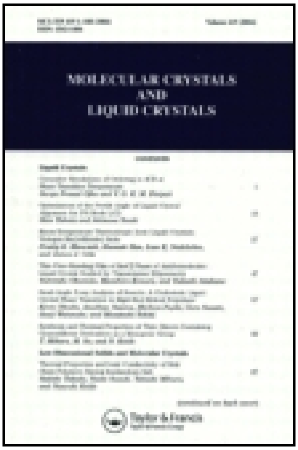

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NEW THERMAL MEMORY EFFECT IN CLC

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Abstract A new thermal memory effect in high-melting cholesteric compositions is described

INTRODUCTION

The isotropic state memory effect in cholesteric liquid crystals (CLC) has been known[1] for a long time and studied sufficiently to understand the physical phenomena underlined[1-4] and to recognize the possibilities for practical applications[2,3,5]. The effect is based on the ability of CLC to form two types of texture with different optical properties and different time stability; these types are: (i) a planar texture exhibiting a property of selectively reflecting the light, which makes the CLC layer appearing colored, and (ii) a metastable confocal texture exhibiting a property of strongly scattering the light, which makes the CLC layer appearing milky. The metastable confocal texture can be formed in the course of cooling of the isotropic CLC phase; with the time, it transforms to a stable planar texture[1-4]. The thermal memory of CLC, thus, manifests itself as a property to exhibit a time delay in the color response of a cooling CLC layer. The CLC exhibiting the thermal memory effect permits one to record only a single isothermal line corresponding to the clearing temperature of the CLC (T_{cl}) or to a certain temperature exceeding T_{cl}. Such CLCs can be effectively applied for vizualizing and storing thermal information on locally heated surfaces[3-5].

Recently, in studies of high-melting (with T_{cl} up to 200 ^{o}C) thermal-sensitive CLC compositions capable of becoming strongly supercooled, we found that some of these compositions exhibit, in addition to the property of isotropic state memory, a property of memorizing a non-uniform surface temperature field in the form of a series of colored bands with distinct boundaries corresponding to particular isotherms. In the present paper, we describe the new memory effect in some detail.

EXPERIMENTAL

Materials Characterization

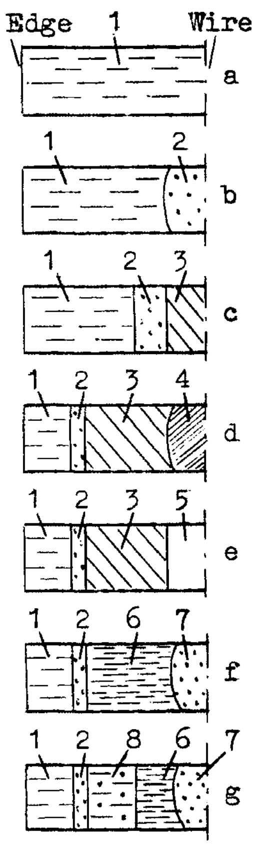
In this study, use was made of specially developed four-component nematic-cholesteric compositions containing up to 85 wt.% of various derivatives of cholesterol and to 15 wt.% of a nematic compound with positive dielectric anisotropy. The compositions' T_{cl}'s ranged between 130 and 165 ^{o}C. The mixtures were thermal-sensitive and displayed the whole color spectrum while heated to T_{cl}. Upon cooling of a molten sample of such a CLC composition to the room temperature, there is formed a very viscous and sticky, colored cholesteric phase which is glassified upon further cooling to negative temperatures (of -20^{o}C and lower). In thin layers, the supercooled cholesteric phase is even more viscous and adheres to the glass slides in such a way that can hardly be deformed (e.g., by shifting the cover glass). If, yet, the displacement can be made, the uniformly colored cholesteric phase transforms to a turbid light-scattering state which appears to be smectic.

Specimens for Investigation

The cells for studying the thermal behavior of the above CLC compositions were made of two glass slides separated by spacings of 10 to 50 microns thick. The cell was filled by the CLC composition heated to above T_{cl} through the use of the capillary effect. To ensure the uniform coloration of the CLC layer, the upper slide was shifted (or pressed) slightly at a temperature 5 to 10 °C below T_{cl}; then the cell was moved away from the hot stage used and left to stay at a room temperature.

Heating Procedure

The samples prepared in the above way were heated from below by means of a nichrome wire (70 to 150 microns in diameter); the cell was held at a temperature "T_{room}" which could be varied from ~20 to 30 °C (though kept constant during a specific run). Under these conditions, a moving thermal "front" could be seen on the surface of the CLC layer upon heating, which was running from the center (wire heater) to the edges of the cell. The horizontal temperature gradients in such an arrangement could reach several tens of °C.



Results

Figure 1 schematically illustrates the dynamics of color changes observed upon locally heating and subsequently cooling a CLC layer in the above cell.

The initial state of the CLC layer is a red, uniformly colored cholesteric phase (1 in Fig. 1). In a few seconds after the heater is switched on, there appears an oval zone in the center of the cell over the heater, which corresponds to the light-scattering state of the CLC (2 in Fig. 1b); this turbid whitish zone 2, initially of about 6 mm wide, extends to the cell edges upon further heating, while in the center a transparent green colored zone 3 appears (Fig. 1c) and widens gradually, until a

FIGURE 1 Schematic illustration of color changes upon local heating (a to e) and cooling (f, g) of CLC layer. The patterns are plane-symmetrical, so only left sides are displayed. For designations, see text thin (~ 1 mm wide) whitish zone ("oreol") remains between the red and green zones (2 in Fig. 1c). With increasing temperature, the front of this green zone, along with its whitish oreol, is moving to the cell edge, but eventually the position of this boundary becomes stabilized at a certain distance from the center (Fig. 1, d-e), and only changes within the green zone occur with the further increase of temperature: first, a blue zone 4 (Fig. 1d) appears in the center; then, this becomes violet and, at last, colorless, when T_{cl} is reached (Fig. 1e). In the result, the surface of the CLC layer becomes broken up to a number of stable zones with clear boundaries between them.

When the heater is moved away and the cell is left to cool down to T_{room}, zone 3 becomes dark red (6 in Fig. 1f) in a fraction of a second. In the next 2 to 10 min, a new zone is formed within the dark red zone 6, and some other color changes occur. Finally, a stable zonal picture is established, with the following series of colored zones (Fig. 1g): (i) turbid whitish (zone 7); (ii)dark red (zone 6); (iii) orange (zone 8); (iv) whitish "oreol" (zone 2); and (v) red (zone 1). The first of these (zone 7) corresponds to the known property of "isotropic state memory"; all the other zones (ii to v) are concerned with the new memory effect (see Figure 2).

Figure 1 displays the most reproducible patterns observed in experiments. In particular cases, the zonal picture may be different depending on the specific conditions of the experiment and properties of the composition used; it is determined by a whole number of factors such as the rate and maximum temperature of local heating; the average temperature of the cell; the cooling procedure, etc. For instance, upon heating at a slow rate (for 20-30-60 s), the green zone 3 becomes wider than in Figure 1c; upon cooling, one to three additional zones may appear within zone 6, each surrounded by a narrow whitish oreol.

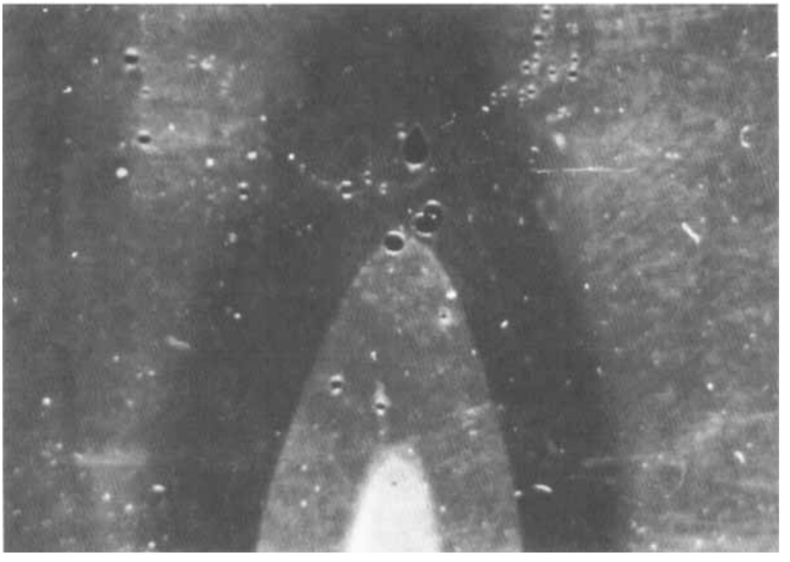
If the maximum temperature in the zone of local heating is below T_{cl}, the new memory effect is exhibited in the pure form, with no zone of isotropic state memory appearing (Fig. 2b, see Color Plate). The zonal color patterns such as displayed in Figure 2, are stable for months when holding at T_{room} below ~ 25 °C, but gradual alterations appear (in color, transparency, contrast of boundaries, etc.) if T_{room} exceeds 25 °C.

Microscopic Study

Figure 3a displays the texture of a starting layer. In the general case, however, this may be different, depending on the thickness and forming procedure of the CLC layer in the cell. This may be the well-known texture of confocal domains; in thick layers (above 50 µm), this may be a fine-grained texture similar to that observed in Fig. 3d; in thin layers (5 to 15 µm), elongated filaments and short bands can occur (such as in Fig. 3a or in Fig. 3b, left), resembling rope scraps at higher magnifications.

In locally heated samples examined immediately after the stable zonal picture has been established, a striated texture (such as in Fig. 3b, left) is observed in all the zones except for the zone of isotropic melting (Fig. 3b, right). In the microscope, the clear boundaries are observable only between the zone of isotropic melting and dark red zone (Fig. 3b) and in thick layers (Fig. 3d).

In samples left to stand under the ambient conditions, various texture changes occur (at T_{room} above 25 °C, in particular) to result in the formation of striated textures of various complexity (striated confocal domains, finger-print and polygonal patterns, etc.), an enhancement of texture distinctions in the zones and, as a consequence, more easily observable boundaries between the zones (Fig. 3c). When kept for 40 days at T_{room}, even more complex textures are formed such as terrace-like patterns with paired bands (Fig. 3e), double spirals (Fig. 3f), polygonal textures with double spirals, etc. In the result of all these changes, the macroscopic appearance of the layer (zone colors, transparency, etc.)becomes changed, too.



See Color Plate IV   Gorina et al., Figure 2a

See Color Plate V   Gorina et al., Figure 2b

FIGURE 2 Zonal pictures of locally heated CLC layer

(a) Local heating to above T(clear). Central whitish region is due to the well-known effect of "isotropic state memory"; the other zones are due to the new effect of the "temperature field memory".

(b) Local heating to below T(clear). The new memory effect is exhibited in the pure form, with no zone of isotropic memory.

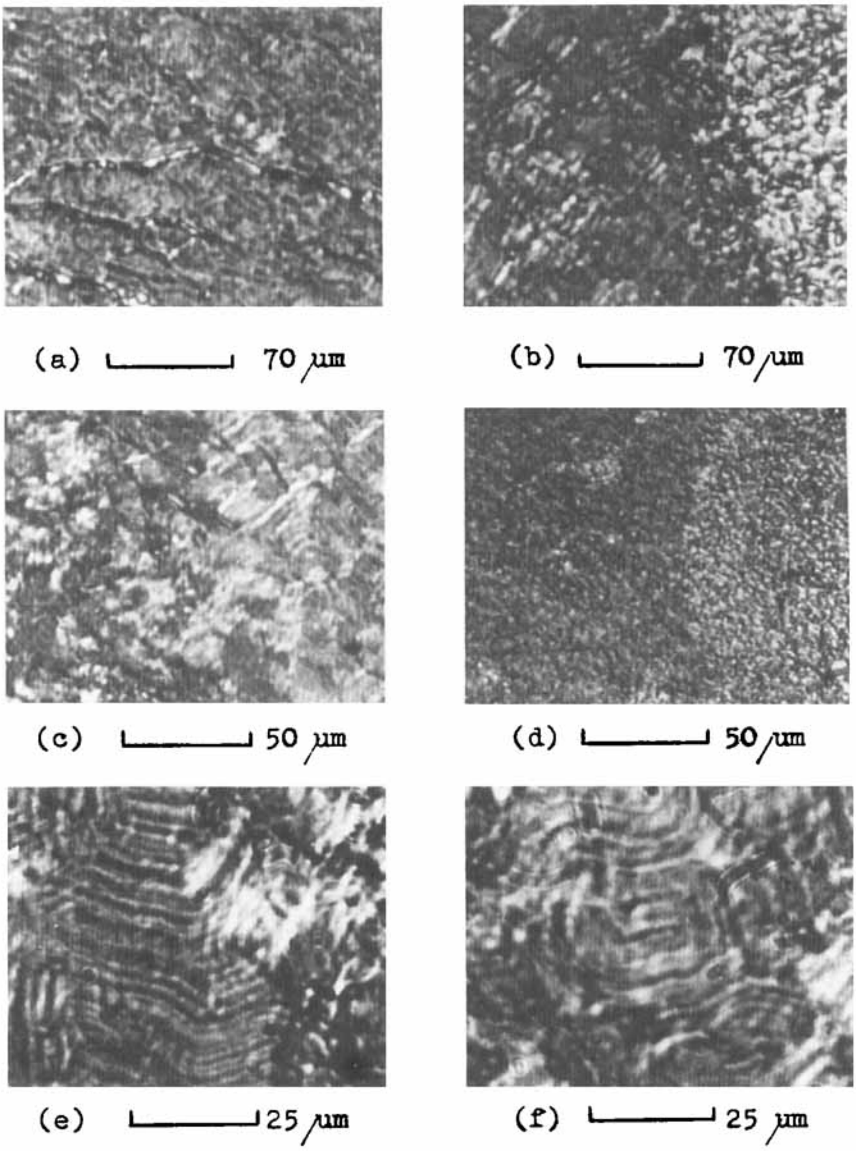


FIGURE 3 Microscopic patterns from various zones
(a) Texture of starting sample. (b) Texture of light-scattering whitish zone 7 (right) and short bands in dark red zone 6 (left). (c) Short bands in zone 6 (left) and "finger-print" type pattern in zone 8 (right).
(d) Boundary between zone 6 and zone 8 in thick layer.
(e) Terrace-like pattern consisting of paired bands.
(f) Double-spiral pattern

CONCLUSIONS

From the above experiments it may be suggested that the new memory effect observed in nematic-cholesteric liquid crystal compositions, is to a large extent determined by the structurizing processes induced by non-stationary temperature gradients. Under these conditions, a structurally inhomogeneous cholesteric phase may be formed, with a variable helix pitch depending on the value of the temperature gradient.

The temperature-gradient effects on the behavior of liquid crystals have been described in a number of works (Refs 6 to 10). It has been found[6] that reversible structural instabilities of the band type occur in the smectic-A phase as a result of dividing of the confocal domains into groups of layers. Stable bandlike textures in smectic A have been described in Ref.7; the "memory effect" was explained in terms of stability of systems of disclinations and dislocations. Instabilities of planarlike texture with various helix pitches have been observed in compensated cholesterics.[8] Oswald et al.[9,10] have studied the behavior of phase interfaces. In smectic-cholesteric mixtures of 4-(*n*-octyl)cyanobiphenyl (CB) with 3 to 10 wt.% of cholesteryl nonanoate (CN), it was observed that on moving a thin layer of the mixture through a region of constant temperature gradient from the "hot" to "cold" region, a narrow nematic zone was formed between the cholesteric and smectic zones and four types of structural instability were observed in the cholesteric phase near the interface. The behavior of the mixtures on cooling has not been studied.

It should be noted that the CB+CN mixtures studied by Oswald et al.[10] may, even on cooling under normal conditions, i.e. with no temperature gradient, undergo various texture changes and exhibit relaxation effects, which plays an important role in thermooptical phenomena.[11] It was of interest for us to test these compositions in our experimental conditions. A stable pattern has been obtained on the layer surface; it had the form of a series of colorless whitish zones (of various degrees of turbidness) divided by colorless transparent bands. The whitish zones consisted of scattering confocal domains of the smectic phase, while the transparent bands, of homeotropic smectic.

The nematic-cholesteric mixtures studied in the present paper are multicomponent systems containing liquid-crystal compounds with different molecular structure and properties; because of their tendency to become supercooled, these systems readily give nonequilibrium states and appear to be capable of exhibiting the reentrant behavior. The temperature gradient can induce in them instabilities of various types, texture transformations, etc., similar to those observed in smectic-cholesteric mixtures.[10-11]

In order to understand the behavior of these complex systems in temperature-gradient fields and to elucidate the physical nature of the memory effect revealed, further investigations are necessary and are in progress in our laboratory.

REFERENCES

1. R.A. Soreff, J. Appl. Phys., 41, 3022 (1970).
2. H. Melchior, F. Kahn, D. Maydan and D. Fraser, Appl. Phys. Lett., 21, 392 (1972).
3. P.L. Carrol, Cholesteric Liquid Crystals, Their Technology and Applications (Ovum, London, 1973).
4. A.G. Kleopov, M.V. Kurik, O.D. Lavrentovich and V.G.Tishchenko, Zh. Fizich. Khimii, 56, 2422 (1982).
5. G. Meier, E. Sakmann and J.G. Grabmaier, Applications of Liquid Crystals (Springer, Berlin et al., 1975).
6. M. Fernandez, Atti Fondaz. G. Ronchi, 38, 112 (1983).
7. A.P. Kapustin and S.A. Pikin, Wiss. Beitr. M.-Luther-Univ. Halle-Wittenberg, No. 12, 86 (1983).
8. N. Eber, Undulation Instability in Compensated Cholesterics (Central Research Institute for Physics, Hungarian Academy of Sciences, Budapest, KFKI-1984-86), p. 1-12.
9. P. Oswald, J. Bechhoefer and A. Libchaber, Phys. Rev. Lett., 58, 2318 (1987).
10. P. Oswald, J. Bechhoefer, A. Libchaber and F. Lequeux, Phys. Rev. A: Gen. Phys., 36, 5832 (1987).
11. N. Nawa and W.-r. Liu, Japan. J. Appl. Phys., 28, 1206 (1989).