Ideality of Pressure-Sensitive Paint. II. Effect of Annealing on the Temperature Dependence of the Luminescence

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ABSTRACT: This article reports the effect of annealing on a pressure-sensitive paint (PSP) consisting of platinum tetra(pentafluorophenyl)porphine (PtTFPP) in a fluoro-acrylic polymer called FIB (Puklin, E.; Carlson, W. B.; Gouin, S.; Costin, C.; Green, E.; Ponomarev, S.; Tanji, H.; Gouterman, M. J Appl Polym Sci 2000, 77, 2795). Samples annealed at 150°C, 75°C, annealed by a heat gun, and dried at room temperature are compared to nonannealed samples. Temperature dependences of luminescence intensity and lifetime are studied as a function and pressure and temperature and fit with Arrhenius and Stern–Volmer equations. We find that heating above T_g is more important than drying at room temperature in lowering the temperature dependence and obtaining ideal PSP, ideal meaning independent effect of pressure and temperature on luminescence properties of the paint. Ideality is achieved by lowering the activation energy for oxygen diffusion, presumably by relaxation of the polymer network. It is shown that ideal behavior occurs only over a limited temperature region. This range is more useful for PtTFPP in FIB than for ruthenium bathophenanthroline in polydimethylsiloxane (PDMS), another common PSP formulation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2805–2814, 2000

Key words: pressure-sensitive paint; luminescence

INTRODUCTION

Pressure-sensitive paint (PSP) based on the quenching of luminescent molecules in polymers has become over the last few years a viable technique for the measurement of surface pressure in the aerodynamic studies of aircraft[1–4] and other devices such as rotating machinery.[5] Static pressure over the surface of an aerodynamic model is customarily measured by the use of pressure taps connected to pressure transducers, which are monitored by an external computer. Installation of hundreds of these pressure taps is not only time-consuming and very expensive, but it also allows only a finite number of pressure values. The pressure-sensitive paints are much more af-fordable and, with charge coupled device (CCD) camera sensors, produce a virtually continuous pressure map. However, major problems limit the use of these paints in aerodynamical studies: correction for the model movements during analysis,[6,7] slow response time of many paints,[8,9] temperature dependence of the luminescence,[10,11] and self-illumination.[12,13] In this article, we explore one feature of practical value for the use of PSP: the role of annealing the paint in achieving ideal PSP properties. The nature and value of ideal PSP is described in the next section. Paper III of this series discusses the effect on ideality of using polymers with different permeabilities and Paper IV shows how nonideal paints can be idealized by adding pigment.

IDEAL PSP

Before defining ideal PSP and showing its value, it is important to give a brief outline of the fun-

damental physicochemical processes involved in the study of PSP. The sensor luminophor (S) incorporated in the paint is photoexcited to a metastable state (S^*), which lives long enough for oxygen quenching. The excited luminophor (S^*) can return to the ground state radiatively by emitting a photon:

$$S^* \xrightarrow{k_r} S + h\nu_{em} \tag{1}$$

or nonradiatively by emitting heat:

$$S^* \xrightarrow{k_{nr}} S + \text{heat} \tag{2}$$

The luminophor can also return to the ground state by transferring energy to molecular oxygen:

$$S^* + {}^3O_2 \xrightarrow{\kappa_q} S + {}^1O_2 \tag{3}$$
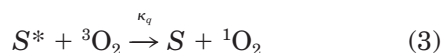
where ${}^3O_2$ is the ground state of molecular oxygen (in a triplet state) and ${}^1O_2$ is the first singlet excited state of molecular oxygen. The lifetime decay rate of the excited luminophor is described by eq. (4)

$$\frac{1}{\tau} = k_r + k_{nr} + \kappa_q[O_2] \tag{4}$$

where $[O_2]$ is the oxygen concentration in the polymer. Both the radiationless decay rate, k_{nr}, and the oxygen-quenching decay rate, κ_q, are temperature dependent, but the radiative decay rate, k_r, is almost temperature independent except for the weak temperature dependence of the refractive index of the medium.[14]

The radiationless decay rate is typically described by an Arrhenius-like equation:

$$k_{nr} = A_{nr}e^{-\Delta E_{nr}/RT} \tag{5}$$

where A_{nr} and ΔE_{nr} are, respectively, the frequency factor and the activation energy of the radiationless decay. Henry's law expresses the linearity of $[O_2]$ with the partial pressure of oxygen over the film. We shall take the partial pressure of oxygen as directly proportional to the total air pressure over the film and substitute:

$$[O_2] = C_0\left(\frac{P}{P_0}\right) \tag{6a}$$

where $C_0 = [O_2]$ when the air pressure is P_0. The solubility of diatomic gases in polymer is not affected over the temperature range used in the wind tunnel, so we shall consider C_0 temperature independent. The temperature dependence of the quenching decay rate can also be described by an Arrhenius-like equation. We thus get an oxygen-quenching term:

$$\kappa_q[O_2] = \kappa_q C_0\left(\frac{P}{P_0}\right) = A_q^0 e^{-\Delta E_q/RT}\left(\frac{P}{P_0}\right) \equiv A_q e^{-\Delta E_q/RT} \tag{6b}$$

where A_q and ΔE_q are the frequency factor and the activation energy of the quenching decay and where we have absorbed $C_0(P/P_0)$ into A_q. An article has been published in which the behavior of a ruthenium complex dissolved in a polydimethylsiloxane (PDMS) matrix is analyzed according to the preceding equations.[10]

The observed emission intensity is related to the excited state lifetime:

$$I_{em} = D_a k_r \tau \Phi^* \tag{7}$$

where D_a is a constant dependent on the apparatus and Φ^* is the quantum yield of the metastable excited state S^* on photoexcitation. Quite generally photoexcitation first produces an initial excited state that then radiationlessly decays to a metastable excited state. In the case of the luminophor platinum tetra(pentafluorophenyl)porphine, the initial excited state formed by 390-nm excitation is a second-excited singlet, ${}^1S_2$, whereas the metastable sensing state is the lowest excited triplet, ${}^3T_1$. In that case it has been shown that the yield of the metastable triplet under constant illumination, ${}^3\Phi(T)$, is temperature dependent mostly because the absorbance is changing.[15] The theoretical temperature dependence of the luminescence is then summarized by

$$I_{em} = \frac{D_a k_r{}^3\Phi(T)}{k_r + A_{nr}e^{-\Delta E_{nr}/RT} + A_q e^{-\Delta E_q/RT}} \tag{8}$$

It is obvious from eq. (8) that the temperature dependence of luminescence intensity in PSP is far from simple and a better understanding of those processes is necessary to develop a PSP with a possibility of temperature correction.

Many studies proposing methods for temperature correction of PSP have already been published.[3,16−22] Some methods involve pressure taps used as an *in situ* calibration of the PSP luminescence.[3,16,17] Other methods involve isothermal calibration[18,19] or referenced temperature calibration[11] of the PSP. Those methods assume that the model is isothermal, but this is obviously not true, because air flux and internal design of the airfoil can induce important temperature gradients on the model. Other groups have proposed a pixel-by-pixel temperature correction using a temperature sensor incorporated in the PSP.[20,21] This is the most promising correction method, even if the choice of luminophor is complicated by the needs of minimum overlap of the emission spectra of the two sensors. Some researchers have even proposed a liquid crystal layer for the temperature mapping of models in the wind tunnel.[24] A good comparison of different temperature correction methods was published by Woodmansee and Dutton.[11] However, the possibility of effective and useful temperature correction of PSP is limited by the nonideal behavior of most of the PSP available.

In an earlier article,[23] which we consider Paper I of this series on PSP, we describe the synthesis of the polymer FIB made from hexafluoroisopropyl and heptafluoro-*n*-butyl methacrylate and show that it is a nearly ideal PSP, in that pressure and temperature dependencies are independent. Because the present article concerns the requirements for the parameters of the various decay rates necessary to ideal behavior, we here review the concept of an ideal PSP.

The wind-tunnel measured intensity ratio is

$$\frac{I(P_0, T_0)}{I(P, T)} \equiv \left[\frac{I(P_0, T_0)}{I(P_0, T)}\right]\left[\frac{I(P_0, T)}{I(P, T)}\right]$$

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

$$\equiv \left[\frac{I(P_0, T_0)}{I(P, T_0)}\right]\left[\frac{I(P, T_0)}{I(P, T)}\right] \equiv f_{T_0}(P, P_0)$$

$$\times \frac{1}{g_P(T, T_0)} \quad (9)$$

where $I(P_0, T_0)$ is the intensity measured with wind-off at a reference pressure and temperature and $I(P, T)$ is the intensity measured with wind-on, where both pressure and temperature have changed. Here we define the functions $f_T(P, P_0)$ and $g_P(T, T_0)$ as

$$f_T(P, P_0) = \frac{I(P_0, T)}{I(P, T)} \quad (10a)$$

$$g_P(T, T_0) = \frac{I(P, T)}{I(P, T_0)} \quad (10b)$$

Thus $f_T(P, P_0)$ represents a pressure scan at temperature T with the intensity at P_0 as a reference, and $g_P(T, T_0)$ represents a temperature scan at pressure P with the intensity at temperature T_0 as a reference. The functions defined in eq. (10a) $f_T(P, P_0)$ form a family of pressure functions, and the functions $g_P(T, T_0)$ defined in eq. (10b) form a family of temperature functions. These functions are easily measured in the laboratory. We have found that for PtTFPP in FIB

$$f_T(P, P_0) \approx f(P, P_0) \quad (10a)$$

i.e., the functions $f_T(P, P_0)$ have very little temperature dependence, and

$$g_P(T, T_0) \approx g(T, T_0) \quad (10b)$$

i.e., the functions $g_P(T, T_0)$ have very little pressure dependence. This leads us to define ideal paints as paints such that

$$\frac{I(P_0, T_0)}{I(P, T)} \approx \frac{f(P, P_0)}{g(T, T_0)} \quad (10c)$$

Ideality is not generally the case. In fact, some paints show a temperature dependence at atmospheric pressure four to five times higher than at vacuum.[5] Ideal paints have the unique character that if a way is found to determine T on the model and the function $g(T, T_0)$ is measured in the laboratory, then the function

$$g(T, T_0) \frac{I(P_0, T_0)}{I(P, T)} \approx f(P, P_0) \quad (10d)$$

That is, we can multiply the wind-tunnel ratio $I(P_0, T_0)/I(P, T)$ by a single function $g(T, T_0)$ to obtain $f(P, P_0)$ from which pressure can be determined. On the other hand, if the paint is not ideal, then we must multiply the wind-tunnel ratio $I(P_0, T_0)/I(P, T)$ by a function $g_P(T, T_0)$ that depends on the pressure which we are trying to determine. Thus temperature correction becomes far more difficult, if not impossible.

EXPERIMENTAL

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 used as the binder in the paint formulation were determined on a DSC 2910 apparatus (TA Instruments, Madrid, Spain) with a heating rate of 20°C/min between −100 and 400°C.

The PSP formulation used in this study was comprised of a platinum tetra(pentafluorophenyl)-porphine (PtTFPP) sensor, purchased from Porphyrin Products (Logan, UT), dissolved in FIB.[23] The paint was sprayed from p-chlorotrifluorotoluene (which was obtained under the trade name Oxsol-100 made by Occidental Chemical Corp., Dallas, TX) on clean aluminum coupons (2.5 × 2.5 cm). Samples with a thickness of about 12–15 μm and an average smoothness (measured with a Surtronic 10 profilometer) of 1 μm were generally obtained. The paint formulation is typically 5 mg of luminophor for each gram of polymer dissolved in 25 mL of unpurified solvent. The dry coat contains about 6.7 mM of PtTFPP.

The lifetimes of the luminophor were measured on a homemade apparatus comprised of a 540-nm nitrogen-pumped dye laser (Oriel, Stratford, CT) and a pressure- and temperature-controlled chamber designed in our laboratory. The emission light received at the detector was filtered by a 645-nm narrow bandpass filter (20-nm width at half-height). The intensities of the phosphorescence as a function of time were measured at least 50 times and then averaged. The lifetimes were extracted from the intensity data by a single exponential curve fitting for vacuum experiments and by a double-exponential curve fitting for atmospheric pressure experiments. The intensities of the luminescence as a function of pressure and temperature were measured with a homemade apparatus comprised of a tungsten lamp and a pressure- and temperature-controlled chamber similar to the one used in the lifetime apparatus. The excitation light was filtered through a 390 narrow bandpass filter and the emission light received at the detector was filtered through a 640 narrow bandpass filter; both filters have a 20-nm width at half-height.

The samples were sprayed and then annealed in different ways to verify the effect of solvent loss and/or heating of the sample on the paint properties as a PSP. Three samples were prepared for each annealing procedure. The first annealing was conducted at 150°C for 45 min. The second
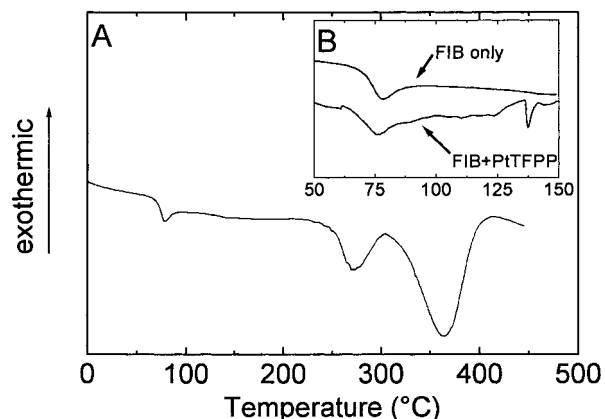

Figure 1   (a) Thermogram of polymer alone. (b) Thermogram of the polymer plus PtTFPP. The y axis represents the heat flow and a downward deflection means heat given to the system.

was conducted at 75°C for 45 min, and the third annealing procedure used a heat gun for two short bursts of 45 s. Three samples were also vacuum dried for 1 week and three other samples were analyzed right after spraying, with no annealing or drying. The weight losses of all samples during annealing were determined by gravimetry.

RESULTS AND DISCUSSION

The thermal characterization of the polymer used in the paint formulation is essential for an understanding of the annealing effect on the properties of the paint as a PSP. The differential scanning calorimetry (DSC) of the polymer, shown in Figure 1, exhibits a transition at about 70°C that can be attributed to the glass transition temperature (T_g). This result is in good agreement with the so-called Fox equation,[24] which predicts a T_g of about 65°C. The Fox equation can predict the T_g of a copolymer based on the T_g's of the corresponding high molecular weight homopolymers:

$$[T_g(\text{copolymer})]^{-1} = w_1[T_g(\text{polymer 1})]^{-1}$$
$$+ w_2[T_g(\text{polymer 2})]^{-1} \quad (11)$$

where w_1 and w_2 are the weight fraction of the monomer 1 and 2, respectively, in the final copolymer and T_g(polymer 1) and T_g(polymer 2) are the T_g's of the homopolymers of monomer 1 and 2, respectively. At higher temperature, the thermogram has two endothermic peaks. The first peak,
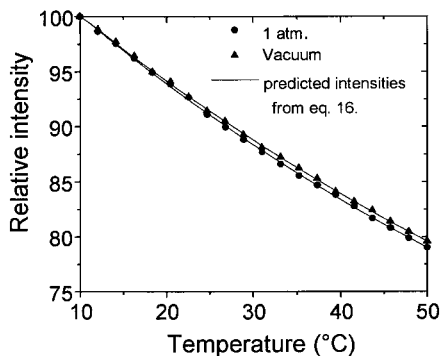
Figure 2 Temperature dependence of the paint luminescence in vacuum (▲) and at atmospheric pressure (●): $g_P(T, T_0)$ for $P = 1$ atm and $P =$ vacuum, $T_0 = 25°C$. Straight lines represent the temperature dependence predicted by eq. (15).

at 260°C, is attributed to the melting of the crystallites in the polymer network and the second peak, at 370°C, is probably the result of the thermal deterioration of the polymer. This assumption is confirmed by the fact that a sample previously heated at 400°C does not show a glass transition temperature nor a melting peak at 260°C nor an endothermic peak at 370°C. It seems that the polymer is totally degraded when heated at temperature above 370°C.

The paint formulation developed in our lab shows remarkable properties as a PSP. The paint has nearly ideal behavior (i.e., temperature dependence is independent of the pressure) and has also a very low temperature dependence (about −0.52%/°C), as shown in Figure 2, which plots $g_P(T, T_0)$ for $P = 1$ atm and $P =$ vacuum with $T_0 = 25°C$. However, we noticed that those good properties are only exhibited by samples that have been annealed at high temperature for a long period of time before analysis. Samples analyzed right after spraying do not behave ideally at all. Nonannealed samples show a greater temperature dependence of the intensity at atmospheric

pressure, about −0.80%/°C, compared to about −0.54%/°C at vacuum.

Annealing at high temperature has two possible effects on the paint layer: a thermal effect and a drying effect. We wanted to separate and determine the individual contribution of those two effects to understand the idealization of the paint during annealing. Table I summarizes the different ways samples were treated and their solvent weight loss. Table II summarizes the fitting parameters obtained for these samples. We see in Table I that drying in vacuum (#4) leads to 13% weight loss, but Table II shows that this does not appreciably change the pressure paint parameters compared to the nonannealed sample (#5). On the other hand, heating above T_g (75°C for #2) and also heating with two short bursts of heat (#3) lead to similar pressure paint parameters in Table II. Note that the weight loss for #2 and #4 are the same. Finally, heating above 150°C (#1) appears to lead to irreversible changes in the polymer. As we discuss in more detail below, we believe this shows that the changes in PSP parameters produced by annealing that lead to ideal PSP come from heating the polymer above T_g rather that from loss of solvent.

The temperature dependence of the luminescence lifetime was measured for each sample at atmospheric pressure and also in vacuum. Although the temperature dependence of the intensity of luminescence is somewhat easier to measure and also less time-consuming, more information can be extracted from the lifetime data and this method was used preferably to the intensity experiments. Lifetimes were extracted from the raw intensity data as a function of time by a single exponential fitting for the vacuum experiments. The intensity decay in vacuum is well described by a simple exponential decay and thus characterized by a well-defined τ value.[15] The residue plots for these analyses show only randomly dispersed data. On the other hand, it is generally

Table I   Weight Loss of Paint Samples During Annealing

Sample	#1	#2	#3	#4	#5
T annealing	150°C	75°C	Heat gun (approx. 175°C)	25°C in vacuum	Nonannealed
Weight loss	18%	13%	20%	13%	0%
Time of annealing	30 min	30 min	2 short bursts of 45 s	2 days	—

Table II   Parameters Obtained from Temperature Dependence Data Fitted to Eqs. 12 and 13

| Sample	#1	#2	#3	#4	#5
T of annealing	150°C	75°C	Heat gun	Vacuum dried	Nonannealed
k_r (s^{-1})	$1.0 \pm 0.2\text{E}^2$	$9.8 \pm 0.3\text{E}^3$	$9.8 \pm 0.3\text{E}^3$	$9.8 \pm 0.3\text{E}^3$	$9.8 \pm 0.3\text{E}^3$
A_{nr}	$2.0 \pm 0.1\text{E}^3$	$4.7 \pm 0.1\text{E}^5$	$4.8 \pm 0.1\text{E}^5$	$4.7 \pm 0.1\text{E}^5$	$4.7 \pm 0.1\text{E}^5$
ΔE_{nr} ($\pm$0.3 kJ/mol)	13.3	14.1	14.1	14.1	14.1
A_q^0 ($\pm$0.1 E5 s^{-1})	—	1.6	1.6	1.8	1.9
ΔE_q ($\pm$0.09 kJ/mol)	—	1.50	1.51	1.72	1.73

accepted that the luminescence decay rates in solid matrix at atmospheric pressure do not follow a single exponential curve due to inhomogeneity of the medium.[25] Although triple exponential curve fitting has been used by some researchers,[10,25] both the physical significance of the parameters and the meaning of the exponential decay for these systems are debatable.[26–27] However, the problem can be eliminated by considering the value of the mean lifetime $\langle \tau \rangle$, determined by the best high-order exponential fitting. (The intensity is described by a sum of exponential terms $I(t) = \sum_i A_i e^{-t/\tau_i}$ and the mean lifetime $\langle \tau \rangle = \sum_i A_i \tau_i / \sum_i A_i$.) With this approach, the Stern–Volmer equation is obeyed[10] and the deviations are small, thus the lifetimes τ were determined from a double exponential fitting at atmospheric pressure.

The lifetime of the PtTFPP at 25°C is typically 87 μs in vacuum and between 9.0 and 10.5 μs at atmospheric pressure, depending on the annealing history. The temperature dependencies of the PtTFPP lifetime in vacuum for samples #2–5 are shown in Figure 3. We can see that the annealing procedure does not affect significantly the temperature dependence of the PtTFPP in vacuum and the curves are almost superposed. Equations (4) and (5) lead to eq. (12), which describes the temperature dependence of lifetime in vacuum:

$$\frac{1}{\tau} = k_r + A_{nr}e^{-\Delta E_{nr}/RT} \tag{12}$$

The data from Figure 3 were fitted according to eq. (12) and the radiative decay rate, the frequency factors, and the activation energy of the radiationless decay rate were calculated. The results from this fitting are presented in Table II. As expected, the radiative decay rate and the frequency factors and activation energy of the radiationless decay rate are very similar for samples #2–5. Annealed sample #1 (30 min at 150°C) gave anomalous results. This can be seen in the contrast between its vacuum parameters and those of the other samples, as shown in Table II. It is possible that this change in parameters relates to the small endothermic peak at 135°C in Figure 1(b), which at first sight looks like noise, but is reproducible in the paint, i.e., polymer plus PtTFPP. This is reproducible and is present on all thermograms of the polymer and the paint (polymer plus PtTPP). The thermograms imply that something is happening at 135°C, which may relate to the anomalous parameters in Table II for sample #1, which has been heated above 135°C. So sample #1 is not considered further.

The temperature dependencies of the lifetime at atmospheric pressure for samples #2–5 are
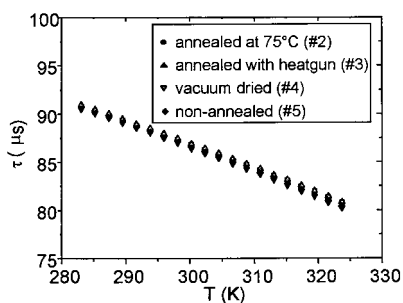
Figure 3   The temperature dependence of the lifetime in vacuum for sample #2–5, Table I.
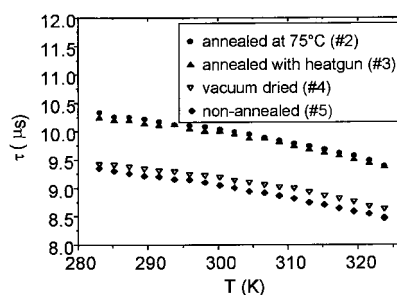
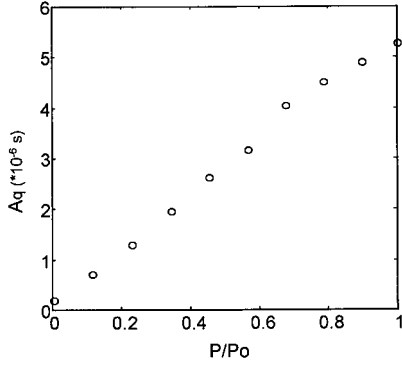**Figure 4**   The temperature dependence of the lifetime at atmospheric pressure for sample #2–5.

Figure 5 Pressure dependence of the preexponential term A_q, as calculated from eq. (12) at different partial pressures.

shown in Figure 4. There is no significant difference between the temperature dependencies of lifetime for samples #2 and #3. However, there is an obvious difference in the temperature dependencies between the samples that have been heated (#2 and #3) and the samples that have been kept at room temperature (#4 and #5). Even though sample #4 is almost dry and sample #5 is still wet, they exhibit a remarkable similarity in their temperature dependence plot. The data obtained from the atmospheric temperature experiments were fitted according to

$$\frac{1}{\tau} = k_r + A_{nr}e^{-\Delta E_{nr}/RT} + A_q^0 e^{-\Delta E_q/RT} \qquad (13)$$

where k_r, A_{nr}, and ΔE_{nr} are assumed to be equal to the values obtained from the experiments in vacuum. The fitting parameters A_q^0 and ΔE_q are shown in Table II for samples #2–5. We can see, as expected, that there is no difference between the parameters A_q^0 and ΔE_q determined for sample #2 and #3. However, the parameters found for samples #4 and #5 are significantly different from those found for sample #2 and #3. Because #2 and #3 are close to ideal, heating seems to be much more important than drying in the idealization of the FIB PSP.

The pressure sensitivity of the luminescent paint is related to the pressure dependence of the preexponential term A_q. The lifetimes of sample #2 were measured as a function of pressure in isothermal condition. The fitting parameters k_r, A_{nr}, ΔE_{nr}, and ΔE_q were kept constant and the parameters A_q were extracted from eq. (12) for each pressure run. The pressure dependence of the preexponential term A_q is shown in Figure 5.

The relationship between A_q and the relative pressure is nearly linear, as expected by eq. (6b).

Intensity of luminescence is related to lifetime as shown by eq. (7) and the theoretical temperature dependence of the lifetime is described in eq. (13). Those equations were used to validate the parameters found with the lifetime experiments. The temperature dependence of the triplet yield for the luminophor has to be determined first. A rearrangement of eq. (7) gives

$$\frac{I_{em}}{\tau} = D_a k_r^3 \Phi(T) \qquad (14)$$

The plot of the intensity (I_{em}) over the lifetime (τ) as a function of temperature, at vacuum, is shown in Figure 6. The nearly linear relationship obtained is solely due to the temperature dependence of $^3\Phi(T)$, because the radiative decay rate is assumed to be temperature independent. The nearly linear temperature dependence of the triplet yield is incorporated in eq. (8) and gives the more detailed

$$I_{em} = D_a \frac{1 - \eta T}{k_r + A_{nr}e^{-\Delta E_{nr}/RT} + A_q e^{-\Delta E_q/RT}} \qquad (15)$$

where η is the slope the temperature dependence of the triplet yield. The parameters describing the temperature dependence of the lifetime and the triplet yield for sample #2, both at atmospheric pressure and vacuum, were used to generate the temperature dependence of the intensity according to

$$\begin{aligned} g_P(T, T_0) &\equiv \frac{I_{em}(P, T)}{I_{em}(P, T_0)} \\ &= \left(\frac{k_r + A_{nr}e^{-\Delta E_{nr}/RT} + A_q^0(P/P_0)e^{-\Delta E_q/RT}}{k_r + A_{nr}e^{-\Delta E_{nr}/RT_0} + A_q^0(P/P_0)e^{-\Delta E_q/RT_0}} \right) \end{aligned} \qquad (16)$$
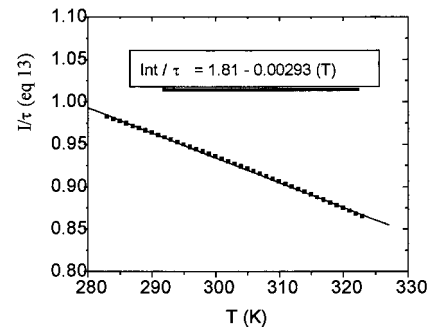

Figure 6 Temperature dependence of the triplet yield of PtTFPP in vacuum.

The experimental data and the generated curves are shown in Figure 2. There is a very good correlation between the experimental and the predicted data, which even explains the small deviation from ideality at high temperature. Such a good fit allows us to consider those parameters reliable and use them to give an explanation of the annealing effect based on the different results obtained for samples #2–5. Notice that all the parameters used in eq. (16) were determined by lifetime measurements and that they were used to describe accurately the temperature dependence of the intensity of the phosphorescence. A better fit would have been obtained, of course, with a simpler function, but the point here is that the temperature dependence of the intensity can be predicted from the lifetime measurements with eq. (16).

The ideality of our luminescent paint, in the range of temperature used, comes from the very low activation energy of the diffusion of oxygen through the paint layer. An activation energy for the diffusion of oxygen of 1.5 kJ/mol has been found for FIB, the polymer used in this study, which is much lower than any usual polymer. For instance, PDMS, well known for its oxygen permeability, has an activation energy of about 11 kJ/mol.[28] The remarkably low activation energy of the oxygen diffusion makes this polymer a good candidate for the development of quantitative PSP. However, it seems that the polymer has to be heated above the T_g to get this ideal behavior. The diffusion of oxygen through polymer is an energy activated process which involves the cooperation of the polymer chains. We can see from Table II that the activation energies of the oxygen diffusion for nonpreviously heated sample (#4 and #5) are somewhat higher than the activation energies found for previously heated sample (#2 and #3). Heating a polymer network above T_g allows the chains to relax, loosens the entanglements in the network, and, more generally, allows the system to become thermodynamically stable. The relaxation of the network can have an effect on the oxygen diffusion through the polymer, because fewer entanglements mean easier diffusion and lower activation energy. From those results, it seems that the thermal contribution is the most important effect of annealing on the idealization of the luminescent behavior of the formulation. The drying of the paint layer does not seem to affect significantly the properties of the paint as a PSP.

One can suggest the utilization of a low T_g polymer as the binder in the paint formulation and therefore, no annealing would be necessary. However, many mechanical problems are associated with a polymer having a T_g below the room temperature. The hardness of the paint layer is generally low and the paint tends to come off the model. Annealing remains necessary to improve adhesion. Finally, a polymer with such a low-activation energy and also a significantly lower T_g is not known yet.

Ideality Temperature Limits (ITL). We now will reexamine the condition of ideality in terms of the temperature dependent rates. From eq. (14) we can derive

$$\frac{I_{em}(P_0, T_0)}{I_{em}(P, T)} = \left(\frac{\Phi^*(T_0)}{\Phi^*(T)}\right)$$
$$\times \left(\frac{k_r + A_{nr}e^{-\Delta E_{nr}/RT} + A_q^0 e^{-\Delta E_q/RT}(P/P_0)}{k_r + A_{nr}e^{-\Delta E_{nr}/RT_0} + A_q^0 e^{-\Delta E_q/RT_0}}\right) \quad (17)$$

To better understand ideality it is handy to rewrite eq. (17) in terms of

$$\gamma(T) = \left(\frac{A_q^0 e^{-\Delta E_q/RT}}{k_r + A_{nr}e^{-\Delta E_{nr}/RT}}\right) \quad (18)$$

This is the ratio of the oxygen quenching rate at 1 atm pressure to the vacuum decay rate. With this substitution, eq. (17) becomes

$$\frac{I_{em}(P_0, T_0)}{I_{em}(P, T)} = \left(\frac{\Phi^*(T_0)}{\Phi^*(T)}\right)$$
$$\times \left(\frac{(k_r + A_{nr}e^{-\Delta E_{nr}/RT})}{k_r + A_{nr}e^{-\Delta E_{nr}/RT_0} + A_q^0 e^{-\Delta E_q/RT_0}}\right)$$
$$\times \left[1 + \gamma(T)\left(\frac{P}{P_0}\right)\right] \quad (19)$$

This is in the form of the ideality condition eq. (10c) (i.e., a function of pressure divided by a function of temperature) insofar as $\gamma(T) = $ const. In eq. (17) we have expressed $\gamma(T)$ in terms of parameters evaluated in Table II.

To understand the meaning of ideality, we use these parameters to generate a plot of $\gamma(T)$ over a wide temperature range. (We are aware that the temperature range in Fig. 7 is far wider than is physically reasonable, because PSP will decompose at high temperature and not allow oxygen diffusion at low temperature.) The plot shows that $\gamma(T)$ rises and falls and has only a narrow range where it is relatively temperature indepen-
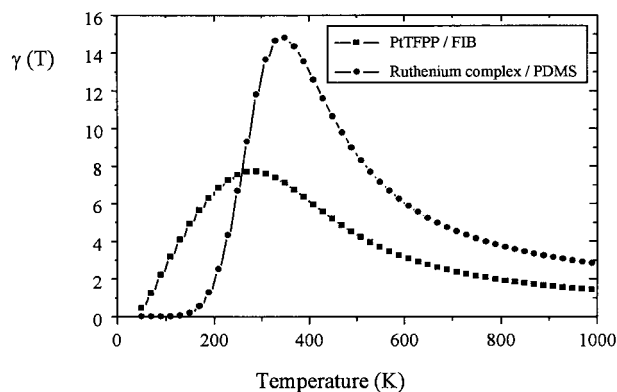
Figure 7   Temperature dependence of the ratio $\gamma(T)$, as generated by eq. (17), over a wide temperature range for the FIB/PtTFPP system and a ruthenium/PDMS system. The parameters for the Ru system were taken from Shanze article.[10]

dent. For PtTFPP in FIB, the region of approximate temperature independence is between 225 and 350 K. A plot of $\gamma(T)$ has also been generated in Figure 7 for another paint based on ruthenium bathophenanthroline in a PDMS matrix using parameter values given by Shanze et al.[10] It seems that this paint has relatively constant $\gamma(T)$ and could behave ideally in the temperature range 325–400 K. We believe that each pressure-sensitive paint has a range of temperature where the luminescence properties behave ideally. The temperature range where ideality is preserved seems also to be larger for a system with a low activation energy of the oxygen diffusion. However, it seems that ideality near room temperature could only be reached by a paint formulation comprised of a polymer with a very low activation energy of oxygen diffusion, such as the FIB polymer used in this study.

CONCLUDING REMARKS

This study gave an explanation of the ideal behavior of the PSP made of PtTFPP in FIB. The very low activation energy of oxygen diffusion for the polymer developed in our laboratory is an exceptional feature and allows the possibility of temperature correction by an internal temperature sensor. Moreover, ratioing the ideal pressure and temperature luminescence to a temperature-dependent but pressure-independent reference could reduce or eliminate the temperature dependence of the paint and open the door to more accurate and quantitative PSP measurements.

Besides the very good diffusivity properties described in this article, our paint formulation shows a short response time (~ 1 s) and a very low photodegradation rate. Those features and also the effect of the basecoat on the paint properties will be discussed in a companion article.

REFERENCES

1. Gouterman, M. J Chem Educ 1997, 74, 697–702.
2. Morris, M. J. ICIASF 95 Record, International Congress on Instrumentation in Aerospace Simulation Facilities, Wright Patterson, OH. IEEE, NY: 1995; pp 31.1–31.10.
3. Kavandi, J.; Callis, J.; Gouterman, M.; Khalil, G.; Wright, D.; Green, E. Rev Sci Instr 1990, 61, 3340–3347.
4. Morris, M. J.; Donovan, J. F.; Kegelman, J. T.; Schwab, S. D.; Levy, R. L.; Crites, R. C. AIAA 1993, 31, 419–425.
5. Burns, S. P.; Sullivan, J. P. ICIASF 95 Record, International Congress on Instrumentation in Aerospace Simulation Facilities; Wright Patterson, OH. IEEE, NY: 1995; pp 32.1–32.14.
6. Bell, J. H.; McLachlan, B. G. AIAA Paper 1993, 93-0178.
7. Le-Sant, Y.; Deleglisse, B.; Mebarki, Y. ICIASF 97 Record, International Congress on Instrumentation in Aerospace Simulation Facilities; Pacific Grove, CA. IEEE, NY: 1997; pp 57–65.
8. Carroll, B. F.; Abbitt, J. D.; Lukas, E. W.; Morris, M. J. AIAA J 1996, 34, 521–526.
9. Di Marco, G.; Lanza, M.; Pieruccini, M.; Campagna, S. Adv Mater 1996, 8, 576–580.
10. Schanze, K. S.; Carroll, B. F.; Korotkevitch, S. AIAA J 1997, 35, 306–310.
11. Woodmansee, M. A.; Dutton, J. C. Exp Fluids 1998, 24, 163–174.
12. Ruyten, W. M. Rev Sci Instr 1997, 68, 3452–3457.
13. Ruyten, W. M. App Opt 1997, 36, 3079–3085.
14. Ware, W. R. J Chem Phys 1965, 43, 1194.
15. Coyle, L. M. Ph.D. Thesis, University of Washington at Seattle, December, 1999.

16. McLachlan, B. G.; Bell, J. H.; Park, H.; Kennelly, R. A.; Schreiner, J. A.; Smith, S. C.; Strong, J. M.; Gallery, J.; Gouterman, M. J Aircraft 1995, 32, 217–227.

17. McLachlan, B. G.; Kavandi, J.; Callis, J.; Gouterman, M.; Green, E.; Khalil, G.; Burns, D. Experiments in Fluids 1993, 14, 33–41.

18. Volan, A.; Alati, L. ICIASF 91 Record, International Congress on Instrumentation in Aerospace Simulation Facilities, Rockville, MD. IEEE, NY: 1991; IEEE Paper No. 91CH3028–8.

19. Troyanovsky, I.; Sadovskii, N.; Kuzmin, M.; Mosharow, V.; Orlov, A.; Radchenko, V.; Phonov, S. Sensors Actuators B Chem 1991, 11, 201–206.

20. Morris, M. J.; Donovan, J. F. 25th AIAA Fluid Dynamics Conference, June 20–23, Colorado Spring, CO. AIAA, NY: 1994; AIAA Paper No. 94-2231.

21. Chapman, D. M.Sc. Thesis, University of Washington at Seattle, Jun. 1998.

22. Bize, D.; Lempereur, C. H.; Mathé, J. M.; Mignosi, A.; Séraudie, A.; Serrot, G. ICIASF 97 Record, International Congress on Instrumentation in Aerospace Simulation Facilities, Pacific Grove, CA. IEEE, NY: 1997; pp 66–75.

23. Puklin, E.; Carlson, W. B.; Gouin, S.; Costin, C.; Green, E.; Ponomarev, S.; Tanji, H.; Gouterman, M. J Appl Polym Sci 2000, 77, 2795.

24. Wicks, Jr., Z. W.; Jones, F. N.; Pappas, S. P. in Organic Coatings: Science and Technology; Wiley, New York, 1992, Vol I, p 55.

25. James, D. R.; Liu, Y. S.; DeMayo, P.; Ware, W. R. Chem Phys Lett 1983, 20, 460–465.

26. Horie, K. in Photophysics of Polymers, Torkelson, J. M., Ed.; ACS: Washington, DC, 1987, 83–96.

27. Sackesteder, L. A.; Demas, J. N.; DeGraff, A. Anal Chem 1993, 65, 3480.

28. Pauly, S. in Polymer Handbook, 3rd ed.; Bandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; pp VI435–449.