

## Photodegradable Vinyl Plastics. III. Comparison of Ultraviolet Light and Sunlight Exposure

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### Synopsis

Polystyrene (PS), polypropylene (PP), and polyethylene (PE) films, blended with additives to enhance photodegradability, were irradiated with UV light and sunlight. In almost every case, photodegradation was greater with outdoor exposure than under laboratory conditions. Explanations for the differences in degradation obtained by the two methods of irradiation are discussed. Based on IR measurements and molecular weight determinations, photo-oxidative changes that occur in PS induced by UV light appear similar to those induced by sunlight. In addition to the additives previously reported, several new classes of photoinitiators were evaluated. These include selected halocarbonyl compounds, haloalkyl sulfur compounds, and halogen compounds containing certain electron-withdrawing groups. The performance of the additives in vinyl polymer blends is discussed.

### INTRODUCTION

The weatherability of plastics has been intensively investigated in recent years, since at least 25% of all plastics are exposed to weathering in outdoor applications.<sup>1</sup> Because natural weathering involves many variables and is time consuming, much effort has been expended toward developing accelerated laboratory weathering tests. Various aspects of the plastic weatherability problem have been reviewed in a symposium.<sup>2</sup> Accelerated weathering tests have the advantage of allowing much closer control over the variables and reducing time of testing. Unfortunately, correlations between accelerated and natural weathering have often been poor.<sup>3</sup> Considering the many variables involved in natural weathering, this lack of correlation is not surprising.

A variety of instruments have been used to expose plastics to artificial sunlight and other weathering conditions in the laboratory. The most common of these include the carbon arc Fade-Ometer and Weather-Ometer, the xenon arc Weather-Ometer, fluorescent sunlamps and blacklights, and mercury arc lamps such as the S-1 and RS sunlamps. The advantages and disadvantages of these light sources have been compared.<sup>4,5,6</sup> Of these, the xenon arc emission bears the closest similarity to solar energy in the UV region.

For this investigation, an RS sunlamp was chosen as the source of UV light because of its simplicity, low cost, and ease of operation. Our previous investigations have already shown that this lamp is capable of producing extensive photodegradation in vinyl polymers with added photoinitiators.<sup>7,8</sup> Our ob-

jective in using the RS sunlamp in previous research was not to correlate the photodegradation produced by the RS sunlamp with that of sunlight, but rather to quickly screen a large number of potential photoinitiators for degradative effectiveness. The object of the present investigation is twofold: (1) to determine the effectiveness of several new classes of active halogen photoinitiators by both RS sunlamp and sunlight, (2) to compare the extent polymers previously degraded with UV light would degrade with sunlight.

## EXPERIMENTAL

The procedures for film preparation, UV exposure, and determination of photodegradation have been described.<sup>7,8</sup> Intrinsic viscosities of toluene solutions of PS were measured at 30°C using an Ubbelohde dilution viscometer. All additives were commercially available and used as received. For sunlight exposure, films measuring  $\frac{3}{4} \times 1\frac{3}{8}$  in. were placed on a stainless steel rack which was mounted on the roof of a building located at Albany, California, and exposed between September 14 and October 14, 1974. The rack was positioned facing south at an angle of 45° to the horizontal, which is a direction and angle often employed for outdoor exposure.<sup>5</sup> The increase in carbonyl absorbance, as determined by IR spectroscopy before and after sunlight exposure, was used to determine photodegradation.

## RESULTS AND DISCUSSION

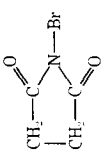
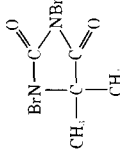


### Infrared Spectroscopy

In comparing a polymer film which was irradiated with the UV lamp versus the same film exposed to sunlight, IR spectra in the carbonyl region were run for both films. A comparison of the carbonyl bands would indicate whether a similarity exists between the photooxidation induced by UV lamp and sunlight. The IR carbonyl region of three polymers (PS, PP, and PE), irradiated with UV lamp and sunlight is shown in Figure 1. In each of these cases, the carbonyl bands produced by the two types of irradiation are similar. Thus, the photo-oxidation processes appear similar. These results do not imply that the RS sunlamp is a good substitute for natural weathering, but that the sunlamp can be used for screening purposes. For final evaluation, outdoor exposure tests must be employed.

### Photodegradation of Polystyrene Polymers by UV Lamp and Sunlight

The degradation resulting from exposure to UV lamp and sunlight of PS films blended with different photoinitiating additives is shown in Table I. Quantitative differences of the IR absorption between these two methods of irradiation are tabulated. The UV lamp exposure time of 66 hr was chosen originally for PS and PP because sufficient degradation occurred to permit comparisons of various additives. For PE, 100 hr of exposure was necessary. One month of exposure to sunlight was adequate to produce significant degradation in the polymers tested. No attempt was made to determine a UV irradiation time providing degradation equal to a given sunlight irradiation,

TABLE I  
Effect of Various Additives on the Photodegradation of Polystyrene by UV Lamp and Sunlight

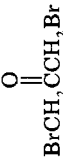
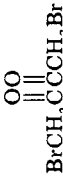


Type	Additive Name	Structure	UV Lamp 66 hr		Sunlight 1 month				
			% additive	Carbonyl <sup>a</sup> increase	AER <sup>b</sup> % additive	Carbonyl increase	AER % additive		
I. N-Halogen	N-bromosuccinimide		1	1.33	5.42	5.42	(0.588) <sup>c</sup>	(7.74) <sup>c</sup>	7.74
	1,3-dibromo-5,5-dimethylhydantoin		1	2.03	8.26	8.26	1.21	7.52	7.52
II. Haloalkene	1,4-dibromo-2-butene	$\text{BrCH}_2\text{CH}=\text{CH}-\text{CH}_2\text{Br}$	5	0.939	3.82	0.764	1.64	10.2	2.04
	2,3-bis(bromomethyl)-1,4-dibromo-2-butene	$(\text{BrCH}_2)_2\text{C}=\text{C}(\text{CH}_2\text{Br})_2$	5	1.34	5.45	1.09	2.92	18.1	3.62
III. Arylmethyl halide	hexachlorocyclopentadiene		5	1.32	5.37	1.07	3.79	23.5	4.70
	cinnamyl bromide	$\phi\text{CH}=\text{CH}-\text{CH}_2\text{Br}$	5	0.997	4.05	0.810	2.12	13.2	2.64
	bromodiphenylmethane	$\phi_2\text{CHBr}$	2	0.997	4.05	2.03	2.05	12.7	6.35
Polymer control	$\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-o-xylene		2	0.912	3.71	1.86	2.95	18.3	9.15
	bromotriphenylmethane (no additive)	$\phi_3\text{CBr}$	5	1.18	4.80	0.960	3.25	20.2	4.04
			0	0.246	1.00	—	0.161	1.00	—

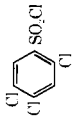
<sup>a</sup>Carbonyl increase is the increase in the carbonyl absorbance measured at 1750–1695  $\text{cm}^{-1}$  by IR before and after irradiation.

<sup>b</sup>Additive effectiveness ratio (AER) is equal to the increase in carbonyl absorbance for polymer and additive divided by the increase in carbonyl absorbance for polymer only.

<sup>c</sup>These values were determined after two weeks rather than one month.

TABLE II  
Effect of Various Additives on the Photodegradation of Vinyl Polymers

Name	Structure	Additive %	Polypropylene			Polyethylene			Polystyrene		
			UV Lamp 66 hr AER <sup>a</sup>	Sunlight 1 month AER	Sunlight 1 month AER	UV Lamp 100 hr AER	Sunlight 1 month AER	Sunlight 1 month AER	UV Lamp 66 hr AER		
1,3-Dibromoacetone		1	1.48	8.00	1.23	0.739	1.23	3.57			
1,4-Dibromo-2,3-butanedione		3-PP 5-PE, PS	1.24	0.80	3.31	0.932	3.31	9.46			
Tetrabromo- <i>o</i> -benzoquinone		5	1.12	7.87	10.8	0.963	10.8	8.27			
2,2,6,6-Tetrachloro- <i>cyclohexanone</i>		3	1.12	4.13	1.54	0.657	1.54	2.91			

Iodoacetic acid	$\text{ICH}_2\text{CO}_2\text{H}$	5	0.152	1.87	0.846	3.00	0.643
1,1,2,2-Tetrachloro-ethylsulfenyl chloride	$\text{Cl}_3\text{CHCCl}_2\text{SCl}$	5	0.329	23.3	0.420	5.46	3.70
1,3,3,3-Tetrachloroethyl disulfide	$(\text{Cl}_3\text{CCHClS})_2$	5	0.370	4.13	0.569	5.15	4.55
Dibromomalononitrile	$\text{Br}_2\text{C}(\text{CN})_2$	3-PP 5-PE, PS	1.27	31.2	1.37	4.31	2.98
Trichloromethanesulfonyl chloride	$\text{Cl}_3\text{CSO}_2\text{Cl}$	3-PP 5-PE, PS	0.807	5.87	0.695	1.62	9.02
2,4,5-Trichlorobenzene-sulfonyl chloride		5	1.15	21.1	1.03	4.00	6.56
Trichloroacetylchloride	$\text{Cl}_3\text{CCCl}$	5	1.03	6.00	0.706	3.31	4.70
Chloropicrin	$\text{Cl}_3\text{CNO}_2$	5	0.350	3.07	0.709	2.85	1.22
Polymer control	—	0	1.00	1.00	1.00	1.00	1.00

<sup>a</sup>See Table I, footnote b.

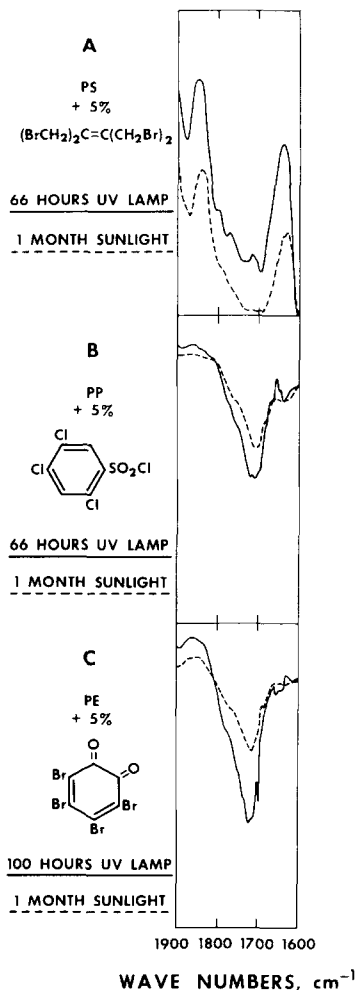


Fig. 1. IR spectra of photodegradable polymers irradiated with UV lamp or sunlight.

but merely to measure how much photo-oxidation occurred at the two given times.

The UV exposure of the N-halogen additives<sup>7</sup> and the haloalkene and aryl-methyl halide additives<sup>8</sup> shown in Table I has already been described. It should be kept in mind that an additive effectiveness ratio (AER) greater than one indicates that the additive functions as a photo-sensitizer, whereas a ratio less than one indicates the additive acts as a photostabilizer. A comparison of the ratios of the UV-exposed films to sunlight-exposed films shows that, with the exception of the film containing the hydantoin, the ratios are significantly higher for the latter films. This indicates that natural weathering conditions have degraded the polymers much more than the laboratory conditions. There are obviously factors present in natural weathering which are absent in the laboratory. Among these are moisture, temperature and temperature variations, ozone, and atmospheric contaminants such as smog, dirt, and soot, etc.<sup>9</sup> Light intensity, periods, and severity of cycling also af-

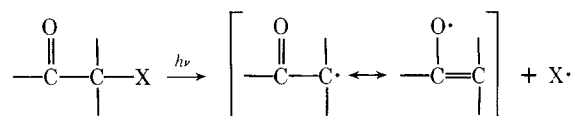
fect the weatherability of plastics.<sup>3</sup> Because of these differences, a direct comparison cannot be made between natural and laboratory weathering conditions. Nevertheless, the polymers containing additives are more responsive to natural weathering than the laboratory weathering employed. Another conclusion from the data in Table I is that generally those additives most effective in inducing photodegradation with UV light are also the most effective with sunlight. Thus, the N-halogen additives, which are superior to the haloalkenes and arylmethyl halides under UV irradiation, maintain that superiority under sunlight irradiation.

### Photodegradation of Vinyl Polymers with Various Active Halogen Additives

The effectiveness of three classes of active halogen photoinitiators not previously discussed are shown in Table II. These classes are halocarbonyl compounds, haloalkyl sulfur compounds, and halogen compounds containing electron-withdrawing groups. Except for the case of iodoacetic acid, exposure of PS with any of these additives to UV light gave good to excellent ratios. The iodo additive also performed poorly when incorporated into PP and PE on UV irradiation. However, PP and PE samples containing iodoacetic acid did degrade more extensively than the controls when subjected to sunlight.

UV exposure of PP samples containing the additives listed in Table II caused degradation only slightly better than the control for most of the samples. PE samples blended with these additives were generally less degraded than the control under similar UV irradiation. If one were to judge these photoinitiators solely on their performance after exposure to UV light they would be regarded as poor to fair. After one month of natural weathering, however, the ratios indicated that moderate to extensive degradation had occurred. Thus, these results suggest that polymers blended with the additives should degrade sufficiently for certain outdoor applications. One such application is agricultural mulching using photodegradable plastics.<sup>10</sup> Degradation can be controlled by varying the concentration of additives in the polymer to render films degradable in a few weeks to many months depending on the desired application. The lack of correlation between the UV lamp and sunlight results is representative of the findings of many other investigators who have exposed plastics to both artificial and natural weathering. Hence, great care must be exercised in predicting natural weathering performance on the basis of accelerated laboratory testing.

The activity of the photoinitiators listed in Table II can be attributed to several sources. The halocarbonyl compounds used in this investigation contain at least one halogen atom bonded to a carbon atom  $\alpha$  to a carbonyl group. This carbonyl group provides a means for delocalization of the electrons produced by cleavage of the C—X bond:



thus providing a reactive free radical.

TABLE III  
Effect of UV Lamp/Sunlight Irradiation on Viscosity and Molecular Weight of Polystyrene

Sample	Before irradiation		After 66 hr UV lamp		After 1 month sunlight	
	$[\eta]^a$	$\bar{M}_v^b$	$[\eta]$	$\bar{M}_v$	$[\eta]$	$\bar{M}_v$
Polystyrene (control)	1.818	917,500	0.997	400,000	1.327	593,500
Polystyrene + 2% $\alpha,\alpha',\alpha'$ -tetrabromo- <i>o</i> -xylene	2.291	1,271,000	0.325	84,550	0.203	43,700
Polystyrene + 5% 2,3-bis(bromomethyl)-1,4-dibromo-2-butene	2.177	1,174,000	0.147	28,000	0.147	28,000

<sup>a</sup> Intrinsic viscosity.

<sup>b</sup> Viscosity-average molecular weight.

The activity of the haloalkyl sulfenyl chloride and disulfide is probably due to the relatively low energy of the S—Cl and S—S bonds (59.7 and 50.9 kcal/mole, respectively), as well as possible contributions from the C—Cl groups. The strong inductive effect of the nitrile and nitro groups in the dibromodinitrile and chloropicrin, respectively, facilitates cleavage of the halogen-carbon bonds in these molecules. The sulfonyl and acyl chlorides contain not only labile chlorine atoms, but also other chlorine atoms bonded to carbon. Both types of chlorine atoms could contribute to photodegradation.

### Viscosity and Molecular Weight Changes in Polystyrene

We have shown that PS films containing additives irradiated with UV light have undergone significantly greater decreases in molecular weight compared to a control containing no additive.<sup>7,8</sup> To ascertain molecular weight changes in sunlight-exposed films, viscosity measurements were made on PS samples as shown in Table III. These data clearly show that a sunlight-exposed film with additive was much more degraded than the same film without additive. Thus sunlight, compared to UV light, can cause an equal or greater molecular weight loss. In conclusion, PS films exposed to both irradiation sources undergo molecular weight losses and form products with similar IR spectra. Hence, the nature of photo-oxidative changes in PS induced by UV lamp and sunlight appear similar.

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