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# (54) Method for the orientation of liquid crystal

(57) This invention describes the orientation of a thermotropic LC volume by means of thermotropic LC molecules which are chemically firmly bound to a matrix. The orientation takes place onto the disordered LC volume by the physical-chemical properties of the chemically bound LC molecules on the matrix.

As matrix, hydrocarbon polymers or organosilanes, to the functional groups of which the thermotropic liquid crystal molecules, which also possess functional groups suitable for binding to the matrix, are chemically bound, are used. The chemically bound thermotropic LC may be a nematic, cholesterinic, discotic or smectic LC, by which nematic, cholesterinic, discotic or smectic LC volumes can be orientated.

The matrix is bound by a chemical homopolar bond to the substrate surface and may be coloured by additional coupling of reactive colouring materials.

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SPECIFICATION

**Method for the orientation of liquid crystals**

This invention relates to a method for the orientation of liquid crystals in liquid crystal displays (LCD), wherein a liquid crystal layer is enclosed hermetically sealed between two transparent electrodes, and an orientation layer for the specific, spatial orientation of the liquid crystals (LC) is chemically bound to their electrode inner surfaces.

In each LCD, the liquid crystal must possess, in the unstressed state, a specific initial orientation which is as heat-resistant as possible and of high durability. This initial orientation can, for example, be obtained in vacuum by means of oblique vapour deposition of the transparent electrodes. As vapour deposition material, SiOx, C, Au, $Al_2O_3$, TiO2 or also organic compounds may be used. Where organic compounds are applied, the binding of the orientation layer to the substrate is not assured. In particular for the orientation of liquid crystals on large areas of substrate, this method is not suitable, because the uniformity of the angle of deposition on the substrate surface is no longer maintained. For this purpose, vapour deposition plants having a large diameter would be necessary, in order to maintain a sufficient distance between vapourization source and substrate. For achieving a specific tilt angle of the liquid crystal relative to the substrate surface, a double oblique vapour deposition may indeed be necessary.

Internationally, success has been achieved by the application of organic orientation coatings onto the transparent electrodes with—of necessity—subsequent mechanical machining. Thus, for example, silane compounds of the type $X_nSiR_{4-n}$, see DE Offenlegungsschrift (published patent) 2635630, hydrocarbon polymers such as polyvinylalcohol, see DE Offenlegungsschrift 2406350 or heat-resistant polyamides/polyimides may be applied in the screen printing process, see US Patent Specification 4 278 326, by photoresist methods, see DE Offenlegungsschrift 2 931 259 or by the dip method with subsequent heating, see DE Auslegeschrift (published patent) 2 638 091. Coloured orientation coatings by the mixing-in of dyes, thus in DE Offenlegungsschrift 3 016 396, or by the coupling of reactive dyestuffs to the orientation coating, as described in DD Patent Specification 221 024, are also known.

The orientation of smectic liquid crystals by oblique vapour deposition in vacuum or by means of hydrocarbon polymers is described in DE Offenlegungsschrifts 3 443 011 and 3 502 160. A firm binding of the polymer orientation coating to the substrate surface, as set out in DD Patent Specification 218 195 and US Patent Specification 4 472 028, as a pre-requisite for a time-independent and temperature-independent qualitative LC orientation, is not taken account of in these Patent Specifications.

The theories of the DE Offenlegungsschrifts 3 513 437, 3 427 597 and 3 508 169 for the orientation of smectic liquid crystals, all relate to the transfer of the known methods for orientation of nematic liquid crystals to smectic liquid crystals.

All the processes to date for the orientation of liquid crystalline molecules are based upon characteristically deforming the surface geometry of the substrates by vapour deposition in vacuum, mechanical machining of an inorganic or organic surface film, making hydrophobic and hydropholic, in order so to impart to the liquid crystal molecule the desired spatial orientation.

Apart from orientation by the surface geometry, physical-chemical interactions between the substrate surface and the LC cannot be excluded. Their determining influence upon the orientation of the LC cannot, however, be exactly predicted, as stated by T. Uchida et al in Mol. Cryst. Liq. Cryst. 60 (1980) 37–52.

The objective of this invention is the uniformly monocrystalline orientation of thermotripic liquid crystals in liquid crystal displays of large area for a high quality and long working life.

The task underlying the invention is to create a method for the orientation of liquid crystal molecules on the substrate surface.

According to the invention this task is achieved in that, for the orientation of liquid crystals, a matrix is applied onto the substrate surface, to the functional groups of which matrix thermotropic liquid crystals are bound, partly before the application onto the substrate surface.

The matrix is bound, either directly chemically and firmly or via a bond promoter, to the substrate surface, which for example consists of glass or polymer.

Functional groups of the matrix that still remain free may be utilized for further specific reactions, for example for the binding of reactive colouring substances.

The thus obtained, orientating matrix, firmly bound to the substrate surface and also coloured, is easily soluble in low-boiling solvents having good wetting properties, so that it can be applied by dipping methods. As further methods, screen printing, centrifuging, spraying and others may be used.

As matrix, there may be used hydrocarbon polymers, which may also possess hetero-atoms in the chain, or organosilanes of the general type $x_nSiR_{4-n}$, where X denotes a hydrolysable group and R an organo-functional residue.

If a matrix is used which itself cannot be chemically bound to the substrate surface, for

example polyvinylalcohol, then a bond promoter is used. Preferably, copolymers of maleic acid or of maleic acid anhydride, copolymers of acrylic acid or of acrylic acid anhydride and copolymers of methacrylic acid or of methacrylic acid anhydride are used as hydrocarbon polymer matrix. Polymers of only one monomer may also be used.

According to the invention, liquid crystals constituting nematic, cholesterinic, discotic, smectic and/or chiral smectic c-phases can be bound to the matrix. Thus subsequently nematic, cholesterinic, discotic and smectic LC layers can be orientated. It is advantageous if the liquid crystal deposited on the matrix constitutes the same phase as the liquid crystal to be orientated, e.g. a matrix having liquid crystals with smectic phase for liquid crystals with smectic phase.

This is, however, not a general requirement. The widest variety of combinations between the individual classes and sub-classes are possible, e.g. smectic a, c, c*, g, h. The basic advantage compared with the known processes for the orientation of LC lies in the fact that the orientation of the LC layer in the LCD takes place not only by a geometric processing of the surface or modification of its surface stress; but the orientation of the LC layer takes place with liquid crystal molecules chemically bound to a matrix.

According to this invention, the orientation of the LC volume by means of thermotropic LC molecules chemically firmly bonded to the substrate surface takes place by transference of the anisotropic orientation forces.

The nematic, cholesterinic, discotic or smectic liquid crystals are chemically bound by functional groups to the reactive groups of the matrix in such a way that the chemical structure of the LC molecule is not or is only slightly modified, and therefore the liquid crystalline anisotropic character is retained.

If the LC molecules do not possess any suitable functional groups for binding to the matrix then such groups are introduced into the LC molecule without the physical-chemical properties being substantially affected.

In the fixing of the LC molecule to a hydrocarbon polymer matrix, the degree of reaction of the matrix with the LC molecule is determined by the molar ratio of the LC to the functional groups of the hydrocarbon polymer.

Where a monomeric starting matrix is used, as for example with the silane compounds, the degree of reaction is dependent upon the ratio of the monomeric or oligomeric organosilanes used, to which an LC molecule is coupled, to the unreacted organosilanes.

The degree of reaction of the matrix with the LC molecules must be sufficiently high for a sufficiently high degree of order to exist at the boundary surface between quasi liquid crystalline orientation layer and LC volume. In the ideal case, the orientation layer has the same degree of order as the LC volume.

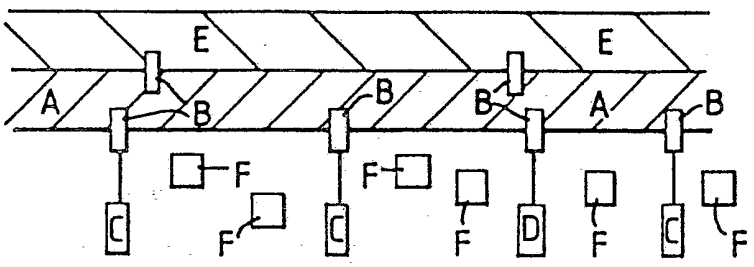
To obtain the quasi liquid crystalline orientation layer according to this invention, LC molecules are deposited on 20–80% of the reactive groups of the matrix, preferably 50–70%. The remaining reactive groups of the matrix are utilized in known manner for the stable chemical binding to the substrate surface. This stable binding of the matrix is achieved by chemical reaction of functional groups of the matrix with the partly hydrolized surface of the substrate. Other free functional groups of the matrix can be utilized for specific reactions.

Thus, reactive colouring substances may be coupled in known manner to these functional groups, in order to obtain coloured quasi liquid crystalline orientation layers. It is sufficient here if reactive colouring substances are deposited on 3–5% of the functional groups of the matrix.

The quasi liquid-crystalline orientation layers produced according to this invention possess the following general structure.

To a matrix A, a thermotropic liquid crystal C is fixed to the greater part of its functional groups B. On further still free functional groups B, reactive colouring substances D may be deposited, and as the case may be secure in particular the stable chemical bond to the substrate surface E.

This matrix A orientates a liquid crystal layer F by the anisotropic properties of the bound LC molecules C, which penetrate into the cells.

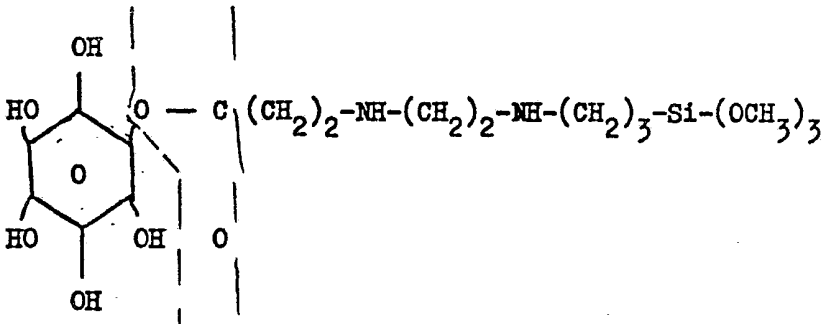



If there is used, as the orientation layer, a matrix on a basis of an organosilane of the general type $SiX_nR_{4-n}$, where

X=hydrolysable group (e.g. alkoxy or haolgen group)
R=organic residue

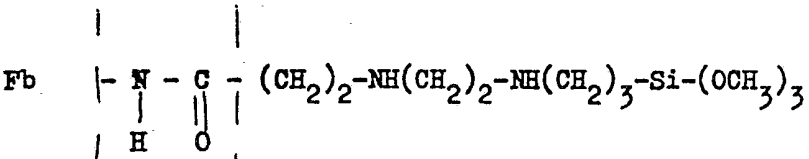
R also contains thermotropic LC molecule (C).

For example



molecule Y — discot-LC — part C — part B — part A with hydrolysable group X

Bond between matrix (A) and LC (C)

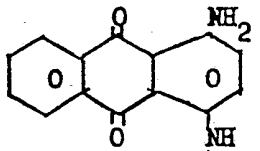


molecule Z — Fb — part D — part B — part A

Bond between matrix (A) and Fb (D)

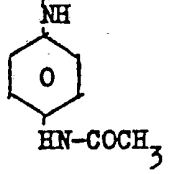
Part D = Reactive colouring material, e.g.

=



(acidic light blue)

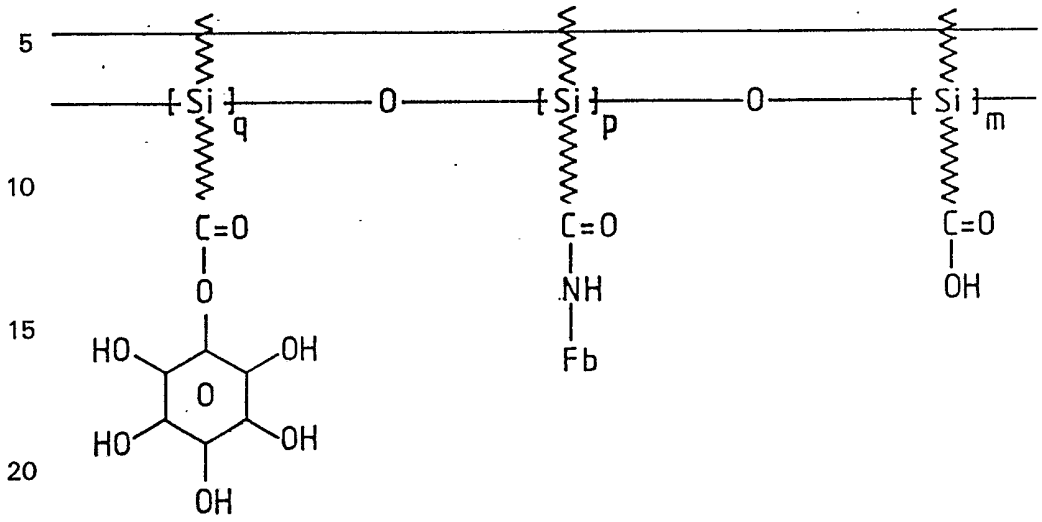
and



Molecule T — $O = C\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_3\text{-}Si\text{-}(OCH_3)_3$

unreacted organosilane ( $\gamma$ - aminosilane)

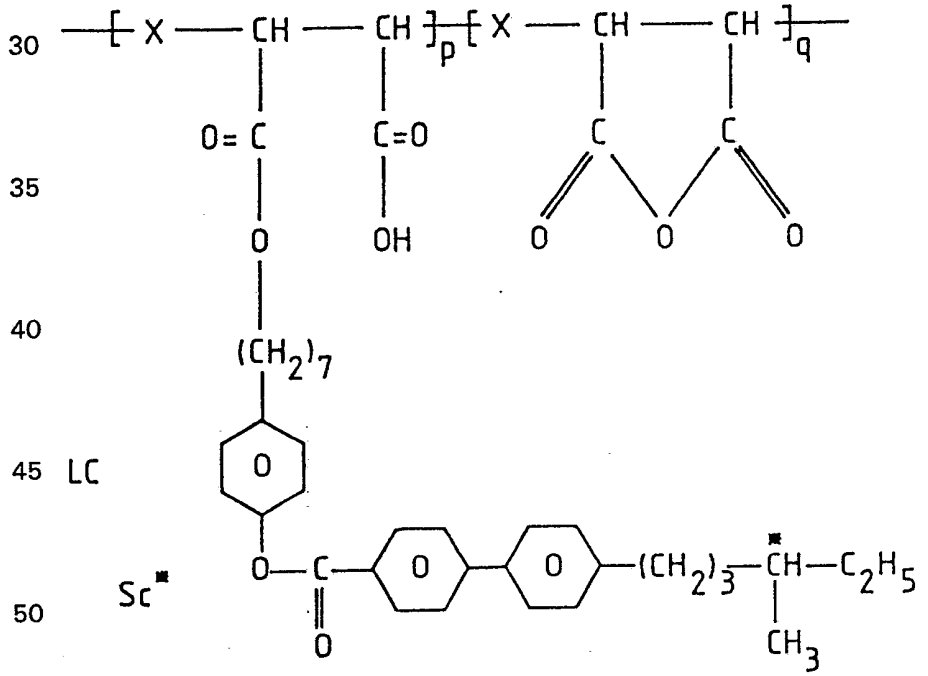
then from the molecules Y, Z and T, dissolved in a solvent, for example in the ratio 20:1:5, the polysilane of the following structure is obtained by known process



A coloured (blue), quasi discotic liquid crystalline orientation layer is obtained; for the orientation of discotic LC layers.

As LC molecule (C) hexaphenol was used.

If a matrix on a basis of a hydrocarbon polymer, which forms a chemical bond with the substrate surface, is used as orientation layer,



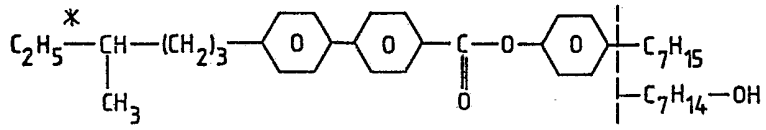
then the process is carried out, for example, at a p:q ratio of 6:4, wherein molecule component p represents a polymer component having chemically bound, smectic chiral liquid crystal and molecule component q a polymer component having free functional groups for binding to the substrate surface. A matrix of the following structure, wherein X denotes a comonomer in the MSA copolymer, is obtained, wherein

vinyl monomers are preferred (e.g. ethylene, propylene, vinyl acetate, isobutyl vinyl ether, styrene etc.).

By these means a thermostable, quasi smectic orientation layer, firmly bonded to the substrate surface, is obtained for the orientation of smectic LC layers.

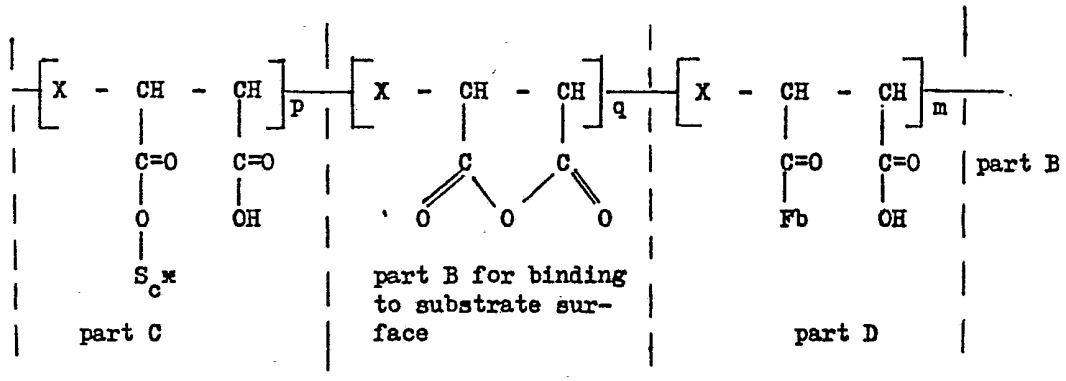
As chiral smectic LC,

4-heptylphenyl-4-(4"methylhexyl)-biphenyl-4'-carboxylate of the formula



was bound to the matrix.

If a portion of the still free functional anhydride groups (in the molecule component q) is reacted with a reactive colouring substance (Fb), then a coloured, quasi smectic liquid crystalline orientation layer of the following structure is obtained.

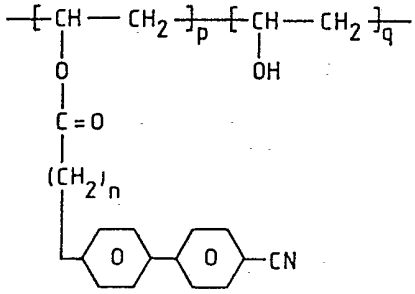



wherein the process is carried out with a ratio p:y:m of 18:10:2.

If a matrix on a basis of a hydrocarbon polymer, e.g. polyvinylalcohol, which cannot itself form a chemical bond to the substrate surface, is used as orientation layer, then a bond-promoting agent is employed to ensure a stable adhesion of the orientation layer to the substrate surface.

As nematic LC, a cyano-substituted biphenyl, which was bonded by a storage group $(CH_2)_n$, was used at the matrix.

A matrix of the following structure is obtained



wherein b:q are used in the ratio 5:1.

The orientation layers manufactured by the process according to this invention can be applied by the dip method, by spraying, by screen printing amongst others, onto the substrate surface formed by the transparent electrodes. The layer thickness of the orientation layer on the surface will depend upon the technology. It lies between 50 and 500 Å.

Example of embodiment

This invention will be explained in more detail below by examples thereof.

*Example 1*

For use as transparent electrode basis plates, glass sheets are vapour-coated on one side with an electrically conducting film of $SnO_2/In_2O_3$. The desired pattern is produced by usual methods. As protection for the electrode film, an $SiO_2$ film is then vapour-deposited, or an $SiO_x$ film is applied from a solution by dipping.

The substrates are then dipped into a 2% solution of a $\gamma$-aminoalkyl silane previously reacted with hexaphenol (10 parts) as LC and acidic pale blue (1 part) as reactive colouring substance.

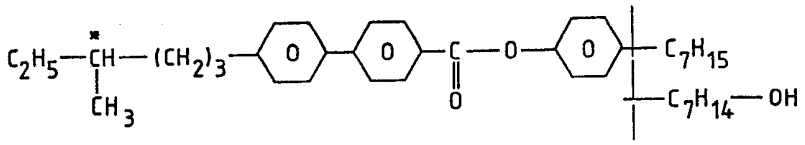
The solvent mixture consists of methanol/ethyl acetate/isobutanol (6:3:1).

Thus treated substrates are subjected to the usual cell structure.

The uniform monocrystalline orientation of the discotic LC layer enclosed in the cell becomes visible in the polarization microscope.

*Example 2*

The transparent electrode plates, as described in example 1, are dipped into an 0.5% solution of a maleic acid anhydride/vinyl acetate copolymer, the anhydride groups of which are reacted via an ester group to 60% with the chiral smectic LC molecule



in a solvent mixture (methanol:ethyl acetate:isobutanol (5:4:1)).

After the dipping process, the substrates dry for twenty minutes at 50°C. The thus treated substrates are assembled into cells and the intermediate space with a cell gap of less than 2 $\mu$m is filled with a chiral smectic LC. The smectic LC layer becomes uniformly orientated.

CLAIMS

1. Method for the orientation of liquid crystals on substrate surfaces, characterized in that a matrix is applied onto the substrate surface as orientation layer, to the functional groups of which matrix thermotropic liquid crystals are bound, partly before the application onto the substrate surface.

2. Method according to Claim 1, characterized in that a hydrocarbon polymer, which can also possess hetero-atoms in the polymer chain, is used as matrix.

3. Method according to Claim 1, characterized in that an organosilane of the general type $x_nSiR_{4-n}$, with

H=hydrolysable group (halogen, alcoxy group etc.)
R=organofunctional residue

is used as matrix.

4. Method according to Claim 1, characterized in that the matrix is bound to the substrate surface by a firm chemical homopolar bond—or via a bond-promoting agent.

5. Method according to Claim 2, characterized in that a copolymer of maleic acid or of maleic acid anhydride is used as hydrocarbon polymer matrix.

6. Method according to Claim 2, characterized in that a copolymer of acrylic acid or of acrylic acid anhydride is used as hydrocarbon polymer matrix.

7. Method according to Claim 2, characterized in that a copolymer of methacrylic acid or of methacrylic acid anhydride is used as hydrocarbon polymer matrix.

8. Method according to Claim 2, characterized in that a polymer of only one monomer is used as hydrocarbon polymer matrix.

9. Method according to Claim 2, characterized in that polyvinylalcohol is used as matrix.

10. Method according to Claim 1, characterized in that liquid crystals constituting nematic, discotic, cholesterinic, smectic and/or chiral smectic c-phases are bound to the matrix.

11. Method according to Claim 1, characterized in that reactive colouring substances are chemically bound additionally to 1%–30%, preferably 2%–4%, of the functional groups of the matrix.

12. Method for the orientation of liquid crystals on substrate surfaces as claimed in Claim 1 substantially as described in any one of the examples disclosed herein.

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