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Inverse angle dependence of the reflection colours of cholesteric polymeric liquid crystals mixed with pigments

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Measurements on thin layers of cholesteric liquid crystals with a cyclic polysiloxane backbone show the usual angle dependence of the reflection wavelength, namely a shift to shorter wavelengths with increasing angle of observation. By mixing these liquid-crystalline side chain polymers with suitable pigments or dyes or by choice of a suitable coloured background, a red shift of the reflection colour with increasing angle can be obtained.

1. Introduction

Ordered layers of cholesteric liquid crystals appear coloured because of selective reflection of light from their helical structure [1]. These colours are highly saturated [2] and change, with increasing viewing angle, to shorter wavelengths [3]. We present measurements of the spectral reflectance of thin layers of cholesterics consisting of cyclic polysiloxanes [4] on black substrates. This type of cholesterics can be oriented very easily on different substrates by mechanical means. Possible applications of these easily orientable liquid-crystalline polymers are optical data storage, non-absorbing optical filters or the decorative sector. For using these materials in the decorative sector, we have mixed them with suitable pigments or used coloured substrates. In this way a red shift of the reflection colour with increasing viewing angle instead of the normal blue shift seen for pure cholesterics on a black substrate can be obtained. Measurements of these effects and a theory based on additive colour mixing are presented.

2. Materials

Liquid-crystalline cyclic polysiloxane side chain polymers [4] (see figure 1) were synthesized by hydrosilylation of cyclic methyl-H-siloxanes with the mesogenic groups 4-allyloxybenzoic-acid–4-phenyl-phenol-ester and 4-allyloxybenzoic-acid–cholesterol-ester according to [5]. These compounds have glass transition temperatures of about 50–60°C (depending on m/n). Above these temperatures they are cholesteric up to 180–200° C; at these temperatures they become isotropic. The pitch of the cholesteric structure and therefore the reflection wavelength depends on the ratio m/n and can be adjusted from 450 to 2000 nm (for normal incidence).

The pigments used were purchased from B.A.S.F. They were mixed with the liquid crystal in concentrations up to 10 per cent (w/w) without greatly disturbing the cholesteric phase. To mix the cholesteric liquid crystals with the pigments, appropriate amounts of both components were dissolved in toluene; the toluene was then removed by evaporation.

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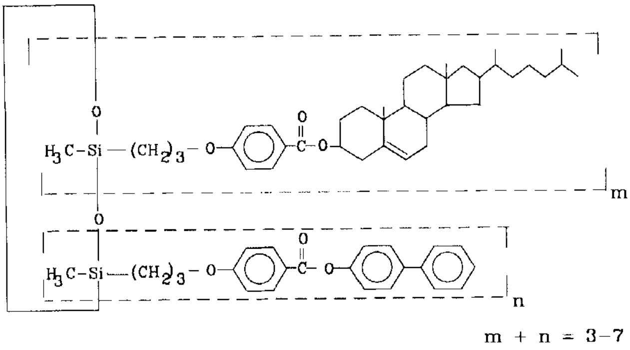


Figure 1. Cholesteric liquid-crystalline side chain polymers with a cyclic polysiloxane backbone.

3. Sample preparation

The liquid crystals (with or without pigments) were oriented on a macroscopic scale as thin films on various substrates (e.g. glass and paper). For this purpose they were heated to 150° C and then oriented mechanically by a stress method with the aid of a knife. The resultant layers had thicknesses of 8–12 μm.

4. Experimental

4.1. *Reflection measurements*

The spectral reflectance $r(\lambda)$, defined by

$$r(\lambda) = I(\lambda)/I_0(\lambda), \tag{1}$$

where λ is the wavelength, $I(\lambda)$ is the reflected light intensity at λ and $I_0(\lambda)$ is the incident light intensity at λ, was measured with the aid of the spectrophotometer shown in figure 2. The light of a tungsten lamp was focussed into the entrance of a fused silica light guide. By means of a goniometer head and a lens system, the light was then focussed on the sample. The variable angle of illumination α was counted counterclockwise from the normal. The light which was reflected at angle β (counted clockwise from the normal) from the sample was collected via a lens system and a second light guide. Then the spectral distribution of the reflected light was determined by means of a grating monochromator. The wavelength was scanned computer-controlled; the data were stored in the computer for further analysis. The system was calibrated with a $BaSO_4$ reference, whose spectral reflectance $r(\lambda)$ (for $\alpha = 45°$, $\beta = 0°$) is well known. By comparison of the reflection intensity of the sample with that of the reference, we obtained the reflectance of the sample:

$$r(\lambda) = \frac{I(\lambda)}{I_r(\lambda)} r_r(\lambda), \tag{2}$$

where $r(\lambda)$ is the spectral reflectance of the sample, $I(\lambda)$ is the measured signal of the sample, $I_r(\lambda)$ is the measured signal of the reference at $a = 45°$, $b = 0°$ and $r_r(\lambda)$ is the known spectral reflectance of the reference ($a = 45°, b = 0°$). The divergences of the illuminating light beam and of the collected light cone, respectively, were less than 5°. With this geometry (for $\alpha = 45°$, $\beta = 0°$ or $\alpha = 0°$, $\beta = 45°$) the requirements of DIN 5033 for the spectrophotometric determination of the chromaticity loci are fulfilled.

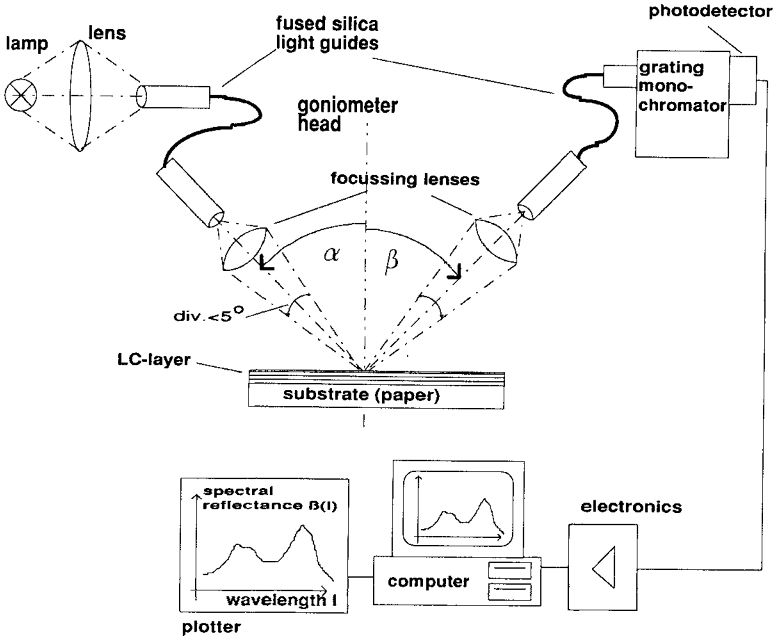


Figure 2. Determination of the spectral reflectance. Note the definition of α and β, the angles of illumination and observation, respectively: α counts counterclockwise and β counts clockwise.

4.2. *Colourimetric system and colour coordinates*

The colour stimulus $f(\lambda)$ for the human eye is determined by the spectral reflectance $r(\lambda)$ of the sample and the spectral composition $L(\lambda)$ of the illuminating light source:

$$f(\lambda) = r(\lambda)L(\lambda). \tag{3}$$

From $f(\lambda)$ we can determine the chromaticity loci x, y of the sample according to DIN 5033 (CIE 1931) [6, 7] (see figure 3). For simplicity, we have always used $L(\lambda) = 1$, i.e. an isoenergetic light source; we can therefore use $r(\lambda)$ instead of $f(\lambda)$. The colour coordinates x, y and the integral intensity J are then given by

$$X = \int r(\lambda)\underline{x}(\lambda)\,d\lambda, \tag{4a}$$

$$Y = \int r(\lambda)\underline{y}(\lambda)\,d\lambda, \tag{4b}$$

$$Z = \int r(\lambda)\,\underline{z}(\lambda)\,d\lambda, \tag{4c}$$

$$J = X + Y + Z, \tag{5}$$

$$x = X/J, \tag{6a}$$

$$y = Y/J. \tag{6b}$$

Here $\underline{x}(\lambda)$, $\underline{y}(\lambda)$, $\underline{z}(\lambda)$ are the sensitivity curves of the human eye for red, green and blue light, respectively. X, Y, Z are the standard colour values and x, y are the chromaticity loci (standard colour value portions). The integrals are taken from 380 to 780 nm.

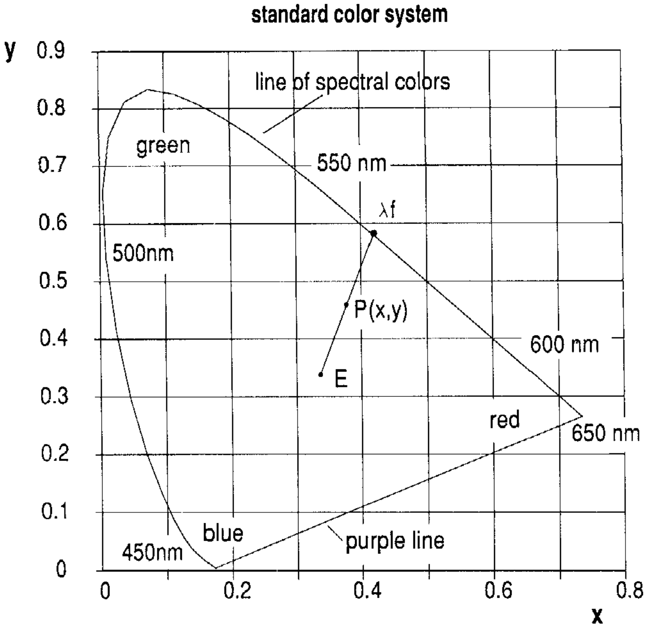


Figure 3. Standard colour table (colour triangle) according to DIN 5033 (based on the CIE 1931 standard observer and illuminating light source E). The wavelength of equal colour, λ_f, for a sample with colour cooordinate $P(x, y)$ is determined as shown: a straight line is drawn through the colour loci of the illuminating light source, E, and P. The intercept of this line with the line of spectral colours gives the desired value. The numbers near the line of spectral colours indicate the corresponding wavelengths.

Figure 3 shows in addition to the standard colour system the determination of the wavelength of equal colour, λ_f, which determines the colour impression of the human eye.

5. Results and discussion

5.1. *Expected angle dependence of the cholesteric reflection*

First we consider the reflection of a substrate coated with a thin layer of an ordered polymeric cholesteric liquid crystal (see figure 4). The incident light (angle α) is partly reflected at the air–liquid crystal boundary. The wavelength-independent specular reflectance can be described quantitatively by the Fresnel law [8]. The penetrating light is diffracted according to Snell's law [8] and reflected by the cholesteric structure, whose helical axis is tilted at an angle h with respect to the surface normal. For the angle γ (i.e. the angle of incidence with respect to the helical axis) and the wavelength of maximum reflection $\lambda_{\max}$ for this angle, we have the following condition, which corresponds to the Bragg law [9]:

$$\lambda_{\max}(\gamma) = pn\cos\gamma, \tag{7}$$

where p is the pitch of the cholesteric helix and n is the mean refractive index of the liquid crystal. For the case of perfect orientation of the cholesteric helices ($h = 0$) we could observe only a cholesteric reflection for $\alpha = \beta$ with

$$\lambda_{\max}(\alpha) = pn\cos[(\sin\alpha)/n]. \tag{8}$$

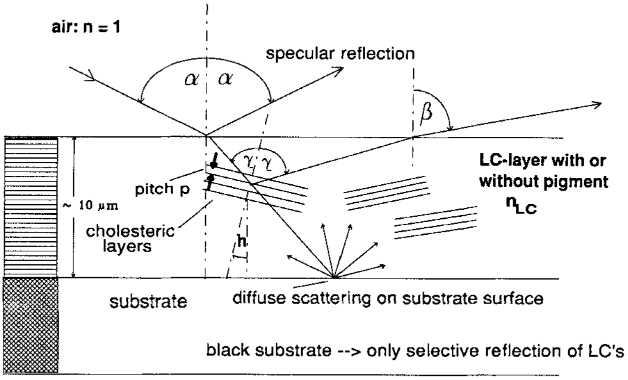


Figure 4. Reflection of a substrate coated with a thin layer of a polymeric cholesteric liquid crystal. Whilst we have only specular reflection for $\alpha = \beta$, we can also observe the cholesteric reflection for $\alpha \neq \beta$ due to the imperfect orientation of the liquid crystal helices. The diffuse scattered light at the substrate surface, whose spectral composition can be influenced by mixing the liquid crystals with pigments or by the colour of the substrate, is superimposed on this reflection. α is the angle of incidence with respect to the surface normal, β is the viewing angle, γ is the angle of incidence with respect to the helix axis and h is the angle between the cholesteric helix axis and the surface normal.

For the real case of a distribution of the helical axes around $h = 0$, we also obtain cholesteric reflection for $\alpha \neq \beta$. A simple calculation shows the dependence of $\lambda_{\max}$ from α and β, the angles of incidence and observation,

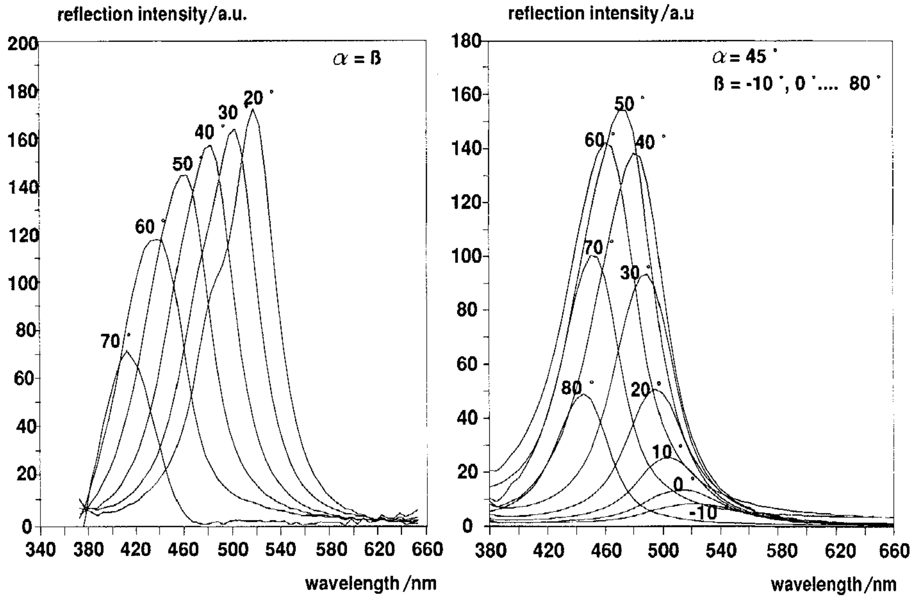
$$\lambda_{\max}(\alpha, \beta) = pn\cos\left\{\frac{1}{2}\left[\arcsin\left(\frac{\sin\alpha}{n}\right) + \arcsin\left(\frac{\sin\beta}{n}\right)\right]\right\}. \tag{9}$$

The reflection intensities at $\lambda_{\max}$ should be greatest for $\alpha = \beta$; for $\alpha \neq \beta$ this intensity should decrease with increasing difference between α and β, depending on the distribution of h.

The remaining light is reflected or, in our case, diffuse scattered at the substrate surface. The spectral composition of this scattered or reflected light can be influenced in different ways. We can mix the liquid crystals with pigments or dyes, which absorb a part of the spectrum or we can use a coloured substrate scattering or reflecting only a part of the incident spectrum. So we have as a result of the structure shown in figure 4 the superposition of the specular reflection at the air–liquid crystal boundary, of the cholesteric reflection and of the light scattered at the substrate surface. If we use a black substrate, we obtain the pure cholesteric reflection, which is superimposed for $\alpha = \beta$ with the wavelength-independent specular reflection.

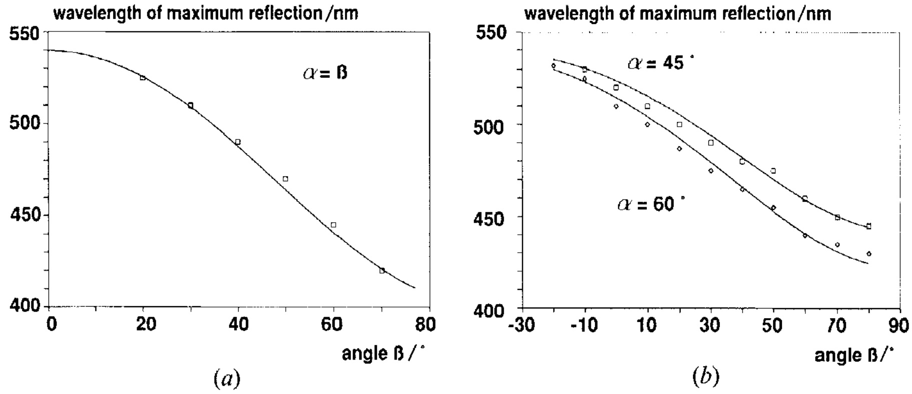
5.2. *Cholesteric liquid crystals on a black substrate*

Figure 5 shows the dependence of the reflection spectra of a black substrate coated with a green reflecting cholesteric polymeric liquid crystal on viewing angle β. The spectra in figure 5(*b*) were recorded with fixed angle of illumination ($\alpha = 45°$), whereas the curves in figure 5(*a*) are valid for $\alpha = \beta$, i.e. the angle of illumination equals the angle of observation. The wavelength-independent contribution of the specular reflection, which can be calculated according to the Fresnel law, was subtracted from the spectra. The variation of the wavelength of maximum reflection with angle β (see figures 6(*a*) and 6(*b*)) can be fitted with the aid of equations (8) and (9),



(*a*) (*b*)

Figure 5. Reflection spectra of a green reflecting polymeric liquid crystal on a black substrate (paper) for different angles, illuminated with an isoenergetic light source. (*a*) The case when the angle of illumination equals the angle of observation. (*b*) The variation of the spectra with the angle of observation for a fixed angle of illumination. The wavelength-independent contribution of the specular reflection at the air–liquid crystal boundary, obeying the Fresnel law, was subtracted from the spectra.



(*a*) (*b*)

Figure 6. The wavelengths of maximum reflection, taken from figure 5, are compared with the theoretical values, which were calculated according to equations (8) and (9). (*a*) □, Experimental values, $\alpha = \beta$; ——, calculated according to equation (8), $pn = 540\,\mathrm{nm}$, $n = 1{\cdot}5$; (*b*) □, ◇, experimental, $\alpha = 45°$ and $60°$, respectively; ——, calculated according to equation (9), $pn = 540\,\mathrm{nm}$, $n = 1{\cdot}5$.

respectively. The observed decrease in reflection intensity with increasing angle in the case $\alpha = \beta$ (see figure 5 (*a*)) can be explained quantitatively: with increasing angle of illumination the specular reflection at the air–liquid crystal boundary increases, and so the amount of light which can be reflected by the cholesteric decreases. For a fixed angle of illumination α, the intensity at maximum versus viewing angle β curves show

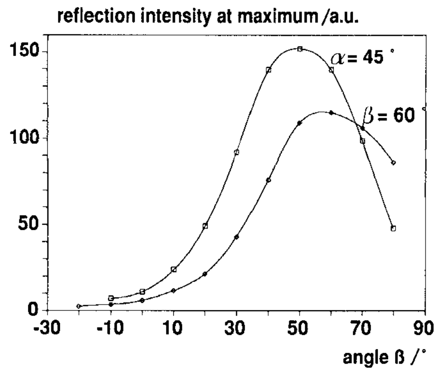


Figure 7. For the case of a fixed angle of illumination (see figure 5(*b*)), the intensity at maximum for different values of the viewing angle shows a pronounced maximum around $\beta = \alpha$. The width of this distribution depends on the orientation of the liquid crystal helices. □, ◇, Experimental values, $\alpha = 45°$ and 60°, respectively.

a gaussian shaped distribution around $\alpha = \beta$ (see figure 7). This effect is explained by the imperfect orientation of the helical axes. From the width of this distribution and from the shape of the reflection spectra, which deviate from the ideal reflection spectra of cholesteric phases [1, 9], the distribution function of the helix axes and the number of cholesteric periods contributing to the reflection could be calculated [10, 11].

5.3. *Pigmented polymeric cholesteric liquid crystals*

For the observation of the effects of mixing liquid crystals with pigments or the use of coloured substrates, both cases are referred to as pigmentation, we have chosen from all the possible angles the special geometry shown in figure 8, which corresponds to real observation conditions. Figure 9(*a*) shows the change of the colour loci of some liquid crystals, partly pigmented, with viewing angle β. The angle of illumination, α, was held constant (corresponding to figure 8). For two different liquid crystals on a black substrate (yellow and green reflecting) the normal blue shift with increasing viewing angle is observed, from yellow to green and from green to blue, respectively. In contrast to this the other examples in figure 9 show a red shift with increasing angle or even purple colours, which we cannot obtain with pure liquid crystals on a black substrate. We can also observe red shifts followed by a blue shift (red liquid crystal on a bright blue paper) and many other effects not presented here.

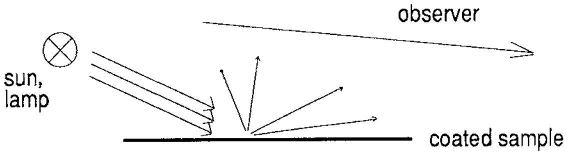


Figure 8. A fixed angle of illumination ($\alpha = 60°$) corresponding to a fixed lamp, and a variable angle of observation corresponding to a moving observer, were chosen for the following measurements.

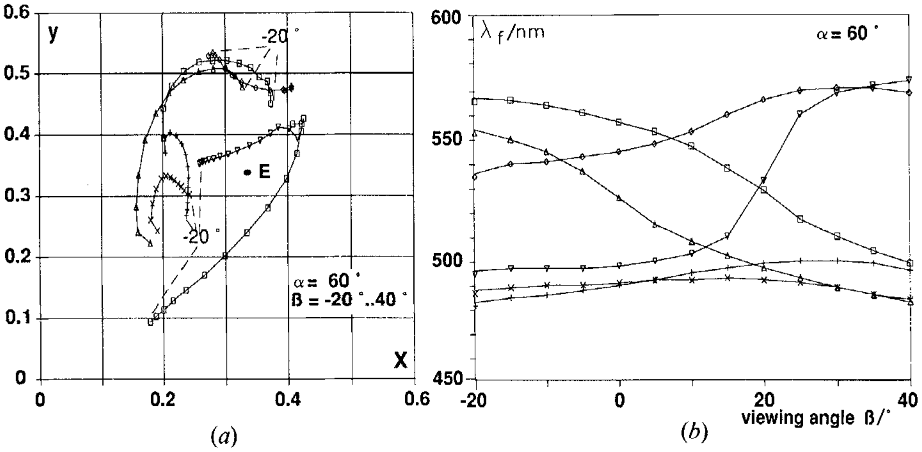


Figure 9. (a) Colour coordinates according to DIN 5033 (CIE 1931) and wavelengths of equal colours, λ_f, determined as indicated in figure 3 (b), for some examples. The angle of illumination was held constant ($\alpha = 60°$); the angle of observation β varied from $-20°$ to $+40°$, the starting and ending points are indicated Δ, green liquid crystal on black paper; □, +, yellow liquid crystal on black and bright blue paper, respectively; ▿, yellow liquid crystal with green pigment (Sicoflush P grün 8730, 2 per cent) on white paper; ◇, ×, □, red liquid crystal on green, bright blue and dark blue paper, respectively.

The dependence of the wavelength of equal colour which was determined according to figure 3 on viewing angle β is shown in figure 9 (b). For pure liquid crystals on a black substrate, the normal decrease in reflection wavelength with angle is observed, whereas for mixtures of liquid crystals with suitable pigments on white paper or for pure liquid crystals on suitably coloured substrates, an increase in the wavelength of equal colour with increasing viewing angle is observed.

5.4. *Theory of colour mixing*

These special colour effects can be explained by simple additive colour mixing. Figure 10 shows, for example, the change of the colour loci with viewing angle for the substrate, the liquid crystal on black paper and the liquid crystal coated substrate (red liquid crystal on blue paper). From the theory of additive colour mixing we obtain for the colour coordinates (x_m, y_m, J_m) of the mixture of two colours with coordinates (x_1, y_1, J_1) and (x_2, y_2, J_2):

$$x_m = \frac{x_1 J_1 + x_2 J_2}{J_1 + J_2}, \tag{10a}$$

$$y_m = \frac{y_1 J_1 + y_2 J_2}{J_1 + J_2}, \tag{10b}$$

$$J_m = J_1 + J_2. \tag{10c}$$

Using these equations we obtain good agreement of the measured colour coordinates of the liquid crystal coated blue paper and the coordinates that were calculated using the values of the single components (see figure 10). The additive nature of this effect

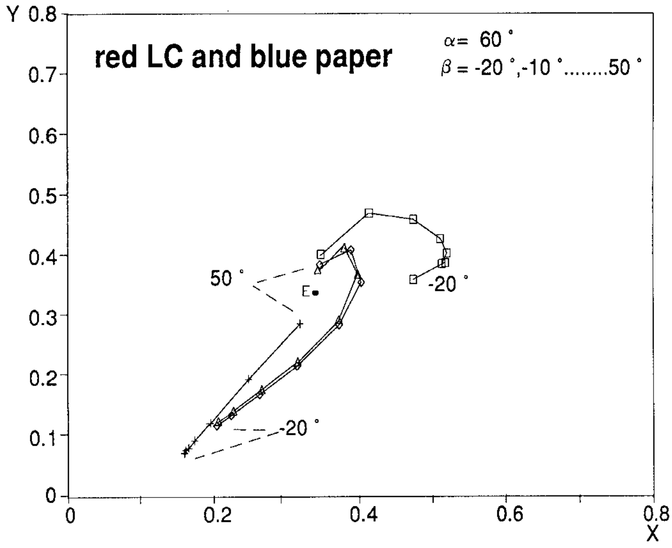


Figure 10. The measured angle dependence of the chromaticity loci (according to DIN 5033 or CIE 1931) of the blue paper, the red liquid crystal on black paper (pure cholesteric reflection) and of the liquid crystal coated blue paper. The angle of observation β varies from $-20°$ to $+50°$, the starting and ending points are indicated, the angle of illumination was held constant ($\alpha = 60°$). The result of additive colour mixing according to equation (10) of the single components is in good agreement with the measured values. +, Blue paper; □, ◇, red liquid crystal on black and blue paper, respectively; △, additive colour mixing of □ and +, calculated according to equation (10).

is best seen with the reflection spectra of the single components and of the liquid crystal coated substrate for some angles (see figure 11).

The reflection intensity of the substrate rarely changes with angle, whereas the reflection intensity of the liquid crystal period is strongly angle dependent (see also figure 5). So, for small (or negative angles β), the colour is dominated by the substrate, while for increasing angles (up to $\beta = \alpha$) the colour is mainly determined by the liquid crystal layer.

By means of this simple theory we are able to predict the effects of the reflection colour of mixing cholesteric polymeric liquid crystals with pigments or by coating coloured substrates with such liquid crystals. So we can obtain the desired effect.

6. Summary

The effects of mixing cholesterics with pigments or by coating coloured substrates with cholesterics can be simply explained with additive colour mixing. These polymeric liquid crystals can be easily oriented on various substrates; mixing them with pigments does not disturb the cholesteric phase to an appreciable extent. Applications of these colour effects are mainly in the decorative sector, and the easy orientability of this class of substances makes them suitable for use as optical filters and for optical data storage.

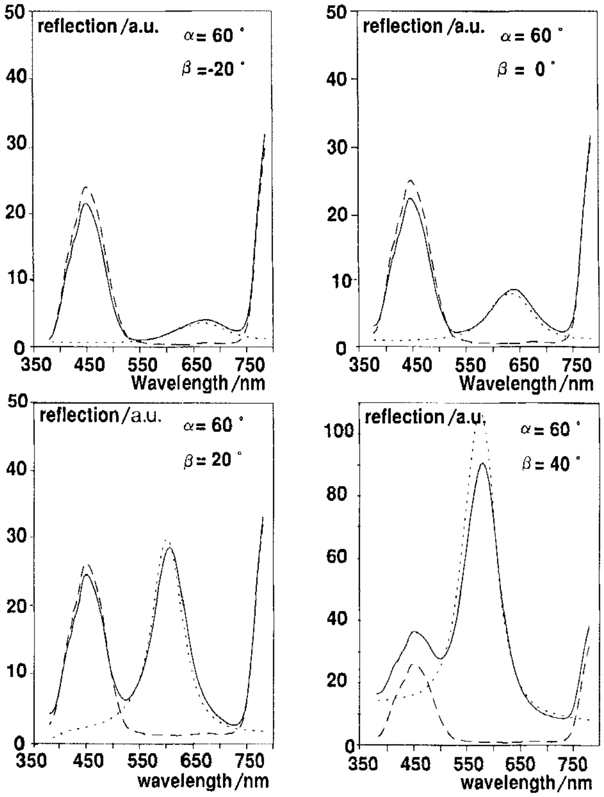


Figure 11. Reflection spectra for different angles of observation β, indicated in the figures, and fixed angle of illumination (α = 60°), showing the additive nature of these effects. – – –, Blue paper; · · · ·, red liquid crystal on black paper and ——, on blue paper.

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