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Dynamics of Texture Transitions in Cholesteric-Nematic Mixtures†

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Several time-dependent electro-optical properties of a cholesteric-nematic mixture have been investigated. In particular, the dynamics of the Grandjean ⇆ focal conic texture transitions have been characterized. A cholesteric-nematic mixture was used comprising molecules having a net tendency to align with their long axes perpendicular to the applied field, allowing the study of the field induced focal conic ↠ Grandjean transition. D.C. electro-hydrodynamic effects were employed in the investigation of the Grandjean ↠ focal conic transition. The driven and relaxation properties of the electro-hydrodynamic induced transition are described. Also, the memory properties of intermediate textures of this transition are discussed. Thickness is found to play a crucial role in the relaxation of the textures. The time to achieve the electro-hydrodynamic induced texture transition (Grandjean ↠ focal conic) is found to be controlled in a non-linear fashion by applied voltage and only weakly by current. For the field induced focal conic ↠ Grandjean transition, it is determined that the transition time varies inversly with the cube of the applied voltage in the material studied. Furthermore, the transition time is found to be a strong function of sample composition, increasing rapidly with cholesteric content.

INTRODUCTION

Films of cholesteric liquid crystals (or mixtures of mesomorphic and/or non-mesomorphic molecules which produce cholesteric behavior) exhibit two stable states called textures.[1] The macroscopic optical properties of these textures are quite different. The Grandjean texture is characterized by dispersive reflection, dispersive optical activity and reflective circular dichroism, whereas the focal conic texture typically appears diffusely scattering. It was recently shown[2] that this distinction is based on domain distribution and that in both textures the

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local molecular symmetry is helical. A third state, observable under certain conditions, and called the homeotropic texture will not be discussed here. In the Grandjean texture, these birefringent domains are oriented such that their screw axes are all approximately parallel (a more complete description would involve order parameter considerations and goes beyond the scope of this treatment) and approximately normal to the substrate. Consequently, at domain" boundaries there is no discontinuity of index of refraction and, in fact, it is not clear to what extent domain boundaries exist. In the focal conic case, the domains are easily observed microscopically and exhibit the anticipated optical properties. In large pitch materials, it is even possible to see a manifestation of the periodic variation of index of refraction within one domain. Domain boundaries represent discontinuities in index of refraction which give rise to diffuse scattering. In addition to this diffuse scattering which causes the focal conic to appear white, the focal conic can exhibit dispersive reflection in the visible when the inversion wavelength is in the infrared.

EXPERIMENTAL

The cells used in the study were of the conventional sandwich layer type utilizing indium oxide coated glass electrodes and Mylar spacers. The material used was 80 wt. % MBBA and 20 wt. % cholesteryl oleyl carbonate, unless otherwise noted. When the turbulent motion is suppressed, the 80/20 mixture has the general tendency of aligning with its helical axis parallel to the field.[3] Electrical stimulus of the cells was provided by either a pulsed D.C. source or a gated A.C. supply.

The 80 wt. % MBBA and 20 wt. % cholesteryl oleyl carbonate mixture has a pitch of approximately 0.5 microns. The dielectric constants of this mixture are expected to be close to those of MBBA,[4] if geometrical factors are taken into account.

The optical arrangement consisted of a Leitz microscope with an attached photodiode to monitor the white light transmission of the cells at a numerical aperture of 0.1. Experimentation indicated that for the material studied, essentially the same results are obtained with monochromatic light. In studying these transitions, two classes of experiments can be performed. The first, reported here, involves collecting the unscattered signal and a fraction of the scattered signal. In general, results depend on numerical aperture, sample dimensions, etc. Therefore, this study relates more strongly to device aspects where finite apertures must be used.

The second method consists of separately measuring the scattered and unscattered signals. This is best done using laser illumination where both the beam diameter and numerical aperture are small. This procedure more accurately probes the microscopic nature of the transitions and will be reported in a separate publication.

Characteristic transformation properties

The application of a D.C. electrical stimulus can cause a hydrodynamic effect converting an initially clear Grandjean texture to the scattering texture.[5,6,7,8] The concomitant change in light transmission during the conversion is illustrated in Figure 1. The relatively clear Grandjean texture is considered the unity transmission level. After a characteristic time, a turbulent scattering condition exists as in conventional dynamic scattering.[9] However, when the stimulus is removed, the liquid crystal relaxes to the light scattering focal conic texture. If the stimulus is removed too quickly, an intermediate texture is retained.[10] The intermediate texture may have varying degrees of memory and light scattering capability, depending on the amplitude and duration of the electrical stimulus. When the degree of transformation is small, the texture appears as localized focal conic islands in a Grandjean sea. As the transformation nears completion, the interpretation becomes less clear as adjacency effects become apparent.

In Figure 2 the general transformation properties of the electro-hydrodynamic induced Grandjean ⟶ focal conic transition are summarized in a composite plot. The driven, memory and relaxation characteristics are shown. The driven response is characterized by an initial overshoot as in dynamic scattering in pure nematics. After the drop, there is a continuous decrease in the transmission asymptotically approaching a steady state value. The top curve shows the memory levels to which the liquid crystal will relax if the stimulus is terminated at the corresponding time shown on the x axis. In these experiments, the transmission

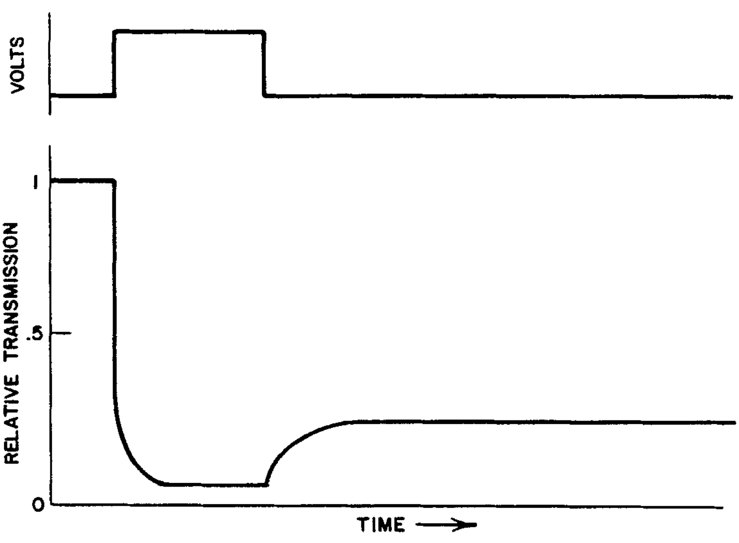

FIGURE 1 Illustration showing optical response to voltage pulse.

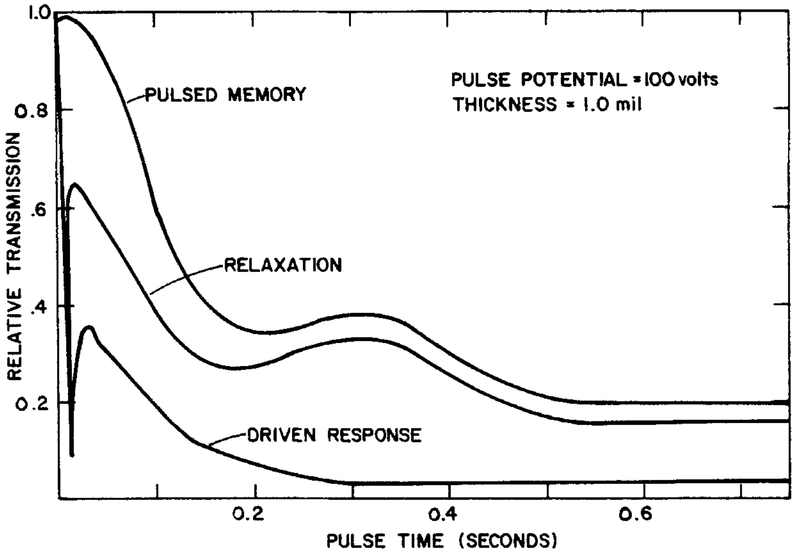

FIGURE 2 Composite transition curves for a numerical aperture of 0.1.

was recorded 15 seconds after removal of the stimulus by which time the texture stabilized. The middle curve is the difference between the upper and lower curves and represents the relaxation which occurred. Note that the relaxation is largest when the degree of transformation is the least. Also, an anomalous bump is observed in the relaxation and memory curves. It is apparent that this is a relaxation characteristic.

In a series of pulse experiments, the memory properties of partially and fully transformed textures were investigated for a family of applied voltages. These results are presented in Figure 3. The unit transmission level again arbitrarily corresponds to the Grandjean texture, while the lowest transmission ($\simeq .18$) is indicative of a fully transformed focal conic texture. Note that every point on the curves below the minimum transmission level corresponds to a memory level for an intermediate texture. It is apparent that the lower voltages require disproportionally longer times to achieve the fully transformed focal conic texture. Thus, non-linearity in voltage is a characteristic of this transition.

Electro-optical reciprocity considerations

The transformation non-linearity between voltage and time also applies to current and time as this material shows virtually ohmic behavior. The resistivity of the mixture used was 5×10^9 ohm-cm; hence, the steady state current can be easily determined. The non-linearity in voltage (or current) can be represented in the form of a reciprocity relationship of electrical stimulus and time. Figure 4 is

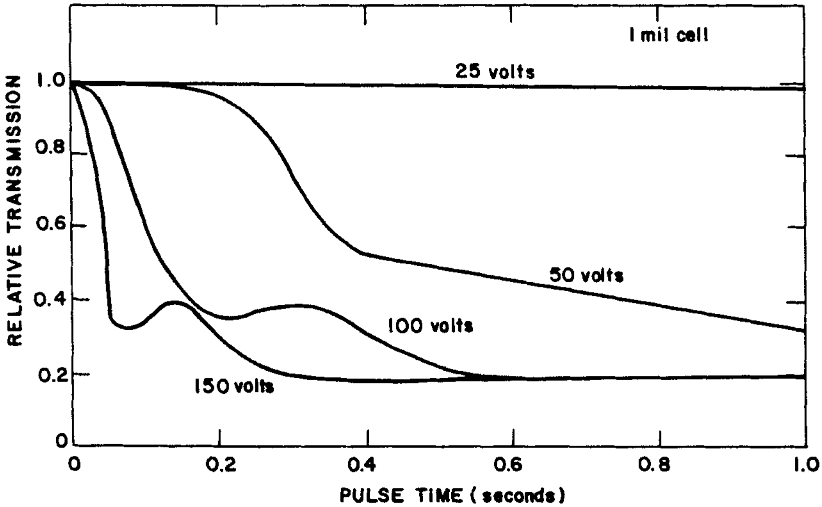

FIGURE 3 Transition curves showing influence of voltage.

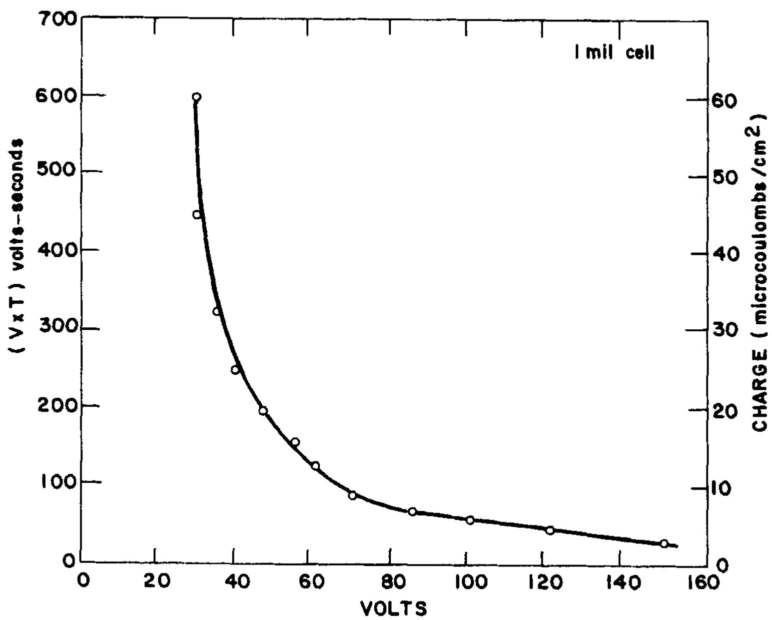

FIGURE 4 Voltage-time reciprocity relationship for complete Grandjean →→ focal conic transformation. Total integrated charge is also shown for a mixture of resistivity $5 \times 10^9\ \Omega$-cm.

a plot of this relationship for the complete Grandjean focal conic transformation. The abscissa chosen is the applied voltage. The voltage – time product to complete the transformation is shown on the left ordinate and the current–time product (or charge) on the right ordinate. If the transformation were a linear process, a straight horizontal line would be obtained. The plot by itself only shows that high voltages and/or currents require disproportionately less time to achieve the transformation. A natural question which follows is. . . what is the relative role of field and current in producing the transformation? Insight can be attained by varying the conductivity by doping. At a given applied voltage, the current can be varied by orders of magnitude. Experimentally, this was done by beginning with high purity MBBA and COC mixtures, and then doping with ionizable salts. The dopant used was tetraethylammonium bromide. Six doped samples were made which varied in resistivity between 8×10^{8} and 8×10^{10} ohm-cm. The high purity starting material had a resistivity of 1.0×10^{11} ohm-cm. Results from the six doped samples gave the same overall shape to the reciprocity curve shown in Figure 4. Very significantly, the *VT* values were not affected, whereas the *IT* values varied directly with conductivity. This results indicates that the transformation time is best correlated to the field, rather than to the current. Deviation from the conductivity independence was observed in the undoped sample (which has the highest resistivity). The shape of the reciprocity curve in that case changed and the sample became non-uniform in appearance. It is apparent that a minimum current must flow, but its absolute value has considerable latitude. It is also worth noting that the samples which had a resistivity in the high 10^{10} ohm-cm regime also suffered from lack of uniformity, but it was of insufficient degree to significantly influence the macroscopic scattering properties.

Relaxation properties

It is seen from Figure 2 that the degree of relaxation (tendency to return to the Grandjean texture after field removal) is greatest for samples which are only slightly transformed and lowest for samples which are almost completely transformed, etc. This characteristic is also observed for the field induced focal conic ↠ Grandjean transition. We now examine the effect of sample thickness on this phenomenon. Conceptually, this is demonstrated in Figures 5 and 6 for relatively thick (2 mil) and thin (1/2 mil) cells. The time scales in Figures 5 and 6 are such that the optical response (turbulent scattering) to the pulses appear as vertical spikes. Pulse amplitudes were scaled in an effort to provide similar stimulus for both cells; however, experiments indicated that this was not necessary to observe the general relaxation properties presented. For the thick cell (Figure 5), a considerable curvature can be detected in the relaxation transient. The curvature is observed to diminish as the sample approaches the complete Grandjean ↠ focal conic transition. This property indicates that the stability of the texture depends on the degree of transformation. It is interesting to note that the turbulent scattering associated with the pulse decreases in amplitude as the degree of turbulent scattering (in response to a pulse) depends on the textural composition of the film. Creagh[11] and Gooch[12] have made similar observations in pure nematics.

In Figure 6, it can be seen for the thin cell case that the stability of the intermediate texture also depends on sample thickness. Little or no curvature exists after the removal of the stimulus. This is most evident for small perturbations of the texture. It should be noted that these characteristics relate to the response (relaxation) of a mixed texture to a perturbation. Recently, Hulin[13] studied the storage properties of textures which had undergone the maximum

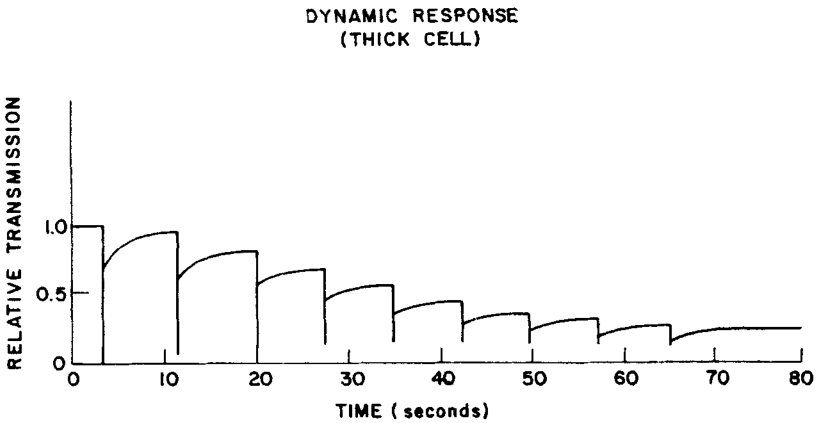

FIGURE 5 Response and relaxation of thick cell (2 mil) to periodic pulse stimuli.

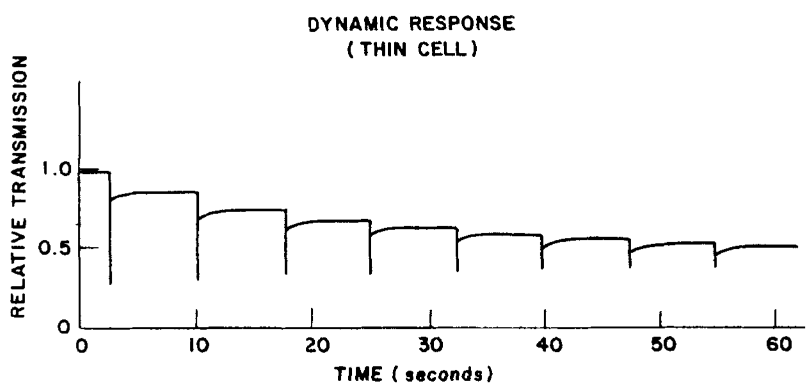

FIGURE 6 Response and relaxation of thin cell (1/2 mil) to periodic pulse stimuli.

degree of transformation. Dielectric measurements were employed to probe molecular distribution. In this case, the sample relaxes from a substantially complete focal conic texture in a characteristic time which is dependent on film thickness and pitch. This behavior is related to response to a perturbation, but only in an indirect fashion. In particular, in the Hulin experiment, a focal conic arrangement is created by an external magnetic field. The relaxation from the "field held" focal conic to the "field of" focal conic modulates the focal conic ↠ Grandjean relaxation.

FOCAL CONIC ↠ GRANDJEAN TRANSITION

A similar investigation was made of the focal conic ↠ Grandjean transition. Instead of using D.C. pulses to provide the stimulus, an A.C. field was gated on for variable lengths of time. Also, the peak amplitude was varied. The frequency of the applied field was held at 3KHz throughout the experiments to suppress turbulence effects, allowing field-dipole interactions to dominate, thus inducing the focal conic ↠ Grandjean transition.

Characteristic transformation properties

As in the reverse transformation, if the field is of insufficient amplitude or applied for too short a time, the transformation will be incomplete and an intermediate texture will result. Figure 7 is the characteristic transformation curve for the A.C. induced transition. The abscissa of this graph is the time a

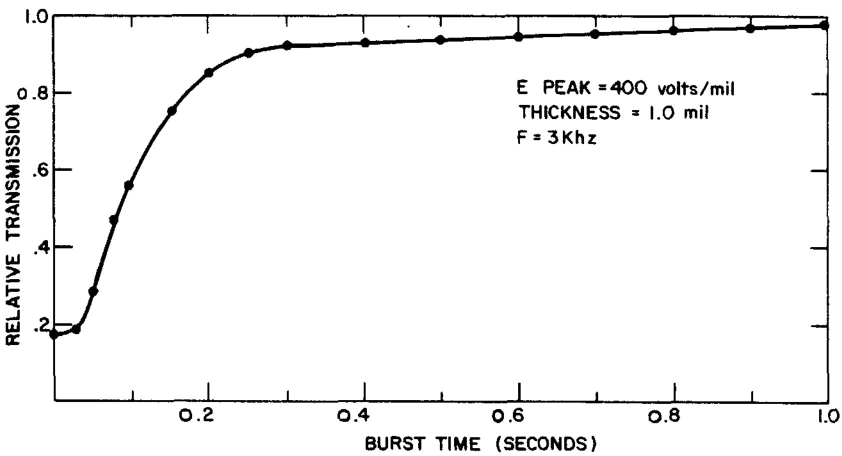

FIGURE 7 Characteristic focal conic↠Grandjean transition curve for a numerical aperture of 0.1.

constant amplitude A.C. field was applied. The ordinate is the transmission of the partially or fully transformed texture after removal of the stimulus. This is sufficient time for the texture to essentially stabilize. The last portion of the transition is the most difficult to achieves as the curve very slowly approaches the unity transmission level corresponding to the Grandjean texture. It has been experimentally observed that the degree of transformation (in the region of the curve where the transmission approaches unity) can influence a subsequent electro-hydrodynamic induced transformation to the focal conic texture.

Voltage dependence

The time dependence for near complete transformation was next investigated as a function of applied voltage. The time to reach 90% transmission was used to circumvent the mentioned difficulty in using a fully transformed Grandjean texture. These results are shown in Figure 8. A log-log plot of the same data

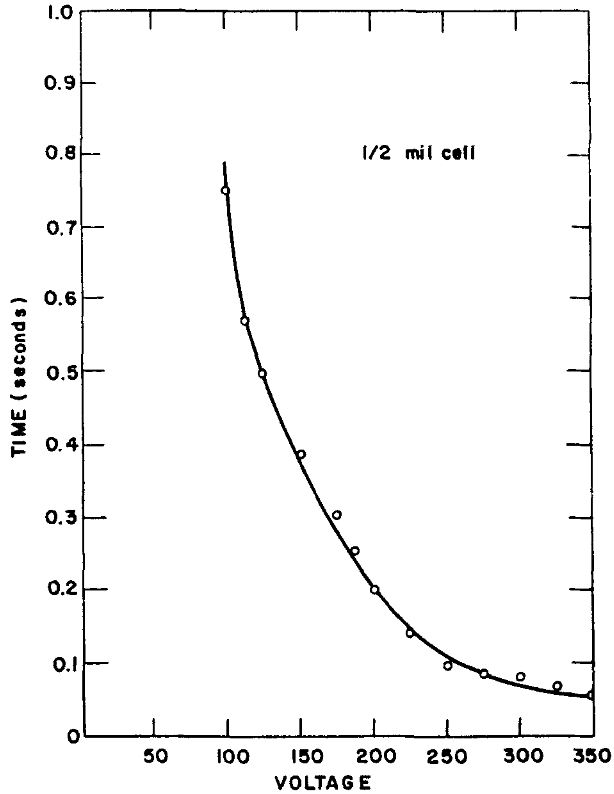

FIGURE 8 Influence of A.C. potential (peak) on focal conic →→ Grandjean transition.

gives a slope of approximately –3. This data was taken using a 1/2 mil cell. Experiments with other thin cells (> 1 mil) gave the same slope. Kerllenevich and Coche[14] have found in MBBA/cholesteryl nonanoate mixtures that the slope depends on the relative concentration of the constituents.

Materials dependence

The ratio of cholesteric-nematic liquid crystals in the cholesteryl oleyl carbonate/MBBA system has been varied and its influence on transition time determined. The field and sample thickness were constant throughout the experiment. Figure 9 is a plot of the results. A linear relationship is observed between cholesteric content and transition time for cholesteric additions up to approximately 20 weight per cent. The addition of further cholesteric material causes an abrupt increase in transition time. Obviously, viscosity and the net dipole moment must bare heavily on this transition property.

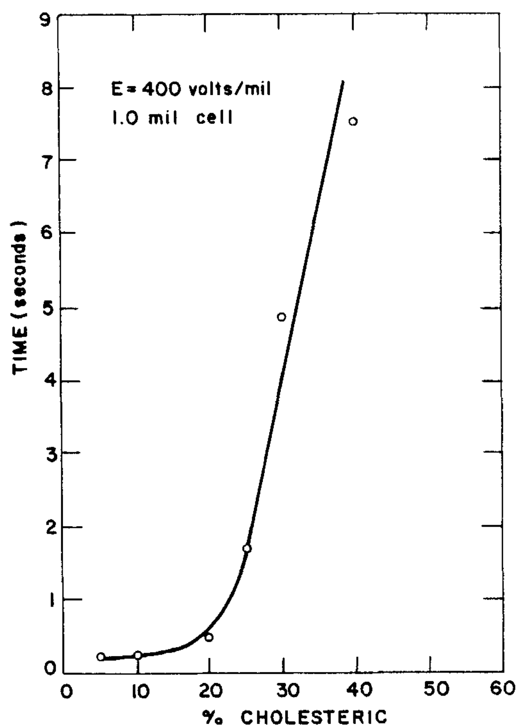

FIGURE 9 Transition time versus weight per cent of cholesteric ingredient.

SUMMARY

The electro-hydrodynamic and field induced texture transitions have been characterized for a certain cholesteric-nematic mixture. These transitions involve a dynamic re-arrangement of the molecules between two stable orientations. In addition, intermediate states are possible. These can appear as regions of focal conic and Grandjean orientation. The intermediate states (textures) are less stable in time than fully transformed textures. However, if thin cells are used, their stability can be considerably enhanced. The driven response of the textures are characterized by transition times which can be related to the applied potential in a non-linear fashion. Current is essential to the Grandjean ↠ focal conic transition. However, its absolute value (over wide ranges) does not significantly effect the transition time when the current is controlled by doping.

The A.C. induced focal conic ↠ Grandjean transition does not require current flow and can be explained in terms of field-dipole interactions. The time to undergo this transition was shown to be related to the A.C. stimulus by a power law. The role of the relative concentration of the constituents on this times was also shown.

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