

## TRANSFORMATIONS OF ANTIOXIDANTS DURING PROCESSING

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**Abstract-** Most antioxidants and stabilisers are partially converted to oxidation products during processing at high temperatures and in the presence of a small amount of oxygen. In some cases the transformation products are more effective antioxidants than the starting materials. Thus for example, hindered nitroxyl radicals are much more effective than the amines from which they are derived as processing and light stabilisers for polypropylene. Similarly, oxidative processing of many sulphur-containing antioxidants markedly improves their antioxidant activity, and in some cases, the processing operation can be used to induce the chemical reaction of the antioxidant with the polymer chain.

### INTRODUCTION

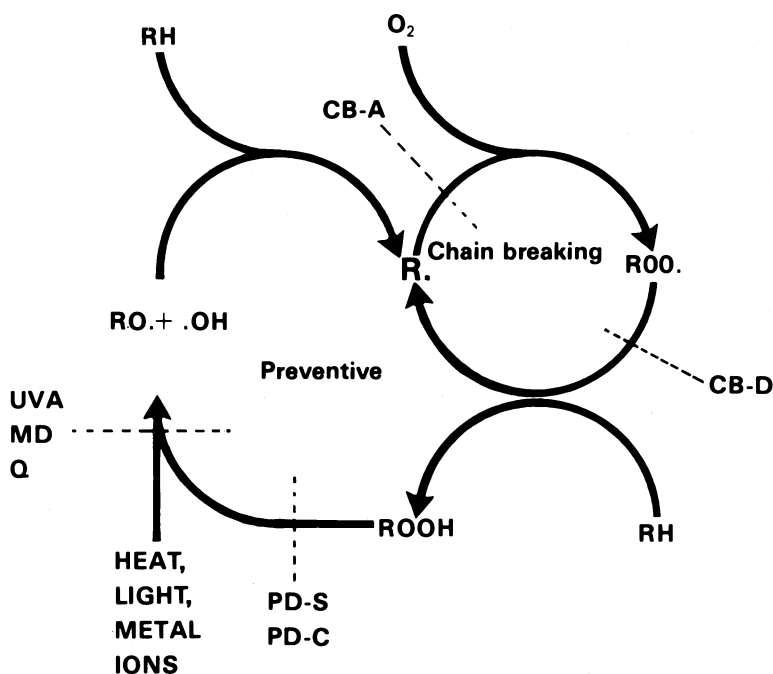
It is important, both theoretically and practically, to know what effect the processing operation has on the subsequent performance of antioxidants and stabilisers in polymers. The study of antioxidant mechanisms is concerned with the way in which the effective inhibitor interferes with the autoxidation chain reaction under the appropriate conditions. Many examples have been noted in recent years of effective antioxidants being produced in situ in the polymer either during processing or during subsequent service. Important practical examples are to be found both among the chain-breaking and preventive antioxidants.

That antioxidants and stabilisers are affected by processing is self-evident in the light of the chemical changes known to occur in polymers under these conditions (Ref.1,2). The passage of a polymer through a screw extruder or plasticisation on a two roll mill leads to shearing of the polymer chain, particularly at the early stages before the polymer has fully liquified and when it is still in the rubbery state. This kind of treatment has been used in the rubber industry for over a century to reduce the molecular weight of the polymer prior to the introduction of compounding ingredients. Early studies in the "mastication" of rubber showed the importance of both shear and oxygen in mechanodegradation. Mechano-oxidation of rubber is characterised by two different phenomena. In the low temperature region (generally below 100°C), mechanical shear of the viscous polymer is the dominating process, whereas at higher temperatures normal oxidation catalysed by macroalkyl radicals is the main process (Ref.3).

Recent studies have shown (Ref. 1,2,4-8) that all the thermoplastic polymers show a high rate of mechanodegradation in the initial stages of a processing operation, leading to the introduction of a variety of irregularities into the macromolecule. The easiest of these to measure are carbonyl compounds (Ref.5,9-13), hydroperoxides (Ref.1,5,9-13) and unsaturation (Ref.5,7,11,13). These "impurities" have been shown to have a profound effect, not only on the subsequent ageing performance of the unstabilised polymer but also on the antioxidants and stabilisers incorporated during processing. This may result either in the partial destruction of the effective species or in its formation from an inert precursor.

### TRANSFORMATIONS INVOLVING CHAIN-BREAKING ANTIOXIDANTS

Chain-breaking antioxidants (CB) are able to interrupt the autoxidation chain reaction shown in Scheme 1 at two points (Ref.14). Reducing agents, of which the hindered phenols and aromatic amines are the best known commercial examples, deactivate alkylperoxyl radicals by electron donation (CB-D). Oxidising agents, such as quinones, "stable" radicals, etc., convert alkyl radicals to carbonium ions or olefinic unsaturation, Scheme 2, by accepting an electron (CB-A). Under normal conditions of thermal oxidation, for example in an air oven, the alkyl radical concentration is low and the CB-D process predominates. However under the conditions existing in a screw extruder or on a closed internal mixer, this is not so, since the shearing forces acting on the polymer lead to a high concentration of free radicals which can survive very much longer than in an open system due to the limited air access to the polymer. Both alkyl and alkylperoxyl radicals can thus co-exist under processing conditions.

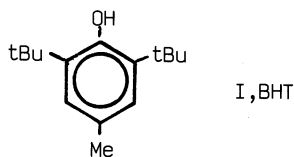


Scheme 1. Antioxidant Mechanisms

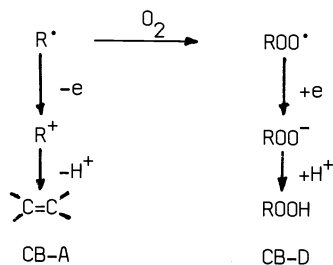
This is confirmed by the fact that some polymers (e.g. polyethylene) undergo macroalkyl radical dimerisation during processing to give molecular enlargement (Ref.10).

#### Hindered phenols as CB antioxidants

Hindered phenols, e.g. BHT(I) are melt stabilisers for polyolefins (Ref.15)



In the course of a typical processing operation, BHT is partially converted to oxidation products which are somewhat more effective in an air oven heat ageing test than BHT itself (Ref. 16,17), see Scheme 3. The stilbenequinone (IV) was shown to be at least partly respons-

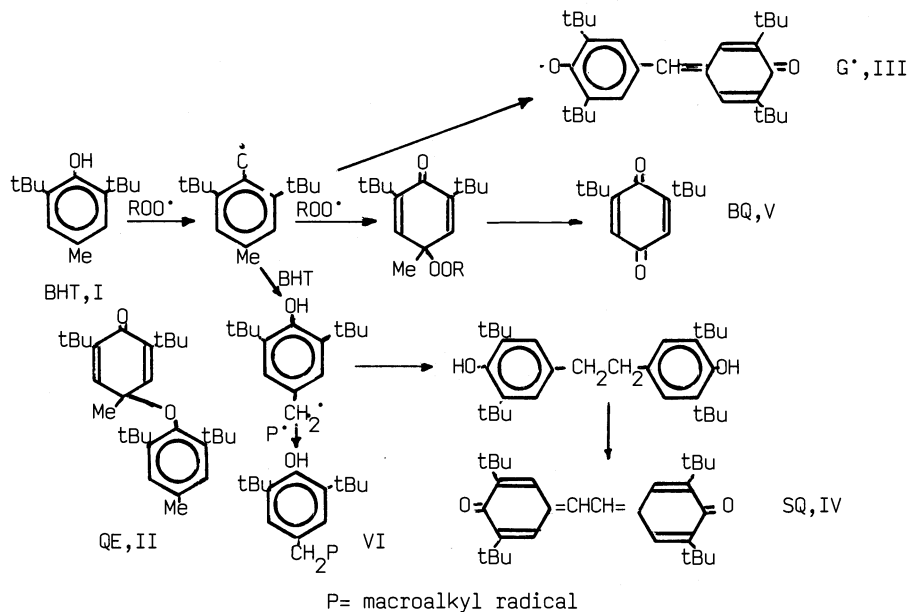


Scheme 2. Oxidative and reductive mechanisms of antioxidant action

ible for this phenomenon, but a polymer-bound antioxidant in which the phenol was bound to the polymer through the methylene group was also implicated (Ref. 16,17). Table 1 shows that the antioxidant is able to withstand exhaustive solvent extraction. However, the extent of polymer binding is low.

Other quinonoid products are known to be formed by oxidation of BHT (Ref.18), see Scheme 3 and these have all been found to be much more effective than BHT itself as melt stabilisers

for polypropylene (Ref.15), see table 2. These products are all oxidising agents and, like the "stable" radicals which will be discussed below, they all act by a CB-A mechanism.



Scheme 3 . Transformation products of BHT(I) in a shearing mixer

TABLE 1. Effect of processing on polypropylene stabilised with BHT (2g/100g)  
Air oven at 140°C

Processing time at 180°C,min	Hydroperoxide conc. (10 <sup>5</sup> mol g <sup>-1</sup> )	Induction Period,h				
		Control	Normally processed		Pre-oxidised	
			U*	E§	U*	E§
0	0.0	0.5	2.0	0.8	2.0	0.8
5	5.0	0.3	4.0	2.0	8.2	3.5
10	9.5	0.1	9.0	2.5	15.0	4.0
15	44.0	-	15.0	2.5	27.0	4.0

\*U= unextracted, §E= extracted

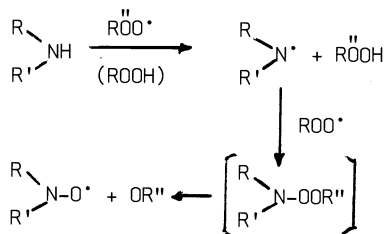
TABLE 2. Effectiveness of BHT transformation products as melt stabilisers for PP at 270°C

Antioxidant	ΔMFI*	
	4.5 <sup>+</sup>	0.5 <sup>+</sup>
BHT, I	100	270
QE, II	40	55
G, III	45	45
SQ, IV	50	60
BQ, V	55	65

\* ΔMFI, Percentage change in MFI on single passage through a screw extruder  
+ Concentration of antioxidant, mmol kg<sup>-1</sup>

### Secondary amines as CB antioxidants

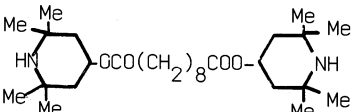
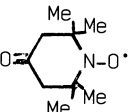
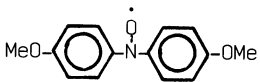
Diarylamines have been used for many years as antioxidants for rubbers. They are considerably more effective than hindered phenols but they are not used in the thermoplastic polymers to any extent because of their tendency to cause discolouration of the end product. They have been shown to be readily oxidised in rubbers to the corresponding nitroxyl radical both during processing (Ref.19), and during subsequent service (Ref. 20), Scheme 4, and it is the nitroxyl radical rather than the parent amine which is primarily responsible for the singular effectiveness of the diarylamines as antifatigue agents in rubbers (Ref. 19,20).



Scheme 4. Oxidation of secondary amines to nitroxyl radicals

Hindered piperidines and related secondary aliphatic amines are also converted to nitroxyl radicals in PP during processing (Ref. 8). They are not themselves effective melt stabilisers but their derived oxidation products are, see Table 3.

TABLE 3. Effectiveness of nitroxyl radicals as melt stabilisers for PP

Antioxidant	Code	$\Delta\text{MFI}^*$	
		4.5 <sup>+</sup>	0.5 <sup>+</sup>
	VI	190	240
	VII	-	55
	VIII	-	45
BHT	I	100	270

\*  $\Delta\text{MFI}$ , Percentage change in MFI on single passage through a screw extruder.  
 + Concentration of antioxidant, mmol kg<sup>-1</sup>

Like the hindered aryloxy radicals, the hindered nitroxyl radicals are CB-A antioxidants, and are incapable of reacting with alkylperoxy radicals.

### Transformation of "stable" radicals in polypropylene during processing

The high activity of hindered aryloxy and nitroxyl radicals as melt stabilisers for polymers during processing results from their ability to oxidise alkyl radicals by the CB-A mechanism, scheme 2 (Ref.21).

Galvinoxyl has been shown to be a melt stabiliser for PP for up to 20 min at 200°C in a close mixer, see Fig.1 (Ref.7). During the first few minutes of processing, 96% of the G<sup>•</sup> initially present is quantitatively reduced to GH (IX). As the viscosity of the polymer is progressively reduced due to melting, some of the GH is re-oxidised to G<sup>•</sup> by alkylperoxy radicals and hydroperoxides. The initial stage of rapid reduction of G<sup>•</sup> to GH is accompanied by the formation of unsaturation in the polymer, Fig.2. The total concentration of G<sup>•</sup>+ GH remains essentially constant for a while and then slowly declines. This indicates that G<sup>•</sup> and GH constitute a reversible redox couple under these conditions. The chemistry is summarised in Scheme 5. The subsequent decrease in concentration of the redox couple must be due to the

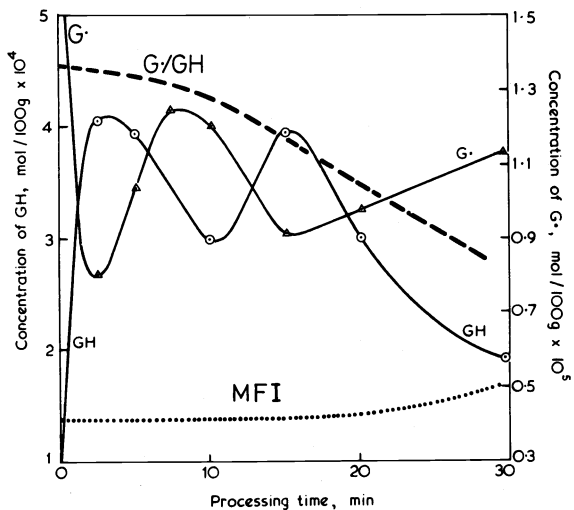


Fig. 1

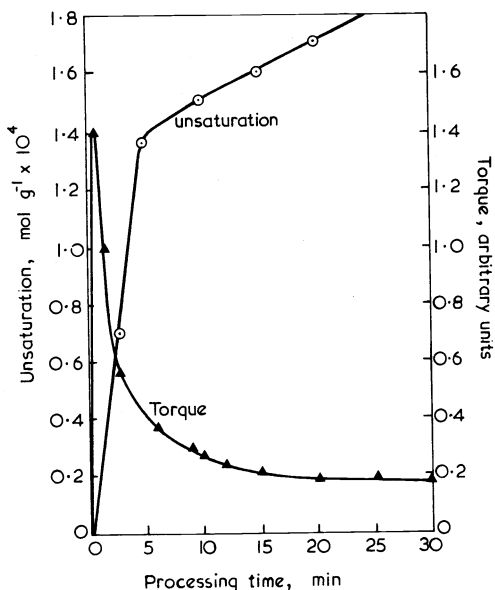
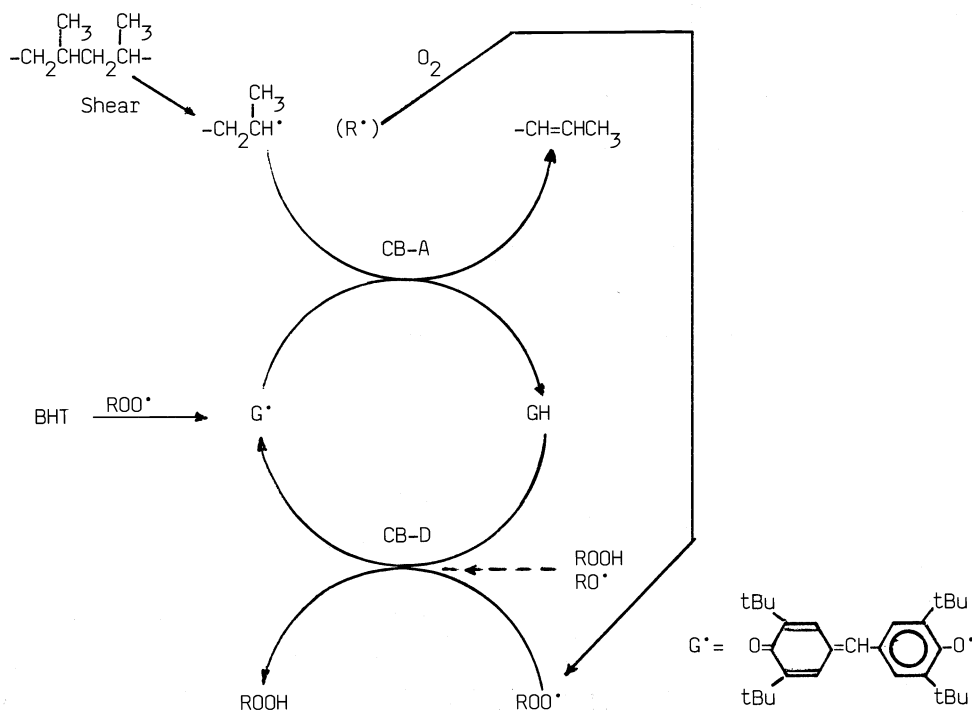


Fig. 2

Fig. 1. Variations of the concentrations of G• and GH during the induction period to MFI change of polypropylene in a closed mixer at 200°C. G•/GH indicates the total concentration of the two species.

Fig. 2. Increase of olefinic unsaturation in polypropylene as a function of applied torque in a closed mixer at 200°C. (After Ref.7 with permission)



Scheme 5. Catalytic role of galvinoxyl (G•) in the melt stabilisation of PP

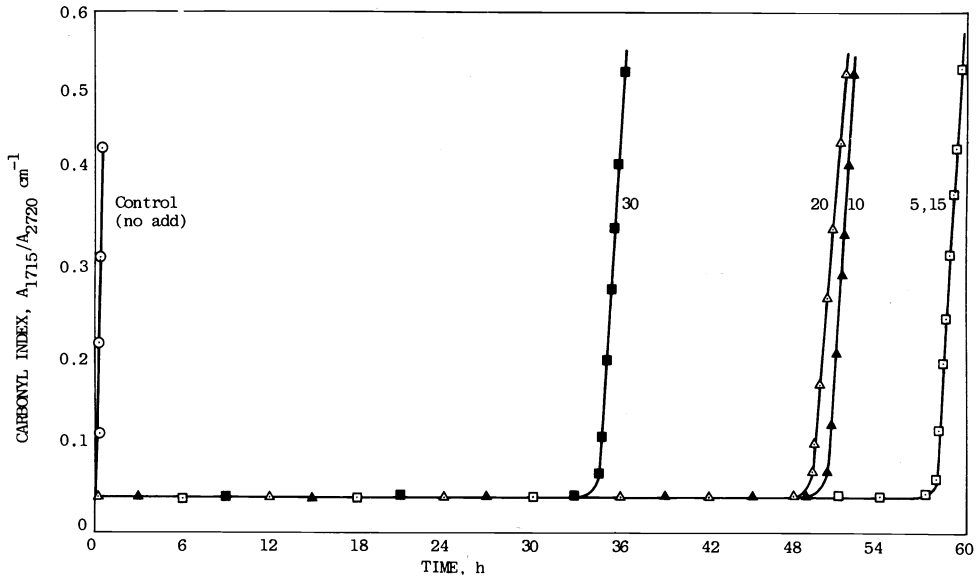


Fig. 3. Formation of carbonyl during the oven ageing of polypropylene at 140°C. Numbers on curves indicate the processing times (min) of PP at 200°.

irreversible destruction of galvinoxyl resulting from the slow diffusion of oxygen into the mixer.

Interesting confirmation for the conversion of the CB-A antioxidant, G\* to the CB-D reduction product, GH comes from a study of the thermal-oxidative stability of polypropylene processed for different times (Ref.22). Fig. 3 shows that the rate of thermal oxidation in an air oven at 140°C varies markedly with the processing time. Comparing Fig.3 with Fig.1 shows that the oxidative stability is directly proportional to the concentration of GH in the film. Under these conditions, due to the ready access of oxygen to the macroalkyl radicals, the CB-A mechanism cannot operate effectively but the CB-D mechanism can. It has been shown that the end of the induction periods in Fig.3 corresponds to the removal of GH by volatilisation (Ref.22).

4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (X) has been shown (Ref.23) to undergo a similar



redox reaction under the same conditions, Fig.4. In this case, however, less of the radical

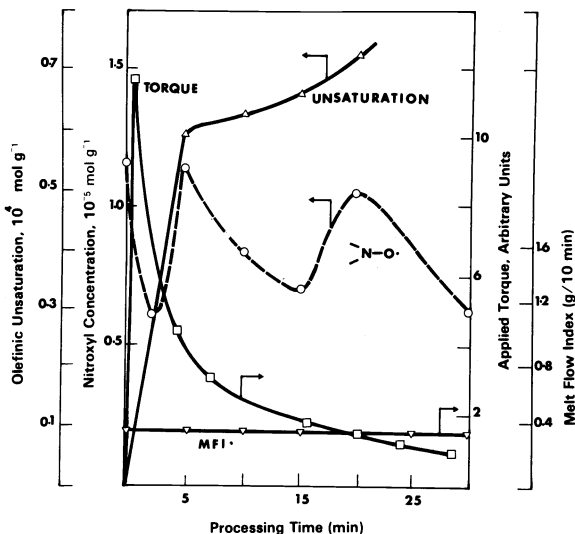
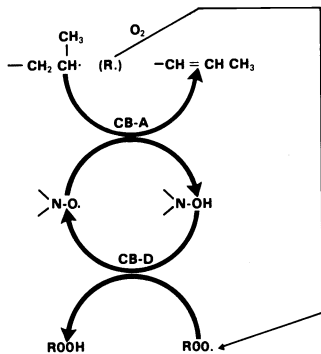


Fig. 4. Effect of processing time on applied torque, nitroxyl concentration [N-O•] and generated unsaturation in PP containing HTMPO at 200°C



Scheme 6

Scheme 6. Catalytic antioxidant mechanism of nitroxyl radicals during the melt stabilisation of polypropylene

Fig. 5. Effectiveness of a hindered piperidinoxyl (X) and its derived hydroxylamine (XI) as melt stabilisers for polypropylene at 180°C in a closed mixer. A commercial hindered piperidine, Tinuvin 770, is also shown for comparison. (All additives at  $3 \times 10^{-4}$  mol/100g)

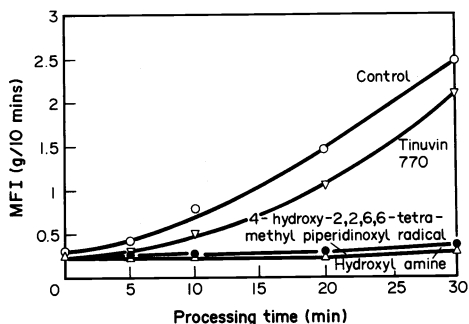


Fig. 5

is converted to the corresponding hydroxylamine during the early stages of processing and it is almost completely regenerated when the shear in the mixer decreases due to melting of the polymer. The mechanism of melt stabilisation by hindered nitroxyls is entirely analogous to that of galvinoxyl, Scheme 6.

Fig. 5 (Ref.8) shows that the hydroxylamine, XI, is almost as effective as the nitroxyl, X, in a closed mixer and Fig.6 shows that the nitroxyls rapidly generated from the hydroxylamine under these conditions. On the other hand, the hydroxylamine is somewhat more effective than the nitroxyl in an open mixer at the same temperature, Fig.7, and the parent hindered piperidine is much less effective than either under all conditions. Under the conditions of an open mixer, as in an air oven, the nitroxyl is less able to compete with oxygen for alkyl radicals and its activity as a melt stabiliser is reduced relative to the hydroxylamine which, as we have already seen, is an effective CB-A antioxidant (Ref.24).

Transformation of hindered piperidines to nitroxyls in polypropylene during processing  
It is now generally accepted that hindered piperidines are not antioxidants (Ref.25-27), and that they are converted to nitroxyls which are effective photostabilisers. The mechanism of photostabilisation by nitroxyl radicals is outside the scope of this paper, but it is now known to involve a similar redox reaction to that described in Scheme 6 (Ref.8). The question of how the hindered piperidines are converted to nitroxyls has not yet been completely resolved, however, it is known that the transformation occurs at least partly during processing (Ref.8). Figure 8 shows that in an open mixer, rapid formation of nitroxyl occurs and that it is also formed in a closed mixer after an induction period. Severely processed polyethylene containing the commercial hindered amine uv stabiliser, Tinuvin 770 (VI), is actually more photostable than normally processed polymer (Ref.28). The derived nitroxyl radicals show quite a different

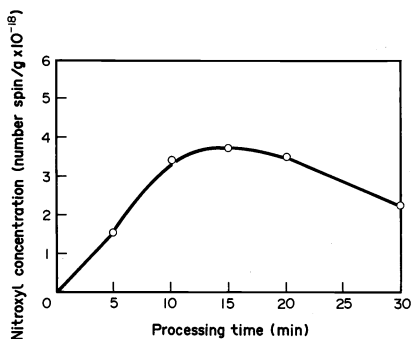


Fig. 6

Fig. 6. Formation of nitroxyl (X) from hydroxylamine (XI) during processing in polypropylene in a closed mixer at 180°C

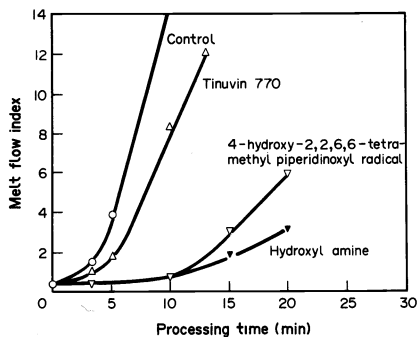


Fig. 7

Fig. 7. Effectiveness of piperidinoxyl (X) and its derived hydroxylamine (XI) as melt stabilisers for polypropylene at 180°C in an open mixer. A commercial hindered piperidine, Tinuvin 770, is also shown for comparison. (All additives at  $3 \times 10^{-4}$  mol/100g)

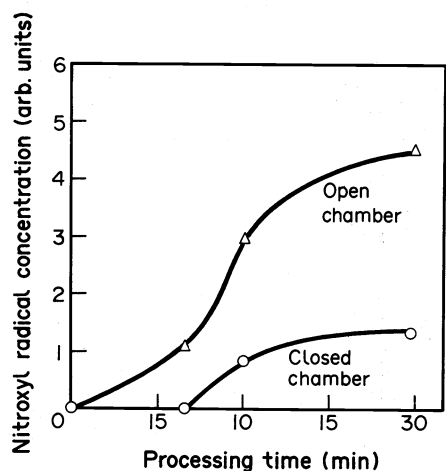


Fig. 8

Fig. 8. Transformation of hindered piperidine, Tinuvin 770, to the corresponding nitroxyl in polypropylene during processing at 180°C

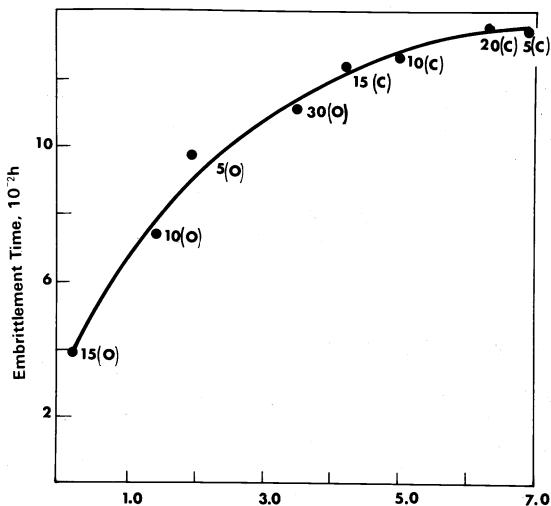


Fig. 9

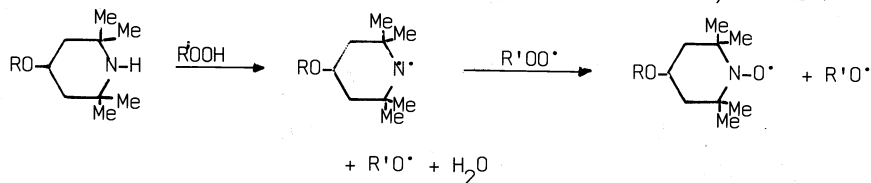
Fig. 9. Relationship between initial [X] and its uv stabilising effectiveness. Numbers on curves indicate processing times. (C), closed mixer; (O), open mixer.

response to processing (Ref.23). Table 4 shows that in a normally processed sample (i.e. closed mixer, 180°C/10 min), the hydroxylamine, XI, is significantly more effective than the corresponding nitroxyl and both are in turn more effective than the hindered piperidine, Tinuvin 770. However severe processing of polypropylene markedly reduces the effectiveness of the nitroxyl. Figure 9 shows that, as might be expected, there is a relationship between the amount of nitroxyl remaining after processing and its stabilising effectiveness (Ref.23).

TABLE 4. U.v stabilising activity of Tinuvin 770 (VI) and derived products

Additive	Time to embrittlement, hours
Tinuvin 770 (VI)	750
XII (bis-nitroxyl of (VI))	960
X	920
XI	1040

The hindered piperidines are virtually without antioxidant activity and indeed, they have been shown to catalyse the formation of hydroperoxides in polyethylene during processing (Ref.28). This pro-oxidant behaviour is consistent with the formation of radicals by a redox reaction with hydroperoxides at the high temperatures involved, Scheme 7



Scheme 7 Formation of nitroxyl radical from hindered piperidine by redox reaction with hydroperoxide

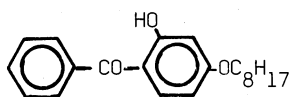
In contrast to this behaviour, nitroxyl radicals completely inhibit the formation of hydroperoxides during processing (Ref.29).

Other effective melt stabilisers for polypropylene, notably iodine, alkyl iodides and cupric salts operate by the same CB-A/CB-D mechanism as galvinoxyl and hindered piperidinoxyls (Ref. 21,29), but as these are not thermal antioxidants, they will not be discussed further in this review.

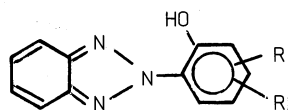


TRANSFORMATION PRODUCTS FORMED FROM PREVENTIVE ANTIOXIDANTS DURING PROCESSING

Unlike the nitroxyls discussed in the previous sections, most uv stabilisers for polymers act by the preventive mechanisms (Ref.25,30). Thus the uv absorbers (UVAs), notably the 2-hydroxybenzophenones (XIII) and the 2-hydroxyphenylbenzotriazoles (XIV) act essentially



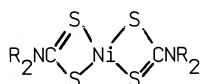
XIII



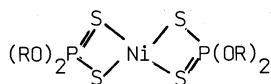
XIV

by protecting potential photosensitisers (hydroperoxides and carbonyl compounds) from the effects of light. A secondary function in both cases is to scavenge "oxyl" radicals (Ref.30,31) and as a consequence, the UVAs are sensitive to the severity of the processing operation. Thus for example, the activity of HOBP (XIII) decreases markedly with processing time in both LDPE (Ref.32) and polypropylene (Ref.12,33). This phenomenon has been shown to be a function of the oxidisability of the substrate and the consequent formation of hydroperoxides which destroy the stabiliser under conditions of uv irradiation (Ref.32).

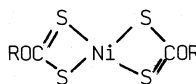
The behaviour of the nickel dithiolate uv stabilisers (XV-XVII) is somewhat different. Again they are all effective UVAs, although their effectiveness in this respect depends on their



XV



XVI



XVII

solubility in the polymer (Ref.34,35). The evidence suggests, however that their primary function is to act as light-stable reservoirs for oxidatively derived antioxidants (Ref.36). Since these species are partially formed during processing in the presence of a trace of oxygen, the metal dithiolates are all effective melt stabilisers for polyolefins (Ref.36) and hydroperoxides are not present in the polymer at the end of the processing operation. Consequentially, the uv stabilising effectiveness of the metal dithiolate group of antioxidants is less sensitive to the effects of the processing operation than are the non-sulphur UVAs (Ref.32). Nevertheless, under severe processing conditions, some reduction in activity does occur, due to the partial conversion of the nickel complex to the disulphide. This is shown typically for nickel dibutyldithiophosphate in polypropylene in Fig.10 (Ref.37). It can be

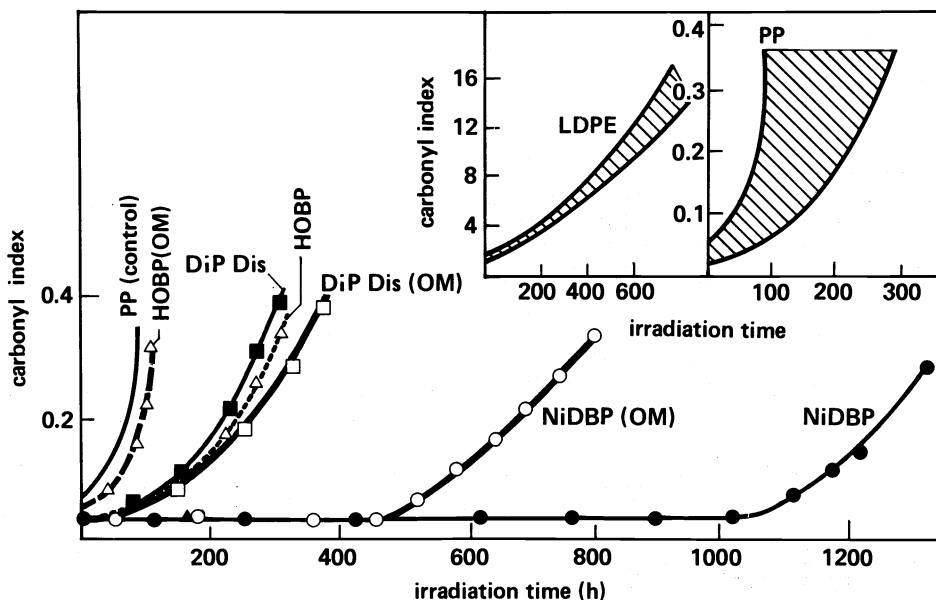


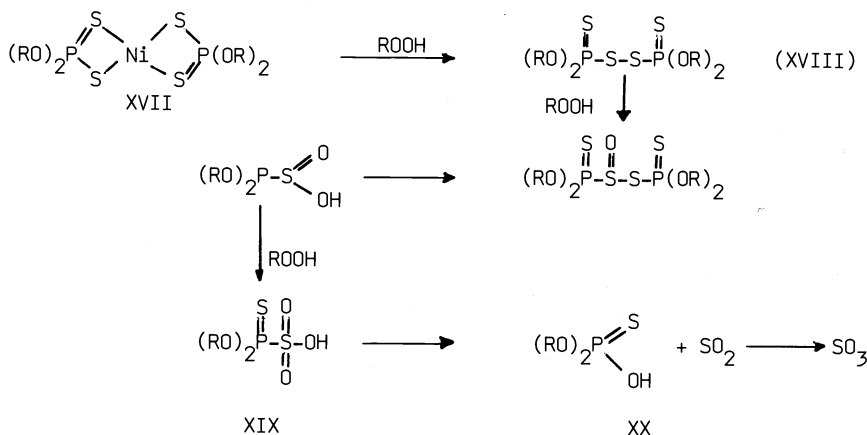
Fig. 10. Effect of processing severity on the effectiveness of uv stabilisers OM indicates open mixer; the rest were processed in a closed mixer

seen that the effectiveness of both HOBP (XIII) and NiDBP (XVI, R=nC<sub>4</sub>H<sub>9</sub>) are substantially reduced by severe processing. However a thiophosphoryl disulphide (XVIII, R=iPr) which is the primary oxidation product of the corresponding nickel dithiophosphate, see Scheme 8, actually improves in performance as a uv stabiliser when subjected to the same severe processing operation, see Table 5.

TABLE 5. Effect of oxidative processing on the uv stability of polypropylene containing antioxidants and uv stabilisers

Additive	Embrittlement time, hours	
	Closed mixer	Open mixer
HOBP (XIII)	835	295
NiDBP(XVI, R=C <sub>4</sub> H <sub>9</sub> )	1370	780
DiPDS(XVIII, R=iC <sub>3</sub> H <sub>7</sub> )	285	400
Control (no additive)	90	45

Scheme 8 shows the changes that have been shown to occur during the oxidation of nickel dialkyl dithiophosphates by hydroperoxides in organic solution at 110°C (Ref.38).



Scheme 8. Oxidation of the nickel dithiophosphates by hydroperoxides

The inset in Fig. 10 compares the effect of severe processing on the uv stabilising activity of bis-isopropylthiophosphoryl disulphide (DiPDS, XVIII, R=iPr) in polypropylene and in polyethylene (the shaded area indicates the difference between mild and severe processing in the two polymers). It is clear that severe processing has resulted in a higher level of stabilising activity in PP than in PE. This is believed to reflect the relative ease of oxidation of PP compared with PE, which is known to give a relatively higher concentration of hydroperoxides in the more oxidisable polymer. Uv stabilising systems of very high activity have been developed using this principle of controlled oxidation of sulphur-based antioxidants during processing. Table 6 compares the effects of normally processed and severely processed combinations of antioxidants on the uv stability of polypropylene.

TABLE 6. Effect of oxidative processing\* on the activity of a synergistic combination of antioxidants

Stabiliser	Concentration g/100g	Embrittlement time, hours	
		Normally processed	Oxidatively processed
DBDS	0.1		
NiDBP	0.1	2100	>4500
HOBP	0.2		

\* As described in Brit. Pat. App. 8208828 (1982)

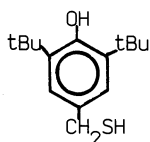
## REACTIONS OF ANTIOXIDANTS WITH POLYMERS DURING PROCESSING

The undesirable effects of shear on polymers during processing was discussed earlier in this paper. It was shown many years ago by Watson and his co-workers (Ref.40) that macroalkyl radicals produced during shearing of polymers could be utilised to initiate polymerisation of vinyl monomers, with the formation of block copolymers. The same process has more recently been applied to the chemical binding of antioxidants to polymers.

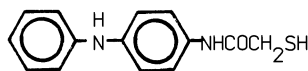
Mechanochemically initiated addition of thiol antioxidants such as XXI and XXII to rubbers is a particularly facile process (Ref.40-42). Substantial conversions have been achieved with both thiols even at quite high loadings in the unsaturated rubbers, Table 7.

TABLE 7 Yield of thiol adducts in rubbers by a mechanochemical procedure

Rubber	Thiol	Temp., °C	Antioxidant loading (g/100g)	Yield*	Ref.
NR	MADA(XXII)	70	10	50	40
SBR	BHBM(XXI)	25	10	43	40
	MADA(XXII)	70	10	58	40
EPDM	MADA(XXII)	150	10	88	42



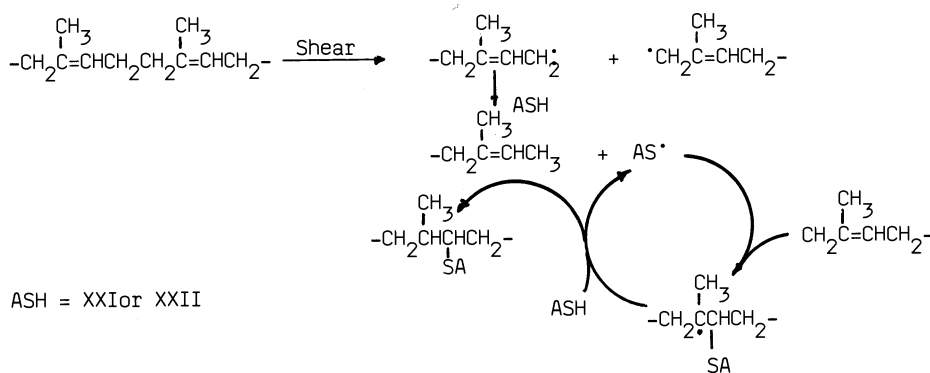
XXI, BHBM



XXII, MADA

\* Percentage of added thiol remaining in the polymer after exhaustive solvent extraction

The chemistry of adduct formation in the case of polyisoprene is summarised in Scheme 9.



Scheme 9. Mechanism of thiol-adduct formation in cis-polyisoprene

Unsaturated thermoplastics such as ABS also react readily with antioxidant thiols (Ref.43), but somewhat more surprisingly so do saturated hydrocarbon polymers. Thus the thiol XXII reacts with polyethylene and polypropylene in a shearing mixer at 150°C and 180°C respectively. In this case, there is insufficient unsaturation in the polymer to account for the level of binding achieved. Figure 11 shows that binding occurs in two stages. Most of the adduct is formed during the first minute while the applied torque in the mixer is high. This stage involves the formation of macroalkyl radicals by mechanical scission of the polymer chain,

see Scheme 10. The second stage utilises the chain end hydroperoxides as radical generators, Scheme 11 (Ref.44).

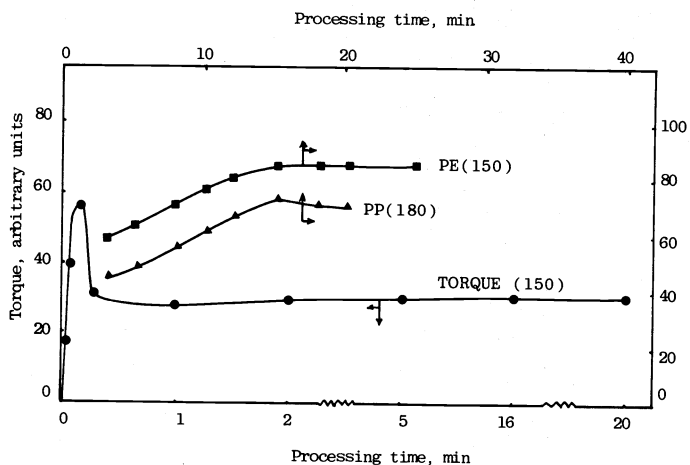


Fig. 11

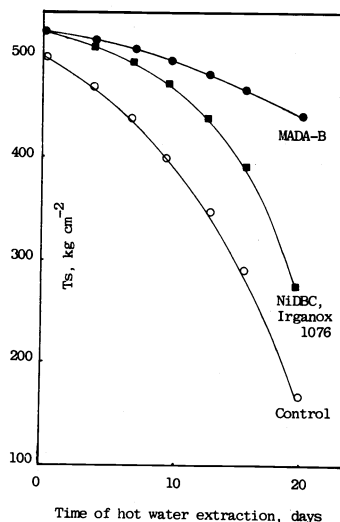
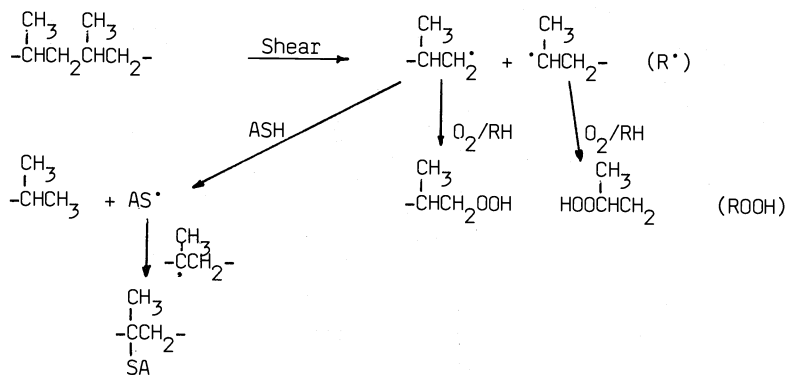


Fig. 12

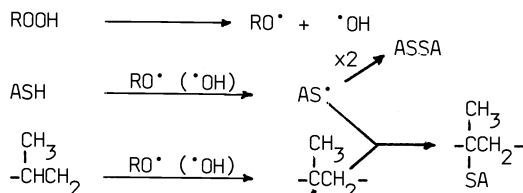
Fig. 11. Effect of processing time on the extent of binding of MADA (XXII) into PP and LDPE (at 2g/100g). Numbers in parenthesis indicate processing temperatures, °C. The applied torque curve for LDPE is also shown.

Fig. 12. Antioxidant activities, as measured by the retention of tensile strength of PP containing antioxidants. (Aerated water at 90°C)

All the polymer-bound antioxidants made by this procedure are very much more resistant to solvent leaching and volatilisation than are conventional additives. This has been discussed in detail elsewhere (Ref.16,45) but a typical example is given in Fig.12 of a comparison of polypropylene-bound MADA (MADA-B) with conventional thermal antioxidants under conditions of hot water extraction (Ref.44)



Scheme 10. Shear-initiated thiol adduct formation in polypropylene



Scheme 11. Peroxide-initiated thiol adduct formation in polypropylene

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