# Color Gamut of Cholesteric Liquid Crystal Films and Flakes by Standard Colorimetry

Ever since cholesteric liquid crystals (CLC's) were discovered in 1888,[1] CLC colors have been noted for their qualitative vividness and luminosity;[2] however, there have been few quantitative colorimetric studies examining CLC's as colorants. We will describe how CLC's produce color, what colorimetric studies have been done on them, and how we have extended and improved on these previous studies.

CLC molecules generally have a large aspect ratio and are often modeled as long thin rods. These rods orient along an average preferred direction in a given plane. This preferred direction, indicated by a unit vector called the director, **n**, rotates slightly from one plane to the next, forming a helix structure that may be right-handed or left-handed depending on the constituents of the molecule.[3] In a typical model (shown in Fig. 73.62) the periodicity of the helix leads to the constructive interference colors of CLC's. The distance it takes the director to rotate through 360° is called the pitch $P$ of the CLC helix. The pitch multiplied by $\bar{n}_n$, the average refractive index of the molecular layers, gives the wavelength of selective reflection, $\lambda_0$, which may range from the ultraviolet through the visible to the infrared.[4] The width of the reflected wavelength band for visible-reflecting CLC's ($\lambda_0$ ranging from 380 to 780 nm) can typically range from 10 to 100 nm.[5]

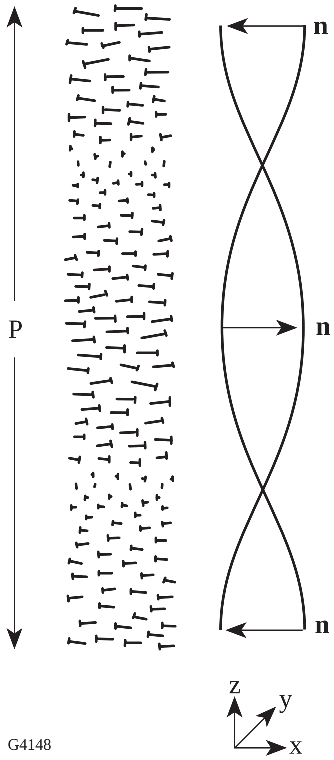

Figure 73.62
Schematic model of CLC structure.

In addition to the selectivity of reflected wavelength, the CLC helix is also selective with respect to polarization. Incident light that is superimposable on the helix, i.e., of the proper wavelength *and* the proper circular polarization, will be reflected.[4] Figure 73.63 shows schematically how randomly polarized white light incident parallel to the CLC helix is selectively reflected by wavelength and polarization.

In the ideal CLC structure, there is no discontinuity in any given plane. In real CLC structures, there may be defects in molecular orientation similar to dislocations in solid crystals. The regions of perfect structure between the defects or other discontinuities are referred to as *domains*.[6] Samples that are defect-free are called *monodomain*. Samples with discontinuous domains are referred to as *polydomain*.

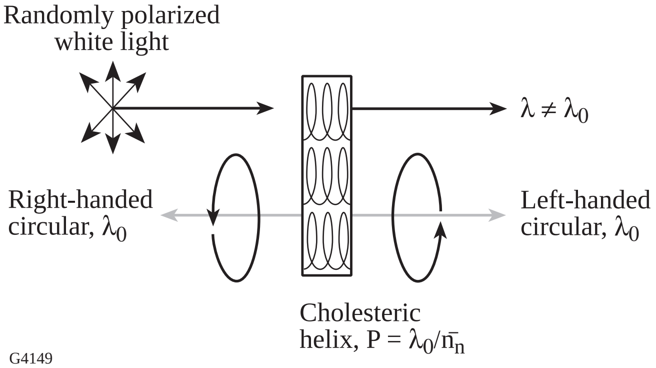

Figure 73.63
Schematic diagram of the wavelength and polarization selectivity of CLC's.

The CLC's that have been used for actively controlled color display purposes are usually polydomain: *polymer dispersed* in which the CLC molecules are found in microdroplets (~0.1 $\mu$m to ~10 $\mu$m in diameter)[7] distributed in an isotropic polymer matrix[8] and *gels* in which the CLC's form a more continuous phase with a small amount of either isotropic or anisotropic polymer to form a network that contributes to CLC molecular orientation.[9] Voltage and frequency are used to control the orientation of the CLC helices within the microdroplets or in the support polymer network; thus the ability to selectively reflect specific wavelength bands can be controlled electro-optically. Kitzerow *et al*.[10] calculated the chromaticities from the reflectivity spectra of a polymer-dispersed CLC system as a function of temperature. Although the chromaticity plot appears to indicate a color gamut covering almost the entire chromaticity diagram, many of the measurement details are unspecified, including the illuminant, the measurement angles, the actual chromaticity and luminosity values, and the voltage required for selective reflection. They indicate, however, that 2 to 3 V/$\mu$m are required to see some reflection, with intensity of the selective reflection increasing with increasing field strength to reach a plateau at 125 V/$\mu$m.

A third form of polydomain CLC that has been used for color display is called *encapsulated*. It is similar to polymer-dispersed CLC except for preparation method and has been used for decorative art[11] and for thermally controlled displays.[12] In the latter, temperature changes twist or untwist the CLC helix, shortening or lengthening the pitch and thereby controlling the reflected color. Makow and Sanders[11] used encapsulated CLC's to elucidate the qualitative color additivity of encapsulated CLC's of different colors in separate layers.

A fourth form of CLC's, *continuous film*, has been used for color filters,[13] optical notch filters,[14,15] polarization isolators,[16] and decorative art.[17] Even CLC continuous films may be polydomain unless some care is taken in the sample preparation.[18] The continuous films may be low-molecular-weight CLC's (LMCLC's) or higher-weight oligomer/polymer materials.

LMCLC's require two support substrates to promote the formation and maintenance of the helix structure across a continuous film. Makow[19] showed that, as with the encapsulated CLC's, layering different colors produces color additivity. Layering of LMCLC films, however, requires separating the layers by thin transparent sheets to prevent physico-chemical mixing that causes pitch averaging/blending.[20,21]

The oligomer/polymer type of CLC is more temperature stable than LMCLC's.[22] Oligomers/polymers can be physically manipulated at temperatures above a certain threshold called the *glass transition temperature* and retain molecular orientation below this temperature. One class of oligomers—cyclic polysiloxanes—has been particularly widely investigated.[23,24]

Cyclic polysiloxanes have been the subject of several colorimetric studies. Makow[25] demonstrated the artistic beauty of CLC polysiloxane films and showed that any spectral color could be produced by simply physico-chemically mixing a short-pitch with a long-pitch CLC. He also suggested that CLC polysiloxane films exhibit chromaticities outside the gamut of available colorants determined by Pointer,[26,27] although Makow actually compared CLC films measured in an 8/*d* geometry of an integrating sphere to Pointer's real surface colors measured by a 45/0 colorimeter. Nevertheless, he did initiate the possibility of comparing CLC's to other colorants. Makow also introduced the qualitative use of isoluminous contour lines as theoretical limits of saturation. As early as 1916, Ostwald[28] had concluded that there was some maximum attainable saturation for any given color. The reflection profile that would yield such a maximally pure or optimal color requires that the spectral reflectance have values of only zero or 100%, with no more than two discontinuous transitions between these values. The reflection profiles of most normal absorptive pigments do not meet these criteria. MacAdam[29] later used the CIE 1931 diagram to define limits of maximum attainable purity for a given luminosity $Y$ and plotted these isoluminosity loci as contour lines within the CIE 1931 diagram. A sample with a given $Y$ can be no purer than its associated isoluminous line.

One other chromaticity study on CLC polysiloxanes was done by Eberle *et al*.[30] They examined CLC polysiloxanes dissolved with dyes and CLC polysiloxanes on colored (paper) substrates, at many combinations of incident and reflection angles. The color additivity of a CLC and a traditional colorant (dye or paper) was quantified, but layers of CLC's of different colors were not examined. In that study, chromaticity and luminosity were shown to be simple averages of the components involved in any pair combination. Although not explicitly stated, Eberle *et al.* used the Center-of-Gravity Color-Mixing Principle.[31]

In its standard form, the Principle describes how two colors, $C_1$ and $C_2$, designated by chromaticity and luminosity coordinates $x_1y_1Y_1$ and $x_2y_2Y_2$ in the CIE 1931 chromaticity system are additively mixed. Using MacAdam's notations,[32] if

$m_1$ units of color $C_1$ are mixed with $m_2$ units of color $C_2$ (where $m_1 = Y_1/y_1$ and $m_2 = Y_2/y_2$), the chromaticity of the mixture color $C_3$ lies on a line connecting $C_1$ and $C_2$ on a CIE 1931 chromaticity diagram and has the following chromaticity values:

$$x_3 = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \tag{1}$$

$$y_3 = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}, \tag{2}$$

$$Y_3 = Y_1 + Y_2 . \tag{3}$$

The distance ratio of the line segments $\overline{C_1C_3}$ and $\overline{C_2C_3}$ shows the center-of-gravity relationship:

$$\frac{|C_1C_3|}{|C_2C_3|} = \frac{Y_2/y_2}{Y_1/y_1}. \tag{4}$$

If each of the two colors occupies a discrete fractional area designated $A_1$ or $A_2$ respectively, Eqs. (1)–(3) may be written as

$$x_3 = \frac{A_1 m_1 x_1 + A_2 m_2 x_2}{A_1 m_1 + A_2 m_2}, \tag{5}$$

$$y_3 = \frac{A_1 m_1 y_1 + A_2 m_2 y_2}{A_1 m_1 + A_2 m_2}, \tag{6}$$

$$Y_3 = A_1 Y_1 + A_2 Y_2 . \tag{7}$$

Since the CLC's with dyes or the CLC's on colored substrates occupied the same area, the form of the Center-of-Gravity Color-Mixing Principle used by Eberle *et al.* invoked Eqs. (1)–(3) and showed good agreement with experiment for their systems. They concluded that the CLC contributed to the measured color significantly near specular geometries (illumination angle ≈ reflection angle), but otherwise the substrate color dominated. This contribution of a colored substrate to the measured color of a CLC confirmed quantitatively what earlier artistic[17] work with CLC's had found: a black backing, contributing no color to the CLC appearance, produces truer CLC color effects.

To date, no *standard* colorimetry has been conducted on continuous CLC films or on discrete CLC domains, that is, at 45/0 and such that all conditions of measurement are explicitly known. No colorimetric experiment has quantified the color additivity of layering CLC's. No deterministic method has been developed for the color additivity of discrete CLC domains. No comparison has been made of CLC's as colorants and traditional absorptive colorants under similar conditions of measurement.

In this article, we address each of these issues. The CLC's used are cyclic polysiloxanes in two forms: continuous film and a new form called *flakes*. These two forms allow us to compare the color of CLC films to other colorants and to compare the large domains of a continuous film to the small domains of flakes. Further, flakes dispersed in a host will serve as a model for polymer-dispersed, gel, and encapsulated CLC forms. Principally, this article will show how the color gamut of CLC's can be affected by the form of the CLC, the size of the domains, and the method of mixing CLC's. Other aspects of CLC colorimetry including CLC flake production, polarization issues, the shape of the selective reflection profile, mixing CLC's with traditional absorptive dyes, and CLC's modeled as optimal colors are addressed elsewhere.[33]

## Sample Preparation and Measurement Methods

The liquid crystal phase of the CLC cyclic polysiloxanes used in this study exists between 50°C and 200°C. At temperatures below this range, the molecular orientation is "frozen." At temperatures higher than this range, these materials are isotropic, noncolored liquids that decompose in the presence of oxygen. Three polysiloxanes were used: CLC670 (red reflecting), CLC535 (green reflecting), and CLC450 (violet reflecting). The number refers to $\lambda_0$, the wavelength in nanometers that is the center of the reflected wavelength band.

Continuous films are prepared by a process referred to as "knife-coating." A sample of CLC on a microscope slide or silicon wafer is heated to ~130°C. Another microscope slide is used on edge as a "knife" to spread the CLC into a thin film ~30 $\mu$m thick. This process produces the proper molecular orientation that results in brilliant reflective color.

A second form of CLC is produced by knife-coating continuous films on silicon wafers[34] and submerging them into liquid nitrogen. The films fracture into smaller pieces called *flakes*.[35] Flakes are collected by rinsing into a methanol slurry. The slurry is washed with methanol through a stack of sieves[36] into four size-groups: 90 to 180 $\mu$m, 45 to 90 $\mu$m, 20 to 45 $\mu$m, and <20 $\mu$m. The average refractive indices of the unfractured films are measured on an Abbe refractometer.[37] The flakes made from the films are mixed into a slurry (12%±3% by weight) with an enamel, filtered[38] from a commercially available paint,[39] providing a very closely index-matched, transparent colorless host. This enamel-and-flake slurry is painted into a 1-cm × 2-cm color patch on black toner paper from a laser printer.[40] A schematic diagram of the typical orientation of CLC flakes brushed onto paper is shown in Fig. 73.64.

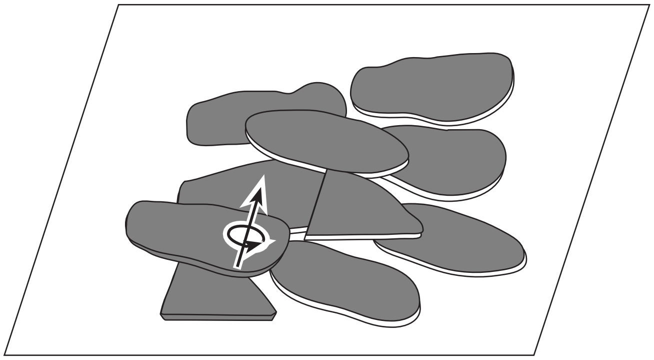

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Figure 73.64
Schematic diagram of CLC flakes painted onto paper.

The chromaticity and luminosity (*x*,*y*,*Y*) of CLC samples were measured with two colorimeters, each using the CIE 1931 basis with $D_{65}$ illuminant. CLC flake samples in enamel painted directly onto black toner paper were measured using the Gretag SPM 100-II colorimeter.[41] Due to the motor action of the Gretag detection head, the measurement of slides was unstable so CLC films on microscope slides with black toner paper backing were measured using the ColorTron II colorimeter.[42] Each sample was measured in five evenly spaced spots along the length of the color patch. These values were averaged, and a standard deviation due to variation across the sample was determined. Inter-instrument agreement was within this standard deviation.

The color of CLC's is angle dependent, following a Bragg-like law;[43] however, since most commonly available colorimeters use the 45/0 geometry, this article will address color effects for this fixed geometry only.

## Experiments and Results

Since this article deals primarily with the nature of the color gamut of CLC's, we will discuss the six main features we have elucidated regarding techniques to access regions of CIE 1931 *x*,*y*,*Y* color space with CLC's as the colorants:

### 1. The Color Gamut of the Three Original CLC Films

Table 73.X lists the *x*,*y*,*Y* values and Fig. 73.65 illustrates the chromaticity positions of the original three CLC films. Geometric color additivity on the CIE 1931 chromaticity diagram ensures that an additive mixture of any two points yields a third chromaticity point *on* the line connecting the two components.[31] Using only the original three CLC's as continuous films, the chromaticities we can access are limited to those *on* the triangle of Fig. 73.65.

Table 73.X: The measured chromaticities and luminosities, *x*,*y*,*Y*, of the three original CLC polysiloxane films.

| CLC ID | *x* | *y* | *Y* |
|---|---|---|---|
| CLC670 | 0.5153 | 0.3459 | 8.83 |
| CLC535 | 0.2306 | 0.4803 | 26.26 |
| CLC450 | 0.1777 | 0.0777 | 4.33 |

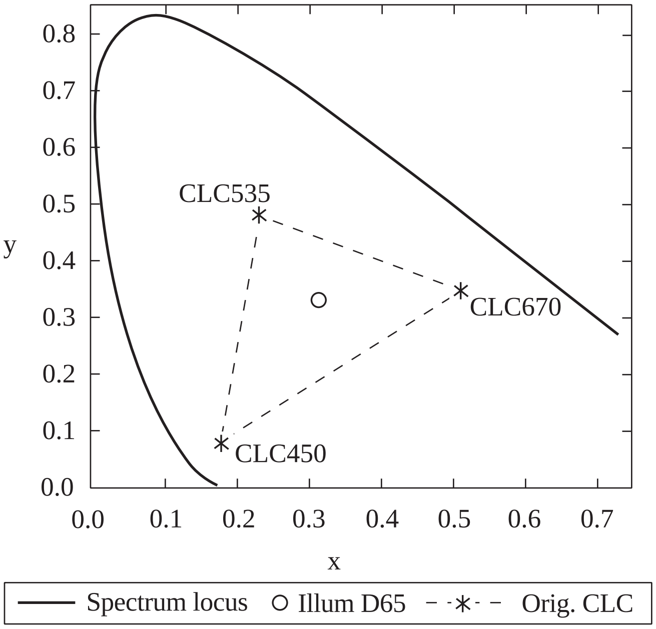

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Figure 73.65
Chromaticities of the three original CLC polysiloxanes as knife-coated films on microscope slides with black toner paper backing.

### 2. Color Additivity by Layering

Unlike traditional inks in which absorption produces subtractive color combination of layers, CLC's are reflective.

Provided that each layer allows reflection from other layers (i.e., each reflecting layer is transparent to the others), the color mixing of CLC layers is *additive*. The knife-coated slides of CLC670, CLC535, and CLC450 were stacked in pairs with black toner paper at the bottom. Chromaticity and luminosity were recorded using the ColorTron II. Table 73.XI lists the results and Fig. 73.66 illustrates that the additive combination does fall on the line connecting the two components. The CIE color gamut is still limited to the triangle formed by CLC670, CLC535, and CLC450.

The color additivity was not a simple 1:1 averaging of the two layers as Eberle *et al.*[30] had found for CLC's layered with colored substrates. In fact, we found a clear difference in chromaticity of layered CLC's based on stacking order. For example, "670 over 450" (meaning the slide with CLC670 was on top and the slide with CLC450 was underneath) is closer to pure CLC670 than "450 over 670," which is closer to pure CLC450. These layers were made by placing the microscope slides together, both face up. This resulted in a layer-to-layer separation of one microscope-slide thickness. The presence of the microscope slide reduced the intensity of the light reaching the detector. The 45/0 geometry of the ColorTron II is designed to illuminate the sample *at* the measurement aperture. The 1-mm-thick microscope slide, displaced one layer from the ideal position, reducing incident intensity and therefore reflected intensity. An alternate way of stacking was to place the CLC layers in contact but separating both layers from the colorimeter by the thickness of a slide. There was virtually no difference in chromaticities from those of Table 73.XI using this alternate method of stacking. The combination chromaticity point fell closer to whichever sample was closest to the colorimeter, even when both films were subjected to the same displacement error from the measurement aperture. This indicated that the upper layer prevented the full reflection of the lower layer due to an imperfect helical structure and some overlap of the reflection bands.

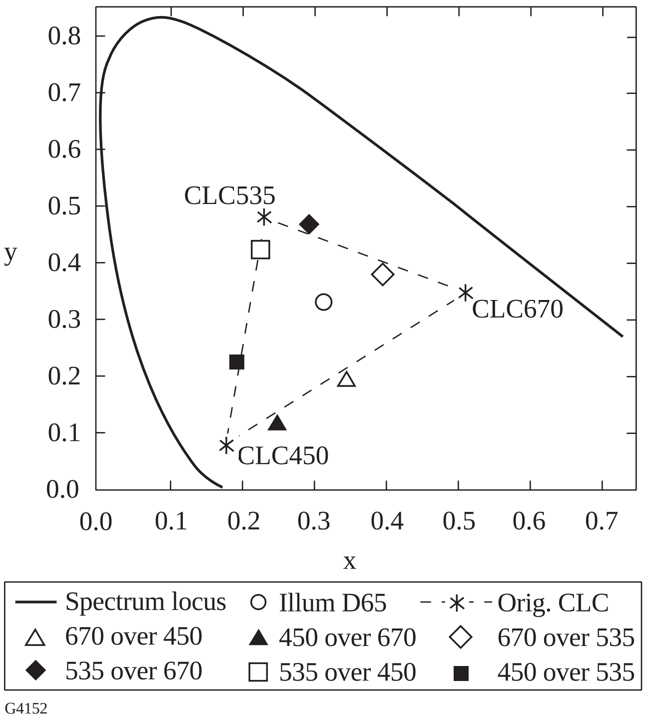

Figure 73.66
Chromaticity plot of layered CLC polysiloxane films.

Table 73.XI: *x*,*y*,*Y* of layered CLC polysiloxane films.

| Sample | | *x* | *y* | *Y* |
|---|---|---|---|---|
| Upper | Lower | | | |
| --- | CLC670 | 0.5153 | 0.3459 | 8.83 |
| --- | CLC535 | 0.2306 | 0.4803 | 26.26 |
| --- | CLC450 | 0.1777 | 0.0777 | 4.33 |
| CLC670 | CLC535 | 0.3972 | 0.3839 | 16.81 |
| CLC535 | CLC670 | 0.2958 | 0.4659 | 30.84 |
| CLC670 | CLC450 | 0.3446 | 0.1984 | 9.69 |
| CLC450 | CLC670 | 0.2491 | 0.1264 | 8.67 |
| CLC535 | CLC450 | 0.2257 | 0.4240 | 27.77 |
| CLC450 | CLC535 | 0.1953 | 0.2320 | 18.21 |

### 3. New Hues by Mixing the Original CLC Polysiloxanes

In this section, we extend Makow's earlier qualitative work[25] by quantifying the chromaticities and luminosities of hues produced by physico-chemically mixing the original CLC polysiloxanes.

Two techniques were used to mix the polysiloxanes. The first technique was simply to place two CLC polysiloxanes in proximity, elevate the temperature to ~130°C, and stir them together with a microspatula. A second technique, which ensured more complete, homogeneous mixing, was mutual dissolution of the two components in dichloromethane, stirring, and evaporation. The resulting mixtures from this second technique were then prepared as knife-coated slides. The chromaticities and luminosities are listed for various weight ratios in Table 73.XII and illustrated in Fig. 73.67. Each mixture has produced a new chromaticity outside the original triangular color gamut, effectively increasing the region of color space that can be accessed by the CLC polysiloxane films.

### 4. Color Gamut of CLC Flakes Made from the Three Original CLC Polysiloxanes

In addition to using the continuous-film form of CLC's, we have also prepared samples of CLC flakes from each of the four different size-groups.

The *x,y,Y* measurements for the CLC flake colorant samples are listed in Table 73.XIII and illustrated in Fig. 73.68. For each of the original materials, decreasing flake size leads to more desaturation of the hue, finally allowing access to the chromaticities *within* the original triangular color gamut. As flake size decreases, the orientation of the periodic molecular planes, responsible for the color, becomes more and more disordered. As a result, the reflection spectrum of CLC flake samples becomes wider and more shallow. This is consistent with the desaturation seen for encapsulated CLC's[20] whose helices are disordered due to the presence of the confining wall.

### 5. Mixing CLC Flakes of Different Colors

Layering CLC films produced an additive color by simultaneous reflection. The use of CLC flakes makes it possible to invoke another kind of color additivity: spatial averaging. By mixing two different colors of flakes and painting the mixture,

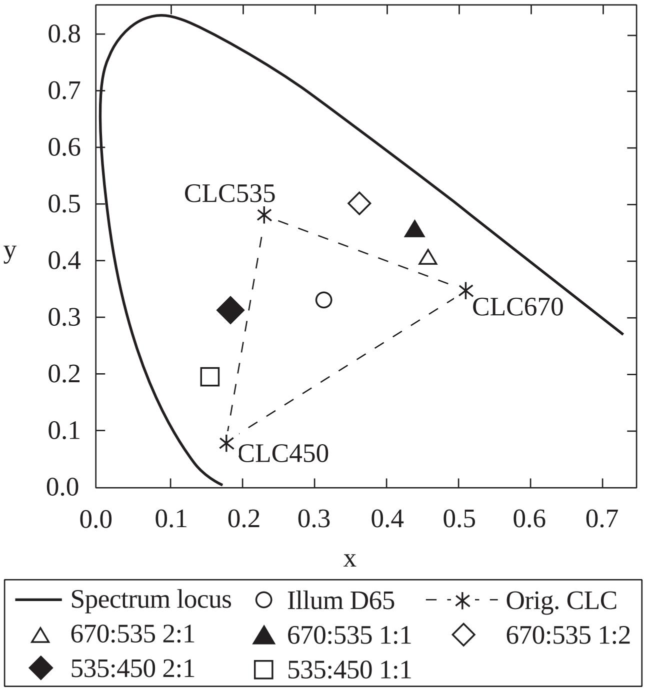

Figure 73.67
Chromaticity plot of CLC polysiloxane mixtures.

Table 73.XII: *x,y,Y* of CLC polysiloxane mixtures. Mixtures of pairs are listed with their mass ratios.

| Sample | *x* | *y* | *Y* |
|---|---|---|---|
| CLC670 | 0.5168 | 0.3541 | 11.83 |
| CLC535 | 0.2270 | 0.4738 | 24.69 |
| CLC450 | 0.1775 | 0.0777 | 4.19 |
| CLC670:CLC535::2:1 | 0.4582 | 0.4088 | 10.26 |
| CLC670:CLC535::1:1 | 0.4409 | 0.4580 | 35.99 |
| CLC670:CLC535::1:2 | 0.3607 | 0.5057 | 31.19 |
| CLC535:CLC450::2:1 | 0.1822 | 0.3086 | 18.58 |
| CLC535:CLC450::1:1 | 0.1562 | 0.1920 | 10.55 |

a color mosaic is produced. The resultant chromaticity of such a color mosaic can be determined by the fractional-area-weighted version of the Center-of-Gravity Color-Mixing Principle. For CLC flakes, instead of using the fractional areas, which are difficult to determine, we used the fractional masses of each type of flake in the mixture as the $A_1$ and $A_2$ factors in Eqs. (5)–(7). Provided the mixture is made with flakes from the same size-group so that the flakes behave similarly, the surface coverage by each color corresponds to the fractional masses and in turn follows the Center-of-Gravity Color-Mixing Principle very well.

Mixtures were made of CLC670, CLC535, and CLC450, in pairs, in weight ratios of 1:0, 3:1, 1:1, 1:3, and 0:1, for each of the flake size-groups separately. Weighting the chromaticities of the unmixed flake samples by these fractional masses, the $x,y,Y$ of the mixtures were predicted and compared to the measured values. The comparison was made by converting the $x,y,Y$ measurement to CIEL*a*b* coordinates through ColorTron II software. The color-difference function[44] $\Delta E^*_{ab}$ was also calculated for each predicted/measured pair, with a difference of 1 $\Delta E^*_{ab}$ unit corresponding approximately to a just-discernible color difference. The $\Delta E^*_{ab}$ values for each size-group were then averaged. The averages and ranges are shown in Fig. 73.69.

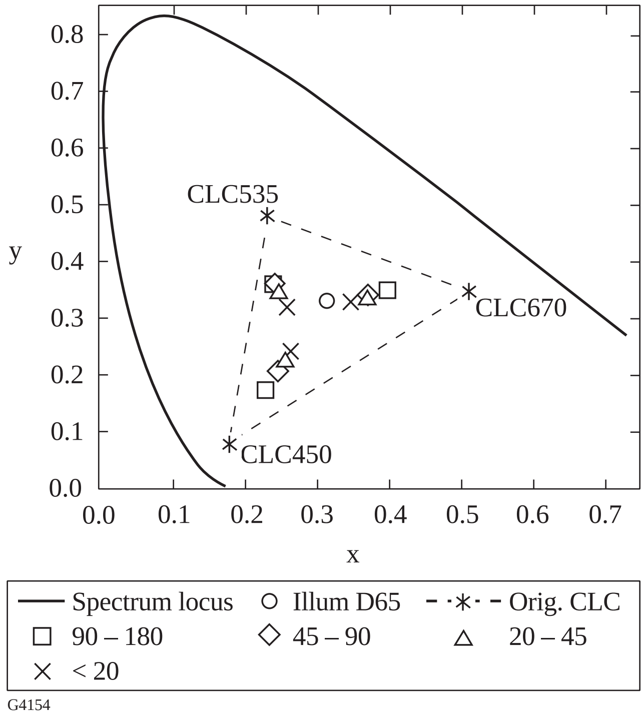

Figure 73.68
Chromaticity of CLC flakes of various size-groups (indicated in microns).

Table 73.XIII: $x,y,Y$ of CLC flakes as a function of size. The film samples are knife-coated microscope slides measured with the ColorTron II. The flake samples are in enamel on black toner paper measured with the Gretag SPM 100-II.

| CLC ID | Size | $x$ | $y$ | $Y$ |
|---|---|---|---|---|
| CLC670 | Film | 0.5153 | 0.3459 | 8.83 |
| | 90 to 180 $\mu$m | 0.3961 | 0.3504 | 5.73 |
| | 45 to 90 $\mu$m | 0.3770 | 0.3468 | 5.86 |
| | 20 to 45 $\mu$m | 0.3710 | 0.3443 | 6.85 |
| | <20 $\mu$m | 0.3510 | 0.3345 | 6.67 |
| CLC535 | Film | 0.2306 | 0.4803 | 26.26 |
| | 90 to 180 $\mu$m | 0.2402 | 0.3603 | 7.43 |
| | 45 to 90 $\mu$m | 0.2419 | 0.3615 | 9.16 |
| | 20 to 45 $\mu$m | 0.2472 | 0.3507 | 8.25 |
| | <20 $\mu$m | 0.2580 | 0.3241 | 7.27 |
| CLC450 | Film | 0.1777 | 0.0777 | 4.33 |
| | 90 to 180 $\mu$m | 0.2306 | 0.1823 | 3.73 |
| | 45 to 90 $\mu$m | 0.2460 | 0.2111 | 3.86 |
| | 20 to 45 $\mu$m | 0.2563 | 0.2315 | 4.51 |
| | <20 $\mu$m | 0.2629 | 0.2473 | 4.86 |

The 20- to 45-$\mu$m size-group had the lowest $\Delta E^*_{ab}$ values, i.e., the best agreement with the center-of-gravity predictions. This is attributed to an optimization of the two factors required for the center-of-gravity principle to hold:

(a) The flakes must be oriented with the normal to the periodic molecular planes normal to the paper. This ensures that all the flakes contribute their full reflection profiles to the combination color. Brushing accomplished this readily except for the <20-$\mu$m flakes. Under a microscope the latter appeared essentially cube-like with no preferred orientation.

(b) The flakes must completely hide the paper support. Samples of the two largest size-groups did not completely cover the measured area, whereas the two smaller size-groups covered it readily. Since the chromaticity of the exposed paper support was not included in the center-of-gravity calculations based on fractional masses, surface hiding was essential.

Figure 73.70 shows the measured $x,y,Y$ values listed in Table 73.XIV for the 20- to 45-$\mu$m size-group. The $Y$ values were very close in magnitude so the distribution of chromaticity points gives approximately the right spacing for 1:0, 3:1, 1:1, 1:3, and 0:1 mass-ratio mixtures for each color pair.

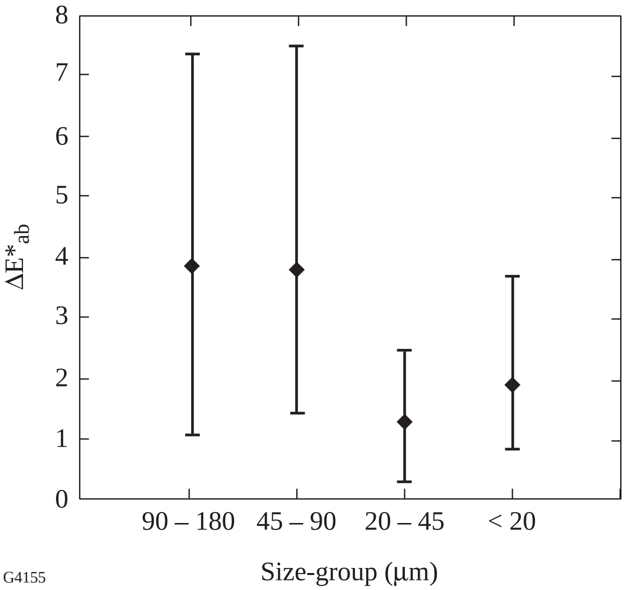

Figure 73.69
$\Delta E^*_{ab}$ averages and ranges for measured versus predicted chromaticity of CLC flakes mixtures.

CLC flake mixtures behave like pixels or pointillist painting. The flakes may be mixed in any proportion, unlike films that can only be layered. Even the layering does not produce a 1:1 weighting of chromaticities as we showed earlier. So use of CLC flakes as colorants allows a range of hues, a range of saturation, and a deterministic method for predicting the resulting chromaticity of a quantifiable mixture. Further, CLC flakes in mixtures of red with violet can be used to predictably produce the nonspectral, that is, purple to magenta, region of $x,y,Y$ color space. Finally, CLC flakes do not require elevated temperature or high voltages for painting since the reflecting molecular orientation is already present and "frozen in" at room temperature.

## 6. CLC Films Compared to Traditional Colorants

In this section, we compare CLC colors to some representative dyes, paints, and inks, i.e., traditional absorptive colorants. We compare these traditional colorants to the most saturated form of CLC, the continuous film, noting that CLC flakes are more versatile, if less saturated, than films.

The CLC film samples included in this comparison are knife-coated samples of CLC670, CLC535, CLC450, and the mixtures CLC670:CLC535::2:1, CLC670:CLC535::1:1, CLC670:CLC535::1:2, CLC535:CLC450::2:1, and CLC535:CLC450::1:1.

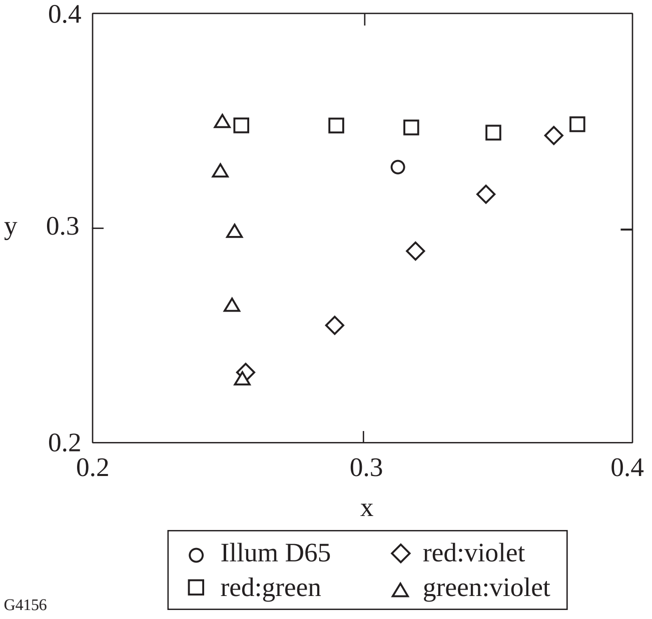

Figure 73.70
CIE diagram illustrating the Center-of-Gravity Color-Mixing Principle for 20- to 45-$\mu$m CLC flakes.

The colorants selected for comparison to these CLC films are (a) commercially available enamel-based paints[45] selected for their subjective vividness, (b) color samples from the Optical Society of America[46] selected for their subjective hue similarity to CLC film samples, and (c) three dyes: sudan III[47] (appears red), malachite green oxalate[48] (appears green), and crystal violet[49] (appears violet). Each dye was mixed with a nonchromatic polysiloxane, CLC850 ($\lambda_0 = 850 \pm 100$ nm), in a 2% by weight mixture. After mutual dissolving in dichloromethane, each dye/CLC850 mix was knife-coated onto a slide. Since CLC850 reflects only near-infrared at normal incidence and is only pale pink, very weakly saturated at 45/0, it is essentially invisible to standard colorimeters (Gretag range = 380 to 730 nm; ColorTron II range = 390 to 700 nm). CLC850 offers the advantage of providing a host for each dye without any significant chromatic contribution.

The CLC films were measured on the ColorTron II under the CIE 1931 $D_{65}$ basis, using black toner paper backing. The dye samples were measured with the same instrument and instrumental settings but with white paper backing. The OSA samples are ink on cardboard, uniquely identified by a sequence of numbers[50,51] no longer in general use (approximately correspondent with brightness, yellowness-blueness, magenta-green-ness). The paint samples were prepared by brushing onto microscope slides until the coating was opaque to the naked eye under ambient room light. They were measured with the same instrument and instrumental settings as the other samples and used a white paper backing behind the slide.

The chromaticities, luminosities, and purities are listed in Table XV. Since CLC's have a definite bandwidth, they can never be as pure as the monochromatic points comprising the spectrum locus. A more practical measurement of purity $P$ is to take the following ratio: the distance from the white point (the $D_{65}$ chromaticity) to the chromaticity of the sample and the distance from the white point along the same line to the isoluminous (same $Y$ value) contour line.

Table 73.XIV: Measured versus calculated $x,y,Y$ of flake mixtures of size-group 20 to 45 $\mu$m. The abbreviations listed under "color" are R ≡ CLC670, G ≡ CLC535, and V ≡ CLC450 with the approximate mass ratios. The actual masses are listed and were used as the $A_1$ and $A_2$ values in Eqs. (5), (6), and (7) of the Center-of-Gravity Color-Mixing Principle.

| Color | Mass (g) Color 1 | Mass (g) Color 2 | Meas $x$ | Meas $y$ | Meas $Y$ | Calc $x$ | Calc $y$ | Calc $Y$ | $\Delta E^*_{ab}$ |
|---|---|---|---|---|---|---|---|---|---|
| R | | | 0.3710 | 0.3443 | 6.85 | | | | |
| V | | | 0.2563 | 0.2315 | 4.51 | | | | |
| R:V 1:1 | 0.0051 | 0.0050 | 0.3197 | 0.2895 | 5.27 | 0.3148 | 0.2891 | 5.69 | 1.43 |
| R:V 1:3 | 0.0042 | 0.0126 | 0.2892 | 0.2556 | 4.68 | 0.2854 | 0.2601 | 5.10 | 2.12 |
| R:V 3:1 | 0.0046 | 0.0015 | 0.3454 | 0.3169 | 6.19 | 0.3432 | 0.3170 | 6.27 | 0.49 |
| | | | | | | | | | |
| G | | | 0.2472 | 0.3507 | 8.25 | | | | |
| V | | | 0.2556 | 0.2300 | 4.52 | | | | |
| G:V 1:1 | 0.0049 | 0.0049 | 0.2517 | 0.2990 | 6.48 | 0.2510 | 0.2958 | 6.39 | 0.80 |
| G:V 1:3 | 0.0027 | 0.0081 | 0.2512 | 0.2638 | 5.80 | 0.2532 | 0.2644 | 5.45 | 1.11 |
| G:V 3:1 | 0.0100 | 0.0033 | 0.2469 | 0.3270 | 8.18 | 0.2490 | 0.3246 | 7.32 | 2.48 |
| | | | | | | | | | |
| R | | | 0.3794 | 0.3493 | 7.75 | | | | |
| G | | | 0.2546 | 0.3488 | 6.79 | | | | |
| R:G 1:1 | 0.00862 | 0.00859 | 0.3179 | 0.3478 | 7.62 | 0.3212 | 0.3491 | 7.27 | 1.00 |
| R:G 1:3 | 0.00514 | 0.01504 | 0.2896 | 0.3483 | 6.95 | 0.2896 | 0.3489 | 7.03 | 0.26 |
| R:G 3:1 | 0.03152 | 0.01066 | 0.3484 | 0.3452 | 6.84 | 0.3508 | 0.3492 | 7.51 | 1.86 |

All the *x*,*y*,*Y* values are plotted for comparison in Fig. 73.71 with a dotted line representing the color gamut provided by CLC polysiloxane films.

Several observations from Table 73.XV and Fig. 73.71 are worth noting. First, we note that there are existing pigments more saturated and less saturated than CLC films. Overall, then, CLC films are not limiting cases in either direction of color purity. For commercial graphic arts applications, this means that CLC films as colorants are as capable of color depth as any other intermediate-saturation colorant.

Secondly, CLC films are more luminous than comparably hued pigments in the blue-violet region of the color gamut. In the lower left "corner" of the CIE diagram in Fig. 73.71, the purities are very similar (86%–96%). The chromaticity points are also very close for the CLC450 film, crystal violet dye, and dark blue paint. The CLC film, however, has a *Y* value four times greater than the dye and 24 times greater than the paint. Recall that the units for tristimulus values such as *Y* are lumens/$m^2$/sr = candelas/$m^2$—in other words, units of luminous flux. The blue-violet CLC film has more light reflecting from it than do pigments of comparable hue. CLC films reflecting in the red-to-green spectral range may show luminosity values comparable to similarly hued pigments; however, the purity values are not as similar. For comparable luminosities, red-to-green pigments are, in general, more saturated than red-to-green CLC films.

## Summary

We have shown that CLC films and flakes can be measured by standard colorimetry. The color gamut of CLC's as colorants, measured by standard techniques, may be accessed by four techniques: layering of continuous films, physico-chemical

Table 73.XV: Chromaticities and purities of CLC films compared to other colorants. The purities are calculated with respect to the isoluminous curve corresponding to each sample's *Y* value.

| Sample Form | Sample ID | Visual color | *x* | *y* | *Y* | *P* (%) |
|---|---|---|---|---|---|---|
| CLC | 670 | red | 0.5043 | 0.3462 | 9.39 | 59 |
| | 670:535::2:1 | gold | 0.4582 | 0.4089 | 8.83 | 63 |
| | 670:535::1:1 | butterscotch | 0.4409 | 0.4580 | 35.99 | 73 |
| | 670:535::1:2 | yellow-green | 0.3607 | 0.5057 | 31.19 | 64 |
| | 535 | green | 0.2257 | 0.4732 | 24.31 | 37 |
| | 535:450::2:1 | turquoise | 0.1822 | 0.3086 | 18.58 | 56 |
| | 535:450::1:1 | light blue | 0.1562 | 0.1920 | 10.55 | 76 |
| | 450 | violet | 0.1793 | 0.0778 | 4.07 | 88 |
| Dyes | sudan III | red | 0.6836 | 0.3130 | 4.13 | 99 |
| | malachite | green | 0.1643 | 0.3902 | 3.68 | 52 |
| | crystal violet | violet | 0.1748 | 0.0341 | 0.94 | 96 |
| Testor's gloss paints | 1103 | red | 0.6445 | 0.3170 | 8.01 | 89 |
| | 1114 | yellow | 0.4961 | 0.4646 | 56.14 | 90 |
| | 1124 | green | 0.2335 | 0.6501 | 9.51 | 73 |
| | 1111 | dark blue | 0.1696 | 0.0688 | 0.17 | 86 |
| OSA color samples | (-1,1,-1) | pink | 0.4362 | 0.3113 | 24.86 | 48 |
| | (-1,5,-5) | orange | 0.4753 | 0.3833 | 26.64 | 59 |
| | (-1,5,5) | green | 0.2991 | 0.4917 | 28.72 | 43 |
| | (-1,-5,3) | blue | 0.2150 | 0.2387 | 22.88 | 54 |
| | (-1,-5,-1) | violet | 0.2698 | 0.2381 | 22.03 | 47 |

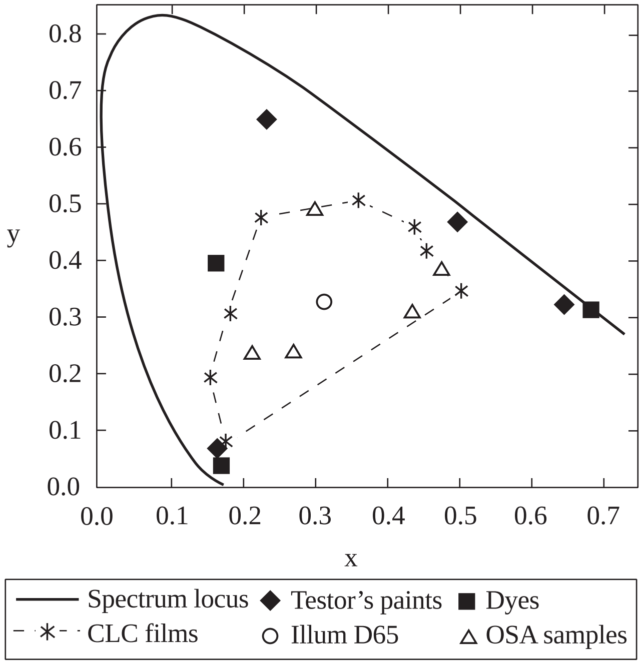

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Figure 73.71
Chromaticity plot of CLC films, dyes, paints, and OSA ink samples.

mixing of CLC's, varying the size of the CLC domains, and spatial averaging of mixed domains. Layering and physicochemical mixing produce new hues, but these new hues can be determined only empirically. The Center-of-Gravity Color-Mixing Principle allows the deterministic prediction of hues of mixed flakes based on their fractional masses in the mixture. Despite their angle dependence and selective polarization behavior, the color gamut of CLC's can be successfully examined with standard colorimetry.

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