Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Prevention of Smectic-A LC Mixtures Electrolytic Degradation

M. V. Mitrokhin [a], L. Johnsen [a], R. Fagerberg [a], C. Kristiansen [b], F. J. Farrand [b], K. H. Holm [b], R. Palm [b], K. Netland [c] & V. L. Aristov [d]

[a] Department of Photonics, SINTEF Electronics and Cybernetics, Trondheim, Norway

[b] Department of Organic Synthesis, SINTEF Applied Chemistry, Oslo, Norway

[c] PolyDisplay ASA, Sandefjord, Norway

[d] R&D Institute "Volga", Saratov, Russia

Version of record first published: 18 Oct 2010

To cite this article: M. V. Mitrokhin, L. Johnsen, R. Fagerberg, C. Kristiansen, F. J. Farrand, K. H. Holm, R. Palm, K. Netland & V. L. Aristov (2004): Prevention of Smectic-A LC Mixtures Electrolytic Degradation, Molecular Crystals and Liquid Crystals, 411:1, 255-263

To link to this article: http://dx.doi.org/10.1080/15421400490435242

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 255/[1297]–263/[1305], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490435242

PREVENTION OF SMECTIC-A LC MIXTURES ELECTROLYTIC DEGRADATION

M. V. Mitrokhin, L. Johnsen, and R. Fagerberg
SINTEF Electronics and Cybernetics, Department of Photonics, Trondheim, Norway

C. Kristiansen, F. J. Farrand, K. H. Holm, and R. Palm
SINTEF Applied Chemistry, Department of Organic Synthesis, Oslo, Norway

K. Netland
PolyDisplay ASA, Sandefjord, Norway

V. L. Aristov
R&D Institute "Volga", Saratov, Russia

The problem with the stability of a smectic A liquid crystal (LC) mixture in a display based on the electrically reversible memory effect is discussed. The degradation of the LC mixture is initiated by the electric field and consists of electrochemical decomposition of one of the mixture components accompanied by gas bubbles arising on the electrodes of the display. The electrochemical degradation was successfully prevented by the introduction of different passivation layers and by the modification of problematic LC mixture component. The obtained results are used for improving the lifetime of a display based on the electrically reversible memory effect.

Keywords: electrolytic dissociation; electrooptics; passivation layer; smectic A

INTRODUCTION

One of the most prevailing applications of liquid crystal (LC) substances is the application as an optical material for electrooptical devices. This is

This work was supported by PolyDisplay ASA (Norway) and by the Norwegian Research Council.

Address correspondence to M. V. Mitrokhin, SINTEF Electronics and Cybernetics, Department of Photonics, Trondheim, Norway.

possible due to the ability of the LC material to change its optical state under the influence of external factors – electric and magnetic fields, thermal and mechanical influence, etc. During operation the electrooptical devices are exposed also to different pernicious factors such as mechanical blows, tensions, vibrations; alteration of the pressure, temperature, and the air moisture; influences of various radiation and so on. The task of the liquid crystal display (LCD) reliability is commonly solved by the design of the display and the properties of the display materials. The modern LCD's have a flat panel design involving glass plates, transparent metal-oxide electrodes, polymer layers for the alignment of LC, thin LC layer and the glue rim hermetically sealing the display cell (1). To provide the device with a long lifetime the LC material as well as any material of the display should possess stable physicochemical properties under the influence of these factors and interaction between each other. At the expense of the material selection the nematic LCD operating time is more than 50 000 hours.

In this paper we discuss the problem with the stability of smectic A LC mixture in the displays based on the electrically reversible memory effect. This problem arises because of influence of electric fields on LC. The influence of the field is both the basis of the display operation and the initiator of LC electrolytic degradation processes leading to the display failure. Here we discuss the mechanism and methods to prevent electrolytic degradation of smectic A LC mixtures in devices based on electrically reversible memory effect.

The effect of electrically reversible memory [2,3] realizes transitions between two structures of smectic A liquid crystal – focal conic (FC) and homeotropic (HP). The influence of a low frequency electric field initiates an electrohydrodynamic (EHD) instability of smectic A LC, causing strong scattering of the transmitted light. After removal of the electric field the electrohydrodynamic vortexes relax to the focal conic structure, accompanied by a small decrease in scattering. The application of a high frequency field to focal conic structure leads to a dielectric reorientation of LC molecules and to the formation of a transparent homeotropic structure. The schematic view of the electrically reversible memory effect is shown in Figure 1. Both transitions have a threshold character. Visco-elastic properties of smectic A LC makes these structures and intermediate ones stable for a long time. The advantages of devices based on this electrooptical effect are the own memory, wide view angles, non-polarizes design, and the ability to form a gray scale.

MATERIALS AND TECHNIQUE

In our experiment a multicomponent mixture on the basis of derivatives of alkylcyanobiphenyls, alkyloxycyanobiphenyls and cyanobiphenyl esters of

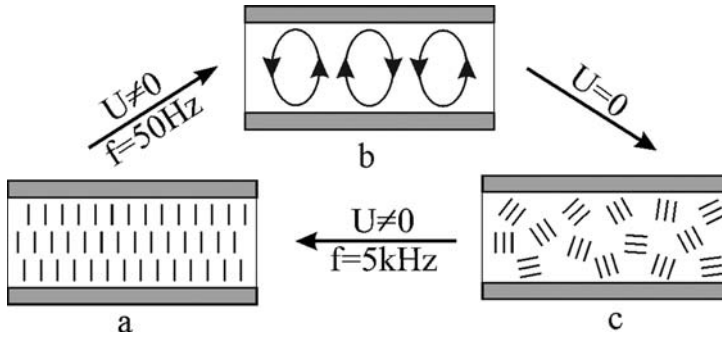
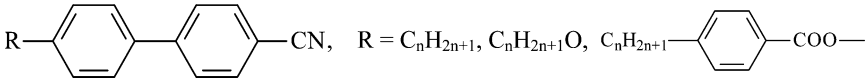


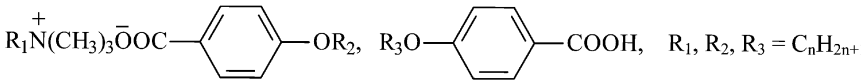
FIGURE 1 The schematic view of electrically reversible memory effect: (a) is the homeotropic transmitting structure of LC, (b) is the electrohydrodynamic instability, (c) is the focal conic scattering structure.

alkylbenzoic acid with the following general structure were used as a LC matrix:



This mixture had the smectic A temperature range from -20 to 73°C.

It is necessary for initiation of the electrohydrodynamic instability to maintain the certain optimal value of LC material electroconductivity. Since the LC has not a noticeable value of electroconductivity, ionic dopants should be used for this purpose. It was found that the most effective dopants investigated by us were the tetraalkylammonium salts of alkyloxybenzoic acid. It was reported previously that an admixture of alkyloxybenzoic acid increases the electroconductivity anisotropy and thus decreases the field threshold (4). The structures of both the substances are as the following:



The test LC cells had a common flat capillary design. The LC layer was sandwiched between two glass substrates with a cell gap of 15 μm maintained by polymeric spherical spacers. Due to the mechanism of the utilized electrooptical effect the polarizers were absent. The transparent indium-tin-oxide electrodes were formed in the matrix order on the glass substrates. Electrooptical characteristics were obtained by measurements of the monochromatic light transmission using a self-made set-up with automatic data acquiring. A red semiconducting laser ($\lambda = 650$ nm) was used

as a light source, the light intensity was detected by silicon pin diode detector, the detector signal was amplified by trans-impedance amplifier. The dynamics of LC texture transformations was studied by Leitz Orthoplan polarizing microscope.

RESULTS AND DISCUSSION

It has been found experimentally that after continuous, long term operation of the display based on such smectic A mixtures gas bubbles arose in some areas. This led to decreased optical density of the focal-conic LC structure, optical spots arising in the LCD informational area, inability to drive these areas and finally to device failure. This process proceeded as a probabilistic one with a random distribution of the reaction areas. When the reaction began, the gas volume increased rapidly. The gas volume increased every low frequency cycle and was not influenced by the high frequency cycles. It was possible to stop the process by switching off the driving field for a while. The gas formation always occurred on the matrix electrodes and then it accumulated between the pixels, where the cell gap is larger, until its volume exceeded the space between the pixels. The gas then penetrated inside the pixel area. Figure 2 demonstrates the common case of this

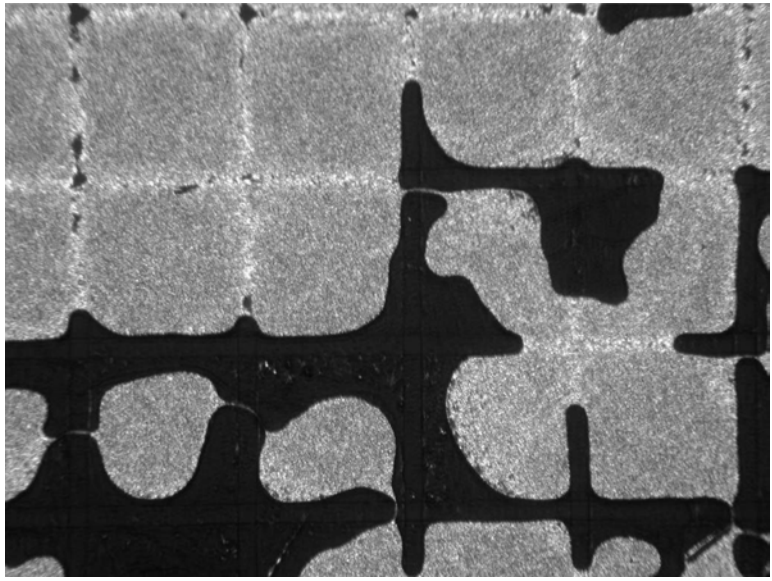


FIGURE 2 Microscope picture of gas inclusions in the focal conic structure of a smectic A LC. Polarizers are crossed.

problem. Here the squares are pixel areas; the black areas with fine edges are gas bubbles.

The peculiarity of EHD instability is that during this process the LC circulates inside the same pixel. This fact in combination with the LC visco-elastic properties restricts the LC mixture component supply to the reaction area and explains the spatial and temporal process localisation.

Such behaviour is common for a radical reaction and the process break can be explained by the radicals' recombination. The value and quantity of the gas bubbles increased with increasing of current density. It is evidence of Faraday's mechanism of LC electrolysis. In such cases the LC medium is the nonaqueous solution of weak electrolytes.

The limiting phase of this electrochemical reaction is the mass transfer to the electrodes, as the reaction proceeds substantially faster when the low frequency field is applied during the EHD instability period. This causes the intensive movement of the LC and the diffusion coefficient is much larger than for static state.

As we have reported earlier (5), this phenomenon can be explained by electrolytic decomposition of the ionic dopant and the alkoxybenzoic acid on the electrodes of substrates in accordance with the mechanism of Kolbe electrosynthesis:

$$\mathrm{RCOO^-} \xrightarrow{-e} \mathrm{RCOO^\bullet}$$

$$\mathrm{RCOO^\bullet} \longrightarrow \mathrm{R^\bullet} + \mathrm{CO_2}.$$

It was found that this process tends to occur near the glue rim. UV curable adhesive was used for the cell glueing and as it can contain free radicals this glue was substituted with an epoxy one. The lifetime of device was improved, but electrolytic degradation was not eliminated.

In order to eliminate this process two methods were successfully applied. The first method consists of an application of passivating layers to isolate the electrode surface from the LC. For this purpose a layer of silica and a polyimide layer were used. Both layers were deposited by a screen-printing technique, the thickness of the silica layers was around 0.25 μm and the thickness of polyimide was around 0.1 μm. The introduction of passivating layers has eliminated the problem of gas production; this was determined by the absence of gas bubbles after 500 thousand switching cycles, but the change of the LC-substrate boundary conditions has influenced the electrooptical parameters of the cell and the permolecular structure of the LC, namely the quality of the homeotropic structure.

The consequence of the silica layer introduction was a strong homeotropic alignment of smectic A LC (Fig. 3b), whereas it was not possible to obtain such a perfect homeotropic structure on the surface of ITO (Fig. 3a). We suppose that this alignment was produced by the long alkyl chains of

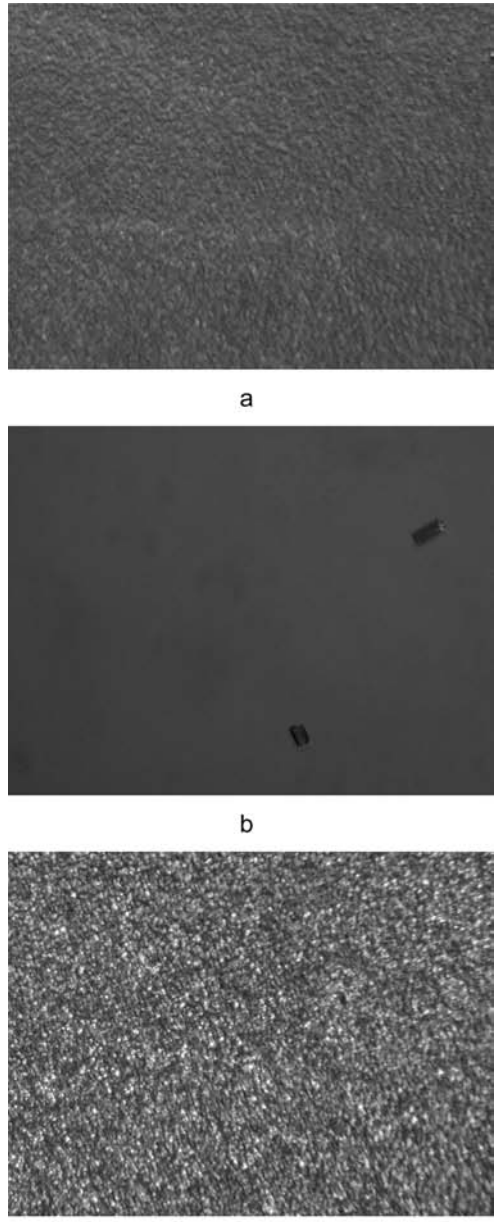


FIGURE 3 Microscope pictures of smectic A LC in homeotropic state on ITO (a), silica (b) and polyimide (c) coatings. Polarizers are crossed.

the ionic dopant, which was adsorbed on the surface of the silica. This homeotropic alignment complicates the creation of grey scale as the intermediate weakly scattering structures lose their stability in the absence of the electric field and relax to the HP one.

The very good homeotropic alignment makes the initiation of EHD instability difficult. This has resulted in an increase in the electrohydrodynamic instability threshold voltage as it can be seen from Figure 4, where the transmittance – voltage curves for both transitions are shown. According to the table, the EHD instability threshold voltage has increased form 81 V to 100 V (rms values, U_{rms}), whereas the focal conic – homeotropic threshold decreased by 15 V due to the alignment layer obtained. The increase of EHD instability threshold voltage raises the EHD response time; the homeoptropically aligning surface makes both the transmittance–voltage curve of FC-HP transition steeper and the transition response faster.

The coating of ITO with the polyimide layer influences the homeotropic structure as it became less transparent because of the planar alignment of LC molecules at the LC/polyimide phase boundary (Fig. 3c). The layer of polyimide levels out the defects and steps of electrodes that increase the threshold voltage of EHD instability with 11 V, as the instability initiates on surface defects and the smectic A layer discontinuity.

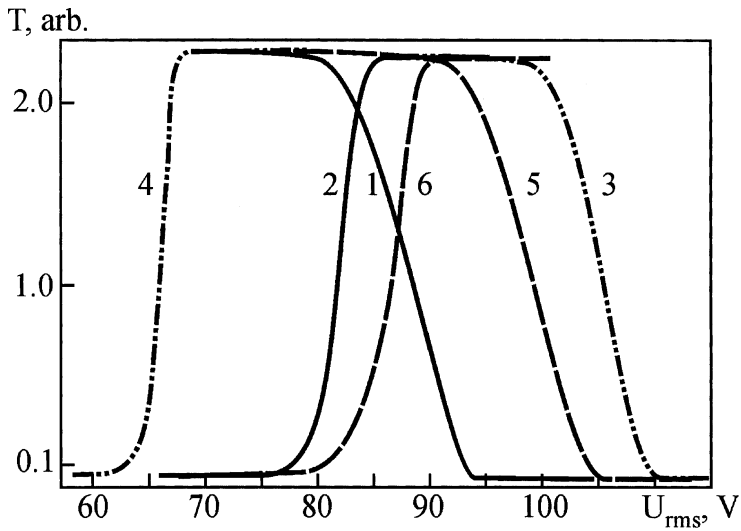


FIGURE 4 Transmittance – voltage curves for electrohydrodynamic instability (1,3,5)and for focal conic – homeotropic transition (2,4,6) of smectic A LC contacting with ITO (1,2), silica (3,4) and polyimide (5,6) coatings. Cell gap is 15 μm.

TABLE Dynamic and Threshold Characteristics of Smectic A LC Mixture on the Different Coatings. The U_{rms} for Measurements of Response Times was 190 V

Coating	EDH response time, ms	FC-HP response time, ms	EHD threshold voltage, V	FC-HP threshold voltage, V
ITO	58	9	81	78
Silica	230	5	100	63
Polyimide	98	10	92	81
ITO*	80	13	65	64
ITO*, modified dopant	120	7	71	52

*Response time measurements were performed in 11 μm cell at $U_{rms} = 130$ V.

In a further attempt to eliminate the electrolytic decomposition the ionic dopant was modified by substitution of the anion with a more stable one. Instead of tetraalkylammonium alkyloxybenzoate we used tetraalkylammonium bromide, which has solved the decomposition problem. The LC mix-

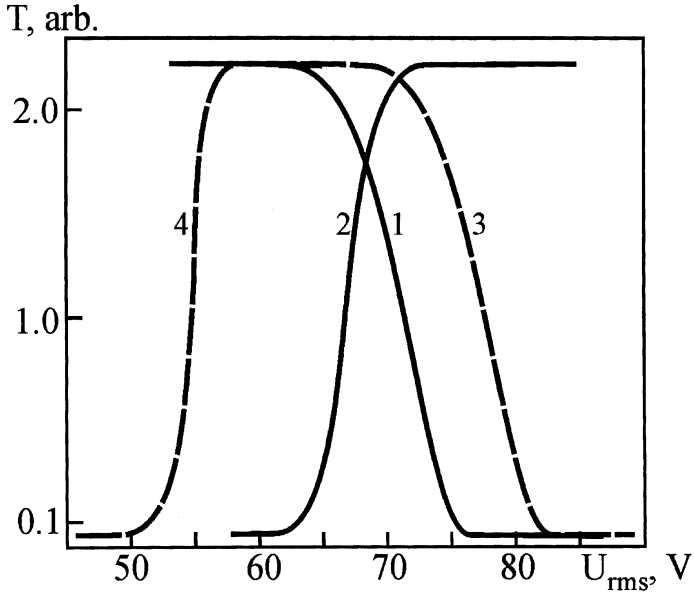


FIGURE 5 Transmittance – voltage curves for electrohydrodynamic instability (1,3) and for focal conic – homeotropic transition (2,4) of smectic A LC containing tetraalkylammonium alkyloxybenzoate (1,2) and tetraalkylammonium bromide (3,4). Cell gap is 11 μm.

ture with the modified dopant had the same density of focal conic structure, as this is determined by the visco-elastic and birefringent properties of LC medium, but the electrooptical parameters were still influenced. The efficiency of the dopant to the initiation of electrohydrodynamic instability is lower, so the EHD threshold voltage was increased and the response of instability became slower, as can be seen form the Figure 5 and from the table. The parameters of focal conic – homeotropic transition were improved: the threshold voltage decreased by 12 V and the response became twice faster.

CONCLUSION

The electrochemical decomposition of a smectic A LC mixture during long term operation has been found. This process leads to gas bubbles arising on the electrodes of the display. Two methods for solving the problem were proposed: the isolation of the electrodes from contact with the LC mixture and the modification of the dopant. It was proved that both methods eliminate the problem, but the electrooptical characteristics and quality of homeotropic structure were influenced. Both the introduction of passivating layers and the dopant modification lead to the deterioration of EHD instability characteristics, the use of silica isolation layer and modified dopant improves the FC-HP transition. The silica layer improves the quality of the homeotropic structure, but at the same time makes the creation of the grey scale difficult. The homeotropic structure obtained on the polyimide layer has more defects than one created on ITO.

The obtained results are used for improving of lifetime of display based on the electrically reversible memory effect.

REFERENCES

[1] Chigrinov, V. G. (1999). *Liquid crystal devices: physics and applications*, Artech House: Boston.

[2] Chirkov, V. N., Aliev, D. F., & Zeinally, AKh. (1977). Electrically reversible memory effect in smectic liquid crystals. *J. Tech. Phys. Lett.*, in Russian, *3*, 1016–1019.

[3] Coates, D., Crossland, W. A., Morrisy, J. H., & Needham, B. (1978). Electrically induced scattering textures in smectic A phases and their electrical reversal. *J. Appl. Phys.*, *11*, 2025–2034.

[4] Aliev, D. F., Bayramov, G. M., Mitrokhin, V. V., & Shikhalibeyly, ShSh. (1992). On the electrophysical properties of polycomponent mixtures exhibiting the smectic A phase. *Mol. Cryst. Liq. Cryst.*, *213*, 137–143.

[5] Aristov, V. L., Mitrokhin, M. V., & Sevostyanov, V. P. (1998). Electrolytic decomposition of S_A liquid crystal mixtures. In: *Proceeding of 7th SID International Symposium Advanced Display Technologies*. Minsk, Byelorussia, 75–77.