

# UV Screen Progenitors. Thermally Labile Urethane Derivatives of Hydroxyphenylbenzotriazoles and Hydroxybenzophenones\*

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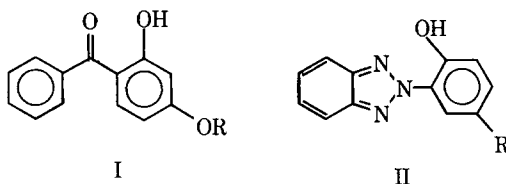
## Synopsis

UV-curable formulations do not UV cure when hydroxybenzophenone or hydroxyphenylbenzotriazole UV screens are added to them. Reaction of these UV screens with alkyl or aryl isocyanates gives urethane derivatives in high yields. These derivatives do not impede UV cures when they are incorporated in UV-curable formulations at relatively high levels (3%–5%). After completion of the UV cure, the urethane derivatives are catalytically decomposed by heating to regenerate the corresponding UV screen within the cured coating.

## INTRODUCTION

UV polymerization of resins, "UV curing," offers the potential to react solventless formulations at high speeds with minimal energy usage.<sup>1-3</sup> Due to the rapid cures, the temperature of the substrates is raised only to a small extent. These aspects make it particularly attractive to use UV for the cure of specialty coatings on thermally sensitive substrates such as plastics.

For many applications involving plastic materials, it is desirable to incorporate UV screens such as hydroxybenzophenones (I) or hydroxyphenylbenzotriazoles (II) in the coatings:

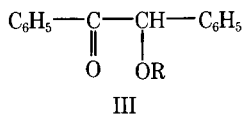


UV screens protect plastics from degradation by long-wavelength ultraviolet light and prevent autoacceleration of aging by color bodies formed during thermal aging.<sup>4</sup>

Achieving a UV cure of a material that is highly UV protective presents an inherent problem. When UV screens such as I or II are incorporated in UV-curable resins, satisfactory cures cannot be obtained even when the concentration of screens is very low, for the following reasons: although common UV initia-

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tors<sup>1,3</sup> such as benzoin ethers (III) have a strong absorption at 250 nm (Fig. 1),



the resin and monomer generally absorb nearly all of the incident short-wavelength UV light below 300 nm. On the other hand, most resin/monomer combinations have virtually no absorption in the 300–370 nm range where benzoin ethers absorb modestly (Fig. 1). UV cures are thus possible unless UV screens such hydroxybenzophenones (I) or hydroxyphenylbenzotriazoles (II) are added. These screens absorb highly in the long-wavelength UV region (Fig. 2), thus screening light from the UV initiator III and thereby preventing UV-initiated polymerization.

Phenolic derivatives of hydroxybenzophenones (IV) ( $R \neq H$ ) do not absorb as strongly in the 350–400 nm region as the parent compound I.<sup>6</sup> The same holds true for derivatives of hydroxyphenylbenzotriazoles (V) ( $R \neq H$ ). Figure 3 shows the UV spectrum of such a “protected” hydroxyphenylbenzotriazole. UV-curable formulations containing relatively large amounts of such “protected” derivatives might be expected to cure efficiently with common initiators such as III due to the relative absorptions of III and IV or V in the 365-nm region where medium-pressure mercury lamps have a high light output. By proper choice of the phenolic derivative, it should be possible to release the UV screen *in situ* in the coating after UV cure.

In principle, the generation of a UV screen can be accomplished by a number of methods such as heat, hydrolysis, or photolysis. In earlier work in this laboratory,<sup>7</sup> trimethylsilyl derivatives IVa and Va were prepared and incorporated

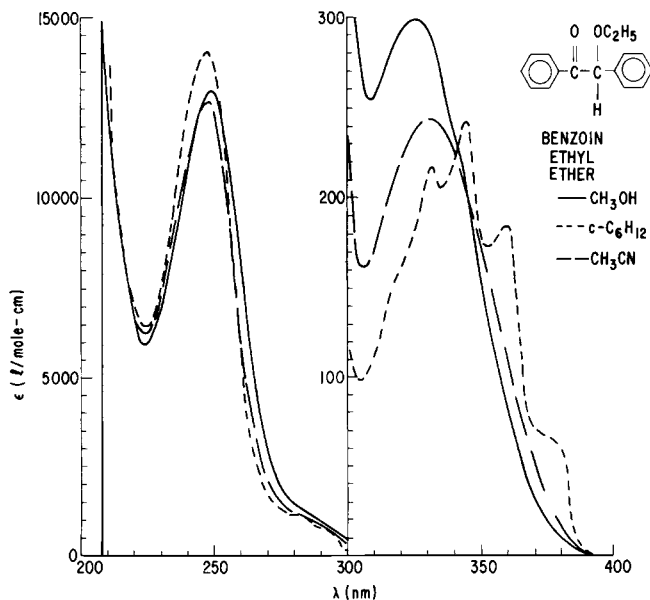


Fig. 1. Ultraviolet absorption spectra of benzoin ethyl ether in various solvents.

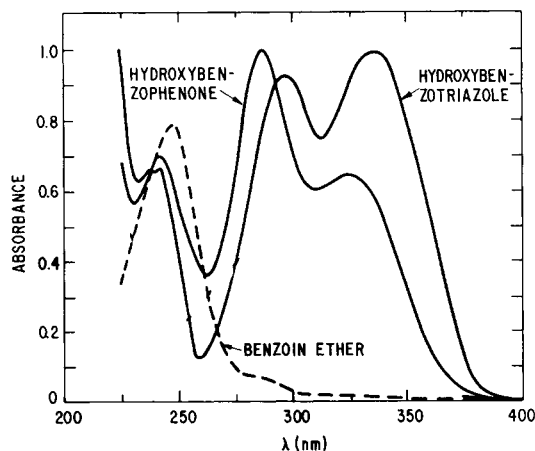
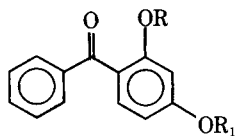
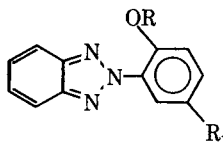


Fig. 2. Ultraviolet absorption spectra of UV screens (hydroxybenzophenone, I, and hydroxybenzotriazole, II) and of a UV-sensitizer (benzoin methyl ether) at concentrations of 15 mg/l. ethanol.

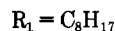
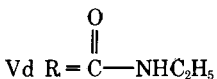
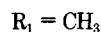
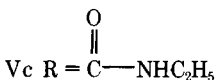
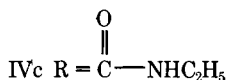
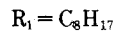
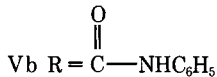
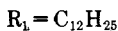
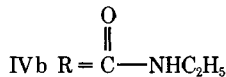
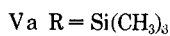
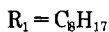
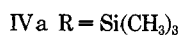
in UV-curable resins. These derivatives can be hydrolyzed after UV cure. However, some of the films containing these silylated derivatives develop color on exposure to UV light. For this reason, other classes of UV screen progenitors have been developed. In this paper, we describe a series of thermally labile UV screen precursors:



IV



V



## RESULTS AND DISCUSSION

For coatings that undergo subsequent heat treatment such as vacuum forming, thermally labile phenolic derivatives of a UV screen can be used as UV screen progenitors. We have found that urethane derivatives of both hydroxybenzophenones (IV,  $R = \text{CONHR}'$ ) and hydroxyphenylbenzotriazoles (V,  $R = \text{CONHR}'$ ) are suitable for this purpose. The urethane derivatives are conveniently and easily prepared in yields of 60%–90% by the reaction of common

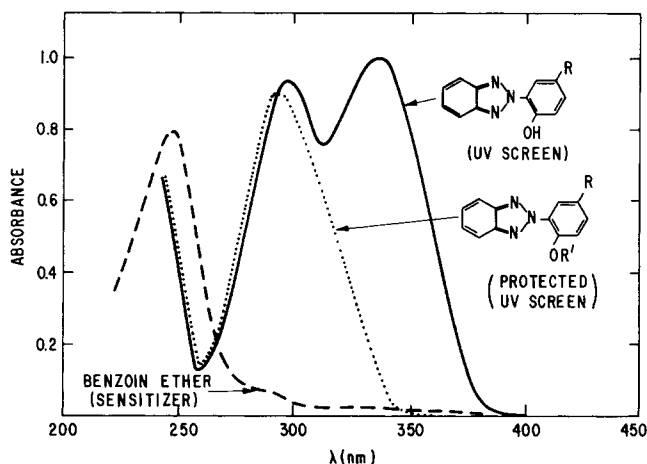


Fig. 3. Ultraviolet absorption spectra of a benzoin ether UV sensitizer, a hydroxyphenylbenzotriazole UV screen (II), and a "protected" hydroxyphenylbenzotriazole (V) at concentrations of 15 mg/l.  $\text{CHCl}_3$ .

commercially available UV screens with isocyanates such as phenyl isocyanate or ethyl isocyanate.

**Aryl Urethanes.** Phenyl urethane (Vb) thermally decomposes at an appreciable rate in solution or in the pure state by a process that regenerates the hydroxyphenylbenzotriazole UV screen (II,  $\text{R} = \text{C}_8\text{H}_{17}$ ) and phenyl isocyanate. Heating Vb for 7 min at  $170^\circ\text{C}$  or 90 min at  $130^\circ\text{C}$  results in complete conversion. However, when the urethane is incorporated in relatively small amounts of about 3% in solid polymer films, no decomposition takes place after heating for 4 hr at  $130^\circ$  or even  $180^\circ\text{C}$ . This suggests that the decomposition reaction is autocatalytic. It has been reported<sup>8</sup> that the thermal decomposition of urethanes can be catalyzed by a variety of compounds such as amines or certain tin derivatives. We have found that these catalysts also effectively promote urethane decompositions in polymer films. Our data, collected in Table I, show that 0.1%–0.2% catalyst is sufficient for the decomposition of urethane Vb. In general,

TABLE I  
Effect of Catalysts on the Thermal ( $130^\circ\text{C}$ , 3 Hr) Decomposition of Urethane Vb in Poly(ethyl Methacrylate) Films

Catalyst	Catalyst, wt-%	Urethane, wt-%	Yield of regenerated UV screen II ( $\text{R} = \text{C}_8\text{H}_{17}$ ), %
None	none	1–10	0
Tetramethyl-1,3-butanediamine	2.5	3.2	69
N,N-Dimethylaniline	0.98	3.7	<10
$\text{Et}_3\text{N}$	0.05	2.9	27
$\text{Et}_3\text{N}$	0.08	3.5	30
$\text{Et}_3\text{N}$	0.24	2.8	63
$\text{Bu}_2\text{SnIau}_2^a$	0.33	3.6	68
$\text{Bu}_2\text{SnIau}_2$	0.17	4.4	67
$\text{Bu}_2\text{SnIau}_2$	0.09	2.9	61

<sup>a</sup> Dibutyltin dilaurate.

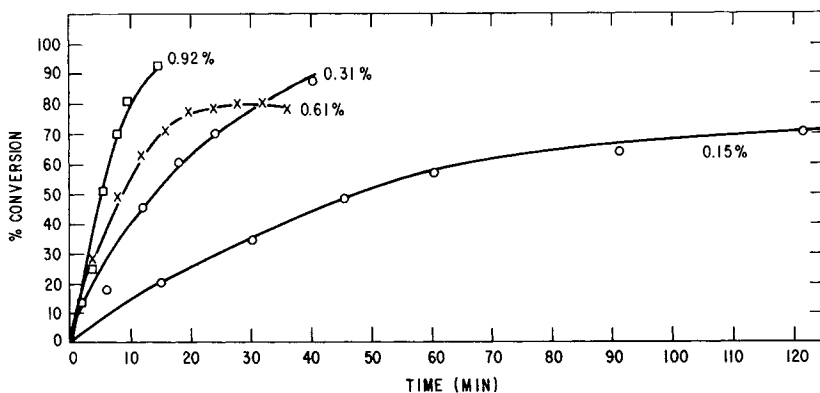


Fig. 4. Effect of dibutyltin dilaurate concentration on generation of UV screen II ( $R = C_8H_{17}$ ) from ethyl urethane Vd in a 2-mil poly(ethyl methacrylate) film.

tertiary alkyl amines function as effective catalysts whereas amines such as *N,N*-dimethylaniline are apparently not sufficiently basic to promote the decomposition. Dibutyltin dilaurate is an even more efficient catalyst than the alkyl amines.

**Alkyl Urethanes.** Alkyl urethanes, prepared by reacting UV screen I or II with an alkyl isocyanate, decompose less readily than phenyl urethanes. For example, heating ethyl urethane Vd at  $170^\circ C$  for 7 min in the absence of a catalyst does not lead to any detectable generation of UV screen II ( $R = C_8H_{17}$ ), whereas phenyl urethane Vb decomposes completely under these conditions. However, alkyl urethanes readily undergo a catalyzed thermal decomposition. Figure 4 shows the effect of catalyst (dibutyltin dilaurate) concentration on the rate of generation of UV screen II ( $R = C_8H_{17}$ ) from its ethyl urethane Vd. It can be seen that the reaction is highly dependent on catalyst level. With 1% dibutyltin dilaurate, the regeneration is nearly quantitative after 15 min at  $130^\circ C$ . A catalyst level of 0.15% is sufficient to give greater than 70% conversion to UV screen in 2–3 hr at  $130^\circ C$ .

**Benzophenone Derivatives.** The urethane decomposition reaction is not restricted to derivatives of hydroxyphenylbenzotriazoles and can be applied equally well to hydroxybenzophenones. As shown in Table II, urethane IVb, prepared by reacting 2-hydroxy-4-dodecyloxybenzophenone with ethyl isocyanate, generates UV screen I ( $R = C_{12}H_{25}$ ) in nearly quantitative yield in a catalyzed reaction after 3 hr of heating at  $130^\circ C$  in a poly(ethyl methacrylate) film.

**Kinetics.** The catalyzed decomposition of urethanes IV and V ( $R = CONHR$ ) follows first-order kinetics through at least one half-life. Table III shows the rate constants calculated from the data in Figure 4. The dependence of the rate on the catalyst concentration indicates that the reaction is *pseudo*-first order.

TABLE II  
Yield of UV Screen I ( $R = C_{12}H_{25}$ ) Regenerated at  $130^\circ C$  from Its Ethyl Urethane in PEMA Film Containing 0.15% Dibutyltin Dilaurate as a Function of Time

Time, min	0	15	30	45	60	75	90	120	200
Yield, %	0	27	46	56	66	72	81	79	90

TABLE III  
Rate Constants at 130°C for the Generation of UV Screen II (R = C<sub>8</sub>H<sub>17</sub>) from Urethane Vd in a PEMA Film at Various Catalyst Concentrations

Catalyst, %	<i>k</i> , min <sup>-1</sup>
0.15	1.4 × 10 <sup>-2</sup>
0.31	5.2 × 10 <sup>-2</sup>
0.62	8.4 × 10 <sup>-2</sup>
0.92	20 × 10 <sup>-2</sup>

The catalyzed urethane decomposition reaction proceeds efficiently at elevated temperatures but also occurs to some extent at room temperature. A UV-curable resin containing 3% ethyl urethane Vd and 0.15% dibutyltin dilaurate showed 10% regeneration of UV screen II (R = C<sub>8</sub>H<sub>17</sub>) after one month at room temperature.

**UV Cures.** Essentially the same degree of cure is achieved for 2-mil films of UV-curable acrylic syrup formulations containing either 3% ethyl urethane Vd or 3% ethyl urethane IVb, or no UV screen progenitor. Details are found in the experimental section. Likewise, the UV screen progenitors can be used in the UV-initiated cure of other resins. Examples are vinyl polymerizations of polyesters<sup>5,9</sup> or multifunctional acrylates,<sup>2,3,10</sup> addition polymerizations of thiol/enes,<sup>11</sup> and cationic polymerizations of cyclic ethers or vinyl compounds.<sup>2,3,12</sup>

### EXPERIMENTAL

**2-(2H-Benzotriazol-2-yl)-4-*t*-octylphenyl N-Phenylcarbamate (Vb).** A solution of 2-(2'-hydroxy-5'-*t*-octylphenyl)benzotriazole (12.92 g, 40 mmoles), phenyl isocyanate (7.87 g, 66 mmoles), and triethylenediamine (0.05 g) in 60 ml methylene chloride was stirred at room temperature for 48 hr. Evaporation of the solvent followed by recrystallization of the residue from ethyl acetate-hexane gave 15.1 g (85%) 2-(2H-benzotriazol-2-yl)-4-*t*-octylphenyl N-phenylcarbamate, (Vb) mp 165–175°C. Infrared (KBr) absorptions at 3.08 (NH) and 5.71 μ (C=O); UV (CHCl<sub>3</sub>): λ<sub>max</sub> 290 nm (17,600); NMR (CDCl<sub>3</sub>): δ 0.82, 1.45 and 1.85 (three singlets, 17H) and 6.8–8.1 (complex, 13 H).

ANAL. Calcd for C<sub>27</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>: C, 73.28; H, 6.83; N, 12.66. Found: C, 73.2; H, 7.0; N, 12.6.

**2-(2H-Benzotriazol-2-yl)-4-*t*-octylphenyl N-Ethylcarbamate (Vd).** A solution of 2-(2'-hydroxy-5'-*t*-octylphenyl)benzotriazole (12.9 g, 40 mmoles), ethyl isocyanate (4.49 g, 63 mmoles), and triethylenediamine (0.05 g) in 25 ml methylene chloride was stirred 24 hr at room temperature. Evaporation of the solvent followed by recrystallization of the residue from ethyl acetate-hexane gave 11.55 g (73%) 2-(2-benzotriazol-2-yl)-4-*t*-octylphenyl N-ethylcarbamate, mp 152°–154°C. Infrared (KBr) absorptions at 3.01 (N-H) and 5.75 μ (C=O); UV (CHCl<sub>3</sub>) λ<sub>max</sub> 300 nm (18,000); NMR (CDCl<sub>3</sub>) δ 1.00 (*t*, *J* = 7), 0.80, 1.45, and 1.80 (three singlets, total area 0.8–2.0 ppm corresponds to 20H), 3.12 (complex, 2H), 5.48 (*t*, *J* = 5, 1H), and 7.1–8.2 (complex, 7H).

ANAL. Calcd for C<sub>23</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>: C, 70.02; H, 7.67; N, 14.20. Found: C, 69.9; H, 7.7; N, 14.1.

**2-Benzoyl-4-dodecyloxyphenyl N-Ethylcarbamate (IVb).** A solution of 2-hydroxy-4-dodecyloxybenzophenone (7.64 g, 20 mmoles), ethyl isocyanate (2.7 g, 38 mmoles), and triethylenediamine (0.005 g) in 5 ml dry methylene

TABLE IV  
Amount of Unreacted Monomer Remaining in UV-Cured Resins Containing UV Screens

UV exposure time, min	Unreacted monomer, %		
	Solution A (no screen)	Solution B (urethane Vd)	Solution C (UV screen II, R = C <sub>8</sub> H <sub>17</sub> )
3	6	6	25
4	5.5	5.5	20
5	5.5	5	18
6	5	5	16

chloride was stirred at room temperature for 100 hr. Evaporation of the volatiles followed by crystallization from hexane gave 4.4 g (49%) 2-benzoyl-4-dodecyloxyphenyl N-ethylcarbamate, mp 70°–72°C. Infrared (KBr) absorptions at 2.97 (N—H), 5.82 (C=O), and 6.04  $\mu$  (C=O); UV (CHCl<sub>3</sub>) $\lambda_{\max}$  285 (12, 150); NMR (CCl<sub>4</sub>)  $\delta$  0.7–2.0 (complex, 26H), 2.0 (complex, 2H), 3.95 (triplet, J = 6, 2H), 5.18 (broad singlet, 1H), 6.70 (3H, complex), and 7.2–7.8 ppm (complex, 5H).

ANAL. Calcd for C<sub>28</sub>H<sub>39</sub>NO<sub>4</sub>: C, 74.2; H, 8.7; N, 3.1. Found: C, 74.6; H, 8.7; N, 3.1.

**Urethane Decompositions in PEMA Films.** Four films were prepared by casting on glass methylene chloride solutions containing 42.6 mg 2-(2-benzotriazol-2-yl)-4-*t*-octylphenyl N-ethylcarbamate (Vd) varying amounts of dibutyltin dilaurate, and 1.20 g of a commercial high molecular weight poly(ethyl methacrylate). After the solvent had evaporated, the resultant films were floated from the glass with water. The films were cut into strips which were suspended in a 130°C oven for various amounts of time. The heated strips were dissolved in chloroform and quantitatively analyzed by UV. Yields of the regenerated UV screen in the various strips were calculated from the amount of absorption at 345 nm. Results at various catalyst levels are shown in Figure 4.

Similarly, a film containing 43.7 mg 2-benzoyl-4-dodecyloxyphenyl N-ethylcarbamate (IVb), 1.9 mg dibutyltin dilaurate, and 1.20 g poly(ethyl methacrylate) was prepared and heated as above. Yields of the regenerated UV screen in the various strips were calculated from the amount of absorption at 327 nm. Results are listed in Table II.

**UV Cures.** The following example illustrates the UV cure of an acrylic resin using ethyl urethane derivative Vd. An acrylic resin blend (A) was prepared from 40 pbw of a poly(methyl methacrylate) resin (molecular weight of ca. 12,000), 60 pbw methyl methacrylate, 1 pbw benzoin ethyl ether, and 0.5 pbw paraffin wax. A second blend (B) consisted of 3 pbw ethyl urethane derivative Vd and 0.2 pbw dibutyltin dilaurate in 98 pbw of solution A. Two-mil films of the resins on Lexan polycarbonate sheet were then exposed to UV light, and the cure of the resin after exposure was measured by baking out unreacted monomer for 1 hr at 150°C. The data in Table IV illustrate that the same degree of monomer conversion was obtained with and without the added UV screen progenitor.

For comparison, 0.5 pbw of the unreacted UV screen II (R = C<sub>8</sub>H<sub>17</sub>) was added to solution A. Films of this solution (C) were then exposed to UV as described above. The data in the table show that this formulation did not UV cure. Essentially the same results were obtained using the ethyl urethane IVb.

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