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A METHOD OF COATING PHOTOMULTIPLIERS WITH WAVELENGTH SHIFTERS

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A simple procedure to coat photomultipliers with PTP wavelength shifter is described and results of some measurements are discussed.

1. Introduction

The spectral sensitivity in the UV region of modern photomultipliers is normally limited by the transmission properties of the window material. The glass windows commonly used typically absorb light below a 300 nm wavelength. In many applications, the interest lies in extending the spectral sensitivity below this limit. For example, in modern gas Cherenkov counters with very low light yields, the aim is to extend the sensitivity down to the absorption region of the gas radiator so as to make use of the $1/\lambda^2$ increase of photon production due to Cherenkov radiation.

Photomultipliers with quartz or LiF windows are difficult and expensive to produce and are not yet in mass production for large-area photomultipliers. An alternative method of enhancing the UV sensitivity of photomultipliers is to coat the glass window with wavelength shifters that convert the light of a certain wavelength region into light of a longer wavelength which can pass the window[1,2]). A common procedure consists of depositing some fluorescent organic compound, under vacuum, onto the glass window by evaporation. PTP (1,4 diphenylbenzol $C_{18}H_{14}$) has been widely used because of its short wave absorption maximum of ~ 277 nm, its re-emission around 350 nm (close to the peak sensitivity of bialkali photocathodes), its high quantum efficiency, and its short decay time. A disadvantage of this method is that the coating has a very weak mechanical resistance. A further inconvenience is that of having to use a vacuum-coating unit. Therefore a simple and quick procedure has been developed to overcome these drawbacks.

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2. The method

This consists of dissolving the wavelength shifter and some transparent plastic binder in an organic solvent. After proper cleaning, the photomultiplier windows are briefly dipped in the solution. After evaporation of the organic solvent, a layer of the plastic binder and wavelength shifter remains. Various wavelength shifters and binders in a wide range of concentrations have been tried. Very satisfactory results were obtained with a mixture of 1 g PTP* and 2 g of paraloid† in 250 cm^3 of methylene dichloride (CH_2Cl_2). Chloroform ($CHCl_3$) can be equally well used as the solvent but requires special safety precautions. Instead of paraloid, polystyrene can be used as the binder, yielding a slightly reduced performance owing to a certain absorption around 210 and 260 nm but with superior

* From Fluka, Chem. Fabrik, Buchs, Switzerland.
† Paraloid B72, from Rohm and Haas, Philadelphia, U.S.A.

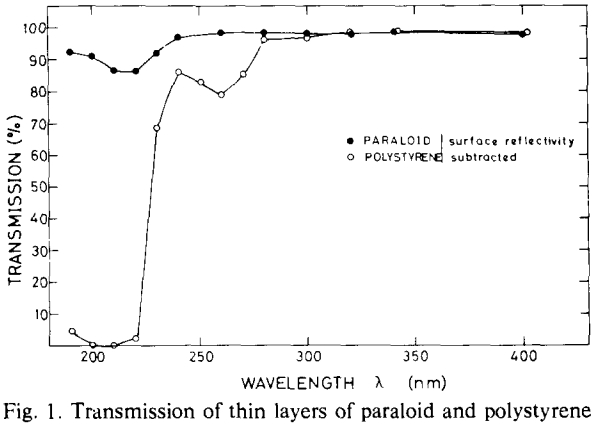

Fig. 1. Transmission of thin layers of paraloid and polystyrene as a function of wavelength. (The data point at 190 mm is less reliable.) The layers were deposited on quartz flats using the same technique as for photomultiplier coating.

mechanical resistance. Fig. 1 shows the transmission of paraloid and polystyrene. In the case of polystyrene, one has to select a type without UV stabilizer. The ratio of PTP to binder is not critical. While a ratio of 1 to 1 gives unsatisfactory mechanical resistance, a fraction below 25% of PTP gives a poor sensitivity below 220 nm wavelength because of the increased absorption of the binder. The solvent concentration of PTP in plastics or organic liquids is very low, typically less than 2%. Therefore, during the evaporation phase of the solvent, the PTP begins to crystallize inside the plastic binder, sometimes giving the finished photomultiplier a pattern like zinc-coated iron. Depending on the working temperature and ventilation these embedded crystals can vary substantially in size, but no significant dependence in sensitivity as a function of the size has been observed.

The advantages of the method described are its extreme simplicity, short implementation time (typically less than 5 min), and the mechanical resistance of the coating. Disadvantages come from the increased optical absorption of the binder below 200 nm and an apparent difficulty in controlling the layer thickness of the deposit. Whilst above 220 nm wavelength a wide variation in thickness results in minimal changes of sensitivity, the sensitivity below 220 nm depends significantly on the layer thickness and on the variation of binder to PTP concentration. No further quantitative studies have been done.

A further advantage of the method seems to be the increased sensitivity compared to the vacuum deposit technique above 200 nm, as will be discussed in the next section.

3. Results

The over-all gain of sensitivity of a photomultiplier depends also on its mode of operation, i.e. on the collection efficiency of photoelectrons inside the electron optics system. In order to obtain a more quantitative measurement of the spectral sensitivity effects, photomultipliers have been operated as photocells, and their photocurrent has been measured as a function of wavelength. As a standard, a 2″ RCA C31000 M with quartz window and bialkali photocathode has been used, i.e. all measurements have been normalized to the sensitivity of this photomultiplier. In a first series of measurements, this photomultiplier was coated under vacuum with 10 000 Å PTP. The resulting change in sensitivity is plotted in fig. 2. The results show

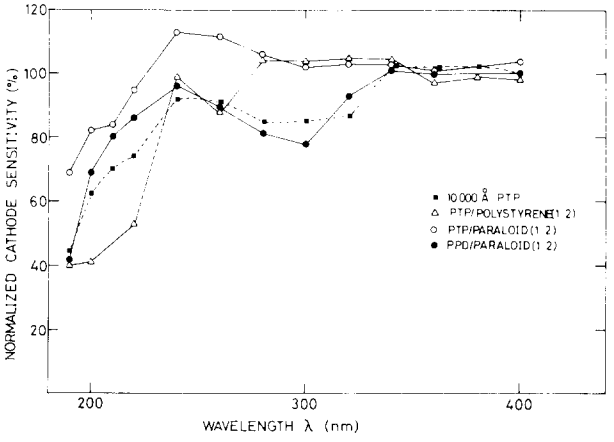

Fig. 2. Cathode sensitivity of a photomultiplier RCA 31000 M coated with various combinations of wavelength shifters and binders as a function of wavelength. The curves are normalized to the sensitivity of the untreated tube.

a) that the wavelength shifter is only effective in a certain wavelength region around 260 nm, while below 230 nm its quantum efficiency sharply decreases;
b) that below 320 nm wavelength the quantum efficiency of a photomultiplier with quartz windows cannot be reached with the technique of vacuum deposition used.

Fig. 2 shows the results for the new procedure of coating. Again the decrease in sensitivity at short wavelength is observed, while around 250 nm an increase in sensitivity over the value of the untreated tube has been observed (except for polystyrol binder, which has an absorption around 260 nm wavelength). The most probable explana-

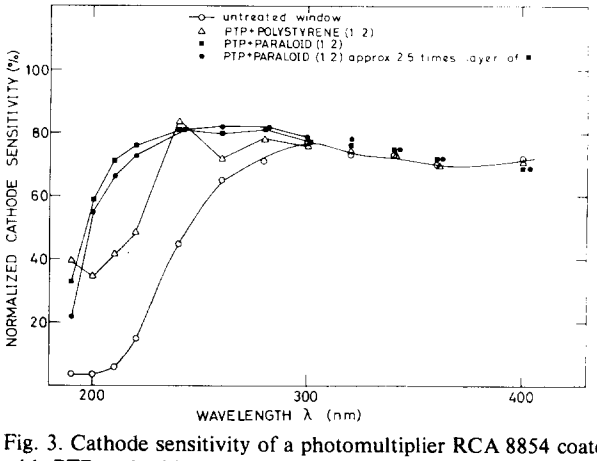

Fig. 3. Cathode sensitivity of a photomultiplier RCA 8854 coated with PTP and with polystyrene or paraloid as binder, as a function of wavelength. The curves are normalized to the sensitivity of the RCA 31000 M of fig. 2.

tion for the difference between the two methods is the following. The PTP shifts the light to 350 nm, where the bialkali photocathode has a higher quantum efficiency than in the region around 250 nm[3]) but the re-emitted light is radiated isotropically. While the use of a plastic binder leads to a good optical contact and a perfectly smooth surface with high internal optical trapping, the vacuum deposition technique leads to a much more structured surface due to recrystallization resulting in a higher emission in the wrong direction. A significant backward emission can be observed by eye when the vacuum coated photomultiplier is illuminated by an intense UV light source.

Fig. 2 also shows the results for a PTP wavelength shifter embedded in polystyrene and for PPD (2,5 diphenyl-1,3,4 oxadiazole; $C_{14}H_{10}N_2O$) in paraloid. Both samples show somewhat lower gains. In order to study the yields of photomultipliers with glass windows, an RCA 8854 has been coated with PTP with paraloid or polystyrene as binder; also the layer thickness has been varied. Fig. 3 shows the results of the measurements and compares them with the cathode sensitivity of the untreated tube. A significant increase in sensitivity below 300 nm wavelength is observed. Other photomultipliers such as the Valvo 56 AVP/DVP and XP 2041, and the RCA 8850, have been tested with similar results.

In order to test the over-all gain of the photomultiplier RCA 8854 for Cherenkov application, 20 of these have been coated and tested in two Cherenkov counters. In a counter with helium filling, an increase in detected photoelectrons of about 35% has been observed, and in a counter with a CO_2N_2 mixture there was an increase of 25%. No correction due to the spectral reflectivity of the intermediate mirror system has been made. During a nine-month operation, no decrease in sensitivity has been seen.

In a second series of measurements, various 5″ photomultipliers have been tested in a small Cherenkov counter filled with air at atmospheric pressure (965 mb, 19 °C). The radiator had a length of 30 cm and was traversed by pions of 12 GeV momentum. The Cherenkov light was deflected by a 45° mirror onto the photomultipliers mounted outside the region of the particle passage. The reflectivity of the mirror is shown in fig. 4. The illuminated area had a diameter of approximately 5 cm. Further details of the procedure are given elsewhere[4]).

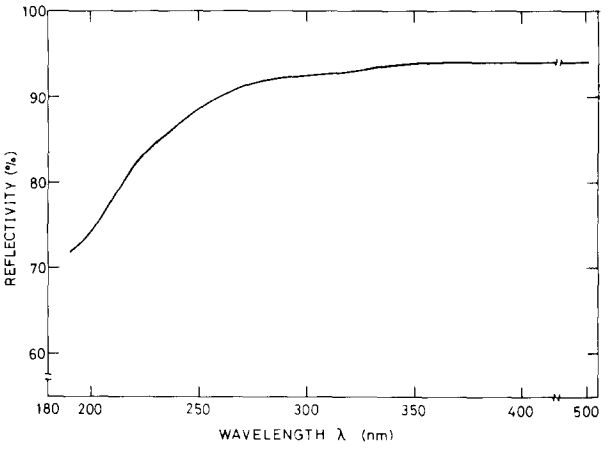

Fig. 4. Spectra reflectivity of the mirror used in the test counter.

As a figure of merit, the numbers of photoelectrons converted to $\beta = 1$ particles are listed in table 1 for the PTP–paraloid combination. Depending on the transmission of the window material, the gain varies between 36% and 85%. For comparison, a tube with a quartz window (EMI 9823QB) was also tested. As expected, the yield decreases with the wavelength shifter, owing to the absorption below 220 nm. The numbers quoted have to be taken only as an approximate yield for improvements because the over-all effect is a complex function of

a) the $1/\lambda^2$ dependence of the intensity of the Cherenkov light,
b) the UV absorption of the air below 180 nm wavelength,
c) the wavelength dependence of the reflectivity of the mirror,
d) the photomultiplier operating conditions.

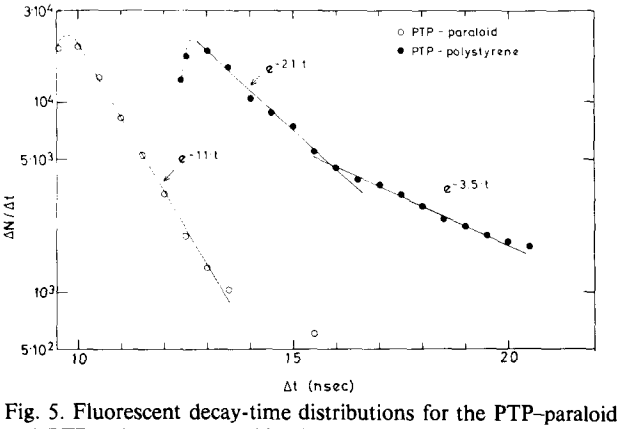

Fig. 5. Fluorescent decay-time distributions for the PTP–paraloid and PTP–polystyrene combinations. Arbitrary zero point.

TABLE 1

Numbers of photoelectrons converted to $\beta = 1$ particles.

Photo-multiplier	Cathode diameter	Number of tubes tested	Average sensitivity μA/Corning blue	Number of observed photo-electrons for $\beta = 1$ particles		Gain due to WLS (%)	Comments
				Plain tube	Coated tube		
RCA 8854	5″	3	10.7	1.62	2.21	36%	$U_{CD1} = 1320$ V [a]
VALVO 58 DVP	5″	3	–	1.01	1.74	72%	[a]
VALVO XP2041	5″	3	85 mA/Watt (401 nm)	1.04	1.48	42%	History of tubes unknown[a].
EMI D325B	5″	1	8.3	0.84	1.48	76%	Test tube. Data outside specifications of manufacturer[a]
EMI 9823QB	5″	1	10.0	2.31	2.04	−12%	Tube with quartz window[a].
EMI 9870B	5″	1	10.0	1.19	2.20	85%	Specially shaped window, venetian-blind dynodes for high collection efficiency. U_{CD1} between 300 and 1000 V [b].
EMI 9829QA	2″	36	10.6	3.14	–	–	2″ quartz tube, two reflections on intermediate mirrors, $U_{CD1} \approx 850$ V.

[a] Divider chain according to ref. 4.
[b] Divider chain according to data sheet of manufacturer.

The collection efficiency for photoelectrons between the photocathode and the first dynode (25–60%) is a particularly critical parameter for 5″ photomultipliers, strongly affecting the absolute numbers of observed photoelectrons. For 2″ photomultipliers a higher collection efficiency can normally be achieved; therefore the results for samples of quartz photomultipliers are also quoted.

The binder slightly affects the optical decay time of the wavelength shifter. Fig. 5 shows the decay time distributions for the fast component for the PTP–paraloid and PTP–polystyrene combinations. The resolution of the measuring system of approximately 0.7 ns has not been unfolded. While the PTP–paraloid combination shows a decay distribution consistent with a single exponential function for a factor of 10 drop in intensity, two exponential decay functions with significantly different decay constants are necessary to describe the data for the PTP–polystyrene combination.

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References

1) E. L. Garwin et al., Nucl. Instr. and Meth. **107** (1973) 365.
2) P. Baillon et al., Nucl. Instr. and Meth. **126** (1975) 13.
3) S. Sabieski, Appl. Opt. **15** (1976) 2297.
4) E. Lorenz, Max Planck Institute Report MPI-PAE/Exp. El. 57 (1976).