The analysis of cured paint media and a study of the weathering of alkyd paints by *FT*i.r./PAS

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Fourier transform infra-red/photoacoustic spectroscopy (*FT*i.r./PAS) has been used to characterize alkyd, silicone alkyd, epoxy, acrylic and polyurethane paints. The convenient sampling arrangement of the photoacoustic technique, and the spectral accumulation and subtraction facilities of the *FT*i.r. spectrometer, permit the study of the artificial weathering of alkyd paints. These paints each contained one of a series of white pigments selected to provide different weathering properties. The changes observed included those due to variation in pigment concentration, loss of binder and binder oxidation. The rate of loss of aliphatic binder material was used as a measure of the resistance to weathering.

(Keywords: Fourier transform infra-red/photoacoustic spectroscopy; paint; analysis; weathering)

INTRODUCTION

The type of binder and pigment in a paint critically affect its performance and properties. It is therefore important to have a rapid and easy method of identifying paints, and of assessing the weathering performance or paints formulated with new pigments of binders. There are already a wide range of techniques[1-5]‡ available for the analysis of paints but most of these suffer from some disadvantage. Many of the existing procedures use infra-red spectroscopy[1] with a variety of sampling techniques. The formation of a halide disc is time consuming, limits the spectral range and cannot be applied to pigmented samples which do not transmit infra-red radiation. Samples coated on halide discs cannot be subjected to artificial weathering cycles which include water washing. However, the use of transmission *FT*i.r. to study the cure of varnish on halide discs has been reported[6]. Techniques such as diffuse reflectance (DRIFT) or attenuated total reflectance (ATR)[7] require the sample to have light reflecting properties, and both the quality and intensity of the spectra decrease with the deterioration of the paint surface during weathering. Emission *FT*i.r. spectroscopy[8] has been applied to the study of the weathering of acrylic coatings, and the identity of some of the new carbonyl containing species created on weathering was established. However, emission *FT*i.r. spectroscopy is experimentally difficult.

Laser Raman spectroscopy[9,10] has proved to be a valuable technique for providing both qualitative and quantitative information on paints and paint weathering processes. However, this technique is very time consuming, not applicable to samples which are poor Raman scatterers and often fluorescence causes interference preventing the acquisition of a useful spectrum.

Nuclear magnetic resonance (n.m.r.) spectroscopy[11] is not generally applicable to cured paints although some useful qualitative studies have recently been carried out[12]. Pyrolysis techniques followed by gas chromatography[2] or infra-red spectroscopy are often limited to providing a fingerprint of the paint. Pyrolysis mass spectrometry[3] provides valuable information on the major and minor components of a cured paint but is expensive, time consuming and will generally only provide qualitative information.

In this paper we describe the use of *FT*i.r./photoacoustic spectroscopy (PAS) for the analysis of alkyd, silicone alkyd, epoxy, acrylic and polyurethane paints. Several comprehensive reviews[13,14] of *FT*i.r./PAS are available and so only a brief account of the technique will be provided here. The photoacoustic experiment involves the production of heat, generated by absorption of infra-red radiation by the sample, from a modulating infra-red source. As the sample is contained in a gas tight cell and the frequency of modulation of the source corresponds to the audio region, sound waves are generated in the cell and are detected by a microphone. The interferogram produced from the microphone output in the first instance is converted to a recognizable infra-red spectrum by Fourier transformation. PAS may therefore be regarded as an alternative sampling procedure for infra-red spectroscopy and it is essentially a surface technique.

The *FT*i.r./PAS technique has been found to be qualitative, at least semiquantitative, applicable to most cured paint systems, rapid and capable of yielding information on weathering mechanisms and curing.

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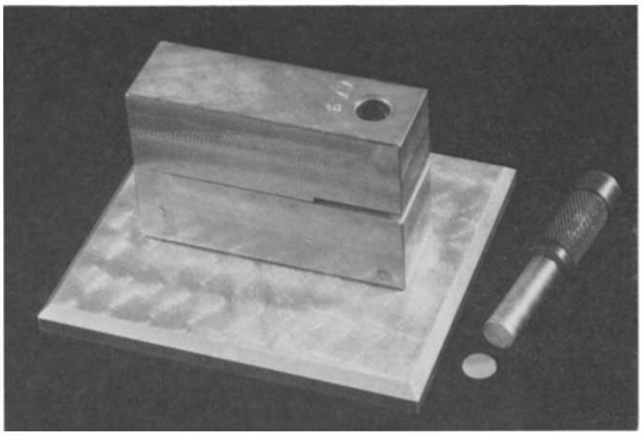

Figure 1 Die and punch used to produce 9 mm discs

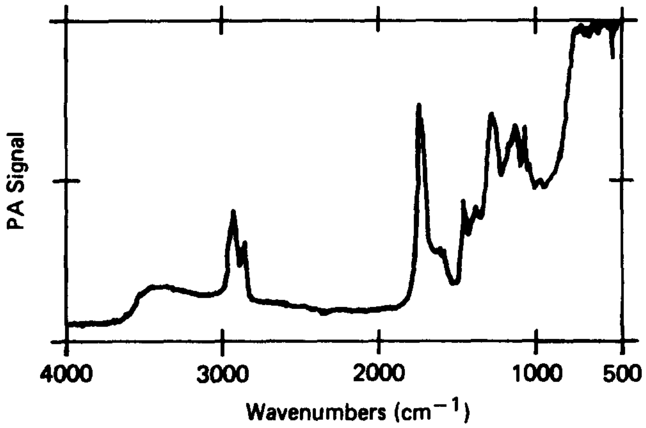

Figure 2 *FT*i.r./PA spectrum of white alkyd paint

EXPERIMENTAL

Samples of cured paint were provided as ~20 μm thick films on polished aluminium. A die (*Figure 1*) was used to punch out 9 mm diameter discs. All samples were examined in this way except for the acrylic paint which was collected from the painted surface with silicon carbide paper. A disc was then punched from the silicon carbide paper in the same manner.

The artificial weathering studies were carried out on a paint consisting of a white pigment and a linseed/pentaerythritol/*o*-phthalate alkyd resin with calcium, lead and cobalt naphthenate driers. The pigments used were anatase titanium dioxide, uncoated rutile titanium dioxide, rutile titanium dioxide coated with alumina and silica, zinc oxide and zirconium dioxide. Artificial weathering was carried out in a QUV Weatherometer, with a cycle of four hours UVA light exposure at 60°C, followed by four hours water condensation at 40°C. The samples were weathered for periods extending up to 24 days.

The infra-red photoacoustic spectra were obtained from a Digilab FTS-15E Fourier transform infra-red spectrometer, with a photoacoustic cell also supplied by Digilab. A spectral resolution of 8 cm^{-1} was used, and the cell volume of 0.2 cm^3 was flushed with helium. Fourier transformation was carried out on interferograms produced from up to 1000 scans of the spectrometer and charcoal was used as reference material. Spectra were drawn by plotting photoacoustic signals against wavenumber. Standard Digilab subtraction routines were used and the difference spectra were plotted with smoothing applied and on a scale of +10 to −10 arbitrary units.

RESULTS AND DISCUSSION

Qualitative analysis of paints

Figures 2–6 show the infra-red photoacoustic spectra of a variety of paints. *Figure 2* shows a spectrum which is characteristic of a cured alkyd paint based on *o*-phthalate and pentaerythritol, and infra-red absorptions from both aliphatic and aromatic components are observed. The spectrum shows ester carbonyl stretching at 1734 cm^{-1}; aromatic and aliphatic C–O stretching at 1273 cm^{-1} and 1134 cm^{-1} respectively; a doublet due to an aromatic ring at 1589 cm^{-1} and 1562 cm^{-1}; an alcohol C–O absorption at 1065 cm^{-1}; CH_2 and CH_3 stretching at 2932 cm^{-1} and 2858 cm^{-1} respectively and a CH_2 bending mode at 1454 cm^{-1}. The presence of titanum dioxide pigment can be seen from the signals at 500–750 cm^{-1}.

The spectrum of a cured silicone modified alkyd paint is shown in *Figure 3*. It is similar to *Figure 2*, but shows the presence of a phenyl silicone modification. This is indicated by an additional peak at 1420 cm^{-1} due to Si–phenyl vibrations, enhancement of the peaks at 1134 cm^{-1} and 1065 cm^{-1}, due to Si–phenyl and Si–O stretching respectively, and an additional peak at 737 cm^{-1} indicating a mono-substituted aromatic ring.

Figure 4 shows the infra-red photoacoustic spectrum of an epoxy paint derived from Bisphenol A and

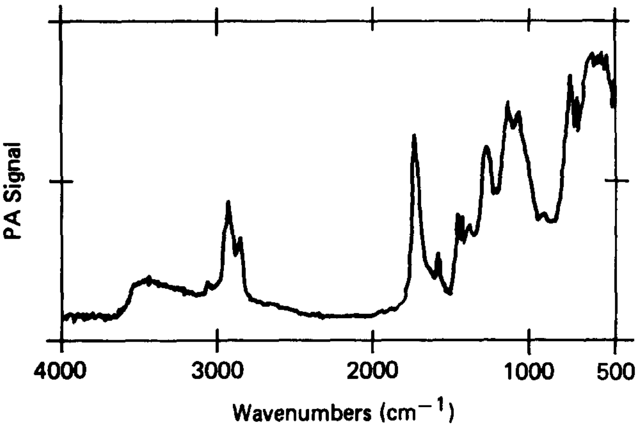

Figure 3 *FT*i.r./PA spectrum of silicone modified white alkyd paint

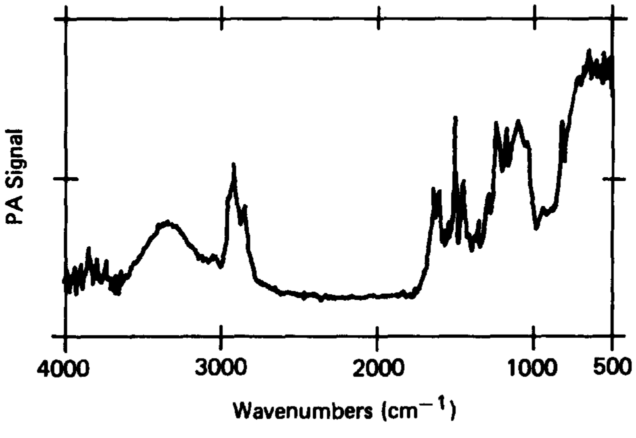

Figure 4 *FT*i.r./PA spectrum of white epoxy paint

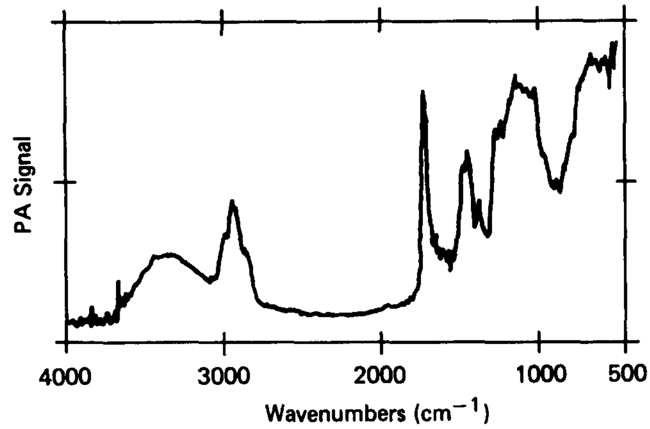

Figure 5 *FT*i.r./PA spectrum of white acrylic paint collected on silicon carbide paper

epichlorohydrin. Characteristic absorptions due to CH_3 stretching, CH_2 stretching and CH_2 bending occur at 2859 cm^{-1}, 2932 cm^{-1} and 1458 cm^{-1} respectively. A *gem* dimethyl group is indicated by the doublet at 1354 cm^{-1} and 1381 cm^{-1}. Aliphatic C–O stretching occurs at 1038 cm^{-1}, and vibrations due to a 1,4-disubstituted aromatic ring are seen at 825 cm^{-1}. The presence of signals at 3348 cm^{-1} due to free phenolic –OH and 921 cm^{-1} due to epoxy groups indicate that the paint was not fully crosslinked and no evidence of the presence of a curing agent could be found in the spectrum.

The spectrum of an acrylic paint sample collected on silicon carbide paper is shown in *Figure 5*, and the quality of the spectrum is comparable to that obtained from the paint films on aluminium. Since both the alkyd and the acrylic paints contain polyester binders their spectra are similar but sufficiently different to provide useful fingerprints to distinguish between the two paints.

The spectrum shown in *Figure 6* is that of a typical polyurethane paint. There are characteristic absorptions at 1732 cm^{-1} and 1690 cm^{-1} (amide I band) due to ester and amide carbonyl stretchings respectively; at 1258 cm^{-1} and 1065 cm^{-1} due to urethane and alcohol C–O stretching respectively, and at 2855 cm^{-1} and 2928 cm^{-1} due to CH_3 and CH_2 stretching. An additional absorption due to the amide occurs at 1535 cm^{-1} (amide II band).

Paint weathering studies

It is valuable to be able to study the mechanism of weathering and the extent of degradation of a paint for two main reasons. The first is to assess the durability of new paint systems and the second is to provide a means of comparing and correlating natural and artificial weathering.

Figure 7 shows the difference spectrum obtained by subtracting the spectrum of an unweathered alkyd paint, pigmented with uncoated rutile titanium dioxide, from that of the same paint after 24 days artificial weathering. It is possible to observe some of the changes in infra-red absorptions due to the destruction and generation of various chemical groups during weathering. The changes include loss of aliphatic material indicated by a decrease in the CH_3 and $-CH_2-$ absorptions at 2855 cm^{-1} and 2930 cm^{-1} respectively. This is due to chain scission reactions occurring in the binder following radical attack. Small increases in the intensity of the absorptions at around 3500 cm^{-1} and 3000 cm^{-1} may be attributed to the generation of species containing –COOH and –OH. Loss of ester carbonyl and formation of several new carbonyl species may also be noted. These changes are due to hydrolysis and oxidation of the binder including the decomposition of hydroperoxy groups formed on weathering. A loss of titanium dioxide pigment was observed from changes in the signal in the 500–700 cm^{-1} region.

Anatase titanium dioxide

Figure 8 shows the results of subtracting the spectrum of an unweathered alkyd paint pigmented with anatase titanium dioxide from the spectra of the same paint after 3, 10 and 17 days artificial weathering. With this paint system, the photocatalytic oxidation cycle (POC) is the dominant weathering mechanism[15] and contributes more to the binder destruction than direct degradation due to the effects of ultraviolet light[16]. The binder is degraded close to the pigment particles[15] and the difference spectrum shows a slight increase in the signal at 500–700 cm^{-1}, due to the increased pigment concentration. Attack on the binder by radicals generated by the POC results in loss of aliphatic material as indicated by a decrease in signals at 2928 cm^{-1} and 2851 cm^{-1}. Increases in the concentration of carbonyl species at 1775 cm^{-1} and 1624 cm^{-1} are accompanied by a decrease in signals due to the alkyd ester at 1748 cm^{-1} and 1270 cm^{-1}. The new absorption around 1775 cm^{-1} is possibly due to the formation of acid peroxides[17], percarboxylic acids[18] or anhydrides[19]. The large new absorption at 833 cm^{-1} may also contain contributions,

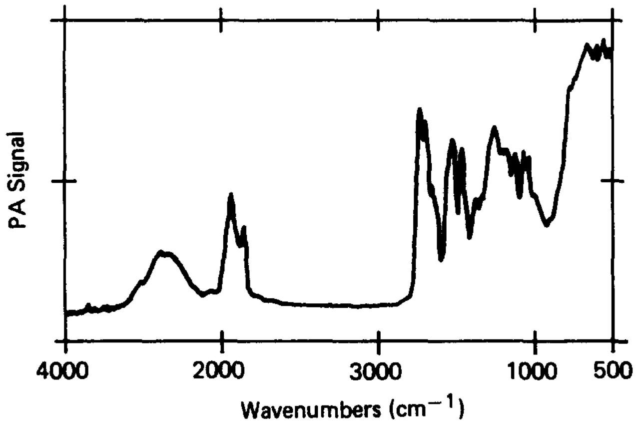

Figure 6 *FT*i.r./PA spectrum of green polyurethane paint

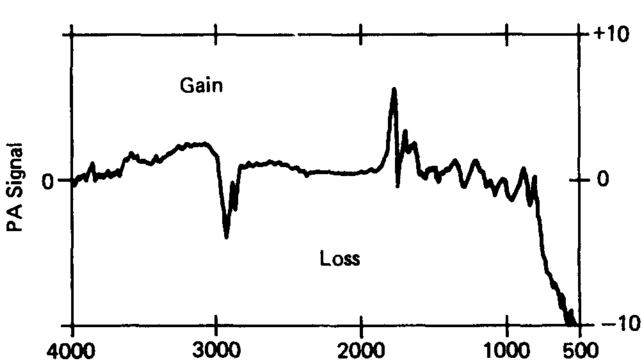

Figure 7 Difference spectrum for alkyd paint, with rutile TiO_2 pigment, obtained by subtracting a spectrum of unweathered paint from a spectrum obtained from a paint after weathering for 24 days

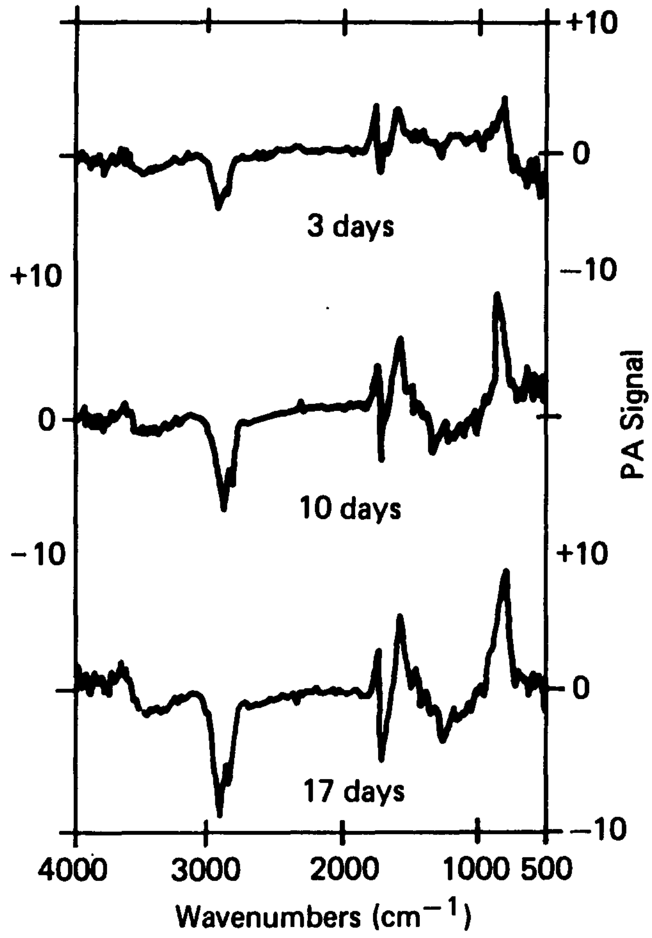

Figure 8 Difference spectra for alkyd paint, with anatase TiO_2 pigment, obtained by subtracting a spectrum of unweathered paint from spectra obtained from a paint weathered for 3, 10 and 17 days

due to –O–O– stretching, from percarboxylic acid and other hydroperoxides[19]. Absorptions at around 830 cm^{-1} have been produced in the infra-red spectra of paints treated with hydrogen peroxide solution[20]. The other new carbonyl absorption centred around 1624 cm^{-1} is a composite signal probably made up of components from carboxylates, aldehydes and ketones generated during weathering[21].

Coated rutile titanium dioxide

Rutile titanium dioxide provides an improved resistance to weathering in alkyd paints especially when, as is the case here, it is coated with silicon and aluminium oxides to reduce photocatalytic activity[22]. A difference spectrum obtained by subtracting the spectrum of unweathered paint from the spectrum of a paint artificially weathered for 24 days is shown in *Figure 9*. This spectrum is much less intense than those obtained from paint pigmented with anatase titanium dioxide, and although similar changes occur on weathering, losses of aliphatic material and ester carbonyl are smaller. In addition there is no evidence of hydroperoxides being generated due to the catalytic activity of the pigment.

Zinc oxide

Figure 10 shows the difference spectrum obtained after subtraction of the spectrum of an unweathered paint, containing zinc oxide pigment, from the spectrum obtained from the paint after it had been artificially weathered for 24 days. Relatively small losses of aliphatic hydrocarbon, as indicated by absorptions at 2928 cm^{-1} and 2851 cm^{-1}, and of ester groups, indicated by absorptions at 1748 cm^{-1} and 1038 cm^{-1}, occur. A new signal at 1600–1650 cm^{-1} may be observed and this is probably due to the formation of zinc carboxylates during weathering[23].

Zirconium dioxide

A considerable loss of aliphatic material, after 24 days artificial weathering, is shown by the difference spectrum in *Figure 11*. Several new absorptions also appear and the

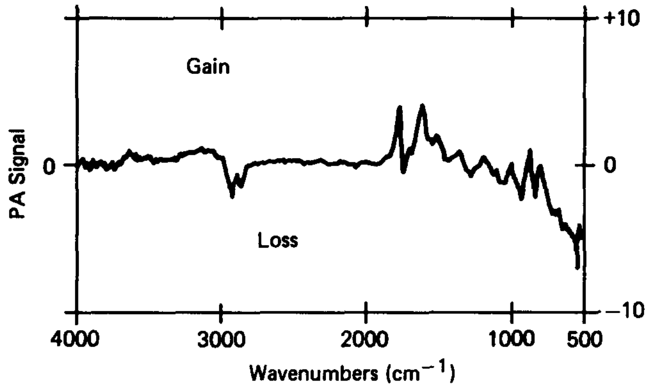

Figure 9 Difference spectrum for alkyd paint, with coated rutile TiO_2 pigment, obtained by subtracting a spectrum of unweathered paint from a spectrum obtained from a paint after weathering for 24 days

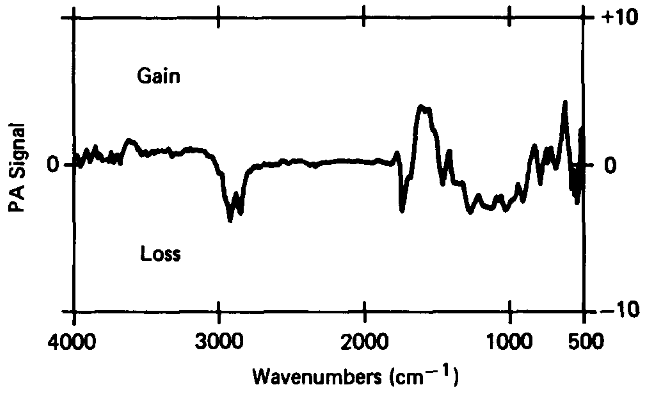

Figure 10 Difference spectrum for alkyd paint, with ZnO pigment, obtained by subtracting a spectrum of unweathered paint from a spectrum obtained from a paint after weathering for 24 days

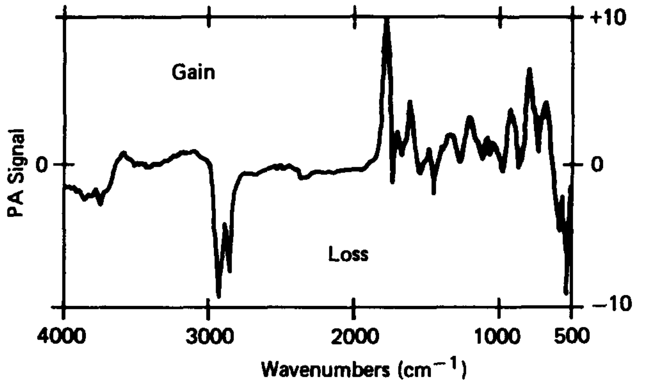

Figure 11 Difference spectrum for alkyd paint, with ZrO_2 pigment, obtained by subtracting a spectrum of unweathered paint from a spectrum obtained from a paint after weathering for 24 days

Table 1 Light reflected at various wavelengths from some pigments incorporated into alkyd paints

Pigment	Wavelength (nm)	% Reflected light
Anatase titanium dioxide	300	6
	350	10
	400	65
	450	79
Coated rutile titanium dioxide	300	7
	350	7
	400	35
	450	79
Zinc oxide	300	7
	350	6
	400	52
	450	66
Zirconium dioxide	300	16
	350	29
	400	50
	450	64

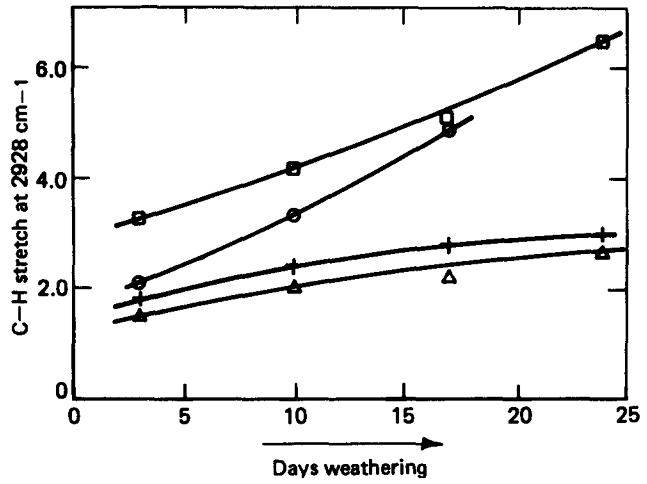

Figure 12 Plot of the intensity of the C–H stretch absorption in the difference spectra, for each of the paint systems, against weathering time: □, ZrO_2 pigment; ○, anatase TiO_2 pigment; +, ZnO pigment; △, coated rutile TiO_2 pigment

strongest of these occur at 1774 cm^{-1}, 1620 cm^{-1}, 1207 cm^{-1}, 800 cm^{-1} and 660 cm^{-1}. These signals indicate the formation of acid peroxides, percarboxylic acids or anhydrides together with the –O–O– containing components also noted in the difference spectrum obtained from the weathering study with anatase titanium dioxide. The complexity of the spectrum in the carbonyl region indicates the generation of numerous carbonyl components such as aldehydes, ketones, acids and metal carboxylates and the signal due to loss of alkyd ester carbonyl is completely obscured by new absorptions.

Comparison of pigment performance

The two main factors influencing the performance of the pigment are its ability to absorb harmful short wavelength radiation and any catalytic effects it may have. *Table 1* shows the proportion of light reflected at various wavelengths from some pigments incorporated into alkyd paints and compared with a barium sulphate reference.

The most useful infra-red absorption in the difference spectra for assessing the total binder degradation is the C–H stretching frequency at 2928 cm^{-1}. *Figure 12* shows the result of plotting the intensity of the C–H stretching absorption in the difference spectra, for each of the paint systems, against weathering time. Comparison of the rate of degradation of the aliphatic portion of the paint binder containing the various pigments shows that the pigments may be ranked as follows, in order of decreasing magnitude of C–H stretching absorption and increasing resistance to weathering: $ZrO_2 <$ anatase $TiO_2 <$ ZnO $<$ coated rutile TiO_2. *Table 1* shows this is approximately the same order as the ability of the pigments to absorb the u.v. radiation, thereby reducing u.v. absorption by the binder. These observations are in good agreement with Raman spectroscopy studies[24] and visual comparisons of naturally and artificially weathered paints containing these pigments.

On the basis of the ability to absorb harmful radiation alone, it might be expected that zinc oxide and anatase titanium dioxide would perform similarly in weathering studies. The fact that anatase titanium dioxide is inferior to zinc oxide has been explained by the former pigment's activity as a photocatalyst[15]. Zirconium dioxide has poor spectral properties that account for its poor weathering resistance. It is unlikely that ZrO_2 undergoes a photocatalytic oxidation cycle similar to TiO_2 since for zirconium the lower oxidation state, essential for the POC, is of minor importance[25]. The difference in photocatalytic activity of the two forms of titanium dioxide is attributed to the higher energy content of the exciton formed in anatase titanium dioxide[15].

CONCLUSIONS

*FT*i.r./PAS is a rapid technique for the classification of the polymeric binder in paints. This technique has advantages in its ease, wide applicability, speed, the fact that the sample is available for further analysis and the ability to sample remotely using silicon carbide paper.

*FT*i.r./PAS has also been used to monitor some of the range of reactions that occur in paints on weathering, and this application of the technique is of great value. The quantitative results obtained in this study have given a comparison of the weathering resistance of alkyd paints containing various white pigments.

It is anticipated that the application of *FT*i.r./PAS in the monitoring of surface reactions will be extended to the study of polymer weathering and curing, and of the natural weathering of paint media.

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