A STUDY OF MECHANOCHEMICAL REACTIONS OF SPIN TRAPS IN HYDROCARBON POLYMERS

PART I

THE PHOTOSTABILITY OF POLYPROPYLENE MODIFIED WITH SPIN TRAPS DURING PROCESSING

PART II

THE EFFECT OF NATURAL RUBBER MODIFICATION BY SPIN TRAPS ON THE FATIGUE LIFE AND THERMAL ANTIOXIDANT ACTIVITY OF THE VULCANISATE

by:

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A Thesis submitted for the degree
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THE UNIVERSITY OF ASTON IN BIRMINGHAM

PART I

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Summary

The identification and quantification of spin adducts and their reduction products (>NOH, >NOR) formed from nitroso compounds and nitrones in EPR and PP during spin trapping techniques have been examined. The nitroxyl yield and polymer bound nitroxyl percentage formed from these spin traps were found to be strongly dependent on the nature of spin trap and radical generator, processing temperature, and irradiation time. The nitroxyl yield and % bound nitroxyl of the spin traps improved significantly in the presence of Trigonox 101 and 2-OH benzophenone.

The effect of these spin traps used as normal additive and their spin adducts in the form of EPR-masterbatch on the photo and thermal-oxidation of PP have been studied. Aliphatic nitroso compounds were found to have much better photo-antioxidant activity than nitrones and aromatic nitroso compounds, and their antioxidant activity improved appreciably in the presence of, a free radical generator, Trigonox 101, before and after extraction.

The effect of heat, light and oxidising agent (meta-dichloro per benzoic acid) on the nitroxyl yield of nitroso tertiary butane in solution as a model study has been investigated and a cyclic regenerative process involving both chain breaking acceptor and chain breaking donor process has been proposed.

Keywords Spin trap, Spin trapping technique,Nitroxyl radicals,Polymer-bound nitroxyls, Photo-antioxidant activity.

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ST = Spin trap
R-ST· = Spin adduct
EPR = Ethylene propylene rubber
ESR = Electron spin resonance
RG = Radical generator
Bph = Benzophenone
AIBN = Azo bis isobutyronitrile
DCP = Dicumyl peroxide
MCPBA = meta-Dichloroperbenzoic acid
>NOR = Alkyl hydroxylamine
>NOH = Free hydroxylamine
>NO· = Nitroxyl radical
CB-A = Chain breaking acceptor
CB-D = Chain breaking donor
EPDM = Ethylene propylene terpolymer rubber
CV = Controlled viscosity
Phr = Parts per hundred parts of rubber(g/g)

Abbreviation of the spin traps used in this study is given in table 4.

CHAPTER 1

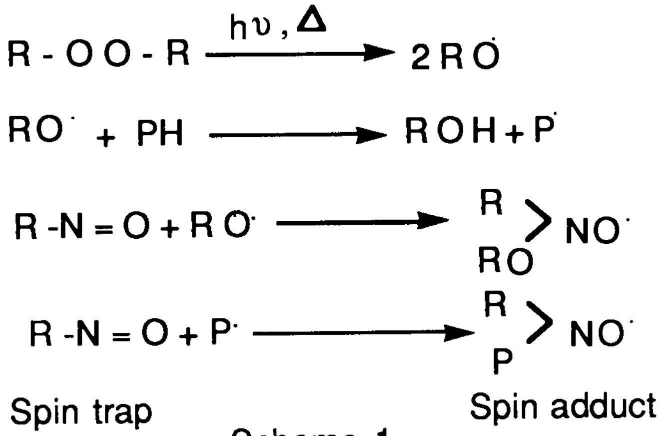
INTRODUCTION

1.1 Introduction

Antioxidants and light stabilisers are used to extend the service life of polyolefins. The useful properties and relatively low cost of polyolefins make them very suitable for use in many applications. However, because of their poor stability to sunlight, polyolefins, and especially polypropylene, have to be light-stabilised for outdoor applications. Two factors are responsible for the effectiveness of a stabiliser in a polymer, namely the intrinsic stabiliser behaviour and the permanence of stabiliser in polymer. Polymer-bound antioxidants might provide a solution to the problem of stabiliser loss from polymers during processing and use.

Polyolefins which are subjected to shear and heat (150-300°C) during processing and fabrication, in the absence of melt stabilisers, build up hydroperoxides, which are the subsequent cause of photo-oxidation during environmental exposure.

It is increasingly being recognised that the low activity of many antioxidants and UV stabilisers during service is due not to the low intrinsic activity of the chemical species used but rather to the fact that they are too readily lost from the polymer due to volatilisation and leaching (1-3). Therefore, polymer scientists are becoming interested in using internal mixers and extruders as chemical reactors to bind the polymer matrix. This can be done, by making use of the macroalkyl radicals produced either under high shear conditions (4) or by photolytic fission. The addition of radical generators to these mechanochemical and photochemical reactions, which will produce additional free radical sites on the polymer chain, could also be advantageous in spin trapping techniques, according to Scheme 1:



$$R\text{-}OO\text{-}R \xrightarrow{h\upsilon,\Delta} 2R\dot{O} \qquad 1$$

$$RO^{\cdot} + PH \longrightarrow ROH + P^{\cdot} \qquad 2$$

$$R\text{-}N{=}O + RO^{\cdot} \longrightarrow \overset{R}{\underset{RO}{>}}NO^{\cdot} \qquad 3$$

$$R\text{-}N{=}O + P^{\cdot} \longrightarrow \overset{R}{\underset{P}{>}}NO^{\cdot} \qquad 4$$

Scheme 1

According to Scheme 1, the alkoxy radical formed may abstract a hydrogen from the polymer chain (reaction 2), followed by reaction 4, or react with the spin trap (reaction 3). However, the concentration of spin traps normally used as antioxidant is quite low relative to the substrate so there is a higher probability of the alkoxy radical reacting with polymer (reaction 2).

1.2 Oxidative Degradation of Commercial Polymers

Most commercial polymers are relatively stable to oxidation as they are manufactured. For example, PE, PP and EPR as they come from the polymer synthesis process show only slow chemical or physical changes if stored at ambient temperatures in the dark. However, during their conversion to fabricated end products in which they are subjected to high temperatures and high shearing forces, oxidative degradation is inevitable.

Degradation of polymers may be regarded as a type of modification involving the main chain backbone and/or side groups, these modifications are chemical in nature i.e, they require the rupture or formation of primary valence bounds, leading to lower molecular weight, cross linking, cyclisation or elimination. Since degradation is a chemical process it affects not only the chemical compositions of the polymer but also physical parameters such as molecular weight, molecular weight distribution, crystallinity, cross-linking, branching and chain flexibility. Such modifications have a profound effect on its subsequent service performance. Oxidative degradation reactions are generally believed to involve a free radical chain reaction as proposed by Bolland and Gee (5).

The main steps of this reaction are:

Chain initiation $RH + O_2 \xrightarrow{h\upsilon,\ \Delta} R^{\cdot} + {}^{\cdot}OOH$ 5

Chain reaction $R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$ 6

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$ 7

Chain branching

$ROOH \xrightarrow{h\upsilon,\ \Delta} RO^{\cdot} + HO^{\cdot}$ 8

$2ROOH \longrightarrow RO^{\cdot} + ROO^{\cdot} + H_2O$ 9

$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$ 2

$HO^{\cdot} + RH \longrightarrow HOH + R^{\cdot}$ 10

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$ 11

Chain termination

$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R$ 12

$R^{\cdot} + RO^{\cdot}_2 \longrightarrow ROOR$ 13

$2ROO^{\cdot} \longrightarrow ROH + R'COR'' + O_2$

14

Scheme 2

Radicals formed during the initiation step react with oxygen leading to a chain reaction (equations 6, 7). The decomposition of hydroperoxide by heat or U.V. light (equation 8) causes formation of alkoxy and hydroxyl radicals leading to chain branching. At sufficiently high concentrations of dissolved oxygen chain termination proceeds particularly exclusively by reaction 13.

1.2.1 Thermal degradation during melt processing and service

The conversion of a thermoplastic polymer to a finished article normally involves heating it to the liquid state followed by extrusion through a die into a mould. During this processing operation, considerable shear is applied to the viscous polymer melt which causes some of the chains to undergo homolytic scissions at the carbon-carbon bonds with the formation of macro-alkyl radicals. These radicals initiate the radical chain sequence 6 and 7.

Reduction in molecular weight of thermoplastic polymers during processing is thus a serious problem, since the final properties of the fabricated product depends on the molecular weight of the polymer. Furthermore, hydroperoxides and their breakdown products are a potential source of oxidation instability in the product.

The temperature at which thermoplastic polymers are used is limited by the fact that they undergo dimensional changes (creep) at high temperatures. With trend towards fiber reinforcement, however, this situation is rapidly changing and oxidative stability of some plastics up to temperatures of 120°C for considerable lengths of time may be demanded in some end uses (e.g in the motor car engine)

Vulcanised rubbers on the other hand, can be and are used at high temperatures because of their cross-linked structure. Although rubbers have good short term dimensional stability, unless effectively stabilised they undergo long term dimensional changes (creep and permanent set) in the presence of oxygen.

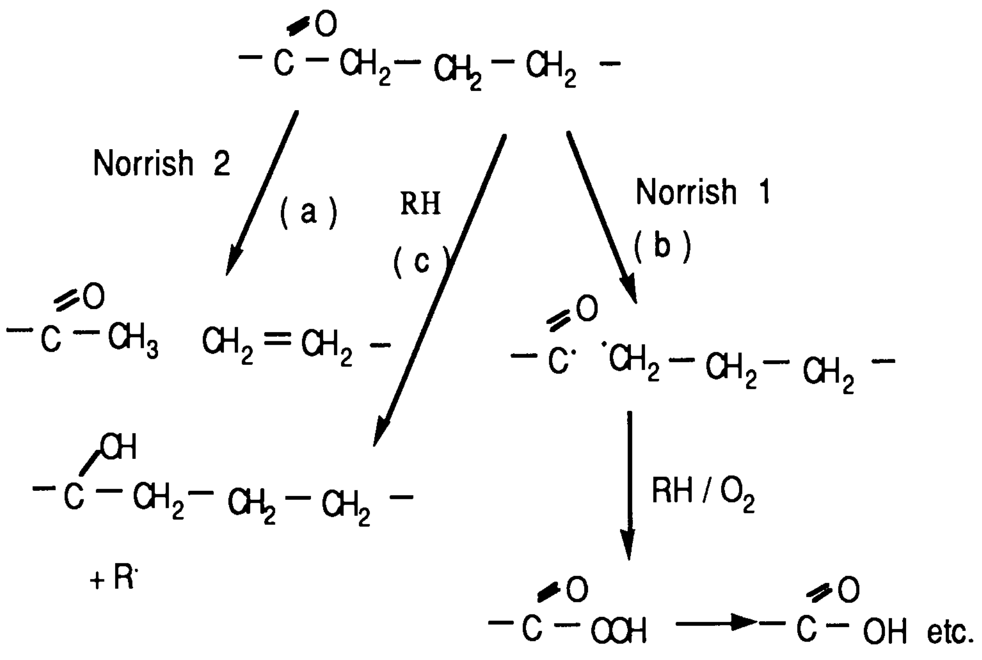
1.2.2 Photo-oxidation

Scott points out (6) that the most important accelerating environmental influences, apart from oxygen which cause deterioration of the polymer are heat, light, ozone and mechanical stress.

The early studies of Bolland and Gee (7,8) established that the basic mechanism of photo-oxidation of olefinic polymers is the same as that involved in thermal oxidation, the main difference lies in the much more rapid formation of hydroperoxides in photo-oxidation which are the common initiators of both processes. Photo-oxidation is oxygen diffusion controlled and higher termination from R· + ·OOR etc. occurs. This leads to higher radical concentration and shorter kinetic chains (9).

Although the energy distribution in the solar spectrum in space extends to short wavelength 200nm (10,11) almost all incident radiation of wavelength less than 290nm is absorbed in the earth's atmosphere. Therefore, very little of the shorter wavelength radiation reaches the earth's surface (11,12). Most of the absorption at the shorter wavelength is caused by a layer of ozone which exists at high altitudes. Therefore, only light having a wavelength exceeding 290nm reaches the earth's surface. Polyolefins, unlike pure hydrocarbons, absorb weakly at longer wavelengths than this and it has been recognised for many years that the sensitivity of unstabilised hydrocarbon polymers can be attributed to impurities, particularly oxygen-containing species, introduced during the manufacturing and/or fabrication processes, that may initiate photochemical reaction. The main light absorbing species are believed to be unsaturation, carbonyl groups, hydroperoxides and metallic impurities. Recent research indicates that carbonyl and hydroperoxide groups are the major initiators (13,14).

The predominant reaction occurring, at least during the early stages of polyolefin photodegradation is the Norrish II reaction (Scheme 2(a)) (15,16). This process, can occur equally readily in the absence of oxygen and since it does not involve the production of free radicals it is not an initiating reaction for photo-oxidation. The Norrish I process (Scheme I(b)) does give rise to free radicals but with a lower quantum efficiency (16), since the radicals have difficulty in escaping from the "cage" in the viscous polymer medium. A third reaction (Scheme 2 (c)) can also give rise to free radicals and this is probably a major source of free radicals in the later stages of photo-oxidation when carbonyl groups are present in substantial amounts. The evidence suggests (17-23) that hydroperoxides rather than carbonyl compounds are the important initiators for photo-oxidation of polyolefins during the initial stages of photo-oxidation.



Scheme 3

Since the chemical processes occurring during photo-oxidation of polyolefins are basically similar to those occurring during the thermal processing operation, 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.

1.3 The Chemical Mechanisms of Antioxidant Action

The radical chain reaction of hydrocarbon oxidation involves three main processes, initiation (scheme 2 reaction 5), propagation (scheme 2 reaction 7,8) and termination (scheme 2 reactions12-14), and antioxidants can be classified by the way in which they interfere with these processes (24).

The chain-breaking mechanism of antioxidant action has been extensively studied in industry and in academic laboratories since the pioneering work of Lowry (25) and of Bolland and his coworkers (26,27) who showed that reducing agents were able to intercept the chain-propagating alkylperoxyl radical and replace it by a radical which is too stable to continue the kinetic chain:

$$\mathrm{ROO^{\cdot} + AH \xrightarrow{CB-D} ROOH + A^{\cdot}} \qquad 15$$

This process, which is now known as the chain-breaking hydrogen(or electron) donor (CB-D) mechanism (28), is the basis of many commercial antioxidants, notably phenols and aromatic amines.

Recently, however, it has been recognised that under certain circumstances, A· can also be reduced back to AH by a second chain-breaking mechanism in which a hydrogen (or an electron) is transferred from an intermediate chain carrying alkyl radical to the antioxidant radical (28-30):

$$\mathrm{R^{\cdot} + A^{\cdot} \xrightarrow[CB-A]{(a)} RA \xrightarrow[h\nu,\,\Delta]{(b)} AH + {>}C=C{<}} \qquad 16$$

The conditions favouring this process are (30):

(a) when A· is a relatively stable radical or an oxidation state of a metal ion and can form a Redox couple with AH;

(b) when oxygen access to the site of the reaction is limited, for example, as a result of diffusion in a solid polymer or in a melt processing operation;

(c) a high rate of initiation, particularly when this is mediated by stress, for example, by mechanical scission of the polymer chain (reaction 17), or by U.V. irradiation:

$$\mathrm{R-R \xrightarrow{Shear} 2\,R^{\cdot}} \qquad 17$$

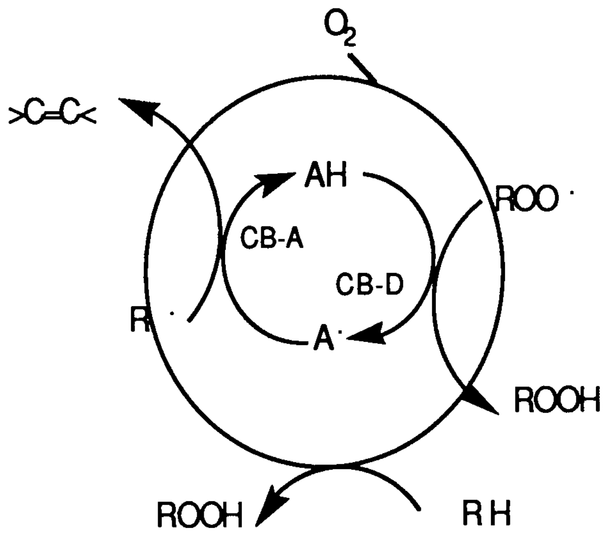
which leads to photolysis of hydroperoxides always present in polymers (reaction 18):

$$ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH \qquad 18$$

(d) when the substrate is very sensitive to oxidation (e.g. in olefinic polymers so that termination can occur through the alkyl radical (reactions 12,13 and consequently reaction 16 can successfully compete with reaction 6), since reactions 6 and 7 constitute a chain reaction in which the reactive intermediates are continually regenerated, reactions 15 and 16 can also be cyclical provided one or more of the above conditions are satisfied. In these circumstances the antioxidant species of the main antioxidant cycle (see Scheme 4), gives rise to a highly effective catalytic antioxidant process. This mechanism has been shown to operate in the mechano-oxidation of polymers in the melt (31,32) and during mechano-oxidation (fatiguing) of rubbers subjected to cyclical deformation (e.g. in tyres) (33,34). It also explains the very high activity of the hindered amine light stabilisers in polymers. The mechanism is somewhat more complex in this case, but it is known that the CB-A antioxidant is the nitroxyl formed by oxidation of secondary amine (reaction 19).

$$>NH \xrightarrow{ROOH} >NO^{\cdot} \qquad 19$$

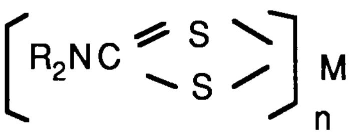
There is conflicting evidence as to the nature of the CB-D antioxidant, some authors believe it to be the alkylhydroxylamine initially formed in reaction 16 (a) (27), but others believe that the free hydroxylamine may also be involved as a result of reaction 16(b) (35):



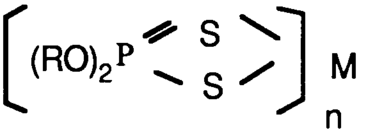
Scheme 4. Mechanism of catalytic chain breaking antioxidants

There is evidence that nitroxyl can also be readily reformed from both the alkylhydroxylamine and the free hydroxylamine by oxidation with hydroperoxides and peroxides present in the polymer (36).

The preventive mechanism of antioxidant action is concerned with the removal of indigenous initiators for the autoxidation process. Most preventive antioxidants are concerned either with preventing the breakdown of hydroperoxides by metal catalysis (i.e. by metal deactivator), or by photolysis (i.e. by UV absorption), or with the decomposition of hydroperoxides by reactions which do not lead to the formation of free radicals. The peroxide decomposing mechanism is by far the most important preventive mechanism in polymer technology because of the fundamental importance of hydroperoxides in autoxidation (37,38). The most widely used class of peroxidolytic antioxidants are the organo-sulphur compounds which include the dialkyl dithiocarbamate (I), the dialkyl dithiophosphates (II), and the well known synergists, the dialkyl thiodipropionate esters (III).



I



II

$(ROCOCH_2CH_2)_2S$

III

They all act by being slowly oxidised by hydroperoxide to sulphur acids which are effective catalysts for peroxide decomposition (37,38). The dithiocarbamates are used in a wide range of polymers as antioxidant in their own right. These include vulcanised rubbers, where they are formed in situ in the vulcanising system and are the basis of the high temperature oxidation resistant EV rubbers and in polyolefins, where the transition metal complexes are highly effective broad spectrum (processing, heat and light) stabilisers (39).

1.4 The Spin Trapping Technique

The direct detection and identification of short-lived free radicals by electron spin resonance (ESR) is possible only if the radicals are produced in relatively high concentrations ($>10^{-8}$M) in the ESR cavity by intense in situ irradiation or by rapid mixing flow system. However, in the last two decades, three independent groups, Lagercrantz and Forshult (40), Janzen and Blackburn (41) and Chalfont et al. (42), recognised that a general procedure for the investigation of free radical reactions might be available if the addition of reactive free radicals to nitroso and nitrone compounds was combined with the ESR observation of the resulting persistent nitroxyl free radical product (spin adduct) (43). The procedure was called "spin trapping" by Janzen (44) in 1969.

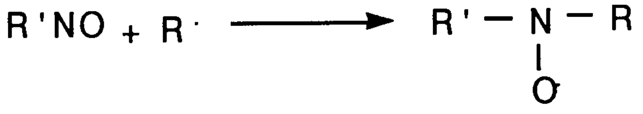
Spin trapping involves the reaction of a reactive free radical, R·, with a diamagnetic spin trap, ST, to form a less reactive free radical product, the spin adduct, R-ST·

$$ST + R^{\cdot} \xrightarrow{\text{Spin trapping}} R - ST^{\cdot}$$

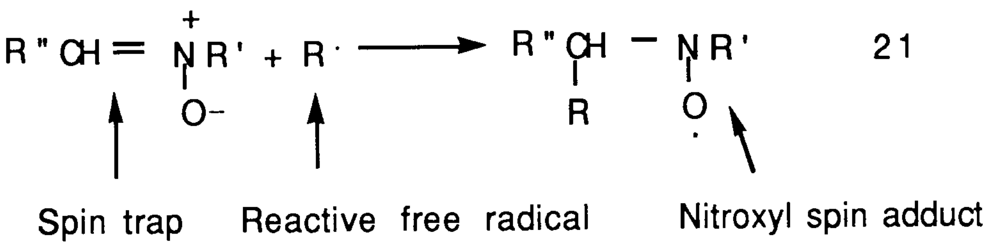
The spin adduct is paramagnetic and has an ESR spectrum with hyperfine parameters sensitive to the type of reactive free radical trapped. Ideally, the number of hyperfine parameters and the magnitude of the hyperfine splitting constants in the ESR spectrum of the spin adduct are characteristic of reactive free radicals from which the spin adduct was derived, and the spin adduct concentration can be related to the cumulative concentration of free radicals from which the spin adduct is derived. Theoretically, spin trapping can give both a full qualitative and quantitative analysis of the formation of reactive free radical intermediates.

1.4.1 Spin trapping agents

Many spin trapping agents have been developed but, only a few have found use in studies of free radicals by spin trapping:



$$R'NO + R^{\cdot} \longrightarrow R' - \underset{\underset{O^{\cdot}}{|}}{N} - R \qquad 20$$

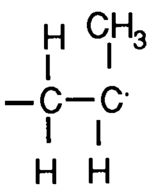


$$R''CH = \overset{+}{\underset{\underset{O^-}{|}}{N}}R' + R^{\cdot} \longrightarrow R''\underset{\underset{R}{|}}{CH} - \underset{\underset{\dot{O}}{|}}{N}R' \qquad 21$$

1.4.2 Techniques in alkyl radical formation

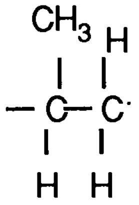
In the last two decades, ESR has been successfully applied to the investigation of polymers fracture. It has been established (45,46) that mechanical actions, such as processing, cutting, milling, grinding, sawing and large deformations, result in the scission of polymer chain to produce free radicals, such radicals of mechanical origin are appropriately called "mechanoradicals". Their formation is usually manifested by a decrease in molecular weight.In order to observe clear spectra from primary mechanoradicals it is desirable to break down a solid polymer at temperatures as low as 77K and in vacuum. A ball milling method was published at first by Butyagin and Abagyan (47), and cutting by a metal saw in liquid nitrogen (48). ESR spectra from PP mechano-radical was reported by Radtsig and Butyagin (49) and these radicals were identified as A and B.

A



$-CH_2-\dot{C}H(CH_3)$

B



$-CH(CH_3)-\dot{C}H_2$

Mechanical degradation also occurs in solution as a result of shaking, high speed stirring and turbulent flow. Mechanical degradation in solution has usually been measured by a decrease in the viscosity of the solution.

Chain scission may also be induced in solution by ultrasound, photo and high-energy radiation. The reactivity of mechano-radicals can play a crucial role in any mechanochemical process. The mechanical methods, such as grinding, milling, processing and ultrasound, are sometimes deliberately utilised for graft copolymerisation and the radicals can be identified by spin trapping

1.4.3 Kinetic aspects of spin trapping

a) The rate of the spin trapping reaction

For spin trapping reactions where there is negligible decomposition of the spin adduct,

$$ST + R^{\cdot} \xrightarrow{rT} R - ST^{\cdot}$$

The rate of spin trapping rT is given by

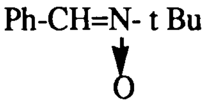
$$rT = \frac{d[R - ST\cdot]}{dt} = KT[ST][R\cdot]$$

where KT is the bimolecular rate constant of spin trapping. Alternative fates for R· other than spin trapping reaction can be decreased by using a high concentration of spin trap. Under these conditions, the spin adduct concentration gives a cumulative measure of reactive free radical:

$$[R - ST.] = \int_{o}^{t} [R\cdot]\, dt$$

Some bimolecular rate constants for the spin trapping reaction are given in table 1.

Table 1 = some bimolecular rate constants for spin trapping

Spin trap	Radical, $R^{\cdot}$	Temperature(°C)	Rate constant, KT, ($M^{-1}\ S^{-1}$)
$(CH_3)_3C\text{-}N{=}O$	$R\dot{C}H_2$	40	9×10^6
(NTB)	$RR\dot{C}H$	40	6×10^6
	$RRR\dot{C}$	26	3×10^6
	$t\text{-}Bu\dot{O}$	25	1.5×10^6
 $Ph\text{-}CH{=}\underset{\displaystyle O}{\overset{}{\underset{\downarrow}{N}}}\text{-}t\,Bu$	$R\dot{C}H2$	40	1.3×10^5
	$RR\dot{C}H$	40	7.0×10^4
(PBN)	$RRR\dot{C}$	26	1.0×10^4
	$t\text{-}BUO^{\cdot}$	25	5.5×10^6
	$ROO^{\cdot}$	60	1.0×10^2

$R\dot{C}H2$=5-hexenyl,$RR\dot{C}H$=6-heptan-2-yl,$RRR\dot{C}$= t-Butyl.

Table data taken from references (50 - 58).

For spin trapping reactions with a finite and significant rate of decay

$$\begin{tikzcd} ST + R^{\cdot} \arrow[r] & {[\,R - ST^{\cdot}\,]} \arrow[r, "r_{P1}"] \arrow[rd, "R - ST^{\cdot}", "r_{P2}"'] & P_1 \\ & & P_2 \end{tikzcd}$$

There are usually two important kinetic components to the decay process: a unimolecular and bimolecular process. The unimolecular decay process typically represents fragmentation and rearrangement reactions of spin adduct or the reaction of the spin adduct with a third component in the reaction mixture, e.g. oxidation or reduction of nitroxyl function of the spin adduct. The bimolecular decay process is typically disproportionation of the nitroxyl to a hydroxylamine and a nitrone.The observed rate of spin adduct formation is given by(54,59,60).

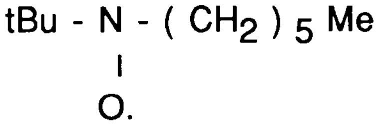
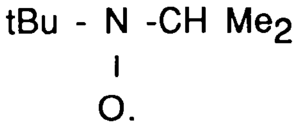
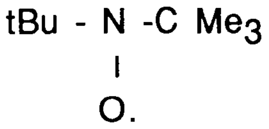
$$rT = \frac{d[R - ST\cdot]}{dt} = KT[ST][R\cdot] - K_d[R - ST\cdot]$$

where

$$K_d = K_{p1} + K_{p2}[R - ST\cdot]$$

Kd is the observed rate constant for the spin adduct decay process. The bimolecular route of spin adduct decay becomes increasingly favourable with increasing spin adduct concentration. Some bimolecular decay rate constants for nitroxyl radicals are given in Table 2

Table 2- Second order rate constants for the disproportionation of some nitroxyl (54, 59, 60).

Spin adduct		$2\ K_d/M^{-1}S^{-1}$
 $\underset{O.}{tBu - N - (CH_2)_5 Me}$	(NTB - nhexyl)	$2.5x10^2$
 $\underset{O.}{tBu - N - CH\ Me_2}$	(NTB - ipr)	$1x10^{-2}$
 $\underset{O.}{tBu - N - C\ Me_3}$	(NTB - tBu)	Stable

b) Factors affecting the magnitude of KT

(i) The spin trap: a comparison of some Kt values for the spin trapping of primary and secondary alkyl radicals, with NTB and PBN, shows the following gradation of KT, N T B > P B N (Table I) with a different reactive free radical this order can change, C-butoxy radicals t-BuO· for example, PBN is more reactive than NTB.

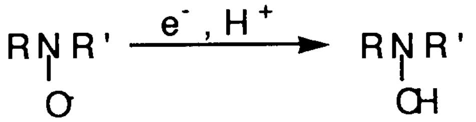
(ii) The reactive free radical: the rate of spin trapping of reactive free radicals R· by PBN shows the gradation given below:

$\mathrm{HO} \gg \mathrm{ph\ CO\cdot_2} > \mathrm{t\text{-}BuO\cdot} > \mathrm{Ph\cdot} > \mathrm{R\cdot\ (1\cdot)} > \mathrm{R\cdot\ (2\cdot)} > \mathrm{R\cdot\ (3\cdot)} > \mathrm{ROO\cdot}$

The order of reactivity for alkyl radicals R· suggest there is steric effect on the transition state controlling the magnitude of KT.

(iii)The solvent: The spin trapping rate constant KT is influenced by the solvent system of the spin trapping reaction. For the spin trapping of primary alkyl radicals with NTB and PBN, the observed rate constant for spin trapping, KT, is increased when the spin trapping reaction is performed in a solvent of high dielectric constant.

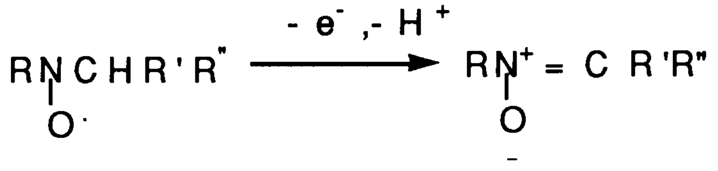
c) Factors affecting Kd: The decay of nitroxyl spin adducts occurs by several mechanisms: fragmentation, rearrangement, combination, disproportionation reactions and also by interaction with other species (reactants, reactive free radicals, miscellaneous oxidants and reductants) present in the spin trapping reaction medium. The most common reactions giving rise to unimolecular kinetics in the decomposition of adducts are oxidation and reduction reactions where the oxidants and reductants are present in large excess in the trapping mixture (a pseudo first order kinetic process). Nitroxyl functions in spin adducts may be reduced by one electron and a proton to form the corresponding hydroxylamine:



$$\mathrm{R}\underset{\substack{| \\ \mathrm{O}}}{\mathrm{N}}\mathrm{R'} \xrightarrow{e^-,\,H^+} \mathrm{R}\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{N}}\mathrm{R'}$$

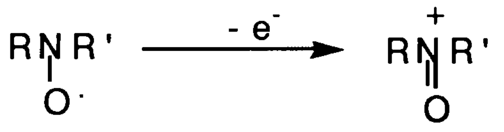
The oxidation of nitroxyls may proceed by two pathways:

(i) for nitroxyls bearing an α-hydrogen atoms, the nitroxyl radical is usually oxidised to a nitrone:



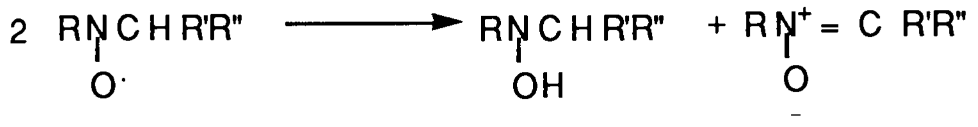
$$R\underset{\overset{|}{O^{\cdot}}}{N}CHR'R'' \xrightarrow{-e^{-},\,-H^{+}} R\underset{\overset{|}{O^{-}}}{N^{+}}=CR'R''$$

and where the nitroxyl has no α-hydrogen atoms, it is oxidised to an oxoammonium salt:



$$R\underset{\overset{|}{O^{\cdot}}}{N}R' \xrightarrow{-e^{-}} R\overset{+}{\underset{\overset{\|}{O}}{N}}R'$$

The most common bimolecular mechanism for nitroxyl decay is disproportionation. Spin adducts which have an α-hydrogen atom in their nitroxyl group (which occurs for all aldehydic nitrone-derived spin adducts), may disproportionate to hydroxylamine and nitrone products:



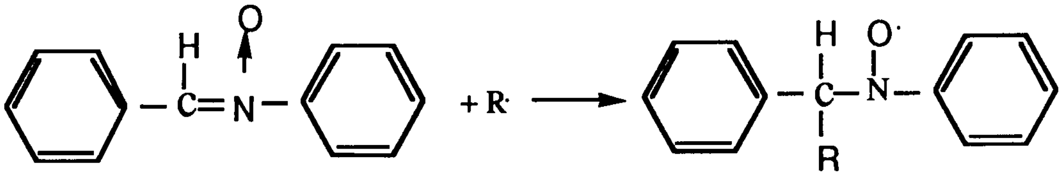
22

$$2\ R\underset{\overset{|}{O^{\cdot}}}{N}CHR'R'' \longrightarrow R\underset{\overset{|}{OH}}{N}CHR'R'' + R\underset{\overset{|}{O^{-}}}{N^{+}}=CR'R'' \tag{22}$$

The rate of spin adduct decay is influenced by temperature, substituent groups on the nitroxyl centre, solvent and steric factors (61). High temperatures, non-polar or low polarity solvents and bulky substituents, enhance the rate of spin adduct decomposition.

1.4.4 Application of spin trapping reaction in polymer stabilisation

2-methyl-2-nitrosopropane (62), diphenylnitrone(63), and phenyl t-butyl nitrone have been shown to trap free radicals to give stable nitroxyl radicals.



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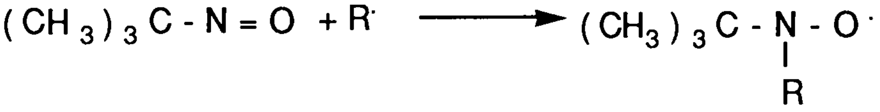


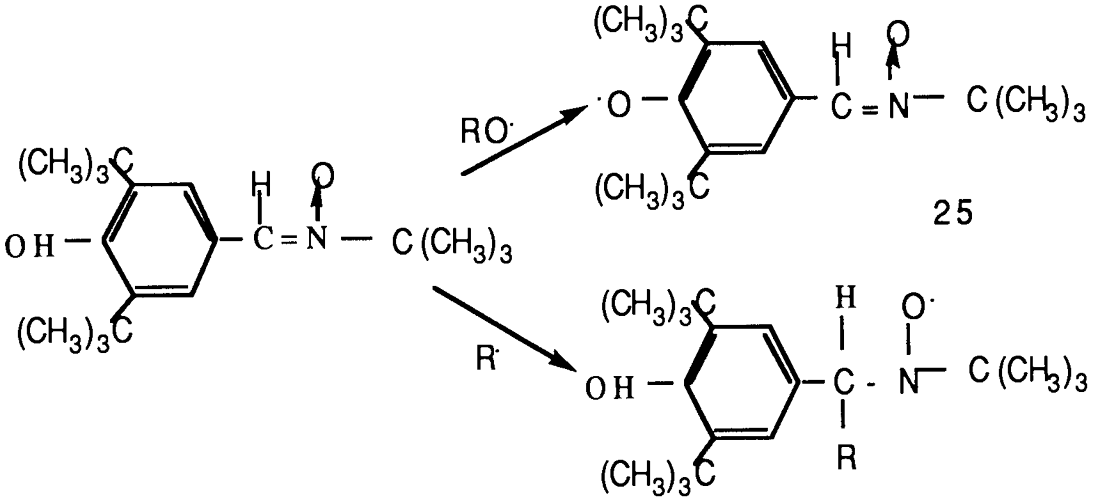
$$(CH_3)_3C-N=O + R^{\cdot} \longrightarrow (CH_3)_3C-\underset{R}{\underset{|}{N}}-O^{\cdot}$$

24

Spin traps   Spin adducts

When tert-butyl radical reacts with nitroso tert-butane to form di-tert-butyl nitroxyl, kinetic studies(64) 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 adducts cannot go above a certain level. The relative rate constants for the reaction of spin traps with tert-butyl were determined to be 0.07, 1.0, 41, for 2, 4, 6-tributyl nitroso benzene, nitroso-tert-butane and pentamethyl nitrosobenzene, respectively. It is important to note that aromatic nitroso compounds generally trap tert-butyl radicals more effectively than the nitroso-alkanes. Phenyl-N-tert-butyl nitrone was found to be less efficient in trapping the tert-butyl radical than aliphatic and aromatic nitroso compounds. Schmid and Ingold (65) have reported that nitroso compounds in general appear to be better traps for n-alkyl radicals than nitrone.

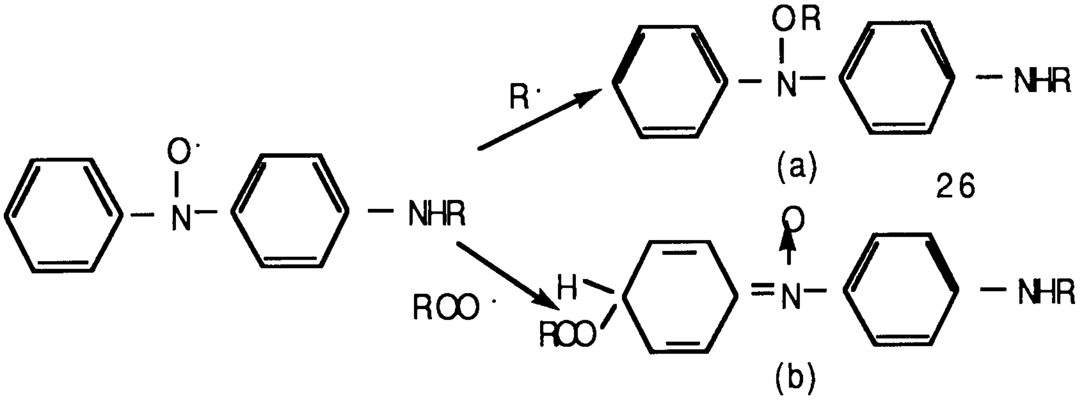
In 1962, utilisation of the nitroxyl radicals was suggested for inhibition of oxidative degradation of thermoplastic polymers (66). It is now clearly established that polyolefins produce alkyl radicals both during processing (in limited oxygen) and on U.V. irradiation (67, 68). Carbon-nitroso compounds with radical scavenging properties, and their derived nitroxyl radicals, are known to be effective stabilisers for polyolefins both during processing and/or on U.V exposure. It has been reported that the nitrones are efficient alkyl and alkoxy radical scavenger (69-70). Therefore, nitrones incorporated during thermal processing of polypropylene terminate macroalkyl radicals formed during processing, thus forming nitroxyl radicals. Nitroxyl reacts with alkyl radicals faster than the nitrone itself to form an O-alkyl hydroxylamine (71). Alternatively, nitroxyl radicals possessing hydrogen on the α- carbon to the nitroxyl function may disproportionate to nitrone and hydroxylamine (72)(reaction 22). Pacific and Browning (73) have employed phenolic nitrones as bifunctional radical traps, they found that alkyl radicals added to 3,5 di-tert-butyl-4- hydroxyl phenyl-tert butyl nitrone to give a nitroxyl radical, whereas the alkoxy radical produced the stable phenoxyl radical by phenyl hydrogen abstraction:



25

It has been suggested (74-76) that an important function of antifatigue agents in rubber subjected to cyclic stresses is to scavenge macroalkyl as well as macroperoxyl radicals, therefore, the antifatigue activity of α-(3,5 dimethyl 4-hydroxyl phenyl) N-tert-butyl nitrone is attributed to its capability to take part in CB-A/CB-D cycle similar to that proposed for galvinoxyl (76,77) and diaryl nitroxyls (74,76,78).

It is well known that fully hindered amine light stabilisers (HALS) are excellent photostabilisers for polyolefins (79-81), and most authors agree that stable nitroxyl radicals formed from HALS compounds play an important role in the photostabilising process (82-84). These radicals function as chain breaking electron acceptors in the free radical oxidative mechanism (78). Although both aliphatic and aromatic amines are converted to nitroxyl radicals during autoxidation, the hindered aliphatic amines have no antioxidant activity. The nitroxyl radicals derived from aliphatic amines are capable of scavenging alkyl radicals (85-87), whereas aromatic nitroxyls are capable of scavenging both R· and ROO· (87) :



The former occurs through the formation of alkylhydroxylamine (a) and latter by attack at the aromatic ring to give a nitrone (b) which is itself capable of scavenging alkyl radicals (88). The aromatic nitroxyls thus have both CB-D and CB-A activity, that is, capability to deactivate both alkylperoxy radicals and alkyl radicals.

The effective inhibiting action of HALS has been shown to result from the regeneration of intermediate nitroxyl radicals (>NO·). One >NO· terminates many oxidation chains. Different mechanisms for the antioxidant activity of nitroxyl radicals in polymers have been proposed :

The first includes the attack of peroxyl radical on the molecule of O-alkyl hydroxylamine >NOR (89),

$$P^{\cdot} + {>}NO^{\cdot} \longrightarrow {>}NOP \qquad 27$$

Followed by regeneration of the nitroxyl by alkylperoxy radical attack.

$$POO^{\cdot} + {>}NO-\overset{\wr}{C}(CH_3)\overset{\wr}{C}H_2 \longrightarrow POOH + {>}NO^{\cdot} + CH_3-\overset{\wr}{C}=\overset{\wr}{C}H$$

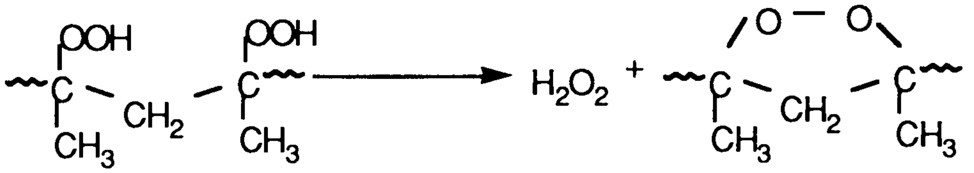
28

The second mechanism of nitroxyl regeneration involves the decomposition of >NOR with hydroxylamine formation (90-92):

$$PON{<} \rightleftharpoons P^{\cdot} + {>}NO^{\cdot} \longrightarrow {>}NOH + CH_3\overset{\wr}{C}=\overset{\wr}{C}H \qquad 29$$

$$POO^{\cdot} + {>}NOH \longrightarrow POOH + {>}NO^{\cdot} \qquad 30$$

It has been recently reported (93), that hydrogen peroxide formed in oxidising polypropylene gives $HO^{\cdot}_2$ radicals by reaction with macromolecular peroxyl radicals:



31

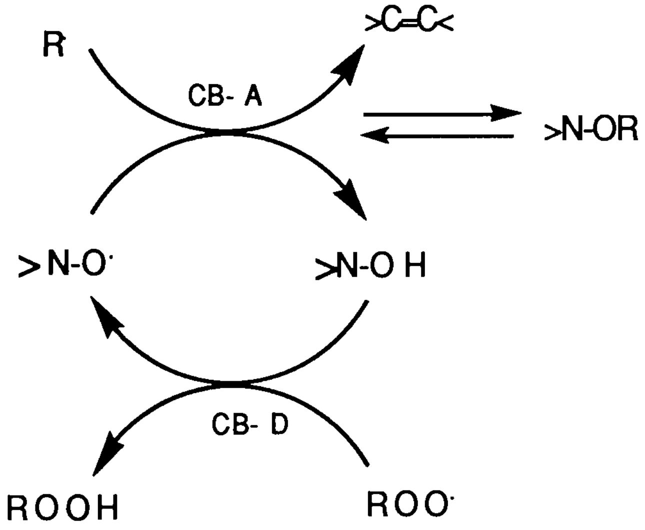
$$PO_2^{\cdot} + H_2O_2 \longrightarrow POOH + HO_2^{\cdot} \qquad 32$$

Hydroperoxyl radicals can oxidise as well as reduce (94). So nitroxyls in oxidising polypropylene may terminate the chains by the reactions 30 and 33:

$$>NO^{\cdot} + HO_2^{\cdot} \longrightarrow >NOH + O_2 \qquad 33$$

This mechanism explains why inhibitors such as sterically hindered amines, >NH, which form >NO·, retard the oxidation of polymers more effectively when they are preoxidised and contain hydroperoxide groups.

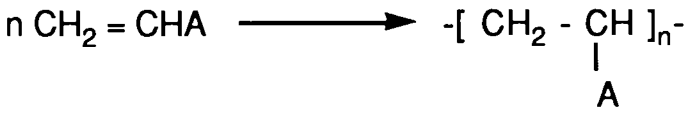
It has been shown (78,90,95) that the mechano-and photo-antioxidant activities of the hindered piperidinoxyls (e.g. 2,2, 6,6-tetramethyl-4-hydroxylpipidinoxyl, >NO·) are due to their involvement in a catalytic cycle. Available evidence suggests that the hydroxylamine >NOH and the nitroxyl >NO· constitute a redox couple with the ability to deactivate a large number of kinetic chains in a redox process summarised in scheme 5 .



Scheme 5

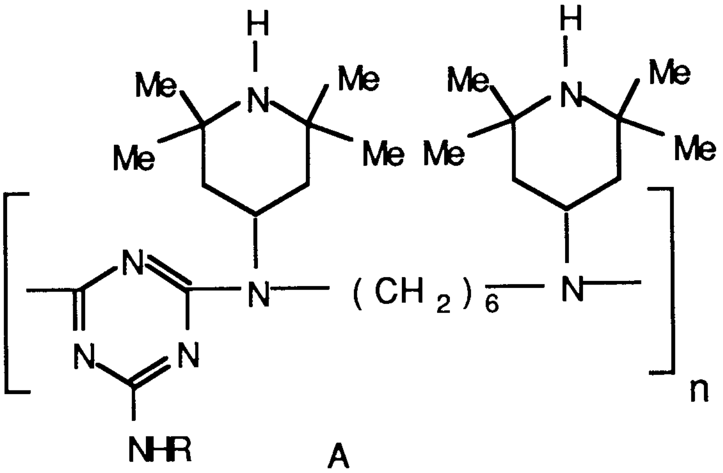
1.5 Polymer-bound antioxidant and polymer bound nitroxyl radicals

From the practical point of view, significant amount of stabilisers are often lost from polymeric materials due to volatilisation during fabrication or service, leaching out, solvent extraction during end use. This problem is especially severe with some crystalline polymers which have relatively small amorphous fractions and with articles having high surface to volume ratio such as film or fibers. In practice a good deal has been achieved by empirical modifications of additive structures. For example increasing molecular mass has a remarkable effect on molar heat stabilising activity (96). However, this stratagem is self-limiting since the usefulness of antioxidant in other tests may actually be reduced on weight basis simply because the weight ratio of functional group to inert residue is steadily reduced in the antioxidant (97). The problem of functional group dilution can, in principle, be overcome by incorporating an antioxidant group into a polymer as a conventional vinyl or condensation polymer so that the antioxidant function is repeated at short intervals along the polymer chain:



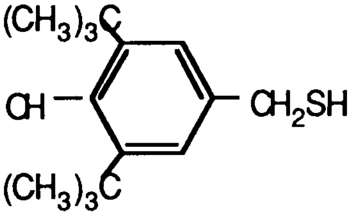
$$n\,CH_2 = CHA \longrightarrow -[\,CH_2 - \underset{A}{\underset{|}{CH}}\,]_n-$$

Antioxidants of high molecular mass made in this way are in general not very effective due to their limited miscibility with commercial polymers (98). Oligemeric antioxidants (e.g.A) have been found to be effective as U.V.stabilisers, but although they may be much more substantive at high temperatures, oligomeric antioxidants and stabilisers are still slowly lost by solvent leaching:



A

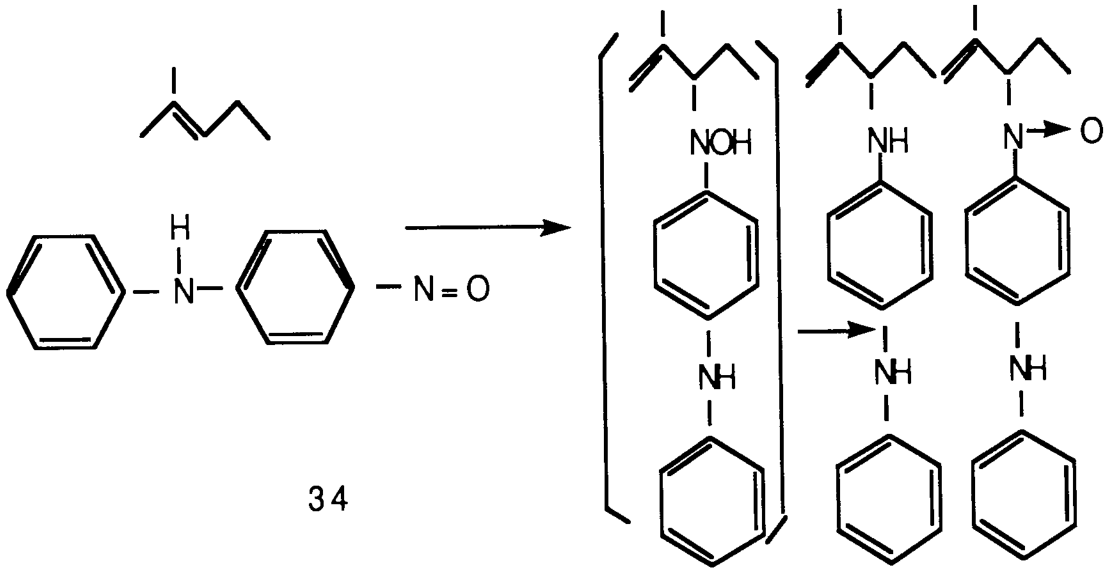
Vinyl antioxidants incorporated by co-polymerisation during synthesis (99,100) or by grafting (101-103) and polymer adduct antioxidants and stabilisers made by the latex or mechanochemical procedures (e.g. the incorporation of the polymer adduct antioxidant BHBM-polymer-bound onto SBR) show exceptional activity as antifatigue agents(104), and provide a potential solution to the problem of loss by volatilisation since they can only be removed by breaking chemical bonds.



BHBM

In addition, they are molecularly dispersed along the polymer chain. It seems that the limitation of molecular mobility associated with this polymer-bound antioxidant is not important in heat aging tests, that the limited movement of molecular chains in the amorphous phase is sufficient for them to diffuse to surface and scavenge alkylperoxy radicals.

One of the earliest polymer-bound antioxidants to be made during processing was the adduct of nitroso antioxidants with rubbers during vulcanisation. Nitrone structures have generally been assigned to the products of the reaction of mono and dinitrosobenzenes with olefins (105) and rubbers (106-109) based on an 'ene' mechanism, e.g. the reaction of 4-nitrosoanilines with olefins with formation amine and nitrone (110).



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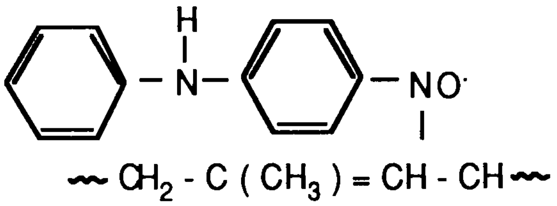
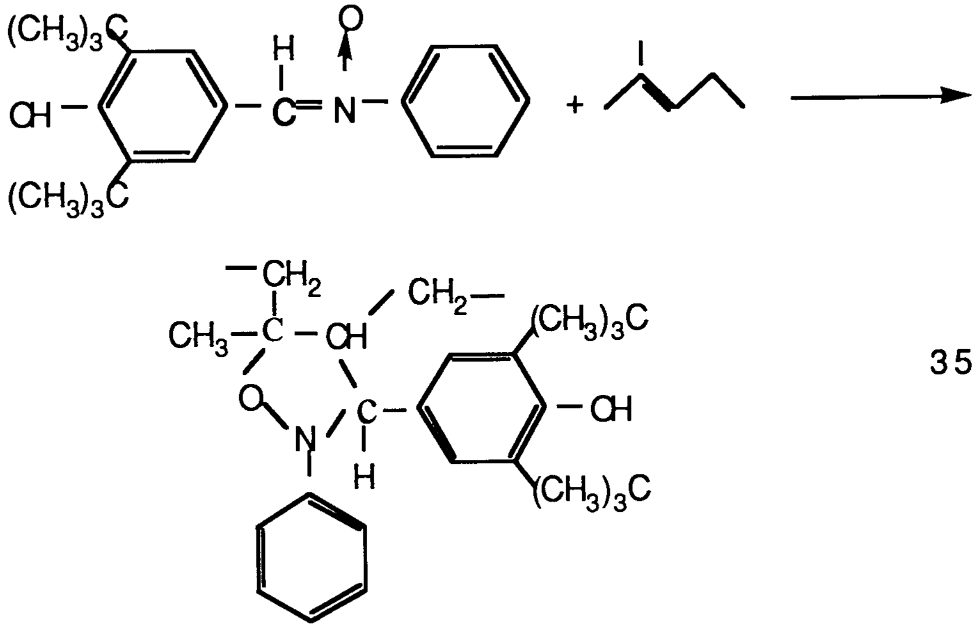
However a radical mechanism has also been suggested for the reaction between polyisoprene and p-nitroso diphenylamine, with formation of a macronitroxyyl radical (111).



The preparation of polymer-bound antioxidants by 1,3-cyclo addition reaction was first described by Saltman and Auerbach (112,113). They prepared a series of compounds including 3,5 di-tert-butyl-4-hydroxyl phenyl N-phenyl nitrone. This material was found to add readily to unsaturated polymers to provide a bound antioxidant. A more detailed academic study of these types of materials was later performed by Scott and Smith (88,114).



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1.6 Object and Scope of present work

Polyolefins, particularly polypropylene, are susceptible to photo-degradation, which limits their use in outdoor applications where they are exposed to sunlight. The UV stability of polyolefins can be improved by incorporation of several types of additives, such as substituted 2-hydroxybenzenophenones, metal chelates and hindered amine derivatives (115).

It has been established that photo-oxidation of a stabilised polymer is accompanied by loss of the effective organic U.V. stabilisers (116). The decrease in concentration of a stabiliser can be caused by such factors as instability of the stabiliser itself to U.V. light, by poor compatibility of the stabiliser with the polymer resulting in exudation, or by high volatility. The photo-oxidation rate of a polymer often shows a marked rise when the concentration of stabiliser falls below a certain level (116), therefore, the polymer-bound antioxidants might provide a solution to the problem of stabiliser loss from polymers during processing and service life.

Recent work (117) has shown that spin traps, particularly aliphatic nitroso compounds with alkyl radical scavenging properties, are efficient U.V. stabilisers for polypropylene. Their antioxidant activity is believed to be due to their ability to scavenge the intermediate propagating radicals by the well known chain breaking radical electron acceptor mechanism (CB-A). However, the spin adducts derived from mechano-chemical reaction of these compounds with polypropylene were substantially extractable from the polymers, suggesting that these were not macroradicals, but low molecular weight spin adducts (see reactions 20, 21).

The first objective of this work is, therefore, to improve the polymer bonding of spin traps (nitroso compounds and nitrones) in ethylene propylene rubber masterbatch or in polypropylene by using radical initiators during processing and/or photochemical radical formation. The quantification of spin adducts formed in these polymers will also be examined.

The second objective is to modify polypropylene during processing by making use of their concentrated bound antioxidant adducts (EPR-masterbatch), and compare their photoantioxidant activity in polypropylene with these spin traps incorporated as normal additives.

CHAPTER 2

PREPARATION OF NITROSO COMPOUNDS AND NITRONES AND GENERAL EXPERIMENTAL TECHNIQUES

2.1 Synthesis of Nitroso Compounds and Nitrone

The synthesised compounds were characterised by elementary analysis (table 3) and spectroscopy methods of analysis.The chemical structures and code names of compounds so prepared are given in table 4.

2.1.1 Preparation of nitroso compounds

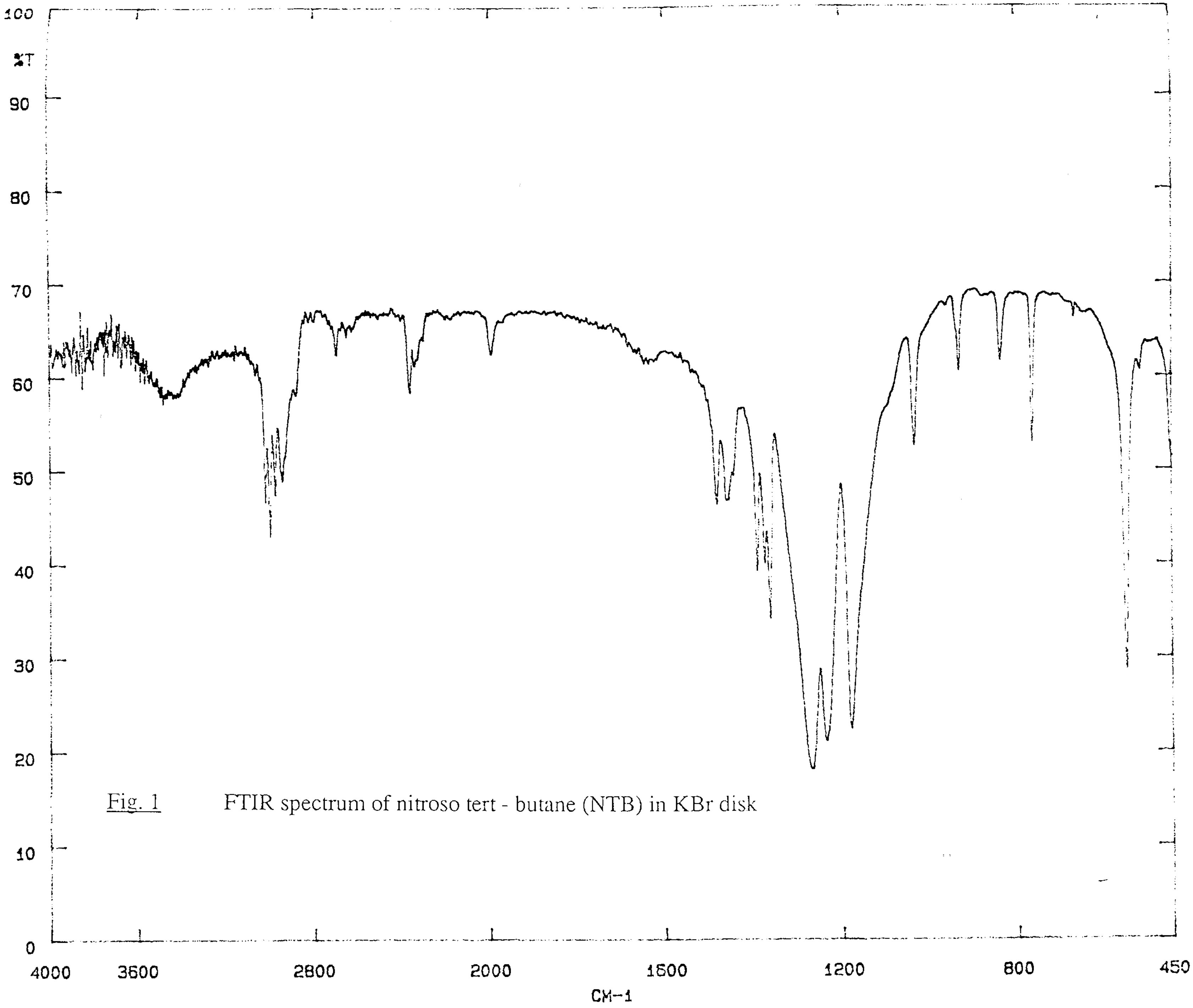
2.1.1.1 2-methy 2-nitroso propane (nitroso tert-butane)(118)

$$(CH3)_3C\text{-}NH_2 + H_2O_2 \xrightarrow{Na_2WO_4} (CH3)_3C\text{-}N{=}O$$

A solution of tert-butylamine (36.6 g. 0.5mol) and Na_2WO_4, $2H_2O$ (4.0 g.) in 50ml of water was cooled in an ice bath. Hydrogen peroxide (170 gr of 21%, 1.0 mole) 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 g. of NaCl was added to break the emulsion and the blue organic layer was separated. this was washed with HCl (dilute) and dried over $MgSO_4$. Distillation gave 10.0 g. (23%) Of the dark blue nitroso compound, which rapidly solidified in an ice bath to solid colourless crystals. m.p 80-81°C (Lit 79-81°C) (118).

IR(KBr); Trans-dimer showed a diagnostic strong absorption at 1176–1290 Cm-1(Fig. 1)

^{1}H-NMR ($CDCl_3$): $\delta(\text{-}CH3) = 0.45$ ppm



<u>Fig. 1</u> FTIR spectrum of nitroso tert - butane (NTB) in KBr disk

2.1.1.2 2,4,4-Trimethyl-2-nitrosopentane(nitroso tert-octane) (118)

Hydrogen peroxide (0.8 mol, 130 g. of 21 %) was added over a 30 minutes period to a mixture of 4.0 g. of Na_2WO_4, $2H_2O$, 50 ml of water and 52 g. (0.4mol) of tert-octyl amine 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 organic layer was separated with 25ml of pentane. The blue organic layer was then dried ($MgSO_4$) and distilled to give nitroso compounds bp 90-92°C (140mm) a bath liquid which slowly crystallised (ice bath). m.p 63-65°C (lit. 63-65°C)(118).

^{1}H-NMR ($CDCl_3$): δ(-CH3)=0.5 ppm

2.1.1.3 Pentamethyl nitrosobenzene (119)

(a) Acetoxymercuripentamethylbenzene was prepared as follows (120): pentamethylbenzene (37 g. ,0.24 mol) and mercuric acetate (80 g., 0.25 mol) were dissolved in 200ml methanol. Enough acetic acid (25ml) was added to prevent hydrolysis of the mercury salt and the solution was refluxed for 5 days. The acetoxy mercuripentamethylbenzene was insoluble in the hot reaction mixure, the product was filtered and recrystallisation from methanol gave white crystals, yield 80%, m.pt. 179° C (lit 180°C) (120).

(b) n-butylnitrite was prepared as follows (121): in a three-necked round bottom flask, fitted with a mechanical stirrer and a separating funnel extending to the bottom of the flask, 38 g. (0.55 mol) of sodium nitrite and 250ml of water was added; the flask was surrounded by an ice salt mixture and the solution was stirred until the temperature fell to 0°C. A mixture of 13.6ml (25 g. 0.25mol) of concentrated sulphuric acid (Sp. gr 1.84) and 46ml (37 0.5mol) Of n-butyl alcohol is cooled to 0 ° and by means of a separatory funnel, was introduced slowly beneath the surface of nitrite solution with stirring. The alcohol solution was added slowly enough so that the temperature was kept at ± 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 separator funnel. The lower aqueous layer was removed and the butyl nitrite layer was washed twice with 20ml portions of a solution containing 1g. of sodium carbonate and 2.5 g. of sodium chloride in 40ml of water. After drying over 2.0 g. of $MgSO_4$, the yield of pure butyl nitrite was 42 g.(81% of theoretical amount). Butyl nitrite decomposes slowly on standing and was kept in a cool place and used within a few days.

(c) The acetoxymercuripentamethylbenzene (20g) was dissolved in chloroform (100ml). the solution was cooled in an ice bath and stirred mechanically. n-butyl nitrite (9ml) was added, this was followed by the addition, in one portion of a mixture of hydrochloric acid (15ml) and acetic acid (20ml). The reaction mixture was washed with water (mercury salt removed). The precipitate was crude nitroso compound, the green filtrate evaporated to 40ml and cooled, and an additional amount of nitroso compound was deposited. The nitroso compound was crystallised from chloroform, the yield was 80 %, m.pt. 158° C(lit 160°C) $^{(119)}$.

Infra-red (KBr disc) : 2960, 2940 cm^{-1}, (aliphatic C-H stretch), 1480 cm^{-1}(aromatic N-O stretch);1260 cm^{-1}(C-N stretch).

2.1.1.4 P-nitroso 2,6 di-tert- butyl phenol(122)

To a solution of 0.05 mole 2,6 di-tert butyl phenol in 50ml methanol, was added 0.0275 mole sulphuric acid. The mixture was cooled to -5°C in dry ice, 3.45 g. (0.05mol) of sodium nitrite in 10 ml of water was added to it. The precipitate was removed, washed with water and petroleum-ether to remove quinoid compounds. Recrystallisation from aqueous alcohol gave yellow crystals. m.pt 212°C (lit 211-213°C) (122).

Infra-Red (KBr disk)

3328cm^{-1} (broad -OH stretch); 3000cm^{-1} (aromatic C-H stretch); 2957cm^{-1} (C-H stretch in tert-butyl); 1608cm^{-1} (aromaticity); 1417, 1455cm^{-1} (N-O stretch); 1250cm^{-1} (C-N stretch); 884cm^{-1} (1,4 disubstituted benzene ring)

2.1.2 Preparation of nitrones

2.1.2.1 α, N-Diphenyl nitrone (123)

a) N-phenyl hydroxylamine was prepared as follows (124): 25g (0.217mole) of ammonium chloride, 800ml of water and 50g (41.6ml) of nitrosobenzene was placed in a 2 litre beaker. The mixture was stirred vigorously by means of a mechanical stirrer, and 59 g. of zinc powder of 90% purity was added for about 15 minutes. As the reaction proceeded, the temperature rose to 45-50°C. Stirring was continued for 15 minutes after all the zinc dust was added, the completion of the reaction was indicated by the fact that the temperature of the mixture ceased to rise. The warm reaction mixture was filtered with suction to remove the zinc oxide,and washed with 100 ml of hot water. filtrate was saturated with sodium chloride (300g.) and cooled in an ice bath for two hours in order to get maximum crystallisation. The pale yellow crystals of N-phenyl hydroxylamine was filtered with suction and drained well. The crude product recrystallised from benzene, mpt 80°C (lit 81° C) (124).

b) N-phenyl hydroxylamine (1.9 g. 0.01mole) and benzaldehyde (1.06 g. 0.01 mole) 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. Recrystallisation from ethanol gave white needles, mpt 114°C (lit 112-113° C) (125).

Infra-Red(KBr):3030 cm^{-1}(aromaticC-Hstretch); 1545 cm^{-1} strong (C=N stretch); 1395 cm^{-1}strong (C-H in-plane bend); 1190 cm^{-1}strong(N^{+}-O^{-}stretch);830 cm^{-1}(substituted ph- ring)

2.1.2.2 α-phenyl-N-tert-butylnitrone (126-128)

3.5 g. (0.033 mole) of benzaldehyde and 3.0 g. of the N-tertiary-butyl hydroxylamine were dissolved in the minimum volume of absolute ethanol and allowed to stand at room temperature for a few days. Pale yellow/white crystals were obtained. The rate of formation of the product could have been speeded up by adding a few ml of water to the reaction solution. The crystals were separated by filtration and recrystallised from ethanol. The yield was 4.0 g. (0.023 mole, 70% theoretical) melting point 72-74°C (lit:75°C) (126-128).

Synthesis of N-tert-butyl hydroxylamine.

a) Synthesis of 2-methyl-2-nitropropane :

this compound was prepared by the oxidation of tertiary butylamine using hydrogen peroxide according to the procedure described by Stowell (129).

A solution of tert-butylamine (36.6 g., 0.50 mol), $Na_2WO_42H_20$ (4.0g), and 25ml of water was cooled in an ice bath. Hydrogen peroxide (225g of 21%, 1.50 mole) was added dropwise over a 2.0 hr period with stirring. The first 100 g was added at 15-20°C, 100ml of methanol was then added, and the H_2O_2 addition was continued at 25-32°C. This was stirred for an additional hour at 25°C. The organic layer was separated and the water layer was extracted with three 25ml portions of ether. The combined organic layer and the extract were dried (over $MgSO_4$) and distilled. The yield was 25 g. (57% theoretical) bP 126-128°C (lit bP 126 -127°C) (129).

b) Synthesis of tert-butyl hydroxylamine.

The hydroxylamine was synthesised by the reduction of the 2-methyl-2-nitropropane (from previous experiment)using zinc dust and ammoniun chloride according to the method described by Greene et al. (130).

To a mixture of 2-methyl-2-nitropropane (20g, 0.19 mole) and a solution of ammonium chloride (8.5 g. in 300ml of water) cooled to10°C with an ice bath was added 28 g. of zinc in small portions over 1 hour, never letting the temperature rise above 20°C. The mixture was stirred for one additional hour at 0°C and 30 minutes at room temperature. The reaction mixture was filtered and the solid was filtered , the solid was washed with 100 ml of hot water (60°C). the filtrate was made basic with

25 g. of sodium hydroxide and 100g of potassium carbonate (to crystallise out the hydroxylamine). The solution mixture was extracted with 350ml portions of ether. The ether was dried over $MgSO_4$ and evaporated, yielding 12 g. (68%) of t-butylhydroxylamine. mp (60-62°C) (lit 60-62°C) $^{(130)}$.

2.1.2.3 N-phenyl-dimethylniotrone (ketonitrone) $^{(131)}$

57.0 g. of β-phenylhydroxylamine was dissolved in dry acetone (68.3 cc) and the filtered solution was kept for several days at room temperature, the condensation product began to crystallise. Thereafter, the mixture was kept, with daily agitation, in an ice-chest for several weeks until further separation occurred. The condensation product, after being washed with cold acetone in which it was only slightly soluble,was obtained almost colourless.It crystallised from ethyl alcohol in hard glassy rhombs, mp 136°C) (lit 136°C) (131).

Table 3 - Elemental analysis of nitroso compounds and nitrones

Compound	Formula	C%		H%		N%	
		Calcu.	Found	Calcu	Found	Calcu.	Found
Nitroso tert- butane	C_4H_9NO	55.17	54.8	10.34	10.2	16.9	16.18
Nitroso tert- octane	$C_8H_{17}NO$	67.13	66.9	6.29	6.0	9.79	10.02
Pentamethyl nitrosobenzene	$C_{11}H_{15}NO$	74.15	74.0	8.98	8.8	7.86	7.65
p-Nitroso 2,6 di tert-butyl phenol	$C_{14}H_{21}NO_2$	71.48	71.1	8.98	8.9	5.95	6.1
α,N-diphenyl nitrone	$C_{13}H_{11}NO$	79.18	78.9	5.58	5.5	7.11	7.0
α,phenyl-N- tert butyl nitrone	$C_{11}H_{15}NO$	75.54	74.60	8.53	8.55	7.90	7.62
N-phenyl- dimethylnitrone	$C_9H_{11}NO$	72.54	72.20	7.43	7.41	9.39	9.48

2.2 Mechanical Modification of Polypropylene during Processing

This was carried out using two different methods: in the first method, spin traps are added directly to the polypropylene (PP) HF22 (supplied by ICI) during processing, whereas the second method involves the use of previously prepared masterbatch from ethylene propylene rubber (EPR) Vistalon MDE 7815 containing 45% polyethylene (supplied by ESSO). The major reasons for the use of EPR for masterbatch preparation are as follows:

a) Structural similarity with polypropylene

b) In view of the low decomposition temperature of aliphatic nitroso compounds, processing was then carried out at lower temperatures.

All processing was carried out in a RAPRA torque-rheometer (132), which is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds (133). The chamber may be operated either open to the atmosphere or sealed by pneumatic ram. A full charge was calculated out for each polymer according to its density. In the modification of PP, 35 g. PP were premixed with additive by tumble mixing prior to the processing step. The processing was carried out in the closed chamber at high rotor speed (70 rpm) at 180°C for 10 minutes. The processed polymers were chilled in water on removal from the mixer to avoid thermal oxidation.

2.2.1 Preparation of EPR-spin adducts (masterbatch)

a) By high shear during processing (mechanochemical) 35g of ethylene propylene rubber was processed with 5% w/w spin traps and in the presence of different concentrations of a variety of radical initiators at different temperatures for 10 minutes in an oxygen free atmosphere (Argon). On completion of mixing, the samples were rapidly removed and quenched in cold water to prevent oxidation. The nitroxyl radical concentration of these samples was assessed by ESR measurements.

b) By ultra-violet irradiation in solution (photochemical):

Benzene or hexane solutions of ethylene propylene rubber containing 5% of nitroso tert-butane together with various radical generators were placed in a quartz tube. The addition of spin trap to the polymer solution was carried out in total darkness because nitroso tert butane in solution in the presence of daylight readily generates di-tert-butyl nitroxyl radical. The quartz tube was then bubbled with Argon gas, sealed and subjected to U.V. irradiation in an U.V. cabinet for different lengths of time and the ESR spectrum run. EPR-masterbatch was recovered by a non-solvent (methanol) from the benzene solution and by evaporation from hexane solution. The recovered masterbatches were dried over vacuum. The [>NO·] of the samples was quantified by ESR measurements.

2.2.2 Polypropylene formulation with and without masterbatch of spin traps

Polypropylene was modified with 0.2% nitroso compounds and nitrones used as normal additives, or with 0.2% spin adducts used as EPR-masterbatch. The modification was carried out in a closed mixer (RPRA-Hampden Torque Rheometer) at 180°C for 10 minutes.On completion of mixing, the samples were rapidly removed and quenched in cold water to prevent further thermal oxidation.

2.3 Preparation of Polypropylene Films

7.0 g. of the modified PP was placed between sheets of a special grade of cellophane.The cellophane sheets were then placed between two stainless steel plates.The plates were placed between the platens of an electrically heated press, the polypropylene samples were preheated for one minute and pressed with a pressure of 50 tonnes on a 15 inches diameter ram for one minute 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 through press platens.

The pressure was released and the films removed from the press at a temperature 100°C. The strips with 0.08 inch thickness were cut from the film for IR and ESR measurements.

2.4 Identification and Quantification of Nitroxyl Radicals by ESR Spectroscopy

A Jeol-PE, ESR spectrometer was used. From the ESR spectrum of the samples run under the identical experimental conditions (mode width, amplitude, magnetic field etc.), the nitroxyl radicals were identified by their g values, and their concentrations were calculated relative to copper sulphate which is used as an internal standard of known concentration . For this purpose 0.1 g. of samples as thin strips, before and after methanol extraction, were placed into a quartz tube. A sealed capillary tube containing 10 microlitre of 0.1M $CUSO_4$, $5H_2O$ solution was fastened to the outside of the quartz tube as a standard, and the tube was then immersed into the cavity of the spectrometer.The [>NO·] of samples were measured before and after methanol extraction and also after oxidation of the polymer samples. The [>NO·] before extraction and after extraction correspond to the initial nitroxyl radical during processing and to the polymer-bound nitroxyl respectively. The [>NO·] after oxidation is the sum of initial nitroxyl radical and that regenerated from free hydroxylamine and/or alkyl hydroxylamine (conversion %).

2.4.1 Procedure for the oxidation of polymer samples containing spin adducts

Oxidation of masterbatch strips was carried out with 0.1% w/v meta di-chloroperoxybenzoic acid (MCPBA) in the cavity of the ESR spectrometer at room temperature for the times indicated in the Results Section. The ESR spectra of samples were run successively until the maximum nitroxyl radical concentration formed during oxidation under the same experimental conditions were recorded

2.4.2 The principle of ESR spectroscopy

ESR spectroscopy depends on the fact that the unpaired electron in a radical is like a spinning magnet by virtue of its charge and spin. When placed in an external magnetic field the unpaired electrons align themselves against and in the direction of the applied field. This causes the normally degenerate energy level occupied by the electron to be split into two states of different energy, the population within these levels is determined by Boltzmann's statistical distribution. If the populations of the two states (the higher energy state and the lower energy state) approach equality, no further net absorption of energy will occur and the observed resonance signal will fade out. This phenomenon is called saturation of the ESR signal. Under normal measurement conditions, the populations in the two states are not equal because high energy electrons are constantly returning to the lower energy state.

The precessing electron in the parallel orientation can absorb energy from the microwave-frequency source and pass into the antiparallel orientation under one particular condition:

if the precessing frequency is the same as the frequency of the microwave beam (such a condition is called an electron spin resonance), the absorbed energy is recorded in the form of an ESR spectrum. A radical is normally characterised by the g-value and the hyperfine splitting value (a). The g-factor is a dimensionless constant and equal to 2.0023 for unbonded electrons. The exact value of the g-factor reflects the chemical environment, particularly when heteroatoms are involved.

Hyperfine interaction: since the radical electron is usually delocalised over the whole molecule or at least a large part of it, the unpaired electron comes into contact-interaction with many nuclei. Nuclei possessing a magnetic moment may interact and cause a further splitting of the electron resonance line. From the number and intensity distribution of spectral lines, one can tell how many nuclei interact with the radical electron. Ordinarily, the hyperfine coupling constant is a small fraction of electron splitting on spectrum it is the distance between associated peak of a submultiple, measured in gauss.

2.4.3 Determination of g value

The ESR spectrum of manganese Mn^{+2} contained in MgO shows six lines. The g-values of the fourth line counted from the low magnetic field side is (g=1.98) as reported in the spectrometer handbook .

The $Mn^{+2}$was used as a marker throughout this work to calculate the g-value of different radicals . In the Jeol cavity resonator, this value remains constant for cavity resonator frequency between 9200 and 9400 MHz. the distance between the third line and the fourth line is 86.9 gauss .

A typical ESR spectrum is shown in figure (2). In this figure

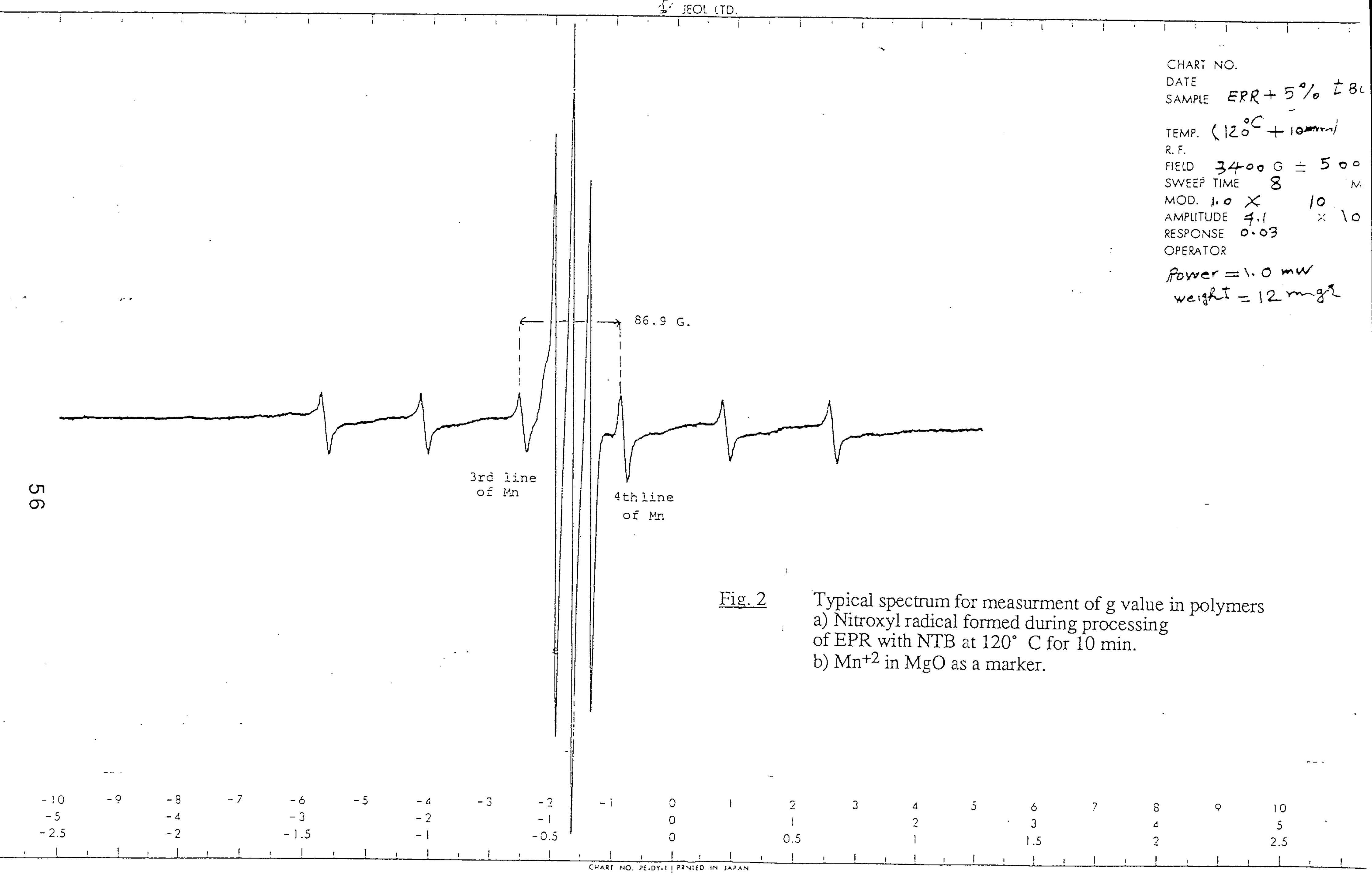


CHART NO.
DATE
SAMPLE EPR + 5% t B
TEMP. (120°C + 10min)
R. F.
FIELD 3400 G ± 500
SWEEP TIME 8 M
MOD. 1.0 × 10
AMPLITUDE 7.1 × 10
RESPONSE 0.03
OPERATOR
Power = 1.0 mW
weight = 12 mg

Fig. 2 Typical spectrum for measurment of g value in polymers
a) Nitroxyl radical formed during processing of EPR with NTB at 120° C for 10 min.
b) Mn^{+2} in MgO as a marker.

the distance between the centre of sample spectra and the fourth line spectra of Mn^{+2} in gauss represents ΔH, which is easily calculated by proportional calculation.

Once ΔH is obtained, the g-value of the measured sample can be calculated as follow :

$$E = g_1 \beta H_0$$

$$h \upsilon = g_1 \beta H_0$$

$$h \upsilon = g \beta (H_0 - \Delta H)$$

Hence $$g = \frac{h \upsilon}{\beta (H_0 - \Delta H)} = \frac{h \upsilon / \beta}{h \upsilon / g_1 \beta - \Delta H}$$

β = Bohr magneton constant (9.27×10^{-21} erg G^{-1})

h = Plank constant (6.62×10^{-27} erg . sec.)

g = g - value of unknown sample

g_1= g - value of the reference (1.891)

H_0=The strength of the applied external magnetic field

If 9300 MHz is substituted for υ, the center frequency of 9200 ~ 9400 MHz , then the following equation is obtained :

$$g = \frac{6651}{3357 - \Delta H}$$

Thus the unkown g-value can be obtained without measuring the microwave frequency. The above equation was used to measure the g-factor of radicals in the masterbatches, processed polypropylene films, and natural rubber.

2.4.4 Measurement of radical concentration

To measure the concentration of nitroxyl radicals in polypropylene samples, a reference was used in the cavity with the polymer sample, so that both spectra could be recorded simultaneously.This technique was essential for the reproducibility of results. The total area enclosed by the absorption signal is proportional to the number of unpaired electron spins in the samples. The ESR spectrum of EPR-masterbatch containing nitroso tert butane recorded simultaneously with copper sulphate reference is shown in fig3.

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

$$\frac{Y_m\ (\Delta Hpp)2}{Y'_m\ (\Delta H'_{pp})^2} = \frac{\text{Concentration of radicals in test sample}}{\text{Concentration of radicals in reference sample}}$$

This method is a close approximation of the summation method of Wyard (134).

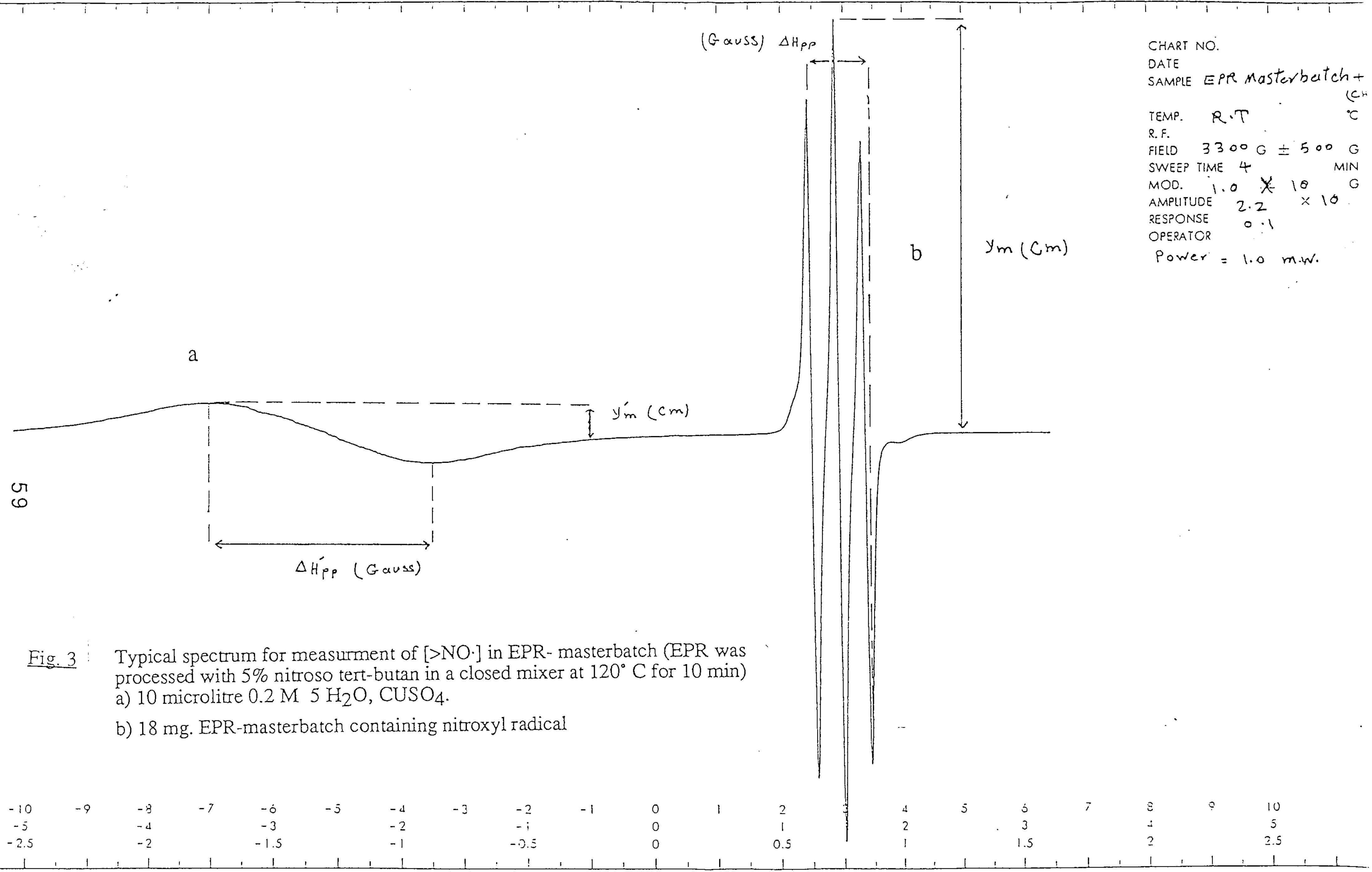


CHART NO.
DATE
SAMPLE EPR Masterbatch + (C
TEMP. R.T °C
R.F.
FIELD 3300 G ± 500 G
SWEEP TIME 4 MIN
MOD. 1.0 ~~×~~ 10 G
AMPLITUDE 2.2 × 10
RESPONSE 0.1
OPERATOR
Power = 1.0 m.w.

Fig. 3 Typical spectrum for measurment of [>NO·] in EPR- masterbatch (EPR was processed with 5% nitroso tert-butan in a closed mixer at 120° C for 10 min)
a) 10 microlitre 0.2 M 5 H_2O, $CUSO_4$.

b) 18 mg. EPR-masterbatch containing nitroxyl radical

2.5 Ultra-violet irradiation of polymer samples

Irradiation of polypropylene films and EPR-masterbatch formation via solution was carried out in an ultra violet light aging cabinet, in which eight fluorescent (Westinghouse sunlamp F 1520) and twenty four Phillips actinic blue lamps were arranged in symmetrical sequence in the ratio 1:3. The light intensity inside the cabinet was 4.6 $W/h/m^{-2}$. The Samples are mounted on a rotary drum fixed inside the cabinet and in this manner the light beam falls perpendicularly on the film samples . The distance of the sample from the light source is 10 cm and the temperature inside the cabinet with the light on is 30 °C. The combined distribution spectra of of both types of lamps has shown (135) that the maximum in the relative intensity occurs within the range 280 -370 nm.

2.6 Measurement of embrittlement times of polymer films

Embrittlement times were recorded as the time required to break the film when it is manually flexed onto itself i.e through an angle of 180°C. Each test was carried out in duplicate

2.6.1 Infra-red analysis of the photooxidised PP films

The rate of photo-oxidation of the polymer films was measured by monitoring the increase in non-volatile carbonylic oxidation products ,absorbing at 1710 cm^{-1}. A Perkin-Elmer 599 infra-red spectrophotometer was used to observe this absorption. Carbonyl function at 1710 cm^{-1} was measured and calculated using the base line technique (136). This was carried by drawing a tangential line between two adjacent shoulders of an absorption maxima. A perpendicular line was dropped to intersect the peak absorption base line. The distance between the tangential line and base line was taken as the absorbance which could be read directly from the chart paper. The increase in the carbonyl index during photo-irradiation of polymer films was calculated as follows :

$$\text{Carbonyl index} = \frac{\text{log of carbonyl absorption at } 1710\ \text{cm}^{-1}}{\text{log of reference absorption at } 2720\text{cm}^{-1}}$$

The reference peak is used to minimise errors caused by deviation in film thickness.

2.7 Thermal oxidation of polypropylene films

The accelerated thermal oxidation of polypropylene films was carried out in a Wallace oven at 140° C. The oven contains seven individual cells with a good temperature control. There is an arrangement for controlling air flow through the cells. The films were aged at 1.3 cubic-feet per hour air flow individually to prevent cross-contamination, due to absorption of volatile degradation products and antioxidant between films. The embrittlement times of oxidised films were recorded by flexing onto itself. i.e. through an angle of 180 ° .

2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis has been used for many years to study degradation process in polymers. Reaction mechanisms have been elucidated kinetically, and accelerated aging tests has been developed which use TGA to predict relative thermal stability of a wide range of materials.

TGA provides the analyst with a quantitative measurement of the mass change associated with a transition. For example thermogravimetry can directly record the loss in weight with time or temperature due to degradation or decomposition. Thermogravimetry curves are characteristics for a given compound or system because of the unique sequence of physicochemical reactions which occurs over a definite temperature ranges and the rate of weight loss that are a function of molecular structure . Changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products.

Experimental method

In the present work, the apparatus used was the Perkin-Elmer 7 series thermal analysis system. The TGA 7 is made up of two major components: a sensitive ultramicrobalance and a furnace element. The microblance used with the TGA is extremely sensitive, capable of detecting weight changes as small as 0.1µg. The nullbalance design of this microbalance uses a servo-contolled torque motor to automatically compensate for weight changes in the sample material. The amount of current necessary to maintain the system in the "null" state is directly proportional to the weight change in the sample.

The apparatus is connected to PE 7000 series professional computer. Under the control of the PE 7000 series, the TGA is programmed from an initial to a final temperature and measure weight changes resulting from chemical reactions, decomposition, evolution of solvent & water, and oxidation in sample materials.

About 10 mg of unextracted and extracted polymer samples with thickness of 0.007 inch in the form of small pieces (1-2 mg) heated under nitrogen and air atmosphere at the rate of 10 °C per minute in the temperature range 50 up to 700°C. In order to measure the dissociation temperature of NTB, this compound was heated up to 180°C at the rate of 4°C and 10°C and the thermograms obtained are shown in the result section.

CHAPTER 3

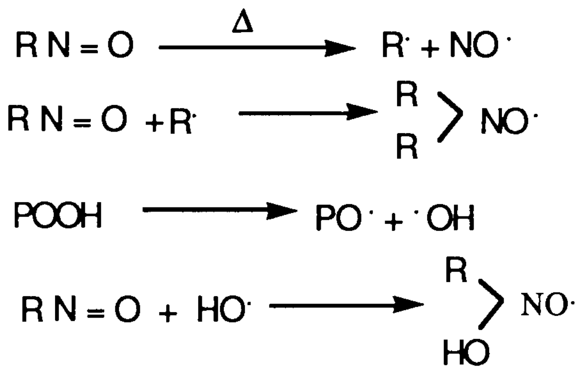
THE IDENTIFICATION AND QUANTIFICATION OF THE SPIN ADDUCTS IN POLYMERS (EPR-MASTERBATCH &PP) BY PROCESSING IN HIGH SHEAR

3.1 Object and plan

Hindered piperidine compounds and aliphatic nitroso compounds are highly effective as photo-stabilisers for polyolefins. The corresponding nitroxyl radicals formed as intermediate from these compounds function as polymer stabilisers. One >NO· terminates many oxidation chains.

If this is the case, then the spin adduct yield (nitroxyl radical and its reductive products >NOH and >NOR) may play a key factor in polymer stabilisation.

It has been reported recently that nitroxyl radicals derived from the processing of aliphatic nitroso compounds with polypropylene were substantially extractable from the polymer(117), suggesting that these are not macro nitroxyl radicals, but are low molecular weight nitroxyl radicals i.e, the spin adducts are not chemically attached to polymer matrix.In the above work the processing was carried out at high temperature and no attempt was made to exclude oxygen. This may have resulted from the formation of low molecular weight nitroxyl radical according to scheme 6



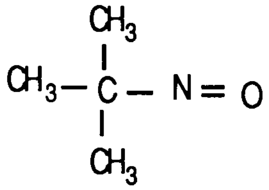
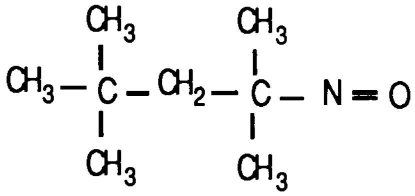
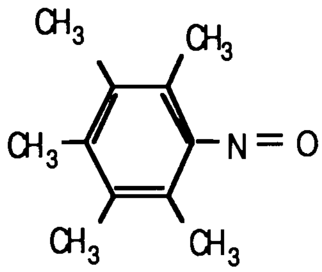
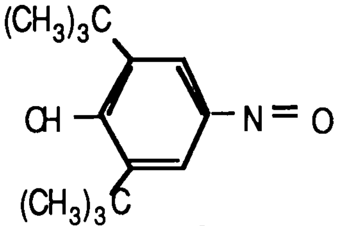
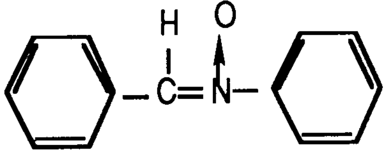
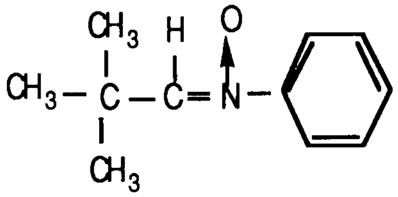
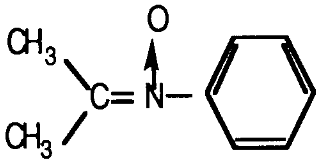
Scheme 6

In the present study, owing to low dissociation energy of nitroso compounds, particularly aliphatic ones,the effect of temperature, inert atmosphere (Argon), radical initiator, and light on the spin adduct yield and polymer bound nitroxyl will be assessed by ESR measurements.The photo-antioxidant activity of the spin adducts generated at low processing temperatures or by UV light (i.e in EPR-masterbatch) will be examined in polypropylene.

The effect of different radical generators on the photo-antioxidant activity and thermal antioxidant activity of the spin traps added directly to PP during processing, will also be assessed.

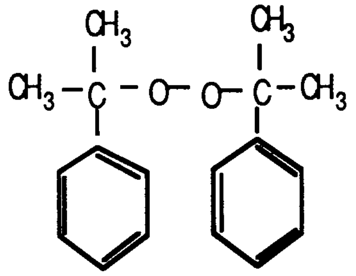
The chemical structures and the code names of additives used in this study are listed in table 4 and the experimental procedure has been summarised in chart flow 1.

Table 4

Spin trap	Chemical structure	Code name
Nitroso tert butane	 $CH_3-C(CH_3)_2-N=O$	NTB
Nitroso tert octane	 $CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-N=O$	NTO
Pentamethyl-nitrosobenzene		PMNB
4-Nitroso-2,6-di-tertbutylphenol		NDBPh
α-N-diphenyl nitrone		DPN
α-Phenyl-N-tert butyl nitrone		PBN
N-Phenyl di-methyl nitrone		PDMN

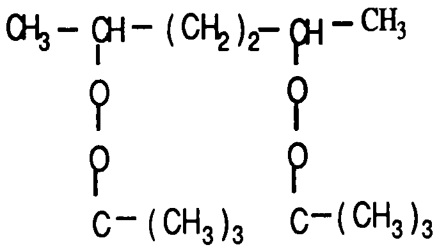
Radical generator

Dicumyl peroxide



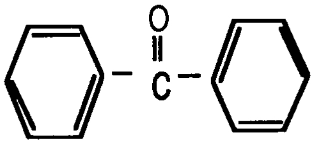
DCP

2.5-dimethyl-
2.5-t.butyl-
peroxy hexane



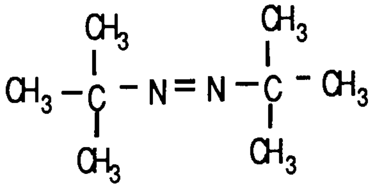
Trigonox 101

Benzophenone



B Ph

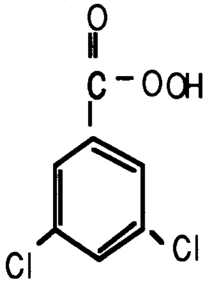
Azo bis iso butyro-
nitrile



AIBN

Oxidizing agent

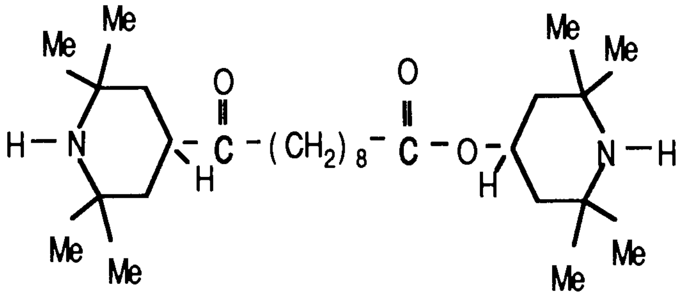
Meta-dichloro peroxy
benzoic acid



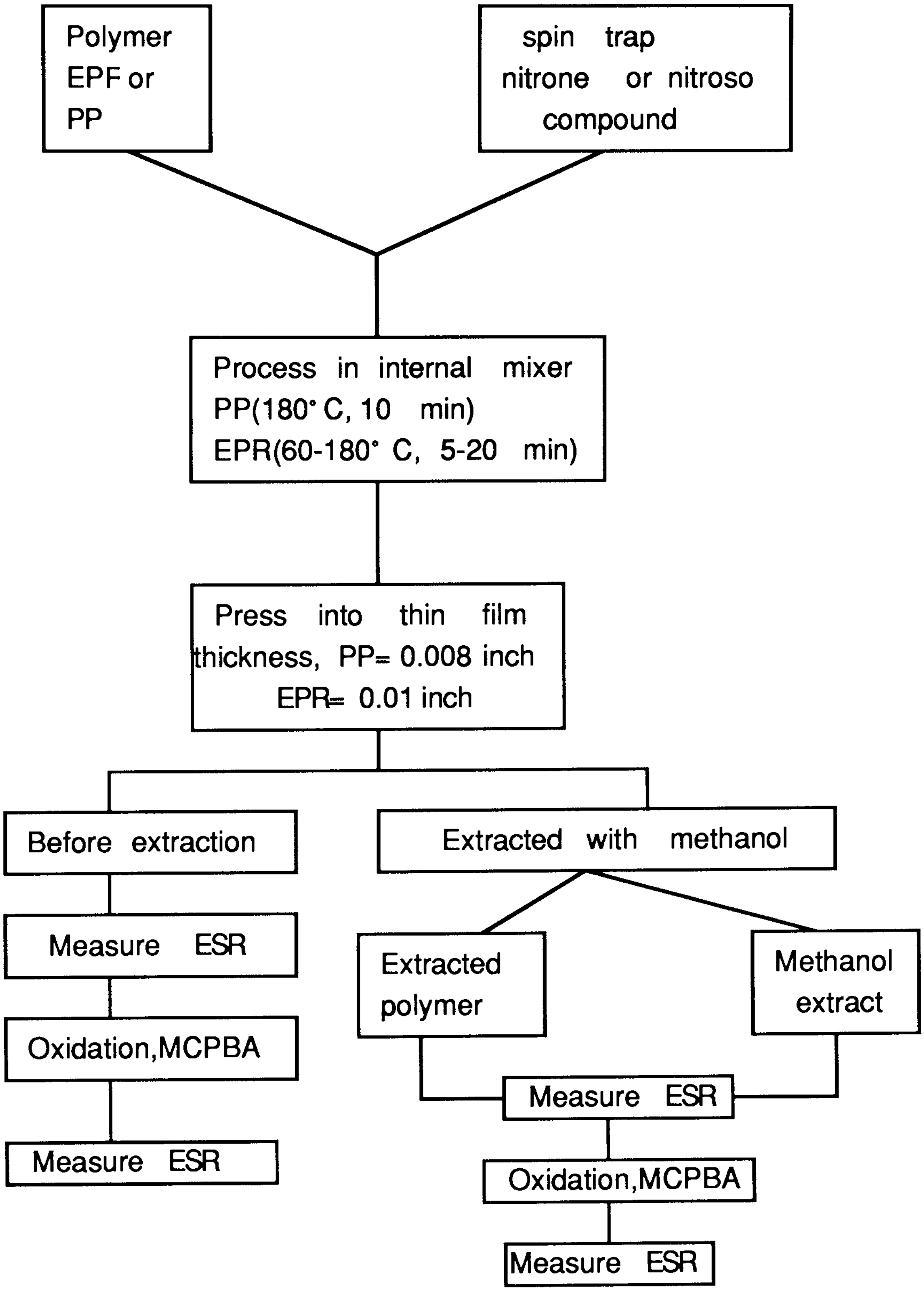
MCPBA

Standard photostabiliser

Bis (2 ,2,6, 6 - tetra methyl - 4 - pipiriydyl) sebacate



Tinuvin 770


Polymer EPF or PP
spin trap nitrone or nitroso compound
Process in internal mixer PP(180° C, 10 min) EPR(60-180° C, 5-20 min)
Press into thin film thickness, PP= 0.008 inch EPR= 0.01 inch
Before extraction
Measure ESR
Oxidation,MCPBA
Measure ESR
Extracted with methanol
Extracted polymer
Methanol extract
Measure ESR
Oxidation,MCPBA
Measure ESR

Flow chart 1

Results

ESR examination of processed EPR-masterbatches and polypropylene samples containing spin adducts showed well resolved symmetrical triplet spectra in the case of aliphatic nitroso compounds and unsymmetrical doublet and singlet spectra in the case of aromatic nitroso compounds and nitrones with the characteristic g values of nitroxyl radicals at low modulus width settings. The g value of nitroxyl radicals which were measured according to the procedure described in section (2.4.3), are given in table14.

The nitroxyl radical concentration generated during processing from 5% and 0.2% spin traps in EPR-masterbatches and polypropylene films respectively, were calculated according to procedure in section (2.4.4).

The nitroxyl radical concentration generated from 5% nitroso tert- butane (NTB) under different processing conditions with ethylene propylene rubber are shown in table 5.

These results show that [>NO·] depends on processing temperature as well as processing time. The amount of nitroxyl radical increases as temperature and/or processing time increases. However [>NO·] reached a maximum and then levelled off with increasing processing time at a given processing temperature. Under these conditions, the [>NO·] reached a maximum with 10 minutes processing at 120° C. The results are also summarised in fig. 4. The formation of maximum nitroxyl from NTB during processing with EPR at 120°C is consistent with maximum dissociation of this compound at this temperature as it was found by thermogravimetry analysis (fig.21).

The effect of solvent extraction on the above system when processed at different temperatures for 10 min is given in table 6. This result reveals that a small fraction of the derived spin adducts are in the form of macroalkyl nitroxyl radical which remains in the polymer after solvent extraction. The addition of peroxides to this system, when processed for 10 min decreased the initial amount of nitroxyl radical formed (table 7). A similar behaviour was also observed when polypropylene was processed with nitroso tert-butane in the presence of Trigonox 101,(table 8).

A marked reduction in the concentration of nitroxyl radicals in the EPR-masterbatches under different processing conditions was observed, on oxidation with (1% w/v) benzene solution of meta-dichloro peroxy benzoic acid (MCPBA). Therefore, the formation of reductive products O-alkyl hydroxylamine and free hydroxylamine under such processing condition is unlikely. This reduction can be due to oxidation of nitroxyl radical to diamagnetic products.

A similar behaviour was seen (tables 9, 10) in the effects of peroxides on the spin trapping properties of nitroso tert-octane (NTO) during polymer processing, compared with NTB. However, in general the percentage conversion of NT0 to spin adducts is much less than NTB at the same weight ratio.

ESR measurements on processed EPR-masterbatches containing spin adducts showed an unsymmetrical doublet spectra in the case of pentamethylnitrosobenzene and a singlet spectra in the case of p-nitroso 2, 6-di tert-butyl phenol. However, symmetrical triplets were obtained after oxidation with the g values of corresponding nitroxyl radicals at low modulus width settings(fig.5-8)

The results in table 10 reveal that, the addition of peroxide to the above systems during processing, reduces the initial nitroxyl radical concentration to some extent. This result also show that the nitroxyl radical concentration reaches a maximum then levels off with time of oxidation. However, in general the nitroxyl radical generated from aromatic nitroso compounds (PMNB, NDBPh) are much lower than aliphatic nitroso compounds (NTB, NTO) under the same processing conditions (shear, heat and time) and at the same weight ratio .

In contrast to aliphatic nitroso compounds, there was a marked increase in the nitroxyl radical concentration of aromatic nitroso compounds, on oxidation which is associated with the oxidation of nitroxyl derivatives, >NOR and >NOH, formed during processing. The bound nitroxyl content of these compounds in EPR is also much higher than in the case of the aliphatic nitroso compounds (compare tables 7 & 11). This could be due to the formation of macro nitroxyl radical in the case of aromatic only, since macro alkyl radicals are more likely to be trapped during processing of aromatic nitroso compound with EPR, whereas aliphatic nitroso compounds particularly NTB may trap both their own alkyl radical and macro alkyl radical from polymer. However the observation of low solubility of aromatic nitroso compounds at high concentration in EPR-masterbatch and their discoloration due to formation of conjugated unsaturation, could be a practical disadvantage in their possible application as antioxidants.

Examination of the ESR spectra of processed EPR-masterbatches containing nitrones showed unsymmetrical doublets with characteristic g value of nitroxyl radicals (fig 9). It is quite common to observe that the lines in the first derivatives ESR spectrum show variation in linewidth. One contributory feature is the anisotropy of the nitroxyl grouping, as a consequence of which the high field component of the nitroxyl triplet may be apparently broadened. This effect is particularly noticeable when free tumbling of the nitroxyl molecule is restricted when incorporated onto a large molecule(137)

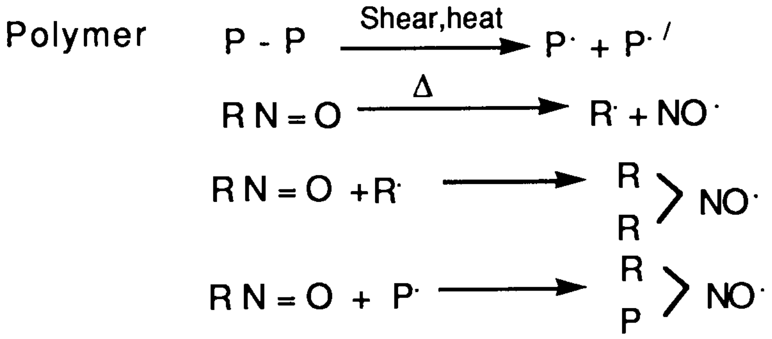
It appears from the ESR measurements (table 12) that [>NO·] is reduced when aldonitrones DPN and PBN are processed with EPR in the presence of dicumyl peroxide .In contrast, an increase in [>NO·] was observed in the case of ketonitrone PDMN. The results are shown in table 12 also reveals that the maximum conversion of DPN and PBN to the spin adducts during processing with EPR is 22 % (88 % unreacted) and 16 % (84 % unreacted), and from the reacted parts 90 % and 83 % remains in the polymer after hot methanol extraction respectively. i.e, they are in the form of macro nitroxyl radicals.

The use of Trigonox101 as radical generators during thermal processing of polypropylene with nitrones affects the amount of nitroxyl radical formed to varying extents in the case of aldonitrones DPN and PBN, the [>NO·] is declined to some extent in both EPR and PP in the presence of peroxides. However, the ketonitrone shows an increase in the [>NO·] with increasing Trigonox 101 ratio (table 13).

In general nitrones are less efficient in trapping the alkyl radical than aliphatic nitroso compounds. Nevertheless polymer -bound nitroxyl of the former DPN and PBN is much higher than the latter. A possible explanation concerning this results will be discussed fully later.

3.2.1 DISCUSSION

During processing, thermal decomposition of C-aliphatic nitroso compounds NTB, NTO in EPR leads to the formation of nitroxyl radicals by homolytic cleavage of the nitroso compound. This is followed by trapping of radical generated both from the polymer or from the spin trap itself, (scheme 7).



Polymer $P-P \xrightarrow{\text{Shear,heat}} P^{\cdot} + P^{\cdot\prime}$

$$RN{=}O \xrightarrow{\Delta} R^{\cdot} + NO^{\cdot}$$

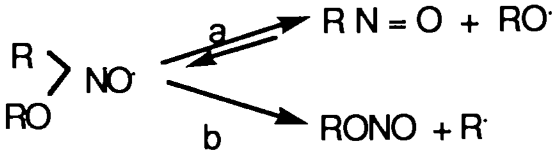
$$RN{=}O + R^{\cdot} \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!\!> NO^{\cdot}$$

$$RN{=}O + P^{\cdot} \longrightarrow \begin{matrix} R \\ P \end{matrix}\!\!\!> NO^{\cdot}$$

Scheme 7

As it is clear from table 5 the nitroxyl radical start to form during processing of NTB at about 50°C,the >NO· was also generated at the same temperature during heating of a benzene solution of NTB in the dark (see section 4.4) . This temperature is in agreement with the dissociation temperature (weight loss) of NTB in nitrogen which was obtained by TGA measurement(fig. 21) and also with the results obtained from differential scanning calorimeters(fig 20), The radical species (tert butyl radical , nitrogen oxide and di tert-butyl nitroxyl radical) so formed during heating function as impurities and decline the melting point of NTB from 81 to 75 °C (fig. 20). The results in table 5 also show that [>NO·] increases as the temperature of processing increases to 120°C. This can be attributed to the higher dissociation of NTB(dissociate to tert-butyl radical and nitrogen oxide) at the higher temperatures, as it is found from first derivative curve of this compound by TGA (fig.21). However, at longer processing time (>15 min.) at any given temperature, the [>NO·] reduced to some extent. The oxidation of rubber samples at this point with MCPBA reduced the [>NO·] almost to zero. It appears then that the formation of reductive products such as O-alkyl hydroxylamine and free hydroxylamine do not occur at longer processing times. This reduction in [>NO·] then is probably due to the oxidation of nitoxyl radical to oxoamminum salt(138).

The addition of Trigonox 101 to above system resulted in a reduction in [>NO·] under identical processing conditions (table7). This may occur by unimolecular reactions, formation of tert butoxy, tert butyl nitroxyl radical which is known to be a relatively short-lived species, and decomposes to tert-butyl nitrite and tert-butyl radical(139), or reversibly to tert-butoxy radical and nitroso tert butane (140)(reaction 36).



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In the absence of any substrate to react with the butoxyl radical, the principal decay of the nitroxyl radical was most likely involve formation of t-butyl nitrite (path b). According to the results shown in table 7, reaction 36-b is expected to be the predominant reaction. It has also been reported that the photolysis of NTB with 540-800 nm radiation in the presence of oxygen leads to the formation of tert butoxy, which can be detected by ESR spectroscopy (141).

The oxidation of EPR-masterbatches containing spin adducts (formed from NTB and Trigonox 101) with MCPBA was not associated with an increase in [>NO·]. However, an immediate sharp increase in [>NO·] in the extract solution of both EPR-masterbatches (with and without employing Trigonox 101), was observed on oxidation (table 7). It appears from this result that the spin adduct formation is not high in the case of NTB at relatively low processing temperatures and in the dark (i.e in the closed mixer), compared with in solution in daylight. In fact, the ideal medium for a high spin adduct yield is in solution and in the presence of light due to the ease of dissociation of C-aliphatic nitroso compounds in light and also to higher dimer to monomer equilibrium and ease of mobility of the generated alkyl radicals toward nitroxyl radical in solution.

Model study of NTB also confirms the formation of higher nitroxyl radical in light when compared to heat and when in the dark (section 4.4).

Trigonox 101 generally increased the spin adduct yield (initial nitroxyl radical and that obtained from oxidation of nitroxyl derivatives, >NOR, >NOH) by factor of 2, and EPR-bound nitroxyl percentage by at least a factor of six. The higher spin trapping efficiency can be accounted for by the additional formation of alkyl radical sites from the polymer in the presence of peroxide.

A general similar trapping behaviour was observed during processing of ethylene propylene rubber and PP with NTO in the presence of peroxide. The nitroxyl radical concentration in PP and EPR decreased with increasing Trigonox 101 ratio (tables 9, 10), presumably due to formation of nitroxyl derivatives. This needs further investigation, and will be discussed later.

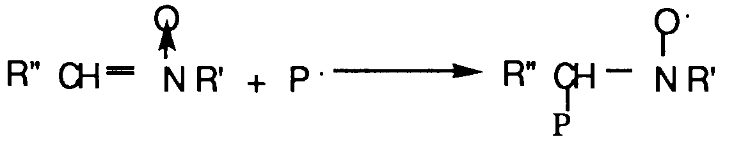
The spin trapping characteristics of aromatic nitroso compounds during processing has also been studied. A doublet spectra and singlet spectra were observed during processing in EPR from pentamethylnitrosobenzene (PMNB) and p-nitroso 2,6 di-tert-butyl phenol(NDBPh) respectively (figs. 5,7). This abnormality in the line shape could be due to restriction of free tumbling of macronitroxyl radical in the high viscosity medium of EPR. However, the formation of symmetrical triplets after oxidation with benzene solution of MCPBA, supports the effect of media on the line shape of nitroxyl radical.

The maximum nitroxyl concentration from NDBPh was formed at 100°C. when processed with EPR for 10 minutes. As the processing temperature exceeded 120°C, the nitroxyl radical almost completely disappeared(table 11). FTIR measurements of NDBph before processing in KBr disk and after processing with EPR at 120° C are compared in figures 10,11. the formation of absorption bands at 1634 and 1685 cm^{-1} at 120°C confirms the formation of quinonoid structures at high processing temperatures. The formation of quinonoid structure under processing also needs to be investigated by UV spectroscopy.

In contrast, to aliphatic nitroso compounds, aromatic nitroso compounds, when processed with EPR in the presence or absence of radical initiator, showed a marked increase in the initial nitroxyl concentration, on oxidation with MCPBA. This is attributed to the formation of reductive products (>NOR ,>NOH) during processing.

The unsymmetrical doublet spectra of nitroxyl radical formed during processing of nitrones with EPR, before and after oxidation (fig.9) could be due to coupling of nitroxyl radical with the hydrogens of the benzene ring of these compounds (142).

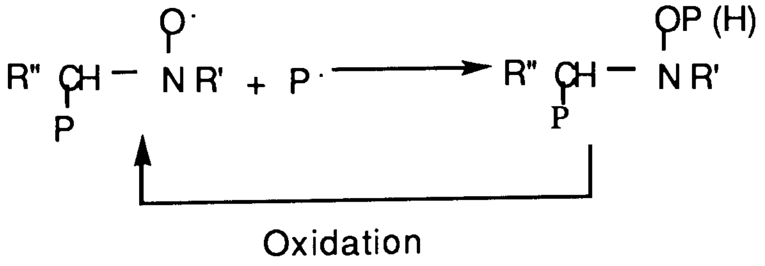
The percentage conversion of nitrones to spin adducts during processing, unlike aliphatic nitroso compounds, is quite low. However, the nitroxyl radicals generated from nitrone, exhibit much higher resistance to solvent extraction compared with aliphatic nitroso compounds, since in the former case, the only alkyl radical reservoir during processing is the polymer macroalkyl radicals, whereas in the latter case low molecular alkyl radicals are also generated from the nitroso compound. The possible reactions are given in scheme 6 and reaction 37.



$$R''\,CH{=}\overset{\overset{O}{\uparrow}}{N}R' + P^{\cdot} \longrightarrow R''\underset{P}{CH}-\overset{O^{\cdot}}{N}R'$$

37

Nitrones, like aromatic nitroso compounds (PMNB, NDBPh) and unlike aliphatic nitroso compounds (NTB, NTO), form >NOR and >NOH during processing with EPR in the presence and absence of dicumyl peroxide. This was confirmed indirectly by an increase in the initial nitroxyl concentration, on oxidation with MCPBA.

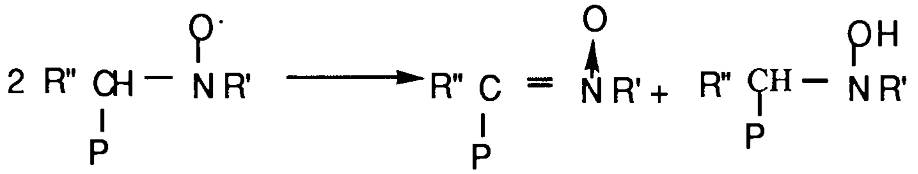


$$R''\underset{P}{CH}-\overset{O^{\cdot}}{N}R' + P^{\cdot} \longrightarrow R''\underset{P}{CH}-\overset{OP\,(H)}{N}R'$$

38

The formation of nitroxyl derivatives and regeneration of nitroxyl radical from them is shown in reactions (37, 38). The reduction in [>NO·] obtained from aliphatic nitroso compounds at longer processing times also suggests that the nitroxyl radical derived from these compounds is thermally less stable than aromatic nitroxyl radicals.

It has been reported that nitroxyls derived from aldonitrones (DPN and PBN), possessing hydrogen on the α-carbon, disproportionate to the corresponding nitrone and hydroxylamine (143)(reaction 39) which they can still be effective spin traps



$$2\,R''\underset{P}{CH}-\overset{O^{\cdot}}{N}R' \longrightarrow R''\underset{P}{C}=\overset{O}{\overset{\uparrow}{N}}R' + R''\underset{P}{CH}-\overset{OH}{N}R' \qquad 39$$

If this is the case, then the behaviour of ketonitrones with no hydrogen on α-C would be different. Results are shown in table 12 indicate that the amount of nitroxyl radical formed in this case is less than both aldonitrones, DPN & PBN under similar experimental conditions (weight ratio, temperature and processing time). The formation of hydroxyl compound which followed by the 1,3 addition of ketonitrone with hydroxylamine (144), (reaction 40) might also be another reason for the above difference.

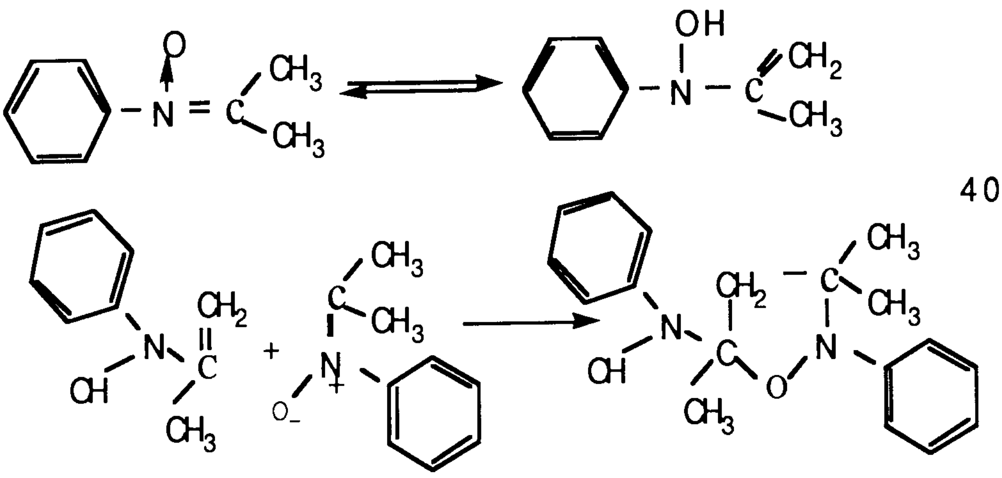


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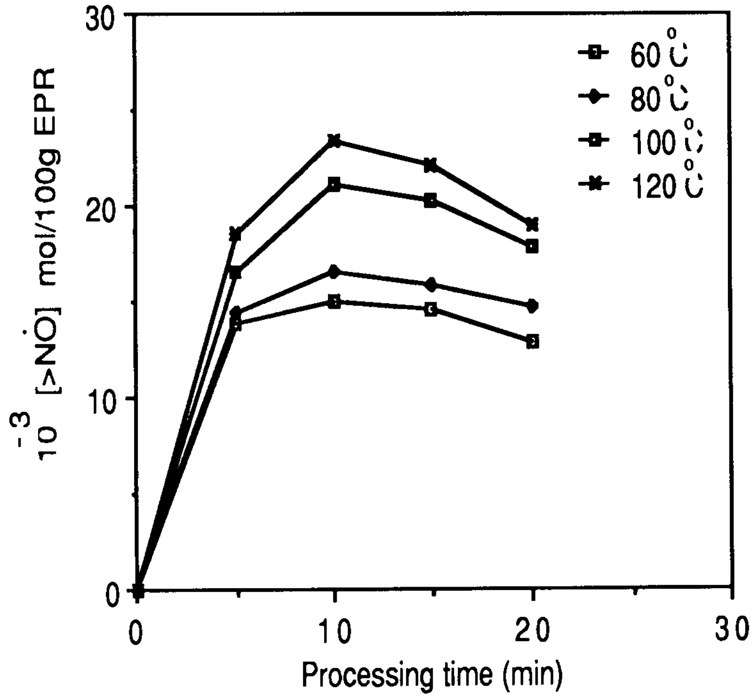
Fig. 4 The effect of processing conditions on spin trapping behaviour
(EPR was processed with 5% NTB in a closed mixer in Argon)



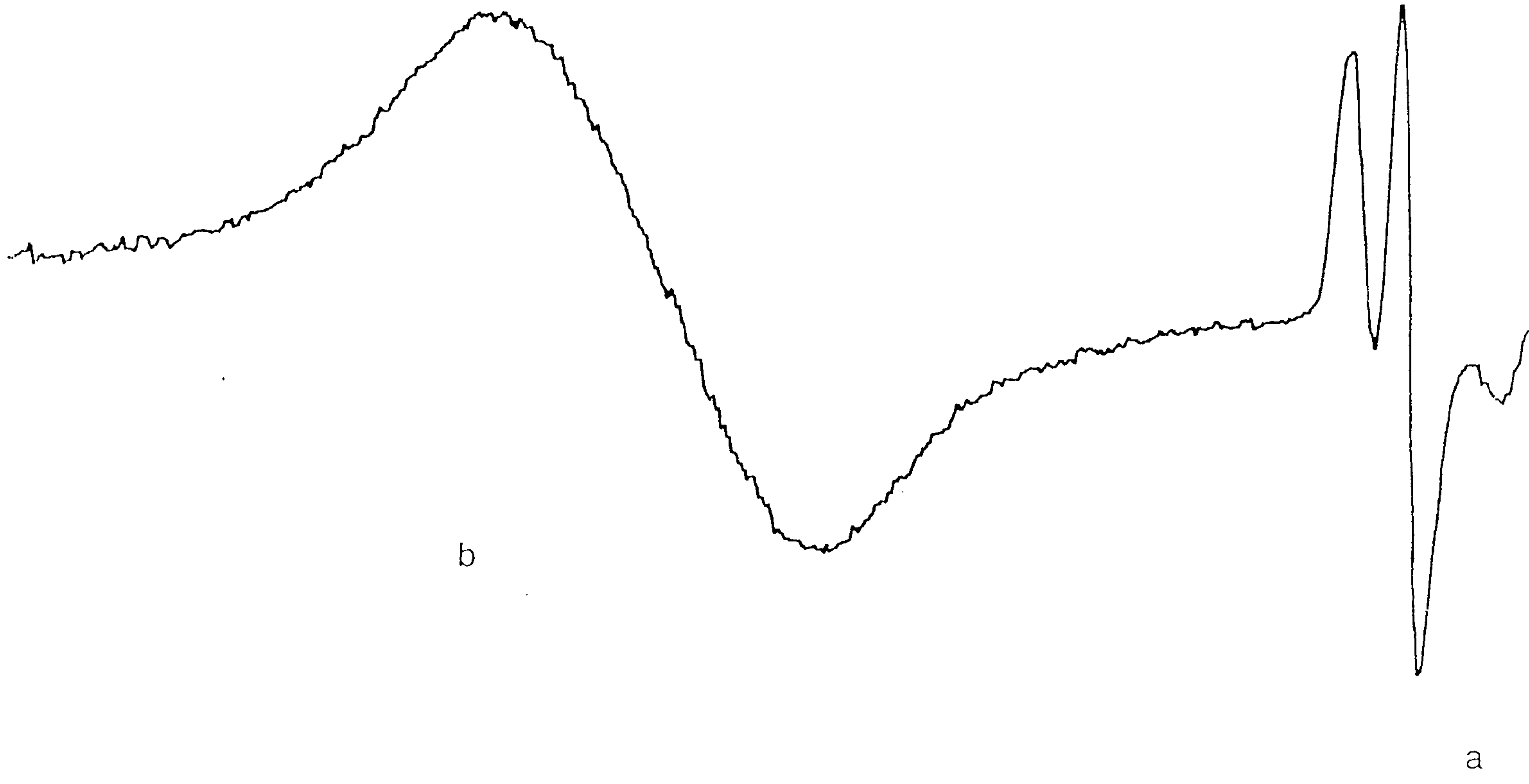


Fig. 5 ESR Spectrum of EPR-masterbatch containing 5% Pentamethylnitrosobenzene (PMNB) processed at 120°C
a) Nitroxyl radical of corresponding nitroso compound before extraction b) The reference $5H_2O$, $CUSO_4$.

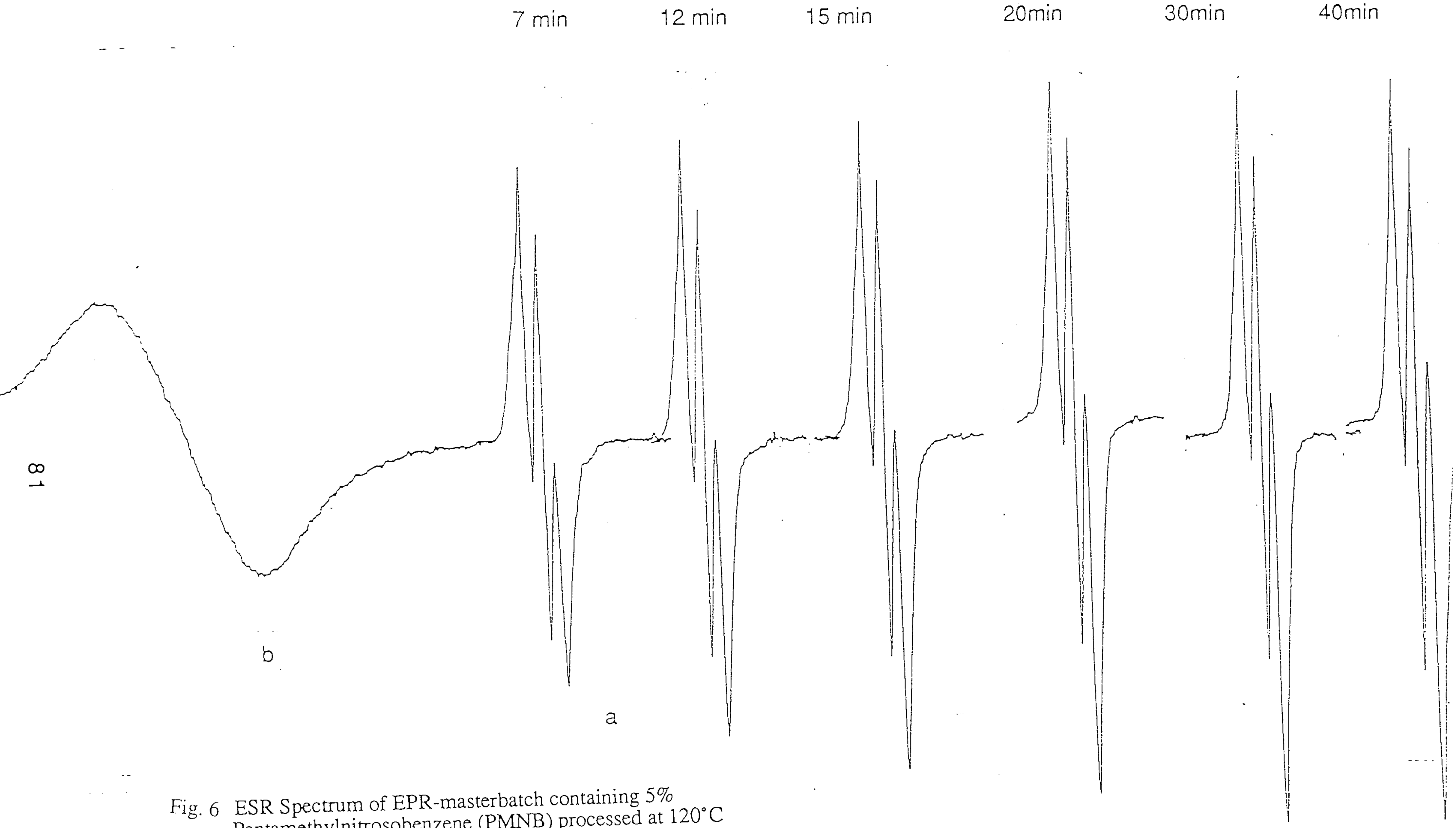


Fig. 6 ESR Spectrum of EPR-masterbatch containing 5% Pentamethylnitrosobenzene (PMNB) processed at 120°C
a) Nitroxyl radical of corresponding nitroso compound before extraction and during 40 minutes oxidation b) The reference $5H_2O$, $CUSO_4$.

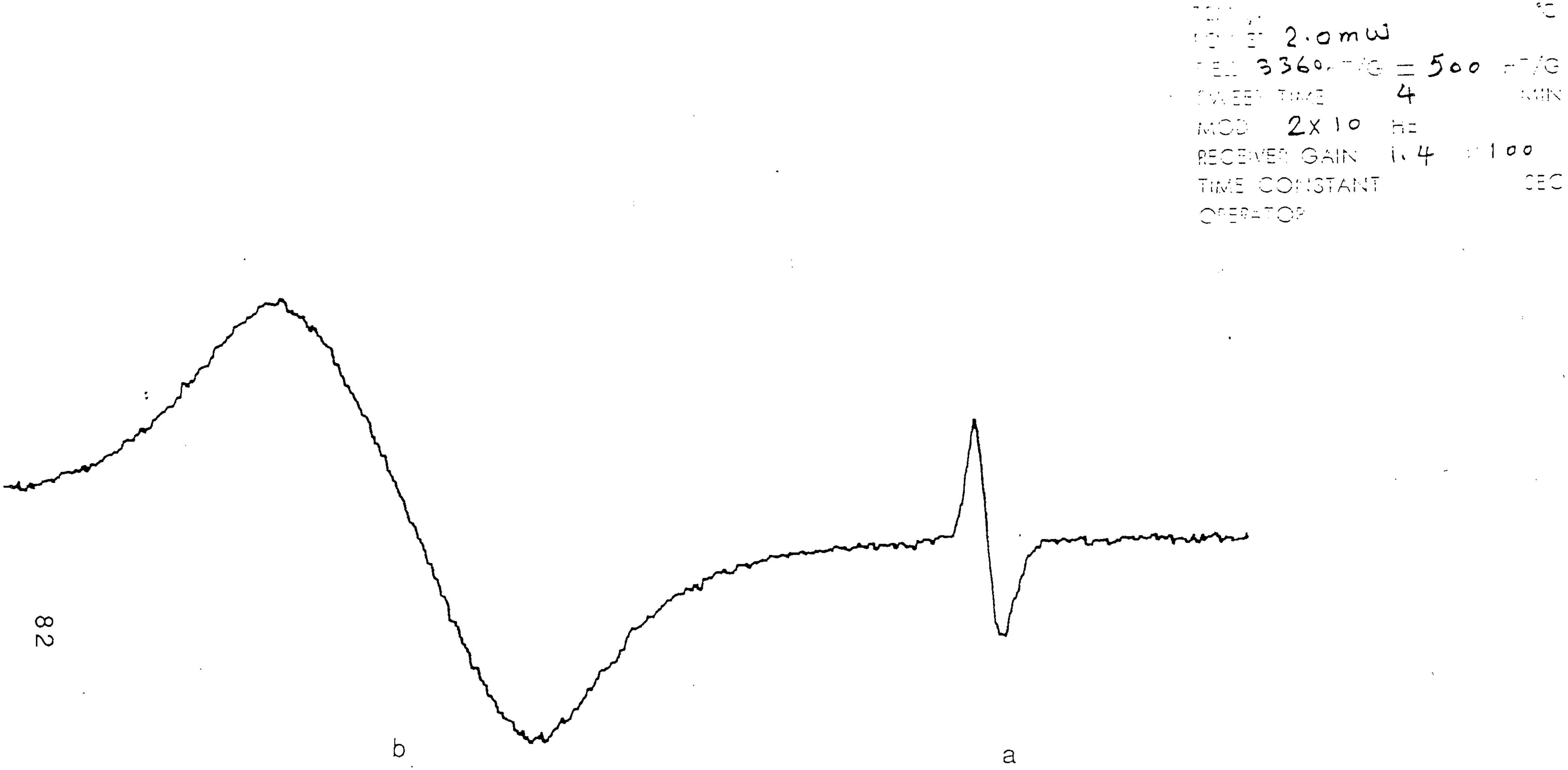


Fig. 7: ESR Spectrum of EPR-masterbatch containing 10% p-nitroso 2,6 di-tert butyl phenol(NDBPh) processed at 100°C
a) Nitroxyl radical of corresponding nitroso compound before extraction b) The reference $5H_2O$, $CUSO_4$.

TEMP. R·T °C
POWER 2· mW
FIELD 3360 mT/G ± 500 mT/G
SWEEP TIME 4· MIN
MOD. 2 x 10 Hz
RECEIVER GAIN 1·4 x 100
TIME CONSTANT SEC
OPERATOR

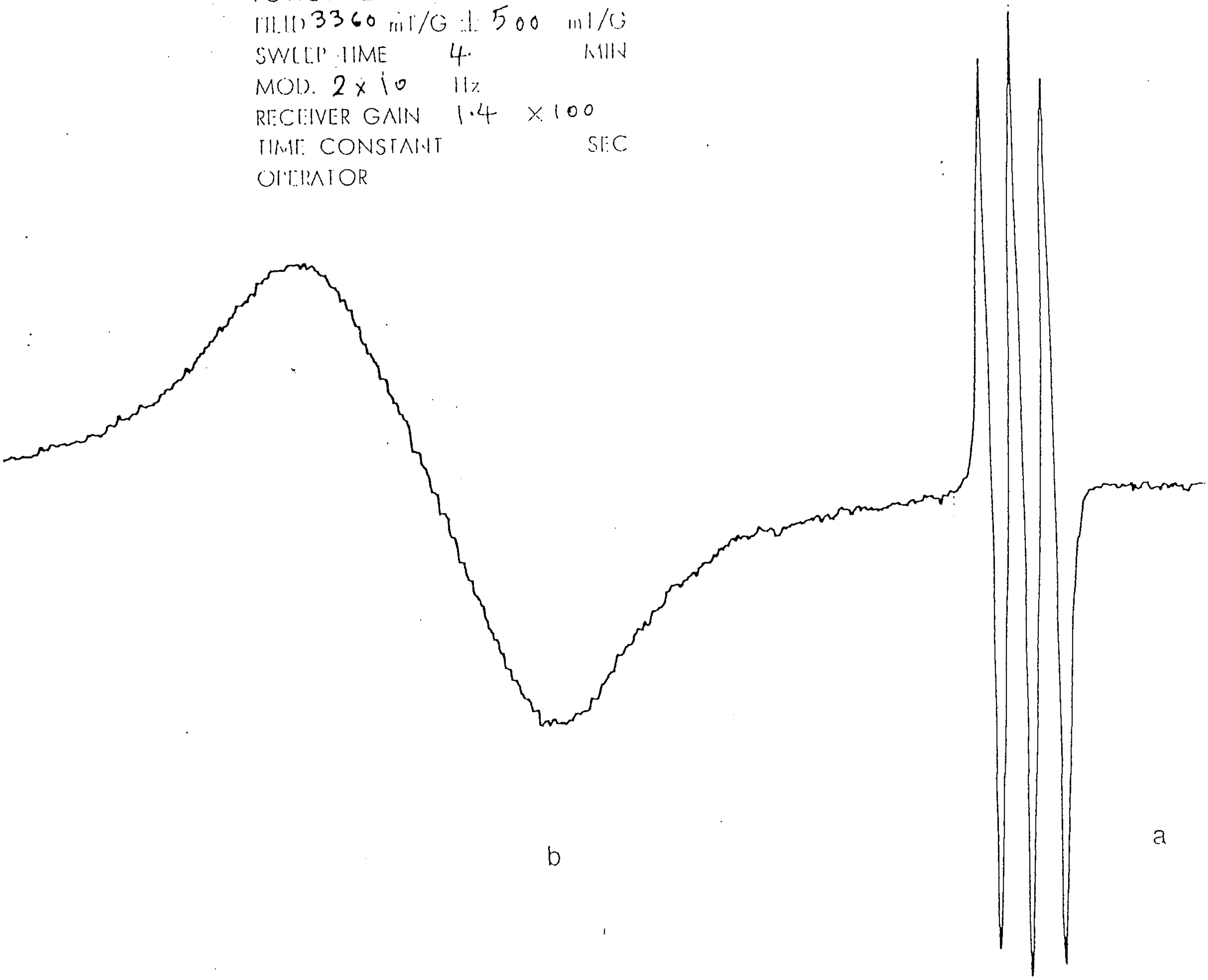


Fig. 8 ESR Spectrum of EPR-masterbatch containing 10% p-nitroso 2,6 di-tert butyl phenol(NDBPh) processed at 100°C
a) Nitroxyl radical of corresponding nitroso compound before extraction and after 4 hours oxidation with MCPBA at room temperature b) The reference 5H_2O, $CUSO_4$.

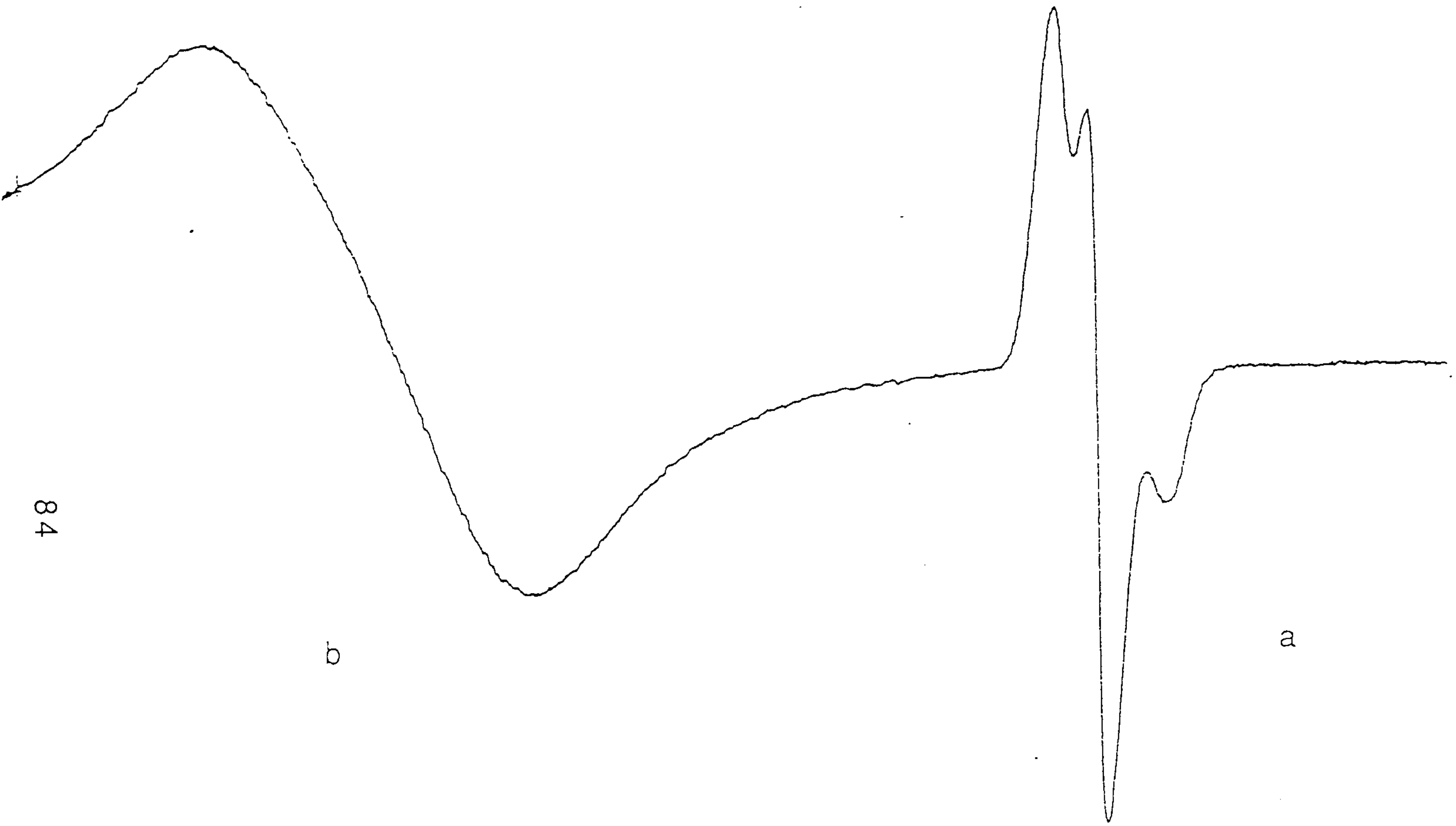


Fig.9 ESR spectrum of EPR- Masterbach containing 5 % Diphenylnitrone (DPN) processed at 60 ° C for 10 min.
a) Nitroxyl radical of corresponding nitrone
b) The reference $5H_2O$, $CUSO_4$.

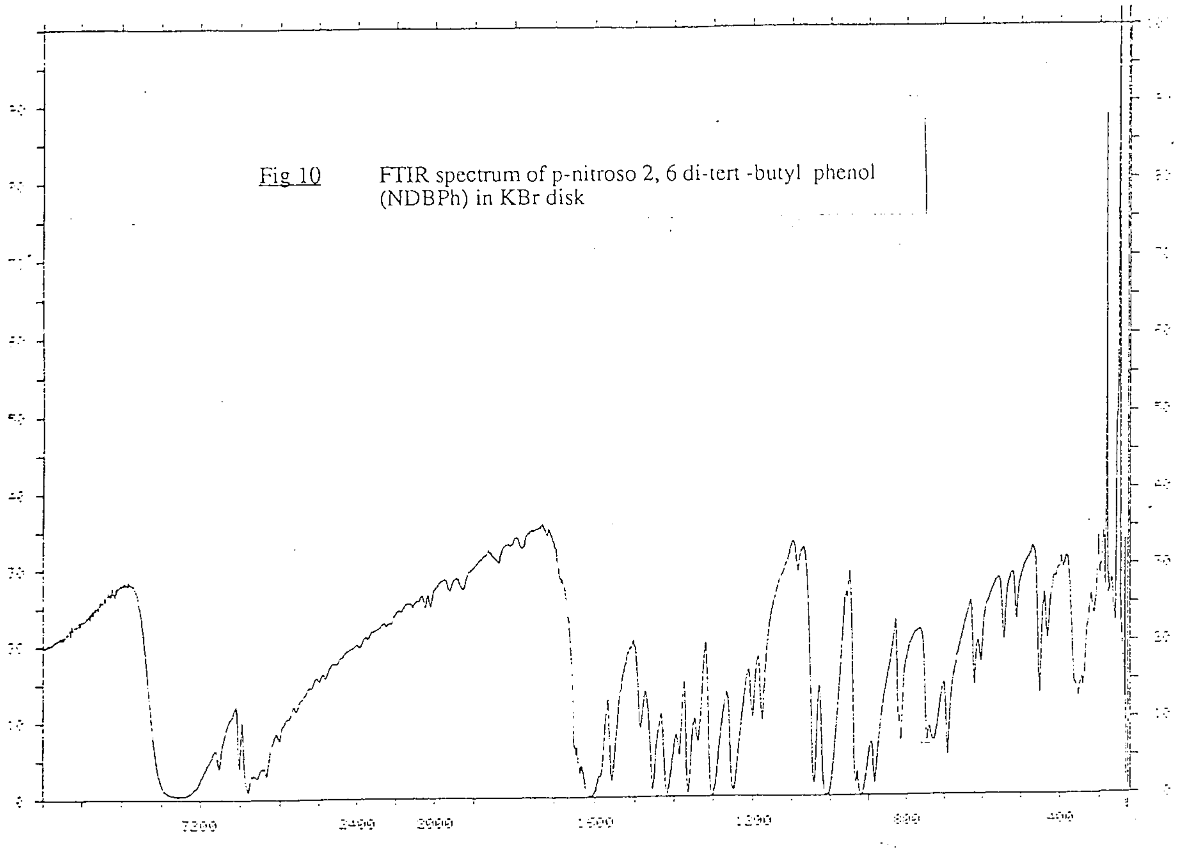


Fig 10 FTIR spectrum of p-nitroso 2, 6 di-tert -butyl phenol (NDBPh) in KBr disk

PEAK THRESHOLD = 1.00

CM-1	%T
3632.0	26.31
3328.0	0.44
3102.0	3.84
3000.0	4.03
2957.0	0.22
2866.0	2.93
2649.0	24.90
2030.0	25.08
1943.0	37.05
1932.0	37.34
1840.0	30.39
1721.0	32.55
1647.0	5.41
1598.0	0.03
1553.0	3.08
1457.0	3.07
1435.0	1.10
1417.0	0.51
1387.0	5.47
1364.0	6.47
1339.0	7.35
1302.0	9.25
1250.0	0.97
1202.0	16.77
1177.0	14.06
1085.0	29.44
1043.0	1.77
1007.0	6.13
974.0	1.47
931.0	-0.03
874.0	1.77
815.0	7.12
742.0	[illegible]
739.0	7.05
663.0	8.34
631.0	14.33
584.0	17.74
544.0	10.17

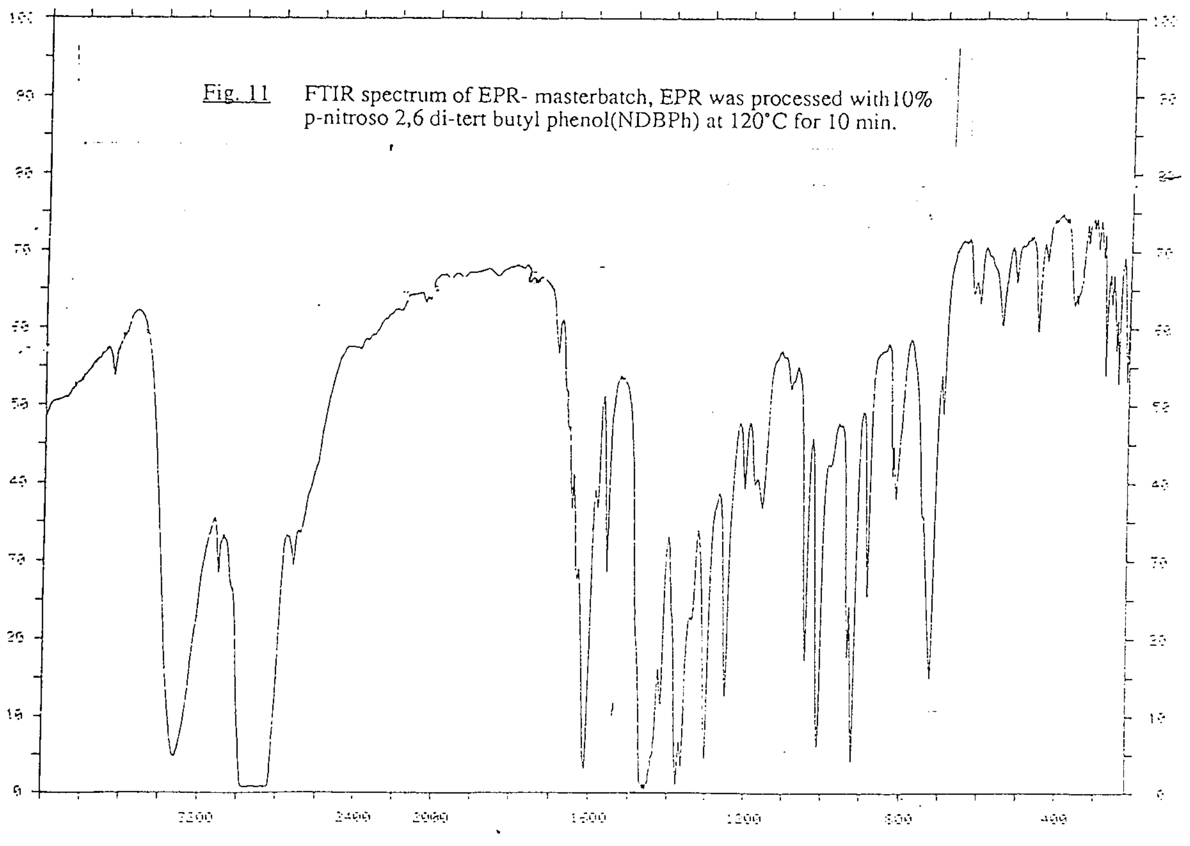


Fig. 11 FTIR spectrum of EPR- masterbatch, EPR was processed with10% p-nitroso 2,6 di-tert butyl phenol(NDBPh) at 120°C for 10 min.

PEAK THRESHOLD = 1.00

CM-1	%T
3643.0	53.86
3318.0	4.73
3193.0	23.56
2852.0	9.78
2722.0	29.50
2649.0	63.34
1963.0	66.28
1939.0	66.69
1849.0	66.76
1754.0	65.83
1740.0	66.95
1688.0	55.94
1647.0	76.29
1634.0	37.73
1611.0	3.26
1582.0	75.85
1558.0	33.51
1461.0	9.53
1456.0	9.42
1419.0	11.55
1377.0	1.19
1364.0	7.67
1302.0	4.55
1255.0	13.62
1202.0	33.38
1175.0	33.86
1155.0	37.02
1094.0	52.33
1042.0	17.34
1010.0	6.16
973.0	17.71
921.0	4.15
883.0	35.46
823.0	46.96
813.0	78.12
733.0	15.94
693.0	49.05
620.0	64.83

Table 5 The effect of processing temperature and time on spin trapping behaviour. EPR was processed with 5 % NTB in a closed mixer under different processing conditions in Argon.

Processing time (min .)	10^{-3}[>NO·] mol/100 g. EPR Processing temperature (°C) 60	80	100	120
5	13.9	14.4	16.5	18.5
10	15	16.5	21.1	23.5
15	14.5	15.9	20.3	22.2
20	12.8	14.7	17.9	19.0

Table 6 . The effect of solvent extraction on nitroxyl radical formed from NTB in EPR-masterbatch. EPR processed with 5 % NTB under Argon in a closed mixer for 10 minutes. Samples are extracted with methanol.

Processing temperature (°C)	10^{-3}[>NO·] mol/100g. masterbatch Before extraction	After extraction	%Conversion (nitroxyl)*	%EPR-bound nitroxyl**
60	12.7	1.1	22.2	8.6
80	14	1.8	25	12.8
100	21	2.0	36	9.5
120	23.5	2.2	41	9.0

* Conversion percentage of spin trap to nitroxyl radical

** Bound percentage of high molecular weight nitroxyl radical

Table 7 The effect of peroxides on the nitroxyl yield of nitroso tert-butane. EPR was processed with 5 % (0.057 mol)NTB and different concentrtion of peroxides in a closed mixer for 10 min. in Argon.

Radical generator	Molar ratio $\frac{[RG]}{[NTO]}$	Processing temperature (^{o}C)	10^{-3} [>$\dot{N}$O] mol / 100 g EPR						% Spin adduct yield (g)	% EPR - bound nitroxyl (h)
			Before extraction (a)	After extraction (b)	Before extraction & after oxidation (c)	After extraction & after oxidation (d)	Extract solution (e)	Extract solution & after oxidation (f)		
None	-	120	23.5	2.2	0.0	0.0	5	19	37	9.0
Trigonox 101	0.05	120	16	10.5	0.0	0.0	1.5	36	82	65
	0.1	120	13.1	8.9	0.0	0.0	1.2	39.5	85	68
Dicumyl peroxide	0.075	120	20.6	12	0.0	0.0	2.1	22.6	60.0	53
	0.15	120	18.3	11.1	0.0	0.0	3.0	27	66.8	60.6

$$(g) = \frac{100\ (b\ +f)}{[NTB]}\ ,\quad (h) = \frac{100(\ b\ )}{(\ a\ )}$$

Table 8 The effect of radical generators (RG) on the spin trapping behaviour of NTB. (Polypropylene was processed with 0.2 % NTB and different concentrations of radical generators at 180 °C for 10 min)

Radical generator	Molar ratio $\frac{[RG]}{[NTB]}$	$10^{-5}[>NO\cdot]$ mol /100 g PP		% PP-bound nitroxyl
		Before extraction	After extraction	
None	0.0	13.8	2.1	15
Trigonox 101	0.2	5.8	3.9	67
	0.4	3.1	2.2	70
	0.8	1.9	1.6	81
	0.12	0.5	0.4	80
Dicumyl peroxide	0.15	10.3	8.2	79
	0.3	7.1	5.2	73
Benzophenone	0.45	10.9	3.9	35
	0.9	8.9	3.5	39
AIBN	0.5	4.6	0.7	15
	1	3.9	0.6	15

Table 9 The effect of Trigonox101 ratio on the spin trapping behaviour of NTO (PP was processed with 0.2% NTO and different concentrations of Trigonox101 at 180 ° C for 10 min).

Peroxide	Molar ratio [Trigonox101] / [NTO]	10^{-4} [>NO·] mol/100g. PP		%PP-bound nitroxyl
		Before extraction	After extraction	
None	0	7.0	0.9	13
Trigonox 101	0.7	5.9	3.3	56
	0.14	2.1	1.5	71
	0.21	0.4	0.3	75

Table 10 The effect of peroxides on the nitroxyl yield of nitroso tert-octane. EPR was processed with 5 % (0.035 mol)NTO and different concentrtion of peroxides in a closed mixer at different temperatures for 10 min .

Radical generator	Molar ratio $\frac{[RG]}{[NTO]}$	Processing temperature (^{o}C)	10^{-3} [>NȮ] mol / 100 g EPR						% Spin adduct yield (g)	% EPR - bound nitroxyl (h)
			Before extraction (a)	After extraction (b)	Before extraction & after oxidation (c)	After extraction & after oxidation (d)	Extract solution (e)	Extract solution & after oxidation (f)		
None	-	80	12.5	1.5	0.0	0.0	4.2	8.1	27.7	12
	-	120	13.2	1.4	0.0	0.0	3.9	9.0	29	10.6
Trigonox 101	0.05	120	10.0	4.3	0.0	0.0	0.8	16	58	43
	0.1	120	11.2	5.6	0.0	0.0	0.6	34	70	50
Dicumyl peroxide	0.075	120	12	3.8	0.0	0.0	1.6	13	48	31.6
	0.15	120	13.5	3.2	0.0	0.0	0.9	14	49	23.2

$$(g) = \frac{100\ (b + f)}{[NTO]}, \quad (h) = \frac{100(b)}{(a)}$$

Table 11 The effect of dicumyl peroxide on the spin trapping behaviour of nitroso aromatic compounds

(EPR was processed with 5 % of these spin traps and DCP in a closed mixer for 10 min)

Nitroso compound	Molar ratio $\frac{[DCP]}{[\text{Spin trap}]}$	Processing temperature (° C)	10^{-3} [$>N\dot{O}$] mol/ 100 g EPR				Spin adduct Yield (%)	% EPR - bound nitroxyl
			Before extraction	After extraction	Before extraction & after oxidation	After extraction & after oxidation		
PMNB	0.0	120	0.4	0.2	2.1	2.0	10	50
	0.1	120	0.32	0.25	2.5	2.3	12.5	78
NDBph	0.0	100	0.05	0.02	0.4	0.2	2.0	40
	0.1	100	0.03	0.025	0.8	0.4	4.0	83

Table 12 The effect of radical generator, solvent extraction, and oxidation on the yield of nitroxyl.

EPR was processed with 5 % nitrones at different temperature for 10 min. Extracted with methanol Oxidized with MPBA

Nitrone	Molar ratio (DCP) / (Nitrone)	Processing temperature (°C)	10^{-3} [>NO] mol / 100 g EPR						% Spin adduct yield	% EPR - bound nitroxyl
			Before extraction	After extraction	Before extraction & after oxidation	After extraction & after oxidation	Extract solution	Extract solution & after oxidation		
DPN	0.0	80	1.1	0.8	4.0	2.7	0.0	0.02	16	72
	0.02	80	1.0	0.7	3.0	3.9	0.0	0.01	12	70
	0.0	120	1.46	1.26	5.3	2.9	0.0	0.02	21.2	90
	0.02	120	1.25	1.0	4.0	4.35	0.0	0.01	16	85
PBN	0.0	80	0.99	0.77	3.7	2.5	0.0	0.05	12	72
	0.02	80	0.91	0.74	3.9	3.0	0.0	0.04	13	81
	0.0	120	1.3	1.02	4.3	3.19	0.0	0.04	14	78
	0.02	120	1.1	0.92	4.8	4.35	0.0	0.02	16	83
PDMN	0.0	80	0.537	0.46	1.5	0.455	0.0	0.03	5	80
	0.02	80	0.597	0.38	1.6	1.12	0.0	0.05	5.3	63
	0.0	120	0.40	0.25	1.2	0.3	0.0	0.02	4.0	62
	0.02	120	0.46	0.21	1.35	0.9	0.0	0.02	4.5	45

Table 13 The effect of radical generator on spin trapping behaviour.(PP was processed with 0.2 % nitrones in a closed mixer at 180 ° C for 10 min)

Nitrone	Molar ratio $\frac{[\text{Trigonox101}]}{[\text{ nitrone }]}$	10^{-5}[>NO·] mol/100 g PP		
		Before extraction	After extraction	% PP- bound nitroxyl
NDP	0.0	6.4	5.0	78
	0.17	6.1	5.0	81
	0.34	5.7	4.9	85
	0.51	4.2	3.8	88
PBN	0.0	4.3	2.0	46
	0.15	4.1	3.2	78
	0.30	3.8	3.2	84
	0.45	3.0	2.6	86
PDMN	0.0	2.6	0.3	11
	0.13	2.9	0.45	15
	0.26	3.1	0.45	14.5
	0.39	3.8	0.6	15.7

Table 14 g value of nitroxyl radicals derived from nitroso compounds and nitrones . The g values of ESR spectra was measured at low setting width according to the method described in section 2.4.3

Spin trap	g values (± 0.0005)
NTB	2.006
NTO	2.0062
PMNB	2.0066
NDBPh	2.0059
DPN	2.0061
PBN	2.0065
PDMN	2.006
NDPA	2.005

CHAPTER 4

The identification and quantification of the spin adducts formed from nitroso tert butane (NTB) in masterbatch prepared by photochemical reaction

4.1 Object and Plan

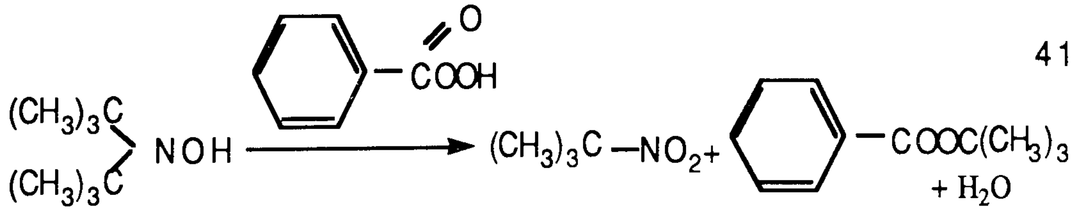
The spin trapping technique could be carried out more effectively in solution than in the solid phase. This could be attributed to the following reasons

1) It is possible to carry out the experiments in absence of air (i.e in argon) in order to reduce the complexity involved in the radicals formed.
2) In the pure state, NTB exists as a colourless crystalline dimer, therefore the dissociation constant, KC= $[\text{monomer}]^2/[\text{dimer}]$, of the spin trap used is an important parameter in the quantitative application of the spin trapping technique. It has been reported that this compound dissociates almost completely in solution to the blue monomer (145,146).
3) In addition, NTB creates monomer vapour during processing and therefore loss of part of the compound is inevitable because it is not completely a closed system, so with employing this technique in solution in a closed system, the risk of the compound loss could be reduced.

4.2 Results

ESR examination of U.V irradiated EPR solution containing nitroso tert-butane and radical initiators showed a well resolved symmetrical triplet spectra with the characteristic g value of a nitroxyl radical. A marked change in the amount of nitroxyl radical of the EPR-solution containing NTB was observed where the solutions were irradiated in the presence of radical generators. The amount of nitroxyl radical formed in all the solutions examined increased to a maximum , then decreased and disappeared. However, the time dependent behaviours are different from each other. The experimental method is indicated in flow chart 2, and the result are summarized in fig .12

An immediate increase in the [>NO·] of NTB solutions irradiated at different intervals, was observed on oxidation with MCPBA. It appears from these results that, besides nitroxyl radical, other compounds presumably >NOR and >NOH are simultaneously formed during UV irradiation (table 15). These results also confirm that there is a non-linear relationship between decay of nitroxyl radical and the formation of its derivatives during UV irradiation. This non-linearity could be attributed to the higher reactivity of the generated nitroxyl radical than the original spin trap toward alkyl radicals in solution. It was also found experimentally that the regenerated nitroxyl radicals of oxidised solution almost disappeared at longer oxidation time, presumably due to formation of nitro compound. The formation of nitrobutane in high yield from oxidation of disubstituted hydroxylamine having no α-hydrogens, such as tBu_2NOH, with peroxy benzoic acid has been also reported (147,148) (reaction 41)



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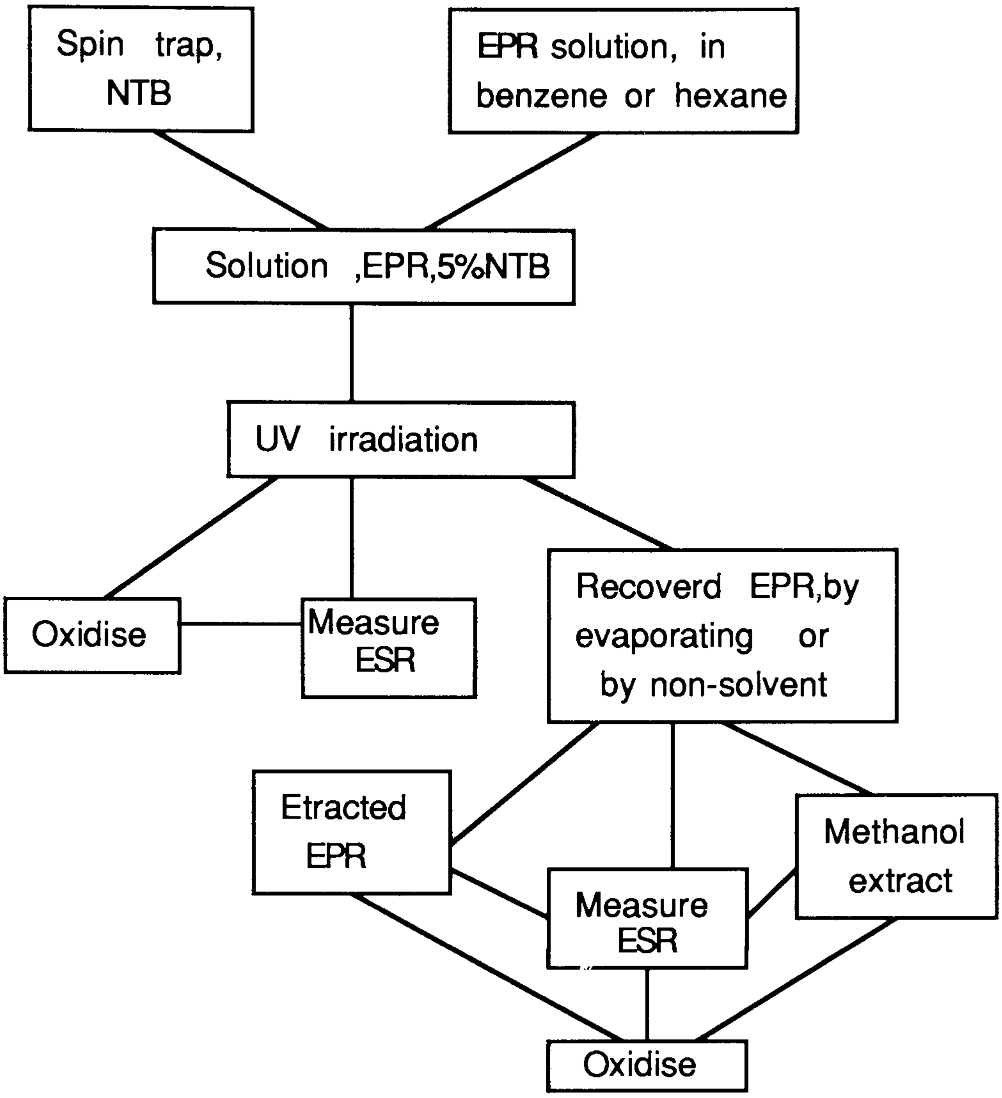


Flow chart 2

The effect of different solvents and oxidising agents such as MCPBA, on the concentration of nitroxyl radical formed from NTB in EPR solutions irradiated at interval times are given in (fig 13 and table 15) and in EPR-masterbatches recovered from solutions according to procedure described in flow chart 2 are given in table 17.

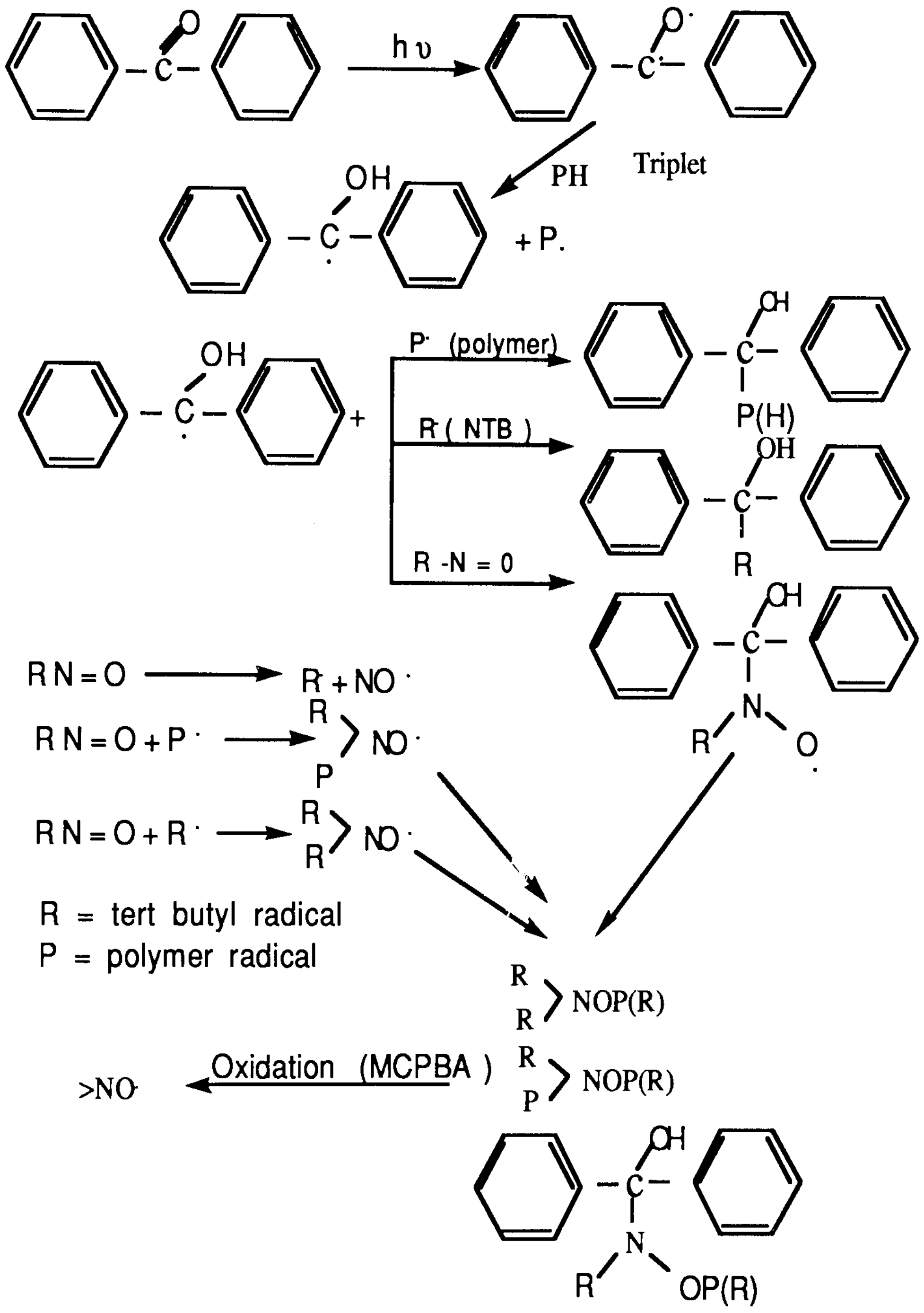
The effect of benzophenone sensitisation on the spin trapping properties of NTB in EPR in benzene solution is shown in fig 12. This result indicates that not only is the amount of nitroxyl radical much higher in the presence of benzophenone during UV irradiation, but its rate of decay is also higher. The regeneration of a higher nitroxyl radical concentration, on oxidation, confirms the formation of a higher initial concentration of nitroxyl derivatives during UV irradiation in this case (table 16). ESR measurements of unextracted and hot methanol extracted EPR samples recovered from benzene solution by addition of a non-solvent (methanol) after 2 hours UV irradiation, reveals that at least 90% of the nitroxyl is in the form of macroalkyl nitroxyl which remains in the polymer during extraction (table 16)

DISCUSSION

The extent of transformation of alkyl nitroso compounds to nitroxyl and polymer bound nitroxyl percentage of NTB increased in the presence of radical initiators, particularly with benzophenone. This is attributed to the formation of additional free radical sites on the polymer by abstraction of hydrogen from polymer chains.

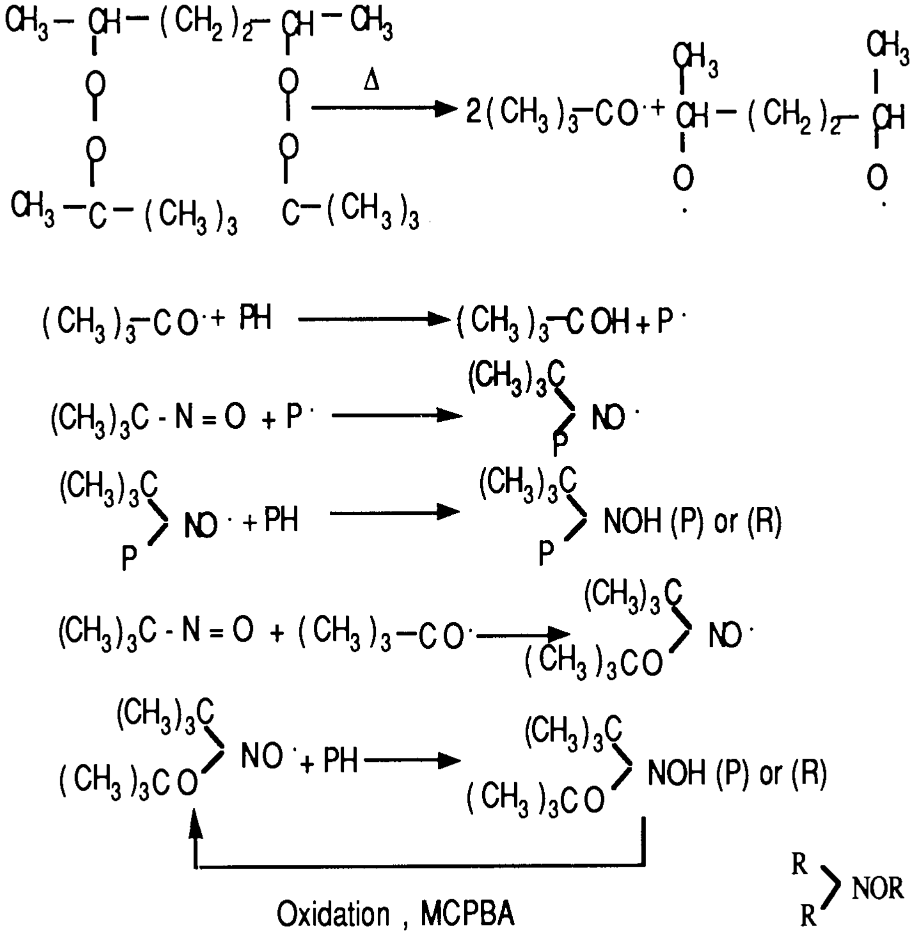
The rate of formation and decay rate of nitroxyl radical formed from NTB in the case of benzophenone is also much higher than in the case of Trigonox 101. This may be consistent with the fact that energy required to cleave the O-O bond in peroxides is higher than the excitation of π electron in C=O bond in benzophenone. The possible reactions occur during photolysis of benzophenone and Trigonox 101 are given in schemes 8 and 9.

It is also apparent from fig. 13, that spin trapping efficiency is solvent dependent. The spin adduct yield of NTB in benzene was higher than in hexane under similar conditions.



R = tert butyl radical
P = polymer radical

Scheme 8



R = tert butyl from NTB

Scheme 9

This could be due to a better solubility of polymer in benzen than hexane and in turn to the formation of higher macroalkyl radical on the effect of UV light.

Oxidation of these solutions with MCPBA at intervals during UV exposure, showed an increase in the [>NO·] suggesting that the formation of nitroxyl derivatives (>NOR, >NOH) from NTB in solution is possible because the diffusion of alkyl radicals to nitroxyl is not limited by the viscosity of the medium. Grattan et al (149) have shown the formation of nitroxyl radicals from model O-alkyl-substituted hydroxylamines under photo-oxidative conditions in solution.

It is therefore to be expected that nitroxyl radicals would be formed under oxidative conditions from macroalkyl hydroxylamine attached to the polymer chain. However, all attempts to identify by FTIR a band at 1140 cm^{-1} which has been reported (150) to be due to O-alkyl hydroxylamine were unsuccessful.

Comparison of the spin trapping behaviour of NTB along with or without radical initiator during photolysis in solution and thermolysis (processing) reveals that polymer-bound nitroxyl is increased to some extent in solution. This could be again due to the ease of migration of macroalkyl radical toward spin trap or spin adduct.

Fig. 12 The effect of radical generator on [>NO·] formed during EPR-masterbach preparation (Benzene solution of EPR containing 5 % NTB and 1x10 $^{-4}$ mole radical generator UV irradiated).

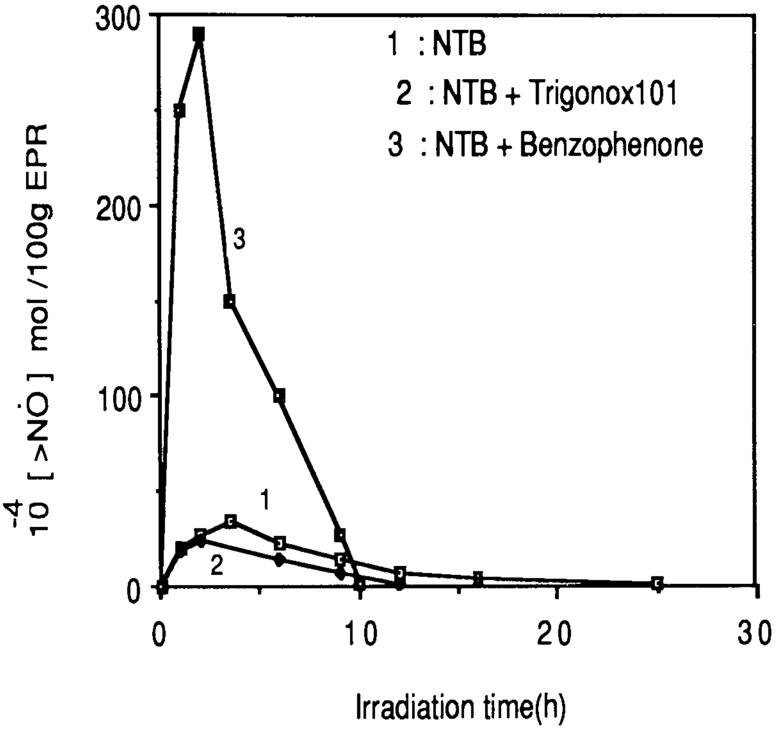


Fig. 13 The effect of solvent on the yield of nitroxyl of NTB,EPR solution containing 5% NTB & 1% DCP was exposed to UV light in Argon, ESR spectra of samples irradiated at intervals run before and after oxidation with MCPBA at room temperature.

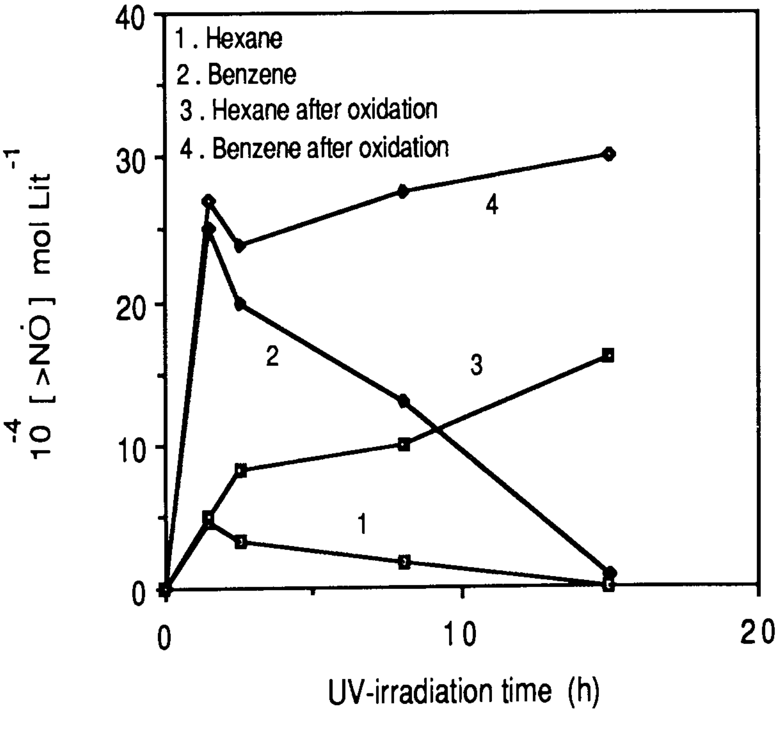


Table 15 The effect of solvent on the nitroxyl yield of nitroso tert-butane. EPR solutions containing 0.028 mole lit^{-1}NTB and 10^{-4} mole lit^{-1} DCP in the presence of Argon was exposed to UV light and ESR spectra run at intervals. Oxidised with MCPBA.

		10^{-4} [>NO·]mol lit^{-1}		
UV-irradiation time (h)	Solvent	**Before** oxidation	After oxidation	% maximum conversion of NTB to>NO· after oxidation
1.5	hexane	4.5	5.0	1.7
	benzene	25	27	9.4
2.5	hexane	3.3	8.3	2.8
	benzene	17	20	7.0
8	hexane	1.8	10	3.5
	benzene	13	22	7.7
16	hexane	0.09	35	12
	benzene	0.8	62	22

Table 16 The effect of benzophenone (BPh) on the spin trapping properties of NTB . Benzene solution of EPR containing 5% NTB and 10 % benzophenone was UV irradiated for 2.0 hours in the presence of Argon, extracted with methanol, oxidized with1 % W / V benzene solution of MCPBA

Molar ratio $\frac{[BPh]}{[NTB]} \times 10^{-4}$	10^{-4} $[>N\dot{O}]$ mole /100g rubber						%	
	Before extraction	After extraction	Before extraction & after oxidation	After extraction & after oxidation	Solution of extract	Solution of extract after oxidation	Spin adduct Yield	% EPR - bound nitroxyl
None	20	2.3	23	5.9	10	18	4.0	11.5
1	290	265	390	360	20	5.0	70	91

Table 17 The effect of oxidation on the regeneration of nitroxyl radical from EPR - masterbatch . EPR solution containing 5 % (0.057 mol)NTB was exposed to UV light for 16 hours, recoverd masterbatch was oxidized with 1% solution of peracid at room temperature .

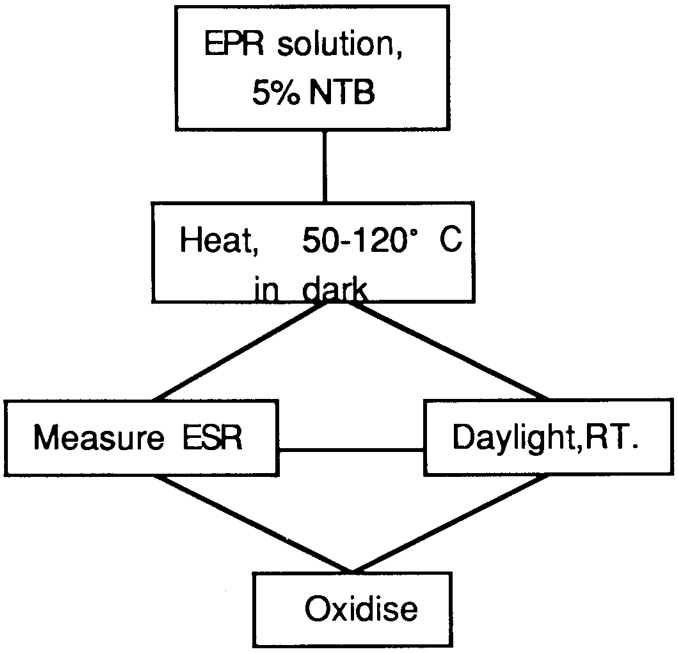
Solvent	$\frac{10^{-4}\,[\text{NTB}]\,\text{mol}}{100\text{g EPR}}$	Molar ratio $\frac{[\text{DCP}]}{[\text{NTB}]}$	10^{-4} [>NO$^{\bullet}$] mole / 100g EPR					
			Before extraction (a)	After extraction (b)	Before extraction & after oxidation (c)	After extraction & after oxidation (d)	%Spin adduct Yield (e)	% EPR - bound nitroxyl (f)
Benzene	570	0.0	1.4	0.9	125	65	22	64
		1	1.5	1.25	187	110	33	83
Hexane	570	0.0	1.2	0.7	69	45	12	58
		1	1.3	1.0	140	89	25	76

$$(e) = \frac{100\ x(c)}{[\text{NTB}]}\ , \qquad (f) = \frac{100\ (b)}{(a)}$$

4.4 A STUDY OF THE SPIN TRAPPING BEHAVIOUR OF NITROSO TERT-BUTANE IN SOLUTION (MODEL STUDIES)

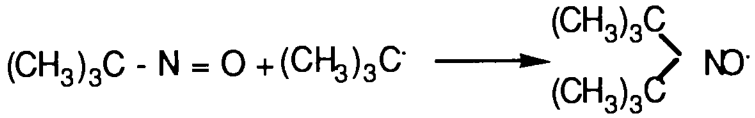
It is important to investigate the reaction behaviour of nitroso tert butane in the absence of polymer under thermal and light conditions, in order to explore the optimum conditions of spin trapping and the mode of action of NTB as photostabiliser.

An ESR quartz tube containing $2.0\text{x}10^{-4}$ mole NTB in benzene solution was deoxygenated by bubbling Argon gas, sealed, and then heated gradually in an oil bath in total darkness up to 120°C. ESR examination showed that nitroxyl radicals start to form at about 50°C and their concentration increases with temperature up to 120°C. This is consistent with the maximum dissociation of this compound at 120°C(dissociate to tertiary butyl radical &nitrogen oxide)found by TGA in Nitrogen (fig.21). After leaving the deoxygenated quartz tube in daylight at room temperature, the nitroxyl radical sharply increased in the first few hours, reaching a maximum within a few days. The [>NO·] then decayed to nearly zero within two weeks and was not eventually detectable by ESR. Discolouration also observed at this stage (initially blue changing to yellow), presumably due to formation of O-alkyl hydroxyl amine. Oxidation of the yellow solution with 1% w/v benzene solution of meta-di chloro per benzoic acid was associated with an immediate regeneration of nitroxyl radical. The nitroxyl radical concentration reached a maximum within 15 min., and then decreased almost to zero with further oxidation time. The experimental method is shown in flow chart 3 and the results are summarised in fig. 14.



The thermal decomposition or photolysis (151,152) of NTB leads to formation of nitroxyl radicals. This is produced by homolytic cleavage followed by trapping of radicals formed (reactions 42,43). An ESR spectrum with the hyperfine splitting due to a nitrogen nucleus (15.7 gauss) developed.

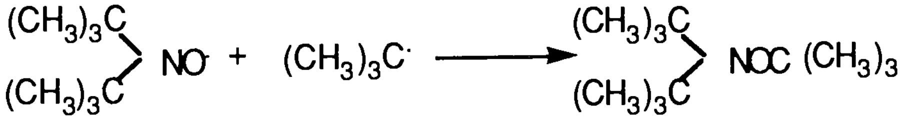
$$(CH_3)_3C - N = O \xrightarrow{h\upsilon\ ,\ \Delta} (CH_3)_3C^{\cdot} + NO^{\cdot} \qquad 42$$



$$(CH_3)_3C - N = O + (CH_3)_3C^{\cdot} \longrightarrow \begin{matrix}(CH_3)_3C \\ (CH_3)_3C\end{matrix} > NO^{\cdot} \qquad 43$$

The more rapid increase in the [>NO·] during photolysis as compared to thermolysis could be attributed to a higher rate of alkyl radical formation from the photodissociation of the spin trap agent.

The decay of the spin-adduct radical is attributed to its reaction with tert butyl radical, giving a diamagnetic product;



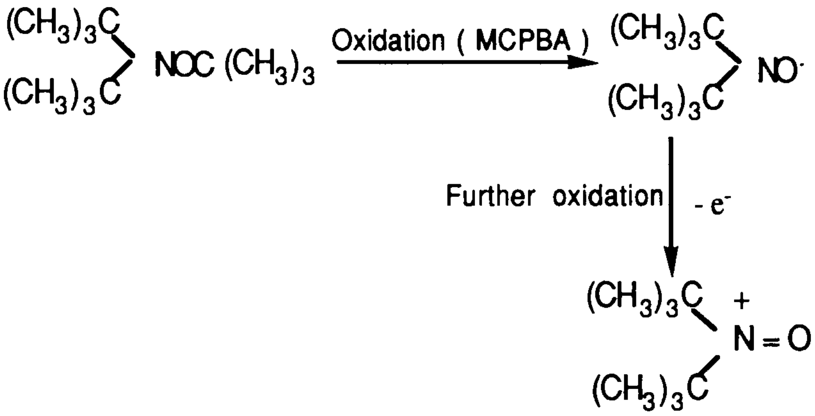
$$\begin{matrix}(CH_3)_3C \\ (CH_3)_3C\end{matrix} > NO^{\cdot} + (CH_3)_3C^{\cdot} \longrightarrow \begin{matrix}(CH_3)_3C \\ (CH_3)_3C\end{matrix} > NOC\,(CH_3)_3 \qquad 44$$

The reaction between di-tert butyl nitroxyl and the tert-butyl radical was presumed to occur in the gas-phase pyrolysis of NTB (153). The adduct radicals do not combine with themselves, and so such a combination reaction can not be a reason for their decay. this decay in the spin adduct can also not be due to the formation of free hydroxylamine, because there is not any opportunity for the spin adduct to abstract hydrogen from the medium. Therefore, the sharp increase in the [>NO·] in solution (six times more than initial [>NO·]) on oxidation with MCPBA at room temperature might be associated with the regeneration of nitroxyl only from O-alkyl hyroxylamine formed during photolysis.

The tert butyl radical reacts with its spin-adduct radical formed from NTB more readily than with spin trap itself, the rate constant of this process was found to be 10 times as large as that of the spin trapping, so that the yield of the spin radical can not go above certain level (154).

The solution at the point (A) in fig 14, where the nitroxyl radical was completely converted to its reduction products was examined by FTIR. All attempts to identify a peak at 1140 cm^{-1} which has been reported to belong to O-alkyl hydroxylamine (150) was unsuccessful. Further investigation by HPLC-MS is required, in order to analyse the nature of the compounds at different stages of photolysis.

On further oxidation the regenerated nitroxyl radical disappeared, presumably due to formation of an oxoammonium salt, which may decompose via several pathways(139). The oxidation process is given in reaction 45.



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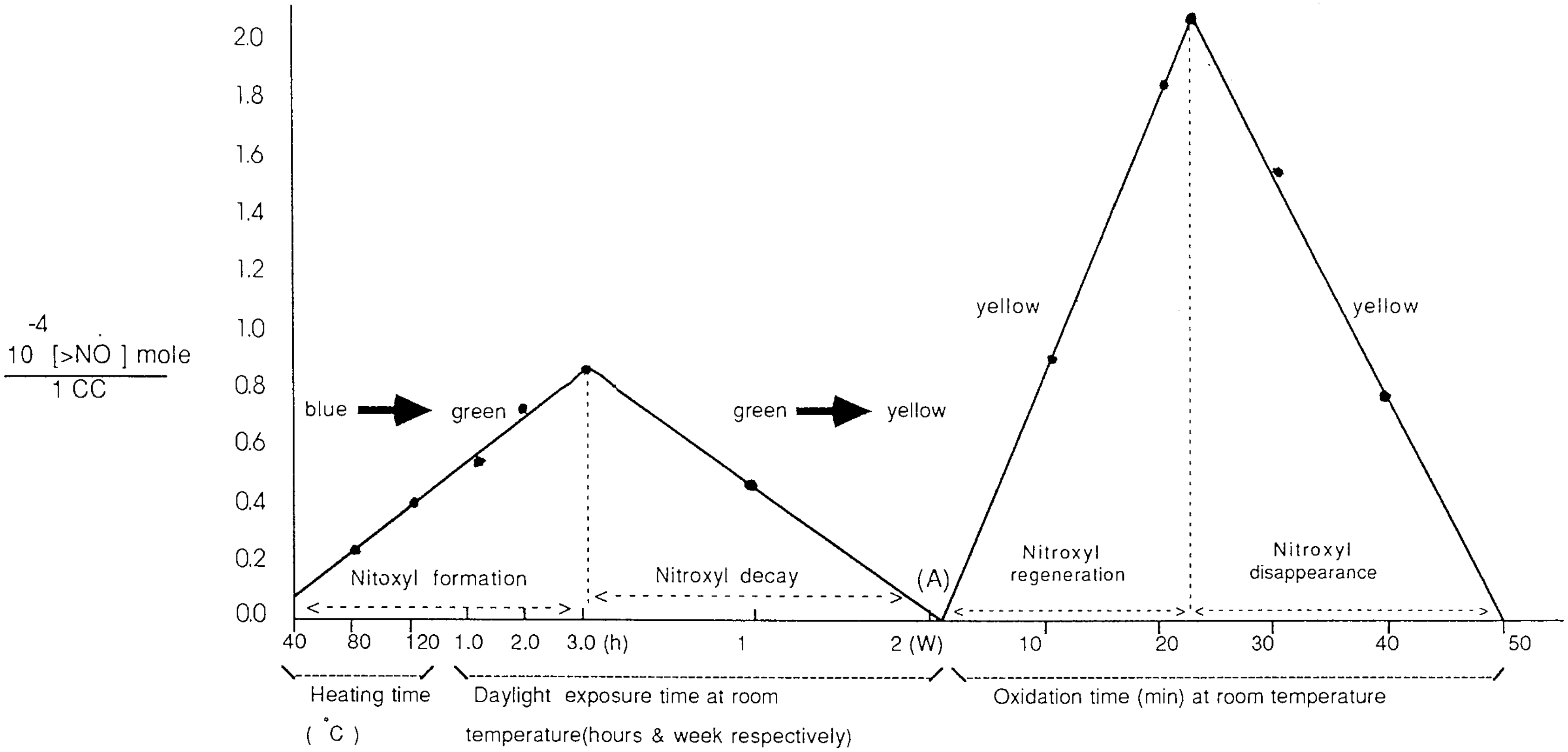


Fig .14 The effect of heat, light , and oxidation on nitroxyl yield of NTB in benzene solution

CHAPTER 5

The photostabilisation of polypropylene by spin traps

5.1 Object and Plan

The importance of free radical trapping reactions in the inhibition mechanisms of polymer photo-oxidation by a number of U.V stabilisers of different types is now well recognised. This subject has been reviewed recently by Scott(155). Hindered amine light stabiliser are finding application in the photostabilisation of polypropylene in both thick and thin sections.The mechanisms of photo-stabilization by these compounds have been studied extensively since their discovery and commercial introduction. Free radical scavenging (156,157) hydroperoxide decomposition(158,159), and excited state carbonyl deactivation effects (160) have been suggested.

Among these effects it is generally agreed that free radical scavenging of polymer radicals by the nitroxyl radicals from the hindered amine light stabilisers is dominant in photo-stabilisation. However, due to their relatively rapid rate of loss by evaporation and leaching, polymeric hindered amine light stabilisers, which are resistant to loss by migration, are used for the photostabilisation of polypropylene fiber (161).

It is also reported that C-nitroso aliphatic compounds with radical scavenging properties are also effective U.V stabilisers for polypropylene (117), and it is now clearly established that polyolefines produce alkyl radicals predominantly both during processing (in limited oxygen) and on U.V irradiation (162,163). However, after solvent extraction, their photo-antioxidant activity almost completely disappeared.

In the present work an attempt was made to study the behaviour of polymer-bound antioxidants in the photostability of polypropylene.
Spin traps and radical generators used in the present work, with code names, are listed in table 4.

Polypropylene was processed with 0.2 % of spin traps at 180°C. for 10 minutes in a closed mixer. spin traps are added to PP either as normal additive or in the form of masterbatch.

5.2 THE PHOTOSTABILISATION OF POLYPROPYLENE BY C-NITROSO COMPOUNDS

Radical initiators were found to improve the photo-antioxidant activity of aliphatic nitroso compounds to varying degrees when used as normal additives in polypropylene. Dicumyl peroxide and benzophenone decrease the photoantioxidant activity of NTB and NTO to some extent, Trigonox 101 improves the antioxidant activity of these compounds outstandingly. Carbonyl induction time of the above inhibitor systems in the extracted polymer samples formed during internal U.V irradiation time was compared with the commercial U.V stabiliser Tinuvin 770 (fig.15). This result reveals that the incorporation of radical initiator containing aromatic rings to this photostabilisers will affect adversely their photoantioxidant activity, despite an improvement in the spin adduct yield and polymer-bound nitroxyl yield. The antioxidant activity of NTB and NTO in polypropylene was improved by 212 % and 19 % respectively before extraction and by 830 % and 400 % after extraction, when Trigonox 101 was used as radical generator (tables 18,19). However, introduction of 0.2 % of nitroso compounds in the form of EPR-spin adducts (masterbatches) in polypropylene, decrease to a high extent the U.V stability of these compounds before extraction. However, some improvement was observed after extraction (table 20).

The effect of the Trigonox 101 to nitroso molar ratio on the embrittlement time of PP containing 0.2 % NTB and NTO is shown in figures 13 and 16. These results indicate that the photoantioxidant activities of aliphatic nitroso compounds increase as the concentration of Trigonox 101 increases up to a certain limit. In fact, the ratio of Trigonox101 is an important factor in controlling the photoantioxidant activity of aliphatic nitroso compounds in PP.

Table 18 lists the embrittlement times for polypropylene containing NTB and a variety of radical initiators after processing for 10 min. at 180°C. Although not quite as effective as bis(2,2,6,6-tetra methyl-4-piperidinyl)sebacate (Tinuvin 770), a commercial UV stabiliser which also acts by generating nitroxyl, at the same weight ratio, NTB is much more efficient than Tinuvin 770 after solvent extraction in the presence of Trigonox 101 (fig.15).

In spite of the fact that, Trigonox 101 increases the photoantioxidant activity of NTB and NTO, the concentration of nitroxyl radicals from these spin traps decreased with increasing peroxide ratio (table 7); and it is therefore of interest to relate photooxidative embrittlement time not only to nitroxyl concentration but also to the formation of its reduction products O-alkyl hydroxylamine and free hydroxylamine. The possible reactions that may occur during processing of PP with NTB in the presence of Trigonox 101 are shown in scheme 9.

The effect of Trigonox 101 ratio on the photoantioxidant activity of NTB in PP was also evaluated by carbonyl formed during interval UV irradiation time, this result is consistent with the results obtained from embrittlement tests. The carbonyl induction time increases as the mole ratio of Trigonox 101 to NTB is increased to a certain limit, fig 17.

The effect of solvent extraction on the carbonyl induction time of the inhibition system (NTB and Trigonox 101) is shown in fig.16, this results clearly indicate that the addition of Trigonox 101 to NTB is associated with formation of higher macroalkyl radical during processing.

Generally speaking, the extent of spin trapping by C-nitroso aliphatic compounds was considerably improved in EPR by processing or UV irradiation in the presence of radical initiator(see sections 3.2, 4.2). This improvement was intensified with benzophenone during UV irradiation, 70 % conversion (spin adduct yield) of nitroso tert butane to nitroxyl was obtained which of this 90 % was attached to the polymer chains. However, dilution of masterbatches of these adducts in polypropylene by processing dramatically decreased the photoantioxidant activity of these spin traps (table 20). Further explanation is given in the discussion section.

Aromatic nitroso compounds PMNB and NDBPh exhibit poor photoantioxidant activity. Their activity does not change appreciably in the presence of peroxides, used either as normal additive or in the form of EPR spin adducts (masterbatches). Table 20 and 21, show the photo-embrittlement time of PP modified by the above systems. However the spin adducts yield and polymer-bound nitroxyl concentration of this spin traps was increased considerably by incorporating peroxides during processing. The lack of UV stabilisation effectiveness of these compounds is presumably due to the quinonoid compounds formed during processing (fig. 11)as the yellow colour of pure state change to brown during processing with EPR and FTIR confirmed the formation of such structure(fig.11).

5.3 The photostabilisation of polypropylene by nitrones

The photoantioxidant activity of nitrones was explored in polypropylene by measurement of photo-oxidative embrittlement time and carbonyl formation during UV irradiation. The formation of only a small amount of nitroxyl radical during processing with EPR or polypropylene was associated with low antioxidant activity of these compounds. In order to increase the level of spin adduct formation of these compounds during processing, Trigonox 101 was used . In this case different photostability behaviours were observed (table 22). A marked increase in the photostabilising effectiveness of PBN in PP was observed in the presence of Trigonox 101, whereas the UV stability of DPN and DMPN is reduced to some extent. The effect of concentration of Trigonox 101 on the carbonyl induction time and on photooxidative embrittlement time of tert butyl phenyl nitrone (PBN) is shown in figures 18 and 19. The poor photo-antioxidant activity of DPN could be due to the presence of aromatic rings which undergo chemical modification upon irradiation. Therefore, besides nitoxyl concentration, instability of nitroxyl radical, some other factor such as chemical structure or permanence of the nitroxyl radical in the polymer must also be considered.

Thus although the spin adduct concentrations of nitrones was increased in the presence of peroxides during masterbatch preparation in EPR (table 13), the photo-antioxidant activity of these compounds where used in the form of EPR-spin adducts in polypropylene either remained unchanged or decreased.

5.3 Assessment of the thermal stability of polypropylene in the presence of nitroso tert-butane by thermogravimetric analysis (TGA) and oven aging

The accelerated thermal aging oxidation of moulded polypropylene films containing NTB with and without Trigonox 101 before and after solvent extraction was carried out in a Wallace oven at 140 ° C with air flow of 1.3 cubic feet per hour. The effect of Trigonox 101 on the thermal antioxidant activity of NTB is shown in table 23. The insignificant antioxidant activity of NTB in PP, despite the formation of nitroxyl radicals is attributed not only to its incapability to trap alkylperoxy radical but also to its,volatility during aging. The thermal stabilising effectiveness of this compound, is increased considerably in the presence of Trigonox 101, due to formation of high molecular weight nitroxyl radical and its transformation products (>NOR ,>NOH).

Thermogravimetry was used to understand better the effect of polymer-bound and the relative thermal antioxidant activity of nitroso tert-butane in polypropylene, in the thermographs shown in figs. 22-30. Polypropylene films containing 0.2 % NTB in the presence and absence of Trigonox 101, before and after extraction were heated at a programmed rate(10 degree C. min^{-1}) under different atmospheres. Each composition showed its characteristic weight loss curve in a certain temperature region. The decomposition temperature of PP samples containing NTB & NTB+Trigonox101 does not vary after extraction under nitrogen atmosphere. However in unstabilised PP after extraction the decomposition temperature is lower than before extraction. The effect of air on the decomposition temperature of these protective systems shown in figs. 28-30. The rate of weight loss of these compounds are as follows :

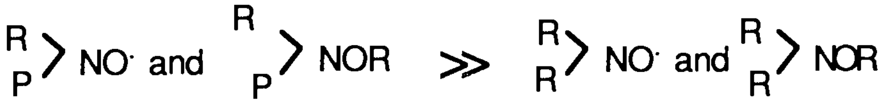
PP > PP+NTB+Trigonox101 > PP+NTB

The effectiveness of polymer-bound nitroxyl is evident from both measurement techniques (oven aging & UV cabinet).

5.5 Discussion

The photoantioxidant activity of C-nitroso alkanes is appeared to be related not only to the concentration of their nitroxyl radical, but also to the amounts of their transformation products (>NOR, >NOH) formed during processing. An increase in the transformation products in the presence of radical initiator was observed in model study and in masterbatches. The formation of these reduction products from these compounds was simply identified by regeneration of nitroxyl radical on oxidation with meta di chloro per benzoic acid (MCPBA). It has been shown earlier (164) that alkyl hydroxylamine and free hydroxylamine together act as a reservoir for nitroxyl radicals on oxidation with alkylperoxyl and hydroperoxides. The role of nitroso compounds is to terminate alkyl or alkoxy radicals during thermal processing or photolysis and to form bound nitroxyl radical within polymer chains, this is followed by abstraction of hydrogen or trapping alkyl radical from medium to form reduction products. These reaction of nitroso compounds during processing result in the inhibition of hydroperoxide formation, which are the key photoinitiator.

Although, Trigonox 101 increases the photoantioxidant activity of C-nitroso alkanes considerably in extracted and unextracted PP, benzophenone and dicumyl peroxide decrease the photo-antioxidant activity of these compounds to varying extents, despite of an increase in their spin trapping efficiency. The outstanding photo-and thermal antioxidant activity of C-nitroso butane in the presence of Trigonox 101, in the extracted and unextracted PP samples, is attributed to the formation of high molecular weight spin adducts formed mainly from macro radicals, i. e



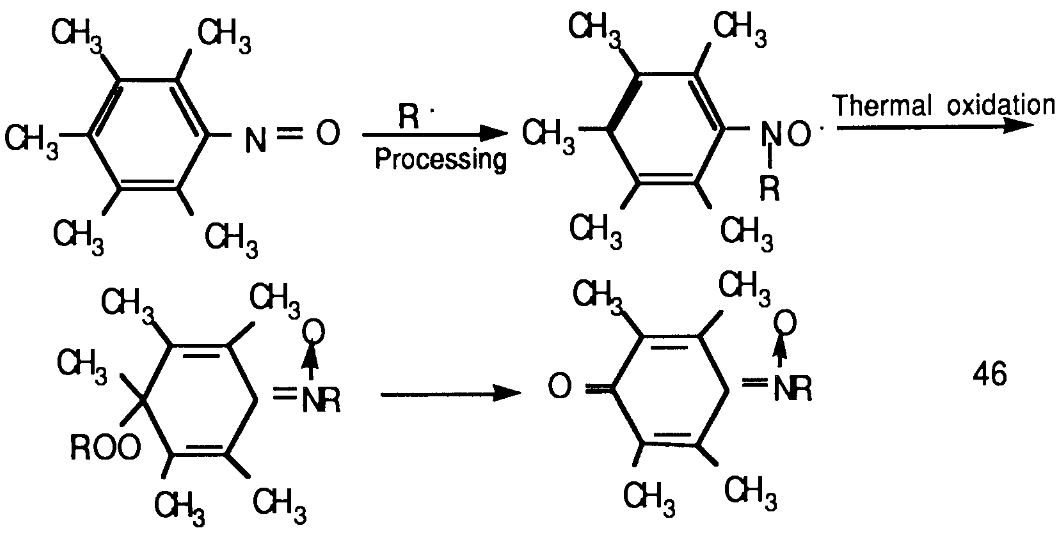
$$ {}^{R}_{P}\!\!>\mathrm{NO^{\cdot}} \text{ and } {}^{R}_{P}\!\!>\mathrm{NOR} \gg {}^{R}_{R}\!\!>\mathrm{NO^{\cdot}} \text{ and } {}^{R}_{R}\!\!>\mathrm{NOR} $$

which are resistant to extraction and volatilisation. The results given in table 6 suggest that photo-antioxidant activity of a protective system in a polymer in addition to intrinsic stabiliser behaviour, and permanence, some other factor such as UV sensitivity of radical initiators must have to be considered. Generally, additives containing chromophoric groups are sensitive to UV light and affect adversely the UV life of polymer. It has been suggested(165) that the main factors which determine the effectiveness of stabiliser are :

(a) intrinsic stabiliser behaviour which is determined primarily by the chemical structure of the stabiliser

(b) permanence of the stabiliser in the polymer. The importance of polymer-bound antioxidant in the stabilisation of polymer, particular in the case of low molecular weight stabilisers such as nitroso tert-butane is completely evident. Aromatic nitroso compounds (PMNB and NDBP) are relatively ineffective as UV stabilisers for PP compared with C-nitroso alkanes. Their poor performance on UV exposure is, therefore not only due to the formation of sensitising products (quinonoid compounds), but is also due in part to their chemical structure (both PMNB and NDBPh possess aromatic ring). It is observed visionary that these compounds are not compatible with polyolefins as they bloom to the surface of polymer on standing, particularly at high concentrations (>2% in EPR). The low solubility of these stabilisers in a polymer encourage physical loss by exudation of the stabiliser to the surface (i.e blooming). The poor solubility of aromatic nitroso compounds could be due to their low equilibrium concentration. It has been reported (166,167) that, when the concentration of antioxidants in the polymer are greater than their equilibrium concentration, they diffuse to the surface of the polymer, where they may be lost by volatilisation or they may deposit on the surface.

The formation of quinonoid products during processing of aromatic nitroso compounds was identified with FTIR. The formation of coloured products (initially yellow to brown in the case of NDBPh and initially white to yellow in the case of PMNB) supports the formation of qunonoid products contain conjugated unsaturation (reaction 46).



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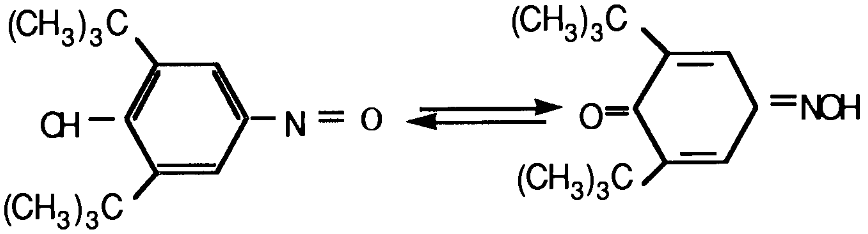
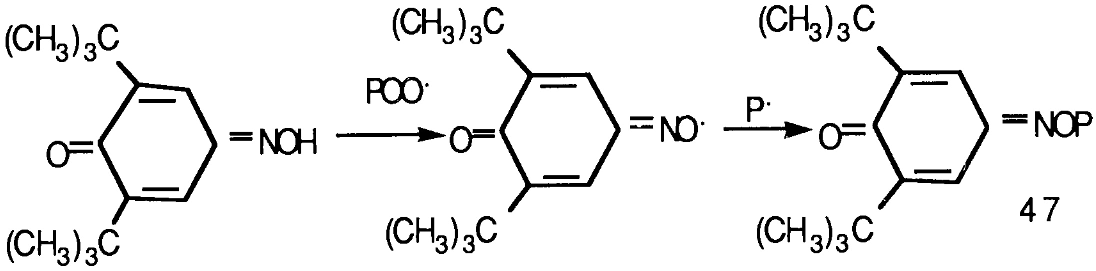
It is also known that nitroso phenols tautomerise into the oxime form



Such an oxime could easily be oxidised by ROO· into iminoxy radicals which are relatively stable. The iminoxy radicals are known highly reactive towards alkyl radicals (168).



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The poor antioxidant activity of nitrones, besides those factors which leads to ineffectiveness of aromatic nitroso compounds, is attributed to low yield of spin adducts formed from these compounds in polymer during processing (table 12).

In general, the addition of spin traps (nitroso compound and nitrones) in the form of EPR-spin adducts (masterbatches), to the polypropylene during processing decreased the photo-antioxidant activity of these spin traps in the extracted and unextracted compounds. The inefficient UV stability of this polymer blend system may be consistent with low affinity of the two components ethylene propylene rubber and polypropylene, despite showing the same paraffinic molecular structure. Electron scanning microscopy reveals a two phase structure in which EPR remains embedded in the form of small particles. Phase contrast micrograph (fig 31) shows a clear picture of a two-phase fine structure that such an EPR-PP blend may assume. Other factors , may also be responsible for the poor stabilising inefficiency of spin traps used in the form of masterbatch, such as cross linked oxidation products that leads to incompatibility,and possible oxidation of nitroxyl radical at longer processing time also have to be considered.

Table 18 The effect of radical generators on the photooxidative embrittlement time of NTB. PP was processed with 0.2 % NTB and different concentration of radical generators in a closed mixer at 180°C for 10 min.

Radical generator	Molar ratio [RG] / [NTB]	Embrittlement time (h) Before extraction	Embrittlement time (h) after extraction
None	-	660	120
Trigonox 101	0.2	950	330
	0.4	1200	630
	0.8	1400	950
	1.2	1320	970
Benzophenone	0.45	300	230
	0.9	250	240
Dicumyl peroxide	0.15	630	190
	0.3	450	170
AIBN	0.5	750	130
	1.0	520	100

Table 19 The effect of Trigonox 101 on the photooxidative embrittlement time of NTO. PP was processed with 0.2 % NTO and different concentration of trigonox 101 in a closed mixer at 180°C for 10 min.

Peroxide	Molar ratio [RG] / [NTO]	Embrittlement time (h) Before extraction	Embrittlement time (h) After extraction
None	-	500	110
Trigonox 101	0.3	670	260
	0.6	900	400
	0.9	900	450
Dicumyl peroxide	0.15	430	170
	0.3	390	160

Table 20 The effect of processing on the photoantioxidant activity of EPR-spin adducts. (EPR-masterbatch diluted to 0.2 % with PP during processing in a closed mixer at 180° C for 10 min).

Spin* trap	Radical generator	peroxide conc.* (g/100)	Processing temp. (° C) *	Embrittlement time (h) Before extraction	Embrittlement time (h) After extraction
	None	-	120	500	100
NTB	DCP	0.1	120	210	270
	Trigonox101	0.1	120	450	350
	Bph**		-	320	200
	None	-	120	350	180
NTO	DCP	0.1	120	200	220
	Trigonox101	0.1	120	340	300
	None	-	120	170	150
PMNB	DCP	0.1	120	150	150
	Trigonox101	0.1	120	170	160
	None	-	100	110	90
NDBPh	DCP	0.1	100	100	80
	Trigonox101	0.1	100	110	100

* = Applied for preparation of the masterbatches

**= Masterbatch was prepared in solution by UV light

Table 21 The effect of Peroxides on the photoantioxidant activity of 0.2% aromatic nitroso compounds in PP films, processed in a closed mixer at 180 °C for 10 min.

Spin trap	Peroxide	Peroxide conc.(g/100)	Embrittlement time (h) Before extraction	Embrittlement time (h) After extractio
	None	-	150	140
PMNB	DCP	0.1	140	140
	Trigonox 101	0.1	160	150
	None	-	120	110
NDBPh	DCP	0.1	110	110
	Trigonox 101	0.1	140	120

Table 22 The effect of Trigonox 101 on the photo-antioxidant activity of nitrones. PP was processed with 0.2 % nitrones and different concentration of Trigonox 101 in a closed mixer at 180°C for 10 min.

Nitrone	Molar ratio $\frac{[\text{Trigonox 101}]}{[\text{Nitrone}]} \times 10$	Embrittlement time(h)	
		Unextracted	Extracted
	0.0	100	90
PBN	0.4	370	180
	0.8	400	360
	1.2	300	380
	0.0	180	90
DPN	0.48	170	90
	0.96	150	80
	0.0	350	170
DMPN	0.36	180	100
	0.72	150	90

Table 23 The effect of Trigonox101 ratio on the thermal antioxidant activity of NTB in polypropylene (PP was processed with 0.2 % NTB and different concentration of 101 in a closed mixer at 180°C for 10 min.)

Molar ratio $\frac{[\text{Trigonox 101}]}{[\text{NTB}]}$	Embrittlment time (h)		%Bound
	Before extraction	After extraction	
0.0	1	0.5	15
0.2	3	2.0	67
0.4	6	3.5	70
0.8	7.5	4.5	81
1.2	7.0	5.0	80

Fig. 15 The effect of radical generators on photo-antioxidant activity of NTB in solvent extracted PP. PP was processed with 0.2 % NTB and appropriate concentration of RG in a closed mixer at 180°C for 10 min.

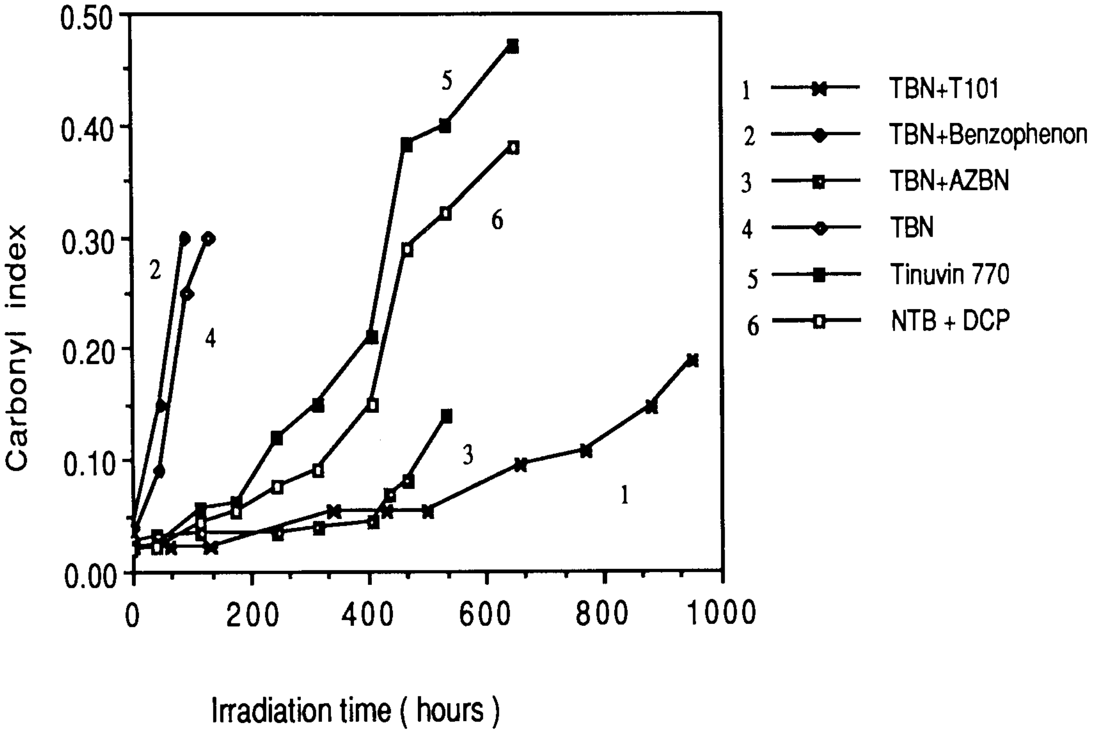


Fig. 16 The effect of Trigonox 101 on photooxidative embrittlement time of NTB. PP was processed with 0.2 % NTB and different concentration of Trigonox 101 at 180°C for 10 minutes.

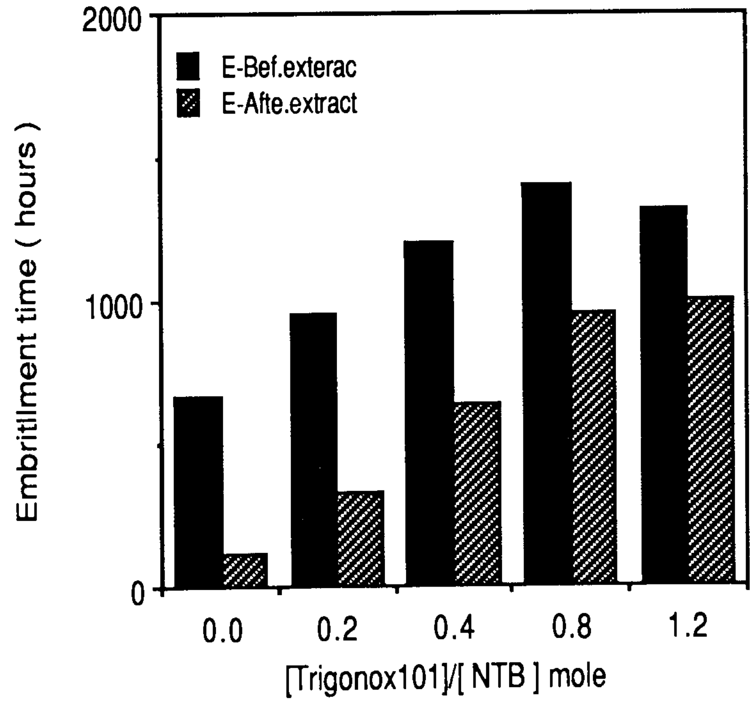


Fig . 17 The effect of Trigonox 101 concentration on the photo antioxidant activity of NTB, PP was processed with 0.2 % NTB and with different concentration Trigonox 101 in a closed mixer at 180°C for 10 min.

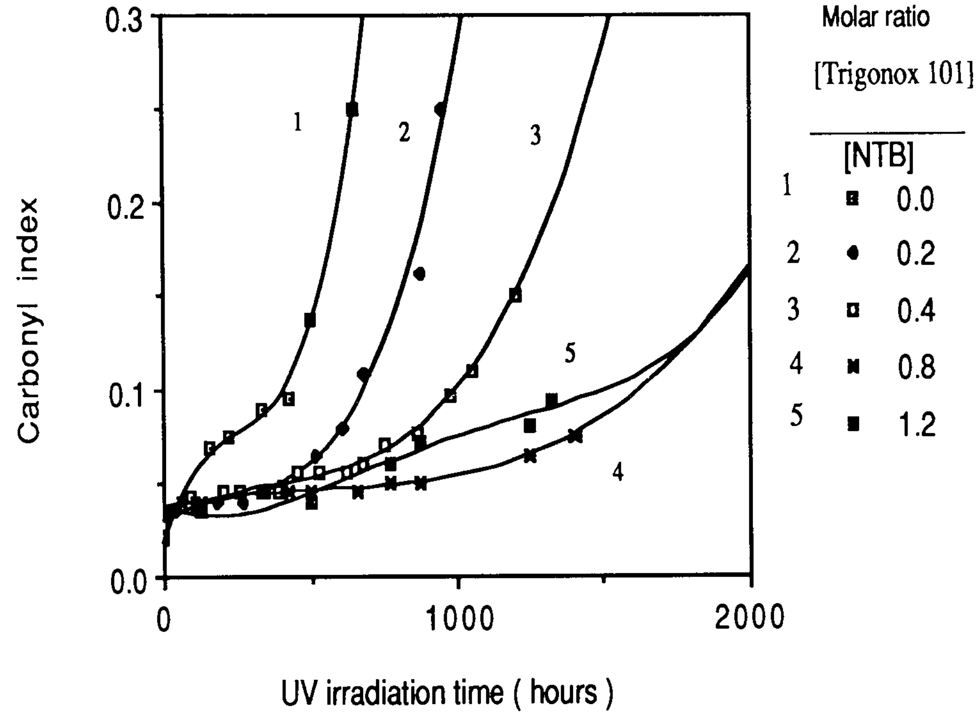


Fig. 18 The effect of Trigonox 101 concentration on the photo antioxidant activity of tert butylphenyl nitrone in extracted and unextracted PP samples, PP was processed with 0.2 % PBN and different concentrations of Trigonox 101 in a closed mixer at 180° C for 10 min.

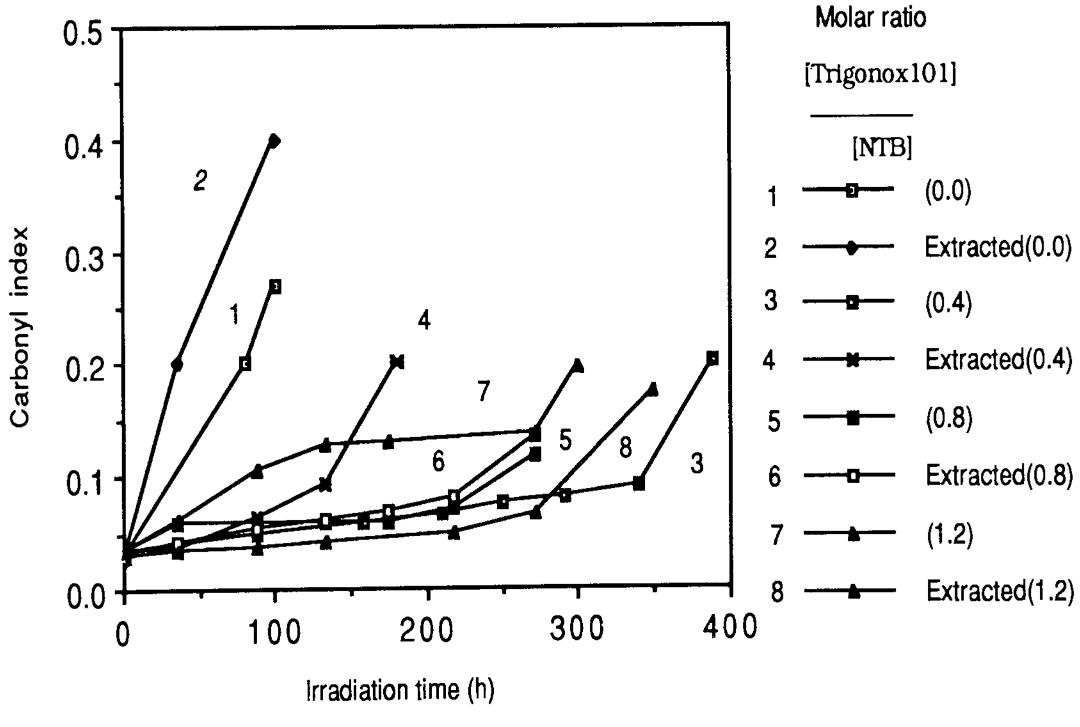
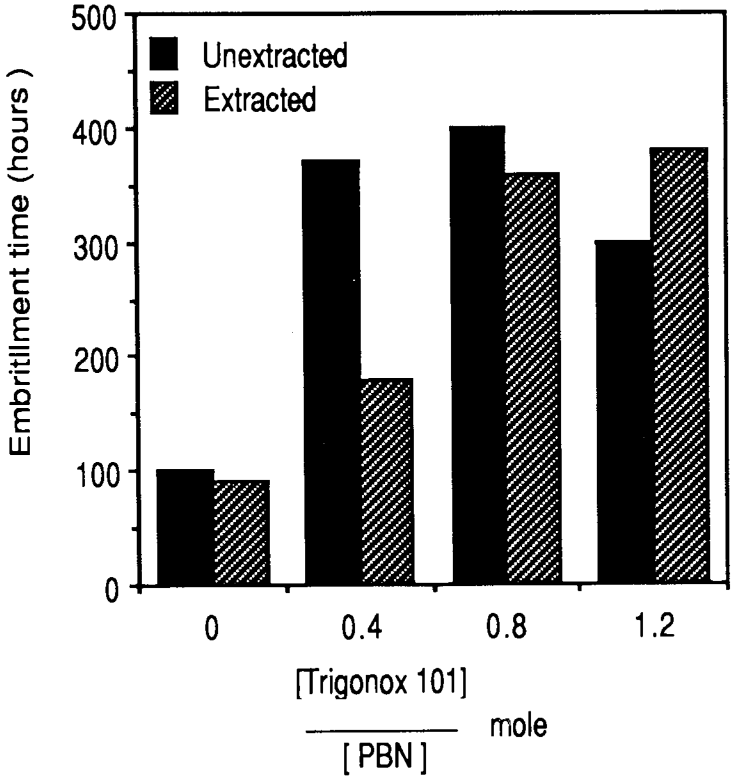
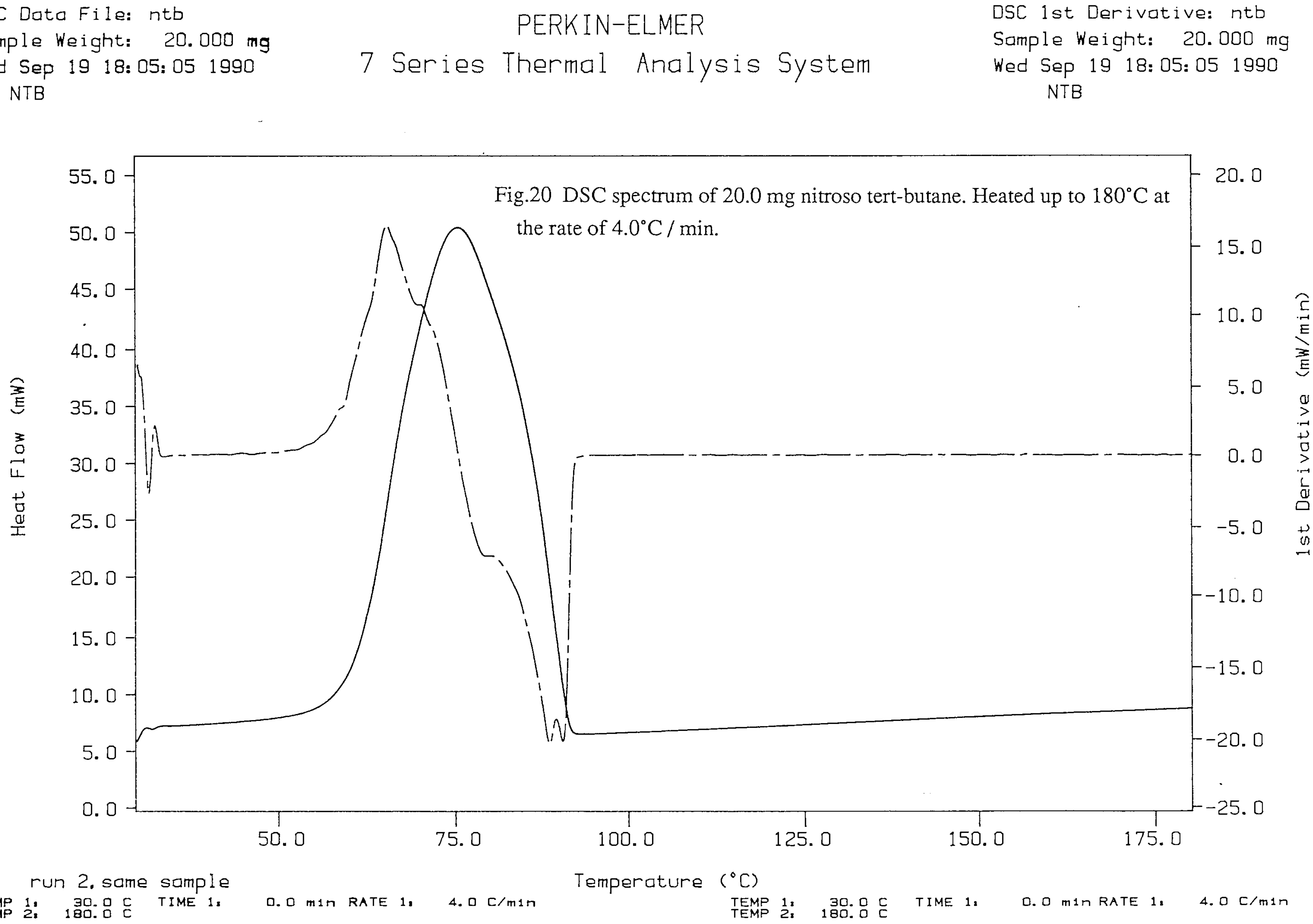


Fig.19 The effect of Trigonox 101 on photooxidative embrittlement time of PBN, PP was processed with 0.2 % PBN and different concentration s of Trigonox 101 in a closed mixer at 180°C for 10 minutes.




DSC Data File: ntb
Sample Weight: 20.000 mg
Wed Sep 19 18:05:05 1990
NTB

PERKIN-ELMER
7 Series Thermal Analysis System

DSC 1st Derivative: ntb
Sample Weight: 20.000 mg
Wed Sep 19 18:05:05 1990
NTB

run 2, same sample
TEMP 1: 30.0 C TIME 1: 0.0 min RATE 1: 4.0 C/min
TEMP 2: 180.0 C

TEMP 1: 30.0 C TIME 1: 0.0 min RATE 1: 4.0 C/min
TEMP 2: 180.0 C

Fig.20 DSC spectrum of 20.0 mg nitroso tert-butane. Heated up to 180°C at the rate of 4.0°C / min.

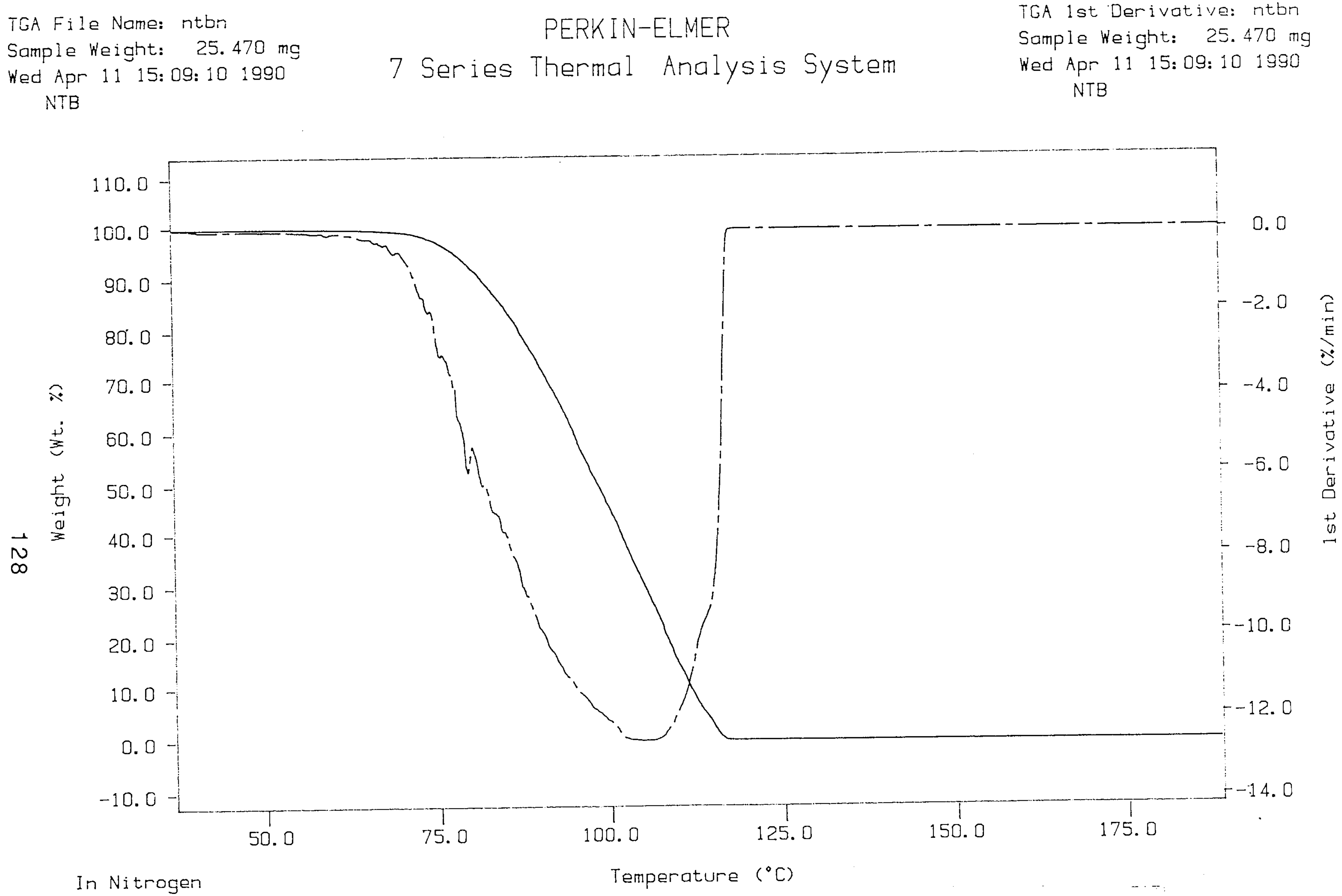


Fig. 21 TGA spectrum of 25.47 mg nitroso tert-butane .Heated up to 180°C at the rate of 4.0°C / min.in Nitrogen.

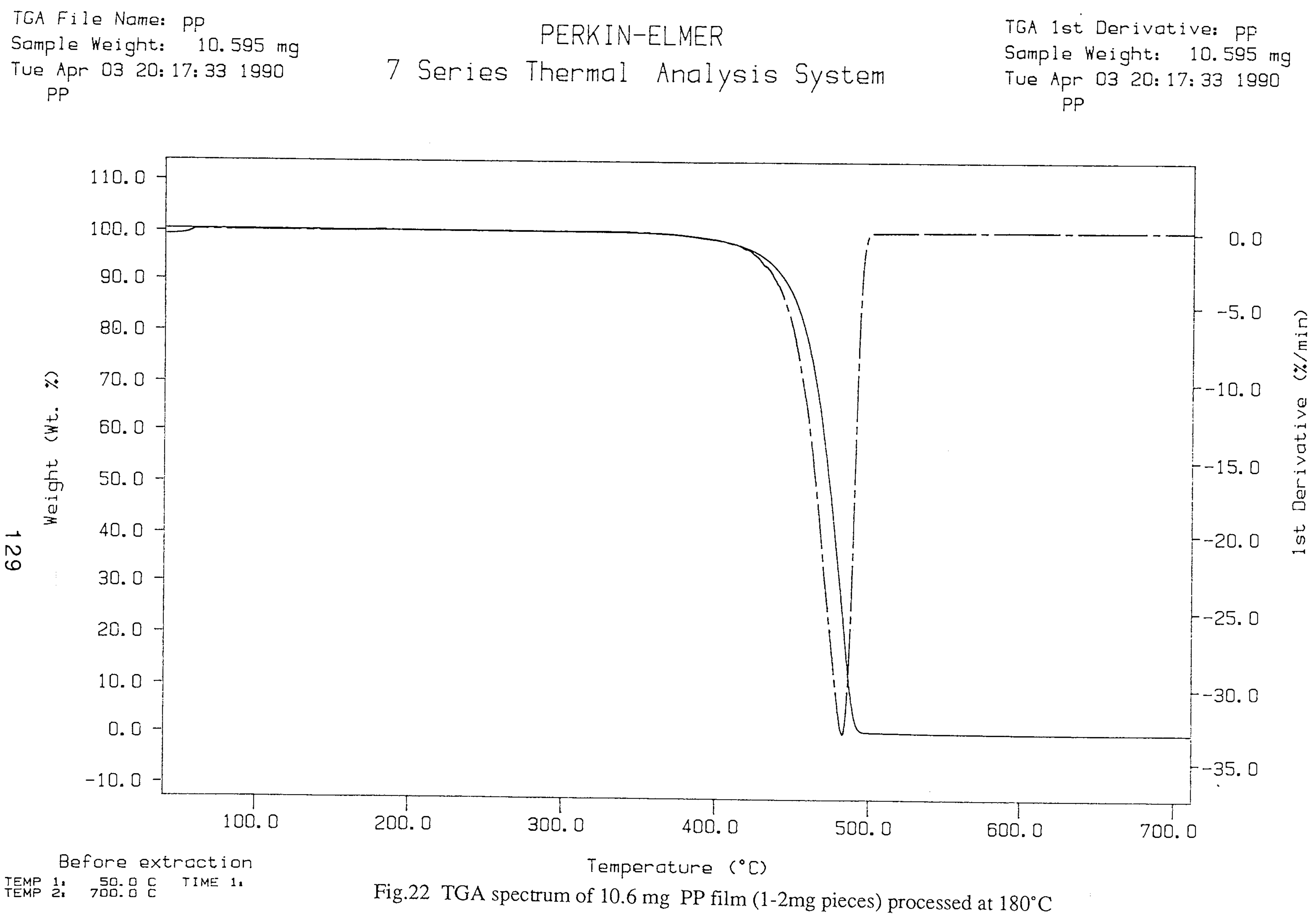


Fig.22 TGA spectrum of 10.6 mg PP film (1-2mg pieces) processed at 180°C in Argon before extraction . Heated up to 700°C at 10°C/min in Nitrogen

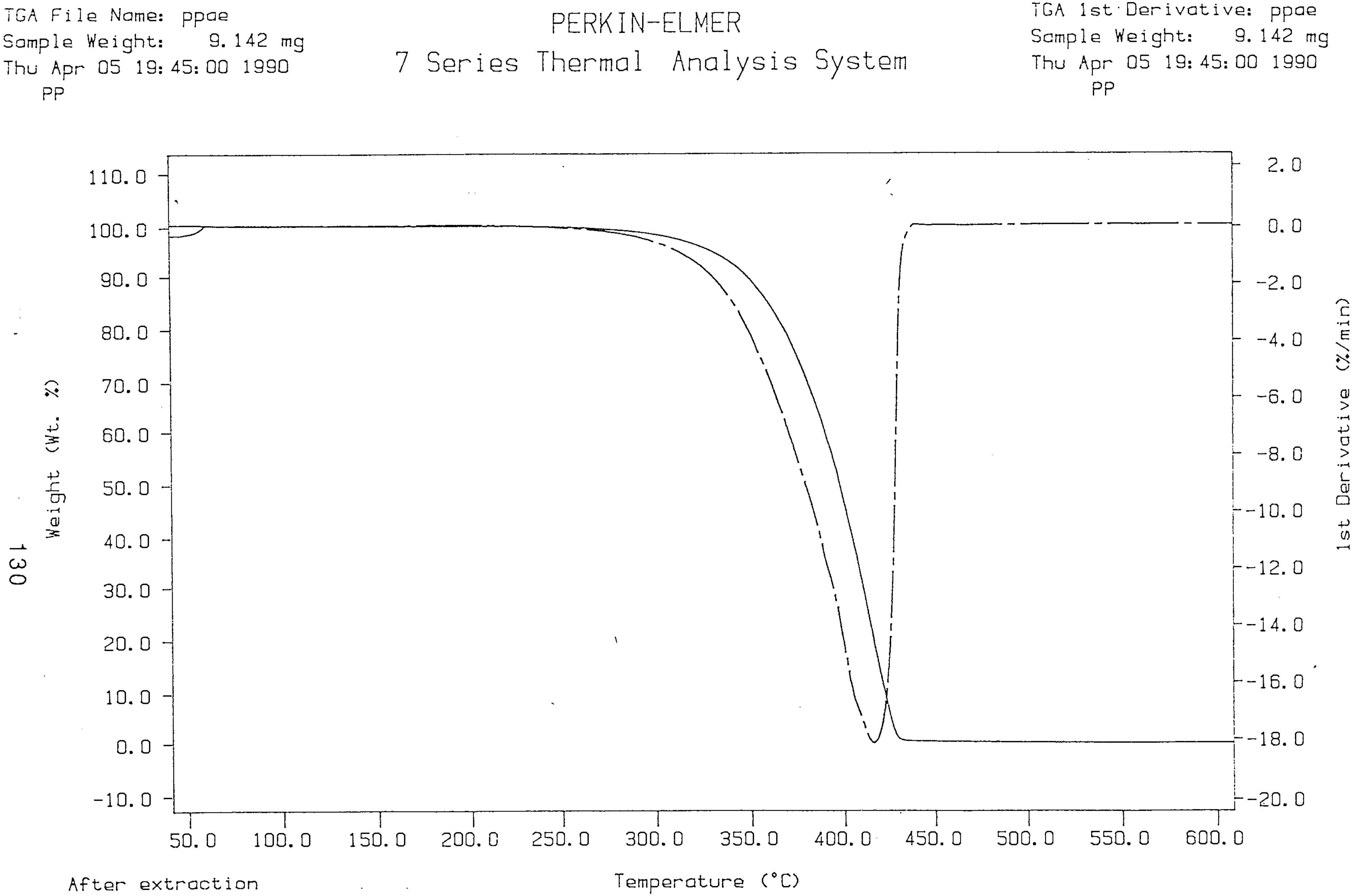


Fig.23 TGA spectrum of 9.15 mg PP film (1-2mg pieces) processed at 180°C in Argon after extraction . Heated up to 700°C at 10°C / min in Nitrogen

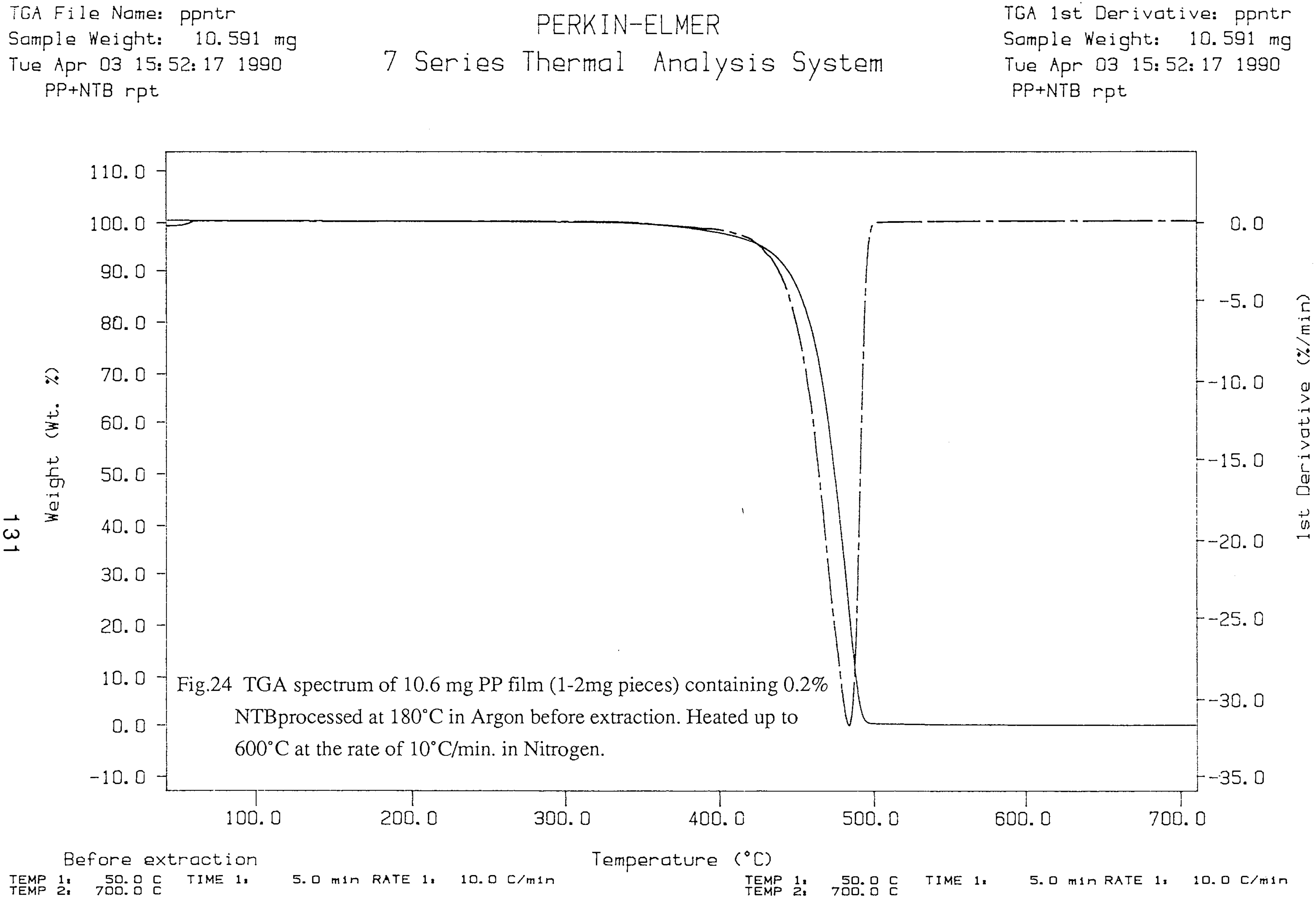


Fig.24 TGA spectrum of 10.6 mg PP film (1-2mg pieces) containing 0.2% NTBprocessed at 180°C in Argon before extraction. Heated up to 600°C at the rate of 10°C/min. in Nitrogen.

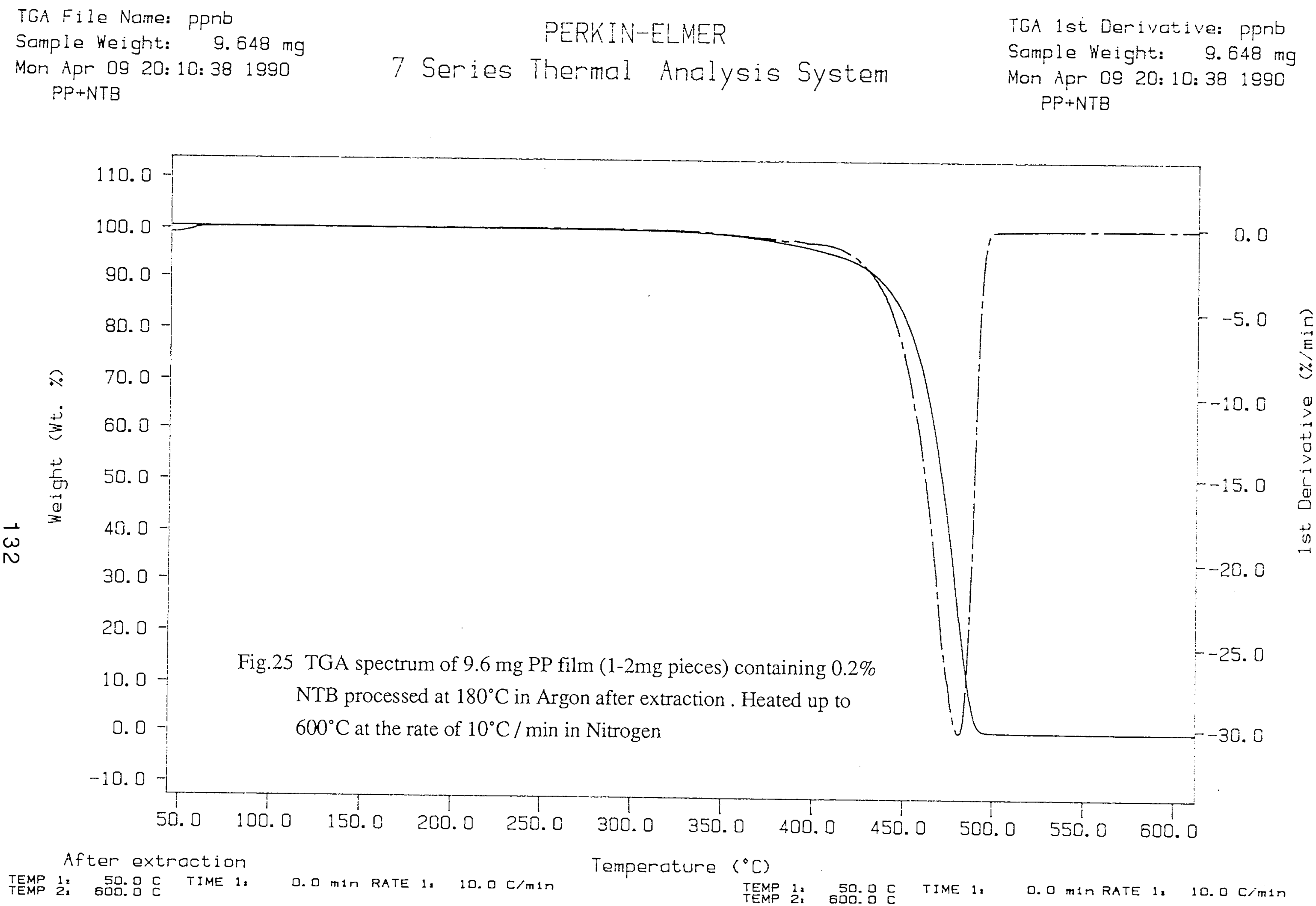


Fig.25 TGA spectrum of 9.6 mg PP film (1-2mg pieces) containing 0.2% NTB processed at 180°C in Argon after extraction . Heated up to 600°C at the rate of 10°C / min in Nitrogen

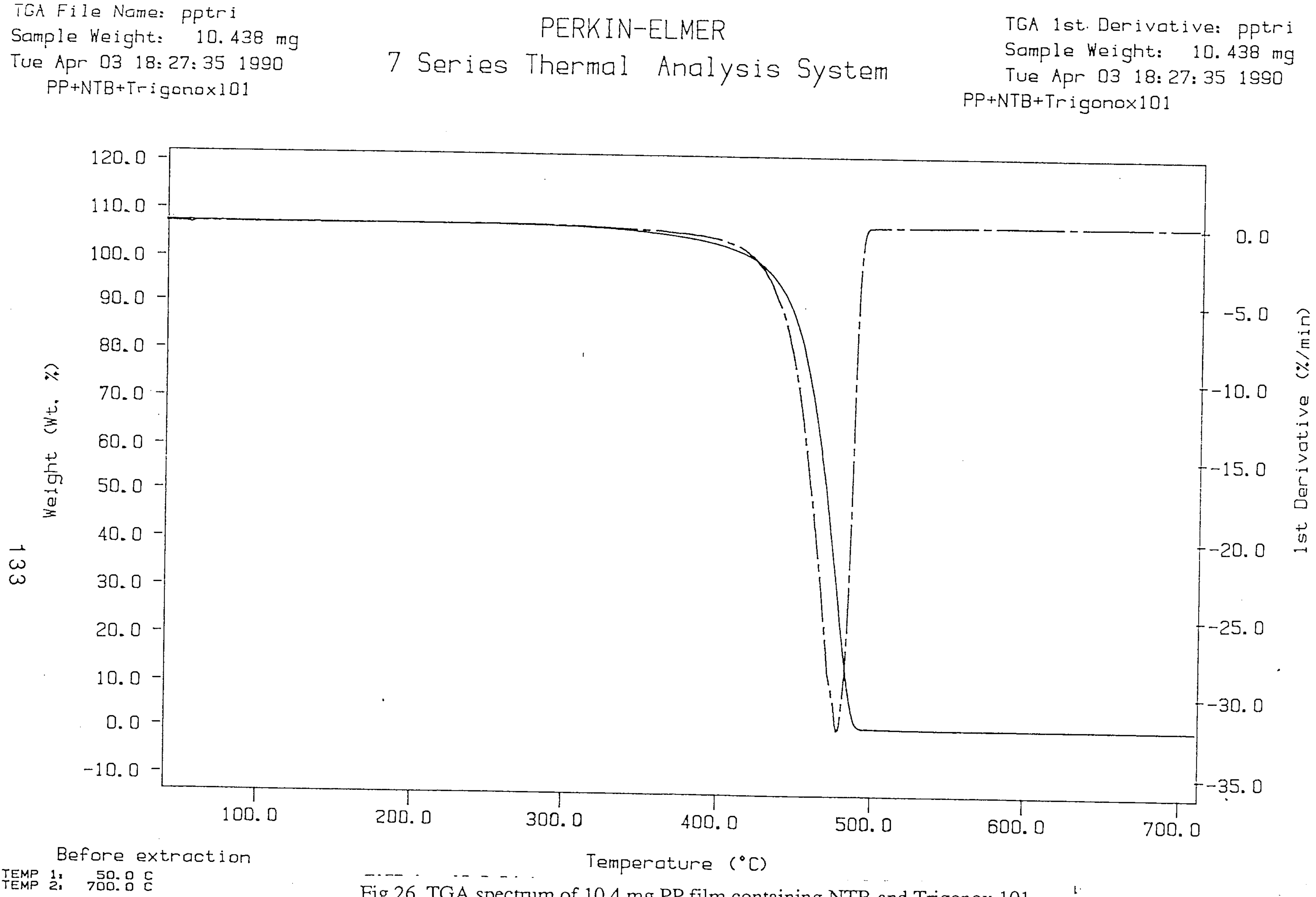


Fig 26 TGA spectrum of 10.4 mg PP film containing NTB and Trigonox 101 with molar ratio (Trigonox101/NTB = 0.4) processed at 180°C in Argon before extraction . Heated up to 700°C at the rate of 10°C / min in Nitrogen

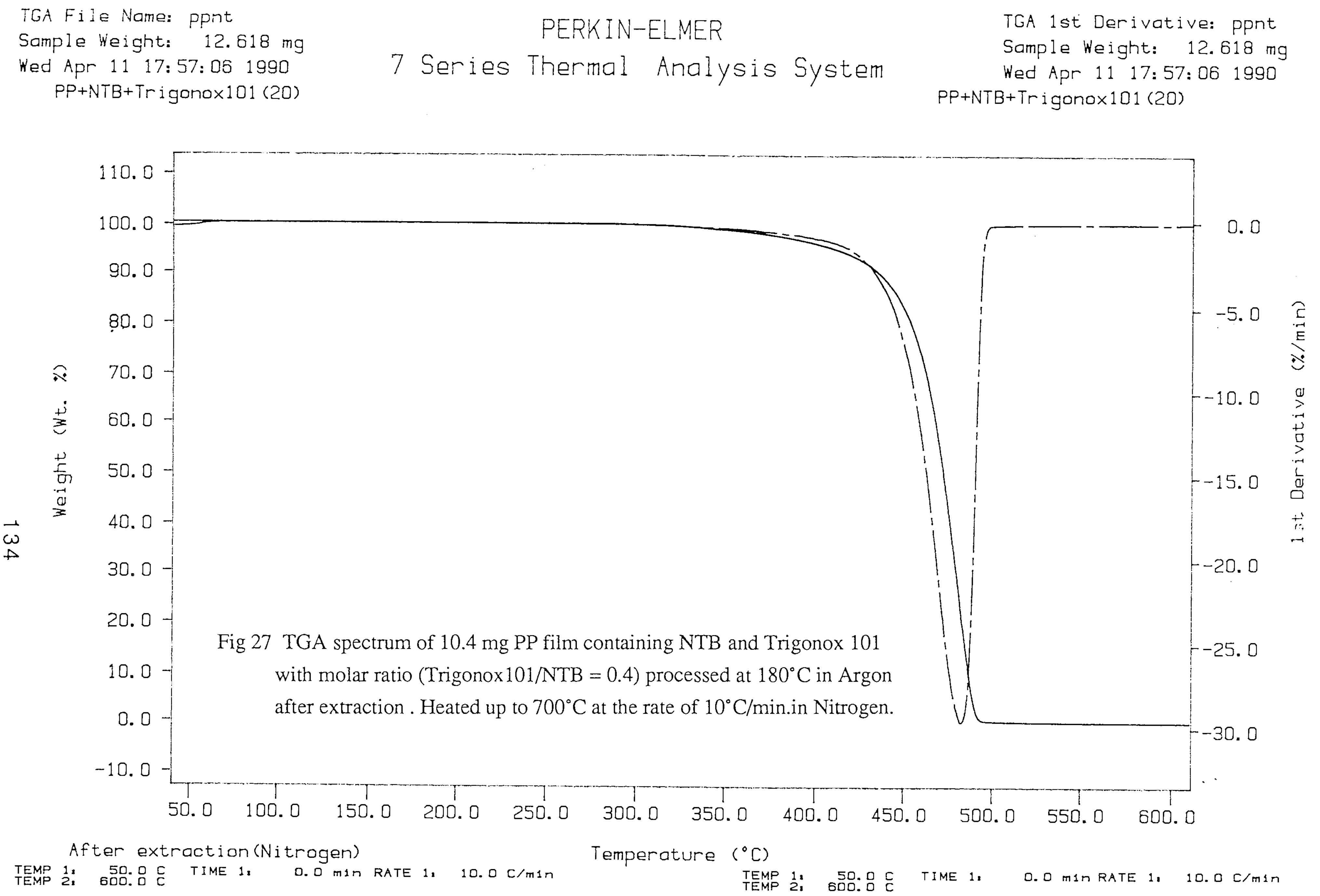


Fig 27 TGA spectrum of 10.4 mg PP film containing NTB and Trigonox 101 with molar ratio (Trigonox101/NTB = 0.4) processed at 180°C in Argon after extraction . Heated up to 700°C at the rate of 10°C/min.in Nitrogen.

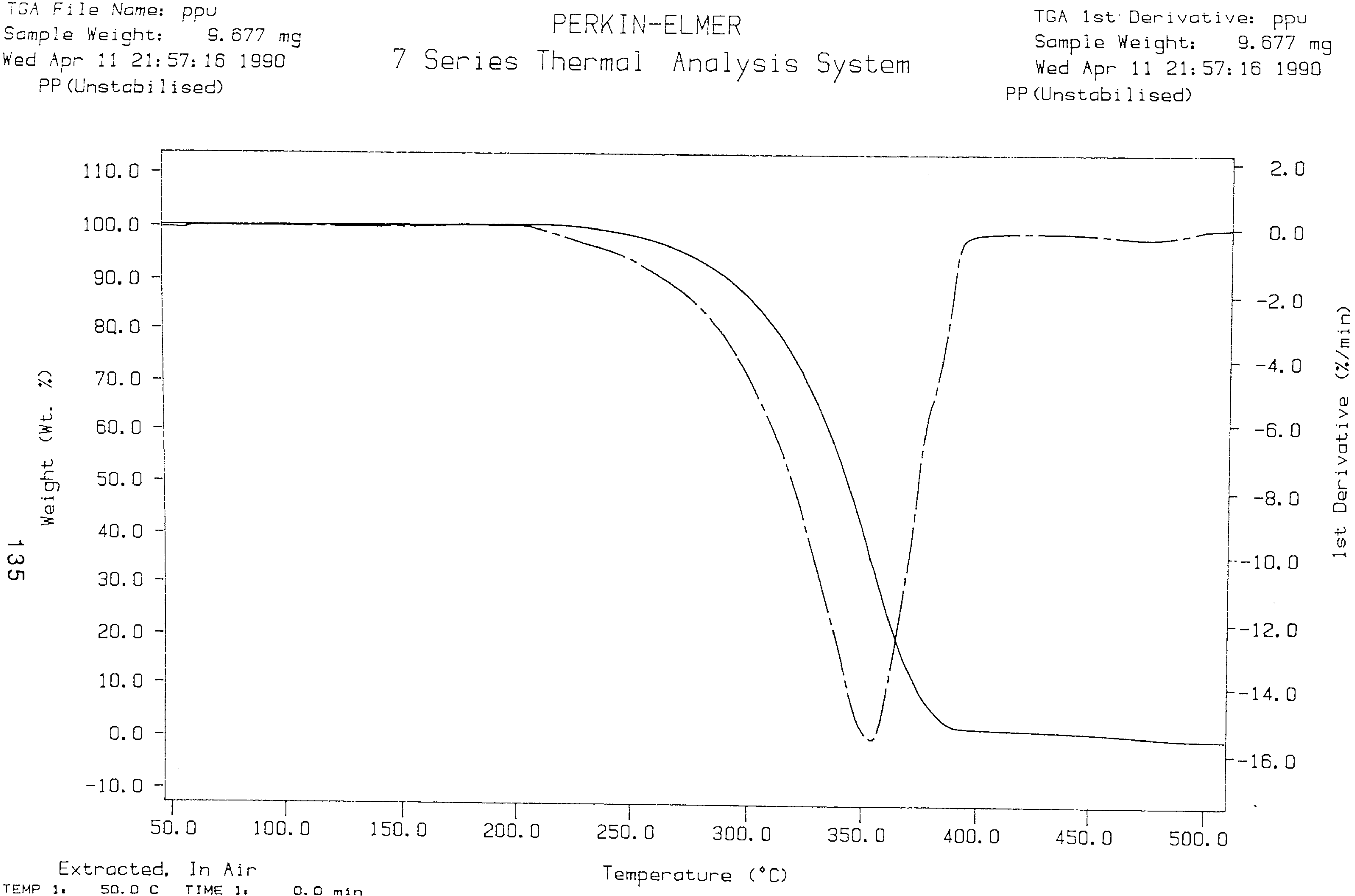


Fig.28 TGA spectrum of 9.7 mg PP film (1-2mg pieces)processed at 180°C in Argon after extraction in Air. Heated up to 500°C at 10°C/min

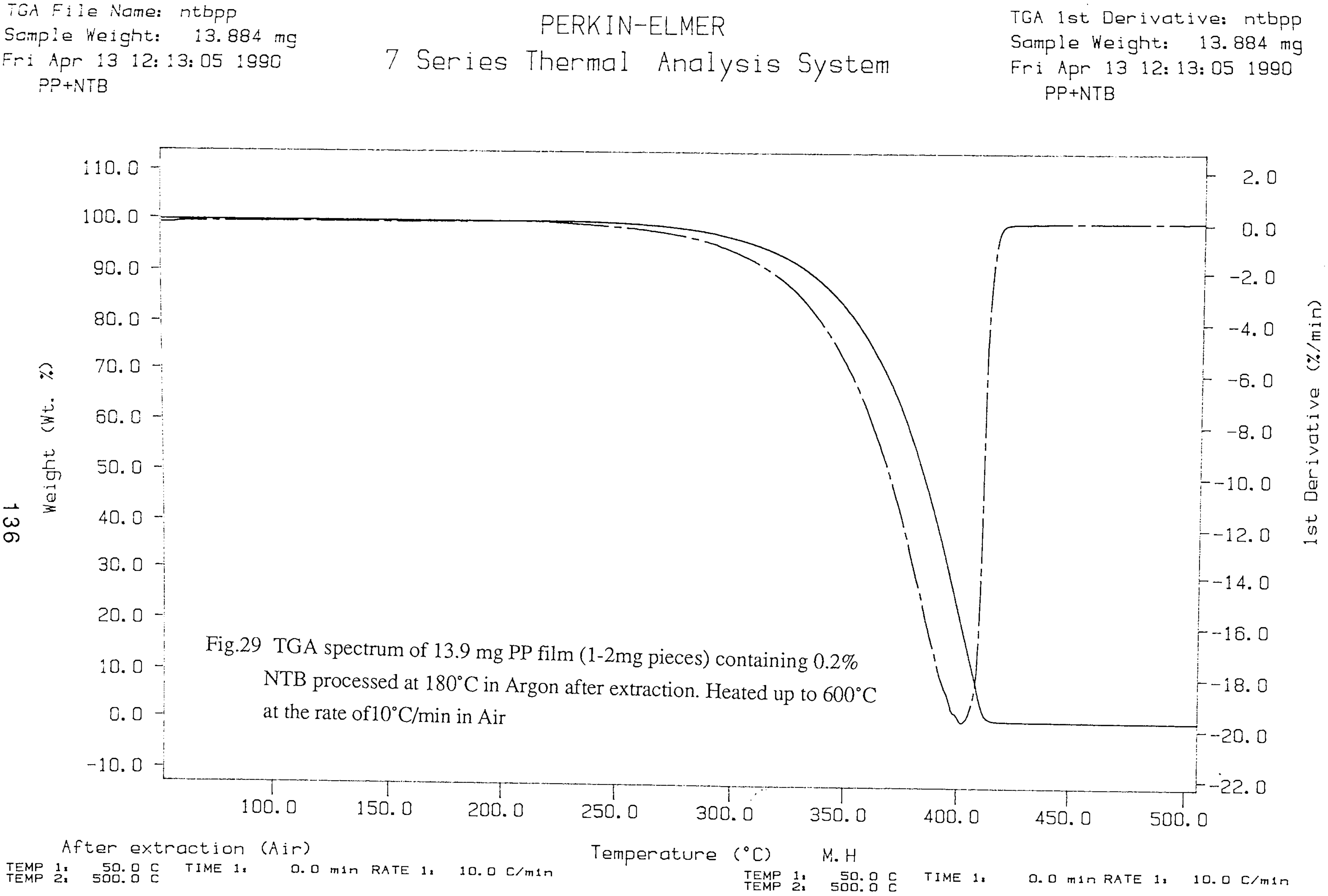


Fig.29 TGA spectrum of 13.9 mg PP film (1-2mg pieces) containing 0.2% NTB processed at 180°C in Argon after extraction. Heated up to 600°C at the rate of10°C/min in Air

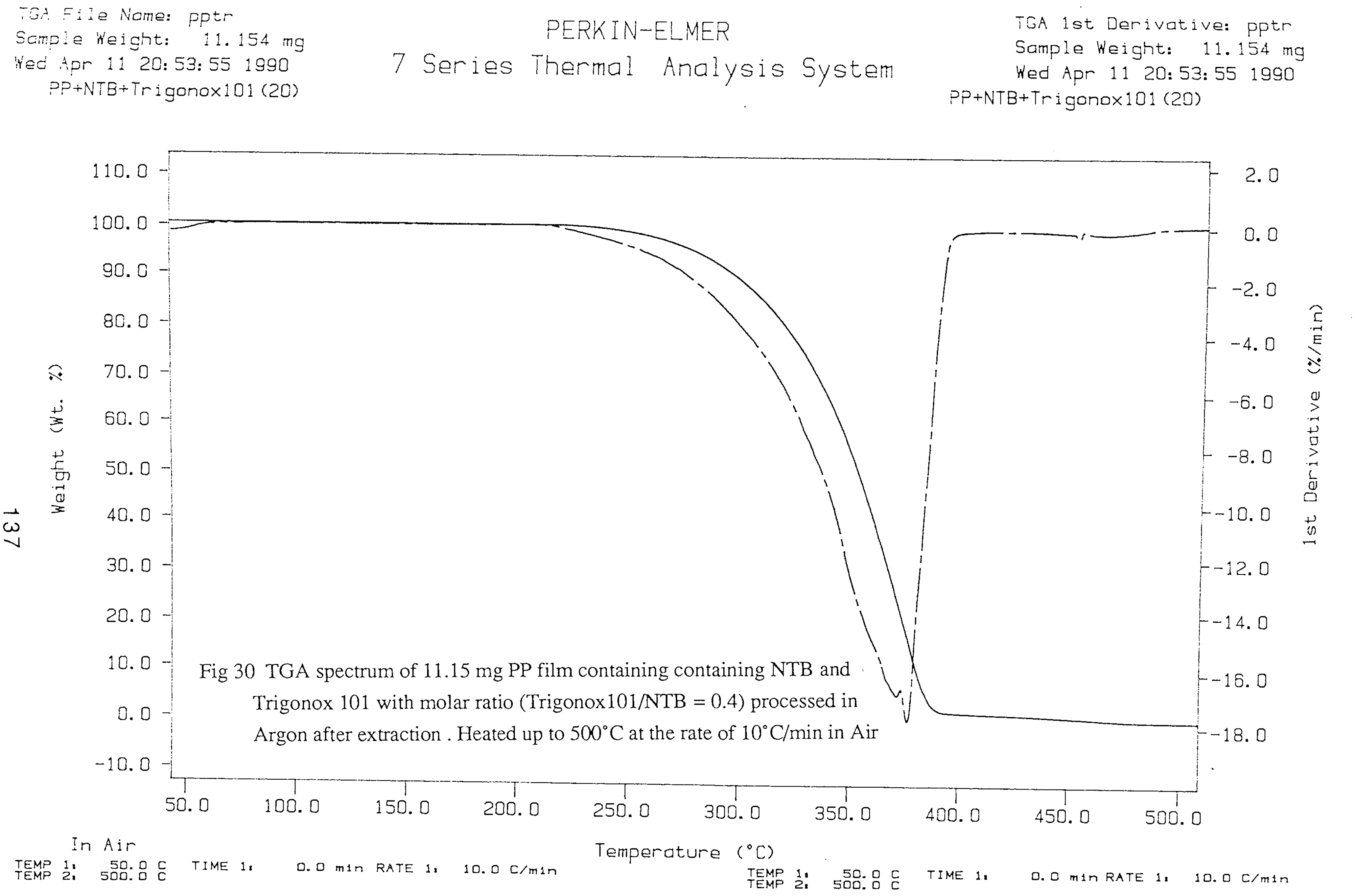


Fig 30 TGA spectrum of 11.15 mg PP film containing containing NTB and Trigonox 101 with molar ratio (Trigonox101/NTB = 0.4) processed in Argon after extraction . Heated up to 500°C at the rate of 10°C/min in Air

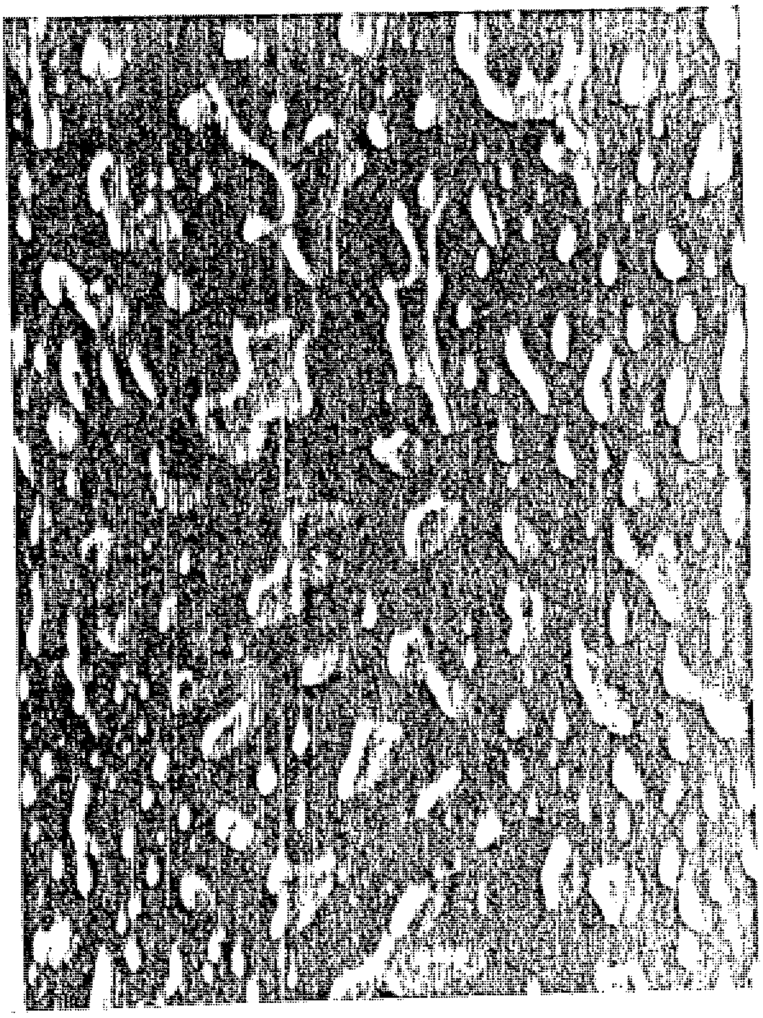


Fig. 31 Typical phase contrast micrography of EPR dispersed in homopolymer PP

CONCLUSIONS:

The main conclusions that can be drawn from these studies are summarised below :

1) The concentration of nitroxyl radical formed from NTB/EPR solution masterbatch as determined by ESR measurements was found to increase to a maximum, then slowly decayed as a function of UV exposure time. The spin trapping technique of the above system is also found to be solvent and radical generator dependent. The incorporation of radical generator in this system gave rise to an increase in both the rates of formation and subsequent decay of the nitroxyl radicals, particularly in the case of benzophenone. Furthermore, the oxidation of the masterbatch solution with MCPBA was associated with a distinct increase in the original nitroxyl radical, the nitroxyl decay is in agreement with the literature data regarding the formation of transformed nitroxyl products (>NOH,>NOR). The formation of O-alkyl hydroxylamine (>NOR) is also confirmed indirectly in model compound studies of NTB/benzene solution.

2) The concentration of nitroxyl radical has been determined by ESR in EPR processed with spin traps as a function of processing conditions. The spin trapping technique is found to be temperature- and time-dependent. The nitroxyl concentration normally increases with increasing processing temperature, presumably due to formation of higher amount of alkyl radical. Nitrones are generally less efficient in trapping alkyl radicals than nitroso compounds. This is associated with the formation

of additional alkyl radical formed from decomposition of alkyl nitroso compounds during thermal processing. The formation of nitroxyl derivatives (>NOH,>NOR) during processing of EPR with nitrones and aromatic nitroso compounds also indirectly identified by an increase in original nitroxyl radical, on oxidation with MCPBA.

3) The quantitative measurements of polymer samples indicated that polymer-bound nitroxyl in the case of nitrones and aromatic nitroso compounds is much higher than aliphatic compounds. This is attributed to the formation of less macronitroxyl radical in the latter. However the poor photoantioxidant activity of the former in the polymer before and after extraction is related to their low solubility and chemical structures rather than permanence of their nitroxyl radicals

4) Trigonox101 was found to improve appreciably the antioxidant activity of C-nitrosoalkanes in the extracted and unextracted PP films. This is believed to be due to formation of a higher amount of macronitroxyl radical and hence decreased the vapour pressure (volatility) of the nitroxyl radical formed in the polymer during photo- and thermal antioxidant activity. However, DCP and benzophenone reduce the photo-antioxidant activity of the above system to varying extents. Hence the importance of chemical structure of additives in the UV stability of polymers is evident

5) Factors which influence the photo antioxidant activity of a spin trap can be outlined as follows: Spin trap,the spin trapping technique, Nitroxyl radical concentration, permanence of nitroxyl radical, nitroxyl transformed products(>NOH,>NOR), the chemical structure of spin trap and radical initiator, the solubility of additive in polymer during thermal processing.

6) ESR studies showed that alkyl hydroxylamines and free hydroxyl amines act as a reservoir for nitroxyl radicals by oxidation by MCPBA. Therefore these species also function as UV stabilisers

Suggestion for further work

1) To increase the spin trapping efficiency of spin traps in polymer solutions without help of radical initiators, would be desirable to carry out this technique in a high speed stirring under thermolysis or photolysis condiations. It has been suggested that high speed stirring of polymer solution lead to rupture of the main chain of polymers (169). It is also interesting to carry out the above technique with the action of ultrasonic, as it has been believed that the decrease in molecular weights of polymer is caused by scission of the main chains by ultrasound irradiation of polymer solutions (170).

2) Although all attempts to identify a band at 1140 cm-1 by FTIR which has been reported to be due to formation of O-alkyl hydroxylamine was unsuccessful in both solution and processed samples containing spin traps (nitroso compounds and nitrones), the formation of this compound (>NOR) was confirmed indirectly in model study (i.e photolysis of benzene solution of NTB) by an increase in the initial concentration of nitroxyl radical in subsequent oxidation with meta-di chloro per benzoic acid. Therefore, it would be desirable to analyse the nature and the amount of nitroxyl transformation products (>NOR and >NOH) individually either by chromotographic method of analysis LC-MS or by NMR. Investigation of the nature of alkyls trapped by nitroso compounds or nitrones or derived nitroxyl radicals when processed with EPR or PP by ESR would be of interest.

3) It was found in this study that nitroxyl radical readily regenerated in the processed polymeric samples or in the photolysed polymer solution containing originally spin traps, on oxidation with a strong oxidising agent (MCPBA). In order to fully understand the fate and mechanism of action of nitroxyl radicals and its transformation products in UV exposure and thermal aging, it is suggested to monitor the changes in nitroxyl radical concentration in the UV exposed polypropylene films at intervals by ESR measurements.

4) IR measurements revealed that 4, Nitroso 2,6,di tert butyl benzene, formed a quinonoid structure during thermal processing with polymers. The poor antioxidant activity of this compound might be in part due to the formation of this compound. Therefore, it is essential to check the photo-antioxidant activity of the synthesised quinone of the corresponding nitroso compound in polypropylene.

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PART II

The effect of Natural Rubber modification by spin traps on the fatigue life and thermal antioxidant activity of the vulcanisate

Mohammad Hassan Zarif Najafi Nooshin

Summary

Aromatic nitroso compounds and their corresponding spin adducts as EPDM-masterbatch have been evaluated as antifatigue agents and antioxidants in natural rubber.

The formation of nitroxyl radicals and their precursors (free hydroxylamine and O-alkylhydroxylamine) from nitroso compounds during processing were shown to be temperature dependent. The concentration of these active species and bonding percentage to polymer have decisive influence upon antioxidant activity of these compounds. However, polymer-bound nitroxyl appeared to have opposite effects on antifatigue activity of antidegradants presumably in part due to restriction in mobility of antioxidant moiety.

p-Nitroso diphenylamine(NDPA) was shown to be highly effective antioxidants and antifatigue agent compared with N-phenyl-N'-isopropyl-p-phenylene diamine (IPPD), under aggressive environmental conditions due to formation of high percentage of polymer-bound nitroxyl.

This work has shown that with the appropriate modification and curing conditions, the antidegradant performance of the commercial stabilisers can be improved significantly.

Keywords: EPDM-Masterbatch,Antifatigue,Rubber-bound nitroxyl

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CHAPTER 1

INTRODUCTION

1-1 INTRODUCTION

The oxidative degradation of elastomers containing only a linear hydrocarbon chain is believed to be through cleavages of carbon-carbon bonds into smaller fragments(1). Consequently, gum-like tactic materials are formed reducing physical strength, shear stress, and elasticity.

The extent of degradation depends on the polymer structure and on the environment. The common environmental factors responsible for degradation are, oxygen, ozone, heat, light, oxidising chemicals, mechanical stress, and metal contamination.

The degradation mechanism is a sequence of free-radical induced chain reactions such as

$$\begin{array}{lll}
\text{Initiation} & \text{Initiator} \xrightarrow[\text{Stress}]{h\upsilon\ ,\ \Delta} R^{\cdot} & \\
\text{Propagation} & R^{\cdot} + O_2 \longrightarrow & ROO^{\cdot} \\
 & ROO^{\cdot} + RH \longrightarrow & ROOR + R^{\cdot} \\
\text{Termination} & 2R^{\cdot} \longrightarrow & R\text{-}R \\
 & ROO^{\cdot} + R^{\cdot} \longrightarrow & ROOR \\
 & 2ROO^{\cdot} \longrightarrow & ROH + ROR
\end{array}$$

Scheme 1

Thus the formation of alcohol (ROH) ether (ROR), Carbonyl (RCOR) Carboxyl (-COOH), and ester (-COOR) functional groups are the major oxidation degradations products from the peroxide initiated free-radical reactions.

However, the presence of many components in the vulcanisation system either accelerate or retard oxidative degradation processes. Natural rubbers contain traces of peroxides from internal sources which could provide free radicals for the initiation of the degradation process. Even in the most carefully prepared raw rubber, peroxides are always present(1,2). Therefore, protective additives, antioxidants and antiozonants are needed for extended oxidation resistance during compounding and use.

The high operating temperatures of modern polymers in engineering applications and increasing public concern about the migration of polymer additives into the human environment, have all contributed to the present demand for improved non-extractable antioxidants and stabilisers. Research during the last two decades has not led to the introduction of any fundamentally new types of antidegradant, but has emphasised the effect of conditions met in service on antioxidant efficiency and the need for proper selection of the protective systems. For satisfactory performance, the antioxidant must not only be designed to have activity against degradation, but must also be resistant to physical loss in an aggressive environment (e.g. oils, solvents, etc.)

There are basically two ways of obtaining a substantial improvement in antioxidant permanence in rubber:

Selecting or creating a high molecular weight antioxidant.

Reacting the antioxidant with the rubber (i.e chemically bind the antioxidant to the polymer backbone).

1.2 Mechanisms of Antioxidant Action:

Antioxidant may be broadly classified into two types based on the mechanism by which they function.

1.2.1 Preventive Antioxidant

The most important classes of preventive antioxidants either remove hydroperoxides in a process which does not involve free radical formation, or protect hydroperoxides from decomposition, thus effectively inhibiting oxidation.

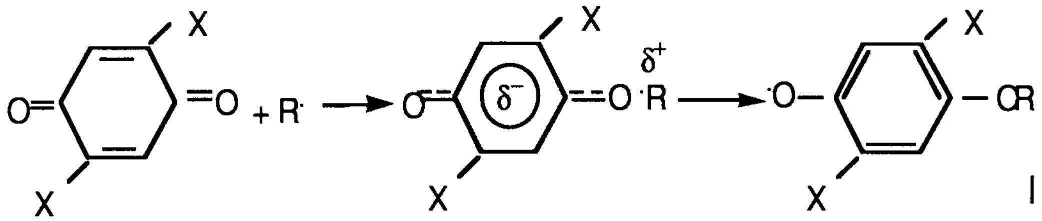
1.2.2 Chain Breaking Mechanism

The free radical oxidation chain reactions (scheme 1),indicates that there are two ways in which the propagating cycle could be interrupted.

1.2.2.1 Chain Breaking Acceptor (CB-A) Mechanism

This mechanism involves the removal of alkyl radicals by an oxidation process to give a carbonium ion or a derived product.This class includes quinones(3), nitroso compounds, nitrones and a variety of stable nitroxyl(4-9) and phenoxyl radicals(3,10,11).

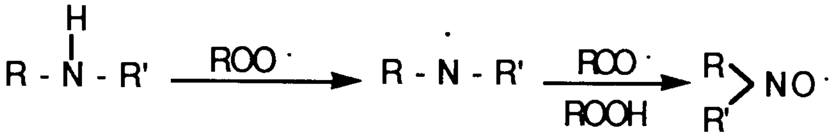
This mechanism is demonstrated by quinones.



Electron withdrawing and delocalising groups increase the alkyl radical affinity and consequently enhance the oxidation activity of quinone(12).

1.2.2.1.1 Nitroxyl Radicals as Chain Breaking Acceptors

One of the most important development in the understanding of the inhibition of oxidation by amines was the discovery that relatively stable nitroxyl radicals are produced from the corresponding amines during the inhibition process. These nitroxyl radicals are efficient alkyl radical traps and thus operate through the CB-A mechanism.



$$R-\overset{H}{\underset{|}{N}}-R' \xrightarrow{ROO\cdot} R-\dot{N}-R' \xrightarrow[ROOH]{ROO\cdot} \begin{matrix}R\\R'\end{matrix}\!\!>NO\cdot \qquad 2$$

The antioxidation activity of the amine is therefore attributed to the termination of alkyl radicals according to reaction 3.

$$>NO\cdot + R\cdot \longrightarrow\ >NOR \qquad 3$$

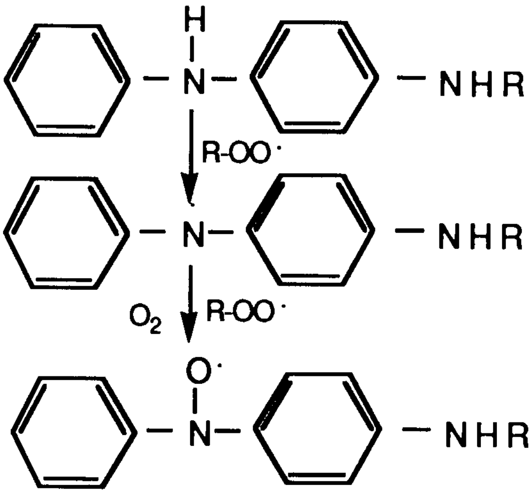
1.2.2.2 Chain Breaking Donor (CB-D) Antioxidants

Electron donor compounds, after donating a labile hydrogen, give rise to a stable radical, are used as CB-D antioxidant. This type of compound is involved in the removal of alkylperoxy radicals.

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad 4$$

The two well known sub-classes of this type of antioxidant are the hindered phenols and aromatic amines(13).

In contrast to the phenolic antioxidants, the oxidation products of secondary aromatic amines (the nitroxyls) are believed to be effective CB-A antioxidant. However, the amines are initially CB-D antioxidants and some phenols also give stable aryloxyls which are CB-A antioxidants. eg galvinoxyl.



Scheme 2

The effectiveness of this type of the p-phenylene diamine, particularly under conditions where alkyl radicals are the predominant species (e.g. fatigue) is believed to be due to the regeneration of nitroxyl in a cyclical mechanism involving the hydroxylamine(14,15).

1.3 FATIGUE OF POLYMERS :

Fatigue is a dangerous form of fracture which occurs in materials when they are subjected to cyclic or fluctuating loads. It occurs by development and progressive growth of a crack and one of the unfortunate features of fatigue fracture is that it can occur at loads much lower than those required to produce failure by static loading. The fatigue failure of polymers is not well understood. This is mostly because of the need to take account of certain factors, such as, molecular weight, degree of cross-linking, crystallinity, transition effect and thermal effects (internal heating).

The importance of thermal effects means that fatigue in polymers is very sensitive to the frequency of cyclic stressing. If conditions are not isothermal, the hysteretic heating effect generated during each cycle of stress causes the elastic modulus to decrease, so that eventually the specimen is unable to support the load and therefore fails prematurely.

One of the most important factors influencing the fatigue resistance of plastics is degree of crystallinity. The lowest fatigue crack growth rates are found in crystalline polymers such as nylon and polyacetal. In contrast, amorphous polymers exhibiting a high degree of cross-linking exhibit very high crack growth rates. Their low toughness and ductility presumably account for poor fatigue performance. The molecular weight of a polymer also appears to be important in relation to fatigue resistance. According to Hertzberg and Manson(16) resistance to fatigue crack propagation resistance at a given stress level is dramatically improved by increasing the molecular weight or by addition of a high molecular weight fraction to the matrix. They also comment that fatigue resistance is enhanced by the addition of second-phase particles that leads to enhancement of toughness.

1.3.1 Initiators of Fatigue Failure

The presence of inhomogenities and naturally occuring flaws are two of the chief initiators of fatigue failures in rubber vulcanisates.Hess and Burgess(17) and Smith(18) have reported that during fatigue, reagglomeratioon of materials, normally dispersed in rubber occurred to form areas of heterogeneity. These areas serve as loci for fatigue failure by forming highly localised stress concentrations (19,20).

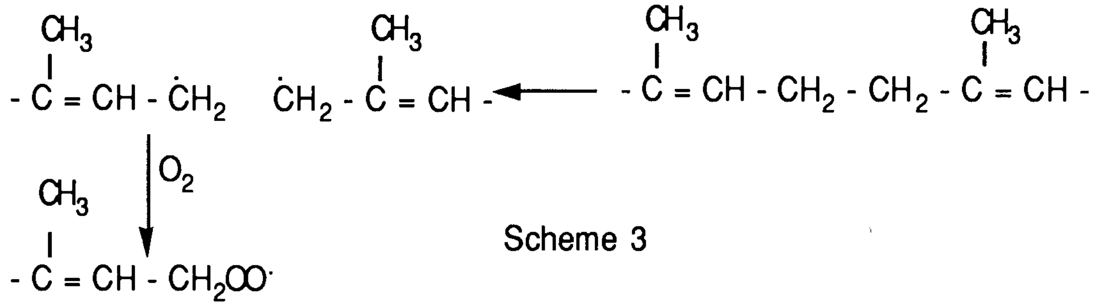
1.3.2 Mechanochemistry to Fatigue

Kuzminsky(21) reported that during the fatiguing process mechanochemically activated destruction takes place, rather than mechanical destruction as suggested by others(22).

Gent(23) studied the chemical reaction involved in flex cracking by measuring fatigue life in controlled atmosphere. His results indicated that oxidative scission take place at the tips of mechanically induced cracks.

Two processes were proposed to account for the activation of vulcanisates toward oxygen.

1) Cleavage of the weakest carbon-carbon bond forming free macroradicals (scheme 3)



Scheme 3

2) The activation of double bonds toward oxygen by distortion of the tetrahedral band angles giving practical double bond character (21-24). Both processes increase the rate of autooxidation. The mechanically activated oxidation processes develop rapidly in thin layer vulcanisates, where the reaction rate with oxygen is not diffusion controlled . In thick samples, and because of limited oxygen diffusibility, mechanically activated thermal processes become more important(25).

1.3.3 Factors Affecting Fatigue Life of Vulcanisates

Many factors control the fatigue life of vulcanisates of these the following are the most important:

1.3.3.1 The Nature of the elastomers

The most important variable affecting fatigue life is the nature of the rubbers. Fatigue lives of different rubbers tested under the same experimental conditions,showed that natural and butyl rubbers give the longest fatigue lives compared with SBR, nitrile and neoprene at strain cycle of 0 to 100% extension(26). Lake and Thomas(27) have shown that crystallising rubbers such as natural rubbers and polychloroprene show a marked improvement in the fatigue life if the specimen is not allowed to relax completely during cycling.It is also shown(27)that by increasing the minimum strain during a cycle from zero to 50% a hundred fold improvement in fatigue life is obtained. This effect is considerably smaller in non-crystallising SBR(28).This effect is attributed(27,29)to strain induced crystallisation at the tip of the crack. This phenomenon can be understood from the mechanism for the effect of hysteresis, since if the minimum strain is sufficiently high, the crystalline structure at the crack tip will be partially retained and will impede the advance of stress concentration on the next loading cycle. Amorphous rubbers display hysteresis resulting from viscoelastic behaviour(30,31) and although this is generally of a lower order than that arising from crystallisation. The extent of the hysteresis again markedly influences crack growth and fatigue.

It has been shown that EPDM appears to have a higher ratio for time to crack initiation to time for crack growth than any other elastomer, due to the high resistance of the rubber to ozone and oxygen. A mixture of different rubbers is sometimes found to have better fatigue life than the individual rubber components. The increased fatigue life of binary compounds is usually accounted for by the resistance of transitional layers which promote the distribution of stress more evenly.

1.3.3.2 Temperature

The effect of temperature on the fatigue life of rubbers is complicated by simultaneous rapid chemical changes of an irreversible nature.

Kervizic and Lloyd(33) reported that for conventionally vulcanised rubbers fatigue life increase to a critical temperature of 70°C above which there is a dramatic fall, due to the softening of the compound and reduction of work input.Nado et al, found that at elevated temperatures there was an increase in the degree of modification of rubber chains by cyclically bound sulphur, this seems to be one of the causes of the low fatigue life.

It should be born in mind that above the critical temperature mentioned above, compounds having inherently high oxidation resistance, exhibit higher fatigue lives than conventional compounds.

1.3.3.3 Effect of Curing System and State of Cure

The fatigue resistance of a rubber is strongly dependent on the nature of the network structure and hence, upon the curing system used and the curing time. Increasing the degree of cross-linking decrease the fatigue resistance of rubbers. Presumably the capacity of the segments of rubber molecules to reorientate is reduced by resulting increase in modulus leading to increased molecular stresses. Curing systems that give a high proportion of polysulphide to monosulphide cross-links provide improved fatigue resistance(34,35).

A state of overcure in a conventional vulcanisate, which leads to a significant decrease in the density of polysulphidic cross-links and the generation of more mono and disulphide cross-links, causes a reduction in fatigue. This is because the mono-sulphide cross-link is a stable link compared with polysulphide, so that when the rubber is strained no stress induced rearrangement of links can take place. This results in higher localised strains and hence, a higher probability of chain scission. Undercure produces a vulcanisate of low elasticity due to insufficient formation of cross-links thus resulting in poor fatigue life.

1.3.3.4 Oxygen and Ozone

An oxygen or ozone environment over an elastomer, which is being subjected to repeated deformation can affect the time for complete failure in different ways. In the case of ozone, a series of reaction leads to the formation of cracks on the surface of the specimen. These cracks can act as points for stress concentrations, and thus reduce the induction period before fatigue cracking begins. Once cracks are formed during continuous deformation, these tips represent a good site for ozone attack, and cracks will propagate as long as adequate stress is available. So ozone, and mechano-oxidation are, essentially additive processes in crack growth(36-38). Oxygen plays a major part in the fatigue failure of rubber. Neal and Northam(37) found the development of flex cracks to be about four times faster in oxygen that in nitrogen. However, it was already shown (39) that in an inert atmosphere, vulcanisates of NR, SBR and butyl show less difference in their fatigue life than in air.

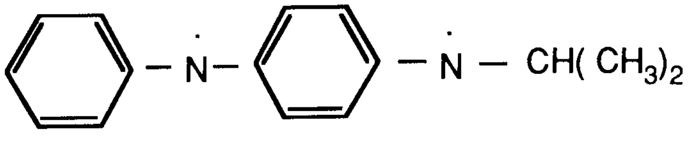
1.3.3.5 Effect of Fillers

The flex cracking tendency of a natural rubber conventional CBS vulcanisates was found to decrease with increasing filler content. Flex cracking rate is high at high loadings of carbon black(40), but it decreases as the carbon black loading decreases. It has been reported that the overall cross-linking density and the proportion of polysulphide cross-links increases between 0-5 phr HAF black in a conventional system(41).

In general, small particle size fillers have little effect on fatigue life if comparison is made on an equal energy input basis(42). The effect of filler must, however, be affected not only by particle size by the adhesion, compatibility and bonding. Any filler which contains particles larger than 10^{-3} cm can initiate failure by acting as points of stress concentration.

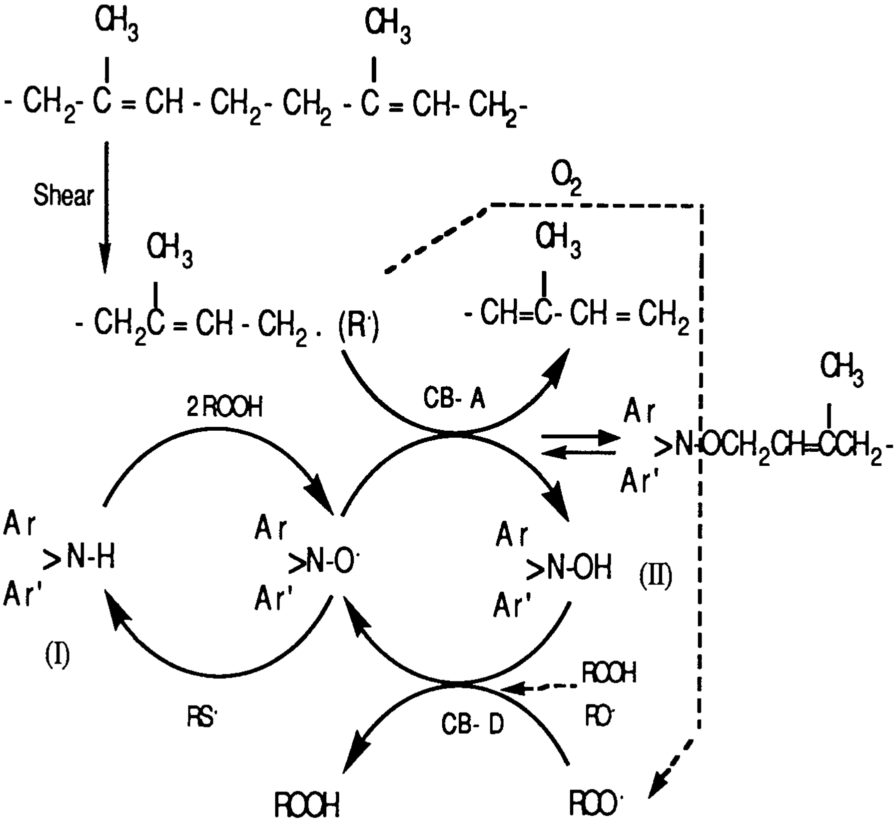
1.3.4 Rubber Antifatigue Agents and their Protective Mechanisms

Additives which retard crack initiation under conditions of cyclic deformation are called anti-fatigue agents. All effective antifatigue agents are antioxidants of the secondary arylamine class. Kuzminsky(43) has suggested the "Cage Theory" as one possible mechanism by which substituted p-phenylene diamines inhibit mechanochemical degradation during flexing. During flexing alkyl radicals are produced, and because the rate of their relaxation is higher than their rate of recombination of these macroradicals, tend to come out of the cage. The moving gradient of stress could also prevent the achievement of the cage. The presence of antifatigue agent, which generate biradicals on oxidation, such as,



could join broken ends of different chains and regenerate three dimensional networks of the broken vulcanisates. Macroalkyl and macrothiyl radicals formed by scission of the hydrocarbon chain or of the cross-links respectively during fatiguing act as initiators for oxidation. In the absence of antidegradant, recombination takes place with shortening of the sulphur cross-links. it is evident, then that antifatigue agents interfere with this process.

An important clue to the mechanism of the p-phenylene diamine antidegradants was the discovery that during fatiguing of rubber containing 4-isopropyl amino diphenylamine (IPPD), nitroxyl radicals can be detected in the vulcanisate by ESR(44). It has also been shown(45,46) that a number of diarylamines behave in the same ways as IPPD and that the derived nitroxyl radicals are more effective as an antifatigue agents than the parent amines. The mechanism which has been proposed to account for this is outlined in scheme (4). It involves the oxidation of alkyl radicals by nitroxyl in a chain-breaking acceptor process (CB-A) followed by re-oxidation of hydroxylamine (II) by alkylperoxy by the more useful chain-breaking donor (CB-D) process (44,46,47).



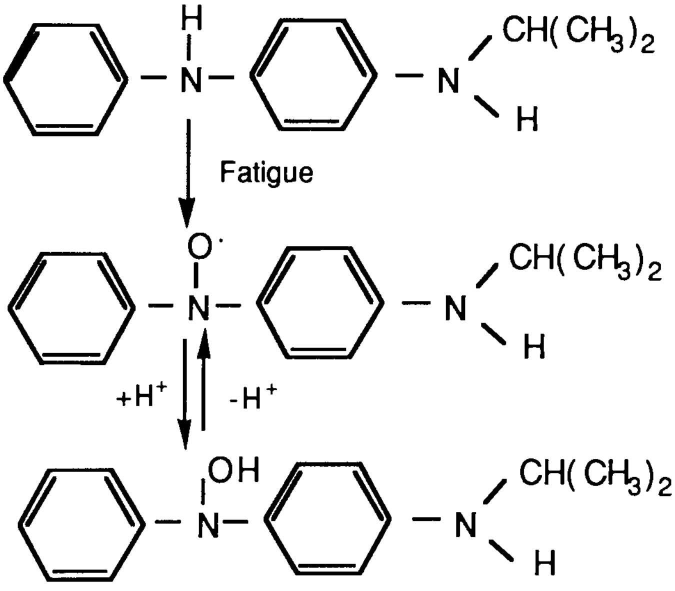
CH3
CH3
- CH2- C = CH - CH2- CH2 - C = CH- CH2-
Shear
O2
CH3
CH3
- CH2C = CH - CH2 . (R·)
- CH=C- CH = CH2
CB- A
2 ROOH
Ar >N-OCH2CH=CCH2-
Ar'
CH3
Ar >N-H Ar'
(I)
Ar >N-O· Ar'
Ar >N-OH Ar'
(II)
ROOH
RO·
RS·
CB- D
ROOH
ROO·

Scheme 4

1.4 Scope and Object of the Present Project

Fatigue failure of rubbers is one of the most important, but at the same time least studied, problems in mechanochemistry. Fatigue results from various mechanochemical processes developing under dynamic and static loading and is intensified by the presence of oxygen, ozone, heat and light.

The most effective antifatigue agents so far identified is N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD). It has been reported(44) that the antifatigue activity of this compound is associated with the generation of the diarylnitroxyl and hydroxylamine, when rubber containing it is subjected to repeated mechanical stress (fatigue).



Scheme 5

The antifatigue activity of this compound is believed to be related to scavenging of macroalkyl as well as macroperoxyl radicals, according to scheme (4). The main disadvantages of this compound are that it is not resistant to aggressive environment(48)(e.g. water, organic solvents,etc.) and it gives rise to intense discolouration in the rubber.

Depletion of antioxidant either by leaching or by thermal oxidation is known to reduce the fatigue life of vulcanisates(49-51). Therefore, reactive antioxidants (aromatic nitroso compounds) with spin trapping properties which attach chemically to the polymer molecules with formation of nitroxyl radicals, cannot be removed even by most exhaustive extraction may overcome this problem.

The objectives of the present project are:

I. To modify the natural rubber (NR) either with the spin traps (aromatic nitroso compounds) or synthesised EPDM-bound spin adducts (Masterbatch) during compounding,and to investigate the effect of spin adducts formed during compounding on the curing characteristics of final vulcanisates.

II. The identification and quantification of spin adducts generated from nitroso compounds in EPDM-masterbatch by the formation of electron spin resonance measurements.

III. To evaluate antidegradant behaviour of modified natural rubber conventional CBS vulcanisates by oxidative stress-relaxation and fatigue to failure test.

IV- To examine the possibility frequently stated in the literature that polymer-bound antioxidant may not be able to function as effectively as conventional antiaging additives.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 MATERIALS

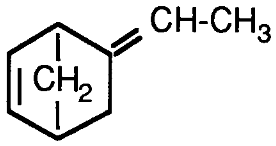
2.1.1 ELASTOMERS

A - Natural Rubber

All dry natural rubber used throughout this work was SMR CV (Controlled Viscosity Standard Malaysian Rubber), containing 0.15% of hydroxylamine salt, which has been added to the latex before coagulation to inhibit the rise in viscosity or storage hardening. It was sheeted on a two-rolled mill and extracted with hot acetone under nitrogen then dried at 25°C under vacuum.

B - Ethylene Propylene Diene Terpolymer Rubber

EPDM V6505 containing 44% PE and 9% diene (Ethylidene norbornene)was supplied by ESSO Chemicals Limited, and used



either for preparation of masterbatch (EPDM-Spin Adducts) or as a blend copolymer during compounding of natural rubber on a two roll mill.

2.1.2 COMPOUNDING INGREDIENTS AND ANTIOXIDANTS

A - Compounding Ingredients

N-Cyclohexyl benzothiazole-2-sulphenamide (CBS), Monsanto Chemical Limited.

Sulphur, Anchor Chemcial Limited.

Zinc Oxide, Amalagamated Zinc Limited.

B - Antidegradants

N-phenyl-N'-isopropyl-p- phenylene diamine (IPPD), Monsanto Chemical Limitd.

P-Nitroso diphenyl amine, (NDPA) Supplied by Aldrich Chemcials Limited. It was welted with 25% water and was dried under vacuum at room temperature.

3, 4, 5, 6-pentamethyl nitroso benzene (PMNB) and 2, 5-di- tert butyl-p-nitroso phenol (NDBph) were synthesised according to the procedures(part1,sections2.11.3 and 2.1.1.4) respectively

2.2 PREPARATION OF RUBBER VULCANISATE

2.2.1Modification of Natural Rubber During Compounding

2.2.1.1 By Nitroso Compounds as Reactive Antioxidants

The compounding ingredients were mixed with natural rubber on a 12 inch water cooled (70-80°C) and hot steam (130°C) two roll mill. A friction ratio of 1:2 was employed. Antidegradants were added as normal additive immediately after mastication. Sulphur was added after all the other ingredients had been incorporated.

Gum rubbers were prepared according to the following formulations:

Natural Rubber	100 g
Antidegradant	1.0 g
Stearic Acid	3.0 g
CBS	0.6 g
Sulphur	2.5 g

The total compounding time of 10 minutes was kept constant in all the formulation procedures.

2.2.1.2 Modification by both EPDM and spin trap

The gum rubbers were prepared according to the following formulation:

Natural Rubber	90g
EPDM	10. g
Antidegradant	1.0 g
Stearic Acid	3.0 g
CBS	0.6 g
Sulphur	2.5 g

This mixing procedure is as described in section 2.2.1.1. EPDM was masticated along with NR prior to addition of other ingredients.

2.2.1.3 Modification by EPDM-Spin Adducts(Masterbatch)

2.2.1.3.1 Preparation of EPDM-Spin Adducts

In order to obtain optimum conditions for maximum [>NO·], EPDM was processed with 10% of aromatic nitroso compounds in the presence and absence of radical generator at different temperatures in an internal mixer for 10 minutes and under an oxygen free atmosphere(Argon).

The [>NO·] of the masterbatch samples were measured by ESR before and after extraction and after oxidation by the benzene solution of meta-di-chloroperbenzoic acid (MCPBA) according to the procedure (part-1,section 2.4.4). $CuSO_4,5H_2O$ was used as an internal standard.

2.2.1.3.2 Procedure for Mechanomodification:

In this case, modification was carried out by introducing EPDM-masterbatches with maximum conversion of spin traps to spin adducts to natural rubber on a water cooled two roll mill (70-80°C). Compounding was carried out according to the following formulation in order to achieve 1.0 phr nitroso compounds in the gum rubber.

Natural Rubber	91.0g
EPDM-masterbatch	10.0g(Containing1phr nitrosocompound)
Stearic Acid	3.0 g
CBS	0.6 g
Sulphur	2.5 g

The mastebatches were introduced to natural rubber during mastication.

2.3 Measurements of Wallace Plasticity

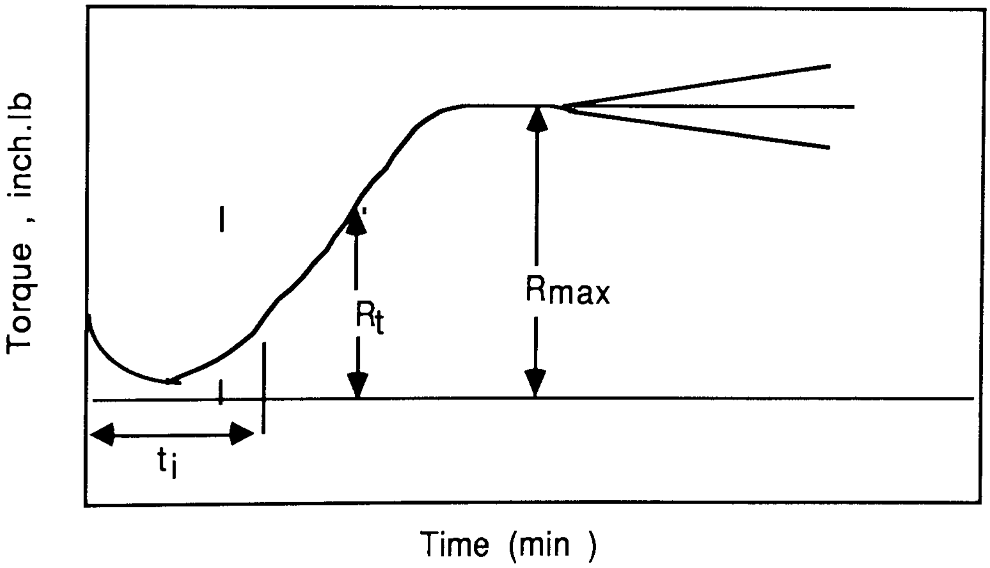
Plasticity may be defined as 'ease of deformation' so that a highly plastic rubber is one that deforms or flow easily. Viscosity is the resistance to plastic deformation or flow. The plasticity of a rubber stock is important because it gives a measure of processability of the rubber. It also gives a measure of the initial molecular weight of the raw rubber which has an influence on the physical properties of the vulcanisate produced(52). In the present work, in order to investigate the effect of the modification systems on natural rubber, the plasticity number (P°), which is inversely related to plasticity of gum rubber was measured at 100°C by The Wallace Plastometer.

2.4 Monsanto Oscillating Disc Rheometer

The curing and processing characteristics of the modified-natural rubber samples were determined by the Monsanto Oscillating Disc Rheometer (model 100). The rubber specimen is placed in a cylindrical cavity and has embedded in it a biconal rotor which is oscillated continuously. The cavity and specimen are maintained at a temperature 140 ± 0.5°C. The dies which from the cavity are held together by a force of 50 PSi. On the arm of the eccentricity are mounted strain gauges which measure the force required to oscillate the disc. The torque applied to the disc and the resistance of the rubber to deformation causes a voltage proportional to the stiffness of the rubber. This is directly recorded on a potentiometer flat-bed recorder.

A typical Torque-time curve produced on the Monsanto Rheometer is shown in Fig. 1. There is an initial decrease in viscosity of the stock due to increasing temperature which then flattens out until the onset of cross-linking produces a sharp rise in viscosity and therefore in the torque exerted by the oscillating rotor embedded in the specimen. This torque increase until cross-linking is complete. The curve may show a decrease in torque with time if chain scissions takes place on extended heating or these may be a continual increase if a slow cross-linking reaction takes place.

Fig. 1 A typical Monsanto rheograph for the vulcanisation of rubbers.



The following vulcanisation characteristics can be measured from Monsanto rheographs:

The overall first order rate Constant, K.

The maximum Torque developed (Rmax), which is a measure of cross-linking density.

The scorch time (t_i), which is a measure of the time for the formation of an active sulphurating agent, and the reaction of this with the hydrocarbon to form rubber-bound intermediate, the precursor to cross-link formation.

The rheographs of the modified natural rubber vulcanisates were obtained at 140°C with arc±:3 by means of the Monsanto reheometer and the corresponding curing parameters were read from a programmed computer. The readings will be shown in the results section.

2.5 VULCANISATION OF COMPOUNDS

2.5.1Vulcanisation of Compounds used for Fatigue Test

Compounds were moulded as rectangular sheets (22.9x7.6x 0.25 cm) with a beaded edge. About 60 g. of gum stock was required for each sheet. Samples were first sheeted out on a mill to 2.5 mm thickness and then cured in a compression mould at pressure 50 Kg/cm^2 and 140°C for the time to get 95% cure.

2.5.2 Vulcanisaton of Compounds used for Stress relaxation Measurements

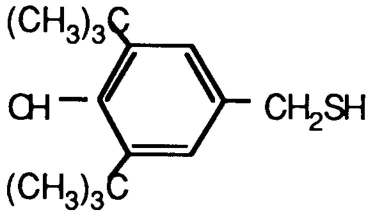
Vulcanisate sheets with a thickness of 50 mm were prepared in a stainless steel mould. 3.0 g of gum stock was milled into a thin sheet and placed in the mould cavity. The mould was cured in compression mould at a pressure 30 Kg/cm^2 and 140°C for the time to obtain 95% cure.

2.6 TECHNOLOGICAL AGEING TESTS

2.6.1 Introduction:

For satisfactory performance, a stabiliser must function at the right place and at the right time. It was a question for many years, that why antioxidants with the same functional group and with similar activity in polymers, particularly under heat aging conditions, appeared to differ considerably in their activity(53). Furthermore, antioxidants that are effective in rubbers when tested in an air oven at temperatures below 100°C were found to be relatively ineffective in polypropylene which is generally evaluated at 130-150°C (54). The factor responsible for this difference was shown to be the volatilisation of conventional rubber antioxidant at the higher temperature used in accelerated aging of polypropylene (53,54). Under these conditions, the intrinsic antioxidant activity of the molecule becomes much less important than its tendency to diffuse through the polymer and volatilise from the surface (54,55).

No solution has so far been proposed for the physical loss of antidegradants from the tyre thorough carcase, in spite of the through investigation of this problem carried out by Kuzminsky and his coworkers who have shown (56) that conventional antidegradants are "extruded" from the inside to the outside at a tire with subsequent loss from the surface. A potential solution may lie in the developing technology of polymer-bound antioxidants. A significant improvement in fatigue resistance of BHBM over IPPD before and after solvent extraction, at least in part is attributed to its capability to bind chemically to rubber during mechanochemical process (57).



BHBM

In this work, the quantitative estimation of rubber-bound antioxidant was determined by ESR measurements according to the following formulation.

[>NO·]* - [>NO·]** = % bound-spin trap

* = Before extraction & after oxidation

** = After extraction & after oxidation

The rate of the loss of antioxidants in the modified rubber vulcanisates before and after azeotropic extraction were evaluated at 100°C by a stress-relaxation. The tensile flex resistance was assessed by Monsanto fatigue to failure tester to determine the life time of the modified vulcanisates before and after azeotropic extraction under dynamic service conditions.The theory behind these techniques is fully described in the relevant sections.

2.6.2 STRESS-RELAXATION OF VULCANISATES

2.6.2.1 Apparatus

The conventional stress-relaxation measurements were made using Wallace Shawbury agetester (Wallace Instruments Limited), in conjunction with a six cell aging oven set to have a block temperature due to a 1.3 cubic-feet per hour air flow.

The agetester consists of a balanced beam, on which the tension exerted by a rubber strip is counterbalanced by that of a helical spring. By means of electrical contacts at the end of the beam and a motor, the tension in the spring is automatically adjusted to balance the tension in the rubber. A pen attached to the moving end of the spring records the stress in the sample on a cylindrical chart revolving at constant speed of one revolution every 12 hours.

During the test, the force exerted by the spring equals that of the specimen. Any imbalance between the two forces will cause tilting of the beam in one or the other directions. Thus, electrical contacts are closed and current is supplied to the servo-motor. This motor rotates and transmission is obtained through a small gear box which moves the vertical thread to restore a position of balance.

2.6.2.2 Procedure

Rectangular samples with thickness 50 mm were cut from adjacent areas of a vulcanised sheet by the Wallace stress-relaxometer cutter. Samples were examined for nicks and any so marked were discarded. The specimen, was located between and clamped in two grips.

The instrument was zeroed for the weight of the specimen after which the lower specimen grip was tightened around the sample. The sample was extended, the instrument being used with a brass collar, so that the initial extension of the sample was a constant 60%. The instrument was then placed in the air aging oven, which was maintained at the aging temperature (100°C) and after allowing 5 minutes for expansion, the pencil lead was adjusted to 100% stress and zero time on the chart.

The specimen was then allowed to relax continuously in stress. The instrument recorded stress as a function of time.

2.6.2.3 Continuous Stress-Relaxation in Rubber Materials

Stress relaxation of rubber materials at elevated temperatures was first investigated by Tobolsky and co-workers(58,59). After applying a constant deformation to a specimen, the retractive force and its change with time are recorded. The retractive force is usually found to decrease with time. In the statistical theory of rubber elasticity, Equation (1), it is claimed that the stress acting on an uniaxially strained rubber item is completely determined by the tension, the temperature and the network density (60). This equation provides a better curve fit to experimental data in compression than in tension and is claimed by Treloar(61) to be valid up to 60% compression.

$$\frac{f}{A} = S\ nom = V.R.T. \left[\frac{Lx}{Lu} - \left(\frac{Lu}{Lx}\right)^2 \right. \qquad (1)$$

$$\frac{ft}{fo} = \frac{Vt}{Vo}$$

A = area of undeformed specimen
S nom = nominal stress
v = network chains per unit volume or network density
g = gas constant
T = absolute temperature
Vt = network density at time t
Vo = network density at the normalization time
Lx = length of specimen deformed
Lu = length of specimen undeformed
f = restoring force
f_o = restoring force at the normalization time
ft = restoring force at time t

Directly after applying the deformation, the retractive force usually declines rapidly because of conformational changes and alignment of polymer chains (62). Entanglement effects have an influence on the modulus of the rubber, at least at shorter times, but these effects are difficult to analyse in a reproducible way. After sometime, these effects no longer dominate the stress relaxation, especially not at higher temperatures. A way of minimising these complicating effects is to normalise the data which means that all measured values are divided by the value at a certain time, e.g. 5 min. after applying the deformation.

When the influence of conformational changes, alignment of polymer chains and entanglement effects are neutralised in this way, it is mainly chemical degradation of the network that contributes to stress-relaxation at the normalisation time will thus be the same as the rates between the network density at the normalisation time, as indicated in equation (1). This analysis of chemical rupture in a rubber network is the idea behind the concept of chemical stress-relaxation(63). Results of stress relaxation are very often (and also in this project) plotted as log (f/f0) against linear time. This is because, when random scission along the main chains is the dominating degradation mechanism, the slope of this plot gives the rate of chain scission (64). The rubber network can degrade in different ways(65):

A. Irreversible network scission

B. Reversible network scission, rearrangements or exchange reactions .

C. Cross-linking reactions, generation of a secondary network.

Scission can occur at different sites in the network.

a. Scission at the cross-links, or junction points.

b. Random scission along the main chains.

2.6.2 FATIGUE RESISTANCE OF VULCANISATION

2.6.2.1 Apparatus

The Monsanto fatigue to failure tester has been developed to provide a simple reproducible method of determining the fatigue life or cut growth properties of cured stocks. Dumbbell samples are subjected to repeated strain cycles and the number of cycles to fatigue failure recorded automatically. The maximum strain imposed may be varied over a wide range and the fatigue properties of vulcanisates are compared directly at equal strain. The samples are subjected, for a quarter of each cycle, to an increasing strain at uniform acceleration which is then relaxed a further quarter cycle.The sample is then held at zero strain for half a cycle to allow recovery of the unstrained length.The maximum applied strain may be varied by changing the drive cam.

2.6.2.2 SAMPLE PREPARATION AND TESTING

2.6.2.2 - A Sample Cutting

Individual dumbbell samples were cut from a rectangular vulcanised sheet, prepared according to section (2.6.1), at right angles to the grain by BS type 'E' dumbbell cutter. The die cutting edge was maintain evenly sharp. Samples with flaws at the sample edge caused by faulty cutting were discarded, since they cause premature failure on fatigue.

2.6.2.2-B Sample Mounting

The dumbbell samples were mounted at zero strain. At zero strain the major axis of the drive cams had to be horizontal and coincided with the horizontal line on the lower carriage. Each sample holder was adjusted so that zero strain was obtained when samples were mounted. This was done by inserting a 6 cm long calibration rod between the upper and lower shackles and adjusting the thumb nut until a snug fit was obtained. After the machine was run for 10 and 100 cycles, the power was turned off and the drive cams were set for zero extension by adjusting each upper shackle with the thumb nut so that when the lower shackle was raised, a slight bow appeared in sample. Then the machine was run and fatigue life was recorded as the number of cycles to failure. The drive cams used gave an extension ratio of 1.61±0.04 (Cam Number 4) and samples were flexed at a frequency of 100 cycles per minute. Replicated experiments were carried out (normally 6) and the fatigue lives quoted are the average values obtained from the four highest values using the Japanese industrial standard (JIS) averaging formula. The purpose of this practice is to eliminate discrepancies due to physical flaws in the samples. JIS AV = 0.5 A+0.3 B+0.1(C+D).

CHAPTER 3

3.1 THE IDENTIFICATION AND QUANTIFICATION OF SPIN ADDUCTS AND THEIR PRECURSORS IN EPDM-MASTERBATCH

3.1.1 Results and Discussion

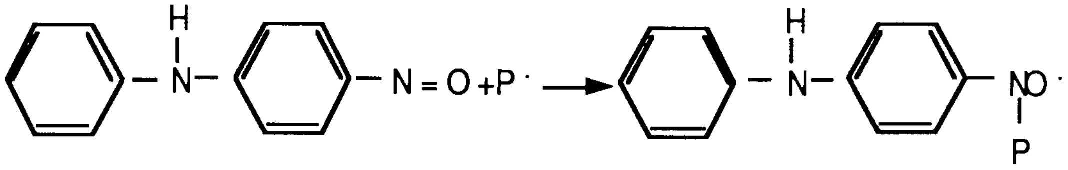
The chemical names and structures and code names of antidegradants used in this study are listed in table -1

ESR examination of processed EPDM-masterbatches showed a singlet spectrum in the case of NDPA(fig.2) and NDBPh (fig.3)and an unsymmetrical doublet in the case of PMNB, with the characteristic g values of nitroxyl radicals at low modulus width settings (Table 5). The g value of nitroxyl radicals were measured according to procedure described in part-1, section 2.4.3. However, the line shape of spectra changed after oxidation with MCPBA in benzene (figs 3, 4), due to free tumbling of nitroxyl radical in a dilute medium. The nitroxyl radical concentrations generated during processing conditions from 10% of these spin traps with EPDM, were calculated according to the procedure (part-1,section 2.4.4). The nitroxyl radical concentrations generated from NDPA, PMNB and NDBPh varied under different processing temperatures.

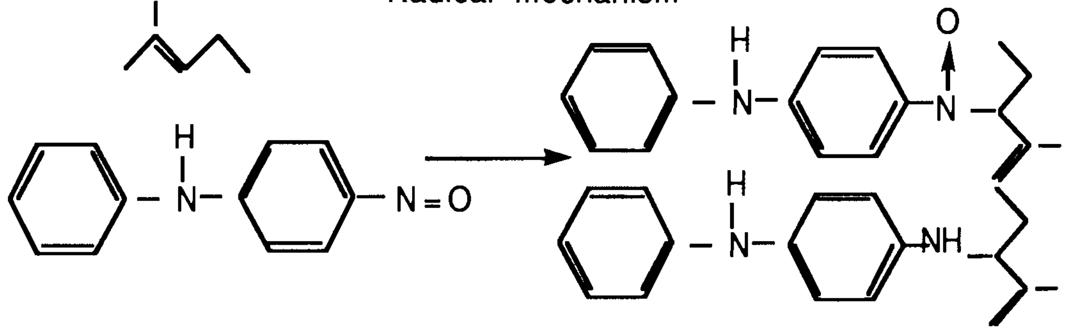
As it is evident from tables 2,3, and 4; the [>NO·] increases with increasing processing temperature to a limiting value. In the case of NDPA and PMNB up to 130°C Whereas, in the case of NDBPh the [>NO·] reached a maximum at 100°C and then disappeared at temperatures exceeding 120°C. The same explanation as (part-1 section 3.2.1) is invoked here. An increase in the [>NO·], when NDPA and PMNB processed at higher temperature, may be attributed to the formation of higher amount of macroalkyl radical under the higher thermal conditions.

Identification of nitroxyl radicals by ESR from NDPA, PMNB and NDBPh during processing with EPDM, confirms that these reactions proceed predominantly via a radical mechanism. However, an 'ene' reaction mechanism with formation of p-phenylene diamine has been reported (66) between the reaction of 4-nitroso diphenylamine with olefins. These mechanisms are schematised below;

$$P\text{-}P \xrightarrow[\text{Heat}]{\text{Shear}} 2P^{\cdot}$$

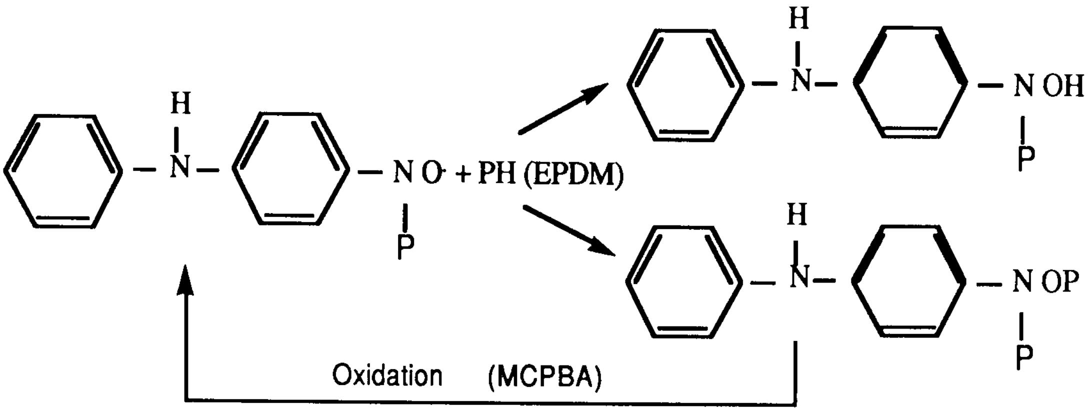


Radical mechanism



"ene" mechanism

A marked increase in the initial concentration of nitroxyl radicals after oxidation with meta-di-chloroperbenzoic acid (MCPBA), confirms the formation of considerable amount of nitroxyl precursors such as hydroxylamines and alkyl hydroxylamines,in addition to nitroxyl radical, during processing of aromatic nitroso compounds with EPDM. The formation of nitroxyl derivatives (free hydroxylamine and O-alkyl hydroxylamine) has already been reported (67). However, all attempts to identify the latter compound by FTIR failed. The formation of this nitroxyl derivatives and the regeneration of nitroxyl radical from this compounds on oxidation are shown in scheme 6.



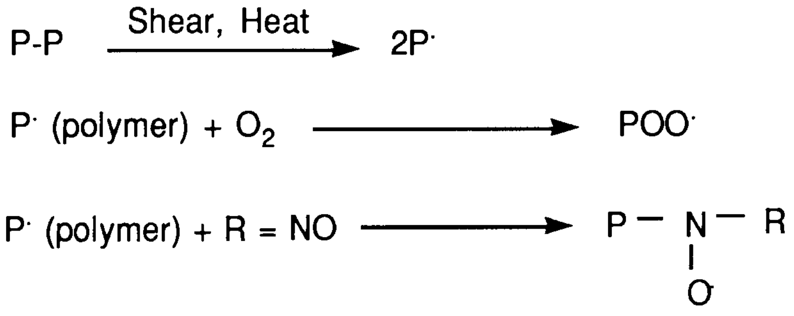
Scheme 6

The order of the maximum nitroxyl radical yield (i.e initial nitroxyl generated after oxidation with MCPBA) and EPDM-bound nitroxyl (i.e. High MW nitroxyl radical which is non-extractable) of C-aromatic nitroso compounds under identical experimental conditions (processing temperature, processing time, inert atmosphere) according to table (5) are: NDPA > PMNB > NDBPh. The results also reveal that approximately 60% of NDPA is converted to spin adducts in the absence of radical generator and of this 96% resists exhaustive solvent extraction, suggesting that not only this compound is chemically attached to the backbone of polymer but also it is in the form of high molecular weight spin adducts.

The regeneration of nitroxyl radical from free hydroxylamine by oxidation with hydroperoxides and peroxides present in the polymer has also been reported (68).

A general reduction in the amount of original nitroxyl radical was observed, when these compounds were processed in the presence of DCP, however, the regenerated nitroxyl radicals of this systems, on oxidation with MCPBA were much greater than the regenerated nitroxyl radicals in the absence of this radical generator i.e the nitroxyl yield is higher in the presence of the peroxide(table 5). This results clearly suggest that the addition of DCP to the masterbatch leads to the formation of higher amount of nitroxyl derivatives (>NOR and >NOH).

A question may be raised concerning the use of this spin traps in the form of masterbatch which is more cost effective. In respect to the following reasons, the preparation of antidegradants in the form of masterbatches would be preferred: Firstly to achieve maximum spin adducts in the rubber in an oxygen free atmosphere (internal mixer) compared with open two roll mill, which interfere with the spin trapping efficiency of these compounds due to competition reaction between spin trap and oxygen toward macroalkyl radicals according to scheme 6 :



$$\text{P-P} \xrightarrow{\text{Shear, Heat}} 2\text{P}^{\cdot}$$

$$\text{P}^{\cdot}\ (\text{polymer}) + O_2 \longrightarrow \text{POO}^{\cdot}$$

$$\text{P}^{\cdot}\ (\text{polymer}) + \text{R} = \text{NO} \longrightarrow \text{P}-\underset{\underset{\text{O}^{\cdot}}{|}}{\text{N}}-\text{R}$$

Scheme 7

The formation of a high concentration of spin adducts in the masterbatches, expected to change the physical and mechanical properties of final vulcanisate in a desirable direction as it has been reported (69), that the antifatigue activity of the most powerful antifatigue IPPD is associated at least in part with the generation of nitroxyl radical and its reductive products during fatiguing.

Secondly, due to ease of handling, dusty and hazardous nature of aromatic nitroso compounds, particularly NDPA, the use of these compounds in the form of masterbatch is also preferred.

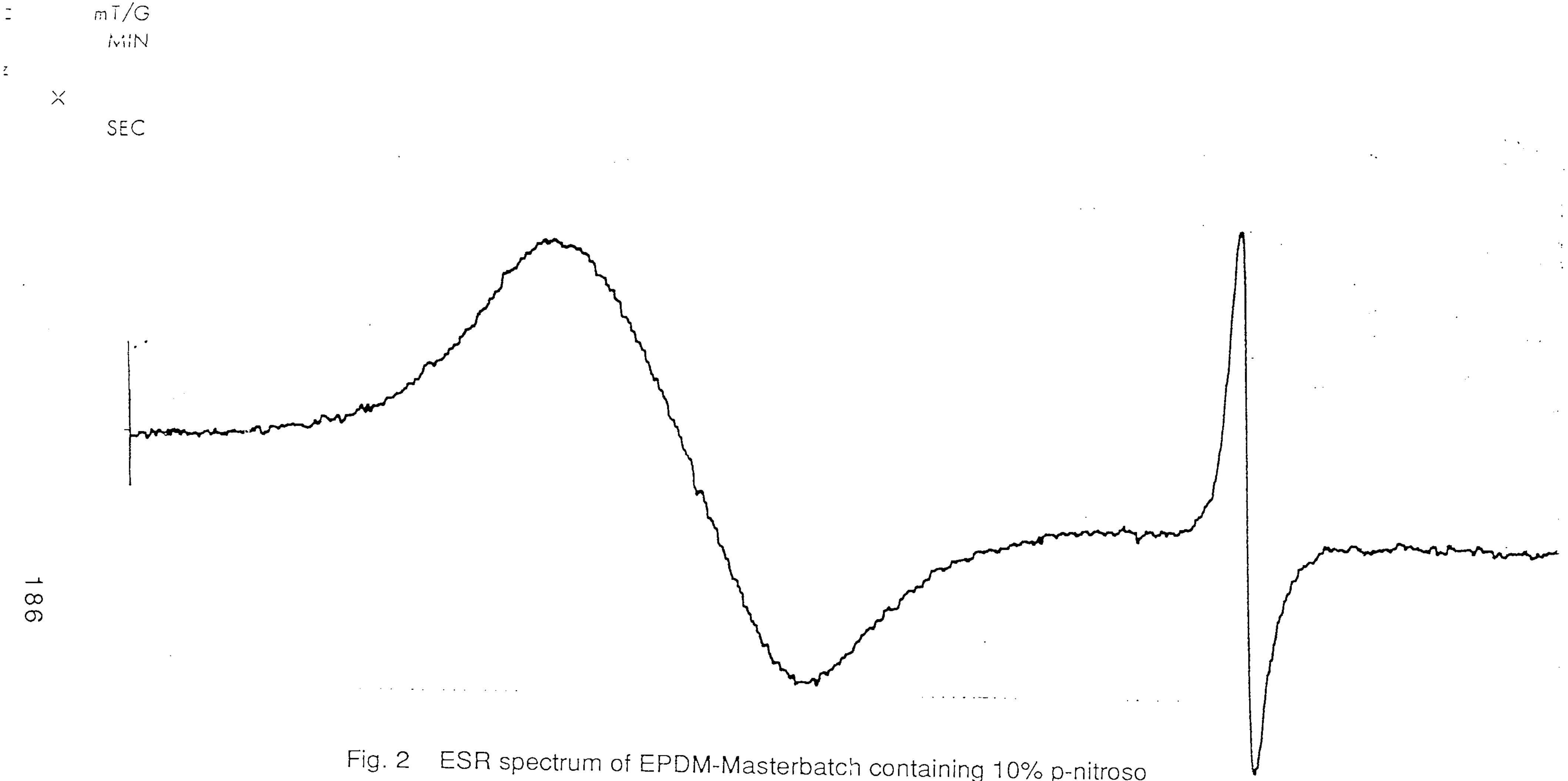


Fig. 2 ESR spectrum of EPDM-Masterbatch containing 10% p-nitroso diphenylamine (NDPA) processed at 130°C.
a) Nitroxyl radical of corresponding nitroso compound before extraction
b) The reference $5H_2O$, $CUSO_4$

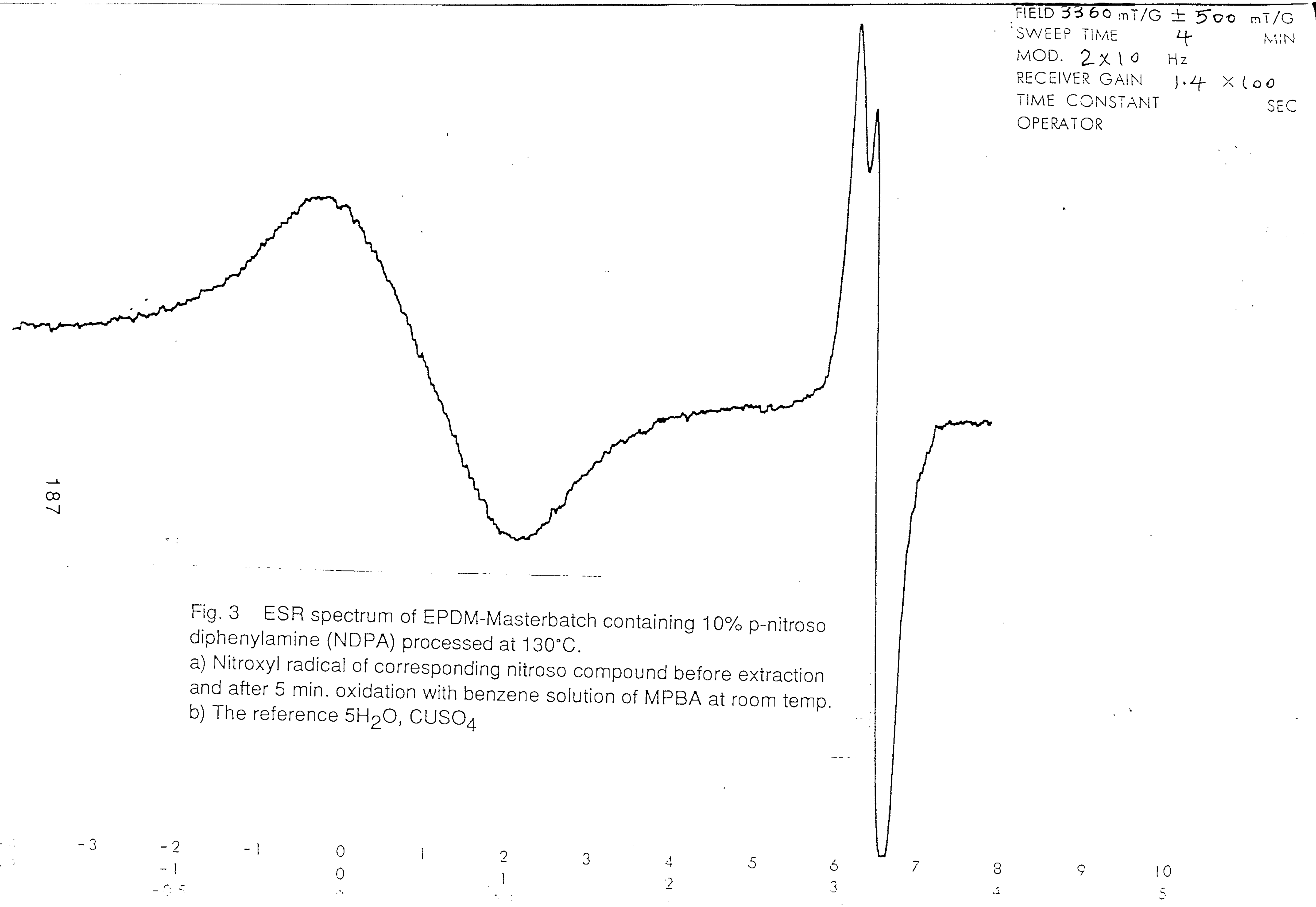


Fig. 3 ESR spectrum of EPDM-Masterbatch containing 10% p-nitroso diphenylamine (NDPA) processed at 130°C.
a) Nitroxyl radical of corresponding nitroso compound before extraction and after 5 min. oxidation with benzene solution of MPBA at room temp.
b) The reference $5H_2O$, $CUSO_4$

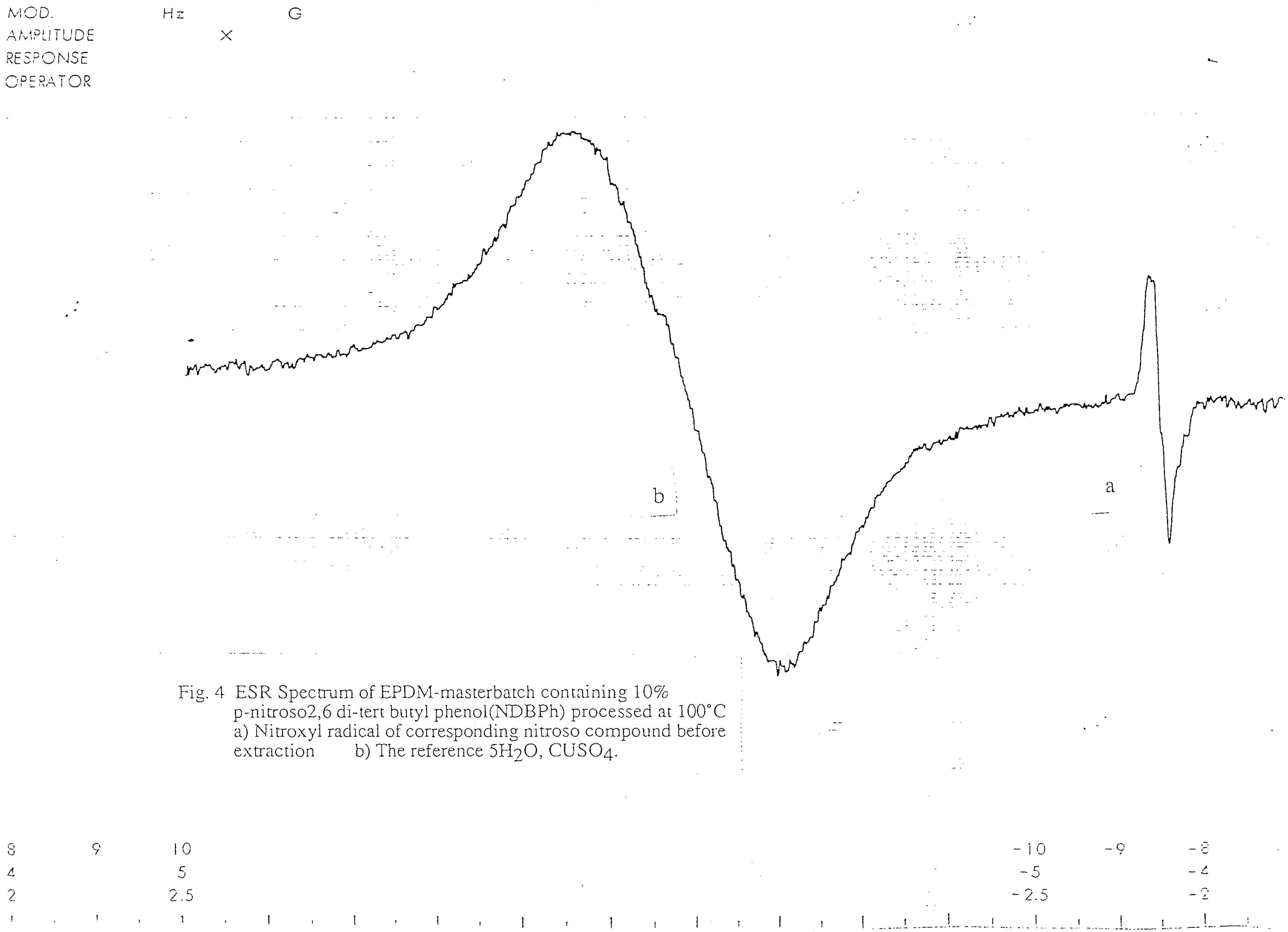


Fig. 4 ESR Spectrum of EPDM-masterbatch containing 10% p-nitroso2,6 di-tert butyl phenol(NDBPh) processed at 100°C a) Nitroxyl radical of corresponding nitroso compound before extraction b) The reference $5H_2O$, $CUSO_4$.

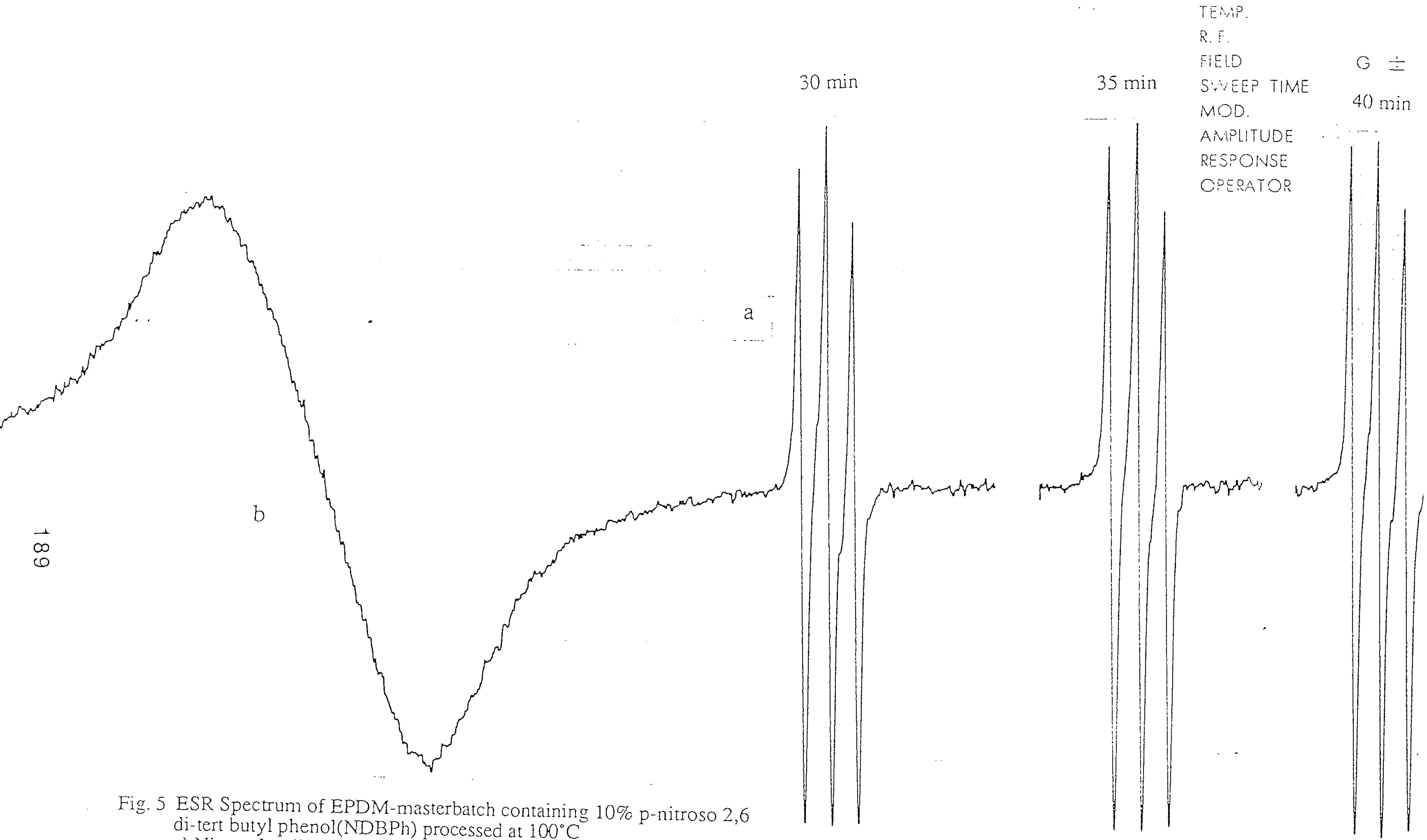


Fig. 5 ESR Spectrum of EPDM-masterbatch containing 10% p-nitroso 2,6 di-tert butyl phenol(NDBPh) processed at 100°C
a) Nitroxyl radical of corresponding nitroso compound before extraction and after 40 min. oxidation with MCPBA at room temperature b) The reference $5H_2O$, $CUSO_4$.

Table 1 Chemical names,structures and code names of antidegradant

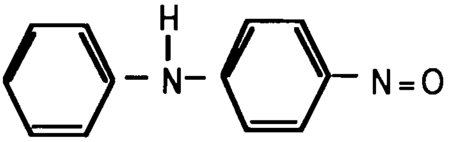
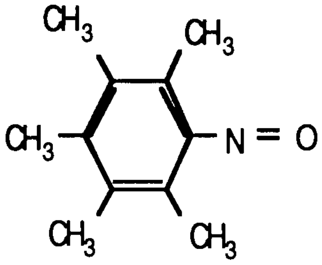
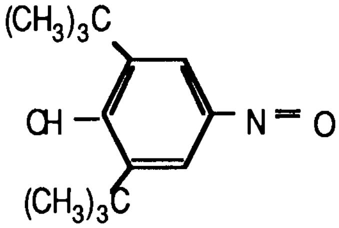
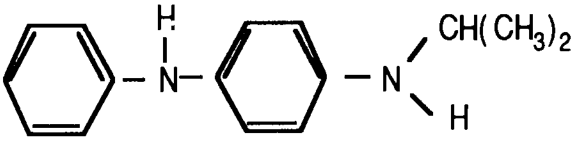
Chemical name	Chemical structure	Code name
p-Nitroso diphenylamine		NDPA
Pentamethyl nitrosobenzene		PMNB
4-Nitroso-2,6-di-tertbutylphenol		NDBPh
N-Phenyl-N'-isopropyl-p-Phenylene diamine		IPPD

Table-2 The effect of processing temperatures, extraction and oxidation on [>NO·] of masterbatch, EPDM was processed with 10% (0.05 mole) NDPA in a closed mixer for 10 min in an oxygen free atmosphere.Extraction: Methanol. oxidation: meta-di chloroperbenzoic acid in ESR cavity.

	10^{-3} [>NO·] mol/100g EPDM			
Processing temp.(C°)	Before extraction	Before extraction after oxidation	After extraction	After extraction after oxidation
80	4.5	13.5	3.95	12.0
90	5.4	16.2	4.68	14.0
100	6.4	19.2	5.7	17.0
110	7.35	22.1	6.57	19.71
120	8.5	25.65	7.85	23.5
130	9.0	30	8.6	28.5
140	8.2	24.3	7.2	21.6

Table-3 The effect of processing temperature, extraction and oxidation on [>NO·] masterbatch. EPDM was processed with 10% (0.056 mole) PMNB in a closed mixer for 10 min in an oxygen free atmosphere(Argon). Extraction: methanol. oxidation: meta choloroperbenzoic acid in ESR cavity.

	10^{-3} [>NO·] mol/100g EPDM			
Processing temperature(C°)	Before extraction	Before extraction after oxidation	After extraction	After extraction after oxidation
80	5.25	16.15	3.25	13.0
100	6.5	18.2	3.9	16.1
120	8.1	27.5	5.09	21.2
140	8.0	27.1	4.99	20

Table-4 The effect of processing temperature, extraction and oxidation on [>NO·] masterbatch. EPDM was processed with 10% (0.056 mole) NDBPh in a closed mixer for 10 min in an oxygen free atmosphere. Extraction: methanol oxidation: meta chloroperbenzoic acid in ESR cavity.

	10^{-3} [>NO·] mol/100g EPDM			
Processing temperature(C°)	Before extraction	Before extraction after oxidation	After extraction	After extraction after oxidation
80	-	8.9	-	8.1
100	2.9	11	0.9	8.1
120	0.3	3.5	-	1.0
140	0.1	2.8	-	0.7

Table-5 The comparison of maximum percentage of conversion (nitroxyl radical yield) and EDPM-bond, bound nitroxyl produced from different aromatic nitroso compounds in the presence and in the absence of radical generator in the masterbatches during processing.

Spin trap	$\frac{[DCP]}{[Spin trap]}$ mol	Processing temperature (C°)	Total nitroxyl yield (10^{-3} mol/100g) after oxidation	Bound-nitroxy %
NDPA	0.0	130	60	96
NDPA	0.07	130	72	97
NDPA	0.14	130	75	97
PMNB	0.0	120	49.1	62.8
PMNB	0.07	120	55	64
PMNB	014	120	58	65
NDBPh	0.0	100	20	31
NDBPh	0.07	100	25	31
NDBPh	0.14	100	26	31

3.2 THE EFFECT OF SPIN TRAPS ON THE CURE PARAMETERS OF NATURAL RUBBER CONVENTIONAL CBS SYSTEM

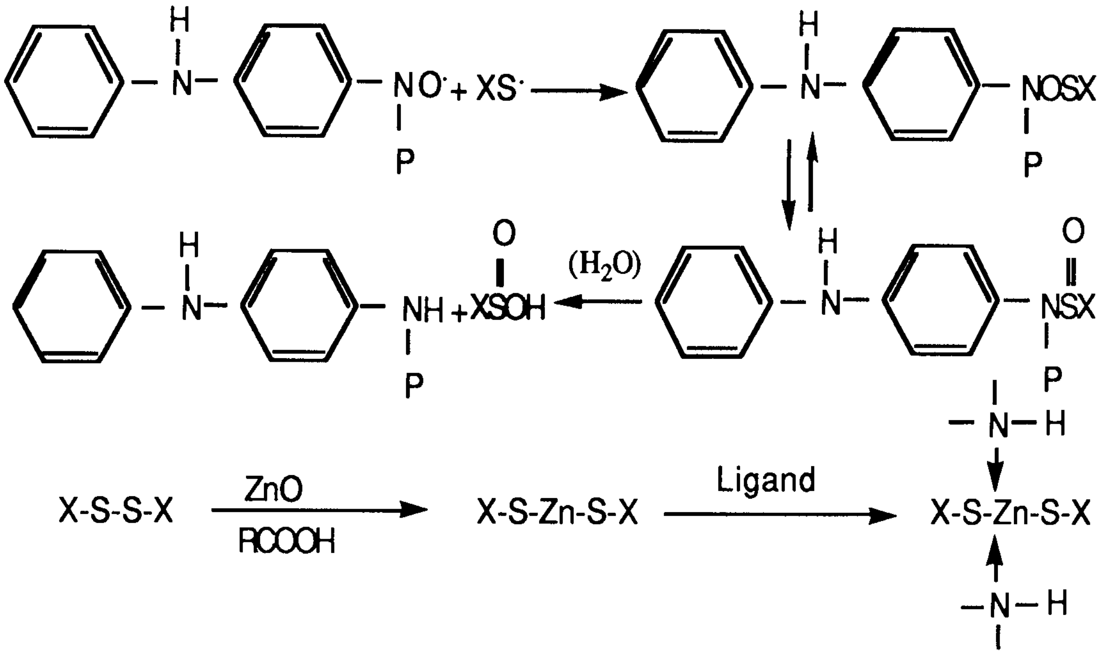
3.2.1 Object and Plan

The extensive chemical modification of the main polymer chains greatly affects the physical properties of the rubber by inhibiting strain induced and low temperature crystallisation and by decreasing resilience. Since the fatigue life of rubber is strongly dependent on the cross-link density (70), in the present work it was necessary to evaluate the antifatigue agents at similar level of cure, (i.e. similar sulphur cross-link density). In addition, it is important to investigate the effect of nitroso modifictions on the vulcanisation characteristics of natural rubbers, since certain disadvantages during mixing of natural rubber with nitroso compounds on the open mill, particularly a severe reduction in processing safety (scorch time) and undue peptization during mixing at high temperature has been reported (71).

3.2.2 Results and Discussion

The vulcanisation behaviour of samples containing 1 phr aromatic nitroso compounds used as normal additive under different compounding temperatures (water cool and steam open two roll mill) or added in the form of EPDM-masterbatch, was investigated by using the Monsanto oscillating disc rheometer. This results were compared to samples containing no additive and to that containing the commercial santoflex IP (IPPD).

Formulated rubbers were prepared according to the procedures in section 2.2.1, cured at 140°C and vulcanisation characteristics were directly read from Monsanto equipped to a programmed computer. The results in table-6 indicate that the C-aromatic nitroso compounds affect the curing parameters to varying extent. The scorch time reduced drastically whereas the rate of cure increased. This effect was particularly severe, in the case of NDPA. Approximately, 50% reduction in scorch time and up to 20% increase in cure rate was observed when this antidegradant used as normal additive or added in the form of masterbatch compared to a control containing no additive. The addition of Trigonox 101 to this system particularly at high compounding temperature i.e steam milling, reduced the scorch time and increased the rate of cure yet to higher degree,(Table 7).A marked decrease in scorch time and increase in first order rate of cure, in the case of NDPA-modified NR vulcnisate, is understood in view of the acceptable fact that amine type antioxidant are known to accelerate the rate of cure because of their ability to donate electrons to the complex A (scheme 8). Therefore, the formation of free amine from nitroxyl radical during vulcanisation enhances nucleophilicity of XS^- and hence increases sulfuration rate.



X is either part of the rubber vulcanisate or is derived from an accelerator residue.

Scheme 8 (A)

It has been shown (72) that when a diaryl nitroxyl radical is incorporated into rubber by normal compounding, it is partially converted back to the free amine during vulcanisation. The cure characteristics of different aromatic nitroso compounds when used as normal additives, are compared with control in Table 7. The order of rate of cure is as follow:

Control = NDBph < NPMB < NDPA, which is reversely proportional to the order of nitroxyl radical, [NDBph] < [PMNB] < [NDPA], (See Table 5), suggesting that the original concentration of nitroxyl radical formed during processing and the formation of subsequent corresponding amines are the main factor in enhancing rate of cure.The present experimental data (chapter 3-1) indicate that the amount of nitroxyl radical increase as a function of processing temperature, when NDPA was processed with EPDM at higher temperatures. Hence in order to achieve the optimum [>NO·], that is maximum nitroxyl yield during spin trapping stage,compounding of NR was carried out in steam two roll mill (130°C). The effect of compounding temperature and Trigonox 101 on curing properties of NR vulcanisate was compared in table 7.

The results in table-7 indicate that the scorch time decreases to a higher level at higher compounding temperature, particulary in the presence of Trigonox 101 .whereas the cross-link density and rate of cure increase up to 13 % and 8% respectively.This behaviour is undoubtedly associated with formation of higher amount nitroxyl radical in NR during compounding at higher temperature and in the presence of radical generator.

The effect of 10% EPDM on the curing characteristics of NR vulcanisate containing 1.0 % NDPA was examined. The results are compard to that of a control containing no additive and to that of a standard containing the commercial IPPD in table 8. These results indicate that the addition of 10% EPDM to NR conventional CBS vulcanisates during compounding does not significantly affect curing parameters. However, the maximum torques were reduced to some extent, which could be associated with plasticising character of EPDM (less shear stress is required).

In the NR vulcanisates modified by EPDM-bound nitroxyl (masterbatch), a similar results was observed. That is, the scorch time reduced and both cross-link density and cure rate increased . As it is clear from the comparison of tables 6,8 and 9 the reduction in scorch time and an increase in maximum torque of vulcanisates in the case of modification by masterbatches is higher than the other systems due to formation of higher spin adducts. Thus it could be concluded that there is a linear relationship between [>NO·] and the curing properties.

Plasticity number (P°) of gum stocks which is a measure of molecular weight of natural rubber and was measured by Wallace Rapid Plastimeter are given in corresponding tables. Plasticity number of gum rubbers containing 10% EPDM reduced to some extent. It appeared that EPDM functions as a plasticizer for NR during compounding. But, the gum rubber modified with NDPA-masterbtch exhibits the maximum plasticity number, which may be associated with the poor dispersion of the highly cross-linked EPDM-bound nitroxyl precursor into natural rubber during compounding.

Table-6 Curing characteristics of NR vulcanisates containing 1Phr aromatic nitroso compounds used as normal additive at 140°C. Compounding was carried out at 70°C.

Compound	$\frac{[\mathrm{DCP}]}{[\mathrm{Spin\ trap}]}$ mole	Scorch time (min)	Time to optimum cure (min)	Maximum torque (inch.lbs)	Firstorder crosslinking rate constant min-1	Plasticity number
Control		13.23	31.0	56.2	0.10	6.0
NDPA	0.00	7.01	22.0	55.0	0.12	5.5
NDPA	0.075	7.07	22.0	55.8	0.12	6.0
NDPA	0.15	7.16	22.0	55.8	0.12	6.0
PMNB	0.00	11.09	28.0	52.5	0.11	5.5
PMNB	0.075	10.95	27.5	52.9	0.11	5.5
PMNB	0.015	10.9	27.1	53	0.12	6.0
NDBPh	0.00	9.01	29.5	56.0	0.10	6.0
NDBPh	0.075	9.0	29.2	56.0	0.10	6.0
NDBPh	0.15	9.0	29.0	56.2	0.10	6.0
IPPD		13.2	30.5	54.8	0.11	5.0

Table 7 The effect of compounding temperature and concentration of Trigonox 101 on the curing parameters of NR vulcanisates containing 1phr NDPA at 140° C.

[Trigonox101] / [NDPA] mol	Compounding temperature (°C)	Scorch time (min)	Time to optimum cure (min)	Maximum torque (inch.lbs)	First order cross-linking rate constant min-1	Plasticity number
0.0	70	7.01	22.0	55.0	0.12	5.5
0.0	130	6.34	22.0	59.4	0.12	6.0
0.07	130	5.58	20.45	59.3	0.12	6.0
0.14	130	6.24	21.40	62.0	0.13	6.5
0.21	130	6.13	21.30	61.7	0.13	7.0

Table 8. The effect of 10% EPDM on the curing parameters of NR vulcanisates containing 1phr antidegradants at 140° C.

Compound	Scorch time (min)	Time to optimum cure (min)	Maximum torque (inch.lbs)	First order cross-linking rate constant min-1	Plasticity number
Control	13.23	31.0	56.2	0.10	6.5
Control+EPDM	13.57	29.5	53.6	0.09	5.5
NDPA	7.01	22.0	55.0	0.12	5.5
NDPA+EPDM	7.15	22.0	54.5	0.12	5.0
IPPD	13.21	30.5	54.8	0.11	5.5
IPPD+EPDM	12.41	30.0	53.4	0.11	5.0

Table 9. Curing characteristics of NR vulcanisates containing 1Phr aromatic nitroso compounds as masterbatch. Masterbatch preparation in a closed mixer. Compounding on water cool mill(70°C). Cured at140°C

Compound	[DCP] ——mole [Spin trap]	Scorch time (min)	Time to optimum cure (min)	Maximum torque (inch.lbs)	First order cross-linking rate constant min-1	Plastic number
Control		13.23	31.0	56.2	0.10	6.0
NDPA	0.00	6.49	25.0	59.3	0.12	8.0
NDPA	0.07	6.25	25.0	59.3	0.12	8.0
NDPA	0.14	6.23	24.5	60.2	0.12	8.0
PMNB	0.00	9.8	27.0	56.5	0.12	6.5
PMNB	0.07	9.6	26.0	56.6	0.12	6.5
PMNB	0.14	9.5	25.5	56.8	0.12	6.7
NDBPh	0.00	8.4	29.0	55.7	0.11	6.5
NDBPh	0.07	8.0	28.5	55.7	0.11	6.5
NDBPh	0.14	8.0	28.0	55.8	0.11	6.5
IPPD		13.2	30.5	54.8	0.11	5.5

3.3 ANTIOXIDANT ACTIVITY BY OXIDATIVE STRESS-RELAXATION STUDIES

3.3.1 Object and Plan

The oxidative degradation of rubber articles is normaly retarded during compounding, by using antioxidants or antiozanants.

The chemicals are most usually phenols or aromatic amines, dithiocarbamates, dithiophosphates. It is an essential feature of their use that they should not undergo chemical reaction during the manufacturing and vulcanisation process, and this may be demonstrated by their recovery from the manufactured articles by extraction with organic solvents. In application where the article is at any time in contact with such solvents the resultant loss of the protective agents increases the rate of degradation. Therefore, reactive antioxidant (C-aromatic nitroso compounds) with spin trapping properties, which attach chemically to the polymer molecules with formation of nitroxyl radical, possessing chain-breaking acceptor (CB-A) characteristics, and can not be removed even by the most exhaustive extraction procedures may overcome this problem.

Stress-relaxation experiment involve the measurment of the force required to maintain the deformation produced initially by an applied stress as a function of time. Stress relaxation measurements, are particularly useful in the evaluation of antioxidant in polymers, especially elastomers, because they are sensitive to bond rupture in the network.
It has been shown (73) that in the temperature range of 100 to 150°C natural and synthetic vulcanisate rubbers show a fairly rapid decay to zero stress at constant extension. Since in principle, a cross-linked rubber network in the rubbery range showed little stress relaxation and certainly no decay to zero stress, the phenomenon was attributed to chemical rupture of rubber network.

In this study it is essential to ensure that the rubber samples used are thin enough to permit steady state conditions of oxygen diffusion, otherwise the rate of chemical stress-relaxation may become diffusion controlled (74, 75). In vulcanisates having a high surface area to volume ratio, such as elastic fibers and films, the stres-relaxation test has technological advantage over the technique of oxygen absorption, in which the test is more indicative of inherent activity of the antioxidant involved. In rubber articles with high surface area to volume ratio, factors such as the volatility and ease of removal of antioxidant by solvent extraction are more important than inherent antioxidant activity (76).

3.3.1 Results and Discussion

In the present work, the ageing resistance of various modified natural rubber vulcanisates was assessed by the use of continous stress-relaxation at 100°C in air, according to procedure described in section (2.6.2.2). The chemical structure & code name of these aromatic compounds are given in table 1.

The continuous stress-relaxation curves of unextracted and azeotrope extracted vulcanisate containing 1Phr C-aromatic nitroso compounds used as normal additive (in the presence or the absence of radical generator) under different compounding temperature (cool and hot open mill) or as masterbatch (only cool mill), are compared to that of control and to that of *vulcanisate containing an equal weight ratio santoflex IPPD in* figs. 6-11.

The decay of stress in continous relaxation measurements provides a measure of the degradation reaction in the network. A comparison of the thermal antioxidant activities of C-aromatic nitroso compounds both before and after azeotropic extraction is given in figs.6 and 7. The antioxidant activity of the examined compounds follow the following order:

NDPA>IPPD>PMNB>NDBPh> Control

These results indicate that although the concentration of nitroxyl-bond is a key factor in determination of antioxidant effectiveness. Nevertheless some other factors such as solubility and chemical structure of these compounds must also be considered.

The ability of C-nitroso compounds to trap alkyl and alkoxy radicals, and their tendency to form intermediates such as nitroxyl radical, free hydroxylamine, and alkyl hydroxylamine has been discussed previously in detail, and evidence for the formation of these compounds in EPDM-masterbatch has been shown before(see chapter 2). The order of nitroxyl yield in the masterbaches is: NDPA>PMNB>NDBPh. The low solubility (bloomed to the surface), formation of low concentration of nitroxyl radical, and probably the formation of quinone structure are responsible for the ineffectiveness antioxidant activity of NDBPh. Moreover, because of the presence of an electron withdrawing group (N=O) at the para position in this compound, the CB-D activity of the hindered phenol moiety will decrease.

It seems very likely that during thermal oxidation the nitroxyl derivatives are converted to nitroxyl radical. Therefore the original amount of this components formed during processing could be at least in part responsible for the antioxidant activity of nitroso compounds.

As it is apparent from figs. 10, 11, the antioxidant activity of NDPA is improved by using Trigonox 101 as a radical generator. these results also indicate that antioxidant activity of NDPA in the presence or absence of Trigonox 101, particularly after solvent extraction is much better than IPPD.

Tables (10,11) compared the T40 of the various vulcanisates to that of control and to that of standard IPPD. T40 is the time taken for the stress to decay to 40% of the original. This value is considered an adequate representation for the evaluation of the thermal antioxidant activities of additives. These results are outlined in the histograms (figs.12-17).

The effect of NDPA as normal additive, EPDM-spin adduct, and along with EPDM on the T40 of NR vulcanisate is compared with control and commercial IPPD in table 14.

Fig.6 Comparison of antioxidant activity of different antidegradants by stress-relaxation at 100°C. NR was compounded with 1Phr antidegradants on a cool open mill at 70°C.Cured at 140° C.

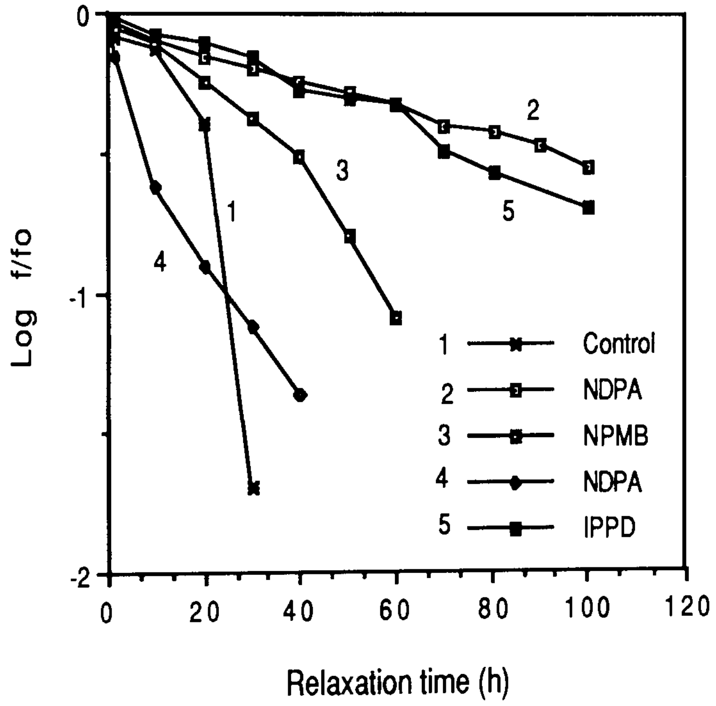


Fig.7 Comparisonof antioxidant activity of different antidegradants by stress-relaxation at 100°C after azeotrope extraction . NR was compounded with 1Phr antidegradants on a cool open mill at 70°C.Cured at 140° C.

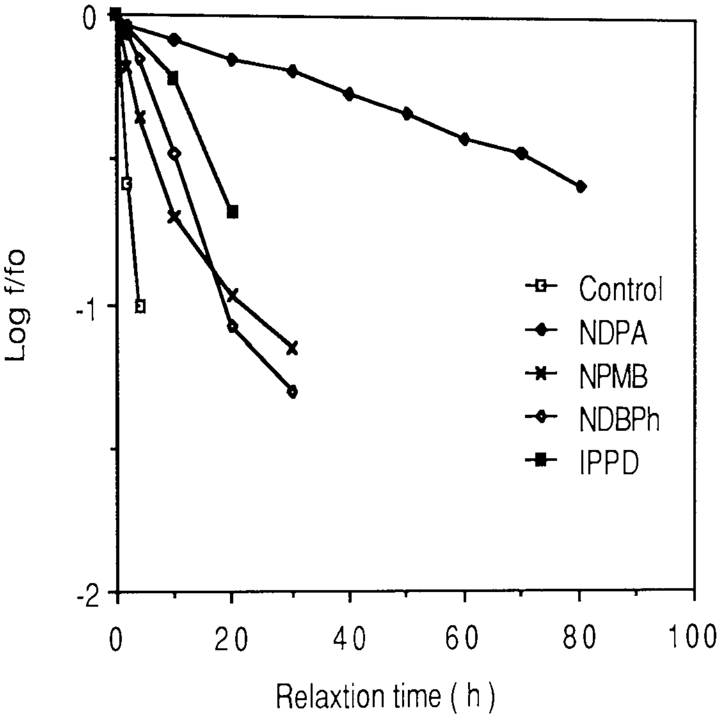


Fig.8 Oxidative stress-relaxation of NR vulcanisate containing 1% nitroso compounds in the form of EPDM-bound nitroxyl before azeotrope extraction at 100°C. Compounding at 70°C. Cured at 140° C.

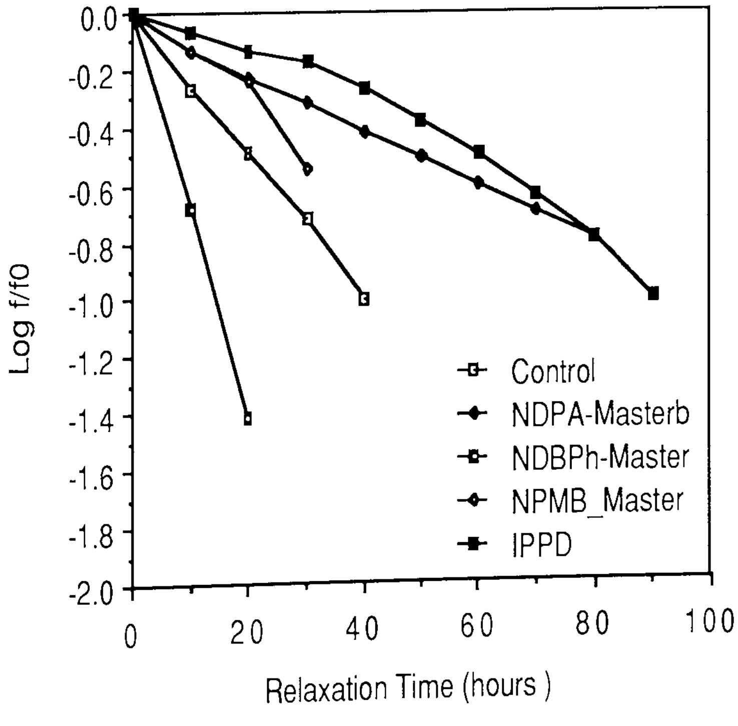


Fig.9 Oxidative stress-relaxation of NR vulcanisate containing 1% nitroso compound in the form of EPDM-bound nitroxyl after azeotropic extraction at 100°C.

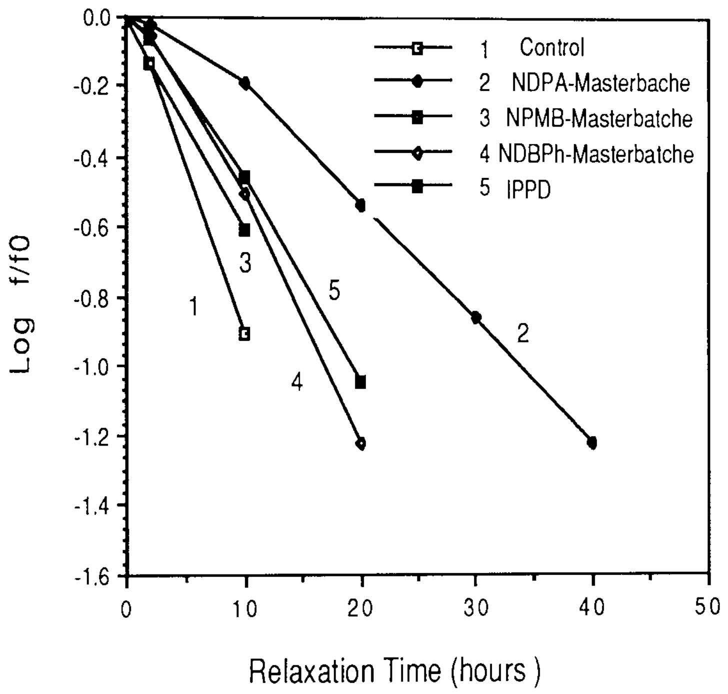


Fig.10 The effect of Trigonox 101 on the antioxidant activity of NDPA used as normal additive by stress-relaxation studies at 100°C before extraction. NR was compounded on an open mill at 130°C.

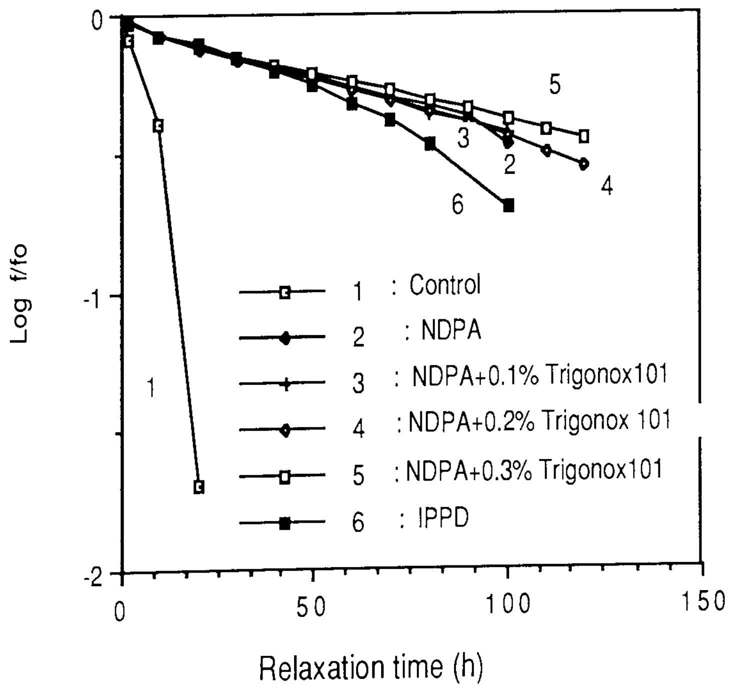


Fig.9 Oxidative stress-relaxation of NR vulcanisate containing 1% nitroso compound in the form of EPDM-bound nitroxyl after azeotropic extraction at 100°C.

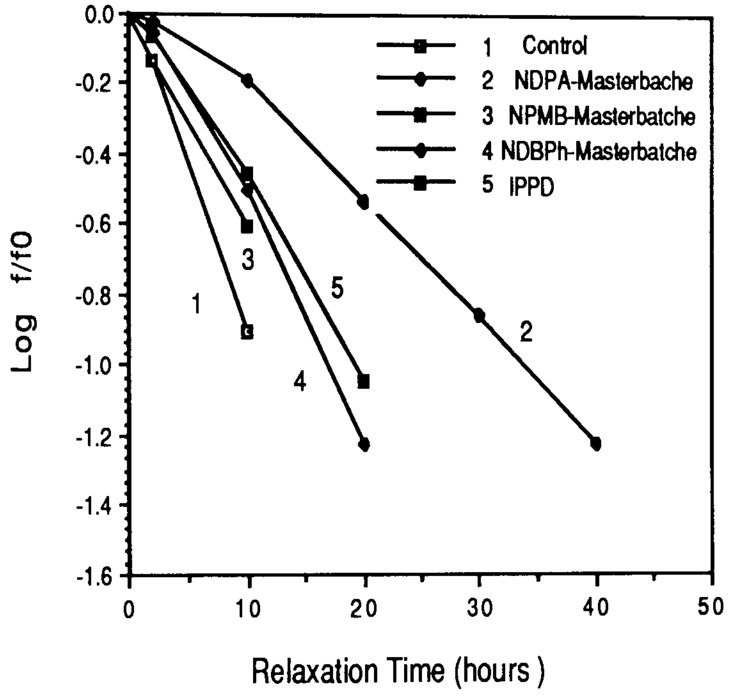


Fig.10 The effect of Trigonox 101 on the antioxidant activity of NDPA used as normal additive by stress-relaxation studies at 100°C before extraction. NR was compounded on an open mill at 130°C.

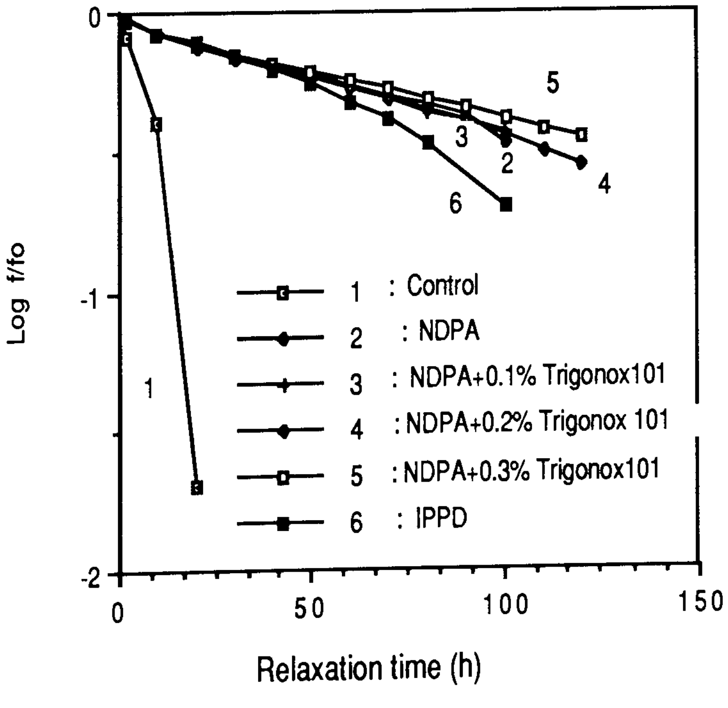


Fig.11 The effect of Trigonox 101 on the antioxidant activity of NDPA by stress-relaxation at 100° C after extraction .NR was compounded on a hot open mill at 130°C. Cured at 140°C.

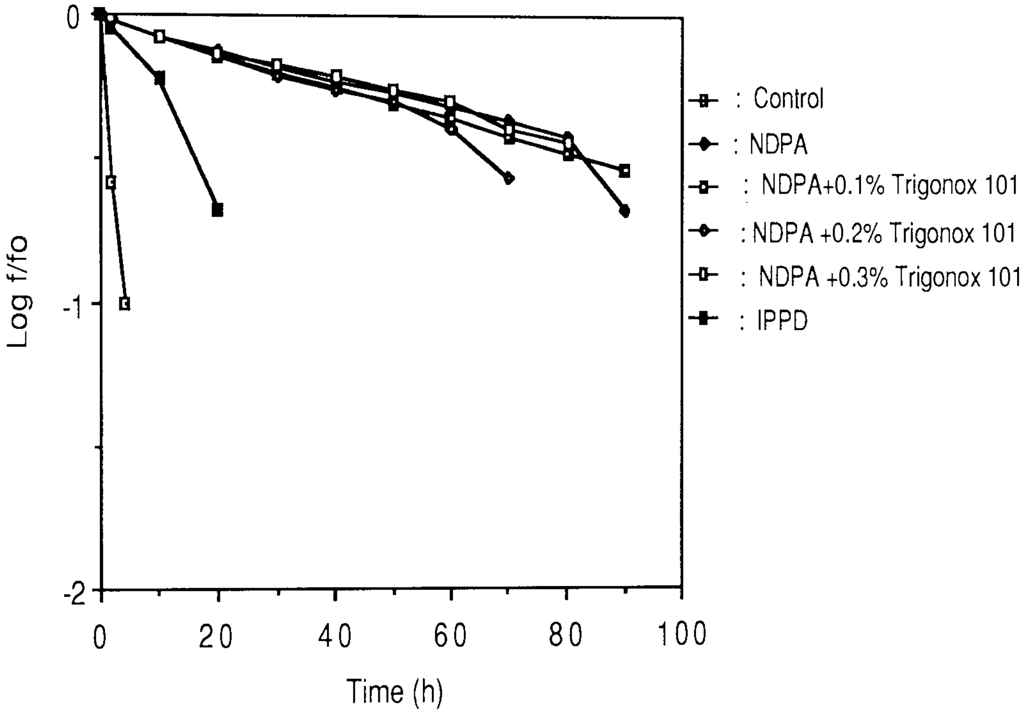


Fig12 The effect of azeotropic extraction on the T40 of NR vulcanisates modified by 1 Phr nitroso compounds

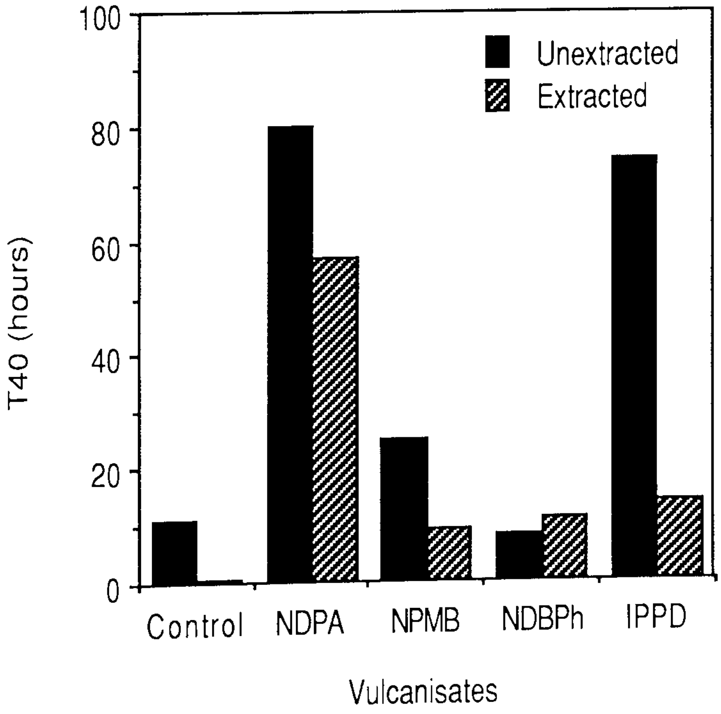


Fig.13 The effect of radical generator on the T40 of unextracted and extracted NR vulcanisate containing 1% NDPA at100°C. compounded at 70°C. Cured at 140°C.

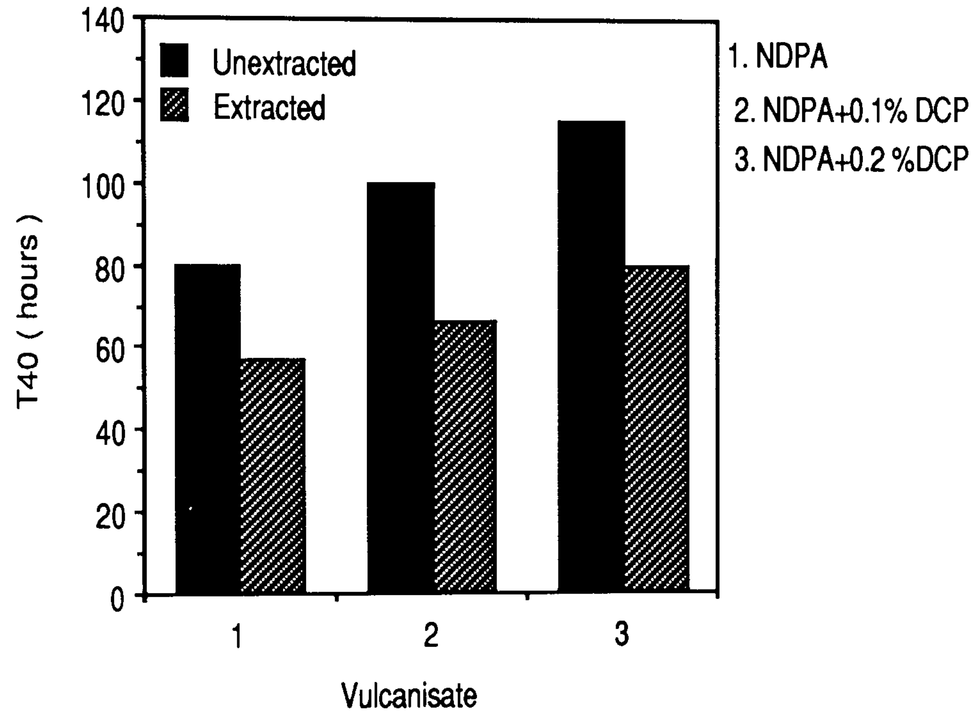


Fig.14 The effect of azeotrope extraction on the T40 of NR vulcanisates modified by 1 Phr of antidegradants in the form of EPDM-masterbatch.

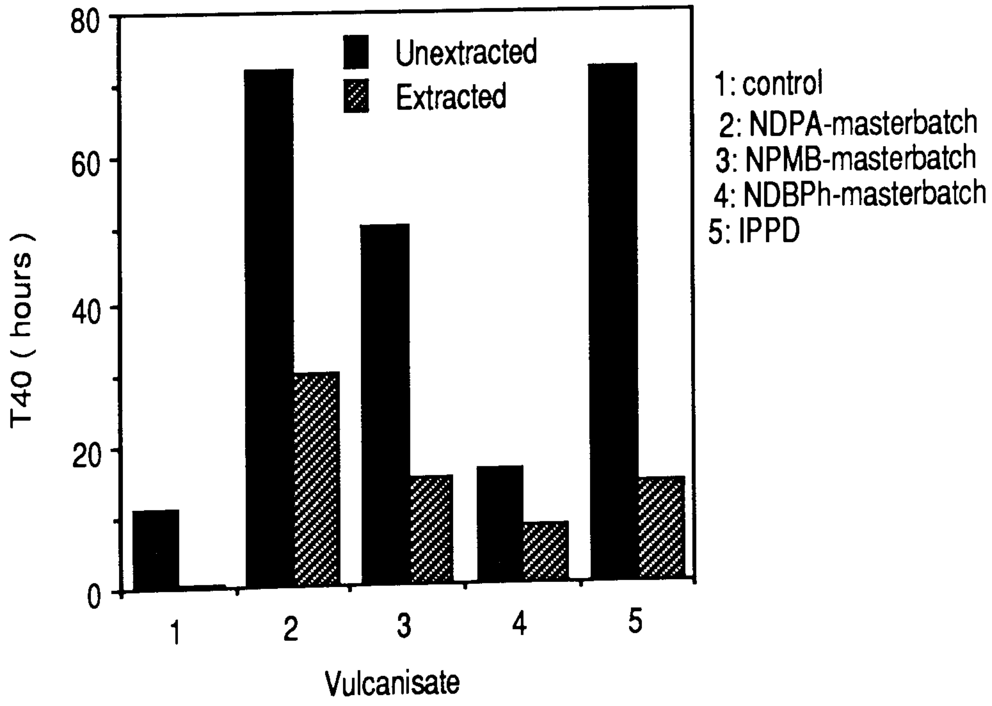


Fig.15 The effect of EPDM-masterbatch containing 1% NDPA and different concentration of DCP on the T40 of NR vulcanisate at 100°C. Compounding 70°C. Curing 140°C.

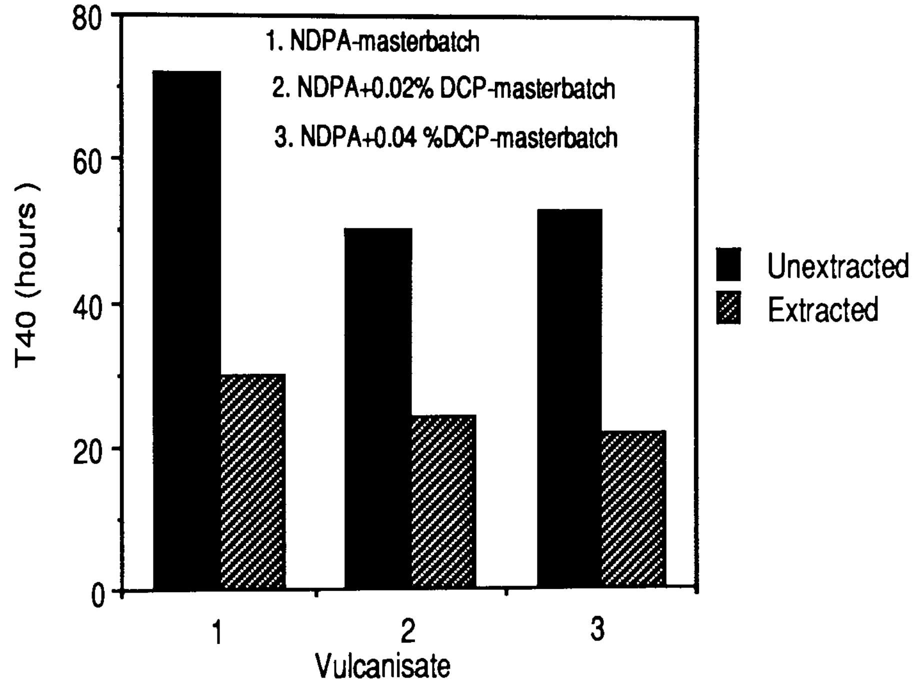


Fig.16 The effect of solvent extraction on the antioxidant activity of NDPA by stress-relaxation at 100°C (NR was compounded with 1Phr antidegradants on a hot open mill at 130°C, cured at 140°C)

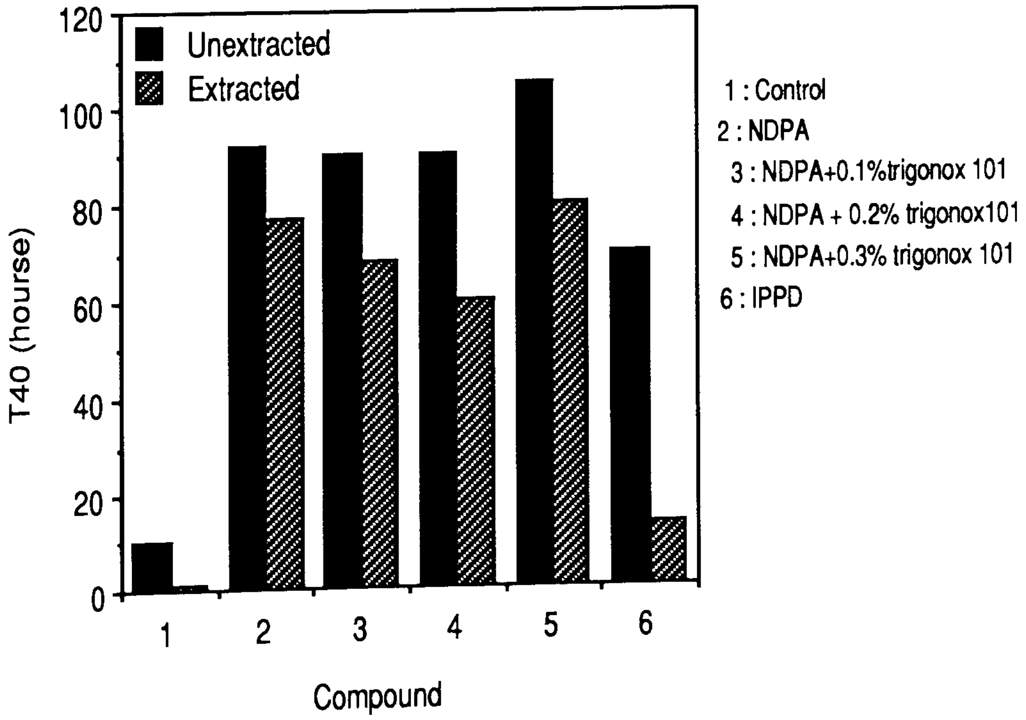


Fig.17 The effect of 10% EPDM on T40 of unextracted and azeotropic extracted NR vulcanisate containing 1phr antidegradant at 100°C. Compounded at 70°C. Cured at 140°C.

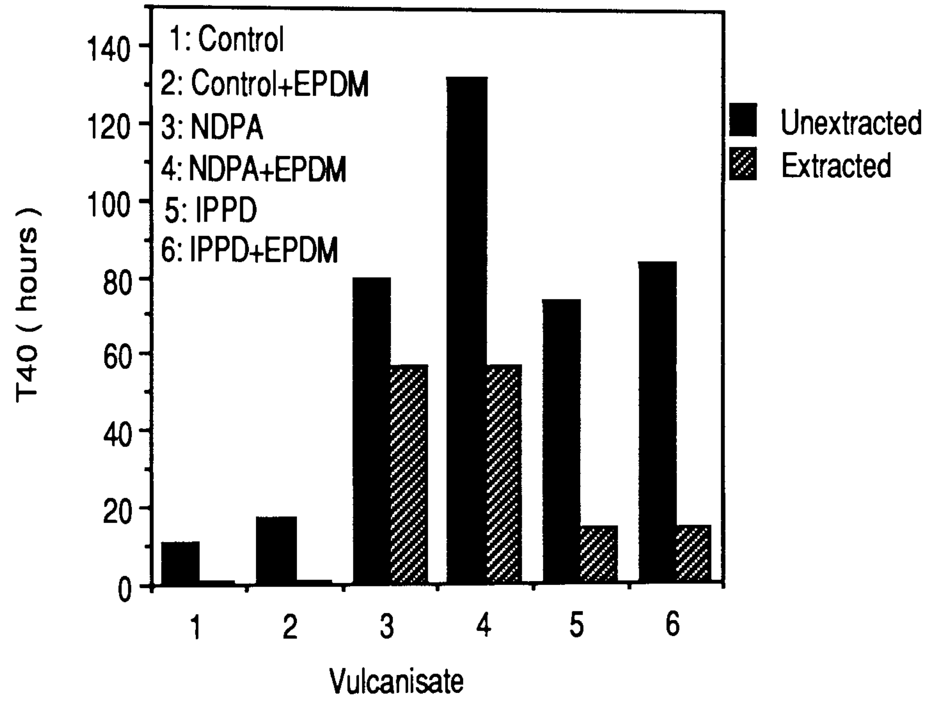


Table10 Time to 40 stress decay during the continuous stress-relaxation of NR conventional CBS vulcanisates containing 1Phr aromatic nitroso compounds as EPDM-bound nitroxyl.Compounded at 70°C. Cured at 140°C.

Vulcanisate containing	Processing temperature (C°)*	Time to 40 % stress decay (T40) at 60 % extention (hours) Unextracted	Extracted
Control	-	11	0.5
NDPA-Master	130	72	16
NPMB-Master	120	50	6
NDBph-Master	100	15	8.2
IPPD	-	74	14

* maximun nitroxyl radical formed during processing in a closed mixer in Argon.

Table11 Time to 40 stress decay during the continuous stress-relaxation of NR conventional CBS vulcanisates containing 1Phr aromatic nitroso compounds used as normal additive.Compounded at 70°C. Cured at 140°C.

Vulcanisate	Time to 40 % stress decay (T40) at 60% extension (hours)	
	Unextracted	Azeotropic extracted
Control	11	0.5
NDPA	80	57
NPMB	16	4.25
NDBPh	6	8.1
IPPD	74	14

Table12 Comparison of time to 40% stress decay using the continous stress-relaxation of modified NR conventional CBS vulcanisates containing 1Phr NDPA, control, and commercial IPPD at 100°C. Compounded at 70°C. Cured at 140°C. EPDM (10%).

Vulcanisate containing	Time to 40% stress decay at 60% extension(hours)	
	Unextracted	Azeotropic extracted
Control	11	0.5
Control+EPDM	17	0.5
NDPA	80	57
NDPA+EPDM	132	56
NDPA-spin adducts	72	30
IPPD	74	14
IPPD+EPDM	84	14

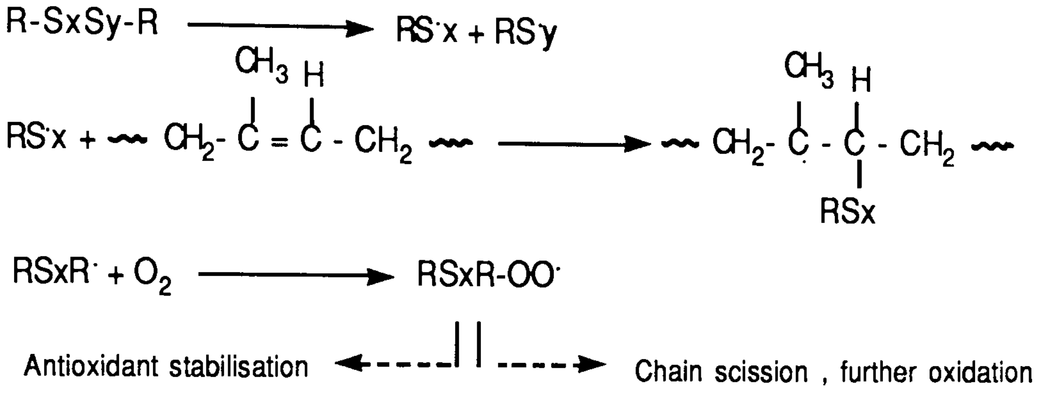
3.4 FATIGUE RESISTANCE OF VULCANISATES

The formation of mechano-alkyl radical in bulk polymers with sulphur linkage has been studied and a typical asymmetrical spectrum was reported (77), the rate of alkyl radical formation would be high, when vulcanised rubber is subjected to dynamic mechanical stresses (fatigue), as a result the concentration of O_2 in the rubber is depleted. A direct consequence of this is that both alkyl and alkylperoxyl radicals will be involved in the termination process under fatiguing conditions.

CBS accelerated vulcanisates provide superior fatigue resistance compared with other curing systems. This is attributed to the slippage or exchange of polysulphide linkage under stress (78), which results in a decrease in stress concentration at individual sites in the vulcanisates. Structurisation of cross-links, takes place during the fatiguing process. It has been reported(78) that there is an increase in the concentration of monosulphide and disulphide linkage but a decrease in the total polysulphide sulphur, Sx, with no change in cross-link density.

During the fatiguing process, the polysulphide linkage not only undergoes exchange, but it also homolytically cleaves and polythiyl radicals thus formed add to the polymer double bound. In the absence of oxygen the effect is an increase in the cross-link concentration, but in the presence of oxygen the polymer radicals thus formed add oxygen causing main chain scission, similar to thermal oxidation.

Schematically, the suggested mechanism may be expressed as:(79)



$$R\text{-}S_xS_y\text{-}R \longrightarrow RS^{\cdot}x + RS^{\cdot}y$$

$$RS^{\cdot}x + \sim CH_2\text{-}\overset{CH_3}{\overset{|}{C}} = \overset{H}{\overset{|}{C}}\text{-}CH_2 \sim \longrightarrow \sim CH_2\text{-}\overset{CH_3}{\overset{|}{C}}\text{-}\underset{\underset{RSx}{|}}{\overset{H}{\overset{|}{C}}}\text{-}CH_2 \sim$$

$$RSxR^{\cdot} + O_2 \longrightarrow RSxR\text{-}OO^{\cdot}$$

$$\text{Antioxidant stabilisation} \dashleftarrow \, || \, \dashrightarrow \text{Chain scission , further oxidation}$$

Macroalkyl and macrothiyl radicals formed by scission of the hydrocarbon chain or the cross-links respectively during fatiguing act as initiators for oxidation. if this species are the only oxidative initiators, then spin adducts formed from aromatic nitroso compounds, possessing chain-breaking acceptor characteristics could interfere with proceeding of oxidative process.

It has been thought(80) that the activity of antifatigue agents may be related to their ability to bloom to the rubber surface as there is evidence of increased diffusion during flexing. Improvements in fatigue life are obtained through the addition of antioxidants which appear to reduce mechano-oxidative growth (49). However, depletion of antioxidant either by leaching or thermal oxidation is known to reduce the fatigue life of vulcanisates(49-51). The antifatigue activity of IPPD is believed to be related to scavenging macroalkyl as well as macroperoxy radicals, according to the scheme (4). However the main disadvantage of this compound is that it is not resistant to aggressive environment(48) (e.g. water, organic solvents, etc.) .

In order to investigate the effect of diffusion and the problem of leaching, a numbers of spin traps, with spin trapping potentials which attach to polymer chains with formation of nitroxyl radical were examined

3.4.2 Results

In the present work, an attempt is made to bind the reactive antioxidants into NR conventional CBS vulcanisate, and to study the effectiveness of these polymer-bound antioxidant in fatigue resistance and radical scavenging potentials (R·,ROO·). For this purpose the aromatic nitroso compounds with the ratio of 1 Phr are introduced into NR by three different methods during compounding:

I) As normal additives,II) As normal additive along with EPDM

III) EPDM-masterbatch.

The antifatigue activity of these compounds was compared to that of a control without additive, and to that of the *commercially used antifatigue agent* IPPD. The fatigue resistance of vulcanisates was assessed as described in section (2.6.2.1).

The fatigue resistance of unextracted and azeotropic extracted modified NR vulcanisates containing 1Phr nitroso compounds and their corresponding spin-adducts are compared with vulcanisate having the equal weight ratio IPPD is given in tables (13-15) and the histograms are shown in figs. (25-29).

The nitroso compounds, particularly NDPA, will be of special interest in application where volatilisation at high temperatures or leaching by liquid in direct contact with rubber cause commercial antioxidant to be lost, and where additives with low vapour pressure (80), low solubility in the extracting medium, and low diffusion coefficient are required. Considerable evidence is available that losses of antidegradant do occur. Amine and phenolic antidegradants in polyethylene sheet are rapidly lost in water(82,83), which also dissolves p-phenylene diamines, particularly IPPD, from the surface of rubber articles(84), losses increase as PH falls due to increased solubility(85),and the formation of soluble acid salts(86). Several methods are available to reduce the effect of antioxidant depletion. The use of p-phenylene diamine of increased molecular weight has been proposed (86,87), and other methods of producing rubber-bound antioxidants studied (57). The modification of NR by NDPA described here should therefore provides another means of improving aging resistance in service, since the spin adduct and its precursors formed from NDPA are resistance to solvent extraction. The rubber-bound nitroxyl also improves considerably the fatigue life of NR vulcanisate after azeotropic extraction.Depletion of antioxidant either by leaching or thermal oxidation known to reduce the fatigue life of vulcanisates (49-51). However, NDPA can not compete with commercial IPPD before extraction, suggesting that movement (diffusion) and also attachment of antidegradants to the rubber both are important factors in the fatigue life of rubber, particularly in an aggressive atmosphere,that must be considered.

The fatigue resistance of NR conventional CBS vulcanisates modified with 1 % aromatic nitroso compounds in the form of EPDM-spin adducts (table 15)is improved compared to that of a control containing no additive. This results also reveal that,although the antifatigue activity of these compounds does not reach to IPPD before extraction. Nevertheless after solvent extraction, the antifatigue activity of these compounds particularly NDPA is much higher than IPPD. An extensive conversion of these spin traps to rubber-bound nitroxyls during processing in a closed mixer, which restrict the spatial mobility of nitroso moiety, could be a reason for poor antifatigue activity of these compounds after extraction. Moreover, the poor dispersity of the EPDM-masterbatch during compounding with NR could be another factor which reversely affects the antioxidant activity and fatigue life of final vulcanisate.This needs to be studied by Electron microscopy.

A general reduction in the fatigue resistance of nitroso compounds, particularly NDPA where used as EPDM-spin adducts is observed (see tables 13 & 15).This could be associated with the formation of a hard (cross-linked) EPDM-spin adducts in a closed mixer which makes the dispersity of the adducts difficult in the subsequent compounding.

Table13 Comparison of fatigue failure times of unextracted and azeotropic extracted of nitroso-modified NR conventional CBS vulcanisates . NR was modified with 1 Phr aromatic nitroso compounds in a water cool open two roll mill ,(70°C).

Compound	[DCP] / [Nitroso] mol	Fatigue life(number of cycles to break x10^2) Before extraction	After extraction	% improvement after extraction over IPPD
Control		400	345	9.5
NDPA	0.0	1760	750	138
NDPA	0.1	1050	820	160
NDPA	0.2	1360	700	120
PMNB	0.0	960	390	23
PMNB	0.1	940	350	11
PMNB	0.2	920	360	14
NDBPh	0.0	920	310	-
NDBPh	0.1	900	290	-
NDBPh	0.2	880	270	-
IPPD		2200	315	-

Table14 The effect of compounding temperature on the fatigue life of NR vulcanisate.NR was compounded with 1 Phr NDPA and different concentration of Trigonox 101 in a cold and hot two roll mill.

Compounding temperature (°C)	[Trigonox101] / [NDPA] mol	Fatigue life,numberof cycles to break x10^2 Before extraction	After extraction
70	0.0	1760	750
130	0.0	1500	580
130	0.14	1250	600

Table15 Comparison of fatigue failure times of unextracted and azeotropic extracted of modified NR conventional CBS vulcanisates. NR was modified with 1 Phr aromatic nitroso compounds in the form of EPDM-spin adducts

Compound	$\frac{[\text{DCP}]}{[\text{Nitroso}]}$ mole	Fatigue life (number of cycles to break x10^{2})		
		Before extraction	After extraction	% improvement after extraction over IPPD
Control		400	345	9.5
NDPA	0.0	1150	500	59
NDPA	0.075	1120	400	
NDPA	0.15	930	410	
PMNB	0.0	860	380	
PMNB	0.075	830	350	
PMNB	0.15	800	330	
NDBPh	0.0	690	340	
NDBPh	0.75	680	330	
NDBPh	0.15	670	330	
IPPD		2200	315	

Table16 The effect of EPDM on fatigue failure times of NR conventional CBS vulcanisates . NR modified by 10% EPDM and 1% of antidegradants in a water cool two roll mill .

Compound	Fatigue life (number of cycles to breakx10^{2})		
	Before extraction	After extraction	% improvement after extraction over IPPD
Control	400	345	9.5
Control+EPDM	390	320	1.6
NDPA	1760	750	138
NDPA+EPDM	1400	690	123
IPPD	2200	315	-
IPPD+EPDM	1745	310	-

Fig.18 The effect of azeotropic extraction on the fatigue life of NR vulcanisates modified with 1 Phr antidegradant as normal additive

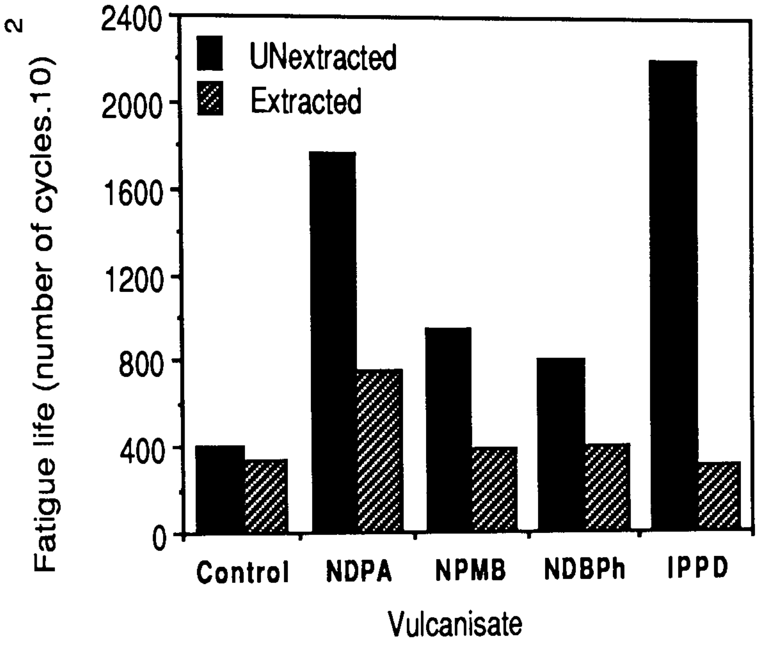


Fig. 19 The effect of radical generator on the fatigue life of unextracted and extracted NR vulcanisate modified with 1% NDPA in a water cool two roll mill (70°C).

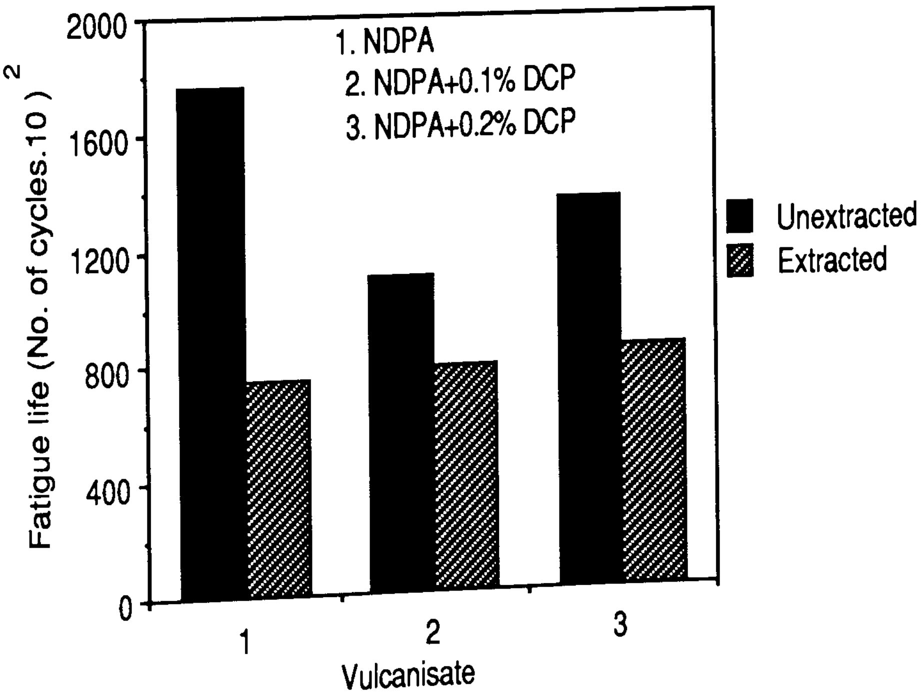


Fig. 20 The effect of azeotropic extraction on the fatigue life of NR vulcanisates containing 1Phr nitroso compounds in the form of EPDM-spin adduct

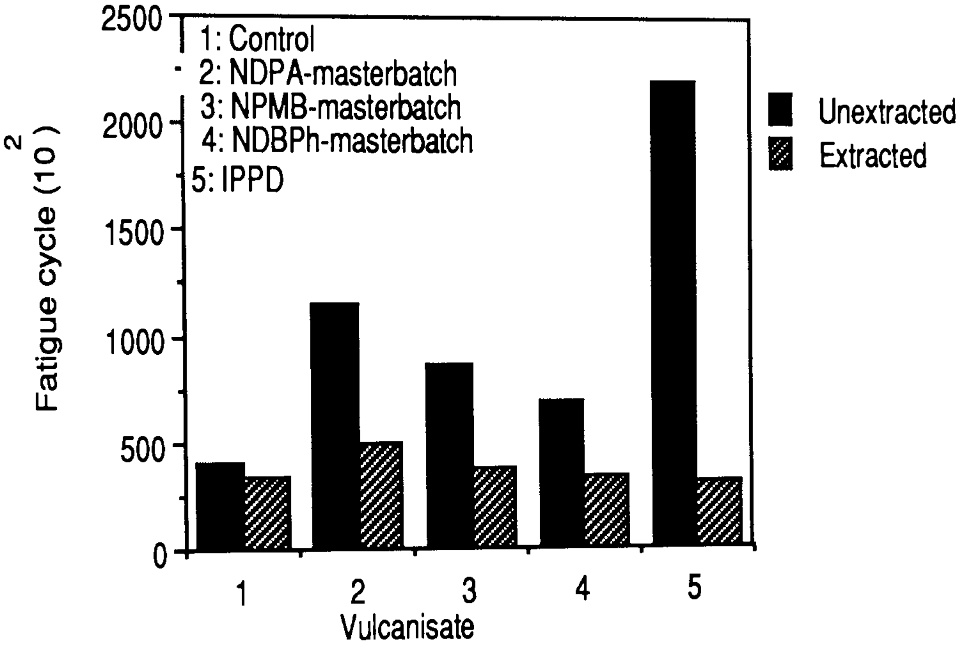
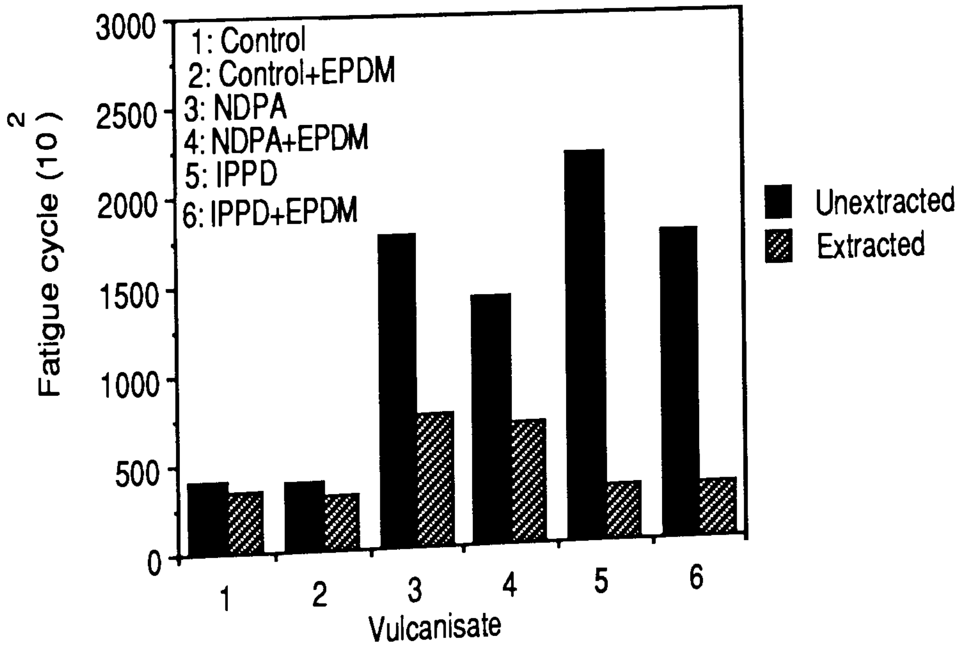


Fig. 21 The effect of 10% EPDM on fatigue failure times of unextracted and azeotropic extracted of NR vulcanisates containing 1 Phr antidegradants used as normal additives



Conclusion

The work described in this part evaluates the spin trapping behaviour, antioxidant activity, and antifatigue activity of aromatic nitroso compounds, added in the form of spin adducts concentrates or as normal additive to NR conventional CBS vulcanisates. The effects of the method of introduction of nitroxyl radicals on the cure parameters of the vulcanisates have also been investigated.

1. The identification of nitroxyl radical (spin adduct) from nitroso compounds in the masterbatches by ESR confirms that mechanochemical reactions of these compounds with polymers proceeds predominantly by a radical mechanism. Identification of nitroxyl radicals in solvent extracted samples indicates that these are macroradical, (ie. they are chemically attached to the polymer). Quantification of [>NO·] during different processing conditions revealed that the formation of adducts is temperature dependent up to a limiting value. A sharp increase in nitroxyl radical concentration of the samples on oxidation with meta-di-chloroperbenzoic acid suggests that, apart from nitroxyl radicals, nitroxyl precursors such as hydroxylamines, and alkyl hydroxylamines were formed in the masterbatches.
2. In general aromatic nitroso compounds and their corresponding spin adducts reduced the scorch time, and increased the rate of cure of final vulcanisates to a varying extent compared to that of control and to that of commercial standard IPPD. This disadvantage was at its maximum when NDPA along with Trigonox 101 was compounded at higher temperature (steam two roll mill) as a normal additive

3. Plasticity number (viscosity)of NR gum rubber were at their highest level when modified by the NDPA-masterbatch, due to the low solubilities of these hard cross-link moieties in NR.

4. Aromatic nitroso compounds vary in their antioxidant activities from highly effective to almost ineffective. The activity of these compounds appeared to be dependent apart from chemical structure on the ability to form nitroxyl radical, free hydroxylamine, and O-alkyl hydroxylamine. These intermediates can function in CB-D/CB-A cycle

5. The antioxidant activity of NDPA, when compounded with NR as normal additive at higher temperatures (steam mill) was highly improved in the presence or absence of Trigonox 101. However, the antifatigue activity of the above systems was declined to some extent under similar conditions. The generation of higher nitroxyl radical from NDPA at higher processing temperatures which is associated with higher polymer-bound nitroxyl could be at least in part responsible for such behaviour. Therefore, the importance of polymer-bound antioxidant in antioxidant activity rather than antifatigue activity is evident.

6. Oxidative stress-relaxation measurements of NR vulcanisates modified with NDPA as a normal additive or as masterbatch revealed that the antioxidant activity and permanence of these systems before and after extraction under different compounding temperatures is better than commercial antioxidant IPPD.

7. Although the antifatigue activities of NR vulcanisates modified with nitroso compounds and their masterbatches do not compete with IPPD, due to formation of higher amount of rubber- bound nitroxyl, which restricts the diffusion of antidegradant in the rubber matrix. However, their antifatigue activities are much better than IPPD after azeotropic extraction, confirms the effectiveness of rubber-bound antioxidant.

8. The addition of 10 % EPDM to NR containing 1% NDPA improved the thermal aging of NR considerably before extraction whereas this effect on NR containing the same weight ratio of IPPD was insignificant. this matter needs more investigation.

9. No solution has already been proposed to the physical loss of antidegradants from the tire carcass, in spite of this problem carried out by Kuzminsky and his coworkers who have shown (22) that conventional antidegradants are "extruded" from the inside to the outside of a tire with subsequent loss from the surface. The spin trapping reaction of NDPA with the formation of rubber-bound nitroxyl can therefore provide a means of improving fatigue resistance of NR vulcanisate under aggressive environmental conditions.

3.7 Suggestion for further work

1. In general aromatic nitroso compounds,particular PMNB and NDBPh show poor solubility when processed with EPDM or NR. The poor antioxidant activity and antifatigue activity of these compounds at least in part is due to their insolubility. The introduction of long alkyl groups in benzene ring of these compounds is suggested.

2. p-Nitroso diphenylamine presents much better antioxidant activity than IPPD in the presence or absence of Trigonox101. The formation of a great deal nitroxyl radical and the corresponding free hydroxylamine and O-alkyl hydroxylamine during processing of this compound with rubber was confirmed by ESR studies. However it would be desirable to study the effect of each one of the components individually.

3. In respect to the results obtained from stress-relaxation studies and fatigue to failure tests , NDPA is not only an excellent antioxidant for thermal aging but also could be a promising antifatigue agent, this however, needs some structural modification.

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