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Recent Advances in the Photo-oxidation and Stabilization of Polymers

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1 Introduction

Stability to sunlight exposure is one of the most important criteria in determining the practical application of all polymeric materials out-of-doors.[1–4] All unstabilized organic polymers oxidize and/or degrade upon exposure to sunlight in the presence and/or absence of oxygen respectively.[3] The rates of photodeterioration vary enormously with polymer structure and range from a few months out-of-doors for polypropylene to perhaps several years for poly(tetrafluorethylene). The chemical and physical changes that result from sunlight attack often take the form of discoloration, crazing, loss of gloss, erosion, cracking, and loss of tensile and impact strengths and extensibility.

Of all the polymer systems studied to date the polyolefins have been by far the most intensively studied.[1] Indeed, much of our understanding in this field emanates from this class of polymer. Therefore, much of the following discussion centres on these polymers although reference will be made to other polymers wherever appropriate.

2 Photo-oxidation Mechanisms

Photo-oxidation mechanisms in polymers are classified into two main types depending on the mode of light absorption, which itself is governed by the cut-off point for terrestrial sunlight *i.e.* wavelengths >290 nm. The first class of mechanism is based upon the absorption of light through impurity chromophores and the second class of mechanism is based on direct absorption of solar radiation by units or groups which form part of the chemical constitution of the polymer. Polymers of the first type include the polyolefins, aliphatic polyamides, polydienes, poly(vinylhalides), polyacrylics, polystyrenes, polyvinylalcohol, aliphatic polyesters, polyethers and polyurethanes, and polyacetals while polymers of the second type include aromatic polyesters, polyamides and polyurethanes, polyphenylene oxides, polyethersulphones, polycarbonates, and phenoxy resins. Many workers will argue that light absorption by some of these polymers, polystyrene and

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[1] J. F. McKellar and N. S. Allen, 'Photochemistry of Man-Made Polymers', Elsevier Applied Science Publishers Ltd., London, 1979.

[2] 'Degradation and Stabilisation of Polyolefins', ed. N. S. Allen, Elsevier Applied Science Publishers Ltd., London, 1984.

[3] N. S. Allen and J. F. McKellar in 'Developments in Polymer Degradation', Vol. 2, ed. N. Grassie, Applied Science Publishers, London, 1979, p. 129.

[4] F. Gugumus in 'Developments in Polymer Stabilisation', Vol. 1, ed. G. Scott, Applied Science Publishers, London, 1979, p. 261.

aliphatic polyamides, involves both processes[1,3] and this adds a further complication to the overall process of oxidation and for that matter stabilization.

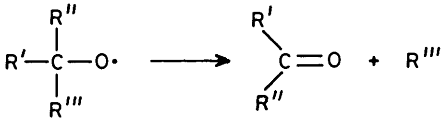
A. Impurity Chromophores.—By far the most common and important impurity chromophore in practically all carbon-containing polymers is the peroxide or hydroperoxide group. These species are incorporated during polymerization and/or processing by the well-established Bolland–Gee auto-oxidation mechanism[2,3] and exhibit very weak light absorption up to 380 nm in the near ultraviolet region. Following light absorption in this region, bond dissociation occurs spontaneously with high efficiency to produce alkoxy and hydroxy free radicals.

$$PO_2H \xrightarrow{h\nu} PO^{\cdot} + {}^{\cdot}OH \qquad (1)$$

The radicals $PO^{\cdot}$ and ${}^{\cdot}OH$ can then start the free radical chain process *via* hydrogen atom abstraction *e.g.*

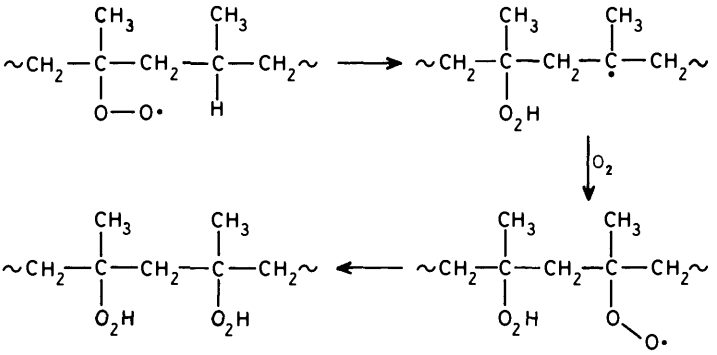
$$^{\cdot}OH + P\text{-}H \longrightarrow P^{\cdot} + H_2O \qquad (2)$$

In the case of the alkoxy free radical β-scission is the dominant mechanism and gives a macroketone or aldehyde and a macroalkane *e.g.*



(3)

In polypropylene, hydroperoxides are considered to be the major photoinitiators since here they can be produced quite rapidly through an intramolecular hydrogen atom abstraction process *e.g.*[5,6]



(4)

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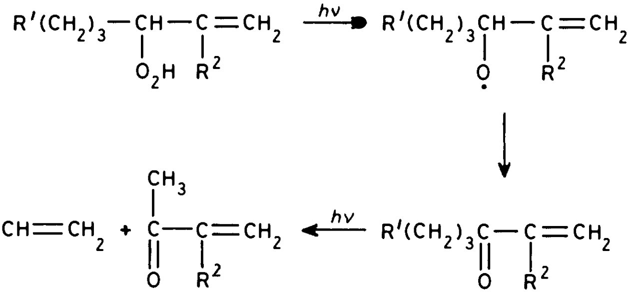
[5] A. Garton, D. J. Carlsson, and D. M. Wiles, in 'Developments in Polymer Photochemistry-1', ed. N. S. Allen, Elsevier Applied Science Publishers Ltd., London, 1980, p. 93.

[6] F. R. Mayo, *Macromolecules*, 1978, **11**, 942.

Intermolecular hydrogen atom abstraction also occurs but to a much lesser extent. In-chain hydroperoxides as in polystyrene will give rise to two alkoxy radicals *e.g.*[7]

$$\mathrm{POOP} \xrightarrow{h\nu} \mathrm{PO}^{\bullet} + \mathrm{PO}^{\bullet} \qquad (5)$$

Vinylidene groups are believed to be associated with hydroperoxides in the photo-oxidation of polyethylene *e.g.*[8]



$$\mathrm{R'(CH_2)_3{-}CH(O_2H){-}C(R^2){=}CH_2} \xrightarrow{h\nu} \mathrm{R'(CH_2)_3CH(O^{\bullet}){-}C(R^2){=}CH_2} \longrightarrow \mathrm{R'(CH_2)_3C({=}O){-}C(R^2){=}CH_2} \xrightarrow{h\nu} \mathrm{R'CH{=}CH_2} + \mathrm{CH_3C({=}O){-}C(R^2){=}CH_2} \qquad (6)$$

These groups photolyse to give α,β-unsaturated carbonyl groups which can then lead to further photochemical breakdown.

The importance of hydroperoxides in inducing photo-oxidation of polymers is often demonstrated through an examination of the effects of prior thermal processing history. This effect is demonstrated in Figure 1 for high density polyethylene. Here it is seen that increasing the time of processing of the polymer in a Brabender Plasticorder decreases its light stability quite dramatically and this can be correlated with the concentration of hydroperoxide groups.[9] Destruction of the thermally generated hydroperoxides almost always results in a restoration or improvement in light stability of the polymer.[8,10] Other methods for destroying hydroperoxides involve treatment of the oxidized polymer with SO_2 gas.[11] This effect is demonstrated in Figure 2 for polypropylene where it is seen that both unprocessed and processed polymer samples are stabilized by this treatment. Complete stabilization was not attained, however, demonstrating the importance of other chromophoric species.

Carbonyl chromophores are closely connected with the involvement of hydroperoxides in photo-oxidation and, for that matter, in thermal oxidation processes. They are often considered to play a more important role in the photo-oxidation of polyethylene than in polypropylene and *vice versa* for hydro-

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[7] G. A. George and D. K. C. Hodgeman, *Polym. Sci., Part C*, 1976, **55**, 195.

[8] K. B. Chakraborty and G. Scott, *Eur. Polym. J.*, 1977, **13**, 731.

[9] N. S. Allen, A. Parkinson, F. F. Loffelman, and P. V. Susi, *Polym. Deg. Stab.*, 1984, **6**, 65.

[10] N. S. Allen and K. O. Fatinikun, *Polym. Deg. Stab.*, 1981, **3**, 327.

[11] N. S. Allen, K. O. Fatinikun, and T. J. Henman, *Polym. Deg. Stab.*, 1982, **4**, 59.

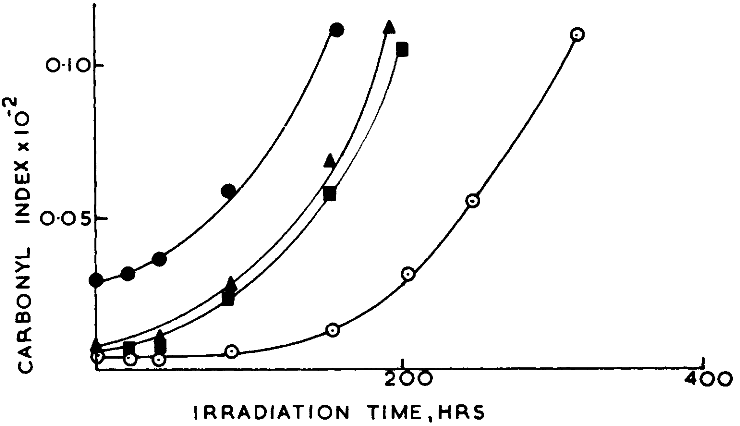

Figure 1 *Rate of photo-oxidation of unstabilized HDPE films in a Microscal unit after processing for* ○, 0 min; ■, 10 min; ▲, 20 min; ●, 30 min *in a Brabender Plasticorder at* 170 °C. *Hydroperoxide concentrations* (μ g/g) are ○, 34; ■, 69; ▲, 20; ●, 84, *respectively* (Reproduced by permission from *Polym. Deg. Stab.*, 1984, **6**, 65)

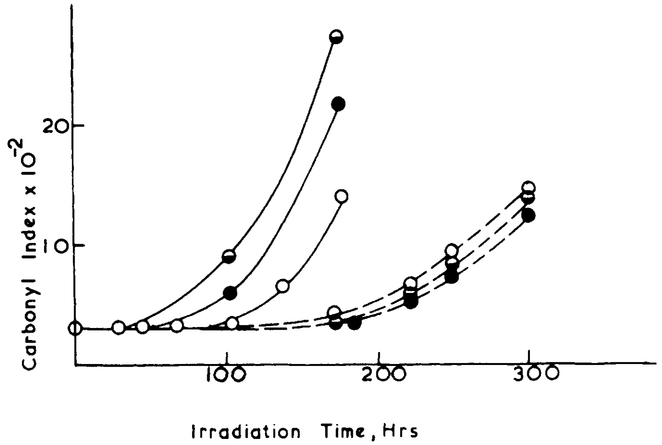

Figure 2 *Rate of photo-oxidation of polypropylene film in a Microscal unit* (~ 200 μm *thick*); ○, *control;* ◒, *thermally oxidized for* 30 min *at* 130 °C; *and* ●, *thermally oxidized for* 4 h *at* 100 °C *before* (——) and after (– – –) *sulphur dioxide treatment*
(Reproduced by permission from *Polym. Deg. Stab.*, 1982, **4**, 59)

peroxides.[12] Whilst the higher extinction coefficients of carbonyl groups (*i.e.* ketones and aldehydes) is an important factor in their favour as photoinitiatiors,

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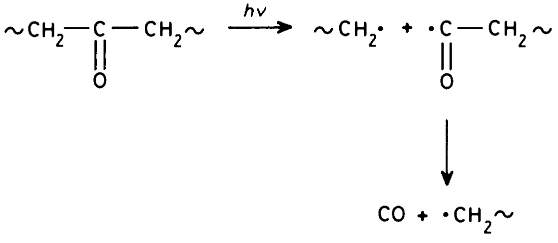
[12] D. M. Wiles and D. J. Carlsson in 'New Trends in the Photochemistry of Polymers', ed. N. S. Allen and J. F. Rabek, Elsevier Applied Science Publishers Ltd., London, 1985, p. 147.

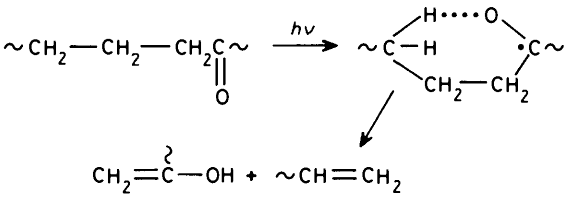
hydroperoxides are nevertheless certainly more efficient free radical generators.

Carbonyl groups, when present in the molecular backbone of the polymer as ketone groups, undergo two primary photochemical reactions. These were described by Bamford and Norrish in their pioneering work on the photochemistry of liquid-phase aliphatic ketones.[13] The first, the Norrish Type I process, leads to the formation of free radicals in which the excited singlet or triplet states of the carbonyl groups are precursors.[14]



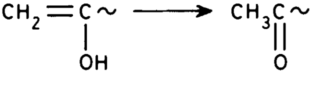
(7)

The second, the Norrish type II process, only occurs when the ketone passes at least one hydrogen atom on the γ-carbon atom with respect to the carbonyl group. The reaction occurs *via* a six-membered cyclic intermediate involving intramolecular hydrogen atom abstraction and produces one olefinic and one enolic group in the polymer:[15]



(8)

The enolic group then rearranges to give a ketone:



$$\underset{\displaystyle\mathrm{OH}}{\mathrm{CH_2{=}C{\sim}}} \longrightarrow \underset{\displaystyle\mathrm{O}}{\mathrm{CH_3\overset{}{C}{\sim}}}$$

(9)

The importance of the rôle of carbonyl groups in photo-oxidation continues to be in serious dispute. Their absorption of solar radiation resulting in the build up of oxidation products is evidenced by the results shown in Figure 3 for polypropylene. Here it is seen that exposure of polypropylene film behind a u.v. filter (1% $NaNO_2$)

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[13] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1935, **150**, 4.

[14] G. H. Hartley and J. E. Guillet, *Macromolecules*, 1968, **1**, 165.

[15] A. M. Trozzolo and F. H. Winslow, *Macromolecules*, 1968, **1**, 98.

prolonged the induction period indefinitely despite the absorption of light by hydroperoxides under these conditions.[11] Many workers have suggested that hydroperoxide groups are inefficient in the absence of ketonic groups and various theories have been proposed to account for this. Only a few years ago it was suggested that light energy absorbed by carbonyl groups could be transferred to the more labile hydroperoxides.[16–19] Whilst studies on model systems have verified that this is a possibility, no direct evidence for such a mechanism in solid-phase polyolefins has appeared. Again controversies exist here. For example, while some workers believe that carbonyl and hydroperoxide groups form an exciplex *e.g.*

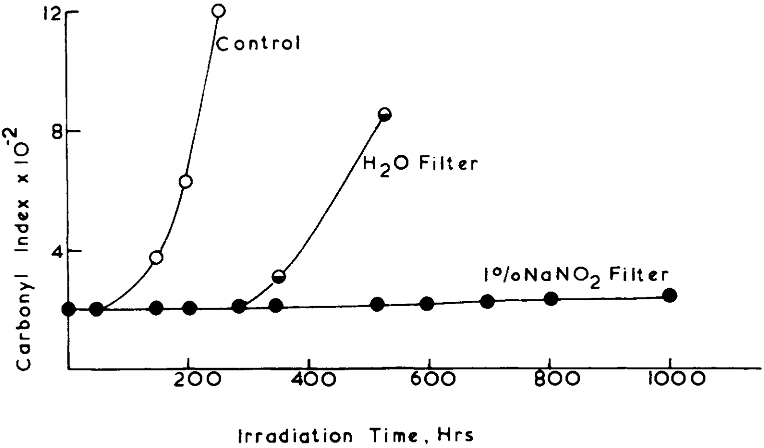
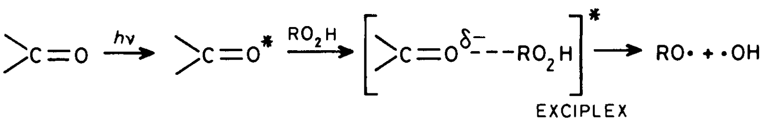
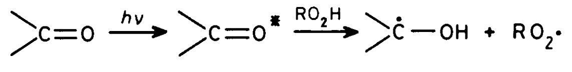


Figure 3 *Rate of photo-oxidation of polypropylene film* (200 μm *thick*): ○, without a filter; ⊖, *with a water filter; and* ●, *with a 1% aqueous sodium nitrite filter in a Microscal unit* (Reproduced by permission from *Polym. Deg. Stab.*, 1982, 4, 59)



$$\rangle C{=}O \xrightarrow{h\nu} \rangle C{=}O^{*} \xrightarrow{RO_2H} \underbrace{\left[\rangle C{=}O^{\delta-}\text{---}RO_2H\right]^{*}}_{\text{EXCIPLEX}} \longrightarrow RO\cdot + \cdot OH \quad (10)$$

through which dissociation of the latter can be more efficient,[17] others have shown that photoexcited aliphatic ketones can abstract a hydrogen atom from the hydroperoxide group to give a peroxy free-radical *e.g.*[18]



$$\rangle C{=}O \xrightarrow{h\nu} \rangle C{=}O^{*} \xrightarrow{RO_2H} \rangle\dot{C}\text{—}OH + RO_2\cdot \quad (11)$$

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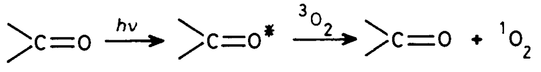
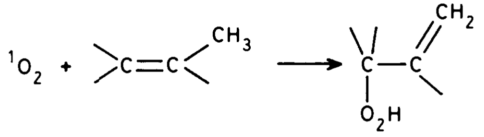
[16] G. Geuskens and C. David, *Pure Appl. Chem.*, 1979, **51**, 233.
[17] H. C. Ng and J. E. Guillet, *Macromolecules*, 1978, **11**, 937.
[18] L. C. Stewart, D. J. Carlsson, D. M. Wiles, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 3605.
[19] G. Geuskens and M. S. Kabamba, *Polym. Deg. Stab.*, 1982, **4**, 69.

Carbonyl groups may also participate in the photo-oxidation of polymers by a less direct route. The photoexcited triplet carbonyl groups may be quenched by ground-state molecular oxygen to form excited singlet oxygen ($^1O_2$).[15] The singlet oxygen may then react with any unsaturation in the polymer *e.g.* vinyl groups produced in the Norrish type II process, to form hydroperoxides:



(12)

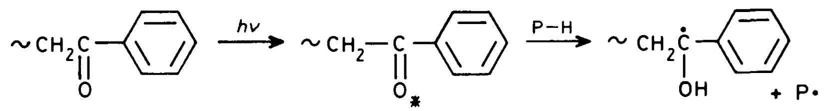


(13)

This mechanism has been supported by the detection of traces of hydroperoxides in polymer films such as polyethylene and polypropylene after treatment with singlet oxygen gas.[20,21] However, the importance of singlet oxygen in the photo-oxidation of many polymer systems is still in serious dispute. Much of the evidence is based on model system work, often where the role of this species is dominant. The only types of polymers where singlet oxygen could conceivably play an important role are polydienes such as polybutadiene.[22]

Aromatic carbonyl groups are an important source of initiation in many polymers *e.g.* acetophenone end-groups in polystyrene[7] and benzophenone derivatives in aromatic polyurethanes based on 4,4′-diphenylmethane diisocyanate.[23] These chromophores can abstract hydrogen atoms from the polymer substrate (P–H) by the following mechanism to give a ketyl radical *e.g.*

(14)



More recent research using luminescence spectroscopy has identified the presence of α,β-unsaturated carbonyl groups as important photoinitiators in the photo-oxidation of a number of polymers such as polyethylene,[24] polypropylene,[24] poly(4-methylpent-1-ene),[25] aliphatic polyamides[25] such as nylon 6 and nylon 6,6,

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[20] M. I. Kaplan and P. G. Kelleher, *J. Polym. Sci., Polym. Lett. Ed.*, 1971, **9**, 565.

[21] D. J. Carlsson and D. M. Wiles, *Rubb. Chem. Technol.*, 1974, **47**, 991.

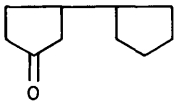
[22] V. B. Ivanov and V. Ya. Shlyapintokh, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **16**, 899.

[23] N. S. Allen and J. F. McKellar, *J. Appl. Polym. Sci.*, 1976, **20**, 1441.

[24] N. S. Allen, *Polym. Deg. Stab.*, 1984, **6**, 193.

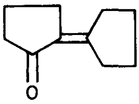
[25] N. A. Allen and M. J. Harrison, *Eur. Polym. J.*, 1985, **21**, 517.

polyoxymethylene,[26] and polybutadiene.[27] The exact nature of the luminescent species in polymers has, however, been the subject of much controversy. Some workers believe that the fluorescent species in polyolefins and PVC, for example, are almost wholly associated with naphthalene which is absorbed from the atmosphere.[28–30] Examination of the corrected fluorescence excitation and emission spectra of n-hexane extracts of polypropylene with those of naphthalene clearly show that they are not one and the same (Figure 4).[24] Furthermore, following n-hexane extraction of polypropylene the regeneration of the fluorescent species is an oxidation process, as shown by the results in Figure 5.[24] Similar results were obtained for nylon 6,6 polymer[25] but in this particular case α,β-unsaturated carbonyl compounds were identified by using GC-mass spectral analysis. Here, the luminescent species in nylon 6,6 polymer were found to originate from 'aldol'-condensation products of cyclopentanone; the latter being produced as a major product of nylon 6,6 degradation. Some characterized products were as follows:



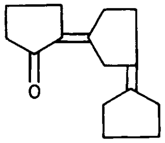
CYCLOPENTYLCYCLO-PENTANONE

(1)



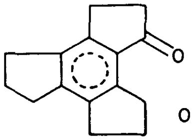
CYCLOPENTYLIDENE-CYCLOPENTANONE

(2)



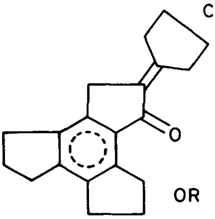
CYCLOPENTYLIDENE-(2'-CYCLOPENTYLIDENE)-CYCLOPENTANONE

(3)



OR ISOMER

(4)



OR ISOMER

(5)

Structures (1)—(3) were associated more closely with the structured phosphorescence emission from nylon 6,6 while structures (4) and (5) were associated with the short-wavelength fluorescence (excitation at 230 and 290 nm) and phosphorescence emission at 407 nm.

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[26] N. S. Allen and J. F. McKellar, *Polym. Deg. Stab.*, 1979, **1**, 51.

[27] S. W. Beavan and D. Phillips, *Rubb. Chem. Technol.*, 1975, **48**, 692.

[28] D. J. Carlsson and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.*, 1973, **11**, 759.

[29] Z. Osawa and H. Kuroda, *J. Polym. Sci., Polym. Lett. Ed.*, 1982, **20**, 577.

[30] Z. Osawa, T. Taba, and Y. Kobayashi, *Macromolecules*, 1984, **17**, 119.

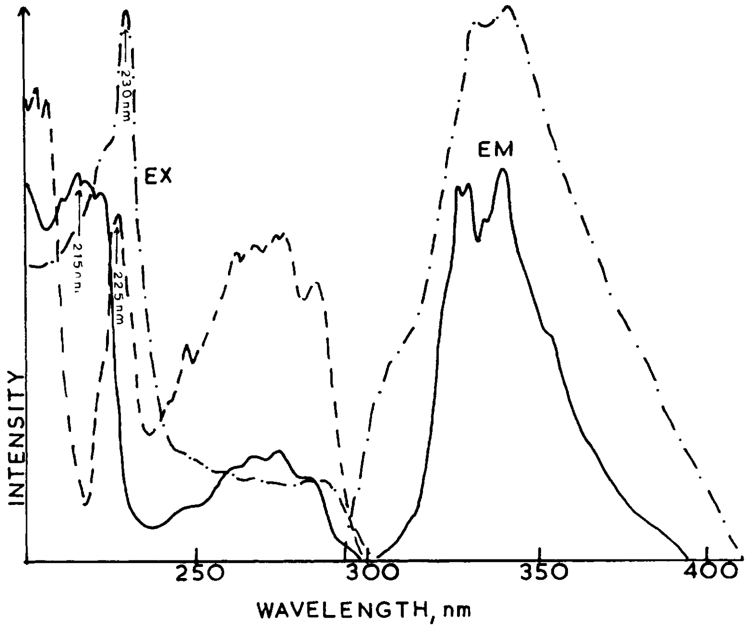


Figure 4 *Fluorescence excitation and emission spectra of* (——) *naphthalene in a n-hexane* (5 × 10^{-6}M) *and* (– • –) *polypropylene n-hexane extracts* (1g *powder*/40 cm^3 *n-hexane*). (*Sensitivity* × 4) (— —) *Naphthalene excitation spectrum at* 10^{-5}M *in n-hexane*
(Reproduced by permission from *Polym. Deg. Stab.*, 1984, **6**, 193)

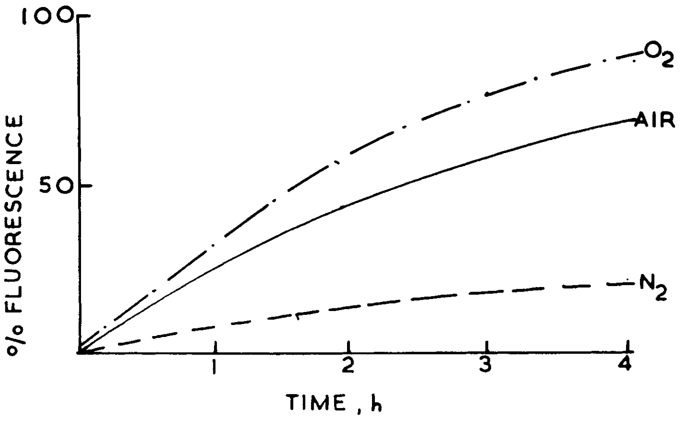
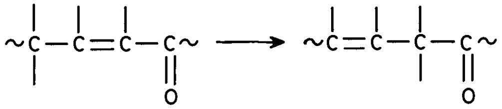


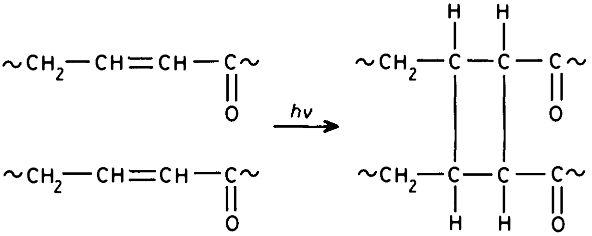
Figure 5 *Rate of regeneration of fluorescence emission from polypropylene film in* (——) *air,* (– – –) N_2, *and* (– · – · –) O_2 *atmospheres.* (*Ex*, 280 nm; *Em*, 340 nm)
(Reproduced by permission from *Polym. Deg. Stab.*, 1984, **6**, 193)

Aliphatic α,β-unsaturated carbonyl groups in a main chain are initially converted into β,γ-unsaturated carbonyl groups *via* the following initial step:



$$\sim\mathrm{C{-}C{=}C{-}C({=}O)}\sim \longrightarrow \sim\mathrm{C{=}C{-}C{-}C({=}O)}\sim \qquad (15)$$

The β,γ-unsaturated carbonyl groups may then react further *via* the Norrish type I and II processes to give eventually non-luminescent carbonylic products. In polydienes where the concentration of these chromophores is high, another reaction involving crosslinking may also occur:



(16)

Metals are another important class of impurity. Traces of transition metals such as Fe, Ni, Ti, and Cr are almost invariably present in many polymer systems.[31–34] They may be incorporated during the manufacture of the polymer or during its fabrication and are now becoming increasingly more important, particularly with regard to the 'new process'-type polyolefins made *via* the gas-phase processes. Iron is a common contaminant in most polymers originating from contact with processing equipment. On light absorption, transition-metal compounds can produce free radicals by an electron-transfer process such as:

$$M^{n+}\,X^- \xrightarrow{h\nu} [M^{(n-1)+}\,X^\bullet] \qquad (17)$$

$$[M^{(n-1)+}\,X^\bullet] \longrightarrow M^{(n-1)+} + X^\bullet \qquad (18)$$

The hydroxyl radical may then abstract a hydrogen atom from the polymer. Transition-metal ions are also able to catalyse the decomposition of hydroperoxides to give alkoxy and peroxy radicals by:

$$RO_2H + M^{2+} \longrightarrow RO^\bullet + OH^- + M^{3+} \qquad (19)$$

$$RO_2H + M^{3+} \longrightarrow RO_2^\bullet + H^+ + M^{2+} \qquad (20)$$

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[31] N. Uri, *Israel J. Chem.*, 1970, **8**, 126.

[32] P. Richters, *Macromolecules*, 1970, **3**, 262.

[33] C. Kujirai, S. Hashiya, H. Furuno, and N. Terada, *J. Polym. Sci., Polym. Chem. Ed.*, 1968, **6**, 589.

[34] N. S. Allen, K. O. Fatinikun, and T. J. Henman, *Eur. Polym. J.*, 1983, **19**, 551.

$$(2\,RO_2H \xrightarrow{[M^{2+}]} RO^{\bullet} + RO_2^{\bullet} + H_2O) \qquad (21)$$

Such a reaction will accelerate the thermal breakdown of polymers during processing and consequently reduce their subsequent photostability. This is confirmed by the results shown in Table 1 where it is seen that there is a correlation between the concentration of Ti residues in various polypropylene film samples [diluent (D) and gas phase types (G)] and photo-oxidative stability as measured by embrittlement times. Earlier work[33] indicated that catalyst residues, such as Ti and Al, in polypropylene might also induce crosslinking by hydrogen atom abstraction.

Table 1 *Comparison of embrittlement times during photo-oxidation with catalyst residues for polypropylene samples*[a]

Polymer		*T* 0.06[b]	[Ti]	[Al]
Type	*Sample*	(h)	(p.p.m.)	(p.p.m.)
DP	C	140	25	140
GP	D	125	30	230
	E	125	30	180
	F	90	65	200
	G	80	70	260

[a] Reproduced by permission from *ref.* 34. [b] *T* 0.06, time to 0.06 carbonyl units as measured by i.r. spectroscopy.

Finally, another chromophore, and one which has been actively studied in recent years, is the polymer–oxygen charge-transfer complex. Such complexes are now believed to be important in inducing the photo-oxidation of many polymers, particularly polyolefins and polystyrene.[36–38] The exact mechanism is not too clear but originates from the early work of Chien[39] where olefins were found to exhibit enhanced absorption up to 400 nm when saturated with oxygen gas. On absorption of u.v. light these species generate hydroperoxides by the following mechanism:

$$R{-}H + O_2 \longrightarrow [R{-}H - - - O_2]_{\text{C-T Complex}} \xrightarrow{h\nu} RH^{+} - - - O_2^{-} \longrightarrow$$
$$R\cdot + \cdot O_2H \longrightarrow RO_2H \qquad (22)$$

The efficiency of this mechanism is believed to be low but it could be argued that only one hydroperoxide group need be generated to start the auto-oxidative chain process—an argument often put forward in favour of hydroperoxide initiation. More definite evidence is obviously required here. Some workers have shown that compression-moulded polyolefin films have the same light stability as vacuum

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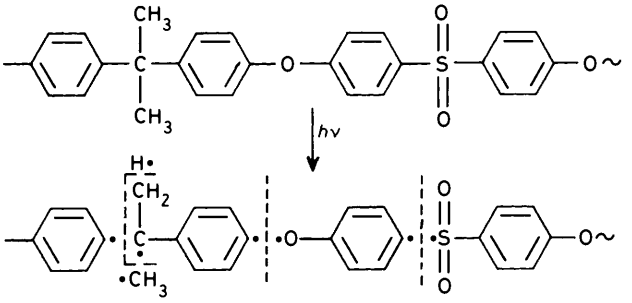
[35] D. G. M. Wood and T. M. Kollman, *Chem. Ind.* (*London*), 1972, 423.
[36] N. S. Allen, *Polym. Deg. Stab.*, 1982, **2**, 155.
[37] J. F. Rabek and B. Ranby, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 273.
[38] J. R. MacCallum and D. A. Ramsay, *Eur. Polym. J.*, 1977, **13**, 945.
[39] J. C. W. Chien, *J. Phys. Chem.*, 1965, **69**, 4317.

pressed films.[35] On the basis of this work chromophores generated in the former case, such as hydroperoxide groups, would not be expected to be important in accelerating the photo-oxidation rate of the polymer. In a related sense, prior destruction of hydroperoxide and carbonyl groups by pre-irradiation of polymer films in an inert atmosphere has no effect on the subsequent photo-oxidative stability of the polymers.[36]

B. Polymer Constitution.—The second class of mechanisms for polymer photo-oxidation is based on the absorption of light through chromophoric units that form part of the backbone structure of the polymer.[1–3] Examples of these are the aromatic polyesters, polyethersulphones, polycarbonates, polyphenylene oxides, aromatic polyamides, and polyurethanes, and phenolic-based resins. All of these polymers possess strong absorption in the near ultraviolet region (300—350 nm) and on photo-oxidation they can undergo several possible bond scission processes. For a polyethersulphone we have:



(23)

Many of these free radical species have been identified through e.s.r. and conventional/laser flash photolysis spectroscopy.[1] Stabilization of these polymers is quite difficult compared with polyolefins.

3 Mechanisms of Photostabilization

It is evident from the above discussion that for almost all polymers some form of photostabilization is essential if adequate protection against the destructive effects of solar radiation is to be achieved. The photostabilization of light-sensitive polymers involves the retardation or elimination of the various photophysical and photochemical processes that occur during photo-oxidation and may be achieved in many ways, depending on the type of stabilizer and type of mechanism that is operative in the polymer. Complete, effective stabilization is, of course, never achieved in commercial practice. A further complication is the influence of processing history and this is not always fully combatted. In many cases, antioxidant and light stabilizer degradation products can reduce the final stability of the polymer.

Over the years four different classes of stabilizing systems have been developed.[1,4] These rely for their stabilizing action on the presence of

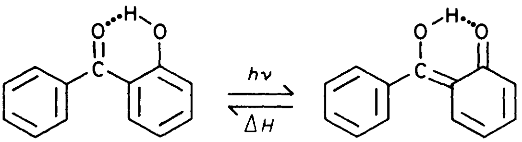
(*a*) an ultraviolet screener
(*b*) an ultraviolet absorber
(*c*) an excited-state quencher
(*d*) a free-radical scavenger and/or hydroperoxide decomposer.

Of these it is generally believed that (*c*) and (*d*) are the most effective methods. In the latter category the terms chain-breaking acceptor and chain-breaking donor have become widespread in use. The former is simply a molecule possessing a free radical that is capable of reacting with another free radical species, whereas the latter is a molecule which possesses a labile atom, usually a H-atom, that will react or terminate another free-radical species. These are exemplified below for different types of stabilizer. It is now an accepted fact that many light stabilizers are multifunctional in their mode of operation in inhibiting photo-oxidation of a polymer. However, this does not necessarily imply that the more diverse the functionality the more effective will be the stabilizer. Many other factors have to be taken into consideration such as light and heat stability of the stabilizer and its compatability with the polymer. Current theories surrounding the mode of action of various stabilizer types will be considered.

A. *o*-Hydroxyaromatics.—These compounds are often still referred to as the classical 'absorber' system since they were originally designed to absorb the ultraviolet portion of the sunlight spectrum in the range 290—400 nm *i.e.* the region which is detrimental to most polymer systems. There are three major types namely the 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, and 2-hydroxyphenyl-S-triazines. The modes of action of these stabilizers are now classified into three distinct types:

(1) ultraviolet absorbers
(2) excited-state quenchers
(3) chain-breaking donors.

Ultraviolet absorption is based on the fact that the stabilizer molecule is capable of harmlessly dissipating the absorbed energy by one or more non-radiative processes, such as internal conversion. Taking the 2-hydroxybenzophenones first, they dissipate their absorbed energy by a mechanism that involves the reversible formation of a six-membered hydrogen-bonded ring.[1–4] The following two tautomeric forms in equilibrium provide a facile pathway for deactivation of the excited state induced by the absorption of light:



(24)

The result of this mechanism of light absorption and dissipation thus leaves the stabilizer chemically unchanged and still able to undergo a large number of these activation–deactivation cycles, provided, of course, no other processes interfere.

Until the advent of modern photochemical techniques direct evidence for such a mechanism was difficult to obtain because the role of the stabilizer is essentially that of a 'passive' nature. One feature that did serve as indirect evidence for this mechanism was that the more effective of these stabilizers exhibited correspondingly stronger intramolecular hydrogen bonding (as measured by n.m.r. spectroscopy) with the carbonyl group and this, of course, is an essential feature of the above reaction (24).[40] However, over the years the concept of photostabilization in commercial polymers by ultraviolet absorption alone has become unacceptable from both a theoretical and practical basis.[41] For example, for effective u.v. absorption all the light would have to be absorbed at the near surfaces of the polymer and not through the bulk since it is well-known that polymer photo-oxidation is a surface phenomenon. Experimental results given in Table 2 show that the photostabilizing effect of 2-hydroxy-4-n-octoxybenzophenone in polypropylene film is much more effective when present as an additive in the polymer than when used simply as a surface screen.[42] Even at a 1% w/w concentration the additive is seen to be ineffective as a screener. For the 2-hydroxyphenylbenzo-

Table 2 *U.v. embrittlement times for polypropylene films containing different concentrations of 2-hydroxybenzophenone light stabilizers*[a]

Additive concentration (% w/w)	*Embrittlement time* (h)	
	Microscal	365nm *light No Screening*
Control	70	100
0.01 4-Methoxy	60	78
0.05 4-Methoxy	80	104
0.10 4-Methoxy	198	260
0.50 4-Methoxy	275	350
1.00 4-Methoxy	294	380
0.01 4-Octoxy	50	125
0.05 4-Octoxy	1 020	2 550
0.10 4-Octoxy	1 140	2 850
0.50 4-Octoxy	4 000	—
1.00 4-Octoxy	>5 000	—
		Screening
Control	61	76
0.01 4-Octoxy	63	44
0.05 4-Octoxy	72	65
0.10 4-Octoxy	58	59
0.50 4-Octoxy	109	117.5
1.00 4-Octoxy	185	130

[a] Reproduced by permission from *ref.* 42

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[40] J. H. Chaudet, G. C. Newland, H. W. Patton, and J. W. Tamblyn, *Soc. Plast. Eng. Trans.*, 1961, **1**, 26.

[41] N. S. Allen, *Polym Photochem.*, 1983, **3**, 167.

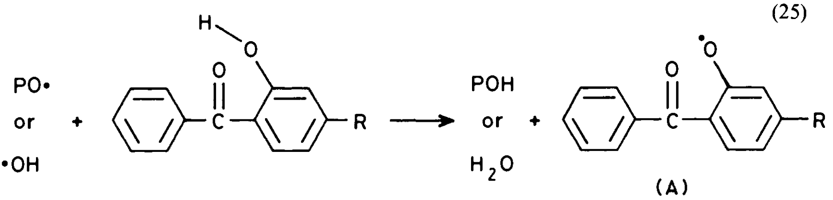
[42] N. S. Allen, M. Mudher, and P. Green, *Polym. Deg. Stab.*, 1984, **7**, 83.

triazoles, screening was found to be effective only at concentrations approaching 1% w/w and above.

Many workers maintain that *o*-hydroxyaromatic compounds owe their stabilizing efficiency to their ability to quench the excited singlet and triplet states of impurity chromophores in polymers. Much of the evidence has originated from the observation of a reduction in the fluorescence and phosphorescence emission intensities and lifetimes of impurity carbonyl species in polymer systems.[43–45] However, whilst quenching has been demonstrated, no correlation between quenching efficiency and stabilizing activity for a range of structures has been found.[45] Furthermore, the simple observation of luminescence quenching is clearly insufficient evidence to justify the implication of energy transfer in photostabilization.

The photostabilizing efficiency of these compounds has been found to be dependent on processing history and this leads us into their mode of action as chain-breaking donors.[46,47] A reduction in photostabilizing activity after processing has been associated with the presence of hydroperoxides which on photolysis give alkoxy and hydroxy radicals that are capable of abstracting the *ortho*-hydroxyl hydrogen atom by the following mechanism:

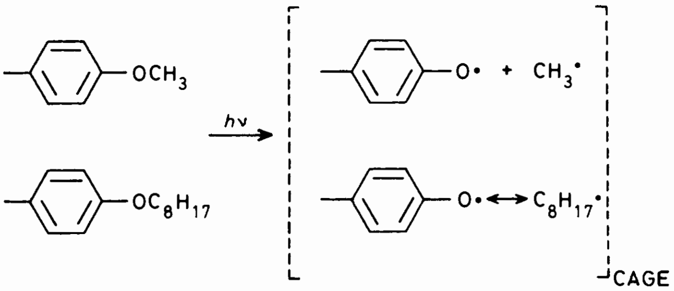
(25)



The radical product (A) is no longer capable of intramolecular hydrogen bonding. This mechanism is induced by light since 2-hydroxybenzophenones have no reaction with hydroperoxides in the dark. The photosensitivity of 2-hydroxybenzophenones in the presence of hydroperoxides is demonstrated by the results shown in Figure 6.[42] This compares the relative photostabilities of both 4-methoxy- and 4-n-octoxy-substituted 2-hydroxybenzophenones under aerobic and anaerobic propan-2-ol conditions in the absence and presence of cumene hydroperoxide. In deoxygenated propan-2-ol both stabilizers are photolysed, the 4-n-octoxy derivative being the most stable. In oxygenated solution the 4-n-oxtoxy derivative is quite stable over the irradiation period studied compared with the 4-methoxy derivative. In deoxygenated solution the rate of photolysis is faster indicating that oxygen is quenching the photoexcited triplet states of the stabilizers. Since one would expect both the stabilizers to have the same photolytic stability in solution, the nature of the long n-octoxy group is clearly playing an important role here.

[43] A. P. Pivovarov, Yu. A. Ershov, and A. F. Lukovnikov, *Vysokomol. Energii*, 1974, **2**, 220.
[44] T. Werner, H. E. A. Kramer, B. Kuster, and H. Herlinger, *Angew. Makromol. Chem.*, 1976, **54**, 15.
[45] N. S. Allen, J. Homer, and J. F. McKellar, *Makromol. Chem.*, 1978, **179**, 1575.
[46] K. B. Chakraborty and G. Scott, *Eur. Polym. J.*, 1977, **13**, 1007.
[47] N. S. Allen, J. L. Gardette, and J. Lemaire, *Polym. Deg. Stab.*, 1981, **3**, 199.

These results essentially follow the photobehaviour of the two stabilizers in polyolefins[41,42] which is associated with the relative stability of the *para*-substituent. Here the methyl radical will move out of the polymer cage compared with the n-octyl radical:



(26)

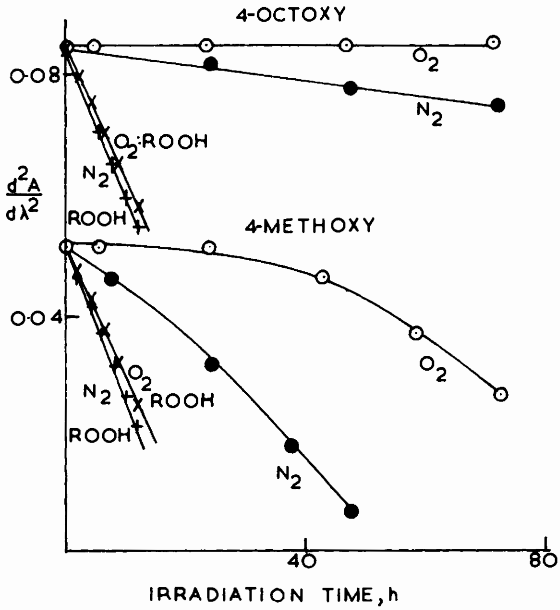
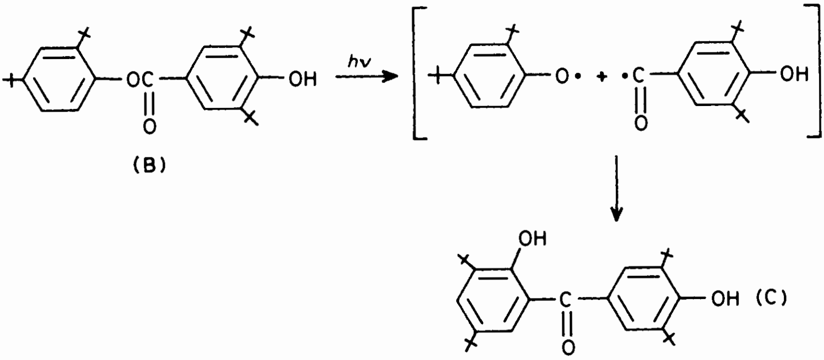


Figure 6 *Rates of photodecomposition in a Microscal unit of* 4-*n-octoxy- and* 4-*methoxy-substituted* 2-*hydroxybenzophenones* (10^{-4}M) *in* ○ *aerobic and* ● *anaerobic propan-2-ol and* × *aerobic and* + *anaerobic propan-2-ol containing* 10^{-3}M *cumene hydroperoxide*
(Reproduced by permission from *Polym. Deg. Stab.*, 1984, 7, 83)

It is evident from Figure 6 that cage effects may even be operative in solution. In the presence of cumene hydroperoxide there is a strong sensitizing effect on the rates of photodecomposition of both stabilizers, confirming reaction (25).

These stabilizers still have widespread use, but mainly in conjunction with other light stabilizers such as the hindered piperidines. Only in short-term applications do they tend to be used alone in conjunction, of course, with an antioxidant for process stability.

B. *p*-Hydroxybenzoates.—Phenyl-substituted *p*-hydroxybenzoates have been used as light stabilizers in polyolefins for some time. They were shown to operate through a photo-Fries rearrangement to give a more effective 2-hydroxybenzophenone product by the following reaction sequence:[48]

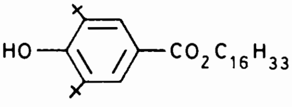


(27)

Obviously, for such a reaction to occur, the original stabilizer must absorb appreciably in the near ultraviolet region and be effectively converted into the product (C) which operates as the light stabilizer.

An alkyl-substituted *p*-hydroxybenzoate light stabilizer of the structure (6) has also been found to operate as an effective light stabilizer, particularly for use in high density polyethylene.[49–53]

Cyasorb UV 2908
(American Cyanamid Company)



(6)

In this case, the photo-Fries reaction above is not feasible, indicating that some other mechanism must be operative. Research studies to date[50–53] show two

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[48] H. J. Heller and H. R. Blattmann, *Pure Appl. Chem.*, 1972, **30**, 145.

[49] J. A. Stretanski, *Soc. Plast. Eng. Reg. Techn. Conf.*, Houston, Texas, 23rd Feb., 1981, pp. 141—161.

[50] N. S. Allen, A. Parkinson, F. F. Loffelman, and P. V. Susi, *Polym. Deg. Stab.*, 1983, **5**, 241.

[51] N. S. Allen, J. L. Kotecha, A. Parkinson, F. F. Loffelman, M. Rauhut, and P. V. Susi, *Polym. Deg. Stab.*, 1985, **10**, 1.

[52] N. S. Allen, A. Parkinson, F. F. Loffelman, P. MacDonald, M. M. Rauhut, and P. V. Susi, *Polym. Deg. Stab.*, 1985, **12**, 363.

[53] N. S. Allen, A. Parkinson, F. F. Loffelman, M. Rauhut, and P. V. Susi, *Polym. Deg. Stab.*, 1984, **7**, 153.

mechanisms to be operative: (*a*) a chain-breaking hydrogen donor particularly for alkoxy and hydroxyl radicals, and (*b*) inhibition of auto-oxidation during processing through (*a*).

The stabilizer (6) is non-absorbing in sunlight and therefore its concentration dependence on simulated sunlight exposure is a function of its reaction with free radicals in the polymer. The photobehaviour of this stabilizer molecule in polypropylene film before and after processing is shown in Figure 7.[50] It is seen that the photostability of the stabilizer decreases with increasing processing time up to 20 minutes, thereafter for 30 minutes processing the stability increases somewhat. The results follow closely the initial hydroperoxide concentrations in the films immediately after processing, indicating that the stabilizer stability and hence its performance is dependent upon hydroperoxide concentration.

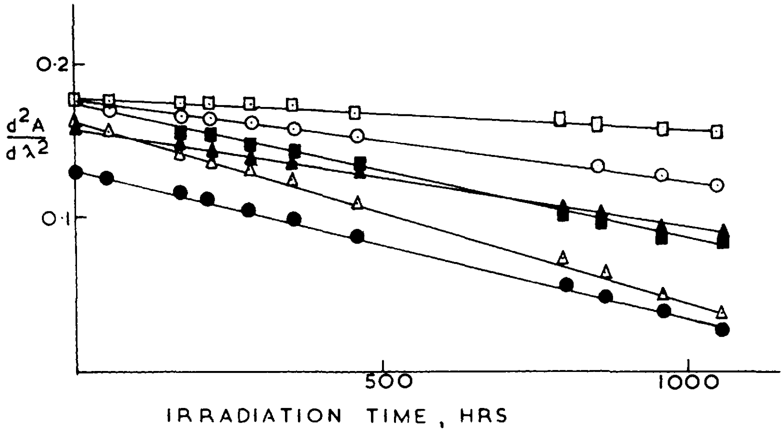

Figure 7 *Rate of decomposition of Cyasorb UV* 2908 *light stabilizer* (0.1% w/w) *in polypropylene film* (300 μm *thick*) *in a Microscal unit after processing for:* ○, 0 min; ●, 10 min; △, 20 min; ▲, 30 min; *and with* 0.1% w/w *Weston* 618, □, 0 min; ■, 10 min *in a Brabender Plasticorder at* 200 °C. *Hydroperoxide concentrations* (μg/g) are ○, 30; ●, 55; △, 70; ▲, 45; □, 0; ■, 43
(Reproduced by permission from *Polym. Deg. Stab.*, 1983, 5, 241)

Thus, hydrogen atom transfer to alkoxy and hydroxy radicals produced from the photolysis of hydroperoxides is the dominant mechanism. Similar results were obtained using 365 nm monochromatic light where only the hydroperoxide groups absorb.

$$\text{PO}^{\bullet} \text{ (or }^{\bullet}\text{OH)} + \text{AH} \longrightarrow \text{POH (or } H_2O\text{)} + \text{A}^{\bullet} \qquad (28)$$

Confirmation of the importance of hydroperoxides is shown by the result that an incorporation of Weston 618, which is a hydroperoxide decomposer, markedly improves the photostability of the stabilizer (Figure 7).[50] Further support for the reaction of this stabilizer with alkoxy and hydroxyl radicals is shown by the dramatic effect of residual catalysts in linear low-density polyethylene (Figure 8).[52] In this polymer the residual Ti and Al catalysts destroy the hydroperoxides on processing and this is seen to have a dramatic effect in improving the photostability of the stabilizer (6). The selectivity of stabilizer (6) in reacting specifically with only active free-radicals such as $^{\bullet}$OH is demonstrated by the results in Figure 9. This compares the reaction of stabilizer (6) and a number of conventional thermal antioxidants with the 2,2'-diphenyl-1-picrylhydrazyl radical. This coloured free-

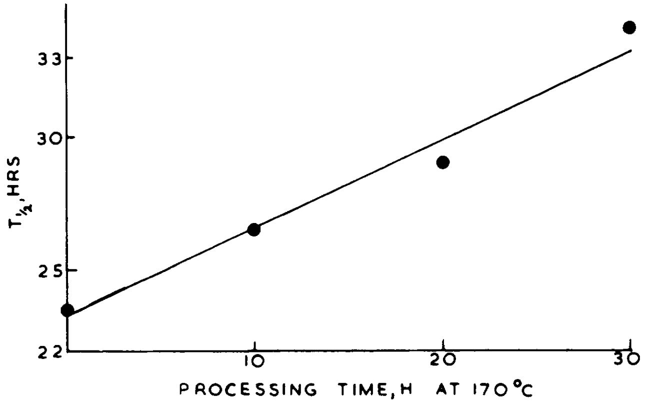

Figure 8 *Plot of the half-life of Cyasorb UV* 2908 *in LLDPE during irradiation in a Microscal unit* versus *processing time at* 170 °C. *Hydroperoxide concentrations* (μg/g) *are:* 48 *at* 0 min; 30 *at* 10 min; 25 *at* 20 min; 20 *at* 30 min
(Reproduced by permission from *Polym. Deg. Stab.*, 1985, **12**, 363)

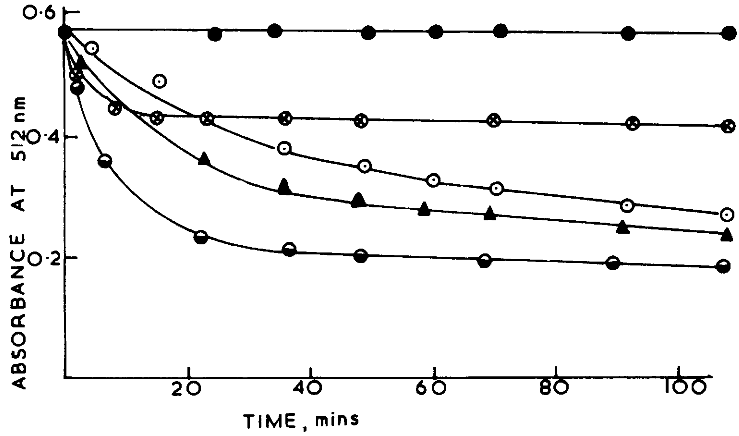

Figure 9 *Reaction of* 2,2-*diphenyl-picrylhydrazyl radical* ($\sim 10^{-4}$M), *absorbing at* 512 nm, *in* n-*hexane solution with* 10^{-4}M *of:* ○ *Topanol OC;* ●, *Cyasorb UV* 2908; ⊗, *Goodrite* 3114; ◒, *Irganox* 100; ▲, *Irganox* 1076
(Reproduced by permission from *Polym. Deg. Stab.*, 1985, **12**, 363)

radical species absorbs strongly at 512 nm and is seen to be terminated at various rates by a chain-breaking donor mechanism (H-atom transfer) by the various antioxidants, namely Topanol OC (I.C.I. Ltd), Goodrite 3114 (B. F. Goodrich Co.), Irganox 1010 and Irganox 1076 (Ciba-Geigy Corp.). However, in the case of structure (6) (Cyasorb UV 2908) there is no reaction, showing that this type of structure is much more stable and will only terminate the more active free-radical species in the polymer such as $^{\bullet}OH$.

Advantages of this type of stabilizer in practical use include its ability to synergize with phosphites and hindered piperidine compounds, especially when used in conjunction with pigments, notably inorganic types.[52]

C. Metal Complexes.—Despite the advent of the newer and more efficient hindered piperidine stabilizers, metal complexes still occupy much attention in the polymer stabilization field, particularly in applications where the former are inefficient, *e.g.* in agricultural use where pesticides can have a detrimental effect on performance. Metal complexes have probably attracted by far the most controversial arguments in the field—particularly in the 1970s. However, with the realization of the multifunctionality of many types of stabilizers, metal complexes have aquired a list of feasible functions; not all applicable, of course, in every structural case.

(1) Hydroperoxide decomposition in a dark reaction at ambient temperatures or during processing by
  (i) the complex itself
  (ii) decomposition products of the metal complex.
(2) Radical scavenger during processing/photo-oxidation
(3) Singlet-oxygen quencher
(4) Excited-state quencher
(5) U.v. absorption

The development of metal complexes, particularly those based on nickel, resulted in compounds which exhibited relatively low extinction coefficients in the near u.v. region and yet in many instances were found to be superior in performance to the currently available *o*-hydroxyaromatic compounds. This finding resulted in a search for some other feasible mechanistic function. Since carbonyl photolysis was considered to be an important initiation process which gives rise to both free radicals and backbone cleavage, then deactivation of the excited-state precursor should prove an effective means of photoprotection. Many early studies, in fact, demonstrated the efficiency of metal complexes in quenching potentially active excited singlet and triplet states of both aliphatic[54] and aromatic carbonyl compounds[55] and polynuclear aromatic hydrocarbons.[56] Effective stuctures in this respect were tris(dibenzoylmethanato) chelates of Fe and Cr (7), nickel oxime chelates (8), and the nickel complex of structure (9) [Cyasorb UV 1084, nickel(II) 2,2′-thiobis(4-t-octylphenolato)-n-butylamine]:

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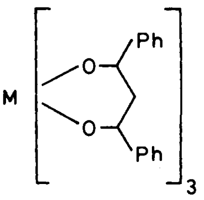
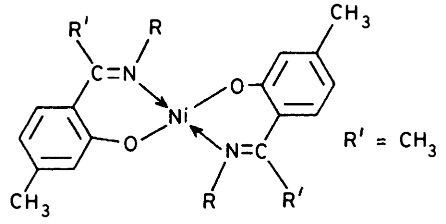
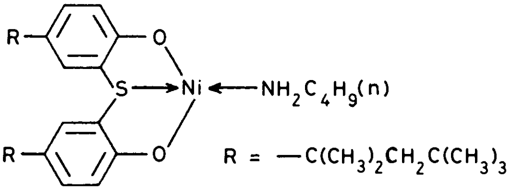
[54] J. C. W. Chien and W. P. Conner, *J. Am. Chem. Soc.*, 1968, **90**, 1001.
[55] D. O. Cowan, R. P. Foss, and G. S. Hammond, *J. Phys. Chem.*, 1964, **68**, 3747.
[56] P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, 1968, **12**, 1825.



(7)



(8)



(9)

In the case of (8) for example, variation in the substituent R produced stabilizers whose quenching efficiencies of triplet anthracene[56] and benzophenone[57] correlated with their corresponding photostabilizing effects in polypropylene and polystyrene films. Excited-state quenching has, however, been strongly disputed as an important stabilizing mechanism,[58–62] particularly on a practical basis where it is calculated that up to 10% w/w of uniformaly distributed stabilizer would be required in order to produce effective quenching.[61]

Apart from the ability of metal complexes to quench the excited states of photoactive chromophores they have also been found to be effective quenchers of singlet oxygen ($^1\Delta g$), especially those chelates containing sulphur donor-ligands such as (9).[63–65] The interrelationships between the structure of the metal complex and singlet-oxygen quenching efficiency are far from being understood however, and although there is no doubt about the ability of some complexes to quench singlet oxygen the absence of large amounts of unsaturation in polyolefins and many other polymers suggests that this stabilizing function is insignificant in the overall process.

[57] D. J. Harper and J. F. McKellar, *J. Appl. Polym. Sci.*, 1974, **18**, 1233.

[58] N. S. Allen, A Chirinos-Padron, and J. H. Appleyard, *Polym. Deg. Stab.*, 1982, **4**, 223.

[59] N. S. Allen, A Chirinos-Padron, and J. H. Appleyard, *Polym. Deg. Stab.*, 1984, **5**, 323.

[60] R. P. Ranaweera and G. Scott, *Eur. Polym. J.*, 1976, **12**, 591.

[61] D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1976, **C14** (2), 155.

[62] S. Al-Malaika, K. B. Chakraborty, and G. Scott, in 'Developments in Polymer Stabilisation', Vol. 6, ed. G. Scott, Applied Science Publishers Ltd., London, 1983, p. 73.

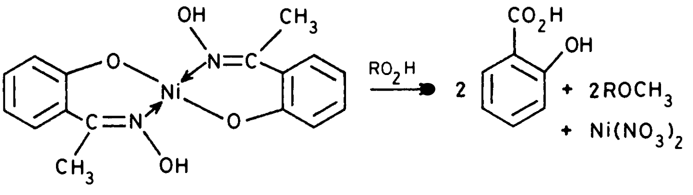
[63] C. F. Cook and J. P. Guillory, *J. Am. Chem. Soc.*, 1968, **93**, 4885.

[64] J. Flood, K. E. Russell, and J. K. S. Wan, *Macromolecules*, 1973, **6**, 669.

[65] W. A. Henderson and A. Zweig, *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 717 and 993.

Essentially, the mode of action of metal complexes is now associated almost wholly with their ability to prevent formation of, or catalytically to destroy, hydroperoxides either during processing and/or photo-oxidation.[62] Peroxide decomposers fall into two classes, namely stoicheiometric reducing agents and catalytic hydroperoxide decomposers.[4,62]

In the former case the light stabilizers such as those based on structure (8) react stoicheiometrically with hydroperoxides to give salicylic acid;[60]



(29)

This mechanism is believed to occur faster in light.

Catalytic hydroperoxide decomposers apparently destroy hydroperoxides through the formation of an acidic product in a radical generating reaction involving the hydroperoxides.[4] Here the parent compound acts as a reservoir for the 'real' antioxidant. A wide variety of sulphur-containing antioxidants fall into this category, including (9), which destroys cumene hydroperoxide by two different processes, depending on the mole ratio of hydroperoxide to stabilizer.[66] When the latter is in excess the hydroperoxide is completely decomposed with no induction period by a homolytic mechanism (Figure 10). Under these conditions the stabilizer (9) showed no change in composition. When the hydroperoxide is in excess there is an induction period up to a certain temperature, indicating that the

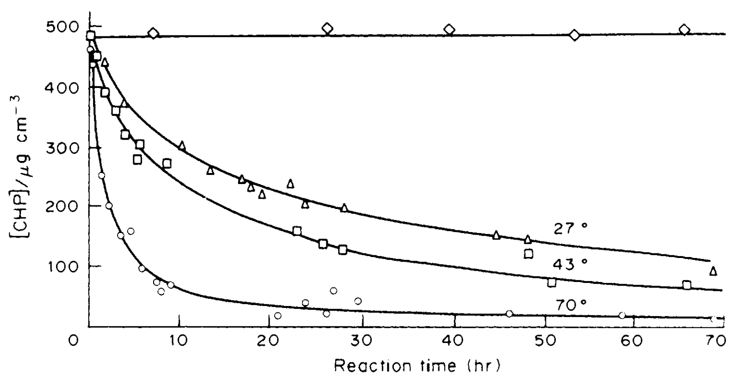


Figure 10 *Decomposition of CHP* (2.33 × 10^{-3}M) *by Cyasorb UV* 1084 (1.21 × 10^{-2}M) *at:* Δ, 27 °C; □, 43 °C; ○, 70 °C; *in n-hexane solution. The control CHP containing no stabilizer is also shown,* ◇

(Reproduced by permission from *Eur. Polym. J.*, 1985, **21**, 101)

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[66] N. S. Allen, A. J. Chirinos-Padron, and J. H. Appleyard, *Eur. Polym. J.*, 1985, **21**, 101.

complex is producing some intermediate which is responsible for the peroxidolysis (Figure 11).[66] Zinc and and nickel complexes of the dithiocarbamates, dithiophosphates, xanthates, mercaptobenzothiazoles, and dithiolates all destroy hydroperoxides by a peroxidolytic mechanism.[4,62] In all cases there is a pro-oxidant stage, the contribution of which is a function of the particular anti-oxidant. Scheme 1 is typical for the metal dialkyldithiocarbamates.[62]

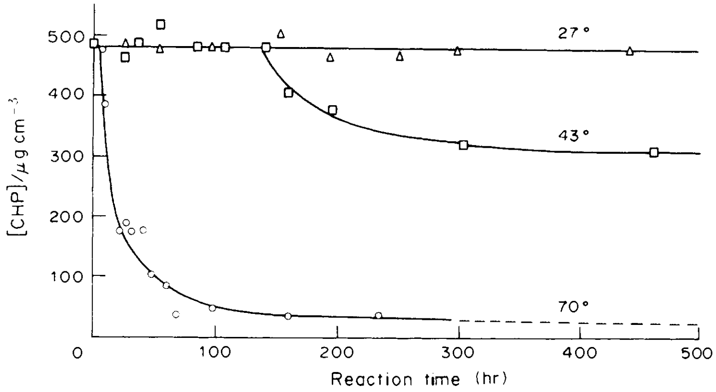
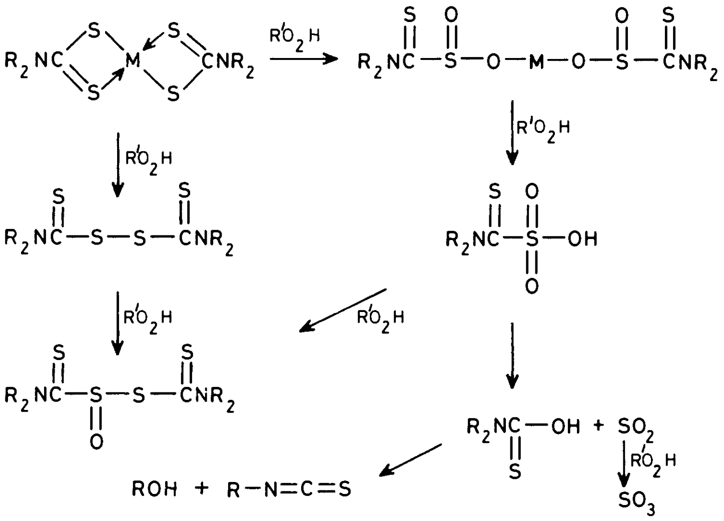
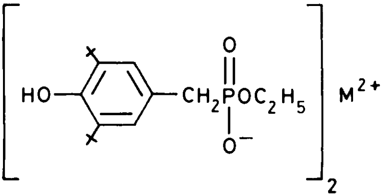


Figure 11 *Decomposition of CHP* (2.33×10^{-3}M) *by Cyasorb UV* 1084 (1.21×10^{-3}M) *at:* △, 27 °C; □, 43 °C; ○, 70 °C; *in n-hexane solution*
(Reproduced by permission from *Eur. Polym. J.*, 1985, **21**, 101)



Scheme 1

Most of these types of metal complexes owe their light-stabilizing action to their ability to operate as effective thermal antioxidants as well as extending this behaviour to a light-catalysed reaction.[62] The results in Tables 3 and 4 demonstrate this effect for three commercial complexes, namely Cyasorb UV 1084 (9), Irganox 2002, and Irganox 1425.[67] The last two are nickel and calcium complexes of structure (10):



(10)

Table 3 *Effect of thermal oxidation at* 140 °C *on hydroperoxide concentration in polypropylene films containing* 0.1% w/w *metal chelates*[a]

	POOH (μg/g)			
Additive	0 h[b]	1 h	3 h	6 h
None	75	119	5 160	13 950
Cyasorb UV 1084	12	15	24	24
Irganox 1425	26	26	50	357
Irgastab 2002	38	26	34	53

[a] Reproduced by permission from *ref.* 67. [b] Heating time

Table 4 *Effect of thermal oxidation at* 140 °C *on subsequent photostability of polypropylene films containing* 0.1% w/w *metal chelates*[a]

	U.v. embrittlement times			
Additive	0 h[b]	1 h	3 h	6 h
None	135	75	—	—
Cyasorb UV 1084	580	870	550	470
Irganox 1425	270	260	250	235
Irgastab 2002	780	690	730	530

[a] Reproduced by permission from *ref.* 67. [b] Heating time

Table 3 compares the thermal antioxidant action of the three metal complexes in polypropylene in terms of hydroperoxide formation. Their antioxidant efficiency follows the order Cyasorb UV 1084 > Irgastab 2002 > Irganox 1425 which is the same order as their light stabilizing effect in the polymer (Table 4). Correlations have also been observed between actual processing history and light stabilizing performance of metal complexes.[68]

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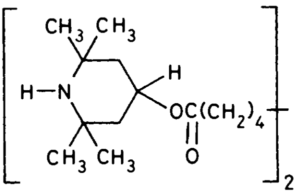
[67] N. S. Allen, A. Chirinos-Padron, and J. H. Appleyard, *Polym. Deg. Stab.*, 1984, **5**, 55.

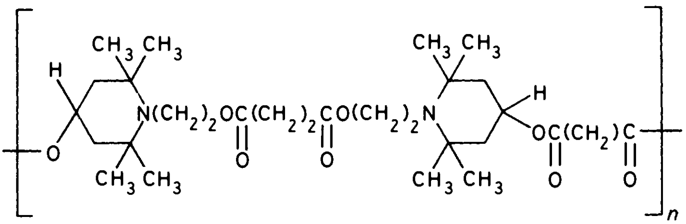
[68] G. Scott, *Pure Appl. Chem.*, 1980, **52**, 365.

D. Hindered Piperidine Compounds.—This is the newest and most efficient class of light stabilizer and, in fact, is now widely established in many polymer applications.[1–5] A range of different commercially acceptable monomeric and polymeric types for polyolefins are now available and are listed below:[4,69]



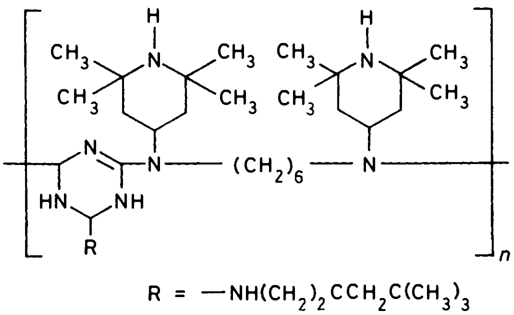
(11)

Tinuvin 770 (Ciba-Geigy): bis (2,2,6,6-tetramethyl-4-piperidinyl)sebacate.



(12)

Tinuvin 622 (Ciba-Geigy): polyester of succinic acid with *N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine.



(13)

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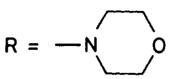
[69] N. S. Allen in 'New Trends in the Photochemistry of Polymers', ed. N. S. Allen and J. F. Rabek, Elsevier Applied Science Publishers Ltd., London, 1985, p. 209.

Chimassorb 944 (Ciba-Geigy): poly[2-*N*,N^1-di(2,2,6,6-tetramethyl-4-piperidinyl)-hexanediamine]-4-(1-amino-1,1,3,3-tetramethylbutane)symtriazine.

(13)



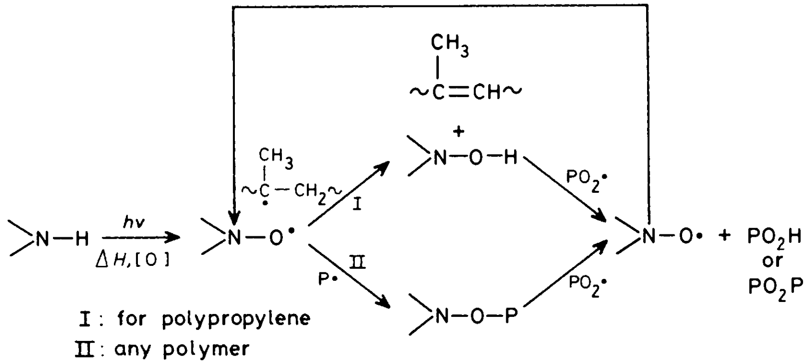
(14)

Cyasorb UV 3346 (American Cyanamid Company).

These light stabilizers have also attracted much controversy with regard to mode of action, and these mechanisms may be summarized as follows:

(1) Chain-breaking donor/acceptor redox mechanism through the nitroxyl/substituted-hydroxylamine intermediates.
(2) Decomposition of hydroperoxides by the amine during processing.
(3) Inhibition of photoreaction of α,β-unsaturated carbonyl groups in polyolefins.
(4) Reduction in quantum yield of hydroperoxide photolysis.
(5) Singlet-oxygen quenching—polydienes only.
(6) Complexation with hydroperoxides/oxygen.
(7) Complexation with transition-metal ions.

These compounds certainly exhibit no absorption in the near u.v. region and are ineffective excited-state quenchers,[2,4,70] although there is some evidence to suggest that in polybutadiene they quench singlet oxygen.[71] The overall stabilizing efficiency of these compounds is associated with the following cyclic (regenerative) mechanism (Scheme 2):[2,4,12,69]



Scheme 2

Here the amine is initially oxidized through to the nitroxyl radical by reaction with hydroperoxides or *via* the breakdown of an amine–oxygen complex:[72]

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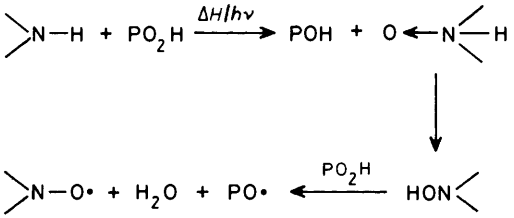
[70] J. Sedlar, J. Marchal, and J. Petruj, *Polym. Photochem.*, 1982, **2**, 175.
[71] Y. Y. Yang, J. Lucki, J. F. Rabek, and B. Ranby, *Polym. Photochem.*, 1983, **3**, 47 and 97.
[72] J. Lucki, J. F. Rabek, B. Ranby, and G. S. Dai, *Polym. Photochem.*, 1984, **5**, 385.



(30)

There is much evidence in the literature in favour of this mechanism occurring in the polymer at elevated temperatures,[73–75] despite room-temperature model-system studies to the contrary.[76] During irradiation the concentration of nitroxyl radicals grows rapidly but thereafter falls to a very low steady-state value of 10^{-4}M.[2,4,70] This low level of nitroxyl radicals is suggested to be insufficient to account for the high photoprotective efficiency of hindered piperidines. Much of the nitroxyl is converted into either the hydroxylamine (>N–OH) or substituted hydroxylamine (>N–O–P) produced by reaction of the nitroxyl radicals with different types of macroalkyl radicals.[2,4] These reactions are now well-established and, in fact, may occur thermally or photochemically. The hydroxylamine and substituted hydroxylamines are now clearly established as the most effective stabilizing intermediates and act as reservoirs for nitroxyl radicals by reaction with peroxy radicals. This latter reaction is somewhat controversial since for each nitroxyl radical generated one molecule of hydroperoxide is produced. The main problem in this area has been identification and confirmation of the involvement of the substituted hydroxylamine in stabilization. Studies using FTIR claim to have identified this intermediate in polypropylene during irradiation but no hydroxylamine could be found.[77] Oven-ageing studies on polypropylene film containing the bis-nitroxyl form of stabilizer (11) have given rise to a very significant improvement in stabilizing activity which is tentatively assigned to substituted hydroxylamine production.[78] The results of this work are shown in Table 5. Here it is interesting to note that the bis-nitroxyl version of (11) is the most efficient starting material. A similar effect to that in Table 5 is seen in Table 6 for the two polymeric hindered piperidine structures (13) and (14). These two compounds differ only by the nature of the 4-substituent on the triazine ring. Stabilizer (14) is seen to be a much more effective light stabilizer in polypropylene before oven ageing but, in fact, after just 10 hours at 130 °C the light stability of the polymer is nearly doubled. For stabilizer (13) maximum stability is evident only after 25 hours of heating, but the effect is marginal. Both effects are, however, consistent with maximum nitroxyl radical formation as shown by the e.s.r. data in Table 7.

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[73] K. B. Chakraborty and G. Scott, *Polymer*, 1980, **21**, 252.

[74] N. S. Allen, *Polym. Photochem.*, 1981, **1**, 243.

[75] N. S. Allen, *Makromol. Chem.*, 1980, **181**, 2413.

[76] J. Sedlar, J. Petrij, J. Pac, and A. Zahradnickova, *Eur. Polym. J.*, 1980, **16**, 659.

[77] D. J. Carlsson and D. M. Wiles, *Polym. Deg. Stab.*, 1984, **6**, 1.

[78] N. S. Allen, A. Parkinson, J. L. Gardette, and J. Lemaire, *Polym. Deg. Stab.*, 1983, **5**, 135; *idem*, *Polymer*, 1984, **25**, 235.

Table 5 *U.v. embrittlement times* (0.6 *carboxyl index*) *and unsaturated index at* 1640 cm^{-1} *for stabilized polypropylene films oven aged at* 140 °C *in air* (0.1% w/w)[a]

Heating time (h)	*Tinuvin 770 Embrittlement* (h)	$\left[>\mathrm{C}=\mathrm{C}< \right]$	*Mono-nitroxyl Embrittlement* (h)	$\left[>\mathrm{C}=\mathrm{C}< \right]$	*Bis-nitroxyl Embrittlement* (h)	$\left[>\mathrm{C}=\mathrm{C}< \right]$
0	1 375	0.032	2 020	0.037	3 050	0.032
1	2 750	0.044	360	0.040	3 875	0.043
4	1 875	0.044	900	0.042	3 925	0.046
8	2 000	0.044	2 200	0.045	3 375	0.046

[a] Reproduced by permission from *ref.* 78

Table 6 *Influence of prior thermal oxidation at* 130 °C *on photostability of polymeric hindered piperidines in polypropylene film*[a]

	U.v. embrittlement times (h)	
Heating time (h)	Chimassorb 944	Cyasorb UV 3346
0	920	1 300
10	1 110	2 270
25	1 200	1 920
50	1 160	1 860

[a] Reproduced by permission from *ref.* 78.

Table 7 *Effect of thermal oxidation on nitroxyl radical concentration in polypropylene and low density polyethylene films containing hindered piperidine compounds*[a]

	Relative nitroxyl concentration (*by e.s.r.*)			
	Polypropylene (130 °C)		*Polyethylene* (100 °C)	
Heating time (h)	(14)[b]	(13)[c]	(14)	(13)
0	0.5	1.0[d]	0.5	1.0
10	11.0	11.0	1.0	1.5
25	10.5	19.5	1.5	5.0
50	10.7	15.0	4.0	15.0
100	—	—	4.0	8.0

[a] Reproduced by permission from *ref.* 78. [b] Cyasorb UV 3346. [c] Chimassorb 944. [d] All values measured at same instrument sensitivity using compound (13) in a solvent blended film as the comparison. This is set at an arbitrary intensity of 1—all other measurements being related to it. Film thicknesses were constant throughout (200 ± 20 μm)

The above cyclic mechanism (Scheme 2) has been carefully scrutinized by many workers in the past few years and, in fact, it has been concluded that it alone cannot fully account for the high photoprotective efficiency of the parent amine molecule. The nitroxyl radical itself is a radical scavenger but is not as effective as hindered phenols in competing with oxygen for alkyl radicals. To account for this deficiency in the cyclic mechanism it has been suggested, and indeed confirmed by many workers, that hindered piperidine stabilizers and their derived nitroxyl radicals form weakly bonded localized complexes with hydroperoxides in the polymer, *e.g.*[2,4,79]

$$\rangle N{-}O\bullet{-}{-}{-}P{-}H + PO_2H \rightleftharpoons \rangle N{-}O\bullet{-}{-}{-}PO_2H + P{-}H \quad (31)$$

This mechanism raises the local concentration of nitroxyl radicals in regions where alkyl radicals are generated after the photocleavage of hydroperoxide groups followed by, of course, hydrogen atom abstraction from the polymer by the derived

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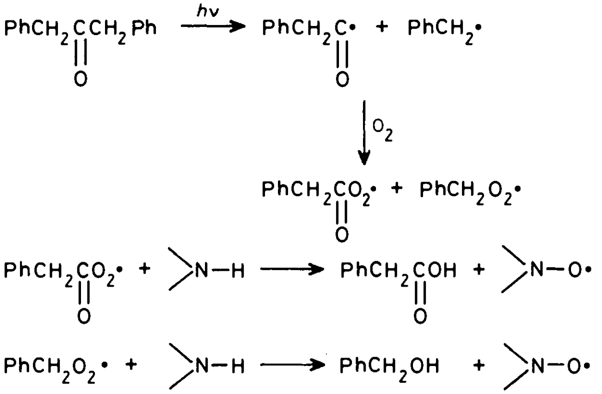
[79] D. J. Carlsson, K. H. Chan, J. Durmis, and D. M. Wiles, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 575.

hydroxyl/alkoxy free radicals. Under these conditions the nitroxyl radicals would then effectively compete with oxygen for the alkyl radicals. Evidence for the association mechanism originates from infra-red solution studies[2,4,70] and the observation of an increase in stabilizer absorption from solution by oxidized polypropylene containing higher concentrations of hydroperoxide groups.[79] One recently observed effect of this mechanism is to reduce the quantum yield of hydroperoxide photolysis.[80]

Other mechanisms originate from the inhibition of the dibenzoyl ketone sensitized photo-oxidation of 7-tetradecene by the following sequences.[81,82]



$$PhCH_2\underset{\underset{O}{\|}}{C}CH_2Ph \xrightarrow{h\nu} PhCH_2\underset{\underset{O}{\|}}{C}\cdot + PhCH_2\cdot \qquad (32)$$

$$\downarrow O_2$$

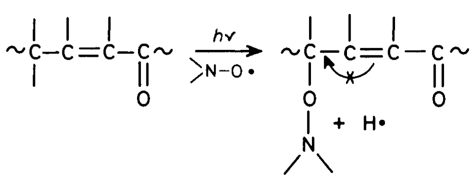
$$PhCH_2\underset{\underset{O}{\|}}{C}O_2\cdot + PhCH_2O_2\cdot \qquad (33)$$

$$PhCH_2\underset{\underset{O}{\|}}{C}O_2\cdot + \rangle N{-}H \longrightarrow PhCH_2\underset{\underset{O}{\|}}{C}OH + \rangle N{-}O\cdot$$

$$PhCH_2O_2\cdot + \rangle N{-}H \longrightarrow PhCH_2OH + \rangle N{-}O\cdot \qquad (34)$$

Reaction of the parent amine with transition-metal ions is also a possibility.[70,83]

The hindered piperidines have also been found to inhibit the photolysis of the impurity, luminescent α,β-unsaturated carbonyl groups in polypropylene[74,75] by the nitroxyl free-radical binding into the γ-carbon radical site and thus preventing the isomerization process:



(35)

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[80] A. Zahradnickova, J. Petruj, and J. Sedlar, *Polym. Photochem.*, 1983, **3**, 295.

[81] B. Felder, R. Schumacker, and F. Sitek, *Chem. Ind.* (*London*), 1980, **4**, 155.

[82] B. Felder, R. Schumacker, and F. Sitek, *Helv. Chim. Acta*, 1980, **63**, 132.

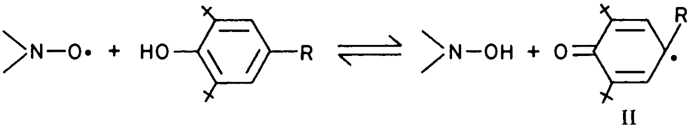
[83] S. P. Fairgrieve and J. R. MacCallum, *Polym. Deg. Stab.*, 1984, **8**, 107.

E. Interactions with Hindered Piperidine Light Stabilizers

Despite the high efficiency of these stabilizers they often interact unfavourably with many other additives used in commercial polymers for various purposes, such as antioxidants and fire-retardents.[2,69,70] Hindered phenolic antioxidants vary widely in terms of their interactions with hindered piperidine compounds depending on the nature of the polymer and processing history. A recent wide ranging survey of phenolic antioxidants and hindered piperidine compounds and their interactions during thermal and photochemical oxidation in both polypropylene and high density polyethylene has been carried out.[84] During thermal oxidation (oven ageing) the interactions are seen to be synergistic in most cases, whereas on photo-oxidation the majority of the effects are seen to be antagonistic.

For high density polyethylene the effects were also highly synergistic during oven ageing, whereas during photo-oxidation the effects were found to be variable, both synergism and antagonism being operative. In many cases the stability of the phenolic antioxidant itself was the main determining factor in controlling performance. Synergism thermally and photochemically is probably associated with the fact that the generated nitroxyl and hydroxylamine products from the parent amine are scavenging macroalkyl and macroperoxy radicals and protecting the phenolic antioxidant. Antagonism on photo-oxidation is associated with any of the following three process:

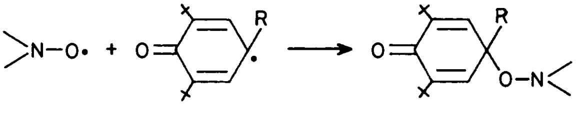
(1) Oxidation of the phenol to an active quinone by the nitroxy radical:[41,42,69]



(36)

(2) Inhibition of hydroperoxide formation by the phenolic antioxidant, thus preventing mechanism (30) above.[41,42,69]

(3) Reaction of the nitroxyl radicals with radical intermediates from the phenol such as II in reaction (36) above:[85]



(37)

This would effectively remove nitroxyl free radicals from the cyclic mechanism (Scheme 2) above.

With thioesters there is very strong antagonism,[84] both thermally and photochemically, which is associated with reaction of nitroxyl radicals with sulphenyl radicals to give inactive sulphonamides:[86]

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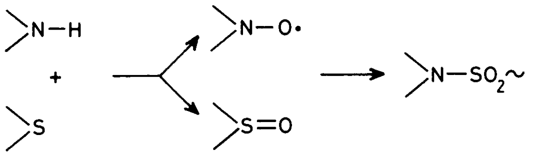
[84] N. S. Allen, A. Hamidi, F. F. Loffelman, P. MacDonald, M. Rauhut, and P. V. Susi, *Plant Rubb. Process Appl.*, 1985, 5, 259 and in press.

[85] J. Lucki, J. F. Rabek, and B. Ranby, *Polym. Photochem.*, 1984, 5, 351.

[86] J. Lucki, S. Z. Jian, J. F. Rabek, and B. Ranby, *Polym. Photochem.*, 1986, 7, 27.


(38)

With phosphites the effects are variable, being generally antagonistic thermally and both antagonistic and synergistic photochemically.[84]

With the *o*-hydroxybenzophenones the effects are not synergistic[86] but are nevertheless greater than that of the original hindered piperidine alone. The former are protected by the hindered piperidine compound due to the ability of the latter to destroy hydroperoxides stoicheiometrically, thus preventing the radical scavenging reaction (25) from occurring.

F. Factors Controlling the Choice of a Light Stabilizer.—The following factors are critical for obvious commercial reasons:

(1) Compatability—stabilizer must not exude from the polymer after fabrication. Long alkyl substituents or polymeric types are preferred.
(2) Volatility—loss of stabilizer during fabrication is to be avoided.
(3) Stability to light—the more photostable the additive the more photostable will be the polymer. Some stabilizers, however, are merely reservoirs for active stabilizing intermediates.
(4) Stability to processing temperatures.
(5) Stabilizer must not react with the polymer *e.g.* nickel forms black complexes with nylon 6,6.
(6) Low toxicity—for example food packaging.
(7) Colour—undesirable except in certain pigment applications.
(8) Cost—lowest consistent with stabilizer performance.