

Mechanisms of Antioxidant Action: The Antioxidant Activity of Nitrones in Polypropylene

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Synopsis

Aldonitrones are effective melt stabilizers for polypropylene, the most effective being benzaldonitrones containing a partially hindered 4-hydroxy group in the aromatic ring. They form nitroxyl radicals in the polymer during processing, and these and the related hydroxylamines are believed to be involved in a catalytic CB—A/CB—D antioxidant cycle during mechano- and photooxidation. During thermal oxidation (oven aging) they behave as stoichiometric CB-D antioxidants.

INTRODUCTION

It has been shown that appropriately substituted nitrones are effective antifatigue agents (mechanochemical stabilizers) for vulcanized rubbers.^{1,2} Furthermore, there is evidence^{3,4} that the conditions under which antifatigue agents are effective (high shear) are similar to those existing during melt processing of polymers. Both involve a high rate of macroalkyl radical formation due to shear of the polymer chains (reaction 1) and in both cases, the concentration of oxygen at the site of the reaction is restricted, in the first case by oxygen diffusion and in the second by deliberate exclusion of oxygen from the shearing zone:



There is also evidence^{5,6} that the conditions which lead to the effective operation of a CB-A/CB-D catalytic antioxidant cycle during photooxidation also have features in common with mechanooxidation, and in particular the fact that "stable" radicals can compete with oxygen for macroalkyl radicals implies oxygen diffusion limitation under these conditions too. The purpose of the present investigation is therefore to pursue the analogy between mechano- and photooxidation, which has been observed in previous papers in this series.^{5,7,8} In particular, it was shown⁸ that nitroso-*tert*-alkanes [e. g., 2-nitroso-2-methyl propane (I)] are effective melt stabilizers and photoantioxidants for polypropylene. Some of these have the ability to "repair"

TABLE I
Aldonitrones Used in the Present Study

				Code	mp (°C)	Elemental Analysis (%)
R	X	Y	Z			
Ph	H	H	H	DPN	110	C,78.8(79.18);H,5.5(5.58);N,7.0(7.11)
Ph	OH	H	H	HDPN	211	C,73.4(73.2);H,5.0(6.2);N,6.3(6.6)
Ph	OH	Me	Me	MHDPN	112	C,74.3(74.1);H,7.1(7.0);N,5.9(5.8)
Ph	NO ₂	H	H	NDPN	176	C,64.1(64.46);H,4.0(4.13);N,11.3(11.57)
Ph	OMe	H	H	MDPN	117	C,73.6(74.0);H,5.4(5.72);N,6.3(6.16)
tBu	H	H	H	PBN	74	C,75.4(74.6);H,8.6(8.49);N,7.8(7.9)
tBu	OH	H	H	HPBN	228	C,68.5(68.4);H,7.8(7.8);N,7.4(7.3)
tBu	OH	Me	Me	MHPBN	178	C,70.1(70.0);H,9.2(9.4);N,6.4(6.3)

RESULTS

Antioxidant Activity of Nitrones in the Polymer Melt during Processing

The nitrones listed in Table I were examined as melt stabilizers for polypropylene at 180°C in a Hampden-RAPRA torque rheometer with the ram in position to exclude oxygen from the atmosphere. The results for diphenyl nitron (DPN) and its 4-hydroxy derivatives (V,X = OH) are summarized in Figure 1. MDPN and NDPN which do not contain a phenolic group (see Table I) behaved almost identically to DPN and are therefore not included in Figure 1. The *N-tert*-butyl nitrones, PBN, HPBN, and MHPBN, did not

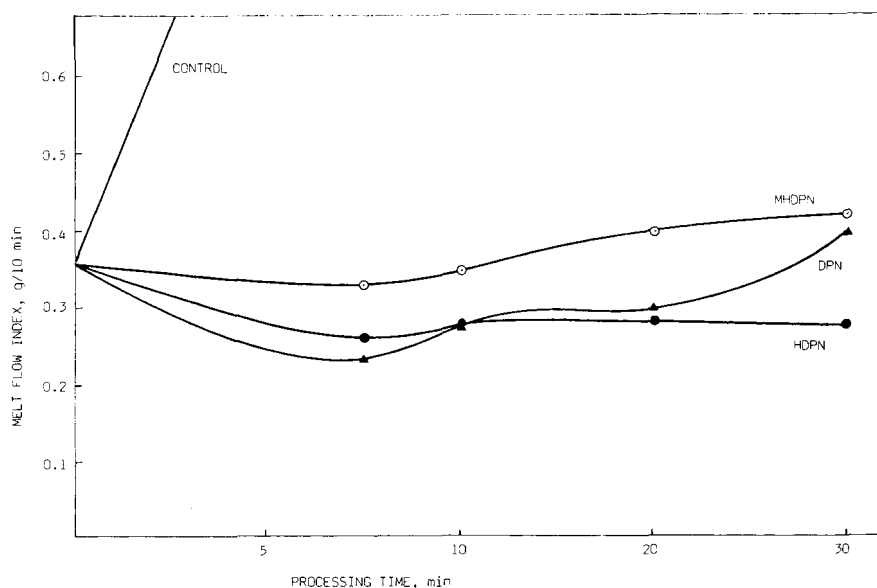


Fig. 1. Effects of *N*-phenyl nitrones (10^{-3} mol/100 g) on the melt stability of polypropylene on processing in a closed mixer at 180°C.

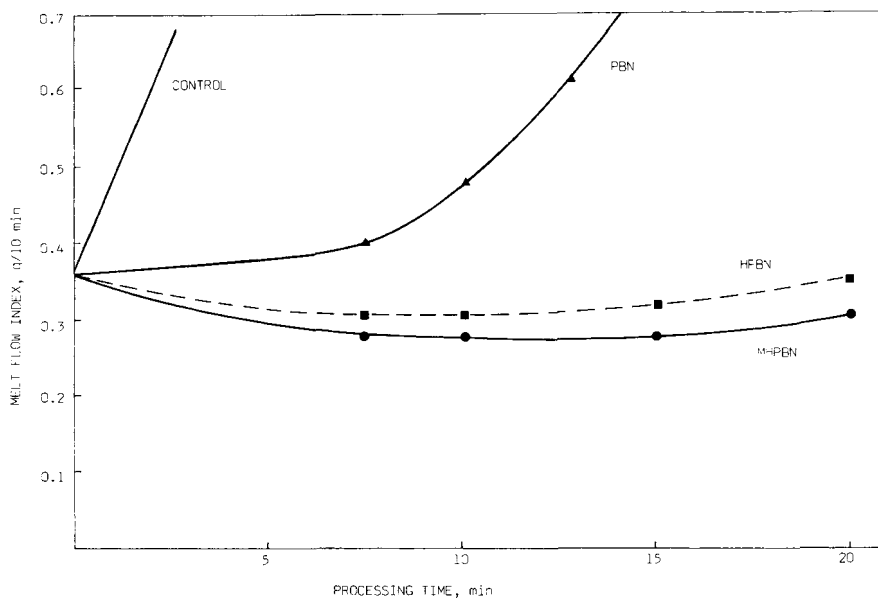


Fig. 2. Effects of *N-tert*-butyl nitrones (10^{-3} mol/100 g) on the melt stability of polypropylene on processing in a closed mixer at 180°C .

cause the same typical melt viscosity fluctuation, and typical curves are illustrated in Figure 2.

It is clear that all the nitrones, except PBN, which is somewhat less effective as a melt stabilizer than the others, crosslink PP to a greater or lesser extent. A gel permeation chromatogram of PP containing DPN processed for 7.5 and 20 min is shown in Figure 3. The upward shift in molecular mass at 7.5 min is clear evidence for the "repair" mechanism previously observed with C-nitroso compounds⁸ and is entirely consistent with the decrease in MFI at the same time observed in Figure 1. This behavior is less obvious with the hydroxy compounds, but HPBN does show a slight upward shift of molecular mass distribution at 10 min processing (see Fig. 4).

NDPN and MDPN show similar melt stabilizing activity to DPN, whereas all the phenolic analogues stabilize for a longer time under the same conditions (see Fig. 1). All the nitrones become more effective with increase in concentration. This is shown for MDPN, NDPN, HPBN, and HDPN at constant processing time in Table II. It can be seen that the crosslinking process increases with increasing concentration but does not increase further above 5×10^{-4} mol/100 g for the hydroxy nitrones. The nonphenolic nitrones are as effective as the phenolic nitrones only at appreciably higher concentrations.

It is known from previous studies⁵ that typical alkyl trapping antioxidants acting by the CB-A mechanism are generally much more effective in a closed mixer than in an open mixer, where the alkylperoxyl radical is the predominant radical species.^{14,15} Figure 5 shows that hydroperoxide formation, which is a concomitant of MFI change, is completely inhibited in a closed mixer in the presence of MHDPN and is effectively retarded even in the presence of air.

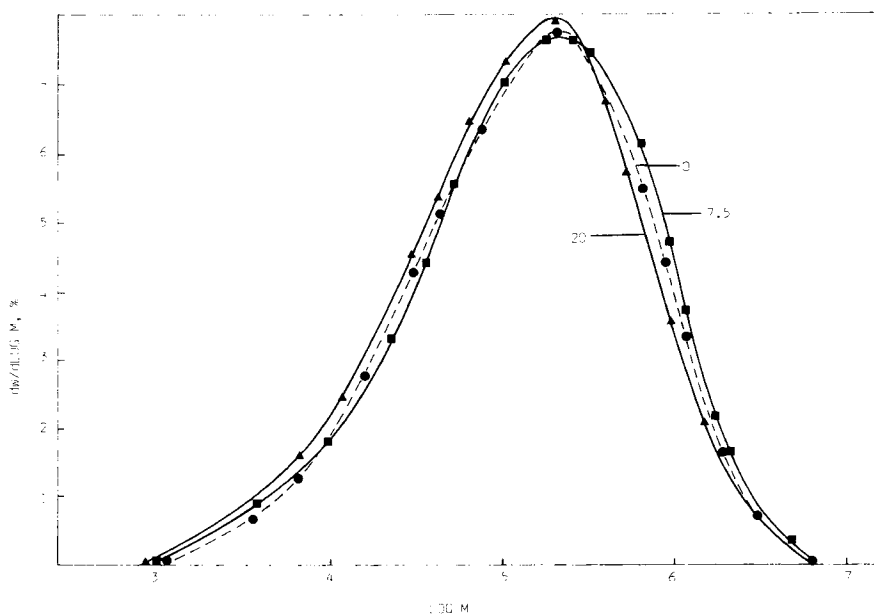


Fig. 3. Effect of DPN on the molecular mass distribution of polypropylene during processing in a closed mixer at 180°C. Numbers on curves are processing times (min).

Formation of Nitroxyl Radicals during Processing

Figure 6 shows the triplet spectrum of MHDPN processed in PP for 10 min at 180°C. Figure 7 shows that about 5% of the MHDPN originally added is converted to the corresponding nitroxyl after 10 min, and slightly less in the case of DPN. However, by measuring the concentration of nitrones

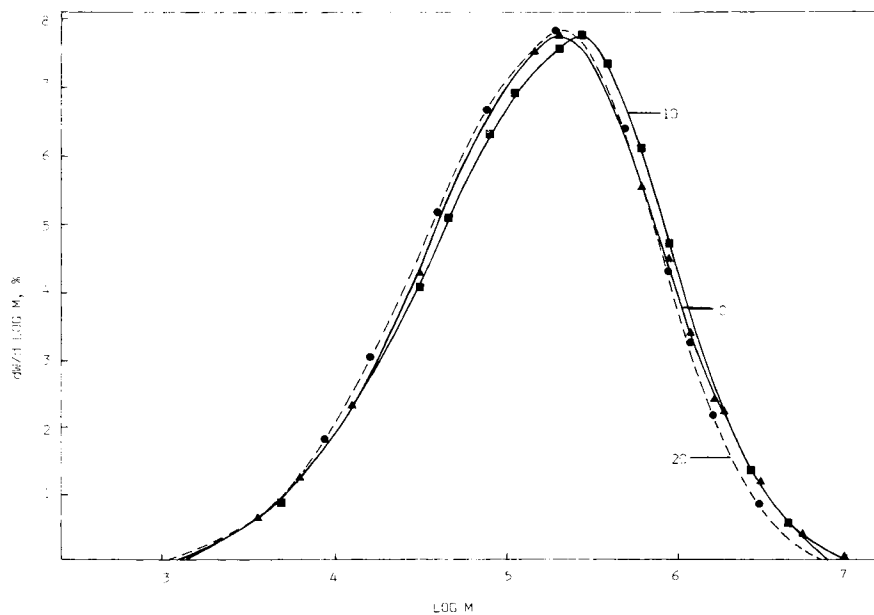


Fig. 4. Effect of HPBN on the molecular mass distribution of polypropylene during processing in a closed mixer at 180°C. Numbers on curves are processing times (min).

TABLE II
Effect of the Concentrations of Nitrones in Polypropylene on Melt Flow Index (MFI) at
Constant Processing Time (10 min/180°C in Closed Mixer)^a

Nitrone	Concn (10 ⁴ mol/100 g)	Melt flow index			
		1	5	10	15
MDPN	0.63	0.38	0.36	0.36	0.36
NDPN	0.44	0.42	0.37	0.37	0.37
HPBN	0.39	0.31	0.31	0.31	0.31
HDPN	0.28	0.28	0.28	0.28	0.28

^a MFI of unstabilized control, 0.37.

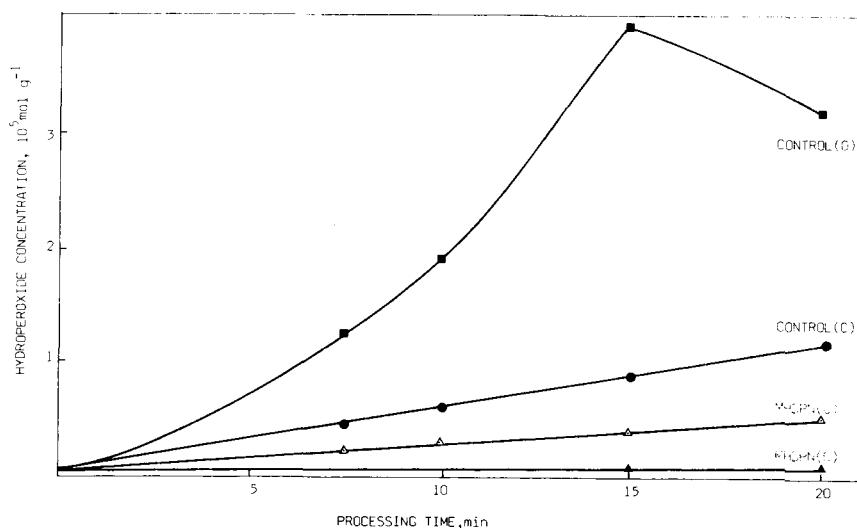


Fig. 5. Formation of hydroperoxides during the processing of polypropylene at 180°C with and without MDPN (10⁻³ mol/100 g). (C) closed mixer; (O) open mixer.

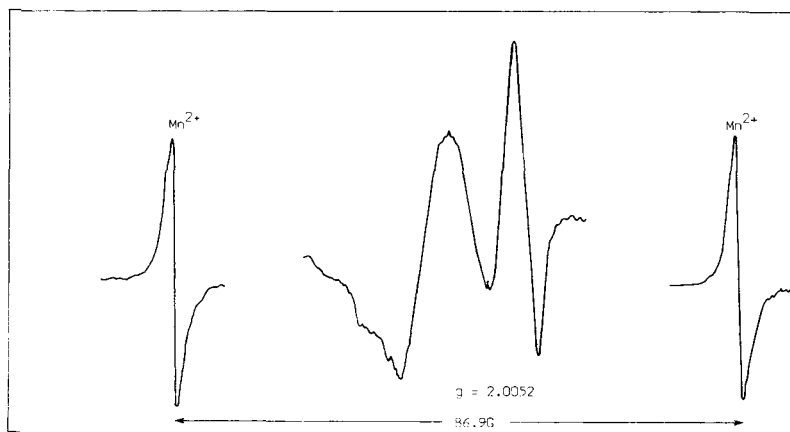


Fig. 6. ESR spectrum of a nitroxyl radical derived from MDPN in polypropylene film after processing in a closed mixer at 180°C/10 min.

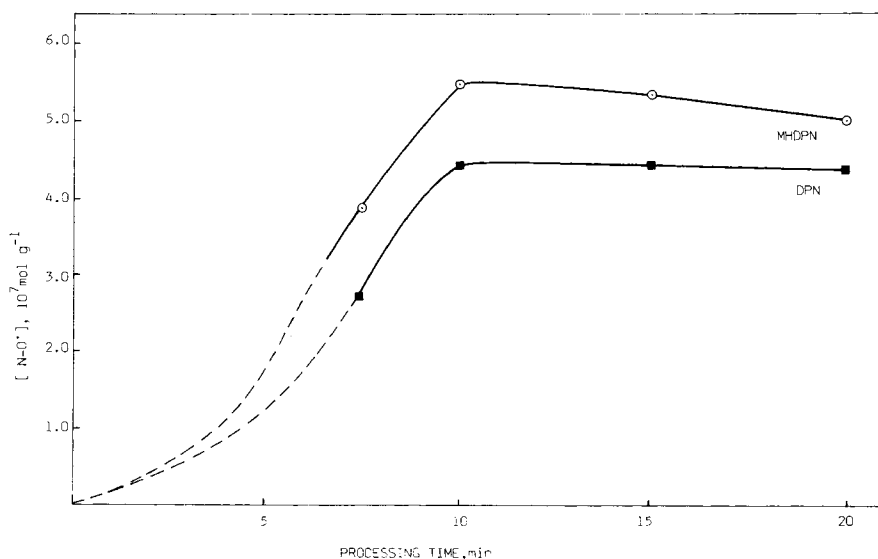


Fig. 7. Formation of nitroxyl radicals during processing (180°C) of polypropylene containing nitrones (10^{-3} mol/100 g).

remaining in the polymer at the same time (by means of the appropriate UV absorbance), it was found that 42% and 45%, respectively, had been converted to other products. No unsaturation could be detected in the polymer during processing in the presence of nitrones, but hydroxylamines were detected by methods described previously.¹⁶

Photoantioxidant Activities of Nitrones

Table III lists the embrittlement times for PP films containing nitrones, which have been processed for varying times, on UV irradiation. Two kinds of behavior are observed. In the case of PBN, MDPN, and HPBN, photoantioxidant activity increased to a maximum with increasing processing time. With the rest, however, including the control, the activity decreased with processing time. None of the nitrones were very powerful UV stabi-

TABLE III
Effect of Processing on the UV Stability of PP Containing Nitrones^a

Processing time (min)	Embrittlement time (h)				
	7.5	10	15	20	10 (extracted)
Nitrone					
Control (no additive)	85	85	75	—	—
DPN	200	245	290	185	—
HDPN	240	210	210	200	130
MHDPN	140	140	140	120	100
NDPN	230	210	210	210	120
MDPN	130	150	160	140	95
PBN	90	90	90	90	90
HPBN	120	140	160	200	109
MHPBN	130	130	130	130	90

^a (10^{-3} mol/100 g; processed in a closed mixer at 180°C).

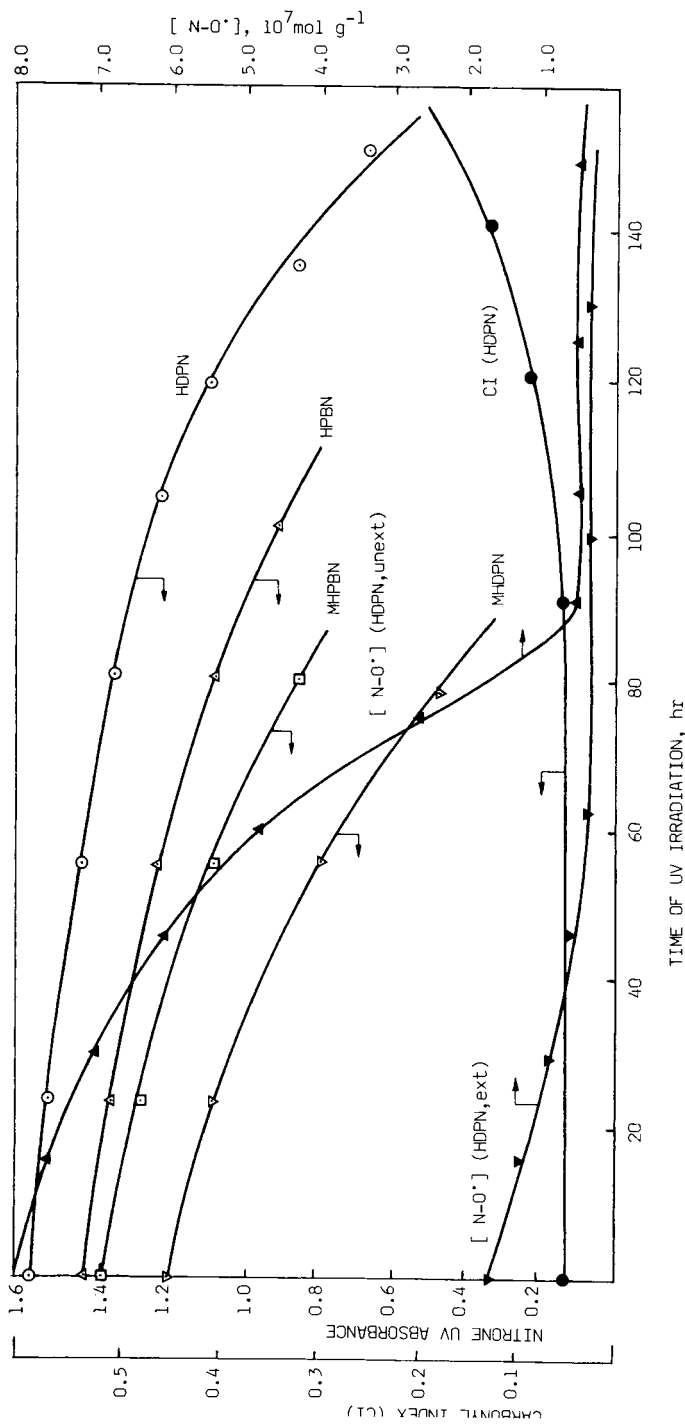


Fig. 8. Change in concentration of nitrones and derived nitroxyl radicals (from HDPN) during photooxidation. The carbonyl induction period (CI) for PP containing HDPN is also plotted.

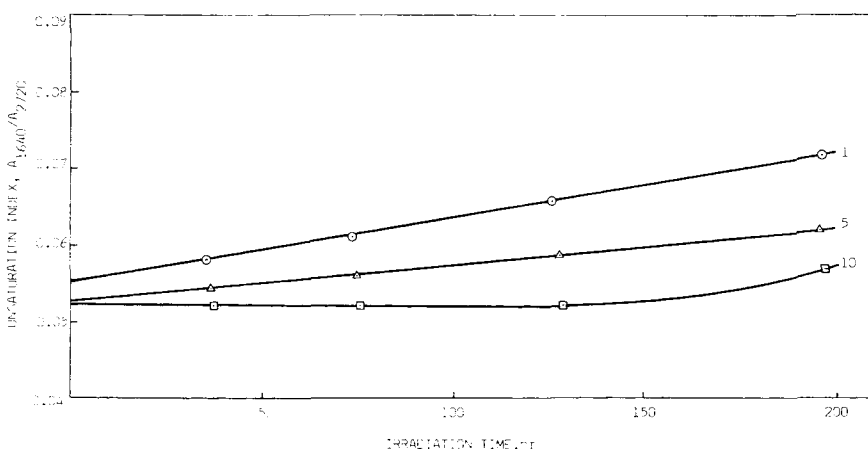


Fig. 9. Formation of olefinic unsaturation in polypropylene (as measured by the IR absorption at 1640 cm^{-1}) containing HDPN, as a function of UV irradiation time. Numbers on curves are HDPN concentrations ($10^4\text{ mol}/100\text{ g}$).

lizers (compared, for example, with the hindered nitroxyls⁵), and PBN was not a UV stabilizer at all.

Figure 8 shows that, in the case of HDPN, the photooxidative induction period correlates with the loss of nitroxyl from the polymer. However, the rate of photooxidation is retarded at the end of the induction period, and this fact, together with the evidence that embrittlement does not occur until after 200 h and that a low, stationary concentration of nitroxyl persists in the polymer up to the embrittlement time, suggests that nitroxyl radicals are continuously formed from the nitrone during this time. Figure 9 shows the formation of unsaturation in the polymer as a function of UV irradiation time for HDPN.

Antioxidant Activities of Nitrones in an Air Oven Test

Table IV compares the embrittlement time for polypropylene film containing nonphenolic and phenolic nitrones. It is clear that the presence of a phenolic hydroxyl group is essential to the antioxidant activity and that

TABLE IV
Effect of Processing Conditions on the Thermal Antioxidant Activity of Nitrones in an Air Oven at 140°C^a

Nitrone \ Processing time (min)	Embrittlement time (h)					
	7.5	10	15	20	10 (open mixer)	10 (closed mixer, extracted)
Control (no additive)	—	0.5	—	—	—	—
DPN	1.5	1.5	1.5	1.5	1.0	0.5
HDPN	7.0	10.0	8.5	6.0	7.5	3.0
MHDPN	18.5	14.0	11.0	9.0	7.0	3.0
PBN	1.0	1.0	1.0	1.0	0.5	0.5
HPBN	3.0	4.0	2.5	2.0	2.0	1.0
MHPBN	9.0	7.5	4.5	2.5	1.5	2.0

^a Concentration, $10^{-3}\text{ mol}/100\text{ g}$.

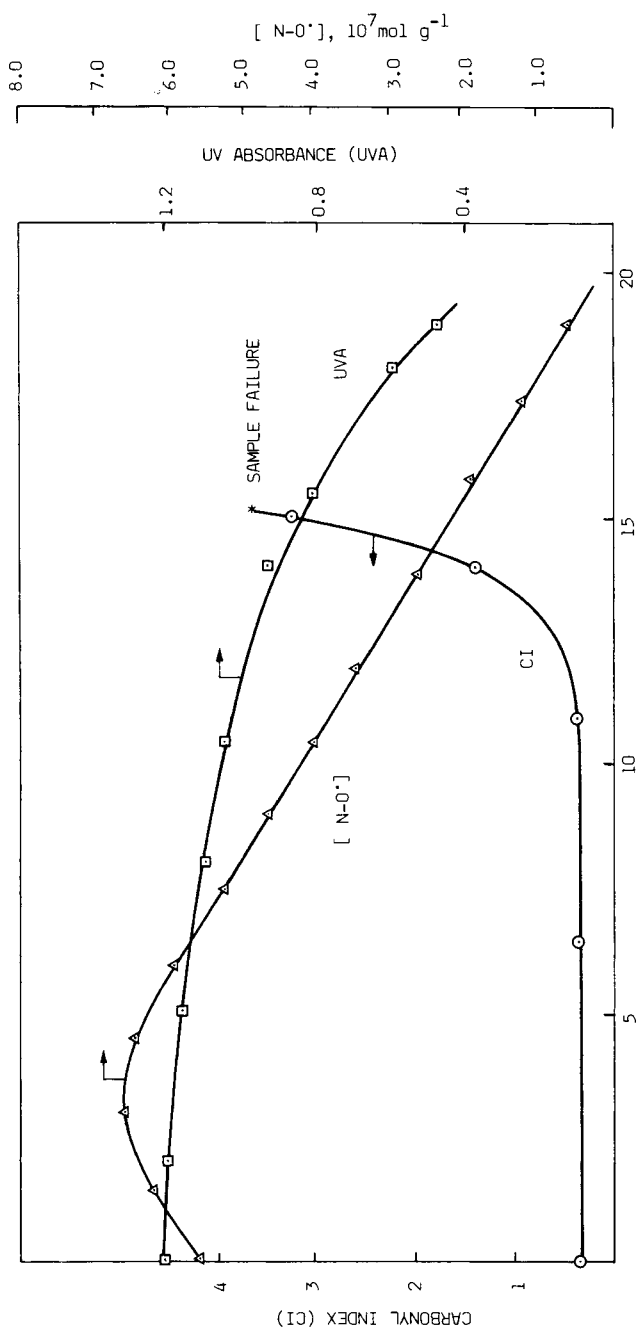


Fig. 10. Disappearance of MHPDN absorbance (at 325 nm) and nitroxyl (by ESR) and their relation to the carbonyl induction period during the thermal oxidation of polypropylene containing MHPDN (10^{-3} mol/100 g) in an air oven at 140°C .

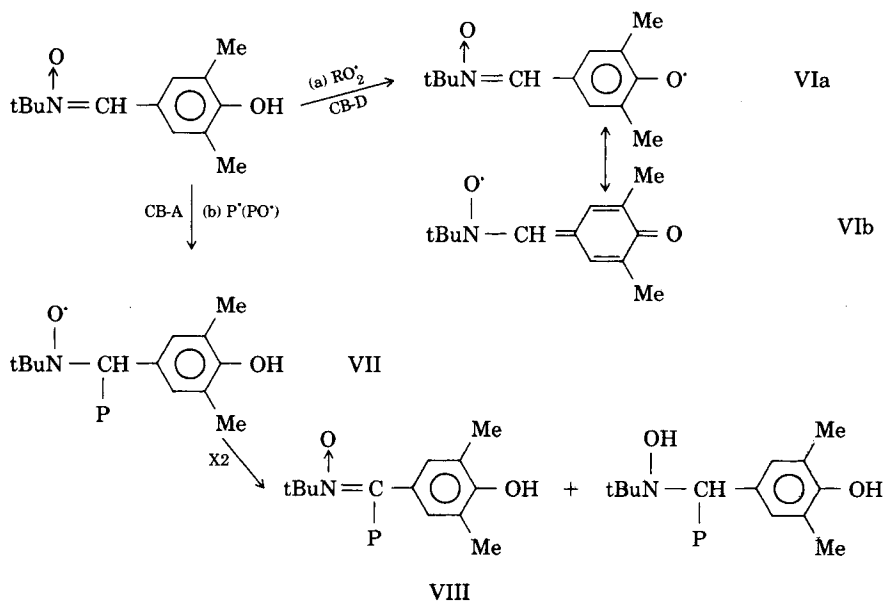
the more severely the formulations are processed, the less effective are the nitrones as thermal antioxidants. The induction period to the commencement of oxidation was found to be somewhat shorter than the time required for the complete loss of the nitroxyl radical from the polymer film (see Fig. 10).

Autoxidation of *p*-Xylene in the Presence of MHDPN

Figure 11 shows that the formation of nitroxyl radicals from MHDPN in *p*-xylene in the presence of oxygen at 110°C and initiated by AIBN. Nitroxyl was formed only during the first 5 min; it decayed slowly during the oxidation induction period.

DISCUSSION

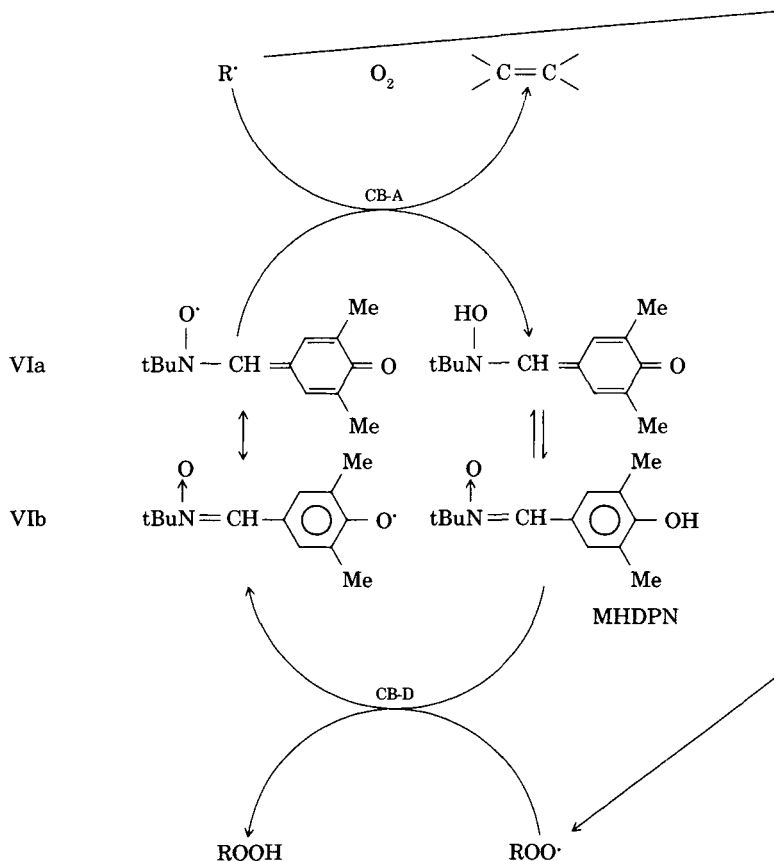
Nitrones do not normally react with alkylperoxyl radicals, but phenolic nitrones of structure V, X = OH, have been shown to be effective inhibitors for the autoxidation of cumene initiated by an alkyl radical generator (AIBN).¹⁷ Figure 10 confirms that nitroxyl radicals are formed from MHPBN by hydrogen abstraction by alkylperoxyl under conditions where the concentration of alkyl radicals is vanishingly small. Nevertheless, in spite of the obvious facility of reaction 1, Figures 1–4 show that the phenolic nitrones cause some relinking of broken polymer chains during processing. This indicates competition between hydrogen abstraction [scheme 2, reaction (a)] and crosslinking [scheme 2, reaction (b)] under these conditions¹⁸:



Scheme 2. Competitive reactions of a phenolic nitron in polypropylene during processing

These complementary reactions should give rise to different nitroxyl radicals, VIb and VII, of which VII rather than VIb might be expected to be formed only in the early stages of processing when the macroalkyl radical concentration is high.⁵ Further work is required to establish this.

The mechanism that has been proposed previously to account for the activity of nitroxyl radicals as melt stabilizers for polypropylene is modified in scheme 3 for the phenoxyl/nitroxyl radical, VI:



Scheme 3. Catalytic mechanism involved in the mechanoantioxidant and photoantioxidant action of phenolic nitrones

This scheme demands the formation of unsaturation in the polymer chain, and this has been observed previously in the case of hindered piperidinoxyl radicals under similar conditions.⁵ However, no unsaturation was observed in the polymer in the present study. This may be because nitrones react rapidly with unsaturation at elevated temperatures by a 1,3 addition reaction.¹⁹ On the other hand, unsaturation was detected in the polymer under conditions of UV irradiation, but the amount decreased with increasing concentration of nitrone initially added to the polymer (see Fig. 9), suggesting that even under these conditions, nitrones when present in excess, are able to react with unsaturation in the polymer. Hydroxylamines, the other products formed in the CB-A reaction (scheme 3), were also detected in the polymer, suggesting that these had at least a transient existence, although it seems likely that the tautomeric form (i. e., the parent phenol MHDPN; see scheme 3) is the predominant species.

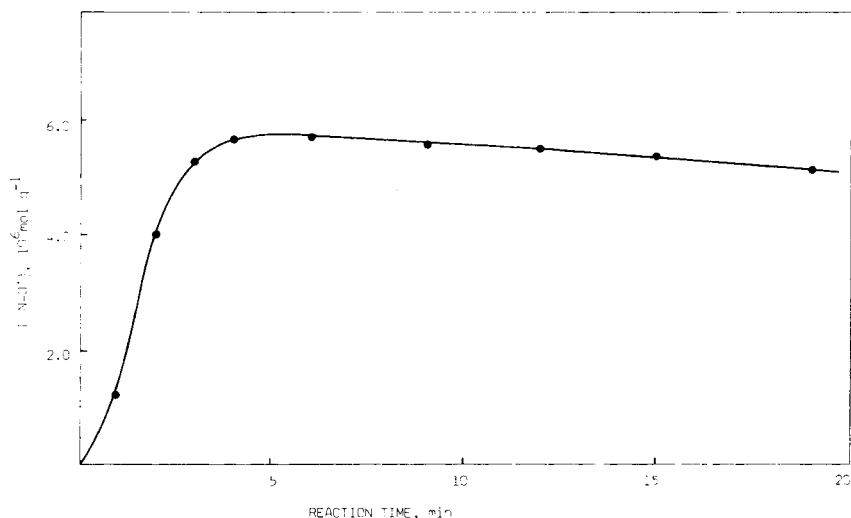
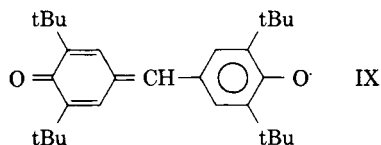


Fig. 11. Formation of nitroxyl radicals from MHDPN (10^{-3} mol/100 g) in *p*-xylene at 110°C in the presence of AIBN (10^{-3} mol/100 g) and in an oxygen atmosphere.

The phenoxy/nitroxyl radical, VI, showed the typical triplet splitting and g value of a nitroxyl. Furthermore, it showed a strong IR absorbance at 1655 cm^{-1} characteristic of quinonoid compounds, suggesting again that VIa is the major species present.

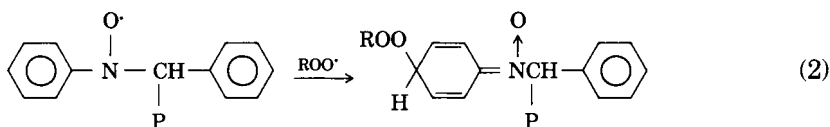
All the phenolic nitrones absorbed strongly in the UV in the region 285–325 nm and were rapidly destroyed in the polymer film (see Fig. 8). In this respect they resemble galvinoxyl, IX, which is a highly effective melt stabilizer for PP^{13,20} and is also an antifatigue agent for rubber,²¹ but is only moderately effective as a UV stabilizer for PP due to its relatively low photostability²²:



Both VI and IX contain a similar conjugated system which is the probable cause of their photoinstability. Figure 8 shows that the decay of VI to a very low level in the polymer corresponds to the induction period to photooxidation. However, the phenolic nitrone itself is somewhat more stable than the radical under these conditions, and the rate of photooxidation at the end of the induction period must reflect the slow conversion of MHDPN to VI.

Figure 8 also shows that the nitroxyl radical is substantially removed from the polymer by solvent extraction, indicating that the radical is combined with the polymer to only a minor extent. This is confirmed by the marked reduction in its photoantioxidant activity on extraction (see Table II). The same correlation is found for the thermal antioxidant activity of HDPN before and after extraction (see Table III).

It is clear from Table III that the partially hindered phenolic nitrones are much more effective as thermal antioxidants than the simple nitrones, DPN and PBN. The virtual absence of antioxidant activity of the latter may be due in part to the higher volatility of the low molecular weight compounds, but it also seems likely that it is partly due to the inability of the nonphenolic nitrones to participate in reaction (a) in scheme 2. The absence of chain-breaking donor (CB-D) activity also accounts for the relative ineffectiveness of PBN as a melt stabilizer (see Fig. 2). DPN is somewhat more effective (see Fig. 1) since, like other aryl nitroxyls, but unlike the aliphatic nitroxyls, it has the ability to scavenge alkylperoxyl radicals through the aromatic ring, reaction 2:



Similarly, the effectiveness of MDPN and NDPN as photoantioxidants compared with the *tert*-alkyl nitrones may be associated with the same ability to scavenge alkylperoxyl radicals.

CONCLUSIONS

The aldonitrones form nitroxyl radicals during processing in PP, and their powerful melt stabilizing effect is almost certainly due to their ability to participate in a catalytic (CB-A/CB-D) process with the cognate hydroxylamine. They are less effective as UV stabilizers than other nitroxyl generators, probably due to the photoinstability of both the nitroxyl and the parent phenolic nitron.

The phenolic nitrones are also effective thermal antioxidants, but the simple nitrones which do not contain a chain breaking electron donor (CB-D) function are ineffective.

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