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14. ABSTRACT

This report results from a contract tasking University of Wales Swansea as follows: This project aims to harness new techniques developed to assess the mechanisms and kinetics of paint failure in short term exposure to the results from traditional weathering experiments. This will enable a rapid test system to be developed for polyurethane coatings which currently are showing premature failures.

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TITANIUM DIOXIDE PHOTO-CATALYZED DEGRADATION OF POLYURETHANES
(PROJECT CODE - 053030)

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Introduction

Titanium dioxide (TiO_2) is widely used to pigment[1] polymers for organic coatings in the paint industry and for structural plastics. TiO_2 can be excited by ultra-band gap UV irradiation (<380 nm) generating electron hole pairs, which have important redox properties[2,3] that can result in degradative attack on the polymer[4,5]. Photo-degradation of polymers yields mineral oxidation products such as CO_2[6,7] and water as well as volatile oxidation products that are precursors to CO_2. In this report we describe the photoactivity testing of several grades of TiO_2 in an unplasticised PVC matrix and the oxidation rates of a variety of polyurethane coating systems prepared using different ratios of cross linking agent and containing different photoactivity grades of TiO_2. We also describe the effects of rutile TiO_2 loading and UVB exposure on rates of degradation.

Experimental Procedures

Model UPVC paints

For standard UPVC films, 3 grams of the pigment was dispersed in a small quantity of THF (Tetrahydrofuran) to ensure good pigment dispersion and de-agglomeration. The remainder of the 100 ml of THF was then added. 10g of PVC was then added slowly over 15 minutes while the mixture was rapidly stirred using a high shear mixer. Once the polymer had dissolved the paint was transferred to a solvent bottle and stored in darkness. A Hegmann draw down gauge was used to ensure consistent particle de-aggregation (<5μm). Before any films were cast from a new batch it was stirred for 24 hours to ensure even mixing and the expulsion of any tiny air bubbles and complete particle de-agglomeration. Dry films of 20 (±2) μm were prepared by casting onto flat glass plates using tape guides and a draw down bar as described previously[8]. A range of TiO_2 grades were incorporated and their properties are summarized in Table 1.

TiO₂ Code	Manufacturer	Nominal Grade	Coating
K2300	Kronos	B	Al,Si,Zr oxides
R960	TiPure	A	Unknown
K2310	Kronos	A	Al,Si oxides
K2220	Kronos	A	Al,Si oxides

Table 1: pigment details for UPVC films

Model polyurethanes (PU)

A range of PU paints were prepared by Captain Kris Hardy and their composition is summarized in Table 2. It can be seen that there are two principle variables. Firstly the grade of TiO_2 was altered with three systems studied. These were no pigment (clear system) an unclassified anatase pigment (Tiona AT-1) and a stabilized TiO_2 grade (TiPure 960). The second variable that was altered was that of the ratio of Demosdur (the isocyanate cross linker) to Desmophen (the polyol) as shown in Table 2. In the later sections the samples X-1.2 to X-1.8, X is A for rutile TiO_2, B for anatase TiO_2 and C for unpigmented.

Code	Target Desmophen (g)	Target Desmodur (g)	Index	Target TiO_2 (g)
X-1.2	25	12	1.2	17
X-1.5	25	15	1.5	18.5
X-1.8	25	18	1.8	20

Table 2: typical compositions of model PU systems

A second series of panels were also prepared in which the loading of titania was altered from 5 – 20 % pigment volume concentration as described in Table 3
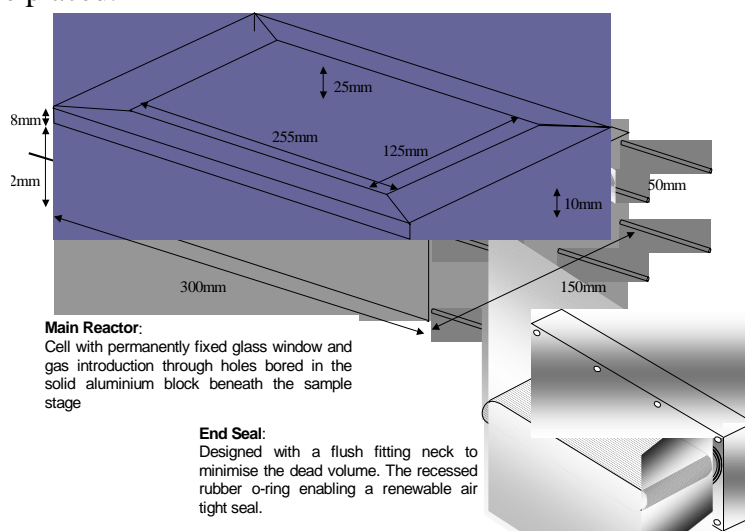
.Code	Target Desmophen (g)	Target Desmodur (g)	Index	Target TiO_2 % PVC
A1.5-5	25	15	1.5	5
A1.5-10	25	15	1.5	10
A1.5-15	25	15	1.5	15
A1.5-20	25	15	1.5	20

Table 3: typical compositions of second series model PU systems

The coating systems also included a tin stabilizer and each was sprayed in 9 coats onto aluminum substrates by Captain Hardy.

Exposure of test panels

The Flat Panel Reactor used in this work has been fully described elsewhere[8] and is shown schematically in Figure 1. The reaction cell was machined from a single block of aluminium, has a quartz window and a sample stage onto which the coated samples can be placed.

25mm

8mm

255mm 125mm

2mm

10mm

50mm

300mm 150mm

Main Reactor:
Cell with permanently fixed glass window and gas introduction through holes bored in the solid aluminium block beneath the sample stage

End Seal:
Designed with a flush fitting neck to minimise the dead volume. The recessed rubber o-ring enabling a renewable air tight seal.

Figure 1: Schematic of the flat panel reactor cell

The cell can be sealed and the headspace circulated *via* an infrared spectrophotometer. The irradiation of the flat panel cell was achieved using a bank of 6×8 W Coast Wave Blacklight UVA lamps (Coast Air: radiation λ_{max} = 355-365 nm, length = 30 cm Intensity = 4 x10^{17} photons s^{-1} measured by potassium ferrioxalate actinometry[9]) set against a flat polished aluminium reflector. The flat panel cell was connected in series with a diaphragm pump to circulate the gas phase at 6 dm^{-3} min^{-1} in the sealed system via an infrared flow cell (path length 2.4 m) mounted inside a Fourier Transform Infrared Spectrophotometer (FTIR Perkin Elmer System 2000). The whole system has a volume of *ca*. 770 cm^3. All the tubing used to connect the different parts was stainless steel with short flexible connectors made from Masterflex tubing (TYGON® R-3603), which has very low gas permeability. The reaction was, in each case, initiated by removing a solid shutter that was inserted between the lamps and the flat panel cell. In this way the lamps could be pre-warmed and be at maximum intensity from the start of the irradiation. The system is calibrated by successive injections of CO_2 as shown in Figure 2 from which it can be seen that there is a linear relationship between the integrated area peak and the amount of CO_2 injected and that the system is completely sealed (since there is no reduction in CO_2 area peak with time).
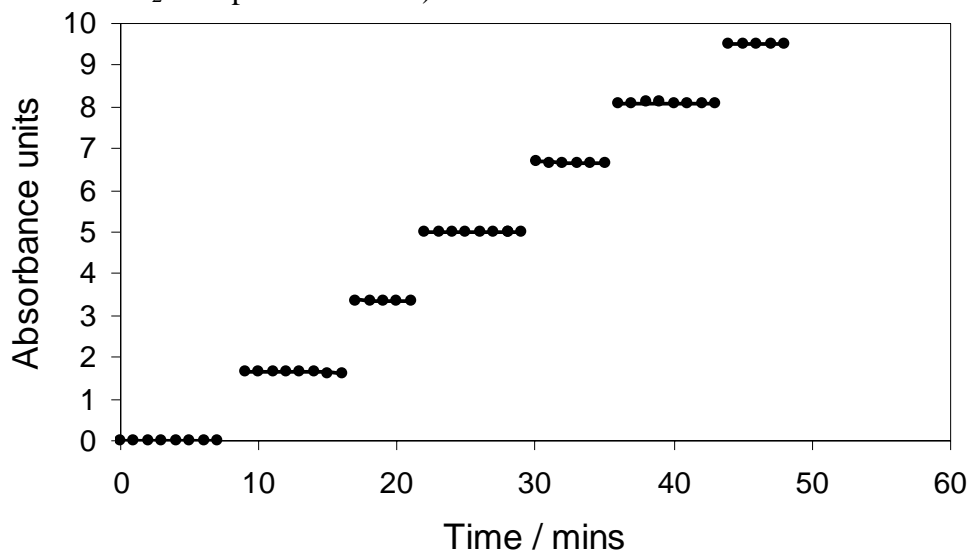

Figure 2: calibration of the flat panel reactor through successive injections of CO$_2$

Results and Discussion

UPVC films.

Much of the previous work undertaken using this technique has been aimed at quantifying the degradation rates of UPVC. In order to determine and rank the photoactivity of the precise grade of TiO_2 used by the USAF in their coatings a series of experiments were performed to determine the CO_2 evolution kinetics from a series of model UPVC paints pigmented with 30 PHR TiO_2 of the different types shown in Table 1. The typical CO_2 evolution plots for such experiments are shown in figure 3 for the pigments tested. There is a clear distinction between activity as demonstrated by the differing CO_2 evolution profiles. This is shown further in figure 4 which illustrates the effect of pigment type on the evolution rate of CO_2 from UPVC films. It can be seen from these plots that the most stable grade of TiO_2 tested is that produced by Kronos (grade K2220). The grade currently in use by the USAF is over twice as photoactive as the most stable grades tested. An immediate recommendation is that the USAF consider

3

testing K2220 in a PU system since it could offer a considerable improvement in chalking resistance and overall coating performance.
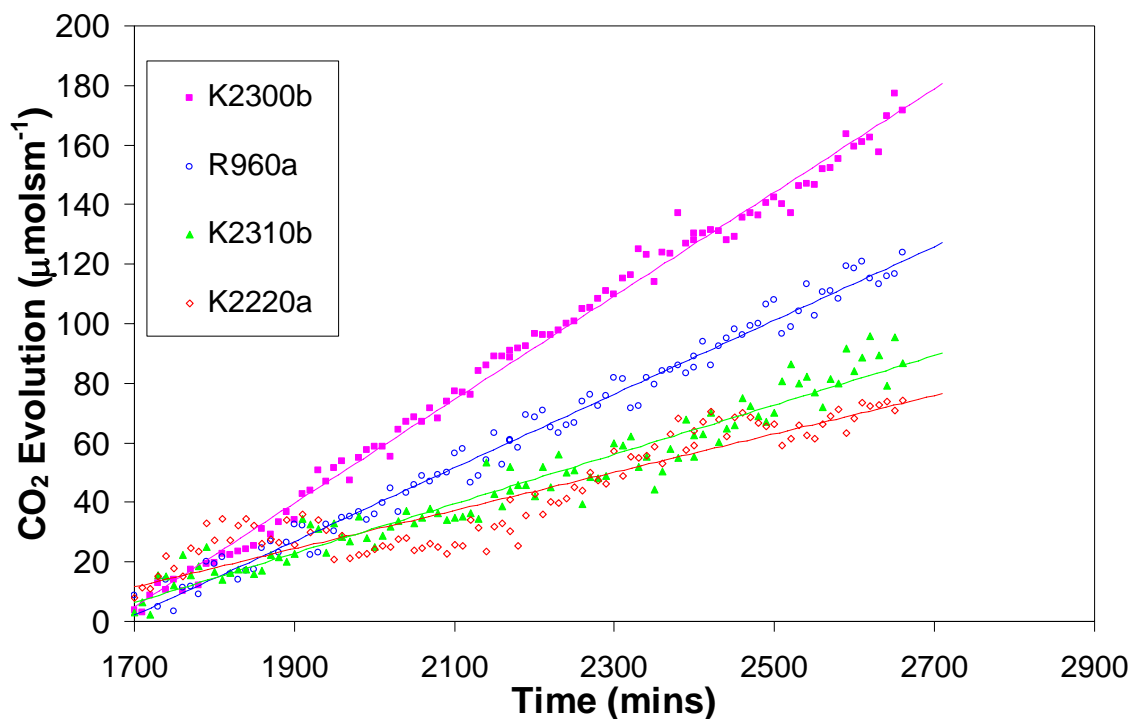

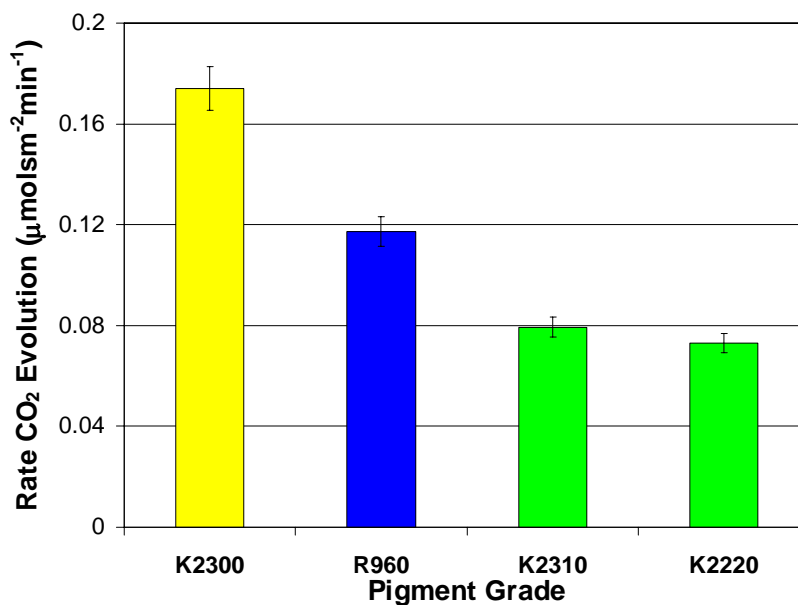*Figure 3: CO_2 evolution as a function of time for different pigments*

Figure 4: CO_2 evolution rates as a function of pigment type. NB K2220 and K2310 are grade A pigments and K2300 is a grade B material. R960 is the rutile TiO_2 used in the USAF polyurethane coatings.

4

Figures 5, 6 and 7 illustrate the CO_2 evolution profiles for unpigmented, anatase pigmented and grade A pigmented PU systems prepared according to Table 2 with differing ratios of Desmodur to Desmophen. These samples were irradiated immediately upon arrival in the UK.
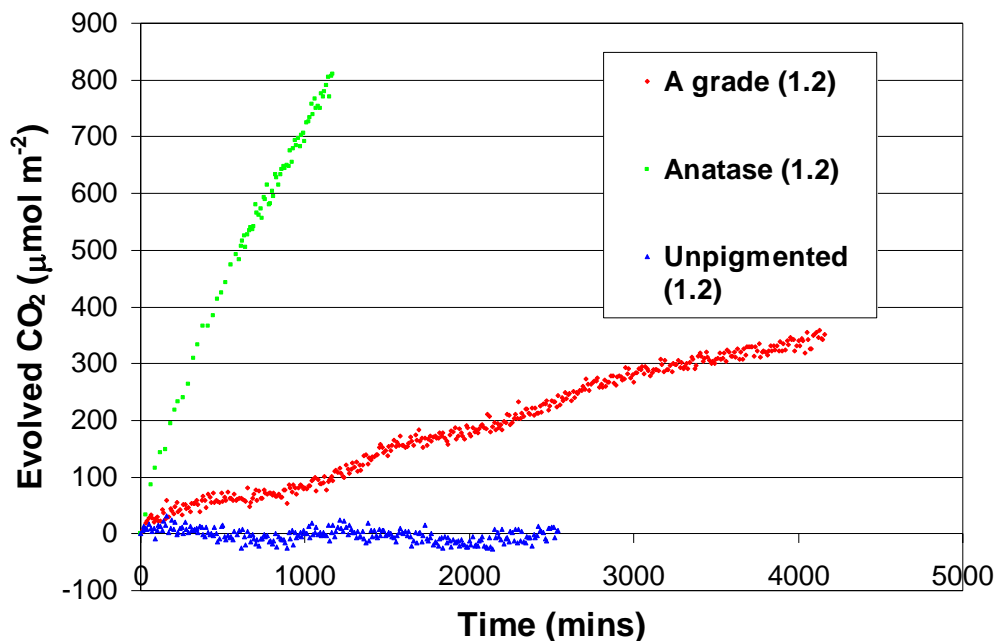

Figure 5: CO_2 vs time profile for X1.2 samples irradiated with UVA containing no pigment (blue), a stable grade A pigment (red) and an unstable anatase pigment (green).
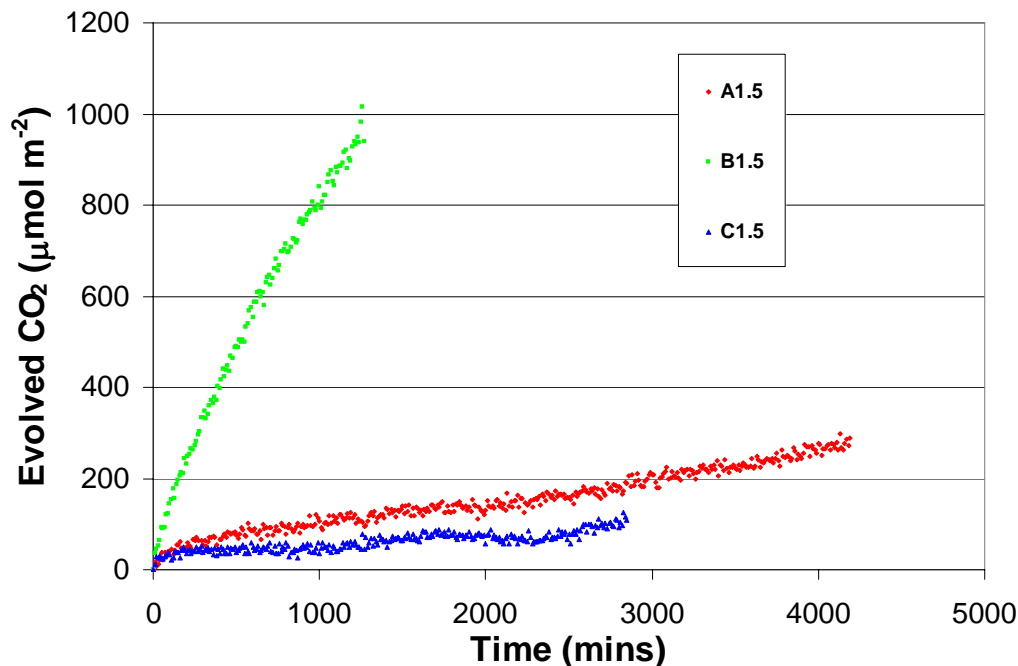

Figure 6: CO_2 vs time profile for X1.5 samples irradiated with UVA containing no pigment (blue), a stable grade A pigment (red) and an unstable anatase pigment (green).
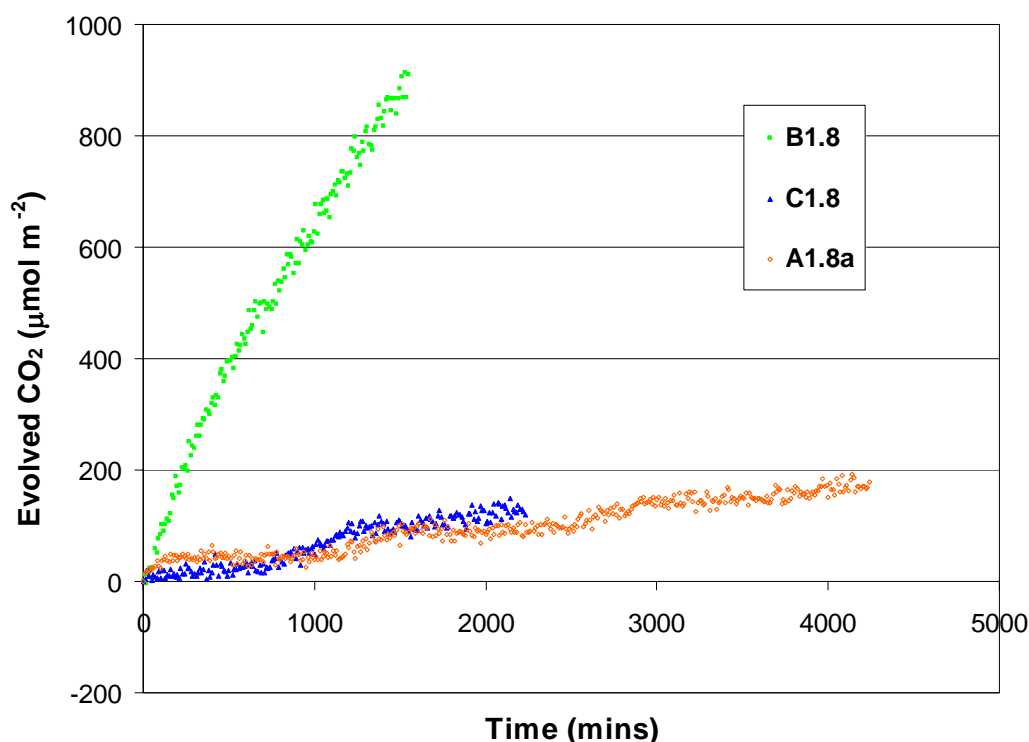
Figure 7: CO_2 vs time profile for X1.8 samples irradiated with UVA containing no pigment (blue), a stable grade A pigment (red) and an unstable anatase pigment (green).

It is clear from Figures 5, 6 and 7 that the addition of an anatase pigment in all cases leads to rapid photodegradation. It is also clear that in most cases the most stable matrix is the PU without pigmentation and that the grade A pigment used in this work is generally leading to elevated rates of photodegradation over the unpigmented material. This is probably due to the rather higher than anticipated inherent photoactivity of this pigment shown in Figures 3 and 4 as compared to other grade A materials that are available. It would be expected that a fully stabilized Titania would actually reduce degradation through shielding the polymer as a result of efficient light scattering. This is further evidence that the grade used could be improved upon.

What is also clear from the data presented is that there is some variation in the signal which appears to be periodic in the samples containing the least active rutile pigments. To enhance the signal to noise ratio in the apparatus the whole cell system has been redesigned. It became apparent that the rate of CO_2 production was very low leading to problems of laboratory personnel emitting competing quantities of CO_2 detectable by the FTIR. To overcome this problem a new long path length cell was purchased and the instrument re-designed to include a nitrogen purged cell chamber. The new apparatus is shown in Figure 8. The success of the shielding is illustrated in Figure 9 which shows the reduction in background signal and increase in reproducibility upon shielding.
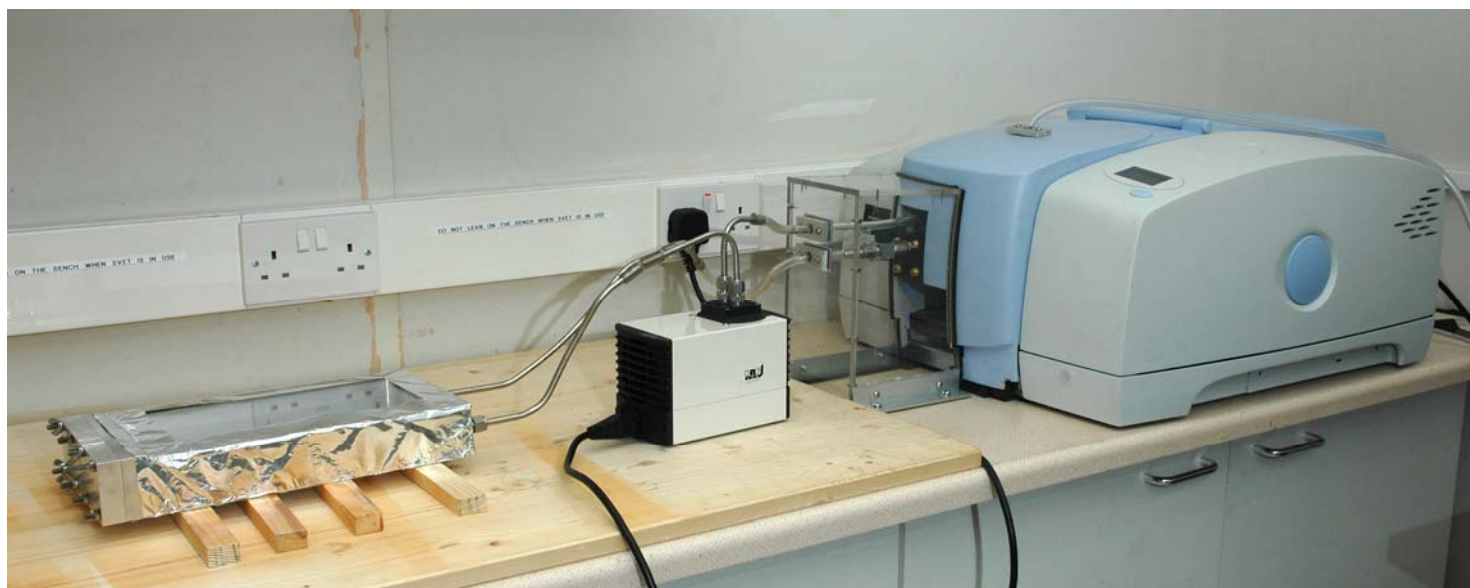
Figure 8: photograph of the re-designed cell with nitrogen encapsulation to minimize interference from lab occupants (NB lamp unit is not shown but fits over aluminum reactor.
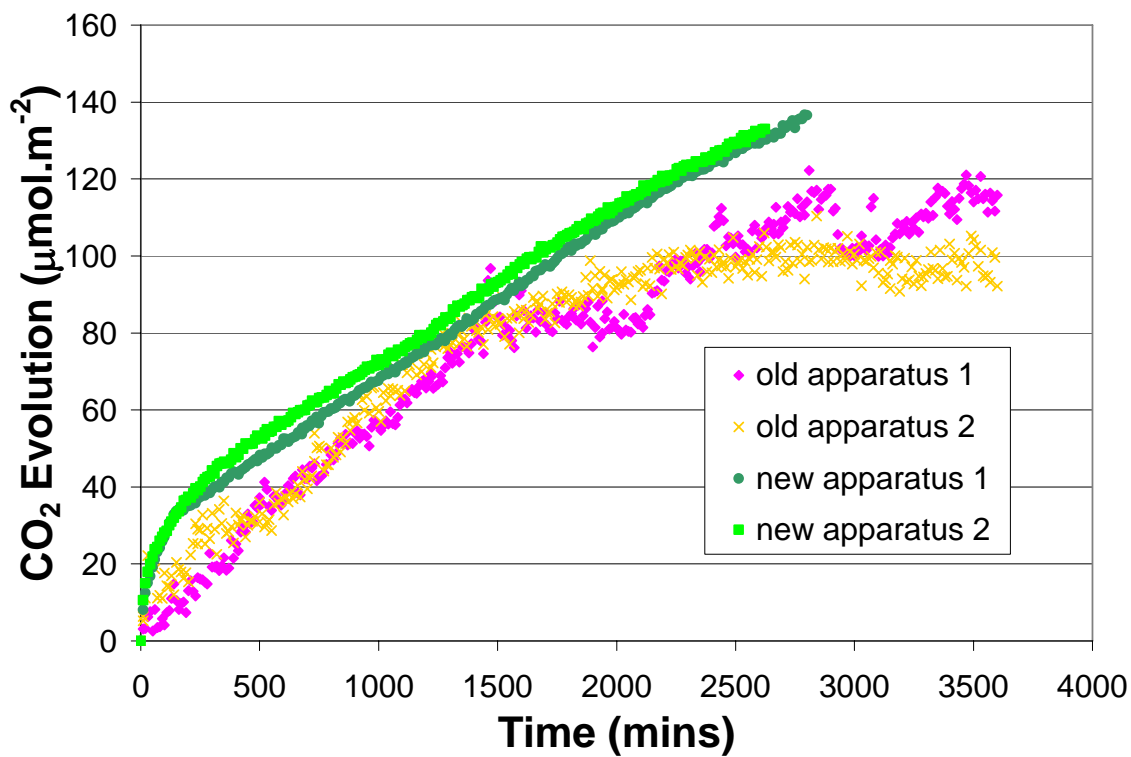

Figure 9; plot showing sample noise and reproducibility before and after addition of nitrogen purging to cell system using an architectural PU pigmented with Kronos K2220.

The redesigned apparatus was then used to measure the rates of degradation for the second series in which the stable titania was used at a series of different loadings and then the first series of panels repeated after 6 months storage.

Testing of CO_2 evolution in new reactor A: different photostable TiO_2 loadings

To illustrate the effectiveness of the new reactor setup in preventing user contamination the first series of panels investigated were those containing a stable grade A rutile pigment at different loadings in the matrix X1.5 (see table 3). The CO_2 evolution profiles for the pigmented paints are shown in Figure 10.
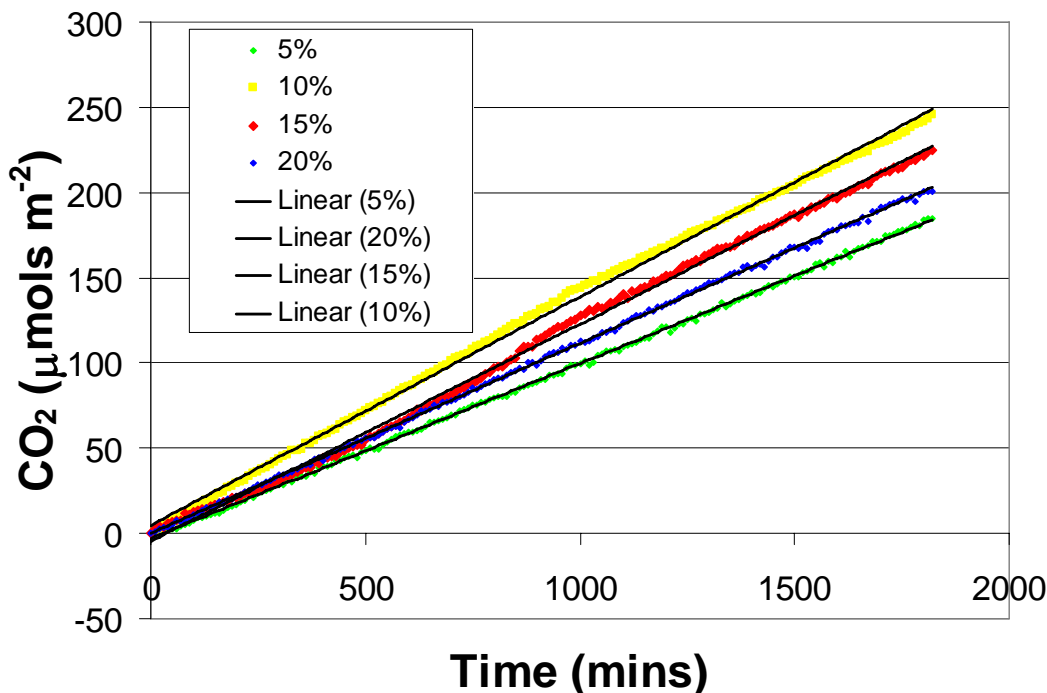

Figure 10; plot showing the evolution of CO_2 from a series of X1.5 paints containing 5, 10, 15 and 20% rutile TiO_2.

The rates of CO_2 production can be obtained from the slope of the CO_2 vs time profile. In this instance the rates have been recorded and are displayed for comparison with a clear un-pigmented blank with the same isocyanate/polyol ratio in Figure 11. From this plot it can be seen that the level of photo-degradation increases as the quantity of TiO_2 is increased to a maximum at 10% loading and then begins to tail off. Again, this is a reflection of the activity of the grade of TiO_2. At lower level additions there is increasing activity but as loading goes above 10% the overall degradation decreases as the TiO_2 more effectively shields the matrix. One potential issue is that our test measures total degradation and it is unknown whether there would be a focus of degradation in the surface of the coating leading to gloss and color alteration (but not to degradation of barrier properties).
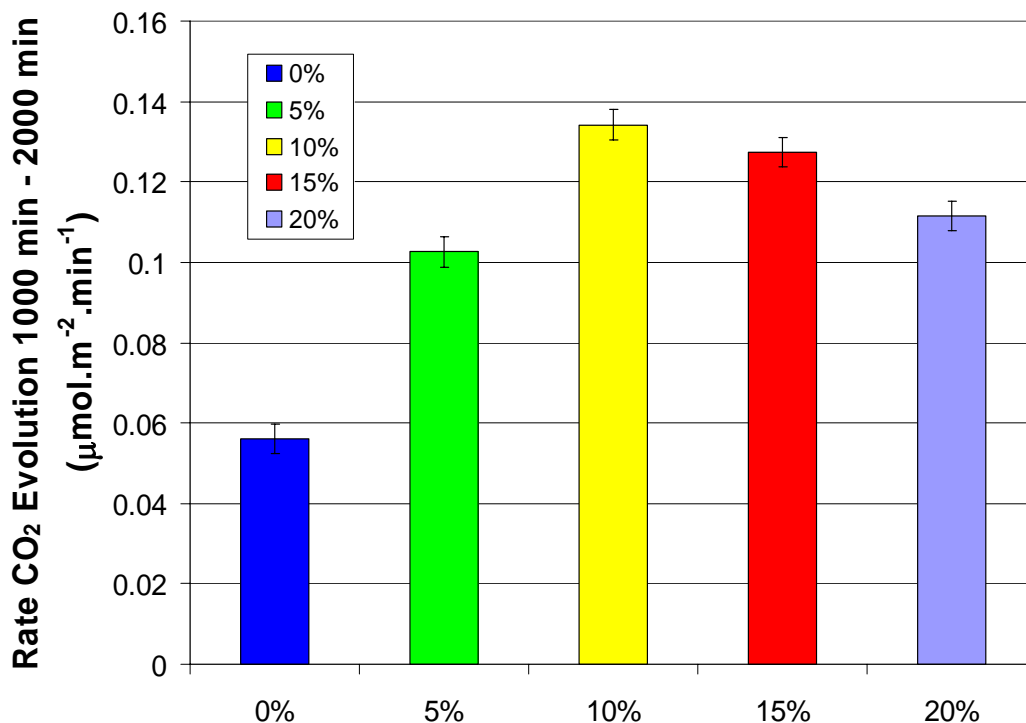
Figure 11; plot of the rate of CO_2 evolution determined from UVA irradiation of X1.5 PU panels containing various amounts of stable rutile TiO_2. (NB TiO_2 is a pigment volume %)

Testing of CO_2 evolution in new reactor: different photoactivity TiO_2 grades

The panels containing different grades of TiO_2 were again irradiated in the apparatus shown in figure 8 to include nitrogen shielding of the IR gas cell. Figure 12 is an illustration of the effect of changing the polyol to isocyanate relationship for the clear non pigmented panels (C 1.2, C1.5 and C1.8). It is clear from the data shown that for the purpose of carbon dioxide evolution determined in this test the greater additions of the cross linking isocyanate is increasing the rate of degradation to CO_2. Similar results are obtained in terms of the CO_2 evolution for both the non stabilized anatase pigments (B1.X) and stable rutile systems (A1.X) shown in Figures 13 and 14. It is clear that addition of the anatase TiO_2 results in very rapid degradation. In this instance the CO_2 evolution profile is non linear and as such, to compare degradation, the final carbon dioxide amount evolved over 2500 mins irradiation is presented. In comparing the CO_2 evolution rates between non pigmented and 'A grade' pigmented paints, the titania appears to stabilize the system with the highest urethane/polyol ratio (X1.8) but there is still a photocatalytic effect at the other ratios. One point of interest is that the panels have aged. Comparison of the rates in figures 12, 13 and 14 with those in figures 5, 6 and 7 show that as the paints have been stored the rate of CO_2 evolution has dropped for TiO_2 pigmented systems. We have observed this with other paints and it relates to slow volatile loss from the paints with storage; the volatiles are more readily degraded by the TiO_2 since they adsorb on the surface so the rate of evolution changes with storage time.
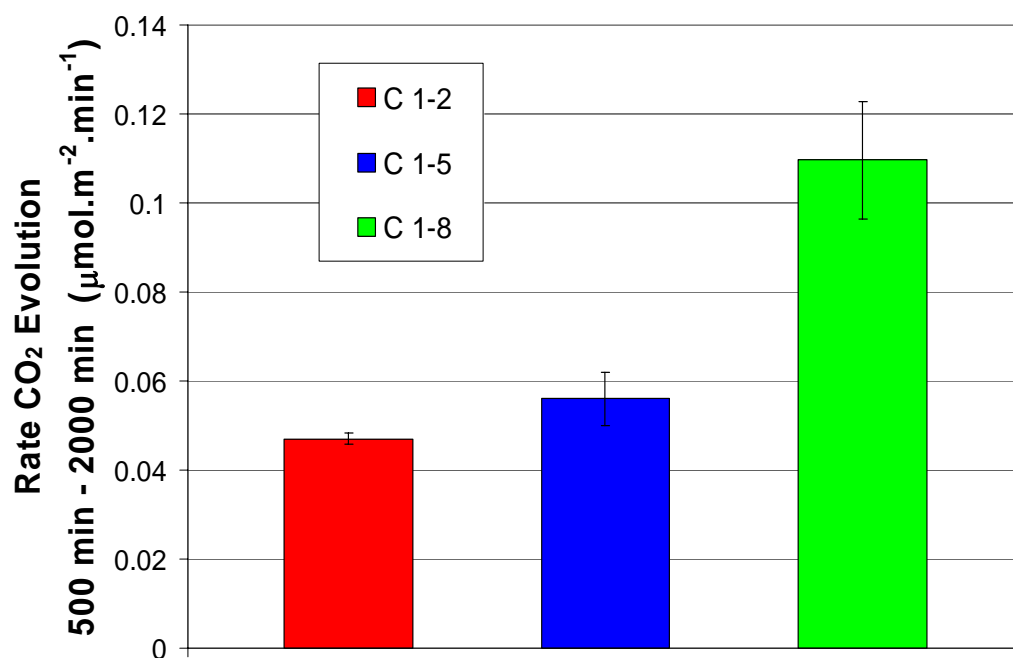
Figure 12: rates of CO_2 evolution from UVA exposed panels of the series C1.X which are unpigmented and contain different ratios of polyol and urethane cross linker described in table 2.
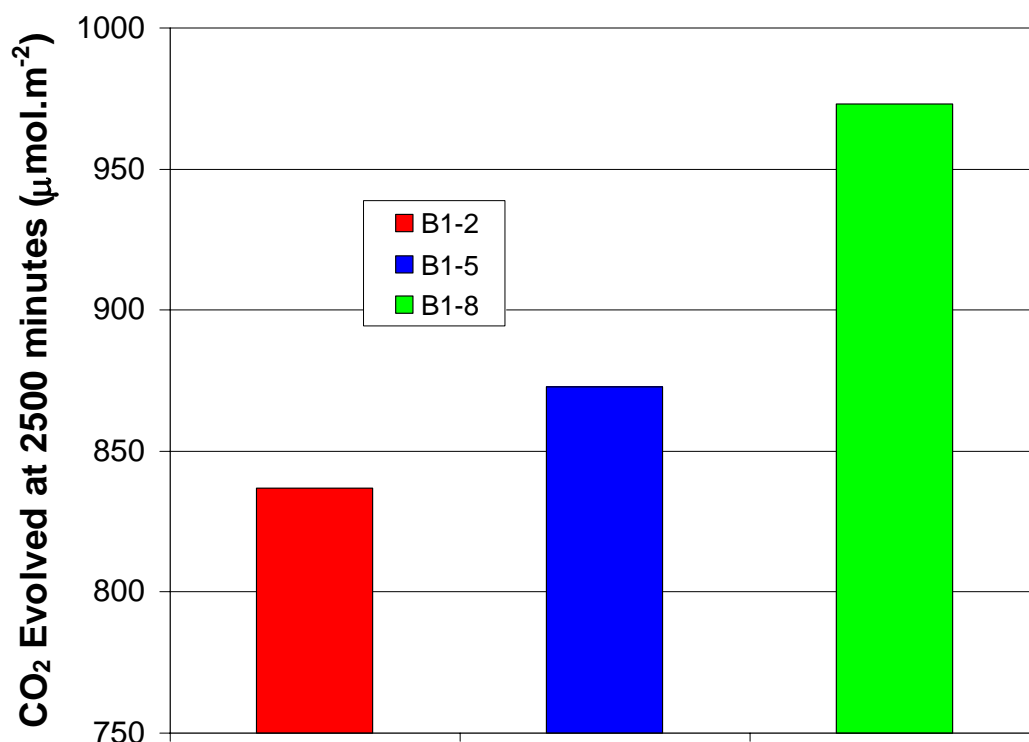

Figure 13: total CO_2 evolution from 2500 mins UVA exposed panels of the series B1.X which are pigmented with anatase TiO_2 and contain different ratios of polyol and urethane cross linker described in table 2.
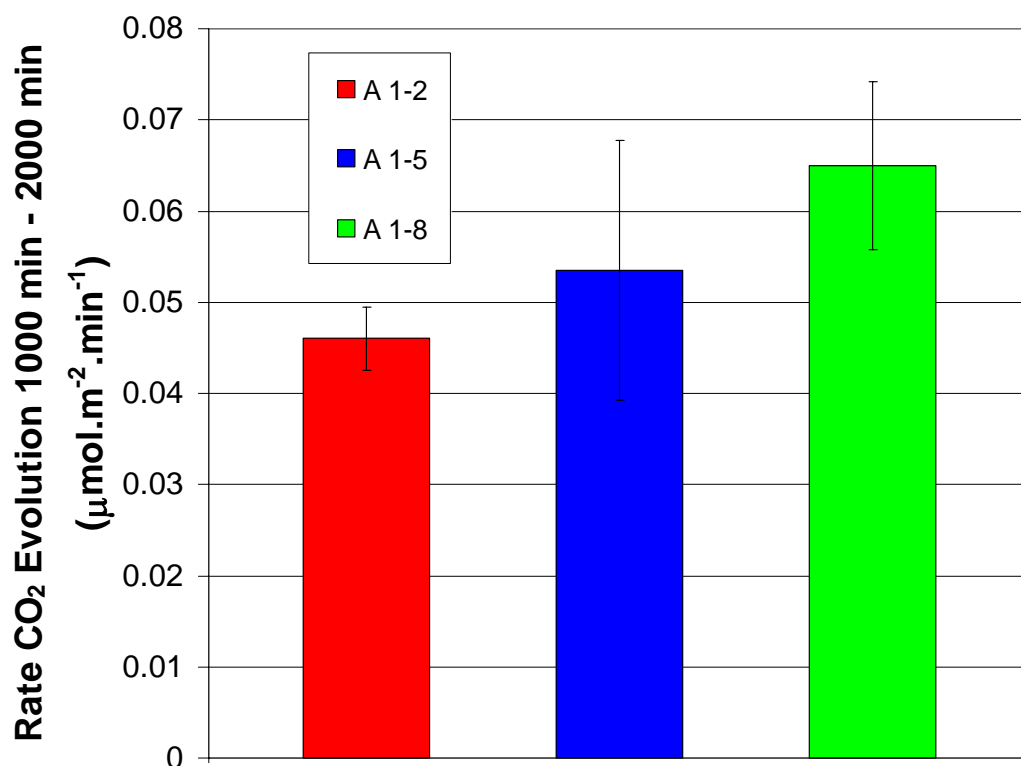
Figure 14: rates of CO_2 evolution from UVA exposed panels of the series A1.X which are pigmented with rutile TiO_2 and contain different ratios of polyol and urethane cross linker described in table 2.

Testing of CO_2 evolution in new reactor: effects of UVB illumination

Since aircraft are flying at such elevated levels in the atmosphere it is likely that their exposure to UVB will be greater than for ground level coatings used on automobiles and in the construction industry. To briefly investigate the effects of a component of UVB irradiation the system was modified to incorporate a quartz window (transparent to UVB) and also one of the six UVA lamps was replaced with a UVB tube. It is the case that this small component of UVB dramatically alters the paint system performance. In the first instance the rates of carbon dioxide evolution are much more rapid. It is also the case that within the 2500 minute irradiations, the panels began to discolor. Figure 15 shows typical CO_2 evolution profiles and figure 16 the amount of degradation determined from the final CO_2 level in the apparatus (since a linear kinetic was not observed in this instance). It is significant that the addition of a single UVB lamp has dramatically altered the degradation rate. Despite this being the most stable pigmented system the rates of degradation are an order of magnitude worse than those pigmented with anatase TiO_2 and irradiated with UVA alone. Hence the UVB component of the light falling on the airframe will critically determine the lifetime of the coating. Even small levels of UVB will accelerate failure by orders of magnitude compared to the results achieved through accelerated testing in QUVA cabinets. In the case of UVB irradiation it is clear from figures 17-20 that adding TiO_2 provides stabilization at all loadings and for all of the isocyanate to polyol ratios used in this programme. Hence further work is required to evaluate the extent of potential UVB exposure of the airframe paints to develop a realistic accelerated test. Figure 21 shows the discoloration of the panels exposed following the test.
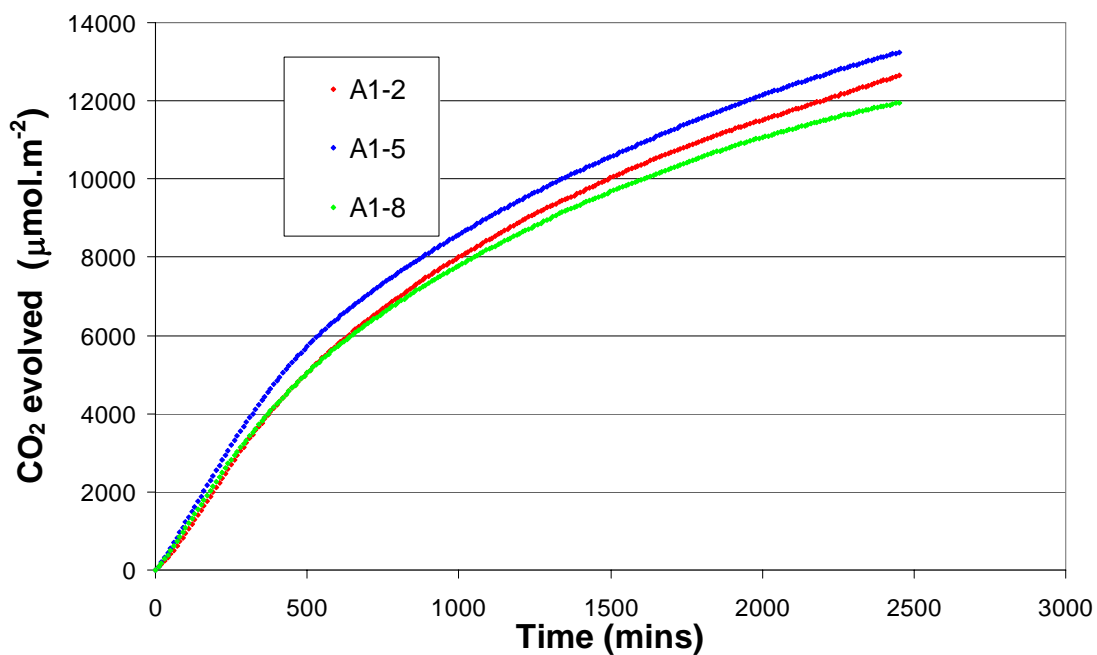
Figure 15: UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of A1.X samples pigmented with stable rutile TiO_2.
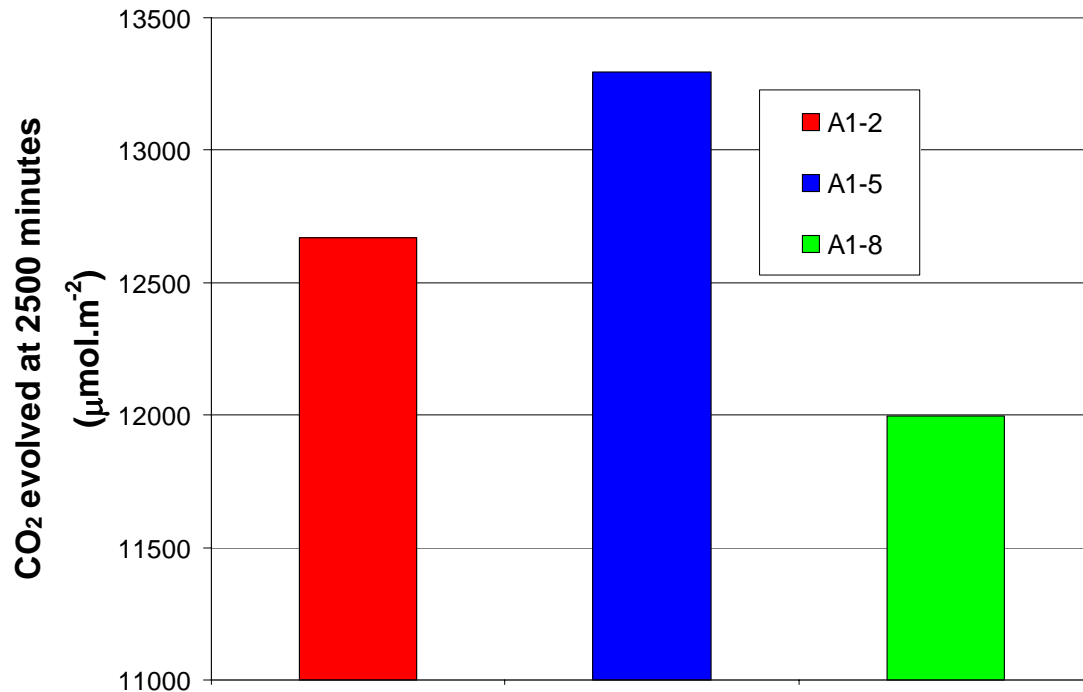

Figure 16; total CO_2 evolved from UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of A1.X samples pigmented with stable rutile TiO_2.
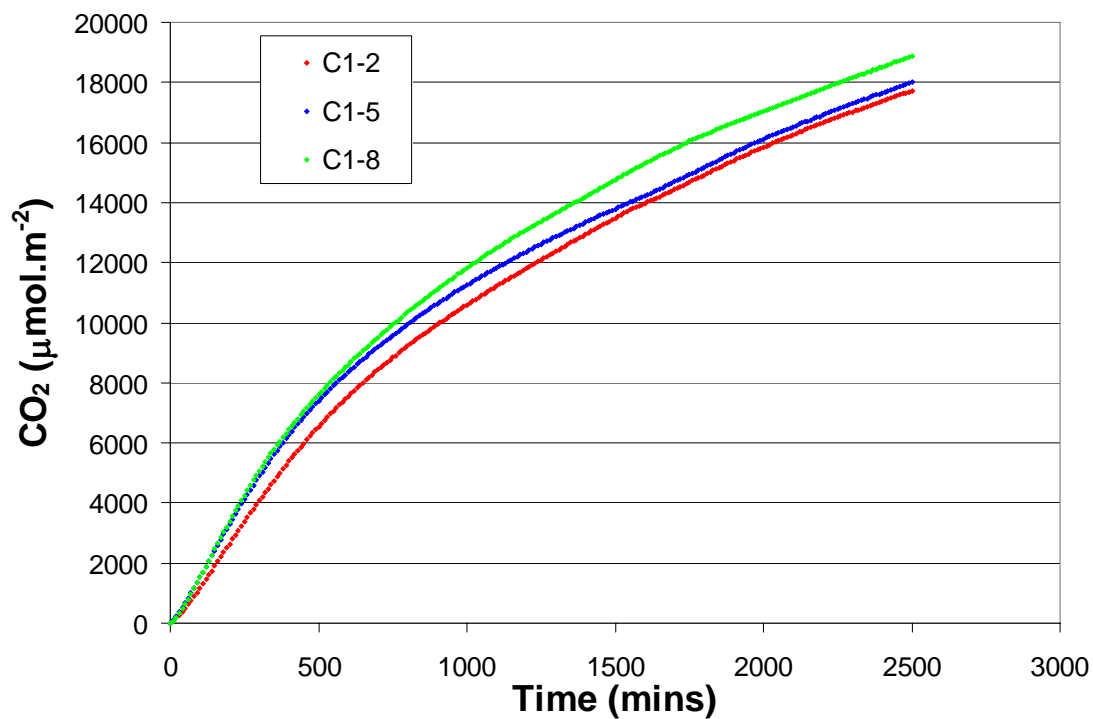
Figure 17; CO_2 evolved from UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of C1.X samples (unpigmented).
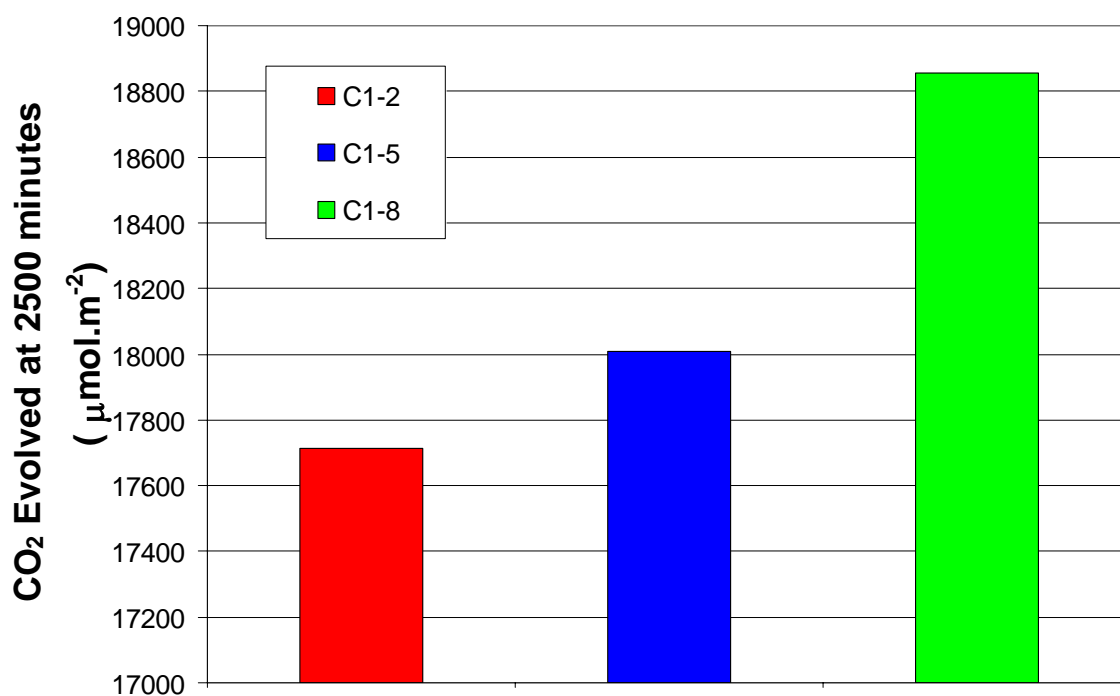

Figure 18; total CO_2 evolved from UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of C1.X samples (unpigmented).
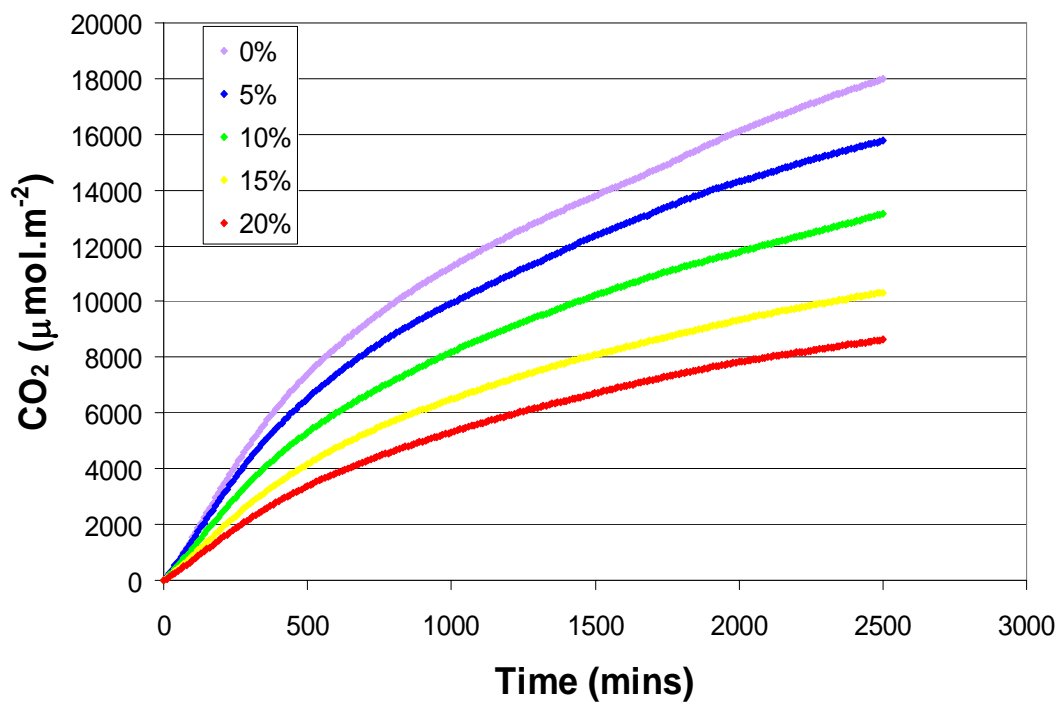
Figure 19; CO$_2$ evolved from UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of samples of the 1.5 PU matrix loaded with different quantities of stable rutile titania.

Figure 20; total CO$_2$ evolved from UVA and UVB (5 UVA lamps 1 UVB lamp) irradiation of samples of the 1.5 PU matrix loaded with different quantities of stable rutile titania.
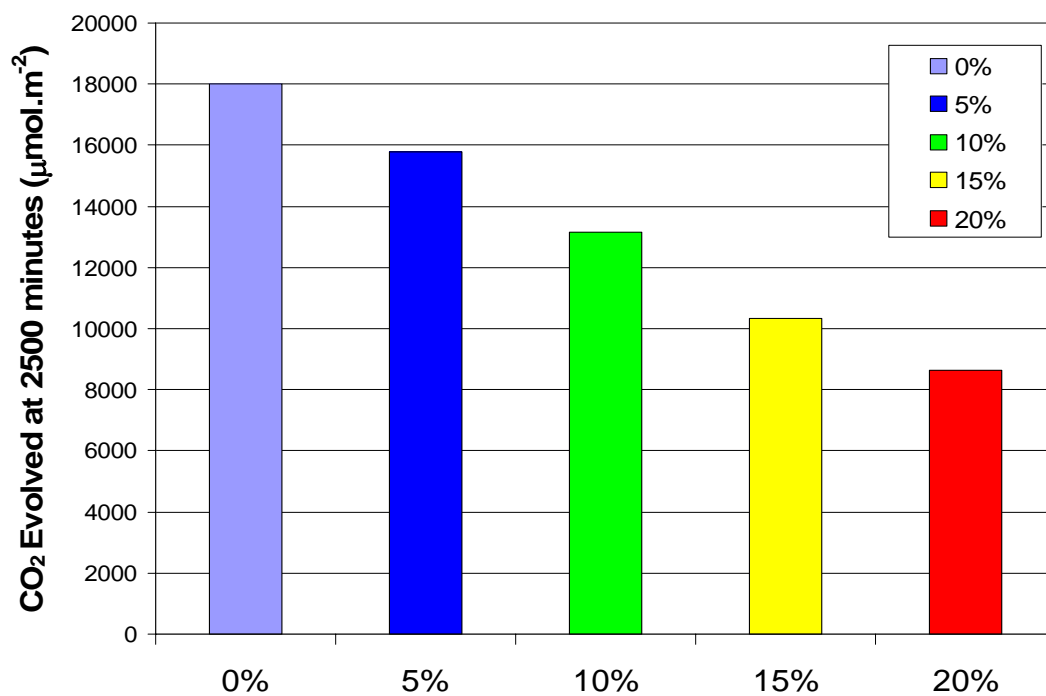
Figure 21; photograph of the UVB irradiated panels showing increasing discoloration with TiO₂ loading reduction.

Conclusions

From the initial study we have shown that

- The flat panel reactor can determine CO_2 levels given off from the degradation of aerospace PU systems exposed to UVA and UVB irradiation.
- The rate of CO_2 evolution depends on the grade of TiO_2.
- The grade of TiO_2 currently in use is quite photoactive and could be improved upon to reduce photodegradation and chalking.
- 10 % additions represent a maximum of degradation rate and should be avoided.
- The rate of CO_2 evolution increases with the amount of cross linker.
- The rate of CO_2 evolution is increased for all systems when anatase TiO_2 is used.
- UVB irradiation (at low levels) increases degradation by several orders of magnitude.
- TiO_2 additions stabilize the PU matrix against UVB irradiation at all levels.

Recommendations

- Replacement of R960 TiO_2 with a more photostable grade following appropriate tests (suggest Kronos K2220).
- Use of TiO_2 at higher loadings of 20% PVC for maximum shielding.
- Comparison of results from flat panel reactor with QUVA and EMMAQUA.
- Evaluate what effect UVB has over a wider range of conditions since even small amounts present at high altitude will radically affect PU performance.

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