Vacuum ultraviolet scintillators: sodium salicylate and *p*-terphenyl

Vijay Kumar and A. K. Datta

Some of the characteristic properties of sodium salicylate and *p*-terphenyl have been studied at a convenient incident wavelength of 253.7 nm. These include the fluorescent spectrum, relative quantum efficiency as a function of scintillator thickness, absolute quantum efficiency, and its possible decline with time. It has been shown that the rotary pump and diffusion pump oil vapors in contact with phosphors affect the stability of fluorescence in a marked but complicated manner. The effect of humidity on relative fluorescent quantum efficiency of the phosphors has also been discussed. *p*-Terphenyl has been found to be a useful alternative to sodium salicylate.

I. Introduction

Of all the known vacuum uv scintillators, sodium salicylate has been widely used as a fluorescent wavelength converter for the detection of vacuum uv radiation from 30 nm to 350 nm. The possible reasons for its widespread use are the following: (1) Phosphor coatings can be prepared in a much simpler way. (2) The fluorescent spectrum matches well with the spectral response (*S*-11) of commonly manufactured photomultipliers. (3) Its relative quantum efficiency is nearly constant[1] over a wide range of incident radiation. (4) Absolute quantum efficiency at these vacuum uv wavelengths is very high. (5) It does not sublime at room temperature in vacuum and does not tend to deteriorate when exposed to air like some other phosphors (diphenyl stilbene and tetraphenyl butadine). (6) Incident vacuum uv radiation does not seem to damage the phosphor coatings.[2,3] (7) It is a cheap chemical commercially available in large quantity. Some other phosphors like liumogen and coronene are very expensive and are not readily available. Sodium salicylate has, though, certain disadvantages like its hygroscopic nature and the possible aging effect, which it shows in the fluorescent quantum efficiency. In spite of these disadvantages, sodium salicylate has been widely accepted as the phosphor without substitution. The result is that practically no measures have been undertaken to search for alternative fluorescent coatings with characteristics similar to those for sodium salicylate. Some work, though, has been reported on a few other phosphors.[1,4]

It is felt that *p*-terphenyl may be a useful alternative to sodium salicylate. Vasseur and Cantin[5] have measured the absolute fluorescent efficiency for *p*-terphenyl from 50 nm to 300 nm and found it to be relatively constant below 150 nm. Also its quantum efficiency was found to be maximum between 280 nm and 300 nm. Again, *p*-terphenyl appears to be quite stable under vacuum conditions and is not hygroscopic. We have investigated a few different characteristics of *p*-terphenyl as a vacuum scintillator. Sodium salicylate has also been thoroughly investigated for the purpose of comparison.

The present paper describes the preparation of coatings for both *p*-terphenyl and sodium salicylate, the fluorescent spectra, the relative quantum efficiency as a function of phosphor thickness, absolute quantum efficiency at 253.7 nm, and the primary effect of aging of the coatings. All characteristic properties of the two phosphors have conveniently been measured at 253.7 nm. It is felt that at wavelengths in vacuum uv spectral regions, the properties would be similar to what have been observed at 253.7 nm.

II. Preparation of the Coatings

The sodium salicylate coatings were prepared by a solvent spray technique developed by Knapp,[6] resulting in fine grained uniform layers on glass substrates. The *p*-terphenyl coatings were prepared by standard vacuum evaporation technique. The glass substrate was cooled by liquid nitrogen during evaporation with the result that the coatings were more adherent to the substrate and uniform.

The authors are with Physical Research Laboratory, Navrangpura, Ahmedabad 380009, India.

Received 6 September 1978.
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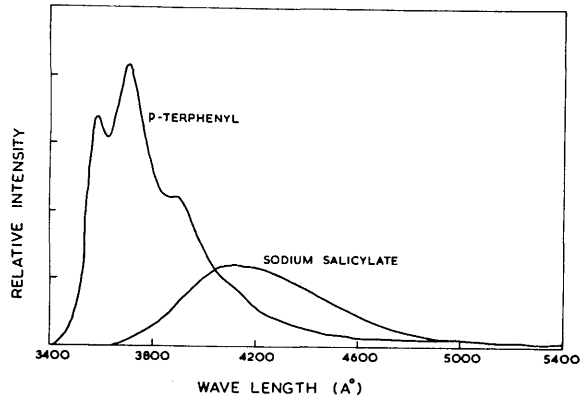

Fig. 1. Fluorescent emission spectra of sodium salicylate and *p*-terphenyl.

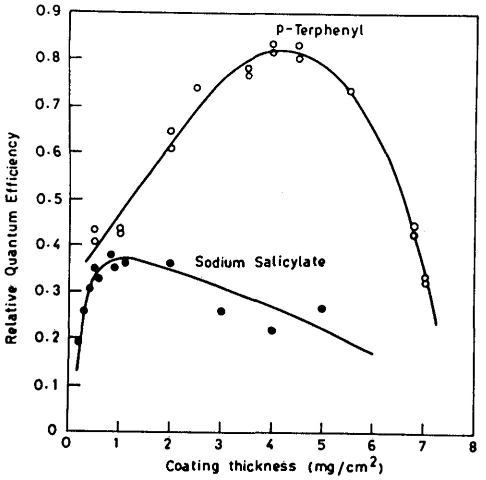

Fig. 2. Relative quantum efficiency of *p*-terphenyl and sodium salicylate as a function of coating thickness.

III. Fluorescent Emission Spectrum

The fluorescent emission spectra for the two phosphors at 253.7 nm were observed using a quartz-enveloped mercury lamp, an interference filter around 253.7 nm, a grating monochromator (Carl Zeiss SPM-2), and an EMI 6256 S photomultiplier. The fluorescent spectra are shown in Fig. 1. The spectrum for sodium salicylate was similar to that observed by Allison *et al.*,[7] peaking at around 416.0 nm, while the *p*-terphenyl spectrum extended from 341.0 nm to about 530.0 nm with three broad peaks at 359.0 nm, 371.5 nm, and 390.0 nm, respectively. The average emission band wavelengths for sodium salicylate and *p*-terphenyl were found to be about 443.0 nm and 382.0 nm, respectively. The measurements as shown in Fig. 1 clearly indicated that the fluorescent efficiency of *p*-terphenyl was relatively much higher than that of sodium salicylate.

IV. Relative Quantum Efficiency vs Phosphor Thickness

The dependence of the relative quantum efficiency on the layer thickness for sodium salicylate and *p*-terphenyl was measured and is shown in Fig. 2. For *p*-terphenyl, the relative quantum efficiency was measured for layer thickness ranging from 0.5 to 7.5 mg/cm², and a maximum was observed at 4.0–4.5-mg/cm² layer thickness of the phosphor. This contradicts what was observed by Vasseur and Cantin.[5] Their measurements ranging from 0.2 to 2 mg/cm² of layer thickness showed a maximum at around 1-mg/cm² thickness of *p*-terphenyl coating. The relative quantum efficiency vs layer thickness curve for sodium salicylate was found to be similar in character as that shown by Nygaard.[8] This lends credibility to our results in case of *p*-terphenyl.

V. Absolute Fluorescent Quantum Efficiency

Absolute fluorescent quantum efficiency for the two phosphors was measured at 253.7 nm. The monochromatic radiation emerging from the SPM-2 Carl Zeiss grating monochromator was allowed to strike the scintillator with an unbaffled area of 1-mm diam, and the fluorescent radiation was collected by the EMI 6256 S photomultiplier with an open area of 10-mm diam. The direct 253.7-nm light was collected by the photomultiplier through 1-mm diam baffle placed in the same position as in the previous case. The absolute fluorescent quantum efficiency in the present setup was measured as

$$\epsilon = \frac{I'}{I}\cdot\frac{Q_\lambda}{Q_{\lambda'}}\cdot\frac{1}{T}\cdot\frac{4\pi}{\Omega}\cdot\frac{1}{f(\cos\theta)}, \tag{1}$$

where I' and I are the photomultiplier currents as viewed with and without scintillator; Q_λ and $Q_{\lambda'}$ are the quantum efficiencies of the photomultiplier at 253.7 nm and the average emission band wavelength of the phosphor, respectively; T is the transmission of the glass substrate at λ'; Ω is the solid angle subtended by the point source of the phosphor at the photomultiplier; $f(\cos\theta)$ is the angular distribution function for the fluorescent radiation emerging at an angle with respect to the incident exciting radiation. A cosine distribution was reported by Allison *et al.*[7] for sodium salicylate layers with thickness between 2 and 4 mg/cm². No measurement for angular distribution function for *p*-terphenyl has been reported. It was assumed, for the purpose of our calculation, to follow cosine law. Again, the fact that the response of the photomultiplier varied with the angle of incidence of the radiation[9] was not taken into account in Eq. (1) because the phosphor size in the experiment was reduced to a point source of fluorescent radiation by using an aperture of 1-mm diam before the scintillator coating.

The absolute quantum efficiencies at 253.7 nm for the two phosphors are reported in Table I. The quantum efficiencies refer to thickness in the optimum region as determined by different investigators. Our value of 37% for sodium salicylate is less than what has been quoted by most of the other experiments[7,8,10,11] but is more than the absolute quantum efficiency measured by Inokuchi *et al.*[10] A close comparison into the relative quantum efficiencies for *p*-terphenyl and sodium salicylate in the present work shows that the efficiency for *p*-terphenyl is more than twice that for sodium salicylate. Following this argument, it would be interesting to note that the values of absolute quantum efficiency for sodium salicylate as given by Allison *et al.*[7] (99%), Kristianpoller[11] (64%), and Nygaard[8,9] (50%) were quite on the higher side. In case of measurements of Inokuchi *et al.*,[10] the layer thickness of sodium salicylate was not known. It was felt that our value of 37% and 82% for absolute quantum efficiencies of sodium salicylate and *p*-terphenyl, respectively, may be right within experimental errors.

VI. Aging of Phosphor Coatings

A slow decline in the uv fluorescence efficiency of phosphor coatings with time has been conveniently named as aging. The aging for sodium salicylate has been studied in some detail in the past. The possible reasons suggested for the gradual loss of quantum efficiency were contamination by ambient atmosphere of the experimental chamber (including vacuum pump oils), effect of uv radiation on phosphor, and absorption of experimental and/or residual gases and water vapor. No systematic study to date has been made to identify the qualitative contribution of the various different effects individually on aging of the phosphor coatings. Only a collective picture is available. The authors have studied in great detail the aging resulted by contamination of phosphor coatings due to atmosphere of rotary pump oil, diffusion pump oil, and water vapor, respectively.

Diffusion pump and rotary pump oils affected the stability of fluorescence of sodium salicylate and *p*-terphenyl in a complicated manner. The vacuum pumps would deposit a significant layer of oil on the phosphor coating over a period of time, resulting in the decline of absolute quantum efficiency. The decline with time would probably follow a systematic law if the oils would not fluoresce themselves at vacuum uv and middle uv wavelengths. The oils have been found to fluoresce when excited by incident radiation at 253.7 nm. The fluorescent spectra measured for two oils, rotary Vac Oil (Lynx 8A), and silicone oil (704 from Dow Corning) are shown in Fig. 3. A thin oil film between two lithium fluoride windows was used to observe the fluorescent spectra. The spectrum for rotary oil extended from 340.0 nm to 610.0 nm with a broad peak around 423.0 nm and a shoulder at 522.0 nm. The diffusion pump oil was found to fluoresce with spectrum ranging from 290.0 nm to 490.0 nm with a broad peak around 361.0 nm and three shoulders at around 308.0 nm, 333.0 nm, and 384.0 nm, respectively. The absolute quantum efficiency measured at 253.7 nm was found to be approximately the same for both oils and was equal to about 0.5% of the quantum efficiency for *p*-terphenyl for an unknown thickness of oil layer.

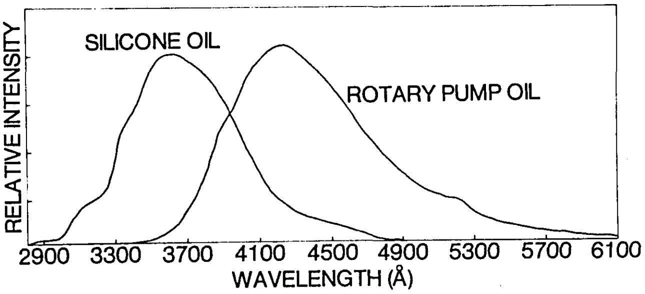

Fig. 3. Fluorescent emission spectra for rotary vac oil (Lynx 8A) and silicone oil (704 from Dow Corning).

Table I. Measurement of Absolute Quantum Efficiencies at 253.7 nm

Phosphor coatings	Author(s)	Layer thickness (mg/cm^2)	ε %
Sodium salicylate	Allison *et al.*[7]	2–4	99
	Inokuchi *et al.*[10]	Unknown	25
	Kristianpoller[11]	6	64
	Nygaard[8,9]	1–2	50
	Present work	2	37
p-Terphenyl	Vasseur and Cantin[5]	1.7	75
	Present work	4	82

Sodium salicylate and *p*-terphenyl coatings were subjected to environmental tests. Two coatings each were kept in the atmosphere of the rotary pump oil and diffusion pump oil vapor separately over a period of time, and the decline in relative quantum efficiency of the two phosphors was measured at 253.7 nm as a function of exposure time. Figure 4 shows the aging of the two coatings in the rotary oil vapor atmosphere. In the figure, the relative quantum efficiency for sodium salicylate and *p*-terphenyl has by no means been shown relative to each other. The decline in efficiency for the two coatings was found to be slow over a long period up to 5 days but showed a definite but slow increase in efficiency later, peaking on the 8th day for both sodium salicylate and *p*-terphenyl. This shoulder was found to be genuine and was definitely not due to some experimental error. The relative quantum efficiency with time seemed to decline much faster when the two

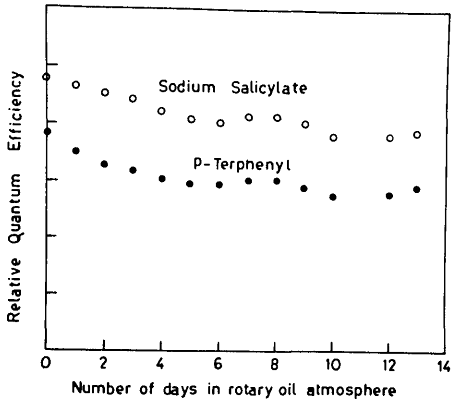

Fig. 4. Relative quantum efficiency of sodium salicylate and p-terphenyl as a function of exposure time in a rotary oil vapor atmosphere.

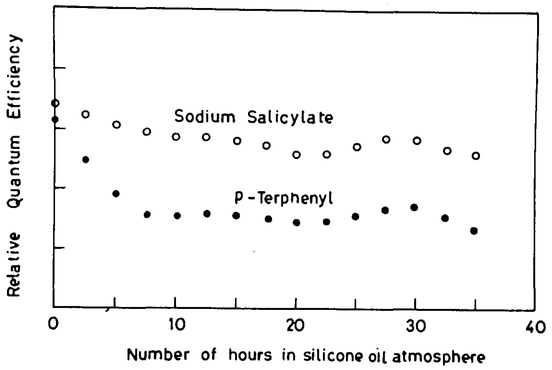

Fig. 5. Relative quantum efficiency of sodium salicylate and p-terphenyl as a function of exposure time in diffusion oil vapor atmosphere.

coatings were kept in a diffusion oil vapor environment (Fig. 5). For sodium salicylate, the efficiency decreased up to an exposure time of 20 h but increased later giving a shoulder around 27.5-h of exposure time. In case of p-terphenyl, the decline in efficiency was much faster than even for sodium salicylate for the first 7.5 h of exposure time. The relative quantum efficiency was constant between 7.5 h and 20 h within experimental error but showed a pronounced shoulder around 30 h of exposure time.

The shoulders as seen in Figs. 4 and 5 can be explained in terms of fluorescence of the vacuum pump oils. To start with, only a small number of oil vapors formed a layer on the phosphor coating. This layer decreased the quantum efficiency of the phosphor but was not significant enough to give an appreciable contribution from its own fluorescence. After a large exposure time, the oil layers on the phosphor coating were thick enough to give a large amount of fluorescence, thus producing a shoulder. To understand the formation of the shoulder in a better way, it is suggested that the relative fluorescent quantum efficiency of the oil layer should be studied as a function of layer thickness. This, though, has not been done by the authors of the present paper. These shoulders may explain the discrepancies observed by some experimenters in the measurement of quantum yields of sodium salicylate at different wavelengths. Samson[12] reported about 14% higher yield at 1610 Å as compared with yield at 1216 Å.

It was qualitatively observed that the relative quantum efficiency of the two phosphors, in the presence of noncorrosive experimental gases like N_2 and O_2, still decreased even after having a clean vacuum free from oil vapors. The only factor for the observed decline could possibly be attributed to the impurity water vapor in the experimental gases. This effect could be observed in an indirect way by observing the effect of humidity on quantum efficiency of the two scintillator coatings.

The two phosphor coatings were kept in a dust free humid atmosphere for 24 h with an average relative humidity of 55%. The relative quantum efficiencies of sodium salicylate and p-terphenyl declined by about 16% and 10%, respectively, during this period.

VII. Conclusion

The measurements reported in this paper demonstrate that p-terphenyl with much higher absolute quantum efficiency may be a useful and better alternative to sodium salicylate. The observations show that the aging of the two phosphors due to vacuum pump oil vapors can be avoided by using a clean vacuum system fitted with liquid nitrogen cooled traps, but the effect due to water vapor of the atmosphere may be difficult to avoid.

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