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# Measurements of carbon dioxide evolution from alkyd paint films

## Part I *Oxidative scission during film ageing*

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A recently developed *in situ* FTIR method of monitoring $CO_2$ evolution during oxidation of paint films has been used to measure $CO_2$ produced by alkyd paints when enclosed in a high humidity oxygen atmosphere. Evolution of $CO_2$ from paint films in the dark was observed and was found to persist over long periods. It is likely that this is the result of $\beta$-scission of fatty-acid side-chains which accompanies oxidative cure of alkyd films: it decreases as these processes go to completion. The rate of $CO_2$ evolution from aged films is reduced after the initial rate of cure has been accelerated by oven ageing or by increasing the concentration of catalytic driers. It has also been shown that resistance to photo-degradation increases as ageing of the films proceeds. Our results demonstrate that the sensitivity of $CO_2$ detection by FTIR provides a useful method for following film cure and ageing. The technique has wider potential, e.g. for the study of oxidation in food oils and cosmetic preparations. *© 2002 Kluwer Academic Publishers*

## 1. Introduction

In earlier work by this group, *in situ* FTIR measurements of $CO_2$ evolution were used to follow the photodegradation of acrylic paint films pigmented with titanium dioxide [1, 2]. It was shown that the technique could distinguish between commercial $TiO_2$ pigments in terms of their photocatalytic activity and results were reported showing the effects of UV intensity and wavelength and of humidity.

The results reported here are part of a study extending the earlier work to alkyd paints. Alkyd resins are widely used in exterior decorative paints where photostability is important and so measurements of UV degradation in these systems are relevant to predicting the lifetime of paint films in the environment. As will be shown below, however, early results showed significant rates of $CO_2$ evolution from alkyd paint films in the dark which interfered with measurement of photo-degradation. The nature of this dark evolution is explored in this paper. Results of photo-degradation experiments will be given in Pt 2.

Alkyd resins are polyesters formed from phthalic anhydride and fatty acid monoglycerides [3]. The monoglycerides are derived from drying oils in which the fatty acid component is high in unsaturated acids; linoleic (cis, cis 9, 12 octadecadienoic) acid is typically the most important of these. Film formation involves first solvent loss and then oxidative cross-linking of the unsaturated acid side-chains which proceeds through formation of hydroperoxides [3–6]. The oxidative process is outlined for linoleate chains in Scheme 1. It is a free radical process assisted by catalytic "driers" such as cobalt compounds. Initiation may be facilitated by the driers, according to:

$$RH + Co^{3+} \rightarrow R^{\cdot} + H^{+} + Co^{2+} \qquad (1)$$

and is favoured by delocalisation of the resultant radical across the diene. Oxygen is added at position A or B to form peroxide radicals which can extract hydrogen from adjacent groups to form the hydroperoxides:

$$ROO^{\cdot} + R'H \rightarrow ROOH + R'^{\cdot} \qquad (2)$$

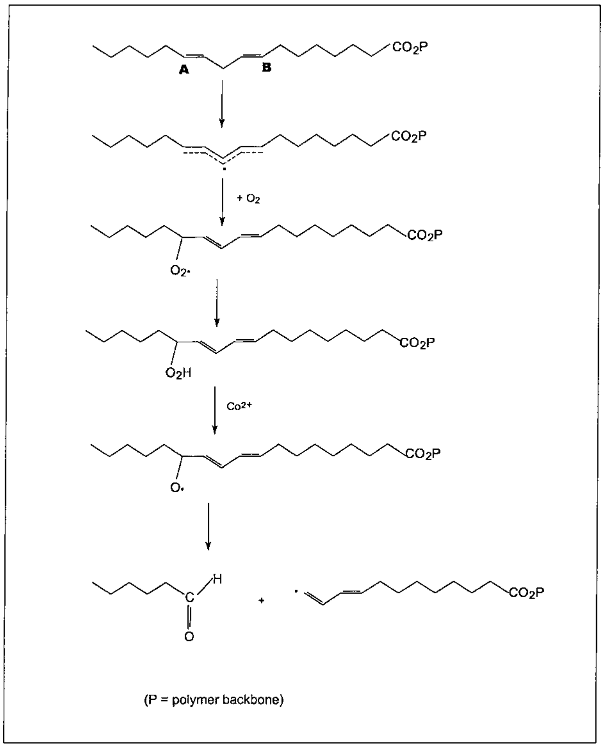
The hydroperoxides are relatively stable but break down in the presence of the catalytic driers to form more radicals:

$$ROOH + Co^{2+} \rightarrow RO^{\cdot} + OH^{-} + Co^{3+} \qquad (3)$$

$$ROOH + Co^{3+} \rightarrow ROO^{\cdot} + H^{+} + Co^{2+} \qquad (4)$$

These radicals can react with each other and with unsaturated groups to form bonds between side-chains and effect cure of the resin.

Scheme 1 also shows how decomposition of hydroperoxides can lead to chain scission. Falla, in a study of the autoxidation of methyl linoleate [4], concluded that most of the unsaturated chains underwent scission during polymerisation, while Muizebelt *et al.* [5],



*Scheme 1* Oxidation of linoleate chains to give hydroperoxides and $\beta$-scission of these intermediates.

working on ethyl linoleate, found that 20–30% of the chains were cleaved over a few months. Typically this produces an aldehyde such as hexanal [7–9] but a wide range of products have been reported.

Scission products of drying oils and of related materials have been extensively studied, particularly in the context of how they affect the flavour and aroma of cooking oils (see for example [10, 11]). Because of this emphasis, very little has been published relating to autoxidation to carbon dioxide. An exception is the early work by Loury and Forney [12, 13] which will be discussed below.

## 2. Experimental

### 2.1. Materials

All the measurements reported here were carried out on paints formulated from Sobral P470. This is a long oil (60% fatty acid content) soya alkyd with acid value of 13 mg KOH/g, supplied by Scott Bader (for an explanation of alkyd resin terminology, see for example [3]).

Most of the films studied were pigmented with rutile $TiO_2$ pigments. These included both coated and uncoated rutile, prepared by both sulphate and chloride routes [14], which were selected to give a range of photocatalytic activity. The pigments were dispersed in a solution of the resin in white spirit by ballmilling for 16 hours in glass jars with glass ballotini. The dispersions were let down to give a pigment volume concentration in the dried paint of 15%, at which stage mixed cobalt (Nuosyn Cobalt 10)/zirconium (Nuosyn Zircon 18) driers were added. The standard level of driers corresponded to 0.13% w/w Co and 1.34% Zr on dried resin.

The gases used to purge the cell were standard BOC cylinder products.

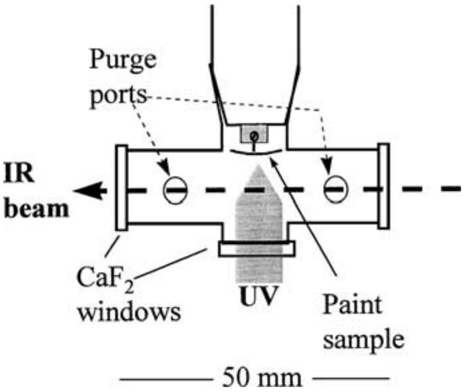


*Figure 1* Plan view of the photochemical infrared cell used for *in situ* measurements of paint film oxidation.

### 2.2. The sample cell

The equipment used was essentially the same as that described previously [1, 2]. Paint films were applied to one surface of metal substrate discs, ca. 10 mm in diameter with an axial mounting pin, by dip coating. The films were allowed to dry in air for at least a week, with light excluded. Variations in drying times and conditions are detailed below. Film thicknesses were estimated by weighing the substrate before and after coating. The discs were secured by a screw to a bayonet mount attached to a B19 ground-glass stopper. This was introduced into the IR cell shown in Fig. 1, using Apiezon T vacuum grease to seal the joint. The cell had two purge ports, each with a greased vacuum tap: it was shown that the vacuum grease did not produce $CO_2$ with oxygen under the experimental conditions used (although it can do under UV irradiation) and that, with reasonable care, the cell was gas-tight to $CO_2$ and to water vapour. The total enclosed volume was 13.9 $cm^3$. This cell volume corresponds to 0.6 mmole $O_2$. A typical fatty acid content of the dried paint film was 0.017 mmole: thus there was a large excess of oxygen.

Calcium fluoride windows were used for the IR beam and to allow irradiation of the paint film by UV. The UV source was a 150 W Xenon arc lamp with an Oriel AM1.5D solar filter to remove radiation of wavelength below 300 nm, simulating the spectral distribution of sunlight, and a 100 mm water filter to remove IR thus minimising heating of the sample. The temperature of the sample pin was shown to vary by $\leq 2°C$ during an experiment. The beam was directed at the sample through a flexible liquid-light-guide which also helped filter out short wavelength UV.

### 2.3. Procedure

After assembly, the cell was normally purged with moist oxygen for one hour to give a $CO_2$-free atmosphere at controlled humidity. The oxygen was bubbled through deionised water which had previously been sparged for 30 minutes to remove dissolved $CO_2$. (Experiments were also carried out after purging with nitrogen and a 20/80 v/v oxygen/nitrogen mixture as described below). The cell was then mounted in the sample compartment of an FTIR spectrometer (Bio-Rad FTS-60A with a liquid-nitrogen-cooled MCT detector) and allowed to equilibrate overnight ($16.5 \pm 0.5$ h) before measurement. The spectrometer chamber was purged

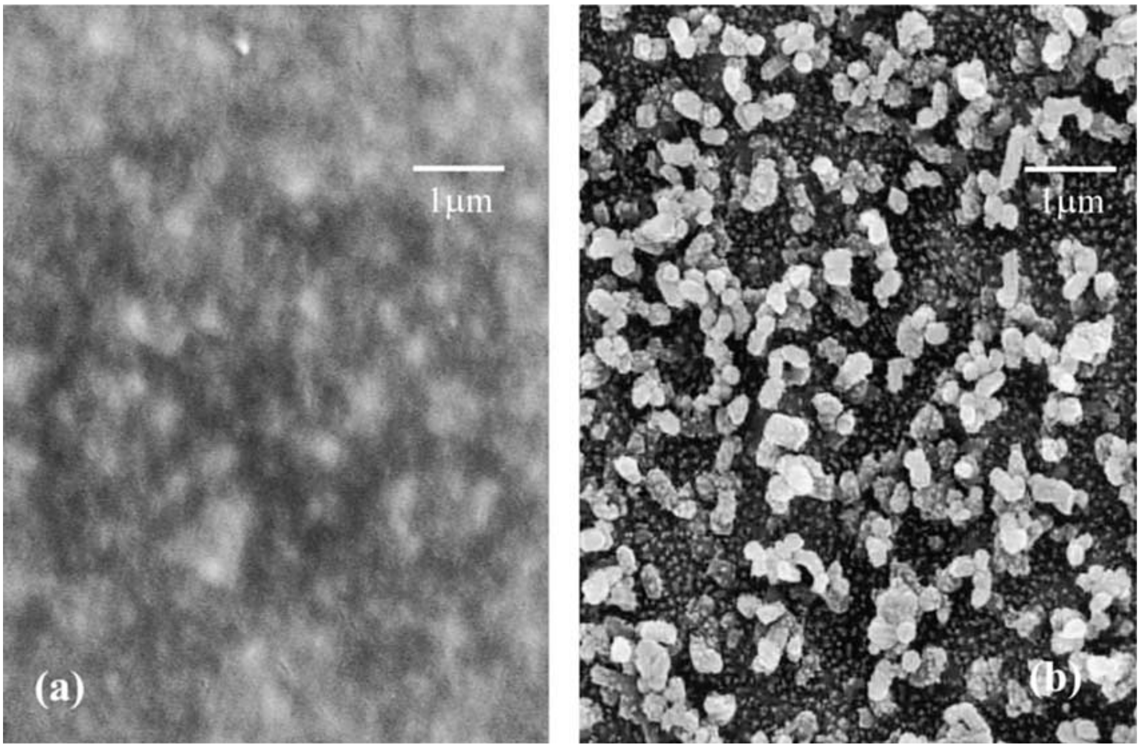


*Figure 2* Scanning electron micrographs of an alkyd film pigmented with $TiO_2$, a) before etching; b) after etching for 40 s with excited oxygen.

with dry nitrogen gas for at least an hour. After this time it was shown that $CO_2$ levels outside the cell were insignificant: much longer purge times were needed to achieve stable $H_2O$ signals and for measurements of water absorbance the $N_2$ purge was extended overnight. When this was done, results indicated relative humidities within the cell of 85–95% [1].

A single-beam reference spectrum was first recorded in the dark and then absorbance spectra were collected over a period of 60 min. before UV exposure commenced. All spectra were an average of 100 co-added scans at 4 $cm^{-1}$ resolution. Peak heights in the reference spectrum were used to estimate initial absorbances from $CO_2$ and $H_2O$ in the cell. In UV exposure experiments, the light pipe was then connected to the source and further absorbance spectra recorded, typically over 3 hours. Finally, spectra were recorded after the lamp was switched off to show whether changes continued and whether there was any leakage from the cell.

## 2.4. Etching

Paint films were surface etched on their metal disc substrates by exposure to RF plasma-excited oxygen in a BioRad barrel etcher operating at 0.1 mbar $O_2$. Examination of etched, pigmented alkyd films by scanning electron microscopy showed that etching for 30 seconds was sufficient to remove clear resin from the surface and to expose a pigment-rich layer. Micrographs in Fig. 2 show the unetched surface and the effect of etching for 40 seconds.

## 3. Results

Changes in $CO_2$ concentration were followed by measuring the height of the IR absorbance peak at 2360 $cm^{-1}$. It is calculated that, in the cell used, an absorbance of $10^{-4}$ corresponds to 0.02 $\mu$g $CO_2$. A typical weight of polymer in the paint film was ca. 8 mg. Thus, if it is assumed that $CO_2$ was produced by oxidation of $(CH_2)$ groups, an overnight increase in absorbance of $200 \times 10^{-4}$, typical of a film dried naturally for one month, would correspond to oxidation of 0.02% by weight of the polymer. A reasonable estimate of 2% over 3 months is consistent with Muizebelt's assertion that $\sim$25% of the chains in ethyl linoleate were cleaved over a few months [5].

For acrylic paints examined by the same technique, there was no evolution of $CO_2$ in the dark [1, 2]. Surprisingly, this was not so for alkyds. Fig. 3 shows how the $CO_2$ peak developed in the dark overnight, during UV irradiation and again in the dark after irradiation. The dark evolution indicates thermal oxidation of the alkyd resin taking place at room temperature. For films dried in air at room temperature the rates of evolution in the dark were less than, but of the same order as rates from photodegradation.

## 3.1. Effect of drying time

The IR absorbance from $CO_2$ evolved overnight in the dark was estimated from the initial single-beam spectrum. Results in Fig. 4 show that the amount produced decreased with the age of the paint film. Similarly, there was a decrease in the rate of $CO_2$ evolution during the 60 minutes before UV exposure. The decrease in $CO_2$ evolution continued for over a month at room temperature but the rate of evolution was still significant after 45 days.

## 3.2. Effect of driers

The level of catalytic driers in an alkyd paint has a significant effect on cure rate. For paint films dried at room temperature for four weeks, doubling the loading of catalytic driers reduced the absorbance from $CO_2$ given off overnight from 200 to $164 \times 10^{-4}$.

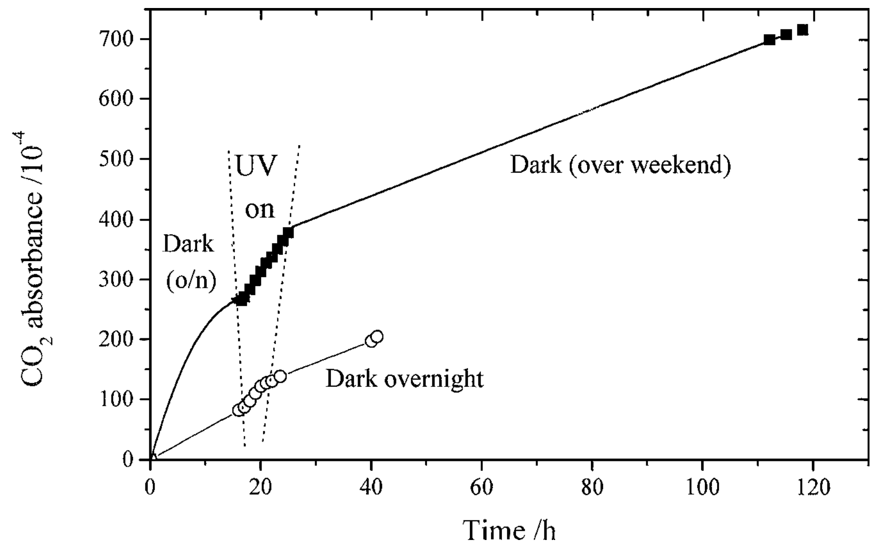


*Figure 3* Growth of the $CO_2$ peak in the dark and under UV irradiation for two alkyd paint films (of different age).

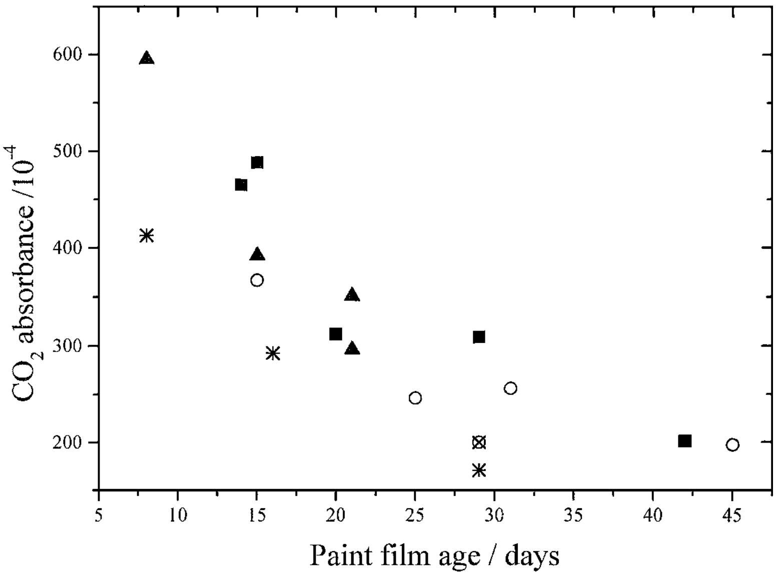


*Figure 4* Dependence of the overnight, dark evolution of $CO_2$ on the paint film drying time at room temperature: (*) unpigmented alkyd; other symbols, pigmented with various uncoated $TiO_2$ pigments.

### 3.3. Effect of cure temperature

The rate of decrease in the rate of $CO_2$ evolution with increasing paint film age was accelerated by ageing at higher temperatures. Table I shows results for one paint, pigmented with $TiO_2$. The rate of evolution was substantially reduced by ageing in air at 60–65°C. Similar reductions were observed for unpigmented films.

TABLE I The effect of oven ageing on $CO_2$ evolution from pigmented alkyd films

| Total drying time (days) | Oven ageing | | $CO_2$ absorbance/$10^{-4}$ | |
|---|---|---|---|---|
| | Days | °C | Overnight[a] | Rate/h[b] |
| 14 | 0 | | 465 | 23 |
| 15 | 0 | | 488 | 21 |
| 15 | 5 | 60 | 141 | 6 |
| 22 | 5 | 60 | 122 | 9 |
| 16 | 1 | 65 | 184 | 8 |
| 20 | 4 | 65 | 81 | 3 |

[a] IR absorbance 16–17 h after purging the cell with wet $O_2$.
[b] The rate of increase in absorbance at the end of this period.

### 3.4. Effect of film thickness

The dip-coating technique gives variable film thickness depending on the paint viscosity and on drainage time. With care, dried-film thickness could be controlled between 80 and 90 $\mu$m and unless shown otherwise results are for films in this range.

To show the effect of film thickness, a wider selection was made. The results shown in Fig. 5 are for paint films which had been oven-aged at 60°C. They show that the amount of $CO_2$ produced in the cell overnight increased with film thickness over the range examined. Thus, the more alkyd resin in the sample, the more $CO_2$ was evolved.

### 3.5. Effect of surface etching

The air interface of a pigmented alkyd paint film is depleted in pigment [15]. The so-called "clear layer" is only about 0.5 $\mu$m thick and is lost during weathering of the paint film before the onset of chalking. To show what effect this surface layer has on oxidation to $CO_2$ and, it was hoped, to simulate weathered paints, films

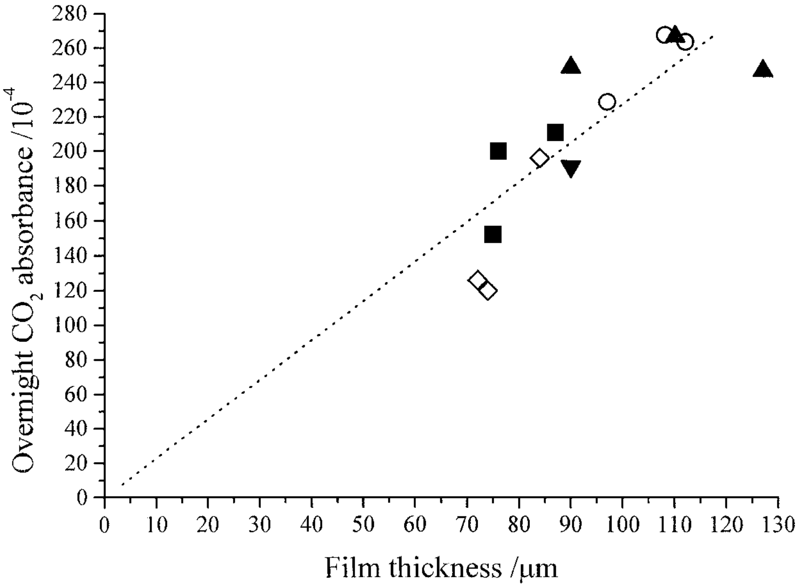


*Figure 5* Dependence of the overnight, dark evolution of $CO_2$ on the paint film thickness for films of various ages but all oven-aged in air for 5 days at 60°C. The films were pigmented with different commercial, coated $TiO_2$ pigments distinguished by the symbols.

were surface etched with activated oxygen as described above. This transformed the glossy surface to matt. A few days were allowed for unstable species produced in the etching process to decay before films were examined in the FTIR cell.

The etching process had no obvious effect on the evolution of $CO_2$. For example one paint, pigmented with an uncoated $TiO_2$ pigment and dried for about 4 weeks (including 5 days at 60°C), gave average absorbance from overnight $CO_2$ of $107 \times 10^{-4}$ for zero etch; 111 for 40 s etch and 108 for 60 s etch.

### 3.6. Effect of oxygen concentration

It was convenient to use cylinder oxygen as a $CO_2$-free oxidising medium but it could be argued that this would accelerate the reactions taking place. The effect of reducing the oxygen partial pressure was therefore investigated, first by purging with a 20/80 v/v $O_2/N_2$ mixture and then by purging with $N_2$ alone. Both gases were bubbled through water. Results are given in Table II for pigmented alkyd films which had been aged at 60°C for 5 days after drying.

There was no difference in the rate of $CO_2$ evolution between pure oxygen and the oxygen/nitrogen mixture. Rather more surprisingly, there was also no difference after purging with nitrogen for an hour. After a longer nitrogen purge, in which the cell was purged for an hour and then the paint sample was left under nitrogen for three days before being purged again for an hour, there was a marked reduction in $CO_2$ evolution but the reaction was still observed.

TABLE II The effect of purge gas on $CO_2$ evolution from a pigmented alkyd film

| | | $CO_2$ absorbance/$10^{-4}$ | |
|---|---|---|---|
| Purge gas | Purge time (h) | Overnight | Rate/h |
| $O_2$ | 1 | 115 | 4 |
| 20/80 $O_2/N_2$ | 1 | 114 | 4 |
| $N_2$ | 1 | 115 | 4 |
| $N_2$ | 2×1 with intervening 3 days under $N_2$ | 57 | 1 |
| $O_2$ | 1: empty cell | 50 | 0 |

### 3.7. Effect of $TiO_2$ pigment

There were no obvious differences between different samples of $TiO_2$. There was insufficient evidence from this work to show a clear effect of pigmentation with $TiO_2$. In Fig. 4, unpigmented alkyd films appeared to give lower levels of $CO_2$ than pigmented films of similar age. The unpigmented films were slightly thinner than the pigmented ones but contained approximately the same amount of resin phase.

### 3.8. Effect of alkyd film ageing on photodegradation

The changes occurring during ageing of the alkyd films are accompanied by increased resistance to photodegradation as measured by evolution of $CO_2$ under UV irradiation. Fig. 6 shows how the rate of photo-oxidation to $CO_2$ for a pigmented alkyd decreased with drying time and with oven ageing. The changes in rate under UV were more than could be accounted for by the decrease in dark rate but paralleled this decrease.

## 4. Discussion

It has been shown that autoxidation of alkyd paint films in the dark produces $CO_2$. Although production of $CO_2$ by thin layers of linoleic acid has been reported [12, 13], we are not aware of similar results for practical alkyd paints. The sensitivity of the technique used here has allowed us to monitor evolution of $CO_2$ over several months and to show that the rate of the reaction decreases with the age of the film over this time scale. Further reductions in rate are observed after oven-ageing at 60–65°C. This is interpreted as an acceleration in

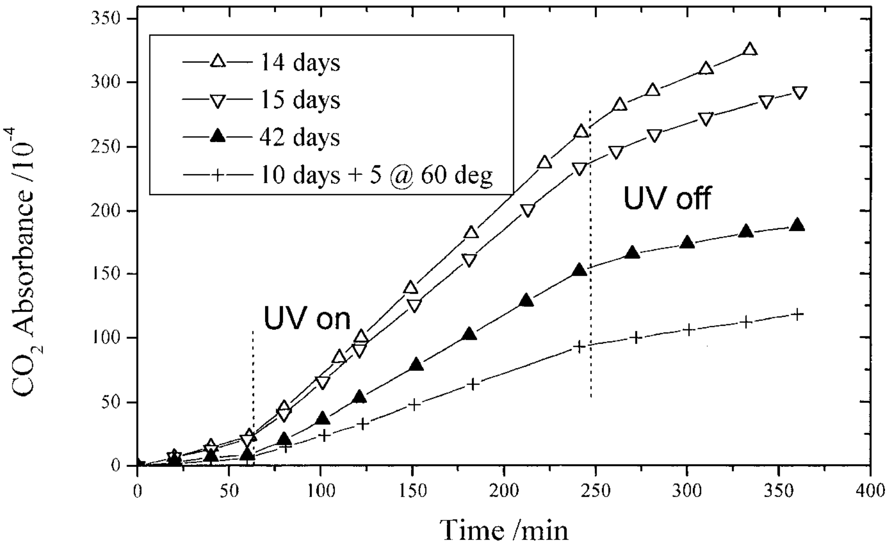


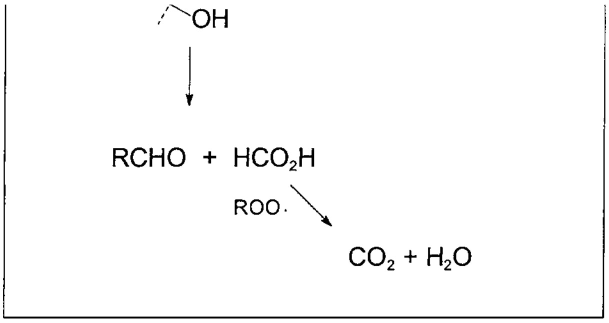
*Figure 6* The effect of ageing time and temperature on $CO_2$ evolution through photodegradation: paint pigmented with uncoated $TiO_2$.

the ageing process: increasing the concentration of catalytic driers in the paint appears to have a similar effect. The difference between unpigmented films and those containing $TiO_2$ pigments was small. This suggests that any effect, for example, of adsorption of the driers on the pigment is small.

To explain the formation of $CO_2$, we look to the oxidation processes occurring during cure of alkyd films. The formation of hydroperoxides, as shown in Scheme 1, is well documented. Experiments on drying oils have shown an induction period followed by a sharp increase in peroxide value then a slow decay [16]. The hydroperoxides break down to initiate further free-radical reactions that lead to cross-linking of the polymer chains and also to chain scission. Key degradation products are alkanals, particularly hexanal, which are responsible for the characteristic odour of drying alkyd paints. For commercial alkyd paints, evolution of hexanal peaked and fell away to very low levels within 4–5 days [9]. Formation of hydroperoxides and other oxidation processes are accelerated by the presence of driers [17].

Several mechanisms for the formation of $CO_2$ in the oxidation process have been suggested, usually only as side reactions associated with minor products [10]. Loury and Forney, however, in a study of the autoxidation of linoleic acid in thin films, found $CO_2$ and $H_2O$ as significant products [12, 13]. They also found formic acid and formic esters among the volatile products and proposed the route to $CO_2$ shown in Scheme 2. In this, alkanal intermediates undergo scission, again by a free-radical process, to form $HCO_2H$ which is oxidised *in situ*, possibly by peroxide radicals.

In some studies the lack of emphasis given to $CO_2$ may simply have been a consequence of the difficulties in detecting it: flame ionisation detectors, for example, would not show $CO_2$ as peaks eluted in gas chromatography. Similarly, alkanals, formic acid and other possible volatile products have not been detected in this work: the small sample size and relatively low extinction coefficients mitigate against their being observed. However, the presence of low concentrations cannot be ruled out. The presence of strong water peaks is a further complication as they could obscure IR absorption by other species. Experiments were carried out at high humidity (estimated at 85–95% RH from water absorbance [1]). Under these conditions there is an equilibrium between water adsorbed on the cell walls and in the atmosphere: this equilibrium is disturbed by small changes in temperature. Significant increases in water peak heights were observed for a temperature increase of 1°C making it impossible to follow evolution of $H_2O$ as a coproduct of $CO_2$ in the current apparatus.



*Scheme 2* Oxidation of alkanals to formic acid and $CO_2$ (after M Loury and M Forney [12, 13]).

Thus there is no direct evidence from this work to support the mechanism shown in Scheme 2. Nonetheless, it remains a plausible explanation of $CO_2$ formation and of how it decreases as residual unsaturation, indirectly the source of the alkanals, is consumed in the oxidation process.

The continued observation of $CO_2$ evolution after purging with nitrogen suggests that oxygen dissolved in the polymer film is very slow to escape. An alternative explanation is that $CO_2$ is formed indirectly, e.g. by secondary reactions of formic acid, possibly with chemically bound oxygen in the form of peroxides and hydroperoxides.

Overall, the oxidative processes occuring in alkyd paints are slow. Uptake of oxygen by alkyds continues for months [6] while film hardness increases over a similar timescale [5]. The timescale for $CO_2$ evolution reported here is consistent with these observations and it is proposed that the technique offers a way of following the ageing process.

The same technique could be used to study oxidative degradation of, say food oils or cosmetic preparations.

The long timescale of the changes is significant for studies of the environmental stability of alkyd paint films, particularly of photodegradation. The results presented here show that during the first months of exposure films are still undergoing slow changes through cure and scission reactions. Moreover, it has been demonstrated that these changes are accompanied by increased resistance to photodegradation.

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