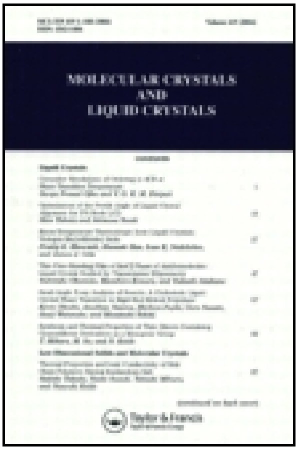

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Improved Liquid Crystal Mixtures for STN Displays

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IMPROVED LIQUID CRYSTAL MIXTURES FOR STN DISPLAYS

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Supertwisted nematic (STN) liquid crystal displays remain a leading technology for mobile communications applications, personal digital assistants (PDA) and personal convergence devices. Higher demands on display information content place ever increasing demands on the physical parameters of the liquid crystal mixture. To satisfy current and future display requirements, it is necessary to develop mixtures showing:

- *Fast response times achieved by rotational viscosity reduction and birefringence increase.*
- *Small temperature dependence of the operating voltage (dV/dT), especially at low temperatures.*
- *Small frequency dependence of the operating voltage (dV/df), necessary for multi-level greyscale operation.*
- *Improved steepness (V_{90}/V_{10}) of the electro-optical curve to enable higher duty multiplexing of the display.*

In order to fulfil these requirements, liquid crystal mixtures with improved physical properties were developed. Examples of these mixtures are presented.

Keywords: birefringence; dielectric anisotropy; nematic liquid crystal mixtures; response times; STN

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1. LIQUID CRYSTAL SINGLE MATERIALS

Liquid crystal (LC) mixtures usually comprise a mixture of about 10–20 individual LC singles to achieve the desired nematic phase range, optical and electro-optical properties. Application-related properties of LC mixtures are strongly dependent on the design of individual LC singles. In the following we will present the status of standard LC singles and the obtained property improvements with the use of newly developed LC singles. As most LC singles are not nematic at room temperature, their individual parameters are derived from a linear extrapolation to 100%, measured from a given concentration of test substance in a nematic host mixture. Elastic constant data is that measured in the nematic host without extrapolation.

1.1. Response Time Improvement

Improvement of response times, in an attempt to achieve video frame rates of optical response is a high priority for the development of electro-optical LC mixtures. It is also important to achieve a faster response time without affecting other properties in a negative way. In high-resolution displays, response times can be reduced by using a mixture design that results in a flatter electro-optical curve. From the materials side this can be achieved by the use of LC singles with smaller ratio of elastic constants K_{33}/K_{11} or increased dielectric parameter $\Delta\varepsilon/\varepsilon_{\perp}$ [1]. However this approach also causes a change of contrast which in most cases is not acceptable. The response time is directly proportional to the rotational viscosity γ_1 and the square of the cell thickness d [2]. As the product of cell thickness d and birefringence Δn is fixed for a certain set of cell parameters (e.g. twist angle), improved response times can be achieved by increasing the Δn value of the mixtures and so decreasing the required cell thickness.

1.1.1. Neutral LC Singles with Low Birefringence

A majority of neutral LC singles show linear relationship of the logarithmic value of rotational viscosity γ_1 vs. clearing point. Alkyl chain length influence on the ratio of rotational viscosity vs. clearing point is shown in Figure 1. The open square and the line represent the status of standard LC single materials. “CC-nV-m” is an abbreviation for a molecule consisting of two cyclohexane [C] rings, a vinyl [V] group and alkyl chains of length n, m.

From the data in Figure 1, it can be seen that the shorter alkyl chain length n results in a smaller ratio of rotational viscosity/clearing point and therefore LC mixtures with improved response time over standard materials can be formulated. The elastic constant ratio K_{33}/K_{11} is essentially not affected by alkyl chain length n.

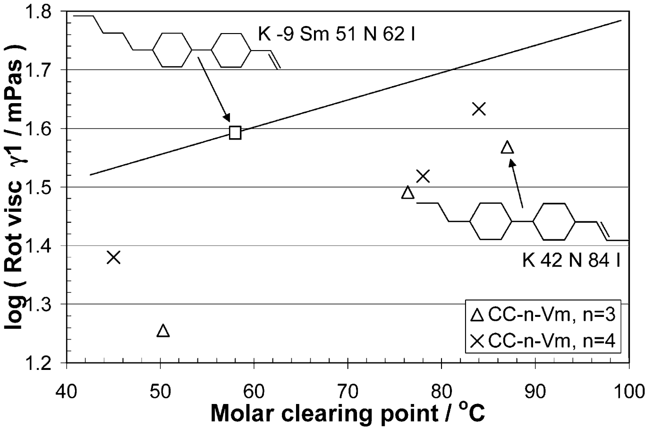


FIGURE 1 Logarithm of rotational viscosity vs. molar clearing point for standard neutral LC singles (open square and line) and new neutral LC singles (cross and open triangle).

1.1.2. Neutral LC Singles with High Birefringence

All LC mixtures for STN applications contain a certain proportion of highly birefringent LC singles to adjust the specified birefringence Δn. Most highly birefringent LC singles have an inherent problem of limited solubility in a nematic host before crystallisation occurs, especially at low temperatures. The maximum achievable Δn value of LC mixtures is therefore limited. In Tables I and II, groups 1 and 2 represent standard singles with Δn values of 0.3 and 0.25 respectively while group 3 represents newly developed LC materials with a Δn value of about 0.32.

The advantages of the new group 3 LC singles compared to group 1 and 2 LC singles are:-

a. Lower melting points result in improved solubility, allowing the realisation of LC mixtures with large Δn values and excellent low temperature

TABLE I Structure and Phase Behaviour of Highly Birefringent Materials (1, 2: Standard; 3: New)

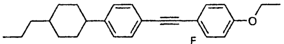
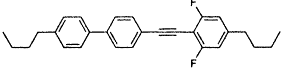
	Structure	Phases
1		K 88 N 95 I
2		K 110 N 253 I
3		K 34 N 156 I

TABLE II Physical Parameters of Highly Birefringent Materials (1, 2: Standard; 3: New)

Structure	Clp. extr./°C	Δn	γ_1/mPas
1	88	0.300	54
2	288	0.252	356
3	198	0.318	69

stability. A typical example for a LC mixture with very high birefringence is given in chapter 2.

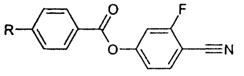
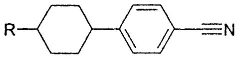
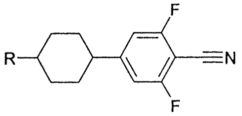
b. Improved clearing point vs. rotational viscosity ratios allows the realisation of mixtures with improved response times.

1.2. Improvement of the Temperature Dependence of the Operating Voltage

Structures 4 and 5 in Table III represent typical polar LC materials.

Structure 4 is characterised by a very strong dielectric anisotropy $\Delta\varepsilon$ while structure 5 shows a very large elastic constant ratio K_{33}/K_{11}. Structure 5 is however well known to form partial antiparallel ordering at low temperatures, which changes to a parallel ordering with increasing temperature. This results in an almost flat temperature dependence of the dielectric anisotropy and hence a strong temperature dependence of the operating voltage. In addition the dielectric anisotropy is frequency dependent which limits the multiplexability of a display and is the main reason for the often-observed strong increase of the operating voltage at low temperatures. Polar materials that display a strong temperature depen-

TABLE III Polar LC Singles (4, 5: Standard; 6: New)

Structure	$\Delta\varepsilon$	K_{33}/K_{11}
4 	50	1.78
5 	20	1.91
6 	32	1.93

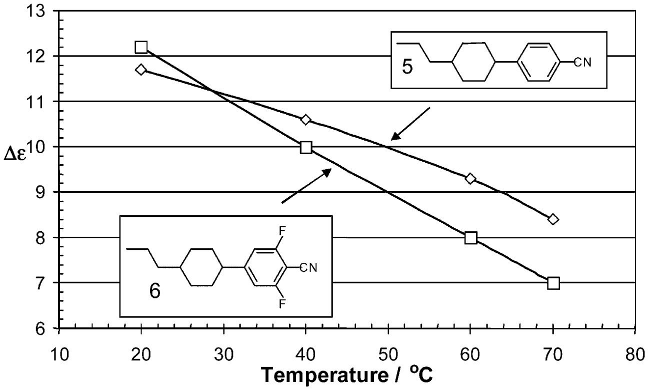


FIGURE 2 Temperature dependence of the dielectric anisotropy Δε of a LC mixture (5: Standard; 6: New).

dence and a weak frequency dependence of the dielectric anisotropy are of particular interest.

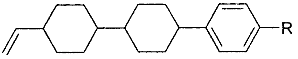
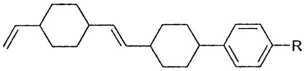
Newly developed LC materials of structure 6 are characterised by the following properties

a. The elastic constant ratio K_{33}/K_{11} is similar to the values of structure 5.
b. Lateral fluorosubstitution results in an increased Δε value.
c. Lateral fluorosubstitution favours parallel association, resulting in a stronger change of the temperature dependence of the dielectric anisotropy (see Fig. 2) and hence a smaller temperature dependence of the operating voltage.
d. Frequency dependence of the dielectric properties is improved which allows the design of LC mixtures with very small temperature dependence of the operating voltage especially at low temperatures (e.g. −20°C).

1.3. Steepness Improvement

Use in mixtures of LC singles containing only cyano-endgroups as a polar terminal group will result in a very steep electro-optical curve but there is a negative impact on the temperature dependence of the operating voltage. Neutral materials with very high elastic constant ratios K_{33}/K_{11} are most interesting for realisation of LC mixtures with very steep electro-optical curves. Structure 7 represents a typical neutral LC single incorporating one double bond in the side chain. The newly developed

TABLE IV Standard (7) and New (8) LC Singles with Improved K_{33}/K_{11} Values

	Structure	K_{33}/K_{11}
7		1.6–1.7
8		1.85–1.95

structure 8 incorporates an additional double bond in the core structure resulting in an increase of the K_{33}/K_{11}values (see Table IV).

2. LIQUID CRYSTAL MIXTURES

Liquid crystal mixtures were electro-optically characterised in single pixel STN cells with a twist of 240 deg, $d^*\Delta n = 0.85$, $d/p = 0.53$ in the normally yellow mode. Values of V_{10} and V_{90}/V_{10} were measured with squarewave addressing (80 Hz). Operating voltages V_{op} and response times $t_{ave} = (t_{on} + t_{off})/2$ were determined for the given multiplex/bias ratios.

2.1. LC Mixtures for Low to Medium Information Content Applications

Table V represents LC mixture data for a typical mobile communications application with maximum multiplex ratio of 1/64.

Cellgaps are in the range of about 6 μm. Main foci are a low absolute value and a small temperature dependence of the operating voltage.

TABLE V Typical LC Mixture with Low Operating Voltage

Clearing point/°C	86	
Δn	0.140	
V_{10}/V	1.15	
V_{90}/V_{10}	1.07	
	duty 1/48 bias 1/7	duty 1/64 bias 1/9
V_{op}/V @ −20 C	6.9	8.5
V_{op} @ 20 C	6.4	7.7
t_{ave}/ms @ −20 C	5000	5700
t_{ave}/ms @ 20 C	270	300

TABLE VI Typical LC Mixture for 3G Mobile Phone Application

Clearing point/°C	90	
Δn	0.160	
V_{10}/V	1.75	
V_{90}/V_{10}	1.07	
	duty 1/64	duty 1/128
	bias 1/9	bias 1/12
V_{op}/V @ −20 C	12.6	17.6
V_{op} @ 20 C	11.9	16.1
t_{ave}/ms @ −20 C	1200	1500
t_{ave}/ms @ 20 C	105	135

2.2. LC Mixtures for Medium to High Information Content Applications

3G mobile phone application requires an increased display resolution and faster switching. This is realised by increased operating voltage and smaller display cellgaps in the range of around 5 μm (see Table VI). Fast switching favours the use of LC singles as described in Section 1.1.1 and those like structure 3, as opposed to the standard LC singles.

Table VII represents typical data for a high-resolution application as e.g. personal digital assistants (PDA). High resolution favours by the use of LC singles like structures 6 and 8, as opposed to the standard LC singles.

2.3. LC Mixtures with Very Large Birefringence

As mentioned in chapter 1.1.2, new highly birefringent materials allow the generation of LC mixtures with a very high birefringence (see Table VIII).

A typical application for such a mixture could be the so-called ECB-STN where 4 colours are generated without the need for colour filters [3]. Although this application can only be found in few products, the mixture

TABLE VII Typical LC Mixture for High-Resolution Application

Clearing point/°C	98
Δn	0.147
V_{10}/V	2.22
V_{90}/V_{10}	1.044
	duty 1/240
	bias 1/16
V_{op} @ 20 C	26.3
t_{ave}/ms @ 20 C	168

TABLE VIII Typical LC Mixture with Very High Birefringence

Clearing point/°C	110
Flow visc./mm^2/s	30
Rot visc γ_1/mPas	198
Δn	0.2670
V(10,0,20)/V	1.77
V_{90}/V_{10}	1.10

data represent well the potential of the new materials to easily generate highly birefringent LC mixtures. This will become quite important for the internet mode mobile phone application, where cell gaps may go down to values of around 4 μm. High birefringence is realised with LC singles like structure 3 which can be used in much larger concentrations because of the vastly improved solubility but also have the additional benefits of good clearing point and low rotational viscosity, as opposed to the standard LC singles.

3. SUMMARY

New LC singles to improve the response times, contrast, temperature and frequency dependencies of the operating voltage of existing LC mixtures were presented. Some typical mixture examples incorporating these new singles were given. Additional influences of cell parameters could not be discussed in the frame of this presentation. This paper presents some status of our research activities in the field of LC mixtures for supertwisted nematic displays and further improvements, e.g. response time reduction, are under investigation.

LITERATURE

[1] Scheffer, T. J. & Nehring, J. (1984). A new highly multiplexable liquid crystal display. *Appl. Phys. Lett.*, *45*, 1021–1023.; Scheffer, T. J. & Nehring, J. (1992). Twisted nematic and supertwisted nematic mode LCDs. In: *Liquid Crystals: Applications and Uses*, Bahadur, B. (Ed.), World Scientific: Singapore, Vol. 1, Chap. 10, 231–274.

[2] Tarumi, K., Finkenzeller, U., & Schuler, B. (1992). Dynamic behaviour of twisted nematic liquid crystals. *Jpn. J. Appl. Phys.*, *31*, 2829–2836.

[3] Ozeki, M., Hori, H., Shidoji, E., Hirai, Y., & Koh, M. (1996). A super reflective color LCD with white, red, blue, and green using electrically controlled birefringence technology. *SID Digest of Technical Papers*, *XXVII*, 107–110.