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Infrared spectroscopic evaluation of the photodegradation of paint

Part II: *The effect of UV intensity & wavelength on the degradation of acrylic films pigmented with titanium dioxide*

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This paper reports the application of a previously described i.r. spectrometric method, which measures the evolution of carbon dioxide, and hence the rate of photo-oxidation, caused by UV irradiation of paint films, to a study of the dependence of paint degradation on UV wavelength. Measurements have been made on both unpigmented and TiO_2-pigmented acrylic films. Preliminary measurements demonstrate that, for both pigmented and unpigmented acrylic films, the rate of carbon dioxide generation is proportional to $I^{0.5}$, the square root of the UV intensity. As the rate of carbon dioxide generation is a measure of paint film degradation, this implies that the rate of film degradation is proportional to the square root of UV intensity. This is the first time that this square root dependence, previously predicted from photo-oxidation studies of model compounds, has been directly measured on a practical paint film. Photo-oxidation of unpigmented, anatase-pigmented and rutile-pigmented acrylic films has been measured by using optical filters to isolated selected portions of the output of a Xenon lamp. Results have been analyzed semi-quantitatively taking into account the measured transmission characteristics of the filters, the lamp output and the $I^{0.5}$ relationship. The disproportionate deleterious effects of short wavelength, <300 nm, radiation on unpigmented films have been confirmed and the stability of anatase pigmented films to 405 nm radiation has been demonstrated directly. The FTIR assay of carbon dioxide produced by paint film degradation could be applied to other polymer films and combined with measurements of carbonyl band development.

1. Introduction

Titanium dioxide is the most widely used white pigment in both paints and plastics [1] and its presence affects the photo-degradation of paints and polymers in two ways. Firstly, by absorbing incident UV, the titanium dioxide protects the paint from direct photochemical reaction of the organic binder [2]. Secondly, a small portion of the absorbed UV leads to the generation of highly reactive hydroxyl radicals at the TiO_2 pigment surface, which catalyse polymer breakdown [3]. In this paper we shall refer to the direct UV-induced reaction process as *photochemical* and the second, TiO_2 mediated generation of hydroxyl radicals, as *photocatalytic*. The wavelength dependency of these two processes can be expected to differ. In particular, depending on its form, titanium dioxide absorbs from ~410 nm (rutile) or ~385 nm (anatase) as shown below, Fig. 1b. By contrast, most film-forming organics do not absorb until shorter wavelengths, the precise wavelength dependence varying with the types of chromophore that are present [4].

An earlier paper [5] described the development and evaluation of Fourier transform infrared spectroscopy (FTIR) to monitor the photo-degradation of a series of acrylic paints. This paper describes the extension of this approach to the study of the effect of irradiation intensity and wavelength on the photo-oxidative formation of carbon dioxide from acrylic paint films. The behaviour of the unpigmented acrylic film is contrasted with films pigmented with both relatively inert (coated rutile) and catalytically active (uncoated anatase) varieties of titanium dioxide pigment.

As in the previous study, oxidation of the acrylic films was measured by an i.r. spectrometric determination

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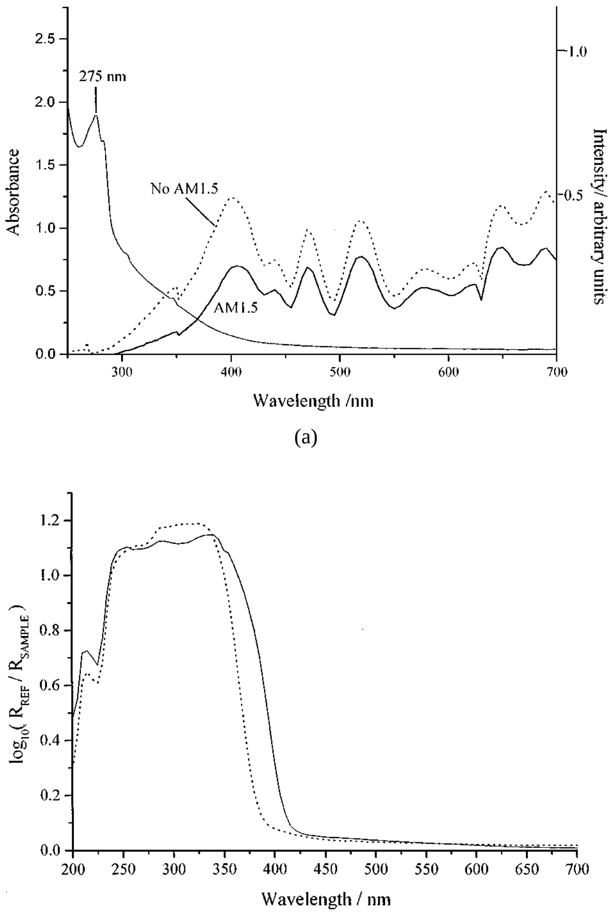

(a)

(b)

Figure 1 (a) The absorption spectrum of a 138 μm dry unpigmented film formed from the acrylic co-polymer emulsion used in these studies compared with the output of the xenon lamp, before and after filtration by the AM1.5 filter. (b) The absorption spectra of titanium dioxide pigmented acrylic films.

of the amount of carbon dioxide released to the gas phase as a result of the oxidation. The effect of incident wavelength on film breakdown was studied by using optical filters to isolate selected spectral portions of the xenon lamp output. Since the use of different filters entails a change in the intensity of the incident radiation, the effect of UV intensity on the rate of carbon dioxide evolution was monitored, in preliminary measurements, by using neutral density filters to reduce the output from a xenon lamp. By combining the two sets of measurements it was possible to infer the relative effectiveness of different wavelengths for photo-oxidation of unpigmented acrylic films and to evaluate the effect of both anatase and rutile titanium dioxide on the photo-oxidation of pigmented paint films.

The principles defined by studies of this type are highly relevant to practical testing of a wide range of pigmented systems, and in particular to the evaluation of accelerated tests, because the comparison of the results of different tests must take into account both the intensity variation and the different spectral distribution of the many different lamp types that are used. Observed differences associated with the varying lamps used in practical weathering tests are frequently interpreted in terms of wavelength distributions [6, 7]. However, there is little direct information on the effect of wavelength and what there is assumes that degradation rate is directly proportional to intensity [8]. The CO_2/FTIR method provides a convenient method of obtaining such information for practical systems.

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, Fig. 1a, of a 138 μm dry film of this emulsion demonstrates that, although the first absorption peak does not occur until 275 nm, significant UV absorption extends to ca. 400 nm. (Beyond 400 nm the small and constant loss in transmission is probably due not to absorption but to reflection losses at the air/polymer and polymer/substrate interface.) The reflectance spectra, measured on a Hitachi U3410 spectrometer fitted with an integrating sphere, of corresponding films pigmented with either anatase or rutile, Fig 1b, show that the anatase and rutile paints begin to absorb strongly at ca 385 nm and ca 410 nm respectively.

Details of the pigments used in this study are summarized in Table I. The rutile was chosen as an example of a pigment with a low photoactivity and had been surface treated (coated [9]) with an inorganic layer, consisting mainly of a hydrous oxide of aluminium, in order to further reduce the low levels of photocatalytic activity characteristic of the rutile form of titanium dioxide. The anatase was selected as an example of a pigment with a high photoactivity. The photocatalytic activity of anatase is generally higher than that of rutile [10], and no inorganic surface coating was applied. Pigmented paint samples were made up as described earlier [5]. Paint films were applied by dip-coating metal substrate discs and dried for ca. 150 hrs. The pigment volume concentration, p.v.c., in the dried paint film was 19% (v/v).

2.2. Apparatus and procedure

The apparatus and procedure were as described in reference [5]. Film samples were positioned, in a specially constructed i.r. cell, opposite a CaF_2 window, which could be illuminated, via a 1m flexible light guide, with UV radiation from an 150W Xenon lamp (Oriel). A 100 mm water filter was used to remove IR and so minimize sample heating. The temperature rise during irradiation was monitored by attaching a thermocouple to the back of the metal substrate, and was shown to be less than 0.5°C. Selected portions of the lamp output could be isolated with the use of appropriate filters (Table II)

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

Sample	Crystal form	Production process	Coated or uncoated
A	Anatase	Sulphate process	Uncoated
R	Rutile	Chloride process	Silica & alumina coated

TABLE II Transmission of filters used in this work

Filter number	% transmission	λ/nm of maximum transmission	Band width, nm.
G-66-74	50	Neutral density	
G-66-67	7	Neutral density	
Oriel 59805	48 @ 400 nm	385	300–450
Oriel 56410	17	315	10
Oriel 56430	32	367	11
Oriel 56440	44	405	10

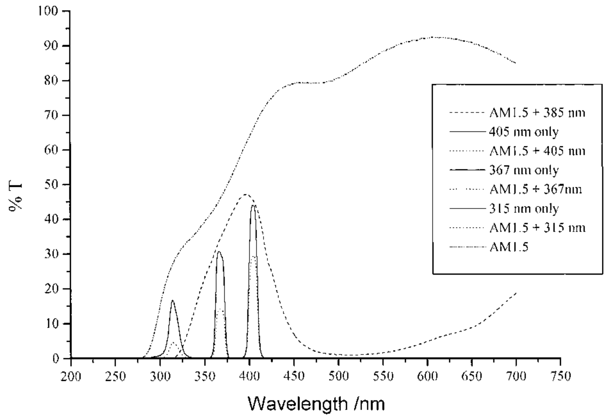

Figure 2 Transmission characteristics of the optical filters, singly or in combination with AM1.5 filter.

whose transmission characteristics are shown in Fig. 2. The assembled cell was sparged with moist oxygen for 30 minutes and was then mounted in the spectrometer sample compartment which was itself purged with nitrogen until the levels of both water vapour and carbon dioxide were constant. A single-beam reference spectrum of the gas-phase in the dark was first recorded and then to confirm the stability of the system, absorbance spectra (1000 scans at 4 cm^{-1} resolution: collection time 105 sec.) were recorded over a period of 60 minutes. The flexible light guide was then connected to the xenon-light source via appropriate optical filters, a new single beam reference spectrum was recorded and absorbance spectra were then recorded at regular intervals over 210 minutes whilst continuing to irradiate. Finally, absorbance spectra were collected for ca. 60 minutes after the light was switched off.

Because of the effects of paint film thickness and atmosphere humidity on the measured rate of carbon dioxide formation, demonstrated in the first part of this study [5], all measurements were made in the same cell, using moist oxygen (relative humidity ~80% monitored by the absorbance of water vapour at 1653 cm^{-1}) on films of similar thickness (150 ± 15 μm).

3. Results
3.1. Dependence of carbon dioxide evolution rate on UV intensity

Fig 3. compares carbon dioxide evolution from unpigmented (U), anatase-pigmented (A), and rutile-pigmented (R) acrylic films. It demonstrates clearly that anatase promotes and rutile retards degradation of the acrylic film. As outlined above, the promotion by uncoated anatase is considered a consequence of the high photocatalytic activity of this form of titanium dioxide.

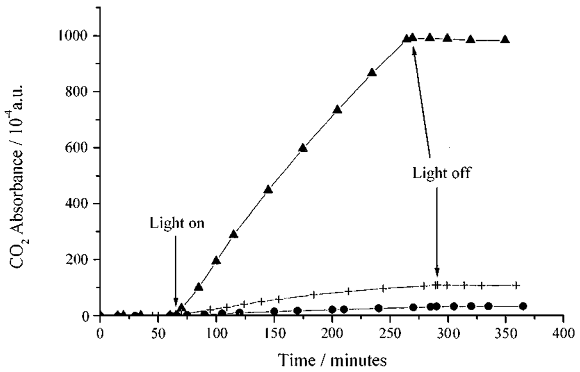

Figure 3 Carbon dioxide evolution from unpigmented (U, +), anatase-pigmented (A, ▲), and rutile-pigmented (R, ●) acrylic films.

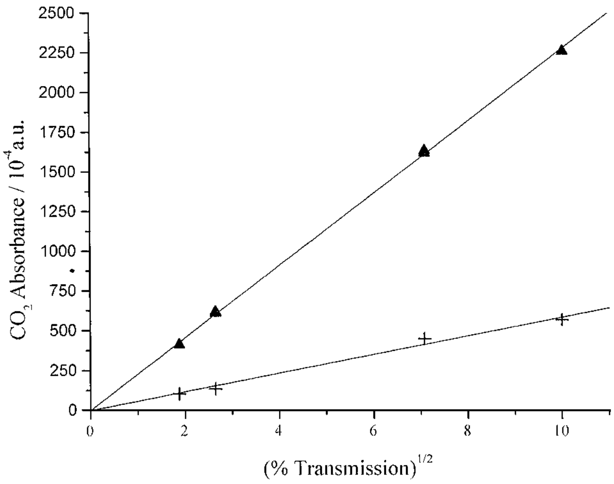

Figure 4 Carbon dioxide evolution after 210 minutes as a function of variation in incident UV intensity. The UV intensity was varied by using neutral density filters, either singly or in combination.

In order to facilitate subsequent normalization of results from different filter combinations, the effect of intensity on the rate of carbon dioxide formation was then assessed by using neutral density filters of known transmission. Fig. 4 shows the affect of reduced UV intensity on carbon dioxide evolution from both unpigmented and anatase-pigmented acrylic films. The UV intensity, of AM1.5 filtered radiation measured at the end of the light pipe was $\sim 1.5 \times 10^{15}$ quanta sec^{-1} and as this was incident on an area of ~ 100 mm^2, the UV intensities corresponding to those shown in Fig. 4 are estimated to range from $\sim 1.5 \times 10^{13}$ quanta mm^{-2} s^{-1} to 5×10^{11} quanta mm^{-2} s^{-1}. This compares with estimated UV intensities of 2×10^{13} quanta mm^{-2} s^{-1} received during outdoor exposures, assuming 5% of sunlight is UV [3]. The linear relationship between the rate of carbon dioxide evolution and the square root of filter transmission shows that the degradation rate varies as the square root of the intensity of the incident radiation. The variation of rate with $I^{0.5}$ occurs with both the unpigmented and the pigmented films.

For the unpigmented film the only degradation route is photochemical. For the anatase-pigmented film both

TABLE III A comparison at different wavelengths of the rates of breakdown of unpigmented, rutile pigmented and anatase pigmented acrylic films

Filter type and λ_{max}, nm	Transmission at λ_{max}, %	CO_2 generated in 210 minutes. [Tabulated as $10^4 \times$ absorbance at 2350 cm^{-1}] (Results in brackets are as a % of the rate measured with AM1.5 filters).		
		Rutile	Unpigmented	Anatase
No Filter		60	1080	2240
AM1.5 alone. (With Xenon lamp simulates solar radiation)	.	50	355	1555
385 Broad band (Oriel 59805)	6.5 at 450 nm 48 at 400 nm 20 at 350 nm	23 (45%)	—	984 (63%)
315	17	7 (14%)	36 (10%)	49 (3.1%)
367	14.3	7 (14%)	29 (8%)	250 (16%)
405	30	14 (28%)	16 (4.2%)	21 (1.3%)

(Individual filters were all used in conjunction with the AM1.5 filter).

photochemical and photocatalytic routes are possible, but the observed large increase in carbon dioxide evolution demonstrates that the photocatalytic route dominates. Thus the $I^{0.5}$ dependence occurs with both the photochemical and photocatalytic mechanisms.

3.2. Dependence of carbon dioxide evolution rate on UV wavelength

In this series of experiments optical filters were used to select defined portions of the UV spectrum and the effect on carbon dioxide evolution rates were monitored. The results are summarized in Table III.

3.2.1. The effect of the Air-Mass Filter

The output of the unfiltered 150W xenon lamp is shown in Fig. 1a and is compared with the output of the same lamp filtered by an AM1.5 optical filter. (The designation AM1.5 signifies a filter designed to modify the output of the xenon lamp so that it more fully simulates solar radiation that has been filtered by an 'air mass' corresponding to a path length 1.5 times that experienced by light from the directly overhead sun—i.e. it corresponds to the air mass when the sun is at an elevation of 34°.) The degradation rates in Table III follow the sequence $A > U > R$ (where U, A and R designate Unpigmented, Anatase-pigmented and Rutile-pigmented films respectively) for both unfiltered and broad band (AM1.5 or 385 nm) filtered xenon radiation and confirm that anatase promotes photo-oxidation of the acrylic film whilst rutile protects it. The effect of the AM1.5 filter is to reduce the carbon dioxide generation by 17 to 30% for the pigmented films and ca 70% for the unpigmented film. The air mass filter reduces the intensity by 64% at 350 nm and ~45% at 400 nm. If oxidation depends on $I^{0.5}$ the expected reduction in oxidation rate would be 40 to 26%. Therefore, it seems reasonable to assume that for the pigmented films the major consequence of the use of the air mass filter is to reduce the UV intensity. Most probably, the larger decrease in rate of carbon dioxide generation from the unpigmented film is mainly a consequence of the fact that the AM1.5 preferentially removes radiation with wavelengths near and below 300 nm. Absorption is a necessary pre requisite for photochemical oxidation and the absorption of the unpigmented acrylic film is mainly below 300 nm, Fig. 1a. Therefore, removal of these short wavelengths exercises a disproportionate effect on the oxidation of the unpigmented film. By contrast the pigmented films absorb to much longer wavelengths, ~385 nm with anatase and ~410 nm with rutile, and the preferential removal of wavelengths near and below 300 nm has only a marginal effect on their oxidation, particularly for rutile.

3.2.2. Results for individual narrow band filters

To minimize the relatively well known effects of short wavelength radiation summarized above, the remainder of these results are presented for a combination of the AM1.5 filter and the specified narrow band filters. The carbon dioxide generation results are expressed relative to those for the AM1.5 filtered xenon lamp by itself.

For each filter combination there is a different radiation intensity. However, for any given combination all films were subjected to the same radiation. Table III compares the amount of carbon dioxide generated from the different paints in a fixed time (210 min.) at a given wavelength.

For the (AM1.5 + 315 nm) filter combination film A oxidizes 7 times faster then R. For AM1.5, (AM1.5 + 385 nm broad band), and (AM1.5 + 367 nm) filters, film A oxidizes 35 to 45 times faster than film R. However, for AM1.5 + 405 nm radiation A and R are comparable. Qualitative inspection of Table III suggests that these changes in relative activity are associated with the marked decrease in the sensitivity of film A to 405 nm radiation. By contrast degradation rates of film R are relatively insensitive to the wavelength of the incident radiation.

3.2.3. Semi-quantitative analysis

To make this qualitative interpretation more robust, a semi-quantitative analysis has been attempted by

TABLE IV A comparison, at selected wavelengths, of measured carbon dioxide with semi-quantitative estimates of the amounts of carbon dioxide

		CO_2 generated from film R in 210 minutes. [Tabulated as $10^4 \times$ absorbance at 2350 cm^{-1}]			CO_2 generated from film U in 210 minutes. [Tabulated as $10^4 \times$ absorbance at 2350 cm^{-1}]			CO_2 generated from film A in 210 minutes. [Tabulated as $10^4 \times$ absorbance at 2350 cm^{-1}]		
λ	F	Calculated from F	Calculated from $F^{0.5}$	Exptl	Calculated from F	Calculated from $F^{0.5}$	Exptl	Calculated from F	Calculated from $F^{0.5}$	Exptl
315[a]	0.00139	(0.07)	1.9	9.0	(0.49)	13.3	71	(2.2)	58	106
315	0.000392	(0.02)	1.0	7.2	(0.14)	7.0	36	(0.61)	31	49
367	0.00160	(0.08)	2.0	7.4	(0.57)	14.2	29	(2.5)	386	250
405	0.00433	(0.22)	3.3	13.9	(1.53)	23.3	16	(6.7)	102	21

[a] Result for 315 nm filter by itself, without the AM1.5 filter.

normalizing the measured carbon dioxide evolution rate for any given filter combination to the rate of evolution associated with the AM1.5 (only) filtered xenon radiation.

For the basis of this calculation only, we made the necessarily crude and approximate assumption that all wavelengths from 300 to 410 nm are equally effective for paint degradation and summed the total output $I(\lambda)$ of the AMD1.5 filtered xenon lamp over this wavelength interval. For each filter combination we then calculated and summed the product $I(\lambda)T(\lambda)$, where T is wavelength dependent filter transmission, over the same wavelength interval, and defined a normalization factor F as

$$F = \frac{\sum I(\lambda)T(\lambda)}{\sum I(\lambda)}.$$

(Clearly the product $I(\lambda)T(\lambda)$ is zero except at those wavelengths at which the filter transmits.) Expected rates of carbon dioxide evolution can then be calculated for each of the filter combinations.

Table IV summarises the results of these calculations and compares the results of two normalisation procedures. The results in brackets were calculated by multiplying the reference rate for each film by the factor F—i.e. the calculation assumed that the oxidation rates are proportional to light intensity, the agreement between measured and calculated rates is strikingly poor-calculated and measured values differ by up to two orders of magnitude. The unbracketed results were calculated on the basis of the square root relationship derived from the results of the preliminary experiments reported above. The discrepancies are much less and overall the semi-quantitative analysis supports the conclusion that normalization on the basis of the square root of light intensity provides a surer basis for analysis of the wavelength experiments.

More specifically, at 367 nm the overall agreement between measured and calculated results for the more active (less stable) unpigmented and anatase-pigmented films is within a factor of ∼2—perhaps as good as can be expected given the errors associated with the numerical summation process described above, and the assumption that all wavelengths between 300 and 410 nm are equally effective. At 405 nm the measured oxidation of these unpigmented and anatase-pigmented films is significantly *less* than the value calculated on the basis that all wavelengths are equally effective. This is most probably because, as Fig. 1 shows, neither film absorbs 405 nm radiation. Conversely, at 315 nm the ratio of measured to calculated oxidation increases-probably because of the increased contribution of direct photochemical oxidation.

4. Discussion

The oxidation rates of anatase-pigmented (A) and rutile pigmented (R) acrylic films relative to the corresponding unpigmented film are shown in Table IV.

4.1. Dependence of carbon dioxide evolution rate on UV intensity

The conclusions from the preliminary experiments, that, for both the photochemical and photocatalytic reactions, the rate of formation of carbon dioxide is proportional to the square root of the incident intensity, are at first sight counter-intuitive.

Kinetic treatments of the decomposition of solid polymers have shown that pair recombination of polymer peroxy radicals, $POO^\bullet$, is of much greater importance in the degradation of solid polymers than would be expected on the basis of solution studies [11, 12]. This is because radical pairs are not free to diffuse away from one another. It is probable that in paint films, as in solid polymers, the restricted radical mobility emphasises the importance of such recombination processes. A kinetic analysis that leads, if chain branching is negligible, to a predicted dependence of degradation rate on the square root of light intensity has been proposed by Gerlock and co-workers in the context of e.s.r. studies of nitroxide radical decay in acrylic-melamine and acrylic urethane coatings [13]. We therefore suggest that in the case of the photochemical reaction the $I^{0.5}$ dependence is a result of the concentration of radicals, that are the key intermediates in the breakdown to carbon dioxide, being controlled by a bimolecular recombination process, as has been suggested for oxidation of liquid hydrocarbons [14].

For the photocatalysed reaction the $I^{0.5}$ dependence is exactly what would be predicted for a process in which recombination of the electrons and holes generated by UV radiation of titanium dioxide is the controlling step in the mechanism. A simple model [3] led to the relationship

$$\text{Rate} = KI^{0.5}$$

where

$$K = \left\{ \frac{k_3^2 k_1}{k_2} \right\}^{0.5}$$

where I is the intensity of UV, k_1 is the absorption coefficient, k_2 is the rate coefficient for electron-hole recombination and k_3 is a rate constant for the surface reaction. Studies of the photo-oxidation of a model compound, isopropanol, by rutile pigments, at intensities from ca 2×10^{11} to 10^{16} quanta mm^{-2} s^{-1}, have confirmed the prediction that rate is proportional to the square root of radiation intensity [3] and subsequently a significant number of other oxidation reactions photo-catalyzed by other forms of titanium dioxide have been shown to depend on $I^{0.5}$ [15]. However, to our knowledge this is the first time that the square root relationship has been demonstrated for the photocatalytic degradation of a *practical* paint film.

4.2. Dependence of carbon dioxide evolution rate on UV wavelength

For the unpigmented film, U, degradation to carbon dioxide increases with decreasing wavelength and this increase is particularly prominent in the absence of the AM1.5 filter. This trend is totally consistent with the absorption spectrum shown in Fig.1. The trend would be even more pronounced in thinner paint films since absorption of the 400 nm photons would then be proportionately less. The first consequence of the minimal absorption above 350 is that at 405 nm the measured oxidation rate is lower than the calculated value. The second consequence is that the calculated denominator, $\sum I(\lambda)$, in the expression used to normalise the data, is too large and therefore the semi-quantitative analysis led, for 315 nm radiation, to calculated rates of carbon dioxide evolution lower, by a factor of $\sim$5, than the measured values.

As shown in Table III and Fig. 3, the overall degradation of the rutile-pigmented film, R, is significantly less, ×7, than that of film U because of the broad optical absorption of rutile, which extends to ca 410 nm, coupled, with the low photocatalytic activity of the coated rutile pigment i.e. the rutile *protects* the organic compound. Because the absorption of rutile at 400 nm is greater than that of the unpigmented acrylic, U and R degrade at comparable rates when irradiated at 405 nm. The similar ratio of measured to calculated activity of R at 367 and 405 nm is consistent with a similar balance of photochemical to photocatalytic degradation at the two wavelengths. Hird [16] has demonstrated that in alkyd-melamine films with 20 volume percent of rutile pigment (comparable to the 19% of the present films) 70% of 400 nm radiation, and 92% of 365 nm radiation is absorbed within 1 μm. Therefore photons of both wavelengths will be completely absorbed by the present comparatively thick films. Equal amounts of carbon dioxide will be generated, but with the 367 nm radiation the breakdown may occur closer to the surface.

The anatase-pigmented film A degrades to carbon dioxide much faster than either R or U, as expected. However, the most significant feature of the results is that for this film there is a marked decrease in the effectiveness of the 405 nm radiation, a consequence of the minimal absorption by anatase at 405 nm. At 367 nm the anatase pigment absorbs strongly and as a result, the measured ratios of carbon dioxide generation rates increase by a factor of 12 (cf 2 for U and 0.5 for R). The difference in absorption coefficients is so large that despite the thick paint films used, degradation of film A is not initiated by 405 nm radiation.

5. Conclusions

This research has demonstrated the usefulness of the FTIR assay of product carbon dioxide in studies of paint film degradation. Similar studies of polymer films could usefully be allied with i.r. assay of the carbonyl intermediates in polymer degradation. The sensitivity and convenience of the technique has allowed the $I^{0.5}$ dependence of photocatalytic degradation of practical paints to be demonstrated for the first time. In its turn, this has allowed the effect of radiation wavelength to be conveniently and directly measured for both unpigmented and pigmented paint films.

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