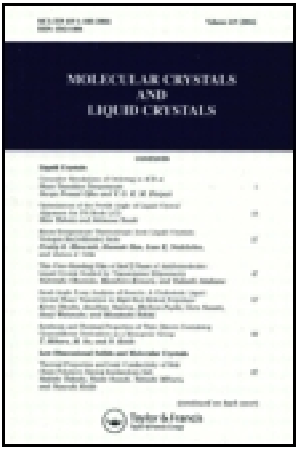

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Fast-Switching Low-Temperature Liquid Crystal Mixtures

W. Kuczyński [a] [b], S. T Lagerwall [a], M. Matuszczyk [a], K. Skarp [a], B. Stebler [a] & J. Wahl [a]
[a] Physics Department, Chalmers University of Technology, S-412 96, Göteborg, Sweden
[b] Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17/19, PL 60-179, Poznan, Poland

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Fast-Switching Low-Temperature Liquid Crystal Mixtures

W. KUCZYŃSKI,[†] S. T. LAGERWALL, M. MATUSZCZYK, K. SKARP, B. STEBLER and J. WAHL

Physics Department, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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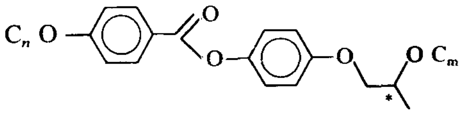
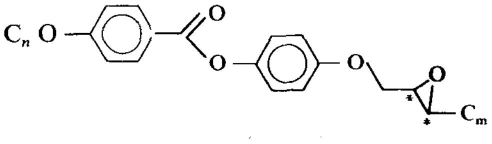
The metastable chiral smectic C phases of the compounds



have been made technically useful by alloying to different two- and three-component systems with enantiotropic behaviour. These systems can serve as a base for multicomponent systems of higher order for optimizing various properties.

In a similar way, the inconveniently high-lying ferroelectric phases of the compounds



have been taken down to a useful temperature range. The mixtures have an excellent UV stability and are well adopted for use in high speed bistable SSFLC devices.

[†] On leave of absence from Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17/19, PL 60-179 Poznań, Poland.

I. INTRODUCTION

Surface-stabilized ferroelectric liquid crystals (SSFLC) are tilted chiral smectics which are made helix-free due to a "book shelf" geometry arrangement[1] (layers standing up perpendicular to the glassplates of the electro-optic cell) under the condition that the distance between the confining plates is very small. During the last few years notable achievements have been made in the physics and technology of the SSFLC devices. The multiplexibility, taking advantage of the bistable properties, has been confirmed and thus the applicability to large screens handling high density information in real time demonstrated. Thin cells with a typical thickness of 1 to 3 μm are capable of fast and bistable operation, with voltages of 5 to 50 volts giving corresponding response times in the range of 1 to 50 μs. These characteristics are typical for certain high-temperature materials, operating at about 60 to 80 degrees Celsius. In order to be useful in devices, however, correspondingly fast liquid crystals should be developed operating at ambient temperature. A number of room-temperatures ferroelectric mixtures have been reported by Isogai *et al.*[2] with response times of about 1 millisecond or longer. In this paper we report on novel mixtures with response times of typically 20–50 microseconds at room-temperature.

II. PROBLEMS WHEN DESIGNING FERROELECTRIC MIXTURES

Three kinds of important problem have to be distinguished in designing ferroelectric liquid crystal materials. First there is the task of developing stable, that is, non-monotropic, C* phases, or eventually also more ordered tilted smectic phases, which are broad-band and centered around ambient temperature. The substances have to have a high electric resistivity and be of high chemical stability; especially they have to be resistant to moisture (which essentially rules out Schiff bases) and to UV-light (which leads to a certain care e.g. when using cinnamates). The second task is to choose compounds and mixtures that are compatible with available surface coatings giving the desired boundary condition of the molecular axis parallel to the confining surface.

At the present stage this problem can only be investigated by trial and error, and whereas several classes of chemical compounds, especially phenyl pyrimidine compounds, show excellent affinity for this boundary condition in combination with a wide variety of precoatings, just as they do in the nematic phase, other substance classes have been found which rather show the opposite tendency of never aligning themselves to the "book shelf" geometry, regardless of coating materials and application of mechanical shear. The third task is the optimization of material parameters like polarization, viscosity, birefringence, dielectric anisotropy, tilt and pitch. In this connection it is of special importance to recognize that the sign and value of dielectric anisotropy is of high relevance to the alignment problem and to the general problem of matrix-addressing the SSFLC cell.

III. MATERIALS

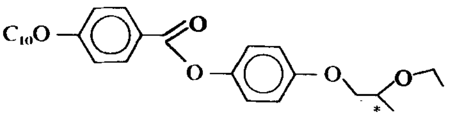
Among available materials having the chiral smectic C phase only non-coloured, chemically stable substances were chosen. Their liquid crystal phases were identified when possible and the phase transition temperatures were determined using both a polarizing microscope equipped with a Mettler FP 52 hot stage and a Perkin-Elmer DSC-7 differential scanning calorimeter. In the latter the transition enthalpies were also measured. Finally, the spontaneous polarization for some materials was measured using the Diamant bridge[3] and the helical pitch Z was estimated by microscope observation or measured by laser diffraction.

Moreover, care was taken to determine not only Z, but also its sign, + or −, $+Z$ designating a right-hand helix in space, and $-Z$, designating a left-hand helix. Further, the sign of P has been determined, according to the proposed convention[4,5] thus the sign pair (P,Z) $(+/-,\ +/-)$ has been determined for all compounds used, which is important for compensating the twisting power of the C* phase without letting one of the compounds' polarization counteract that of the others in the mixture.

The used compounds are listed below (Table I) and the transition temperatures given below each formula. X,S,C,A,N and L stand for crystalline, smectic (with no further designation), smectic C, smectic A, nematic and (isotropic) liquid phase. An asterisk denotes a chiral-asymmetric phase and a parenthesis indicates a monotropic (metastable) phase;

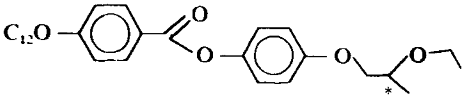
TABLE I

(1)



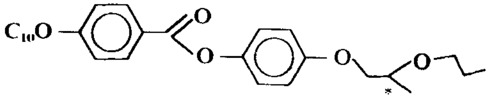
X40 ($S_3$10 C^*28) A 42 L

(2)



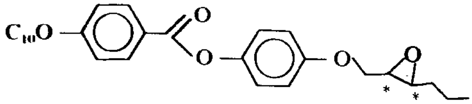
X44 (S_3 18 C^*35) A 45 L

(3)



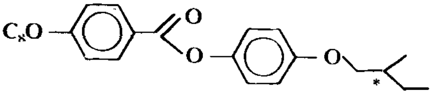
X38 (C^*37) A 43 L

(4)



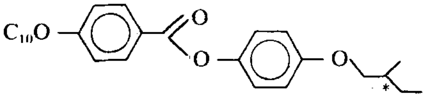
X73 ($S_3$57) C^*78 A 80 N^* 95 L

(5)



X48 ($S_4$12 $S_3$21 C^* 43) A 59 L

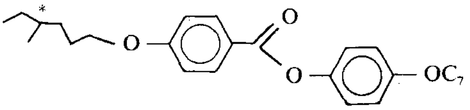
(6)



X 45 C^* 47 A 64 L

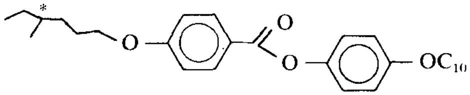
TABLE I (*Continued*)

(7)



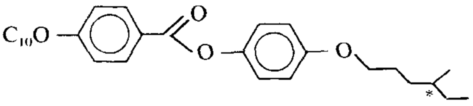
X36 C^* 47 N^* 63 L

(8)



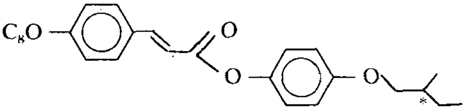
X39 C^* 51 N^* 66 L

(9)



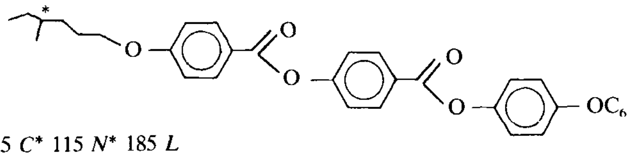
X38 ($S_3$30) C^* 70 A 73 N^* 74 L

(10)



X84 (C^*86) A 99 N^* 105 L

(11)



X95 C^* 115 N^* 185 L

Compounds (1) to (4) have been synthesized by D. M. Walba.[6,7] The synthesis of compounds (5) to (9) has been described by P. Keller[8]; the synthesis of (10) by T. Leslie.[9] Compounds 1–9 are available from Display Tech, Inc., P. O. Box 7246, Boulder, CO, 80306 USA

In Table II approximate values of the helical pitch and of the spontaneous polarization are given as well as the sign pair polarization-helicity for the investigated substances.

IV. DETERMINATION OF THE HELIX HANDEDNESS

Despite its obvious importance the handedness of the helix in the chiral smectic C phase has been reported in but a few cases.[10] Its determination is far from trivial, but fortunately, we can take advantage of the existing experience concerning cholesteric liquid crystals. Generally it is not possible to draw conclusions about the handedness from the absolute configuration of the molecule in question, known from optical activity measurements in the isotropic phase or in solutions. Further, if a given material has a cholesteric phase above the smectic C*, the knowledge of the handedness in the former can not be used as a guideline for the handedness in the latter phase, because the nature of the correlation—if any—is not known. There is even an example of inversion of the handedness in the cholesteric (but not in the C*) phase in a pure compound on changing the temperature[11]; in this case the lack of correlation is obvious.

The determination of handedness from observation of the pitch change in mixtures may also give erroneous results, and it is known that the dependence of the cholesteric pitch on concentration may be non-linear and sometimes quite complicated (for instance, a helix inversion may occur in a cholesteric-nematic mixture[12] or even, a

TABLE II

		Z (micrometer)	Sign Z/sign P	P(nC/cm^2)
Substance	(1)	<3	−/+	6
	(2)	<3	−/+	
	(3)		−/+	
	(4)	3	+/+	30
	(5)	3	−/−	2
	(6)	10	−/−	
	(7)	5	−/−	
	(8)	5	−/−	
	(9)	5	−/−	
	(10)	3	−/+	

double helix inversion in a mixture of two components with the same handedness[13]). One cannot exclude a similar behaviour in the case of smectic C* liquid crystals.

One of the most reliable methods for handedness determination in the cholesteric phase has been developed by Heppke and Oestreicher[14]. In this "mechanical" method the handedness is determined by means of observation of the motion of Cano lines in a wedge-shaped sample, caused by rotation of the lens placed on the supporting plate with the sample in between. Unfortunately, this method is hardly applicable to smectic C* liquid crystals because of the difficulty in obtaining stable and well-visible Cano lines.

In our handedness determinations we used instead the rotation of the polarization plane of light. The method, explained in Figure 1, is very simple and gives unambiguous results, if proper precautions are taken. It requires, however, the knowledge of the position of the selective Bragg reflexion wavelength λ_R with respect to the measuring

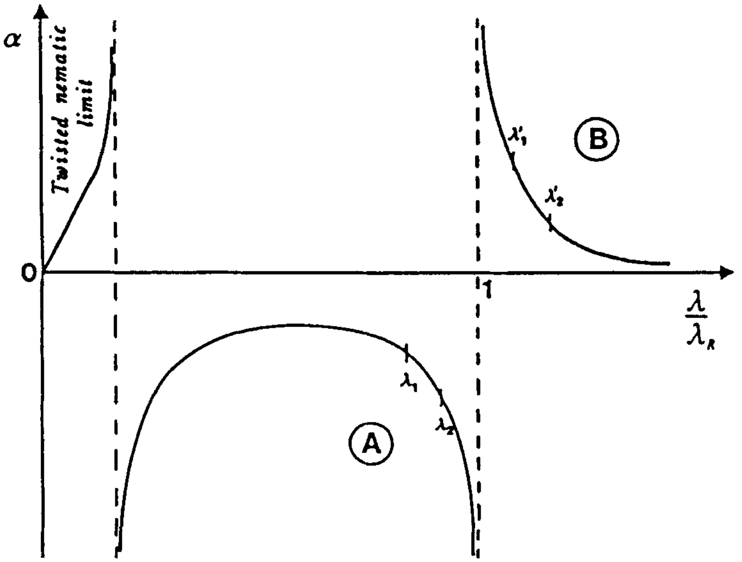


FIGURE 1 Illustration of the method for the determination of the helical handedness in chiral smectics. The Figure shows schematically the angle α of the rotation of polarization plane (plane polarized light) as a function of transmitted wavelength λ. λ_R is the Bragg reflexion wavelength $\lambda_R = nZ$ (n – index of refraction). For $\lambda > \lambda_R$ the sense of rotation is the same as the sense of the helix, for $\lambda < \lambda_R$ (the common case) it is the opposite. Increasing the wavelength ($\lambda'_2 > \lambda'_1$ $\lambda_2 > \lambda_1$) gives, for the absolute value of α, a decrease in the former, an increase in the latter case, which can be used to determine the relative position of the reflexion band in the case that $\lambda \approx \lambda_R$.

wavelength λ. In the common case the situation is fairly simple because normally the C* phase periodicity is on a much larger scale than the wavelength of visible light used for the measurement. Then, applying de Vries theory[14] to the smectic C* case, we conclude that the polarization plane of the light passing the sample along the helix axis (homeotropic orientation) is turned in the sense opposite to the sense of the helix (or, otherwise but less conveniently expressed, a right helix turns the polarization plane anti-clockwise for an observer looking from the light source in the direction of light propagation). We are then to the left of λ_R in Figure 1.

Some doubts can appear, when the pitch is comparable to the wavelength of light. In this case (in which the microscope field of view is coloured) one can decide whether the measuring wavelength is higher or lower than λ_R using two wavelengths (λ_1, λ_2 in case A; λ_1' λ_2' in case B shown in the Figure). In case A $|\alpha(\lambda_1)|<|\alpha(\lambda_2)|$ and in case B $|\alpha(\lambda_1')| > |\alpha(\lambda_2')|$.

V. TWO-COMPONENT MIXTURES

The first task to be solved was lowering the melting temperature by mixing two different substances. Some eutectic temperatures could either be determined or directly found to lie below room-temperature by using a contact preparation, which also in many cases helped us to identify the liquid crystal phases and to draw approximate phase diagrams. These served for selecting materials and pairs of materials for further investigation.

For more accurate determination of the phase diagrams small samples of known composition were prepared. After careful mixing of the substances in the isotropic phase both microscopic and calorimetric investigations were carried out. Melting temperatures and enthalpies as measured by DSC are presented in Table III. The melting curves were plotted using the van Laar equation

$$\frac{1}{T_i} = \frac{1}{T_{oi}} - \frac{R \ln X_i}{\Delta H_i} \tag{1}$$

where T_{oi} is the melting temperature of the pure component i, T_i is the melting temperature of a mixture with molar fraction X_i of the i-th component, ΔH_i is the melting enthalpy of the pure substance i and R is the gas constant.

For the selection of materials giving low-melting mixtures, we used a very convenient parameter $T(1/2)$ which is presented in the last column of the Table III. $T(1/2)$ is a characteristic melting temperature

TABLE III

Thermal properties of the investigated materials

Material No	Molar weight	Melting point	Latent heat	T_{CA} (T_{CN})	$T(1/2)$
	g	°C	kj/mole	°C	°C
1	456	40	31.5	28	22
2	470	44	35.0	35	28
3	484	38	35.3	37	23
4	468	73	34.6	78	54
5	412	48	21.1	43	22
6	440	45	33.4	47	28
7	426	36	19.2	(47)	10
8	468	39	38.8	(51)	25
9	468	38	26.2	70	18
10	438	84	24.1	86	58
11	532	95	22.6	(115)	63

(real or fictitious) calculated from the van Laar equation for a mixture in which the molar fraction of a given substance equals 0.5. $T(1/2)$ takes into account the effect of both T_o and ΔH for any pure substance and is independent of the second mixing component. It thus describes the a priori ability for any substance to depress the melting temperature in a mixture. In the case of substances possessing metastable solid modifications, the highest $T(1/2)$ value was chosen.

The van Laar equation (1) was also used for calculating the eutectic temperature and concentration. Both parameters agree quite well with the values obtained from the investigations of contact preparations and calibrated mixtures, which is clearly seen from Figure 2, where some examples of phase diagrams are shown.

On the basis of the described two-component systems some mixtures were chosen as the new basic mixing components used for making three- and four- component compositions, in which other parameters like the upper limit of the C* phase, the spontaneous polarization, or the pitch, were optimized. Examples of binary starting mixtures are the eutectics of (2) and (5), (5) and (7), (6) and (9), (4) and (5), and (3) and (5).

VI. MULTI-COMPONENTS MIXTURES

The basic low temperature mixtures generally have sufficiently low melting temperatures to be useful. Thus, the next parameter to be optimized was the upper limit of existence of the C* phase. It was

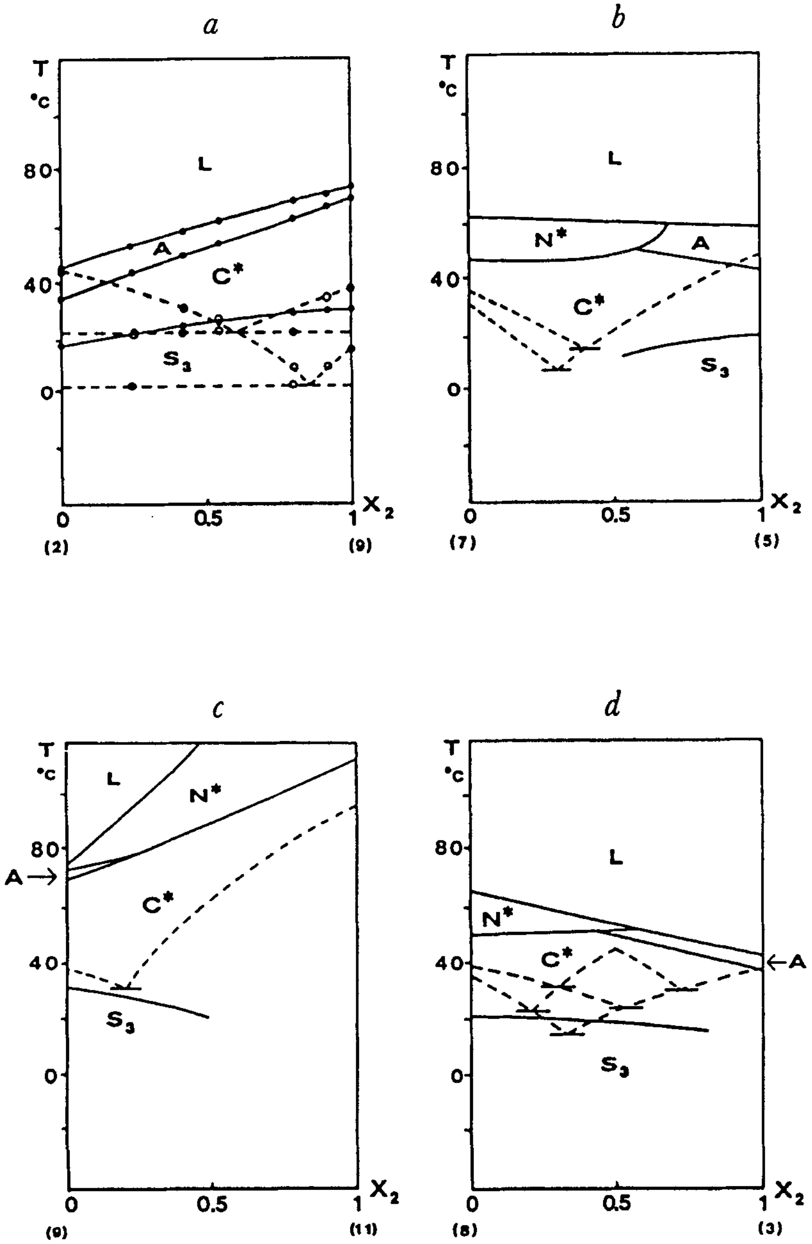


FIGURE 2 Examples of phase diagrams of binary mixtures. The substances are identified below each diagram. The diagram *d*) shows an example of mixed crystals formation.

achieved by adding a third component, which was one of the substances (4), (10) and (11). In this manner the range of the C* phase has been extended up to 60 degrees in some cases. The addition of the third component lowered simultaneously the melting point. To achieve the maximum lowering of the melting point the actual composition was close to the eutectic composition. The method of approximate determination of the eutectic composition used in this work is illustrated in Figure 3. Here the ternary composition diagram for components A, B, C is shown. The eutectic concentrations of each pair of components, known from two-component mixture investigations, are marked on the triangle sides. Then the lines of constant concentration ratio for each pair is plotted (lines $A - X_{BC}$, $B - X_{AC}$, $C - X_{AB}$). Those three lines create a small triangle inside the concentration triangle ABC. The center of gravity of this small triangle can be assumed to represent the approximate eutectic composition of the three-component mixture.

Eutectic two-component mixtures of substances having high temperature smectic C* phases were also prepared. After mixing some of them with the low-temperature basic mixtures we obtain low-

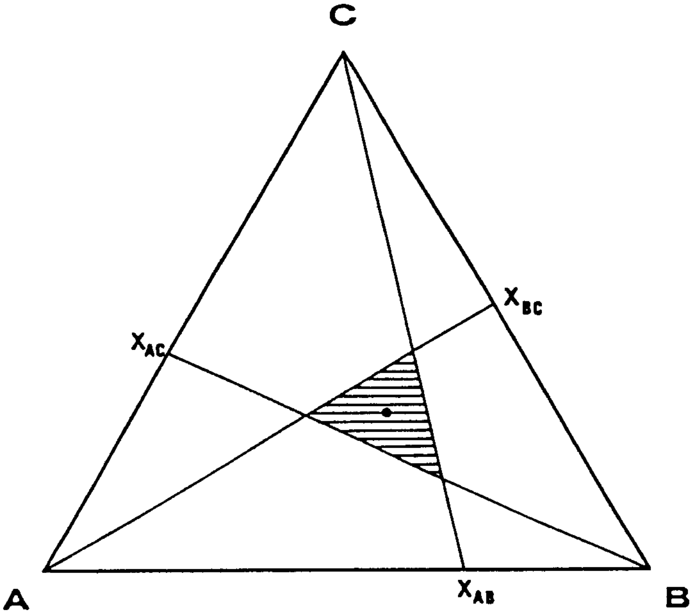


FIGURE 3 Illustration of the approximate method used for determination of eutectic composition of ternary mixtures.

melting four-component systems with broad range of existence of the Sm C* phase. The phase transition temperatures of some three- and four-component mixtures are shown schematically in Figure 4. In the following Table IV compositions of the mixtures shown in Figure 4 are given.

Choosing the composition we took into account the sign and value of the spontaneous polarization and the handedness of the helix of each component in order to achieve large values both of the polarization and of the helical pitch.

VII. DISCUSSION

Some multicomponent mixtures presented have properties which make them suitable for technical applications in liquid crystalline displays and matrices. The existence region of the smectic C* phase could be brought to a range of about 50 degrees. The mesophase range has been extended down to below −25°C, which in practice means, that

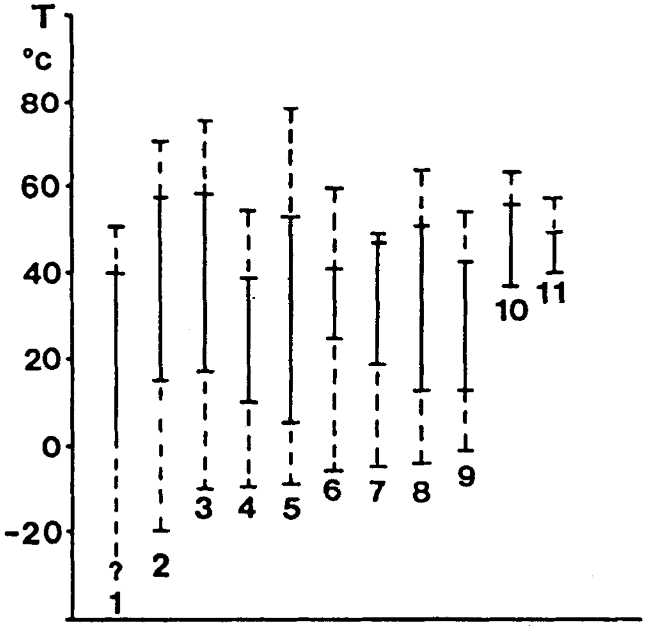


FIGURE 4 The diagram of transition temperatures for some ternary and quarternary mixtures. The number shown below each line refers to the Table IV. Dotted lines go from melting point to clearing point with the solid part showing the stable smectic C* range. The melting point of the mixture 1 lies below −25°C.

TABLE IV

Compositions of some ternary and quarternary mixtures

Mixture No (Figure 4)	Substances used	Composition
1	(1), (5), (7)	35:33:32
2	(3), (7), (10)	30:38:32
3	(5), (7), (10)	50:17:33
4	(3), (5), (7)	29:39:32
5	(3), (5), (7), (11)	25:32:26:17
6	(3), (4), (5)	44:15:41
7	(3), (4), (5), (8)	26:11:30:33
8	(3), (5), (8), (11)	32:27:30:11
9	(3), (5), (8)	36:31:33
10	(3), (4), (8)	33:15:52
11	(3), (8), (9)	51:35:14

the melts never crystallize. The upper limit of the C* phase is still not satisfactory. The preliminary check of electrooptic behaviour shows that the switching times are of the order of 100 μs or less.

There are, however, still many problems to be solved. Probably, the most serious is that of a high-order smectic phase (generally called S_3 in our schemes) lying below the smectic C* phase. Most substances used in the present investigation exhibit these phases, which also normally appear in the mixtures. If the low temperature phase is another tilted phase (for instance F^* or J^*), the problem may not be serious, but if it is non-tilted (as for instance smectic B), this drastically limits the usefulness of the mixture at low temperatures. The miscibility of the high-order smectic phases of different components is here of great importance. If those phases are miscible, one can expect an approximately linear dependence of the transition temperature on concentration, with little gain on mixing, as illustrated in Figure 5a. If they are immiscible the broadening of the C* phase downwards may be achieved in many cases, as illustrated in Figure 5b.

In practice, the identification of the low-temperature smectic phases is difficult. The differences between some of the high-order phases are relatively subtle and the information obtained from microscopy and calorimetry is normally not sufficient for uniqueness. Thus the identification has been done in a few cases only, when simultaneous microscopic, calorimetric and miscibility investigations were possible. Work below room-temperature demands, however, special equipment. In addition, some unexpected phenomena may appear in the

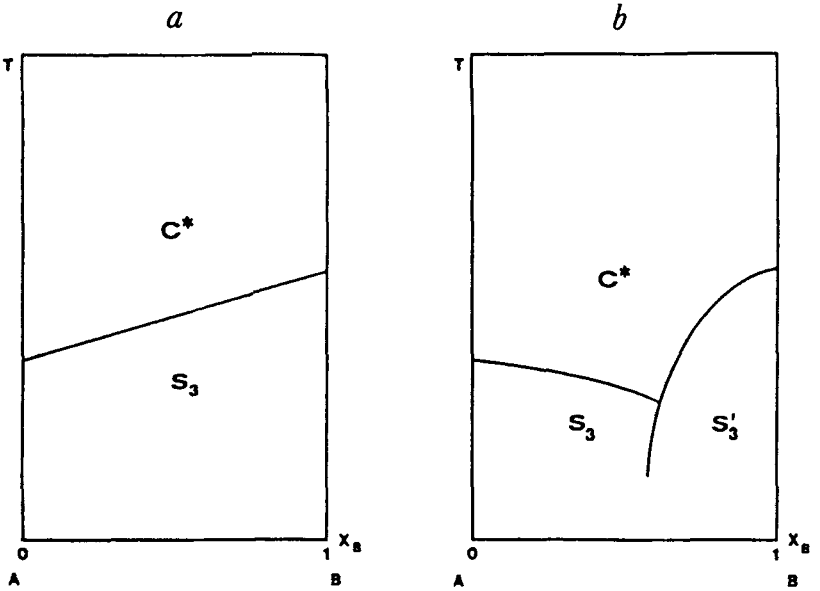


FIGURE 5 Schematic binary phase diagrams for miscible (a) and immiscible (b) high-order smectic phases.

phase diagram, like hidden and induced phases, metastable solid phases and mixed crystals.

VIII. CONCLUSIONS

Besides being fast-switching at low temperature, the substance compositions for the basic mixtures presented below respond to the following demands:

1. They are non-coloured.
2. The C* phase is thermodynamically stable.
3. The upper temperature limit is reasonably high, 44–45°C.
4. The lower temperature limit is reasonably low, 15–20°C, highly supercoolable, and easily extendable down to lower temperatures by very small additions of other substances.
5. $\Delta\epsilon < 0$, but not of too large magnitude.
6. They show good aligning properties both with polyimide and silane coatings.
7. They have a long helical pitch Z, larger, or typically much larger than the typical cell thickness, both in the working phase (C^*) and the alignment phase (N^*).

Acknowledgments

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