

Study of the mechanism of degradation of pyrene-based pressure sensitive paints

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Abstract

Even though pyrene-based pressure sensitive paints have some special advantages like high quantum efficiency, good pressure sensitivity and low temperature sensitivity, these paints exhibit steady degradation of the fluorescent intensity after each wind tunnel test. It has been reported that pyrene-based paints degrade because pyrene has a tendency to evaporate. It is necessary to understand the mechanism of degradation of pyrene-based paints in order to find a solution to this problem. Thermal aging tests and UV exposure tests of the paint specimens are carried out to study the effect of experimental parameters like temperature, pressure and UV exposure on the paint stability. This study has shown that the paint degradation in wind tunnel is mainly due to diffusion and evaporation of pyrene. The effect of pyrene concentration in the paint and the thickness of the active layer on the paint stability were also studied.

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1. Introduction

In recent times, pressure sensitive paint (PSP) technique has been increasingly used for the measurement of surface pressure distribution in wind tunnel studies [1–9]. This technique has some important advantages in comparison to the conventional methods like pressure taps. The high spatial resolution is the main advantage of the PSP technique that has attracted the attention of aerodynamic researchers all over the world. The technique is based on the principle of luminescence quenching of some materials by oxygen. The principle of PSP is the same as that of optical oxygen sensors. PSP is composed of luminescent molecules embedded in a polymeric binder and this paint can be applied over the wind tunnel models. The details of the PSP technique and the paint are described elsewhere [1–5,7,8]. The important characteristics required for a good paint are high pressure sensitivity, low temperature coefficient, high fluorescence quantum efficiency, good photo stability and fast response time. Since the paint has to function in wind tunnel conditions, it also should have good adhesion and stability.

The luminescence intensity of the paint is inversely proportional to the air pressure and directly proportional to ex-

citation light intensity. The accuracy of the surface pressure measurements by PSP is reduced by the variation of the excitation intensity over the model surface during the test [1–7]. The error introduced by the non-uniformities of the excitation intensity can be eliminated by incorporating a second reference luminophore which is insensitive to pressure but sensitive to variations in excitation intensity. Such binary pressure sensitive paints are reported to give more accurate surface pressure data [4–7].

Three kinds of luminescent molecules or luminophores are generally used for the preparation of PSPs. They are platinum porphyrin complexes [1–5,7–10], ruthenium di-imine complexes [1–5,7,11–13] and pyrene [6,7,14–17]. Paints based on platinum and ruthenium dyes as the luminophores possess high temperature coefficients. Temperature sensitivity is a serious drawback of PSP that decreases the accuracy of the surface pressure measurements [8,11–13]. Hence corrections have to be applied for the pressure data obtained by these paints. There are certain advantages in using pyrene as the active luminophore for PSP since it has relatively high quantum efficiency, good pressure sensitivity and low temperature coefficient at ambient temperatures [6,7]. We have developed a pyrene-based binary pressure sensitive paint termed as “NAL-G” [15]. This paint contains two luminophores, pyrene as the pressure sensor and europium doped yttrium oxysulfide ($Y_2O_3:S:Eu$) as the reference luminophore in a single component silicone resin. The

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reference luminophore has a strong phosphorescent emission in the red region. As the luminescence of pyrene is in the blue region, there is no interference between the two emissions. This paint was tested on a delta-wing-body model in 1.2 m wind tunnel at NAL. It was found that the paint had a pressure sensitivity of 75%/bar and a low temperature coefficient ($<0.3\%/^{\circ}\text{C}$). The paint cured in 24 h at room temperature and had good adhesion. The response time of the paint was fast so that it could be used in transonic flows. But NAL-G paint showed a certain degree of degradation in the blue emission intensity after a few blowdowns. Two more paint formulations with improved stability (NAL-G1 and NAL-G2) were developed subsequently [16,17] but they also degraded after several blowdowns.

It has been reported that pyrene-based paints undergo degradation because of the evaporation of pyrene under wind tunnel blow down conditions [6,7]. Mebarki has studied the degradation of pyrene-based PSP in the temperature range from 40 to 100 °C and found that the emission intensity of pyrene decreased at 50 °C and above [7]. Since pyrene is an organic luminophore, the degradation of the paint may occur either due to UV exposure or due to the evaporation of pyrene. We have carried out systematic investigations to understand the degradation of pyrene-based paints in wind tunnel. Thermal aging studies of the paint specimens with different pyrene concentrations were carried out to study the effect of temperature and pressure on the paint stability. This study has brought to light some interesting results and these are described here.

2. Experimental

2.1. Materials

Pyrene was obtained from Acros Organics. The reference luminophore, $\text{Y}_2\text{O}_2\text{S:Eu}$ (red phosphor, type QKL63/N-C1) was procured from M/s Phosphor Technology, UK. The silicone resin, RTV IS 9188 was obtained from GE Silicones and used as the binder for the paint. RTV IS 9188 is a translucent one component neutral cure silicone resin and selection of this resin as the binder for our PSP was done based on our previous investigations [15]. Toluene (sulfur-free) was used as the diluent for the paint. A blue pigment from KEROL Pigments Corporation was used for coloring the paint.

Paint formulations of pyrene-based binary pressure sensitive paint were prepared by mixing 1 g of silicone resin with a solution of pyrene in 6 ml toluene, 1 ml 0.5% blue pigment solution in toluene and 0.3 g red phosphor well. This mixture was filtered through a silk screen cloth into a spray gun and sprayed onto 15 cm \times 5 cm aluminum sheets of 0.3 mm thickness coated with a white reflecting undercoat [15]. This undercoat known as screen layer was prepared by spraying a two-component white paint onto the clean and dry aluminum sheets and curing for 12 h at room temperature. The PSP layer was sprayed on the screen layer

and allowed to cure for 24 h at room temperature. Five paint coupons of size 3 cm \times 5 cm were cut from each aluminum sheet painted with each PSP formulation. The thickness of the coating was about $35 \pm 5 \mu\text{m}$. Blank coupons were prepared by spraying a similar silicone resin mixture without pyrene and red phosphor.

2.2. Methods

2.2.1. Fluorescence measurements

Fluorescence emission spectra were recorded using a fiber optic spectrometer, model SD1000 from Ocean Optics Inc., USA and a 300 W xenon arc lamp (model no. 6258 from Oriel Instruments) as source. The infrared radiation from the xenon lamp was filtered by means of a water filter. A bandpass filter (Oriel cat. no. 51650) was used to transmit UV radiation from the source in the wavelength range of 300–380 nm and to illuminate the coatings with UV radiation. The coatings were mounted in a sample chamber fabricated in our laboratory so that emission was measured by the front face technique. There was provision to pass nitrogen through the chamber to record the emission spectra in the absence of oxygen. The blue emission counts (I_{blue}) due to pyrene excimer emission was measured at 475 nm and the red emission counts (I_{red}) due to the red phosphor was measured at 626 nm. Normalized intensity was determined using the equation $(I_{\text{blue}}/I_{\text{red}}) \times 100$. The oxygen quenching sensitivity or the pressure sensitivity of the paint was calculated using the equation

$$\frac{I_{\text{N}_2} - I_{\text{air}}}{I_{\text{N}_2}} \times 100$$

where I_{N_2} and I_{air} are the normalized intensity values of the PSP coating in nitrogen and air, respectively.

2.2.2. Thermal aging studies

Thermal aging studies of the coatings were carried out by exposing the paint specimens to different temperatures of 40, 50, 60 °C and 100 mbar for 1 h in a vacuum oven and measuring the blue emission and red emission counts before and after the thermal aging. A comparison of the normalized intensity values before and after the thermal aging test was used in order to check the stability of PSP coatings.

3. Results and discussion

3.1. Effect of UV irradiation on the fluorescent intensity of the coating

The effect of UV exposure on the emission intensity of the paint coatings was studied. The pyrene concentration in the PSP coatings was 40 mM and these paint coupons were prepared as described in Section 2.1. Fig. 1 shows the fluorescent emission spectra of a pyrene-based binary PSP coating in air and in the presence of nitrogen. The broad

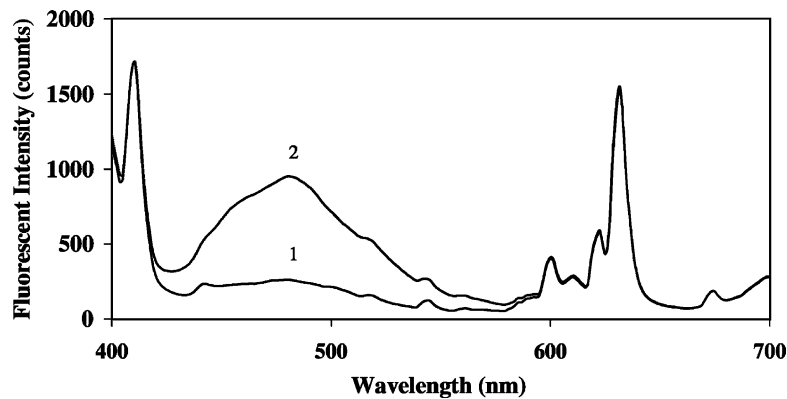


Fig. 1. Fluorescent spectra of a coating of the binary pressure sensitive paint in (1) air and (2) in the presence of nitrogen.

emission peak at 480 nm is due to pyrene excimer and it can be seen from the figure that this peak is sensitive to oxygen. The blue emission intensity of the coating increased in the absence of oxygen, whereas the red emission intensity of the reference luminophore at 626 nm was independent of the partial pressure of oxygen.

The coatings were exposed to continuous UV radiation from the xenon arc lamp filtered through ORIEL UV transmitting filter and water filter. Fluorescent emission spectra were recorded at regular intervals of exposure for a period of 1000 s. The intensity values for blue and red emission were measured at the peak maxima. The normalized intensity was calculated. Fig. 2 shows the plot of normalized intensity versus UV exposure time. It was seen that the decrease in normalized intensity was about 2.6% on continuous UV exposure of the coating for 1000 s.

In the actual PSP measurements, a pulsed xenon lamp is often used for excitation of the paint and the painted model surface is illuminated only for the duration of data acquisition in order to minimize the photodegradation. The UV exposure of the painted surface for a single blowdown is about 5–20 s. The distance between the source and the

painted model also is much larger than that used here. Thus the UV exposure of the painted model during wind tunnel studies will be much less than that used for this study. A lower excitation intensity could not be used because of the limitation of the detector efficiency of our spectrometer. This study shows that the contribution of UV degradation to paint instability is negligibly small.

3.2. Effect of thermal aging at three different temperatures on the paint emission intensity

The effect of thermal aging on the fluorescent emission intensity of the paint coupons was studied. The paint coupons were subjected to aging at three different temperatures, 40, 50 and 60 °C and 100 mbar in a vacuum oven for 1 h and the emission intensity was measured before and after the aging test and compared. The paint coatings used for this study had a thickness of about $30 \pm 5 \mu\text{m}$ and the pyrene concentration in the coatings was maintained at 40 mM. It was seen that there was no change in the normalized intensity of the paint coupons after thermal aging at 40 °C and 100 mbar for 1 h and also at 50 °C and 100 mbar for 1 h.

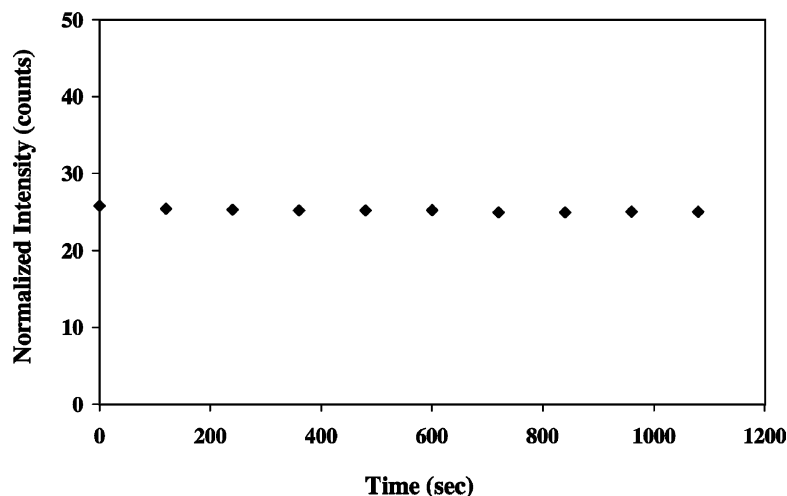


Fig. 2. Effect of UV exposure on the normalized intensity of a coating of pyrene-based PSP.

Table 1

Photophysical characteristics of the PSP coatings with different pyrene concentrations^a

Pyrene concentration (mM)	Normalized intensity in		Pressure sensitivity (%)
	Air	Nitrogen	
10	18.9	101.2	81.3
20	21.8	100.5	78.3
30	23.6	99.1	76.2
40	25.0	100.3	75.1
50	30.7	101.0	69.6
60	35.1	99.3	64.7

^a Thickness of the coating is $40 \pm 10 \mu\text{m}$.

A decrease in normalized intensity was observed after thermal aging at 60°C and 100 mbar for 1 h. This indicated that the paint degradation occurred at temperatures higher than 50°C . Several thermal aging tests were carried out to study the mechanism of pyrene loss from PSP coatings and the results are described in the following sections.

3.2.1. Effect of pyrene concentration on the thermal stability of the paint coatings

Paint coupons with different pyrene concentrations of 10, 20, 30, 40, 50 and 60 mM in the coating were prepared to study the effect of thermal aging on them. The photophysical characteristics of the paint coatings with different pyrene concentrations are given in Table 1. It can be seen that normalized intensity values increased with increase in pyrene concentration in the coating. But the pressure sensitivity decreased with increase in pyrene concentration due to self-quenching at higher pyrene concentrations. This is in agreement with the theoretical predictions. In order to select an optimum concentration of pyrene for the PSP, the paint stability factor also has to be considered.

Initially the paint coupons of different pyrene concentrations were thermally aged together at 60°C in the vacuum oven. It was observed that the results were erratic and some of the low-pyrene paint coupons showed an increase in emission intensity after thermal aging and vice versa. This was probably because the pyrene evaporated from paint coupons of high pyrene concentration was collected on coatings of low pyrene concentrations. Therefore, thermal aging study of coatings with different pyrene concentrations was carried out separately at 60°C and 100 mbar for one hour for each set of paint coupons with the same pyrene concentration. The results of this study are summarized in Table 2. It was found that the normalized intensity of coatings with 10 and 20 mM pyrene concentration decreased after thermal aging. For coatings with ≥ 40 mM pyrene the intensity increased after thermal aging.

To understand the fluorescent intensity changes taking place in the coatings of different pyrene concentration during thermal aging, the intensity was measured at intervals of 15 min of thermal aging at 60°C and 100 mbar. The normalized intensity was plotted versus thermal aging time. The results are shown in Fig. 3A and B. It was found that the

Table 2

Effect of thermal aging at 60°C and 100 mbar on the fluorescent intensity of paint coatings with different pyrene concentrations^a

Pyrene concentration in the coating (mM)	Normalized intensity in air		Change in intensity (%)
	Before thermal aging	After thermal aging	
10	19.0	8.36	−56.0
20	21.8	11.6	−47.0
30	23.6	22.2	−6.0
40	25.0	29.0	+16.0
50	30.7	39.6	+29.0
60	35.1	42.1	+19.9

^a Thickness of the coating is $40 \pm 5 \mu\text{m}$.

intensity of 10 mM coupons decreased steadily with aging time. When pyrene concentration in the coating was 20 mM, the intensity increased after 15 min and decreased on further aging as shown in Fig. 3A. When pyrene concentration in the coating was 30 mM, the intensity increased after 30 min of thermal aging at 60°C and decreased on further aging. For coatings with 40 mM pyrene, increase in intensity was observed after 30–45 min of thermal aging at 60°C and the intensity decreased on further aging (Fig. 3B). The normalized intensity of 40 mM coatings after 1 h of thermal aging was often higher than the initial intensity if the thickness of the coating was $\geq 40 \mu\text{m}$. For coatings of higher pyrene concentration (50 and 60 mM), the increase in intensity was observed at 60 min and decreased after 90 min.

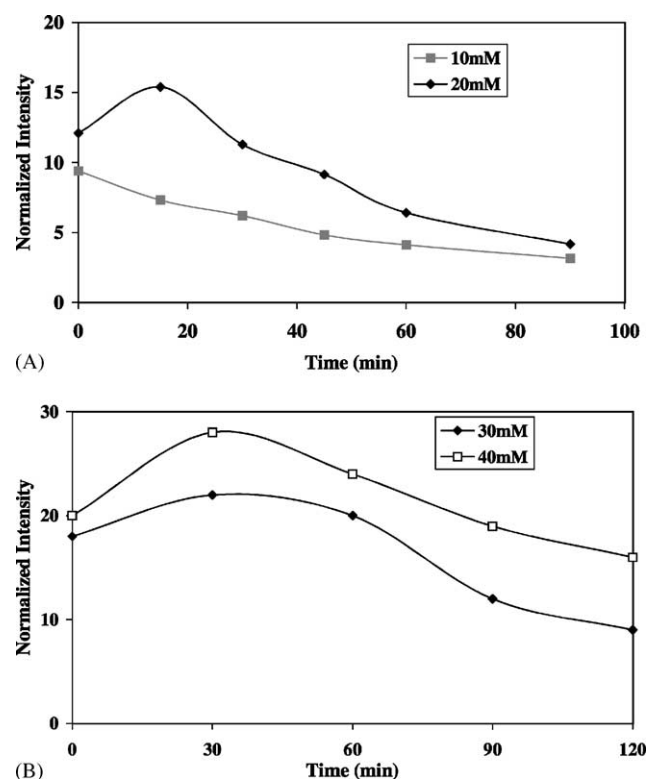


Fig. 3. Effect of thermal aging at 60°C and 0.1 bar on the normalized intensity of coatings with different pyrene concentrations: (A) 10 and 20 mM; (B) 30 and 40 mM.

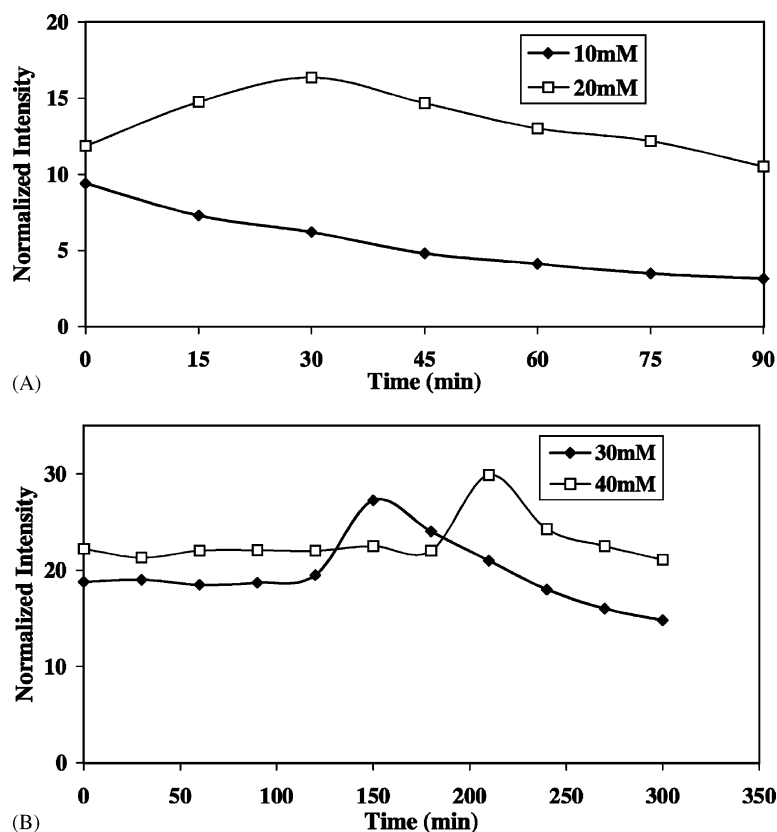


Fig. 4. Effect of thermal aging at 50 °C and 0.1 bar on the normalized intensity of coatings with different pyrene concentrations: (A) 10 and 20 mM; (B) 30 and 40 mM.

The effect of thermal aging at 50 °C and 100 mbar for longer duration was studied for coatings with four different pyrene concentrations. The intensities were measured at periodic intervals of 30 min till the paint coatings started showing steady degradation. The coupons were taken out of the vacuum oven in every 30 min and returned to the oven after fluorescence intensity measurement. The normalized intensity versus time was plotted for each paint coupon and the results are shown in Fig. 4A and B. It was found that the intensity of 10 mM coupons decreased with aging time even at 50 °C as shown in Fig. 4A. When pyrene concentration in the coating was 20 mM, the intensity increased on thermal aging. Maximum increase in intensity at 50 °C was observed after 30 min. When pyrene concentration in the coating was 30 mM, the intensity was constant up to 100 min of thermal aging at 50 °C. Maximum increase in intensity at 50 °C was observed after 140 min. For coatings with 40 mM pyrene, the intensity was constant up to 180 min of thermal aging at 50 °C. Maximum increase in intensity at 50 °C was observed after 210 min (Fig. 4B). After 300 min of aging, the normalized emission was nearly that of the unexposed paint coupon. Further aging resulted in a steady decrease of emission intensity.

It has been reported that a pyrene concentration of 7 mM is most suitable for a pyrene-based PSP [6,7]. This coating is reported to have a high pressure sensitivity of 90%/bar

but very poor stability and undergoes degradation after each wind tunnel test. Generally, a lower luminophore concentration of 10 mM or below is used in PSPs to avoid the effects of concentration quenching. But in the case of pyrene-based PSP, the broad excimer emission band in the 450–550 nm region is used for PSP measurements. Excimer formation is facilitated by higher pyrene concentration as the peak emission intensity at 475 nm increased with increase in pyrene concentration. However, the pressure sensitivity decreased with increase in pyrene concentration as shown in Table 1. Our results of thermal aging at 50 and 60 °C showed that a pyrene concentration of 40 mM is more suitable for PSP from the point of view of stability. The pressure sensitivity of a PSP coating containing 40 mM pyrene was found to be 75%/bar (calculated from the slope of the Stern–Volmer calibration plot of the paint coupon recorded using NAL PSP system) [16].

3.2.2. Effect of thickness of the coating on the thermal stability

Thermal aging at 60 °C and 100 mbar for 1 h for a number of paint coupons of different coating thickness was carried out. The pyrene concentration in the coatings was 40 mM. The normalized intensities of the coatings were measured before and after the thermal aging and the results are shown in Table 3. It was found that the normalized intensity decreased

Table 3
Effect of thermal aging on the normalized intensity of paint coatings of different thickness with 40 mM pyrene concentration

Thickness of the coating (μm)	Normalized intensity		Difference in intensity (%)
	Before thermal aging	After thermal aging	
20	21.2	15.9	−25.0
30	23.5	21.2	−10.80
40	25.0	29.0	+16.0
50	28.0	40.0	+43.0
60	28.5	44.5	+56.1

for thin coatings, whereas the intensity increased for thicker coatings. When the thickness was <30 μm, the intensity decreased after thermal aging. When the thickness of the coating was 40–60 μm, an increase in intensity was observed after thermal aging. Thus thermal stability of the coating was found to be dependent on the thickness of the paint layer.

3.3. Effect of normal aging on the intensity of paint coatings of different pyrene concentrations

The normal aging stability of the paint coating of different pyrene concentrations (10, 20 and 40 mM) was studied. Paint coupons were prepared as described in Section 2.1. The fluorescent emission intensity values of the paint coupons were measured at periodic intervals of time. Initial measurements were done at short intervals of 2 days for the first 15 days and thereafter measurements were made once in a week for about 100 days. The first measurement was done after complete curing of the paint. Generally, complete curing takes place in 24 h for most of the RTV silicone resins.

Normalized intensity versus storage time was plotted for three paint coupons and the results are shown in Fig. 5. A comparison of shelf life of coatings of 10, 20 and 40 mM pyrene showed that 10 mM coating degraded steadily with time, whereas a 20 mM coating was stable for 10 days and showed steady degradation thereafter. But a 40 mM coating was stable for 100 days. These results also indicated that a 40 mM coating had higher stability.

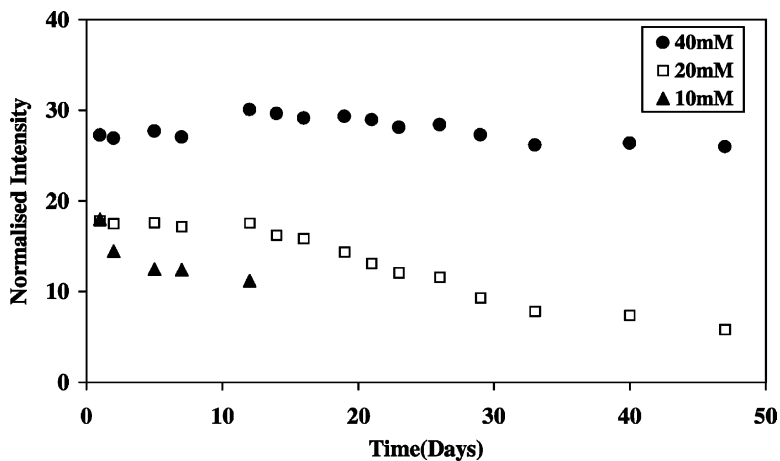


Fig. 5. Normal aging of PSP coatings with 10, 20 and 40 mM pyrene concentration.

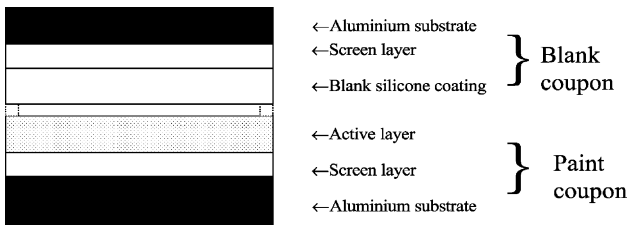


Fig. 6. Schematic diagram of the arrangement of the blank and paint coupons in the oven for thermal aging.

3.4. Experimental evidence for loss of pyrene from the silicone coating

Blank silicone coatings (paint coupons without pyrene) and pyrene-based PSP coupons were prepared as described in Section 2.1. Blank silicone coatings were placed face to face in contact with the PSP coatings as shown in Fig. 6 and thermal aging at 60 °C and 100 mbar was carried out for 1 h in a vacuum oven. The emission intensities of the blank and the paint coupons were measured before and after the thermal aging. Fig. 7 shows the fluorescence emission spectra of the blank coupon before and after thermal aging in contact with the paint coupon. It was found that the blank coupons showed the presence of pyrene after thermal aging as shown by the broad excimer emission peak at 480 nm in Fig. 7. The increased emission intensity of the blank coupon indicates that some amount of pyrene has evaporated from

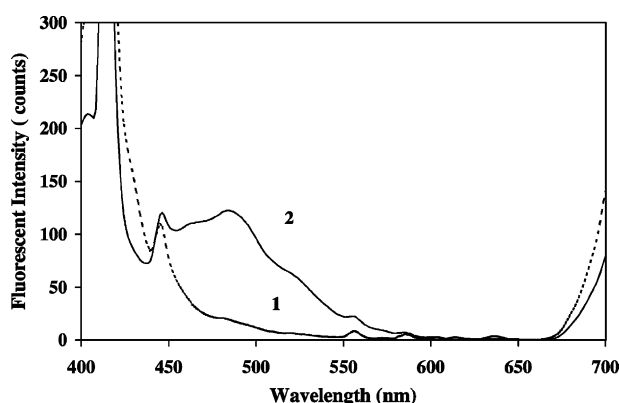


Fig. 7. Fluorescent spectra of a blank silicone coating (1) before and (2) after thermal aging in contact with a PSP coating.

Table 4

Fluorescent emission intensity of blank coupons after thermal aging in contact with PSP coupons of different pyrene concentrations

Blank coupon ^a	Pyrene concentration in the paint coupon (mM)	Intensity of blank coupons after thermal aging (counts)	Increased intensity of blank coupons (counts)
BL-1	20	58	50
BL-2	40	82	74
BL-3	60	118	110

^a The emission intensity of the blank coupon before aging was about eight counts.

the PSP coupon and diffused into the blank coupon during thermal aging.

The effect of concentration of pyrene in the coating on the diffusion of pyrene was studied. Paint coatings with three different pyrene concentrations (20, 40 and 60 mM pyrene) were prepared. Blank coupons were kept in contact with these paint coupons in a vacuum oven and thermal aging at 60 °C and 100 mbar was done for 1 h. The emission intensities of the blank and the paint coupons were measured before and after the thermal aging. The results are shown in Table 4. It was found that the emission intensity of the blank coupons after thermal aging increased with increase in pyrene concentration in the paint coating. The emission intensity of pyrene is a function of the concentration of pyrene in the coating. Thus the collection of pyrene by the blank silicone coating from the paint coating was found to be concentration-dependent.

Table 5

Fluorescent intensity of blank coupons and PSP coupons after aging tests under different conditions of temperature and pressure

Aging conditions	Intensity of the blank coupons after aging ^a (counts)	Normalized intensity of PSP coupons (counts)	
		Before aging	After aging
60 °C and 100 mbar for 1 h	81.5	25.11	18.45
60 °C and 1 bar for 1 h	60.8	25.76	19.83
RT and 100 mbar for 1 h	39.7	25.12	23.15
RT and 1 bar for 1 h	8.6	23.82	23.75

^a The emission intensity of the blank coupon before aging was about eight counts.

3.4.1. Diffusion of pyrene in silicone coatings under different conditions of temperature and pressure

Blank silicone resin coupons were placed on the pyrene-based PSP coupons of 40 mM pyrene during aging tests under different conditions of temperature and pressure for a period of 1 h. The emission intensities of blank coupons and the paint coupons were measured before and after the aging test and the results are shown in Table 5. The emission intensity of the blank coupons before aging was about eight counts. It was found that the increase in emission intensity of the blank coupon was highest at 60 °C and 100 mbar and lowest at room temperature and 1 bar. The increase in emission intensity of the blank coupon is proportional to the amount of pyrene diffused from the PSP coupon to the blank coupon. In the case of paint coupons, the decrease in emission intensity was maximum at 60 °C and 100 mbar compared to the other conditions studied. There was very slight decrease in intensity for the PSP coupon in contact with the blank coupon at room temperature and ambient pressure. The trend in the loss of pyrene of PSP coupons matched with the gain of pyrene of the corresponding blank coupons under each aging condition. Therefore, it was evident that increase in temperature and decrease in pressure accelerated the diffusion of pyrene.

At room temperature and ambient pressure, the diffusion of pyrene from the paint coating into the blank coating was negligibly low for a period of 1 h as shown in Table 5. The effect of time on diffusion was studied by keeping a PSP coupon of 40 mM pyrene and a blank coupon with their surfaces in contact at room temperature and pressure for 10 days. It was found that the intensity of the blank increased to 78 counts. Thus a large amount of pyrene diffused into the blank coupon over 10 days. Even though the rate of diffusion was low at room temperature, the process was taking place continuously as there was a concentration gradient between the two coupons. It was also found that the intensity of the paint coupon in contact with the blank coupon decreased. However, a paint coupon stored in contact with air was quite stable and showed no change in its intensity after 10 days. This shows that the rate of evaporation of pyrene was negligible at ambient temperature and pressure, whereas rate of diffusion within the silicone polymer is quite high even under ambient conditions.

The diffusion of pyrene in the PSP coating was further confirmed by more experiments by accelerating the diffusion

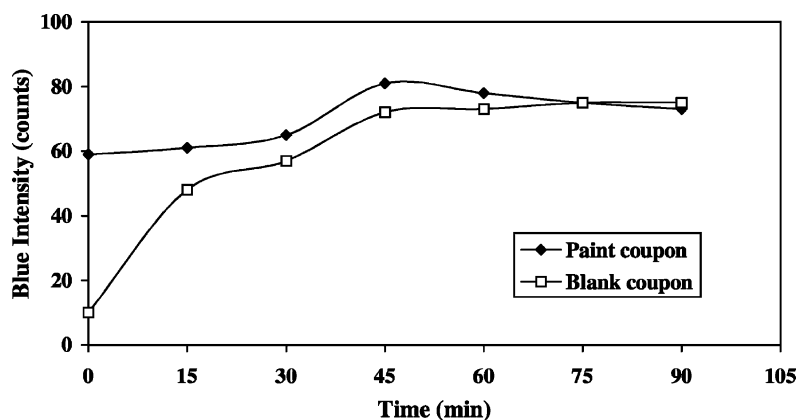


Fig. 8. Change in blue intensity with aging time for a paint coupon and a blank coupon during thermal aging at 60 °C and 0.1 bar.

processes by increasing the temperature to 60 °C. A paint coupon of 40 mM pyrene was thermally aged at 60 °C and 100 mbar with a blank coupon with their surfaces in contact. The thickness of the paint coating was 50 μm . Both paint coupon and blank coupon were taken out at 15 min intervals and the intensities were measured and the coupons were returned to the oven for further aging. The intensities were measured at periodic intervals of 15 min for about 90 min. The blue intensity versus time was plotted for both paint coupon and the blank coupon and the results are shown in Fig. 8. It was found that intensity of the paint specimen and blank increased with aging time and reached the same value by 75 min and did not change on further aging for 15 min. The diffusion of pyrene from the PSP coating to the blank coating at 60 °C continued until both the blank and PSP coupons attained the same pyrene concentration.

3.4.2. Evidence for the absence of diffusion of pyrene in epoxy paint layer

Coupons of white epoxy paint coating (screen layer) were kept in contact with the PSP coupons during thermal aging test at 60 °C and 100 mbar for 1 h. Fig. 9 shows a comparison of the fluorescence emission spectra of blank coupons of

epoxy paint and silicone resin after thermal aging treatment in contact with a PSP coupon. It was found that the epoxy blank coupons showed only very slight fluorescent emission after thermal aging. The pyrene collected on epoxy blank surface was much lower compared to that on a silicone blank surface.

The fluorescent emission spectra of both blank coupons of silicone resin and epoxy paint after thermal aging test at 60 °C and 100 mbar for 1 h in contact with PSP coupons were recorded in air and in the presence of nitrogen and are shown in Fig. 10. It was found that the emission intensity of pyrene in silicone resin blank increased by about four times in the presence of nitrogen, whereas the emission of pyrene on epoxy paint was not increased in the presence of nitrogen. It is known that the epoxy paint coating has very poor oxygen permeability and silicone polymers have high oxygen permeability. But the fact that pyrene collected on silicone resin blank coupon has exhibited dynamic oxygen quenching of fluorescence shows that pyrene has not only condensed on the surface of silicone blank coating but also has diffused into the bulk of the coating. These results are similar to the behavior of pyrene in polydimethyl siloxane (PDMS) reported in literature. Chu and Thomas have

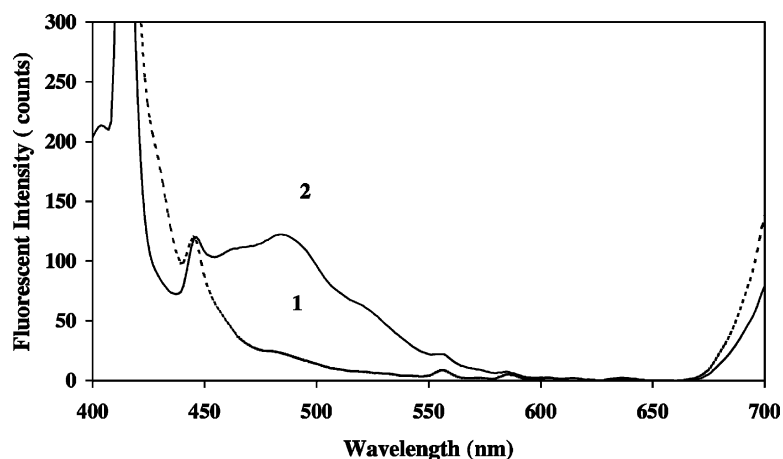


Fig. 9. Comparison of fluorescent spectra of (1) epoxy and (2) blank silicone coatings in contact with PSP coatings during thermal aging.

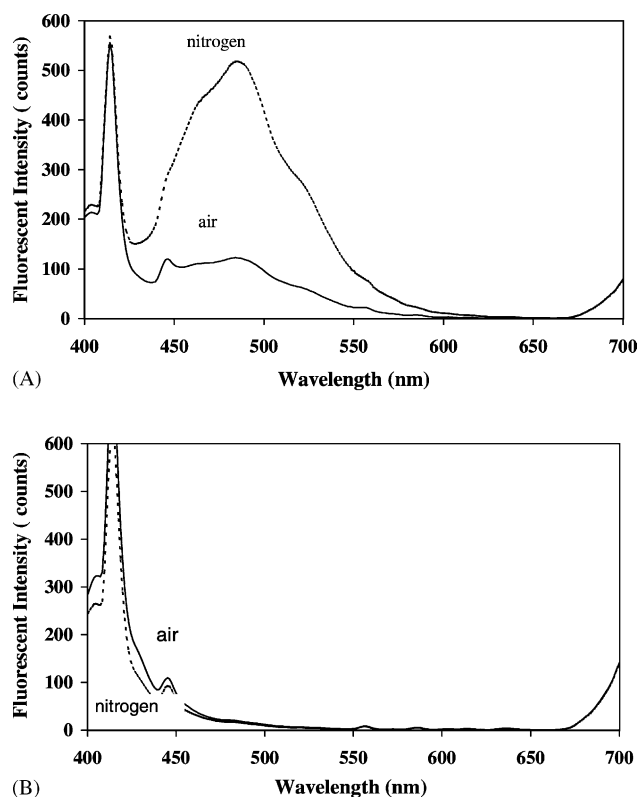


Fig. 10. Fluorescent spectra in air and in the presence of nitrogen of (A) blank silicone and (B) blank epoxy coatings exposed to PSP coatings during thermal aging tests.

reported that pyrene molecules diffuse to form excimers dynamically in PDMS of various viscosity values but not in epoxy resin or polystyrene [18].

3.5. Mechanism of paint degradation

It was shown earlier (Section 3.1) that the contribution of UV degradation to paint instability is small. Therefore, based on the thermal aging studies presented above, it can be easily understood that the decrease in intensity of the paint is due to the loss of pyrene in the coating by evaporation assisted by diffusion. It is well established that pyrene excimer formation is a diffusion controlled process [19]. It has been reported that pyrene has mobility in polymers like polydimethyl siloxanes since these polymers have high free volume [18]. Chu and Thomas have calculated the diffusion coefficient of pyrene in PDMS with high molecular weight and high viscosity and found it to be high. The comparatively long Si–O and Si–C bonds reduce steric conflict, i.e. hindrance between methyl groups on neighboring silicon atoms, which facilitates freedom of rotation of methyl group about the Si–O and Si–C bonds. This unique structural feature leads to a significant free volume in bulk PDMS. The diffusion of pyrene does not require the movement of the whole macromolecule, but a rotation of the side groups of the resin is sufficient for solute diffusion. We have found

that the same is true for pyrene in silicone coatings also. The pyrene molecules are in constant motion within the bulk of the silicone coating and when they reach the surface they undergo evaporation. At room temperature and pressure, these processes of evaporation and diffusion are taking place at a slower rate. The evaporation of a few pyrene molecules from the surface is compensated by molecules diffusing towards the surface from the bulk of the coating. For a thick coating, especially with higher pyrene concentration, there is a balance between these two processes so that no degradation is observed for a long period under ambient conditions. This explains the good shelf-life or normal aging stability of the coatings with 40 mM pyrene.

Pyrene molecules are uniformly distributed in the cured paint coating at lower pyrene concentrations (≤ 10 mM) and the average distance between pyrene molecules at this concentration is approximately 1 nm. Since pyrene cannot diffuse into the epoxy screen layer at the base (as discussed in Section 3.2.2), it has to diffuse towards the surface. As the thermal aging proceeds, pyrene molecules from the surface evaporate and these are replaced by molecules diffusing from the bulk of the coating. These processes lead to accelerated loss of pyrene from the coating during thermal aging. Thus a decrease in intensity is observed for paints with lower pyrene concentration (≤ 10 mM).

But the evaporation cum diffusion process cannot explain the phenomenon of increase in intensity observed at higher concentrations at a certain stage of thermal aging. We propose the following mechanism to understand the anomalous intensity changes of paint coatings of higher pyrene concentrations during thermal aging tests. At higher pyrene concentrations (≥ 30 mM), pyrene molecules are not uniformly distributed in the cured paint coating and there may be several microclusters or aggregates of pyrene molecules. During thermal aging, pyrene molecules from the clusters diffuse out into the coating and are available for excimer formation. Thus, at a particular time during the thermal aging, there is an enrichment of “free” pyrene in the coating due to the disintegration of clusters of pyrene. It has been reported that the excimer formation between a pyrene molecule in ground state and a pyrene molecule in excited state occurs when the interaction distance between them is about 3 Å [20]. The disintegration of pyrene clusters leads to increased excimer formation and an increase in intensity is observed. The maximum intensity is obtained when the free pyrene concentration in the top layer is at the highest and the distribution of pyrene molecules is most favorable for excimer formation. Further, thermal aging results in a steady decrease in intensity as the pyrene accumulated in the top layer continues to evaporate and they are not replenished at the same rate.

4. Conclusions

Our study has shown that evaporation of pyrene assisted by diffusion in the coating as the major factor which con-

tributes to the poor wind tunnel stability of the pyrene-based pressure sensitive paints. The decrease in intensity due to UV degradation was comparatively smaller. The diffusion of pyrene was found to be dependent on pyrene concentration, temperature, pressure and thickness of the coating. It was seen that loss of pyrene was accelerated at higher temperatures and lower pressures. A mechanism is proposed to understand the anomalous increase in intensity after thermal aging for paint coatings with higher pyrene concentrations. An optimum pyrene concentration of 40 mM in the coating and a coating thickness of about 60 μm were found to give improved stability for the PSP applications.

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