# Temperature Compensation for Temporal (Lifetime) Pressure Sensitive Paint Measurements

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#### Abstract

Binary pressure sensitive paints (PSP) are developed for temperature compensation in lifetime-based measurement techniques. The binary systems are evaluated in regards to two and three gate measurement schemes. It is shown that a binary paint system can be designed to yield excellent temperature compensation for both two-gate and threegate measurement approaches.

#### Introduction

A typical PSP is composed of two main parts, as shown in Fig. 1--an oxygensensitive fluorescent molecule and an oxygen-permeable binder. The PSP method is based on the sensitivity of certain luminescent molecules to the presence of When a luminescent molecule oxygen. absorbs a photon, it is excited to an upper singlet energy state. The molecule then typically recovers to the ground state by the emission of a photon of a longer wave-In some materials oxygen can length. interact with the molecule such that the transition to the ground state is nonradiative; this process is known as oxygen quenching.

The rate at which these two processes compete is dependent on the partial pressure of oxygen present, a higher oxygen concentration causing additional quenching of the molecule, resulting in a lower light intensity.

Unfortunately, PSPs are also sensitive to temperature. A rise in temperature will alter (usually increase) the probability that the molecule will transition back to the ground state through a non-radiative process. This process, known as thermal quenching, is the basis of the temperature-sensitive-paint (TSP) technique. A second source of temperature sensitivity occurs when the binder for the pressure-sensitive luminescent molecule has oxygen permeability that is a function of temperature. This is often the case for the polymer-based binders used for PSP. The calibration of two typical PSPs— Ruthenium-complex in Sol-Gel and PtTFPP in FIB--is shown in Fig. 2. From this figure it is clear that the binder can have a significant impact on both the temperature and pressure sensitivity of the system. Temperature sensitivity can lead to errors in converting the intensity distributions to pressure. Regardless of the paint formulation, effective implementation of a PSP requires that temperature effects be characterized and corrected.

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### **Review of Previous Work**

Lifetime-based **PSP** measurement systems have been developed by several groups. Techniques for measuring lifetimes have included both pointwise and imaging approaches. Among the pointwise (scanning) approaches the work of Davies<sup>1</sup>, and Sullivan<sup>2</sup> are prime examples. The imaging approaches include both phasedetection<sup>3</sup> and sensitive multi-gate integration<sup>4-5</sup> techniques. In each of these systems all data are acquired at the wind-on condition, which eliminates--or at least minimizes--illumination as a source of error. With illumination errors eliminated, errors due to temperature become the dominant source of uncertainty in lifetime-based PSP measurements.

Goss et al.,<sup>6</sup> performed an analysis and showed that the signal-to-noise ratio could be maximized using a two-gate approach to lifetime measurements by the appropriate selection of the gate location and width. This two-gate approach could be incorporated into an image-based PSP system using a gated CCD camera. А system employing this two-gate approach been used extensively for has PSP measurements at AEDC. A schematic of the two-gate lifetime approach is given in Fig. 3. The PSP is illuminated using a pulsed LED array. The illumination pulse is approximated as a square wave and has a width of 10-30 µs. The two-gate lifetime measurement is accomplished by integrating the luminescence from the probe during a specified portion of the rise and/or decay of the probe luminescence. The luminescence from the paint is a function of the probe distribution. paint thickness. and illumination field. A ratio of the two gates will eliminate these variations, and the resulting function will be sensitive to pressure and temperature only. The position of the gates is selected to optimize the

pressure sensitivity of the system while maintaining a favorable signal-to-noise ratio.

Temperature compensation for lifetime based PSP's systems has been discussed by several authors<sup>1,7-15</sup>. Davies claimed success with a multi-gate scheme measuring both temperature and pressure with his pointwise system, however, he has not formally published his results beyond the early report of Ref 1. Coyle<sup>7</sup> proposed a method of correcting lifetime measurements for temperature which involved the addition of a non-oxygen quenched, temperaturedependent phosphor to a PtTFPP/FIB paint.

Hradil<sup>8</sup> demonstrated a dual-lifetime approach using a short-lived Ruthenium complex as the pressure sensor and a longlived phosphor as the temperature sensor. The temperature measurements are then used to correct the temperature-induced errors in the PSP data. Among the issues of concern for their system are the low temperature sensitivity of the phosphor (~ 0.3%/K) compared to the temperature sensitivity of the pressure sensor (~ 1%/K). The reported accuracy of the temperature measurement was  $\pm 3$  K.

In 2002, Mitsuo, et al.<sup>9</sup>, demonstrate a lifetime imaging system to simultaneously measure pressure and temperature. In their approach, three separate time gates were used to form two distinct ratios from which both the temperature and pressure could be uniquely determined. While the initial system proved to be noisy due to laser speckle and photon shot noise, a subsequent system<sup>10</sup> reported in 2004 indicated that the accuracy of reconstructed pressure could be greatly improved by using LED excitation and a low-noise non-intensified gated camera.

Watkins, et al.<sup>11</sup>, have demonstrated a similar three-gate approach as Ref 9 for temperature correction.

In 2004, Ruyten<sup>12</sup> published an elegant review of physical models for lifetime analysis of PSP's. In subsequent work he reported a lifetime analysis of the PtTFPP/FIB paint system<sup>13</sup> (the industrial standard for PSP measurements in the USA). He also reported on the optimization of three-gate lifetime pressure and temperature base systems<sup>14</sup>.

Recently, Goss et al.<sup>15</sup>, reported on the development of a binary paint system for compensation temperature in lifetime measurements. This approach was based on a two-gate method in which a second nonoxygen quenching probe was added to the PtTFPP/FIB (ISSI-UniFIB) paint to compensate for temperature. In this work, the temperature sensitivity of the second probe was chosen to closely match that of the pressure sensitive probe so that a single ratio would be sufficient to produce a temperature independent surface pressure.

# Absolute Verses Relative Temperature Measurement

In the development of a temperaturecorrecting paint, an issue of significant importance is the type of temperature measurement that is needed (namely, absolute or relative). To understand this issue, one must consider the property of a PSP that Gouterman<sup>16</sup> defined as ideality. For a simple description of ideality, consider the slope of the pressure-calibration curve as a function of temperature. In the case of the calibration data that were shown in Fig. 2, the intensity at a single pressure and temperature was used as the reference point for all data. This plot demonstrates the temperature sensitivity of the paint. To demonstrate the ideality of the paint, data along each isotherm are normalized using the intensity at a reference pressure. The resulting plot (see Fig. 4) shows the slope of the paint curve at different temperatures. If the paint is ideal, the slope will be independent of temperature; the ISSI PtTFPP/FIB, shown in Fig. 4, achieves this result.

Two basic approaches can be use for temperature compensation of pressure paint--whether in the time-resolved or in the intensity-measurement mode. The temperature channel can be used for compensation by either directly determining the absolute temperature or matching the temperature sensitivity of the pressure channel. In the former approach, we have the more difficult assignment of making an absolute temperature measurement. In the latter approach, only the relative temperature profile is needed.

In terms of paint ideality, as discussed above, the non-ideal paint is characterized by variable temperature sensitivity, while the ideal paint is characterized by constant temperature sensitivity. Thus, matching the temperature sensitivity of the pressure and temperature channels is much easier in the ideal paint case. In the non-ideal paint case, compensation of temperature by matching sensitivities can only occur over a very limited temperature range. Thus, an absolute temperature measurement is the only way to ensure compensation over а wide temperature range for a non-ideal paint.

Fortunately, the ISSI PtTFPP/FIB (UniFIB) is an ideal paint, and temperature compensation over a wide temperature range can be realized by choosing the appropriate temperature probe. ISSI has developed and demonstrated a temperature-compensating binary PSP based on the ideal FIB binder. This binary paint minimizes the impact of temperature over a range of temperatures (5  $-45^{\circ}$ C) and pressures (1 -20 psia). Unfortunately, the system is designed specifically for radiometric detection and will not work in the lifetime mode. However, the system does demonstrate the value of using an ideal paint when developing a temperature-correcting or compensating system. Absolute measurements of temperature are no longer necessary because the slope of the independent sensitivity curve is of temperature. In fact, no attempt is made to measure temperature directly. The system employs a ratio-of-ratios approach that eliminates the need to measure temperature directly. The calibration of this paint is included in Fig. 2.

# Lifetime Temperature Compensation

One mode of isolating the emission of the signal and reference probes is based on the luminescent lifetime of the probes, as demonstrated by Hradil.<sup>8</sup> Each probe is pumped using a pulse from a single excitation source, however the luminescence from the probes is distinguished by the lifetime difference in the of the luminescence. Radiometric binary systems based on the idea of temporal isolation have proposed and demonstrated been bv Mosorov,<sup>17</sup> Orlov,<sup>18</sup> and Crafton.<sup>19</sup> In each case, the system was composed of probes with significantly different lifetimes. It can be shown that the degree to which the probes are isolated is a function of the difference in the lifetimes of the probes. Effective isolation requires that the probe lifetimes be different by two to three orders of magnitude.

In principle, complete isolation of the two probes may not be necessary or desirable. Consider the two-gate lifetime method shown in Fig. 3. In the case of UniFIB the reference gate, gate 1, exhibits little sensitivity to pressure but also exhibits little sensitivity to temperature. Gate 2, exhibits good sensitivity however. to pressure and some sensitivity to temperature. The temperature sensitivity of the calibration that results from ratioing these two gates is due mostly to gate 2. If

one could enhance the temperature sensitivity of gate 1 without affecting gate 2, one could, in principle, nullify or cancel the temperature sensitivity of gate 2.

# Binary Paints for Temperature Compensation

Several binary paints were developed in this study for evaluation of two and threegate temperature compensation approaches. As mentioned earlier, the UniFIB paint system is uniquely suited for the development of temperature compensating binary paints. It was thus used as the base for all binary paints in this study.

<u>MgTFPP/UniFIB</u>. One of the main issues concerning the stability of a binary paint system is the sensitivity of the probes to singlet oxygen attack. Because singlet oxygen is formed by most oxygen sensitive probes, the binder, and probes of the paint platform must be able to withstand this highly reactive radical. The high degree of fluorination of both the PtTFPP probe and the FIB binder help to minimize the attack by singlet oxygen. Magnesium(II) meso-Tetra(Pentafluorophenyl)porphine

(MgTFPP) is very similar to PtTFPP and is temperature sensitive, but displays little pressure sensitive. It also has absorption and emission characteristics very similar to PtTFPP and thus can be easily excited by 470 nm LEDs.

*RuBath/UniFIB*. Another probe that was considered for a binary system was Tris(Bathophenanthroline) Ruthenium(II) Chloride (RuBath). This probe is not only temperature sensitive (>1%/°C) but also pressure sensitive. It was chosen because of its resistance to singlet oxygen attack. The introduction of additional pressure sensitivity in the reference gate may seem contrary, however, as will be shown this results in both two-gate temperature

compensation and three-gate temperaturepressure determination.

<u>*RuBPy/UniFIB.*</u> A second pressure probe Tris(2,2'bipyridyl) Ruthenium(II) Chloride (RuBPy) was chosen for the development of a binary paint system based on its short lifetime (~ 1  $\mu$ sec ) and its high temperature sensitivity. Again, like most pressure probes, it is relatively immune to singlet oxygen attack.

<u>*Py2/UniFIB*</u>. Pyridine 2 is a laser dye which has a relatively high temperature sensitivity (>1%/°C), short lifetime (< 100 nsec), and absorption and emission characteristics that are compatible with PtTFPP.

# **Calibration Apparatus**

The calibration apparatus that was used to measure the luminescence of the binary paint systems is shown in Fig. 5. A 10 µs 470 nm LED (ISSI-LM2-470) pulse was used to excite the paint emission, which was recorded by a PMT and a digitizing oscilloscope. A single long pass filter was employed to block the LED lamp and to transmit the paint emission. A photodiode (PD) was used to capture the excitation pulse envelope. The captured waveforms were recorded as a function of temperature and pressure. Because the entire waveform was recorded, it can be analyzed with a vast number of different time gates. An analysis code was written to allow the integration of the emission waveforms with multiple time gates. These ratios were then further processed to determine temperature and pressure sensitivities. Along with the temporal characteristics, the light stability of the binary paint could be recorded with this setup.

# **Results and Discussion**

*Two-Gate Results.* То evaluate the effectiveness of a binary paint to compensate for temperature, a series of waveforms were captured during а temperature-pressure calibration. Next the waveforms were analyzed by using various gate combinations and the resulting sensitivity to pressure and temperature determined for each gate ratio. The gates utilized to study the binary paints in the twogate mode are listed in Table 1. In this case gate 1 was chosen to be constant and set to the 0 - 5 µsec region during the LED excitation. Nine different Gate 2's were studied to determine the best two-gate minimize combination that would temperature effects (see Table 1).

### Table 1. Reference (Gate 1) and Pressure (Gate 2) Gates Used to Evaluate Binary Paints. All times in µsec. LED start at t=0.

Gate 1.	0-5		
Gate 2	10-20,	15-25	20-30
	25-35	30-40	30-50
	30-60	30-100	30-200

The first paint to be evaluated in this manner was ISSI's UniFIB. This paint represented the "state of the art" in that it specifically engineered for low was temperature sensitivity. The temperature sensitivities for the various gate combinations are shown in Fig. 6. As would be expected when using the ideal binder FIB, the temperature sensitivity is nearly constant over a wide range of gates. Also note that the temperature sensitivity is ~0.5% C which is quite low as compared to most pressure paints.

The binary paint, RuB/UniFIB displays the least amount of compensation among the tested binary paints (see Fig. 6). Note that adequate temperature compensation does not occur until pressure gates that are delayed 30 µsec after the start of the LED excitation. This is likely due to the long lifetime of the RuB probe as compared to the other temperature probes used in the binary paints. The pressure gates less than 30 µsec contain both pressure and temperature probe and thus show less compensation. Delays larger than 30 usec contains only the PtTFPP signal and show some temperature compensation.

The MgP probe of the MgP/UniFIB binary displays good temperature compensation despite its low temperature sensitivity (see Fig. 6). This is due to it's very short lifetime that ensures its emission is only in Gate 1 plus it has no pressure sensitivity which would act to reduce the pressure sensitivity of the gate ratios.

The RuBPy probe, like the RuBath, has both pressure and temperature sensitivity. However, unlike RuBath, its short lifetime ensures its emission is mostly in Gate 1. The result is nearly a factor of 2 reduction in the temperature sensitivity over UniFIB alone (see Fig. 6).

The best result was obtained with the Py2 probe whose short lifetime ensures that its emission is strictly in Gate 1 and whose temperature sensitivity is a close match for the pressure probe. The addition of this probe reduces the temperature sensitivity from ~ 0.5%/°C to less than 0.08%/°C (see Fig. 6).

<u>Three-Gate Results.</u> As discussed earlier, several groups have looked into the development of three-gate approaches in which both the temperature and pressure are determined from gate ratios. Ruyten<sup>14</sup> has shown that the relationship between the RMS error of a three-gate to two-gate system is

$$\frac{\sigma_P^{(3)}}{\sigma_P^{(2)}} = \left| \frac{\eta_{13}}{\eta_{12} - \eta_{13}} \right| \qquad (1)$$

where  $\sigma^{(3)}$  and  $\sigma^{(2)}$  are the RMS errors of the three-gate and two-gate measurements, respectively, and  $\eta_{12}$  and  $\eta_{13}$  are the temperature sensitivities of gate ratios,  $r_{12}$ and  $r_{13}$ , respectively. As concluded by Ruyten, a necessary condition for a threegate measurement to out perform a two-gate measurement is that the relative temperature sensitivities  $\eta_{12}$  and  $\eta_{13}$  should be substantially different from each other.

To evaluate the binary paints for a three gate scheme, the series of gates shown in Table 2 were used to determine relative temperature sensitivities.

Table 2. Reference (Gate 1) and Pressure (Gate 2) Gates Used to Evaluate Binary Paints for Three-Gate Approach. All times in µsec. LED start at t=0.

Gate 1.	0-2		
Gate 2	10-15,	15-20	20-25
	25-30	30-35	35-40
	40-50	40-60	40-70
	40-80	40-90	40-110
	40-130	40-150	40-200

The first paint to be evaluated was ISSI's UniFIB. A plot of the temperature sensitivities as a function of gate ratio is shown in Fig. 7. Note as expected the temperature sensitivities of the various gates are relatively constant. This indicates that PtTFPP/FIB cannot be used by itself in a three-gate scheme.

As shown in Fig. 7, the temperature sensitivity of the ratios for RuB/UniFIB varies by a factor of 2-3 for ratios  $r_{1,2} - r_{1,9}$ . This indicates it would be a good candidate for a three-gate scheme.

Similarly, the temperature sensitivities shown in Fig. 7 for RuBPy/UniFIB vary by a factor of ~ 2.5 between ratios  $r_{1,2}$  and  $r_{1,7}$ . This binary would also be a good candidate for a three-gate scheme.

The temperature sensitivities of the MgP/UniFIB binary different from the other binaries at the low gate ratios  $(r_{1,2}-r_{1,3})$  in that they do not increase in this area. Instead they show a steady decline from high ratios to low (see Fig. 7). However, the total variation of the temperature sensitivity is approximately a factor of 2 from  $r_{1,2}$  to  $r_{1,16}$ .

The Py2/UniFIB binary displays the largest variation in temperature sensitivity varying from ~0.99%/°C at  $r_{1,2}$  to 0.10%/°C at  $r_{1,16}$ . This order of magnitude change would allow for an excellent three gate system.

# Conclusions

A series of binary paints specifically designed for lifetime based multiple-gate systems have been developed for temperature compensation. In the two-gate displays the best mode, Py2/UniFIB temperature compensation reducing the temperature sensitivity of UniFIB from 0.5%/°C to 0.08%/°C. In the three gate mode, all the tested binaries display a good temperature sensitivity range, (a factor of 2-3). Py2/UniFIB again was a standout in that its variation of temperature sensitivities was over a factor of 9.

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Fig. 1. Components of a PSP system.



Fig. 2 Calibration of UniFIB, Rutheniumcomplex in Sol-Gel, and Binary FIB. Note the high pressure sensitivity and low temperature sensitivity of the FIB binder and the extremely low temperature sensitivity of the intensity-based Binary



Fig. 3. Luminescent lifetime of a pressuresensitive probe, demonstrating the twogate lifetime measurement approach.



Fig. 4. Ideality of PtTFPP in FIB and Ruthenium-complex in Sol-Gel. Calibration data along each isotherm were normalized using the intensity at that temperature and the reference pressure. The resulting plot shows the sensitivity of the paint at different temperatures.



Fig. 5. Experimental setup used to evaluate time-resolved binary paints.



Fig. 6 Plot of Temperature Sensitivities for Binary Paints in Two-Gate Mode. Gates start at  $r_{1,2}$  on left of plot and end at  $r_{1,9}$  at right of plot. Gate values are listed in Table 1.



Fig. 7 Plot of Temperature Sensitivities for Binary Paints in Three Gate Mode. Gates start at  $r_{1,2}$  on left of plot and end at  $r_{1,16}$  at right of plot. Gate values are listed in Table 2.