Ideality of Pressure-Sensitive Paint. IV. Improvement of Luminescence Behavior by Addition of Pigment

SÉBASTIEN GOUIN, MARTIN GOUTERMAN

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received 25 September 1999; accepted 15 January 2000

ABSTRACT: We report the effect of inorganic pigments on the diffusion properties of a polymer matrix. The presence of pigments has a large effect on the frequency factor and the activation energy of the diffusion of oxygen in the polymer matrix. This effect is used to modify the overall temperature dependence of the luminescence in pressure sensitive paint (PSP). Ideality of luminescence (i.e., independent effect of pressure and temperature on the luminescence intensity) can be achieved with a PSP formulation by using a low-cost and commercial silicone polymer using Al_2O_3 as the pigment. Ideality temperature limits (ITL) can be tailored by adjusting the pigment volume concentration (PVC) in the paint formulation. With the appropriate adjustment of PVC, the luminescence characteristics of the PSP can be designed to suit the particular needs of the wind-tunnel researchers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2824–2831, 2000

Key words: luminescence quenching; pressure-sensitive paint

INTRODUCTION

Pressure-sensitive paint (PSP) is increasingly popular as an alternative to conventional pressure taps used in wind-tunnel research for pressure mapping.¹⁻³ PSP technology is now expected to supplant pressure taps, its much more expensive but less informative predecessor, because many breakthroughs have been made during the last few years. Paint formulations with good photostability, fast response time, and low-temperature dependence are now available.^{1,3,4} However, some problems still prevent PSP technology from becoming an efficient quantitative tool for windtunnel research.⁵⁻⁹

The main inaccuracy comes from the inherent temperature dependence of the luminescence of

Journal of Applied Polymer Science, Vol. 77, 2824–2831 (2000) © 2000 John Wiley & Sons, Inc. PSP. The temperature of the model in the wind tunnel drifts over a temperature range by as much as 40°C. Moreover, temperature gradients are established over the model, due to different flow rates and to the internal morphology of the model. The temperature inhomogeneity of the model leads to a discrepancy between the pressure values found with the PSP and with the taps.^{10,11} temperature-independent pressure Some paints have been developed with low-temperature dependency,¹ which limits the divergence of the measurements due to temperature changes. Errors induced by the temperature change are not substantial, but can be fatal in low-speed wind-tunnel experiments, where intensity changes due to pressure variations are small and comparable to intensity changes caused by temperature drift.

The inherent temperature dependence of pressure-sensitive paints comes from the temperature dependence of the different decay rates involved in the luminescence processes.^{4,12,13} The intensity of the luminescence is given (as in Paper II) as:

Correspondence to: M. Gouterman.

Contract grant sponsor: NASA–Ames Research Center; contract grant number: NAG 2-1157.

$$I_{em} = D_a \left(\frac{k_r \Phi^*(T)}{k_r + k_{nr} + \kappa_q [O_2]} \right)$$
$$= D_a \left(\frac{k_r \Phi^*(T)}{k_r + A_{nr} e^{-\Delta E_{nr}/RT} + A_q e^{-\Delta E_q/RT}} \right) \quad (1)$$

where k_r and k_{nr} are, respectively, the radiative and the radiationless decay rates and κ_q is the bimolecular oxygen quenching rate constant. D_a is the apparatus constant. In eq. (1), we express k_{nr} in terms of a frequency factor A_{nr} and an activation energy ΔE_{nr} .^{12,13} The concentration of molecular oxygen in the layer is represented by $[O_2]$. Equation (2) expresses Henry's law that the oxygen concentration in the polymer is linear with the oxygen pressure over the layer:

$$[O_2] = C_0 \left(\frac{P}{P_0}\right) \tag{2}$$

where C_0 is the solubility of oxygen in the paint layer at reference pressure P_0 usually taken as 1 atm and is not temperature dependent over the range of interest. Expressing κ_q in terms of a frequency factor and an activation energy^{12,13} and making use of eq. (2) we obtain:

$$\kappa_q[\mathcal{O}_2] = A_q e^{-\Delta E_q/RT} = A_q^0 \left(\frac{P}{P_0}\right) e^{-\Delta E_q/RT} \qquad (3)$$

Equations (1) and (3) give the pressure and temperature dependence of k_{nr} and κ_q . The radiative decay rate, k_r , is temperature independent,¹⁴ and the oxygen concentration in the polymer, C_0 , is considered temperature independent over the temperature range normally used in wind-tunnel research,^{15,16} and we absorb it into the frequency factor A_q .

In Paper I of this series we defined an ideal paint as one such that

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

where the functions $f(P, P_0)$ and $g(T, T_0)$ are generally defined as

$$f_T(P, P_0) = \frac{I(P_0, T)}{I(P, T)}$$
(5)

$$g_P(T, T_0) = \frac{I(P, T)}{I(P, T_0)}$$
 (6)

Thus, in general, $f_T(P, P_0)$ is a set of functions of pressure that slowly change with temperature; $g_P(T, T_0)$ is a set of functions of temperature that slow change with pressure. In the case of ideal paints a single function $f(P, P_0)$ adequately represents all functions $f_T(P, P_0)$ and a single function $g(T, T_0)$ adequately represents all functions $g_P(T, T_0)$. In the laboratory we carry out pressure runs at constant temperature. In this case using eqs. (1) and (2), we obtain

$$f_{T}(P, P_{0}) = \frac{I(P_{0}, T)}{I(P, T)}$$
$$= \frac{k_{r} + k_{nr}^{T} + \kappa_{q}^{T}C_{0}(P/P_{0})}{k_{r} + k_{nr}^{T} + \kappa_{q}^{T}C_{0}} \equiv \left(\frac{\tau_{0}(T)}{\tau(T)}\right) \quad (7)$$

In using eq. (7), we take the decay times as average times if the decays are nonexponential. If the intensity is described by a sum of exponential terms, $I(t) = \sum_i A_i e^{-t/\tau_i}$, then the mean lifetime is $\langle \tau \rangle = (\sum_i A_i \tau_i / \sum_i A_i)$. The *T* indicates temperature dependence, and the subscript 0 refers to P = 1atm. We then get

$$\frac{\tau_0(T)}{\tau(T)} = A_T + B_T \left(\frac{P}{P_0}\right) \tag{8}$$

where

$$A_{T} = \frac{k_{r} + k_{nr}^{T}}{k_{r} + k_{nr}^{T} + k_{q}^{T}C_{0}}; \quad B_{T} = \frac{\kappa_{q}^{T}C_{0}}{k_{r} + k_{nr}^{T} + \kappa_{q}^{T}C_{0}}$$
(9)

Because eq. (9) requires that $A_T + B_T = 1$, only the ratio

$$\frac{B_T}{A_T} \equiv \gamma(T) = \frac{\kappa_q^T C_0}{k_r + k_{pr}^T}$$
(10)

can vary with temperature. Thus for $f_T(P, P_0)$ to be independent of T, the condition of ideality, then $\gamma(T) = \text{const.}$ Expressing this in terms of the frequency factors and activation energies, we have

$$\frac{B_T}{A_T} = \gamma(T) = \frac{A_q^0 e^{-\Delta E_q/RT} C_0}{k_r + A_{nr} e^{-\Delta E_{nr}/RT}}$$
(11)

In Paper I we show that the condition of ideality is very important for temperature correction of PSP. In the case of ideal paints, one can replace the wind-off measurement by a suitable temperature dependent but pressure-independent reference, i.e.,

$$g(T, T_0)I(P_0, T_0) \to I_{ref}(T)$$
 (12)

Thus replacing the wind-off over wind-on intensity ratio by

$$\frac{I(P_0, T_0)}{I(P, T)} \to \frac{I_{\rm ref}(P, T)}{I(P, T)} = \frac{I_{\rm ref}(T)}{I(P, T)}$$
(13)

can lead to an experimental ratio that has less temperature dependence. In fact, a referenced PSP has been made that reduces temperature dependence by nearly a factor of 2.17 However, ideality requires $\gamma(T) = \text{const}$, and eq. (11) makes it clear that this cannot be true for all temperatures. However as pointed out in Paper II, there can be ideality temperature limits (ITL) over which this is approximately true to within 1%. Although the parameters k_r , A_{nr} , and ΔE_{nr} cannot be significantly modified, it is known that the diffusion of oxygen in the layer, which is related to κ_q ,¹² is affected by the presence of inert pig-ment in the polymer.¹⁶ In this article, we use decay time as a function of temperature to determine the frequency factors A_{nr} and A_q^0 and the activation energies ΔE_{nr} and ΔE_q of eqs. (1) and (3). In this article, we show A_q^0 and ΔE_q can be modified by adding pigment to a polysiloxane polymer-based PSP, thereby idealizing this PSP.

EXPERIMENTAL

Paint Formulations

The PSP formulations used in this study comprised a polysiloxane, named SR-900 purchased from GE Silicones (Pittsfield, MA), mixed with a platinum tetra(pentafluorophenyl)porphine (PtTFPP) sensor purchased from Porphyrin Products (Logan, UT). The SR-900 polymer solution contains 50% (v/v) silicone polymer dissolved in toluene. The silicone solution is diluted to an adequate viscosity by adding *p*-chlorotrifluorotoluene, purchased from Occidental Chemical Corp. (Dallas, TX) under the name of Oxsol-100. A certain amount of pigment (Al₂O₃ of size 1–5 μ m) is added to the solution and the mixture is ballmilled at room temperature for 2 days. Typically, the paint formulation contains 11.3 g of silicone solution, 7 mg of PtTFPP, and 36 mL of Oxsol-100. Paints with different pigment volume concentrations (PVC) (see Paper II for a definition of PVC) are prepared by adding 0, 1.5, 3.0, 3.5, 4.0, and 4.5 g of pigment to the solution above, leading to PVC values of approximately 0, 13, 27, 31, 36, and 40%. The paint is sprayed on clean aluminum coupons (6.2 and 1 cm²) with a spray gun, using argon at a pressure of 20 psi as the carrier gas. The samples are annealed at 75°C for half an hour and then cooled at room temperature on the bench for about 15 min.

Luminescence Analysis

Lifetimes of the luminophor as a function of pressure and temperature, for the different samples, were measured on a homemade apparatus. This lifetime apparatus comprises a nitrogen-pumped dye laser (Oriel) as the excitation source and a pressure- and temperature-controlled chamber. The excitation wavelength is set at 390 nm and the emission light is filtered through a bandpass (20-nm width at half-height) filter centered at 645 nm. The intensity of the luminescence as a function of time was measured 50 times and then averaged for each experiment. The lifetime values were extracted from the raw intensity data by a single exponential fit for experiments conducted in vacuum and the mean lifetime of a double exponential fit for those conducted at atmospheric pressure.¹³

The intensity of luminescence as a function of temperature, pressure, and time was measured with a homemade system called the PMT survey apparatus, similar to the lifetime apparatus. Here the excitation light comes from a tungsten lamp filtered through a bandpass (20-nm width at half-height) filter centered at 390 nm.

The response times of the different paints were determined by measuring the intensity change as a function of time after a very rapid pressure change. Those experiments were conducted on a homemade apparatus similar to the PMT survey apparatus. In that apparatus, the pressure- and temperature-controlled chamber is much smaller (thus allowing pressure jump from vacuum, ~ 1 Pa) to atmospheric pressure in about 0.6 ms.

RESULTS AND DISCUSSION

Thickness is not believed to affect the diffusion rate of oxygen in the layer, nor the permeability of the coating. However, the response time is certainly affected by the thickness of the sample.¹⁸ Therefore, particular care has been taken to prepare samples with consistent characteristics, such as the thickness, roughness, and dryness. It has been shown in a previous paper¹³ that annealing has an effect on the diffusion properties of the coating. Samples in this study have been annealed all together at 75°C for 30 min. Sample thicknesses range from 20 to 22 μ m and roughness of all samples is about 1.0 μ m.

The luminescence and the diffusion properties of the paint have been studied as a function of PVC. It is known that the diffusion characteristics of polymers are affected by the presence of solid particles.¹⁶ Researchers have followed the original work of Stern and Volmer¹⁹ and, assuming Henry's law linearity of oxygen concentration in the polymer with oxygen partial pressure over the polymer, have derived a Stern–Volmer equation for the emission of luminophors in polymer:

$$\frac{I^{\text{vac}}}{I} = \frac{\tau^{\text{vac}}}{\tau} = \frac{k_r + k_{nr} + \kappa_q C_0 (P/P_0)}{k_r + k_{nr}} = 1 + K_{SV} P$$
(14)

where the Stern–Volmer constant, K_{SV} , is

$$K_{SV} = \left(\frac{\kappa_q^T}{k_r + k_{nr}^T}\right) \frac{C_0}{P_0} = \kappa_q \tau^{\text{vac}} \frac{C_0}{P_0} = \frac{B_T}{A_T} = \gamma(T)$$
(15)

where τ^{vac} and I^{vac} are, respectively, the lifetime and the intensity measured at vacuum and A_T and B_T are given in eq. (9). The solubility of oxygen in the coating is represented by C_0/P_0 , where C_0 is the concentration of the quencher (O₂) at an air pressure of P_0 . The quenching rate coefficient κ_q is related to the diffusivity of the quencher in the layer:

$$\kappa_q = \alpha \kappa_{\rm diff} \tag{16}$$

where α is the probability for quenching after the formation of the excited luminophor/quencher complex and κ_{diff} is the diffusion-controlled rate of complex formation. We expect that α is near unity. Smoluchowski²⁰ related κ_{diff} to the diffusion coefficient of the quencher:

$$\kappa_{\rm diff} = 4 \,\pi r_{AB} N_A D \tag{17}$$



Figure 1 Stern–Volmer intensity plot for PtTFPP in SR-900 at various temperatures. The superposition of the plot represent the near-ideality of the paint formulation.

where r_{AB} is the collision radius of the complex (in cm), D is the diffusion coefficient (in cm²/s), and N_A is Avogadro's number. [To get units of cm³ (STP) cm⁻³, divide N_A by 22,400 cm³ (STP)/mol.] Rearrangement of eqs. (15–17) gives

$$\frac{I^{\text{vac}}}{I} = \frac{\tau^{\text{vac}}}{\tau} = 1 + 4 \pi r_{AB} N_A \alpha \tau^{\text{vac}} (DC_0/P_0) P$$
$$= 1 + K_{\text{SV}} P \quad (18)$$

where (DC_0/P_0) is the permeability of the coating. Because we expect that $(r_{AB}\alpha)$ will be similar for the various polymer matrices, then comparison of the Stern–Volmer constants for the different samples gives an idea of the relative permeability of the paints and the effect of the PVC on the permeability coefficient.

The Stern–Volmer equation either as eq. (8) or (18) predicts a linear relationship between the intensity ratio and the air pressure if we assume the partial pressure of oxygen in air is constant. Figure 1 shows the Stern–Volmer plot for sample #4, with a 31% PVC of the Al_2O_3 pigment in the silicone polymer. We can see that the experimental data are not precisely linear, and thus the Stern–Volmer equation does not fully describe the quenching of a luminophor immobilized in a polymeric matrix. However, this equation gives a good approximation of the luminescence properties, and the Stern-Volmer equation was used in this study. Table I shows the Stern-Volmer constants as a function of PVC, at 25°C. We can see that the relative permeability, as reflected in K_{SV} , is re-

Paint	Al ₂ O ₃ PVC (%)	$K_{SV}^{a} \times 10^{3} (Pa^{-1})$	ITL ^b (°C)	%Nonideality ^c	Response Time ^d (ms)
1	0	4.11	130-477	2.10	60
2	13	3.71	177-686	1.22	120
3	27	3.60	19 - 158	0.88	135
4	31	3.55	11-161	0.22	145
5	36	3.65	42-263	0.95	130
6	40	3.74	122 - 583	2.14	120

Table I Diffusion and Ideality Characteristics for Paint Formulations with Different Amounts of Aluminum Oxide (CPVC of aluminum oxide used in this study is about 30%)

^a K_{SV} values are determined at 25°C. $K_{SV} = \kappa_q \tau^{\text{vac}} (C_0/P_0)$. ^b ITL is the ideality temperature range, temperature range where the ratio B_T/A_T is independent of temperature at ±1%. ^c From 10 to 50°C.

^d Time required for the intensity to complete 95% of its total change when pressure rises from near vacuum to 1 atm.

lated to the pigment concentration and goes through a minimum around 31% PVC, which is about the CPVC of aluminum oxide, the pigment used in the paint.

The diffusion properties of oxygen in the coating are known to be affected by the presence of pigment.¹⁶ Therefore, it is important to know how the parameters of eq. (11) (i.e., the frequency factor and the activation energy for the diffusion of oxygen) are affected by the pigment. A better comprehension of the effect of the pigment would allow the possibility of predictable modification of the PSP properties.

The lifetime of the luminescence for every sample has been studied as a function of the temperature. The lifetime values were extracted from the raw intensity data as a function of time by a single exponential fit for experiments conducted in vacuum. Data taken at atmospheric pressure were fitted by a double exponential fit, because a single exponential fit does not describe correctly the experimental results. The mean lifetime was calculated from the fitting parameters. A multisites model has been proposed by researchers to legitimize the use of a multiexponential fitting,^{12,21} but controversy remains on this subject. However, this study does not require an absolute and accurate determination of the lifetime and these average lifetimes are considered satisfactory for this particular study. The luminescence properties of the paint were extracted from the lifetime as a function of temperature, in vacuum, according to

$$\frac{1}{\tau} = k_r + A_{nr} e^{-\Delta E_{nr}/RT}$$
(19)

The three-parameter function gives an excellent fit to the experimental data for all the samples studied in this article. The lifetime values as a function of temperature, determined at atmospheric pressure, were fitted according to

$$\frac{1}{\tau} = k_r + A_{nr} e^{-\Delta E_{nr}/RT} + A_q^0 e^{-\Delta E_{q}/RT}$$
(20)

In eq. (20), the radiative decay rate k_r , the preexponential term A_{nr} , and the activation energy ΔE_{nr} were taken as the same value found in vacuum. Therefore, the lifetime values as a function of temperature, at atmospheric pressure, were fitted with only two parameters, A_q^0 and ΔE_q . Equation (20) describes properly the experimental data for all the samples, even though the lifetime values determined at atmospheric pressure are the average lifetimes determined from the parameters of a double exponential fit.

Figure 2 shows the luminescence and diffusion parameters as a function of the PVC. As expected, the luminescence parameters k_r , A_{nr} , and ΔE_{nr} are not much affected by the presence of pigments. On the other hand, the effect of the pigment concentration on the frequency factor A_q^0 is unambiguous. The frequency factor A_q^0 decreases over an order of magnitude as the PVC increases up to the CPVC. A_a^0 goes through a minimum at the CPVC. The activation energy ΔE_q is only slightly affected by the presence of pigments and variations might be due to the uncertainties associated with the measurements, although it seems to go through a minimum at a PVC of 31%. Figure 2 clearly shows that the diffusion properties are affected by the pigments, but it also



Figure 2 Fitting parameters from eq. (20) $(k_r, A_{nr}, \Delta E_{nr}, A_q, \Delta E_q)$ as a function of the Al₂O₃ PVC in the paint formulations #1–6.

shows that the Arrhenius parameters of the quenching rate constants are selectively affected by the presence of pigments. This very important selectivity could be exploited to design and predict properties of PSP with the addition of inorganic pigments such as aluminum oxide.

We showed in a previous paper¹³ that ideality of paints is achieved only over a narrow temperature range and is dependent mostly on the diffusion properties of oxygen in the coating. The plot of the ratio $B_T/A_T = \gamma(T)$ as a function of temperature of eq. (11) gives an idea of the temperature range where ideality of paint is achieved. Figure 3 shows the plots generated from eq. (11) using the parameters of Table II. In Figure 3, the effect of the glass temperature transition on the diffusion properties of the paint is not considered. We can see that for each sample, there is a fragment of the curve where the ratio B_T/A_T is almost independent of temperature. This is called the ITL and is defined as the temperature range where the ratio B_T/A_T is independent of temperature at $\pm 1\%$. Table I shows the ITL for paints with different amounts of pigments. We can see that paint #4 has the lowest ITL, from 11 to 161°C. It is important to note that this sample also has the lowest frequency factor A_q^0 (see Table II).

To verify those assumptions, we measured the temperature dependence of the different paints in vacuum and at atmospheric pressure from 10 to 50°C, the usual temperature range in wind tunnels. The comparison of the temperature dependencies at different pressures is a good indication of the ideality of the paint. Figure 4 shows the temperature dependencies $g_P(T, T_0) = I(P, T)/$ $I(P, T_0)$ of eq. (6) at atmospheric pressure for paint formulations #1, 2, 4, 6 and the temperature dependence of the luminescence in vacuum (which is independent of PVC). We can see that the temperature dependence of the intensity of luminescence varies greatly with PVC. Below CPVC (PVC \leq 31%), the presence of pigment decreases the temperature dependence of the luminescence intensity at atmospheric pressure and above CPVC, the temperature dependence of the luminescence intensity starts to increase again. This profile parallels the PVC dependence of the frequency factor of the oxygen diffusion in the polymer matrix, as shown in Figure 2. Figure 4 shows that the temperature dependence of the luminescence intensity can be fine-tuned from roughly 1.0 to 0.7%/°C by incorporation of inorganic pigment in the paint formulation. At a PVC of 31%, the temperature dependence of the luminescence intensity at atmospheric pressure is al-



Temperature (K)

Figure 3 Temperature dependence of the ratio B_T/A_T generated from eq. (11). The effect of the glass transition temperature is not considered.

Sample	#1	#2	#3	#4	#5	#6
Al_2O_3 PVC	0%	13%	27%	31%	36%	40%
$ \begin{array}{c} k_r ~(\mathrm{s}^{-1}) \\ A_{nr} ~(\mathrm{s}^{-1}) \\ \Delta E_{nr} ~(\mathrm{kJ/mol}) \\ A_q^0 ~(\mathrm{s}^{-1}) \\ \Delta E_q ~(\mathrm{kJ/mol}) \end{array} $	$1.06E^4$ $1.54E^6$ 15.0 $5.91E^7$ 12.0	$1.07{ m E}^4 \ 6.86{ m E}^5 \ 13.8 \ 2.45{ m E}^7 \ 10.5$	$1.04{ m E}^3$ $5.60{ m E}^5$ 12.3 $4.55{ m E}^6$ 5.9	$1.04{ m E}^3 \ 4.96{ m E}^5 \ 11.3 \ 3.12{ m E}^6 \ 5.8$	$1.03E^{3}$ $4.07E^{5}$ 11.0 $6.64E^{6}$ 6.5	$1.04E^4$ $3.35E^5$ 11.1 $1.01E^7$ 7.7

Table II Parameters Obtained from Temperature Dependence Data Fitted to eqs. (11) and (12)

most equal to the temperature dependence of the luminescence intensity in vacuum. This is called ideality. Ideality is attained when the temperature dependence $g_P(T, T_0)$ is independent of pressure. Thus we define percentage nonideality by

$$\% \text{NID}(T_N, T_1) \equiv [(N-1)^{-1} \sum_{T_j = T_1}^{T_j = T_N} (g_{\text{atm}}(T_j, T_0) - g_{\text{vac}}(T_j, T_0))^2]^{1/2} \times 100\% \quad (21)$$

where N is the number of data. Here T_0 is a particular temperature (we used 25°C). Note that $g_P(T_0, T_0) = 1$, which is why we use N - 1 in eq. (21). Summary of the percentages of nonideality for the samples studied are presented in Table I. We can see that the predicted ideality of paint #4 between 10 and 50°C is verified in Table I, because the percentage of nonideality is very low over this temperature range.

The response time of the paint is also an important characteristic for practical considerations. The response times were expected to be



Figure 4 Temperature-dependence $g_P(T, T_0)$ of eq. (6) for PtTFPP paint sample #1, 2, 4, and 6 at atmospheric pressure and the temperature dependence of luminescence in vacuum (independent of PVC).

affected by the presence of pigments, because the permeability of the polymer is reduced by addition of solid particles up to the CPVC (Table I). The response time is defined in this article as the time necessary for the intensity to complete 95% of the total change when pressure rises from I to 10^5 Pa. For example, the paint formulation #4 has a 95% response of about 145 ms, which is very short compared to wind-tunnel research needs. This short response time occurs at an even shorter time if the PVC < 31% = CPVC, where response time reaches its maximum (see Table I). This time is significantly longer than 60 ms shown by the pure polymer (sample #1). The inorganic particles restrain the diffusion of oxygen through the layer and therefore increase the response time of the paint. However, at PVC above CPVC, the coating contains voids filled with air that increases the diffusion rate of oxygen and thus lowers the response time.

The pigments can also influence the photostability of the probes incorporated in the polymer matrix. It is known that titanium dioxide is a powerful oxidation agent when irradiated with UV light. Paints prepared with titanium dioxide showed the same ideality profile with PVC as the paints prepared with aluminum oxide. However, paints using titanium dioxide as the pigment show a significantly higher photodegradation rate with time. Because the effect on the diffusion properties does not depend on the nature of the pigment but only on the PVC, any pigment could be used. The pigments used in this study, aluminum oxide, do not increase the photodegradation rate of the sensor, compared to paint without pigments. However, titanium dioxide could be used in paint formulations where the sensor is excited by a longer wavelength (>400 nm). A longer excitation wavelength would not promote the degradation of the paint containing titanium dioxide.

CONCLUDING REMARKS

We have shown in this article that the luminescence properties of pressure-sensitive paints can be modified and idealized by the addition of inorganic pigments. The ideality temperature limits of a low-cost and readily available silicone resin have been tailored to suit the particular needs of wind-tunnel research. Although the response time of luminescence is increased by the presence of pigments, it is shown that it still remains in the limit of the wind tunnel exigencies. We have demonstrated that the PSP luminescence characteristics can be designed a priori to fulfill prerequisites. Comprehension and control of the factors affecting the PSP characteristics facilitate the design of paint formulations and minimize trial and error experiments.

Funds for the support of this study were allocated by the NASA-Ames Research Center, Moffett Field, California, under Grant No. NAG 2-1157. M.G. acknowledges Dr. Sergei Ponomarev for first presenting the concept of ideality in pressure-sensitive paints and the role of PCV on response time. Colin Costin is gratefully acknowledged for helping in different parts of the project. Our apparatus was designed and set up by Sheldon Danielson and kept working by Eugen Schibli. Lisa Coyle helped set up the decay time studies.

REFERENCES

- 1. Gouterman, M. J Chem Educ 1997, 74, 697-702.
- Kavandi, J.; Callis, J.; Gouterman, M.; Khalil, G.; Wright, D.; Green, E. Rev Sci Instrum 1990, 61, 3340–3347.
- 3. Liu, Y.; Campbell, B. T.; Burns, S. P.; Sullivan, J. P. Appl Mech Rev 1997, 50, 227.

- 4. Gouin, S.; Gouterman, M. J Appl Polym Sci to appear.
- Bell, J. H.; McLachlan, B. G. AIAA Paper 1993, 93-0178.
- Le-Sant, Y.; Deleglisse, B.; Mebarki, Y. ICIASF 97 Record, International Congress on Instrumentation in Aerospace Simulation Facilities, Pacific Grove, CA; IEEE: New York, 1997; pp 57–65.
- 7. Ruyten, W. M. Rev Sci Instr 1997, 68, 3452-3457.
- 8. Ruyten, W. M. App Opt 1997, 36, 3079-3085.
- Bullock, J. P.; Baron, A. E.; Gouterman, M. in Flow Visualization VII. Proceedings of the Seventh International Symposium on Flow Visualisation, Crowder, J. P., Ed.; Begell House: New York, 1995; pp 795–799.
- Gallery, M. G.; Gouterman, M.; Callis, J.; Khalil, G.; McLachlan, B.; Bell, J. Rev Sci Instrum 1994, 65, 712–720.
- Woodmansee, M. A.; Dutton, J. C. Exp Fluids 1998, 24, 163–174.
- Schanze, K. S.; Carroll, B. F.; Korotkevitch, S. AIAA J 1997, 35, 306–310.
- Gouin, S.; Gouterman, M. J Appl Polym Sci 2000, 77, 2805.
- 14. Ware, W. R. J Chem Phys 1965, 43, 1194.
- Naylor, T. in Comprehensive Polymer Science, Vol. 2; Allen, G.; Bevington, J. C., Eds.; Pergamon: Oxford, England, UK, 1989; pp 643–668.
- Pauly, S. in Polymer Handbook, 3rd ed.; Bandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; pp VI435–449.
- Chapman, D. M.S. Thesis, University of Washington, Seattle, 1998.
- Yekta, A.; Zahra, M.; Winnik, M. A. Can J Chem 1995, 73, 2021–2029.
- 19. Stern, O.; Volmer, M. Phys Z 1919, 20.
- Smoluchowski, M. J Phys Chem 1917, 92, 129– 138.
- James, D. R.; Liu, Y. S.; DeMayo, P.; Ware, W. R. Chem Phys Lett 1983, 20, 460–465.