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AN OPTIMISED THIN FILM WAVELENGTH SHIFTING COATING FOR CHERENKOV DETECTION

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Investigations of an appropriate thin film wavelength shifting (WLS) coatings for Cherenkov radiation detection are reported. A number of dyes were investigated and an optimum coating arrived at. This consists of 0.175 mg/cm^2 of p-terphenyl, 0.095 mg/cm^2 of bis-MSB and 16 mg of acrylic matrix (Paraloid B 72) for coating on a perspex substrate. Coating over Pilot 425 is best done with a bis-MSB grammage reduced to 0.052 mg/cm^2. These coatings gave an average quantum efficiency of 91% of that a quartz window PM tube over a wavelength interval of 200–400 nm. A number of hints on the techniques of utilising thin film WLS coatings are also included.

1. Introduction

The application of WLS in increasing the effective area of detectors of ultraviolet radiation is well known [11]. In addition a number of authors have described the use of WLS in improving the UV response of photomultiplier tubes in gas Cherenkov detector applications. Recently two authors [7,5] have adopted a method of coating PM tubes using an acrylic matrix heavily doped with WLS: Viehmann and Frost [17] have discussed coatings for a number of applications. Our purpose here is to show that careful selection of the quantities of WLS and matrix, together with control of the coating process can produce very high efficiencies virtually indistinguishable from a quartz windowed tube at wavelengths above 200 nm. In addition the application of such coatings to large sheets of acrylic or glass can increase the effective area of the tube substantially.

2. Principles of fluorescent collection

Consider a rectangular parallelopiped of transparent material (fig. 1) doped with a fluorescent chemical. Molecules such as P absorb photons of UV light and re-emit isotropically. Thus a re-emitted photon will emerge from a given surface if it makes an angle $\theta < \theta_c$ (the critical angle) to the normal. Keil [11 shows that the fraction of emitted photons escaping through any surface is:

$$0.5\left[1-(n^2-1)^{1/2}/n\right].$$

If we now consider a thin sheet with mirrored edges the same result holds. Light will escape from the upper and lower surfaces only and, neglecting absorption in the sheet, the remaining fraction

$$(n^2-1)^{1/2}/n$$

will be collected by a detector in optical contact with the sheet. In practice, of course, it must be ensured that this detector is sufficiently large to compete successfully with any absorption effects, since a very small detector would imply a long pathlength in the transparent sheet. Fig. 2 shows such a device, coated by our recommended process, which has an effective area, allowing for losses of 4 times the area of the 5″ phototube and a quantum efficiency of > 90% above 200 nm.

In considering the gain of such systems the Fresnel

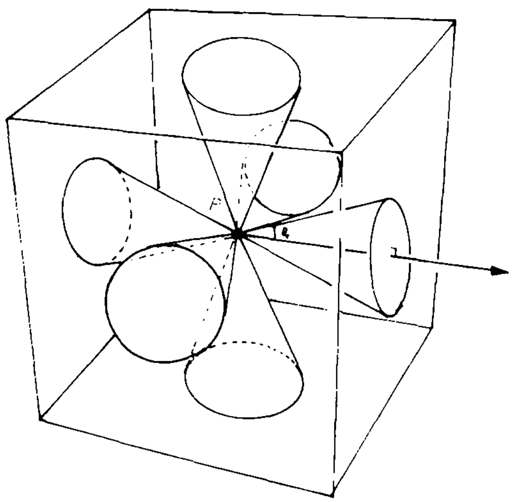

Fig. 1. Light emission from a transparent WLS doped block.

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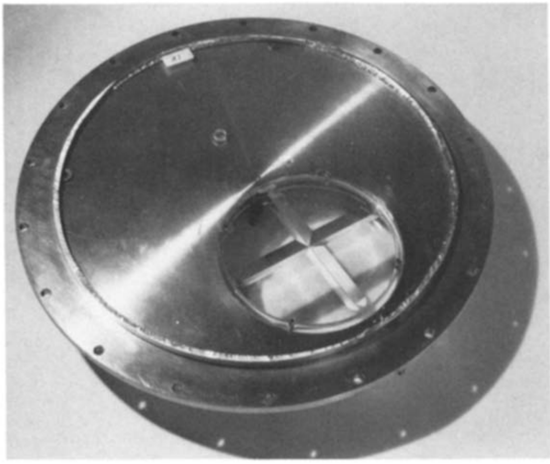

Fig. 2. Coated aerial and mounting.

reflection and the pathlength of the photon in the detector usually a PM photocathode must be considered. If the optical surface above the photocathode is good then it is possible for a photon to be multiply internally reflected at the photocathode, with an increased chance of conversion to an electron. If a coating of WLS crystals [7] rather than molecules in a solid solution such as we discuss here, is applied to the tube face, this can scatter incident light in such a way as to increase the pathlength in the photocathode. This can be desirable in some circumstances. Since we consider the gain in photocathode pathlength due to an optically clear coating to be desirable, we have made no attempt to separate this from our results.

The above discussion applies equally to coatings and bulk doped material. The advantages of coating are several. Firstly, the process is cheap and easy to perform. Secondly, the coating may be tailored to the individual application, in this case the detection of Cherenkov radiation. More importantly, a carefully prepared and applied coating will generally contain much less WLS than a commercially available doped plastic, leading to greatly improved attenuation properties. It should be noted, however, that if the total quantity of WLS in the two cases is the same then no gain will be obtained. Additionally, in general the surface obtained by coating, which is flattened by surface tension effects at the time of application is in general of superior quality to that of bulk doped material, also improving the attenuation length.

3. Objectives

As is well known the spectrum of Cherenkov radiation above the autoionization threshhold of a transparent medium is described by a $1/\lambda^2$ relation. It is therefore desirable to optimise the response of a detector in the UV, preferably at wavelengths below 300 nm. A number of WLS having absorption peaks below this wavelength are known (e.g. ref. 2) and several have been used as coatings evaporated onto photomultiplier windows in gas Cherenkov detectors. The two compounds most widely reported are para-Terphenyl (pT) [8], which has a high quantum efficiency [3] and Tetraphenylbutiadene (TPB) [1,12]. The latter has however been reported to deteriorate with time [6] and is in any case considerably more expensive. The emission and absorption spectra of pT are shown in fig. 3 [4]. It is seen that the peaks are at 290 nm and 360 nm. Vasseur and Cantin [16] have reported a good quantum yield at wavelengths down to 50 nm.

The evaporation coating of pT, however, suffers from the disadvantage of producing a layer which is vulnerable to contamination [13] and mechanical abrasion, which suggests the incorporation of the WLS in a transparent coating. Moreover, such a coating, if it has a good optical surface will remove the loss due to scattering of the isotropically re-emitted light from a rough surface.

The UV emission peak of these substances makes the use of a secondary WLS desirable when coupling to a glass window photomultiplier tube. Our first aim therefore was to investigate the possibility of applying a WLS containing coating to Pilot 425, a Cherenkov detecting plastic manufactured by Nuclear Enterprises, which consists of a PMMA matrix doped with a WLS that has an absorption peak around 360 nm and an emission peak at 425 nm. This we had previously used to provide an enhanced collection area for tubes detecting gas scintillation. The use of such a system in a gas Cherenkov detector has been described in detail by

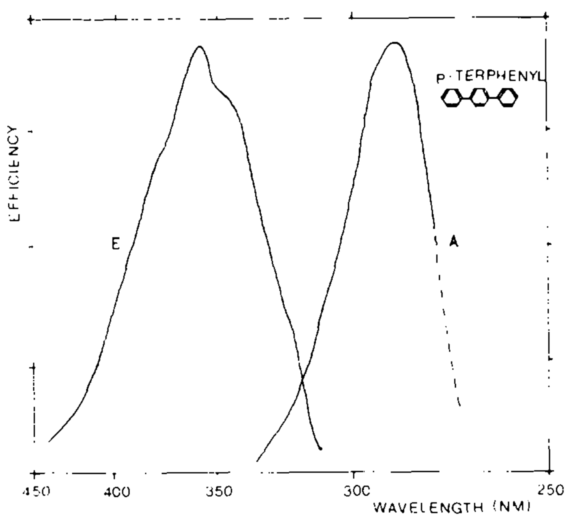

Fig. 3. Absorption and emission spectra of p-Terphenyl.

Swordy [15] and Grande [9,10]. By extending the wavelength response into the UV, however, considerably gains accrue.

4. Optimisation of wavelength shifting properties

A number of WLS were investigated. Table 1 lists a range of coatings incorporating various of these individually. Fig. 4 shows the spectral response of coatings incorporating pT, TPB, PPO, BIBUQ, αNPO, and bis-MSB in Paraloid B-72, on a Pilot 425 substrate. It is seen that pT appears by far the most promising, in agreement with the reports cited above. We therefore decided to further investigate the optimisation of a coating based on this substance.

Initially it was intended to use the Pilot 425 substrate as the sole secondary WLS. However, it was discovered that the efficiency could be further enhanced by adding a small quantity of a secondary WLS, bis-MSB to the coating, since this converts that 13.1% of the 360 nm light emitted from the pT which would otherwise escape from the upper surface of the coating. Subsequently we also investigated the optimisation of a coating containing pT and bis-MSB for the application to undoped perspex and glass.

The acrylic matrix used was Paraloid B72 * (Polyethyl methacrylate PEMA) which has the advantage of being transparent to light of wavelengths above 200 nm [7]. Previous authors have considered that the refractive index of the thin film incorporating the WLS is the same as that of the substrate. In a real situation this will not, of course, be the case. Since the thin layer will in general have inferior properties of transmission to the substrate, the coating should be chosen so as to have a refractive index slightly lower than the substrate, thus ensuring that light is free to enter the substrate. PEMA matrix has a slightly lower refractive index (1.482) than perspex, ensuring that light formed in the film will not be trapped.

5. Method

Small samples of PILOT 425 and perspex were prepared, and coatings applied by dip coating (see section 7), evaporation and pipette. These samples were optically coupled to a Mullard 56 TUVP quartz window phototube and an aluminium foil reflector placed over the arrangement (fig. 5). The sample was illuminated with monochromated light from a stabilised deuterium discharge lamp and the response of the phototube recorded using a Bentham 211 phase sensitive detector.

* Manufactured by Rohm and Haas.

Table 1
Composition and performance of coatings containing single WLS.

	Wavelength shifter in coating	Composition of coating (g l^{-1} in toluene)		substrate	Minimum quantum efficiency		Integrated quantum efficiency 200–400 nm
		WLS	Paraloid-B72		Wavelength (nm)	Quantum efficiency	
Mixture 1	p-Terphenyl	8	170	Pilot 425	240	0.34	0.76
Mixture 2	Pilot 425	–	–		–		0.54
Mixture 3	TPB	8	120	Pilot 425	225	0.43	0.68
Mixture 4	BIBQ	8	120	Pilot 425	260	0.29	0.69
Mixture 5	PPO	8	120	Pilot 425	215	0.44	0.62
Mixture 6	αNPO	8	120	Pilot 425	260	0.47	0.70

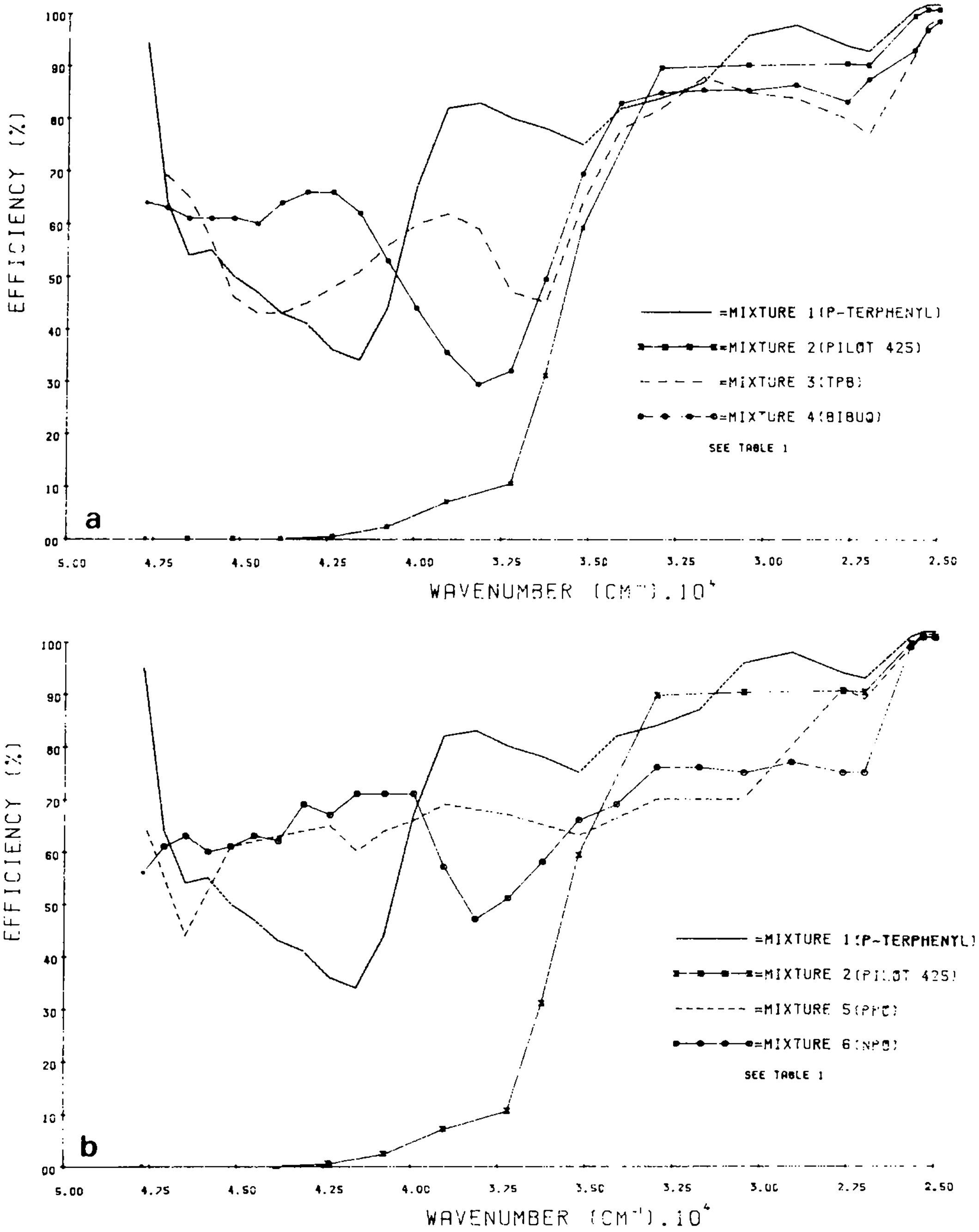

Fig. 4. (a) Spectral response of coatings incorporating pT, TPB, BIBQ. (b) Spectral response of coatings incorporating pT, PPO, NPO.

The samples absorb effectively all the light below 390 nm and transmit visible light. The fluorescence light is re-emitted isotropically and all will reach the phototube except the 13.1% (for $n = 1.48$) which will be within the critical angle for the upper surface and so escape. In order to check our results this escaping fraction was analysed separately using a Beckman ratio recording spectral reflectometer DK-2A. The results from this experiment, which are not presented here, are entirely consistent with those stated.

The phototube response at a given wavelength was compared with that of the bare tube, appropriately weighted for its spectral response.

Table 2
Composition and performance of coatings containing WLS in combination.

	Coating composition (gl^{-1} in toluene)					Substrate	Integrated quantum efficiency
	p-Terphenyl	Bis-MSB	Fluorene	PPO	Paraloid-B72		
Mixture 1	–	–	–	–	–	Pilot 425	0.54
Mixture 2	1	–	2	2	2	Pilot 425	0.54
Mixture 3	1	2	–	8	100	Pilot 425	0.794
Mixture 4	8	2.4	–	2	130	Pilot 425	0.89
Mixture 5	8	2.4	-	–	130	Pilot 425	0.91
Mixture 6	8	4.4		–	130	Perspex	0.91

6. Results of optimisation of WLS mixture

In order to measure the optimum pT grammage, samples were prepared by pipetting quantities of solution onto Pilot 425 discs, a process which does not produce a good optical finish. The effect of varying the total grammage of pT per unit area for a constant matrix thickness is shown in fig. 6. The optimum thickness for Cherenkov detection (assuming a $1/\lambda^2$ spectrum) is found to be 0.175 mg/cm^2, a result in good agreement with the results of Garwin et al. [8], Baillon et al. [1], and Carlson [6] for evaporated coatings. The best pT Paraloid ratio in this regime, where a good optical finish was not stipulated was found to be 1 : 7.

Fig.7, shows the effect of adding bis-MSB indicating an optimum concentration of 55% for a glass or perspex substrate, and 30% for a Pilot 425 substrate. The efficiency of these arrangements is seen to be the same within the experimental errors.

7. Coating

In order to increase the effective area of a PM tube or indeed in any application involving the use of a radiance amplifier, it is essential to ensure that the coating forms an optically perfect surface. At very high

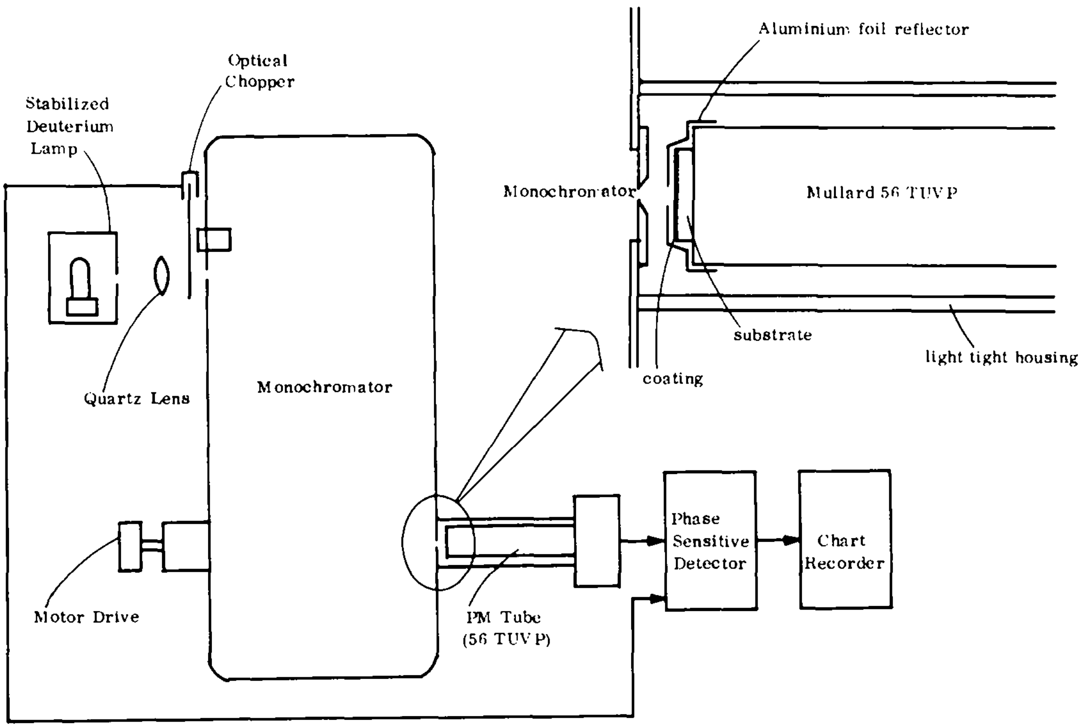

Fig. 5. Apparatus used in determining spectral response of coatings.

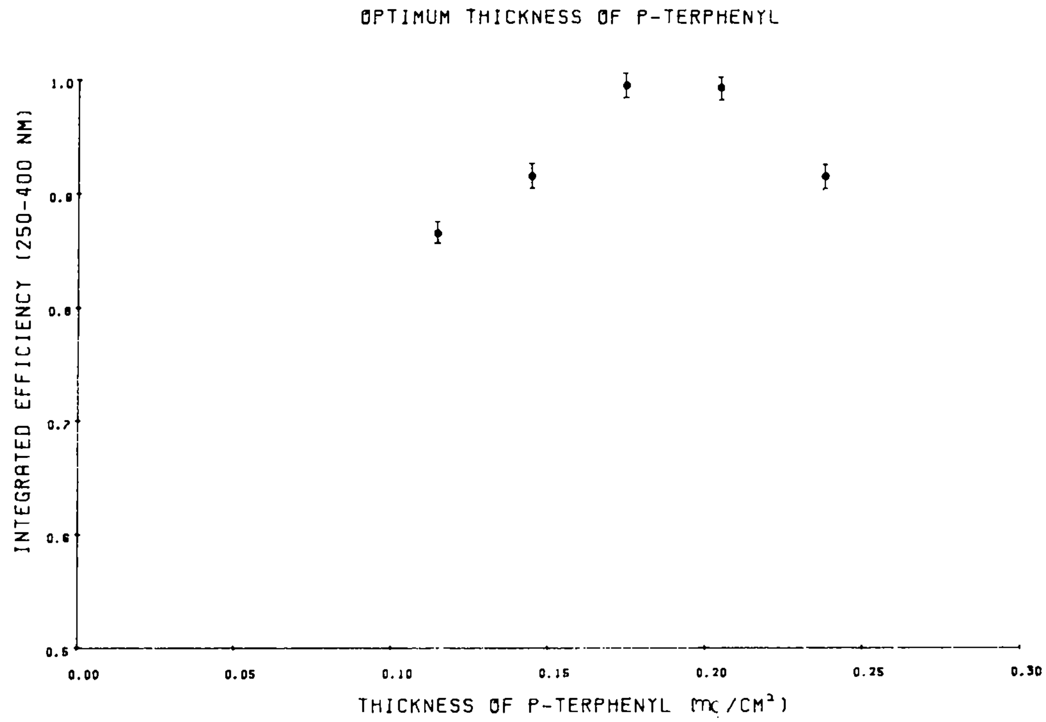

Fig. 6. Optimum concentration of pT for Cherenkov detection.

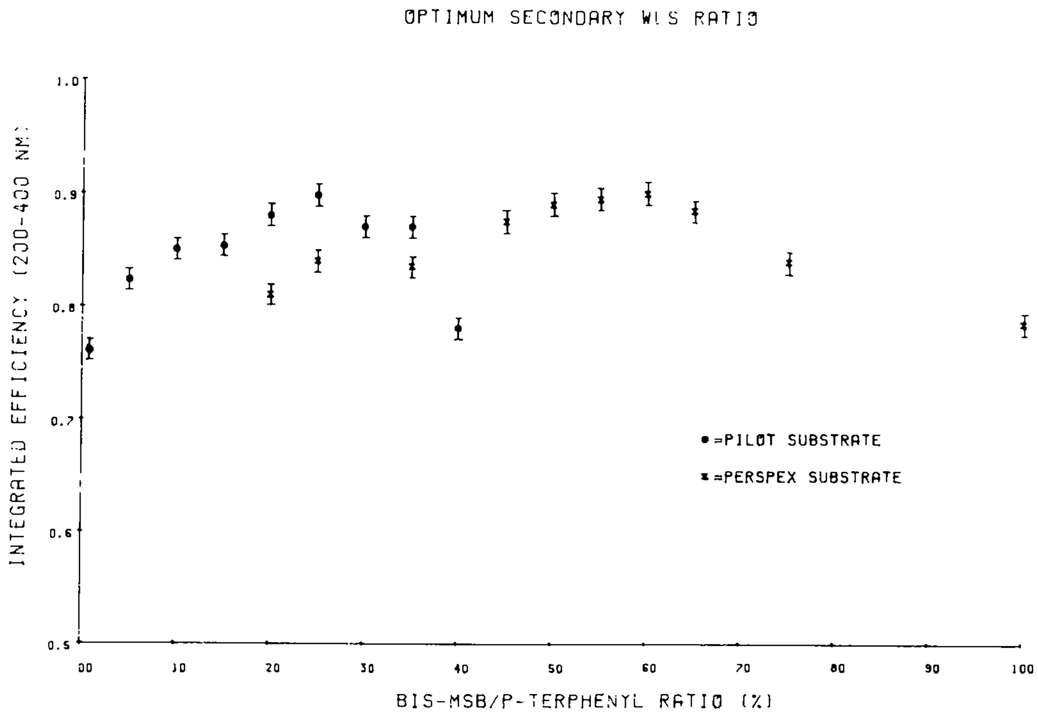

Fig. 7. Optimum bis-MSB/pT ratio for Cherenkov detection.

doping concentrations, however, the rapid evaporation of the solvent used in coating, will in general result in the crystallization of the WLS on the surface (solute re-aggregation) destroying its optical properties. In order to avoid this undesirable state of affairs it is necessary therefore to reduce the mobility of the WLS molecules by having a larger concentration of matrix in the solution than would in general be dictated by considerations of the optimum WLS/matrix ratio (1 : 7) which was observed for applications in which the surface properties were not critical. This in turn increases the viscosity of the mixture, hence making it easier to achieve the optimum thickness of pT of 0.175 g/cm^2.

Fig. 8 shows the performance of varying WLS/matrix ratios in the situation described above, where good optical properties are essential, indicating an optimum performance for a ratio of 1 : 17.5. In addition this ratio represented the lowest for which good optical properties could be easily and reliably obtained. Fig. 9 shows the spectral response of our recommended coating. Applying a $1/\lambda^2$ weighting to this response gives an average efficiency for the detection of Cherenkov light in a bandwidth 200 nm to 400 nm of 91%. Good coatings were obtainable at lower matrix/WLS ratios but only by exerting the most rigorous control of the cleanliness, temperature, humidity and rapidity of the dip coating process. This ratio leads to slightly reduced quantum efficiency in the 235 nm region, where pT has a low cross section for photoabsorption, whereas a large depth of PEMA will produce some attenuation; this appears to be an inevitable consequence of the application of dip coating techniques to a material of such low solubility at pT. No other coating mechanism could be envisaged which would provide the desired quality of coat on the large areas in question.

Of the commonly available solvents the two in which pT has the greatest solubility were found to be chloroform and toluene, and the use of these was extensively investigated. The solubility in toluene is 8 g/l at 20°C [4], while that in chloroform is somewhat higher. The latter, however, will of course attack the surface of the acrylic substrate. This is not necessarily a disadvantage since this tends to increase the viscosity of the layer deposited in the coating process, and this, together with the increased concentrations of pT possible, facilitates the application of an optically thick coating and in addition improves the adhesion. We found that a mixture of equal proportions of the two solvents had very good properties; higher proportions of chloroform again required stringent environmental control of the dip coating process.

It is interesting to note that previous authors [17] have found the solubility of pT in toluene to be substantially lower, and hence have relied on other less efficient WLS; we encountered no such problem.

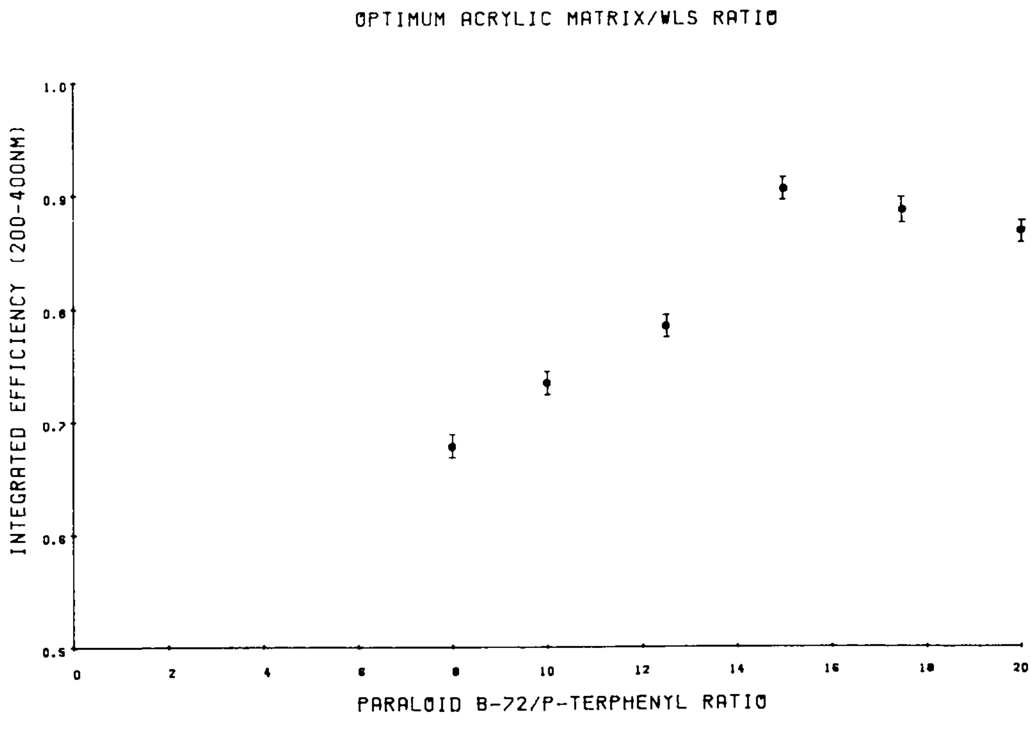

Fig. 8. Optimum acrylic matrix/WLS ratio for Cherenkov detection.

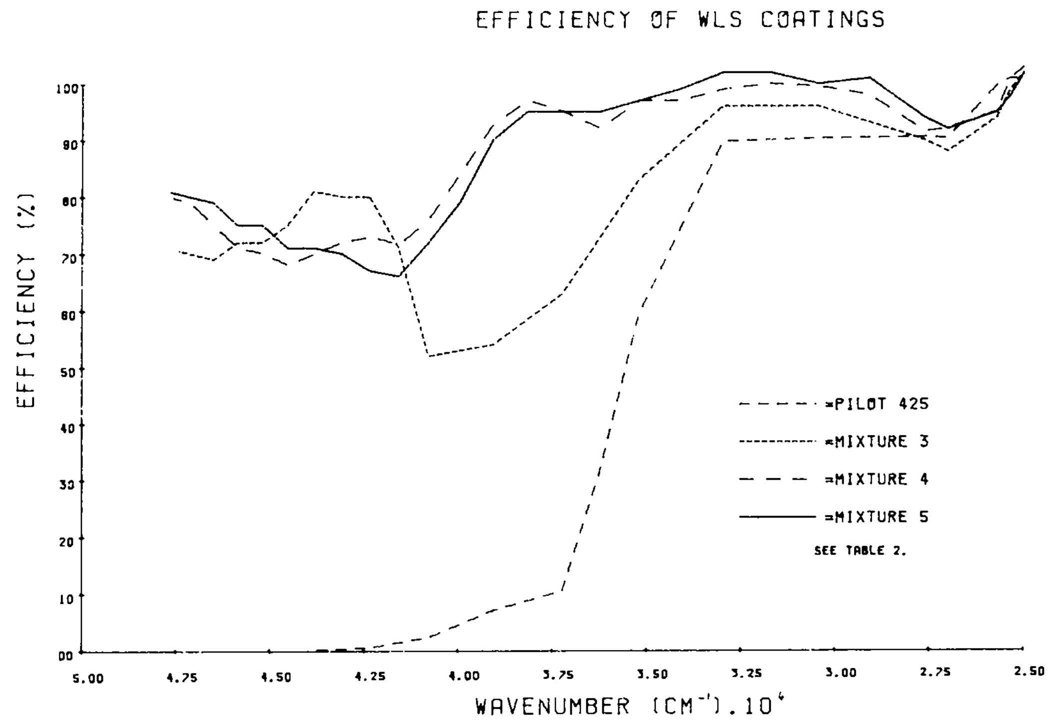

Fig. 9. Spectral response of coatings incorporating combinations of WLS.

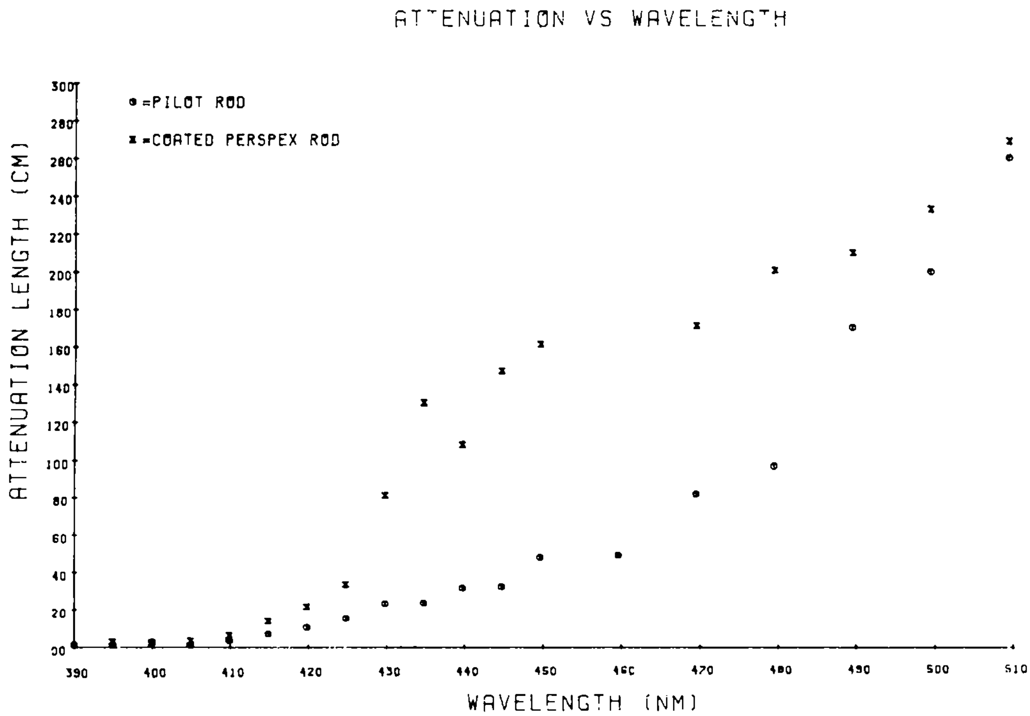

Fig. 10. Variation of attenuation length with wavelength for a Pilot 425 rod and a coated perspex rod.

8. Attenuation

As we have previously remarked, one of the major advantages of using thin films is that the doping in the coating may be chosen such that only the minimum WLS grammage required for efficient conversion is applied.

This means that problems of attenuation due to

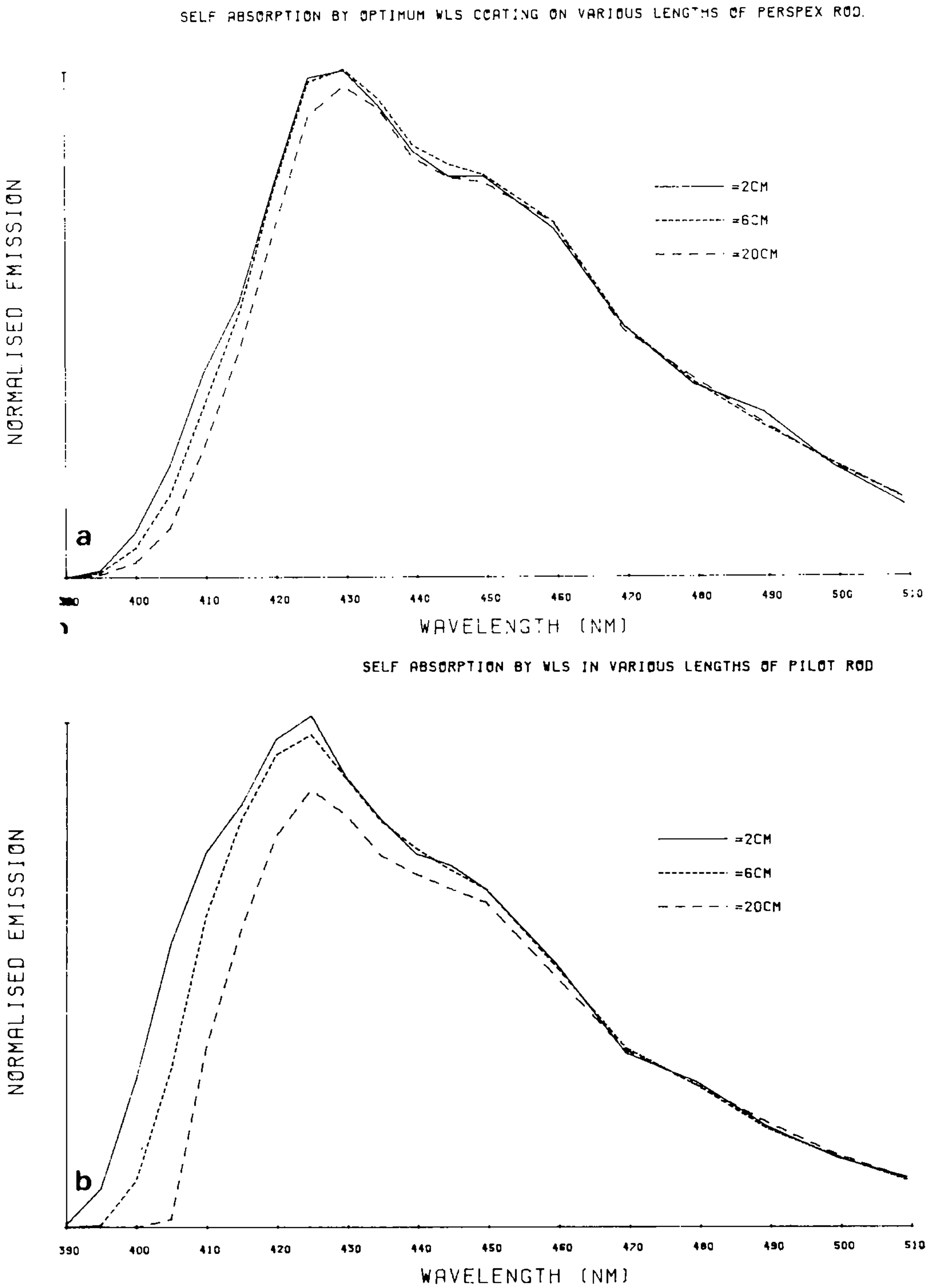

Fig. 11. Emission spectra of (a) coated perspex rod, (b) Pilot 425 rod for light travelling different distances in the rod.

self-absorption in the WLS, compared with commercially doped plastics, can be minimised. Fig. 10 shows the variation of attenuation length with wavelength in a 1 cm diameter rod of Pilot 425 and a similar rod of perspex coated with mixture 6. It is seen that at wavelengths corresponding to the emission peak of bis-MSB, at which the majority of the emitted light emerges, the attenuation length in the coated rod is substantially longer than in the Pilot 425. Fig. 11 shows the variation of emission spectrum from the end of the rod with wavelength.

It should be noted that due to self-absorption the peak emission is always bathochromatically shifted with respect to the emission of the WLS in liquid solution. In theory one would actually expect to see a hysochromatic shift due to the "freezing in" of the Franck Condon transitions in a solid matrix. This is due to the preferential absorption at short wavelengths.

9. Discussion

Coatings involving bis-MSB have been found prone to ageing [14]. A possible explanation for this is that hard UV radiation is capable of exciting triplet states, rather than the singlet states involved in fluorescence. In the presence of oxygen these triplet states form radicals which destroy the WLS molecule. The coating may be protected by avoiding intense UV or oxygen. One advantage of using a Pilot 425 substrate is the avoidance of this restriction. We found no detectable degradation in the performance of pT coated on Pilot 425 which had been exposed to sunlight for several months.

The possibility of using other WLS, both individually and in combination, was also investigated. Table 1 lists a range of coatings incorporating other WLS combinations. The spectral response of these is shown in fig. 9. We see that in none of the mixtures approach the efficiencies obtained with the pT/bis MSB mixture described above.

The possibility of improving our coating by the addition of PPO was extensively investigated. However, it was found that in all cases its presence degraded the performance of the coating by an amount which increased with increasing concentration of PPO.

10. Conclusion

For applications involving radiance amplifiers in the detection of Cherenkov radiation, a coating consisting of 5.7% pT and 3.1% bis-MSB in a PEMA matrix is recommended for a transparent substrate. This coating has an average quantum efficiency of 91% in the wavelength interval 200–400 nm and is transparent above. For coating on a Pilot 425 substrate the bis-MSB concentration should be reduced to 1.7%; this yields the same quantum efficiency. Other coatings involving different WLS did not approach this efficiency. If a good optical surface is unnecessary or undesirable the WLS concentrations should be increased by a factor of 2.5.

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