

Ideality of Pressure-Sensitive Paint. III. Effect of the Base-Coat Permeability on the Luminescence Behavior of the Sensing Layer

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Received 25 September 1999; accepted 15 January 2000

ABSTRACT: The response time and temperature dependence of a pressure-sensitive paint (PSP) based on platinum tetra(pentafluorophenyl)porphine (PtTFPP) in the fluoroacrylic polymer FIB significantly increases for bilayer paint systems that include a base coat made of different polymers with solid TiO_2 added as scattering agent, compared to the single-layer sensor paint. The temperature dependencies at vacuum are the same in the various bilayer coatings (paint/base coat) as compared to monolayer paint, roughly $-0.53\%/^{\circ}\text{C}$. With FIB base coat the percent of TiO_2 is adjusted to reduce photodegradation, in which case only a slight increase in response time ($0.6 \rightarrow 0.8$ s) is caused by the base coat and there is almost no change in temperature dependence at 1 atm. However, in the cases of the less permeable polymers, poly(methylmethacrylate) (PMMA) and poly(vinyl acetate) (PVA), there is increased response time of the bilayer coating (rising, respectively, to 15 and 7 s) and significantly greater temperature dependence at 1 atm. The highly impermeable polyacrylonitrile (PAN) as base coat shows little effect on response time but a somewhat higher temperature dependence at 1 atm compared to vacuum. For the highly permeable polydimethylsiloxane (PDMS), adjustment of the TiO_2 concentration is needed to prevent an increase in temperature dependence but both PDMS base coats tested have response times < 2 s and low-temperature dependence. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2815–2823, 2000

Key words: pressure-sensitive paint; luminescence

INTRODUCTION

Pressure-sensitive paints (PSP) have become a useful tool in aerodynamic research^{1–5} and many different paint formulations have been developed.^{1,3,6,7} Continuous mappings of pressure at the surface of the foil are obtained at a fraction of the cost usually spent on conventional pressure mapping. However, the superiority of the PSP over the traditional method is not yet ensured because some remaining problems affect the ac-

curacy. These problems include photodeterioration of the paint,¹ self-illumination,^{8,9} slow response time,^{6,10} movement of the model during analysis,¹¹ and the inherent temperature dependence of PSP.^{12–14} These factors induce significant errors on the pressure values determined by PSP and restrain the use of PSP in quantitative experiments.

The accuracy of the measurements obtained with PSP directly depends on the uniformity and reproducibility of the conditions in the wind tunnel. Temperature of the model and gradient of temperature on the model have a significant influence on the results. Uniformity of the model surface is also crucial for accurate results. Intensity of light emitted in the direction of the detec-

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

Journal of Applied Polymer Science, Vol. 77, 2815–2823 (2000)
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tor is, to some extent, related to the nature of the substrate and its intrinsic reflectivity. Wind-tunnel research often uses materials such as *Bondo* (e.g., Keylite, Pomona, CA), wax, plaster, etc., on the model, and significant errors are induced due to reflectivity variation of the different substrates. Therefore, a uniform base coat must be used to minimize substrate-related errors. However, it has been shown that the base coat is generally not inert but seriously affects the functionality of the PSP.^{15,16}

Our laboratory has shown that the base coat can modify the response time of the paint to a pressure change.¹⁵ A reservoir model was invoked for the explanation of the substrate effect on the response time of the luminescence. The oxygen concentration dissolved in the sensing layer, and therefore the intensity of emitted light, is related to the partial pressure of oxygen on the surface and is involved in a dynamic equilibrium:



When a base coat is used in the system, the dynamic oxygen equilibrium in the sensing layer is influenced by the exchange rate between air and the PSP and also by the exchange rate between the base coat and the PSP:



The response time is the time necessary for the system to reach equilibrium and to have a constant intensity of emitted light. Equation (2) shows that the response time is closely related to the intrinsic diffusion properties of the base-coat polymer.

Moreover, it is known that the base coat also has a significant effect on the temperature dependence of the PSP luminescence.¹⁷ This topic is very important because it may alter the ideality of the paint and therefore restrain the utilization of PSP in quantitative analysis. Ideality is defined as an independent effect of pressure and the temperature on the luminescence of the sensing layer and is carefully defined in Paper II of this series¹²:

$$\frac{I(P_0, T_0)}{I(P, T)} \approx \frac{f(P, P_0)}{g(T, T_0)} \quad (3)$$

where $I(P_0, T_0)$ is the emission intensity monitored in some standard condition. In the wind tunnel this is generally ambient pressure and

temperature with wind-off, and it represents the intensity monitored at a single pixel in the charge coupled device (CCD) camera. $I(P, T)$ is the intensity monitored during wind-on conditions. (In this article, we neglect any effects of model motion between wind-off and wind-on.) Here P is the variable to be measured, and T has often drifted away from T_0 . The functions $f_T(P, P_0)$

$$f_T(P, P_0) \equiv \frac{I(P_0, T)}{I(P, T)} \quad (4)$$

are a set of functions that represent the variation of intensity as a function of pressure when monitored at constant temperature (T) using the intensity at P_0 as a reference. The functions

$$g_P(T, T_0) \equiv \frac{I(P, T)}{I(P, T_0)} \quad (5)$$

are a set of functions that represent the temperature variation at constant pressure (P) using the intensity at (T_0) as a reference. Now the ideality condition eq. (3) means that one function $f(P, P_0)$ and one function $g(T, T_0)$ adequately represents all functions of their respective sets. Ideality holds for only a limited class of PSP formulations. The ideality of a PSP allows easier temperature correction and thus facilitates utilization of PSP as an accurate, autocalibrated quantitative method for aerodynamic research.

Temperature dependence of PSP was studied and showed that the temperature dependence of the oxygen diffusion through polymer has a significant contribution to the overall temperature sensitivity of the PSP.^{12,13} The diffusion of gases in polymer is an activated process and can be described by an activation energy and a frequency factor.¹⁸ Other contributions to the temperature sensitivity come from the temperature dependence of the radiationless decay rate and the temperature dependence of the triplet yield. In a previous article,¹² we show that the temperature dependence of the emission intensity of the paint can be described by:

$$\begin{aligned} I_{em} &= D_a \left(\frac{k_r \Phi^*(T)}{k_r + k_{nr} + \kappa_q [\text{O}_2]} \right) \\ &= D_a \left(\frac{k_r \Phi^*(T)}{k_r + A_{nr} e^{-\Delta E_{nr}/RT} + A_{q} e^{-\Delta E_q/RT}} \right) \quad (6) \end{aligned}$$

Here $\Phi^*(T)$ is the yield under constant illumination of the metastable state (S^*), which is created

by photoexcitation and is quenched by oxygen, and the notation $\Phi^*(T)$ indicates that this yield may be a function of temperature (T); k_r and k_{nr} are the radiative and radiationless decay rates; κ_q is the bimolecular quenching decay rate; T is the temperature; and D_a is the apparatus constant. In eq. (6), we substituted the Arrhenius form for the decay constants, where A_{nr} and A_q are temperature-independent frequency factors of the radiationless and quenching decay rates, respectively; ΔE_{nr} and ΔE_q are the activation energies of the radiationless and quenching decay rates, and R is the ideal gas constant. We should note that in the Henry's Law model

$$A_q = A_q^0 \left(\frac{P}{P_0} \right) \quad (7)$$

A_q is the term that gives the dependence on pressure,¹² where A_q^0 is the frequency factor at P_0 and is independent of pressure and temperature.

We can see that the diffusion properties of the polymer used in the base-coat formulation might have an impact on the luminescence behavior of the PSP. The diffusion properties of the base coat are affected by the presence of inert pigment in the paint formulation.¹⁹ Diffusion coefficients generally decrease with addition of pigment and go through a minimum at the critical pigment volume concentration (CPVC). (See Appendix for definition.) At higher concentration, the diffusion coefficient generally increases with the addition of pigment.

Generally, the base coats are comprised of polymer and white pigment, such as titanium dioxide. Titanium dioxide is used for its high refractive index and high hiding power. However, titanium dioxide is somewhat reactive and can photooxidize organic compounds when irradiated with wavelengths shorter than 390 nm.²⁰

In this article, we report the results concerning the effect of different base coats on the ideality of a PSP, which consists of platinum tetra(pentafluorophenyl)porphine (PtTFPP) dissolved in FIB, a copolymer of hexafluoroisopropyl and heptafluoro-*n*-butyl methacrylate.²¹ The effect of the pigment volume concentration (PVC) is also studied and related to the ideality of the PSP. Other properties such as response time and photodegradation are also studied.

EXPERIMENTAL

PSP Preparation

The pressure-sensitive paint (top coat) is comprised of PtTFPP, purchased from Porphyrin Products (Logan, UT), dissolved in FIB. The paint uses the solvent *p*-chlorotrifluorotoluene (made by Occidental Chemical Corp. (Dallas, TX) under the trade name of Oxsol-100). The typical formulation is 5 mg of PtTFPP for each gram of polymer, dissolved in 25 mL of solvent.

FIB Base-Coat Preparation

The FIB base coat is prepared by dissolving 2.5 g of polymer in 35 mL of *p*-chlorotrifluorotoluene and then by adding the desired amount of treated titanium dioxide. Base-coat formulations with a PVC (see Appendix) of 24 and 45% were prepared by adding 2.2 and 4.0 g of pigment, respectively. The paint is then ballmilled for 48 h or blended (in a household Osterizer blender) at *purée* for 30 min.

PMMA Base-Coat Preparation

The polymethylmethacrylate (PMMA) base coat was prepared in a similar way as the FIB base coat, but the *p*-chlorotrifluorotoluene was replaced by tetrahydrofuran (THF), because the polymer is only slightly soluble in the former. The PMMA used was purchased from Aldrich and has an average molecular weight in number of 86 kDa. The PMMA formulation has a PVC of 25% and is comprised of 2.8 g of titanium dioxide and 2.5 g of PMMA dissolved in 35 mL of THF.

PAN Base-Coat Preparation

The polyacrylonitrile (PAN) was prepared in a different way, because PAN is not soluble in common solvents or solvents that can be used in the paint industry. Therefore, a suspension paint was prepared. The polymer powder was mixed with nitromethane (Aldrich, Milwaukee, WI) and the particles were divided finely by the use of an ultrasound bath. The mixture was kept at 40°C in the bath for at least 1 h with continuous and vigorous agitation. The resulting suspension is free from deposit and is opaque. Titanium dioxide is then added in the mixture and the paint is ballmilled for 48 h. The PAN formulation is 2.8 g of titanium dioxide, 2.5 g of PAN, and 35 mL of solvent.

PVA Base-Coat Preparation

The polyvinyl acetate (PVA) base coat was prepared in a similar way as the FIB base coat, but the polymer-solvent mixture was heated at 50°C for 1 h, to complete the dissolution of the polymer. The PVA formulation is 2.8 g of titanium dioxide, 2.5 g of PVA, and 35 mL of *p*-chlorotrifluorotoluene.

Silicone Base-Coat Preparation

The silicone solutions (SR-900) were purchased from GE Silicones (Pittsfield, MA) and consist of polysiloxane dissolved in xylene. The solution was first diluted four times with *p*-chlorotrifluorotoluene and mixed carefully. Titanium dioxide was then added and the paint was ballmilled for 48 h. The silicone formulation is 4 mL of silicone solution, 12 mL of *p*-chlorotrifluorotoluene, and 1.1 or 1.8 g of titanium dioxide for a PVC of 27 and 45%, respectively.

Sample Preparation

The base coat was sprayed consecutively on medium (6.5 cm²) and small (1 cm²) square clean aluminum coupons. The samples were then annealed at 100°C for 30 min. Layers approximately 12–15- μ m thick were generally obtained. The samples were then sprayed with top coat (PtTFPP in FIB) and dried again at 100°C for 20 min. Samples with total thickness between 20 and 25 μ m were obtained.

Sample Analysis

The intensity of the luminescence as a function of temperature and pressure was measured with a home-made apparatus comprised of a tungsten lamp and a pressure- and temperature-controlled chamber designed and constructed in our laboratory. The excitation light was filtered through a 390 narrow band pass filter (20 nm width at half-height) and the emission light received at the detector was filtered through a 645 narrow band pass filter (20 nm width at half-height). The large coupons were used in this apparatus. The response time of the paint was measured with a fast pressure jump apparatus described earlier.²² Briefly, the apparatus is comprised of a small sample chamber (\sim 2 mL), three solenoid powered valves, a tungsten lamp, and the same set of filters used in the intensity apparatus. The pressure jump apparatus can measure response times

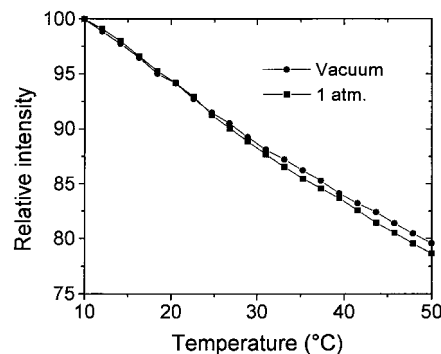


Figure 1 Temperature dependence of the intensity of PtTFPP in FIB film, without base coat. The lines simply connect data points.

as short as \sim 10 μ s. The small coupons were used in this apparatus.

RESULTS AND DISCUSSION

The preparation of the sample is crucial to obtain accurate and reproducible results. As described in a previous article,¹² the annealing procedures affect significantly the luminescence properties of the PSP and the optimal annealing temperature is shown to be above T_g of the polymer used in the paint. The samples were annealed after spraying the base coat to remove remaining solvent and also annealed after spraying the top coat. The samples were annealed at 100°C for 30 min each time. The annealing temperature was chosen to be above the T_g of every polymer used in this study. The base-coat layer for each sample was approximately 10 μ m and the top-coat layer was approximately 8 μ m. Similar overall thicknesses for each sample were obtained. The PAN base coat gave a somewhat rougher surface than the other base coat, because PAN is not soluble in the solvent chosen. The roughness of the PAN base coat was about 2 μ m, and the roughness of the other base coats was between 0.5 and 1.1 μ m.

The temperature dependence of the luminescence was measured for every sample at vacuum and at atmospheric pressure. Figure 1 shows the temperature dependence of the luminescence for a sample with a PtTFPP/FIB layer and no base coat. We can see that the luminescence behavior of the paint is nearly ideal, because the vacuum and the atmospheric curves are almost the same. Percent nonideality (%NID) may be quantified by the use of

Table I Percentage of Nonideality and Response Time of the Different Basecoats Tested (thickness of basecoat is around 12–15 μm and thickness of top coat is around 8–10 μm)

Base-Coat Polymer	PVC ^a	%NID ^b	Response Time (s) ^c	Permeability ^d
No base coat	—	0.35	0.6	
FIB	25	0.45	0.8	2.1×10^{-12}
PMMA	25	8.91	15	1.16×10^{-14}
PVA	25	11.52	7	6.65×10^{-16}
PAN	25	2.15	0.9	1.15×10^{-17}
SR-900	44	2.68	1.1	
	27	0.36	1.9	$\approx 3 \times 10^{-11}$

^aCPVC of the TiO_2 used in this study is 35%.

^bFrom 10 to 50°C.

^cTime to complete 95% of the total intensity drop after a fast pressure jump.

^dUnits: cm^3 (STP) $\text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.

$$\% \text{NID}(T_N, T_1) = \left[(N - 1)^{-1} \sum_{T_j=T_1}^{T_j=T_N} (g_{\text{atm}}(T_j, T_0) - g_{\text{vac}}(T_j, T_0))^2 \right]^{1/2} * 100\% \quad (8)$$

where N is the number of data and $g_P(T, T_0)$ represents the temperature variation of intensity at pressure (P) as defined in eq. (5). Here T_0 is a particular reference temperature for $g_P(T, T_0)$ (we used 25°C). Note that $g_P(T_0, T_0) = 1$ at all pressures, which is why we use $N - 1$ in eq. (8). Summary of the percentages of nonideality for the samples studied are presented in Table I. The ideality of this paint formulation has been explained in Paper II¹² by the low-activation energy of the oxygen diffusion through FIB. The fast diffusion of oxygen through the paint layer is also responsible for the relatively short response time of the paint to a pressure change. Figure 2 shows

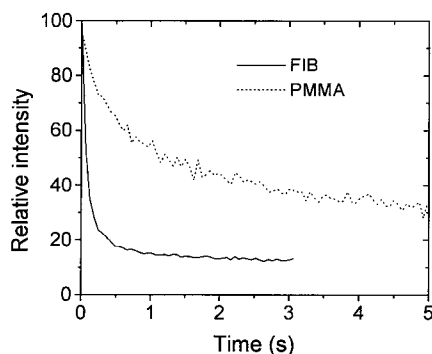


Figure 2 Luminescence intensity of PtTFPP in FIB on a FIB base coat and a PMMA base coat as a function of time after a pressure drop.

that the luminescence is quenched very rapidly after a pressure jump from 10^{-1} to 760 Torr. The luminescence has completed 95% of its total intensity drop after 0.6 s. These characteristics make the PtTFPP/FIB paint a good candidate for eventual quantitative PSP measurement. However, a base coat is needed for such measurements, and several different base coats have been evaluated according to their inertness regarding the luminescence behavior of the PSP layer.

As explained earlier, the diffusion properties of the polymer are important characteristics to consider in the development of a base coat for PSP measurements. The oxygen diffusion is related to the quenching rate^{12,13,23} and is the predominant contribution to the temperature dependence of luminescence at atmospheric pressure. The diffusion profile and the oxygen concentration in the sensing layer as a function of time are complex, because the two boundaries of the sensing layer (air and base coat) do not have the same diffusion properties [see eqs. (1) and (2)]. No quantitative explanation will be proposed, although it would be possible to use the Fickian equations of diffusion with two boundaries to analyze the data, but the main interest here is the study of the effect of different base coats on the temperature dependence of the luminescence. A very impermeable polymer with a small diffusion coefficient might have a negligible effect compared to the oxygen diffusion coefficient in FIB and therefore might have no practical impact on the temperature dependence of the paint. On the other hand, a temperature dependence of the oxygen diffusion in the base coat similar to the one in the top coat

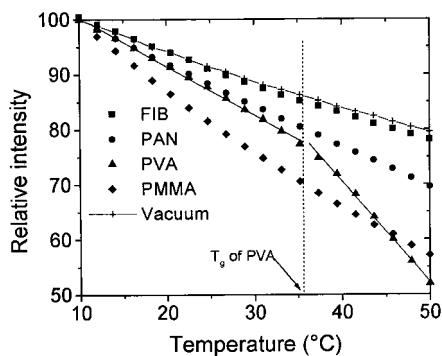


Figure 3 Temperature dependence of the intensity of PtTFPP in FIB film sprayed on various base coats.

would also have only a small impact on the ideality of the PSP. Therefore, different polymers have been chosen according to their extreme diffusion parameters and evaluated as an undercoat for PSP measurements.

First, the FIB polymer has been evaluated as the binder in the base coat. At first sight, it does not seem propitious to use the same polymer in the base coat, because the addition of pigment would alter the diffusion properties and a different temperature dependence of the oxygen diffusion would be expected. However, many different formulations have been tested. We noticed that at higher PVC (45%), problems such as photodegradation of the pressure probe arise. Therefore, the formulation retained includes titanium dioxide at a PVC of 27%, which is a good compromise between the hiding power and the photodegradation rate. Photodegradation becomes a problem when using base coats with a titanium dioxide PVC over the CPVC. Above CPVC, there is not enough binder in the base coat to cover every particle and some of the top-coat polymer is sucked, along with its sensor, into the base coat. The mixing of the well-known photoactive TiO_2 and the sensor sucked into the base coat promotes the photodegradation of the latter. Therefore, the use of a TiO_2 PVC below the CPVC in the base coat can prevent, or minimize, the photodegradation of the pressure sensor. The temperature dependence of the luminescence at atmospheric pressure for a sample painted over a FIB base coat is shown in Figure 3. We can see that the temperature dependence of the PSP is not much influenced by the base coat, but one can notice a small deviation at high temperature. The percentage of nonideality (0.45%) is close to what is obtained without base coat (0.35%). It seems that, contrary to what was

expected, the influence of the pigment on the diffusion properties in FIB is small even if the concentration of titanium dioxide is relatively high.

The most impermeable polymer tested was PAN, which has a permeability coefficient of 1.5×10^{-17} (in usual units) for oxygen.¹⁹ [The permeability has units of [(amount of permeant)(film thickness)]/[(area)(time)(pressure drop across the film)] and are expressed in cm^3 [standard temperature and pressure (STP)] $\text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.] We thought that very low permeability of this polymer would restrain sufficiently the diffusion of oxygen in the base coat and thus would have a negligible impact on the luminescence of the sensing layer. Figure 3 shows the temperature dependence of the sensing layer applied on a PAN base coat containing titanium dioxide at a PVC of 25%. The percentage of nonideality does increase with this polymer base coat (2.15%), but it remains low as expected for a low-permeable polymer. The temperature dependence of the luminescence at atmospheric pressure, directly related to the diffusion properties of the polymer, is close to what is obtained without base coat. However, a small deviation remains at higher temperature. Moreover, the PAN base coat has an inherent problem because of its high insolubility in common organic solvents. Accordingly, a suspension paint formulation has been used, but the mechanical properties are not acceptable for the wind-tunnel research. The roughness, the apparent friability of the coating, and the inhomogeneity of the paint are not acceptable.

Another highly impermeable polymer, but with better solubility characteristics, has been evaluated. PVA has a permeability coefficient of 6.65×10^{-16} for oxygen.¹⁹ This polymer is soluble in *p*-chlorotrifluorotoluene and acceptable mechanical properties (roughness and adhesion) were obtained. The temperature dependence of the sensing layer applied over a PVA base coat containing titanium dioxide at a PVC of 25% is shown in Figure 3. The atmospheric curve shows two distinct parts and an inflection point at about 30°C. This observation was confirmed by a F-test conducted on the atmospheric curve for a parabolic fitting and a double distinct linear fitting. The variance of parabolic fitting is greater than the variance of the double linear fitting with an F ratio of 3.05 with 20 points. That means that the parabolic fitting does not give a better fitting than the double linear fitting at a 0.5% significance level.²⁴ Figure 3 shows the double linear fitting of the temperature dependence: at low temperature

(from 10 to 30°C), the temperature dependence is about $-0.75\%/^{\circ}\text{C}$ and above 30°C, the temperature dependence is about $-2\%/^{\circ}\text{C}$. This peculiar characteristic is related to the glass transition temperature (T_g) of PVA, which is about 35°C. Below T_g , the polymer is in a glass state and the diffusion of oxygen is very slow. At higher temperature, the polymer becomes more flexible and thus the diffusion of oxygen, which involves the cooperation of the polymer chains, becomes easier. The small temperature dependence below T_g is probably due to the very small diffusion coefficient of the base coat compared to the topcoat, as discussed earlier. Above T_g , the diffusion coefficient is not negligible and the high temperature dependence of oxygen diffusion in PVA is the cause of the higher slope observed in Figure 3. This example shows the dramatic effect of the T_g on the diffusion properties and the temperature dependence of the diffusion coefficient. The overall percentage of nonideality obtained (11.52%) is very large and is not acceptable.

PMMA has a permeability coefficient for oxygen of 1.16×10^{-14} .¹⁹ This permeation coefficient is significantly higher than PAN, but is still one of the lowest among common vinylic polymers. The temperature dependence of the luminescence for a sample painted over a PMMA base coat is shown in Figure 3. The very large difference between the temperature dependence at vacuum and at atmospheric pressure is reflected in the high percentage of nonideality (8.91%). The temperature dependence of the luminescence at atmospheric pressure for the PMMA sample is very high compared to the temperature dependencies of the other impermeable base-coat samples. The temperature dependence at atmospheric pressure for the PMMA sample is $-1.06\%/^{\circ}\text{C}$, whereas the temperature dependencies for PVA and PAN are -0.75 and $-0.70\%/^{\circ}\text{C}$, respectively. The diffusion coefficient of PMMA is also higher than that of PVA or PAN. This is further evidence that the luminescence properties of the PSP are directly related to the oxygen diffusion coefficient of the polymer used in the base coat.

A very permeable polymer has also been evaluated as the binder in the base-coat formulation. Polysiloxanes are well known for their diffusion characteristics and are used in many PSP formulations as the binder in the sensing layer.^{13,15} The permeability coefficient of oxygen in polydimethylsiloxane (PDMS), for example, is substantially higher than that of the preceding polymers and has a value of about 3.67×10^{-11} .¹⁹ The temper-

ature dependence of the luminescence for a sample sprayed on a silicone base coat containing titanium dioxide at a PVC of 45% is about $-0.69\%/^{\circ}\text{C}$ at atmospheric pressure. The paint luminescent behavior is near to ideality, with a percentage of nonideality of 2.68%. A similar base coat has been prepared with a lower PVC. The temperature dependence of the luminescence at atmospheric pressure for the sample painted over a 27% PVC silicone base coat is $-0.56\%/^{\circ}\text{C}$. The ideality of this PSP formulation is complete; the paint has almost the same temperature dependence at vacuum and at atmospheric pressure. The percentage of nonideality (0.36%) is very close to that which is obtained without base coat and shows that the base coat has barely any effect on temperature dependence of the sensing layer. This serendipitous characteristic was not predictable because a detailed theoretical model is not yet available. However, an *a posteriori* explanation might involve the right proportion of titanium dioxide added in the paint formulation. The diffusion coefficient obtained for a 27% PVC silicone base coat might be such that the temperature dependence of the oxygen diffusion in this particular base coat is the same as the temperature dependence of the oxygen diffusion in FIB.

It is interesting to note that the temperature dependencies of the luminescence in vacuum for each sample, whatever the base coat used, are almost identical. The temperature dependencies of the luminescence in vacuum vary from -0.52 to $-0.54\%/^{\circ}\text{C}$ among all the samples studied. On the other hand, the temperature dependence of the luminescence at atmospheric pressure varies from -0.52 to $-2.0\%/^{\circ}\text{C}$ among the samples tested. It is obvious that the problems induced by the base coat come from the diffusion of oxygen in the base-coat layer or, more precisely, from the difference of the oxygen diffusion in the two layers. The selection of a base coat for a particular PSP is therefore not a simple task because no theoretical work has been published yet.

The base coat not only affects the temperature dependence of the luminescence, but affects also the response time of the sensing layer. As explained earlier, the response time is related to the rapidity with which the equilibrium of the oxygen concentration in the sensing layer is reached. The response time has been quantified as the time needed for the luminescence to complete 95% of the total intensity drop. The response time for a sample without base coat is about 0.6 s. The response time of a sample sprayed on FIB base coat

is about 0.8 s. Very long response times are generally obtained with impermeable base coat and response times around 10 s have been measured for PMMA and PVA. The response time of the paint with a PMMA base coat is shown in Figure 2. The response time is thought to be around 15 s, but a precise value is hard to obtain, because the sample takes a long time to reach equilibrium after a pressure change (probably many minutes). The response time of the PAN base-coat sample seems to be very short, but it is impossible to compare with the other samples. The short response time observed is probably a result of the inhomogeneity of the coating surface, which seems to be very porous when observed under a microscope. Response times obtained with silicone or FIB base coats are generally acceptable and vary from 0.8 to 1.9 s. The response time is thought to be dependent on the thickness, but the samples used in this study were of comparable thickness, between 20 and 25 μm . The lower limit is probably the intrinsic response time of PtTFPP in FIB, which is around 0.6 s.

CONCLUSIONS

We have shown that the base coat affects significantly the luminescence properties of the PSP and that ideality can only be obtained with a base coat specifically designed for the sensing layer used. It has been shown that the base coat does not affect the temperature dependence of the luminescence of the PSP in vacuum, but has a large effect at atmospheric pressure. Therefore, the base-coat effect is thought to be the result of the difference in the diffusion characteristics between the base coat and the PSP. Although a full theoretical treatment has not been carried out, the results in this article suggest that the base coat greatly increases the PSP response time to pressure change if the permeability of the base coat is much less than that of the paint layer. Furthermore, this increased response time of a paint/base-coat system is associated with an increase in the temperature dependence at 1 atm, hence a loss of ideality compared to the monolayer paint. These findings should reduce the trial and error testing required to develop ideal paint/base-coat systems with lower temperature dependence and short response times.

Funds for the support of this study were allocated by the NASA-Ames Research Center, Moffett Field, California, under Grant No. NAG 2-1157. Dr. Sergei

Ponomarev is thanked for first presenting the concept of ideality in pressure-sensitive paints. Eileen Puklin and Colin Costin are gratefully acknowledged for providing the FIB polymer. 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.

APPENDIX

Pigment Volume Concentration (PVC)

PVC is a measure of the pigment concentration in the dry coating. It is defined by:

$$\text{PVC} = \frac{(m_{\text{pigment}}/\rho_{\text{pigment}})}{(m_{\text{pigment}}/\rho_{\text{pigment}}) + (m_{\text{binder}}/\rho_{\text{binder}})}$$

where m is the mass and ρ is the density in g/cm^3 . The CPVC is defined as the maximum pigment concentration at which all pigment particles are completely covered by the binder. Above CPVC, there is not enough binder to cover all the particles and voids are filled by air bubbles. The CPVC of a pigment is independent of the binder characteristics but depends on the particle size and characteristics.²⁵ CPVC of titanium dioxide ranges typically from 35 to 55%, whereas CPVC of aluminum oxide is usually around 30%.

Ballmilling is a procedure used to separate the pigment aggregates. This procedure homogenizes the distribution of the pigments in the paint. Aggregation of pigments changes the PVC, the hiding power of the paint, and many other characteristics.²⁵

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