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# ORGANIC WAVELENGTH SHIFTERS FOR IMPROVED VACUUM ULTRA-VIOLET DETECTORS\*

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### Abstract

Two organic scintillators, p-p', diphenylstilbene and para-terphenyl, have been investigated for use as vacuum-ultraviolet wavelength shifters. Details of film preparation and overcoating are presented. Data on stability against aging in a conventional monochromator vacuum environment containing oil vapors show that these organic films are not only much more stable, but have quantum yields as high or higher than sodium salicylate in such an environment. Scintillation decay-time measurements show that the organic films are 4 to 10 times faster than sodium salicylate, a property of value for measuring lifetimes in the vacuum ultraviolet.

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### 1. Introduction

The use of fluorescent materials as wavelength shifters in vacuum UV detectors is widespread. Presently the most popular material is sodium salicylate. Its quantum yield is relatively high—around 65%, <sup>1</sup> its response is wavelengthindependent within  $\pm 20\%$  over the range 850 - 2000 Å, <sup>2</sup> it is easily prepared, and at first it was believed to be unaffected by vacuum. Later, an aging effect of the vacuum environment was found to cause a decrease of the fluorescent efficiency for wavelengths shorter than 2000 Å. <sup>3-5</sup>

The oil vapors existing in most vacuum monochromators are believed to be responsible for the aging process. (Allison and Burns<sup>6</sup> demonstrated that sodium salicylate samples kept in a very clean vacuum do not exhibit any deterioration.) Since oil vapors exist in most high-vacuum systems, it is of interest to find a fluorescent material with net efficiency more stable than sodium salicylate, particularly if that material has higher quantum yield and shorter decay time than sodium salicylate. The latter property allows measurements of short-lived emissions in the vacuum UV region. This paper reports on wavelength shifters which were found to be superior in the above aspects to sodium salicylate.

### 2. Experimental Methods

#### 2.1. Sample Preparation

The organic scintillators were obtained from New England Nuclear, Pilot Chemicals Division, in "scintillator grade" and used without any further purification. The measurements were performed on evaporated films, prepared by heating the various materials in a Mo evaporation boat covered by a thin wire mesh screen (in order to prevent explosive scattering) at a pressure of  $\leq 10^{-5}$ mm Hg. A typical rate of deposition was  $10^{-2}$  mg/cm<sup>2</sup>-min. The substrates were pyrex. The variations of the film thickness on the substrate were minimized

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by locating the substrate an appropriate distance above the evaporation boat. The thickness of a film was determined by weighing the substrate before and after the evaporation. The coated substrate was optically coupled by a thin silicone grease layer 7 to the front window of a photomultiplier. Some of the samples, in order to prevent evaporation, were coated with a protective thin layer (  $\sim$  200 Å) of  ${\rm MgF}_2$  or LiF. This coating was accomplished by evaporation (typical rate, 100 Å/min) immediately after the scintillator deposition without venting the vacuum system. The thickness of the  $MgF_2$  or LiF layers was determined by a quartz-crystal thickness monitor technique.<sup>8</sup> We recommend, for regular use, directly coating the photomultiplier window, thus eliminating the necessity for using silicone grease as a means of coupling. The silicone grease used for coupling can be a serious cause of premature aging of the samples, if it creeps onto the sensitive layer and spreads. However, in our experiments, we used the silicone coupling method because it enabled us to change relatively quickly the various samples and to study the aging effects under very harsh conditions.

### 2.2. Lifetime Measurements

An oxygen-filled, nanosecond light source,<sup>9</sup> combined with a 270-Å Optics Technology interference filter, was used for excitation. The emission was detected by a 1P21 RCA phototube combined with a lucite lightguide. The decay curves were obtained on a Tektronix sampling oscilloscope.

# 2.3. Wavelength and Thickness Dependence of the Quantum Yield

The wavelength dependence of the quantum yields of various scintillators was determined in the double beam attachment of a McPherson 225 Vacuum UV Monochromator. The readings of the photomultiplier-A (in Beam A) viewing the scintillators under evaluation were normalized to the readings of photomultiplier-B (in Beam B) viewing a reference layer of p-terphenyl, to eliminate

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the lamp intensity variations between two consecutive measurements. P-terphenyl was used as a working reference because it proved to be quite stable under our conditions of operation. Since the oscillating wedge mirror of the double beam attachment did not have identical reflective coatings on both its sides, a fresh sodium salicylate layer was measured in Beam A. The readings of photomultiplier-A viewing the sodium salicylate were normalized to the readings of photomultiplier-B viewing the reference layer of p-terphenyl. Subsequently, the normalized readings for the scintillators investigated in Beam A were divided by the normalized readings for sodium salicylate and the ratio gave the wavelength dependence of the quantum yield of the scintillator, referred to the well-known published values for sodium salicylate.<sup>1,2</sup>

The thickness dependence of the quantum yield was obtained in a similar way with samples of different thicknesses measured in Beam A.

### 3. Results

In the measured wavelength region (300 - 110 m $\mu$ ), the quantum yields of p-terphenyl (PTP) and diphenylstilbene (DPS) were found to be wavelengthindependent (relative to sodium salicylate) corresponding to the results of Ref. 5. The efficiency of p-terphenyl seems to be higher by 40% than the efficiency of sodium salicylate.<sup>10</sup> DPS was found, in thicknesses greater than 0.1 mg/cm<sup>2</sup>, to be inferior to PTP, due to the relatively low transparency of the DPS layer in the wavelength region of its own emission. (If DPS had the same transparency as PTP, its quantum yield would be roughly 20% higher than that of PTP.) As the thickness of DPS decreases, its transparency increases, as does the <u>apparent</u> quantum yield. For a thickness of 40  $\mu$ g/cm<sup>2</sup>, the quantum yield is as high as the quantum yield of PTP. At this thickness, the absorption of the incident light does not seem to be complete any more but still, for wavelengths below 255 m $\mu$ , the apparent quantum yield is constant to 110 m $\mu$ , the shortest wavelength measured.

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Unlike DPS, the quantum yield of PTP seems to be thickness-independent in the thickness range of 3 to  $0.1 \text{ mg/cm}^2$ . The high transparency of PTP layers and a total absorption of the incident photons (in this thickness range) seem to be the explanation.

Aging experiments were performed for PTP and DPS layers at vacuum and at room atmosphere. The aging in vacuum has two main causes: 1. The organic scintillators have relatively high vapor pressure and therefore they tend to evaporate in a vacuum environment. 2. Oil vapors are adsorbed on the surface of the scintillator and affect its performance. Since oil vapors seem to be the major cause of sodium salicylate deterioration, it was of special interest to compare the stabilities of PTP and DPS to sodium salicylate.

Figure 1 shows the thickness dependence of the quantum yield for various representative wavelengths. The only influence of the thickness is in the neighborhood of the absorption edge near 310 m $\mu$ -a region of no significant importance for vacuum UV.

The silicone grease layer used for optical coupling (see experimental section) was a constant source of vapors to which the samples were exposed. In addition, diffusion pump and forcepump oil vapors were present in the measuring chamber. A sodium salycilate layer already showed considerable deterioration after 24 hours while PTP started to show inferior performance only after weeks. DPS deteriorated slightly more rapidly than PTP upon adsorption of oil.

The rate of evaporation of DPS and PTP was measured by inserting the samples in the vacuum monochromator and weighing them subsequently. The rate of evaporation of PTP was found to be 0.03 mg/cm<sup>2</sup>-day, while the rate of evaporation of DPS was found to be roughly ten times less. Therefore, from the point-of-view of evaporation stability, DPS is superior to PTP. In order to

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eliminate aging due to evaporation, the scintillator layers were coated with  $MgF_2$  and LiF. It was found that  $MgF_2$  coating causes inferior performance only for wavelengths below 140 M $\mu$ . The LiF coating caused generally inferior performance below 2000 Å due to its hygroscopic nature.

It is interesting to note that aging at room atmosphere influences DPS more than PTP. Figure 2 shows the relative change in the intensity from a PTP layer and a DPS layer, as a function of wavelength, due to exposure to room atmosphere. The main effect is at wavelengths shorter than 2000 Å, possibly due to adsorption of water-vapor whose major influence is in the region of its absorption bands below 1900  $A^{0}$ .<sup>11</sup>

The following method of operation is suggested in order to utilize properly the above-mentioned properties of the investigated scintillators: If PTP is to be used, the thickness-independent quantum yield can be used to compensate for the relatively high rate of evaporation, by depositing a layer of  $3 \text{ mg/cm}^2$ . Since evaporation does not influence the quantum yield, at least to thicknesses of 0.1 mg/cm<sup>2</sup>, this layer can be effective for a couple of months.

DPS seems to be inferior to PTP but it can still be utilized successfully for vacuum UV conversion purposes. In the region of thicknesses near  $0.2 \text{ mg/cm}^2$ , halving the thickness causes a change in net yield of only 10%. Such a change, using the measured rates of evaporation, again takes months. The disadvantage of the DPS is that at these thicknesses, its quantum yield is lower than that of the PTP and is comparable with the quantum yield of sodium salicylate. In the thinner layers where the quantum yields of PTP and DPS are comparable, the influence of the rate of evaporation is too significant to be ignored.

The excited state lifetimes of PTP and DPS were measured for the possible use of these scintillators in measurement of vacuum UV emission decay time.

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Again PTP was found to be superior to DPS. Its lifetime was between 1 and 2 nsec, while the lifetime of DPS was slightly longer, 2 - 3 nsec. For sake of comparison, it is interesting to note that the lifetimes of sodium salicylate are reported to be between 8.5 and 10 nsec.<sup>12</sup>

## 4. Conclusions

We have demonstrated that PTP and DPS used as vacuum UV converters are superior in all aspects to sodium salicylate in an oil-pumped high-vacuum system, while in an oil-free, ultra-high vacuum system, sodium salicylate might be superior because of its lower vapor pressure.

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# **Figure Captions**

- Figure 1: Photon yield from p-terphenyl (normalized to sodium salicylate)  $\underline{vs}$  thickness in mg/cm<sup>2</sup>, for various wavelengths of incident light.
- Figure 2: Photon yield, for samples exposed to room atmosphere, compared to yield for a fresh sample, <u>vs</u> wavelength. Curve (a) is for a p-terphenyl sample (0.38 mg/cm<sup>2</sup>) aged for 4 days. Curve (b) is for a diphenylstilbene sample (0.04 mg/cm<sup>2</sup>) aged for 2 days.





