

Photo-oxidation of Polypropylene Films. VI. Possible UV-stabilization Mechanisms

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Synopsis

The effects of the chemical nature, concentration, stability, and location of various additives on the ultraviolet stability of polypropylene are discussed. It is shown that effective stabilizers of thin films do not depend on UV absorption for their protective action, whereas some relatively inefficient additives operate solely as UV screeners. Adequate UV protection was observed when small amounts (~ 0.01 wt-%) of effective stabilizers were concentrated in or on the surfaces of commercial films, and the remaining bulk of the film contained only a very low concentration (~ 0.01 wt-%) of uniformly blended additive. Previous attempts at demonstrating energy-transfer stabilization of the polymer are discussed with reference to the present data; it is concluded that effective polypropylene stabilizers probably operate by a combination of chromophore quenching, radical scavenging, and hydroperoxide decomposition.

INTRODUCTION

Since polyolefins do not themselves absorb beyond ~ 2200 Å, the photo-oxidative deterioration of these polymers by the ultraviolet (UV) component of terrestrial sunlight (>2900 Å) is believed to be initiated by the presence of chromophoric impurities and/or by the direct photolysis of oxygen or oxygen-polymer charge transfer complexes.¹ Possible photoinitiating impurities in polypropylene include macrocarbonyl² and peroxidic derivatives³ (produced by either inadvertent thermal oxidation, O_3 , or 1O_2 attack), traces of metals⁴ (especially Ti compounds), and C—C unsaturation.⁵ However, most of these possible sources of initiation will begin to generate macrocarbonyl and macroperoxidic products as soon as irradiation starts. Consequently the photolyses of these latter polymer chromophores probably dominate the initiation of photo-oxidative degradation soon after the onset of degradation.

In practice, several types of impurities may contribute to photoinstability simultaneously, the relative importance of any one depending on the synthesis and processing conditions of the resin and the subsequent history and irradiation conditions of the polymer. For example, the photo-oxidation of commercial 22- μ polypropylene films has been found to occur predominantly in the surface layers of the films (less than ~ 2000 Å thick).⁶

This effect was attributed to the presence in the film surfaces of thermal oxidation products, probably resulting from the exposure of the molten extruded polymer to air, prior to quenching.⁷

There are already many commercially available additives which are reputed to improve the photostability of polymers.⁸ An UV stabilizing additive might inhibit the photo-oxidative deterioration of the solid polymer by either preventing the initiation of degradation or preventing radical propagation. Photoinitiation can be reduced either by the additive preventing the damaging UV wavelengths from reaching the chromophores (i.e., acting as an UV absorber) or by the additive promoting the deactivation of the excited chromophore (produced by UV absorption) back to the ground state (i.e., chromophore quenching). In this quenching process, the absorbed energy of the excited chromophore must be dissipated harmlessly by, for example, reemission at longer wavelengths, so that subsequent damage to the polymer does not occur. Scavenging of free radicals produced during photooxidation (alkyl R·, alkoxy RO·, or peroxy RO₂·) will also inhibit photodegradation.⁹ Reactions involving the mobility of the additive or reactive species will be somewhat limited by the solid matrix. However, both chromophores and additives¹⁰ will be largely concentrated in the amorphous zones of the polymer where mobility is most favored. In addition, some association between chromophores and the usually polar UV-stabilizer additives can be expected to occur during the cooling of the molten polymer, and this is likely to enhance the efficiency of subsequent quenching processes. Alternative means of reducing photoinitiation rates can involve a reduction in the effective chromophore concentration by, for example, complexing between the additive and the chromophore or by additive-promoted chemical destruction of chromophores. Alternatively, complexing might result in a reduction in the quantum yield for reactions leading to photo-oxidation.

The practical evaluation of the UV-stabilizing effectiveness of an additive for polymer films involves a comparison of the lifetime of a film containing 0.5 w-% or less of the additive with the lifetime of an unstabilized film, both films receiving identical UV exposures. However, the results of this type of test are frequently difficult to interpret in terms of the mode of action of the additive owing to various complications. For example, the true stabilizing effectiveness of an additive may be obviated by its volatility or instability during irradiation, by photosensitizing certain reactions, or by its instability under extrusion conditions. Hence, a search for efficient classes of UV-stabilizing additives for polymer films must involve at least a continuous monitoring of the additive concentration during the degradation.

Despite the growing awareness that polypropylene articles, in particular thin films, fibers, and split films, cannot be effectively stabilized simply by a UV-absorption mechanism,^{11,12} the polymer additives are still frequently referred to as "UV absorbers" in the literature. For those additives which do stabilize thin polypropylene materials efficiently, it is important to identify and understand what alternative stabilization mechanisms are

involved. In this paper, we discuss the use of a simple screening test which allows the rapid discrimination between stabilizer types and clearly demonstrates the ineffectiveness of additives that protect solely by absorption of the incident UV. In addition, the importance of type, concentration, stability, and location of the stabilizer additive within an article are discussed. Evidence is also presented which indicates that the quenching of excited carbonyl impurities by effective additives can contribute only partially to the stabilizing effect of some efficient polypropylene stabilizers.

EXPERIMENTAL

Materials

Films of known thickness (25–30 μ) were prepared from an isotactic polypropylene powder (Moplen, Montecatini Edison). The unstabilized powder had not been previously processed apart from the removal of catalyst residues. Prior to film fabrication, additives were dissolved in a suitable solvent, the solution was added to the resin powder, and the additives deposited by evaporating the solvent (5 hr at 10^{-2} torr). Only thermally stable additives were employed. The criterion for thermal stability was taken to be an unchanged melting point after heating at 225°C in air for 3 min. Films were prepared by pressing the powder between quartz plates at 225°C in an N_2 -blanketed press, quenching in Dry Ice/methanol, and vacuum drying.

Additives were also introduced into unstabilized 22- μ commercial film samples (Eastman, isotactic polypropylene) subsequent to manufacture, either by a brief diffusion of the additive from a suitable solvent or by vacuum sublimation to produce surface coatings. Samples to be treated in the latter manner were attached to a drum which rotated in a bell jar above a boat containing a weighed amount of the required additive. The jar was evacuated to 2.0 torr (N_2), rotation was started, and the boat was heated to the predetermined sublimation temperature so that the additive transferred uniformly to the film sample. The film was then identically treated on its opposite surface. Total loadings were determined from the weight increase of the films or by UV spectroscopy. Additives were shown to be concentrated on or close to the film surfaces by attenuated total reflection spectroscopy in the infrared, using the method described previously.²

Photo-oxidation

Films were irradiated with UV in air in an Atlas carbon-arc Fade-Ometer (ambient temperature 35°C). The onset of deterioration was detected by transmission infrared (IR) spectroscopy, and the failure point was taken to be an —OH optical density (at 3400 cm^{-1}) of 0.010 (corrected to 22- μ thickness). This point corresponds closely to the sudden loss of flexibility of the samples (elongation less than 50%, as compared to $\sim 700\%$ before irradiation).² The deterioration of some samples was also studied during irradiation in an Atlas xenon-arc Weather-Ometer at 46°C (Pyrex inner,

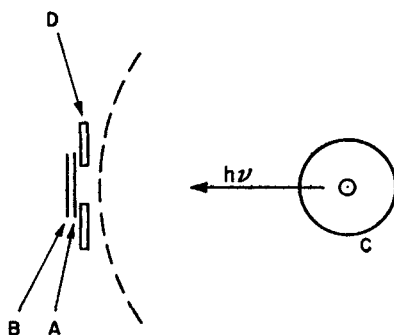


Fig. 1. Film irradiation arrangement.

"clear glass" outer filters). These results were very similar to those from the carbon-arc irradiations, and irradiation lifetimes usually only differed by less than 20% despite the significant differences in spectral outputs of the sources.

Blank experiments showed that neither the solvents nor the vacuum sublimation conditions employed in the addition of stabilizers to films influenced the subsequent photostability of the films.

The mechanism of stabilization by each additive was studied, as shown in Figure 1, by monitoring the effects of radiation from the carbon-arc D on an unstabilized film sample B mounted immediately behind each additive containing film A. The unstabilized film only received UV radiation which had passed through the additive-containing film. Film samples were mounted on the metal Atlas SL-LSR holders C.

After irradiation, additive concentrations in films were determined by transmission IR or UV spectroscopy, using multiple film thicknesses where necessary. Crystallization rates were estimated by visually observing, under polarized light, the crystallization of film samples melted on a Mettler FP52 Hot Stage.

RESULTS AND DISCUSSION

Importance of UV Absorption

Photodegradation of polypropylene films results in the buildup of —OH products (largely hydroperoxides in the early stages) and carbonyl products, which are readily monitored by IR spectroscopy.¹³ When certain additives were blended into the A films (Fig. 1) which were directly irradiated in the carbon arc, the practical lifetime of these films (as shown by the slower rate of build-up in —OH absorption) was markedly increased beyond that of other directly irradiated, but unstabilized samples. In addition, unstabilized B films (Fig. 1) which were exposed behind the stabilized films A showed either little or no increase in UV stability (as compared to a directly irradiated unstabilized film), or alternatively were found to have lifetimes close to those of the A films. These effects are illustrated by the

TABLE I
 UV Stability of Films with Blended Additives

Additive	Additive concn., wt-%	Irradn. lifetime, hr	
		Stabilized film ^a	Screened film ^b
—	—	110	90
I Resorcinol monobenzoate	0.1	150	150
II 4-(<i>tert</i> -Octyl)phenyl salicylate	0.1	135	135
III Substituted 2(2'-hydroxyphenyl)- benzotriazole ^c	0.3	200	210
IV Ethyl 2-cyano-3,3-diphenyl acrylate	0.1	190	140
V 2-Hydroxy-4-dodecyloxybenzophenone	0.2	560	100
VI Octadecyl 3-(3',5'-di- <i>tert</i> -butyl-4'- hydroxyphenyl) propionate	0.1	440	110
VII Dimethylglyoxime	0.05	300	100
VIII Zinc di-isopropylidithiophosphate <i>Ni(II)</i> chelates of:	0.1	380	95
IX Glyoxime	0.1	570	140
X Dimethylglyoxime	0.1	650	140
XI Butyl 3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl phosphonate	0.3	800	110
XII 2,2'-Thiobis(4- <i>tert</i> -octylphenol)	0.1	250	110
XIII 2,2'-Thiobis(4- <i>tert</i> -octylphenol) plus <i>n</i> -butylamine	0.1	470	110
XIV 2-Hydroxy-5-methoxyphenyl- <i>N-n</i> - butylaldimine	0.1	380	140
XV Di- <i>n</i> -butyldithiocarbamate	0.1	1310	110
XVI 2-Hydroxy-4-methoxybenzophenone	0.5	190	95
XVII 2,6-Di- <i>tert</i> -butyl-4-methylphenol	0.1	195	115
XVIII 1,3,5-Trimethyl-2,4,6-tri(3',5'-di- <i>tert</i> - butyl-4'-hydroxybenzyl)benzene	0.1	205	110

^a Moplen films (pressed from powder).

^b Screened Eastman film (commercially extruded) free of additives. Irradiated directly behind the stabilized film.

^c Tinuvin 328 (Ciba-Geigy Corp.).

data in Table I. Additives I to IV resulted in similar lifetimes for the A film and the unstabilized B film. These compounds were usually relatively ineffective UV stabilizers, requiring high concentrations to produce a significant stabilization. Under our irradiation conditions, compounds I to IV apparently operate mainly by a simple UV-screening mechanism, since the B film was protected to the same degree as the A film, and so these compounds must be relatively ineffective in protecting thin substrates despite high UV extinction coefficients. Additives V to XV, however, which produced very long A film lifetimes in comparison with the unstabilized B film, apparently stabilize the polymer by a mechanism other than UV absorption, which probably only contributes ~10% or less to the stabilization effect. These compounds might either interfere with the photoinitiation step(s) or introduce additional termination steps by acting as R·, RO·, or RO₂·

scavengers. The screening test does not allow differentiation between these other possible protective mechanisms.

Chromophore Destruction in the Melt

The possibility of the UV protective action of nonabsorbing additives being the result of their reaction with and destruction of macrochromophores during film preparation can be readily discounted by extraction experiments. Film samples into which 0.1 wt-% of compounds V, VI, X, or XIII had been compounded were acetone- or pentane-Soxhlet extracted for 40 hr. The extracted films contained no detectable stabilizer and had the same lifetime on UV irradiation (~ 110 hr) as films which were initially additive free. This similarity also precludes the possibility of additives preventing chromophore formation (by, for example, an antioxidant effect) during film production.

Additive Concentration

Compounds V and XV are all very effective UV stabilizers and can provide comparable protection at concentrations which are at least ten times lower than those required for protection by a UV absorber (such as compounds I to IV). The lifetimes of polypropylene films containing various concentrations of nickel dimethylglyoxime are shown in Figure 2. Increasing the concentration beyond ~ 0.1 wt-% ($\sim 3 \times 10^{-3} M$ of additive) produces little increase in UV stability. However, it is doubtful that any quantitative conclusions can be drawn from this apparent concentration

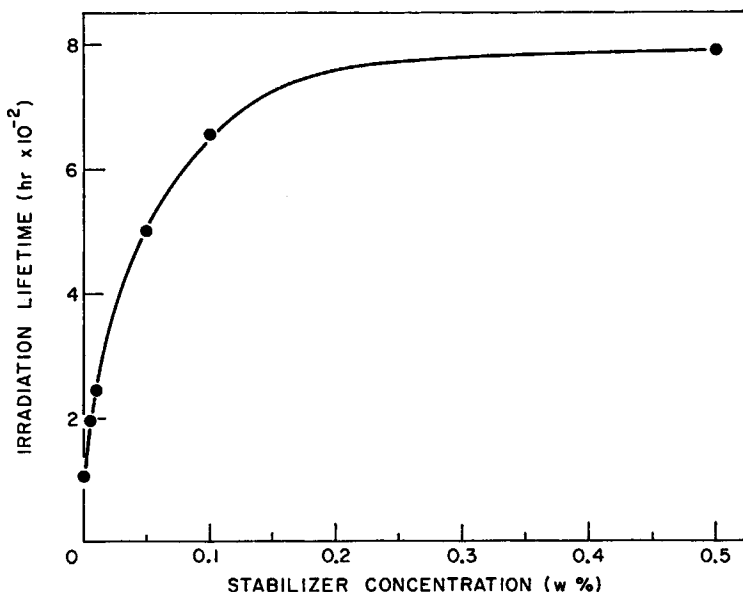


Fig. 2. Effect of nickel dimethylglyoxime concentration on polypropylene film photostability.

dependence owing to the certain presence of additive aggregates which result from both insufficient additive dispersion in the melt and from additive exclusion from the crystalline zones of the polymer.¹⁰ In addition, additive-chromophore association is also possible because of the polar nature of additives and impurities and the nonpolar nature of the polymer. Concentration-lifetime curves similar to those shown in Figure 2 were also obtained with other Ni(II) chelates and 2-hydroxy-4-dodecyloxybenzophenone.

The concentrations of compounds I to IV (Table I) in the film samples changed little during the relatively brief irradiation lifetimes of these samples. However, for all other additives listed in Table I, gradual loss of the additives occurred during irradiation, and film failure ensued soon after this loss became extensive. In some cases loss resulted from additive volatility. For example, the large difference in practical protective efficiency of the substituted 2-hydroxybenzophenones (compounds V and XVI) largely results from the high volatility of the 4-methoxy derivative (compound XVI), which completely sublimates out of the sample during about 40 hr of irradiation or exposure to an air oven at 40°C in the dark. The phenols (compounds XVII and XVIII) are both rapidly decomposed under irradiation conditions, and so the true effectiveness of these conventional radical scavengers cannot be inferred. The concentrations of all of the nickel chelates were steadily reduced to zero during the irradiation lifetime of the films. However, this was not due to a volatility effect, because the respective nickel concentrations before and after the irradiation of the films initially containing compounds X and XIII were roughly identical (as shown by atomic absorption spectroscopy), indicating extensive destruction of the chelates by the UV radiation and/or chemical or radical attack.

Nucleation Effects

Schonhorn and Luongo¹⁴ have shown that the presence of 3 wt-% of certain high surface free energy fillers (such as KBr) causes a marked decrease in the UV stability of low-density polyethylene films, possibly by modifying the initial crystallinity of the films. Remaly and Schultz¹⁵ have shown that sodium benzoate acts as an effective nucleating agent for polypropylene, and this was confirmed in our work by the dependence of film density on nucleator concentration and by the enhancement of crystallization rates by the nucleator, which were observed when these film samples were allowed to cool on a microscope hot stage. However, little variation in UV stability was detected when varying concentrations (0.05–1.0 wt-%) of sodium benzoate or KBr were melt blended into 30- μ films and the films quenched as usual by immersion in Dry Ice/methanol. Consequently, nucleation and crystallinity effects attributable to the low concentration (\sim 0.1 wt-%) of additives employed in our work (Table I) can probably be ignored.

Surface Stabilization

The photo-oxidative degradation of thin ($\sim 22 \mu$) commercially extruded polypropylene films was previously found to be confined to a thin surface layer on both surfaces of the films.⁶ Although only a small fraction of the total thickness is photooxidized during irradiation, this surface oxidation and associated restructuring is sufficient to render the samples extremely brittle, because of the presence or ready generation of microcracks in the surface layers and the ready propagation of these cracks across the film. Surface photo-oxidation has been shown to originate from the presence of chromophores predominantly in the surface layers of the films.⁷ Since the UV absorption mechanism for additives apparently contributes little to the stabilization of thin films, it is of interest to examine the effects of applying stabilizers solely to the surface or surface layers of such films, since energy quenching, chromophore-additive complexing, and radical scavenging will all depend on the proximity of additive and chromophores.

Additives were applied to commercial unstabilized film samples either by a brief diffusion from solution or by vacuum sublimation. In both cases, conditions were chosen to give add-ons (averaged over the total film weight) of less than 0.5 wt-%. The lifetimes found using the arrangement shown in Figure 1 for the directly irradiated A films and the unstabilized B films are shown in Table II. These A films displayed the same general behavior as A

TABLE II
UV Stability of Films with Surface Additives

Additive ^a	Av. additive concn., ^b wt-%	Irradiation lifetime, hr	
		Stabilized film	Screened film ^c
—	—	90	90
I	0.5	200	150
II	0.5	210	200
V ^d	0.05	290	90
V ^e	0.2	505	100
VI ^e	0.4	400	150
IX ^e	0.3	450	100
X ^e	0.01	220	95
X ^f	0.01	100	90
XI ^d	0.05	230	90
XII ^g	0.05	300	90

^a Compounds listed in Table I.

^b Additives incorporated into a preformed commercial film; additive loading averaged over the total film weight.

^c Unstabilized film, irradiated directly behind stabilized film.

^d Additive diffused into film (1 hr) from xylene solution (3.0 wt-%, 40°C).

^e Additive vacuum deposited onto both film surfaces.

^f As for (e), but only film surface facing UV source coated.

^g Ligand vacuum deposited on both film surfaces, and chelate subsequently formed by reaction with an aqueous Ni(II) salt solution.

films that had been prepared by the addition of compounds prior to melt processing. That is, compounds I and II again acted only as UV absorbers, whereas compounds V and VI, and X to XII, appeared to operate by a more effective mechanism. Surface coating also represents the ideal location for maximum UV absorption effects. However, this latter mechanism is relatively unimportant for effective stabilization, as shown by the low degree of stabilization of the B films when shielded by the effectively stabilized A films (Table II). Furthermore, when only the surface directly facing the UV source was coated with a nickel dimethylglyoxime layer (compound X, 0.01 wt-% add-on), the film was little stabilized, whereas when both film surfaces were coated (to give roughly the same total add-on as before), a significant increase in UV stability was recorded (Table II).

The results shown in Table II are relevant to the practical problem of inexpensively photostabilizing polypropylene. The bulk of a stabilizer which is uniformly distributed throughout a polypropylene article apparently contributes relatively little to the immediate stability of the article (although it may provide a reservoir of stabilizer capable of replenishing the surface region when depleted by extraction or migration of the additive¹⁶). Since low loadings of certain stabilizers can provide adequate UV stabilization for certain applications when incorporated in the vicinity of the chromophores, i.e., in or on the surface layer of commercial polypropylene samples, it may be practicable to stabilize films and fibers by this method and so use only very small amounts (0.05 wt-% or less) of the expensive stabilizers. Surface application of the stabilizer might be achieved by sublimation or diffusion as described above. Alternatively, the additive may be blended with a small amount of polymer which is conjugate extruded as a thin continuous layer around a fiber of unstabilized polymer or on both sides of a film of unstabilized polymer. Another possibility would involve the adjustment of the melt properties and additive mobility so that the involatile, extraction-resistant additive preferentially migrates to the surface during extrusion. The optimum stabilization can probably be achieved by incorporating a very low level of UV stabilizer in the bulk of the polymer and a higher concentration in the surface skin. For example, 0.01 wt-% of uniformly blended nickel dimethylglyoxime gave an irradiation lifetime of 240 hr; the same total loading as a (sublimed) surface coating gave 220 hr. However, a loading of 0.01 wt-% present as coatings on both surfaces of a film which already contained 0.01 wt-% of uniformly blended additive (i.e., a total concentration of 0.02 wt-%) gave a lifetime of 420 hr. This value is comparable with the stability resulting from a uniform blend of 0.05 wt-% of this additive (Fig. 2).

Energy Quenching and UV Stabilization

The possibility that UV absorption alone cannot account for the protective action of many effective stabilizers in thin films and fibers has been suggested several times^{11,12} and demonstrated by the use of solution filters for 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole or 2-hy-

droxy-4-*n*-octyloxybenzophenone.¹² Some of the highly effective UV stabilizers for polypropylene have been proposed to operate by an "energy transfer" mechanism.^{17,18} Energy transfer involves the quenching of an excited chromophore which has absorbed energy from the incident UV. Quenching is proposed to occur by transfer of this excitation energy to a stabilizer molecule. For effective UV stabilization, this type of additive must be capable of dissipating most of the accepted energy harmlessly, that is, without destroying polymer bonds or its own structure. Efficient energy transfer may occur over 10–20 Å (transfer by an exchange interaction) or up to ~50 Å (transfer by a dipole–dipole interaction)¹⁹; both mechanisms require extensive overlap between the appropriate emission spectrum of the donor chromophore and the UV absorption spectrum of the acceptor additive.¹⁹

Various attempts have been made to demonstrate energy-transfer processes in both the liquid and solid phases for additives which are known to stabilize polyolefins. For example, Briggs and McKellar¹⁷ have shown that certain nickel [Ni(II)] chelates are efficient acceptors for the excitation energy of triplet (E_T^*) anthracene in liquids and that some of these chelates are also effective UV stabilizers for polypropylene articles. However, anthracene cannot be expected to be an adequate model for the polypropylene carbonyl chromophores.¹ In particular, E_T^* (anthracene) is ~42 kcal/mole, whereas the value for an aliphatic ketone is ~74 kcal/mole.²⁰ Efficient energy transfer usually occurs from a donor energy level to an acceptor level of lower energy than that of the donor.¹⁹ Hence it is possible for an additive to quench ketone triplets but to be incapable of quenching anthracene triplets. The inadequacy of the anthracene system is illustrated by the reported failure of the Ni(II) complex of 2,2'-thiobis(4-*tert*-octylphenol) (compound XII) to quench triplet anthracene,¹⁷ in comparison with the effective stabilization shown by the data in Tables I and II for this compound. Chien and Conner²¹ have also concluded that the same Ni(II) complex effectively prevents the diethyl ketone photosensitized oxidation of cumene in the liquid phase, possibly by a dipole–dipole type of energy-transfer process.

Pivovarov and Lukovnikov¹⁸ have attempted to make a more meaningful test of the energy-transfer ability of additives which are actually present in a given polymer. Their test is based on the efficiency of quenching of the fluorescence emission which is detected from polymers, such as polyolefins, polyamides, and polystyrene, due to the presence of certain impurities. These fluorescent impurities are assumed to be responsible for the photo-instability of these polymers. Some effective polypropylene UV stabilizers were found to efficiently quench the fluorescence emission of polypropylene observed at 3300 Å. The UV stability of various unstabilized commercial polypropylene samples has been shown to be roughly proportional to the initial fluorescence emission intensity of these samples,⁷ and the fluorescence has been attributed to the presence of macroaldehydes.²² The established photochemistry of aldehydes indicates that these impurities might well

initiate the deterioration of polypropylene. However, aldehydes probably represent only a small fraction of the impurities in the polymer, since thermal oxidation of polypropylene near the extrusion temperature has been shown to produce mainly macroketones,² which do not contribute to the fluorescence emission from polypropylene at 3300 Å,²² but are reported to emit weakly at 3850 Å.²³ In addition, we have found that polypropylene emission decreases slowly during photo-oxidation, despite the rapid build-up in hydroperoxides and various carbonyl products.⁷ Thus, the fluorescence emission at 3300 Å from polypropylene is probably not a true indication of the nature or concentration of the UV-sensitive chromophoric impurities present in the polymers.

Some of the data shown in Tables I and II appear to be in disagreement with the results of Pivovarov and Lukovnikov derived from the degree of quenching of polypropylene fluorescence by similar stabilizers.¹⁸ They concluded that the protective action of 4-*tert*-butylphenyl salicylate and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole was largely due to energy transfer and that these compounds were more effective than 2-hydroxy-4-octoxybenzophenone which they believed to stabilize by acting both as an UV absorber and an energy-transfer agent. Our data (Tables I and II) indicate that the salicylate and triazole are purely UV absorbers, whereas the 2-hydroxybenzophenone derivative is not, and our data are in agreement with the results of Guillery and Cook.¹²

Based on the conflicting published data and our own experimental results, we feel that energy transfer probably does occur from carbonyl chromophores to certain stabilizers, but this quenching is by no means the sole protective action of all effective additives, or necessarily the most important mechanism. For example, certain additives, such as the oximes and zinc di-isopropyl dithiophosphate (compounds VII and VIII), have little absorption beyond 3000 Å and yet provide good UV protection at 0.1 wt-%. These compounds cannot take part in exchange or dipole-dipole resonance energy transfer from excited ketones or aldehydes, since spectral overlap with the donor emission will be negligible. The effectiveness of the oxime and the zinc di-isopropyl dithiophosphate must stem from entirely different sources; for example, oximes can operate as effective traps for ·OH and alkoxy radicals^{24,25} under certain conditions, and the metal dialkyl dithiophosphates are well known to be exceptionally effective hydroperoxide decomposers in the liquid phase²⁶ and possibly also in the solid phase.²⁷ The possibility of certain additives operating by completely different UV-protecting mechanisms as compared to other additives is consistent with the synergistic effects reported between, for example, nickel chelates and 2-hydroxybenzophenones.^{27,28}

CONCLUSIONS

Effective polypropylene UV stabilizers do not operate simply as "UV absorbers." The additives do not necessarily prevent chromophore formation or permanently complex with chromophores during processing.

Nucleation and crystallization effects of additives appear to be unimportant. Additives probably operate by a combination of carbonyl quenching, radical scavenging, and hydroperoxide-photolysis interference, the relative importance of each mechanism depending on the nature of the additive.

A thorough investigation of these possible stabilization mechanisms will involve a systematic evaluation of (i) the effect of additives on the primary quantum yield for the photolyses of polypropylene derivatives and/or model compounds of both the carbonyl type and the peroxide type, and (ii) the effects of additives on the photo-oxidation of polypropylene or a liquid analog when sensitized by the presence of carbonyl or peroxidic model compounds, or the equivalent polypropylene derivative.

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