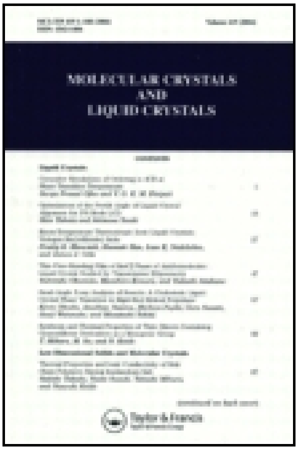

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Interaction Between UV Radiation and Cholesteric Liquid Crystals

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Interaction Between UV Radiation and Cholesteric Liquid Crystals

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Abstract—Mixtures of cholesteryl iodide and cholesteryl bromide with cholesteryl nonanoate were exposed to UV radiation and the resultant color shifts were measured as a function of exposure and composition. The formation of images by this process will be described, and the presiding mechanism will be briefly discussed.

Our interest in this subject was initiated by a short reference in a report to the U.S. Government by Westinghouse. The authors Jones, Fergason, *et al.*[1] indicated that UV sensitive liquid crystals exist and that images could be made using the UV induced color shifts.

Since we did not know which liquid crystals were used and what wavelengths and irradiation levels were required we selected a number of liquid crystal compositions and, guided by absorption measurements, subjected them to UV radiation below 3000 Å, either from a Xenon flashtube Novatron-186 or a GE-H6 mercury arc lamp.

The first positive results were obtained with mixture of cholesteryl iodide and cholesteryl nonanoate.

Later, it was established that cholesteryl bromide-cholesteryl nonanoate mixtures are also UV sensitive and that cholesteryl chloride-cholesteryl nonanoate mixtures become much more sensitive after addition of oleyl cholesteryl carbonate.

In the majority of our experiments we used the following 3 compositions, by weight:

(1)	cholesteryl iodide	50%
	cholesteryl nonanoate	50%
(2)	cholesteryl iodide	20%
	cholesteryl nonanoate	80%
(3)	cholesteryl bromide	50%
	cholesteryl nonanoate	50%

The mixtures were dissolved in petroleum ether, 1 g/10 cc, and applied to the substrate. The solvent was allowed to evaporate and we will call the colorless liquid crystal film so obtained, undisturbed, in opposition to a mechanically disturbed film which shows beautiful reflection colors.

Contact exposure of an undisturbed film through a suitable mask generally does not result in an immediately visible image. A latent image however is produced which can be developed by heating the film or by exposing it to an organic vapor like chloroform.

The development step is not necessary if a mechanically disturbed film is exposed.

Films may be disturbed in a variety of ways; a method which results in a smooth surface is to move a glass slide over the free surface. The film then acquires an intense color which changes in the exposed areas as shown in Fig. 1.

If the surface is smooth, and close enough to the mask, images with good resolution can be obtained. An electron microscope grid held between the cleavage planes of a piece of mica is a suitable mask and resolution in excess of 10 1/mm are easily obtained. The images are not stable in time and tend to disappear completely. Fifteen minutes after exposure the borders lose their original crispness. We attribute this loss of resolution to thermal diffusion.

In the case of cholesteryl iodide the observed color changes appear associated with breaking of the cholesteryl iodide bond and release of iodine. If the liquid crystal film is deposited onto a filter paper soaked in starch solution and exposed through a mask to UV a purple image is formed due to the iodine-starch reaction. If we deposit our liquid crystal film onto a polished copper plate a

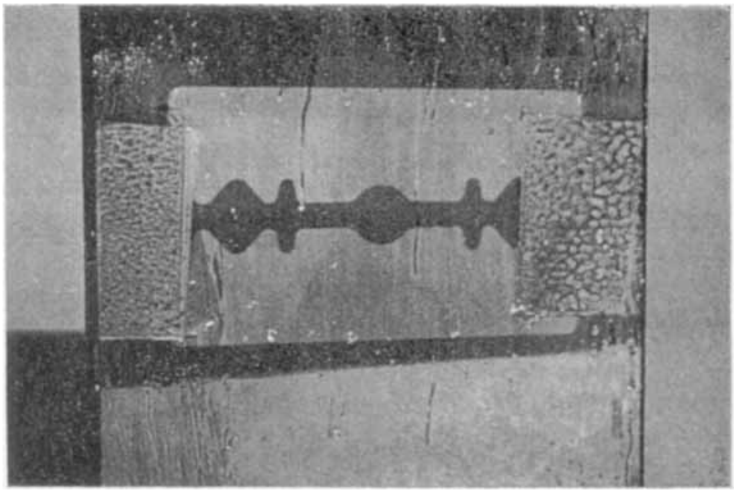

Figure 1. Image resulting from UV radiation.

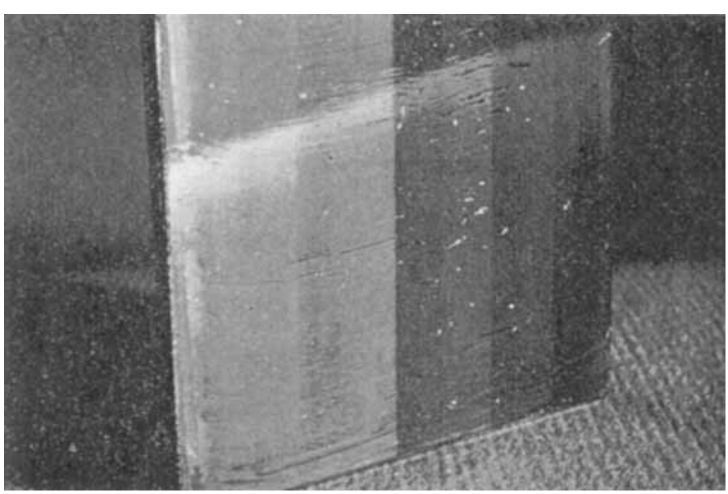

Figure 2. Image resulting from sequential UV radiation.

high resolution pattern is produced on the copper plate after exposure. This pattern is presumably due to the formation of CuI and of course only becomes visible after cleaning off the liquid crystal film.

Exposure of a disturbed cholesteryl iodide-nonanoate film (50% cholesteryl iodide) results in a shift of the reflection color toward red, as shown in Fig. 2 which was obtained by successive increase of the exposure time.

The color shift was measured as a function of exposure with the apparatus shown schematically in Fig. 3.

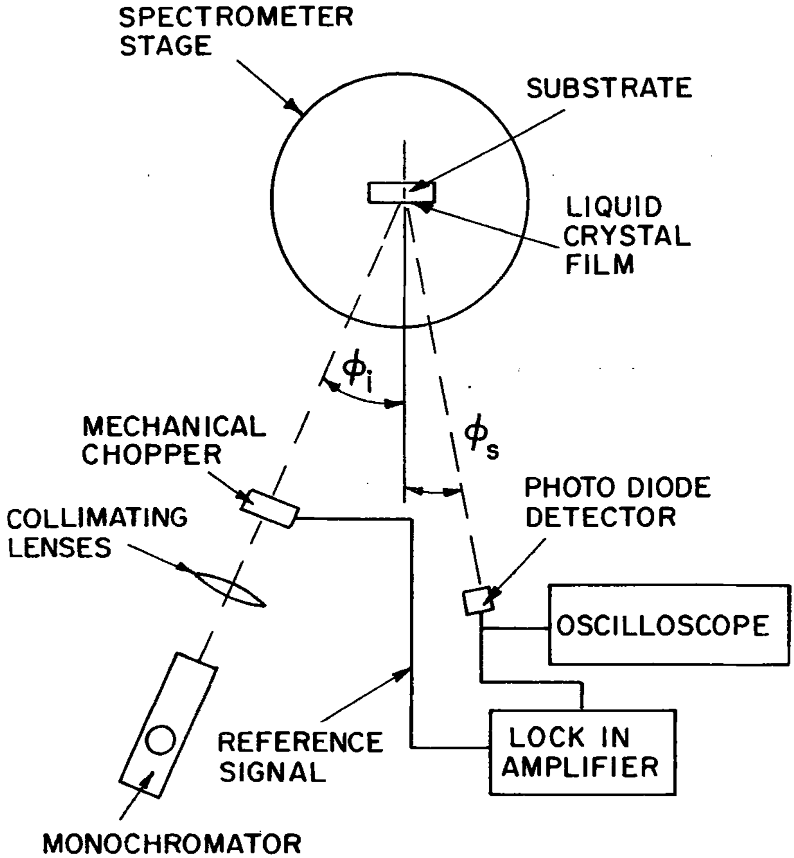

Figure 3. Experimental configuration of apparatus.

A beam of light from the monochromator was allowed to fall onto the liquid crystal film and was detected with the photodiode. A mechanical chopper provided a reference signal for use with a lock-in amplifier or to provide a signal for oscilloscope viewing. The sample was mounted on a black substrate on a spectrometer stage for reflectance measurements.

The color of light scattered from a liquid crystal film is a function of the angle of incidence and of the angle of observation. For

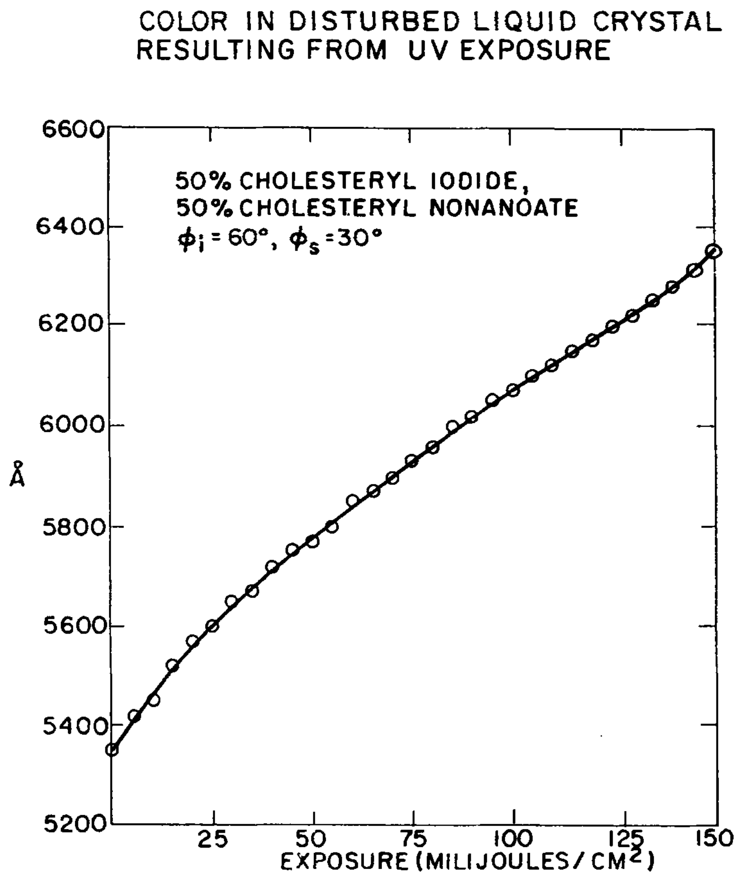

Figure 4. Color in disturbed liquid crystal resulting from UV exposure.

convenience we fixed the angle of incidence of light ϕ_i at 60° and the angle of observation ϕ_s at 30°. ϕ_i and ϕ_s are measured from the normal; we measured the wavelength of maximum output by scanning the monochromator. Corrections for the spectral sensitivity of the diode and output of the monochromator were made.

A plot of the color versus radiation is shown in Fig. 4. As stated, the effect of UV radiation is a shift toward red. This effect cannot be explained simply by removal of the cholesteryl iodide molecules from the light scattering process.

We measured the wavelength of the maximum light output of a disturbed unexposed film as a function of the cholestery iodide content. The color shift is toward blue with decreasing cholesteryl iodide content as shown in Fig. 5. The optical effect of UV light is opposite to the effect caused by decreasing the cholesteryl iodide content. This must mean then that the new species formed

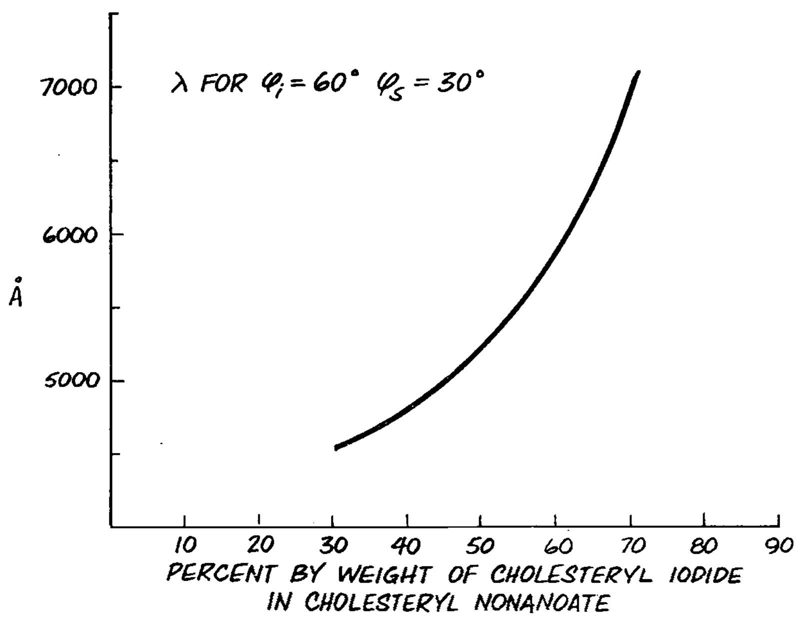

Figure 5. Reflected color versus composition.

by iodine removal acts in the same direction as cholesteryl iodide but in a more pronounced fashion.

Another effect associated with UV radiation which we would like to describe is a shift in the transition temperature between the smectic and cholesteric mesophase. In this experiment we used a liquid crystal film with 20% cholesteryl iodide and 80% by weight cholesteryl nonanoate deposited from a solution of 1 g in 10 cc petroleum ether. The film was deposited onto a microscope slide and observed between crossed nicols at room temperature.

The field is essentially dark except for some pretty structures of radial symmetry. The conoscopic figure of the dark areas is a neat uniaxial cross. The positive sign indicates that the film is in the smectic mesophase. Let us now examine what happens if part of the film is UV irradiated. At room temperature between crossed polarizers the field of the exposed and unexposed areas is still dark, and the conoscopic figure shows no change.

If we heat now the film slowly, at 31.5 °C the exposed area starts to undergo the transition to the cholesteric phase. The exposed area becomes gradually brighter and no conoscopic figure is obtainable. The unexposed area remains dark until about 36.2 °C is reached. It then starts in turn to become cholesteric. The contrast between exposed and unexposed regions reaches its maximum just below 35.2 °C.

The exposed area is clearly outlined against the almost dark background as shown in Fig. 6. If heating is continued both exposed and unexposed areas become cholesteric. The difference between them becomes very small between crossed polarizers but in reflected light, the various colours show a clear difference. If heating is continued up to the isotropic transition it can be observed that this transition temperature is also lowered by UV radiation.

Another phenomenon associated with UV radiation is a deformation of the boundary between exposed and unexposed regions. This deformation becomes clearly visible after heating the film above the isotropic transition and can reach a height of several microns. At this point we do not yet have any satisfactory explanation for the deformation. One possibility is that it is

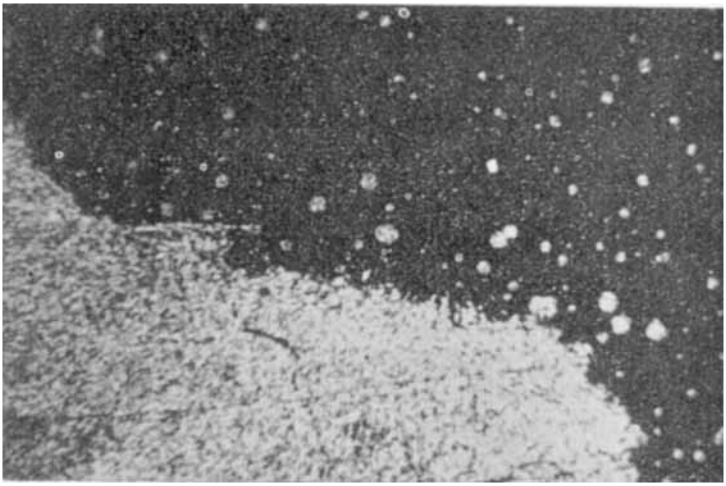

Figure 6. Smectic-cholesteric liquid crystal film between crossed polarizers.

caused by electrostatic forces due to charged species generated by photooxidation or photoreducation processes such as postulated by Gaynor in his paper entitled "Photocharge Process".[2] Gaynor used this mechanism to explain the deformation after illumination of polymer films containing iodoform, carbon tetrachloride or other polyhalogenated aliphatic hydrocarbons. He observed that thermoplastic films could be used for deformation image recording by illuminating the films imagewise with light of wavelengths between 3500–4500 Å and heating them afterwards to reduce the viscosity sufficiently to permit deformation.

Another possible explanation for the deformation is the following:

Since photochemical reactions lower the cholesteric-isotropic transition temperature of the exposed material, deformation may be due to differential migration properties. At some temperature the exposed region is isotropic while the unexposed region is cholesteric. Both the surface tension and viscosity are quite different in the two regions and a material imbalance is expected at the interface.

Summarizing

Color shifts can be induced in a number of liquid crystals by irradiation with ultraviolet light below 3000 Å.

A study of the system cholesteryl iodide-cholesteryl nonanoate showed that in addition to the color shift the transition temperatures are lowered by UV exposure and deformation occurs at the boundaries between exposed and unexposed regions.

We believe that those three phenomena are not exclusive to the system studied, but are in a lesser or larger degree present in all cholesteric liquid crystals.

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