Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: G. D. Dixon & L. C. Scala (1970): Thermal Hysteresis in Cholesteric Color Responses, Molecular Crystals and Liquid Crystals, 10:3, 317-325

To link to this article: http://dx.doi.org/10.1080/15421407008082817

Molecular Crystals and Liquid Crystals. 1970. Vol. 10, pp. 317–325

Printed in Great Britain

Thermal Hysteresis in Cholesteric Color Responses

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Received January 1, 1970

Abstract—The magnitude of the thermal hysteresis exhibited by cholesteric liquid crystals is mainly dependent upon the material composition of the system and the operating range.

1. Introduction

The lack of reproducibility of the color response of cholesteric liquid crystals used as sensors in electro-optical devices has been a serious obstacle to the utilization of such apparatus. This lack is exemplified by the delay in the thermally or electrically induced color responses due to a hysteresis phenomenon which appears to be inherent to the liquid crystal systems explored by us.

As a first step in reducing the magnitude of hysteresis, we have endeavored to determine the parameters governing this phenomenon by examining the thermal hysteresis of a number of liquid crystal mixtures. We thus hope to be in a position to distinguish between hysteresis effects due to thermal and electrical stimuli.

In the course of this work we encountered a situation, with mixtures operating at higher temperatures, in which the actual solid-liquid crystal transition appears to show hysteresis.

This paper will deal with thermal hysteresis only.

2. Experimental

The apparatus used to measure color response temperature on heating and cooling is shown in Fig. 1. The instrument consists of a tungsten source giving a beam of white light which has an angle of incidence of 20°. The reflected light passes through a collimating

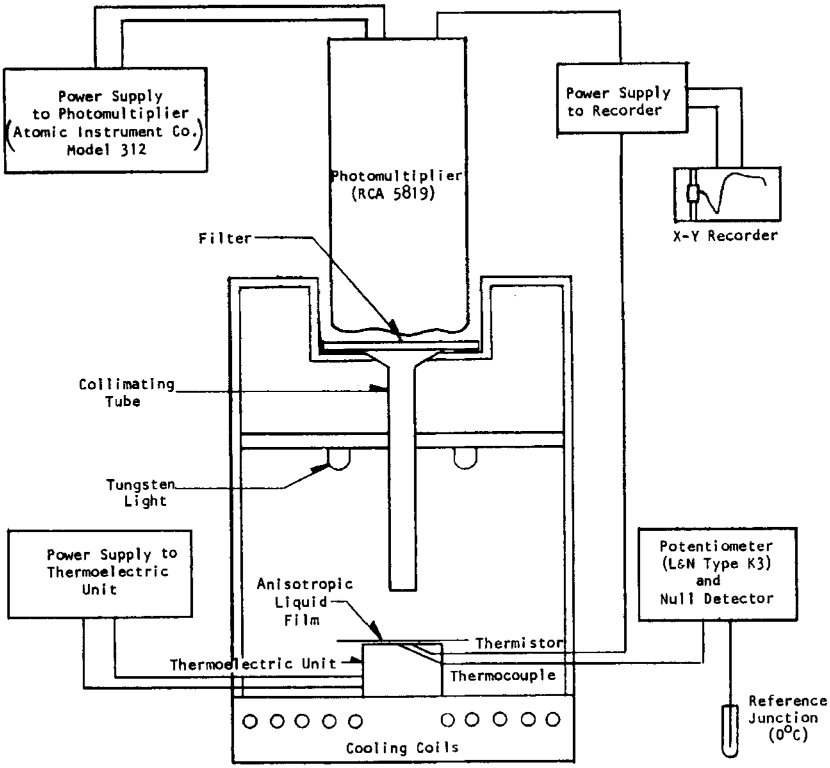

Figure 1. Thermo-optical apparatus.

tube, an interference filter, and then on to a photomultiplier. The samples consisted of thin films of liquid crystal (1 mil = 0.001 in = 0.0025 cm) on a Mylar substrate. They were heated and cooled using a thermoelectric device (8°–10°/min), and an X-Y recorder gave a trace of temperature versus the intensity of the reflected radiation. Figure 2 shows a typical hysteresis curve obtained using a series of interference filters, where the wavelength of the reflected light is plotted against the temperature of the sample.

In order to simplify matters, the measure of the magnitude of the hysteresis was taken as the difference between the peak reflectance temperatures on cooling and heating for 5000 Å reflected radiation.

Figure 3 is an example of how this difference, ΔT, was measured. In this example, the temperature of maximum reflectance on heating

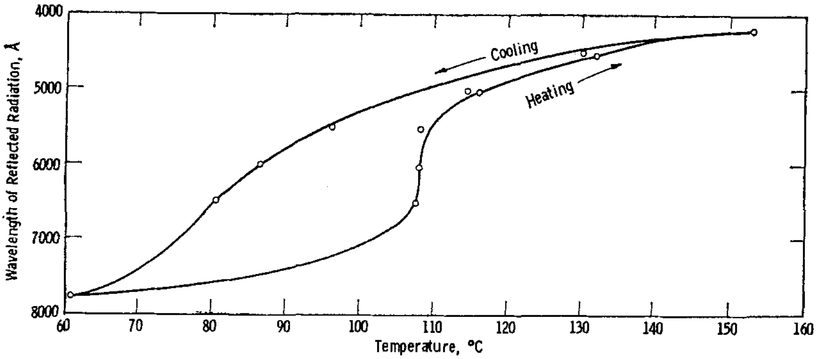

Figure 2. Hysteresis of a mixture of chol. cinnamate: chol. benzoate (45:55).

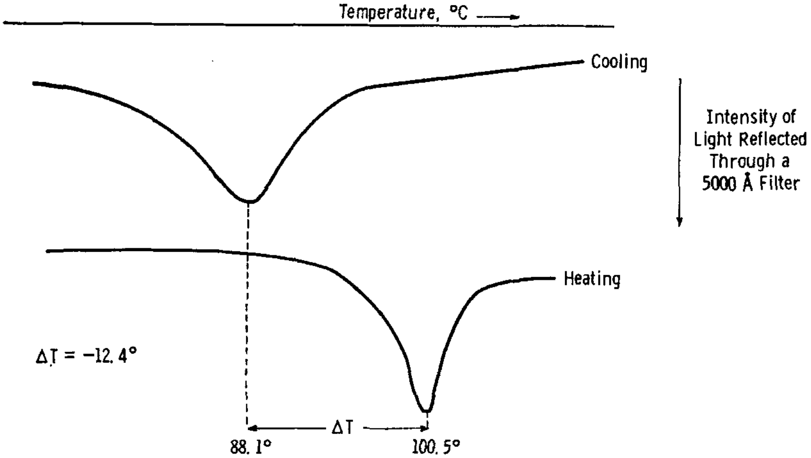

Figure 3. Method of determining ΔT as the measure of hysteresis.

was subtracted from the temperature of maximum reflectance on cooling to give $\Delta T = -12.4°$. ΔT can be positive or negative.

This method is taken as the most significant means of giving a single value for the magnitude of the hysteresis because many mixtures do not exhibit a color display in the red or green on heating.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were carried out using a DuPont 900 analyzer with the samples hermetically sealed in aluminum pans.

X-ray photographs were taken using a 19 cm Debye–Scherrer camera and Cr, K_α radiation. Powdered samples containing aluminum were held in quartz tubes (1 mm dia.), in a thermostatted environment and could be heated to any desired temperature.

Cholesteryl nonanoate was obtained from Eastman Chemicals; all other chemicals were synthesized in this laboratory. Materials were recrystallized until only two peaks were obtained by DTA.

3. Results and Discussion

At first it was thought that the magnitude of the hysteresis depended upon the operating temperature; for example, after handling many samples, it seemed that the hysteresis was always small for systems operating at low temperatures (below 50°) and was always large for systems operating at high temperatures (above 100°). In fact, this phenomenon turned out to be mainly material-dependent and only secondarily related to the operating temperature.

This effect is clearly shown in Fig. 4 where ΔT, our measure of the hysteresis, is plotted against composition for the addition of cholesteryl nonanoate to cholesteryl cinnamate. On adding cholesteryl

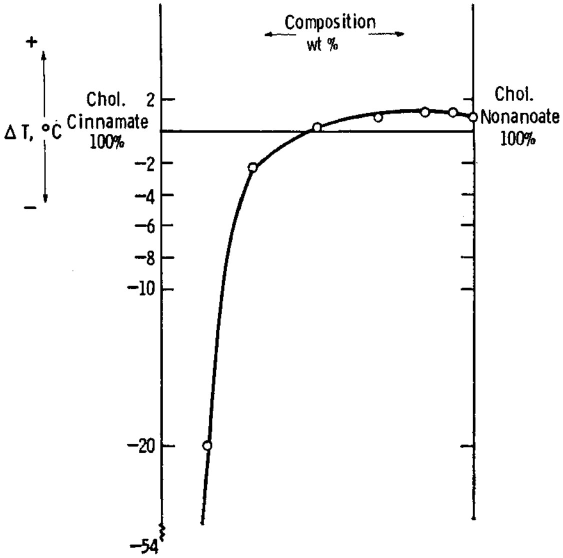

Figure 4. Hysteresis of chol. cinnamate: chol. nonanoate mixtures using a 5000 Å filter.

nonanoate, with $\Delta T = 0.9°$ (72.7°–71.8°), to cholesteryl cinnamate, with $\Delta T = -53.7°$ (164.8°–111.1°), the ΔT for the mixture decreases in magnitude as the concentration of cholesteryl nonanoate increases until it is barely measurable, at approximately 50 wt-% cholesteryl nonanoate.†

A second parameter affecting the magnitude of the hysteresis is the actual operating range with respect to the melting point of the system examined, i.e. the magnitude depends upon the temperature at which the heating cycle begins, and on whether this is above or below the melting point.

This is illustrated in Fig. 5 where sample temperature is plotted against the intensity of the reflected light passing through a 5000 Å filter. This shows the hysteresis of a 50:50 mixture of cholesteryl cinnamate and cholesteryl benzoate as a function of the temperature limits of the thermal cycle. The mixture has a melting point of 58° and a clearing point of 148°. Figure 5 shows that the magnitude of the hysteresis (ΔT), for 5000 Å reflected light, decreases from

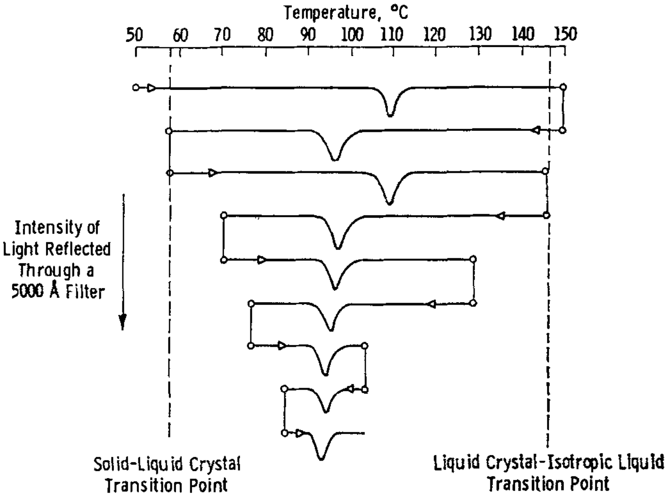

Figure 5. Hysteresis of a mixture of chol. cinnamate: chol. benzoate (50:50).

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† J. A. Fergason of the Liquid Crystal Institute, Kent State University, Ohio, has indicated to us that there is some evidence that cholesteryl nonanoate does not exhibit hysteresis. If this is so, then our value for ΔT of cholesteryl nonanoate is a measure of the error of these measurements.

−12.2° to +0.3° as the operating range narrows and as the starting temperature is raised above the melting point of the mixture.

It may be noted that the peak reflectance temperatures on the cooling legs are almost unaffected by the limits of the operating range. On the other hand, the peak reflectance temperatures on the heating legs are greatly affected and the closer the limits of the operating range are to the maximum reflectance temperature, the smaller is the hysteresis.

As mentioned above, the peak reflectance temperatures on the cooling legs do drift slightly to lower values. This is a separate phenomenon which is due to the progressive degradation of the materials at these high temperatures. Figure 6 shows the peak

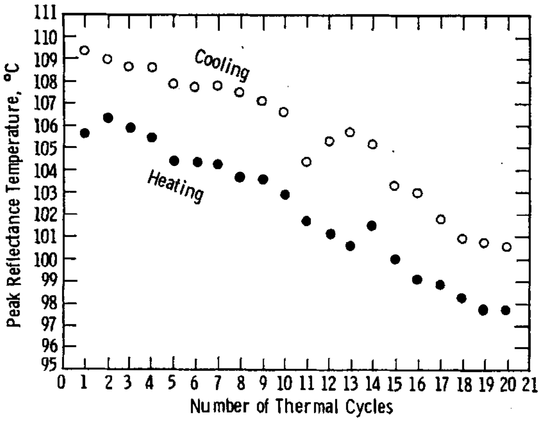

Figure 6. Degradation of the color response of a 50:50 mixture of chol. cinnamate and chol. benzoate using a 5000 Å filter.

reflectance temperatures through a 5000 Å filter, on heating and cooling, plotted against the number of thermal cycles to which the sample is subjected. The peak reflectance temperatures become progressively lower on repeated cycling, dropping from 109° to 101° after 20 cycles; there is no noticeable change in the magnitude of the hysteresis.

A third parameter consists of the rate of heating, which would also be expected to affect the magnitude of the hysteresis; however, this case was not investigated by us.

As stated previously, some mixtures do not exhibit a red or green color on heating from the solid state. This is illustrated in Fig. 7, where wavelength of reflected light is plotted against temperature for a 60:40 mixture of cholesteryl benzoate:cholesteryl cinnamate. On heating, the solid becomes liquid crystalline at 110° and reflects 5500 Å radiation. The reflected light progresses to shorter wavelength up to the clearing point at 140 °C. Cooling produces the complete spectrum (blue to red) down to the crystallization temperature at 78°. If the mixture is cooled below 50°, the cycle mentioned above can be repeated. However, if cooling is stopped at or above 78°, then a complete spectrum (from red to blue) is obtained on reheating. In effect, one has two solid-liquid crystal transitions and the abbreviated color response on heating suggests superheating. That this was not the case was shown by the fact that the mixture was still crystalline after it had been heated up from 25° and then held at 106° for two hours. We attempted to show that supercooling was not responsible by heating a film until it became liquid crystalline. It was then cooled and held between 90° and 100° for about 20 hours. No crystallization was noted during this period, the film having degraded in the course of this treatment. One suggestion to account for the transition temperature difference was that higher melting impurities could affect the temperature at which the transition took place, especially if supercooling prevented them from crystallizing out above the transition temperature on the cooling leg.

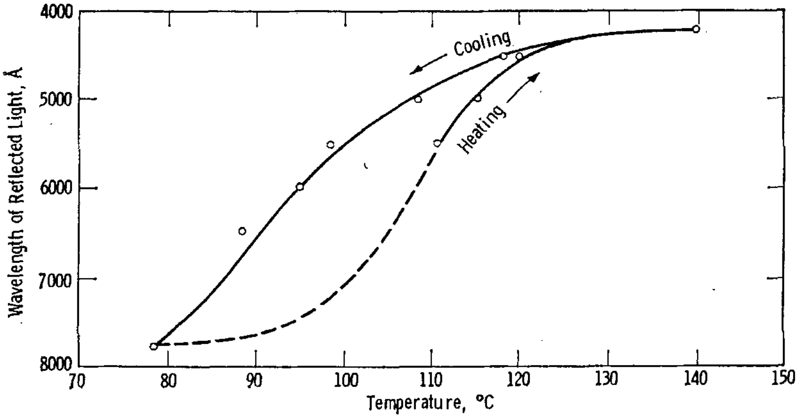

Figure 7. Hysteresis of a mixture of chol. cinnamate: chol. benzoate (40:60).

Therefore we examined the DTA of the cholesteryl cinnamate (40):

cholesteryl benzoate (60) mixture which gave a broad endothermic peak for the first transition. Melting started at 104° and the maximum was 115° for a heating rate of 5° per minute. Cooling gave a sharp exotherm at 82°. DSC showed that the enthalpy of the transition on heating was consistently greater than the enthalpy of the transition on cooling. Since the width of the endotherm suggested the presence of impurities, the materials were crystallized again using *n*-pentanol, this step having been recommended as being highly effective in removing impurities (Davis and Porter, Am. Chem. Soc. 158th National Meeting, N.Y., 1969). This had very little effect upon the DTA of the cholesteryl cinnamate, but the endotherm maximum for the cholesteryl benzoate increased from 148° to 154°. There was no effect on the DTA of the mixed components, the endotherm still started at 104° with a maximum at 115° and the exotherm on cooling still occurred at 82°. However, DSC showed that the enthalpy for the transition on heating was now the same as that on cooling. These results indicate that impurities were not responsible for the hysteresis in the transition point.

One expects there to be some relationship between the elevation of the transition temperature on heating and the odd behavior in the color display. An explanation for this behavior is as follows:

After passing through the crystal-liquid crystal transition, the liquid crystal retains enough energy to produce the molecular geometry which reflects blue light. However, the liquid crystal can now cool to display the full spectrum (blue to red) before passing through the phase transition, to give a crystalline form having a molecular configuration similar to that of the anisotropic liquid. No drastic change in molecular organization would occur in this cooling process in contrast to the heating leg. Further cooling then causes this second crystal form to revert to the lower temperature form.

In order to determine whether crystalline phase changes did occur, X-ray photographs of this mixture were taken at 26°, 61°, 104°, and 125° as the material was heated and at 75° and 26° on cooling. These photographs show that there is a change in the crystal form on heating, between 61° and 104°, and that the solid produced on cooling (at 82°) has a similar form, but with a distorted lattice, to that form which exists above 60° on heating.

Obviously, crystalline phase changes are occurring which cannot be explained at this time and these may well be the reason for the hysteresis in the melting behavior of the liquid crystal systems investigated. However, these results do not suggest the cause of the peculiar color response of the cholesteryl cinnamate (40): cholesteryl benzoate (60) mixture.

On the basis of these investigations, it should be possible to select a mixture of liquid crystals having a minimum thermal hysteresis.

Acknowledgements

The authors wish to thank Prof. G. H. Brown and Dr. A. de Vries of the Liquid Crystal Institute, Kent State University, Ohio, for stimulating discussions and help in the analysis of X-ray photographs.

This work was sponsored by the Advanced Research Projects Agency of the Department of Defense and was monitored by the Air Force Office of Scientific Research.