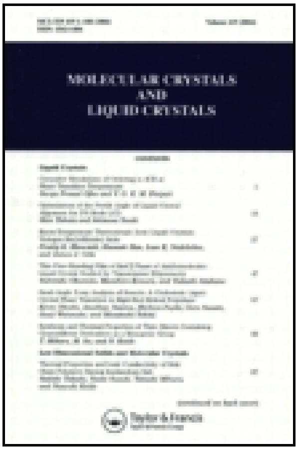
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Long Term Stability of Cholesteric Liquid Crystal Systems

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Long Term Stability of Cholesteric Liquid Crystal Systems

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Abstract—Aging cholesteric liquid crystals in various atmospheres resulted in little change in the temperatures at which their color responses occurred. However, the intensity of the color display was drastically reduced. Evidence is produced to show that the cholesteric plane texture is unstable in the presence of substrates and readily converts to another, which has the appearance of the smectic fan shaped texture, under the influence of a variety of stimuli, such as UV radiation, atmospheric contaminants, and substrate effects.

Introduction

The unusual optical properties of cholesteric liquid crystals have made these compounds very attractive from the point of view of practical applications. In particular, these materials are being considered for use in electro-optical devices. The usefulness of such devices is strongly dependent upon the reproducibility of the color response of these materials for a reasonable length of time. It then becomes important to identify the processes by which these cholesteric liquid crystals lose their color response with time so that steps can be taken to prevent or reduce these color losses.

Instrumentation

Any change brought about by aging, or external stimuli, is only relevant to our research if it affects the optical properties of the chosen liquid crystal system. For our purposes, the color response as a function of temperature was the phenomenon chosen as the criterion of aging effects. Figure 1 shows the thermo-optical apparatus used in this work to measure the temperature–wavelength characteristics of liquid crystal systems.

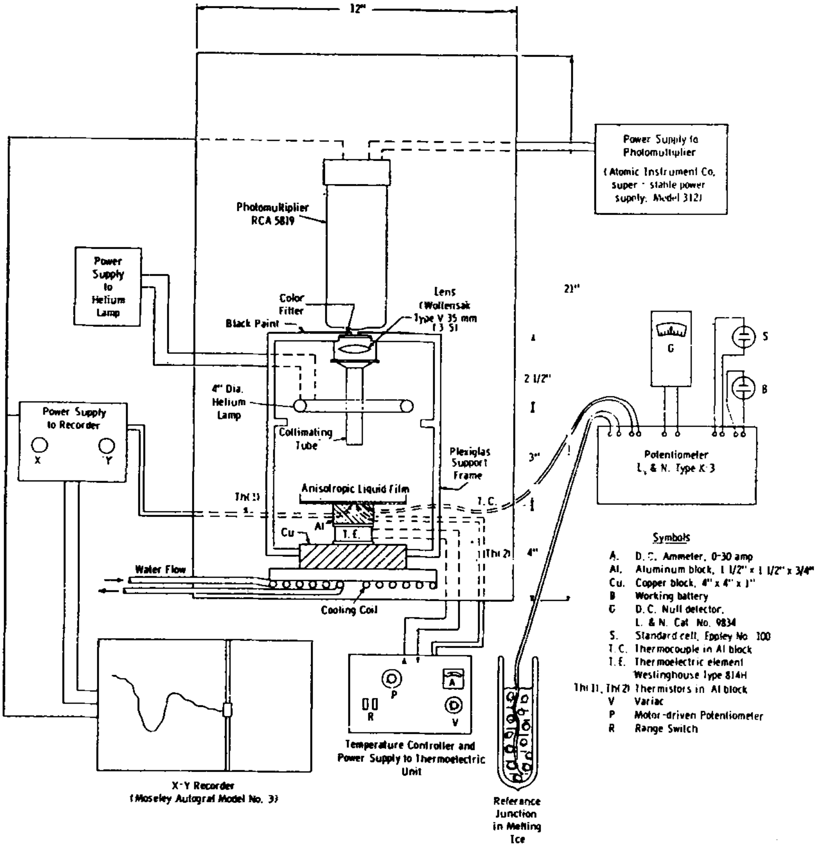

Figure 1. Thermo-optical apparatus

In particular, this apparatus indicated the temperature at which a test sample of a liquid crystal system reflected light of a known wavelength, usually given by a helium lamp.

The test samples consisted of brass hoops over which was stretched Mylar‡ film covered by a film of liquid crystal under examination. The samples were heated and cooled at controlled rates using a thermoelectric heating element. Simultaneously, light from a He lamp illuminated the surface of the film. The reflected light passed through a collimating tube, then through a filter, and was detected by a photomultiplier. This information was fed to an X–Y recorder from which a trace of temperature vs. intensity of reflected light at a given wavelength was obtained.

Experimental

The materials used in these investigations were oleyl cholesteryl carbonate (OCC), cholesteryl chloride (CC), and cholesteryl nonanoate (CN). These compounds were purified by repeated recrystallizations from hot methanol (CC, CN) or hot acetone (OCC) until the presence of impurities could not be detected by differential thermal analysis (DTA). Standard mixtures consisted of: OCC 44%, CC 27%, and CN 29% by weight.

Long Term Aging Effects in Different Environments

INTRODUCTION

Aging tests were carried out on the mixture described above in the form of thin films (*ca.* 20 μ) and in bulk. The bulk individual components were also aged separately in the same environments. The bulk materials consisted of 20 g aliquots which filled Petri dishes (3 in. diam.) to a depth of about 1 in. The dishes were loosely covered to prevent contamination by relatively large particles of atmospheric dust. Samples taken contained portions of the surface and of the body of the material. Two sets of aging conditions were used:

A. Room temperature, all light excluded, and atmospheres of (a) 21 : 79 oxygen : argon, (b) bottled air, (c) bottled air in the presence of 50% humidity, and (d) 0.001% carbon dioxide in argon.

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‡ Mylar is a trade name of E. I. duPont de Nemour Company for polyethylene terephthalate film.

B. Room temperature, in the presence of ultraviolet radiation and a 21 : 79 oxygen : argon atmosphere.

The materials were sampled periodically. The aged bulk ingredients were made into films and the aged films were tested as such. The most meaningful results were obtained using the thermo-optical screening device and DTA methods. Very interesting results were obtained by microscopic examination.

RESULTS

A. *Temperature Response of Aged Liquid Crystal Films*

Figure 2 shows the effect of aging liquid crystal films in four different atmospheres. After a common rise of about 5 °C in the temperature at which maximum reflectance occurred, which was later shown to be an instrument error, no further significant change in the temperature response of the films was observed with a total aging period of about 22 weeks. However, the intensity of the color responses decreased as a function of time, so that after only 10–12 weeks the color was difficult to detect. At 22 weeks or later most of the samples had lost all their response.

B. *Microscopic Examination of Degraded Films*

The deterioration of liquid crystal films manifested itself not only by diminished color response intensity but especially by the presence of craters which destroyed their homogeneity.

Initial observations of degrading liquid crystal films led one to believe that crater formation was associated with the presence of airborne, solid contaminants. Microscopic examination of many degrading films (aged 1 week to 6 months) showed that there were in fact foreign bodies (dust particles or fibers) in a great number of the craters which had formed. In one case, a crater was observed to have formed within half an hour of preparing a film. A large fiber was present in the center of this crater.

The larger craters ($\frac{1}{8}$ in. diam.) usually had a region that no longer contained liquid crystalline material, which had apparently migrated to the edges. One often gained the impression that a raised lip occurred at the periphery of these craters. Infrared

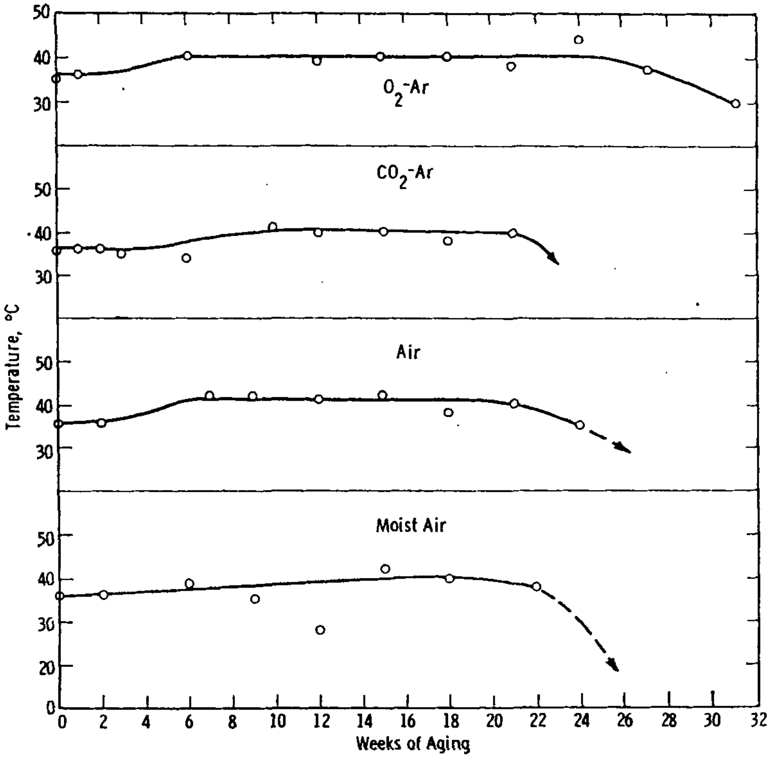

Figure 2. Effect of aging in various atmospheres of liquid crystal films on color response temperature (6000A peak).

spectra of material taken from the lip and the main body of material were not significantly different. Infrared analysis of the body of the crater showed only an intense spectrum of Mylar.

In the majority of cases where craters had formed, the following observations were made: There was a ring of small, focal-conic spherulites having definite boundaries inside and out (Fig. 3). The outside of this ring made contact with the main body of the liquid crystal which exhibited the cholesteric plane texture. In some instances the focal-conic spherulites rapidly diminished in size on approaching the center of the crater, especially when a foreign body was present. In such cases, the surfaces of massive inclusions were covered by liquid crystalline material.

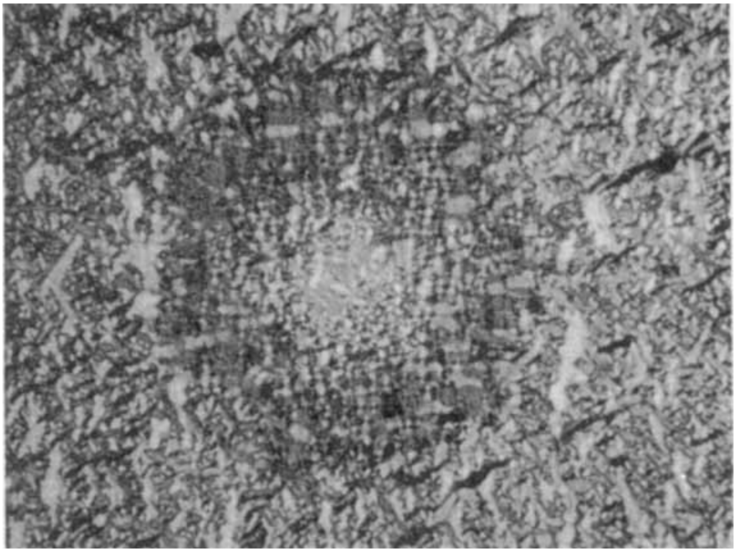

Figure 3. Ring of focal-conic spherulites (300μ diameter) in a cholesteric matrix.

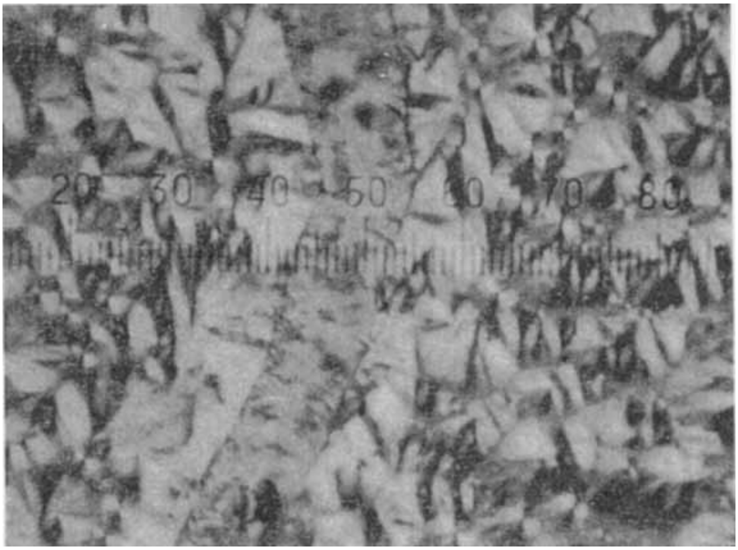

Figure 4. Fan-shaped structure in the immediate vicinity of a fiber (center). Magnification 380 ×.

Many smaller craters ($< 300\mu$ diameter) did not have a definite inner boundary and, occasionally, the focal-conic spherulites extended to the center of the disturbance. When this occurred, no visible foreign particle could be observed. It could be that, in these cases, migration of material had just started or, alternatively, the driving force which causes migration was not sufficient to give a dry crater.

The immediate effect of a foreign body, such as an airborne fiber, is to cause a drastic change in the orientation of the liquid crystal surrounding the impact area. This may then develop into a crater as described. An unusual situation, or possibly an intermediate state of degradation, occurred when a particular fiber made contact with a liquid crystal film. In this case the fiber caused a recognizable change from cholesteric plane texture to the fan-shaped smectic texture in the region surrounding the fiber (Fig. 4). In all other instances, the cholesteric plane texture was converted to the focal-conic texture.

The rings of focal-conic material mentioned above disappeared on heating the liquid crystal film, on which they were originally present, through its isotropic melting point. They spontaneously reappeared at the same loci on cooling.

C. *Temperature Response of Films Made from Liquid Crystal Components Aged in Bulk*

Although there was little or no change in the temperature responses of films made from bulk-aged materials, except perhaps in the oxygen-argon environment (Fig. 5), there was a drastic decrease in the intensities of these responses.

The intensity of a film response was compared with that of a film freshly made from materials stored in a refrigerator, having an arbitrary intensity of one.

The most impressive effect was that observed for samples bulk-aged in the oxygen-argon atmosphere (Fig. 6), especially when compared with the intensity of a film which was stored under nitrogen in the absence of light (as shown by the large dot on Fig. 6). The actual drop in intensity on aging is shown for a particular atmosphere (air containing 50% humidity) in Fig. 7.

DTA and IR studies of the aged bulk materials used in these tests revealed no significant changes in the transition points of the chemical composition of each of the three components.

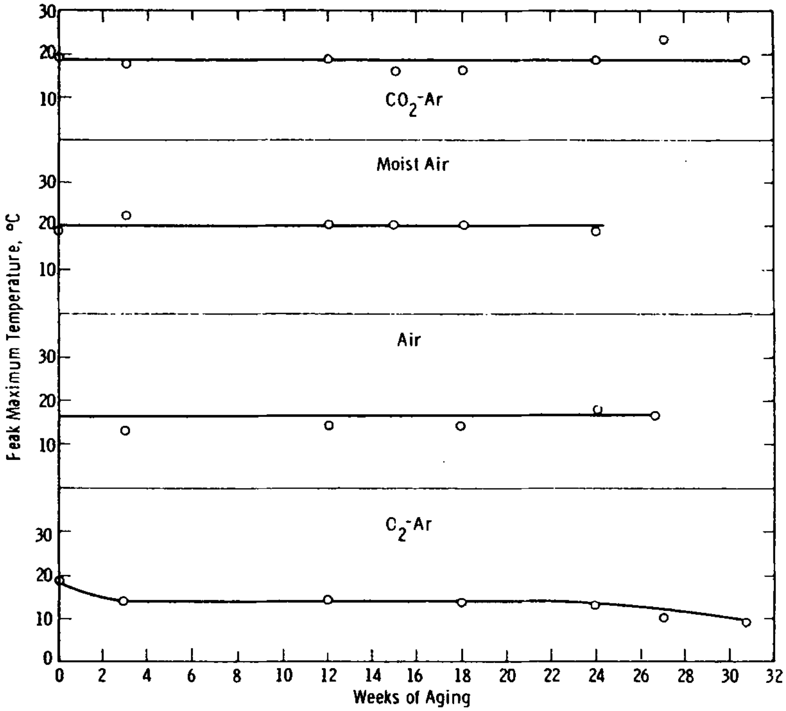

Figure 5. Effect of aging in various atmospheres of bulk liquid crystals on color response temperature (5875A peak) of corresponding films.

D. *Effects of Aging Under UV Irradiation in the Presence of Oxygen*

Ultraviolet radiation has long been suspected of being responsible for much of the damage to liquid crystals. Therefore, the usual liquid crystal mixture was exposed to 254 mμ radiation in the form of thin films, in bulk mixture, and as a 10% chloroform solution. Individual components were also irradiated. The actinic exposure was carried out in an atmosphere of 21 v/v% oxygen in argon.

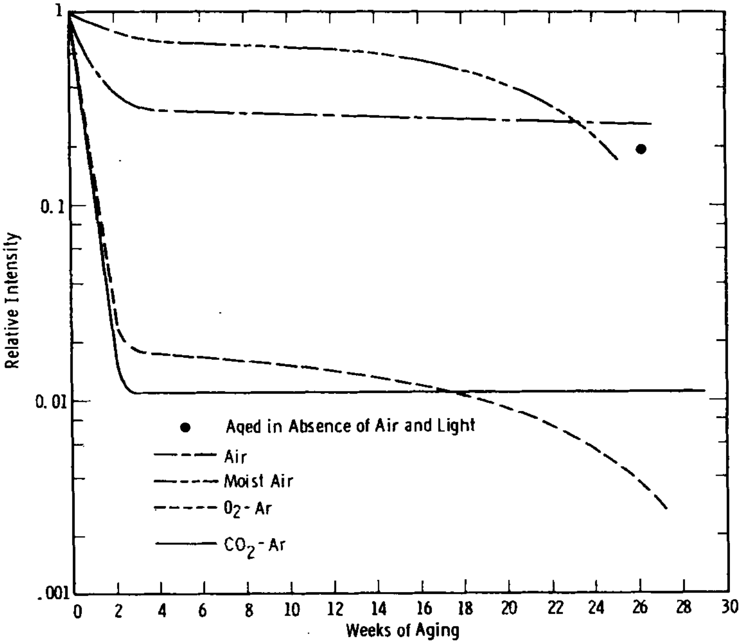

Figure 6. Effect of aging of bulk liquid crystals in various atmospheres on intensity of color response (5875A peak) of corresponding films.

The irradiated films ceased to function as image forming devices after 15 days exposure (Fig. 8), and the irradiated solution no longer gave films with a color response after 27 days. The bulk mixture degraded much more slowly, exhibiting a shift of about 10 °C in the color response after 48 days, and 20 °C after 72 days. However, liquid crystal films made from mixtures in which one or two of the ingredients were irradiated for 40 days under the same conditions, showed no change in their temperature response. DTA of irradiated bulk materials showed no detectable change in the transition points of all three mixture components.

In an attempt to see if the irradiation had only caused structural changes a film, which no longer gave a color response between 0° and 90° (normal response being over the range 5° to 45°), was redissolved in chloroform and recast. The new film also failed to give the characteristic cholesteric color display. No

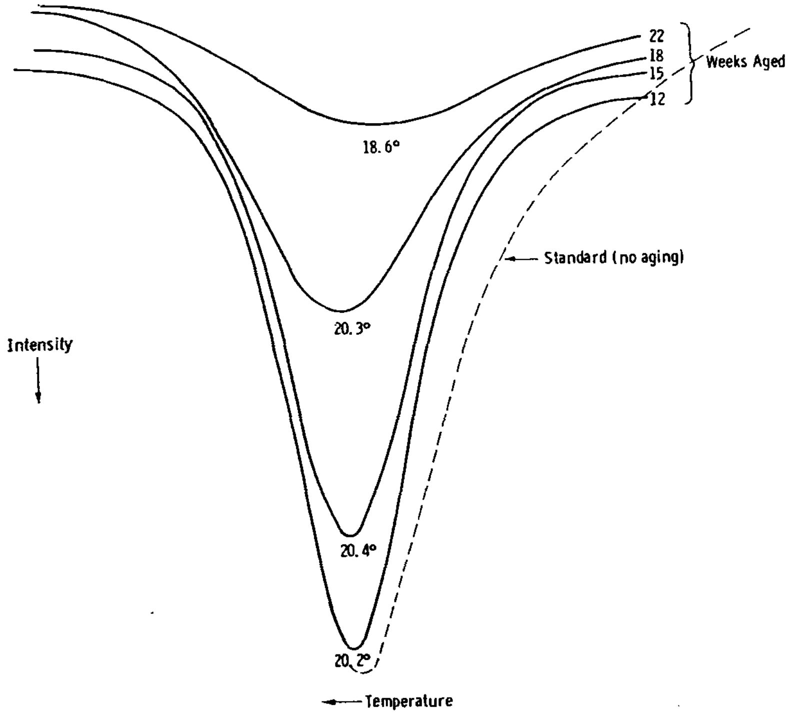

Figure 7. Effect of aging of bulk liquid crystals in moist air on intensity of color response (5875A peak) of corresponding films.

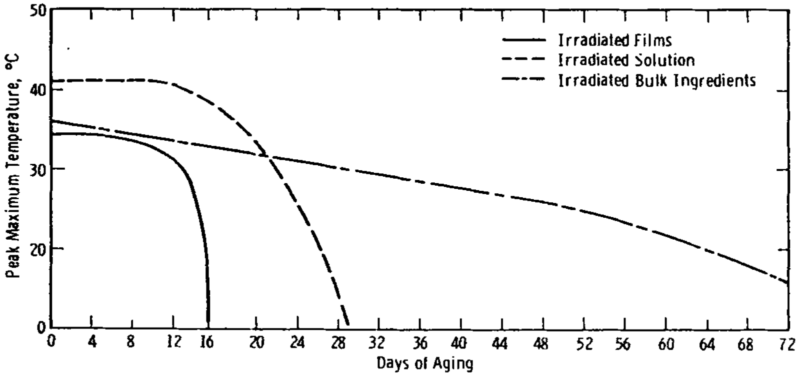

Figure 8. Effect of UV irradiation (2540A) on liquid crystal film, solution, and bulk as shown by variations of peak maximum (6000A) temperature.

significant difference could be detected between the infrared spectrum of the above chloroform solution and that of a solution of a non-irradiated mixture.

Discussion

The presence of UV irradiation and oxygen combined is extremely deleterious to the optical properties of cholesteric liquid crystals, affecting the temperature at which maximum reflectance of a given color occurs. It appears that a surface reaction or interaction is principally involved as shown by the much more rapid degradation of a film over the bulk mixture. It is probable that the effects which occurred in irradiated solutions were due to the formation of solvent free radicals initiated by the UV irradiation.

The thin liquid crystal films examined, aged in the absence of light, did not show an appreciable change in the temperature of maximum reflectance. From this, it appears that no chemical reaction had occurred. Also, IR and DTA studies of the individual components and of some mixtures could not detect any chemical changes.

On the other hand, there was a remarkable loss in the intensity of reflected light from these same films. The loss of intensity was continuous until no color could be detected except by a photomultiplier. Microscopic examination showed that, in all the films examined, there was a multitude of small areas, ranging in diameter from 300μ to 3000μ in which the cholesteric plane texture had changed to a focal-conic (presumably smectic) texture. It seems probable that the loss of color intensity is a function of the amount of material converted to this focal-conic texture.

In the transformations described, the focal-conic material traverses the full depth of the film. This is seen at actual crater sites. The causes of this phenomenon are probably manifold. Those that have been considered are occlusions, airborne foreign particles, surface tension and interface effects, and physical separation or preferential precipitation of the components of the liquid crystal mixture.

Because of the physical properties of the components used in the mixtures, physical separation would result in precipitation or crystallization. This was not detectable under a magnification of 400 ×.

In many instances foreign particles could readily be seen and it is considered that the free energy change brought about by the mixing of a solid and a fluid may be sufficient to cause the textural change.

In many other cases, no foreign body was visible. However, it is known that the substrate, Mylar, does contain small amounts of both crystalline and amorphous polymer. It is possible that surface interactions occur here causing the textural change. This is borne out by the fact that these small ring structures of focal-conic material reappear at the same positions after heating through the isotropic melting point.

Another phenomenon, which may not be related to the above effects, was observed on the surface of the liquid crystal films after aging. While many of these films still showed a well-developed cholesteric color display, it was observed that the surface of these films was partly converted to a focal-conic texture. The implication is that this was a surface change and that the material underneath this transparent layer still retained the cholesteric plane texture.

The decrease in color intensity of films prepared from bulk-aged materials is difficult to explain. Since these films were examined within hours of their preparation, it is reasonable to assume that the films were still wholly cholesteric so that a change in texture would not be sufficient to explain the cause of this decrease.

In summary, there is evidence that cholesteric liquid crystals under the influence of external stimuli are converted from the cholesteric plane texture to a focal-conic texture and, in some cases, to a fan-shaped texture which is known to occur only in the smectic mesophase. In these instances the different textures coexist for long periods of time. It is not known if the conversion is total, as would occur on cooling below the mesophase transition point.

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