

# The Permanence of UV Absorbers in a Rubber-Modified Acrylic Film by UV/Visible Spectrophotometry

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## SYNOPSIS

A new analysis technique for UV/visible spectrophotometry is described. This technique is used to accurately determine the retention of several UV absorbers (UVAs) in a rubber-modified acrylic film during xenon arc accelerated weathering. The effects of reflectance, light scattering, and matrix absorbance are deconvoluted from the total apparent absorbance, resulting in an absorbance spectrum due to the UVA alone. All of the UVAs studied exhibit significant losses upon xenon arc exposure, which has important implications for the long-term durability of polymers that utilize these stabilizers. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Transparent polymer films are used in numerous weatherable applications such as clear top coats, film laminates, and free-standing films. Acrylics are a typical example of a transparent, weatherable polymer. Acrylics may also be modified with a dispersed rubber phase, generally an acrylate rubber, to enhance toughness.

When a transparent polymer film is used as a clear coating or laminate, it is necessary to protect the substrate from damaging wavelengths of UV light to prevent substrate degradation and delamination. A UV absorber (UVA) is often included in the coating in order to provide substrate protection or to minimize the depth of UV damage. These absorbers function by absorbing the damaging UV radiation and converting most of the radiation energy to heat energy (ground state vibrational relaxation).<sup>1,2</sup> The effectiveness of the UVA depends on many factors, including its absorptivity spectrum and concentration in the polymer. The light and heat stability and extraction resistance of the UVA are also important to maintain this effectiveness with time.

A physical loss of UVA can occur by diffusion to the polymer surface and subsequent loss through evaporation or physical removal.<sup>3,4</sup> Solubility, volatility, and diffusion coefficient of the UVA are all important to physical loss. Clearly, environmental conditions such as temperature and water or solvent exposure also play a role in UVA loss. If evaporation rates of the UVA are greater than their migration rates in the polymer, as in the case of many UVAs in polycarbonate,<sup>3</sup> the overall loss rate of UVA is diffusion limited. Oligomeric and polymeric UV absorbers show greater compatibility, and also higher retentions with time (lower diffusion, volatility, exudation, and solvent extractability) than low molecular weight UVAs.<sup>5,6</sup>

UVA loss could also occur by chemical reactions including thermo-oxidation or photo-oxidation. UVAs are usually considered extremely light stable because of the rapid deactivation of the excited state via proton transfer.<sup>1</sup> However, in work exploring UVA light stability in acrylic coatings using a reflectance spectroscopy technique, the permanence of benzophenone and oxanilide UVAs were shown to be much worse than a benzotriazole UVA after 28 months of Florida weathering,<sup>7</sup> implying photo-induced UVA chemical change. More recently, all of the major classes of UVAs were shown to photodegrade in a PMMA matrix.<sup>8</sup>

The UVA concentration can be monitored during outdoor exposure by extracting it from the polymer

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and quantifying it though UV or GC analysis.<sup>9</sup> This technique not only assumes complete extraction may be achieved, but it is also a destructive test to the sample. UV/visible reflectance<sup>10</sup> and modified transmission<sup>8,11</sup> spectrophotometry have also been developed to measure the UVA level nondestructively *in situ*, but these methods are only semiquantitative due to uncorrected reflection, matrix absorbance, and/or light-scattering errors.

This work presents a novel, nondestructive analysis method of transmission UV/visible spectrophotometry that allows an accurate determination of UVA concentration in a rubber-modified thermoplastic acrylic film that also contains a low level of a benzotriazole UVA. The concentrations of these UVAs are followed in time with exposure to xenon arc accelerated weathering. It is believed that this technique is broad enough to allow similar analyses of other UV and/or visible absorbing species in a variety of matrices.

## EXPERIMENTAL

### Sample Preparation

Blends of a rubber-modified polyacrylate resin containing approximately 0.06 wt % of UVA-1 and a variety of other UV absorbers were prepared. The compositions shown in Table I were chosen to give approximately 50% UV transmission in the final samples in order to optimize the signal-to-noise ratio.

The samples were compounded in a counter-rotating twin-screw extruder, and tapes were extruded to a thickness of 2 mil on a Brabender tape extruder. The standard deviation of the film thick-

**Table I** Composition of UV Stabilized Acrylic Samples

Sample	Stabilizer	Wt Added (%)	UVA Mol Wt
1	UVA-1*	None	225
2	UVA-2	0.137	323
3	UVA-3	0.217	510
4	UVA-4	0.167	394
5	UVA-5	0.190	448
6	UVA-6	0.152	358
7	UVA-7	0.137	323

\* The base polyacrylate resin contained ~ 0.06% UVA-1 as received.

**Table II** Xenon Arc Conditions

Borosilicate inner and outer filters
0.35 Watts/sq meter irradiance level
63°C black panel temperature
50% relative humidity
Cycle: 102 min. light, 18 min. light + water spray

ness over the film surface is  $\pm 10\%$ . The sample tapes were attached at the edges to quartz slides with heat-resistant tape. The slides were marked to ensure reproducible location in the spectrophotometer window.

### Xenon Arc Exposure

Samples were exposed to xenon arc accelerated weathering in an Atlas Ci65 xenon arc Weather-Ometer using the ASTM D2565 conditions listed in Table II. The samples were removed at intervals to record their UV/visible spectra and then returned to the Weather-Ometer for continued exposure.

### UV Absorbance Measurements

The sample slides were periodically measured for UV absorbance using a Shimadzu model 3101PC UV/visible spectrophotometer. The sample is oriented so that the UV beam first passes through the quartz slide upon which the samples are mounted, as shown in Figure 1. The structures of the UVAs used in this experiment are given in Table III. The absorbance spectra of the UVAs were obtained in acetonitrile to determine their absorptivities. A typical absorptivity spectrum is given in Figure 2 for UVA-1.

## THEORY

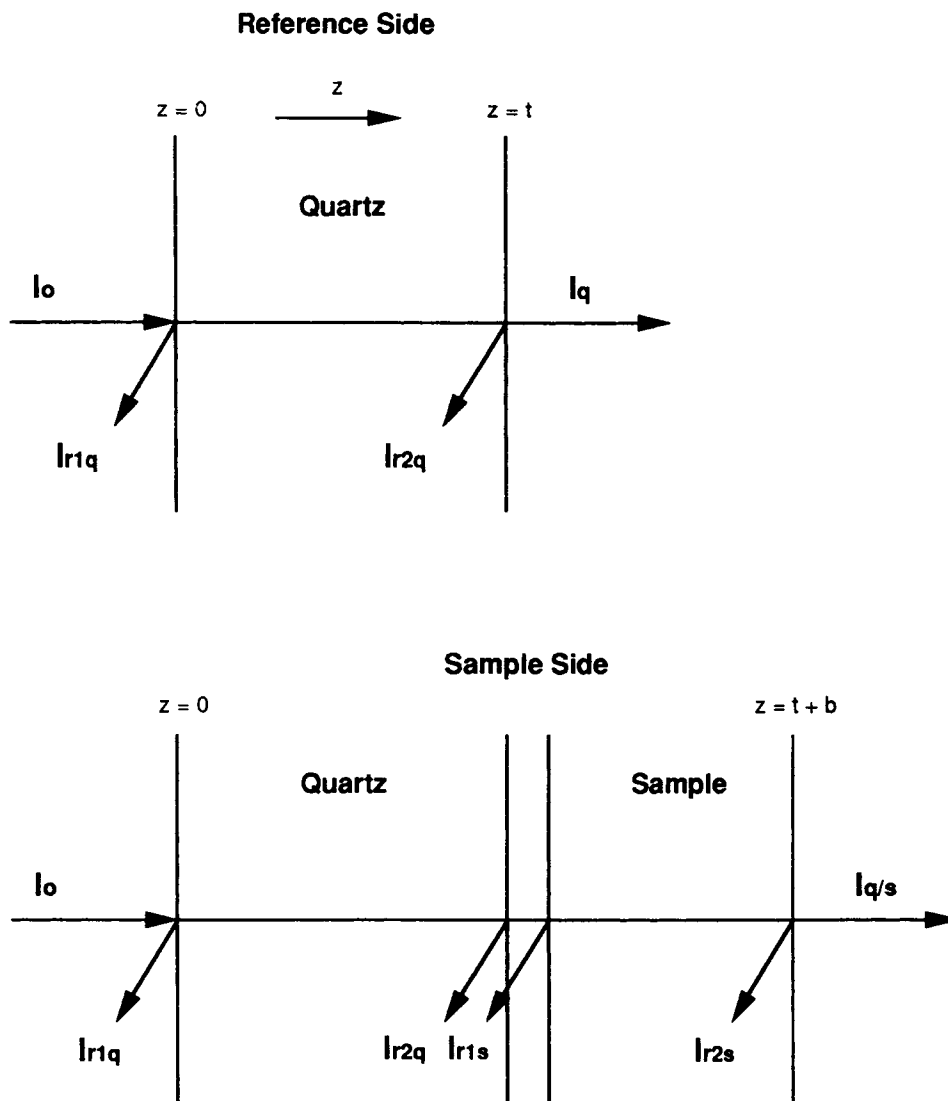
### Apparent Absorbance of Slide-Mounted Sample

The intensity of radiation,  $I$ , through a material in the  $z$  direction is governed by

$$\frac{dI}{dz} = -I\gamma'$$

where  $\gamma'$  is the absorptivity coefficient. Solving this equation gives

$$I_z = I_0 e^{-\gamma'z}$$



**Figure 1** Sample geometry for UV/visible spectrophotometry.  $I_{r1q}$  and  $I_{r2q}$  represent the light intensity reflected from the first and second quartz surfaces.  $I_{r1s}$  and  $I_{r2s}$  represent the light intensity reflected from the first and second sample surfaces. All other notations are as defined in the text.

The intensity transmitted through a reference quartz slide of thickness,  $t$ , and absorptivity coefficient,  $\gamma'_q$ , as shown in Figure 1, is given by

$$I_q = (I_0 - RI_0)e^{-\gamma'_q t} - R(I_0 - RI_0)e^{-\gamma'_q t}$$

where the second term accounts for the second surface reflectivity, and

$$R \approx \left( \frac{n - 1}{n + 1} \right)^2$$

represents the fraction of intensity reflected from each surface<sup>12</sup> where  $n$  is the refractive index of the matrix. The UV transmission of the quartz slides used in these experiments are independent of wavelength to a good approximation over the wavelengths of interest but show about a 7% reflection loss for all wavelengths ( $\sim 3.5\%$  for each surface).

For a sample film with an absorptivity coefficient,  $\gamma'_s$ , and a thickness,  $b$ , mounted on the quartz slide, the transmitted intensity is

$$I_{q/s} = I_q e^{-\gamma'_s b} (R' - 1)^2$$

where  $R'$  ( $\sim 0.039$ ) is the fraction of intensity reflected from the surface of the sample film. The spectrophotometer uses the radiation that passes through the blank quartz slide as a reference. This provides a ratio of intensities or transmittance,  $T_s$ , given by

$$T_s = \frac{I_{q/s}}{I_q} = e^{-\gamma'_s b (R' - 1)^2}.$$

Because  $R'$  is small,  $T_s$  reduces to

$$T_s = e^{-\gamma'_s b} e^{-2R'} = e^{-(\gamma'_s b + K'_r)}$$

where the reflection,  $K'_r$ , is independent of wavelength above 250 nm. By definition, the total apparent absorbance,  $A$ , is given by

$$A = -\log T_s = \gamma'_s b + K'_r,$$

where  $\gamma'_s = 2.303 \gamma_s$  and  $K'_r = 2.303 K_r$ .

The total apparent absorbance includes absorbance from the polymer matrix,  $A_{\text{electronic}}$ , and UV absorbers,  $\sum_i A_{i,\text{Beer-Lambert}}$ , as well as intensity re-

duction due to the scattering,  $A_{\text{scattering}}$ , and reflection,  $K'_r$ , of light as given here

$$A = A_{\text{scattering}} + A_{\text{electronic}} + \sum_i^{\text{UVA}} A_{i,\text{Beer-Lambert}} + K'_r,$$

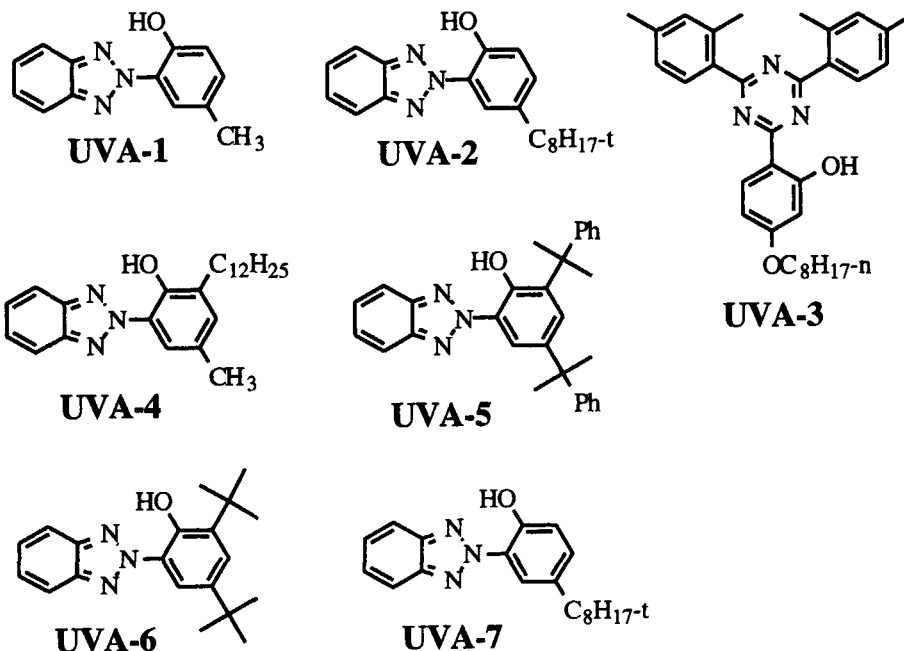
or

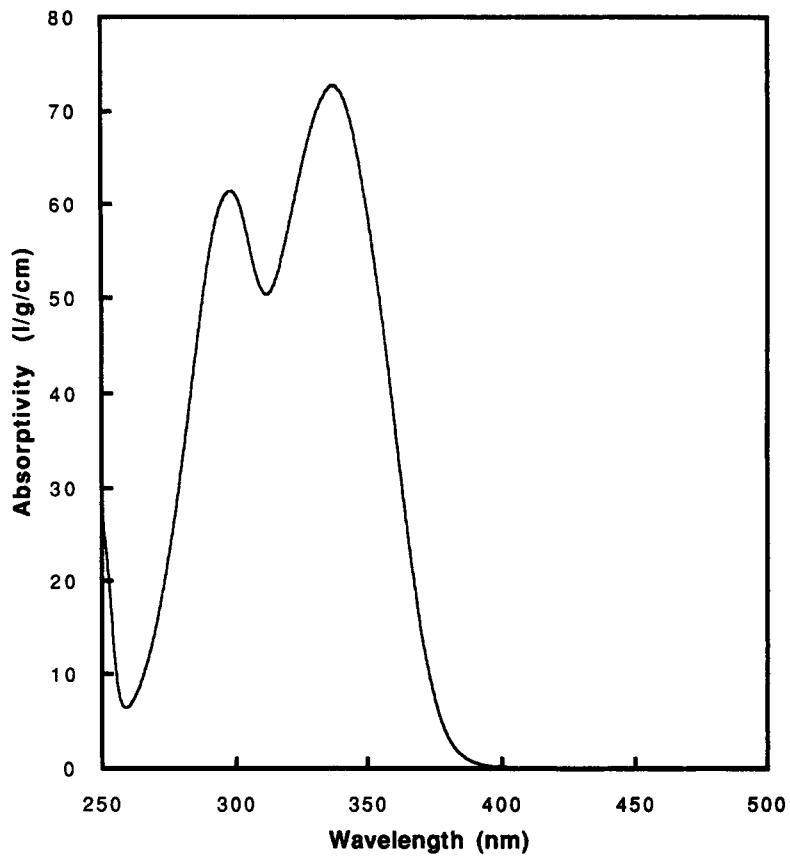
$$A = \alpha b + \sum_i^{\text{UVA}} A_{i,\text{Beer-Lambert}} + K'_r,$$

where  $\alpha$  is the combined absorptivity coefficient of the rubber-modified acrylic matrix consisting of light scattering "absorbance" and electronic absorbance. Both absorbances are proportional to the sample thickness and independent of UVA concentration. The typical relative magnitudes of light scattering, matrix absorbance, and UVA absorbance are shown for one of the samples in Figure 3.

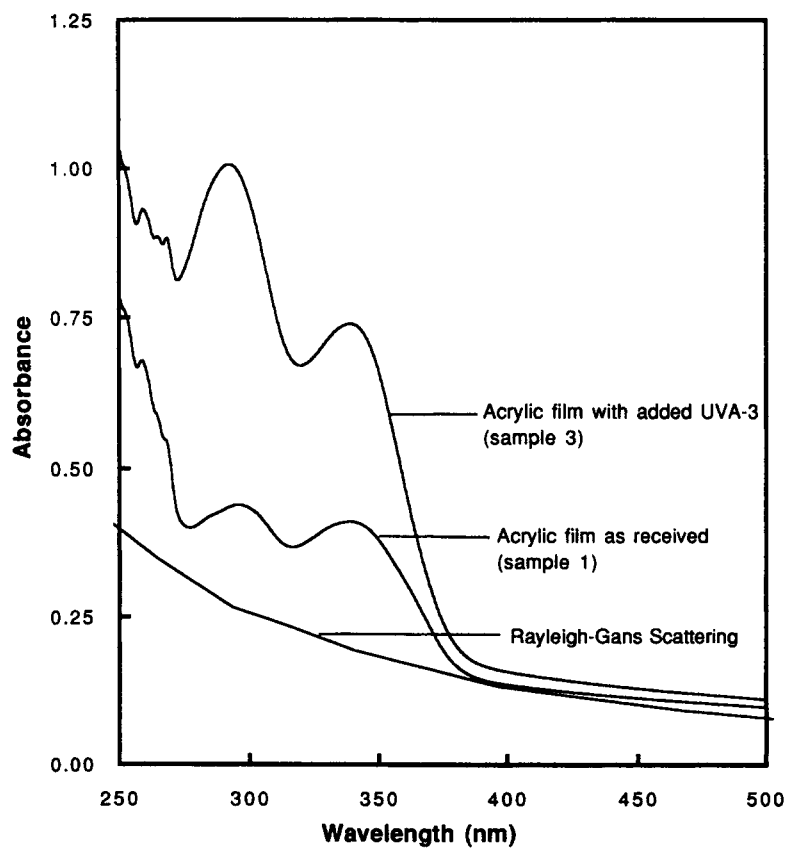
Light scattering is important to consider because the polyacrylate resin contains small rubber particles. The absorbance may be approximated using Raleigh-Gans scattering theory<sup>13</sup> which is wavelength dependent. The scattering absorbance for a 0.002 inch film of the rubber-modified acrylic is calculated to be approximately 0.36 at 260 nm and 0.08

Table III Structures of UV Absorbers





**Figure 2** UVA-1 absorptivity spectrum.



**Figure 3** Scattering absorption for rubber-modified acrylic film.

**Table IV Absorbance Data for Rubber-modified Acrylic Films Containing UV Absorbers**

Hours	UVA-1	UVA-2	UVA-3	UVA-4	UVA-5	UVA-6	UVA-7
Absorbance at 260 nm							
0	0.669	0.678	0.927	0.788	0.812	0.816	0.932
519	0.655	0.690	0.935	0.855	0.823	0.907	0.937
1011	0.727	0.826	0.925	0.903	0.783	0.902	0.837
1509	0.676	0.683	0.890	0.787	0.800	0.805	0.936
2028	0.669	0.796	0.907	0.848	0.695	0.892	0.832
3040	0.682	0.588	0.770	—	0.708	0.827	0.852
Absorbance at 500 nm							
0	0.098	0.112	0.112	0.112	0.115	0.105	0.119
519	0.092	0.111	0.110	0.106	0.110	0.103	0.112
1011	0.095	0.124	0.113	0.115	0.136	0.102	0.101
1509	0.088	0.102	0.104	0.094	0.099	0.092	0.100
2028	0.085	0.105	0.102	0.096	0.092	0.092	0.096
3040	0.090	0.009	0.009	—	0.010	0.007	0.008

at 500 nm. The electronic absorbance of the same rubber-modified acrylic film is approximately 0.30 at 260 nm and negligible at 500 nm.

The Beer-Lambert law relates absorbance to the concentration of the absorber,  $c$ , the thickness of the sample (path length),  $b$ , and the absorptivity of the absorber,  $a(\lambda)$ . This may be stated for one ( $i$ th) UV/visible absorber as

$$A_{i,\text{Beer-Lambert}} = a_i(\lambda)bc_i$$

The UVAs all have negligible absorbance at 500 nm. Most UVAs studied here have an absorbance minimum at about 260 nm and, in particular, this is a relative minimum absorbance for UVA-1. Therefore, 260 nm was chosen for normalizing spectra at low wavelengths as described below.

### Wavelength and Time Dependence of Absorbance

Each measurement made in the series of measurements in time has slight variation in  $\alpha b$  and in  $K_r$ , i.e.,  $\alpha(\lambda, t)b$  and  $K_r(t)$ . This may be seen by inspection of the absorptions at 260 nm and 500 nm listed in Table IV, which shows scatter of absorbance values measured at various exposure times.

The reflection intensity vs. incident angle is nearly a flat function for low incident angles ( $< 20^\circ$ ).<sup>12</sup> This means that variations of  $K_r$  are

small, although still significant, with variations in film orientation during the experiment and in surface quality between samples. The films taped to the quartz slides are not absolutely flat against the slide and, therefore, do not provide constant reflectance from measurement to measurement for the same sample. Finally, because it is possible that the surface of the film may be affected during the exposures of this experiment, the reflection term must include time dependence and, therefore,  $K_r = K_r(t)$ .

The rubber phase could be slightly altered (e.g., oxidized) during exposure. This could change the value of rubber index of refraction,  $n_r$ . Small changes in  $n_r$  can significantly affect the light scattering absorptivity coefficient. Such variations are reflected to a greater extent at the 260 nm wavelength where the scattering is stronger. It is also possible other light scattering changes can be obtained by variation in the amount of water absorbed by the matrix resin resulting in secondary light scattering from water ( $n_w = 1.33$ ). Therefore, the absorptivity coefficient should include time as well as wavelength dependence to give  $\alpha = \alpha(\lambda, t)$ .

Because the acrylic resin contains some residual UVA-1, the total absorbance for the sample (1) of acrylic resin only, without added UVA, may then be expressed as a function of wavelength, time, and thickness as

$$A_1(\lambda, t, b_1) = a_1(\lambda)b_1c_1(t) + \alpha(\lambda, t)b_1 + K_{r1}(t).$$

Because all samples have residual UVA-1 as well, the absorbance for the samples (2) of acrylic resin with added UVA are given by

$$A_2(\lambda, t, b_2) = a_1(\lambda)b_2c_1(t) + a_2(\lambda)b_2c_2(t) + \alpha(\lambda, t)b_2 + K_{r2}(t)$$

where to a good approximation,  $\alpha$ , is determined mainly by the matrix that is common to all samples, i.e.,

$$\alpha_1(\lambda, t) = \alpha_2(\lambda, t) = \alpha(\lambda, t)$$

### Absorbance Spectra Corrections

The objective of these experiments is to monitor  $c_2$  as a function of time. To accomplish this, it is necessary to remove not only the UVA-1 time-dependent contribution to the absorbance, but also the scattering and reflection time variations. The following procedure was used in the analysis of the data.

#### Subtraction of $K_r$

The absorbance of UVA is very small at 500 nm and may be neglected. Therefore, it may be neglected in the expression for absorbance,

$$A_1(500, t, b_1) = \alpha(500, t)b_1 + K_{r1}(t)$$

For example, at 500 nm and 2 mil thickness,  $A_{\text{UVA-1}} = 0.00039$ ,  $A_{\text{Matrix}} \cong 0$ ,  $A_{\text{Scattering}} \cong 0.08$ , and  $K_r = 0.034$ . This results in  $A_1 = 0.114$  in approximate agreement with the data in Table IV for 500 nm.

Similarly,

$$A_2(500, t, b_2) = \alpha(500, t)b_2 + K_{r2}(t)$$

Subtraction of  $A(500, t, b)$  values remove the reflection term  $K_r(t)$  resulting in baseline normalized absorbances as

$$\Delta A_1(\lambda, t, b_1) = a_1(\lambda)b_1c_1(t) + \Delta\alpha(\lambda, t)b_1$$

where

$$\Delta\alpha(\lambda, t) \equiv \alpha(\lambda, t) - \alpha(500, t)$$

and similarly,

$$\Delta A_2(\lambda, t, b_2) = a_1(\lambda)b_2c_1(t) + a_2(\lambda)b_2c_2(t) + \Delta\alpha(\lambda, t)b_2$$

### Thickness Normalization

In order to match the baselines of each spectrum, a second and lower wavelength point must be chosen. That this is necessary may be seen from the scatter in the  $A(260 \text{ nm})$  values listed in Table IV. Normalizing to the absorbance at 260 nm after the subtraction of absorbance at 500 nm gives a thickness normalized absorbance

$$A_{1N} = \frac{\Delta A_1(\lambda, t, b_1)}{\Delta A_1(260, t, b_1)} = \frac{a_1(\lambda)c_1(t) + \Delta\alpha(\lambda, t)}{a_1(260)c_1(t) + \Delta\alpha(260, t)}$$

and

$$\begin{aligned} A_{2N} &= \frac{\Delta A_2(\lambda, t, b_2)}{[\Delta A_2(260, t, b_2) - a_2(260)b_2c_2(t)]} \\ &= \frac{a_1(\lambda)c_1(t) + a_2(\lambda)c_2(t) + \Delta\alpha(\lambda, t)}{a_1(260)c_1(t) + \Delta\alpha(260, t)} \end{aligned}$$

### Subtraction of Absorbance of Rubber-Modified Acrylic Film

The absorbance of the acrylic film (1) is subtracted from the absorbance of the film sample (2) with UVA to give

$$\{A_{2N} - A_{1N}\}(\lambda, t) = \frac{a_2(\lambda)c_2(t)}{a_1(260)c_1(t) + \Delta\alpha(260, t)}$$

Using the maximum UVA absorptivity at the "340" nm peak, the UVA retention fraction,  $RF_2$ , may be expressed as

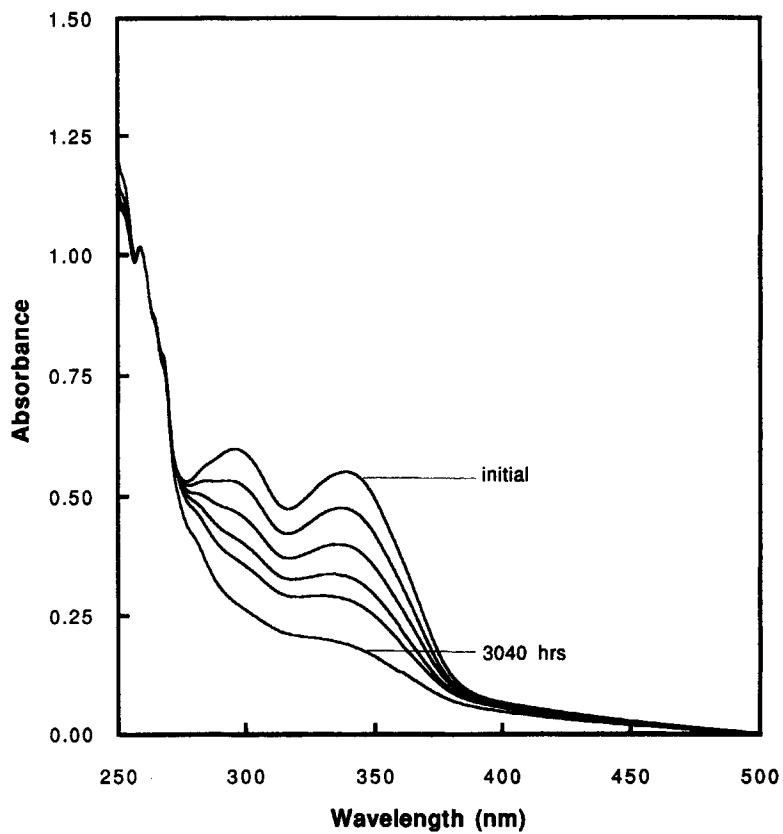
$$RF_2(t) = \frac{\{A_{2N} - A_{1N}\}(340, t)}{\{A_{2N} - A_{1N}\}(340, 0)}$$

giving upon substitution

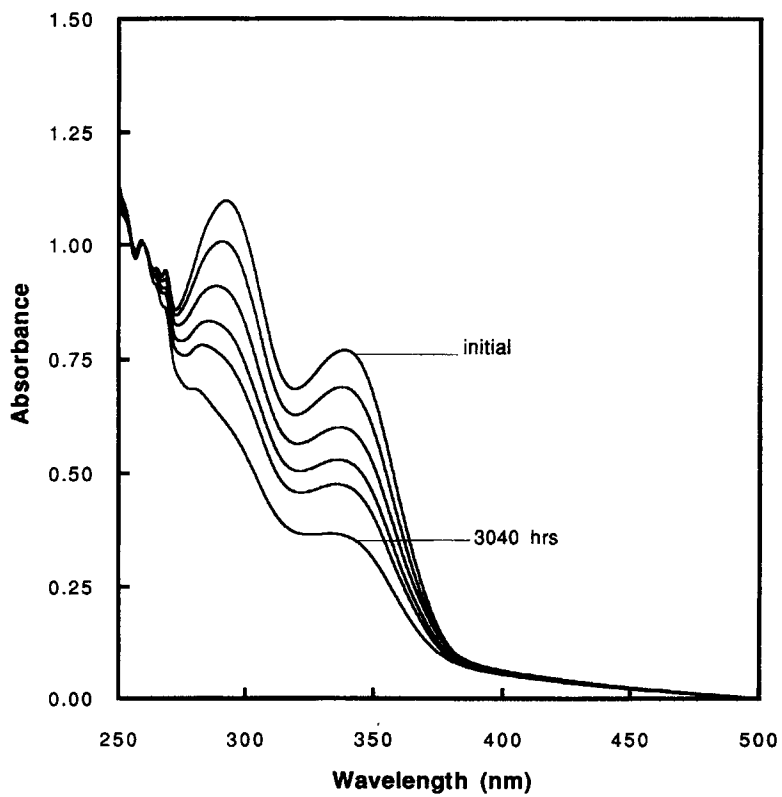
$$RF_2 = \frac{a_2(340)c_2(t)/[a_1(260)c_1(t) + \Delta\alpha(260, t)]}{a_2(340)c_2(0)/[a_1(260)c_1(0) + \Delta\alpha(260, 0)]}$$

The absorptivity coefficient difference,  $\Delta\alpha(260, t)$ , is about  $59 \text{ cm}^{-1}$ , whereas as  $a_1(260)c_1(t) < a_1(260)c_1(0) = 4.6 \text{ g/L}$ . Furthermore, the time variation of  $\Delta\alpha(260, t)$  is not substantial so that  $\Delta\alpha(260, t) \approx \Delta\alpha(260, 0)$ . Therefore,  $RF_2$  reduces approximately to

$$RF_2 \cong \frac{c_2(t)}{c_2(0)}$$

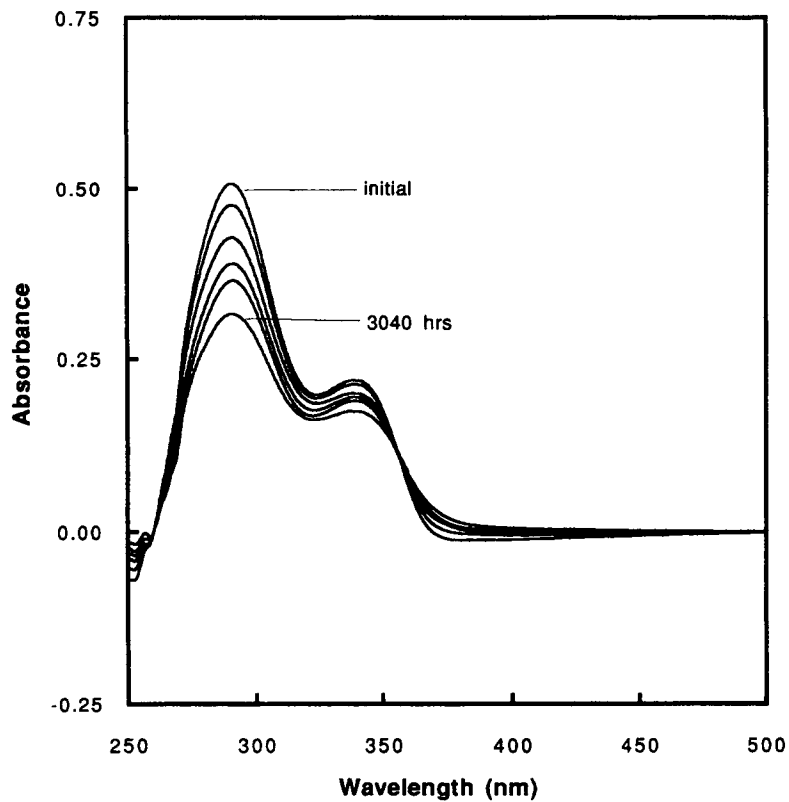


**Figure 4** Absorbance spectra of acrylic film containing only UVA-1 (sample 1) after xenon arc exposure.

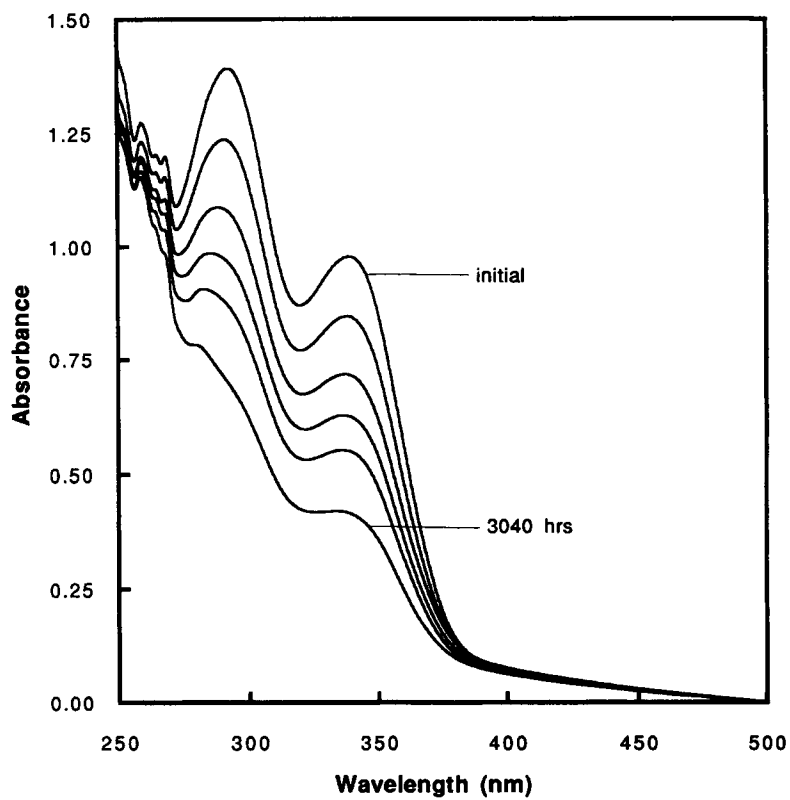


**Figure 5** Absorbance spectra of acrylic film containing UVA-3 (sample 3) after xenon arc exposure (uncorrected).

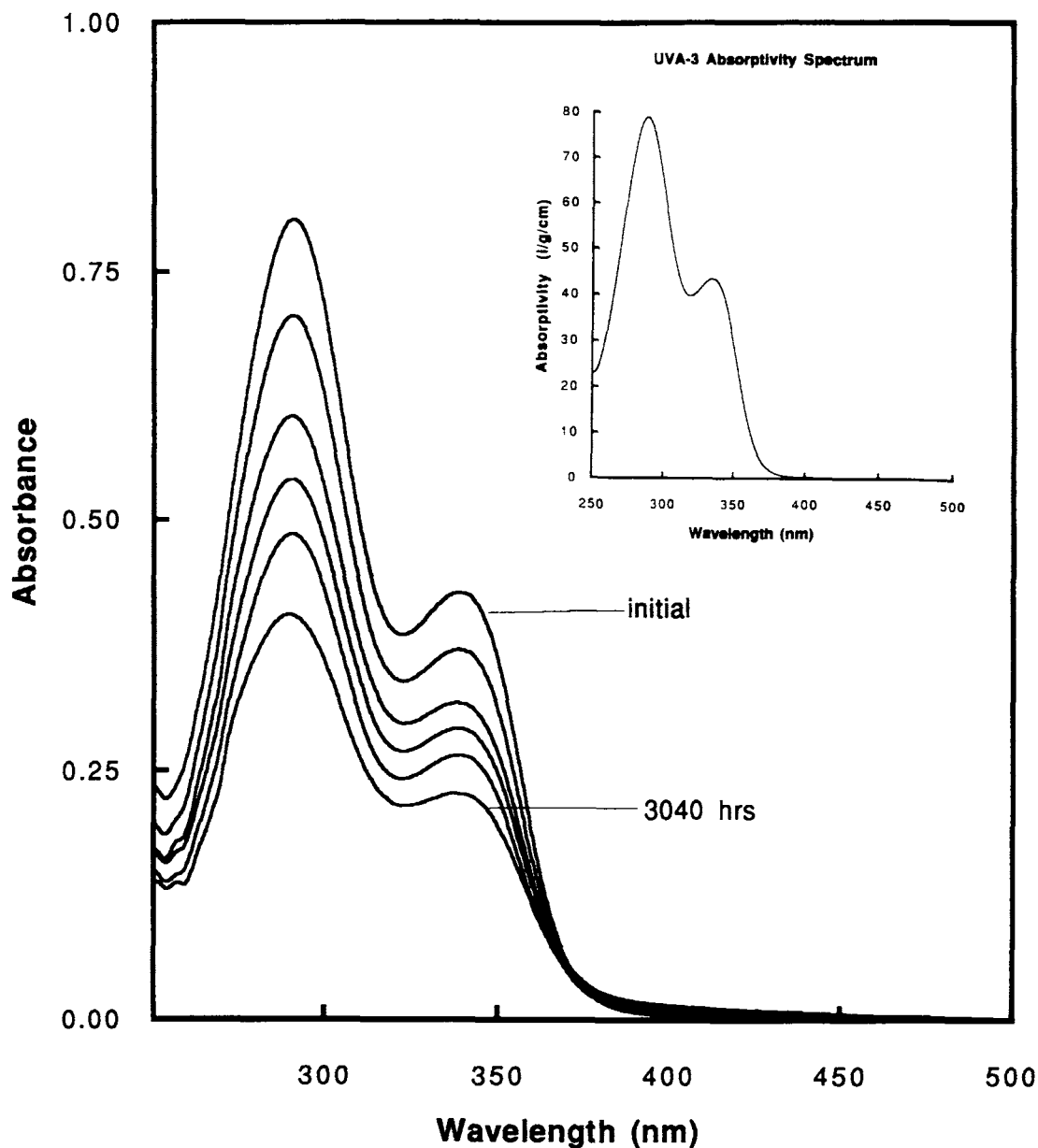




**Figure 6** Absorbance difference spectra of acrylic film containing UVA-3 (sample 3) after xenon arc exposure (uncorrected).



**Figure 7** Corrected absorbance spectra of acrylic film containing UVA-3 (sample 3) after xenon arc exposure (final iteration).



**Figure 8** Absorbance difference spectra of acrylic film containing UVA-3 (sample 3) after xenon arc exposure (final iteration).

This allows a new expression to be written for  $A_{2N}$  that includes  $RF_2$ ,

$$A_{2N} = \frac{\Delta A_2(\lambda, t, b_2)}{\Delta A_2(260, t, b_2) - a_2(260)b_2c_2(0)RF_2}$$

Because  $c_2(t)$  is unknown prior to the experiment, it is determined by using an iterative process. This results in convergence after, at most, four iterations and often after only a single iteration.

## RESULTS AND DISCUSSION

The iterative procedure described above is used here to determine the UVA retentions in the rubber-modified acrylic films. The absorbance data, corrected for reflection and normalized to only their  $A(260, t, b)$  values, are plotted for the films containing UVA-1 and UVA-3 in Figures 4 and 5, respectively. The family of curves shows that the UVA is lost with increasing time of xenon arc exposure. The

**Table V** Percent Retention of UV Absorbers

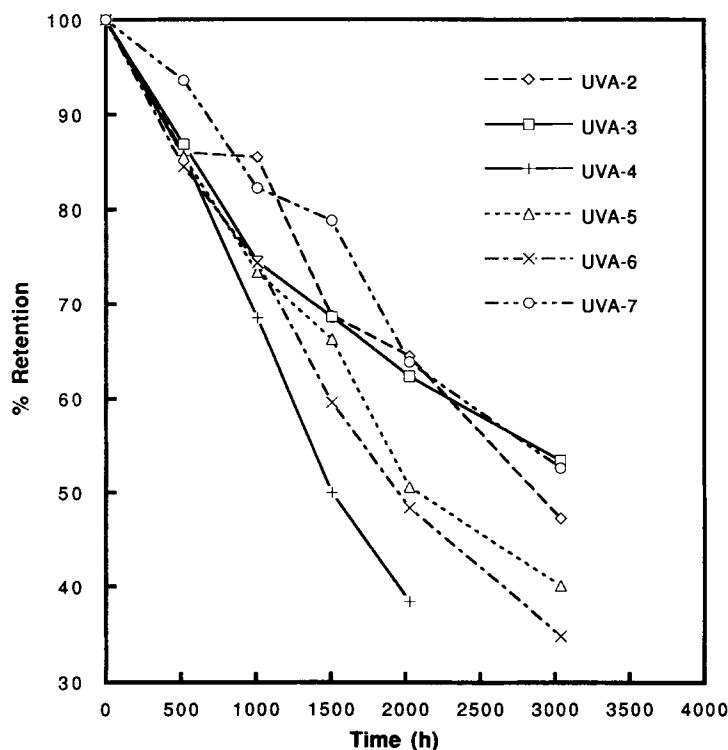
Hours	UVA-2	UVA-3	UVA-4	UVA-5	UVA-6	UVA-7
By UV Absorbance						
519	86	87	86	86	84	94
1011	85	74	68	73	74	82
1509	69	69	50	66	60	79
2028	64	62	38	51	48	64
3040	47	53	—	40	35	53
By GC						
3040	50	50	—	46	31	60

difference spectra between the UVA-3 film and the UVA-1 film are plotted in Figure 6. By using the retentions obtained from Figure 6, the UVA-3 absorbance data may be normalized using an iterative correction procedure. Convergence is considered to be obtained when the  $A(260,t,b)$  values are within 0.003 from the previous  $A(260,t,b)$  values. For the UVA-3 sample, convergence occurs after three iterations. The results of the final iteration are shown in Figures 7 and 8 for the absorbance and absorbance difference spectra, respectively. It is noteworthy that the absorbance spectrum of UVA-3 in Figure 8,

which represents the final converged iteration, exhibits a shape similar to the absorptivity spectrum of this UVA. For each of the samples, the final iteration absorbance spectra match the absorptivity spectra of the corresponding UVA.

The retentions of the UVAs are listed in Table V. At the end of the xenon arc exposure, the samples were analyzed by an extraction/gas chromatography technique as described in ref. 14. The data obtained by GC compares very well to the data obtained from the analysis presented in this article.

The data in Table V is plotted in Figure 9. The



**Figure 9** Retention of UV absorbers in an acrylic film upon xenon arc exposure (samples 2 through 7).

shapes of the retention profiles suggest first-order kinetics. Recent work by Pickett and Moore<sup>8</sup> shows that UVA retention in PMMA follows zero-order kinetics at high concentrations but transitions to first-order kinetics at lower concentrations, such as those used in this study. This is consistent with a photochemical degradation mechanism, because the internal filtering effect would limit the rate of UVA loss at high absorbance. Other literature<sup>3,4</sup> suggests that the more likely loss mechanism is a diffusion of the UVA to the surface followed by subsequent evaporation. The internal filter effect would, again, be important if the UVA vibrational relaxation enhances UVA diffusion. However, additional work reported in an accompanying article<sup>15</sup> shows that the loss mechanism in these samples is a combination of photochemical and photo-oxidative degradation, and that physical losses are insignificant under these conditions.

## CONCLUSION

This work presents a novel, nondestructive analysis technique for UV/visible spectroscopy that allows the accurate determination of a UV absorber in a rubber-modified polyacrylate film with time. The effects of reflectance, light scattering, and matrix absorbance are deconvoluted from the total apparent absorbance, resulting in an absorbance spectrum due to the UVA alone. All of the UVAs studied exhibit significant losses upon xenon arc exposure, which has important implications for the long-term durability of polymers that utilize these stabilizers.

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## REFERENCES

1. F. Gugumus, in *Oxidation Inhibition in Organic Materials*, Vol. 2, J. Pospisil and P. P. Klemchuk, Eds., CRC Press, Boca Raton, FL, 1990.
2. G. Geuskens, in *Comprehensive Chemical Kinetics*, Vol. 14: *Degradation of Polymers*, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, New York, 1975.
3. D. R. Olson and K. K. Webb, *Macromolecules*, **23**, 3762 (1976).
4. N. C. Billingham, in *Oxidation Inhibition in Organic Materials*, Vol. 2, J. Pospisil and P. P. Klemchuk, Eds., CRC Press, Boca Raton, FL, 1990.
5. D. Bailey and O. Vogl, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C14**, 267 (1976).
6. D. K. C. Hodgeman, *Polym. Degrad. Stabil.*, **1**, 155 (1979).
7. G. Berner and M. Rembold, *Org. Coat.*, **6**, 55 (1984).
8. J. E. Pickett and J. E. Moore, *Polym. Degrad. Stabil.*, **42**, 231 (1993).
9. D. R. Bauer, J. L. Gerlock, and R. A. Dickie, *Prog. Org. Coat.*, **15**, 209 (1987).
10. G. Berner and M. Rembold, *ACS Org. Coat. Proc.*, **47**, 624 (1982).
11. B. Lindberg, *VTT Symp. No. 49*, Int. Conf. Durability Build. Mater. Compon., 3rd, Vol. 2, 1984, p. 318.
12. M. Born and E. Wolf, *Principles of Optics*, 3rd ed., Pergamon Press, New York, 1965.
13. H. C. Van de Hulst, *Light Scattering by Small Particles*, John Wiley, New York, 1957.
14. C. G. Smith, W. C. Buzanowski, J. D. Graham, and Z. Iskandarani, in *CRC Handbook of Chromatography—Polymers*, Vol. 2, J. Sherma, Ed., CRC Press, Boca Raton, FL, 1994.
15. B. Bell, D. Beyer, N. Maecker, R. Papenfus, and D. Priddy, *J. Appl. Polym. Sci.*, **54**, 1605 (1994).

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