NEW METHODS OF STABILISING POLYPROPYLENE AGAINST THE DELETERIOUS EFFECTS OF LIGHT

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Summary

The effects of C-nitroso compounds, nitrones and N-nitrosamines on the melt stabilisation, thermal and photo-oxidation have been studied under a variety of processing conditions. The stabilising effects of these compounds were found to be strongly dependent on the amount of oxygen present in the mixture and were shown to be due to termination of macro-alkyl radicals.

The mechanism of nitroxyl radical action has been investigated and a cyclic regenerative process involving both chain-breaking electron acceptor (CB-A) and chain-breaking electron donor (CB-D) processes has been proposed.

Aliphatic and aromatic nitroso compounds were found to be effective melt stabilisers. Some nitroso compounds (e.g. tetramethylnitrosobenzene, nitroso-tert-octane) cause cross linking of the polymer, whilst others, notably nitroso-tert-butane and nitrosobenzene did not. Aliphatic nitroso compounds were much more effective U.V. stabilisers than the aromatic derivatives.

All nitrones examined were effective melt stabilisers in a closed mixer but phenolic nitrones were also found to be good melt stabilisers in an excess of oxygen and most were found to cause cross-linking. Nitrones were less effective U.V. stabilisers than aliphatic nitroso compounds possibly due to the formation of quinonoid structures.

N-nitrosamines were effective melt stabilisers only in the presence of limited amounts of oxygen. They were photo-stabilisers and again, this activity was found to be dependent on the nitroxyl radicals formed during processing.

All aliphatic and cyclo-aliphatic N-nitrosamines were ineffective thermal antioxidants, whereas diphenylnitrosamine was a very effective antioxidant.

Key Words

POLYPROPYLENE, BOUND NITROXYL, MELT STABILISATION,
PHOTO-STABILISATION, SYNERGISM

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CHAPTER ONE

INTRODUCTION

1. OXIDATIVE DEGRADATION AND STABILISATION OF POLYPROPYLENE

Polypropylene contains many tertiary hydrogen atoms, each of which constitutes a weak spot open to attack by oxygen. This structure leads to a high sensitivity to oxidation and subsequent molecular breakdown. This is particularly severe at elevated temperatures and in the presence of ultra-violet light. Molecular breakdown occurs during processing of the polymer in the molten state, melt viscosity drops sharply during extrusion and injection molding operations and the molded products have low impact strength unless stabilized.

1.1 Thermal Oxidation

Polypropylene just like other polyolefins is oxidized according to a radical chain mechanism(1,2) with degenerate branching. The resulting radical can then combine with oxygen and an oxidation chain propagation sequence follows. The proposed scheme to explain the results of polypropylene oxidation may be summarised as follows:

$RH + O_2 \longrightarrow R. + .OOH$ (Initiation) (1)

$R. + O_2 \longrightarrow RO_2.$ (2)

$RO_2. + RH \longrightarrow RO_2H + R.$ (Propagation) (3)

$2RO_2\cdot \longrightarrow$ Products (Termination) (4)

$R + ROO \longrightarrow ROOR$

$R. + R. \longrightarrow R - R$

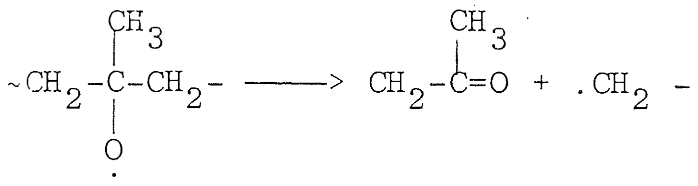
As the hydroperoxide yield increases (reaction 3) the rate of chain initiation and hence the rate of oxidation will increase:

$ROOH \longrightarrow RO. + .OH$ (5)

or

$2ROOH \longrightarrow RO. + H_2O + ROO^{\bullet}$ (6)

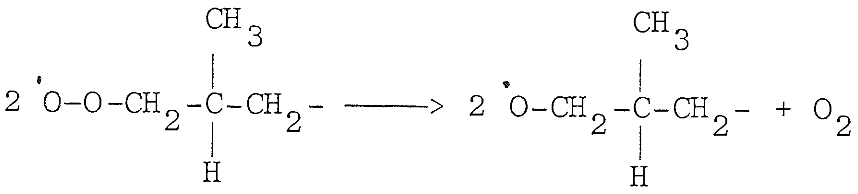
Numerous authors$^{(4-6)}$ have reported that the tertiary alkoxy radical thus formed undergoes cleavage; such cleavage would produce a ketone and a primary alkyl radical.



$$\sim CH_2-\overset{CH_3}{\underset{O\cdot}{C}}-CH_2- \longrightarrow CH_2-\overset{CH_3}{C}=O + .CH_2 -$$

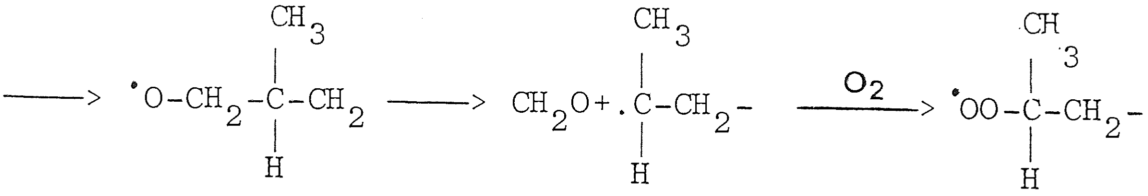
(7)

Formaldehyde and acetaldehyde are primary oxidation products in the oxidation of isotatic polypropylene. These volatile aldehydes can be accounted for in the following reactions$^{(7)}$.



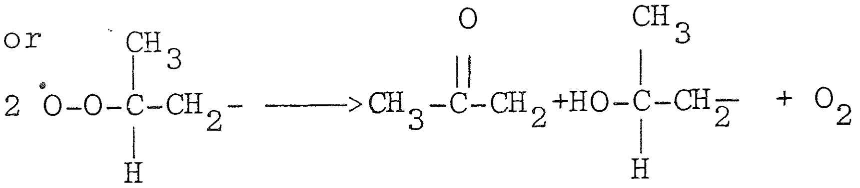
$$2\,{}^{\bullet}O-O-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2- \longrightarrow 2\,{}^{\bullet}O-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2- + O_2$$

(8)



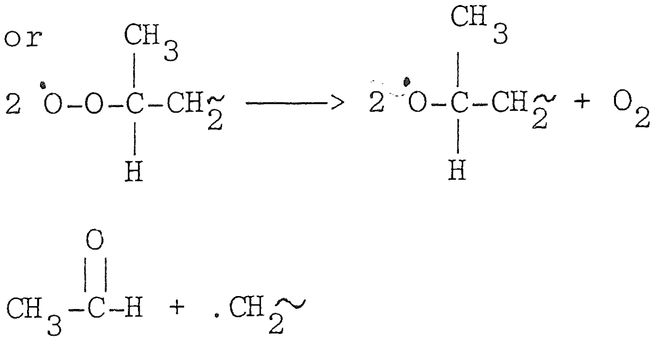
$$\longrightarrow {}^{\bullet}O-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2 \longrightarrow CH_2O+.\overset{CH_3}{\underset{H}{C}}-CH_2- \xrightarrow{O_2} {}^{\bullet}OO-\overset{CH_3}{\underset{H}{C}}-CH_2-$$

or



$$2\,\dot{O}-O-\overset{CH_3}{\underset{H}{C}}-CH_2- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2+HO-\overset{CH_3}{\underset{H}{C}}-CH_2\!\sim + O_2 \qquad (9)$$

or

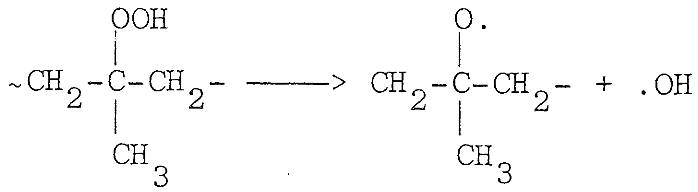


$$2\,\dot{O}-O-\overset{CH_3}{\underset{H}{C}}-CH_2\!\sim \longrightarrow 2\,\dot{O}-\overset{CH_3}{\underset{H}{C}}-CH_2\!\sim + O_2 \qquad (10)$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H + .CH_2\!\sim$$

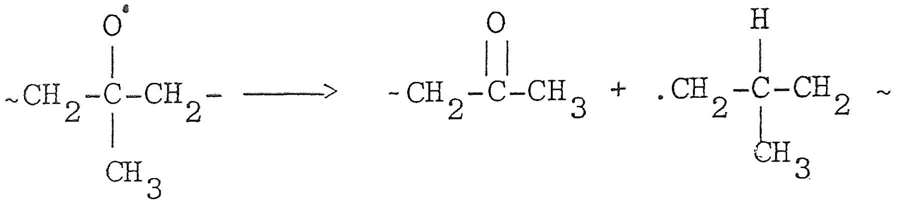
These oxidative unzipping reactions may be rapid enough to form several molecules of aldehydes before two primary, two secondary or a primary and a secondary peroxy radical interacts to give termination.

Schooten and Wijga(8) have provided strong evidence that the degradation of polypropylene in the absence of oxygen at temperatures around 250°C is due to hydroperoxide already present in the polymer. They concluded that the polymer molecule itself would be stable. The authors have suggested the following reaction mechanism to explain their results of degradation experiments. The initiation reaction in the thermal decomposition of the hydroperoxide:



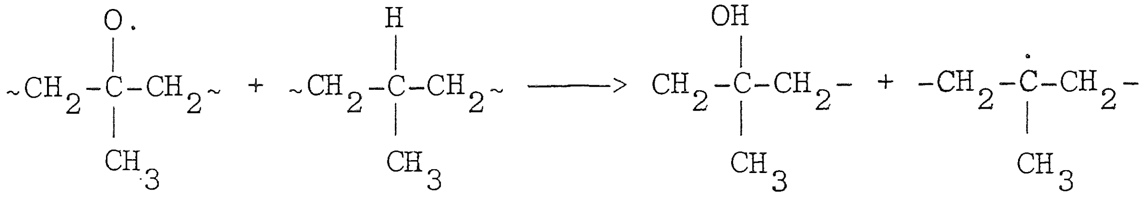
$$\sim CH_2-\overset{OOH}{\underset{CH_3}{C}}-CH_2- \longrightarrow CH_2-\overset{O.}{\underset{CH_3}{C}}-CH_2- + .OH \qquad (11)$$

The alkoxy radical formed may react further in two ways, viz:



$$\sim CH_2-\overset{\overset{\textstyle O^{\bullet}}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2- \longrightarrow -CH_2-\overset{\overset{\textstyle O}{||}}{C}-CH_3 + .CH_2-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2 \sim \qquad (12)$$

The alkoxy radical may also react with another molecule without giving rise to degradation, viz by hydrogen abstraction and formation a tertiary alcohol:



$$\sim CH_2-\overset{\overset{\textstyle O.}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2\sim + \sim CH_2-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2\sim \longrightarrow CH_2-\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2- + -CH_2-\underset{\underset{\textstyle CH_3}{|}}{\dot{C}}-CH_2- \qquad (13)$$

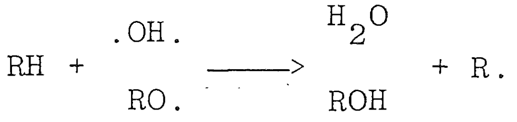
1.2 Photo-oxidation

The U.V. light absorbed by the polyolefines between 300 and 340 nm is commonly attributed to absorption by peroxide and carbonyl groups(9,10). These groups are introduced into the polymer by air oxidation during polymerization or processing (moulding, extrusion, spinning, etc.), or by very slow metal catalysed oxidation at room temperature(11). Photo-oxidation involves the same reaction sequence of thermal oxidation including the three stages, i.e. initiation, propagation and termination, but the rate of initiation is much higher in the case of photo-oxidation than it is for thermal oxidation, and hence the rate of termination is also higher, consequently the length of the kinetic propagation sequence is shorter(12). Photo-chemical reactions in polymers may be better explained after the effect of light on hydroperoxides and carbonyl groups has been discussed.

1.2.1 Photo-degradation due to hydroperoxide groups:

Hydroperoxide has been considered the key initiators for photo-initiated degradation and the mechanism can be summarised as follows:

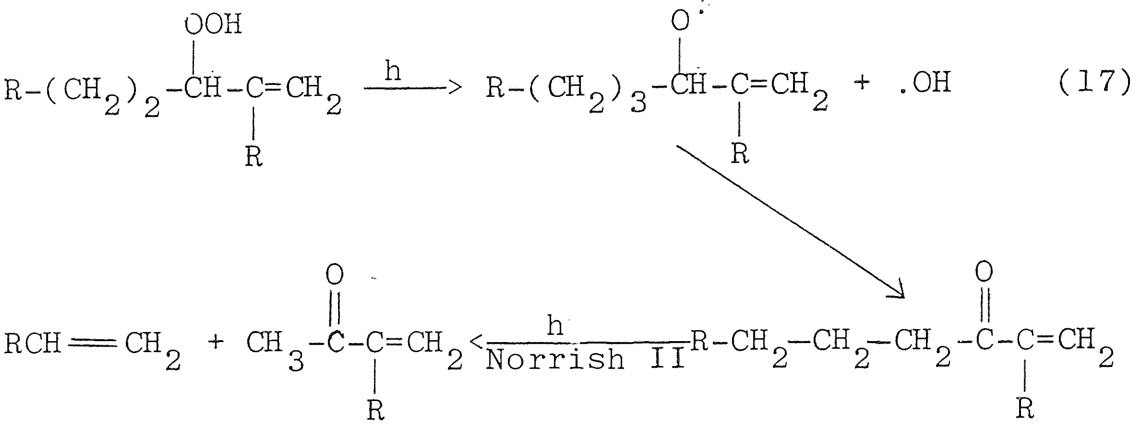
$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO.} + \mathrm{.OH} \qquad \text{(initiation)} \qquad (14)$$



$$\mathrm{RH} + \begin{matrix}\mathrm{.OH.} \\ \mathrm{RO.}\end{matrix} \longrightarrow \begin{matrix}\mathrm{H_2O} \\ \mathrm{ROH}\end{matrix} + \mathrm{R.}$$

It has been shown(13) that polypropylene is markedly sensitized to photo-oxidation by the thermal processing involved in its conversion to fabricated products. The absence of significant carbonyl formation during the early stages of this thermal oxidation suggests that hydroperoxides rather than carbonyl compounds are responsible for the photo-activation process. This suggestion has also been proved by Scott and Chakraborty(14). This is consistent with the study of other polyolfines(15,16). Although there is little evidence that carbonyl compounds participate in photo-initiation process during the early stages of photo-oxidation, the observations indicated the carbonyl groups play some part as a secondary photo-initiator during the latter stages of photo-degradation(15,17).

Scott has also suggested(16) that unsaturated and not saturated hydroperoxide are mainly responsible for the photo-initiated degradation of polyethylene. He considered that only in the later stages of photodegradation the Norrish type II mechanism of carbonyl group photolysis became an important process

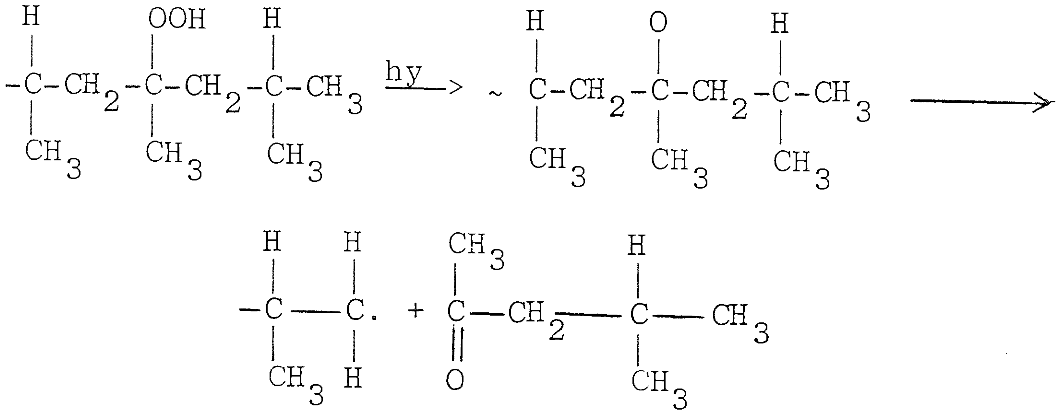


$$R-(CH_2)_2-\overset{OOH}{CH}-\underset{R}{C}=CH_2 \xrightarrow{h} R-(CH_2)_3-\overset{O^{\cdot}}{CH}-\underset{R}{C}=CH_2 + .OH \qquad (17)$$

$$RCH=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{C}=CH_2 \xleftarrow[\text{Norrish II}]{h} R-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\underset{R}{C}=CH_2$$

Therefore Scott concluded that hydroperoxides formed during thermal processing of the polymer are the precursors to carbonyl formation and hence primarily involved in initiation.

Wiles et al$^{(18)}$ have shown that the quantum efficiency of radical initiation for polypropylene hydroperoxide is much higher than it is for the derived carbonyl compounds, such high quantum yield would cause appreciable scission in the polymer. The authors postulated that photolysis of polypropylene hydroperoxide generated by prior thermal oxidation of the polymer is a key step in the photodegradation mechanism:

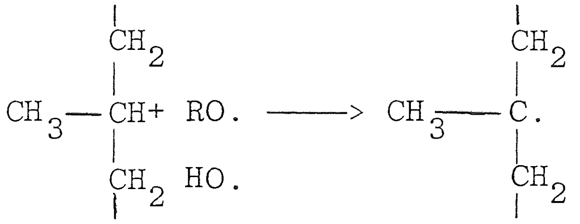


$$-\underset{CH_3}{\overset{H}{C}}-CH_2-\underset{CH_3}{\overset{OOH}{C}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_3 \xrightarrow{hy} \sim \underset{CH_3}{\overset{H}{C}}-CH_2-\underset{CH_3}{\overset{\dot{O}}{C}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_3 \longrightarrow \qquad (18)$$

$$-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}. + \underset{O}{\underset{\|}{\overset{CH_3}{C}}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_3$$

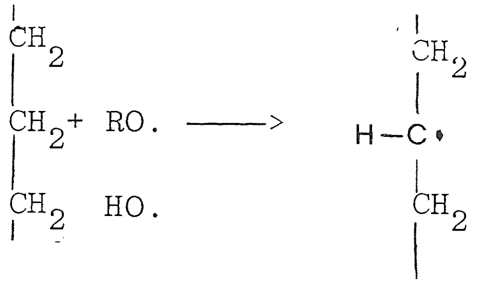
Their postulation of hydroperoxide initiated photodegradation of polymer was later supported by evidence from E.S.R. studies.

Veseley et al$^{(19)}$ suggested that free radicals can attack the polypropylene in the middle of the chain and interpreted the greater light stability of polyethylene compared with polypropylene in terms of the two radical reactions



$$\begin{array}{c} | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_3{-}CH} + \mathrm{RO.} \\ | \\ \mathrm{CH_2}\;\; \mathrm{HO.} \\ | \end{array} \longrightarrow \begin{array}{c} | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_3{-}C.} \\ | \\ \mathrm{CH_2} \\ | \end{array}$$

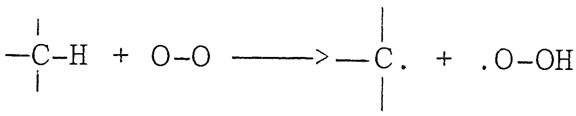
fast (19)



$$\begin{array}{c} | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} + \mathrm{RO.} \\ | \\ \mathrm{CH_2}\;\; \mathrm{HO.} \\ | \end{array} \longrightarrow \begin{array}{c} | \\ \mathrm{CH_2} \\ | \\ \mathrm{H{-}C\cdot} \\ | \\ \mathrm{CH_2} \\ | \end{array}$$

slow (20)

In addition polypropylene probably shows greater readiness to form hydroperoxide by direct reaction with oxygen.



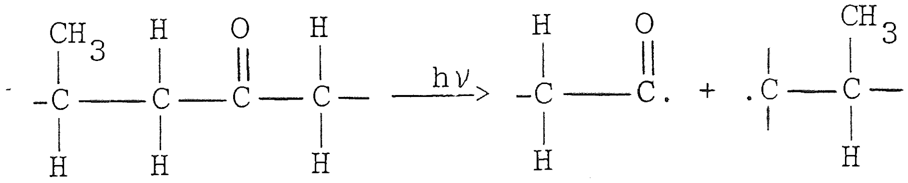
$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{H} + \mathrm{O{-}O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{C}}}. + \mathrm{.O{-}OH} \qquad (21)$$

1.2.2 Photodegradation due to carbonyl groups

Study of the photochemical reactions of carbonyl compounds may provide some insight into the relative importance of the chemical and physical processes. The known photochemistry in the liquid phase of aliphatic ketones(20-25) containing hydrogen on the carbon atom in the α position with respect to C= O group (simulating polyolefines with carbonyl group in the polymeric chain) suggests that the photochemical reactions to be considered in the mechanism of oxidative photodegradation are Norrish I and Norrish type II.

(a) Norrish type I:

This process leads to the formation of free radicals



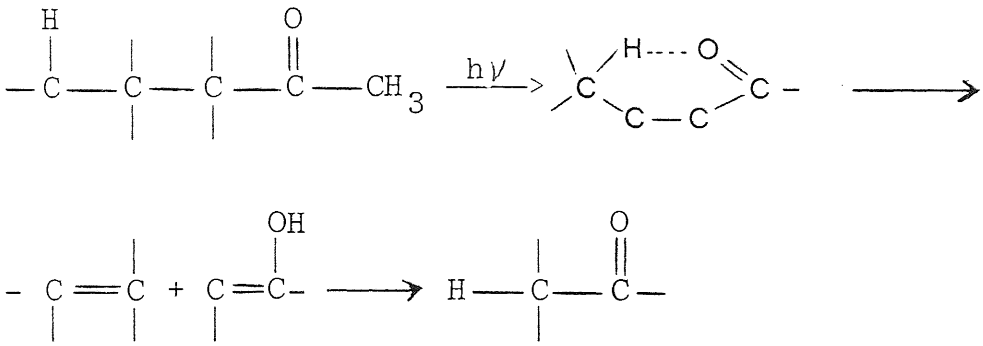
$$-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}- \xrightarrow{h\nu} -\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}}-\overset{CH_3}{\underset{H}{C}}-$$

(22)

It has been shown(25) that the excited states of carbonyl groups are the precursors of the reaction.

(b) Norrish type II

This process only occurs when the Ketone possesses at least one hydrogen atom on the α-carbon with respect to the carbonyl group.



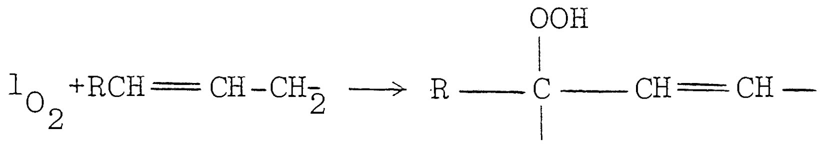
(23)

The Norrish type II reaction proceeds by intermolecular hydrogen transfer to yield one molecule of olefin and one enol which then rearranges to ketone(26-27). It was suggested that the hydrogen transfer takes place via a six-membered cyclic intermediate. The Norrish type II process does not directly produce free radicals but it is considered to be the most important reaction in the mechanism of the oxidative photodegradation of polyolefines containing carbonyl groups with random distribution along the hydrocarbon chain.

Hartly and Guillet(28) studied the photolysis of ethylene-carbon monoxide copolymer, which is a ketone polymer. They explained the products obtained due to Norrish type I and type II reaction of ketones.

Winslow et al(29) have suggested that the carbonyl groups can sensitise the photo-oxidation of polyethylene in which the C=O group is activated by U.V. light to the singlet state, and then crosses over to a longer life triplet state. It is then able to activate an oxygen molecule to excited singlet oxygen ($^1O_2$). This might attack the unsaturated bonds in the polymer, formed by photolytic breakdown of ketone groups by Norrish type II.

$$>C=O \xrightarrow{h\nu} >C=O^* \xrightarrow{O_2} >C=O + {}^1O_2 \qquad (24)$$



$${}^1O_2 + RCH=CH-CH_2 \longrightarrow R-\overset{\overset{\displaystyle OOH}{|}}{\underset{|}{C}}-CH=CH- \qquad (25)$$

Foot and Wexler(30) have proposed a similar mechanism for the oxidation of unsaturated hydrocarbon.

Gollnick and Schenck(31) have suggested that an excited C=O group can remove a H atom directly from the hydrocarbon chain, a process which would also contribute to the greater light sensitivity of polypropylene compared with polyethylene owing to the large number of tertiary carbon atoms in polypropylene.

1.2.3 Photodegradation Due to Metal Impurities

Polypropylene always contains transition metal residues, which cannot easily be removed.

It has been suggested(32) that the transition metal residue in the polymer acts as sensitiser in photo-oxidation of polyolfins according to a mechanism that should involve light absorption and the production of free radicals through photo-excited electron transfer from the anion to the cation

$$M^{n+}X^{-} \xrightarrow{h\nu} [M^{(n-1)*}X\cdot] \longrightarrow M^{(n-1)^{+}} + \dot{X} \qquad (26)$$

The free radicals should initiate the oxidation of the substrate.

The catalytic effect of the metal residues on hydroperoxide decomposition involved oxidation-reduction reactions to produce free radicals from hydroperoxide depending on the metal and its state of oxidation

$$ROOH + M^{n+} \text{ —— } RO. + M^{(n+1)} + OH^{-} \qquad (27)$$

$$ROOH + M^{(n+1)} \longrightarrow RO_2. + M^{n+} + H^{+} \qquad (28)$$

When the metal has two valence states of comparable stability, both reactions will occur and a trace amount of the metal can convert a large amount of hydroperoxide to free radicals according to the sum of the two reactions(34). In the case of cobalt for example, the equation is the same as for uncatalysed bimolecular hydroperoxide decomposition, but the rate is much faster and the reaction occurs readily at room temperature.

$$2ROOH \xrightarrow{Co^{+2}/Co^{+3}} RO. + RO_2. + H_2O \qquad (29)$$

1.3 Stabilisation of Polypropylene

1.3.1 Thermal Stabilisation

The thermal oxidation of polypropylene leads to the formation of hydroperoxides by means of which a chain process is effected. Since the reaction proceeds with the participation of free radicals, it is natural to use inhibitors (antioxidants) to suppress the development of a radical chain. Since ROOH is easily broken down into free radicals which contribute to oxidation process, a complementary process is used to decompose the ROOH into inert compounds.

1.3.1.1 Mechanism of Chain-breaking Antioxidants

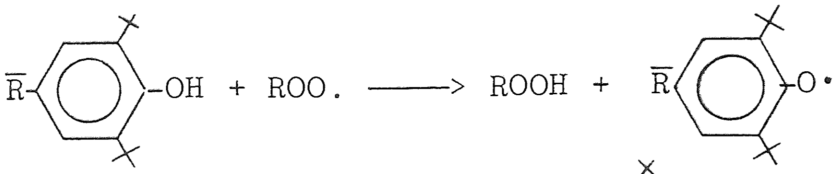
Consideration of the free radical chain mechanism of autoxidation suggests the use of materials capable of reacting with either R. or RO_2. free radicals to interrupt the propagation cycle and thus retard the oxidation process. Most antioxidants of this type react with peroxy radicals in some way to terminate the kinetic chain. There are two familiar kinds of chain breaking antioxidants which can be distinguished according to the way they react; (1) hydrogen or electron donors and (2) free radical traps or electron acceptors.

The presence of a reactive N-H and O-H functional groups in the hindered secondary amine and phenol types of antioxidants suggest that they compete with the polymer for the RO_2. radical, and thus terminate a kinetic chain by transfer of hydrogen to form ROOH and a radical derived from the antioxidant. The antioxidant radical will then function as a radical trap and terminate a second kinetic chain according to the following general reaction

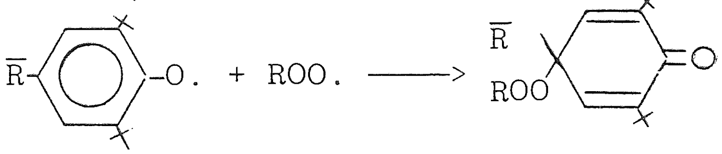
$$ROO. + AH \longrightarrow A. + ROOH \qquad (30)$$

$$ROO. + A. \longrightarrow ROOA \qquad (31)$$

In reaction 30 the labile hydrogen donor or chain terminator (AH) reacts with the peroxy radical to form a molecule of hydroperoxide and as a by-product the radical A., the antioxidant radical (A.) may react with peroxy radical through radical trapping (35) For example, hindered phenols terminate peroxy radicals in a stoichiometric fashion



(32)



(33)

It has been reported that the catalytic inhibition(36-39) of the autoxidation of hydrocarbon at high temperature by the secondary aromatic and aliphatic amines, is attributed to the radical scavenging efficiencies of these compounds. The use of electron spin resonance(40-42) has resulted in the observation and identification of the nitroxyl radical as a result of the interaction of the secondary amines with peroxy radicals. It was found that the reaction of ROO. with the secondary amines proceeded according to reactions leading to the formation of nitroxyl radical.

$$>NH + ROO. \longrightarrow ROOH + >N. \qquad (34)$$

$$>N. + ROO. \longrightarrow RO. + >N\text{-}O. \qquad (35)$$

Later it was revealed(43) that the interaction of $>NO.$ with R. radicals occurs which has been confirmed by direct experiments.

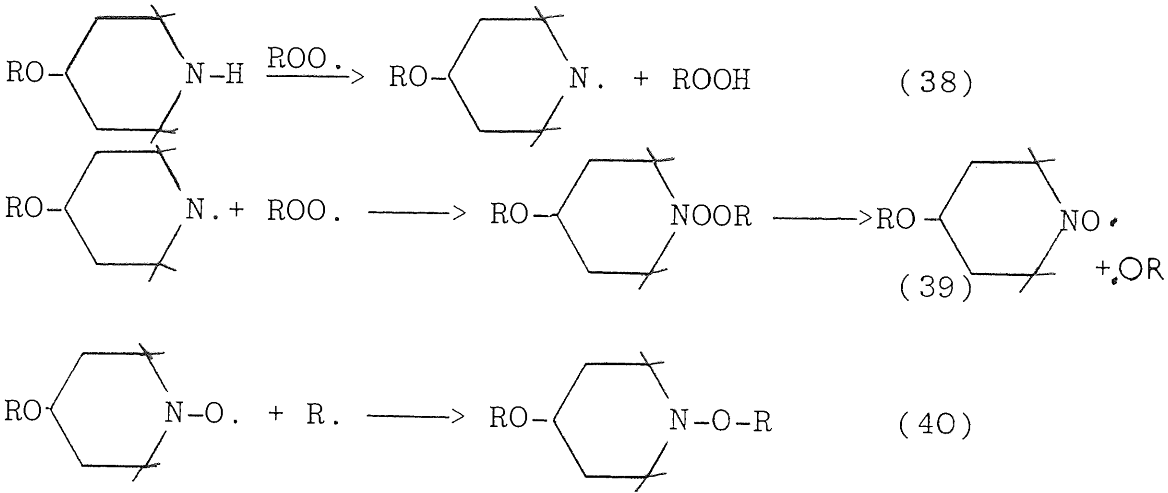
$$R. + >NO. \longrightarrow RON< \qquad (36)$$

Thus, when amines are used, the oxidation chains can be terminated not only on account of the reaction of hydrogen transfer according to reaction (34), but also by reactions of disproportionation (35) and recombination (36).

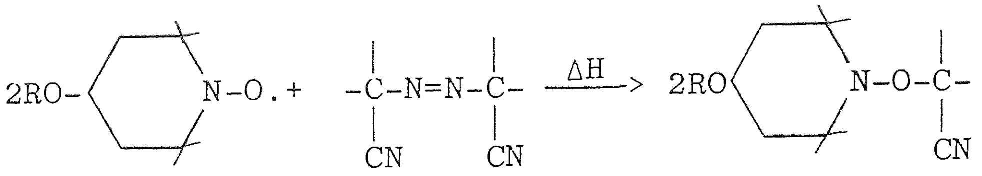
The inhibition effect$^{(44)}$ of nitroxyl radicals of piperidine derivatives during the thermal oxidation of polymers has been investigated. The inhibition process is attributed to the trapping of active radicals by nitroxyl radicals$^{(45)}$.

$$>NO. + R. \longrightarrow NOR \xrightarrow{ROO.} >NO. + ROOR \qquad (37)$$

It has also been reported$^{(46-49)}$ that hindered piperidine derivatives can effectively stabilise polyolefines against photo-oxidation. They are converted rapidly to the corresponding nitroxyl radicals under oxidising conditions

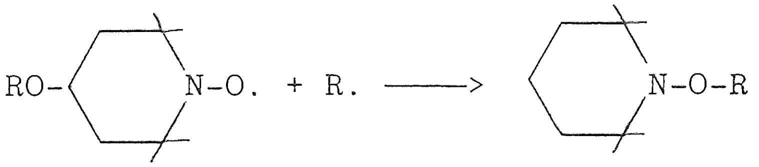


The reaction of nitroxyl radicals of pip dine derivatives with alkyl radicals (reaction 40) have also been confirmed by isolating coupled products due to the reaction of nitroxyl radicals with C-radicals derived from α, α azobis-isobutyronitrile

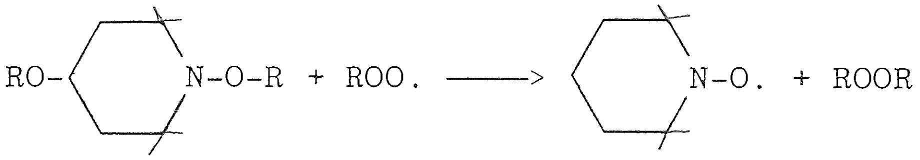


(41)

But the mechanism of the hindered piperidine light stabilisers appears to involve a nitroxyl regeneration mechanism(52,53). Rozantsev et al,(45) have suggested the cyclical mechanism for nitroxyl regeneration according to reaction 40 and 42



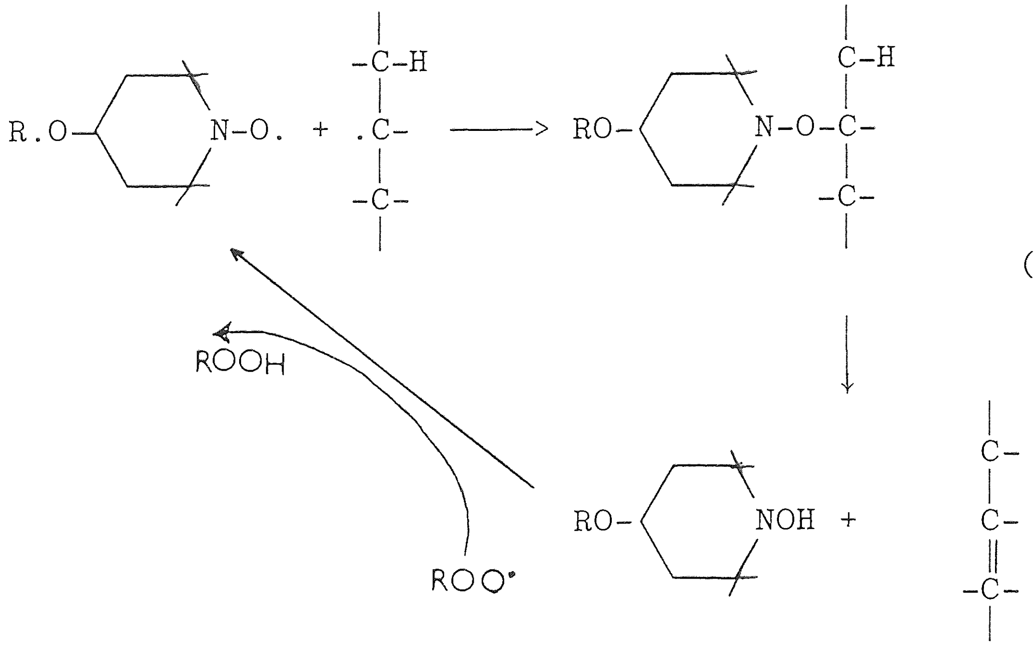
(40)



(42)

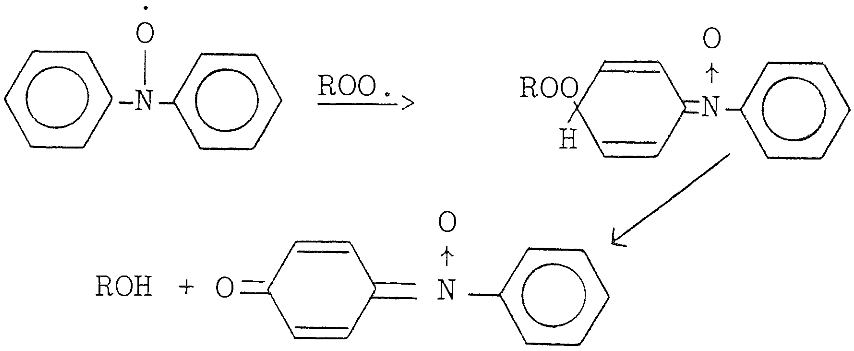
This suggestion is not entirely satisfactory since it has been shown that the rate of reaction (42) is not high enough to account for the observed facts. An alternative regeneration process(43,50,51) has been suggested with appropriate evidence that the nitroxyl is continuously regenerated in a cyclic mechanism involving the corresponding hydroxyl amine.

While the nitroxyl radicals derived from piperidine did not react with alkyl peroxy radicals(43,54) (ROO.), aromatic nitroxyl radicals such as diphenyl nitroxyl radicals do react with both alkyl radicals and peroxy



(43)

radicals(55). It is likely that the latter reaction involves an initial addition of the peroxyl radical to the aromatic ring to give eventually an p-benzoquinone-imine N-oxide and an alcohol



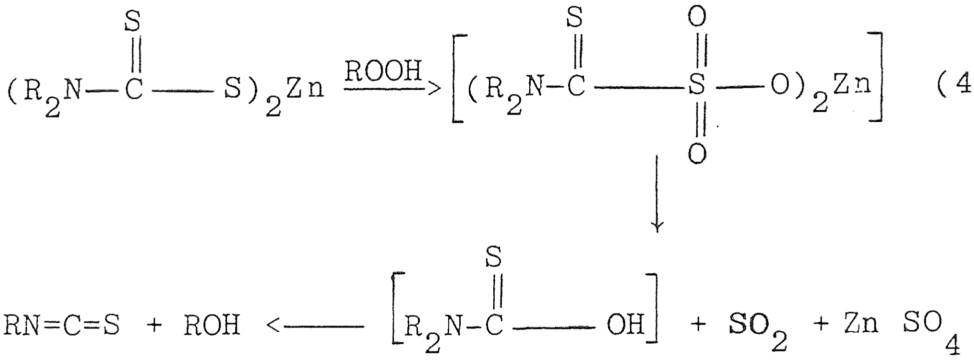
1.3.1.2 Mechanism of Stabilisation by Hydroperoxide Decomposers

It is now well-established that hydroperoxides are key initiators for the oxidative degradation of polymers. Decomposition of hydroperoxides into radicals is believed to be responsible for initiation of new oxidative chains, and hence autocatalysis. Thus any compound added to the system which might induce decomposition of the hydroperoxides into inert products would be an effective stabiliser.

The familiar classes of hydroperoxide decomposers are esters of phosphorous acid $(RO_3)P$, metal complexes of dialkyldithio carbamates $(R_2N\ C{-}S)_nM$,metal complexes of dialkyldithiophosphates $|(RO)_2{-}P{-}S|_nM$ and thiodipropionate esters $ROCO(CH_2)_2{-}S{-}(CH_2)_2COOR$. The other three classes are effective U.V. stabilisers(59).

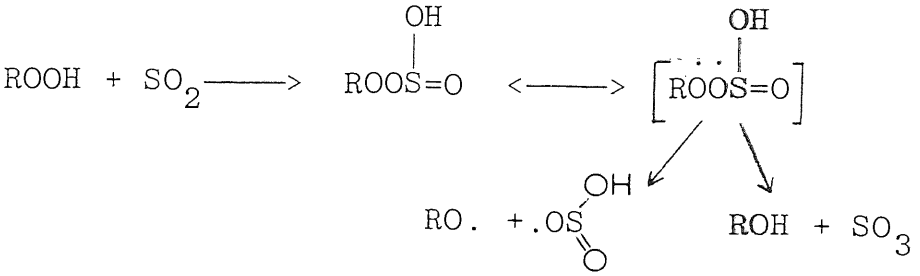
Dithiocarbamate transition-metal complexes vary in both thermal and U.V. stability. The nickel and cobalt complexes act as U.V. stabiliser because besides decomposing hydroperoxides they can also absorb U.V. light and re-emit the absorbed energy as thermal energy. The iron complexes of dithiocarbamates are much less stable to U.V. light and they behave as stabilisers or as activators, depending on their concentration(13). At low concentration they act as peroxide decomposers during processing and then become powerful U.V. activators.

Holdsworth(60) et al have studied the peroxide decomposing effect of metal diethyldithiocarbamate and they found the formation of sulphur dioxide and isothiocynate. It was suggested that the reaction sequence involved the formation of an unstable sulphate.



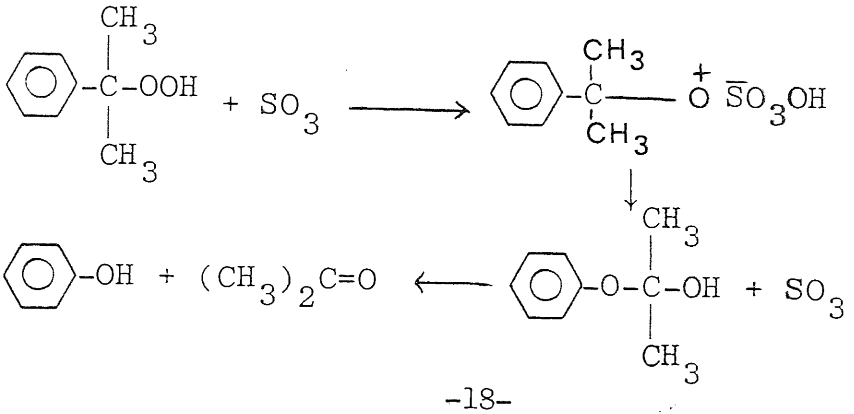
(45)

It has been proposed that SO_2 act as a catalyst for the decomposition of hydroperoxide to alcohols and ketones. Recently,(61) the evidence shows that sulphur dioxide is not a catalyst for the decomposition of hydroperoxide. It initially reacts with hydroperoxides stoichiometrically in a homolytic process, giving rise to sulphur trioxide (SO_3), which is a powerful catalyst for hydroperoxide decomposition.



(46)

The catalytic effect of sulphur trioxide on the decomposition of hydroperoxides can be accounted for on the basis of the following regenerative process



(47)

Ranaweera and Scott(62,63) have shown that nickel dibutyldithiocarbamate gives rise to a powerful catalyst for non-radical hydroperoxide decomposition; in the presence or absence of light and the mechanism appears to be similar. They have found also that nickel acetophenone oxime reacts stoichiometrically with hydroperoxide and the reaction involves the consumption of at least six molecules of hydroperoxide per molecule of nickel complex. The authors concluded that the nickel complex functions by an auto-synergistic mechanism involving hydroperoxide decomposition and U.V. screening.

Humphris and Scott(64) have investigated the effect of phosphorous compounds on the polyolefines and found the catechol phosphite esters are powerful stabilisers for polymer and appear to behave differently from simple alkyl or aryl phosphites in that they destroy hydroperoxides in a Lewis acid catalysed reaction, whereas the alkyl or aryl phosphite act stoichiometrically with hydroperoxide(65).

$$(RO_3)P + ROOH \text{ —— } (RO)_3P{=}O + ROH \qquad (48)$$

1.3.2 Photo-stabilisation of Polypropylene

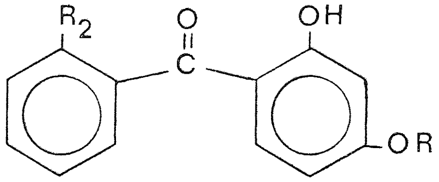
There are several ways in which a polymer can be protected from the action of U.V. apart from the obvious expedient of using an opaque screen or coating to prevent light from reaching the polymer. One way is to mix with the polymer a compound which will absorp most of the light and use up the energy in some way, which does not harm the polymer. To do this the stabiliser must usually have a very high absorption coefficient in the near U.V. range of spectrum. However, the requirement of a high absorption coefficient is not sufficient, since if the compound re-emits radiation of the same wavelength (fluorescence), it will be ineffective. It must have a route for dissipating the energy of U.V. which does not lead to the emission of harmful U.V. radiation or the formation of active chemical intermediates which might attack the polymer. U.V. stabilisers have been classified into four types, as follows:

(i) U.V. absorbers
(ii) Excited state quenchers
(iii) Peroxide decomposers
(iv) Chain-breaking agents.

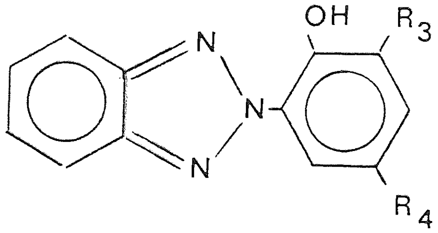
(i) Mechanism of Stabilisation by U.V. Absorbers

In this case the compounds added to the polymers preferentially absorb ultraviolet light. These compounds may become electronically excited and then emit the U.V. energy at nondestructive wavelength such as the infra red. The excited molecules may also release absorbed ultraviolet energy as fluorescence or phosphorescence which has less degradative effect.

The most effective compounds belonging to this class are 2-hydroxybenzophenones (I) and 2-hydroxybenzotriazoles (II).



(I)



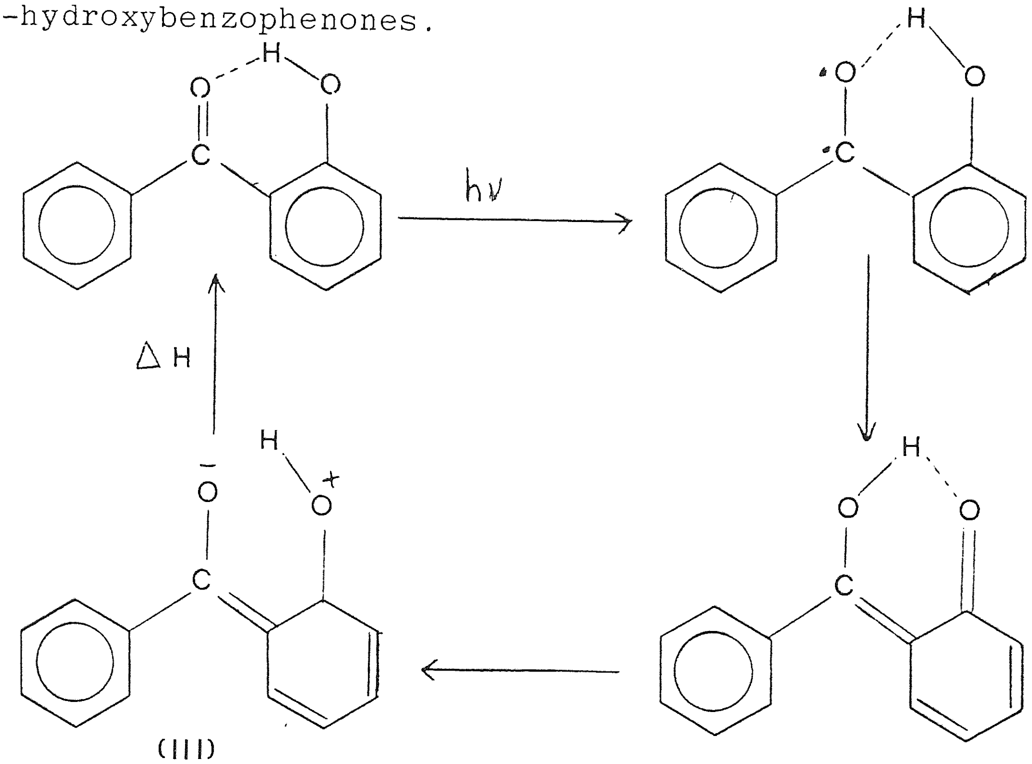
(II)

Where generally, R_1=n-alkyl, $R_2 = H_1R_3$ = t-butyl, R_4 = methyl, t-butyl.

A large number of investigations carried out on benzophenone compounds have indicated that the length of the alkyl group is of critical importance(66). It has been found that polyethelyene was better protected by long alkyl groups, the protection efficiency was attributed to better compatibility and probable reduction in migration. However, it has recently been shown(67,68) by compatibility and diffusion measurements on homologous series of 2-hydroxy-4-n-alkyloxy-benzophenones that in the case of isotatic polypropylene, migration decreases with increasing alkyl chain length R_1 and compatibility is practically independent of the chain length. In the case of high density polyethylene, diffusion is lower when the alkyl group is n-octyl and compatibility is better with longer side chains.

The effectiveness of orthohydroxybenzophenone in degrading electromagnetic energy without giving rise to free radicals or to other active forms is associated with the possible formation, through a six membered cycle, of an internal hydrogen bond between hydroxyl and carbonyl groups(69,70). The presence of this bond would allow energy transfer from the triplet state and hence formation of enolic quinone in the ionic form (III), by emission of degraded energy, the latter would reconduct to the ground singlet ketone.

The experimental evidence for this theory has come from nuclear magnetic resonance studies of a number of 2-hydroxybenzophenones.



(III)

As to 2-hydroxybenzotriazoles, it may be assumed that hydrogen bonds form between triazolic nitrogen and phenolic hydroxyl, thus creating an analogous mechanism for dissipation of the absorbed energy.

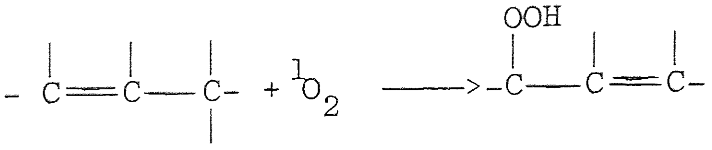
(ii) Mechanism of Stabilisation by Quenching of Excited States

This type of stabiliser depends on energy transfer from the excited states induced in the polymer molecule by the absorption of light. This involves a direct transfer of the excitation energy from the polymer molecule to an acceptor molecule which has excited state energy levels slightly lower than the polymer molecule(1). Since the quencher is raised to an excited state in the quenching process, the mere fact that a compound quenches a photosensitiser does not necessarily mean that this compound acts a a light protective agent. Only if the excited quencher can dissipate its accumulated energy harmlessly has it a chance to reduce photodegradation.

Heskins and Guillet concluded(66,71) the photoexcited state of carbonyl groups may indirectly initiate degradation by being quenched in its triplet state by oxygen to form excited singlet state oxygen.

$$>C = O^* + O_2 \longrightarrow >C = O\ (S.) + {}^1O_2 \qquad (24)$$

The singlet oxygen produced may react with double bonds of polyolefines and give hydroperoxide(72,75).



$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}- + {}^{1}O_2 \longrightarrow -\overset{OOH}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}- \qquad (25)$$

Therefore deactivation of excited states of chromopheres can be achieved in a number of ways and this adds a further complicating factor to the assessment of the stabilising action of the quencher. Therefore an effective quencher should be capable of deactivating the excited state of carbonyl group preventing Norrish type I or II reaction in the polymer, as well as deactivating ${}^{1}O_2$ preventing hydroperoxide formation by interaction of ${}^{1}O_2$ with double bonds.

Several workers(35,59,65) have reported that some nickel (II) chelates are effective quenchers of singlet oxygen, particularly those chelates with sulphur donor legands. In this case, therefore, a stabilising effect by the chelate could be possibly by acting as a singlet oxygen quencher preventing the attack by ${}^{1}O_2$ in the polymer matrix.

(iii) Effect of Hydroperoxide Decomposers on U.V. Stabilisation

Peroxide decomposers are reported to be U.V. stabilisers(9). The compounds which belong to this class are dithiocarbamate metal complexes, transition metal complexes of dithiophosphates and xanthates. The difference in behaviour of dialkyldithiocarbamate complexes of various transition metals in photo-oxidation is not a reflection of a difference in their activity as hydroperoxide decomposer since under thermal oxidative conditions they have very similar antioxidant activity and this appears to relate to the U.V. stability of the antioxidants, thus nickeldiethyldithiocarbamate is more U.V. stable than zincdiethyldithiocarbamate.

(iv) Effect of Chain Breaking Antioxidants on U.V. Stabilisation

It has been reported that the chain breaking antioxidants act as U.V. stabilisers. The mechanism of their action is not different from their effect as an antioxidant. Phenolic antioxidants have shown little value as light stabilisers due to their destruction under U.V. irradiation(53,78). Many workers have shown that hindered piperidines effectively stabilise polyolefins against photo-oxidation. It is generally agreed(45,53) that the starting structure of the hindered amines is converted to the corresponding nitroxyl (I) during thermal processing(49) and in the initial U.V. irradiation stages.

$$>NH \xrightarrow{\text{oxidation}} >N\text{-}O. \qquad (I)$$

Nitroxyl radicals are effective alkyl radicals scavengers to give a substituted hydroxylamine (II).

$$>NO. + R. \longrightarrow >NOR \qquad (II)$$

Nitroxyl radical regeneration has been suggested(45,53,76) to explain the ability of nitroxyl radicals to scavenge other radicals many times their stoichiometric equivalent.

1.4 Synergism and Antagonism

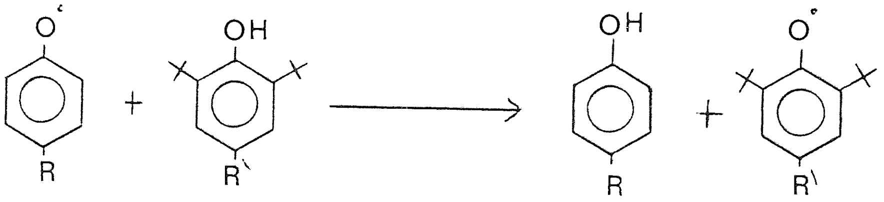
When two or more different types of antioxidants or/and U.V. stabilisers are used during polyolfine oxidation, the resistance of the substrate to oxidation may often be enhanced to an extent which is greater than would be expected based on strict addivity. The antioxidants or U.V. stabilisers are said to be synergistic towards one another. The opposite of synergism is termed antagonism.

Synergistic effects may occur when (1) chain breaking antioxidants are mixed with hydroperoxide decomposers; (2) a weak chain breaking antioxidant is mixed with a strong chain breaking antioxidant and (3) U.V. stabilisers are mixed with hydroperoxide decomposers or chain breaking antioxidants.

Case 1: Although the chain breaking antioxidant can inhibit the formation of long reaction chains, hydroperoxides can form by reaction $ROO^{\bullet} + AH \longrightarrow ROOH + A$. If this hydroperoxide then reacts with a peroxide decomposer to form inert products, rather than decomposing into free radicals, the two antioxidants act together in a synergistic manner. Furthermore, the chain breaking antioxidants prevent peroxy radicals from attacking the peroxide decomposer while the peroxide decomposer reduces the hydroperoxide that is formed from the hydrogen-donor chain breaking antioxidant.

Case 2: A mechanism which may be operative in case 2 involves the transfer of hydrogen atom from one inhibitor to another after the latter had lost its active hydrogen to a peroxy radical. In this manner an efficient antioxidant may be regenerated from its oxidation products by a hydrogen donor which may itself be a weak antioxidant. For example(77), a mixture of a non-hindered phenol and a hindered phenol can complement one another as illustrated by the following reaction

(50)



(51)

(33)

Case 3: Both the hydroperoxide and carbonyl groups might act as initiators in photoxidation of polymer, the excitation of carbonyl groups by U.V. irradiation leads to degradation of polymer by Norrish type I and II, this excitation of carbonyl group can be inhibited by U.V. stabiliser (by quenching or U.V. absorption). Hydroperoxides can form during oxidation process. If this hydroperoxide then reacts with hydroperoxide decomposer to form inert products, rather than decomposing into free radicals, the U.V. stabilisers and hydroperoxide decomposer act together in a synergistic manner. For example Chakraborty and Scott(78) have investigated the synergistic effect of U.V. absorber 2-hydroxy-4-octyloxy benzophenone with both hydroperoxide decomposer metal dithiocarbamate and a phenolic chain breaking antioxidant Iraganox 1076 during photoxidation of LDPE, the authors suggested the function of the U.V. absorber is at least in part, to remove the reactive species formed from the antioxidants during irradiation and this protects the dithiocarbamate from photolysis. By contrast, the peroxide decomposing and chain breaking antioxidants which are effective synergists during thermal oxidation of LDPE are antagonists during photo-oxidation. It is suggested that this may be due to sensitisation of the photolytic destruction of the dithiocarbamate, by oxidation products of the phenols.

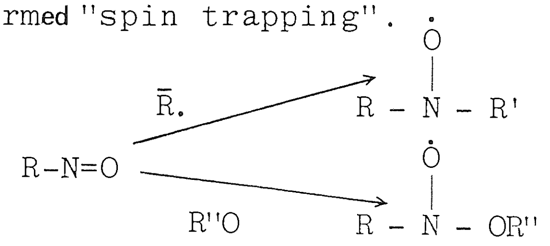
Antagonism between inhibitors suggests(79) that the two substances interact directly with one another. Thus when fairly acidic phenols and fairly basic amines are involved, antagonism may be due to the formation of a complex between the two inhibitors which is inactive towards peroxy radicals. Another possible explanation(80) for antagonism is that the radicals derived from the two inhibitors, may undergo a rapid cross termination reaction.

$$A. + \bar{A}. \longrightarrow A - \bar{A} \qquad (52)$$

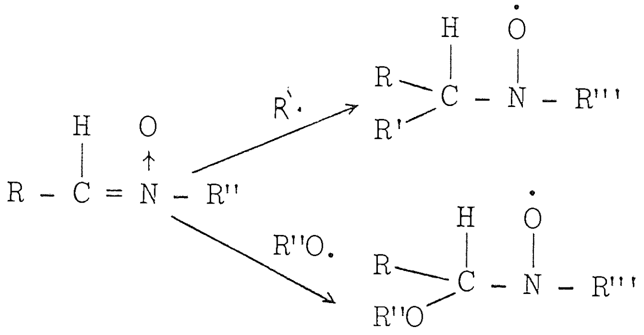
Consequently, both inhibitor radicals are prevented from reacting with peroxy radicals. Accordingly, the inhibiting power is decreased.

1.5 Review of C-nitroso, Nitrosoamine and Nitrone Compounds as Trapping Agents for Free Radicals

The reaction of nitroso and nitrone compounds with alkyl and alkoxy radicals to form substituted nitroxides(81,88) has been utilized by a number of authors, and the use of these compounds to detect and identify radicals present is termed "spin trapping".

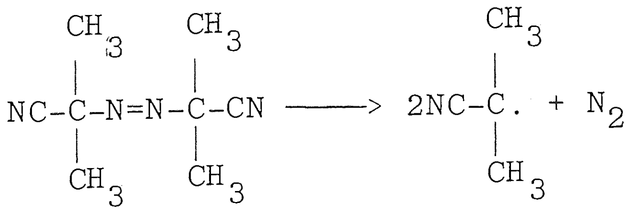


(53)



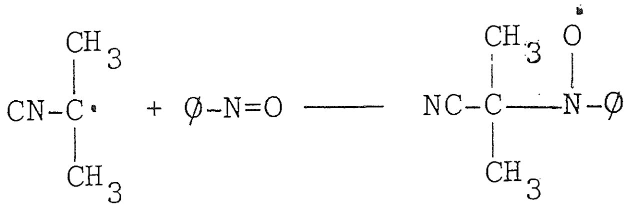
(54)

In the thermal reaction of azo-bis-isobutyronitrile (AIBN) with nitroso benzene(89), the nitroxyl is formed by addition of 2-cyano-2-propyl radicals to the nitroso compound.



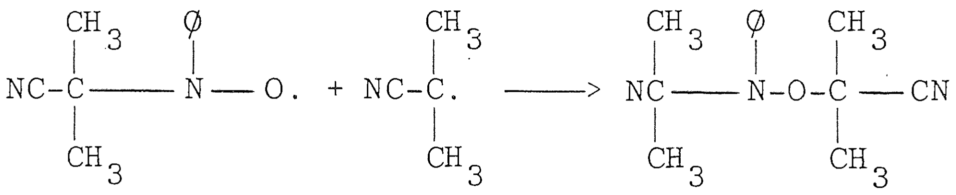
$$NC-\overset{CH_3}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-CN \longrightarrow 2NC-\overset{CH_3}{\underset{CH_3}{C}}. + N_2$$

(56)



$$CN-\overset{CH_3}{\underset{CH_3}{C}}\cdot + \phi-N=O \text{ ——— } NC-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\dot{O}}{N}-\phi$$

When an excess[(90)] of AIBN was reacted with nitrosobenzene, nitroxyl was not detected, but di-t-alkyl-phenylhydroxylamine obtained in a yield of 75%, probably formed by addition of second radical to the oxygen atom of the intermediary nitroxyl.

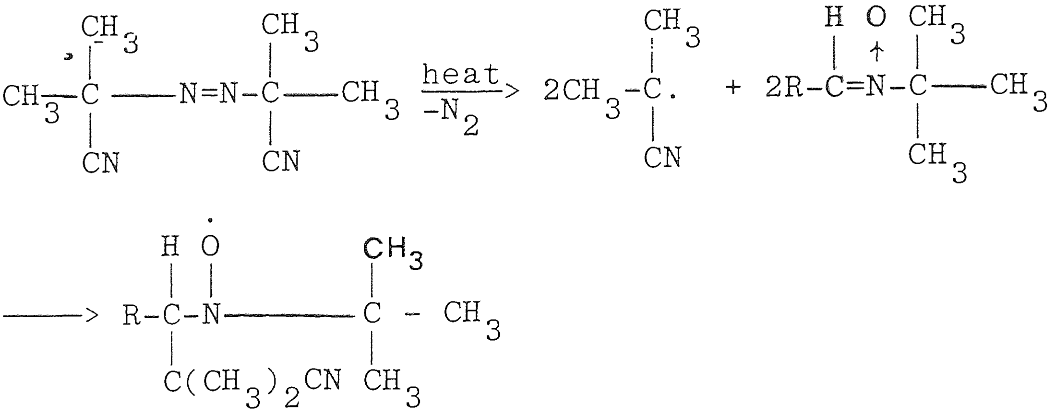


$$NC-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\phi}{N}-O. + NC-\overset{CH_3}{\underset{CH_3}{C}}. \longrightarrow \overset{CH_3}{\underset{CH_3}{NC}}-\overset{\phi}{N}-O-\overset{CH_3}{\underset{CH_3}{C}}-CN$$

(57)

The reaction of N-t-butyl-containing nitrones[(91)] with alkyl radicals gives stable nitroxyl radicals. Reaction of AIBN with phenyl-N-t-butylnitrone and similar compounds in xylene at 110°C gave stable nitroxyl radical derivatives.

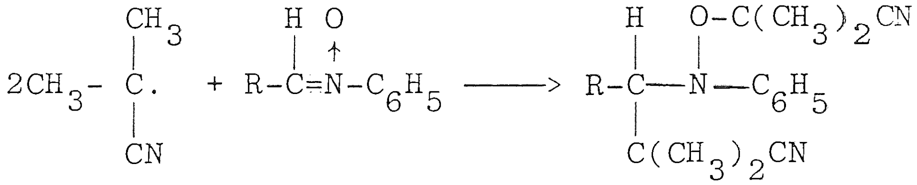
In another study[(92)] it has been shown that diphenyl-containing nitrones react with AIBN to form trisubstituted hydroxylamine through addition reactions. When AIBN was



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-N_2]{heat} 2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + 2R-\overset{H}{C}{=}\overset{\overset{O}{\uparrow}}{N}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad (58)$$

$$\longrightarrow R-\underset{C(CH_3)_2CN}{\overset{H}{C}}-\overset{\dot{O}}{N}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

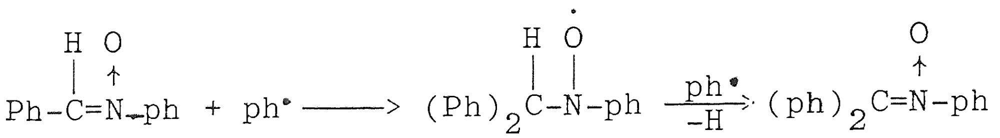
decomposed in xylene containing α,N-diphenyl nitrone at 90-110°C gave trisubstituted hydroxylamine in a 63%. Similar compounds gave the same addition reaction.



$$2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + R-\overset{H}{C}{=}\overset{\overset{O}{\uparrow}}{N}-C_6H_5 \longrightarrow R-\underset{C(CH_3)_2CN}{\overset{H}{C}}-\overset{O-C(CH_3)_2CN}{N}-C_6H_5 \qquad (59)$$

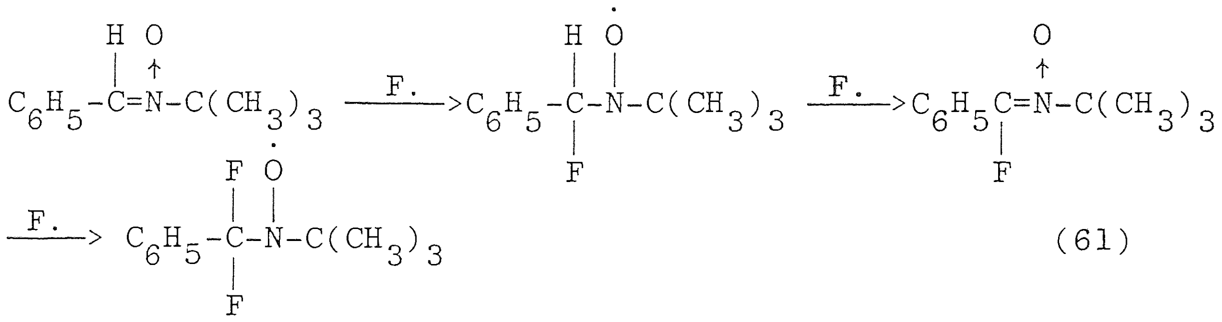
where R = C_6H_5 or $C_6H_5CH_2$.

As the addition products are trisubstituted hydroxylamines it is reasonable to consider that two radicals could add to the nitrones in a 1,3 fashion. It has been found that nitroxyl was formed instead of the expected trisubstituted hydroxylamine in the case of the N-t-butyl containing nitroxyl. These facts indicate that, in the reaction of the nitrones with free radicals, radicals first add to the carbon atom and then to the oxygen atom of the nitrone system. It has also been shown(93) that the reaction of α-N-diphenyl nitrone with phenyl radical gave α,α,N-triphenylnitrone(ketonitrone) through nitroxyl radical from which reactive phenyl radical abstracts the tertiary hydrogen atom to give a new ketonitrone.



$$\mathrm{Ph{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}ph} + \mathrm{ph}^{\bullet} \longrightarrow \mathrm{(Ph)_2\overset{\overset{H}{|}}{C}{-}\overset{\overset{\dot{O}}{|}}{N}{-}ph} \xrightarrow[-H]{ph^{\bullet}} \mathrm{(ph)_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}ph} \qquad (60)$$

When fluorine atoms reacted(82) with α-phenyl-N-t-butyl nitrone α,αdifluorobenzyl-t-butyl nitroxyl is formed. It would appear that the initial monofluronitroxide adducts react with fluorine atoms by hydrogen abstraction to produce phenyl fluoromethyl-t-butyl nitrone which in turn traps one more fluorine atom.

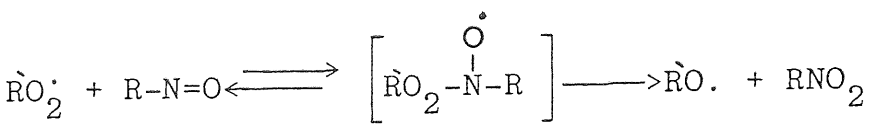


$$\mathrm{C_6H_5{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}C(CH_3)_3} \xrightarrow{F.} \mathrm{C_6H_5{-}\underset{\underset{F}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{\dot{O}}{|}}{N}{-}C(CH_3)_3} \xrightarrow{F.} \mathrm{C_6H_5\underset{\underset{F}{|}}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}C(CH_3)_3}$$

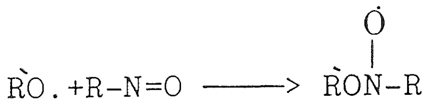
$$\xrightarrow{F.} \mathrm{C_6H_5{-}\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}{-}\overset{\overset{\dot{O}}{|}}{N}{-}C(CH_3)_3} \qquad (61)$$

These observations may mean that the tertiary nature of the hydrogen would be very vulnerable to abstraction by radicals.

The spin trapping of peroxy radicals(87,88) using nitrone and C-nitroso compounds as scavengers gives rise to alkoxy rather than expected alkylperoxy nitroxide adducts. But at very low temperatures (-90°C) alkylperoxy derivatives of nitroxyl adducts were detected. When the temperature was increased, this radical was not stable and was replaced by alkoxy derivatives of nitroxyl adducts. Pfab(94) has studied the reaction of C-nitroso compounds with peroxy radicals in detail and shows appropriate evidence for the following reactions.



$$\dot{R}O_2^{\cdot} + R\text{-}N{=}O \rightleftharpoons \left[\dot{R}O_2\text{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}\text{-}R\right] \longrightarrow \dot{R}O. + RNO_2 \qquad (62)$$



$$\dot{R}O. + R\text{-}N{=}O \longrightarrow \dot{R}O\overset{\overset{\cdot}{O}}{\overset{|}{N}}\text{-}R \qquad (63)$$

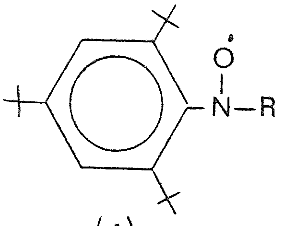
According to reactions (62) and (63), each mole of peroxy radicals needs two moles of nitroso compound to form more persistent alkoxy derivatives of nitroxyl adducts. The alkoxy radicals produced by O-O fission(95) of unstable adduct (eq. 62) will give rise to more persistent alkoxy derivatives of nitroxyl adducts (eq. 63).

When tert-butyl radical reacts with nitroso-tert-butane to form di-tert-butyl nitroxyl kinetic studies(96) have shown that the tert-butyl radical reacts with di-tert-butyl nitroxyl more readily than with nitroso-tert-butane itself, so that the yield of the spin adduct radical cannot go above a certain level. The relative rate constants of spin trapping toward the tert-butyl radical were determined to be 0.07, 1.0, 41, 63 and higher than 50 for 2,4,6, tributyl nitroso benzene, nitroso-tert-butane, pentamethylnitrosobenzene, 2,3,5,6, tetramethylnitrosobenzene and nitrosobenzene respectively. It is important to note that aromatic nitroso compounds are generally more efficient in trapping the tert-butyl radical than the nitroso-alkane. Phenyl N-t-butyl nitrone was found to be less efficient in trapping the tert-butyl radical than the nitroso compounds (either aromatic or aliphatic nitroso compounds).

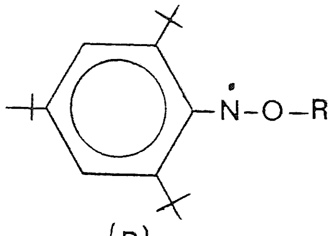
Schmid and Ingold(97) have reported that nitroso compounds would in general appear to be better traps for n-alkyl radicals than nitrones. Aromatic nitroso compounds trap n-alkyl radical faster than nitroso alkanes (2,3,5,6 tetramethylnitrosobenzene > nitroso-t-butane) unless steric hindrance is very pronounced (2,4,6 tri-tert-butylnitrosobenzene). This behaviour of nitroso and nitrone compounds appears to be consistent with that reported(96,98) previously.

It has been found that with the nitrones, electron withdrawing groups enhance the rate of n-alkyl radical addition to substituted α-phenyl-N-t-butylnitrones, while electron donating groups reduce such an addition reaction. The authors(97) assumed that the ground states of nitrone function will be stabilised (i.e. made less reactive) by an electron-donating substituent and will be destabilised (i.e. made more reactive) by electron-withdrawing substituent.

Konaka(99) has shown that small-sized radicals react with 2,4,6-tri-tert-butylnitrosobenzene to give the nitroxyl (A), while the bulky radicals are trapped in the form of alkoxy amine radical (B).

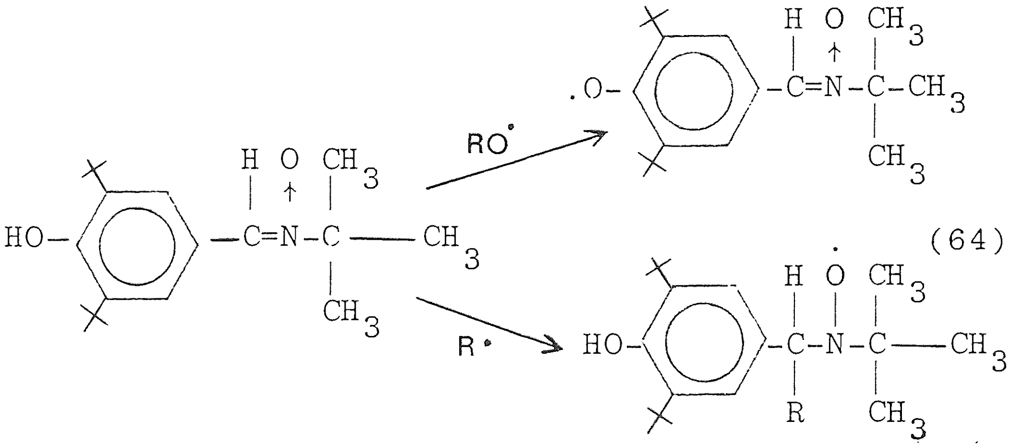


(A)



(B)

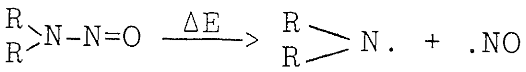
Pacifici and Browning(100) have employed the phenolic nitrone as a bifunctional radical trap. They found that alkyl radicals add to 3,5 di-tert-butyl-4-hydroxy phenyl-tert-butyl nitrone to give nitroxyl adducts. However the alkoxy radicals produced the stable phenoxy radical by phenol hydrogen abstraction.



(64)

Investigations(101-107) have shown that N-nitrosamines are decomposed thermally or by irradiation with production of nitric oxide and that RRN. radical is one of the primary products.

Rickatson and Stevens(101) investigated the thermal decomposition of many N-nitrosamines. Nitric acid was observed among the decomposed products



$$\begin{matrix}R\\R\end{matrix}\!>\!N\text{-}N{=}O \xrightarrow{\Delta E} \begin{matrix}R\\R\end{matrix}\!>\!N\cdot + \cdot NO \qquad (65)$$

Other studies(102-104) showed additional evidence for the thermal decomposition of N-nitrosamines by N-N=O bond dissociation.

The direct observation(105) of the dimethylamino-radical by E.S.R. during the photolysis of N-nitrosodimethylamine supported the primary photochemical N-N=O bond breakage. In the presence(106) of azobisbutyronitrile, the photolysis of dimethylnitrosamine in benzene gave a nitroxyl radical spectrum, probably formed in the following reactions:

$$(CH_3)_2N\text{-}N{=}O + h\nu \longrightarrow (CH_3)_2N. + \dot{N}O \tag{66}$$

$$CN(CH_3)_2CN{=}NC(CH_3)_2CN + h\nu \longrightarrow 2CN(CH_3)_2\dot{C} + N_2 \tag{67}$$

$$CN(CH_3)_2 + \dot{N}O \longrightarrow CN(CH_3)_2C\text{-}N{=}O \tag{68}$$

$$CN(CH_3)_2C\text{-}N{=}O + CN(CH_3)_2\dot{C} \longrightarrow (CN(CH_3)_2C)_2 + NO. \tag{69}$$

The amino radical was not detected under the experimental conditions and may well combine with the $CN(CH_3)_2\dot{C}$ radical to form a tertiary amine. Also in the presence(106) of benzoyl peroxide, the photolysis of dimethylnitrosamine in benzene gave dipheny nitroxyl radical, which can be expected to form via the following reactions.

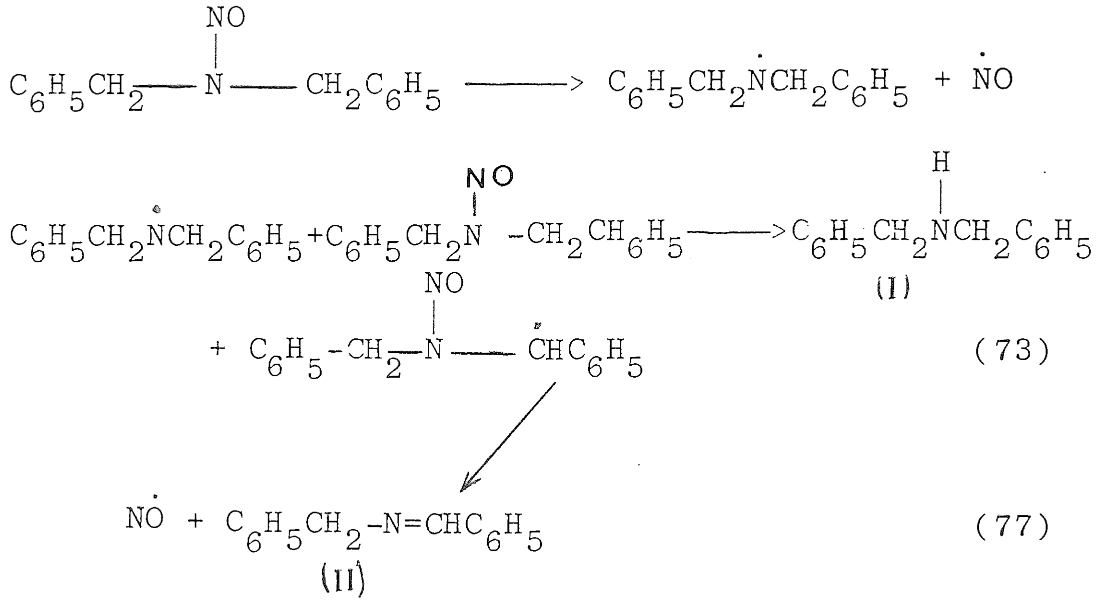
$$(CH_3)_2N\text{-}NO + h\nu \longrightarrow (CH_3)_2\dot{N} + \dot{N}O \tag{66}$$

$$(PhCO_2)_2 + h\nu \longrightarrow 2\dot{P}h + 2CO_2 \tag{70}$$

$$\dot{P}h + \dot{N}O \longrightarrow Ph\text{-}N{=}O \tag{71}$$

$$PhN{=}O + \dot{P}h \longrightarrow Ph_2NO. \tag{72}$$

Burgess and Lavanish(107) have reported that when N-dibenzyl-nitrosamine has irradiated with U.V. light, it was converted to 1:1 mixture of dibenzylamine, I, and N-benzylidene benxylamine, II, isolated by gas chromotography and identified by comparison with authentic samples



$$C_6H_5CH_2-\overset{NO}{N}-CH_2C_6H_5 \longrightarrow C_6H_5CH_2\dot{N}CH_2C_6H_5 + \dot{N}O$$

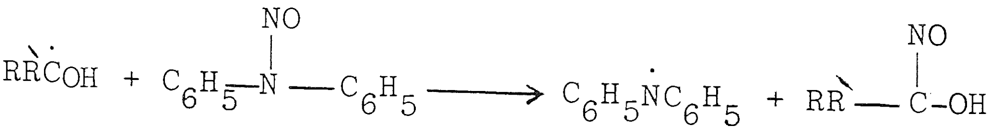
$$C_6H_5CH_2\dot{N}CH_2C_6H_5 + C_6H_5CH_2\overset{NO}{N}-CH_2CH_6H_5 \longrightarrow \underset{(I)}{C_6H_5CH_2\overset{H}{N}CH_2C_6H_5} + C_6H_5-CH_2-\overset{NO}{N}-\dot{C}HC_6H_5 \quad (73)$$

$$\dot{N}O + \underset{(II)}{C_6H_5CH_2-N=CHC_6H_5} \quad (77)$$

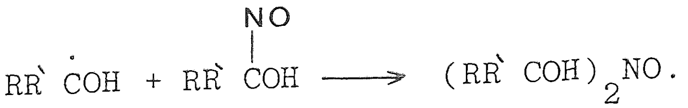
Nitroxyl radicals were generated(108) when N-nitroso-dicyclohexylamine was irradiated with U.V. light in alcohol solution containing di-t-butyl peroxide. The presence of the nitroxyl radicals under this experimental condition suggests the following reaction, in part the effect of adding di-t-butyl peroxide was to generate alcohol-derived radical.

$$t\text{-BuOOt-Bu} \xrightarrow{h\nu} 2t\text{-BuO} \quad (78)$$

$$t\text{-BuO}. + RR'CHOH \longrightarrow t\text{-BuOH} + RR'\dot{C}OH \quad (79)$$



$$RR'\dot{C}OH + C_6H_5-\overset{NO}{N}-C_6H_5 \longrightarrow C_6H_5\dot{N}C_6H_5 + RR'-\overset{NO}{C}-OH \quad (80)$$

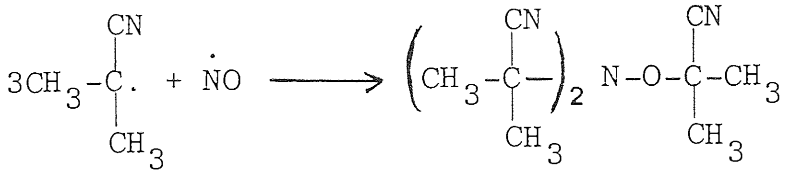


$$RR'\dot{C}OH + RR'\overset{NO}{\overset{|}{C}}OH \longrightarrow (RR'COH)_2NO.$$

(81)

The C-nitroso compound formed in reaction (80) can then act as a radical trap to form the nitroxyl radicals observed in reaction (81).

When azobisbutyronitrile, thermally decomposed in the presence of nitric oxide(109), is used as a source of alkyl radicals, trisubstituted hydroxylamine could be isolated in yield of 50%



$$3CH_3-\underset{CH_3}{\overset{CN}{C}}\cdot + \dot{N}O \longrightarrow \left(CH_3-\underset{CH_3}{\overset{CN}{C}}-\right)_2 N-O-\underset{CH_3}{\overset{CN}{C}}-CH_3$$

(82)

Also, in the decomposition of di-tert-butyl peroxide at 160°C in the presence of nitric oxide, tert-butyl nitrite is formed(109), and the rate of association has been measured

$$(CH_3)_3CO. + \dot{N}O \longrightarrow (CH_3)_3C-O-N=O \qquad (83)$$

CHAPTER 2

PREPARATION OF NITRONES AND NITROSO COMPOUNDS AND GENERAL EXPERIMENTAL TECHNIQUES

2.1 Synthsese of Nitrones and Nitroso Compounds

2.1.1 Preparation of Nitrones

2.1.1.1 α-N-Diphenylnitrone(111)

(a) N-phenylhydroxylamine was prepared as follows(112):

25 gm (0.217 mol) of ammonium chloride, 800 ml of water and 50 gm (0.4 mol) of nitrobenzene was placed in a 2L round bottom flask. The mixture was stirred vigourosly by means of mechanical stirrer, and 62 gm of zinc dust of 85% purity was added during the course of 15-20 min. As the reaction proceeded the temperature rose to 60-65°C. Stirring was continued for 15 minutes after all the zinc dust was added, and completion of the reaction was indicated by the fact that the temperature of the mixture ceased to rise. While still hot the solution was filtered with suction in order to remove the zinc oxide, which was washed with 200 ml of hot water (60°C). The filtrate was saturated with sodium chloride (350 gm) and cooled to 0°C. The phenyl-hydroxyl-amine which crystalised out in long light yellow needles was filtered by suction, the crude produce recrystalized from benzene, M.P 80°C (lit 81°C). It was used freshly prepared or kept for no longer than two days at 0°C in the dark.

(b) N-phenylhydroxylamine (1.09 gm, 0.01 mol) and benzaldehyde (1-06 gm, 0.01 mol) were dissolved in the minimum quantity of ethanol and allowed to stand overnight. The white needles which formed were filtered off, washed with a little ethanol and dried. Recrystalisation from ethanol gave white needles, M.P. 110°C (lit 112°C$^{(113)}$. Details of elemental analysis are shown in Table 2.1.

2.1.1.2 α-(4-Hydroxyphenyl)-N-phenylnitrone

The above procedure repeated by using N-phenylhydroxylamine (1.09 gm, 0.01 mol) and hydroxy benzaldehyde (1.22 gm, 0.01 mol). The product pale yellow needles, M.Pt 211°C (lit 212°C)$^{(114)}$.

2.1.1.3 α-(3,5-Dimethyl-4-hydroxyphenyl)-N-phenyl-nitrone (NPNC)

(a) 3,5-Dimethyl-4-hydroxybenzaldehyde was prepared according to the method of Nikiforov and co-workers,$^{(115)}$ as follows.

Boric acid (35 gm), hexamethylene tetramine (25 gm) and ethylene glycol (100 ml) were placed in a beaker and the mixture was heated to 130°C with stirring. 2,6-xylenol (12.2 gm; 0.1 mol) was slowly added over a period of 10 minutes, after which time heating was continued for a further 30 minutes. A colour change to deep orange was observed. The beaker was removed from the heat and cooled slightly. 30% sulphuric acid (150 ml) was added, and the mixture left to stand for 1 hour. The aldehyde separated and was filtered off. Recrystalisation from aqueous methanol gave long needles, M.Pt. 112°C)$^{(115)}$. The elemental analysis was correct (Table 2.1).

(b) N-phenylhydroxylamine (2.1 gm; 0.02 mol) and 3.5 dimethy-4-hydroxybenzaldehyde (3.0 gm; 0.02 mol) were dissolved in the minimum quantity of ethanol, mixed and allowed to stand overnight. On dilution with water and vigourous stirring, a cream solid precipitated. Recrystalisation from ethanol and water gave yellow needles, M.Pt 167°C. The elemental analysis was correct (Table 2.1).

2.1.1.4 α-(4-Nitrophenyl)-N-phenylnitrone

N-phenyl-hydroxylamine (1.09 gm; 0.01 mol) and 4-nitrobenzaldehyde (1.51 gm; 0.01 mol) were dissolved in the minimum quantity of ethanol and allowed to stand overnight. The yellow needles which formed were filtered off, washed with a little ethanol and dried. Recrystalisation from ethanol gave pale yellow needles, M. Pt 176°C.

I.r. (KBrdisc): 1605, 1590 cm^{-1}, strong (Ph ring); 1185 cm^{-1}, strong (Ph-N stretch), 1055 cm^{-1}, strong (N-O stretch); 1520 m.strong (NO_2 stretch).

2.1.1.5 α-(Methoxyphenyl)-N-phenylnitrone

N-phenylhydroxylamine (1.09 gm; 0.01 mol) and methoxybenzaldehyde were dissolved in the minimum quantity of ethanol and allowed to stand overnight. The cream needles which formed were filtered off, washed with a little ethanol and dried. Recrystalisation from ethanol gave pale cream needles, M. Pt 116-117°C.

I.r (KBr disc) 1570 cm^{-1} strong (C=N stretch); 1195 cm^{-1}

strong (Ph-N stretch); 1150 cm^{-1}, v. strong (C-O stretch); 1075 cm^{-1} v. strong (N-O stretch).

2.1.1.6 α-Phenyl-N-tert-butylnitrone

(a) 2-Methyl-2-nitropropane was prepared according to the method of Stowell(116), as follows.

A solution of tert-butylamine (36.6 gm, 0.5 mol), Na_2WO_4-$2H_2O$ (4.0 gm) and 25 ml of water was cooled in an ice bath. Hydrogen peroxide (255 gm of 21%, 1.5 mol) was added dropwise over a 2 hour period with stirring. The first 100 gm was added at 15-20°C, 100 ml of methanol was then added, and H_2O_2 addition was continued at 25-35°C. This was stirred for an additional hour at 25°. The organic layer was separated and the water layer was extracted with three 25 ml portions of ether. The combined organic layer and the extract was dried ($MgSO_4$) and distilled b.p 126-127°C.

(b) Tert-Butyl hydroxylamine was prepared as follows(117).

To a mixture of 2-methyl-2-nitropropane (nitro-tert-butane), (20 gm, 0.19 mol) and a solution of ammonium chloride (8.5 gm in 300 ml of water) cooled to 10°C with an ice bath was added 28 gm of zinc in small portions over 1 hour, never letting the temperature rise above 20°C. The mixture was stirred for 1 additional hour at 0°C and 30 minutes at room temperature. The reaction mixture was strong (Ph-N stretch); 1150 cm^{-1}, v. strong (C-O stretch); 1075 cm^{-1} v. strong (N-O stretch).

2.1.1.6 α-Phenyl-N-tert-butylnitrone

(a) 2-Methyl-2-nitropropane was prepared according to the method of Stowell(116), as follows.

A solution of tert-butylamine (36.6 gm, 0.5 mol), Na_2WO_4-$2H_2O$ (4.0 gm) and 25 ml of water was cooled in an ice bath. Hydrogen peroxide (255 gm of 21%, 1.5 mol) was added dropwise over a 2 hour period with stirring. The first 100 gm was added at 15-20°C, 100 ml of methanol was then added, and H_2O_2 addition was continued at 25-35°C. This was stirred for an additional hour at 25°. The organinic layer was separated and the water layer was extracted with three 25 ml portions of ether. The combined organic layer and the extract was dried ($MgSO_4$) and distilled b.p 126-127°C.

(b) Tert-Butyl hydroxylamine was prepared as follows(117).

To a mixture of 2-methyl-2-nitropropane (nitre-tert-butane), (20 gm, 0.19 mol) and a solution of ammonium chloride (8.5 gm in 300 ml of water) cooled to 10°C with an ice bath was added 28 gm of zinc in small portions over 1 hour, never letting the temperature rise above 20°C. The mixture was stirred for 1 additional hour at 0°C and 30 minutes at room temperature. The reaction mixture was filtered and the solid was washed with 100 ml of hot water (60°C). The filtrate was made basic with 25 gm of sodium hydroxide and 100 gm of pottassium carbonate (to crystallise out the hydroxylamine). The solution mixture was extracted with three 50 ml portions of ether. The ether was dried ($MgSO_4$) and evaporated, m.pt 60-62 (lit 60)(117).

(c) tert-Butyl-hydroxylamine (1.8 gm, 0.02 mol) and benzaldehyde (2.1 gm, 0.02 mol) were dissolved in the minimum quantity of ethanol and allowed to stand 24 hours, then diluted with 10 ml water and allowed to stand another 48 hours, white needles which formed were filtered off, washed with a little mixture of water and ethanol m.pt 74°C (lit 73°C)(118). The elemental analysis was correct (Table 2.1).

2.1.1.7 α-4Hydroxyphenyl-N-tert-butylnitrone

tert-Butylhydroxylamine (1.8 gm, and 0.02 mol) and 4-hydroxybenzaldehyde (2.44 gm, 0.02 mol) were dissolved in the minimum quantity of ethanol and allowed to stand for 24 hours, then diluted with 10 ml of water and allowed to stand for another 48 hours. The pale yellow needles which formed were filtered off, washed with a little mixture of ethanol and water, M.pt. 228°C.

I.r (KBr disc) 3210 cm^{-1}, v. broad (OH); 1580 cm^{-1}, m. strong (C=N stretch) 1560, strong (Ph ring) 1165 cm^{-1}, m. strong (t.butyl); 1195 cm^{-1}, strong (N-O stretch); 944 cm^{-1}, m.strong (C-N stretch)

2.1.1.8 α-(3,5-Dimethyl-4-hydroxyphenyl)-N-tert-butyl-nitrone

tert-Butylhydroxylamine (1.8 gm, 0.02 mol) and 3,5 dimethyl-4-hydroxybensaldehyde (3.0 gm; 0.02 mol) were dissolved in the minimum quantity of ethanol, mixed and allowed to stand 24 hours, then diluted with 10 ml of water and allowed to stand another 48 hours. The pale yellow needles which formed were filtered off, washed with a little mixture of ethanol and water, M.pt. 178°C.

I.r (KBr disc) 3100-3300 cm^{-1} broad (OH); 1580 cm^{-1}, strong (C=N stretch); 1390 cm^{-1}, m. strong (CH_3 sym.-deformation); 1168 cm^{-1}, strong (N-O) stretch.

2.1.1.9 2,5,5-Trimethyl-1-pyrroline N-oxide(119)

(a) 5-Methyl-5-nitro-2-hexanone was prepared as follows:(120)

Methyl vinyl ketone (70 gm, 1.0 mol) was added dropwise over 3 hours to a refluxing mixture of 2-nitropropane (89 gm; 1.0 mol), ethyl ether (100 ml) and benzyltrimethylammonium hydroxide (Tritan B, 7 ml). The reaction was then stirred and heated for 15 hours. The mixture was cooled and washed with water and saturated sodium chloride. The mixture was dried over anydrous sodium sulphate, then filtered. Distillation of the product at reduced pressure at 124-127°C (10 mm), (lit 123-125°C)(120).

(b) 5-Methyl-5-nitro-2-hexanone (40 gm, 0.25 mol) was stirred with a solution of ammonium chloride (14 gm, 0.25 mol) in 350 ml of water, while zinc dust (115 gm) was added in 2 hours. The temperature was kept below 15°C. After filtration, the cake of zinc oxide was washed with hot water, and the combined washing and filtrate were evaporated under reduced pressure at 70-75°C. The residual oil was saturated with potassium carbonate and extracted with chloroform. After drying ($MgSO_4$), the solution was evaporated and the nitrone was distilled from the residue at reduced pressure (2 mm) at 73-75°C (lit 71-72°C(119)). The elemental analysis was correct. (Table 2.1).

2.1.2 Preparation of C-nitroso Compounds

2.1.2.1 2-Methyl-2-nitrosopropane(116) (nitroso-tert-butane)

A solution of tert-butylamine (36.5 gm, 0.5 mol) and Na_2WO_4-$2H_2O$ (40 gm) in 50 ml of water was cooled in an ice bath. Hydrogen peroxide (170 gm of 21%, 1 mol) was added dropwise over 1-3 hours at 15-20°C with stirring. Stirring was continued for 30 minutes more at 20-25°C. About 3 gm of Na Cl was added to break the emulsion and the blue organic layer was separated. This was dried over Mg SO4. Distillation gave the dark blue nitrose compound. The distillate should be kept in an ice bath until it solidified to colourless crystals. M.pt. 80-81°C (lit 79-81°C).(116)

2.1.2.2 2,4,4-Trimethyl-2-nitrosopentane(116) (Nitroso-tert-octane

Hydrogen peroxide 0.8 mol, 130 gm of 21%) was added over a 30 minute period to a mixture of 4.0 gm of Na_2WO_4-$2H_2O$, 50 ml of water and 52 gm (0.4 mol) of tert-octylamine with stirring. A temperature of 18-22°C was maintained by occasional ice bath cooling. The blue mixture was stirred for an additional 3.5 hours at 18-22°C. The organiclayer was separated with 25 ml of pentane. The blue organic layer was then dried (Mg SO_4) and distilled to give the nitroso compound, bP 90-92°C (130 mm), a blue liquid which slowly crystallized (by using ice bath), M.pt 63-65°C (lit.63-65°C)(116). The elemental analysis was correct (Table 2.2).

2.1.2.3 Preparation of Nitrosobenzene(121)

In a 2-litre beaker, equipped with a thermometer and mechanical stirrer, 30 gm (0.56 mol) of ammonium chloride, 1 litre of water and 61.5 gm (51 ml, 0.5 mol) of pure nitrobenzene was placed. The mixture was stirred vigorously and 75 gm (1.03 mol, 90%, purity) of zinc powder was added during about 15 minutes, the rate of addition was such that the temperature rose rapidly to 60-65°C and remained in this range until all the zinc was added. The stirring was continued for a further 15 minutes. Zinc oxide was removed by filtration and washed with 600-700 ml warm water. The filtrate was cooled immediately to 0°C by the addition of sufficient crushed ice. Concentrated cold H_2SO_4 (50 ml) was added immediately to the cold solution and also ice-cold solution of 34 gm (0.11 mol) of crystallised sodium dichromate in 125 ml of water added as rapidly as possible to the stirred solution. After 2-3 minutes, the straw-coloured precipitate of nitrosobenzene was filtered and washed with 200 ml of water. Nitrosobenzene was obtained as white solid using steam distillation method. Elemental analysis was correct (Table 2.2).

2.1.2.4 Preparation of 2,4,6-trichloronitrosobenzene(122)

To a mixture of glacial acetic acid (200 ml), 30% aqueous hydrogen peroxide (50 ml, 0.44 mol) and 3 ml of concentrated sulphuric acid was added 20 gm (0.102 mol) of 2,4,6-trichloro-aniline. The mixture was warmed gently in order to bring all the amine into solution, and was then kept at 35-40°C for 10 hours. The warm solution was diluted with an equal volume of water and the solid removed and recrystallised from boiling acetic acid (150 ml) and gave colourless crystals melting at 142-143°C (lit 145-146°C)(122). The elemental analysis was correct (Table 2.2).

2.1.2.5 Tetramethylnitrosobenzene(125) (nitrosodurene)

(a) Acetoxymercuritetramethylbenzene was prepared(123) as follows. Tetramethylbenzene (34 gm, 0.25 mol) and mercuricacetate (80 gm, 0.25 mol) were dissolved in 200 ml of methanol. Enough acetic acid (25 ml) was added to prevent hydrolysis of the mercury salt and the solution was refluxed for 5 days. The products was soluble in the hot reaction mixture, the hot solution was filtered from the undesirable insoluble products. When the solution was cooled, the acetoxymercuritetramethylbenzene precipitated. Recrystallisation from methanol gave white crystals, M.pt 158-159 (lit 158-159°C(123)).

(b) n-Butylnitrite was prepared as follows:(124)

In a round bottom flask, fitted with a mechanical stirrer and a separating funnel extended to the bottom of the flask, 38 gm (0.55 mol) of sodium nitrite and 150 ml of water was placed; the flask was surrounded by an ice-salt mixture, and the solution was stirred until the temperature fell to 0°C. A mixture of 14 ml (25 gm, 0.25 mol) of concentrated sulphuric acid (s.p.gr. 1.84) and 46 ml (37 gm, 0.5 mol) of n-butyl alcohol and by means of separatory funnel was introduced slowly beneath the surface of the nitrite solution, with stirring. The alcohol solution was added slowly enough so that the temperature was kept ± 1°C.

The resulting mixture was allowed to stand in the ice bath until it separated into layers, and the liquid layer decanted from the sodium sulphate into a separatory funnel. The lower aqueous layer was removed and the butyl nitrite layer was washed twice with 20 ml portions of a solution containing 1 gm of sodium carbonate and 2.5 gm of sodium chloride in 40 ml of water. After drying over 2 gm of

$Mg\ SO_4$, the yield was pure butyl nitrite. Butyl nitrite decomposes slowly on standing and was kept in a cool place and used within a few days.

(c) Acetoxymercuritetramethylbenzene (20 gm) was dissolved in chloroform (100 ml); the solution was cooled in an ice-bath and stirred mechanically, n-butyl nitrite (9 ml) was added, this was followed by the addition in one portion, of a mixture of hydrochloric acid (15 ml) and acetic acid (20 ml). The reaction mixture was stirred for one hour at 10°C. The chloroform solution was washed by water, warmed to dissolve all the products, then 20 ml of methanol was added to the chloroform solution, filtered, concentrated to 40 ml by evaporation under reduced pressure, pure white crystalline nitroso product was precipated, M.pt. 158°C (lit 160°C)(125).

2.1.2.6 Pentamethylnitrosobenzene(125)

(a) Acetoxymercuripentamethylbenzene was prepared(123) as follows:

Pentamethylbenzene (37 gm, 0.25 mol) and mercuric acetate (80 gm, 0.25 mol) were dissolved in 200 ml methanol. Enough acetic acid (25 ml) was added to prevent hydrolysis of the mercury salt and the solution was refluxed for 5 days. The acetoxymercuri-pentamethylbenzene was insoluble in the hot reaction mixture; the product was filtered and recrystallisation from methanol gave white crystals, M.pt. 179 (lit 180°C)(123).

(b) The acetoxymercuripentamethylbenzene (20 gm) was dissolved in chloroform (100 ml), the solution was cooled in an ice-bath and stirred mechanically. n-Butylnitrite (9 ml) was added, this was followed by the addition, in one portion of a mixture of hydrochloric acid (15 ml) and acetic acid (20 ml). The reaction mixtures were stirred for fifteen minutes to one hour. The reaction mixture was washed with water (mercury salt removed). The precipitate was crude nitroso compound, the green filtrate evaporated to 40 ml and cooled, and an additional amount of nitroso compound was deposited. The nitroso compound was crystallised from chloroform, M.pt. 157°C (lit 160°C(125).

2.1.2.7 1-Nitroso-2-naphthol

1-Nitroso-2-naphthol was prepared by the method of Vogel(126) as follows:

100 gm (0.7 mol) of 2-naphthol was dissolved in a warm solution of 28 gm (0.7 mol) of sodium hydroxide in 1200 ml of water contained in a 2.5 litre round-bottom flask fitted with a mechanical stirrer. The solution was cooled to 0°C in a bath of ice and salt and 50 gm (0.72 mol) of powdered sodium nitrite was added, 220 gm (166.5 ml) of sulphuric acid was then added at such a rate that the temperature was kept at 0°C. The mixture was stirred for an additional hour, keeping the temperature at 0°C. 1-Nitroso-2-naphthol was filtered and washed with water thoroughly. The pale yellow product changed to dark brown on drying at room

temperature. 1-Nitroso-2-naphthol was recrystallised from light petroleum ether, M. pt. 103°C (lit 106°C)(126).

2.1.2.8 2,6-Di-tert-butyl-4-nitrosophenol

2,6-Di-tert-butyl-4-nitrosophenol was prepared(127) by the method of Barnes and Hickinbottom as follows:

2N-hydrochloric acid was slowly added to a stirred solution of sodium nitrite (7.0 gm) and powdered sodium hydroxide (7.0 gm) in an alcoholic solution of 2,6 di-tert-butylphenol (20 gm, 0.1 mol), until a slight excess of acid was present (PH4.0). Dilution with water precipitated the nitroso compound, which was extracted with ether (very soluble). Recrystallisation of the ether residue from chloroform and 60/80 petroleum ether and then twice from ethanol, the product was bright yellow crystals, M.Pt. 216°C (lit 218°C)(127).

2.1.3 Preparation of Nitrosamine

2.1.3.1 Preparation of Diphenylnitrosamine(112)

17 gm (0.1 mol) of pure diphenylamine was dissolved in 140 ml of warm ethanol. The solution was cooled to 5°C and 12 ml of concentrated hydrochloric acid was added slowly with stirring to the diphenylamine solution, and 8 gm of sodium nitrite in 12 ml water was added rapidly into the well-stirred mixture. The temperature soon went up to 20-25°C and the diphenylnitrosamine crystallised out. The mixture was cooled in ice for 15-20 minutes. The product was filtered and washed with water to remove

sodium chloride. Recrystalisation from industrial methylated spirit gave a yellowish product, M.pt. 68°C (lit 68°C)(112). The elemental analysis was correct (Table 2.3).

2.1.3.2 N-nitroso-2,2,6,6-tetramethyl piperidinyl sebacate

9.6 gm (0.02 mol) of 2,2,6,6 tetramethyl-4-piperidinyl sebacate, (supplied by Ciba-Gagy Ltd., Switzerland, under the commercial name Tinuvin 770), was dissolved in 100 ml alcohol and the solution was cooled in ice until the temperature fell to 5°C. 3 ml concentrated HCl was added slowly with stirring to the alcoholic solution of amine, followed by the addition of sodium nitrite solution (1.6 gm, 0.045 mol in 5 ml water). The reaction was exothermic, and temperature was kept at 5°C by using an ice bath. The reaction mixture was concentrated and white cream crystalline product was precipitated. The crude product recrystallised from methanol M.pt. 108-109°C. The elemental analysis was correct (Table 2.3).

I.r(KBr disc) 1600 cm^{-1}, Strong (NO stretching); 1040 cm^{-1} m. strong (N-N stretching), 550 cm^{-1}, (N -N=O deformation); 2920 cm^{-1}, strong (C-H stretching.

2.1.3.3 N-nitrosopiprazine

14.4 gm (0.1 mol) of piprazine was dissolved in 150 ml of water. The solution was colled in an ice-bath until the temperature fell to 5°C. Add 12 ml of concentrated hydrochloric acid (35%) to the cooled aqueous solution of piprazine slowly with stirring and immediately pour sodium nitrite solution (8 gm/15 ml of water, 0.11 mol) into the well-stirred mixture. The temperature soon rises to 15-25°C, the nitrosamine crystallises out, re-crystallisation from methanol gave cream crystals, M.pt. 154°C (lit 156°C)$^{(135)}$. The elemental analysis was correct (Table 2.3).

2.1.3.4 N-Nitrosodicyclohexylamine

The above procedure was repeated with 0.1 mol of dicyclohexylamine instead of piprazine. The elemental analysis was correct (Table 2.3).

2.1.3.5 N-nitroso dibenzylamine

The same procedure as for the N-nitroso piprazine was repeated with 0.1 mol of alcoholic solution of di-benxylamine. The elemental analysis was correct (Table 2.3).

2.2 Experimental Techniques

2.2.1 Preparation of Polymer Films

The additives were initially tumbled with a polymer which was then processed using the prototype RAPRA Torque Rheometer, which is essentially a small internal mixture, containing mixing screws contrarotating at different speeds. It has good temperature control and the jackets are heated by oil, circulated by means of a pump. The chamber may be

TABLE 2.1

ELEMENTAL ANALYSIS OF NITRONS COMPOUNDS

	Formula	C%		H%		N%	
		Calcu.	Found	Calcu.	Found	Calcu.	Found
α,N-diphenyl nitrone	$C_{13}H_{11}NO$	79.18	78.8	5.58	5.5	7.11	7.0
α,(4-hydroxyphenyl).N-phenyl nitrone	$C_{13}H_{11}NO_2$	73.23	73.4	6.16	5.0	6.57	6.3
α,(3,5 dimethyl-4-hydroxy phenyl)-N-phenyl nitrone	$C_{15}H_{15}NO_2$	74.1	74.3	6.99	7.1	5.76	5.9
α,(4-methoxy phenyl)-N-phenyl nitrone	$C_{14}H_{10}NO_2$	74.0	73.6	5.72	5.4	6.16	6.3
α,(4-nitrophenyl)-N-phenyl nitrone	$C_{13}H_{10}N_2O_3$	64.46	64.1	4.13	4.0	11.57	11.3
α,phenyl-N-t-butyl nitrone	$C_{11}H_{15}NO$	74.57	74.4	8.47	8.6	7.9	7.8
α-(4-hydroxy phenyl)-N-tert butyl nitrone	$C_{11}H_{15}NO_2$	68.39	68.5	7.77	7.8	7.25	7.4
α,(3,5 dimethyl-4-hydroxy phenyl)-tert -butyl nitrone	$C_{13}H_{19}NO_2$	69.95	70.1	9.41	9.2	6.27	6.4
2,5,5-trimethyl pyrroline-N-oxide	$C_7H_{13}NO$	66.14	65.9	10.23	10.0	11.02	10.9

TABLE 2.2

ELEMENTAL ANALYSIS OF C-NITROSO COMPOUNDS

Compound		C%		H %		N %	
		Calcu.	Found	Calcu.	Found	Calcu.	Found
Nitrosobenzene	C_6H_5NO	67.28	67.0	4.67	4.7	15.88	15.6
tetramethyl nitrosobenzene	$C_{14}H_{13}NO$	73.6	73.4	8.0	8.2	8.59	8.4
pentamethyl nitrosobenzene	$C_{11}H_{15}NO$	74.15	74.0	8.98	8.7	7.86	7.6
trichloronitrosobenzene	$C_6H_2Cl_3NO$	34.78	34.9	1.0	1.1	6.76	6.9
4-nitroso,2,6 di,tert-butyl phenol	$C_{14}H_{21}NO_2$	71.48	71.2	8.98	8.8	5.95	6.1
4-nitrosophenol	$C_6H_5NO_2$	58.53	58.8	4.16	4.0	11.38	11.1
1-nitrosonaphthol	$C_{10}H_7NO_2$	69.36	69.5	4.04	4.0	8.1	7.9
nitroso-tert-butane	C_4H_9NO	55.17	54.9	10.34	10.1	16.09	16.2
nitroso-tert-octane	$C_8H_{17}NO$	67.13	66.8	6.29	6.0	9.79	10.0

TABLE 2.3

ELEMENTAL ANALYSIS OF N-NITROSO COMPOUNDS (NITROSAMINE)

Compound	Formula	C%		H%		N%	
		Calcu.	Found	Calcu.	Found	Calcu.	Found
4-N-nitroso 2,2,6,6 tetramethyl piperidinyl sebacate	$C_{28}H_{48}N_4O_6$	62.45	62.3	9.29	9.5	10.40	10.1
N-nitrosopiprazine	$C_4H_8N_4O_2$	33.33	33.5	5.55	5.2	38.88	38.5
N-nitroso dicyclohexyl-amine	$C_{12}H_{22}N_2O$	69.23	69.0	9.61	9.2	13.40	13.6
N-nitroso dibenxylamine	$C_{14}H_{14}N_2O$	74.33	74.5	6.19	6.4	12.38	12.1
N-nitroso diphenylamine	$C_{12}H_{10}N_2O$	72.72	27.3	5.05	4.9	14.14	14.5

operated either to the atmosphere or sealed by means of a ram operated by compressed air. A full charge was 35 gm of polypropylene was used when the chamber was sealed, and 20 gm was used when the chamber was left open to the atmosphere. Mixing time at 180°C was used in all experiments.

On completion of mixing, the polymer samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. The material was allowed to dry and compression moulded into sheets 0.008 in. in thickness as follows. The processed polymer (5 gm) was placed between sheets of a special grade of cellophane, which was used as mould release agent , which themselves were located between stainless steel glazing plates. The glazing plated and enclosed samples were placed between the platens of an electrically heated press, the temperature of which had been previously raised to the required melt temperature. A pressure of 20 tons on a 15 in. diameter ram was used to obtain the required thickness. Polypropylene films were preheated for 30 sec. and pressed for 2 minutes at 180°C. At the end of the pressing time, the heater was switched off and the films rapidly cooled under pressure by means of circulating water to the press platens. The pressure was released and the films removed from the press at a temperature of 40-50°C.

The films were then cut into strips for different examinations and their thickness checked with a thickness gauge.

2.2.2 Ultra-violet Cabinet

All the film samples were irradiated in an ultra-violet light ageing cabinet (supplied by Ciba-Geigy Limited), cylindrical in shape and composed of 1:3 combination of fluorescent sun lamps and black lamps each of 20 watts power and mounted alternately around the periphery of the metallic cylindrical board which was mounted vertically on the circumference of a rotating drum fixed inside the cabinet. In this manner, the light beam fell perpendicularly on the surface of the film. The distance of the sample from the light source was 10 cm.

2.2.3 Thermal Oxidation of Polypropylene Films

The accelerated thermal oxidation of polypropylene films was carried out in a Wallace oven at 140°C. This has separate seven cells and has a good temperature control. There is an arrangement for controlling air flow through the cells. The films were aged individually to prevent cross-contamination, due to absorption of volatile degradation products and antioxidants between films.

2.2.4 Ultra-violet Spectroscopy Studies

Ultra-violet spectra of polymer film with additives and model solutions was carried out using the Unicam UV/visible spectrophotometer model SP 800. For the former, an unprocessed additive-free polymer film of identical thickness was used (as a compensator) in the reference beam. In the case of the model solution, the spectra were recorded using quartz cells of 1 cm path length with the pure solvent being used in the reference beam.

2.2.5 Electron Spin Resonance Spectrascopy

Electron spin resonance spectra of polypropylene samples were obtained using a JEOL-PE spectrometer. Samples of polypropylene films (30 mg each) were cut and placed into a quartz tube. The tube was then immersed into the cavity of the spectrometer. The machine was calibrated using a marker sample made up of MgO powder containing diffused Mn^{+2} ions before the spectrum of samples were recorded.

Since with this marker sample the sharp hyperfine structure of Mn^{+2} $(I=\frac{5}{2})$ consisting of six lines could be observed, g-values of radicals were measured using the above marker sample as reference. When the spectrum of each sample was obtained, the sample was replaced by the marker sample and its spectrum was recorded under the same conditions used for the sample and g-values were measured with respect to the third and fourth lines of Mn^{+2} peaks according to the instruction written in the handbook of the spectrometer as follows.

2.2.5.1 Determination of g-values

Among the six line ESR spectrum of Mn^{+2} contained in MgO used as marker sample, the g-value of the fourth line counted from the low magnetic field side is g=1.981 (reported in the handbook of the spectrometer). In the JEOL cavity resonator, this value remains constant for cavity resonator frequency between 9200 MHz and 9400 MHz. Furthermore, the distance between the third and fourth lines is 86.9 gauss. Let us assume that the following measured sample and ESR marker signals were recorded and that the data as shown in Fig.2.1 was obtained

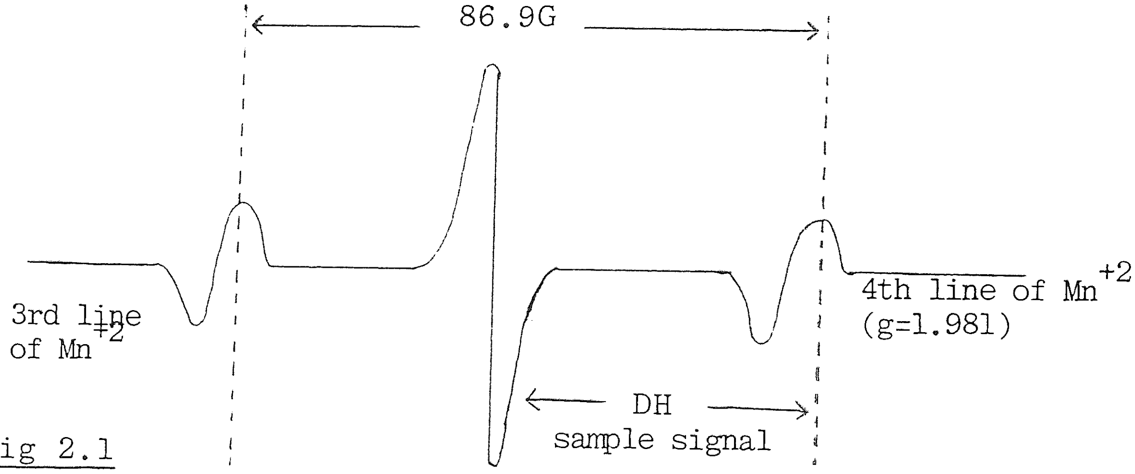


Fig 2.1

according to the equation(2) which was used to measure the g-factors of radicals in all samples.

The splitting constant (a) of radicals was obtained as a proportional calculation. Let us assume that the spectrum obtained is a triplet as shown in Fig. 2.2 If we assume that d is the distance between the third and fourth lines of Mn^{+2} and d' is the separation between the two hyperfine lines of the detected signal as shown in Fig.2.2, the value of splitting constant ($a = \Delta H'$) can be calculated according to the following equation:

$$a = \Delta H' = \frac{86.96}{d} \times d' \qquad (1)$$

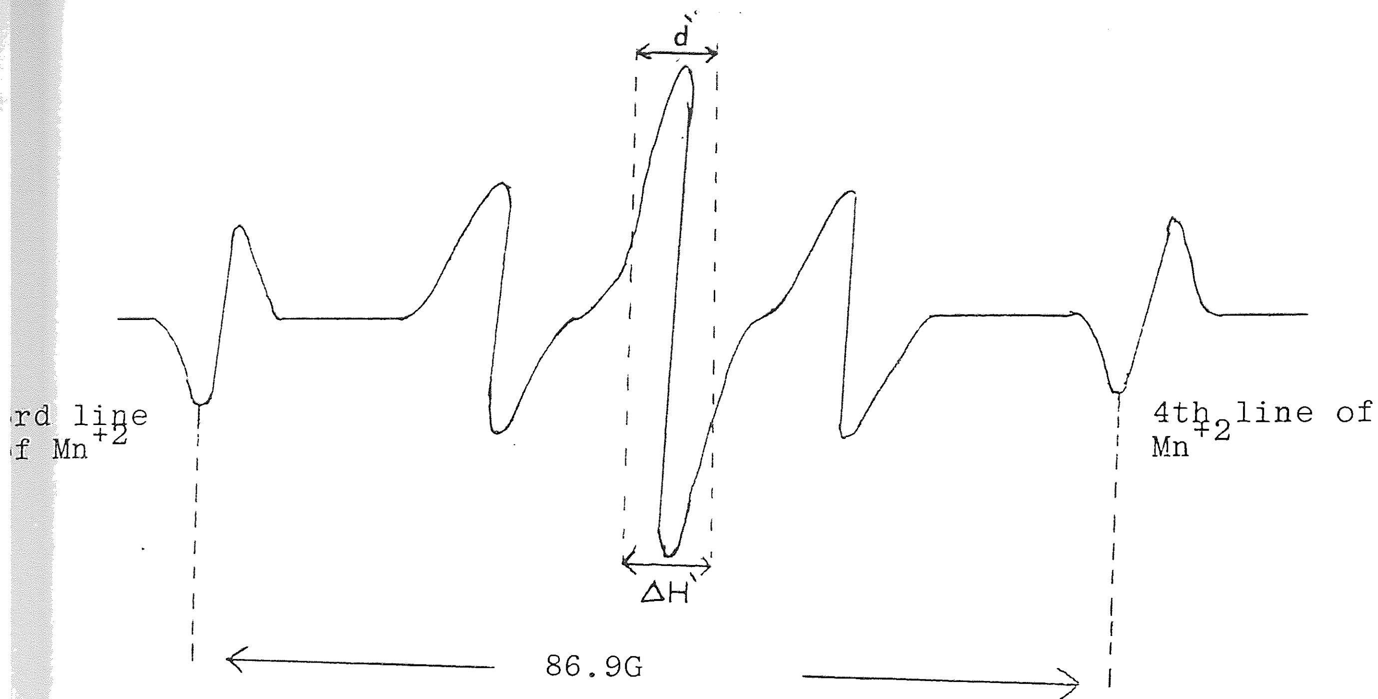


Fig. 2.2

In Fig.2.1, ΔH (gauss) represents the distance between the measured sample spectra and the fourth spectra of Mn^{+2} which can easily be obtained by proportional calculation. Once ΔH has been obtained, the g-values of the measured sample can be calculated as follows:

$$h\nu = g_{,}\beta H_o$$

$$h\nu = g\beta(H_o - \Delta H)$$

Therefore:

$$g = \frac{h\nu}{\beta(H_o - H)} = \frac{\frac{h\nu}{\beta}}{\frac{h\nu}{g_{,}\beta} - \Delta H} \qquad (2)$$

β = Bohermagneton constant

h = Planks constant

g = g-value of the unknown sample

$g_{,}$ = g-value of the reference

If 9300 MHz is substituted for ν (the centre frequency of 9200-9400 MHz), the following equation is derived:

$$g = \frac{6651}{3357-\Delta H} \qquad (3)$$

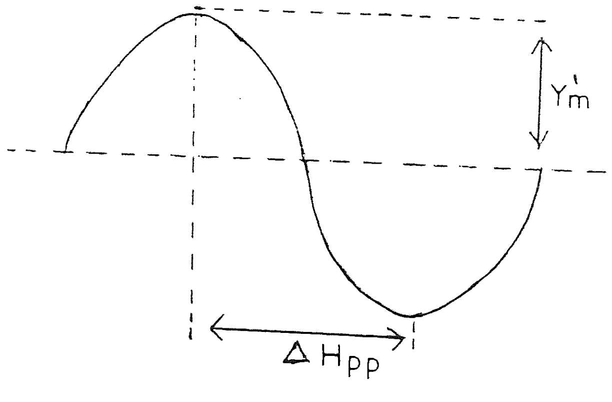
Thus the unknown g-value can be obtained.

2.2.5.2 Measurement of Radical Concentration

To measure the concentration of radicals in polypropylene samples, a reference sample was used in the cavity with the polypropylene sample so that both spectra could be recorded simultaneously. For this purpose, a sealed capillary tube containing a known weight (10 mg of 0.1M $CuSO_4$) of copper sulphate solution was fastened to the outer surface of the glass tube inside which the polypropylene sample had been placed. This technique was found to be essential for the reproducibility of results.

The radical concentration was calculated by comparing the ratio $Y'm(\Delta Hpp)^2$ for the polypropylene samples to $Y'm(\ Hpp)^2$ for the reference sample.

$$\frac{Y'm(\Delta Hpp)^2 \text{sample}}{Y'm(\Delta Hpp)^2 \text{reference}} = \frac{\text{concentration of radicals in test sample}}{\text{concentration of radicals in reference sample}}$$



This method was found to be a close approximation of the summation method of Wyard(128), and has been used by others(129).

2.2.6 Infra-red analysis of the Oxidised Films

Infra-red spectroscopy was used to estimate the oxidation kinetics of polymer samples since polymer oxidation of polymers results in the build up of carbonyl oxidation products. The kinetics of the growth of this functional group, as the oxidation proceeds were followed by observing the changes in the characteristic absorption peak at a definite wavelength, and these were assigned by a comparison with the values for long chain ketones(130).

In the quantitative analysis of infra-red, the following combined form of Beer-Laberts equation was used(131).

$$A = \log_{10} \frac{I_o}{I} = ec\ell$$

where

A = Absorbance or optical density

I_o = Intensity of radiation falling on the sample

I = Intensity of radiation emerging from the sample

e = Molar extinction coefficient

c = Concentration of the absorbing group present in the sample in moles per litre.

ℓ = Path length of radiation within the sample in centimeters.

The samples were oxidised under certain conditions for regular intervals of time and the spectra were run on the same chart paper for comparison purposes.

The functional group index calculated from these spectra, which is defined as the ratios

$$\frac{\text{Absorbance of the function group}}{\text{Absorbance of a standard peak}}$$

The standard peak used here corresponds to an absorption band that does not change with oxidation of the sample and this will help minimise errors due to variations of the film thickness as well as errors due to the instrument.

Hence: $\text{Carbonyl index} = \frac{A(1710\ cm^{-1}}{A(2710\ cm^{-1}}$

2.2.7 Measurement of Melt Flow Index

Melt flow index was determined on polypropylene samples which have been processed with or without additives.

The melt flow index (MFI) is defined as the amount of polymer in grammes extruded through a standard die in a given time (e.g. 10 minutes). It is an inverse measure of melt viscosity of the polymer which is again related to the molecular weight. The melt flow index decreases as the molecular weight of the polymer increases.

Since the thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such reactions as chain-scission, cross linking, etc. Such changes are expected to be reflected in the melt flow index values. Hence melt flow index measurement provides a means of detecting any oxidation which may occur during heat treatment of the polymer.

The apparatus was brought to a steady extrusion temperature of 230°C ± 0.5°C for beginning an experiment. The barrel was then charged with 4 gm of polymer. The time taken to charge the barrel should not exceed one minute. The polymer extruded under certain load through the die. The extrudate was cut with a suitable sharp tool. The time interval for the first extrudate was 60 seconds and was discarded; then five successive cut-offs were taken each at 30 seconds, each cut-off was weighed separately and their average weight was determined.

2.2.8 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermo-analytical technique which enables the change in weight of material as a function of temperature, or as a function of time at a certain specified temperature.

The basic instrument consists of a precision balance, a furnace capable of being programmed either for linear rise of temperature or a constant temperature and weight continuously on a moving paper chart.

2.2.8.1 Thermal Balance

In the present work, the apparatus used was a "Stanton" TR-01 Thermo-recording balance which comprised a precision air-damped analytical balance surmounted by a bifilar-wound tube furnace capable of temperatures up to 1000°C. The furnace (internal bore 2") was designed to take an inner refractory sheath so that samples can be heating in air. One limitation of the apparatus is that work cannot be carried out at pressures other than air. The sample is placed in a silica crucible mounted on a silica support rod rising from the top of the rear balance suspension piece. Furnace temperature and changes of weight are registered simultaneously on a twinpen electronic recorder. The temperature of the furnace is controlled by an on-off switch device which is itself governed by a simple cam mechanism driven by an electronic servo-motor. The samples can be studied at any fixed temperature or under constant rate of heating conditions which are determined by the speed of the motor controlling the rotation of the cam. In this work the rate of heating was 4°C per minute. The thermal balance has a full scale deflection of 10 mg and a sensitivity of 0.1 mg. The whole balance beam is arrested automatically for a few seconds every 5 minutes to prevent movement of the balance beam or the pans on their knife edges and to curb any oscillations which may develop.

A slow heating rate was used because it was thought the automatic temperature recorder would give a truer indication of the temperature inside the crucible. It would be an improvement if the thermocouple was situated at the base of the crucible instead of on the furnace.

2.2.8.2 Experimental Method

The weight of each sample used was 35 mg of chemical samples. All samples used were pre-dried over P_2O_5 for 48 hours. The dried sample was placed in a silica crucible which was mounted on a silica support rod rising from the top of the rear balance suspension piece, then the furnace and recording system for both temperature and weight switched on. The samples were heated in the temperature range 20°C - 700°C.

It was found necessary to make a correction for negative buoyance to the results for total weight loss (i.e. up thrust as the air becomes hotter). A calibration experiment was performed on the empty crucible from 20-700°C.

2.2.9 Measurement of Unsaturation in Polypropylene(132)

0.5 gm of the polypropylene film was swollen in 75 ml of $CHCl_3$ in a conical flask for about 48 hours (about 3 hours in an oil bath at 50°C), 5 ml of 20% trichloroacetic acid in $CHCl_3$ was added, followed by 25 ml of 0.1N iodine.

25 ml of 5% mercuricacetate in glacial acetic acid

was added, the contents were swirled gently and stored in the dark for 2 hours. After the addition of 75 ml of 7.5% KI solution, the excess of iodine was titrated with 0.1N $Na_2S_2O_3$ employing the customary starch end point (the starch end point noted in the aqueous phase).

2.2.10 Chemical Measurement of Hydroperoxide in Polypropylene

The method used by Manasek et al(133) and Geddes(134) was modified as follows: 0.5 - 1.0 gm of polymer film (in small pieces) was introduced into 20 ml of chloroform and purged with nitrogen for half an hour. The polymer was then allowed to swell for 18 hours - 3.3 ml of glacial acetic acid was added and the solution was purged with nitrogen for 3-5 minutes before and after the addition of freshly prepared 5% solution of sodium iodide in methanol. After storage for 4 hours in the dark for complete reaction, the liberated iodine was titrated using 0.01N sodium thiosulphate.

2.2.11 Gel Permeation Chromatography

Molecular weight changes during thermal degradation of polymers have usually been explained by chain scission or cross linking. The study of competitive cross linking and chain scission reactions is facilitated by the use of G.P.C.

A chain scission process shifts the molecular weight distribution (MWD) to lower molecular weight. A molecular enlargement will be observed as an increase of the high molecular weight tail. Molecular weight and molecular weight distribution (MWD) for the processed polypropylene with different additives were obtained using G.P.C. and were kindly carried out by the Polymer Supply and Characterization Centre of RAPRA. Experimental conditions used were as follows:-

Solvent:- o-dichlorobenzene stabilized with 2,6-di-tert-butyl-p.cresol.

Temperature: 138-140^{o}C, Columns packed with Styragel in series of 1 x 500A^{o}, 1 x 10^{-4}A^{o}, 1 x 10^{6}A^{o} and 1 x 10^{7}A. Flow rate was 1 ml/min. Polystyrene standards supplied by Waters Associates was used for calibration and Mark-Houwink constants ($|\eta| = KM^{\alpha}$) used for conversion of calibaration:

Polystyrene $K = 1.38 \times 10^{-4}$ $\alpha = 0.70$

Polypropylene $K = 1.30 \times 10^{-4} \alpha = 0.78$.

Molecular weight distribution curves were obtained by the plot of dw/dlogM versus logM.

2.2.12 Identification of Hydroxylamine(136)

1 ml of test solution (extracted product dissolved in CH_2Cl_2), just acidified with dilute HCl, was treated with 1 ml of 1% (W/V solution of oxine (8-hydroxy quinoline) in ethyl alcohol, followed by 1 ml of 2N sodium carbonate solution. The whole was well shaken and the green colouration which developed immediately (indo-oxine formation) indicated the presence of hydroxylamine.

CHAPTER 3

EFFECT OF C-NITROSO COMPOUNDS ON MELT STABILISATION, PHOTO-OXIDATION AND THERMAL OXIDATION OF POLYPROPYLENE

3.1 Effect of C-nitroso Compounds on Melt Stability of Polypropylene

3.1.1 Introduction

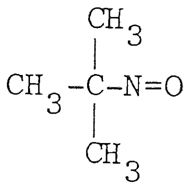
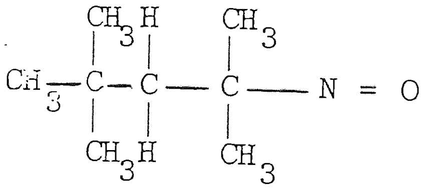
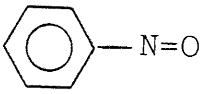
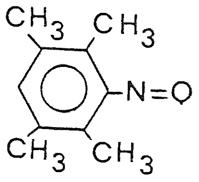
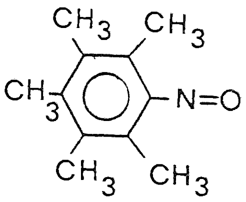
Evidence from the literature clearly shows that in model compounds carbon-nitroso compounds are very efficient as alkyl and alkoxy radicals trapping agents (Chapter 1), but no evidence so far has been put forward to show that carbon nitroso compounds are effective as stabilisers in polymers. It is now clearly established that polyolefines produce alkyl radical predominantly both during processing (in limited oxygen) and on U.V. irradiation$^{(62,139)}$.

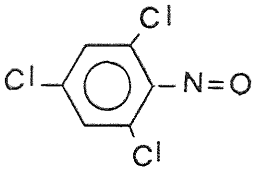
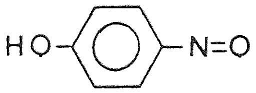
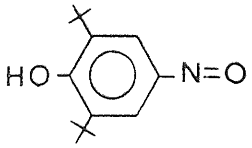
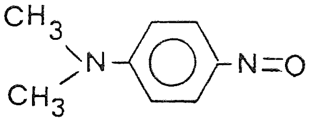
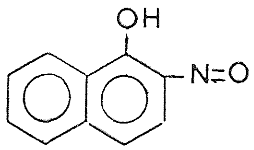
In the presence of oxygen, alkyl radicals are oxidised to new peroxy radicals which abstract hydrogen from the polymer producing hydroperoxides which are initiators for the oxidative degradation by polymers. Molecular weight reduction by thermal oxidation could in theory be prevented by 100% effectiveness in inhibiting any of the following steps:

$$RH \xrightarrow{\Delta H} R. \xrightarrow{O_2} RO_2. \xrightarrow{RH} ROOH \xrightarrow{\Delta H} RO. + HO.$$

An effective melt stabiliser should thus be a compound that can act in one of several ways but preferably by deactivating alkyl radicals before they react with oxygen. Since carbon-nitroso compounds are know to be very effective alkyl and alkoxy radical traps, these compounds could be effective stabilisers for polyolefines both during processing and on U.V. exposure.

This study examines in detail the behaviour of carbon-nitroso compounds as melt stabiliser in polypropylene and the compounds used in this study are listed below with the code name:

Name of the compounds	Molecular formulae	Code Name
Nitroso-tert-butane	 $CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}N=O$	NTB
Nitroso-tert-octane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-N=O$	NTO
Nitrosobenzene		NB
Tetramethylnitrosobenzene		TMNB
Pentamethylnitrosobenzene		PMNB

Trichloronitrosobenzene		TCNB
4-Nitrosophenol		4-NP
4-Nitroso-2,6-di-tert-butyl phenol		4-NDBP
N,Ndimethylnitroso aniline		DMNA
2-Nitroso-1-naphthol		2-N-1-N

3.1.2 Effect of Aliphatic Nitroso Compounds on Melt Stability of Polypropylene

Fig. 3.1 illustrates the variation of melt flow index of polypropylene with processing time in the presence of aliphatic nitroso compounds (nitroso-tert-octane "NTO" and nitroso-tert-butane "NTB"). The polymer was processed at 180°C in the RAPRA Torque Rhometer in a closed mixture at concentration of 1×10^{-3} mole/100 gm. The control sample without additives showed a high rate of chain scission as evidence by the increase in melt flow index value of polymer. Incorporation of the nitroso-tert-butane inhibited the change in MFI up to 20 mins. of processing. However, nitroso-tert-octane resulted in a significant decrease in MFI up to 10 mins. of processing to a level less than the unprocessed polymer. This implies the occurrence of a cross

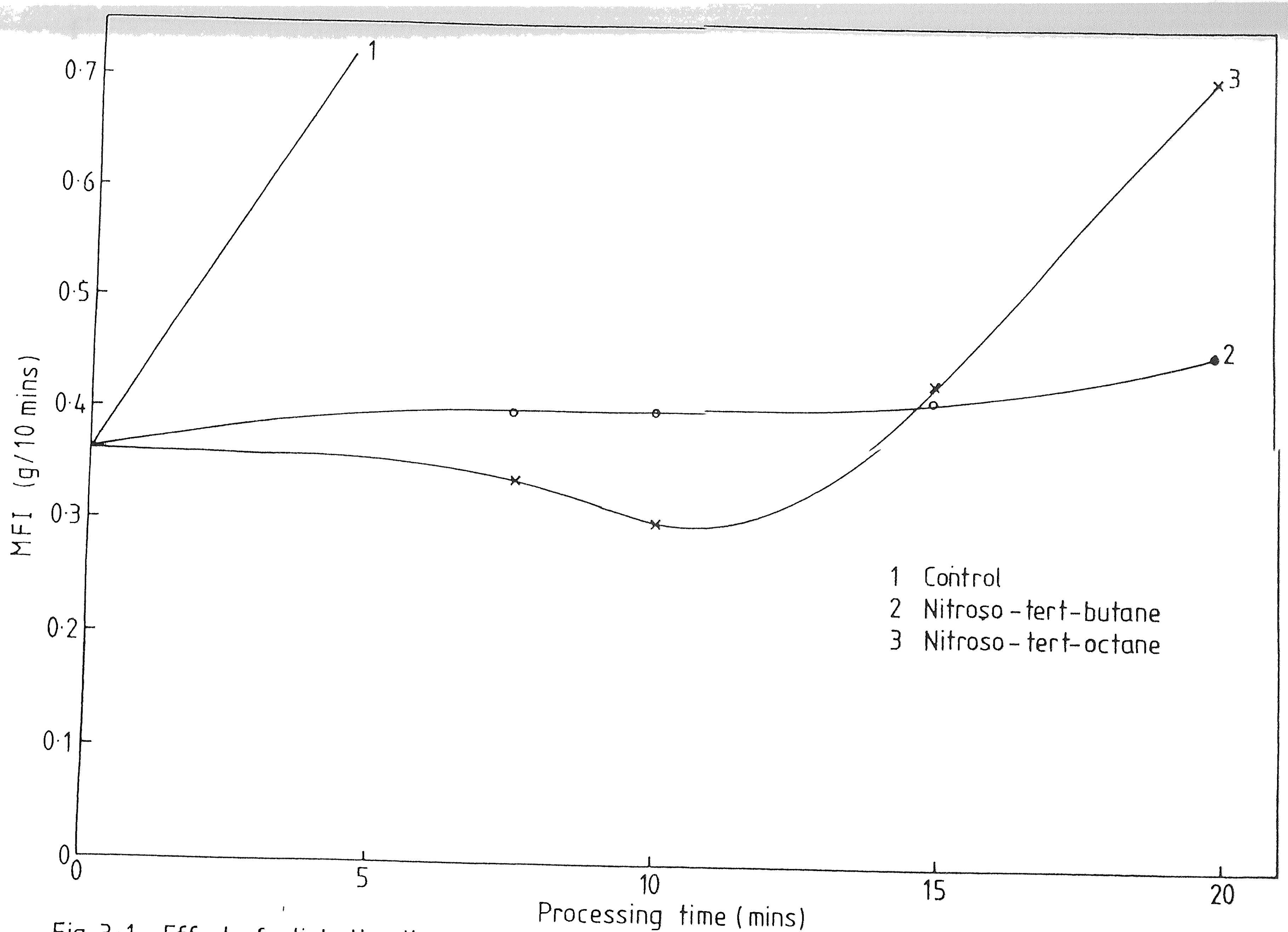


Fig 3:1 Effect of aliphatic nitroso compounds on the melt flow index (MFI) of pp processed at 180°C in a closed mixer at different time (Conc 1×10^{-3} mole/100 gm)

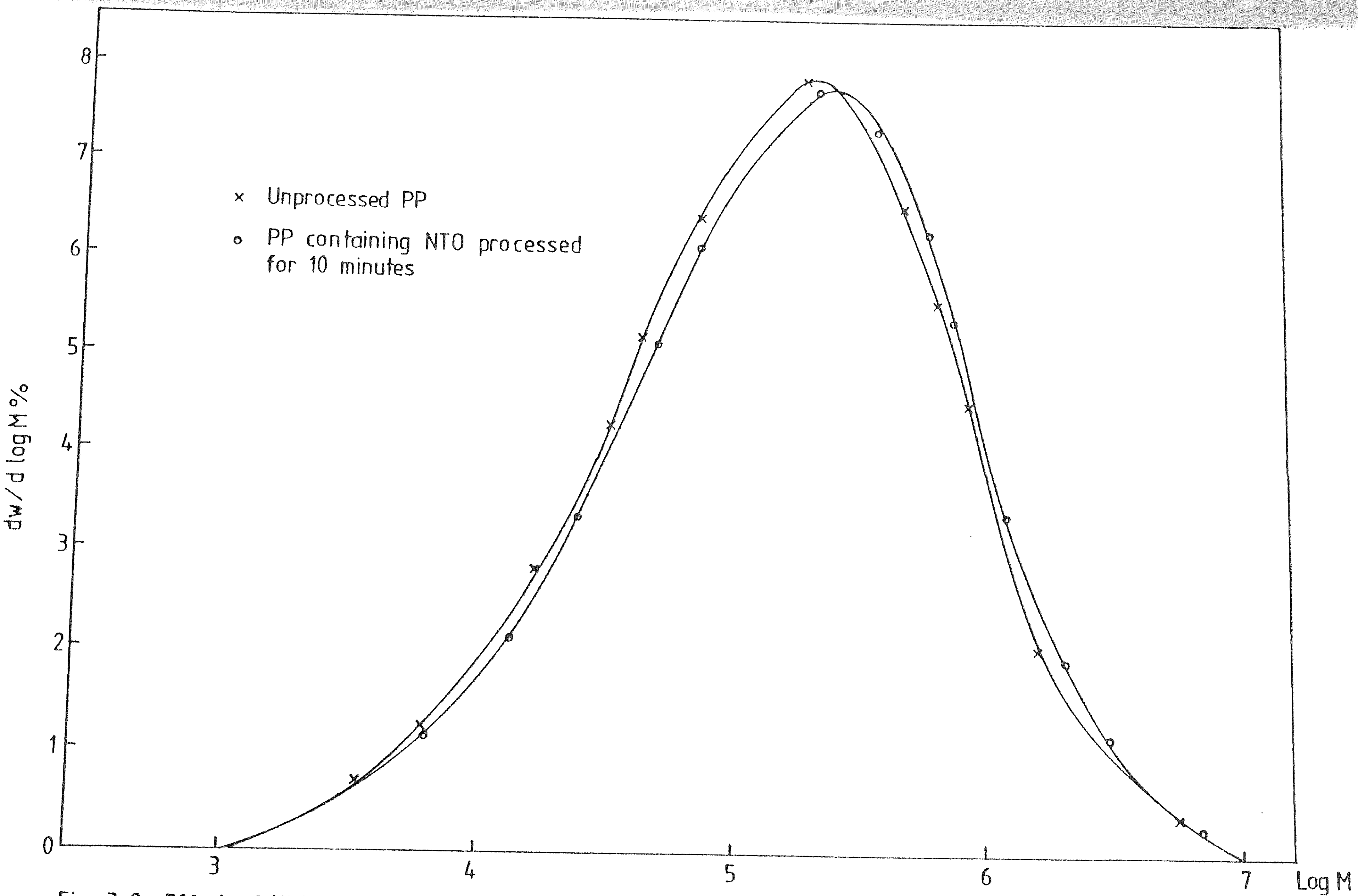
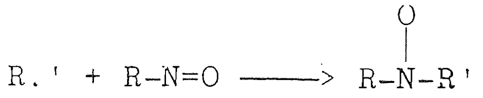


Fig 3:2 Effect of NTO on the molecular weight distribution of polyprapylene during processing for 10 minutes

linking reaction between the polymer chains. Prolonged processing, up to 20 min., could result in an increase in the MFI in an auto-accelerating reaction.

ESR examination of processed polypropylene samples containing both NTO and NTB showed the formation of nitroxyl radicals. Table 3.1 shows that the concentration of radicals produced from NTB increased with processing time. However, the concentration of nitroxyl radicals produced from NTO remained almost constant with processing time. Nitroxyl radicals could be formed from the nitroso compounds according to the following reaction



$$R^{\cdot\prime} + R{-}N{=}O \longrightarrow R{-}\overset{\overset{\dot{O}}{|}}{N}{-}R' \qquad (1)$$

Fig. 3.2 shows the effect of nitroso-tert-octane on the molecular weight distribution of pp with processing time. It is also apparent from this figure that molecular weight distribution is slightly shifted to higher molecular weight at 10 mins. of processing, indicating cross-linking of polymer chains, as is also indicated from MFI measurement (Fig. 3.1, curve 3).

3.1.3 Effect of Aromatic Nitroso Compounds on the Melt Stability of Polypropylene

Fig. 3.3 shows the effect of processing time on polypropylene in the presence of aromatic nitroso compounds as melt stabiliser in polypropylene. 4-Nitroso phenol (4-NP) showed no sign of polymer breakdown up to 30 mins. of processing. However, 4-nitroso-2,6 -

di-tert-butylphenol and 1-nitroso-2-naphthal showed good melt stabilising effect up to 15 mins. of processing and then MFI of pp started to increase at longer processing times.N,N dimethyl-4-nitrosoaniline showed a significant decrease in MFI compared with unprocessed polymer, even at long processing times, implying cross linking reactions of polymer molecules. Nitrosobenzene is seen to be a fairly good melt stabiliser for pp up to 10 mins. of processing. However, the melt stabilising effectiveness of aromatic nitroso compounds varies with the nature of the aromatic substituent.

Fig. 3.4 shows the effect of trichloronitrosobenzene (TCNB) and pentamethylnitrosobenzene (PMNB) on the melt stabilisation of pp. The MFI of polypropylene containing TCNB was found to be critically dependent on the processing time. At 10 mins. the MFI was reduced compared with samples processed at shorter processing time of 7.5 mins. and longer processing time of 15 and 20 mins. The significant reduction of MFI of pp containing PMNB to levels less than the unprocessed polymer up to 20 mins. indicates the formation of cross links.

Fig. 3.5 shows the effect of the concentration of TCNB and PMNB on MFI of pp at constant processing time. This increases with increasing concentration of TCNB and decreases with increase in concentration of PMNB.

Fig. 3.6 compares the molecular weight distribution

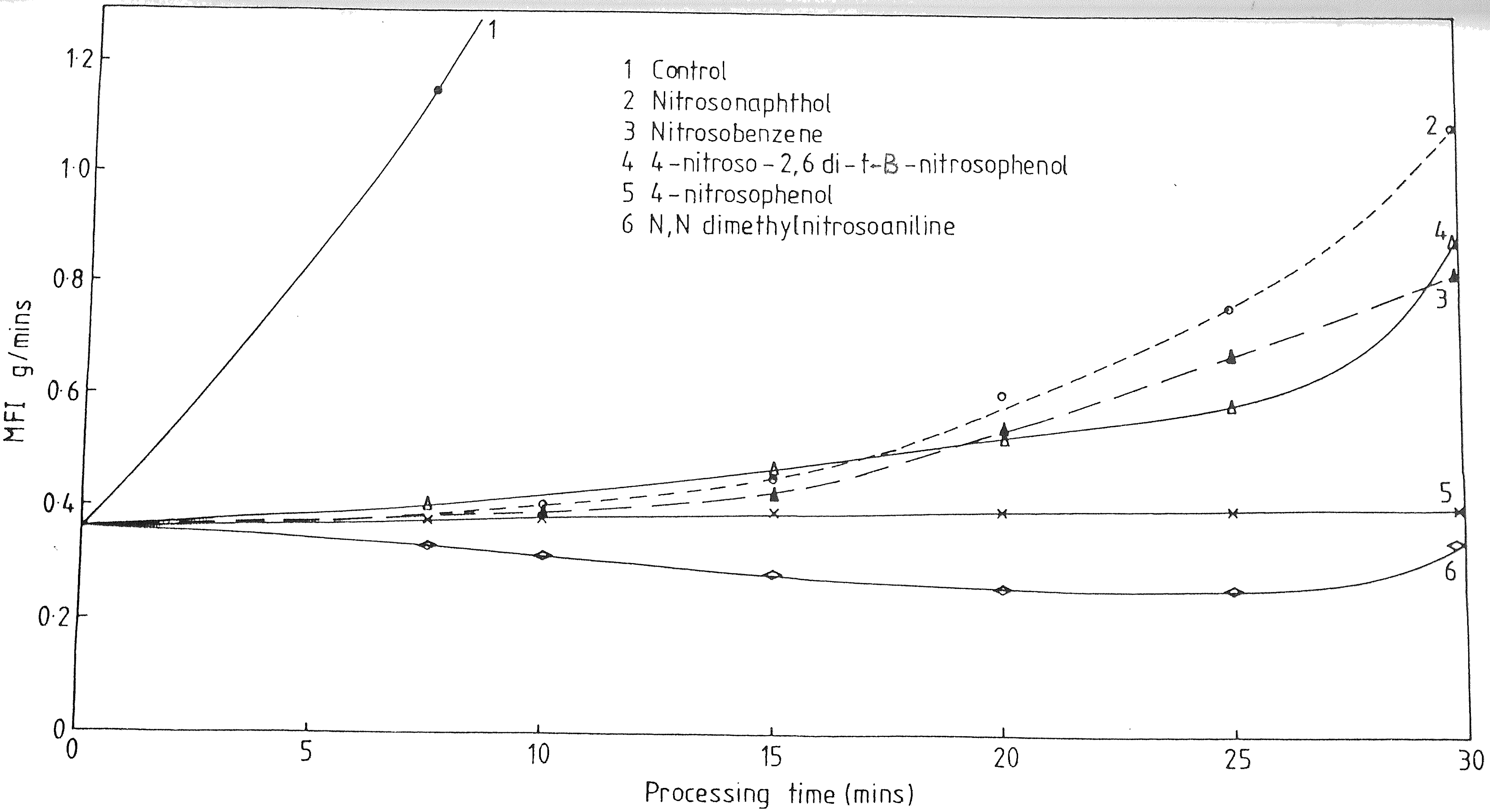


Fig 3:3 Effect of aromatic nitroso compounds on the melt flow index of pp processed at 180°C in closed mixer at different time (Conc 1×10^{-3} mole/100 gm)

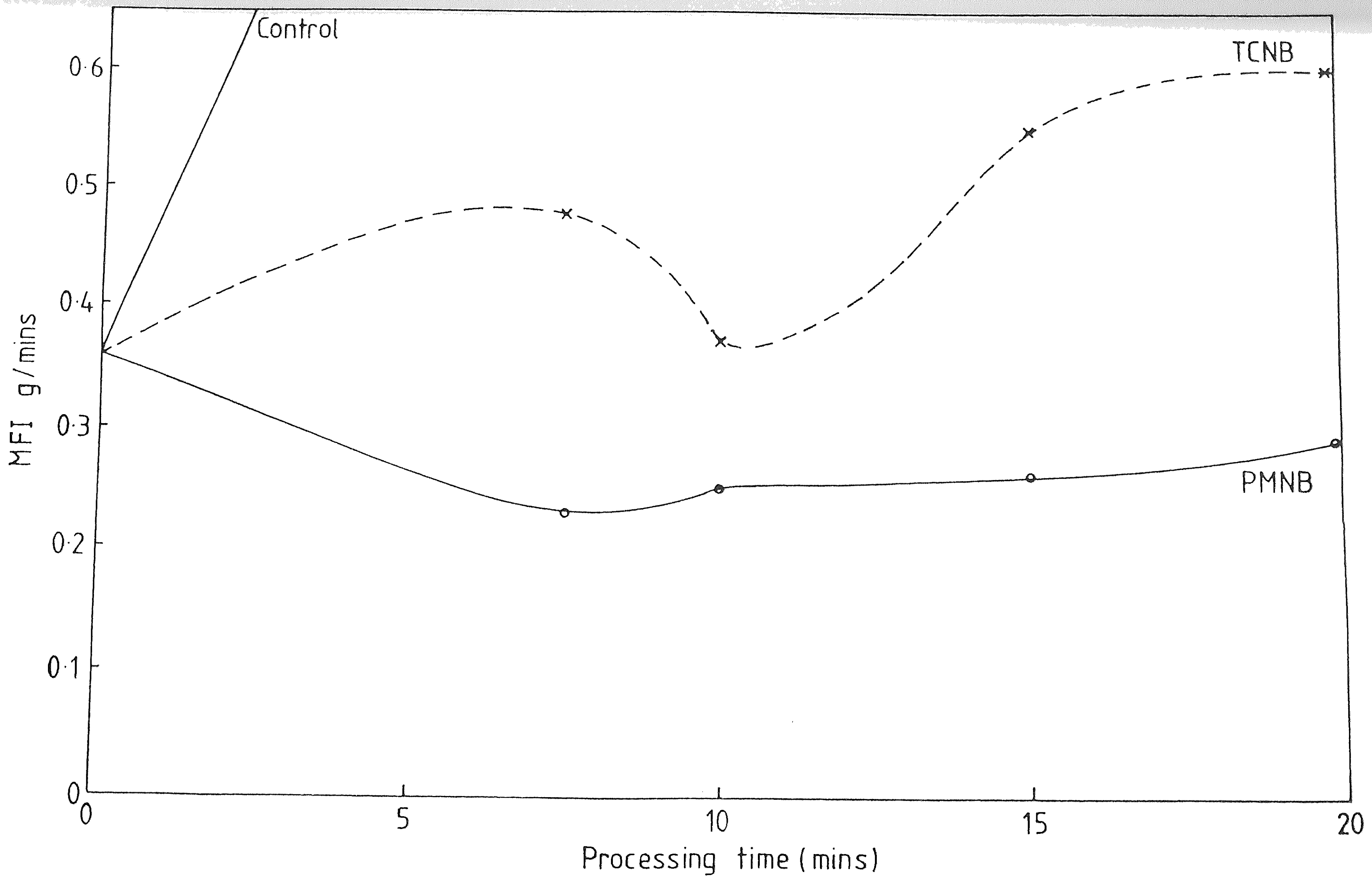


Fig 3:4 Effect of TCNB and PMNB on the MFI of PP processed at 180°C in closed mixer at different time (Conc 1 $\times 10^{-3}$ mole/100 gm)

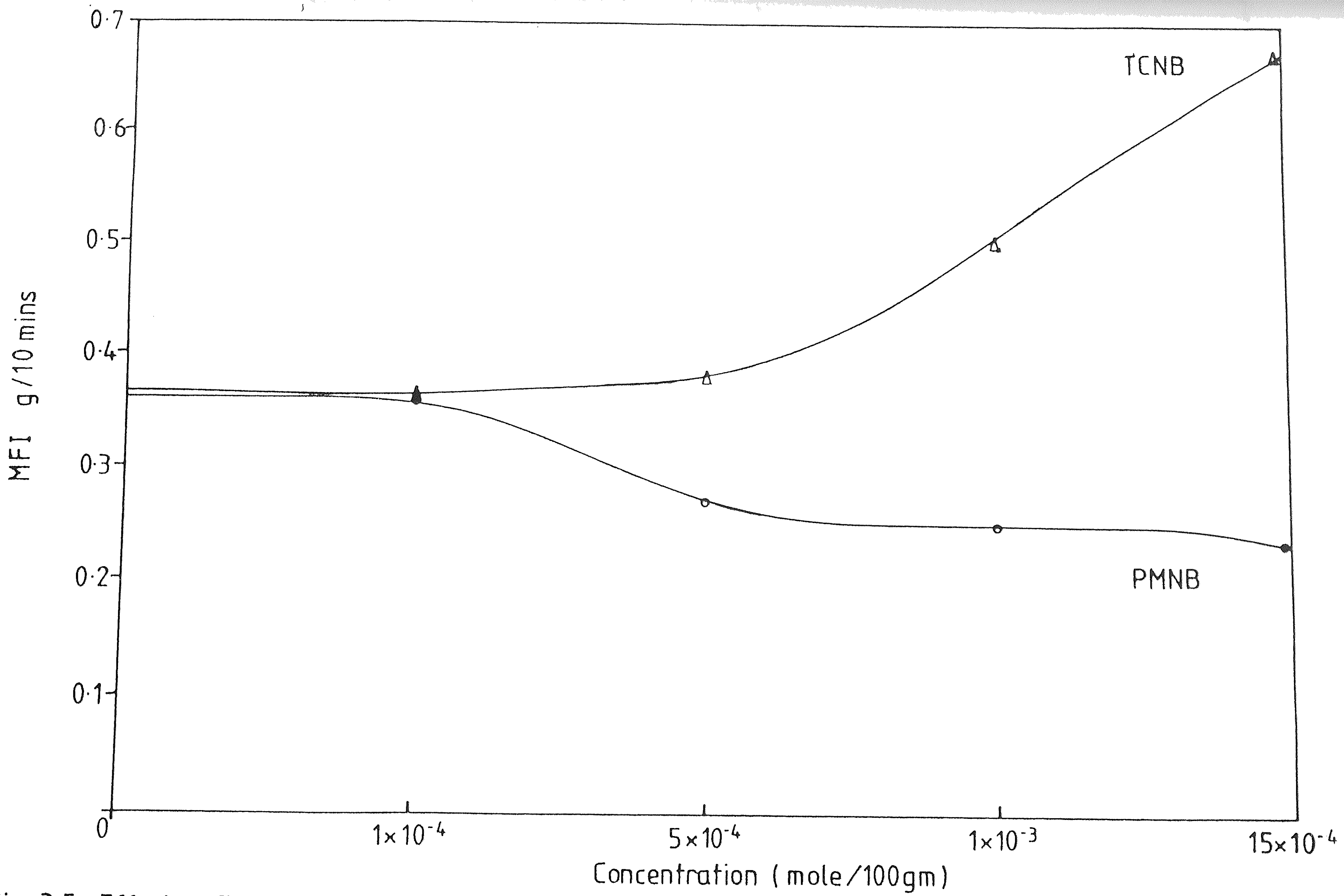


Fig 3:5 Effect of TCNB and PMNB concentration on the MFI of PP processed in a closed mixer at 180°C for 10 minutes

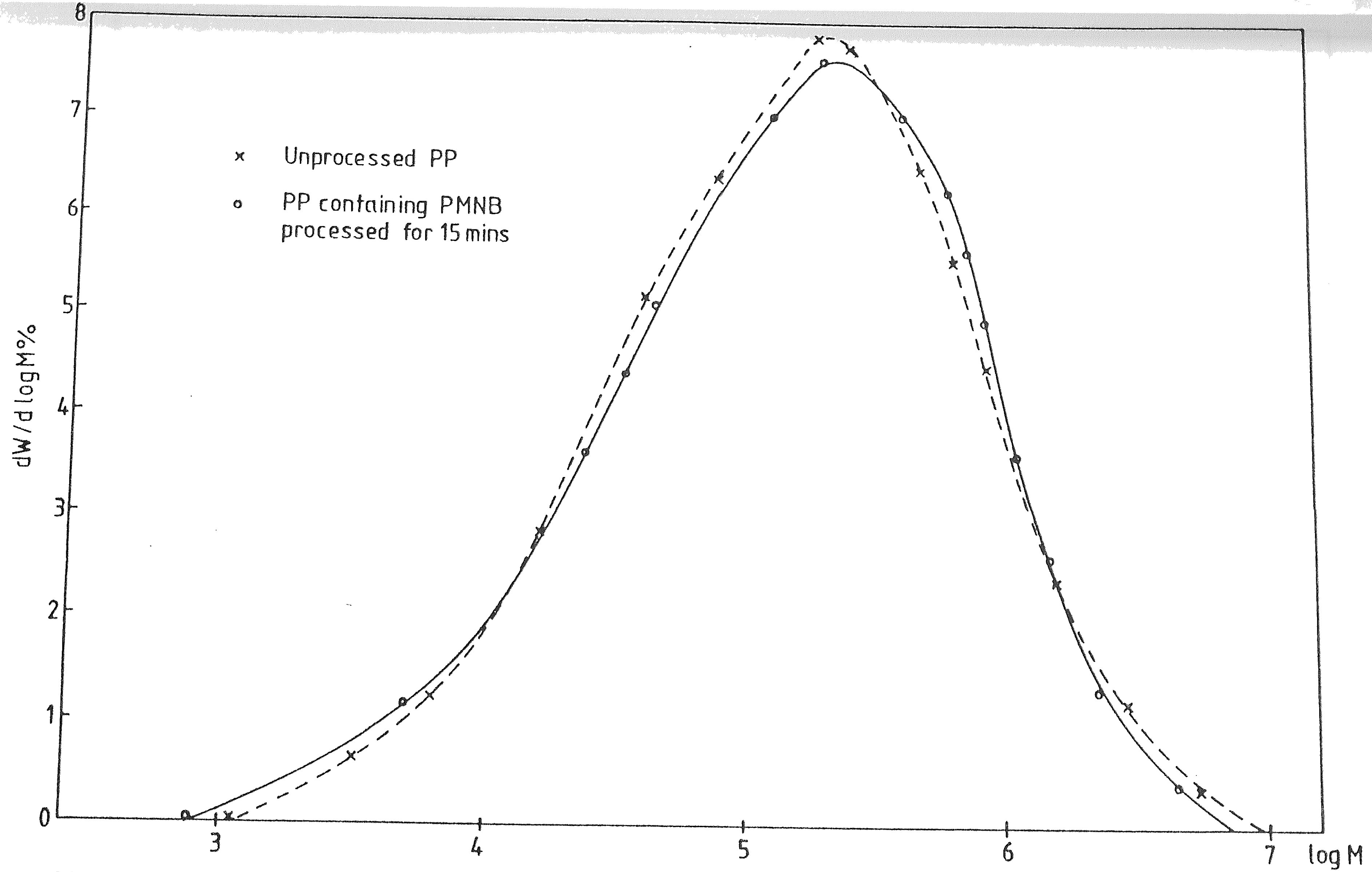


Fig 3:6 Effect of PMNB on the molecular weight distribution of PP processed at 180°C in closed mixer at 15 minutes

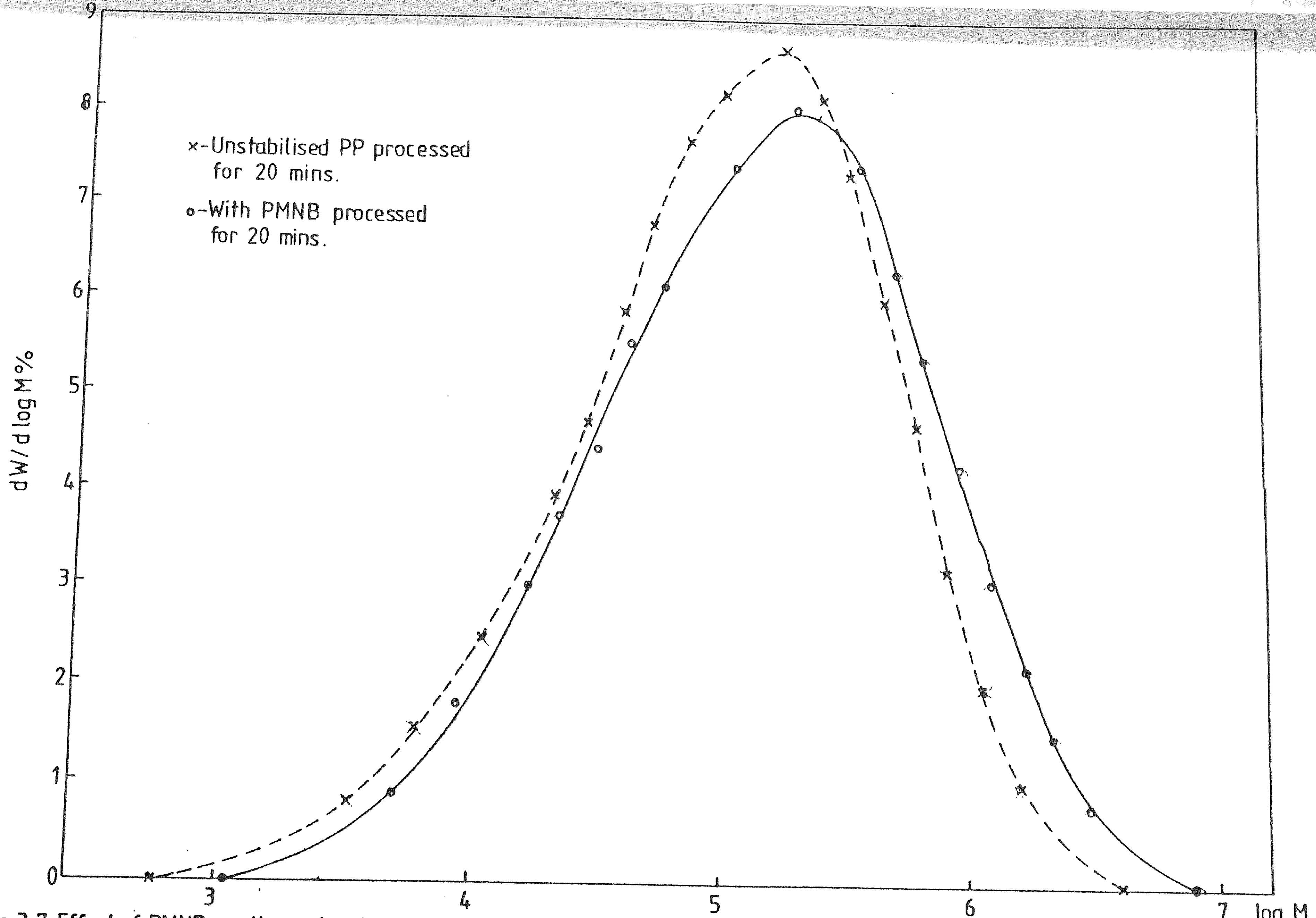


Fig 3:7 Effect of PMNB on the molecular weight distribution of PP processed at 180°C in closed mixer for 20 minutes

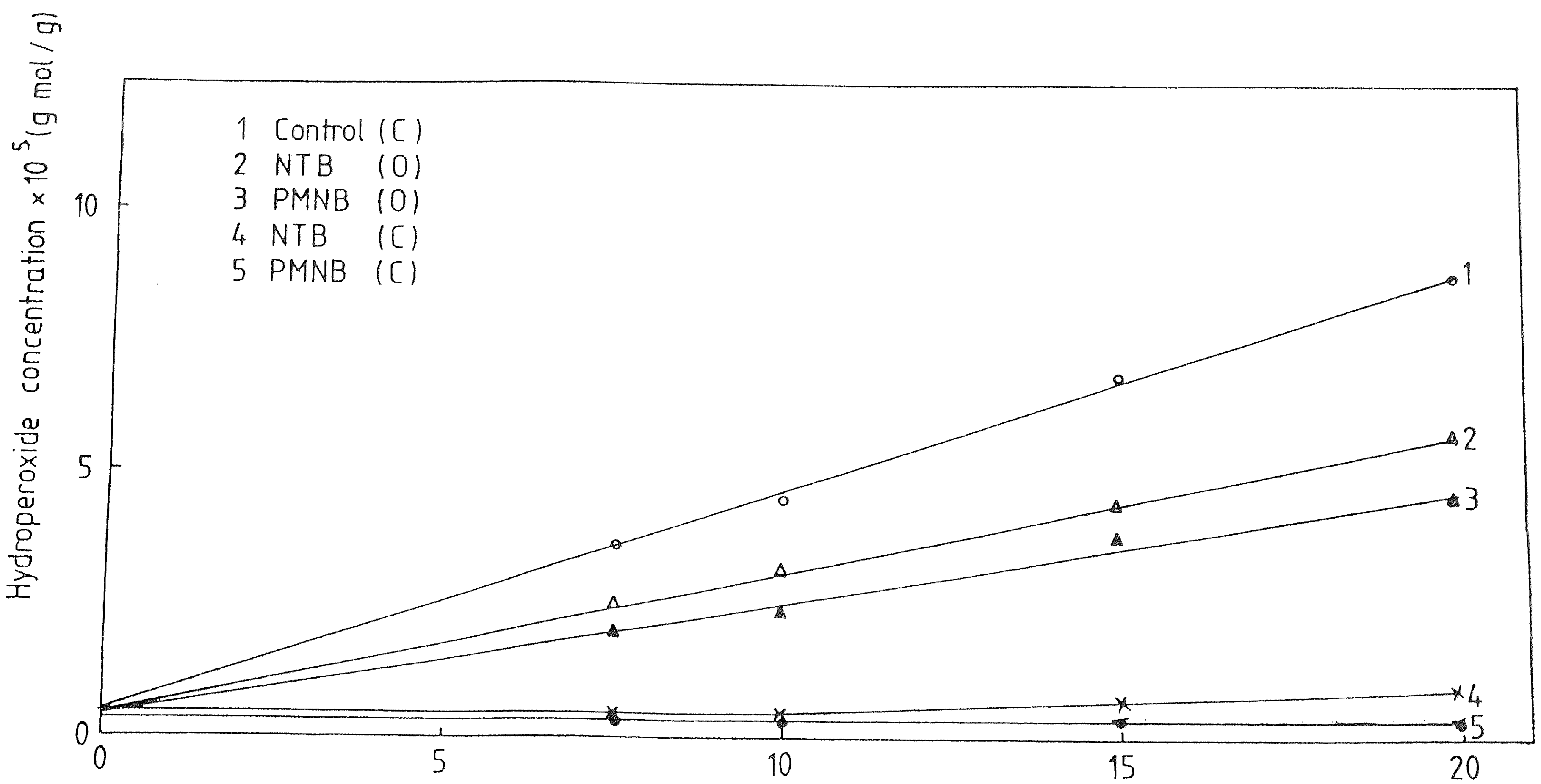


Fig 3:8 Effect of NTB and PMNB on the formation of hydroperoxide during processing of PP in closed (C) and open (O) mixer at 180°C (Conc 1×10^{-3} mole/100 gm)

of processed polymer containing PMNB with that before processing, and shows an increase in average molecular weight corresponding to the decrease in MFI (Fig. 3.4) indicating that the cross linking occurred under these conditions. Fig. 3.7 demonstrates the change in molecular weight distribution of pp processed for 20 mins. in the presence and absence of PMNB.

The detection of nitroxyl radicals by E.S.R. in pp samples processed thermally with aromatic nitroso compounds (Table 2.2) indicates that a major effect of these compounds could be their ability to terminate the polymeric alkyl radicals (CB-A mechanism) to produce nitroxyl radicals (Reaction (1)).

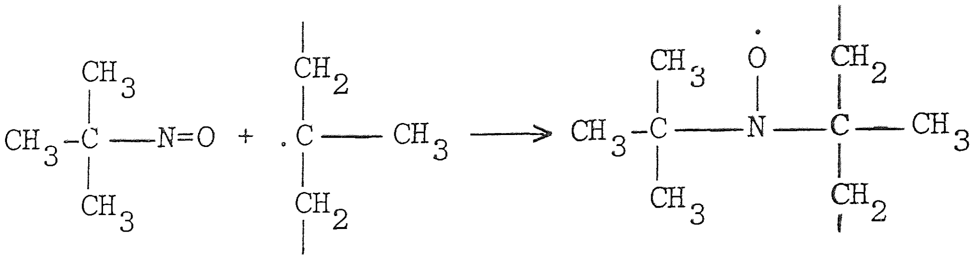
The formation of hydroperoxides was almost completely inhibited in pp samples containing NTB and PMNB when processed in a closed mix (Fig. 3.8), curves 4 and 5). However, hydroperoxide formation was not completely inhibited when processed in an open mixture. Furthermore, the MFI values reduced remarkably during processing in open mixt compared with processing in closed mix . Such results show oxygen competes strongly with alkyl radicals during processing time in open mix .

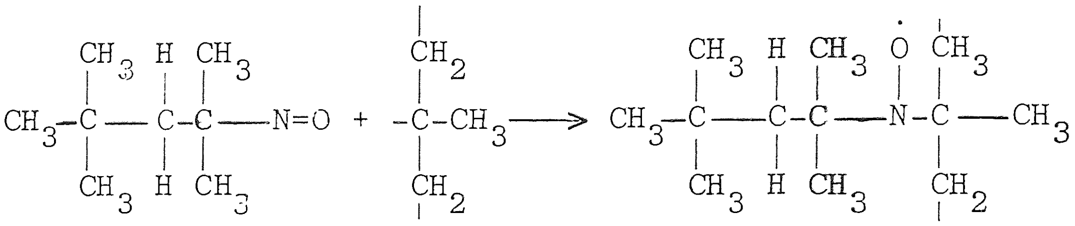
3.1.4 Discussion.

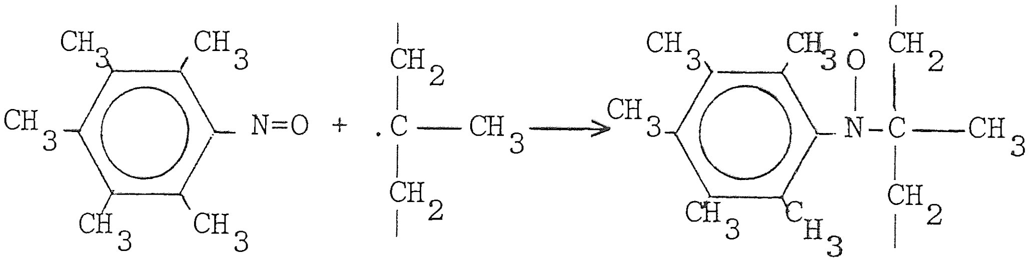
During the thermal processing of pp, once initiation step has started by alkyl radical formation, the polymer propagation then follows in a series of reactions. The first of these is a rapid reaction of R. with oxygen to form alkylperoxy radicals the propagating species for polymer degradation. When the nitroso compounds are incorporated in to the polymer during the thermal processing operation, particularly when there is a deficiency of oxygen, (processing in closed chamber) it seems possible that alkyl radicals are oxidised by nitroso compounds (CB-A mechanism) to produce stable nitroxyl radicals (reaction I).

The investigation of pp films containing nitroso compounds after the thermal processing by means of ESR at room temperature showed signals characteristic of nitroxyl radicals. The calculated g values are shown in Table 3.2.

The formation of nitroxyl radicals is certainly due to the reaction of macro alkyl radicals with nitroso compounds. Such a reaction would inhibit the formation of alkylperoxy radicals which are the precursor of hydroperoxides which leads to polymer degradation. Consequently they would preserve the polymer chains without significant breakdown. The reactions of nitroso compounds with macro alkyl radical to form nitroxyl radicals may be represented by the following representative reactions:







The above reaction of nitroso compounds with macro alkyl radicals implies that the nitroxyl radical becomes chemically bound to the polymer chains.

It has been shown(95) that the reaction of alkyl radicals with nitroxyl radicals producing alkylated hydroxylamine is faster than its reaction with nitroso compounds. This fact suggest the bound nitroxyl radicals attached to the polymer chains react again with another macro alkyl radical to produce an alkylated hydroxylamine. This will result in cross linking reactions and is reflected in the decrease of MFI of polypropylene in the case of some nitroso compounds (PMNB, NTO and DMNA), i.e. each molecule of nitroso compound should terminate

Table 3.1 Concentration of nitroxyl radicals in pp containing nitroso compounds at concentration of 1 x 10^{-3} mole/100 gm, before and after extraction with CH_2Cl_2

Compound	Nitroxyl radical concentration x10^{-5} mole/100 gm		
	pp films processed for 10 mins.		pp films processed for 15 mins
	before extraction	after extraction	unextracted
NTB	3.9	2.1	4.2
NTO	1.9	1.1	2.1
NB	4.1	1.4	4.1
PMNB	2.5	0.9	2.4
TMNB	2.3	1.2	2.1

Table 3.2 g values of nitroxyl radicals obtained from pp films processed with different nitroso compounds

Nitroso compounds	g values (±0.0005)
NTB	2.0059
NTO	2.0067
PMNB	2.0065
TMNB	2.0062
NB	2.0071
DMNA	2.0068
4-NDBP	2.0061
TCNB	2.0069

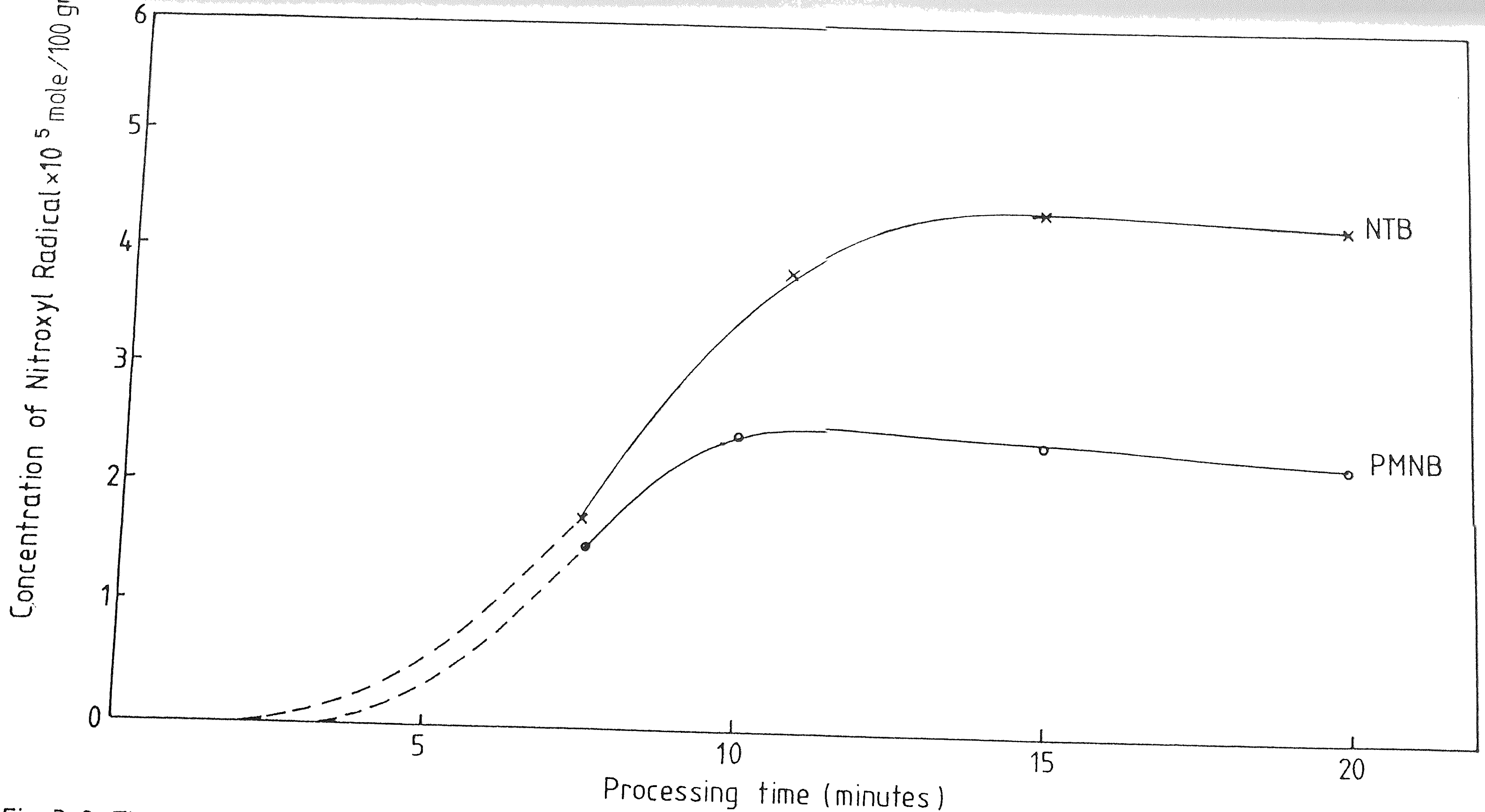
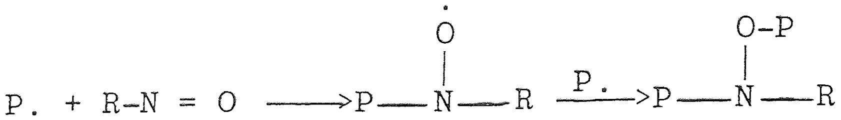


Fig 3:9 The concentration of nitroxyl radials formed during processing of PP containing NTB and PMNB at 180° C, concentration 1×10^{-3} mole/100 gm

two macro alkyl radicals and act as cross linking sites



$$P. + R\text{-}N = O \longrightarrow P-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-R \xrightarrow{P.} P-\overset{O-P}{\overset{|}{N}}-R \qquad (2)$$

The above reaction explains the reason for the shift of molecular weight distribution of polypropylene containing nitroso compounds to higher values (Figs. 3.2 and 3.6). However, some nitroso compounds viz NTB and nitrosobenzene did not show any cross linking reactions in polypropylene during processing. This could be due to the slow rate of formation of the alkylated hydroxylamine which is produced by trapping macro alkyl radicals by nitroxyl radicals. The stability of alkylated hydroxylamine seems to depend on the inductive effect due to the substituents.

Fig. 3.9 and Table 3.1 show that the concentration of nitroxyl radicals derived from NTB increased with processing time up to 15 mins. and then remained almost constant up to 20 mins. of processing. A similar phenomenon is observed with aromatic nitroso compound (PMNB), but in this case the rate of nitroxyl formation was slower. The slower increase in nitroxyl radical concentration increase observed at longer processing times could be due to the reaction of nitroxyl radicals with alkyl radicals to form alkylated hydroxylamines (cross linking reaction) according to reaction (2).

The effect of the processing time on the activity of nitroso compounds could be related to the formation of nitroxyl radicals. Presumably processing of pp in a limited amount of oxygen allowed more formation of alkyl radicals, which are essential to react with nitroso compounds to produce nitroxyl radicals. Under these circumstances the concentration of nitroxyl radicals depends on the reactivity of nitroso compounds which again depend on the substituents reacting with alkyl radicals to produce nitroxyl radicals. It is important to bear in mind that the concentration of nitroxyl radicals observed within the pp films could be less than the real amount of nitroso compound converted into nitroxyl radicals due to the formation of alkyated hydroxylamines and hydroxylamine.

The inhibition of hydroperoxide formation by nitroso compound (Fig. 3.8) during processing in a closed mixter is consistent with the idea that nitroso compounds terminate alkyl radicals which would otherwise form hydroperoxides.

The ESR measurements show that the concentration of nitroxyl radicals is reduced by hot extraction (with $CH_2C\ell_2$) of pp samples containing NTB and NTO (Table 3.1). Nitroxyl radicals were detected in the extracts suggesting that some low molecular mass alkyl radicals also react with nitroso compounds.

It is now clearly evident from the measurements of MFI values, molecular weight distribution, and hydroperoxide contents that nitroso compounds act as very powerful melt stabilisers in polypropylene when processed in closed system and the evidence suggests that nitroso compounds produce some bound nitroxyl radicals in the polymer chains.

Although some aromatic nitroso compounds show cross linking in polypropylene (reaction (2)), nitrosophenol and its derivatives did not show any decrease in MFI of polypropylene during processing. Nitrosophenols act in a somewhat different manner from other carbon nitroso compound and its mechanism of action will be discussed in detail in the next section.

3.2 Effect of C-nitroso Compounds on Photo-oxidation of Polypropylene

It has been reported(138) that there is a linear relationship between initial photo-oxidation rate and initial hydroperoxide concentration during photo-oxidation of pp which implies that hydroperoxide formed during the thermal processing can account for the photo-initiation. Further evidence supporting this view was also provided by an experiment during which hydroperoxides were removed from a processed sample by heating in argon at 110°C for 50 hrs. before U.V. exposure and it was found that in spite of the high concentration of ketonic carbonyl, the initial photo-oxidation rate is reduced to zero. When substantial amounts of carbonyl groups are present in the polymer either by thermolysis or photolysis of hydroperoxides they are intimately involved as initiators in the later stages of photo-oxidation. In the previous section it has been observed that hydroperoxide formation is almost inhibited in polypropylene during processing in the presence of nitroso compounds. It follows therefore, that carbon nitroso compounds could act as U.V. stabiliser in polypropylene.

3.2.1 Effect of Aliphatic Nitroso Compounds on Photo-oxidation of Polypropylene

The results of this section demonstrate the effect of aliphatic nitroso compounds as U.V. stabiliser for pp films. It was desirable to evaluate the contribution of different processing times and different concentrations on the photo-stabilisation activity.

Fig. 3.10 shows the effect of processing time on the photo-stability of polyropylene containing nitroso-tert-butane (NTB) at concentration of 1.5×10^{-3} mole/100 gm (0.2%) as measured by carbonyl formation. Increasing the processing time from 7.5 mins. up to 15 mins. improved the photo-stabilisation activity, but at 20 mins. of processing the photo-stabilisation activity slightly decreased compared to 15 mins. processed samples. It appears that there is an optimum processing time for the stabilisation activity of NTB. The performance of NTB is characterised by a long induction period of about 450 hours followed by a gradual increase in carbonyl formation. The embrittlement times of exposed pp films were consistent with carbonyl formation, i.e. the highest embrittlement time was provided by samples processed at 15 mins. (Fig. 3.11). It has been shown (Fig. 3.9 and Table 3.1) that the concentration of nitroxyl radicals derived from nitroso compounds depends on the processing time and reaches a maximum of 15 mins. It may be concluded therefore that the photo-stabilisation activity is related to nitroxyl formed prior to photo-oxidation.

Fig. 3.12 shows the relationship between the concentration of NTB, the U.V. embrittlement times of pp and the concentration of nitroxyl radicals in pp prior to UV irradiation. It is apparent that there is a linear relationship up to certain concentrations between the embrittlement times and NTB concentration, which in turn has a relation with nitroxyl radical concentration derived from NTB. The limitation in the nitroxyl radical concentration with increasing NTB concentration, may be due to the preferred reaction of alkyl radicals with nitroxyl radicals, rather than with NTB itself, so that the yield of the nitroxyl radical will attain an equilibrium concentration.

Fig. 3.13 shows the U.V. stabilisation effect of NTO processed with pp at different concentrations. Increase in concentration leads to increase in photo-stabilisation activity up to 1×10^{-3} mole/100 gm. However, on further increase in concentration, no further increase in U.V.

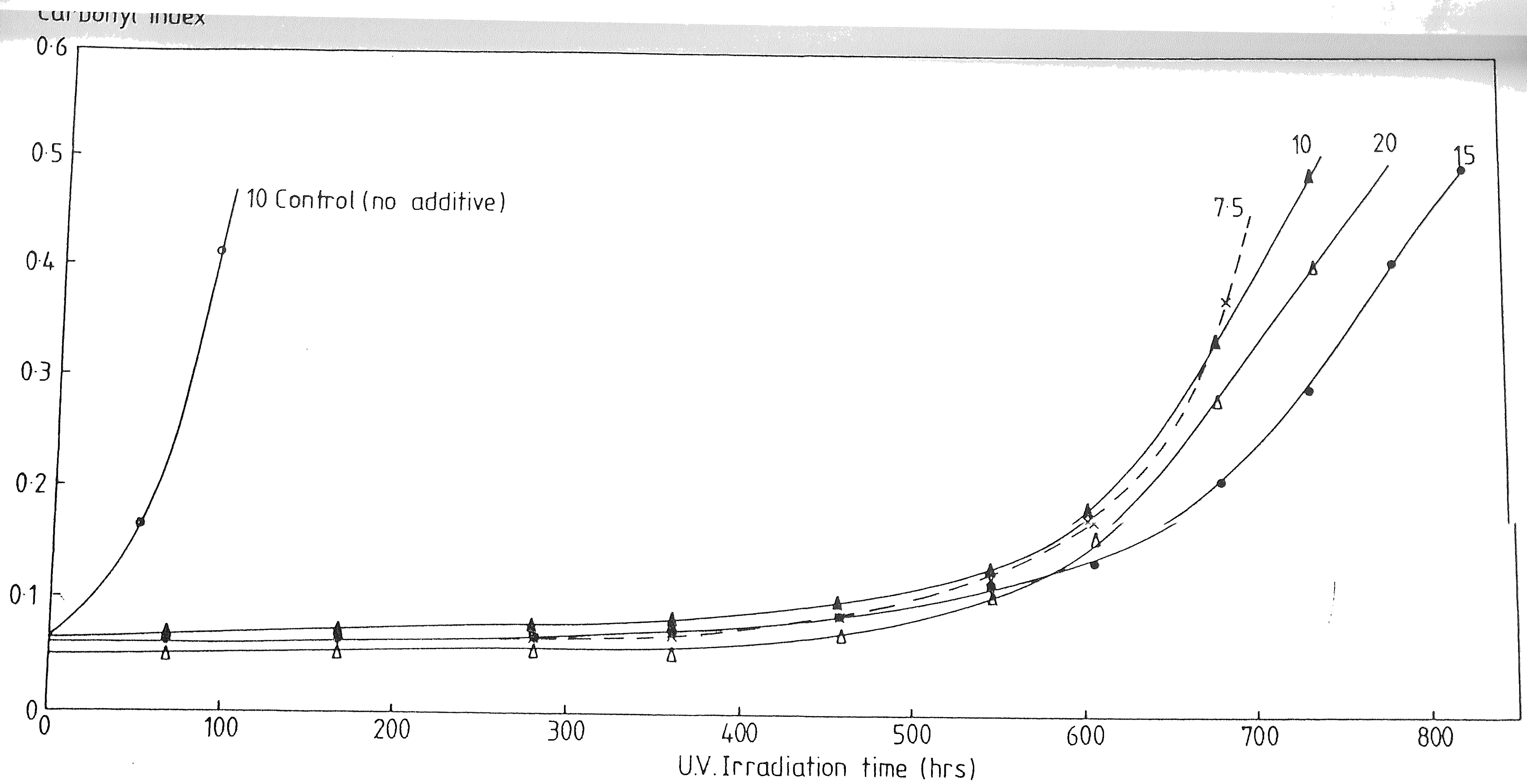


Fig 3:10 Effect of processing time on the U.V. stabilization of PP containing nitroso - tert - butane
(All samples were processed at 180°C, Conc $1{\cdot}5 \times 10^{-3}$ mole / 100 gm)
The number on the curve represents the processing time

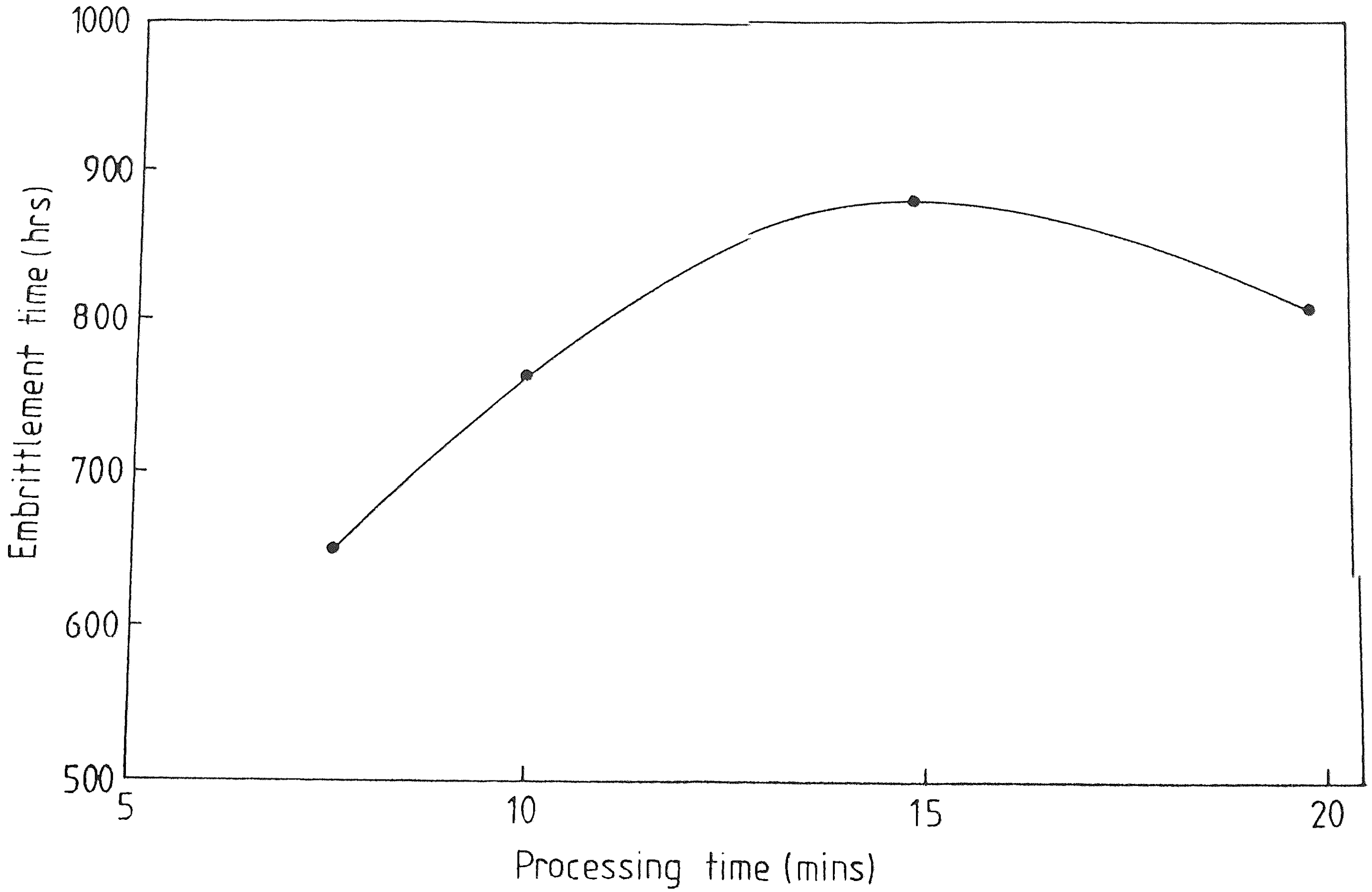


Fig 3 : 11 Effect of processing time on the embrittlement time of PP containing NTB, Conc $1{\cdot}5 \times 10^{-3}$ mole/100 gm

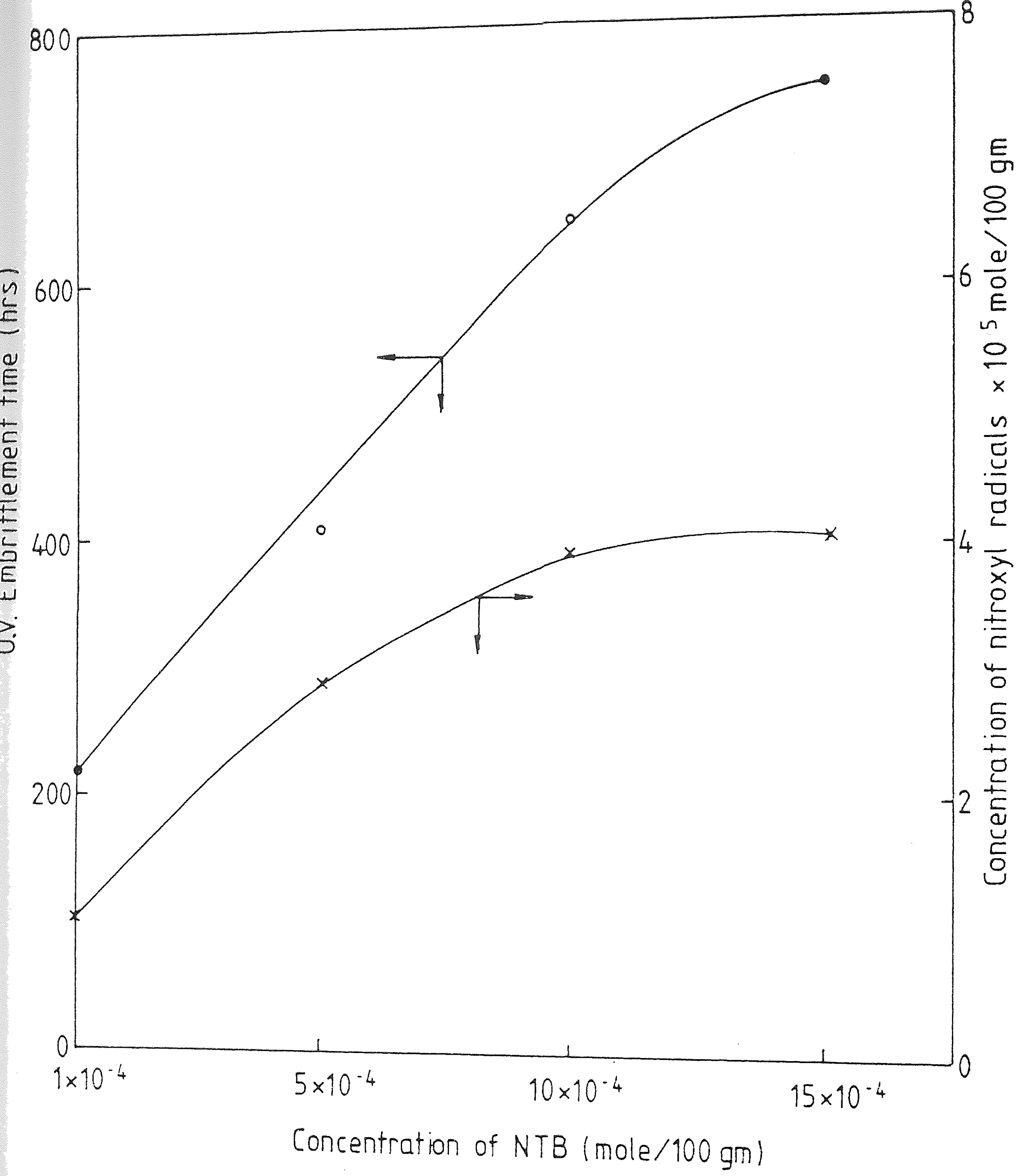


Fig 3: 12 A The effect of NTB concentration on the formation of nitroxyl radicals and U.V. embrittlement time of PP processed at 180°C in closed mixer for 10 mins.

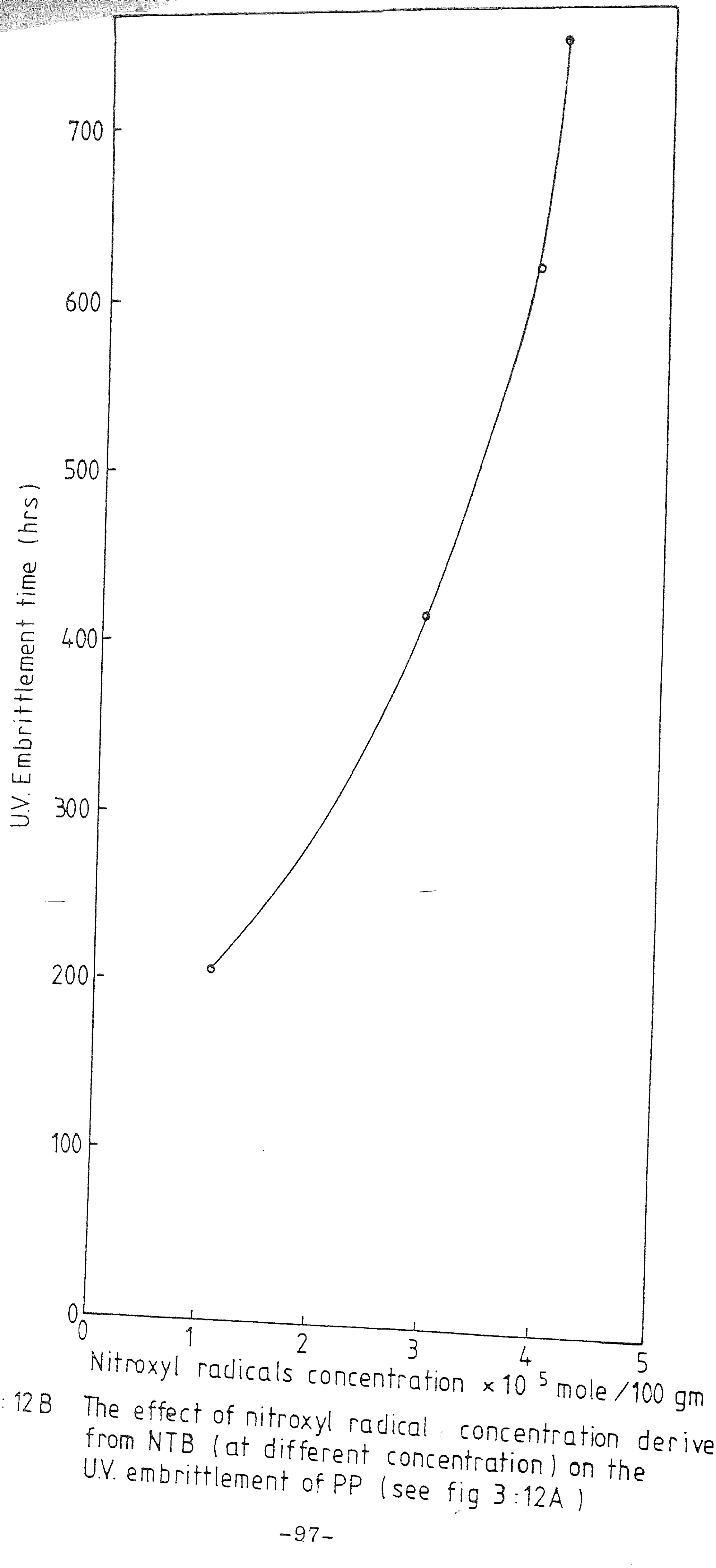


Fig 3 : 12 B The effect of nitroxyl radical concentration derived from NTB (at different concentration) on the U.V. embrittlement of PP (see fig 3 : 12A)

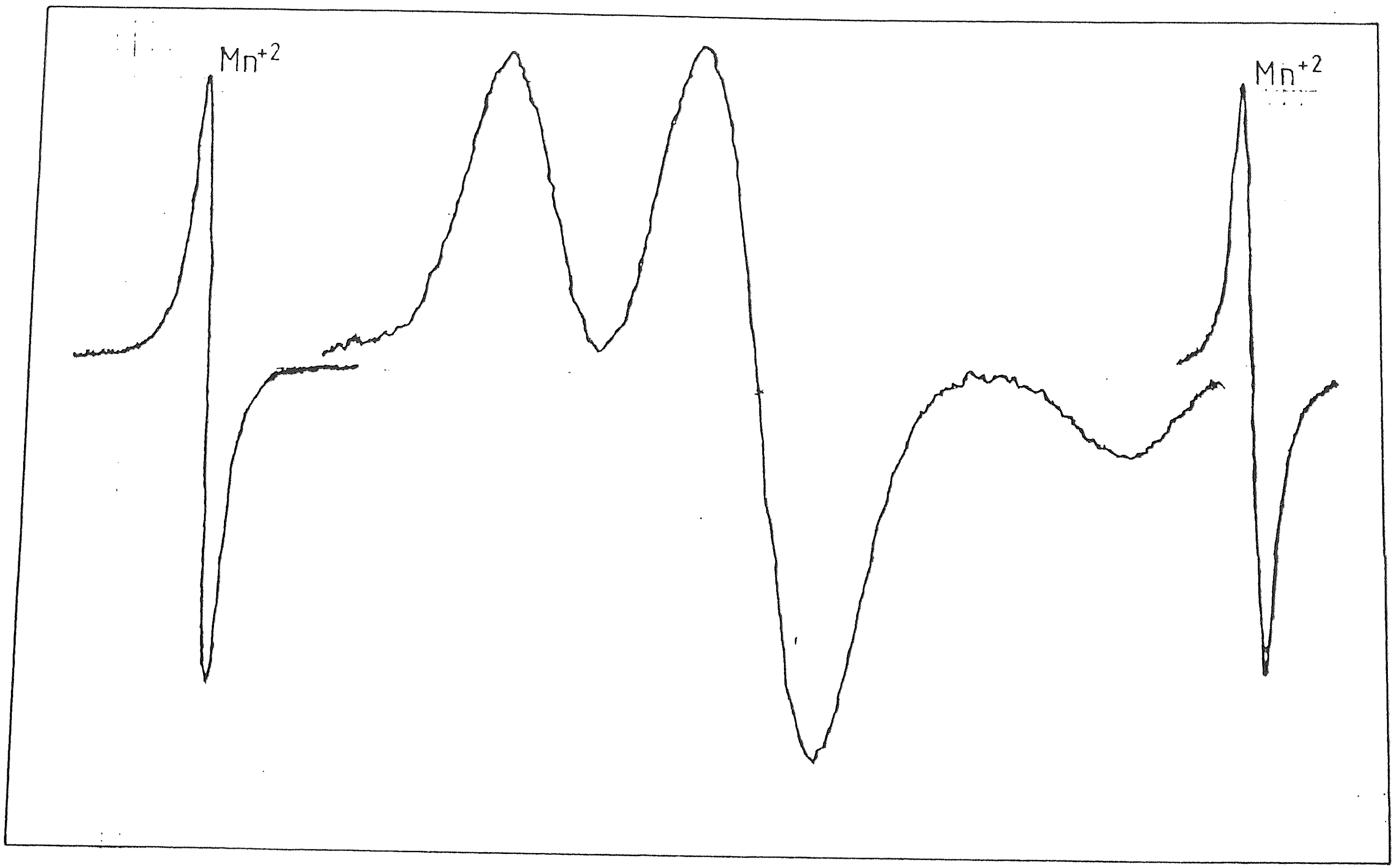


Fig 3 : 12 C ESR spectrum of nitroxyl radical in PP film containing NTB processed for 10 mins at 180°C

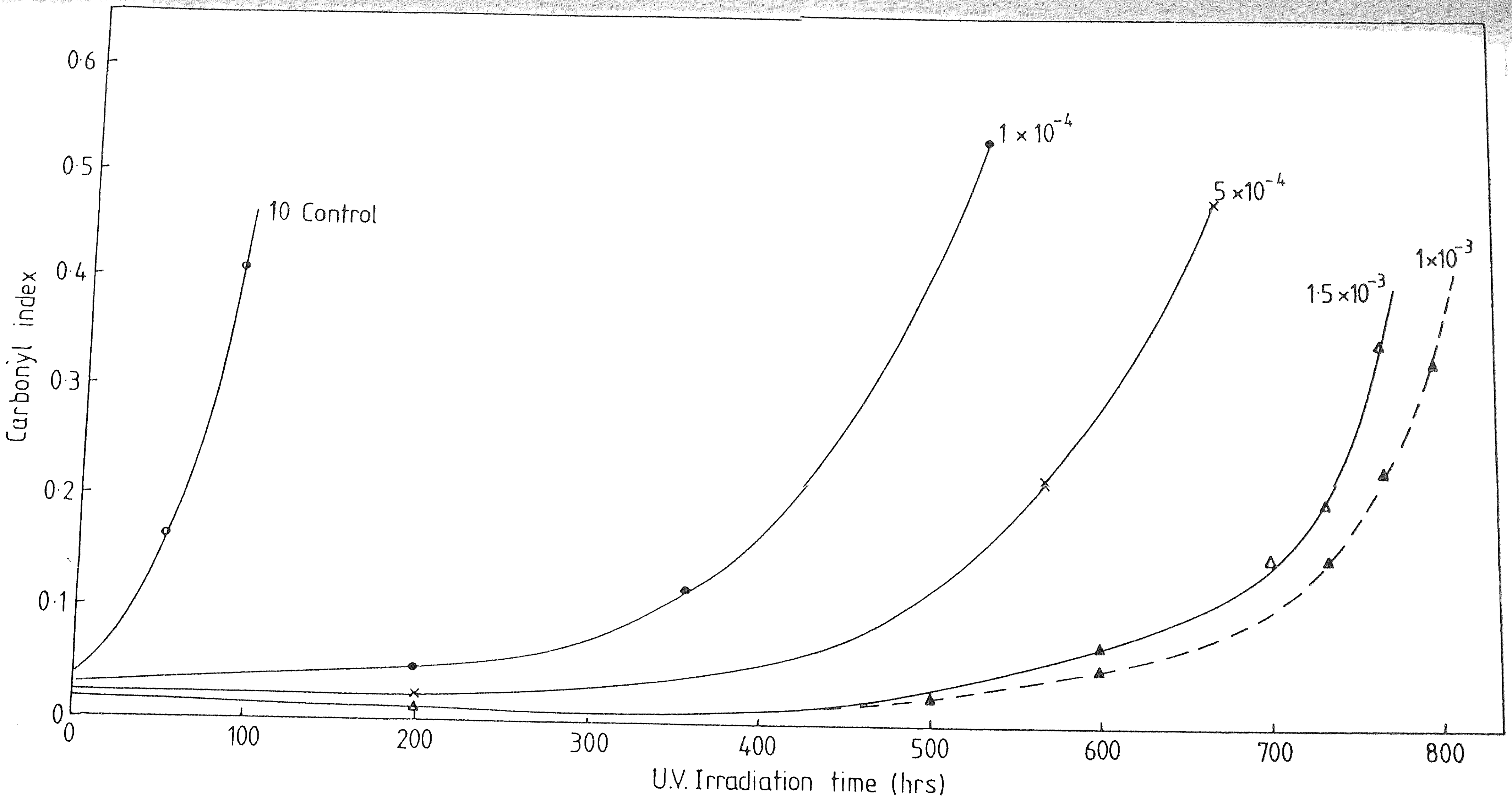


Fig 3:13 The rate of photo-oxidation of PP films containing different concentration of nitroso-tert-octane processed at 180°C in closed mixer at 10 minutes. Number on curve represents conc. in mole/100 g

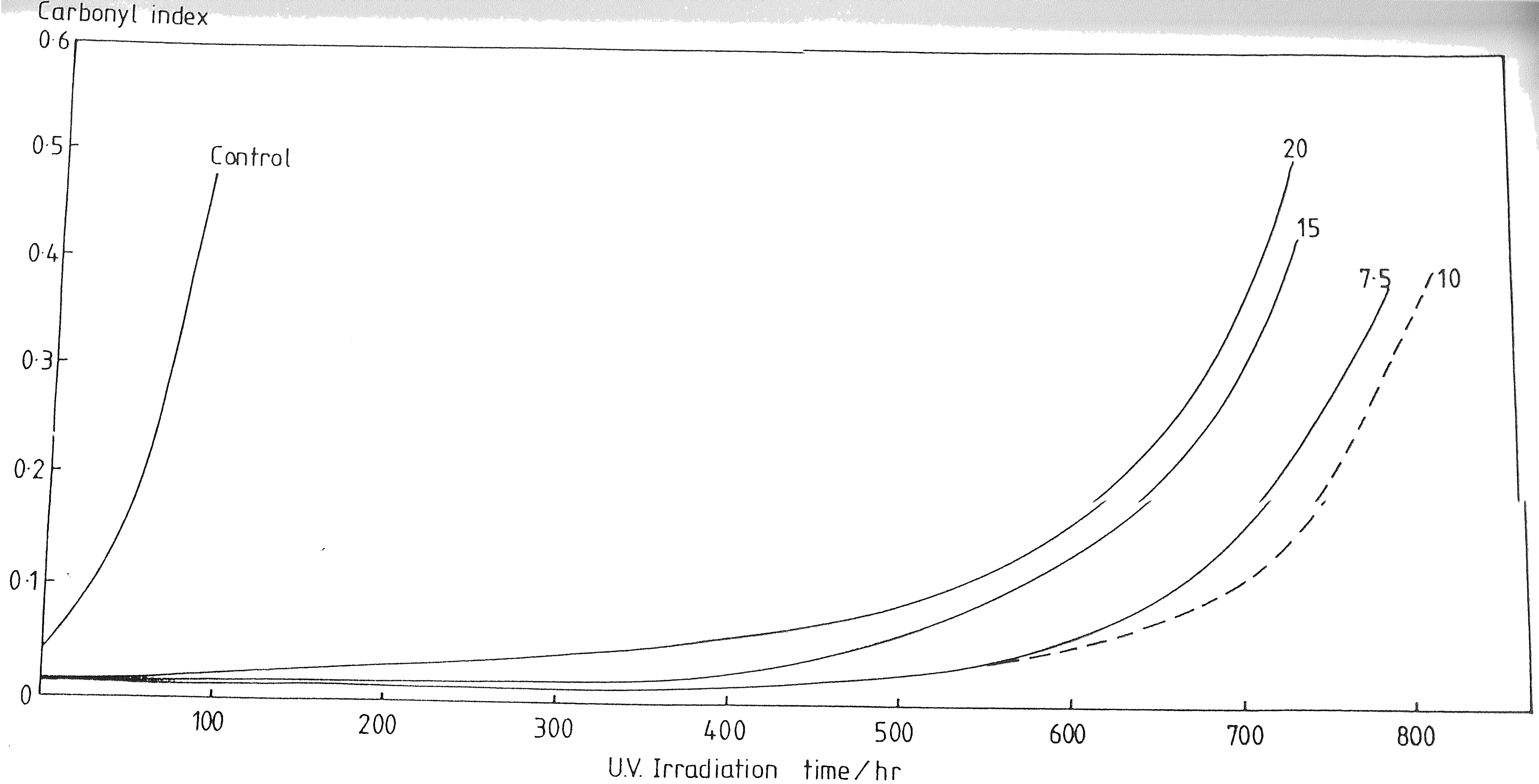


Fig 3:14 Effect of processing time on the rate of photo-oxidation of PP films containing nitroso-tert-octane processed at 180°C in closed mixer, concentration 1 × 10 mole/100 gm. Number on curve represents processing time

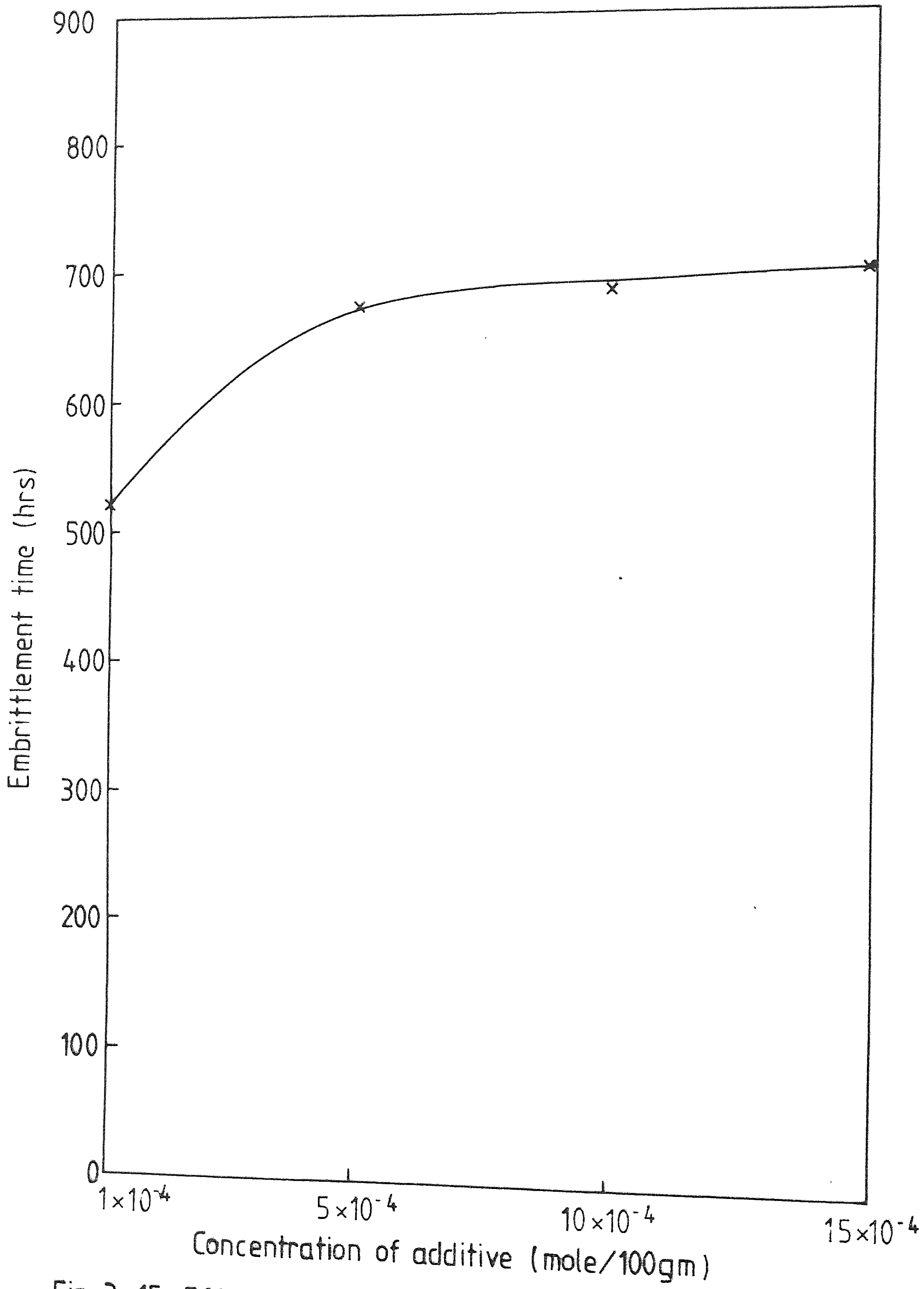


Fig 3 : 15 Effect of conc. of nitroso-tert-octane on the U.V. embrittlement time of PP processed in closed mixer at 10 minutes stabilisation occurs. This is also reflected in the embrittlement time (Fig. 3.15). Increasing processing time from 7.5 mins. to 10 mins. leads to an increase in the U.V. stabilising activity of NTO in pp (Fig.3.14), but further increase in processing time decreased the efficiency of NTO. The U.V. stabilising activity of NTO is characterised by a long induction period to carbonyl formation followed by a high rate of carbonyl formation.

On comparison of the U.V. stabilising activity of 15 mins. processed extracted and unextracted pp films containing NTB and NTO, it is found that the stabilising activity of extracted films is reduced, compared to unextracted films, and this reduction in activity seems to depend on the amount of nitroxyl radicals removed during extraction (Table 3.4).

3.2.2 Effect of Aromatic Nitroso Compounds on Photo-oxidation of Polypropylene

This section is concerned with a study of the effect of concentration and processing time on the U.V. ageing behaviour of aromatic nitroso compounds containing different substituents in polypropylene.

3.2.2.1 Effect of Nitrosobenzene Derivatives

Fig. 3.16 shows the effect of concentration of PMNB on the photo-oxidation of pp films. Increasing the concentration of PMNB from 5×10^{-4} mole/100 gm to 1.5×10^{-3} mole/100 gm progressively increased carbonyl formation and effectively decreases the induction period. In spite of the differences in the carbonyl formation rate with varying concentration of additive, the polymer embrittlement time was almost at the same time for given concentration (170 hours). Fig. 3.17 shows the effect of processing time on the photo-stability of polypropylene containing PMNB at 1 x 10^{-3} mole/100 gm. Carbonyl formation during photo-oxidation of pp varies slightly with different processing times. However the embrittlement time of pp was found to be more or less similar (≃170 hours). Tetramethylnitrosobenzene (TMNB) gives similar results to PMNB and the U.V. stability of pp containing PMNB or TMNB is almost independent of either concentration or processing time.

The effect of TCNB concentration on the photo-stability of pp is shown in Fig. 3.18. TCNB causes an initially high rate of carbonyl formation which increases with increasing concentration. However the overall stabilisation activity is higher with increasing concentration. Fig. 3.19 shows the effect of processing time on the photo-stability of pp containing TCNB. This figures indicates that the photo-stability of polypropylene increased up to 10 mins. of processing but decreased on further processing. The embrittlement time is generally consistent with the rate of carbonyl formation (Table 3.3).

The considerable effect of processing time on the photo-stabilising activity of nitrosobenzene is shown in Fig. 3.20 A. Increasing processing time reduced photo-stabilisation effectiveness. The embrittlement times of the exposed films were consistent with carbonyl formation (see Table 3.3).

The photo-stabilisation afforded by the N.N dimethyl-4-nitrosoaniline at different processing times is shown in Fig. 3.21. Increasing processing time was again found to reduce the stabilisation activity although this compound has the ability to stabilise the polymer melt up to 30 mins. (see Section 3.1.2). This compound exhibited an induction period as is shown by the insignificant increase in carbonyl index up to 100 hours of U.V. exposure. U.V. embrittlement times of pp containing N.N dimethylnitrosoaniline are shown in Table 3.3 again to correlate with photo-oxidation rates.

The ESR spectra obtained from pp samples containing different nitrosobenzene derivatives (i.e. pentamethyl-nitrosobenzene, tetramethyl nitrosobenzene, nitroso-benzene and N.N.dimethyl-4-nitrosoaniline) during U.V. irradiation clearly shows the presence of nitroxyl radicals in each case, characterised by different g values (Table 3.2). This suggests that the photo-stabilisation activity of nitrosobenzene derivatives, could be due to the nitroxyl radicals and their concentration formed during the thermal processing.

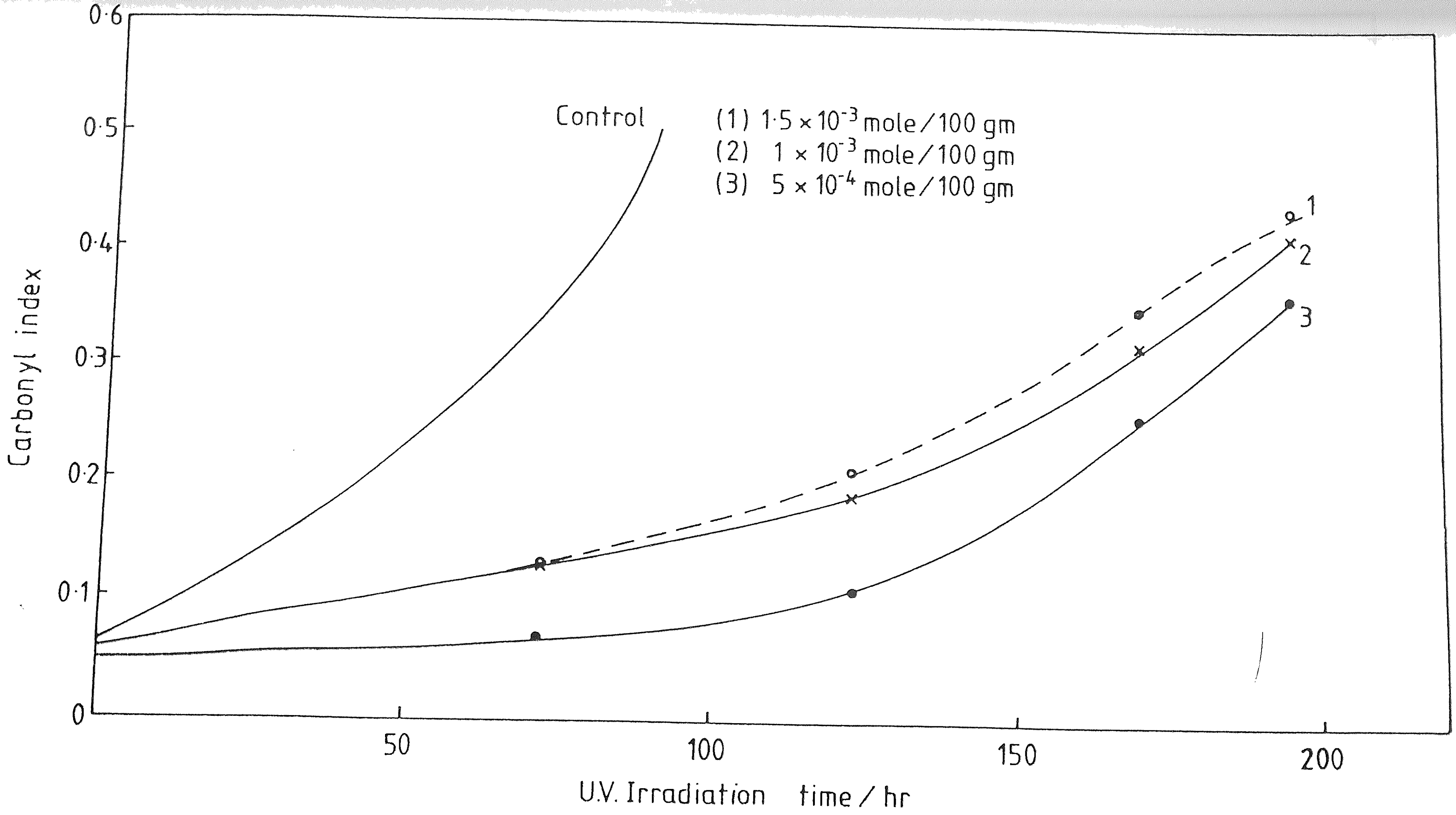


Fig 3:16 Effect of PMNB concentration on the photo-stabilisation of PP processed at 180°C in closed mixer at 10 minutes

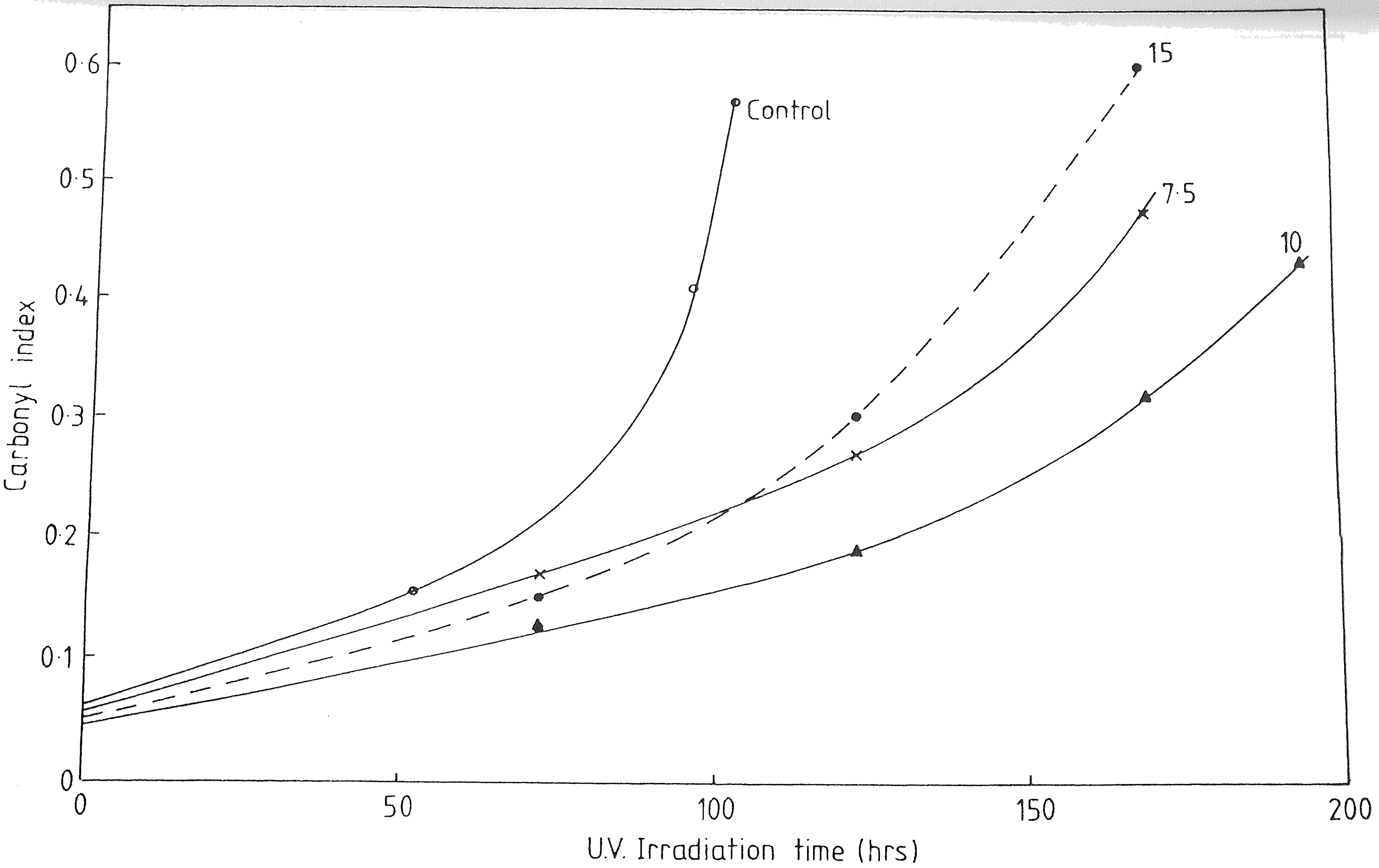


Fig 3 : 17 Effect of processing time on the photo-stabilisation of PP containing PMNB processed at 180°C in closed mixer at concentration of 1×10^{-3} mole/100 gm
Number on curve represents processing time in minutes

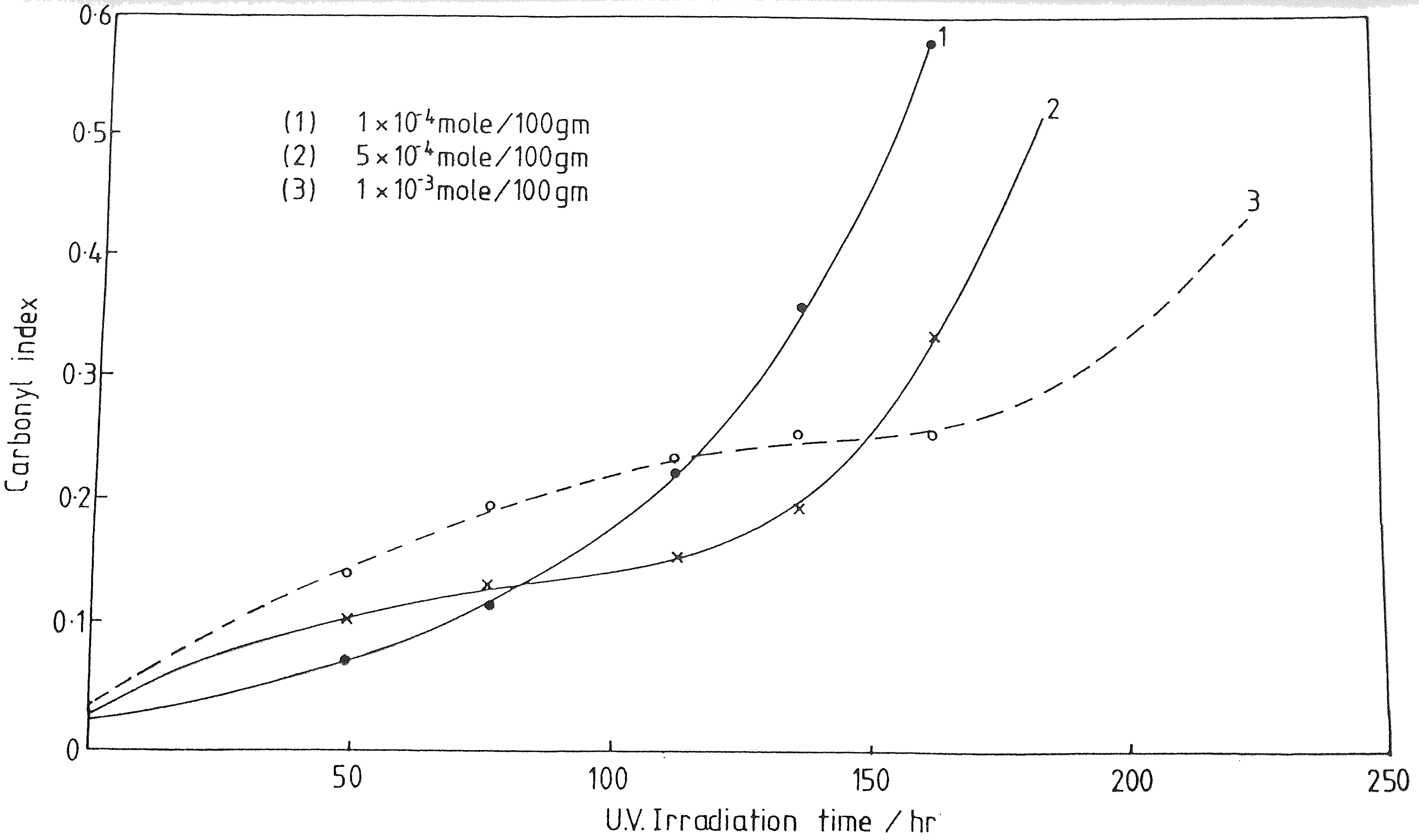


Fig 3:18 Effect of TCNB concentration on the photo-stabilisation of PP processed at 180°C in closed mixer at 10 minutes

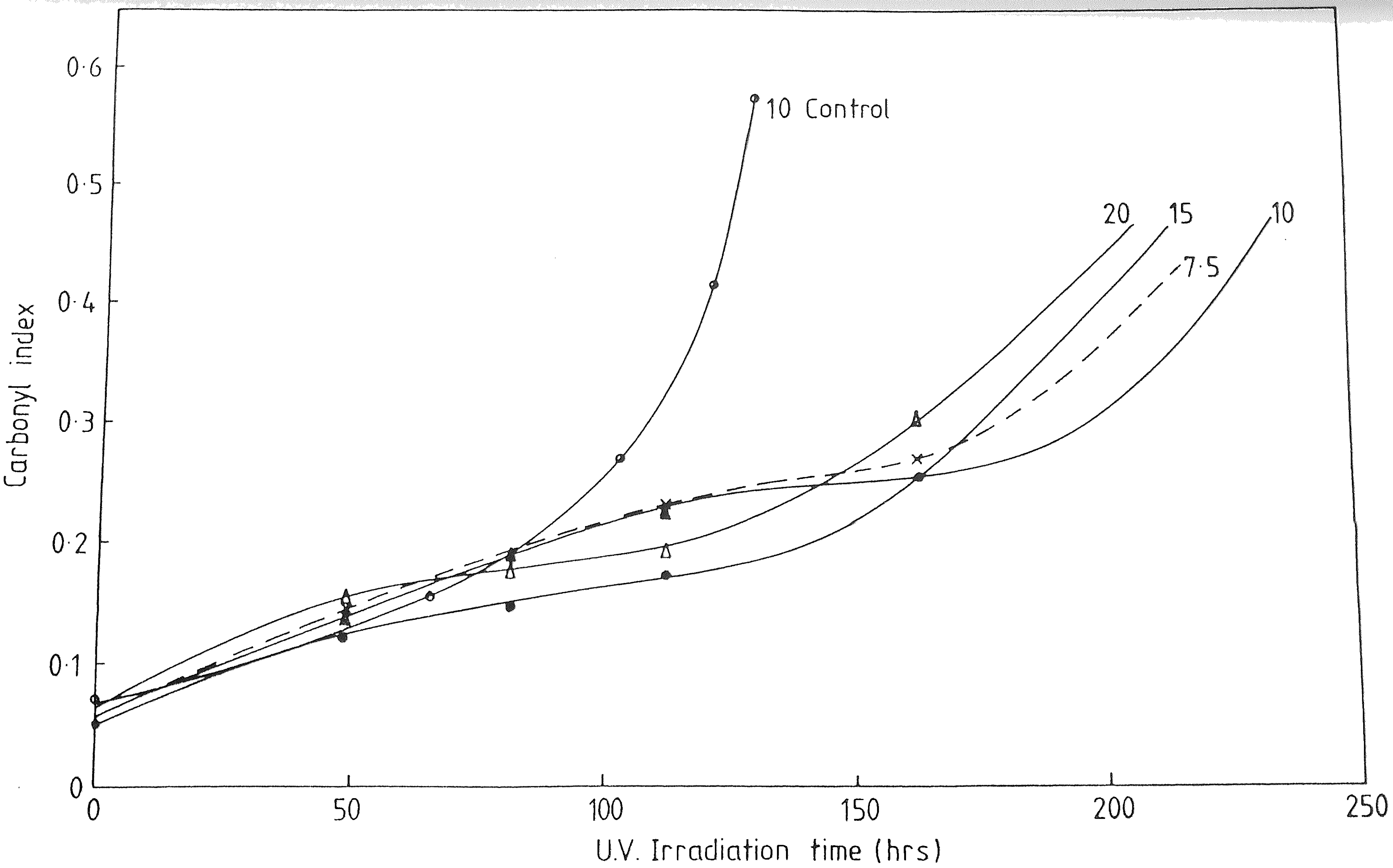


Fig 3:19 Effect of processing time on the photo-stabilisation of PP containing TCNB processed at 180°C in closed mixer at concentration of 1×10^{-3} mole/100 gm. Number on curve represents processing time

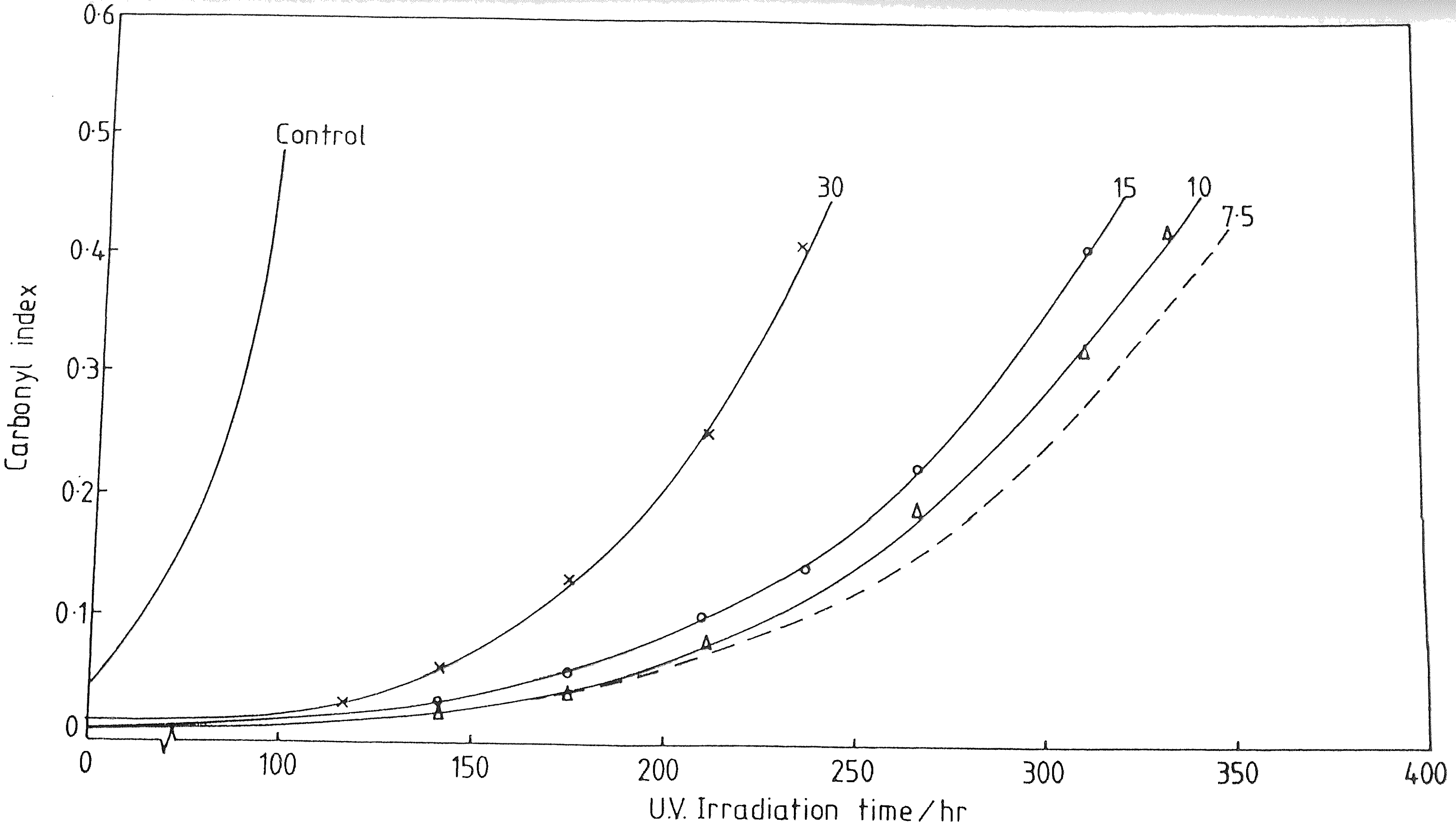


Fig 3:20A Effect of processing time on the photo-stabilisation of PP containing nitrosobenzene processed at 180°C in closed mixer at concentration of 1×10^{-3} mole/100gm. Number on curve represents processing time in minutes

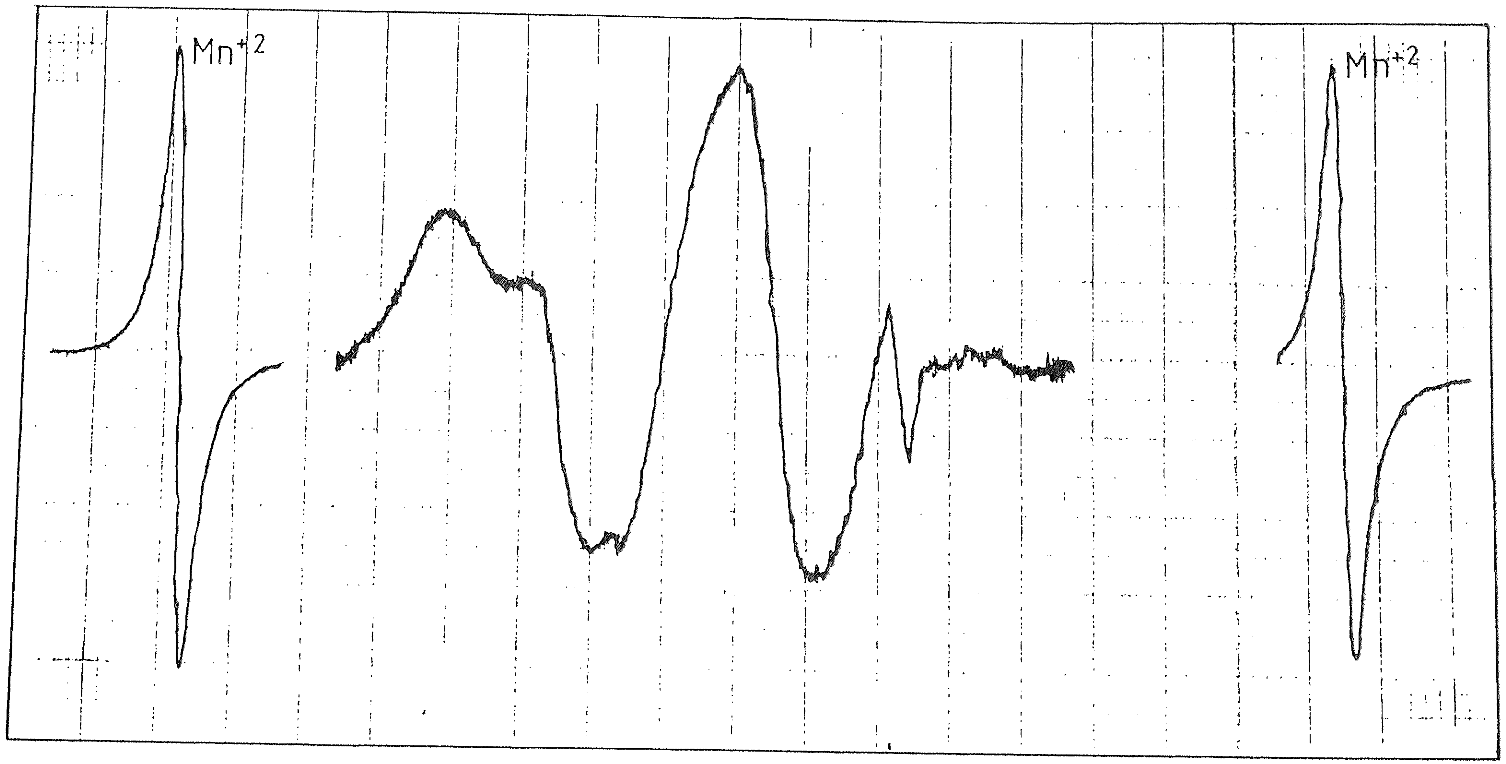


Fig 3:20 B ESR spectrum of nitroxyl radical in PP film containing nitrosobenzene processed for 10 mins at 180° C

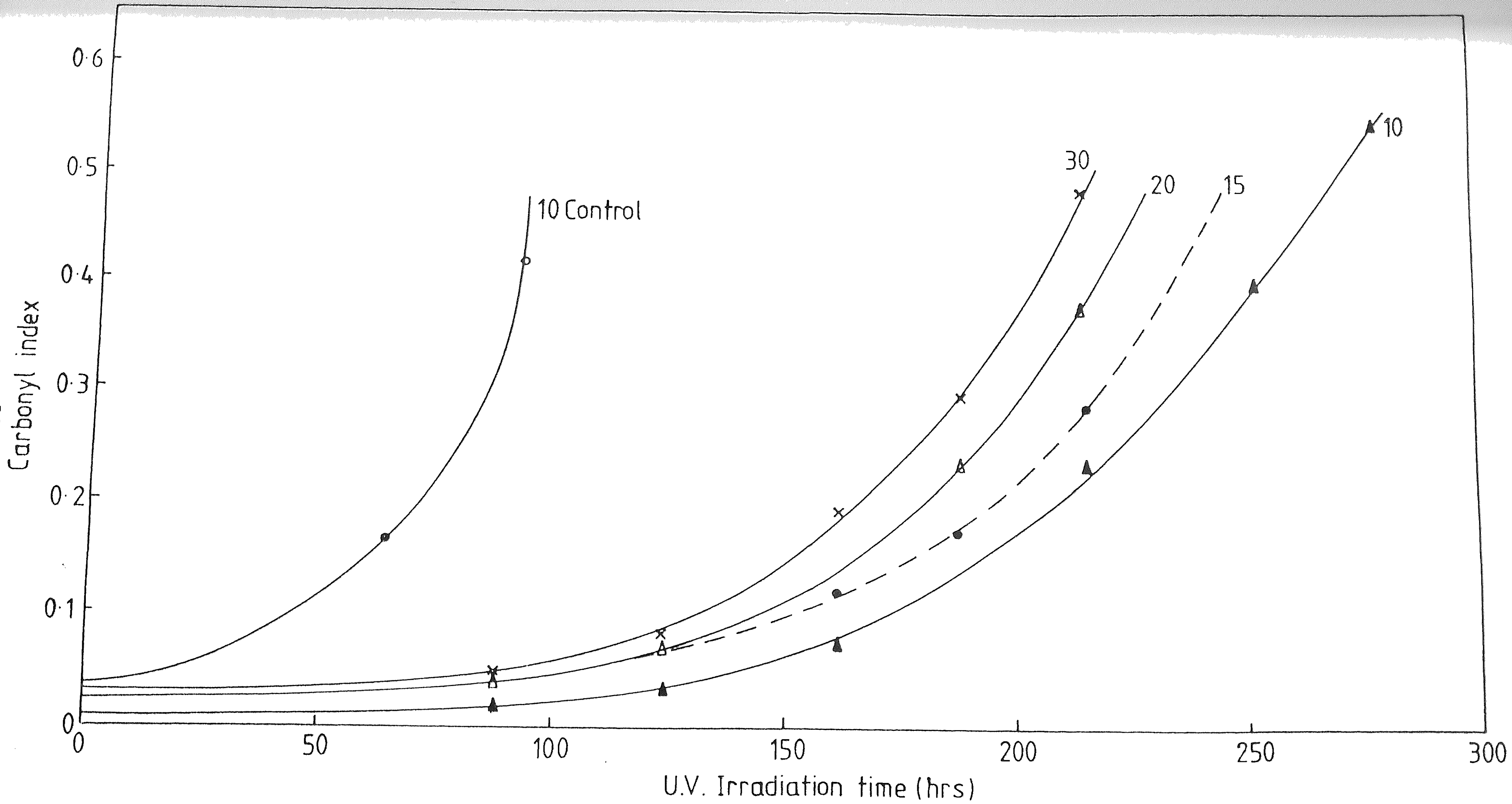


Fig 3:21 Effect of processing time on the photo-stabilisation of PP containing N,N Dimethylnitrosoaniline processed at 180°C in closed mixture at concentration of 1×10^{-3} mole/100 gm. Number on curve represents processing time in minutes.

TABLE 3.3 - U.V. embrittlement time (in hours) of pp containing nitroso compounds, processed at different times in closed mixer at concentration of 1 x 10^{-3} mole/100 gm.
*(concentration 1.5 x 10^{-3} mole/100 gm.)

Processing time Additives	7.5 mins	10 mins	15 mins	20 mins
No additive	85	85	75	--
Nitroso-tert-butane*	660	770	870	800
Nitroso-tert-octane	660	690	650	630
Nitrosobenzene	330	330	280	240
Trichlornitrosobenzene	180	200	180	160
N,N,Dimethylnitrosoaniline	230	260	210	190
Nitroso,2,α,di-tert-butylphenol	---	160	185	200

TABLE 3.4

Compound	PP films processed for 10 minutes		PP films processed for 15 minutes	
	Before extraction	After extraction	Before extraction	After Extraction
Nitrosobenzene*	330 hrs.	125 hrs.	280 hrs.	125 hrs.
Nitroso-tert-butane	770 hrs.	195 hrs.	875 hrs.	255 hrs.
Nitroso-tert-octane	770 hrs.	210 hrs.	630 hrs.	170 hrs.

Effect of the extraction on the U.V. embrittlement time of PP containing nitroso compounds, processed at different time and same concentration of 1.5 x 10^{-3} mole/100 gm (*concentration 1 x 10^{-3} mole/100 gm).

3.2.2.2 Effect of Nitrosophenols

Nitrosophenols possess nitroso and phenolic functional groups which could have an autosynergestic effect during stabilisation processess, the phenolic group acting by a CB-D mechanism (i.e. by hydrogen donation) and the nitroso group act by trapping alkyl and alkoxy radicals (CB-A mechanism). The following study deals with the effect of these compounds on polypropylene stabilisation.

Figs. 3.22, 3.23 and 3.24 show the effect of nitrosophenol compounds (4-nitroso-2,6di-tert-butylphenol "4-NDBP", 4-nitrosophenol and 1-nitroso-2-naphthol) on the photostabilisation of pp processed for different times at the same molecular concentration (5 x 10^{-4}mole/100 gm). Longer processing times slightly improved the photostabilisation activity of 4-NDBP. All the processed samples show auto-accelerating behaviour. After 100 hrs. of U.V. irradiation the rate of carbonyl formation showed a sharp increase (Fig.3.22). Fig. 3.22 clearly shows that processing time does not have a significant effect on the U.V. stabilisation activity of 4-nitrosophenol.

It was found that hydroperoxide formation was inhibited in pp samples processed at different times in the presence of 4-nitrosophenol and 4-NDBP prior to U.V. irradiation. This indicates the activity of nitrosophenols to terminate active radicals and it may be expected that the extent to which the nitrosophenols, have the ability to inhibit the formation of hydroperoxides should be reflected on their U.V. stabilisation effectiveness. However, ESR examination of pp films containing NDBP after processing showed the presence of a nitroxyl radical as is evidenced by its g value of 2.0061. After hot extraction of pp films processed with NDBP, the E.S.R. signal intensity was found to decrease. This implies that some nitroxyl radical may have been extracted during extraction.

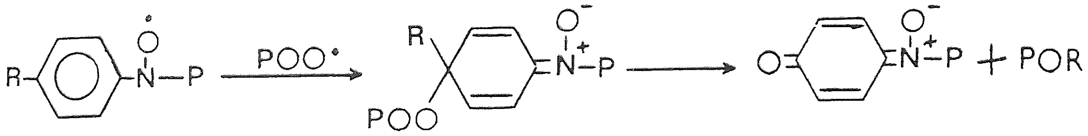
Fig. 3.24 shows the effect of 1-nitroso-2-naphthol on the photo-stabilisation of pp processed at 10 and 30 mins. It is apparent the carbonyl formation shows an induction period of 65 hours followed by gradual increase in carbonyl formation. Longer processing reduced the effectiveness of 1-nitroso-2-naphthol whereas other nitrosophenols provided better stabilisation activity at longer processing times.

3.2.3 Discussion

It seems that the photo-stabilisation activity of nitroso compounds is primarily dependent on the nitroxyl radicals formed in pp during processing. As demonstrated previously (Section 3.1) the role of nitroso compounds is to terminate alkyl or alkoxy radicals during thermal processing and to form bound nitroxyl radicals within polymer chains. Such nitroxyl radicals are highly reactive to alkyl radicals and their concentrations are highly dependent on the thermal processing time. These reactions of nitroso compounds during processing result in the inhibition of hydroperoxide formation (Fig. 3.8) which are the key photo-initiators. It is apparent that there is correlation between photo-stabilisation effectiveness and thermal processing time, so that usually longer processing time results in better U.V. stabilisation activity due to higher initial concentration of nitroxyl radicals (Fig. 3.9). During photo-oxidation, alkyl radicals predominate owing to the high rate of initiation and oxygen diffusion limitation(147) Hence nitroxyl radicals which are effective CB-A anti-oxidants may compete with oxygen for alkyl radicals resulting in alkylhydroxylamine(148). It will be shown later (see section 3.4) that there is no evidence for the direct effect of nitroso compounds in the photo-stabilisation process and that the photo-stabilisation was related to initial concentration of nitroxyl radicals formed prior to the U.V. irradiation (see Section 3.4).

Most of the aromatic nitroso compounds did not show an induction period to carbonyl formation during U.V. irradiation. IR spectroscopy indicated a quinonoid structure at 1630 cm^{-1} attributed to carbonyl stretching of quinone structure in hexane extract of U.V. irradiated pp samples containing PMNB. This could be due to the attack of the aromatic ring by ROO. leading to the decay of nitroxyl radicals, and formation of a quinoniod structure which may act as a sensitiser(141) during U.V.

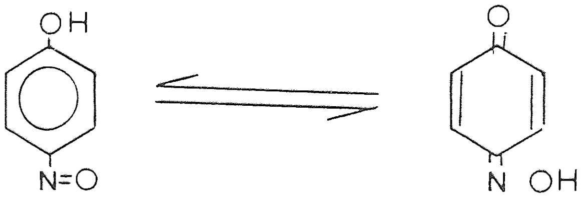
irradiation



(8)

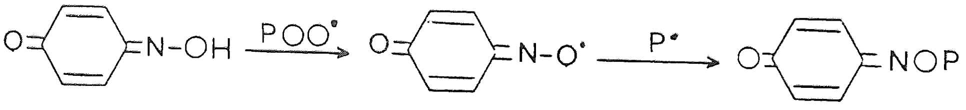
Hence, such quinonoid structures could reduce the efficiency of aromatic nitroso compounds as U.V. stabilisers compared with aliphatic nitroso compounds (Fig. 3.25).

It is also known that nitroso phenols tautomerise into the oxime form.



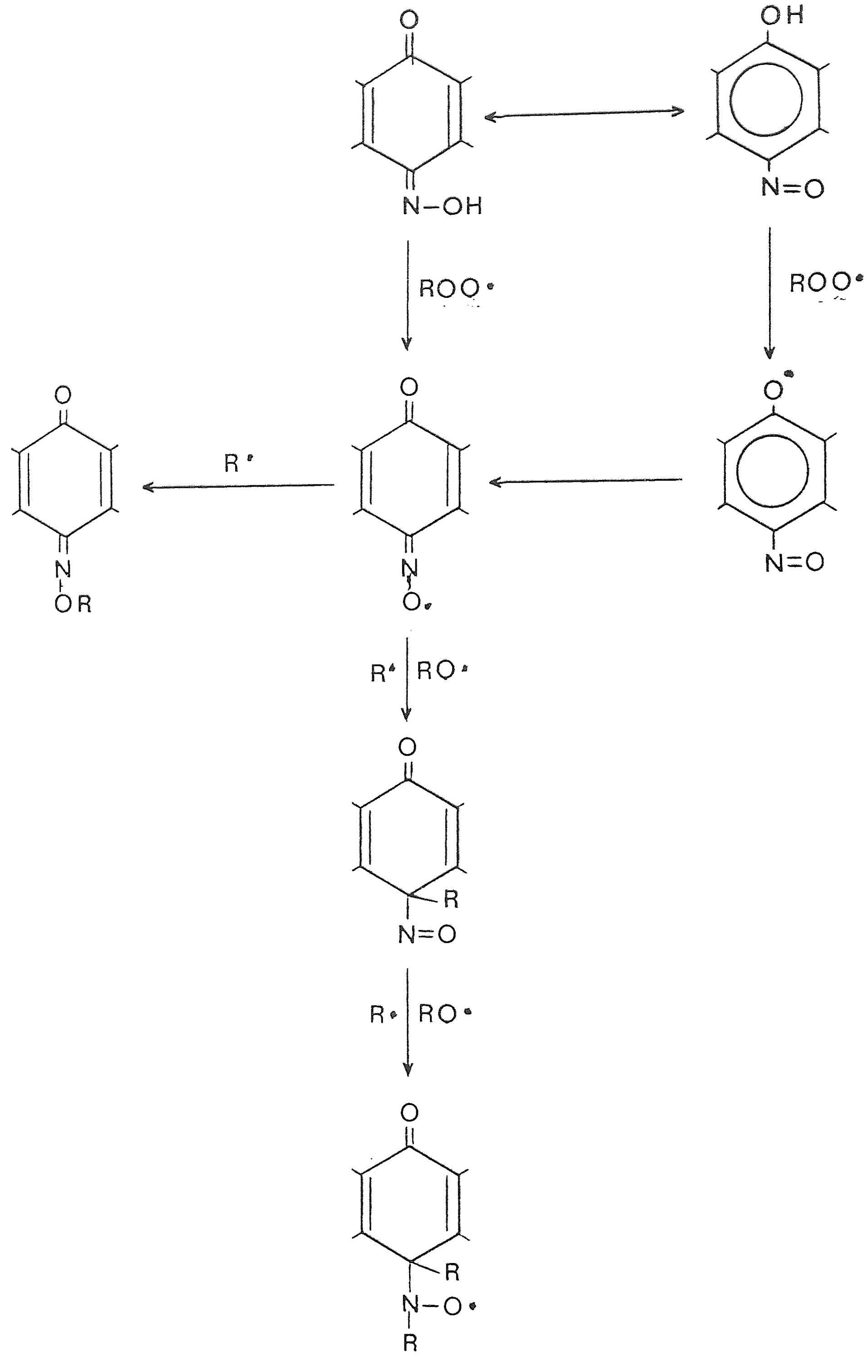
(9)

Such an oxime could easily be oxidised by ROO. into iminoxy radicals which is relatively stable. The iminoxy radicals are highly reactive towards alkyl radicals(143).



(10)

Ingold et al reported(144) that during the oxidation of oximes into iminoxy radicals with butoxy radicals, the ESR spectra indicated the presence of more than one nitroxyl radical among the oxidation products which could be formed according to the following reaction(143) [11].



Scheme 12

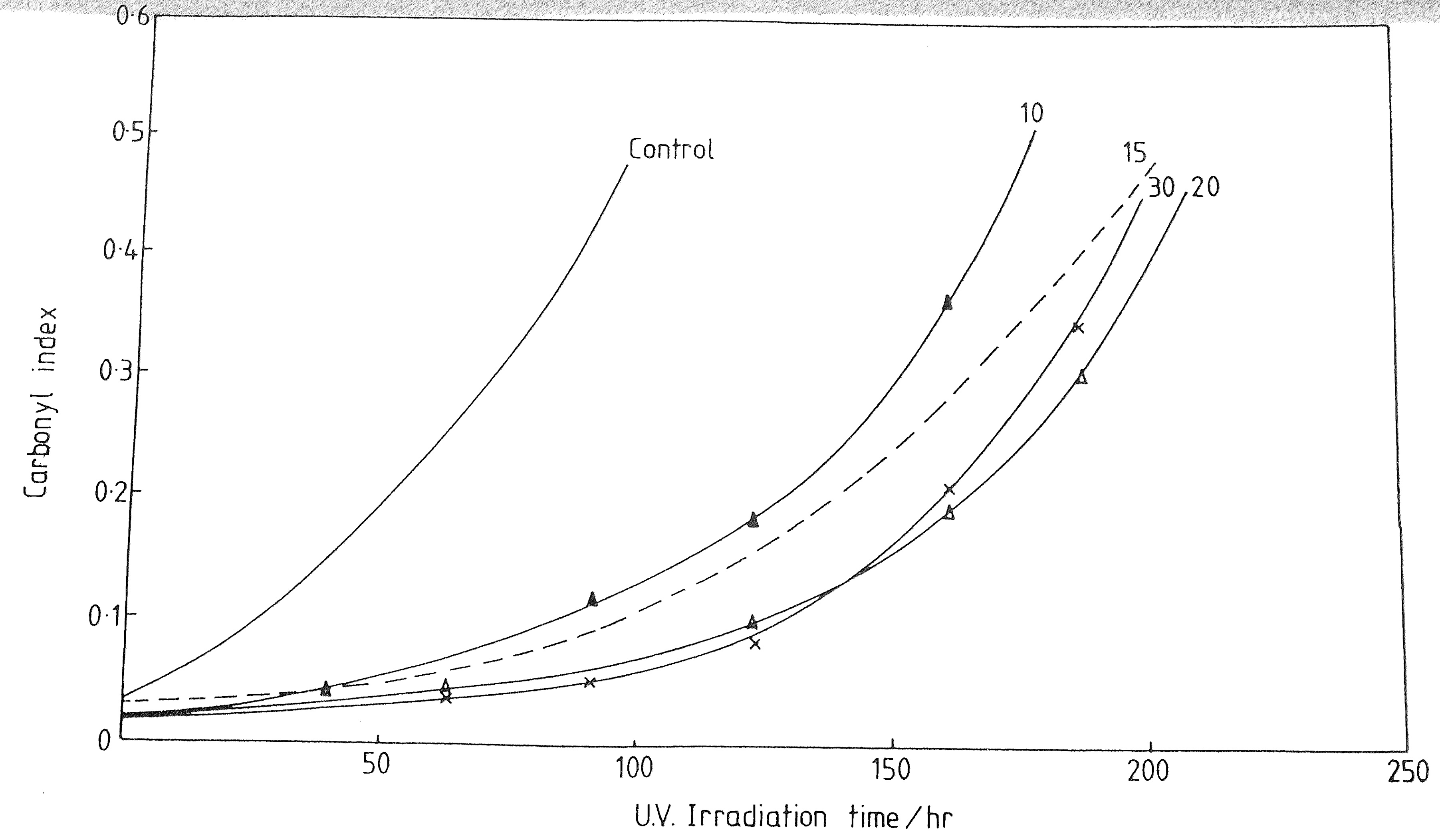


Fig 3:22 Effect of processing time on the photo-stabilisation of PP containing NDBP processed at 180°C in closed mixer at concentration of 5×10^{-4} mole/100 gm. Number on curves represents processing time in minutes

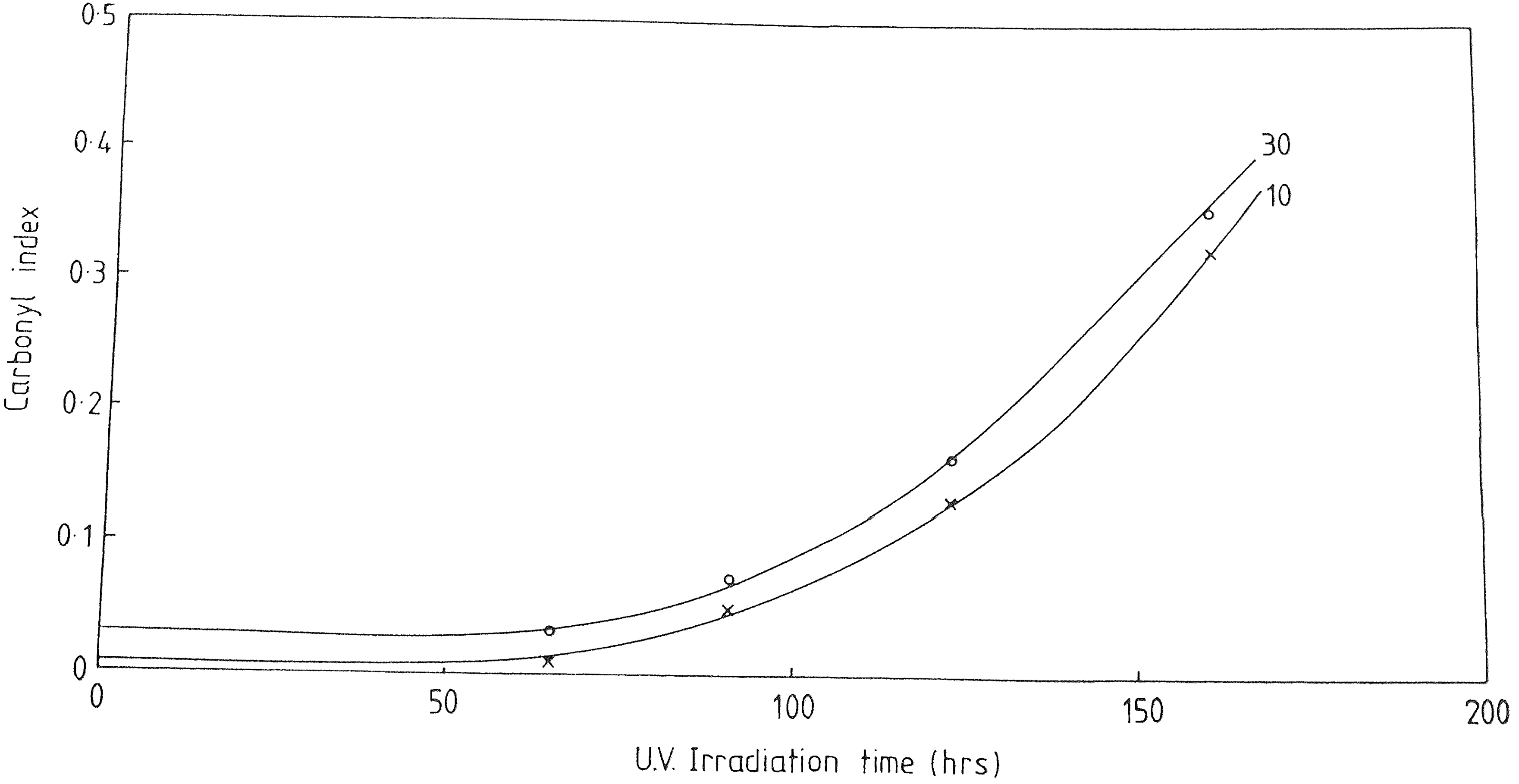


Fig 3:23 Effect of processing time on the photo-stabilisation of PP containing 4-nitrosophenol processed at 180°C in closed mixture at concentration of 5×10^{-4} mole/100 gm. Number on curve represents processing time in minutes.

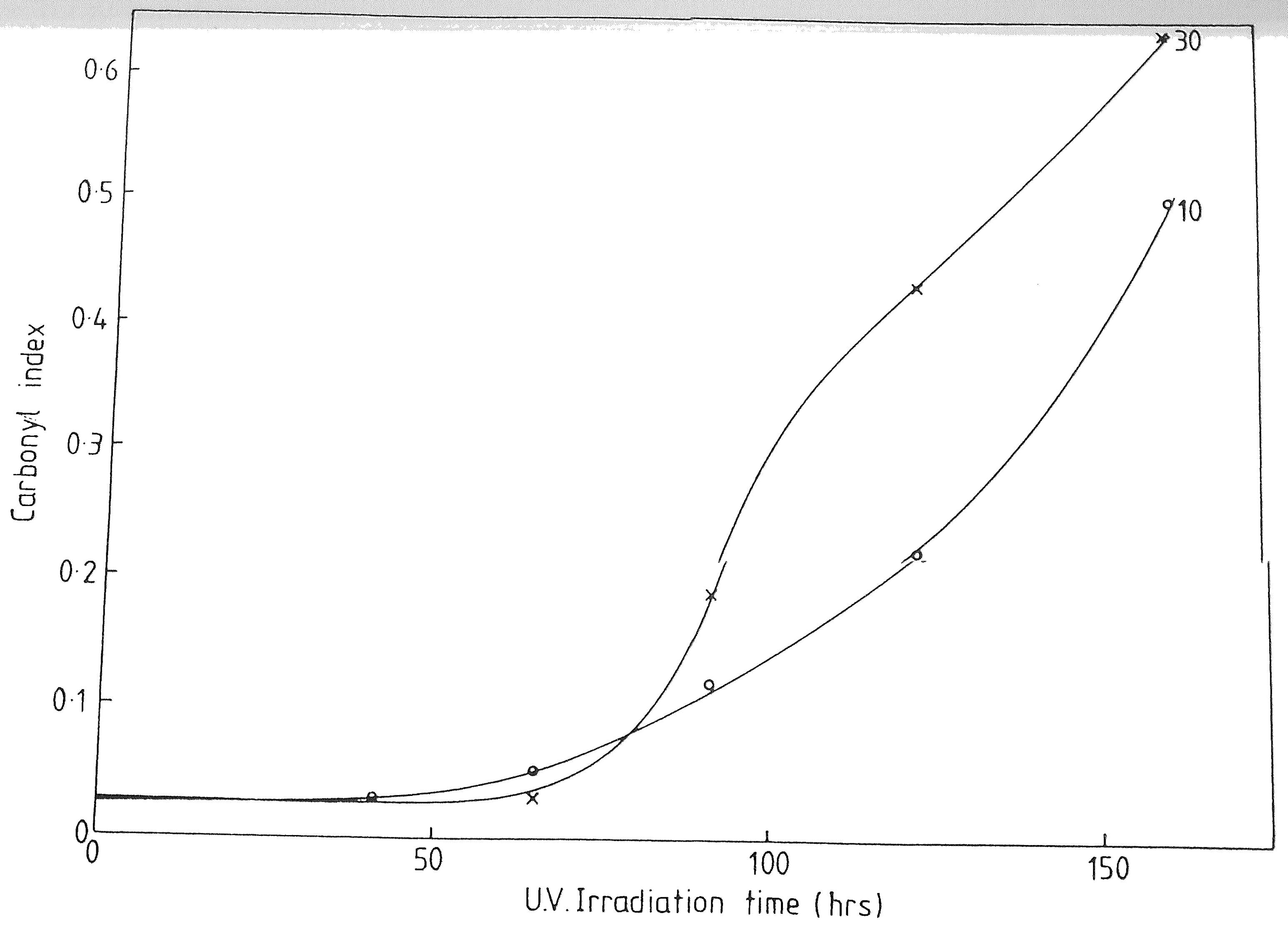


Fig 3:24 Effect of processing time on photo-stabilisation of PP containing 4-nitroso-2-naphthol processed at 180°C in closed mixture at concentration of 5×10^{-4} mole/100gm. Number on curve represents processing time.

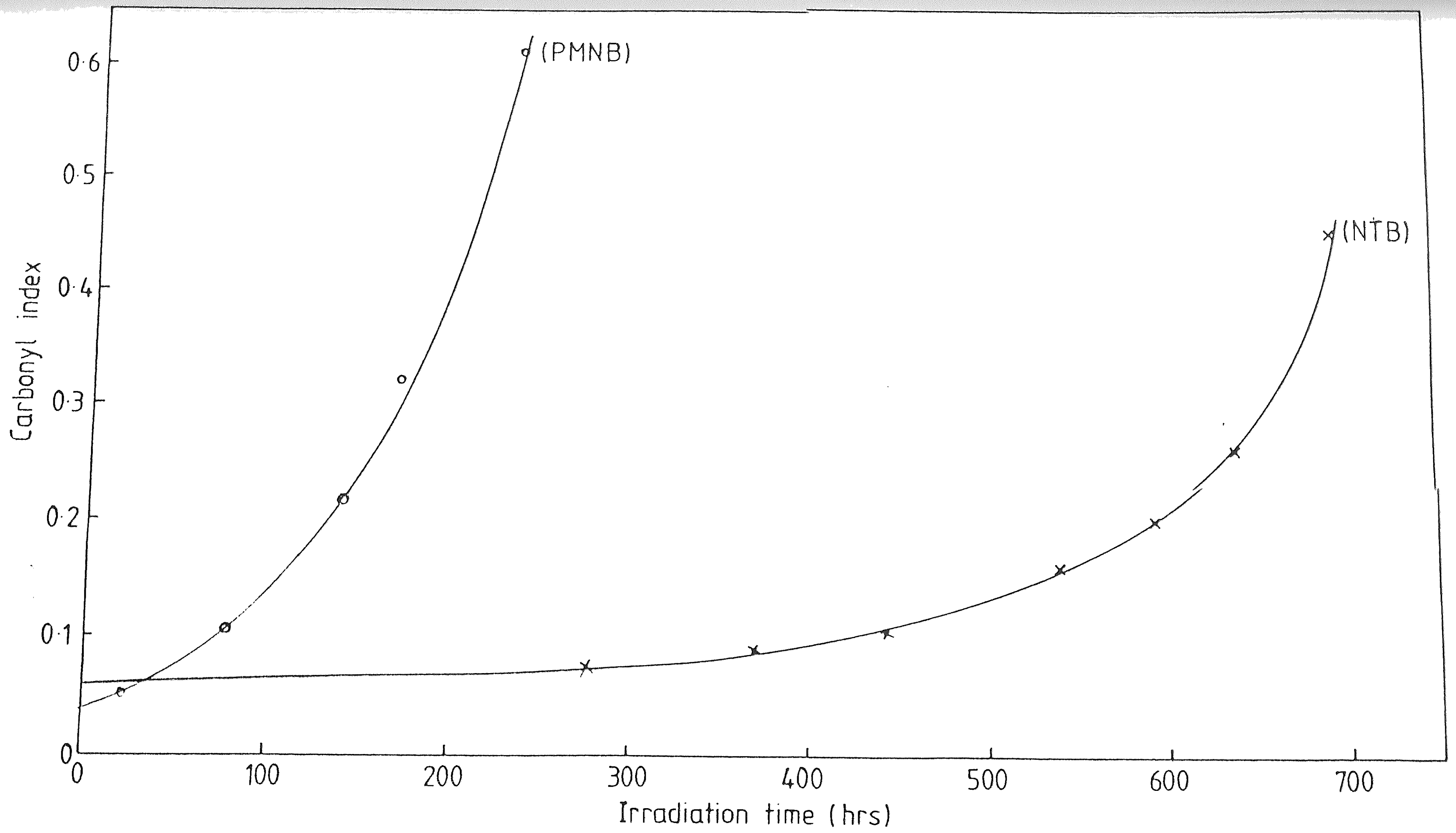
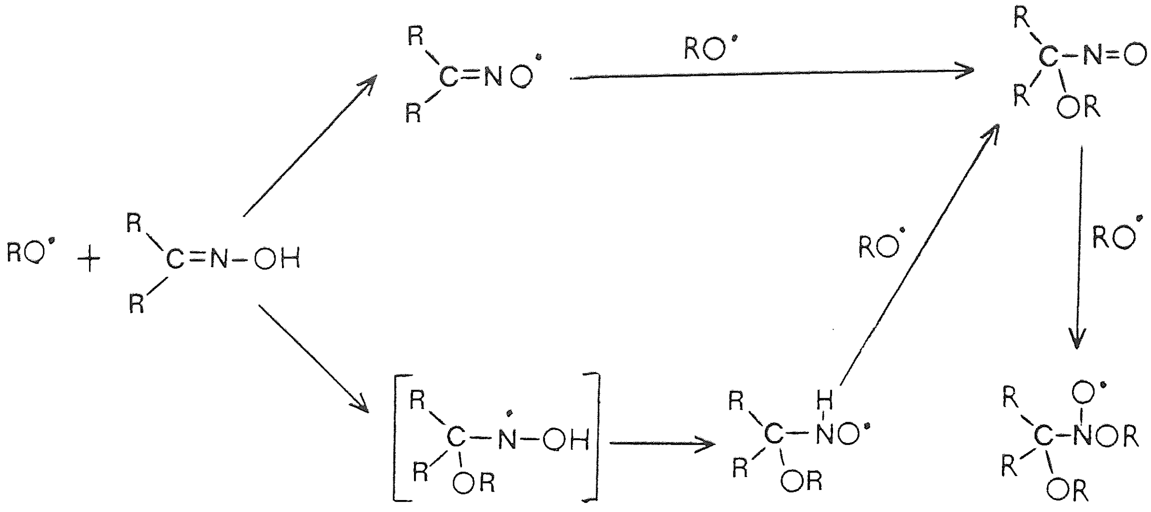


Fig 3:25 Comparison of effect of NTB (aliphatic nitroso) and PMNB (aromatic nitroso) on the photo-stabilisation of PP processed at 180°C in closed mixture at 10 minutes. Concentration 1×10^{-3} mole / 100 gm



(11)

The observation of nitroxyl radicals and disappearance of phenoxy radicals within pp films processed with NDBP suggests that the stabilisation process could be due to the tautomeric oxime form making the major contribution to melt stabilisation and subsequently U.V. stabilisation processes according to reaction scheme (12). Even when the phenolic form participates in the stabilisation process this could result in iminoxy radical formation, as outlined in reaction scheme (12). Therefore, the photo-stabilisation effectiveness of NDBP with extended thermal processing could be attributed to the formation of nitroxyl radicals.

3.3 Effect of C-Nitroso Compounds on Thermal Oxidative Stability of Polypropylene

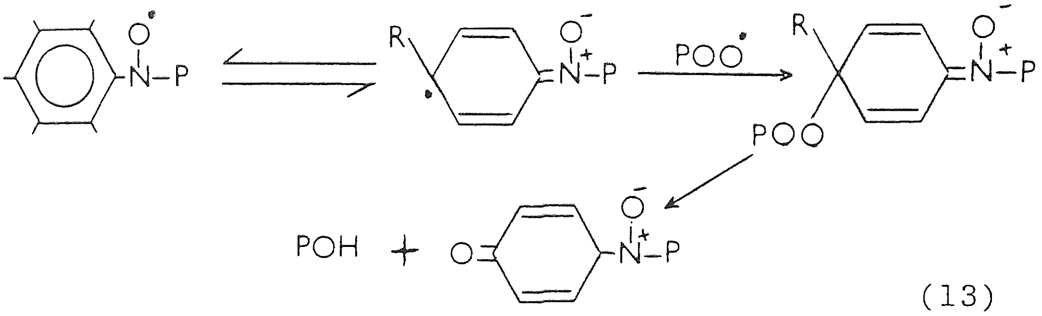
Results and Discussion

The behaviour of aromatic and aliphatic nitroso compounds was shown to be very powerful melt stabiliser in pp under various processing conditions. This section shows the subsequent behaviour of nitroso compounds during thermal oxidation of pp. The accelerated thermal oxidation of compression moulded samples was carried out in a Wallace oven at 140°C.

3.3.1.1 Effect of Aromatic Nitroso Derivatives

Fig. 3.26 illustrates the effect of processing time on the subsequent thermal oxidative stability of pp in the form of compression moulded film containing PMNB at 140°C. All the samples show an induction period to carbonyl formation during thermal oxidation and the induction period was found to be dependent on the prior processing time. The length of the induction period seems to correlate with the concentration of nitroxyl radicals derived from PMNB during processing (Fig.3.9). In other words, the antioxidant mechanism involves the termination of alkyl radicals by PMNB, these inhibiting the formation of hydroperoxide, the initiator of polymer degradation.

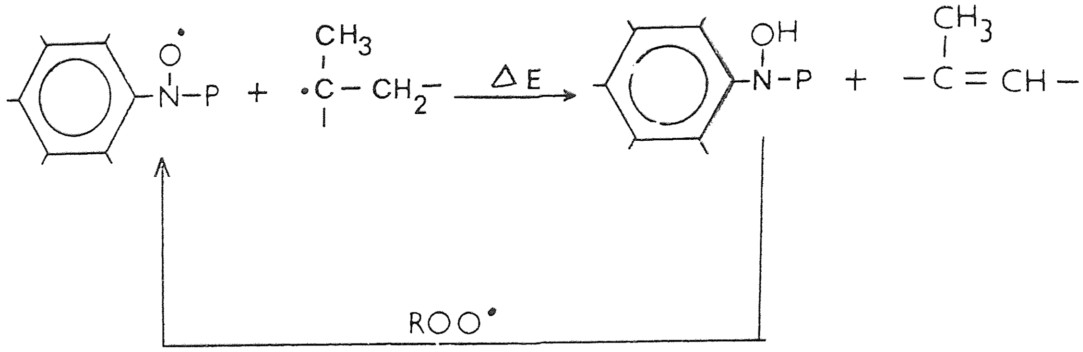
The presence of excess of air might be expected to promote the reaction of alkyl radicals with oxygen rather than the nitroso compound or nitroxyl radicals, thus forming alkylperoxy radicals. The latter do not react with either nitroso compounds or nitroxyl radicals. It has been shown(145) that the unpaired electron density in aromatic nitroxyls is strongly delocalized. As a result, radical reactions will occur not only at the nitroxyl function, but also at the aromatic rings, preferably in the para position(146). Consequently the nitroxyl will be attacked by peroxy radicals on the aromatic ring



(13)

Fig. 3.27 demonstrates the rate of decay of nitroxyl radicals derived from PMNB in polypropylene during thermal oxidation. The high rate of initial decay of nitroxyl radicals during first 4.5 hours possibly is attributed to both the reaction of the alkyl radical with nitroxyl (due to slow diffusion of oxygen on early stages of thermal oxidation) as well as the reaction of peroxy radicals with the aromatic ring resulting in the destruction of the nitroxyl. Prolonged thermal oxidation leads only to alkylperoxy radical formation, which may react with the aromatic ring of the nitroxyl according to reaction (13), such a reaction resulted in a slower rate of nitroxyl decay in later stages of oxidation process.

The activity of aromatic nitroso compounds in the stabilisation of thermal oxidation could be accounted for by reaction (14) involving thermal decomposition of alkylhydroxylamine



(14)

Table 3.5 and Fig.3.28 show the thermal embrittlement times given by the aromatic nitroso derivatives to pp films at different processing times, subjected to oven ageing at a temperature of 140^{o}C. It is apparent that the thermal oxidation stabilisation is highly dependent on the processing time and also on the nature of the nitroso compound. For example, maximum embrittlement times were obtained using PMNB at 15 and 20 mins., tetramethylnitrosobenzene provided maximum embrittlement time at a processing time of 10 mins.

Increasing the concentration of aromatic nitroso compounds results in an increase in stabilisation effectiveness as reflected by the improvement of embrittlement time (Table 3.6).

TABLE 3.5 Effect of processing on the thermal embrittlement time (hours) of pp containing nitroso compounds, processed at 180°C in closed mixer at concentration of 1 x 10^{-3} mole/100 gm.

Processing time Additives	Colour	7.5 mins.	10 mins.	15 mins.	20 mins.
No additive	White	0.5	0.5	0.5	0.5
Pentamethylnitrosobenzene	Yellowish	9.5	11.5	20.5	19.o
Tetramethylnitrosobenzene	Yellowish	9.o	12.o	11.	6.5
Trichloronitrosobenzene	Yellowish	3.5	4.5	3.5	3.o
2,6 Di-tert-butylnitrosophenol	Yellowish	14.o	21.o	18.5	16.o
N,N dimethyl-4-nitrosoaniline	Brown	--	11.o	--	--
Nitrosobenzene	White	--	7.o	--	--
Nitrosophenol	Brown	--	5.o	--	--
2-Nitroso-1-naphthol	Brown		8.5		
Nitroso-tert-butane	White	1.o	1.o	0.7	0.7
Nitroso-tert-octane	White	1.o	1.o	0.7	0.7

TABLE 3.6

Conc. Compound	1x 10^{-4}	5x10^{-4}	11 x 10^{-3}
Pentamethylnitrosobenzene	1.0	4.5	11.5
Tetramethylnitrosobenzene	1.0	4.o	12.o
Trichloronitrosobenzene	1.o	2.o	4.5
2,6 Di-tert-butyl-4-nitroso-phenol	1.7	16.o	21.o
N,N Dimethyl-4-nitrosoaniline	2.o	8.5	11.o

Effect of concentration of different aromatic nitroso compounds on the thermal embrittlement time of pp films processed at 180°C in closed mixer at 10 minutes.

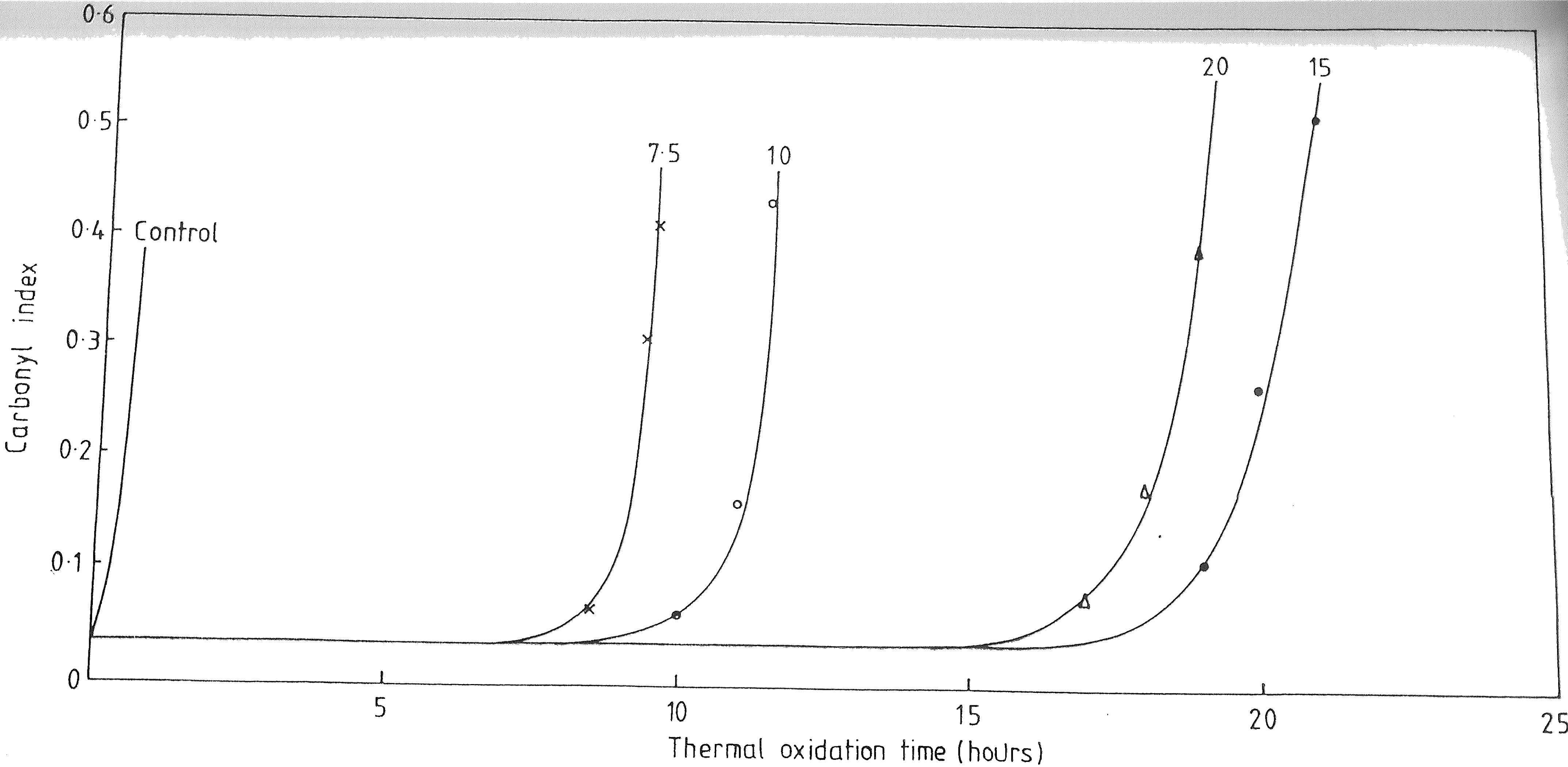


Fig 3:26 Effect of processing time on the thermal oxidation of PP films containing PMNB at 140°C processed at 180°C in closed mixture at concentration of 1×10^{-3} mole / 100 gm. Number on curve represents processing time in minutes

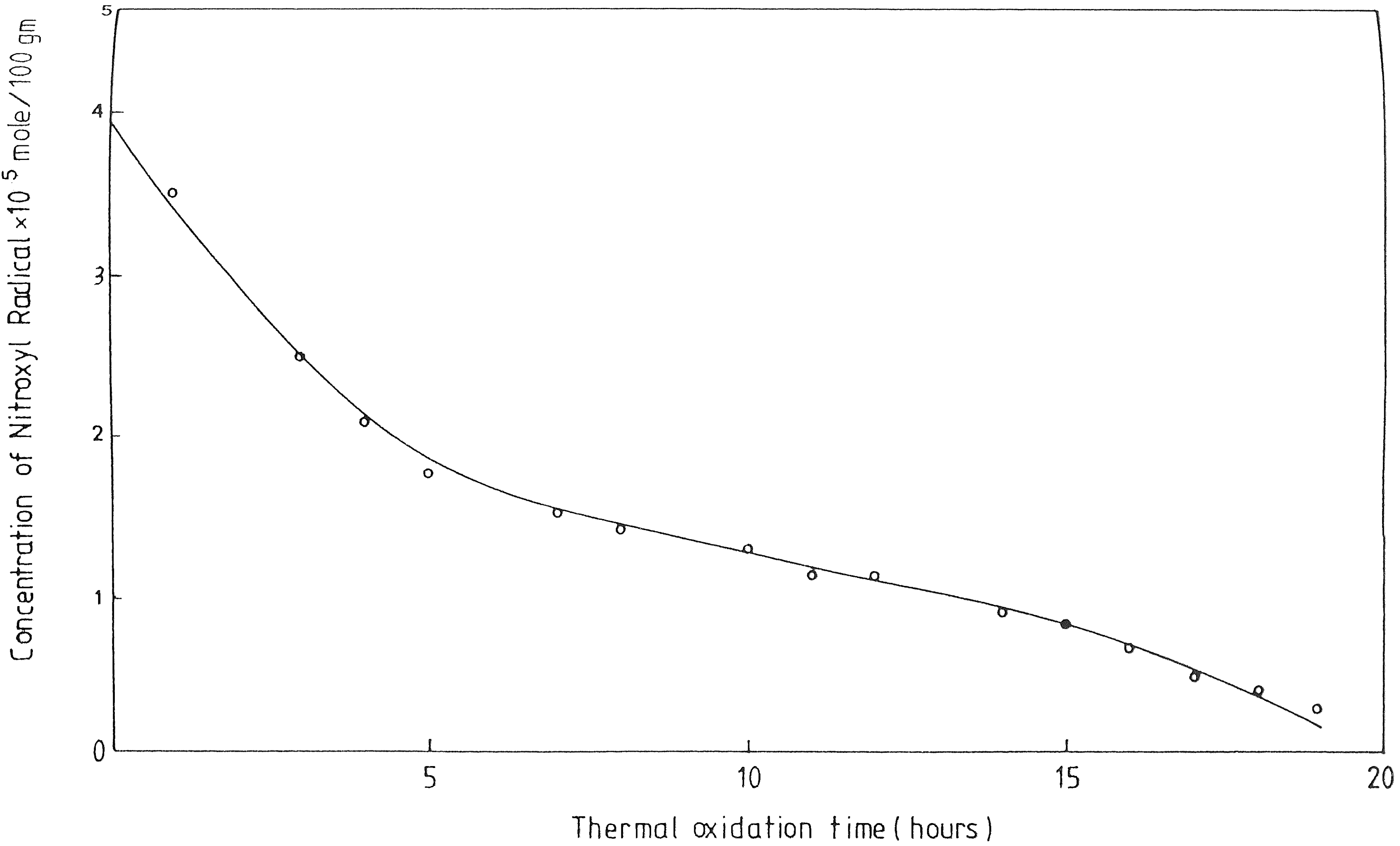


Fig 3:27 Rate of decay of nitroxyl radical, derived from penta methyl nitrosobenzene during thermal oxidation of PP at 140°C processed in closed mixture at 10 minutes, concentration 1×10^{-3} mole/100 gm

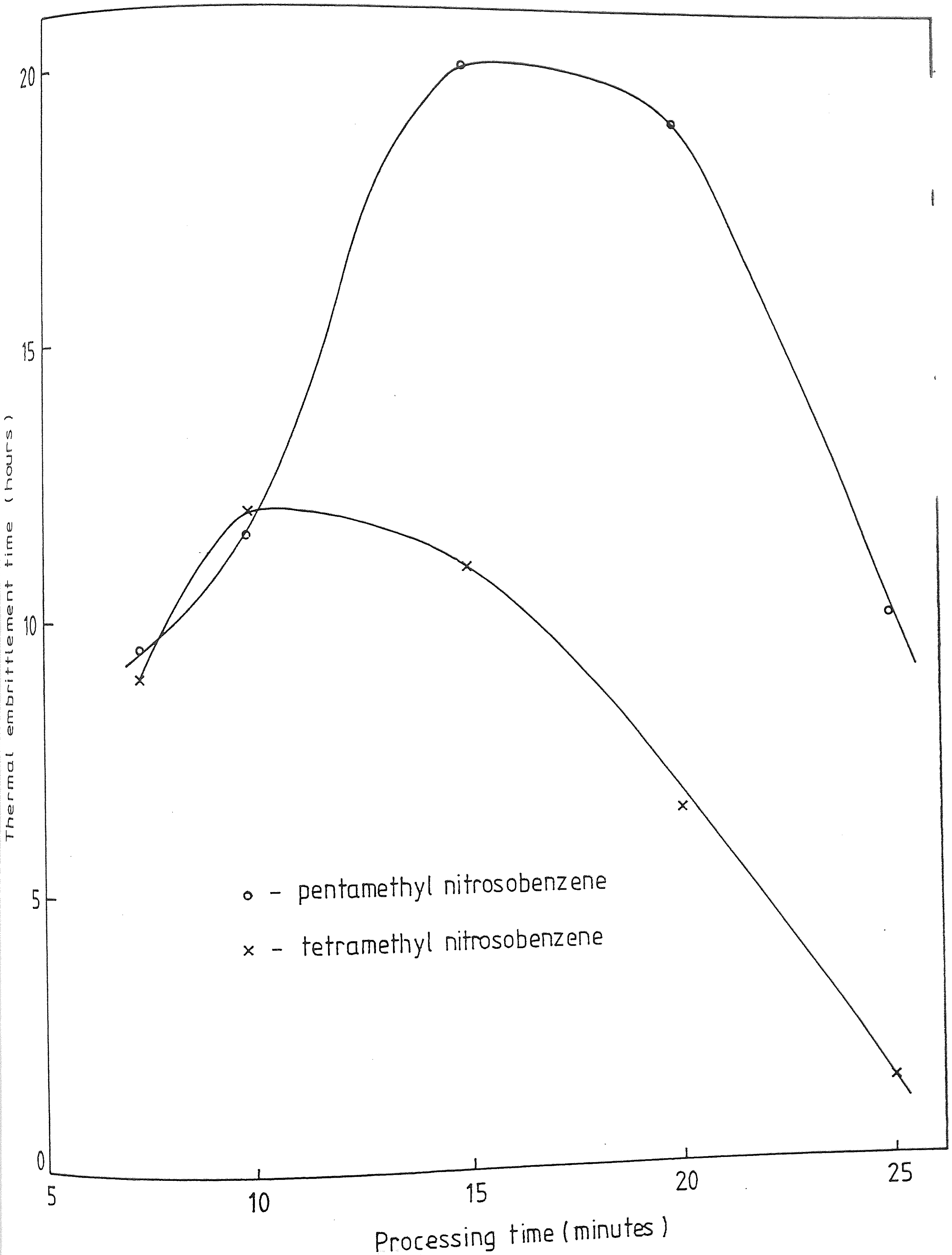


Fig 3:28 Effect of processing on the thermal embrittlement time of PP containing PMNB and TMNB

3.3.1.2 Effect of Aliphatic Nitroso Compounds on the Thermal Oxidative Stability of Polypropylene

Nitroso-tert-butane and nitroso-tert-octane do not show a significant thermal stabilisation of polypropylene during oven ageing at 140°C compared with aromatic nitroso derivatives, (Table 3.5), in spite of the fact that both aromatic and aliphatic nitroso compounds are very powerful melt stabilisers for polypropylene, when processed in a limited amount of air. However, it was found (see Section 3.1.2) that the melt stabilisation efficiencies of aliphatic nitroso compounds were very much reduced when processed in an excess of air.

Aliphatic nitroso compounds react efficiently with alkyl and alkoxy radical radicals, but not with peroxy radicals to form aliphatic nitroxyl radicals which subsequently are very effective alkyl radical scavengers. Since in thermal oxidation oxygen is able to compete strongly with nitroxyl for alkyl radicals to form peroxy radicals, aliphatic nitroxyl are not able to effectively scavenge peroxy radicals, the propagating species in polymer degradation.

3.4 Model Studies of the Mechanism of Action of Nitroso Compounds.

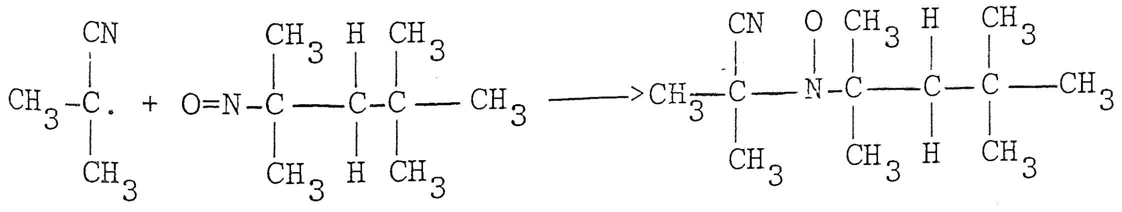
3.4.1 Results and Discussion

It is important to investigate the reaction behaviour of c-nitroso compounds with alkyl radicals under thermal conditions in order to understand the mode of action of these compounds as melt stabilisers, thermal antioxidants and photo-stabilisers.

The kinetics of the reaction of NTO with alkyl radicals was investigated in an inert atmosphere (nitrogen) in p-xylene containing 1.5×10^{-3} mole/100 gm of azobisisbutryronitrile (AZBN) 1×10^{-3} mole/100 gm.of NTO at two different temperatures; 110°C and 130°C. The ESR signal obtained shows the formation of nitroxyl radicals. The reaction kinetics were studied by following the change in nitroxyl radicals concentration (Fig.3.29).

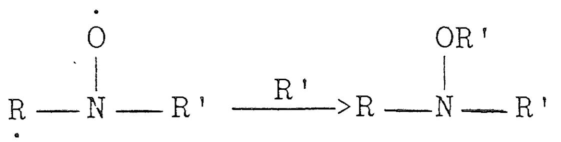
The concentration of nitroxyl radicals initially increased rapidly, reached a maximum, then decreased gradually to minimum, followed again by a further slow increase at both temperatures. However, the concentration of nitroxyl radicals at 130°C was always higher than that at 110°C during the course of the reaction.

The rapid increase in nitroxyl radical concentration during the reaction can be accounted for by the reaction of alkyl radicals with the nitroso compounds.



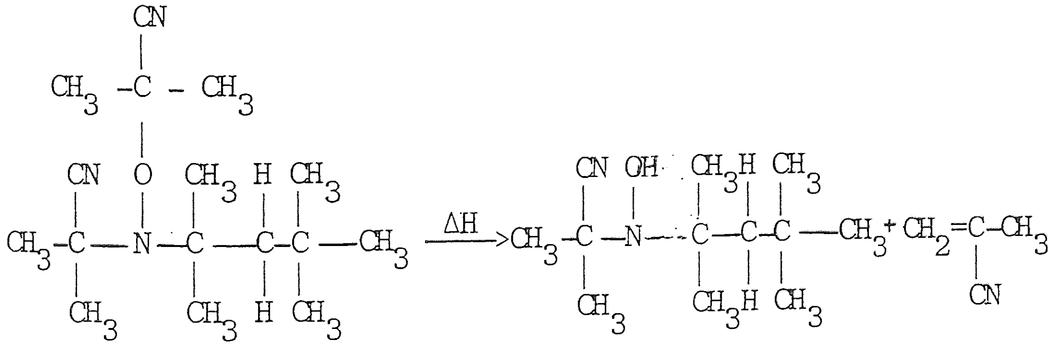
$$CH_3-\overset{CN}{\underset{CH_3}{C}}\cdot + O=N-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{CN}{\underset{CH_3}{C}}-\overset{\dot{O}}{N}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \qquad (13)$$

Several studies(57,96,140,147,148) have shown that nitroxl radicals are highly reactive toward alkyl radicals to form alkylated hydroxylamines. Therefore, the decrease in nitroxyl radical concentration is attributed to the reaction of alkyl radicals with nitroxyl radicals. This means that the alkyl radicals react with nitroxyl radicals formed from NTO more readily than with NTO itself, so that the yield of the nitroxyl radicals cannot go above a certain level



$$R-\overset{\overset{\displaystyle \dot{O}}{|}}{N}-R' \xrightarrow{R^{\cdot}{}'} R-\overset{\overset{\displaystyle OR'}{|}}{N}-R' \qquad (14)$$

The slow increase of nitroxyl concentration with extended reaction time may be attributed to the thermolysis of alkylated hydroxylamine to give hydroxylamines and olefines under the experimental conditions



(15)

The exposure of reaction mixture to air during experimental measurement lead to oxidation of the hydroxylamine by peroxy radicals into the corresponding nitroxyl, leading to a slow increase in nitroxyl radical concentration. The isolation of methacrylonitrile from the reaction mixture by thin layer chromatography (TLC) provides the

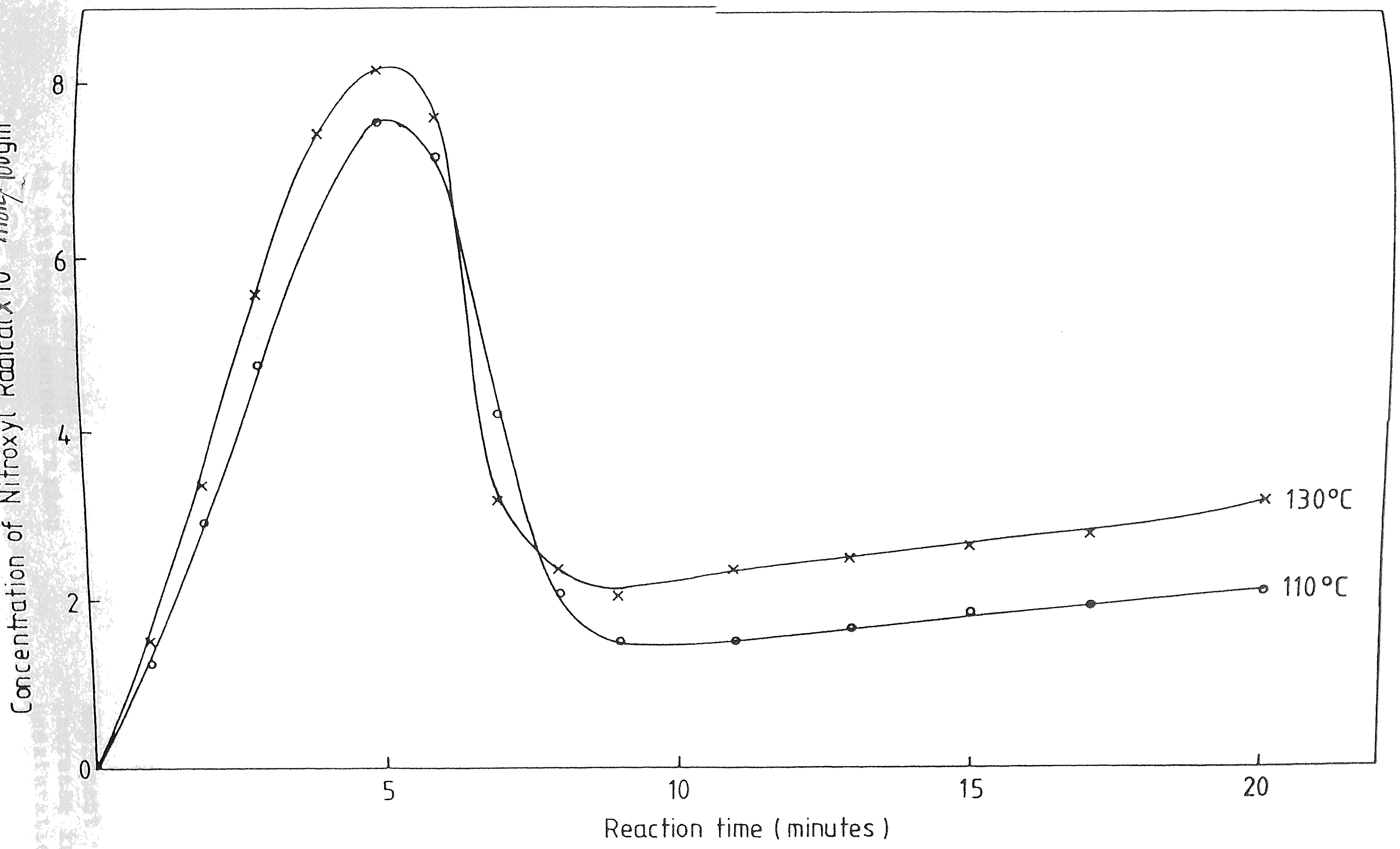
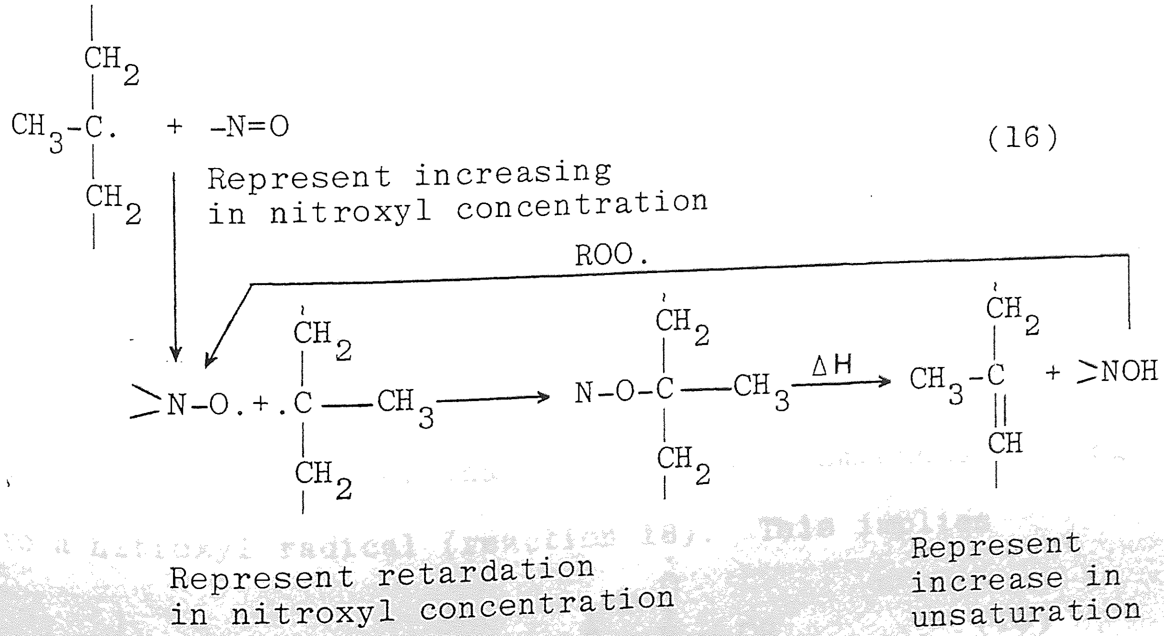


Fig 3:29 The rate of nitroxyl radical formation during reaction time of ZBAN with NTO at 130°C and 110°C in p-xytene.

evidence for the reaction (15). However the higher rate of increase of nitroxyl radical concentration at 130°C compared to that at 110°C provides additional evidence for the higher rate of alkyl hydroxylamine thermolysis. The subsequent rate of regenration of nitroxyl radicals depends on the rate of alkyl hydroxylamine thermolysis.

Similar results have been reported by other workers(43,149) and shown that hydroxylamine is eliminated from alkylhydroxylamine at high temperature.

The increase of nitroxyl radical concentration in PP containing nitroso-tert-butane on increasing the processing time up to 15 mins. (Fig.3.9) is evidence for the reaction of nitroso compound with alkyl or alkoxy radicals. Nitroxyl radical formation on extended processing time is associated with increase in unsaturation (Fig. 3.30), which indicates the formation and thermolysis of alkylhydroxylamine.

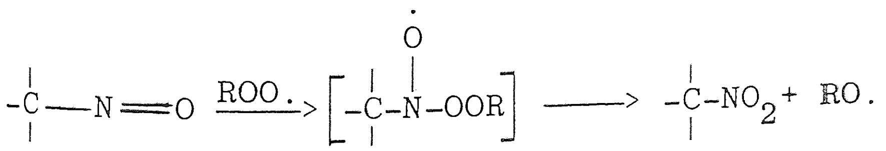


(16)

The chemical identification of hydroxylamine (see section 2.2.12) in the extract of polypropylene samples containing NTB and PMNB again shows additional evidence of reaction (16).

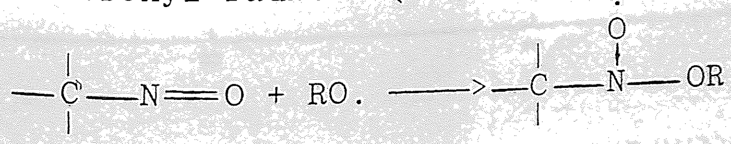
It is proposed that the melt stabilising activity of nitroso compounds is primarily due to the CB-A mechanism leading to macro alkyl radical trapping and formation of nitroxyl radicals. Since nitroxyl radicals are themselves effective alkyl radicals traps they also act as CB-A antioxidants leading to the formation of alkylhydroxylamines, which further decompose into hydroxylamines and olefines (see Fig. 3.29). The hydroxylamine are effective CB-D antioxidants and terminate ROO. These reactions together constitute a cyclic regenerative process (reaction 16).

The isolation of nitro-tert-butane by TLC from the products of the extract of polypropylene samples containing nitroso-tert-butane after processing suggests the oxidation of nitroso-tert-butane with peroxy alkyl radicals formed during processing (reaction 17).



$$-\overset{|}{\underset{|}{C}}-N=O \xrightarrow{ROO.} \left[-\overset{|}{\underset{|}{C}}-\overset{\dot{O}}{\overset{|}{N}}-OOR\right] \longrightarrow -\overset{|}{\underset{|}{C}}-NO_2 + RO. \qquad (17)$$

RO. could then be terminated by nitroso compounds leading to a nitroxyl radical (reaction 18). This implies



$$-\overset{|}{\underset{|}{C}}-N=O + RO. \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\dot{O}}{\overset{\uparrow}{N}}-OR \qquad (18)$$

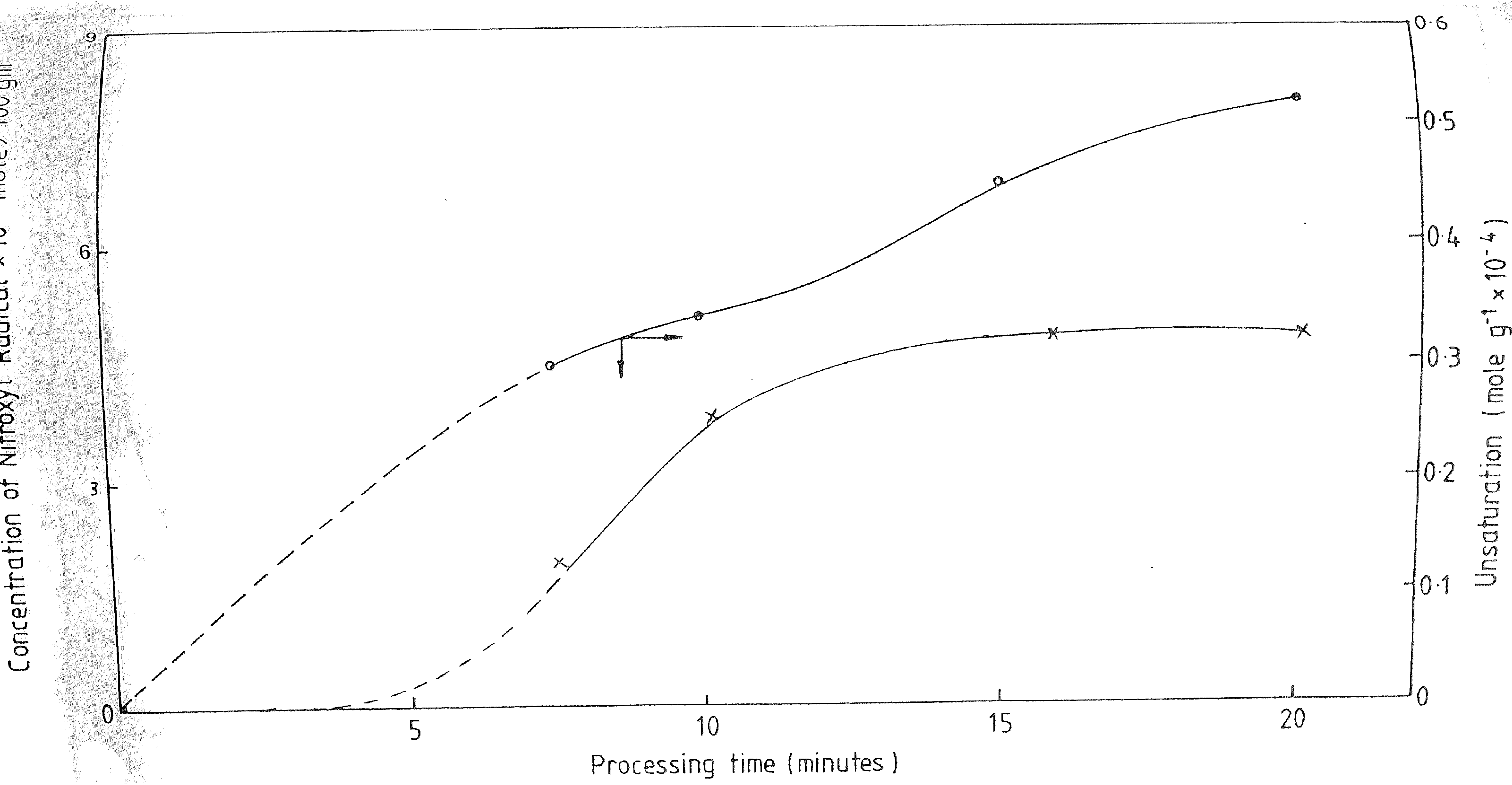


Fig 3 : 30 Rate of formation of unsaturation and nitroxyl radicals during thermal processing of PP containing nitroso-tert-butane at 180°C in closed mixture at concentration of 1×10^{-3} mole / 100 gm

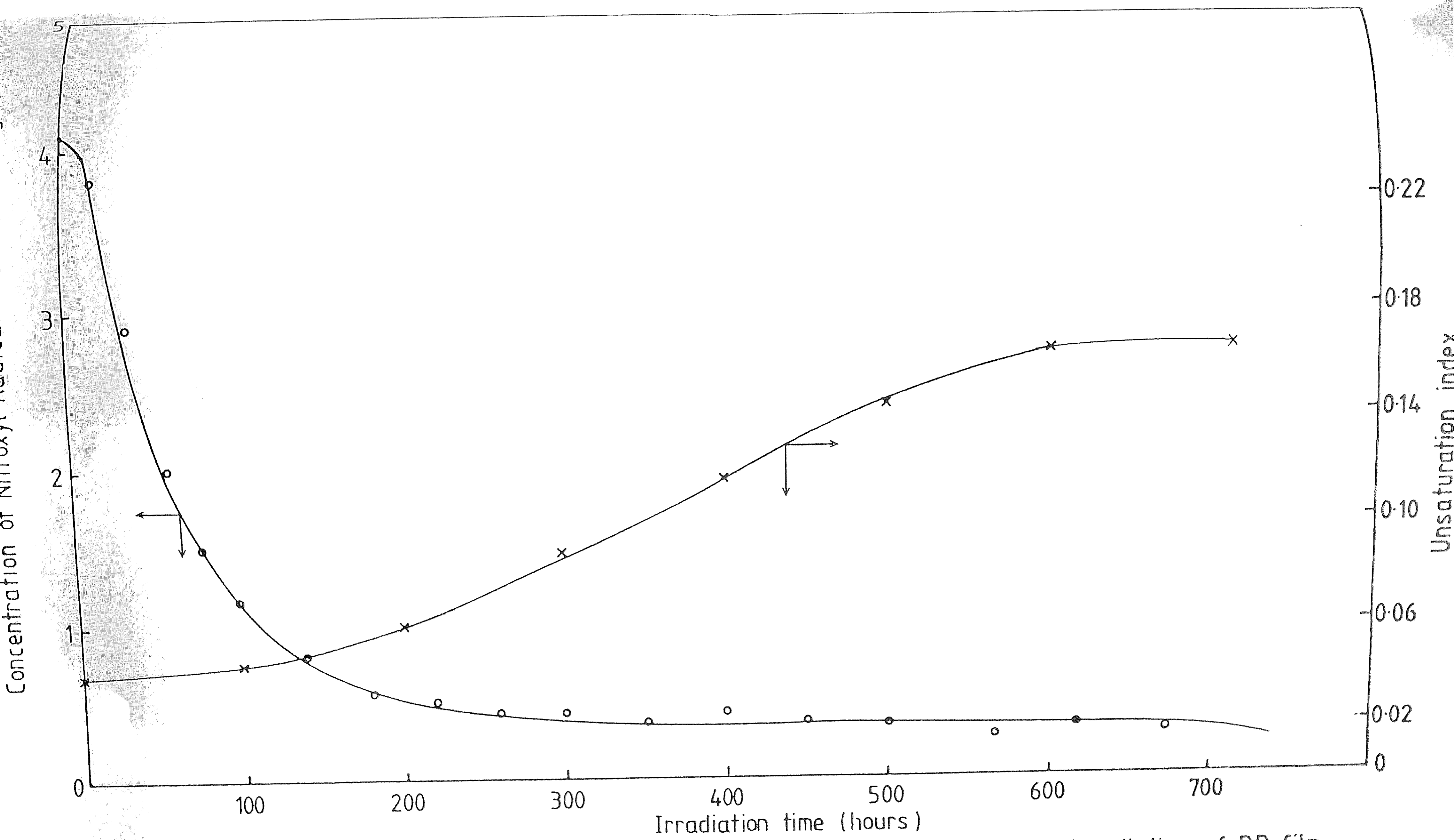


Fig 3:31 The rate of nitroxyl radicals decay and unsaturation formation during photo - irradiation of PP film containing NTB at concentration of $1{\cdot}5 \times 10^{-3}$ mole/100 gm

nitroso-tert-butane could terminate peroxy radicals in indirect way according to reactions 17 and 18. Similar results have been reported(94) by other workers who show the formation of both nitro compounds and nitroxyl radicals as a result of the reaction of peroxy radicals with nitroso compounds.

It seems then that nitroso compounds do not contribute directly to the photo-stabilisation of polypropylene. Fig. 3.31 shows a rapid change in nitroxyl radical concentration during the first 70 hours of U.V. irradiation, subsequently the rate decreased gradually to reach a stationary concentration up to 600 hours, when it was difficult to detect the nitroxyl radical, the sample embrittled.

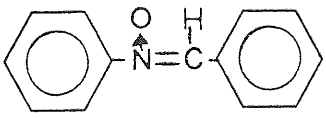
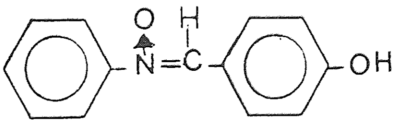
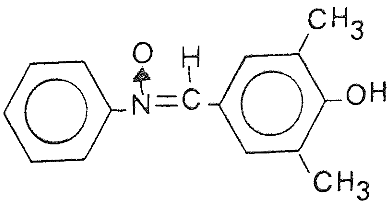
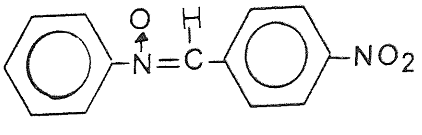
This result shows that the photo-stabilisation process is dependent only on the nitroxyl radicals formed during the thermal processing, prior to photo-irradiation. Consequently the photo-stabilisation process is highly dependent on the melt processing conditions, particularly on the processing time (Fig. 3.9). However, there is no doubt that decrease in the concentration of nitroxyl radical during U.V.irradiation is due to the reaction of nitroxyl radicals with alkyl radicals to give alkylhydroxylamine.

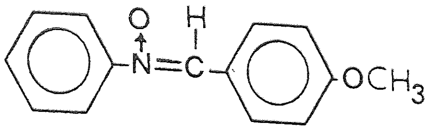
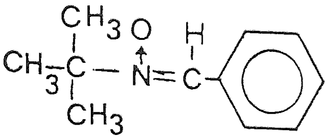
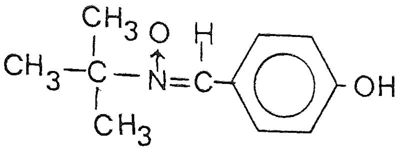
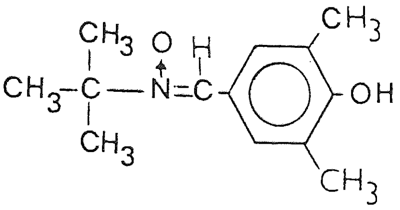
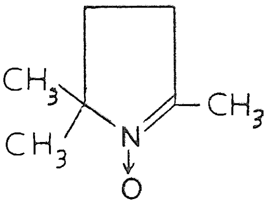
CHAPTER 4

EFFECT OF NITRONES ON MELT STABILISATION, PHOTO-OXIDATION AND THERMAL OXIDATION OF POLYPROPYLENE

4.1 Introduction

This chapter deals with the effect of nitrones on the melt stabilisation, thermal oxidation and photo-oxidation of PP and the mechanisms of their action are discussed. The nitrones are listed below with the code name used in this chapter.

Nitrones	Structure	Code
α,N-diphenylnitrone		DPN
α -(4-hydroxyphenyl)-N-phenylnitrone		HDPN
α-(3,5dimethyl-4-hydroxy-phenyl)-N-phenylnitrone		DHDPN
α-(4-nitrophenyl)-N-phenylnitrone		NDPN

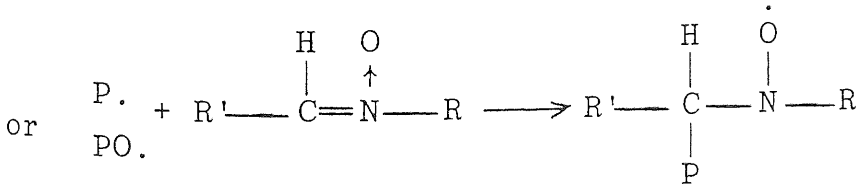
α-(4-methoxyphenyl)-N-phenylnitrone		MDPN
α-phenyl-N-tert-butylnitrone		PBN
α-(4-hydroxyphenyl)-N-tert-butylnitrone		HPBN
α-(3,5 dimethyl-4-hydroxyphenyl)-N-tert-butylnitrone		DHPBN
2,5,5 Trimethyl-pyrroline-N-oxide		TPN

4.2 Effect of Nitrones on Melt Stability of Polypropylene

4.2.1 Results

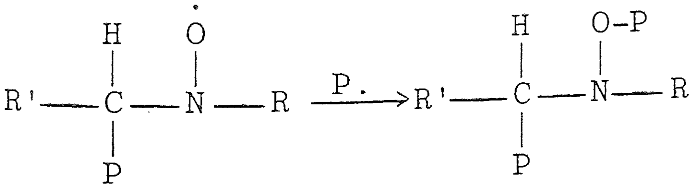
Fig. 4.1 illustrates the variation of melt flow index (MFI) of polypropylene containing α,N diphenylnitrone and its substituent derivatives (1 x 10^{-3} mole/100 gm) processed at different times. Curve (1) shows the effect of α,N-diphenylnitrone (DPN) on the MFI of polypropylene. The MFI was found to decrease significantly to a level lower than that of unprocessed polypropylene up to 15 minutes of processing followed by an increase. Curve (2) represents the MFI of polypropylene containing α-(4-hydroxyphenyl)-N-phenylnitrone (HDPN). The MFI of polypropylene at all processing times was found to be lower than that of the unprocessed polymer. Similarly, the processing of α-(3,5 dimethyl-4-hydroxyphenyl)-N-phenylnitrone (DHDPN) with polypropylene reduced the MFI up to 10 mins. of processing to a level lower than the unprocessed polymer (curve 3, Fig.4.1), followed by a slight increase with further processing.

Examination by ESR technique (see section 2.2.4) showed the presence of nitroxyl radicals (Table 4.2) and this coupled with the decrease in MFI of polypropylene indicates that nitrones inhibit polymer degradation during thermal processing, by terminating alkyl or alkoxy radicals to form polymer bound nitroxyl radicals (reaction 1). Since nitroxyl radicals are themselves highly reactive towards alkyl radicals cross-linking of the polymer chains should result (reaction 2)



$$\begin{array}{l}P\cdot\\ \text{or}\quad PO.\end{array} + R'-\overset{H}{C}=\overset{O}{\overset{\uparrow}{N}}-R \longrightarrow R'-\underset{P}{\overset{H}{C}}-\overset{\dot{O}}{N}-R$$

(1)



$$R'-\underset{P}{\overset{H}{C}}-\overset{\dot{O}}{N}-R \xrightarrow{P\cdot} R'-\underset{P}{\overset{H}{C}}-\overset{O-P}{N}-R$$

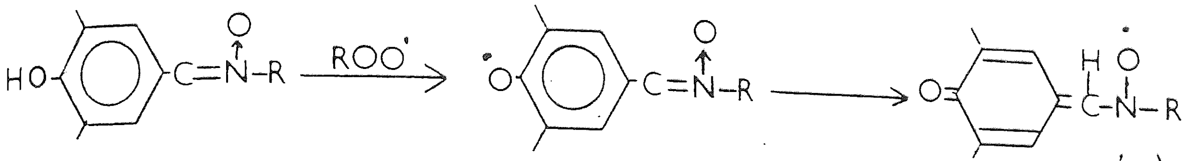
(2)

Fig. 4.2 shows that the molecular weight distribution of polypropylene processed for 7.5 mins. containing DPN shifts upward compared with unprocessed polypropylene. The increase in molecular weight confirms that cross-linking occurs during thermal processing according to reactions 1 and 2.

Fig. 4.3. compares the melt stabilisation effect of α-phenyl-N-tert-butylnitrone derivatives on polypropylene. It is apparent that whilst α-N-phenyl-tert-butylnitrone (PBN) gave melt stabilisation up to 7.5 mins. at 180°C, α-(4-hydroxyphenyl)-N-tert-butylnitrone (HPBN) and α-(3,5 dimethylphenyl)-N-tert-butylnitrone (DHPBN) showed significant decrease in MFI up to 20 mins. of processing compared to unprocessed polypropylene.

The upward shift in molecular weight distribution of polypropylene processed for 10 mins. in the presence of HPBN (Fig.4.4) again provides evidence for cross-linking. Processing for up to 20 mins did not cause a significant decrease in molecular weight distribution compared with unprocessed polymer (Fig. 4.4, curve 1).

The E.S.R. spectra obtained from polypropylene samples containing phenolic nitrones, shows the presence of nitroxyl radicals only; there is no evidence for the formation of phenoxyl radical (see Section 4.5). This observation could suggest that the formation of nitroxyl radical derived from nitrones containing phenolic group is not based only on reaction (1) but could also be attributed to reaction 3. The IR spectra of the extract of processed



(3)

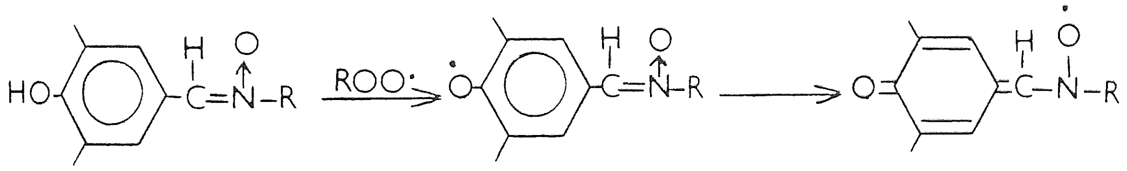
polypropylene containing phenolic nitrones (HPBN, HDPN, DHDPN and DHPBN) showed carbonyl peaks between 1660 and 1670 cm^{-1} attributed to quinonoid structure. This is additional evidence for reaction (3) and implies that nitrones possessing phenolic groups have the ability to terminate R., RO. and ROO. radicals according to reactions 1, 2 and 3.

Fig. 4.5 shows the effect of processing time on melt stabilisation of polypropylene containing p-methoxyphenyl-N-phenylnitrone(MDPN),p-nitrophenyl-N-phenylnitrone (NDPN) and 2,5,5 trimethyl-pyrroline-N-oxide (TPN) at concentration of 1×10^{-3} mol/100 gm. It is apparent that TPN is not as good a stabiliser as NDPN and MDPN. This may in part, result from the volatility of this additive (BP of TPN = $137^{\circ}C$). Processing of NDPN and MDPN with polypropylene up to 7.5 mins. showed a marked decrease in MFI, again suggesting cross-linking of the polymer chain. This was followed by a rapid increase in MFI up to 10 mins. and a slower increase up to 20 mins. Fig. 4·6 shows the broadening of molecular weight distribution of pp containing NDPN processed for 7.5 mins compared with unprocessed polypropylene.

However, on further processing (up to 20 mins.) the molecular weight distribution shifted into a lower range, indicating that chain scission had occurred.

Another important feature shown in Figs. 4.7 and 4.8 is that the activity of nitrone function depends on the substituents attached to it. Fig. 4.7 shows that NDPN is more effective than MDPN at concentration of 1 x 10^{-4} mol/100 gms. under the same processing condition. This observation could be attributed to the presence of the electron attracting nitro-group in the para position which reduces the electron density on the nitrone function and consequently makes it more susceptible to attack by alkyl radicals, whilst the presence of the electron releasing methoxy group increases the electron density at nitrone function and consequently reduces its reactivity towards alkyl radicals. Furthermore, to demonstrate the effect of substitution at nitrone function. Fig. 4.8 shows that HDPN is more effective as a melt stabiliser than HPBN at concentrations of 1 x 10^{-4} mol/100 gm under the same processing condition and both compounds are thermally stable at processing temperature (180°C), (see section 2.2.7). This presumably is due to the inductive effect of the phenyl group attached to nitrone function which reduces the electron density, consequently activating the nitrone function to react on alkyl radicals. When the phenyl group is replaced by tertiary butyl group (i.e. HPBN) the electron density is relatively increased at the nitrone function, consequently reducing its reactivity towards alkyl radicals.

An important characteristic of most nitrones is that they are good melt stabilisers for polypropylene processed in an excess of air (open mixture), (Table 4.1). Under these conditions the oxygen competes strongly with the nitrones to produce ROO.. This is presumably due to the activity of the phenolic group to terminate ROO. radicals by CB-D mechanism in the case of nitrones (reaction 3), consequently hydroperoxide formation is inhibited (see Section 2.2.9). But



stabilisation activity of DPN, MDPN and NDPN during processing in air could also be attributed to the ability of nitrone function to act as a hydroperoxide decomposer.

Hydroperoxide formation is inhibited by all nitrones containing phenolic groups (DHDPN, HDPN, DHPBN and HPBN) as well as by DPN and MDPN during processing in closed chamber and mostly inhibited during processing in air excess, although it is present in substantial amounts in control samples (without additives)

Table 4.1 MFI values of pp containing nitrones at concentration 1 x 10^{-3} mole/100 gm, processed in open and closed chamber at 180°C.

Additives	Processing Time(mins)	MFI (gm/10mins) (open mixer)	MFI (gm/10mins) (closed mixer)
pp (no additives)	10	1.7	
Unprocessed pp	-	0.36	0.36
DPN	10	0.41	0.28
HDPN	10	0.41	0.28
DHDPN	10	0.38	0.35
HPBN	10	0.36	0.31
DHPBN	10	0.38	0.28
MDPN	10	0.40	0.35

Table 4.2 Concentration of nitroxyl radicals formed in pp processed with nitrones for 10 mins in closed mixer at concentration 1 x 10^{-3} mole/100 gm ($180^{o}C$).

Additives	Concentration of nitroxyl radicals x 10^{-5} mole/100 gm		g values (± 0.0005)
	Before extraction	After extraction	
DPN	4.42	2.12	2.0058
HDPN	8.25	1.4	2.0071
DHDPN	5.56	3.34	2.0052
PBN	2.30	0.9	2.0066
HPBN	4.52	1.6	2.0069
DHPBN	3.1	1.1	2.0051

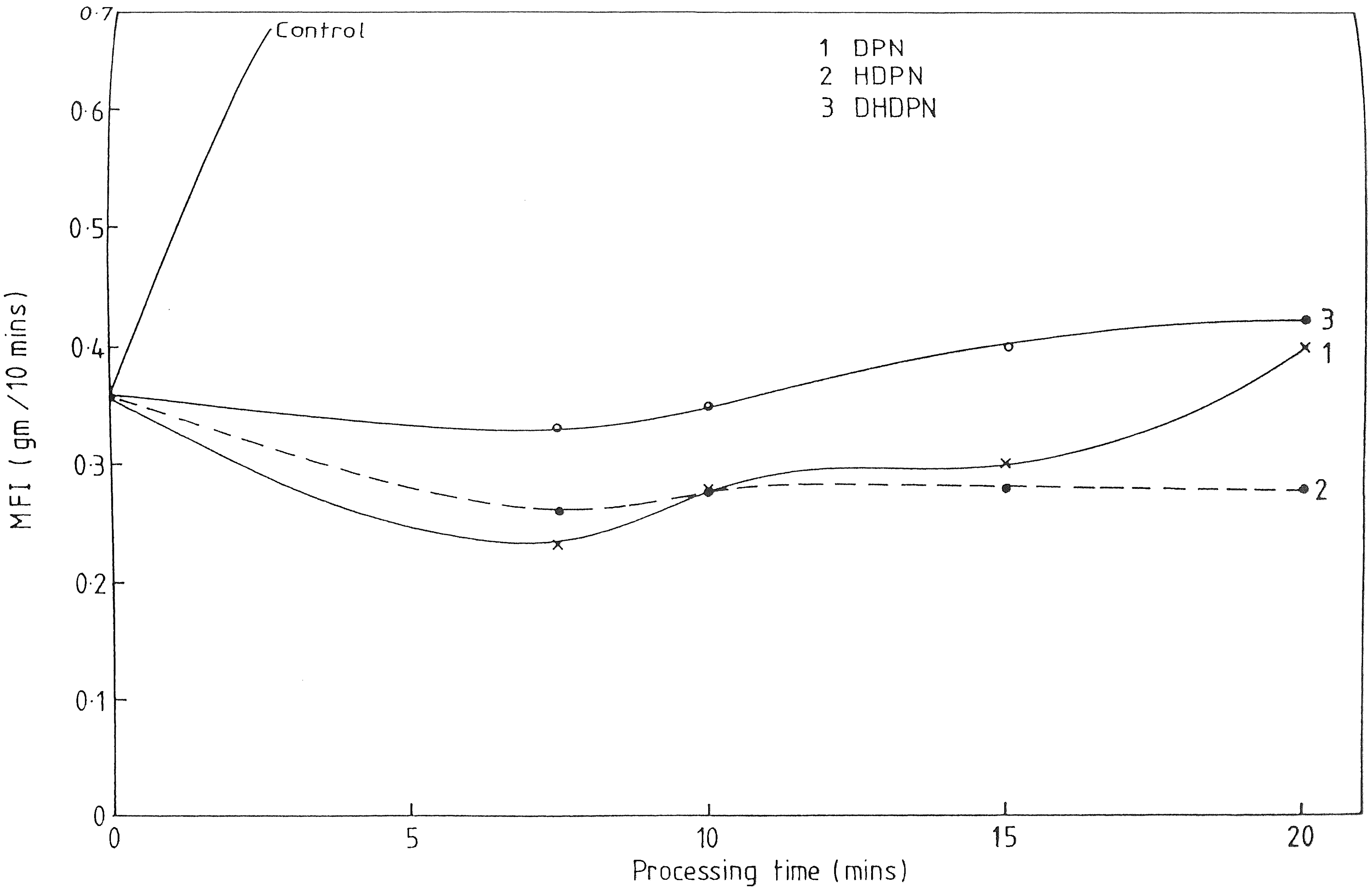


Fig 4:1 Effect of diphenylnitrones derivatives on melt flow index of PP processed at 180°C in closed mixture at different time (Concentration 1×10^{-3} mole/100 gm)

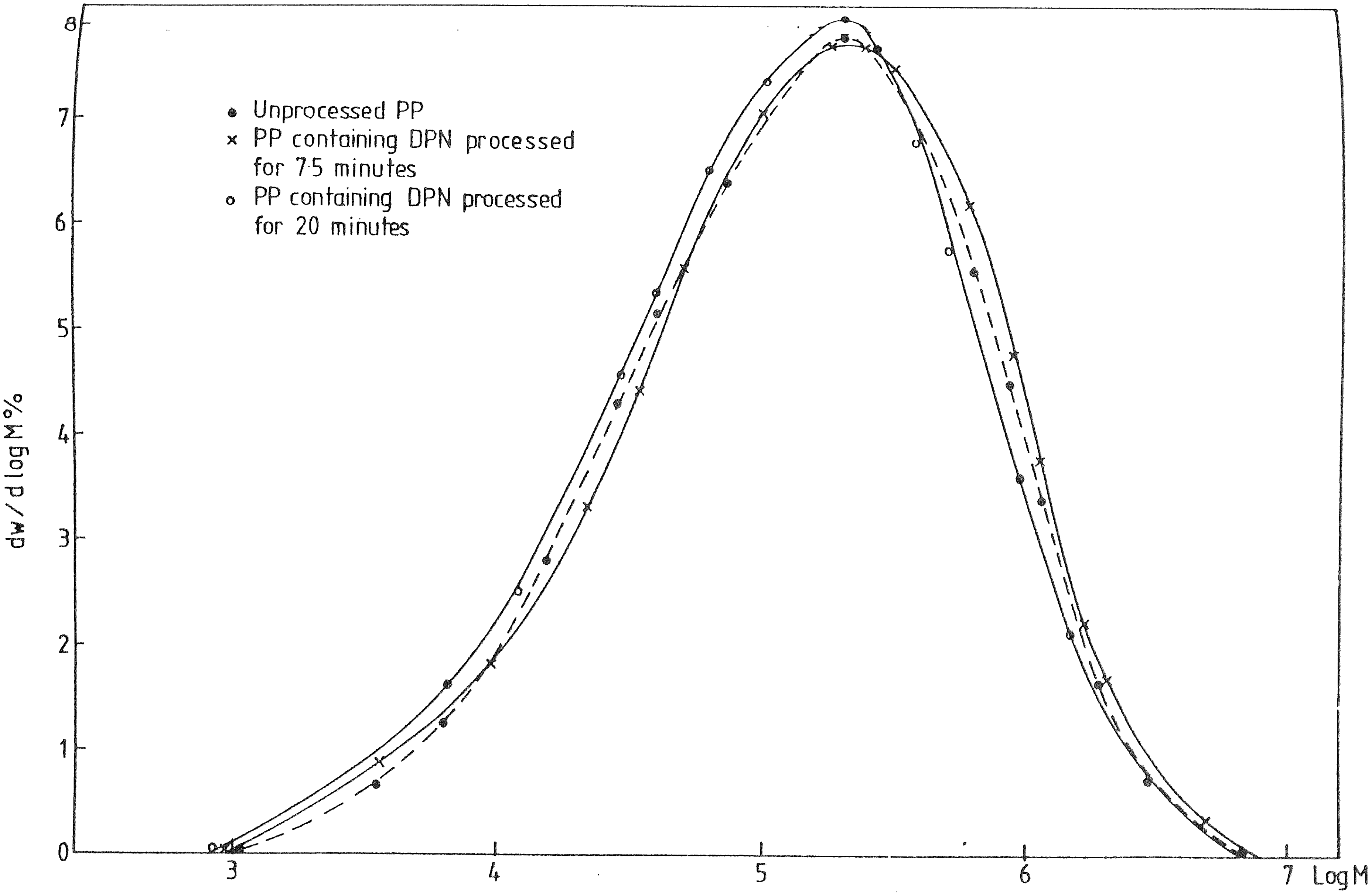


Fig 4:2 Effect of DPN on the molecular weight distribution of PP processed at 180°C in closed mixture at different times

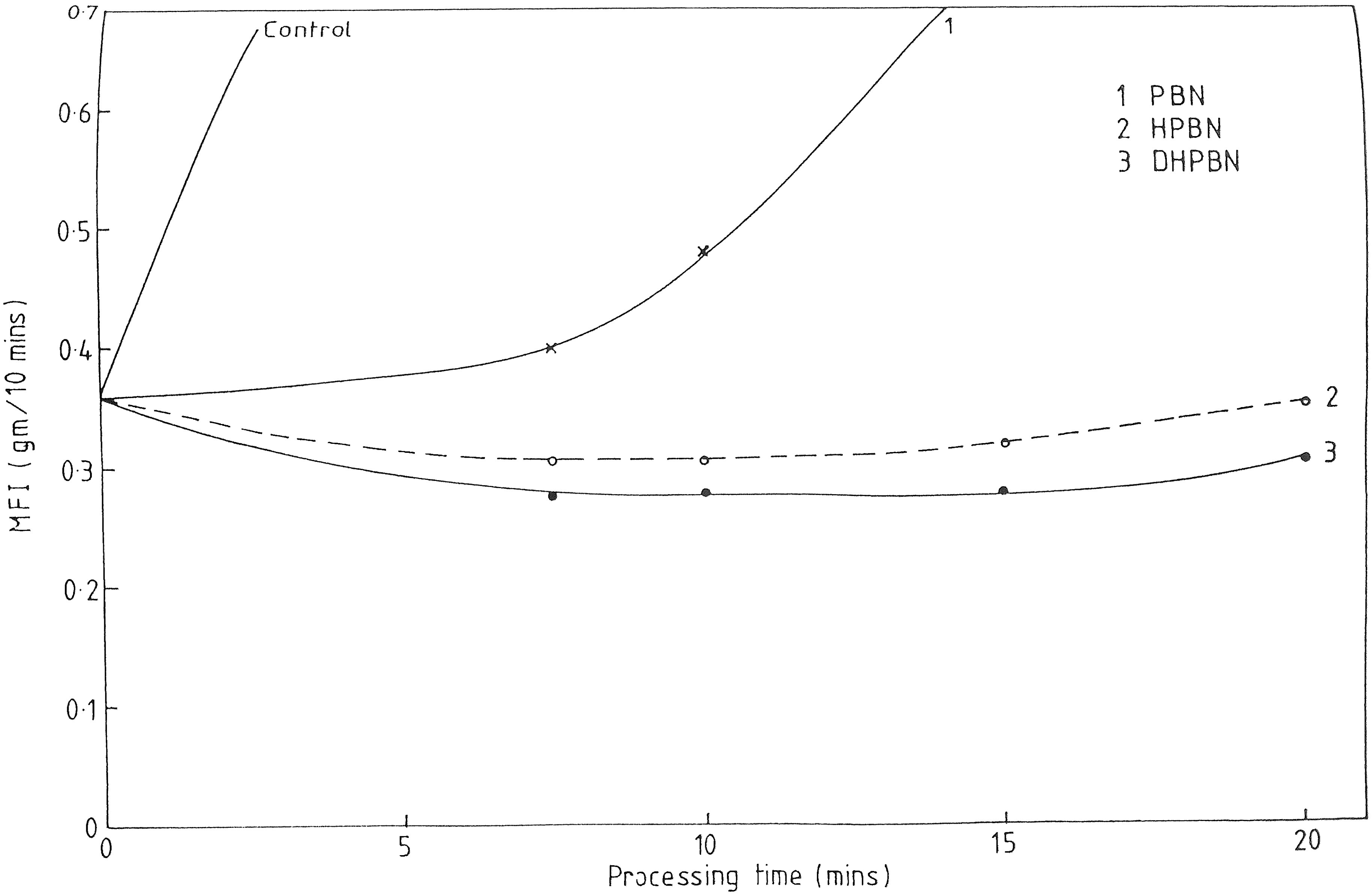


Fig 4:3 Effect of phenyl-tert-butyl nitrone derivatives on MFI of PP processed at 180°C in closed mixture at different times (Concentration 1×10^{-3} mole/100 gm)

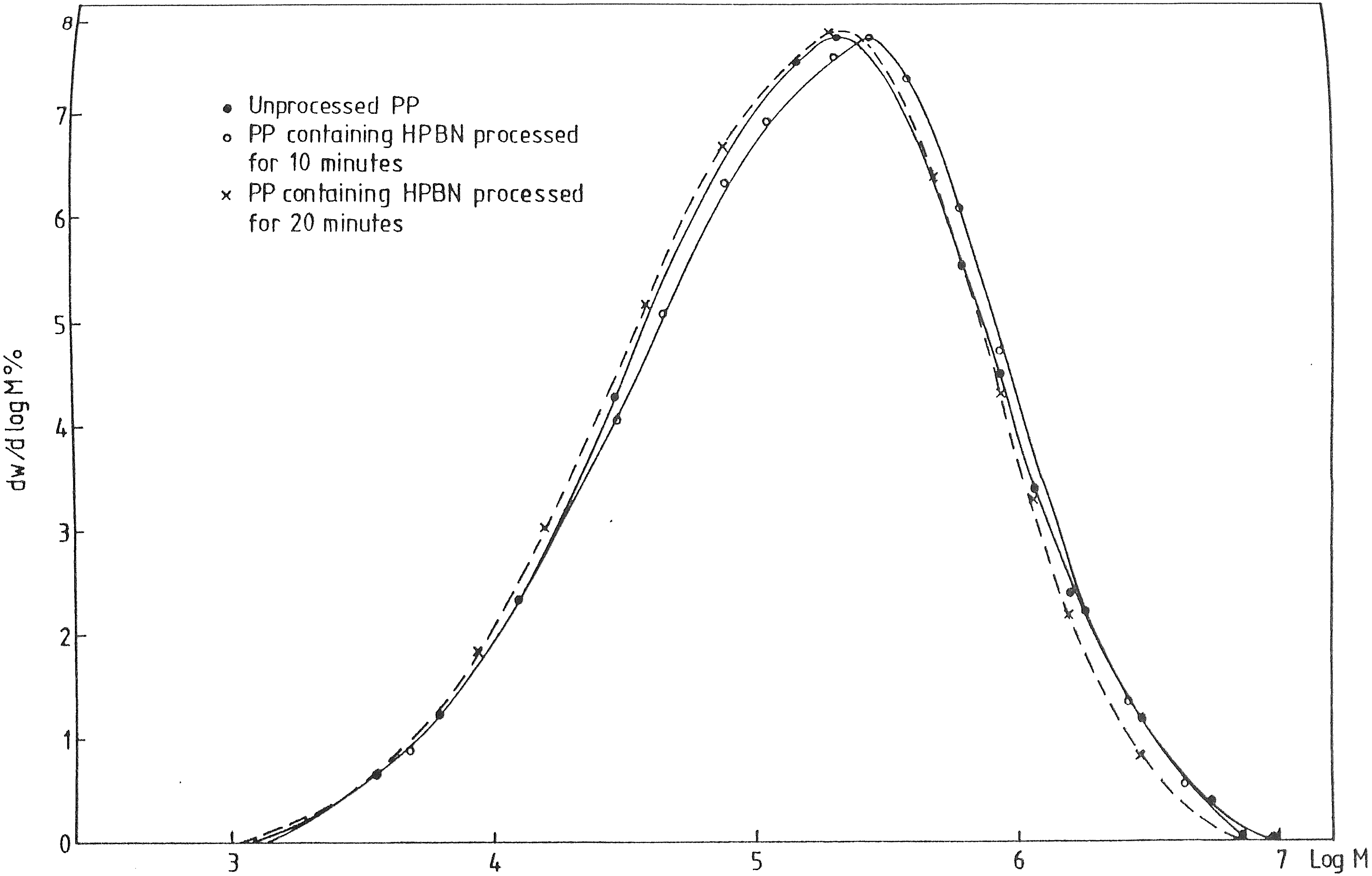


Fig 4:4 Effect of HPBN on the molecular weight distribution of PP processed at 180°C in closed mixture at different times

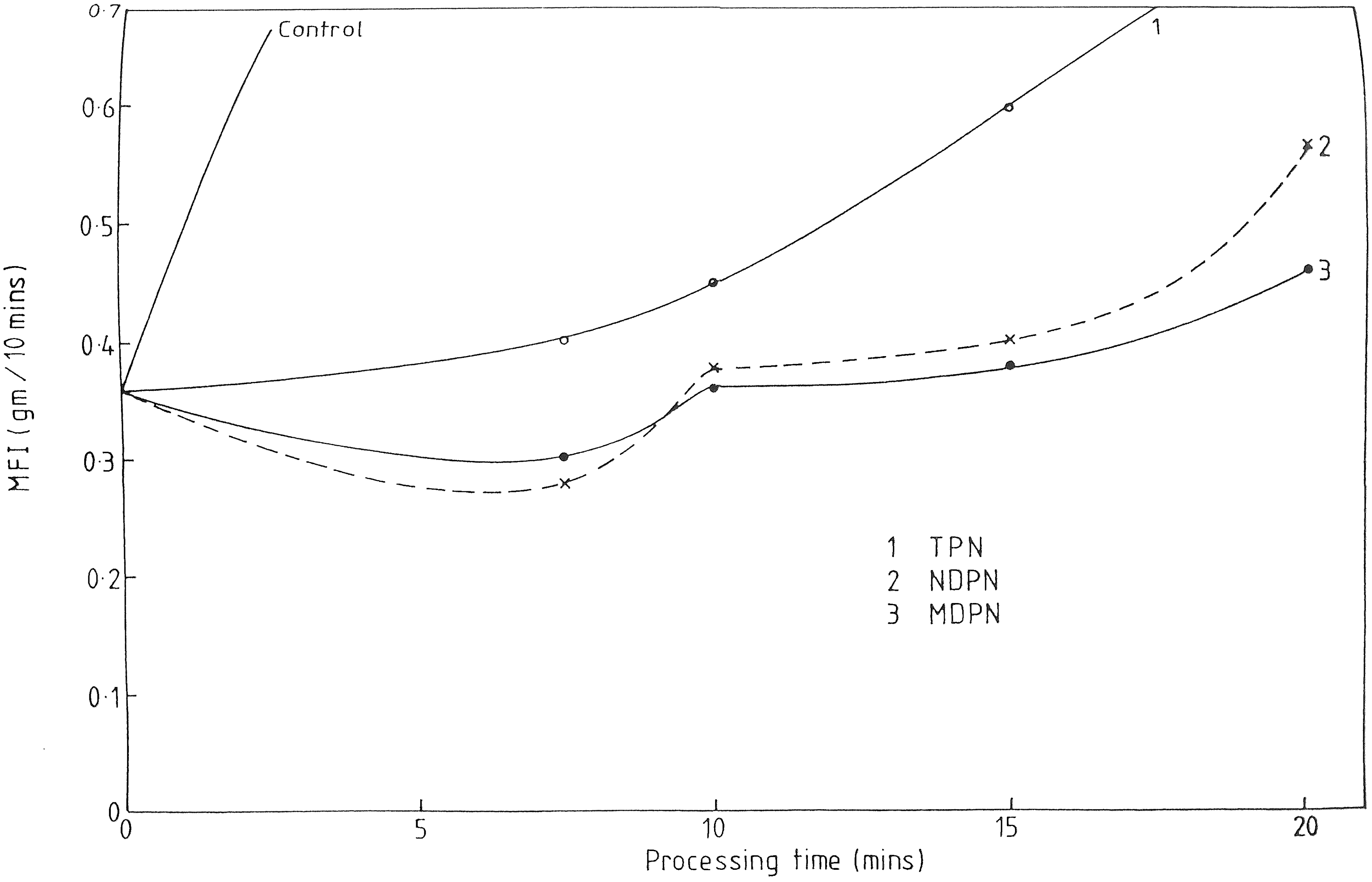


Fig 4:5 Effect of TPN, NDPN and MDPN on melt stabilisation of PP processed at 180°C in closed mixture at different time (Concentration 1×10^{-3} mole/100 gm)

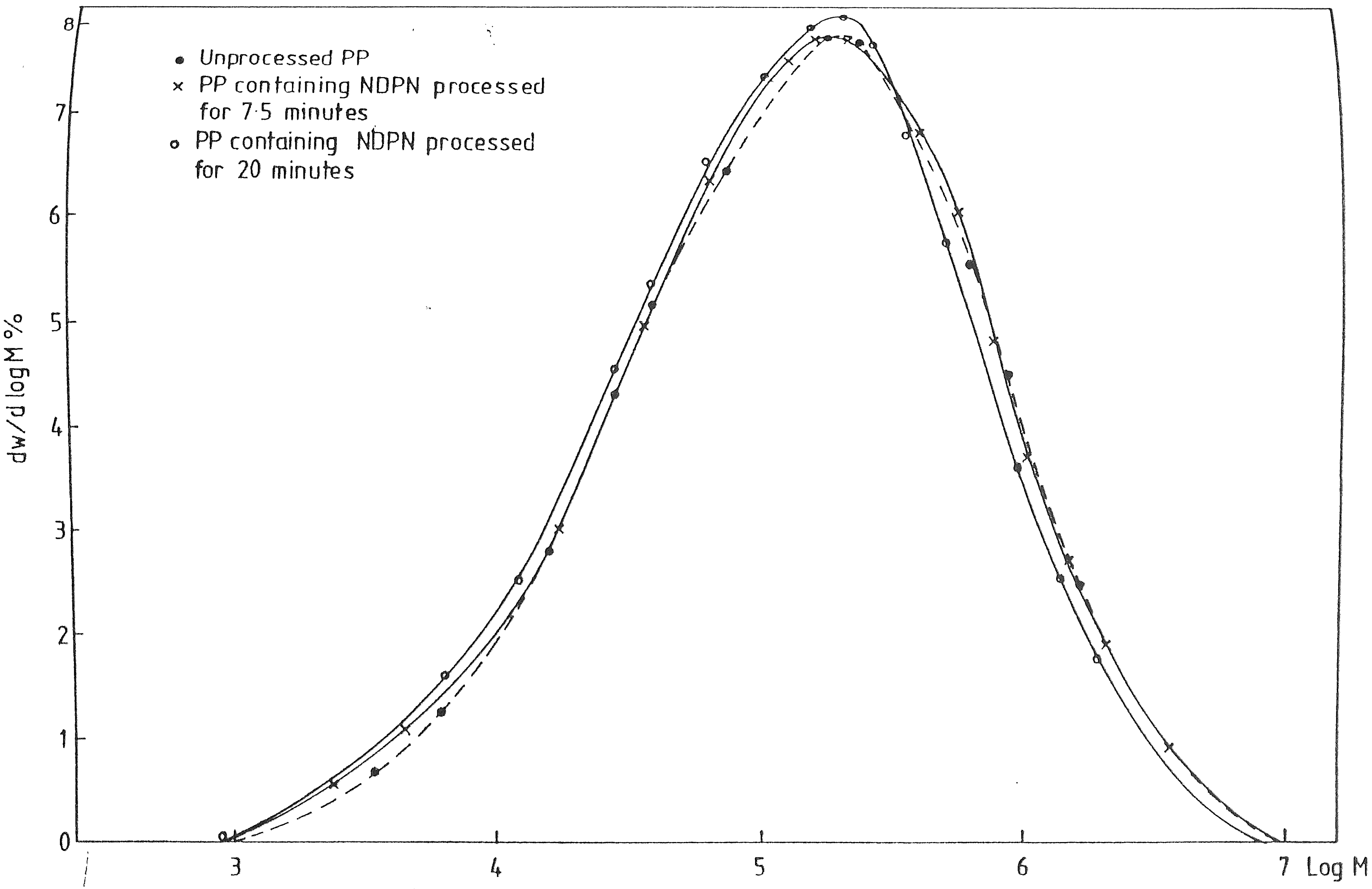


Fig 4:6 Effect of NDPN on the molecular weight distribution of PP processed at 180°C in closed mixture at different times

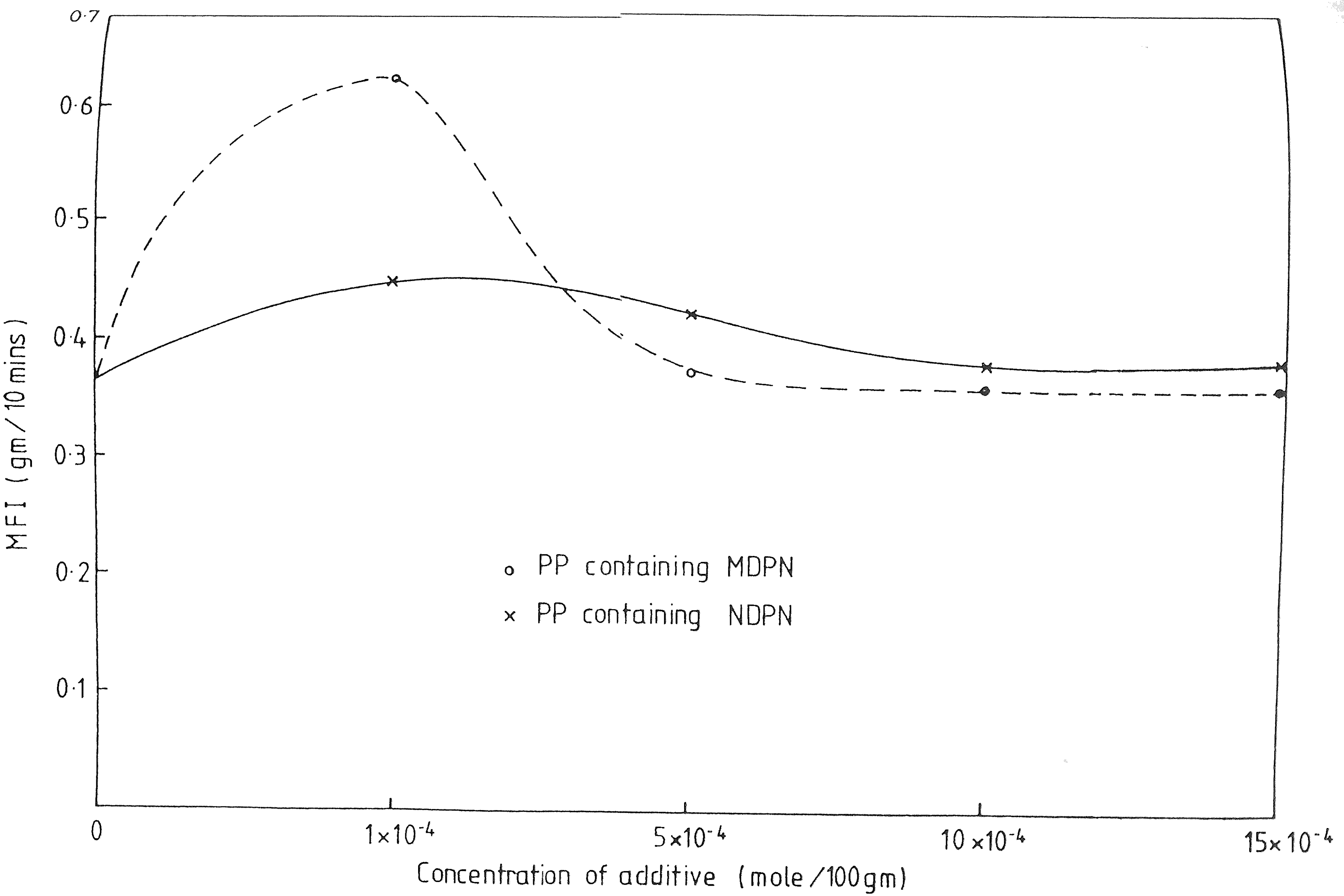


Fig 4:7 The change in MFI of PP due to the inductive effect of different substituent in nitrons at different concentrations (processing time 10 mins at 180°C in closed mixer)

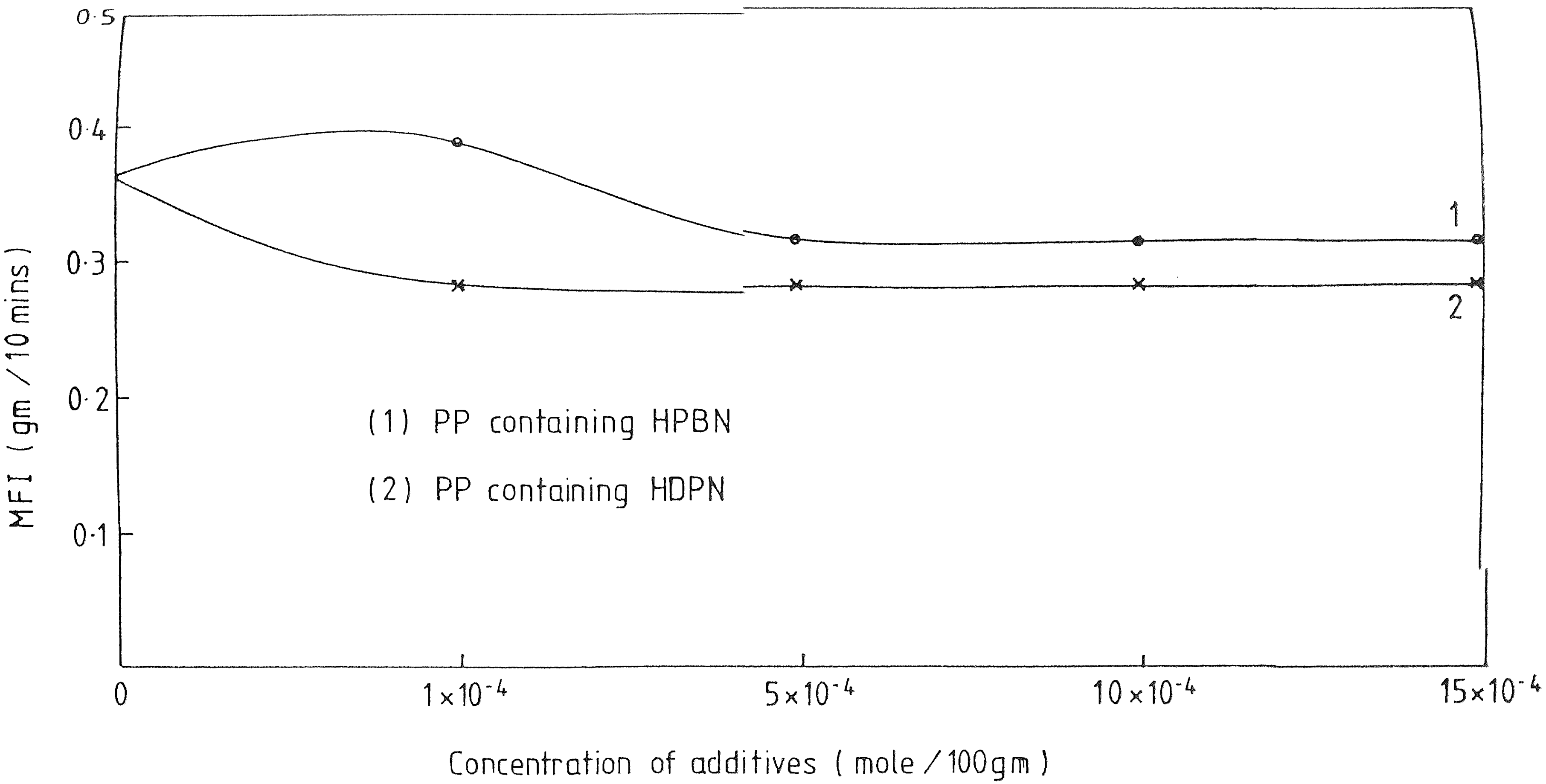


Fig 4:8 The change in MFI of PP due to the inductive effect of different structure of nitrons at different concentrations (processing time 10 mins at 180°C in closed mixer)

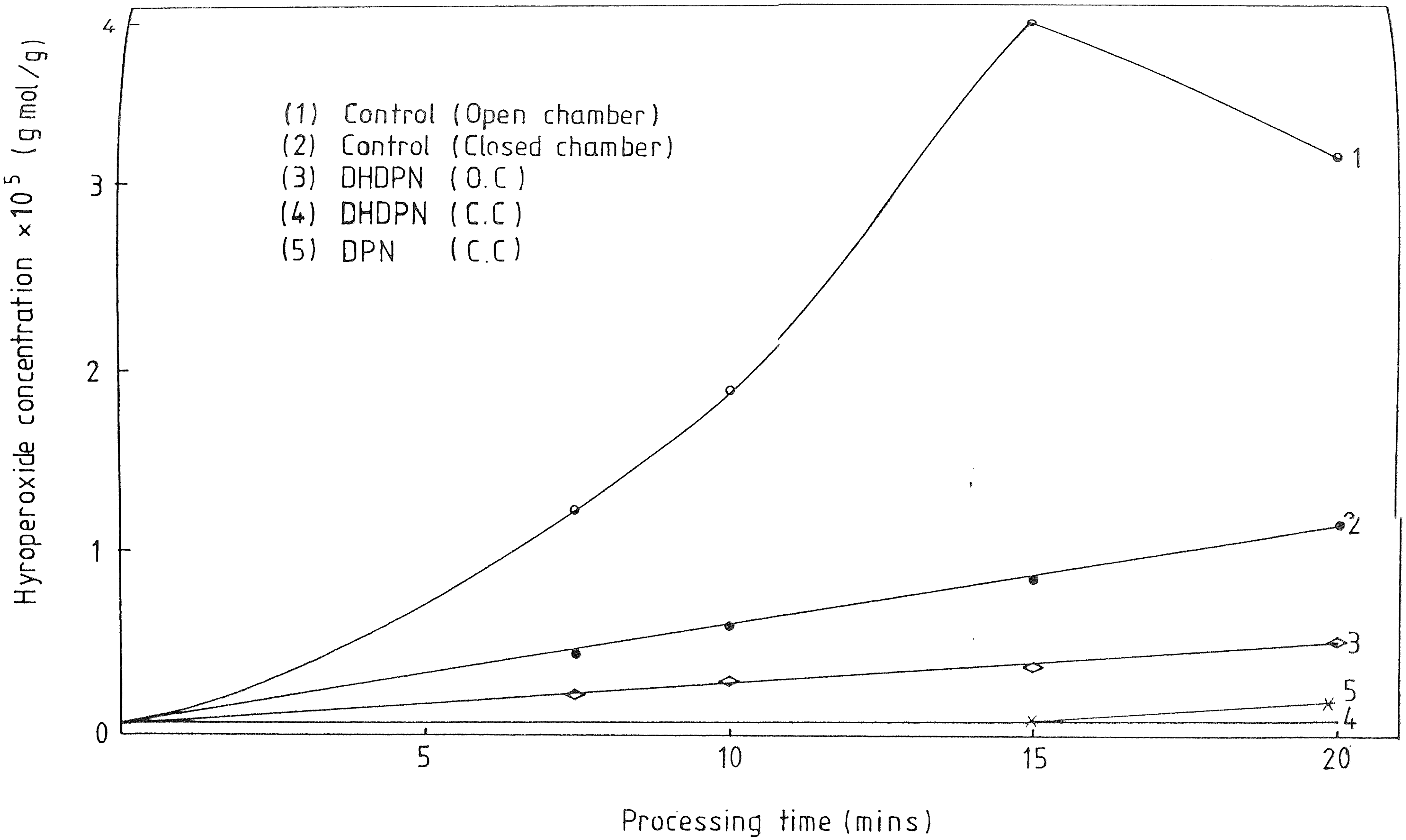


Fig 4:9 Concentration of hydroperoxide formed during processing of PP containing DHDPN at different conditions (Concentration of DHDPN 1×10^{-3} mole /100 gm, processed at 180° C)

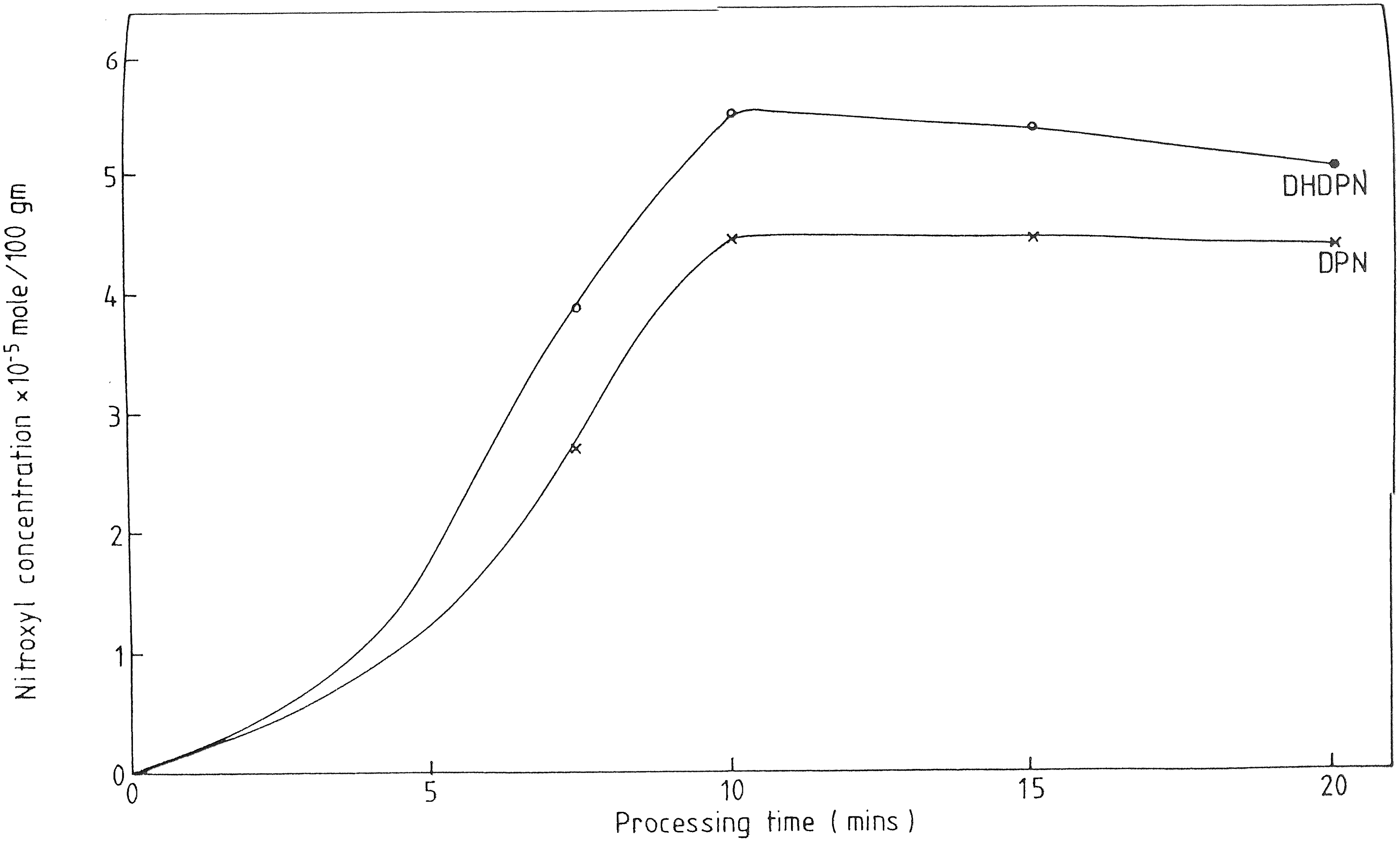
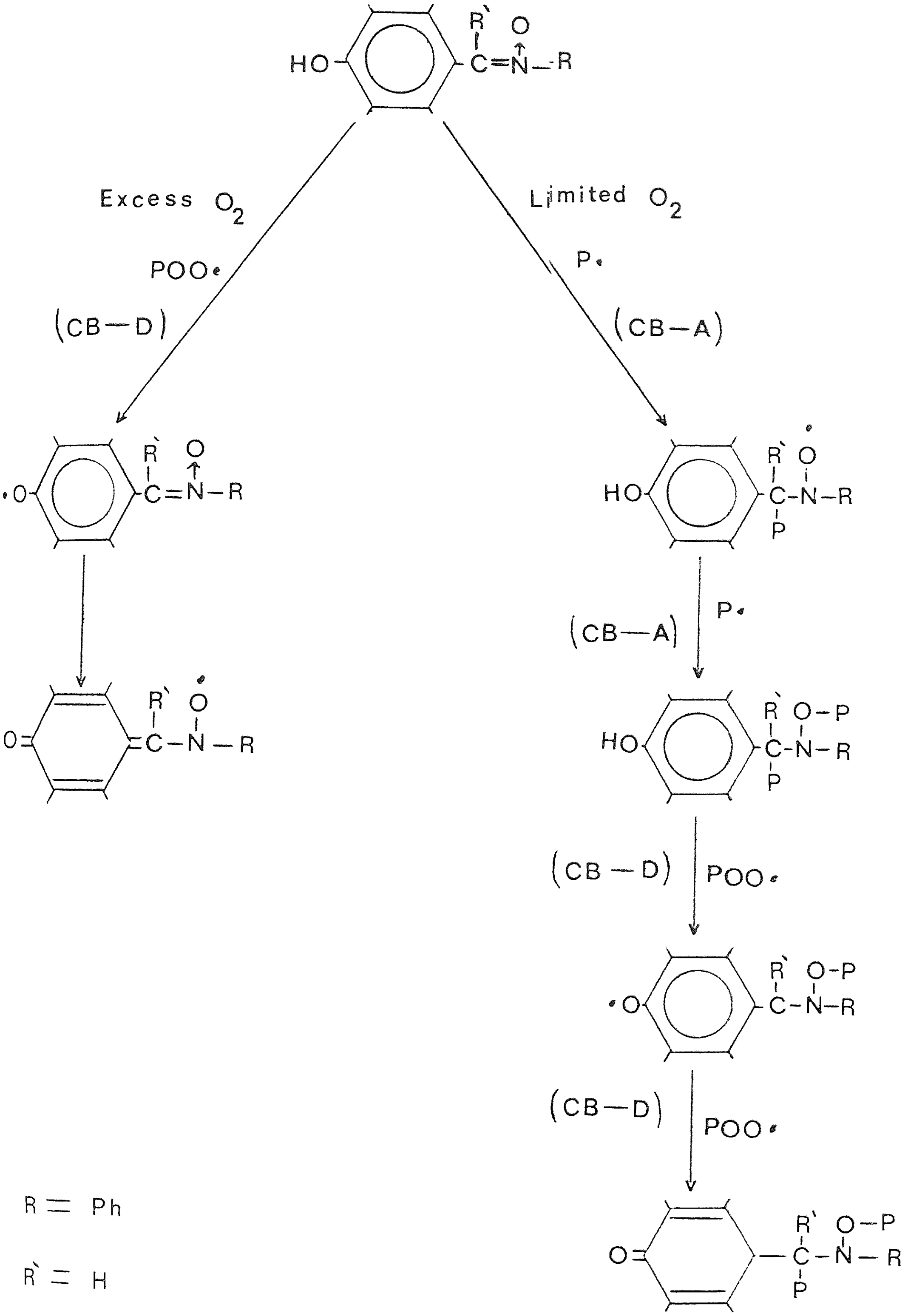


Fig 4: 10 Concentration of nitroxyl radicals formed during processing of PP containing DHDPN and DPN at 180°C, concentration 1×10^{-3} mole / 100 gm



R = Ph

R' = H

Scheme 1

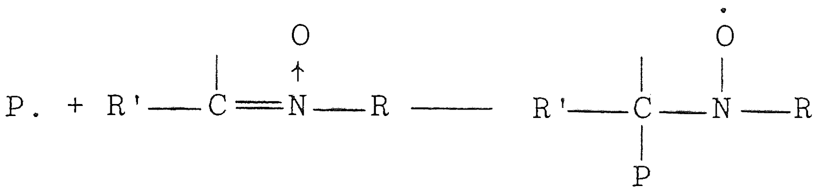
processed under the same conditions. For example, the effect of DHDPN and DPN on the inhibition of hydroperoxide formation in polypropylene is shown in Fig. 4.9.

The conversion of nitrones into nitroxyl radicals seems to be dependent on the processing time. The nitroxyl radicals concentration derived from DPN rises to maximum at 10 mins. and then remains almost constant up to 20 mins. of processing (Fig. 4.10). The same phenomenon is observed with DHDPN, but the rate of nitroxyl formation is higher and rises to maximum at 10 mins., followed by a slow decay with processing (Fig. 4.10). Table 4.2 shows the concentration of nitroxyl radicals formed within polypropylene samples containing nitrones before and after extraction. It is important to note that the observed nitroxyl radicals does not represent the real amount of reacted nitrones during thermal processing due to the formation of nitroxyl radicals derivatives of hydroxylamine and alkylated hydroxylamine.

The unreacted nitrones calculated from the U.V. spectra(152) (see Section 2.2.4) of polypropylene containing nitrones (1×10^{-3} mole/100 gm) processed for 10 mins. was found to be 55%, 61%, 58% and 65% respectively for DPN, HDPN, DHDPN and DHPBN.

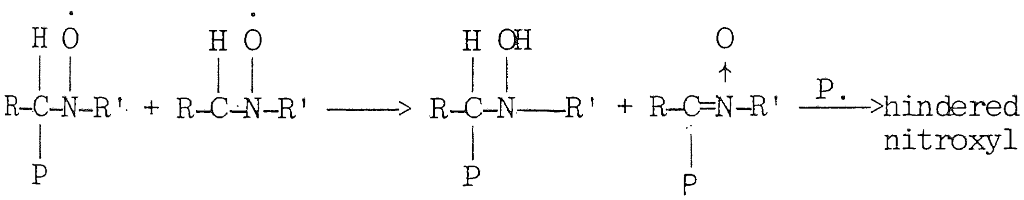
4.2.2 Discussion.

It has been reported that the nitrones are efficient alkyl and alkoxy radical scavengers(82,153). Therefore the incorporation of nitrones during thermal processing of polypropylene terminates macro alkyl radicals formed during processing by coupling macro alkyl radicals and nitrones both on the carbon atom α to nitrone function to form bound nitroxyl radicals according to the reaction (1).



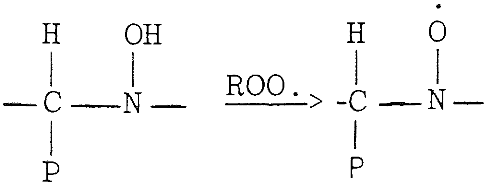
$$P^{\cdot} + R'-\overset{|}{C}=\overset{\overset{O}{\uparrow}}{N}-R \longrightarrow R'-\underset{\underset{P}{|}}{\overset{|}{C}}-\overset{\overset{\dot{O}}{|}}{N}-R \qquad (1)$$

Once nitroxyl radicals are formed, they react with alkyl radicals faster than the nitrones themselves to form alkylated hydroxylamine(91). Alternatively, nitroxyl radicals possessing hydrogen on the α-carbon to the nitroxyl function may be disproportionate to nitrone and hydroxylamine(154) (reaction 4).

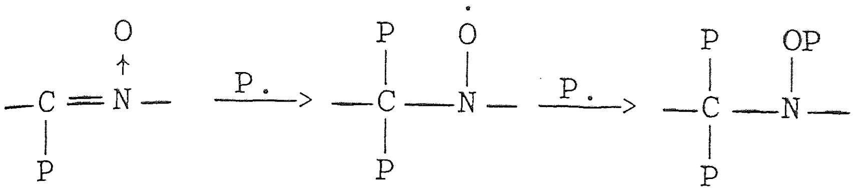


$$R-\underset{\underset{P}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{\dot{O}}{|}}{N}-R' + R-\overset{\overset{H}{|}}{C}-\overset{\overset{\dot{O}}{|}}{N}-R' \longrightarrow R-\underset{\underset{P}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{OH}{|}}{N}-R' + R-\underset{\underset{P}{|}}{C}=\overset{\overset{O}{\uparrow}}{N}-R' \xrightarrow{P^{\cdot}} \text{hindered nitroxyl} \qquad (4)$$

Hydroxylamines(155,156) and nitrones(82,153) react with ROO. and R. or RO. radicals respectively to form nitroxyl, which may react with R. radical to form alkylated hydroxylamine(191) (reactions 5 and 6).



$$-\underset{\underset{P}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{OH}{|}}{N}- \xrightarrow{ROO^{\cdot}} -\underset{\underset{P}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{\dot{O}}{|}}{N}- \qquad (5)$$

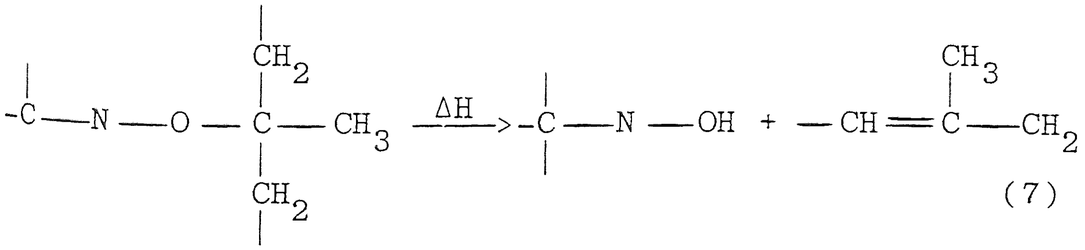


$$-\underset{P}{\underset{|}{C}}=\overset{O}{\overset{\uparrow}{N}}- \xrightarrow{P\cdot} -\overset{P}{\underset{P}{C}}-\overset{\dot{O}}{N}- \xrightarrow{P\cdot} -\overset{P}{\underset{P}{C}}-\overset{OP}{N}- \qquad (6)$$

A rapid rate of nitroxyl radical formation during the early stages of processing under limited air access (Fig. 4.10) followed by stationary state on further processing, indicates that the nitroxyl radicals derived from nitrones react more readily with alkyl radicals than with the nitrones to form alkylhydroxylamine(96), so that the yield of nitroxyl radicals does not exceed a certain level.

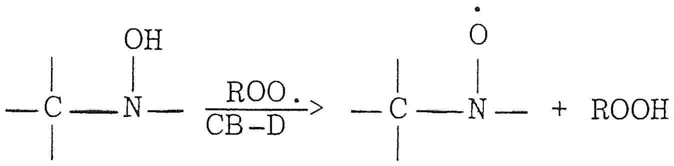
The reduction in MFI (Figs. 4.1 and 4.3) as well as the increase in molecular weight (Figs. 4.2 and 4.4) is certainly due to the cross-linking effect of nitrones according to reactions 2 and 6. Similar cross-linking reaction has also been observed in rubber containing nitrones(150).

The detection of hydroxylamines in the polypropylene extract which still contained nitrones, suggests that these species are produced by thermal decomposition of alkylated hydroxylamine(48,149,159)(reaction 7) or disproportionation of nitroxyl containing α-hydrogen (reaction 4).



$$-\overset{|}{C}-N-O-\overset{\overset{|}{CH_2}}{\underset{\underset{|}{CH_2}}{C}}-CH_3 \xrightarrow{\Delta H} -\underset{|}{\overset{|}{C}}-N-OH + -CH=\overset{CH_3}{\overset{|}{C}}-CH_2 \qquad (7)$$

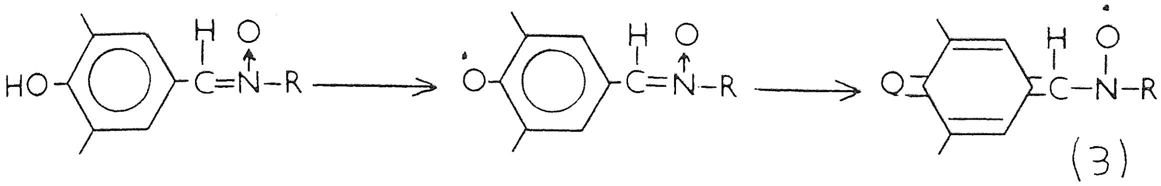
It was not possible in the present case to measure the change in the unsaturation in the polymer (according to reaction 7) due to reactivity of nitrones towards double bonds by the 1,3-cyclo-addition reaction 9. The hydroxylamine was reported to be a better melt stabiliser than the corresponding nitroxyl radicals in excess of oxygen indicating CB-D activity of hydroxylamine(155).



$$-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{N}}}- \xrightarrow[\text{CB-D}]{\text{ROO.}} -\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\dot{\mathrm{O}}}{\overset{|}{\mathrm{N}}}- + \mathrm{ROOH} \qquad (8)$$

Since nitroxyl radicals are effective alkyl radical traps, reaction 7, together with reaction 8 constitute a cyclic regeneration process.

It is clear from the above discussion that the nitrones such as DPN, NDPN and MDPN are autosynergestic since they operate by terminating alkyl radicals (CB-A) as well as decomposing hydroperoxides(158). Nitrones containing a phenolic group operate by an additional mechanism, since they can also terminate ROO. radicals (CB-D) (this will be discussed later, see Section 4.5). The CB-A, CB-D and peroxide decomposing activity of phenolic nitrones therefore explain the very good melt stabilisation activity of these nitrones in pp even under severe processing conditions. However the absence of phenoxy radicals signals from the E.S.R. spectra, and the detection of nitroxyl radicals could be attributed to the tautomerisation of phenoxyl radicals with nitroxyl radicals. (This will be discussed in the mechanism Section 4.5). The presence of quinonoid


(3)

structure (IR absorbance at 1660 cm^{-1} in polyproplene extracts containing DHDPN confirms the above mechanism.

4.3 Effects of Nitrones on the Photo-oxidation of Polypropylene

4.3.1 Results

The effect of thermal processing on the subsequent U.V. stabilising activity of nitrones in pp is investigated in this section.

Fig. 4.11 shows the effect of DPN on the photo-oxidation of pp processed at different times and at concentration of 1 x 10^{-3} mole/100 gm. As the processing time was increased from 7.5 up to 15 mins., the induction period to carbonyl formation as well as the overall photo-stabilisation activity was improved. U.V. embrittlement times of pp were found to be consistent with carbonyl formation (Table 4.3). The improvement of photo-stabilisation process with increase in processing time is consistent with the higher formation of nitroxyl radicals. However the initially colourless sample containing DPN gradually changed to yellow colour during U.V. irradiation and embrittlement of pp occurred when the films were quite yellow.

Fig. 4.12 shows the relationship between the U.V. embrittlement time of pp containing DPN and the concentration of nitroxyl radicals formed during processing prior to U.V. irradiation. It is apparent that there is no direct relationship between the nitroxyl radical concentration observed and the U.V. embrittlement time. Although nitroxyl radical concentration remained constant in the later stage of processing, the U.V. embrittlement time of pp was found to decrease.

Fig. 4.13 shows the effect of processing on the photo-oxidation of polypropylene containing 1 x 10^{-3} mol/100 gm. of HDPN. All samples showed an initial induction period to carbonyl formation up to 100 hours, followed by a slower rate of photo-oxidation compared to the control. In this case, however, the severity of processing does not seem to have any significant effect on the overall photo-stabilisation activity (Table 4.3).

Fig. 4.14 compares the effect of processing under limited oxygen and excess oxygen for 10 mins. at a concentration of HDPN, 1 x 10^{-3} mole/100 gm. It is apparent that the processing conditions do not have a significant effect on the U.V. activity of HDPN. This suggests that the ability of HDPN to terminate both ROO. and R. radicals during processing (reaction scheme 1) thus inhibiting hydroperoxide formation. However the unreacted HDPN may also play an important role during U.V. irradiation by terminating either ROO. or R. radicals to form nitroxyl radicals. Whereas under conditions of U.V. irradiation the ratio [R.]/[ROO.] is higher than in thermal oxidation due to the slow rate of oxygen diffusion, alkyl radicals can react with nitroxyl radicals to form alkylated hydroxylamine(43).

Fig. 4.15 shows the formation of unsaturation during the photo-oxidation of pp films containing different concentrations of HDPN (process for 10 mins. in closed mixer). The unsaturation growth is reduced by increasing HDPN concentration during U.V. irradiation, so that there is no change in the olefinic unsaturation at concentration of 1 x 10^{-3} mole/100 gm. up to 140 hours of irradiation (unsaturation was measured by following a bond at 1640 cm^{-1}). This seems to suggest that unreacted HDPN consumed the unsaturation formed during irradiation by 1,3 cyclo-addition reaction(157). This is supported by the fact that an irradiated pp film containing HDPN after extraction with dichloromethane showed the formation of unsaturation from the very beginning of irradiation.

Fig. 4.16 shows the U.V. ageing behaviour of pp films containing HPBN processed at different times (at 1 x 10^{-3} mole/100 gm. processing temperature 180°C). The induction period to carbonyl formation and to the overall stabilisation activity was found to increase significantly with increase in processing time.

Figs. 4.17 and 4.18 illustrate the photo-oxidation behaviour of pp containing MDPN and NDPN with processing (1×10^{-3} mole/100 gm.). It is apparent that there is no significant effect of processing on the photo-stabilisation activity of NDPN and that carbonyl starts to form from the beginning of U.V. irradiation at a very slow rate. This is reflected in the embrittlement times of pp (Table 4.3). It seems that the photo-stabilisation behaviour of MDPN differs from the behaviour of NDPN. The carbonyl values of pp.containing MDPN are initially low up to 90 hours. At the end of this time the rate of carbonyl formation increased rapidly (Fig. 4.17). MDPN is less effective as a photo-stabiliser compared to NDPN (Fig. 4.19 and Table 4.3). This suggests that the inductive effect of NO_2 and MeO groups of unreacted NDPN and MDPN effected the stabilisation activity during U.V. irradiation. Due to the electron withdrawing nature of the nitro group, the activity of NDPN towards alkyl radicals is increased. As a result the overall U.V. stabilisation activity of NDPN in found to be higher compared to MDPN.

Fig. 4.20 shows the decay of U.V. absorbance peaks at 325, 290, 290, 285 nm indicating the decrease in concentration of DHDPN, HDPN, DHPBN and HPBN respectively

Table 4.3 Fffect of processing time on the U.V. embrittlement time of pp containing nitrones at concentration 1 x 10^{-3} mole/100 gm, processed in closed mixer at 180°C.

Additives	U. V. Embrittlement Time (hours)				
	Unextracted Samples				Extracted Samples
	7.5mins	10mins	15mins	20mins	
Control	85	85	75	-	-
DPN	200	245	290	185	130
HDPN	240	210	210	200	130
DHDPN	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
DHPBN	130	130	130	130	90
TPN	110	110	110	90	90

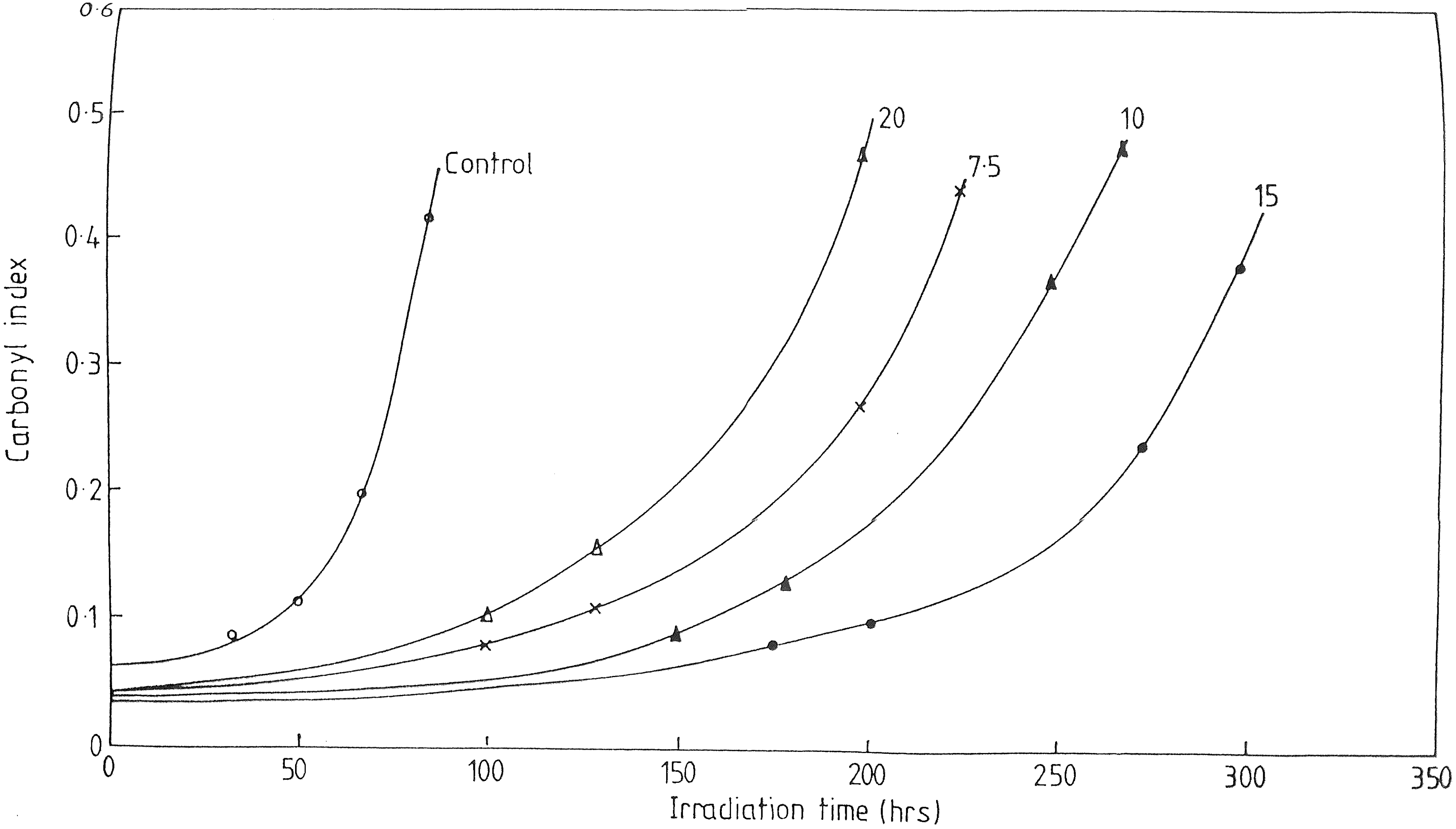


Fig 4:11 Effect of processing time on the photo - stabilisation of PP containing DPN processed at 180°C in closed mixer at concentration of 1×10^{-3} mole/100 gm
Number on curve represents processing time in minutes.

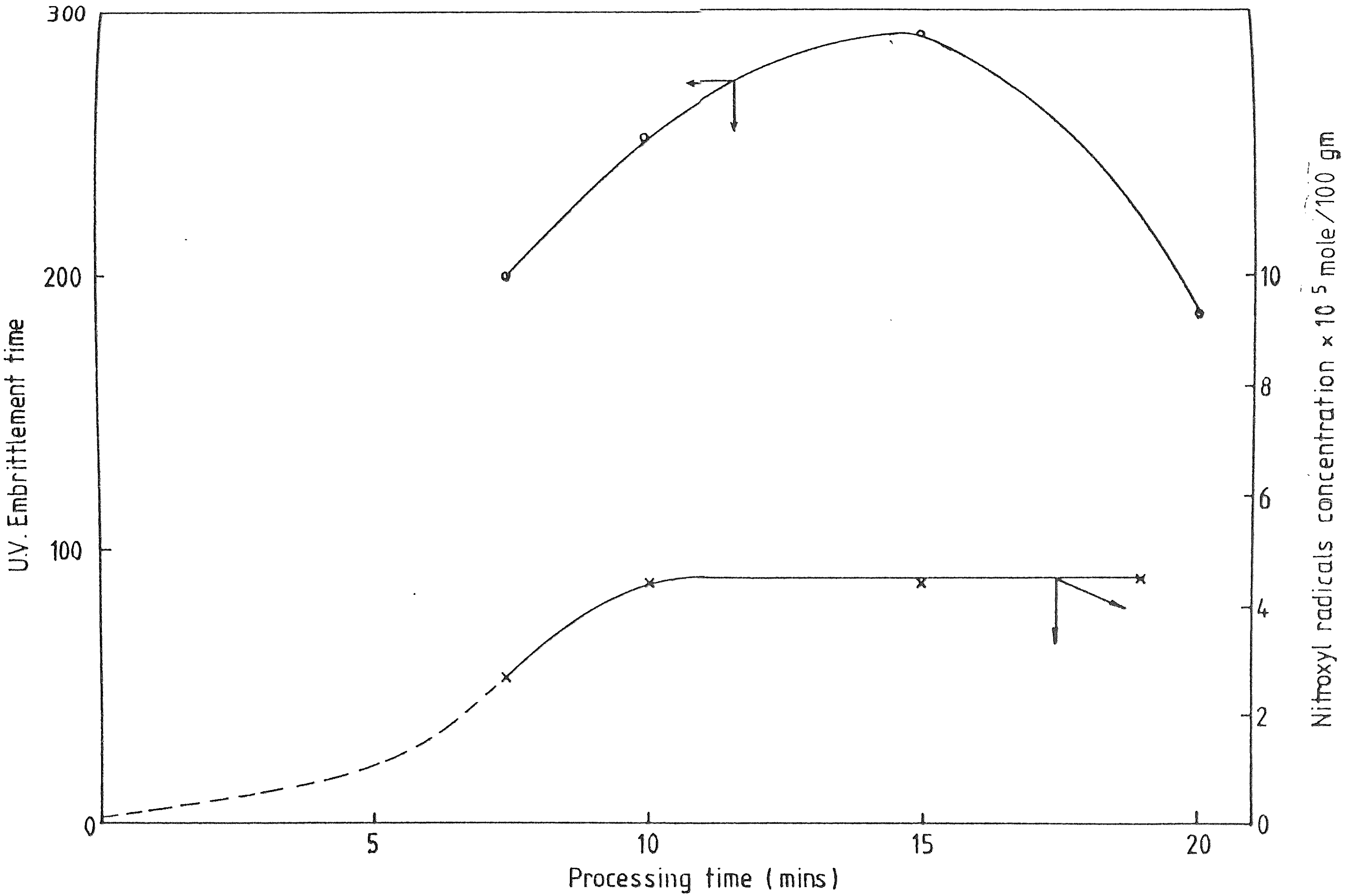


Fig 4:12 Effect of processing on nitroxyl radicals formation and U.V. embrittlement time of PP containing DPN at concentration of 1×10^{-3} mole/100 gm

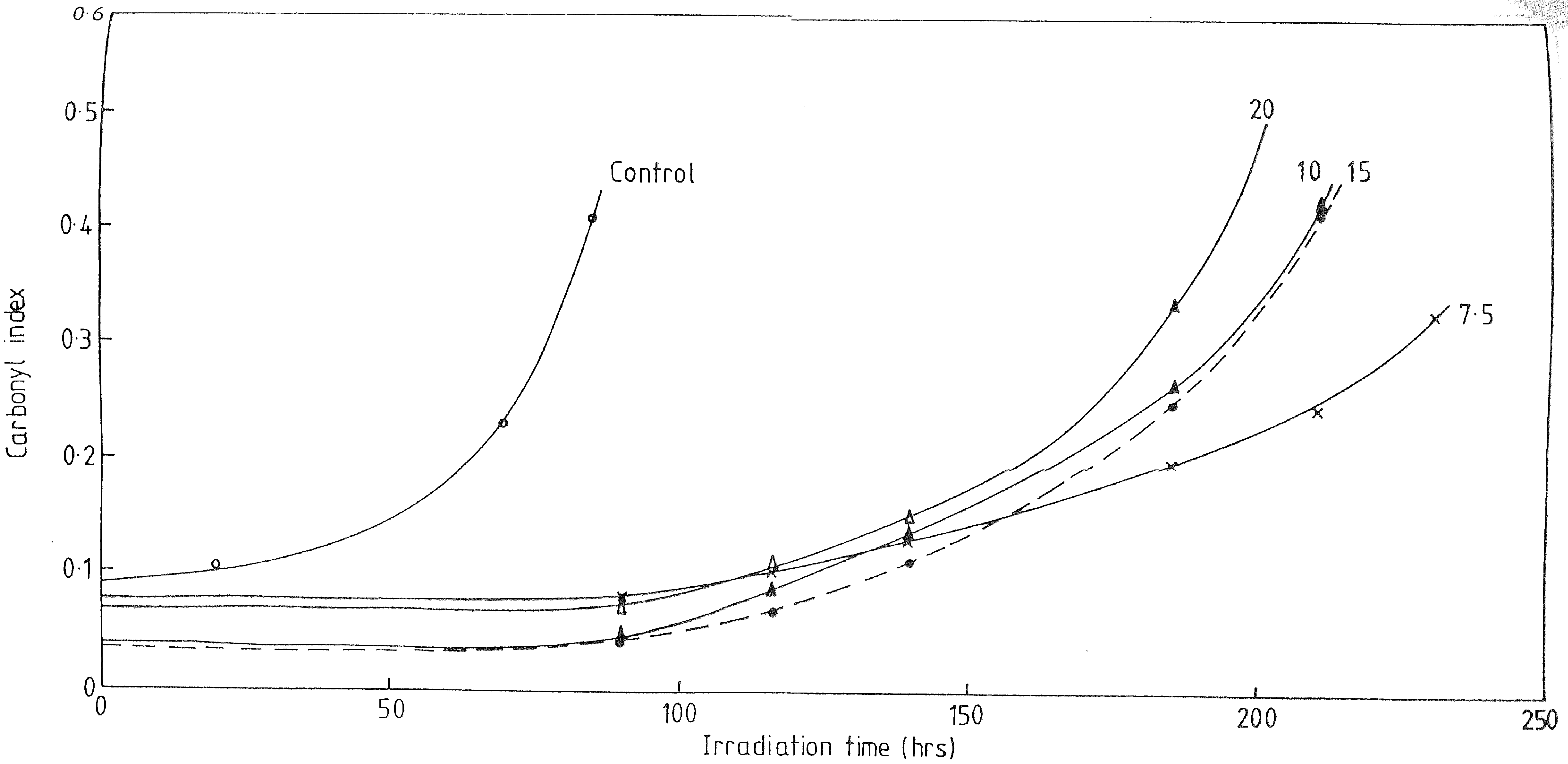


Fig 4:13 Effect of processing time on the of photo-oxidation of PP film containing HDPN processed at 180°C in closed mixer concentration 1×10^{-3} mole/100gm. Number on curve represents processing time.

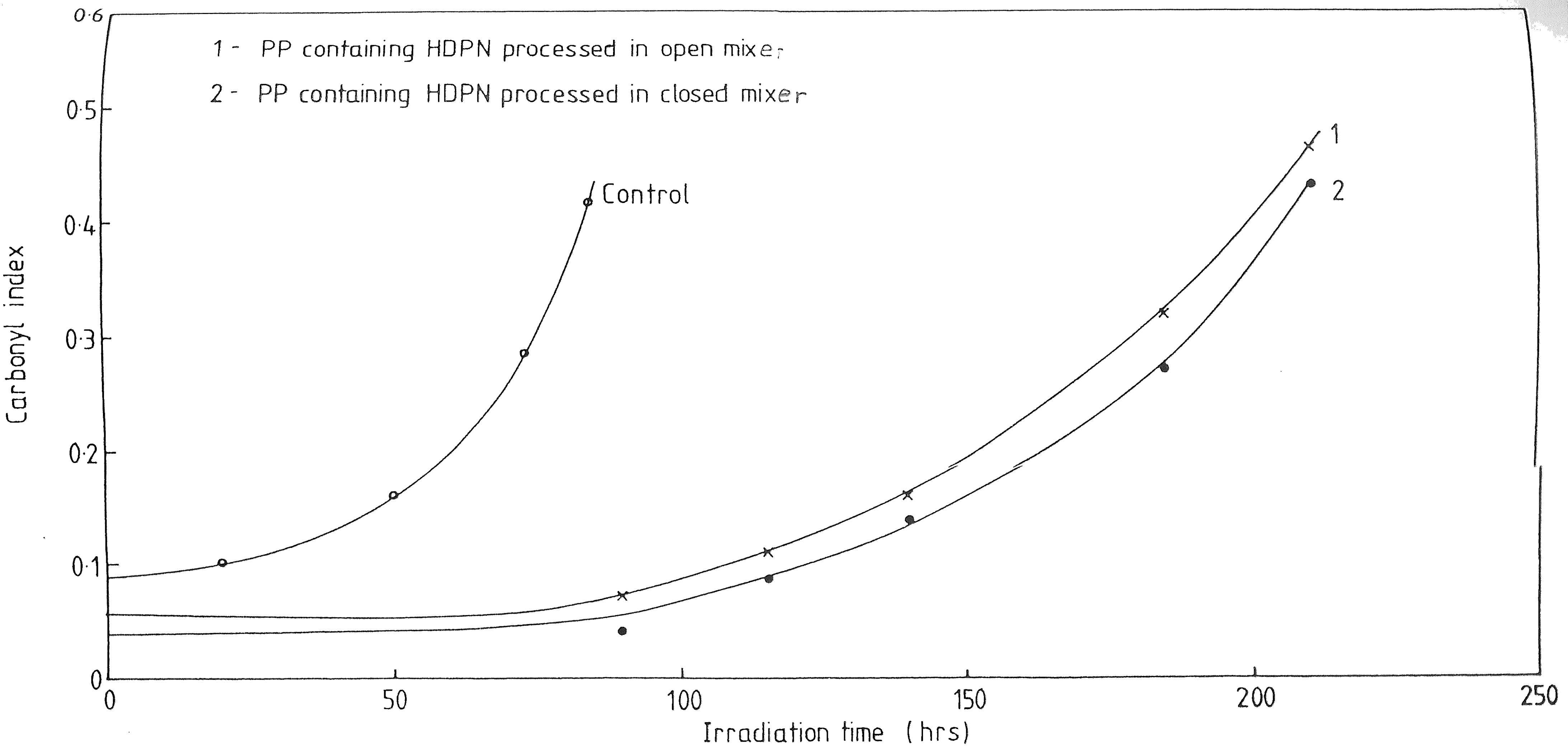


Fig 4:14 Effect of processing conditions on the photo - stabilisation of PP containing HDPN processed at 180°C for 10 minutes at concentration of 1×10^{-3} mole/100 gm

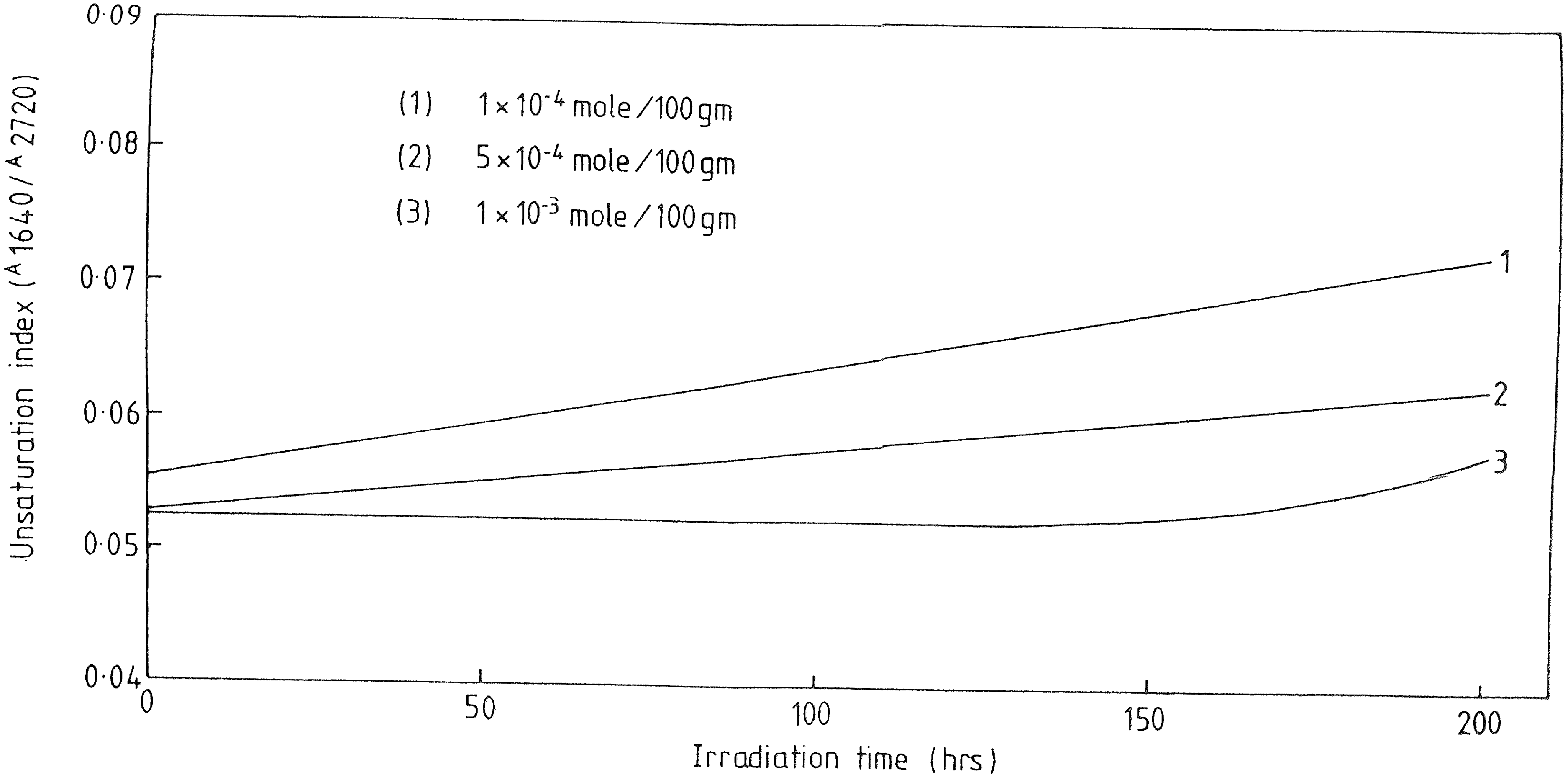


Fig 4:15 Effect of HDPN concentration on the unsaturation formation in PP processed at 180°C in closed mixer at 10 minutes

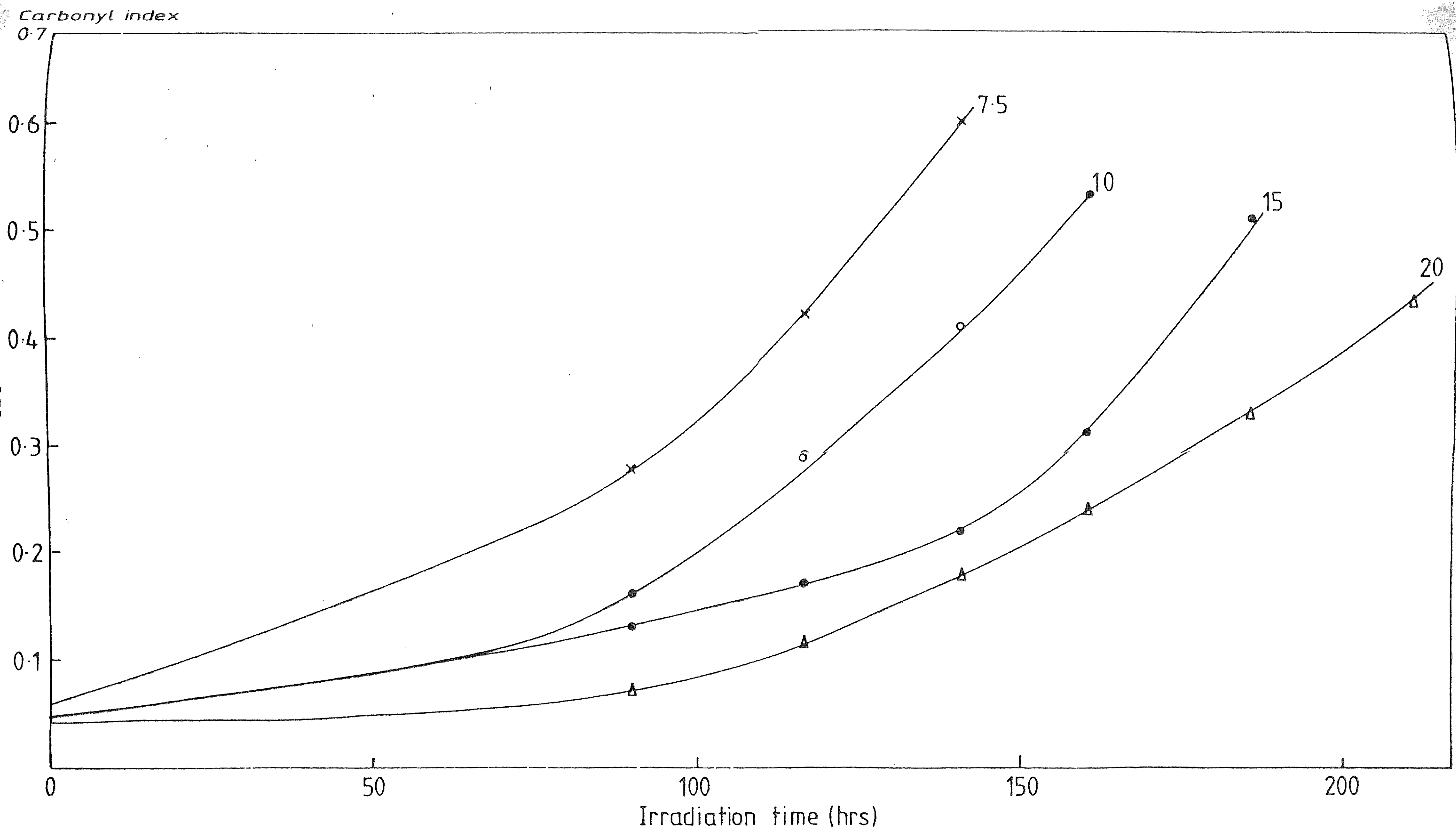


Fig 4:16 Effect of processing time on the photo-stabilisation of PP containing HPBN processed at 180°C in closed mixer at concentration 1×10^{-3} mole/100 gm. Number on curve represents processing time in minutes

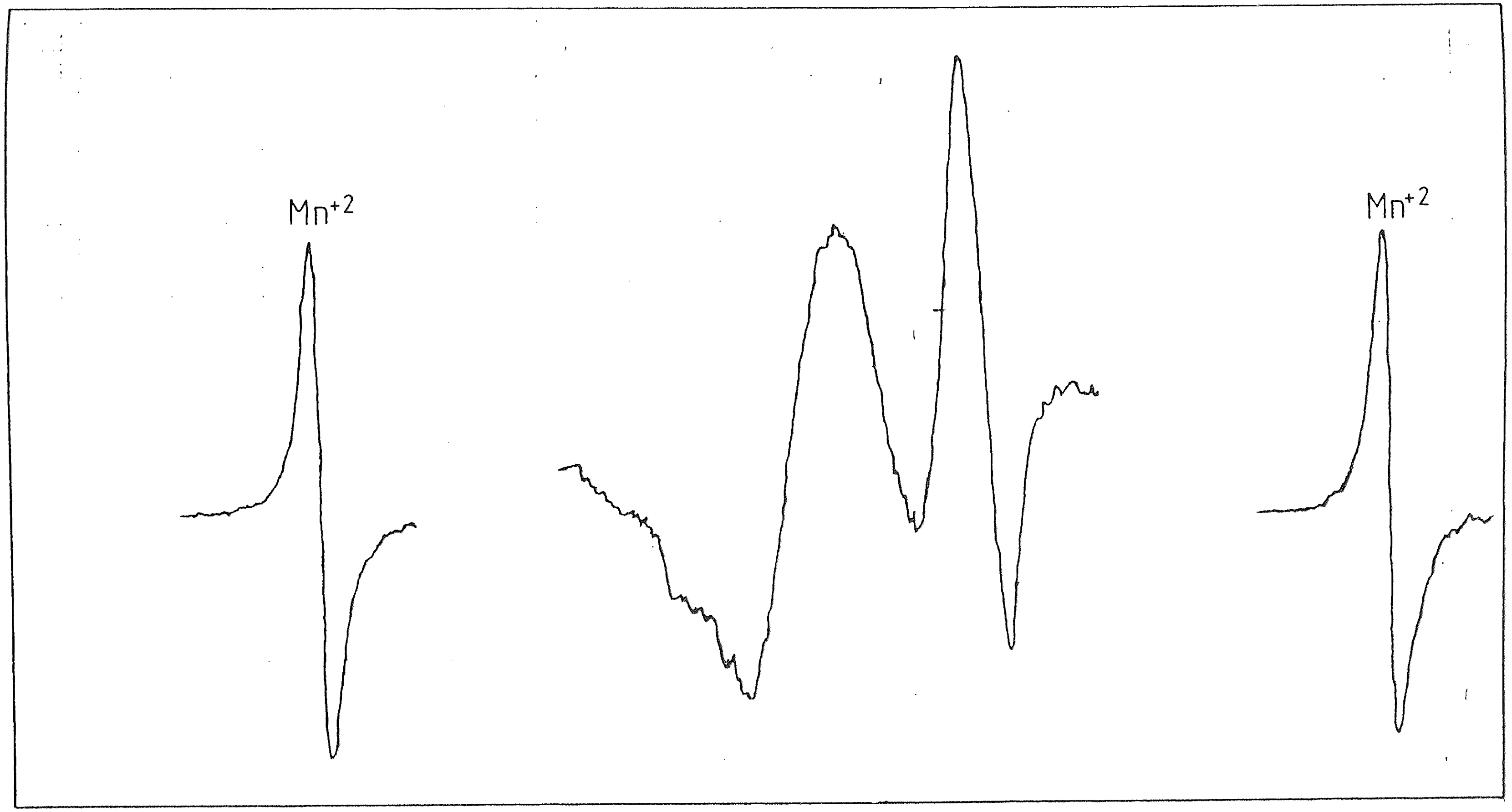


Fig 4:16B ESR spectrum of nitroxyl radical in PP film containing DHDPN processed for 10 mins at 180°C

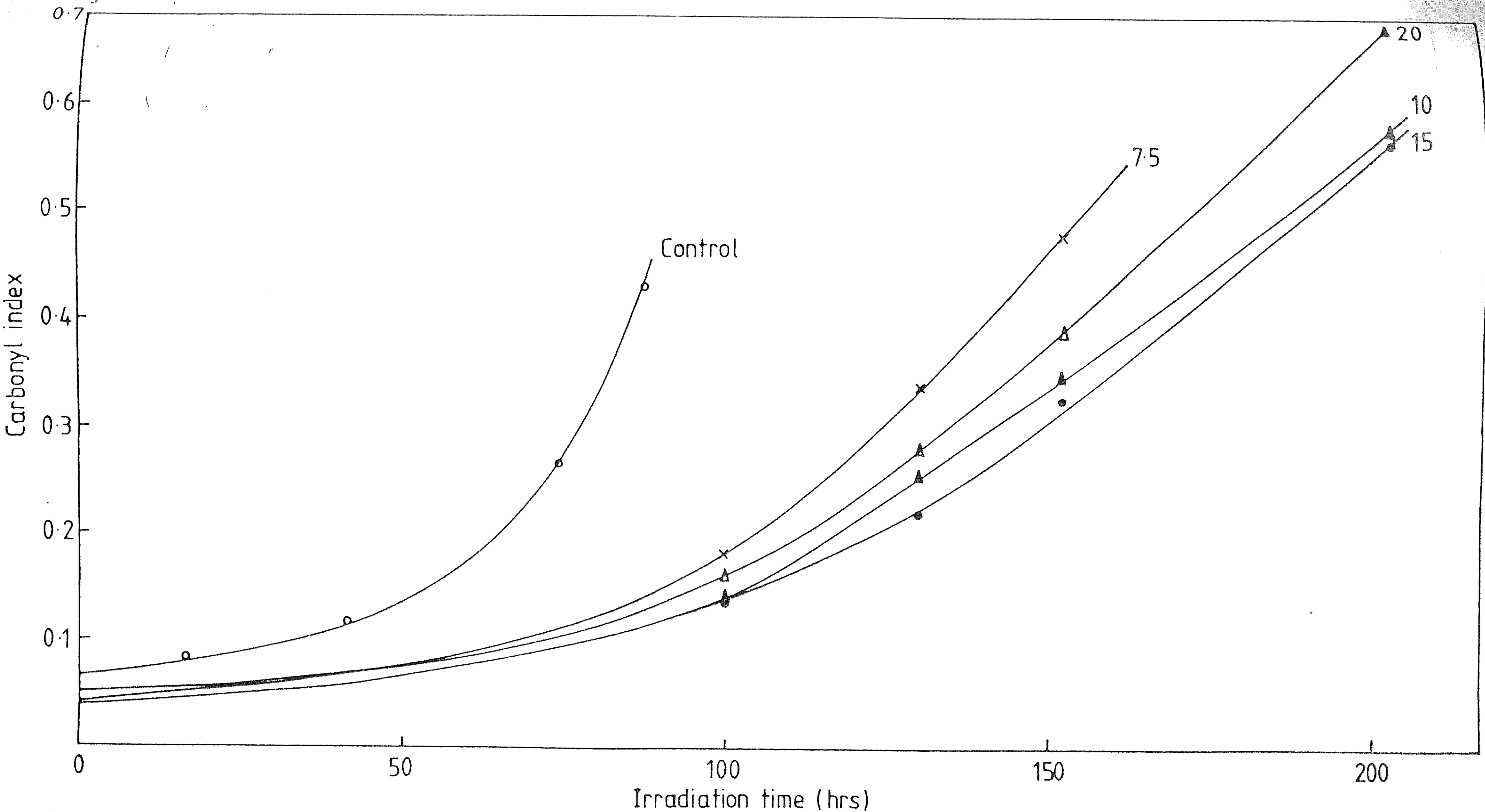


Fig4:17 Effect of MDPN on the photo-oxidation of PP processed at different times at 180°C in closed mixer at concentration of 1×10^{-3} mole/100gm. Number on curve represents processing time in minutes.

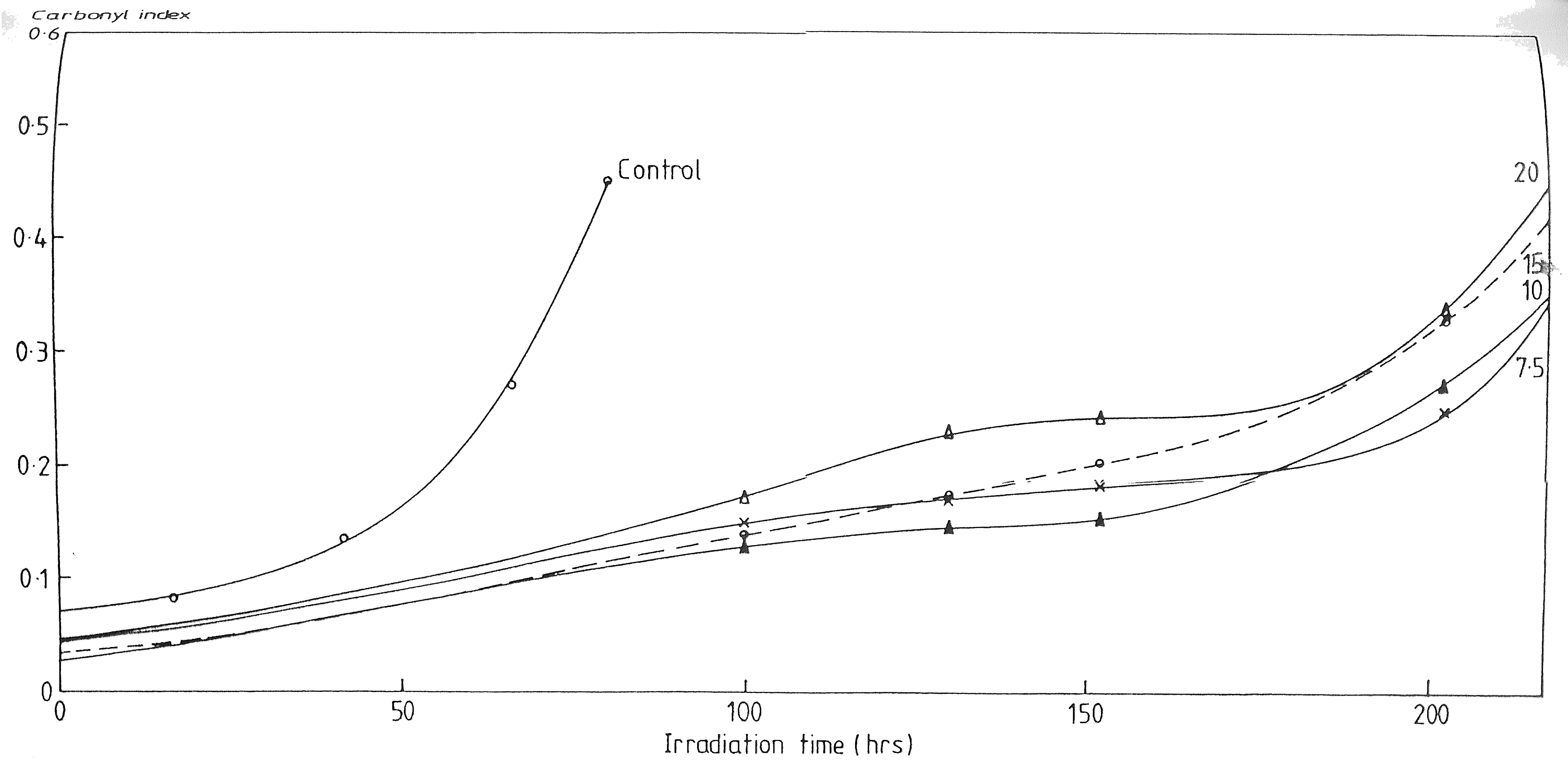


Fig 4:18 Effect of NDPN on the photo-oxidation of PP processed at different times at 180°C in closed mixer at concentration of 1×10^{-3} mole/100 gm. Number on curve represents processing time in minutes.

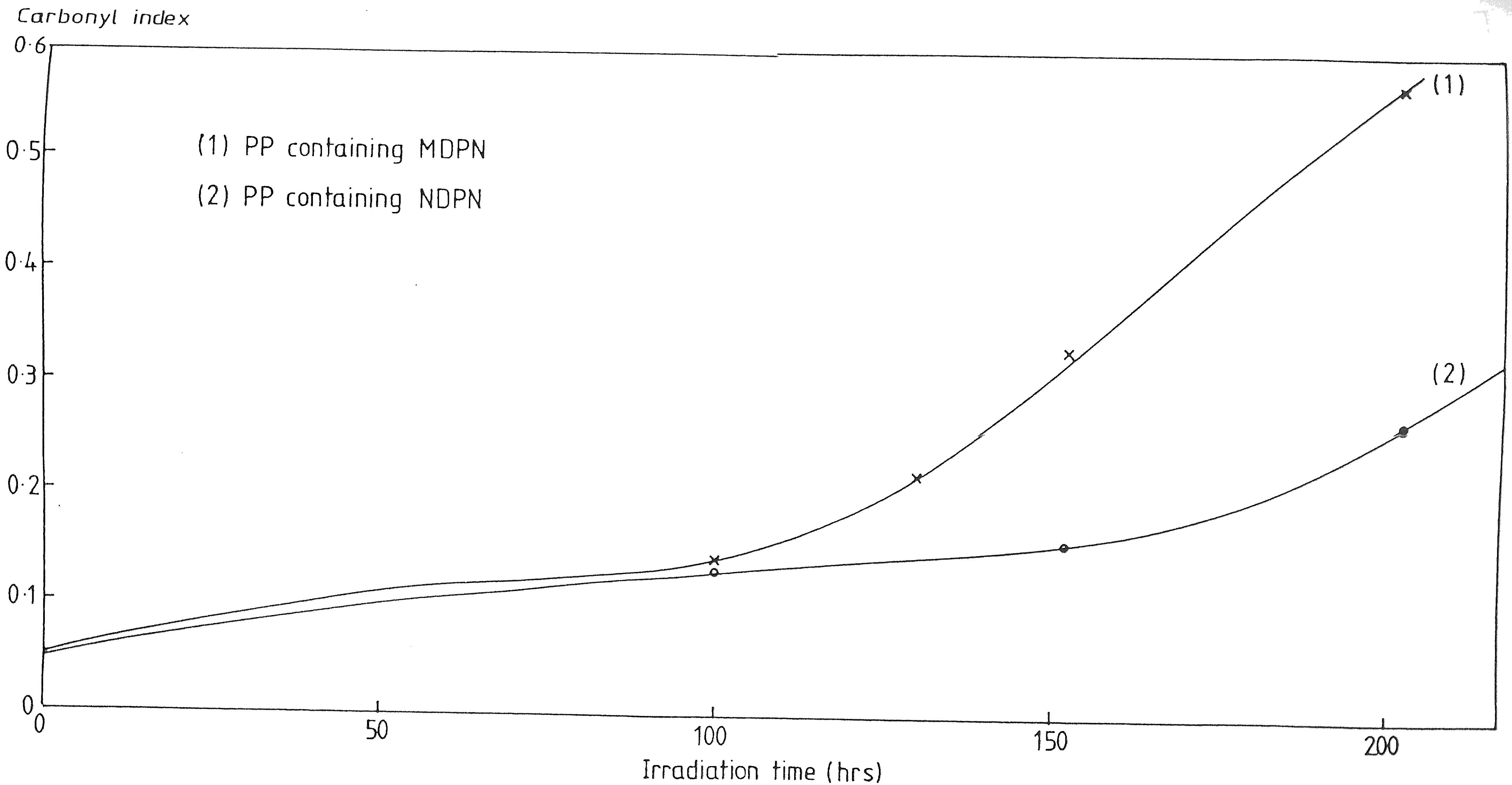


Fig 4:19 The change in rate of photo-oxidation of PP due to the inductive effect of different substituent in nitrons at concentration of 1×10^{-3} mole/100 gm. (Processing time 15 minutes at 180° C)

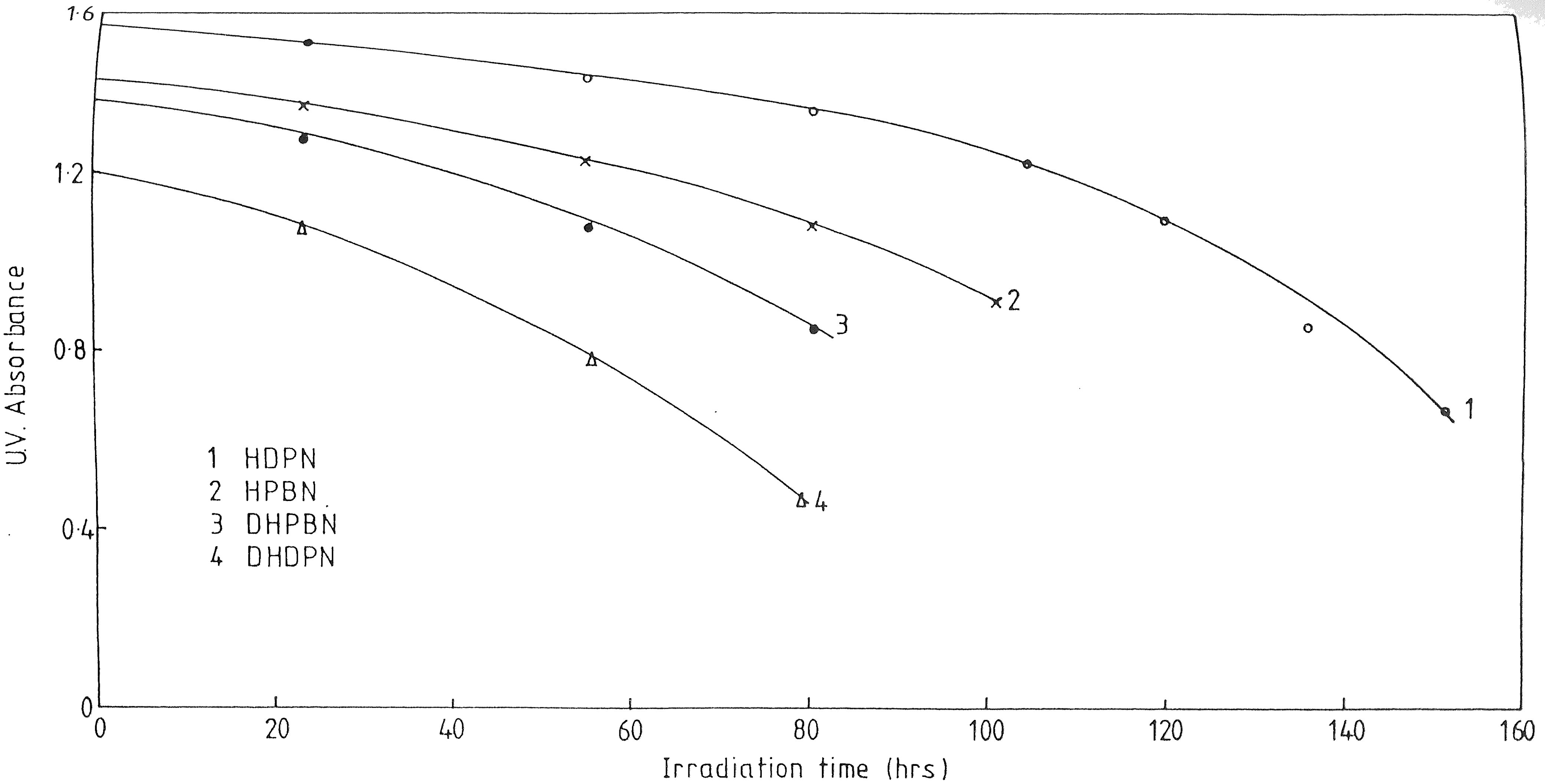


Fig 4:20 Decay of unreacted nitrones in PP during U.V. irradiation, concentration of additives 1×10^{-3} mole/100 gm processing time 10 mins

in polypropylene films during U.V. irradiation. All the nitrones showed gradual initial decay followed by a much more rapid decay on further irradiation.

4.3.2 Discussion

The photo-stabilisation activity of nitrones seems to be dependant on their ability to terminate short lived radicals produced during thermal processing of pp as well as on the presence of unreacted nitrones prior to U.V. irradiation.

It has been shown previously (Section 4.2) that nitrones have the ability to terminate R. and RO. radicals (reaction 1) to produce bound nitroxyl radicals within polymer chains. In addition the phenolic group can terminate ROO., producing nitroxyl radicals (reaction 3) during thermal processing. Consequently, such effects could lead to inhibition of the formation of hydroperoxide the key factor in photo-initiation process. However, it is difficult to establish a correlation between the photo-stabilisation effectiveness and the processing time due to the involvement of unreacted nitrones in the photo-stabilisation process. During photo-oxidation the ratio $[R.]/[ROO.]$ is higher than in thermal oxidation due to the slow rate of oxygen diffusion. Hence nitroxyl radicals already formed during thermal processing and which are effective CB-A antioxidants may compete with oxygen for alkyl radicals, resulting in alkylhydroxylamine formation (Fig.4.21). Moreover the presence of unreacted nitrones plays an important role in photostabilisation process by terminating alkyl radicals to produce more nitroxyl radicals (Figs. 4.20 and 4.21).

The variation in nitroxyl radical concentration in pp films containing HDPN during U.V. irradiation before and after extraction is shown in Fig. 4.21, as measured by E.S.R. It is apparent that the nitroxyl radicals concentration of unextracted samples initially decreases slowly followed by high rate of decay and finally attains a stationary low concentration. But the concentration of nitroxyl radicals in extracted samples is characterised by high rate of decay in the very beginning of irradiation and followed by a stationary state at low concentration. Presumably, during U.V. irradiation of unextracted films, alkyl radicals are the predominant species. These tend to react with either nitroxyl radicals formed during thermal processing prior to U.V. irradiation to form alkylated hydroxylamine or with unreacted nitrone (Fig. 4.20) to replenish nitroxyl radicals. This accounts for the initial slow rate of decay of nitroxyl radicals. The subsequent increase in rate of decay as the reaction proceeds, is due to the consumption of nitrones which is the precursor of nitroxyl radicals. In extracted films, where there is no nitrone to compete with nitroxyl radicals for alkyl radicals, therefore, the

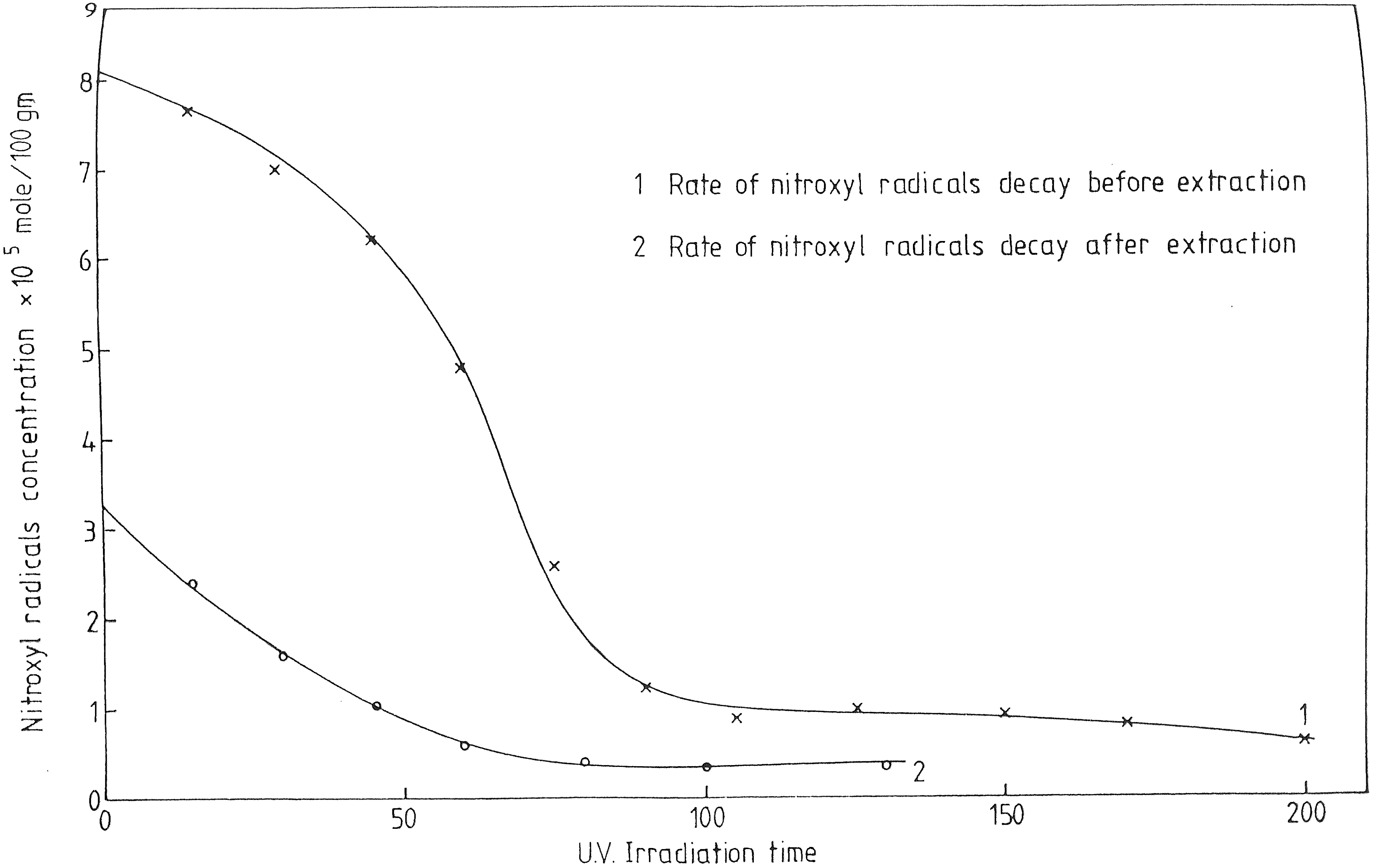
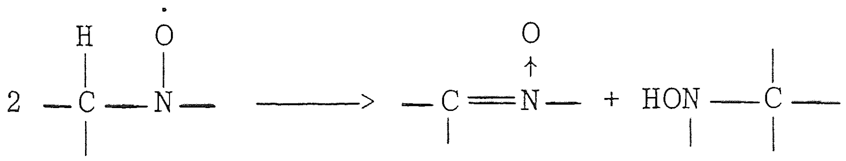


Fig 4:21 Kinitic of nitroxyl radical decay during U.V. Irradiation of PP film containing HDPN at concentration of 1×10^{-3} mole/100 gm

decay of nitroxyl radicals is faster. Furthermore, the removal of nitrone on extraction eliminates the reaction of nitrone with alkyl radical which serves to replenish nitroxyl radicals.

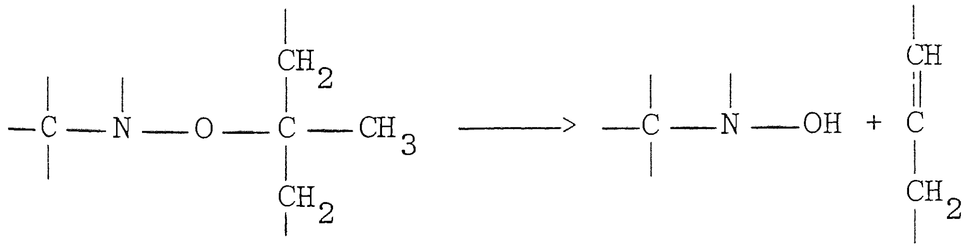
Hydroxylamines have been shown to be formed during thermal processing of pp in the presence of nitrone. Hydroxylamine has also been detected in the extract of U.V. irradiated pp containing nitrones (DPN and HDPN). Two possible ways may be suggested for the formation of hydroxylamine

(a) nitroxyl radicals derived from nitrones having α-hydrogens could be disproportionate to give the corresponding nitrones and hydroxylamine



$$2\ -\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{\dot{O}}{\overset{|}{N}}- \longrightarrow -\underset{|}{C}=\overset{O}{\overset{\uparrow}{N}}- + HON-\underset{|}{\overset{|}{C}}-$$

(b) Decomposition of alkylated hydroxylamine



$$-\underset{|}{\overset{|}{C}}-\overset{|}{N}-O-\overset{|}{\underset{\underset{|}{CH_2}}{\overset{CH_2}{\overset{|}{C}}}}-CH_3 \longrightarrow -\underset{|}{\overset{|}{C}}-\overset{|}{N}-OH + \overset{\overset{|}{CH}}{\underset{\underset{|}{CH_2}}{\overset{\|}{C}}}$$

Although unreacted nitrones within pp films represent a potentially versatile reagent for double bonds by the 1,3-cyclo-addition reaction(157) (Fig. 4.15), the unsaturation was detected by IR (bond at 1645 cm^{-1}) during U.V. irradiation, both before and after extraction of the processed samples, but the unsaturation is more pronounced in the extracted samples. This suggests that the second mechanism is the most likely for the formation of hydroxylamine and unsaturation leading to the regeneration of nitroxyl radicals $(-\overset{|}{N}-OH \xrightarrow{ROO.} -\overset{|}{N}-\dot{O} + ROOH)$ and hence to the stationary nitroxyl radical concentration (Fig. 4.21).

The presence of quinonoid structures in the extract of polypropylene films containing phenolic nitrone after thermal processing could reduce the photo-stabilisation activity of such nitrones due to the sensitisation effect of quinonoid structures under U.V. irradiation(151).

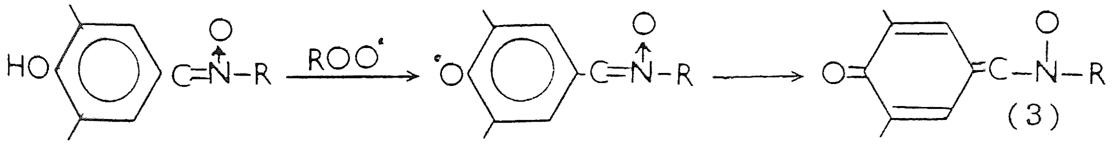
4.4 Effect of Nitrones on Thermal Oxidation of Polypropylene

4.4.1 Results and Discussion

It has been shown in the preceding section (4.2) that melt degradation is completely inhibited during the processing of polypropylene with most of the nitrones and nitroxyl radicals are formed as main products from the nitrones. This section is concerned with the effect of the melt stabilisation process on the subsequent thermal oxidative stability of polypropylene.

Fig. 4.22 illustrates the effect of processing time on the subsequent thermal oxidative stability of polypropylene in the form of compression moulded film containing DHDPN at 140°C. Fig. 4.23 shows the rate of decay of DHDPN during thermal oxidation as measured by U.V. technique (λ_{max} 325 nm). The induction period of carbonyl formation during thermal oxidation was found to be dependent on the processing time, i.e. longer processing reduced the induction period. This could be due to depletion of DHDPN during processing time.

During the thermal oxidation process, the unreacted DHDPN may have been consumed in stabilising polypropylene (Fig. 4.23) both by terminating radicals$^{(82,153)}$ (R. and ROO.) and by decomposing hydroperoxide$^{(158)}$. In oven ageing, because of the presence of a high concentration of oxygen which competes with unreacted DHDPN for alkyl radicals, the nitrone function is relatively ineffective under these conditions. However, the phenolic group of DHDPN acts as a powerful CB-D antioxidant removing alkylperoxyl radicals from the system, resulting in the formation of phenoxyl radicals. However, ESR examination of thermally oxidised samples containing DHDPN does not show a phenoxy radical signal; nitroxyl radicals are detected instead. This observation suggests that the phenoxy radicals which are formed mesomerise to nitroxyl radicals according to reaction 3.



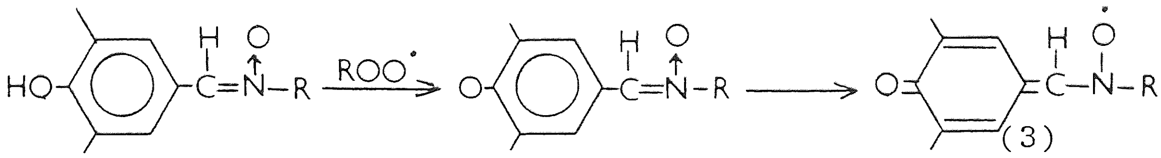
(3)

The detection of quinonoid structure by IR (absorbtion band at 1660 cm^{-1}) in the extract of pp films containing DHDPN during thermal oxidation process shows an additional evidence for the above reaction (reaction 3). On extraction of pp samples containing phenolic nitrones prior to thermal oxidation, the thermal stabilisation activity was found to reduce significantly. This is an indication of the important role played by unreacted phenolic nitrones in the thermal oxidation process (Table 4.4). Both CB-D and hydroperoxide decomposing mechanisms could be involved in thermal oxidative stabilisation activity of the unreacted phenolic nitrones.

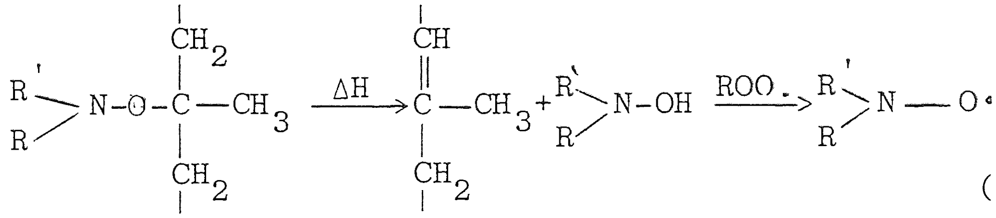
Table (4.4) shows that nitrones possessing a phenolic group are more effective antioxidants than DPN, TPN, and MDPN during the thermal oxidation of pp. This suggests that the phenolic group of the unreacted nitrones play a significant part in the thermal oxidative stabilisation process (reaction 3).

Fig. 4.24 follows the kinetics of nitroxyl radical decay by E.S.R. in the polymer films, containing DHDPN during thermal oxidation process at 140°C. It is apparent that the nitroxyl radical concentration initially increased during the first 3 hours of thermal oxidation, then started to decrease gradually at a slow rate. The initial increase in nitroxyl radicals concentration could be accounted for by two possible processes:

(a) reaction of unreacted DHDPN with ROO. according to reaction 3 (Fig. 4.23).


(3)

(b) thermal decomposition of alkylated hydroxylamine(43) formed during thermal processing (section 4.2) prior to thermal oxidation process.



$$\begin{matrix} R' \\ R \end{matrix}\!\!>\!N{-}O{-}\overset{\overset{|}{CH_2}}{\underset{\underset{|}{CH_2}}{C}}{-}CH_3 \xrightarrow{\Delta H} \overset{\overset{|}{CH}}{\overset{\|}{\underset{\underset{|}{CH_2}}{C}}}{-}CH_3 + \begin{matrix} R' \\ R \end{matrix}\!\!>\!N{-}OH \xrightarrow{ROO.} \begin{matrix} R' \\ R \end{matrix}\!\!>\!N{-}O\cdot$$

(11)

It is difficult to quantify the occurrence of reaction (11), because hydroxylamine could not be identified in the extract of pp samples containing DHDPN during thermal oxidation. Nor was the absorbance due to unsaturation at 1645 cm^{-1} observed during thermal oxidation. This could be due to the fact that under thermal oxidative conditions hydroxylamine is easily oxidised(155,156) by ROO· to nitroxyl radicals and due to the high reactivity of nitrones towards double bonds by 1.3 cycloaddition. This leads to the disappearance of the double bonds (reaction 11). Thus both hydroxylamine and unsaturation are transient. It has been reported that hydroxylamines are readily eliminated from alkyl hydroxylamines at elevated temperatures(149). Therefore the initial increase in nitroxyl radicals concentration during thermal oxidation may be

Table 4.4 Effect of processing time and processing conditions on thermal embrittlement of pp containing nitrones at concentration 1×10^{-3} mole/100 gm before and after extraction (oven temperature 140°C).

Additives	Thermal Embrittlement Time (hours)					
	Unextracted Films					Extracted
	Closed Chamber				Open Chamber	Closed Chamber
	7.5mins	10mins	15mins	20mins	10mins	10mins
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
DHDPN	18.5	14.0	11.0	9.0	7.0	4.5
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
DHPBN	9.0	7.5	4.5	2.5	1.5	2.0
Control	-	0.5	-	-	-	-

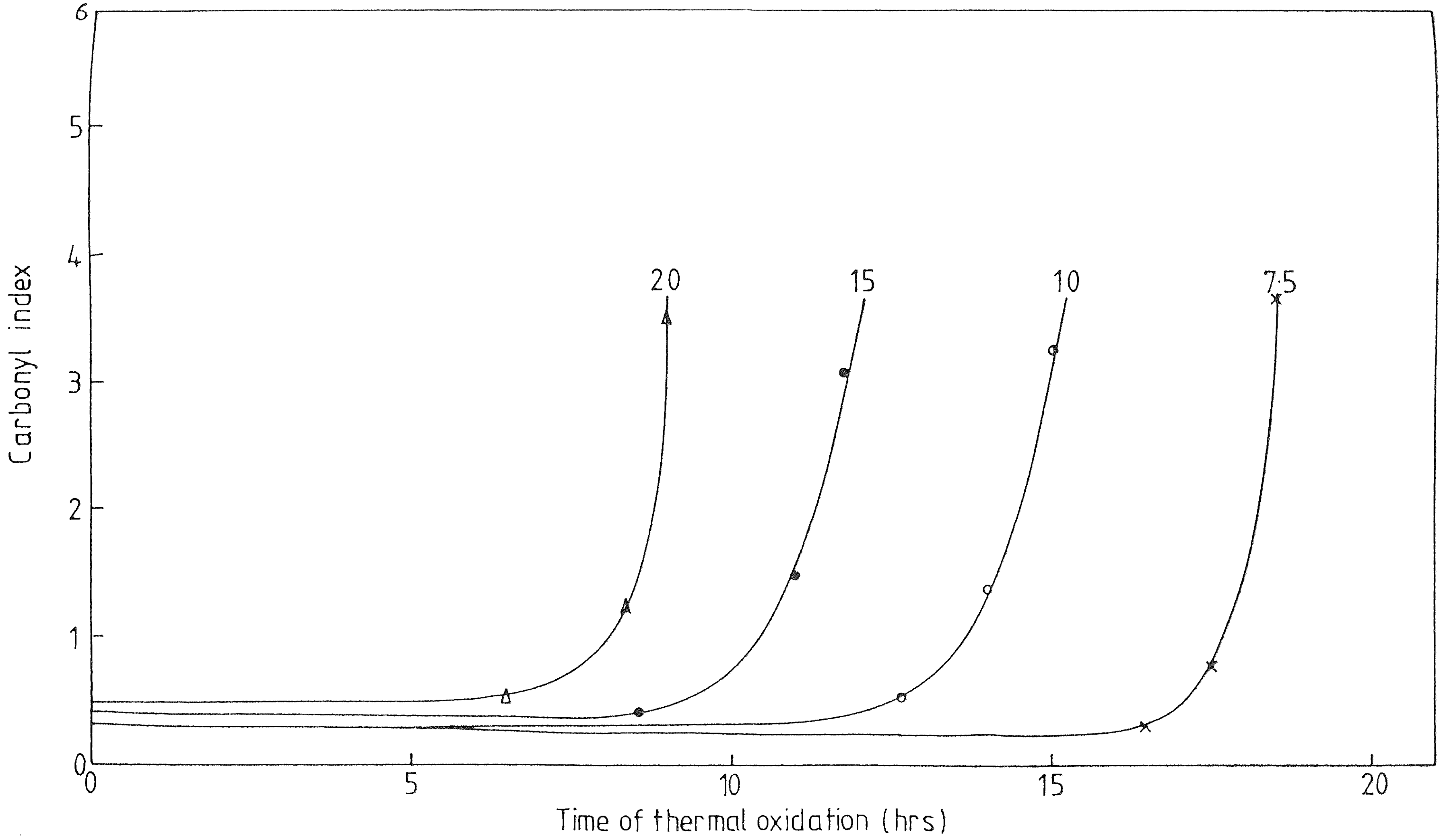


Fig 4:22 Effect of DHDPN on thermal oxidation of PP at 140 °C processed at different time, at 180°C
Concentration 1×10^{-3} mole / 100 gm
Number on curve represents processing time in minutes

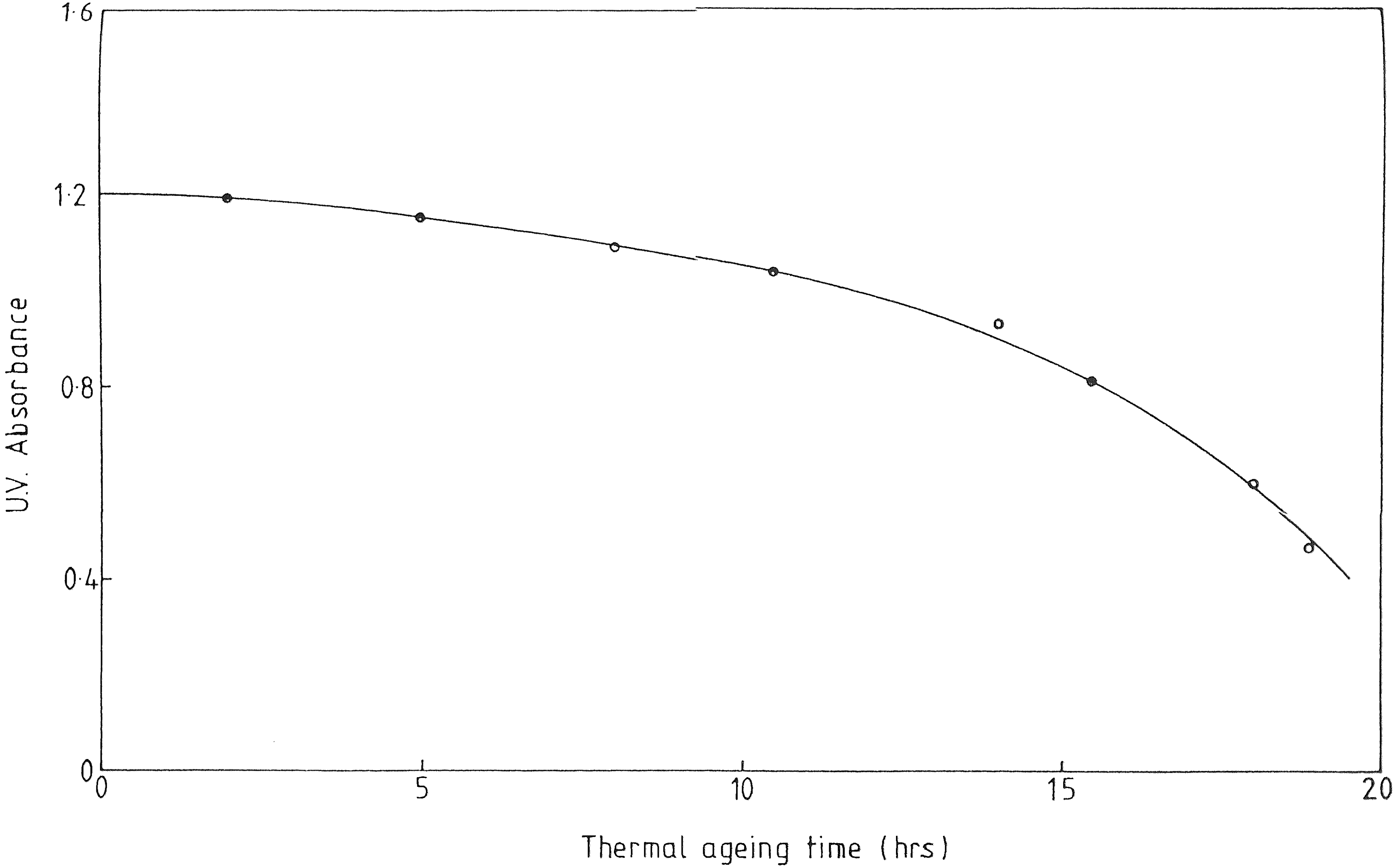


Fig 4:23 Decay of DHDPN during thermal oxidation of PP at 140°C, concentration 1×10^{-3} mole/100 gm, processing time 10 mins at 180°C.

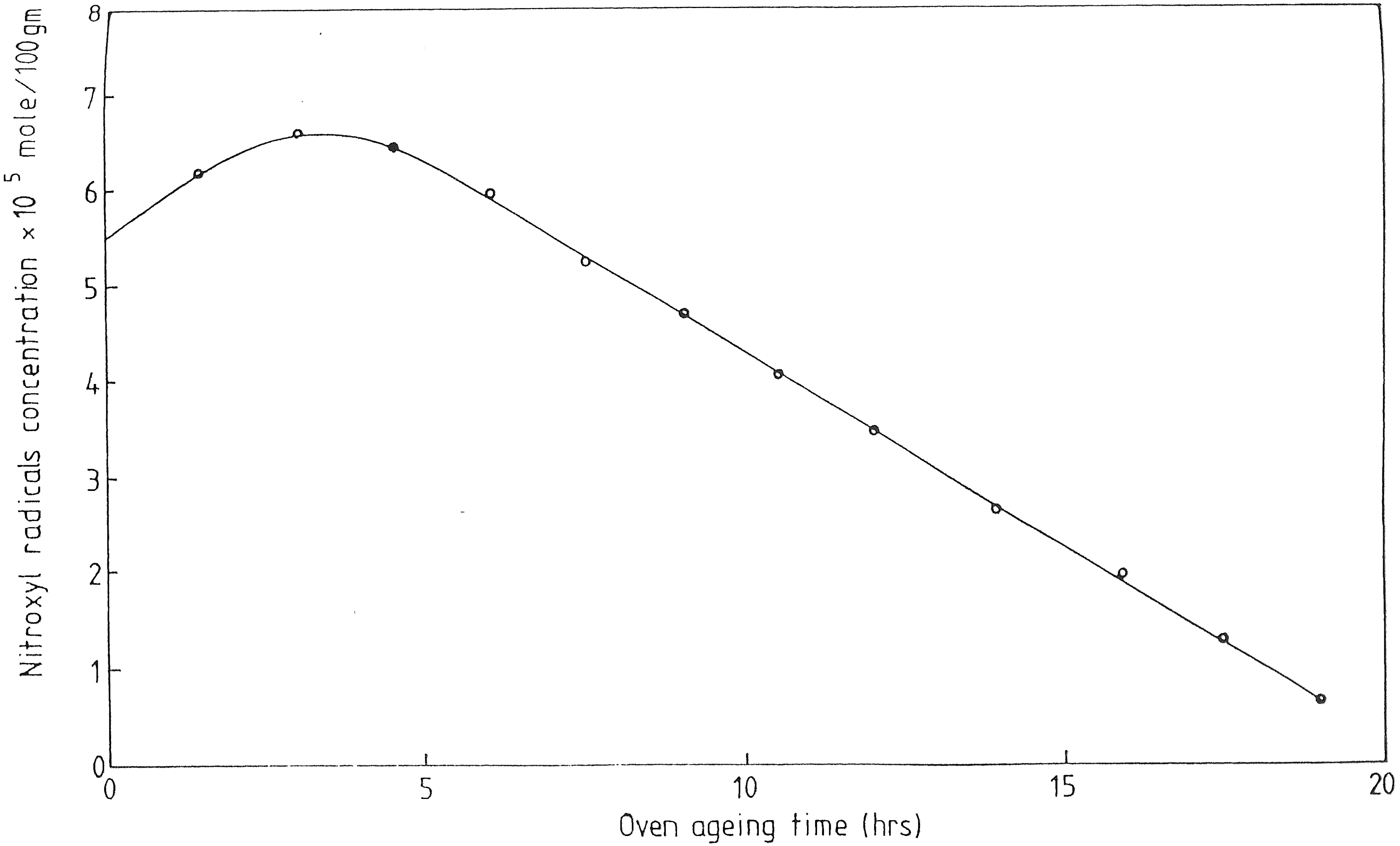
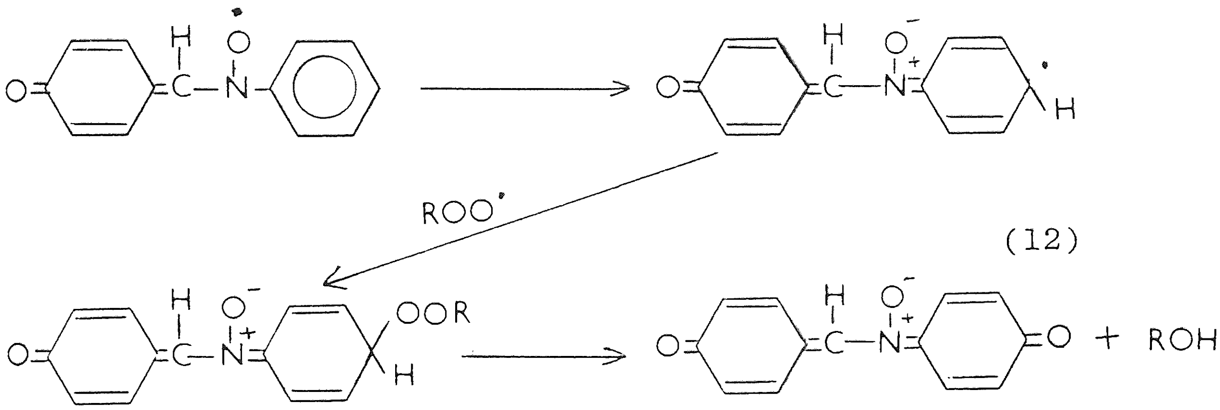


Fig 4:24 Kinitic of nitroxyl radical decay during thermal oxidation of PP film containing DHDPN at concentration of 1×10^{-3} mole/100 gm. (Oven temperature 140°C)

attributed to the occurrence of reactions 3 together with reaction 11. The slow rate of nitroxyl radicals decay may be due to attack of ROO. at the aromatic ring preferably at para position, because of the delocalization of unpaired electron density in aromatic nitroxides (see reaction 12)



(12)

4.5 Mechanism of Action of Phenolic Nitrones

4.5.1 Results and Discussion

The kinetics of the reaction of phenolic nitrones with alkylperoxy radicals under thermal condition was studied using the model compound azoisobutyronitrile (AIBN) as the source of alkylperoxy radicals. The formation of nitroxyl radical during the reaction was followed by ESR spectroscopy.

To carry out the reaction, a solution of DHDPN and AIBN in p-xylene (1×10^{-3} mole DHDPN and 1×10^{-3} mole AIBN per 100 gm of p-xylene) was placed in a round bottom flask and the flask was immersed in an oil both maintained at a temperature of 110°C. The reaction was carried out in the presence of oxygen.

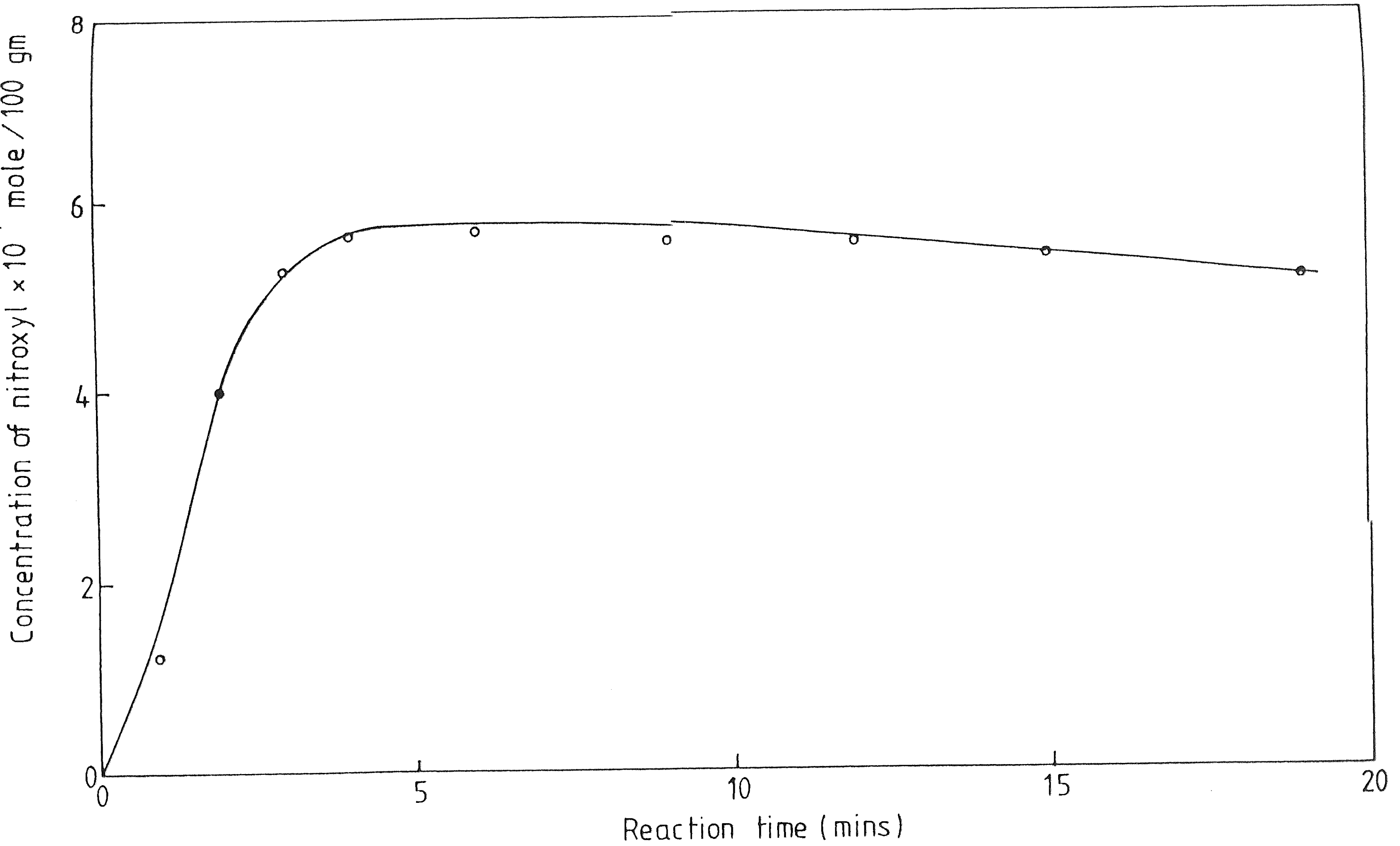
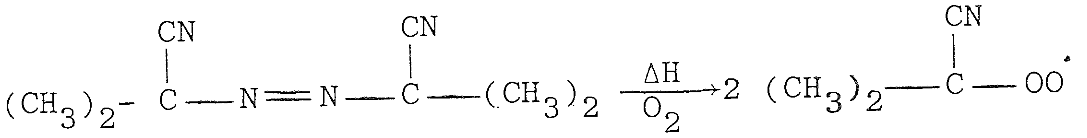


Fig 4:25 Rate of nitroxyl formation derived from DHDPN at 110°C in the presence of alkyl peroxyl radical in p-xylene.

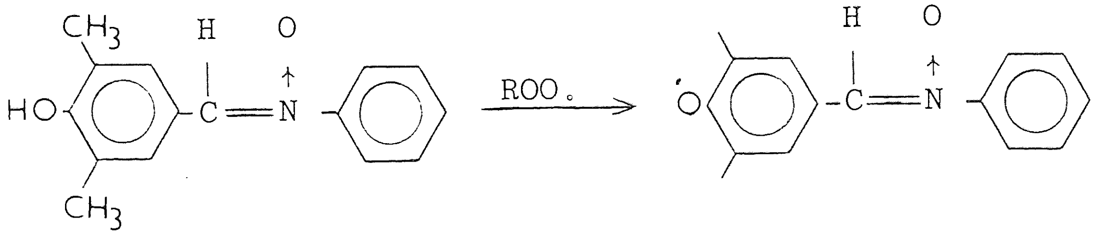
Fig. 4.25 shows the build up of nitroxyl radicals with reaction time. There is an initial high rate of nitroxyl radical formation which reaches a maximum after 5 mins. then followed by a steady state as the reaction proceeded.

The formation of nitroxyl radicals can be explained on the basis of the fact that during the reaction alkylperoxy radicals are formed from AIBN as shown in reaction 1. In the presence of DHDPN alkylperoxy

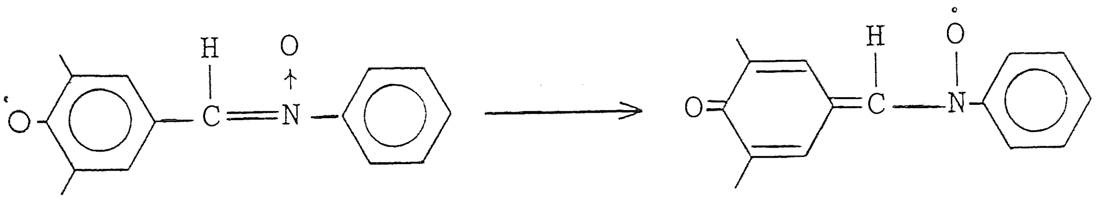


$$(CH_3)_2-\overset{\overset{CN}{|}}{C}-N=N-\overset{\overset{CN}{|}}{C}-(CH_3)_2 \xrightarrow[O_2]{\Delta H} 2\ (CH_3)_2-\overset{\overset{CN}{|}}{C}-OO^{\bullet} \qquad (1)$$

radicals are terminated by the hydrogen of the phenolic group of DHDPN (CB-D mechanism) as shown in reaction 2. The nitroxyl radicals observed may have been formed from the mesomerisation of the



(2)



(3)

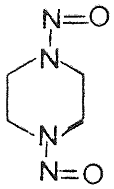
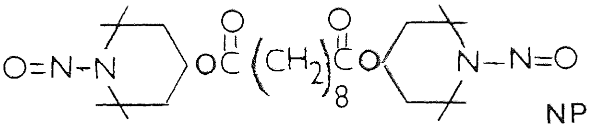
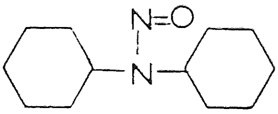
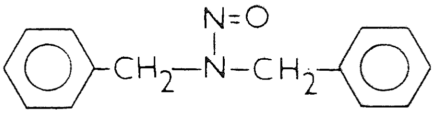
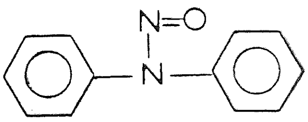
phenoxy radicals. This could account for the fact that no phenoxy radicals were detected by ESR. Moreover, it is well known(82) that alkylperoxy radicals do not react with nitrone functional group to form nitroxyl radical. The initial high rate of nitroxyl formation during the reaction suggests that the formation of nitroxyl radicals from phenoxyl radical by mesomerism is very fast. It has been reported(168) that phenoxy radicals with two methyl groups is unstable. The high concentration of nitroxyl radicals is maintained at a steady state when no DHDPN. Furthermore, the presence of an absorption band at 1655 cm^{-1} (IR) in the reaction mixture attributed to the quinonoid structure confirms the above mechanism.

CHAPTER 5

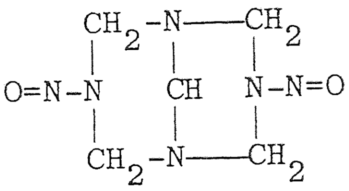
EFFECT OF N-NITROSAMINES ON MELT STABILISATION, PHOTO-OXIDATION AND THERMAL OXIDATION OF POLYPROPYLENE

In this chapter the effect of N-nitrosamines has been investigated as melt stabilisers, antioxidants and U.V. stabilisers for polypropylene and the mechanisms of action are discussed. So far no studies have been reported in the literature regarding the stabilising activity of N-nitrosamines on polymers.

The N-nitrosamines are listed below with the code name used in this chapter.

Dinitrosopiprazine		NPZ
Bis(N-nitroso-2,2,4,4- tetramethyl-4-piperidinyl) sebecate		NPS
N-nitrosodicyclohexylamine		NDCA
N-nitrosodibenzylamine		NDBA
N-nitrosodiphenylamine		NDP

Dinitrosopenta-
methyl-tetramine



DPTA

5.1 Effect of N-nitroso amines on Melt Stability of Polypropylene

5.1.1 Results

Fig. 5.1 compares the effect of Tinuvin 770 and its N-nitroso derivative bis(N-nitroso-2,2,6,6-tetramethyl-4-piperidinyl) sebecate (NPS) on the melt stability of polypropylene processed at 180°C in closed mixer at 1×10^{-3} mol/100 gm. Tinuvin 770 has only marginal stabilising effect on the polymer under those conditions compared with NPS which is powerful melt stabiliser. Processing for up to 10 mins. reduced the MFI to a level lower than the unprocessed polymer and on increasing processing time up to 20 mins. the MFI increased slightly. Fig. 5.2 which relates the molecular weight distribution of polypropylene containing NPS processed for 10 mins. under limited supply of air to the unprocessed polymer shows that there is a change in M'_w. $\frac{dw}{d\log M}$ decreased and M'_w increased when polypropylene was processed in the presence of NPS compared with the unprocessed polymer. Such a result corresponds to the decrease in the melt flow index (Fig.5.1). Also the slight broadening of molecular weight distribution of polypropylene containing NPS may be explained as being due to a cross-linking reaction.

Fig. 5.3 depicts the effect of NPS and Tinuvin 770 concentrations on the melt flow behaviour of polypropylene processed at 180°C for 10 mins. in closed mixer and indicates significant decrease in MFI with increasing NPS concentration, to a level below that of the unprocessed polymer. On the other hand increasing the concentration of TINuvin 770 leads to significant increase in MFI compared with the unprocessed polypropylene. This implies that Tinuvin 770 is a pro -oxidant, while the MFI decreased with increasing NPS concentration.

Fig. 5.4 illustrates the variation of melt flow index of polypropylene containing N-nitrosodicyclohexylamine (NDCA), N-nitrosodiphenylamine (NDP) and dinitroso-piprazin (NPZ) processed for different times at a molar concentration of 1 x 10^{-3} mole/100 gm in closed mixer (processing temperature 180°C). Curve 1 shows that NPZ stabilises polypropylene for up to 10 mins. of processing, but prolonged processing (up to 20 mins) increased MFI slightly. The MFI of polypropylene processed in the presence of NDCA decreased up to 10 mins. (curve 3) and then started to increase gradually with further processing. NDP is an effective melt stabiliser up to 20 mins. of processing (curve 3). Even more it shows melt stabilisation activity during processing in excess of air although under these conditions ROO. is the most predominant species, whilst all other n-nitrosamines are not effective melt stabilisers in excess of air.

N-nitrosodibenzylamine (NDBA) and dinitrosopentamethyl-tetramine (DPTA) are not effective melt stabilisers. Thermal stability measurements (section 2.2.7) indicated both NDBA and DPTA are decomposed at 90^{o}C i.e. the ineffectiveness of NDBA and DPTA are due to their decomposition before their reaction with the polymer.

Hydroperoxide formation is inhibited in the presence of NDP when polypropylene was processed in closed mixer up to 20 mins. of processing (Fig. 5.5, curve 5). But hydroperoxides are not completely inhibited when polypropylene was processed in the presence of NPS, NPZ and NDCA (Fig. 5.5, curves 2, 3 and 4). However, these show an induction period which corresponds to the effective initial melt stabilisation.

E.S.R. examination of polypropylene samples processed in the presence of N-nitrosamines (NPS, NDP, NPZ and NDCA) for 10 minutes of concentrations of 1×10^{-3} mole/100 gm, indicated the formation of radicals stable at room temperature and with g values corresponding to nitroxyl radicals (table 5.1). When the samples were extracted with CH_2Cl_2, the concentration of nitroxyl radicals reduced, i.e. some of nitroxyl radicals were bound to the polymer chains. The concentration of nitroxyl radicals measured before and after the extraction are stated in Table 5.1.

Table 5.1 Concentration of nitroxyl radicals formed in pp processed with N-nitrosamines for 10 mins in closed mixer at concentration 1 x 10^{-3} mole/ 100 gm (180°C).

N-nitrosamines	Concentration of nitroxyl before extraction (x 10^{-5} mole/100gm)	Concentration of nitroxyl after extraction (x 10^{-5} mole/100gm)	g values (±0.0005)
NPS	5.9	2.1	2.0072
NPZ	4.7	1.2	2.0058
NDCA	3.6	1.4	2.0065
NDP	4.2	1.9	2.0051

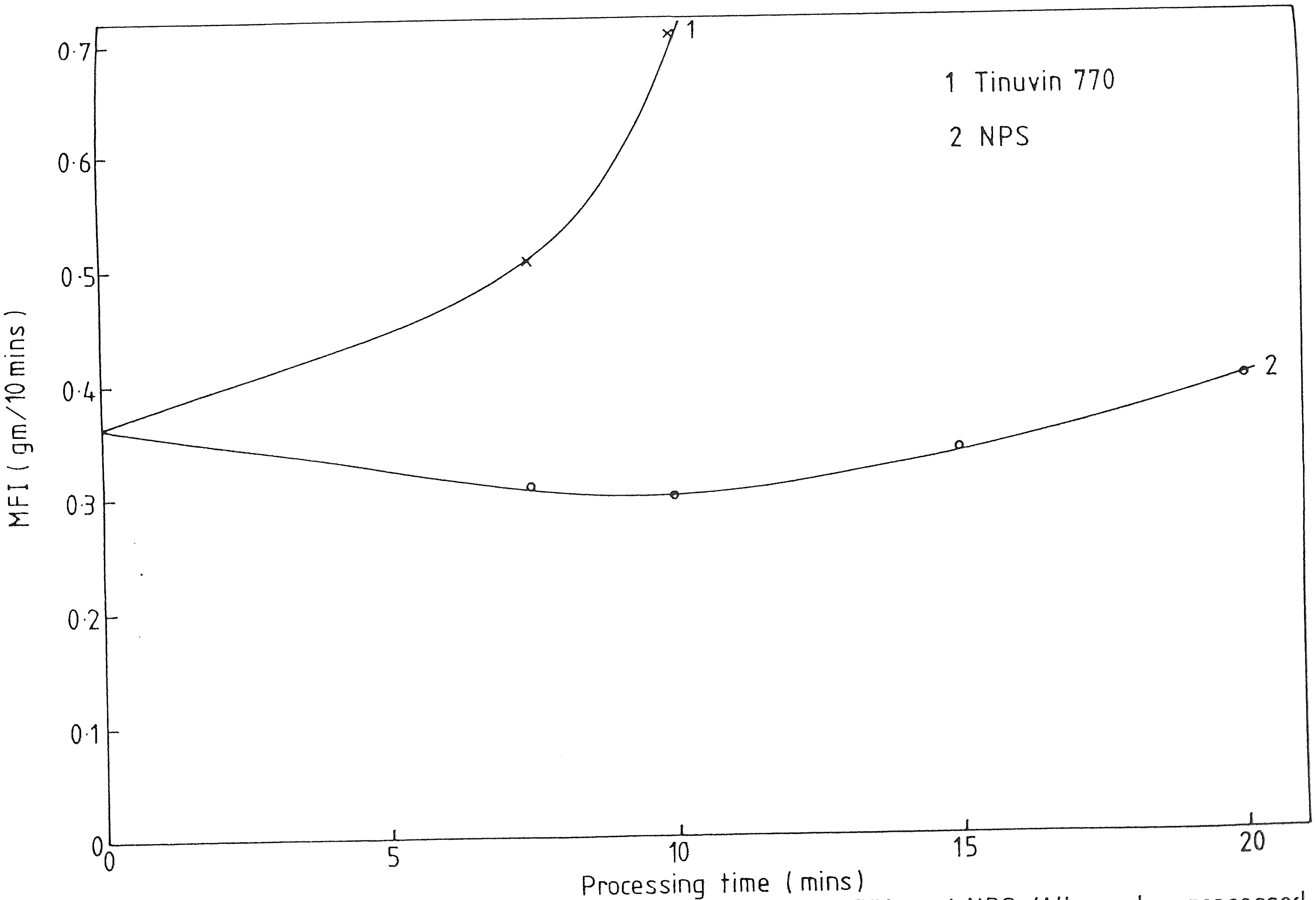


Fig 5:1 Effect of processing time on MFI of PP containing Tinuvin 770 and NPS. (All samples processed in closed mixer at concentration 1×10^{-3} mole/100 gm at °C)

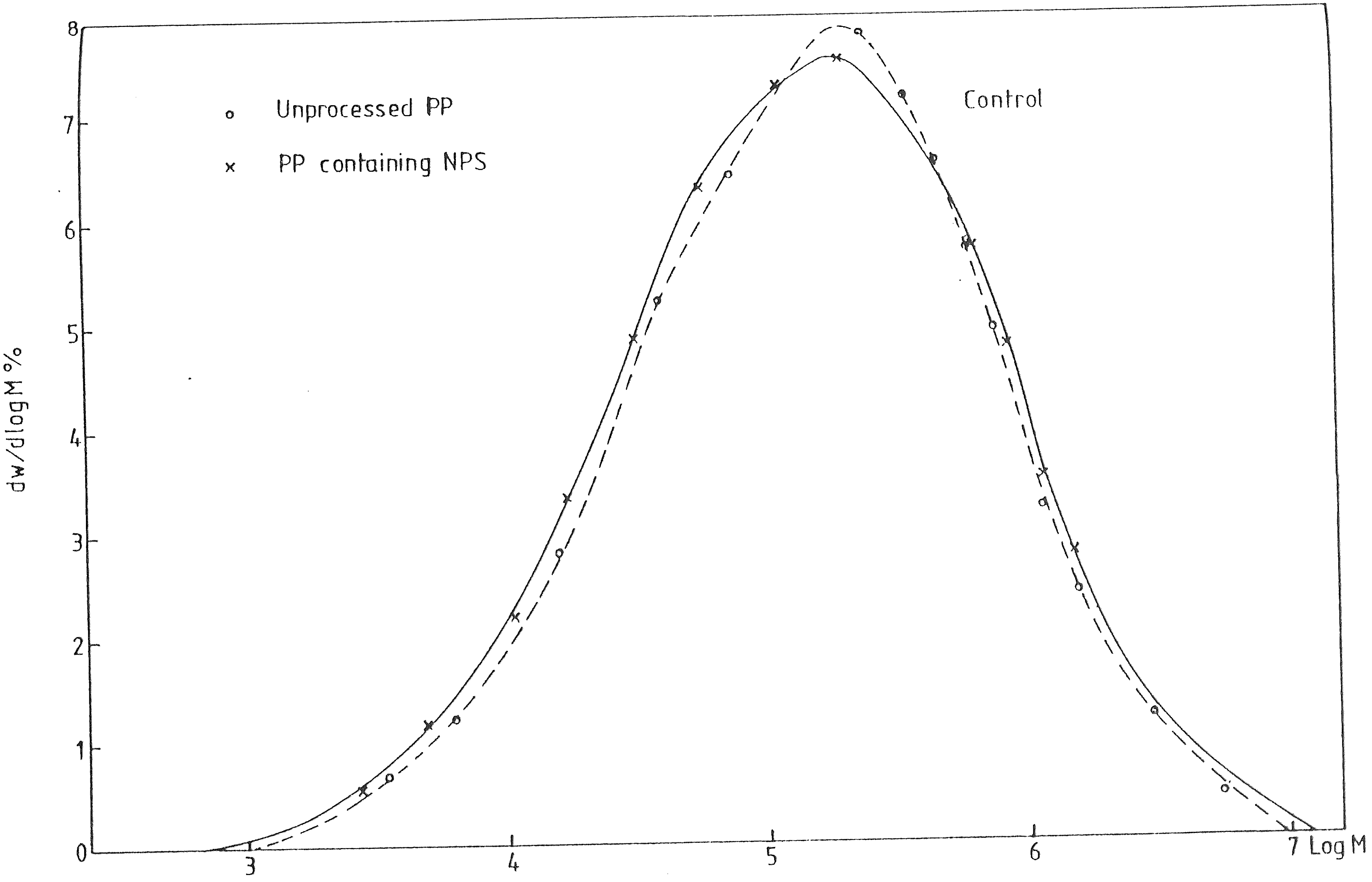


Fig 5:2 Effect of NPS on the molecular weight distribution of polypropylene during processing for 10 mins concentration 1×10^{-3} mole/100 gm

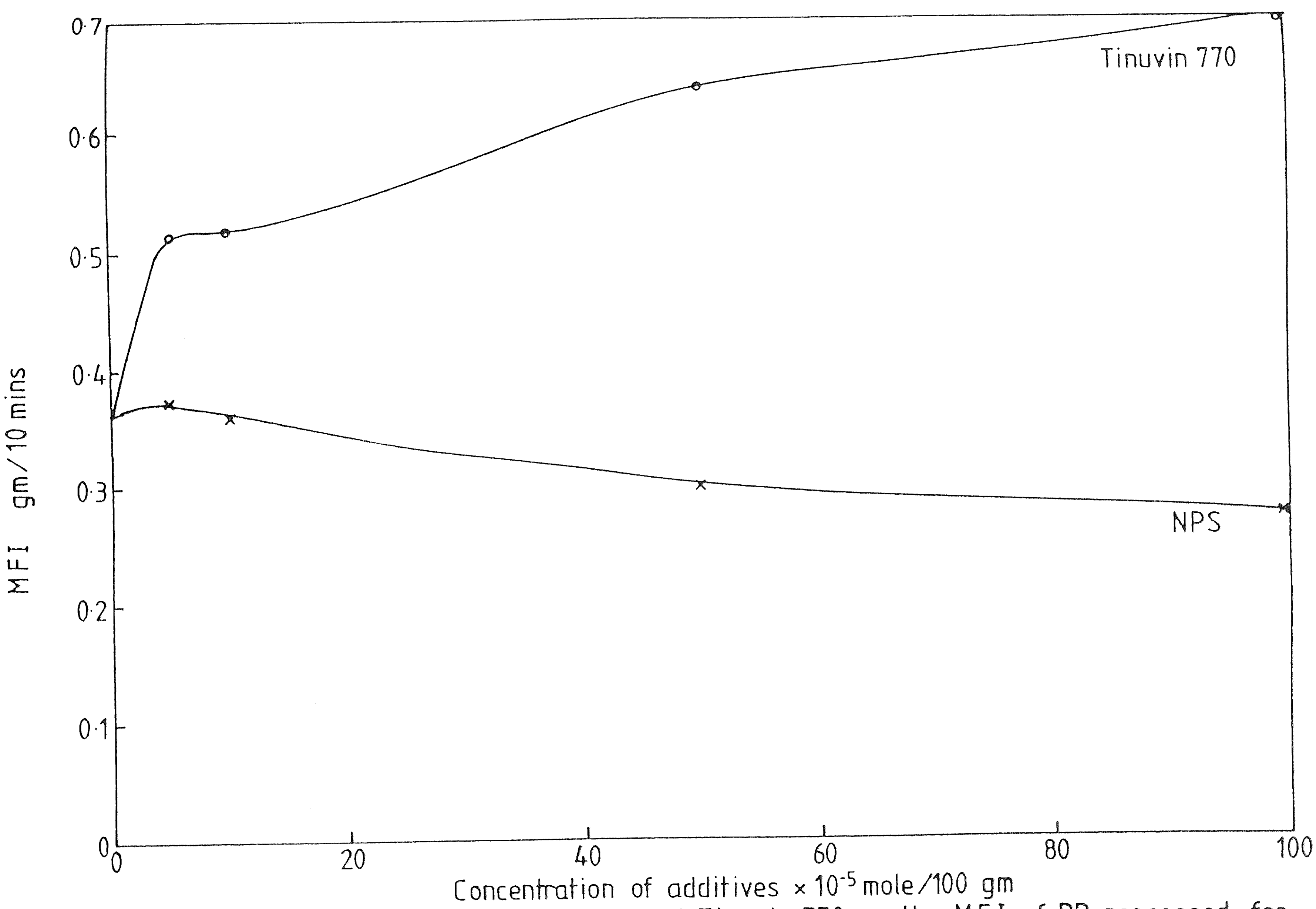


Fig 5:3 Effect of different concentration of NPS and Tinuvin 770 on the MFI of PP processed for 10 mins at 180° C (closed mixer)

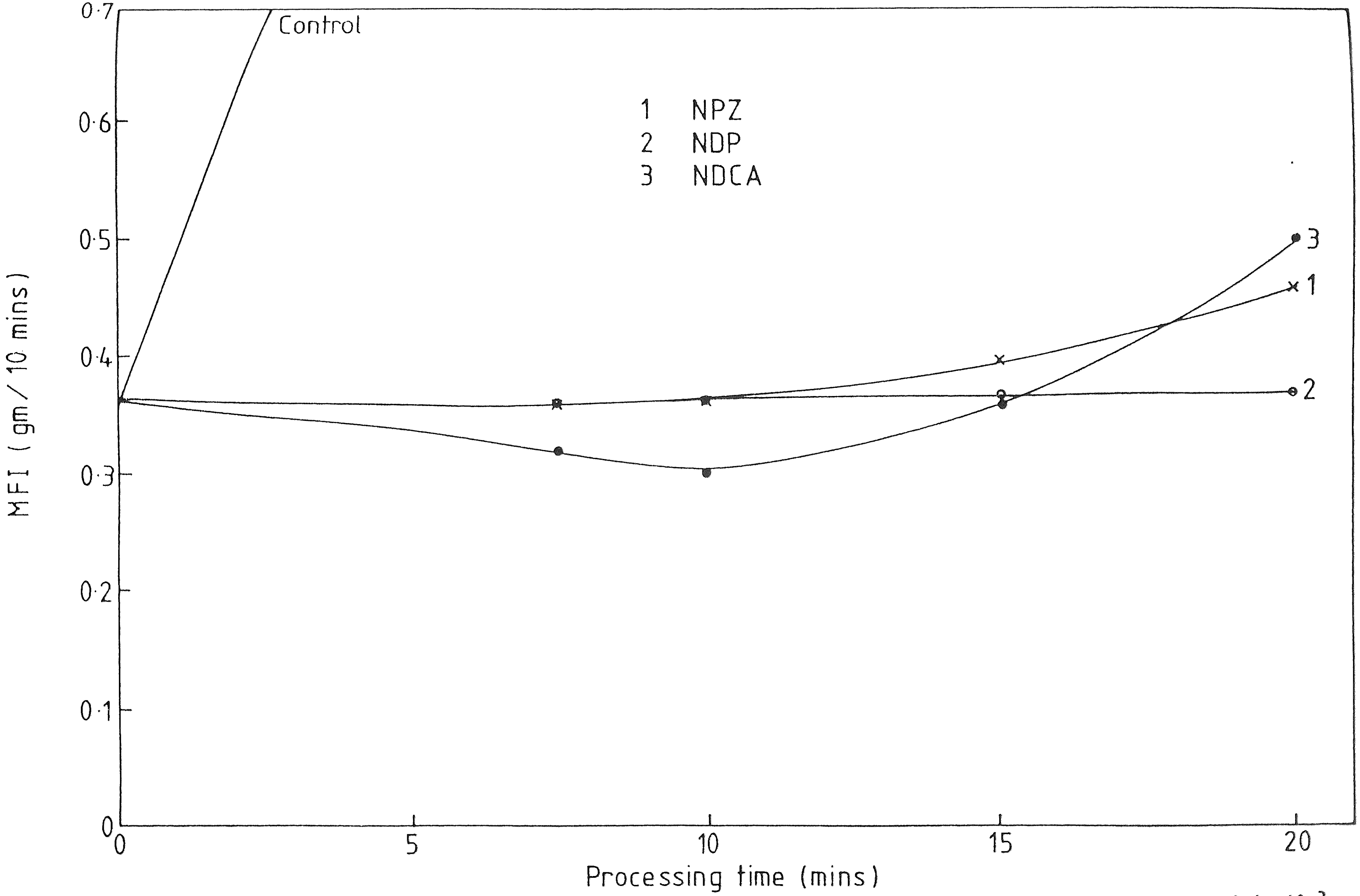


Fig 5:4 Effect of processing on MFI of PP containing NPZ, NDP and NDCA at concentration of 1×10^{-3} mole/100 gm processed in closed mixer

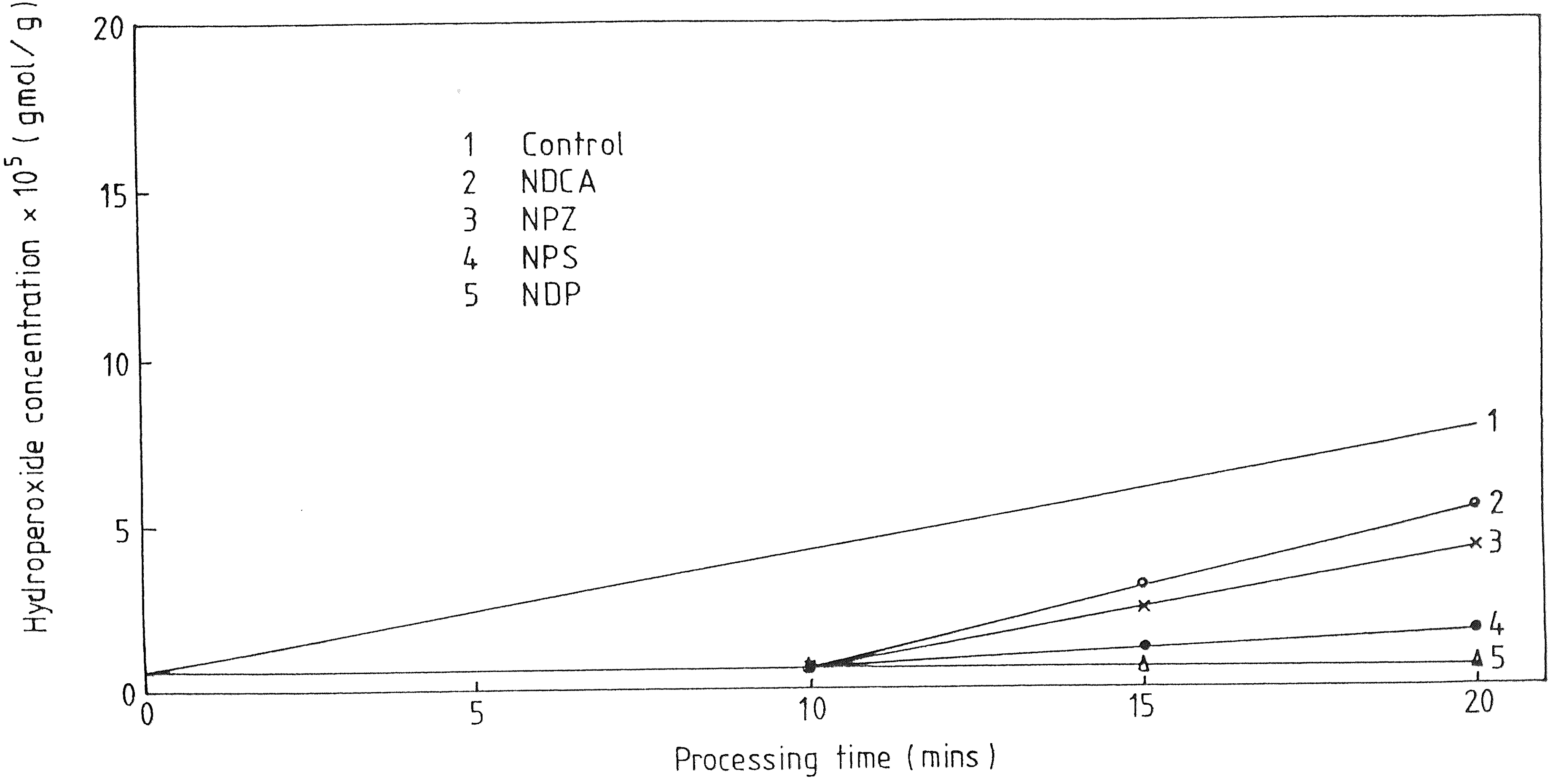


Fig 5:5 Effect of N - nitrosamines on the formation of hydroperoxide during processing of PP at different time in closed mixer (Concentration 1×10^{-3} mole / 100 gm)

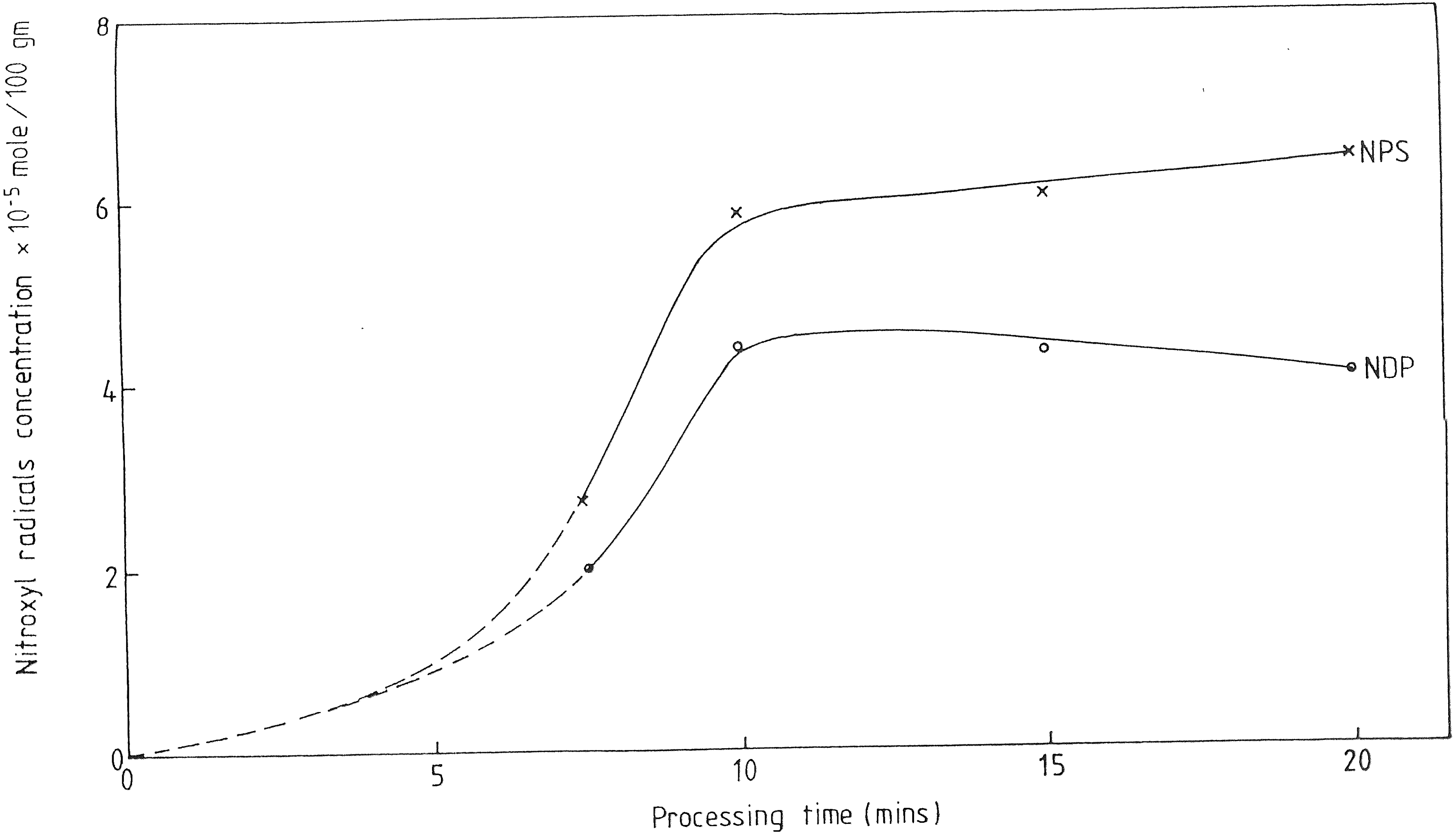


Fig 5:6 Kinitics of nitroxyl radical formation derived from NPS and NDP during their processing with PP at 180°C (Concentration of additive 1×10^{-3} mole / 100 gm)

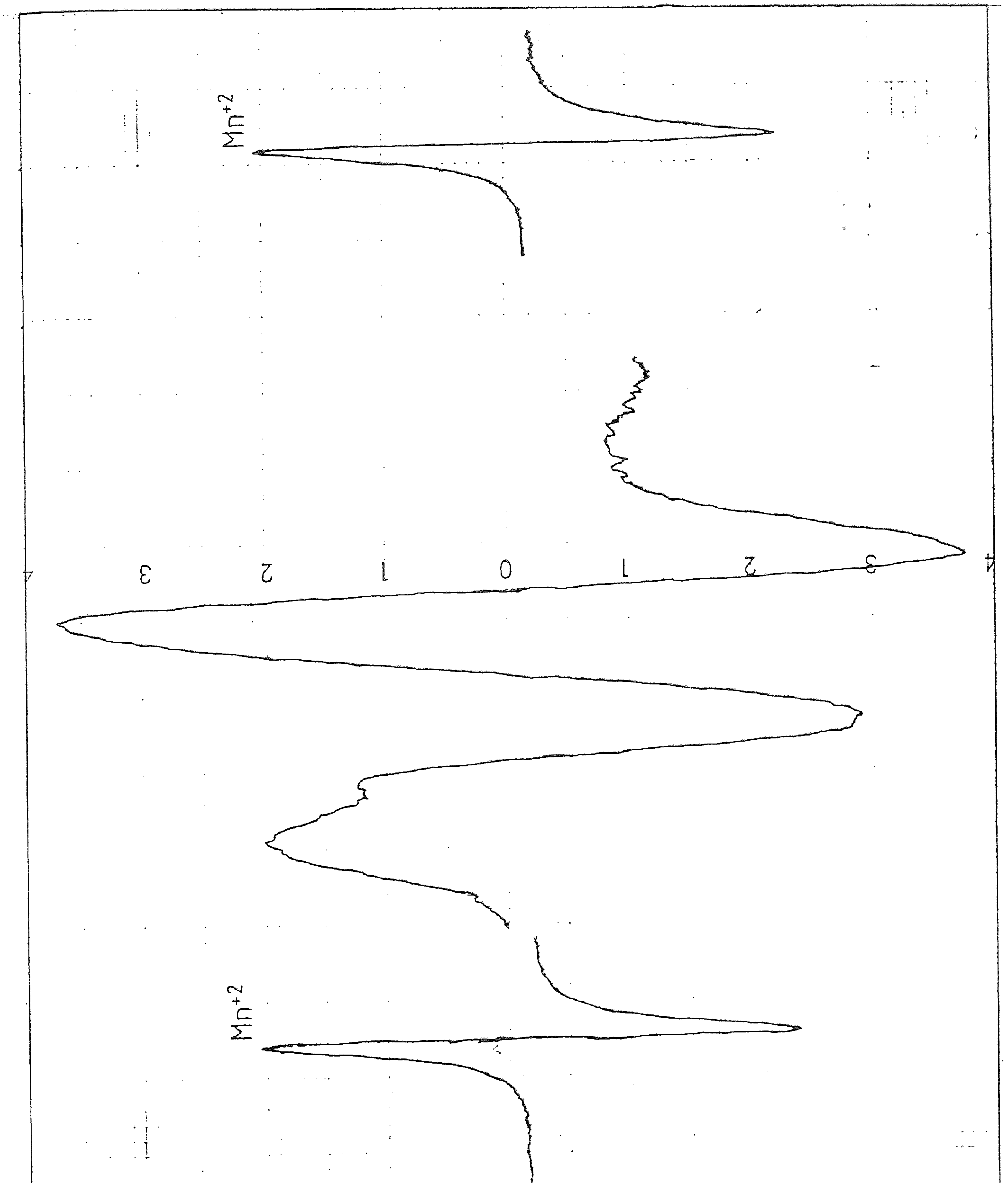


Fig 5:6 B ESR spectrum of nitroxyl radical in PP film containing NPS processed for 10 mins at 180°C

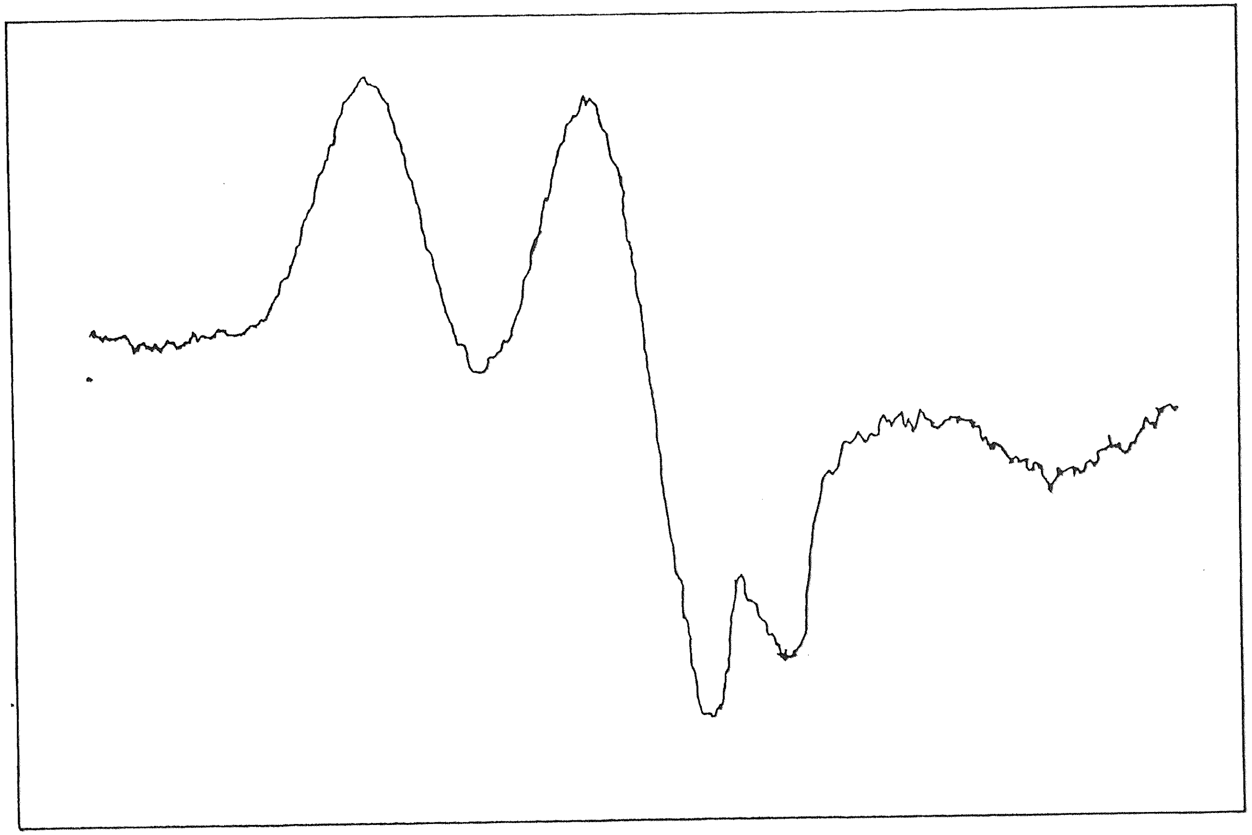
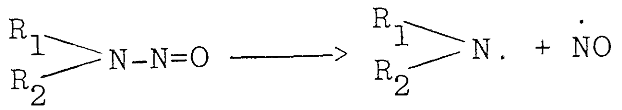


Fig 5:6C ESR spectrum of nitroxyl radical in PP film containing NDP processed for 10 mins at 180°C

Fig. 5.6 shows the kinetics of nitroxyl radical formation in polypropylene derived from NDP and NPS (concentration of additives 1 x 10^{-3} mole/100 gm. and processing temperature 180°C). It is apparent that the rate of nitroxyl radicals formation is high during the first 10 mins. of processing, and after this time the rate of nitroxyl radical formation is significantly reduced.

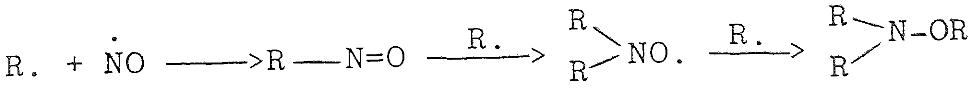
5.1.2 Discussion

The bond energies of $>$N-N=O bonds are of the order of 217-225 KJ mol^{-1} for heterocyclic and aliphatic N-nitrosamines, but only 46 KJ mol^{-1} for N-nitrosodiphenylamine(162). All are significantly lower than values for C-N, C-C or C-H bonds (which lie in the range of 300-450 KJ mol^{-1}). All N-nitrosamines decompose on heating under neutral conditions into nitric oxide ($\dot{N}O$) and an amino radical(101,110,107,163) which is insensitive to oxygen(3). (according to reaction 1). But most nonaromatic compounds require higher temperature than aromatic compounds(162). One of



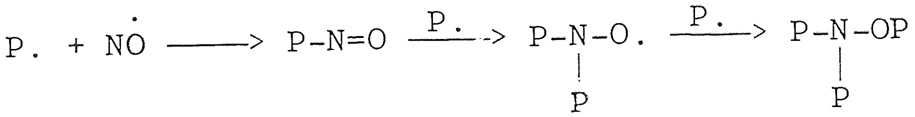
(1)

the characteristic reaction of nitric oxide is its reactions with with alkyl radicals to form nitroso derivatives(90), nitroxyl radicals(90) and alkyl hydroxylamines(90) (reaction 2)



$$R\cdot + \dot{N}O \longrightarrow R{-}N{=}O \xrightarrow{R\cdot} \begin{matrix}R\\R\end{matrix}{>}NO\cdot \xrightarrow{R\cdot} \begin{matrix}R\\R\end{matrix}{>}N{-}OR \qquad (2)$$

The processing of pp in the presence of N-nitrosamines reduced polymer degradation significantly and in some cases cross link formation was observed (NPS, NPZ and NDCA). This suggests that N-nitrosamines were primarily decomposed during thermal processing in a limited amount of oxygen to produce nitric oxide and amino radical (reaction 1). Presumably, nitric oxide is able to terminate macro alkyl radicals in series of reactions to produce nitroxyl radicals and trisubstituted hydroxylamines according to reaction 3, subbsequently such reactions could deactivate ROO. radical formation which is the propagating species in polymer degradation and also could explain the decrease in MFI during the early stages of processing observed in polypropylene containing NPS, NPZ and NDCS (reaction 3). Prolonging



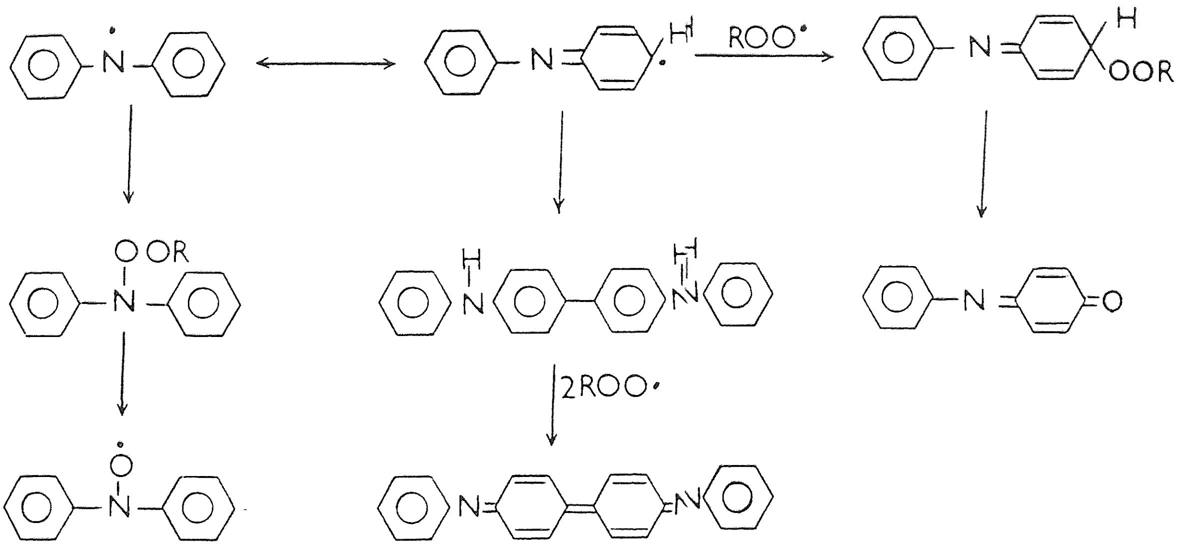
$$P\cdot + \dot{N}O \longrightarrow P{-}N{=}O \xrightarrow{P\cdot} P{-}\underset{\substack{|\\ P}}{N}{-}O\cdot \xrightarrow{P\cdot} P{-}\underset{\substack{|\\ P}}{N}{-}OP \qquad (3)$$

processing (up to 20 mins.) leads to the consumption of nitric oxide, consequently the rate of alkyl radical termination by nitric oxide is reduced, resulting in an increase in MFI. Amino radicals could take part in the melt stabilisation process. Alkylperoxy radical could oxidize the amino radicals into nitroxyl radicals according to reaction 4 (amino radicals insensitive to O_2) and this nitroxyl radical is an effective alkyl radical trap.

$$>N. + ROO. \longrightarrow >NOOR \longrightarrow >NO. + .OR \quad (4)$$

It is obvious that NPS is a more powerful melt stabiliser than Tinuvin 770 (Fig. 5.1). Increasing NPS concentration improved melt stabilisation activity, so that at concentration of 5 x 10^{-4} mole/100 gm. cross-linking formation is observed, by increasing the concentration up to 1 x 10^{-3} mol/100 gm. no significant change in the MFI is obtained, i.e. there is limited effect of NPS concentration on the cross linking formatio This is presumably due to the partial pressure of nitric oxide derived from NPS which is proportional to the concentration of NPS, consequently the rate of alkyl radi trapping by nitric oxide is increased on increasing NPS concentration. It has been reported(166,167) that the reaction rate of alkyl radicals with nitric oxide is independent both of the pressure and of the solubility of nitric oxide, provided that the initial partial pressu of nitric oxide is not less than a certain limiting valu which depends on the nature of the alkyl radicals.

The decomposition of NDP during thermal processing results again in the liberation of nitric oxide which terminates alkyl radicals. Moreover the delocalization of the unpaired electron of diphenylamino radical over the aromatic rings(145), results in the attack of the diphenylamino radical by alkylperoxy radicals (reaction 5). Furthermore, amino radicals disproportionate in a series of complicated reactions which involve



(5)

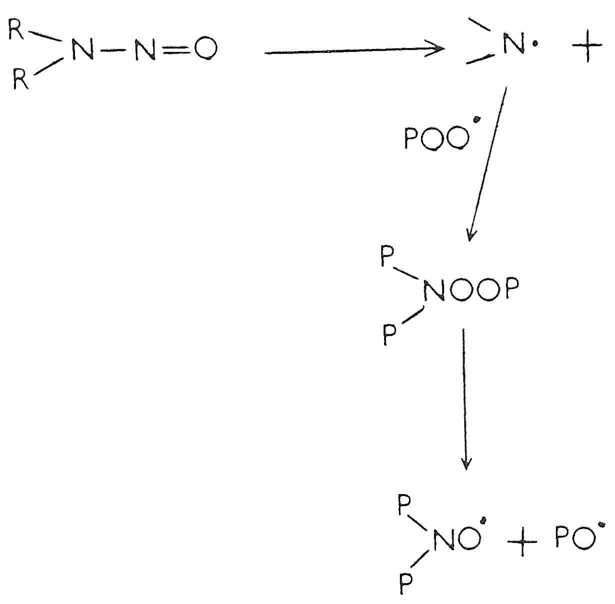
polyconjugated systems containing quinonimine (reaction 5). The investigation of the extract of pp films containing NDP by IR shows two absorption bands at 1690 cm^{-1} and 1625 cm^{-1} attributed to C=N (stretch) and carbonyl (stretch) of quinonoid structure respectively. Such observations are consistent with the formation of quinonimine according to reaction 5.

The inhibition of hydroperoxide formation by N-nitrosamine (NPS, NPZ and NDCA) at early stages of processing (up to 10 mins of processing), (Fig. 5.6) must consequently be due to the termination of alkyl radicals by nitric oxide.

There are two possibilities for nitroxyl radical formation derived from N-nitrosamine during thermal processing.

(a) The most probable one is the reaction of nitric oxide with macro alkyl radical.

(b) By oxidizing amino radical by alkylperoxy radical according to reaction 6.



(6)

The decrease in nitroxyl radical concentration in polymer films after extraction is presumably due to the extraction of unbound nitroxyl radicals derived from the reaction of nitric oxide with small alkyl radicals as well as the extract of nitroxyl radical derived from the oxidation of amino radicals with alkylperoxy radicals (reaction 6).

5.2 Effect of N-nitrosamines on Photo-oxidation of Polypropylene

This section deals with the effect of processing on the subsequent U.V. stabilisation activity of polypropylene containing different N-nitrosamines.

5.2.1 Results.

The processing time has been found to have a significant effect on the photo-stabilisation activity of NPS in polypropylene. Increase in processing time up to 10 mins. improved the photo-stability of polymer, with prolonged processing up to 15 and 20 mins., leads to a decrease in polymer photo-stability (Fig. 5.7). The reduction in U.V. life time of polymer on processing corresponds to the formation of hydroperoxide in the samples before irradiation (Fig. 5.5).

Fig. 5.8 shows that initial carbonyl concentration in the polypropylene containing Timuvin 770 is higher than it is for NPS (at the same conditions of processing and at the same molar concentration). Both Tinuvin 770 and NPS gave long induction period to carbonyl formation, but it is clear that NPS is significantly more effective than Tinuvin 770. It is apparent that the photo-stabilisation activity of NPS is highly dependent on the concentration of the additive (Table 5.2 and Fig. 5.9). Furthermore, it has been observed that the increase in NPS concentration leads to an increase in the initial concentration of nitroxyl radical formation during thermal processing (Fig. 5.9). The improvement of U.V. embrittlement time of pp by increasing NPS concentration is related to the initial concentration of nitroxyl radical. This imples that the increase in NPS concentration results in higher liberation of nitric oxide and hence of nitroxyl radicals.

Fig. 5.10 shows the photo-stabilisation effect of NPZ when processed with polypropylene for different times. It is apparent that the increase of processing from 7.5 up to 10 mins. improved the photo-stabilisation effect remarkably. Prolonged processing up to 20 mins., reduced photo-stabilisation effect of NPZ significantly (Table 5.3). The carbonyl formation at all different processing times is characterized by initial induction period followed by a high rate at later stages of U.V. irradiation. Moreover, the embrittlement times were consistent with the carbonyl formation at different processing times, so that the highest U.V. embrittlement was obtained for samples processed at 10 mins., and the lowest U.V. embrittlement times was obtained for samples processed at 20 mins. (Table 5.3).

Fig. 5.11 shows that there is linear improvement for the U.V. embrittlement time of polypropylene by increasing the concentration of NPZ up to 1×10^{-3} mole/100 gm. then by increasing the concentration up to 1.5×10^{-3} mol/100 gm, U.V. embrittlement of the polymer is reduced. Furthermore, the rates of carbonyl formation are reduced by increasing NPZ concentration up to 1×10^{-3} mole/100 gm., further increase in concentration resulted in an increase in carbonyl formation rate (Fig. 5.12, curve 3). It is apparent that the photo-stabilisation of polypropylene is highly dependent on the concentration of NPZ.

Fig. 5.13 shows that there is an insignificant change in the rate of carbonyl formation in polypropylene containing NDP processed for different times (see also Table 5.2).

E.S.R. examination of polypropylene films containing NPS (processed for 10 mins. at 180°C) showed the decay of nitroxyl radicals derived from NPS in an auto-retarding mode during the early stages of photo-oxidation (Fig. 5.14), and is followed by a decrease at a much slower rate. At embrittlement, the nitroxyl radical could no longer be detected. However there is no significant change in the unsaturation (as measured by the growth of a band at 1640 cm^{-1}), during the initial sharp decrease in nitroxyl radical concentration during the early stages of U.V. irradiation (Fig. 5.14). The increase in unsaturation started when nitroxyl radical concentration started to decrease at a much slower rate.

The extraction of polypropylene films processed in the presence of NPS (concentration 5×10^{-4} mole/100 gm., processing time 10 mins.), reduced the nitroxyl radical concentration by 55% (see Table 5.1), subsequently the U.V. embrittlement time reduced from 1300 hours into 300

TABLE 5.2 Effect of concentration of n-nitrosamines on the U.V. embrittlement time (hours) of pp processed for 10 mins. at 180°C

Concentration / N-nitrosamine	1×10^{-4}	5×10^{-4}	1×10^{-3}
NPS	440	1340	1520
NPZ	155	300	570
NDP	170	200	220
NDCA	135	190	230
DPTA	80	80	80
NDBA	80	80	80

Table 5.3 Effect of processing on the U.V. embrittlemtn time (hours) of pp containging N-nitrosamine at concentration 1×10^{-3} mole/100 gm. at 180°C.

Processing time / Additives	7.5 mins. (unextracted)	10 mins.		15 mins. (unextracted)	20 mins. (unextracted)
		unextracted	extracted		
No additive	85	85	--	75	--
Tinuvin 770	--	760	210	--	--
NPS	1100	1580	300	1120	880
NPZ	370	570	180	440	330
NDP	190	220	150	210	180
NDCA	200	230	120	190	140
DPTA	100	85	--	85	85
NDBA	85	85	--	85	85

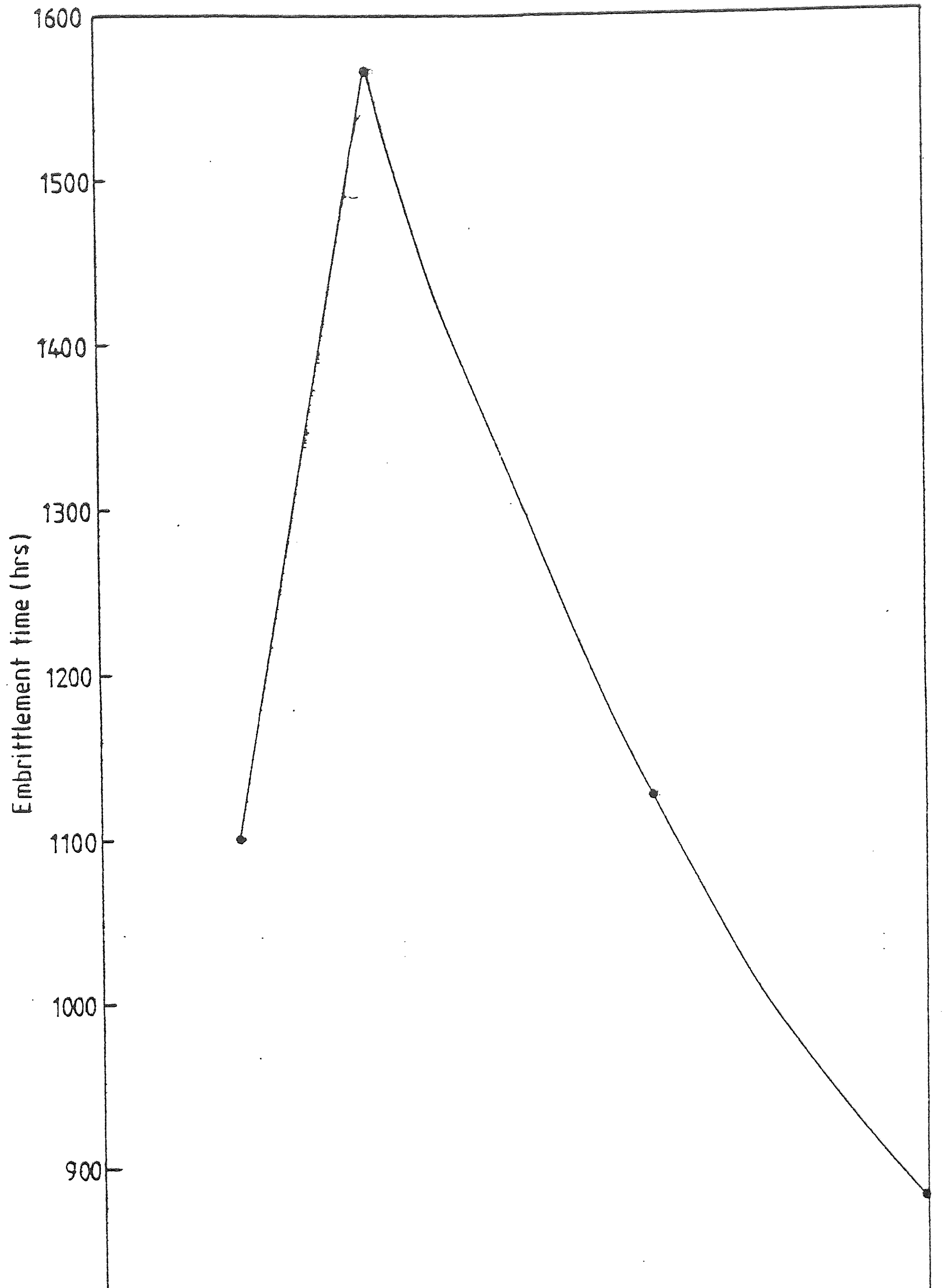


Fig 5:7 Effect of processing time on the U.V. embrittlement of PP containing NPS. (Concentration of additive 1×10^{-3} mole / 100 gm, processing temperature 180 °C at closed mixture)

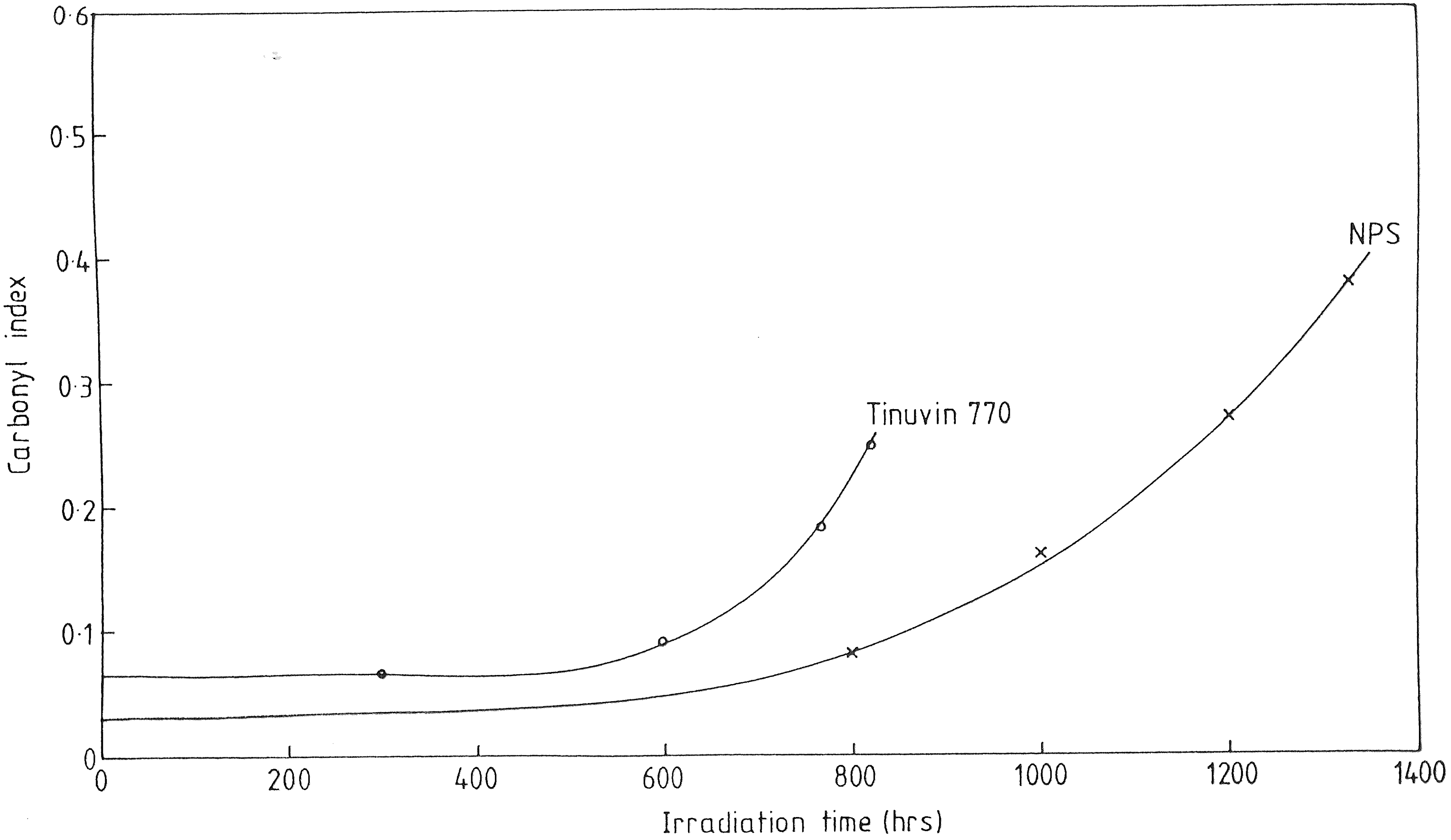


Fig 5:8 Effect of Tinuvin 770 and NPS on carbonyl formation during U.V. irradiation of PP (Concentration 5×10^{-4} mole/100 gm, processing time 10 mins in closed mixer at 180°C)

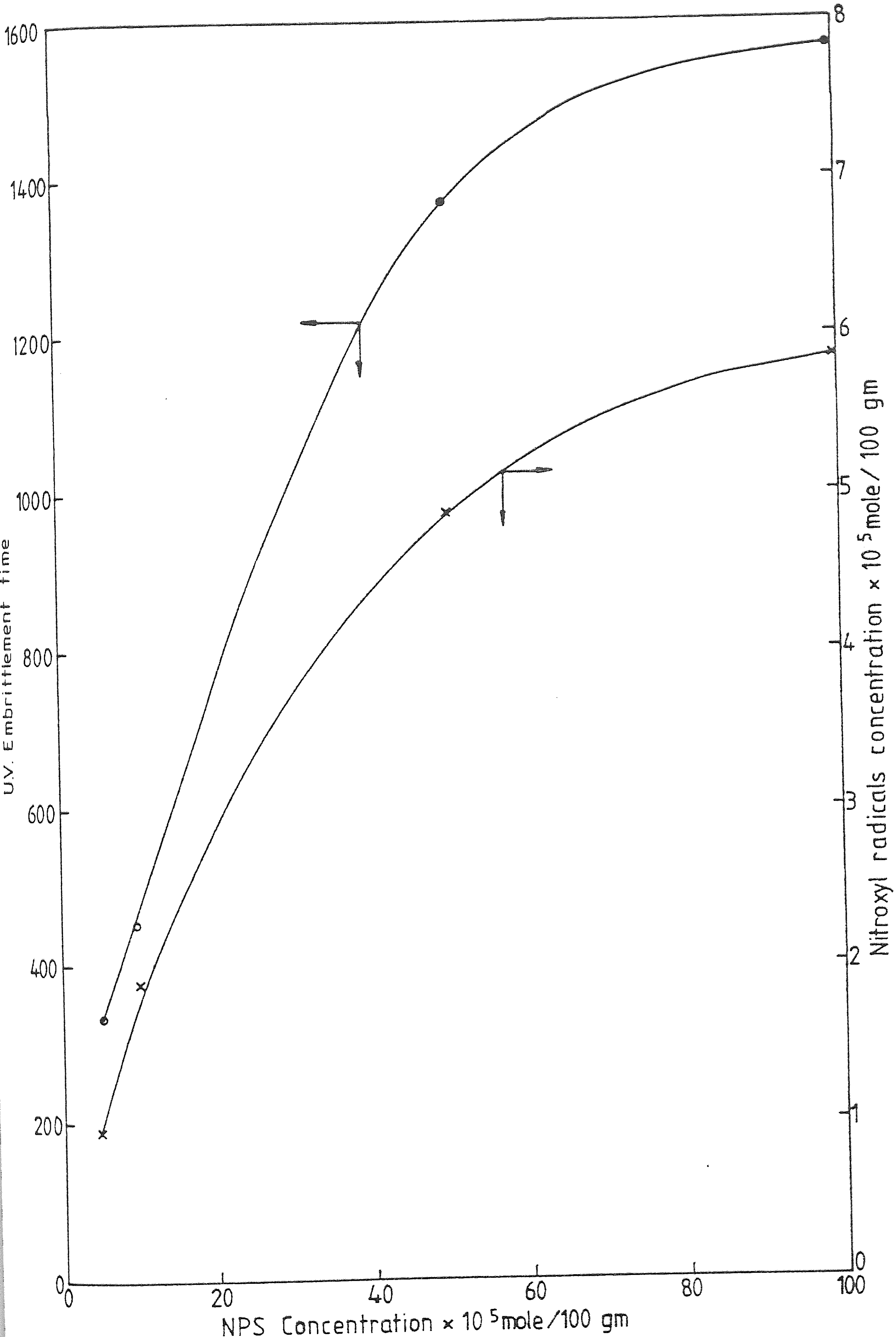


Fig5:9A The effect of NPS concentration on the formation of nitroxyl radicals and U.V. embrittlement of PP processed at 180°C for 10 mins.

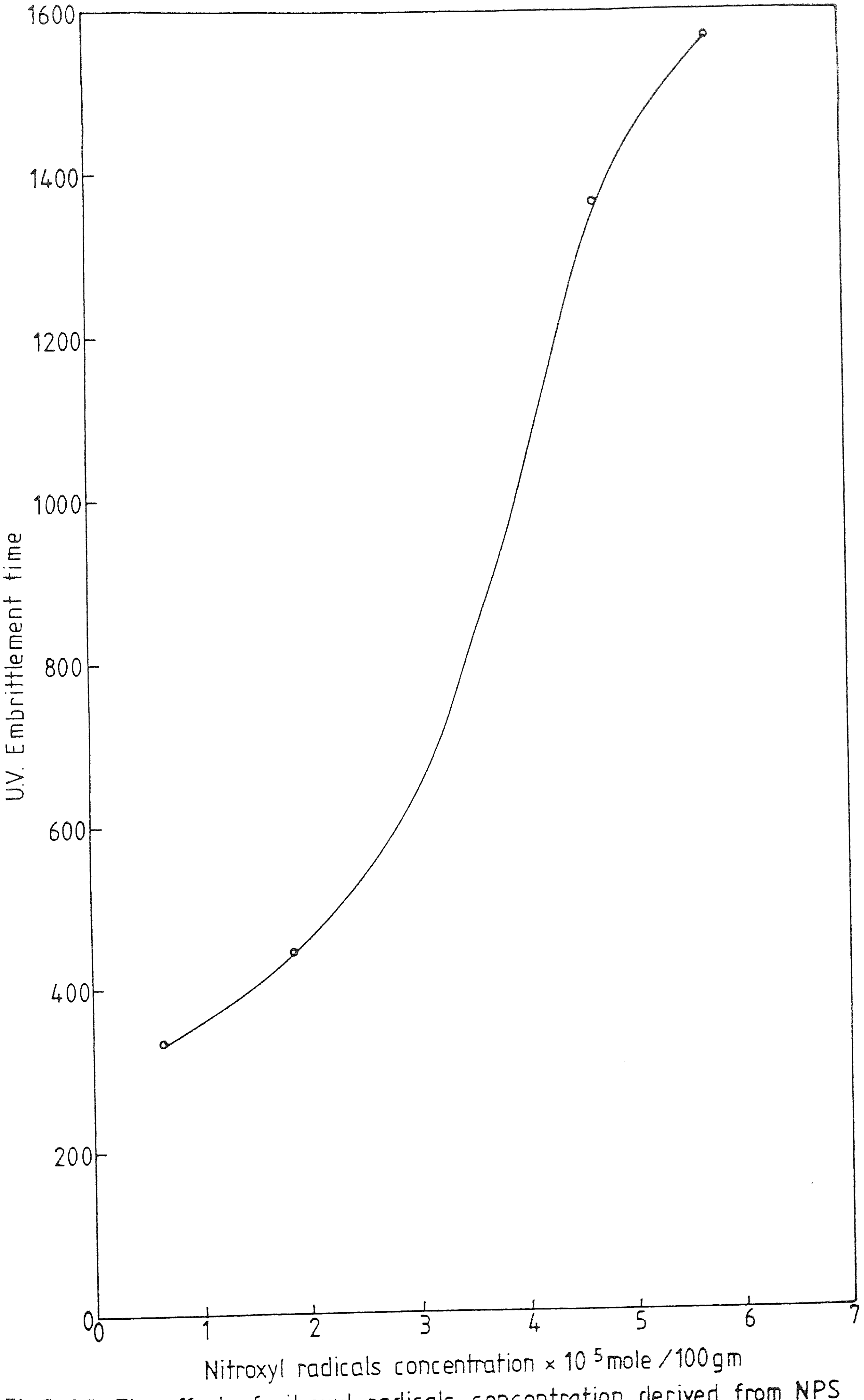


Fig 5:9 B The effect of nitroxyl radicals concentration derived from NPS (at different concentration) on the U.V. embrittlement time of PP (see fig 5:9A)

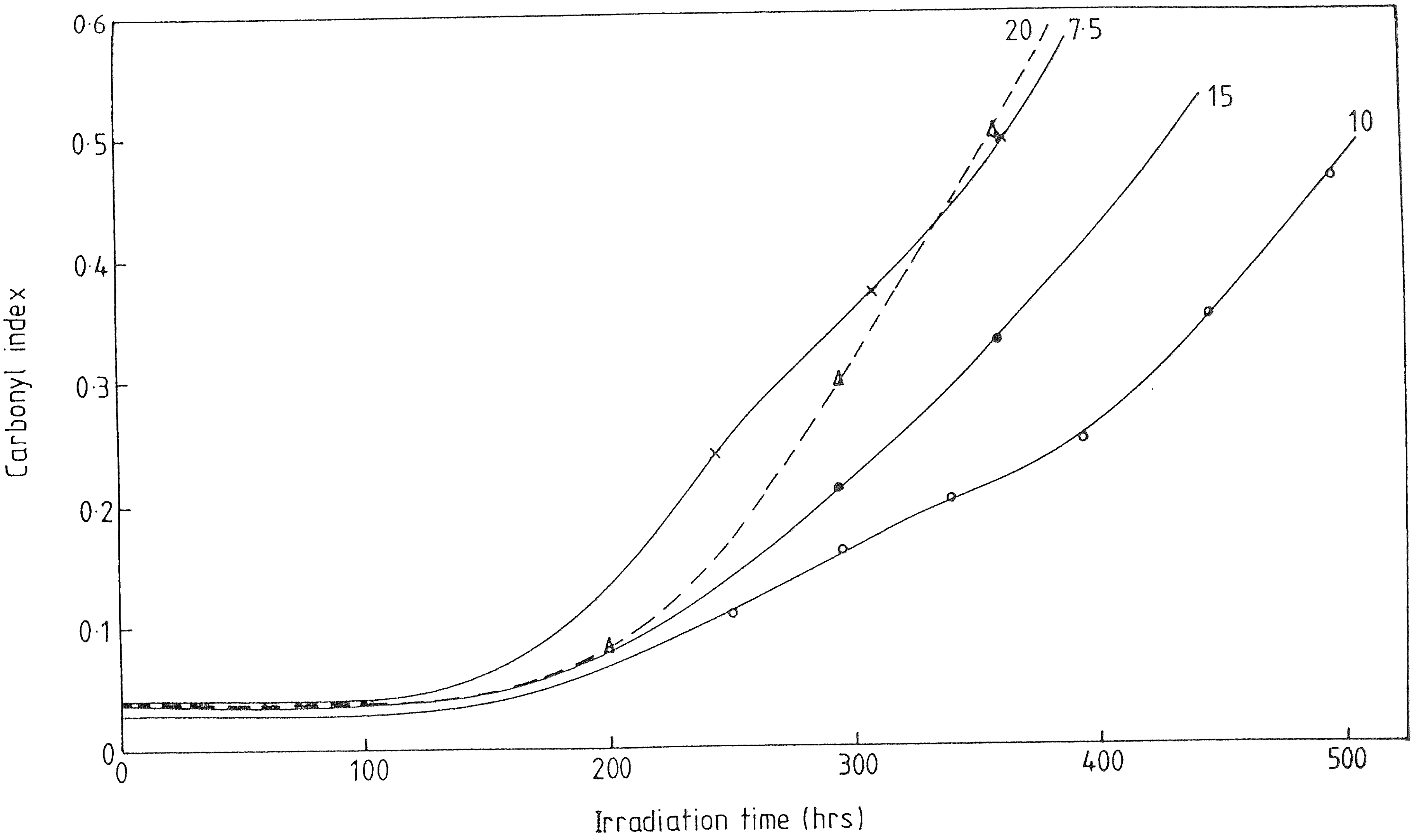


Fig 5:10 Effect of NPZ on photo-oxidation of PP processed at different time (All samples processed in closed mixer at concentration of 1×10^{-3} mole / 100 gm, number on curve represents processing time in minutes.

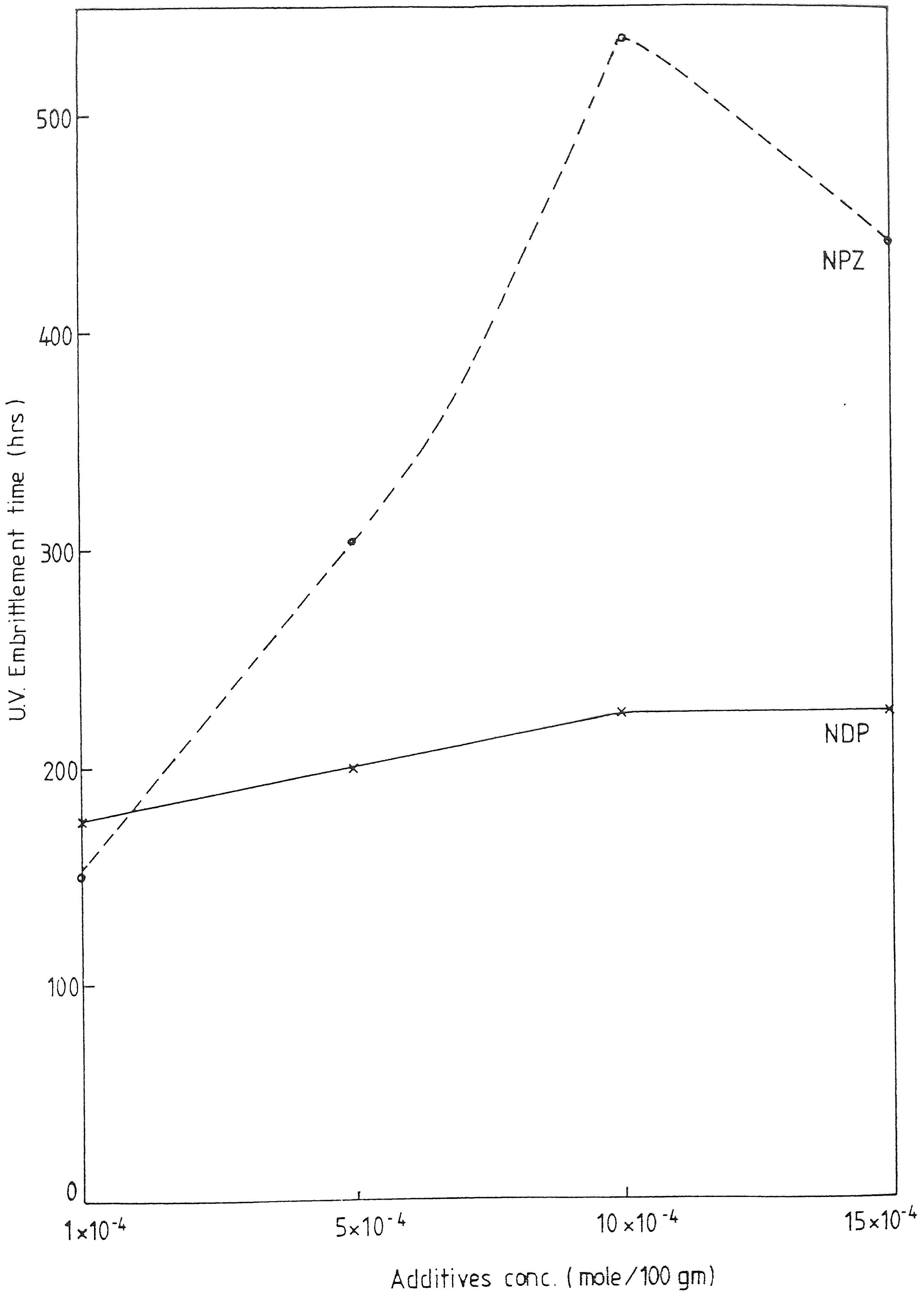


Fig 5:11 Effect of concentration of NPZ and NDP on the U.V. embrittlement of PP processed for 10 mins in closed mixer

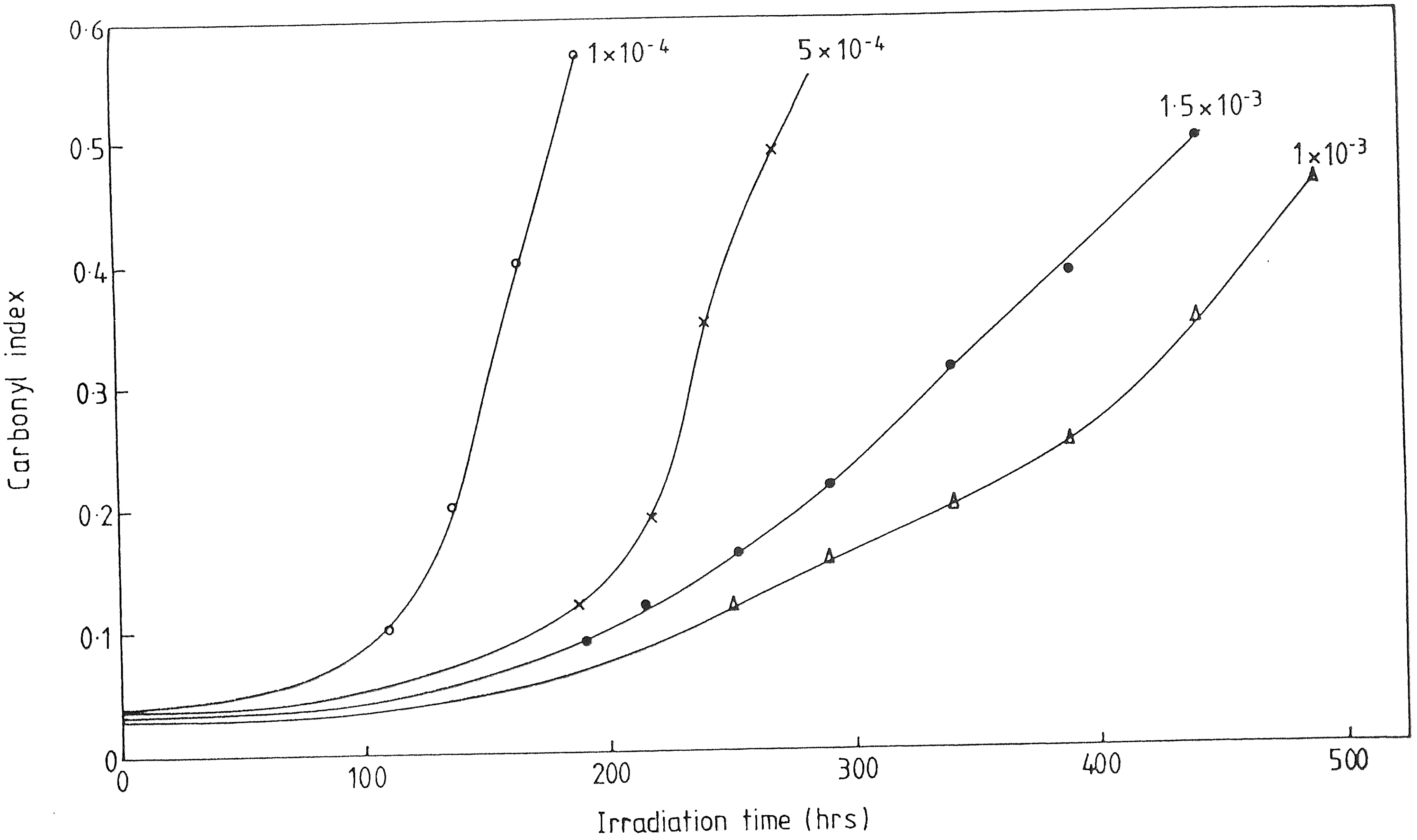


Fig 5:12 Effect of NPZ concentration on photo-oxidation of PP processed for 10 mins in closed mixer at 180°C
Number on curve represents molecular concentration / 100 gm

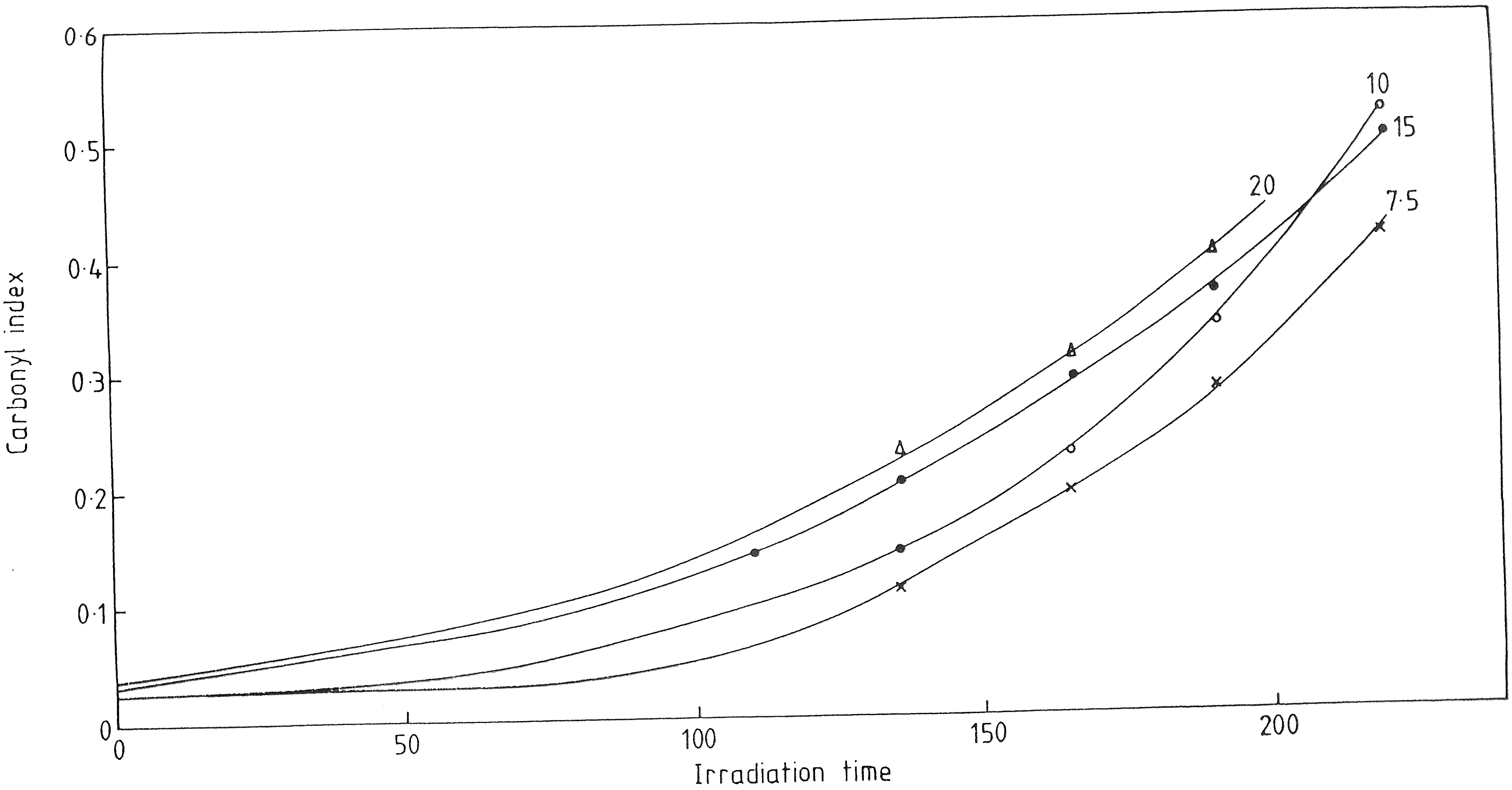


Fig 5:13 Effect of processing time on photo-oxidation of PP containing NDP at concentration 1×10^{-3} mole/100 gm (processed in closed mixer at 180° C), number on curve represents processing time in minutes.

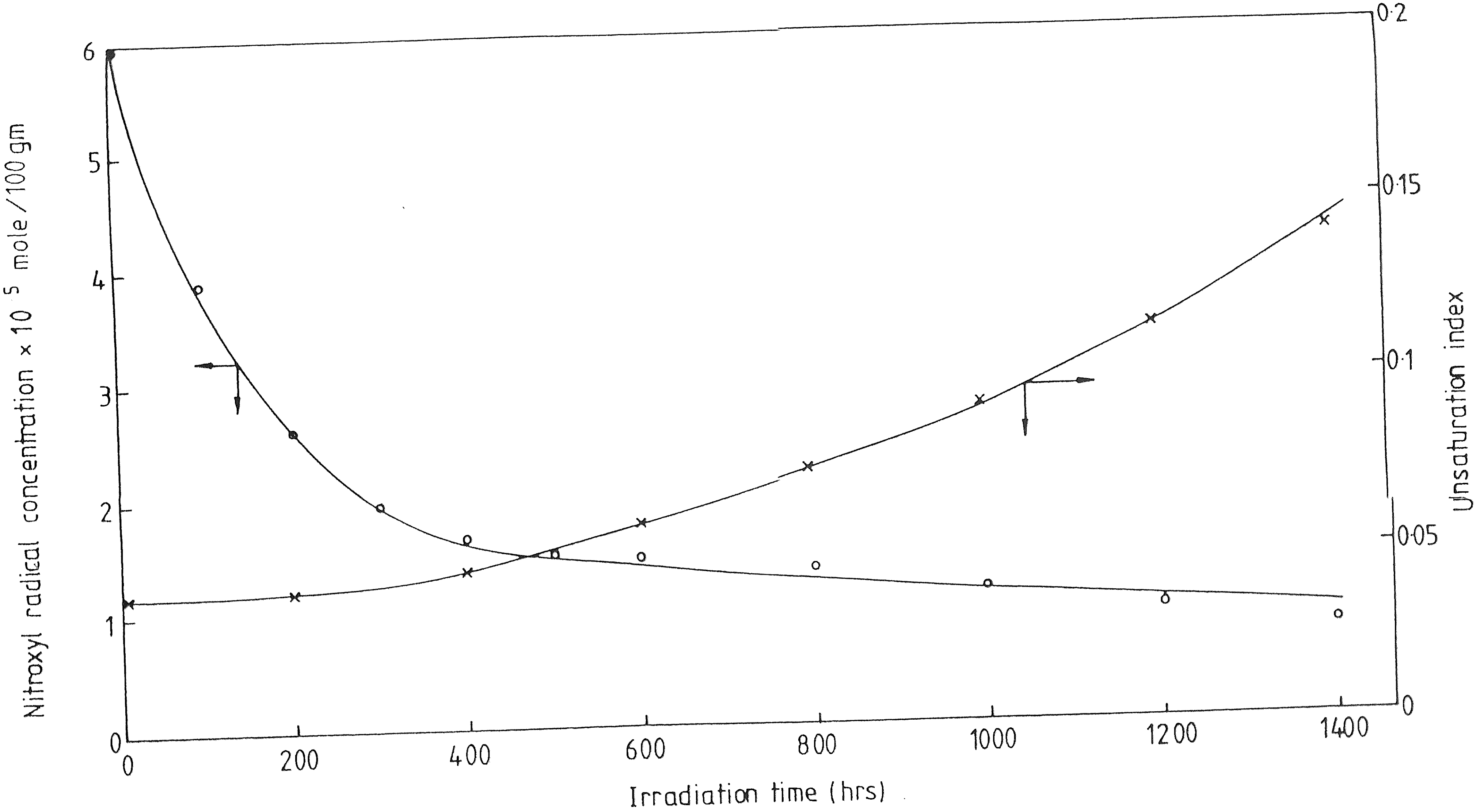


Fig 5: 14 Kinitics of nitroxyl radical decay (formed from NPS) and unsaturation formation in PP during U.V. exposure Concentration of NPS 1×10^{-3} mole/100 gm, processing time 10 mins at 180°C

hours (after extraction).

NPZ and NPS are ineffective U.V. stabilisers when processed in excess of air for 10 mins.. This suggests that under the circumstances of processing, oxygen competes with nitric oxide liberated by thermal decomposition of NPS and NPZ to react with alkyl radicals to form ROO.. Subsequently a large amount of hydroperoxide is formed which is a key factor in the photo-initiation process.

5.2.2 Discussion.

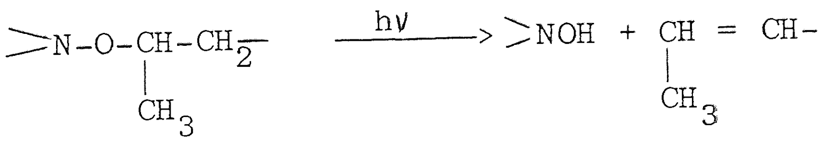
N-nitrosamines decompose into nitric oxide and amino radicals during processing at 180°C (see section 2.2.7) and subsequently the reaction of nitric oxide with alkyl radicals(90) as well as the reaction of amino radical with alkylperoxy radical, results in nitroxyl radical formation (reactions 2 and 4). It seems that nitroxyl radical formed prior to U.V. irradiation play an important role in the photo-stabilistion activity.

Nitroxyl radicals are effective alkyl radical scavengers and since alkyl radicals are the predominant species formed during the early stages of U.V. irradiation. The sharp decrease in nitroxyl radical concentration during the early stages of irradiation (Fig. 5.14) is presumably due to the reaction of nitroxyl radical with macroalkyl radicals to form alkyl hydroxylamine (reaction 7). The U.V. stabilisation process persists whilst the

$$\mathrm{P.} + \mathrm{N\text{-}O.} \longrightarrow \mathrm{N\text{-}O\text{-}P} \qquad (7)$$

concentration of nitroxyl radical remains at a low stationary level and the unsaturation steadily increases at later stages of irradiation (Fig. 5.14). The detection of hydroxylamine (see Section 2.2.11) in U.V. irradiated samples (processed with NPS), suggests that the latter and unsaturation may result from the decomposition of alkylhydroxylamine formed either during thermal processing or during the early stages of U.V. irradiation. Chackraborty and Scott(165) have reported that the formation of hydroxylamine and unsaturation during photo-oxidation of hydrocarbons in the presence of nitroxyl radicals.

It must be concluded that the decomposition of alkylhydroxylamine during U.V. irradiation is necessary for the alternating CB-D, CB-A regenerative cycle to operate effectively according to reaction 8.



$$>\mathrm{N\text{-}O\text{-}}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{\text{-}CH_2\text{-}} \xrightarrow{h\nu} >\mathrm{NOH} + \underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}} = \mathrm{CH\text{-}}$$

(8)

Prolonged processing of polypropylene with NPZ and NPS up to 15 and 20 mins., leads to significant reduction in photo-stabilisation activity (Figs. 5.7 and 5.11,

Table 5.3). This is almost certainly due to hydroperoxide formed during thermal procesing (Fig. 5.5) which subsequently initiates photo-oxidation.

5.3 Effect of N-nitrosamines on Thermal Oxidation of Polypropylene

5.3.1 Results and Discussion

It has been shown that most of the N-nitrosamines are good melt stabilisers for polypropylene when processed in limited amount of air and nitroxyl radicals are formed as one of the main products. However it has been found that the melt stabilising effectiveness of N-nitrosamines are very much reduced when processed in an excess of air except in case of DPN which showed good melt stabilisation activity under this condition.

None of the aliphatic and cyclo-alipatic N-nitrosamines showed significant antioxidant activity during oven ageing (140°C) of polypropylene as compared with N-nitrosodiphenylamine (aromatic nitrosamine) which is very effective antioxidant (Table 5.4).

Nitroxyl radicals are very effective alkyl radical scavengers (i.e. CB-A antioxidant). Since in thermal oxidation condition (oven ageing) oxygen is able to compete with nitroxyl radicals for alkyl radicals, nitroxyl radicals are ineffective under this condition. Nitroxyl function is known not to terminate alkylperoxy radicals during thermal oxidation.

Table 5.4 Effect of processing on the thermal stability (hours) of pp containing N-nitrosamines at concentration 1 x 10^{-3} mole/100 gm (180°C)

Processing time / Additives	7.5 mins.	10 mins.	15 mins.	20 mins.
No additive	0.5	0.5	0.5	
NDP	37.o	39.o	36.o	31.
NPZ	1.o	1.o	0.5	0.5
NDCA	1.o	1.o	1.o	0.5
NPS	1.5	1.5	1.o	1.

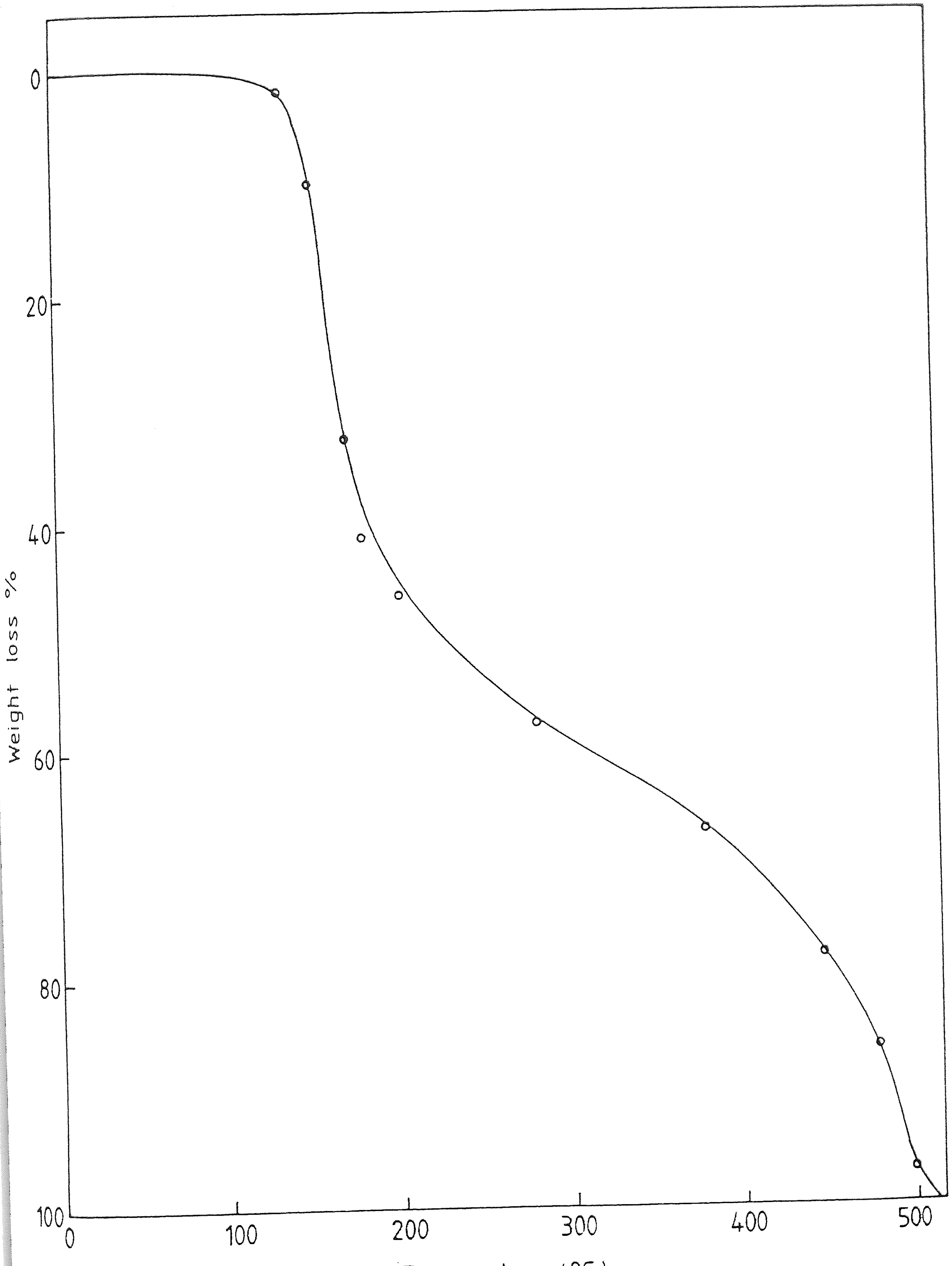


Fig5:15 Thermal stability of DPN at different temperatures

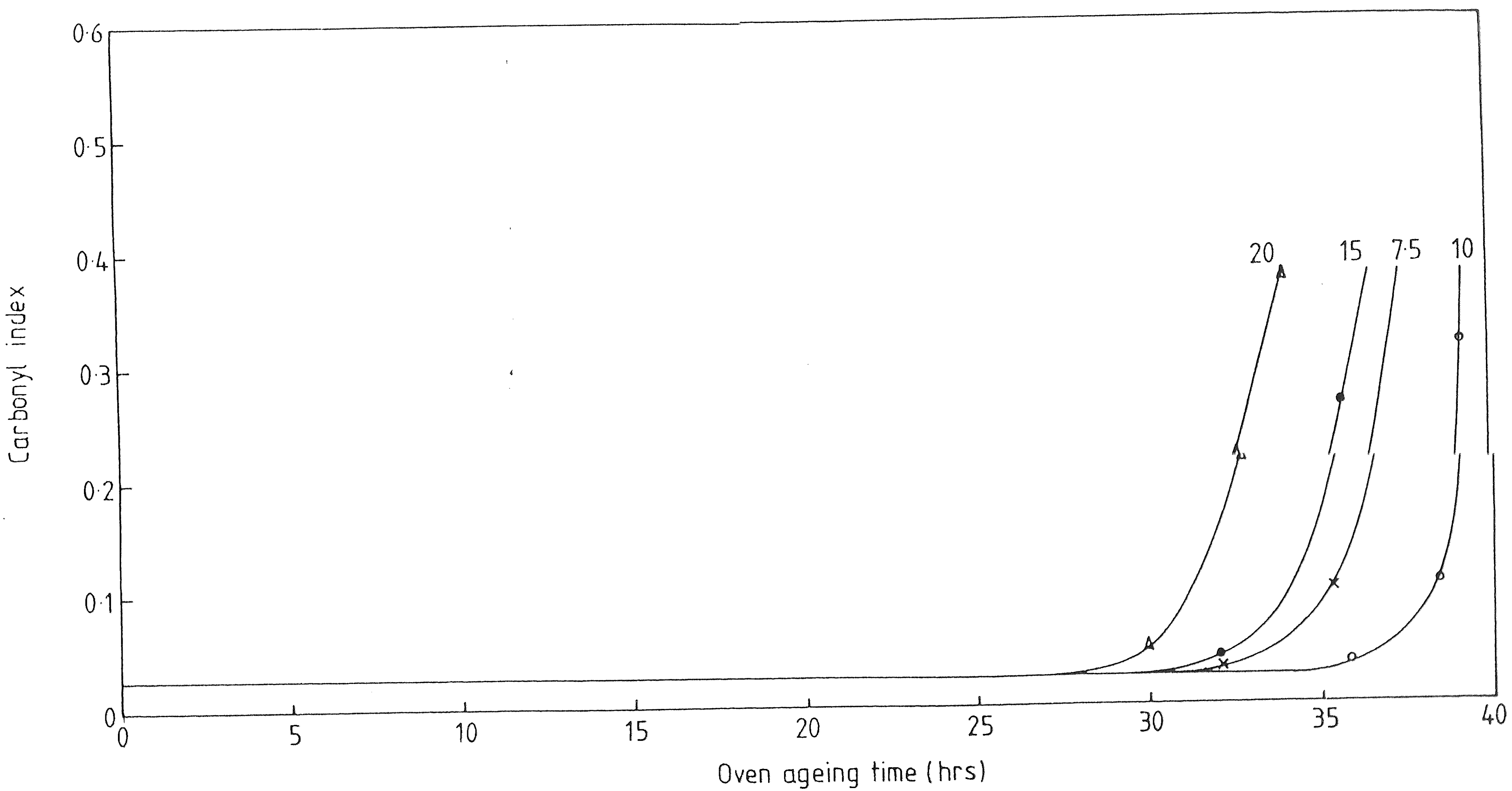


Fig 5:16 Effect of processing on thermal oxidation of PP at 140°C containing NDP at concentration 1×10^{-3} mole/100 gm in closed mixer

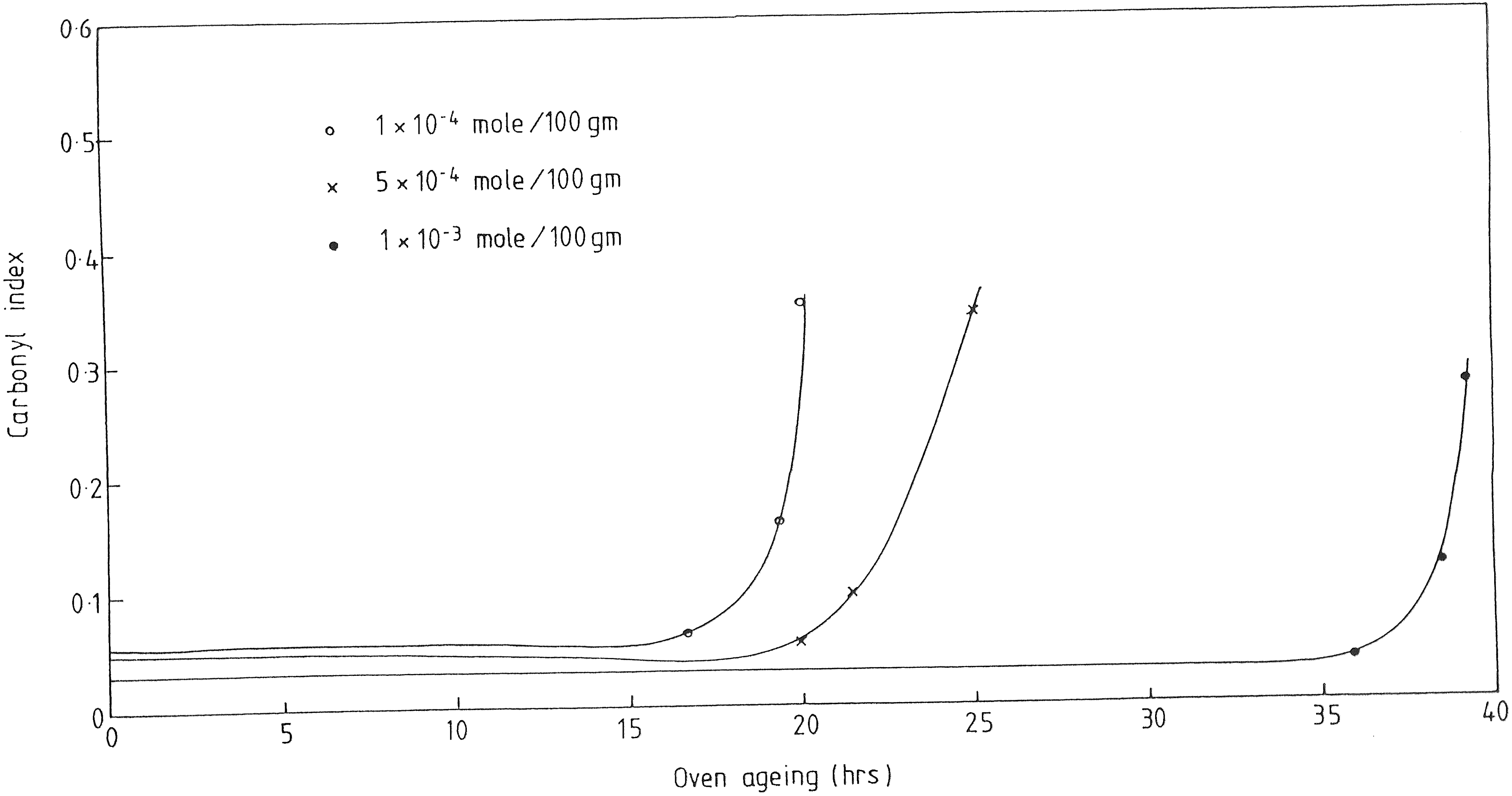


Fig 5:17 Effect of different concentrations of diphenyl nitrosamine on thermal oxidation of PP at·140°C, processing time 10 mins/cl at 180°C

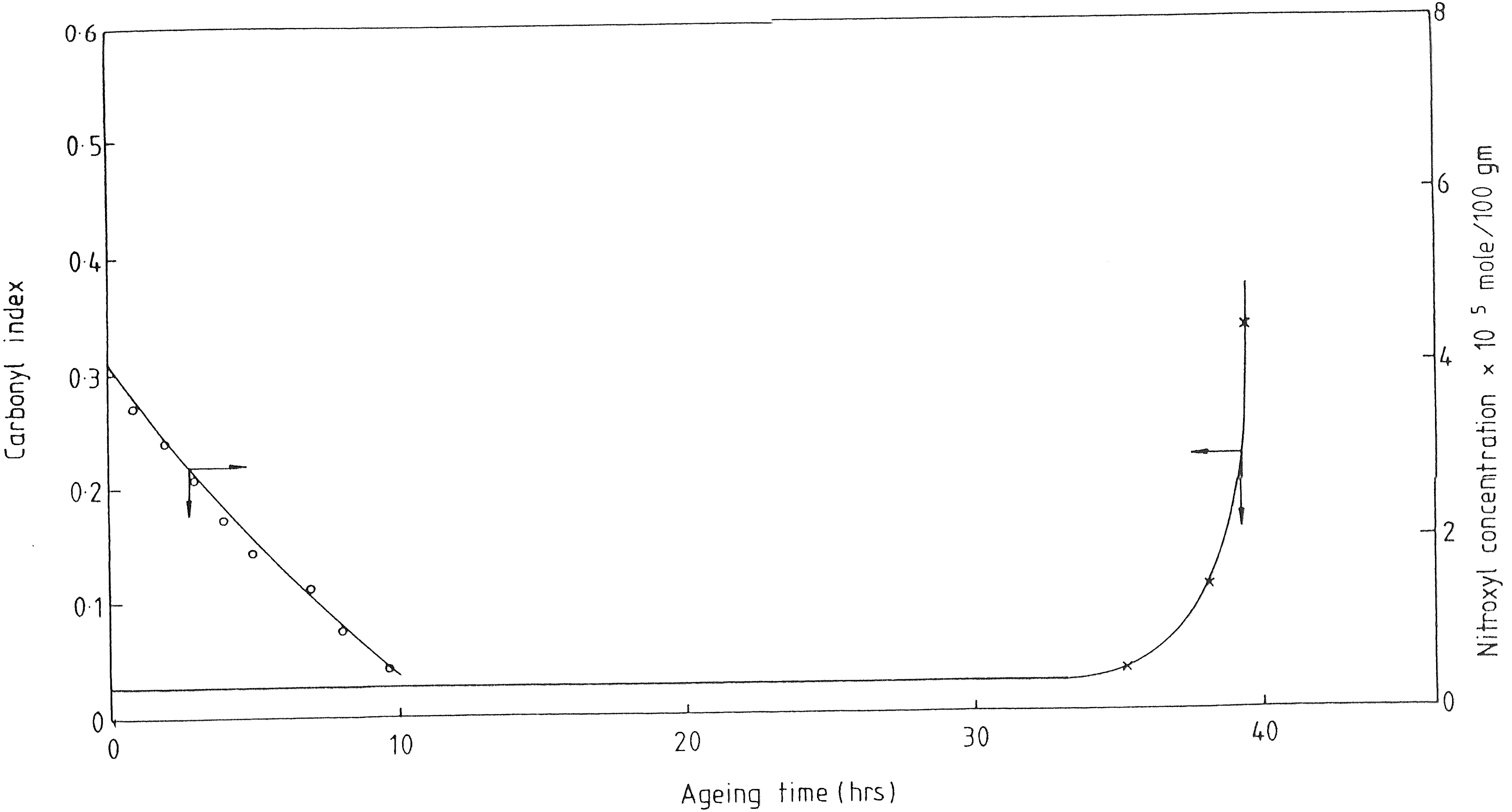
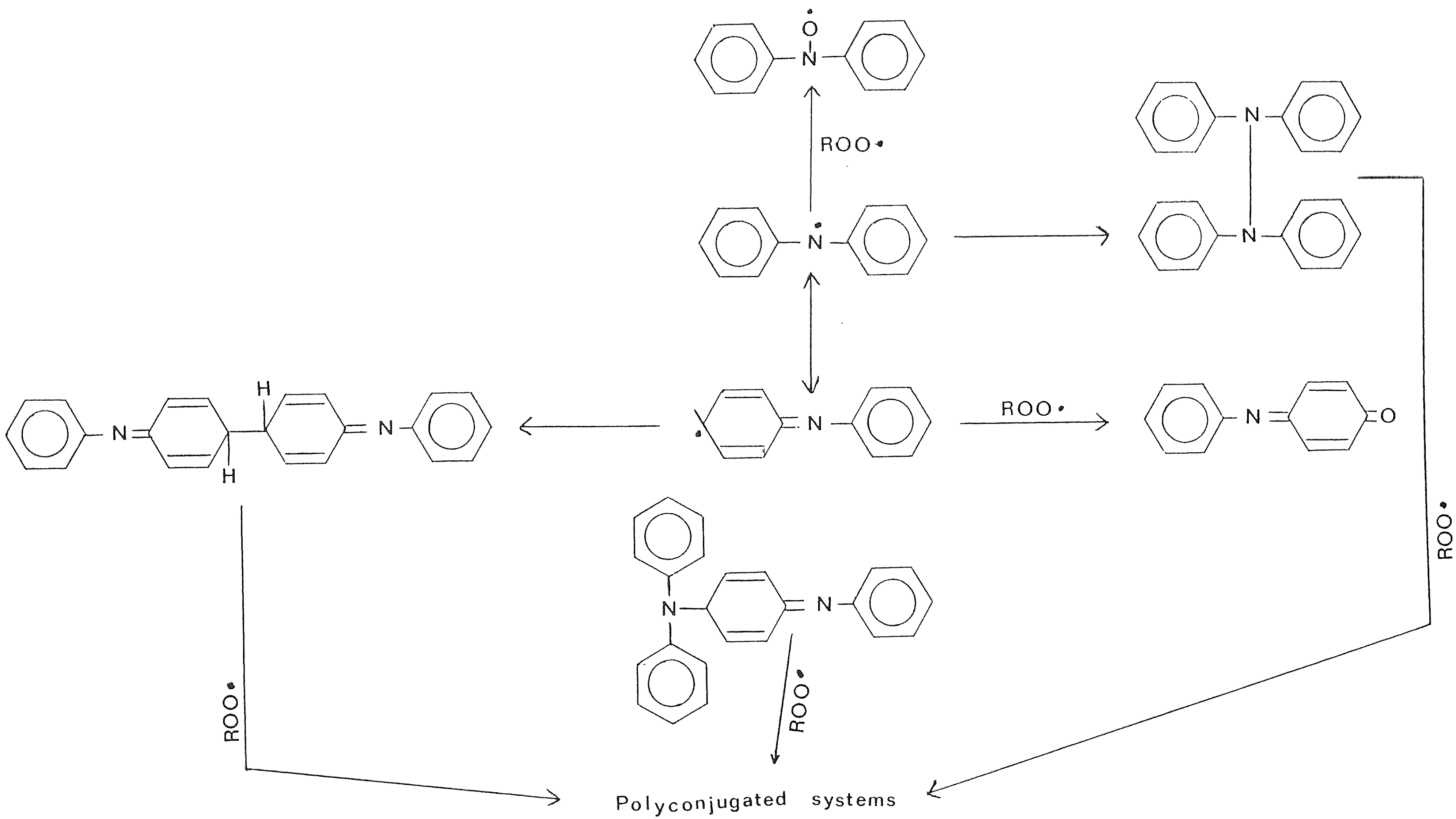


Fig 5:18 Rate of nitroxyl radical decay and carbonyl formation during oven ageing (140°C) of PP containing NDP at concentration 1×10^{-3} mole/100 gm (processing time 10 mins)



Scheme 1

Thermal analysis (TG) (see Section 2.2.7) of NDP shows that the voltalisation occurred in two stages (Fig. 5.15). The first stage starts at 120°C and the second stage of voltalisation started at 260°C. Presumably the weight loss in the first stage is due to the decomposition of NDP into nitric oxide and dipheny amino radical. Fig. 5.15 clearly shows that not only nitric oxide is lost by voltalisation but some amino radicals could also be voltalised. Dimerised products containing quinonimine are formed through the mesomeric forms of diphenylamino radical (see scheme 1). The thermal stability of these products (dimerised products) at 260°C is represented by the induction period before the second stage of weight loss, i.e. the dimerised products are not volatile either at processing temperature (180°C) or at oven ageing temperature (140°C) of polypropylene.

Fig. 5.16 illustrates the effect of processing time on the subsequent thermal oxidative stability of polypropylene in the form of compression moulded film containing N-nitrosodiphenylamine at 140°C (oven temperature). All samples showed an induction period to carbonyl formation during thermal oxidation and the induction period does not seem to depend significantly on the prior processing time. This may be attributed to the thermal stability of the dimerised products of diphenylamine radical, which is also involved in the stabilisation process (see scheme 1).

Increase in the concentration of N-nitrosodiphenylamine leads to a corresponding increase in thermal oxidative stability of the polymer (Fig. 5.17).

Fig. 5.18 shows the kinetics of nitroxyl decay (derived from NDP according to reaction 6) as well as the rate of carbonyl formation during thermal oxidation of polypropylene processed in presence of NDP for 10 mins. in closed mixer at concentrations of 1 x 10^{-3} mol/100 gm. It is apparent that nitroxyl radicals decayed after 10 hours of thermal oxidation, while the stabilisation process lasted for 40 hrs. (carbonyl induction period, curve 2). This indicates that nitroxyl is not the main species involved in thermal oxidative stabilisation. When the sample was extracted, the dark brown colour of the sample was much reduced and the stability of the polymer was reduced from 40 hours to 2 hours. The identification of two absorption bonds in the extract at 1690 and 1610 cm^{-1} corresponds mainly to C=N (stretch) and C=C (stretch) related to conjugated structure respectively. This seems to suggest that the dimerized products of the diphenylamine radical containing quinonimines play the major role in the thermal stabilisation process (see scheme 1). It has also been reported that quinonimine is a highly efficient antioxidant for alkanes at 130°C(43).

CHAPTER 6

SYNERGISTIC ACTION OF NITROSO AND NITRONE COMPOUNDS WITH COMMERCIAL STABILISER

Studies in the preceding chapters described the individual performance of nitroso compounds, nitrones and N-nitrosamines in polypropylene as melt, thermal and U.V. stabilisers. This chapter is mainly concerned with the behaviour of the above compounds in the presence of other commercial U.V. stabilisers and antioxidants in polypropylene in the same performance tests.

In both the two component systems, a total concentration of 1 x 10^{-3} mole additives per 100 gm polymer was used.

6.1 Results and Discussion

Fig. 6.1 illustrates the photo-stability of polypropylene containing nitroso-tert-butane (NTB) in presence of commercial U.V. stabilisers U.V.531 at total concentration of 1 x 10^{-3} mole/100 gm at different molar ratios. It is clear from this figure that NTB and U.V. 531 give a very good synergistic effect in polypropylene under U.V. exposure (Table 6.1). Fig. 6.2 shows that the maximum synergistic effect is obtained at 1:1 molar ratio of NTB to U.V. 531. Fig. 6.3 illustrates the rate of decay of

U.V. 531 (λ max = 330 nm) in the presence and absence of NTB in polypropylene during U.V. irradiation. The same figure also includes the rate of decay of nitroxyl radicals as measured by ESR in the presence and absence of U.V. 531 in polypropylene film under U.V. irradiation. This result seems to suggest that U.V. 531 is protected by NTB both during thermal processing and during U.V. irradiation. This could be due to the scavenging of alkyl radicals by NTB and consequently the formation of peroxy radicals and hence hydroperoxides will be very much reduced in the system. It has been reported that the activity of U.V. 531 is very much reduced in the presence of peroxide(138). It may be suggested that the protection of U.V. 531 by nitroxyl radicals begins at the processing stage and extends over the U.V. exposure stage. Fig. 6.3 confirms that the initial absorbance values of U.V. 531 after processing is higher in the presence of NTB than in its absence.

However, this difference in absorbance of U.V. 531 could also be due to the mutual increased solubility in polymer. However, curves 3 and 4 (Fig. 6.3) show that the rate of decay of nitroxyl radicals produced from NTB during processing is slower and lasts longer in light in the presence of U.V. 531 than in its absence. This could be due to the protection of nitroxyl radicals by the screening action of U.V. 531. U.V. 531 is known (138) to act by a U.V. screening mechanism in addition to free radical scavenging. The above results clearly show that the mechanism of synergism between NTB and U.V. 531 involves the mutual protective effect of the additives. NTB has the ability to protect U.V. 531 from peroxy radicals and peroxide formed during processing and U.V. irradiation and U.V. 531 as well as behaving as screen, can stabilise nitroxyl radicals produced from NTB against photolytic destruction.

However, under thermal conditions (in oven ageing at 140°C) the combined effect of NTB and U.V. 531 is very poor (Table 6.2), although under processing conditions this combination of additives acts as a fairly good melt stabiliser (Table 6.3). This may be due to the physical loss of antioxidants by voltalisation in the air flow during oven ageing.

NTB also synergises very effectively with a hindered amine (Tinuvin 770) under photo-oxidation conditions in polypropylene (Fig. 6.4, Table 6.1). As before a maximum synergistic effect has been observed at 1:1 molar ratio of NTB to Tinuvin 770 (Table 6.1). It is known that Tinuvin 770 itself acts as pro-oxidant(138) to some extent during processing (Table 6.3). However, it acts as a very good U.V. stabiliser for polymers and it has been shown(138) that Tinuvin 770 is converted to nitroxyl radicals by its reaction with hydroperoxides. The nitroxyl radicals so produced undergo cyclical regeneration(155) through the

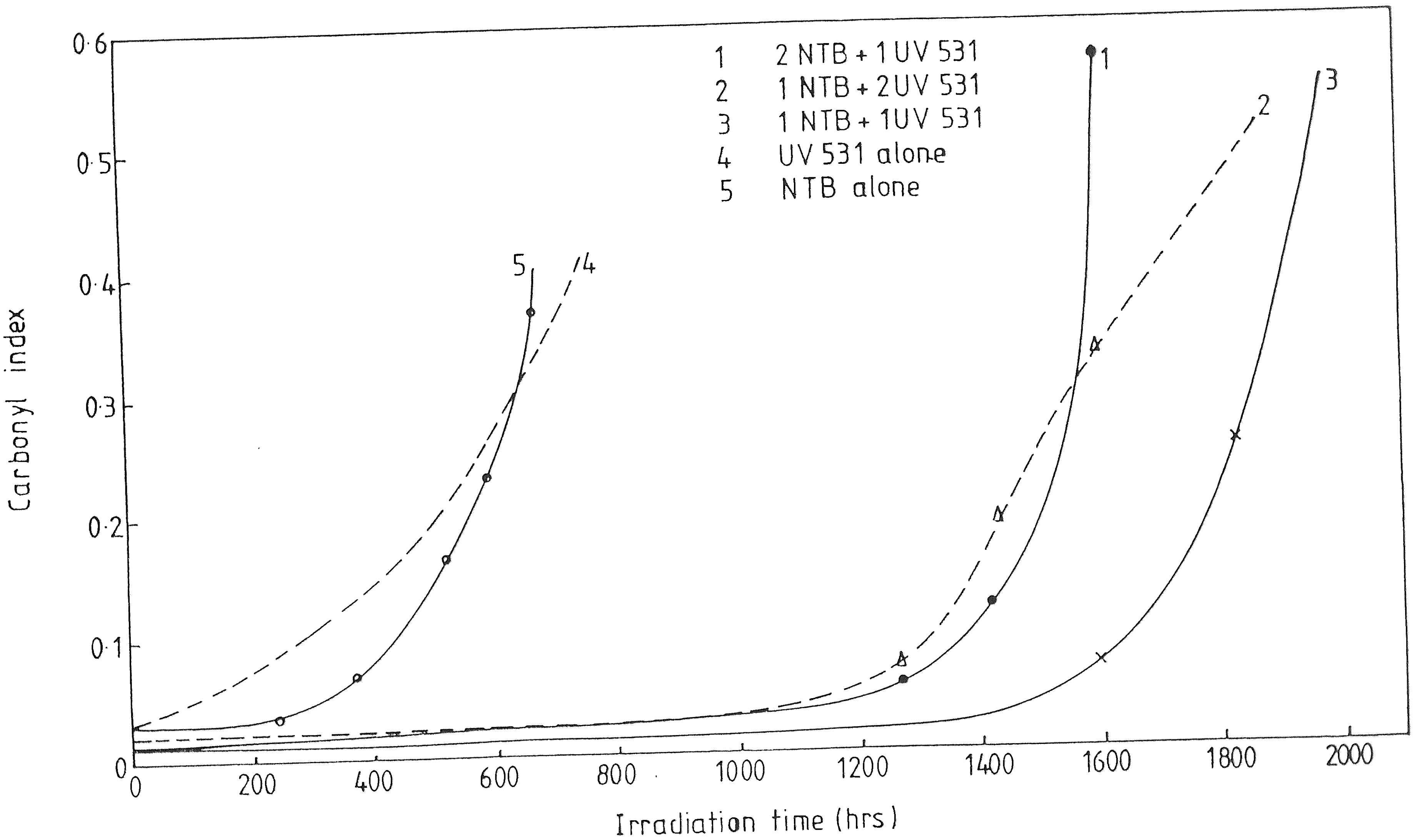


Fig 6:1 Rate of carbonyl formation during photo-oxidation of PP containing UV 531 and NTB at different molar ratios (total conc. 1×10^{-3} mole/100 gm)

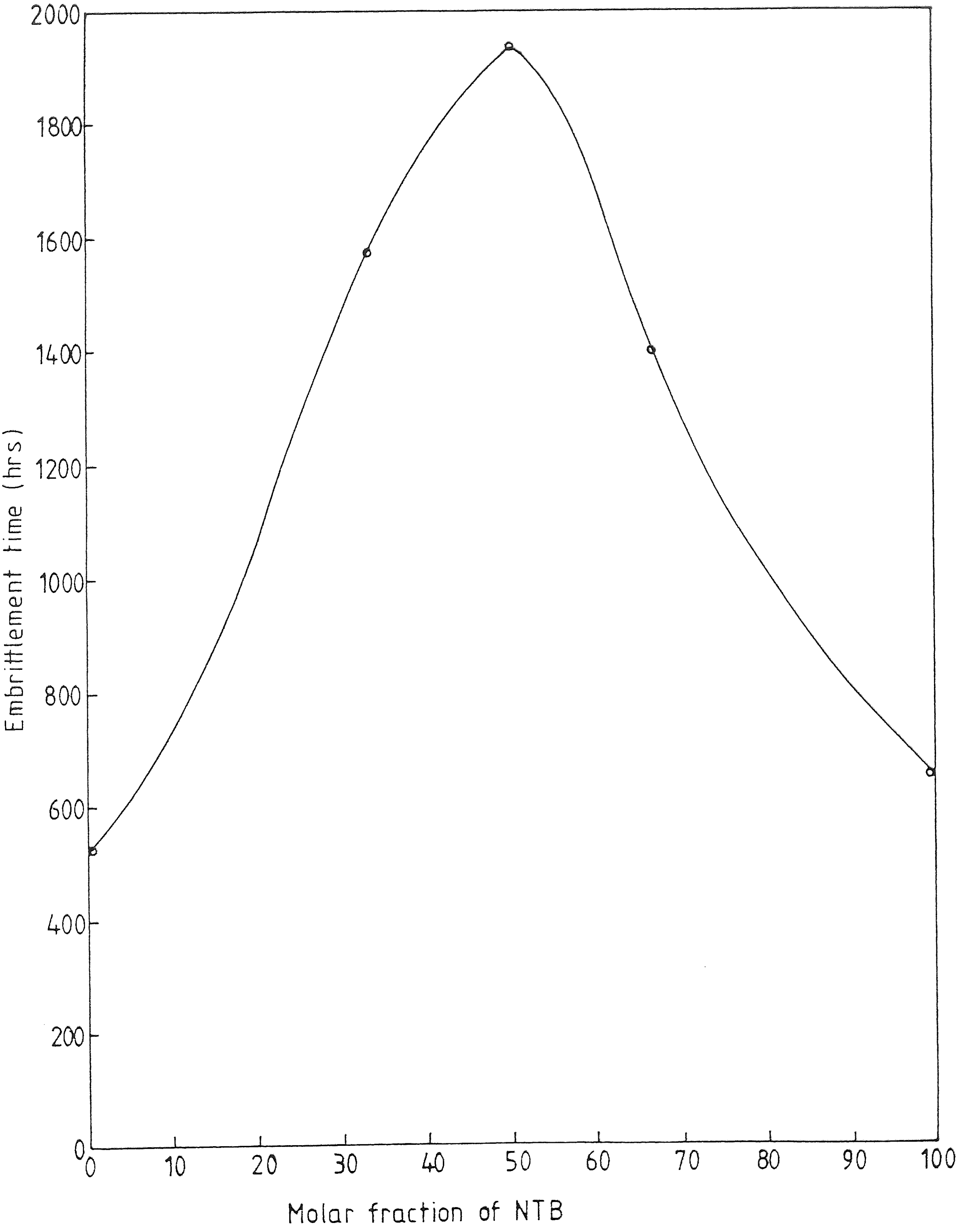


Fig 6:2 Synergistic effect of UV 531 and NTP at different molar ratios on photo-stabilisation of PP (total conc. 1×10 mole /100 gm)

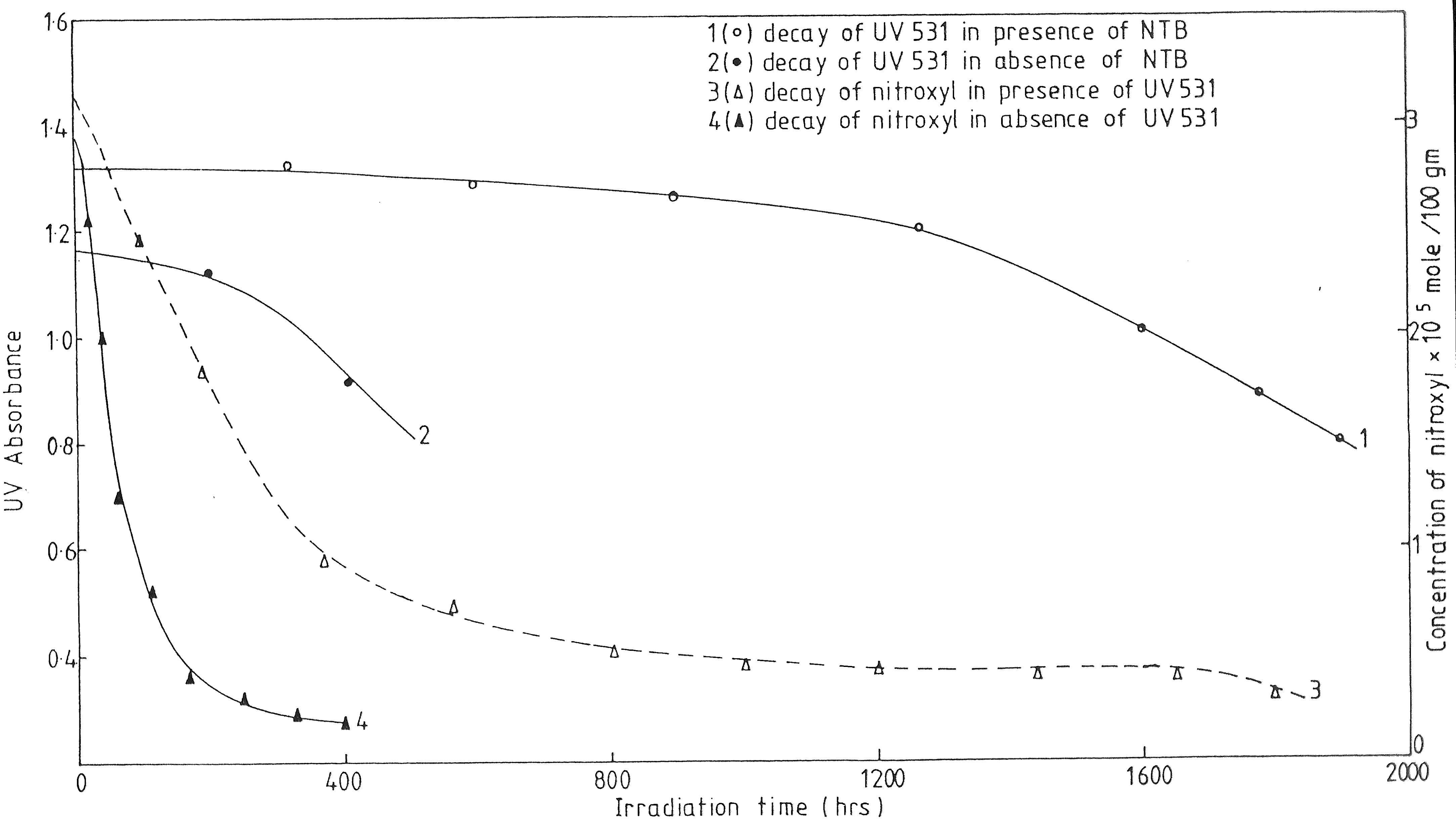


Fig 6:3 Rate of nitroxyl radicals decay (derived from NTB) in presence or absence of UV 531 during photo-oxidation of PP
Concentration of both UV 531 and NTB, 5×10^{-4} mole /100 gm

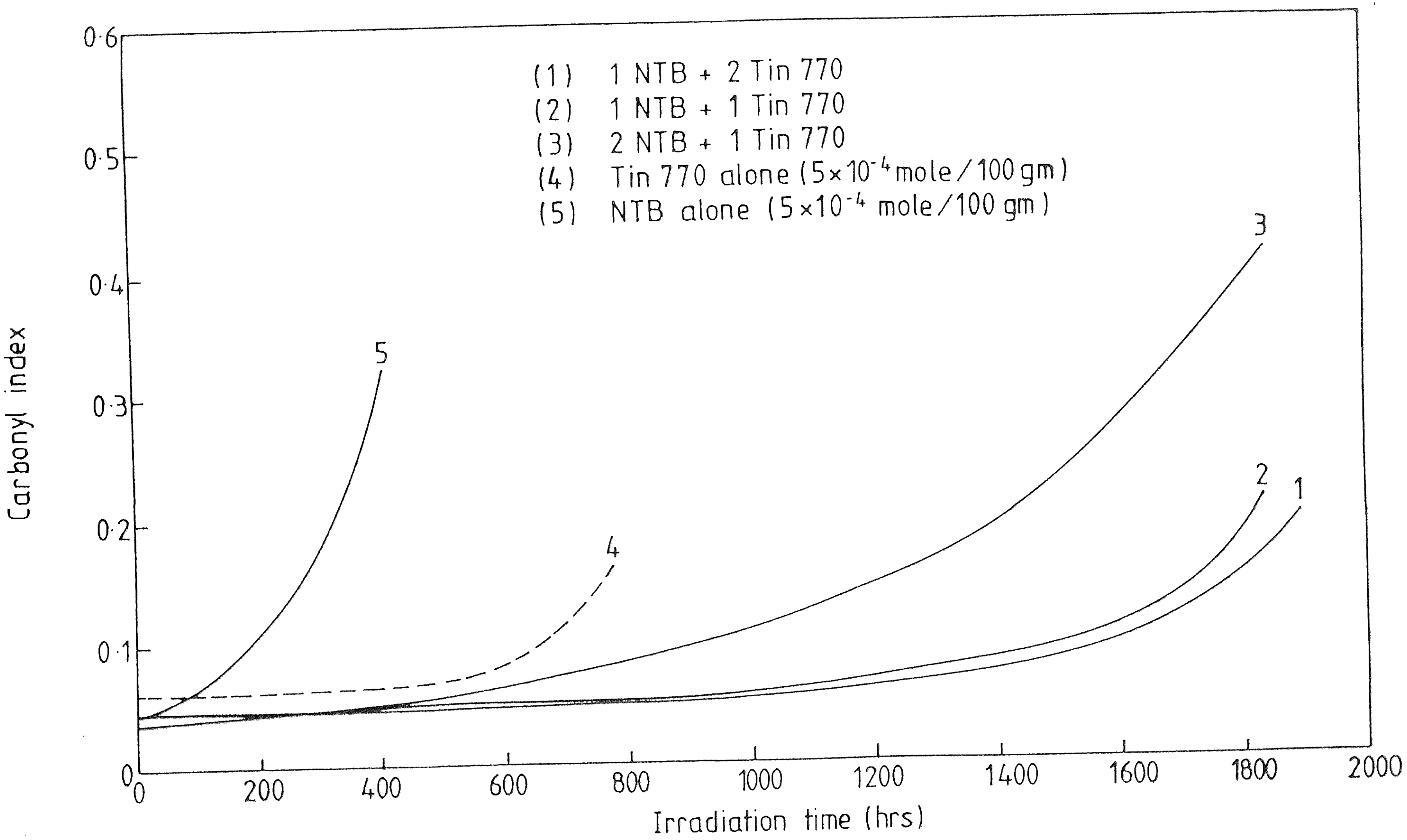


Fig 6:4 Synergistic effect of different molar ratios of UV531 and NTB on photo-oxidation of PP (total conc. 1×10^{-3} mole/100 gm)

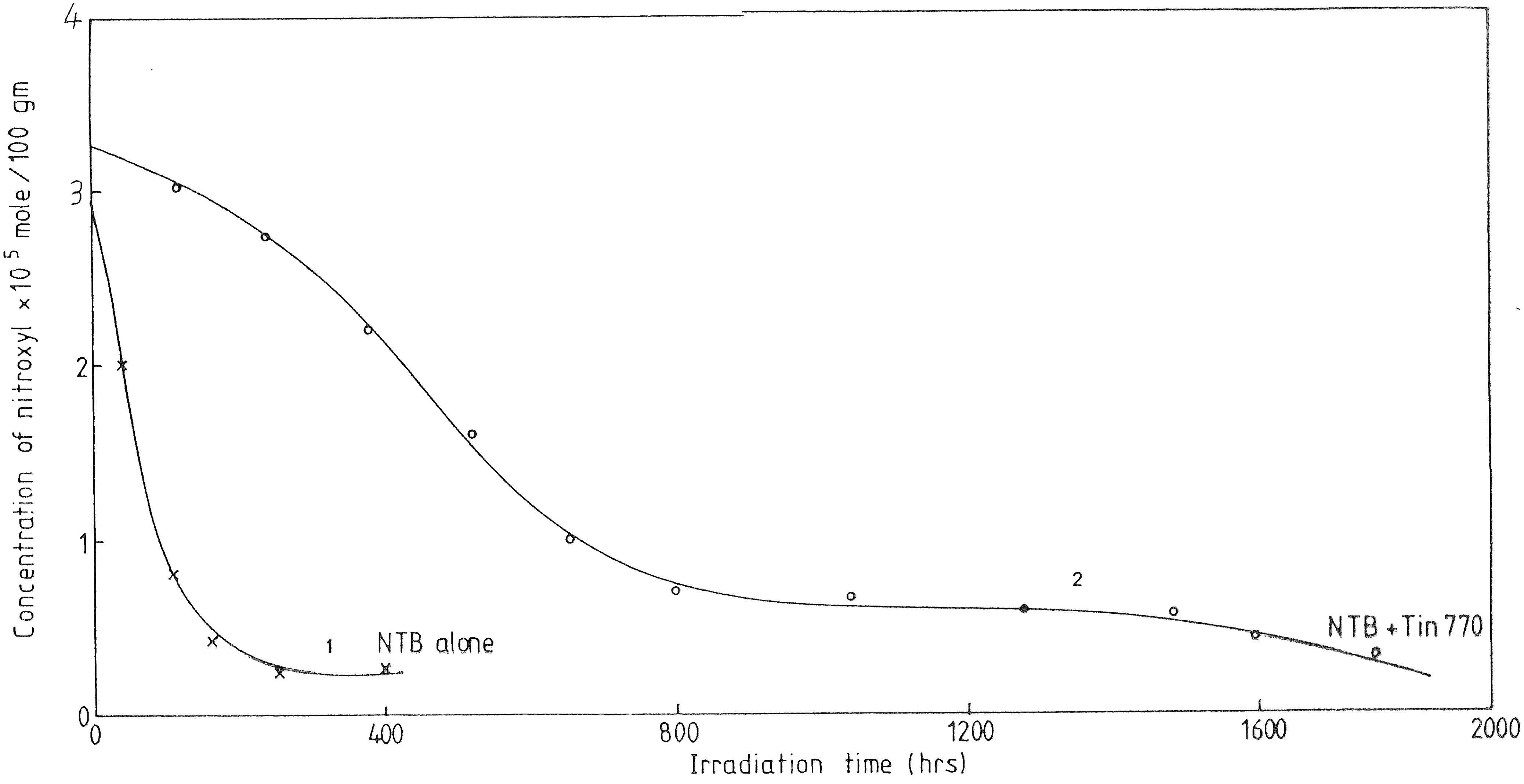


Fig 6:5 Rate of nitroxyl decay during photo-oxidation of PP containing Tinuvin 770 and NTB (Conc. of both 5×10^{-4} mole/100 gm

Table 6.1 Synergistic effect of nitroso and nitrone compounds on the U.V. embrittlement of pp containing other additives.

	Molar ratio	Mole/100gm (total)	UV embrittlement (hours)	Calculated on additive basis
Control		5×10^{-4}	85	
NTB		5×10^{-4}	410	
ZnDEC		5×10^{-4}	170	
Irganex 1076		5×10^{-4}	300	
UV 531		5×10^{-4}	340	
Tinuvin 770		5×10^{-4}	700	
DPN		5×10^{-4}	175	
NB (nitrosobenzene)		5×10^{-4}	210	
Tin + NTB	1:1	10×10^{-4}	≃2000	940
Tin + NB	1:1	10×10^{-4}	≃2000	740
UV 531 + NTB	1:1	10×10^{-4}	≃2000	540
Irg 1076 + NTB	1:1	10×10^{-4}	320	540
ZnDEC + NTB	1:1	10×10^{-4}	460	410
Tin + DPN	1:1	10×10^{-4}	800	705
UV 531 + DPN	1:1	10×10^{-4}	480	345
Irg 1076 + DPN	1:1	10×10^{-4}	275	305
ZnDEC + DPN	1:1	10×10^{-4}	160	175

Table 6.2 Effect of combination of nitroso and nitrone compounds with other additives on the thermal embrittlement of pp processed for 10 mins (Oven temperature 140°C).

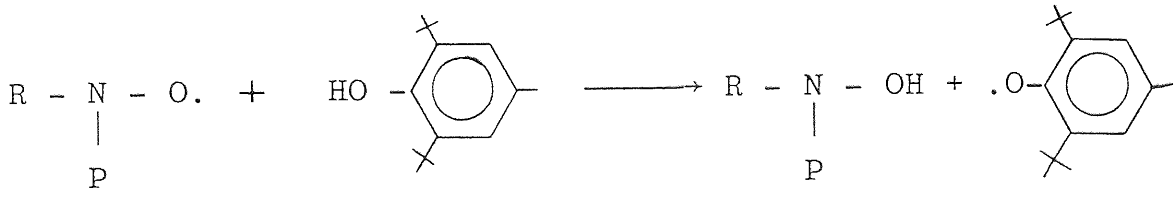
Additives	Molar Ratio	Mole/100 gm	Embrittlement Time (hrs)
pp Alone	-	-	≃ 0.5
UV 531	-	5×10^{-4}	≃ 0.7
Tin 770	-	5×10^{-4}	≃ 0.7
NTB	-	5×10^{-4}	≃ 0.7
ZnDEC	-	5×10^{-4}	≃17.0
Irg 1076	-	5×10^{-4}	≃40.0
Tin + NTB	1:1	10×10^{-4}	≃ 1.0
UV 531 + NTB	1:1	10×10^{-4}	≃ 1.0
ZnDEC + NTB	1:1	10×10^{-4}	≃17.0
Irg 1076 + NTB	1:1	10×10^{-4}	≃41.0
UV 531 + DPN	1:1	10×10^{-4}	≃ 1.0
ZnDEC + DPN	1:1	10×10^{-4}	≃17.0
Irg 1076 + DPN	1:1	10×10^{-4}	≃41.0
Tin + DPN	1:1	10×10^{-4}	≃ 1.0

Table 6.3 Effect of combination of nitroso and nitrone compounds with other additives on MFI of pp (Processing time 10 mins. at 180°C)

Additives	Ratio	Mole/100gm	MFI (Gm/10 mins)
Unprocessed pp			0.36
Irganox		5×10^{-4}	0.36
ZnDEC		5×10^{-4}	0.36
Tinuvin 770		5×10^{-4}	0.66
NTB		5×10^{-4}	0.40
Nitrosobenzene		5×10^{-4}	0.42
Diphenylnitrone (DPN)		5×10^{-4}	0.33 (cross linking)
Tin + NTB	1:1	10×10^{-4}	0.42
Irg + NTB	1:1	10×10^{-4}	0.36
UV531 + NTB	1:1	10×10^{-4}	0.41
ZnDEC + NTB	1:1	10×10^{-4}	0.36
Tin + DPN	1:1	10×10^{-4}	0.39
Irg + DPD	1:1	10×10^{-4}	0.34 (cross linking)
UV531 + DPD	1:1	10×10^{-4}	0.37
ZnDEC + DPN	1:1	10×10^{-4}	0.36
pp processed for 10 mins			1.70

corresponding hydroxylamine (BC-A/CB-D mechanism). NTB in this case, probably protects Tinuvin 770 during processing by trapping alkyl radicals and produces nitroxyl radicals. Nitroxyl radicals subsequently protect Tinuvin 770 during initial U.V. exposure stage by scavenging alkyl radicals; whereby the life time of Tinuvin 770 is increased. Only in the later stages of U.V. irradiation could Tinuvin 770 take part in the stabilisation process by conversion to nitroxyl radicals. It can be seen from the Fig. 6.5 that nitroxyl radicals produced from NTB alone during processing decays to almost zero concentration within 400 hours of irradiation (Curve 1, Fig. 6.5). It is also interesting to note that the nitroxyl radical concentration produced during processing from NTB is more or less the same both in presence and absence of Tinuvin 770. This evidence again suggests that Tinuvin 770 is probably not converted to nitroxyl radicals during processing in the presence of NTB. However, the rate of decay of nitroxyl radicals produced during U.V. irradiation containing both NTB and Tinuvin 770 is much slower compared to nitroxyl radicals produced from NTB alone. This could be due to generation of nitroxyl radicals from Tinuvin 770. In other words, Tinuvin 770 acts as a reservoir to replenish nitroxyl radicals.

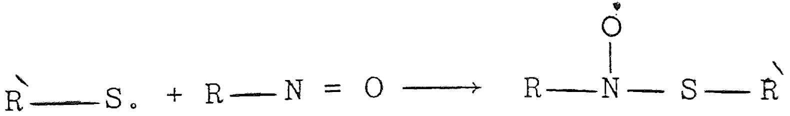
Nitroso-tert-butane in combination with a commercially used hindered phenol viz Irganox 1076 showed clearly antagonistic effect in polypropylene under photo-oxidative conditions (Fig. 6.6, and Table 6.1). However, they gave an almost additive effect in thermal oxidation. It can be seen from the Fig. 6.7 that the effectiveness of NTB is very much reduced in the presence of Irganox 1076 (antagonistic effect). It has already been shown (Chapter 3) that NTB is converted to nitroxyl radicals during processing. However, in the presence of hindered phenol, nitroxyl radicals could extract hydrogen from phenols producing hydroxylamine and phenoxyl radicals$^{(165)}$(reaction 1) subsequently phenoxyl radicals form



(1)

quinone under U.V. exposure condition and quinones are known to photo-sensitise$^{(151)}$ the photo-oxidative degradation of polymers.

NTB again shows antagonistic effect with peroxide decomposer ZnDEC under U.V. exposure in polypropylene (Fig. 6.7 and Table 6.1). The mechanisms of action of NTB in the presence of ZnDEC probably involves the trapping of thiyl radicals (produced from ZnDEC) by nitroso compounds according to reaction (2). Presumably,



$$R'-S\cdot + R-N=O \longrightarrow R-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-S-R' \qquad (2)$$

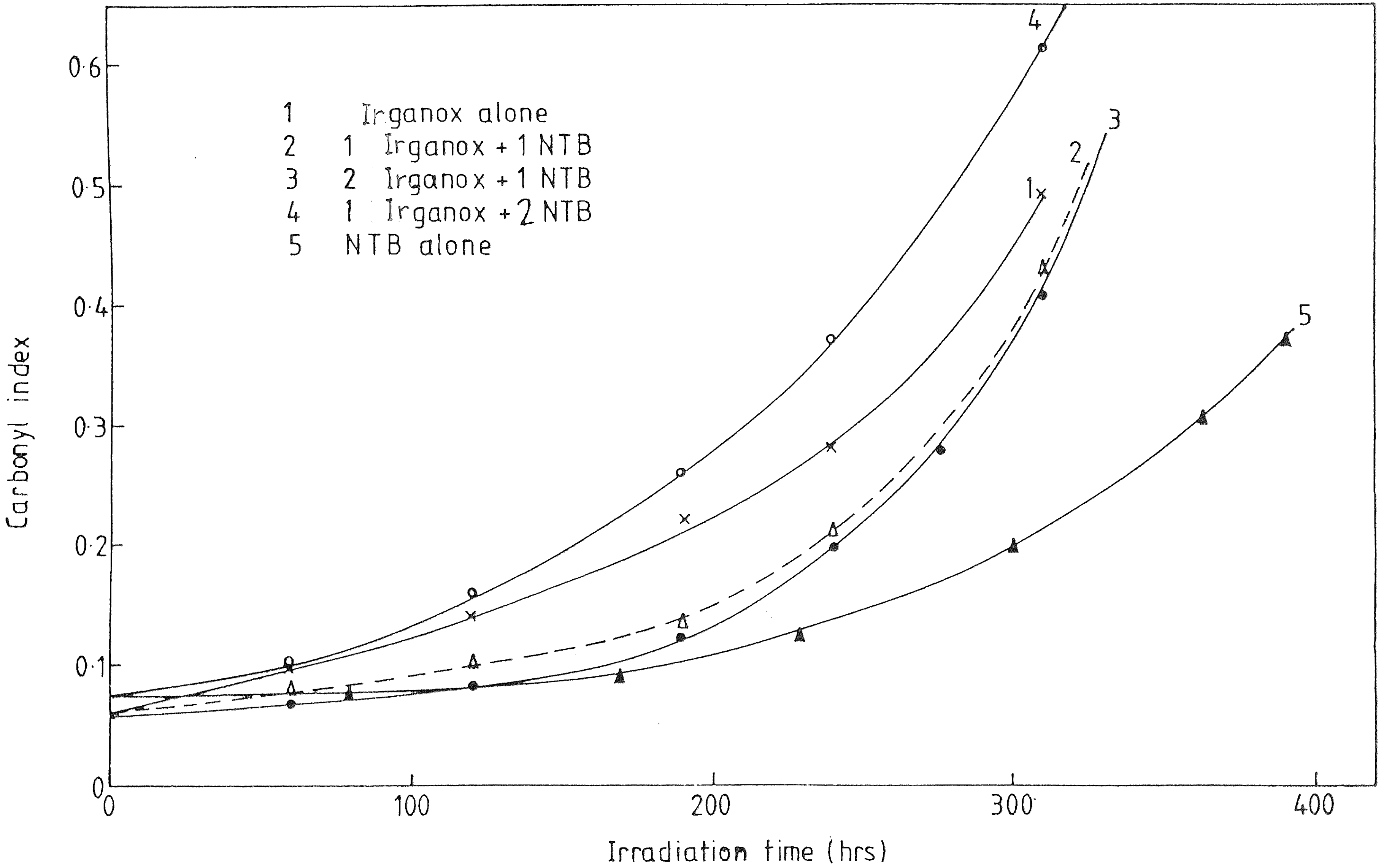


Fig 6:6 Rate of carbonyl formation during photo-oxidation of PP containing Iraganox 1076 and NTB at different molar ratios (total conc. 1×10^{-3} mole /100 gm)

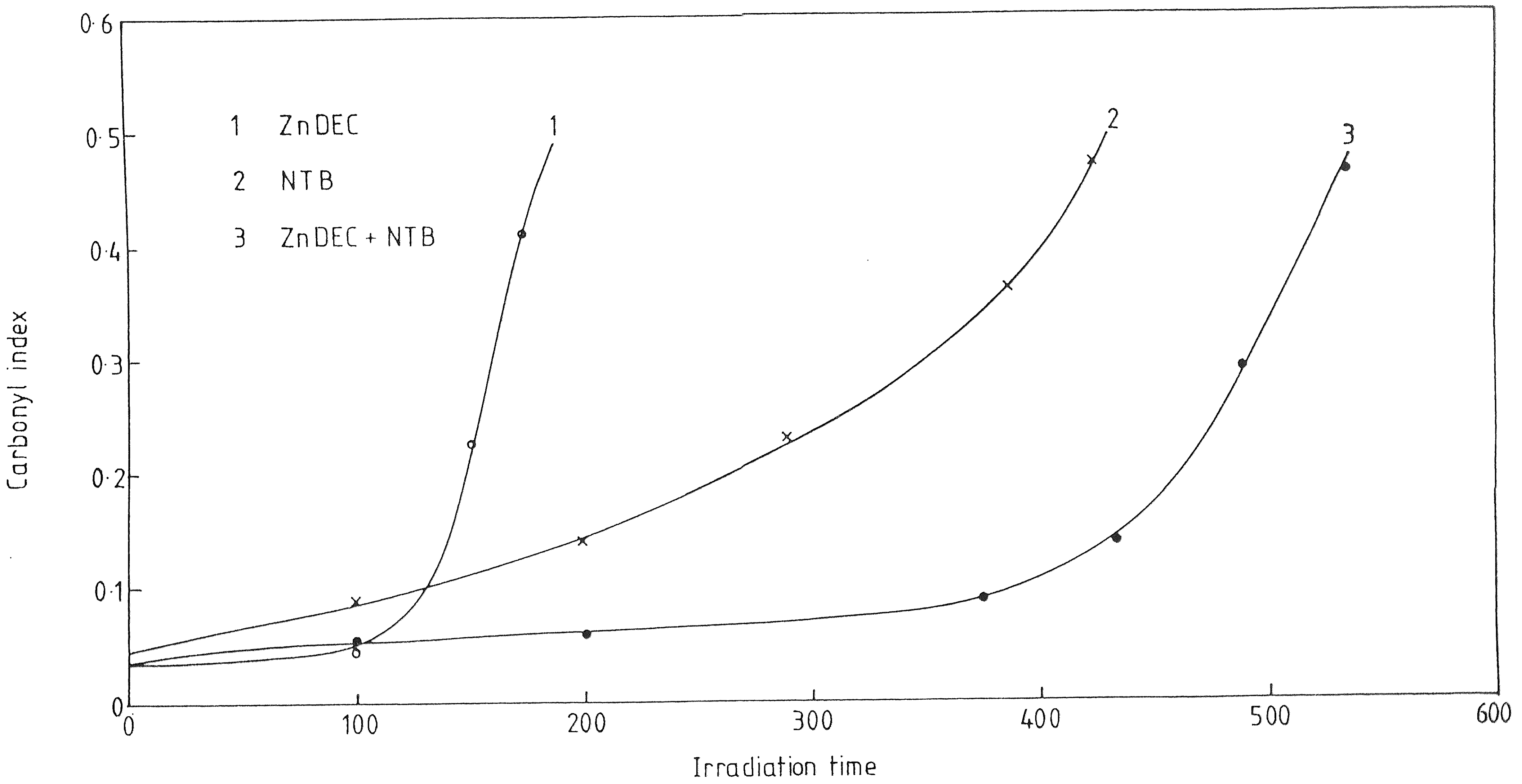


Fig 6:7 Effect of combination of ZnDEC and NTB on the photo-oxidation of PP (concentration of each 5×10^{-4} mole/100 gm)

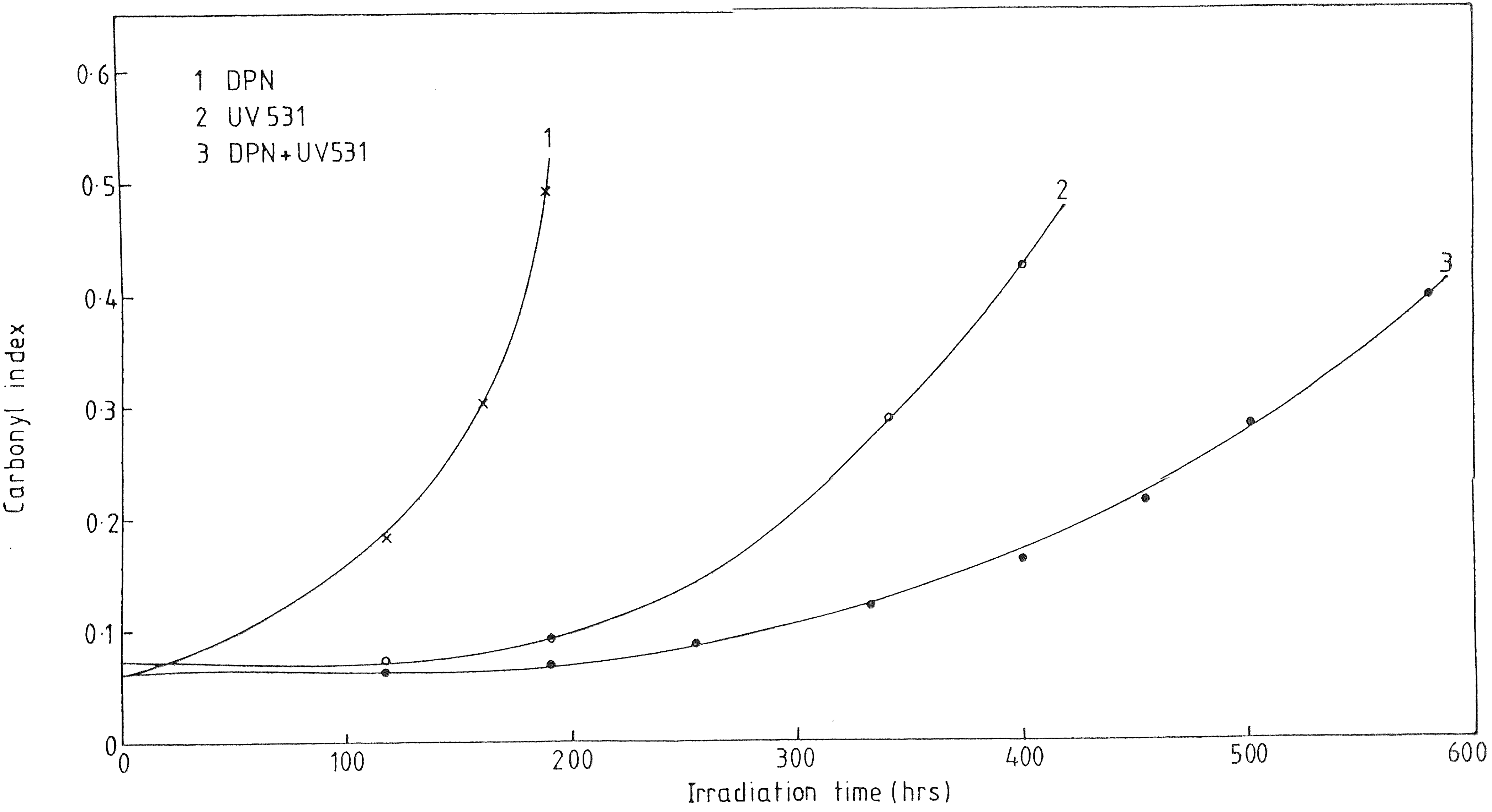


Fig 6:8 Effect of combination of DPN and UV 531 on the photo-oxidation of PP (concentration of each 5×10^{-4} mole/ 100 gm)

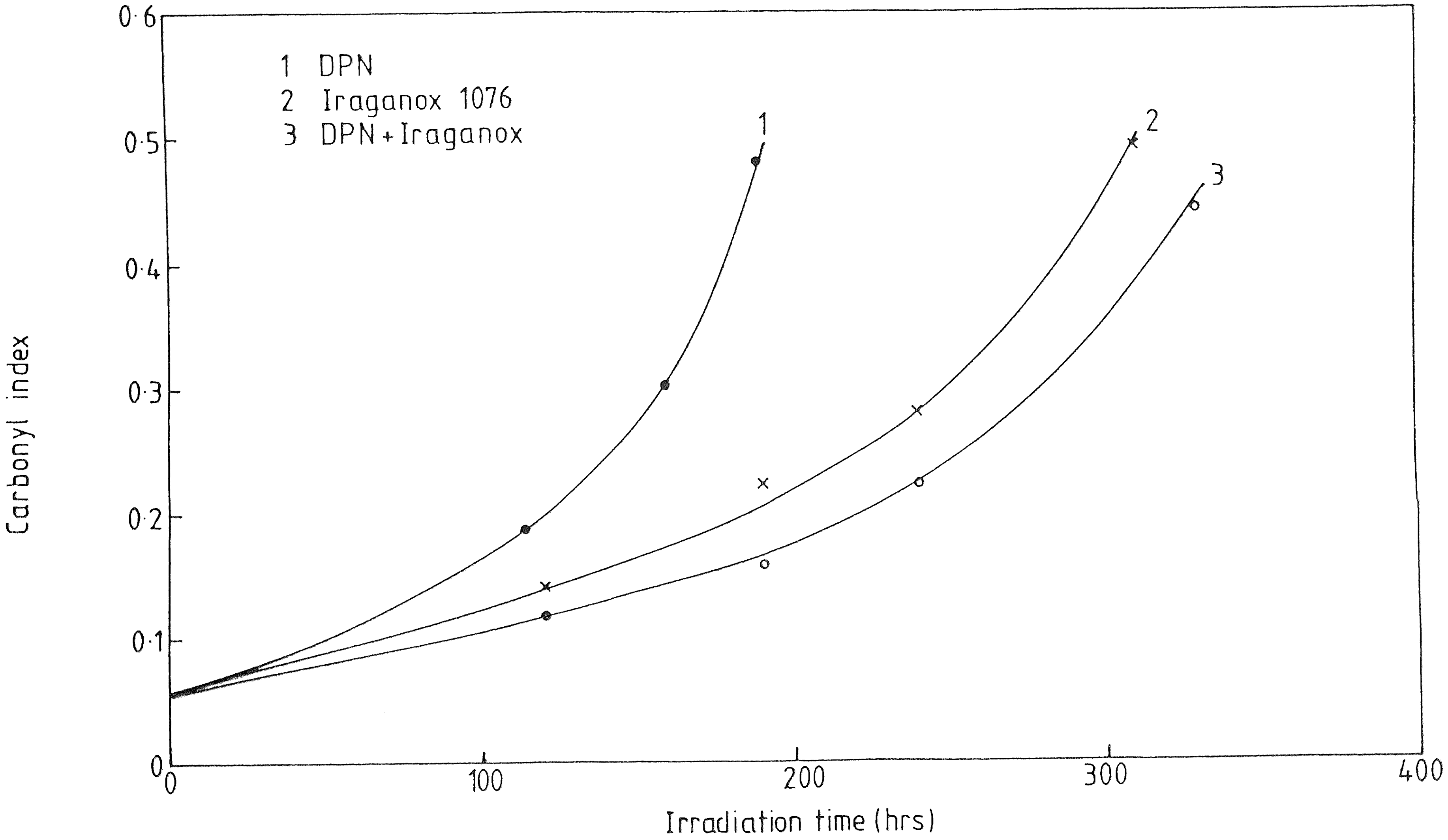


Fig 6:9 Effect of combination of DPN and Iraganox 1076 on the photo-oxidation of PP (concentration of each 5×10^{-4} mole/100 gm)

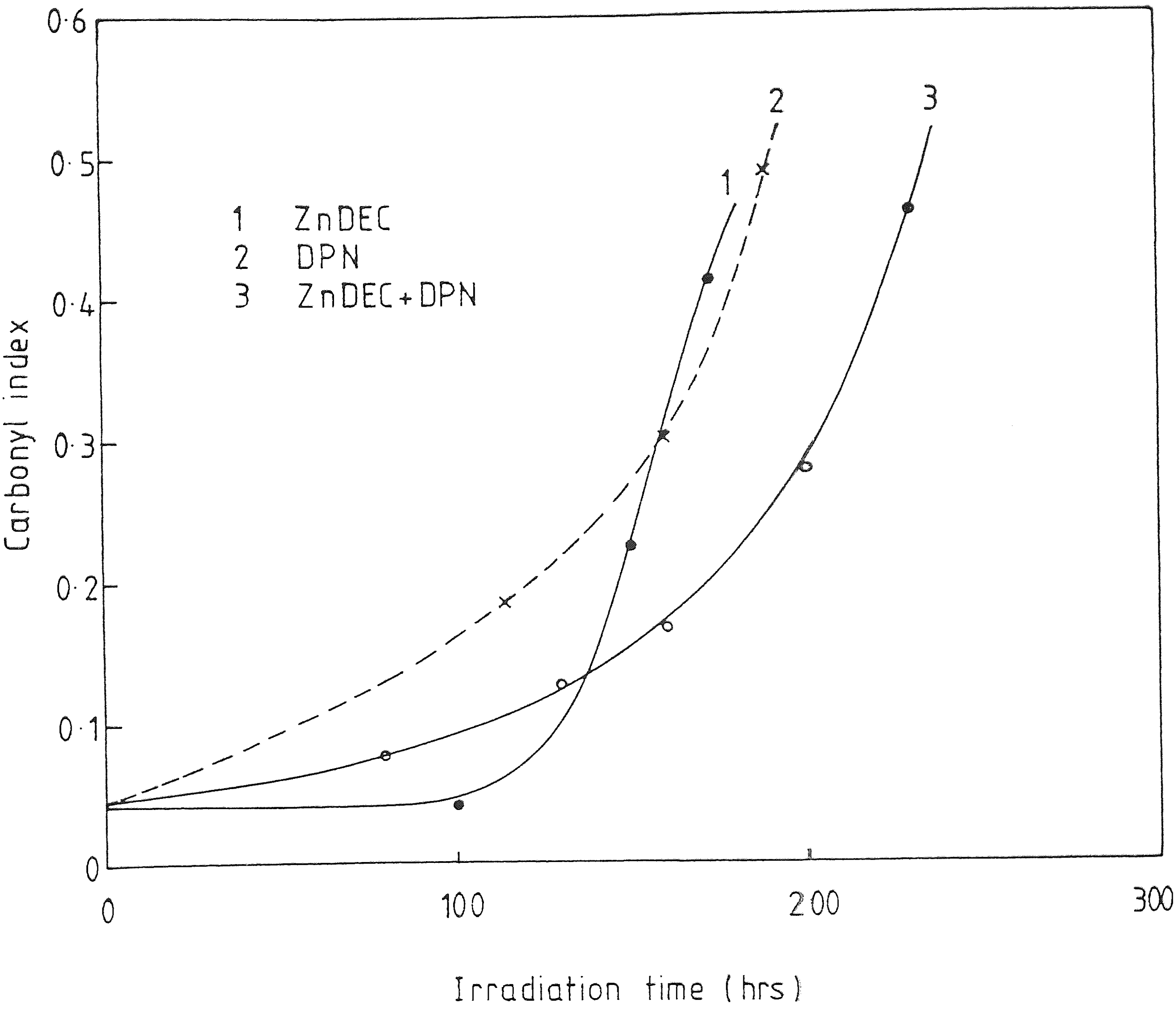


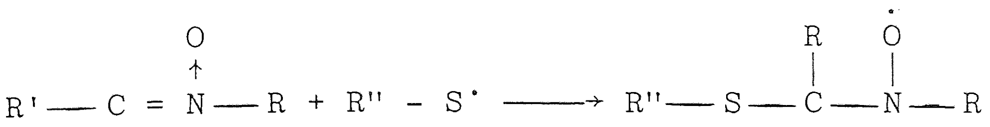
Fig 6: 10

Effect of combination of DPN and ZnDEC on the photo - oxidation of PP (concentration of each 5×10^{-4} mole/100 gm) according to reaction (2), the activity of ZnDEC as a peroxide decomposer as well as scavenging ability of alkyl radicals by nitroso compounds will both be reduced. Moreover, ZnDEC is known(138) to photolyse fairly rapidly and nitroxyl radicals cannot protect ZnDEC from photolysis.

It has been shown in the Chapter 4, that diphenyl nitrone (DPN) is not effective thermally but is a fairly effective U.V. stabiliser in polypropylene. It is known that nitrones are not as efficient as aliphatic nitroso compounds as alkyl radical traps. Moreover, aromatic nitrones form quinonoid structures under U.V. irradiation.

DPN shows an almost additive effect with U.V. 531 and Tinuvin 770 (Fig. 6.8 and Table 6.1) and a clearly antagonistic effect with Irganox 1076 (Fig. 6.9 and Table 6.1) and ZnDEC under photo-oxidative conditions (Fig. 6.10 and Table 6.1).

Thiyl radicals produced from ZnDEC either during thermal processing or U.V. irradiation(140) may react with DPN (reaction 3), consequently the activity of both components



$$R'-C=\overset{\overset{O}{\uparrow}}{N}-R+R''-S^{\bullet}\longrightarrow R''-S-\overset{\overset{R}{|}}{C}-\overset{\overset{\dot{O}}{|}}{N}-R \qquad (3)$$

will be reduced. On the other hand, the trapping of thiyl radicals by DPN instead of alkyl radicals reduced the efficiency of both compounds as alkyl radical scavenger

(DPN) and hydroperoxide decomposer (ZnDEC).

Nitroxyl radicals generated from DPN during polymer processing, probably oxidize(165) Irganox 1076 to the corresponding quinone. The presence of the photoactive(151) quinone form could account for the antagonistic effects observed.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Conclusions

During thermal processing of polypropylene, chain scission occurs and alkyl radicals are produced. Once alkyl radicals are formed, they may react with available oxygen to give alkylperoxy radicals. The peroxy radicals are then converted by radical exchange to hydroperoxide, which in turn will cleave to an alkoxy radical. Since the chemical processes occurring during photo-oxidation of polyolefins are basically similar to those occurring during thermal processing operations, the prior thermal history of these polymers will, to a major extent, determine their behaviour during photo-oxidation. In particular, the extent to which hydroperoxides are formed during thermal processing operations will determine the rate of photo-oxidation during the initial stages of light exposure of the polymer.

Therefore, removal of active radicals ($\dot{R}$, $ROO^{\cdot}$) formed in the initial stage of processing by efficient free radical scavengers will lead to inhibition of hydroperoxides formation. Active radicals could be deactivated by a CB-A or CB-D mechanism. Any compounds possessing both types of the mechanisms will stabilise the polymer effectively during processing, as well as thermal and photo-oxidation.

This study clearly shows that C-nitroso compound, nitrones and N-nitrosamines stabilise polypropylene effectively against heat and light.

(1) C-nitroso compounds terminate macro alkyl or alkoxy radicals during processing forming bound nitroxyl radicals to polymer chains, subsequently inhibited the formation of hydroperoxide. Polypropylene has been found to cross link in the presence of nitroso-tert-octane, tetramethylnitrosobenzene, pentamethylnitrosobenzene and N,N-dimethyl-4-nitrosoaniline.

(2) Aliphatic C-nitroso compounds are more effective U.V. stabilisers than aromatic nitroso compounds. This is due to the fact that the latter produce quinonoid structures which might sensitise photo-oxidation process. The high photo stabilising activity of aliphatic nitroso compounds is due to the inhibition of hydroperoxide formation during processing stage by scavenging alkyl radicals. Aliphatic nitroso compounds are not as effective as antioxidant as aromatic nitroso compounds.

(3) Nitrones act as very effective melt stabilisers and cross linking is observed in the polymer. One of the

characteristic reactions of nitrones is their ability to terminate macro alkyl radicals through nitrone function (CB-A mechanism), forming bound nitroxyl radicals. Phenolic nitrones are more effective melt stabilisers during processing in excess of air. Under this condition phenolic nitrones deactivate short lived radicals (R$^\cdot$, ROO$^\cdot$) either by phenolic group (CB-D mechanism) or nitrone function (CB-A mechanism).

Subsequent thermal and photo-stabilisation activity of nitrones depend on the nitroxyl radical formed and unreacted nitrones during thermal processing. Phenolic nitrones are effective antioxidants due to the activity of phenolic groups of unreacted nitrones to terminate ROO$^\cdot$.

(4) N-nitrosamines are effective melt stabilisers during processing in closed mixer. But their activity is very much reduced when processed in excess of air. The activity of N-nitrosamines is mainly due to their decomposition into amino radicals and nitric oxide which is powerful alkyl radical scavenger, forming bound nitroxyl radicals. This nitroxyl radicals are the active species in polymer stabilisation process during U.V. irradiation. Aliphatic and cyclo-aliphatic N-nitrosamines are ineffective antioxidants, but diphenylnitrosamine is a very effective antioxidant.

In general, it may be concluded that the C-nitroso compounds, nitrones and N-nitrosamines react with alkyl radicals during processing (which predominate during processing in difficiency of oxygen) and produce nitroxyl radicals, and subsequently alkylated hydroxylamine. As a result formation of hydroperoxide is inhibited which is the most important initiator species. The nitroxyl radicals then take part in the U.V. stabilisation process involving CB-A and CB-D stabilisation mechanisms via hydroxylamine.

(5) C-nitroso compounds synergises very effectively with both U.V. 531 and Tinuvin 770 under photo-oxidative conditions, whilst the combined effect of carbon-nitroso compounds, with hindered phenols and peroxide decomposer (ZnDEC) is antagonistic. The studies on the mechanism of synergistic action showed that the additives protect each other during thermal processing and subsequent U.V. exposure stage and hence increased the period of their action. C-nitroso compounds have the ability to protect U.V. 531 from peroxide due to alkyl radical scavenging during processing and initial photo-oxidative stage and in turn U.V. 531 can protect nitroxyl radicals produced from nitroso compounds from photolysis due to its U.V. screening ability. In case of Tinuvin 770, C-nitroso compounds protect Tinuvin 770 during processing and subsequently during the later part of photo-oxidation process, Tinuvin 770 supplies

nitroxyl radicals which is the important photo-stabilising species. The antagonism between C-nitroso compound and Iraganox 1076 and ZnDEC could be due to the interaction in each others actions.

Aromatic nitrones in general showed nearly additive effect with both U.V. 531 and Tinuvin 770 and very antagonistic effect with both hindered phenol (Iraganox) and peroxide decomposer (ZnDEC) during photo-oxidation. The antagonistic effect in all cases has been found to be due to the formation of quinonoid structure derived from nitrone during U.V. irradiation which could photo-sensitise the photo-oxidation process.

7.2 Suggestions for Further Work

Cross-linking reaction in polypropylene suggests that the alkylated hydroxylamine has been formed. It is interesting to investigate the effect of synthesised alkylated hydroxylamine on the thermal processing and U.V. stabilisation process, as well as to examine their stability under thermal and U.V. irradiation conditions and identify the products. The effect of the alkyl hydroxylamines in model compounds under thermal and U.V. irradiation conditions should be studied in detail.

It was found that aromatic nitrones produce quinonoid structure, which might sensitise the photo-oxidation process.

Therefore, it would be necessary to synthesise the quinones (as produced from aromatic nitrones) and to study the effect of their activity on oxidative stability of polypropylene. The stabilisation activity of aliphatic nitrones may also be studied.

It would be useful to study the effect of the bulky chains length (particularly cyclic chains) in C-nitroso compounds on the photo-stability of polypropylene.

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