

# Degradation Studies of Plasticized PVC. I. Multiple Internal Reflection Infrared Spectroscopy

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## Synopsis

Multiple internal reflection infrared spectroscopy (MIR) was used to study surface degradation in commercial and laboratory prepared plasticized PVC samples. Samples were subjected to accelerated (UV exposure) and natural weathering. Ultraviolet-exposed samples show peak formation at  $3200\text{ cm}^{-1}$  (OH), and  $1400\text{ cm}^{-1}$  (CH bend), as well as increased absorption at  $1720\text{ cm}^{-1}$  (CO). Outdoor-exposed samples show essentially similar changes, but the variation in peak ratio shows large variations of a random nature; it has been proposed that rainfall has a major influence on surface plasticizer concentration.

## INTRODUCTION

A large number of papers have appeared in the literature on the degradation and stabilization of poly(vinyl chloride). In many of these papers, infrared spectroscopy has been used to study the degradation processes (e.g., Refs. 1-4); however, only a few have appeared on the use of multiple internal reflection infrared spectroscopy (MIR) for this purpose.<sup>5-7</sup>

Plasticized PVC is used extensively for outdoor applications, e.g., tarpaulins and airhourse membranes. Due to the thickness of these coatings and the presence of a woven fabric between them, conventional transmission spectroscopy is not possible, but MIR allows the surface degradation of these materials to be studied.

Pure PVC is not an absorber in the UV region of the spectrum and should exhibit good UV stability. However, during the polymerization process, impurities and irregularities are included in the polymer chains resulting in a lowered thermal and UV stability.<sup>8-11</sup> During subsequent thermal processing, further degradation can occur.<sup>9,12-15</sup> Various compounds are also added to the PVC during processing, such as stabilizers, plasticizers, fillers, pigments, lubricants, etc., and these may have a marked effect on the stability of the resulting mixture; for instance, it has been reported that the presence of DOP lowers the thermal stability of PVC.<sup>2</sup>

During outdoor exposure, various degradative processes occur. Solar UV causes dehydrochlorination of the polymer chain, resulting in the formation of polyene sequences, which may subsequently lead to oxidation and chain scission, or to crosslinking.<sup>16</sup> Plasticizer may exude from the bulk of the mixture, resulting in decreased flexibility; the addition of a suitable filler reduces this surface migration. Water can also be absorbed into PVC,<sup>17,18</sup> the presence of some fillers, e.g.,  $\text{CaCO}_3$ , enhancing this effect. Microbial attack can also occur, leading to surface hardening and loss of flexibility.<sup>19</sup>

Although a great deal is known about choosing PVC formulations for various

applications, most of this knowledge is empirical; in particular, little is understood of the ways in which different components in a system affect the stability of the whole system. By suitable compounding, useful outdoor lifetimes of up to 10 yr are possible, but little is known of the physical and chemical changes that take place over this long time, most work being concentrated on degradation occurring during processing. Accelerated tests are useful as indicators of relative stability, but are not representative of the actual processes occurring during natural weathering.

This paper is concerned with the usefulness of MIR as a technique for studying degradation in PVC-coated fabrics. To this end, commercial coated fabric samples were weathered artificially in UV-exposure apparatus, and by boiling, as well as being weathered naturally. It was also decided to study the effect of plasticizer concentration on stability, and also to deal with a simpler system; so samples of PVC sheet were prepared in the laboratory, these being subjected to artificial UV radiation only.

## METHOD

Samples were subjected to accelerated weathering in a Hanau suntester. A xenon UV source was used, filtered to simulate the solar UV spectrum. The black body temperature of samples was 43°C, and the radiation intensity was approximately 1000 W/m<sup>2</sup> between 300 nm and 830 nm (manufacturers estimate).

Naturally weathered samples were exposed at 45°, on south facing wooden frames, for up to 2 yr.

Coated fabric material was obtained from B.M. Coatings, Ltd., and consisted of white and orange pigmented samples, apart from which the formulation was stated to be identical.

Laboratory samples were prepared from Breon PVC resin mixed with 50% or 100% (w/w) of Bisoflex DOP (di-2-ethylhexylphthalate), both supplied by B.P. Chemicals, Ltd., Sully. Some samples were also stabilized by the addition of 3% (w/w) of Interstab M103, supplied by Akzo Chemie, U.K., Ltd. The ingredients were mixed for 10 min in a rotary mixer to ensure an even dispersion of paste particles. The resulting paste was then spread onto aluminium sheets and heated in an oven at 180°C for 4 min.

Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrometer, equipped with a Wiltech MIR unit. The optical element was a Wilks KRS-5 prism 52 mm × 20 mm × 2 mm, having 45° faces, and giving approximately 25 reflections with an angle of incidence of the beam of 45°. Spectra were recorded at 45° and 60°, giving incident angles at the sample surface of 45° and 51°, respectively, the latter due to refraction at the prism face, since the beam was not entering normal to its surface. The optical element was sandwiched between two sheets of material, and the sample holder screws tightened down evenly in a diagonal sequence. To obtain good reproducible spectra, it is necessary that the same pressure be applied to samples each time, since sample contact with the prism increases with increasing pressure, resulting in a stronger spectrum.<sup>20</sup> The optical element was cleaned before use, and spectra taken of it regularly to ensure no surface contamination was taking place.

The main regions selected for detailed analysis were the  $\nu$ -OH absorption at

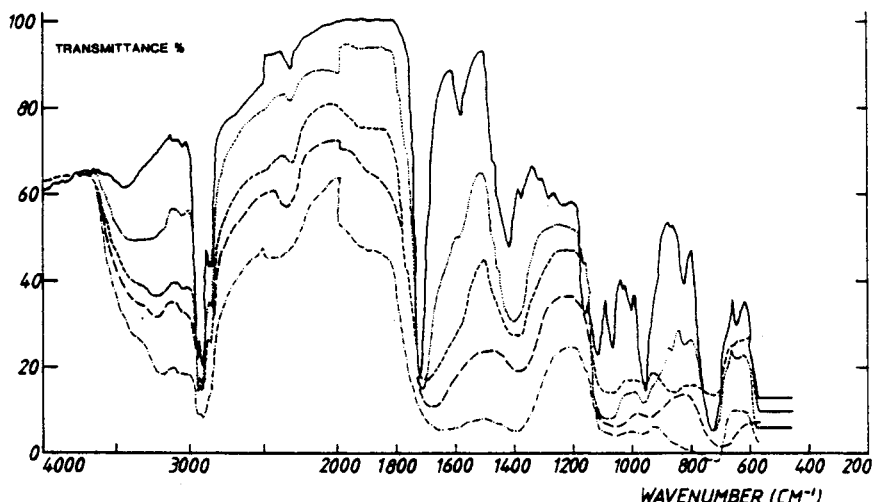


Fig. 1. Comparison of spectra of artificially weathered coated fabric. UV exposure (h): (—) 0; (· · ·) 2198; (---) 3211; (- - -) 4577; (- - -) 6945.

3200 cm<sup>-1</sup>, the  $\nu$ -C = O absorption at 1720 cm<sup>-1</sup>, the  $\nu$ -C = C absorption at 1640 cm<sup>-1</sup>, and the  $\delta$ -CH<sub>2</sub> absorption at 1400 cm<sup>-1</sup>.

Normalized optical density ratios were obtained by determining the absorption of each peak measured from a constructed baseline and dividing by the absorption of the  $\nu$ -CH peak at 2900 cm<sup>-1</sup>. Graphs of the results were plotted, and computer smoothing programs used to obtain best fit curves to the data points.

While perfectly adequate data were obtained using an angle of incidence of 45°, it was found that prolonged UV exposure (more than 6,000 h) resulted in these spectra being of insufficient detail to yield reproducible results. Spectra performed at 60° produced good data to 10,000-h UV exposure; all results pro-

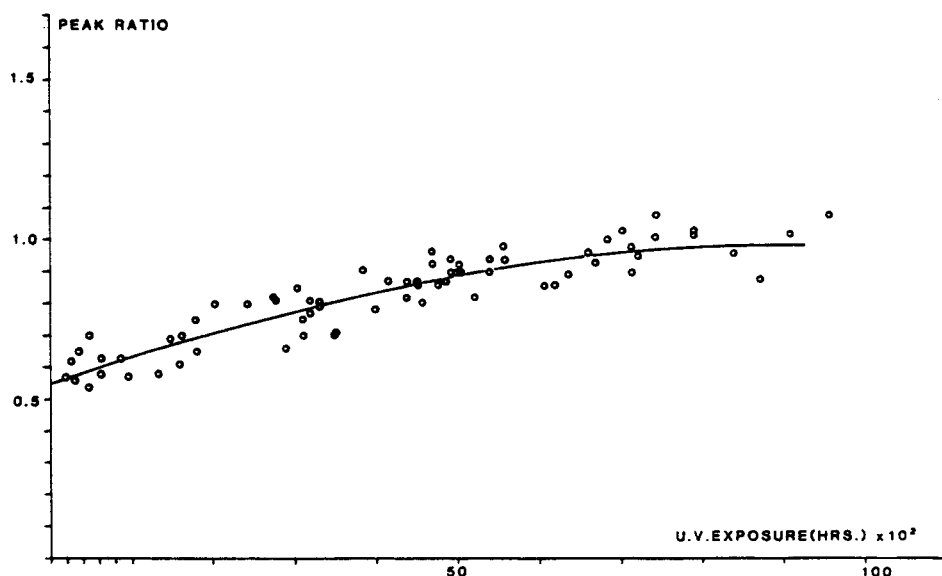


Fig. 2. Variation at 3200 cm<sup>-1</sup> (OH) for UV-exposed coated fabric.

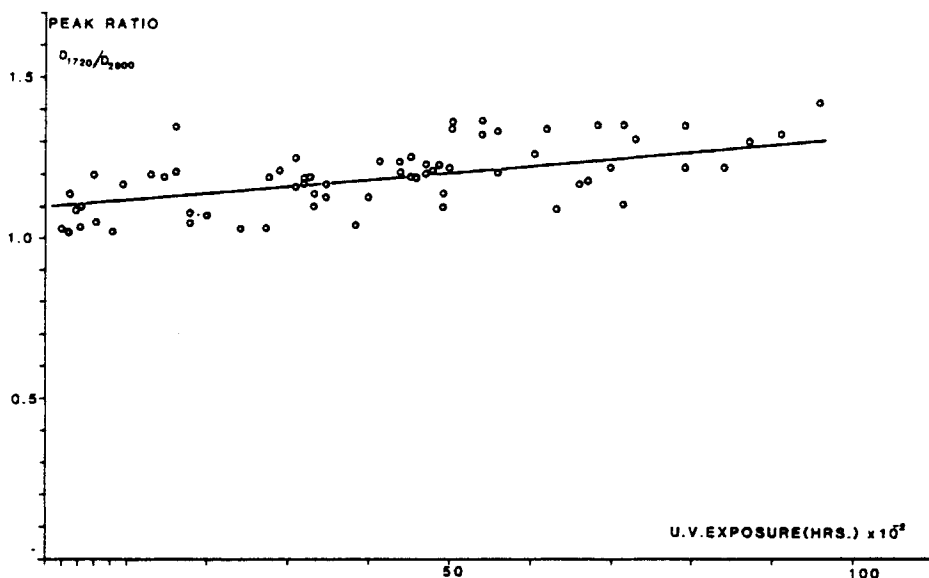


Fig. 3. Variation at  $1720\text{ cm}^{-1}$  (CO) for UV-exposed coated fabric.

duced in this paper have been standardized using spectra obtained at  $60^\circ$ , for this reason.

## RESULTS

### Artificial Weathering of Commercial PVC Coatings

A comparison of spectra of commercial PVC coatings exposed in the suntest from 0–7000 hours is shown in Figure 1. There is considerable growth of the hydroxyl absorption centered on  $3200\text{ cm}^{-1}$  (Fig. 2), the carbonyl peak increases slightly in intensity (Fig. 3), accompanied by a considerable broadening (Fig. 4), while the peak at  $1400\text{ cm}^{-1}$  shows a large increase in absorption (Fig. 5). The spectrum becomes less detailed as UV exposure time increases, with the peaks merging together. There is no evidence of any polyene adsorption.

### Natural Weathering of Commercial PVC Coatings

Changes in spectra during a period of two years outdoor exposure are shown in Figure 6. Similarities with Figure 1 can be seen in the growth of the hydroxyl peak at  $3200\text{ cm}^{-1}$ , and the broadening of the carbonyl band. However, the absorption of the carbonyl band can be seen to vary quite considerably and in an erratic manner. Plots of the optical density ratios against time of outdoor exposure show that these variations occur for the other peaks as well, although the carbonyl peak shows the greatest variability. Variations in the hydroxyl absorption are shown for three samples in Figure 7. The general trend is a gradual increase in absorption, although between May and October 1980 there was no increase, followed by a dramatic increase between October 1980 and January 1981, and a subsequent decline in absorption between January and March 1981.

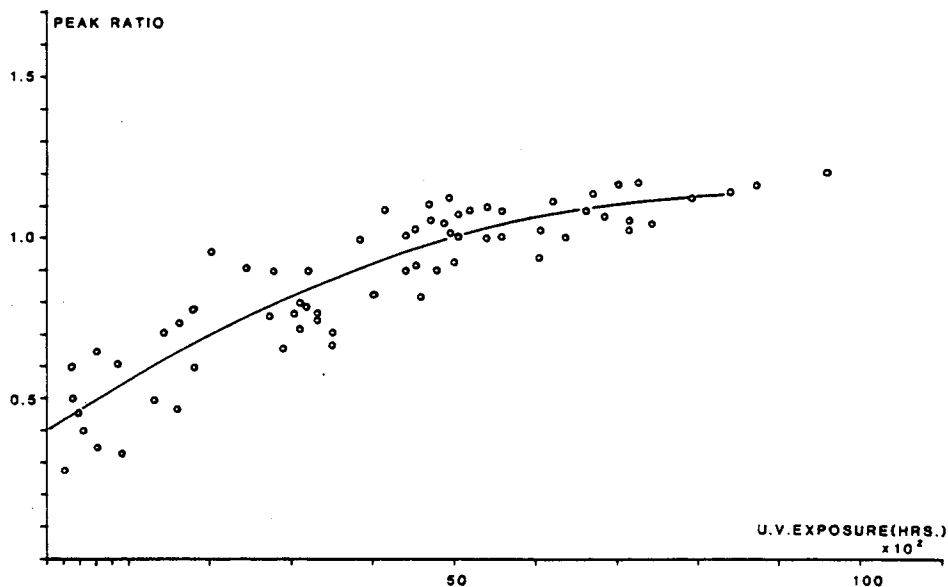


Fig. 4. Variation in absorbance at 1640 cm<sup>-1</sup> for UV-exposed coated fabric.

Similarly the carbonyl absorption shows considerable variation in intensity (Fig. 8). An initial decrease in absorption for the first 9 months of exposure was followed by an increase from March to September 1980 for sample 1, although the effect is less pronounced for sample 2. A decrease beginning September 1980 to November 1980 was followed by a sharp rise in intensity until March 1981, a drop for some months and a further increase.

The measure of absorption at 1640 cm<sup>-1</sup> shows a general increase for over a year and then a dramatic rise followed by a sharp fall at the beginning of 1981. The behavior of the peak at 1400 cm<sup>-1</sup> also shows a rise in intensity in the last few months of 1980 and first few months of 1981.

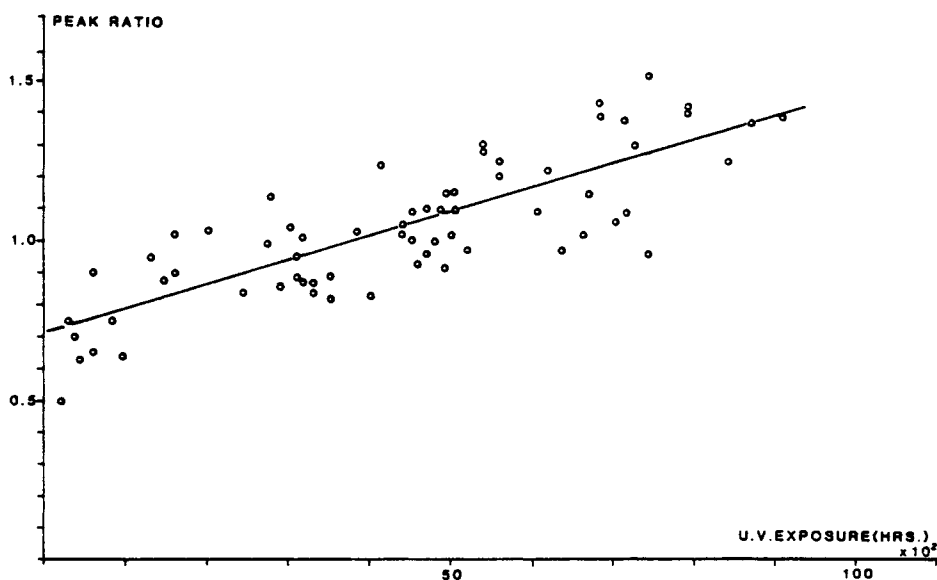


Fig. 5. Variation in absorbance at 1400 cm<sup>-1</sup> (CH bend) for UV-exposed coated fabric.

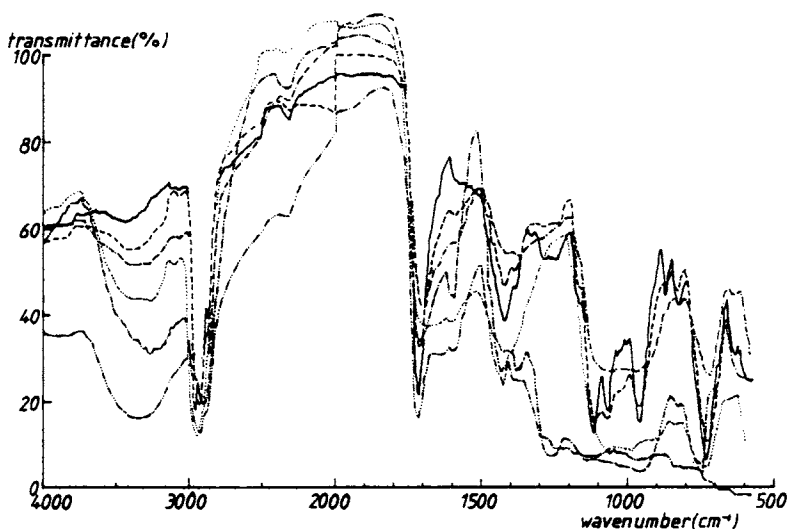


Fig. 6. Comparison of spectra of naturally weathered coated fabric. Outdoor exposure (months): (—) 0; (---) 3; (- - -) 9; (· · ·) 11; (— · —) 19; (— · · —) 24.

The variations in optical density ratio show a greater variation for outdoor than indoor samples. These variations follow largely the same pattern for each of three samples with spectra performed at different times. Furthermore the appearance of the carbonyl peak in the various spectra shows a great variability (Fig. 6). Since there is no reason why there should be a greater error in performing spectra of outdoor compared with indoor samples, it is logical that this variability in the spectra is linked to actual changes taking place at the sample surface.

### COMMERCIAL SAMPLES BOILED IN DISTILLED WATER

In order to determine if there was any relationship between the hydroxyl peak absorption and variations in plasticizer concentration, samples of commercially coated polyester fabric were boiled in distilled water, for up to 8 weeks. Spectra were performed on samples removed at weekly intervals. After 3 weeks boiling,

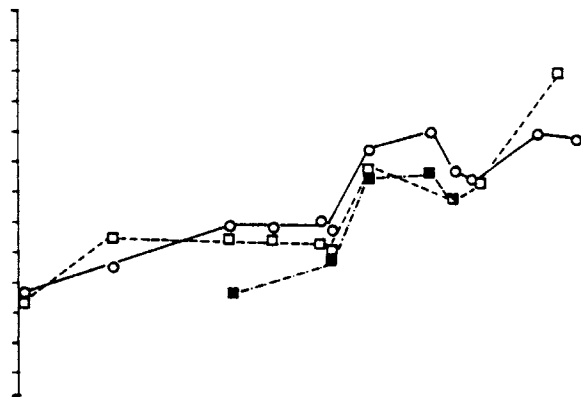


Fig. 7. Variation in absorption at  $3200\text{ cm}^{-1}$  for naturally weathered coated fabric: (—) sample 1; (---) sample 2; (· · ·) sample 3.

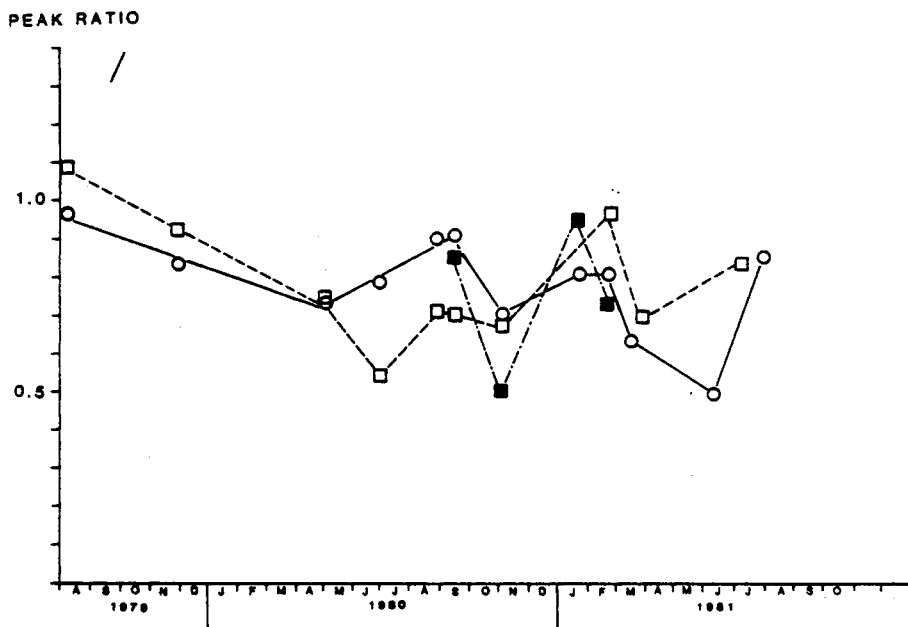


Fig. 8. Variation at  $1720\text{ cm}^{-1}$  for naturally weathered coated fabric.

samples were becoming noticeably stiffer, and this effect increased progressively; however, it was still possible to obtain reasonable spectra in spite of the detrimental effect this would have on sample-prism contact. Variations in peak ratio for hydroxyl, carbonyl, and carbonyl width are shown in Figure 11. The hydroxyl peak absorption increases rapidly for the initial 3 weeks and thereafter levels

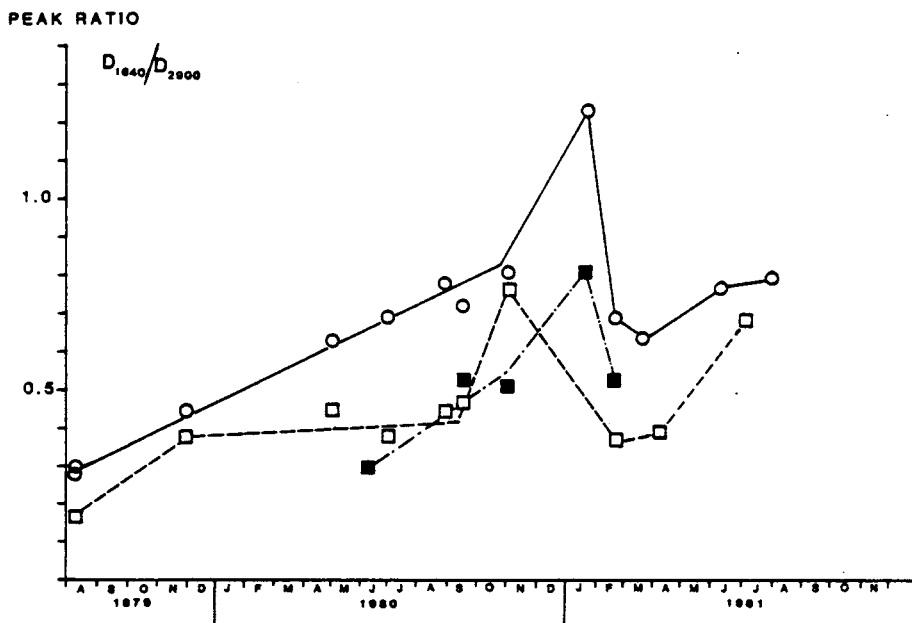


Fig. 9. Variation at  $1640\text{ cm}^{-1}$  for naturally weathered coated fabric.

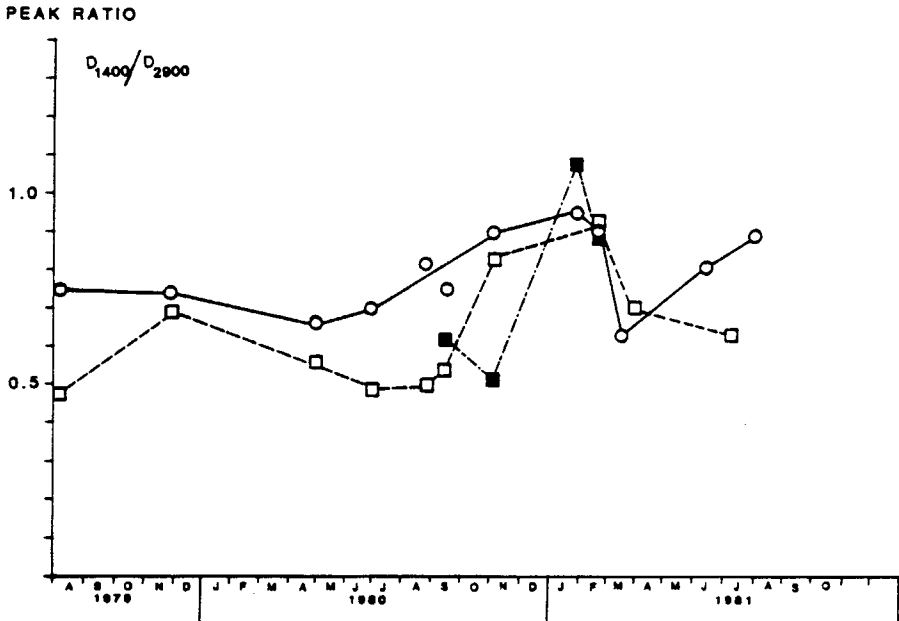


Fig. 10. Variation at  $1400\text{ cm}^{-1}$  for naturally weathered coated fabric.

off, contrasting with the continuous decline of the carbonyl absorption. The absorbance at  $1640\text{ cm}^{-1}$  which is related to the width of the carbonyl peak shows a continuous linear increase with time.

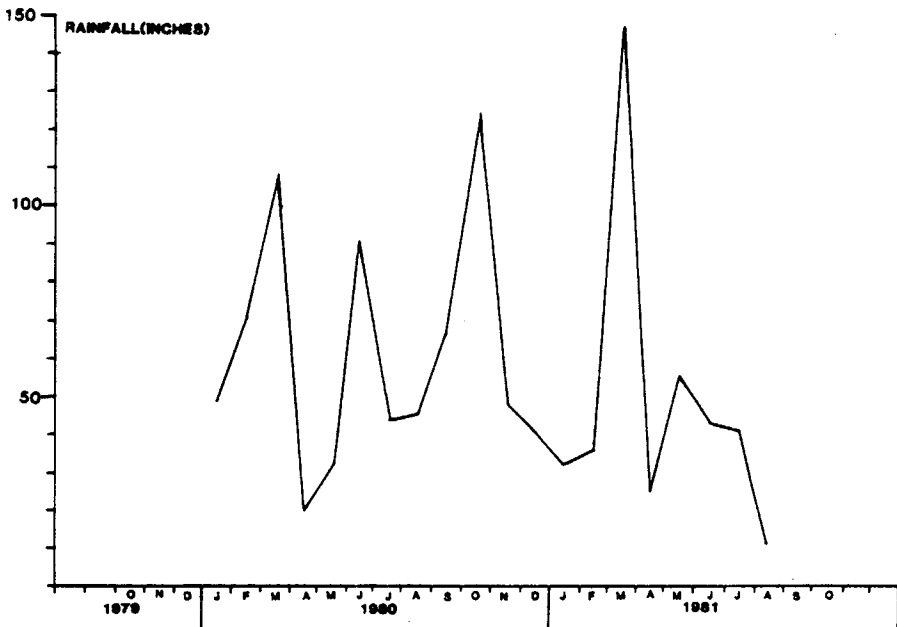


Fig. 11. Monthly rainfall totals for Bath area.



Laboratory-Prepared Samples

Changes in spectra of laboratory prepared samples (containing 50% DOP and 3% M103) are shown in Figure 12. Spectra could not be recorded beyond 1650 h since the sample had degraded to such an extent by this time that it was destroyed on attempted removal from the optical element. (Most spectra were recorded on the same samples which were then returned to the UV cabinet for further exposure.) The main changes are the growth of the hydroxyl peak at  $3200\text{ cm}^{-1}$  (Fig. 13) and the formation of an entirely new peak at  $1400\text{ cm}^{-1}$  (Fig. 16). The carbonyl absorption ratio (Fig. 14) shows an initial decline in intensity followed by an increase after approximately 600 h exposure. The peak ratio measured at  $1640\text{ cm}^{-1}$  (Fig. 15) shows an immediate increase on exposure to the UV source. Also included on the graphs are the variations recorded for samples containing plasticizer but not stabilizer. The variation in hydroxyl absorption shows no significant difference between stabilized and unstabilized samples. However, at the other regions studied, there are significant differences in the behavior of the peaks between stabilized and unstabilized samples. The carbonyl absorption shows an immediate increase with no sign of the induction time noted with the stabilized samples; similarly, the peak at  $1400\text{ cm}^{-1}$  exhibits the same behaviour. The intensity measured at  $1640\text{ cm}^{-1}$  shows an enhanced rate of growth compared with the stabilized sample, but the increase is still linear in nature.

There appears to be little difference in the degradation rates between samples containing 50% and 100% of plasticizer.

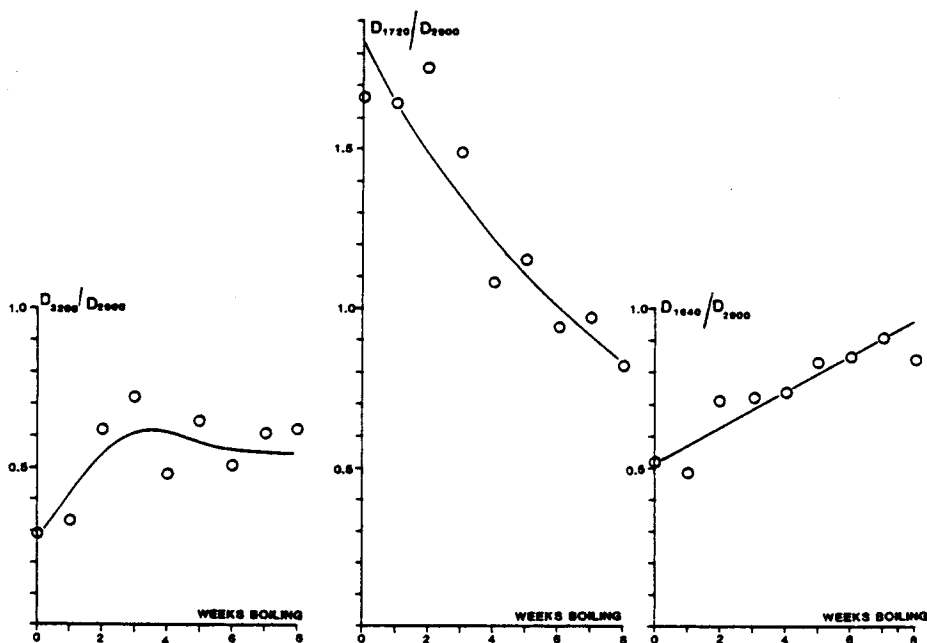


Fig. 12. Variation in absorption for boiled coated fabric samples.

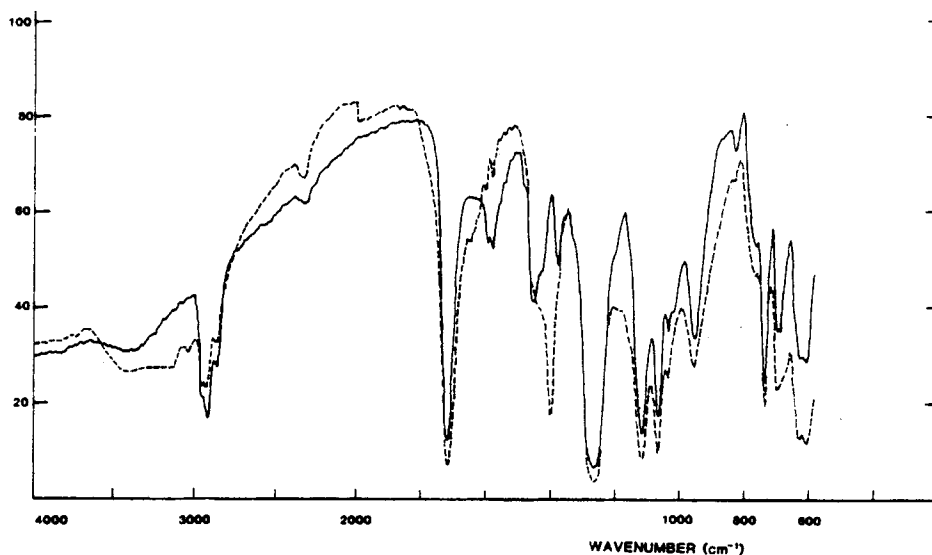


Fig. 13. Comparison of spectra for UV exposed laboratory samples: (—) 0 h; (---) 1650 h.

## DISCUSSION

### Commercial Coated Fabrics—Indoor Exposure

The increase in hydroxyl absorption is most likely to be due to increased concentrations of absorbed water in the sample; this also leads to a broadening of the carbonyl absorption, due to hydrogen bonding. The appearance of the hydroxyl absorption has been noted during photooxidation<sup>5,21,22</sup> and thermal degradation.<sup>2,23,24</sup> Figures 2 and 4 show similar nonlinear trends, suggesting a similar cause for both effects. It is possible that hydroperoxide formation may also make a contribution to the hydroxyl peak, but to what extent cannot be determined. There may be some contribution from the formation of polyene

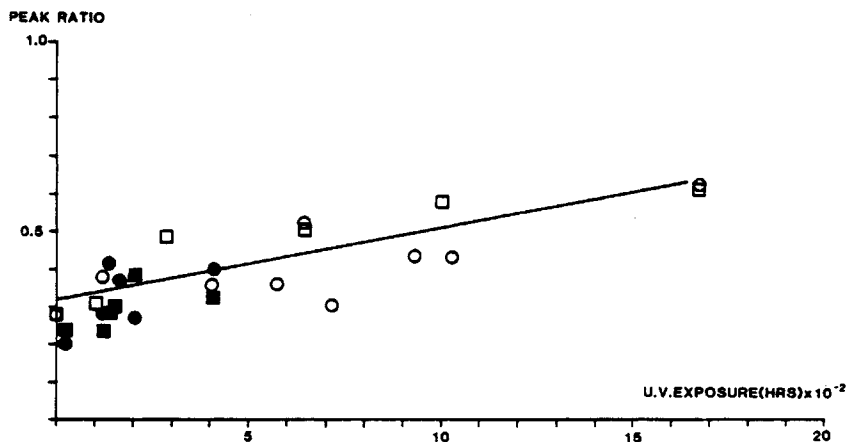


Fig. 14. Variation in absorption at  $3200\text{ cm}^{-1}$  for UV-exposed laboratory samples: (○, □) stabilized; (●, ■) unstabilized; (○, ●) 100 phr; (□, ■) 50 phr.

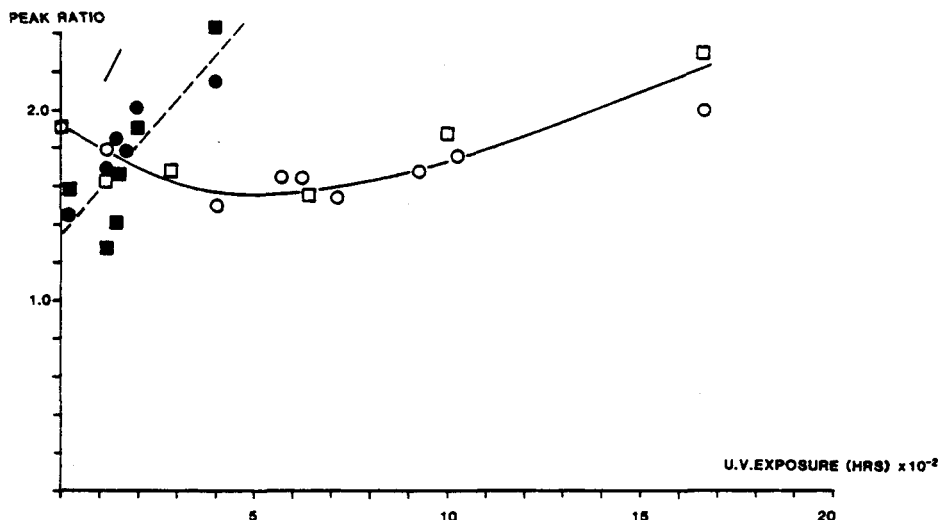


Fig. 15. Variation at  $1720\text{ cm}^{-1}$  for UV-exposed laboratory (—, O, □) stabilized; (---, ●, ■) unstabilized; (O, ●) 100 phr; (□, ■) 50 phr.

sequences to the increase in absorption at  $1640\text{ cm}^{-1}$ , indeed on some spectra a small peak is seen at this point. However, since IR spectroscopy is particularly insensitive at detecting these groups, it would seem that any contribution from this source is small. Laser-Raman spectroscopy is a vastly superior method for investigating polyene formation.<sup>16,25</sup>

The carbonyl absorption increase is slight (Fig. 3), but, nonetheless, observable. Two main mechanisms causing this increase are surface oxidation and migration of plasticiser to the surface, although the sample was not found to have become appreciably tacky after exposure. The presence of a strong carbonyl absorption due to plasticizer would tend to mask any evidence of surface oxidation anyway, so that little can be gained by comparing the rate of carbonyl formation with, say, hydroxyl formation.

The increase in absorption near  $1400\text{ cm}^{-1}$  may represent an increase of CH, or OH bend groups in the surface. Interpretation is difficult because other components (i.e., filler) in the system also absorb in this region.

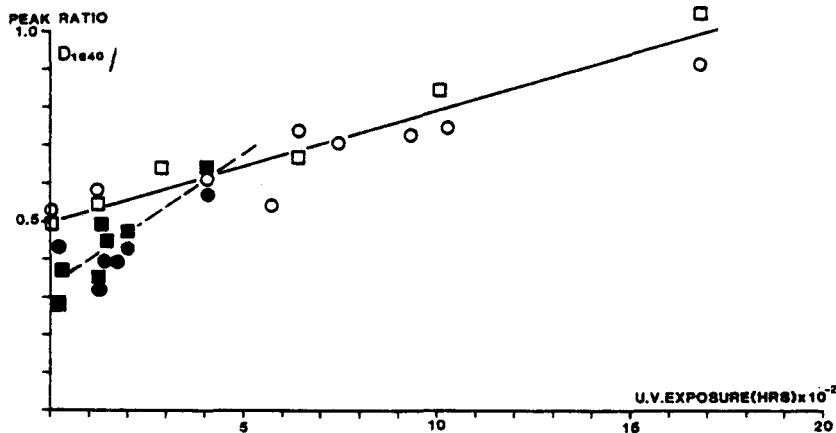


Fig. 16. Variation at  $1640\text{ cm}^{-1}$  for UV-exposed laboratory samples: (—, O, □) stabilized; (---, ●, ■) unstabilized; (O, ●) 100 phr; (□, ■) 50 phr.

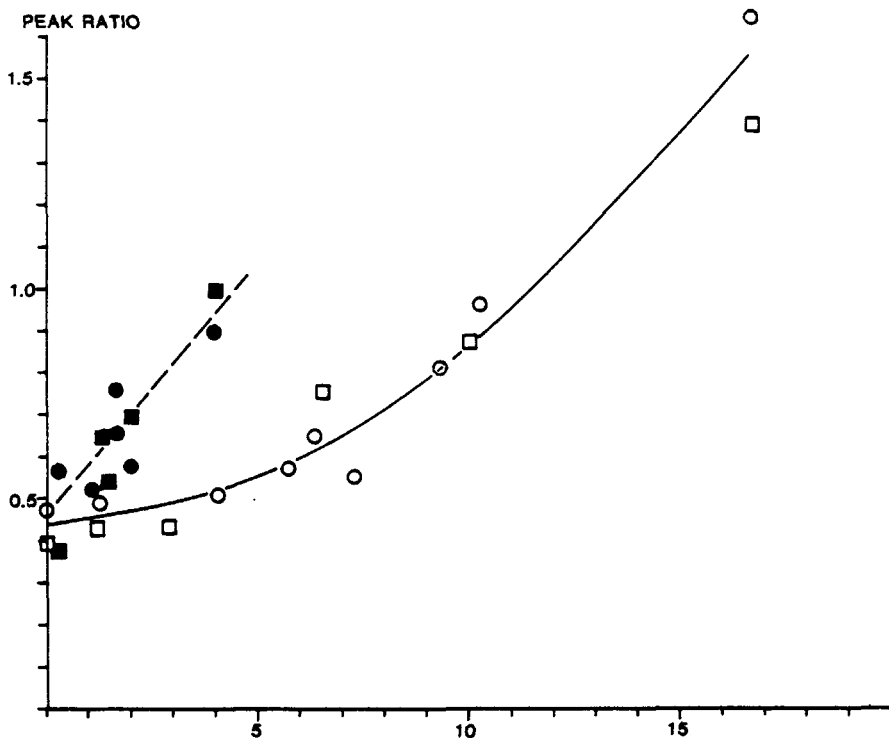


Fig. 17. Variation at  $1400\text{ cm}^{-1}$  for UV-exposed laboratory samples: (—, O, □) stabilized; (---, ●, ■) unstabilized; (O, ●) 100 phr; (□, ■) 50 phr.

### Commercial Coated Fabrics—Outdoor Exposure

Most noticeable in Figure 6 is the large, random variation in the carbonyl peak, illustrated in Figure 8. The intensity of this peak is related to the concentration of plasticizer in the coating to a depth of a few microns below the surface. Some mechanism is therefore responsible for altering the surface plasticizer concentration. A decrease is noted for the first year of exposure, although measurements are taken at such widely spaced intervals that little can be concluded about this. However, observation of the variation of hydroxyl absorption does show an approximately inverse relationship. In particular, the large jump beginning in October 1980 coincides with a fall in carbonyl absorption at the same time. The most likely conclusion is that increased concentrations of water are related to decreased surface concentrations of plasticizer, suggesting that rainfall may be a contributory factor in this plasticiser loss, contrary to the conclusions drawn by Dunn et al.<sup>26</sup>

Comparison of rainfall data (Fig. 11) for the area, compared with variations in hydroxyl and carbonyl intensity, shows that:

(a) Sharp declines in carbonyl intensity in October 1980 and April 1980 are both associated with high rainfall months. Similarly, increases in carbonyl intensity are associated with low rainfall months.

(b) Increases in hydroxyl intensity are associated with high rainfall months, while decreases or levelling off in intensity are associated with low rainfall months.

The behaviour of the peaks at  $1640\text{ cm}^{-1}$  (Fig. 9) show an increased absorption

with a sharp rise and then a fall at the beginning of 1981. The behavior of the peak at  $1400\text{ cm}^{-1}$  (Fig. 10) is similar. Both have a similarity with the behavior of the hydroxyl peak (Fig. 7).

### Boiled Commercial Samples

In this case (Fig. 11) it can be seen that during boiling the OH concentration rapidly reaches a saturation value and thereafter levels off, while the CO absorption decreases continuously. The loss of plasticizer was accompanied by an increased sample stiffness. There is little correlation between the amount of water absorbed into the sample and loss of plasticizer from that sample. There are, however, some important differences occurring in this case: water is absorbed not just in the surface layer, but also the bulk of the material, and secondly a temperature of  $100^{\circ}\text{C}$  applied for many weeks is certain to lead to a continued loss of plasticiser.

### Laboratory-Prepared Samples

The graphs (Figs. 13–16) show significant differences between stabilized and unstabilized samples. With stabilized samples the carbonyl absorption at  $1720\text{ cm}^{-1}$  and the peak at  $1400\text{ cm}^{-1}$  both show an induction period of some 600 h before the peaks start growing significantly; indeed, the carbonyl peak absorption decreases for the initial 500-h exposure. Presumably surface oxidation takes place to some degree during thermal processing, and subsequent migration of stabilizer reacts with the oxidized surface. The induction period before the growth of the carbonyl group has been previously reported,<sup>23</sup> and has been explained as the result of thermal stabilizer remaining after thermal processing, and subsequently behaving as an ultraviolet stabilizer during UV exposure. When this remaining amount has been consumed, photooxidation begins to take place. This explanation is supported by these results; no evidence of this induction period is seen with unstabilized samples. However, there is no guarantee that the growth of the carbonyl peak in this particular case is related to surface oxidation. The result of UV exposure upon stabilized and unstabilized samples is the formation of a brown tacky layer on the exposed surface of the samples. The unstabilized samples are initially slightly brown after thermal processing, this coloration disappears during the first 15 h of UV exposure and formation of the brown surface exudate follows soon after. The stabilized samples require at least 500 h before the exudate appears, at the same time as the peaks at  $1720\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  start increasing. The peak at  $1400\text{ cm}^{-1}$  disappears when samples are soaked in methanol for 48 h. In addition, areas of these samples that have been shielded for the UV radiation exhibit a much lower extractability of plasticizer due to immersion in methanol, and these regions are considerably more flexible and unclouded, in comparison with the exposed areas. Exposure of DOP for in excess of 2000 h in the sun test machine has not altered its IR spectrum at all.

These observations indicate that after thermal processing of plasticised PVC, subsequent UV exposure leads to some reaction of the DOP with degraded segments of the PVC chain, resulting in a DOP-reaction product having little compatibility with the PVC, resulting in exudation of this compound. Studies

with model compounds<sup>27</sup> have suggested that this reaction is with the polyene sequences in the polymer chain. The presence of this reaction compound on the surface of the material is evidenced by the occurrence of a peak at  $1400\text{ cm}^{-1}$  between the  $\text{CH}_2$  scissor absorption of PVC at  $1428\text{ cm}^{-1}$  and the  $\delta\text{-CH}_2$  absorption of DOP at  $1375\text{ cm}^{-1}$ . The fact that the carbonyl peak at  $1720\text{ cm}^{-1}$  and the peak at  $1400\text{ cm}^{-1}$  both exhibit the same induction period suggests that the increase of carbonyl absorption is also related to the exudation of degraded plasticiser. Since the formation of the hydroxyl peak shows no induction period and little difference between stabilized and unstabilized samples, its presence is probably due to absorbed water, rather than formation of hydroperoxide groups. If this is correct, then this would explain the broadening of CO and OH absorption to be due to H bonding.

### CONCLUSIONS

MIR has shown itself to be a useful technique for observing chemical degradation in plasticized poly(vinyl chloride). The importance of obtaining enough spectra for trends to be determined has been illustrated, particularly in the case of naturally weathered samples.

Samples of commercial coated fabrics exposed to a UV source in accelerated weathering exhibit growth of, hydroxyl peak at  $3200\text{ cm}^{-1}$ , the  $\delta\text{-CH}_2$  peak at  $1400\text{ cm}^{-1}$ , a slight growth of the carbonyl peak, and considerable broadening of this peak.

Outdoor exposure of samples of the same type result in growth of the hydroxyl peak and broadening of the carbonyl peak. Absorption of the carbonyl peak decreases. The variations are not continuous, the general trends being broken up by sharp changes in intensity. There is some suggestion of an inverse relationship between hydroxyl and carbonyl intensities. It is suggested that rainfall is a factor in determining plasticizer concentration, analysis of rainfall data indicating loss of plasticizer associated with high rainfall.

Boiling of samples in distilled water leads to a fast increase in hydroxyl intensity which then levels off; the carbonyl peak decreases continuously, however. In this case the continuous application of high temperature and the presence of turbulent water accounts for the continued loss of plasticizer, even though there is no corresponding increase in hydroxyl concentration.

Laboratory prepared samples exposed in the UV cabinet exhibit some growth of the hydroxyl peak. More importantly, samples containing stabilizer exhibit an induction period before peak growth occurs. This induction period is related to the time required to react unconsumed thermal stabilizer during photodegradation. Consumption of stabilizer allows the polymer chain to degrade and subsequently react with plasticizer, resulting in an incompatible product of the plasticizer, which exudes from the material bulk. With unstabilized samples this effect is immediate and appears to be related to the disappearance of discoloration in the material. Degradation, in the initial stages at least, has not been confined to surface regions only. The degradation product has not been analyzed and this remains to be done.

It is suggested that in outdoor applications, i.e., airhouses, it is important that the site for such exposure dictates what formulation is used, since it is to be expected that different outdoor weathering regimes will lead to different degra-

dation processes. Plasticizer loss can occur by different mechanisms, which mechanism is important depends on formulation and environment. Comparison with rainfall data indicates that a correlation exists between rainfall and hydroxyl peak absorption and an inverse relationship occurs with variations in carbonyl intensity. What then are the criteria which decide plasticizer extractability and could surface coating of PVC for outdoor applications lessen the water leaching effect?

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