Preparation and properties of optical notch filters of cholesteric liquid crystals

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We investigated the influence of preparative conditions of cholesteric-liquid-crystal (CLC) solid films on their cholesteric structures. They are made of poly[γ-butyl-L(or D)-glutamate] (PBuL(D)G and triethylene glycol dimethacrylate (TGDM), and have the ability to reflect the light in a specified wavelength region. When these films were combined with conventional colour filters, the colour reproduction region was enlarged by about 25% in the area of the CIE chromaticity diagram.

(Keywords: polypeptide; cholesteric; polymer; notch filter; circular dichroism)

INTRODUCTION

In most of the full colour display devices, a number of pixels which contain red (R), green (G), blue (B) micro filters are aligned in a mosaic pattern. However, the picture is not so vivid and its colour purity is not so high as that of the colour CRT. This is due to the overlapping of the transmission spectrum of each colour filter.

Although a lot of effort has been focused on the development of the R, G and B filters whose transmission spectra do not overlap with each other, it may be difficult to develop a dyestuff which has high enough solubility (that is, a large optical density) and no overlapping region in the spectra. Therefore, optical notch filters (ONFs) which cut off the light of specific wavelength regions are needed.

Some ONFs have been proposed which are based on the circular dichroism of cholesteric liquid crystals (CLCs)[1-3]. They are composed of a dextrorotary and a levorotary CLC film. The former film reflects the left circularly polarized light and the latter the right circularly polarized light. The two films are prepared to show selective reflections at the same wavelength, λ, which is defined as

$$\lambda = pn\cos\theta \quad (1)$$

where θ is an incident angle, p denotes the helical pitch and n denotes the average refractive index of the CLC film. By using these films, only the light in a specified wavelength region can be reflected.

These filters have the following disadvantages which prevent them from being used practically as stable ONFs. First, the helical pitch of the CLC film is very sensitive to external variables such as temperature, pressure, electric field, magnetic field, chemical vapour and ultraviolet rays. Therefore, it should be installed in a thermostated cell covered with a protection film such as a glass plate or a Mylar® sheet. Second, a transparent spacer is needed between a dextrorotary and levorotary CLC film, because the films are liquid. The spacer brings about the reflection and the absorption loss for the filter.

Recently, a technique for producing a solid polymer film has been developed[4]. It is produced by polymerization of lyotropic liquid crystal (LC) made of mesogenic components and monomers having unsaturated bonds. The solid polymer film has a fixed CLC structure, whose helical pitch is very stable against external variables.

We prepared a dextrorotary and a levorotary CLC film by this method, and laminated them to form an ONF. We describe here the influence of preparative conditions of the CLC solid films on their cholesteric structures and the optical characteristics of the laminated films as ONFs.

EXPERIMENTAL

Materials

As polypeptide compounds, poly[γ-butyl-L-glutamate] (PBuLG) which shows the right-handed helical cholesteric structure and poly[γ-butyl-D-glutamate] (PBuDG) which shows the left-handed helical cholesteric structure were used. As a monomer solvent, triethylene glycol dimethacrylate (TGDM) which polymerizes under u.v. irradiation was used.

PBuLG and PBuDG were prepared by transesterification of poly[γ-methyl-L-glutamate] (Ajicoat A-2000, Ajinomoto Co. Inc.) and poly[γ-methyl-D-glutamate] (Mitsui Toatsu Fine Chemicals Inc.) with n-butyl alcohol using p-toluenesulphonic acid as a catalyst. The degree of substitution of the methyl group by the butyl group was nearly 100% from the n.m.r. spectrum measured in trifluoroacetic acid. The degree of polymerization of PBuLG was *ca.* 2000. Two samples of PBuDG with degrees of polymerization of *ca.* 2000 and 3000 were prepared, which we will designate PBuDG (#2000) and PBuDG (#3000).

Preparation of CLC films

PBuLG (or PBuDG) as LC material and TGDM as monomeric solvent were each weighed into small flasks. The concentration of PBuLG (or PBuDG) was above

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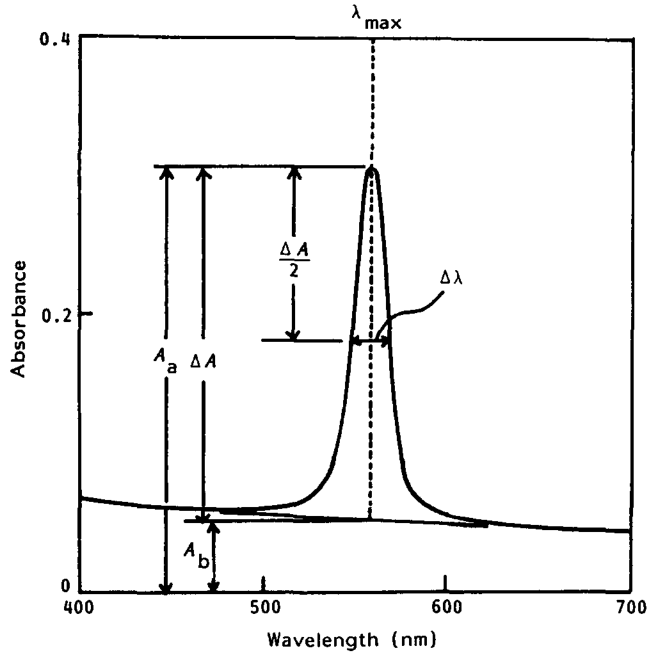

Figure 1 Transmission spectrum of the PBuDG (#2000)/TGDM (56/44) solution at 25.9°C

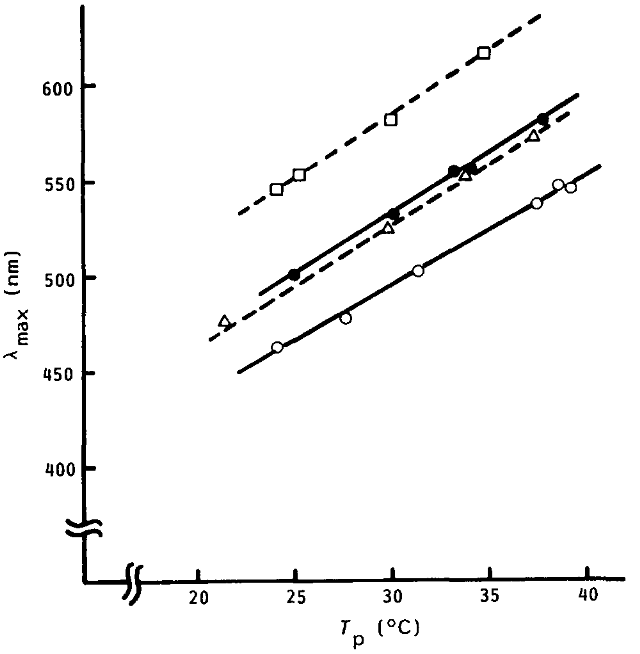

Figure 2 Peak wavelength λ_{max} plotted against polymerization temperature T_p for PBuLG/TGDM solid films (——) and PBuDG (#2000)/TGDM solid films (----). Weight ratios for PBuDG/TGDM: □, 47/53; △, 56/44. Weight ratios for PBuLG/TGDM: ●, 50/50; ○, 55/45

the critical concentration for the formation of lyotropic LC and below the solubility limit. The mixture was stirred by keeping the temperature between 40°C and 50°C, and then 1 wt% of benzophenone as photosensitizer was added to the homogeneous LC solution obtained. The PBuLG/TGDM weight ratio was 50/50 and 55/45, and PBuDG (#2000)/TGDM weight ratio was 47/53, 50/50 and 56/44, and PBuDG (#3000)/TGDM weight ratio was 50/50. After degassing the mixed solution, a small amount of the solution was placed between a pair of microscope slides, allowing a 0.1–0.2 mm gap by spacers, and a shearing stress was applied to the sample cell. The sample cells were immersed 15 cm deep in a thermostated water bath, allowed to stand for 10–15 h, and irradiated with a high-pressure mercury lamp (H1000L, Toshiba Corporation) for 3–4 h to polymerize TGDM. Then a CLC film with a fixed helical structure was obtained. The distance from the u.v. lamp to the surface of the sample was 65 cm. The stiff CLC films were removed from the cells by hand in an ultrasonic cleaning bath.

ONFs were prepared by laminating a pair of PBuLG/TGDM and PBuDG/TGDM films which show the selective reflection in the same wavelength region. After placing a photosetting acrylic monomer (M5700, Toagosei Chemical Industry Co. Ltd) as an adhesive between a pair of films, the adhesive was irradiated with a high-pressure mercury lamp for 5 min to polymerize the monomer. The helical axes of the dextrorotary and the levorotary CLC films were aligned parallel to each other and perpendicular to the surface of the solid polymer films.

Spectroscopic observation

Wavelengths of the selective reflection of cholesteric solutions and polymer films were measured from their transmission spectra using a double beam spectrophotometer (UV-260, Shimadzu Corporation). The spectra of cholesteric solutions were taken in glass cells of 0.2 mm thick. The spectra of solid films were taken at room temperature.

Figure 1 shows the visible transmission spectrum of a polymer film obtained by polymerizing the PBuDG (#2000)/TGDM (56/44) solution at 25.9°C. In the following discussion, we denote the peak wavelength of selective reflection as λ_{max}, absorbance at λ_{max} as A_a, apparent absorbance of the film as A_b, the degree of selective reflection as $\Delta A(=A_a-A_b)$, and half-width of the selective reflection spectrum as $\Delta\lambda$. These quantities are shown in *Figure 1*.

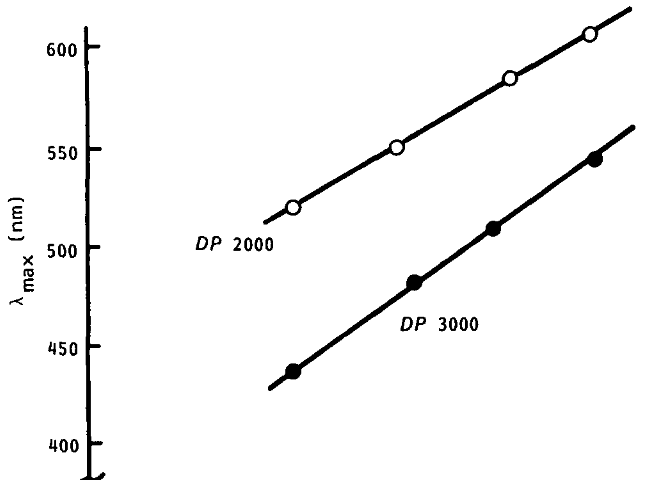

Figure 3 Peak wavelength λ_{max} plotted against polymerization temperature T_p for PBuDG/TGDM (50/50) solid films. ○, PBuDG (#2000)/TGDM; ●, PBuDG (#3000)/TGDM; *DP*, degree of polymerization

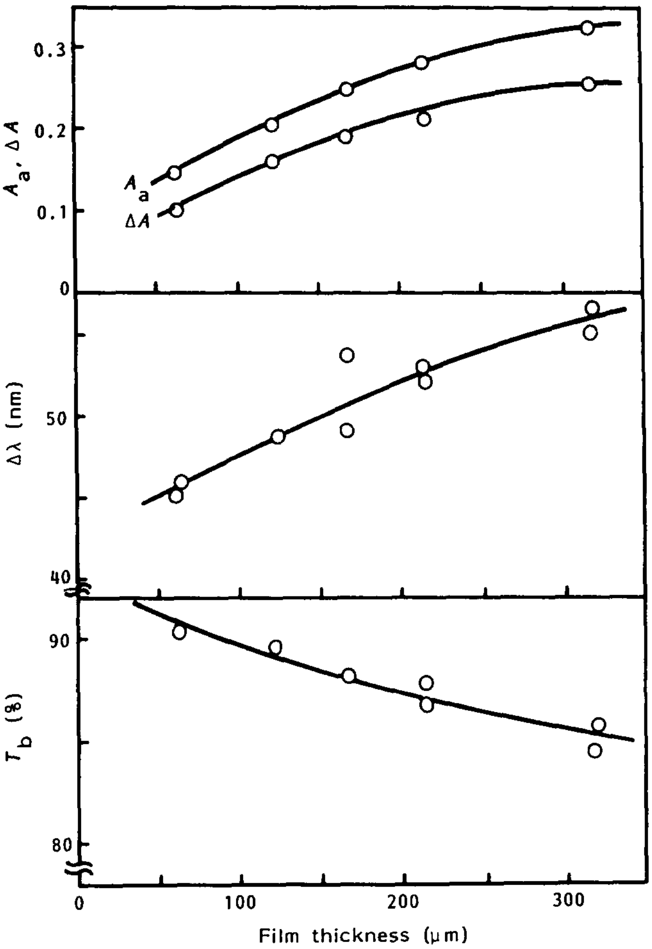

Figure 4 Influence of the film thickness on A_a, ΔA, $\Delta\lambda$, and T_b for PBuLG/TGDM (50/50) solid films

RESULTS AND DISCUSSION

λ_{max} is proportional to the helical pitch p and can be controlled by the combination of polypeptides and monomeric solvents, their mixing ratio, and the polymerization temperature of TGDM[5].

Changes of the peak wavelength λ_{max} with polymerization temperature T_p for the PBuLG/TGDM (50/50, 55/45) films and the PBuDG (#2000)/TGDM (47/53, 56/44) films polymerized at several temperatures are shown in *Figure 2*. Films with λ_{max} below 450 nm could not be obtained by this method because the concentration of polypeptide was beyond the solubility limit and gelation occurred.

It became apparent that λ_{max} can also be controlled by the degree of polymerization of the polypeptide and that films with λ_{max} below 450 nm can be obtained with highly polymerized polypeptide. *Figure 3* represents this influence on the shifts of λ_{max} for PBuDG. The higher the degree of polymerization, the lower the critical concentration necessary for the formation of lyotropic LC. When the degree of polymerization is higher, λ_{max} shows the blue shift even at the same mixing ratio and the same T_p. This means that the cholesteric pitch becomes shorter with increasing the degree of polymerization.

Figure 4 shows the influence of the film thickness on A_a, ΔA, $\Delta\lambda$ *and* $T_b(=10^{2-A_b})$ got PBuLG/TGDM (50/50) films. When the film becomes thick, ΔA, A_a, and $\Delta\lambda$ become large. *Figure 5* shows the influence of the incident angle θ on the peak wavelength λ_{max}. In our experiments, the relationship between λ_{max} and θ does not satisfy equation (1). This phenomenon may be interpreted as follows. At the surface of the solidified CLC film, an optically isotropic layer which does not show the selective reflection is formed. When the light enters the layer with an incident angle θ, the light is refracted according to

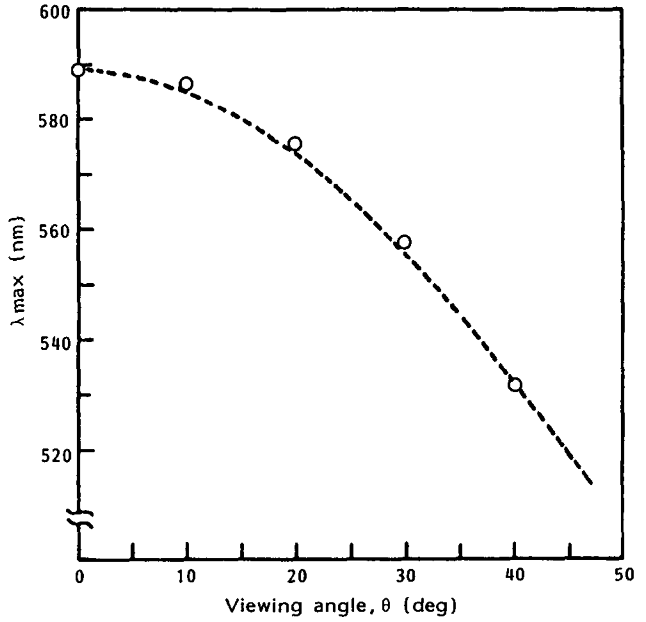

Figure 5 Peak wavelength λ_{max} in a PBuLG/TGDM (50/50) solid film plotted against several incident angles. – – –, Calculated value for the equation: $\lambda_{max}(\theta)=\lambda_{max}(0)\cos(\sin^{-1}((1/n)\sin\theta))$, where $n=1.50$

Table 1 Changes of optical characteristics of films by laminating PBuDG/TGDM and PBuLG/TGDM films

	PBuDG/TGDM film	PBuLG/TGDM film	Notch filter [I]
λ_{max} (nm)	585	583	585
A_a	0.314	0.280	0.785
A_b	0.060	0.060	0.085
ΔA	0.254	0.220	0.700
$\Delta\lambda$ (nm)	26	31	26
T_b (%)	87	87	82

	PBuDG/TGDM film	PBuLG/TGDM film	Notch filter [II]
λ_{max} (nm)	582	583	585
A_a	0.305	0.280	0.902
A_b	0.055	0.060	0.099
ΔA	0.250	0.220	0.803
$\Delta\lambda$ (nm)	30	31	23
T_b (%)	88	87	80

	PBuDG/TGDM film	PBuLG/TGDM film	Notch filter [III]
λ_{max} (nm)	493	485	488
A_a	0.273	0.313	0.815
A_b	0.081	0.062	0.132
ΔA	0.192	0.251	0.683
$\Delta\lambda$ (nm)	35	34	29
T_b (%)	83	87	74

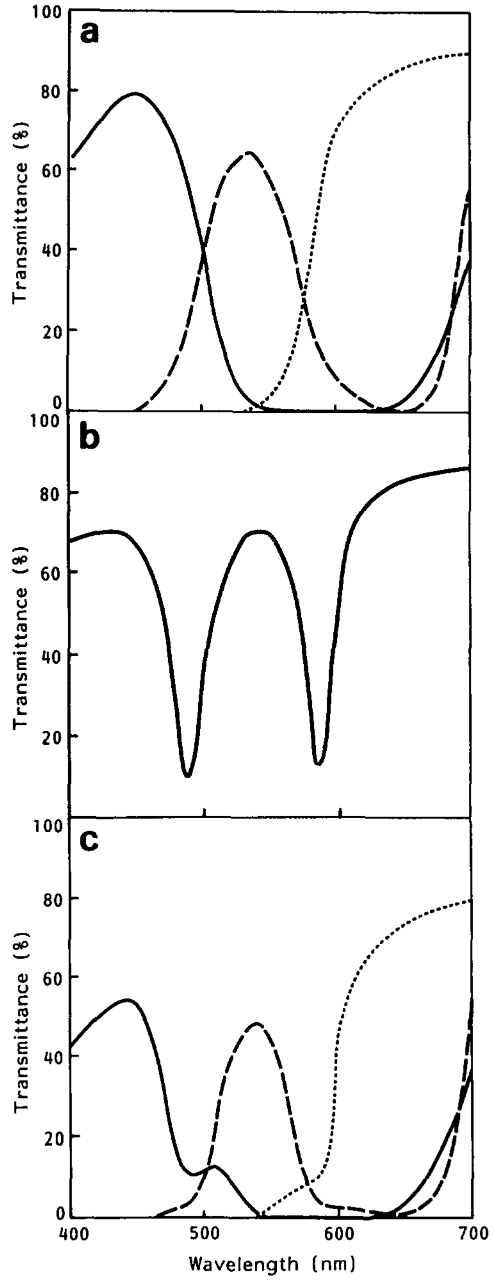

Figure 6 Transmission spectra of (a) typical colour filters (b) an optical notch filter (ONF) made from filters [I] and [III] in *Table 1*, and (c) colour filters (a) with the ONF (b)

Snell's law and enters the successive CLC layer with an angle θ'

$$\theta' = \sin^{-1}((1/n)\sin\theta) \qquad (2)$$

That is, the light with an incident angle θ is selectively reflected, when its wavelength λ satisfies the following relation

$$\lambda = pn\cos(\sin^{-1}((1/n)\sin\theta) \qquad (3)$$

Equation (3) accounts for the experimental data well. (The broken line in *Figure 5* represents the value calculated with this equation.)

The ONFs have been obtained by laminating PBuLG/TGDM films and PBuDG/TGDM films. Changes of optical characteristics by lamination are indicated in *Table 1*. To get an excellent ONF that hardly transmits the light of a specified wavelength, it is necessary to laminate a PBuLG/TGDM film and a PBuDG/TGDM film that have the same λ_{max}. Also an adhesive that has the refractive index of about 1.50 should be transparent and should not dissolve a CLC film. TGDM is not appropriate as an adhesive, as it dissolves the film and disorders the helical structure of the polypeptide largely.

From *Table 1*, it can be seen that the well-defined cholesteric planar structures were kept even if two films were integrated to one ONF by an acrylic adhesive.

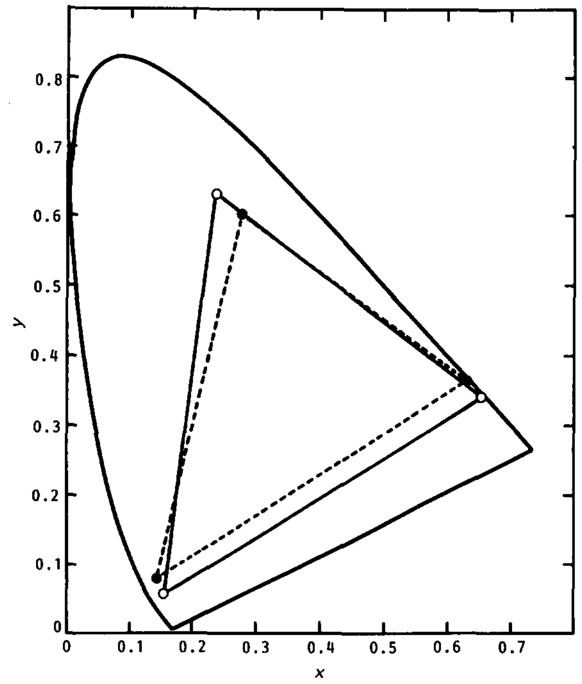

Figure 7 CIE chromaticity diagram of colour filters with (○) and without (●) optical notch filters

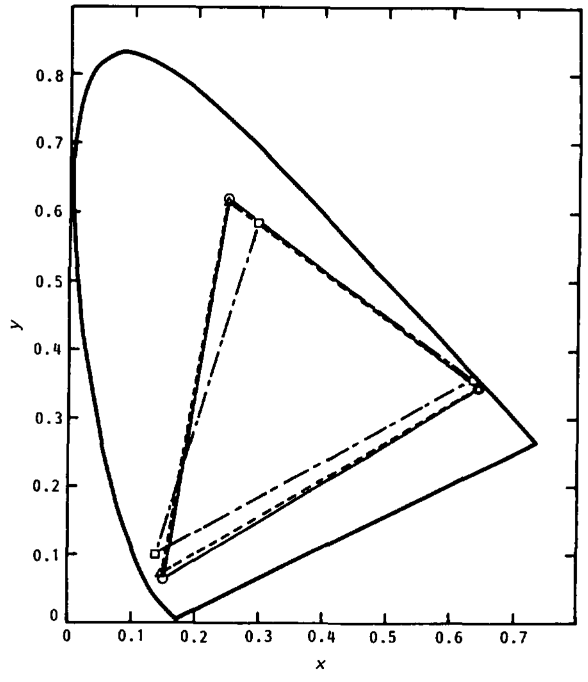

Figure 8 Influence of the incident angle (θ) on the CIE chromaticity diagram of colour filters with optical notch filters. —○—, 0°; – –△– –, 20°; ——□– —, 40°

ONF[I] and [III] selectively reflect the light whose wavelength region corresponds to the overlapped region between the transmission spectra of an R filter and a G filter, and that of a G filter and a B filter, respectively. The transmission spectra of typical colour filters, the transmission spectrum of the ONF made by laminating a filter[I] and a filter[III], and the transmission spectra of colour filters with the above-mentioned ONF are shown in *Figure 6*. With the ONF, the overlapped area between the spectra of an R filter and a G filter was 56%, and the overlapped area between the spectra of a G filter and a B filter was 75%.

Figure 7 shows the change of chromaticity of each R, G, B filter in the CIE chromaticity diagram*, when ONFs[I], [II] and [III] were attached to the R, G and B filters, respectively. The light source was the C-lamp. When these ONFs were combined with conventional colour filters, the colour reproduction region was enlarged by about 25% in the area of the CIE chromaticity diagram.

In *Figure 8*, the influence of the incident angle on the colour reproduction region of colour filters with ONFs is indicated. When the incident angle is below 20°, the region of the colour reproduction does not change very much. When the incident angle is 40°, the region of the colour reproduction decreases, and the hue of the colour filters changes.

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* This chart represents the hue and the purity of colours and their mixtures, and is based on the CIE specifications (CIE: the Commission International de l'Éclairage, International Commission on Illumination). All spectral wavelengths are located along the 'horseshoe' locus shown in *Figure* 7, and the colour purity is highest on this locus. All colours within the confines of the triangular area are reproduced by three filters whose chromaticity coordinates are the coordinates of the apexes of the triangle.