

Wavelength-shifting materials for the use in RICH detectors – p-terphenyl and tetraphenyl-butadiene revisited –

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Abstract

P-terphenyl (PT) and tetraphenyl-butadiene (TPB) in form of thin films have been investigated as possible wavelength shifting material for application in Ring Imaging Cherenkov (RICH) detectors. Films of different thickness were evaporated onto borosilicate windows of photomultiplier tubes (PMT) and the quantum efficiency of the modified PMTs was determined as a function of wavelength. Gain factors for the number of measured photoelectrons in dependence on the cutoff wavelength (energy) for application in Cherenkov counters were established. Using PT, a strong increase in quantum efficiency between 200 nm and 300 nm was observed leading to gain factors as high as 1.71 ± 0.11 for a cutoff energy of 6.2 eV. Due to strong absorption in the wavelength range between 300 nm and 400 nm, TPB shows inferior results. No significant thickness dependence was observed for films thicker than 0.6 μm . Film morphology and wavelength dependent fluorescence was measured to back the results. Simulations encourage the use on flat panel multi-anode photomultipliers.

Key words: Wavelength shifter, RICH detector, Cherenkov radiation

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1. Introduction

High spectral sensitivity and quantum efficiency of photomultipliers for photon detection in the UV region (150 nm onwards to the visible light region) is an important quality criterion in particular for gas Cherenkov counters. With standard bi-alkali photocathodes as well as for the new super-bi-alkali or ultra-bi-alkali photocathodes, the limiting factor is the UV transparency of the window material. Typical borosilicate windows start absorbing light below ≈ 300 nm, UV-extended windows below ≈ 250 nm, and only quartz windows allow to extend the range down to ≈ 180 nm. However, in particular for large areas, quartz windows are still technically difficult to handle and expensive to produce. As a rather inexpensive alternative to enhance the photon detection efficiency in the UV region, the usage of wavelength shifting (WLS) films on top of the photomultiplier window was investigated as early as in the 70's [1, 2, 3, 4] and 80's [5] and since then was regularly used (see e.g. Ref. [6] for a recent application). These WLS films are typically made from organic molecules absorbing light in the UV region and re-emitting fluorescence photons at larger wavelength, ideally at maximum spectral sensitivity of common photocathodes.

Despite the usage of WLS films in a plurality of applications, the number and quality of reported data on their performance are rather scarce. Gain factors comparing uncovered and covered photomultiplier tubes were typically measured in a wavelength integrating manner [1, 2, 6]. Furthermore, the measurements were performed in dedicated setups [1, 2, 6] and are thus dependent on the chosen conditions, e.g. radiator, mirror coat-

ing, windows, etc. Therefore, gain factors vary between the different measurements and are difficult to compare. Results concerning a possible dependence of the gain factor on the WLS film thickness differ between the publications if being reported at all [1, 2, 3, 4].

With upcoming plans for a large acceptance RICH detector for the future Compressed Baryonic Matter (CBM) experiment at the Facility for Antiproton and Ion Research (FAIR) [7], WLS films for the extension of PMT sensitivity into the shorter wavelength region become appealing again. Wavelength extended PMTs offer affordable coverage of large photodetector planes with high efficiency photodetectors. In this context, it furthermore is of interest whether these WLS films can also be used with flat panel multi-anode photomultiplier tubes (MAPMTs) at tolerable crosstalk. Two different types of wavelength shifting films showing good performance in previous investigations [2, 5] have therefore been revisited: p-terphenyl (PT) and tetraphenyl-butadiene (TPB). In particular p-terphenyl is a very promising candidate because of its absorption maximum at about 280 nm and its re-emission of light at around 350 nm [8, 9] close to the peak quantum efficiency of bi-alkali photocathodes. Moreover, its fluorescence decay time has been reported to lie in the 1- to 5-ns-region [1, 3, 5], somewhat depending on whether the film has been evaporated or coated from solution [3]. The absorption maximum of TPB is more unfortunate, i.e. at about 350 nm, and the re-emission of fluorescence photons peaks at 420 nm [8]. Nevertheless gain factors as high as for the use of p-terphenyl have been reported [2].

To overcome the dependence of the gain factor on the specific setup wavelength dependent quantum efficiencies of WLS-covered and uncovered PMTs have been measured. WLS films were evaporated directly on top of the borosilicate window of XP3102 photomultiplier tubes from Photonis, purchased for this study. Different layer thickness was studied in terms of efficiency measurements, fluorescence spectra, and film morphology.

2. Coating method

Films of p-terphenyl¹ and tetraphenyl-butadiene² were deposited with different thickness on the borosilicate window of Photonis XP3102 photomultipliers (1 inch diameter) by evaporation of crystalline PT and TPB from a molybdenum boat which was heated resistively up to 200° in a vacuum evaporator (base pressure about $3 \cdot 10^{-6}$ mbar). The evaporation method was calibrated by means of test evaporation on float glass plates of known size and weight. During these test evaporations the duration and heating current were registered together with readings of a quartz crystal microbalance (QCM) placed at a certain distance from the boat. The material load of the evaporated substance was measured by weighing the glass plates before and after coating. As the photodetector area is much smaller than the distance to the vapor source, homogenous surface coverage is achieved. Layers of different thickness were applied by positioning the plates at different distances to the source and have been verified by SEM measurements. After these tests, the coating process was monitored with good accuracy with the QCM alone.

3. Wavelength dependent quantum efficiency

External quantum efficiencies were measured in a setup operated in air comprising a Xe-lamp and a monochromator allowing to determine the absolute quantum efficiency in the range between 200 nm and 800 nm [10]. A Newport 818-UV Photo Diode is used for light irradiance calibration. The photocurrent extracted from the cathode of the PMT under investigation was measured by applying a voltage of 200 V between the first dynode and the cathode which was kept at ground. This way the amplification chain of the photomultiplier is bypassed and possible collection efficiency losses inside the electron optics system are irrelevant.

From repeated measurements we estimate the uncertainty in the quantum efficiency determination to be below 10%, somewhat depending on wavelength. Including normalization uncertainties, this results in a combined error of 10% for the integrated quantum efficiency and thus for the gain factor calculated as described below.

The gain factor for measuring Cherenkov radiation using WLS films on photomultipliers was estimated as follows: In

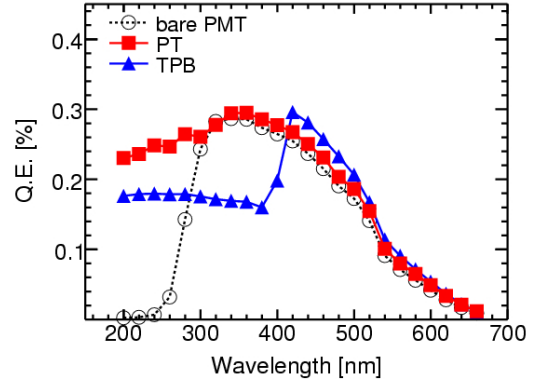


Figure 1: (Color online) Quantum efficiency of the same Photonis XP3102 photomultiplier without and with wavelength shifter coating. The material loads were $95 \mu\text{g}/\text{cm}^2$ for PT and $65 \mu\text{g}/\text{cm}^2$ for TPB, respectively. The estimated uncertainty of this measurement is below 10%.

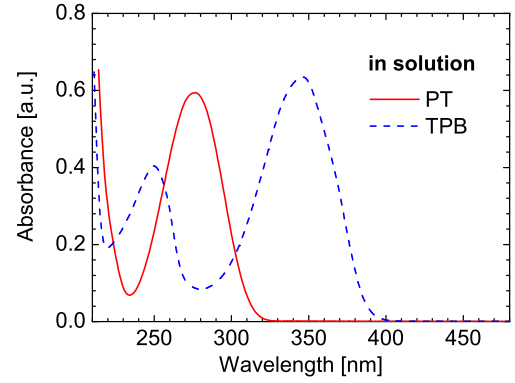


Figure 2: (Color online) Absorption spectra of PT and TPB in cyclohexane; concentration was 2×10^{-5} mol/l. Note the different wavelength scale compared to Fig. 1.

general, in a given device the number of detected photoelectrons from Cherenkov radiation (with Cherenkov cone half angle θ_c) of a particle with charge ze passing a radiator of length L can be written as [11]:

$$N_{p.e.} = L \frac{\alpha z^2}{\hbar c} \int_{E_{min}}^{E_{max}} \epsilon_T(E) \epsilon_R(E) \epsilon_D(E) \sin^2 \theta_c(E) dE \quad (1)$$

with the fine-structure constant α and with the energy dependent efficiencies for light transmission in the radiator, ϵ_T , for reflection if using a mirror, ϵ_R , and for detection in the photodetector, ϵ_D . If written in dependence on the wavelength λ this formula contains the λ^{-2} dependence of Cherenkov light being the reason for the strong interest in UV photons for Cherenkov counters. In context of this investigation the first two efficiencies are irrelevant and the detection efficiency can be reduced to the quantum efficiency as the amplification chain is bypassed. Since the typical energy dependent variation of the index of refraction n and thus θ_c is modest, $\sin^2 \theta_c$ is assumed to be constant. The resulting dependence of the number of detected photoelectrons then reads:

$$N_{p.e.} = \text{const} \cdot \int_{E_{min}}^{E_{max}} \epsilon_{q.e.}(E) dE \quad (2)$$

¹MERCK, Art. No 108099, batch 7469311.

²Sigma, Art. No T4250-25G, 1,1,4,4-Tetraphenyl-1,3-butadiene, minimum 99%.

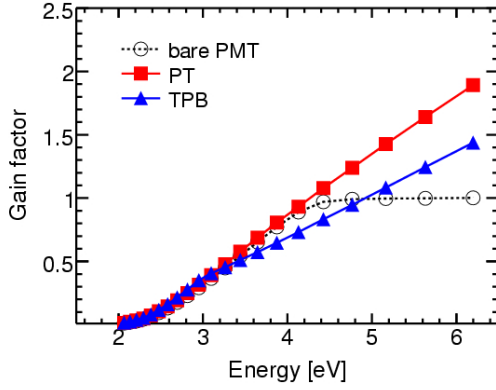


Figure 3: (Color online) Integrated photon yield as deduced from the data in Fig. 1 for Cherenkov photons versus energy; the integral of the untreated PMT is normalized to unity at $E_{max} = 6.2$ eV. The estimated uncertainty of this measurement is 10%.

Measuring wavelength and thus energy dependent quantum efficiencies (Fig. 1), this integral can be calculated as function of the cutoff wavelength λ_{min} , i.e. cutoff energy E_{max} .

In Fig. 1 the measured quantum efficiency for an untreated PMT is compared to the one after PT and TPB was applied. For direct comparison, Fig. 2 shows the absorption spectra of PT and TPB measured in cyclohexane. Checking the coated photomultipliers after 4 months storage under CO_2 flow again showed no deterioration of the quantum efficiencies. Fig. 3 shows the energy dependent gain factor in the number of measured photoelectrons in a Cherenkov counter when using WLS-coverage for the photomultipliers. This gain factor is calculated by normalizing the integrated quantum efficiency (eq. 2) of the uncoated photomultiplier to unity at $E_{max} = 6.2$ eV, and by using the same normalization for the covered photomultipliers.

As seen in Fig. 1 for PT, the WLS film strongly extends the measurable range of photons into the UV region while not affecting the efficiency in the visible part. This results in a significant gain in the integrated number of measured photoelectrons of a factor between 1.6 and 1.9 ($E_{max} = 6.2$ eV) as can be read from Fig. 3 and Fig. 4, the latter showing the gain factor as a function of WLS film thickness. For TPB, an enhanced quantum efficiency for $\lambda \lesssim 300$ nm is observed as well (Fig. 1), however losses in the range from approx. 300 nm to 400 nm are obvious. As a consequence, the gain in the number of measured photoelectrons is smaller if compared to PT (see Fig. 3). Both observations can be understood considering the absorption and emission spectra of the two substances (Figs. 2 and 5 and Ref. [8]): In the PT film photons with $\lambda \lesssim 300$ nm, i.e. outside the sensitive region of the uncoated PMT, are absorbed and re-emitted with a spectrum that peaks near 350 nm (see also Fig. 5) which is close to the maximum quantum efficiency of bialkali photocathodes. However, in the TPB film photons with $\lambda \lesssim 380$ nm are absorbed, i.e. in the range where the PMT photocathode is already sensitive. Furthermore, for TPB the re-emission of fluorescence photons peaks near 450 nm which is beyond the peak efficiency of the photocathode. Therefore a reduced quantum efficiency is observed compared to PT for

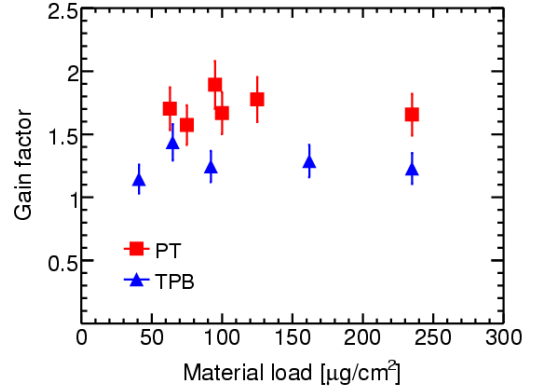


Figure 4: (Color online) Gain factor versus material load (see Fig. 6 for corresponding film thickness) for a cutoff energy $E_{max} = 6.2$ eV ($\lambda_{min} = 200$ nm). Uncertainties of 10% are expressed by the error bars.

$\lambda \lesssim 380$ nm.

As mentioned in the introduction, different gain factors are reported elsewhere; e.g. a factor of ≈ 3.4 for both substances in Ref. [2], or factors of approx. 1.5 and 1.1 for PT and TPB, respectively, in Ref. [6]. Both observations can be understood considering the relevant wavelength range in the different setups. In Ref. [6] Cherenkov photons were generated and transmitted in aerogel. With a corresponding wavelength limit of approx. 240 nm (5.3 eV), the reported gain factors agree well with the results presented in Fig. 3. In ref. [2], a wavelength limit of ≈ 105 nm is claimed, corresponding to a photon energy of approx. 12 eV. The gain factor of ≈ 3.4 can be understood assuming that the quantum efficiency stays constant at the measured level of approx. 22% - 25%. In this case, the gain as plotted in Fig. 3 would continuously increase with cutoff energy. Indeed, a linear extrapolation of the presented measurement reaches gain factors of 3 to 4 for both substances at 12 eV. Since both materials behave more similar towards shorter wavelengths, the measured relative difference in the integrated factors will be smaller. The measurements presented in Fig. 3 provide thus a setup independent evaluation of expectable gain factors in Cherenkov light detection using PT or TPB as wavelength shifters.

4. Thickness dependence

Quantum efficiencies and gain factors were evaluated for PT and TPB films of different thickness (Fig. 4). No significant dependence on the applied material load was found in the evaluated range. On average, for a cutoff wavelength of 200 nm ($E_{max} = 6.2$ eV) a gain factor of 1.71 ± 0.11 for PT and 1.27 ± 0.11 for TPB is achieved. This insensitivity to the material load is clearly a plus for the application in a RICH detector. With many hundreds of PMTs to be coated, there seems to be no need for a restrictive thickness control.

To better understand the thickness dependent results of the measured quantum efficiency, fluorescence measurements and scanning electron microscopy were performed with films grown on glass substrates similar to those on the PMT windows. These

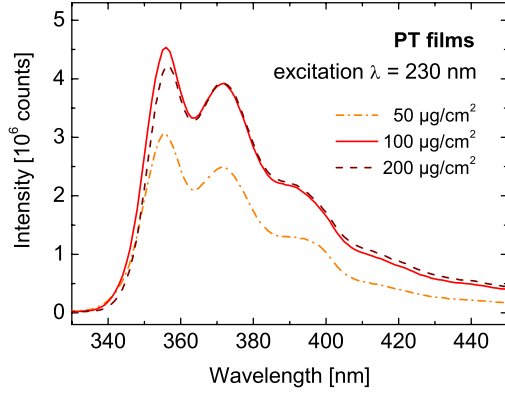


Figure 5: (Color online) Photoluminescence spectra of PT films of different layer thickness (compare Fig. 6). Excitation wavelength was 230 nm.

investigations were performed only for PT films as this has been shown to be the more promising candidate of the two substances under investigation. Fluorescence measurements were performed both with the excitation wavelength at 280 nm and 230 nm. The first one is close to the absorption maximum of PT, the latter is located in the absorption minimum. The measurements of fluorescence intensity as a function of wavelength with excitation at 230 nm as shown in Fig. 5 can therefore be seen as an extreme case with respect to the number of adsorbed photons in the films; the influence of layer thickness on film performance should therefore be most pronounced in this case. In Fig. 5, one observes two emission maxima around 356 nm and 372 nm for all three films, in good agreement with literature [9]. A pronounced increase in intensity can be observed for the 100- $\mu\text{g}/\text{cm}^2$ -film when compared to the 50- $\mu\text{g}/\text{cm}^2$ -film. However, the intensities of the 100- $\mu\text{g}/\text{cm}^2$ -film and 200- $\mu\text{g}/\text{cm}^2$ -film are comparable with a slight drop of the intensity of the 200- $\mu\text{g}/\text{cm}^2$ -film in the shorter wavelength region. Qualitatively the same behavior was observed when exciting the films with 280-nm-light, but with a less pronounced difference between the 50 $\mu\text{g}/\text{cm}^2$ and 100 $\mu\text{g}/\text{cm}^2$ coverage.

SEM images of these films are shown in Fig. 6. The side view in Fig. 6(a) indicates a rather smooth film growth and only minor formation of larger crystals. The thickness of each film was measured in these images and in Fig. 6(b) the values are plotted as a function of the material load applied during the evaporation process. The thickness of the layers is proportional to the applied material load corresponding to a density of $\rho = (1.12 \pm 0.10) \text{ g}/\text{cm}^3$ which is slightly below the reported PT density of $\rho = 1.23 \text{ g}/\text{cm}^3$. However, towards higher material load the thickness variation increases as indicated by the error bars, which represent lowest and highest layer thickness. This increased surface roughness of the thicker layers is also observed in the bird's-eye-view images in Fig. 6(c) and (d). For the thicker film, a pronounced formation of micro-crystals is observed which results in a higher surface roughness.

The observation that the spectra for 100 $\mu\text{g}/\text{cm}^2$ and 200 $\mu\text{g}/\text{cm}^2$ material load in Fig. 5 do not show a pronounced difference in fluorescence intensity leads to the conclusion that the PT film with a thickness of 1 μm (approx. 100 $\mu\text{g}/\text{cm}^2$) ab-

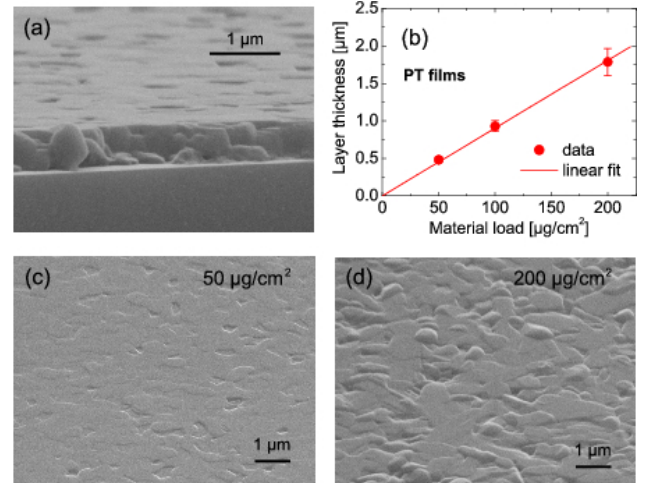


Figure 6: (Color online) (a) SEM side-view of a 0.5- μm -film on glass, viewing angle 80° off normal. (b) Dependence of layer thickness as measured by means of SEM as a function of material load applied during the evaporation process. (c) and (d) SEM bird's eye view of the layers' surface (60° off normal) for the 0.5- μm -film and 2- μm -film, respectively.

sorbs almost all of the incoming photons. As a consequence, the efficiency of the PMTs is not further increased with increased film thickness. For the thinner 50- $\mu\text{g}/\text{cm}^2$ -film, however, a lower fluorescence intensity is observed. This indicates that a substantial number of UV photons is not absorbed anymore. Although this effect is seen in the fluorescence spectrum with excitation at 230 nm, it is not observed in the measured integrated quantum efficiency of the PMTs coated with PT films (Fig. 4), of which the lowest PT material load was 63 $\mu\text{g}/\text{cm}^2$. Apparently, quantum efficiency measurements with films thinner than those investigated so far would be necessary to investigate at which film thickness a significant reduction of the integrated efficiency sets in.

The increased surface roughness and correlated increase in light scattering for the thickest layer shows, if any, a small effect in the fluorescence spectrum. The observed slight reduction of the fluorescence intensity in the short wavelength region might be explained by the fact that this range is affected the most by light scattering. However within the error bars, no effect of the increased light scattering is observed for the measured quantum efficiencies.

5. Simulations on spatial resolution

Simulations with GEANT4 [12] have been performed in order to better understand the observed quantum efficiency as well as to study the applicability of WLS films to flat panel MAPMTs. A 0.8- μm -thick layer of PT ($\text{C}_{18}\text{H}_{14}$, $\rho = 1.234 \text{ g}/\text{cm}^3$, $n = 1.65$) corresponding to a material load close to 100 $\mu\text{g}/\text{cm}^2$ has been implemented on top of a 1.5 mm thick borosilicate window ($\rho = 2.23 \text{ g}/\text{cm}^3$, $n = 1.52$); both geometries were placed in vacuum ($n = 1$). All materials are optically isotropic and the refractive index n does not depend on the wavelength. The emitted fluorescence light was simulated by an isotropic generation of monochromatic optical photons

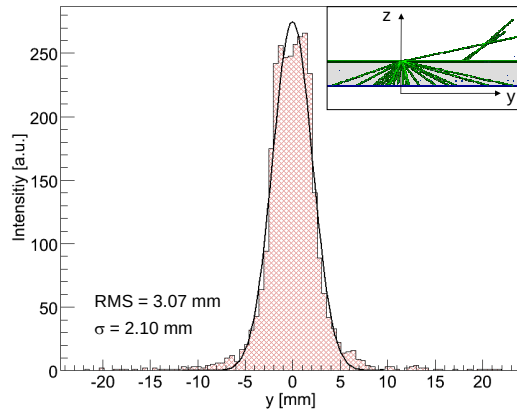


Figure 7: (Color online) Simulated distribution of the y-coordinate of photons recorded at the PMT photocathode on the bottom of the PMT window. The insert shows the simulated setup: photons (green lines) isotropically generated in the center of a $0.8\ \mu\text{m}$ thick PT film on top of a PMT window of $1.5\ \text{mm}$ thickness (grey).

in the middle of the PT layer. Due to total internal reflection at the PT to vacuum interface about 60% of the photons reached the bottom face of the borosilicate window thus could potentially be detected. Assuming a quantum efficiency of 30%, the combined detection probability is 18% which is close to the value observed, see Fig. 1, short wavelength region. This value should be wavelength independent as observed experimentally. Due to the isotropic generation of the fluorescence photons, their detection point is distributed around the generation point; the corresponding distribution is shown in Fig. 7. It is well described by a gaussian distribution ($\sigma = 2.10\ \text{mm}$), however, showing some outliers ($RMS = 3.07\ \text{mm}$).

These results allow a first evaluation on expected resolution losses if using WLS films on the window of flat panel MAPMTs such as the Hamamatsu H8500; geometrical conditions used in the simulation described above were already adopted to this device. This MAPMT has an 8×8 pixel matrix with single pixel sizes of $(5.8 \times 5.8)\ \text{mm}^2$. The variance of a measurement with a 1-dimensional uniform distribution (length $5.8\ \text{mm}$) is $(5.8/\sqrt{12})\ \text{mm} = 1.7\ \text{mm}$. Assuming an additional gaussian broadening with $\sigma = 2.1\ \text{mm}$ for single photons, the resolution degrades to $2.9\ \text{mm}$. As this degradation holds only for photons being converted by the WLS film ($\lambda \lesssim 280\ \text{nm}$), the overall loss in resolution is less. Assuming a fraction of 40% of converted photons according to the measured factor of 1.7 in gain, the combined resolution is $2.3\ \text{mm}$. Whether this is a tolerable loss in resolution which is compensated by the gain in the number of photoelectrons has to be evaluated for the specific application.

6. Summary

Systematic investigations of the quantum efficiency enhancing effect of commonly used wavelength shifting materials, p-terphenyl (PT) and tetraphenyl-butadiene (TPB), have been presented. In order to overcome the shortcomings of the setup-specific measurements reported so far, quantum efficien-

cies were measured in dependence on wavelength for coatings of different thickness on borosilicate windows of Photomultiplier Tubes (PMT) XP3102 phototubes. Gain factors comparing the coated and uncoated phototubes have been established as a function of cutoff energy.

For both substances a strong increase of quantum efficiency was observed in the wavelength region between $200\ \text{nm}$ and $300\ \text{nm}$. Because absorption and emission spectra for PT perfectly match the quantum efficiency spectrum of typical alkali photocathodes, the PT coverage causes no change in the quantum efficiency for $\lambda > 300\ \text{nm}$. This match is not as good for TPB causing a decrease of the quantum efficiency of the covered PMT in the range of $300\ \text{nm}$ to $400\ \text{nm}$. A gain in the number of measured photoelectrons of 1.7 is calculated for an application of PT in Cherenkov light detectors and a cutoff wavelength of $200\ \text{nm}$. For TPB, a gain factor of 1.3 is measured. No significant thickness dependence of the enhanced quantum efficiency is seen between approx. $(60\text{--}230)\ \mu\text{g}/\text{cm}^2$ material load. This observation is in general supported by fluorescence measurements; however a drop in fluorescence intensity is observed for thinner layers. This suggests that for less material load than studied here, the quantum efficiency and gain factor will drop. SEM images show that the film growth by evaporation is rather smooth with larger crystals being formed for thicker films. However, for the maximum layer thickness investigated here they do not significantly affect the performance by increased light scattering.

Although the fluorescence light is emitted isotropically, simulations support the observation that a fraction larger than 50% of the generated photons reach the photocathode and can be detected. Due to the low PMT window thickness, the corresponding spatial distribution of the generated photons is close enough to the absorption point in order to encourage the usage on flat panel MAPMTs.

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References

- [1] E.L. Garwin, Y. Tomkiewicz and D. Trines, Nucl. Instr. Meth. 107 (1973) 365.
- [2] P. Baillon et al., Nucl. Instr. Meth. 126 (1975) 13.
- [3] G. Eigen and E. Lorenz, Nucl. Instr. Meth. 166 (1979) 165.
- [4] M.A.F. Alves et al., Nucl. Instr. Meth. 119 (1974) 405.
- [5] A.M. Gorin et al., Nucl. Instr. Meth. A 251 (1986) 461.
- [6] Y. Allkofer et al., Nucl. Instr. Meth. A 582 (2007) 497.
- [7] C. Höhne et al., Nucl. Instr. Meth. A 595 (2008) 187.
- [8] Reference materials for Molecular Fluorescence Spectrophotometry, Starna Scientific Ltd., <http://www.optiglass.com>
- [9] R. Katoh, K. Suzuki, A. Furube, M. Kotani, K. Tokumaru, J. Phys. Chem. C 113, 2961-2965 (2009).
- [10] P. Hammarstedt, Master Thesis, CERN and Lund University, LUNFD6/(NFFL-7197)2001.
- [11] C. Amsler et al. (Particle Data Group), Phys. Lett. B 667 (2008), 1.
- [12] S. Agostinelli et al., Nucl. Instr. Meth. A 506 (2003) 250.