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THE ANTIOXIDANT ROLE OF UV STABILISERS

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Abstract - The mechanisms of action of the more important classes of uv stabilisers for polyolefins are considered in the light of present views on the mechanisms of antioxidant behaviour.

The metal thiolate catalytic peroxide decomposers (PD-C) are seen to be effective uv stabilisers in their own right and as synergists with 'uv absorbers'. Chain-breaking antioxidants (CB-A), of which the hindered nitroxyl radicals are the most important, are very effective as single-component uv stabilisers but their precursors, the hindered amines, are thermal pro-oxidants. Donor chain-breaking antioxidants (CB-D), as typified by the hindered phenols, are weak photostabilisers with only a small concentration gradient. Their radical scavenging effect, is augmented when they are used in conjunction with the 'uv absorbers' but they antagonise with the peroxide decomposers. The 'uv absorbers' appear to function at least in part by a CB-D mechanism and their effectiveness is due mainly to their uv stability. They are destroyed by both hydroperoxides and by excited carbonyl chromophores and their synergism with the peroxide decomposers (PD-C) is to a large extent due to their protection by this class of uv stabiliser.

INTRODUCTION

Uv stabilisers have always been categorised as a sub-group within the general antioxidant class of polymer additives (1). However, the ability of many photostabilisers to absorb uv light without forming chemically reactive species has led to attention being focussed on light screening or filtering processes. Very adequate explanations for both the excellent screening behaviour and the high photostability of typical 'uv absorbers' have been given in recent reviews (2,3). Many effective photostabilisers do not however function primarily by absorbing uv light but are nevertheless preventive antioxidants. One of the earliest classes of uv stabiliser to be distinguished from the uv absorbers was the metal dithiocarbamates (4) whose function as catalytic peroxide decomposers was already known (5). The contribution of uv screening to the function of these compounds has been shown to be relatively unimportant (6,7). Other types of peroxidolytic agents have since been shown to be effective as uv stabilisers, sometimes alone (6-8) but, more effectively, in combination with the 'uv absorbers' (9,10).

More recently the effectiveness of many nickel complexes as uv stabilisers has been ascribed to the quenching of photo-excited states of impurities present in polymers. This antioxidant mechanism can also be classified as preventive (11) in that it interferes with the initiation of autoxidation by removing potential free radical initiators. Although there is little doubt that many metal complexes can deactivate excited states of potential chromophores in polymers or singlet oxygen formed by their quenching with ground state oxygen, the importance of this kind of process in the stabilisation of polymers under practical conditions is still very much in question (12). The function of some of the more effective uv stabilising metal complexes is generally explained on the basis of other known photo-initiation processes occurring in the polymer; for example, many are either kinetic chain-breaking antioxidants or peroxide decomposers (6,13,14).

Classification of antioxidant mechanisms

Since the sequence of reactions occurring during photo-oxidation is the same as that involved in thermal oxidation it should be possible in principle to interfere with photooxidation in the following ways (15):

(a) Kinetic chain-breaking (CB) – There are two mechanistically distinguishable alternatives of this process:

(i) Alkylperoxyl radical reduction is the most significant process occurring when these radicals are present in excess in the system. This is the normal situation at ambient oxygen pressures during thermal oxidation and when diffusion control is not important. This class of antioxidant behaves by electron or hydrogen atom donation to the radical (CB-D).

$$\mathrm{RO\dot{O} + DH \longrightarrow [RO\bar{O} + \overset{+\bullet}{D}H] \longrightarrow ROOH + \dot{D}} \qquad [1]$$

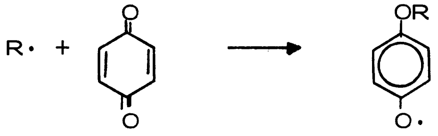
Hindered phenols and aromatic amines are the best known examples in this class (15).

$$\mathrm{ROO\cdot + AH \longrightarrow ROOH + \dot{A}} \qquad [2]$$

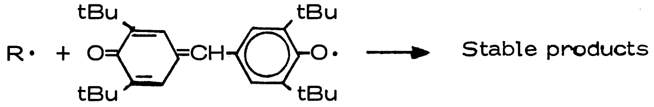
(ii) Alkyl radicals predominate at high rates of initiation and particularly when there is a deficiency of oxygen (either as a result of low ambient oxygen pressure or low rate of diffusion) to the reaction site. Under these conditions, alkyl radical oxidation by an acceptor antioxidant is the most likely deactivating mechanism (CB-A).

$$\mathrm{R\cdot + A \longrightarrow [R^{+} + \bar{A}\cdot] \longrightarrow R\dot{A}} \qquad [3]$$

Quinones [4], nitro compounds, nitrones and stable free radicals [5] are the preferred classes within this group (15).



[4]



[5]

(b) Preventive mechanisms – Screening of uv light from the polymer by stable chromophores is essentially a preventive mechanism which is specific to uv degradation. Destruction of hydroperoxides in a process which does not give rise to free radicals is also preventive; two mechanistically different types of peroxidolytic agents can be distinguished.

(i) The majority of agents falling into this class are catalytic peroxide decomposers (PD-C) containing sulphur and are eventually converted by oxidation into sulphur trioxide or sulphuric acid (16). Examples within this class include the thiodipropionate esters (17), the metal complexes of mercaptobenzthiazole (18), dithiocarbamic acids (5,6) and dithiophosphoric acids (20,21).

(ii) Phosphite esters have been shown to behave primarily as stoichiometric peroxide decomposers (22,23) (PD-S) but certain cyclic esters also have catalytic activity (24). Bis-phenol sulphides show auto-synergistic behaviour due to the presence of both CB-D function (phenol) and a peroxidolytic function (sulphide) which may be either stoichiometric (PD-S) or catalytic (PD-C) depending on the sulphide structure (25).

THE EFFECTS OF ANTIOXIDANTS AND UV STABILISERS ON THE MELT STABILITY OF POLYOLEFINS

The conditions prevailing in a commercial processing operation are very different from those to which the same polymer may be exposed during subsequent service. The most important differences are the high shearing forces to which the polymer is exposed until it reaches its melting transition, and the oxygen deficiency in the extruder barrel. These two conditions lead to a predominance of alkyl radicals over alkylperoxyl radicals (15). This leads to cross-linking of polyethylene during the early stages of processing (see Fig 1) due to dehydro-cross-linking by the hydroperoxides initially formed in the polymer [6] (26).

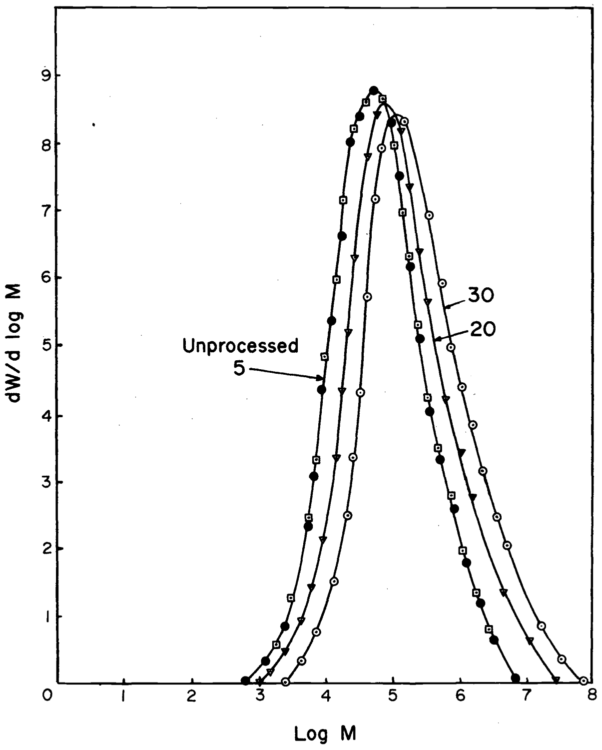
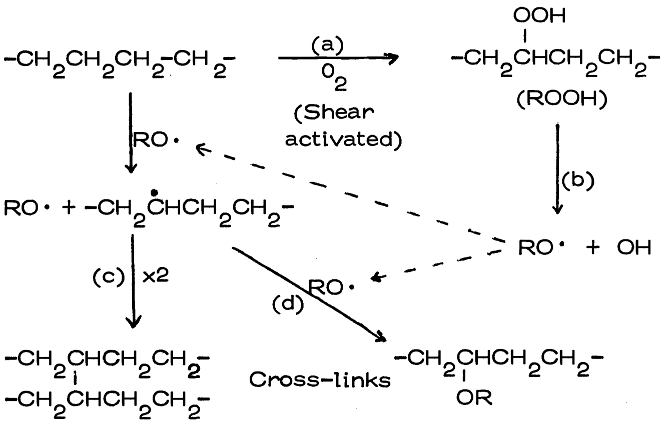
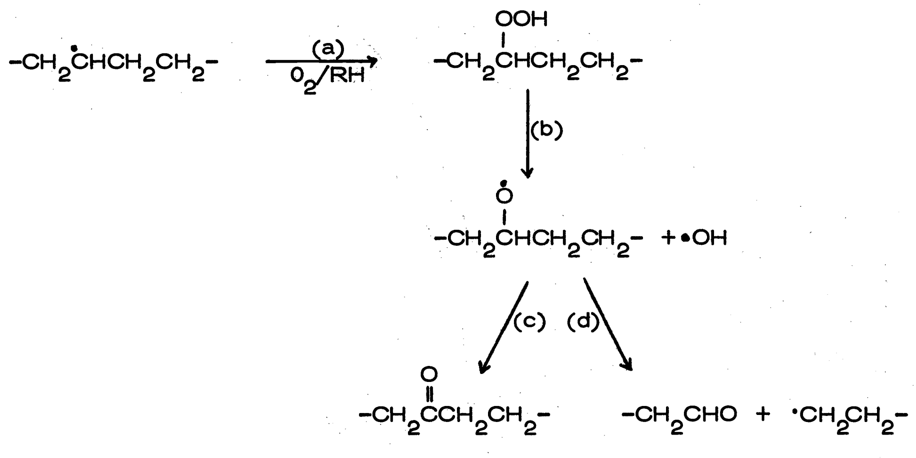


Fig 1. Effect of processing in an oxygen deficient atmosphere on the molecular weight distribution of LDPE (numbers on curves are processing times at 150°C in mins). Reproduced from Chakraborty and Scott, Europ Polym J, 13, 731 (1977) with permission from Pergamon Press Ltd.



[6]

Cross-linking by dehydrodimerisation processes [6(c,d)] is in competition with oxidative chain-scission [7(d)] which supervenes when there is a higher oxygen concentration in the system (26).



[7]

Both cross-linking and chain-scission are effectively inhibited by CB-A, CB-D and PD-C antioxidants but particularly by the first and last. Fig 2 compares the behaviour of some typical antioxidants and stabilisers on the melt stability of polypropylene which is much more sensitive to chain-scission than is polyethylene. A typical chain-breaking (CB-D) antioxidant, Irganox 1076 [I] is an effective melt stabiliser, although it cannot completely inhibit peroxide formation (see Fig 3). Catalytic peroxide decomposers, ZnDEC and NiDEC [II, R = Et; M = Zn or Ni] are also effective melt stabilisers (Fig 2) and completely inhibit the formation of hydroperoxides during processing (Fig 3). No peroxides could be measured over the time of the experiment. A typical 'uv absorber', HOBP [III] had only a minor CB effect on both peroxide and carbonyl formation.

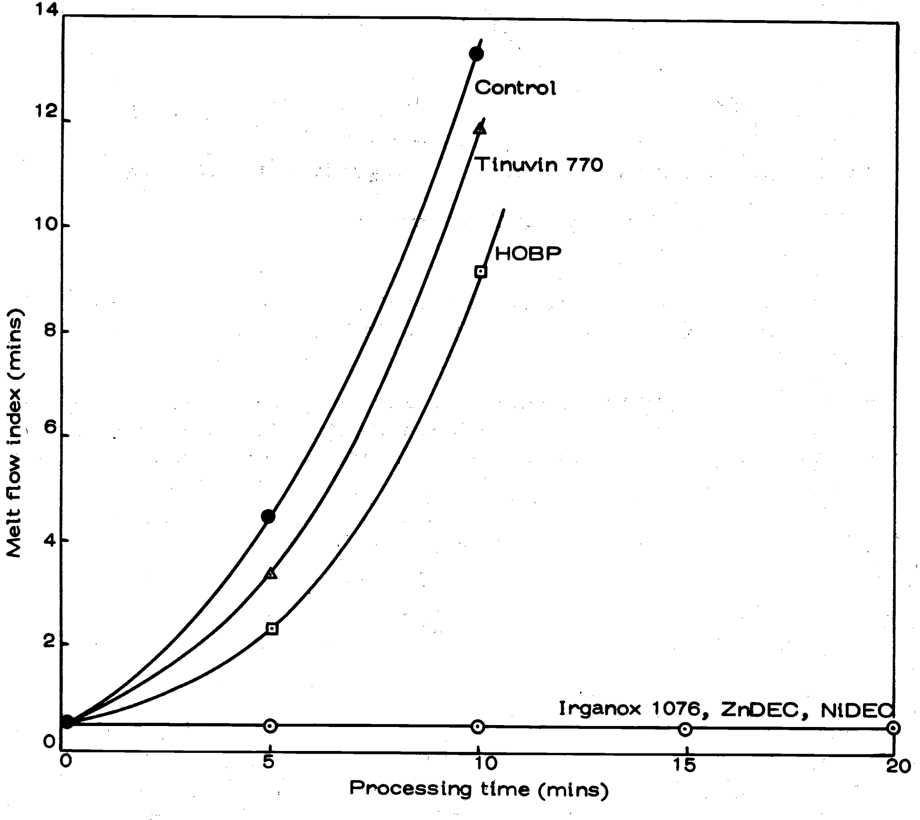


Fig 2. Effect of antioxidants and stabilisers on the change in melt flow index (MFI) of PP processed at 180°C (all additives at 3×10^{-4} mol/100 g).

The recently developed hindered amine class of uv stabiliser, typified by Tinuvin 770 [IV]

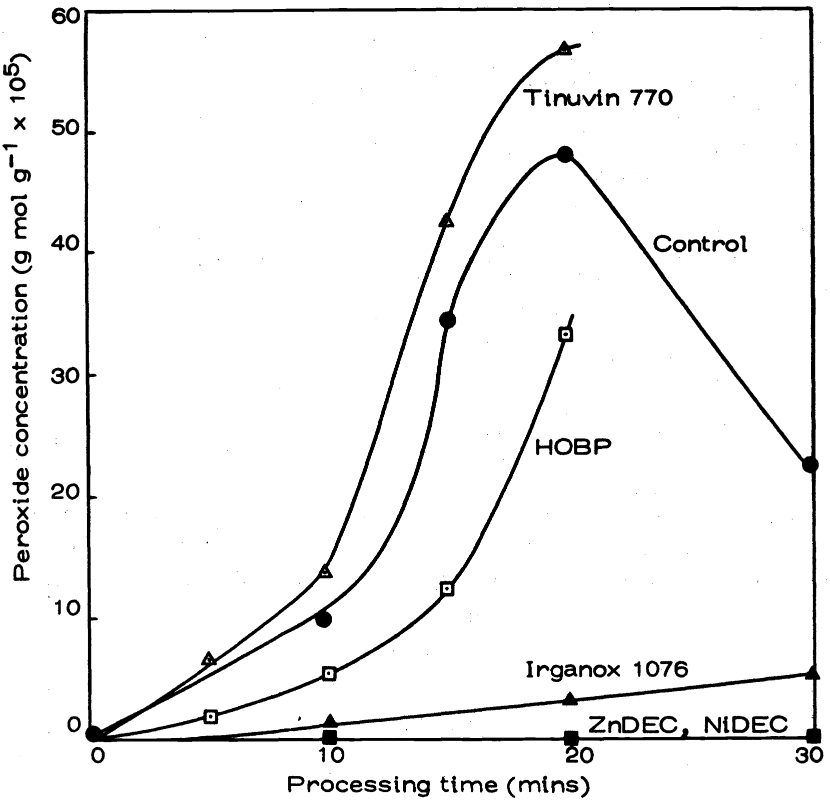
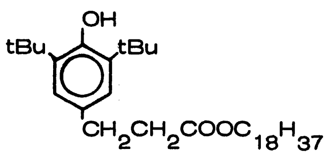
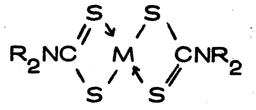


Fig 3. Effect of antioxidants and stabilisers on the formation of peroxides in PP during processing at 180°C (all additives at 3 x 10^{-4} mol/100 g).

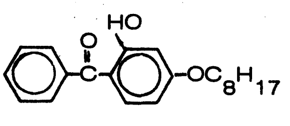
had a positive pro-oxidant effect on the polymer as indicated by hydroperoxide formation (see Fig 3) but it had only a minor effect on melt flow index (Fig 2). A similar pattern of behaviour was observed with the same four classes of antioxidant in thermal oxidative (oven ageing at 110°C) (see Fig 4) (27), although in the case of Tinuvin 770, a much more powerful thermal pro-oxidant effect was evident than during processing.



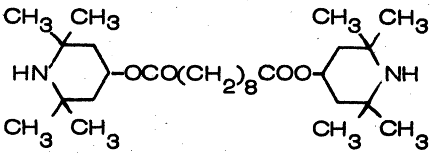
[I] (1076)



[II] (a) M = Zn
(b) M = Ni



[III] (HOBP)



[IV] (Tin 770)

Table 1 compares the effectiveness of these four classes of antioxidant in the thermal oxidation of both LDPE (110°C) and PP (140°C). It is clear that [III] and [IV] cannot be considered to be antioxidants under these conditions and unlike 1076 they do not synergise with the dithiocarbamates.

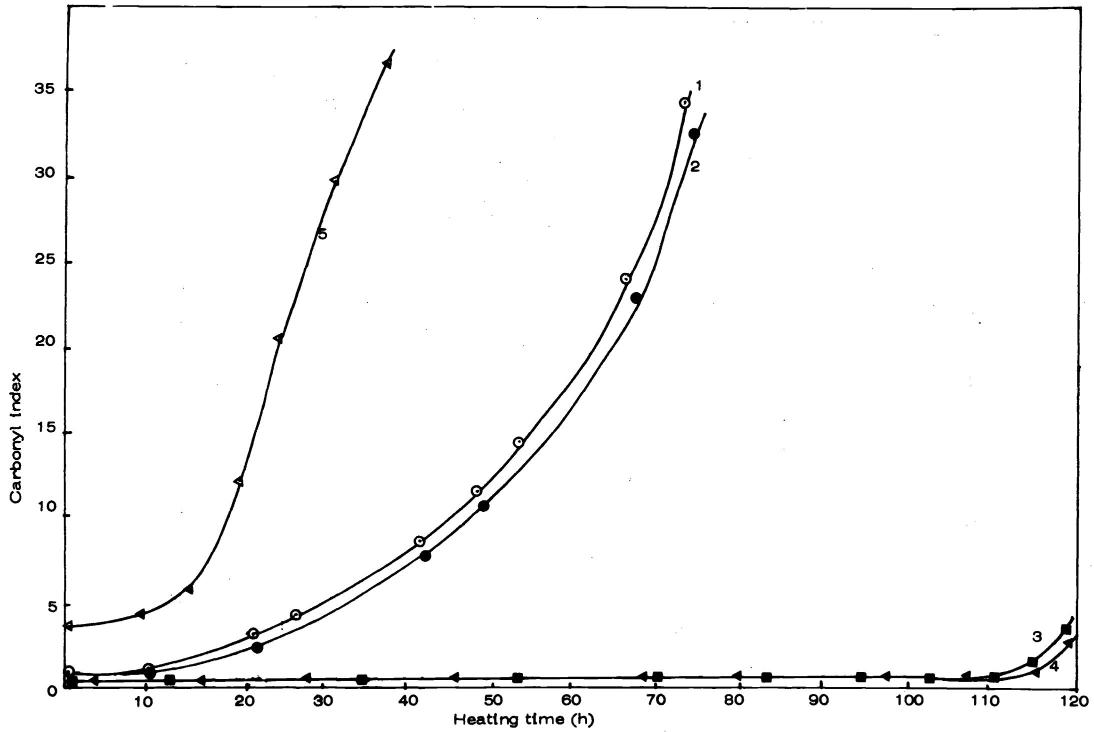


Fig 4. Effect of antioxidants and stabilisers on the rate of thermal oxidation of LDPE at 110°C (all additives at 3 x 10^{-4} mol/100 g). 1, Control, no additive; 2, HOBP; 3, 1076; 4, ZnDEC; 5, Tinuvin 770.

TABLE 1. Thermal oxidative stability of polyolefins in the presence of antioxidants and stabilisers (concentrations of all additives 3 x 10^{-4} mol/100 g)

Antioxidant	PP (140°C)* Embrittlement time (h)	LDPE (110°C)* Induction period (h)
None	0.5	10
HOBP [III]	≃0.5	10
770 [IV]	≃0.5	0
1076 [I]	58	110
ZnDEC [IIa]	32	110
NiDEC [IIb]	28	105
ZnDEC + 1076	165	300
ZnDEC + HOBP	≃32	130
ZnDEC + 770	≃32	-
NiDEC + 770	-	110

* In the case of PP, the embrittlement times follow the end of the induction periods closely whereas they are much longer than induction periods in the case of LDPE

UV STABILISATION OF POLYOLEFINS WITH ANTIOXIDANTS AND UV STABILISERS

The same four mechanistic classes used in the melt stabilisation experiments were also used as light stabilisers for polyethylene and polypropylene. Fig 5 illustrates this for polypropylene (all at the same molar concentration of 3 x 10^{-4} mol/100 g). It is clear that the order of activity is quite different from their order of effectiveness as melt stabilisers.

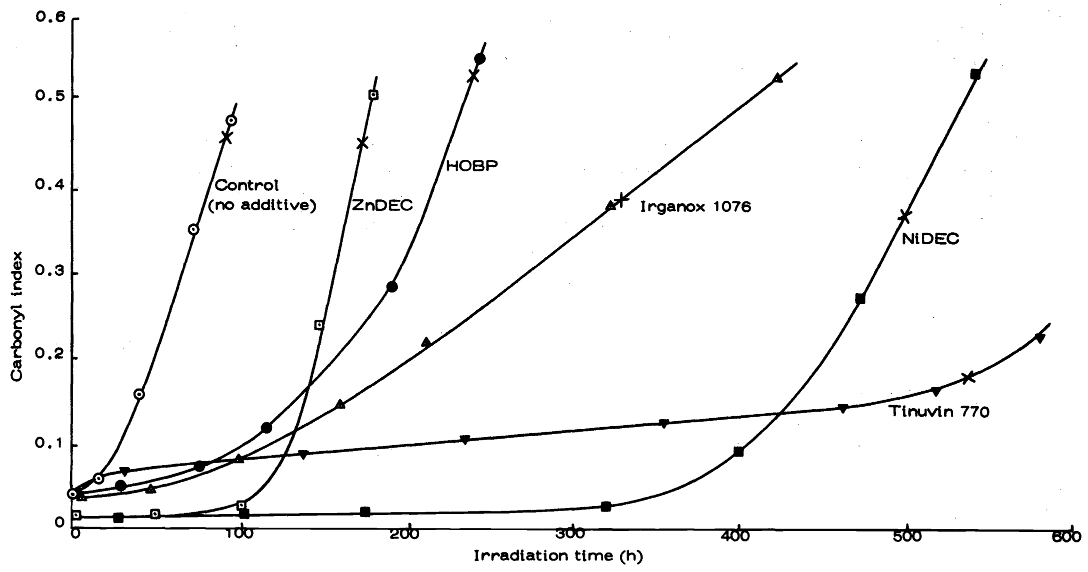


Fig 5. Effect of antioxidants and stabilisers (all at 3 x 10^{-4} mol/100 g) on the uv stability of PP processed at 180°C for 10 mins (x indicates embrittlement of the sample).

The nickel dithiocarbamate (NiDEC) and the hindered piperidine (Tin 770) are more effective than the other additives and this is reflected in the embrittlement lifetimes of the polymer films (see Table 2).

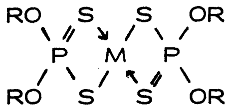
TABLE 2. Embrittlement lifetimes of polyolefin films containing antioxidants and stabilisers (all at 3 x 10^{-4} mol/100 g)

Antioxidant/stabiliser	Time to embrittlement	
	PP (h)	LDPE (h)
Control (no additive)	90	1200
HOBP	245	2200
1076	325	1800
770	540	2250
ZnDEC	175	1400
NiDEC	500	1800

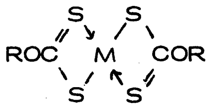
The shapes of the photo-oxidation curves (Fig 5) are a reflection of the distinctly different mechanisms involved in the behaviour of the different classes of uv stabiliser and the compounds chosen are representative of the main classes of uv stabiliser currently in use.

Peroxidolytic agents
A number of transition metal complexes have been shown to fall into this category and two distinct mechanistic sub-classes have been recognised depending on whether they destroy peroxides catalytically or by a stoichiometric mechanism.

(a) Catalytic peroxide decomposers (PD-C) – Although the dithiocarbamate metal complexes [II] are the most extensively studied members of this class (5–7,9,10, 27–31), similar activity has been found with the transition metal complexes of the dithiophosphates [V] (21,32) and the xanthates [VI] (21), whose structural relationship to the dithiocarbamates is obvious. The similarity of the behaviour of the



[V]



[VI]

nickel complexes of [II], [V] and [VI] in the decomposition of cumene hydroperoxide is illustrated in Fig 6. The first stage is a rapid catalytic destruction of

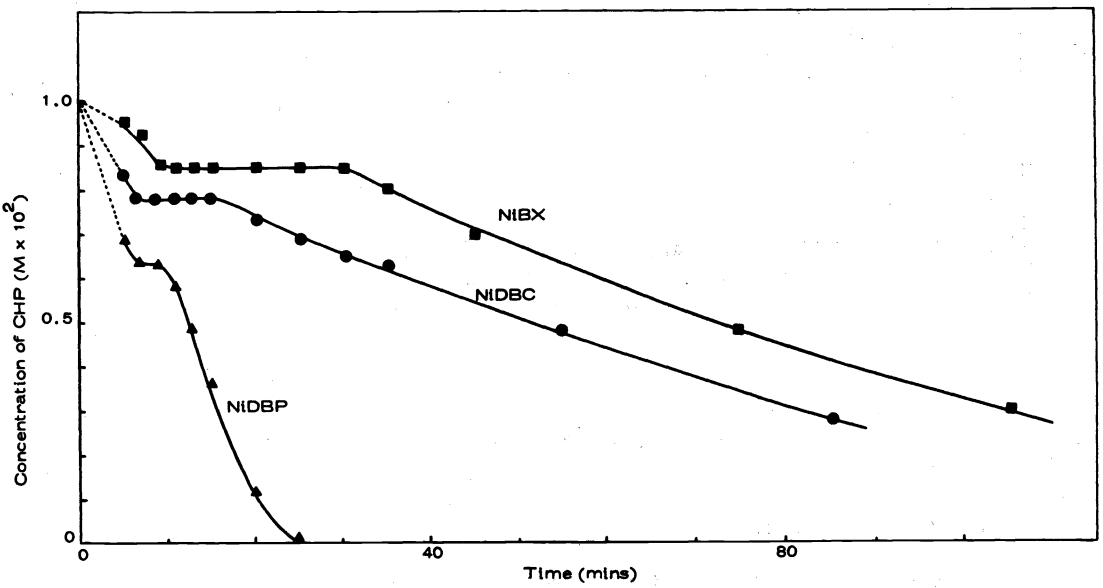


Fig 6. Decomposition of CHP (1 x 10^{-2} M) in chlorobenzene at 110°C (in nitrogen) in the presence of nickel dithiolates (2 x 10^{-4} M).

hydroperoxide involving free radicals (5,21,34,36). An induction period precedes the second stage, an ionic catalytic destruction of peroxides. The first two stages are not observed during photo-oxidation since the powerful Lewis acids responsible for the ionic catalytic decomposition of the hydroperoxides are produced during the early stages of processing. This coupled with the ability of the metal complexes to trap free radicals when present in molar excess leads to the essential elimination of a potential pro-oxidant, the hydroperoxide, during processing (see Fig 3). This alone would not lead to uv stabilisation (32) unless the effective PD-C antioxidant was also active during photo-oxidation. This has been shown to be the case; nickel dialkyldithiocarbamates are even more effective catalysts for the ionic decomposition of hydroperoxides in the presence of light than they are under thermal oxidative conditions (6). This powerful peroxidolytic process, which is known to involve derived inorganic acids [SO_3, H_2SO_4] (5), is the reason for the induction period observed in the photo-oxidation of polyolefins in the presence of these metal complexes (see Fig 5).

The difference in behaviour of ZnDEC and NiDEC (Fig 5) in photo-oxidation is not a reflection of a difference in PD-C activity since under thermal-oxidative conditions they have very similar antioxidant activity (see Table 1). A comparison of the photostabilities of the two complexes shows (Fig 7) that ZnDEC is considerably less uv stable than NiDEC and the length of the induction period to photo-oxidation corresponds almost exactly to the time for the disappearance of the metal complex from the system. Fig 8 shows that the stabilisers fall into two classes; the effective stabilisers (770, NiDEC and HOBP) are strongly concentration dependent whereas the ineffective stabilisers (1076, ZnDEC) are not. This appears to relate to the uv stability of the antioxidant-active species, HOBP and NiDEC are both much more uv stable than 1076 and ZnDEC and the nitroxyl radical has been shown to be uv stable (47).

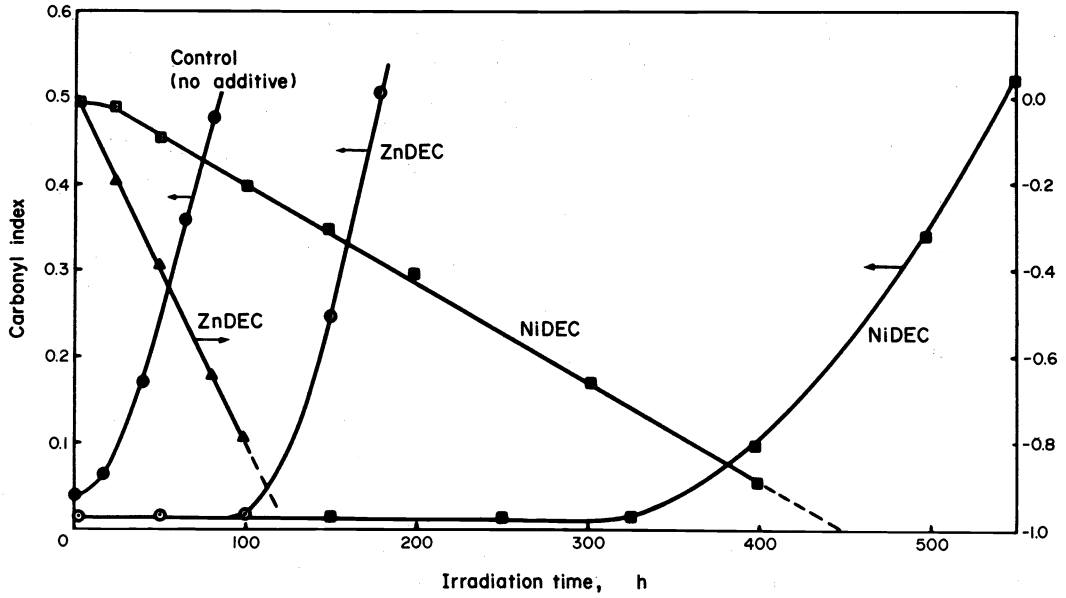
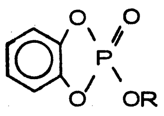


Fig 7. Correlation of the decay of uv absorbance of ZnDEC (285 nm) and NiDEC (330 nm) in LDPE with photo-oxidation induction period (initial additive concentration 3 x 10^{-4} mol/100 g).

A second class of PD-C antioxidants with photo-stabilising activity is the cyclic catechol phosphites and the derived phosphates [VII] (8,24). Unlike their aliphatic analogues which appear to react with hydroperoxides by a stoichiometric reaction (36) compounds in the above class are very effective thermal and uv stabilisers by virtue of their catalytic activity.



R = H, alkyl aryl or transition metal ion

[VII]

(b) Stoichiometric peroxide decomposers (PD-S) - The class of transition metal complexes derived from salicaldoximes and ketoximes [VIII] are effective uv stabilisers. Attempts to show that the activity of the nickel complexes was

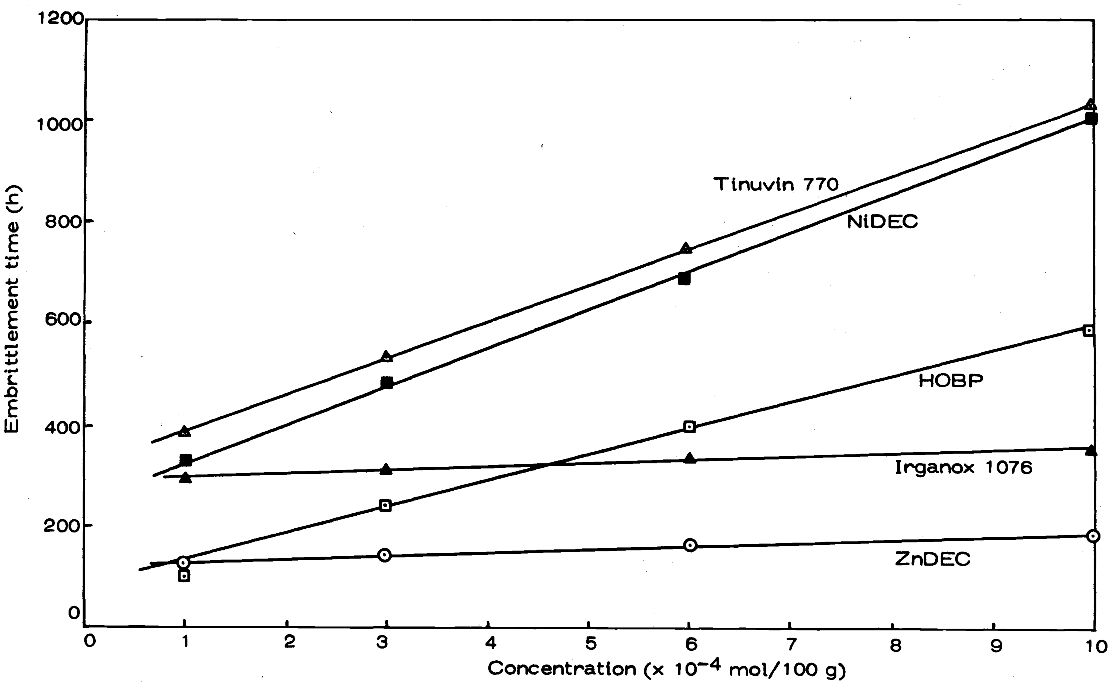
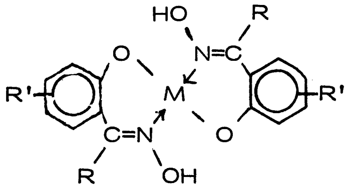


Fig 8. Effects of additives concentrations on the photostability of PP.

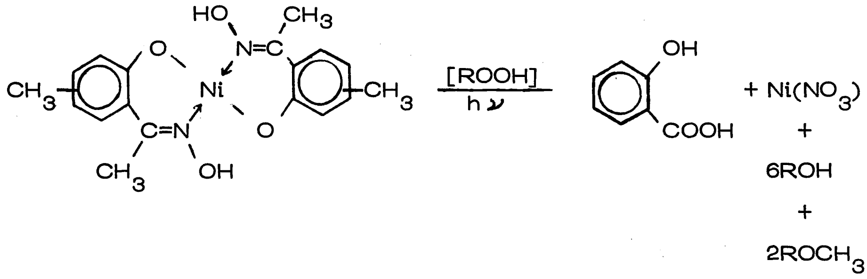


R = H or alkyl

R' = alkyl

[VIII]

associated with their known ability to quench excited states of indigenous chromophores in polymers (37,38) or singlet oxygen (39), the product of their quenching with ground state oxygen have been largely unsuccessful. The stabilising effect seems to receive a more satisfactory explanation on the basis of both CB-D and PD-S activity which has been demonstrated in model systems (6). As in the case of the nickel dithiocarbamates, two additional factors which appear to be important as (i) the high intrinsic light stability of the nickel complexes and (ii) the increased rate of the stoichiometric non-radical reaction [8] in the presence of light.



[8]

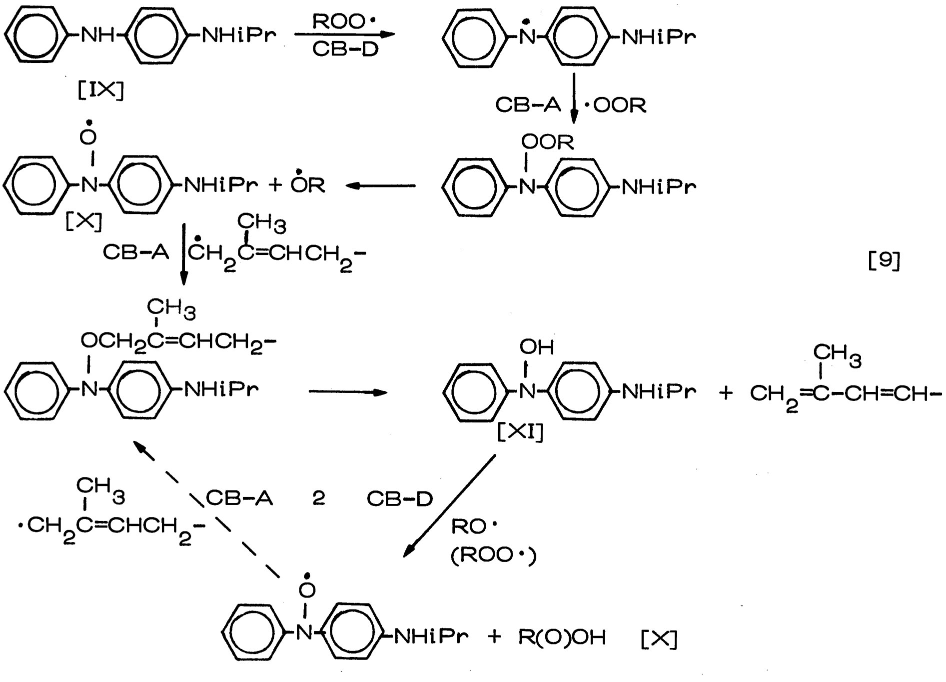
Alkyl or arylphosphites have some activity as light stabilising PD-S antioxidants in polyolefins but they are normally used as synergists with the uv absorbers (40).

Chain-breaking antioxidants

(a) CB-D mechanism - It has been recognised for many years that conventional phenolic antioxidants, although effective thermal stabilisers for polyolefins, by themselves have little value as light stabilisers. Such a conclusion however depends on the conditions of the evaluation. Fig 8 and Table 2 show that at low concentrations, a hindered phenol (1076) compares favourably with a conventional light stabiliser (HOBP) in polypropylene. With increasing concentration, however, the uv absorber becomes much more effective whereas the CB-D antioxidant shows only a marginal increase in activity. As in the case of the zinc dithiocarbamate, this is believed to be due to their photlysis to give non-antioxidant products which are in some cases sensitisers of photo-oxidation; particularly the stilbenequinones (9). However, important synergistic effects may be achieved when CB-D antioxidants are used in conjunction with uv absorbing antioxidants (see later).

(b) CB-A mechanism - 'Stable' nitroxyl radicals have been known to be involved in the function of amine antioxidants for many years (42,43) but relatively little attention has been paid to their function compared with that given to the CB-D mechanism.

(c) Regenerative CB-A, CB-D cycle - It has recently been shown that the exceptional activity of alkylaminodiphenylamine [IX] in rubber under conditions of high shear is almost certainly due to the ability of the derived nitroxyl radical [X] to trap mechanochemically formed alkyl radicals (44). The corresponding hydroxylamine [XI] has been shown to be involved in the antioxidant process and the regenerative process [9] has been proposed to account for the fact that the nitroxyl radical concentration rises to a maximum and then reduces to a low stationary concentration throughout the lifetime of the rubber (44).



[9]

The mechanism of the hindered piperidine light stabiliser [IV] appears to involve a nitroxyl regeneration mechanism (45-47). The cyclical process [10] seems to be generally preferred (45,46) to account for the high f^* value which appears to be associated with the persistence of the nitroxyl radical [XII] in the system (49).

This proposal is not entirely satisfactory for two reasons:

1 The rate constants for the steps involved are not high enough to account for

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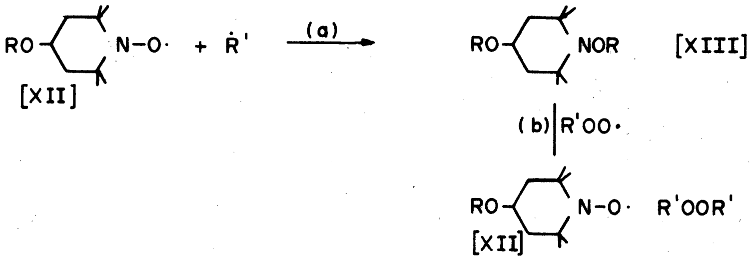
[*] f = no of chains terminated per chain initiation step.

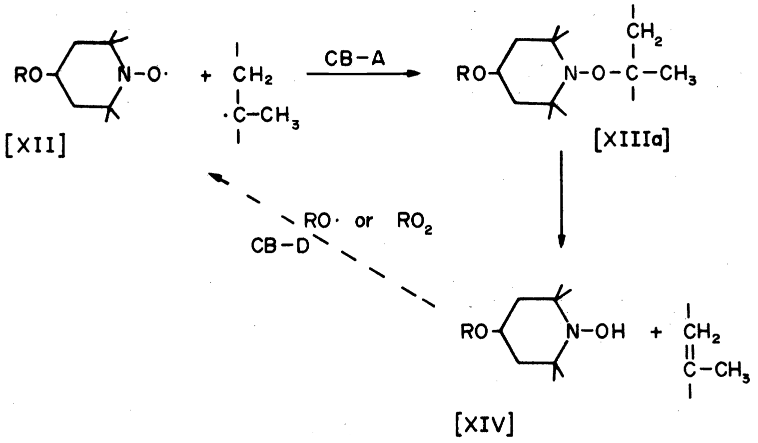


[10]

the effectiveness of the inhibition mechanism and it has to be assumed that reaction [10a] is in some way favoured for example by physical association with the primary radical generator, the hydroperoxide (47).

2 The peroxide produced in reaction [9] is itself a source of new free radicals in the presence of light and the overall process is therefore still branching.

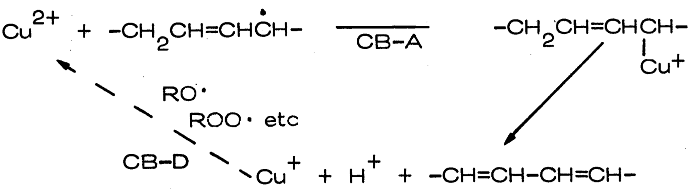
The interpolation of the hydroxylamine [XIV] by reaction [11] overcomes both of these



[11]

difficulties since the alkyl hydroxylamines are known to be extremely efficient CB-D antioxidants (48) which lead to the facile regeneration of nitroxyl radicals.

Evidence will be presented for this process elsewhere (49) but a similar cyclical regenerative process has been found to operate in photostabilisation processes involving transition metal ions. For example, soluble copper salts are very effective photostabilisers for paint media which become discoloured due to the formation of polyconjugated unsaturation. The reaction sequence [12] has been proposed to account for this phenomenon (50).



[12]

Uv absorbers as antioxidants

Although the 2-hydroxybenzophenones have weak thermal stabilising properties under processing conditions (see Fig 3), their activity during photo-oxidation appears at least in part to be the removal of photo-generated initiating radical species (6,51). Fig 9 (6) shows that during the initial stages of photo-oxidation of polyethylene, the activity of HOBP is limited to its screening function; that is it has no significant retarding effect on hydroperoxide initiated photo-oxidation apart from its screening function (6). In the later stages, however, when carbonyl initiation becomes important (52), HOBP appears to show chemical inhibiting activity. In a more detailed study of this effect in heavily oxidised polyethylene

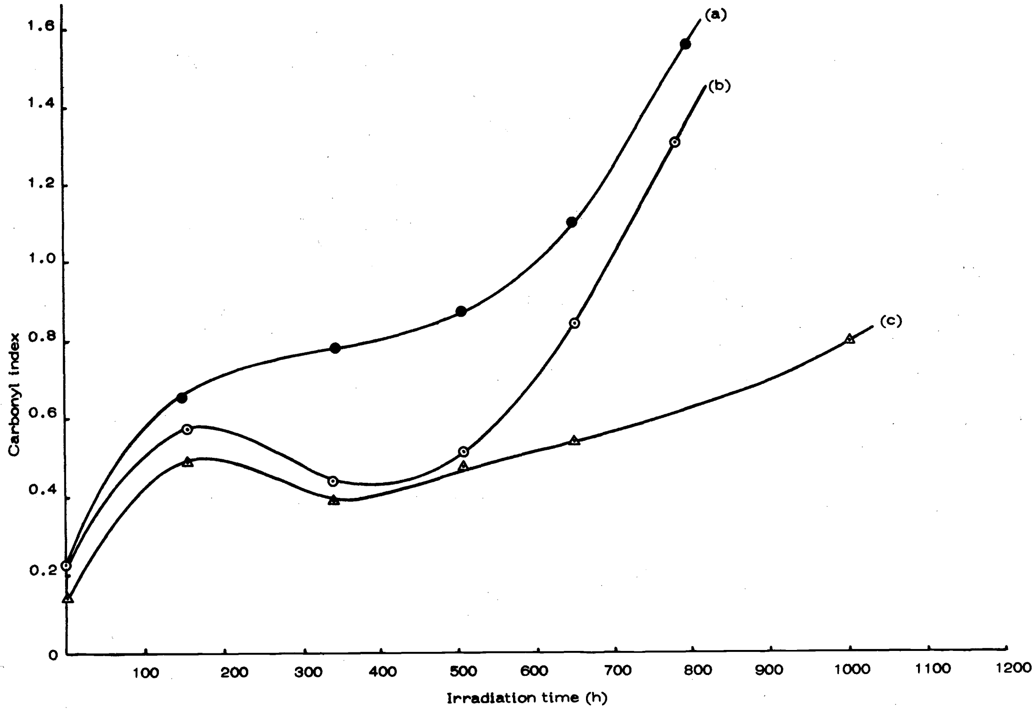
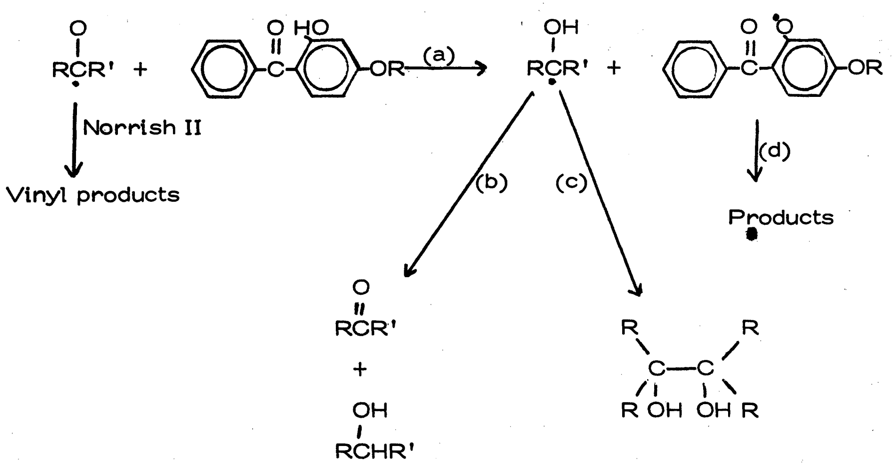


Fig 9. Comparison of the uv stabilising effectiveness of HOBP as a screen and as an additive in HDPE. (a) Control (no additive); (b) as a screen in a separate superimposed film (0.2 g/100 g); (c) as an additive (0.2 g/100 g). Reproduced from Ranaweera and Scott, Europ Polym J, 12, 591 (1976) with permission from Pergamon Press Ltd.

from which hydroperoxide was removed by thermolysis in an inert atmosphere, it was shown (51) that the 2-hydroxybenzophenone appears to play two distinct roles (see Fig 10). The first is physical screening of uv light, which is a relatively minor effect. The second is a sacrificial interaction with the excited carbonyl chromophore. Retardation of the Norrish II formation of vinyl (see Fig 11) suggests that physical quenching of carbonyl might be occurring but this is not yet proven since a redirection of the chemical reactions to other products (including regeneration of carbonyl [13b]) is an equally likely alternative on the basis of the evidence (51).



[13]

Hydroperoxides also lead to the rapid destruction of HOBP under conditions of uv irradiation (see Fig 12) and although there is little evidence at present to suggest that this process plays a significant role in polymer stabilisation, it is clearly relevant to the role of the processing operation on the subsequent effectiveness of the uv stabiliser during

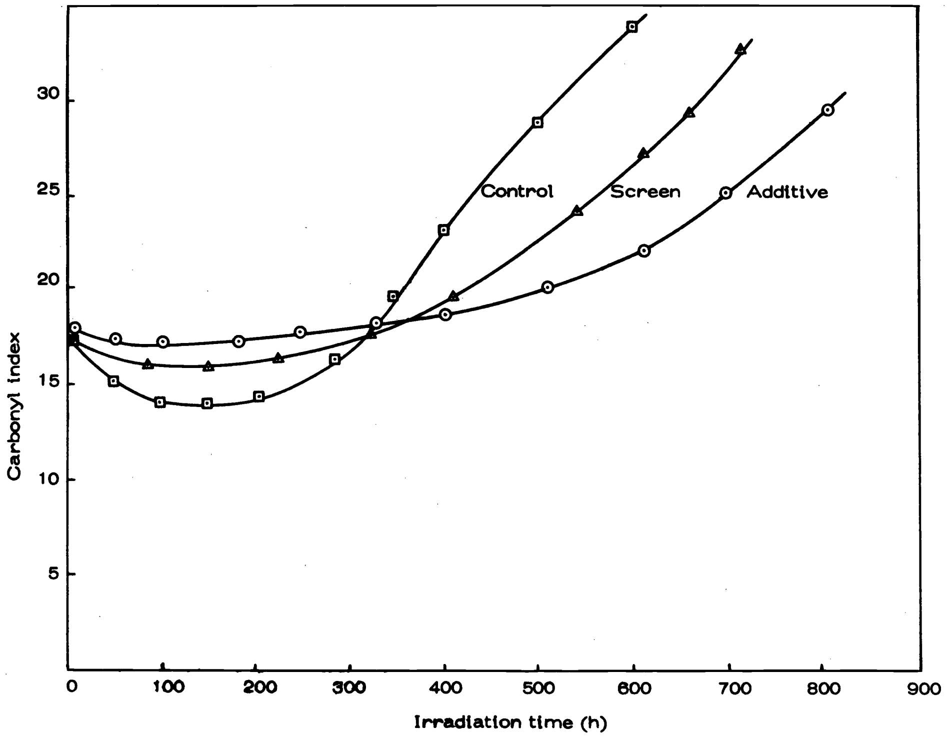


Fig 10. Effect of HOBP on the photolysis of thermally produced carbonyl compounds in LDPE (concentration of HOBP, 3 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Europ Polym J, 15, 35 (1979) with permission from Pergamon Press Ltd.

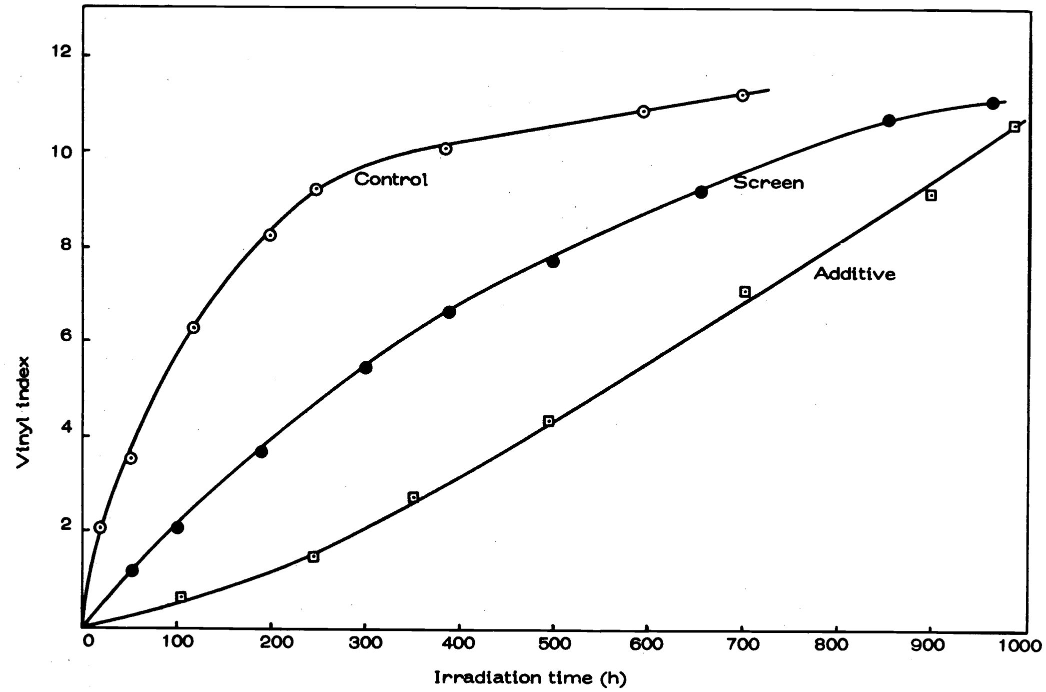


Fig 11. Effect of HOBP on the formation of vinyl in thermally oxidised LDPE during photo-oxidation (concentration of HOBP, 3 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Europ Polym J, 15, 35 (1979) with permission from Pergamon Press Ltd

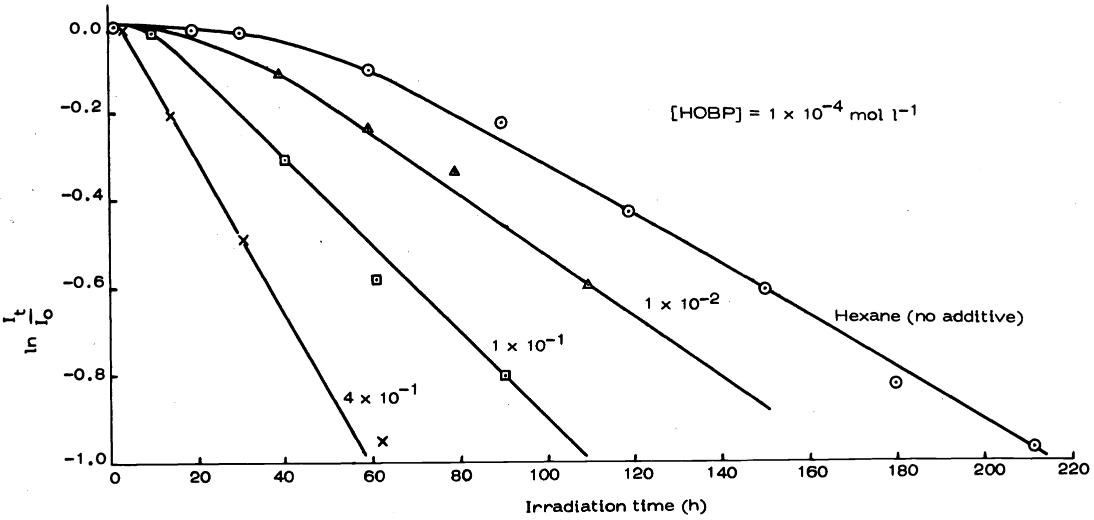


Fig 12. Effect of *tert*-butyl hydroperoxide in the photostability of HOBP in hexane (numbers on curves are TBH concentrations (M)). Reproduced from Chakraborty and Scott, Europ Polym J, **15**, 35 (1979) with permission from Pergamon Press Ltd.

service. It has been shown (27,32) that HOBP is particularly sensitive to the severity of the processing operation (see Table 3).

TABLE 3. Effect of processing time on the uv lifetime of LDPE films containing (3 x 10^{-4} mol/100 g) of antioxidants (27)

Antioxidant	Time to embrittlement (h)	
	10 min processed	30 min processed
None	1200	900
ZnDEC [IIa]	1400	1400
NiDBC [IIb]	1800	1800
HOBP [III]	2200	1600
1076 [I]	1800	1750
770 [IV]	2250	2400

It is clear that the processing operation has no effect on the stabilising effect of the peroxide decomposers, only a minor effect on the chain-breaking antioxidants but a very unfavourable effect on the uv absorber. It can be seen from Fig 3 that HOBP, unlike the thermal antioxidants, does not prevent the formation of hydroperoxides during processing, thus giving rise to its rapid destruction during photo-oxidation (9,10,27,51).

COMBINATION EFFECTS OF ANTIOXIDANTS IN THE UV STABILISATION OF HYDROCARBON POLYMERS

Few if any CB-D antioxidants give adequate protection against thermal or photo-oxidation when used alone. The use of synergistic mixtures of CB-D and PD-C antioxidants in hydrocarbon polymers has been well documented (1,53,54) but antioxidant interaction effects in photo-oxidation have been less systematically studied. In view of the complementary function of the CB-D, PD-C and CB-A antioxidants with the uv absorbers, there clearly seems to be the basis for synergistic effects which should lead to the development of much more cost effective uv stabiliser systems.

Synergism between uv absorbers and CB and PD antioxidants

It was noted earlier that the 2-hydroxybenzophenone class of uv stabiliser is highly susceptible to destruction under photo-oxidative conditions by hydroperoxides formed during processing. HOBP and its analogues should therefore synergise effectively with both CB and PD antioxidants. Fig 13 (10) shows that this is so in polypropylene and similar results have been obtained in polyethylene (9). There appears to be two distinct and complementary aspects to this synergism. The first is the protection of the uv absorber against destruction by thermally formed hydroperoxides during uv exposure. It has been shown that the concentration of hydroperoxides in PP containing the dithiocarbamates is so low as to be undetectable even after a severe processing operation (see Fig 3). The second synergistic interaction is the protection of the metal complex, PD-C antioxidants, from photolysis during uv exposure. Fig 14 shows that the decay of the characteristic uv absorbance of NiDEC at 330 nm is effectively reduced by the presence of HOBP at equimolar concentration. The disappearance of the NiDEC from the system corresponds to the end of the induction period to carbonyl formation in both cases. However, the post induction period rate is very much lower when HOBP is present than in its absence. Fig 15 shows that there is an additional interactive effect between the secondary products formed from the dithiocarbamate and HOBP which lead to a lower rate of destruction of the latter. It is instructive to note that this phenomenon also occurs with the zinc dithiocarbamate (ZnDEC). This PD-C antioxidant is much less effective as a uv stabiliser alone but gives a higher synergistic effect in combination with HOBP. This is illustrated in Table 4 for polypropylene (10).

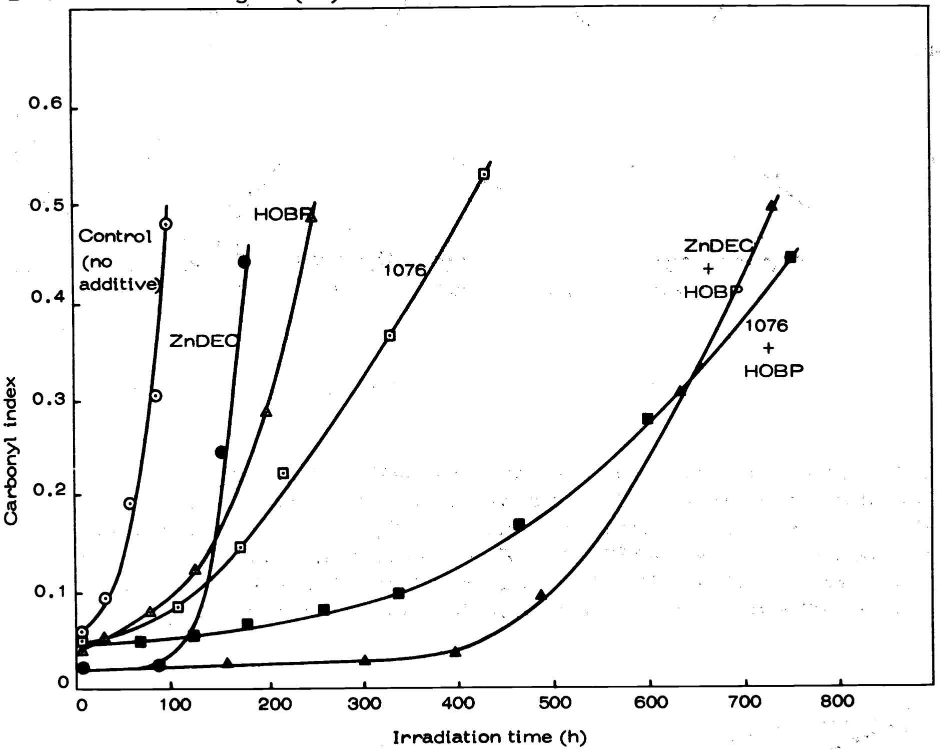


Fig 13. Effects of ZnDEC and 1076 alone and in combination with HOBP on the photo-oxidation of PP (concentrations of all additives, 3 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Polym Degrad and Stab, 1, 37 (1979) with permission from Applied Science Publishers Ltd.

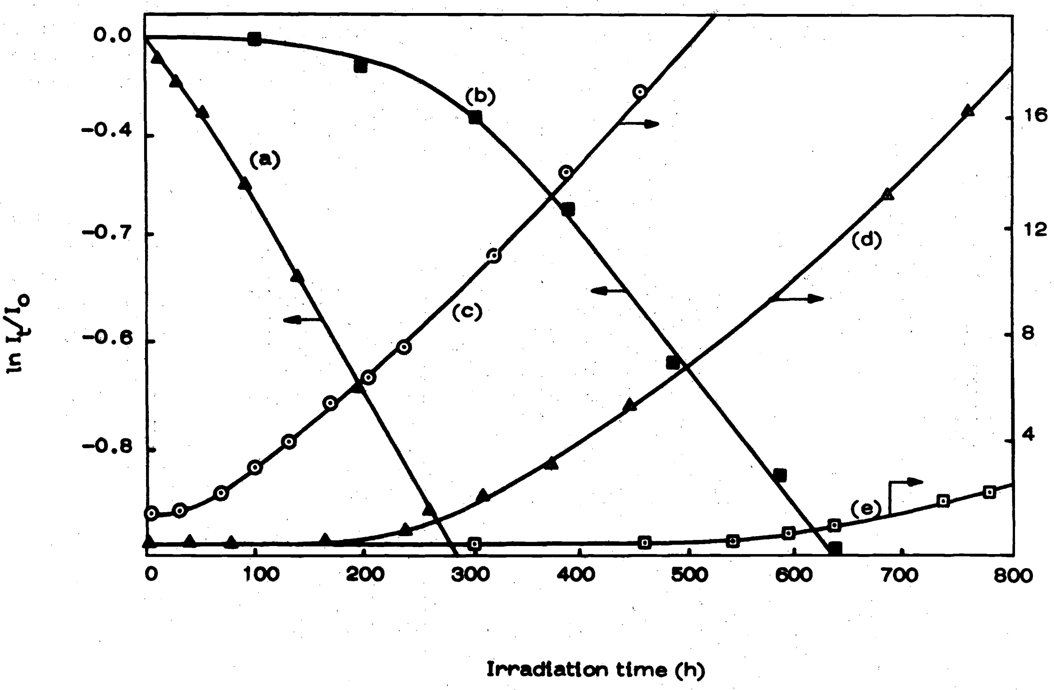


Fig 14. Effect of HOBP on the decay of the NiDEC absorbance at 330 nm and the associated induction period to photo-oxidation. (a) Decay of NiDEC; (b) decay of NiDEC + HOBP; (c) carbonyl formation control; (d) carbonyl formation NiDEC; (e) carbonyl formation NiDEC + HOBP (all concentrations at 3 x 10^{-4} mol/100 g). Reproduced from Scott, Developments in Polymer Degradation -1, (ed N Grassie) (1978), p 205 with permission from Applied Science Publishers Ltd.

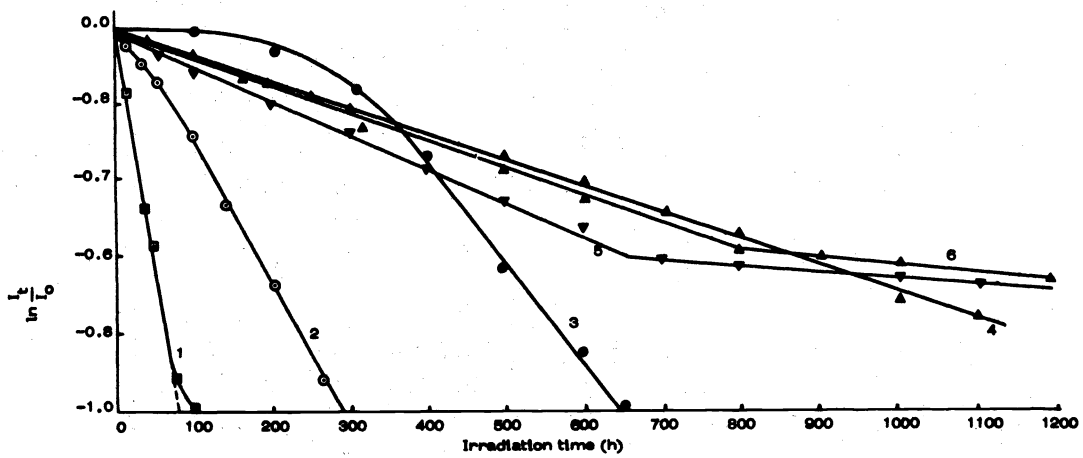


Fig 15. Change in uv absorbance of uv stabilisers during photo-oxidation of LDPE. 1, ZnDEC (330 nm); 2, NiDEC (330 nm); 3, NiDEC + HOBP (390-395 nm); 4, HOBP (330 nm); 5, ZnDEC + HOBP (330 nm); 6, NiDEC + HOBP (330 nm) (all concentrations at 3 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Europ Polym J, 13, 1007 (1977) with permission from Pergamon Press Ltd.

TABLE 4. Comparison of uv stabilisers in polypropylene (concentration of all additives 3 x 10^{-4} mol/100 g) (10)

Antioxidant	Time to embrittlement E (h)	Calculated effect of synergist (h)	Synergism* (%)
Control (no additive)	90	-	-
ZnDEC [IIa]	175	-	-
NiDEC [IIb]	500	-	-
1076 [I]	325	-	-
HOBP [III]	245	-	-
ZnDEC + HOBP	700	240	154
NiDEC + HOBP	850	565	35
1076 + HOBP	650	390	44

$$^{*}\text{Synergism (\%)} = \frac{(E_s-E_c)-[(E_1-E_c)+(E_2-E_c)]}{E_1-E_c+E_2-E_c} \times 100$$

where: E_s = embrittlement time of synergist
E_c = embrittlement time of control
E_1 = embrittlement time of antioxidant 1
E_2 = embrittlement time of antioxidant 2

Table 4 and Fig 13 also illustrate the synergistic activity of the CB-D antioxidant 1076 with the uv absorber. The extent of the synergism is not as high as with ZnDEC but is nevertheless significant. It seems possible that the effective stabilisation of the zinc dithiocarbamate by HOBP is due to a physical quenching process. This possibility has been investigated further by using a typical amine quenching agent, 1,4-diazabicyclo[2,2,2]-octane [DABCO, XV]. This compound was synergistic with ZnDEC (see Fig 16 and Table 5).

[XV, DABCO]

TABLE 5. Synergism of ZnDEC with DABCO

Antioxidant	Concentration (mol/100 g x 10^4)	Embrittlement time (h)	Synergism (%)
None	-	75	-
ZnDEC [IIa]	5	180	-
DABCO [XV]	5	140	-
ZnDEC + DABCO	5 + 2.5	328	-
ZnDEC + DABCO	5 + 5	318	37
ZnDEC + DABCO	5 + 10	336	-

Synergistic optima

The effect of varying the molar ratio of the two components in the HOBP/ZnDEC system is shown in Fig 17. The optimum activity lies at about 2:1, suggesting that the uv absorber is playing a major role. In the case of the phenolic antioxidants 1076 [I] and TBC [XVI], the synergistic optimum lies even further on the side of the uv stabiliser (55) (see Fig 18). The autosynergistic sulphur-containing antioxidants [XVII and XVIII] ($R=C_{12}H_{25}$) although only marginally more effective than the simple hindered phenols when used alone, show much more pronounced synergism with HOBP than do the simple phenols. It has previously been shown (25) that these compounds are effective PD-C antioxidants in addition to being effective chain-breaking antioxidants. It follows from this that the effect of these autosynergists is primarily to protect HOBP against the effects of

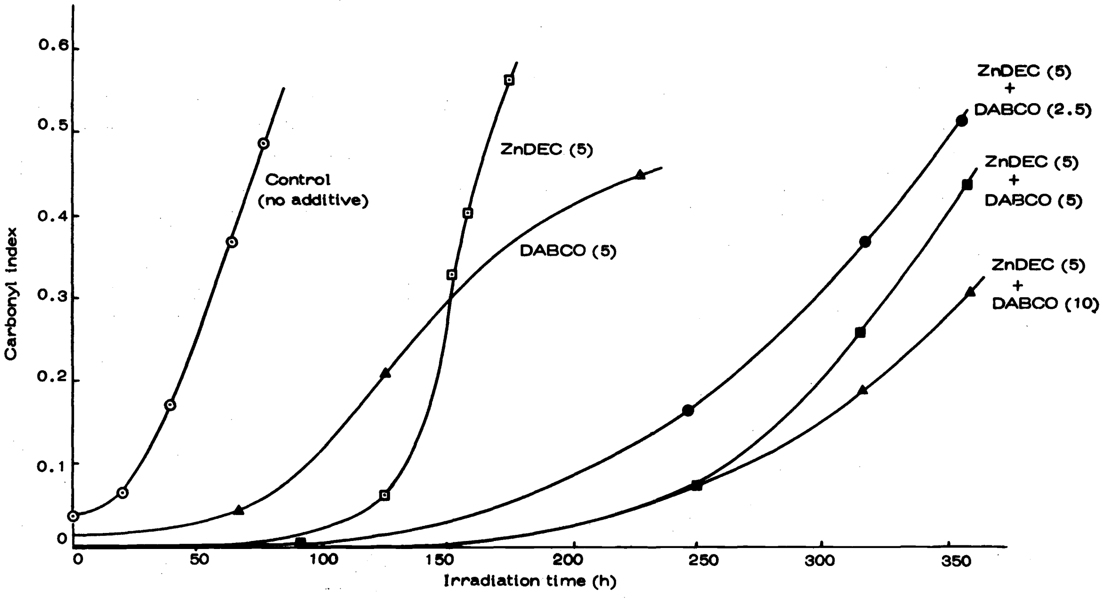


Fig 16. The effect of an amine quenching agent (DABCO) on the photostabilising effect of ZnDEC (numbers in parenthesis are concentrations in mol/100 g x 10^4).

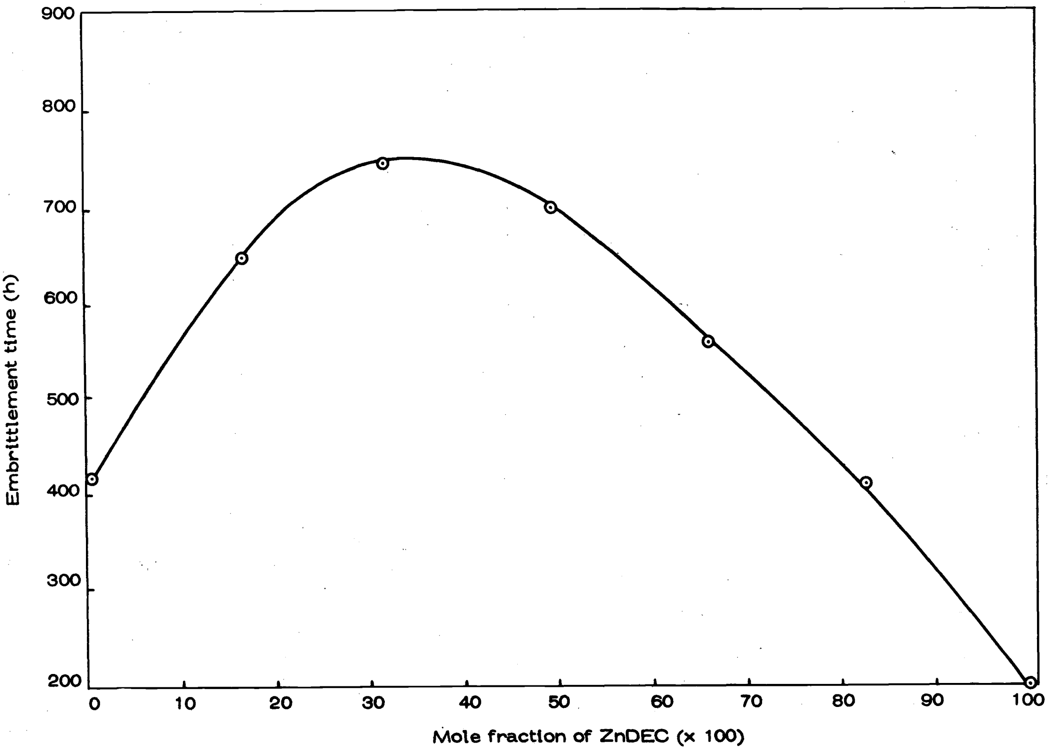


Fig 17. Synergism between ZnDEC and HOBP on the photostabilisation of PP (total concentration, 6 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Polym Degrad and Stab, 1, 37 (1979) with permission from Applied Science Publishers Ltd.

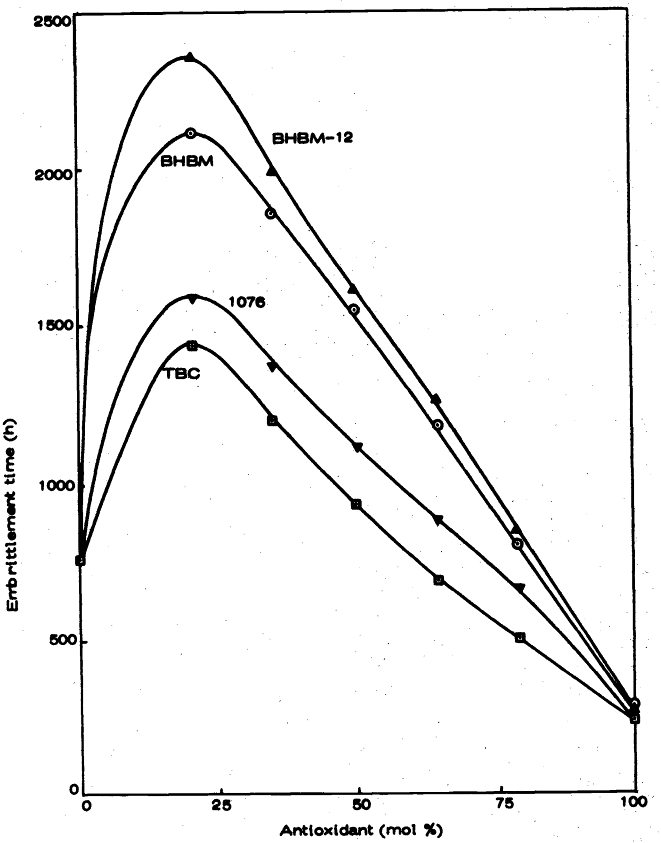


Fig 18. Synergism between phenolic antioxidants and HOBP (total concentration, 10^{-3} mol/100 g).

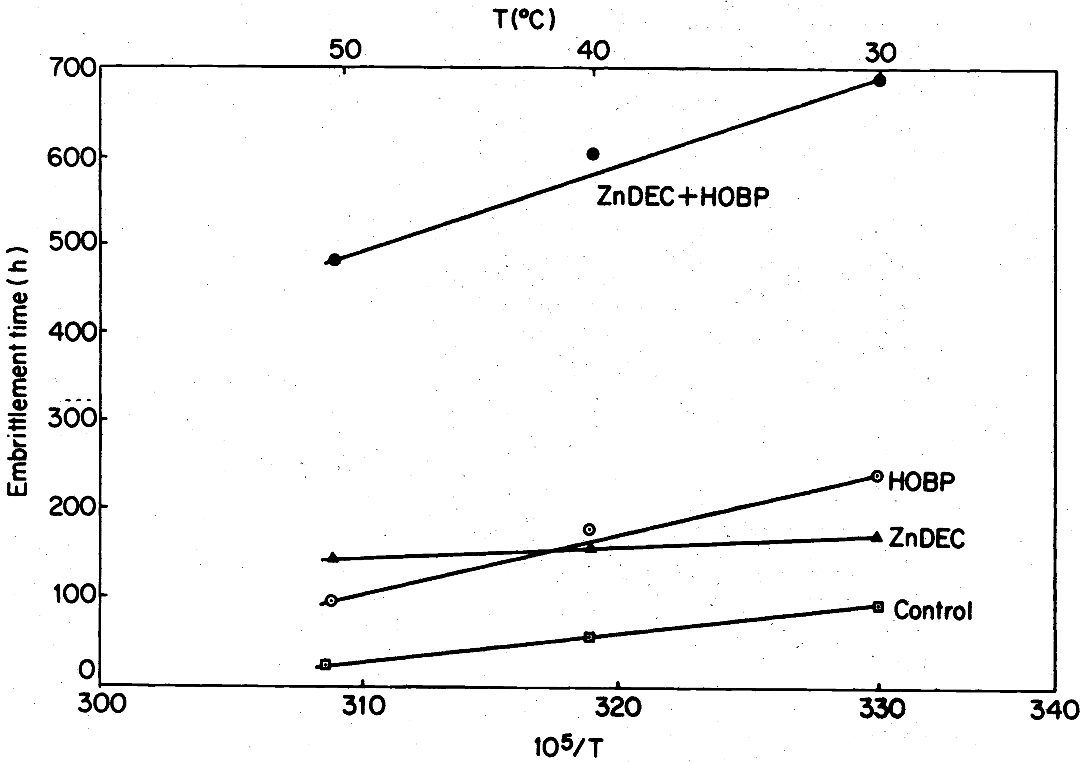
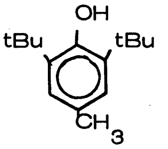
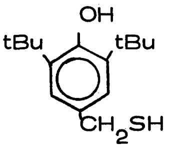


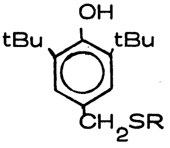
Fig 19. Effect of temperature on the uv embrittlement times of uv stabilisers in polypropylene (concentrations of all additives, 3 x 10^{-4} mol/100 g). Reproduced from Chakraborty and Scott, Polym Degrad and Stab, 1, 37 (1979) with permission from Applied Science Publishers Ltd.



[XVI, TBC]



[XVII, BHBM]



[XVIII, DBHBM, R = $C_{12}H_{25}$]

hydroperoxides during processing and subsequent photo-oxidation (55). In this respect, the autosynergists are much more effective than the single function CB-D antioxidants, as can be seen from Table 6 which lists the first order rate constants for the destruction of HOBP during the photo-oxidation of PP (55). A surprising feature of these results is just how small a proportion of a highly effective autosynergistic antioxidant is required to disproportionately increase the activity of a uv absorber.

TABLE 6. Comparison of the first order rate constants for the decay of HOBP and synergised by antioxidants during the uv irradiation of PP (total synergistic stabiliser concentration, 10^{-3} mol/100 g)

Antioxidant (mol %)	Rate constant (10^4 h^{-1})			
	TBC [XVI]	1076 [I]	BHBM [XVII]	DBHBM[XVIII]
0	3.8	3.8	3.8	3.8
20	1.3	1.1	0.8	0.8
35	1.7	1.4	1.1	1.1
50	2.3	1.8	1.6	1.5
65	7.1	4.1	2.9	2.8
80	8.3	6.0	3.7	3.5

Combined effects of heat and light

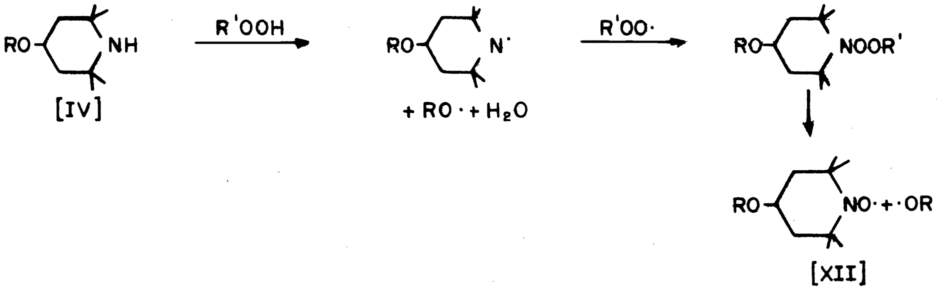
For many purposes, polyolefins have to withstand the effects of light at elevated temperatures. It is clear from what has been said earlier that most recognised uv stabilisers are not very effective under these conditions. This is illustrated in Fig 19 (10) which shows the effect of light on polypropylene at temperatures between 30 and 50°C. It is clear that in keeping with its behaviour during processing (see Table 3), ZnDEC is much less sensitive to temperature during uv irradiation than is HOBP and at 50°C it is superior to it on a molar basis. As might be expected, the synergistic combination is superior at all temperatures to either component alone.

Antagonistic effects

It has been reported that both the PD-C antioxidants (27) and the CB-D antioxidants (56) are antagonistic towards the hindered piperidine uv stabiliser, Tinuvin 770 [IV]. This is illustrated for NiDEC and 770 in Table 7 and Table 3 also shows that the more severe the processing conditions, the more effective is the hindered piperidine as a uv stabiliser. As indicated earlier, the hindered amine [IV] is not itself the effective uv stabiliser, but it has to be first oxidised to the nitroxyl radical [XII]. Unlike the analogous diarylamine [IX], [IV] is not an effective CB-D antioxidant, but like the former it must be converted to [XII] via radical intermediates. The fact that PD-C antioxidants reduce the effectiveness of the nitroxyl precursor coupled with the fact that the hindered amine is a pro-oxidant suggests that the sequence of reaction involved is as shown in [14] (27). An effective CB-D antioxidant would have a similar effect to the peroxide decomposers but at higher concentrations severe processing should have the reverse effect (27).

TABLE 7. Combination effects of stabilisers in LDPE (all concentrations 3×10^{-4} mol/100 g) (9,27)

Stabiliser	Induction period (110°C,h)	Uv embrittlement time (h)
None	10	1200
HOBP [III]	10	2200
1076 [I]	110	1800
ZnDEC [IIa]	110	1400
NiDEC [IIb]	105	1800
770 [IV]	no induction period	2250
1076 + ZnDEC	330	1250
HOBP + ZnDEC	130	4000
770 + NiDEC	110	1850



[14]

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