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Volatiles release from photodegrading, pigmented PVC: kinetic changes*

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Volatile species produced during the ultraviolet irradiation of a rigid, poly(vinyl chloride) construction panel have been established as a function of irradiation time. Residual organic and chloroorganic compounds were detected in the polymer surface after irradiation. Similar species are also directly released during irradiation. In both cases, these were identified and quantified by gas chromatography, with mass spectrometry detection. Rates of volatilisation of organic and chloroorganic compounds were measured directly during accelerated exposure conditions and dropped sharply with irradiation time. This drop may be attributable to the cross-linking of the irradiated surface which becomes chlorine deficient and rich in titanium dioxide pigment (rutile). In contrast, samples exposed to sunlight did not undergo surface cross-linking but did thermally desorb volatiles similar to laboratory exposed samples. Crown copyright © 1998 Published by Elsevier Science Limited. All rights reserved

1 INTRODUCTION

The generation of volatile products has been reported from the photo- and thermal degradation of many polymers (including polypropylene, polyethylene, polyfluoroethers and their copolymer and polyvinylchloride, PVC).^{1–7} For PVC only a few, usually small, molecules have been identified.^{6,7} In most studies of polymer volatiles, only unpigmented polymers have been studied.

Commercial PVC formulations, optimized for outdoor performance, are complex blends of PVC with pigments, impact modifiers, stabilizers, lubricants, etc. Recently, we have reported the wide array of chloroorganic and organic compounds released from both naturally weathered and artificially exposed PVC construction materials (siding panels for exterior cladding).^{8,9} Species directly evolved during ultraviolet (UV) exposure were trapped and concentrated in sorbents, then desorbed for analysis by gas chromatography with electron capture (GC–EC) or mass spectrometry (GC–MS) detection. Volatile residues remaining in

the PVC surface after irradiation were measured by GC–MS after thermal desorption.

In this paper we extend the use of this analytical approach to follow the evolution of volatile species as a function of PVC irradiation times. In addition, changes in molecular weight, gel and surface characteristics have been measured.

2 EXPERIMENTAL

2.1 UV exposures

Outdoor exposed samples were compared with PVC siding samples (40 cm² and 1 mm thick) irradiated in a flat, borosilicate glass cell under a slow flow of pure air (10 ml/min, Praxair, ‘Zero’ air) as described previously.^{8,9} For the laboratory (accelerated) testing, a medium pressure mercury arc (Hanovia Inc., 550 watt) was used, with only wavelengths greater than 290 nm transmitted by the cell.

2.2 PVC Characterization

Although several commercial siding samples were studied, most detailed studies were performed on a

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light gray material produced in 1985. Previously, this was shown to contain 10 wt% TiO₂ (rutile by wide angle, X-ray diffraction), a tin stabiliser (0.18 wt% Sn), undetectable Pb or Cd (<0.005 wt%) and 5 wt% of an acrylate impact modifier (a methyl methacrylate/butyl acrylate copolymer). From differential scanning calorimetry (DSC) measurements made under nitrogen at 10°C/min heating rate, this PVC had a single T_g at 83–85°C. A low level of chlorinated polyethylene might be present as an additional impact modifier, but could not be unambiguously established by infrared spectroscopy.

The molecular weights of PVC samples abraded as a fine powder from irradiated and non-irradiated surfaces were determined by size exclusion chromatography (Waters Millennium SEC system) after solution in tetrahydrofuran (THF) and removal of pigment and other insolubles with an Ahlstrom filter.

Gel formation was established by immersion of small ($0.5 \times 0.5 \text{ cm}^2$) pieces of PVC in THF and observing the solution process at low magnification. Visible gel was separated by decantation, repeatedly washed with fresh THF and dried to constant weight.

2.3 Surface topography and chemistry

Changes in surface topography were measured, after gold coating, by scanning electron microscopy (SEM, JEOL, JSM-5300) equipped with energy dispersive X-ray analysis (EDXA). EDXA was used to monitor Ti and Cl levels, both on virgin and exposed surfaces and on cross-sections produced by freeze fracture. The electron beam of the SEM induces X-ray emissions from a 2–3 μm diameter spherical domain in the sample surface. The X-ray emissions are distinctive of the elemental composition in the domain, although carbon cannot be detected.

2.4 Thermal desorption

Species that are released by thermal desorption of UV exposed PVC plaques have been reported previously, together with the detailed GC-MS methodology used.^{8,9} Briefly, surface material was abraded from the top ~15 m of a 40 cm² area of each sample. This produced a fine powder and volatile species were desorbed from this powder by heating at 120°C for 3 min under helium flow in the GC injection system, followed by

cryo-focusing onto the head of the GC column for GC-MS analysis..

2.5 Direct desorption

Volatile species from PVC samples were released during the irradiation under a stream of pure air in the borosilicate glass cell. These species were trapped in a sorption train for subsequent, off-line GC-MS analysis after cryofocussing as described previously.⁹ The sorbent train consisted of two carbon sorbents (first Carbotrap and then Carbosieve-S tubes, Supelco Inc.). Carbotrap sorbed and released all species above about C₄ and up to at least C₁₂. Carbosieve sorbed and released the C₁–C₃ species not retained by the Carbotrap. Both sorbents were cooled at –5°C in an aluminium, heat-exchanger block to give an adequate sorption period (~8 h) before species eluted completely through the sorption tubes.⁹

2.6 System calibration

The sorption and release capabilities of the two sorbents and the GC-MS sensitivity for specific, liquid compounds were established using the glass apparatus shown in Fig. 1. This contained up to seven liquid standards at once, each in a separate vial equipped with a capillary vent. All of these liquid standards were thermostated together at 20°C. The capillary diameter and length for each compound was chosen to give a rate of volatilization into the pure air stream (10 ml/min flow, Praxair, 'Zero' air) so as to give fluxes comparable to the fluxes from irradiated PVC, when diluted with the large nitrogen cross flows (15–80 l/min). After passing through the manifold designed to ensure complete mixing, the diluted, standard

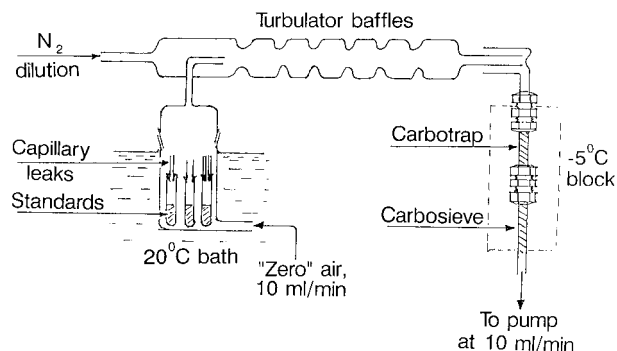


Fig. 1. Dilution equipment for calibration of the sorbents and GC-MS sensitivity. Up to 7 standards were used at once; only 3 are shown. N₂ dilution at 10–80 l/min.

vapours were drawn off at 10 ml/min. through the sorbent train pre-cooled to -5°C , for an 8 h period. Absolute rates of volatilization of each standard were determined gravimetrically over a 14 day period. This method allowed the total system (sorbent train, GC cryo-focusing system and MS sensitivity) to be calibrated over a range corresponding to our emission levels from the irradiated samples. For gaseous species such as chloroethylene, appropriate certified standards (Matheson) were quantitatively diluted and pressurized with nitrogen and then bled into the manifold (Fig. 1) at a known, controlled rate where further dilution with nitrogen occurred. It was found to be essential to maintain trapping conditions close to those used during irradiation to avoid calibration problems especially with the compounds trapped in the second sorbent (Carbosieve).

The total trapping/GC-MS system was calibrated for many of the most prominent species released from irradiated PVC. The system response factors, as measured by total ion abundance/ 10^5 per 100 ng of volatilized compound covered only a small range (about 1.5–5.0) and fell into quite consistent patterns. For example, aromatics such as benzene and toluene give the highest response (about 5.0) and very small chloroorganics (chloroethane, chloroethylene) gave the lowest (~ 1.5).

2.7 HCl evolution

Because the GC method was optimised for volatile organic compounds, no clear HCl peak was observed in the total ion chromatograms. Instead, HCl evolution was measured as a function of UV irradiation or infrared heating times in separate experiments by passing the air stream exiting the irradiation cell through a water trap. (The high purity air was passed through a bed of potassium hydroxide pellets to remove trace acids such as CO_2 before entering the irradiation cell.) The conductometric changes in this water trap were continuously recorded as described previously.¹⁰ The cell was calibrated by comparison with the conductivity of known concentrations of HCl. HCl yields were periodically cross checked by precipitating the chloride ion as silver chloride from the water in the conductivity cell by adding silver nitrate and adjusting to pH 4 with nitric acid. The silver chloride yield was measured by gravimetry. Less than 10% deviation between the two methods was found. When a second conductivity cell was run in series with the first, negligible increase in

conductivity occurred in this second cell during irradiation, indicating that complete HCl sorption had occurred in the first cell.

3 RESULTS AND DISCUSSION

3.1 Thermal desorption

Surface layers ($\sim 15\mu\text{m}$) were carefully abraded from the PVC samples as a fine powder. Species desorbed from the gray siding after mercury arc irradiation changed progressively over long irradiation times (up to 2500 h). Examples of chromatograms are shown in Fig. 2 together with a chromatogram of species desorbed from a non-exposed sample. The latter did not release detectable chloroorganic compounds.

The kinetic dependence of quantities of some dominant species are shown in Fig. 3. It should be noted that many other volatiles have been previously identified.^{8,9} Removal of a second, $\sim 15\mu\text{m}$ layer from a UV exposed surface gave PVC powder which released negligible volatile species upon thermal desorption. Because of the surface nature of the changes in pigmented PVC, the quantities of desorbed compounds are expressed per unit area in Fig. 3.

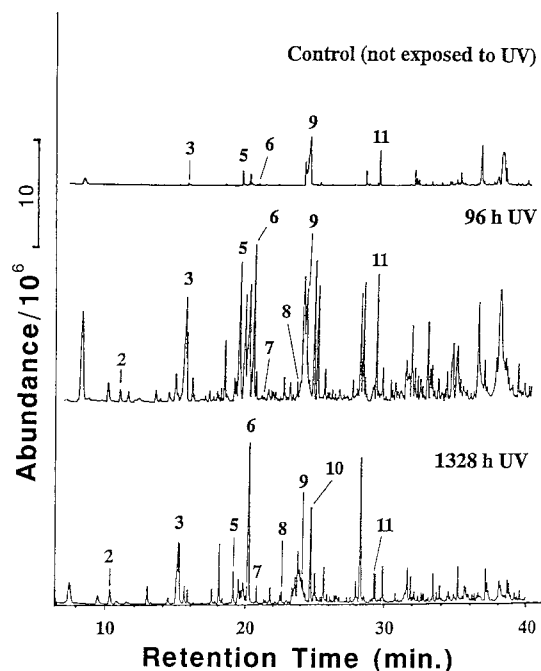


Fig. 2. Chromatograms of species thermally desorbed from abraded PVC powders. UV exposure times as indicated. Identification numbers correspond to those in the captions of Figs 3 and 4.

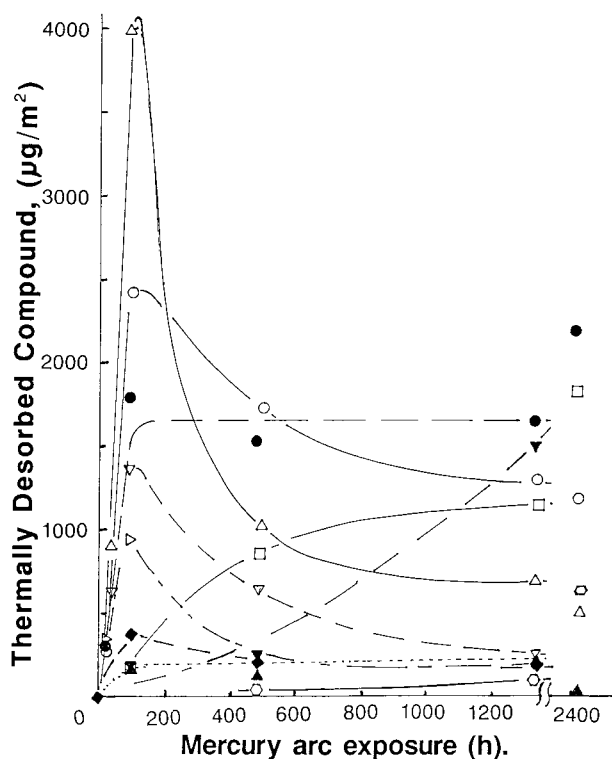


Fig. 3. Time dependence of some species thermally desorbed from abraded PVC powders. ◆, Chloroethane (#2); ○, benzene (#7); o, Acetone (#3); ▼, dichloropropanes (#8); ▲, Dichloromethane (#4); ▽, butanol (#9); △, butanal (#5); □, butyl formate (#10); ●, 1-chlorobutane (#6); ▷, di-*n*-butyl ether (#11).

It is possible that the rapid accumulation, then drop off of species such as butanal, 1-butanol and di-*n*-butyl ether may result from their initial formation followed by their secondary photooxidative destruction in the surface layer.

3.2 Surface molecular weight

Number and weight average molecular weights for unexposed, sunlight exposed and mercury arc exposed surface materials are collected in Table 1. The presence of gel in 'solutions' of surface powder samples in THF could not be detected because of the opacity of these solutions (from the TiO_2 pigment). However, progressive solution in THF of irradiated PVC pieces clearly showed the swelling and detachment of a gelled surface skin from each mercury-arc-exposed sample (≥ 25 h exposure). Visual swelling in THF and gel layers were not observed in any of the sun-exposed samples, consistent with the decline in molecular weight of outdoor weathered samples (Table 1).

Gel formation in unstabilized, unpigmented PVC has been previously reported upon UV exposure.^{11,12}

Table 1. Molecular weight of THF-soluble PVC^a and gel content

Sample	Gel wt% (μm) ^b	M_w	M_n	Poly-dispersity
Unexposed	0 (0)	154 700	79 900	1.9
After 11 year sunlight	0 (0)	109 800	47 700	2.3
After 96 h Hg arc	0.5 (5)	— ^c	— ^c	— ^c
After 2527 h Hg arc	1.6 (15)	1 416 000	319 000	4.5

^aSolutions filtered through a $0.45 \mu\text{m}$ filter to remove pigment and any gel before GPC analysis. Calibration with polystyrene standards.

^bGel layer thickness, assuming that the dried gel has the same density as the pigmented PVC.

^cNot determined.

Gel formation is attributable to cross-linking of the polyene structure during the free-radical driven dehydrochlorination of the surface layer.

3.3 Surface topography and chemistry

The SEM micrographs of an 11 year weathered and a non-irradiated surface are shown in Fig. 4. The non-irradiated surface is relatively smooth, consistent with an amorphous, melt-extruded sheet. After 11 years of outdoor weathering, the surface texture is highly granular. A very similar surface texture was visible after mercury arc exposure (> 1000 h). Cl/Ti EDXA signal ratios from irradiated surfaces and from areas across a freeze-fractured surface of an irradiated plaque are shown in the schematic in Fig. 5. Similar changes in Cl/Ti signal ratio were seen for 11 year weathered and 2500 h mercury arc irradiated plaques. The uncalibrated Cl/Ti signal ratio of 12 from the non-irradiated surface or core regions corresponds to the calculated Cl/Ti atomic ratio of 12.3 (based on 10 wt% TiO_2). The EDXA data is consistent with the formation of a pigment rich, surface layer upon UV exposure. This is presumably the highly granular surface (Fig. 4B), which accounts for the dull, chalked surface of UV exposed PVC siding.

3.4 Direct volatilization

The calibrated sorption train of Carbotrap and Carbosieve sorbents allows the measurement of species directly volatilized from the PVC samples during UV exposure. Typical chromatograms are shown in Fig. 6. Because UV exposure only affects the top most 10–15 m of the pigmented, stabilized PVC, emissions are best expressed on a sample

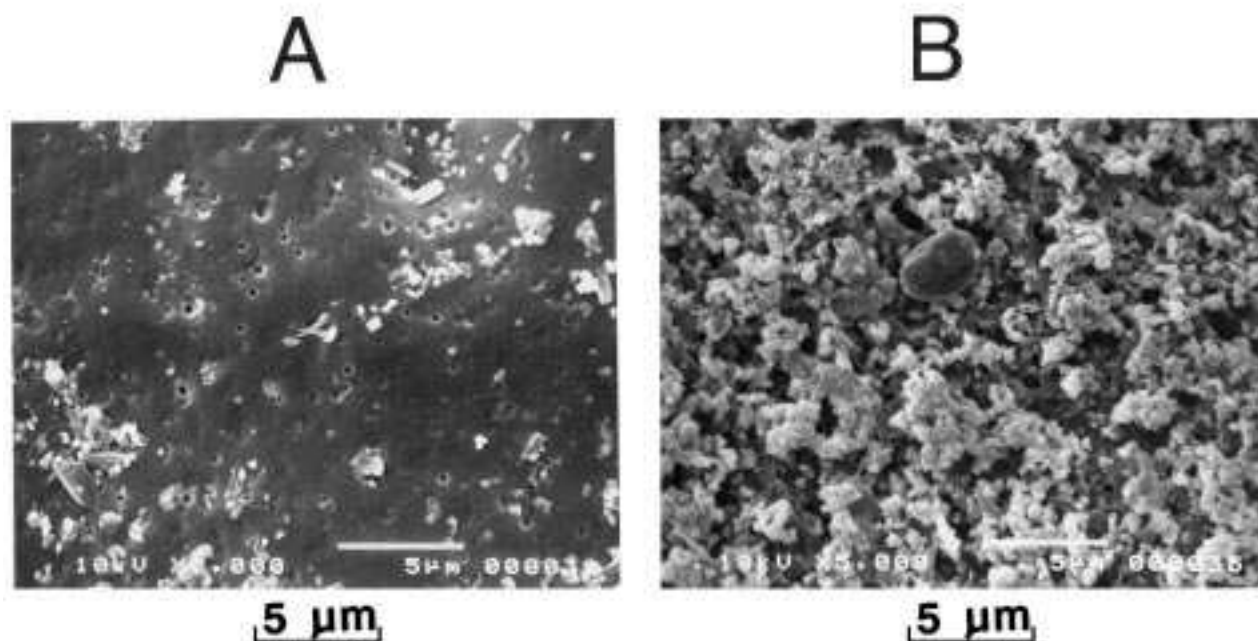


Fig. 4. SEM micrographs of PVC surfaces. (A) Not UV exposed; (B) after 11 year sun exposure.

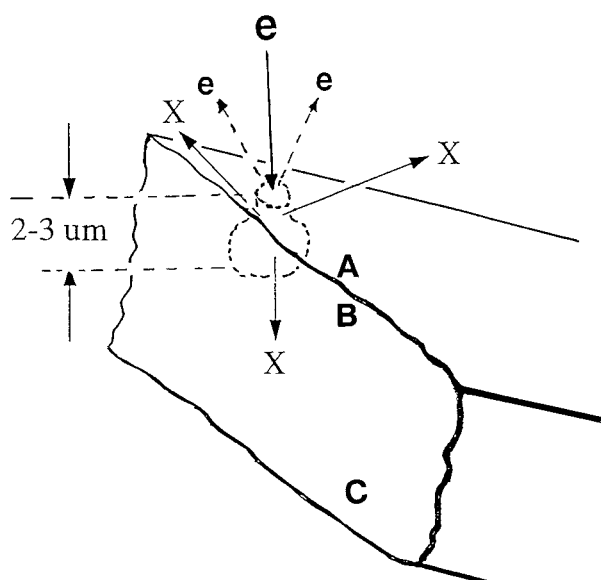


Fig. 5. Schematic of PVC fracture cross-section and EDXA [Cl/Ti] ratios. Initial surface and bulk Cl/Ti = 10 before irradiation. After 2400 h of mercury arc exposure in the flow cell: (A) UV exposed surface, Cl/Ti = 2.5; (B) fracture cross-section, $\sim 5 \mu\text{m}$ from the UV exposed surface, Cl/Ti = 3; (C) fracture cross-section, $\sim 500 \mu\text{m}$ from UV exposed surface, Cl/Ti = 12.

area basis and are collected in this form in Fig. 7. For comparison with the quantities of species thermally desorbed from the abraded PVC powder (Fig. 3), the rates of emission of each compound in Fig. 7 were integrated graphically to give the accumulated emissions shown in Fig. 8.

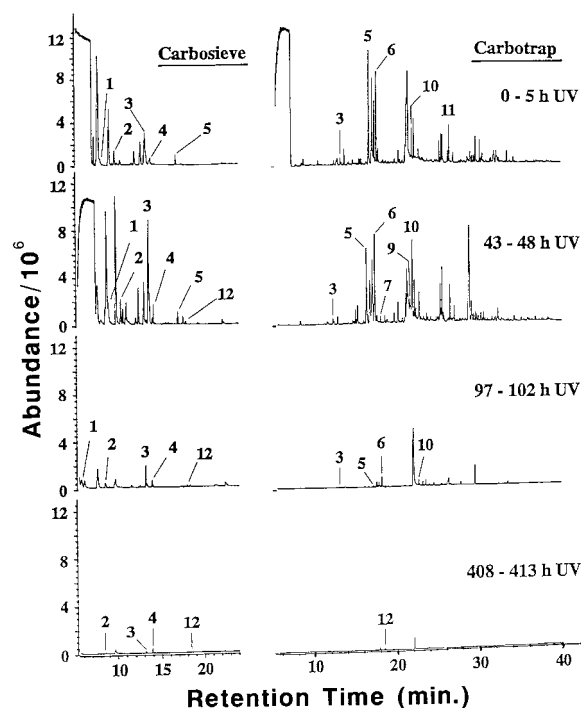


Fig. 6. Chromatograms of species directly desorbed from PVC during irradiation. Identification numbers correspond to those shown in Figs 3 and 7.

The accumulated HCl emission as measured by conductometry is also shown in Fig. 8. After a brief 'induction period' HCl emission proceeded linearly for about 1000 h and then the rate declined monotonically to plateau at about 2000 h. Because

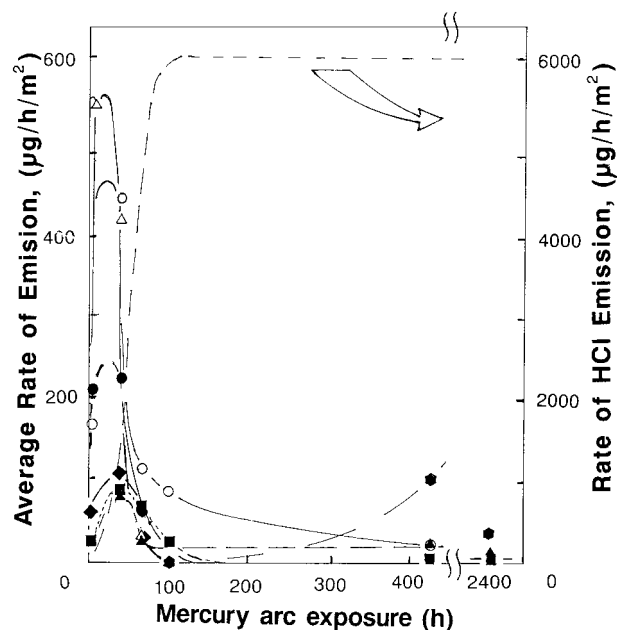


Fig. 7. Total accumulation of key species directly desorbed from PVC during irradiation. Symbols as in Fig. 3 and in addition: ■, Chloroethylene (#1); ●, Chloroform (#12); ---, rate of HCl emission calculated from conductometry.

HCl can come from direct heat alone, some samples were exposed to external infrared heaters in the sample cell, with the sample temperature adjusted to correspond to that experienced during UV exposure (75–80°C). Negligible HCl emission was detected either from fresh (non-irradiated) PVC samples at 80°C or from a sample that had previously received an initial, 300 h UV exposure before the thermal treatment at 80°C.

HCl emission from irradiation (unpigmented) PVC has previously been both reported and denied at wavelengths > 290 nm.^{11,13} TiO₂ is well known both as a UV screen and as a photosensitizer for

polymer degradation.¹⁴ HCl evolution has been found to be initially enhanced by TiO₂, indicating a photo catalytic effect.¹⁵ In contrast, yellowing and photo oxidation of UV exposed PVC are slowed by the presence of coated and uncoated TiO₂ pigments.¹⁶

Formation and release of volatile species from pigmented, stabilized PVC can be expected to be a complex function of many processes, including direct photochemistry, TiO₂-sensitized photochemistry, TiO₂ screening, oxidation, polyene formation and diffusion phenomena. Furthermore the rate of each process will vary (often decrease) as photodegradation proceeds because of the surface-rich TiO₂ layer and molecular weight and gel increase in the residual surface layer. A comparison of Figs 7 and 8 with Fig. 3 shows that direct volatilization is very low beyond 100 h of filtered, mercury arc exposure except for HCl, despite the significant levels of compounds which can be thermally desorbed from surface powder, even after ≥2000 h. This could be explained by changes in PVC surface permeability. 'Pure' PVC has a low diffusivity for O₂ and > 10⁴ times lower values for small organic molecules.¹⁷ For O₂ and other, small molecules, permeability can be expected to drop even lower as a result of surface crosslinking.¹⁷ From gel measurements, this skin is ~15 m thick after ~200 h, increasing steadily from the very early stages of irradiation. The more sustained HCl evolution implies a very high HCl permeation through PVC, even when cross-linked. This is a distinct possibility by analogy with the reported, very high permeation through PVC of another, small, polar molecule, H₂O.¹⁷

Control of the processes for volatiles formation and/or volatiles release by a surface skin effect was confirmed by abrading away the top ~25 µm of a sample after, for example, 100 or 400 h of mercury arc exposure. These samples then showed a similar emissions pattern to that in Fig. 7 when irradiated for a second time. Adam *et al.* have shown that polybutadiene photooxidation is controlled by formation of an oxygen impermeable surface layer.¹⁸ Such a phenomenon could also contribute to the effects in mercury-arc-irradiated PVC.

3.5 Outdoor weathering and accelerated exposure

As reported previously, thermally desorbed species from 11 year, sun-exposed PVC and an ~100 h mercury-arc-exposed sample are very similar in volatile type and distribution.⁹ In addition, quite

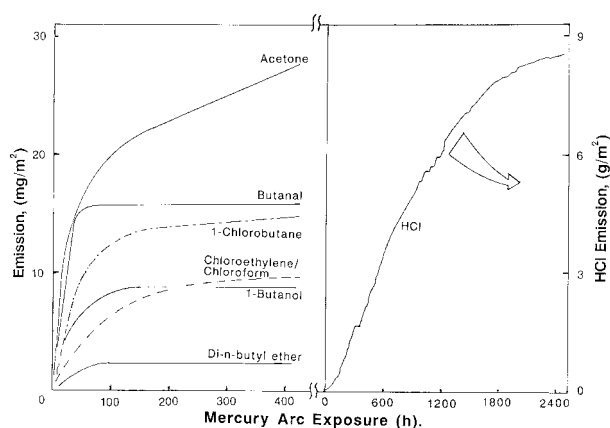


Fig. 8. Cumulative real time emissions. From integration of the curves in Fig. 7. Total HCl evolution measured directly by conductometry.

similar SEM and EDXA changes were found, as described above. The rapid reduction in direct volatilization for laboratory exposed samples may be attributed to the surface crosslinking caused by mercury arc exposure, which contrasts with the chain scission prevalent in the surface of sun-exposed samples (Table 1). This difference could result from the temperature rise in our mercury-arc-exposed cell (up to $\sim 80^{\circ}\text{C}$), to the high UV intensity (accentuating radical-radical reactions, causing O_2 depletion, etc.) or to humidity/rain/thermal cycling effects during outdoor exposure. Such effects could be studied by the use of an infra-red filter (such as a water layer) between the mercury arc and the irradiation cell.

4 CONCLUSIONS

1. During mercury arc exposure, organic, chloro-organic and hydrogen chloride emissions from pigmented PVC show a complex dependence on UV exposure time.
2. Surface crosslinking appears to block release of volatile species after quite short mercury-arc-exposure times, except for very small molecules such as HCl and Cl chlorinated species.
3. Naturally weathered PVC samples do not crosslink and show a loss in surface molecular weight in complete contrast to samples exposed under accelerated test conditions.
4. Analysis of directly released volatiles could form the basis of a highly sensitive method to follow the effects of stabilizers, pigment and other additives on the photodegradation of the complex PVC formulations used in practical applications.

5. The technique of trapping and concentrating volatiles from photodegrading polymers, followed by GC/MS analysis (dynamic head space analysis), should be applicable to other, complex, polymer systems.

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