

# Novel Pigment Approaches in Optically Variable Security Inks Including Polarizing Cholesteric Liquid Crystal (CLC) Polymers

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## ABSTRACT

Optically variable pigment technologies for markings and inks have increased in use as overt protection methods for document and product security. These technologies use optical reflective effects including interference technologies that create angular dependent color changes. Novel developments in different inorganic and organic pigments offer potentially new optical performance for both overt and covert security applications. These developments may lead to unique signature pigment formats that can verify origin and authenticity. Cholesteric Liquid Crystal (CLC) pigment approaches utilize both angular dependent “color flop” and the unique polarization properties to potentially develop markings with both overt and covert detection mechanisms. Continuous improvement in these technologies may lead to new visible and non-visible applications that when integrated with the graphic design will provide novel protection and graphic impact.

**Key words:** Optically variable, color travel, cholesteric liquid crystal polymers, polarization, security markings

## 1. INTRODUCTION

The security industry is in the continuous pursuit of novel overt and covert systems that demonstrate hard to copy dramatic visual effects. Recent innovations in deposition based interference systems have created very unique color travel, and they have successfully penetrated global markets for banknote and brand protection applications.

Cholesteric liquid crystal (CLC) polymers, formed into pigment flake, have similar color travel effects, but through a reflective circular polarization mechanism. CLCs, therefore, have the capability to provide overt color travel (through UV, visible, IR) as well as embedded covert polarization mechanisms of detection. This circularly polarizing effect is unique to CLCs. The design and manufacturing flexibility of CLCs enables customized security pigments.

### 1.1 Color Travel Pigments

The search for color travel coatings that mimic nature’s luster creations, such as the scarab beetle, the butterfly, and the oyster shell, dates back to early civilization and the cosmetic industry. Early Egyptians used facial bases containing bismuth for their pearl-like luster. Man-made imitation pearls first appeared in the 17<sup>th</sup> century in France.

In the 20<sup>th</sup> century, several generations of luster pigments emerged to service the growing cosmetic, coating and plastic industries. Each evolution of technology created pigments with more significant color development and travel. In the 1950’s, crystalline bismuth oxychloride platelet technology was commercialized, followed by pearlescent pigments in the 1960’s. This luster pigments used metal oxide coatings (primarily titanium dioxide) to coat mica at various thickness to create colors. Merck and Mearl (Engelhard) were the first to commercialize these systems<sup>(1)</sup>

The first Fabry-Perot (FP) stack (metal/metal oxide composite with interference properties) was created in 1969 by Dupont using vacuum metal deposition of aluminum on a dielectric (silicon dioxide)<sup>(2)</sup>. These systems, however, have only a weak color travel effect. OCLI improved on the earlier FP systems by creating complex stacks with inner reflectors, thereby dramatically improving brightness and the color travel effect<sup>(3)</sup>. Currently, OCLI (Flex Products) and

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BASF<sup>(4)</sup> are marketing FP based pigments and their adoption has been strong in security applications (banknotes) and in decorative applications (consumer electronics). However, continued growth is limited due to the high cost of the manufacturing process of FP systems.

For nearly a hundred years, the temperature dependent color of cholesteric liquid crystals (CLCs) has been used to create novelty products (mood rings, thermometers, etc.). In the late 80's, crosslinkable CLCs were developed enabling the "locking-in" of their unique reflection properties. In the early 90's, Chelix's parent company, Reveo, was the first to patent the use of CLCs in color travel and polarizing pigment applications<sup>(5)</sup>.

The evolution from simple interference approaches, such as pearlescents, to controlled interference stacks (FP), and to organic circularly polarizing CLC pigments demonstrates the continued development of more effective color travel systems.

### 1.2 Color Development in Interference Pigments

The basic theory behind optically variable pigments is light interference and the angular dependence of the reflected or refracted light.

For pearlescent pigments, the interference occurs in between light reflected by the surface of TiO<sub>2</sub> (or other metal oxides) and light reflected at the interface of TiO<sub>2</sub> and mica substrate (Figure 1). The reflected color (wavelength) and the intensity are dependent on the thickness of the metal oxide film and the oxide's index of refraction. Because of the low level reflection from these two surfaces, the resulting interference is visible (e.g. the pearl-like luster) but not strong enough to create significant angular dependent color travel.

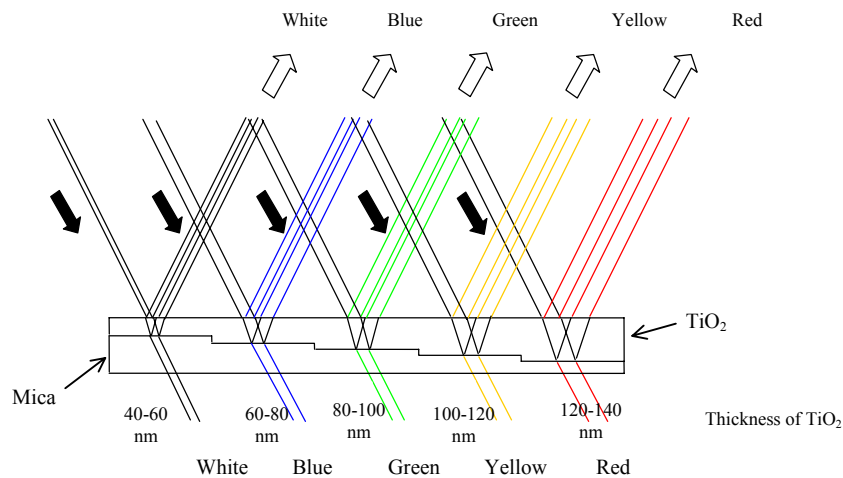


Figure 1 How pearlescent pigments work

The OVP<sup>TM</sup> technology (ChromaFlair<sup>®</sup> from Flex Products, e.g.), however, has much stronger interference effect compare to pearlescent technology because of its use of a modified Fabry Perot stack. With an opaque, highly reflective metal layer in the middle of the coating, the intensity of the reflected beams is much stronger resulting in striking color development. With an increase in reflection, the effect of color travel is improved drastically. The reflectance of such pigment can be much higher than pearlescent's (Figure 2). Color and color travel are dependent on the choice of the semi-transparent reflector, the index and the thickness of the dielectric.

### 1.3 CLC pigment approaches

Cholesteric liquid crystal (CLC) polymer film is a natural reflective polarizer. When the center wavelength is set within the visible spectra, color travel effects can be created through circular polarized reflection.

This organic approach has advantages over the more expensive interference stack technology. Unlike interference systems, CLC pigments are circular polarized creating a simple secondary detection mechanism. Also, in CLC based flakes, center wavelength is easily adjusted enabling a wide set of custom products. Lastly, CLC pigments are manufactured using continuous film based polymerization, allowing for significantly lower cost conversion than vacuum deposition technologies.

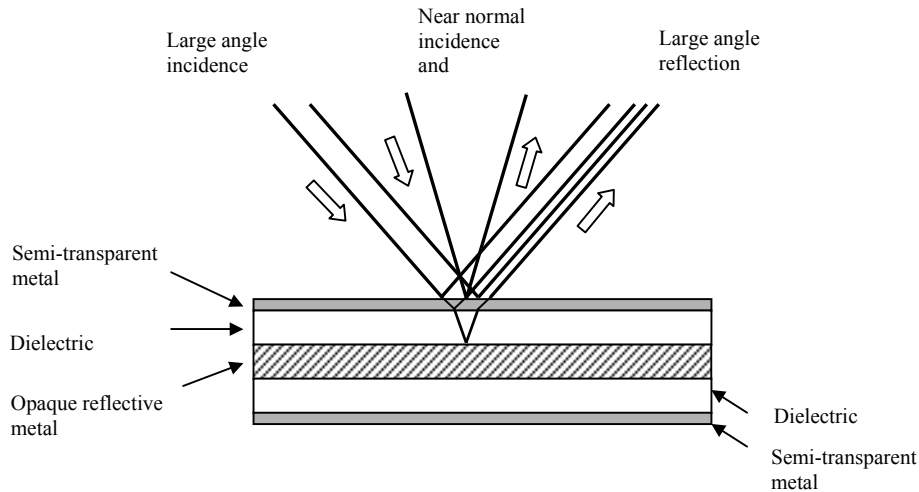


Figure 2 Structure and principle of operation of OVP™

## 2. BASICS OF CLC PIGMENTS

### 2.1 Optical properties of CLC materials

The Cholesteric liquid crystal (CLC) pigments are made with CLC films. Each flake is a piece of microfilm in platelet form with optimal dimensions of 5 micron in thickness and 20-40 microns in diameter.

Liquid crystals (LC) have several known phases, each with different optical characteristics due to different molecular arrangement and orientation. Cholesterics constitute the special case of chiral nematics and are usually formulated by adding chiral additives to a nematic LC. Figure 3 shows that in cholesterics the molecules are aligned in a helical fashion perpendicular to a helical axis. Figure 4 shows that with planar alignment of the molecules at the film interfaces the helical axis is perpendicular to the film interfaces and the continuous twist of the molecules is depicted by a helix. A cholesteric pitch, P, is defined as distance along the helical axis for 360° twist (Figure 4). This periodic structure results in a Bragg reflection centered at a wavelength  $\lambda_0$  which is determined by the pitch:

$$\lambda_0 = nP \quad (1)$$

where n is the average refractive index of the locally birefringent medium. For example, if  $n=1.575$  a green reflecting film ( $\lambda_0 = 550$  nm) corresponds to a pitch of 349.2 nm. The width of the reflection band is given by:

$$\Delta\lambda = \Delta n \lambda_0 / n \quad (2)$$

where  $\Delta n$  is the anisotropy of the material. For a typical CLC polymer,  $\Delta n=0.1$ , the bandwidth of a green reflecting film is approximately 35 nm.

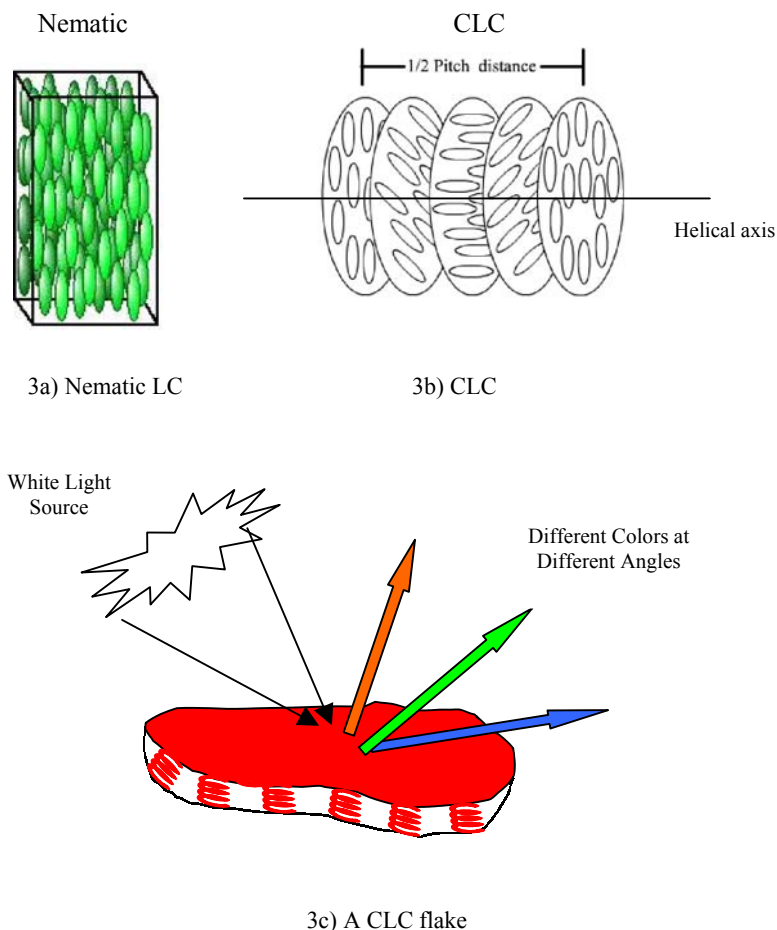


Figure 3 Nematic liquid crystal, cholesteric liquid crystal, and CLC flake

The helical structure of CLC also determined the handedness of the reflected light. For instance, with CLC medium that has a left-handed helical structure, unpolarized light will be reflected as left-handed at wavelength  $\lambda_0$ , while the rest of the wavelengths of left-handed and the entire right-handed light will pass through (Figure 4).

## 2.2 CLC pigments

Cholesteric liquid crystal polymer is a crosslinked organic material with its molecules fixed in the cholesteric phase. Once the film is made, it can be fractured to small platelets. These platelets remain all the optical properties of CLC. Therefore, inks that are made with CLC pigments are also called polarizing inks.

Due to the periodic structure of CLC films, CLC pigments possess strong color travel effect similar to other reflective interference pigments (ChromaFlair<sup>®</sup>, etc.). However, the fact that the reflection is circularly polarized enables the unique applications of CLC pigments in security covert detection. Figure 5 shows a picture printed with the left-handed CLC pigments in red, green, and blue analyzed by left-handed circular polarizer and right-handed polarizer, respectively. The extinction is clear and obvious.

The circular polarization extinction effect can also be used in high-speed machine-read detection mechanisms. A right and left-handed circular polarized detector set at the same wavelength would detect the drastically different signals from the same location indicating an authentic product. Because CLCs can be made in the UV, visible and IR, this effect can be utilized in non-visible systems.

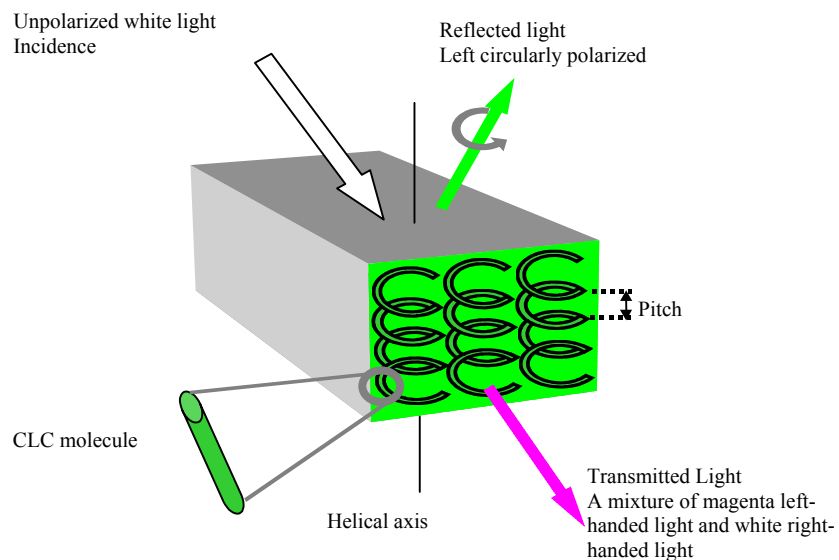


Figure 4 Optical property of cholesteric liquid crystal

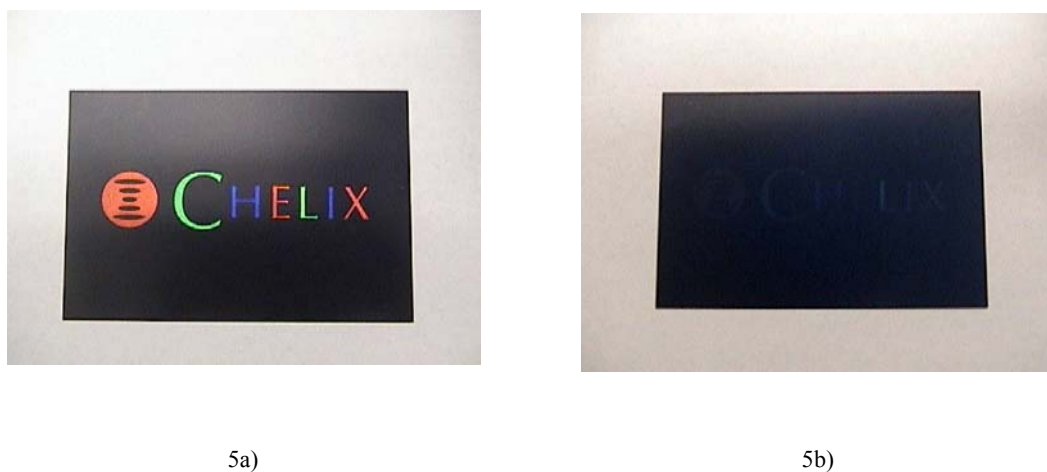


Figure 5 Image printed with left-handed CLC pigments a) viewed by left-handed polarizer, and b) viewed by right-handed polarizer

Figure 6 illustrates the measurement results of color travel (x,y coordinates in a chromaticity chart) of commercially available red and green CLC pigments. Fluorescent light source was used for the measurement. The data was taken by a

colorimeter. The results clearly indicate that at large angle, the red pigment turns to yellowish green, and the green pigment changes to blue (at specula reflection angles).

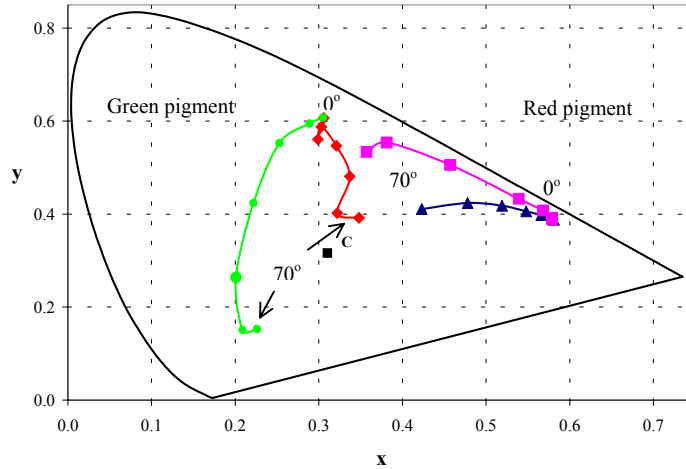


Figure 6 Color travel of red and green CLC pigments  
 Squared line: red pigment with specula reflection; triangled line: red pigment with light source fixed at 0°. Round-dotted line: green pigment with specula reflection; diamond line: green pigment with light source fixed at 0°

### 3. SUMMARY OF TECHNOLOGIES

In compare with pearlescent and OVP™ Technologies, CLC pigments posses significant color travel effect at lower cost and provide unique polarization property. Table 1 lists the performance of the systems outlined.

Table 1: Performance comparison of interference pigments

Property	Pearlescent	Interference stacks	CLC pigments
Interference	Yes	Yes	Yes
Brightness	Low	High	Moderate
Color travel	Insignificant	Significant	Significant
Diameter	5-130 μm	~35 μm	30-50 μm
Thickness	~1 μm	~1 μm	~5 μm
Polarization	No	No	Yes
Cost	Low	High	Medium

### 4. CUSTOM DESIGN AND PROCESS

Because CLC pigments are made with polymeric materials with most of their optical properties determined by the CLC mixtures, color fine-tuning, special wavelength design, and bandwidth control become relatively easy compare to those that use conventional interference technology. Only limited process adjustments are required from changing one product to another. All performance properties are controlled in the initial formulation and photo-polymerization step.

Figures 7 shows the tunability of color of CLC pigments. All measurements were done in film format. Note that the color travel of blue reflecting pigments makes then invisible while invisible IR reflecting pigments become visible. These effects are particularly useful as overt authenticating measure.

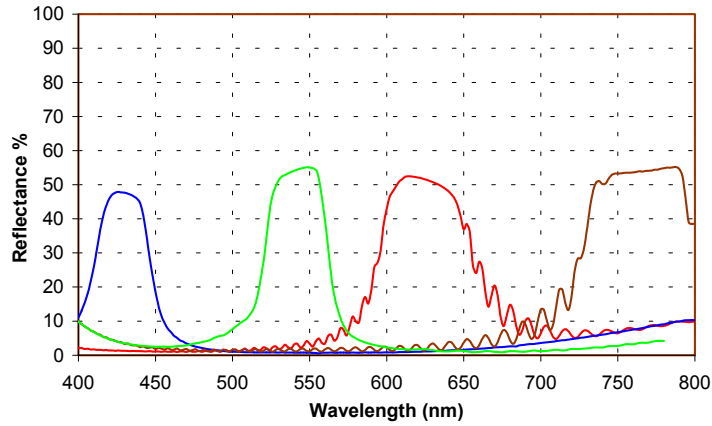


Figure 7 Reflection spectra of blue, green, red and near-IR CLC film

With Chelix’s patented broadening technology, CLC pigments can be made with different bandwidths other than that are determined by Equation 2. Unique formats can be developed in the UV (Figure 8) and red (Figure 9), respectively. Bandwidth is highly controllable enabling, for instance, visible pigment with higher levels of color saturation.

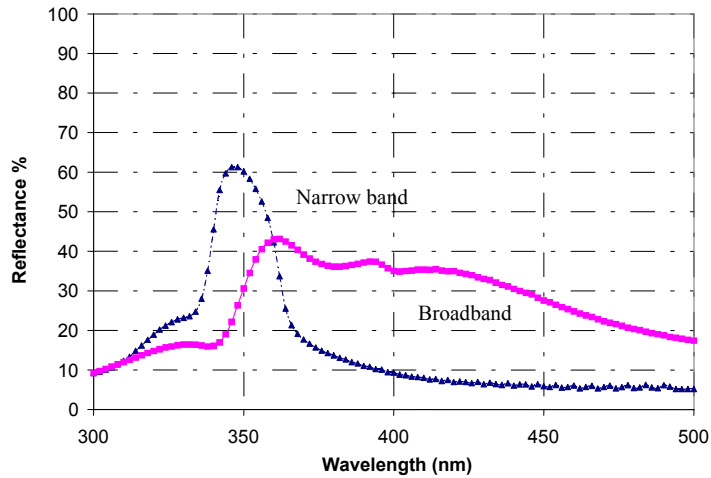


Figure 8 Semi-broadband UV reflecting film compared with a narrow band UV reflecting film

In addition, due to the flexibility of formulations, CLC films can be modified by doping it with other traditional pigments or dyes. These advanced systems will provide multiple signatures for both overt and covert detection from a single pigment source. Moreover, when the thickness of the flakes is reduced to 2-3  $\mu\text{m}$ , stacking of other special effect films becomes feasible allowing CLC pigments to have unique position in counterfeiting.

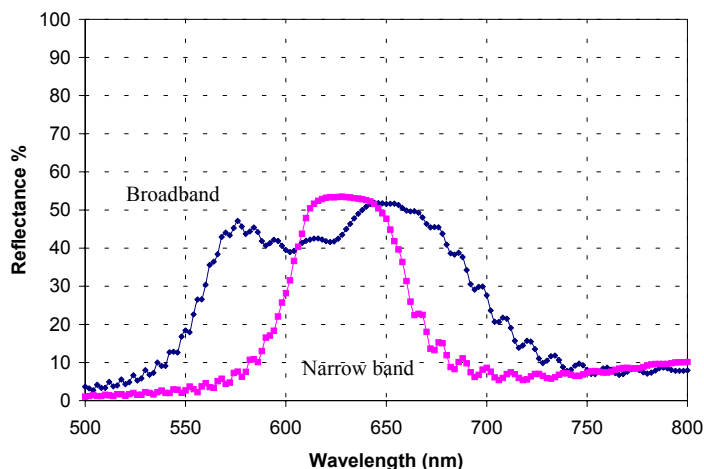


Figure 9 Semi-broadband red reflecting film compared with a narrow band red reflecting film

## 5. CONCLUSIONS

CLC pigments are applicable for both counterfeit deterrence in banknotes and secure documents, and for authentication processes for brand and product protection. CLC technology offers the security applications designer several degrees of new design flexibility. First, as a color travel overt system, CLCs have similar performance to interference stacks, but at lower cost. Due to the manufacture flexibility of CLCs, customized wavelength materials, both narrow and broadband, can be designed in the visible, UV and IR. Second, every CLC pigment is circular polarized, enabling simple detection mechanisms such as opposite handedness extinction. This feature is only found with CLC pigments. This extinction feature can also be used in machine read applications. Lastly, CLCs are polymeric systems allowing other active materials to be incorporated in the pigment. This capability can create an out of band signature that is unique to the designer's systems.

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