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Antioxidant interaction between organic phosphites and hindered amine light stabilisers during processing and thermoxidation of polypropylene

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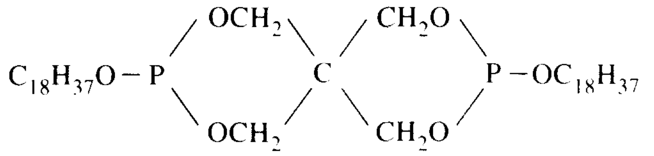
Mixtures of hindered amine light stabilisers (HALS) and their radical analogues, with aromatic and aliphatic phosphites have been examined for their effectiveness as melt and thermal antioxidants in polypropylene (PP). Stabilisers containing two different antioxidant functions in the same molecule (aromatic phosphite and either of the above HALS or related functions), referred to as 'HALS-phosphites', were also examined and their antioxidant effectiveness compared with the optimum performance of the corresponding combination of mixtures of the individual antioxidants. Binary combinations of the phosphites Irgafos 168 (aromatic) and TLP (aliphatic) with Tinuvin 770, its bis-nitroxyl analogue, or with Tinuvin 292 (tertiary amine) exhibited synergistic effects at different molar ratios; the level of synergism was generally higher during thermal ageing than during melt processing. The optimum combination, leading to the most effective synergism, varied with the chemical nature of the phosphite: under thermoxidative conditions, molar excess of the Irgafos 168 is required whereas molar excess of the HALS is needed for optimum of TLP. HALS-phosphites act autosynergistically and show, in most cases, higher efficiency than their corresponding additive mixtures of stabilisers.

1 INTRODUCTION

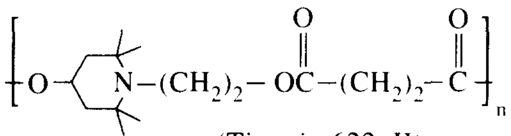
Many commercial antioxidant packages are based on combinations of two or more antioxidants which often function by complementary antioxidant mechanisms. Alkyl and aryl phosphites are normally considered as weak antioxidants and are used in combination with hindered phenols for melt stabilisation and for minimising colour development during processing of polyolefins.[1] The mechanism of antioxidant action of organophosphorous stabilisers has been investigated extensively,[2–6] the exact nature of their action was found to depend on their chemical structure, the nature of the oxidising substrate and the conditions of oxidation. Generally, phosphites and phosphonites act by a preventive mechanism; simple alkyl and aryl phosphites act by a stoichiometric peroxide decomposition process, PD-S. However, sterically hindered aryl phosphite stabilisers have been shown to act also as chain breaking (CB) antioxidants.[2–4,7]

The synergistic action of mixtures of various phosphorous antioxidants and hindered phenols has been well documented.[2,8] Much less is known, however, about the antioxidant interactions in combinations of phosphorous antioxidants with HALS-based stabilisers under processing and thermoxidative conditions. Even less work has been carried out for systems in which two antioxidant functions (such as phosphite and HALS) are present in the same molecule. It was shown[9,10] that combinations of the phosphite, Weston 618, **I**, with either Tinuvin 770 or Tinuvin 622, **II**, lead to synergism, whereas combinations of the former with Chimassorb 944 and Cyasorb UV 3346, **III**, give rise to antagonism when used as thermal antioxidants in PP. (The structures of the other antioxidants are shown below.) It was also shown, however, that in HDPE, Weston 618 synergises with the high molecular weight HALS compounds, Tinuvin 622 and Chimassorb 994, but antagonises with Tinuvin 770. In the case of phosphonites, combinations of Tinuvin 770 and Irgafos P-EPQ, **IV**, as well as, Spinuvex A36, **V**, and Irgafos P-EPQ, gave synergism, whereas Tinuvin 622/Irgafos P-EPQ system led to antagonism during their action as thermal antioxidants (at 170°C) in LDPE.[11] The action of various combinations of HALS/phosphite antioxidants were investigated[12] as light and heat stabilising systems for polypropylene. Synergistic effects were only observed in the case of multifunctional HALS-phosphite antioxidants.[12]

The present work investigates the antioxidant interactions and co-operative effects of combinations of the aliphatic phosphite, TLP, and hindered aromatic phosphite, Irgafos 168, with different HALS and related compounds, as well as, the effects of multifunctional HALS-phosphites on the melt and thermoxidative stability of PP.



(Weston 618, I)



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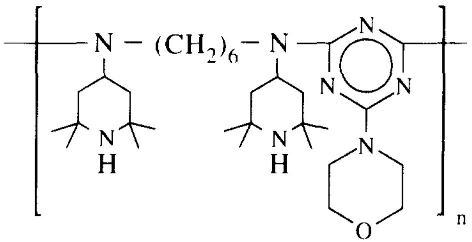

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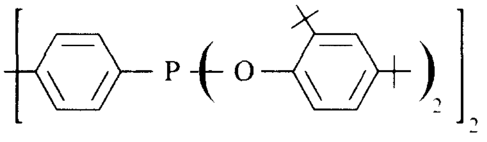

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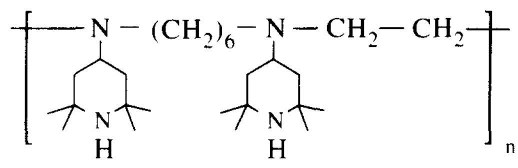


(Spinuvex A36, V)

2 EXPERIMENTAL

Unstabilised PP powder (ICI, Propathene HF 32) was used. The antioxidants Irganox 1010, Irganox 1076, Irgafos 168, Tinuvin 770, Tinuvin 292 and Chimassorb 994 (for structures, see Table 2) were used as received from Ciba Geigy, Basel. The HALS-phosphite and the HALS-phosphonite antioxidants (Pbd$_2$, Pbe$_2$, Pbf$_2$, Pad$_2$, Paf$_2$, P$_2$cd$_4$, P$_2$cf$_4$, Pd$_3$ and Pf$_3$) were synthesised according to literature methods (for structures see Table 2).[13,14]

The antioxidants were mixed with PP in small amount of dichloromethane. The polymer–antioxidant mixture was then processed in a closed chamber of an internal mixer (a RAPRA-Hampden torque rheometer) for 10 min at 190°C and rotor speed of 40 r.p.m. Polymer films (0.15 mm thick) were prepared by compression moulding in a Daniel press (190°C, pressure of 85 kg/cm^2).

Melt flow index (MFI) was measured on a Davenport melt flow indexer (230°C, 2.16 kg, die diameter = 1 mm; five measurements were taken for each MFI value recorded). Polymer films were aged in single cell Wallace ovens at 140°C and under continuous air flow of 85 l/h. Embrittlement time and induction period to carbonyl formation were used to compare the stability of different polymer samples. Some of the HALS-containing films were subjected to a prior photoxidation before studying their thermoxidative stability. Exposure to uv light was carried out in Sunlamp-Blacklamp accelerated UV ageing cabinet (light intensity = 4.4 W h m^{-2}).

Table 1. Effect of HALS-phosphites and some commercial antioxidants on the melt flow index (MFI) of PP[a]

Sample	Concentration (10^{-3} mol/kg)	MFI (g/10 min)
Polypropylene	Unstabilised	0.74
Tinuvin 770	7	0.50
Irganox 1010	7	0.32
Irgafos 168	7	0.35
Pbd2	3.5	0.35 (0.44; Irgafos 168 + Tinuvin 770)
Pbd2	7	0.30 (0.39; Irgafos 168 + Tinuvin 770)
Pbe2	3.5	0.33 (0.32; Irgafos 168 + 770-NO ·)
Pbe2	7	0.31 (0.36; Irgafos 168 + 770-NO ·)
Pbf2	3.5	0.35 (0.43; Irgafos 168 + Tinuvin 292)
Pbf2	7	0.30 (0.36; Irgafos 168 + Tinuvin 292)
Pad2	7	0.34
Paf2	7	0.33
P2cd4	3.5	0.30
P2cf4	3.5	0.29
Pd3	8.4	0.63
Pf3	2.6	0.35

[a] Numbers in parentheses are MFI values for combinations of Irgafos 168 with HALS or related compounds at a molar ratio of 1:1 and the same total concentration as the HALS-phosphites.

3 RESULTS AND DISCUSSION

3.1 Effect of antioxidant mixtures (containing phosphites and hindered amines or related antioxidant functions) and multifunctional antioxidants (HALS-phosphites) on the melt stability of PP

The melt stability of PP in the presence of various antioxidants, used individually and in combination, was determined by measuring the melt flow index (MFI). In order to assess the effect, and optimise the performance of combinations of antioxidants, different molar ratios of any two antioxidant combinations were examined at a given constant total concentration.

Figure 1 shows the MFI values for PP processed in the presence of different antioxidants. Compared to the hindered amines

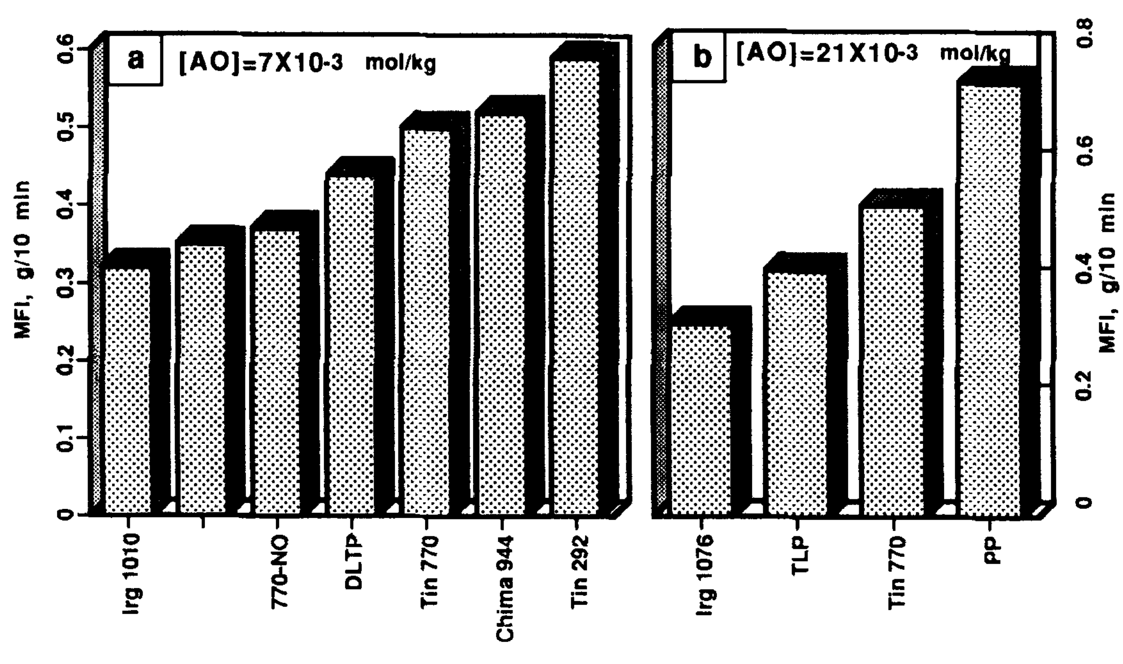
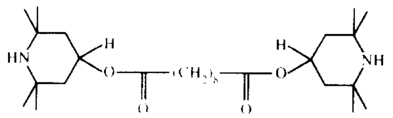
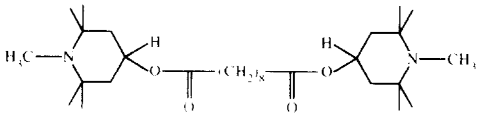
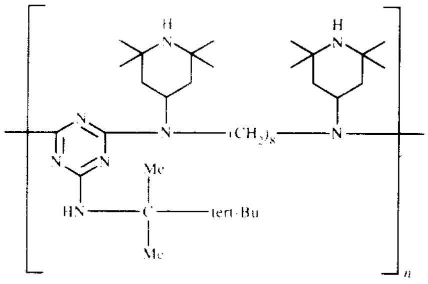
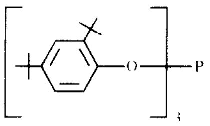
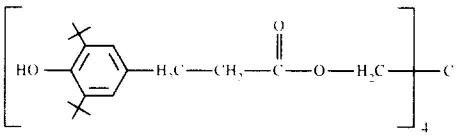
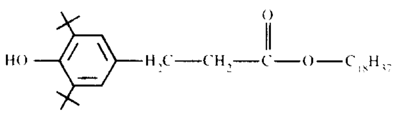
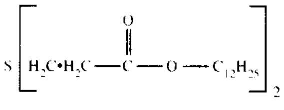
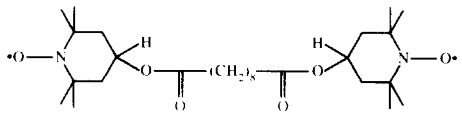


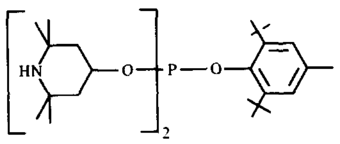
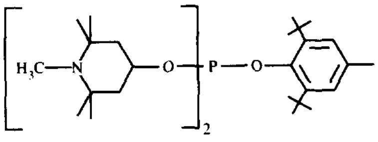
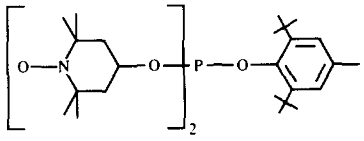
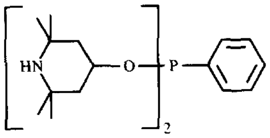
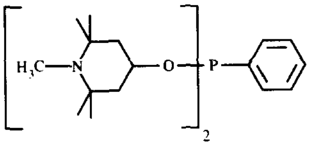
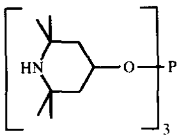
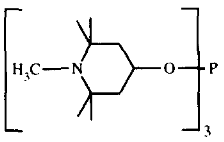
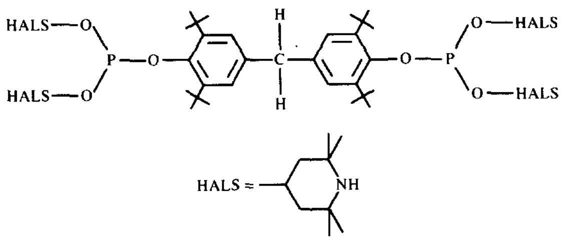
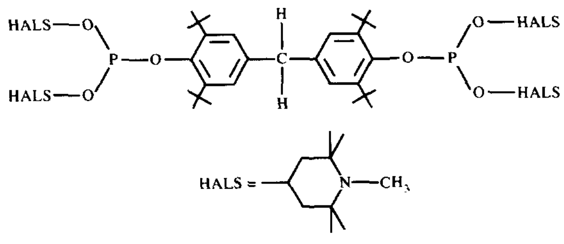
Fig. 1. Melt flow index (MFI) of PP stabilised with commercial antioxidants.

Table 2. Structures of antioxidants

Antioxidant code	Structure
Tinuvin 770	
Tinuvin 292	
Chimassorb 944	
Irgafos 168	
Irganox 1010	
Irganox 1076	
DLTP	 $S\left[H_2C{\cdot}H_2C-\overset{O}{\overset{\|}{C}}-O-C_{12}H_{25}\right]_2$
TLP	$(C_{12}H_{25}O\!-\!)_3\,P$
770-NO (synthesised)	

(*Cont.*)

Table 2. (*continued*)

Antioxidant code	Structure
Pbd_2	
Pbf_2	
Pbe_2	
Pad_2	
Paf_2	
Pd_3	
Pf_3	
P_2cd_4	
P_2cf_4	

(HALS) and phosphite, the hindered phenols (Irganox 1010 and 1076) showed the highest stabilising effect. Phosphites are known to be generally weaker antioxidants than hindered phenols[2] and are normally used in synergistic combinations with the latter for melt stabilisation of polyolefins. Simple alkyl and aryl phosphites decompose hydroperoxides by a stoichiometric ionic (non-radical) mechanism to form an alcohol and a phosphate (phosphonites act by a similar mechanism), see reaction 1. The lower efficiency of the aliphatic phosphite, TLP, as a melt stabiliser for PP, compared to the sterically hindered aromatic phosphite, Irgafos 168 (see Fig. 1) is attributed to the fact that the former acts by a PD-S mechanism only, whereas the latter acts primarily by a CB mechanism in addition to its peroxidolytic activity. Thus reaction of Irgafos 168 with the propagating radicals, alkylperoxyl (ROO $\cdot$) and alkoxyl (RO $\cdot$), gives a hindered phenoxyl radical, reactions 2 and 3 (see also Scheme 1, rn b and c) which can terminate the autoxidation chain process, reaction 4,[3,4] whereas similar reactions of the aliphatic phosphite, TLP, lead to the formation of alkyl radicals which can propagate further the polymer chain oxidation, reactions 5 and 6. Figure 1 also shows that the melt stabilising effect of the hindered amine light stabilisers (Tinuvin 770, Chimassorb 994 and Tinuvin 292) is much lower than that of the phosphite, Irgafos 168. The ineffectiveness of HALS as melt stabilisers for polyolefins has been attributed[15,16] to the fact that secondary amines are not effective CB-D antioxidants; oxidation of the NH to the corresponding NO $\cdot$ by hydroperoxides formed during processing occurs through the intermediacy of aminyl radicals and formation of further radicals, e.g. RO $\cdot$, which propagate the oxidative chain, see Scheme 1, rn d.

$$(OR)_3P + ROOH \xrightarrow{\text{PD-s}} (OR)_3P = O + ROH \qquad (1)$$

For sterically hindered aryl phosphites

$$(OPh)_3P + ROO^{\cdot} \xrightarrow{\text{CB}} \left[ROO\dot{P}(OPh)_3\right] \longrightarrow (OPh)_3P = O + RO^{\cdot} \qquad (2)$$

$$(OPh)_3P + RO^{\cdot} \xrightarrow{\text{CB}} \left[RO\dot{P}(OPh)_3\right] \longrightarrow (RO)(OPh)_2P + PhO^{\cdot} \qquad (3)$$

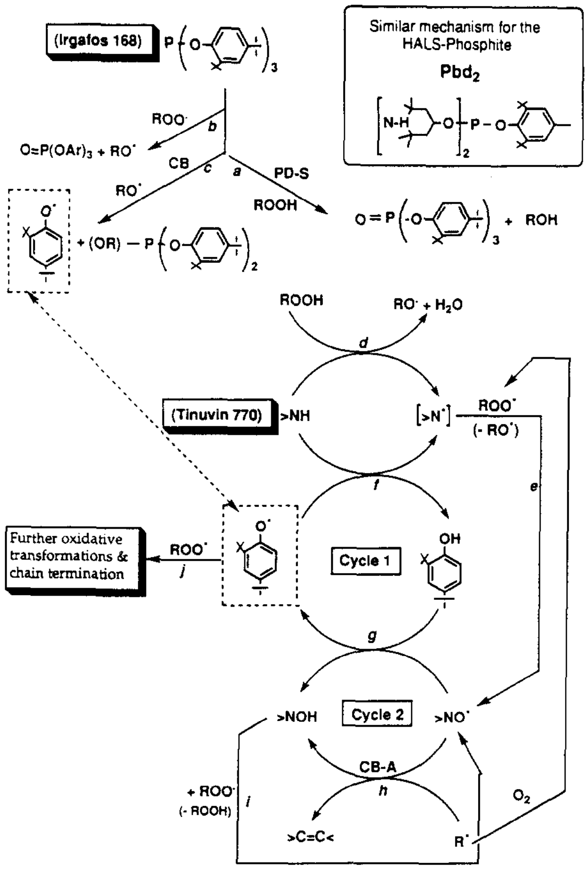
$$PhO^{\cdot} + ROO^{\cdot} \longrightarrow \text{Inactive products (chain termination)} \qquad (4)$$

For simple alkyl phosphites

$$(OR)_3P + RO^{\cdot} \longrightarrow \left[RO\dot{P}(OR)_3\right] \longrightarrow O = P(OR)_3 + R^{\cdot} \qquad (5)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \quad \text{(chain propagation)} \qquad (6)$$

The effect of varying the molar ratios (at a constant total molar concentration of 7×10^{-3} mol/kg) of antioxidant combinations, based on sterically hindered aryl phosphite and HALS or related functions and the effect of the multifunctional HALS-phosphite on changes in MFI of PP is shown in Fig. 2 (see also Table 1) and although hindered amines are themselves not useful as processing antioxidant for polyolefins, it is clear that their combinations with an aliphatic or an aromatic phosphite, at all molar ratios, lead to effective synergism for the stabilisation of PP melt (see Table 3 and Figs 3 and 4); the optimum combination varies with the nature of the phosphite used. It is interesting to note also, that all the HALS-phosphites and HALS-phosph(on)ites examined, except Pd3, showed high melt stabilising effect (Table 1). Synergistic effect of the HALS-phosphites, Pbd$_2$, Pbe$_2$ and Pbf$_2$, was either similar or slightly better than



Scheme 1

those of the corresponding additive mixtures of HALS and phosphites at the same molar ratio (1:1) of the antioxidant functions, see Table 3 and Fig. 2.

The efficiency of additive combinations of Irgafos 168 with HALS was found to be highest with the bis-nitroxyl compound (Irgafos 168/770-NO); these were the only combinations which gave better overall melt stability than the phosphite alone, see Fig. 3. Although slightly less effective than the aromatic phosphite, the bis-nitroxyl radical of Tinuvin 770 (770-NO) is a better melt stabiliser than Tinuvin 770, see Fig. 1. Under processing conditions, the relatively high [R ·]/[ROO ·] ratio allows the NO to compete (as a CB-A antioxidant[17,18]) with oxygen for the polymer radical (R ·) forming a hydroxylamine, NOH, see Scheme 2, rn a versus b. The synergism observed for Irgafos 168/770-NO combinations is most likely due to the ability of the NOH formed to reduce the phenoxyl radical (formed from the phosphite in a CB process, via reactions 2 and 3 and Scheme 2 rn g) to the hindered phenol in a process which also regenerates the NO · , Scheme 2, rn c. The phenol/phenoxyl-radical redox couple will continue to participate in regenerative antioxidant cycles involving the other redox couple, NO/NOH, until it is irreversibly destroyed. The overall co-operative effect leads to the efficient removal of both propagating radicals, the alkyl and alkylperoxyl radicals, from the system (e.g. Scheme 2 rns a and f), as well as the deactivation of the hydroperoxides formed during processing and as a consequence of the CB-D process of phenol, Scheme 2, rn d, by the PD-S action of the phosphite itself, see Scheme 2, rn h.

The synergism between Irgafos 168 and Tinuvin 770 (see Table 3) is thought to be due to the generation of the hindered phenol (see Scheme 1, rn f) which becomes involved in a similar complementary antioxidant regenerative mechanism leading to the removal of R · and ROO · (see Scheme 1, rns g to j). However, the first co-operative step which leads to the formation of this phenol also involves the formation of an iminyl radical (scheme 1, rn f) and more propagating radicals (scheme 1, rn e) resulting in a lowering of the overall efficiency of such antioxidant mixtures. The fact that the NO · is a better melt stabiliser than NH (see Fig. 1), and that the synergistic step involving the reaction of its reduced form, NOH, with the hindered phenoxyl radical, does not involve the formation of pro-oxidant species (see Scheme 2, rn c), would certainly account for the observation of better overall melt stability and higher extent of synergism for all combinations of bis nitroxyl (770-NO ·) with Irgafos 168 compared to the corresponding additive combinations of the individual, see Fig. 3.

Although TLP is much less effective (even at threefold excess) than Irgafos 168, as a melt stabiliser for PP, combinations of TLP with Tinuvin 770, especially at higher molar proportions of the latter, do show some synergistic activity, see Fig. 4 and Table 3. Both the CB-A/CB-D modes of action of the HALS products (NO · and NOH) and the peroxidolytic function of TLP must contribute to the observed synergism.

3.2 Effect of antioxidant mixtures containing phosphites and hindered amines or related antioxidant functions on the thermoxidative stability of PP

The thermoxidative stability of PP processed in the presence of different antioxidants is shown in

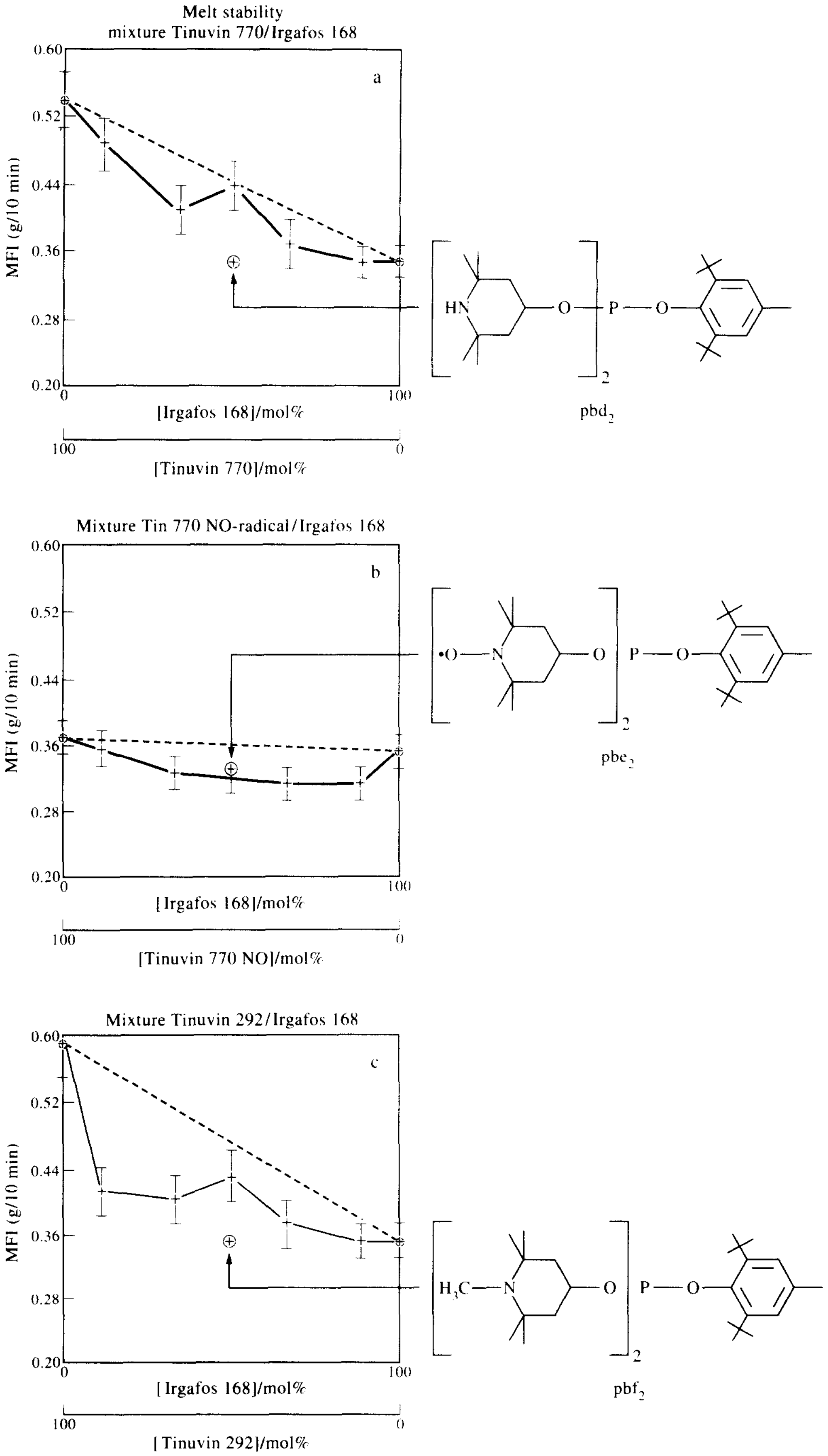


Fig. 2. Effect of molar composition of mixtures of HALS and Irgafos 168 (total [AO] = 7×10^{-3} mol/kg) on the melt flow index of PP. The melt flow indexes of the corresponding HALS-phosphites (Pbd$_2$, Pbe$_2$ and Pbf$_2$; concentration of 3.5×10^{-3} mol/kg) are also shown.

Table 3. Effect of molar ratios of combinations of phosphites and Tinuvins on extent of synergism during the melt processing (measured from MFI) of PP. Percentage synergism of the corresponding HALS-phosphites is also shown

Antioxidants	Concentration (10^{-3} mol/kg)	Synergism[a] (MFI) %
Irgafos 168 + Tinuvin 770	0.8 + 6.2	6
Irgafos 168 + Tinuvin 770	2.3 + 4.7	14
Irgafos 168 + Tinuvin 770	3.5 + 3.5	1
Irgafos 168 + Tinuvin 770	4.7 + 2.3	10
Irgafos 168 + Tinuvin 770	6.2 + 0.8	6
TLP + Tinuvin 770	14 + 7	19
TLP + Tinuvin 770	7 + 14	33
Pbd_2 (HALS-phosphite)	7	21
Irgafos 168 + Tinuvin 770-NO	0.8 + 6.2	21
Irgafos 168 + Tinuvin 770-NO	2.3 + 4.7	12
Irgafos 168 + Tinuvin 770-NO	3.5 + 3.5	11
Irgafos 168 + Tinuvin 770-NO	4.7 + 2.3	13
Irgafos 168 + Tinuvin 770-NO	6.2 + 0.8	12
Pbe_2 (HALS-phosphite)	7	8
Irgafos 168 + Tinuvin 292	0.8 + 6.2	27
Irgafos 168 + Tinuvin 292	2.3 + 4.7	22
Irgafos 168 + Tinuvin 292	3.5 + 3.5	9
Irgafos 168 + Tinuvin 292	4.7 + 2.3	14
Irgafos 168 + Tinuvin 292	6.2 + 0.8	7
Pbf_2 (HALS-phosphite)	7	25

[a] Percent synergism = $(Es/[X2(E2 - E1) + E1] - 1) \times 100$, where Es = MFI of antioxidant mixture or multifunctional antioxidant, $E1$ = MFI of antioxidant 1 (lower embrittlement time at 7×10^{-3} mol/kg), $E2$ = MFI of antioxidant 2 (higher embrittlement time at 7×10^{-3} mol/kg), $X2$ = molar fraction of antioxidant 2.

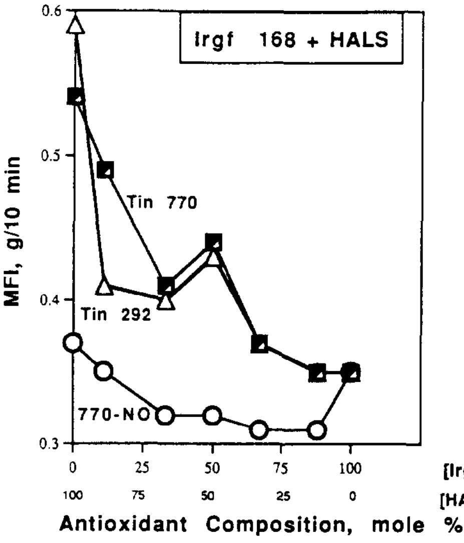


Fig. 3. Comparison of melt flow index of PP containing different molar compositions of mixtures of Irgafos 168 with various HALS compounds (Tin 770, Tin 292 and 770-NO) at total [AO] = 7×10^{-3} mol/kg.

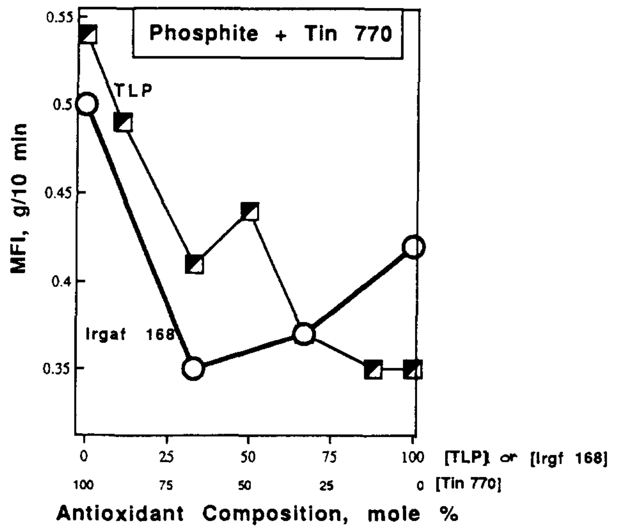
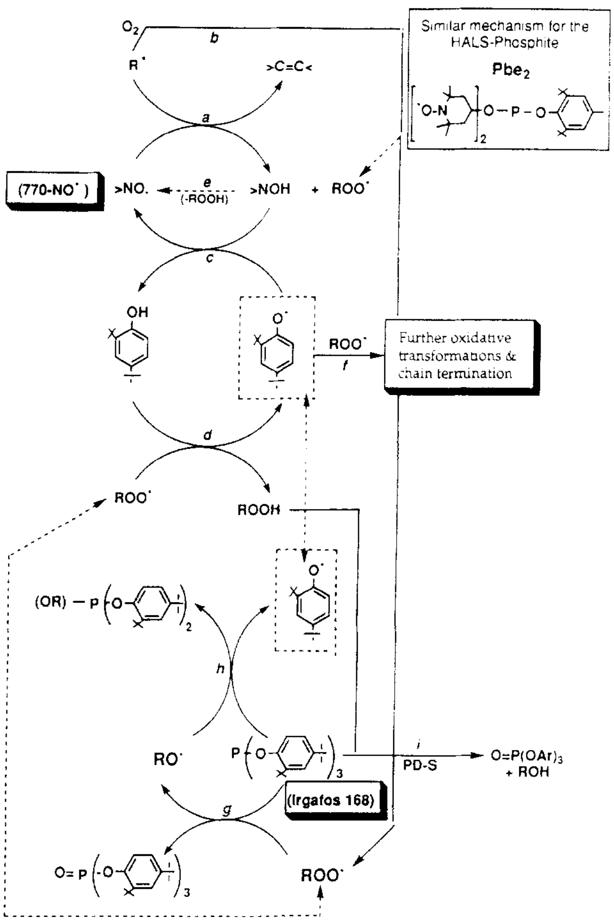


Fig. 4. Comparison of melt stability of PP containing different molar compositions of mixtures of Irgafos 168 and Tin 770 (at total [AO] = 7×10^{-3} mol/kg) with mixtures of TLP and Tin 770 (at total [AO] = 21×10^{-3} mol/kg).



Scheme 2

Fig. 5(a). Irganox 1010 shows a superior antioxidant activity compared to all the other antioxidants. By comparison, both Irgafos 168 and Tinuvin 770 are inferior to Irganox 1010; the bis-nitroxyl of Tinuvin 770 is, however, considerably better than the parent amine, Tinuvin 770. The high molecular weight secondary amine, Chimassorb 944, leads to much higher antioxidant effect under these conditions compared to Tinuvin 770 due to the lower volatility of the former.

Thermoxidative stability of PP film containing Tinuvin 770 was re-examined also but after an initial period of photoxidation (corresponding to one third of its photo-embrittlement time) with the aim of producing the corresponding nitroxyl radical *in situ*. Figure 5(b) shows clearly that this sample has led to a considerable improvement in the thermoxidative lifetime of the polymer compared to the untreated Tinuvin 770-containing sample. Further, a PP film containing the bis-nitroxyl of Tinuvin 770 subjected to the same photo pre-treatment, followed by thermoxidative ageing at 140°C, showed only a relatively small improvement in the thermoxidative stability of the PP film. However, both pre-photoxidised polymer samples (i.e. NH ox. and with NO ox.) gave quite similar induction periods at 140°, see Fig. 5(b). It is known that photoxidation of HALS leads to a constant stationary concentration of nitroxyls;[17] the level of the nitroxyl formed in pre-photoxidised PP samples containing Tinuvin 770 and 770-NO must be of the same order, hence the similarity in the thermoxidative lifetime of the polymers in both cases.

Figure 6 shows the co-operative effect of combinations of Irgafos 168 with Tinuvin 770, its corresponding bis-nitroxyl (770-NO), and the methyl hydroxyl amine analogue (Tinuvin 292), as well as that of the corresponding HALS-phosphites (Pbd_2, Pbe_2 and Pbf_2), on the thermoxidative stability of PP. Examination of Table 4 shows that all combinations give, in all cases, very high levels of synergism with the optimum lying towards large molar excess of Irgafos 168. In contrast to the Irgafos 168/Tinuvin 770 system, combinations of TLP with Tinuvin 770 (at a total concentration which is threefold that of the Irgafos 168/Tinuvin 770 mixtures) become much more effective at higher molar ratios of Tinuvin 770, see Fig. 7 and Table 3. The HALS-phosphites, Pbe_2 and Pbf_2, gave higher levels of synergism than the corresponding mixtures of the individual compounds (at the same molar ratio of the antioxidant functions, see Table 4).

The most interesting feature of these results is that the addition of a very small concentration of a completely ineffective thermal antioxidant, such as Tinuvin 770, to the aromatic phosphite, Irgafos 168 (which itself has no thermal antioxidant effect) leads to a remarkable improvement (of up to over 6000%) in the thermoxidative stability of the PP, see Fig. 8 and Table 4. Furthermore, the extent of synergism, for all the antioxidant mixtures studied, is shown to be much higher under thermoxidative conditions than under processing conditions (compared at the same total antioxidants concentration), see Tables 3 and 4.

Under thermoxidative conditions, RO· and ROO· radicals predominate (whereas alkyl radicals, R·, become more important during melt processing). The higher levels of synergism

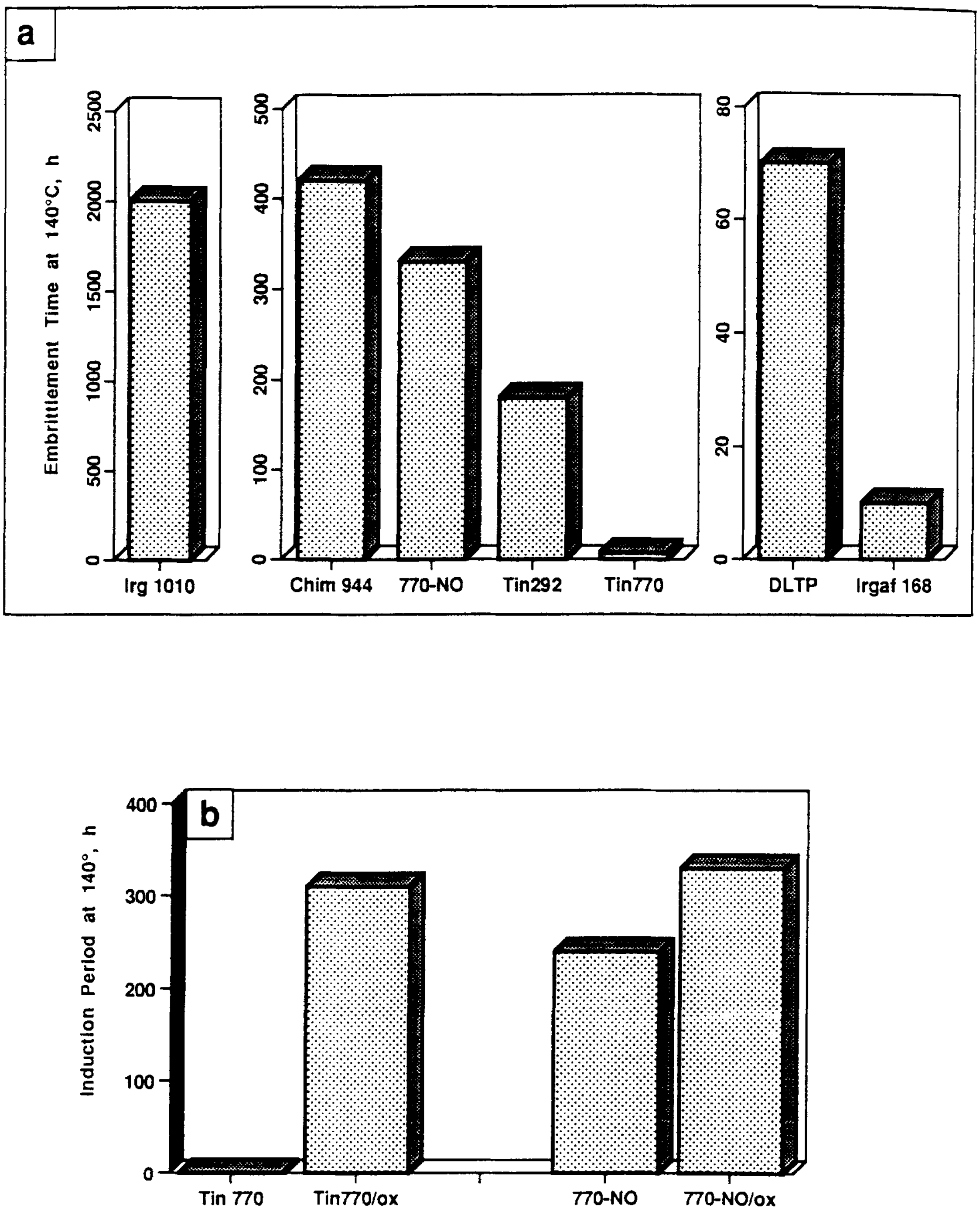


Fig. 5. Thermoxidative stability (at 140°C and air flow 6.8×10^{-2} m^3/h) of PP stabilised with antioxidants ($[AO] = 7 \times 10^{-3}$ mol/kg): (a) commercial antioxidants; (b) Tinuvin 770 (Tin 770) and the di-nitroxyl analougue (770-NO) before and after initial pre-photoxidation to one third of their photo-embrittlement time ('Tin 770/ox' and '770-NO/ox').

observed under thermoxidative conditions is almost certainly due to the prevailing environmental conditions which are conducive to the formation of phenoxyl radicals from the hindered aryl phosphite, Irgafos 168, see (Scheme 1) rn b and c. Only a small concentration of a hindered amine (e.g. Tinuvin 770) is required in the antioxidant mixture composition, but this is absolutely essential in order to create and maintain the regenerative co-operative cyclical processes involving two effective redox couples (PhOH/PhO· and NO·/NOH, see Scheme 1 cycles 1 and 2). These complementary co-operative cyclical processes, coupled with the additional peroxidolytic activity of the phosphite antioxidant must be primarily responsible for the

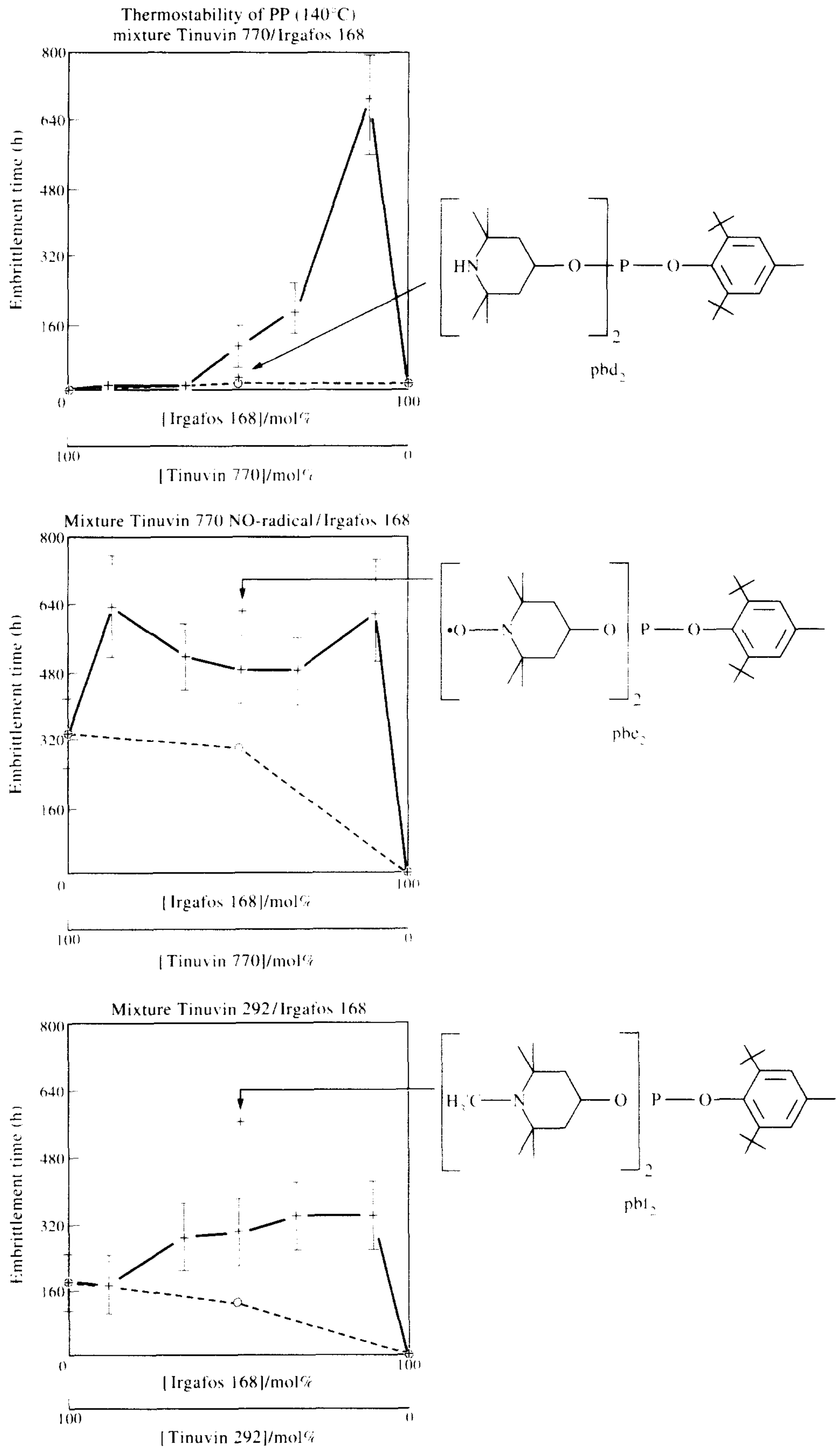


Fig. 6. Effect of molar composition of mixtures of Irgafos 168 and various HALS compounds (total [AO] = 7×10^{-3} mol/kg) on the thermoxidative stability (at 140°C and air flow 6.8×10^{-2} m^3/h) of PP. The thermoxidative stability of PP containing the corresponding HALS-phosphites (Pbd_2, Pbe_2 and Pbf_2; concentration of 3.5×10^{-3} mol/kg) is also shown.

Table 4. Effect of molar ratios of combinations of phosphites and Tinuvins on extent of synergism during oven ageing (measured from thermoxidative embrittlement time, EMT) of PP. Percentage synergism of the corresponding HALS-phosphites is also shown

Antioxidants	Concentration (10^{-3} mol/kg)	Synergism[a] (EMT) (%)
Irgafos 168 + Tinuvin 770	0.8 + 6.2	105
Irgafos 168 + Tinuvin 770	2.3 + 4.7	25
Irgafos 168 + Tinuvin 770	3.5 + 3.5	1076
Irgafos 168 + Tinuvin 770	4.7 + 2.3	178 6
Irgafos 168 + Tinuvin 770	6.2 + 0.8	6941
TLP + Tinuvin 770	14 + 7	200
TLP + Tinuvin 770	7 + 14	620
Pbd_2 (HALS-phosphite)	7	253
Irgafos 168 + Tinuvin 770-NO	0.8 + 6.2	118
Irgafos 168 + Tinuvin 770-NO	2.3 + 4.7	131
Irgafos 168 + Tinuvin 770-NO	3.5 + 3.5	188
Irgafos 168 + Tinuvin 770-NO	4.7 + 2.3	325
Irgafos 168 + Tinuvin 770-NO	6.2 + 0.8	1277
Pbe_2 (HALS-phosphite)	7	276
Irgafos 168 + Tinuvin 292	0.8 + 6.2	6
Irgafos 168 + Tinuvin 292	2.3 + 4.7	134
Irgafos 168 + Tinuvin 292	3.5 + 3.5	216
Irgafos 168 + Tinuvin 292	4.7 + 2.3	416
Irgafos 168 + Tinuvin 292	6.2 + 0.8	1057
Pbf_2 (HALS-phosphite)	7	489

[a] Percent synergism = $(Es/[\times 2(E2 - E1) + E1] - 1) \times 100$, where Es = embrittlement time of antioxidant mixture or multifunctional antioxidant, $E1$ = embrittlement time of antioxidant 1 (lower embrittlement time at 7×10^{-3} mol/kg), $E2$ = embrittlement time of antioxidant 2 (higher embrittlement time at 7×10^{-3} mol/kg), $\times 2$ = molar fraction of antioxidant 2.

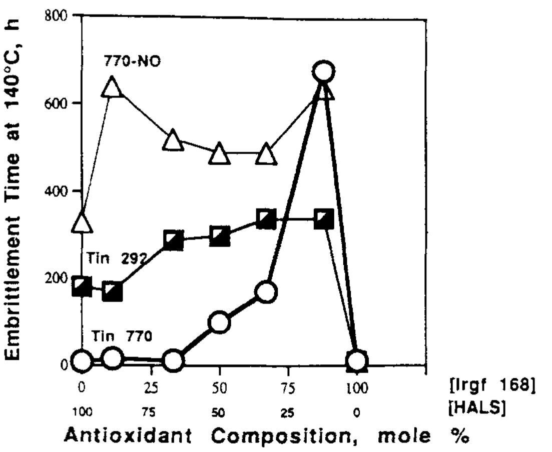


Fig. 7. Comparison of thermoxidative stability of PP containing different molar compositions of mixtures of Irgafos 168 with various HALS compounds (Tin 770, Tin 292 and 770-NO) at total [AO] = 7×10^{-3} mol/kg.

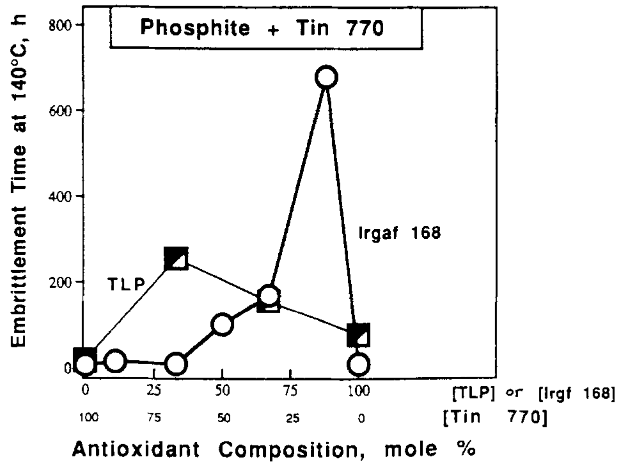


Fig. 8. Comparison of thermoxidative stability of PP containing different molar compositions of mixtures of Irgafos 168 with Tinuvin 770 (total [AO] = 7×10^{-3} mol/kg) and mixtures of TLP with Tinuvin 770 (total [AO] = 21×10^{-3} mol/kg).

very effective synergism observed, see Table 4.

The behaviour of combinations of the aliphatic and the hindered aromatic phosphites with hindered amines and related compounds during the photostabilisation of PP will be the subject of a further publication.

4 CONCLUSIONS

The hindered aromatic phosphite, Irgafos 168, is almost as effective as the hindered phenol, Irganox 1010, as melt stabiliser in PP but is much more inferior under thermoxidative (at 140° with air flow) conditions. The bis-nitroxyl, Tinuvin 770-NO, is a better processing and thermoxidative stabiliser than the parent amine, Tinuvin 770, and the corresponding methyl hydroxylamine, Tinuvin 292. Whilst the hindered amine, Tinuvin 770, itself offers no thermal oxidative stability (no induction period) to PP, a pre-photoxidised Tinuvin 770-containing PP sample in which a stationary NO concentration has formed leads to an induction period of about 300 h, and this is similar to that obtained from a similarly pre-treated NO-containing PP film.

Secondary and tertiary HALS and their nitroxyl radicals show effective synergism at all molar ratios with aromatic and aliphatic phosphites, both as melt processing and thermoxidative antioxidants. However, the synergistic optima are obtained at different molar ratios depending on the structure of the phosphite; excess HALS is necessary in the case of the aliphatic phosphite whereas a molar excess of the phosphite is required for the sterically hindered phosphites.

In all cases, a much higher extent of synergism was obtained under thermoxidative conditions than under melt processing conditions.

All HALS-phosph(on)ite antioxidants give rise to synergism under both processing and thermoxidative conditions. In most cases their efficiency was slightly higher than their corresponding additive mixtures.

Further detailed investigations are necessary to confirm the nature of the co-operative antioxidant mechanisms discussed above and to provide a rationale for some of the experimental observations reported.

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