Abstract
Pressure-sensitive paints (PSP) have recently been extended to high-frequency flowfields. Paint formulations have effectively been used to characterize pressure fluctuations on the order of 100 kHz. As the limits of PSP are extended, various experimental results indicate that the unsteady response characteristics are non-linear. A thorough understanding of the photo physical mechanisms in paint response is needed. Gas transport properties, coupled with the non-linear nature of the Stern-Volmer relationship have an effect on the paint response. This work extends a diffusion-based model to porous paints, and incorporates the highly non-linear nature of porous PSP calibrations. Based on this model, it is shown that the indicated pressure response of PSP is typically faster for a decrease in pressure than a corresponding increase. Effects of other factors, such as pressure-jump magnitude, pressure-jump range, and Stern-Volmer non-linearity, are evaluated. Furthermore, a fluidic oscillator is used to experimentally demonstrate the quenching kinetics of anodized aluminum PSP. Results from the oscillator operated with argon, nitrogen, and oxygen gases demonstrate behavior that agrees with the diffusion model.

Introduction
Pressure-sensitive paint (PSP) has recently emerged as a powerful measurement tool for global pressure distributions. PSP is an optical method for measuring surface pressures based on the principle of oxygen quenching of a luminescent molecule. Recent reviews by Bell et al. and Liu et al. have summarized the PSP technique and common applications.

Even more recently, the development of porous PSP formulations has allowed measurement of unsteady pressures in flowfields with frequency content on the order of 100 kHz. Common binders in use today for unsteady measurements are thin-layer chromatography plate (TLC-PSP), anodized aluminum (AA-PSP), polymer/ceramic (PC-PSP), and poly(TMSP). Dynamic calibrations with a shock tube and a fluidic oscillator have shown that porous PSP formulations have typical frequency responses in excess of 40 kHz. Unsteady pressure fields such as the fluidic oscillator, a turbocharger compressor, or the oscillating shock in a Hartmann tube have been characterized. Some of these experimental results apparently indicate that the dynamic response of PSP is non-linear. Experimental results suggest that the response to an increase in oxygen concentration may be slower than the response to a corresponding increase in nitrogen concentration.

The purpose of this paper is to develop a model for the quenching dynamics of pressure-sensitive paint. The implications of the model on the dynamic response of PSP are discussed. Furthermore, it will be shown that the diffusion-based model is applicable to porous PSP formulations. Experimental results from the fluidic oscillator will illustrate the effects of the quenching dynamics and will be compared with the theoretical model.

Background
Polymer chemists have done a large amount of experimental and theoretical work on the quenching kinetics of luminescent molecules immobilized in a polymer binder. It has been known for quite some time that the luminescent response of a luminophore in a polymer matrix is different for oxygen sorption or desorption experiments. Chemists have used these observations, along with simple diffusion models to determine the diffusivity of a polymer film. The first known published work involving this method was the work of MacCallum and Rudkin. Cox and Dunn also published some early work involving this method. Carraway et al. discussed the kinetics of quenching due to several possible models, including pure diffusion, adsorption, and other combinations of models. Perhaps the clearest explanation of the diffusion model and its interaction with the Stern-Volmer relation is given by Mills and Chang. Subsequent researchers have used the diffusion modeling technique extensively, and most report a fast luminescent response to oxygen sorption, and a slower response to oxygen desorption.
Within the field of PSP research, there has been some work done to model and experimentally determine the dynamic response characteristics of pressure-sensitive paints. Liu, et al.\textsuperscript{33} have used a diffusion-based model with porous paints, lending credence to the current use of a diffusion model with anodized aluminum PSP. Schairer\textsuperscript{34} also employed a diffusion model in his analysis of optimum thickness of a PSP layer, which he found to be a tradeoff between signal-to-noise ratio and dynamic response. Carroll, et al.\textsuperscript{35} modeled the PSP step-response with a diffusion-based model, and compared the response times of three different polymer-based PSP formulations. Winslow, et al.\textsuperscript{36} then further developed the model to compensate for delay in PSP response. Winslow demonstrated that the indicated pressure will respond quicker to a step-decrease in pressure. Although these models have shown the basic behavior of the quenching kinetics of PSP, an exhaustive evaluation of the PSP dynamics is needed. The effects of factors such as the pressure-jump magnitude, the range over which the jump occurs, the direction of the pressure jump need to be evaluated.

Stern-Volmer Quenching Model

Model Development

The response of the PSP may be modeled by considering the diffusion of oxygen into or out of the binder. It is assumed that the diffusion process, rather than the much faster luminophore quenching process, controls the paint response characteristics. If the paint layer is thin and uniform, the oxygen diffusion is assumed to be one-dimensional and Fickian,\textsuperscript{37} expressed as

\[ \frac{\partial [O_2]}{\partial t} = D_m \frac{\partial^2 [O_2]}{\partial z^2} \] (1)

where \([O_2]\) is the oxygen concentration, \(D_m\) is the diffusivity of oxygen (assumed constant), \(t\) is time, and \(z\) is distance measured from the paint surface. Fickian diffusion also assumes that there is no mass convection present in the flow. In addition, the time scales of adsorption effects are assumed to be negligible relative to the diffusion and unsteady pressure time scales. The boundary conditions for the diffusion equation are

\[ \frac{\partial [O_2]}{\partial z} = 0 \text{ at } z = h \] (2)

and

\[ [O_2] = [O_2]^0 f(t) \text{ at } z = 0 \] (3)

where \(h\) is the paint thickness, \(f(t)\) is a function describing the variation with time of oxygen concentration at the paint surface, and \([O_2]^0\) is a reference oxygen concentration (constant). The physical model is shown in the diagram in Figure 1.

The diffusion equation may be rewritten as

\[ \frac{\partial n}{\partial t'} = \frac{\partial^2 n}{\partial z'^2} \] (4)

with boundary conditions

\[ \frac{\partial n}{\partial z'} = 0 \text{ at } z' = 0, \]

\[ n = g(t') \text{ at } z' = 1, \]

\[ n = 0 \text{ at } t' = 0 \]

by using the non-dimensional variables

\[ n(t', z') = \left[ O_2 \right] / \left[ O_2 \right]_0 - H(t), \]

\[ z' = z/h, \]

\[ t' = t D_m / h^2. \]

A function \(g(t') = f(t') - f(0)\) is used to satisfy the initial condition \(g(0) = 0\). This differential equation (Equation 4) is solved with the Laplace transform. When the boundary conditions (Equation 5) are applied, a general convolution solution is obtained for the non-dimensionalized oxygen concentration

\[ n(t', z') = \int_0^t g(t' - u) W(u, z') du. \] (7)

The function \(g(t)\) is the derivative \(\frac{\partial g(t)}{\partial t}\), and \(W(t, z)\) is defined as

\[ W(t, z) = \sum_{n=0}^{\infty} \left( -1 \right)^n e^{-\frac{1 + 2k + z}{2t}} \] (8)

For a step change increase in oxygen concentration at the paint surface, the function \(g\) is defined as the delta function, \(g(t) = \delta(t)\), which gives

\[ n(t', z') = W(t', z'). \] (9)

Analogously, a step change decrease in oxygen concentration is given by

\[ n(t', z') = -W(t', z'). \] (10)

From Equations 9 and 10, it can be seen that there is no difference in the time scale of diffusion, whether oxygen is diffusing into or out of the paint binder. The oxygen concentration profiles for several time steps are shown in Figure 2 – diffusion into the paint binder, and Figure 3 – diffusion out of the paint binder.

The key to the difference in time scales of the PSP response is in the characteristic non-linearity of the Stern-Volmer calibration curve. The Stern-Volmer relation may be expressed as

\[ \frac{I}{I_0} = \frac{1}{1 + K [O_2]_0} \] (11)

where \(I\) is intensity, \(K\) is a calibration constant (assuming constant temperature), and the subscript 0 indicates the complete absence of oxygen. A typical plot of the Stern-Volmer relation, with \(K=10\), is shown in Figure 4. The highly non-linear nature of the
intensity response to a change in pressure is the primary cause of PSP dynamic response differences. The rate of change of paint intensity per unit pressure is higher at low pressures, and somewhat lower at high pressures. Therefore, the variation in PSP response will depend on the non-linearity of the PSP calibration curve.

The form of the Stern-Volmer equation typically used for PSP calibrations, given as

$$\frac{I_{ref}}{I} = A \frac{P}{P_{ref}} + B,$$  \hspace{1cm} (12)

is obtained by taking the ratio of Equation 11 at two conditions – a reference and a test condition. When Equation 11 is compared with the Stern-Volmer form used for PSP calibrations (Equation 12), the value of $K$ can be derived as

$$K = \frac{A}{B[O_2]_{ref}},$$ \hspace{1cm} (13)

since the concentration of oxygen in air is proportional to the air pressure. A variation of Equation 12 is the Stern-Volmer relation following the Freundlich Isotherm, namely

$$\frac{I_{ref}}{I} = A \left( \frac{P}{P_{ref}} \right)^\gamma + B.$$ \hspace{1cm} (14)

This calibration behavior is characteristic of porous PSP formulations, particularly anodized aluminum PSP. Typical PSP calibration curves for $\gamma=1.0$ and $\gamma=0.1$ are shown in Figure 5, with A=0.9 and B=0.1.

For a given time after the step-change in oxygen concentration, there will be a distribution of oxygen within the binder, according to the diffusion relation (Equation 1). Therefore, there will also be a variation in paint luminescence within the PSP binder, depending on the local oxygen concentration. In the current diffusion-based model, an elemental intensity contribution throughout the paint thickness is determined from the local oxygen concentration. Assuming an optically thin paint layer and a uniform distribution of luminophore in the binder, the luminescent intensity can then be integrated over the thickness of the paint,

$$I(t) = \int_{0}^{h} I(t,z) dz$$ \hspace{1cm} (14)

to give the total luminescent intensity of the paint as a function of time.

Intensity Response

In order to discretize and solve the diffusion equations, a total of 1000 time steps are used. In addition, the paint thickness is divided into 1000 elemental areas. The summation in Equation 8 is carried out to 10 terms. These parameters are sufficient to ensure convergence of the solution, and are greater than the values used by Winslow, et al.$^{36}$

The first case to be considered is a step-change in pressure from atmospheric conditions down to vacuum, and back again. The intensity response for the step-increase and step-decrease are shown in Figure 6, along with the shape of the actual oxygen concentration time history. If a perfectly linear calibration is used, then the intensity response for the rise and fall will both collapse to the oxygen concentration curve. Note that the Stern-Volmer relation is not linear (see Equation 11), and a perfectly linear calibration is not a physical reality.

The validity of the diffusion-based model is evaluated by comparing the model results with published experimental results. Watkins et al.$^{38}$ published work with a polymer film showing the response to nitrogen, air, and oxygen. The polymer film was quite thick, and therefore exhibited long response times (on the order of minutes). These experimental results serve as a useful benchmark for comparison. A simulation of the experimental results is shown in Figure 7, with the rise in intensity being much slower than the intensity decay. This behavior matches the experimental results of Watkins.

Pressure Response

Before meaningful comparisons may be made, however, the integrated intensity profile must be converted to an indicated pressure via the Stern-Volmer calibration. When the intensity time-histories shown in Figure 6 are converted to pressure, the shapes of the curves change such that the indicated pressure-response to a decrease in pressure leads that of an increase in pressure. This result is shown in Figure 8, for the same parameters used in the solution represented in Figure 6. The change in behavior (contrasted with the intensity profiles) is due to the inversion process within the Stern-Volmer relation. This result also highlights the importance of calibrating intensity results before drawing conclusions about PSP behavior. For both modeling and experimental work (even flow visualization), the observed trend may be altered significantly if the intensity is not calibrated to pressure or gas concentration.

The effect of $\gamma$ in the Freundlich Isotherm calibration on the PSP response is also evaluated. Figure 9 shows the results with A=0.9, B=0.1, and $\gamma=1.0$ or 0.1. The Freundlich Isotherm does have some effect on the shape of the indicated pressure-time history, although the effect is minimal. The basic trend
remains the same – there is a fast response to a step-decrease, and a slower response to a step-increase in pressure.

The effects of a small change in pressure are shown in Figure 10. For this case, a change in pressure of 1.0 psi above atmosphere was considered. As expected, a smaller change in pressure produces a much smaller difference between the rise and fall in indicated pressure. The response to a pressure decrease remains faster than the response to a pressure increase.

The effect of the overall range of the pressure change is shown by comparing Figure 8 with Figure 11. Both cases have a pressure change of 1 atmosphere, but the first case is a change to vacuum and back, while the second case is a change from 1-atm to 2-atm and back. Note that the pressure change at lower pressures produces a greater difference in the time scales of the indicated pressure than the case at higher pressures. The trend remains the same, however – a decrease in pressure produces a faster response than a corresponding increase in pressure.

**Experimental Results**

**Fluidic Oscillator**

In order to experimentally evaluate the quenching kinetics of porous PSP, a fluidic oscillator is used. The unsteady flow of the oscillator is ideal for making dynamic measurements. A typical fluidic oscillator design is shown in Figure 12. In this design, a jet of fluid emerges from an orifice called the power nozzle. The issuing jet will tend to attach to one of the side walls – called the Coanda effect. The wall attachment occurs because a region of low pressure between the jet and the wall is generated by the jet flow, thus pulling the jet towards the wall until it is attached. Now, if flow is injected at one of the control ports, a separation bubble can be formed between the jet and the wall. If enough fluid is injected, the separation bubble grows to the point of jet detachment. The momentum of the jet, along with pressure gradients, causes the jet to swing to the opposite wall. This motion can be accomplished cyclically by introducing a feedback loop from the jet exit back to the control port. In this way, whenever the jet is attached to an adjacent wall, it feeds fluid into the feedback tube and initiates the separation bubble. In this way, self-sustaining oscillations can be established. Miniature fluidic oscillators are capable of sustained oscillations on the order of several kilohertz, all without any moving parts. The oscillation frequency depends primarily on the supply pressure for the jet issuing from the control port. Flow visualization of typical jet oscillations are shown in Figure 13. Note that this fluidic oscillator is not the same type used in the current experiments, but serves to illustrate the basic nature of the oscillatory flow.

The fluidic oscillator used in these experiments is one that produces a square-wave flow pattern. This is the same identical oscillator that has been characterized by Gregory, et al. and Raman et al. in the past. The flow pattern of the oscillator is somewhat bimodal, as shown in the previous work. This device is used for characterizing the unsteady response of PSP because it has a very fast rise time, and the entire oscillation cycle is on the order of 629 µs long.

The rise time of the PSP response to the issuing jet can be compared when the oscillator is operated with different test gases. Argon, nitrogen, and oxygen are all used in the current experiments. Argon and nitrogen will both purge the oxygen in the AA-PSP, simulating a pressure decrease to vacuum conditions. The oxygen will have the opposite quenching behavior, with the luminophore being nearly quenched under the presence of pure oxygen. The pure oxygen condition simulates a large pressure increase, up to 4.76 atmospheres. If the fluid dynamic behavior of the oscillator is independent of the test gas used, then the PSP response to these three cases may be compared and the response behavior evaluated. Commonality of fluid dynamics among the test gases can not be immediately assumed, however. Each gas has a different molecular weight, and a different speed of sound, as summarized in Table 1. Because of this, the supply pressure required of each gas to generate a given oscillation frequency varies widely. To evaluate the flow commonality, a hot-film probe was placed in the fluidic oscillator flowfield, and subjected to flow from air, argon, nitrogen, and oxygen. The normalized time history from each of these gases is shown in Figure 14. Despite differences in supply pressure, the normalized waveforms have collapsed into one shape. This indicates that the oscillator may be used with different test gases to evaluate the PSP response.

The experimental setup for the fluidic oscillator is shown in Figure 15. The anodized aluminum PSP sample was prepared with bathophen ruthenium as a luminophore. The supply gases were either argon, nitrogen, or oxygen – all three were set at a pressure such that the oscillation frequency was maintained constant at 1.59 kHz. The corresponding supply pressures were 7.64 psig for argon, 5.11 psig for nitrogen, and 6.00 psig for oxygen. A Kulite pressure transducer was positioned adjacent to the oscillator to provide a reference signal for triggering and phase-locking. The Kulite signal was low-pass filtered at 1.6 kHz to eliminate all but the primary frequency...
component. This filtered signal was sent to an oscilloscope with a gating function and trigger output. The TTL output from the oscilloscope was used to phase lock the LED illumination with the oscillation frequency. Successive delays within the oscillation period were set with a delay/pulse generator. The pulse width was set to 15.723 µs (2.5% of the oscillation period), and the successive delays were at 31.447 µs intervals. A 14-bit CCD camera was used with an f/2.8 macro lens. Both long-pass colored glass and band-pass interference filters were used in series to filter out the excitation light. An ISSI blue LED array was used for paint excitation. The camera shutter was set open for 3 seconds to integrate enough light, while the LED array was strobed to freeze and phase-average the oscillatory motion. Acquired intensity images were converted to normalized gas concentration levels through an assumed calibration curve, based on previous experiments and calibrations.

Results

Typical full-field PSP images of the fluidic oscillator, in response to nitrogen gas, are shown in Figure 16. Full-field results for the other gases are similar. More detailed information can be gleaned by evaluating a cross-section of the full-field image, as shown in Figure 17. For this data, the cross section was taken horizontally across the full-field image, crossing both regions of the bimodal jet flow. In Figure 17(a), the peak on the left of the image is increasing, indicating that the jet is emerging on that side. In the same figure, the peak on the right side of the image is decreasing, indicating that the jet is retreating from that side. The motion of the peaks in Figure 17(b) is the same, with this figure being captured 220 µs after the first (126° phase delay). Notice that the profiles for all three gases correlate well in Figure 17(a), when the peak is just beginning to rise. In Figure 17(b), however, as the peak has begun to rise for some time, the PSP response due to oxygen has begun to lag behind the argon- and nitrogen- response. This behavior agrees with the diffusion-based model, which predicts that a rise in pressure (or oxygen concentration) will be slower than a corresponding decay.

Further details of this behavior may be observed in Figure 18 and Figure 19. These figures correspond to a time-history generated from a single point in the full-field images. Figure 18 corresponds to a point near the top of the left peak, while Figure 19 corresponds to a point near the top of the right peak (as shown in Figure 17). Notice that in both figures, the overall behavior of the PSP signal correlates well between the three gases. At one point within the cycle, however, a delay in the response to oxygen can be observed – shortly after the gas concentration has begun to increase. This may be observed in both figures, and agrees with the diffusion-based model.

Conclusions

This work has shown, through modeling and experiments, that the unsteady response of pressure-sensitive paint is affected by the nature of the Stern-Volmer calibration. A calibration that is highly non-linear will cause the paint to respond quickly to a decrease in oxygen concentration (pressure decrease), and relatively slowly to oxygen sorption (pressure increase). In addition, it has been shown that this observed effect is more pronounced for larger changes in pressure, particularly if the pressure change covers the non-linear portion of the Stern-Volmer curve at low pressures. Interestingly, because of this non-linearity, pressure-sensitive paint will respond faster to a decrease in pressure if the mean pressure is near vacuum rather than atmosphere. The effect of the Freundlich isotherm on the Stern-Volmer relationship produced a minimal variation from the effects of the basic Stern-Volmer relation.

Experimental results with anodized aluminum PSP showed that the Stern-Volmer non-linearity effect is present in porous paints. The AA-PSP response to the fluidic oscillator with three test gases showed good agreement overall, but with slight delays for an increase in oxygen concentration (when compared to nitrogen and argon). Furthermore, the gaseous adsorption/desorption hysteresis effect observed by Egami et al. at cryogenic temperatures was not observed in these room-temperature experiments.

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References


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Figure 1: Diagram of modeled PSP geometry.

Figure 2: Oxygen diffusion into the paint layer.

Figure 3: Oxygen diffusion out of the paint layer.

Figure 4: Typical Stern-Volmer relation with $K=10$.

Figure 5: Typical Stern-Volmer calibration curves for PSP, with linear calibration ($\gamma=1.0$) and Freundlich Isotherm ($\gamma=0.1$) curves.

Figure 6: PSP intensity step-response, integrated over paint thickness, compared to oxygen concentration; $A=0.9$, $B=0.1$, $\gamma=1.0$. 

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Figure 7: Simulated PSP intensity response to pressure cycles, similar to the experimental results of Watkins, et al.\textsuperscript{18}

Figure 10: PSP indicated pressure step-response, variation with pressure jump magnitude; $A=0.9$, $B=0.1$, $\gamma=1.0$, $\Delta P=1.0$ psi.

Figure 8: PSP indicated pressure step-response, variation from atmosphere to vacuum; $A=0.9$, $B=0.1$, $\gamma=1.0$.

Figure 11: PSP indicated pressure step-response, variation from 1 atmosphere to 2 atmospheres; $A=0.9$, $B=0.1$, $\gamma=1.0$.

Figure 9: PSP indicated pressure step-response, variation with $\gamma$; $A=0.9$, $B=0.1$, $\gamma=1.0$ or 0.1.

Figure 12: Fluidic oscillator design, demonstrating the operating principle of jet wall-attachment.
Figure 13: Typical schlieren images of fluidic jet oscillations, (a) 0° phase, (b) 180° phase

Table 1: Gas properties.

<table>
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<tr>
<th>Gas</th>
<th>Molecular Mass (g/mol)</th>
<th>Sound Speed (m/s), $a=\left(\gamma \cdot \frac{R}{T}\right)^{0.5}$</th>
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<tr>
<td>Air</td>
<td>28.967</td>
<td>346.0</td>
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<tr>
<td>Oxygen</td>
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<td>Nitrogen</td>
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<tr>
<td>Argon</td>
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Figure 14: Hot-film probe characterization of fluidic oscillator flow with various gases; normalized data indicates no variation.

Figure 15: Experimental setup for fluidic oscillator.

Figure 16: AA-PSP response to nitrogen jet at (a) 0 µs and (b) 314 µs (180° phase delay). Color scale indicates normalized gas concentration.
Figure 17: AA-PSP response to fluidic oscillator flow, cross-section of full-field image. Left peak is increasing in magnitude, right peak is decreasing. (a) 0 $\mu$s, with the peak beginning to rise (b) 220 $\mu$s, with oxygen response lagging nitrogen and argon.

Figure 18: AA-PSP response to fluidic oscillator at one point in the flowfield (left peak). Note the slight delay of the oxygen rise time, compared to nitrogen or argon.

Figure 19: AA-PSP response to fluidic oscillator at one point in the flowfield (right peak), also showing the delay in oxygen rise time.