JOURNAL OF MATERIALS SCIENCE **37** (2002) 4901 – 4909

Photocatalytic oxidation of alkyd paint films measured by FTIR analysis of UV generated carbon dioxide

P. A. CHRISTENSEN, A. DILKS*, T. A. EGERTON†, E. J. LAWSON
Department of Chemistry, Bedson Building, University of Newcastle upon Tyne,
NE1 7RU, UK
E-mail: T.A.Egerton @ ncl.ac.uk

J. TEMPERLEY
Research & Development Department, Huntsman Tioxide, West Site,
Haverton Hill Road, Billingham, TS23 1PS, UK

FTIR assay of UV generated gaseous CO_2 has been used to monitor the photo-degradation of alkyd paint films in oxygen of controlled humidity. The three contributions to CO_2 evolution from such paint films are (a) a dark reaction associated with the drying process, (b) direct photochemical reaction, and (c) photocatalysis by the TiO_2 opacifier. As this paper is focused on the photocatalysis by TiO_2, the dark reaction has been minimized by accelerated drying of the paint films and the photocatalytic component has been emphasised by studying films pigmented with TiO_2 that has not been surface treated. This methodology allows the UV stability of alkyd paints to be monitored rapidly by an FTIR measurement of the UV-generated carbon dioxide. CO_2 evolution was greater for films made with high (35%) than for low (15%) TiO_2 pigment volume concentration (p.v.c.) paints. This behaviour, which parallels weight losses from similar films exposed in conventional accelerated weathering equipment, shows that photocatalysis by the TiO_2 is dominant. The CO_2 evolution rates from films opacified with different grades of rutile pigment correlate with weight loss measurements made from identical paints exposed to glass-filtered carbon arc irradiation in conventional accelerated weathering equipment. These two comparisons confirm the relevance, to conventional accelerated testing, of paint durability of the FTIR assay of carbon dioxide evolution from alkyd paints. Because the experimental procedure allows the ready interposition of suitable optical filters, the method is well suited to studies of e.g., incident wavelength & intensity. In addition, deliberate variations in the humidity of the atmosphere in the FTIR cell were monitored by using the i.r. absorption of water vapour. Not only did the observed rates of carbon dioxide evolution decrease with decreasing humidity, they extrapolated to zero at zero humidity. This is consistent with mechanisms, derived from studies of model systems, that identify hydroxyl radicals as the key catalytic intermediate in photocatalytic oxidation of TiO_2 pigmented paint. © *2002 Kluwer Academic Publishers*

1. Introduction

FTIR analysis of gas phase carbon dioxide has been shown to be sufficiently sensitive to monitor quantitatively the evolution of carbon dioxide generated by the photo-degradation of acrylic emulsion paints pigmented with commercial grades of titanium dioxide pigments [1–3]. Using this method, it was possible to demonstrate that incorporation of a surface modified rutile pigment decreased the rate of carbon dioxide generation, relative to that from the unpigmented acrylic film, because the dominant role of the pigment was to absorb UV and thus decrease the relative rate of photochemical generation of CO_2 [1]. Even though the effect of rutile pigments was to lower the rates of carbon dioxide evolution, it was possible to compare the relative rates of polymer photo-degradation of three paints made with different rutile pigments. Further, the relative orders correlated with the order of gloss deterioration measured on test panels exposed in Florida [1].

By contrast the anatase form of titanium dioxide increased the formation of carbon dioxide relative to the rate of generation from an unpigmented sample of the

---

*[*] *Present Address*: British Sugar Corporation, British Sugar Plc, Wissington Sugar Factory, Stoke Ferry, Kings Lynn, PE33 9QG, UK.

[†] Author to whom all correspondence should be addressed.

0022–2461

same acrylic polymer because the much greater photocatalytic activity of anatase outweighed the beneficial effect of UV absorption—i.e., increased photocatalysis by the TiO_2 out-weighed the decreased direct photochemical degradation. FTIR analysis of evolved CO_2 was then used to investigate the effects on photocatalysis of variation in incident intensity (I), wavelength and humidity of the oxygen [2]. The rate of CO_2 evolution was shown to be proportional to $I^{0.5}$, as expected if photocatalysis by TiO_2 is controlled by recombination of the photo-generated charge carriers [4].

More recently we have shown that the same method can be used to monitor the carbon dioxide that is evolved from alkyd paints in the dark. In alkyd paints, unlike acrylic emulsions, drying is associated with cross-linking of the polyester chains as a result of autooxidation [5] and we suggested that during this cross-linking carbon dioxide is evolved. The rate of evolution decreases as the paint ages and the ageing can be accelerated by drying the paint at 50°C [6].

In this paper we report a study of carbon dioxide evolution from alkyd paint films pigmented with different forms of TiO_2 on exposure to UV. There are three components to the carbon dioxide evolved from such films. These are (a) a dark reaction as result of the cross-linking/drying processes, (b) direct photochemical Reaction, and (c) photocatalysis by the TiO_2. Since we have sought to focus on the photocatalysis by TiO_2, we have minimized the dark reaction by accelerated drying of the paint films and have emphasised the photocatalytic reactions by, in the main, studying the degradation of paints pigmented with different types of uncoated (i.e., not surface-treated) TiO_2.

2. Experimental

2.1. Paint preparation

All the paint and resin films studied in this work were prepared from Sobral P470, a long oil (60% fatty acid content), soya alkyd with an acid value of 13 mg KOH g^{-1}, supplied by Scott Bader. Paints were prepared by dispersing rutile TiO_2 pigments in a solution of the resin in white spirit. The pigments were ball-milled in the solution for 16 hours in glass jars with glass ballotini. After milling, mixed cobalt/zirconium catalytic driers (Nuosyn D216) were added to promote oxidative cross-linking in the final films [5] and further resin solution was added to adjust the pigment concentration in the dried film to 15% or 35% by volume. For unpigmented resin films, the same level of driers on resin solids was used.

Most of the measurements reported here were on paints pigmented with uncoated rutile. The pigments were selected from materials produced commercially by both the sulphate and chloride routes [7] to give a range of photocatalytic activity. Codes used to identify the paints are explained in Table I. To test the sensitivity of the technique, paints prepared from less active, coated commercial pigments were also examined. These contained 17.5% v/v pigment in the dried film.

TABLE I A summary of the different paint films used in this work

Paint code	TiO_2 pigment sample	Pigment conc. in dried film (by vol.)
ALU	None	0
AL1/AH1	Rutile, high (>1%) Al_2O_3	AL1 15% AH1 35%
AL2/AH2	Rutile, low (<0.2%) Al_2O_3	AL2 15% AH2 35%
AL3/AH3	Rutile, intermediate (~0.3%) Al_2O_3	AL3 15% AH3 35%
AL4	Duplicate paint made with same pigment as AL3	AL4 15%
AL5/AH5	Rutile, high (>1%) Al_2O_3	AL5 15% AH5 35%
AL6/AH6	Rutile, high (>1%) Al_2O_3	AL6 15% AH6 35%

The paint or resin solution was applied to one surface of a metal disc substrate, ca. 10 mm in diameter, as described in earlier papers [1, 6]. Films were allowed to dry in air for at least a week, with light excluded. Film thickness was estimated from dried weights: typical values were 105 μm for the unpigmented films, 85 μm for the AL series, 40 μm for AH and 90 μm for paints prepared from coated rutile pigments. To stabilise the films, they were then oven-aged at 50°C for five days. After this treatment, they were again kept in the dark until required.

2.2. The FTIR cell

The coated disc was mounted in a gas-tight cell with calcium fluoride windows which allowed the paint film to be irradiated with UV and the atmosphere surrounding the disc to be probed with an IR beam. Two versions of the cell have been described previously [1, 6]. Preliminary experiments were carried out in a cell with a rubber seal [1] but most of the results were obtained in a cell with greased glass joints and taps [6]. The cell was purged for an hour with oxygen (BOC cylinder product), then allowed to equilibrate overnight (16.5 ± 0.5 h). Controlled high humidity was normally attained by bubbling the oxygen through de-ionised water. Humidity variations were achieved by using oxygen direct from the cylinder or passing it through a column of silica-gel.

Apiezon T high vacuum grease (Edwards Vacuum Products), was used to seal glass joints in early work. Initial blank runs indicated that it did not degrade to CO_2 under the conditions used. Later blanks, however, showed that this grease did undergo photo-oxidation. It was inferred that continued use of the sample port had pushed grease from the joint onto the internal surface where it was exposed to UV and the cell atmosphere. Therefore, Fomblin (Edwards Vacuum Products) perfluorinated polyether grease, which is very resistant to oxidation, was used in later experiments.

The cell was mounted in the chamber of a Bio-Rad FTS-60A FTIR spectrometer before overnight equilibration and the chamber was flushed with nitrogen from a liquid nitrogen source. Flushing for an hour was sufficient to reduce CO_2 outside the cell to negligible levels but the chamber had to be flushed overnight to give stable, low H_2O peaks in the IR.

2.3. UV illumination

The optical arrangement has been described in earlier reports [1]. Radiation from a 150 W xenon arc lamp (Oriel) was filtered through water to remove infrared then through two air-mass filters, AM0 and AM1.5 (also Oriel), to adjust the spectral distribution to that of solar radiation reaching the surface of the earth at a solar elevation of 42°. The beam was directed through a flexible liquid-light-guide, which also removes some short wavelength UV, to the FTIR cell. If required, as for the study whose results are shown in Fig. 7, an additional filter could be mounted between the light-pipe and the cell window.

Measurements of UV intensity and spectral distribution were made with a spectro-radiometer (Spex Minimate; Optronics Inc.) with the collector mounted in the FTIR cell position. The spectro-radiometer was not calibrated but was used to give relative values of irradiance to monitor the effects of lamp age and filters. Results presented in any given figure are directly comparable, but those in different figures should not be compared directly, because of possible changes in light intensity associated with replacement of a failing lamp—or because of changes in background levels of CO_2 associated with different vacuum greases.

2.4. Measurement procedure

A measure of CO_2 concentration in the cell atmosphere was obtained from the IR absorbance peak height at 2360 cm^{-1}. Absorbance could be measured to 10^{-4}: it was calculated that this corresponds to 0.02 μg CO_2 in the cell volume of 13.7×10^{-6} m^3. The peak height at 1560 cm^{-1} was used as a measure of H_2O concentration.

All spectra were averages of 100 scans, taken over ~40 s, at 4 cm^{-1} resolution. A single beam reference spectrum was recorded first in the dark and used to give measures of the starting concentrations of CO_2 and H_2O. Subsequent spectra were referenced to this. Absorbance spectra were collected for one hour prior to UV exposure. The light pipe was then connected and the evolution of CO_2 under UV was measured, typically over 3 h. Finally, spectra were collected in the dark again to show whether changes continued and to check for leakage from the cell.

It was observed that H_2O peak heights were not stable but varied with temperature in the spectrometer. This fell when liquid nitrogen was added to the MCT detector at the beginning of a run and then rose slowly, typically by ~2°C, over the course of an experiment. It appears that there is an equilibrium between water in the water-saturated oxygen atmosphere and absorbed water on the walls of the cell or on the paint film and water is released as the temperature rises. It follows that under these conditions, the H_2O peak height cannot be used to monitor water formed during paint film degradation in water-saturated oxygen, because an equilibrium concentration is reached in the atmosphere at any temperature.

As reported in Table I, duplicate paints, AL3 and AL4, were prepared from the same titanium dioxide sample. The photo-generation of carbon dioxide from these separately made paints is directly compared in Fig. 4—which therefore represents a demonstration of the overall reproducibility of the measurement.

2.5. The Marr artificial weathering equipment

To link the present FTIR measurements of CO_2 generation with conventional accelerated tests of paint photodegradation we measured the weight loss, resulting from total oxidation of the organic, of P470 alkyd paint films applied to stainless steel panels and exposed on a drum which rotated around a carbon arc UV source. The design of this Marr Artificial Weathering equipment is based on a UK Ministry of Defence Specification but modified by replacing the specified 1600 W single carbon arc by two 850 watt carbon arcs. Prior to weight loss measurements the painted panels were exposed with their backs to the carbon arcs for 100 hours (24 hours for the paints whose weight losses are plotted in Fig. 5)—an ageing step which roughly parallels the oven ageing used in our FTIR experiments. During UV exposure the paint panels were sprayed with distilled water at the same point in the cycle—i.e., at intervals of ~15 minutes. At appropriate intervals the paint panels were removed from the weathering equipment dried, weighed, on a balance sensitive to 0.1 mg, and then replaced in the weathering equipment for further UV exposure.

3. Results

3.1. CO_2 evolution: the effect of coating TiO_2

Fig. 1 shows typical results for the evolution of CO_2 from alkyd paint films. As shown previously [6], there is slow evolution through oxidation in the dark but the rate is accelerated under UV. The two pigments shown are an uncoated rutile (AL3) and a coated product made on the same base crystal. This has a mixed ZrO_2/Al_2O_3 coating, one of several types of surface treatment which can be used to reduce the photocatalytic activity of TiO_2 pigments. Electron micrographs in Fig. 2a and b illustrate the bare and coated rutile surfaces, showing an uneven coating layer of ca. 2–10 nm on the coated rutile. The uncoated pigment gave an increase in CO_2 absorbance rate from 5 h^{-1} in the dark to 22 h^{-1} under UV; the coated pigment only gave an increase from 6 to 8 h^{-1}.

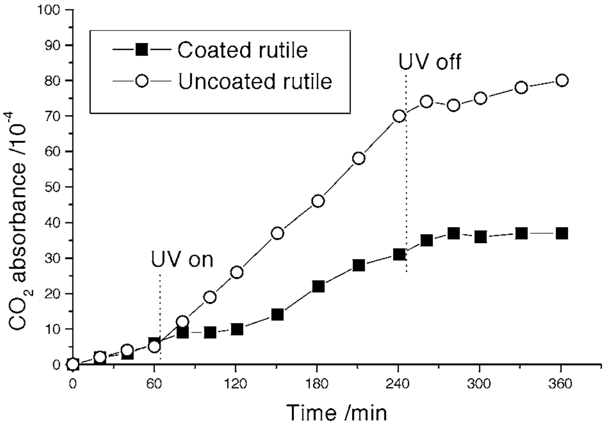


Figure 1 Growth of the CO_2 peak before, during and after UV irradiation for alkyd paint films pigmented with uncoated (AL3) and coated rutile at 15% v/v in the film. The ZrO_2/Al_2O_3 coating greatly reduces photocatalytic activity.

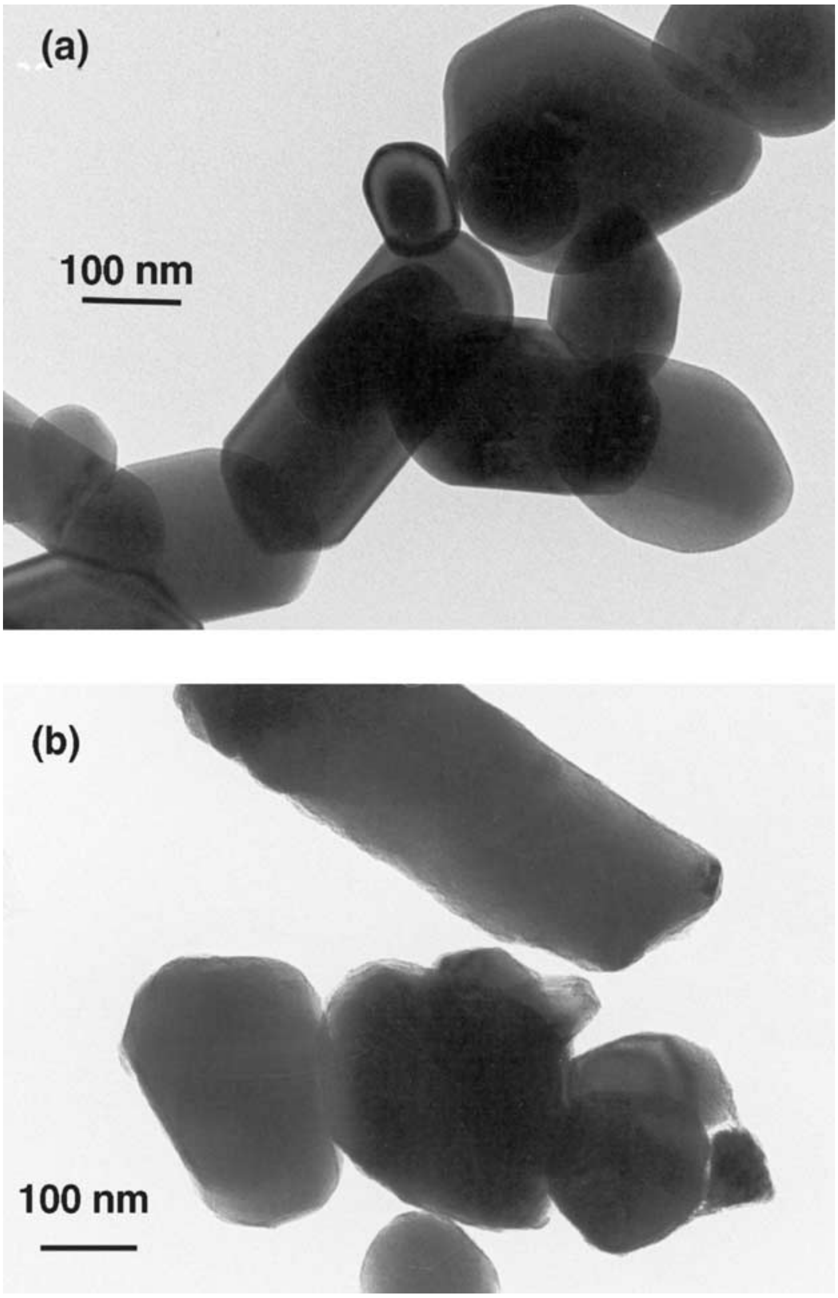


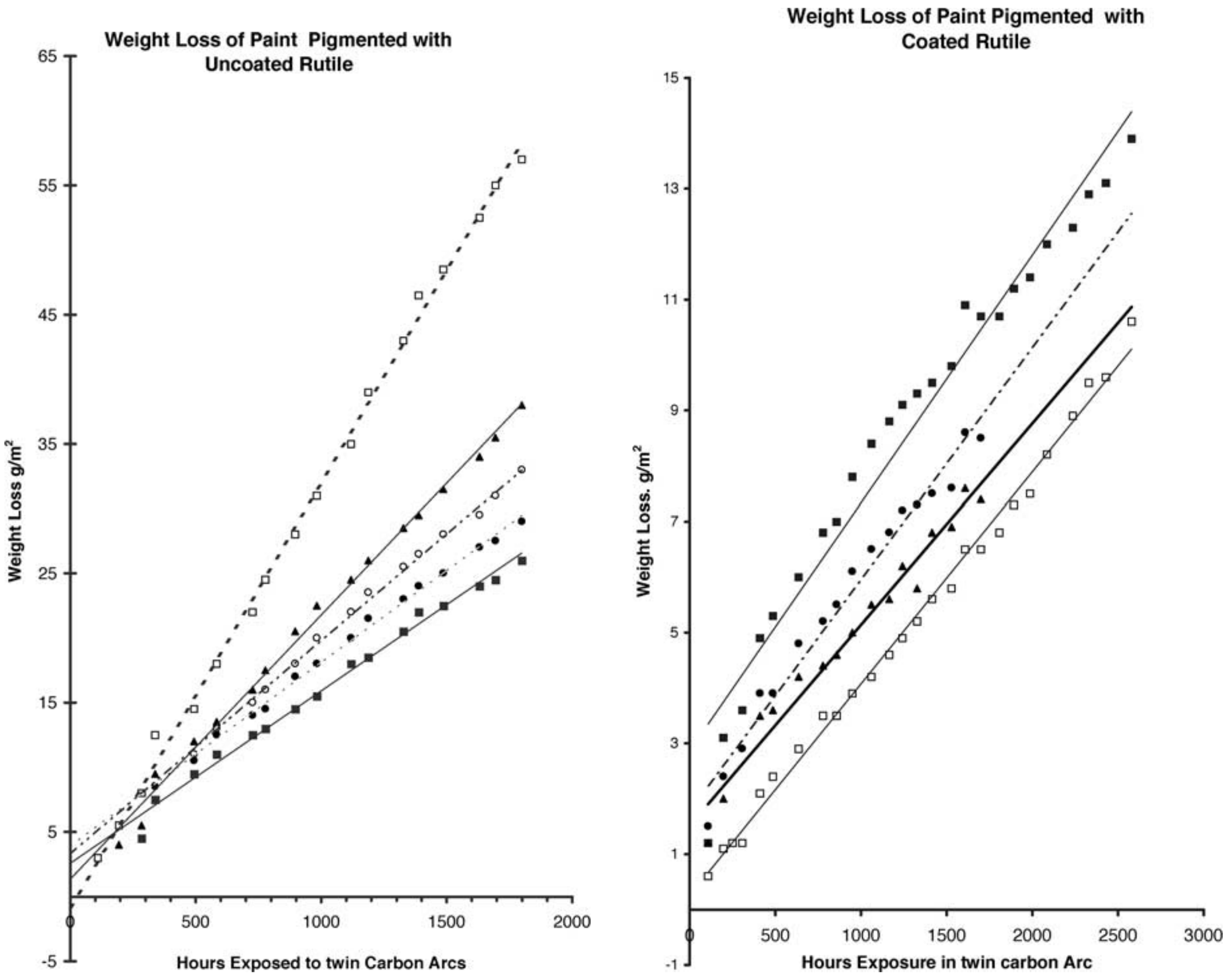
Figure 2 Transmission electron micrographs showing (a) the uncoated TiO_2 crystals and (b) surface treated (coated) TiO_2 rutile pigment. The ZrO_2/Al_2O_3 coating shows as a less dense outline to the images, with a thickness of 3–10 nm.

3.2. Weight loss: effect of TiO_2 coating and volume concentration

Figs 3a and b compare the weight loss from alkyd paints pigmented with (a) an uncoated and (b) a coated pigment similar to, but not the same as, those used in these FTIR studies. The weight loss from the paints made with uncoated pigments is $\sim$20 mg m^{-2} h^{-1}, significantly greater than the $\sim$4 mg m^{-2} h^{-1} measured for a paint made with a coated pigment—and this demonstrates the decreased photocatalytic activity associated with surface modification of the TiO_2 surface. For the uncoated pigment the weight loss increases as the pigment volume concentration (p.v.c.) increases from 5 to 40 and this is interpreted as a consequence of the increased photocatalytic degradation of alkyd polymer, to carbon dioxide and water vapour, associated with an uncoated rutile pigment—even though the photocatalytic activity of rutile is significantly less than that of anatase. By contrast the weight loss from the alkyd paints pigmented with a coated pigment decreases as the p.v.c. increases. This is attributed to the fact that, as a consequence of the reduced photocatalytic activity, the dominant effect of the surface modified TiO_2 is to act as a UV absorber and protect the alkyd from direct photochemical degradation. The higher the p.v.c., the more effective this protection is.

3.3. Discrimination between uncoated TiO_2 pigments

Results in Fig. 4 for alkyd paints at 15% pigment volume concentration show that the FTIR method discriminates between the different uncoated pigments in terms of rate of CO_2 formation under UV. The ranking of the pigments in these experiments on heat-treated films was the same as obtained in preliminary experiments on unheated films which gave a greater spread of rates.



(a) (b)

Figure 3 (a) The weight loss, as a function of exposure time in a carbon arc Marr weathering apparatus, of alkyd paint films opacified with an uncoated rutile pigment, showing the increase in weight loss in the sequence 5 (■), 10 (●), 17 (○), 25 (▲) and 40 (□) % p.v.c. (b) The weight loss, as a function of exposure time in a carbon arc Marr weathering apparatus, of alkyd paint films opacified with a coated rutile pigment, showing the decrease in weight loss in the sequence 5 (■), 19 (●), 25 (▲) and 40 (□) % p.v.c.

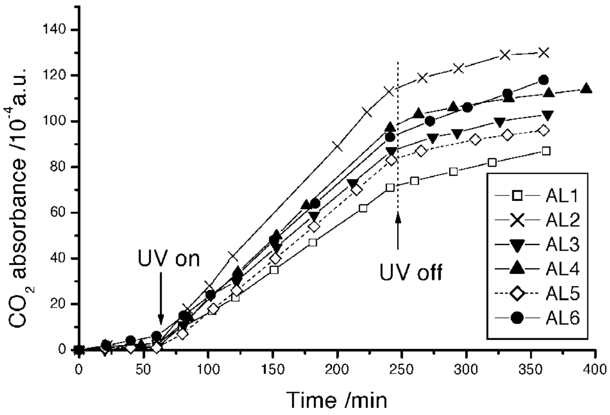


Figure 4 CO_2 evolution from alkyd paint films, all made at 15% p.v.c., with a range of uncoated rutile samples (see Table I) of different photocatalytic activity. All paint films were heat treated at 50°C for 5 days before exposure.

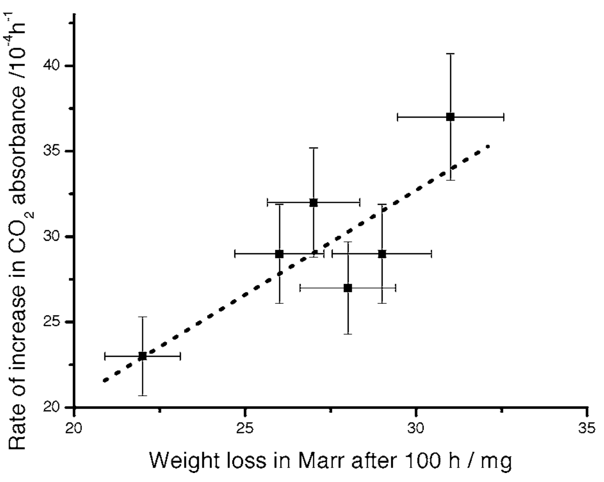
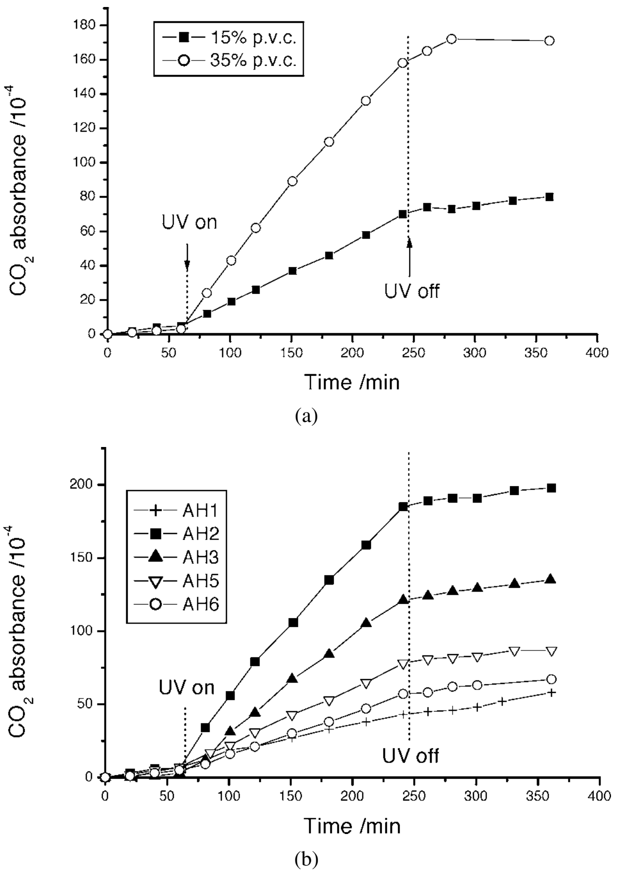


Figure 5 The correlation between CO_2 evolution in the FTIR cell and initial weight loss in the Marr Weatherometer for the paints in Fig. 4. The dotted line is a linear fit to the results.

The CO_2-absorbance rates are plotted in Fig. 5 against weight losses, measured after 100 h exposure in the Marr equipment, of paints made to the same formulation. Although the ranking is not identical, there is a reasonable correlation, $R^2 = 0.68$, between the two methods.

3.4. CO_2 evolution at higher pigment loading

To accentuate photocatalytic degradation of the alkyd by the TiO_2 over photochemical oxidation of the resin itself, a second series of paints containing uncoated



(a)

(b)

Figure 6 CO_2 evolution from alkyd paint films at 35% pigment volume concentration (p.v.c.). (a) A comparison of low and high TiO_2 concentrations for the same pigment: paints AL3 and AH3; (b) the results for a range (see Table I) of uncoated rutile pigments at 35% p.v.c.

rutile pigments at much higher volume concentration was examined. Fig. 6a shows CO_2 absorbance results for paints AL3 and AH3 at 15% and 35% pigment volume concentration (p.v.c.) respectively. The higher TiO_2 loading gave a markedly enhanced rate of CO_2 evolution indicating that, for this pigment, photocatalysis is dominant.

Results for the whole series at 35% p.v.c. are given in Fig. 6b. Although, because of lamp and grease changes (see Sections 2.2 and 2.3) that were made between the two sets of measurements, the results recorded in Fig. 6b cannot be compared directly with those in Fig. 4. Nevertheless, it is clear that a greater spread of rates was obtained at the higher pigment loading. The ranking of pigments, however, in terms of CO_2-absorbance rate, was similar to that at lower p.v.c., viz.

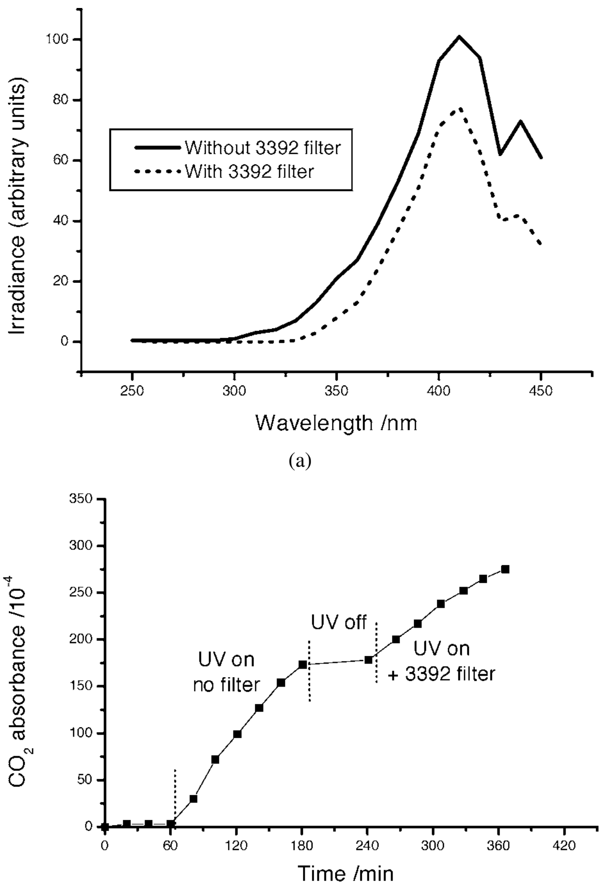
AH2 > AH3 > AH5 > AH6 > AH1 (at 35% p.v.c.)

AL2 > AL4 > AL3 = AL6 > AL5 > AL1

(at 15% p.v.c.)

3.5. The effect of filters

Both TiO_2 and the unpigmented alkyd resin absorb strongly in the UV. Whereas rutile TiO_2 has a fairly sharp absorption edge at ca. 400–420 nm, the resin absorption increases more slowly with decreasing wavelength and is strongest below ca. 350 nm (see below and Fig. 9). Therefore, cutting-out radiation below 350 nm should favour photocatalytic oxidation over photochemical.



(a)

(b)

Figure 7 Use of an additional UV filter. (a) Spectroradiometer results showing the effect of the 3392 filter on the intensity and spectral distribution of UV falling on the cell; (b) the effect of the filter on CO_2 evolution for alkyd paint AH2.

Fig. 7b shows that the reduction in rate of CO_2 evolution from paint AH2 when an Oriel 3392 filter, which filters most strongly below 350 nm and also reduces the intensity, integrated from 250 to 420 nm, by ~20% (Fig. 7a), was inserted between the light guide and the cell window. For AH2, the absorbance rate fell from 85 h^{-1} to 49 h^{-1}, for AH5 from 29 h^{-1} to 23 h^{-1}. That is, the insertion of the filter caused the rates to fall to ~66% of their initial value.

3.6. Effect of humidity

The effect of deliberately varying the humidity in the FTIR cell is shown in Fig. 8. The minimum water peak height, corresponding to residual water in the spectrometer chamber, was consistently $\sim 100 \times 10^{-4}$, but values near 600×10^{-4} were obtained after the cell had been purged with essentially water free cylinder oxygen and was then equilibrated overnight. This increase is probably attributable to water desorption from the paint film or to water formation in the overnight dark reaction. The corresponding values for oxygen bubbled through water were $\sim 1200 \times 10^{-4}$ and intermediate values were obtained by passing the oxygen through a silica-gel column: the cylinder oxygen extracted water from the gel!

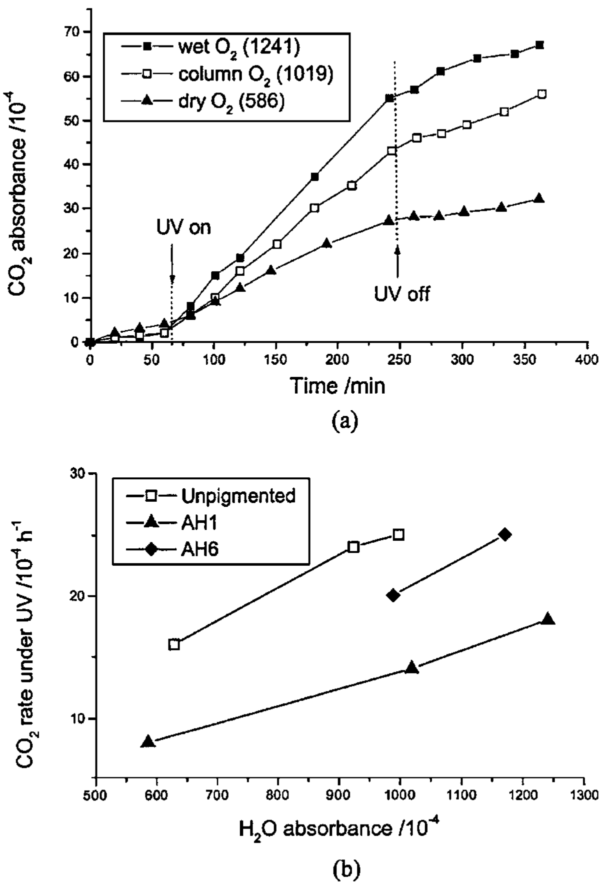


Figure 8 The effect of varying humidity in the FTIR cell. (a) CO_2 evolution from alkyd paint AH1: values in parentheses are H_2O absorbance peak heights ($\times 10^{-4}$) at the start of the run; (b) CO_2 absorbance rate against initial H_2O absorbance peak height for pigmented and unpigmented films.

Fig. 8a gives data for paint AH1 showing a clear reduction in the rate of CO_2 evolution under UV with decreasing humidity. The absorbance rates are replotted against H_2O peak height in Fig. 8b with results for paint AH6 and unpigmented alkyd films. All showed the same trend with reduced humidity.

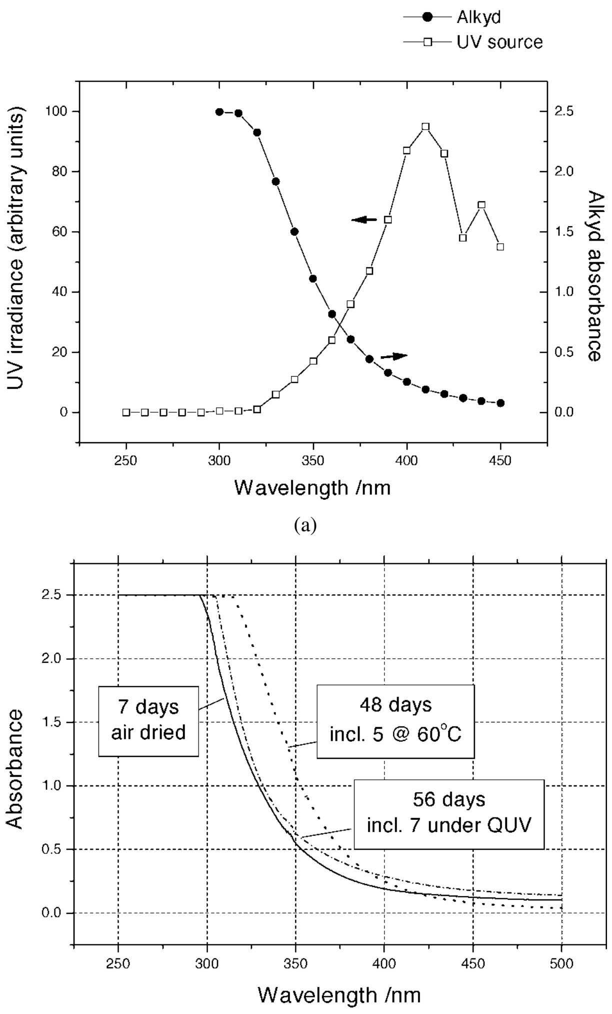
4. Discussion

The results in Fig. 1 show that the evolution of carbon dioxide alkyd paints increases significantly above the background value ($\sim 5 \times 10^{-4}$ absorbance units/hour, caused by continued slow drying [6]) when the paints are irradiated. Further, surface treatment (coating) of the TiO_2 pigment to give the differences exemplified in Fig. 2 causes a decrease, by a factor of ~3, in the CO_2 generation rate. This factor is comparable with the different weight loss rates, shown in Fig. 3 observed on ~18% p.v.c. paints made with other coated and uncoated pigments. This confirms that, as expected, the FTIR assay of carbon dioxide evolution provides information that is relevant to conventional accelerated testing of paint durability.

The comparison, in Fig. 4, of the relative rates of photo-degradation of 6 paints (all made from uncoated rutile pigments) shows clear differences in the rate of CO_2 generation. All these paints have the same TiO_2 concentration, and since the pigments have similar crystal sizes, the optics of the different paints would be expected to be broadly similar. Therefore, UV absorption by the pigments is, to at least a first order approximation, the same and consequently the contribution of direct photochemical degradation is expected to be closely similar in all six paints (though we recognise that second order effects will result from differences in the thickness of a pigment-depleted layer—the 'clear layer' [9] manifested in variations in the gloss levels of the different samples.) Therefore the differences in the CO_2 generation rates are caused primarily by differences in photoactivity of the different uncoated rutile samples. The different photoactivities reflect manufacturing differences such as variations in the additives (e.g., the aluminium level) used in the manufacture of different grades of proprietary pigments, as outlined in Table I. A series of recent papers [e.g., 10, 11] gives useful background information on the factors concerned, but commercial considerations preclude the disclosure of additional specific information. In Fig. 5 the measured rates of CO_2 generation are plotted as a function of the weight loss of paint films made from identical pigments exposed in a Marr accelerated-weathering equipment. Taking into account the errors—exemplified by the results for duplicate paints (AL3 and AL4) made from the same uncoated rutile—associated with both sets of measurements, there is a reasonable correlation between the CO_2 assay and the weight loss. In addition, the $41 \pm 6\%$ increase in weight loss between the least and most photo-active rutiles parallels the $48 \pm 5\%$ change in CO_2 generation rates. This suggests that the proportion of carbon dioxide in the UV generated volatiles remains the same, despite the changes in activity of the rutile. This suggestion is supported by the result of an approximate calculation (assuming that each CO_2 molecule results from the oxidation of one —CH_2— group) that indicates that for both the most and least active uncoated pigments the weight loss during the first 100 hours Marr exposure (32 and 23 $mg\,m^{-2}\,hr^{-1}$ respectively) correspond closely with (30 and 18 $mg\,m^{-2}\,hr^{-1}$ respectively) weight losses calculated from the measured growth in carbon dioxide intensity. That is, at this level of accuracy there is no need to assume that any of the weight loss is caused by 'chalking'—detachment of TiO_2 particles from the film [12].

Fig. 6 shows that increasing the TiO_2 p.v.c. in the alkyd paint increases the rate of carbon dioxide generation by a factor of ~2—again quite consistent with the changes observed in weight loss rates in similar paints (Fig. 3a). Any increased UV absorption/protection of the type associated with coated rutile (Fig. 3b) is more than compensated for by the increased photocatalysis associated with the increased concentration of TiO_2. This suggests that differences in photoactivity should be amplified if the p.v.c. of the test paints is increased. A qualitative comparison of the results in Fig. 4 and Fig. 7 shows that this is indeed the case.

All of the above analysis has demonstrated that, for alkyd paints, as with the much simpler acrylic emulsion films, the results of FTIR CO_2 method are relevant to practical paint durability. Therefore, the method may be usefully exploited to probe details of the mechanism of the photo-degradation of alkyd paints and we conclude



(a)

(b)

Figure 9 UV absorption by the alkyd resin. (a) Absorbance spectrum of a 90 μm alkyd film on CaF_2 compared with the spectral distribution of the UV/visible radiation used in photodegradation experiments; (b) changes in the absorbance spectrum during oxidative drying and after exposure to UV using a Q-Panel UVA-340 lamp.

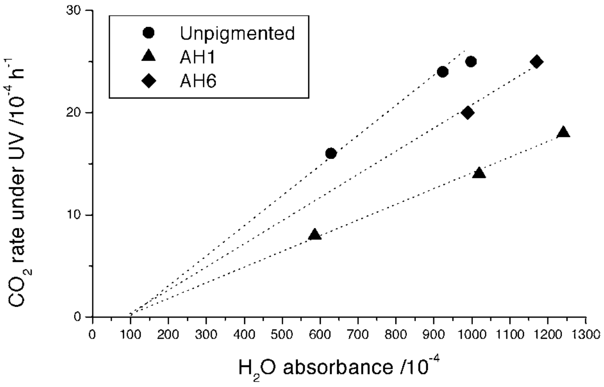


Figure 10 Dependence of the CO_2 generation rate on the humidity in the cell for unpigmented alkyd and for paints AH1 and AH6. The results are plotted as a function of the H_2O absorbance peak height ($\times 10^{-4}$) at the start of the run. As explained in the text, an H_2O absorbance peak heights of 100×10^{-4} is associated with residual water vapor in the spectrometer and therefore approximates to a dry cell.

this paper with two examples of the type of study that becomes possible.

The first example concerns the effect of the UV wavelength. The practical importance of wavelength in accelerated weathering tests has received significant attention [13] and we have shown [2] how the effects of photochemical and photocatalytic degradation can be differentiated in acrylic paints. The results of Fig. 7b illustrate that the FTIR method can directly monitor changes in alkyd degradation rates when relatively subtle changes (as shown in Fig. 7a) are made to the incident UV spectral intensity distribution. This is particularly important because, for alkyd paints, the significant absorption of the organic medium, which extends throughout the UV and into the visible (Fig. 9a), changes as the paint ages thermally or photochemically (Fig. 9b). Because the FTIR experiments can be completed sufficiently quickly for the absorption of the medium to be regarded as constant, this enables meaningful studies of the effect of wavelength to be conducted.

The second example is the increased rate of oxidation, associated with increased humidity, shown in Fig. 8a and b . An unpigmented alkyd film gave the same trend. In practical paints this effect has been widely accepted in a qualitative way [14], and for photocatalysed oxidation by TiO_2 is consistent with the mechanism, for the oxidation of isopropanol in the vapour phase, put forward by Stone and Bickley [15]. This requires the initial presence and subsequent regeneration of hydroxyl groups at the TiO_2 surface. It is striking that when the results are plotted in an alternative manner (Fig. 10) a provocative/speculative conclusion emerges. The rate of photo-oxidation would be zero if the cell were completely dry. (The measured water absorbance of 100×10^{-4} was the minimum achieved and was attributed above to residual water in the spectrometer). The FTIR method has enabled an effect to be investigated which could not be observed in practical tests because water is a product of degradation and because pigments are initially hydrated.

5. Conclusion

This work has shown that, despite their much greater complexity, the UV stability of alkyd paints, may be monitored rapidly by an FTIR measurement of the UV-generated carbon dioxide. Despite the experimental complications associated with the previously reported dark evolution of carbon dioxide—a consequence of β-scission during drying—the measured rates of carbon dioxide evolution are consistent with the results of weight losses measured during conventional artificial weathering tests lasting weeks or months. Therefore the technique may be used reliably to probe details of the degradation mechanism. The unexpected implication of the results, that no photocatalytic oxidation of a paint would occur in a completely and permanently dry atmosphere, merits further testing—e.g., in a perfluorinated medium that does not oxidize to water.

Acknowledgements

We are grateful for the financial assistance of Huntsman Tioxide (EJL & AD) & EPSRC (AD). It is a pleasure to acknowledge the experimental work on paint weight loss measurements by Mr. D. Newton

(Huntsman Tioxide) and helpful discussions with Professor J. R. White (University of Newcastle upon Tyne).

References

1. P. A. CHRISTENSEN, A. DILKS, T. A. EGERTON and J. TEMPERLEY, *J. Mater. Sci.* **34** (1999) 5689.
2. *Idem.*, *ibid.* **35** (2000) 5353.
3. A. DILKS, Ph.D. thesis, University of Newcastle on Tyne, 1999.
4. T. A. EGERTON and C. J. KING, *J. Oil Col. Chem. Assoc.* **26** (1979) 386.
5. G. P. A. TURNER "Introduction to Paint Chemistry and Principles of Paint Technology" 3rd ed. (Chapman & Hall, London 1983).
6. P. A. CHRISTENSEN, A. DILKS, T. A. EGERTON and E. J. LAWSON, J. TEMPERLEY, *J. Mater. Sci.* **37** (2002) 3667.
7. T. A. EGERTON and A. TETLOW, in "Industrial Inorganic Chemicals: Production and Uses," edited by R. Thompson (The Royal Society of Chemistry, Cambridge UK, 1995) ch. 13.
8. U.K. Ministry of Defence Specification, DEF 1053, Method 26, 1953.
9. R. D. MURLEY and H. SMITH, *J. Oil Col. Chem. Assoc.* **52** (1970) 292.
10. U. GESENHUES, *J. Photochem. Photobiol. A : Chemistry* **139** (2001) 243.
11. *Idem.*, *Chem. Eng. Technol.* **24** (2001) 685.
12. G. KAEMPF, W. PAPENROTH and R. HOLM, *J. Paint. Technol.* **46** (1974) 56.
13. L. CUTRONE and D. V. MOULTON, in Proc. Oil Col. Chem. Assoc. Eastbourne, June 1987, p. 1
14. W. F. SULLIVAN, *Prog. Org. Coatings* **1** (1972) 157.
15. R. I. BICKLEY and F. S. STONE, *J. Catalysis* **31** (1973) 389.

Received 28 March
and accepted 6 June 2002