Ideality of Pressure-Sensitive Paint. I. Platinum Tetra(pentafluorophenyl)porphine in Fluoroacrylic Polymer

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ABSTRACT: The pressure sensitive paint (PSP) properties of a fluoroacrylic polymer, FIB, with the luminophor platinum tetra(pentafluorophenyl)porphine (PtTFPP) are presented. This paint forms a hard coating that displays Stern–Volmer plots with a high dynamic range ($\sim$ 0.9) [defined as $(I_{vac} - I_{atm})/I_{vac}$], good photostability, a response time of less than 1 s and a relatively low temperature dependence ($\sim$ 0.6% per degree). The temperature dependence is low because FIB has a unusually low activation energy for the diffusion of oxygen. Pressure and temperature affect intensity independently making this PSP "ideal." The basecoat affects the functionality of the PSP it underlies, and the optimal basecoat used to date also includes the FIB polymer. The synthesis of the FIB polymer is a copolymerization that occurs in one step with a peroxide initiator. Annealing the painted model above $T_g = 70°C$ procures adhesion and ideality. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2795–2804, 2000

Key words: pressure-sensitive paint; fluoroacrylic polymer FIB; Stern–Volmer plots; luminescence; oxygen quenching; platinum porphyrin

INTRODUCTION

As the B-17 Flying Fortress Bomber did to World War II, pressure sensitive paint (PSP) has utterly transformed the field of quantitative pressure measurements on aerodynamic surfaces. Relative to conventional pressure taps, PSP costs less, collects more data at faster rates, and provides significantly improved spatial resolution via a virtually continuous map of the pressure field that the surface of a geometrically complex aircraft experiences in flight.

The word "paint" has two meanings: (a) the mixture of nonvolatiles (e.g., pigment and chro-

mophore) and volatiles that are applied to a surface and (b) the coating left behind on the surface after evaporation of the volatiles. "Pressure sensitive paint" and the abbreviation "PSP" have been used in both contexts. In this paper, the word *formulation* refers specifically to (a) and the word *coating* refers specifically to (b).

The technique of using PSP and digital video imaging to measure pressure fields in wind tunnels began at the University of Washington in 1987. Several detailed presentations of PSP theory precede this paper.[1–4] PSP coatings consist of a luminophor dispersed in an oxygen-permeable binder. Absorption of short wavelength light takes the luminophor to a metastable excited state. The luminophor can return to the ground state by emitting radiation with rate k_r or by nonradiative conversion to heat by rate k_{nr}. Molecular oxygen introduces a new path for nonradiative decay, thereby reducing the number of

emitted photons. In the presence of abundant oxygen, quenching by oxygen dominates.

The quenching of luminescence by molecular oxygen is described in the Stern–Volmer relation.[5] The Stern–Volmer relation assumes that the oxygen concentration in the PSP coating (in our case a polymer) is in equilibrium with the oxygen pressure above the coating as described by Henry's Law[6]:

$$C = \sigma P \qquad (1)$$

where C is the molar concentration of oxygen in the paint coating when the partial pressure of oxygen over the paint is P, and σ is Henry's constant, which has units mol/L · atm. Since the goal is measuring air pressure under conditions where the partial pressure of oxygen is constant, we shall henceforth think of P as total air pressure with the value of σ appropriately modified.

Laboratory experiments vary the pressure and measure the luminescence intensity of the paint at a constant temperature. This data is presented as Stern–Volmer[5] plots at different temperatures:

$$f_T(P, P_0) = \frac{I(P_0, T)}{I(P, T)} \qquad (2)$$

where $I(P, T)$ is the luminescence intensity of the PSP at a particular pressure P and temperature T, and P_0 is some reference pressure (generally 1 atm). For temperature-dependence plots, laboratory experiments vary the temperature and measure the luminescence intensity of the paint coating at constant pressure. The intensity ratio for temperature dependence plots is

$$g_P(T, T_0) = \frac{I(P, T)}{I(P, T_0)} \qquad (3)$$

where T_0 is some reference temperature (generally room temperature). We define an "ideal" PSP as one for which the functions $f_T(P, P_0)$ are approximately independent of temperature and the functions $g_P(T, T_0)$ are approximately independent of pressure. The wind tunnel measurement is the ratio of luminescence intensity measured at ambient pressure and temperature divided by intensity measured with airflow, when both temperature and pressure are usually different. For an ideal paint this can be expressed as

$$\frac{I(P_0, T_0)}{I(P, T)}$$

$$= \frac{I(P_0, T_0)}{I(P_0, T)} \cdot \frac{I(P_0, T)}{I(P, T)} \equiv \frac{1}{g_{P_0}(T, T_0)} \cdot f_T(P, P_0)$$

$$\approx \frac{f(P, P_0)}{g(T, T_0)} \qquad (4)$$

An ideal PSP can more easily achieve temperature correction despite the temperature dependence that is inherent to the phenomenon of luminescence.[7] This is because if temperature is known, the wind tunnel ratio $I(P_0, T_0)/I(P, T)$ can be multiplied by a single function $g(T, T_0)$ to obtain the single function $f(P, P_0)$ from which the pressure on the airfoil can be determined. For the FIB PSP described in this paper, plots of $g_P(T, T_0)$ over the temperature range 10°C to 50°C made at vacuum and ambient pressure are approximately the same, showing only a small deviation from ideality. We also find the functions $f_T(P, P_0)$ are independent of temperature over this same temperature range. Because the Stern–Volmer constant (K_{SV}, defined below) exhibits a temperature dependence, PSPs can only be ideal over a limited temperature range.[7]

The original Kavandi PSP was based on a commercial mix, Genesee-197.[2] It had several problems including a slow response time, a high temperature dependence, and serious photodeterioration. In addition, the Genesee-197 PSP coating turned brittle and chipped away in the wind tunnel. We synthesized the fluoroacrylic polymer FIB described below in hopes of correcting these problems. Fluorinated polymer was studied because it is well known that oxygen is very soluble in fluorinated hydrocarbons.

Platinum tetra(pentafluorophenyl)porphine (PtTFPP) replaced the original luminophor, platinum octaethylporphine (PtOEP), because it showed much less photodeterioration. Presumably this is because the electronegativity of fluorine makes photooxidation much less favorable.

We sought a solvent with a high boiling point to avoid rapid evaporation during the process of spraying and to produce a smoother surface. Oxsol 100 (parachlorobenzotrifluoride) was chosen for three reasons: it is environmentally benign,[8] it exhibits a high boiling point, and relative to other solvents, it dissolves the polymer best.

We make our basecoat with FIB polymer as well. In addition to providing uniformity for the PSP coating by hiding blemishes on the surface of the model, an underlying white basecoat affects the functionality of the PSP coating, most particularly the response time.[9–11] Commercial white basecoats often induce a slower response time, increased photodeterioration, and increased temperature dependence.[9] It seemed natural enough to try FIB itself for the basecoat, and it was found to work well (see below).

THEORETICAL BACKGROUND

The quantum yield of the PSP is defined as the number of photons emitted divided by the number of photons absorbed. Under steady-state conditions, the quantum yield is given by the rate of radiative decay (k_r) divided by the total rate of decay of the excited luminophor molecules (k_{tot}):

$$\phi = \frac{k_r}{k_{tot}} \quad (5)$$

The total rate of decay (k_{tot}) is the sum of the rates of the three possible paths of decay: radiative decay (k_r), nonradiative decay (k_{nr}), and oxygen quenching ($\kappa_q \sigma P$):

$$\phi = \frac{k_r}{k_r + k_{nr} + \kappa_q \sigma P} \quad (6)$$

where the assumption of the linearity of quenching is based on the Stern–Volmer relation.[5] Here P refers to the air pressure over the polymer that is measured, and σ refers to Henry's constant (eq. 1). In eq. 6, we use k for monomolecular decay rates (units s^{-1}) and κ for a bimolecular rate (units $M^{-1} s^{-1}$), where M is molarity.

Under fixed conditions of illumination and detection, the observed phosphorescence intensity, I, is directly proportional to the quantum yield. In the wind tunnel, the standard method for measuring pressure is the image intensity ratio I_{atm}/I, obtained from ratioing wind-off and wind-on CCD camera images. This intensity ratio corresponds to the quantum yield ϕ_{atm} divided by the quantum yield ϕ at any other pressure P, where atm indicates at 1 atm:

$$\frac{\phi_{atm}}{\phi} = \frac{I_{atm}}{I} \quad (7)$$

By the definition of quantum yield ϕ and some basic algebra,

$$\frac{I_{atm}}{I} = \frac{k_r + k_{nr} + \kappa_q \sigma P}{k_r + k_{nr} + \kappa_q C_{atm}} = A + B(P/P_{atm}) \quad (8a)$$

where $C_{atm} = \sigma P_{atm}$, i.e., C_{atm} is the concentration of oxygen in the polymer at 1 atm.

$$A = \frac{k_r + k_{nr}}{k_r + k_{nr} + \kappa_q C_{atm}}; \quad B = \frac{\kappa_q \sigma P_{atm}}{k_r + k_{nr} + \kappa_q C_{atm}} \quad (8b)$$

At vacuum, where there is no rate of oxygen quenching, the luminescence intensity ratio becomes

$$\frac{I_{vac}}{I} = \frac{k_r + k_{nr}}{k_r + k_{nr}} + \frac{\kappa_q \sigma P}{k_r + k_{nr}} = 1 + K_{SV}P \quad (9a)$$

where K_{SV} is the Stern–Volmer quenching coefficient, with units of atm^{-1}. It follows that

$$K_{SV} = B/(AP_{atm}) \quad (9b)$$

The Stern–Volmer quenching coefficient, K_{SV}, times 1 atm is the ratio of the rate of oxygen quenching at atmospheric pressure to the rate of decay in vacuum:

$$K_{SV}P_{atm} = \frac{\kappa_q C_{atm}}{k_r + k_{nr}} \quad (10)$$

A PSP is ideal when the Stern–Volmer constant K_{SV} exhibits the least degree of temperature dependence possible. In other words, a PSP is ideal when the Stern–Volmer plots taken at different temperatures lie on top of each other. The radiative decay k_r is almost temperature independent because of the weak temperature dependence of the refractive index of the medium.[12] The temperature dependence in the Stern–Volmer constant stems from the temperature dependencies of the rate constant of oxygen quenching κ_q and the rate constant of nonradiative decay k_{nr}.[13] The Arrhenius equation defines the nature of the temperature dependencies of these rate constants:

$$\kappa_{\mathrm{q}} = A_{\mathrm{q}}e^{-\Delta E_{\mathrm{q}}/RT} \qquad (11a)$$

$$k_{\mathrm{nr}} = A_{\mathrm{nr}}e^{-\Delta E_{\mathrm{nr}}/RT} \qquad (11b)$$

where A and ΔE are, respectively, the frequency factors and the activation energies of oxygen quenching and nonradiative decay. When ΔE_{q} is low, the rate of oxygen quenching changes little with temperature. Because κ_{q} depends on the oxygen diffusion coefficient of the polymer in the PSP coating, ΔE_{q} must depend on the nature of the polymer.

EXPERIMENTAL

Synthesis of FIB

FIB (Fluoro/Isopropyl/Butyl) is a fluorinated copolymer synthesized in one step from hexafluoroisopropyl methacrylate and heptafluoro-n-butyl methacrylate purchased from Lancaster Synthesis Inc. at 98% and 99% purity, respectively. The monomers come inhibited with methoxyhydroquinone, which is removed by swirling the monomers in activated charcoal powder at room temperature. A glass-fritted filter connector to an aspirator separates the charcoal from the deinhibited monomers. Trifluorotoluene was added in twice the volume of the monomers and lauroyl peroxide, the initiator, was added in approximately 0.2% the weight of the monomers, w/w (weight of peroxide/weight of monomers). Both the solvent and the initiator were purchased from Aldrich and used as received. The polymerization took place in a four-neck flask equipped with a mechanical stirrer, a sparger, a reflux condenser, and a temperature controller. The flask was purged with argon for 1 h at a flow rate of 61 ± 8 mL/min before the temperature controller was turned on. The polymerization was carried out at 74°C for 48 h and then at 100°C for 1 h. During this time, a mixture of ethylene glycol and distilled water circulated through the reflux condenser at -20°C via a refrigerated, circulating bath to reduce loss of material to evaporation. At the end of this time, the polymerization was finished, producing "polymer liquor."

The polymer was purified and isolated by precipitation. The polymer liquor was first diluted with twice its volume of trifluorotoluene. This diluted solution was added 400 mL at a time drop-wise (over the course of 4–6 h) to 1200 mL of swirling hexanes (a mixture of n-hexane, methylcyclopentane, and methylpentane called "hexanes," from Fisher Chemicals). A glass-fritted filter connected to an aspirator separated the precipitated polymer from the hexanes. The collected polymer was rinsed with methanol and hexanes and allowed to dry on the filter for $\frac{1}{2}$ hour. When the precipitated polymer resembled a white powder, it was dried under a vacuum overnight to remove all residual solvent. Every step of the precipitation was done at room temperature.

Characterization of FIB

The density of FIB (reported below) was ascertained by means of a "flotation" method, meaning that the relative speeds with which a sample of FIB sank and/or rose to the top of four, separate CsCl solutions of various densities were measured.[14]

^{1}H-NMR spectra of FIB were taken in deuterated acetone on a Bruker AMX-200 spectrometer operating at 200.1 MHz for ^{1}H. The residual protonated acetone signal (2.04 ppm) served as the internal reference. The spectra were recorded using a spectral window of 3200 Hz.

The transition temperatures, such as the glass transition temperature (T_g), the melting temperature (T_m) and the degradation temperature (T_d) of the copolymer FIB were determined on a differential scanning calorimeter (DSC) 2910 apparatus (TA Instruments) with a heating rate of 20°C/min, from -100°C to 400°C.

Size exclusion chromatography [(SEC) also known as gel permeation chromatography (GPC)] determined the relative molecular weight distribution of FIB. We coupled together a 5×10^4 Å column to a 5×10^5 Å Phenomenex column packed with Phenogel porous beads and calibrated it using polystyrene standards. Tetrahydrofuran (THF) served as the mobile phase. The L-4250 Hitachi UV-Vis HPLC detector is hooked up to a L-6200 Hitachi Intelligent Pump and a PC on which we integrate the data using EZChrome software. The chromatography was monitored for polymer at 220 nm, near the polymer absorption peak.

Preparation of PSP and Basecoat

To prepare 1 L of PSP formulation with the ratios of 5 mg of luminophor to 1 g of polymer to 25 mL of solvent, we dissolved 200 mg of the PtTFPP

sensor (obtained from Porphyrin Products) and 40 g FIB into 1000 mL of unpurified parachlorobenzotrifluoride (Oxsol 100; Occidental Chemical Corporation) in a tinted bottle. Based on the density of polymer as 1.55 g/cm^3, the molarity of PtTFPP in the final FIB coating was 6.4×10^{-3} mol/L.

To prepare the basecoat, we dissolved 71 g FIB in 1000 mL Oxsol 100. Then 63 g of titanium dioxide (Tronox CR-800; Kerr-McGee Chemical Co.) was added, and the mixture was blended for 30 min in an Osterizer Imperial blender.

Application

Before painting, a 1 in × 1-in aluminum square was scrubbed with a Scotch-Brite 7447+ abrasive hand pad and then rinsed with acetone. It then was wiped dry, taking care to avoid finger prints. Spraying was done with a Baasch model H air brush, using dry nitrogen as propellant at about 16 psi. [Use of piped building air is risky, as it often is contaminated.] Keeping the brush nozzle 15 cm from the aluminum surface, the painter applied the basecoat first, until sufficient hiding power is achieved, and it is allowed to dry in the oven at 100°C for 30 min before applying the topcoat. The PSP topcoat is applied in a similar fashion. The freshly painted sample then spends 30 more minutes annealing in the oven at 100°C.

Apparatus

The Stern–Volmer data plots, temperature sensitivity data plots, and photodegradation data plots were obtained using the "PMT survey apparatus," a locally designed computer-controlled system, described more fully elsewhere,[15] that can control and monitor temperature and pressure in the sample chamber while measuring emission from a paint coupon with a photomultiplier tube. Pressure can be varied over a pressure range of 0 (under 1 Torr) to 1 atm and a temperature range of 0°C to 50°C. Temperature and pressure scans may be taken separately, allowing the option of obtaining either a Stern–Volmer plot at constant temperature, $f_T(P, P_0)$ or a temperature sensitivity plot at constant pressure, $g_P(T, T_0)$. Photostability studies are conducted at constant pressure and temperature. A tungsten–halogen lamp, fitted with a 405 nm (bandwidth 30 nm) interference filter, excites the PSP coating of a sample in the PMT survey apparatus and an RCA C31043

photomultiplier, also fitted with the appropriate interference filter, detects the phosphorescence of the sample. For PtTFPP, the excitation filter had a band pass centered at 400 nm (58+% transmittance, 40 nm width at half height) and the emission filter had with a band pass centered at 650 nm (55+% transmittance, 10 nm width at half height).

The response time is the time necessary for the system to reach equilibrium and to have a constant intensity of emitted light after a fast pressure jump (∼ 1 ms). Response time was determined on a fast pressure jump apparatus described elsewhere.[16] This apparatus consists of a small sample chamber (capable of holding a 1 cm × 1-cm sample), three solenoid powered valves to control pressure, a tungsten lamp, and the same set of filters used in the PMT survey apparatus. With convolution fitting, the fast pressure jump apparatus can measure response times as short as ∼ 10 μs.

Coating thickness was measured with a Positector 6000 micrometer eddy current thickness gauge (Mausner Equipment). Coating smoothness was measured with a Surtronic 10 profilometer (Mausner Equipment).

Characterizations of PSP

To characterize our PSP, we applied a coating to a 2.5 cm × 2.5-cm aluminum square coupon and tested it in the PMT survey apparatus. Typical protocol meant three Stern–Volmer runs, $f_T(P, P_0)$, at 10°C, 30°C, and 50°C, two temperature runs, $g_P(T, T_0)$, at vacuum and ambient pressure, two photodegradation runs at vacuum and ambient pressure, and one response time measurement at ambient temperature.

For the Stern–Volmer runs, the PMT survey apparatus scanned the pressure at fixed temperature from 1 atm to vacuum, and 21 emission intensities $I(P, T)$ were recorded. Temperature scans, $g_P(T, T_0)$, were run between 10°C and 50°C for both vacuum and ambient pressure. For the photodegradation plots, a tungsten lamp (with interference filter as above) connected to a stabilized dc power supply irradiated the sample continuously for 60 min at room temperature and constant pressure (either ambient or vacuum). A power density of 925 $\mu W/cm^2$ was maintained for each photodegradation study in this paper. The power density was recorded using a power density meter from Newport. At ambient pressure, a
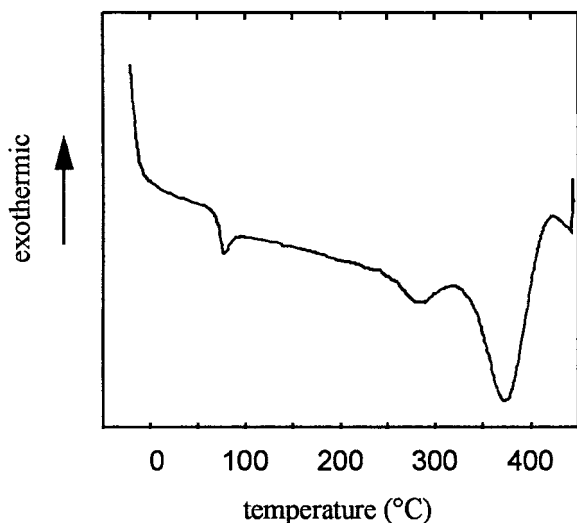
Figure 1 Thermogram of the FIB polymer. The y axis represents the heat flow, and a downward deflection means heat given to the system. $T_g = 70°C$. See Ref. 7.

12-V, 0.5-W fan by Sunon was used on the sample to prevent heating. For the response time data, 2000 data points were taken at 2000 ms each, for a total run time of 4 s on the fast pressure jump apparatus.

RESULTS AND DISCUSSION

FIB Polymer

For FIB polymer synthesis, the two monomers were in a 1 : 1 molar ratio. Typical yields were ~ 50% purified polymer. The integration ratios of the polymer's NMR spectrum[17] indicated that the monomer proportions in the polymer were more on the order of 60 : 40, heptafluoro-n-butyl methacrylate to hexafluoroisopropyl methacrylate. From the mode of synthesis, we presume that this is a random copolymer.

The thermogram of the FIB polymer showed that the glass transition temperature was 70°C (Fig. 1). Annealing the freshly painted PSP coating improves its ideality and possibly its adherence to the aluminum surface.[7]

The weight average molecular weight of precipitated FIB from the synthesis described here is $\langle M \rangle_W \sim 109,300$ Da. The number average molecular weight of precipitated FIB is $\langle M \rangle_N \sim 74,800$ Da. Accordingly, the copolymer's average polydispersity, the ratio of these numbers is 1.46. FIB

showed a density of 1.55 ± 0.04 g/cm^3, as determined by flotation.

The NMR and IR spectra of the polymer are reported elsewhere.[17] We found that the polymer has essentially no UV absorption at wavelengths longer than 245 nm.[17] A UV peak in tetrahydrofuran (THF) was observed at 218 nm. This peak would give a 10-μm film an absorbance of 1.2. The THF prevented observation of absorbance at wavelengths shorter than 215 nm.

PSP

Figure 2 shows the maximum absorbance of the sensor molecule PtTFPP [TFPP = tetra(pentafluorophenyl)porphine] to be 388 nm. For this spectrum, 13.5 mg of PtTFPP (lot no. 071497) was diluted first with trifluorotoluene, a second time with a mixture solvent called EPAF (diethylether, isopentane, dimethylformamide, and ethanol, 12 : 10 : 6 : 1 volumetric ratio), degassed, frozen, and sealed before thawing.[14]

To quantitatively measure the degree of ideality, we used $g_P(T, T_0)$, as defined in eq. (3) and then defined percent nonideality over a given temperature range as

$$\%\text{NID}^{50°C–10°C} = 100\%[(N_j - 1)^{-1} \sum_j (g_{\text{atm}}(T_j, T_0)$$
$$- g_{\text{vac}}(T_j, T_0))^2]^{1/2} \quad (12)$$

where N_j is the number of temperatures studied. $(N_j - 1)$ appears in the summation which includes the point $T_j = T_0$, which makes no contribution. Percent nonideality is zero if the paint is ideal.

Recently we measured the activation energies for the rates κ_q and k_{nr}, defined in eqs. (11).[11] The polymer FIB exhibits a significantly low ΔE_q, which makes FIB PSP the most ideal, single polymer formulation at room temperature to date.

In addition to a temperature dependence of approximately 0.52% per degree (Fig. 3) and good photostability (Fig. 4), the FIB polymer produces a smooth, robust PSP coating, whereas the Genesee-197 polymer paint turned brittle and chipped away. Because of its high boiling point and its high solubility for the FIB polymer, the solvent Oxsol 100 (parachlorobenzotrifluoride) also produces a smooth coating.

PtTFPP in FIB polymer has a response time of less than 1 s (Fig. 5 and Table I). It takes 0.6 s for
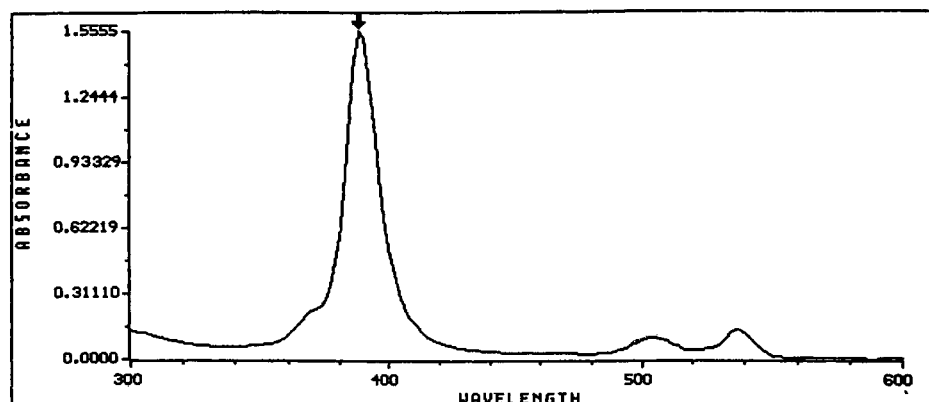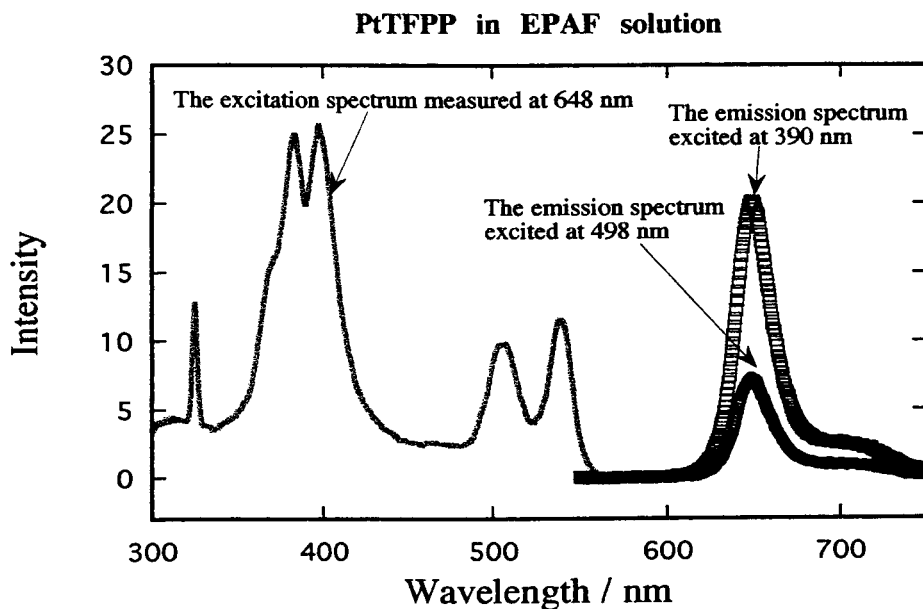
Figure 2 Top: Excitation and emission spectrum of PtTFPP in EPAF degassed solution (6.13 × 10^{-6} mol L^{-1}) taken on a Perkin–Elmer Luminescence Spectrometer LS 50. [The excitation spectrum shows two artifacts: a front face dip at 390 nm and a second-order peak at 325 nm.] Bottom: The absorption spectrum taken on a Hewlett Packard 8452A Diode Array Spectrophotometer. See Ref. 14.

the intensity of the coating to drop 95% in response to a sudden jump in pressure. A response time of 1 s is sufficient for wind tunnel tests, so 0.6 s is quite satisfactory.

Samples with a thickness of about 12–15 μm and an average smoothness of 1 μm are generally used for Stern–Volmer and response time studies. One liter of PSP [proportions 5 mg of PtTFPP : 1 g polymer : 25 mL solvent] covers an area of 2.6 m^2. This coating is nearly unobtrusive, meaning that the coating itself minimally affects the aerodynamic properties of the model to which it is applied and tested in the wind tunnel.[18]

In practice, the Stern–Volmer relationship is plotted as I_{atm}/I versus P/P_{atm} (Fig. 6). In general we do not fit with parameters A and B as in eq. (8a) but rather use
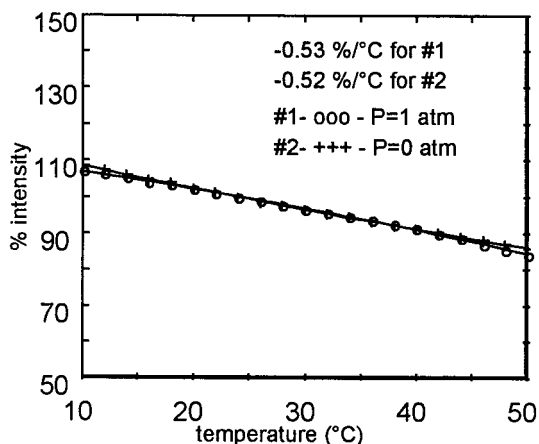
Figure 3 Overlaid plots of the temperature dependence of the paint luminescence in a vacuum and at atmospheric pressure for PtTFPP in FIB polymer. The % $NID^{50°C-10°C} = 0.35$.

$$f_T(P, P_0) \equiv \frac{I(P_0, T)}{I(P, T)} = f_T^{(0)} + f_T^{(1)} \left(\frac{P}{P_0}\right) + f_T^{(2)} \left(\frac{P}{P_0}\right)^2 \quad (12a)$$

where

$$f_T^{(0)} + f_T^{(1)} + f_T^{(2)} = 1 \quad (12b)$$

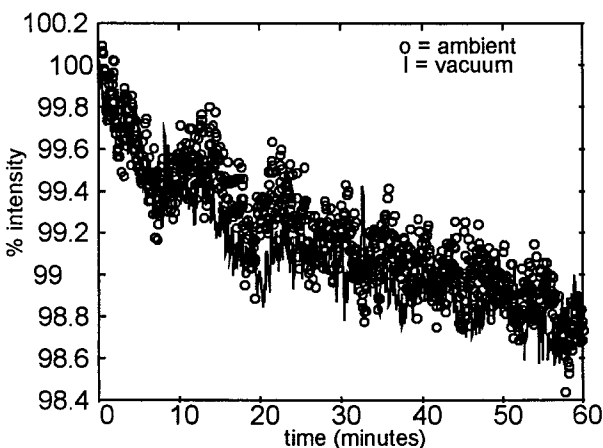In Figure 6 the value of coefficient is $f_T^{(1)} \approx 1.1$ independent of temperature.

Figure 4 Overlaid photodegradation plots at vacuum and ambient pressure. PtTFPP in FIB polymer was irradiated continuously for 60 min, and power density of 925 $\mu W/cm^2$ was maintained at room temperature and constant pressure each time. Photodegradation = 1.5%.
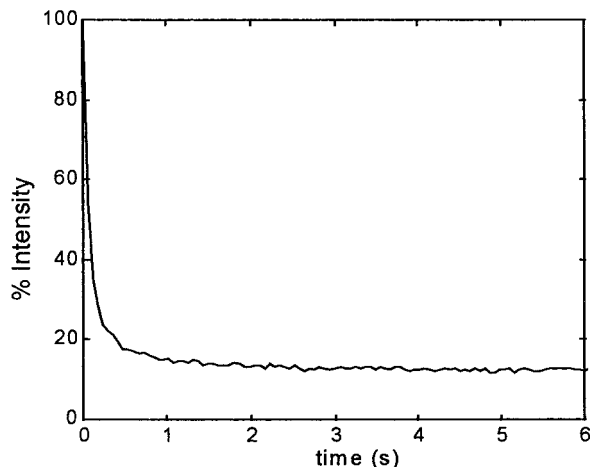

Figure 5 Luminescence intensity of PtTFPP in FIB polymer on aluminum as a function of time after a pressure drop. See Ref. 8.

Basecoat

We estimate that 1 L of the FIB basecoat prepared as described above covers a surface area of 6.5 m^2 at a thickness of 10 μm. Generally, the basecoat provides sufficient hiding power at a thickness of 10–12 μm. Prior to trying FIB in the basecoat, we considered the phenomenon of pigments such as titanium dioxide, which tend to retard the diffusion of small molecules such as molecular oxygen, and hoped that the polymer and titanium dioxide pigment together would not change the oxygen diffusion properties of the basecoat. Serendipitously enough, the FIB/TiO_2 basecoat reported here does not alter the response time of the luminescence of the FIB with the PtTFPP topcoat. Indeed, the FIB basecoat appears to affect the functionality of the PSP the least, exhibiting minimal temperature depen-

Table I   Response Times: The Time Required for the Luminescence Intensity to Drop 10%, 90% and 99% of Its Total Change

ΔI	10%	90%	99%
Time FIB on aluminum (s)	0.06	0.35	1.90
Time FIB on FIB basecoat (s)	0.08	0.50	2.60

Values given are for pressure increases from near vacuum to 1 atm for PtTFPP in FIB polymer on aluminum and on FIB basecoat.
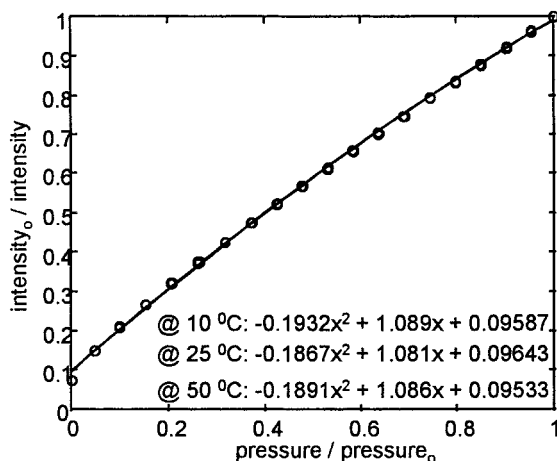
Figure 6 Overlaid Stern–Volmer plots at 10°C, 25°C, and 50°C of PtTFPP with FIB ($M_W \sim 47{,}500$ Da) on aluminum. Here $f_T^{(1)} = 1.09$.

dence, as evidenced by comparison of temperature dependence plots of PSP without basecoat, with FIB basecoat, and with a basecoat made from a poly(methyl methacrylate) (PMMA) polymer (Figs. 3, 7, and 8).[17] Percent nonidealities of the three plots are given in Table II. The preparation of the PMMA basecoat was similar to that of the FIB basecoat, and the PMMA formulation consisted of 2.8 g of titanium dioxide and 2.5 g of PMMA dissolved in 35 mL of THF. This compatibility allows the basecoat to stay as inert as possible and still provides sufficient hiding power.
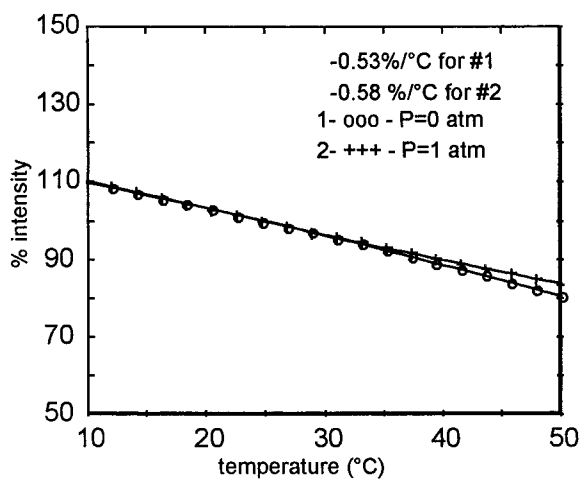

Figure 7 Temperature dependence of the intensity of PtTFPP in FIB polymer on a FIB polymer basecoat. The % $\mathrm{NID}^{50°C-10°C} = 0.45$.
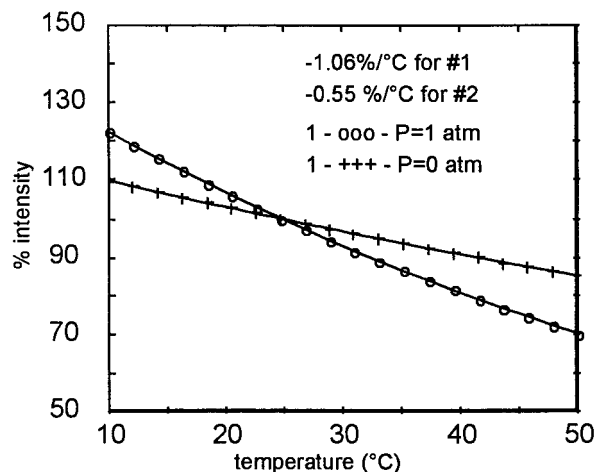

Figure 8 Temperature dependence of the intensity of PtTFPP in FIB polymer on a PMMA polymer basecoat. The % $\mathrm{NID}^{50°C-10°C} = 8.91$.

CONCLUSION

PtTFPP in FIB is the most ideal PSP formulation based on a single polymer binder without additives.[7,10,11] Here ideal means that temperature dependence and pressure dependence are nearly independent. It forms a hard, smooth coating, displays Stern–Volmer plots with a high dynamic range (~ 0.9), a response time of less than 1 s, and a temperature dependence of under 0.6%/°C. In part because of the significant electronegativity of the PtTFPP luminophor, the PSP exhibits good photostability. Because of the notably low activation energy involved in FIB's oxygen diffusion coefficient, the PSP exhibits a relatively low temperature dependence. This low temperature dependence and nearly "ideal" PSP, i.e., independence of pressure and temperature dependence, should ease the problem of temperature dependence and the need to compliment PSP aerodynamic studies with large numbers of pressure taps.

Table II Percent Nonidealities from 10°C to 50°C, as Calculated Using Eq. (14)

	% NID
PSP on aluminum	0.35
PSP on FIB basecoat	0.45
PSP on PMMA basecoat	8.91

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