

# Colorimetry of Fractured Cholesteric Liquid Crystal Polymers

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## Abstract

Cholesteric liquid crystals produce reflection or transmission which is selective with regard to both polarization and wavelength. Thermal fracturing of the polymer form of cholesteric liquid crystals creates a new form called flakes. Light-, scanning electron-, and atomic force microscopies confirm that these cholesteric flakes maintain the same periodic structure that is responsible for the selective optical effects of the unfractured cholesteric.

Because they can be mixed with a host and because of their color gamut, cholesteric flakes are being developed as a new kind of paint. Applications for cholesteric flake paint focus on its ability to selectively reflect one handedness of circular polarization within a narrow wavelength band and on its ability to produce a wide color gamut by classic color additivity. Colorimetric techniques specify the chromaticity of this new type of colorant which is both polarization- and angle-sensitive.

## Introduction

Cholesteric liquid crystal (CLC) polymers consist of rod-like molecules arranged in layers. Within each layer, molecules are aligned with their long directions oriented parallel to each other. This direction rotates slightly for each subsequent layer creating a helical macrostructure with a characteristic pitch,  $P$ , and an average refractive index,  $n$ . Light whose wavelength,  $\lambda$ , (such that  $\lambda = \lambda_0 = nP$ ) and polarization orientation (right- or left-handed circular) allow it to be superimposed on the helix will be reflected. All other light will be transmitted. The color reflected by a particular CLC polymer is determined primarily by its chemical composition. The layered structure also gives rise to Bragg-like viewing-angle dependence of color.

The CLCs used for inks and paints in this study are polysiloxane polymers<sup>1</sup>. Their refractive indices are measured using an Abbe refractometer, and  $\lambda_0$  of the unfractured films is determined using a Perkin-Elmer  $\lambda 9$  spectrophotometer. From these optical data, the pitch of the unfractured CLC can be calculated.

The polymers are helically aligned by knife-coating at elevated temperature. The aligned films are then ther-

mally fractured into flakes<sup>2</sup>. We have shown by scanning electron and atomic force microscopies that flakes maintain the helical structure of the cholesteric. In particular, the pitch of the helix as measured physically by atomic force microscopy agrees well with the pitch determined by optical methods. This agreement indicates that flakes maintain the selective wavelength reflection properties of the original sample. The selective polarization properties were confirmed in transmission profiles determined by spectrophotometer.

## CLC Flakes as Colorants

The evaluation of the colorimetric nature of CLC before now was inconvenient and often simply not possible on many surfaces: Monomeric CLC, usually liquid at room temperature, requires two substrates in a sandwich configuration to provide alignment surfaces. Polymer-dispersed CLC requires high voltages to produce the helical structure<sup>3</sup>. Unfractured polymer CLC, highly viscous or even solid at room temperature, requires elevated temperatures to flow easily enough to be aligned.

In contrast, CLC flakes can be used to produce a colorant which is stably aligned over wider temperature ranges than is low-weight CLC<sup>4</sup>, does not require special surfaces or electro-optic control, and can be applied at room temperature by paintbrush, airbrush, roller, or even fountain pen.

CLC flakes can be ground and sieved to achieve particles of relatively uniform diameter. Samples have been produced with diameters as small as  $15 \pm 5 \mu\text{m}$ , comparable to traditional pigment particle sizes. Like traditional pigments, fractured CLC polymer can be mixed, or embedded, in a host fluid. This enables CLC flake paints to be manipulated like traditional paints, while maintaining the reflective and polarizing selectivity of the cholesteric structure.

## Colorimetry of CLC Flakes

The reflectance amplitude of CLC colorants is strongly affected by both the polarization of the incident beam and the angle of observation. Consequently, colorimetric measurements will be dependent on these two factors. To establish a basis for comparing CLC flake paint

to traditional paint, we chose to measure color coordinates using the standard 45/0 geometry and the CIE 1931 xyY system. It should be noted that for traditional paints, changes in measurement geometry can lead to changes in the values of the chromaticity and luminosity measured. These changes, though, are usually relatively small compared to those that result from measurement geometry changes for CLC paints. For CLCs, shifts in observing angle lead to significant differences in perceived hue but shifts in illumination angle lead to only slight differences in hue. The 45/0 choice describes CLC flake paints, therefore, in a very specific viewing condition.

Colors are measured on a Gretag SPM 100 spectrophotometer and on a LightSource ColorTron (on loan through Lucid Technologies, Henrietta, NY) which have been set for standard daylight illuminant  $D_{65}$  and are plotted as x,y chromaticity coordinates on the CIE 1931 Chromaticity Diagram.

When cholesteric liquid crystals are extremely well-aligned in a continuous film, they show a reflection profile which is minimal outside the selective wavelength band. Within the selective band, the reflectance reaches some maximum. The profile shows no more than two transitions between the minimum reflectance and this maximum reflectance. For incident illumination of the proper polarization handedness, this maximum can approach 100% R. As such, CLCs come very close to meeting the Ostwald/Schrödinger criteria (as summarized by MacAdam<sup>5</sup>) for yielding maximum visual efficiency. Consequently, purity of CLC color approaches the maximum attainable for real colorants.

CLC flakes painted onto a surface do not show the same level of purity as the well-aligned film. Studies of light scattering and Bragg's Law for CLC flake samples suggest that as flakes become smaller in size, they scatter more light and show greater randomization of the helix axis direction. The effect of scattered light does not change the chromaticity but does decrease Y. The effect of helical axis direction randomization serves to broaden the selective reflection profile which strongly reduces purity. We believe that addressing the materials processing techniques of CLC flake manufacture to produce small flakes but with higher aspect ratios will increase the color purity of the CLC flake colorants.

If different CLC coatings are mixed, the perceived color is a spatially-averaged-type additive mixture of the different colors of light reflected. While dominant wavelength and purity can be determined for any individual sample, CLC flake mixtures can be further characterized by distance ratios. Distance ratios on the CIE 1931 Chromaticity diagram correspond to ratios of amounts of light being added. For CLC flake mixtures, these distances also roughly correspond to ratios of masses of CLC flakes in the mixture. Unlike opaque colorants, if flakes of different colors cover each other, provided their reflection profiles do not overlap, they are transparent to each other. Both will contribute to the perceived color. However, when flakes of the same color overlap, color saturation does not increase once a threshold thickness has been reached.

## Applications

In addition to the color gamut made available by the mixing of CLC flakes, CLC coatings provide the capability of painting a surface to reflect only right-handed or only left-handed circularly polarized light. This suggests many new display possibilities.<sup>2</sup> For example, painting an image using right-handed CLC ink and then painting the same image stereoscopically offset and using left-handed CLC ink would allow an observer wearing the appropriate circularly polarizing glasses to view a three-dimensional full-color passive image.

CLC flakes could also be used instead of or in conjunction with traditional pigments for document identification and security. Currency, for example, is in ever greater danger of being counterfeited due to the improvement in color copiers<sup>6</sup>. Normal copiers, however, would be incapable of reproducing the selective polarization behavior of embedded CLC coatings.

Polymer CLCs have already been proposed for document security based on their angle-dependent color properties<sup>7</sup>. Well-suited to simple first-line inspection as well as machine detection, CLCs polymer coatings have a higher structural order, therefore allowing more freedom of optical manipulation, than multilayers, thin films, or gratings. Before now, typical CLC polymer coatings were limited by high-temperature requirements for application (e.g. hot stamp transfer). CLC flake paints, on the other hand, provide all the optical versatility of unfractured CLC polymers, but may be applied at room temperature. CLC flake coatings may be painted onto the document, enmeshed in the document fibers itself, or painted directly onto other surfaces, such as metal, plastic, or cloth. Further, CLC flakes provide another variable with which to complicate counterfeiting: mixing CLC polymers before fracture to select a color based on the particular  $\lambda_0$  reflected, or mixing CLC flakes after fracture to select a color based on spatial averaging.

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