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Infrared spectroscopic evaluation of the photodegradation of paint

Part I *The UV degradation of acrylic films pigmented with titanium dioxide*

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In situ, quantitative infrared spectrometry has been used to measure the evolution of carbon dioxide during the photo-degradation of pigmented and unpigmented acrylic-emulsion paint films. It is demonstrated that the method permits a fast and convenient way of assessing the resistance of such paints to UV degradation. However, it is also shown that valid comparisons of paints prepared with different grades of titanium dioxide, but with the same acrylic emulsion, require careful selection and control of the experimental conditions. Thus, the relative importance of (a) direct photochemical oxidation of the binder and (b) indirect photo-catalysed oxidation (mediated by titanium dioxide) depend not only on the spectral distribution of the radiation source, particularly the output between 300 and 400 nm, but also on the humidity of the ambient atmosphere. The increased rate of oxidation with increased humidity is not unexpected, but the size of the effect is unexpectedly high. In addition, there is some carbon dioxide formation during irradiation of the paint film in nitrogen and further investigation of this phenomenon is in hand. For both pigmented and unpigmented films, the rate of carbon dioxide evolution is sensitive to the film thickness. The dependence of the oxidation rate on the thickness of clear, unpigmented films is consistent with the measured UV absorption. However, for pigmented films, this dependence extends over greater film thicknesses than predicted by a simple model based on paint film optics.

1. Introduction

This paper describes the use of FTIR to measure the carbon dioxide generated during the UV-induced oxidation of an acrylic paint pigmented with titanium dioxide. In such systems, degradation of the acrylic polymer film, induced by the ultra-violet component of solar radiation, can occur both by direct photochemical oxidation and by indirect, heterogeneously photo-catalysed, oxidation. The consequent destruction of the polymer film detracts not only from the appearance of the paint, through changes in gloss and colour, but also from the coating's protective action, both through erosion and because the consequent embrittlement promotes cracking and loss of adhesion to the underlying substrate [1]. Therefore, manufacturers of resins, paints and varnishes devote considerable research and development effort towards improving the photo-stability of their products. In most cases a natural-weathering study is the rate-determining step in the development of these materials and many accelerated tests, in which paints are exposed to artificial UV, are used. Commercial equipment may use carbon arcs (Atlas, Marr), xenon arcs (Xenotest, or Atlas Ci65a) or fluorescent tubes with enhanced UV emission (QUV), but even these accelerated tests take many months [2].

Alternatively, the photo-stability of a product may be inferred more rapidly from measurement of the photo-stability of its components, and many physicochemical methods have been employed in order to assess the photo-activity of the most widely used pigment, titanium dioxide. They include studies of the photo-chemical oxidation of isopropanol [3–5], measurements of the generation of hydroxyl radicals by e.s.r. spin-trapping experiments [6] and the photo-induced darkening caused by the reduction of lead oxide/titanium dioxide compacts [7]. However, the correspondence of these rapid tests with the behaviour of the corresponding pigmented systems has, in the main,

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been disappointing. One reason is that, as identified above, the practical weathering of a pigmented system is a result of at least two separate processes (a) the direct homogeneous photochemical oxidation of the organic medium and (b) the heterogeneous photo-catalytic oxidation caused by the titanium dioxide pigment [8]. An accelerated test should reflect the natural balance between these two contributions and physico-chemical studies of just one component can never fully reflect the practical system.

This paper reports the use of infrared spectroscopy to measure the evolution of carbon dioxide during the degradation of both pigmented and unpigmented acrylic emulsion paint films in different atmospheres. Commercial titanium dioxide pigments are made in either the Anatase or Rutile crystalline forms. Both forms may be sold as an 'uncoated' titanium dioxide base crystal or as a 'coated' grade in which a hydrous oxide layer, typically silica and/or alumina, is deposited on the titanium dioxide in order to reduce further the photocatalytic activity [9]. We show that, for pigments of widely differing activity, the amount of carbon dioxide evolution mirrors the results of conventional paint tests. Significantly, for paints of similar activity the amount of carbon dioxide evolved is also similar. This is most important because a key property of any photoactivity test is that it should reflect the constancy of pigments which, whilst chemically different, have the same photoactivity in practical paints.

2. Experimental

2.1. Materials

All of the measurements reported here were made on paints formulated from the same acrylic commercial emulsion—(a methyl acrylate/methyl methacrylate/ butyl acrylate emulsion: XK90, Zeneca Specialities). The transmission spectrum of dried films of this emulsion is shown in Fig. 1 and demonstrates that there is a weak UV absorption between 300 and 400 nm.

TABLE I Description of the titanium dioxide samples used in this study

Sample	Crystal form	Production process	Uncoated or coated
A1	Anatase	Sulphate process	Uncoated
R1	Rutile	Chloride process	Coated: Alumina
R2	Rutile	Chloride process	Coated: Alumina & silica
R3	Rutile	Sulphate process	Coated: Alumina & zirconia
R4	Rutile	Chloride process	Coated: Alumina, silica & zirconia
R5	Rutile	Chloride process	Coated: Alumina & silica

The pigments used in this study are listed in Table I. They include an uncoated anatase—selected as an example of a pigment with a very high photoactivity—and coated rutile samples, made by both the chloride (R1,R2,R4,R5) and sulphate (R3) processes, selected as examples of pigments with low photoactivity. The comparison of anatase and coated rutile allows measurements to be made with pigments of widely differing photoactivity whilst the comparison of several coated rutile samples allows more subtle differences in photoactivity to be probed.

To make pigmented paint samples, a mill-base was first prepared by slowly adding titanium dioxide pigment (180 g) to a milling solution (74.3 g; mainly water, propane 1.2 diol and Neocryl BT 24 coalescing solvent) in a 250 ml lacquered tin using a high speed disperser (Dispermat F105 with 50 mm/Impeller at 400 rpm). When all the TiO_2 had been added, incorporation was continued for a further 20 min at 4000 rpm. The resulting mill base was then allowed to cool and 74 g of XK90 emulsion was added to it. The mixture was then slowly stirred until homogeneous and finally a diethyl glycol based thickener solution (8.6 g) was added. The resulting paint had a solids content of 20%. It was stirred for a further 10 min and allowed to stand overnight, to remove air bubbles, before use. The pigment volume concentration, p.v.c., in the dried paint film was calculated to be 19% (v/v).

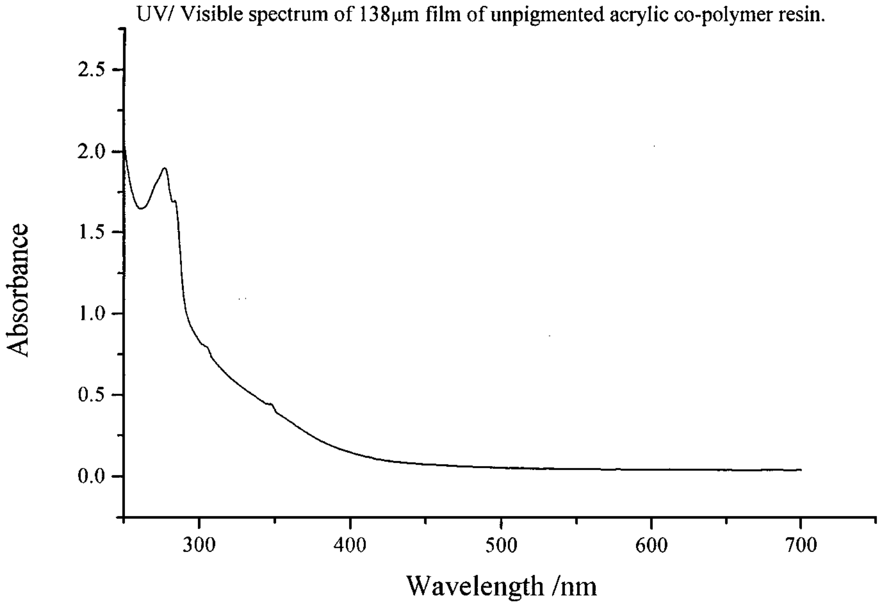

Figure 1 Absorption spectrum of a 138 μm unpigmented film formed from the acrylic co-polymer emulsion used in these studies.

2.2. Conventional weathering tests

Natural weathering tests on these paint films were carried out in Florida. The panels were exposed on south facing racks and were inclined at 45° to the horizontal. The film degradation was monitored by measuring the paint gloss as a function of time. (Paint 'gloss' is the specular reflection of the paint film and is measured, at a fixed angle, relative to that from a standard tile using a standard source and photoelectric receiver.) For these measurements the glosses were measured at a glancing angle of 60°, at intervals of 1 month, over a total period of more than two years.

2.3. The sample cell

For the research measurements described below, the paint films were applied, by dip-coating, to metal substrate discs (ca. 10 mm in diameter and mounted on an axial pin which could be located in a rubber base plate) and allowed to dry for ca. 150 h. The discs were then positioned in a specially constructed I.R. cell, see Fig. 2, fitted with calcium fluoride windows. During the course of the research, various modifications of this cell were employed. Typically the internal cell diameter was 16 mm and the total volume, including inlet and outlet ports was 14 cm^3.

The sample, which was located in the cell opposite a CaF_2 window, could be illuminated, via a 1 m flexible light guide, with UV radiation from an 150 W Xenon lamp (Oriel) as shown in Fig. 3. The UV light was filtered by a Solar filter (Oriel) to remove radiation with wavelength below 300 nm, and a 100 mm water filter to remove IR and so minimize sample heating.

Measurement with a UV-Visible Radiometer (Optronic Laboratories Model 730A) demonstrated that the

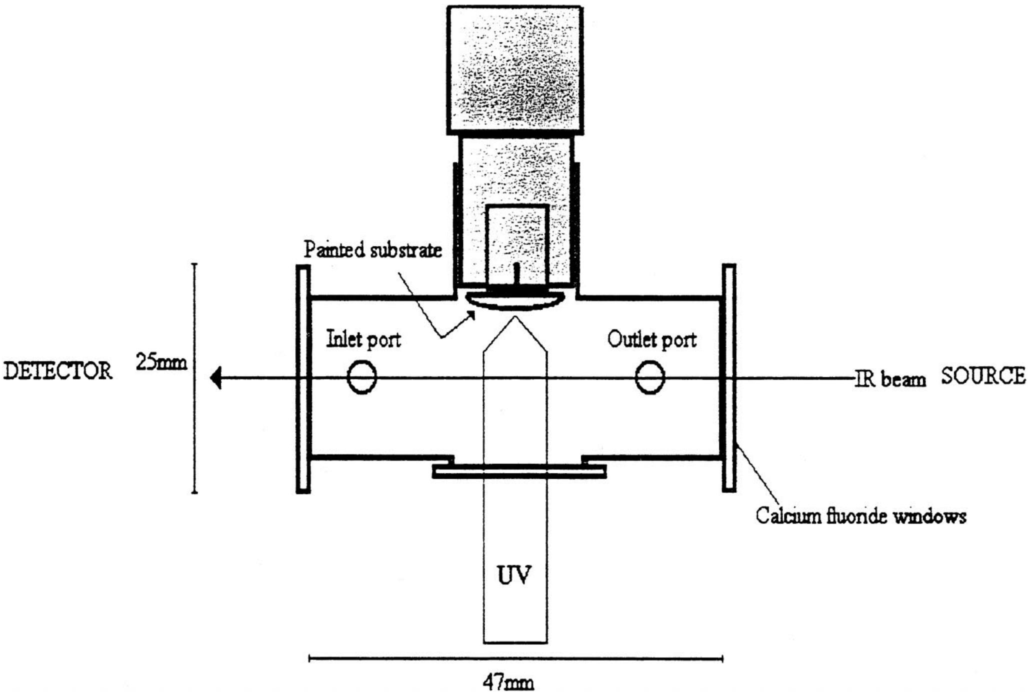

Figure 2 Plan view of the photochemical infra-red cell used for *in situ* studies of paint film degradation.

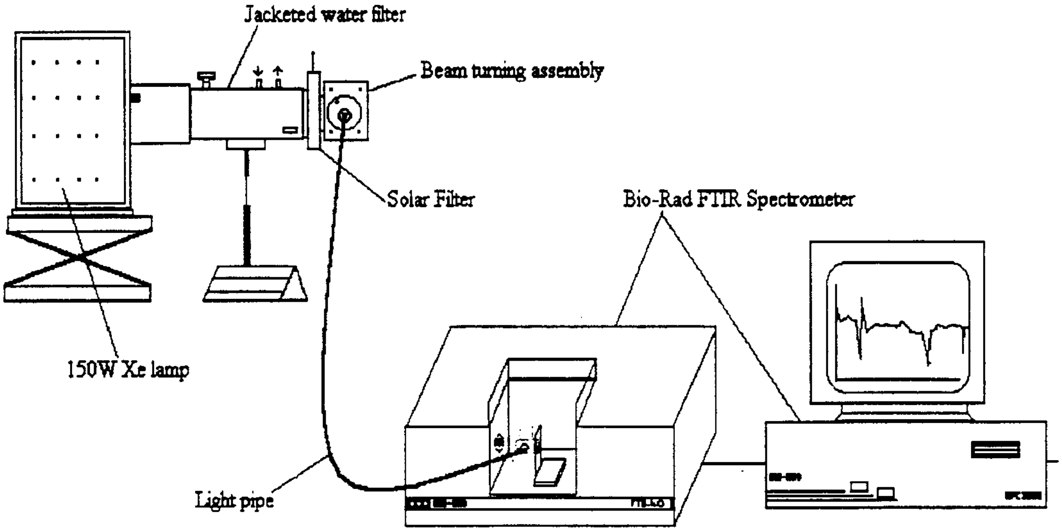

Figure 3 The arrangement of the radiation source, infra-red cell and spectrometer.

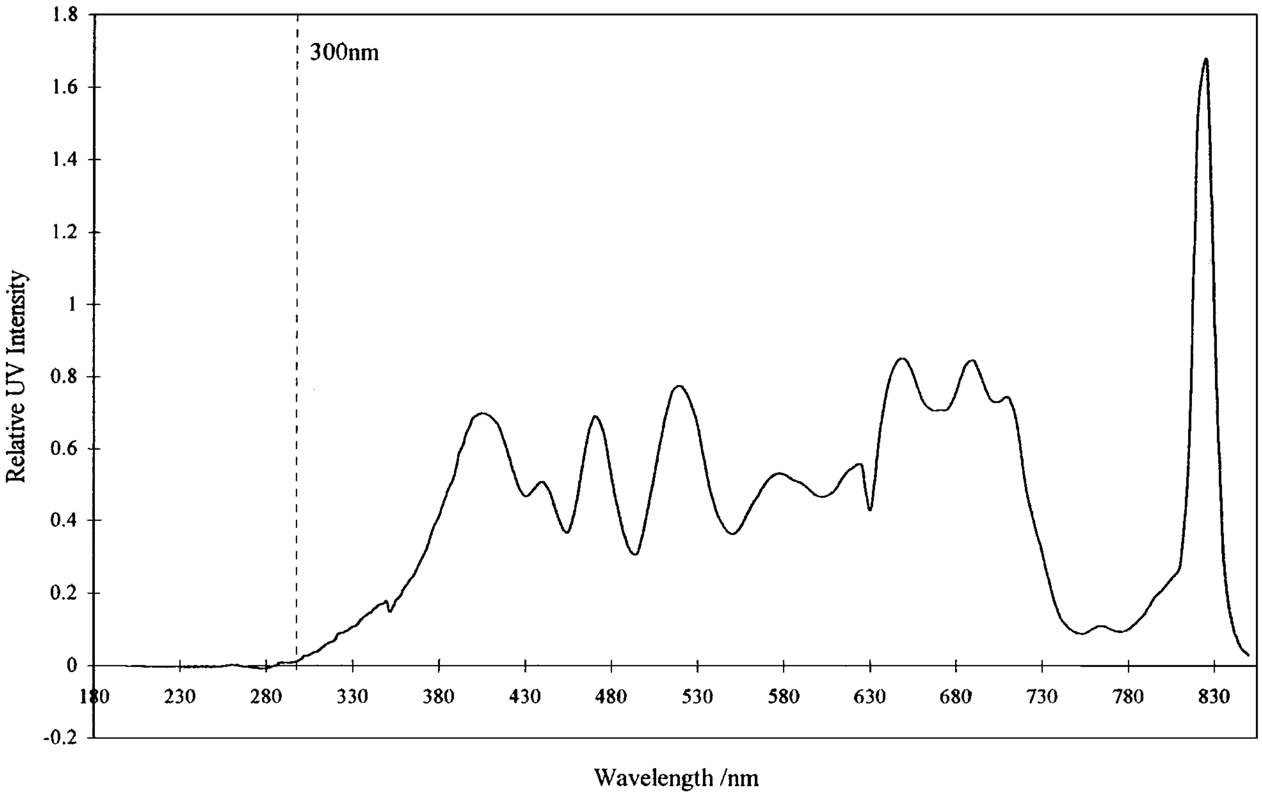

Figure 4 The spectral distribution of the 150 W Xenon lamp system with IR filter and Solar filter (Air Mass 1.5). Measured with a UV-Visible Radiometer (Optronic Laboratories Model 730A) using 10 nm slits.

radiation incident upon the paint film was indeed free of wavelengths below 300 nm (see Fig. 4).

2.4. Procedure

After assembly, the cell was sparged with moist oxygen for 30 min and was then mounted in an FTIR spectrometer (Bio-Rad FTS-60) fitted with a liquid nitrogen cooled MCT detector. The spectrometer sample compartment was then purged with gaseous nitrogen, until spectra showed that the levels of both water vapour and carbon dioxide were constant.

To provide a reference to which all subsequent spectra could be normalised, a single-beam reference spectrum of the gas-phase in the dark was first recorded. Next, to confirm the stability of the spectrometer/cell system, absorbance spectra (1000 scans at 4 cm^{-1} resolution) were recorded over a period of 60 min. The flexible light guide was then connected to the xenon-light source via the beam turning assembly, a new single beam reference spectrum was recorded and absorbance spectra were then recorded at regular intervals during the irradiation of the sample film. Finally, absorbance spectra were collected after the light was switched off.

3. Results

In order to assess the relative contributions of direct photochemical and TiO_2-mediated heterogeneous photocatalytic oxidation in pigmented films it is necessary first to measure the oxidation of the unpigmented acrylic film.

3.1. Unpigmented acrylic film

Fig. 5 shows the infrared absorbance of gaseous carbon dioxide before, during and after UV irradiation of unpigmented acrylic films. The film weights were approximately constant, 24 ± 1 mg, corresponding to thicknesses of ca. 280 ± 10 μm (assumed film density of 1100 kg m^{-3}) and agreement between replicate measurements on different films of the same thickness is excellent. CO_2 bands increase only during UV irradiation. A carbon dioxide absorbance of 4×10^{-2} corresponds to a mass loss of ca. 8.8×10^{-6} g; i.e. the amount of paint destroyed in 3 h is ca. 0.04% of the total film weight. It follows that total oxidation of the organic component would occur in ca. 8000 h. This is comparable with exposure times in natural weathering tests at, e.g., Florida (2 years at 12 h/day is equivalent to 8760 h.) Fig. 5 also shows that the rate of CO_2 evolution decreases during the course of the experiment. This decrease in oxidation rate has also been observed during conventional accelerated paint testing e.g. in Marr, Carbon Arc accelerated testing equipment. It has been suggested [5] that it is due either to ongoing polymerization of the binder or disappearance of residual solvent.

Fig. 6 shows the effect of variations in the composition of the ambient atmosphere on the oxidation of the unpigmented acrylic. Film degradation to carbon dioxide still occurs, though more slowly ($\times 0.6$) in a nitrogen atmosphere. In both oxygen and nitrogen the rate of carbon dioxide generation is sensitive to humidity, as monitored by the 1653 cm^{-1} water vapour band. Carbon dioxide generation is greatest in the presence

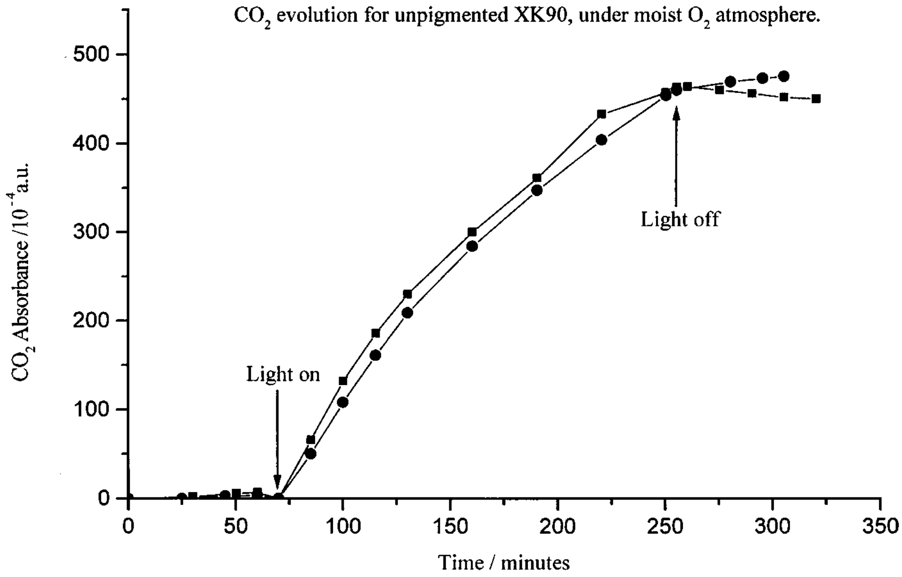

Figure 5 The infrared absorbance of gaseous carbon dioxide before, during and after UV irradiation of duplicate unpigmented acrylic films. (Film weights were approximately constant, ■ 23 mg, ● 25 mg, corresponding to thicknesses of ca. 280 ± 10 μm.)

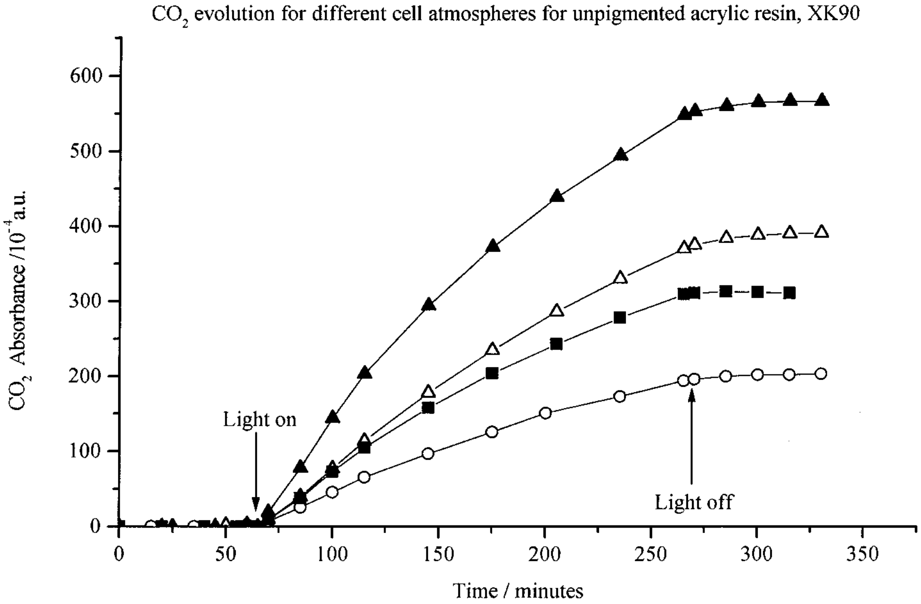

Figure 6 Dependence of carbon dioxide evolution from unpigmented acrylic films on the composition of the atmosphere in the infrared cell. (The numbers in brackets are the absorbances of the 1653 cm^{-1} band of water.) ○ nitrogen @ 80% humidity (0.117): ■ nitrogen at 48% humidity (0.090); △ oxygen @ 47% humidity (0.089); ▲ oxygen at 84% Humidity (0.122).

of moist oxygen, i.e. in the presence of oxygen, water accelerates CO_2 formation but in the nitrogen, CO_2 formation decreases as the humidity increases. The dependence of oxidation rate on humidity although well known in practical paint testing is often ignored in the development of rapid tests. However, the present results demonstrate that it is essential to control humidity if reproducible comparisons of paint films are to be made by monitoring the carbon dioxide produced during film breakdown.

It was not possible directly to interpret the water absorbance in terms of relative humidity because of the presence of residual low levels of water in the spectrometer light path. However, separate experiments, employing solutions saturated with different salts, suggest that variations from 0.065 to 0.145 in the measured absorbance of the 1653 cm^{-1} band correspond to changes in relative humidity from 20 to 96%. In this paper, activity comparisons within a particular set of results are made at the same humidity level. However, it was not always possible to maintain constant humidity between different sets of experiments and small differences between sets may occur.

Fig. 7 shows the dependence of oxidation rate on film thickness. Because the incident UV first traverses the acrylic film and is then reflected by the metallic substrate before traversing the film once more, the results are plotted as a function of $2t$, where t is the film

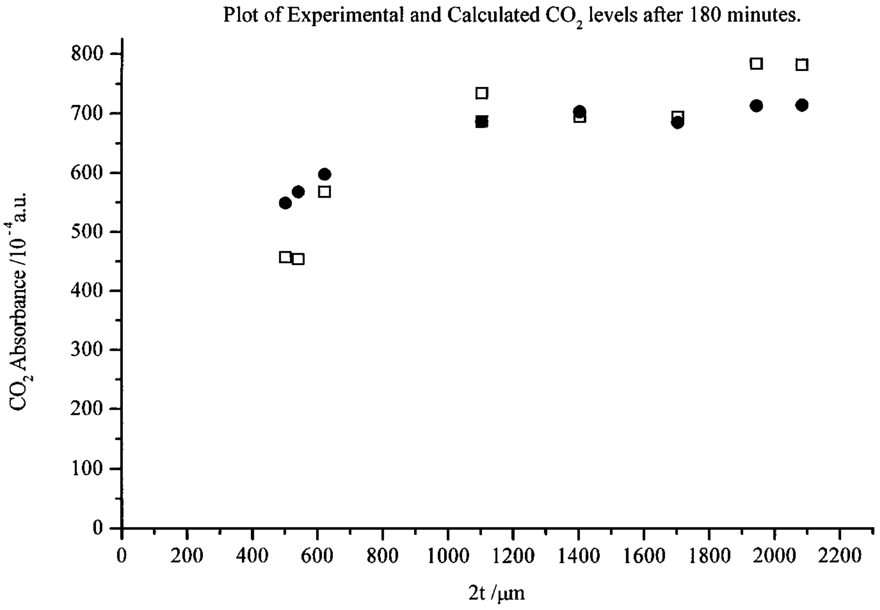

Figure 7 A comparison of experimental (measured after 180 min) and calculated carbon dioxide levels from unpigmented acrylic films of increasing thickness, *t*. □ Experimental results; ● Results calculated as described in the text.

thickness. (This assumes that any diffuse component at the film/substrate interface is negligible.) Separate transmission measurements, made on films applied to a CaF_2 substrate gave an absorbance, A, of ca. 0.40 at 350 nm wavelength for a 140 μm film, where A is defined as

$$A = \log_{10}(I_0/I) = \varepsilon t/2.303$$

and I_0 is the incident intensity and I the intensity of the beam transmitted by a film of extinction coefficient ε and thickness t. It follows that $(I_0/I) = 2.5$ and that 40% of the incident intensity is transmitted (60% absorbed) by the 140 μm film. Successive 140 μm thicknesses will therefore absorb ca. 60%, 24% (60% × 40%), 10% (60% × 16%) and 4% (60% × 6%) of the incident radiation. For a 280 μm film—an effective path length of 560 μm—more than 97% of the incident radiation is absorbed and further increases in film thickness should have negligible effect on carbon dioxide generation. More generally, the fraction of the incident energy absorbed is given by

$$I_{\text{abs}}/I_0 = 1 - e^{-\varepsilon t} \qquad (1)$$

From a single experimental measurement of the rate of carbon dioxide evolution for a 550 μm film, the rates for other films were calculated on the assumption that CO_2 evolution is directly proportional to UV absorption and the fraction of UV absorbed, I_{abs}/I_0, is given by Equation (1) and ε (derived from a 350 nm wavelength absorbance value of 0.4 for a 140 μm film) is $6.6 \times 10^3\ \text{m}^{-1}$. The calculated results, filled circles, are compared with the experimental points, empty squares, in Fig. 7. The agreement, even without allowing for the wavelength dependence of film absorbance, is sufficiently good to suggest that the model is broadly correct.

3.2. Pigmented films

XK90 acrylic films pigmented (19% v/v) with either anatase (A) or one of the four rutile pigments (R1–R5) described in Table I were then examined. These films—designated by the letters used to describe the relevant pigments—were used as received, i.e. without further dilution, as anomalously low rates of carbon dioxide generation were obtained on paint films thinned with acetone prior to film formation (Fig. 8). As with unpigmented acrylic films, CO_2 evolution from uncoated anatase (Fig. 8) and coated rutile (Fig. 9) pigmented paint films occurs only during UV irradiation. The rate of carbon dioxide generation for the coated rutile pigments is more than one order of magnitude less than for the uncoated anatase, consistent with the known lesser photoactivity of rutile [10]. However, even at these low activities the reproducibility of the measurements is good (±5%) provided that the humidity is held constant. Therefore, it is possible to differentiate clearly and unambiguously between the different grades of rutile.

The effects of changes in humidity on carbon dioxide generation from anatase and rutile are shown in Figs 10 and 11. In the presence of oxygen, water dramatically increases the rate of carbon dioxide formation but has a much smaller effect on the oxidation of rutile pigmented paints. In the presence of nitrogen, water has only a small effect on carbon dioxide generation from (rutile or anatase) pigmented paints. Results of the effect of humidity for unpigmented acrylic, anatase and rutile (R1) are summarised in Fig. 12.

Fig. 13 shows the dependence of CO_2 generation on the thickness, in the range 100 to 1000 μm, of films pigmented with rutile, R1. For these films, in contrast with the unpigmented acrylic, the carbon dioxide generation is independent of film thickness over the range 200–1000 μm. This much reduced dependence of oxidation rate on film thickness is a consequence of the

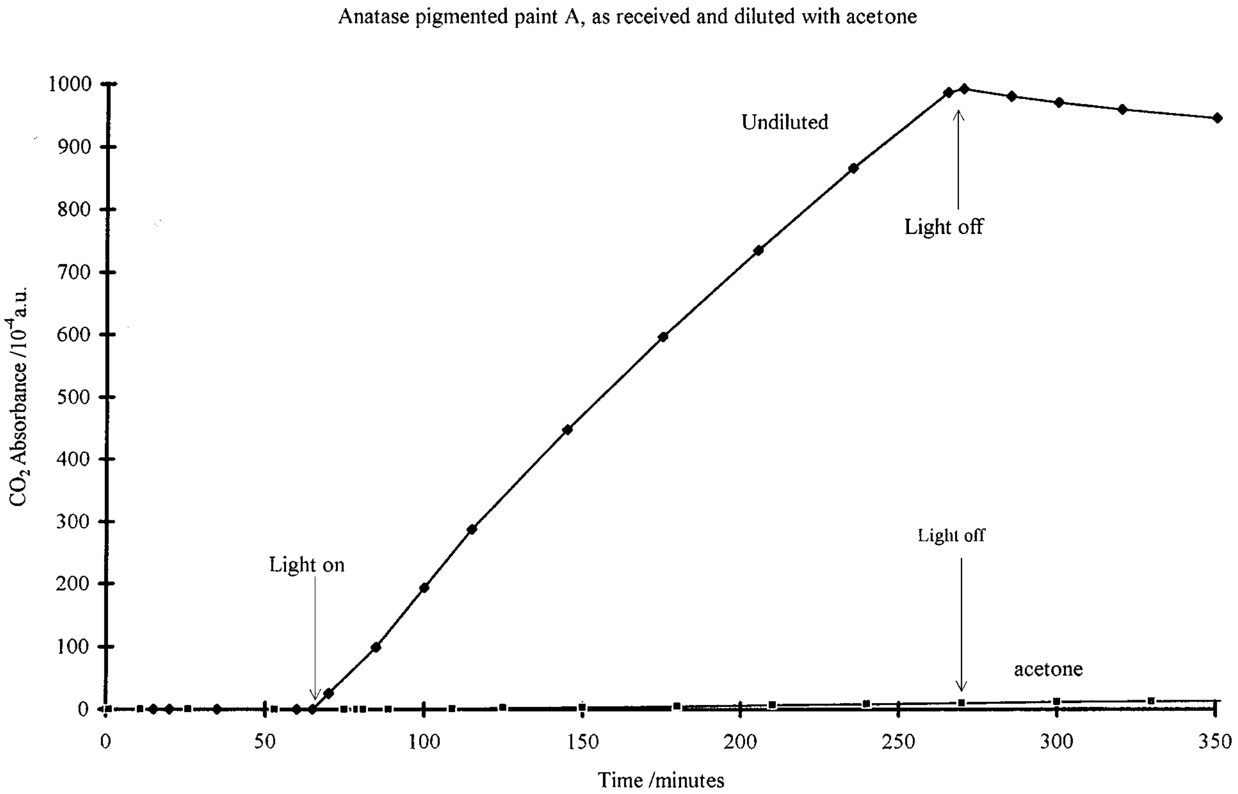

Figure 8 Increase of carbon dioxide absorbance during the irradiation of acrylic film pigmented with uncoated Anatase (A) showing the sensitivity to thinning with acetone.

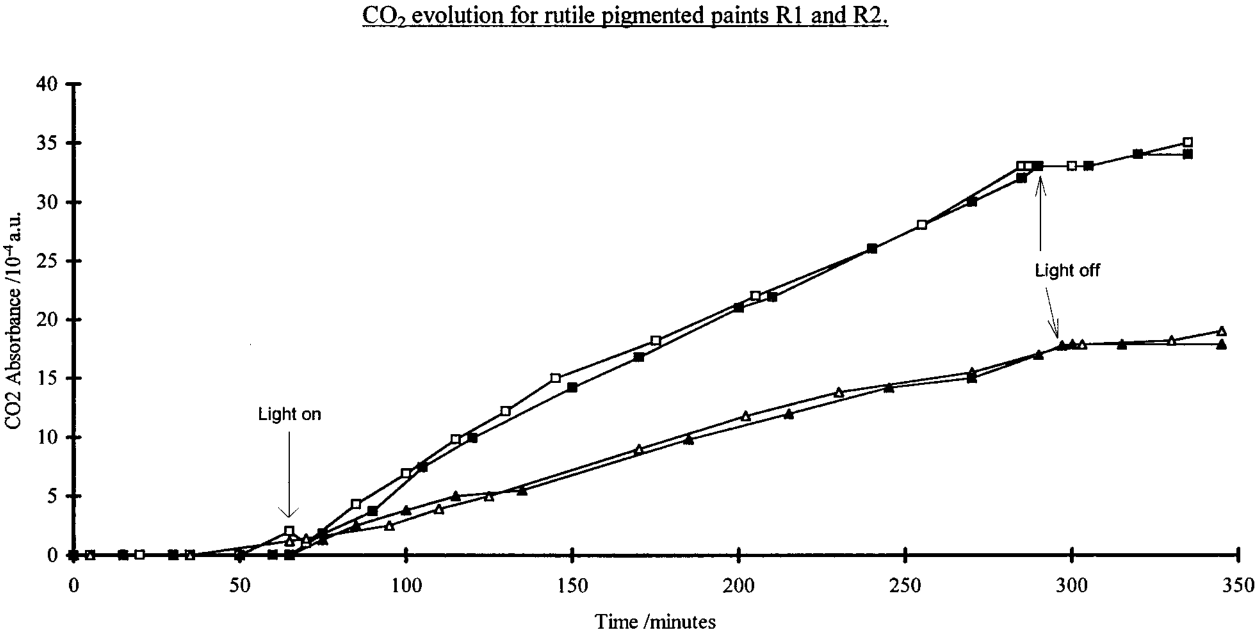

Figure 9 Carbon dioxide evolution from duplicate irradiations of Rutile pigmented acrylic paints R1 ■□ and R2 ▲△.

strong absorption of UV by rutile pigment and is discussed further below.

Fig. 14 shows the CO_2 evolution curves for rutile pigments R3, R4 and R5. R3 was made by the sulphate process, R4 and R5 by the chloride process and the details of the coatings also differed. However, all three showed excellent gloss retention when exposed to natural weathering at Florida. The CO_2 evolution measurements are able to discriminate between the three and rank the relative photo-activities as

$$R3 > R5 > R4$$

The Florida gloss results, corresponding to the CO_2 evolution curves shown in Fig. 14, are shown in Fig. 15. Pigments of high photoactivity lose gloss more quickly than those of low photoactivity because oxidative loss

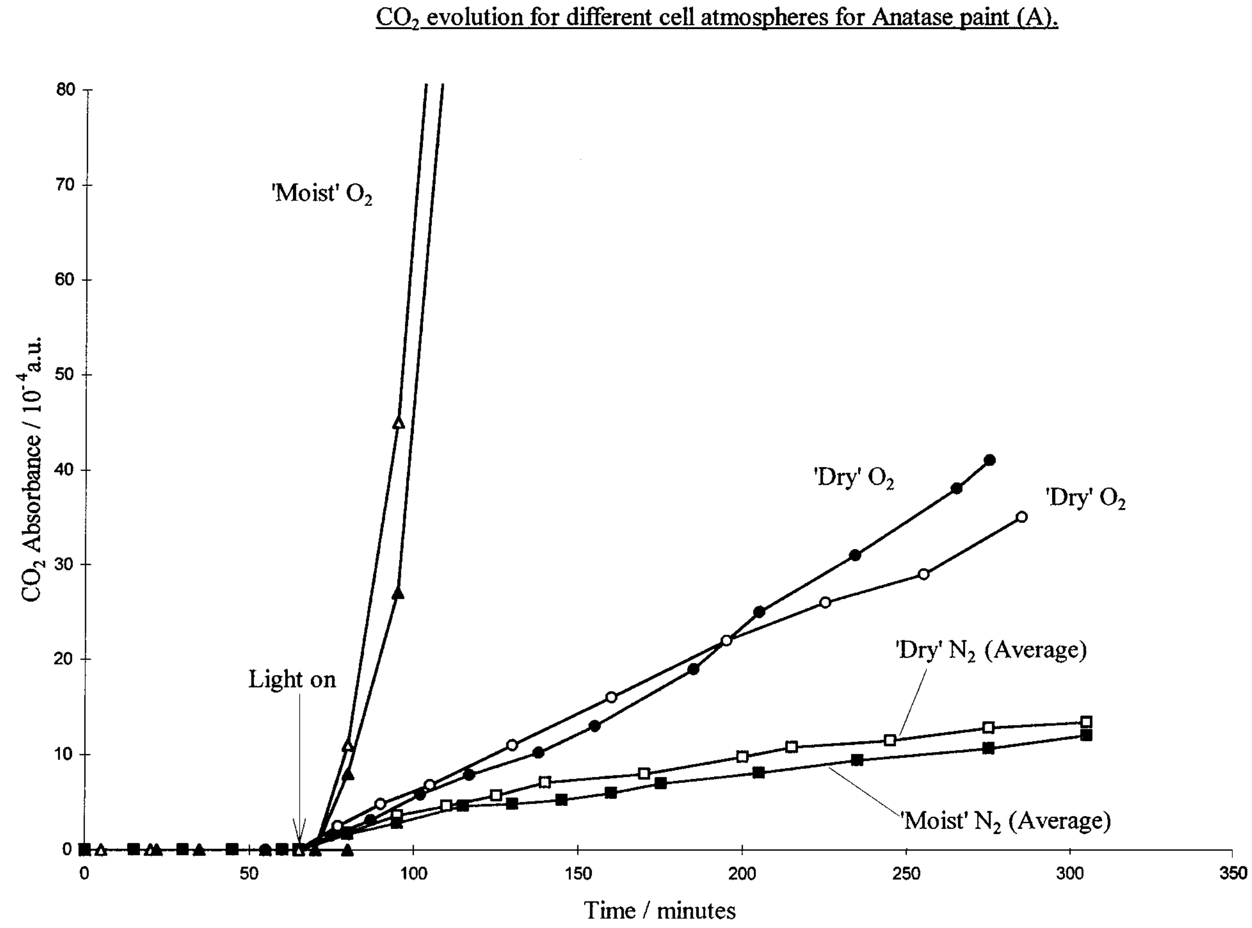

Figure 10 Carbon dioxide evolution as a function of atmosphere for Anatase pigmented paint. ▲△ 'Moist' Oxygen; ○● Dry Oxygen; □ Dry Nitrogen 40%; ■ Moist N_2.

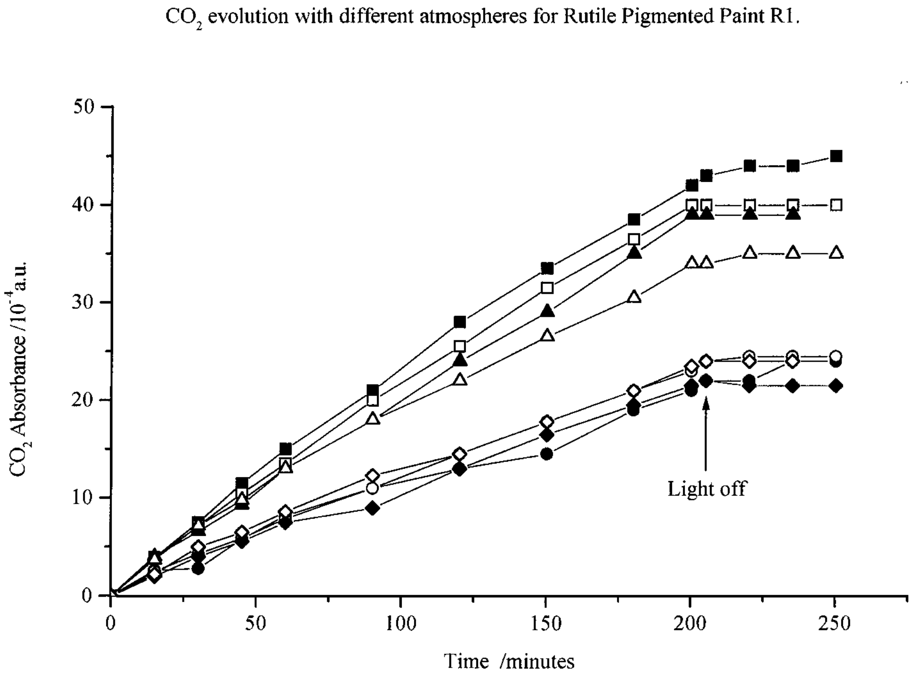

Figure 11 Carbon dioxide evolution in different atmospheres from paint pigmented with R1 Rutile. Oxygen ■ 85%; □ 60%: ▲46%; △ 31% humidity. Nitrogen ○ 47%; ● 40%; ◆ 67%; ◇ 86% humidity.

of the organic binder causes the surface to roughen more quickly. The results are less easy to interpret—partly because the pattern of measured gloss values show fluctuations that are influenced by seasonal climatic changes—and in order to make quantitative comparisons a Gloss Ratio (*GR*) may be calculated by comparing the gloss of the test paint, G_t, measured at different times during the paint exposure, with the

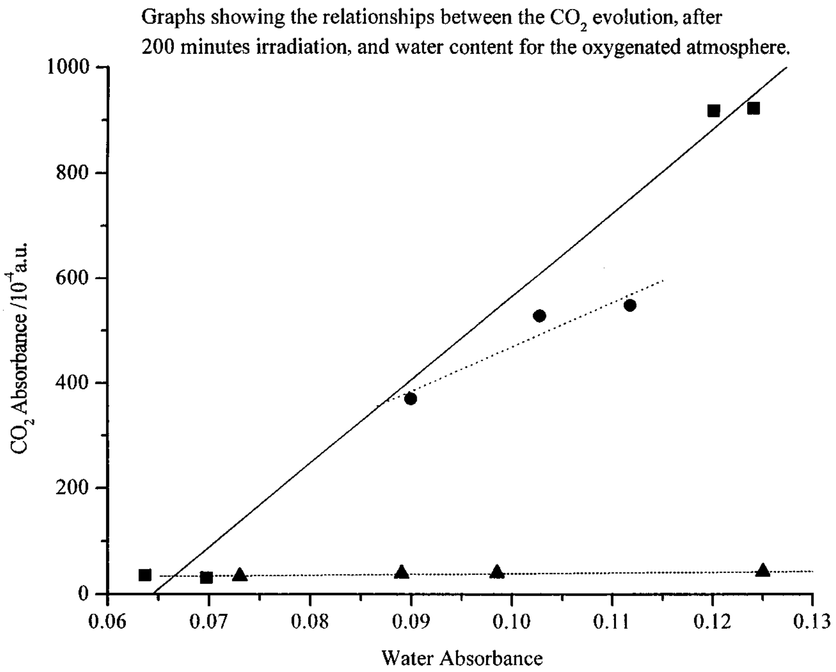

Figure 12 Comparison of carbon dioxide evolution of ■ anatase, ▲ rutile R1, and ● unpigmented acrylic films after 200 min irradiation in oxygen.

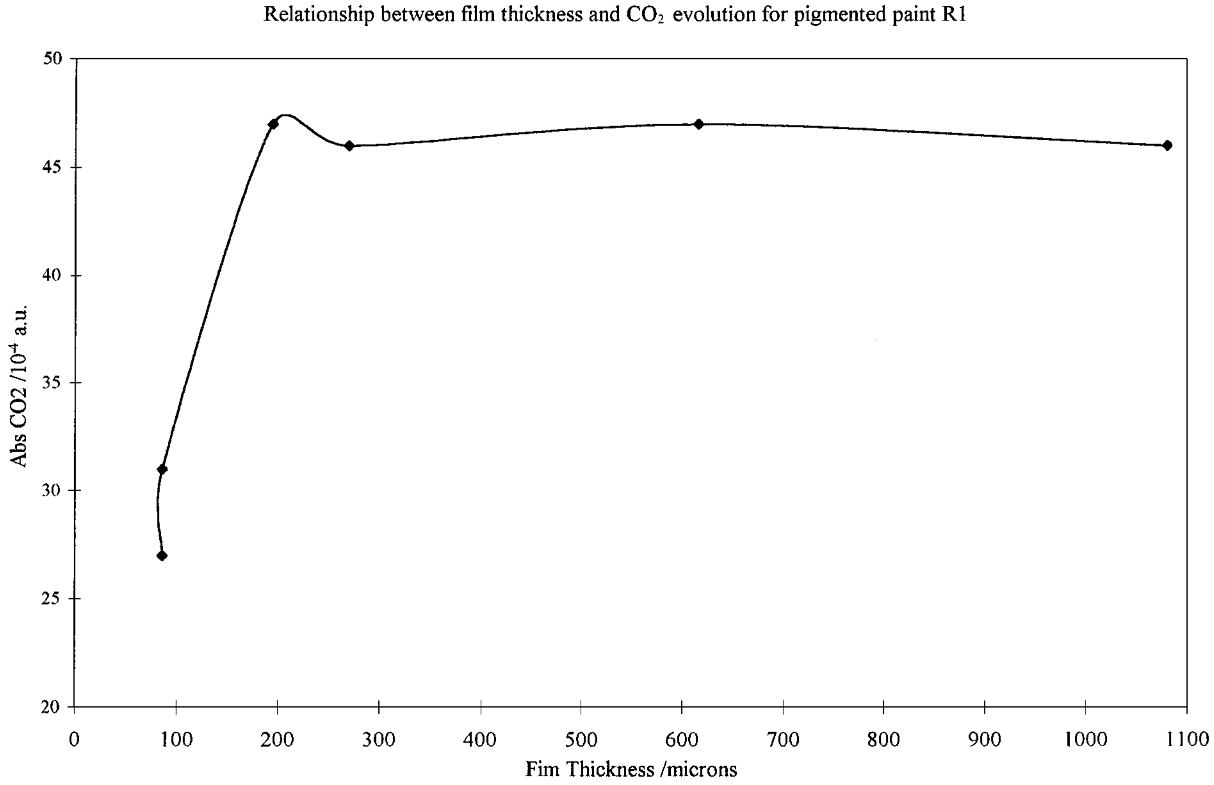

Figure 13 Dependence of CO_2 evolution on thickness of rutile (R1) pigmented acrylic film.

corresponding measurements, G_s, on a standard paint film exposed at the same time and place. The GR may then be defined by summing the measured values over the exposure period

$$GR = \Sigma G_s / \Sigma G_t$$

A large GR indicates that the test pigment has a worse gloss retention than the standard, and, if the film-forming organic is the same throughout, this is normally attributed to a higher photoactivity of the pigment. The photo-activity pattern based on the GR values is

$$R3(GR = 1.16) > R5(GR = 1.03) = R4(GR = 1.03)$$

Even for these low activity, coated-rutile pigments the differences in CO_2 evolution can be distinguished clearly and correlate reasonably well with the natural weathering results measured at Florida. The similarity of R4 and R5 measured at Florida may be a consequence

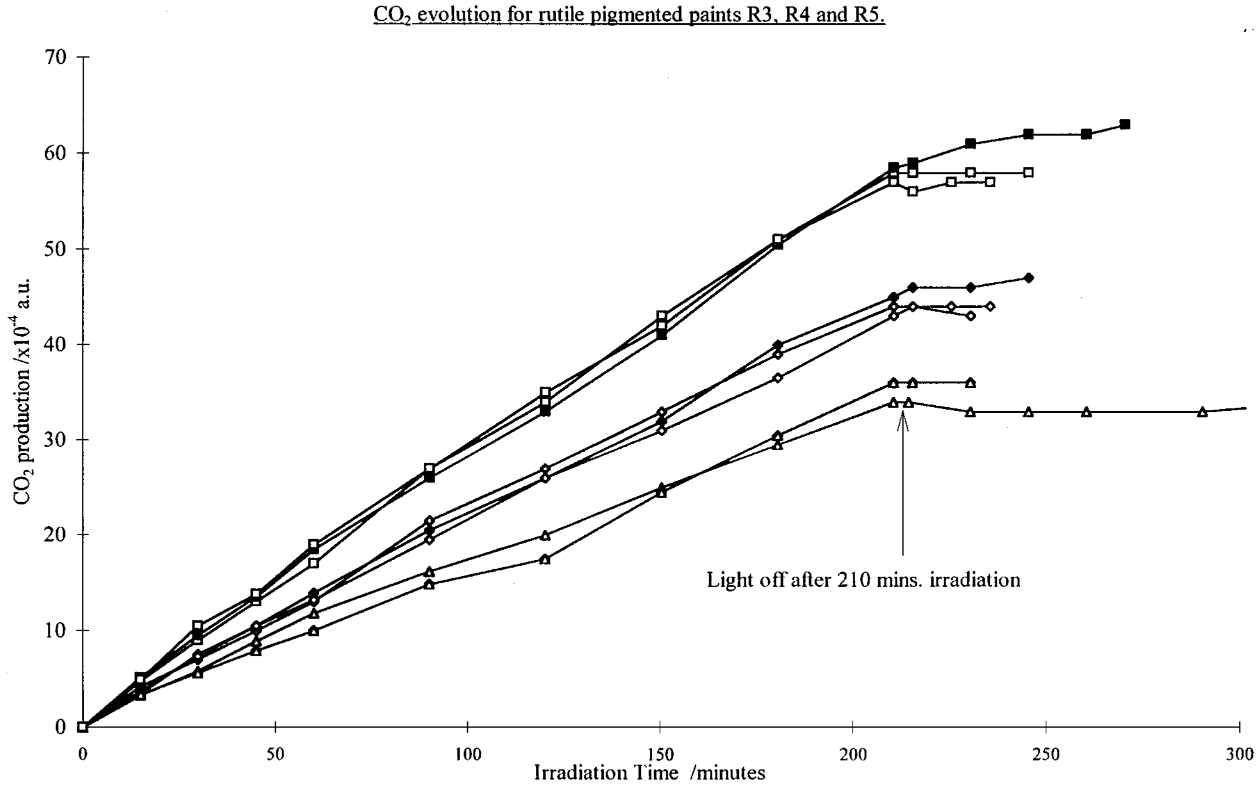

Figure 14 CO_2 evolution from CO_2 evolution from coated rutile (■ R3, ▲ R4 and ◆ R5 different shadings represent replicate experiments) pigmented acrylic films.

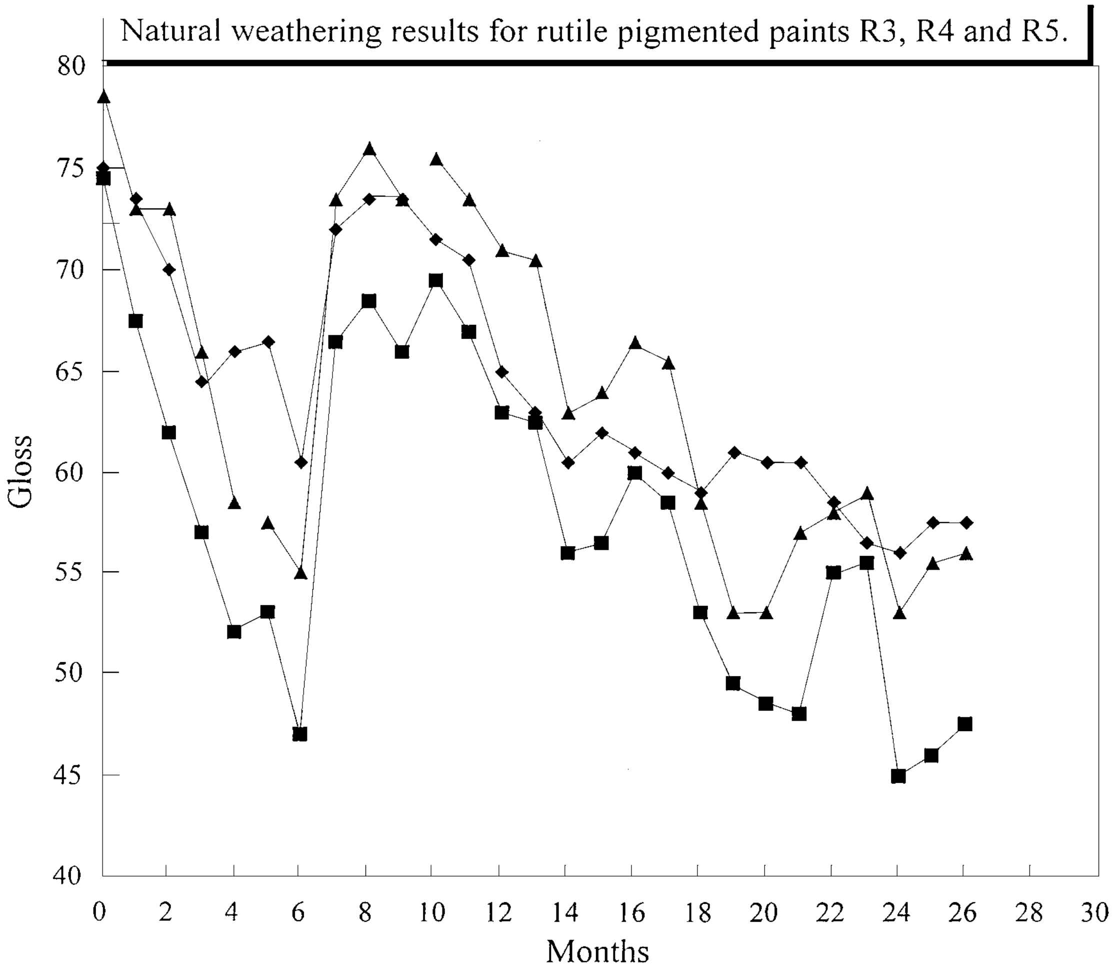

Figure 15 Reduction of Gloss with increasing exposure time for coated rutile (■ R3, ▲ R4 and ◆ R5) pigmented acrylic films exposed to natural Florida sunlight.

of the fact that the gloss retention curves depend not only on the photoactivity of the titanium dioxide but also on the state of dispersion of the pigment. Both the reproducibility of the CO_2 plots and their regular, monotonic nature—in marked contrast with the natural weathering results—inspire confidence in the FTIR method.

4. Discussion

The first conclusion from this work is that carbon dioxide evolution from *conventional paints* can be measured using *in situ* FTIR spectroscopy. This work, therefore, extends previous studies by Mackor and co-workers [5] who used chromatographic determination of CO_2 to monitor the photo-oxidation of paint films.

In order to use this method to determine the relative photoactivity of different titanium dioxide pigments it is necessary to understand and quantify the relative contributions of the direct photochemical oxidation of the organic and the indirect photocatalytic contribution of the pigments. For example, this paper demonstrates that direct photochemical oxidation of the unpigmented XK90 using a filtered xenon arc lamp is possible. This was an unexpected result because complementary studies—to be reported in detail in a separate paper—had demonstrated that the direct photochemical oxidation of these acrylic films by radiation from a glass filtered carbon arc is very slow. The apparent anomaly results from the fact that the major emission of the carbon arc is at 385 nm [10]—a wavelength at which there is negligible absorption by XK90 (see Fig. 1). By contrast the emission for the xenon lamp—a much closer simulation of solar UV—extends to 300 nm and there is increasing UV absorption of the acrylic at these shorter wavelengths. It follows that, when an XK90 paint pigmented with titanium dioxide is exposed to a carbon arc, there will be an increased breakdown of the organic binder because of the catalytic oxidation. However, if the same paint is exposed to a filtered xenon arc, the apparent effect of the titanium dioxide will be much less because the increased photocatalytic oxidation will be, to some extent, offset by absorption of UV by titanium dioxide and the consequent reduction in direct photochemical oxidation. Therefore, although carbon arc sources are a poor simulation of solar UV, and may not rank acrylic paints in the same sequence as natural exposure at Florida, they do differentiate effectively between the photocatalytic contributions to oxidation of different titanium dioxide pigments.

The observation that the oxidation rate of both pigmented and unpigmented films increases with humidity is fully consistent with the known importance of humidity in the natural weathering of paint films. It is also consistent with a mechanism in which the rate-determining step is the formation of hydroxyl radicals via the capture of positive holes at the titanium dioxide surface [3, 4]. However, *in situ* measurements, as described here, offer the possibility of probing the details of this mechanism in a manner that has not hitherto been possible with paint film. In particular the significantly greater sensitivity of Anatase to variations in humidity, shown in Fig. 12, has not previously been reported. The clear and important conclusion is that determination of the relative photo-activity of Anatase and Rutile *must* be made at constant humidity.

Since the primary focus of this work has been to develop a rapid test for assessing paint degradation we have not probed further the mechanism by which carbon dioxide is formed in the presence of nitrogen. Mackor and co-workers [5], on the basis of contrasting results for alkyd and acrylic films, have suggested that the effects are associated with dissolved oxygen in the acrylic films. Therefore we intend to further elucidate the mechanism of film degradation both by studies of alkyd films and by the use of complementary spectroscopic techniques such as photo-acoustic spectroscopy (PAS) and reflection- absorption.

Finally, we comment on the dependence of carbon dioxide evolution on film thickness. For unpigmented films, the 350 nm absorption is relatively weak and as Fig. 7 demonstrates the calculated increase in the number of photons absorbed at increasing film thickness is paralleled by the increased film degradation as shown by increased carbon dioxide generation. By contrast for a pigmented paint film the UV absorption at 350 nm is very much increased. Hird has reported [11] that only 20% of the incident 350 nm radiation is transmitted by a 1.3 μm alkyd/melamine film containing 10% (v/v) of anatase and only 8% of the incident UV was transmitted by a 1.5 μm film pigmented with 10% (v/v) of 0.20 μm rutile. Therefore $>$99% of the 350 nm UV incident upon an 8 mg (ca. 85 μm) acrylic film would be absorbed, but Fig. 11 shows that the amount of CO_2 generated increases significantly as the film thickness increases from 85 to 200 μm. Similar results, i.e. an increase in oxidation over a thickness range at which all the UV is expected to be absorbed have been reported previously for alkyd films by one of the present authors [12]. At present the explanation of this phenomenon is unclear. One possibility is that radiation with a wavelength of ca. 410 nm, much longer than previously suspected, can play a role in the photocatalytic degradation of films pigmented with rutile. A second possibility is that the OH radicals formed at the titanium dioxide/organic interface are generated near (within 10 μm of) the paint surface and then by a process of chain transfer the hydroxyl radicals form other more stable radicals that can diffuse within the film over lengths of ca. 100 μm. If substantiated, this possibility would have significant implications for the degradation of a wide range of pigmented polymers.

Acknowledgements

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