

# Photosensitized Dehydrochlorination of Poly(vinyl Chloride). I. Effect of Commercial Additives

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## Synopsis

A commercial formulation of thermal antioxidant has been shown to photosensitize the dehydrochlorination of poly(vinyl chloride). The species responsible was shown to be a *p*-alkyl-substituted phenol, and this was confirmed using *p*-cresol as a model compound.

## INTRODUCTION

The irradiation of poly(vinyl chloride) (PVC) with light in the 300–350 nm region is well known to give rise to strong color development as a result of a dehydrochlorination reaction forming strongly absorbing polyenes.<sup>1</sup> Since the "pure" polymer does not absorb radiation in this wavelength region, there has been speculation as to the identity of the absorbing chromophore responsible for the sensitization of this process. One possibility is peroxides remaining as initiator residues from polymerization or produced by thermal processing,<sup>2,3</sup> and added peroxides have been shown to accelerate polyene formation.<sup>2</sup> Ketone impurities have also been implicated,<sup>4</sup> and aromatic<sup>5</sup> and aliphatic ketones<sup>4</sup> have both been shown to sensitize the process. Plasticizers have also been shown to have an effect upon color formation due to conjugated polyene production.<sup>6</sup>

In view of the variety of species capable of sensitizing the photodehydrochlorination of PVC, it is not surprising that a sample of the polymer containing commercial additive formulations was found to discolor rapidly in outdoor use. We present here the results of a brief investigation in which the component of the commercial additives principally responsible for this observation is identified.

## EXPERIMENTAL

### Materials Studied

All materials were supplied by Bakelite-Xylonite Ltd. Two samples, I and II, of unstabilized PVC in powdered form were investigated being suspension homopolymers with isoviscosity numbers 87 and 125, respectively. The following commercial additives were also used: S, a thermal antioxidant described as a liquid Ba/Cd/Zn type containing a phosphate chelator in a predominantly aliphatic hydrocarbon solvent; M, a dibutyltin maleate-type stabilizer; L, a C<sub>16</sub>–C<sub>18</sub> alcohol lubricant; and B, a lubricant manufactured from C<sub>7</sub>–C<sub>9</sub> linear branched and cyclic alcohols.

TABLE I  
Samples Prepared

Sample no.		
1	Polymer I	100 parts
	M	1 part
	L	1 part
2	Polymer I	100 parts
	S	1 part
3	Polymer I	100 parts
	L	1 part
4	Polymer II	100 parts
	B	30 parts
	M	1 part
	L	1 part
5	Polymer II	100 parts
	B	30 parts
	S	1 part
6	Polymer II	100 parts
	B	30 parts
	L	1 part

PVC sheets of various formulations shown below were milled on a two-roll mill at 160°/155°C using a nip setting of approximately 0.012 in. Two minutes after gelling the milled formulations were removed and pressed in a 10 in. × 10 in. steam-heated press at a maximum temperature of 170°C. These sheets were prepared by Bakelite-Xylonite Ltd.

### Samples Prepared

The samples prepared are shown in Table I.

PVC films with and without additives were cast from purified tetrahydrofuran (THF) solution into a brass mold, with the THF allowed to evaporate over a period of several days in a closed atmosphere maintained by an inverted glass tank. The films obtained were of good optical quality.

### RESULTS AND DISCUSSION

Upon irradiation with the light emitted by a Hanovia SH-100 mercury arc transmitted through a Corning CS 7-54 glass filter (transmission profile shown in Fig. 1), color formation was observed only in samples 2 and 3. It is evident that only the low-viscosity PVC is affected by the additives, and moreover, the color formation in sample 3 was an order of magnitude weaker than that in sample 2. The depth of color found in this sample after various irradiation times is indicated in Figure 2. Figure 3 shows the UV-visible absorption spectrum of this sheet as a function of irradiation time. Figure 3 also shows that upon irradiation through a filter combination (Corning CS-7-54 plus CS-0-53, Fig. 1) such that no light below 290 nm reached the film, no strong color formation was observed on the time scale of these experiments. However, on exposure to sunlight outdoors for a six-month period, considerable color development was observed (Fig. 3). There is sufficient ambient insolation in the 300–330 nm region to suggest

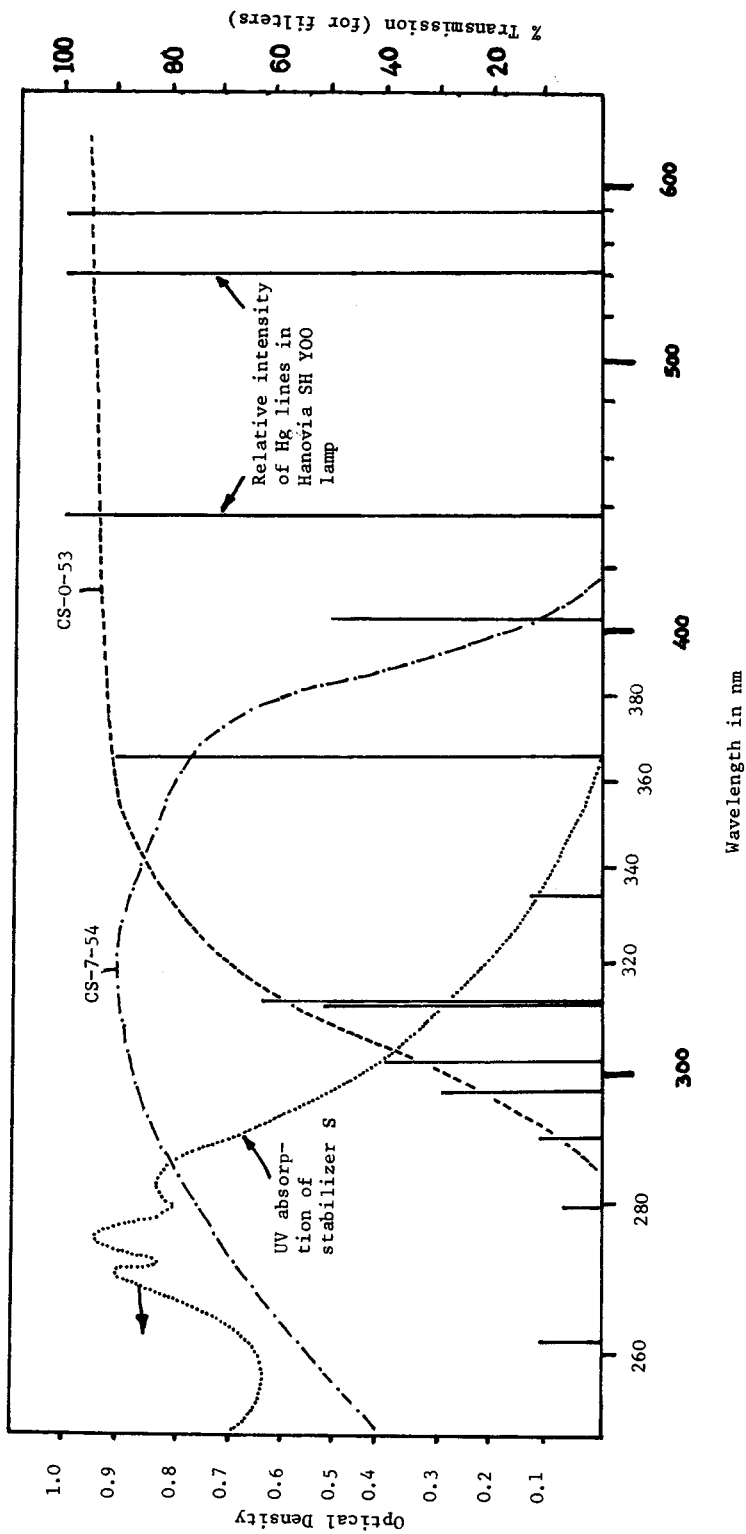


Fig. 1. Spectral output of Hanovia SH 100 mercury arc and transmission characteristics of CS-7-54 and CS-0-53 glass filters, together with absorption spectrum of stabilizer formulations S in THF (one part in 10<sup>4</sup>).

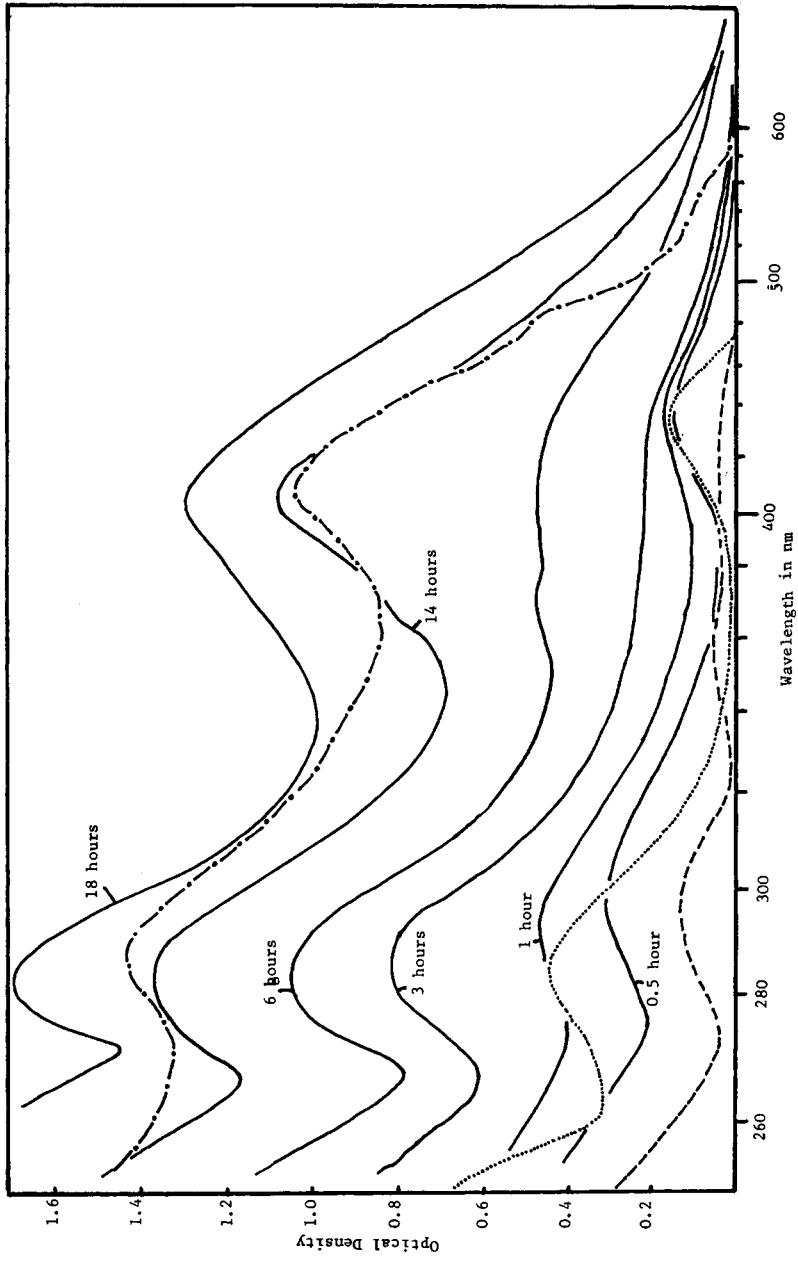


Fig. 2. Discoloration of PVC due to photosensitized dehydrochlorination. (A) Pure PVC irradiated for 6 hr; (B, C, D) cast film of 1% stabilizer S in PVC irradiated 1.25 hr (B), 6 hr (C), and 24 hr (D) through CS-7-54 filter.

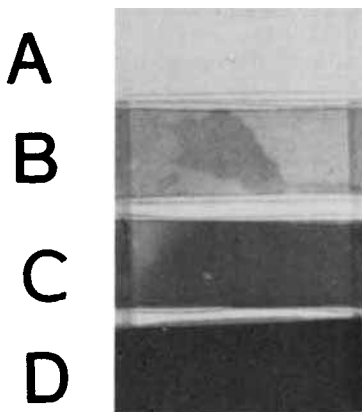


Fig. 3. Solid lines, UV visible absorption spectra of sample 2 after periods of irradiation indicated using CS-7-54 filter alone. (---) Result of 18 hr of irradiation of sample 2 through CS-7-54-CS-0-53 filter combination. (— · —) Sample 2 weathered out of doors for six months (approx. 1180 hr of sunlight). (···) Cast a film PVC containing 1% *p*-cresol irradiated through CS-7-54 filter for 0.33 hr.

that a component of the stabilizer formulation S with an absorption maximum in the 280-nm region is responsible for the photosensitization of the color formation at 400 nm. Exactly comparable results were obtained in films cast from THF with the same range of additives. The absorption spectrum of stabilizer S in THF is shown in Figure 1 to have such an absorption at 280 nm.

The identity of the species responsible for the sensitized dehydrochlorination was established in the following way. An ethereal solution of the stabilizer was separated into basic, phenolic, acidic, and neutral components by first adding sodium carbonate, filtration of inorganic carbonates, and then separating the aqueous layer, which was neutralized with hydrochloric acid and extracted. The phenolic components were obtained from the ethereal solution remaining after removal of the aqueous fraction by addition of sodium hydroxide, and the basic fraction was obtained from the solution remaining by extraction with HCl.

The UV spectrum of the stabilizer solution after removal of the phenolic fraction showed a vastly diminished UV absorption at 280 nm, pointing to the involvement of a phenol as the sensitizer. The phenolic fraction was separated into components by preparative TLC (1 mm silica gel plates in petroleum ether:ethyl acetate 3:1). A major component was shown by mass spectrometry NMR and UV absorption to be a *p*-substituted nonyl phenol. Thus, the mass spectrum had peaks at  $m/e$  220 ( $C_{15}H_{24}O^+$  parent), 205 ( $-CH_3$ ), 191 ( $-C_2H_5$ ), 177 ( $-C_3H_7$ ), 163 ( $-C_4H_9$ ), 149 ( $-C_5H_{11}$ ), 135 ( $-C_6H_{13}$ ), 121 ( $-C_7H_{15}$ ), and 107 ( $-C_8H_{17}$ ). The NMR spectrum was consistent with this identification ( $\tau$  3.2–6.4/4H,  $\tau$  3.4/1H,  $\tau$  7.9–9.2 19H).

Since phenols, typically of the hindered type such as 2,6-ditertiary butylcatechol, are commonly used as thermal antioxidants in which capacity they act as radical scavengers, the isolation of a compound of this type is not surprising. However, the capacity for the phenol to act as a potent photosensitizer of dehydrochlorination was unexpected. This property was confirmed, however, by the use of *p*-cresol as a model compound. As shown in Figure 3, irradiation of a cast film of PVC containing 1% *p*-cresol results in color formation very similar

in extent to that observed in the polymer with commercial additive formulation. Clearly, for outdoor applications, the use of such thermal oxidants should be used with caution.

The work reported here was carried out as part of the M.Sc. projects of P.H.W. and R.J.F., University of Southampton 1973-1974. The authors are grateful to the Science Research Council for financial support and to Bakelite-Xylonite Ltd. for provision of materials.

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Received January 14, 1977

Revised April 1, 1977