended to fully colour-capable displays, in which a mosaic of red.

green and blue filters is arranged in such a way that a filter element is opposite each switchable pixel.

The term MLC displays here covers any matrix display with integrated nonlinear elements, i.e. besides the active matrix, also displays with passive elements, such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for TV applications (for example pocket TVs) or for high-information displays in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to insufficiently high specific resistance of the liquid-crystal mixtures ITOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORI-MACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, pp. 141 ff., Paris; STROMER, M., Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, pp. 145 ff., Paris]. With decreasing resistance, the contrast of an MLC display deteriorates. Since the specific resistance of the liquid-crystal mixture generally drops over the life of an MLC display owing to interaction with the inside surfaces of the display, a high (initial) resistance is very important for displays that have to have acceptable resistance values over a long operating period.

25

30

10

15

20

There, thus continues to be a great demand for MLC displays having very high specific resistance at the same time as a large working-temperature range, short response times and a low threshold voltage with the aid of which various grey shades can be produced. The disadvantage of the frequently-used MLC-TN displays is due to their comparatively low contrast, the relatively high viewing-angle dependence and the difficulty of generating grey shades in these displays.

35

VA displays have significantly better viewing-angle dependencies and are therefore principally used for televisions and monitors. However, there continues to be a need here to improve the response times, in particular with respect to the use of televisions having frame rates (image change

frequency/repetition rates) of greater than 60 Hz. At the same time, however, the properties, such as, for example, the low-temperature stability, must not be impaired.

5

10

The various display technologies have been developed for a lot of applications. The flexible display, 3D display and transparent display etc. have been mentioned as the future display. The liquid crystal display is the non-emissive type which means the backlight is essential. In most LC optical devices, the incident light of LCD panel is absorbed, reflected and blocked by the several layers of LCD. For this reason, the optical efficiency of LCD is very low as 7~8 %. Thus, the object of the display manufacturers is to improve the transmittance of LCD and to decrease the cost. This could be achieved for example by removing some substrates or eliminating polarizers in the LCD.

The object of the present invention is to provide LC mixtures which can be used for all kind of applications, especially for LCD panels with one glass substrate only.

20

15

Furthermore, the invention is based on the object of providing liquid crystalline mixtures, in particular for monitor and TV applications, which are based on the ECB effect or on the IPS or FFS effect, which do not have the above-mentioned disadvantages or only do so to a reduced extent. In particular, it must be ensured for monitors and televisions that they also operate at extremely high and extremely low temperatures and at the same time have short response times, have improved reliability behaviour, in particular have no or significantly reduced image sticking after long operating times.

30

35

25

Surprisingly it has been found that LCD which contain LC mixtures with at least two polymerisable compounds (reactive mesogens = RMs), preferably with different polymerization reactivities, can be operated with a single substrate in the display only. With the mixtures according to the present invention, it is possible to build the RM polymer layer in order to replace the top glass substrate in the LCD through UV exposure process.

The built RM polymer layer stores the LC mixture in the polyimide wall. The polyimide (PI) is used as orientation layer in the display.

The LC mixtures according to the present invention especially improve the response times, especially the response times of PS-VA mixtures.

The invention thus relates to a liquid-crystalline medium which contains at least two polymerisable compounds or reactive mesogens (RM)

and

at least one compound selected from the group of compounds of the formula IIA, IIB and IIC,

15

10

$$R^{2A} = \begin{bmatrix} & & \\ & B & \end{bmatrix}_{p} Z^{2} = \begin{bmatrix} & & \\ & O & \end{bmatrix}_{0} C_{v} H_{2v+1}$$
IIA

20

$$R^{2B} \underbrace{ \left( \begin{array}{c} L^{2} \\ H \end{array} \right)}_{q} \underbrace{ \left( \begin{array}{c} L^{2} \\ O \end{array}$$

25

in which

30

35

$$R^{2A}$$
,  $R^{2B}$  and  $R^{2C}$ 

each, independently of one another, denote H, an alkyl or alkenyl radical having up to 15 C atoms which is unsubstituted, monosubstituted by CN or  $CF_3$  or at least monosubstituted by halogen, where, in addition, one or more  $CH_2$  groups in these radicals may be replaced by -O-, -S-,  $\longrightarrow$ , -C=C-, -CF<sub>2</sub>O-,

-OCF<sub>2</sub>-, -OC-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

5 denotes

Y<sup>1-6</sup> each, independently of one another, denote H or F.

L<sup>1</sup> and L<sup>2</sup> each, independently of one another, denote F, CI, CF<sub>3</sub> or CHF<sub>2</sub>,

each, independently of one another, denote H, F, Cl, CF<sub>3</sub> or CHF<sub>2</sub>, but at least two of L<sup>3-6</sup> denote F, Cl, CF<sub>3</sub> or CHF<sub>2</sub>

 $Z^2$  and  $Z^{2'}$  each, independently of one another, denote a single bond,  $-CH_2CH_2$ -, -CH=CH-,  $-C\equiv C$ -,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2O$ -,  $-OCH_2$ -, -COO-, -OCO-,  $-C_2F_4$ -, -CF=CF-,  $-CH=CHCH_2O$ -,

p denotes 1 or 2, and, in the case where  $Z^2$  = single bond, p may also denote 0,

q denotes 0 or 1,

25

(O) $C_vH_{2v+1}$  denotes  $OC_vH_{2v+1}$  or  $C_vH_{2v+1}$ , and

v denotes 1 to 6.

The mixtures according to the invention preferably exhibit very broad nematic phase ranges having clearing points ≥ 70 °C, preferably ≥ 75 °C, in particular ≥ 80 °C, very favourable values for the capacitive threshold,

15

20

25

30

35

relatively high values for the holding ratio and at the same time very good low-temperature stabilities at -20 °C and -30 °C, as well as very low rotational viscosities and short response times. The mixtures according to the invention are furthermore distinguished by the fact that, in addition to the improvement in the rotational viscosity  $\gamma_1$ , relatively high values of the elastic constant  $K_{33}$  for improving the response times can be observed.

The invention further relates to the use of the LC mixture in LC displays, especially in PS or PSA displays.

The invention further relates to a method of preparing an LC medium as described above and below, by mixing one or more compounds of formula IIA, IIB and/or IIC with two or more polymerisable compounds or RMs and optionally with one or more further liquid-crystalline compounds and/or additives.

Especially preferred PS and PSA displays are PSA-VA, PSA-OCB, PS-IPS, PS-FFS and PS-TN displays, very preferred PSA-VA and PSA-IPS displays.

The mixture according to the invention is highly suitable for panel structures wherein one of the outer plate is substituted by the polymer layer and the PI layer in the bottom side is not rubbed for VA.

The invention further relates to an LC medium, its use in PS and PSA displays, and to PS and PSA displays containing it as described above and below, wherein the polymerisable components or polymerisable compounds or RMs are polymerised.

The mixtures according to the present invention containing at least two polymerisable compounds and at least one compound of the formula IIA, IIB or IIC show an advantageous rotational viscosity  $\gamma_1$ /clearing point ratio. They are therefore particularly suitable for achieving liquid crystalline mixtures having low  $\gamma_1$ , high transmittance and a relatively high clearing point. In addition, the compounds of the formulae IIA, IIB and IIC exhibit good solubility in LC media. LC media according to the invention containing

with high transmission.

5

10

15

20

25

30

35

at least one compound of the formula IIA, IIB and/or IIC have a low rotational viscosity, fast response times, a high clearing point, very high positive dielectric anisotropy, relatively high birefringence and a broad nematic phase range and a high transmittance. They are therefore particularly suitable for mobile telephones, video applications, smart phones, tablet PC and especially for TV, flexible displays and for displays

Polymerisable compounds, so-called reactive mesogens (RMs), for example as disclosed in U.S. 6,861,107, are added to the mixtures according to the invention in concentrations of preferably 0.1 - 5 % by weight, particularly preferably 0.2 - 2% by weight in total, based on the mixture. These mixtures may optionally also contain an initiator, as described, for example, in U.S. 6,781,665. The initiator, for example Irganox-1076 from Ciba, is preferably added to the mixture containing polymerisable compounds in amounts of 0-1 %. Mixtures of this type can be used for so-called polymer-stabilised VA modes (PS-VA) or PSA (polymer sustained VA), in which polymerisation of the reactive mesogens is intended to take place in the liquid-crystalline mixture. The prerequisite for this is that the liquid-crystal mixture does not itself contain any polymerisable components.

In a preferred embodiment of the invention, the polymerisable compounds are selected from the compounds of the formula I

$$R^{Ma}-A^{M1}-(Z^{M1}-A^{M2})_{m1}-R^{Mb}$$

in which the individual radicals have the following meanings:

R<sup>Ma</sup> and R<sup>Mb</sup> each, independently of one another, denote P, P-Sp-, H, halogen, SF<sub>5</sub>, NO<sub>2</sub>, an alkyl, alkenyl or alkynyl group, where at least one of the radicals R<sup>Ma</sup> and R<sup>Mb</sup> preferably denotes or contains a group P or P-Sp-,

P denotes a polymerisable group,

Sp denotes a spacer group or a single bond,

A<sup>M1</sup> and A<sup>M2</sup> each, independently of one another, denote an aromatic, heteroaromatic, alicyclic or heterocyclic group, preferably having 4 to 25 ring atoms, preferably C atoms, which may also encompass or contain fused rings, and which may optionally be mono- or polysubstituted by L,

denotes P, P-Sp-, OH, CH<sub>2</sub>OH, F, CI, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)N(R<sup>x</sup>)<sub>2</sub>, -C(=O)Y<sup>1</sup>, -C(=O)R<sup>x</sup>, -N(R<sup>x</sup>)<sub>2</sub>, optionally substituted silyl, optionally substituted aryl having 6 to 20 C atoms, or straight-chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 25 C atoms, in which, in addition, one or more H atoms may be replaced by F, Cl, P or P-Sp-, preferably P, P-Sp-, H, OH, CH<sub>2</sub>OH, halogen, SF<sub>5</sub>, NO<sub>2</sub>, an alkyl, alkenyl or alkynyl group,

20 Y<sup>1</sup> denotes halogen,

25

30

35

 $R^{x}$ 

Z<sup>M1</sup> denotes -O-, -S-, -CO-, -CO-O-, -OCO-, -O-CO-O-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>S-, -SCF<sub>2</sub>-, -(CH<sub>2</sub>)<sub>n1</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, -(CF<sub>2</sub>)<sub>n1</sub>-, -CH=CH-, -CF=CF-, -C≡C-, -CH=CH-, -COO-, -OCO-CH=CH-, CR<sup>0</sup>R<sup>00</sup> or a single bond,

R<sup>0</sup> and R<sup>00</sup> each, independently of one another, denote H or alkyl having 1 to 12 C atoms,

denotes P, P-Sp-, H, halogen, straight-chain, branched or cyclic alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl, P or P-Sp-, an optionally substituted aryl or aryloxy

WO 2013/124040 PCT/EP2013/000407

group having 6 to 40 C atoms, or an optionally substituted heteroaryl or heteroaryloxy group having 2 to 40 C atoms,

5 m1 denotes 0, 1, 2, 3 or 4, and

n1 denotes 1, 2, 3 or 4,

30

35

where at least one, preferably one, two or three, particularly preferably one or two, from the group R<sup>Ma</sup>, R<sup>Mb</sup> and the substituents L present denotes a group P or P-Sp- or contains at least one group P or P-Sp-.

Particularly preferred compounds of the formula I are those in which

15 R<sup>Ma</sup> and R<sup>Mb</sup> each, independently of one another, denote P, P-Sp-, H, F, CI, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, SF<sub>5</sub> or straight-chain or branched alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may each be replaced, independently of one another, by -C(R<sup>0</sup>)=C(R<sup>00</sup>)-, -C≡C-, -N(R<sup>00</sup>)-, -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, CI, Br, I, CN, P or P-Sp-, where at least one of the radicals R<sup>Ma</sup> and R<sup>Mb</sup> preferably denotes or contains a group P or P-Sp-,

A<sup>M1</sup> and A<sup>M2</sup> each, independently of one another, denote 1,4-phenylene, naphthalene-1,4-diyl, naphthalene-2,6-diyl, phenanthrene-2,7-diyl, anthracene-2,7-diyl, fluorene-2,7-diyl, coumarine, flavone, where, in addition, one or more CH groups in these groups may be replaced by N, cyclohexane-1,4-diyl, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may be replaced by O and/or S, 1,4-cyclohexenylene, bicyclo[1.1.1]-pentane-1,3-diyl, bicyclo[2.2.2]octane-1,4-diyl, spiro[3.3]heptane-2,6-diyl, piperidine-1,4-diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl, indane-2,5-diyl or octahydro-4,7-methanoindane-2,5-diyl, where all these

groups may be unsubstituted or mono- or polysubstituted by L,

- denotes P, P-Sp-, OH, CH<sub>2</sub>OH, F, CI, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)N(R<sup>x</sup>)<sub>2</sub>, -C(=O)Y<sup>1</sup>, -C(=O)R<sup>x</sup>, -N(R<sup>x</sup>)<sub>2</sub>, optionally substituted silyl, optionally substituted aryl having 6 to 20 C atoms, or straight-chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 25 C atoms, in which, in addition, one or more H atoms may be replaced by F, CI, P or P-Sp-,
  - P denotes a polymerisable group,
- 15 Y<sup>1</sup> denotes halogen,

20

25

30

35

WO 2013/124040

R<sup>x</sup> denotes P, P-Sp-, H, halogen, straight-chain, branched or cyclic alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl, P or P-Sp-, an optionally substituted aryl or aryloxy group having 6 to 40 C atoms, or an optionally substituted heteroaryl or heteroaryloxy group having 2 to 40 C atoms.

Very particular preference is given to compounds of the formula I in which one of  $R^{\text{Ma}}$  and  $R^{\text{Mb}}$  or both denote(s) P or P-Sp-.

Suitable and preferred polymerisable compounds for use in liquidcrystalline media and PS mode displays, preferably PS-VA and PSA displays, according to the invention are selected, for example, from the following formulae:

**I-3** 

$$P^1-Sp^1-O$$
  $Sp^2-P^2$ 

5

$$P^1-Sp^1$$
  $O$   $Sp^2-P^2$ 

10

30

35

15 
$$(L)_s \longrightarrow O \longrightarrow Sp^2-P^2$$

$$P^1-Sp^1 \longrightarrow O \longrightarrow Sp^2-P^2$$

1-5 20

$$P^{1}-Sp^{1} \longrightarrow O \longrightarrow Sp^{2}-P^{2}$$

$$P^1-Sp^1$$
  $O$   $O$   $Sp^2-P^2$   $I-7$ 

1-8

$$P^1-Sp^1$$
  $O$   $Z^1$   $O$   $Sp^2-P^2$ 

$$P^1$$
- $Sp^1$   $O$   $O$   $O$   $Sp^2$ - $P^2$ 

$$P^{1}-Sp^{1}$$
 $P^{1}-Sp^{1}$ 
 $O$ 
 $O$ 
 $O$ 

$$P^1-SP^1$$
 $P^2-SP^2$ 
 $P^2-SP^2$ 
 $P^3-SP^3$ 
 $P^3-SP^3$ 
 $P^3-SP^3$ 
 $P^3-SP^3$ 

$$P^{2}-Sp^{2}$$
  $O$   $Sp^{1}-P^{1}$   $Sp^{1}-P^{1}$  35

$$P^1-Sp^1$$
  $H$   $O$   $Sp^2-P^2$   $I-22$ 

$$(L)_{t}$$

$$(L)_{t}$$

$$(L)_{t}$$

$$X^{3}-Sp^{3}-P^{3}$$

20 
$$(L)_{t}$$
  $X^{2}-Sp^{2}-P^{2}$   $Y^{3}-Sp^{3}-P^{3}$ 

$$P^1$$
 $P^2$ 
 $P^2$ 
 $P^2$ 
 $P^2$ 

$$P^{1}$$
 $P^{2}$ 
 $P^{2}$ 
 $P^{2}$ 
 $P^{3}$ 

$$P^{1} \longrightarrow P^{2}$$

$$P^{3}$$

$$I-28$$

$$P^1$$
 $P^2$ 
 $P^3$ 
 $P^2$ 
 $P^3$ 

$$P^1$$
- $Sp^1$   $Sp^2$ - $P^2$  I-31

$$P^{1}-Sp^{1} \longrightarrow Sp^{2}-P^{2}$$
 I-32

$$P^1$$
-Sp<sup>1</sup> I-34

25 
$$P^1-Sp^1$$
  $Sp^2-P^2$  I-35

$$P^{1}-Sp^{1} \longrightarrow Sp^{2}-P^{2}$$
I-36

$$P^{2}-Sp^{2} - Sp^{1}-P^{1}$$

$$Sp^{1}-P^{2}$$

$$I-38$$

$$P^{1}-Sp^{1}$$
  $Sp^{2}-P^{2}$   $I-39$ 

10

15

20

25

30

in which the individual radicals have the following meanings:

 $P^1$  and  $P^2$ 

each, independently of one another, denote a polymerisable group, preferably having one of the meanings indicated above and below for P, particularly preferably an acrylate,

 $R^{aa}$ 

15

20

25

30

35

methacrylate, fluoroacrylate, oxetane, vinyloxy or epoxy group,

Sp¹ and Sp² each, independently of one another, denote a single bond or a spacer group, preferably having one of the meanings indicated above and below for Sp, and particularly preferably -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p1</sub>-O-, -(CH<sub>2</sub>)<sub>p1</sub>-CO-O- or -(CH<sub>2</sub>)<sub>p1</sub>-O-CO-O-, in which p1 is an integer from 1 to 12, and where the linking of the last-mentioned groups to the adjacent ring takes place via the O atom, where one of the radicals P¹-Sp¹- and P²-Sp²-may also denote R<sup>aa</sup>,

denotes H, F, Cl, CN or straight-chain or branched alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may each be replaced, independently of one another, by -C(R<sup>0</sup>)=C(R<sup>00</sup>)-, -C=C-, -N(R<sup>0</sup>)-, -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl, CN or P<sup>1</sup>-Sp<sup>1</sup>-, particularly preferably straight-chain or branched, optionally mono- or polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyloxy having 1 to 12 C atoms (where the alkenyl and alkynyl radicals have at least two C atoms and the branched

R<sup>0</sup>, R<sup>00</sup> each, independently of one another and on each occurrence identically or differently, denote H or alkyl having 1 to 12 C atoms,

radicals have at least three C atoms),

 $R^{y}$  and  $R^{z}$  each, independently of one another, denote H, F, CH<sub>3</sub> or CF<sub>3</sub>,  $Z^{1}$  denotes -O-, -CO-, -C( $R^{y}R^{z}$ )- or -CF<sub>2</sub>CF<sub>2</sub>-,

WO 2013/124040 PCT/EP2013/000407

$Z^2$ and $Z^3$	each, independently of one another, denote -CO-O-, -O-CO-,
	-CH <sub>2</sub> O-, -OCH <sub>2</sub> -, -CF <sub>2</sub> O-, -OCF <sub>2</sub> - or -(CH <sub>2</sub> ) <sub>n</sub> -, where n is 2, 3
	or 4,

5

L

on each occurrence, identically or differently, denotes F, Cl, CN, or straight-chain or branched, optionally mono- or polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyloxy having 1 to 12 C atoms, preferably F,

10

L' and L" each, independently of one another, denote H, FCI or CF<sub>3</sub>,

r denotes 0, 1, 2, 3 or 4,

15

s denotes 0, 1, 2 or 3,

t denotes 0, 1 or 2, and

20 x

denotes 0 or 1.

Especially preferred polymerisable compounds of the formula I are listed in Table D.

The liquid-crystalline media in accordance with the present application preferably contain in total 0.1 to 10 %, preferably 0.2 to 4.0 %, particularly preferably 0.2 to 2.0 %, of at least two polymerisable compounds. Preferred mixtures contain 2, 3 or 4 polymerisable compounds, preferably two polymerisable compounds.

30

35

Particular preference is given to the polymerisable compounds of the formula I.

Especially preferred mixtures contain the following two polymerisable compounds

5 F O O

10 or

25 or

10

or

15

20

Preferred mixtures contain RM-1 or RM-15 or RM-17 in amounts of 0.1 -1.0 wt.%, preferably 0.2 - 0.5 wt.%, based on the total mixture.

25

Preferred mixtures contain RM-41 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

Preferred mixtures contain RM-56 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

30

Preferred mixtures contain RM-32 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

35

Preferred mixtures which contain two polymerisable compounds, contain RM-1 in amounts of 0.1 -1.0 wt.%, preferably 0.2 - 0.5 wt.% and RM-41 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

10

15

25

30

35

In another preferred embodiment, the mixtures according to the present invention which contain two polymerisable compounds, contain RM-1 in amounts of 0.1 - 10 wt.%, preferably 0.2 - 0.5 wt.% and RM-56 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

In another preferred embodiment, the mixtures according to the present invention which contain two polymerisable compounds, contain RM-1 in amounts of 0.1 - 10 wt.%, preferably 0.2 - 0.5 wt.% and RM-32 in amounts of 0.1 - 5 wt.%, preferably 0.2 - 2.0 wt.%, based on the total mixture.

Preferred mixtures are VA mixtures which contain two polymerisable compounds with different polymerisation reactivity and different miscibility in the LC mixture.

RMs with different UV absorption band show different reactivity under the certain UV exposure. By measurement of the UV-visible spectrum of each RM it is possible to determine the reactivity of each RM.

20 Preferred mixtures contain at least one RM (RM-A) which is responsible for the building of the RM polymer layer and at least one RM (RM-B) which is responsible for the pre-tilt generation via PS-VA process.

RM-A for polymer layer should be separated from LCs easily, move towards the LC-air interface, and be polymerized by UV exposure to build the polymer layer not polymer network in the bulk. RM-B should be alive during the 1<sup>st</sup> UV exposure for the next PS-VA process.

The mixture according to the present invention contains at least one compound selected from the compounds of the formula IIA, IIB and IIC. The compounds of the formulae IIA, IIB and IIC have a broad range of applications. Depending on the choice of substituents, they can serve as base materials of which liquid-crystalline media are predominantly composed; however, liquid-crystalline base materials from other classes of compound can also be added to the compounds of the formulae IIA, IIB, IIC in order, for example, to modify the dielectric and/or optical anisotropy

25

30

35

of a dielectric of this type and/or to optimise its transmittance, threshold voltage and/or its viscosity.

- In the pure state, the compounds of the formulae IIA, IIB and IIC are colourless and form liquid-crystalline mesophases in a temperature range which is favourably located for electro-optical use. They are stable chemically, thermally and to light.
- The compounds of the formulae IIA, IIB and IIC are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can also be made here of variants known per se, which are not mentioned here in greater detail.

The compounds of the formulae IIA, IIB and IIC are known, for example, from EP 0 364 538 and US 5,273,680.

If R<sup>2A</sup>, R<sup>2B</sup> and R<sup>2C</sup> in the formulae above and below denote an alkyl radical and/or an alkoxy radical, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6 or 7 C atoms and accordingly preferably denotes ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy, hexyloxy or heptyloxy, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tridecyloxy or tetradecyloxy. R<sup>2A</sup>, R<sup>2B</sup> and R<sup>2C</sup> in the formulae above and below preferably denote straight-chain alkyl having 2-6 C atoms.

Oxaalkyl preferably denotes straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

WO 2013/124040 PCT/EP2013/000407

If R<sup>2A</sup>, R<sup>2B</sup> and R<sup>2C</sup> denote an alkyl radical in which one CH<sub>2</sub> group has been replaced by -CH=CH-, this may be straight-chain or branched. It is preferably straight-chain and has 2 to 10 C atoms. Accordingly, it denotes, in particular, vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl, oct-1-, -2-, -3-, -4-, -5-, -6- or -7-enyl, non-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-enyl, dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or -9-enyl.

5

20

30

If R<sup>2A</sup>, R<sup>2B</sup> and R<sup>2C</sup> denote an alkyl or alkenyl radical which is at least monosubstituted by halogen, this radical is preferably straight-chain, and halogen is preferably F or Cl. In the case of polysubstitution, halogen is preferably F. The resultant radicals also include perfluorinated radicals. In the case of monosubstitution, the fluorine or chlorine substituent may be in any desired position, but is preferably in the ω-position.

In the compounds of the formulae IIA and IIB,  $Z^2$  may have identical or different meanings. In the compounds of the formula IIB,  $Z^2$  and  $Z^{2'}$  may have identical or different meanings.

In the compounds of the formulae IIA, IIB and IIC,  $R^{2A}$ ,  $R^{2B}$  and  $R^{2C}$  each preferably denote alkyl having 1-6 C atoms, in particular CH<sub>3</sub>,  $C_2H_5$ ,  $n-C_3H_7$ ,  $n-C_4H_9$ ,  $n-C_5H_{11}$ .

In the compounds of the formulae IIA, IIB and IIC,  $L^1$ ,  $L^2$ ,  $L^3$ ,  $L^4$ ,  $L^5$  and  $L^6$  preferably denote  $L^1 = L^2 = F$  and  $L^5 = L^6 = F$  and  $L^3 = L^4 = H$ , furthermore  $L^1 = F$  and  $L^2 = CI$  or  $L^1 = CI$  and  $L^2 = F$ ,  $L^3 = L^4 = F$  and  $L^6 = F$  and  $L^5 = H$ .  $Z^2$  and  $Z^2$  in the formulae IIA and IIB preferably each, independently of one another, denote a single bond, furthermore a  $-CH_2O$ - or  $-C_2H_4$ - bridge.

In the compounds of the formulae IIA and IIB,  $Z^2$  may have identical or different meanings. In the compounds of the formula IIB,  $Z^2$  and  $Z^2$  may have identical or different meanings.

If in the formula IIB  $Z^2 = -C_2H_{4-}$ ,  $-CH_2O_{-}$ ,  $-COO_{-}$  or  $-CH=CH_{-}$ ,  $Z^{2'}$  is preferably a single bond or, if  $Z^{2'} = -C_2H_{4-}$ ,  $-CH_2O_{-}$ ,  $-COO_{-}$  or  $-CH=CH_{-}$ ,  $Z^2$  is preferably a single bond. In the compounds of the formulae IIA and IIB,

 $(O)C_vH_{2v+1}$  preferably denotes  $OC_vH_{2v+1}$ , furthermore  $C_vH_{2v+1}$ . In the compounds of the formula IIC,  $(O)C_vH_{2v+1}$  preferably denotes  $C_vH_{2v+1}$ . In the compounds of the formula IIC,  $L^3$  and  $L^4$  preferably each denote F.

5

Preferred compounds of the formulae IIA, IIB and IIC are indicated below:

IIA-1

IIA-2

15

IIA-3

20

$$\begin{array}{c|c} CI & F \\ \hline & O \end{array}$$

IIA-4

25

IIA-5

30

IIA-6

35

IIA-7

$$\begin{array}{c|c} CI & F \\ \hline & D & alkyl^* \end{array}$$

alkyl—
$$H$$
  $H$   $O$   $O$ -alkyl\* IIA-12

\_\_

alkyl—
$$C_2H_4$$
— $O$ —alkyl\* IIA-13

alkyl—
$$C_2H_4$$
— $O$ —O-alkyl\* IIA-14

alkyl—
$$C_2H_4$$
— $O$ —alkyl\* IIA-15

alkyl 
$$-C_2H_4$$
 O  $-O$ -alkyl\* IIA-16

alkyl—
$$C_2H_4$$
— $O$ —alkyl\* IIA-17

alkyl—
$$C_2H_4$$
— $O$ —O-alkyl\* IIA-18

alkyl—
$$H$$
— $CF_2O$ — $O$ -alkyl\* IIA-19

$$F F$$

$$O = O = O$$

alkyl—
$$H$$
— $OCF_2$ — $O$ — $O$ alkyl\* IIA-22

~ ~

alkyl—
$$CH_2O$$
— $O$ — $O$ alkyl\* IIA-26

alkyl—
$$H$$
— $CH_2O$ — $O$ — $O$ )alkyl\* IIA-28

\_\_

alkenyl—
$$H$$
— $C_2H_4$ — $O$ —O-alkyl\*. IIA-43

alkyl—
$$H$$
— $CH=CH$ — $O$ — $O$ )alkyl\* IIA-44

15 
$$F$$
  $F$   $O$  alkyl\* IIA-54

30

10 F F O O-alkyl\*

15 alkyl— H O alkyl\* IIA-62

alkyl—
$$\left(\begin{array}{c} F \\ O \end{array}\right)$$
—O-alkyl\* IIB-2

$$alkyl \longrightarrow H \longrightarrow O \longrightarrow alkyl* \qquad IIB-5$$

alkyl—
$$C_2H_4$$
 O  $C_2H_4$  O  $C_2$ 

alkyl—
$$\left(\begin{array}{c} F \\ O \end{array}\right)$$
— $\left(\begin{array}{c} F \\ O \end{array}\right)$ — $\left(\begin{array}{c} O \\ O \end{array}\right)$ alkyl\* IIB-10

$$\begin{array}{c|c}
F & CI \\
\hline
O & O-alkyl*
\end{array}$$
IIB-14

$$alkyl \longrightarrow O \longrightarrow O \longrightarrow alkyl^* \qquad IIC-3$$

10

15

20

25

in which alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms and alkenyl denotes a straight-chain alkenyl radical having 2-6 C atoms.

Particularly preferred mixtures according to the invention contain one or more compounds of the formulae IIA-2, IIA-8, IIA-14, IIA-26, IIA-29, IIA-35, IIA-45, IIA-57, IIB-2, IIB-11, IIB-16 and IIC-1.

30

The proportion of compounds of the formulae IIA, IIB and/or IIC in the mixture as a whole is preferably 3-40 %, preferably 5-30 % by weight, most preferably 3-20 %, by weight.

35

Particularly preferred media according to the invention contain at least one compound of the formula IIC-1,

$$alkyl \longrightarrow O \longrightarrow O \longrightarrow alkyl^*,$$

in which alkyl and alkyl\* have the meanings indicated above, preferably in amounts of  $\geq 3$  % by weight, in particular  $\geq 5$  % by weight and particularly preferably 5-15 % by weight.

10

Preferred mixtures contain one or more compounds of the formula IIA-66 and/or IIA-67:

$$C_2H_5O \longrightarrow OC_3H_7$$

IIA-66a

20

$$C_2H_5O \longrightarrow OC_4H_5$$

IIA-66b

$$C_2H_5O - OC_5H_1$$

IIA-66c

25

$$C_2H_5O \longrightarrow OC_6H_{13}$$

IIA-66d

30

$$C_3H_7O \longrightarrow O \longrightarrow OC_3H_7$$

IIA-66e

35

$$C_3H_7O \longrightarrow O \longrightarrow OC_4H_9$$

IIA-66f

WO 2013/124040 38

PCT/EP2013/000407

$$C_3H_7O \longrightarrow O \longrightarrow OC_5H_{11}$$
 IIA-66g

5

25

35

IIA-66h

10 F F 
$$C_4H_9O - OC_4H_9$$
 IIA-66i

15 
$$C_4H_9O \longrightarrow OC_5H_{11}$$
 IIA-66j

$$C_4H_9O \longrightarrow OC_6H_{13}$$
 IIA-66k

$$C_5H_{11}O$$
 O  $OC_5H_{11}$  IIA-66I

$$C_3H_7O \longrightarrow OCH_2CH=CH_2$$
 IIA-67a

$$C_4H_9O \longrightarrow OCH_2CH=CH_2$$
 IIA-67b

$$C_5H_{11}O$$
 O O O O O IIA-67c

$$C_6H_{13}O$$
 O O O O IIA-67d

$$C_3H_7O \longrightarrow OCH_2CH=CHCH_3$$
 IIA-676

$$C_4H_9O \longrightarrow OCH_2CH=CHCH_3$$
 IIA-67

$$C_6H_{13}O \longrightarrow OCH_2CH=CHCH_3$$
 IIA-67h

$$C_3H_7O \longrightarrow OCH_2CH=CHC_2H_5$$
 IIA-67i

$$C_4H_9O \longrightarrow OCH_2CH=CHC_2H_5$$
 IIA-67j

10

$$C_5H_{11}O$$
 OCH<sub>2</sub>CH=CHC<sub>2</sub>H<sub>5</sub> IIA-67k

15

$$C_6H_{13}O$$
 OCH<sub>2</sub>CH=CHC<sub>2</sub>H<sub>5</sub> IIA-67I.

Preferred mixtures contain at least one compound of the formula IIA-66a to IIA-66n.

Preferred mixtures contain one or more tolan compound(s) of the formula IIB-T1 and IIB-T2,

25

30

35

The mixtures according to the invention additionally can contain at least one compound of the formula To-1

$$R^{1} \longrightarrow O \longrightarrow R^{2}$$
 To-1

in which  $R^1$  has the meaning for  $R^{2A}$  and  $R^2$  has the meaning of  $(O)C_vH_{2v+1}$ .  $R^1$  preferably denotes straight-chain alkyl having 1-6 C atoms.  $R^2$  preferably denotes alkoxy having 1-5 C atoms, in particular  $OC_2H_5$ ,  $OC_3H_7$ ,  $OC_4H_9$ ,  $OC_5H_{11}$ , furthermore  $OCH_3$ .

10

The compounds of the formulae IIB-T1 and IIB-T2 are preferably employed in concentrations of 3 - 25 % by weight, in particular 5 - 15 % by weight based on the total mixture.

15

Preferred embodiments of the liquid-crystalline medium according to the invention are indicated below:

20

 Liquid-crystalline medium which additionally contains two or more compounds selected from the group of the compounds of the formulae IIA, IIB and IIC.

b) Liquid-crystalline medium which additionally contains one or more compounds of the formula III,

25

$$R^{31}$$
  $A$   $R^{32}$ 

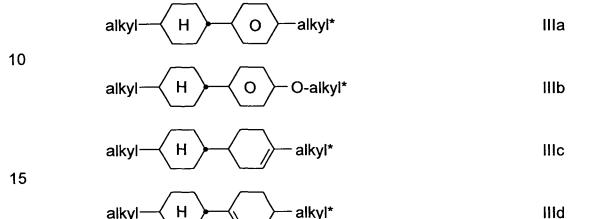
in which

30

R<sup>31</sup> and R<sup>32</sup> each, independently of one another, denote a straightchain alkyl, alkoxyalkyl or alkoxy radical having up to 12 C atoms, and

Z<sup>3</sup> denotes a single bond, 
$$-CH_2CH_2$$
-,  $-CH=CH$ -,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2O$ -,  $-OCO$ -,  $-OCO$ -,  $-C_2F_4$ -,  $-C_4H_8$ -,  $-CF=CF$ -.

Preferred compounds of the formula III are indicated below:



in which

20

alkyl and

alkyl\*

each, independently of one another, denote a straightchain alkyl radical having 1-6 C atoms.

25

The medium according to the invention preferably contains at least one compound of the formula IIIa and/or formula IIIb.

The proportion of compounds of the formula III in the mixture as a whole is preferably at least 5 % by weight.

30

c) Liquid-crystalline medium additionally containing a compound of the formula

$$H_7C_3$$
  $H$   $H$  and / or

15

35

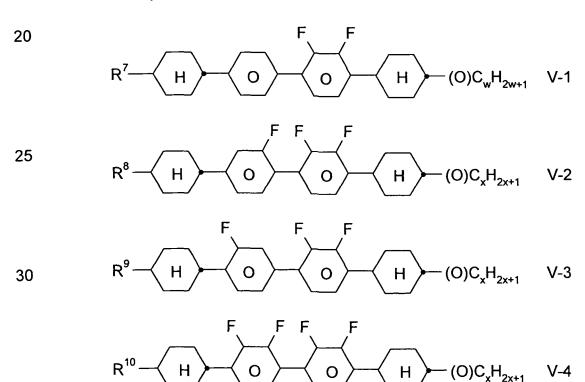
$$H_9C_4$$
 H and / or

preferably in total amounts of  $\geq 5$  % by weight, in particular  $\geq 10$  % by weight.

Preference is furthermore given to mixtures according to the invention containing the compound

$$H_7C_3$$
  $H$   $H$ 

d) Liquid-crystalline medium which additionally contains one or more tetracyclic compounds of the formulae



WO 2013/124040 44

$$\mathbb{R}^{10}$$
  $\longrightarrow$   $\mathbb{R}^{10}$   $\longrightarrow$   $\mathbb{R}^{10}$ 

PCT/EP2013/000407

5

10

15

20

in which

25

R<sup>7-10</sup> each, independently of one another, have one of the meanings indicated for R<sup>2A</sup> in Claim 2, and

w and x

each, independently of one another, denote 1 to 6.

30

35

Particular preference is given to mixtures containing at least one compound of the formula V-9.

e) Liquid-crystalline medium which additionally contains one or more compounds of the formulae Y-1 to Y-6,

$$R^{14}$$
  $H$   $H$   $O$   $CH2)z-O-CmH2m+1 Y-1$ 

$$R^{15}$$
  $H$   $O$   $OCH=CH_2$   $Y-2$ 

$$R^{16} \longrightarrow H \longrightarrow O \longrightarrow OCH_2CH = CH_2 \qquad Y-3$$

$$R^{17}$$
  $\longrightarrow$   $C_2H_4$   $\longrightarrow$   $O$   $\longrightarrow$   $\longrightarrow$   $O$   $\longrightarrow$ 

$$R^{18}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $\longrightarrow$   $O$   $\longrightarrow$   $O$ 

in which  $R^{14}$ - $R^{19}$  each, independently of one another, denote an alkyl or alkoxy radical having 1-6 C atoms; z and m each, independently of one another, denote 1-6; x denotes 0, 1, 2 or 3.

The medium according to the invention particularly preferably contains one or more compounds of the formulae Y-1 to Y-6, preferably in amounts of  $\geq$  5 % by weight.

f) Liquid-crystalline medium additionally containing one or more fluorinated terphenyls of the formulae T-1 to T-21,

$$R \longrightarrow 0 \longrightarrow 0 \longrightarrow F$$
 T-1

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-2$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-3$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-6$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-8$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-9$$

$$\begin{array}{c|c} F & F \\ \hline R & O \end{array} \begin{array}{c} F & F \\ \hline O & O \end{array} \begin{array}{c} C & O \\ \hline O & O \end{array} \begin{array}{c} C & O \\ \hline O & O \end{array} \begin{array}{c} T-10 \\ \hline O & O \end{array}$$

$$F \qquad F \qquad CF_{3}$$

$$R \qquad O \qquad O \qquad O \qquad (O)C_{m}H_{2m+1} \qquad T-11$$

10 
$$F CF_3$$
  $O O O O OOO_mH_{2m+1}$  T-12

$$R - O - O - O - O - O - O - O - T - 15$$

$$R \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} F$$

$$Q \xrightarrow{O} \xrightarrow{O} (O)C_{m}H_{2m+1} \qquad T-16$$

30 
$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-17$$

$$R = O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-18$$

$$R \longrightarrow O \longrightarrow F \qquad T-19$$

$$R - O - O - C_m H_{2m+1}$$
 T-20

10

$$R - O - O - C_n H_{2n} - C_m H_{2m+1}$$
 T-21

in which

15

R denotes a straight-chain alkyl or alkoxy radical having 1-7 C atoms, and m = 0, 1, 2, 3, 4, 5 or 6 and n denotes 0, 1, 2, 3 or 4.

20

R preferably denotes methyl, ethyl, propyl, butyl, pentyl, hexyl, methoxy, ethoxy, propoxy, butoxy, pentoxy.

The medium according to the invention preferably contains the terphenyls of the formulae T-1 to T-21 in amounts of 2-30 % by weight, in particular 5-20 % by weight.

25

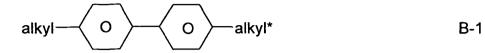
Particular preference is given to compounds of the formulae T-1, T-2, T-20 and T-21. In these compounds, R preferably denotes alkyl, furthermore alkoxy, each having 1-5 C atoms. In the compounds of the formula T-20, R preferably denotes alkyl or alkenyl, in particular alkyl. In the compound of the formula T-21, R preferably denotes alkyl.

30

The terphenyls are preferably employed in the mixtures according to the invention if the  $\Delta n$  value of the mixture is to be  $\geq 0.1$ . Preferred mixtures contain 2-20% by weight of one or more terphenyl compounds selected from the group of the compounds T-1 to T-21.

g) Liquid-crystalline medium additionally containing one or more biphenyls of the formulae B-1 to B-3,

5



•

10

in which

15

alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, and

20

alkenyl and alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms.

25

The proportion of the biphenyls of the formulae B-1 to B-3 in the mixture as a whole is preferably at least 3 % by weight, in particular  $\geq$  5 % by weight.

Of the compounds of the formulae B-1 to B-3, the compounds of the formula B-2 are particularly preferred.

30

Particularly preferred biphenyls are

B-1a

35

B-2a

in which alkyl\* denotes an alkyl radical having 1-6 C atoms. The
medium according to the invention particularly preferably contains
one or more compounds of the formulae B-1a and/or B-2c.

h) Liquid-crystalline medium containing at least one compound of the formulae Z-1 to Z-7,

15
$$R \longrightarrow O \longrightarrow O \longrightarrow (O)alkyl$$

Z-1

$$R \longrightarrow F F$$
 $O \longrightarrow O$ 
 $O \longrightarrow O$ 
 $O \longrightarrow O$ 

20

25

35

Z-2

Z-3

$$R \xrightarrow{O} OCF_{2} \xrightarrow{F} F$$

$$O(O)alkyl$$

Z-4

$$R \longrightarrow CF_2O \longrightarrow O \longrightarrow (O)alkyl$$

Z-5

$$R \longrightarrow CF_2O \longrightarrow O \longrightarrow (O)$$
alky

Z-6

10

20

30

 $R \longrightarrow CH_2O \longrightarrow O \longrightarrow OCH_2 \longrightarrow H \longrightarrow (O)$ alkyl Z-7

in which R and alkyl have the meanings indicated above.

 i) Liquid-crystalline medium containing at least one compound of the formulae O-1 to O-16,

$$R^{1}$$
  $H$   $CH_{2}O$   $H$   $R^{2}$   $O-1$ 

$$R^1$$
  $H$   $CH_2O$   $H$   $R^2$   $O-2$ 

$$R^1$$
 H COO H  $R^2$  O-3

 $R^1 \longrightarrow H \longrightarrow COO \longrightarrow O \longrightarrow H \longrightarrow R^2$  O-4

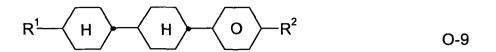
$$R^1 \longrightarrow H \longrightarrow H \longrightarrow R^2$$
 O-6

$$R^1 \longrightarrow H \longrightarrow R^2$$
 O-7

$$R^{1} \longrightarrow H \longrightarrow R^{2}$$

20

25



 $R^{1} \qquad H \qquad O \qquad R^{2} \qquad O-10$ 

10 R<sup>1</sup> H O R<sup>2</sup> O-11

 $R^1$  H H  $R^2$  O-12

 $R^1$  H O O H  $R^2$  O-13

 $R^1$  H O H  $R^2$  O-14

 $R^1 \longrightarrow H \longrightarrow O \longrightarrow R^2$  O-15

 $R^1$  H H  $R^2$  O-16

in which R<sup>1</sup> and R<sup>2</sup> have the meanings indicated for R<sup>2A</sup>. R<sup>1</sup> and R<sup>2</sup> preferably each, independently of one another, denote straight-chain alkyl.

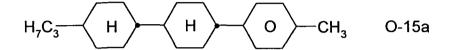
Preferred media contain one or more compounds of the formulae O-1, O-3, O-4, O-5, O-9, O-13, O-14, O-15 and/or O-16.

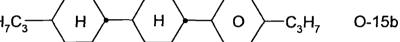
Mixtures according to the invention very particularly preferably contain the compounds of the formula O-9, O-15 and/or O-16, in particular in amounts of 5-30 %.

5

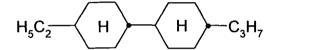
Preferred compounds of the formulae O-15 and O-16 are indicated below:

10





15



O-16a

20

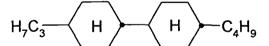
$$H_5C_2$$
  $H$   $H_5C_5H_1$ 

O-16b

Н

O-16c

25



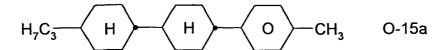
O-16d.

30

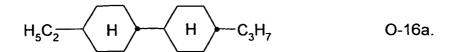
The medium according to the invention particularly preferably contains the tricyclic compounds of the formula O-15a and/or of the formula O-15b in combination with one or more bicyclic compounds of the formulae O-16a to O-16d. The total proportion of the compounds of the formulae O-15a and/or O-15b in combination with one or more compounds selected from the bicyclic compounds of the formulae O-16a to O-16d is 5-40 %, very particularly preferably 15-35 %.

Very particularly preferred mixtures contain compounds O-15a and O-16a:

5



10



Compounds O-15a and O-16a are preferably present in the mixture in a concentration of 15-35 %, particularly preferably 15-25 % and especially preferably 18-22 %, based on the mixture as a whole.

15

Very particularly preferred mixtures contain compounds O-15b and O-16a:

20

$$H_7C_3$$
  $H$   $O$   $C_3H_7$  O-15b

 $H_5C_2$  H  $H_7$ 

O-16a.

25

Compounds O-15b and O-16a are preferably present in the mixture in a concentration of 15-35 %, particularly preferably 15-25 % and especially preferably 18-22 %, based on the mixture as a whole.

30

Very particularly preferred mixtures contain the following three compounds:

$$H_7C_3$$
  $H$   $H$   $O$   $CH_3$   $O-15a$ 
 $H_7C_3$   $H$   $H$   $O$   $C_3H_7$   $O-15b$ 

$$H_5C_2$$
  $H$   $H$   $C_3H_7$  O-16a.

Compounds O-15a, O-15b and O-16a are preferably present in the mixture in a concentration of 15-35 %, particularly preferably 15-25 % and especially preferably 18-22 %, based on the mixture as a whole.

j) Preferred liquid-crystalline media according to the invention contain one or more substances which contain a tetrahydronaphthyl or naphthyl unit, such as, for example, the compounds of the formulae N-1 to N-5,

15 
$$R^{1N}$$
  $H$   $Z^1$   $O$   $O$   $R^{2^*N}$   $N-1$ 

20 
$$\xrightarrow{F} \xrightarrow{O} \xrightarrow{O} R^{2N}$$
 N-2

$$R^{1N} \longrightarrow H \longrightarrow Z^1 \longrightarrow H \longrightarrow Z^2 \longrightarrow O \longrightarrow R^{2N} N-3$$

$$R^{1N} \longrightarrow H \longrightarrow Z^1 \longrightarrow H \longrightarrow Z^2 \longrightarrow O \longrightarrow R^{2N} N-4$$

20

30

35

$$R^{1N} \longrightarrow H \longrightarrow Z^1 \longrightarrow H \longrightarrow R^{2N}$$
N-5

in which R<sup>1N</sup> and R<sup>2N</sup> each, independently of one another, have the meanings indicated for R<sup>2A</sup>, preferably denote straight-chain alkyl, straight-chain alkoxy or straight-chain alkenyl, and

Z<sup>1</sup> and Z<sup>2</sup> each, independently of one another, denote  $-C_2H_{4-}$ , -CH=CH-,  $-(CH_2)_{4-}$ ,  $-(CH_2)_3O-$ ,  $-O(CH_2)_3-$ ,  $-CH=CHCH_2CH_2-$ ,  $-CH_2CH_2CH=CH-$ ,  $-CH_2O-$ ,  $-OCH_2-$ , -COO-, -OCO-,  $-C_2F_{4-}$ , -CF=CF-, -CF=CH-, -CH=CF-,  $-CF_2O-$ ,  $-OCF_{2-}$ ,  $-CH_2-$  or a single bond.

k) Preferred mixtures contain one or more compounds selected from the group of the difluorodibenzochroman compounds of the formula BC, chromans of the formula CR, fluorinated phenanthrenes of the formulae PH-1 and PH-2, fluorinated dibenzofurans of the formula BF,

$$R^{CR1}$$
  $H$   $CR$   $CR$ 

$$R^{1}$$
  $O$   $O$   $R^{2}$  PH-1

$$R^1$$
  $O$   $O$   $O$   $R^2$   $PH-2$ 

$$R^1 = 0$$
  $C = 0$   $C$ 

in which

 $R^{B1}$ ,  $R^{B2}$ ,  $R^{CR1}$ ,  $R^{CR2}$ ,  $R^1$ ,  $R^2$  each, independently of one another, have the meaning of  $R^{2A}$ . c is 0, 1 or 2.

The mixtures according to the invention preferably contain the compounds of the formulae BC, CR, PH-1, PH-2 and/or BF in amounts of 3 to 20 % by weight, in particular in amounts of 3 to 15 % by weight. Particularly preferred compounds of the formulae BC and CR are the compounds BC-1 to BC-7 and CR-1 to CR-5,

$$\begin{array}{c|c}
F & O & F \\
\hline
O & O & O-alkyl*
\end{array}$$
BC-3

$$\begin{array}{c|c}
F & O & F \\
\hline
 & O & O & O-alkyl^*
\end{array}$$
BC-4

$$alkyl \longrightarrow H \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow CR-3$$

in which

15

20

alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, and

alkenyl and

alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms.

Very particular preference is given to mixtures containing one, two or three compounds of the formula BC-2.

25 Preferred mixtures contain one or more indane compounds of the formula In,

$$R^{11} = \begin{pmatrix} I \\ I \end{pmatrix}_{i} \qquad H \qquad \qquad \begin{pmatrix} R^{12} \\ R^{13} \end{pmatrix} \qquad \qquad ln$$

in which

each, independently of one another, denote a straightchain alkyl, alkoxy, alkoxyalkyl or alkenyl radical having 1-6 C atoms,

30

35

R<sup>12</sup> and R<sup>13</sup> additionally denote halogen, preferably F,

i denotes 0, 1 or 2.

Preferred compounds of the formula In are the compounds of the formulae In-1 to In-16 indicated below:

20 
$$R^{11}$$
  $H$   $O$  In-1  $R^{11}$   $H$   $H$   $O$   $F$   $F$   $F$   $F$  In-3

$$R^{11}$$
  $H$   $H$   $O$   $F$  In-4

$$R^{11}$$
  $H$   $O$   $F$  In-6

$$R^{11} \longrightarrow H \longrightarrow F \qquad \qquad In-8$$

$$R^{11} \longrightarrow R^{11} \longrightarrow R$$

$$R^{11}$$
  $H$   $H$   $O$   $CH_3$  In-11

$$R^{11}$$
  $H$   $H$   $O$   $F$   $E$   $In-12$ 

$$R^{11}$$
  $H$   $H$   $O$   $C_2H_5$  In-13

$$R^{11}$$
  $H$   $H$   $C_2H_5$  In-14

10

$$R^{11}$$
  $H$   $H$   $O$   $C_3H_7$ - $n$  In-15

15

$$R^{11}$$
  $H$   $H$   $F$   $F$   $F$  In-16

Particular preference is given to the compounds of the formulae In-1, 20 In-2, In-3 and In-4.

> The compounds of the formula In and the sub-formulae In-1 to In-16 are preferably employed in the mixtures according to the invention in concentrations ≥ 5 % by weight, in particular 5 - 30 % by weight and very particularly preferably 5 - 25 % by weight.

m)

Preferred mixtures additionally contain one or more compounds of the formulae L-1 to L-11,

30

25

$$R \longrightarrow F F$$
 $O \longrightarrow (O)$ -alkyl

CI

$$R \longrightarrow O \longrightarrow O$$
 (O)-alkyl

$$R^{1} = \begin{bmatrix} H \\ S \end{bmatrix}_{S} = \begin{bmatrix} C \\ C \\ C \end{bmatrix} = \begin{bmatrix} C \\ C \\ C \end{bmatrix}$$
 L-11

35 in which

R, R<sup>1</sup> and R<sup>2</sup> each, independently of one another, have the meanings indicated for R<sup>2A</sup> in Claim 1, and alkyl denotes an alkyl radical having 1-6 C atoms, s denotes 1 or 2.

5

WO 2013/124040

Particular preference is given to the compounds of the formulae L-1 and L-4, in particular L-4.

10

The compounds of the formulae L-1 to L-11 are preferably employed in concentrations of 5 - 50 % by weight, in particular 5 - 40 % by weight and very particularly preferably 10 - 40 % by weight.

Particularly preferred mixture concepts are indicated below: (the acronyms used are explained in Table A. n and m here each denote, independently of one another, 1-6).

The mixtures according to the invention preferably contain

20

15

- CPY-n-Om, in particular CPY-2-O2, CPY-3-O2 and/or CPY-5-O2, preferably in concentrations > 5 %, in particular 10-30 %, based on the mixture as a whole,

and/or

25

 CY-n-Om, preferably CY-3-O2, CY-3-O4, CY-5-O2 and/or CY-5-O4, preferably in concentrations > 5 %, in particular 15-50 %, based on the mixture as a whole,

and/or

30

 CCY-n-Om, preferably CCY-4-O2, CCY-3-O2, CCY-3-O3, CCY-3-O1 and/or CCY-5-O2, preferably in concentrations > 5%, in particular 10-30%, based on the mixture as a whole,

35

and/or

WO 2013/124040 PCT/EP2013/000407 65

- CLY-n-Om, preferably CLY-2-O4, CLY-3-O2 and/or CLY-3-O3, preferably in concentrations > 5%, in particular 10-30%, based on the mixture as a whole,

5

and/or

- CK-n-F, preferably CK-3-F, CK-4-F and/or CK-5-F, preferably in concentrations of > 5%, in particular 5-25%, based on the mixture as a whole.

10

Preference is furthermore given to mixtures according to the invention which contain the following mixture concepts: (n and m each denote, independently of one another, 1-6.)

15

- CPY-n-Om and CY-n-Om, preferably in concentrations of 10-80%, based on the mixture as a whole,

and/or

- CPY-n-Om and CK-n-F, preferably in concentrations of 10-70%, based on the mixture as a whole.

and/or

25

20

- CPY-n-Om and CLY-n-Om, preferably in concentrations of 10-80%. based on the mixture as a whole.

The invention furthermore relates to an electro-optical display having active-matrix addressing based on the ECB, VA, PS-VA, IPS or FFS effect, characterised in that it contains, as dielectric, a liquid-crystalline medium according to one or more of Claims 1 to 12.

30

The liquid-crystalline medium according to the invention preferably has a nematic phase from ≤ -20 °C to ≥ 70 °C, particularly preferably from  $\leq$  -30 °C to  $\geq$  80 °C, very particularly preferably from  $\leq$  -40 °C to  $\geq$  90 °C.

The expression "have a nematic phase" here means on the one hand that no smectic phase and no crystallisation are observed at low temperatures at the corresponding temperature and on the other hand that clearing still does not occur on heating from the nematic phase. The investigation at low temperatures is carried out in a flow viscometer at the corresponding temperature and checked by storage in test cells having a layer thickness corresponding to the electro-optical use for at least 100 hours. If the storage stability at a temperature of -20°C in a corresponding test cell is 1000 h or more, the medium is referred to as stable at this temperature. At temperatures of -30°C and -40°C, the corresponding times are 500 h and 250 h respectively. At high temperatures, the clearing point is measured by conventional methods in capillaries.

The liquid-crystal mixture preferably has a nematic phase range of at least 60 K and a flow viscosity  $v_{20}$  of at most 30 mm<sup>2</sup> · s<sup>-1</sup> at 20°C.

The values of the birefringence  $\Delta n$  in the liquid-crystal mixture are generally between 0.07 and 0.16, preferably between 0.08 and 0.12.

20

5

10

The liquid-crystal mixture according to the invention has a  $\Delta\epsilon$  of -0.5 to -8.0, in particular -2.5 to -6.0, where  $\Delta\epsilon$  denotes the dielectric anisotropy. The rotational viscosity  $\gamma_1$  at 20°C is preferably  $\leq$  165 mPa·s, in particular  $\leq$  140 mPa·s.

25

The liquid-crystal media according to the invention have relatively low values for the threshold voltage ( $V_0$ ). They are preferably in the range from 1.7 V to 3.0 V, particularly preferably  $\leq$  2.5 V and very particularly preferably  $\leq$  2.3 V.

30

For the present invention, the term "threshold voltage" relates to the capacitive threshold  $(V_0)$ , also known as the Freedericks threshold, unless explicitly indicated otherwise.

35

In addition, the liquid-crystal media according to the invention have high values for the voltage holding ratio in liquid-crystal cells.

In general, liquid-crystal media having a low addressing voltage or threshold voltage exhibit a lower voltage holding ratio than those having a higher addressing voltage or threshold voltage and vice versa.

5

10

15

For the present invention, the term "dielectrically positive compounds" denotes compounds having a  $\Delta\epsilon$  > 1.5, the term "dielectrically neutral compounds" denotes those having -1.5  $\leq$   $\Delta\epsilon$   $\leq$  1.5 and the term "dielectrically negative compounds" denotes those having  $\Delta\epsilon$  < -1.5. The dielectricanisotropy of the compounds is determined here by dissolving 10% of the compounds in a liquid-crystalline host and determining the capacitance of the resultant mixture in at least one test cell in each case having a layer thickness of 20  $\mu$ m with homeotropic and with homogeneous surface alignment at 1 kHz. The measurement voltage is typically 0.5 V to 1.0 V, but is always lower than the capacitive threshold of the respective liquid-crystal mixture investigated.

All temperature values indicated for the present invention are in °C.

20

The mixtures according to the invention are suitable for all VA-TFT applications, such as, for example, VAN, MVA, (S)-PVA, ASV, PSA (polymer sustained VA) and PS-VA (polymer stabilized VA). They are furthermore suitable for IPS (in-plane switching) and FFS (fringe field switching) applications having negative  $\Delta \epsilon$ .

25

The nematic liquid-crystal mixtures in the displays according to the invention generally contain two components A and B, which themselves consist of one or more individual compounds.

30

Component A has significantly negative dielectric anisotropy and gives the nematic phase a dielectric anisotropy of  $\leq$  -0.5. Besides the polymerisable compounds, it preferably contains the compounds of the formulae IIA, IIB and/or IIC, furthermore compounds of the formula III.

35

The proportion of component A is preferably between 45 and 100%, in particular between 60 and 100%.

For component A, one (or more) individual compound(s) which has (have) a value of  $\Delta \varepsilon \le -0.8$  is (are) preferably selected. This value must be more negative, the smaller the proportion A in the mixture as a whole.

5

Component B has pronounced nematogeneity and a flow viscosity of not greater than 30 mm<sup>2</sup>·s<sup>-1</sup>, preferably not greater than 25 mm<sup>2</sup>·s<sup>-1</sup>, at 20°C.

10

Particularly preferred individual compounds in component B are extremely low-viscosity nematic liquid crystals having a flow viscosity of not greater than 18 mm<sup>2</sup>·s<sup>-1</sup>, preferably not greater than 12 mm<sup>2</sup>·s<sup>-1</sup>, at 20°C.

15

Component B is monotropically or enantiotropically nematic, has no smectic phases and is able to prevent the occurrence of smectic phases down to very low temperatures in liquid-crystal mixtures. For example, if various materials of high nematogeneity are added to a smectic liquid-crystal mixture, the nematogeneity of these materials can be compared through the degree of suppression of smectic phases that is achieved.

20

The mixture may optionally also contain a component C, containing compounds having a dielectric anisotropy of  $\Delta \varepsilon \ge 1.5$ . These so-called positive compounds are generally present in a mixture of negative dielectric anisotropy in amounts of  $\leq 10$  %, preferably  $\leq 5$  % by weight, based on the mixture as a whole.

25

A preferred compound of the component C is the compound of the formula

30

$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $F$   $O$   $F$ 

wherein n denotes 1, 2, 3, 4, 5 or 6, preferably n is 3.

35

A multiplicity of suitable materials is known to the person skilled in the art from the literature. Particular preference is given to compounds of the formula III.

15

20

30

In addition, these liquid-crystal phases may also contain more than 18 components, preferably 18 to 25 components.

The mixture according to the invention preferably contain 4 to 15, in particular 5 to 12, and particularly preferably ≤ 10, compounds of the formulae IIA, IIB and/or IIC and optionally III.

Besides compounds of the formulae IIA, IIB and/or IIC and optionally III, other constituents may also be present, for example in an amount of up to 45 % of the mixture as a whole, but preferably up to 35 %, in particular up to 10 %.

The other constituents are preferably selected from nematic or nematogenic substances, in particular known substances, from the classes of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexylbiphenyls or cyclohexylpyrimidines, phenyl- or cyclohexyldioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acid esters.

The most important compounds which are suitable as constituents of liquid-crystal phases of this type can be characterised by the formula IV

 $R^{20}$ -L-G-E- $R^{21}$ 

in which L and E each denote a carbo- or heterocyclic ring system from the group formed by 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

G denotes -CH=CH- -N(O)=N
-CH=CQ- -CH=N(O)-C≡C- -CH<sub>2</sub>-CH<sub>2</sub>-CO-O- -CH<sub>2</sub>-O-

15

35

	-CO-S-	-CH₂-S-
	-CH=N-	-COO-Phe-COO-
	-CF <sub>2</sub> O-	-CF=CF-
5	-OCF <sub>2</sub> -	-OCH <sub>2</sub> -
	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> O-

or a C-C single bond, Q denotes halogen, preferably chlorine, or -CN, and R<sup>20</sup> and R<sup>21</sup> each denote alkyl, alkenyl, alkoxy, alkoxyalkyl or alkoxycarbonyloxy having up to 18, preferably up to 8, carbon atoms, or one of these radicals alternatively denotes CN, NC, NO<sub>2</sub>, NCS, CF<sub>3</sub>, SF<sub>5</sub>, OCF<sub>3</sub>, F, Cl or Br.

In most of these compounds, R<sup>20</sup> and R<sup>21</sup> are different from one another, one of these radicals usually being an alkyl or alkoxy group. Other variants of the proposed substituents are also common. Many such substances or also mixtures thereof are commercially available. All these substances can be prepared by methods known from the literature.

- It goes without saying for the person skilled in the art that the VA, PS-VA, PSA, IPS, PS-IPS, FFS or PS-FFS mixture according to the invention may also contain compounds in which, for example, H, N, O, Cl and F have been replaced by the corresponding isotopes.
- The mixtures according to the invention may furthermore contain conventional additives, such as, for example, stabilisers, antioxidants, UV absorbers, nanoparticles, microparticles, etc.
- The structure of the liquid-crystal displays according to the invention corresponds to the usual geometry, as described, for example, in EP-A 0 240 379.

For PS-VA applications the preferred process can be carried out for example by using a band pass filter and/or a cut-off filter, which are substantially transmissive for UV light with the respective desired wavelength(s) and are substantially blocking light with the respective undesired wavelengths. For example, when irradiation with UV light of

20

35

wavelengths  $\lambda$  of 300-400nm is desired, UV exposure can be carried out using a wide band pass filter being substantially transmissive for wavelengths 300nm <  $\lambda$  < 400nm. When irradiation with UV light of wavelength  $\lambda$  of more than 320 nm is desired, UV exposure can be carried out using a cut-off filter being substantially transmissive for wavelengths  $\lambda$  > 320 nm.

PCT/EP2013/000407

"Substantially transmissive" means that the filter transmits a substantial part, preferably at least 50 % of the intensity, of incident light of the desired wavelength(s). "Substantially blocking" means that the filter does not transmit a substantial part, preferably at least 50 % of the intensity, of incident light of the undesired wavelengths. "Desired (undesired) wavelength" e.g. in case of a band pass filter means the wavelengths inside (outside) the given range of λ, and in case of a cut-off filter means the wavelengths above (below) the given value of λ.

This preferred process enables the manufacture of displays by using longer UV wavelengths, thereby reducing or even avoiding the hazardous and damaging effects of short UV light components.

UV radiation energy is in general from 6 to 100 J, depending on the production process conditions.

The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner which is conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing.

By means of suitable additives, the liquid-crystal phases according to the invention can be modified in such a way that they can be employed in any type of, for example, ECB, VAN, IPS, GH or ASM-VA LCD display that has been disclosed to date.

10

15

20

30

The dielectrics may also contain further additives known to the person skilled in the art and described in the literature, such as, for example, UV absorbers, antioxidants, nanoparticles and free-radical scavengers. For example, 0-15 % of pleochroic dyes, stabilisers or chiral dopants may be added. Suitable stabilisers for the mixtures according to the invention are, in particular, those listed in Table B.

For example, 0-15 % of pleochroic dyes may be added, furthermore conductive salts, preferably ethyldimethyldodecylammonium 4-hexoxybenzoate, tetrabutylammonium tetraphenylboranate or complex salts of crown ethers (cf., for example, Haller et al., Mol. Cryst. Liq. Cryst. Volume 24, pages 249-258 (1973)), may be added in order to improve the conductivity or substances may be added in order to modify the dielectric anisotropy, the viscosity and/or the alignment of the nematic phases. Substances of this type are described, for example, in DE-A 22 09 127, 22 40 864, 23 21 632, 23 38 281, 24 50 088, 26 37 430 and 28 53 728.

Throughout the patent application, 1,4-cyclohexylene rings and 1,4-phenylene rings are depicted as follows:

Besides the compounds of the formulae IIA and/or IIB and/or IIC, one or more compounds of the formula I, the mixtures according to the invention preferably contain one or more of the compounds from Table A indicated below.

#### Table A

The following abbreviations are used:

35 (n, m, m', z: each, independently of one another, 1, 2, 3, 4, 5 or 6; (O) $C_mH_{2m+1}$  means above and below  $OC_mH_{2m+1}$  or  $C_mH_{2m+1}$ )

15

20

$$C_nH_{2n+1}$$
 $C_pH_{2n+1}$ 
 $C_pH_{2n+1}$ 

AIK-n-F

$$\mathsf{C_nH_{2n+1}} - \hspace{-0.5cm} \longleftarrow \hspace{-0.5cm} \mathsf{O} \hspace{-0.5cm} \longrightarrow \hspace{-0.5cm} \mathsf{O} \hspace{-0.5cm} \longrightarrow \hspace{-0.5cm} \mathsf{C_mH_{2m+1}}$$

10 BCH-nm

$$C_nH_{2n+1}$$
  $H$   $O$   $C_mH_{2m+1}$ 

BCH-nmF

$$C_nH_{2n+1}$$
  $H$   $H$   $C_mH_{2m+1}$ 

BCN-nm

<sup>25</sup> C-1V-V1

$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $OC_mH_{2m+1}$ 

30 CY-n-Om

$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $OC_mH_{2m+1}$ 

35 CY(F,CI)-n-Om

$$C_nH_{2n+1}$$
  $H$   $O$   $OC_mH_{2m+1}$   $CY(CI,F)-n-Om$ 

$$C_{n}H_{2n+1} - H + O - OC_{m}H_{2m+1}$$
10
$$CCY-n-Om$$

15
$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow OC_{m}H_{2m+1}$$

$$CCY(F,CI)-n-Om$$

$$C_{n}H_{2n+1} - H + O - OC_{m}H_{2m+1}$$

$$CCY(CI,F)-n-Om$$

CCY-V-m

$$C_{n}H_{2n} \xrightarrow{F} F$$

$$C_{n}H_{2m+1}$$

$$CCY-Vn-m$$

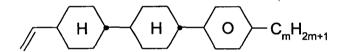
$$C_nH_{2n+1}$$
  $H$   $H$   $O$   $O-C_mH_{2m}$ - $CH=CH_2$ 

5 CCY-n-OmV

$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $O$   $\longrightarrow$   $H$   $\longrightarrow$   $C_mH_{2m+1}$ 

10 CBC-nmF

15 CBC-nm



20 CCP-V-m

25

30

35

CCP-Vn-m

$$C_nH_{2n+1} - H - O - C_mH_{2m+1}$$

CCP-nV-m

$$C_nH_{2n+1}$$
  $H$   $O$   $C_mH_{2m+1}$   $CCP-n-m$ 

$$C_{n}H_{2n+1} - H - O - O - (O)C_{m}H_{2m+1}$$

$$CPYP-n-(O)m$$

$$C_{n}H_{2n+1} - H - O - O - H - C_{m}H_{2m+1}$$

$$C_{n}H_{2n+1} - H - C_{m}H_{2m+1}$$

$$CYYC-n-m$$

$$C_{n}H_{2n+1} - H - OC_{m}H_{2m+1}$$

$$CCH-nOm$$

$$C_nH_{2n+1}$$
  $H$   $O$   $C_mH_{2m+1}$ 

30 CCP-n-m

35

$$C_nH_{2n+1}$$
  $H$   $O$   $C_mH_{2m+1}$ 

CY-n-m

$$C_{n}H_{2n+1} \xrightarrow{H} C_{m}H_{2m+1}$$

$$CCH-nm$$

$$C_{n}H_{2n+1} \xrightarrow{H} H$$

$$CC-n-V$$

$$CC-n-V1$$

$$CC-n-Vm$$

$$CC-n-Vm$$

$$CC-n-Vm$$

$$C_nH_{2n+1} H - C_mH_{2m+1}$$

30 
$$C_nH_{2n+1}$$
  $H$   $C_mH_{2m}$ -CH=CH<sub>2</sub>

CC-n-mV

CVC-n-m

$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow CH_{2}O \longrightarrow H \longrightarrow C_{m}H_{2m+1}$$

$$CCOC-n-m$$

$$C_nH_{2n+1}$$
  $H$   $COO$   $O$   $OC_mH_{2m+1}$ 

5 CP-nOmFF

$$C_nH_{2n+1}$$
  $H$   $COO$   $H$   $C_mH_{2m+1}$ 

10 CH-nm

15 CEY-V-n

$$\begin{array}{c|c} & F & F \\ \hline & O & C_n H_{2n+1} \end{array}$$

20 CVY-V-n

25

30

$$\begin{array}{c|c}
F & F \\
O & OC_nH_{2n+1}
\end{array}$$
CY-V-On

FF

$$C_nH_{2n+1}$$
  $H$   $O$   $OCH_2CH=CH_2$ 

CY-n-O1V

CY-n-OC(CH<sub>3</sub>)=CH<sub>2</sub>

$$C_nH_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow CH_2$$

$$C_nH_{\overline{2n+1}} \underbrace{H} CN \\ H_{2m+1}$$

5 CCN-nm

$$C_nH_{2n+1}$$
  $H$   $O$   $OCH=CH_2$ 

10 CY-n-OV

$$C_nH_{2n+1} - H - COO - O - H - C_mH_{2m+1}$$

CCPC-nm

15

$$C_{n}H_{2n+1} - \left(H\right) - \left(CH_{2}\right)_{z} - OC_{m}H_{2m+1}$$

20 CCY-n-zOm

25 CPY-n-(O)m

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

30 CPY-V-Om

$$C_nH_{2n+1}$$
  $H$   $CF_2O$   $O$   $C_mH_{2m+1}$ 

35 CQY-n-(O)m

15

25

30

$$C_nH_{2n+1}$$
  $H$   $OCF_2$   $O$   $O(O)C_mH_{2m+1}$ 

5 CQIY-n-(O)m

$$C_nH_{2n+1}$$
  $H$   $CF_2O$   $O$   $CO)C_mH_{2m+1}$   $CCQY-n-(O)m$ 

 $C.H_{O.J.}$  H H  $OCF_{O}$  O  $O(O)C.H_{O.J.}$ 

CCQIY-n-(O)m

$$C_{n}H_{2n+1} \longrightarrow CF_{2}O \longrightarrow COC_{m}H_{2m+1}$$

$$CPQY-n-(O)m$$

$$C_nH_{2n+1}$$
  $H$   $O$   $OCF_2$   $F$   $O$   $OCF_mH_{2m+1}$ 

CPQIY-n-(O)m

35 
$$H \rightarrow G$$
  $OC_mH_{2m+1}$   $OCY-V-Om$ 

CPGP-n-m

10

30

$$C_nH_{2n+1} - \begin{pmatrix} H \\ O \end{pmatrix} - (O)C_mH_{2m+1}$$

CY-nV-(O)m

### CENaph-n-Om

15
$$C_{n}H_{2n+1} \longrightarrow H$$

$$O \longrightarrow O$$

# COChrom-n-Om

25 COChrom-n-m

CCOChrom-n-Om

$$C_nH_{2n+1} - H - C_mH_{2m+1}$$

CCOChrom-n-m

# CONaph-n-Om

# CCONaph-n-Om

### CCNaph-n-Om

$$C_{n}H_{2n+1} \xrightarrow{\qquad \qquad H \qquad \qquad } O \xrightarrow{\qquad \qquad } F$$

### CNaph-n-Om

$$C_{n}H_{2n+1} - H - OC_{m}H_{2m+1}$$

$$C_nH_{2n+1}$$
 $H$ 
 $O$ 
 $OC_mH_{2m+1}$ 

CTNaph-n-Om

$$C_nH_{2n+1}$$
 $H$ 
 $F$ 
 $F$ 
 $F$ 
 $F$ 

CK-n-F

5

$$C_{n}H_{2n+1} - H - OC_{m}H_{2m+1}$$

$$CLY-n-Om$$

$$C_nH_{2n+1} \longrightarrow C_mH_{2m+1}$$

$$CLY-n-m$$

$$C_{n}H_{2n+1} - C_{m}H_{2m+1}$$
**LYLI-n-m**

$$C_nH_{2n+1} \longrightarrow C_0C_mH_{2m+1}$$

$$C_{n}H_{2n+1} - H - C_{m}H_{2m+1}$$

$$COYOICC-n-m$$

$$C_{n}H_{2n+1} - H - C_{m}H_{2m+1}$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$COYOIC-n-V$$

$$CCOY-V-O2V$$

$$C_nH_{2n+1} \longrightarrow H \longrightarrow COO \longrightarrow OC_mH_{2m+1}$$

D-nOmFF

$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $C_mH_{2m+1}$ 

$$C_nH_{2n+1}$$
  $\longrightarrow$   $O$   $\longrightarrow$   $OC_mH_{2m+1}$  **PCH-nOm**

$$C_nH_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow F$$

PGIGI-n-F

5

10

25

30

$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $C_mH_{2m+1}$ 

PGP-n-m

$$C_nH_{\overline{2n+1}}$$
 O  $-C_mH_{2m+1}$ 

15 **PP-n-m** 

$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $C_mH_{2m}$ 

20 PYP-n-mV

$$C_nH_{2n+1}$$
  $O$   $C_mH_{2m+1}$ 

PYP-n-m

$$C_nH_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow OC_mH_{2m+1}$$

PYP-n-Om

$$C_nH_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow C_mH_{2m+1}$$

PPYY-n-m

$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $F$   $F$ 

PPGU-n-F

$$C_nH_{2n+1} \longrightarrow C_mH_{2m+1}$$

YPY-n-m

15 
$$C_nH_{2n+1}$$
  $O$   $O$   $C_mH_{2m}$ -CH=CH<sub>2</sub>

YPY-n-mV

PY-n-(O)m

C-DFDBF-n-(O)m

DFDBC-n(O)-(O)m

15

20

35

$$C_nH_{2n+1}O \longrightarrow O \longrightarrow OC_mH_{2m+1}$$

Y-nO-Om

$$C_nH_{2n+1}O \longrightarrow O \longrightarrow OC_mH_{2m}$$

10 Y-nO-OmV

$$C_nH_{2n+1}O \longrightarrow O \longrightarrow OC_mH_{2m} \longrightarrow C_mH_{2m'+1}$$

Y-nO-OmVm'

Table B shows possible dopants which can be added to the mixtures according to the invention. If the mixtures contain a dopant, it is employed in amounts of 0.01-4% by weight, preferably 0.1-1.0% by weight.

#### Table B

C 15 CB 15

30 
$$C_6H_{13}$$
-CH-O-OOOOOOOOOOOOOOO

**CM 21** 

20

25

$$C_{6}H_{13}O - O - O - O - O - CH - C_{6}H_{13}$$

$$C_{1}H_{13}O - O - CH - C_{6}H_{13}$$

R/S-811

### **CM 44**

**CM 47** 

# CM 45

CN

$$C_5H_{11}$$
  $H$   $O$   $COO$   $O$   $H$   $C_5H_1$ 

30 R/S-1011

$$C_3H_7$$

H

O

F

CH<sub>3</sub>

O

CH-C<sub>6</sub>H<sub>13</sub>

35 **R/S-2011** 

10

$$C_3H_7$$
 $H$ 
 $H$ 
 $O$ 
 $O$ 
 $O$ 
 $O$ 

R/S-3011

$$C_5H_{11}$$
O
O
F
CH<sub>3</sub>
O
C<sub>6</sub>H<sub>13</sub>

R/S-4011

#### R/S-5011

Stabilisers which can be added, for example, to the mixtures according to the invention in amounts of up to 10% by weight, based on the total amount of the mixture, preferably 0.01 to 6% by weight, in particular 0.1 to 3% by weight, are shown below in Table C. Preferred stabilisers are, in particular, BHT derivatives, for example 2,6-di-tert-butyl-4-alkylphenols, and Tinuvin 770.

### Table C

$$(n = 1-12)$$

$$C_nH_{2n+1}$$
  $H$   $O$   $OH$ 

n = 1, 2, 3, 4, 5, 6 or 7

n = 1, 2, 3, 4, 5, 6 or 7

$$C_nH_{2n+1}O$$
 O OH

20 0 0 O O O O O O O O O O

25 HO\_O\_O

30

n = 1, 2, 3, 4, 5, 6 or 7

35

$$C_nH_{2n+1}$$
 OH OH

n = 1, 2, 3, 4, 5, 6 oder 7

Suitable reactive mesogens for use in the mixtures according to the invention, preferably in PSA and PS-VA applications are shown in Table D below:

# Table D

$$10 \qquad \begin{array}{c} \\ \\ \\ \\ \end{array}$$

RM-38

5

RM-39

10

RM-40

15

RM-41

20

RM-42

25

RM-43

30

RM-44

RM-45

35

RM-46

RM-47

RM-48

$$10 \qquad \begin{array}{c} F \\ \hline \end{array}$$

RM-75

$$C_3H_7$$
 RM-77

20

25

RM-82

RM-83

25

30

RM-84

5

15 RM-85

20

RM-86

The LC media preferably contain at least two reactive mesogens selected from the group consisting of compounds from Table D.

Unless explicitly noted otherwise, all temperature values indicated in the present application, such as, for example, the melting point T(C,N), the transition from the smectic (S) to the nematic (N) phase T(S,N) and the clearing point T(N,I), are indicated in degrees Celsius (°C).

All physical properties are and have been determined in accordance with "Merck Liquid Crystals, Physical Properties of Liquid Crystals", Status Nov. 1997, Merck KGaA, Germany, and apply for a temperature of 20°C, and  $\Delta n$  is determined at 589 nm and  $\Delta \epsilon$  is determined at 1 kHz, unless explicitly indicated otherwise in each case.

For the present invention, the term "threshold voltage" relates to the capacitive threshold ( $V_0$ ), also known as the Freedericksz threshold, unless explicitly indicated otherwise. In the examples, as is generally usual, the optical threshold for 10% relative contrast ( $V_{10}$ ) may also be indicated. The display used for measurement of the capacitive threshold voltage has two plane-parallel outer plates at a separation of 4  $\mu m$  and electrode layers with overlying alignment layers of rubbed polyimide on the insides of the outer plates, which cause a homeotropic edge alignment of the liquid-crystal molecules.

The polymerisable compounds are polymerised in the display by UV irradiation for a pre-determined time, with a voltage simultaneously being applied to the display (usually 10 V to 30 V alternating current, 1 kHz). In the examples, unless indicated otherwise, a 25 mW/cm² mercury vapour lamp was used, the intensity was measured using a standard UV meter (model Ushio UNI meter) fitted with a band-pass filter and/or cut-off filter transmitting the desired UV wavelengths.

25

35

5

10

15

20

The tilt angle is determined by a rotational crystal experiment (Autronic-Melchers TBA-105). A small value (i.e. a large deviation from a 90° angle) corresponds to a large tilt here.

The ranges of parameters given in this application are all including the limiting values, unless explicitly stated otherwise.

Throughout this application, unless explicitly stated otherwise, all concentrations are given in mass percent and relate to the respective complete mixture, all temperatures are given in degrees centigrade (Celsius) and all differences of temperatures in degrees centigrade.

The optical anisotropy ( $\Delta n$ ) is determined at a wavelength of 589.3 nm. The dielectric anisotropy ( $\Delta \epsilon$ ) is determined at a frequency of 1 kHz. The threshold voltages, as well as all other electro-optical properties are been determined with test cells prepared at Merck KGaA, Germany. The test cells for the determination of  $\Delta \epsilon$  have a cell gap of approximately 20 µm. The electrode is a circular ITO electrode with an area of 1.13 cm² and a guard ring. The orientation layers are JALS 2096-R1 from JSR (Japan Synthetic Rubber), Japan for homeotropic orientation ( $\epsilon_{II}$ ) and polyimide AL-1054 also from JSR for planar homogeneous orientation ( $\epsilon_{IL}$ ). The capacities are determined with a frequency response analyser Solatron 1260 using a sine wave with a voltage of 0.3 V<sub>ms</sub>. The electro-optical data are determined in a VA cell. These test cells used have a cell gap selected to have an optical retardation ( $d \cdot \Delta n$ ) matching the first transmission minimum according to Gooch and Tarry at an optical retardation ( $d \cdot \Delta n$ ) of 0.5 µm at 20°C, unless expressly stated otherwise.

5

10

15

20

25

30

35

The light used in the electro-optical measurements is white light. The set up used is an equipment commercially available from Autronic Melchers, Karlsruhe, Germany. The characteristic voltages are determined under perpendicular observation. The threshold  $(V_{10})$  - mid grey  $(V_{50})$  - and saturation  $(V_{90})$  voltages are been determined for 10 %, 50 % and 90 % relative contrast, respectively.

The response times are given as rise time  $(\tau_{on})$  for the time for the change of the relative contrast from 0 % to 90 %  $(t_{90}-t_0)$ , i.e. including the delay time  $(t_{10}-t_0)$ , as decay time  $(\tau_{off})$  for the time for the change of the relative contrast from 100 % back to 10 %  $(t_{100}-t_{10})$  and as the total response time  $(\tau_{total}=\tau_{on}+\tau_{off})$ , respectively.

The rotational viscosity is determined using the transient current method and the flow viscosity in a modified Ubbelohde viscometer. For liquid-crystal mixtures ZLI-2293, ZLI-4792 and MLC-6608, all products from Merck KGaA, Darmstadt, Germany, the rotational viscosity values determined at 20°C are 161 mPa·s, 133 mPa·s and 186 mPa·s respectively, and the flow viscosity values (v) are 21 mm<sup>2</sup>·s<sup>-1</sup>, 14 mm<sup>2</sup>·s<sup>-1</sup> and 27 mm<sup>2</sup>·s<sup>-1</sup> respectively.

Then the liquid crystal mixtures are stabilized by in situ polymerisation of a polymer precursor, preferably of a reactive mesogen. To this end the respective mixture is introduced into a respective test cell and the reactive compound is polymerized via UV-irradiation from a high-pressure mercury lamp. The energy of the UV exposure is 6 J. A wide-band-pass filter (300 nm  $\leq \lambda \leq$  400 nm) together with soda-lime glass are applied, which decreases intensity of the UV radiation at shorter wavelengths. During an electrical field is applied. A rectangular wave electric voltage (14 V<sub>PP</sub>) is applied to the cells.

The following abbreviations and symbols are used in the present application:

5

15	$V_0$	threshold voltage, capacitive [V] at 20°C,
	n <sub>e</sub>	extraordinary refractive index measured at 20°C and 589 nm,
	n <sub>o</sub>	ordinary refractive index measured at 20°C and 589 nm,
	Δn	optical anisotropy ( $\Delta n = n_e - n_o$ ) at 20°C and 589 nm,
	$\epsilon_{\perp}$	dielectric permittivity perpendicular to the director at 20°C and
20		1 kHz,
	3	dielectric permittivity parallel to the director at 20°C and 1 kHz,
	Δε	dielectric anisotropy at 20°C and 1 kHz,
		$(\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}),$
	ν	flow viscosity measured at 20°C [mm <sup>2</sup> ·s <sup>-1</sup> ],
25	γ1	rotational viscosity measured at 20°C [mPa·s],
	K <sub>1</sub>	elastic constant, "splay" deformation at 20°C [pN],
	K <sub>2</sub>	elastic constant, "twist" deformation at 20°C [pN],
	K <sub>3</sub>	elastic constant, "bend" deformation at 20°C [pN],
	LTS	low-temperature stability (phase stability) determined in test cells,
30	$V_0$	capacitive threshold voltage also called Freedericks threshold
		voltage,
	V <sub>10</sub>	threshold voltage, i.e. voltage for 10% relative contrast
	$V_{50}$	mid-grey voltage, i.e. voltage for 50% relative contrast and
	$V_{90}$	saturation voltage, i.e. voltage for 90% relative contrast
35		$(V_{10},V_{50}$ and $V_{90}$ all for a viewing angle perpendicular to the
		plate surface),
	cl.p., T(N,I)	clearing point [°C],

HR<sub>20</sub>

denotes voltage holding ratio at 20°C [%], and

HR<sub>100</sub>

denotes voltage holding ratio at 100°C [%].

The following examples are intended to explain the invention without restricting it. In the examples, m.p. denotes the melting point and C denotes the clearing point of a liquid-crystalline substance in degrees Celsius; boiling points are denoted by b.p. Furthermore:

10 C denotes crystalline solid state, S denotes smectic phase (the index denotes the phase type), N denotes nematic state, Ch denotes cholesteric phase, I denotes isotropic phase, T<sub>g</sub> denotes glass transition temperature. The number between two symbols indicates the conversion temperature in degrees Celsius.

15

20

The host mixture used for determination of the optical anisotropy  $\Delta n$  of the compounds of the formula I is the commercial mixture ZLI-4792 (Merck KGaA). The dielectric anisotropy  $\Delta \epsilon$  is determined using commercial mixture ZLI-2857. The physical data of the compound to be investigated are obtained from the change in the dielectric constants of the host mixture after addition of the compound to be investigated and extrapolation to 100 % of the compound employed. In general, 10% of the compound to be investigated are dissolved in the host mixture, depending on the solubility.

The display used for measurement of the threshold voltage has two planeparallel outer plates at a separation of 20 µm and electrode layers with overlying alignment layers of SE-1211 (Nissan Chemicals) on the insides of the outer plates, which effect a homeotropic alignment of the liquid crystals.

30

The following examples are intended to explain the invention without limiting it. Above and below, per cent data denote per cent by weight; all temperatures are indicated in degrees Celsius.

### Mixture examples

### Example M1

5

### To the following host mixture H1

	CY-3-O2	15.00 %	Clearing point [°C]:	75.5
	CCY-4-02	9.50 %	∆n [589 nm, 20°C]:	0.1075
10	CCY-5-O2	5.00 %	Δε [1 kHz, 20°C]:	-3.0
	CPY-2-O2	9.00 %	ε <sub>ll</sub> [1 kHz, 20°C]:	3.5
	CPY-3-O2	9.00 %	ε⊥ [1 kHz, 20°C]:	6.5
15	CCH-34	9.00 %	K <sub>3</sub> [pN, 20°C]:	13.0
	CCH-23	22.00 %	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.01
	P-2-3	7.00 %	γ₁ [mPa⋅s, 20°C]:	115
	PYP-2-4	7.50 %	V <sub>0</sub> [20°C, V]:	2.20
	PCH-301	7.00 %		

are added two reactive mesogens with different reactivity:

20

25

30

RM-1 and RM-41 show a different UV absorption behaviour as shown in figure 1.

35

The PS-VA mixture is introduced into a cell with homeotropic alignment. The polymerization of RM-1 and RM-41 is done selectively. RM-41 is polymerized first by using an UV cut filter and the RM polymer layer is formed. In the next step the PS-VA process takes place with RM-1 under

2<sup>nd</sup> UV exposure (UV light with a power of 100 mW/cm²) and the pretilt angle is generated.

5

### Example M2

To the following host mixture H1

10	CY-3-O2	15.00 %	Clearing point [°C]:	75.5
	CCY-4-02	9.50 %	Δn [589 nm, 20°C]:	0.1075
	CCY-5-O2	5.00 %	Δε [1 kHz, 20°C]:	-3.0
	CPY-2-02	9.00%	ε <sub>ll</sub> [1 kHz, 20°C]:	3.5
	CPY-3-O2	9.00%	ε⊥ [1 kHz, 20°C]:	6.5
15	CCH-34	9.00%	K <sub>3</sub> [pN, 20°C]:	13.0
	CCH-23	22.00%	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.01
	PYP-2-3	7.00%	γ₁ [mPa⋅s, 20°C]:	115
	PYP-2-4	7.50%	V <sub>0</sub> [20°C, V]:	2.20
	PCH-301	7.00%		

20

are added two different reactive mesogens with different reactivity:

30

35

# Example M3

30

35

To the following host mixture H1

5				
	CY-3-O2	15.00 %	Clearing point [°C]:	75.5
	CCY-4-02	9.50 %	∆n [589 nm, 20°C]:	0.1075
	CCY-5-O2	5.00 %	Δε [1 kHz, 20°C]:	-3.0
	CPY-2-O2	9.00%	ε <sub>II</sub> [1 kHz, 20°C]:	3.5
10	CPY-3-O2	9.00%	ε⊥ [1 kHz, 20°C]:	6.5
	CCH-34	9.00%	K <sub>3</sub> [pN, 20°C]:	13.0
	CCH-23	22.00%	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.01
	PYP-2-3	7.00%	γ₁ [mPa⋅s, 20°C]:	115
	PYP-2-4	7.50%	V <sub>0</sub> [20°C, V]:	2.20
15	PCH-301	7.00%		

are added two different reactive mesogens with different reactivity:

## Example M4

15

30

35

# To the following host mixture H1

5				
	CY-3-O2	15.00 %	Clearing point [°C]:	74.7
10	CY-5-O2	6.50 %	∆n [589 nm, 20°C]:	0.1082
	CCY-3-O2	11.00 %	Δε [1 kHz, 20°C]:	-3.0
	CPY-2-02	5.50%	$\epsilon_{\parallel}$ [1 kHz, 20°C]:	3.6
	CPY-3-02	10.50%	ε⊥ [1 kHz, 20°C]:	6.6
	CC-3-V	28.50%	K <sub>3</sub> [pN, 20°C]:	15.7
	CC-3-V1	10.00%	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.22
	PYP-2-3	12.50%	γ₁ [mPa⋅s, 20°C]:	97
	PPGU-3-F	0.50%	V <sub>0</sub> [20°C, V]:	2.42

are added two different reactive mesogens with different reactivity:

### Example M5

15

30

35

## To the following host mixture H1

5				
	CY-3-O2	15.00 %	Clearing point [°C]:	74.7
	CY-5-O2	6.50 %	∆n [589 nm, 20°C]:	0.1082
	CCY-3-O2	11.00 %	Δε [1 kHz, 20°C]:	-3.0
	CPY-2-02	5.50%	$\epsilon_{\parallel}$ [1 kHz, 20°C]:	3.6
10	CPY-3-O2	10.50%	ε⊥ [1 kHz, 20°C]:	6.6
	CC-3-V	28.50%	K <sub>3</sub> [pN, 20°C]:	15.7
	CC-3-V1	10.00%	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.22
	PYP-2-3	12.50%	γ₁ [mPa⋅s, 20°C]:	97
	PPGU-3-F	0.50%	V <sub>0</sub> [20°C, V]:	2.42

are added two different reactive mesogens with different reactivity:

30

35

### To the following host mixture H1

5				
	CY-3-O2	15.00 %	Clearing point [°C]:	74.7
	CY-5-O2	6.50 %	∆n [589 nm, 20°C]:	0.1082
	CCY-3-O2	11.00 %	Δε [1 kHz, 20°C]:	-3.0
10	CPY-2-O2	5.50%	ε <sub>∥</sub> [1 kHz, 20°C]:	3.6
	CPY-3-O2	10.50%	ε⊥ [1 kHz, 20°C]:	6.6
	CC-3-V	28.50%	K <sub>3</sub> [pN, 20°C]:	15.7
	CC-3-V1	10.00%	K <sub>3</sub> /K <sub>1</sub> [20°C]:	1.22
	PYP-2-3	12.50%	γ₁ [mPa⋅s, 20°C]:	97
	PPGU-3-F	0.50%	V <sub>0</sub> [20°C, V]:	2.42

are added two different reactive mesogens with different reactivity:

#### **Patent Claims**

Liquid-crystalline medium based on a mixture of polar compounds
having negative dielectric anisotropy, characterised in that it contains
at least two polymerisable compounds or reactive mesogens (RM)
and

at least one compound selected from the group of compounds of the formula IIA, IIB and IIC,

15
$$R^{2A} = \begin{bmatrix} & & & \\ & B & & \end{bmatrix}_{p} Z^{2} = \begin{bmatrix} & & \\ & O & & \end{bmatrix}_{(O)} C_{v} H_{2v+1}$$
IIA

in which

25

R<sup>2A</sup>, R<sup>2B</sup> and R<sup>2C</sup>

each, independently of one another, denote H, an alkyl or alkenyl radical having up to 15 C atoms which is unsubstituted, monosubstituted by CN or CF₃ or at least monosubstituted by halogen, where, in addition, one or more CH₂ groups in these radicals may be replaced by -O-, -S-, -C≡C-, -CF₂O-, -OCF₂-, -OC-O- or -O-CO- in such

a way that O atoms are not linked directly to one another,

$$-\underbrace{\circ}, -\underbrace{\circ}, -\underbrace{\bullet}, -\underbrace{\bullet},$$

10

15

Y<sup>1-6</sup> each, independently of one another, denote H or F.

L<sup>1</sup> and L<sup>2</sup> each, independently of one another, denote F, CI, CF<sub>3</sub> or CHF<sub>2</sub>,

 $L^{3-6}$  each, independently of one another, denote H, F, Cl,  $CF_3$  or  $CHF_2$ , but at least two of  $L^{3-6}$  denote F, Cl,  $CF_3$  or  $CHF_2$ 

 $Z^2$  and  $Z^2$ 

each, independently of one another, denote a single bond,  $-CH_2CH_2$ -, -CH=CH-,  $-C\equiv C$ -,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2O$ -,  $-OCH_2$ -, -COO-, -OCO-,  $-C_2F_4$ -, -CF=CF-,  $-CH=CHCH_2O$ -,

25

p denotes 1 or 2, and, in the case where  $Z^2$  = single bond, p may also denote 0,

q denotes 0 or 1,

30

35

(O) $C_vH_{2v+1}$  denotes  $OC_vH_{2v+1}$  or  $C_vH_{2v+1}$ , and

v denotes 1 to 6.

PCT/EP2013/000407

I

5

25

2. Liquid-crystalline medium according to Claim 1, characterised in that the polymerisable compounds are selected from the compounds of the formula 1,

$$R^{Ma}-A^{M1}-(Z^{M1}-A^{M2})_{m1}-R^{Mb}$$

in which the individual radicals have the following meanings:

- 10 R<sup>Ma</sup> and R<sup>Mb</sup> each, independently of one another, denote P, P-Sp-, H, halogen, SF<sub>5</sub>, NO<sub>2</sub>, an alkyl, alkenyl or alkynyl group, where at least one of the radicals R<sup>Ma</sup> and R<sup>Mb</sup> preferably denotes or contains a group P or P-Sp-,
- 15 P denotes a polymerisable group,
  - Sp denotes a spacer group or a single bond,
- A<sup>M1</sup> and A<sup>M2</sup> each, independently of one another, denote an aromatic, heteroaromatic, alicyclic or heterocyclic group, preferably having 4 to 25 ring atoms, preferably C atoms, which may also encompass or contain fused rings, and which may optionally be mono- or polysubstituted by L,
- denotes P, P-Sp-, OH, CH<sub>2</sub>OH, F, CI, Br, I, -CN, -NO<sub>2</sub>, -NCO, -NCS, -OCN, -SCN, -C(=O)N(R<sup>x</sup>)<sub>2</sub>, -C(=O)Y<sup>1</sup>, -C(=O)R<sup>x</sup>, -N(R<sup>x</sup>)<sub>2</sub>, optionally substituted silyl, optionally substituted aryl having 6 to 20 C atoms, or straight-chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having 1 to 25 C atoms, in which, in addition, one or more H atoms may be replaced by F, Cl, P or P-Sp-, preferably P, P-Sp-, H, OH, CH<sub>2</sub>OH, halogen, SF<sub>5</sub>, NO<sub>2</sub>, an alkyl, alkenyl or alkynyl group,
  - Y<sup>1</sup> denotes halogen,

I-1 to I-44

5	Z <sup>M1</sup>	denotes -O-, -S-, -CO-, -CO-O-, -OCO-, -O-CO-O-, -OCH <sub>2</sub> -, -CH <sub>2</sub> O-, -SCH <sub>2</sub> -, -CH <sub>2</sub> S-, -CF <sub>2</sub> O-, -OCF <sub>2</sub> -, -CF <sub>2</sub> S-, -SCF <sub>2</sub> -, -(CH <sub>2</sub> ) <sub>n1</sub> -, -CF <sub>2</sub> CH <sub>2</sub> -, -CH <sub>2</sub> CF <sub>2</sub> -, -(CF <sub>2</sub> ) <sub>n1</sub> -, -CH=CH-, -CF=CF-, -C≡C-, -CH=CH-, -COO-, -OCO-CH=CH-, CR <sup>0</sup> R <sup>00</sup> or a single bond,
10	R <sup>0</sup> and R <sup>00</sup>	each, independently of one another, denote H or alkyl having 1 to 12 C atoms,
10	R <sup>x</sup>	denotes P, P-Sp-, H, halogen, straight-chain, branched or cyclic alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH <sub>2</sub> groups may be
15		replaced by -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-o- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl, P or P-Sp-, an optionally substituted aryl or aryloxy group having 6 to
20		40 C atoms, or an optionally substituted heteroaryl or heteroaryloxy group having 2 to 40 C atoms,
	m1	denotes 0, 1, 2, 3 or 4, and
25	n1	denotes 1, 2, 3 or 4,
25	where at least one from the group R <sup>Ma</sup> , R <sup>Mb</sup> and the substituents present denotes a group P or P-Sp- or contains at least one group P-Sp	
30 3.	Liquid-crystalline medium according to Claim 2, characterised in that in formula I one of $R^{Ma}$ and $R^{Mb}$ or both denote(s) P or P-Sp	
4. 35	characterise	alline medium according to one or more of Claims 1 to 3 ed in that it contains at least two polymerisable selected from the group of the compounds of the formula

1-7

$$P^1-Sp^1-O$$
  $Sp^2-P^2$ 

$$P^1$$
-Sp<sup>1</sup> O Sp<sup>2</sup>-P<sup>2</sup>

$$P^{1}-Sp^{1} \longrightarrow O \longrightarrow Sp^{2}-P^{2}$$

$$Sp^{3}-P^{3}$$

$$P^{1}-Sp^{1} \longrightarrow O \longrightarrow Sp^{2}-P^{2}$$

$$P^1$$
-Sp<sup>1</sup> O N  $\stackrel{(L)_r}{\longrightarrow}$  Sp<sup>2</sup>-P<sup>2</sup>

$$P^1-Sp^1$$
  $O$   $N+C$   $O$   $Sp^2-P^2$ 

$$P^1-Sp^1$$
  $O$   $O$   $Sp^2-P^2$  I-8

$$P^1-Sp^1$$
  $O$   $Z^1$   $O$   $Sp^2-P^2$ 

$$P^1$$
-Sp<sup>1</sup>  $O$   $Z^2$   $O$   $Z^3$   $O$   $Sp^2$ - $P^2$ 

$$Sp^2-P^2$$
 $P^1-Sp^1$ 
 $O$ 
 $O$ 
 $O$ 
 $O$ 
 $O$ 
 $O$ 

10 
$$P^{1}-Sp^{1}$$
  $O$   $O$   $O$ 

15 
$$Sp^2-P^2$$
  $Sp^1-P^1$  I-18

20 
$$Sp^{1}-P^{1}$$
 I-19  $Sp^{2}-P^{2}$ 

$$P^{1}-SP^{1}$$
  $P^{2}-SP^{2}$  I-20

$$P^{2}-Sp^{2}$$
  $O$   $Sp^{1}-P^{1}$   $Sp^{1}-Sp^{2}$   $Sp^{2}-Sp^{3}$   $Sp^{2}-Sp^{3}$   $Sp^{3}-Sp^{3}$   $Sp^{3}-Sp^{3}$   $Sp^{3}-Sp^{3}-Sp^{3}$   $Sp^{3}-Sp^{3}-Sp^{3}-Sp^{3}$   $Sp^{3}-S$ 

$$P^{1}-Sp^{1}$$
  $H$   $O$   $Sp^{2}-P^{2}$   $I-22$ 

$$(L)_{t}$$

$$(L)_{t}$$

$$(L)_{t}$$

$$(L)_{t}$$

$$X^{3}-Sp^{3}-P^{3}$$

$$X^{3}-Sp^{3}-P^{3}$$

$$X^{2}-Sp^{2}-P^{2}$$
(L)<sub>t</sub>
 $X^{3}-Sp^{3}-P^{3}$ 
 $X^{3}-Sp^{3}-P^{3}$ 

$$P^1$$
 $P^2$ 
 $P^3$ 
 $P^2$ 
 $P^3$ 

$$P^{1} \xrightarrow{\text{(L)}_{r}} P^{2}$$

$$I-27$$

$$P^1$$
 $P^2$ 
 $P^3$ 
 $P^2$ 
 $P^3$ 

$$P^1$$
 $P^2$ 
 $I-29$ 

5 P<sup>5</sup>

10

20

35

$$P^1$$
 $P^2$ 
 $I-30$ 

 $P^1$ - $Sp^2$ - $P^2$ 

15 
$$P^1-Sp^1$$
  $Sp^2-P^2$  I-32

 $P^1-Sp^1$   $Sp^2-P^2$ 

 $P^1$ - $Sp^1$  I-34

25 
$$P^1-Sp^1-Sp^2-P^2$$
 I-35

 $P^{1}-Sp^{1} \longrightarrow Sp^{2}-P^{2}$ I-36

$$P^{2}-Sp^{2}$$

$$Sp^{2}-P^{2}$$

$$Sp^{1}-P^{2}$$

$$I-37$$

$$P^{2}-Sp^{2}$$
  $Sp^{1}-P^{1}$  I-38

$$P^{1}-Sp^{1}$$
  $Sp^{2}-P^{2}$   $I-39$ 

10

15

20

25

30

in which the individual radicals have the following meanings:

 $P^1$  and  $P^2$ 

each, independently of one another, denote a polymerisable group, preferably having one of the meanings indicated above and below for P, particularly

PCT/EP2013/000407

R<sup>aa</sup>

R<sup>0</sup>, R<sup>00</sup>

15

20

25

30

35

preferably an acrylate, methacrylate, fluoroacrylate, oxetane, vinyloxy or epoxy group,

Sp¹ and Sp² each, independently of one another, denote a single bond or a spacer group, preferably having one of the meanings indicated above and below for Sp, and particularly preferably -(CH<sub>2</sub>)<sub>p1</sub>-, -(CH<sub>2</sub>)<sub>p1</sub>-O-, -(CH<sub>2</sub>)<sub>p1</sub>-CO-O- or -(CH<sub>2</sub>)<sub>p1</sub>-O-CO-O-, in which p1 is an integer from 1 to 12, and where the linking of the last-mentioned groups to the adjacent ring takes place via the O atom, where one of the radicals P¹-Sp¹- and P²-Sp²- may also denote R<sup>aa</sup>,

denotes H, F, Cl, CN or straight-chain or branched alkyl having 1 to 25 C atoms, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may each be replaced, independently of one another, by -C(R<sup>0</sup>)=C(R<sup>00</sup>)-, -C=C-, -N(R<sup>0</sup>)-, -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O- in such a way that O and/or S atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by F, Cl, CN or P<sup>1</sup>-Sp<sup>1</sup>-, particularly preferably straight-chain or branched, optionally mono- or polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyl-oxy having 1 to 12 C atoms (where the alkenyl and alkynyl radicals have at least two C atoms and the branched radicals have at least three C atoms),

each, independently of one another and on each occurrence identically or differently, denote H or alkyl having 1 to 12 C atoms,

 $R^{y}$  and  $R^{z}$  each, independently of one another, denote H, F,  $CH_{3}$  or  $CF_{3}$ ,

Z<sup>1</sup> denotes -O-, -CO-, -C( $R^yR^z$ )- or -CF<sub>2</sub>CF<sub>2</sub>-,

 $Z^2$  and  $Z^3$  each, independently of one another, denote -CO-O-, -O-CO-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>- or -(CH<sub>2</sub>)<sub>n</sub>-, where n is 2, 3 or 4,

5

on each occurrence, identically or differently, denotes F, CI, CN, or straight-chain or branched, optionally monoor polyfluorinated alkyl, alkoxy, alkenyl, alkynyl, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyloxy having 1 to 12 C atoms, preferably F,

10

L' and L" each, independently of one another, denote H, FCI or  $CF_3$ ,

15

r denotes 0, 1, 2, 3 or 4,

s denotes 0, 1, 2 or 3,

t

denotes 0, 1 or 2, and

20

x denotes 0 or 1.

25

5. Liquid-crystalline medium according to one or more of Claims 1 to 4 characterised in that the polymerisable compounds of the formula I are selected from the group of compounds of the formula RM-1 to RM-86:

30

35

RM-3

WO 2013/124040 PCT/EP2013/000407

PCT/EP2013/000407 136

RM-84

**RM-85** 

**RM-86** 

5

10

15

20

25

30

35

 Liquid-crystalline medium according to one or more of Claims 1 to 5 characterised in that the compounds of the formula IIA, IIB and IIC are selected from the formulae IIA-1 to IIC-6,

$$\begin{array}{c|c} & & & & \\ \hline & & \\$$

$$\begin{array}{c|c} CI & F \\ \hline & O \\ \hline & O-alkyl^* \end{array}$$

$$alkyl - C_2H_4 - O - alkyl^*$$
IIA-13

alkyl 
$$-C_2H_4$$
  $O$   $O$ -alkyl\*

alkyl—
$$C_2H_4$$
— $O$ —alkyl\* IIA-15

alkyl—
$$C_2H_4$$
— $O$ -alkyl\* IIA-16

alkyl—
$$H$$
— $C_2H_4$ — $O$ — $O$ -alkyl\*

$$alkyl \longrightarrow H \longrightarrow OCF_2 \longrightarrow O-alkyl^* \qquad IIA-20$$

alkyl—
$$CH_2O$$
— $O$ — $O$ )alkyl\* IIA-26

alkyl—
$$H$$
— $CH_2O$ — $O$ — $O$ )alkyl\* IIA-28

alkyl—
$$H$$
— $OCH_2$ — $O$ — $O$ alkyl\* IIA-29

alkenyl—
$$C_2H_4$$
— $O$ —alkyl\* IIA-42

alkenyl—
$$C_2H_4$$
— $O$ — $O$ -alkyl\*

10 
$$F$$
  $F$   $O$  O-alkyl\* IIA-47

$$alkyl \longrightarrow H \longrightarrow O \longrightarrow O-alkyl^* \qquad IIB-2$$

30 CI F alkyl
$$\overset{\bullet}{\text{H}}$$
 O  $\overset{\bullet}{\text{O}}$  alkyl $\overset{\bullet}{\text{H}}$  IIB-3

$$\begin{array}{c|c} CI & F \\ \hline & O & O & O-alkyl^* \end{array}$$

alkyl—
$$H$$
 O O-alkyl\* IIB-6

alkyl—
$$C_2H_4$$
— $O$ — $O$ — $O$ alkyl\*

alkyl—
$$H$$
 O OCF $_2$  O (O)alkyl\* IIB-9

alkyl—
$$H$$
— $O$ — $CF_2O$ — $O$ — $O$ )alkyl\* IIB-10

$$alkyl \longrightarrow O \longrightarrow alkyl^* \qquad IIB-12$$

$$\begin{array}{c|c} CI & F \\ \hline O & O-alkyl^* \end{array}$$

$$\begin{array}{c|c}
\hline
 & F & F \\
\hline
 & O & & \\
\hline
 & O &$$

$$alkyl \longrightarrow O \longrightarrow O \longrightarrow O-alkyl^* \qquad IIC-4$$

in which alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms and alkenyl denotes a straight-chain alkenyl radical having 2-6 C atoms.

10

7. Liquid-crystalline medium according to one or more of Claims 1 to 6, characterised in that it additionally contains one or more compounds of the formula III,

15 
$$R^{31}$$
  $\longrightarrow$   $A$   $\longrightarrow$   $R^{32}$  III

in which

20

R<sup>31</sup> and R<sup>32</sup> each, independently of one another, denote a straightchain alkyl, alkoxyalkyl or alkoxy radical having up to 12 C atoms, and

25

30

Z<sup>3</sup> denotes a single bond, 
$$-CH_2CH_2$$
-,  $-CH=CH$ -,  $-CF_2O$ -,  $-OCF_2$ -,  $-CH_2O$ -,  $-OCO$ -,  $-OCO$ -,  $-C_2F_4$ -,  $-C_4H_9$ -,  $-CF=CF$ -.

8. Liquid-crystalline medium according to one or more of Claims 1 to 7, characterised in that the medium additionally contains at least one compound of the formulae L-1 to L-11,

$$F CI$$

$$R \longrightarrow O O O - (O)-alkyI$$

$$L-2$$

$$R \longrightarrow H \longrightarrow O \longrightarrow (O)$$
-alkyl

15 
$$F$$
  $CI$   $O$   $O$ -alkyl  $C$ -5

$$R \longrightarrow H \longrightarrow O \longrightarrow (O)$$
-alkyl

$$R \longrightarrow H \longrightarrow O \longrightarrow O$$
 Cl F CO)-alkyl L-9

in which

5

10

25

30

R, R<sup>1</sup> and R<sup>2</sup> each, independently of one another, have the meanings indicated for R<sup>2A</sup> in Claim 1, and alkyl denotes an alkyl radical having 1-6 C atoms, and

s denotes 1 or 2.

 Liquid-crystalline medium according to one or more of Claims 1 to 8, characterised in that the medium additionally contains one or more terphenyls of the formulae T-1 to T-21,

$$R - O - O - O - O - O - O - O - T-2$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-3$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow T-4$$

$$R \xrightarrow{F} O \xrightarrow{F} O \xrightarrow{F} F O \xrightarrow{O} C_m H_{2m+1} T-6$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow CHF_2$$

$$R \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow COC_mH_{2m+1} \longrightarrow T-13$$

$$R - O - O - O - O - O - O - O - T-17$$

$$R - O - O - C_m H_{2m+1}$$
 T-20

$$R - O - O - C_n H_{2n} - C_m H_{2m+1}$$
 T-21

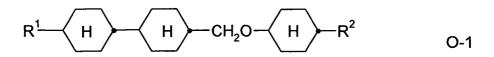
in which

R denotes a straight-chain alkyl or alkoxy radical having 1-7 C atoms, and

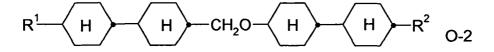
m denotes 1-6.

10. Liquid-crystalline medium according to one or more of Claims 1 to 9, characterised in that the medium additionally contains one or more compounds of the formulae O-1 to O-16,

5

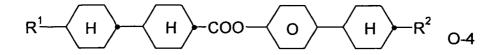


10

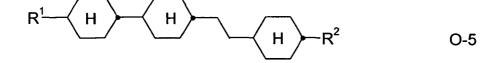


$$R^1 - H - COO - H - R^2$$

15



20



 $R^1 \longrightarrow H \longrightarrow H$ 

O-6

25

$$R^1 \longrightarrow H \longrightarrow R^2$$
 O-7

30

35

$$R^1$$
  $H$   $H$   $Q-8$ 

 $R^1 - H - H - O - R^2$ 

O-9

$$R^1$$
  $H$   $O$   $R^2$   $O-10$ 

$$R^1$$
  $H$   $O$   $R^2$   $O-11$ 

10

$$R^1$$
  $H$   $R^2$   $O-12$ 

15

$$R^1 - H O O H R^2$$
 O-13

$$R^1$$
  $H$   $O$   $H$   $R^2$  0-14

20

$$R^1 \longrightarrow C$$
  $O \longrightarrow R^2$   $O-15$ 

25

30

35

$$R^{1}$$
  $H$   $H$   $R^{2}$   $O-16$ 

in which

R<sup>1</sup> and R<sup>2</sup> each, independently of one another, have the meanings indicated for R<sup>2A</sup> in Claim 1.

11. Liquid-crystalline medium according to one or more of Claims 1 to 10, characterised in that the medium additionally contains one or more indane compounds of the formula In,

$$R^{11}$$
  $H$   $Q$   $R^{12}$   $R^{13}$   $R^{13}$ 

in which

5

10

R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> denote a straight-chain alkyl, alkoxy, alkoxyalkyl or alkenyl radical having 1-5 C atoms,

R<sup>12</sup> and R<sup>13</sup> additionally also denote halogen, ·

i denotes 0, 1 or 2.

- 25 12. Liquid-crystalline medium according to one or more of Claims 1 to 11, characterised in that the proportion of the polymerisable compounds of the formula I in the mixture as a whole is 0.1 to 5 % by weight.
- 13. Process for the preparation of a liquid-crystalline medium according to one or more of Claims 1 to 12, characterised in that at least two polymerisable compounds are mixed with at least one compound of the formula IIA, IIB or IIC with at least one further mesogen compound, and additives are optionally added.
- Use of the liquid-crystalline medium according to one or more of Claims 1 to 12 in electro-optical displays.

- 15. Use according to Claim 14, wherein the polymerisable compounds or reactive mesogens in the liquid crystalline medium are polymerised.
- 5 16. Use according to Claim 15, wherein at least two polymerisable compounds in the liquid crystalline medium are polymerised by UV radiation, by applying a voltage, by use of appropriate UV filters and/or by controlling the temperature for enhancement of the reaction.
- 17. Electro-optical display having active-matrix addressing, characterised in that it contains, as dielectric, a liquid-crystalline medium according to one or more of Claims 1 to 12.
- 18. Electro-optical display according to Claim 17 characterised in that it is
   a VA, PSA, PS-VA, PALC, FFS, PS-FFS, IPS, PS-IPS or flexible display.
  - 19. PS or PSA display according to Claim 17 or 18 characterized in that a display cell containing two substrates and two electrodes, wherein at least one substrate is transparent to light and at least one substrate has one or two electrodes provided thereon, and a layer of an LC medium containing two polymerised compounds located between the substrates, wherein the polymerised components are obtainable by polymerisation of one or more polymerisable compounds between the substrates of the display cell in the LC medium, preferably while applying a voltage to the electrodes.
- 20. PS or PSA display according to Claim 19 characterized in that a display cell contains two substrates wherein one substrate is a glass substrate
   30 and the other substrate is a flexible substrate made by RM polymerisation of at least one polymerisable compound of the formula I.

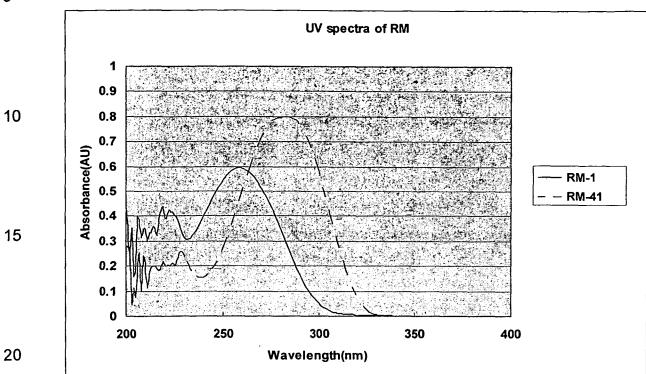
- 21. Method of producing a PS or PSA display according to claim 19 or 20 by providing a LC mixture according to one or more of claims 1 to 12 into a display cell containing two substrates and two electrodes, wherein at least one substrate is transparent to light and at least one substrate has one or two electrodes provided thereon, and polymerising at least two polymerisable compounds.
- 22. Method of according to claim 21, characterized in that the polymerisable compounds are polymerised by exposure to UV light having a wavelength from 320 nm to 400 nm.

WO 2013/124040 PCT/EP2013/000407

## **Figures**

# Figure 1

5



25

30

#### INTERNATIONAL SEARCH REPORT

International application No PCT/EP2013/000407

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K19/44 C09K19/04 C09K19/54 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  $c09\,\text{K}$ 

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Х	US 2008/236727 A1 (HSIEH CHUNG-CHING [TW] ET AL) 2 October 2008 (2008-10-02) paragraphs [0003], [0063] - [0066]	1-22		
А	WO 2011/137986 A1 (MERCK PATENT GMBH [DE]; LEE SEUNG-EUN [KR]; LEE SANG-KYU [DE]; JIN HEU) 10 November 2011 (2011-11-10) claim 1; examples 1.1-1.4; table 4a	1-22		
A	WO 2009/156118 A1 (MERCK PATENT GMBH [DE]; LEE SEUNG-EUN [KR]; KIM EUN YOUNG [KR]; SONG D) 30 December 2009 (2009-12-30) claims; page 55, lines 1-10; example M1; table 11	1-22		

X Further documents are listed in the continuation of Box C.	X See patent family annex.	
"A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier application or patent but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  "&" document member of the same patent family	
Date of the actual completion of the international search  12 April 2013	Date of mailing of the international search report $19/04/2013$	
Name and mailing address of the ISA/  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040,  Fax: (+31-70) 340-3016	Authorized officer Schoenhentz, Jérôme	

## **INTERNATIONAL SEARCH REPORT**

International application No
PCT/EP2013/000407

ategory*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
•	US 2004/011996 A1 (MERCK PATENT GMBH [DE]) 22 January 2004 (2004-01-22) mixtures P1A,P1B; example 1	1-22
A	mixtures PIA,PIB; example 1  DE 10 2009 055829 A1 (MERCK PATENT GMBH [DE]) 24 June 2010 (2010-06-24) claims; examples; paragraphs [0076], [0077]; table 1; compounds N1-3,RM1	1-22

### **INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No
PCT/EP2013/000407

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008236727 A1	02-10-2008	TW 200838989 A US 2008236727 A1 US 2011001919 A1	01-10-2008 02-10-2008 06-01-2011
WO 2011137986 A1	10-11-2011	EP 2566934 A1 TW 201211215 A US 2013056680 A1 WO 2011137986 A1	13-03-2013 16-03-2012 07-03-2013 10-11-2011
WO 2009156118 A1	30-12-2009	CN 102076821 A EP 2288672 A1 JP 2011525553 A KR 20110033847 A TW 201009053 A US 2011095229 A1 WO 2009156118 A1	25-05-2011 02-03-2011 22-09-2011 31-03-2011 01-03-2010 28-04-2011 30-12-2009
US 2004011996 A1	22-01-2004	AT 354623 T CN 1475547 A DE 10329140 A1 EP 1378557 A1 JP 4562357 B2 JP 2004131704 A KR 20040005616 A TW I330659 B US 2004011996 A1	15-03-2007 18-02-2004 15-01-2004 07-01-2004 13-10-2010 30-04-2004 16-01-2004 21-09-2010 22-01-2004
DE 102009055829 A1	24-06-2010	CN 102264866 A DE 102009055829 A1 EP 2361290 A1 JP 2012513482 A KR 20110116020 A TW 201033337 A US 2011255048 A1 WO 2010072302 A1	30-11-2011 24-06-2010 31-08-2011 14-06-2012 24-10-2011 16-09-2010 20-10-2011 01-07-2010