# Development of Low Anchoring Strength Liquid Crystal Mixtures for Bistable Nematic Displays

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#### **Abstract**

The recent Bistable Nematic (BiNem®) LCD technology presents long term bistability, high level passive matrix multiplexing, gray levels capabilities and high optical quality. The BiNem® device, based on anchoring breaking, needs specific low anchoring strength materials – alignment layers and liquid crystal mixtures. We present here our approach to develop nematic mixtures with wide enough temperature range and low zenithal anchoring energy.

Keywords: anchoring stregth, weak anchoring, nematic mixtures, bistable displays

### 1. Introduction

Most liquid crystal devices are monostable, with unique off-field state. They require permanent voltage application and frequent image refreshment, increasing the energy consumption and limiting the passive matrix multiplexability.

Bistable displays have at least two stable states and intrinsic memory of the pixel. They have lower power consumption if frequent update is not required. For some applications, e.g. e-book, the energy saving can increase the battery lifetime by orders of magnitude. Passive bistable devices can be driven line-by-line, memorizing the displayed information and removing the limitations of the multiplexing ratio.

Some bistable devices, like the 360° BTN [1] and the bistable cholesteric display [2], depend mainly on the bulk properties of the liquid crystal and use standard strong anchoring. The alignment films and the liquid crystal mixtures for these devices are similar to the traditional monostable materials. Other devices [3-5] are based on the surface properties and need specific weak anchoring materials.

Here we present our approach to the development of "weak anchoring" nematic mixtures, covering the needs of

the BiNem<sup>®</sup> bistable nematic technology [4]. We study the anchoring properties of different chemical families of pure nematics, then binary and more complicated mixtures, in order to understand how the mixture anchoring strength is related to the anchoring of the components. The results of the present work, together with the progress of weak polymer alignment layers, enabled us to develop BiNem<sup>®</sup> mixtures for the temperature range 0-50°C.

## 2. BiNem® Operation and Materials

# 2.1 Basic principles of BiNem® operation

The two BiNem bistable textures [4] are the untwisted (U) and 180° twisted (T) states (Fig. 1). They are realized with simple monostable anchorings on the two substrates. On the upper plate the anchoring is tilted and strong (zenithal anchoring energy  $W_z \approx 10^{-3} \text{ J.m}^{-2}$ ) – this anchoring is hardly perturbed when the field is applied. On the bottom plate the anchoring is weaker ( $W_z \approx 3 \times 10^{-4} \text{ J.m}^{-2}$ ) and without pretilt – this anchoring breaks under strong fields.

Without field both textures are stabilized by the surface anchoring torques, zenithal and azimuthal. The textures U and T differ by  $\pi$ -twist and are topologically different; they cannot be transformed one into the other, except by defect propagation or anchoring breaking. By suitable chiral doping (pitch P almost 4 times larger than the cell gap d) the energies of these two textures are equalized, giving a true bistability.

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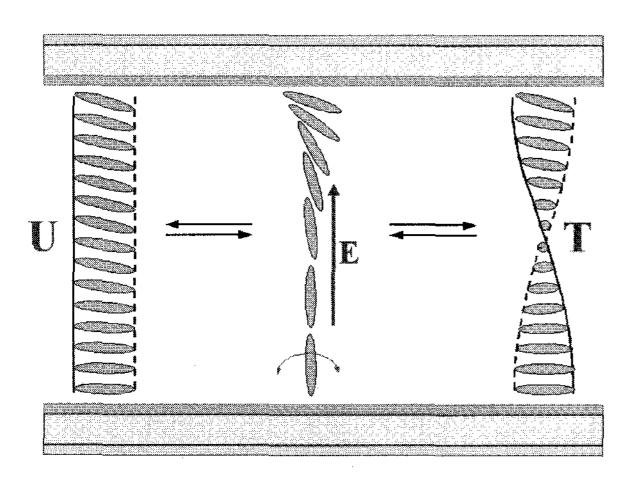


Fig. 1. BiNem textures and transitions.

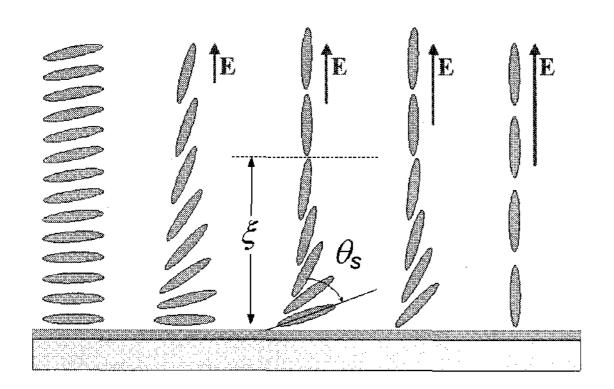


Fig. 2. Zenithal breaking of an uniform anchoring.

Under electric field **E** (we suppose  $\Delta \varepsilon > 0$ ) the bulk director is oriented along **E** ( $\theta \cong 0$ ), except in a surface layer of thickness  $\xi = \sqrt{K/\varepsilon_0}\Delta\varepsilon$  / E. usually called electric correlation length (Fig. 2).

For  $\xi > L_z$  (where  $L_z = K_{33} / W_z$  is the zenithal extrapolation length and  $K_{33}$  is the bend elastic constant), the surface director orientation  $\theta_s$  ( $0 < \theta_s < \pi/2$ ) is defined by the torque equilibrium. At a threshold field given by  $\xi_c = L_z$  (typically  $E_c$ =10-30 V/ $\mu$ m) the anchoring is broken – the anchoring torque vanishes and the surface director is oriented homeotropically, parallel to the field. After the field removal this surface can relax to either one of the bistable states.

The final state selection is obtained by the form of the electric driving pulse back-front. Fast switching-off of the field creates a strong flow in the vicinity of the unbroken upper plate. Diffusing to the unstable-equilibrium bottom plate, the flow imposes relaxation toward the T-state. On the other hand, progressive decrease of the field (100 µs

time scale) favors the static (elastic) coupling between the surfaces and gives the U-texture. Once the final state is selected, the surface relaxation is rapid (10 µs time scale) and irreversible.

The voltage thresholds depend both on the bulk properties of the nematic and the anchoring energy. We present the results of our studies concerning the optimization of the liquid crystal mixtures of weak anchoring and more precisely for BiNem devices.

# 2.2 Bulk properties of the nematic mixture

At a first glance, the properties of the mixtures designed for BiNem devices appears to be not so different of the usual technology ones. The main requirements imposed to the bulk properties of the nematic mixture in the BiNem device are:

- Large enough nematic temperature range, usually larger than  $-20^{\circ}$ C to  $+60^{\circ}$ C.
- Strong positive dielectric anisotropy, decreasing the anchoring breaking voltage, typically  $\Delta \epsilon > 20$ .
- The birefringence  $\Delta n$  should be adapted to the cell thickness in order to optimize the optical properties.
- Low rotational viscosity is needed for fast switching and relaxation of the display.
- The elastic anisotropy can be arbitrary it plays only a minor role in the BiNem technology.
- High electrochemical stability of the mixture is required, due to the strong anchoring breaking fields (up to 20 V/μm at low temperatures).

All these bulk properties are similar to the usual LCD technologies needs. After more than 40 years of basic and applied research, the measurement techniques and the rules of design of the mixtures are well developed for the bulk properties and only a limited effort is needed to adapt them to the BiNem needs. The big difference is that we need particular anchoring on the substrate (weak zenithal anchoring). We have found that this property depends strongly on the chemical structure of the liquid crystal components of the mixture.

### 2.3 Anchoring properties of the nematic

The nematic anchoring on the weak alignment layer side is the key property for the BiNem. Here we focus only on the mixture properties, supposing that the alignment layer is already developed. In the anchoring studies we use either a SiO evaporated layer or the rubbed polymers BP11 and BP16, developed by Nemoptic, all of them giving weak anchoring of the nematic pentyl-cyanobiphenyl (5CB).

The most important surface properties we need are:

- Weak zenithal anchoring strength. In practice we need  $U_c = d.E_c = d.W_z / \sqrt{K\varepsilon_0 \Delta \varepsilon} < 30 \text{ V}$ , implying  $W_z < 5.10^{-4} \text{ J.m}^{-2}$ . In some cases we can measure directly  $U_c$  from the switching threshold in BiNem cells. Otherwise, we measure  $W_z$  with a modified high-field technique from the birefringence saturation above the anchoring breaking threshold. This technique is limited only by the dielectric breakdown of the test cell above 30-40 V/ $\mu$ m.
- Strong azimuthal anchoring strength, typically  $W_a>5.10^{-5}$  J.m<sup>-2</sup>, is needed to stabilize the bistable textures against the defect propagation. High  $W_a$  improves also the optical contrast by decreasing the twist of the U-state due to the chiral doping of the nematic. We have developed simple techniques [6] to measure  $W_a$  with satisfactory precision.
- Pretilt  $\psi$  on the weak anchoring plate. The best conditions for the BiNem operation are obtained for  $\psi$ <0.5°. To measure  $\psi$ , its temperature variation and uniformity we have developed a local electro-optic technique [7].
- The temperature dependences of the surface properties should be as weak as possible, the BiNem temperature range being limited above from too weak W<sub>a</sub> and below by too strong W<sub>z</sub>.
- The anchoring should also remain stable in the time even under strong torques easy axis gliding [6,8] and other anchoring memory phenomena can disturb seriously the BiNem switching.

# 3. Anchoring Studies and Results

## 3.1 Study of pure nematic compounds

For the choice of the components in our mixtures we measured the zenithal anchoring strength of more than 30 among the most common families of nematics. On Fig. 3 we present the temperature dependence of  $W_z$  for 5CB on two different substrates. The observed fast increase of  $W_z$  with the nematic order parameter S,  $W_z \sim S^{\beta}$ , where  $\beta = 4$ 

7, is confirmed for all weak anchoring nematics.

As expected, the anchoring strength variation with the reduced temperature  $T_r=T/T_c$  is approximately the same within each homologous series (for the same substrate).

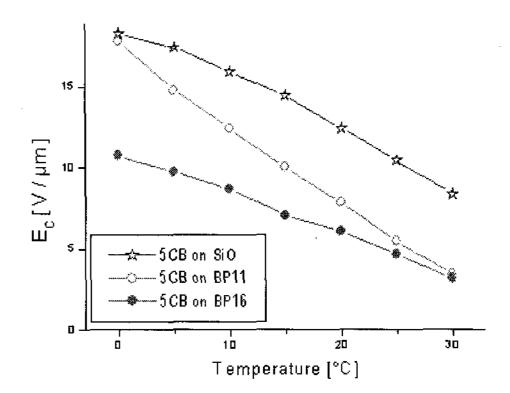


Fig. 3. Temperature dependences of the anchoring breaking threshold of the nematic 5CB on three different alignment layers.

Table 1. Breaking thresholds of some nematic compounds

| Nematic compound |     | $E_C$ on BP16 at $Tr=0.9$ |
|------------------|-----|---------------------------|
| 5CB              | CN  | 9.8 V/µm                  |
| 60СВ             |     | 18 V/μm                   |
| РСН-5            | -CN | 27 V/μm                   |

From one series to the other, however, the variation can be spectacular (Table 1).

For example, the replacement of one phenyl ring in the 5CB molecule by a saturated (cyclohexane) ring increases W<sub>z</sub> by a factor of 3 (point 18 on Fig. 4)! Even minor changes, like the replacement of the alkyl- with alkoxy- in the CB series, increase twice the anchoring breaking threshold (point 6 on Fig. 4).

## 3.2 Anchoring strength of binary mixtures

In a large number of cases it is impossible to measure the anchoring strength of a pure compound, either due to the very high value of  $W_z$ , or to the narrow nematic

temperature range, or to the low  $\Delta \varepsilon$ , not enabling to apply high enough electric torque for the anchoring breaking. These compounds have been studied in binary mixtures with 5CB, and the results have been extrapolated to 100% concentration of the studied molecule. This approach, quite

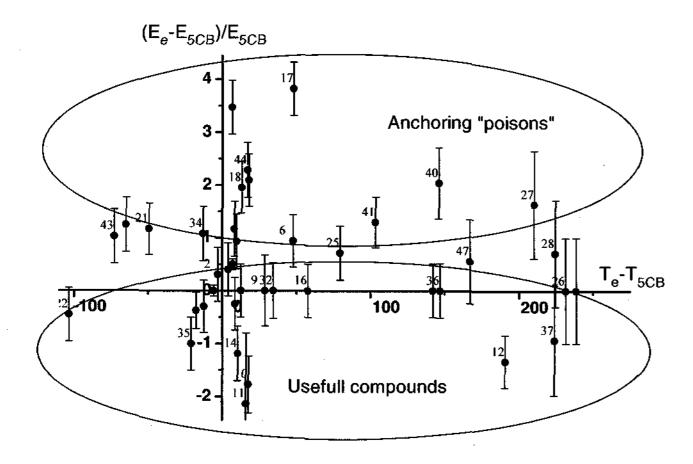


Fig. 4. Extrapolated anchoring breaking thresholds and clearing temperatures of the studied nematic compounds on the BP11 alignment layer.

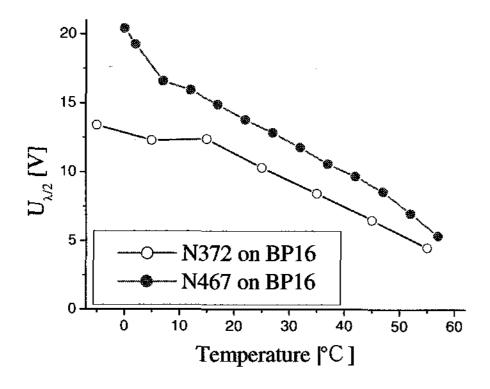


Fig. 5. Anchoring breaking voltage of two weak anchoring mixtures on the BP16 alignment layer.

usual for most of the bulk properties, is not obvious for the anchoring properties: the interaction of the nematic with the alignment polymer can be strongly non-linear due to a segregation of the mixture on the surface and other selective physico-chemical interactions.

However, limiting our studies to diluted solutions, we observed experimentally a reasonable agreement of the anchoring strength of the mixture as a weighted linear combination of the anchoring energies of the components. For small concentrations c the anchoring breaking field of the mixture can be approximated as  $E_c = (1-c)E_{5CB} + c.E_e$ ,

where  $E_e$  is the extrapolated threshold for the pure compound. On Fig. 4 we plot the values of  $E_e/E_{5CB}-I$  for different nematic compounds, extrapolated from measurements in 10-20% mixture with 5CB. On Fig. 4 we see the limitations of the extrapolation procedure: for some nematics the extrapolated threshold  $E_e$  is negative, due to the non-linearity of the mixing laws for the anchoring strength. We note also that the large error bars are due to the extra-polation from low-concentration data.

## 3.3 Design rules for the mixtures

The data presented on Fig. 4 enable us to make the initial choice of the main mixture components, ensuring relatively low anchoring breaking thresholds. The most interesting compounds are those on the bottom part of the figure, with anchoring strength comparable or weaker than the 5CB one. To obtain a large temperature range we need components with clearing temperatures covering a large range, if possible distributed over all the abscissa axis. Varying the proportions of the high-T<sub>c</sub> components we can adjust the mixture clearing temperature to the wanted value.

On the contrary, the compounds on the upper side of the figure are a kind of "anchoring poisons": even small amount of them can seriously increase the anchoring strength. These components should be avoided even when they are expected to improve some others, secondary properties of the mixture - their price in anchoring energy is excessively high.

Finally, the compounds lying between these two extreme groups, with moderate anchoring strength, are very useful to adjust the final mixture properties. Typically, we need up to 30-40% of these compounds in order to match the miscibility of the low anchoring strength components, to increase the electrochemical stability and to decrease the viscosity.

# 3.4 Examples of low anchoring strength mixtures

The above findings have enabled us to design several weak anchoring mixtures specially adapted to the BiNem technology [9] and to our rubbed polymer weak anchoring alignment layers. On Fig. 5 we show the anchoring breaking voltage for two of these mixtures, renormalized to the optimal cell thickness given by d.  $\Delta n = \lambda/2$ .

The data presented on Fig. 4 enabled us to combine high  $\Delta \varepsilon$  and low anchoring strength, avoiding the "anchoring poisons". The mixtures have been optimized for

BiNem devices operating, with driving signals not exceeding 30 V in the pixel. The electro-chemical stability was also improved, in particular for N467, by testing the components and their simple mixtures for long term stability under strong fields ( $E=20~V/\mu m$ ). The basic physical properties of these two mixtures are presented in Table 2.

Table 2. Some basic properties of Nemoptic's weak-anchoring mixtures

| Mixture                        | N372                                  | N467                           |
|--------------------------------|---------------------------------------|--------------------------------|
| Nematic range                  | -20 − 59 °C                           | -24 – 62 °C                    |
| $\Delta \varepsilon$ at 25°C   | 29                                    | 26                             |
| ∆n at 25°C                     | .198                                  | .166                           |
| W <sub>z</sub> on BP16 at 25°C | 4.2 10 <sup>-4</sup> J/m <sup>2</sup> | $3.6 \ 10^{-4} \ \text{J/m}^2$ |
| W <sub>a</sub> on BP16 at 25°C | $4.0 \ 10^{-5} \ \text{J/m}^2$        | $2.2 \ 10^{-5} \ \text{J/m}^2$ |

#### 4. Conclusions

We have shown that the surface properties of the weak-anchoring mixtures can be predicted, by study of the anchoring in pure compounds and simple mixtures. We show the strong variation of the anchoring strength even with minor changes in the chemical formula of the molecule, especially in the case of polar compounds. On the same substrate some chemical families of nematics have extremely strong anchorings and have to be definitely avoided in weak anchoring mixtures. The linearity of the "mixing laws" for the anchoring strength have been

confirmed experimentally, at least for low to moderate concentrations of the components.

Our present work demonstrates the way to achieve nematic mixtures with weak zenithal anchoring, low pretilt, high electrochemical stability and wide temperature range for use in bistable displays. Further improvement of these mixtures, by introducing new components and by matching the alignment layer process and the mixture composition, is under way in collaboration between Nemoptic and Dainippon Ink and Chemicals, Japan.

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