# Accelerated weathering of UPVC

# A. TURNBULL, N. FALLA\*, A. SMITH\*, D. WHITE Centre for Materials Measurement and Technology, National Physical Laboratory, Teddington, Middlesex, TW11 OLW, UK and \*Paint Research Association, 8 Waldgrave Road, Teddington, Middlesex, TW11 8LD, UK

A detailed study has been conducted to assess the effect of various artificial weathering cycles on the degradation of three formulations of window-grade UPVC. The results were compared with samples which had been exposed outdoors in the north-east of England for periods of up to 16 years. Microhardness, loss of calcium carbonate filler, intensity of the C–O stretching band, colour and gloss were used as measures of degradation. The samples tested in the laboratory exhibited the characteristic surface degradation and partial recovery predicted for these materials. Cyclic variation of certain properties was exhibited for long laboratory exposures. In contrast, the naturally exposed material gave no definitive indication of a recovery process. The various measures of degradation employed gave reasonably consistent indications of degradation, particularly with regard to the onset of partial recovery. The complexity of the degradation process for these materials inherently limits the establishment of quantitative rate equations to predict the durability of naturally exposed materials. Nevertheless, four of the five exposure cycles gave consistent ranking of the different materials which compared well with the ranking deduced from natural exposure. An optimum artificial weathering cycle was derived. It is recommended that laboratory tests should involve testing of a reference sample in parallel for the purposes of quality control and interlaboratory comparison. By choosing a material with established outdoor performance, a basis for prediction of relative service life is also provided.

# 1. Introduction

Polymeric materials subjected to the atmospheric exposure effects of ultraviolet (UV) radiation, temperature, wetting and drying cycles, and pollutants will degrade with exposure time resulting in the loss of gloss, colour, and mechanical properties. In addition, the formation of a degraded surface layer creates difficulties in effective recycling of exposed material.

The very extensive research performed on the weathering of polymers in general [1–3] and PVC in particular [4-8], has led to significantly improved formulations, but there remains considerable debate concerning the efficacy of accelerated exposure tests in simulating natural exposure conditions [2, 9-11]. The inherent difficulties are the range of environmental factors and their complex time and spatial variation, coupled with the need to accelerate testing in a meaningful way. Advanced weathering machines with appropriate filtering can generate a reasonable simulation of the solar spectrum, with the acceleration factor being the intensity of the source and the time of exposure, coupled with elevated temperature, humidity and water spraying. Accelerated natural exposure is also used, in the context of using more severe environments compared to the intended application or using mirror reflection to intensify the irradiance.

The advantage of laboratory testing is control and convenience but the degree of success in relation to

correlation with natural exposure has been very mixed and indeed it has been argued that there appears to be no correlation between natural and artificial weathering [1, 9]. However, the term correlation is often used without a clear definition. The principle requirements for a meaningful accelerated test are that ranking of materials should be successfully predicted and that a functional relationship should be established which enables long term prediction in service. In practice, a damage function which takes account of the range of weathering parameters and can be applied to a wide variety of locations and hence exposure conditions seems unrealistic. The more realistic goal would be to focus on predicting behaviour for a particular climatic condition.

The primary objective of this research was to evaluate the effect of artificial weathering parameters on chemical and mechanical properties of a commercial polymer and to assess the capability for correlation of the results with the effects of natural exposure. A parallel activity using plasma erosion as an ultrafast degradation process is described elsewhere [12]. The main material for study was PVC-U window grade, the basis of choice being the availability of naturally weathered samples of known history and the provision of new extrusions of identical formulation. Material property variation was measured by Fourier transform infra red spectroscopy (FTIR), microindentation, colour and gloss measurement, and scanning electron microscopy (SEM). A range of techniques were used because of the broader interest in the correlation between different property measurements with exposure. Nanoindentation was also used in this study and the results are reported in detail in a separate publication [13]. Impact tests and tensile tests were not feasible because of the non-uniform geometry of the profiles.

# 2. Experimental procedure

## 2.1. Materials

Three formulations of PVC-U window profiles were used including Hostalit<sup>®</sup>Z (Hoechst AG) chlorinated polyethylene-modified window-sill section, denoted AHS8; acrylic modified "tropical" PVC window section denoted AHS7; RW00 acrylic modified window profile, denoted AHS2. The composition of these materials is described in Appendix 1.

For the laboratory exposure tests newly extruded profiles of AHS8 and AHS7 with formulations identical to the naturally exposed material were utilized but equivalent material could not be obtained for AHS2. Accordingly, sections of the original material not exposed to sunlight were used but the available material was limited and this is reflected in more limited laboratory exposure data.

# 2.2. Exposure conditions

## 2.2.1. Artificial exposure

The samples were exposed in an Atlas weatherometer Model Ci 35A which utilizes a xenon arc radiation source. For these tests the radiation was filtered using borosilicate glass to give a Miami "average"  $45^{\circ}S$  daylight spectrum in the range 300-800 nm. The radiant energy per unit area is measured only at 340 nm. The total radiant energy per unit area (irradiance) in the energy band 300-800 nm was estimated [14] by multiplying the measured value at 340 nm by a factor of 1160.

#### TABLE I Artificial weathering cycles: conditions used

The exposure conditions for this test programme are listed in Table I and involved five specific weathering cycles in which primarily the irradiance or temperature was modified. Cycle 1 is based on the draft CEN Comité Européen de Normalisation standard [15]. Cycle 4 is similar to cycle 2 with the exception of an extended water spray period.

# 2.2.2. Natural exposure

The AHS8 and AHS7 samples were exposed with a south-facing aspect at Wilton, Cleveland, UK,  $(54^{\circ}N, 1^{\circ}W)$ . The AHS8 sample was exposed for a total of 16 years between 10 December 1975 and 2 December 1991 and the AHS7 sample for about eight years between 20 August 1984 and 13 April 1992. The AHS2 sample was exposed at Newton Aycliffe, Co Durham, UK,  $(54^{\circ}N, 1^{\circ}W)$  over a nine year period between 18 April 1983 and 5 March 1992. The relevant climatological data for the locality are given in Table II. All samples were exposed at an incline at  $45^{\circ}$ .

The solar spectrum extends from about 300– 3000 nm. However, the spectrum of the artificial radiation source in this study extends from 300–800 nm. In calculating the solar radiant energy density in the range 300–800 nm it was assumed that this wavelength range represents about 55% of the total value, which is close to the value reported elsewhere [16]. For comparison with the artificial weathering the solar energy data have been scaled accordingly. A dose per unit area of 10 GJ m<sup>-2</sup> calculated in this way would correspond approximately to 5.3 years of natural exposure at 54°N.

# 2.3. Measurement methods

Microindentation measurements were made using a Vickers microhardness tester with a 15 s period at maximum load. The load applied was 0.29 N but the effect of varying this load on the hardness was evaluated in a few tests. Indents were made for any

	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
Black standard temperature	65	65	72	65	58
Black panel temp $\approx 58 ^{\circ}\text{C}$					
White panel temperature (°C)	44	44	54	44	46
Air temperature (°C)	36	36	48	36	41
Wet bulb depression (°C)	6	6	7	6	6
Relative humidity 65%					
Light/dark cycle			Continuous light		
Water spray cycle	102 min/18 min	(light/light + water	90 min/30 min	102 min/18 min	
				light/light + water spray	(light/light + water spray)
Irradiance at 340 nm (Wm <sup>-2</sup> )	0.35	0.5	0.35	0.5	0.25
Inner filter			Borosilicate		
Outer filter	Borosilicate				
Maximum radiant exposure	AHS2: 5116	AHS7:)	AHS7:)	AHS7:)	AHS7: 3654
$(MJ m^{-2})$	AHS7: 5846	AHS8:) 8352	AHS8:) 5846	AHS8:) 4176	AHS8: 3654
	AHS8: 6577				
Maximum duration (h)	AHS2: 3500	AHS7:)	AHS7:)	AHS7:)	AHS7: 3500
	AHS7: 4000	AHS8:) 4000	AHS8:) 4000	AHS8:) 2000	AHS8: 3500
	AHS8: 4500				

TABLE II	Climatological	data for	naturally	exposed	samples
----------	----------------	----------	-----------	---------	---------

Year	Temperatur	e (°C)		Relative Humidity (%)			Rain (mm)	Rain (h)	Wet (h)	Solar max. (°C)	Bright sun (h)	Sun (1) (L)
	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Total	Total	Total	Mean	Total	Total
1975	30	- 4	8.9	95	60	78	431	420	1864	36.7	1376	93855
1976	30	- 9	8.9	93	62	77	552	488	2174	35.7	1294	85677
1977	26	- 11	8.4	94	67	80	522	540	2406	35.4	1179	85103
1978	26	- 11	8.4	94	62	79	636	610	2381	35.1	1056	65759
1979	26	- 15	7.9	92	64	78	708	628	2017	32.6	1209	81087
1980	27	- 7	8.6	93	61	77	646	573	2271	32.9	1158	78 596
1981	26	-17	8.4	92	61	77	591	488	2475	34.8	1273	84788
1982	27	-16	8.9	93	61	77	521	476	2099	34.2	1313	85879
1983	29	-8	9.0	93	64	78	569	533	1920	33.4	1244	81214
1984	27	- 8	8.7	91	58	75	540	517	2229	34.9	1303	86282
1985	25	-10	8.1	93	61	77	564	572	1981	Δ	1152	76 584
1986	27	-12	7.2	92	56	74	644	366	1082	38.2	Δ	54769
1987	26	- 7	8.2	96	71	84	667	552	1961	Δ	1174	75086
1988	26	-10	9.0	93	66	80	557	557	1945	40.8	1464	81 243
1989	30	- 6	9.5	93	64	78	339	334	1611	41.3	1645	87271
1990	34	- 6	9.8	Δ	Δ	Δ	536	Δ	1556	40.9	1491	81 187

1. Wetness (h) – total wetness due to rain and dew.

2. Bright sun hours - measured using a Campbell-Stokes sunshine recorder.

3. The Solar maximum temperature refers to a standard black bulb thermometer (made by Solar Max).

4. Solar radiation data applies to surfaces facing south  $45^{\circ}$ .

5. L (Langley) =  $4.19 \times 10^{-4}$  J m<sup>-2</sup>.

6. Symbol  $\Delta$ : Equipment failure

Data supplied by Tioxide UK Ltd. Technical Service Dept. Weathering Station, Cleveland, England

particular sample at ten different locations on the exposed surface. The repeatability of the mean value of the ten indents was within 10%. The choice of *ten* indents was based on repeated determination of hardness on a sample until the mean value of the hardness, as a function of the number of indents, converged.

Chemical composition was measured using FTIR (B10-Rad FTS-7) with photoacoustic cell attachment, and a scanning electron microscope with energy dispersive X-ray (EDX) analysis. The SEM was used mainly in plan (i.e., from the top surface) but measurements were also made in profile after sectioning of the sample. In order to ensure reliable statistics at different depths in the latter case a rectangular section of height 6  $\mu$ m and length of about 20  $\mu$ m was scanned and this was repeated at 10 to 12 different locations along a plane at the same distance from the top edge.

Colour measurements were recorded on a Pacific Scientific Spectrogard colour system and conformed to BS 3900 Pt D9. Gloss measurements were made generally using a Rhopoint Labgloss instrument with a  $60^{\circ}$  head and a large port hole (about 420 mm<sup>2</sup>) in accordance with BS 3900 Pt D5. However, for assessment of the effect on gloss of ultrasonic cleaning of the samples a Rhopoint Novogloss Gloss Comparator with a port hole of about 75 mm<sup>2</sup> was used because of limitations in size of the particular samples evaluated.

Mechanical tests to fracture were not possible on the particular window profiles because of the distinctive non-uniform geometry of the extruded material and, in the case of naturally exposed samples, limited availability of material.

#### 3. Results

The work in this study involved three materials, five exposure cycles and a natural exposure, and different indices of degradation. The range of data is too great to reproduce in its entirety in this paper and a number of the figures, illustrating colour change for example, have been excluded. Nevertheless, the full set of figures are included in a National Physical Laboratory report [17].

#### 3.1. Hardness

The measured values of the microhardness of the artificially weathered AHS8 material are shown as a function of dose per unit area (for brevity this will be referred to simply as dose) and weathering cycle in Fig. 1. The depth of indent for the 0.29 N load ranged from about 14 µm for the aged but unweathered material to 19  $\mu$ m for cycle 1 at a dose of 6.6 GJ m<sup>-2</sup>. There is indication of the onset of recovery of properties, certainly in cycles 1 and 2. These results would appear supportive of loss of surface layer as reported elsewhere [4] and indeed the surface is very powdery after this degree of exposure. Cycle 3, for which the temperature was elevated with respect to the other cycles, shows significant hardening. In practice, the surface was very powdery indeed at a dose of  $4.0 \text{ GJm}^{-2}$  and, although tests at longer duration were conducted, it was not possible to optically resolve the indents because of the degraded surface state.

The effect of varying the indenter load was evaluated for cycle 1 (Fig. 2). At a dose of 6.6 GJ m<sup>-2</sup> the nominal indent depths were 19, 23 and 30  $\mu$ m for the



*Figure 1* Variation of the mean values of the Vickers hardness with exposure period for the AHS8 material. Key: ( $\Box$ ) cycle 1, ( $\bigcirc$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamondsuit$ ) cycle 5.



*Figure 2* Effect of load on the mean value of the Vickers hardness with exposure period for the AHS8 material (cycle 1). Key: ( $\Box$ ) 0.29 N, ( $\bigcirc$ ) 0.54 N, ( $\triangle$ ) 1.03 N.

three applied loads. The details of the variation of hardness with dose changed slightly but the general trend was maintained. The lack of recovery in hardness at the lowest (standard) load is surprising in view of the evident recovery at the higher loads. For this pyramidal indenter, the layer constituting the first 10% of overall indent depth contributes 49% of the volume of the indent. A change in hardness of the very top surface could then have a significant effect on the hardness measurements. The lack of apparent recoverv for the smallest load may reflect greater sensitivity to the very near surface conditions, and thus subsequent exposure damage to the newly exposed surface. Alternatively, the sustainment of softening of the shallower indents may be due to the gradual loss of the thin hard outer crust ( < 150 nm) detected in nanoindentation measurements [13].

Cyclical variation in hardness is observed more obviously for AHS7 (Fig. 3). The distinctive features in contrast to AHS8 are the more rapid onset of surface loss, indicated by the minimum at smaller values of dose, and the more limited degree of recovery relative to the initial hardness value. Mid-thickness measurement of hardness confirmed that the hardness of the unexposed material represents the bulk material and not simply a surface hardened region which had subsequently been removed by weathering. The minimum



*Figure 3* Variation of the mean value of the Vickers hardness with exposure period for the AHS7 material. Key: ( $\Box$ ) cycle 1, ( $\bigcirc$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamondsuit$ ) cycle 5.



*Figure 4* Variation in the mean value of the Vickers hardness with exposure period for the AHS2 material. cycle 1.

in hardness for cycles 1 and 2 occurs at fairly similar values of radiant exposure, paralleling the results for AHS8. Cycle 4 shows the lowest value of hardness, although the minimum occurs at the same dose as for cycle 2. In contrast to AHS8, there is a clear decrease and partial recovery in hardness for cycle 3.

The limited availability of AHS2 material limited its exposure solely to cycle 1 (Fig. 4). Nevertheless, the data show the same trend as for the other materials. The minimum in hardness occurs at a somewhat smaller value of dose relative to AHS7.

The results for the naturally weathered samples (Fig. 5) suggest a minimum in hardness for the AHS2 material but there is no recovery distinguishable for the AHS8 or AHS7 materials despite being subjected to greater doses. Interestingly, the minimum in the value of hardness for naturally weathered AHS2 is similar to that for cycle 1.

#### 3.2. Chemical composition

The measurement of the chemical composition was made using the complementary techniques of scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and FTIR with a photoacoustic attachment.



*Figure 5* Variation of mean value of Vickers hardness with exposure period for naturally weathered material. Key: ( $\Box$ ) AHS8, ( $\bigcirc$ ) AHS7 and ( $\triangle$ ) AHS2.

# 3.2.1. SEM-EDX measurements

The SEM-EDX was used to monitor the relative concentrations of calcium, titanium and chlorine as a function of exposure conditions in plan and to a limited extent in profile. Estimation of the depth of sampling for composite material analysed in plan by this method is very uncertain but would be about 7  $\mu$ m. The SEM only gives information about relative concentrations (i.e., relative to the total counts) of detectable species and should only be considered a semi-quantitative technique.

The loss in the calcium content was significant and strongly affected by exposure conditions and time.  $TiO_2$  is very insoluble and will have little tendency to be lost. Indeed, loss of adjacent material may leave  $TiO_2$  standing proud on the surface with a consequent loss of gloss. The limitation with the SEM technique in this context is the depth of sampling which may not allow the very near surface detail to be resolved. No loss of Ti was observed for either the naturally weathered material or artificially weathered material. The SEM data appeared to show a slight increase of Ti but this was probably an artefact associated with the loss of Ca and the derivation of concentration as a percentage of the total count.

The loss of Ca (at %) from AHS7 and AHS8 samples investigated in plan are shown in Figs 6 and 7 for the artificially weathered samples and in Fig. 8 for the naturally weathered materials. The Ca content is observed to decrease in all cases but the magnitude and rate of change are strongly affected by the exposure conditions and investigated material. The AHS8 sample shows a slightly greater loss rate (versus dose) than the AHS7 sample under natural weathering conditions while they both show indications of cyclical variation of calcium concentration. Cycles 1 and 5 would appear to be the least severe in relation to the rate of loss of calcium with dose for AHS8, although cycle 1 was aggressive for AHS7. For both materials, the high temperature cycle, cycle 3, was aggressive in terms of calcium loss.

In assessing the effect of different exposure cycles it is important to recognise that, for the same dose, the exposure *time* will be different for different levels of



*Figure 6* Variation of the Ca content with exposure period on the surface of the AHS8 material. Key: ( $\Box$ ) cycle 1, ( $\bigcirc$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.



*Figure 7* Variation of the Ca content with exposure period on the surface of the AHS7 material. Key: ( $\Box$ ) cycle 1, ( $\bigcirc$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.



*Figure 8* Variation of the Ca content with exposure period on the surface of naturally weathered material. Key: ( $\Box$ ) AHS8 and ( $\bigcirc$ ) AHS7.

irradiance. The loss of calcium carbonate will be a time dependent process and, for example, the timebased rate of loss of calcium for cycle 2 relative to cycle 1 is even faster than is apparent from Fig. 6.

The reproducibility of these measurements was tested for a range of exposure conditions by a different

![](_page_5_Figure_0.jpeg)

*Figure 9* Variation of the Ca content with cross-sectional depth for the AHS8 material (cycle 1,  $5.12 \text{ GJ m}^{-2}$ ).

![](_page_5_Figure_2.jpeg)

*Figure 10* Variation of the Ca content with cross-sectional depth for naturally weathered AHS8 material ( $30.07 \text{ GJ m}^{-2}$ ).

operator. The maximum difference in measured value was less than 25%. In addition, measurements were made at different positions along the sample to allow for any variability in sampling position. The variability was less than 10%. Thus, the detailed variations in the Ca content for AHS7, cycle 1, for example, would be inferred to be real.

Depth profiling of the calcium content is time consuming because of the requirement for good statistics, and the range of investigation was confined mainly to AHS8 and to cycle 1 and naturally-exposed material only. Examples of the profile for these exposure conditions are given in Figs 9 and 10. In order to simplify comparisons, the depth of depletion relative to the bulk value was evaluated and plotted against dose as is shown in Figs 11 and 12. An evident peak in value occurs between  $4.0-5.0 \text{ GJm}^{-2}$  for the artificially weathered material and matches the minimum in hardness for cycle 1 in Fig. 1. The rate of change of the depth of the depletion zone of calcium after the peak (Fig. 11) would imply that the surface is eroding at a rate of about 88 µm per annum for these artificial weathering conditions. The variation of depth of depletion of calcium with exposure period for the naturally weathered sample has a very similar characteristic trend to the variation in hardness.

![](_page_5_Figure_7.jpeg)

*Figure 11* Variation of Ca depletion depth with exposure period for 12 AHS8 material (cycle 1).

![](_page_5_Figure_9.jpeg)

*Figure 12* Variation of Ca depletion depth with exposure period for naturally weathered AHS8 material.

#### 3.2.2. FTIR measurements

The measurement of interest from the perspective of FTIR are the stretching bands associated with CO<sub>3</sub>, CO and polyene. However, problems of water vapour and CO<sub>2</sub> contamination in this instrument interfered with measurements in the critical wavenumber range of interest, 1400–1800 cm<sup>-1</sup>. Accordingly, characterization of the variation of the polyene absorbence peak with weathering was not feasible. Fortunately, the CO<sub>3</sub> moiety exhibits a characteristic absorbence band at 875 cm<sup>-1</sup> associated with the three C-O bonds bending towards each other. Absorbence bands corresponding to aliphatic C-O (C-O-C or C-O-H) stretching in the range 1050–1150 cm<sup>-1</sup> should give a measure of the build up of oxidation products such as ethers, peroxides and/or hydroxyl groups. No attempt was made to specifically identify the various degradation species since this was not a critical requirement within the context of the project objectives and has been discussed elsewhere  $\lceil 6 \rceil$ . In quantifying the variation in carbonate concentration with exposure period the ratio of the peak area, after subtraction of the background, to that for a C-H deformation  $(1329 \text{ cm}^{-1})$  was used on the basis that the latter would be unaffected by exposure and there would be a consistent reference. In determining the variation in

![](_page_6_Figure_0.jpeg)

*Figure 13* Variation of CO<sub>3</sub> with exposure period for the naturally weathered materials: ( $\square$ ) AHS8, ( $\odot$ ) AHS7 and ( $\triangle$ ) AHS2.

![](_page_6_Figure_2.jpeg)

*Figure 14* Variation of CO<sub>3</sub> with exposure period for the AHS8 material. Key: ( $\square$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\nabla$ ) cycle 4 and ( $\diamond$ ) cycle 5.

C–O concentration the peak height at  $1095 \text{ cm}^{-1}$  was used in calculating the relevant ratio to the reference peak. Peak height rather than area was used in this case because of the overlap of neighbouring peaks. Where absorbance bands overlap there will be uncertainty in reliable quantification, whether using peak area or peak height. Much will depend on the detailed shape of the spectral bands and extent of overlap. The peak height was considered more reliable for these data.

The variation with dose of the intensity of the absorbence band associated with CO<sub>3</sub> for the naturally weathered samples is shown in Fig. 13 and an example for the artificially weathered samples in Fig. 14. Comparison of the FTIR and SEM results for the naturally exposed samples (Figs 13 and 8) indicates similarity for AHS8 but less accord for AHS7 in relation to the rate of loss of calcium carbonate. The loss of carbonate detected by FTIR compares reasonably well with the loss of calcium determined by SEM for the artificially exposed AHS8 material in terms of the dependence on dose and exposure cycle (Figs 14 and 6). The basic cyclic variation of the data with dose was matched also for the AHS7 material but there were some specific differences. The depth of sampling of the material for the SEM and FTIR techniques will be different and hence some variations in detail might be

![](_page_6_Figure_6.jpeg)

*Figure 15* Variation of C–O abs. with exposure period for the AHS8 material. Key: ( $\boxdot$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.

![](_page_6_Figure_8.jpeg)

*Figure 16* Variation of C–O abs. with exposure period for the AHS7 material. Key: ( $\Box$ ) cycle 1, ( $\Box$ ) cycle 2, ( $\odot$ ) cycle 3, ( $\triangle$ ) cycle 4 and ( $\nabla$ ) cycle 5.

![](_page_6_Figure_10.jpeg)

Figure 17 Variation of C–O abs. with exposure period for the AHS2 material.

expected although uncertainty in measurement may also be a factor.

The change with artificial weathering of the intensity of the absorbance band associated with the C–O stretching mode is shown in Figs 15–17. The range of uncertainty indicated in these figures represents the

![](_page_7_Figure_0.jpeg)

*Figure 18* Variation of C–O abs. with exposure period for naturally weathered samples of  $(\Box)$  AHS8,  $(\odot)$  AHS7 and  $(\triangle)$  AHS2.

variability of results obtained for the unweathered sample determined in a series of repeated tests. This is reflective of general measurement variability associated with the particular measurement process.

In view of the magnitude of the uncertainty associated with the results, emphasis on detailed variation would be inappropriate. Nevertheless, some broad trends can be reasonably identified. For example, in Fig. 15, a peak at  $5.0 \text{ GJ m}^{-2}$  for exposure of AHS8 to cycle 2 can be discerned, whilst an initial decrease and subsequent increase to a plateau can be identified for cycle 1. The AHS2 material exposed to cycle 1 appears to show a peak although, again, uncertainty levels for these measurements are significant.

The variation of C–O with exposure period in the naturally weathered samples (Fig. 18) is comparatively small but some indication of a build up in concentration with exposure for the AHS2 and AHS8 materials is evident although the loss of C–O for AHS2 is not easy to rationalize.

#### 3.3. Colour

Colour variations with exposure were evaluated in terms of the quantitative colour indices da, db, dL and dE where a denotes the red/green value; b the yellow/blue value and L defines lightness. The total difference in these parameters is denoted by a single value, dE. The most significant change in colour for these materials is generally towards the yellow. In all materials, for most artificial weathering cycles, the colour index showed indications of a cyclic variation with dose, or at least the first stages of change and recovery (Figs 19-21). In the case of the AHS8 material (Fig. 19), the artificial weathering in cycles 1 and 2 resulted in an initial peak in db (and dE), associated with yellowing of the material followed, by a subsequent minimum. Cycle 3 gives rise to an almost continuous increase in yellowing but with a maximum occurring towards the end of the exposure period. The AHS7 material showed an initial increase in yellowing for cycle 1 with a subsequent peak and then a minimum, but for cycles 2 and 3 an initial decrease in db was observed before some degree of partial recovery ensued. The AHS2 material exposed to cycle 1 showed

![](_page_7_Figure_8.jpeg)

*Figure 19* Variation of colour (db) with exposure period for the AHS8 material. Key: ( $\boxdot$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.

![](_page_7_Figure_10.jpeg)

*Figure 20* Variation of colour (db) with exposure period for the AHS7 material. Key: ( $\boxdot$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.

![](_page_7_Figure_12.jpeg)

*Figure 21* Variation of colour (db) with exposure period for the AHS2 material (cycle 1).

a generally similar response with exposure but with the peak and the minimum shifted, and with the extent of change also being different.

The behaviour of the naturally weathered material (Fig. 22) is more complex. A concern with these latter measurements was the long duration after removal from exposure before measurements were made. In order to investigate the effect of ageing, artificially weathered samples were stored in the dark and

![](_page_8_Figure_0.jpeg)

*Figure 22* Variation of colour (db) with exposure period for the naturally weathered samples of  $(\boxdot)$  AHS8,  $(\odot)$  AHS7 and  $(\triangle)$  AHS2.

![](_page_8_Figure_2.jpeg)

*Figure 23* Colour (db) variation with storage period after 2000 h  $(2.92 \text{ GJ m}^{-2})$  artificially weathered of the AHS8 material.

removed for colour measurement at regular intervals. The results are shown in Fig. 23 and indicate a marked ageing effect. In contrast, variation in  $CO_3$ , for example, with storage period was minor. The consequence is that the colour measurements of the naturally weathered samples do not provide a good reference framework for the evaluation of the effects of artificial weathering.

Whilst the shift in db was the most significant feature for most exposure cycles, the AHS8 material experienced a very significant shift to red for the higher temperature cycle 3 with a correspondingly visible "pinking" of the material. This pinking is most probably associated with the photoactivity level of  $TiO_2$  in the AHS8 material which results in the production of radicals and enhanced degradation [18]. The photocatalytic activity of  $TiO_2$  tends to become more pronounced with increasing temperature [19].

Ultrasonic cleaning of the naturally weathered samples was carried out to assess the impact of dirt accumulation on the surface of the window profiles. The cleaning had a marked effect on the whiteness of the samples and for each sample an increase in whiteness of the order of 2–4 L units was observed. No discernible variation in the other colour parameters was observed.

#### 3.4. Gloss

The results of gloss measurement of the artificially weathered samples (Figs 24–26) show a fairly consistent pattern. A steady decrease in gloss with exposure period occurs followed by a more rapid fall off, consistent with surface erosion, and then a levelling off at a very low value. The dose corresponding to the onset of the more rapid degradation was sensitive to material and exposure conditions. There was indication of a slight partial recovery of gloss of AHS7 prior to the onset of erosion which may reflect the loss of surface asperities. The uncertainty in the reported gloss measurements mainly arises from variations across the sample, the magnitude of which varies with exposure conditions. The error bars in Figs 24–26 reflect the maximum uncertainty in the data.

In view of the accumulation of dirt on the naturally exposed samples, measurements were also made after ultrasonic cleaning in distilled water. Differences were observed but since the tests carried out on artificially weathered samples also showed a significant change this approach was abandoned.

The results for AHS7 showing a marked increase in gloss of the naturally exposed samples (Fig. 27) are

![](_page_8_Figure_11.jpeg)

*Figure 24* Percentage gloss retention with exposure period for the AHS8 material, after: ( $\boxdot$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.

![](_page_8_Figure_13.jpeg)

*Figure 25* Percentage gloss retention with exposure period for the AHS7 material, after: ( $\boxdot$ ) cycle 1, ( $\odot$ ) cycle 2, ( $\triangle$ ) cycle 3, ( $\bigtriangledown$ ) cycle 4 and ( $\diamond$ ) cycle 5.

![](_page_9_Figure_0.jpeg)

*Figure 26* Percentage gloss retention with exposure period for AHS2 material (cycle 1).

![](_page_9_Figure_2.jpeg)

*Figure 27* Percentage gloss retention with exposure period for naturally weathered samples of  $(\Box)$  AHS8,  $(\odot)$  AHS7 and  $(\triangle)$  AHS2.

exceptional. Manhandling of the material was considered unlikely since this would show up under optical observation. The likely explanation is inconsistency in gloss of the original sample with respect to the control, aged, sample. The rate of loss of gloss for the naturally exposed AHS8 shows very different behaviour from that of the artificially exposed with no evidence of the marked increased in rate associated with erosion observed for the artificially exposed samples. Indeed, the rate of loss of gloss decreases at the longer exposures.

#### 4. Discussion

The objectives of accelerated testing are to provide a satisfactory ranking of materials and a measure of the potential life of a product. In both cases it is important that the degradation of properties generated by the artificial weathering follows the same mechanism path. The prediction of long term performance in natural conditions depends on the ability to predict the *rate* of degradation in natural weathering. It is insufficient to demonstrate that 2 months in the weatherometer with a specified weathering cycle is equivalent to 2 years say in natural conditions, for which data may be known as a reference point, unless there is a framework for predicting the extent of degradation at 15 years for example. In any degradation process there will usually be a single point equivalence.

For the ranking of materials the requirement is less stringent and it is simply necessary to demonstrate that the relative performance of the different materials in terms of the extent of degradation is consistent with that observed in natural conditions. Nevertheless, it is conceivable that problems could arise if the rate of degradation is not varying consistently for the different materials, so that a cross-over occurs.

In assessing which weathering cycle best simulates natural behaviour a minimum requirement is that it should adequately rank the materials. In the absence of specific rate equations for degradation this enables confidence that broad predictions can be made based on comparison with practical experience of the performance of materials already in service for an extensive period.

A range of property measurements were made in this study, some directly related to performance such as colour and gloss and others indirect such as hardness. Direct in this context represents practical measures of degradation such as loss of cosmetic appearance or mechanical integrity while indirect measures may be considered indices of change in properties related to those parameters. A first step in the evaluation is to establish the extent of consistency in the varied measures of degradation and to use the critical parameters as a basis for identifying the most effective weathering cycle capable of predicting temperate exposure while retaining the maximum degree of acceleration.

Thus, the three key issues to be resolved are:

- (1) the extent to which individual measurement methods give consistent indicators of degradation;
- (2) the effect of changing artificial weathering parameters on the material properties; and
- (3) the extent to which artificial weathering correlates with natural weathering in terms of rate prediction and ranking.

# 4.1. Consistency of measurement parameters

The parameters measured in this study reflect mechanical, chemical and physical properties of the material. An explicit functional relationship between these would be surprising. Nevertheless, it might be expected that similar trends in behaviour would be observed since in different ways they will reflect degradation of the material. The most distinguishing feature of accelerated degradation of this UPVC material is the recovery of properties in a number of cycles associated with erosion of the surface. The steps in the degradation of UPVC have been summarized succinctly by Magnus [4]:

(1) Dehydrochlorination leads to the formation of conjugated double bonds. When their number exceeds eight the double bonds absorb visible light and yellowing results.

(2) Oxidation of the double bonds causes disruption of the polyene sequence leading to the reduction and

possible disappearance of yellowing. Also, water-sensitive molecules are formed and are removed from the surface. The oxidation can also lead to chain scission. (3) Disintegration of the surface can result from oxidation and crosslinking leading to high surface stresses and microcracking. The microcracks cause a diminution of mechanical properties and the loss of surface due to erosion is accompanied by a loss of gloss. A recovery of certain properties is obtained and the process repeats itself leading to a cyclical variation in properties with exposure time.

The relative effects of ultra-violet (UV) bond dissociation and oxidation processes will be a function of distance from the exposed surface and exposure conditions. Thus, a high UV irradiance might be expected to consume oxygen close to the surface. The presence of a dark period in natural exposure can allow ingress of oxygen to greater depths and influence the detailed reaction processes.

In temperate climates, the cyclical nature of the degradation process is not commonly observed. Nevertheless, the AHS2 material examined in this study did show some indication of the commencement of recovery in relation to hardness, and to some extent in the blue-yellow colour index db [17].

The accelerated artificial weathering provides a more extensive framework for comparing different measures of material properties. In that context, there is a consistent pattern of degradation and recovery identifiable for the most extended exposure cycles, cycles 1 and 2. For AHS8 exposed to cycles 1 and 2 this appears as a recovery in hardness after initial softening (Fig. 2), in calcium concentration (Figs 6 and 11), in the colour parameter db (Fig. 19), in the C-O concentration to some extent (Fig. 15, cycle 2), and as a discrete acceleration in the rate of loss of gloss (Fig. 24). For example, the minimum in hardness for cycle 1 occurs at about  $5.0 \text{ GJ m}^{-2}$  and this is consistent with the minima and/or maxima in the other parameters. Hence, all of the parameters show a consistent and characteristic trend for these two cycles. This is illustrated in Fig. 28 in which the various property measurements have been compared using simple scaling.

There are more detailed fluctuations in colour, with a peak followed by a minimum. This behaviour most probably reflects initial yellowing due to the formation of the polyene sequence, oxidation causing bleaching, and then surface removal.

The depth of depletion of calcium carbonate (Fig. 11) is interesting. The loss of calcium carbonate in laboratory exposures is due to dissolution in the presence of water and HCl generated by dehydrochorination. The depth of depletion, up to about 15  $\mu$ m, implies that there is a pathway for the ingress of water, reaction with the carbonate and removal of product. The conceptual image is a network of cavities linked by small cracks carrying the water. Indeed, examination of the weathered surface with the scanning electron microscope indicated a very porous structure [17]. The porous structure appears to develop most significantly for the naturally weathered material. The calcium carbonate particles or their remnant

![](_page_10_Figure_6.jpeg)

*Figure 28* Variation of property measurements with exposure period for the AHS8 material (cycle 1). Key: ( $\boxdot$ ) HV, ( $\odot$ ) % Ca, ( $\triangle$ ) gloss and ( $\nabla$ ) C–O abs.

cavities may act as local stress/strain raisers amplifying the thermal stresses and strains inherent in the heating and spraying cycle and causing cracking between. The loss of calcium carbonate will also affect the hardness of the material. The reduction in hardness will reflect not only chain scission but also loss of filler.

For cycle 3, in which the temperature was significantly elevated, the exposure conditions were so severe for the AHS8 material that cyclic behaviour was not observed for all parameters. The hardness and colour index db did not show simple behaviour, in the former case because of very marked disintegration of the surface.

The pattern of behaviour of the AHS7 material is broadly similar to the AHS8 material in showing a correlation between different parameters with respect to the onset of recovery.

It may be concluded that all of the parameters measured at different exposure periods for the different cycles give a reasonably consistent indication of the recovery of properties, with exception of cycle 3. However, it does not appear possible to predict the onset of surface loss and recovery in properties in relation to any critical change in any measured parameter.

Perhaps the most surprising overall feature is that the recovery is a gradual process in all cases even with respect to the calcium level (Fig. 11). If extensive micro-cracking and porosity is developing on the surface it might have been anticipated that when a sufficient degree of deterioration of the surface was achieved some discontinuous loss of material may have occurred. In practice, this may happen but on a small scale and in the approximate 500 h exposure interval it would not be apparent as a discontinuous process. The surface removal appears as a slow continuous erosion which at the same time is "competing" with the effect of radiation on the newly exposed surface. This would imply that the onset of erosion may not be at the minimum in hardness but occurs prior to that perhaps in a very near surface region. As will be discussed in a later section, the rate of change of hardness undergoes a minimum at doses less than that associated with the minimum in hardness.

The indications from the long exposures are that the rate of degradation and surface removal reach a dynamic balance once the initial surface of the material is degraded. This is most clearly apparent for a AHS7 sample exposed to cycle 2.

#### 4.2. Effect of weathering parameters

Five weathering cycles were investigated in this study focusing on the effect of changing the level of irradiance, of temperature and of water spray cycle. Cycle 1 corresponds to the draft CEN standard on artificial weathering.

In comparing cycles 1, 2 and 5 the white panel temperatures are approximately the same with only the irradiance changing. Nevertheless, the exposure time at a given level of radiation will increase with a decrease in irradiance. Cycles 2 and 4 differ solely in the water spray cycle. The variation in white panel temperature for these two cycles was insignificant.

In some cases, the exposure period was limited so that full evidence of the cyclic characteristics of the degradation process did not appear. This is particularly true for cycle 5. Also, it was not possible to obtain the full range of property measurement in every case.

The perception of the effect of different cycles depends to an extent on the particular material and property measurement. In comparing cycles 1 and 2 for AHS8, the hardness diminishes most significantly for cycle 1, perhaps due to reduced oxygen penetration as a consequence of the higher irradiance (and hence oxygen consumption) of cycle 2. The onset of recovery in hardness appears at a slightly lower value of the dose. The latter trend is observed also with respect to the measurements of the colour index db, but for cycle 5 there is little variation of db with exposure period. The loss of calcium carbonate with radiant energy density is more rapid for cycle 2. There is also little difference with respect to the loss of gloss for the different cycles.

The response of AHS7 to cycles 1, 2 and 3 is broadly similar to that for the AHS8 with respect to hardness. There was little apparent sensitivity of this material with respect to colour changes. The increased rate of loss of calcium carbonate for cycle 2 in relation to cycle 1 is also repeated for this material. The loss of gloss is somewhat more rapid for cycle 2 relative to cycles 1 and 5.

On the whole, the differences between cycles 1, 2 and 5 are not particularly distinct in character or in magnitude. However, the test time for cycle 2 is inherently shorter for the same dose level. Solely on the basis of the artificial weathering, cycle 2 would be the optimum choice. This cycle is reasonably similar to that suggested in the draft International Standards Organisation ISO standard (ISO/DIS2 4892-2).

A comparison of cycles 2 and 4 should give an indication of the impact of the water spraying period. Differences in the hardness were apparent only for AHS7 for which the minimum in hardness was lower for the longer spray cycle. There was no distinction of the different cycles in terms of dE [17] but there was

a difference in detail with respect to db although the distinction for both AHS8 and AHS7 samples largely rests on single data points. The rate of loss of carbonate for the AHS8 and AHS7 samples would appear to be broadly similar, within the measurement uncertainty, for both cycles. There was no discernible difference in gloss for the different cycles. Thus, it may be inferred that an extended water spraying has a distinguishable but only a small impact on the material properties relative to the conventional test. This conclusion is in agreement with the summary of Decker [7] although it would not apply to outdoor weathering for which acid rain and pollutants would potentially have an effect.

In essence, the overall differences between cycles 1, 2, 4 and 5 may be considered to be minor. However, cycle 3, in which the white panel temperature was  $55 \,^{\circ}$ C, showed very distinctive behaviour. The AHS8 material developed a very powdery surface after a short time period making hardness evaluation difficult and the loss of hardness and the onset of recovery was more rapid for the AHS7 material. Similarly, the loss of calcium carbonate from the surface was more rapid than for cycles 1 and 2. The colour of samples exposed to cycle 3 showed very marked variations in all parameters with respect to the other cycles. The loss of gloss of both the AHS7 and AHS8 samples was most rapid for cycle 3.

It may be suggested that significantly raising the temperature as a method of accelerating weathering will introduce very marked changes compared to the effect of the variations in level of irradiance investigated in this study. The appropriateness or otherwise of this approach depends on comparison with natural weathering and that is discussed in the next section.

### 4.3. Correlation of artificial weathering with natural weathering

### 4.3.1. Predicting rates of degradation

The difficulty in quantitative prediction of natural weathering is illustrated by comparison of the hardness data for the AHS8 sample exposed to cycle 1 (Fig. 1) with the data for natural weathering (Fig. 5). This is set out more explicitly in Fig. 29 in which the

![](_page_11_Figure_15.jpeg)

*Figure 29* Rate of change of Vickers hardness with dose for the AHS8 material (( $\boxdot$ ) cycle 1 and ( $\odot$ ) naturally weathered) for a 0.29 N load.

rate of change of hardness with dose is plotted as a function of dose. In the case of the artificially weathered sample, the rate of change of degradation with dose is greatest at  $3.0 \text{ GJ m}^{-2}$  (appearing as a minimum in Fig. 29 simply by virtue of the negative sign representing a loss of hardness) and then diminishes as the character of the surface changes. This may represent shielding of the underlying substructure as the degraded layer builds up or the onset of gradual erosion of the surface.

Although not apparent for AHS8, the continuing exposure of the samples leads to a *cyclic* process of surface damage and erosion. This process is observed most evidently for AHS7 exposed to cycle 2 (Fig. 3). After the initial hard surface layer is removed the amplitude of the cyclic change diminishes and the hardness then dynamically depends on the competitive processes of damage and recovery. Dampening of the cyclic change with exposure period occurs until the cyclic change is small.

Resistance to colour change is probably the most important performance parameter for the application of these materials. Unfortunately, the dependence of colour on the time of removal from exposure, demonstrated in Fig. 23, means that there is no reference basis in the naturally exposed samples with which to make comparison, since the samples were stored for years prior to measurement. The correlation in behaviour between colour and hardness described earlier suggests that quantitative prediction of the rate of change of the colour parameters will also be difficult.

The degradation of gloss is simpler in character with three stages being clearly apparent namely initial decay; loss of surface and more rapid degradation; levelling off at a low level of gloss. A consideration of Fig. 27 (e.g., AHS8 gloss data) suggests that the behaviour of the naturally weathered samples is not simple, with an initial high rate of degradation followed by a slower rate. It is inconceivable that fitting of equations to the gloss data of the artificially exposed samples (prior to surface erosion) can predict this behaviour even with scaling of the data. A problem here may be the contamination of the naturally exposed samples with other material of one form or other, and the uncertain effect of pollutants on degradation. Unfortunately, the destructive effect of cleaning means that it is not possible to isolate the "intrinsic" gloss. The accumulation of dirt on the surface may be a factor also in the extent of UV absorption.

In conclusion, the intrinsic dependence of the development of the degraded layer on exposure conditions and, for these materials, the subsequent erosion means that it can be inherently difficult to establish rate equations which can be meaningfully transferred from artificial weathering to natural exposure discussions. The prediction of life times then greatly depends on the relative ranking based on known performances of specific materials.

# 4.3.2. Ranking of materials

For the ranking of materials, it is necessary to demonstrate that the relative performance of the different materials, in terms of the extent of degradation, is consistent with that observed in natural conditions. Implicit in this evaluation is an assessment of the relevance of the weathering cycle since the relative performance of the material could change according to the artificial exposure conditions. The important performance criterion is the resistance to change of the key parameters. The three materials will be compared with respect to a range of performance parameters.

In relation to colour change, for which satisfactory reference data for natural exposure are not available, the basis for comparison is solely with respect to the laboratory exposures. In that context, AHS2 would appear the least resistant material in so far as it showed the greatest change in db and dE when exposed to cycle 1. The AHS7 sample is more resistant to yellowing than AHS8 and does not show the marked deterioration in colour observed for AHS8 in the elevated temperature cycle, cycle 3. The TiO<sub>2</sub> concentration in the AHS7 sample is almost double that for AHS8 and this most probably accounts for its increased resistance to colour change.

The AHS7 sample can only be compared with the other materials with respect to loss of gloss solely on artificial exposure because of the anomalous natural weathering data. In terms of the exposure period to attain the minimum in gloss the AHS8 sample performs better than AHS7 sample which in turn performs better than the AHS2 sample. It would also appear that the more rapid decrease in gloss associated with surface erosion occurs at shorter exposure periods for the AHS7 sample with respect to AHS8 sample although the differences for the higher temperature cycle, cycle 3, are less obvious. A comparison of the AHS8 and AHS2 samples with respect to the loss of gloss of the naturally exposed samples indicates little difference. However, this may simply reflect the limited period of exposure.

A comparison of the resistance to change in hardness requires consideration of the initial value of the hardness which is similar for the AHS2 and AHS7 samples but much lower for the AHS8 sample. This is associated with the use of a chlorinated polyethylene impact modifier in the AHS8 material. The rate of loss of hardness of the materials exposed naturally is greatest for the AHS2 material with the AHS8 sample showing the most modest rate of change. The AHS8 sample also shows the greatest resistance to change in hardness for all cycles except for cycle 3 for which very rapid erosion of the surface appeared to occur.

The artificial weathering results may be summarized as follows:

- (1) AHS2 exhibits the poorest performance in all tests;
- (2) AHS7 shows best resistance to colour change;
- (3) AHS8 shows the greater resistance to change in hardness and surface erosion with the exception of cycle 3;
- (4) AHS8 shows the slowest rate of loss of gloss.

The natural weathering results may be summarized as:

(1) AHS2 shows the poorest performance in all reliable tests; (2) AHS8 shows the greatest resistance to change in hardness.

It is evident that the ranking of these materials is consistent for the natural and artificial weathering conditions provided that the artificial weathering is not too extreme, e.g., cycle 3 with regard to its effect on the AHS8 sample. All of the cycles would have been satisfactory for ranking of the materials but cycle 2 would be the most cost effective. In deciding which material has the best resistance to weathering the key issue is the critical performance criterion. Clearly, the AHS2 sample generally performs less well, although the lack of reliable colour data for the natural exposures precludes a definitive conclusion with respect to this parameter. The AHS7 sample shows a lower tendency for yellowing than the AHS8 sample although the magnitude of the change in either sample is comparatively small with the exception of AHS8 exposed to cycle 3. The AHS7 sample exhibits a greater rate of deterioration in hardness (a reflection of the mechanical properties) and gloss and a more rapid onset of surface erosion.

The explanation for the performance of the AHS7 material namely good colour stability but greater ease of erosion, may be associated with the suggestion that particular mixes of anastase and free chalking rutile grades of  $TiO_2$  produce faster bleaching which may lead to more rapid erosion [8].

It should be emphasized that the materials tested no longer represent current formulations. Hence, while useful for indicating the effectiveness of the artificial weathering cycles in predicting natural exposure the results do not reflect the properties of materials currently supplied by the different manufacturers.

In view of the conclusion in the previous section with respect to long term prediction for outdoor conditions and the need to depend more on ranking rather than quantitative prediction it is reassuring that consistent behaviour is predicted. In that context, it is important that a reference material, for classes of material, should be adopted for laboratory testing. This would provide a basis for quality control and for comparison of different weathering apparatus. More importantly, by utilizing a material whose long term outdoor performance is reasonably established there is then the possibility of obtaining an assessment of relative life prediction.

#### 5. Conclusions

The exposure of three different formulations of window-grade UPVC to artificial weathering conditions results in a process of surface damage followed by partial recovery which becomes cyclic in nature at long exposures, as described previously by Magnus [4].

The rate of degradation and surface removal by erosion achieves a competitive dynamic balance with the cyclic amplitude of the variation in properties gradually diminishing with exposure period.

Exposure of these materials outdoors in the temperature climate of the north east of England gave no indication of recovery for two of the materials despite exposure in one case for up to 16 years. One of the materials did exhibit a trend towards some recovery but the data were limited and firm conclusions could not be drawn.

The varied measures of degradation employed, namely microhardness, loss of calcium carbonate filler, colour and gloss, gave reasonably consistent indications of degradation, particularly with regard to the onset of partial recovery.

Varying the incident irradiance in the range  $0.25-0.5 \text{ Wm}^{-2}$  at approximately the same white panel temperature had an impact on the details of the variation of properties with dose but the general trends were not affected. Similarly, increasing the water spray period from 18 and 120 min to 30 and 120 min had only a small influence on behaviour. In contrast, increasing the white panel temperature from 44 to 54 °C at the same irradiance resulted in a dramatic deterioration in the performance of one of the materials.

Cycle 2, which utilizes the higher irradiance, is considered the most efficient weathering cycle, of the cycles studied, for characterizing the weathering resistance of these materials.

The intrinsic dependence of the development of the degraded layer on exposure conditions and, for these materials, the subsequent erosion means that it can be inherently difficult to establish rate equations which can be meaningfully transferred from artificial weathering to natural exposure conditions. Quantitative prediction of service life, based on laboratory testing, is not feasible in an absolute sense.

The four weathering cycles at moderate temperatures (1, 2, 4, 5) all gave a consistent ranking of the different materials and within the range of reliable data available gave ranking consistent with natural weathering.

The prediction of the relative resistance to natural weathering depends on the performance criteria used. One of the materials exhibited greater colour resistance but was more sensitive to surface erosion.

It is recommended that a reference material, of a specific material class, be established for testing in parallel with other materials being evaluated. This would enable quality control of testing, interlaboratory comparison and, by choosing a material with an established outdoor performance, a measure of potential service life.

# Appendix

#### Materials

## AHS2 specification

Various naturally weathered, acrylic modified, window and window sill profile extrusions; no control specimens available.

Supplied by Hydro Polymers, Newton Aycliffe, Co Durham UK.

#### Composition

Suspension PVC (K value, 66–68)	100 (phr)
Acrylic impact modifier	10.0

Acrylic processing aid	1.5
Ba/Cd/Pb-Lubricant master batch	4.5-5.0
(stabilizers are in the ratio 1:1:1 as salts,	
actual % metal, 25% Pb, 4.5% Cd and	
2.5% Ba; lubricants usually comprise poly-	
ethylene PE wax, paraffin wax and/or long	
chain fatty acids $\approx 2.5$ phr)	
TiO <sub>2</sub>	4.0-6.0
CaCO <sub>3</sub>	6.0
-	

## Natural exposure history

Samples were exposed at Newton Aycliffe, Co Durham (54°N 1°W) over a nine year period between the 18 April 1985 and the 5 March 1992. Sampling periods were 3, 6, 7 and 9 years.

## AHS7 specification

"Tropical" PVC window section supplied by EVC UK Ltd, Runcorn, Cheshire, UK, small control specimen and various naturally weathered cuttings from the faces of Corvic<sup>®</sup> (PVC resin) based, acrylic modified, profile extrusion; also  $\approx 5$  m of newly extruded profile based on the same composition.

## Composition

Corvic 68/173 (SPVC resin)	100 (phr)
Paraloid KM323B (impact modifier)	8.7
Stabilizer/Lubricant masterbatch	
(Pb/Ba/Cd)	6.5
Omyalite ( $CaCO_3$ filler)	6.5
Tioxide RS3230 (TiO <sub>2</sub> )	7.6

## Natural exposure history

Samples were exposed at Wilton Cleveland, UK  $(54^{\circ}N, 1^{\circ}W)$  over an eight year period between the 20 August 1984 and the 13 April 1992. Sampling periods were 1, 3, 5 and 8 years.

# AHS8 specification

Hostalit<sup>®</sup>Z (Hoechst AG) CPE (chlorinated polyethylene) modified window sill section; small control specimen and various naturally weathered cuttings from the exposed surface; also 3 m of newly extruded profile based on original formulation, kindly prepared by parent company in Sendenhorst, Germany. Supplied by EVC UK Ltd, Runcorn, Cheshire.

Composition	
SPVC/70	100 (phr)
CPE impact modifier	10.0

Ba/Cd stabilizer	2.0
Lubricants	1.7
CaCO <sub>3</sub>	6.0
TiO <sub>2</sub>	4.0

# Natural exposure history

Samples were exposed at Wilton, Cleveland, UK  $54^{\circ}N$   $1^{\circ}W$ ) over a 16 year period between the 10 December 1975 and 2 December 1991. The sampling periods were 1, 3, 5, 8, 15 and 16 years.

## Acknowledgements

This work was carried out as part of the 'Environmental Degradation of Materials Programme', a programme of underpinning research financed by the United Kingdom Department of Trade and Industry. The authors are grateful to the project advisory group consisting of N. Allen, D. Gardiner, J. Greig, P. Guy, R. Stephenson, N. Thomas and J. White, for their constructive comments during this programme.

#### References

- W. D. KETOLA and D. GROSSMAN, "Accelerated and outdoor durability testing of organic materials," ASTM STP 1202 (American Society for Testing and Materials, Philadelphia PA, 1993).
- 2. J. WHITE and A. TURNBULL, J. Mater. Sci. 29 (1994) 584.
- 3. P. PAGAN, Polymer Paint Colour J. 177 (1987) 648.
- 4. R. MAGNUS, Kunstoffe German Plastics 81 (1991) 19.
- 5. E. D. OWEN, "Degradation and stabilisation of PVC" (Elsevier, 1984).
- 6. J. SUMMERS and E. B. RABINOVITCH, *J. Vinyl Tech.* **5** (1983) 91.
- 7. C. DECKER, in "Degradation and Stabilisation of PVC", edited by E. D. Owen (Elsevier, 1984).
- 8. E. B. RABINOVITCH and B. F. GOODRICH, Polymers Paint Colour J. 183 (1993) 521.
- 9. R. B. BROWN, Polymer Testing 10 (1991) 3.
- 10. P. PAGAN, Polymers Paint Colour J. 176 (1986) 715.
- 11. L. CREDSON, Eur. Coat. J. 1-2 (1993) 34.
- 12. A. TURNBULL, N. FALLA, A. SMITH and D. WHITE, *Polymer Testing* **15** (1996) 455.
- 13. A. TURNBULL and D. WHITE, J. Mater. Sci. 31 (1996) 4189.
- 14. A. WOOTON, Alpas Technology, Private communication (1993).
- 15. Draft CEN standard, CEN/TC33/WP1/TG5 11GE, 1991.
- Commission Internationale de L'Eclairage, Technical Report– Solar Spectral Irradiance, Publ. No. CIE 85, Ist Edn. (1989).
- A. TURNBULL, N. FALLA, A. SMITH and D. WHITE, NPL Report CMMT (A) 45 (1996).
- W. WALRAEVENS, Solway S. A. Central Laboratory report, LC4 – WWS/RDC, (1993)
- 19. N. ALLEN, H. HASSAN and F. THOMPSON, *Eur. Polym. J.* **28** (1992) 817.

Received 19 April and accepted 19 December 1996