A study of some artificially weathered paints by laser Raman spectroscopy

Charles M. Jenden
DQA/TS, MOD(PE), Materials Centre, Royal Arsenal East, Woolwich, London SE18 6TD, UK

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Laser Raman spectroscopy has been used to monitor artificial weathering of alkyd and silicone modified alkyd varnishes. Preliminary weathering data are also reported for these binders after pigmentation with rutile titanium dioxide. The Raman technique has been used for the first time to yield semi-quantitative structural data which are sensitive to chemical changes even during the initial stages of weathering. Data reported show the improved weather resistance of silicone modified coatings compared to alkyds, which appears to be related to the large dissociation energy of silicon–oxygen bonds. Mechanisms are postulated to account for spectroscopic observations which imply crosslinking, chain scission and hydrolysis reactions. Photo-oxidation by the formation and decomposition of hydroperoxy groups is also reported during the weathering of both varnishes. The Raman spectra provide evidence of binder erosion which is in part due to evolution of volatile materials. A self-stabilization mechanism is proposed to account for the initial rapid evolution of aliphatic hydrocarbons, which gradually slows down after continued exposure. The Raman data obtained from the titanium dioxide pigmented paints are discussed in relation to the photostability of titanium dioxide which appears to be consistent with a photocatalytic oxidation cycle.

(Keywords: Raman spectroscopy; paint; weathering; alkyd; silicone–alkyd; varnish)

INTRODUCTION

An understanding of the photochemical degradation mechanisms of paints is important, for it is the nature and rate at which these reactions take place that largely determine their service life. Once these photochemical mechanisms have been established then it may be possible to control or manipulate the degradation of a surface coating by modifying its formulation.

In the past, the most common methods of examining weathered paints have utilized physical techniques such as weight loss, gloss factor, or average height of roughness irregularities (*AHRI*). Although valuable, these data do not give any information about the chemistry of paint degradation. Previously, chemical methods of analysis have largely been neglected due to the general insolubility of cured paint films. However, nuclear magnetic resonance (n.m.r.) spectroscopy provides some useful data if the paint is first saponified[1,2], but a more direct form of analysis is required. Infra-red spectroscopy, employing ATR, pyrolysis or mulling techniques, has also been used, but the spectra obtained are generally poor and the results often unreliable[3].

This paper describes how laser Raman spectroscopy has been used for the first time as a non-destructive tool to follow chemical changes in cured paint media after artificial weathering. A study has been made of alkyd and silicone modified alkyd varnishes and preliminary data regarding the effects of titanium dioxide pigments on these binders during weathering are reported along with postulated photochemical degradation mechanisms to account for these observations.

EXPERIMENTAL

Samples of commercially available linseed oil/pentaerythritol/*o*-phthalate based alkyd resin and silicone modified alkyd resin were cured on aluminium panels. Samples of each binder were also pigmented with rutile titanium dioxide (20% PVC) and cured in a similar manner. The thickness of each coating was approximately 25 μm.

The coated panels were artificially weathered in a Xenotest 1200 Weatherometer with exposure times varying between 56 h and 956 h. The weathered panels were then presented to a Spex Ramalog 4 laser Raman spectrometer employing a 180° viewing platform, and were irradiated with an argon ion laser (supplied by Coherent Radiation Ltd., Cambridge, UK) operating at 488 nm and 200 mW power. Raman scattering was detected in the photon counting mode with a cooled RCA model C31034 photomultiplier detector. The double monochromator was scanned at 0.5 $\mathrm{cm^{-1}\,s^{-1}}$ with slits set at 10 $\mathrm{cm^{-1}}$ resolution and spectra were recorded with a 10 s time constant. Prior to this, samples were left in the laser beam for one hour to quench any fluorescence scattering.

RESULTS AND DISCUSSION

Before discussion of the degradation of the surface coatings in detail, consideration must be given to the photochemical effects, if any, that laser radiation may have on the paint during the analysis. After 8 h irradiation at 488 nm and 200 mW laser power, which is considerably longer than the typical analysis time, no sample de-

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gradation was observed. This is consistent with the absorption spectra of alkyd and silicone modified alkyd binders reported by Hughes[4], which show little absorption at long wavelengths.

Alkyd varnish

The laser Raman spectra of the artificially weathered alkyd binder after various periods of exposure are shown in *Figure 1*. The spectra reflect that the alkyd is based on a polyester formed from the condensation of linseed oil, pentaerythritol and *ortho*-phthalic anhydride starting materials. The Raman spectrum of the cured binder (0 h weathering) is dominated by the 'linseed oil' type bands at 2920 and 2855 cm^{-1} due to aliphatic CH stretching vibrations. Further bands at 1640, 1450, 1300 and 850 cm^{-1} are also characteristic of the 'linseed' portion of the polymer network and are assigned to C=C stretching, CH_2 deformations, long chain CH_2 twist and rock and C–C skeletal vibrations respectively. The presence of the band at 1640 cm^{-1} shows that even after curing some unsaturation still remains in the varnish. Strong aromatic ring signals at 1597 and 1578 cm^{-1} and the aromatic CH stretching peak at 3070 cm^{-1} along with the *ortho*-substituted aromatic band at 1040 cm^{-1} are indicative of the *ortho*-phthalate part of the coating. The prominent feature of 1725 cm^{-1} is due to the ester carbonyl which with other ester bands at 1085, 1155 and 1260 cm^{-1} confirms the polyester nature of the binder. Identification of the polyol type by Raman spectroscopy is difficult, but bands observed at 1395, 1217 and 945 cm^{-1} are peculiar to the pentaerythritol based alkyd and are not present in glycerol based alkyds[5].

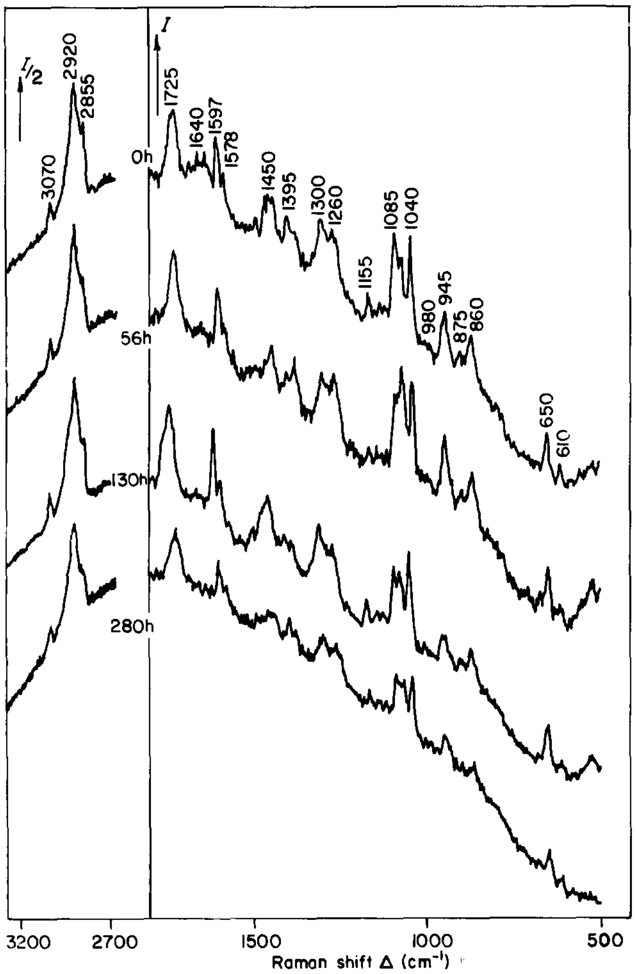
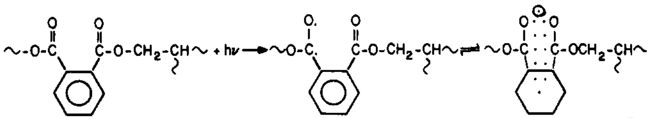


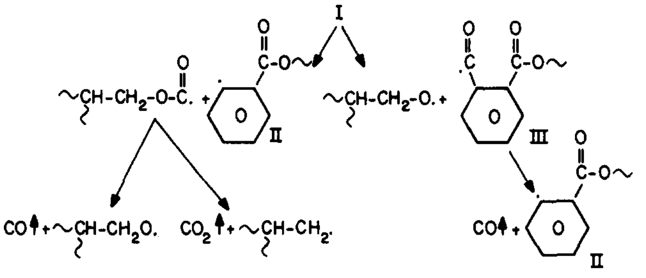
Figure 1 Raman spectra of an alkyd varnish after artificial weathering

The Raman spectra show a marked decrease in signal-to-noise ratio after artificial weathering. This observation is a consequence of binder erosion taking place during weathering resulting in diminished Raman scattering. Sullivan[6] has reported that drying oils exposed to u.v. radiation experience weight loss and that erosion takes place due to evolution of volatile material after chain scission and molecular rearrangement. The Raman spectra suggest that a similar mechanism is responsible for erosion of the alkyd coating. If volatile material rich in methylene groups, for example, is released during weathering of a paint, then this will be apparent in the Raman spectrum as a decrease in intensity of the aliphatic CH_2 band at 2920 cm^{-1} relative to, say, the aromatic CH stretching band at 3070 cm^{-1}. The latter band is chosen as a suitable reference as there is little evidence for volatile aromatic material being released, particularly during the early stages of weathering. *Figure 2* confirms the release of aliphatic volatiles due to the decrease of this ratio with increased exposure. The Raman spectra also give some indication of the kinetics of this degradation reaction. The release of aliphatic material is initially fast and then slows down. A similar profile is reported in *Figure 9* for the silicone modified alkyd. Both sets of data may be interpreted in terms of a self-stabilization mechanism similar to that postulated by Lucki *et al.*[7] for the photolysis of poly(propylene 1,2-phthalate). Light is primarily absorbed through ester carbonyl groups as shown below:

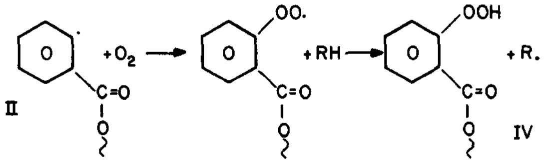


I

Hyperconjugation may take place to form I which may then undergo Norrish type I chain scission to give CO and CO_2 gases, which have been observed previously[6].



As the weathering was carried out in air photooxidation takes place to produce hydroperoxides; for example **II** behaves as follows:



where R is the polymer network.

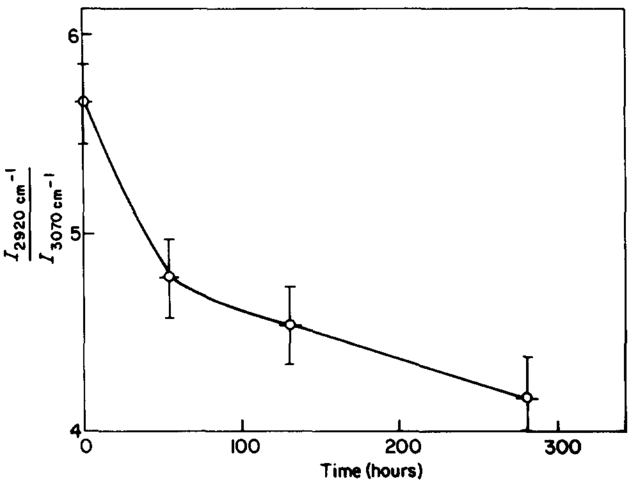
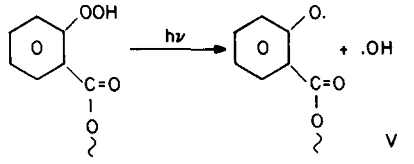


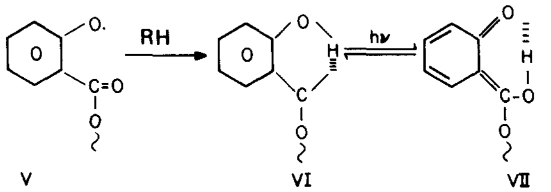
Figure 2 Relative Raman intensities *versus* time of weathering for an alkyd binder

The hydroperoxide **IV** may then decompose in light to give **V**.

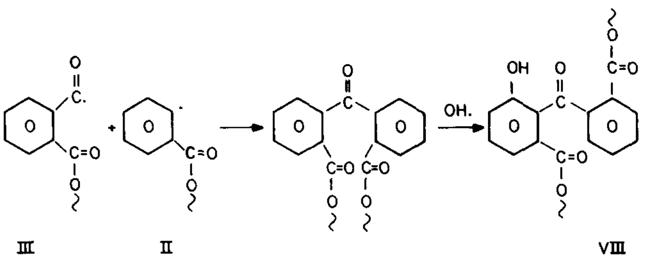


The self-stabilization mechanism described by Lucki *et al.*[7] may then be due to reactions (1) or (2) below or a combination of both.

(1) Formation of hydroxyester end groups.

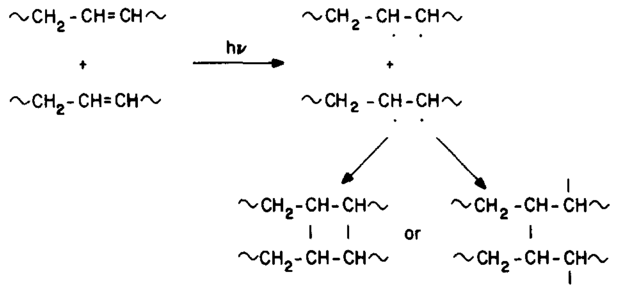


(2) Formation of ortho-benzophenone structures from **II** and **III**.



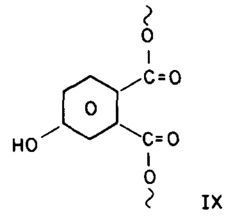
The stabilization mechanism of the *ortho*-hydroxyester, **VI**, is based on absorbing light whilst converting **VI** to **VII** and the photostabilization of the *ortho*-hydroxybenzophenone structure **VIII** is well known[8,9]. It is considered that mechanisms of this type are responsible skeletal band at 945 cm^{-1} relative to the aromatic band at concentration of radical species that can cause chain scission leading to the release of volatile hydrocarbons.

The unweathered alkyd binder spectrum shows some Raman scattering at 1640 cm^{-1} due to C=C stretching. This band noticeably decreases during the early stages of weathering indicating that further crosslinking reactions have taken place after the initial curing period, and completely disappears after 130 h. Raman spectra are particularly sensitive to these reactions as the C=C group scatters strongly. They are initiated by u.v. radiation and are generalized below:



Crosslinking may also take place between carbonyl and carbon–carbon double bond groups yielding C–O–C crosslinks. *Figure 3* lends further evidence for these reactions. It shows that the Raman intensity ratio of the skeletal band at 945 cm^{-1} relative to the aromatic band at 1597 cm^{-1}, increases after 56 h weathering due to formation of crosslinks and then, as chain scission reactions become more abundant, slowly decreases.

Hydroperoxy and hydroxy radicals play an important role in the degradation of paint binders. It has already been shown that the former is involved in the self-stabilization mechanism. Lucki *et al.*[7] have shown that poly(propylene 1,2-phthalate) reacts with hydroxyl radicals converting the phthalate to a monohydroxyphthalate, **IX**.



The alkyd binder degrades in a similar way. This is manifested by a decrease in the relative intensity ratio of the *ortho*-substituted aromatic band at 1040 cm^{-1} to the aromatic ring mode at 1597 cm^{-1} as shown in *Figure 4*, for the newly formed tri-substituted compound **IX** will not have a Raman band at 1040 cm^{-1}. Previous infra-red studies have also described a similar decrease in phthalate concentration[6].

Hydroperoxy groups are also produced at the site of methyl groups adjacent to C=C bonds[6] to produce the weathered product CH(OOH)–CH=CH– or by the

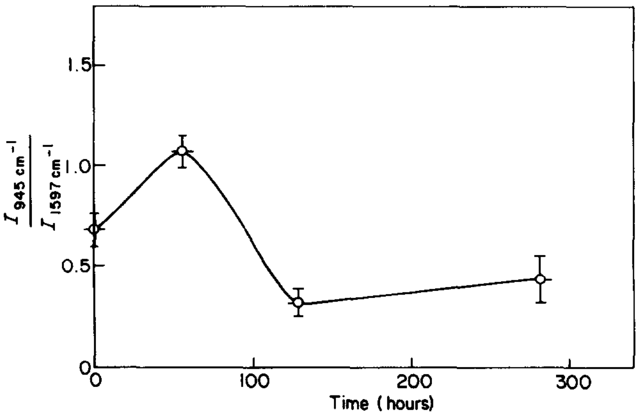


Figure 3 Relative Raman intensities *versus* time of weathering for an alkyd binder

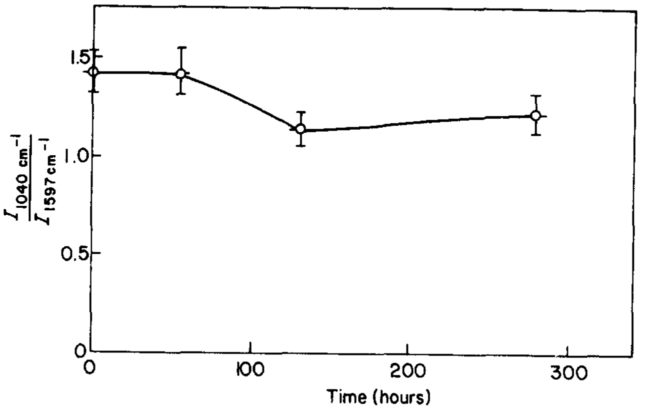
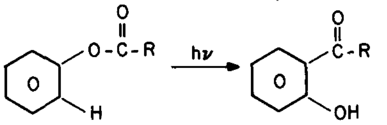


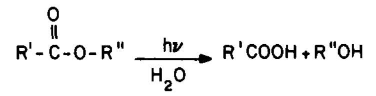
Figure 4 Relative Raman intensities *versus* time of weathering for an alkyd binder

formation of aromatic compounds similar to IV above. They decompose during weathering to give –OH and C=O groups. O'Neill[10] has reported an increase in infra-red intensity of the carbonyl band relative to CH_2 groups for weathered alkyd paint. The equivalent Raman signal shows a similar slight increase and confirmation is derived from *Figures 5* and *6*. They depict the Raman intensity ratios of the aliphatic and aromatic ester type C–O vibrations respectively relative to the carbonyl band at 1725 cm^{-1}. The small decrease observed is interpreted as formation of non-ester carbonyl species on the surface of the alkyd binder from the decomposition of the hydroperoxy groups. Unfortunately the large half-width of the Raman carbonyl band makes it impossible to distinguish between these species. A further, although less important, contribution to the general trend of these data may arise from a Fries rearrangement in a similar way to the degradation of poly(ethylene terephthalate)[11], which,



although not breaking the backbone of the polymer, may leave it more susceptible to oxidation as shown above.

Hydrolysis reactions are evident from the Raman spectra, published infra-red and gas evolution data[6]. These are of the general type



$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R'' \xrightarrow[H_2O]{h\nu} R'COOH + R''OH$$

Formic acid and formaldehyde have been detected from the gas evolution studies and are consistent with an increase in the OH stretching band at 3450 cm^{-1} in the infra-red spectrum on weathering. The resulting products arise from chain scission reactions which are indicated by the Raman data in *Figure 3*.

Silicone-modified alkyd varnish

The chemistry of the silicone-modified binder will differ from that of the simple alkyd due to the inclusion of Si–C and Si–O bonds in the polymer backbone. Many of the reaction mechanisms reported for the alkyd also contribute to the degradation of the silicone-modified binder. This section highlights significant differences in weathering due to the silicone modifying groups. The Raman spectra obtained from the weathered varnish are depicted in *Figure 7*. Many of the bands present in the spectrum of the alkyd varnish are common to the silicone-modified

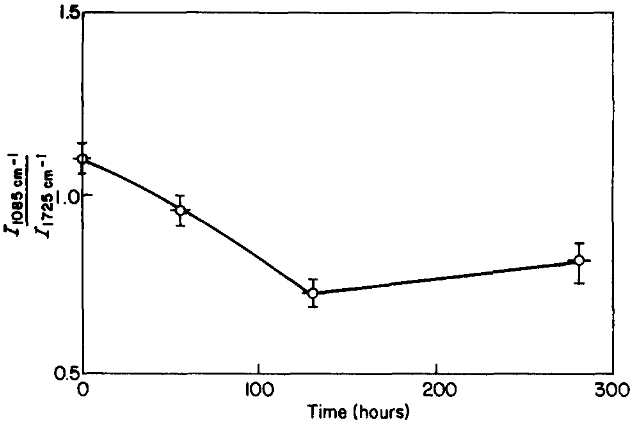


Figure 5 Relative Raman intensities *versus* time of weathering for an alkyd binder

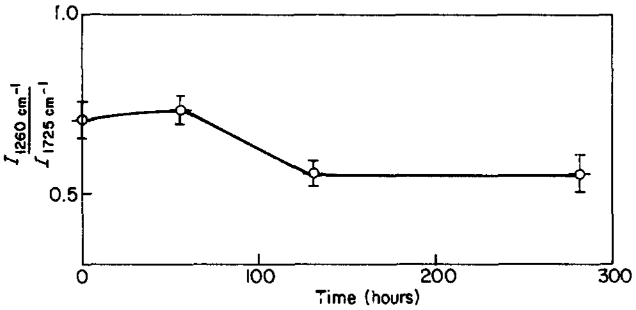


Figure 6 Relative Raman intensities *versus* time of weathering for an alkyd binder

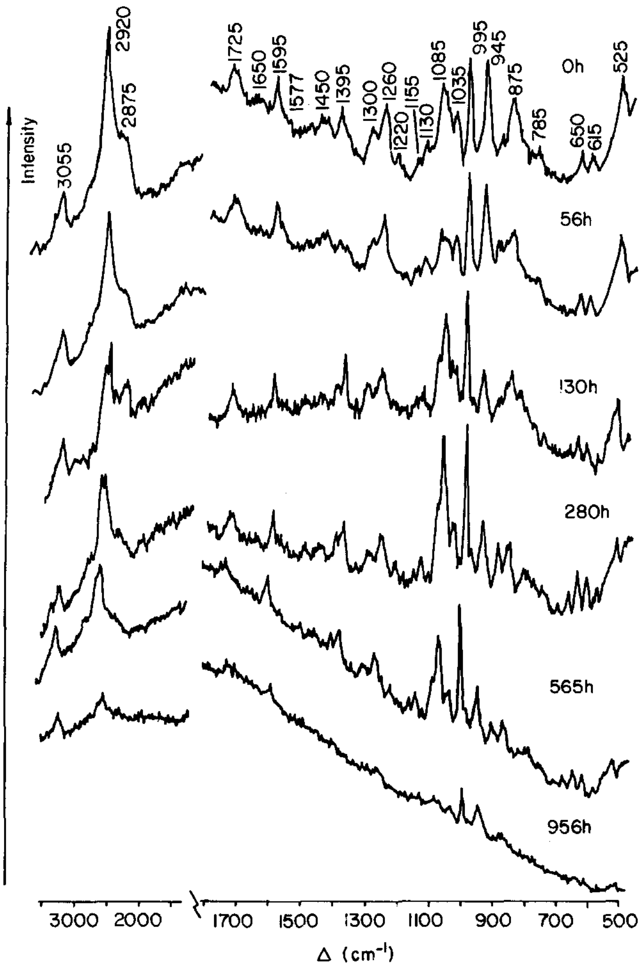


Figure 7 Raman spectra of a silicone alkyd varnish after artificial weathering. Δ is the Raman shift

varnish along with the new peak at 995 cm^{-1} due to the presence of the Si–O–CH$_2$ group and an increase in the relative intensity of the band at 1260 cm^{-1} due to the overlap of Si–C vibrations with alkyd ester bands. The introduction of silicon atoms into the polymer produces a further spectral difference as it lowers the frequency of the aromatic CH stretching band to 3055 cm^{-1}.

During weathering, the signal to noise (S/N) ratio of the Raman spectra decreases quite dramatically, confirming binder erosion in a similar manner to the alkyd varnish. However, for the silicone-modified varnish, Raman spectra could be recorded after 956 h artificial weathering, albeit of poor S/N ratio, whilst no Raman spectrum could be obtained from the alkyd binder after 565 h. This observation suggests that the silicone-modified binder is more resistant to weathering than its alkyd counterpart, for presumably after 565 h weathering there was insufficient alkyd coating left on the aluminium panel to obtain a spectrum.

This improvement in weather resistance is considered to be imparted to the silicone-modified alkyd by the Si–O bonds rather than the Si–C bonds as the former have a larger bond dissociation energy.

The inherent strength of the Si–O bond is reflected in the Raman spectra for even after 956 h weathering the 995 cm^{-1} band still dominates the spectrum. *Figure 8*, which shows the relative intensity ratio of this band to the aromatic vibration at 1595 cm^{-1}, lends support to these observations. The ratio increases after 280 h weathering, which suggests that there is some loss of aromatic components after this long period of exposure which, although less volatile than the aliphatic material, may be washed away by the spray cycle in the Xenotest weatherometer. The subsequent decrease in this ratio after 956 h indicates some breakdown of the strong Si–O bonds too, but there are large errors associated with this measurement due to the poor S/N ratio of the Raman spectrum; however, they do confirm the stability of this bond relative to others in the polymer.

Like the alkyd varnish, the spectra in *Figure 7* reveal the loss of volatile products rich in methylene groups. *Figures 9* and *10* show the ratio of the CH$_2$ stretching band at 2920 cm^{-1} relative to the aromatic band at 1595 cm^{-1} and the Si–O–CH$_2$ band at 995 cm^{-1} respectively. Both display an initial large loss of aliphatic material followed by a period of less activity. These volatiles are considered to arise from similar chain scission reactions to those described for the alkyd and lend further support to the self-stabilization mechanism proposed above.

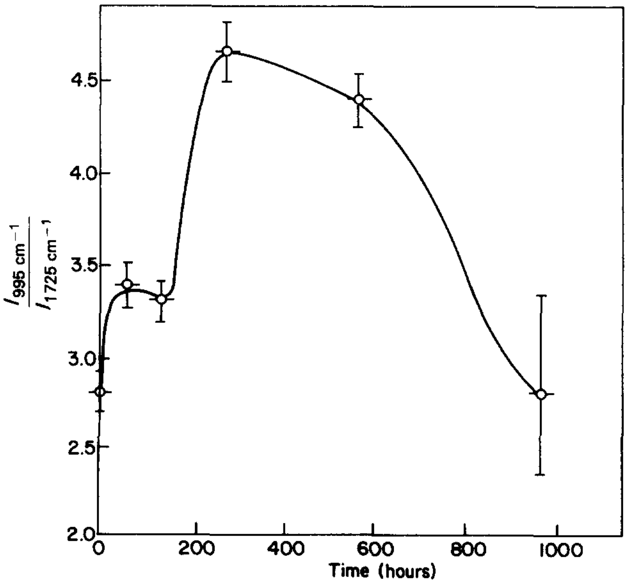


Figure 8 Relative Raman intensities *versus* time of weathering for a silicone modified alkyd binder

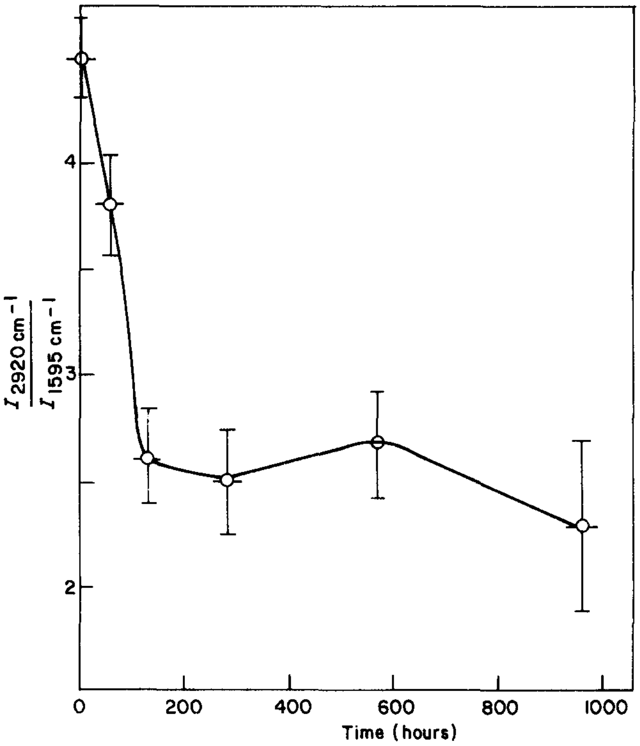


Figure 9 Relative Raman intensities *versus* time of weathering for a silicone modified alkyd binder

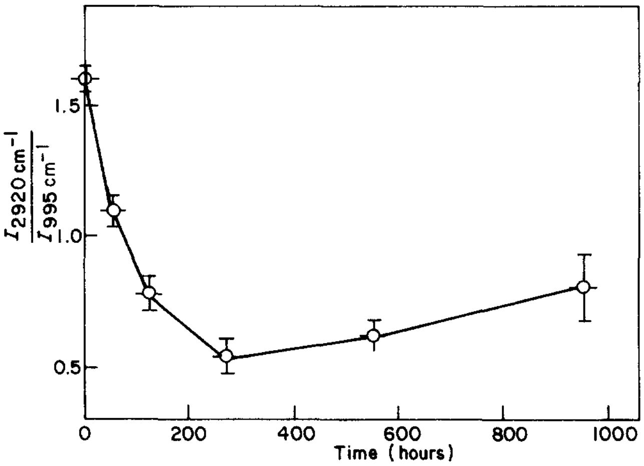


Figure 10 Relative Raman intensities *versus* time of weathering for a silicone modified alkyd binder

The peak at 1650 cm^{-1} in the Raman spectrum of the unweathered silicone-modified varnish is due to C=C stretching in the binder polymer, indicating that in this varnish too some unsaturation remains even after the initial curing period. However after 56 h weathering crosslinking reactions have reduced the concentration of these groups below the Raman detection limit. The skeletal band at 875 cm^{-1} in *Figure 7* gives a further insight into the photochemistry of the silicone binder. This band shows a gradual broadening up to 130 h weathering, but after 280 h splits into two sharper peaks which persist up to 980 h. This observation is considered to be due to continued crosslinking reactions up to 130 h, after which chain scission reactions dominate the weathering of the varnish, for the two sharp peaks observed after 280 h are similar to those found in the spectra of short chain aliphatic compounds.

Hydroperoxy radicals again play an important part in the degradation of silicone-modified binders. The data in *Figure 11* depict the intensity ratio of the aromatic ester C–O stretching band at 1260 cm^{-1} relative to the carbonyl band at 1725 cm^{-1}. It decreases on weathering, suggesting the formation of carbonyl groups on the surface of the varnish due to degradation of hydroperoxy groups. However evidence for this conclusion is not as clear cut as in the alkyd case as there is some overlap of the ester peak with the 1250 cm^{-1} Si–C vibration.

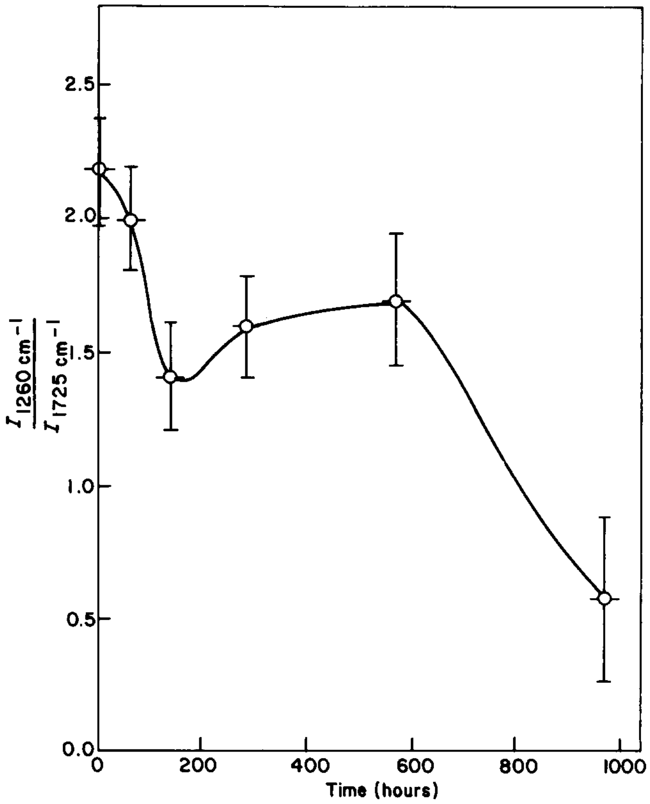


Figure 11 Relative Raman intensities *versus* time of weathering for a silicone modified alkyd binder

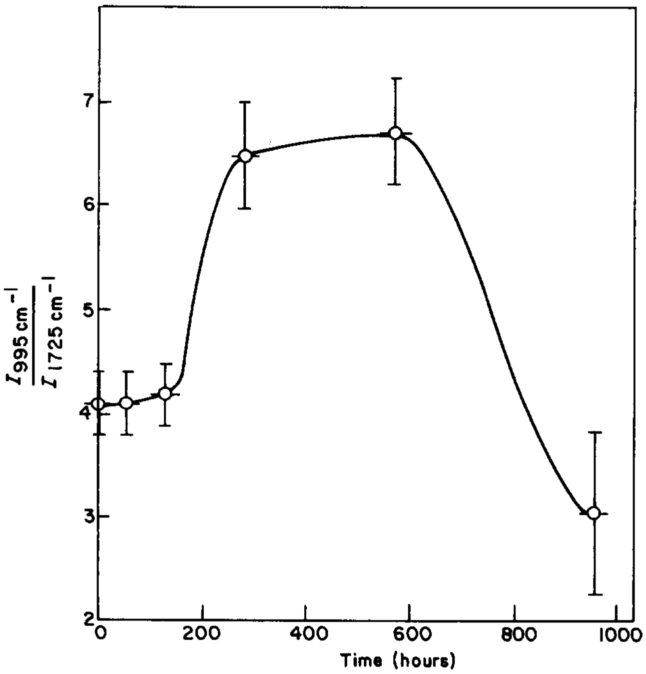


Figure 12 Relative Raman intensities *versus* time of weathering for a silicone modified alkyd binder

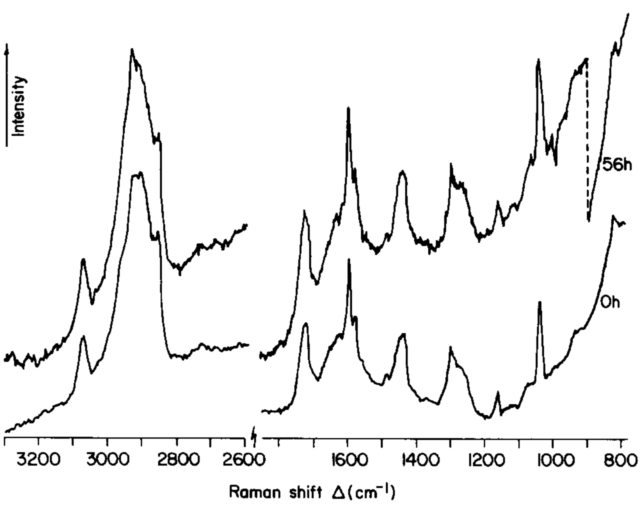


Figure 13 Raman spectra of a white alkyd paint

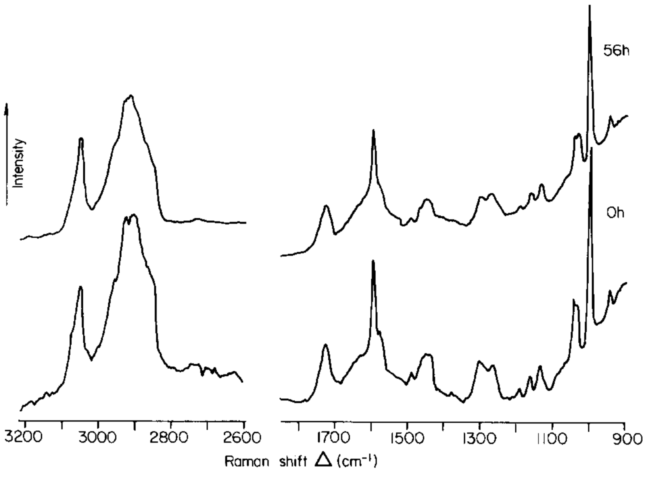


Figure 14 Raman spectra of a white silicone modified alkyd paint

Hydrolysis of the silicone binder is also observed by the rise in the ratio of the relative intensities of the $SiOCH_2$ band (995 cm^{-1}) to the C=O bands (1725 cm^{-1}) up to 565 h as depicted by *Figure 12.*

Titanium dioxide pigmented alkyd and silicone-modified alkyd paints

The laser Raman spectra of both pigmented paints are presented in *Figures 13* and *14*. Each Figure shows the spectrum before and after 56 h artificial weathering. The very intense Raman scattering from the rutile titanium dioxide pigment appears at 141, 236, 442 and 607 cm^{-1}. These Raman bands are not affected by the weathering process and they show no sign of crystallographic changes, which would be readily seen in the Raman spectra[12]. Therefore these peaks are omitted from the spectra for the sake of clarity. The remaining peaks above 700 cm^{-1} are some thirty times less intense than the pigment bands and are attributed to the binder. They are very similar to their unpigmented analogues and share the same assignments.

Differences in the Raman spectra of the varnish and pigmented paint, both before and after weathering, shed light on changes in the curing mechanism and photodegradation mechanisms due to the inclusion of the titanium dioxide pigment. The effect of pigmentation on the curing of the alkyd binder is seen as a decrease in intensity of bands at 1085, 1305 and 2700 cm^{-1}. The consequence of these observations is not yet fully understood but may reflect differing degrees of crosslinking within each paint system. A similar situation is also observed for the silicone-modified paints.

The Raman spectra highlight the enhancement or suppression of photochemical reactions due to the presence of pigment particles. The ratio of the peak intensities of the CH_2 stretching mode at 2920 cm^{-1} to the aromatic peak at 3070 cm^{-1} decreased substantially for the alkyd varnish after 56 h artificial weathering, whilst this ratio for the white alkyd paint indicated only a small decrease. This observation highlights the well known stabilizing influence of titanium dioxide by absorbing much of the u.v. radiation and therefore minimising binder breakdown due to chain scission reactions and subsequent release of volatile material rich in methylene groups. Weight loss data reported by Hughes[4] are consistent with these Raman data and show that the bulk mass of an alkyd paint film decreases on weathering as pigment loading increases up to the critical pigment volume concentration. This stabilizing influence of the pigment was also observed in the silicone-modified alkyds studied.

Like the varnishes, hydroperoxy and hydroxyl radicals are prominent in the degradation of the titanium dioxide pigmented paints, for they are not only produced during the photochemical degradation of the binder polymer as described above, but also during the photocatalytic oxidation cycle (POC) of the titanium dioxide pigment as reported by Völz *et al.*[13]. It was also shown that the hydroperoxy groups formed on the binder polymer decompose photolytically to give –OH and C=O groups. The increased concentration of these radicals in the white alkyd paint is underlined by the spectra after weathering. The intensity ratio of the band at 1725 cm^{-1} due to C=O vibrations relative to the aromatic signal at 1597 cm^{-1} is larger for the white coating after weathering than for the varnish, implying that there are a larger number of carbonyl groups formed on the surface of the former due to increased hydroperoxy radical activity. These Raman data are consistent therefore with the POC mechanism. The white silicone-modified alkyd paint however behaves differently. After 56 h weathering, this same ratio shows a small decrease, suggesting that hydroperoxy radicals play a less important part in the photochemistry than they do in the white alkyd paint, providing evidence for its improved weather resistance. Another reaction, probably hydrolysis, would appear to dominate the degradation at this early stage in the weathering process. A small decrease was also observed in this intensity ratio for the silicone-modified alkyd varnish, showing that the effects of pigmentation on this binder are not so apparent after 56 h as they were for the corresponding alkyd coating.

The intensities of the pigment peaks relative to all the binder peaks, for both paint systems, increased on weathering, indicating erosion of the binder. These observations are also consistent with the POC model, which postulates that binder erosion in the vicinity of a pigment particle may be greater than in the binder alone for a photocatalytically active pigment such as titanium dioxide. If the binder is sufficiently flexible this will result in an increased PVC. However the Raman data, although consistent with the model, do not verify its authenticity unless they are compared with data from anatase titanium dioxide or a photocatalytically less active pigment such as zinc oxide.

Finally, comparison of *Figures 13* and *14* shows a noticeable decrease in *S/N* ratio for the white alkyd after weathering, which is not as apparent for the silicone-modified paint. This observation suggests that the white silicone-modified coating is more resistant to weathering than the alkyd paint in a similar way to the varnishes.

CONCLUSIONS

Laser Raman spectroscopy has been successfully used for the first time to monitor the photochemical processes that take place during artificial weathering of paints. These new data suggest that the following reactions play an important part in the degradation of alkyd and silicone-modified alkyd varnishes. At first crosslinking takes place at the site of C=C and C=O groups, followed by the dominance of chain scission reactions. Evolution of volatile material rich in methylene groups results from these chain scission reactions. Evidence is also provided for hydrolysis and the formation of carbonyl groups on the surface of these binders due to the photodecomposition of hydroperoxy groups formed during weathering.

The kinetics of photodegradation may be followed by Raman spectroscopy. For example, the rate of evolution of aliphatic volatiles slows down rapidly after the initial stages of weathering, which is explained in terms of a self-stabilization mechanism.

An estimation is made concerning the relative weather-resistance of the alkyd and silicone-modified alkyd varnishes and paints from Raman signal-to-noise considerations. It is concluded that the silicone-modified coatings are more resistant to weathering than their alkyd counterparts due to the large bond dissociation energy of Si–O bonds in the former.

From the preliminary study of the titanium dioxide pigmented paints encouraging results are obtained which highlight the effects of pigmentation on initial curing and subsequent weathering. They show that binder degradation is slower in comparison with the varnish and that the evolution of volatile material rich in methylene groups is reduced when the pigment is introduced into the coating, thereby demonstrating the stabilizing properties of titanium dioxide. Unfortunately however the pigment also possesses photocatalytic properties which lead to binder degradation. This is demonstrated by the white alkyd paint which on weathering exhibits a relative increase in the observed carbonyl concentration compared to the alkyd varnish, which is explained by the increased formation and subsequent decomposition of hydroperoxy groups produced by this photocatalytic activity[13].

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