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

The Selective Light reflection by Plane textures

R. D. Ennulat [a]
[a] U.S. Army Electronics Command Night Vision Laboratory, Fort Belvoir, Virginia, 22060
Version of record first published: 28 Mar 2007.

To cite this article: R. D. Ennulat (1971): The Selective Light reflection by Plane textures, Molecular Crystals and Liquid Crystals, 13:4, 337-355

To link to this article: http://dx.doi.org/10.1080/15421407108083550

Molecular Crystals and Liquid Crystals. 1971. Vol. 13, pp. 337–355

Printed in Great Britain

The Selective Light Reflection by Plane Textures†

R. D. ENNULAT

U.S. Army Electronics Command
Night Vision Laboratory
Fort Belvoir, Virginia 22060

Received October 31, 1970; *in revised form December* 11, 1970

Abstract—The dependence of the selective reflection on wavelength and temperature is determined for cholesteryl nonanoate (CN), cholesteryl oleyl carbonate (COC), cholesteryl erucyl carbonate (CEC) containing five weight percent of cholesteryl chloride, and a 1 : 1 mixture of COC and CEC. In addition the wavelength at peak selective reflection is measured as a function of temperature. For each of the materials both the half-width of the spectral response curve and the maximum temperature coefficient of selective reflection of monochromatic light increase with wavelength. COC exhibits the highest temperature coefficient of 13,000 percent intensity change per degree centigrade (at a wavelength of 700 mμ), which may also be the highest temperature coefficient observed for any optical effect. A brief discussion deals with the scientific and technological significance of the results.

Selective reflection of visible light by cholesteric mesophases may not only be the most spectacular optical effect exhibited by liquid crystals but also the most promising phenomenon that could be utilized for displays,[1] thermal mapping,[2] thermal radiography[3] and detection of microwave energy.[4] Therefore it is surprising that relatively few investigations deal with the temperature dependence and the theory of this effect.[5] However, the recent extension of the theoretical work, begun by Oseen[6] in 1921 and advanced by de Vries[7] in 1951, resulted in a phenomenological theory of selective reflection, which agrees very well with the experimental results.[8]

This investigation is concerned with the determination of the extremely large temperature coefficient of selective reflection exhibited by: cholesteryl nonanoate (CN), cholesteryl oleyl carbonate (COC), cholesteryl erucyl carbonate (CEC) containing 5% cholesteryl chloride, and a 1 : 1 mixture of COC and CEC. The measurements

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

were performed with monochromatic light incident and selectively reflected within a fourteen degree cone which was perpendicular to the sample surface. The schematic overview shown in Fig. 1 indicates the results of the measurements performed: wavelength at peak selective reflection versus temperature; intensity versus wavelength at constant temperature; intensity versus temperature at constant wavelength.

Experimental Set-up

The experimental scheme shown in Fig. 2 consists of a thermostated miscroscope stage (Leitz, Model 350) containing the sample and a metallurgic microscope (Leitz, Ortholux) using a grating monochromator (Bausch & Lomb, Type 33–86–44) for illumination, a binocular eyepiece for observation, and a photomultiplier mounted on the third microscope tube for the measurement of the light intensity. The light coming from the sample can either be measured by the photometer (El Dorado, Model PH-200) or by simply flipping in a mirror (dashed lines), viewed through the eyepiece. This feature is essential because it enables the operator to frequently inspect the texture of the sample. Two copper constantan thermocouples are imbedded in the liquid crystal outside of the field of view. One is connected to a potentiometer (Rubicon, Type B-1) and measures the sample temperature within ± 0.01 °C. The other is connected over a bucking circuit with a microvolt amplifier (Keithly, Model 190) to measure temperature differences of the order of millidegrees

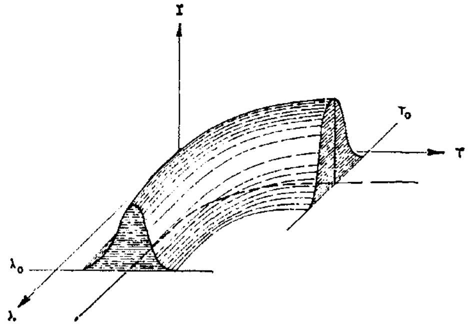

Figure 1. The intensity of light selectively reflected by the plane texture of the cholesteric mesophase as a function of wavelength and temperature.

against a chosen temperature level. The output of this amplifier drives the x axis of the xy recorder while the intensity of the photometer drives the y axis.

The sample temperature is stabilized by a circulator (Haake, Type Fe) pumping constant temperature water through the jacket of the microscope stage. To achieve higher temperature stability, the electrical on-off control of the water temperature was replaced by an on-partial-off control. In the partial off mode a constant heater current compensates for the minimum heat loss of the system, while in the on-control mode heat is added to counter temporary additional heat losses which are reduced by careful insulation. Since the ambient temperature usually changed by less than one degree during the day, these measures resulted in a temperature reproducibility and reversibility of ± 0.002 °C over the test period (5 to 10 minutes).

Sample Preparation and Handling

To obtain a sufficient amount of selectively reflected light for the measurement, the sample had to be illuminated over an area of

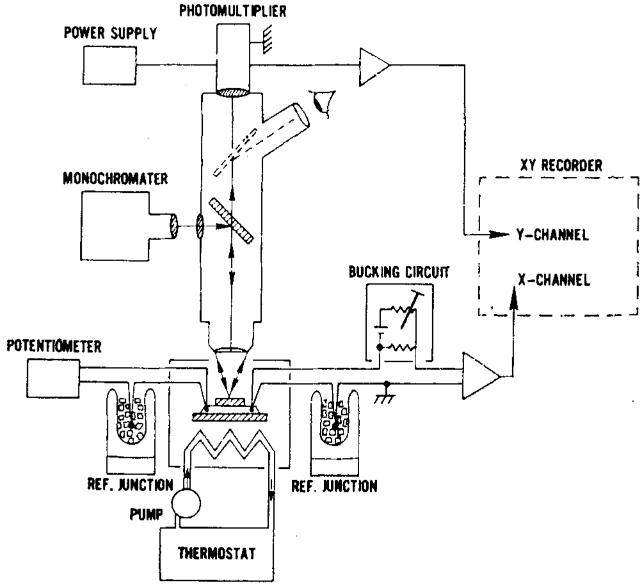

Figure 2. Measurement of selective reflection.

about 0.5 mm diameter. This requires a plane texture uniform over this extension. However, known methods of sample preparation yielded only a mosaic of uniform texture elements, the latter ranging in dimensions from 10 to 50 μm. These non-uniformities could be caused by impurities and as indicated by the angular dependence of selective reflection by deviations of the helical symmetry axis of the elements from the normal of the sample surface. Since the degree of non-uniformities depends on purity, unknown interactions at interfaces, and on thermal history, we developed empirical procedures yielding reproducible results for a given sample by controlling these factors.

COC and CEC were carefully prepared in-house to avoid the formation of hard to remove impurities,[9] while reasonably pure CN was obtained from commercial sources. After purification of these materials by column chromatography, the total amount of known impurities was reduced below the detection limit of thin layer chromatography, which is about one mole percent.

To avoid effects due to surface structures and to electrostatic and chemical interactions, the liquid crystal was supported and covered by clean, degreased glass slides. Manipulation of the melted material on a glass slide usually resulted in a smooth coherent liquid crystal film, which was then covered by a thin heated cover slip. Care was taken to avoid trapping of dust and air bubbles. Only CEC causes severe difficulties because it does not wet the glass surface. The addition of 5% cholesteryl chloride eliminated this problem but at the cost of obtaining data not characteristic of the pure CEC. Since perfect alignment of the plane texture could not be achieved, we did not measure the absolute magnitude of the selective reflectivity and therefore did not need to know the thickness of the liquid crystal film. We adjusted the thickness by simply squeezing the assembly until bright and relatively pure spectral colors appeared for incident white light.† This procedure allowed the experimenter to apply a variety of mechanical disturbances in order to eliminate undesirable textures and to obtain plane textures with a high degree of alignment. The thermal history of the sample has a pronounced

† This occurred for sample thicknesses between 10 to 20 μ. Thicker samples had a milky appearance which may be due to light scattering by strongly misaligned plane texture elements.

influence on the texture. For example, fast cooling of CN from above the clearing point results in spherulites formed by elliptical focal conics, the long axis of which are radially oriented. The rapidly growing spherulites finally displace all other textures. At the transition from the cholesteric to the smectic mesophase the spherulites maintain their diameter while the focal conics convert into segments of fan-shaped textures. The latter are arranged in concentric rings with the ribs of the fan-shaped texture aligned approximately parallel to concentric circles. Subsequent heating reverses the changes of the textures. On the other hand, slow cooling from above the clearing point induces a grayish texture, which readily exhibits the colorful selective reflection in the appropriate temperature interval. All the investigated materials favor the plane texture on slow cooling (about 1 °C per minute and less) once the few persistent focal conic bands are eliminated by mechanical manipulation of the sample. To start with a well defined thermal history, all experiments were conducted on samples cooled from above the clearing point. As expected, the experimental results indicate that prior thermal history is annealed out at temperatures above the clearing point.

Experimental Results

The experimental results were obtained under the following conditions:

1. The polarizers of the microscope were always crossed to reduce the background level of light caused by specular reflection.

2. The field stop of the microscope illuminator limited the investigated sample area to circular disc of 0.75 $mm.^2$

3. The microscope objective illuminated and received the selectively reflected light within a cone of fourteen degrees.

4. The monochromator slit was set to a 1 mm opening in order to obtain monochromatic light with a spectral half-width of 1.2 mμ.

5. All intensity data were corrected for the spectral response of the apparatus.

Wavelength at Peak Selective Reflection versus Temperature

The temperature dependence of the wavelength at peak intensity was measured by adjusting the monochromator to a desired wavelength and by changing the temperature in one direction. When the photometer indicated the intensity peak, the temperature was determined with the thermocouple connected to the potentiometer. Figure 3 shows the results with the error bars indicating the ± 0.01 °C uncertainty of the temperatures. Clearly CEC exhibits the narrowest color band. Also notice the cross-over of the 1 : 1 mixture of COC and CEC at 550 mμ which indicates that the mixture apparently approaches the behavior of CEC for longer wavelengths. Measurements repeated on successive days revealed that except for CN these curves shifted by about 0.1 degree centigrade per day towards lower temperatures without change of shape and that samples not covered by a glass slide exhibited even a larger effect. Apparently oxygen, which was adsorbed on the coverslip in the first case and which was more readily available in the second case, must have reacted with the liquid crystal and formed products which depressed

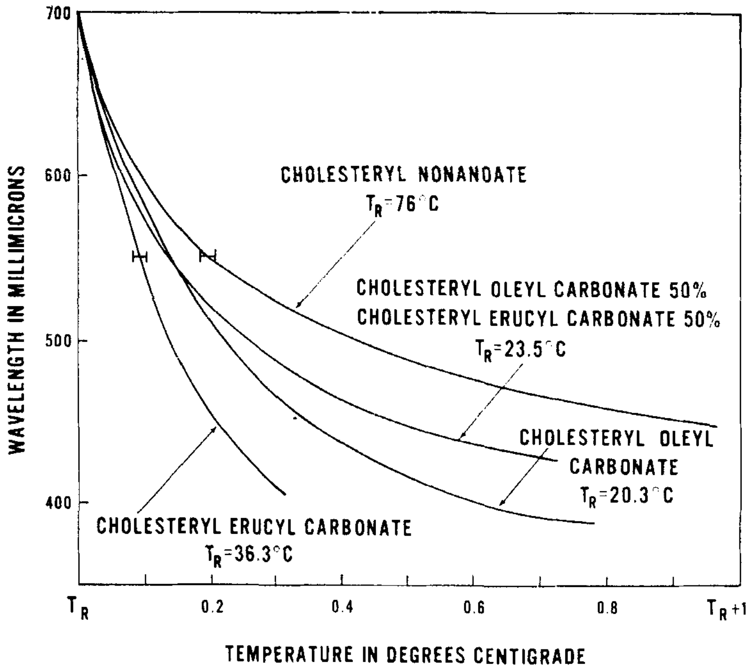

Figure 3. Wavelength of maximum selective reflection as a function of temperature.

the temperature range of the selective reflection.[10] This was confirmed by the fact that unknown impurities were detected by thin layer chromatography after the test and that the initial test results were repeated after their removal.†

Intensity versus Wavelength at Constant Temperature

The spectral response of the selective reflection was measured at constant temperature for increasing and subsequently for decreasing wavelength. Since the same wavelengths were used in either case, intensity differences at a given wavelength indicated changes in sample temperature. We rejected data associated with temperature variations larger than ± 0.002 degree centigrade. The error bars in Figs. 5 to 6 show the remaining uncertainties of the measurements. Considering the fact that the half-width of the spectral response curves approach that of customary interference filters (7mμ to 25 mμ), we conclude that our samples were reasonably well aligned.

Intensity versus Temperature at Constant Wavelength

The temperature dependence of the selective reflection of monochromatic light was measured by imparting a temperature drift on

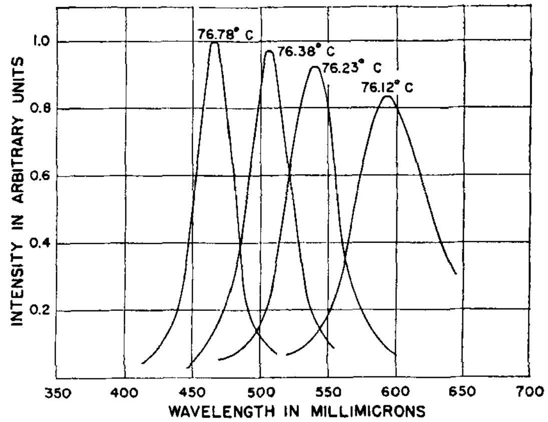

Figure 4. Intensity of selectively reflected light as a function of wavelength. Material: Cholesteryl nonanoate.

† This impurity effect is utilized to detect the presence of certain gases with the aid of liquid crystals.[11]

the sample and by plotting intensity versus temperature with the set-up shown in Fig. 2. Errors caused by time lags in the recording channels were avoided by keeping the drift rate below 0.05 degree centigrade per minute. The capability of the equipment is best demonstrated by the trace of a typical recording shown in Fig. 7. The superimposed spikes mark the calibration points, independently determined with the thermocouple connected to the potentiometer.

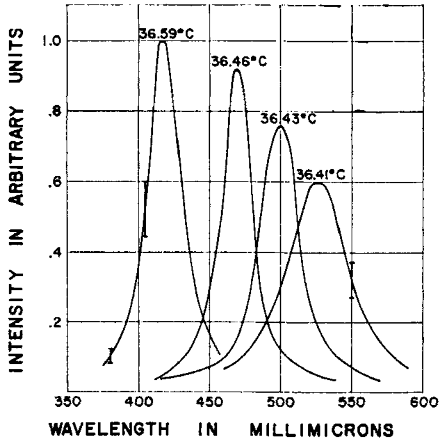

Figure 5. Intensity of selectively reflected light as a function of wavelength. Material: Cholesteryl erucyl carbonate with 5% cholesteryl chloride.

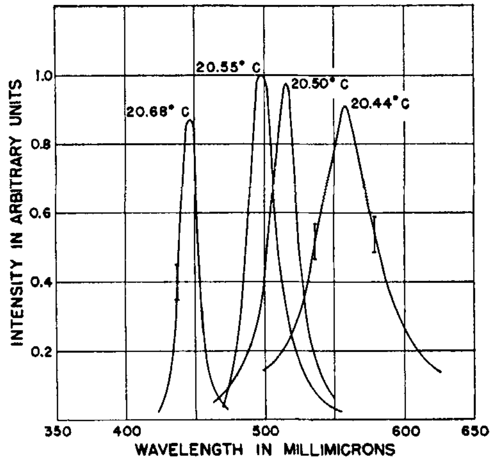

Figure 6. Intensity of selectively reflected light as a function of wavelength. Material: Cholesteryl oleyl carbonate.

Smoothness and shape of this curve indicate that the sample was well aligned and uniformly heated. This is based on the fact that drastic changes in alignment, the appearance of birefringent textures, and non-uniformities of the temperature travelling across the sample strongly modulate the recorded light intensity in a way not systematically related to the temperature. To interpret more subtle distortions of the measurements it is necessary to inspect the sample with the microscope at the beginning and at the end of each run.

After cooling a sample from above the clearing point, we determined the intensities obtained for heating and cooling within a narrow temperature interval. We found that the intensities of the heating curves were consistently lower by 10 to 20% than those of the cooling curves. The temperatures of peak intensity are

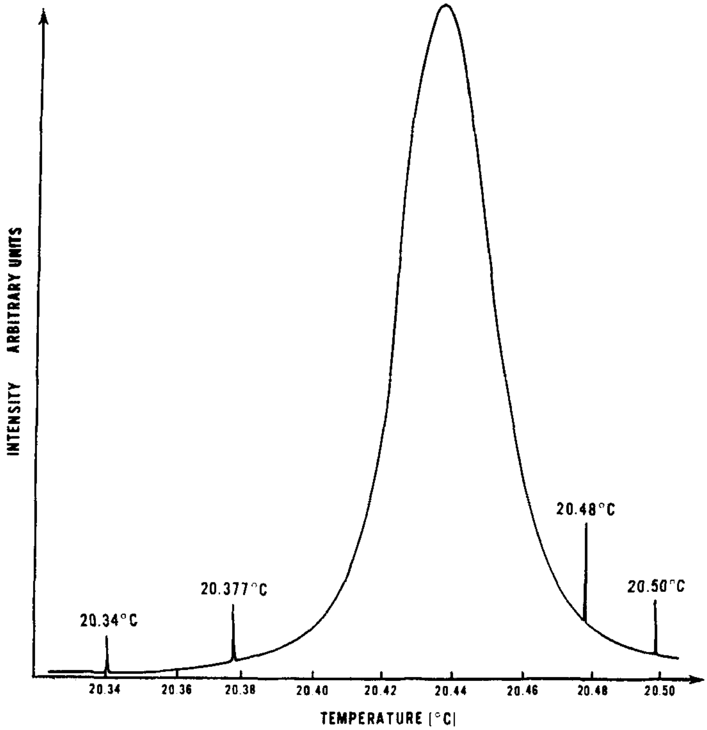

Figure 7. Intensity of selectively reflected light in dependence of temperature as plotted by XY recorder.

Material: Cholesteryl oleyl carbonate.

Wavelength: 575 mμ.

reproducible within ± 0.002 degree centigrade for heating and cooling regardless of the magnitude of the temperature interval. This indicates that the alignment variations of the plane texture were only minor. But samples containing detectable amounts of oxidation products exhibited a temperature shift of the cooling curve. Since the selective reflection occurs only a fraction of a degree above the cholesteric to smectic phase transition, this hysteresis may be linked with the undercooling of the phase transition due to impurities.

Figures 8 through 10 show the temperature dependence of selective reflection determined for the various materials at the same wavelengths. These results indicate that neither peak height nor half-width exhibit a simple dependence on the temperature T_p at peak intensity. The latter can be better recognized on the normalized presentations of the data in Figs. 11 and 12. Notice that the half-width generally decreases with wavelength and that COC exhibits the smallest width of 0.024 degree centrigade.

The Temperature Coefficients

In Figs. 13 through 16 the temperature coefficients of the selectively reflected light intensity are plotted as a function of the temperature

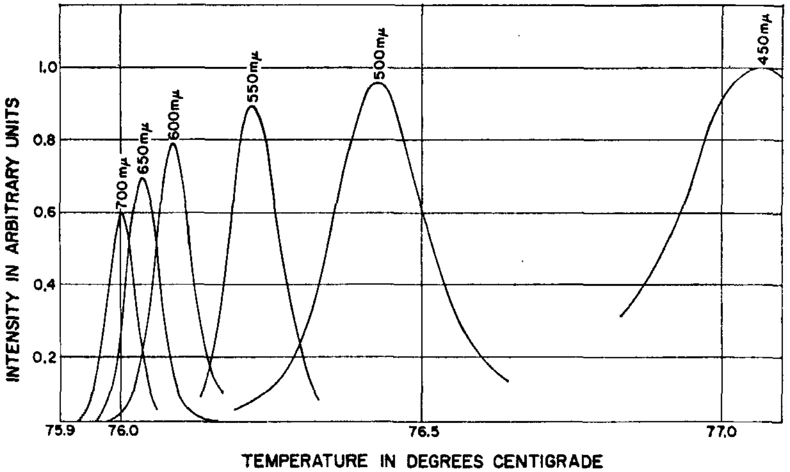

Figure 8. Intensity of selectively reflected light in dependence of temperature.

Material: Cholesteryl nonanoate.

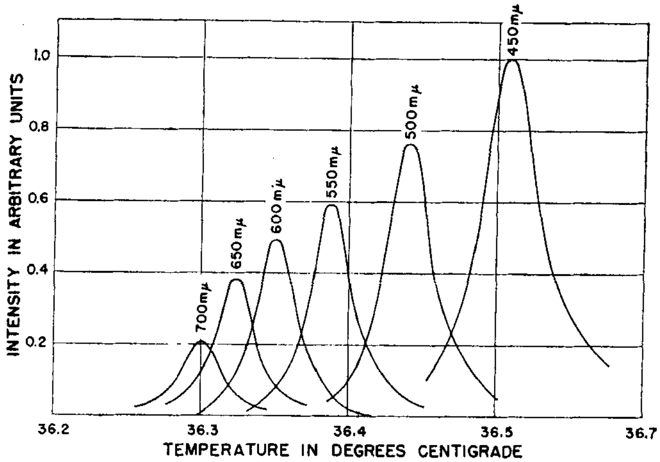

Figure 9. Intensity of selectively reflected light in dependence of temperature.

Material: Cholesteryl erucyl carbonate with 5% cholesteryl chloride.

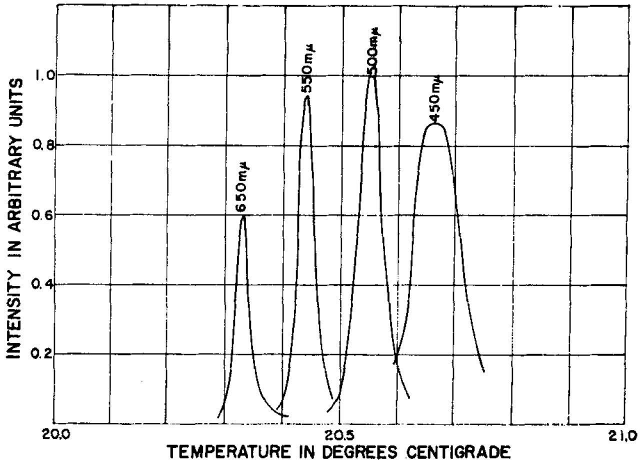

Figure 10. Intensity of selectively reflected light in dependence of temperature.

Material: Cholesteryl oleyl carbonate.

relative to the temperature T_p of peak intensity. For a given wavelength these coefficients have a relative maximum on either side of temperature T_p and decrease rapidly within a few hundredths of a degree. Depending on material and wavelenth these maxima occur at intensities ranging from 10 to 60% of peak intensity. The high magnitude of the coefficients underlines the importance of obtaining a slow but definite temperature drift and of ascertaining the calibration of a temperature interval at the beginning and at the end of each test run. The sensitivity and the high short time stability of the temperature measurement (see Fig. 7) made it possible to determine the temperature coefficients within ± 10 to ± 25%. This estimate is based on numerous test runs and on thermostated samples. For example, using a sample of COC in the most temperature sensitive region, we observed that a galvanometer deflection, indicating a

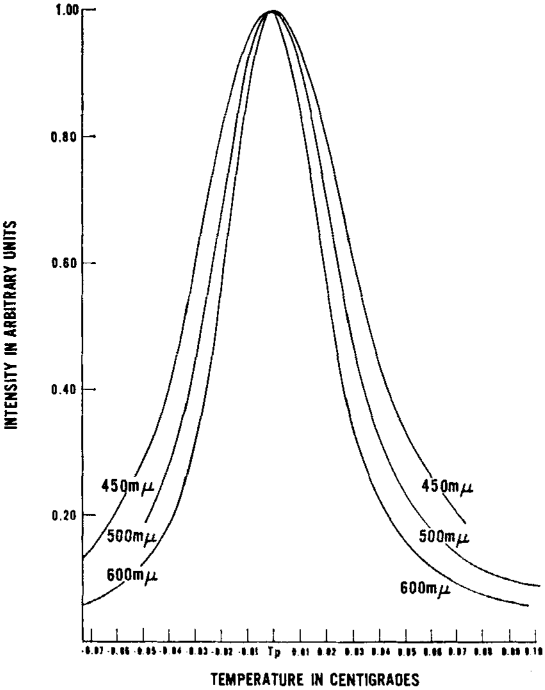

Figure 11. Normalized intensity of selectively reflected light versus temperature.
Material: 1 : 1 mixture of cholesteryl erucyl carbonate and cholesteryl oleyl carbonate.

control oscillation of $\pm$ 0.001 °C, was concurrent with a brightness oscillation of $\pm$ 10% displayed by the photometer. This effect could be observed for many minutes until an adjustment was required to compensate for drifts.

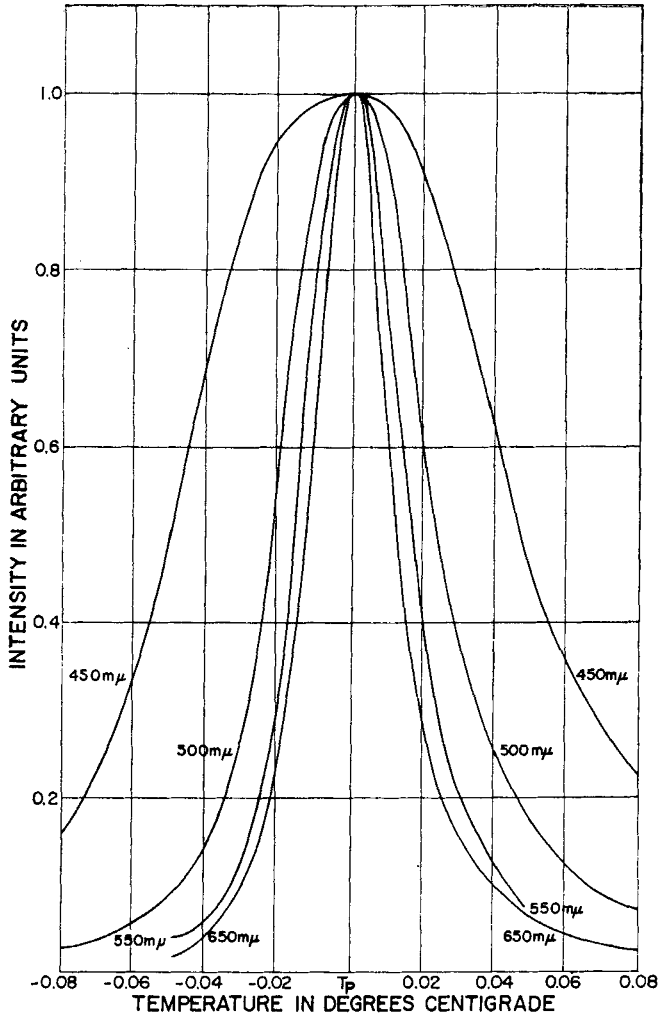

Figure 12. Normalized intensity of selectively reflected light versus temperature.

Material: Cholesteryl oleyl carbonate.

Discussion

The scientific assessment of the experimental results is restricted to a few speculative statements primarily because the degree of alignment of the plane texture is not known quantitatively. However, the narrowness of the half-width of the spectral response and the high degree of the temperature reproducibility of the wavelength at peak intensity both indicate that our experimental results may differ only slightly from those obtained on perfectly aligned textures. The curves in Fig. 3 suggest an interesting analogy to a Curie-Weiss law dependence. This view is supported by our experience that a material exhibits a steeper initial slope of the peak wavelength versus

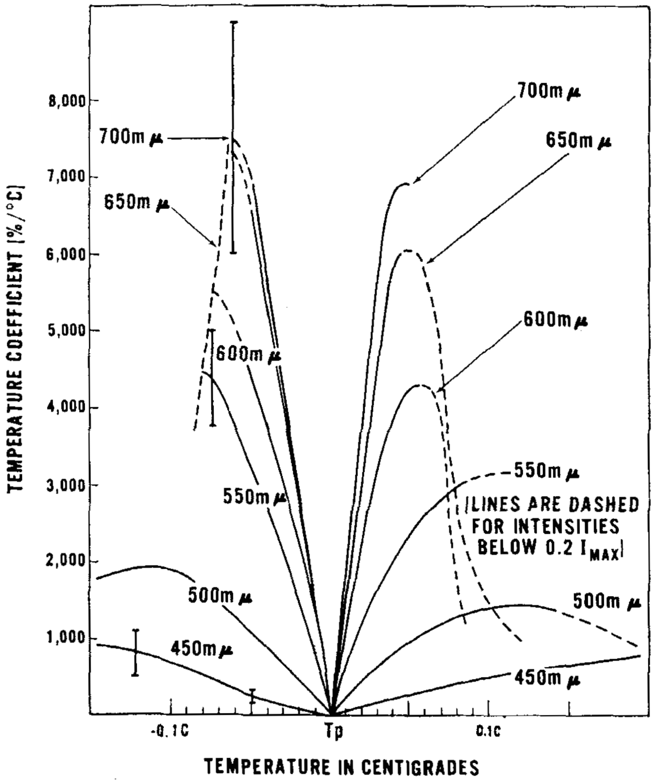

Figure 13. Temperature coefficient of selective reflection versus temperature. Material: Cholesteryl nonanoate. T_p: Temperature of peak intensity.

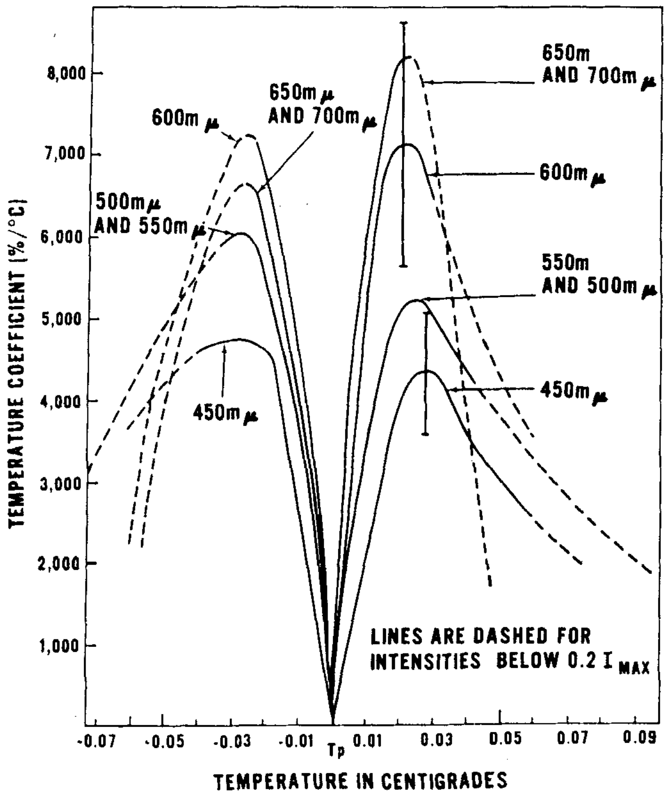

Figure 14. Temperature coefficient of selective reflection versus temperature. Material: Cholesteryl erucyl carbonate with 5% cholesteryl chloride. T_p: Temperature of peak intensity.

temperature curve (see Fig. 3) the smaller the difference is between the reference temperature T_R (i.e. the arbitrarily chosen point on the curve at 700 mμ) and the cholesteric to smectic transition temperature. However, cholesteric-smectic phase transitions are of first order, while phase transitions in the vicinity of the Curie points of magnetic and certain ferroelectric materials are of second order. Furthermore, the curves in Fig. 3 are not hyperbolas required by the Curie-Weiss law. But the latter discrepancy could be explained as follows: Assume a hyperbolic dependence for a plane texture element of given orientation with respect to incident parallel light and with respect to the angle of observation; in addition assume that hyperbolas associated with different angles of incidence and observation

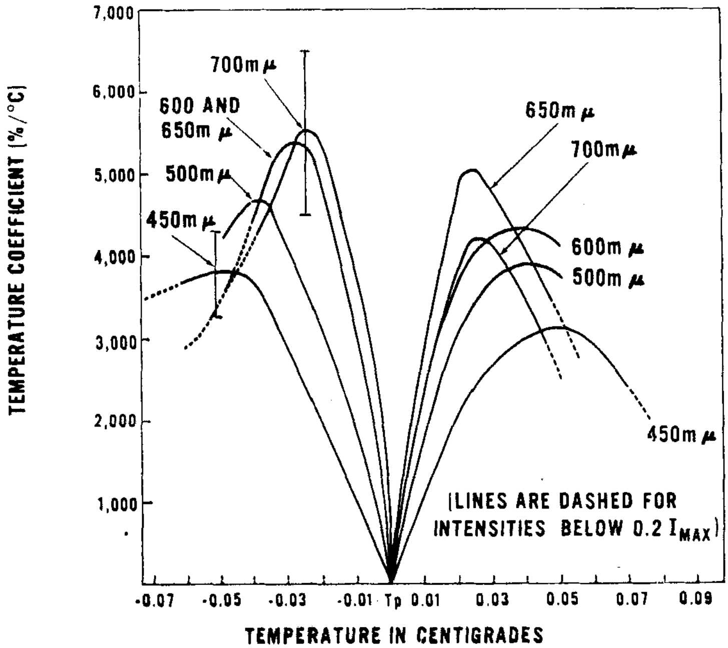

Figure 15. Temperature coefficient of selective reflection versus temperature. Material: 1 : 1 mixture of cholesteryl erucyl carbonate and cholesteryl oleyl carbonate.
T_p: Temperature of peak intensity.

are equal in shape but shifted against each other along the temperature axis.† Since our experimental set-up illuminates and observes the mosaic of slightly misaligned plane texture elements within a cone of fourteen degrees, a hyperbolic dependence of the peak wavelength cannot be expected. Thus we can conclude that our results do not contradict the theoretical consideration,[12] which predicts a hyperbolic dependence of peak wavelength versus temperature.

The experimental results show that liquid crystals have great technological potential as temperature indicators and as extremely sensitive detectors of temperature differences. In the former application the wavelength at peak selective reflection is calibrated with respect to temperature. If the liquid crystal is kept in a chemically inert environment and if it is shielded from radiation (such as

† The angular dependence of selective reflection[5] indicates such a possibility.

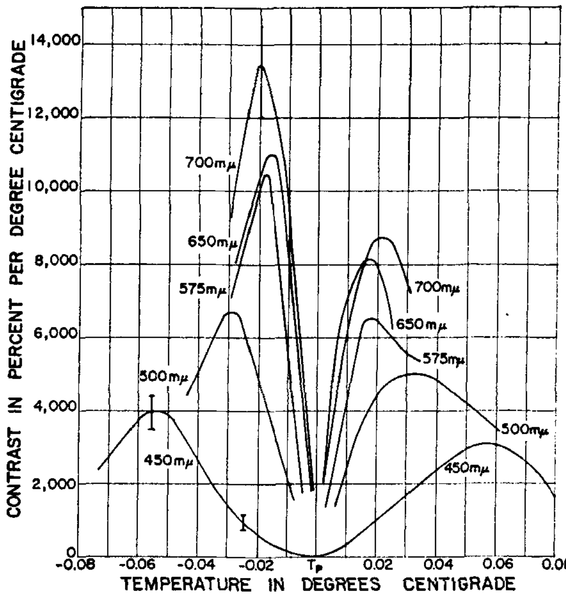

Figure 16. Temperature coefficient of selective reflection versus temperature. Material: Cholesteryl oleyl carbonate. T_p: Temperature of peak intensity.

UV) that causes chemical reactions, the temperature calibration should be maintainable within the order of a few hundredths of a degree centigrade. The latter application relies on the high temperature sensitivity of the selective reflection of monochromatic light. The maximum temperature coefficients of this effect are shown in Fig. 17 for CN, COC, and CEC containing 5% cholesteryl chloride. It should be pointed out that the presence of cholesteryl chloride may have substantially decreased the temperature sensitivity of CEC. Notice that all coefficients increase with wavelength and that, except for CEC, they are generally higher on the low than on the high temperature flank of the selective reflection curve. We conclude that the temperature coefficient of 13,000 percent per degree centigrade exhibited by COC is the highest one in our investigation and may be the highest one observed for any optical effect. This material is capable of indicating temperature differences of less than a millidegree directly to the human eye.

c

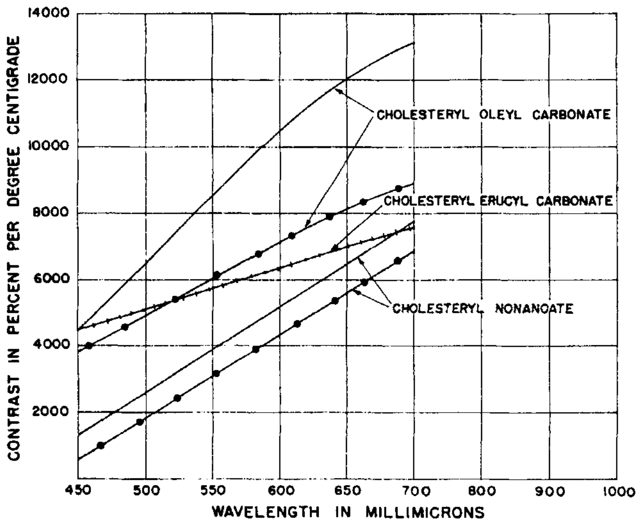

Figure 17. Maximum temperature coefficients of selective reflection versus wavelength.
——— Low temperature side —·—·— High temperature side
of intensity curve at constant wavelength.

Acknowledgements

I am ingratiated to Drs. W. Elser and J. L. W. Pohlmann for the preparation of the compounds and to our former co-workers Messrs. F. M. Schaer and R. Sherman for their work during 1963 and 1964 when most of the experiments were conducted.

REFERENCES

1. Fergason, J. L., Fr. Pat. Nr. 1 527 311 (1968).
2. Fergason, J. L., *Scientific American* **211,** 77 (1964); Selawry, O. S. and H. S., Holland, J. F., *Mol. Cryst.*, **1,** 495 (1966); Lukianoff, G. V., *Mol. Cryst. and Liq. Cryst.*, **8,** 389 (1969).
3. Ennulat, R. D. and Fergason, J., *Mol. Cryst. and Liq. Cryst.*, to be published.
4. Dev. of Liq. Cryst. Microwave Power Density Meter, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Electronic Products, BRH/DEP 70–8.
5. Fergason, J. L., *Mol. Cryst.*, **1,** 293 (1966).
Ittner, G., Böttcher, B., *Mol. Cryst. and Liq. Cryst.*, to be published.
6. Oseen, C. W., Fortschritte der Chemie, Physik and Physikalischen Chemie, Band 20, Heft 2, Serie B, Verlag von Gebr. Borntraeger, Berlin (1929).
7. DeVries. Hl., *Acta. Cryst.*, **4,** 219 (1951).

8. Chandrasekhar, S., Prasad, J. S., *Mol. Cryst. and Liq. Cryst.*, to be published.
Berreman, D. W., Scheffer, T. J., *Mol. Cryst. and Liq. Cryst.*, to be published.
Dreher, R., Meier, G., Saupe, A. O., *Mol. Cryst. and Liq. Cryst.*, to be published.
9. Elser, W., to be published.
10. Scala, L. C. and Dixon, G. D., *Mol. Cryst. and Liq. Cryst.*, **7**, 443 (1969).
Scala, L. C. and Dixon, G. D., *Mol. Cryst. and Liq. Cryst.*, **10**, 411 (1970).
11. Fergason, J. L., Willey, D., and Sharpless, E., Private Communication.
12. Keating, P. N., *Mol. Cryst. and Liq. Cryst.*, **8**, 315 (1969).