Accelerated Photo-Oxidation of Polyethylene. II. Further Evaluation of Selected Additives

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Synopsis

A number of additives previously observed to promote photo-oxidative degradation of polyethylene films have been evaluated with respect to their relative photoinitiating effectiveness at wavelengths near 300 nm and their effects on thermal-oxidative stability of polyethylene. Depending on the nature of the additive, the photo-oxidation process may display autoretarding or autoaccelerating behavior. Thermomechanical analyses and gel content measurements on UV-exposed films containing substituted anthraquinones suggest that at short exposure times, photo-oxidative degradation is accompanied by photochemical crosslinking.

INTRODUCTION

The preceding paper in this series[1] described the results of preliminary "screening" studies intended to identify substances capable of accelerating the environmental photo-oxidative degradation of polyethylene and discussed the mechanisms by which such additives may initiate photodegradation. Those studies utilized an ultraviolet source exhibiting peak emission at 300 nm, since we were particularly interested in identifying compositions which would be sensitive to sunlight but insensitive to normal indoor lighting. The present paper reports the results of further studies in which a variety of additives were evaluated with respect to their effectiveness as photoinitiators and their effects on thermal-oxidative stability of polyethylene.

COMPARATIVE EXAMINATION OF PHOTOINITIATING EFFECTIVENESS

Low-density polyethylene films, typically containing 2% by weight of the selected additive, were prepared as described previously.[1] The exposure technique described previously[1] was modified in an effort to provide a better simulation of exposure to the "erythemal" region of the solar spectrum and to provide a basis for a semiquantitative evaluation of the photoinitiating effectiveness of various additives. Light from a source exhibiting peak emission at 300 nm was filtered through borosilicate glass in order to ensure the elimination of light having wavelengths shorter than 290 nm.

The infrared absorption spectrum of each film was measured both before and after exposure to this filtered source for a period of 24 h in ambient air. The increase in absorbance in the carbonyl region (ca. 1720 cm^{-1}) was taken as an indication of the extent of photo-oxidative degradation. In certain cases it was

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also possible to detect increased absorbance in the hydroxyl region (ca. 3360 cm^{-1}) as a result of the formation of polymer hydroperoxide. Similar infrared methods have been employed in a number of other studies of photo-oxidation of polyethylene.[2–12]

The results of a number of these experiments are summarized in Table I. Unless otherwise specified, the additives were employed at a concentration of 2% by weight of the resulting film.

Alkyl-substituted anthraquinones such as 2-tert-butylanthraquinone and 2-ethylanthraquinone appear to be more effective as degradation-promoting additives than anthraquinone itself. This observation is tentatively attributed to the higher solubility of the substituted anthraquinones in the polymer.

The following additives displayed negligible or slight accelerating effects (increase in IR absorbance 0.010 or less): anthraquinone-2-carboxylic acid, 4'-benzyloxypropiophenone, 4,4'-bis(diethylamino)benzophenone, benzanthrone, benzoin, p-benzyloxybenzylideneacetophenone, coumarin, 2-chloroanthraqui-

TABLE I
Examination of Photoinitiating Effectiveness[a]

Additive	Increase in carbonyl absorbance	Increase in hydroxyl absorbance
Cobalt octoate (1%)	0.415	0.035
Iron octoate (1%)	0.250	0.040
2-tert-butylanthraquinone	0.105	0.030[b]
2-ethylanthraquinone	0.105	—
Ferrous stearate (1%)	0.095	0.025
4-Dimethylaminobenzophenone	0.085	0.035[b]
Flavanone	0.085	0.010
Thioxanthone	0.080	0.005
Chalcone	0.055	—
Cinnamylideneacetophenone	0.045	—
Flavone	0.045	—
4,4''-oxydibenzophenone	0.045	—
2-methylanthraquinone	0.035	0.030[b]
Xanthone	0.030	—
9-anthraldehyde	0.025	—
p-anisyl benzyl ketone	0.025	—
4,4'-bis(dimethylamino)benzophenone	0.025	—
Decanophenone	0.025	—
Phenanthrenequinone	0.025	0.015
9-anthracenylideneacetophenone	0.020	—
4-allyloxybenzylideneacetophenone	0.020	—
Benzoin acetate	0.020	—
Dibenzocycloheptadienone	0.020	—
Leuco-malachite green	0.020	—
2,2'-methylenebis(benzothiazole)	0.020	—
1-methoxyanthraquinone	0.020	—
Anthraquinone (2%)	0.015	
Deoxybenzoin	0.015	—
1,4-naphthalenediol	0.015[b]	—
4-octyloxybenzylideneacetophenone	0.015	
Triphenylamine	0.015	—

[a] UV irradiation (24 h) in air, using borosilicate-filtered radiation from 300-nm source.
[b] Intensity of "additive" peaks reduced as a result of exposure.

none, desoxyanisoin, 2,5-di-*tert*-butylhydroquinone, 1,4-dibenzoylbutane, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, diphenyl carbonate, fluorene, *p*-hydroxypropiophenone, 2-methyl-1,4-naphthoquinone, 4'-methoxychalcone, 4,4'-methylenebis(*N*,*N*-dimethylaniline), 2-mercaptobenzothiazole, α-pentyl-cinnamaldehyde, phenyl disulfide, *N*-phenyl-2-naphthylamine, *N*-phenyl-1-naphthylamine, phenyl salicylate, α-phenylindole, and 1,3,5-triacetylbenzene. The failure of these materials to exhibit significant photoinitiating effects may be attributed to one or more of the following factors:

(1) A poor "match" between the absorption spectrum of the additive and the ultraviolet wavelengths present in the incident radiation.

(2) Limited solubility or dispersibility of the additive in polyethylene.

(3) The availability of an efficient pathway for intramolecular photochemical deactivation of the excited state of the additive.

(4) The availability of nonphotochemical pathways, such as fluorescence, phosphorescence, or radiationless conversions, for deactivation of the additive's excited state.

EVALUATION OF AUTO-OXIDATIVE REACTIVITY OF ADDITIVE-CONTAINING POLYETHYLENE COMPOSITIONS

In order to have practical utility as an initiator of environmental photodegradation, it is not sufficient that an additive only display good efficiency in initiating photo-oxidative processes. The effect of the additive on the ease of *thermal*-oxidative degradation is also of interest, since in most cases it is desired to incorporate the additive into the polymer prior to the fabrication of a film, sheet, or molded article by conventional melt processing technology. Undesired thermal reactions during the melt processing step can have adverse effects on the processibility and physical properties of the polymer and on the reusability of scrap. While others have approached this problem by adding conventional antioxidants along with additives known to accelerate thermal-oxidative degradation, we preferred to begin by examining the influence of a variety of photoinitiating additives on thermal oxidation; it was hoped that it would be possible to identify some photoinitiating additives which have little or no effect on thermal oxidation processes.

The technique selected for initial evaluation of autoxidative reactivity was differential thermal analysis (DTA) of additive-containing films in an oxygen atmosphere at a slow heating rate (2°C/min). Similar techniques have been employed by other workers for similar purposes.[13-16] The "onset temperature," at which the oxidation exotherm first causes detectable deviation from the baseline, was taken as a rough indication of oxidative reactivity. The results are given in Table II. Those additive-containing polyethylene samples which exhibited onset temperatures higher than the additive-free polyethylene sample were considered to display a stabilizing or inhibiting effect on autoxidation, while lower onset temperatures were interpreted as enhanced autoxidation. Unless otherwise specified, each additive was present at a concentration of 2% by weight.

Reviewing the results in Table II, several points are worthy of mention. Additives which would be expected to function as antioxidants, such as *N*-phenyl-2-naphthylamine and 1,4-naphthalenediol, do cause a shift of the oxidation

TABLE II
DTA Studies of Effect of Selected Additives on Polyethylene Autoxidation

Additive	Onset temperature °C
None	162
N-phenyl-2-naphthylamine	222
Ferric dibutyldithiocarbamate	216
1,4-naphthalenediol	210
Phenanthrenequinone	184
Thioxanthone	183
2-methylanthraquinone	170
4-dimethylaminobenzophenone	166
Triphenylamine	165
2-chloroanthraquinone	164
Flavanone	162
2-tert-butylanthraquinone	160
Chalcone	160
4,4″-oxydibenzophenone	160
Anthraquinone	156
Xanthone	156
2-ethylanthraquinone	154
Flavone	154
Iron octoate (1%)	128
Ferrous stearate	116

onset to higher temperatures. Transition metal compounds which would be expected to function as pro-oxidants, such as iron octoate and stearate, have the opposite effect. Ferric dibutyldithiocarbamate exhibits a substantial stabilizing effect; this observation is in accord with the reports of Scott et al.[10,17–19] Phenanthrenequinone and thioxanthone appear to confer a modest increase in oxidative stability. Photosensitizers of the anthraquinone and aromatic ketone types do not appear to cause major changes in susceptibility to autoxidation.

It should be emphasized that these DTA studies are qualitative and preliminary; more detailed studies would be required in order to reach firm conclusions about the relative effects of different additives on oxidative stability, the role played by additive concentration, and so on.

FURTHER STUDIES OF PHOTO-OXIDATION OF POLYETHYLENE FILMS CONTAINING SELECTED ADDITIVES

The photo-oxidation behavior of polyethylene films containing a few selected additives was examined in greater detail. Effects of time and additive concentration on the extent of photo-oxidative degradation were determined by infrared measurements of carbonyl absorbance in ultraviolet-exposed films. Figures 1 and 2 show the results for the cases of film containing anthraquinone and 4,4″-oxydibenzophenone, respectively, after exposure to an unfiltered source having peak emission at 300 nm. In both these cases, it was possible to resolve infrared peaks arising from carbonyl groups in oxidized polyethylene from those attributable to the additive. While the "oxidized polyethylene" peaks show a gradual increase over the course of the ultraviolet exposure, the "sensitizer" peaks diminished substantially in intensity during the early stages of the photo-oxi-
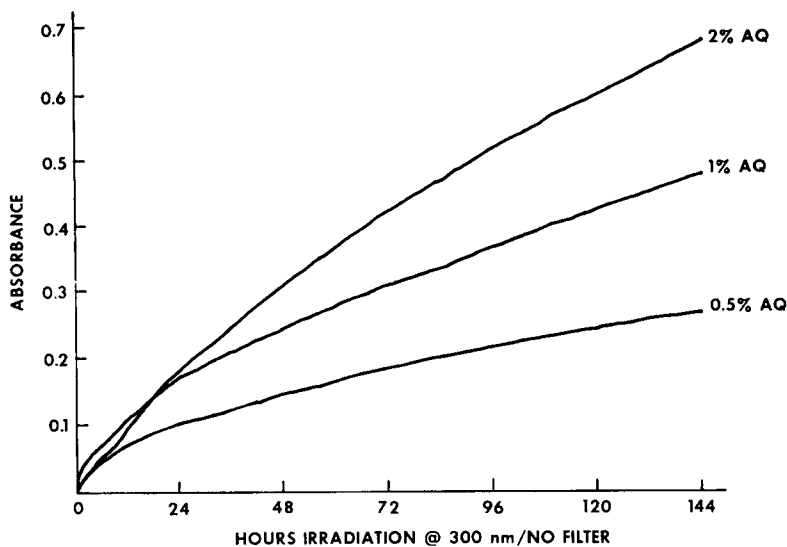
Fig. 1. Carbonyl infrared absorbance changes in irradiated anthraquinone-sensitized polyethylene films.

dation. Presumably, the retardation of the photo-oxidation process as irradiation proceeds can be attributed to the chemical conversion of the additive to another species which is less prone to initiate photo-oxidation. This supposition is further supported by the results of supplementary experiments in which UV-exposed films containing substituted anthraquinones were subjected to
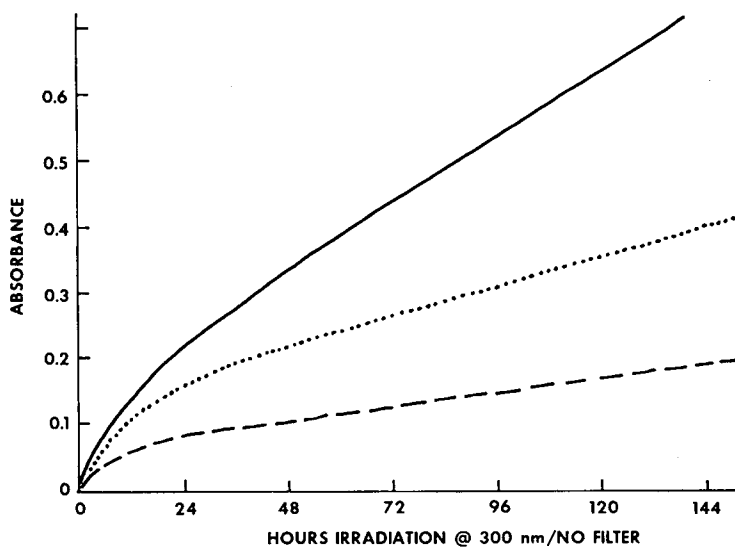
Fig. 2. Carbonyl infrared absorbance changes in irradiated polyethylene films sensitized with 4,4″-oxydibenzophenone.   (——) 2% ODP, (· · · ·) 1% ODP, (- - -) 0.5% ODP.

solvent extraction with 1,4-dioxane. Ultraviolet spectrophotometric mea-
surements on the extracts indicated that the level of extractable photoinitiator
decreased rapidly during the first few hours of irradiation under a borosilicate-
filtered source having peak emission at 300 nm. Similar observations have been
reported by Scott.[22]

Very different behavior was observed when ferric dibutyldithiocarbamate was
employed as a photoinitiator. The results, shown in Figure 3, indicate that an
initial induction period is followed by the initiation of rapid, extensive, and
continuing photo-oxidation. These observations are in accordance with those
reported by Scott et al.[10,11,19] Ferrous stearate (Fig. 4) likewise causes substantial
and continuing photo-oxidation, but without an initial induction period.

While infrared measurements provide evidence of the nature and extent of
chemical changes occurring during photo-oxidation, they do not provide direct
evidence concerning changes in the polymer's mechanical or thermal properties.
Figure 5 depicts the results of a study in which unexposed and UV-exposed films
containing 2% 2-tert-butylanthraquinone were characterized by thermome-
chanical analysis (TMA). All samples exhibit extensive distortion at 110–120°C,
as would be expected in the vicinity of the crystalline melting point of low-density
polyethylene. Complete penetration of the sample by the TMA probe is ob-
served with the unexposed material. In the case of exposed samples, however,
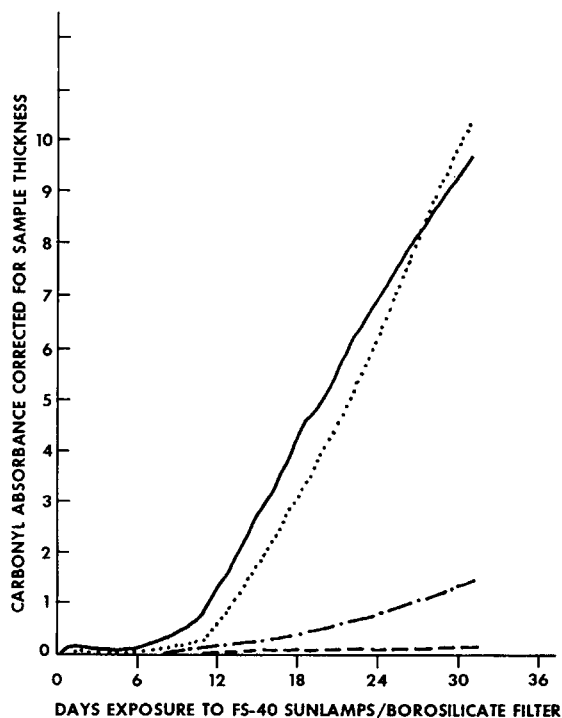the thermal distortion does not lead to complete penetration of the probe; instead,

Fig. 3. Photo-oxidation of polyethylene films sensitized with Ferric dibutyldithiocarbamate. (·····)
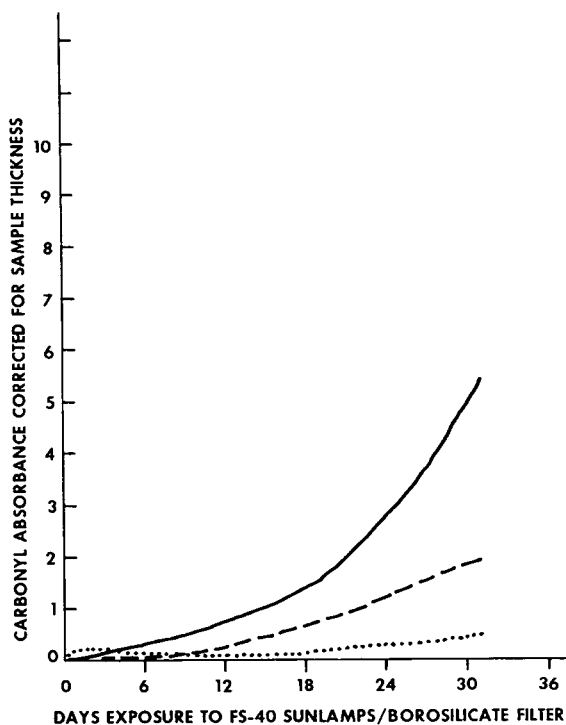0.10% FeDBDTC, (——) 0.05% FeDBDTC, (—·—) 0.01% FeDBDTC, (- - -), 0.50% FeDBDTC.

Fig. 4. Photo-oxidation of polyethylene films sensitized with ferrous stearate. (———) 0.05% Fe stearate, (‑ ‑ ‑) 0.01% Fe stearate, (· · · ·) no additive.

the samples exhibit a degree of resistance to distortion which varies as a function of irradiation time. These results suggest that photo-oxidation is accompanied by crosslinking—a suggestion that has received support from the work of several groups.[8,11,19–22]

Further evidence for crosslinking was obtained by measurement of the gel content of irradiated additive-containing samples. Figure 6 shows the gel content, as well as the carbonyl absorbance, as functions of the concentration of the photoinitiator 2-ethylanthraquinone under selected exposure conditions (48 h irradiation in air, borosilicate-filtered source having peak emission at 300 nm).

EXPERIMENTAL

Materials

An additive-free grade of low-density polyethylene (Sinclair-Koppers Super Dylan WPD-367F) was used. Laboratory or commercial additives employed were of the highest available purity and were used without further purification; in most cases they were reagent-grade laboratory chemicals.
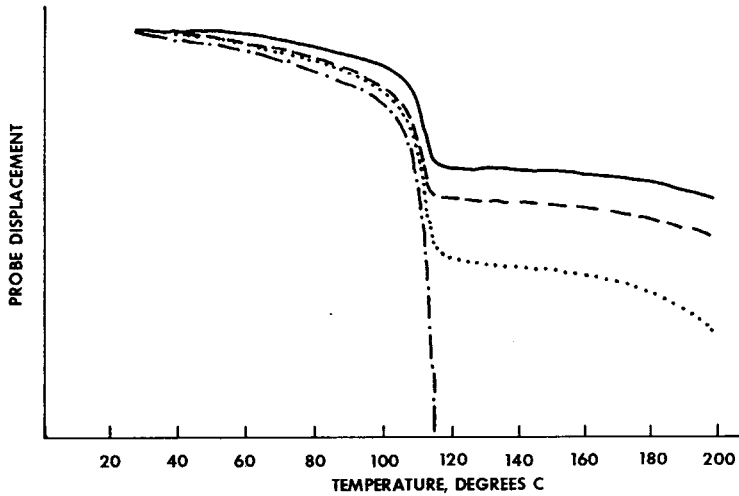
Fig. 5. Thermomechanical analyses of polyethylene films sensitized with 2% 2-*tert*-butylanthraquinone and irradiated at 300 nm/borosilicate.   (——) 12-h exposed, (- - -) 8-h exposed, (· · · ·) 4-h exposed, (-·-) unexposed.

Sample Preparation

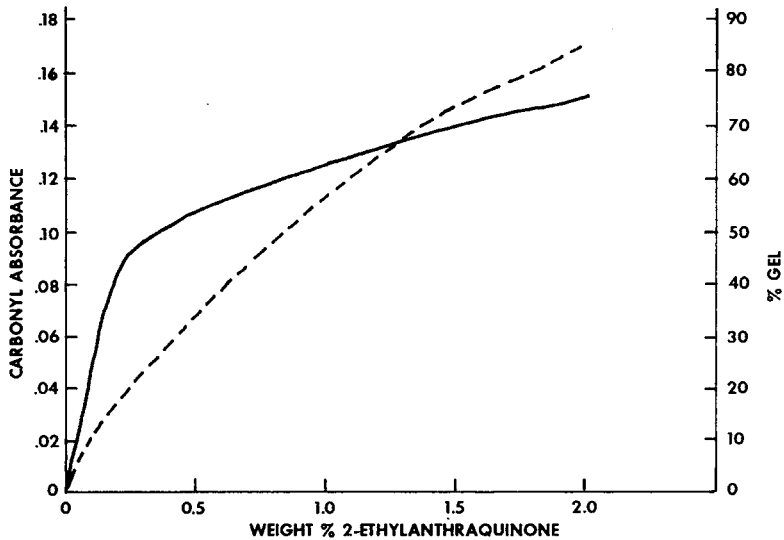Additive containing films were prepared by the solution-cast method described earlier.[1]

Fig. 6. Gel content and carbonyl absorbance of polyethylene films as functions of sensitizer concentration.   Films irradiated 48 h at 300 nm/borosilicate.   (——) % gel, (- - -) carbonyl absorbance.

Ultraviolet Exposure

If an additive was shown to cause significant degradation of the polyethylene after preliminary screening exposure conditions, which were described earlier,[1] samples were then examined further using filtered irradiation. This involved 24-h irradiation under a 300-nm fluorescent U-tube measuring 17 in. in length and 4 in. in width (RUL—3000 lamp, Southern New England Ultraviolet Co.). These lamps are phosphor coated on the inside surface and are equipped with a reflector. Each lamp produces a total output energy of ca. 35 watts. A $1/4$-in. borosilicate glass filter was placed between the light source and the sample to filter out wavelengths less than 290 nm. Source-to-sample distance was 3 in.

Infrared Measurements

Infrared spectra were obtained using a Perkin–Elmer model 237B spectrophotometer as described earlier.[1]

Thermal Analysis

Two thermal analysis techniques—differential thermal analysis (DTA) and thermomechanical analysis (TMA)—were employed during the course of this work. DTA measurements were performed on a du Pont model 900 Differential Thermal Analyzer equipped with a DSC cell and with an electronic signal differentiator. Samples (generally 5–10 mg) were weighed into miniature aluminum pans, which were used without lids; an empty aluminum pan was used as reference. Studies of thermal oxidation were performed with oxygen flowing through the DSC cell (flow rate typically 0.5 L/min). The usual DTA curve and its derivative were recorded simultaneously; recording of the derivative aided in locating the "onset temperature" of thermal auto-oxidation. A heating rate of 2°C/min was employed in most of the experiments.

TMA was employed in an attempt to observe directly physical changes in polymer samples resulting from degradation and/or crosslinking. A modified du Pont model 941 Thermomechanical Analyzer was used. Samples of polyethylene film were held by a pair of concentric stainless steel rings which snapped together to hold the sample (ca. 7 mm in diameter) like the head of a drum. A quartz probe with a spherical tip was brought into contact with the sample under a constant load of 2 g. The deformation of the film was recorded as a function of temperature during linear temperature programming (heating rate 10°C/min).

Gel Content Measurements

"Gel content" measurements were used to estimate the extent of crosslinking in irradiated film samples. Samples (0.1–0.2 g) were weighed into glass extraction thimbles with coarse fritted-glass discs (Kimflow type 25EC); each thimble was then immersed for 16 h in 100-mL refluxing xylene. The thimble was then removed, allowed to drain, and dried in an oven at 105°C. The gel content was then taken as the per cent of the original sample weight remaining after this treatment.

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