TO MY WIFE CHAMPICA

AND

MY FAMILY

ALIPHATIC NITROXYL RADICALS AS ANTIFATIGUE AGENTS FOR RUBBERS

by

LAKSHMAN PREMAL NETHSINGHE

Submitted for the
Degree of Doctor of Philosophy
at the
University of Aston in Birmingham

December 1982

ACKNOWLEDGMENTS

I wish to acknowledge with gratitude the guidance, advice and encouragement given by my supervisor, Professor Gerald Scott, throughout the course of this work.

I am grateful to the British Technology Group for the financial support of this project.

I acknowledge with thanks the co-operation of the Technical staff in the Chemistry Department, and the staff in the Library of the University of Aston in Birmingham. My thanks are also extended to my friends and colleagues in the Chemistry Department.

Special thanks go to Miss Shobhna Thakrar for typing this thesis.

Last but by no means least my sincere appreciation goes to my wife Champica for her constant encouragement, patience and morale support throughout the duration of this work.

THE UNIVERSITY OF ASTON IN BIRMINGHAM

ALIPHATIC NITROXYL RADICALS AS ANTIFATIGUE AGENTS FOR RUBBERS

LAKSHMAN PREMAL NETHSINGHE

Submitted for the Degree of
Doctor or Philosophy

December 1982

SUMMARY

The antifatigue activity of hindered nitroxyl radicals and their precursors have been studied. It was demonstrated that hindered alicyclic nitroxyl radicals and their precursors have weak antifatigue activities. However the trend increased in the order: amine < nitroxyl radical < hydroxylamine. The activity was improved by attaching PD-C and CB-D antioxidant functions to the alicyclic nitroxyl radicals. On the other hand N-alkyl aldonitrones containing semi-hindered phenolic antioxidant functions were good antifatigue agents. Optimum activity was achieved when they were premilled with the rubber for two minutes on an open two-roll mill prior to the compounding operations.

Mechanistic studies showed that the role played by O-alkylated hydroxylamines during the antifatigue activity of the hindered alicyclic nitroxyl radicals is small. It was also shown that the nitrones probably function in part as antifatigue agents by a chain repair mechanism.

The hindered piperidines and hydroxylamines did not greatly affect the curing characteristics of the vulcanisation process. However their nitroxyl radicals were found to retard cure. The nitrones did not particularly affect the curing characteristics either, except for the N-primary-alkyl nitrones. These were found to activate cure. None of the hindered piperidine nitroxyl radicals nor their precursors possessed any antiozonant or antioxidant activity. The nitrones on the other hand, were found to be weak anti-oxidants but very good static antiozonants. All the compounds were non-discolouring and non-staining. Combinations of the nitrones with other non-discolouring/non-staining stabilisers did not impair their antidegredant activities very much. Furthermore the nitrones were shown to be better static antiozonants than the commercially available agents. Moreover they represent a new class of compounds which can potentially be used to protect light coloured rubber goods against fatigue and ozone deterioration.

KEY WORDS: Antifatigue; nitroxyl radicals; nitrone; antiozonant; discolouration/stain.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

p.h.r. = Parts per hundred parts of rubber

p.p.h.m. = Parts per hundred million parts

For the abbreviations (code names) of the compounds used in this thesis see table 2.1

CHAPTER ONE

GENERAL ASPECTS OF THE DETERIORATION OF RUBBERS

1.1 INTRODUCTION

An important consideration in the design of rubber components is that they should have an adequate service life. Premature failure can occur by a variety of processes. These include shelf ageing, metallic poisoning, heat ageing, light ageing, fatigue, flex cracking, oxidation and ozone cracking. In all these cases, except for the last, the fundamental reaction responsible for the ageing process is always the same: oxidation of the rubber hydrocarbon or of the cross-link by molecular oxygen [1-10]. In each case the reaction is initiated by a different initiating process.

A direct consequence of oxidation is rupture of the polymer molecules [1,2,4]. In natural rubber, this is manifested as a loss in mechanical properties such as tensile strength, elasticity, elongation at break and resilience. In some synthetic rubbers [1,3], for example styrene butadiene rubber (SBR), ageing may be accompanied by an increase in tensile strength due to cross-linking reactions taking place during the oxidative process.

Mechanical working of polymers causes a much more rapid deterioration which is not normally uniform throughout the bulk of the polymer[8]. Thus the continual flexing of rubber leads to the development of surface cracks which rapidly propagate through the rubber component and may in severe cases lead to complete severage. This type of breakage is referred to as fatigue and is aggravated by oxygen and ozone. Typical of this kind of failure are groove cracking in tyres, tread and ply separation in tyres, cracking of torsion springs and motor mounts, the cracking of carcass beltings and the cracking of boot uppers and shoe soles.

1.2 MECHANISM OF OXIDATIVE DETERIORATION

1.2.1. The Autoxidation Cycle

All organic polymers are hydrocarbon materials and hence are susceptible to oxidation. The oxidative deterioration of polymers takes place by a process known as autoxidation. By definition "autoxidation is the spontaneous oxidation of hydrocarbon materials when exposed to oxygen" [1]. Bolland and co-workers[1,9-11] have suggested that the oxidation is a chain reaction proceeding via a free radical mechanism with the formation of hydroperoxides. The essential steps of this chain reaction are shown in scheme 1.1.

				Reaction rate
Initiator	(1) →	R·	Initiation	$V_1 = r_1$
$R\cdot + O_2$	(2) →	ROO·	Propagation	$V_2 = k_2 [R\cdot][O_2]$
$ROO\cdot + RH$	(3) →	ROOH + R·		$V_3 = k_3 [ROO\cdot][RH]$
$R\cdot + R\cdot$	(4) →	R-R	Termination	$V_4 = k_4 [R\cdot]^2$
$ROO\cdot + R\cdot$	(5) →	ROOR		$V_5 = k_5 [R\cdot][ROO\cdot]$
$ROO\cdot + ROO\cdot$	(6) →	ROOR + O_2		$V_6 = k_6 [ROO\cdot]^2$

Scheme 1.1

Assuming a stationary concentration of free radicals and that under these conditions

$$r_1 = V_4 + V_5 + V_6$$

and also

$$V_3 = V_2$$

$$\text{then} \quad [ROO\cdot]^2 = \frac{r_1}{\frac{k_4 k_3}{k_2^2}\frac{[RH]^2}{[O_2]^2} + \frac{2k_5 k_3 [RH]}{k_2 [O_2]} + k_6}$$

Now

$$\frac{-d[O_2 \text{ absorbed}]}{dt} = V_2 = V_3 = k_3[ROO\cdot][RH]$$

substituting for $[ROO\cdot]$,

$$\frac{-d[O_2 \text{ absorbed}]}{dt} = \frac{r_1^{\frac{1}{2}}}{\left(\frac{k_4}{k_2^2[O_2]^2} + \frac{k_6}{k_3^2[RH]^2} + \frac{2k_5}{k_3k_2[RH][O_2]}\right)^{\frac{1}{2}}}$$

if it is assumed that $k_4k_6 = k_5^2$, then

$$\frac{-d[O_2 \text{ absorbed}]}{dt} = \frac{r_1^{\frac{1}{2}}}{\left(\frac{k_4^{\frac{1}{2}}}{k_2[O_2]} + \frac{k_6^{\frac{1}{2}}}{k_3[RH]}\right)}$$

Thus at 'high' oxygen pressures

$$\frac{-d[O_2 \text{ absorbed}]}{dt} = r_1^{\frac{1}{2}} \frac{k_3[RH]}{k_6^{\frac{1}{2}}} \quad \cdots\cdot(\text{eq } 1)$$

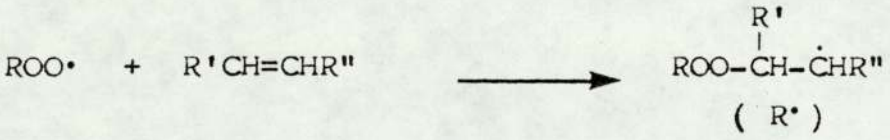
and at 'low' oxygen pressures

$$\frac{-d[O_2 \text{ absorbed}]}{dt} = r_1^{\frac{1}{2}} \frac{k_2[O_2]}{k_4^{\frac{1}{2}}} \quad \cdots\cdot(\text{eq } 2)$$

Equation (1) describes satisfactorily the kinetics of oxidation of a large number of hydrocarbons at pressures greater than 100 mm[1].

These equations suggest that in the excess of oxygen, the overall oxidation processs is determined by the reaction step 3 of the autoxidation cycle. However, in the deficiency of oxygen, alkyl radicals may predominate in the system and consequently the rate of propagation and termination is expectedly different from that taking place in the excess of oxygen.

In the case of olefins, an alternative propagation step has been reported [1,8,11] to account for the products of oxidation. This is the addition of alkylperoxyl radicals to the reactive double bond.



The radical (R•) formed in this reaction is alkyl and continues the chain reaction by addition to oxygen. Although this step is in competition with step 3 in the autoxidation cycle, chemical identification is necessary to distinguish between them since the kinetics of their formation are the same [1].

The initiation step may be brought about in a number of ways the most important being heat, light and mechanical activation [1,2,11].

Chain scission occurs after thermolysis and photolysis reactions of the hydroperoxides and other peroxy entities formed during the autoxidation cycle[1]. Hydroperoxidation is thus of major chemical significance in olefin autoxidation, and in polymers it is a precursor to the physically important scission and cross-linking processes which result in a loss of the mechanical properties.

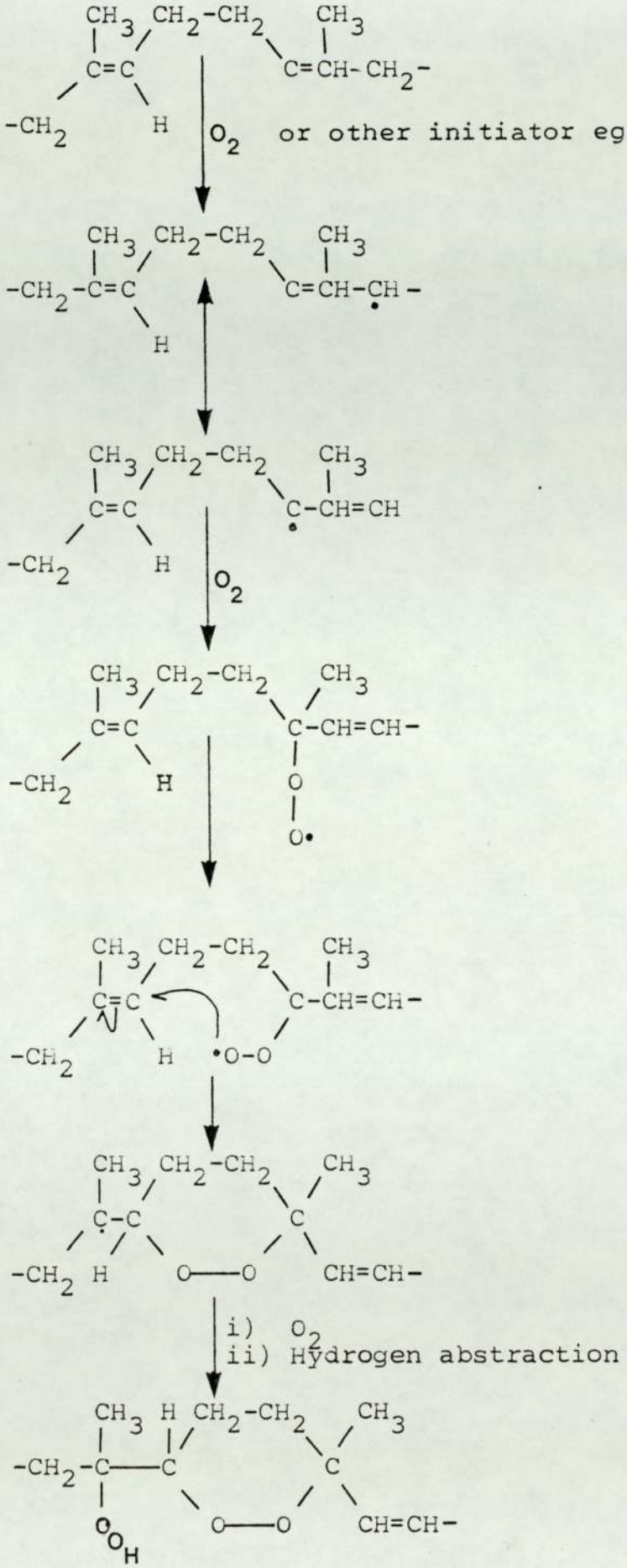
When applied to polymers, this autoxidation reaction scheme has been criticised[11] for not taking into account the chain scission reactions, as hydroperoxidation by itself does not alter the mechanical properties of the polymer significantly. These properties are lost only after the scission of the oxygenated species which are formed during the autoxidation cycle. Furthermore, for sulphur cross-linked rubbers, the scheme does not take into account oxidation of the sulphur cross-links, the products of which are known to retard the oxidative deterioration of the rubber[1]. Despite these limitations however, the autoxidation cycle describes satisfactorily the kinetics of oxidation of most polymers including rubbers.

1.3 THE MECHANISM OF THE OXIDATION OF RUBBER

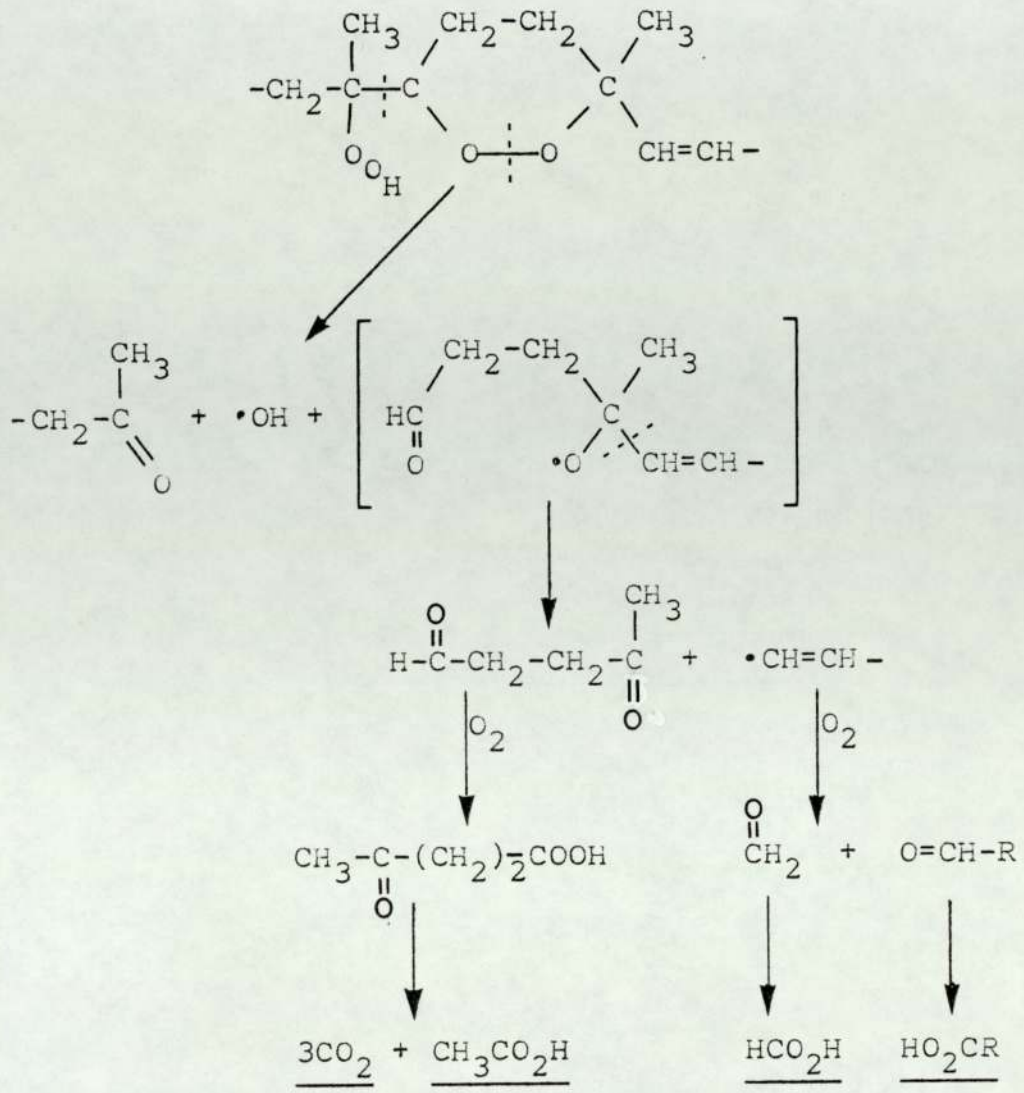
1.3.1 The Oxidation of Raw Rubber

There are a number of proposed mechanisms, but the most widely accepted scheme is that suggested by Bevilaqua[1,7,11]. The essential steps of this mechanism are outlined in scheme 1.2.

According to this scheme, hydrogen atoms are abstracted from the methylene groups of the polyisoprene chain and this constitutes the propagation step of the autoxidation cycle. The main primary product is thus a polymer chain having hydroperoxy groups attached to the methylene carbons. Some of the peroxyl radicals however, attack a neighbouring double bond before hydrogen abstraction can occur. This leads to the formation of cyclic dialkyl peroxides. Secondary reactions then lead to chain scission, cross-linking and formation of various functional groups along the polymer chain. In natural rubber and in cis-polyisoprene chain scission predominates over cross-linking, thus softening occurs on ageing. In the synthetic rubbers, like SBR, cross-linking reactions can occur by radical addition across pendant vinyl groups that are inherent in the polymer[3]. These pendant vinyl groups are formed during the polymer manufacturing stage.



Scheme 1·2 continued overleaf



Scheme 1.2 Oxidative degradation of raw rubber

Natural rubber also behaves differently to cis-polyisoprene during oxidation due to the presence of naturally occurring antioxidants in the former.

1.3.2 The Oxidation of Vulcanised Rubber

The essential difference between raw rubber and

vulcanised rubber is that the latter contains cross-links which impart the useful service properties to the rubber. These cross-links may be of the type:

(i) C-C as obtained from a peroxide or radiation cure.

(ii) $C-S_x-C$ as obtained from a typical sulphur formulated conventional cure.

(iii) $C-S_1-C$ and $C-S_2-C$ as obtained from a TMTD sulphurless cure.

The difference between the vulcanised and unvulcanised rubbers is highlighted in their behaviour to creep and stress relaxation under conditions where chain scission is negligible[1]. Raw rubber exhibits rapid decay of stress when held at constant extension at various temperatures ranging from $-50^{o}C$ to $0^{o}C$.[12] In contrast vulcanised rubbers do not show any comparable relaxation behaviour between $-40^{o}C$ and $+40^{o}C$[13]. At higher temperatures, relaxation occurs due to chemical scission of the cross-links.

In contrast to raw rubbers, the oxidation of vulcanised rubbers is complicated by the presence of the cross-links. The oxidative degradation of peroxide cured vulcanisates corresponds closely with that observed for the raw rubber since the cross-links are direct carbon-carbon links[16].

In the case of sulphur cross-linked vulcanisates however, besides main chain scission occurring as a result of autoxidation, cross-links are also oxidised[1,14-18]. Oxidation of the cross-links gives rise to oxygenated sulphur compounds which are known to protect the rubber against further oxidative deterioration[1,18,19]. However, chain scission is normally associated with the formation of these antioxidant species.

1.4. THE FATIGUE OF RUBBER

One of the ways in which failure of rubber components can occur is by the development and propagation of cracks resulting from the cyclic mechanical working of the rubber. This kind of failure is known as fatigue. By definition[2] 'fatigue is the change in physical structure and properties of the mass of a rubber component when it is subjected to repeated deformation'.

In general there are three causes for the failure of rubber by fatigue[1,2,7]. These are:

(1) The mechanical rupture of the polymer molecules.
(2) Oxidation of the polymer chains.
(3) The action of ozone.

The mechanical rupure of the polymer molecules is

accelerated in the presence of oxygen and when this occurs the failure is termed as 'mechano-oxidative' rupture. Fatigue failure is also accelerated by ozone due to the initiation of cracks caused by ozonisation of the rubber hydrocarbon.

The roles played by the oxygen and the ozone are clearly distinct phenomena, although the combined effects of the two stimulants may be synergistic. Oxidation leads to a random development of shallow cracks, known as crazing, on the surface of the rubber. Ozonisation leads to the formation of deep cracks, always perpendicular to the direction of the applied strain.

1.4.1 The Mechanics of Crack Propogation

Growth and propagation of cracks in rubber has been studied extensively using test pieces containing deliberately inserted cuts and subjecting them to static or dynamic strain.

It has been shown that fatigue is primarily a physico-chemical phenomenon. The initial crack formation may be a physical phenomenon however, the rate of crack growth is certainly dependent on both the presence of oxygen and on the tearing energy at the tip of the crack. Oxygen accelerates the rate of deterioration of the rubber by

combining with the alkyl radicals produced during the mechanical scission of the rubber molecules. The nature of the role played by oxygen will be discussed further in section 1.4.6.

Crack growth during fatigue has been shown to take place from minute flaws on the surface of the rubber. These flaws include small indentations, hard particles, small regions of abnormal local cross-linking density and cracks initiated by ozone[5].

1.4.2 The Tearing Energy Concept

Much of the work reported in the literature on fatigue has involved the study of the tearing energy at the tip of the growing crack[19-29].

The tearing energy is defined as 'the energy produced at the tip of a crack when an external force is applied for the propagation of that crack'. For an edge crack the tearing energy is mathematically defined as:

$$T = 2KWC$$

where T is the tearing energy, K is a constant which slowly varies as a function of strain, C is the length of the cut in the unstrained rubber and W is the work done

or the strain energy at a maximum extension during each cycle.

1.4.3 The Relation Between the Tearing Energy and the Fatigue Life

When expressed in terms of T, the crack growth per cycle for a repeated loading through zero strain is[20]:

$$\frac{dc}{dn} = F(T)$$

where C = crack length

n = number of cycles

T = maximum tearing energy attained during the cycle

The number of cycles for a crack to grow from a length C_1 to C_2 is then:

$$n = \int_{C_1}^{C_2} \frac{dc}{F(T)}$$

Now $T = 2KWC$

and since T increases with C, rupture of a sample will occur when the tear strength Tc is exceeded. Therefore

the number of cycles to failure, N, is given by:

$$N = \int_{Ti}^{Tc} \frac{dT}{2KW\ F(T)} \qquad \text{(Eq 1.3)}$$

where Ti is the tearing energy at the start of the test.

Equation 1.3 thus relates the fatigue life to the crack growth characteristics of a rubber, the magnitude of the deformation and the size of the initial crack or flaw.

Using power law approximations of the form:

$$F(T) = \beta T^{\beta}$$

and integrating equation (1.3)

$$N = \frac{1}{(\beta - 1)\ (2KW)^{\beta}\ Co^{\beta-1}} \qquad \text{(Eq 1.4)}$$

where Co is the effective size of the natural flaws.

β is known as the strain exponent and is influenced by the hysterisis and morphological characteristics of the rubber. For natural rubber β has been shown to equal 2 and for SBR vulcanisates β equals 4[20,21].

The flaw size, Co, required to give the best quantitative correlation with the experimental results is 2.5×10^{-3} cm, for natural rubber, and Ca. 5×10^{-3} cm for SBR[20].

The fatigue life of a vulcanisate can, therefore, be predicted mathematically by the use of the fracture mechanics treatment. When expressed in these terms, the cut growth behaviour is strongly dependent on the magnitude of the tearing energy and on the loading conditions.

1.4.4 The Effect of the Loading Conditions and the Morphological Factors

The cut growth characteristics of a rubber are greatly influenced by the type of loading conditions and the morphological characteristics of the base rubber[20-27]. The loading conditions are classified into static conditions and dynamic conditions[5,20,21]. In both cases, the rate of cut/crack growth is affected by whether the rubber is able to undergo strain induced crystallisation and also on the associated hysteresis loss. In a perfectly elastic material, where there is no hysteresis loss, the stress pattern around the tip of a growing crack would advance at a speed approaching that of sound[2]. However if hysteresis loss occurs then the rate of propagation of the crack is greatly retarded[5].

For natural rubber, at high strain, the hysteresis loss caused by the strain induced crystallisation is very great, thus under static strain, the crack growth for natural rubber is not very significant unless Tc is exceeded[30]. For the same reason, under dynamic strain, crack propagation for a crystallising rubber only occurs when the rubber is allowed to return to zero strain during each cycle. If it is not allowed to return to zero strain, the fatigue life of the rubber will be substantially higher.

In contrast, a rubber like SBR has very little hysteresis loss since it does not undergo strain induced crystallisation[31]. Thus for this rubber, crack propagation occurs at the same rate whether the loading conditions are static, dynamic with return to zero strain during each cycle, or dynamic with return to non-zero strain during each cycle.

1.4.5 Other Factors Affecting Fatigue Life

Other factors which affect the rate of crack propagation and the fatigue life of rubber components have been reported to include[1,20,25,26] the state of cure, compounding variation, the energy input during each cycle, the temperature and the nature and loading of any filler. Probably, the most important of these are the state of cure,

variations in the compounding formulation and the energy input per cycle.

The state of cure affects the degree of cross-linking and an increase in cross-link density decreases the fatigue life of the rubber component[1]. This is probably related to the capacity of the rubber molecules to be reorientated and dissipate the applied molecular stresses.

The type of cross-link also affects the fatigue life significantly. Generally sulphur cross-linked rubbers have a higher fatigue life than carbon-carbon cross-linked rubbers and this is particularly pronounced for the polysulphide cross-linked rubbers. This effect is due to a combination of two facts. A polysulphide cross-linked network is more flexible than a carbon-carbon cross-linked network. Hence the molecular stresses in the former is less than that in the latter case. Furthermore, polysulphide cross-links are able to break and reform during the fatiguing operations, thus imparting a greater lifetime to the vulcanisate. Mono and disulphide cross-linked rubber have intermediate fatigue properties.

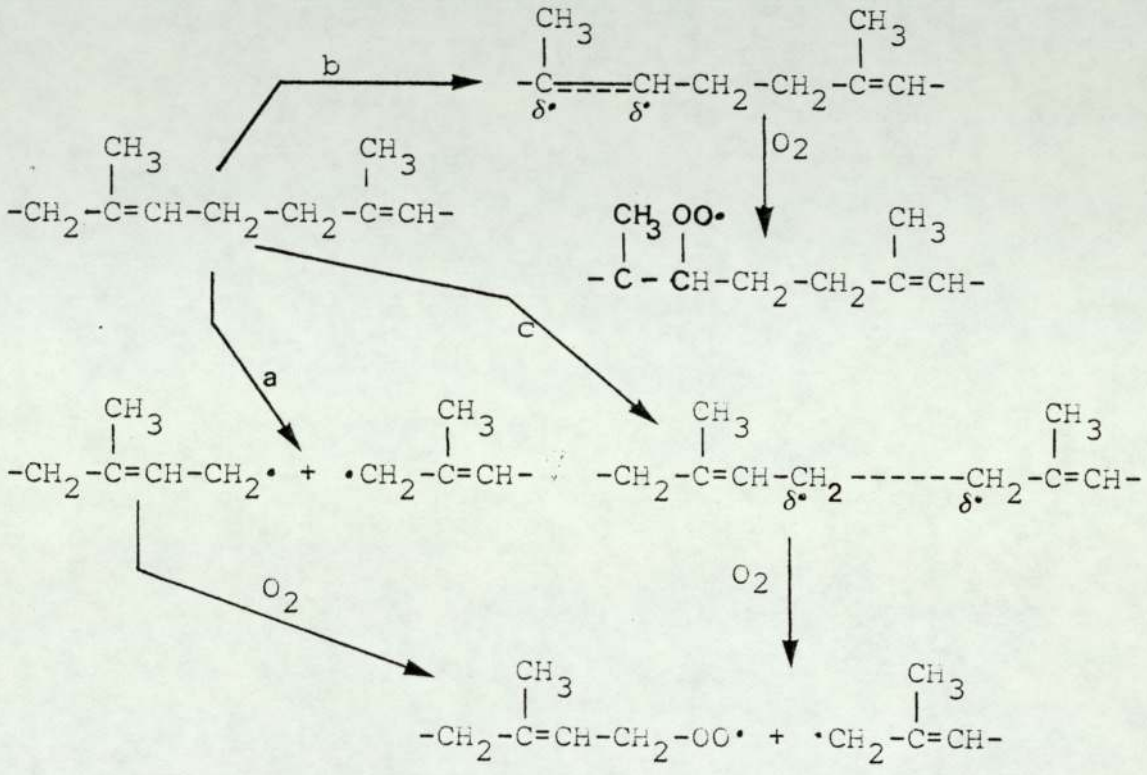
The dispersion of the compounding system also affects the fatigue properties, since the uniformity of the distribution

of cross-linking sites will be affected.

The energy input during a deformation cycle has a significant effect on the fatigue life of the rubber[26]. Generally an increased energy input decreases the fatigue life. The effect is obviously due to the greater amount of work done which causes the rubber to deteriorate more rapidly. Because of this effect, rubber vulcanisates having different moduli owing to changes in compounding formulations, should not be compared at the same strain. Instead they should be compared at the same strain energy per cycle. If tested in the former manner, the results may be erroneous, due to variations in the energy input[26].

Effects of temperature on crack growth and fatigue are mainly associated with changes in hysteresial behaviour of the rubber. At temperatures up to about 100°C the fatigue life of natural rubber is not greatly affected. In contrast, for a non-crystallising rubber such as SBR, the fatigue life decreases very markedly[20].

Inclusion of small particle size fillers have little effect on the fatigue life if comparisons are made on an equal energy input basis. Constant amplitude comparisons, however, will tend to penalise the high modulus compounds, since the energy input will be greater. Filler particles



Scheme 1.3

larger than 10^{-3} cm however, can initiate failure[24, 26].

1.4.6 The role of Oxygen

It has been known for a long time that atmospheric oxygen plays a major role in the fatigue failure of rubber. The process is quite distinct from thermal oxidative ageing in that the rate of alkyl radical formation is much higher and the oxygen concentration may become diffusion controlled[1, 32, 33]. However, the effect of oxygen is detrimental since when the fatigue operations are carried out in the absence of oxygen, for example, in very pure nitrogen or in a vacuum, the fatigue life is increased tremendously[20, 26].

The precise mechanism by which the fatigue failure is accelerated by oxygen is not quite understood yet. Two processes have been suggested[1].

(1) The oxygen can combine with the very liable alkyl radicals formed by the mechanical scission of the polymer chain (scheme 1·3 path a)

(2) The activation of the rubber hydrocarbon towards oxygen by the partial unpairing of the π electrons in the double bonds (scheme 1·3 path b) or by giving allylic methylene groups a partial free radical character (scheme 1·3 path c).

A direct consequence of this is that both alkyl and alkylperoxy radicals are involved in the terminating process under fatiguing conditions.

Kuzminsky[34] has suggested that the radicals formed by mechanical rupture do not recombine as would be expected according to the cage theory because their rate of relaxation is higher than their rate of recombination. Thus the broken chain ends come out of the cage and a large number of terminal alkyl radicals are formed which have a very high liability towards oxygen.

Kromov et al[35] have suggested that the oxidation of the rubber substantially reduces the number of polymer molecules which are amenable to the orientational and crystallisational strengthening effects.

1.5 THE OZONE CRACKING OF RUBBER

The very small concentrations of ozone in the atmosphere at ground level, normally a few parts per hundred million, may cause cracking in deformed rubber components[1,2,11]. The cracks are always formed on the surface of the rubber and are orientated perpendicular to the direction of the applied strain[1,2,11].

1.5.1 The Mechanics of Ozone Crack Growth

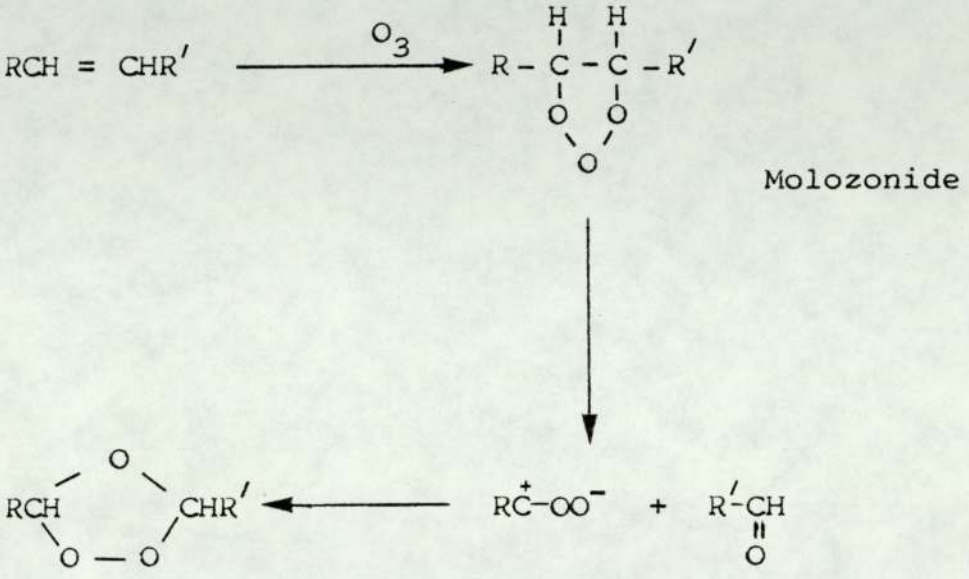
When a rubber surface is held at constant extension and exposed to ozone, crack formation does not occur unless the strain exceeds a certain critical value[1,2,36-38]. At this critical strain, the rate of crack growth is a maximum. Below and above this strain, the failure of the rubber, when exposed to ozone, is slower. Up to the critical strain, the cracks formed are few but deep. Above this strain, although the time to failure is longer, the density of cracks formed per unit area is greater, but these are very small and shallow.

Studies of single crack growth under static conditions have shown that the cut growth only occurs when the tearing energy exceeds a certain critical value[2,36,27]. When compared with the critical tearing energy value for rubber during fatigue, the value here is about ten times less. Furthermore, the rate of cut growth is directly proportional to the ozone concentration[1].

Under dynamic conditions, ozone crack growth occurs all the time the rubber surface exposed to ozone is strained, providing the critical extension is exceeded. In contrast to static exposure however, the minimum critical tearing energy is reduced[38,39].

1.5.2 The Mechanism of Ozone Rupture

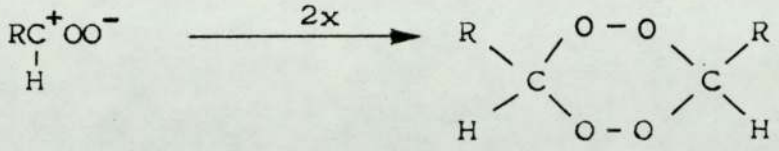
Ozone rupture occurs through ozone attack at the double bonds of the polymer to give an unstable molozonide, which subsequently rapidly rearranges to give the iso-ozonide[1,8,11,40] (scheme 1·4).



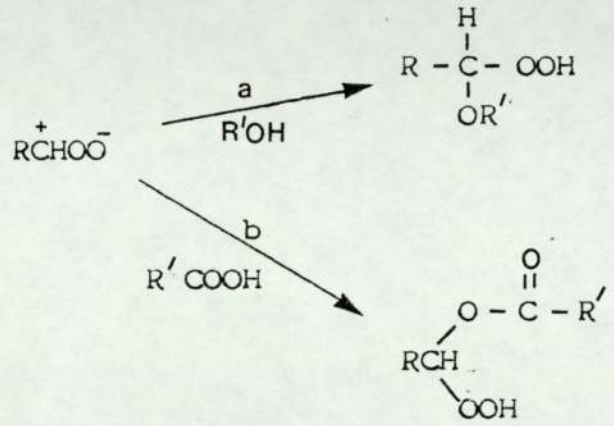
Scheme 1.4

In unstrained rubber, the recombination of the zwitterion and carbonyl can take place readily, and the effect is to produce a protective skin on the surface of the rubber[8]. In strained rubber this recombination is not possible and crack development occurs[8]. Hence the need for the critical strain before significant ozone cracking occurs.

Dimerisation of the zwitterion to give cyclic peroxides is also known [1,11,40].



Other peroxidic products could also be formed from hydroxyl containg reagents.



These peroxide entities are detrimental to the rubber because they can initiate oxidative degredation.

There is some evidence that ozone could also be regenerated by the reaction of the zwitterion with oxygen [1]. A similar regenerative process could occur in rubber too, by reaction of the zwitterion with the dissolved oxygen in the rubber.

Popov et al [41] have suggested a free radical mechanism for the ozone attack on polymers. It is however universally

accepted that ozone attack in rubber occurs by the ionic mechanism described earlier.

The decrease in the rate of ozone cracking at extensions above the critical strain appears to be anamolous. This effect is however explained in terms of retardation of crack growth due to hysterisis loss caused by strain induced crystallisation and orientation effects[34]. Kuzminsky has also suggested that at strains above the critical value, the double bonds become more single bond like in character and becomes increasing so at higher strains. Therefore the rate of ozone attack is correspondingly decreased.[34]

1.5.3 Other Factors Affecting Ozone Cracking

Ossefort[6] and Cox[42] have reviewed the criterion which affect the rate of ozone cracking in rubber vulcanisates. The most important of these are concentration of ozone, the strain on the specimen, the chemical nature of the base polymer, the state of cure the type of curing system and the temperature at which the test is done.

Vulcanisates in which the base rubber tends to crystallise when strained are more succeptible to ozone cracking than those which do not crystallise.[1,6] The reason for this

could be associated with the observation that the lower the tendency to crystallise the higher is the critical elongation value.

At room temperature the rate of crack growth differs for different rubbers. However at elevated temperatures the rate of crack growth becomes similar for all types of rubber. This is because the rate of ozone cracking depends on the ability of the chain ends to separate[1] and this in turn is affected by the internal viscosity of the polymer.

The rate of ozone crack growth is considerably influenced by the chemical nature of the base polymer, in particular the nature of the substituent at the double bond [1,6,42]. Neoprene rubbers, for instance, are more resistant to ozone cracking than natural rubber. The reasons for this effect is two fold. Firstly, the double bonds in the neoprene rubber are deactivated towards ozone attack by virtue of the electron withdrawing effects of the chlorine atoms attached to the double bond carbons[34]. Secondly, because of the presence of the chlorine atom in place of the alkyl substituent of the double bond, the glass transition temperature (Tg) for neoprene rubber is higher than the Tg for natural rubber[50]. This difference in Tg affects the internal viscosities of the two rubbers, and hence the

ability of broken chain ends to separate.

The state of cure, the nature of the curing system and the treatment of the rubber prior to vulcanisation all affect the rate of ozone crack growth. Peroxide vulcanisates have been found to be more resistant to ozone cracking than sulphur vulcanisates[1,6]. The accelerator system also affects the ozone resistance of the vulcanisate. Guanides impart no protection towards ozone cracking, but mercaptobenzthiazoles and dithiocarbamates do.[1]

1.6 THE FLEX CRACKING OF RUBBER

Failure of rubber as a result of cracks formed due to cyclical bending or compression fatigue is termed flex cracking[40]. This contrasts to fatigue which is failure by crack formation due to cyclical extension. Like fatigue, flex cracking is caused by mechano-oxidative scission of the polymer molecules[7,40,43,44]. There is evidence[1,46-49] however that ozone is generated during the flexing of rubber, and that flex cracking and dynamic ozone cracking are very similar processes. Indirect evidence[40] to suggest that flex cracking is primarily a mechano-oxidative process arises from the fact that many antioxidants which delay flex cracking are ineffective in retarding ozone crack growth.

1.7 STABILISERS

Rubber vulcanisates may be protected from detremental effects of heat, ultraviolet light, fatigue, oxidation and ozone cracking by a variety of stabilisers.

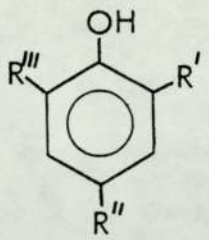
They are catagorised into two distinct classes which operate through different mechnisms. The first are chain breaking antioxidants which interrupt the chain propogating cycle by reacting with the free radicals produced during the autoxidation process. The second class are known as preventive antioxidants. These inhibit or retard the formation of the source of free radicals in the initiating step. Often a combination of these two classes are used in which case the phenomenon of synergism may occur where the overall effects of the combination is greater than the additive effects of each component.

1.7.1 Chain Breaking Antioxidants

1.7.1.1 Definition and the Factors Affecting Their Activity

Any substance capable of reacting with the alkyl or alkyl-peroxyl radicals produced in the autoxidation cycle are potential chain breaking antioxidants. Typical compounds in this catagory are aryl amines and phenolic

antioxidants.



Studies[1,8] made on phenolic antioxidants have shown that

1) electron releasing substituents (ortho and para to the hydroxyl group) markedly increase the antioxidant efficiency (e.g. tertiarybutyl, methyl or methoxy groups).

2) Electron abstracting groups in the same positions decrease the antioxidant activity (e.g. nitro, carboxyl and halogen groups).

3) α - branched ortho alkyl groups considerably increase the antioxidant activity. Such groups in the para position decrease the activity. For the amines too electron releasing nuclear substituents increase the antioxidant effeciency tremendously[8].

1.7.1.2 The Mechanism of Chain Breaking Activity

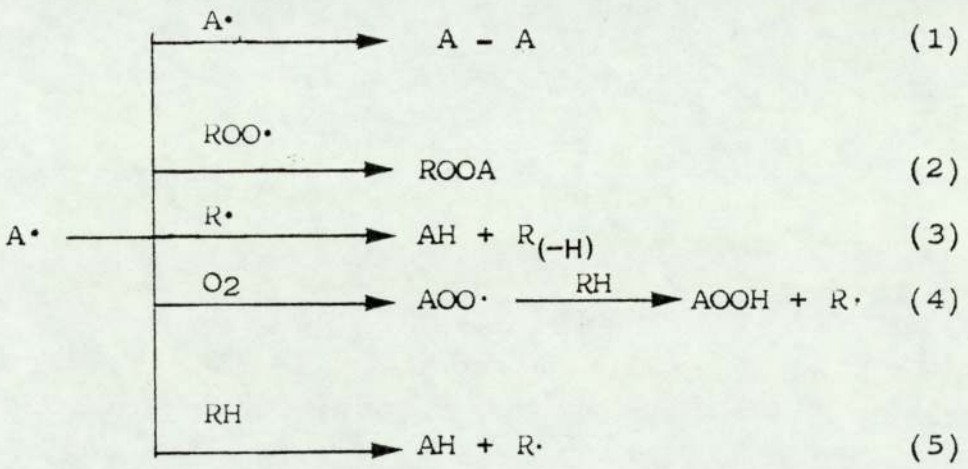
Both the phenols and the amines possess labile hydrogens

which compete with the hydrocarbon for the alkylperoxyl radicals.

i.e. $ROO\cdot + AH \longrightarrow ROOH + A\cdot$

Since the free radical A· is generated, the effectiveness of the chain breaking antioxidant depends not only on the rate of interaction of the antioxidant with the alkylperoxy radical but also on the stability of A..

The possible reactions of A. are[1,8,50]



Reactions (1), (2) and (3) are terminating steps. Steps (4) and (5) however are chain transfer steps and lead to a continuation of the autoxidation cycle.

A single antioxidant may act in all of these ways more or less simultaneously. Thus in some circumstances the material may appear primarily as an antioxidant and in

other circumstamces it may show proxidant tendencies[1,50,51].

The substituents on the aromatic rings of the phenols and on the aromatic amines affect their antioxidant effenciences by -

1) increasing or decreasing the rate of reaction of AH with the alkylperoxy radicals.
2) affecting the stability of the radical A· and hence the ratio of the chain transfer to terminating steps.

Chain breaking antioxidants are further classified into chain breaking donor and chain breaking acceptor antioxidants depending on whether they function by an oxidative or a reductive mechanism. This will be discussed further in section 1.8.1.

1.7.2 Preventive Antioxidants

These antioxidants act by preventing or retarding the initial formation of free radicals. Materials that function this way may be classified into:

i) metal deactivators
ii) agents which absorb or screen U.V. light
iii) agents which decompose hydroperoxides into non-radical products.

Although the preventive antioxidants are classified into

one of these three catagories, often they can act in two or more ways.

1.7.2.1 Metal Ion Deactivators

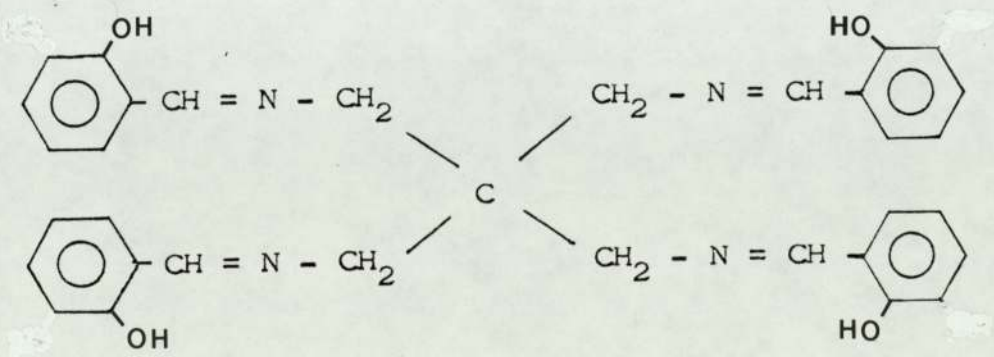
Traces of transition metals ions such as copper, manganese, nickel and iron can catalyse the decomposition of the hydroperoxides which are formed during the autoxidation cycle[1,51].

$$ROOH + M^{n} \longrightarrow RO\cdot + OH + M^{n+1}$$

$$M^{n+1} + ROOH \rightleftharpoons ROO + H^{+} + M^{n+1}$$

The harmful effect of these metal ions may be inhibited by the use of chelating agents which act by forming cordination complexes with the metal ions.

A chelating agent effective against all the metal ions described above is N^{I}, N^{II}, N^{III}, N^{IIII} - tetrasalicylidinetetra (aminomethyl) methane (I)[11,52].



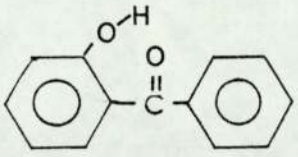
(I)

1.7.2.2 Ultraviolet Screeners and Absorbers

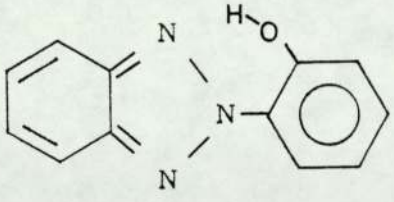
Ultraviolet light is known to cause ageing of unfilled white rubbers. The effect is to cause surface resinification and crazing of the rubber component[8]. The ultraviolet light causes photolysis of the peroxides and other photo-excitable chromaphoric groups in the polymer[1].

Carbon black filled rubbers are protected from this radiation by the screening and light absorbing capacity of the filler itself[1,53].

White rubbers may be protected against U.V. light by ultraviolet absorbers such as substituted ortho-hydroxy-benzophenones (II) and ortho-hydroxyphenylbenzotriazoles (III).



(II)

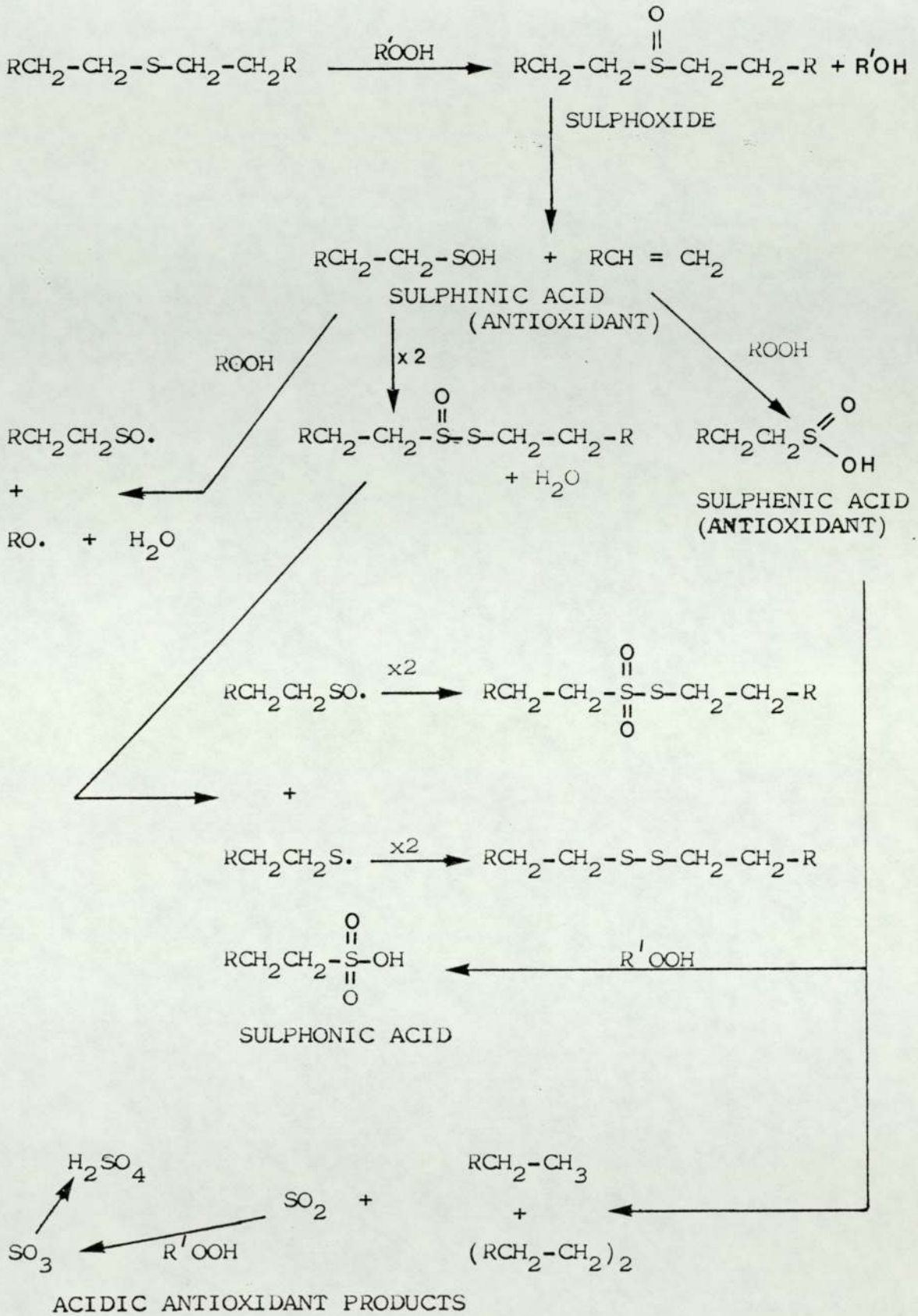


(III)

Nickel dithiocarbamates and xanthates[2,23] have also been reported to prevent photolytic ageing of white rubbers.

1.7.2.3 Peroxide Dexomposing Agents

In saturated polymers these are the most important of the


R'OOH
SULPHOXIDE
SULPHINIC ACID
(ANTIOXIDANT)
ROOH
x 2
ROOH
SULPHENIC ACID
(ANTIOXIDANT)
x2
x2
R'OOH
SULPHONIC ACID
H_2SO_4
SO_2 +
SO_3
R'OOH
ACIDIC ANTIOXIDANT PRODUCTS

Scheme 1.5

preventive antioxidants. They transform hydroperoxides into stable non radical products in reactions which do not involve free radicals. A wide variety of sulphur containing compounds fall into this catagory, the most important being:

i) thiopropionate esters

ii) metal complexes of dithiocarbomates

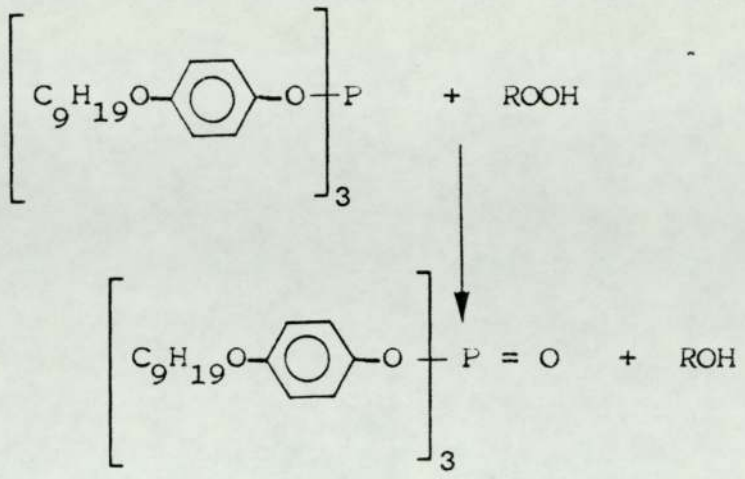
iii) metal complexes of dithiophosphates.

The chemistry of the protective action of these compounds involves the production of a powerful Lewis acid such as sulphur trioxide which can catalatically decompose hydroperoxides. The sulphur trioxide is formed via a series of oxygenated sulphur intermediates. The chemistry is typified by the sequence for dilauryl - β - thiodipropionate (D L T P)[54-59] as shown in scheme 1.5.

Scott[1,18] has classified this type of preventive antioxidant as catalytic peroxide decomposers or PD - C antioxidants.

This PD - C mechanism most certainly operates in sulphur cross-linked vulcanisates too. During the thermal ageing the cross-links are oxidised to give a variety of oxygenated sulphur species which are known to protect the rubber against subsequent ageing[1,19,60].

Phosphite esters such as trisnonyl phenyl phosphite are



Scheme 1.6

used as commercial stabilisers for raw rubber[18]. These too are classed as preventive antioxidants. However they function by decomposing peroxides stoichiometrically.

Therefore they are called stoichiometric peroxide decomposers or PD - S antioxidants[18]. They operate as shown in scheme 1.6.

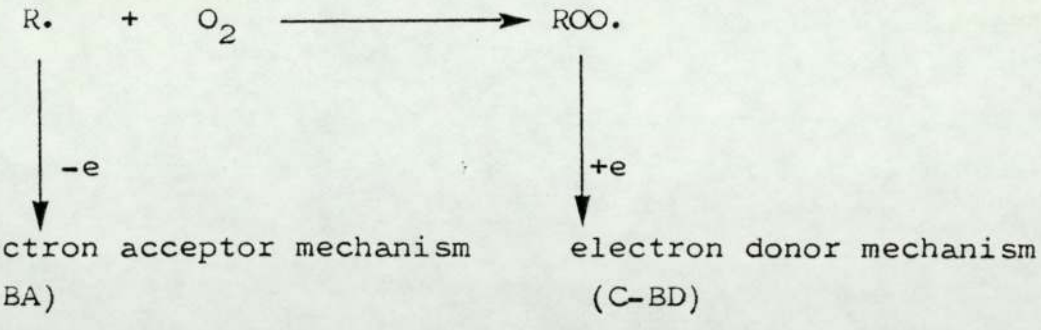
1.8 THE ANTIOXIDANTS ENCOUNTERED IN THE STABILISATION OF RUBBER AGAINST FATIGUE, OZONE ATTACK AND FLEX CRACKING

The largest class of compounds encountered in the stabilisation of rubbers against thermal oxidation, fatigue failure, flex cracking and ozone cracking are the chain breaking antioxidants. Amongst these only the aryl amines show a high level of activity. Phenols and their derivatives are used extensively as antioxidants, however they do not have any significant antiozonant or antifatigue activity. Almost all the commercial antifatigue agents and antiozonants are diarylamines and derivatives thereof. Another essential difference between these two classes of antioxidants is the degree of discolouration and staining they impart to the rubber.

1.8.1 The Mode of Activity of the Chain Breaking Antioxidants

As described in section 1.7.1 the chain breaking antioxidants interrupt the autoxidation cycle by reacting with the alkyl or alkylperoxyl radicals.

Chain breaking antioxidants function through two distinctive mechanisms. The first involves oxidation of the alkyl radical by an oxidation process to give a carbonium ion or derived product. This is known as the chain breaking acceptor (CB-A) mechanism. The second involves the reduction of alkylperoxyl radicals to give a hydroperoxide and is known as the chain breaking donor (CB-D) mechanism. The redox process is conveniently summarised in scheme 1.7[1,18,61].



Scheme 1.7

1.8.1.1 The Chain Breaking Donor Mechanism (CB-D)

Alkylperoxyl radical reduction is the most significant

process occuring in an air excess condition. This is the normal situation at ambient oxygen pressures during thermal oxidation and when diffusion control is not important. CB-D antioxidants function by electron or hydrogen atom donation to the radical.

$$ROO\cdot + AH \rightleftharpoons \left[ROO^- + A^+H^\cdot\right] \longrightarrow ROOH + A^\cdot$$

Hindered phenols and aromatic amines are typical of this class.

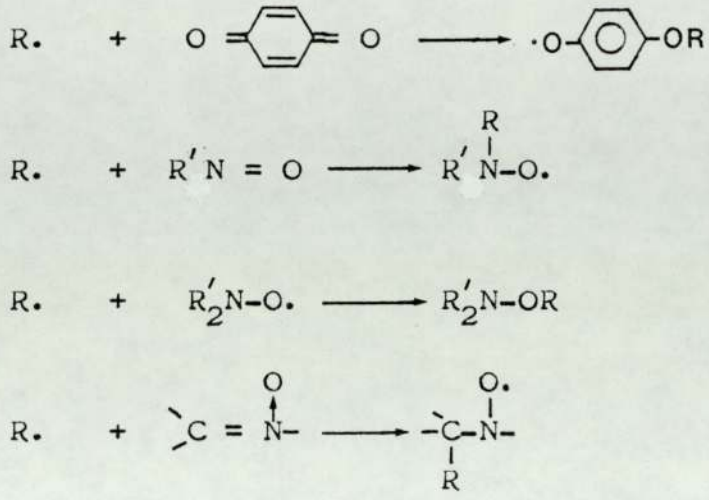
1.8.1.2 The Chain Breaking Acceptor Mechanism (CB-A)

At high rates of alkyl radical initiation and when there is a deficiency of oxygen the ratio of alkyl radical to alkylperoxyl radical concentration is very much higher than during normal thermo-oxidative conditions. Under the former conditions therefore, alkyl radical oxidation by the chain breaking antioxidant is a much more likely deactivating mechanism than in the latter case. A variety of oxidising agents are capable of removing alkyl radicals from an autoxidising system, and provided they are able to do this in competition with alkylperoxyl radicals they have antioxidant activity.

$$R\cdot + A \longrightarrow \left[R^+ + A\cdot\right] \longrightarrow RA\cdot$$

$$\text{or } R\cdot + A\cdot \longrightarrow \left[R^+ + A^{(-)}\right] \longrightarrow RA\cdot$$

Quinones, nitro[SO] compounds, nitrones and stable free radicals are the best known examples of this class.



1.8.1.3 Complementary Antioxidant Mechanisms Involving Both CB-D and CB-A Reactions

CB-D antioxidants function most effectively when alkyl-peroxyl radicals are present in the highest concentration in the autoxidising system. CB-A antioxidants are effective only when the ratio of alkyl radical to alkyl-peroxyl radical concentration is high. Since both types of radicals are present to some extent in most oxidation processes, antioxidants which exhibit both kinds of activity are superior to those operating by a single mechanism alone. Several types of antioxidants are known which involve both mechanisms. The best known example is hydroquinone. This is converted by the CB-D mechanism to benzoquinone which itself is an effective alkyl radical

trap.[18] Another example is stilbenequinone.[62,18]

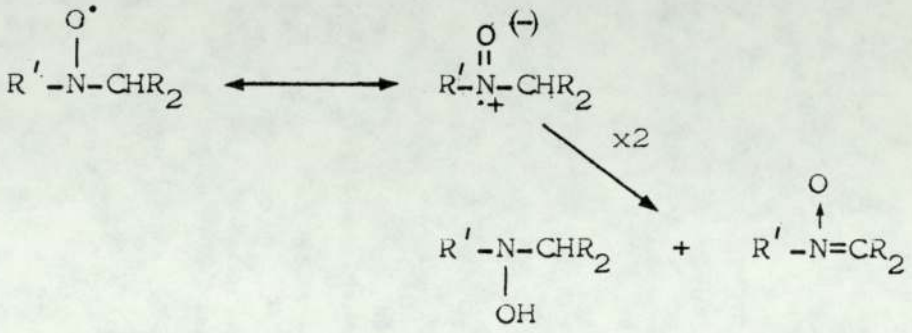
1.8.1.4 Regenerative Chain Breaking Antioxidants

Some chain breaking antioxidants have the ability to regenarate by a sequence of alternating CB-A and CB-D reaction mechanisms in which both alkyl and alkylperoxyl radicals are consumed. The polymer melt stabilisation mechanism by galvinoxyl radical is one such example.[63] The galvinoxyl radical is converted to hydrogalvinoxyl by a CB-A mechanism, and converted back to the galvinoxyl radical by a CB-D mechanism. Another such example is the melt stabilisation of polypropylene by sulphoxides.[62] Nitroxyl radicals too are efficient alkly radical traps, and are regenerated though a cyclic mechanism involving CB-A and CB-D reactions.[18] This particular example will be discussed at length in sections 1.82 and 1.9.

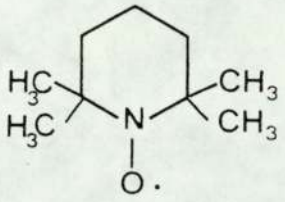
1.8.2 Nitroxyl Radicals

A recent class of compounds that have been found to be powerful alkyl radical traps are nitroxyl radicals.[18] They trap the alkyl radicals through the CB-A mechanism[18]. Nitroxyl radicals have long been known to be generated as intermediates in the oxidation of secondary amines, however their importance in the inhibition of autoxidation has been recognised only about two decades ago. The only nitroxyl

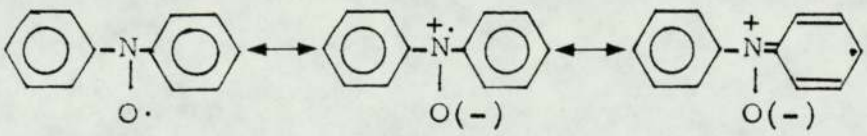
radicals which are of significance in the inhibition of autoxidation are those which are stable [64-72]. Nitroxyl radicals contain the structural group >N-O. [70-73]. Generally they are only stable when they have no hydrogens on the groups α to the nitrogen. If they do posess hydrogens then the nitroxyl radical disproportionates to the corresponding hydroxylamine and a nitrone. [64-69]



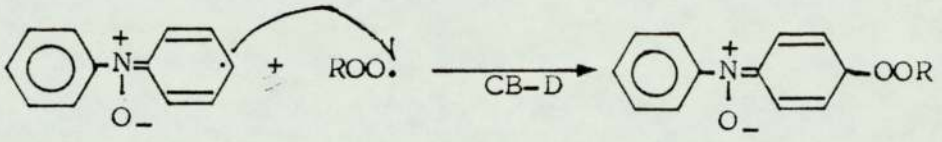
A typical stable nitroxyl radical is [70-75]



Unlike in the aliphatic series, aromatic nitroxyl radicals exhibit extensive delocalisation of the unpaired electron. Because of this delocalisation, the ortho and para ring sites are activated and are prone to oxidation inhibition



reactions by a CB-D mechanism.



In fact this reaction can lead to the destruction of the inhibitor[76].

1.8.2.1 The Role of Nitroxyl Radicals in the Stabilisation of Polymers

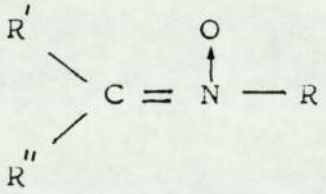
Much of the technological work done on the stabilisation of polymers with nitroxyl radicals has centered around the light protective action of sterically hindered piperidines[78-87]. Other studies have included the inhibitive action of diphenylamine on the oxidation of cumene[88], the inhibition of radiation induced chemical oxidation of n - octane by aliphatic nitroxyl radicals[89], and the inhibition of thermoxidation of a variety of hydrocarbons by arylamines, hindered piperidines and their related nitroxyl radicals and hydroxylamines[77,90]. It is now known that the protective action of these amines is due to formation and regeneration of the nitroxyl radical. The regeneration involves a cyclic mechanism with the involvement of the O-alkylated hydroxylamine and the hydroxylamine[70-83]. Studies[68,69,72,79,90] have shown that stable aliphatic nitroxyl radicals react exclusively with alkyl radicals whereas the aromatic nitroxyl radicals are able to react with alkylperoxyl radicals too. This is due to the

delocalisation of the electron over the aromatic system as described in section 1.8.2.

The hydroxylamines corresponding to the nitroxyl radicals whether aliphatic or aromatic have been reported to react exclusively with alkylperoxyl radicals by a CB-D mechanism[68]. The O - alkylated hydroxylamines derived from the nitroxyl radicals also react only with alkyl-peroxyl radicals[76,89].

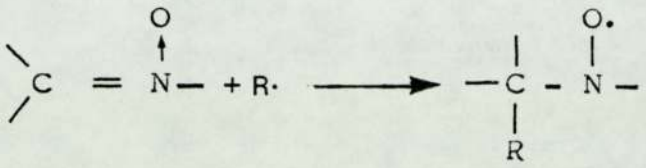
1.8.3 Nitrones

Nitrones have the general formula[91,92]



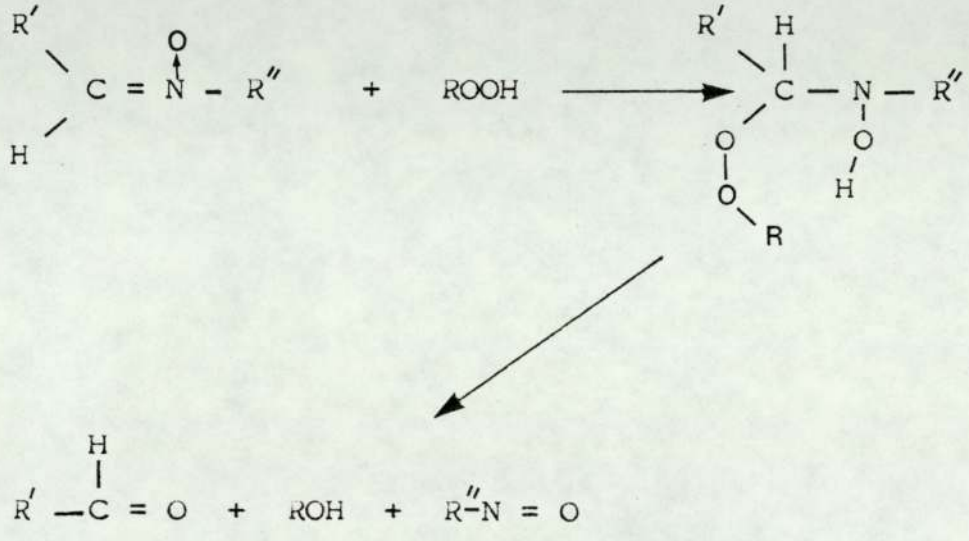
When R′ = H the nitrone is called an aldonitrone. When R′ is some other group the nitrone is a ketonitrone.

Nitrones are very efficient radical trapping agents[93,94] and have found wide usage as spin traps in many systems. They are known to react with alkyl radicals[84-87], aryl radicals[91-94] and alkoxy radicals[95]. Thus they can function by both the CB-A and CB-D antioxidant mechanisms. However, they are unable to react with peroxy radicals.



R = alkyl, aryl, RO.

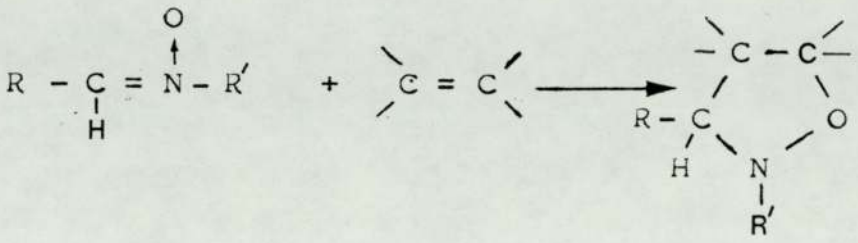
Aldonitrones can also react with hydroperoxides stoichiometically and are themselves decomposed to aldehydes and nitroso compounds[96]. (scheme 1.8)



Scheme 1.8

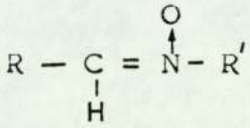
Aldonitrones have recently been used as stabilisers in polymers and have been shown to exert good melt stabilising and thermal antioxidant activity[97,98]. They have also been examined in rubber as substantive antioxidants[99]. The N - aryl nitrones were found to bind to the rubber in high yields. In contrast an N - methyl nitrone which was also tested[99] did not show any significant binding to the rubber.

The binding reaction is thought to occur by a 1, 3 - addition to the double bonds in the rubber to form a 5 - membered ring[99] (see scheme 1.9)



Scheme 1.9

An interesting feature is that for nitrones of the type



where R = phenyl, phenol or hindered phenol the normal structure - activity relationships for antioxidant efficiency do not appear to be operative[99,100]. In fact greater antioxidant efficiency was found for the nitrones containing the less hindered phenols[99].

During vulcanisation of the rubber some of the nitrones were found to be scorchy and exhibit premature curing[99].

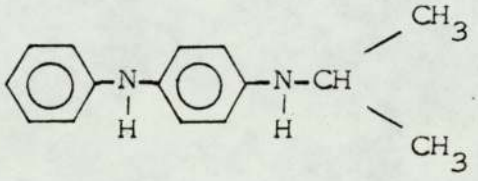
1.9 ANTIFATIGUE AGENTS FOR RUBBER

It was described in section 1.4.6 that fatigue

of vulcanised rubbers causes the activation of the rubber to oxygen by the generation of alkyl (alkenyl) radicals and by activation of the double bonds.

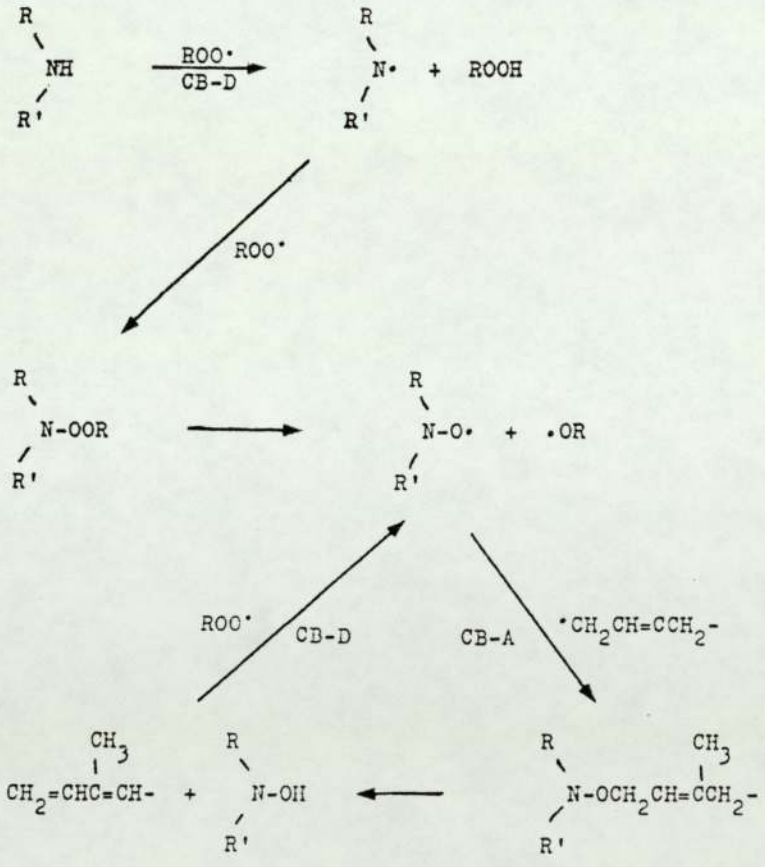
Both these processes have the effect of increasing the rate of autoxidation by introducing mechanochemically formed radicals. Fatiguing of rubber differs from thermal oxidation in that the rate of alkyl radical formation is much higher than in the latter case and the oxygen concentration is limited by diffusion. A direct consequence of this is that both alkyl and alkylperoxyl radicals are involved in the fatiguing process.

As mentioned in section 1.8 all the effective antifatigue agents are chain breaking antioxidants and among these the aromatic amines are significantly more effective than other classes of antioxidants. Typical commercial agents are 4 - alkylamino - diphenylamines, the best known agent being N - iso-propyl-N'-phenyl p-phenylene diamine (IV) (I P P D) commercially known as Santoflex I.P., Antioxidant-4010NA or Nonox ZA.



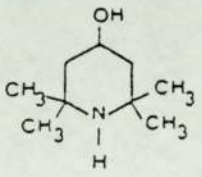
(IV)

Like the hindered phenols the aromatic amines are effective electron donor chain breaking antioxidants, but unlike the former the amines are readily oxidised to stable nitroxyl radicals. In fact it has recently been shown[18,101] that it is the derived nitroxyl radical that are primarily responsible for the antifatigue activity of these compounds. The mechanism of their action involves a cyclical regeneration process in which there is an alternating sequence of CB-A and CB-D reactions as shown in scheme 1.10.

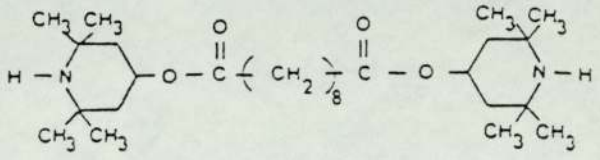


Scheme 1·10

Aliphatic amines too, based on the hindered piperidines (V and VI) were found to have a limited antifatigue activity when swelled into rubber[101]. This activity however was not as pronounced as that for the aromatic amines[101].



(V)



(VI)

(VI) is commercially used as light protective stabiliser for polyolefins and is known by the trade name "Tinuvin 770"[102].

The formation and decay of nitroxyl radicals from these amines during fatiguing was followed using the technique of electron spin resonance spectroscopy[101]. It was found that after an initial induction period the nitroxyl radical concentration built up to a maximum and then decreased to a low steady state concentration till the eventual failure of the rubber. The regeneration cycle was proposed to account for this low steady state. The presence of conjugated unsaturation and the hydroxylamine has also been detected in the rubber[101].

Kuzuminsky has suggested that these aromatic amines could also function by relinking the broken rubber chain ends at the two nitrogen sites[34].

1.9.1 Other Factors Affecting the Antifatigue Activity

It has been suggested in the literature[103,104] that migration of the antifatigue agent to the zones of crack growth is a very important criterion. If the antifatigue agent is not mobile then its protective efficiency is very limited or non-existent[103,104]. Thus network bound antioxidants such as p-nitrosodiphenylamine have been reported to be relatively ineffective as antifatigue agents[103,104]. This directly contrasts with antioxidant activity where network bound antioxidants are superior to the commercial materials[100,105]. Recent evidence[106,107] however has suggested that network bound antioxidants do infact have a certain antifatigue efficiency although in the presence of unbound material the effectiveness is much greater.

Certain sulphur containing compounds such as dilauryl β-thiopropionate and its oxidised products have been shown to have some antifatigue activity[108]. Work is still going on in this area to establish the precise mechanism by which they function.

1.10 ANTIOZONANTS

From the early days of the rubber industry, protection of stressed rubber against ozone has been achieved by the incorporation of soluble waxes and chemical antiozonants[1,6,40,42,109].

Waxes impart antiozonant protection by rising (blooming) to the surface of the rubber and forming a surface layer which effectively acts as a barrier between the ozone and the rubber surface. The waxes are supplied as two major types[110] - paraffin and microcrystalline. They differ in molecular weight and in the rate of migration to the surface.

One disadvantage of waxes is that they can only be used for static applications. Under dynamic conditions (cyclic strain) they offer no protection against the ozone as the protective film cracks leaving the rubber unprotected. Under these conditions therefore the use of chemical antiozonants is required. As with the antifatigue agents, the best protective agents against ozone cracking are N-alkyl -N′ phenyl p-phenylene diamines. N-isopropyl-N′-phenyl-p-phenylene diamine is commercially used widely as an antiozonant. N, N′- dialkyl-p-phenylene diamines, especially the heptyl and octyl derivatives are reported to be even more effective for static applications[1,40].

When chemical antiozonants are used in combination with small amounts of waxes the ozone cracking protection is enhanced[1,2,34,40]. The action of the wax is described as "carrying" the antiozonant to the surface of the rubber.

The mechanism of activity of the para-phenylenediamines has been subject to a great deal of controversy. Several different theories have been proposed. They are:[111]

(a) the scavenger mechanism. This theory suggests that the antiozonant diffuses to the surface where it competes with the double bonds for ozone.

(b) the protective film theory. This theory suggests the antiozonant migrates to the surface of the rubber, reacts with the ozone and forms a protective layer over the rubber surface thus preventing the ozone from contacting the rubber surface.

(c) the relinking theory. This theory states that the antiozonant recombines the rubber chains broken during the ozonolysis.

(d) the self healing theory. This theory states that the antiozonant reacts with the zwitterion or ozonide to give a low molecular weight inert self healing film on the rubber surface.

In fact all four of these mechanisns could contribute during the protective action of the antiozonants. Probably the scavenger mechanism is the most important.

Aromatic amines are known to react with ozone to give a variety of products including nitroxyl radicals, nitroso alkyls, nitroso aryls, oximes and nitro compounds[112,114]. N-isopropyl-N'-phenyl-p-phenylenediamine is known to consume three molecules of ozone per molecule of inhibitor[114]. Most aromatic nitroxyl radicals themselves however do not have any significant antiozonant activity[34].

Recently [115,116] the Malasian Rubber Producer's Research Association have developed a new class of antiozonants based on para-phenelenediamines bearing side chains containing selenide linkages. These are reported to react much more rapidly with ozone than the para-phenylenediamines themselves, and act as superior chemical antiozonants for rubber vulcanisates.

It has been found that certain bound antioxidants too can impart some antiozonant protection to rubber[117]. Further investigations into this area are in progress.

1.11 ANTIFLEX CRACKING AGENTS

All the effective antiflex cracking agents are antioxidants

of the secondary aryl amine class[1,40]. Their mode of action is probably a combination of that described for the antifatigue and antiozonant activities.

1.12 STAINING AND DISCOLOURATION

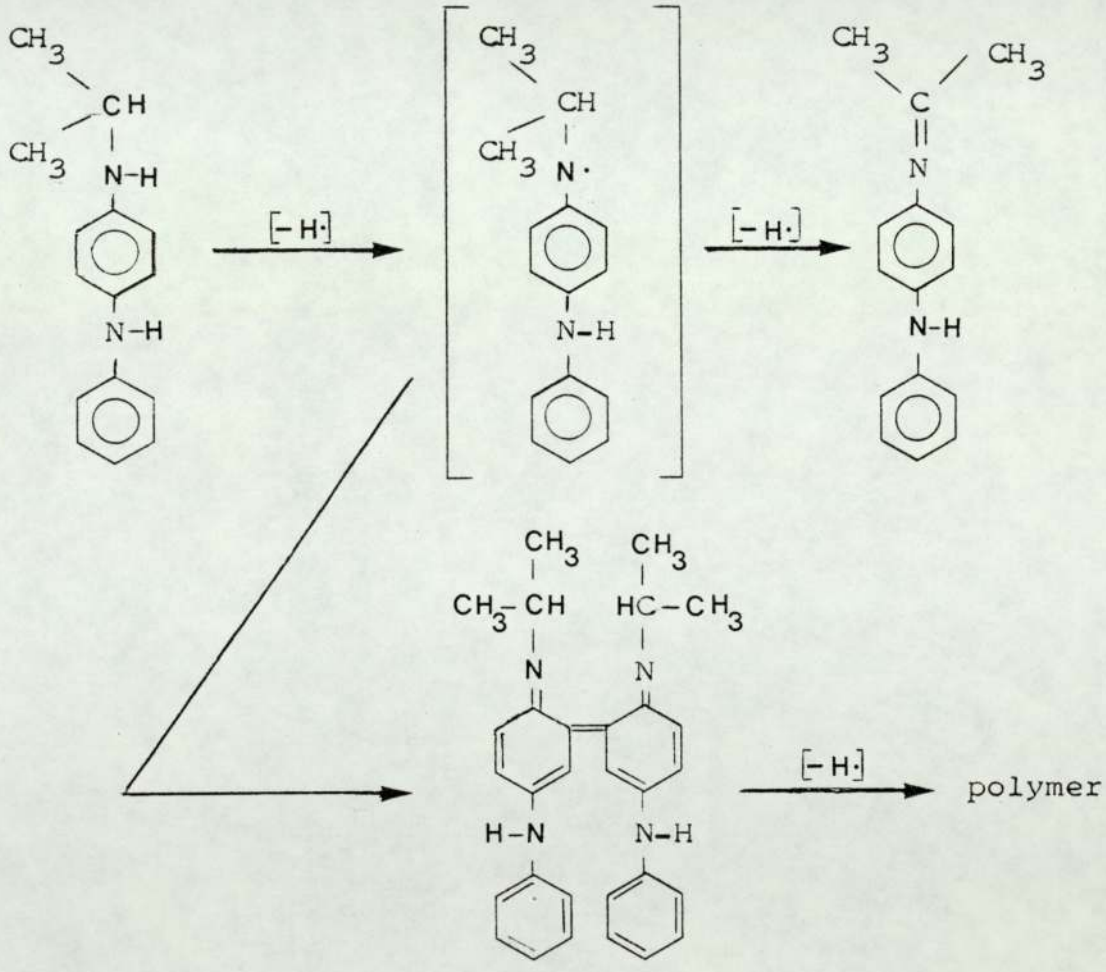
A disadvantage of the aryl amine antioxidants is that they cause severe discolouration and staining of the rubber. By definition[118] a non-discolouring antioxidant is one which does not discolour the rubber to which it has been added, even after exposure to heat and light. A non-staining antioxidant is one which does not discolour another surface onto which it has migrated.

For most applications discolouration of the rubber is not important, especially since the largest outlet for antioxidants is in tyres where carbon black is used[119].

However a wide variety of light coloured vulcanised products are manufactured today. These include industrial products such as hoses, and beltings; shoe products such as shoe soles, insoles and waterproof wear; domestic products such as rug underlays, insulation, gaskets and toys and a variety of latex products. Recently white side tyre walls have become popular especially in the United States of America[120]. All these goods are protectd with non-staining antioxidants. Most of these are of the

hindered phenol class and do not possess significant antifatigue, antiflex cracking or antiozonant activities.

The discolouration and staining caused by the para-phenelene diamines is due to the formation of conjugated dehydro-dimers and trimers which are insoluble in the rubber system and migrate to the surface. The mechanism[1] of formation of these conjugated dimers and trimers is represented in scheme 1.11



Scheme 1.11

Because of the increasing use of light coloured rubbers for many applications, the development of a suitable non-discolouring/non-staining antifatigue agent or antiozonant would be of significant commercial value.

1.13 SCOPE AND OBJECTIVES OF THE PRESENT WORK

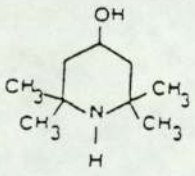
In section 1.9 it was shown that aromatic amines owe their antifatigue activity to the derived nitroxyl radical. Nitroxyl radicals are powerful alkyl radical traps and during fatiguing they function as such terminating the maro-alkyl radicals that are produced in the rubber. Their action involves a cyclical regeneration mechanism where both alkyl and alkylperoxyl radicals are removed from the system (scheme 1.10).

Hindered piperidines too (structure V and VI or TMP, TMPS; table 2.1) have been found to exhibit some anti-fatigue activity when swelled into rubber[101] and their mode of action is believed to be similar to the commercial antifatigue agent, IPPD (IV) involving the formation and regeneration of the nitroxyl radical.

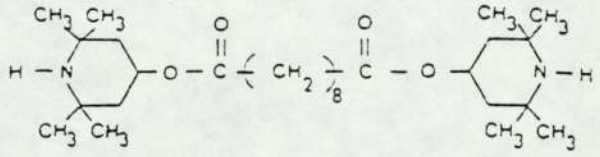
The regeneration of the nitroxyl radical may proceed through the O-alkylatedhydroxylamine but definitely through the hydroxylamine intermediate since it is also accompanied by the formation of conjugated unsaturation.

The hydroxylamine and conjugated unsaturation have already been detected in the rubber during the anti-fatigue action of the amines[101]. However neither the hydroxylamine nor the O-alkylated hydroxylamine have been tested as antifatigue agents in rubber.

In the first part of this work, nitroxyl radicals and hydroxylamines of the hindered piperdines series will be synthesised, incorporated into the rubber during the compounding stages and tested for antifatigue activity in the rubber. Their performance will be compared to the activity of the parent amine. The parent amines will have the structures shown below (V and VI).



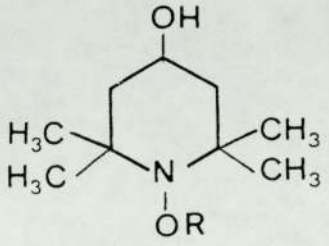
(V)



(VI)

The contributory role of the hydroxylamine and the O-alkylated hydroxylamine to the overall antifatigue mechanism of the nitroxyl radical will be studied.

For this purposes attempts will be made to synthesis O-alkylated hydroxylamines of type VII, where the nature of R will be changed from primary to tertiary alkyl groups and their antifatigue performance in the rubber will be assessed.



(VII)

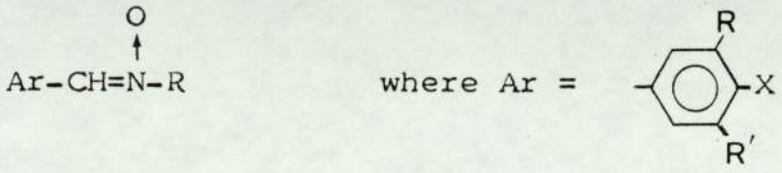
Mechanistic work involving a study of the regeneration of the nitroxyl radical from V will be undertaken both in solution (squalene) and in the rubber. The purpose of this study is to establish the role of the rubber alkylated hydroxylamine in the overall antifatigue mechanism.

The antifatigue activity of the hindered piperidines and their derived nitroxyl radicals and hydroxylamines will be compared with the commercial agent IPPD. Appropriate modifications to the structure of the piperidines will be made to improve their activity if required. The modifications will involve the attachment of peroxide decomposing groups such as disulphides and also the attachment of CB-D antioxidant functions on to the base nitroxyl radical (i.e. the synthesis and evaluation of

compounds such as TMOPX and BPTMOP shown in table 2.1).

The effect of these compounds on the vulcanisation characteristics will also be studied.

In the second part of this work nitroxyl radical precursors, especially nitrones of the type VIII, will be synthesised and tested for antifatigue activity in the rubber.



VIII

The nature of the substituents on Ar will be varied as shown in table 2·1 in order to assess the contributory effects of Ar to the antifatigue activity of the nitrone. The nature of R will also be changed from primary alkyl to tertiary alkyl in order to optimise activity. The curing characteristics of these compounds will also be assessed. The effects of premilling the nitrones with the rubber prior to the compounding operations and the mechanism of the antifatigue activity of nitrones will also be studied.

All the compounds will be evaluated for other technological performance in the rubber with special emphasis given to those compounds having good anti-fatigue activity. The technological studies will include:

a) a study of antiozonant activity,

b) a study of antioxidant activity,

c) a study of the discolouration and staining properties of the additives.

Combinations of compounds which have good antifatigue activity with those having good antioxidant or good antiozonant properties will also be assessed.

In addition the technologically acceptable compounds will be studied for antifatigue, antiozonant and antioxidant activity in carbon black filled rubbers.

Finally the technological performance of the compounds will be compared with the commercially available stabilisers IPPD, HPPD and WSP (see table 2·1 for structures and names).

IPPD (Santoflex IP) is a commercial antifatigue agent and antiozonant.
HPPD (Santoflex 77) is a commercial static antiozonant.
WSP (Permanax WSP) is a commercial non-discolouring antioxidant.

CHAPTER TWO

THE SYNTHESES

2.1 LIST OF COMPOUNDS

The compounds listed in table 2.1 were either purchased or synthesised and evaluated in the rubber for their technological activity.

The I.U.P.A.C. Nomenclature[121] for these compounds is listed in table 2.2

2.2 GENERAL METHODS FOR THE PREPARATIONS

2.2.1 General Syntheses for the Nitroxyl Radicals

Stable nitroxyl radicals may be synthesised by the following general methods[70-74, 122-126]:-

1) the dehydrogenation of N,N′-disubstituted hydroxylamines.
2) the oxidation of secondary amines.
3) the reduction of nitro and nitroso compounds.
4) the reaction of nitroso compounds with Grignard reagents.
5) the addition of free radicals to nitrones.

TABLE 2.1

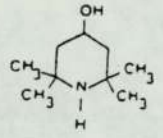
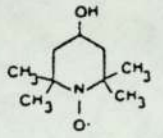
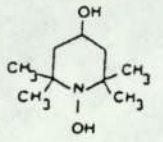
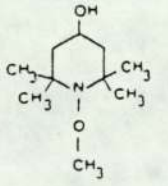
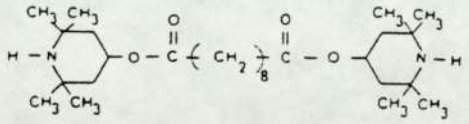
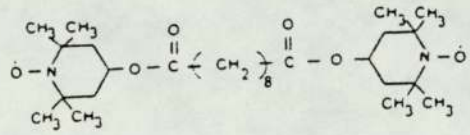
CODE NAME	STRUCTURE	NOMENCLATURE	SOURCE
TMP		2,2,6,6-tetramethyl-4-piperidinol	purchased (see section2.3)
TMOP		2,2,6,6-tetramethyl-1-oxyl--4-piperidinol	synthesised (section 2.4.1)
TMPD		2,2,6,6-tetramethyl-1,4--piperidinediol	synthesised (section 2.4.2)
TMMP		2,2,6,6-tetramethyl-1-methoxyl-4-piperidinol	synthesised (section 2.4.3)
TMPS		Bis(2,2,6,6--tetramethyl -4-piperidyl) sebacate	donated (see section 2.3)
TMOPS		Bis(2,2,6,6--tetramethyl -1-oxyl-4-piperidyl) sebacate	synthesised (section 2.4.4)

Table 2.1 continued

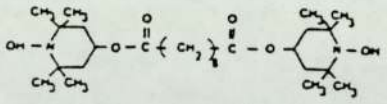
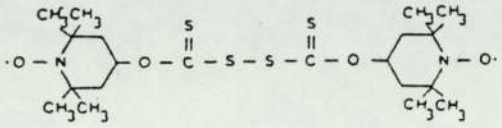
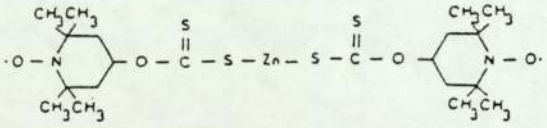
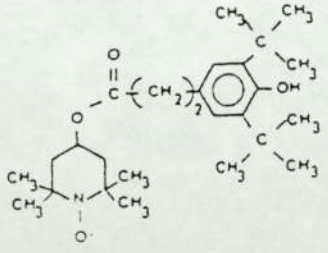
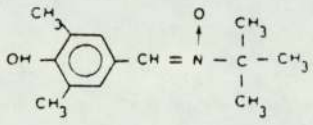
TMPDS		Bis(2,2,6,6--tetramethyl--4-piperidyl--1-ol)sebacate	synthesised (section 2.4.5)
TMOPX		Bis(2,2,6,6--tetramethyl--1-oxyl-4--piperidyl) dixanthogenate	synthesised (section 2.4.6
TMOXPZ		Bis(2,2,6,6--tetramethyl--1-oxyl-4--xanthogenato-piperidyl) zincate	synthesised (section 2.4.7)
BPTMOP		4-(3,5-ditert-iarybutyl-4--hydroxyphenyl--1-propianato) 2,2,6,6-tetramethyl-1-oxyl--piperidine.	synthesised (section 2.4.8)
MHPBN		α-(3,5-dimethyl -4-hydroxy-: phenyl)-N-tertiarybutylnitrone	synthesised (section 2.4.9)

Table 2.1 continued

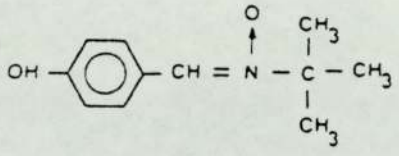
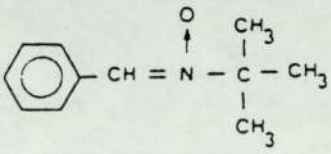
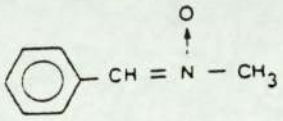
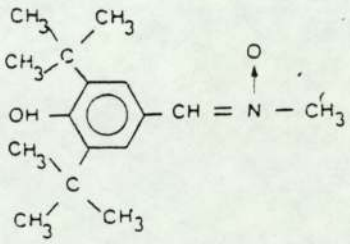
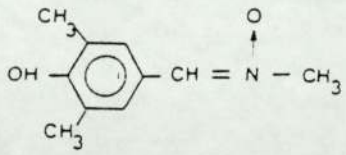
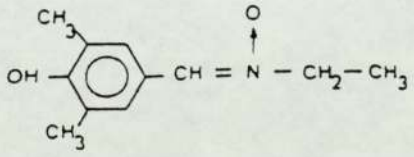
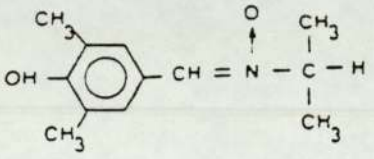
HPBN		α-(4-hydroxy-phenyl)-N-tert-iarybutyl-nitrone	synthesised (section 2.4.10)
PBN		α-phenyl-N-tertiarybutyl-nitrone	synthesised (section 2.4.11)
PMN		α-phenyl-N-methylnitrone	synthesised (section 2.4.12)
BHPMN		α-(3,5-diter-tiarybutyl-4--hydroxyphenyl)-N-methylnitrone	synthesised (section 2.4.13)
MHPMN		α-(3,5-dimethyl--4-hydroxy-phenyl)-N-methylnitrone	synthesised (section 2.4.14)
MHPEN		α-(3,5-dimethyl--4-hydroxy-phenyl)-N-ethylnitrone	synthesised (section 2.4.15)
MHPPN		α-(3,5-dimethyl--4-hydroxy-phenyl)-N-isopropyl-nitrone	synthesised (section 2.4.16)

Table 2.1 continued

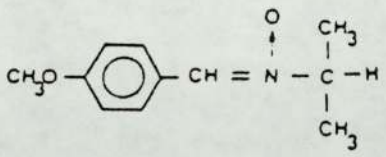
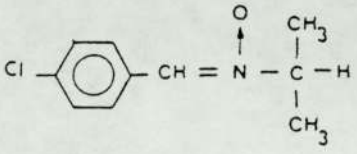
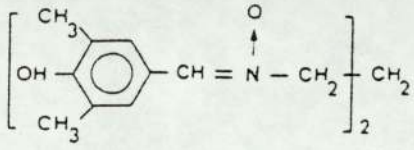
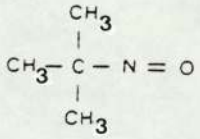
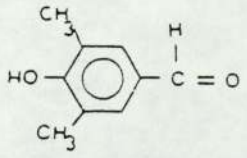
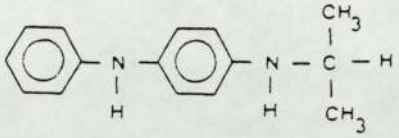
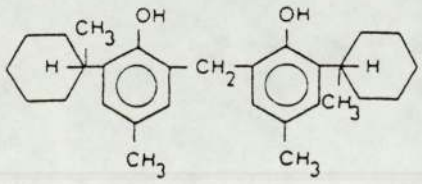
MPPN		α-(4-methoxy-phenyl)-N-iso-propylnitrone	synthesised (section 2.4.17)
CPPN		α-(4-chloro-phenyl)-N-iso-propylnitrone	synthesised (section 2.4.18)
BMHPPN		Bis(α-(3,5-di-methyl-4-hydro-xyphenyl))-1,3--N-propyl-nitrone	synthesised (section 2.4.19)
MNP		2-methyl-2--nitroso-propane	synthesised (section 2.4.20)
MHB		3,5-dimethyl--4-hydroxy-benzaldehyde	synthesised (section 2.4.9)
IPPD		N-phenyl-N′-isopropyl-p--phenlene diamine	purchased (section 3.2)
WSP		2,2′-dihydroxy-3,3′-di(α-methyl-cyclohexyl)-5,5′-dimethyldi-phenyl-methane	purchased (section 3.2)

Table 2.1 continued

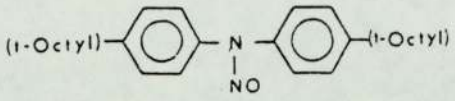
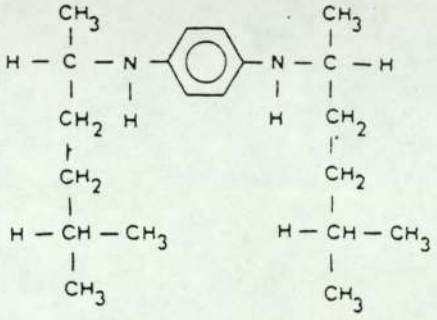
NODP		4,4′-ditertiaryoctyl-N--nitrosodiphenylamine	synthesised by H.S. Dweik and kindly given for testing
HPPD		N,N′-di(1,4--dimethyl--pentyl)-p--phenlenediamine	purchased (see section 3.2)

TABLE 2.2

CODE NAME	I.U.P.A.C. NOMENCLATURE
TMP	2,2,6,6-tetramethyl-4-piperidinol
TMOP	2,2,6,6-tetramethyl-1-oxyl-4-piperidinol
TMPD	2,2,6,6-tetramethyl-1,4-piperidinediol
TMMP	2,2,6,6-tetramethyl-1-methoxyl-4-piperidinol
TMPS	Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate
TMOPS	Bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) sebacate
TMPDS	Bis(2,2,6,6-tetramethyl-1-hydroxy-4-piperidyl) sebacate
TMOPX	Bis(2,2,6,6,-tetramethyl-1-oxyl-4-piperidyl) dixanthagonate
TMOXPZ	Bis(2,2,6,6-tetramethyl-1-oxyl-4-xanthagenato-piperidyl) zincate
BPTMOP	4(3,5-di-(tert-butyl)-4-hydroxy-1-propianato-phenyl) 2,2,6,6-tetramethyl-1-oxyl-piperidine
MHPBN	N-(3,5-dimethyl-4-hydroxybenzylidene)tert-butyl-amine N-oxide
HPBN	N-(4-hydroxybenzylidene)tert-butylamine N-oxide

Table 2.2 continued

PBN	N-benzylidene-tert-butylamine N-oxide
PMN	N-benzylidene methylamine N-oxide
BHPMN	N-(3,5-di-tert-butyl-4-hydroxybenzylidene) methylamine N-oxide
MHPMN	N-(3,5-dimethyl-4-hydroxybenzylidene)methylamine N-oxide
MHPEN	N-(3,5-dimethyl-4-hydroxybenzylidene)ethylamine N-oxide
MHPPN	N-(3,5-dimethyl-4-hydroxybenzylidene) isopropylamine N-oxide
MPPN	N-(4-methoxybenzylidene)isopropylamine N-oxide
CPPN	N-(4-chlorobenzylidene)isopropylamine N-oxide
BMHPPN	Bis(N-(3,5-dimethyl-4-hydroxybenzylidene)) 1,3-propyldiamine N-oxide
MNP	2-methyl-2-nitrosopropane
MHB	3, 5-dimethyl-4-hydroxybenzaldehyde
IPPD	N-phenyl-N′-isopropyl-p-phenylenediamine
WSP	2,2′-dihydroxy,3,3′-di(α-methylcyclohexyl)5,5′-diphenylmethane

Table 2.2 continued

NODP	4, 4′-di-tert-octyl-N-nitroso-diphenylamine
HPPP	N, N′-di(1, 4-dimethylpentyl)-p-phenylene diamine

2.2.2 General Syntheses for the Hydroxylamines

The best method for synthesising hydroxylamines involves the reduction of nitro and nitroso compounds[94,127,128]. Other methods include:-[94,129-131]

1) the alkylation of a mono-or disubstituted hydroxyl amine.
2) the elimination of an olefin from an N-oxide.
3) the reduction of nitrones.
4) the addition of Grignard reagents to nitrones, nitroso compounds or nitro compounds.
5) the reduction of stable nitroxyl radicals with mild reducing agents.

2.2.3 General Syntheses for the O-Alkylated Hydroxylamines

A variety of methods can be used to synthesise acyclic N, N'- O-trisubstituted hydroxylamines[92,129]. For the cyclic series however there are only two or three general methods of preparation. These include:-[79,92,129-141]

1) the alkylation of a hydroxyl amine.
2) the reaction of stable nitroxyl radicals with Grignard reagentsand with lithium alkyls.
3) the radical addition to nitroxyl radicals.
4) the 1,3 radical addition to nitrones.
5) the Meisenheimer rearrangement of trisubstituted amine oxides.

2.2.4 General Syntheses for the Nitrones

There are a number of general methods for the synthesis of nitrones. However the three most important methods are:-[91,92]

1) the hydroxylamine - carbonyl condensation reaction.
2) the alkylation of oximes.
3) the oxidation of N-substituted imines (azomethines).

2.3 LIST OF CHEMICALS AND STARTING MATERIALS

1) 2,2,6,6 tetramethylpiperidine-4-ol (Aldrich Chemical Company).
2) Bis 2,2,6,6 tetramethyl-4-piperidyl sebacate (Tinuvin 770) (kindly donated by Ciba Geigy - Manchester).
3) 30% W/V Hydrogen peroxide (B.D.H. Chemical Company).
4) m-Chloroperbenzoic acid (Aldrich Chemical Company)
5) Sodium tungstate (Aldrich Chemical Company).
6) Hydrazine hydrate (Aldrich Chemical Company).
7) Carbon disulphide (Aldrich Chemical Company).
8) Zinc sulphate (Aldrich Chemical Company).
9) 3,5 ditertary butyl-4-hydroxy benzoic acid.
10) Tertiarybutylamine (Aldrich Chemical Company).
11) 2,6, xylenol (Aldrich Chemical Company).
12) Boric acid (Aldrich Chemical Company).
13) Hexamethylenetetraamine (Aldrich Chemical Company).

14) Benzaldehyde (Aldrich Chemical Company).

15) 4-hydroxy benzaldehyde (Aldrich Chemical Company).

16) 3,5, ditertiarybutyl-4-hydroxybenzaldehyde (Aldrich Chemical Company).

17) Anisaldehyde (Aldrich Chemical Company).

18) P-chloro-benzaldehyde (Aldrich Chemical Company).

19) Nitromethane (B.D.H. Chemical Company).

20) Nitroethane (Aldrich Chemical Company).

21) 2-Nitropropane (Aldrich Chemical Company).

22) 1,3, diaminopropane (Aldrich Chemical Company).

23) Zinc dust (B.D.H. Chemical Company).

24) Ammonium chloride (Aldrich Chemical Company).

2.4 THE SYNTHESES

2.4.1 2,2,6,6- Tetramethyl-1-oxyl-4-piperidinol (TMOP)

This compound was synthesised according to the procedure described by Rassat et al[122] by the oxidation of 2,2,6,6-tetramethyl-4-piperidinol (TMP) using 30% hydrogen peroxide catalysed by sodium tungstate. 20g (0.127 moles) T.M.P was used. The yield was 21.2g (0.123 moles; 95% of the theoretical). Melting point: recrystallised 70-72°C (lit: 72°C)[122].

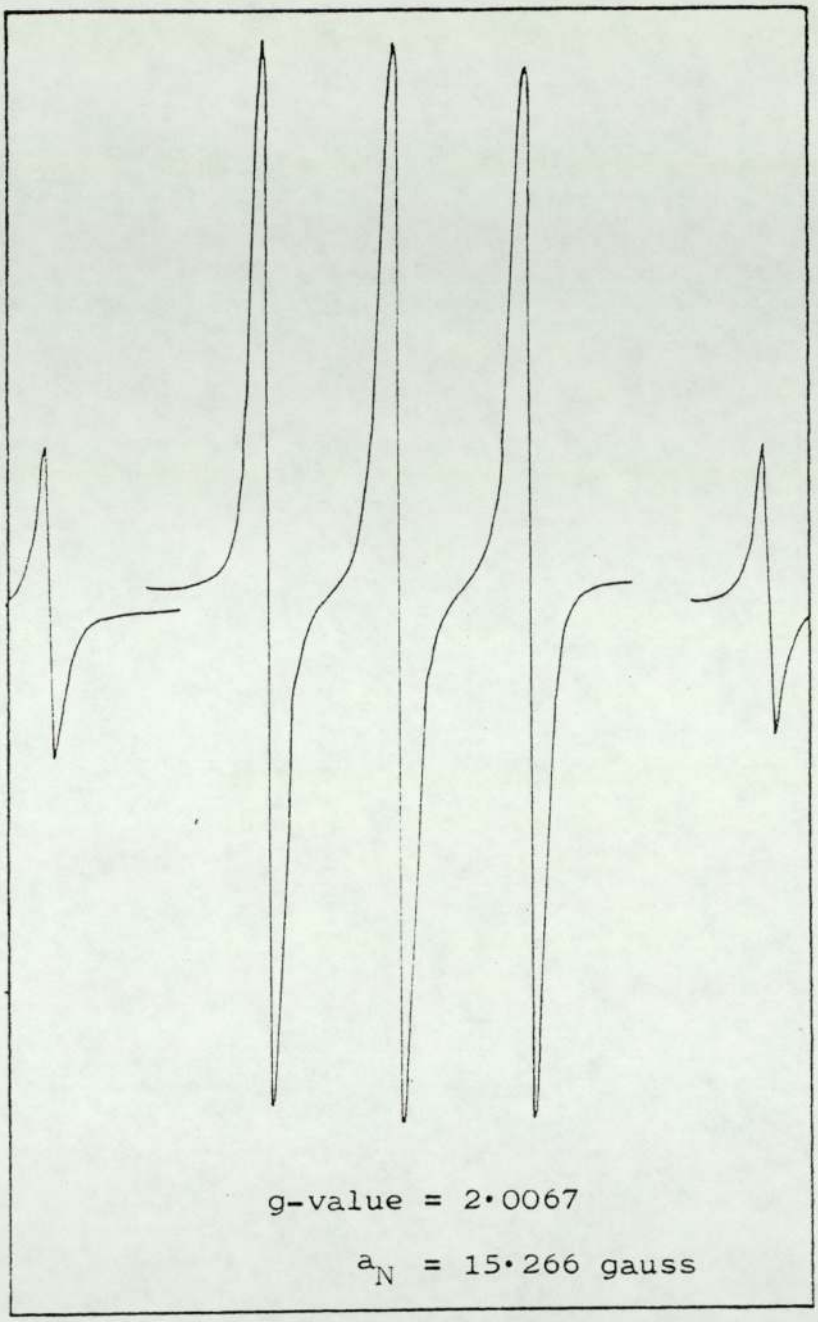


Fig. 2·1: E.s.r. spectrum of TMOP in benzene
Field = 3280 ± 100G; amptitude = 1·5 x 10;
mod-width = 1·1 x 1; output = 8 M.v;
sweep time = 4 minutes

Analytical date:-

(i) Elemental analysis

calculated for $C_9H_{18}NO_2$

element	C	H	N
expected	62.8	10.5	8.1
found	62.9	10.7	9.1

(ii) U.V. analysis: (cyclohexane solvent)
strong absorbance at λ = 248 n.m., weak absorption at λ = 410 n.m extending over the whole visible region.

(iii) Infrared analysis: (K Br disc)
disappearance of absorbance band at 3230 cm^{-1} (N-H stretch of amine); New absorbance at 1355 cm^{-1} (N-O· stretch not shown in parent amine).

(iv) e.s.r. analysis: (in benzene).
The spectrum is a triplet. It is shown in figure 2.1; g-value = 2.0067; a_N = 15.266 gauss.

2.4.2 2,2,6,6-Tetramethyl-1,4-piperidinediol. (TMPD)

This compound was prepared according to the method described by Rozantsev et al[131], using hydrazine hydrate to reduce the TMOP. 10.0g (0.058 moles) TMOP was used. Yield: 7.42g (0.0475 moles; 82% of the throretical).

Melting point: 155-157°C (lit.: 157°C)[131].

Analytical data:-

(i) Elemental analysis:

calculated for $C_9H_{19}NO_2$

element	C	H	N
expected	62.4	10.9	8.1
found	62.3	10.7	8.0

(ii) U.V. analysis:

No absorption in the U.V. or visible region.

(iii) Infrared spectroscopy analysis: (K Br disc)

Disappearance of the absorbance band at 1355 cm^{-1} (N-O· stretch); New absorbtion bands at 1490 cm^{-1} (probably N-OH stretches).

(iv) No e.s.r. spectrum obtained.

2.4.3 2,2,6,6-Tetramethyl-1-methoxyl-4-piperidinol (TMMA)

This compound was synthesised by trapping methyl radicals using TMOP. A clean source of methyl radicals was obtained by the sliver catalysed decarboxylation of acetic acid[142,143].

To 3.40g (0.02 moles) TMOP dissolved 100 ml water, 0.678g

(0.006 moles) silver nitrate was added and dissolved under an atmosphere of nitrogen. 13.8g (0.06 moles) ammonium persulphate dissolved in 20 ml water was added into the reaction mixture over a period of 10 minutes. The reaction mixture was heated at 60-70°C on a waterbath and stirred magnetically until the colour disappeared. The orange colour disappears within four hours and the solution takes on a pale yellow colour. The reaction mixture was heated at 60°C for a further 20 hours. After the reaction time, the solution was allowed to cool and solid sodium bicarbonate was added into the solution till the latter became neutral to litmus paper (B.D.H. Universal litmus paper). The neutral reaction mixture was extracted exhaustively with dichloromethane. The dichloromethane extracts were dried over anhydrous magnesum sulphate and evaporated under reduced pressure at room temperature. A yellow/red product was obtained. This residue was redissolved in dichloromethane(50ml) and cyclohexane added. (Cyclohexane was found to be a non-solvent by trial and error). A pale off white/cream precipitate was formed which was separated by filteration. Yield: 1.63g (0.0087 moles; 43% of theoretical). Melting point 131-133°C (melts and decomposes; becomes red).

Analytical data:-

(i) Elemental analysis:

calculated for $C_{10}H_{21}NO_2$

element	C	H	N
% expected	64.2	11.2	7.5
% found	64.8	11.5	7.8

(ii) Mass spectroscopy

parent peak at 172 (loss of $CH_3\cdot$).

(iii) Infrared analysis: (K Br disc)

absorption band at 1335 cm^{-1} (nitroxyl stretch) disappears. New bands appear at 1338 cm^{-1}, 1218 cm^{-1}, 920 cm^{-1} and 745 cm^{-1} (probably correspond to N-O-Me stretches).

These bands are not present in the infrared spectra of the TMP, TMOP, and TMPD. The absorption band at 1218 cm^{-1} characteristic of ether stretch[144] appears very strongly in the spectrum for TMMP but appears very weakly in the spectrum of the other compounds.

2.4.4 Bis (2,2,6,6-Tetramethyl-1-oxyl-4-piperidyl) sebacate (TMOPS)

To a solution of 4.8g (0.01 moles) of Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TMPS; section 2.3) dissolved in 200ml ether, 8.1g (0.04 moles) m-chloroperbenzoic acid

was added in powder form with stirring over a period of 1 hour. The reaction solution was stirred magnetically for 24 hours at room temperature. At the end of this period the colour of the solution was deep red. The solution was then washed four times with 5% sodium bicarbonate solution (50ml each time) and the ether layer dried over anhydrous magnesium sulphate. The ether was evaporated to dryness under reduced pressure and the orange red residue (powder) was recrystallised from absolute ethanol. Orange crystals were formed. Yield: 3.8g (0.075 moles; 75% of theoretical). Melting point 99-101°C. (lit.:101°C)[145].

Analytical data:

(i) Elemental Analysis:

calculated for $C_{28}H_{50}N_2O_6$

element	C	H	N
% expected	65.8	9.8	5.5
% found	65.2	9.9	5.8

cf. : parent amine:

calculated for $C_{28}H_{52}N_2O_4$

element	C	H	N
% expected	70.0	10.8	5.8
% found	71.8	11.2	6.7

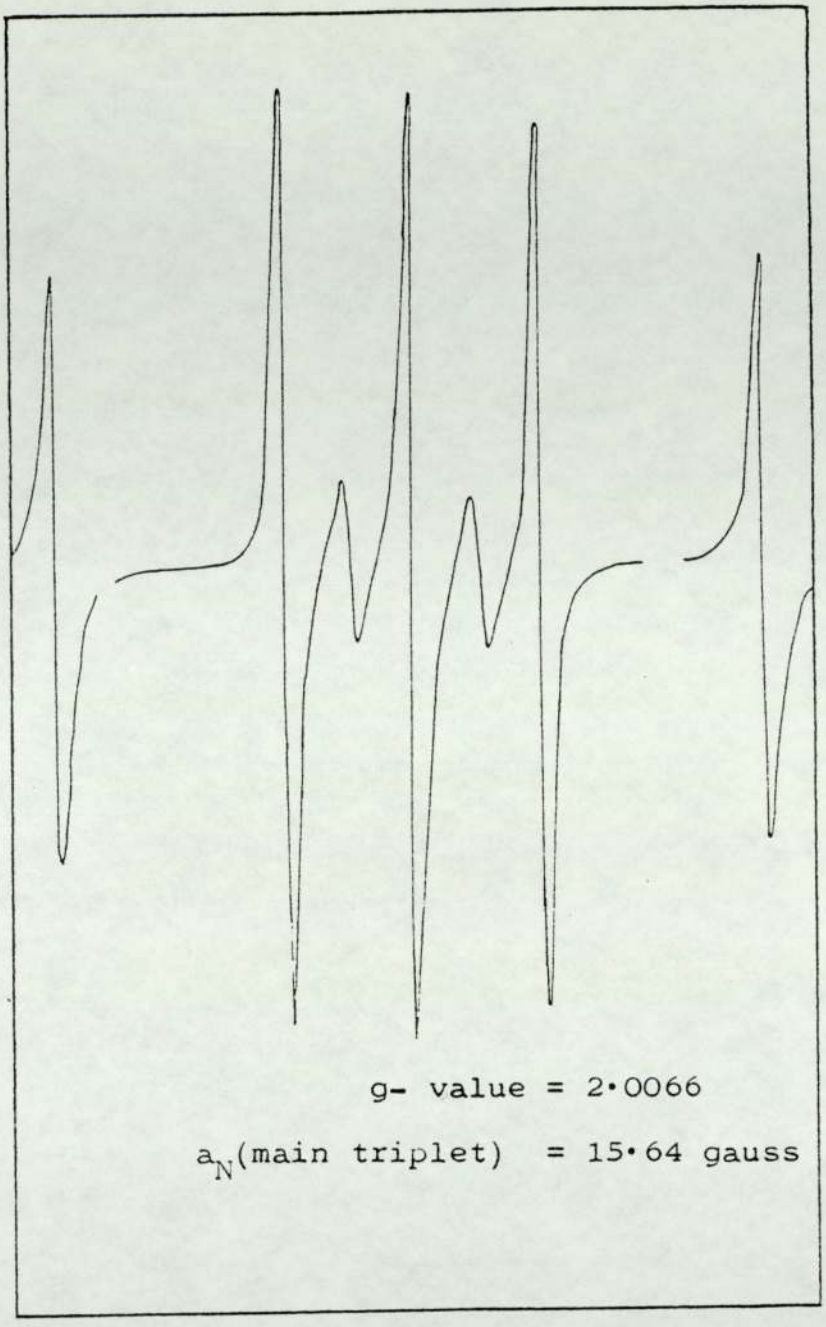


Fig. 2·2: E.s.r. spectrum of TMOPS in benzene
Field = 3300 ± 100G; amplitude = 2·2 x 10;
mod-width = 1·1 x 1; output = 8 m.v;
sweep time = 4 minutes

(ii) U.V. analysis : (cyclohexane solvent)
strong absorbance at 240 n.m. and 450 n.m.
(infact whole of visible region)
Parent amine shows no absorption.

(iii) Infrared analysis : (K Br disc)
Band at 3600 cm^{-1} (N-H stretch) disappears. New absorption band at 1365 cm^{-1} (nitroxyl N-O· stretch).

(iv) e.s.r. analysis : (in benzene)
The spectrum is a quintuplet; g-value = 2.0066, a_N (main triplet) = 15.64 gauss. The spectrum is shown in figure 2.2. The tendency to form five lines is due to long range spacial interaction of the unpaired electrons[145].
Attempts to prepare TMOPS by oxidation of TMPS with hydrogen peroxide were not successful. A red resinous material formed which did not crystallize even though the reaction period in some cases was three weeks.

2.4.5 Bis(2,2,6,6-Tetramethyl-4-piperidyl-1-ol)sebacate (IMPDS)

The general method of Rozantsev el al [131] was modified as follows:

4.5 ml (0.09 moles) of hydrazine hydrate was added to a solution of chloroform (100 ml) containing 3.0g (0.006 moles) of TMOPS. The mixture was then refluxed until decolourised (faint yellow colour). A white precipitate had formed at the end of this period. This was filtered, washed with fresh chloroform (20 ml) and dried under vacuo. Yield: 1.2g (0.0024 moles; 40% of theoretical). Melting point: 168-170°C .

Analytical data:-

(i) Elemental analysis:

calculated for $C_{28}H_{52}N_2O_6$

element	C	H	N
% expected	65.6	10.2	5.5
% found	65.3	10.2	5.8

(ii) Infrared analysis: (KBr disc)

Disappearance of the absorbance band of 1365 cm^{-1} (Nitroxyl stretch) and new absorption bands appear at 1460 cm^{-1}, 3020 cm^{-1}, 3280 cm^{-1} and 3400 cm^{-1} (probably N-OH stretching and bending frequencies). The parent amine TMPS does not have any of these infrared bands. The NH stretching frequency appears at 3320 cm^{-1}.

2.4.6 Bis(2,2,6,6-Tetramethyl-1-oxyl-4-piperidyl) dixanthogenate (TMOPX)

This compound was prepared according to the method described by Kirchenko and Medzhikov[146] via the potassium salt of the 2,2,6,6-tetramethyl-1-oxyl--piperidine-4-xanthogenate. (TMOPXK).

10.00g (0.056 moles) TMOP was used. The yield of the TMOPXK was 13.0g (0.045 moles; 80% of theoretical).

For the synthesis of the disulphide, 3.0g (0.01 mole) of TMOPXK was used. Yield: 1.97g (0.004 moles; 40% of theoretical). Melting point: 134-137°C (lit.:136°C)[146].

Analytical data for the dixanthogenate:-

(i) Elemental analysis

calculated for $C_{20}H_{34}N_2O_4S_4$

element	C	H	N	S
expected	48.5	6.9	5.9	25.9
found	48.0	6.9	6.2	28.2

(ii) Infrared analysis: (KBr disc).

540 cm^{-1} (c-s stretch)

470 cm^{-1} 490 cm^{-1}, 500 cm^{-1} s-s stretch.

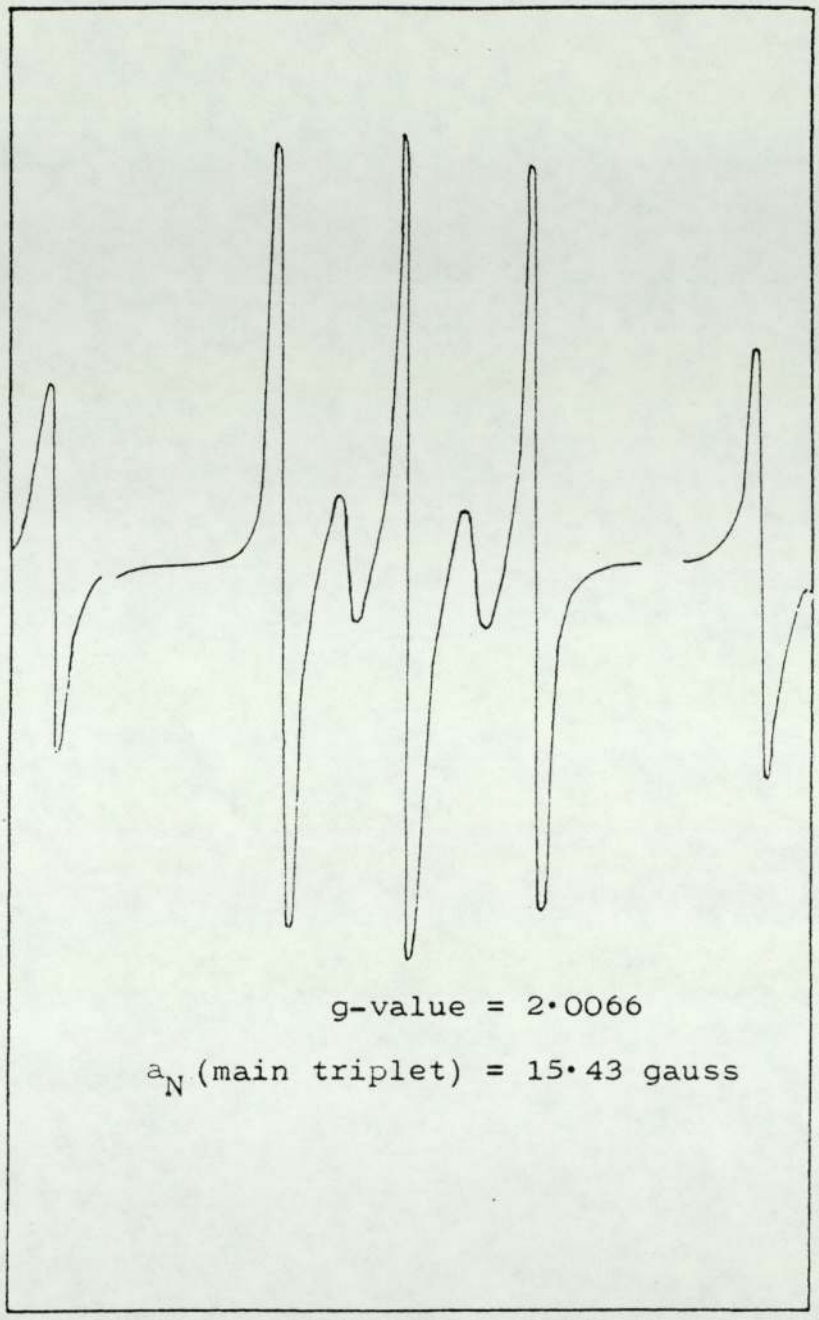


Fig. 2·3: E.s.r. spectrum of TMOPX in acetone
Field = 3280 ± 100G; amplitude = 2·4 x 10;
mod-width = 1·2 x 1; output = 10 m.v.;
sweep time = 4 minutes

(iii) e.s.r. analysis (in acetone)

The spectrum in a quintuplet; g-value = 2.0066; a_N (main triplet = 15.43 gauss. It is shown in figure 2.3. The quintuplet is due to long range inter and intra molecular exchange reactions between the unpaired electrons[146].

2.4.7 Bis(2,2,6,6-Tetramethyl-1-oxyl-4-xanthogenato-piperidyl) zincate. (TMOXPZ)

This compound was prepared according to the procedure of Kirchenko and Medzhikov[146] from the TMOPXK.

3.0g (0.1 moles) of TMOPXK was used. Yield: 2.96g (0.053 moles; 53% of the theoretical). Melting point: decomposes at 157 -160°C.

Analytical data:-

(i) Elemental analysis:

calculated for $C_{20}H_{34}N_2O_4S_4Zn$

element	C	H	N	S
expected	42.9	6.1	5.0	22.9
found	44.1	6.8	4.9	24.4

(ii) Infrared analysis: (KBr disc)

strong band at 620 cm^{-1} (c-s stretch)

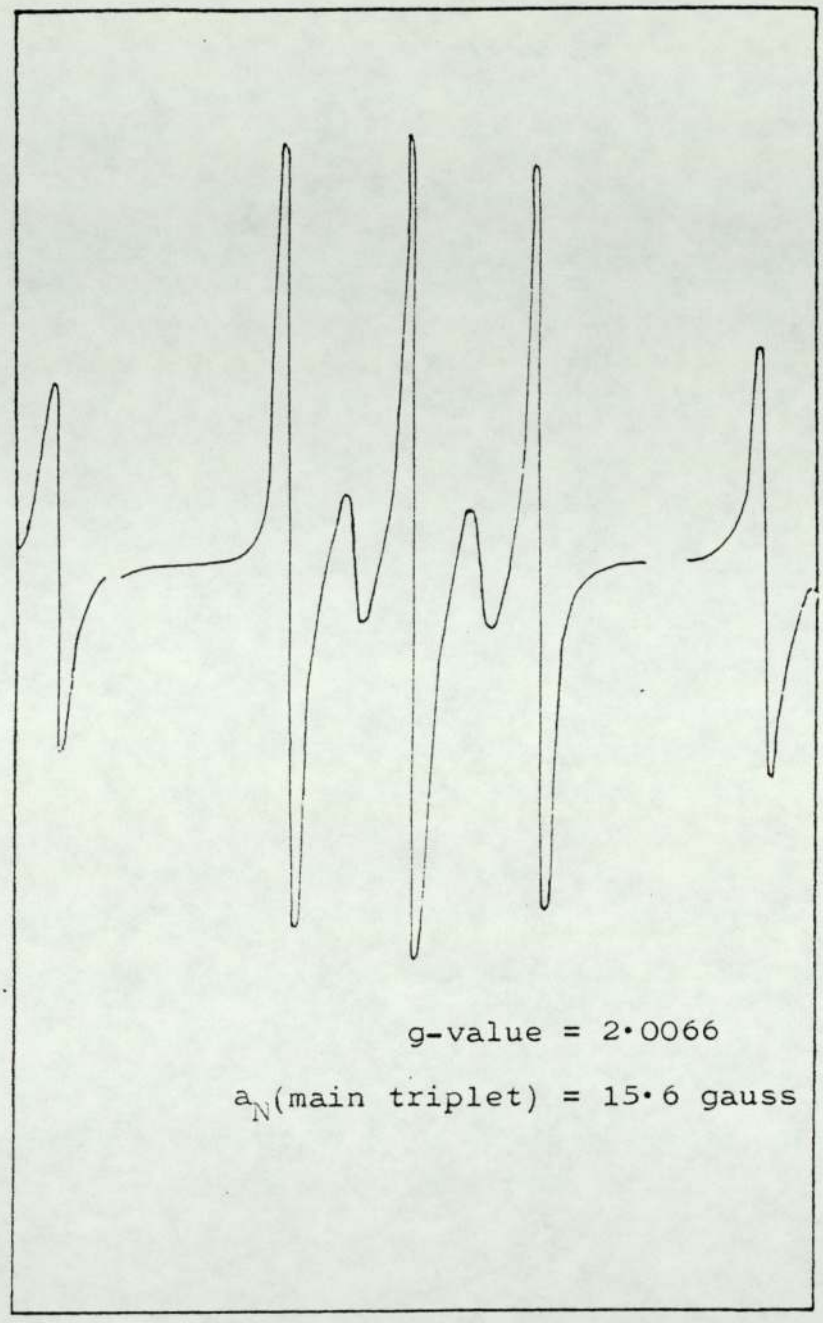


Fig. 2·4: E.s.r. spectrum of TMOXPZ in benzene (field = 3300 ± 100G; amplitude = 2·0 x 10; mod-width = 1·2 x 1; output = 6 m.v.; sweep time 4 minutes)

(iii) e.s.r. spectroscopy analysis: (in benzene)

The spectrum is a quintuplet; g value = 2.0066 a_N (main triplet) = 15.6 gauss. The spectrum is shown in figure 2.4. The quintuplet is due to long range inter-and intra-molecular interactions between the unpaired electrons[146].

2.4.8 4-(3,5-Ditertiarybutyl-4-hydroxyphenyl-1-propionato) -2,2,6,6-tetramethylpiperidine-1-oxyl (BPTMOP)

This procedure was adopted from the general method for preparing 4-esters of TMOP[70].

Equimolar quantities of TMOP 3.1g (0.018 moles) and 3,5-ditertiarybutyl-4-hydroxy-benzyl-1-propionic acid (4.8g ; 0.018 moles) were dissolved separately, each in 25ml anhydrous pyridine, mixed together and refluxed for eight hours. By this time the reaction solution had become dark red in colour. The pyridine was then removed under reduced pressure on the rotory evaprator, and the resulting dark red/brown viscous product was washed thoroughly with water. The material was dried in a vacuum oven and left in a deep freeze at -10°C for a few days to solidify. The brown solid was then recrystallised from minimum acetone. Yield: 4.125g (0.096 moles; 53% of theoretical). Melting point: 91-93°C.

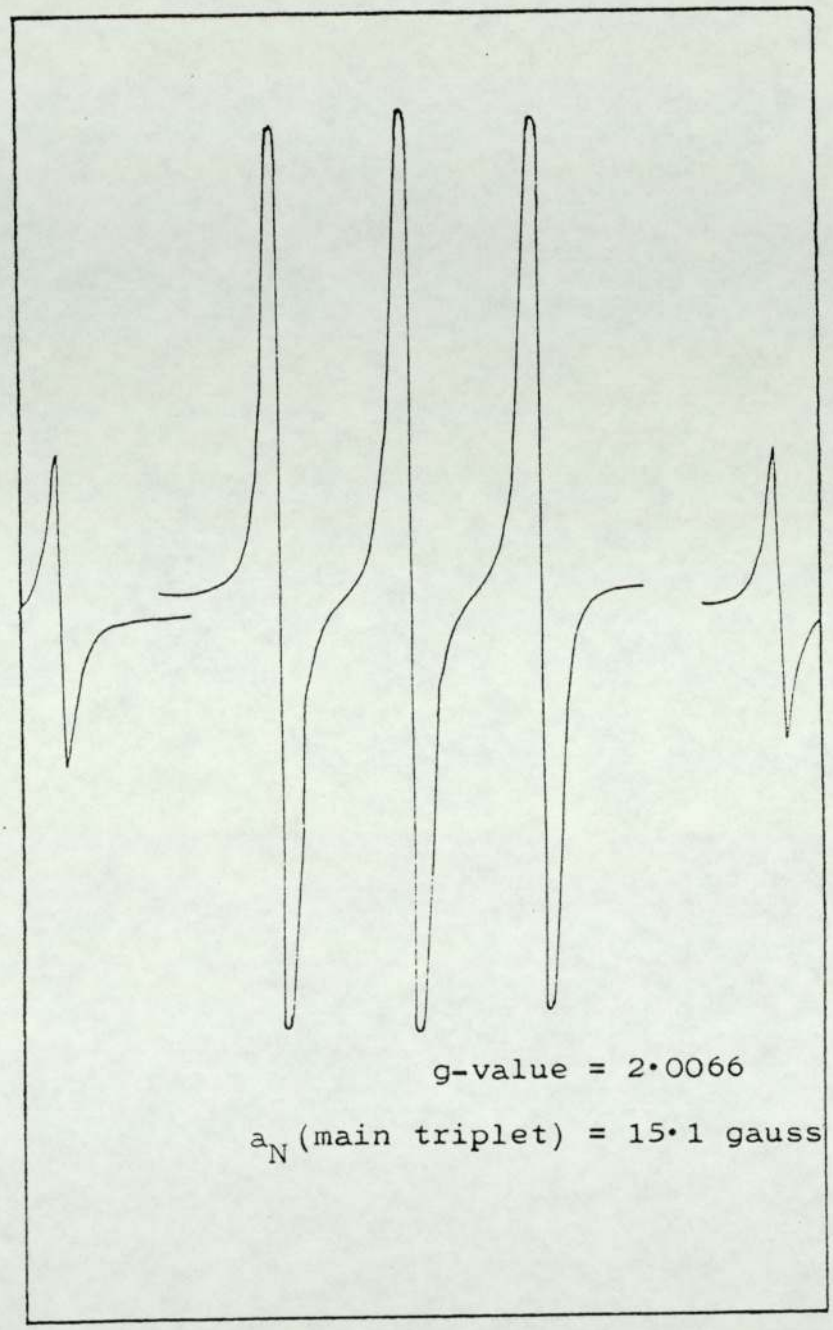


Fig. 2·5: E.s.r. spectrum of BPTMOP in benzene (field = 3300 ± 100G; amplitude = 1·5 x 10; mod-width = 1·1 x 1; output = 7 m.v.; sweep time=4 minutes)

Analytical data:-

(i) Elemental analysis:

calculated for $C_{26}H_{42}NO_4$

element	C	H	N
% expected	72.2	9.7	3.2
% found	69.9	10.1	3.3

(ii) Mass spectroscopy:

Molecular ion peak at m/e = 432.

(iii) Infrared analysis: (KBr disc)

Strong band at 3620 cm^{-1} (OH- stretch of hindered phenol).

Absorption band at 1700 cm^{-1} ($-\overset{O}{\overset{\|}{C}}$ stretch) of acid disappears and new band appears at 1730 cm^{-1}. (carbonyl of ester group).

(iv) e.s.r. spectroscopy analysis: (in benzene)

The spectrum is a triplet; g-value = 2.0066; a_N = 15.1 gauss. The spectrum is shown in figure 2.5.

2.4.9 α -(3,5-Dimethyl-4-hydroxyphenyl)-N-tertiarybutyl-nitrone (MHPBN)

(a) Synthesis of 3,5-dimethyl-4-hydroxybenzaldehyde.

This compound was synthesised by the formylation of 2,6 xylenol according to the procedure described by Nikiforov et al[147]. 12.2g (0.1 moles) of 2,6 xylenol was used together with 35g of boric acid, 25g of hexamethylene-tetraamine and 100ml ethylene gylcol. The yield was 10.5g (70% of theoretical). Melting point: 110-113°C (lit.:112°C)[147].

(b) Synthesis of N-tertiarybutylhydroxylamine

(i) Synthesis of 2-Methyl-2-nitropropane

This compound was prepared by the oxidation of tertiarybutylamine using hydrogen peroxide according to the procedure described by Stowell[148]. 36.6g (52ml; 0.5 moles) of tertiarybutylamine was used. The yield was 25.8g (0.293 moles; 59% of theoretical). Boiling point 126 - 128°C.

(ii) Synthesis of the Hydroxylamine.

The hydroxylamine was synthesised by the reduction of the 2-methyl-2-nitropropane using zinc dust and ammonium chloride according the method described by Greene et al[149].

25g (0.28 moles) of the 2-methyl-2-nitropropane was used. The yield was 18.2g (0.204 moles; 73% of theoretical). Melting point:60-62°C. (lit.: 62°C)[149].

(c) Synthesis of the Nitrone (MHPBN)

The nitrone was synthesised by the condensation reaction of the aldehyde with the hydroxylamine. N-tertiarybutyl-hydroxylamine (3.0g; 0.033 mole) and 3,5-dimethyl-4--Hydroxybenzaldehyde (4.95g; 0.033 mole) were dissolved in the minimum volume of absolute ethanol and allowed to stand at room temperature for a few days. Colourless crystals were formed. 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 filteration and recrystallised from ethanol. Yield: 4.2g (0.190 mole; 58% of theoretical). Melting point: 178-180°C.

Analytical data:-

(i) Elemental analysis:

calculated for $C_{13}H_{19}NO_2$

element	C	H	N
expected	70.6	8.6	6.3
found	71.0	9.2	6.5

(ii) Mass spectroscopy:

Molecular ion at m/e = 221. See section 2.6.1 for the fragmentation of this ion.

(iii) Infrared analysis (KBr disc)

3100-3300 cm^{-1} (broad OH stretch); 1590 cm^{-1} (aromatic C=C stretch); 1570 cm^{-1} (C=N stretch); 1160 cm^{-1} (N-O stretch); disappearance of the carbonyl stretch of the parent aldehyde at 1680 cm^{-1}.

N.B. typical literature values

C=N of nitrones appear at 1560-1580 cm^{-1} [84]; and the N-O stretch appear at 1150-1270 cm^{-1} [84].

(iv) N.M.R analysis: (in acetone d_6).

1.5 δ (S; 9H; N-^{t}Butyl protons); 2.2 δ (S; 6H; ring methyl protons); 7.5 δ (S; 1H; -CH = N(O)-); 8.0 δ (S; 2H; aromatic protons).

S = singlet

2.4.10 α -(4-Hydroxyphenyl)-N-tertiarybutylnitrone (HPBN)

This compound was prepared in the same way as described for MHPBN (section 2.4.9.c.). 3.0g (0.033 mole) of 4-hydroxybenzaldehyde was used with 3.0g of the tertiarybutylhydroxylamine. Orange/colourless crystals were obtained. The yield of the product was 2.0g (0.010 mole;

30% of theoretical). Melting point: 212-215°C (but begins to decompose above 200°C).

Analytical data:-

(i) Elemental analysis:

calculated for $C_{11}H_{15}NO_2$

element	C	H	N
expected	68.4	7.8	7.3
found	68.7	8.2	6.9

(ii) Mass spectroscopy:

Molecular ion peak at m/e = 193. For the fragmentation of this ion see section 2.6.2.

(iii) Infrared analysis: (KBr disc)

3100-3300 cm^{-1} (broad OH stretch); 1570 cm^{-1} (C=N stretch); 1168 cm^{-1} (N-O stretch); 1590 cm^{-1} (aromatic C=C stretch); disappearance of the carbonyl stretch of the parent aldehycle at 1680 cm^{-1}.

(iv) N.M.R. analysis: (in acetone d_6)

1.25 δ (S; 9H; N-^{t}Butyl protons); 6.55 δ (d; 2H; ring protons); 7.5 δ (S; 1H; -CH = N(O)-); 8.10δ(d; 2H; ring protons)

S = singlet; d = doublet.

2.4.11 α -Phenyl N-tertiarybutylnitrone (PBN)

This nitrone was prepared according to the method described for MHPBN (section 2.5.9.c). 3.5g (0.033 moles) of benzaldehyde and 3.0g of the N-tertiarybutylhydroxyamine was used. Pale yellow/white crystals were obtained. The yield was 4.0g (o.023 moles; 70% of theoretical). Melting point: 75-77°C (lit.: 75-77°C).

Analytical data:-

(i) Elemental analysis:

calcualted for $C_{11}H_{15}NO$

element	C	H	N
expected	74.6	8.5	7.9
found	73.5	8.9	7.6

(ii) Infrared analysis: (KBr disc)

1590 cm^{-1} (aromatic C ≡≡ C stretch); 1160 cm^{-1} (N-O stretch); 1570 cm^{-1} (C = N stretch); disappearance of the carbonyl stretch of the parent aldehyde at 1680 cm^{-1}.

2.4.12 α - Phenyl-N-Methylnitrone (PMN)

(a) Synthesis of N-methylhydroxylamine hydrochloride

This compound was prepared by the reduction of nitromethane

by ammonium chloride and zinc dust. 50g (0.82 mole) of nitromethane was used. The yield of the crystals obtained was 14.2g (0.213 moles; 26% of the theoretical). Melting point: 88-90°C. (Lit.: 88-90°C)[97].

(b) Synthesis of the Nitrone (PMN)

This compound was prepared according to the method described by Brady et al[151]. 13.0g (0.12 moles) of benzaldehyde was used together with 10.0g of the hydroxylamine hydrochloride. Yellow/brown crystals were obtained. The yield was 3.0g (0.022 mole; 20% of the theoretical). Melting point: 81-83°C. (Lit.: 82°C)[97,151].

Analytical date for the nitrone:-

(i) Elemental analysis:

calculated for C_8H_9NO

element	C	H	N
expected	71.1	6.6	10.4
found	71.5	7.1	10.8

(ii) Infrared analysis: (KBr disc)

1590 cm^{-1} (aromatic C=C stretch); 1168 cm^{-1} (N-O stretch); 1565 cm^{-1} (C=N stretch) disappearance of carbonyl stretch of the aldehyde at 1680 cm^{-1}.

(iii) N.M.R. analysis: (in acetone d_6)

1.55 δ(S; 3H; N-methyl protons); 7.3δ(t(broad); 3H; ring protons); 7.5δ(S; 1H; -CH = N(O)-); 8.0δ(t(broad); 3H; ring protons)

S = singlet; t = triplet.

2.4.13 α-(3,5-Ditertiarybutyl-4-hydroxyphenyl)-N-methylnitrone (BHPMN)

3,5-ditertiarybutyl-4-hydroxybenzaldehyde (10.0g, 0.042 mole) was dissolved in 2N sodium hydroxide solution (100ml) and was added to N-methylhydroxylamine (9.0g) in 25ml water. The solution was stirred magnetically overnight and the resulting orange coloured reaction solution was neutralized to pH 6-7 (B.D.H. universal litmus paper), by drop wise addition of 50% hydrochloric acid. On standing a brown/yellow precipitate formed. Recrystallisation from methanol yielded yellow crystals. The yield was 5.0g (0.019 mole; 45% of the theoretical). Melting point: 169-170°C.

Analytical data:-

(i) Elemental analysis:

calculated for $C_{16}H_{25}NO_2$

element	C	H	N
expected	73.0	9.5	5.3
found	73.1	10.2	5.3

(ii) Mass spectroscopy:

Molecular ion peak at m/e = 263. For the fragmentation pattern of this ion see section 2.6.3.

(iii) Infrared analysis: (KBr disc)

3100-3400 cm^{-1} (broad OH - stretch); 1590 cm^{-1} (aromatic C===C stretch); 1570 cm^{-1} (C = N stretch); 1170 cm^{-1} (N - O stretch).

(iv) N.M.R. analysis: (in acetone d_6)

2.3 δ (S; 6H; ring methyl protons); 3.8 δ (S; 3H; N-methyl protons); 7.5 δ (S; 1H; -C<u>H</u> = N(O)-); 8.0 δ (S; 2H; ring protons).

2.4.14 α -(3,5-Dimethyl-4-hydroxyphenyl)-N-methylnitrone (MHPMN)

This compound was made according to the procedure described by Smith[97]. 14.0g (0.093 mole) of 3,5--dimethyl-4-hydroxybenzaldehyde was used with 9.0g of N-methylhydroxylaminehydrochloride. Orange crystals were obtained. The yield was 6.0g (0.076 mole; 81.6% of the theoretical). Melting point: decomposes and melts at 205-208°C (lit.: 206°C)[97].

Analytical data:-

(i) Elemental analysis:

calculated for $C_{10}H_{13}NO_2$

element	C	H	N
expected	67.0	7.3	7.8
found	66.4	7.3	7.8

(ii) Infrared analysis: (KBr disc)

3100-3400 cm^{-1} (broad OH strech); 1590 cm^{-1} (aromatic C=C stretch); 1580 cm^{-1} (C = N stretch); 1168 cm^{-1} (N-O stretch); disappearance of the carbonyl stretch of the aldehyde at 1680 cm^{-1}.

(iii) N.M.R. analysis: (in acetone d_6)

2·3 δ (S; 6H; ring methyl protons); 3.8 δ (S; 3H; N-methyl protons); 7.5 δ (S; 1H; -CH = N(O)-); 8.0 δ (S; 2H; ring protons).

S = singlet

2.4.15 α-(3,5-Dimethyl-4- hydroxyphenyl)-N-ethylnitrone (MHPEN)

(a) Synthesis of N-ethylhydroxylamine hydrochloride

Nitroethane (80g), ammonium chloride (30g) were dissolved in 400 ml water, cooled to below 20°C and 137.5 g zinc

dust was added gradually with stirring over a period of 2 hours. The temperature was not allowed to exceed 20°C during this period. After the addition of the zinc dust, the reaction mixture was stirred for a further 45 minutes at room temperature and filtered. The aqueous filterate contained the hydroxylamine hydrochloride (literature[152] refers to this compound being soluble in water). No attempt was made to isolate this material. The filterate was used directly to prepare the nitrone as described in the next section without any further treatment.

(b) Synthesis of the Nitrone (MHPEN)

To the aquesus solution of the ethylhydroxylamine-hydrochloride (obtained as the filterate from section (a)) was added 30g (0.2 mole) of 3,5,dimethyl-4-hydroxybenz-aldehyde which had been previously dissolved in 2N sodium hydroxide solution (100 ml). The reaction solution was stirred magnetically overnight and then acidified to pH 6-7 (universal litmus paper), by drop wise addition of concentrated hydrochloric acid. A cream precipitate formed on standing. This was filtered and recrystallised from methanol. The yield was 10.0g (0.05 mole; 25% of the theoretical). Melting point: 162-164°C.

Analytical data:-

(i) Elemental analysis:

Calculated for $C_{11}H_{15}NO_2$

element	C	H	N
expected	69.5	8.2	6.7
found	69.3	8.0	7.1

(ii) Mass spectroscopy:

Molecular ion peak at m/e = 193. For the fragmentation of this ion see section 2.6.4.

(iii) Infrared analysis: (K Br disc)

3100-3300 cm^{-1} (broad OH stretch); 1590 cm^{-1} (aromatic C===C stretch); 1580 cm^{-1} (C = N stretch; shoulder); 1155 cm^{-1} (N-O stretch); disappearance of the carbonyl stretch of the aldyhyde at 1680 cm^{-1}.

(iv) N.M.R. analysis: (in acetone d_6)

1·4 δ (t; 3H; N-CH_2-$\underline{CH_3}$); 2·2 δ(S; 6H; ring methyl protons); 3·8 δ (q; 2H; N-$\underline{CH_2}$-CH_3); 7·5 δ (S; 1H; -$\underline{CH}$ = N(O)-); 8·0 δ (S; 2H; ring protons).

S = singlet; q = quadruplet.

2.4.16 α-(3,5-Dimethyl-4-hydroxyphenyl)-N-isopropylnitrone (MHPPN)

(a) Synthesis of N-Isopropylhydroxylaminehydrochloride

An aqueous solution of this compound was prepared by the

reduction of 2-nitropropane (72.0g; 0.808 mole) with ammonium chloride and zinc dust using the same procedure as described in section 2.4.15 (a). The filterate containing this hydroxylaminehydrochloride was used directly to prepare the nitrone as described in the next section. (The literature[153] reports that this compound is soluble in water).

(b) Synthesis of the Nitrone (MHPPN)

To the aqueous filterate containing the N-isopropyl-hydroxylaminehydrochloride, 3,5-dimethyl-4-hydroxybenz-aldehyde (20g; 0.133 mole) dissolved in 2N sodium hydroxide solution (100ml) was added and stirred magnetically for 1 hour. The reaction solution was then made to pH 8 (B.D.H. litmus paper) by drop wise addition of concentrated hydrochloric acid, and then stirred overnight. A pale yellow precipitate had formed. This was separated and recrystallised from methanol. The yield was 16.0g (0.077 mole; 58% of the theoretical). Melting point: 192-195^{o}C.

(i) Elemental analysis:

Calculated for $C_{12}H_{17}NO_2$

element	C	H	N
expected	69.5	8.2	6.8
found	67.0	8.2	6.9

(ii) Mass spectroscopy:

Molecular ion peak at m/e = 207. For the fragmentation of this ion see section 2.6.5.

(iii) Infrared analysis: (KBr disc)

3100-3300 cm^{-1} (broad OH stretch); 1590 cm^{-1} (aromatic C=C stretch); 1580 cm^{-1} (shoulder; C = N stretch); 1155 cm^{-1} (N-O stretch); disappearance of the carbonyl stretch fo the aldehyde at 1680 cm^{-1}.

(iv) N.M.R. analysis: (acetone d_6)

1·4 δ (d; 6H; N-CH-($\underline{CH_3}$)$_2$); 2·2 δ (S; 6H; ring methyl protons); 2·8 δ (m; N-$\underline{CH}$-$(CH_3)_2$); 7·5 δ (S; 1H; -$\underline{CH}$=N(O)-); 8·0 δ (S; 2H; ring protons).

S = singlet; d = doublet; m = multiplet.

2.4.17 α -(4-Methoxyphenyl)-N-isopropylnitrone (MPPN)

To an aqueous solution of N-isopropylhydroxylaminehydrochloride (see section 2.16 (a)) anisaldehyde (30g ; 0.2 mole)

dissolved in 2N sodium hydroxide in aqueous ethyl alcohol (100ml) was added. The mixture was stirred at room temperature for three days. A red oil had separated at the bottom of the beaker. The oil was separated from the aqueous layer using a separating funnel, dried over anhydrous magnesium sulphate and distilled under a reduced pressure of 5mm Hg. The distillate boiling at 100-110°C was collected. This was a colourless liquid and infact was revealed to be unreacted anisaldehyde (by infrared and elemental analysis). The yield of the distillate was 10.0g.

The fraction that did not distill was cooled in a fridge for 3-4 days to form a red glassy solid. Upon grinding of this residue a tan coloured powder was obtained. Analysis of this material revealed that this compound in fact was the nitrone.

Analytical data of the tan coloured powder:

(i) Elemental analysis:

Calculated for $C_{11}H_{15}NO_2$

element	C	H	N
expected	68.4	16.1	7.25
found	68.0	16.4	7.8

(ii) Mass spectroscopy

Molecular ion at m/e = 193. For the fragmentation of this ion see section 2.6.6.

(iii) Infrared analysis: (KBr disc)

1595 cm^{-1} (aromatic C=C stretch); 1570 cm^{-1} (shoulder; C=N stretch); 1167 cm^{-1} (N-O stretch); disappearance of carbonyl stretch of the aldehyde at 1680 cm^{-1}.

(iv) N.M.R. analysis (in acetone d_6)

1·2 δ (d; 6H; N-CH-($C\underline{H}_3$)$_2$); 3·2 δ (m(overlaps with tail of singlet at 3·9δ); 1H; N-C$\underline{H}$-(CH_3)$_2$); 3·9δ (S; (broad); 3H; -O-C$\underline{H}_3$); 7·0 δ (S; (broad); 4H; ring protons); 7·6 δ (S; (shoulder on singlet at 7·0 δ; 1H; C$\underline{H}$=N(O)).

S = singlet; m = multiplet; d = doublet.

2.4.18 α-(4-chlorophenyl)-N-isopropylnitrone (CPPN)

To an aqueous solution of N-isopropylhydroxylamine hydro chloride (containing 0.4 moles of the material; see section 2.16 (a)) p-chlorobenzaldehyde (30g: 0·2 moles) in 100ml ethanol containing 4·0g sodium hydroxide was added. The aldehyde was previously brought into solution by stirring with the sodium hydroxide in the ethanol containing 5% water. The reaction solution was

stirred magnetically for six hours and left standing overnight. A dark yellow/brown oil had formed and a yellow sediment had also precipitated. The sediment was filtered and the yellow oil was separated from the aqueous phase using a separating funnel. Ether extraction of the aqueous phase followed by evaporation of the ether layer yielded a white solid (3.5g). The oil was dried over anhydrous magnesium sulphate, and distilled under reduced pressure. The distillate boiling at 70°C was collected. This was an orange liquid which when cooled in the fridge at -5°C formed orange crystals which melted below room temperature.

Analysis of the products showed that the desired product was the white powder. Melting point: 183-185°C (melts and decomposes; melting point of the parent aldehyde: 44-47°C).

Analytical data: (white powder):-

(i) Elemental analysis:

Calculated for $C_{10}H_{12}NO\,Cl$ M.W = 197.5

element	C	H	N	Cl
expected	60.8	6.1	7.1	18.0
found	61.0	6.4	7.5	

(ii) Mass spectroscopy

Molecular ion at m/e = 197.5; $M^+ + 2$ peak at m/e = 199.5 (intensity relative to molecular ion peak = 28%). For the fragmentation pattern of this ion see section 2.6.7. All the ions greater than m/e = 111.5 had a corresponding $M^+ + 2$ peak which had a relative intensity of approximately 30% relative to the M^+ peak.

(iii) Infrared analysis: (KBr disc)

1595 cm^{-1} (aromatic C===C stretch); 1570 cm^{-1} (shoulder; C=N stretch); 1140 cm^{-1} (N-O stretch); 1095 cm^{-1} (C-Cl stretch on aromatic ring; lit.[144]: 1096-1089); disappearance of the carbonyl stretch of the aldehyde at 1700 cm^{-1}.

(iv) N.M.R. data: (in acetone d_6)

1·4 δ (d; 6H; N-CH-($\underline{CH}_3$)$_2$); 3·1 δ (m(W); 1H; N-$\underline{CH}$-(CH_3)$_2$); 7·6 δ (m; 3H; overlap of -$\underline{CH}$=N(O)- and ring protons); 8·0 δ (m; 2H; ring protons).

d = doublet; m = multiplet.

2.4.19 Bis(α-(3,5-Dimethyl-4-hydroxyphenyl))-1,3-N-propylnitrone (BMHPPN)

(a) Synthesis of 1,3,dinitropropane

This compound was prepared by the oxidation of

1,3 diaminopropane by hydrogen peroxide using the same procedure as for the synthesis 2-methyl-2-nitropropane from its amine[148]. 37.0g (52ml; 0.5 moles) 1,3 diaminopropane 8.0g sodium tungstate and 200ml 30% hydrogen peroxide was used. When all the hydrogen peroxide was added the reaction mixture was red/brown in colour. The reaction mixture was then evaporated to dryness by removal of the water on the rotory evaporator, and the dark red oily residue was dried in a vacuum oven. The thick oil was then vacuum distilled at 4mm Hg pressure and the fraction boiling at 104-114°C was collected. The distillate was a yellow oil (lit.[154] B.P: 103°C at 1mm pressure).

Analysis (infrared): (neat)

1515 cm^{-1}, 1680 cm^{-1} and 1360 cm^{-1} (NO_2 stretch); disappearance of the NH stretch at 3280 cm^{-1}.

(b) Synthesis of 1,3-di-hydroxylamino-propane hydrochloride

8.5g (0.083 mole) of 1,3-dinitropropane was mixed with 100ml water and reduced using ammonium chloride (9.0g) and zinc dust (22g) keeping the temperature below 20°C. The procedure used was as described in reaction 2.16 (a). At

the end of the reaction period the reaction mixture was filtered, and the filterate containing the hydroxylamine hydrochloride was used directly to synthesis the nitrone as described below (section c).

(c) Synthesis of the Nitrone (BMHPPN)

The aqueous filterate obtained from section b was added to an aqueous solution (50ml) of 3,5-dimethyl-4-hydroxy-benzaldehyde (20g; 0.133moles) and sodium hydroxide (4.0g). The reaction mixture was stirred at room temperature for 2 hours. A yellow precipitate formed. The pH of the reaction mixture was 8 (B.D.H. universal litmus paper). The precipitate was filtered, recrystallised from ethanol and dried in a vacuum oven. The yield was 3.0g (0.008 mole; 10% of theoretical). Melting point: 134-136°C. In order to increase the yield, the reaction solution was neutralized to pH 7 (B.D.H. universal litmus paper) 6.0g of white precipitate was obtained. However, analysis of this product showed it to be the starting aldehyde.

Analytical data of the nitrone:-

(i) Elemental analysis:

Calculated for $C_{21}H_{26}N_2O_4$

element	C	H	N
expected	68.1	7.0	7.6
found	66.5	7.2	8.0

(ii) Mass spectroscopy

No molecular ion peak; highest M^+ occurs at m/e = 206. For other main fragmentation products see section 2.6.8.

(iii) Infrared analysis: (KBr disc)

1590 cm^{-1} (aromatic C=C stretch); 1140 cm^{-1} (N-O stretch of nitrones); disappearance of absorption bands at 1680 cm^{-1} of the aldehyde and nitropropane, and the band at 1515 cm^{-1} of the latter compound.

(iv) N.M.R. analysis: (acetone d_6)

2·1 δ (S; 12H; ring methyl); 2·3 δ (t (overlaps with singlet at 2·1δ); 4H; N-$C\underline{H}_2$-CH_2-CH_2-N); 2·8 δ (m (weak); 2H; N-CH_2-$C\underline{H}_2$-CH_2-N); 7·5 δ(S; 2H; $C\underline{H}$=N(O)); 8·0 δ(S; 4H; ring protons).

2.4.20 2-Methyl-2-nitrosopropane (MNP)

This compound was synthesised according to the procedure described by Stowell[148]. 36.6g (52ml; 0.5 mole) tertiarlybutylamine was oxidised with 30% hydrogen peroxide. Yield: 8.0g of the monomer (0.09 mole; 18% of theoretical) b.P = 50-55°C. On cooling in the fridge at -5°C the dimer was obtained (M.P.: 70-72°C lit.:[137] 74-75°C.

2.4.21 The attempted Synthesis of α -(3,5-ditertiarybutyl -4-hydroxyphenyl)-N-tertiarybutylnitrone.

The synthesis of this compound was attempted according to the procedure of Pacifici et al[155]. However the desired product was not formed. A white precipitate was obtained. Analysis of this material indicated that this infact was the starting aldehyde.

Attempts to prepare this nitrone by refluxing the reaction mixture for several hours was also not successful. The material that was isolated was always the parent aldehyde. Changing the solvent did not help either.

The fact that this compound was not formed is very unusual especially since its synthesis has been reported in the literature. It must be pointed out however that other workers[97,98,156] too have attempted to synthesise this nitrone and the related N-phenylnitrone according to this procedure but without success.

2.4.22 Attempted Synthesis of α -(3-teritiarybutyl-5-methyl -4-hydroxyphenyl)-N-tertiarybutylnitrone

3-tertiarybutyl-5-methyl-4-hydroxyphenylbenzaldehyde was prepared by the formylation of 2-methyl-5-tertiarybutylphenol

according to the procedure described by Nikiforov et al[97,147]. The synthesis of the nitrone was attempted using by the procedure described in 2.5.9.c. Molar quantities of the aldehyde and the hydroxylamine were used. A white percipitate was obtained. Analysis of this material revealed that in fact it was the starting aldehyde.

2.4.23 Attempted Synthesis of α-(3,5-ditertiarybutyl -4-hydroxyphenyl)-N-isopropylnitrone

The synthesis of this nitrone was attempted according to the procedure described in section 2.5.15. A white material was isolated but analysis showed that this compound was infact the starting aldehyde.

2.4.24 Attempted Synthesis of 2,2,6,6-Tetramethyl-1-ethoxyl -4-piperidinol

The procedure used was as described for the synthesis of TMMP (section 2.4.3). Ethyl radicals were produced in situ by the silver catalysed decarboxylation of propionic acid[142,143] in the presence of TMOP. A mixture of ethanol and water was used to ensure solubility of the propionic acid. During the reaction the characteristic orange colour of TMOP disappeared and the solution took on a pale yellow colour. After the work up with dichloromethane and cyclohexane (non solvent) a pale off white precipitate was formed.

However during the isolation procedure this oxidised back to the parent TMOP on contact with air. Attempts to isolate the product under a stream of nitrogen too were unsuccessful as the product oxidised back to TMOP, but more slowly than before.

2.4.25 Attempted Synthesis of 2,2,6,6-Tetramethyl-1-isopropoxyl-4-piperidinol

The procedure used was as described for the synthesis of TMMP (section 2.4.3). isopropyl radicals were produced in situ by the silver catalysed decarboxylation of 2-methylpropionic acid[142,143] in the presence of TMOP. A mixture of ethanol and water was used to ensure solubility of the 2-methylpropionic acid. During the reaction the characteristic orange colour of TMOP disappeared and the solution took on a pale yellow colour. However on work up and isolation the product oxidised back to TMOP even when the isolation procedure was carried out under a stream of nitrogen.

2.4.26 Attempted Synthesis of 2,2,6,6-Tetramethyl-1-1 tert-butoxyl-4-piperidinol

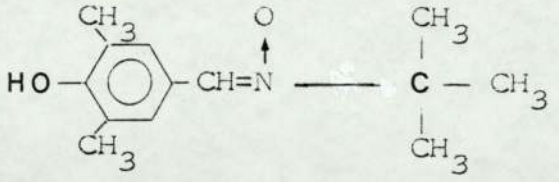
The procedure used was as described for the synthesis of TMMP (section 2.4.3). Tert-butoxyl radicals were produced in situ by the silver catalysed decarboxylation of

2,2-dimethylpropionic acid (pivalic acid)[142,143] in the presence of TMOP. A mixture of ethanol and water was used to ensure solubility of the pivalic acid. During the reaction the characteristic orange colour of TMOP slowly disappeared and the solution took on a pale yellow colour. However on work up and isolation the products oxidised slowly back to TMOP even when the isolation was carried under a stream of nitrogen.

2.5 INTERPRETATION OF THE MASS SPECTRA

In all cases the peaks shown in the tables below were seen in the mass spectra of the respective compounds.

2.5.1 The Fragmentation Pattern for MHPBN



$C_{13}H_{19}NO_2$ M.W = 221

$$C_{13}H_{19}NO_2 \xrightarrow{-e} C_{13}H_9NO_2^{+\cdot}$$

m/e = 221 (molecular ion).

Fragmentation of the molecular ion.

PATH 1		
m/e	M^+	fragment loss
220	$C_{13}H_{17}NO_2^+$	H·
190	$C_{13}H_{18}O^+$	NO
134	$C_9H_{10}O^+$	C_4H_8
105	$C_8H_9^+$	HCO
77	$C_6H_5^+$	C_2H_4
51	$C_4H_3^+$	C_2H_2

PATH 2		
m/e	M^+	fragment loss
164	$C_9H_{10}NO_2^+$	C_4H_9·
134	$C_9H_{10}O^+$	NO
105	$C_8H_9^+$	HCO
Then as for path 1		

PATH 3		
m/e	M^+	fragment loss
191	$C_{13}H_{19}O^+$·	NO
134	$C_9H_{10}O^+$	C_4H_9·
105	$C_8H_9^+$	HCO
Then as for path 1		

PATH 4		
m/e	M^+	fragment loss
205	$C_{13}H_{19}NO^+$	O·
178	$C_{12}H_{18}O^+$	HCN
120	$C_8H_{10}O^+$	C_4H_{10}
92	$C_7H_8^+$	CO
64	$C_5H_4^+$	C_2H_4
38	$C_3H_2^+$	C_2H_2

PATH 5		
m/e	M^+	fragment loss
204	$C_{13}H_{18}NO^+$	·OH
177	$C_{12}H_{17}O^+$	HCN
121	$C_8H_9O^+$	C_4H_8
93	$C_7H_9^+$	CO
91	$C_7H_7^+$	H_2
65	$C_5H_3^+$	C_2H_2

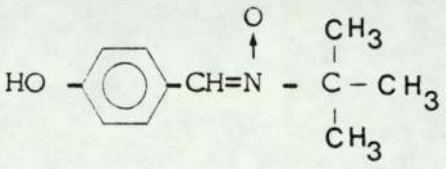
PATH 6		
m/e	M^+	fragment loss
93	$C_7H_9^+$	
65	$C_5H_5^+$	C_2H_4
39	$C_3H_3^+$	C_2H_2

MHPBN continued

PATH 7		
m/e	M^+	fragment loss
121	$C_8H_9O^+$	
92	C_7H_8	. HCO

then as for path 3

2.5.2 The Mass Spectrum Fragmentation pattern for HPBN



$C_{11}H_{15}NO_2$ M.W. = 193

$C_{11}H_{15}NO_2$ $C_{11}H_{15}NO_2^{\cdot+}$

m/e = 193 (molecular ion)

Fragmentation patterns for the molecular ion:

PATH 1

m/e	M^+	fragment loss
192	$C_{11}H_{14}NO_2^+$	H·
162	$C_{11}H_{14}O^+$	NO
106	$C_7H_6O^+$	C_4H_8
77	$C_6H_5^+$	HCO
51	$C_4H_3^+$	C_2H_2

PATH 2

m/e	M^+	fragment loss
136	$C_7H_6NO_2^+$	$\cdot C_4H_9$
106	$C_2H_6O^+$	NO
Then as for path 1		

PATH 3

m/e	M^+	fragment loss
163	$C_{11}H_{15}O^{\cdot +}$	NO
106	$C_7H_6O^+$	$\cdot C_4H_9$
Then as for path 1		

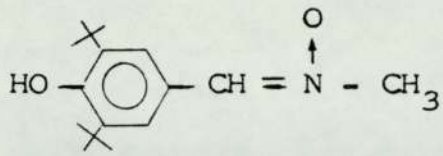
PATH 4

m/e	M^+	fragment loss
177	$C_{11}H_{15}NO^+$	O·
150	$C_{10}H_{14}O^+$	HCN
94	$C_6H_6O^+$	C_4H_8
65	$C_5H_5^+$	HCO
39	$C_3H_3^+$	C_2H_2

PATH 5

m/e	M^+	fragment loss
176	$C_{11}H_{14}NO^+$	$\cdot$OH
149	$C_{10}H_{13}O^+$	HCN
93	$C_6H_5O^+$	C_4H_8
65	$C_5H_5^+$	CO
39	$C_3H_3^+$	C_2H_2

2.5.3 The Fragmentation Pattern for BHPMN



; $C_{16}H_{25}NO_2$; M.W = 263

$$C_{16}H_{25}NO_2 \xrightarrow{-e} C_{16}H_{25}NO_2^{\cdot +}$$

m/e = 263 (molecular ion)

Fragmentation of the molecular ion:

PATH 1

m/e	M^+	fragment loss
262	$C_{16}H_{24}NO_2^+$	H·
232	$C_{16}H_{24}O^+$	NO
216	$C_{15}H_{20}O^+$	CH_4
160	$C_{11}H_{12}O^+$	C_4H_8
131	$C_{10}H_{11}^+$	HCO
105	$C_8H_9^+$	C_2H_2

Then as for MHPBN path 1 (section 2.5.1)

PATH 2

m/e	M^+	fragment loss
248	$C_{15}H_{22}NO_2^+$	$\cdot CH_3$
218	$C_{15}H_{22}O^+$	NO
160	$C_{11}H_{12}O^+$	C_4H_{10}

Then as for path 1

PATH 3

m/e	M^+	fragment loss
233	$C_{16}H_{25}O^{\cdot +}$	NO
218	$C_{15}H_{22}O^+$	$CH_3\cdot$

Then as for path 2

PATH 4

m/e	M^+	fragment loss
247	$C_{16}H_{25}NO^+$	O·
220	$C_{15}H_{24}O^+$	HCN
162	$C_{11}H_{14}O^+$	C_4H_{10}
133	$C_{10}H_{13}^+$	HCO

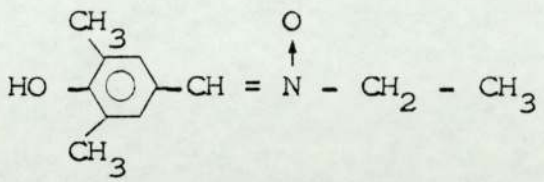
PATH 5

m/e	M^+	fragment loss
246	$C_{16}H_{24}NO^+$	·OH
219	$C_{15}H_{23}O^+$	HCN

BHPMN path 4 and 5 continued.....

PATH 4			PATH 5		
m/e	M^+	fragment loss	m/e	M^+	fragment loss
105	$C_8H_9^+$	C_2H_4	161	$C_{11}H_{13}O^+$	C_4H_{10}
			133	$C_{11}H_{13}$	CO
Then as for path 1 alternately			Then as for path 1-4 alternately		
220	$C_{15}H_{24}O^+$		219	$C_{15}H_{23}O^+$	
164	$C_{11}H_{16}O^+$	C_4H_8	163	$C_{11}H_{15}O^+$	C_4H_8
135	$C_{10}H_5^+$	HCO	135	$C_{10}H_{15}^+$	CO
91	$C_7H_7^+$	C_3H_8	91	$C_7H_7^+$	C_3H_8
Then as for MHPBN path 5 (section 2.5.1)			Then as for MHPBN path 5 (section 2.5.1)		

2.5.4 The Fragmentation Pattern for MHPEN



$C_{11}H_{15}NO_2$ M.W. = 193

$$C_{13}H_{15}NO_2 \xrightarrow{-e} C_{11}H_{15}NO_2^{\cdot +}$$

m/e = 193 (molecular ion)

Fragmentation of the molecular ion:

PATH 1

m/e	M^+	fragment loss
192	$C_{11}H_{13}NO_2^+$	H·
162	$C_{11}H_{14}O^+$	NO
134	$C_9H_{10}O^+$	C_2H_4

Then as for MHPBN path 1 (section 2.5.1)

PATH 2

m/e	M^+	fragment loss
164	$C_9H_{10}NO_2^+$	C_2H_5·
134	$C_9H_{10}O^+$	NO

Then as for path 1

PATH 3

m/e	M^+	fragment loss
163	$C_{11}H_{15}O^{\cdot+}$	NO
134	$C_9H_{10}O^+$	C_2H_5·

Then as for path 1

PATH 4

m/e	M^+	fragment loss
177	$C_{11}H_{15}NO^+$	O·
150	$C_{10}H_{14}O^+$	HCN
122	$C_8H_{10}O^+$	C_2H_4
93	$C_7H_9^+$	HCO

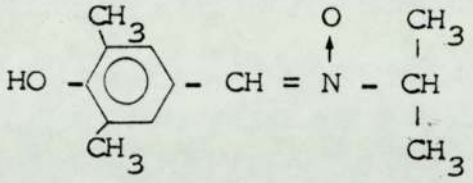
Then as paths 5 and 6 of MHPBN (section 2.5.1)

PATH 5

m/e	M^+	fragment loss
193	$C_{11}H_{15}NO_2^{\cdot+}$	-
176	$C_{11}H_{14}NO^+$	·OH
149	$C_{10}H_{13}O^+$	HCN
121	$C_8H_9O^+$	C_2H_4

Then as for paths 5, 6, and 7 of MHPBN (section 2.5.1)

2.5.5 The Fragmentation Pattern for MHPPN



$C_{12}H_{17}NO_2$ M.W. = 207

$$C_{12}H_{17}NO_2 \xrightarrow{-e} C_{12}H_{17}NO_2^{\cdot+}$$

m/e = 193 (molecular ion)

Fragmentation of the molecular ion:

PATH 1

m/e	M^+	fragment loss
206	$C_{12}H_{16}NO_2^+$	H·
176	$C_{12}H_{16}O^+$	NO
134	$C_9H_{10}O^+$	C_3H_6

Then as for path 1 of MHPBN (section 2.5.1)

PATH 2

m/e	M^+	fragment loss
164	$C_9H_{10}NO_2^+$	$\cdot C_3H_7$
134	$C_9H_{10}O^+$	NO

then as for path 1

PATH 3

m/e	M^+	fragment loss
191	$C_{12}H_{17}O^{\cdot+}$	NO
134	$C_9H_{10}O^+$	$\cdot C_3H_7$

Then as for path 1

PATH 4

m/e	M^+	fragment loss
191	$C_{12}H_{17}NO^+$	O·
164	$C_{11}H_{16}NO^+$	HCN
162	$C_{11}H_{14}O^+$	H_2
118	$C_8H_6O^+$	C_3H_8
90	$C_7H_6^+$	CO
62	$C_5H_2^+$	C_2H_4

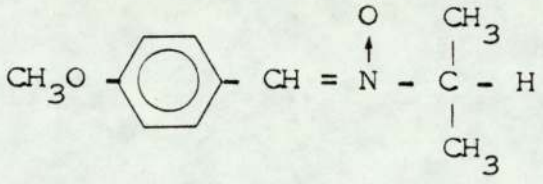
PATH 5

m/e	M^+	fragment loss
190	$C_{12}H_{16}NO^+$	·OH
163	$C_{11}H_{15}O^+$	HCN

MHPPN Path 4 and 5 continued .....

PATH 4			PATH 5		
m/e	M^+	fragment loss	m/e	M^+	fragment loss
alternately					
164	$C_{11}H_{16}NO^+$		119	$C_7H_8O^+$	C_3H_8
120	$C_8H_8O^+$	C_3H_8	91	$C_7H_7^+$	CO
Then as for path 3 of MHPBN (section 2.5.1)			Then as for PHPBN path 5 (section 2.5.1)		

2.5.6 Mass Spectrum Fragmentation Pattern for MPPN



$C_{11}H_{15}NO_2$ M.W. = 193

$$C_{11}H_{15}NO_2 \xrightarrow{-e} C_{11}H_{15}NO_2^{\cdot +}$$

m/e = 193 (molecular ion)

Fragmentation of the molecular ion:

PATH 1

m/e	M^+	fragment loss
192	$C_{11}H_{14}NO_2$	$\cdot H$
162	$C_{11}H_{14}O^+$	NO
120	$C_8H_8O^+$	C_3H_6
90	$C_7H_6^+$	CH_2O
64	$C_5H_4^+$	C_2H_4
38	$C_3H_2^+$	C_2H_2

PATH 2

m/e	M^+	fragment loss
150	$C_8H_8NO_2^+$	$\cdot C_3H_7$
120	$C_8H_8O^+$	NO
Then as for path 1		

PATH 3

m/e	M^+	fragment loss
163	$C_{11}H_{15}O^{\cdot +}$	NO
120	$C_8H_8O^+$	$\cdot C_3H_4$
Then as for path 1		

PATH 4

m/e	M^+	fragment loss
177	$C_{11}H_{15}NO^+$	O$\cdot$
150	$C_{10}H_{14}O^+$	HCN
108	$C_7H_8O^+$	C_3H_6
78	$C_6H_6^+$	H_2CO
52	$C_4H_4^+$	C_2H_2

PATH 5

m/e	M^+	fragment loss
176	$C_{11}H_{14}NO^+$	$\cdot OH$
149	$C_{10}H_{13}O^+$	HCN
107	$C_7H_7O^+$	C_3H_6
77	$C_6H_5^+$	H_2CO
51	C_4H_3	C_2H_2

MPPN continued

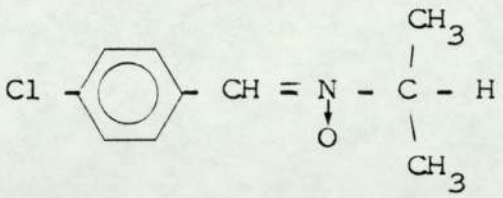
PATH 6		
m/e	M^+	fragment loss
162	$C_{11}H_{14}O^+$	$\cdot NO$
122	$C_8H_{10}O^+$	C_3H_4
92	$C_7H_8^+$	H_2CO

Then as for MHPBN path 4 (section 2.5.1), alternately

121	$C_8H_9O^+$	C_3H_5
91	$C_7H_7^+$	H_2CO

Then as for MHPBN paths 5 and 6 (section 2.5.1)

2.5.7 Mass Spectrum Fragmentation Pattern for CPPN



$C_{10}H_{12}NOCl$ M.W. = 197.5

$$C_{10}H_{12}NOCl \xrightarrow{-e} C_{10}H_{12}NOCl^{\cdot +}$$

m/e = 197.5 (molecular ion)

Fragmentation of molecular ion.

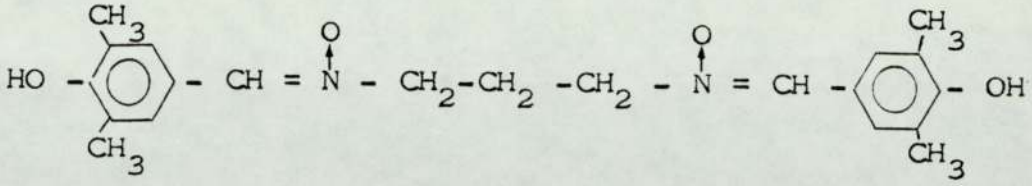
PATH 1		
m/e	M^+	fragment loss
154.5	$C_7H_5NOCl^+$	$\cdot C_3H_7$
124.5	$C_7H_5Cl^+$	NO
88	$C_7H_4^+$	HCl
62	C_5H_2	C_2H_2

PATH 3		
m/e	M^+	fragment loss
181.5	$C_{10}H_{12}NCl^+$	O·
139.5	$C_7H_6NCl^+$	C_3H_6
112.5	$C_6H_5Cl^+$	HCN
76	$C_6H_4^+$	HCl
50	$C_4H_2^+$	C_2H_2
alternatively		
141.5	$C_7H_8ClN^+$	C_3H_4
114.5	$C_6H_7Cl^+$	HCN
78	$C_6H_6^+$	HCl
52	$C_4H_4^+$	C_2H_2

PATH 2		
m/e	M^+	fragment loss
167.5	$C_{10}H_{12}Cl^{\cdot+}$	NO
124.5	$C_7H_5Cl^+$	$\cdot C_3H_7$
Then as for path 1 :		
alternately		
127.5	$C_7H_8Cl^{\cdot+}$	C_3H_4
91	$C_7H_7^{\cdot+}$	HCl
Then as for paths 5 and 6		
of MHPBN (section 2.5.1)		

PATH 4		
m/e	M^+	fragment loss
180.5	$C_{10}H_{11}NCl^+$	·OH
138.5	$C_7H_5NCl^+$	C_3H_6
111.5	$C_6H_4Cl^+$	HCN
75	$C_6H_3^+$	HCl
alternatively		
140.5	$C_7H_7NCl^+$	C_3H_4
113.5	$C_6H_6Cl^+$	HCN
77	$C_6H_5^+$	HCN
51	$C_4H_3^+$	C_2H_2

2.5.8 The Fragmentation Pattern for BMHPPN



$C_{21}H_{19}NO_2$; M.W. = 221

$$C_{21}H_{19}NO_2 \xrightarrow{-e} C_{21}H_{19}NO_2^{+\cdot}$$

m/e = 370

$$C_{12}H_{16}NO_2^{+\cdot} + C_9H_{10}O_2N$$

m/e = 206

Fragmentation pattern for the mass ion at m/e = 206.

PATH 1

m/e	M^+	fragment loss
205	$C_{12}H_{15}NO_2^+$	H·
175	$C_{12}H_{15}O^+$	NO
134	$C_9H_{10}O^+$	C_3H_5

Then as for MHPBN path 1 (section 2.5.1)

PATH 2

m/e	M^+	fragment loss
162	$C_9H_{10}NO^{\cdot+}$	C_3H_6
134	$C_9H_{10}O^{\cdot+}$	NO

Then as for path 1

PATH 3

m/e	M^+	fragment loss
176	$C_{12}H_{16}O^{\cdot+}$	NO
134	$C_9H_{10}O^{\cdot+}$	C_3H_6

Then as for path 1

PATH 4

m/e	M^+	fragment loss
190	$C_{12}H_{16}NO^+$	O·
163	$C_{11}H_{15}O^+$	HCN
121	$C_8H_9O^+$	C_3H_6

Then as for MHPBN path 5 (section 2.5.1)

PATH 5

m/e	M^+	fragment loss
189	$C_{12}H_{15}NO^+$	·OH
162	$C_{11}H_{14}O^+$	HCN
120	$C_8H_8O^+$	C_3H_6

Then as for MHPBN path 4 (section 2.5.1)

2.6 THE INSTRUMENTS USED FOR THE ANALYSES.

The infrared spectra were recorded on either the Perkin Elmer 457 grating infrared spectrometer or the Perkin Elmer 599 grating infrared spectrometer.

The elemental analysis were done using the Perkin Elmer model 240 Elemental Analyser.

The mass spectra were recorded on the Associated Electrical Industries mass spectrometer type M.S.9.

N.M.R. spectra were recorded on the Perkin Elmer model R12B nuclear magnetic resonance spectrometer.

E.S.R. spectra were recorded on the J.O.E.L. P.E. electron spin resonance spectrometer.

CHAPTER THREE

TECHNOLOGICAL TECHNIQUES

The compounds described in section 2.1 were incorporated into rubber and their technological performance was assessed. The following aspects were studied:-

i) curing characteristics
ii) antifatigue activity
iii) antiozonant activity
iv) antioxidant activity (by stress relaxation)
v) degree of discolouration to the rubber and staining characteristics
vi) Presence of nitroxyl radical.

All compounds described in section 2.1 were incorporated into the rubber during the compounding stage.

3.1 MATERIALS

Solid natural rubber (S.M.R. grade 10) was used.

Before compounding, the rubber was sheeted and hot acetone extracted for 48 hours in an atmosphere of nitrogen. This was done to remove the acetone soluble naturally occuring

antioxidants and other acetone soluble naturally occuring non-rubber constituents in the rubber. These include naturally occuring proteins and resins[157]. After extraction the rubber was dried in a vacuum oven at 30°C and stored in a vacuum dessicator in the dark till required.

The vulcanisates were prepared as described below.

3.2 COMPOUNDING

3.2.1 The Compounding Ingredients

The ingredients were:

Zinc oxide (Amalgamated Zinc Ltd.); Stearic acid (B.D.H Chemical Company Ltd.) ; C.B.S. (N-cyclohexylbenzthiazole-2-sulphenamide; Monsanto Chemical Company Ltd.) ;Sulphur (Anchor Chemicals Ltd.);antioxidant. In addition to the compounds synthesised the following commercial antidegradants were tested:

i) Santoflex I.P. (I P P D ; N-isopropyl N′-phenyl-p-phenelene diamine) (Monsanto Chemical Company)

ii) Permanax W.S.P. (W S P ; 2.2′-dihydroxy 3.3′-di(α-methylcyclohexyl) 5.5′ dimethyl diphenyl methane) (Vulnax Ltd)

iii) Santoflex 77 (N, N^{1}di-(1,4-dimethylpentyl)-p-phenlenenediamine) (Monsanto Chemical Company)

3.2.2 The Compounding Technique

The ingredients were mixed into the rubber on a 0.3 meter water cooled laboratory two-roll mill. The proportions used were that corresponding to the C.B.S. formulation indicated below.

C.B.S. formulation:-

Natural rubber	:	100g
Zinc oxide	:	5g
Stearic acid	:	3g
Antioxidant	:	as shown on the tables in the following chapters.
C.B.S.	:	0.6g
Sulphur	:	2.5g

For all the nitroxyl radical series the total compounding time = 10 minutes, and the ingredients were added into the rubber in the order shown.

For the nitrones, the total compounding time was 15 minutes. When premilling with the rubber was done the nitrone was premilled with the rubber alone on the two-roll open mill, and then the other compounding ingredients were added in the same order. Where no premilling was done, the nitrones were added after the stearic acid in the normal way.

The friction ratio used was 1:1

The nip size between the mills was set to 0.05cm.

The Wallace rapid plasticy numbers of all the stocks were measured after the compounding operations using the Wallace Plastimeter. They were all between 6 - 8 units no matter whether the total compound time was 10 minutes or 15 minutes.

Before vulcanisation the time for optimum cure and the curing characteristics were determined for each compounded stock using the Monsanto rheometer.

3.3 THE WALLACE RAPID PLASTIMETER

The Wallace rapid plastimeter was used. The principle of operation of this plastimeter is as follows[158]. A test piece (cut with a specially provided punch) is compressed between two parallel metal discs, at 100°C under a constant force, and the compressed thickness is measured. The thickness is indicated on a dial in the instrument in units of 0.1mm. It is usually expressed in terms of a Wallace Rapid Plasticity number.

The punch has dimensions such that it always cuts a disc of rubber of constant volume ($0.4 \pm 0.04 cm^3$).

3.4 THE MONSANTO OSCILLATING DISC RHEOMETER

The Monsanto rheometer model A-100 was used. This instrument is used to assess the curing characteristics of rubber stocks during vulcanisation at any desired temperature.

The instrument consists essentially of two die plates held together by pressure containing a cavity filled with rubber in which a bi-conical disc oscillates over an angle of 3^{o}. As the rubber vulcanises, the stress required to maintain the constant oscillation of 3^{o} is measured in terms of torque and recorded automatically on a separate chart recorder.

The following information may be obtained from the torque-time curve of a Monsanto rhegraph:the scorch time, the rate of cure, rate of first order cross-linking, the optimum cure time, the 90% cure time and the reversion characteristics.

The rheometer was operated at $140^{o}C$.

A typical Monsonto rheograph is shown in figure 3.1

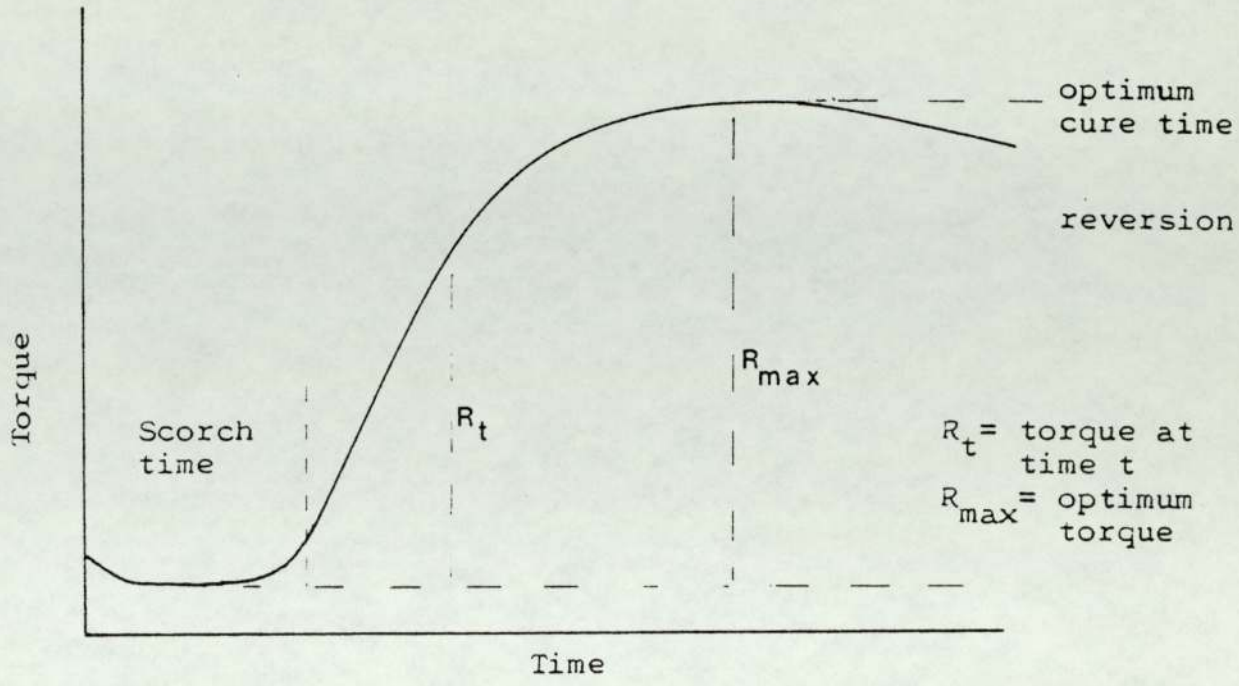


Figure 3·1: Typical Monsanto rheograph for the vulcanisation of rubber

A rough quantitative figure for the scorch time may be obtained directly from the rheograph by taking this time to be a rise in torque of 3 or 5 units above the minimum[159], and the rate of cure may be estimated directly from the slope of the curve[160].

More accurate figures for these values however can be obtained by assuming that the cross-linking rate follows first order kinetics and using the expression[159]

$$\lg_{10}(R_{max} - R_t) = \lg_{10} R_{max} - \frac{k}{2.303} (t - t_i)$$

when R_{max} is the maximum torque ; R_t is the torque at time t, t is the time of cure , ti is the scorch time, k is the rate of first order cross-linking. A plot of log $(R_{max} - R_t)$ against t gives a straight line with slope of k/2.303 and an induction period of t_i (see figure 3.2)

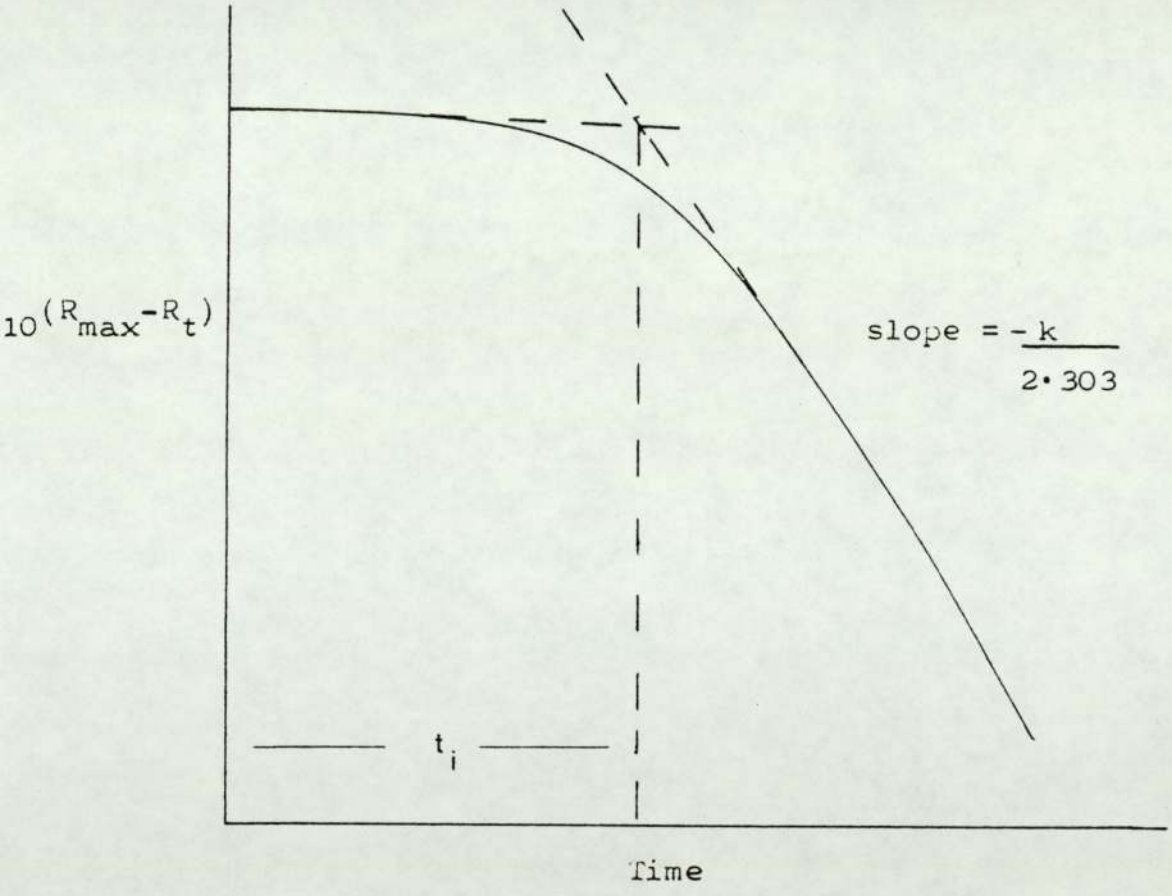


Figure 3·2: Typical first order plot for the vulcanisation of rubber using information from the Monsanto rheograph

3.5 THE VULCANISATION OF THE STOCKS FOR FATIGUE, OZONE AND STRESS RELAXATION TESTS

3.5.1 Vulcanisation for the Fatigue Tests

The vulcanisates were prepared in a rectangular stainless steel mould having dimensions of 22.9cm x 7.6cm x 0.15cm and beaded edges. Sixty grams of stock was required for each sheet. The mould containing the stock placed between the plates of a preheated steam or electric press and a pressure of 30 tons per 8 inch ram was applied to produce the required sheet thickness. The vulcanisates were cured to optimum cure at 140°C (determined earlier from the Monsanto rheograph see section 3.4) and at the end of the cure time they were removed and quenched in cold water.

3.5.2 Vulcanisation for the Ozone and the Stress Relaxation Tests

A stainless steel mould having dimensions of 24cm x 15cm x 0.068cm was used. Twenty grams of stock was used and vulcanised to optimum cure as described in section 3.5.1.

3.5.3 Vulcanisation for the Infrared Spectroscopic Analysis of Rubber

A stainless steel mould having dimensions 13.5cm x 13.5cm

x 0.018cm was used for this purpose. The weight of rubber stock used was 4.5 grams and the thickness of the vulcanised sheet was between 0.015cm - 0.020cm.
The vulcanisation was done as described in section 3.5.1.

3.6 STORING OF THE VULCANISED SHEETS

The vulcanised sheets obtained this way were stored in the dark in a vacuum dessicator or in a deepfreeze at $-10^{\circ}C$ till required.

3.7 SAMPLE CUTTING

For the fatigue experiments, dumbell shaped test pieces were cut using a B.S. type E cutter. The test pieces were cut after alligning the cutter between marks on the beaded edges found on either side of the cured sheet.

For ozone exposure strips of rubber 1cm wide and 7cm long were cut from the vulcanised sheet using the appropriate cutter.

For the stress relaxation tests, samples 0.4cm wide and 7cm long were cut from the vulcanised sheet using the appropriate test cutter.

All the test pieces were cut perpendicular to the grain of the rubber by punching the appropriate cutter onto the rubber sheet with a single stroke of hand operated press.

3.8 CONDITIONING OF THE TEST PIECES

As the properties of vulcanised rubber changes continuosly with time, and since these changes are particularly rapid during first sixteen hours after vulcanisation[158] no tests were carried out during this period.

Before testing the fatigue and stress relaxation test pieces were conditioned for four hours at room temperature.

For the static ozone tests, after mounting the test pieces on the jigs and straining them to the required elongation the stretched test pieces were conditioned for twenty four hours at room temperature before being exposed to the ozone.

As far as possible all tests were carried out after the same time interval after vulcanisation so that the results from different vulcanisates would be comparable.

3.9 THE ASSESSMENT OF THE FATIGUE RESISTANCE OF THE VULCANISATES

3.9.1 Description of the Apparatus

The Monsanto fatigue to failure tester was used for this purpose. The machine subjects dumbell shaped samples to repeated extension and records the number of cycles to failure automatically. During each extension the test pieces are subjected to an increasing strain at uniform acceleration for a quarter of a cycle, then relaxed over the next quarter and held at zero strain for the remaining half of the cycle. The maximum applied strain could be varied by changing the driving cams of the machine.

3.9.2 Operation Procedure

The test pieces were mounted between two horizontal bars containg shackels to hold the test pieces. The driving cams on the machine were set at the positions for zero strain and the distance between the upper and lower shackels were adjusted to be precisely 6cm apart with the aid of a callibration rod. The test pieces were then mounted and the machine was run for 1000 cycles. Any set developed in the test pieces was then eliminated, and the machine was run until the test pieces failed.

The samples were strained to a maximum of 61% of the original length at a frequency of 100 cycles per minute.

A minimum of six test pieces were used from each vulcanisate, the average number being nine pieces.

3.9.3 Presentation of the Results

The fatigue to failure results were expressed in terms of the Japanese Industrial Standard (J.I.S.) average. This value is obtained from the highest four results for the samples tested using the formula[161].

J.I.S. average = 0.5A + 0.3B + 0.1C + 0.1D where A, B, C and D are the fatigue lives of the samples and $A > B > C > D$.

The J.I.S. average is biased towards the high readings. However it is prefered to the simple arithmatic mean because the latter average does not represent the true fatigue life of the vulcanisate. The reason for this is because small imperfections on the surface of the rubber will cause the test piece to fail prematurely. These imperfections may be either present on the surface due to flaws in the mould, or they be be brought about during the cutting of the test pieces (flaws in the cutting surface). Therefore because premature failure is caused by flaws on the test pieces the arithmatic mean will not be a true representative value of the fatigue life of the vulcanisate. However the J.I.S. average makes allowance for these flaws and the premature failure of the rubber.

3.9.4 Comparison of the Fatigue Life of the Vulcanisates at Equal Energy Input

When the modulus of the stocks are nearly equal all the vulcanisates can be compared at a single extension. However comparison of vulcanisates, whose moduli differ significantly, at a single extension would give erroneous results since the energy input into the vulcanisate having the higher modulus would be greater than that fed into the vulcanisate with a lower modulus. In order to eliminate the effect of modulus the fatigue lives must be compared at the same strain energy input[26,161]. Comparisons made at equal energy input requires the computation of the strain energy per cycle and evaluation of the fatigue lives at the same strain energy value.

3.9.4.1 The Strain Energy Measurement

Stress-strain curves were plotted for the test pieces and the strain energy was obtained from these curves.

3.9.4.1.1 Method

The stress-strain curve was obtained for a fatigue test piece which had been previously fatigued for 30 cycles. The sample was suspended from a clamp, known weights

loaded onto the free end of the test pieces and the strain after each loading was measured with travelling microscope.

The stress was calculated using the expression

$$\text{stress} = \frac{\text{load}}{\text{cross-sectional area}}$$

and a stress strain curve was plotted. A typical curve is shown in figure 3.3

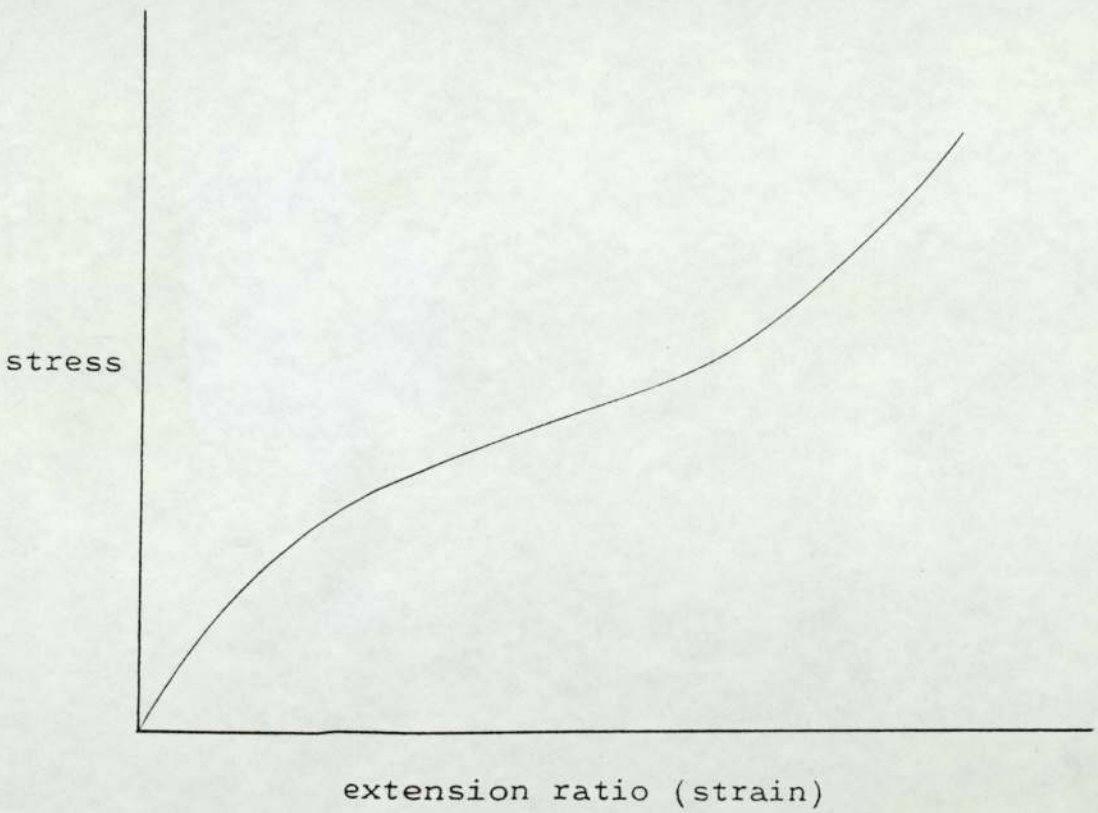


Figure 3·3: Stress-strain curve for rubber vulcanisate

3.9.4.1.2 The Strain Energy Calculation

The work done on the strain energy per cycle was obtained by calculating the area under the stress strain curve. This was done by applying Simpson's rule[161,162].

3.9.4.1.3 The Relationship of Strain Energy to Fatigue Life

It was shown in section 1.4.2 that the fatigue life N is related to strain energy W by the expression

$$N = \frac{1}{(\beta - 1)\beta(2KW)^{\beta} C_o^{\beta-1}}$$

Since B, K and Co are effectively constant this expression can be rewritten as

$$N = \frac{G}{W^{\beta}}$$

where G is a constant encompassing β, K and Co. Taking logs we get

$$\lg N = \lg G - \beta \lg W$$

Therefore the log of the fatigue life and the log of the strain energy have a straight line relationship.

Using this relationship the fatigue life of vulcanisates having different moduli can be compared at equal strain energy values.

3.10 THE ASSESSMENT OF THE OZONE CRACK RESISTANCE OF THE VULCANISATES

3.10.1 Description of the Apparatus

The Hampden-Shawbury Ozone test cabinet was used. The ozone cabinet consists essentially of a non illuminated chamber into which ozonoised air of known concentration is passed. The ozone is generated by exposing a stream of air to an ultraviolet source. The test pieces are hung from a mobile carrier inside the chamber. The mobile carrier ensures that all the samples are exposed to identicle concentrations of ozone.

The concentration of ozone inside the cabinet is measured electro-chemically using the ozometer model OZT-2. This measurement relies on the reaction of ozone with a solution of potassium iodide to produce iodine, according to the reaction

$$2KI + O_3 + H_2O \longrightarrow I_2 + 2KOH + O_2$$

The iodine effectively conducts the current through the solution by being reduced at the cathode to iodine anions,

and being reoxidised back to iodine at the anode.

The potassium iodide solution is made up according to the following formulation:-

potassium iodide : 1.500 ± 0.025 g/l

anhydrous sodium monohydrogen phosphate : 1.500 ± 0.025 g/l

anyhdrous potassium dihydrogen phosphate: 1.400 ± 0.025 g/l

3.10.2 Procedure for Static Ozone Testing

The rubber test strips having dimensions 7cm x 1cm x 0.068cm were mounted on jigs and held in tension at the required strain. The samples were all initially tested at a single strain level of 20%. The technologically interesting vulcanisates were further tested at strain levels of 5%, 10%, 15% and 30% as well.

Before the test samples were exposed to the ozone they were conditioned in the manner described in section 3.7.

The ozone concentration of the ozonoised air inside the test chamber in the ozone cabinet was set to 25 ± 5 p.p.h.m. The test temperature was set at 30°C, and the rate of air inflow into the chamber was set at 180(l/hour).

The strained test pieces were placed inside the ozone

chamber on the rotating test piece holder, exposed to the ozonoised air and the surface inspected for crack development at various time intervals. The examination was done using a stand lens of x 5 magnification[163]. An average of three test pieces per vulcanisate were studied.

3.10.3 Presentation of the Results

The size of the cracks were graded on an arbitary scale as follows:-

0) no cracks
1) cracks (0.5 - 1mm long) visible only under a magnification of x5.
2) fine cracks 1 - 2mm long just visible to the naked eye.
3) cracks 2 - 5mm long
4) cracks penetrate through the test piece
5) test piece broken

For the more interesting cases, a permanent record of the cracks was made on a photograph.

3.11 THE ASSESSMENT OF THE STRESS RELAXATION OF THE VULCANISATES

3.11.1 Description of the Apparatus

The Wallace Shawbury self recording age tester was used

for this purpose. The technique involves the monitoring of the stress in a sample of rubber whilst subjecting it to an accelerated ageing procedure, usually oxidative ageing. The decay in stress is recorded automatically on a chart by a pencil on the apparatus.

3.11.2 Testing Procedure

The test pieces having dimensions of 7cm x 0.4cm x 0.068cm were mounted between two clamps on the instrument and were strained by an extension of 60%, after first having zeroed the instrument. The test piece in the instrument was placed in an air oven set at 100 $\pm$ 2^{o}C with an air inflow rate of 0.071 cubic meters per hour. After allowing 5 minutes to equilibriate, the pencil was adjusted to 100% stress and allowed to decay. An average of two test pieces per vulcanisate was studied.

3.11.3 Presentation of the Results

The decay of the stress for each specimen was plotted using 1st order kinetics, and the time to 50% loss in stress was recorded.

3.12 THE ASSESSMENT OF THE DISCOLOURATION AND THE STAINING OF THE ADDITIVES

3.12.1 The Assessment of Discolouration

The discolouration tendency of the antidegradant in the vulcanised rubber was assessed relative to the control before and after ultraviolet radiation. Test pieces having dimensions of 5cm x 3cm x 0.15cm were exposed for 25, 50 and 100 hours to U.V. radiation in a U.V. cabinet. The severity of the discolouration after each period of exposure was assessed visually in diffused light. A numerical grading system was adopted using an arbitary scale fron 0 - 10. In cases where the additive was considered to have technological significance the discolouration was also assessed quantitatively by reflectance spectroscopy. The Colour Master-V was used for this purpose.

3.12.2 The Assessment of Staining

The degree of staining produced by the antidegradant relative to the control was tested according to the method specificied in the I.S.O. 3865 standard. Rectangular rubber test pieces (dimensions 5cm x 3.8cm x 0.068cm) were sandwiched between white enammel painted metal panels having the same dimensions and aged in an oven for 24 hours

at 70 ± 1°C. One plate was directly examined for staining and the other panel without the rubber sample, was exposed to U.V. light in the U.V. cabinet for 50 hours before the stain was examined.

The development of stain on the white panels, relative to the blank and a control, was assessed visually and graded qualitatively from 0 - 10 on an arbitary scale.

The stain was also measured quantitatively by reflectance spectroscopy on the Colour Master-V.

3.13 THE ASSESSMENT OF THE DEGREE OF THE BINDING OF THE ADDITIVE TO THE RUBBER

The vulcanisates moulded in the infrared mould were used. The degree of binding was assessed using infrared spectroscopy by measuring the decrease of an absorbance characteristic of the additive after extraction.

3.13.1 Testing Procedure

Sheets of vulcanised rubber 0.015 - 0.020cm thick were mounted on special holders and infrared spectra were recorded before and after extraction. The absorbance was measured using the base line technique. The rubber was

extracted in hot acetone under nitrogen. The Perkin - Elmer I.R. 599 grating spectrometer was used to record the spectra.

For each additive a callibration curve was also made by recording the spectra of the vulcanisates containing different amounts of additive from 0 - 2phr. Using this callibration curve the amount of additive left in the rubber could be determined easily.

3.14 THE R.A.P.R.A. TORQUE RHEOMETER

For some experiments it was necessary to mill the additive with the rubber using high shear in an oxygen defficient enviroment. The R.A.P.R.A. torque rheometer[164] was used for this purpose. This machine consists of a small chamber (capacity ca. 30g) containg two Z- bladed mixing screws which contrarotate to each other. Two rates of shear could be used - high or low. The mixing could be done either open to the atmosphere or closed to the atmosphere. The latter was achieved by means of an air operated ram. The temperature of the machine could be set at any desired value.

3.14.1 The Processing Procedure

The rubber (30g) was milled with 1p.h.r. of the additive in the closed chamber at room temperature using the high shear

speed. This speed corresponded to approximately 60 revolutions per minute.

The torque inside the chamber was followed automatically using an attached recorder. Due to the heat produced during the shearing of the rubber, the average temperature inside the chamber was between 40 -45^{o}C. When a series of samples were processed therefore, the machine was loaded as quickly as possible between runs inorder to ensure that the temperature ramained constant for all the processing operations.

After processing the samples were stored in the dark at -5^{o}C till required.

3.15 EVALUATION OF THE VARIATION OF TORQUE WITH PROCESSING TIME

Variations in torque are cuased by changes in the molecular weight of the polymer during shearing.

During the shearing in the R.A.P.R.A. Torque rheometer the torque experienced by the rotors is measured automatically and recorded on an arbitary scale on a separate chart recorder. For reproducibility, an average of three runs were recorded, and since the initial torque

always varies slightly with the degree of packing the initial torque was always equated to 100 and the remaining torque expressed as a percentage of the initial torque.

3.16 MEASUREMENT OF GEL CONTENT

The gel content in the milled rubber was measured as follows:-

1g of rubber was wrapped in lens tissue[165] and then by a wire mesh of known weight, placed inside a sealed bottle containing 200ml toluene and shaken for 72 hours. After this period of time the wire mesh and lens tissue were dried to constant weight in a vacuum oven and reweighed. From the weight difference the gel content was calculated.

The rubber solution was then filtered through a new lens tissue of known weight after which it was dried in a vacuum oven and reweighed. The weight difference was used to support the previous measurement.

For reproducibility an average of three runs were made for each sample.

The lens tissue used for this experiment was Whatman lens tissue grade 105.

3.17 NUMBER AVERAGED MOLECULAR WEIGHT ($\bar{M}_n$) FROM VISCOSITY MEASUREMENTS

A known weight of rubber (0.5g) was dissolved in 250ml purified toluene, filtered through a sintered glass (size 2) to remove insoluble material and the viscosity was evaluated from the flow times of the solvent and the rubber solution using an Ubbeholde suspended level viscometer at 25°C. The bore size of the capillary was such that the flow time for the solvent alone was 60 seconds. Flow times were obtained for various concentrations of the initial solution and the intrinsic viscosity $[\eta]$ was found by plotting the reduced viscosity ($\frac{\eta_{sp}}{c}$) verses c and making a linear extrapolation to zero concentration. Using the Mark-Houwink relationship ($[\eta] = KM^{\alpha}$) and the appropriate rate constants for K and ($K = 7.11 \times 10^{-6}$; $\alpha = 1.25$)[166] $\bar{M}_n$ was obtained.

In order to obtain $[\eta]$ accurately, a linear extrapolation of the plot of inherent viscosity $\frac{(\ln \eta_r)}{c}$ verses c was also made on the same graph for the plot of reduced viscosity verses concentration, and a double extrapolation was performed to the same point (see figure 3·4).

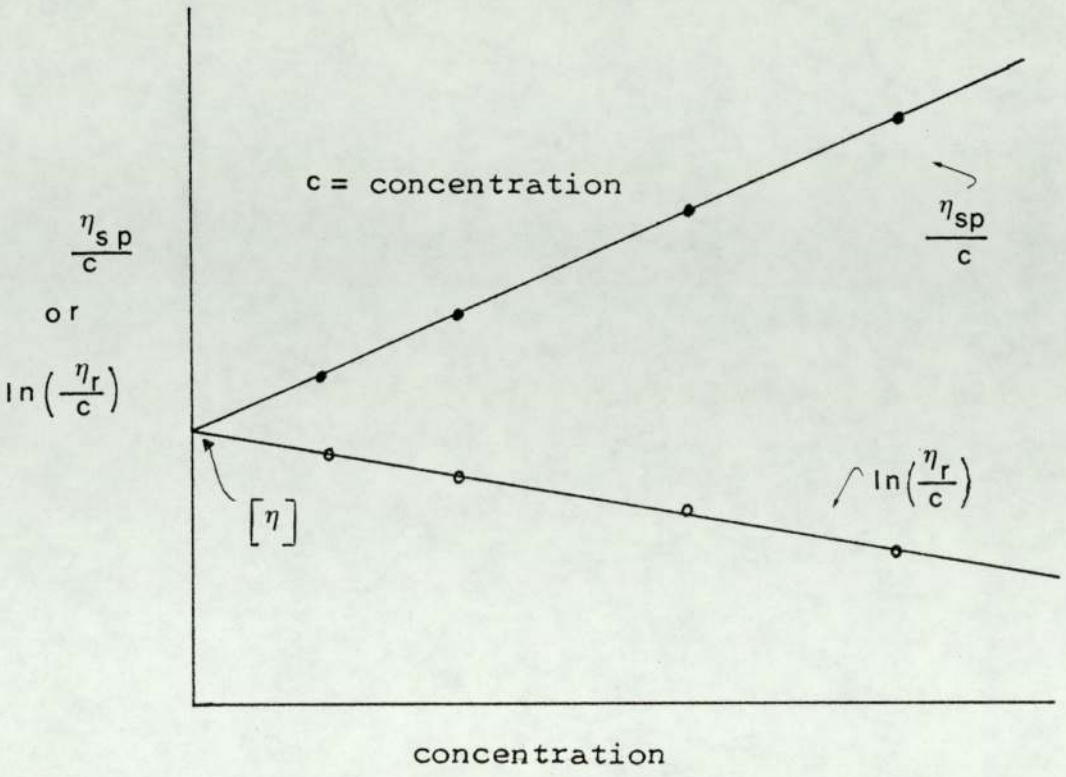


Figure 3·4

η_r was calculated from the ratio of the flow time of the solution to the solvent i.e: $\eta_r = \frac{t}{to}$

and η_{sp} was calculated from η_r by the following expressiion:

$\eta_{sp} = \eta_r - 1$

3.18 GEL PERMEATION CHROMATOGRAPHY (G.P.C.)

To determine changes in the molecular weight distribution of the rubber due to shearing in the torque in the presence of stabilisers G.P.C. was used. Chain scission processes

shift the molecular weight distribution to lower molecular weights. An increase in molecular weight implies cross linking.

The G.P.C. analyses were kindly done by personnel at the Rubber and Plastics Research Association of Great Britain. Samples were sent in duplicate for the G.P.C . analysis.

Polystyrene standards were used for callibration and Mark-Houwink constants were used for conversion via the universal callibration. The following conditions and G.P.C. operating varialles were used:

Columns : 4 columns; 1×10^6 A^o, 1×10^5 A^o, 1×10^4 A^o, 1×10^3 A^o.

flow rate : 1 ml/min

solvent : Tetrahydrofuran stabilised with 2,6 di-tert-butyl-p-cresol.

temperature : ambient

callibration : derived from polystyrene standards.

Mark-Houwink constants ($[\eta] = KM^{\alpha}$) used for conversion via universal callibration

polystyrene	$K = 1.2 \times 10^{-4}$	$\alpha = 0.71$
rubber	$K = 1.09 \times 10^{-4}$	$\alpha = 0.79$

Molecular weight distributions were obtained by the plot of $\frac{d\ W}{d\ \lg M}$ verses lgM. The relative values of $\frac{d\ W}{d\ \lg M}$ and lg M

are computed automatically by a computer attached to the G.P.C. Dispersity ratios of the polymers and other molecular weight data such as the number, weight and viscosity average molecular weights are also computed by the computer.

3.19 THE IDENTIFICATION OF RADICALS AND THE MEASUREMENT OF THEIR RELATIVE CONCENTRATIONS USING ELECTRON SPIN RESONANCE SPECTROSCOPY.

The JEOL - PE electron spin resonance (e.s.r.) spectrometer was used. The radicals were identified by their g and a_N values. The concentrations were measured relative to a copper sulphate standard of known concentration.

3.19.1 The Principle of e.s.r. Spectroscopy[167].

E.S.R. spectroscopy depends on the fact that the unpaired electron in a radical is like a spining magnet by virtue of its charge and spin. When placed in an external magnetic field the unpaired electrons allign 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 - one having a lower energy and the other having a higher energy. The

population within these levels is determined by Bolsman's statistical distribution. The lower energy state contains the spins (electrons) which are alligned parallel to the external field and the upper energy state contains the antiparallel spins. Upon application of a constant energy frequency (usually X-band microwave radiation) and sweeping the magnetic field, the electrons from the lower energy state can be made to "flip" or precess into the antiparallel state, and vice versa. The precession (resonance) requires the absortion of energy, and this absortion is recorded by the spectrometer.

In mathematical terms this behaviour is rationalised as follows:

The magnetic moment associated with a spining electron is

$$\mu = - g\beta S$$

where g = g - factor = spectroscopic splitting factor, the magnitude of which depends on extend of spin-orbit coupling.

β = Bhor magneton = $\frac{e\hbar}{2mc}$

where e = electron charge; $\hbar = \frac{h}{2\pi}$ and h = planks constant; m = mass of electron; c = speed of light.

S = spin

Since the electron spin is quantised, the magnetic moment

in a direction z in space is given by

$$\mu_z = -g \beta Ms$$

where Ms = magnetic spin quantum number = $\pm \frac{1}{2}$ for an electron.

When the electron is placed in a uniform magnetic field acting in the z direction, the energy of the interaction of the magnetic moment of the electron with the magnetic field H is given by

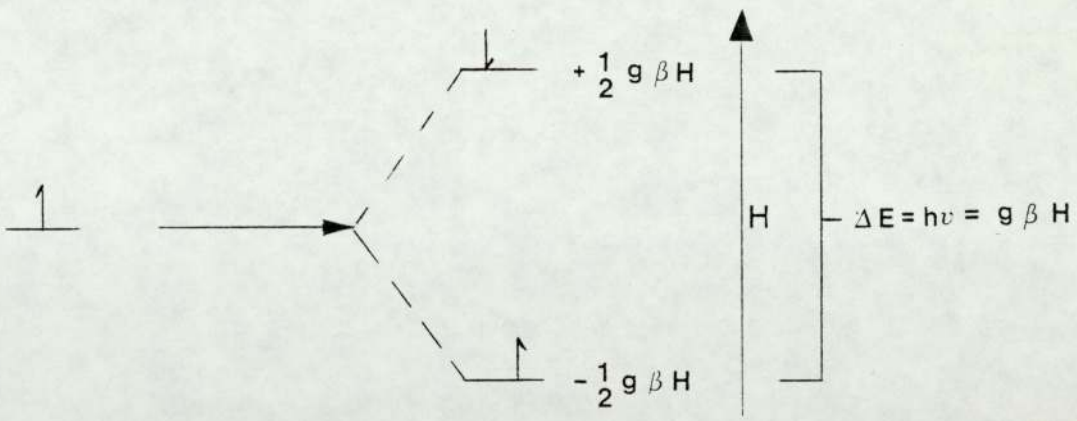
$$E = -\mu h$$

$$= g \beta MsH$$

Since Ms = $\pm \frac{1}{2}$, this represents two energy states differing in energy by: $\Delta E = g \beta H$

In frequency units this is: $h\upsilon = g \beta H$

Thus



i.e: the electron can allign itself either parallel or antiparallel with the applied field, and the normally degenerate energy level will be split into two states.

The lower energy state corresponds to the energy level in which the electron spin is parallel to the applied field, and the energy difference between the upper and lower levels is directly proportional to the applied field H.

The commonest value for the applied field used for organic work is 3300 gauss.

If electromagnetic radiation of frequency ν is absorbed by the system, the electrons in the lower energy state will be excited to the higher level and vice versa. A recording of the field at which this energy is absorbed gives rise to the e.s.r. spectrum.

A radical is normally characterised by the g - value and the hyperfine splitting value "a".

The g - value is a dimensionless quantity known as the spectroscopic splitting factor. It is a unique property of the radical and its magnitude is a measure of the amount of spin orbit coupling. For a "free" electron where there is no spin orbit coupling g = 2.0023 for resonance occuring when the applied field is 3300 gauss and the frequency of the electromagnetic radiation is 9.5 G Hz. Spin orbit coupling causes a small pertubation to the field experienced by the unpaired electron hence the resonance

will occur at a slightly different g - value and field to that of the "free" electron. It is this difference which serves to identify the type of radical present. The g - value is useful to identify different radical types such as carbon centred; oxygen centred or nitrogen centred radicals. However it cannot be used to distinguish between members of the same series of radicals. The hyperfine splitting value "a" however will give this information.

The hyperfine structure arises due to interaction of the unpaired electron with neighbouring nuclei in the radical which have non-zero spin e.g: ^{1}H, ^{2}D, ^{14}N. When the radical is placed in the magnetic field, the non-zero spin nuclei also allign themselves parallel or antiparallel to the applied field, hence modifies the field experienced by the unpaired electron. This causes the original signal of the unpaired electron to be split into a number of lines. The separation of the original signal into the number of lines is known as the hyperfine splitting. Generally if n is the number of equivalent nuclei and I is their spin value the resonance signal of the unpaired electron will be split into (2nI + 1) lines, their relative intensities being given by Pascal's Triangle. The separation between the hyperfine lines is called the hyperfine splitting value and is given the symbol "a".

There are two mechanisms which give rise to hyperfine structure in organic radicals, an isotropic mechanism and an anisotropic mechanism. Isotropic splitting arises when the unpaired electron has a finite probability of being at the position of the nucleus in question, and it is independant of the orientation of the radical. Anisotropic splitting on the other hand is critically dependant on the position of the nucleus and the electrons with respect to each other. Anisotropic interaction is important particularly in solid state studies where the magnetic nucleus is fixed in a particular orientation. The g-value is normally an anisotropic function, having three principle values along the three orthagonal axes (gx, gy, gz corresponding to the x, y, z. directions in space respectively). The anisotropic effect leads to complicated line shapes (figure 3.5). It is typically observed when the rotation of the radical is severely restricted as in single crystals, powders and in a "rigid glass". The spectra for these cases are generally broad and complex.

Apart from the g-value and the hyperfine splitting value, the width and shape of the e.s.r. lines are also of interest and can provide useful information. The line width is affected by the electron-spin reorientation processes, the geometry and nature of the surroundings, the

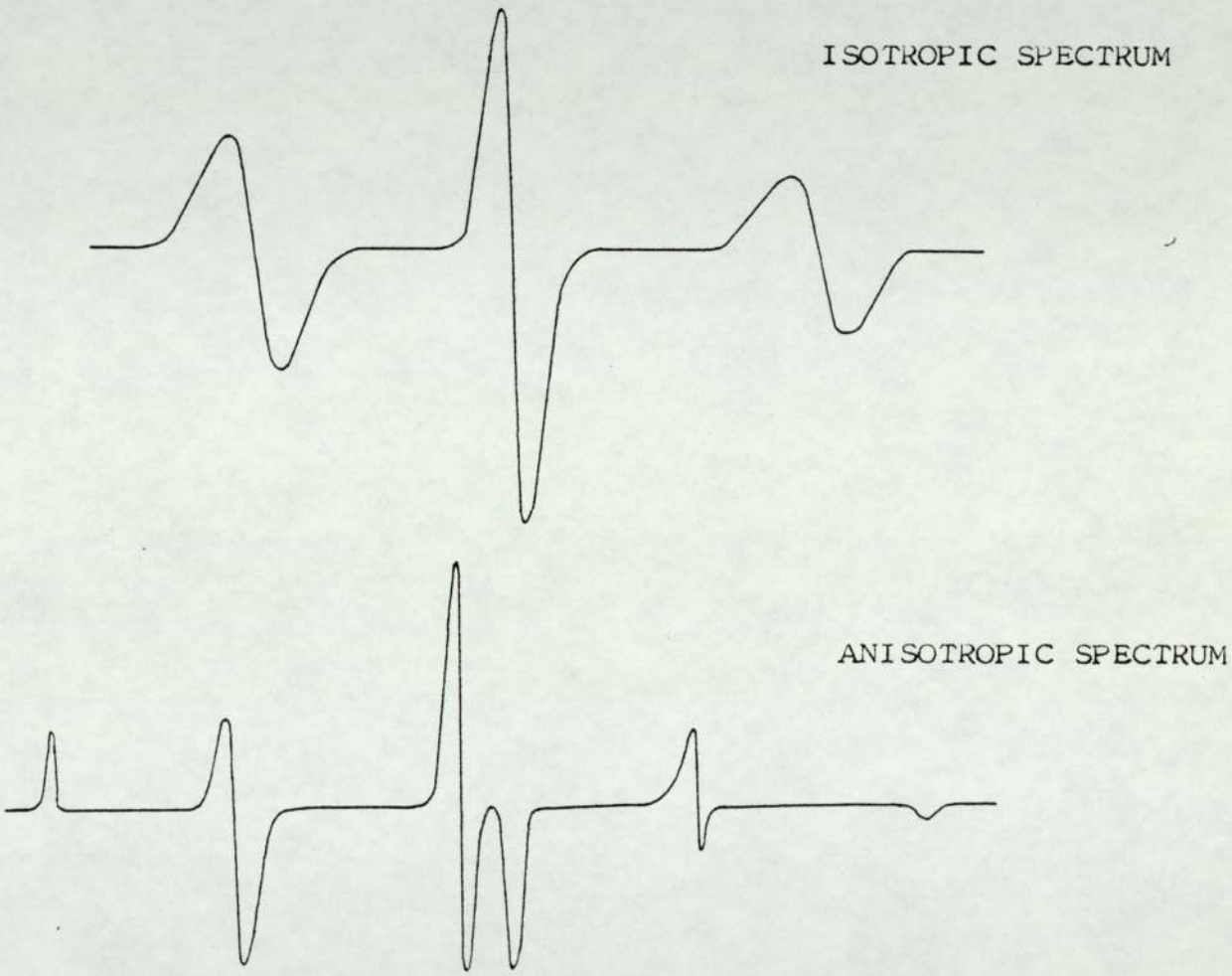


Fig. 3.5: A hypothetical set of spectra to illustrate a typical solution spectrum (isotropic spectrum) and a typical powder spectrum (anisotropic spectrum) for a radical coupled to a nucleus with I = 1

direction of rotation, and the ease of rotation of the radical. Generally when rapid free rotation occurs, the line with is mainly controlled by the electron-spin reorientation processes, and for dilute solutions the line widths are narrow and sharp. For concentrated solutions however due to spin-spin relaxation via electron-electron interactions line broading may occur. Restricted rotation of the radicals also causes line broading of the spectrum. This type of broading is caused by electron-nuclear interactions and is associated with the reorientation of nuclear spins. The broading observed for the e.s.r. lines of radicals in viscous media or in polymers is due to this reason.

3.19.2 Procedure for Recording the e.s.r. Spectra

For solutions usually 10μl in a sealed capillary tube was placed into a quartz tube and placed in the spectrometer cavity.

For the rubber samples, small strips weighing 0.5mg was weighed accurately, fixed on the outside of the quartz tube with cellotape and placed in the spectrometer cavity.

Before recording any spectra, the instrument was callibrated using a manganese reference, containing Mn^{2+} ions thermally fused with MgO powder.

This marker was also used to measure the g value and the hyperfine splitting value "a" for the unknown sample.

For quantitative measurements, copper sulphate solutions of known concentration were used as reference markers.

3.19.2.1 Measurement of the g-value and the Hyperfine Splitting value"a"

The manganese reference marker was used for this measurement. The Mn^{2+} ion gives an e.s.r. spectrum of six lines and a "g value" of 1.981[168] which does not vary significantly between the frequency range 9.2 M Hz to 9.4 M Hz[168]. Hence all measurements were made using electromagnetic radiation between these two limits.

The spectra of most organic radicals fall between the third and fourth of the Mn^{2+} spectrum, and the magnetic field between these two lines is 86.9 gauss.

A typical e.s.r. spectrum is shown in figure 3.6.

The g-value for the unknown sample is obtained by equating the distances x and y to 86.9 gauss and calculating the value of ΔH by a proportional sum and then using the expression[167].

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

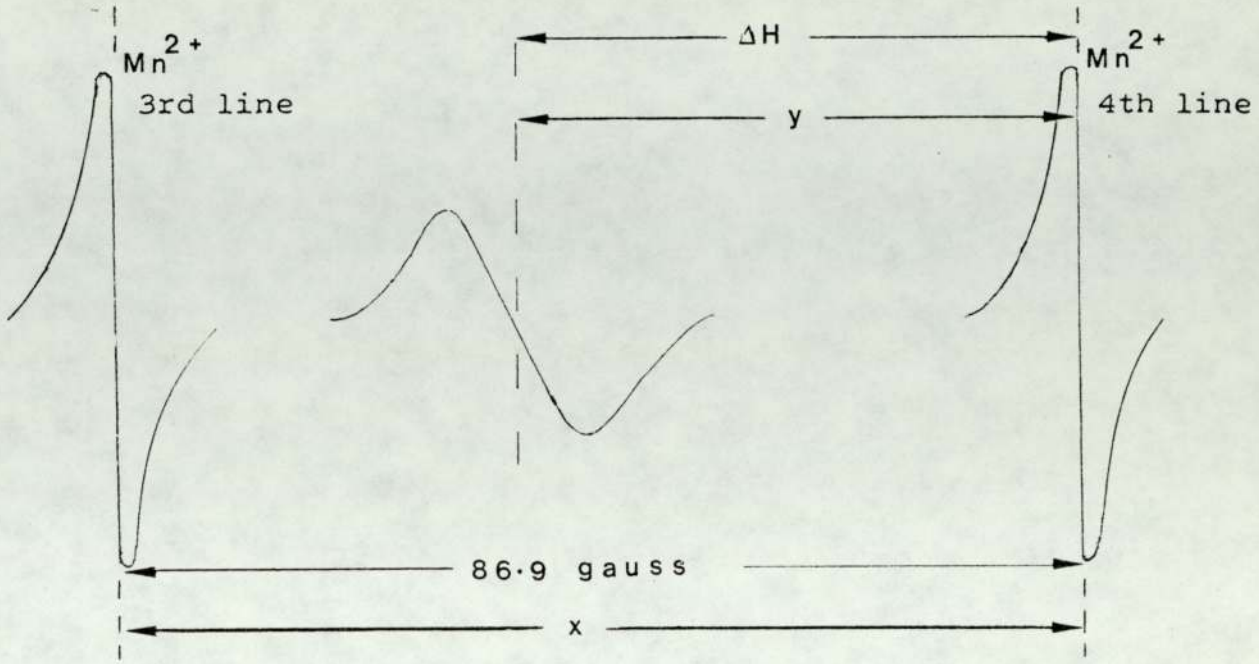


Figure 3·6: A typical e.s.r. spectrum

The hyperfine splitting value a is calculated using the notation in figure 3.2, and the expression

$$a = \Delta H' = \frac{z}{x} \times 86.9 \text{ gauss}$$

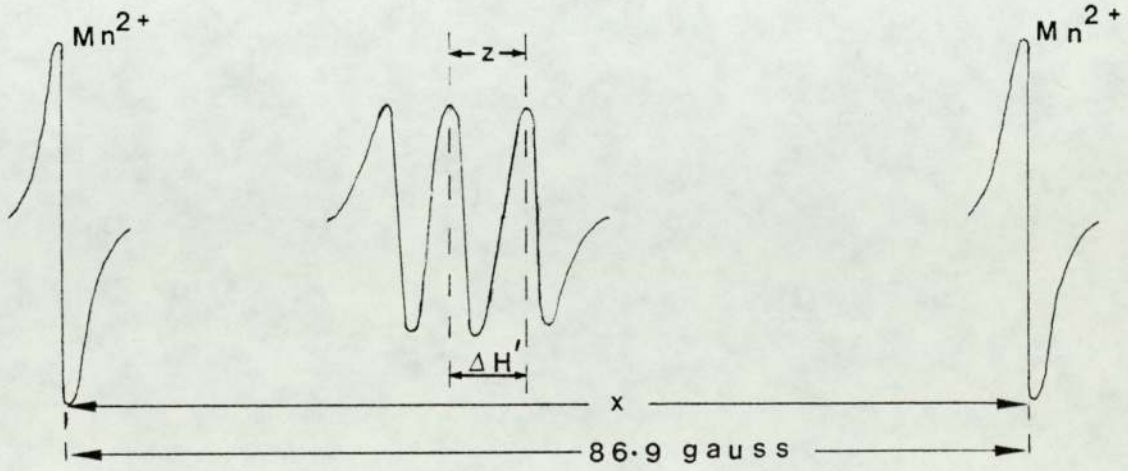


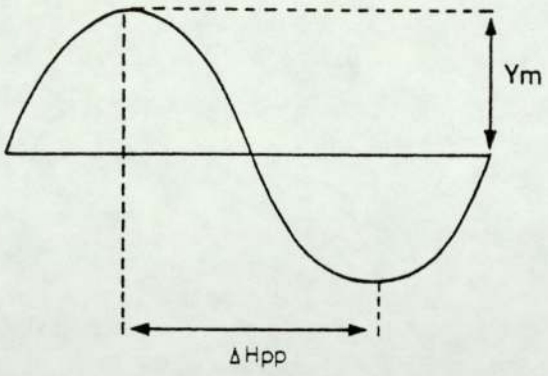
Figure 3·7 : Typical e.s.r. spectrum showing the hyperfine splitting

3.19.2.2 Measurement of Radical Concentration

The reference samples used for the measurement were copper sulphate solutions of known concentration. To avoid errors of reproducibility, the spectra for the unknown sample and the copper sulphate reference were recorded simultaneously.

The radical concentration was calculated by comparing the ratio under the aborption curves for the unknown and the reference sample , by the following equation using the notation in figure 3.8[32,106]

$$\frac{Y_m (\Delta H_{pp})^2 \text{ sample}}{Y_m (\Delta H_{pp})^2 \text{ reference}} = \frac{\text{concentration of radicals in sample}}{\text{concentration of radicals in reference}}$$



where Ym is in centimetres

and ΔHpp is in Gauss.

Figure 3·8

As far as possible for identification purposes and to study the hyperfine splitting instrument settings were used such that the molulus width setting was low.

For concentration measurements however high modulus width settings were used to minimise errors in the measurements of ΔH_{pp}.

CHAPTER FOUR

THE STUDY OF THE CURING CHARACTERISTICS AND THE ANTIFATIGUE EFFICIENCIES OF THE HINDERED PIPERDINES AND THEIR DERIVATIVES.

The hindered piperdines TMP, TMPS and their respective nitroxyl radicals have been reported to show antifatigue activity when swelled into rubber vulcanisates[101]. In view of this it was prudent to study the effect of these additives and their derivatives on the vulcanisation parameters and the antifatigue activities of these compounds after being introduced into the rubber during the compounding stage.

4.1 THE CURING CHARACTERISTICS OF THE HINDERED PIPERIDINES

4.1.1 Introduction

Any vulcanisation system may be described numerically by four parameters[160]. These are the scorch time (the induction period before crosslinking starts to occur), the rate of cure, the optimum cure time and the modulus at optimum cure. The ideal vulcanisation system is one having a scorch time sufficiently long to enable the

processing and the handling of the rubber before being put into the heated press, a fast as possible rate of cure (for obvious economic reasons) and no reversion characteristics. In practice however, this ideal cure is not possible although by the judicious use of the correct accelerator system the ideal vulcanisation can be approached. Indeed this is precisely what has been done in the rubber industry and has led to the development of a number of standard curing formulations. These include the conventional C.B.S/sulphur system where there is a high sulphur to accelerator ratio, the so called "efficient" cure systems where the sulphur to accelerator ratio is low, the T.M.T.D. sulphurless curing system, the peroxide and radiation cures.

Stabilisers which are added to the rubber should not significantly interfere with the vulcanisation process. If they do they are not normally considered to be technologically acceptable, particularly if they affect the scorch time by causing premature crosslinking to occur, or if they retard the cure rate extensively.

Thus a study of the curing parameters yields information on the scorch time and the rate of cure which are important industrial parameters for the vulcanisation process. A further object of the present study is to compare the

effect of additives (stabilisers) relative to the control containing no stabiliser and relative to commercial agents such as I P P D

4.1.2 The Vulcanisation Procedure

Acetone extracted rubber (S.M.R. grade 10) was used. The extraction was done as described in section 3.1. The compounding formulation used was the conventional C.B.S system. The compounding operations were done in the manner described in section 3.2. The vulcanisation temperature was 140°C. The vulcanisation parameters were determined on the Monsanto Rheometer (model A100) and assessed by the kinetic treatment of the cure curves as described in section 3.4. Before vulcanisation the Wallace Rapid Plasticity number of the stocks were measured using the Wallace Rapid Plastimeter (section 3.3) to ensure that all the stocks had plasticity values between 6 and 8 units.

4.1.3 The Effect of the TMP and TMPS Series

Figure 4.1 shows a typical set of cure curves for the hindered piperidines. In fact it shows the curves for TMP, TMOP, TMPD and TMMP. The curing parameters for these compounds are summarised on table 4.1. The table

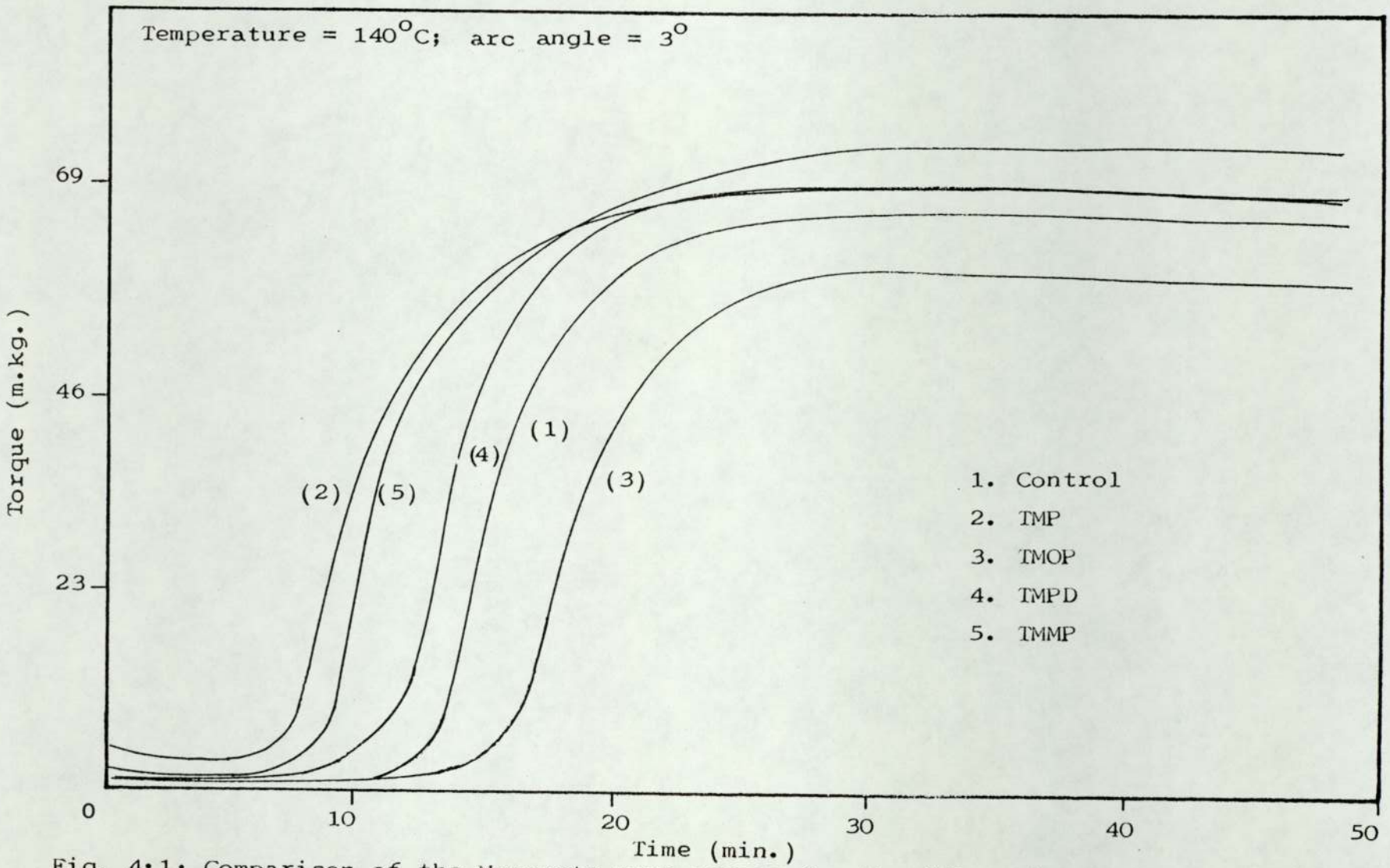


Fig. 4·1: Comparison of the Monsanto cure curves for the TMP series

ADDITIVE	Concentration		CURING CHARACTERISTICS				
	g/100g rubber p.h.r.	moles /100 parts rubber x 10^{-3}	optimum cure time (min.)	scorch time (min.)	1st order rate constant k(min.) $\pm$0.01	90% cure time (min.)	optimum torque (m.kg.)
Control	Nil	Nil	33	12.5	0.26	21	0·67
TMP	1·0	6·37	30	7·5	0·28	18	0·64
TMOP	1·08	6·37	33	16·5	0·23	25	0·58
TMPD	1·1	6·37	30	11·6	0·27	20	0·67
TMMP	1·2	6·37	30	8·5	0·25	20	0·69
TMPS	1·53	3·19	30	9·0	0·24	22	0·67
TMOPS	1·62	3·19	37	14·0	0·22	29	0·60
TMPDS	1·63	3·19	37	6·0	0·22	25	0·69

Table 4·1: The curing characteristics for the TMP and TMPS series

also shows the curing parameters for the TMPS series, namely TMPS, TMOPS and TMPDS.

Inspection of this table shows that the curing parameters for TMPD are not significantly different to the control. However for the stocks containing TMP, TMOP and TMMP, they do differ significantly. In the case of TMOP, the rate of cure appears to be retarded since the scorch time is longer and the optimum modulus is lower than the control. The rate of first order crosslinking is also slightly lower. In contrast the amine and the o-methylated hydroxylamine are scorchy.

The trend is similar for the TMPS series too. However in contrast to TMPD the hydroxylamine of this series is significantly more scorchy. The concentration of the TMPS series is 3.16×10^{-3} moles per hundred parts rubber. This concentration was chosen in order to compare the molar technological activity of these compounds with that of the corresponding monofunctional additives (i.e. the TMP series). The concentration is half of that used for the monofunctional compounds because TMPS and its derivatives are bifunctional. Table 4.2 shows the curing characteristics for TMPS and its nitroxyl radical (TMOPS) at an equiweight concentration of 1 phr. It can be seen from this table that the curing characteristics for these

ADDITIVE	Concentration		CURING CHARACTERISTICS				
	P.h.r. (g)	moles /100 parts rubber x 10^{3}	optimum cure time (min.)	scorch time (min)	1st order rate constant k(min)$^{-1}$ ±0.01	90% cure time (min.)	optimum torque (m.kg)
Control	Nil	Nil	33	12·5	0·26	21	0·67
TMPS	1·0	2·08	30	9·0	0·27	22	0·67
TMOPS	1·0	1·96	37	14·0	0·22	29	0·62
TMPDS	1·0	1·96	37	6·0	0·22	26	0·67
TMOPX	1·0	2·02	35	8·5	0·21	24	0·66
TMOXPZ	1·0	1·79	40	9·6	0·21	26	0·67
BPTMOP	1·38	3·19	45	18·0	0·20	37	0·64
BPTMOP	1·0	2·31	42	14·0	0·20	36	0·69
IPPD	1·0	4·4	35	11·0	0·22	27	0·69

Table 4·2: The curing characteristics for hindered piperidine nitorxyl radicals containing various functional groups.

two additives at the 1 p.h.r. level are similar to that for the equimolar concentration (table 4·1).

Table 4·2 also shows the curing characteristics for TMOPX, TMOXPZ and BPTMOP. Unlike the other nitroxyl radicals examined, TMOPX and TMOXPZ are very scorchy. The curing characteristics for BPTMOP on the other hand do not differ very much from that of the other nitroxyl radicals although the optimum torque is now similar to that of the control. One interesting point is that for BPTMOP, when the loading is reduced from 1.4 p.h.r. the scorch time is also reduced. As a matter of interest the commercial material Santoflex I P (I P P D) at 1.0 p.h.r. was also tested and the results are shown in table 4.2.

A study of the curing parameters for the additives in unextracted rubber showed that the vulcanisation characteristics did not significantly differ to that of the extracted rubber.

Because the nitroxyl radicals were found to cause retardation of the vulcanisation process it was interesting to study the relative concentration of nitroxyl radicals in the rubber before and after vulcanisation and compare it to the relative

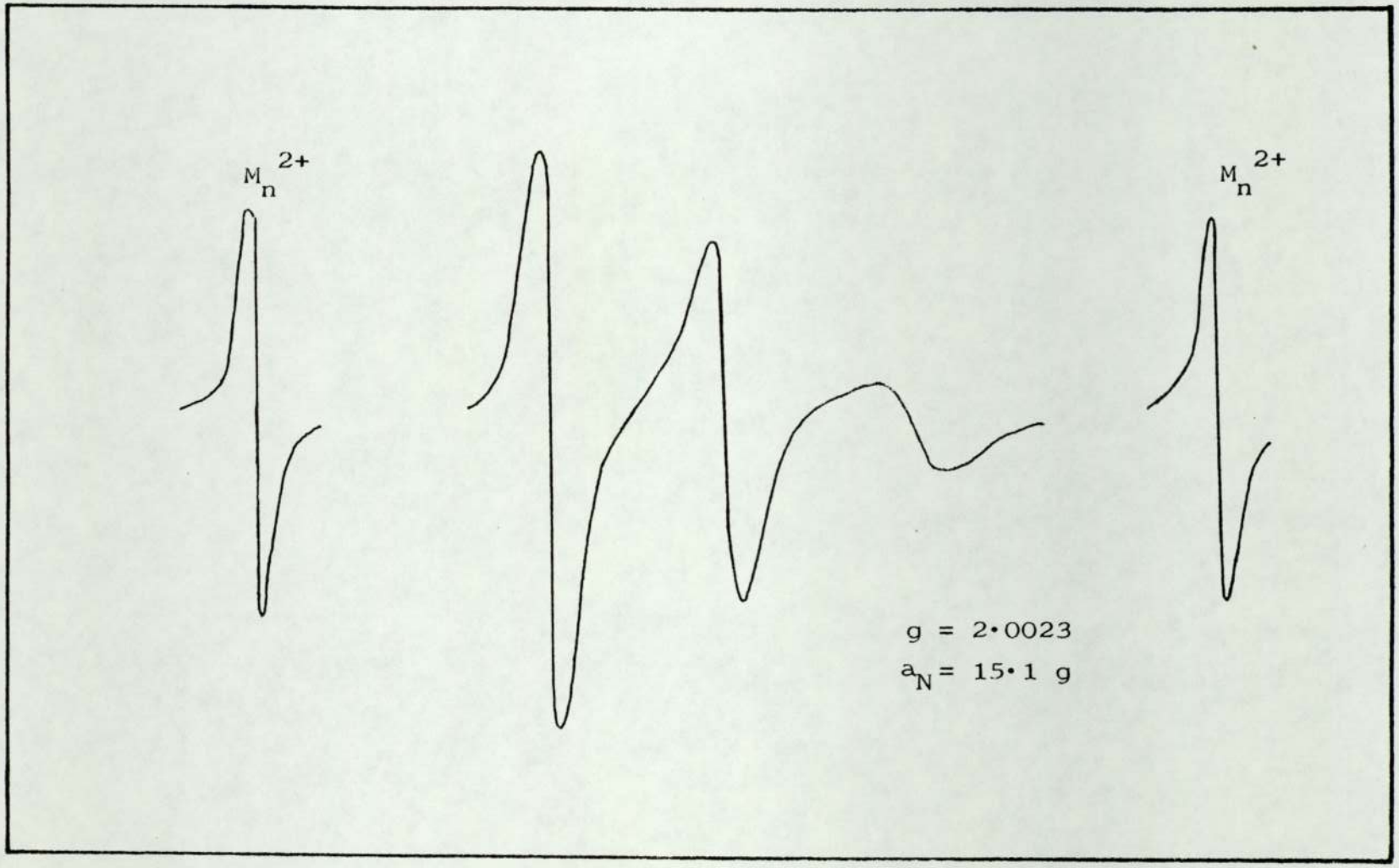


Fig. 4·2: The e.s.r. spectrum of TMOP in conventional C.B.S. vulcanised rubber

STAGE	Relative $[R_2NO\cdot]$ per gram rubber (moles) x 10^5	Percent $R_2NO\cdot$ left relative to that initially put in
a	$1\cdot68 \pm 0\cdot02$	100
b	$1\cdot65 \pm 0\cdot02$	98
c	$0\cdot026 \pm 0\cdot003$	1·5

Notation:

a = 1 p.h.r. TMOP swelled into the rubber

b = 1 p.h.r. TMOP incorporated into the rubber as an additive during the compounding stages - before vulcanisation

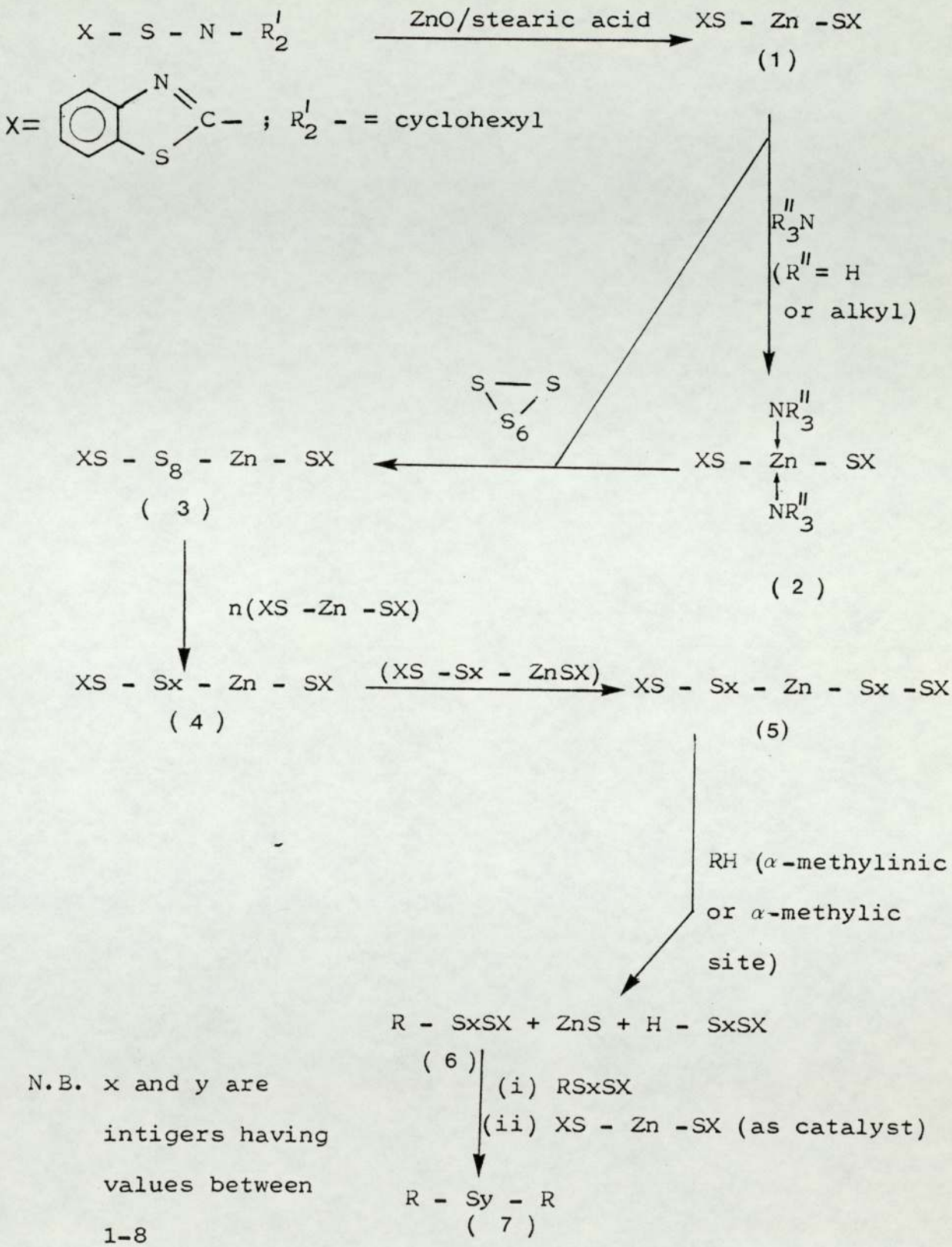
c = b after vulcanisation

Table 4.3: The relative concentration of TMOP before and after vulcanisation

concentration that was initially added into the rubber. TMOP (1 p.h.r.) was used for this study. Figure 4.2 shows a typical e.s.r. spectrum of TMOP in the vulcanised rubber. In contrast to the solution e.s.r. spectrum (figure 2.1) the e.s.r. lines for TMOP in the rubber are broader. Furthermore in the rubber there is a pronounced differential broading of the three e.s.r. lines. As the field is "swept" the lines tend to broaden (figure 4.2). Table 4.3 shows the results for the relative nitroxyl radical concentrations and compares them to that initially added into the rubber. Because absolute concentrations cannot be measured directly from the e.s.r. spectra the relative concentration equivalent to 1 p.h.r. of TMOP was measured from an e.s.r. spectrum which was recorded after 1 p.h.r. of TMOP had been swelled into the rubber. The nitroxyl radical concentrations were measured by the technique described in section 3.19.2.

4.1.4 Discussion

It is generally accepted that the sulphur vulcanisation of natural rubber in the presence of accelerators proceeds via a polar mechanism without involving any ionic or free radical intermediates. The reaction scheme as proposed by workers at the M.R.P.R.A[1] for the N-cyclohexyl-



N.B. x and y are intigers having values between 1-8

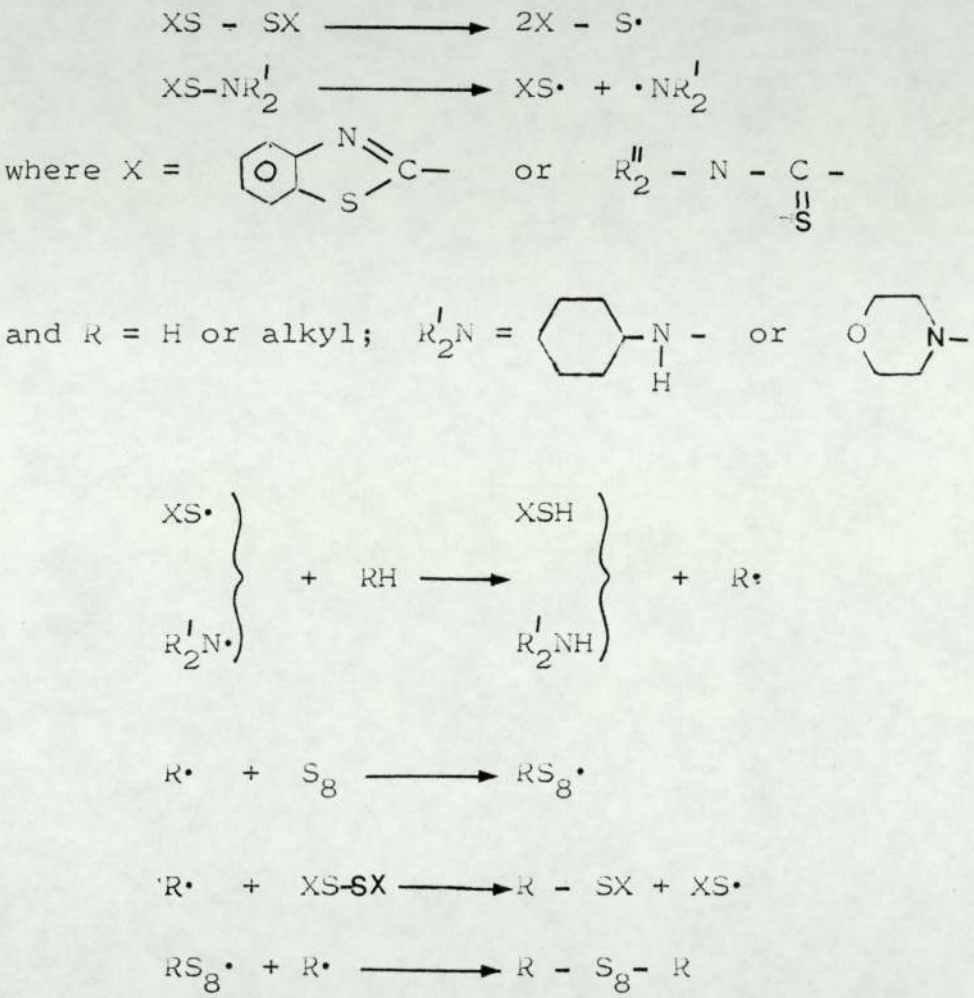
Scheme 4•1

benzothiazole-2-sulphenamide (C.B.S.) accelerated system is outlined in the scheme 4.1. It is believed that the other common accelerators such as thiazoles, other sulphenamides and thiuramdisulphides also act in a similar manner.

The reaction scheme is centered around the role of an active zinc complex of the type (1) in scheme 4.1. This is really a zinc mercaptide species. In fact for C.B.S. the species is zinc mercaptobenzthiazole (ZMBT). This species reacts with elemental sulphur by a polar mechanism to form a zinc perthiomercaptide of the type (5) in scheme 4.1. The reaction of (1) with the sulphur is enhanced by amine co-ordination to the zinc to give compounds of type (2). The amines are generally the naturally occuring nitrogeneous bases or that produced from cleavage of the S-N bond of the sulphenamides. The perthiomercaptide (5) then reacts with the rubber hydrocarbon at the α-methyline or the α-methylic sites also by an essentially polar mechanism to give a rubber bound intermediate of the type (6) shown in scheme 4.1. The initial cross link (7) is formed by catalysis of two of these moieties of type (6) by the active ZMBT complex.

A free radical mechanism for the vulcanisation reaction has also been proposed[170,175]. Although it is generally

regarded as being outdated, there has been evidence[176,177] to suggest that this mechanism also operates to a certain extent. The essential steps for this mechanism are outlined in scheme 4.2.



Scheme 4.2

Because both the polar and the free radical pathways could

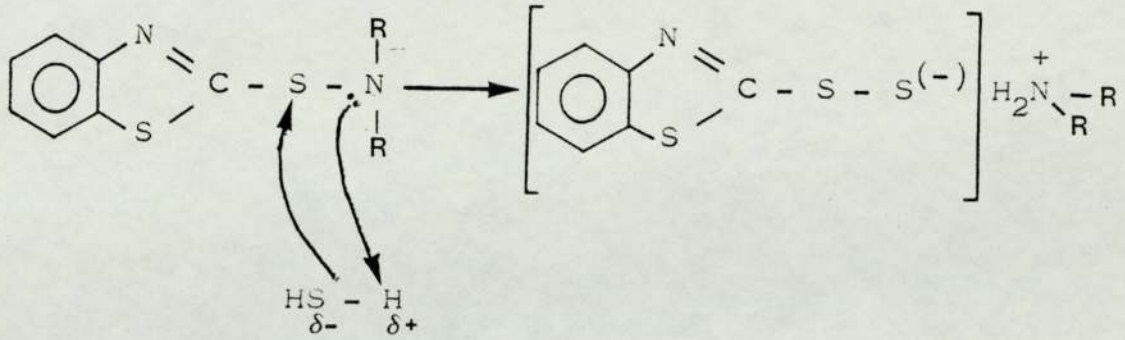
occur to a greater or lesser extent during the severe conditions of the vulcanisation (the temperature of vulcanisation is 140°C or greater) any suggestions that have been made in the following discussion on the effect of nitroxyl radicals and their precursors are such that both the vulcanisation mechanisms are satisfied.

The most significant feature among the hindered piperidines, their nitroxyl radicals and hydroxylamines which were tested is that all the nitroxyl radicals interfere with the curing process. This fact was inferred, because for these compounds the induction period before crosslinking occurs was increased, and the optimum degree of crosslinking was reduced slightly. The latter feature is reflected from the torque values. The only exception to this were the xanthogenetonitroxyl radicals, the reasons for which will be discussed later. The interference with the cure was further supported by the fact that after vulcanisation there was only about 1% of free nitroxyl radical left in the system (see table 1.36). This suggests that the nitroxyl radical is transformed into other products during the vulcanisation reactions, possibly to the amine, the hydroxylamine or the alkylated hydroxylamine, or it may even be destroyed altogether.

The interference was unexpected, however it may be rationalised in terms of the reaction of the nitroxyl radicals with the thiols and other thyl radicals that could be formed during the vulcanisation reactions. Hindered piperidines are known to react with tetramethylthiuramdisulphide[178], aromatic thiols[179] and thyl radicals[179] to give a variety of compounds.

The interference with the cure during vulcanisation can be rationalised in terms of both the polar mechanism and the free radical mechanism. In the case of the free radical mechanism the nitroxyl radical interferes by reacting with the thyl radicals produced during the initial steps.

In terms of the polar mechanism, the initial formation of the activated ZMBT complex from the sulphenamide involves the thermal or reductive scission of the S-N bond[169]. It has been suggested that hydrogen sulphide formed from the thermal reaction of sulphur with the naturally occuring nitrogeneous bases or the amine moiety of the sulphenamide is responsible for the cleavage of the S-N bond[180].



This amine salt of the mercaptobenzothiazole (MBT) then reacts rapidly with the zinc soap (formed from reaction of the zinc oxide with the stearic acid) to give the activated ZMBT complex[181]. Interaction of the nitroxyl radical with either the H_2S or the amine salt of the MBT or the MBT itself would retard the formation of the ZMBT complex.

Furthermore the interaction of the nitroxyl radical with the other perthiomercapto intermediates would certainly affect the overall degree of crosslinking in the rubber. Dweik[182] has reported that aromatic nitroxyl radicals produce the corresponding amines during the vulcanisation reaction, presumably by the interaction of the nitroxyl radical with the curing system.

The scorchiness of the amine and the hydroxylamines of the hindered piperidines respectively may be attributed to their relative basicities. Nitrogeneous bases are

known to activate the vulcanisation process by activating the ZMBT complex[183] and also by activating the elemental sulphur to heterolytic scission[184,185]. Hydroxylamines could probably do this as well, but less efficiently, thus accounting for the difference in the scorch times for these compounds.

Xanthates are known to be very scorchy when used in sulphur vulcanisates. In fact they are often used in the rubber industry as ultrafast accelerators and find application in sulphurless formulations and room temperature vulcanisation of latex[186,187]. A typical commercial material is zinc isopropyl xanthate known as ZIX[50,186-188]. The retardation of the cure that occured in the presence of the nitroxyl radicals was not observed for the case of TMOPX and TMOXPZ probably because of the extreme "scorchiness" of the xanthate functional groups in the molecule.

It can be seen that the commercial material I P P D does not interfere with the cure significantly.

The broading of the e.s.r. lines of the nitroxyl radical in the rubber (figure 4.2) relative to that for the solution (figure 2.1) is due to the restricted mobility of the nitroxyl radical[166]. As described in section 3.19.1,

in liquid solution there is rapid tumbling and rotation of the radicals. This results in the spectrum being isotropic and the e.s.r. lines being narrow and sharp. In the rubber however the tumbling and rotational motions of the radicals are restricted. The radicals are not immobile as the spectrum is still isotropic, but the broading of the spectrum is due to the slow tumbling of the radicals in the rubber. The differential broading of the e.s.r. lines in the spectrum for the radical in the rubber is also an effect of the slow tumbling motion.

4.2 THE ANTIFATIGUE PROPERTIES OF THE HINDERED PIPERIDINES, THEIR NITROXYL RADICALS AND THEIR HYDROXYLAMINES.

4.2.1 Introduction

In section 1.8 it was described that the species primarily responsible for the antifatigue activity of the aromatic amines were the nitroxyl radical derived from the amines. The mechanism of their action was described to be a regenerative cycle involving an alternative sequence of CB-A and CB-D reactions which removed both alkyl radicals and alkylperoxyl radicals from the system respectively. Since the hindered alicyclic piperidines (TMP and TMPS) too were shown to have a limited antifatigue activity when

they were swelled into the rubber, it was decided to evaluate their activities and the activities of their related nitroxyl radicals and hydroxylamines after incorporating them into the rubber during the compounding operations.

4.2.2 Procedure

The procedure for the compounding and the vulcanisation of the rubber was described in sections 3.1 to 3.5. Before vulcanisation the Rapid Wallace Plasticity numbers of each stock was measured to ensure that they were all between 6 - 8 units. The test pieces were cut from the moulded vulcanisates, conditioned as described in section 3.8 and fatigued to faliure on the Monsanto Fatigue to Faliure Tester as described in section 3.9. During the fatiguing operations, the samples were strained to a maximum extension of 61% of the original length at a frequency of 100 cycles per minute. The results were expressed in terms of the J.I.S. average (section 3.9.3).

4.2.3 Results

The fatigue life of conventional C.B.S. cured gum vulcanisates containing the hindered piperidines, their nitroxyl radicals and hydroxylamines for the TMP and TMPS

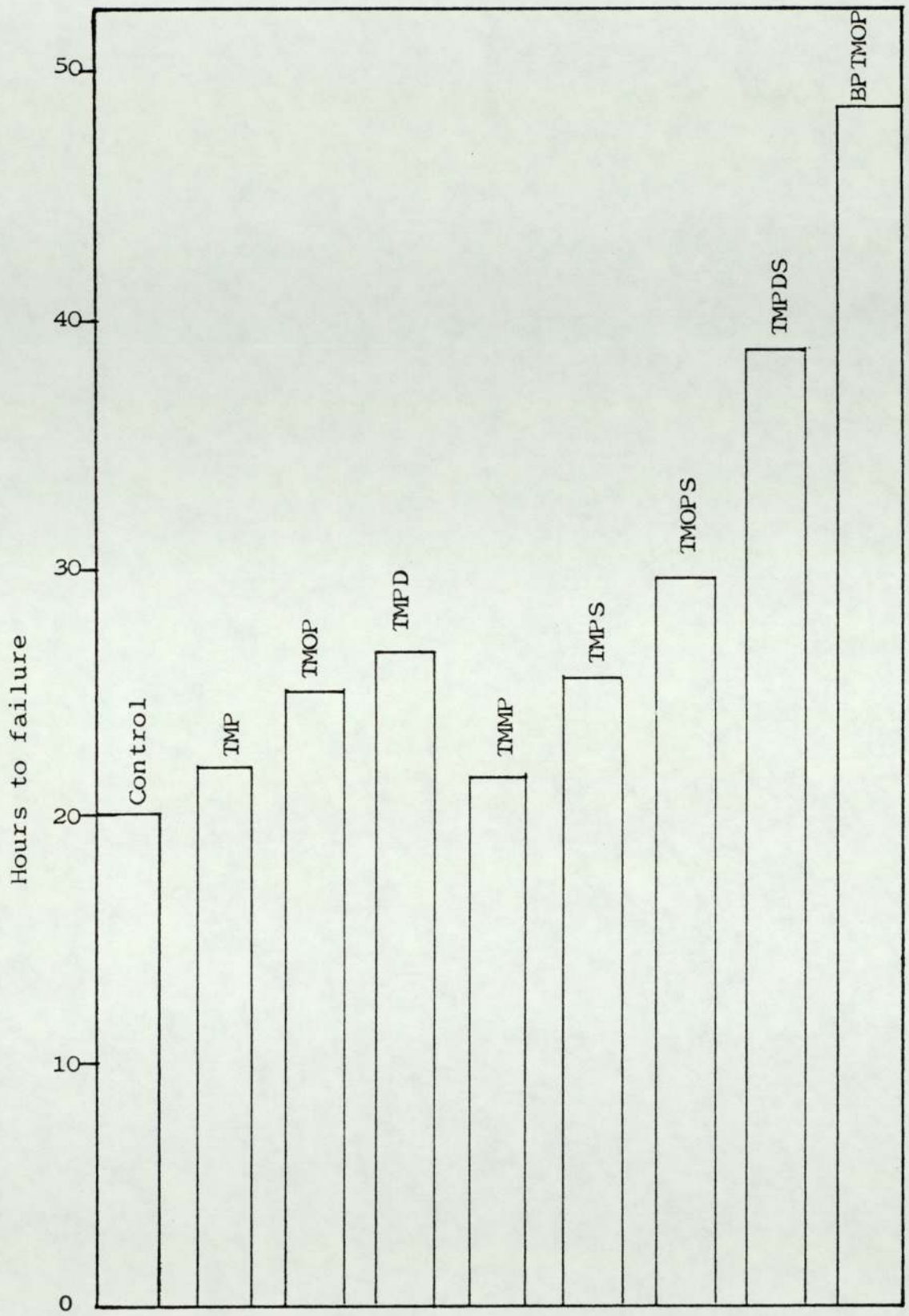


Fig. 4·3: Bar chart showing the influence of the hindered piperidines and their derivatives (at equimolar concentrations) on the fatigue life of conventional C.B.S gum vulcanisates.

ADDITIVE	CONCENTRATION		FATIGUE LIFE 61% max. strain		
	p.h.r. (g)	moles per hundred parts rubber x 10^{3}	Number of cycles to failure x 10^{2}	Number of hours to failure (hrs.)	Percent improvement over the control
Control	Nil	Nil	1204	20·0	-
TMP	1·0	6·37	1301	21·7	8
TMOP	1·08	6·37	1499	24·9	24
TMPD	1·1	6·37	1573	26·3	30
TMMP	1·2	6·37	1268	21·1	5
TMPS	1.53	3·19	1523	25·4	27
TMOPS	1·62	3·19	1742	29·0	45
TMPDS	1·63	3·19	2247	37·5	87
BPTMOP	1·38	3·19	2901	47	135

Table 4.4: The influence of the hindered piperidines and their derivatives on the fatigue life of conventional C.B.S cured gum vulcanisates.

series at the same functional molar concentration is summarised in table 4.4 and in figure 4.3 . Table 4.5 and figure 4.4 show the fatigue life of the vulcanisates when the additives were incorporated into the rubber at a level of 1p.h.r.. Table 4.5 and figure 4.4 also shows the fatigue life of the vulcanisates containing the xanthogeneto nitroxyl radicals and the nitroxyl radical containing the hindered phenol functional groups(BPTMOP). For comparative purposes the fatigue life of the vulcanisate containing 1phr santoflex I.P. (I P P D) is also shown on this table.

It is evident from these tables that the protection of the rubber vulcanisates against fatigue detioration by the hindered piperidine series increases in the order

$$R_2NH < R_2NO\cdot < R_2NOH$$

This effect is particularly pronounced for the TMPS series.

In contrast the O-methylated hydroxylamine does not impart any antifatigue resistance to the vulcanisate.

For the vulcanisates which were protected by the xanthogeneto nitroxyl radicals (TMOPX and TMOXPZ) the protection imparted to the rubber was about 40% greater than the fatigue protection given by the bisnitroxyl radical

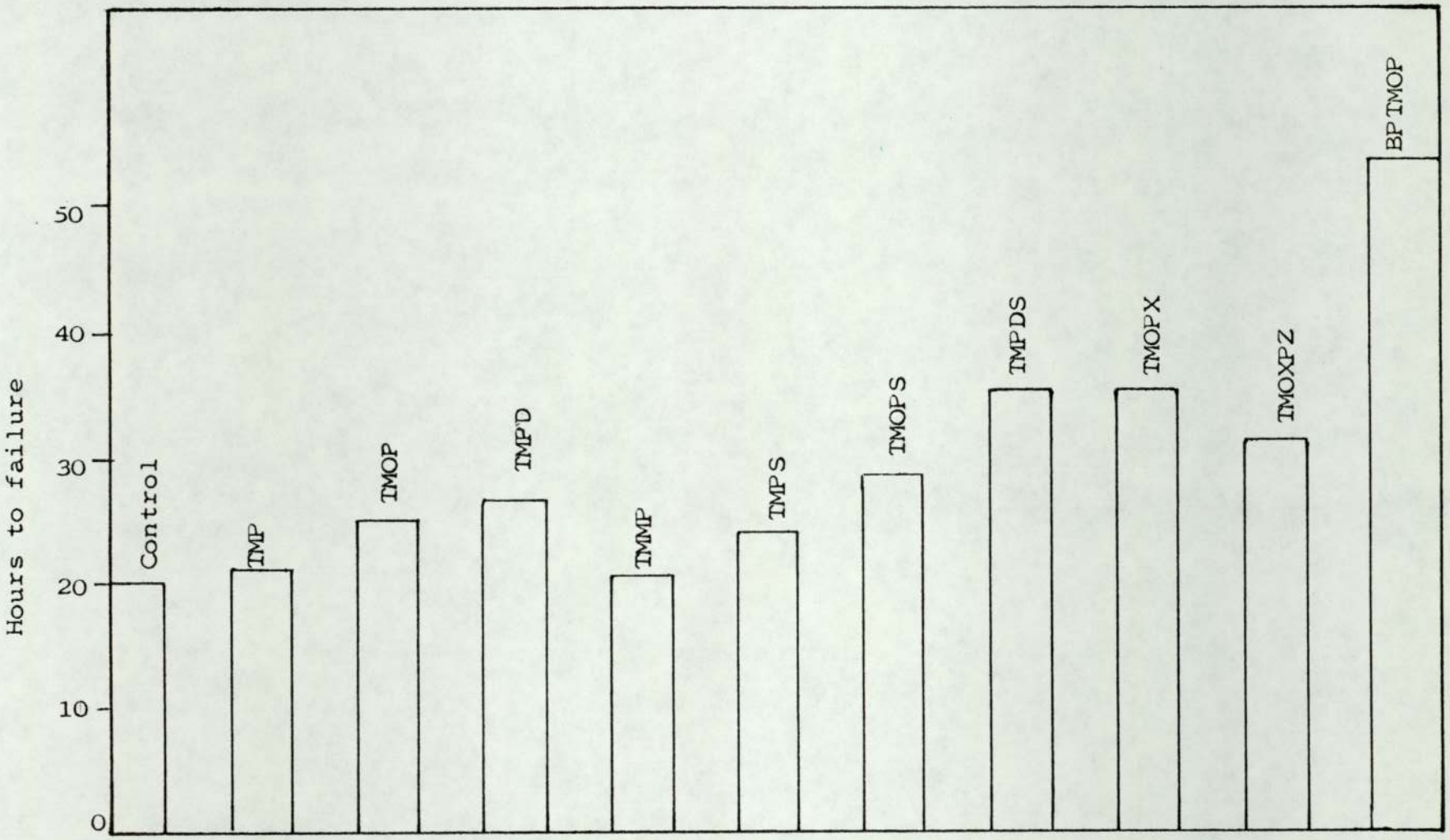


Fig. 4·4: Bar chart showing the influence of the hindered piperidines and their derivatives (each at 1 p.h.r.) on the fatigue life of conventional C.B.S. gum vulcanisates.

ADDITIVE	Loading p.h.r.	FATIGUE LIFE 61% maximum strain		
		Number of cycles to failure x 10^{-2}	Number of hours to failure (hrs.)	percent improvement over control
Control	Nil	1204	20·0	-
TMPS	1·0	1461	24·3	17
TMOPS	1·0	1648	28·0	37
TMPDS	1·0	2097	35	75
TMOPX	1·0	2092	35	75
TMOXPZ	1·0	1905	32	60
BPTMOP	1·0	3159	53	165
IPPD	1·0	16200	270	1250

Table 4·5: The influence of the bis functional nitroxyl radicals and their derivatives at an equiweight level on the fatigue life of conventional C.B.S gum vulcanisates.

alone. For the vulcanisates protected by BPTMOP, the protection against fatigue faliure is even greater. (see tables 4.4, 4.5 and figures 4.3 and 4.4). Table 4.5 also shows that the antifatigue activity of I P P D is significantly greater than any of the hindered piperidine nitroxyl radicals and their derivatives.

None of the additives bloomed to the surface either on storage after vulcanisation or during the fatiguing of the rubber vulcanisates.

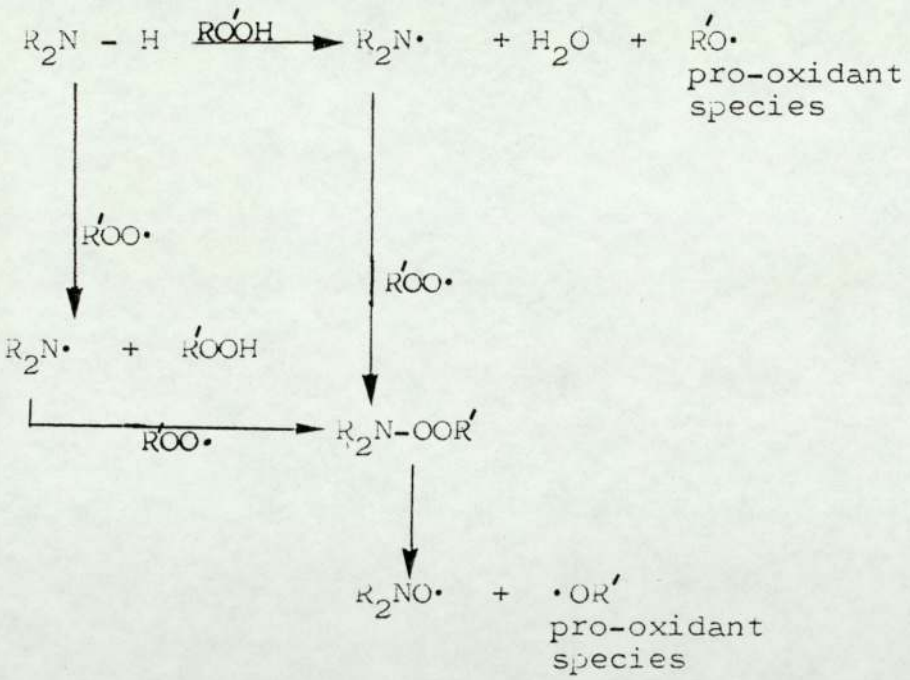
The results for the antifatigue activity of the compounds in unextracted rubber was similar to that of the extracted rubber.

4.2.4 Discussion

In this discussion the effect of the hydroxylamine, the nitroxyl radical and the parent amine will be considered first and then the effect of the xanthogenato nitroxyl radicals (TMOPX and TMOXPZ) and the nitroxyl radical containing the hindered phenolic antioxidant function (BPTMOP) will be discussed separately.

The antifatigue activity of the hydroxylamine was superior to the nitroxyl radical which in turn was superior to the

parent amine. Furthermore the O-methylated hydroxylamine did not have any antifatigue activity. The results were as expected, because when the hydroxylamine or the nitroxyl radical is used in palce of the parent amine, the initial proxidant stages which accompanies the conversion of the amine to the nitroxyl radical is eliminated. This is better illustrated by considering the mechanism of the formation of the nitroxyl radical from the amine the reaction steps of which are shown in scheme 4.3.



Scheme 4.3

These steps involve the generation of radical intermediates (the RO· species) before the nitroxyl radical is formed.

These alkoxyl radicals could accelerate the deterioration of the rubber in the autoxidation cycle. By using the hydroxylamine or the nitroxyl radical directly these initial pro-oxidant reactions are eliminated, therefore the antifatigue activity of the additive is increased. The hydroxylamine is superior to the nitroxyl radicals because it can remove alkylperoxyl radicals more readily from the system itself being converted to the nitroxyl radical. In the case of the nitroxyl radical the removal of the alkylperoxyl radicals takes place only after it has been converted to the hydroxylamine (see scheme 1.10). The results suggest that for efficient anti-fatigue activity peroxyl radical removal is important during the early stages of the fatiguing of rubber. Indeed it will be seen later in this discussion that this is one of the reasons why nitroxyl radicals containing a CB-D function (e.g. BPTMOP) is superior to the nitroxyl radical by itself.

The inability of the O-methylated hydroxylamine (TMMP) to function as an antifatigue agent must be due to lack of a β - hydrogen on the O-alkyl groups[76]. Bolsman et al[76] have reported that for the generation of the hydroxylamine and olefin from the O-alkylated hydroxylamine the presence of a β- hydrogen is essential, otherwise the elimination will not occur. Attempts to make longer chain O-alkylated hydroxylamines of TMOP were not successful (section 2.4.24-2.4.26).

Hence it was not possible to test any other O-alkylated hydroxylamines for antifatigue activity. However the contributory role of this species to the overall antifatigue activity of amines, nitroxyl radicals and hydroxylamines will be discussed further in chapter 6.

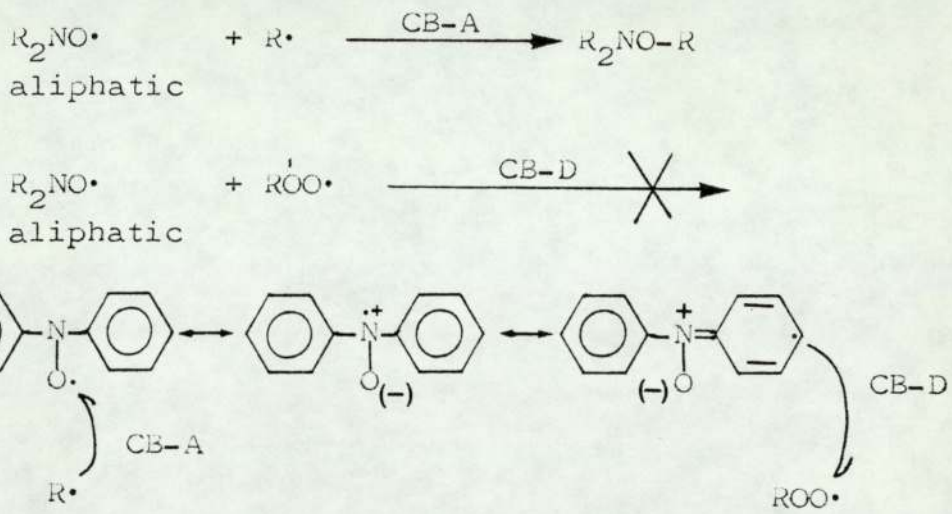
If the antifatigue efficiencies of the alicyclic amines, nitroxyl radicals and hydroxylamines are compared to I P P D the activity of the former is practically insignificant relative to the latter. In fact I P P D nitroxyl radical has been found to be even more efficient than I P P D itself[182], imparting a life time of 337 hours to the rubber vulcanisate. Other aromatic amines, nitroxyl radicals and hydroxylamines have been found to behave similarly[182].

The lack of activity of the hindered piperdines may be due to two reasons:-

1) a compatability effect - the aromatics, being less compatible with the rubber than the aliphatics/ alicyclics, will migrate to the surface (zones of crack growth) faster than the latter compounds. Therefore they will exert a better antifatigue protection.

2) the lack of CB-D activity of the aliphatic nitroxyl radicals:- the alicyclic nitroxyl radicals can only function through the CB-A mechanism and trap only the alkyl radicals. The aromatic nitroxyl radicals on the other hand not only are able to trap alkyl radicals at the nitroxyl function but they are also capable of reacting with alkylperoxyl radicals at the ring sites by delocalisation of the unpaired electron over the ring system

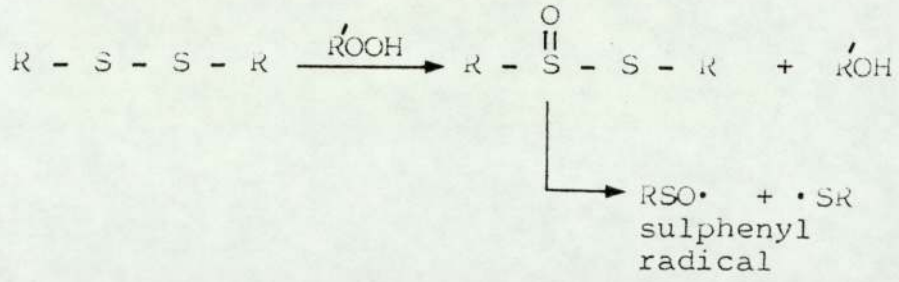
i.e.



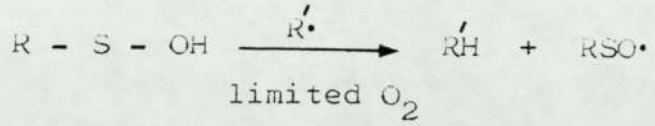
In order to counter this lack of CB-D activity of the alicyclic nitroxyl radicals, it was decided to test the xanthogeneto nitroxyl and the nitroxyl radical containing the hindered phenol function. The former compounds contained the catalytic peroxide decomposing functional group and the latter compound contained the hindered phenol

which is able to function by a CB-D mechanism. The results (tables 4.3, 4.4) have shown that these compounds do possess better antifatigue efficiencies than the corresponding simple nitroxyl radicals by themselves (i.e. TMOP and TMOPS).

The improvement of the xanthogenato nitroxyl radicals over TMOPS is due to a complementary action of the xanthagenato functional group with the nitroxyl radical. In the fatiguing system since there is a defficiency of oxygen (owing to the availability being diffusion controlled) the effective inhibitor formed from the sulphur containing functional group would be the sulphenyl radical[19,108]. This could be formed from the sulphoxide by mechanical activation viz:

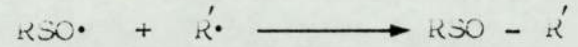


or alternatively from the sulphonic acid[19]



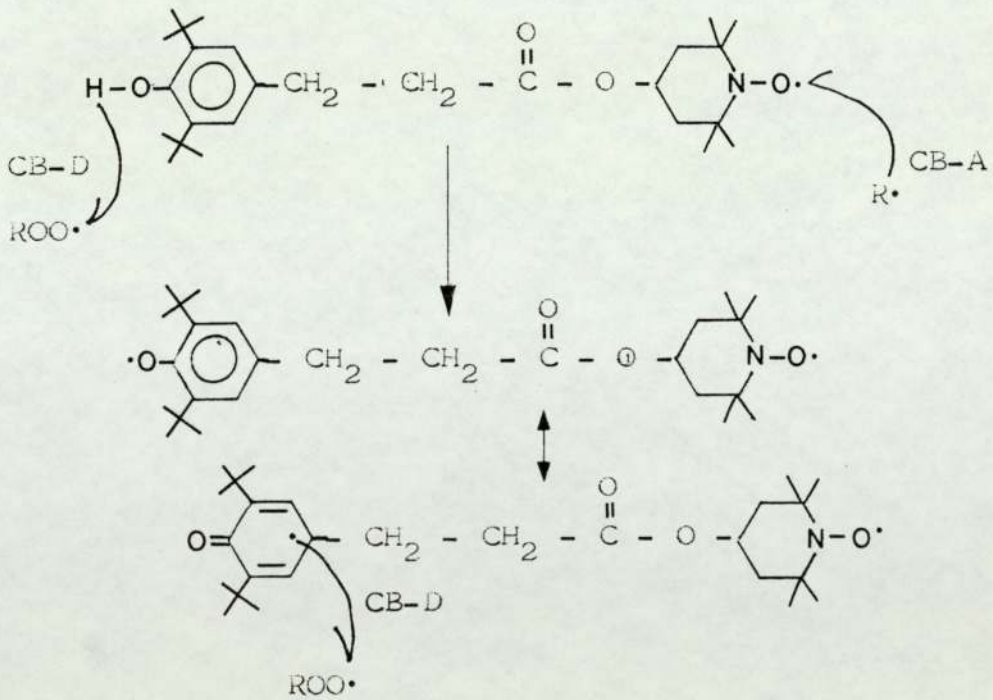
The sulphoxide and sulphonic acid would be formed by oxidation of the xanthate by peroxides in the rubber[1].

The sulphenyl radicals are capable of trapping the alkyl radicals produced in the system during the fatiguing by a CB-A mechanism.



There is also the possibility of suphenyl radical regeneration taking place by a disproportionation of this O-alkylated sulphenate to the sulphenic acid and unsaturation[108].

The improved antifatigue activity of BPTMOP must be due to the complementary CB-D action of hindered phenol functional group together with the CB-A activity of the nitroxyl radical moiety.



Furthermore the element of aromaticity has been introduced into the alicyclic nitroxyl radical, therefore possibly improving the compatability requirements for the antifatigue activity of the molecule.

Other transformation products[18,189] of the hindered phenoxyl radical and a limited galvinoxyl type regeneration of this moiety could also be possible[63,106].

From the results described in this chapter and the ensuing discussion it appears that besides the compatibility requirements, alkylperoxyl radical termination during the early stages of fatiguing is important for efficient antifatigue activity. In view of this conclusion it was decided to investigate aliphatic nitroxyl radical precursors which have a combined CB-A and CB-D activity possesing aromaticity remote to the nitroxyl function. A variety of nitrones were studied and indeed improved antifatigue effeciencies were obtained. This will be discussed in detail in chapter 5.

CHAPTER FIVE

THE CURING CHARACTERISTICS AND ANTIFATIGUE PROPERTIES OF N-ALKYL ALDONITRONES

5.1 INTRODUCTION

Nitrones are efficient radical scavengers and therefore are widely used as radical traps. They are known to scavenge alkyl radicals[69,190] alkoxyl radicals[95] and to decompose hydroperoxides stoichiometrically[96]. However there are no examples in the literature of nitrones being able to trap alkylperoxyl radicals. Many of the nitrones used as spin traps in the literature have been aldonitrones. Presumably ketonitrones could function just as well, however these are generally more difficult to synthesise[91,92,191] (see section 1.8 for the difference between aldo - and ketonitrones).

When nitrones react with a radical the product is a nitroxyl radical[69,91,95,123]. It is this product which makes them so useful as spin traps since they can be readily identified by e.s.r. spectroscopy. Furthermore a study of the hyperfine coupling constants can yield valuable information on the nature of the trapped radical.

Nitrones are also capable of 1,3-addition reactions across double bonds of olefins[139,192]. This reaction has been used to cross-link rubbers using bis-nitrones[193] and to chemically bind antioxidants containing nitrone functional groups into rubber[96].

In chapter four it was concluded that for good antifatigue activity, the antidegradant must not only be able to function by a CB-A mechanism, it must also be able to operate by the CB-D mechanism as well and trap alkylperoxyl radicals, especially during the early stages of fatiguing. Furthermore to satisfy compatibility requirements the compound should contain some aromatic character as well. Therefore it was decided to evaluate the antifatigue performance of a series of N-alkyl-aldonitrones containing α- aryl groups which were capable of CB-D activity, in addition to the alkyl radical trapping activity of the nitrone function.

Because nitroxyl radicals are produced from the nitrone it was decided to generate these in situ in the rubber prior to compounding. With this in mind, prior to the compounding operations, the nitrones were premilled into the rubber for different lengths of time and the effect of premilling on the technological performance of the rubber was assessed.

The nitrones described in section 2.1 were prepared and evaluated in the rubber. Both the substituents of the N-alkyl group and those on the α- aryl group were varied in order to study their contribution to the antifatigue activity.

5.2 EXPERIMENTAL

The compounding was done as described in section 3.2

MHPBN was premilled with the rubber on the laboratory two-roll open mill for 0, 2, 4 and 6 minutes respectively in order to assess the optimum premilling time for best technological performance. It will be seen later (section 5.4) that optimum performance was achieved for the two minutes premilling time. Therefore the other nitrones were all premilled into the rubber for 2 minutes prior to the compounding operations. For the nitrones which appeared to be technologically interesting the compounds were also tested as a normal additive without any premilling being done. For these compounds, the effect of extraction prior to the fatigue testing was also assessed. The extraction of the vulcanised rubber was done in hot acetone under nitrogen for 48 hours.

Since it is known[96] that nitrones react with hydroperoxides generating the aldehyde and nitroso-compound the technological activities of 3,5-dimethyl-4-hydroxybenzaldehyde (MHB) and 2-methyl-2-nitrosopropane (MNP) were studied. These two compounds would be the expected reaction products of the reaction between MHPBN and hydroperoxides. (see section 1.8.3).

A combination of WSP (a commerical phenolic antioxidant) plus a technologically interesting nitrone was also assessed. The combination of the nitrone with a non-discolouring aromatic N-nitroso amine (NODP) was also studied.

5.3 EVALUATION OF THE CURING CHARACTERISTICS OF THE NITRONES

Smith and Scott[99] have reported that N-phenyl and N-methyl nitrones cause premature cross-linking and acceleration of the cure rate during the vulcanisation of rubbers. The reason for this effect was attributed to the formation of nitrone-accelerator adducts. It was therefore of interest to see whether similar behaviour occured with other N-alkyl nitrones as well.

5.3.1 Experimental

The compounding operations were done as described in section

3·2 and 5·2. Before vulcanisation the Wallace Rapid Plasticity numbers of all stocks were measured in order to ensure that they were all between 6-8 units.

The curing characteristics were determined on the Monsanto Rheometer as described in section 3·3.

All the additives were incorporated into the rubber at a level of 1 p.h.r. as the molecular weight of the nitrones were more or less similar.

5.3.2 Results

Table 5·1 and figure 5·1 show that for a typical nitrone (MHPBN) premilling does not greatly affect its curing characteristics.

Table 5·2 shows the curing characteristics for 3,5-dimethyl-4-hydroxybenzaldehyde (MHB and 2-methyl-2--nitrosopropane (MNP). This shows that the aldehyde severly interferes with the cure whereas the nitroso-compound does not.

Table 5·3 shows the curing characteristics for the nitrones listed in table 2·1, all having been premilled with the rubber for 2 minutes on the 2-roll open mill prior to compounding. It is clear that although the substituents on the α-phenyl ring have no effect on the cure, the nature

ADDITIVE	Time of premilling (min.)	Time to optimum cure (min.)	Scorch time (mins)	Rate constant for 1st order crosslinking k $(min.)^{-1}$	Time to 90% cure (min.)	Maximum Torque (m.kg)
Control	-	33	12·0	0·24	27	0·67
MHPBN	0 (as additive)	35	10·0	0·23	27	0·63
MHPBN	2	35	10·0	0·20	28	0·67
MHPBN	4	35	11·0	0·20	29	0·69
MHPBN	6	40	12·0	0·18	32	0·68

Table 5·1: The effect of the premilling time on the curing characteristics of MHPBN (loading level = 1 p.h.r.)

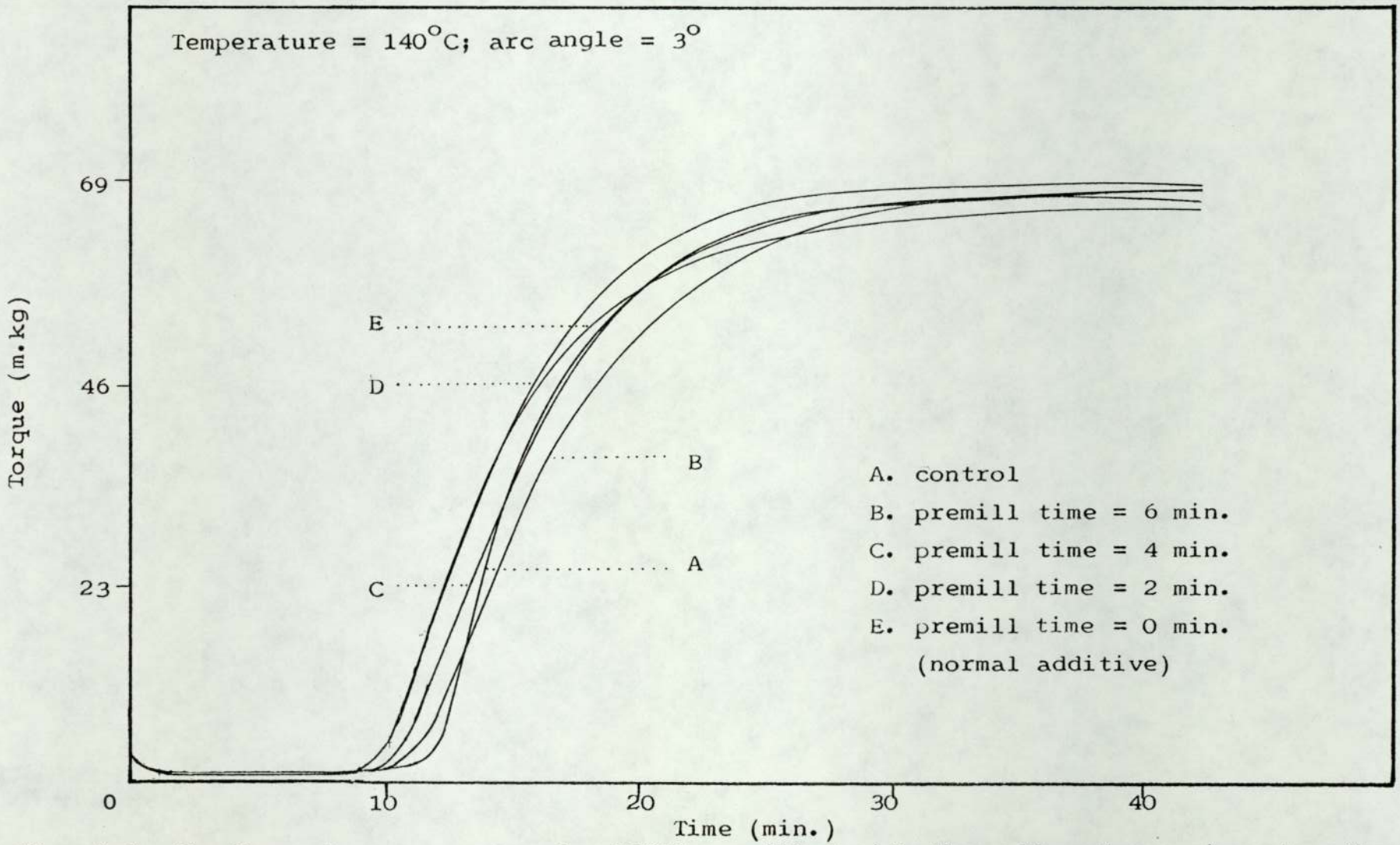


Fig. 5·1: The Monsanto cure curves for MHPBN premilled with the rubber for various lengths of time prior to compounding.

ADDITIVE	loading p.h.r.	Time to optimum cure (min.)	Scorch time (min.)	Rate constant for 1st order crosslinking k $(min.)^{-1}$	Time to 90% cure (min.)	Maximum Torque (m.kg.)
Control	-	33	12·0	0·24	27	0·67
IPPD	1·0	35	11·0	0·22	28	0·69
Santoflex 77	1·0	35	10·0	0·23	28	0·65
MNP	1·0	35	10·0	0·24	28	0·69
MHB	1·0	50	10·0	0·20	35	0·30
MHPPN	1·0	35	11·0	0·24	25	0·69
WSP	1·0	35	12·5	0·16	30	0·69
MHPPN + WSP	1·0	35	11·0	0·26	26	0·67
MHPPN + NODP	1·0 each	35	13·0	0·22	30	0·69

Table 5·2: The curing characteristics for various additives plus combinations of MHPPN and antioxidants

ADDITIVE	Time to optimum cure (min.)	Scorch time (min.)	Rate constant for 1st order crosslinking k $(min.)^{-1}$	Time to 90% cure (min.)	Maximum Torque (m.kg.)
Control	33	12·0	0·24	27	0·67
IPPD	35	11·0	0·22	28	0·69
MHPBN	35	10·0	0·20	28	0·67
HPBN	35	10·0	0·22	26	0·70
PBN	35	9·0	0·19	28	0·70
PMN	30	6·0	0·20	25	0·69
BHPMN	35	9·0	0·20	27	0·70
MHPMN	30	7·0	0·20	24	0·68
MHPEN	35	9·5	0·20	22	0·68
MHPPN	35	11·0	0·24	25	0·69
MPPN	35	11·5	0·17	31	0·69
CPPN	40	14·0	0·14	41	0·69
BMHPPN	35	3·5	0·19	35	0·66

Table 5·3: The curing characteristics of the nitrones, all premilled into the rubber for 2 minutes on the open 2-roll mill (loading level = 1 p.h.r.)

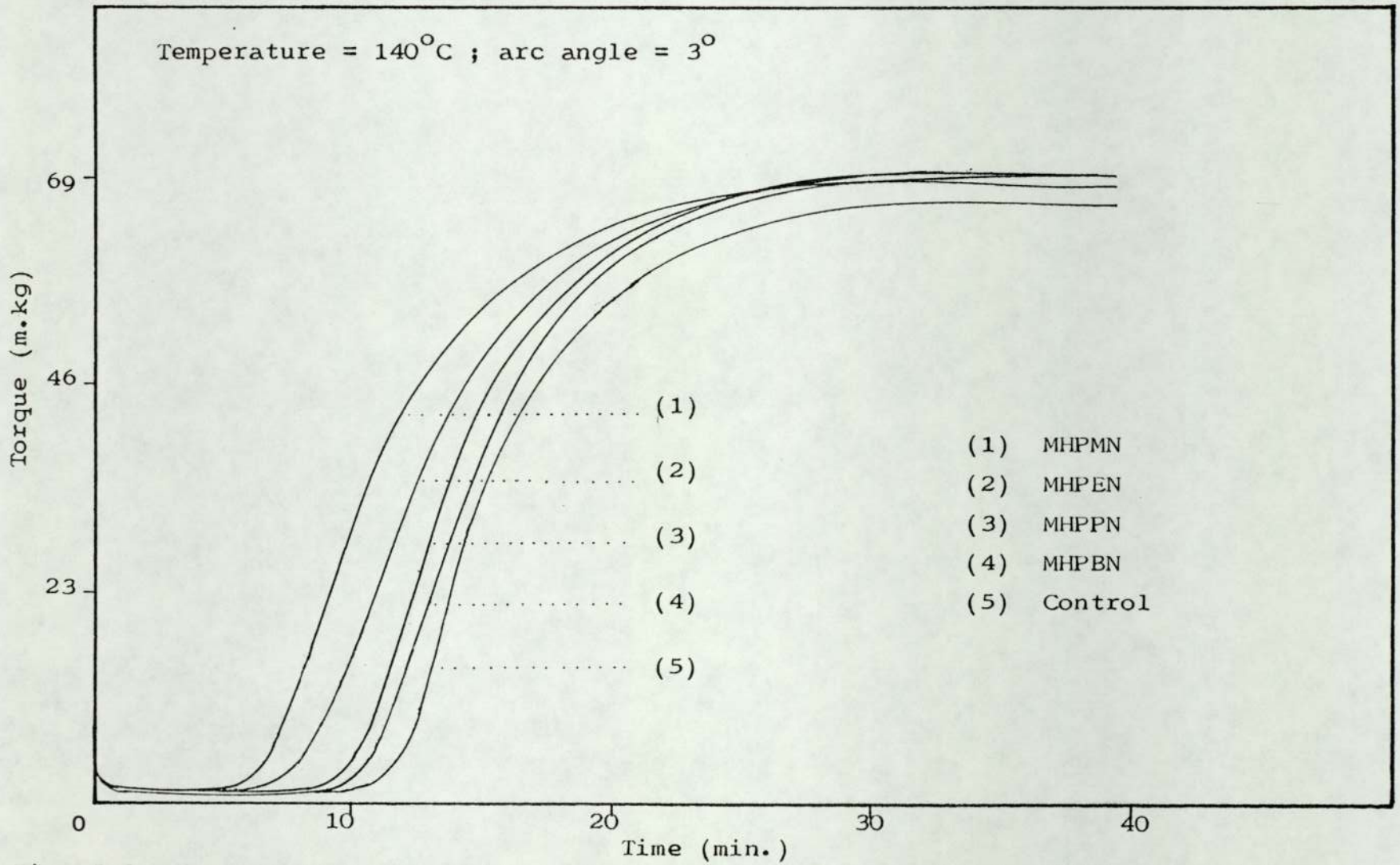


Fig. 5·2: The Monsanto cure curves for the nitrones MHPMN, MHPEN, MHPPN and MHPBN - all the nitrones were premilled with the rubber for two minutes.

of the N-alkyl group does. As the N-alkyl group is changed from a tertiary group to a primary group the nitrones become scorchy (figure 5·2).

This table also shows that the bis-nitrone (BMHPPN) was very scorchy. With this additive in the rubber, the scorch time was reduced to almost three minutes.

Table 5.4 shows that the curing characteristics for the rubber containing the nitrones as a normal additive (with no premilling) do not differ significantly from that with 2 minutes premilling with the rubber prior to compounding.

The curing characteristics for the combination of MHPPN the commercial antioxidant WSP and with NODP (section 2·1) respectively are shown in table 5·2. It is clear that there is no significant interference with the curing characteristics relative to the control.

Table 5.5 shows the relative concentrations of nitroxyl radical formed from MHPBN before and after vulcanisation. It shows that although the concentration of nitroxyl radical does increase with increasing premilling time of rubber and the nitrone, after vulcanisation the concentration of nitroxyl radical is similar in all the

ADDITIVE	Time to optimum cure (min.)	Scorch time (min.)	Rate constant for 1st order crosslinking k $(min.)^{-1}$	Time to 90% cure (min.)	Maximum Torque (m.kg.)x10
Control	33	12·0	0·24	27	0·67
MHPBN	35	12·0	0·23	27	0·64
MHPMN	30	7·0	0·21	25	0·68
MHPEN	35	10·0	0·20	26	0·68
MHPPN	35	11·0	0·21	28	0·67

Table 5·4: The curing characteristics for nitrones incorporated into the rubber as an additive with no prior premilling.

Time of premilling (min.)	Relative concentration of nitroxyl radicals (rel. moles/g rubber) x 10^8	
	Before vulcanisation $\pm$ 0·005	After vulcanisation $\pm$ 0·004
0	0·03	1·28
2	0·034	1·31
4	0·07	1·26
6	0·10	1·29

Table 5·5: Relative nitroxyl radical concentrations formed from MHPBN for the various premilling times before and after vulcanisation.

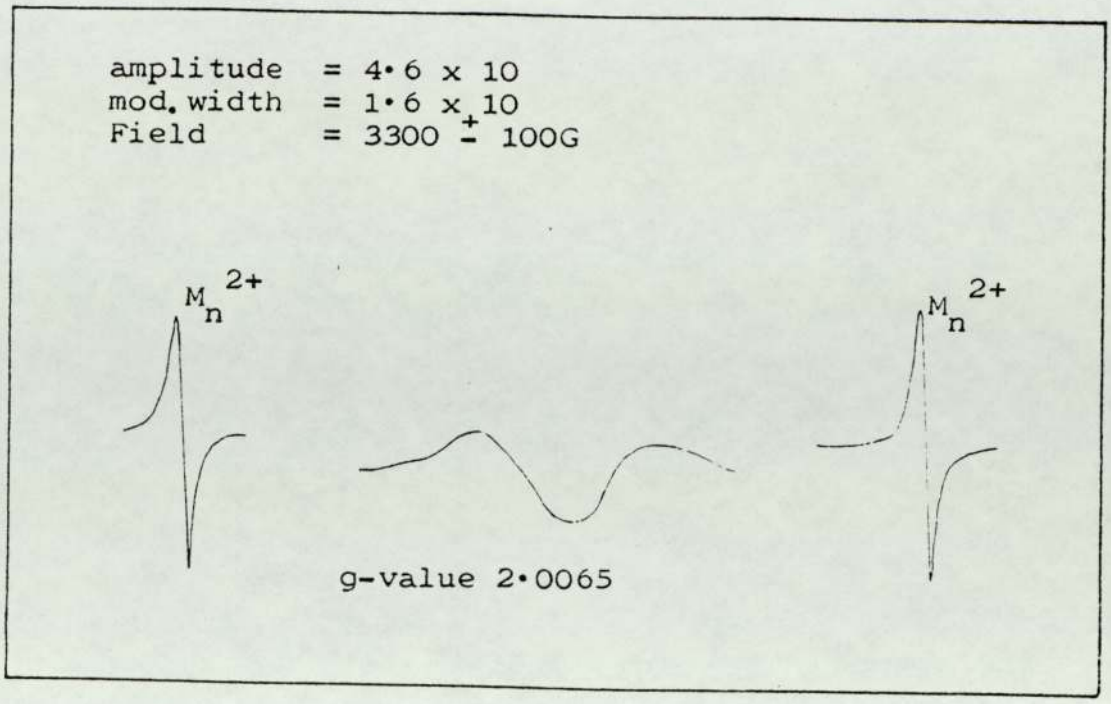


Fig. 5·3(a): The spectrum of nitroxyl radical formed from MHPBN (1 p.h.r.) in C.B.S formulated rubber stock (before vulcanisation) (premill time = 2 min.)

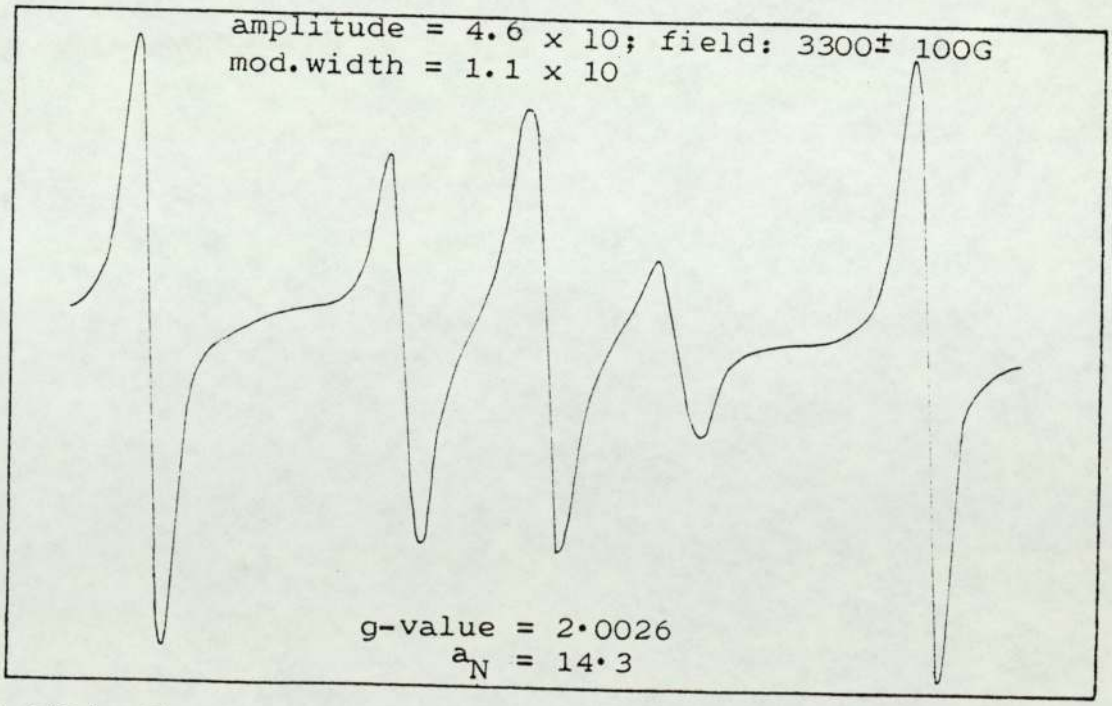


Fig. 5·3(b): The spectrum of nitroxyl radical formed from MHPBN (1 p.h.r.) in a conventional C.B.S. vulcanisate

cases and about ten times greater than that before vulcanisation.

Figure 5·3 shows the nitroxyl radical spectra for MHPBN before and after vulcanisation.

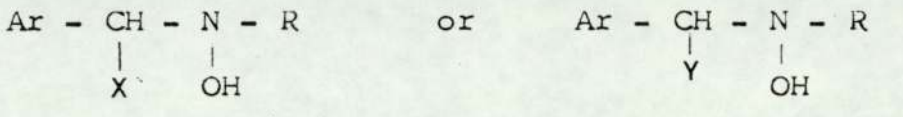
A study of the curing characteristics of MHPBN, MHPMN, MHPEN and MHPPN in unextracted rubber did not show any difference to that in the extracted rubber.

5.3.3 Discussion

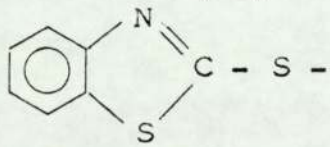
It is clear from the curing characteristics that the vulcanisation parameters were not greatly affected by most of the nitrones. Premilling of the nitrones (MHPBN) with the rubber before compounding, did not affect the curing characteristics very much either.

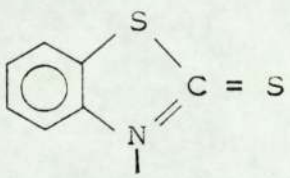
The nature of the N-alkyl group however did affect the scorch time of the vulcanisation. When the N-alkyl group was primary (e.g. Me) the scorch time was short being about 6 minutes. When the group was secondary (i-propyl) or tertiary (tert-butyl) the scorch time relative to the control was not significantly affected.

This interference by the nitrones with the time for cross-linking to start may be rationalised in terms of basicity effect or interaction of the nitrone with free radicals produced during initial stages of vulcanisation or in terms of the interaction of the nitrone with the accelerator system to form a nitrone-accelerator adduct. The ease of fromation of this adduct and its relative stability would affect the scorch time of the vulcanisation process. Smith[97] has suggested that this adduct could be of the type IX or X and could be formed by



(IX) (X)

where X= 

and Y= 

interaction of the nitrone with 2-mercaptobenzothiazole, which is known[194] to be formed during C.B.S. accelerated sulphur vulcanisation of rubber. Decomposition of this adduct would liberate 2-mercaptobenzthyl radicals and/or ionic products such as MBT anions which would activate vulcanisation. Thus irrespective of whether the accelarated

sulphur vulcanisation of rubber proceeds through a polar or a free radical mechanism, the ease of formation of such adducts and their relative stabilities would certainly reduce the time to the onset of cross-linking.

Decomposition of these nitrone — accelerator adducts and/or the trapping of radicals during vulcanisation would give rise to nitroxyl radicals either directly or via the hydroxylamine. This would account for the tenfold increase of nitroxyl radicals after vulcanisation compared to that present before vulcanisation. It would also account for the fact that the nitroxyl radical concentration after vulcanisation was independant of the premilling time of MHPBN with the rubber (table 5.5).

The bis-nitrone (BMHPPN) was found to be very scorchy relative to the control (table 5·3). The scorch time with this compound in the rubber was reduced to almost three minutes. Such a scorch time would normally not be technologically acceptable. The extreme scorchiness must be due to the presence of two nitrone functions in the molecule which probably play some part in the cross-linking of the rubber[193].

The reason for the severe interference of 3,5-dimethyl--4-hydroxybenzaldehyde (MHB) with the vulcanisation

process is not clear. 2-methyl-2-nitrosopropane (MNP) did not interfere with the cure parameters. A comparison with the curing characteristics of the nitrones based on this aldehyde (MHPBN, MHPPN, MHPEN and MHPMN) suggest that the nitrones do not significantly decompose to the aldehyde during the vulcanisation process.

The combination of MHPPN with WSP and NODP respectively did not interfere with the vulcanisation process.

5.4 EVALUATION OF THE ANTIFATIGUE ACTIVITY OF THE NITRONES

5.4.1 Introduction

Nitrones have not been previously investigated as antifatigue agents. Since they are nitroxyl radical precursors and are known to efficiently trap alkyl radicals, alkoxyl radicals and stoichiometrically decompose hydroperoxides, it was interesting to study the behaviour of nitrones as antifatigue agents. In particular it was of interest to study nitrones which contained phenolic antioxidant functional groups which were capable of reacting with peroxyl radicals as well. This study was done because in chapter 4 it was concluded that for efficient antifatigue activity the antifatigue

agent must not only be capable of reacting with alkyl radicals by the CB-A mechanism, it must also be able to function by the CB-D mechanism as well and presumably react with alkylperoxyl radicals that are produced during the fatiguing of rubber as well.

5.4.2 Experimental Procedure

The compounding was done as described in sections 5·1 and 3·2. The vulcanisation and the fatiguing was done as described in sections 3·4 and 3·5-3·9. The modulus of the vulcanisate containing the aldehyde was significantly lower than the other stocks (0·3 m.kg as opposed to about 0·7 m.kg. respectively; table 5·2). Therefore the fatigue life for this vulcanisate was evaluated at the same strain energy per cycle to that produced by the other vulcanisates when strained to 61% extension. This was done by the method described in section 3·9·4.

5.4.3 Results

Table 5·6 and figure 5·4 show the effect of premilling on the antifatigue efficiency for MHPBN. It is clear that optimum activity was obtained when the premilling time was two minutes.

Time of premilling (min.)	FATIGUE LIFE 61% maximum strain frequency = 100 cycles per minute		
	cycles to break x 10^2	Hours to break (hrs.)	percent improvement over control
Control	1200	20	-
0	5800	98	390
2	6600	110	450
4	6120	102	410
6	5580	93	365

Table 5·6: The effect of premilling time on the fatigue life of C.B.S. cured vulcanisates containing MHPBN (1 p.h.r.)

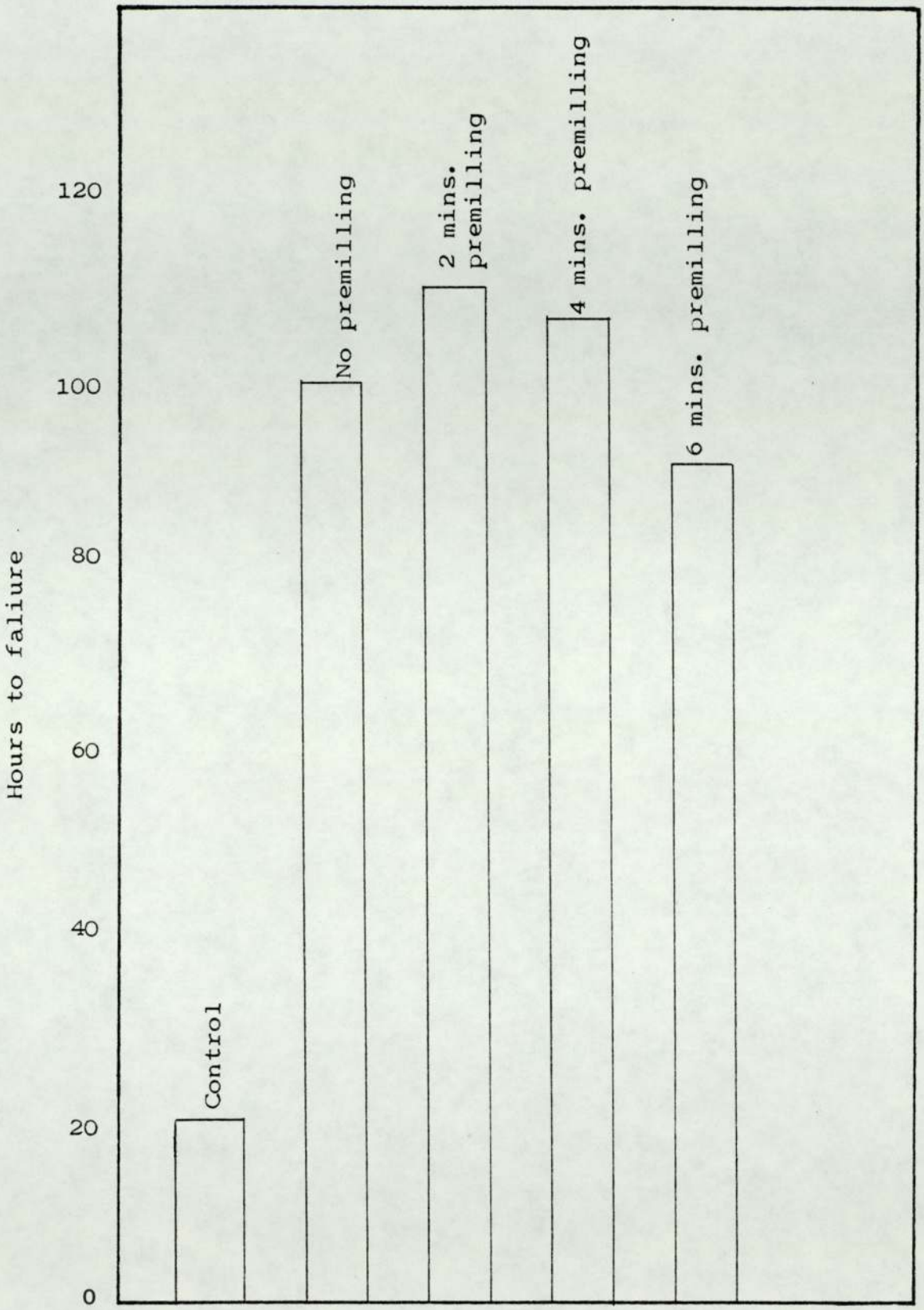
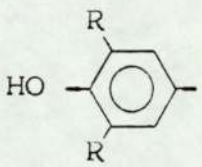


Fig. 5·4: The effect of premilling time on the fatigue life of conventional C.B.S. vulcanisates containing MHPBN (1 p.h.r.)

Table 5·7 and figure 5·5 show the antifatigue activities for the nitrones relative to the control and IPPD. All the nitrones were premilled with the rubber for two minutes prior to the compounding operations. The table and the figure show that optimum antifatigue activity was obtained for MHPPN where the N-alkyl group was iso-propyl and the α-aryl group was a hindered phenolic antioxidant.

When the N-alkyl group of the nitrone was kept constant (e.g. MHPBN, HPBN and PBN; table 5·7) and the nature of the substituents on the 3,4 and 5 positions of the phenyl ring was changed, optimum activity was obtained for the semi-hindered phenol.



where R = CH_3

Although it was not possible to synthesise an N-tertiary-butyl or N-isopropyl nitrone containing a more hindered phenolic antioxidant function, for the N-methyl nitrone where the synthesis was possible it was seen that increasing the bulkiness of the groups ortho to the phenol function (BHPMN; table 5·7) did not increase the antifatigue efficiency of the nitrone. This effect is

ADDITIVE						FATIGUE LIFE 61% maximum strain frequency = 100 cycles per minute		
Structure				Name		cycles to failure x 10^{-2}	hours to failure (hrs.)	percent improvement over control
Control				—		1200	20	-
see table 2·1				IPPD		16200	270	1250
				MNP		2280	38	90
				MHB		1500	25	25
X	R′	R″	R					
OH	Me	Me	^{t}Bu	MHPBN		6600	110	450
OH	H	H	^{t}Bu	HPBN		1800	30	50
H	H	H	^{t}Bu	PBN		1560	26	30
H	H	H	Me	PMN		1740	29	45
OH	^{t}Bu	^{t}Bu	Me	BHPMN		2700	45	125
OH	Me	Me	Me	MHPMN		4800	80	300
OH	Me	Me	Et	MHPEN		5580	93	365
OH	Me	Me	i-Pr	MHPPN		7800	130	550
OCH_3	H	H	i-Pr	MPPN		1980	33	65
Cl	H	H	i-Pr	CPPN		2220	37	85
Bis - nitrone				BMHPPN		6360	106	430

Me = CH_3; Et = $-CH_2-CH_3$; i-Pr = $-CH-(CH_3)_2$; ^{t}Bu = $-C-(CH_3)_3$

Table 5·7: The effect of the nitrones on the fatigue life of C.B.S cured vulcanisates (loading of all additives = 1 p.h.r.; all nitrones premilled for 2 minutes)

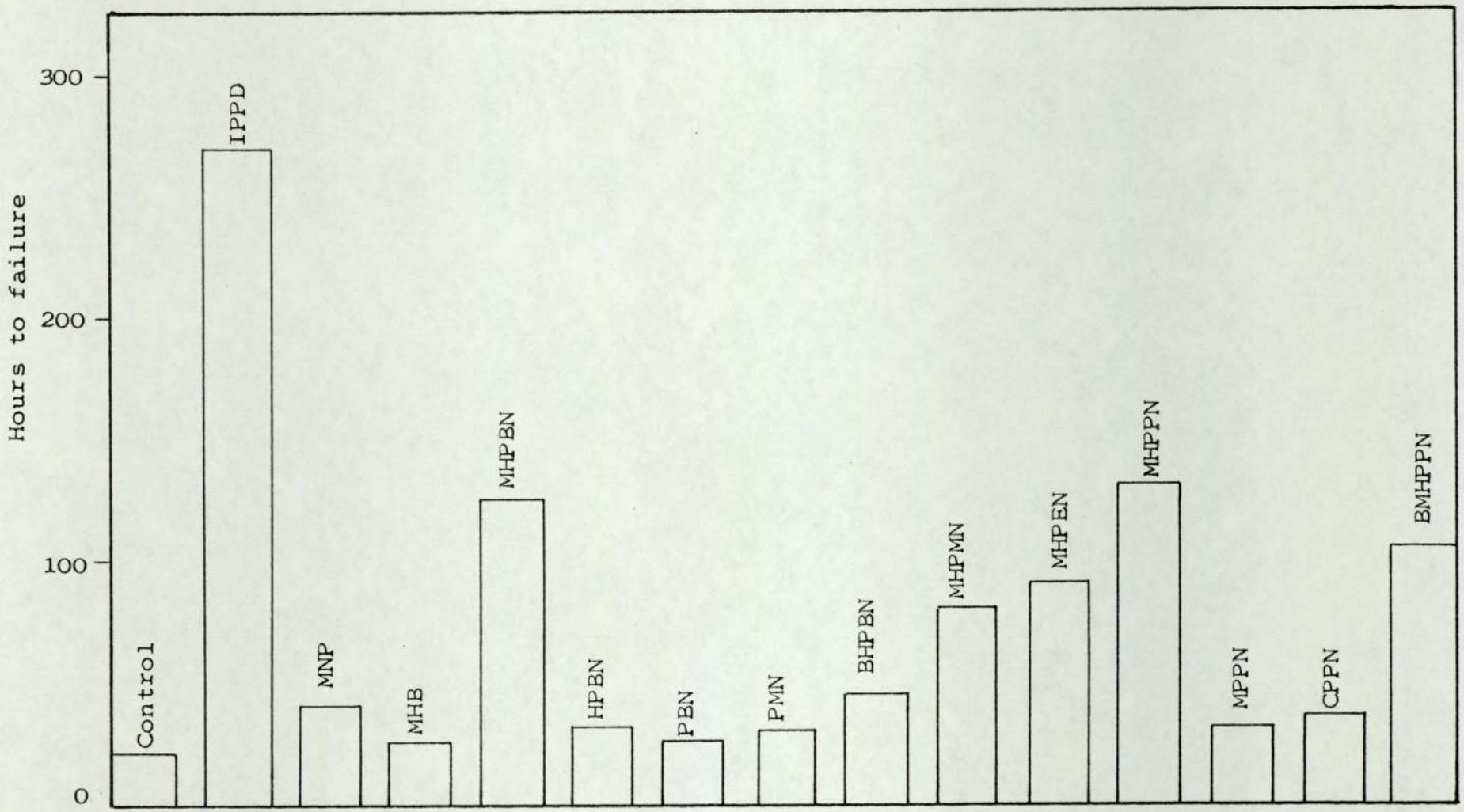


Fig. 5·5: The effect of the nitrones on the fatigue life of conventional C.B.S. vulcanisates ([additives] = 1 p.h.r.; all nitrones premilled for 2 mins.)

better illustrated in table 5·8 and figure 5·6 where the N-methyl nitrones have been evaluated at the same molar concentrations.

The improvement in antifatigue efficiency when the semi-hindered phenolic antioxidant function was introduced into the nitrone was very dramatic. The effect was particularly pronounced for the N-tertiarybutyl nitrone (MHPBN) and the N-isopropyl nitrone (MHPPN) and is clearly seen from table 5·7 and figure 5·5.

When the substituents on the α-aryl group were kept constant (as the semi-hindered phenol) and the nature of the N-alkyl group was changed from a primary group to a tertiary group, optimum antifatigue efficiency was observed when the N-alkyl group was a secondary alkyl moiety (i.e. isopropyl group; MHPPN). When the group was tertiary the antifatigue efficiency was reduced (MHPBN, table 5·7). It was reduced even further when the nature of the N-alkyl group was primary (MHPMN and MHPEN; table 5·7).

Incorporation of the nitrones as a normal additive into the rubber without any prior premilling decreased their antifatigue efficiencies by about 20% (table 5·9; MHPMN, MHPEN, MHPPN and MHPBN).

Table 5·10 shows that after hot acetone extraction of the

ADDITIVE	LOADING		FATIGUE LIFE .61% maximum strain frequency = 100 cycles per minute		
	p.h.r. g.	moles/ 100g $\times 10^{3}$	cycles to failure $\times 10^{-2}$	hours to failure	percent improvement over control
Control	-		1200	20	-
PMN	0·51	3·8	1848	30	50
MHPMN	0·68	3·8	4037	67	235
BHPMN	1·00	3·8	2700	45	125

Table 5·8: The antifatigue activities of N-methyl nitrones at the same molar concentration.

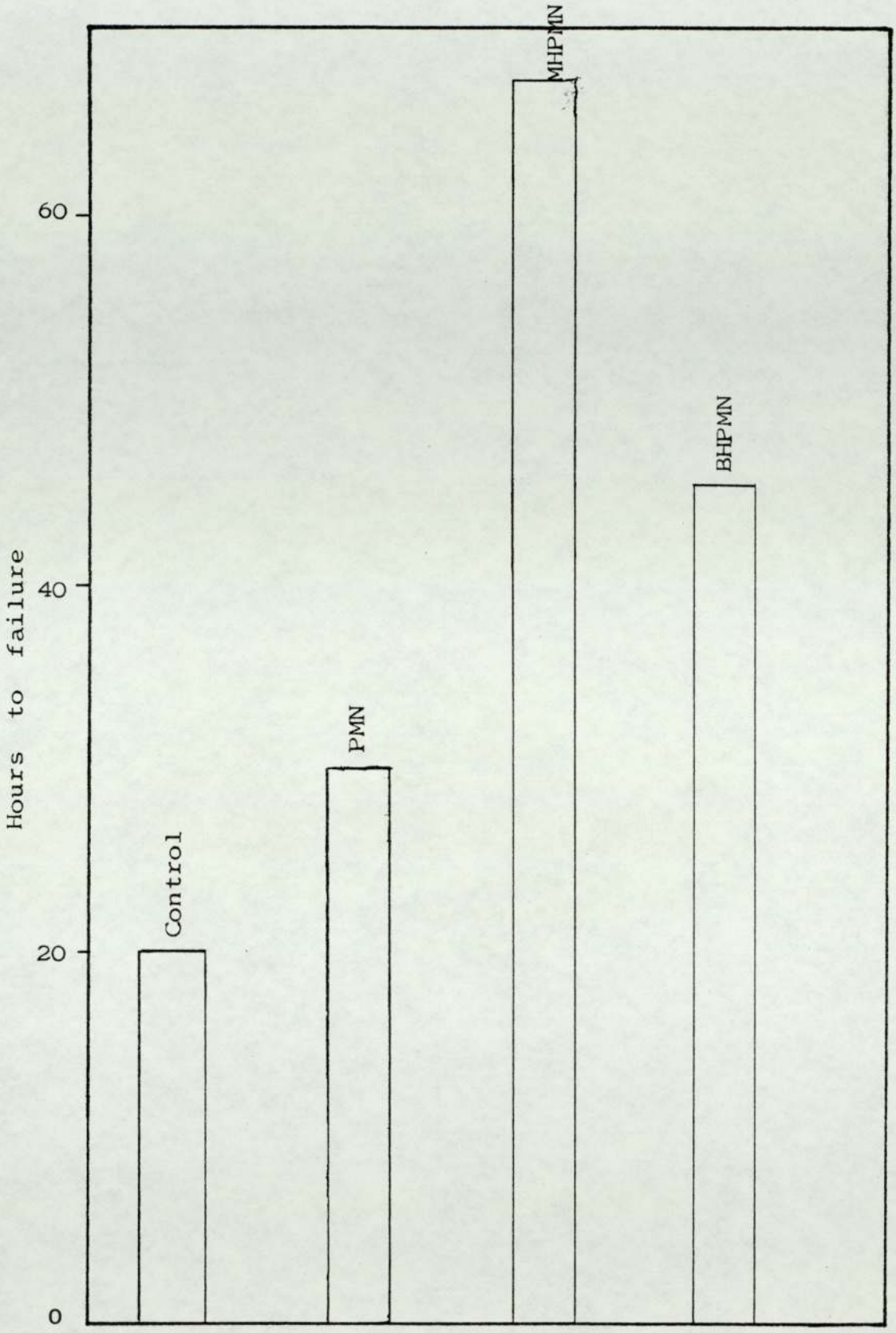


Fig. 5·6: The antifatigue activity of the N-methyl nitrones, each at the same molar concentration ($3·8 \times 10^{-3}$ moles per hundred parts rubber)

ADDITIVE	FATIGUE LIFE (hrs.) 61% maximum strain frequency = 100 cycles per minute	
	2 min. premilling	as addive. no premilling
Control	20	20
MHPMN	80	56
MHPEN	93	81
MHPPN	130	102
MHPBN	110	98

Table 5·9: Comparison of the antifatigue activity of some nitrones with no premilling and after 2 minutes premilling prior to the compounding operations.

ADDITIVE	FATIGUE LIFE (hrs.) 61% maximum strain frequency = 100 cycles per minute	
	Before extraction	After extraction
Control	20	22
MHPMN	80	25
MHPEN	93	25
MHPPN	130	26
MHPBN	110	26

Table 5·10: Comparison of the fatigue life of C.B.S. cured vulcanisates containing nitrones before and after extraction.

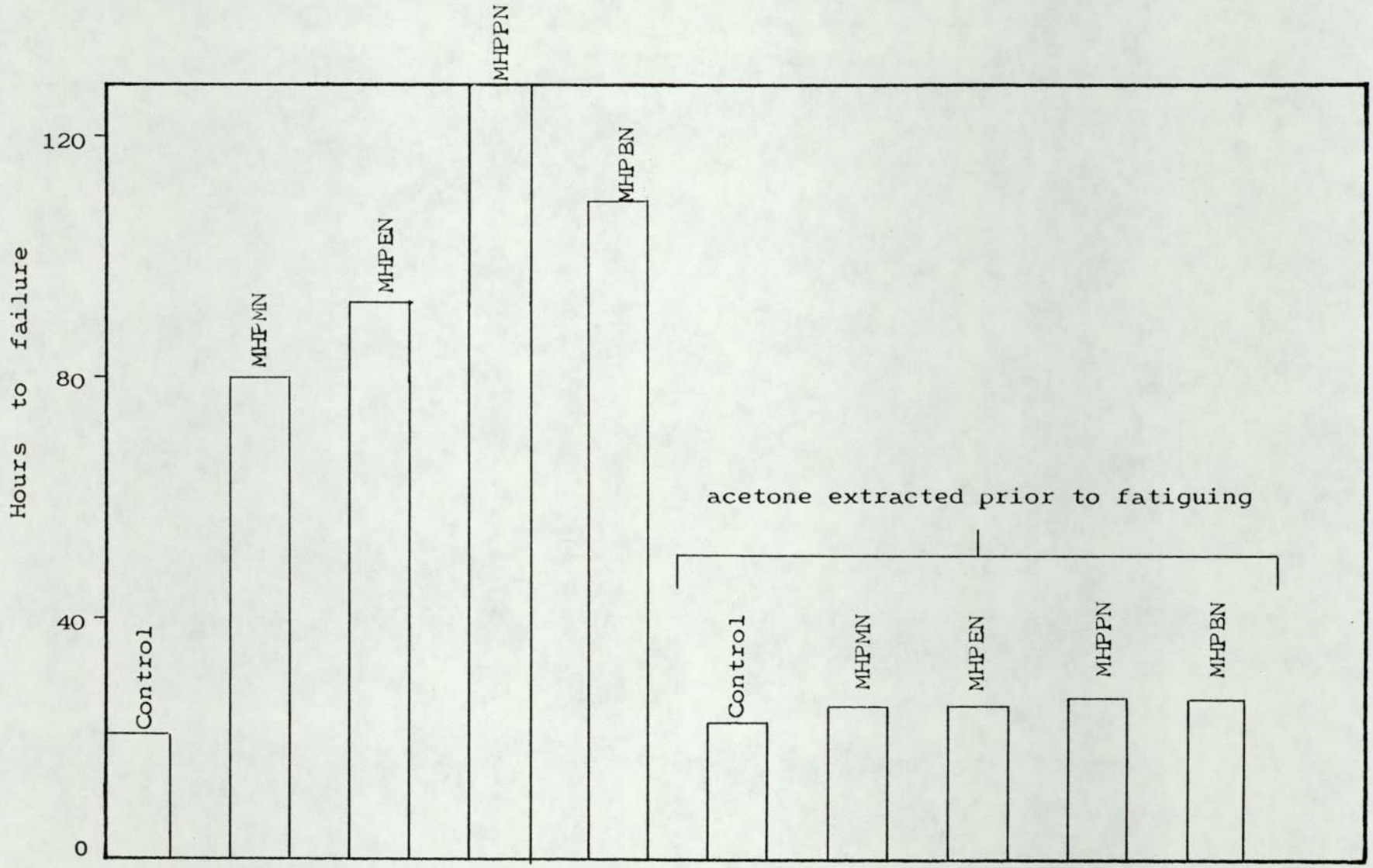


Fig. 5·7: Comparison of the fatigue life for nitrones before and after exhaustive acetone extraction

vulcanisates containing the nitrone, their antifatigue protection was lost. Figure 5.7 highlights this effect.

The nitrones MPPN and CPPN containing an α-(4-methoxyphenyl)-group and an α-(4-chlorophenyl)- group respectively was studied in order to assess the contribution of electron withdrawal and donation to the overall antifatigue activity of the nitrones. CPPN appeared to be slightly more efficient than MPPN (table 5·7). However in comparison to the nitrone containing the semi-hindered phenolic antioxidant function (MHPPN) the antifatigue efficiencies of MPPN and CPPN are small since the activity of these two compounds are 32 hours and 35 hours respectively.

Table 5·7 and figure 5·5 show that 3,5-dimethyl-4-hydroxylbenzaldehyde does not have any significant antifatigue activity. However 2-nitroso-2-methylpropane does have some antifatigue activity relative to the control.

Table 5·11 and figure 5·8 shows the antifatigue efficiency for combinations of MHPPN with W S P and NODP respectively. W S P alone gave the vulcanisate a fatigue life of 65 hours. The vulcanisate containing MHPPN had a fatigue life of 130 hours. The combination of the two compounds (each at 1 p.h.r.) in the rubber gave the vulcanisate a fatigue life of 206 hours. Thus the combination of MHPPN and WSP each at a level of 1 p.h.r., was synergistic.

Additive	Loading p.h.r. g	FATIGUE LIFE 61% maximum strain frequency = 100 cycles per minute		
		cycles to failure x 10^{-2}	hours to failure (hrs.)	percent improvement over control
Control	-	1200	20	-
MHPPN	1·0	7800	130	550
WSP	1·0	3900	65	225
MHPPN + WSP	1·0 each	12360	206	930
NODP*	1·0	6720	112	460
MHPPN + NODP	1·0 each	10440	174	770

* - reference (182)

Table 5·11: The effect of combination of MHPPN with other antioxidants on the fatigue life of C.B.S. cured vulcanisates.

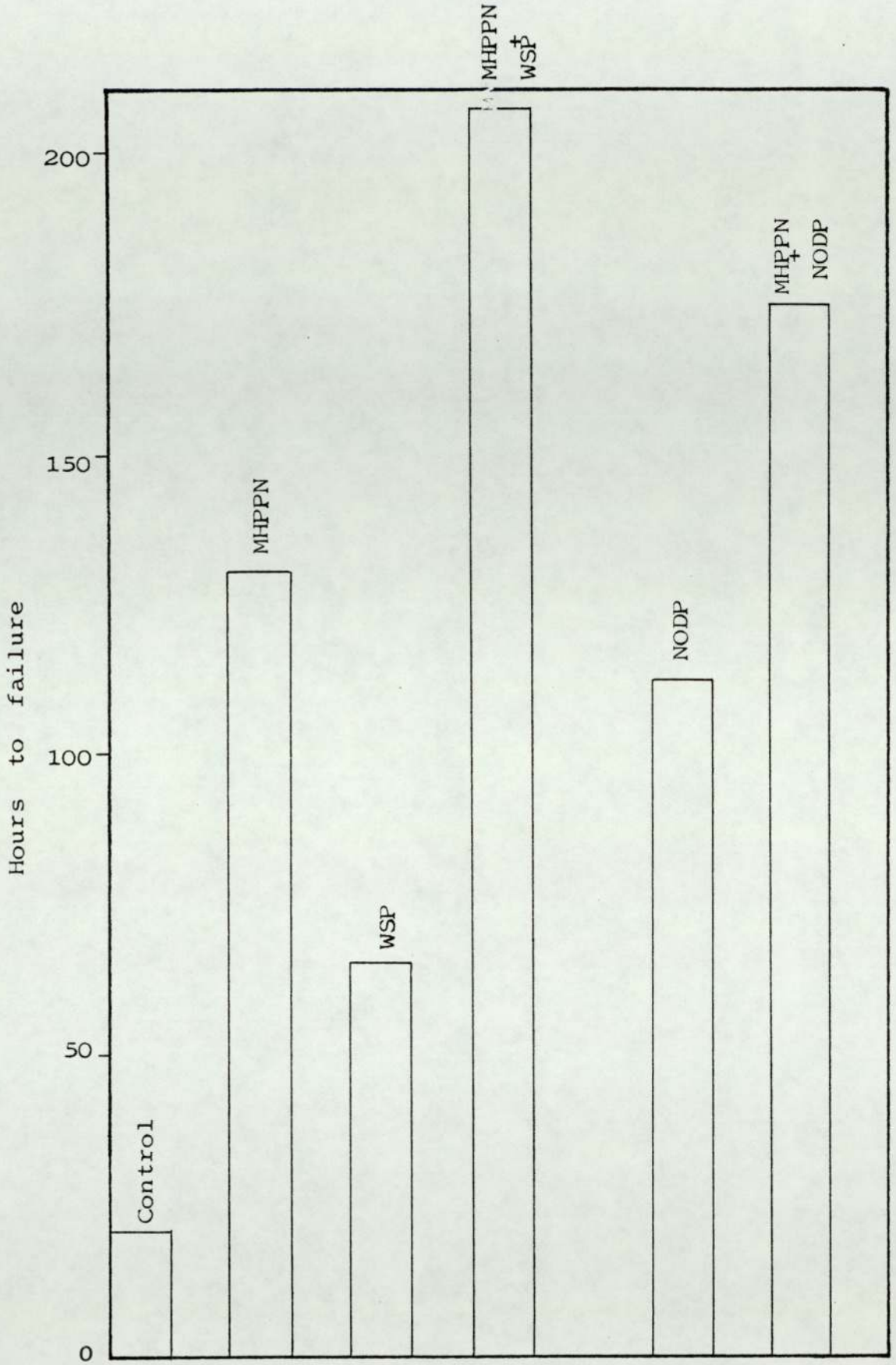


Fig. 5·8: The antifatigue activity for combinations of MHPPN with other antioxidants (1 p.h.r. each)

ADDITIVE	FATIGUE LIFE 61% maximum strain frequency = 100 cycles per minute		
	cycles to failure $\times 10^{-2}$	hours to failure	percent improvement over control
Control	1380	23	-
IPPD	15600	260	1030
MHPMN	3725	62	170
MHPEN	5100	85	270
MHPPN	7440	124	439
MHPBN	5988	100	335

Table 5·12: The effect of nitrones on the fatigue life of C.B.S. cured vulcanisates made from unextracted rubber. (all nitrones premilled for 2 minutes; level of loading = 1 p.h.r.).

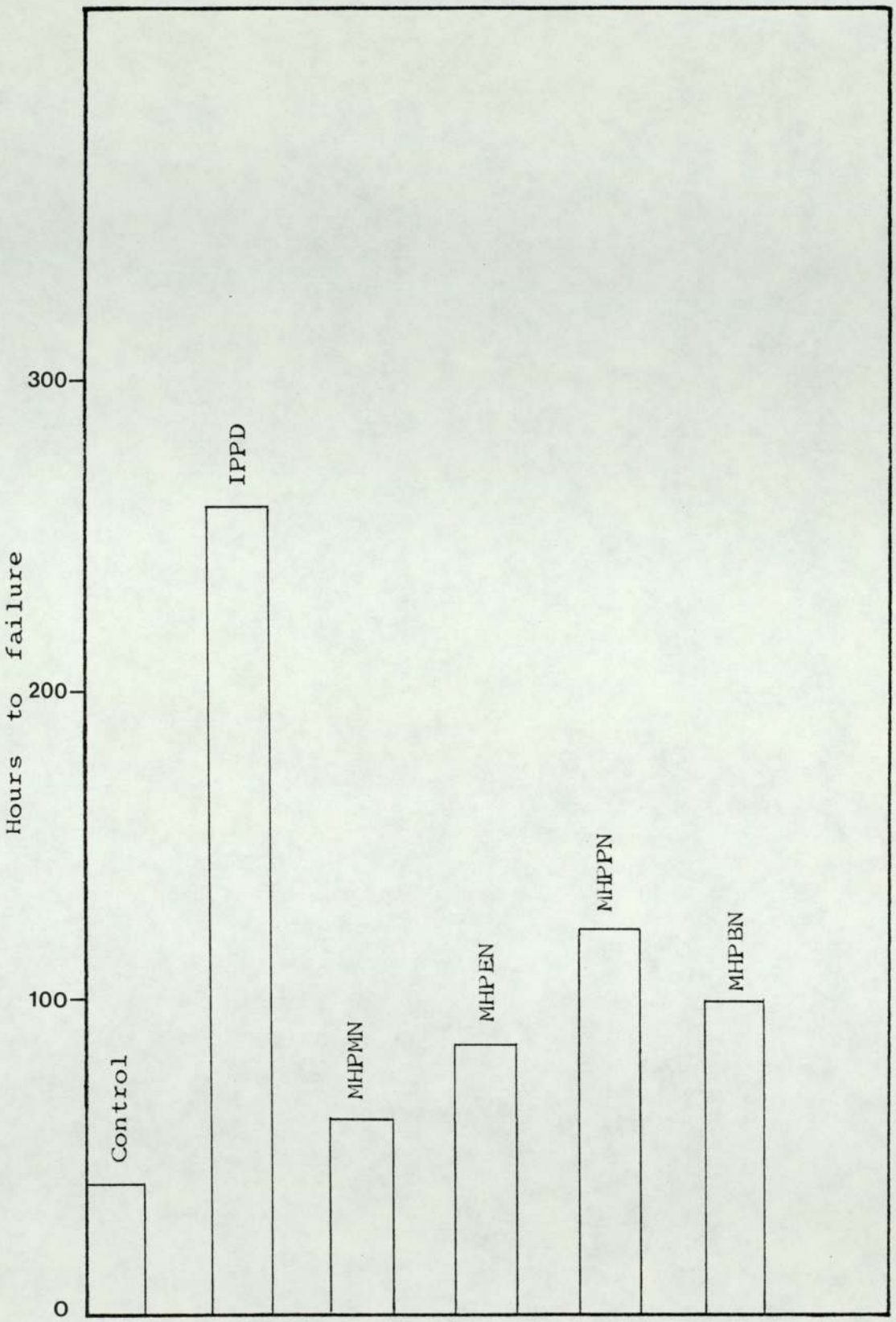


Fig. 5·9: Comparison of the antifatigue activity of nitrones in conventional C.B.S. vulcanisates made up from unextracted rubber ([nitrone] = 1 p.h.r.; premill time of nitrones = 2 mins.)

However the conbination with NODP was slightly antagonistic.

Table 5.12 and figure 5.9 show that the use of unextracted rubber to make the vulcanisates reduces the activities of the nitrones slightly (cf. : table 5.7, figure 5.5)

Table 5.13 shows the relative nitroxyl radical concentration after fatigue to failure for MHPBN premilled into the rubber. The table shows that irrespective of the premilling time the nitroxyl radical concentration after fatigue to failure was the same. Furthermore the relative concentration after fatigue to failure was roughly twice the value present before fatiguing. Figure 5.10 shows the nitroxyl radical spectrum after fatigue to failure. A comparison of the e.s.r. spectra before and after fatiguing (figures 5.3b and 5.10 respectively) show that after 100 hours fatiguing the spectrum of the nitroxyl radical is much broader with a tendency to hyperfine splitting. The growth of the nitroxyl radical concentration during the fatiguing of rubber containing MHPBN is described in the chapter on Mechanistic Studies (chapter 6, section 6.B.2).

5.4.4. Discussion

It is clear that among the nitrones which were tested, those which did not contain a phenolic antioxidant fuction in the molecule had very little or no antifatigue activity. Inclusion of the phenolic antioxidant function

Time of premilling (min.)	Relative concentration moles/g x 10^{-7}		
	before vulcanisation $\pm$ 0·005	after vulcanisation $\pm$ 0·01	after fatiguing $\pm$ 0·01
0	0·003	0·13	0·27
2	0·004	0·13	0·28
4	0·007	0·13	0·26
6	0·011	0·13	0·28

Table 5·13: The relative nitroxyl radical concentrations formed from MHPBN in the rubber after compounding, after vulcanisation and after fatigue to failure.

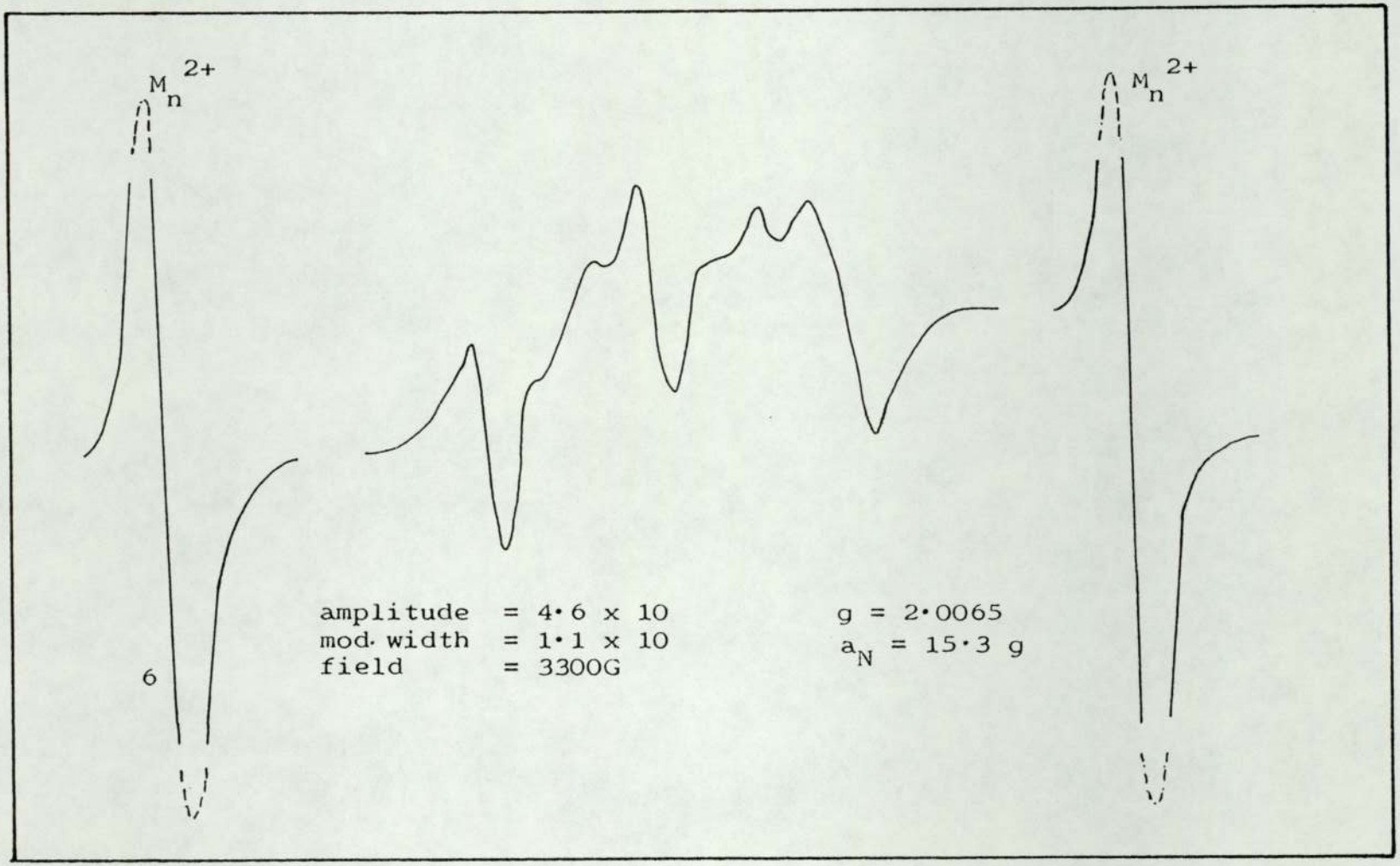


Fig. 5·10: The spectrum of nitroxyl radical formed from MHPBN in a conventional C.B.S. vulcanisate after 100 hours fatiguing.

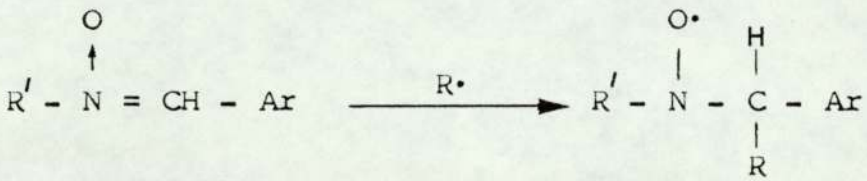
into the nitrone molecule dramatically increased its antifatigue efficiency (table 5·7; PBN, HPBN, MHPBN). However when the steric hinderence of the groups ortho- to the phenol function was increased the antifatigue efficiency decreased slightly (table 5·8, figure 5·6; PMN, MHPMN, BHPMN).

It is well known that nitrones are capable of removing alkoxyl radicals, alkyl radicals and hydroperoxides from an oxidising system[92]. However there is no evidence in the literature which suggests that nitrones are capable of reacting with peroxyl radicals. Indeed Scott and Smith[92] have reported that α,N-diphenyl-nitrone is ineffective in retarding the oxidation of hydrocarbons initiated by azo-bis-isobutyronitrile (AZBN) because it is unable to scavenge the peroxyl radicals formed in the system. In contrast nitrones containing a phenolic antioxidant function were effective retarders for the same system[92]. The effect of the latter nitrones was attributed to the removal of alkylperoxyl radicals from system by the phenolic antioxidant function through the CB-D mechanism (section 1·8·1·1).

In the study of the antifatigue activity of the nitrones only the nitrones which contained the phenolic antioxidant function were effective antifatigue agents. Since the

predominent effect of the latter function is to remove alkylperoxyl radicals from the system by the CB-D mechanism, this suggests that removal of alkylperoxyl radicals, particularly during the early stages of fatiguing, together with the alkyl radicals is necessary for efficient antifatigue activity.

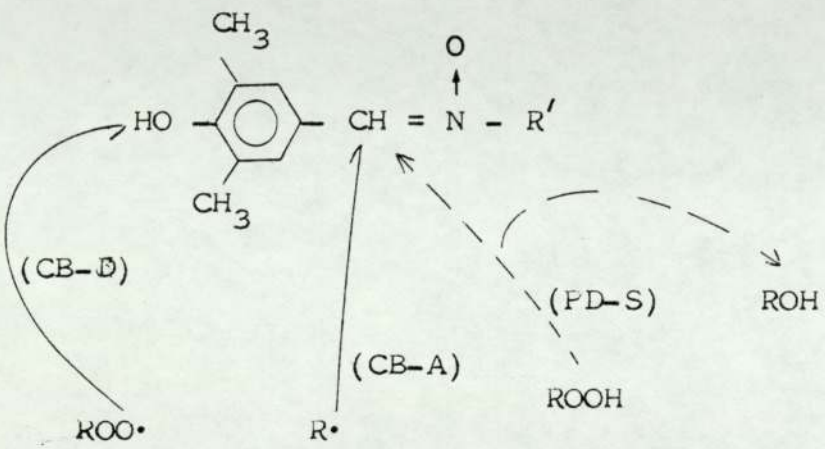
The nitrones without the phenolic antioxidant function are only capable of removing the alkyl radicals and the traces of alkoxyl radicals and hydroperoxides that are produced in the system.



It therefore appears that removal of the alkyl radicals alone from the system is inadequate for efficient antifatigue activity.

This finding infact complements the conclusions made in chapter 4, where it was suggested that the inefficient antifatigue activity of the hindered alicyclic nitroxyl radicals was probably due the inability of these compounds to terminate the alkylperoxyl radicals, especially during the early stages of fatiguing.

Furthermore nitrones are capable of reacting with alkoxyl radicals and hydroperoxides as well, the nitrones containing the phenolic antioxidant function must be functioning auto-synergistically removing the alkyl radicals, alkoxyl radicals and hydroperoxides at the nitrone function and the alkylperoxyl radicals at the phenol function.
i.e.

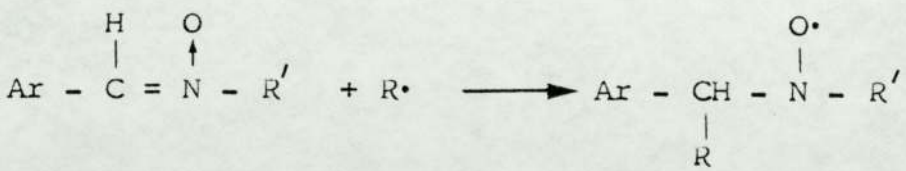


The effect of removing alkylperoxyl radicals from the rubber is highlighted when the combination of MHPPN and W.S.P. was used. The activity of the two was found to be syntergistic, thus exemplifying the need for presence of an alkylperoxyl radical scavenger to operate in conjuction with the alkyl radical trapping mechanism for efficient antifatigue activity. Quinonoid type transformation products are probably also formed from the W.S.P. and their subsequent alkyl radical trapping activity may also contribute to the synergism between the W.S.P. and the nitrone.

It was shown in the present work that the nitrone containing the fully hindered phenolic antioxidant function (BHPMN) was less efficient than the semi-hindered counterpart (MHPMN). Although this finding appears to be inconsistant with the normal structure-activity relationships for hindered phenolic antioxidants, it does conform to the antioxidant trends for the nitrones containing these functions[96,100].

It was shown in this work that optimum antifatigue activity was achieved when the N-alkyl group was isopropyl. The activity was slightly less when the group was tert-butyl, and even less for the N-methyl nitrone. This suggests that the nature of the N-alkyl group is very important for the antifatigue efficiency of the nitrone.

When the nitrone reacts with an alkyl radical a nitroxyl radical is generated.

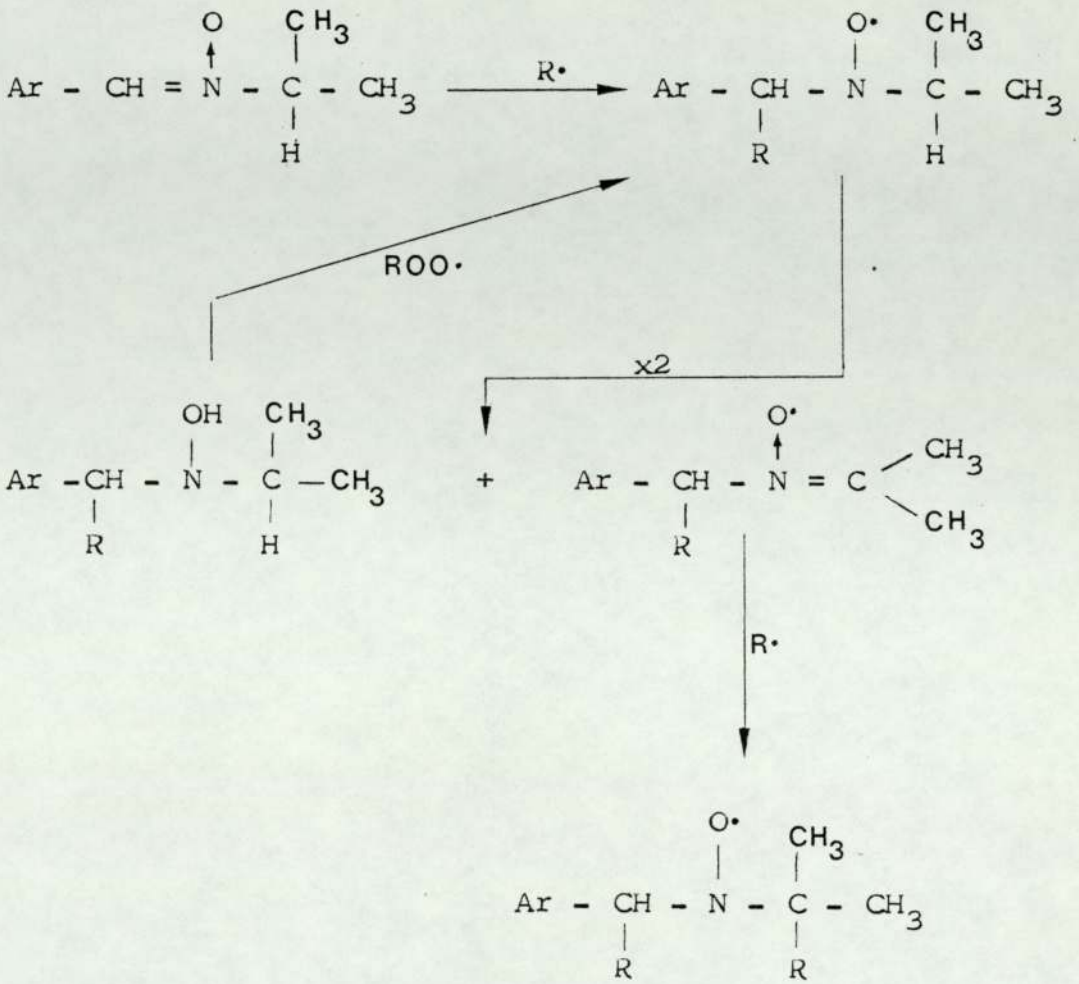


It is well known[194-196] that nitroxyl radicals containing hydrogens on the carbon α to the nitrogen can decompose to the hydroxylamine and nitrone. Exceptions to this general rule are bicyclic nitroxyl radicals[197] where the

disproportionation is forbidden by Bredt's Rule and nitroxyl radicals in which disproportionation is not possible because of "spacial congestion"[123]. Nitroxyl radicals which are derived from nitrones fall into the latter catagory[123]. However it must be pointed out that the latter nitroxyl radicals are stable only in the solid state. Furthermore since they have been isolated in only a 3% yield, Forrester et al[71] have suggested that they must be undergoing slow disproportionation in solution.

The effectiveness of the nitroxyl radical as an anti-fatigue agent will depend on its relative ease of formation from the nitrone, its stability, on its ability to regenerate and on compatability criteria.

If we assume that the compatability criteria are similar for most of the nitrones and since it is known that all nitrones readily trap alkyl radicals to generate nitroxyl radicals, the greater antifatigue efficiency of the N-isopropyl nitrone (MHPPN) over the N-tertiarybutyl nitrone (MHPBN) must be due to the relative stability of the nitroxyl radical derived from the former nitrone. The nitroxyl radical formed from MHPPN would be able to disproportionate on the N-alkyl side to generate another nitrone function which could further trap more alkyl radicals (scheme 1·5).



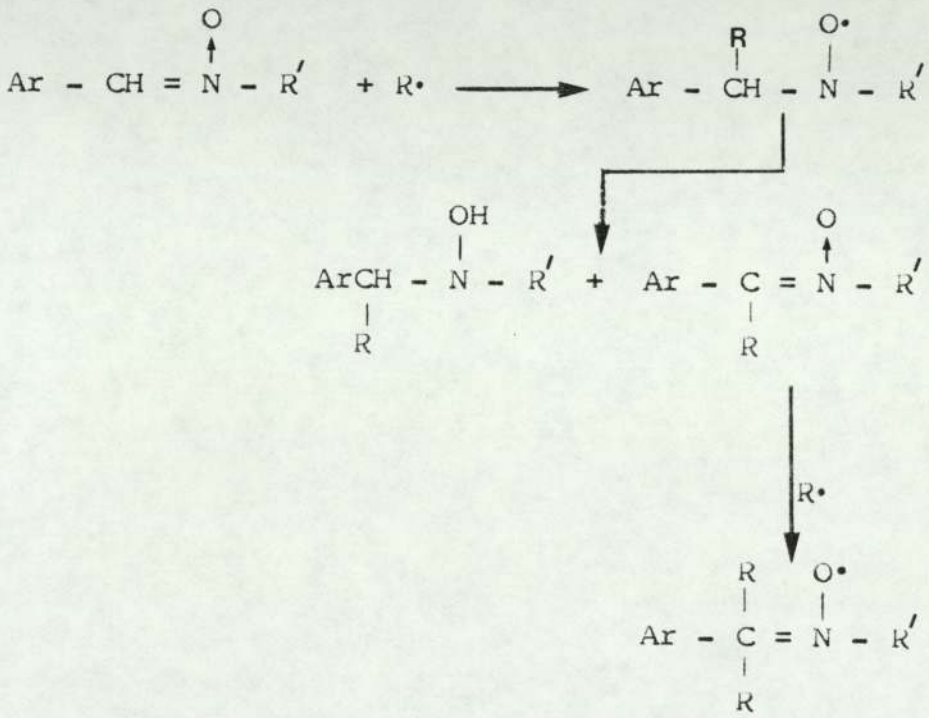
Scheme 5·1

The N-tertiarybutyl nitrone is unable to disproportionate on the N-alkyl side. Disproportionation of the N-methyl nitrone also would not be chemically feasible. However the N-ethyl nitrone presumably could disproportionate in this manner. The fact that it is not as effective as the N-isopropyl nitrone is probably associated with the

lability of the methelynic hydrogen on the $N - CH_2 - CH_3$ group.

Disproportionation of the nitroxyl radicals derived from the nitrones on the aryl side to give a ketonitrone should also not be eliminated.

i.e.



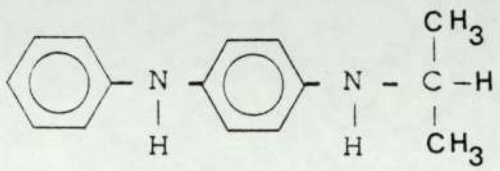
Scheme 5·2

Regeneration of the nitroxyl radical could also occur.

The contributory role of these two mechanisms to the overall activity of nitrones will be discussed further in chapter 6

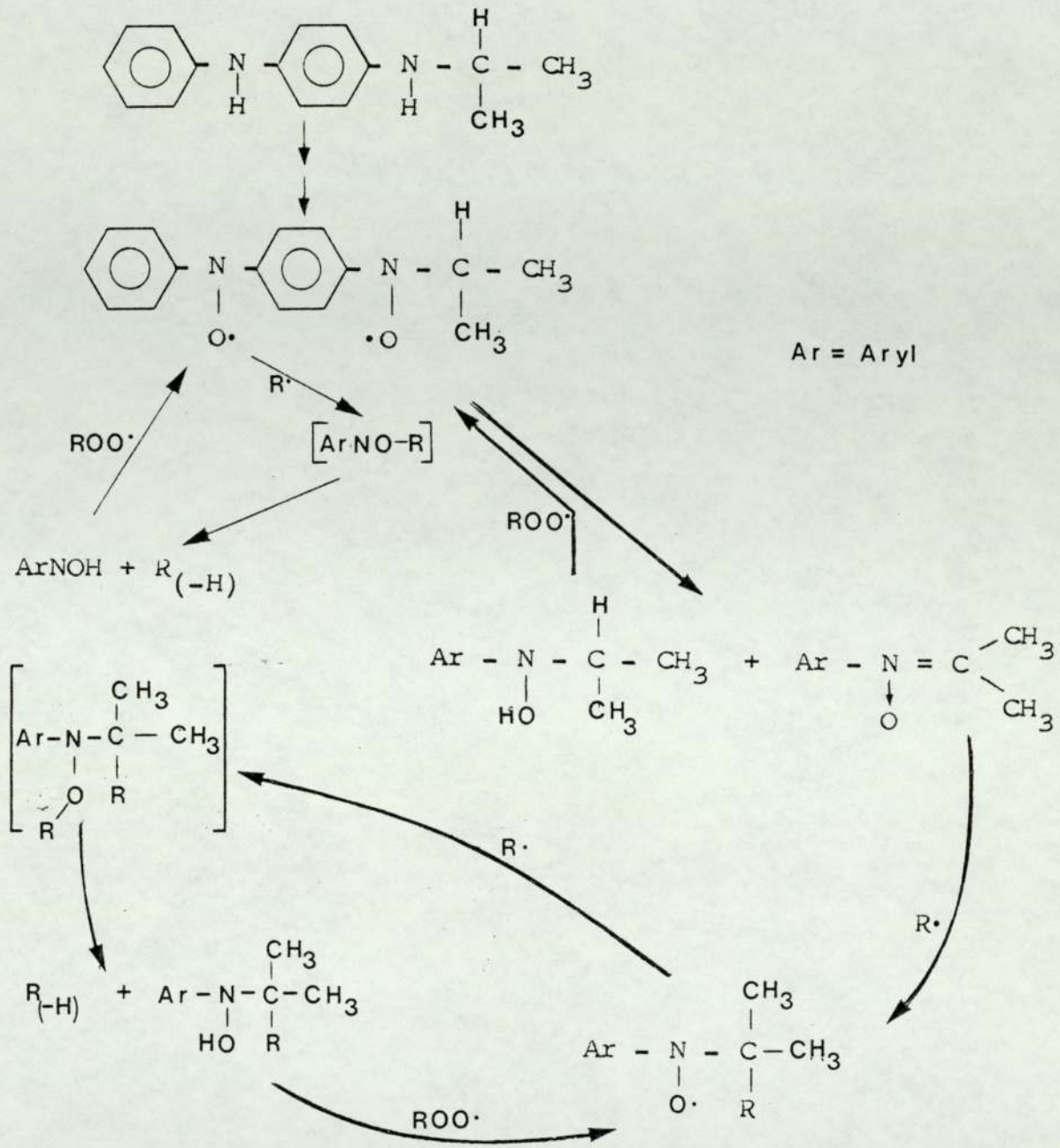
where the mechanism of antifatigue activity of nitrones has been studied.

It is interesting that the nitrone containing the N-isopropyl group has the most efficient antifatigue activity, because IPPD, the commercial antifatigue agent, also has the same functional group. The structure of IPPD is shown below.



So far most of the attention for the antifatigue action of IPPD has centered around the oxidation of the nitrogen between the phenyl rings. The results from the study of the nitrones MHPPN & MHPBN suggest that for IPPD too, the N-isopropyl group could be playing an active contributory role during the antifatigue action.

Thus in addition to the nitroxyl radical regeneration mechanism the following mechanistic path could also be operative during the antifatigue action of IPPD :-



Scheme 5·3: The participation of the N-isopropyl group of IPPD during its antifatigue action

In the study of the antifatigue effectiveness of the nitrones it was found that electron withdrawing or donating substituents on the 4-position of the phenyl ring attached

to the α carbon did not affect the activity of the nitrones significantly (MPPN and CPPN; table 5·7). Electron withdrawl (CPPN) did marginally improve the antifatigue efficiency by about 5 hours, however in relation to MHPPN, which contained phenolic antioxidant function, the antifatigue activities of MPPN and CPPN were very small. The slight improvement of the antifatigue efficiency of CPPN relative to MPPN may be attributed to the electron withdrawing capacity of the chlorine substituent on the phenyl ring of MHPPN Generally, although the effects are very small[198], electron withdrawing groups tend to enhance the rate of alkyl radical addition to the nitrone function.

It was shown that optimum antifatigue activity for the nitrones was achieved only for two minutes premilling of the nitrone with the rubber. Extended premilling decreased the activity slightly. The activity was also reduced for the case where no premilling was done. These results suggest that a certain amount of premilling is necessary probably to produce nitroxyl radicals. On longer premilling however, although the nitroxyl radical concentration increases as shown in table 5·12 perhaps some of the unreacted nitrone is destroyed by interaction with peroxidic entities in the rubber. Thus after long premilling, the total nitrone available to protect the rubber against

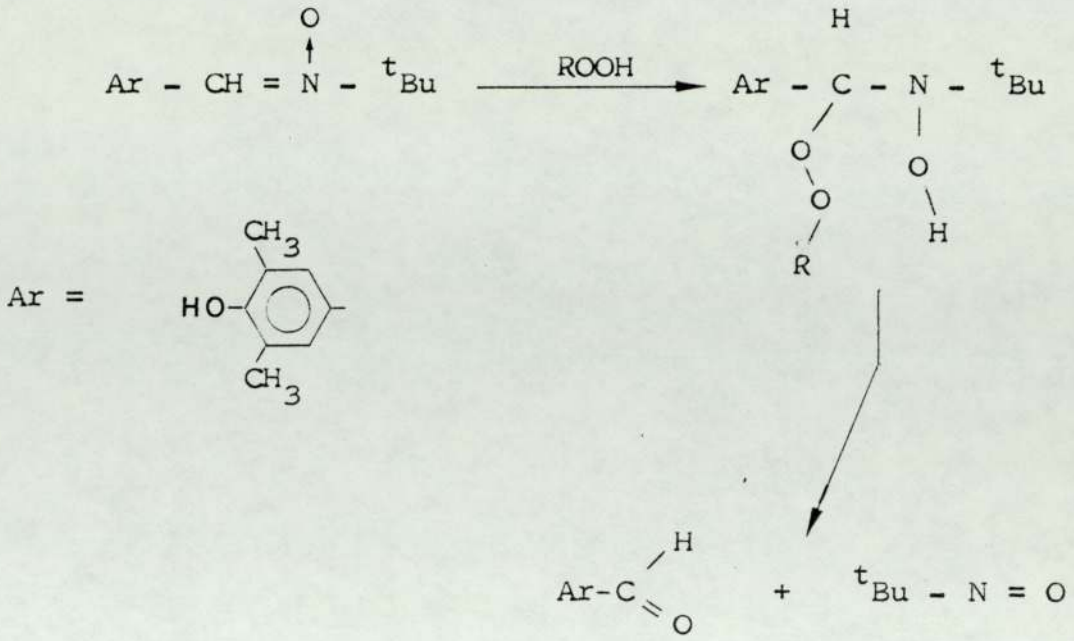
fatigue deterioration would be reduced. Furthermore alkyl peroxyl radicals are produced when the rubber is milled on the open mill[1]. The nitrone that was premilled for various lengths of time was MHPBN which contained the phenolic antioxidant function. If this function reacts with the peroxyl radicals that are produced during the premilling operations, then less phenolic antioxidant function will be available to auto-synergise with the nitrone function during the fatigue activity of the nitrones.

Upon extraction of the rubber prior to fatiguing (for rubber containing MHPBN, MHPPN, MHPEN and MHPMN respectively) it was found that practically all the antifatigue activity was lost. This result suggests that it is the free nitrone in the rubber that was responsible for the antifatigue protection. Extraction removes all the free nitrone and any other acetone soluble product that could be formed from the nitrone. These include the aldehyde and nitroso compound that are formed by interaction of peroxides with the nitrones[96]. The species left in the rubber would only be rubber bound nitroxyl radicals derived from the nitrones and the O-alkylated hydroxylamines. Indeed the presence of nitroxyl radicals was detected in the rubber after extraction. The fact that the antifatigue activity was lost after extraction

suggests that these rubber bound species do not contribute significantly to the antifatigue activity of the nitrones. This conclusion will be elaborated further in chapter 6.

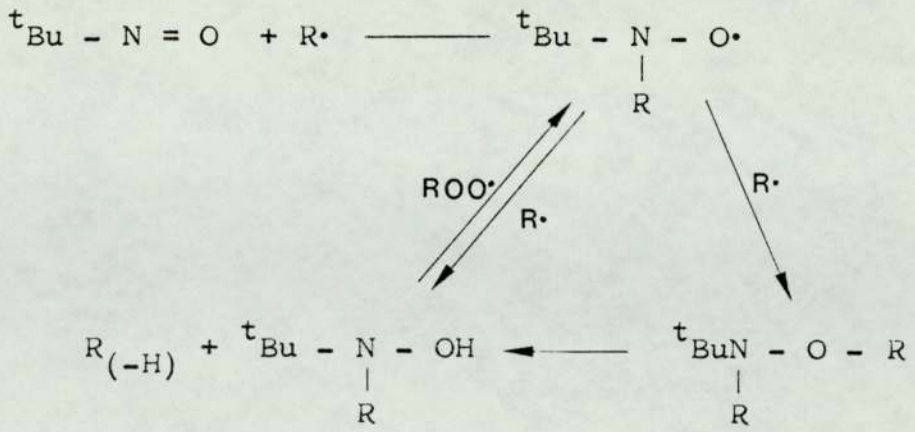
It can be pointed out however, that the loss of activity was not entirely unexpected since only the free nitrones would be sufficiently mobile to protect the rubber against fatigue deterioration. The mobility of nitroxyl radicals which are derived from the trapping of the macro-alkyl radicals by the nitrones would be restricted especially if one nitrone can trap two alkyl radicals. This effect too will be elaborated further during the mechanistic study of the antifatigue activity for nitrones in chapter 6.

The antifatigue activities of 3,5-dimethylbenzaldehyde and 2-methyl-2-nitrosopropane (PMN) were evaluated since nitrones are known to react with peroxides[96] to yield the aldehyde and a nitroso compound, and it was of interest to see whether either of these compounds had any activity by themselves. The products from the interaction of MHPBN with peroxides would be the parent aldehyde and PMN (scheme 5·4).



Scheme 5•4

Neither the phenolic aldehyde nor the 2-methyl-2-nitroso-propane were found to have significant antifatigue activity in the rubber. The nitroso-compound did have a small activity relative to the control. This was probably due to the ability of the nitroso-compound to trap alkyl radicals and generate nitroxyl radicals[198]. Regeneration of the nitroxyl radical would also be possible. (scheme 5•5).



Scheme 5.5

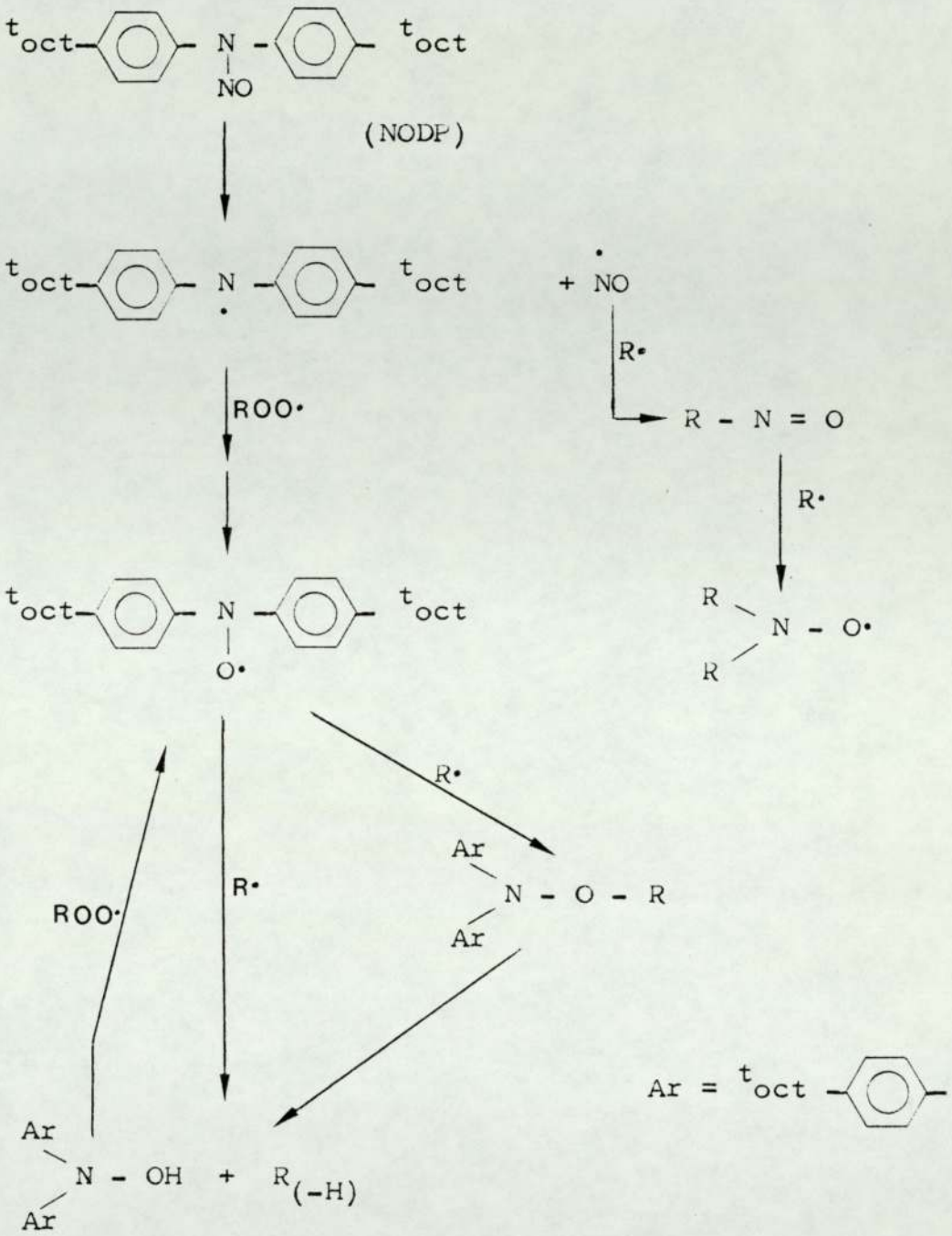
However the antifatigue activity is still small relative to the parent nitrone. Thus although the derived nitroso compound may contribute to the overall antifatigue activity of the nitrone the major alkyl radical trapping site must be the $>C=\overset{\uparrow}{N}-$ function of the nitrone.

When unextracted rubber was used with the nitrones (MHPBN, MHPPN, MHPEN and MHPMN all premilled with the rubber for two minutes before compounding; table 5·12) the antifatigue activity was slightly reduced. This probably was due to interference of the antifatigue activity of the nitrones by the indigenious proteins and other naturally occuring antioxidants that are present in the natural rubber.

After fatiguing, the relative nitroxyl radical concentration derived from the nitrones (MHPBN) became twice the value

that was initially present after vulcanisation. Further more the e.s.r. spectrum was much broader and tendended to show hyperfine splitting than that before fatiguing (figures 5·10 and 5·3·6). The spectrum is still isotropic since it consisted of three lines, however the increased broadning of the e.s.r. lines the increased differential broadning of the lines and the increased complexity of the lines (especially for the second and third lines) suggest[166] a greater tendancy to anisotropy than before fatiguing. This implies that the freedom of movement of the nitroxyl radical is much more restricted after fatiguing than before fatiguing. The implications of this result will be seen after the studies on the mechanism of the antifatigue action of the nitrones (chapter 6 part B).

Table 5·11 and figure 5·8 shows that the combination of MHPPN with NODP was slightly antagonistic as the effect was not additive. NODP itself is an effective antifatigue agent[182] by virtue of the fact that it can disproportinate to the diarylamino radical and nitric oxide radical (·NO). The former can give rise to nitroxyl radicals which will have antifatigue activity. The ·NO too can contribute towards the antifatigue activity by trapping alkyl radicals to give nitroxyl radicals (scheme 5·6).


t oct
N
NO
t oct
(NODP)
ROO·
+ NO
R·
R - N = O
R·
R
N - O·
R
O·
R·
Ar
N - O - R
Ar
ROO·
R·
Ar
N - OH
Ar
+ R(-H)
Ar = t oct

Scheme 5·6

In the presence of MHPPN, the effect of the combination of the nitrone and NODP is not additive probably because some of the $\dot{N}O$ liberated from the NODP is trapped by the nitrone. This reaction would therefore compete with the alkyl radical trapping reactions of the nitrone and that of the nitric oxide radical respectively.

Although the best fatigue life obtained for the nitrones was 130 hours which is approximately 50% of the fatigue life of rubber containing the commercial material IPPD the improvement is significant relative to the alicyclic nitroxyl radicals. Furthermore it will be seen in chapter 7 that these nitrones are relatively non staining compated to IPPD. Therefore further technological studies on these nitrones were warranted and are described in chapter 7. Besides, the combination of MHPPN with a commercial antioxidant (W.S.P.) improved the antifatigue activity to over 200 hours. Therefore a further study of the technological activity of the nitrones was justified.

CHAPTER SIX

MECHANISTIC STUDIES

6.A A STUDY OF THE ROLE PLAYED BY THE ALKYLATED HYDROXYLAMINE DURING THE REGENERATION OF THE NITROXYL RADICAL IN RELATION TO FATIGUE

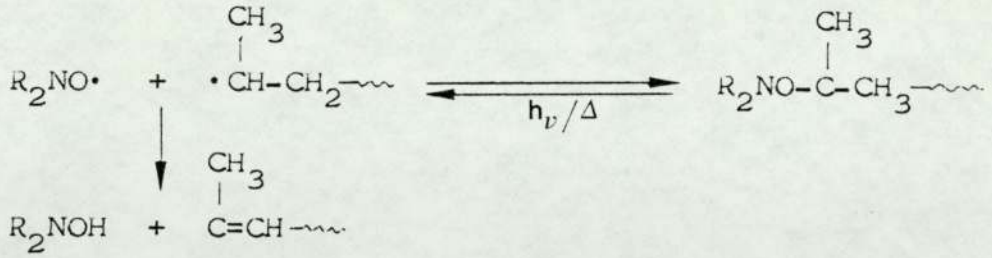
6.A.1 Introduction

The precise role played by the O-alkylated hydroxylamine if any, in the regeneration cycle of nitroxyl radicals is not clear yet and is therefore the subject of considerable controversy. Certainly it is well known that nitroxyl radicals react with low molecular weight alkyl radicals to give the alkylated hydroxylamines. It is also known that these hydroxylamines are unstable at elevated temperatures especially in the presence of traces of oxygen and the nitroxyl radical is rapidly regenerated. Bolsman et al[76] and Grattan et al[199] have shown that this regeneration occurs via the disproportionation of the alkylated hydroxylamine to the free hydroxylamine and unsaturation. This scheme explains the removal of alkyl and alkylperoxyl radicals from the system very well. The alkyl radicals are removed by the trapping of these radicals by the nitroxyl radical. The O-alkylated hydroxylamine then disproportionates to the hydroxylamine and

unsaturation. The alkylperoxyl radicals are removed by reaction with the hydroxylamine in a CB-D mechanism during which the nitroxyl radical is regenerated (see scheme 1·10). Both the hydroxylamine and unsaturation have been found to be present in the polymer[101,200]. However Scott et al[85] have suggested an alternative scheme for the formation of hydroxylamine and unsaturation which occurs in competition with the reaction:

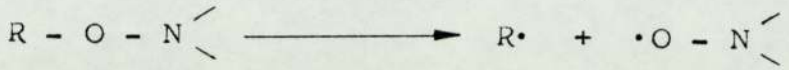
$$R_2NO\text{-}R' \longrightarrow R_2NOH + R'(-H)$$

They have suggested that the formation of the O-alkylated hydroxylamine is reversible and that the alkyl radicals are removed from the system by direct hydrogen abstraction from the latter by the nitroxyl radical to give the hydroxylamine and the unsaturation (see scheme 6·1).



Scheme 6·1

Kovtun et al[135] were the first to suggest dissociation of the alkylated hydroxylamine back to the nitroxyl radical and alkyl radical.



Since then other workers too have found evidence for the feasibility of this reaction[138,199]. Shlyapintokh and Ivanov[201] have suggested that the decomposition rate is strongly dependant on the structure of the O-alkyl group and an increase in the delocalisation of the unpaired electron in the alkyl radical leads to an increase in the rate of decomposition of the O-alkylated hydroxylamine.

Whatever the pathway the formation of the hydroxylamine is central to the efficient operation of the regeneration scheme cycle, and as already stated has been detected in the polymer. However there has been very little evidence to suggest the existence of stable O-alkylated hyrdoxylamines within the polymer formed from the reaction of the nitroxyl radical with the macro-alkyl radicals. Wiles and Carlsson[87] have recently reported that the polymer-alkylated hydroxylamine of Tinuvin 770 (TMPS) is formed to a yield of 80% during the light protection of polypropylene by TMPS. Their evidence is based on Fourrier transform infrared spectroscopy and a peak at 1135 cm^{-1} of the spectrum.

However attempts to prepare long chain O-alkylated hydroxylamines based on TMP series (sections 2·24 -2·26) were not successful as they oxidised back to the nitroxyl radical during the isolation procedure. It was therefore

interesting to study the contributory role of the polymer alkylated hydroxylamine to the overall antifatigue activity of the hindered alicyclic nitroxyl radicals. With this in mind, two studies were carried out.

The first was a study of the formation and decay of species produced when TMOP was reacted with squalene. Squalene is normally used as a model compound for rubber[169]. The second study involved the milling of TMOP with the rubber in the RAPRA torque rheometer (closed chamber) and the indirect estimation of the amount of TMOP bound to the rubber by a technological ageing test, and e.s.r. studies.

6.A.2 A MODEL COMPOUND STUDY OF THE REACTION OF TMOP WITH SQUALENE

Squalene was used as the model substrate for two reasons:

1) Squalene consists of a chain of six isopentenyl units joined in a head to tail manner, hence is very similar to rubber. Therefore it is a good model substrate for the latter.

2) Because of its structure any conjugated unsaturation could be detected easily by infrared spectroscopy at 1430 and 1410 cm^{-1} on the spectrum.

6.A.2.1 Experimental Procedure

Squalene (analar grade; B.D.H. Chemical Company) was purified[96] by passing through a column of silica gel and kept in the dark till required for use.

A number of experiments were carried out in the presence and absence of initiator (benzoylperoxide) and in the presence and absence of air. A typical experimental procedure was as follows:
To 70ml of a 16% (volume:volume) solution of squalene in chlorobenzene, 0·716g of TMOP and 0·05g benzoylperoxide (previously purified by recrystallisation from methanol[202]) was added and dissolved. The molar ratio of squalene to TMOP to benzoylperoxide was 0·023:0·004:0·0001 or 1:0·175:0·004 respectively. In terms of percent of the overall reaction volume the ratios were 16% squalene, 1% TMOP and 0·07% benzoylperoxide. The reaction was carried out in a round bottom flask equipped with a condenser and a nitrogen inlet tube, and was heated in an oil bath at $110 \pm 2^{o}C$.

The progress of the reaction was followed by infrared and e.s.r. spectroscopy at various time intervals. Sample solutions were removed from the reaction flask using a 2·0ml syringe with a long needle.

The infrared spectra were recorded on the Perkin Elmer 599 grating infrared spectrophotometer using sodium chloride solution cells. The path length of the cells was 0·5mm. Approximately 0·5ml of the solution was required to fill the cell. This was small enough to ensure a minimal effect on the reaction solution.

The e.s.r. spectra were recorded on the J.O.E.L. spectrometer. The decay of nitroxyl radical was followed using a copper sulphate standard as described in section 3·15. 10 μl of reaction solution was required for this purpose.

The reaction of the TMOP with squalene was studied under the following conditions:

1) 16% squalene + 1% TMOP + 0·07% benzoylperoxide (as initiator) in chlorobenzene heated at 110 $\pm$ 2°C in an atmosphere of nitrogen.

2) 16% squalene + 1% TMOP (no initiator) heated in chlorobenzene at 110 $\pm$ 2°C in an atmosphere of nitrogen.

3) 16% squalene + 1% TMOP + 0·07% benzoylperoxide in chlorobenzene heated in air at 110 $\pm$ 2°C.

4) 16% squalene + 1% TMOP (no initiator) heated in air at 110 $\pm$ 2°C.

5) 16% squalene in chlorobenzene heated in air.

6.A.2.2 Results

Figure 6·1 shows sections of the infrared spectrum in which pronounced changes occured during the reaction of 16% squalene + 1% TMOP + 0·07% benzoylperoxide in chlorobenzene at 110 $\pm$ 2°C under nitrogen. The changes were:

1) An increase in the absorption band at 3600 cm^{-1}.

2) An increase in the absorption bands at 1630 and 1610 cm^{-1}. The growth of these two bands was simultaneous and paralled each other.

3) A slight decrease in the absorption band at 1360 cm^{-1} accompanied by line broadning as the reaction progressed.

4) A rapid and paralled decrease within the first two hours of reaction time for the bands at 1710 cm^{-1} and 1220 cm^{-1} respectively.

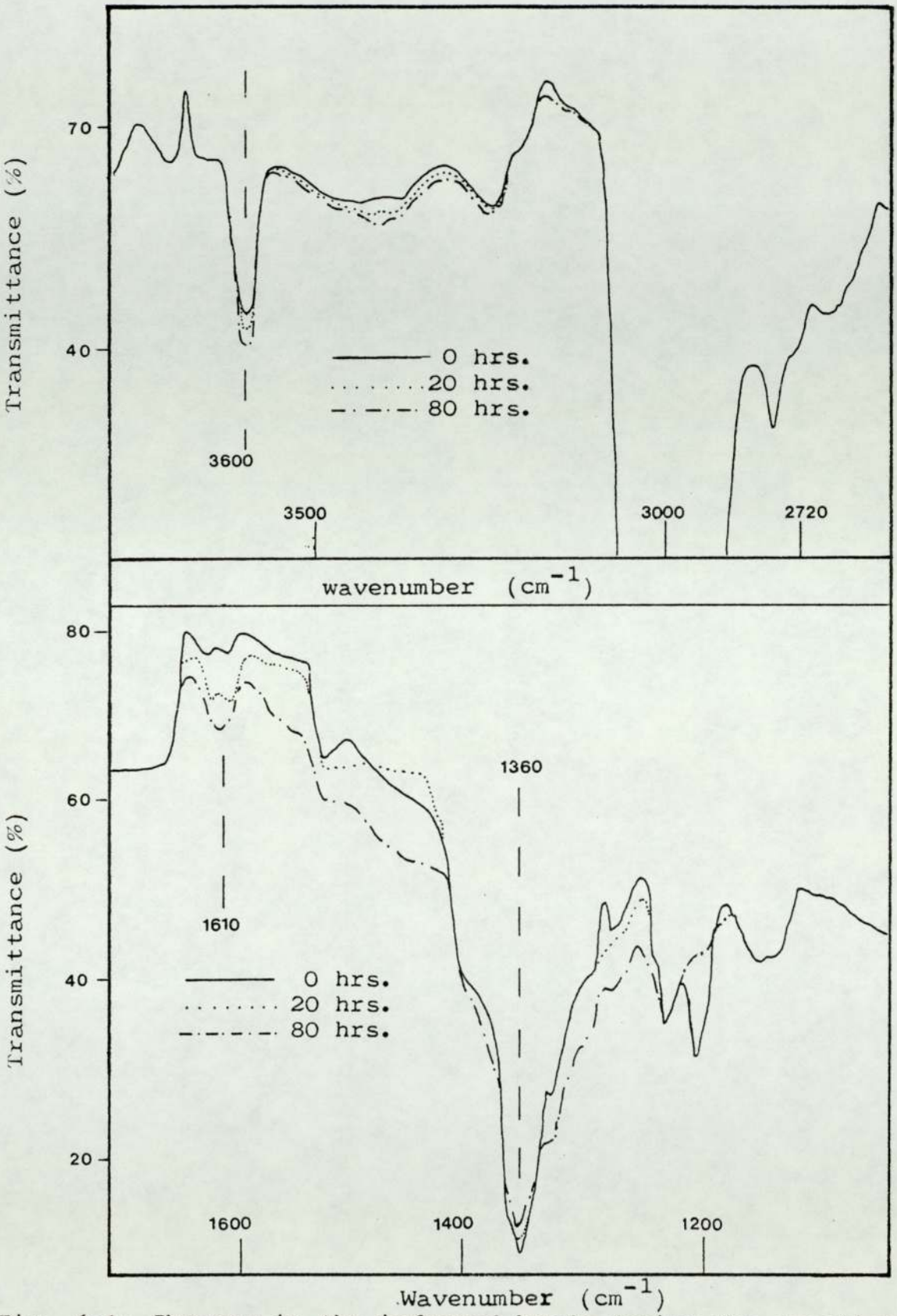


Fig. 6·1: Changes in the infrared bands during the reaction of TMOP with squalene at 110 ± 2°C under N_2 (initiator was benzoylperoxide)

When a compensated infrared spectrum was run (i.e.: a; recording made when the reference cell contained 16% squalene in chlorobenzene instead of chlorobenzene alone) changes were observed in the region of 2800 cm^{-1}. In the normal spectrum where the reference cell contained solvent (chlorobenzene) alone, the changes in this region were masked by the intense C-H stretch absorption in the region of 3000-2700 cm^{-1} (figure 6·1). The changes with reaction time in the region of 2800 cm^{-1} in the compensated infrared spectrum are shown in figure 6·2. It is clear that there is a growth of a new absorption band at 2810 cm^{-1} which shifts to 2780 cm^{-1} as it grows. Its growth is accompanied by a parallel growth of weak absorption bands in the region of 2600 cm^{-1}, an increase in the absorbtion band at 3600 cm^{-1} and an increase in the broad absorption at 3350 cm^{-1} - 3500 cm^{-1}. Changes in other parts of the spectrum as the reaction progressed were similar to that shown in the lower section of figure 6·1 i.e.: a growth in the bands at 1610 and 1630 cm^{-1}; a slight decrease in the band at 1360 cm^{-1} and a rapid decrease of bands at 1710 cm^{-1} and 1220 cm^{-1}.

Figure 6·3 shows that the growth of the bands at 3600 cm^{-1} and 2780 cm^{-1} respectively. The band at 2780 cm^{-1} probably corresponds to free hydroxylamine stretch[203]. Therefore the increase in the absorption band at 3600 cm^{-1} is also

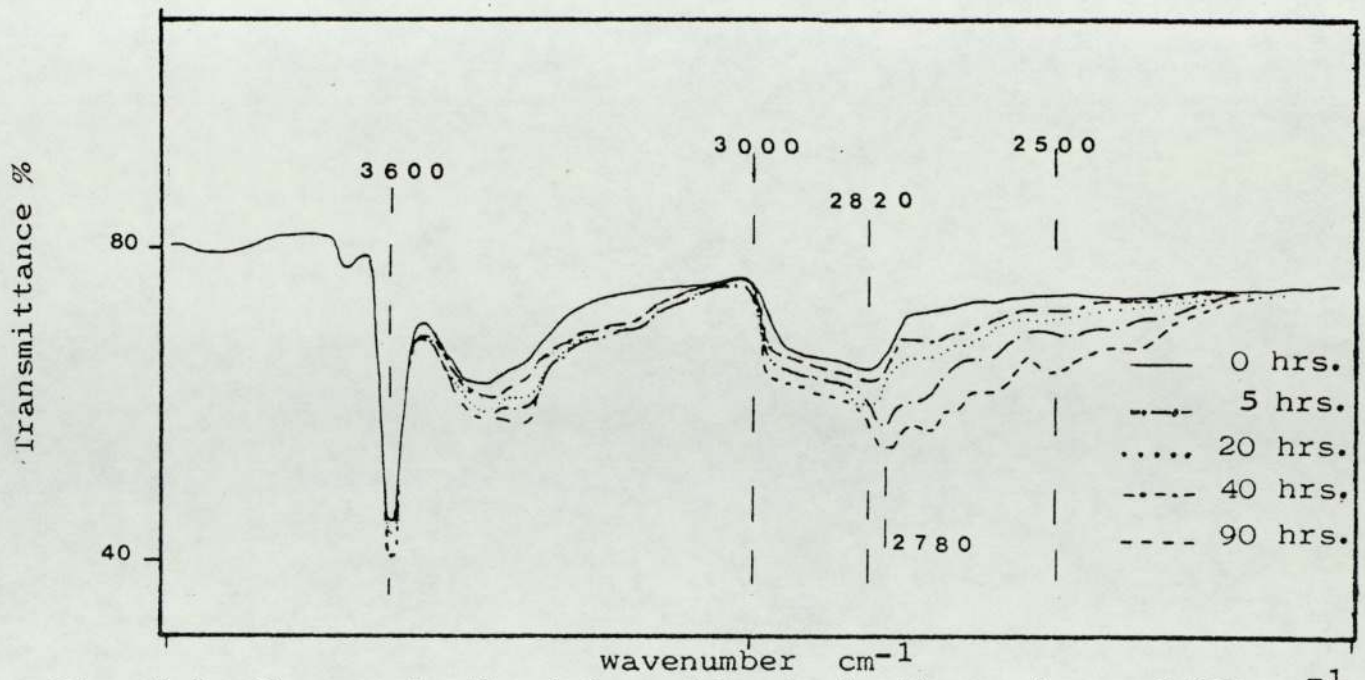


Fig. 6·2: Changes in the infrared bands in the regions of 280 cm^{-1} of a compensated spectrum during the reaction of TMOP with squalene at 110°C under N_2 -(initiator: benzoylperoxide)

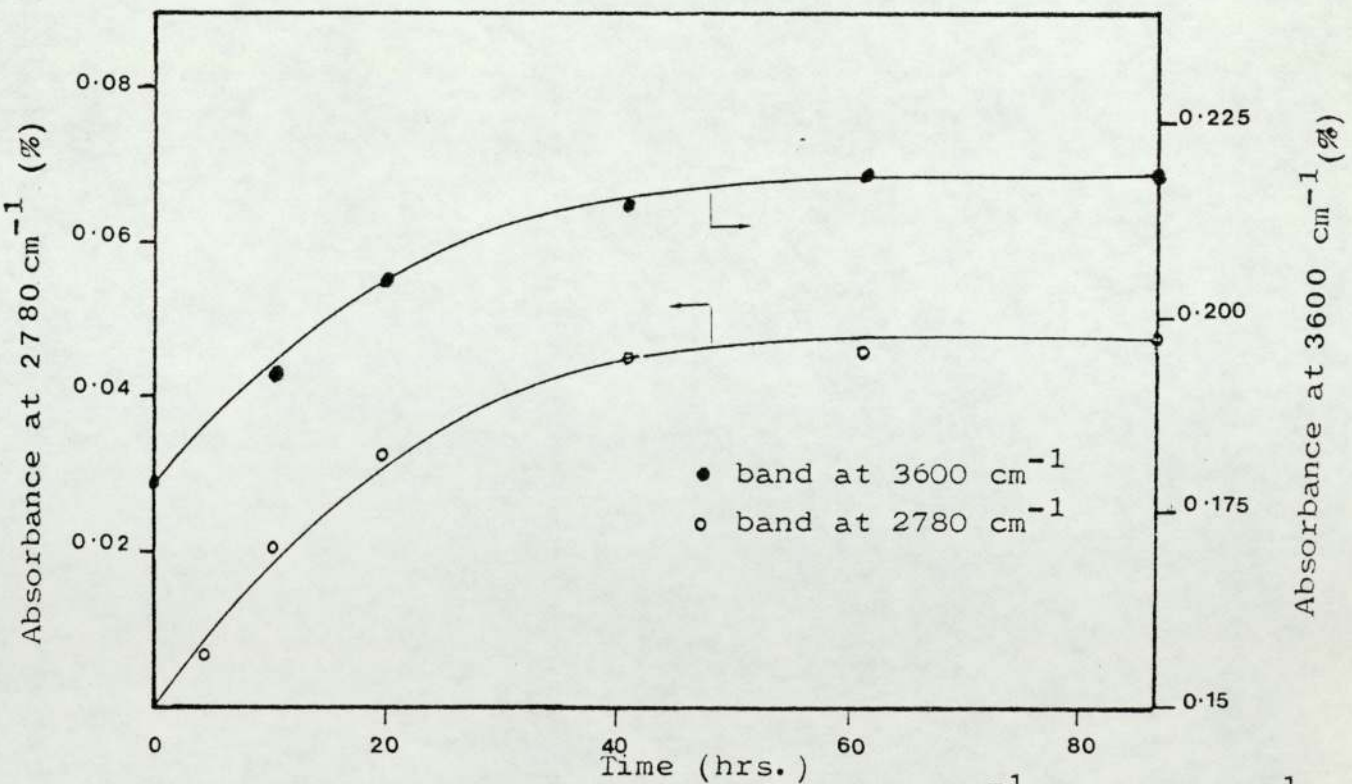


Fig. 6·3: Growth of the infrared bands at 3600 cm^{-1} and 2780 cm^{-1} respectively in the compensated infrared spectrum during the reaction of TMOP with squalene at 110°C under N_2 (initiator: benzoylperoxide)

probably due to the formation of the hydroxylamine.

The bands at 1630 cm^{-1} and 1610 cm^{-1} correspond to unsaturation and conjugated unsaturation C = C stretches respectively[144]. The band at 1360 cm^{-1} probably corresponds to the nitroxyl stretch, however hydroxylamine also absorbs in the same region and overlaps. This band was therefore not used for any quantitative work.

The bands at 1710 cm^{-1} and 1220 cm^{-1} correspond to acid carbonyl[144] and $C-\overset{O}{\overset{\|}{C}}-O$ stretch[144] respectively. Since they dissappear rapidly during the first few hours of reaction they are probably associated with the benzoylperoxide initiator. This is most likely because under reaction conditions where no benzoylperoxide was used, these two bands were absent.

Figure 6·4 shows the growth of the band at 3600 cm^{-1} due to hydroxylamine formation, and the band at 1610 cm^{-1} corresponding to the conjugated unsaturation. The decay of nitroxyl radical concentration (from e.s.r. spectroscopy) and the band at 1710 cm^{-1} are also shown. The bands at 1630 cm^{-1} and 1220 cm^{-1} are not shown since they parallel the growth and the decay of 1610 cm^{-1} and 1710 cm^{-1} respectively. It is clear from this figure that the growth of the hydroxylamine and conjugated unsaturation

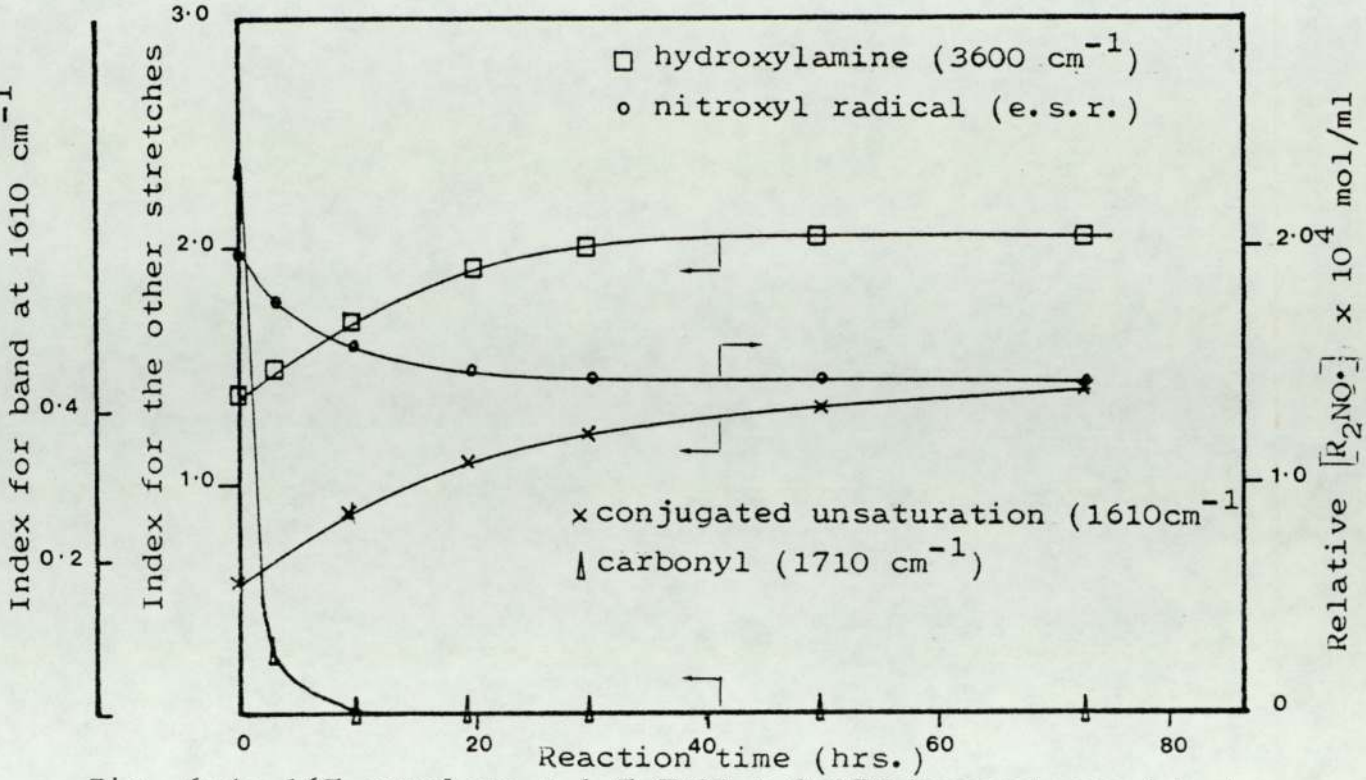


Fig. 6·4: 16% squalene + 1 % TMOP + 0·07% benzoylperoxide in chlorobenzene heated at 110°C under nitrogen

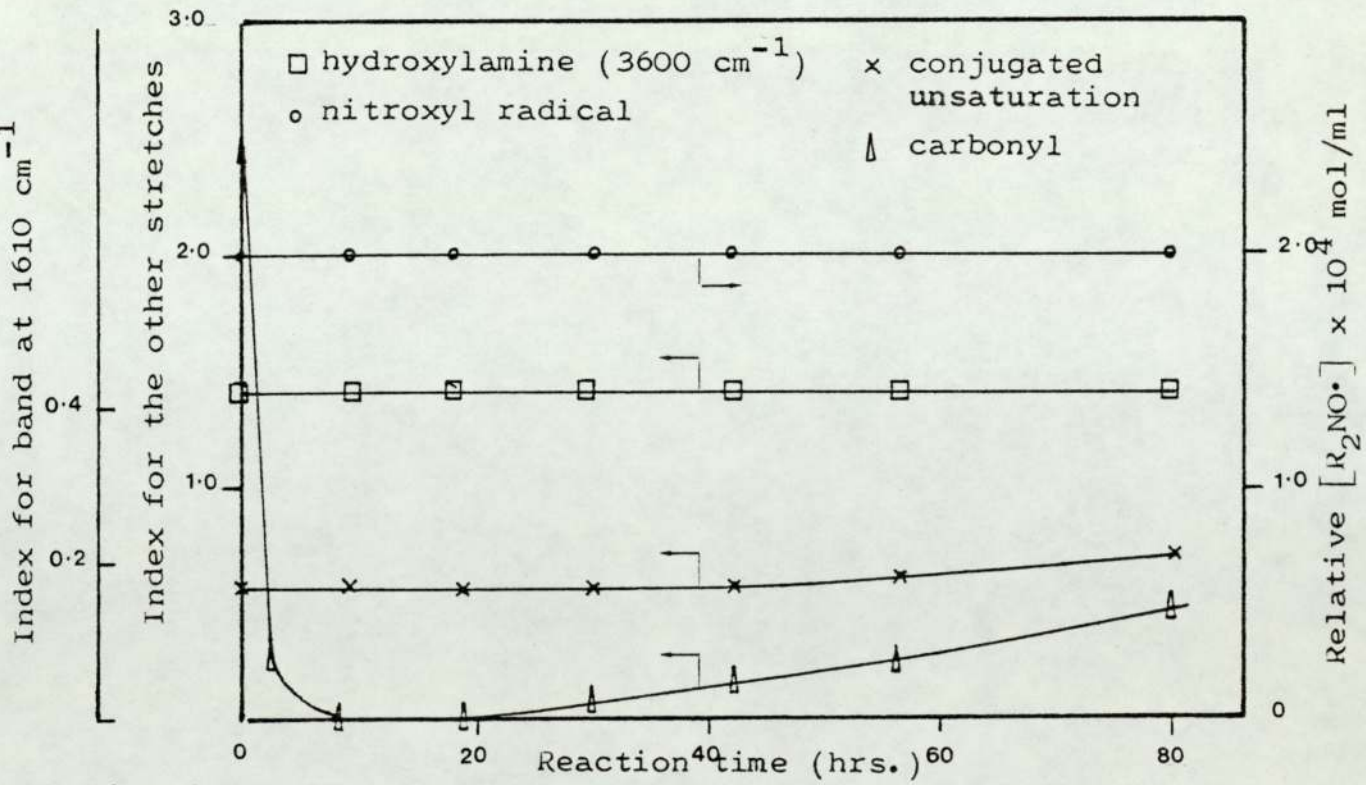


Fig. 6·5: 16% squalene + 1% TMOP + 0·07% benzoylperoxide in chlorobenzene heated at 110°C in air

is a mirror image of the decrease of the nitroxyl radical concentration during the reaction. Unlike the hydroxylamine however, the conjugated unsaturation continues to increase without reaching a steady state, albeit at a slower rate than during the early stages of the reaction.

An examination of the spectra did not reveal the growth of any bands that could have corresponded to alkylated hydroxylamine formation especially in the 1100 cm^{-1} region.

Figure 6·5 shows that when the same reaction is carried out in the presence of air there is no change in the band at 3600 cm^{-1} nor in the concentration of the nitroxyl radical. After the initial rapid decay of carbonyl due to the benzoylperoxide, however there is a gradual growth of carbonyl again probably due to oxidation of the squalene. This oxidation is also accompanied by a slight increase in conjugated unsaturation as well. The induction period before carbonyl growth occurs is about 20 hours.

Figure 6·6 shows there is no change in any of these bands when no initiator is used and in the absence of air.

Figure 6·7 shows that when the reaction is carried out in the presence of air but in the absence of initiator (benzoyl-

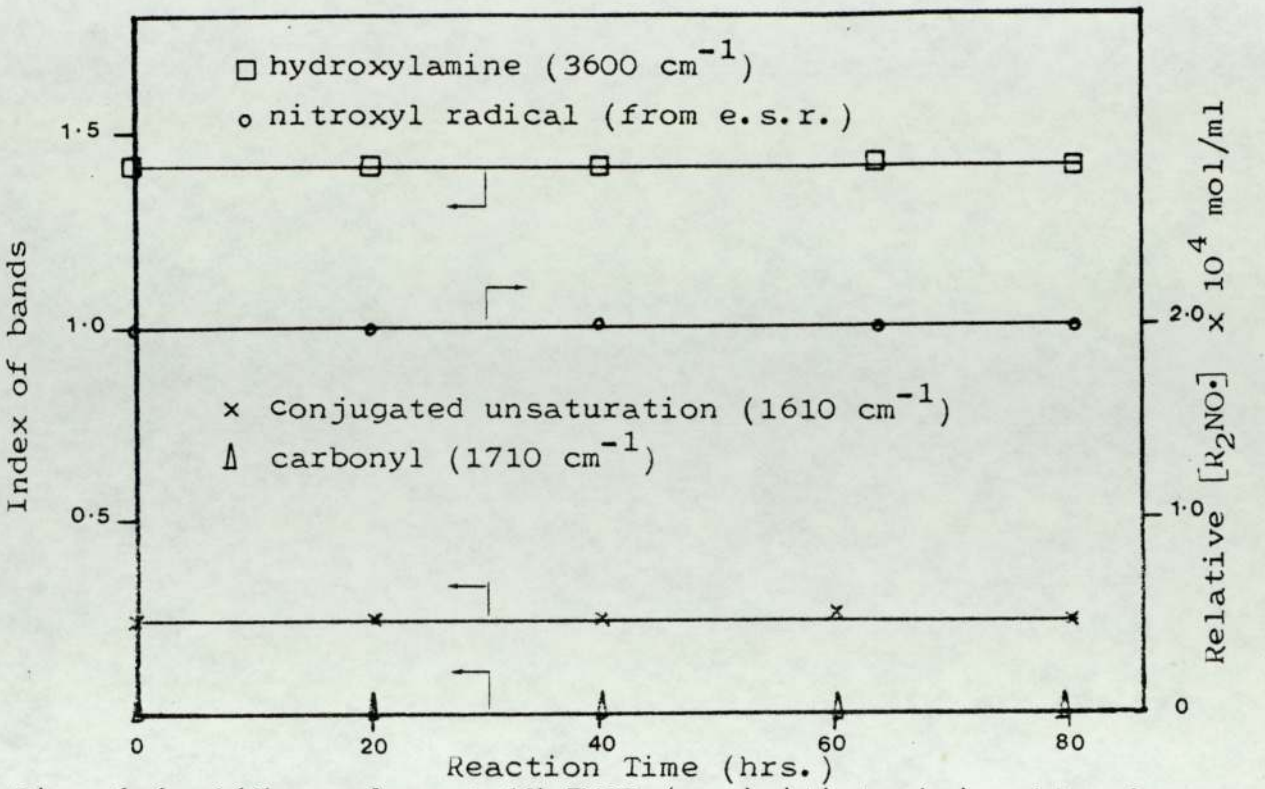


Fig. 6·6: 16% squalene + 1% TMOP (no initiator) in chlorobenzene heated at 110°C under N_2

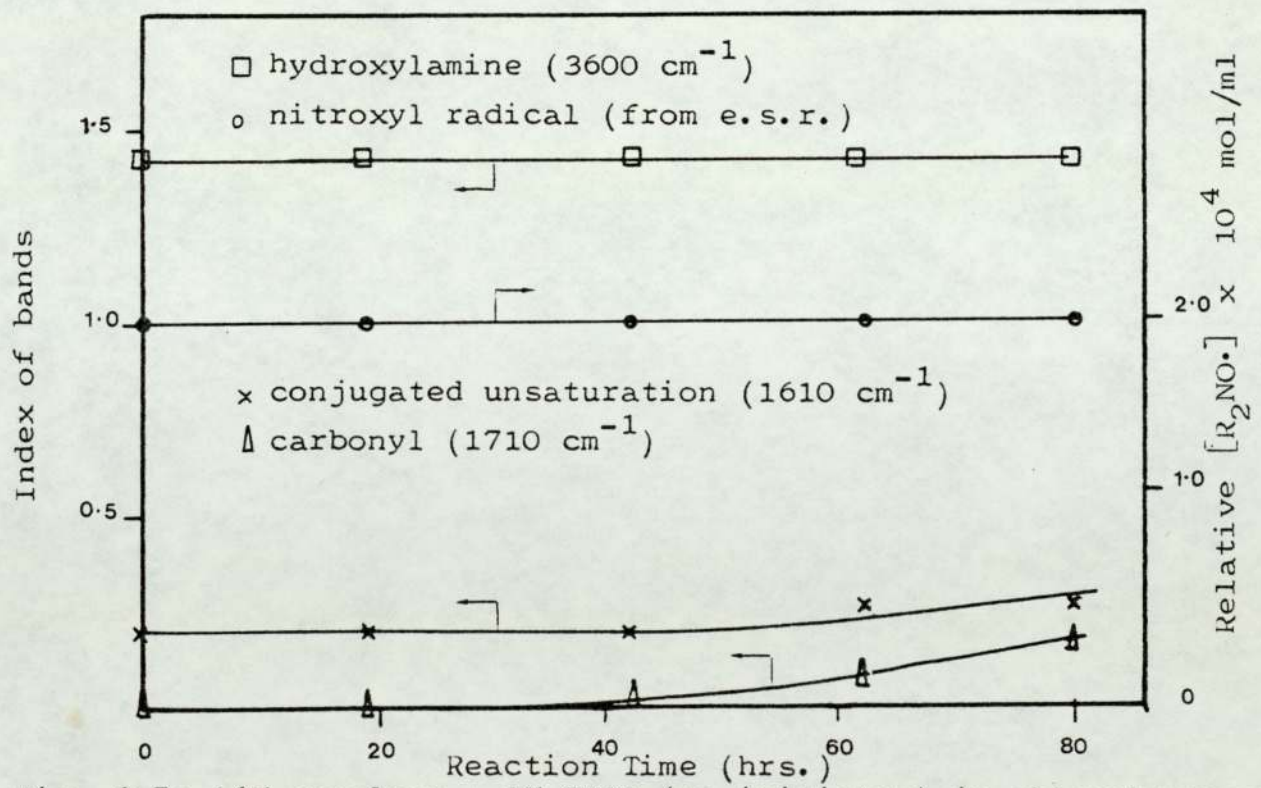


Fig. 6·7: 16% squalene + 1% TMOP (no initiator) in chlorobenzene heated at 110°C in air

peroxide) no growth of hydroxylamine or decay in nitroxyl radical occured. However due to oxidation of the squalene, carbonyl growth occurs after about 30 hours induction period accompanied by a slight growth of the conjugated unsaturation.

Figure 6·8 shows the changes in the infrared spectra when squalene alone in chlorobenzene is heated at 110 $\pm$ 2°C in air. Rapid auto-catalytic carbonyl growth occurs with no induction period due to oxidiation of the squalene. The carbonyl growth is also accompanied by a slight increase in the conjugated unsaturation. A slight broadning and a shift to lower wave number (1690 cm^{-1}) as the reaction progressed indicated the formation of conjugated carbonyl in the system.

6.A.2.3 Discussion

It is clear that the regenerative cycle for the nitroxyl radical operates when TMOP is reacted with squalene in a nitrogen atmosphere by heating at 110 $\pm$ 2°C in the presence of an initiator (benzoylperoxide). The regeneration can be seen by the decrease of the nitroxyl radical concentration to a steady state, accompanied by the mirror image formation of hydroxylamine and conjugated unsaturation.

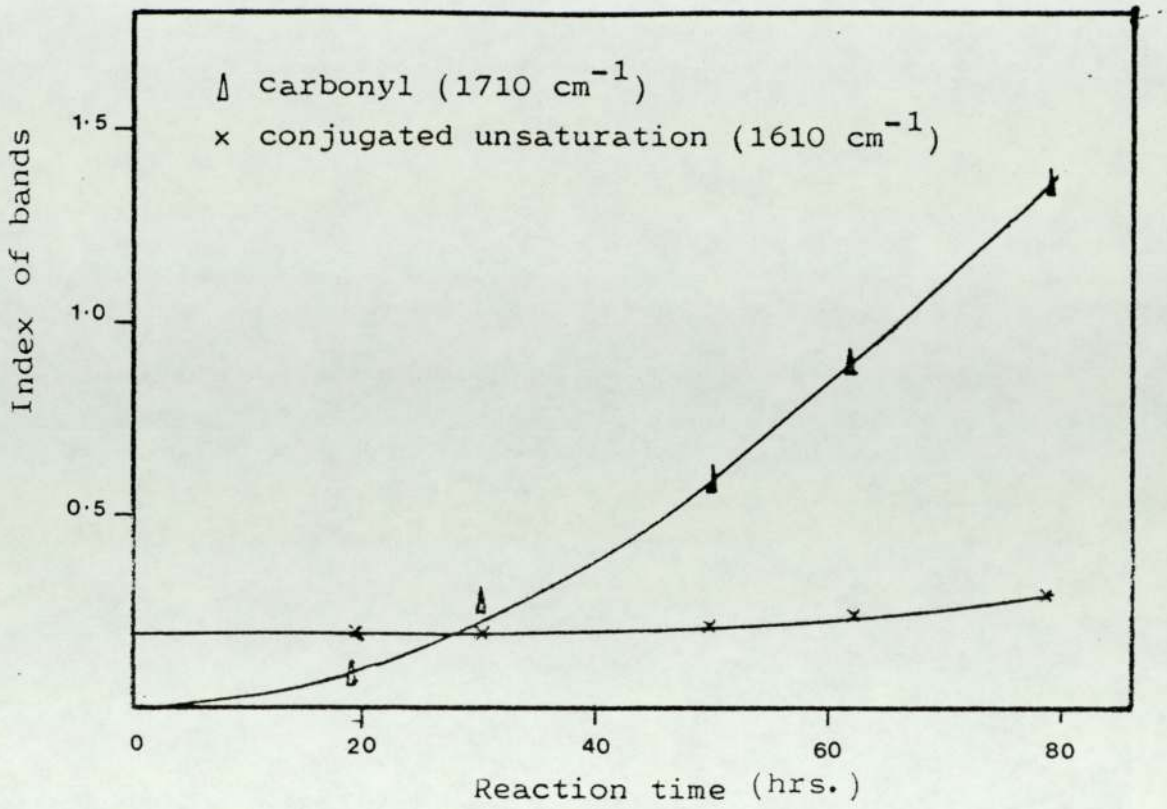


Fig. 6·8: 16% squalene in chlorobenzene heated in air at 110°C

Furthermore the relative rate of decay of the nitroxyl radical, and of the production of hydroxylamine and conjugated unsaturation appear to be of a similar value (figure 6·4). However no absorption bands due to the O-alkylated hydroxylamine were detected under these experimental conditions. This is probably due to the instability of the O-alkylated hydroxylamine in the conditions used. Alternately it suggests that under these conditions the formation of the O-alkylated hydroxylamine is reversible as described by Bagheri, Chakraborty and Scott[85]. Thus alkyl radicals are terminated by direct hydrogen abstraction by the the nitroxyl radical from the former to give the hydroxylamine and unsaturation.

In the absence of initiator under nitrogen the reaction does not proceed at all. Oxidation of squalene does not occur either, due to the inert atmosphere (figure 6·6).

When the reaction was done in the presence of air (oxygen) with initiator no change was observed in the nitroxyl radical concentration, nor was there any growth of hydroxylamine and conjugated unsaturation. Towards the later stages of the reaction conjugated unsaturation did grow slightly, but this was as a result of oxidation of the squalene - shown by the growth of carbonyl (figure 6·5).

These facts suggest that under these conditions, the contribution of chain termination reactions of alkyl radicals with nitroxyl radicals is small relative to the termination with peroxyl radicals.

During the reaction in the presence of air but in the absence of initiator (figure 6·7) once again only oxidation of the squalene occured. The induction period before carbonyl growth occured, was about 30 hours in contrast to 20 hours in the presence of initiator (figure 6·5).

Figure 6·8 shows that the oxidation of squalene is auto-catalytic, with no induction period and a very rapid build up of carbonyl. The induction period that is observed for the oxidation of squalene in the presence of TMOP and the slower rate of build up of the carbonyl must be due to the slight antioxidatant effect of the nitroxyl radical[85]. No change in the nitroxyl radical concentration was observed probably because of the rapid regeneration of the nitroxyl radicals in this oxygen excess condition[89,135]. In the presence of the benzoyl-peroxide the induction period to carbonyl growth is shorter than when it is absent because of the pro-oxidant effects of the peroxide.

6.A.3 ASSESSMENT OF THE AMOUNT OF O-ALKYLATED HYDROXYL AMINE FORMED DURING THE MILLING OF TMOP WITH NATURAL RUBBER IN THE R.A.P.R.A. TORQUE RHEOMETER

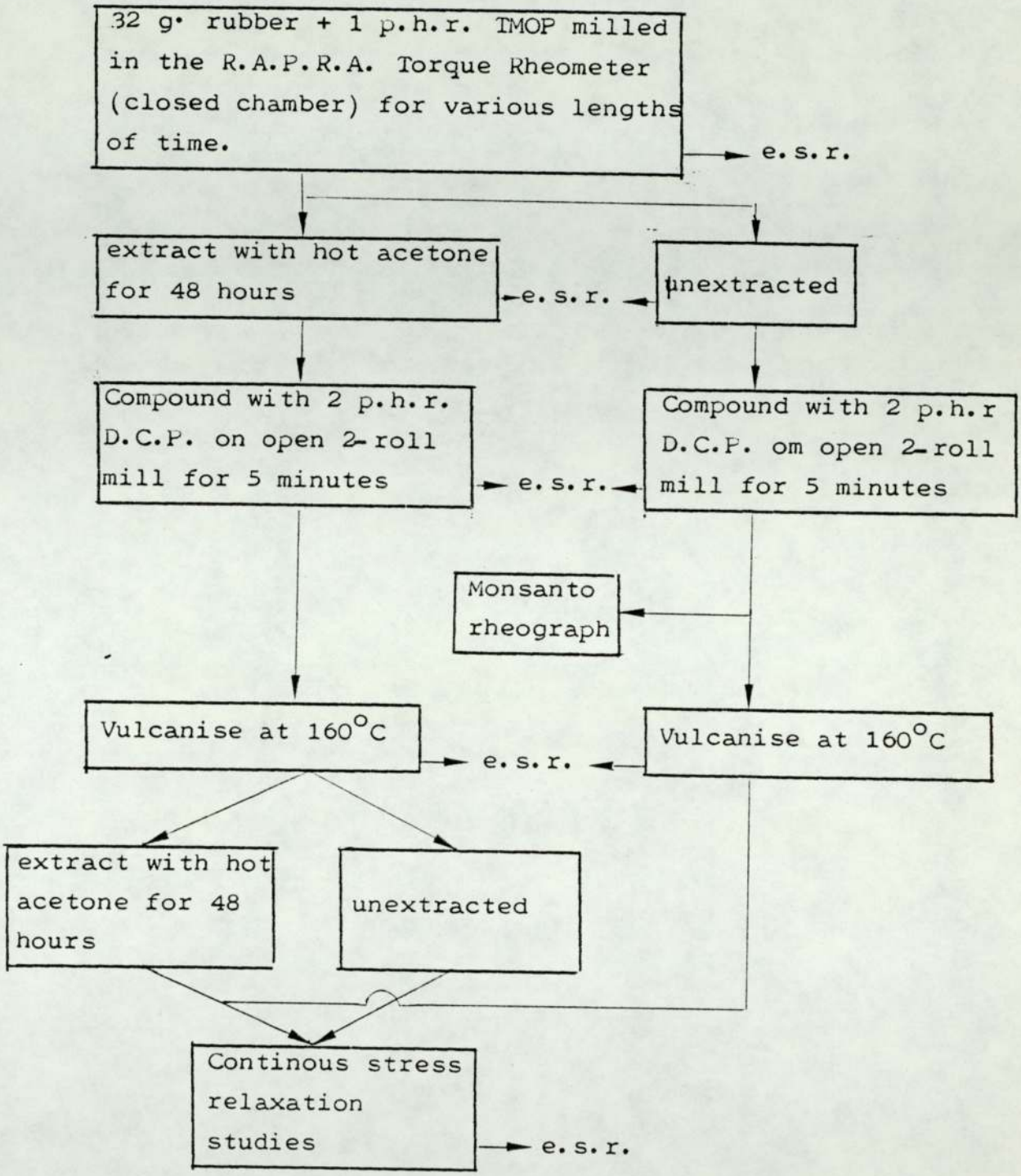
6.A.3.1 Introduction

During the mechanical processing of polymers in a closed high shearing mixer both alkyl and alkylperoxyl radicals are produced. However because the rate of initiation of alkyl radicals is very high, and the oxygen is limited to that dissolved in the system the concentration of alkyl radicals exceeds the concentration of alkylperoxyl radicals. Under these conditions the contribution to chain terminating reactions of the alkyl radicals will be greater than that made by the alkylperoxyl radicals. Therefore the processing of rubber in a high shearing closed mixer provides a good model for fatigue since in both cases the initiation and termination of radicals are governed by similar processes.

Using this model for fatigue the fate of the nitroxyl radical when milled together with the rubber at high shear in a closed chamber of the R.A.P.R.A. Torque Rheometer was studied. The amount of O-alkylated hydroxylamine formed in the system was also assessed by stress relaxation studies of peroxide cured vulcanisates, made using the rubber samples milled with the TMOP.

6.A.3.2 Experimental Procedure

32g of previously hot acetone extracted rubber (S.M.R. grade 10) was milled with 1 p.h.r. of TMOP for various lengths of time in the closed chamber of the R.A.P.R.A. torque rheometer (see section 3.14). The shearing was done at room temperature in a water cooled chamber using high shear. After milling, the concentration of the nitroxyl radicals in each sample of rubber was measured using e.s.r. spectroscopy as described in section 3.19. Each rubber sample was then hot acetone extracted for 48 hours and dried to a constant weight in a vacuum oven. The rubber (31g) was then compounded with 2 p.h.r. dicumylperoxide (D.C.P.; Hercule Chemical Company) on a water cooled 0.3 meter laboratory two-roll open mill using a nip size of 0.038 cm for approximately 5 minutes so that the Rapid Wallace Plasticity number of each stock was 4-5 units (see section 3.3). The nitroxyl radical concentrations in the stocks were measured. The curing characteristics of the stocks were determined on the Monsanto Rheometer at 160°C and thereafter they were cured in the stress relaxation mould for approximately 10 minutes so that the torque on the Monsanto rheograph corresponded to 0.32 m.kg. respectively. This value was chosen becase when the procedure was repeated for the rubber samples premilled with TMOP but without extraction



e.s.r. = nitroxyl radical concentration measurement by e.s.r. spectroscopy.

Scheme 6·2

prior to the compounding with the D.C.P. the maximum torque on the Monsanto Rheograph was 0·32 m.kg. (see figure 6·10).

The concentration of nitroxyl radical in the vulcanised rubber was measured again.

Stress relaxation test pieces were cut from the vulcanisates and the continous stress relaxation was measured at 60% strain and 100°C in an air flow of 0·71 m^3 per hour as described in section 3·11. The continous stress relaxation was also measured for peroxide cured samples treated as outlined above but which were extracted for 48 hours after the vulcanisation operation. During the stress relaxation the growth and decay of nitroxyl radicals were monitored by e.s.r. spectroscopy.

The above operations were repeated for rubber samples premilled with the TMOP but without extractions prior to compounding with the D.C.P.

The operations described above are summarised on scheme 6.2

6.A.3.3 Results

Figure 6·9 shows the relative nitroxyl radical consumption

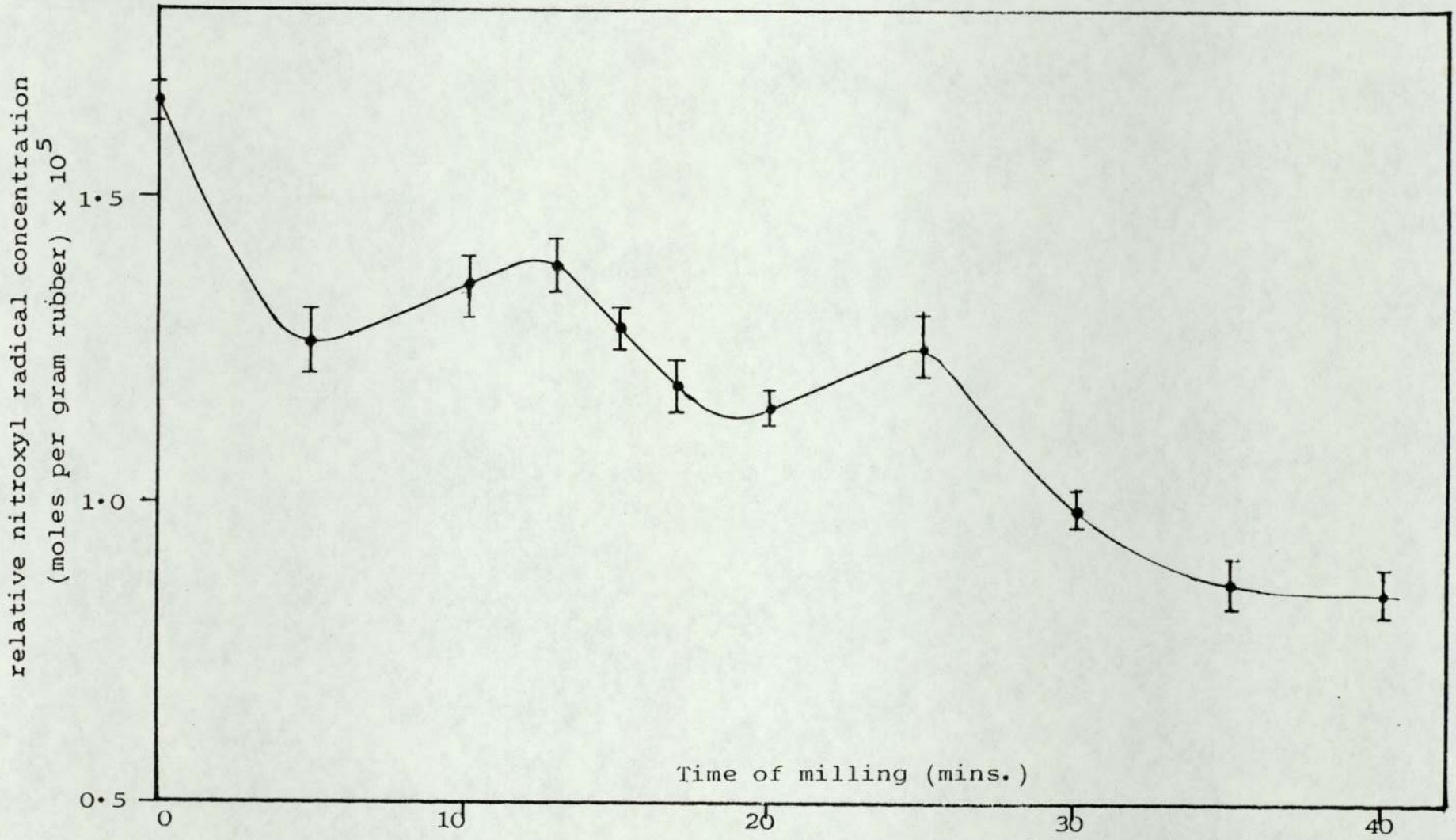


Fig. 6·9: Decay of nitroxyl radical during the milling of TMOP (1 p.h.r.) with rubber in the R.A.P.R.A. Torque Rheometer (closed chamber)

when TMOP is milled with the rubber in the R.A.P.R.A. Torque Rheometer (closed chamber). Table 6·1 shows the relative concentrations of the nitroxyl radical for TMOP milled with the rubber for 5 minutes, 10 minutes and 20 minutes respectively before extraction, after extraction, after compounding with the D.C.P. on the 2-roll open mill, after vulcanisation and the same for the unextracted samples. This table shows that after extraction of the rubber over 95% of the free nitroxyl radical is removed from the rubber samples. It also shows that there is no increase in the nitroxyl radical concentration after the compounding and vulcanisation operations. Infact this table shows that in all cases after vulcanisation the nitroxyl radical concentration was very much less than before vulcanisation by almost a factor of 10.

Figure 6·10 and table 6·2 show the curing charactertistics during the vulcanisation of these stocks. It is clear that for the stocks containing the rubber which were unextracted prior to the compounding the vulcanisation rate and cure rate are retarded significantly. However for the rubber which was extracted prior to the compounding no retardation of cure was observed.

Premill time (min.)	Stage	Relative $[R_2NO\cdot]$ moles/g rubber x 10	Percent $R_2NO\cdot$ left in the rubber relative to that put in
0	1 p.h.r TMOP swelled into the rubber	16·8	-
5	a	12·60	75·0
	b	1·15	6·8
	c	1·07	6·4
	d	0·08	0·5
	e	11·02	66·0
	f	2·02	12·0
10	a	13·40	79·8
	b	0·80	4·8
	c	0·60	3·6
	d	0·06	0·4
	e	10·10	60·1
	f	2·05	12·2
20	a	11·40	67·8
	b	0·78	4·6
	c	0·71	4·2
	d	0·08	0·5
	e	8·96	53·3
	f	1·60	9·5

notation:
a = after premilling
b = after premilling and extraction
c = after premilling, extraction and compounding
d = after premilling, extraction and vulcanisation
e = after compounding without prior extraction
f = after vulcanisation without prior extraction

Table 6·1: Table showing the nitroxyl radical concentration after premilling TMOP into the rubber at the various stages described in the notation.

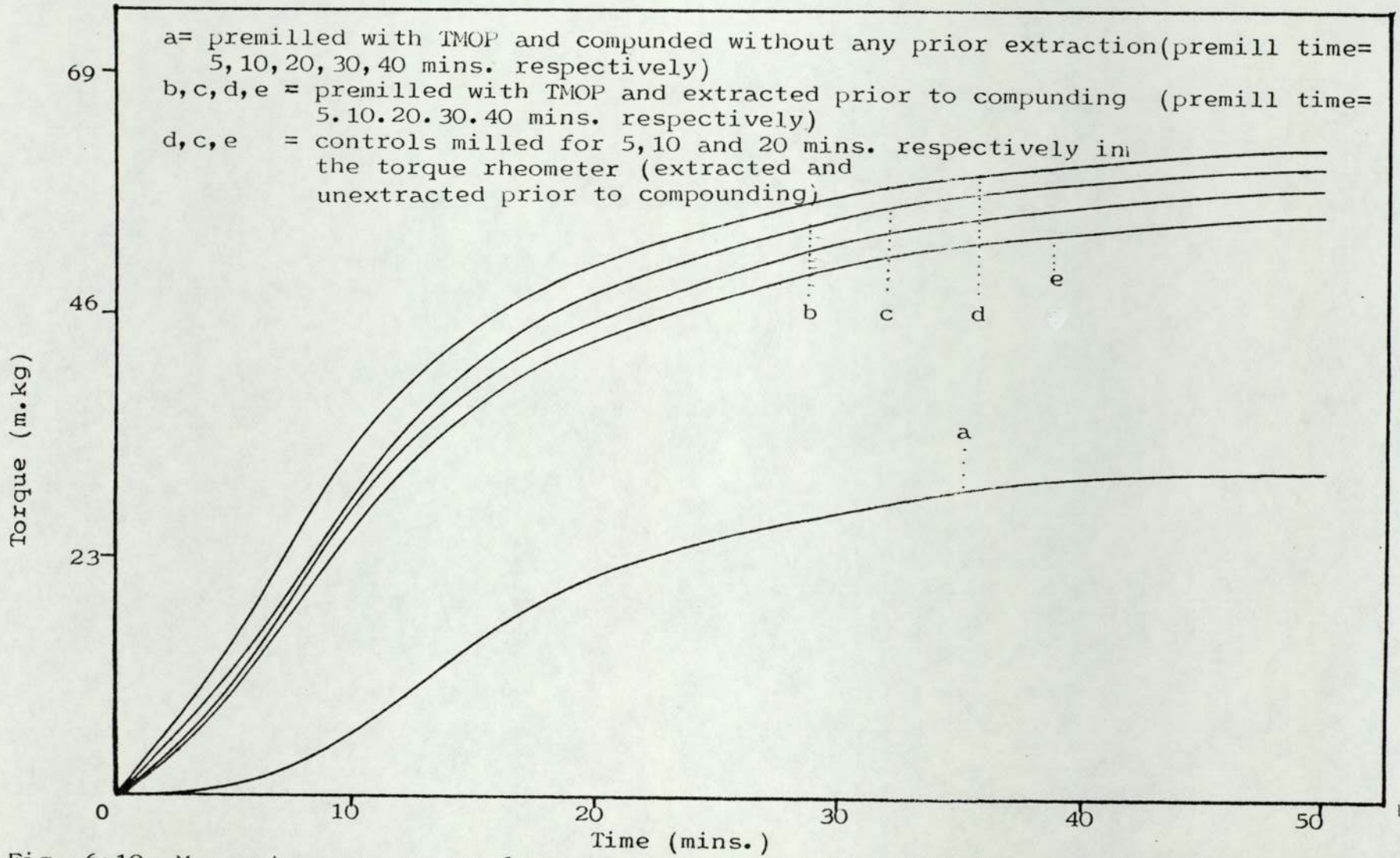


Fig. 6·10: Monsanto cure curves for rubber premilled with TMOP (1 p.h.r.) in the R.A.P.R.A. torque rheometer closed chamber and cured with D.C.P.(2 p.h.r.) at 160°C

	extracted prior to compounding				unextracted prior to compounding			
Additive and time of premill	Scorch time (min.)	1st order cross-link rate k_i ($min.^{-1}$)	rate of vulcanisation (from rheograph) ($m.kg.min.^{-1}$)	Torque at 40 minutes cure (m.kg.)	Scorch time (min.)	1st order cross-link rate k_i ($min.^{-1}$)	rate of vulcanisation (from rheograph) ($m.kg.min.^{-1}$)	Torque at 40 minutes cure (m.kg.)
Control 5 min.	same as for unextracted				3·0	0·12	0·19	0·60
10 min.					3·0	0·11	0·18	0·55
20 min.					3·0	0·12	0·19	0·58
TMOP								
5 min.	3·0	0·11	0·19	0.59	8·0	0·09	0·09	0·32
10 min.	3·0	0·11	0·18	0.56	8·0	0·09	0·09	0·32
20 min.	3·5	0·11	0·19	0.55	8·0	0·09	0·09	0·32
30 min.	3·0	0·11	0·19	0.59	8·0	0·09	0·09	0·32
40 min.	3·5	0·12	0·18	0.60	8·0	0·09	0·09	0·32
Average control	3·0	0·11	0·19	0.58	3·0	0·11	0·19	0·58
Average TMOP	3·0	0·11	0·19	0.58	8·0	0·09	0·09	0·32

Table 6·2: The curing characteristics for rubber premilled with TMOP (1phr) in the R.A.P.R.A Torque rheometer (closed chamber) and compounded with D.C.P. on a 2-roll open mill with and without extraction prior to compounding.

Tables 6·3 and 6·4 show the time to τ_{50} for the vulcanisates containing rubber unextracted prior to compounding and extracted prior to compounding respectively. They also show the τ_{50} times for the vulcanisates before and after extraction. Figures 6·11 (a) and (b) and 6·12 (a) and (b) show the respective stress relaxation curves. It is clear that for the vulcanisates containing the rubber without prior extraction before compounding, the τ_{50} time increases with time of milling. Extraction of the vulcanisates decreases the antioxidant efficiency but does not eliminate it (table 6·3). It is also clear from table 6·4 and figure 6·12 that the τ_{50} values for the vulcanisates containing the rubber which had been extracted prior to compounding do not show any significant difference for the increasing time of premilling of the TMOP either before or after extraction of the vulcanisates. Relative to the controls however they are slightly more efficient since the latter break before or at the time to τ_{50}. The extracted vulcanisates also show a slightly longer time to τ_{50} than the unextracted vulcanisates.

Table 6·5 and figure 6·13 show the nitroxyl radical growth present during the stress relaxation of the rubber which was extracted after the premilling operation, vulcanised for 10 minutes and stress-relaxed. The table and figure also show the relative nitroxyl radical

Milling time of TMOP with the rubber (min.)	Time to τ_{50} (hrs.) Temperatures = 100 $\pm$ 2°C; Strain = 60%	
	Unextracted vulcanisate	extracted vulcanisate
Control	1·5 *	2·3 #
10	2·7	1·5
20	3·5	2·5
30	5·4	3·8

* broken before time to τ_{50}; # broken at τ_{50}

Table 6·3: Time to τ_{50} during the continous stress relaxation of peroxide cured rubber containing TMOP [1 p.h.r.] premilled into the rubber.

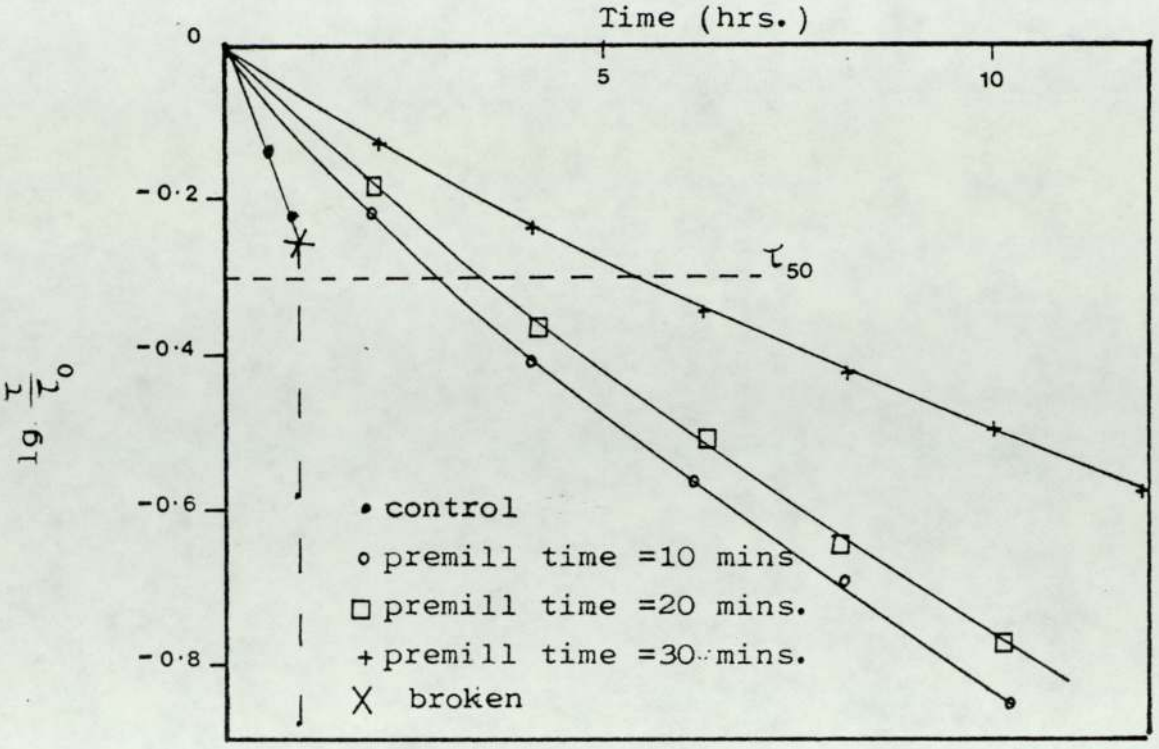


Fig. 6·11 (a): unextracted vulcanisates

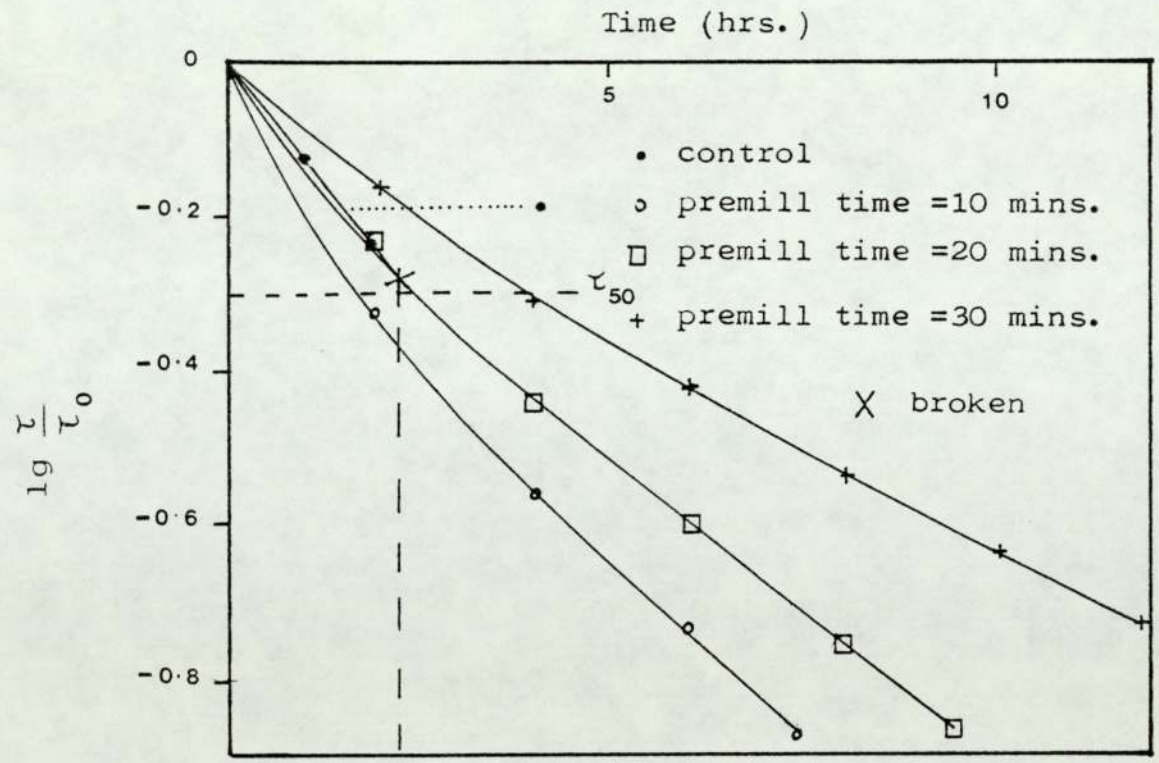


Fig. 6·11 (b): extracted vulcanisates

Fig. 6·11: Continous stress relaxation of peroxide cured vulcanisates made from rubber premilled with TMOP (1 p.h.r.) prior to compounding

Milling time of TMOP with the rubber (min.)	Time to τ_{50} (hrs.) Temperature = 100 ± 2°C; strain = 60%	
	unextracted vulcanisate	extracted vulcanisate
Control	1·5 *	2·0 *
10	1·6	2·3
20	1·5	2·3
30	1·4	2·3

* broken before τ_{50}

Table 6·4: Time to τ_{50} during the continous stress relaxation of peroxide cured vulcanisates containing TMOP [1 p.h.r.] premilled into the rubber and extracted prior to compounding.

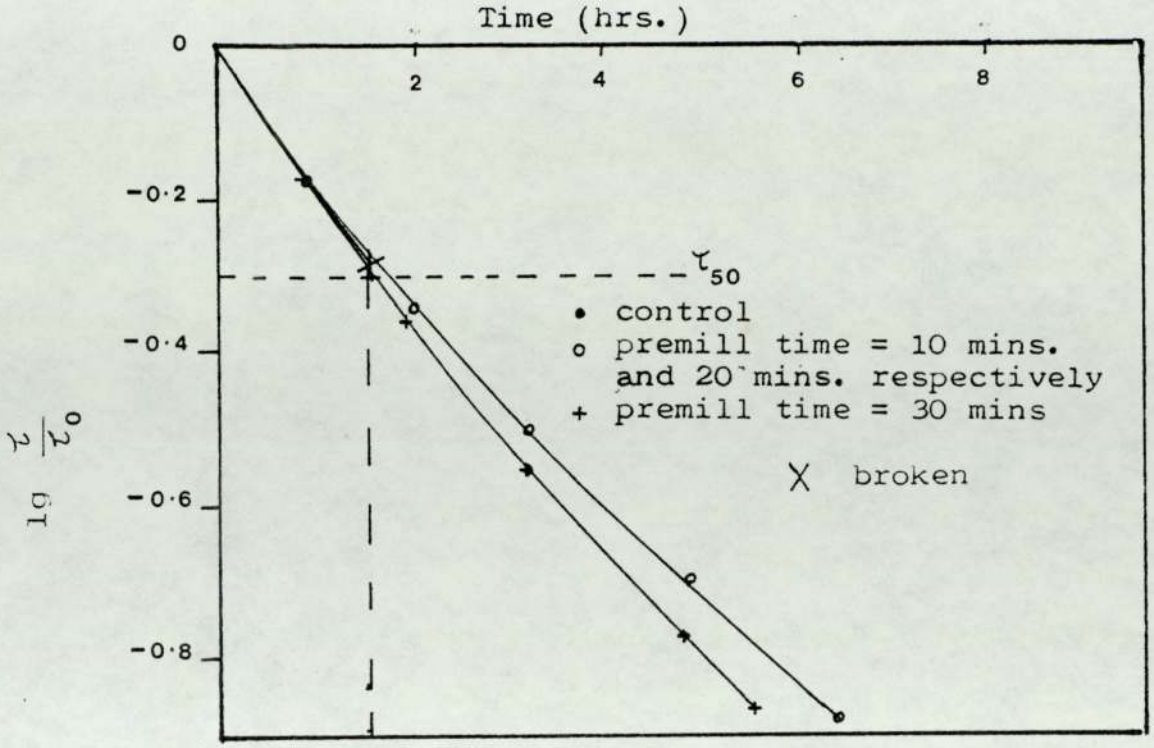


Fig. 6·12 (a): unextracted vulcanisates

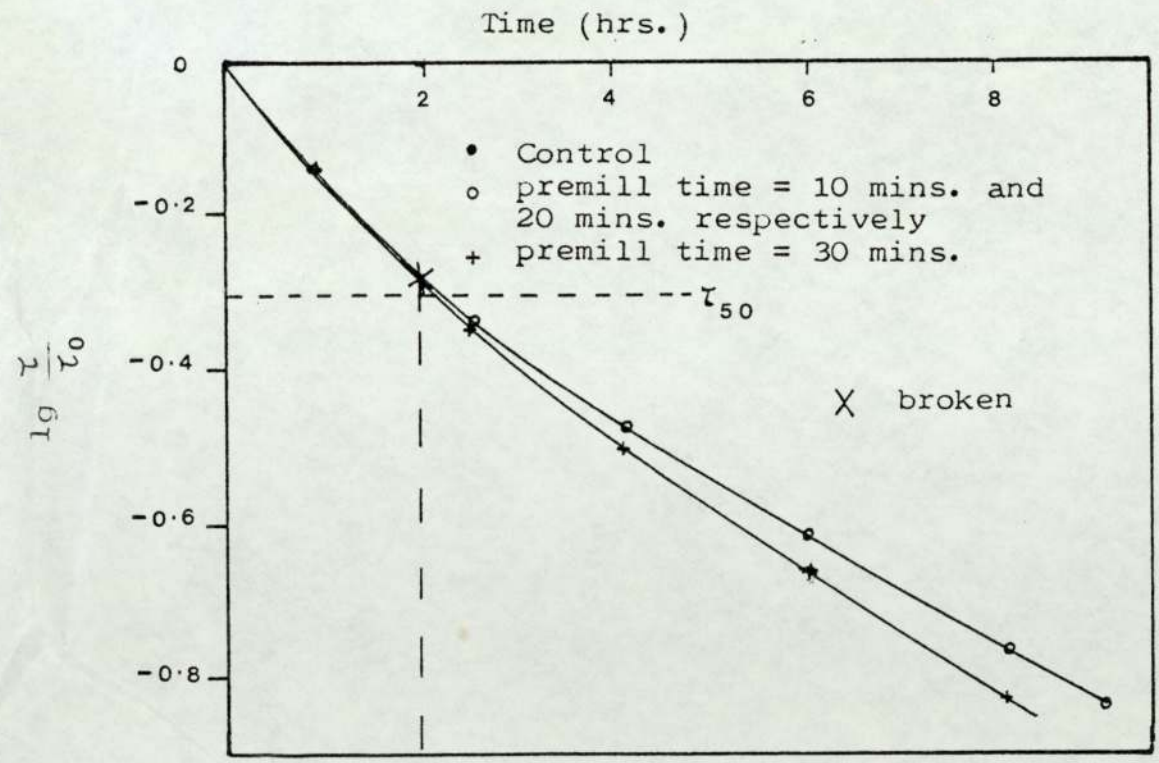


Fig. 6·12 (b): extracted vulcanisates

Fig. 6·12: Continous stress relaxation of peroxide cured vulcanisates made from rubber premilled with TMOP (1 p.h.r.) and extracted prior to compounding

Premill time (min.)	Stage	Time of stress-relaxation (hrs.)	relative ($R_2NO\cdot$) moles/g rubber x 10^6 $\pm$ 0·06	percent $R_2NO\cdot$ relative to that at 0-milling time
0	1 p.h.r. $R_2NO\cdot$ swelled into rubber	-	16·8	-
10	a	0	0·06*	0·4
		½	0·54	3·2
		1	0·96	5·7
		2	0·63	3·7
		3	0·30	1·8
		4	0·15	0·9
20	a	0	0.08*	0·5
		½	0·98	5·8
		1	1·51	8·9
		2	1·05	6·2
		3	0·63	3·8
		4	0·36	2·2

Notation: * $\pm$ 0·006

(a) = 1 p.h.r. TMOP premilled into the rubber (closed chamber) extracted; peroxide cured for 10 minutes; stress relaxed at 100 $\pm$ 2°C and 60% strain.

Table 6·5: Table showing the growth and decay of nitroxyl radical during stress-relaxation of rubber treated as described in notation (a).

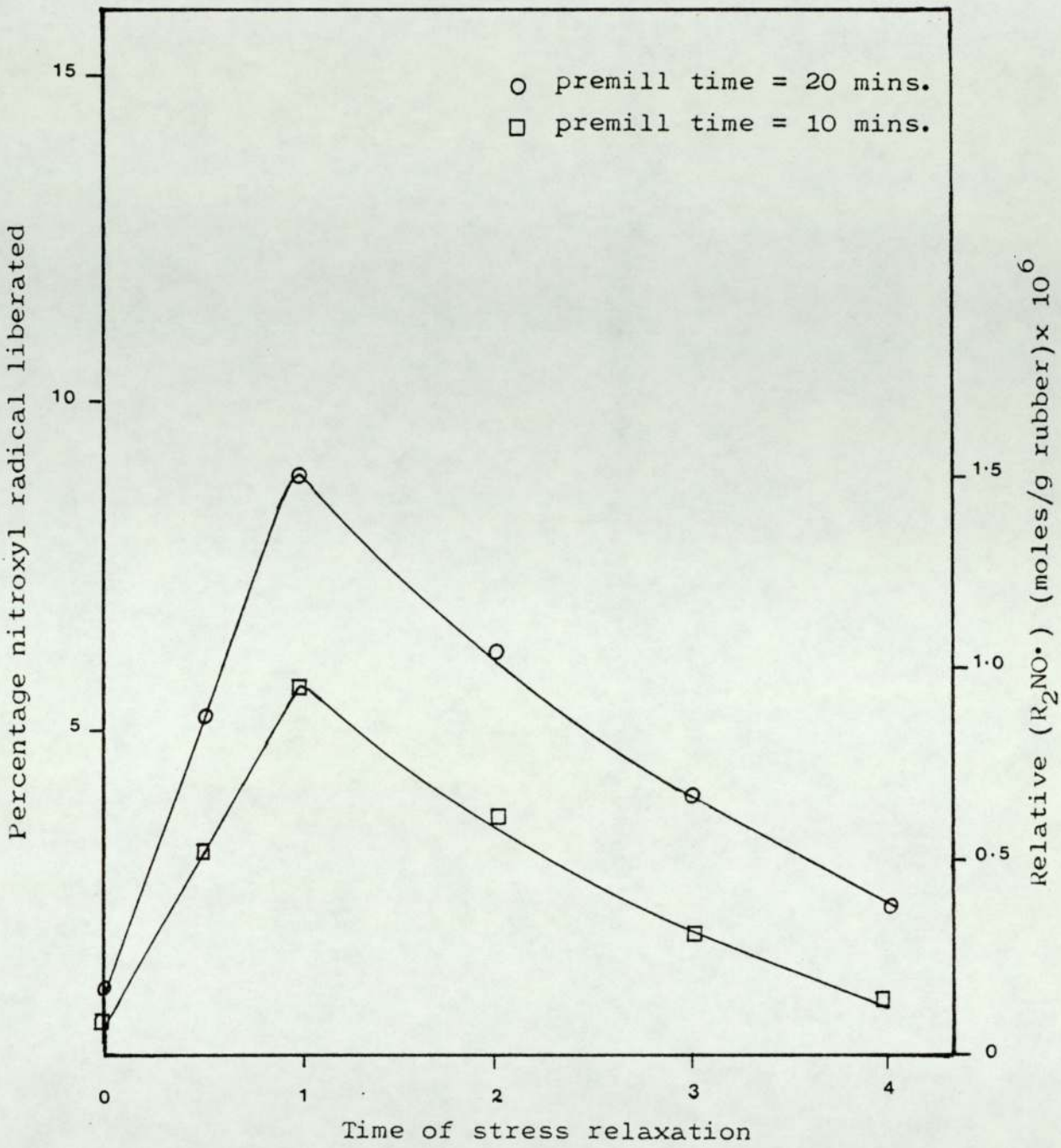


Fig. 6·13: Percentage growth and decay of nitroxyl radical during the stress relaxation of peroxide cured vulcanisates made from rubber premilled with TMOP (1 p.h.r.), extracted, vulcanised with 2 p.h.r. D.C.P. for 10 mins. and extracted again

concentrations. It is clear from this data that after extraction and vulcanisation of the rubber premilled with the TMOP for 20 minutes the percent nitroxyl radical was 0·5%. However during the stress-relaxation, within one hour almost 9%, of the 1 p.h.r. TMOP initially mixed in with the rubber is produced. This nitroxyl radical then decays slowly with time as shown on figure 6.13. For the 10 minute premilled rubber too, which had been treated similarly the nitroxyl radical concentration builds up to about 5·5% before decaying. Some sailent data from tables 6·1 and 6·5 which will be useful in the subsquent discussion are summarised in table 6·6.

6.A.3.4 Discussion

During the milling of the TMOP with the rubber in the R.A.P.R.A. torque rheometer (closed chamber) it was shown that the nitroxyl radical concentration decayed (figure 6·9). The consumption of nitroxyl radical is due to its interaction with the macro-alkyl (alkenyl) radicals produced during the shearing of the rubber. Shearing in the "closed chamber conditions" gives a high rate of alkyl radicals to alkylperoxyl radicals because of the high rates of radical initiation and low availability of oxygen in the system. These alkyl radicals being terminal radicals, have a very high activity[34] and will react with the

Time of premilling (min.)	Stage	Percent nitroxyl radical left in the rubber relative to the 1 p.h.r. TMOP initially mixed into the rubber. (%)
20	a	67·8
	b	4·6
	c	0·5
	d	8·9 *
10	a	79·8
	b	4·8
	c	0·4
	d	5·7 *

Notations:

(a) = 1 p.h.r. TMOP premilled into rubber (closed chamber)

(b) = a + extract

(c) = a + b + peroxide vulcanise for approximately 10 minutes.

(d) = a + b + c + stress relax.

* = maximum nitroxyl radical formed during stress relaxation

Table 6·6: Percent nitroxyl radical in the rubber at the various stages described in the notation.

nitroxyl radicals. The alternating increase and decrease of the nitroxyl radical concentration during its consumption must be due to its regeneration. The first maximum peak (figure 6·9) could be due to regeneration of the nitroxyl radical from free hydroxylamine (as intermediate), owing to the effect of the alkylperoxyl radicals. The second maximum peak (figure 6·9) is probably due to oxidation[200,201] of the hydroxylamine by hydroperoxides formed in the rubber during the extensive milling of 20 to 25 minutes, leading to regeneration of the nitroxyl radical. Bagheri[200] too reports similar results when nitroxyl radical is processed with polypropylene at 180°C, but over a shorter time scale.

Table 6·1 shows that exhaustive hot acetone extraction of the rubber milled with TMOP in the R.A.P.R.A. torque rheometer (closed chamber) removes over 95% of the free nitroxyl radical from the system. Presumably during this extraction free hydroxylamine (TMPD) and other and acetone soluble products such as the amine formed from the TMOP during the milling process would have been extracted as well. Only the rubber grafted nitroxyl ($R_2NO-R'.$; O-alkylated hydroxylamine) would have been left in the rubber. After compounding with the D.C.P. and vulcanisation no increase in nitroxyl radical concentration was observed.

Figure 6·10 and table 6·2 show that when the rubber is vulcanised without extraction prior to compounding, the rate of peroxide vulcanisation was significantly retarded. When the rubber is extracted prior to the compounding operation however, there was no retardation of the cure. During the peroxide cure the D.C.P. dissociates to peroxyl radicals which initiate alkyl radical formation in the rubber by hydrogen abstraction reactions[169]. Termination of these alkyl radicals by combination reactions gives rise to the cross-linked network[169]. In the presence of TMOP some of the macro-alkyl radicals will be scavenged since the nitroxyl radical would compete with the normal termination reactions of the alkyl radicals. This is probably why the cure is retarded. However after extraction prior to compounding no retardation of cure was observed. This was probably because almost all the free nitroxyl radical and its precursors were removed from the system by extraction. This result suggests that the rubber-grafted nitroxyl (R_2NO-R' ; O-alkylated species) is not present in the rubber to a significant extent. If it were, it would be unextractable and should have produced nitroxyl radicals during the compounding and vulcanisation stages which would have interfered with the cure. Infact table 6·1 shows that upon vulcanisation the traces

of the nitroxyl radical remaining in the rubber after extraction decreased by a factor of ten. Presumably the 4% or so of nitroxyl left after extraction would have interacted with the vulcanisation reactions, but no significant interference with the cure was observed because the amount of nitroxyl radical was very small.

After the vulcanisation stress relaxation of the vulcanisates, made from the rubber which was extracted after the premilling stage, showed no difference for the various times of milling (figure 6·12). Table 6·4 which shows the τ_{50} times for these vulcanisates highlights this point. Actually this result is not unexpected since the majority of the species left in the rubber after extraction would have been the rubber-grafted nitroxyl (R_2N-O-R; O-alkylated hydroxylamines) and although these O-alkylated species are known[135,201] to react with hydroperoxides and peroxyl radicals to generate nitroxyl radicals (equations 6·1 - 6·3) they do not exhibit any significant antioxidant properties[135]

$$R_2NO\text{-}R' + R''OOH \longrightarrow R_2NO\cdot + \text{Products} \qquad \text{(Eq 6·1)}$$

$$R_2NO\text{-}R' + R''OO\cdot \longrightarrow R_2NO\cdot + R'OOR'' \qquad \text{(Eq 6·2)}$$

$$R_2NO\text{-}R' + R''OO\cdot \longrightarrow R_2NO\cdot + R'(-H) + R''OOH \qquad \text{(Eq 6·3)}$$

Nitroxyl radicals themselves are not thermal stabilisers[210] although they are known to associate with hydroperoxides[210] (equation 6·4)

$$R_2NO\cdot + ROOH \longrightarrow R_2NO\cdot\text{------}HOOR \qquad \text{(Eq 6·4)}$$

However relative to the control (figure 6·12) the vulcanisates produced from the rubber that were milled with the TMOP and extracted prior to compounding, did have some oxidation resistance. During the test, the control broke ("melted") after two hours of continous stress relaxation, but the others continued to stress-relax longer. The difference between the control and these other vulcanisates must be due to traces of hydroxyl-amine and nitroxyl radical left in the systems after extraction, or alternately to the presence of the unextractable rubber-grafted nitroxyl species.

The e.s.r. study of the relative nitroxyl radical concentration produced during the stress relaxation for the vulcanisate made up from the rubber milled with the TMOP for 20 minutes and then extracted showed that a maximum concentration corresponding to 9% of the original 1 p.h.r. of TMOP that was milled into the rubber was formed during the stress relaxation (figure 6·13; tables 6·5 and 6·6). Taking into account the 4% of nitroxyl

radical concentration left in the rubber after extraction (tables 6·6 and 6·1) this corresponds to approximately 5% of nitroxyl radical that must have been produced from the rubber-grafted nitroxyl species (R_2NO-R'; O-alkylated hydroxylamine). The nitroxyl radical may be produced readily by interaction of the O-alkylated hydroxylamine with alkylperoxyl radicals and hydroperoxides (equation 5·1-5·3) during the stress-relaxation test at the elevated temperature. Certainly there would still have been a lot of excess unreacted D.C.P. in the vulcanisate due to the fact that they were only cured for 10 minutes to a torque of 0·32 m.kg on the Monsanto rheograph. For optimum cure the vulcanisation time is usually 40-45 minutes and the torque achieved is 0·58 m.kg.. Therefore the unreacted D.C.P. would have most certainly given rise to alkylperoxyl radicals and hydroperoxides during the stress-relaxation test, especially since the ageing was done at 100 $\pm$ 2°C.

For the rubber that was milled with the TMOP for ten minutes (closed chamber) the nitroxyl radical concentration formed during the stress-relaxation was a maximum of about 6% Taking into account the relative amount of TMOP left after extraction of the premilled rubber, this corresponds to only about 1-2% of rubber-grafted nitroxyl species in the system (table 6·6).

These results suggest that even after extended premilling (20 minutes) of the 1 p.h.r. TMOP originally mixed into the rubber only about 5%, (i.e: 0·05 p.h.r) of O-alkylated hydroxylamine is formed in the system. As this quantity is so very small no perceptable interference with the peroxide vulcanisation would have been observed.

During the vulcanisation process at the elevated temperatures that are involved, some free hydroxylamine could also have been formed by the thermal decomposition of the O-alkylated hydroxylamine as shown in scheme 6·1. This too could have contributed to the albeit slight antioxidant activity that was observed when compared with the control. During the subsequent ageing, nitroxyl radical would have been regenerated from this hydroxylamine. Therefore irrespective of the stage in which the O-alkylated hydroxylamine decomposes the results show that after extended milling of TMOP with the rubber in a closed chamber only about 5% is converted to O-alkylated hydroxylamine.

Figure 6·13 shows that the maximum nitroxyl radical concentration was liberated in the first hour of stress relaxation and longer ageing only decreased this concentration. The decay is probably due to destruction of the nitroxyl radical by the thermal decomposition

products of the hydroperoxides formed in the system[201]. This could happen by the following reactions[205]:

$$ROOH \xrightarrow{\Delta} RO\cdot + OH$$

$$R_2NO\cdot + \cdot OH \longrightarrow R_2NO-OH \longrightarrow R_2\overset{OH}{\underset{|}{N}}=O$$

The stress relaxation of the vulcanisates made up from the rubber that was not extracted after the initial premilling with the TMOP (figure 6·11 (a), and table 6·3) showed increased antioxidant activity for increased milling time. Since it has been shown above that the O-alkylated hydroxylamine is formed in only very low levels in the rubber during the premilling operations the activity must be due to the free hydroxylamine produced during the premilling operations and subsequent vulcanisation. Free hydroxylamines are known to possess[85] antioxidant activity. They can react with alkylperoxyl radicals and hydroperoxides according to equations 6·5 to 6·7.

$$R_2NOH + R'OO\cdot \longrightarrow R_2NO\cdot + R'OOH \qquad \text{(Eq 6·5)}$$

$$R_2NOH + R'OOH \longrightarrow R_2NO\cdot + R'O\cdot + H_2O \qquad \text{(Eq 6·6)}$$

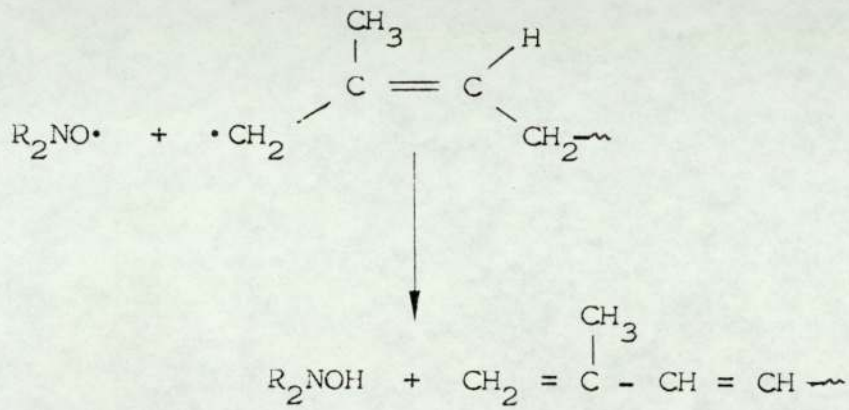
$$R_2NOH + R'O\cdot \longrightarrow R_2NO\cdot + R'OH \qquad \text{(Eq 6·7)}$$

Equation 6·6 is not a chain terminating step. This is probably whey the hydroxylamine is not a very efficient thermal antioxidant.

Extraction of the vulcanisates removes the acetone soluble species but not all since some albeit reduced antioxidant activity is still retained in the rubber (figure 6·11 (b) and table 6·3). This could be due to some hydroxylamine still left in the rubber being trapped in the vulcanised network. The control improves after extraction due to the removal of the unextracted peroxides from the system.

Table 6·6 shows that about 30% of nitroxyl radical which was originally mixed into the rubber is consumed after 20 minutes of premilling. This means that 30% of the nitroxyl radical is in the form of a reduced species of nitroxyl radical. Since it has been shown in the discussion so far that only about 5% of this corresponds to O-alkylated hydroxylamine, the rest must be mainly in the form of the free hydroxylamine. Similar conclusions may be drawn for the 10 minute milling time of TMOP with rubber, although the percent hydroxylamine formed is lower than in the former case. This would account for the increased antioxidant activity with increasing premilling of TMOP with the rubber (figure 6·11).

These conclusions suggest that during the milling of the rubber with the TMOP in a closed chamber in addition to the formation of free hydroxylamine from the O-alkylated species, there must be hydroxylamine formation directly by hydrogen abstraction reactions from the alkyl radicals by the nitroxyl radicals, as suggested by Scott et al[85] i.e:

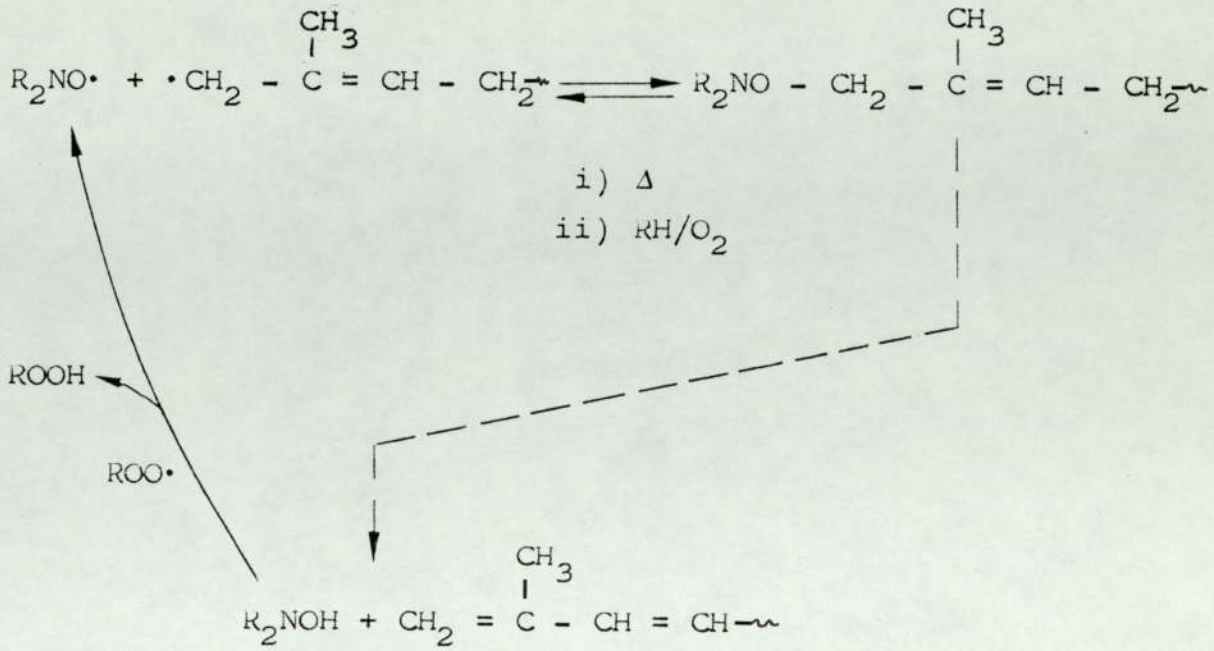


(Eq 6·8)

The conclusions infact complement the findings in the study of TMOP with squalene (section 6·2), namely that stable O-alkylated hydroxylamine species is not formed to a substantial extent during the radical scavenging action of nitroxyl radicals at 110°C. They are also consistent with the reversible formation of the O-alkylated hydroxylamine which was proposed by Scott et al[85].

Therefore taking into account the reversible formation of the O-alkylated hydroxylamine, the regeneration of nitroxyl radical and the formation of hydroxylamine plus conjugated

unsaturation can be represented as outlined in scheme 6·3.



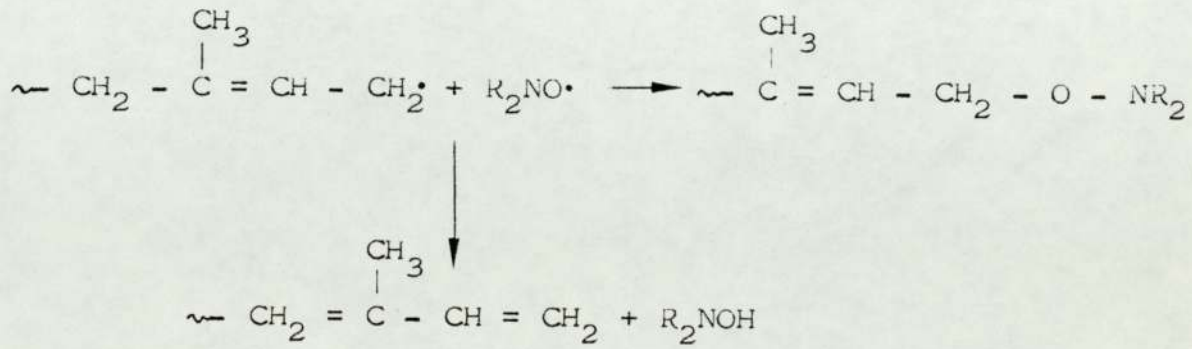
Scheme 6·3

This type of scheme has been proposed for the U.V. stabilisation of polypropylene by hindered nitroxyl radicals[85] and emphasies the central role of the free hydroxylamine in the regeneration cycle. This is probably what happens in the two systems which have been studied in this work as well, and consequently can be extended to the antifatigue activity of these additives too.

Carlsson et al[204] report that model O-alkylated hydroxylamines generate the nitroxyl radical even at relatively mild temperatures of 50-80°C in the presence of air (oxygen)

or hydroperoxide, without the formation of the free hydroxylamine. This too can be explained on the basis of the reversible reaction that has been suggested by Scott et al[85]. Certainly during fatiguing the average internal temperature is well above 50°C[34]. Furthermore traces of hydroperoxides and peroxyl radicals are present in the rubber as well[1]. Therefore disproportionation of the rubber bound hydroxylamine back to the nitroxyl radical would be quite feasible under these conditions. Termination of the alkyl (allyl) radicals produced during the fatiguing would then occur by the mechanism outlined in scheme 6·3.

Another reason why the dissociation reaction of the O-alkylated hydroxylamine will be particularly favoured in the case of the diene rubber is that the alkyl radical formed will be quite stable and the hydrogen abstraction process will be preferred due to diene conjugation.



6.B A STUDY OF THE ANTIFATIGUE MECHANISM OF THE NITRONES.

In chapter 5 it was shown that N-alkyl aldonitrones, particularly those containing phenolic antioxidant functions were effective antifatigue agents for rubber. In view of this result it was relevant to study the mechanism of the antifatigue action of the nitrones. Not only are the nitrones capable of trapping alkyl radicals to generate the nitroxyl radical, they are also capable of binding to the rubber by 1,3-addition reactions across the double bonds in the rubber[99]. The contributory role played by the nitroxyl radicals and the 1,3-addition reaction towards the overall antifatigue mechanism of the nitrones will be assessed. For this purpose the following tests were done.

a) A study of the amount of nitrone bound to the rubber during vulcanisation

b) An e.s.r. study of the growth and fate of the nitroxyl radical derived from the nitrone during the fatiguing operations.

c) An e.s.r. study on the growth and fate of nitroxyl radicals from the nitrone; a torque-time study; a gel content study; the number average molecular weight

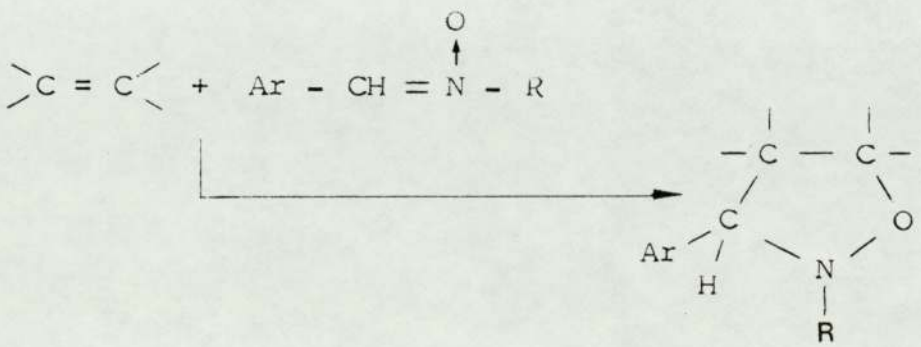
study on the rubber; and molecular weight distribution studies on the rubber by gel permeation chromatography for the effect on the nitrone on rubber in simulated fatigue studies. (i.e. during the milling of the nitrone with the rubber in the R.A.P.R.A. torque rheometer (closed chamber)).

For all these studies except for (a) MHPBN was used as a typical nitrone with good antifatigue activity. The nitrone was always used at a level of 1 p.h.r.. For (a) MHPBN, MHPPN, MHPEN and MHPMN were all used respectively.

6.B.1 A STUDY OF THE AMOUNT OF NITRONE BOUND TO THE RUBBER DURING VULCANISATION

6.B.1.1 Introduction

Nitrones are known to add across double bonds in unsaturated compounds to give 5-membered isoxazolidines[91].



Scott et al[99] have made use of this reaction efficiently to bind several N-aryl nitrones into rubber. Vulcanisation of synthetic rubber too, by bis N-phenyl nitrones has been reported to be quite efficient[193]. N-methyl nitrones however were found not to bind into the rubber to any significant extent[99]. It was therefore of interest to see whether the other N-alkyl nitrones too (MHPBN, MHPPN, and MHPEN) behaved in a similar manner.

6.B.1.2 Experimental Procedure

MHPBN, MHPPN, MHPEN and MHPMN were respectively premilled with extracted rubber for 2 minutes prior to compounding as described in section 5·2. The compounded stocks were vulcanised for half hour each, using the infrared mould as described in section 3·5·3. The vulcanised sheets of thickness 0·020 cm. were mounted on special frames, and the extent of binding was evaluated by infrared analysis before and after extraction with hot acetone (section 3·13).

Attempts to see changes in the spectra of the nitrones before and after extraction in the natural rubber vulcanisates were unsuccessful. The band that was being followed was the aromatic stretch of nitrones at 1590 cm^{-1}[99] and this was masked by the strong absorption of natural rubber peaks in this region.

In order to overcome this problem extracted synthetic cis-polyisoprene (Natsyn 2200) was used together with 2 p.h.r. of the nitrone. The rubber was vulcanised for half an hour at 150°C and infrared spectra were recorded before and after extraction with acetone. The extent of binding was measured by measuring the decrease in the absorbance of the band at 1590 cm^{-1}, and making appropriate callibration curves for the rubber made up with different levels of nitrone.

6.B.1.3 Results

In all cases no significant (measurable level) of binding was achieved during the vulcanisation. Table 6·7 summarises the results.

NITRONE	Percent ANTIOXIDANT LEFT IN RUBBER AFTER EXTRACTION *
MHPMN	Not measurable
MHPEN	Not measurable
MHPPN	Not measurable
MHPBN	Not measurable

* Measured by means of the aromatic absorption in the infrared spectrum at 1590 cm^{-1} after extraction.

Table 6·7: Percent nitrone bound to cis-polyisoprene vulcanisate during vulcanisation

6.B.1.4 Discussion

These results conform to the observations made by Scott et al[99] that N-alkyl nitrones do not bind to the rubbers. The lack of significant 1,3-addition reactions by these compounds may be associated with steric and/or electronic effects around the N → O function of the nitrones.

Since no detectable quantities of bound adduct was present in the rubber after extraction it may be concluded that the 1,3-addition reaction of the nitrones to the double bonds in the rubber does not contribute significantly to the overall antifatigue activity of the N-alkyl nitrones.

6.B.2 A STUDY OF THE GROWTH OF NITROXYL RADICALS FROM MHPBN DURING THE FATIGUING OF RUBBER

6.B.2.1 Introduction

It was shown in table 5·13 that the relative nitroxyl radical concentration doubles when the rubber containing MHPBN is fatigued to faliure and that the relative concentration is more or less the same irrespective of the time of premilling of the nitrone with the rubber.

The present study was made in order to establish the contributory role of the nitroxyl radicals formed from the nitrone (MHPBN) during the fatiguing process.

6.B.2.2 Experimental Procedure

Rubber vulcanised with 1 p.h.r. of MHPBN premilled for two minutes with the rubber prior to compounding on the 2-roll open mill (section 5·4·2), was fatigued. At various time intervals during the fatiguing of the rubber samples were removed and the nitroxyl radical concentration was measured using the J.E.O.L - e.s.r. spectrometer as described in section 3·19.

6.B.2.3 Results

The growth of nitroxyl radical from MHPBN is shown in figure 6·14 (a). Figure 6·14 (b) shows the relative increase in the intensity of the spectrum as the fatiguing progresses, measured under identical instrument settings. The growth appears to be auto-retarding.

The implications of this result will be discussed in section 6.B.4.

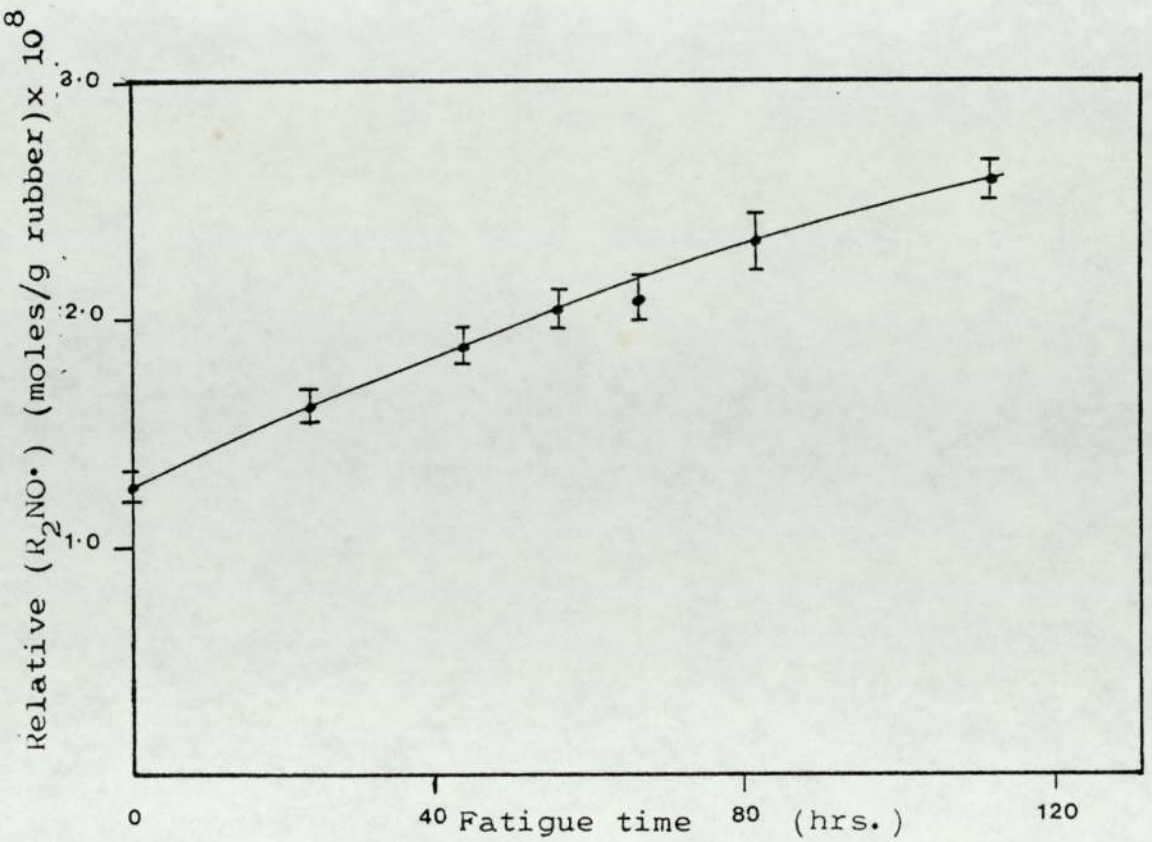


Fig. 6·14 (a): The growth of nitroxyl radical from MHPBN (1 p.h.r.; premilled with rubber for 2 mins.) during the fatiguing of a conventional C.B.S. vulcanisate

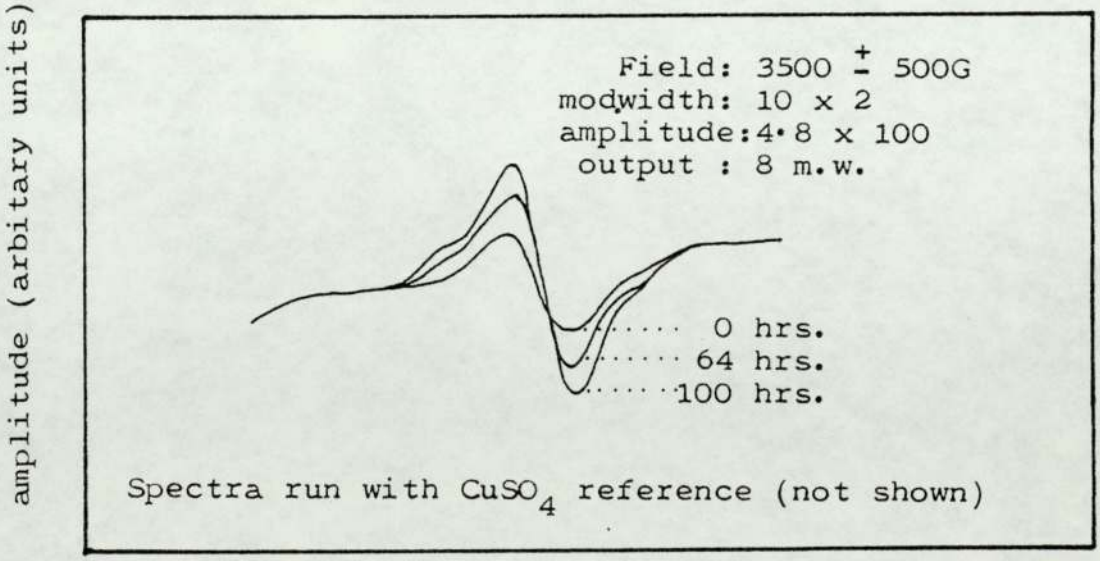


Fig. 6·14 (b): Increase in the intensity of the nitroxyl radical spectrum during the fatiguing of MHPBN (1 p.h.r)

6.B.3 THE STUDY OF THE EFFECT OF MHPBN ON THE RUBBER DURING MECHANOCHEMICAL TREATMENT IN THE TORQUE RHEOMETER

The R.A.P.R.A. torque rheometer was used to provide the simulated fatigue conditions. The similarity of the conditions prevailing during the milling of rubber in the R.A.P.R.A. torque rheometer (closed chamber) and the fatiguing of rubber has been described well in section 6·A·3. MHPBN was used as a typical nitrone for the following studies.

6.B.3.1 MEASUREMENT OF NITROXYL RADICAL GROWTH DURING THE MILLING OF MHPBN WITH RUBBER (CLOSED CHAMBER)

MHPBN (1 p.h.r.) was milled into the rubber in the R.A.P.R.A. torque rheometer (closed chamber) using the same technique outlined in section 6·A·3·2·
E.s.r. spectra were recorded for various times of milling as described in section 3.19.2.2.

Results

The growth of the relative nitroxyl radical concentration from MHPBN during the milling with rubber in the closed chamber is shown in figure 6·15 (a). Figure 6·15 (b) shows the increase in the intensity of the e.s.r. spectra for the same under identical instrumentation settings.

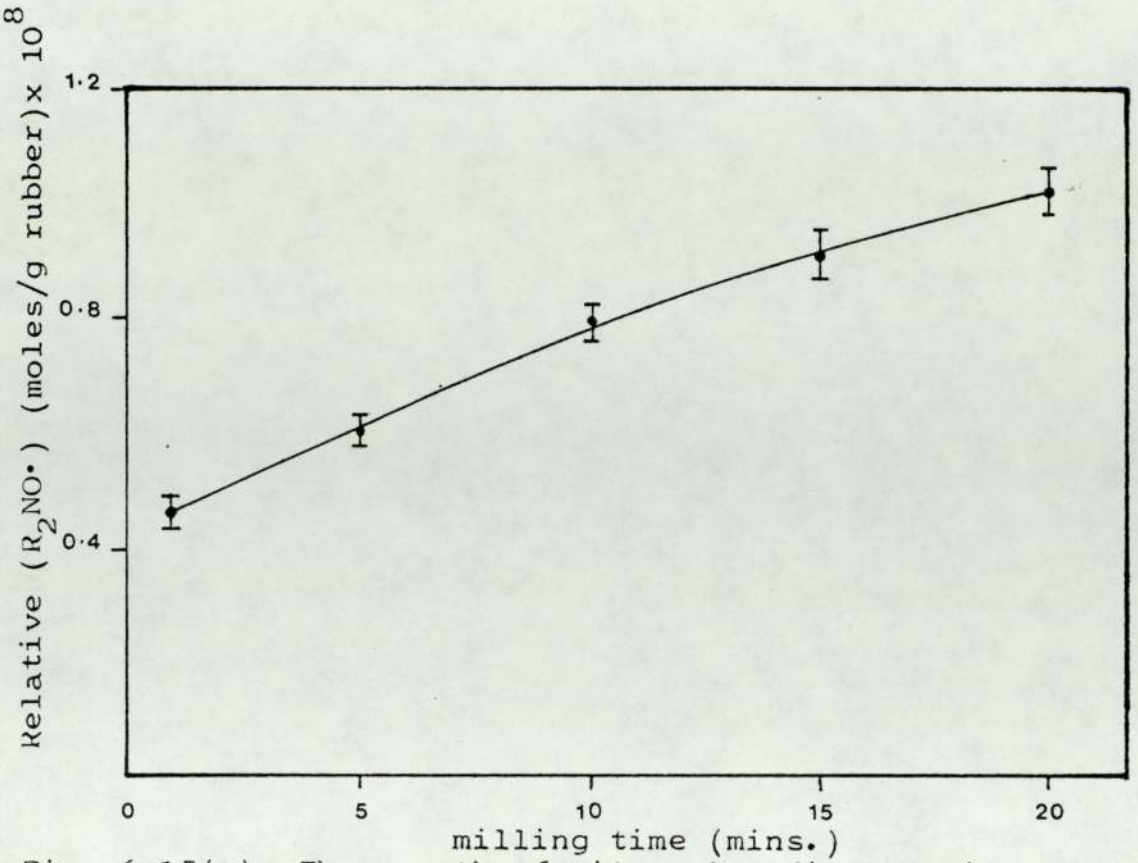


Fig. 6·15(a): The growth of nitroxyl radical during the milling of MHPBN (1 p.h.r.) with rubber in the R.A.P.R.A. torque rheometer (closed chamber)

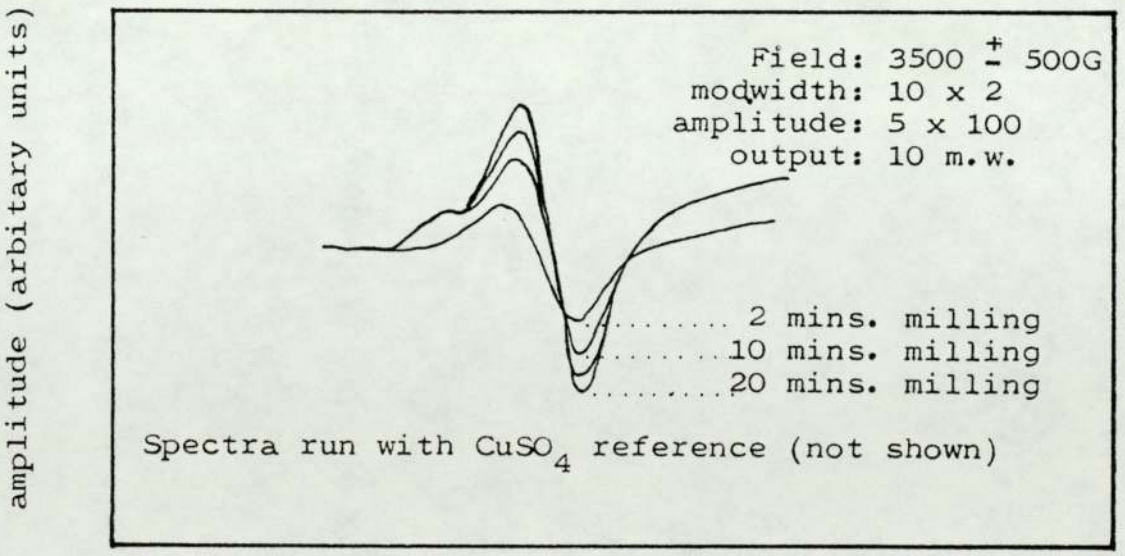


Fig. 6·15(b): Increase in the intensity of the nitroxyl radical spectrum during the milling of rubber with MHPBN (1 p.h.r.) in the R.A.P.R.A. torque rheometer (closed chamber)

6.B.3.2 MEASUREMENT OF TORQUE DURING THE MILLING OF MHPBN WITH THE RUBBER (CLOSED CHAMBER)

MHPBN (1 p.h.r.) was milled with rubber using the conditions described in section 6·B·3·1. The torque experienced by the rotors during the shearing was recorded automatically on a separate chart-recorder as described in section 3·14 and 3·15.

Results

The torque time curves were treated as described in section 3.15. Figure 6·16 shows the decrease in torque with milling time for the rubber with the nitrone and for the rubber without the nitrone (control). The implications of this result will be discussed in section 6.B.4.

6.B.3.3 MEASUREMENT OF GEL FORMATION DURING THE MILLING OF MHPBN WITH THE RUBBER (CLOSED CHAMBER)

MHPBN (1 p.h.r.) was milled into the rubber as described in section 6.B.3.1. Gel content studies were made on the rubber with and without nitrone in the manner described in section 3·16.

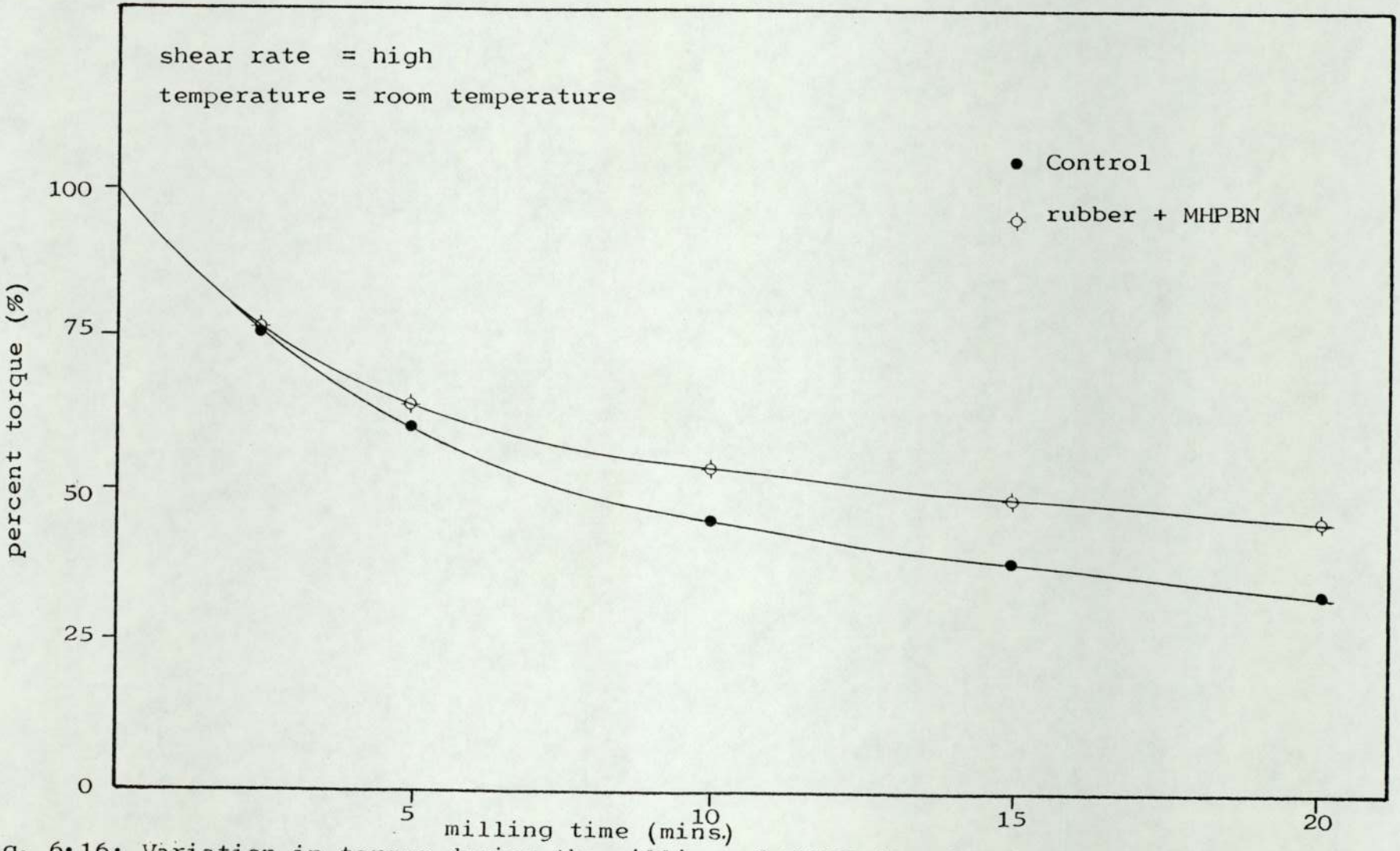


Fig. 6·16: Variation in torque during the milling of MHPBN (1 p.h.r.) with rubber in the R.A.P.R.A. torque rheometer (closed chamber)

Results

No gel formation was observed in the rubber either for the control or for the rubber with the nitrone. Table 6·8 shows typical experimental results for the measurement of gel content.

The implications of this result will be discussed in section 6.B.4.

6.B.3.4 MOLECULAR WEIGHT MEASUREMENTS FROM VISCOSITY STUDIES FOR RUBBER MILLED WITH AND WITHOUT MHPBN (CLOSED CHAMBER)

MHPBN (1 p.h.r.) was milled in the R.A.P.R.A. torque rheometer (closed chamber) as described in section 6.B.3.1. The decrease in the number averaged molecular weight ($\bar{M}n$) was measured from viscosity studies and was obtained by the procedure described in section 3·17.

Results

Figure 6·17 shows the decrease in the number average molecular weight ($\bar{M}n$) for the rubber with and without MHPBN. It is clear that for the rubber containing the

Rubber without nitrone (control)

MILLING TIME (min.)	a (g.)	b (g.)	c (g.)	d (g.)
2	1·00	2·47	1·47	0·00
5	1·00	2·23	1·23	0·00
10	1·00	2·43	1·43	0·00
15	1·00	2·70	1·70	0·00
20	1·00	2·91	1·91	0·00

Rubber with MHPBN

MILLING TIME (min.)	a (g.)	b (g.)	c (g.)	d (g.)
2	1·00	2·38	1·38	0·00
5	1·00	2·21	1·20	0·01
10	1·00	2·54	1·54	0·00
15	1·00	2·92	1·92	0·00
20	1·00	2·19	1·19	0·00

Notation

a = weight of rubber used.

b = weight of rubber + lens tissue wrapping + wire wrapping before dissolution

c = b after dissolution in toluene

d = weight of rubber left inside the lens tissue wrapping after dissolution = weight of gel formed.

Table 6·8: Typical experimental results for measurement of gel formation in the rubber.

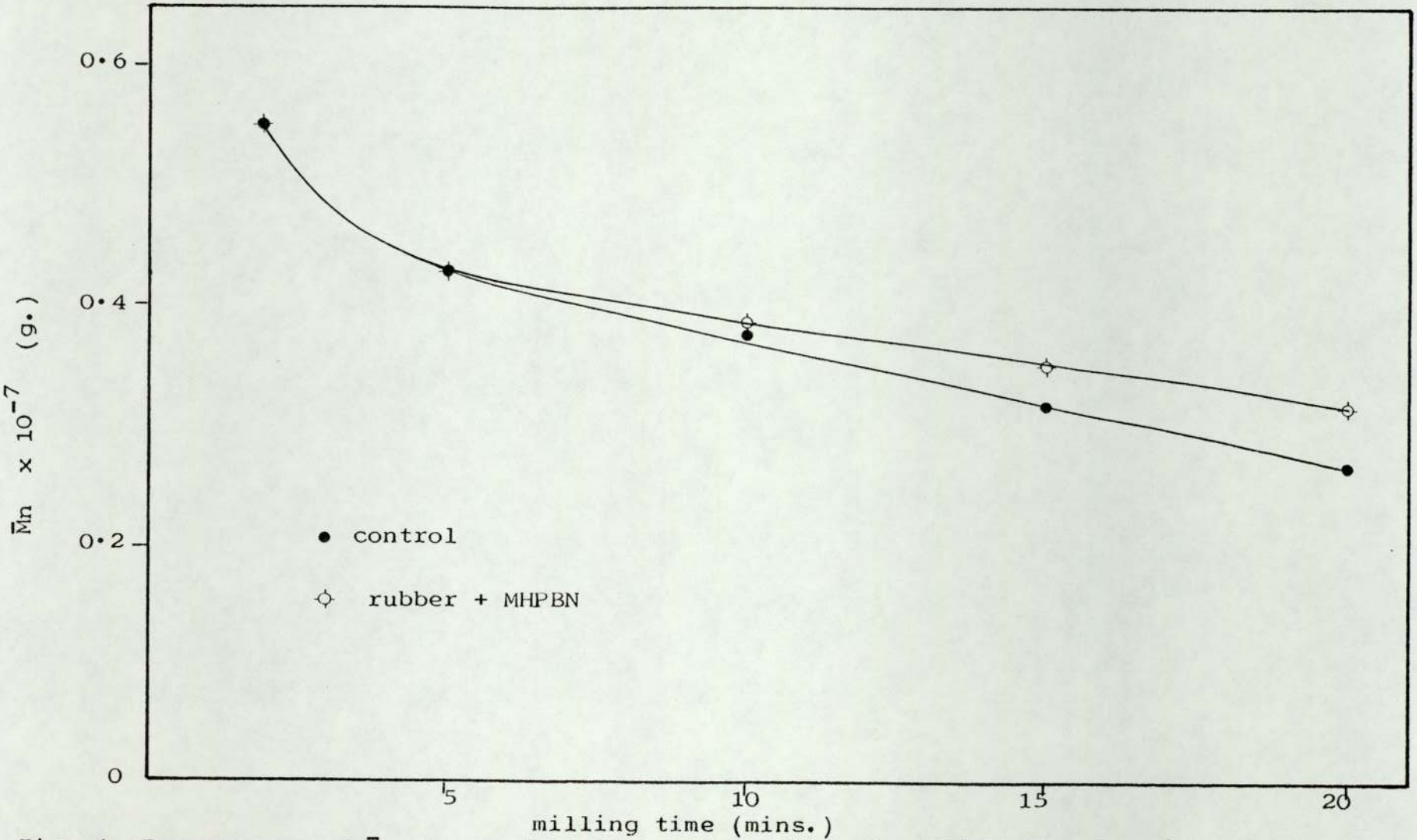


Fig. 6·17: Decrease of $\bar{M}n$ during the milling of rubber with MHPBN (1 p.h.r.) in the R.A.P.R.A. torque rheometer (closed chamber) at room temperature

nitrone, $\bar{M}n$ does not decrease as much with milling time as for the control (rubber without the nitrone). The implications of this result will be discussed in section 6.B.4.

6.B.3.5 CHANGES IN THE MOLECULAR WEIGHT DISTRIBUTION FOR THE RUBBER MILLED WITH AND WITHOUT MHPBN (CLOSED CHAMBER)

MHPBN (1 p.h.r.) was milled into the rubber using the conditions described in section 6.B.3.1. Samples were sent in duplicate for gel permeation chromatography (g.p.c.) analysis to the Rubber and Plastics Research Association of Great Britain. The conditions used for the g.p.c. analysis are described in section 3·18. Molecular weight distributions were obtained by plotting $\frac{dW}{d \lg \bar{M}}$ verses lg M, the values of which had been calculated by the computer attached to the g.p.c. analyser.

Results

The molecular weight distribution for the rubber with and without the nitrone for the various milling times are shown in figures 6·18 (a) to (e). It is clear from these figures that the shearing action during the milling

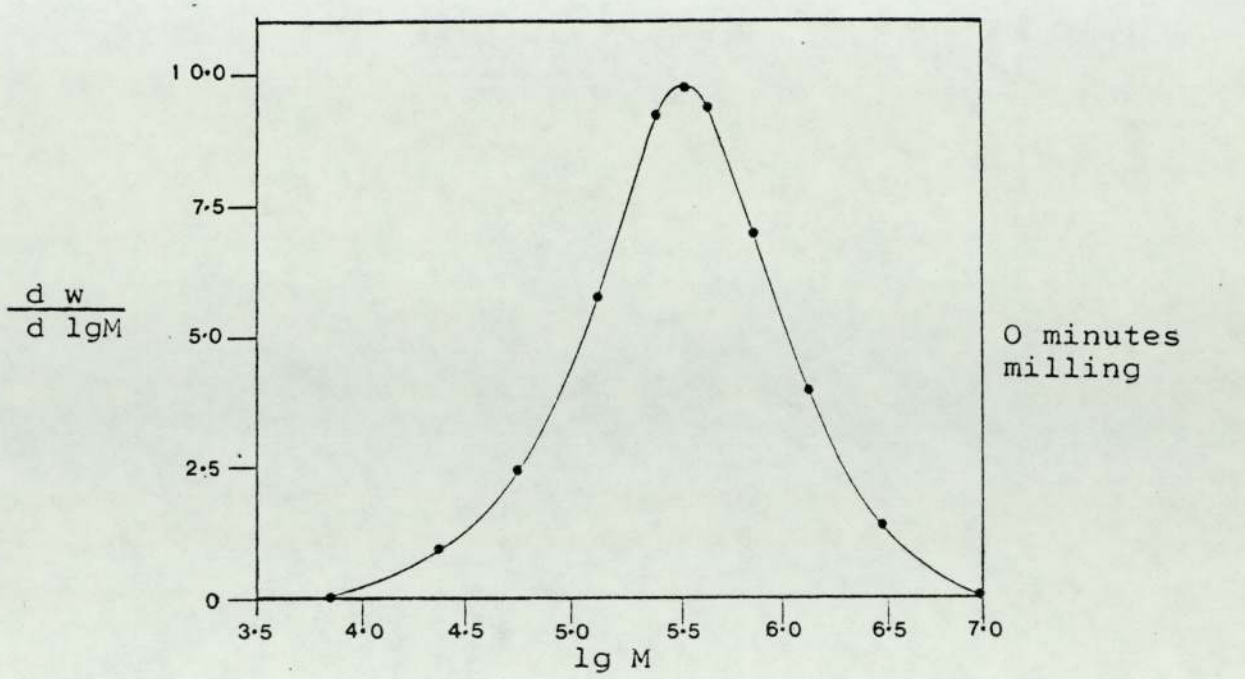


Fig. 6·18(a): Molecular weight distribution curve for rubber prior to any milling in the R.A.P.R.A. torque rheometer: i.e.: 0 mins. milling

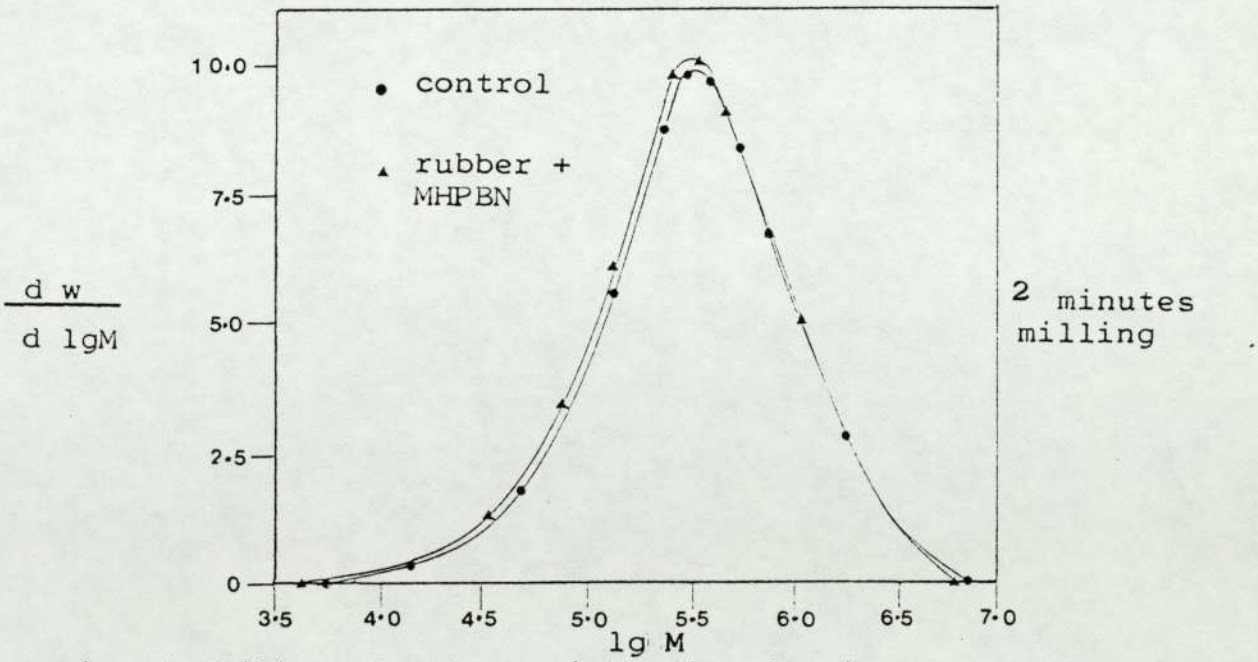


Fig. 6·18(b): Molecular weight distribution curves for rubber with and without MHPBN (1 p.h.r.) milled for 2 minutes in the R.A.P.R.A. torque rheometer (closed chamber) at room temperature

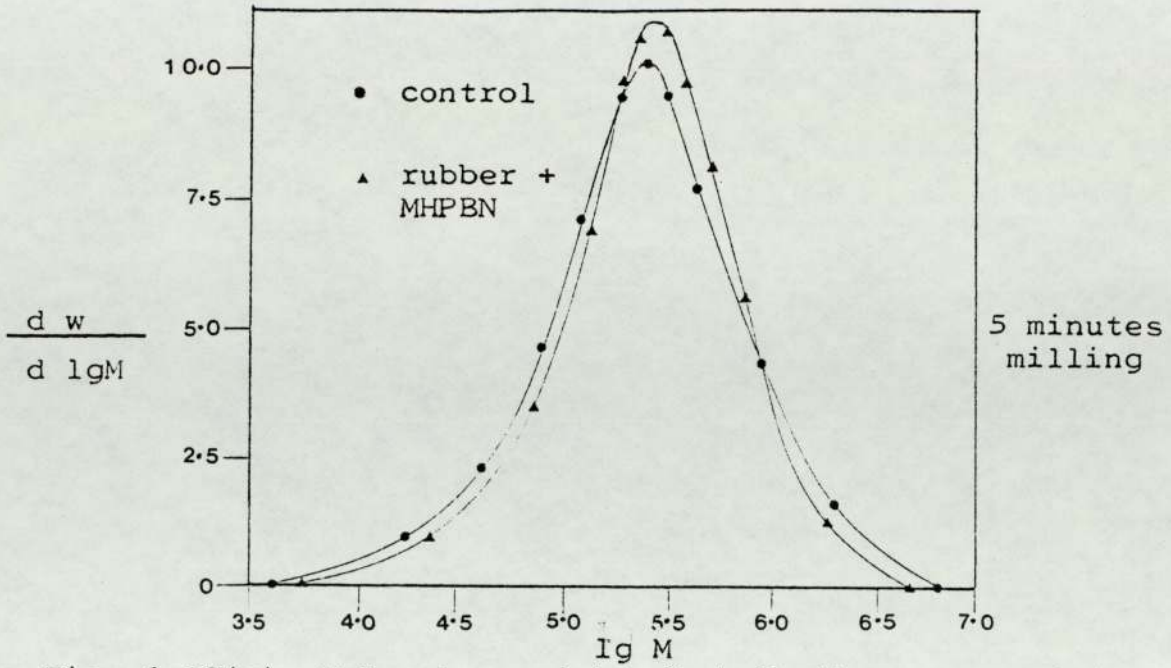


Fig. 6·18(c): Molecular weight distribution curves for rubber with and without MHPBN (1 p.h.r.) milled for 5 minutes in the R.A.P.R.A. torque rheometer (closed chamber) at room temperature

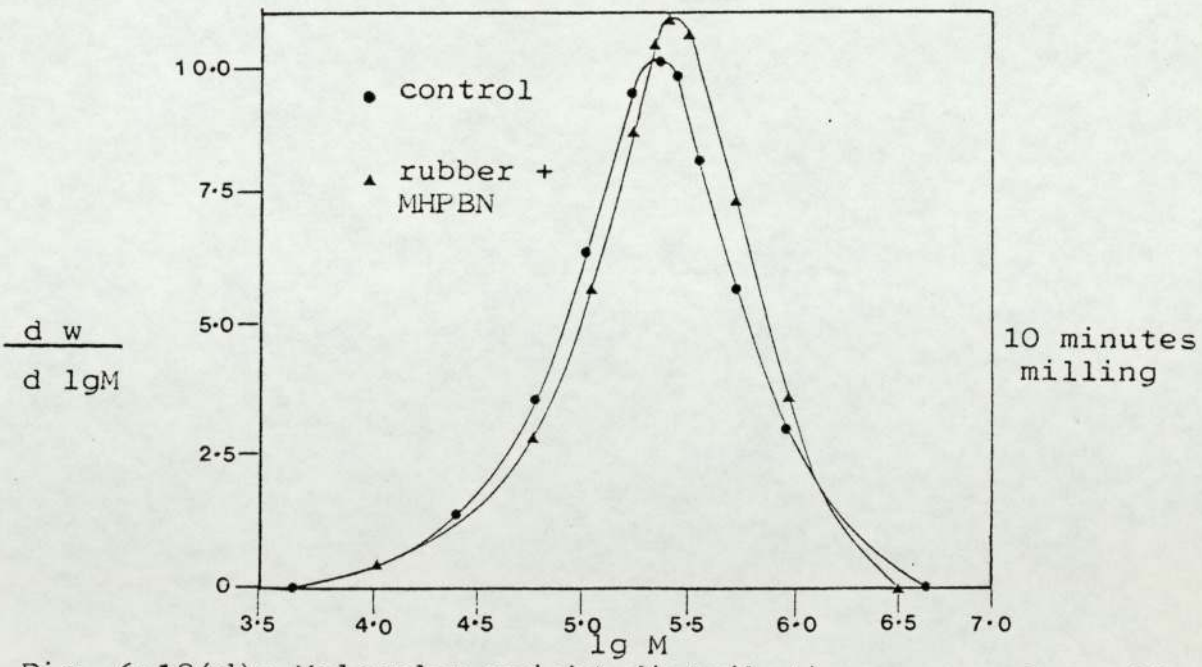


Fig. 6·18(d): Molecular weight distribution curves for rubber with and without MHPBN (1 p.h.r) milled for 10 minutes in the R.A.P.R.A. torque rheometer (closed chamber) at room temperature

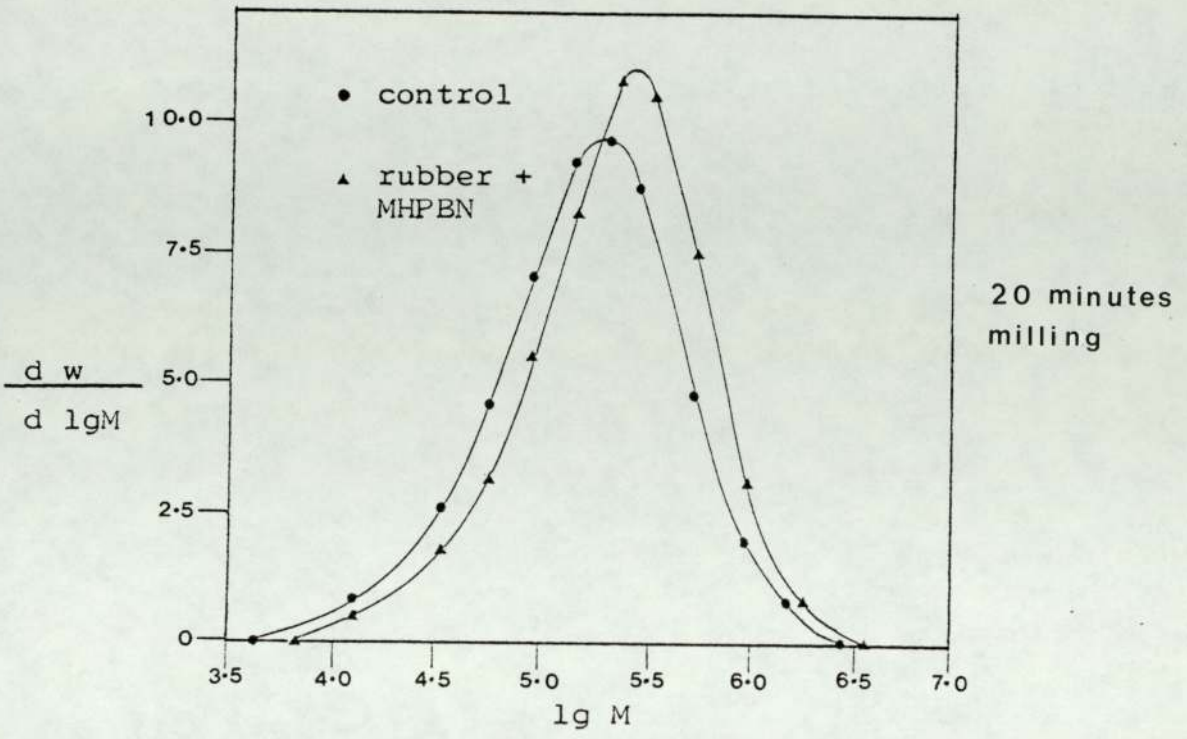


Fig. 6·18(e): Molecular weight distribution curves for rubber with and without MHPBN (1 p.h.r) milled for 20 minutes in the R.A.P.R.A. torque rheometer (closed chamber) at room temperature

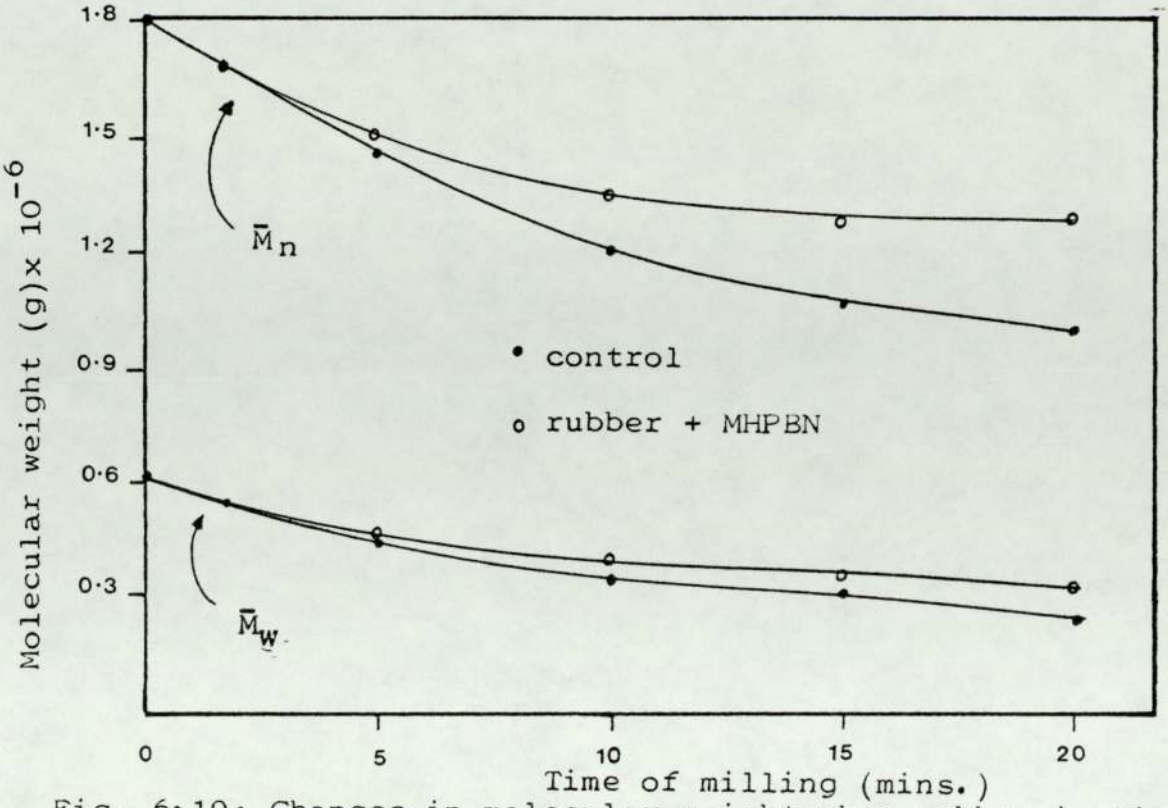


Fig. 6·19: Changes in molecular weight when rubber is milled with MHPBN (1 p.h.r.) with R.A.P.R.A. torque rheometer at room temperature

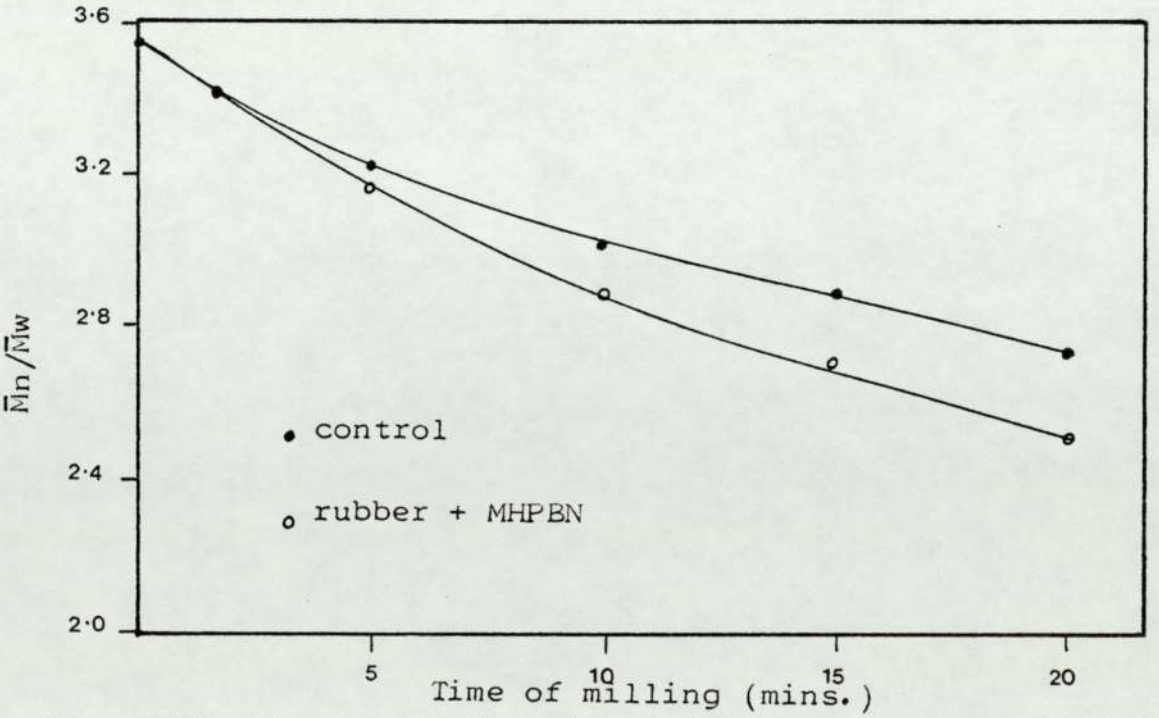


Fig. 6·20: Changes in the dispersivity ratio when MHPBN (1 p.h.r.) is milled with rubber in the R.A.P.R.A. torque rheometer at room temperature

reduces the molecular weight of the control (rubber without MHPBN) to a lower molecular weight distribution much more rapidly than the rubber containing the nitrone. Changes in the number and weight averaged molecular weights ($\bar{M}n$ and $\bar{M}w$) and the dispersivity ratios ($\frac{\bar{M}n}{\bar{M}w}$) for these distribitions as calculated by the g.p.c. computer are shown in figures 6·19 and 6·20 respectively. It is clear that for the control both $\bar{M}n$ and $\bar{M}w$ decrease rapidly with the increased milling time. So does the dispersivity ratio. However for the rubber milled with the MHPBN $\bar{M}n$ does not change as rapidly as for the control, $\bar{M}w$ decreases rapidly as for the control, and $\frac{\bar{M}n}{\bar{M}w}$ changes more rapidly than for the control.

The implications of these results will be discussed in section 6.B.4.

6.B.3.6 STABILITY OF THE NITROXYL RADICAL IN THE RUBBER FORMED FROM MHPBN BY FATIGUING

It was considered important to study the stability of the nitroxyl radical in the rubber produced from MHPBN upon fatiguing.

With this in mind rubber containing MHPBN (1 p.h.r.) was fatigued for 30 hours. The concentration of the nitroxyl

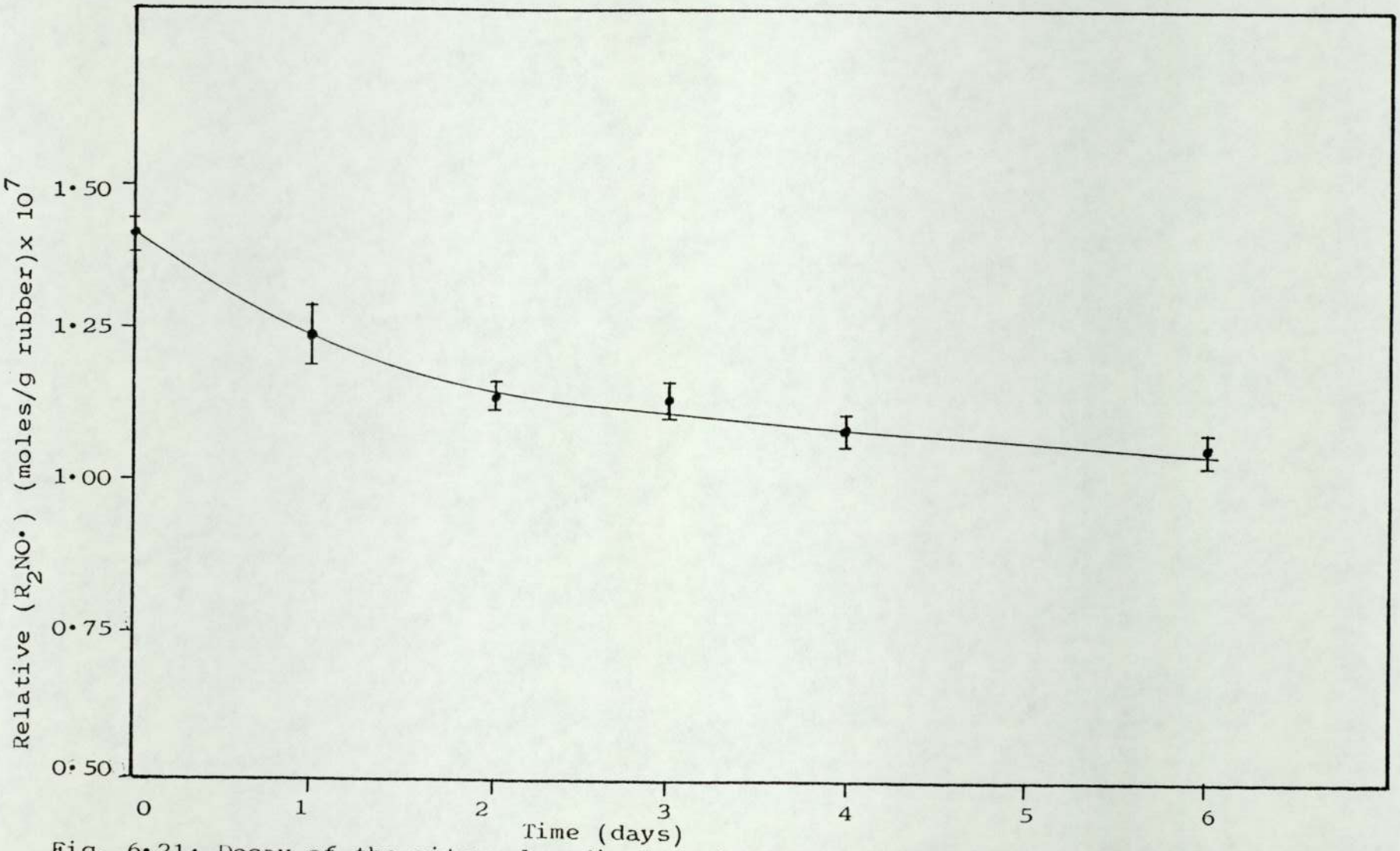


Fig. 6·21: Decay of the nitroxyl radical derived from MHPBN (1 p.h.r.) after fatiguing for 30 hours, the decrease in nitroxyl radical being monitored in the rubber at room temperature

radical in the rubber was then monitored for a period of six days at room temperature.

Result

The decay in the nitroxyl radical concentration in the rubber at room temperature is shown in figure 6·21. It is clear that the concentration of the nitroxyl radicals formed from the nitrone slowly decays to approximately 60% of its original value over six days at room temperature.

The implications of this result will be discussed in section 6.B.4.

6.B.4 Discussion

The nitroxyl radical growth from MHPBN during the fatiguing of rubber (figure 6·14) is similar to its growth during the shearing of rubber with the nitrone in the R.A.P.R.A. torque rheometer (closed chamber; figure 6·15). In both cases the growth of nitroxyl radical is autoretarding with increasing milling time. The similarity of the results under the two conditions serves to emphasise the close relationship between fatiguing of rubber and the shearing of rubber in a closed chamber of a R.A.P.R.A. torque rheometer.

The torque study (figure 6·16) and the $\bar{M}n$ study from viscosity measurements (figure 6·17) indicate that in the case of rubber sheared in the presence of the nitrone there is resistance to the degradation effects. The decrease in the torque and in the $\bar{M}n$ value for the rubber in the presence of the nitrone is less rapid than in its absence (control). These results suggest that during the shearing of the rubber with the nitrone, the nitrone causes cross-linking or chain-repair of the broken rubber chain ends, thus effectively conteracting the destructive effects of the shearing action. This is why the number average molecular weight of the control approaches the limiting molecular weight faster than the rubber containing the nitrone.

The study of gel content showed that no gel was formed during the milling of either the control or the rubber with the nitrone. The result suggests that no significant cross-linking had taken place in the presence of the nitrone. Usually gel occurs[175] when there is sufficient three-dimensional cross-linking to render the rubber insoluble in solvents. Actually the fact that no gel was observed is reflected in the decrease of $\bar{M}n$ with increased milling time. If gel formation had occured, then the $\bar{M}n$ value would have increased dramatically. In

fact such an increase was not observed. Therefore the nitrone must have been functioning by a chain-repair (chain extension) mechanism. If chain extension were to occur during the shearing of the rubber then the molecular weight would not decrease as rapidly as in the case when chain repair did not occur. Furthermore the rubber in which chain extension had occured during the shearing operations would still be soluble in the solvents as no gel had formed.

The molecular weight distributions for the rubber milled in the presence and absence of MHPBN infact confirm this chain extension (repair) mechanism. It is clear that for the control the molecular weight distribution rapidly shifts down with increased milling time. (figure 6·18 a-- e). In the case of the rubber with the nitrone the shift to lower molecular weight is not so great, the distribution narrows and the peak hight increases slightly.

Figure 6·19 shows the molecular weight decrease as computed by the computer attached to the g.p.c. The relative rates of decrease of $\bar{M}n$ for the rubber with and without MHPBN are similar to the results obtained from the viscosity measurements. The $\bar{M}n$ for the rubber containing the nitrone does not decrease with increasing milling time as rapidly as does the control.

However the decrease in $\bar{M}w$ appears to occur at a similar rate for both the control and the rubber milled with the nitrone. There is a small difference between the two, but it is not as dramatic as for the differences in $\bar{M}n$.

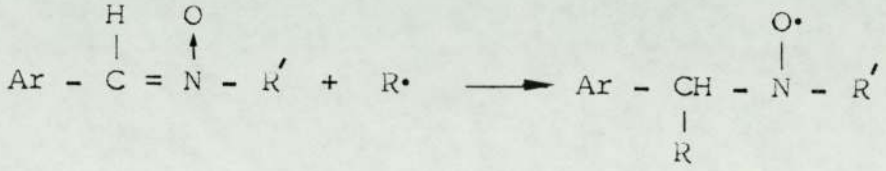
Figure 6·20 shows that the dispersivity ratio $\frac{(\bar{M}n)}{\bar{M}w}$ reduces more rapidly for the rubber milled with the MHPBN than for the control. This implies that for the former case the distribution of the rubber molecules becomes more uniform at a faster rate than for the control.

Chain scission still occurs. This is reflected in the rapid decrease in $\bar{M}w$. However for the rubber milled with the nitrone the polymer molecules become a uniform length faster than the control and this length is of a higher $\bar{M}n$ than the control, therefore chain extension must be occuring when the rubber is milled with MHPBN.

This chain extension occurs because the nitrone must be acting as a relinking agent for the broken polymeric chain ends produced during the shearing of the rubber.

Naturally, during the fatiguing of rubber the nitrone must be functioning by a similar mechanism as well.

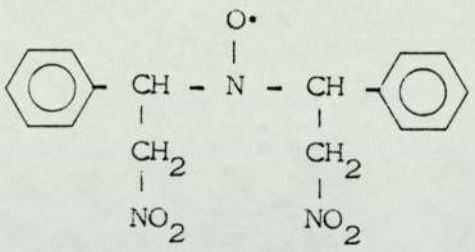
The nitrone MHPBN must be functioning as a relinking agent by trapping two alkyl radicals. The trapping of one alkyl radical by nitrones to give nitroxyl radicals is well known and indeed was the basis for the present work (scheme 6·4).



Scheme 6·4

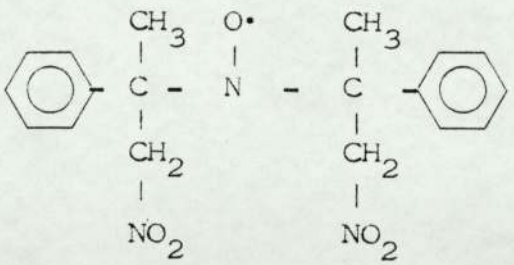
It was pointed out in chapter 5 that nitroxyl radicals containing hydrogens on the carbons α - to the nitrogen can decompose to the hydroxylamine. Nitroxyl radicals derived from nitrones[123] have been reported to be stable due to spacial conjestion. However they are only stable in the solid state and Forrester et al[71] have stated that as these compounds have been isolated in only a three percent yield, they must be undergoing slow disproportionation in solution.

Recently Jantrawaratit[206] has found that radicals of type XI (see below) are stable in solution at room temperature for only about two to three hours.



(XI)

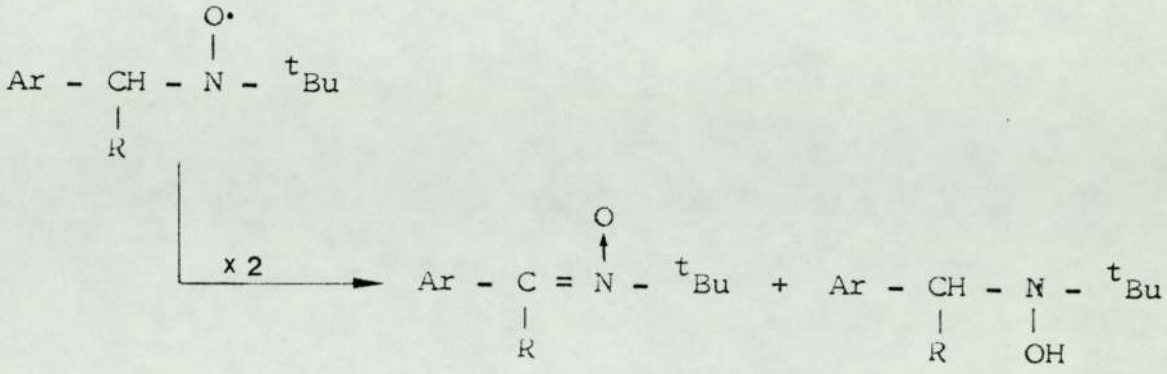
At elevated temperatures (90-100°C) the radical was unstable and could only be detected using high intensity settings on the e.s.r. spectrometer. By contrast[206] the nitroxyl radical of type XII was found to be quite stable in solution at room temperature, and its presence could be detected in high concentration even at 100°C.



(XII)

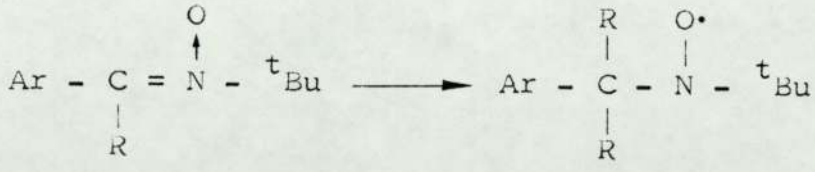
Figure 6·18 shows that at room temperature the nitroxyl radical derived from MHPBN in the rubber after 30 hours fatiguing, slowly decays over a period of six days to approximately two thirds of its original value. This

decay must be due to slow disproportionation (scheme 6·5)



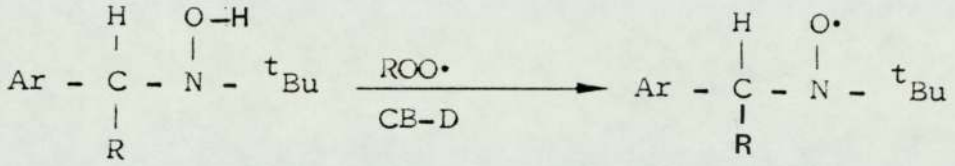
Scheme 6·5

If at room temperature slow disproportionation of the nitroxyl radical derived from MHPBN occurs then certainly at the elevated internal temperatures inside the rubber ($50^{o}C$ above ambient temperature[34]) such disproportionation could occur at a faster rate. Disproportionation of the nitroxyl radical would lead to the formation of a keto-nitrone which could then trap another alkyl radical (scheme 6·6).



Scheme 6·6

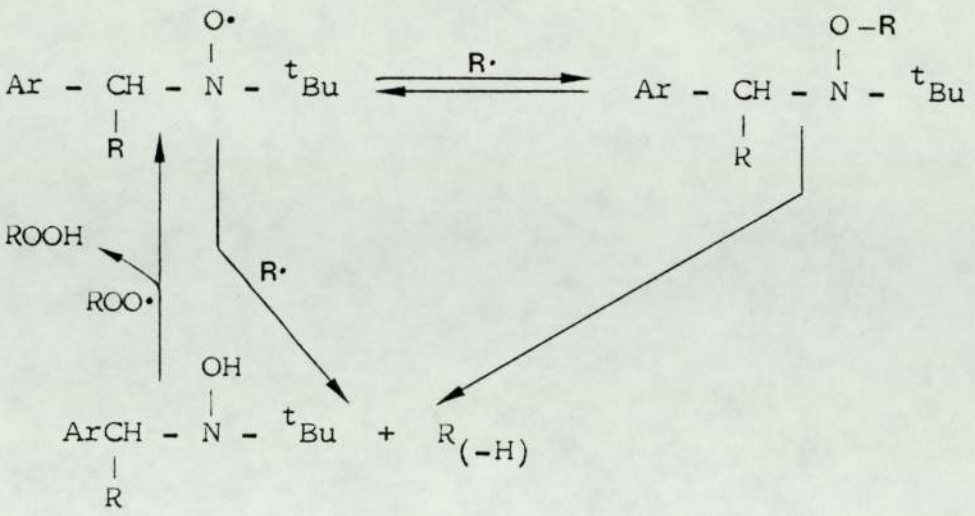
The hydroxylamine formed in scheme 6·5 could regenerate the nitroxyl by a CB-D mechanism (scheme 6·7).



Scheme 6·7

Schemes 6·4 - 6·7 would certainly account for the chain extension observed during the milling of the nitrone with the rubber. These schemes would also account for the auto-retarding nature of the build up of nitroxyl radical from MHPBN during the shearing with the rubber in the closed chamber and during the fatiguing of rubber. The tendency towards saturation of nitroxyl radical concentration during fatiguing and during the shearing operations would be due to a combination of nitroxyl radical formation (scheme 6·4. 6·6 and 6·7) and disproportionation by scheme 6·5.

The results might also possibly be explained by reaction of the nitroxyl radical formed in scheme 6·4 with alkyl radicals at the oxygen site to form an O-alkylated hydroxylamine. This would account for the auto-retarding build up of nitroxyl radicals from MHPBN. However since regeneration of the nitroxyl radical would occur from the O-alkylated hydroxylamine (scheme 6·8), significant chain extension would not be seen as the relinking would not be permanent.

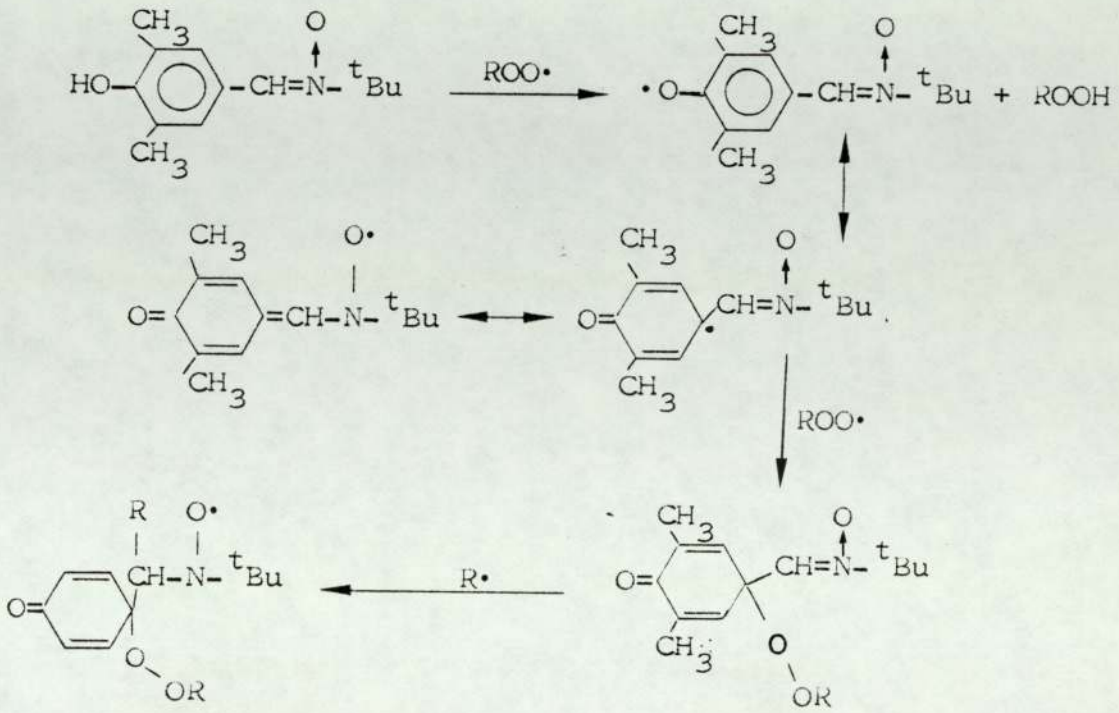


Scheme 6·8

Furthermore in section 6.A.3.4 it was concluded that stable O-alkylated hydroxylamines are not formed to a great extent during the shearing of rubber in the presence of a nitroxyl radical. It is therefore unlikely that the significant chain extension, seen during the shearing of rubber in the presence of MHPBN, could be accounted by the formation of the O-alkylated hydroxyl amine.

It should be borne in mind that only nitrones containing the phenolic antioxidant function had efficient anti-fatigue activity, and it was concluded in chapter 5 that during the initial stages of fatigue peroxyl radical termination was important for efficient antifatigue action.

Therefore the chain extension could be explained by the following mechanism as well (scheme 6·9).



Scheme 6·9

Whatever the scheme for the trapping of two alkyl radicals to produce the chain extension, it is doubtful that the nitroxyl radical would be able to effectively contribute further to the overall antifatigue activity of the nitrones, especially since its mobility would be severely restricted. This would explain why after extraction of the rubber containing the nitrones (chapter 5) no significant antifatigue activity was observed. All

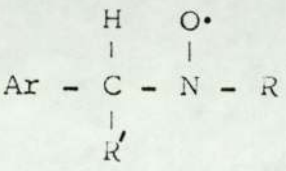
the free nitrone would have been extracted and only the nitroxyl radicals bound to the rubber would have remained in the system.

However the contributory role of the regeneration of the nitroxyl radical in the overall antifatigue activity of nitrones must not be ruled out, as there is no direct evidence to state otherwise. It probably does contribute but the more importnat mechanism is the trapping of two alkyl radicals by the nitrone function (schemes 6·4, 6·6 and 6·9).

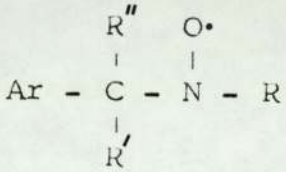
As suggested in chapter 5, disproportionation of the initially formed nitroxyl radical from the nitrone to give the hydroxylamine and keto-nitrone would also explain why MHPPN has better antifatigue activity to MHPBN. In addition to disproportionation on the aryl side of the derived nitroxyl radical (scheme 6·5), the former can also disproportionate on the N-alkyl side (scheme 5·1) by virtue of the hydrogen on the α - carbon. The trapping of alkyl radicals at this site could also occur and therefore provide an additional trapping mechanism in the molecule.

The broadning of the e.s.r. lines relative to before fatiguing (figures 5·10 and 5·3·b), ie. the tendency to

anisotropy, provides further evidence for the trapping of two alkyl radicals by the nitrone. The resulting nitroxyl radical being relatively immobile would certainly give rise to the observed spectral phenomena due to the lack of free rotational and tumbling motions of the radicals. These spectral changes could also be rationalized in terms of the superimposition of the nitroxyl radicals XIII and XIV.



(XIII)



(XIV)

CHAPTER SEVEN

ASSESSMENT OF THE ANTIOZONANT, ANTIOXIDANT, DISCOLOURATION AND STAINING PROPERTIES OF THE ALICYCLIC NITROXYL RADICALS, THEIR PRECURSORS AND THE NITRONES.

7.A. ASSESSMENT OF THE STATIC ANTIOZONANT PROPERTIES

7.A.1 Introduction

The very small quantities of ozone present in the atmosphere at ground level (3-5 parts per hundred million (p.p.h.m.))[1] can cause severe cracking of unsaturated rubbers when they are under strain. The deterioration of rubber by ozone has been known for a long time. The mechanism of the ozone attack and the factors affecting the ozone cracking of rubbers have been reviewed in chapter one section 1.5. Whilst there are rubbers available which are resistant to ozone (e.g. neoprene rubber), the common general purpose rubbers such as natural rubber and S.B.R. are rapidly attacked if unprotected. Ozone cracking only manifests itself in rubbers that are under strain and always occurs at right angles to the applied stress. As the cracks produced are clearly visible and can significantly reduce the strength and the service performance of rubbers, the resistance of the rubber articles to atmospheric ozone

is of key importance. Rubber may be protected from the deterioral effects of ozone by the judicious use of waxes chemical antiozonants or combinations of the two. Practically all the commercial antiozonants used today in the rubber industry belong to the arylamine class of compounds. The probable modes of action of these compounds have been described in chapter one (section 1.10). The antiozonants belonging to the arylamine class of compounds are very effective during the protection of rubber against ozone cracking, however they suffer from a severe disadvantage. They cause gross discolouration and lead to staining by migration to adjacent surfaces. These characteristics are aesthetically undesirable particularly for light coloured applications.

It will be seen later in this chapter (section 7.C) that the hindered alicyclic nitroxyl radicals, their precursors and the nitrones do not discolour or cause staining. In view of their antifatigue activities it was of interest to study the antizonant activities of these compounds.

7.A.2 Experimental Procedure

The compounds described in section 2.1 were incorporated into the rubber using the procedure described in sections 4.2. 5.2 and 5.3.1. The vulcanisation was done as described in section 3.5.2.

Test pieces were cut and conditioned as described in sections 3.7 and 3.8. The static antiozonant activity for the rubber containing the compounds was tested in the Hampden Shawbury Ozone Test Cabinet as described in section 3.10. All test pieces were initially tested at a strain of 20%, in an ozone concentration of 25 $\pm$ 5 p.p.h.m. at 30^{o}C. The technologically interesting compounds, particularly the nitrones MHPBN, MHPPN, MHPEN and MHPMN because of their high antifatigue efficiency, were testd at strain levels of 5%, 10%, 15%, and 30% as well.

The degree of cracking of the test pieces was studied using a stand lens of x 5 magnification[163]. The severity of the cracking was graded numerically on an arbitary scale from 0-5 as described in section 3.10.4.

7.A.3 Results

Table 7.1 and figure 7.1 compare the static antiozonant activities of the alicyclic nitroxyl radicals and their precursors in conventional C.B.S. gum vulcanisates. It is clear that relative to the control none of the compounds have antiozonant activity. The results for the vulcanisates made up from unextracted rubber were the same as that made up from the extracted rubber.

Static test; strain = 20%; [ozone] = 25 ± 5 p.p.h.m; temperature = 30°C		
Additive	Time for appearance of cracks 0·5 mm long (hrs.) ± 1	Time for failure (severage) (hrs.) ± 1
Control	10	20
TMP	12	20
TMOP	12	20
TMPD	12	20
TMMP	12	19
TMPS	5	15
TMOPS	5	18
TMPDS	10	20
TMOPX	4	16
TMOXPZ	4	20
BPTMOP	10	20

Table 7·1: Comparison of ozone test results for the alicyclic nitroxyl radicals, precursers and derivatives. ([additive] = 1 p.h.r.; conventional C.B.S. vulcanisates).

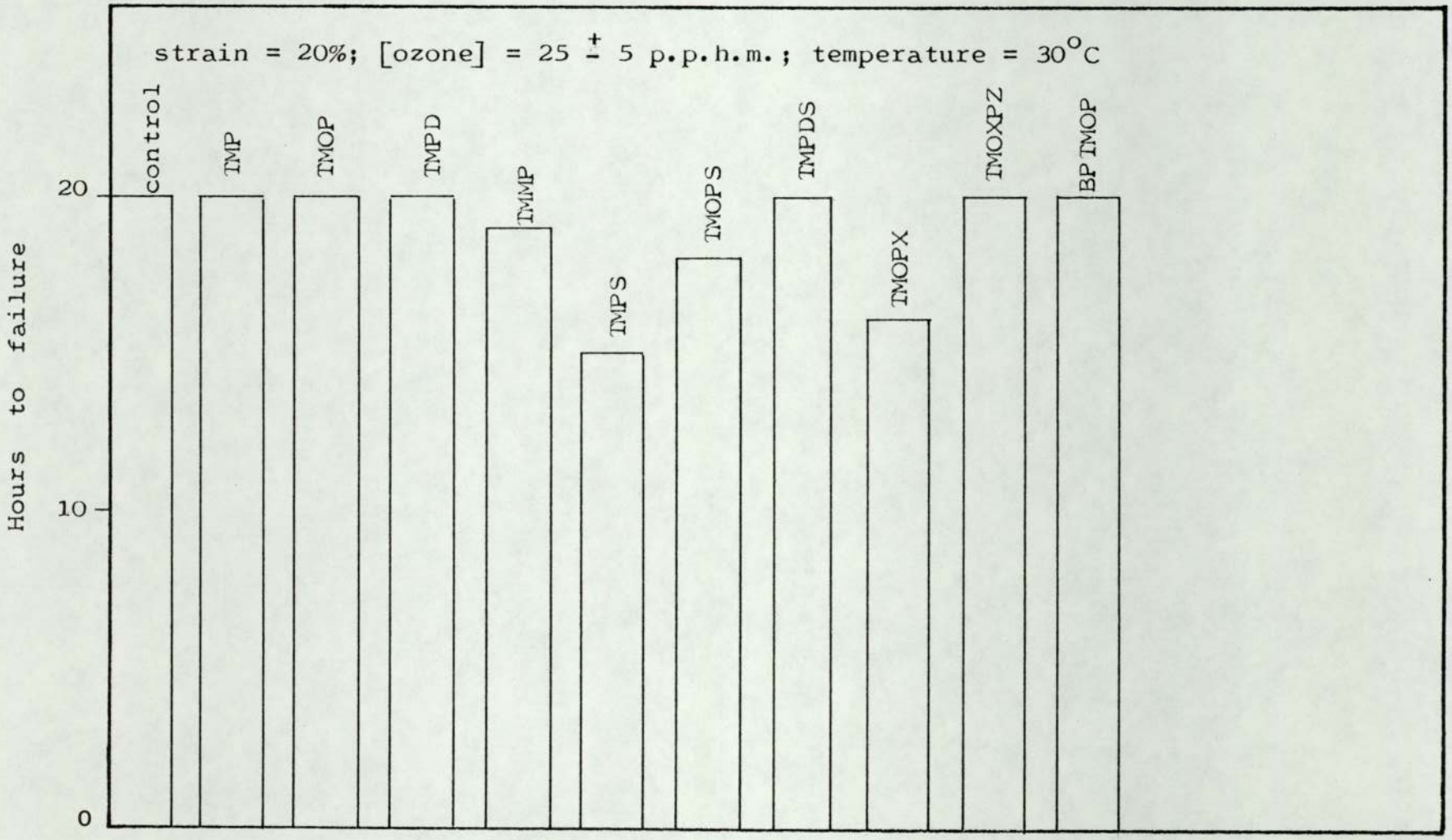


Fig. 7·1: Comparison of the static antiozonant activities of the alicyclic nitroxyl radicals and their precursors (1 p.h.r. each) in conventional C.B.S. vulcanisates

Table 7.2 and figure 7.2 compare the static ozone test results for the conventional C.B.S. vulcanisates protected by the nitrones and other additives. All the additives were used at a 1 p.h.r. level and the nitrones were premilled with the rubber for two minutes prior to the compounding operations. Irrespective of the structure all the nitrones were found to have good antiozonant activity which was superior to even the commercial agents IPPD and HPPD. In fact contrary to expectations HPPD gave very little antiozonant protection to the rubber. The results are shown only for the test pieces which were strained by an elongation of 20%. However for other extensions as well, the trends were similar. The superior activity of the nitrones is particularly pronounced for the time for cracks of length 0.5mm to appear in the test pieces (table 7.2). There does not appear to be a significant structure activity relationship for the time to appearance of the initial cracks. Once the initial crack is formed however, the time to failure (severage) does appear to be affected by the structure of the N-alkyl group. Optimum activity was obtained by MHPPN which has an N-isopropyl group (table 7.2). MHPMN had considerably lower activity and MHPBN was intermediate (table 7.2).

Static test; strain = 20%; [ozone] = 25 ± 5 p.p.h.m; temperature = 30°C		
Additive	Time for appearance of cracks 0·5 mm long (hrs.) ± 2*	Time to failure (severage) (hrs.) ± 2 *
Control	10 ± 1	20 ± 1
IPPD	12	35
HPPD	8 ± 1	23
MNP	30	46
MHB	10	20
MHPBN	30	58
HPBN	30	48
PBN	30	50
PMN	35	60
BHPMN	30	52
MHPMN	30	55
MHPEN	30	68
MHPPN	30	72
MPPN	10	26
CPPN	12	36
BMHPPN	40	80

* unless where otherwise indicated

Table 7·2: Comparison of ozone test results for the nitrones and other additives ([additive] = 1 p.h.r.; premill time for nitrones = 2 minutes; conventional C.B.S. vulcanisate).

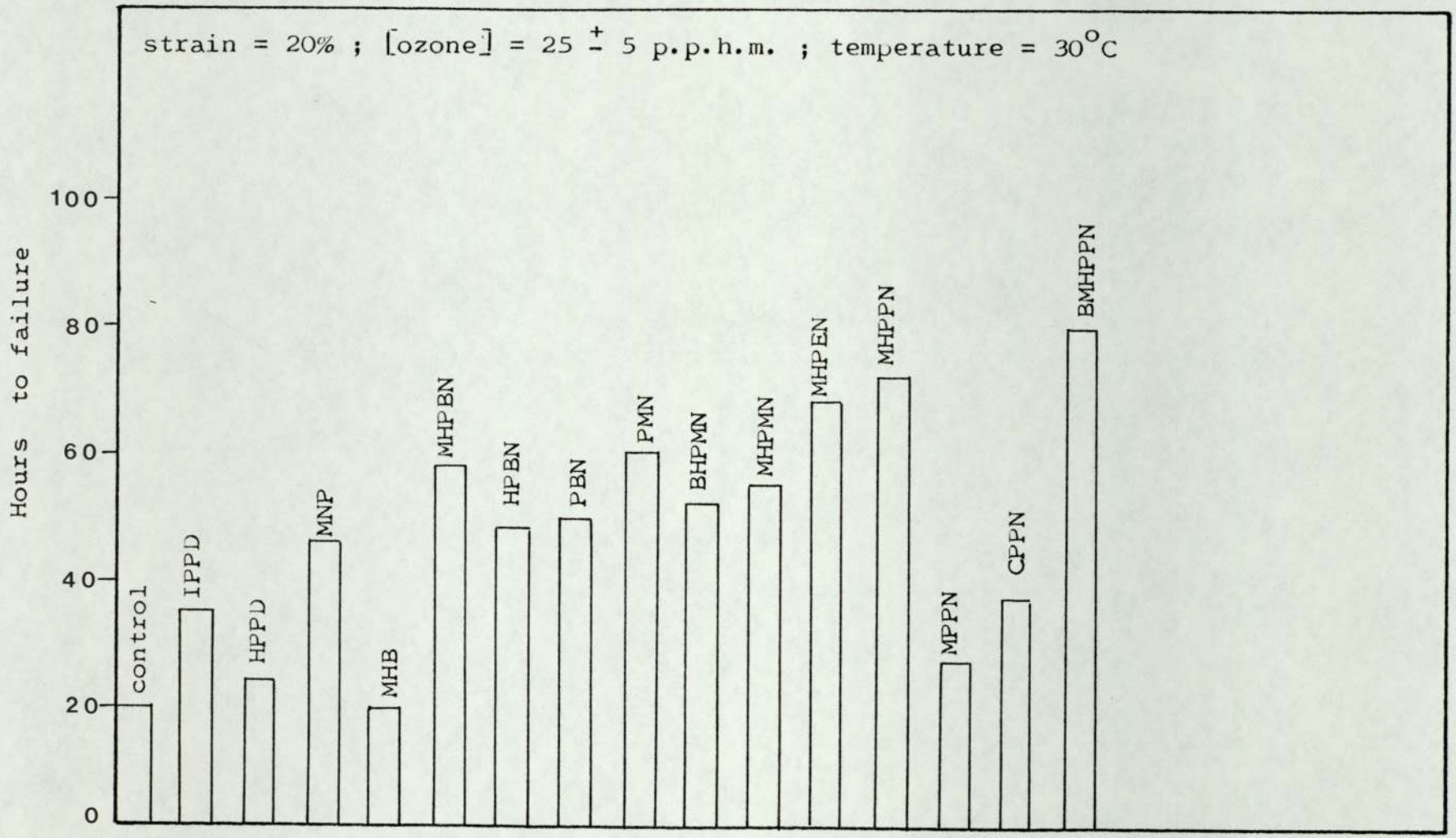


Fig. 7·2: Comparison of the static antiozonant activities of the nitrones, and other additives (1 p.h.r. each) in conventional C.B.S. vulcanisates (premill time for all nitrones = 2 minutes)

2-methyl-2-nitrosopropane an oxidation product of MHPBN (MNP; table 7.2) was also found to exert good protection against static ozone cracking of the rubber. However 3,5-dimethyl-4-hydroxybenzaldehyde (MHB) also an oxidation product of MHPBN did not possess any antiozonant activity.

Figure 7.3 shows the rate of ozone crack growth as a function of time for the control, IPPD, HPPD, MNP and two typical nitrones (MHPBN and MHPPN). The figure shows that the rate of crack development and growth in the vulcanisates protected by the nitrones were considerably slower than in the unprotected rubber or the rubber protected by IPPD. Although not shown, the other nitrones too behaved similarly. Table 7.3 shows that the activity of the nitrones was not affected very much when they were incorporated into the rubber as a normal additive during the compounding operations.

Table 7.4 and figure 7.4 show the antiozonant activities for the combinations of MHPPN with WSP and NODP respectively. WSP by itself did not have any antiozonant activity, nor did NODP. (MHPPN does have good antiozonant activity). The table shows that the combination of WSP + MHPPN were infact slightly antagonistic with respect to the nitrone alone. Similarly for the combination of NODP with MHPPN. It must be pointed out however, that the

Static test; strain = 20%; [ozone] = 25 ± 5 p.p.h.m; temperature = 30°C		
Additive	Time for appearance of cracks 0·5 mm long (hrs.) ± 2	Time to failure (severage) (hrs.) ± 2
MHPBN	30	55
MHPMN	30	50
MHPEN	30	69
MHPPN	30	74

Table 7·3: Comparison of antiozonant activity of nitrones incorporated into the rubber during the compounding stage as a normal additive. (i.e. no premilling; [nitrone] = 1 p.h.r.; conventional C.B.S. vulcanisate).

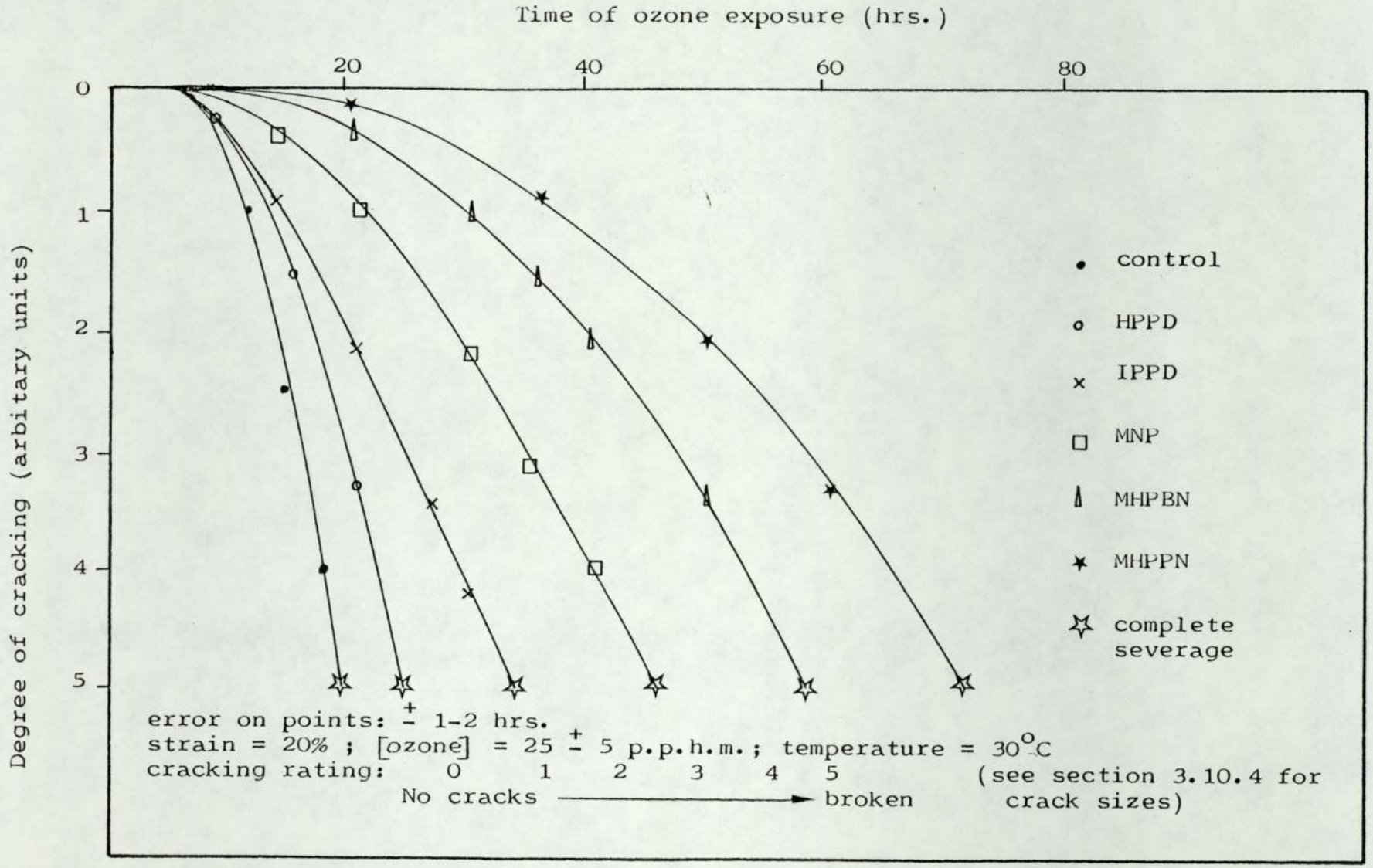


Fig. 7·3: Rate of crack development for rubber protected by two typical nitrones and other additives during static ozone exposure

Static test; [strain] = 20% ozone = 25 ± 5 p.p.h.m; temperature = 30°C		
Additive	Time for appearance of cracks 0·5 mm long (hrs.) ± 2	Time for failure (severage) (hrs.) ± 2
Control	10	21
IPPD	12	36
HPPD	8	23
MHPPN	30	72
WSP	10	20
WSP + MHPPN	25	56
NODP	12	24
NODP + MHPPN	20	60

Table 7·4: Comparison of ozone test results for combinations of MHPPN with other antioxidants ([additive] = 1 p.h.r.; conventional C.B.S. vulcanisate).

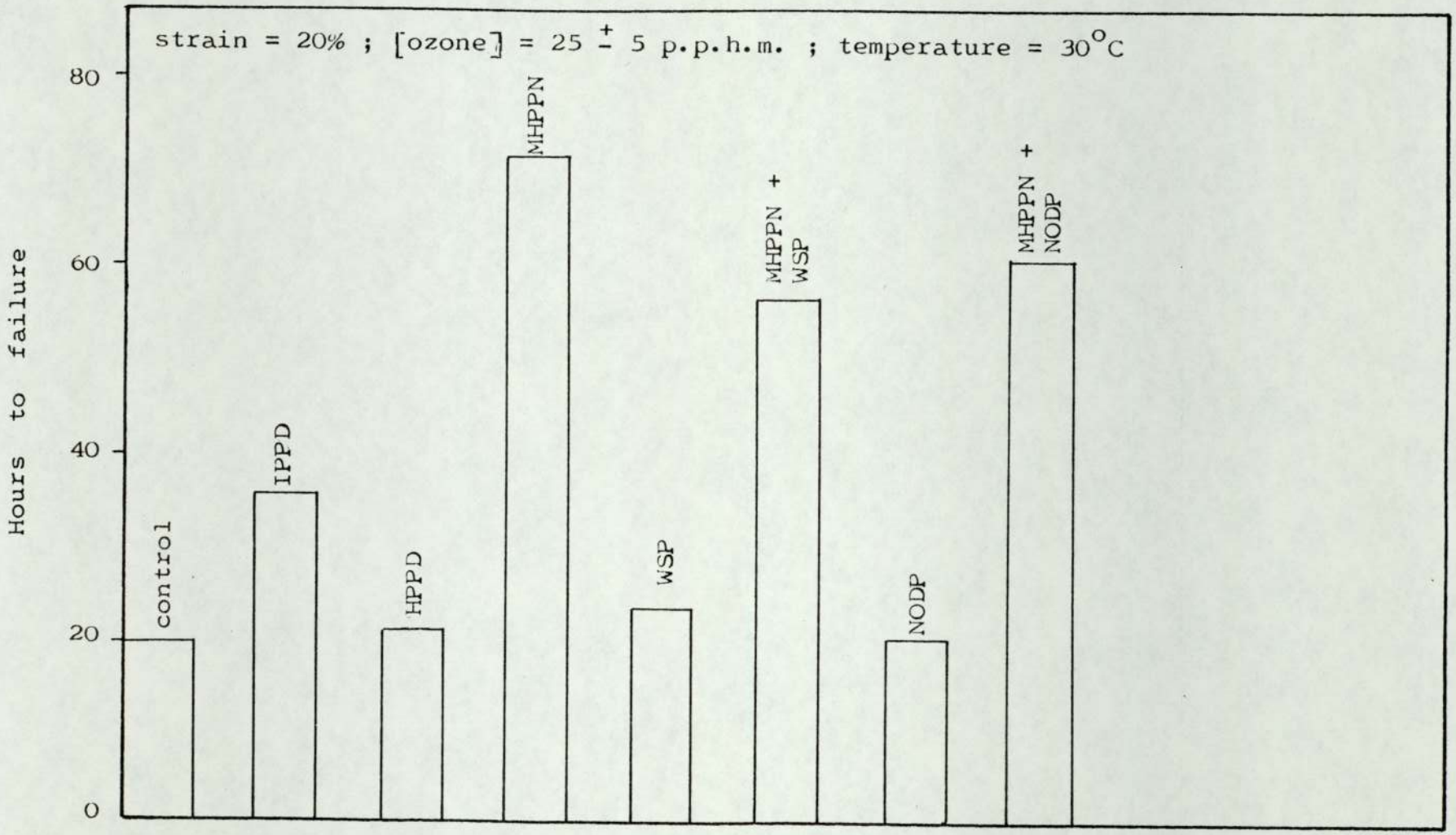


Fig. 7·4: Comparison of the static antiozonant activities for combinations of MHPPN with other antioxidants (1 p.h.r. each) in conventional C.B.S. vulcanisates

activity of the combinations were still superior to that of the commercial antiozonants IPPD and HPPD.

Table 7.5 and figure 7.5 show the effect of premilling MHPBN with the rubber prior to the compounding operations. It is clear that although there is little difference between no premilling and two minutes premilling, increased premilling decreased the antiozonant protective efficiency of the nitrone.

Figure 7.6 shows photographs of the extent of cracks formation as a function of premilling time, after 36 hours exposure to ozone for vulcanisatates protected by MHPBN. The photographs have been enlarged by x5 to highlight the cracks.

Table 7.6 shows that after acetone extraction of the vulcanisates the antiozonant protection of the nitrones and the commercial agents (IPPD and HPPD) was lost.

Table 7.7 compares the antiozonant activities for MHPBN, MHPPN, MNP, the commercial antiozonants and the control at test piece strains of 5, 10, 15, 20 and 30 percent respectively. Table 7.8 compares the rates of ozone deterioration at these strain levels. It is clear that the highest rate of ozone deterioration (cracking) occurs

Static test; strain = 20% ; [ozone] = 25 ± 5 p.p.h.m ; temperature = 30°C		
Time of premilling	Time for appearance of cracks 0.5 mm long (hrs.) ± 2	Time to failure (severage) (hrs.) ± 2
0	30	55
2	30	58
4	25	52
6	22	46

Table 7·5: Effect of premilling MHPBN with rubber prior to compounding on the antiozonant activity ([nitrone] = 1 p.h.r ; conventional C.B.S. vulcanisate)

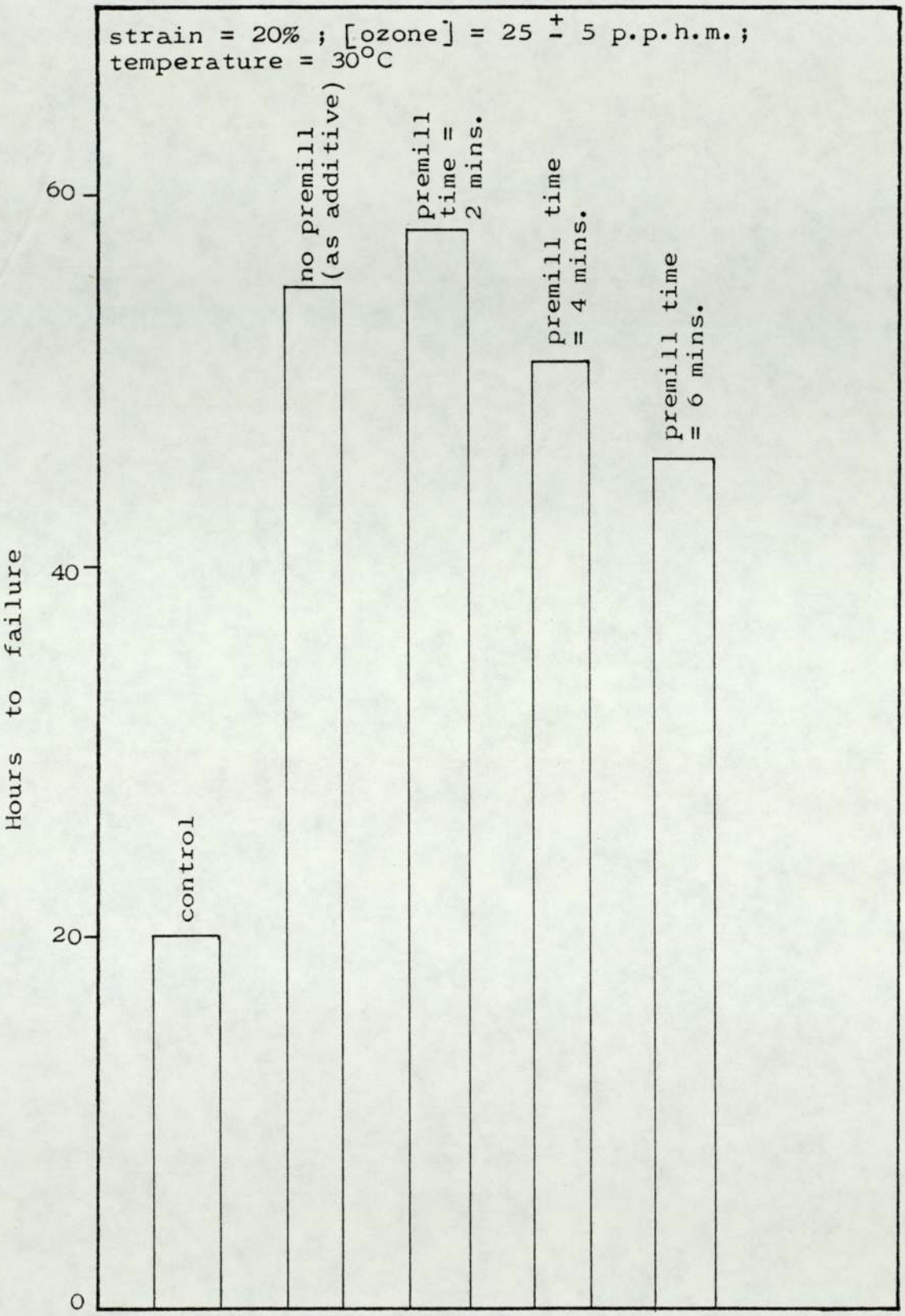


Fig. 7·5: Effect of premilling MHPBN (1 p.h.r.) with the rubber on its static antiozonant activity

Fig. 7.6 Photographs showing the effect of premilling time on the nature of the cracks developed in conventional C.B.S. vulcanisates protected by MHPBN (1p.h.r.) after 36 hours of static ozone exposure (ozone = 25 $\pm$ 5 p.p.h.m.; temperature = 30^{o}C ; strain = 20% ; scale 5cm = 1cm)

Notation:

1. 0/2 mins. premill time
2. 4 mins. premill time
3. 6 mins. premill time

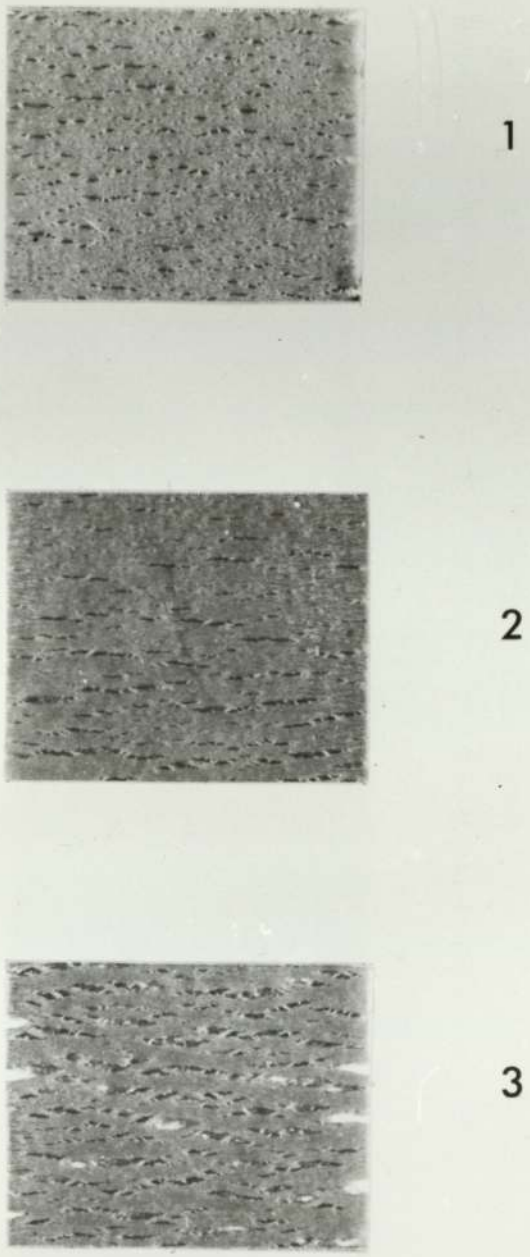


Fig. 7.6

Static test; strain = 20%; [ozone] = 25 ± 5 p.p.h.m; temperature = 30°C		
Additive	Time for appearance of cracks 0·5 mm long (hrs.) ± 1	Time to failure (severage) (hrs.) ± 1
Control	11	20
IPPD	12	22
HPPD	8	19
MHPBN	11	22
MHPMN	12	23
MHPEN	12	24
MHPPN	12	23

Table 7·6: Effect of extraction of the additive after vulcanisation ([additive] = 1 p.h.r.; premill time of nitrones = 2 minutes; conventional C.B.S. vulcanisate).

Static test; strain as shown; [ozone] = 25 ± 5 p.p.h.m. temperature = 30°C										
Strain %	5		10		15		20		30	
additive	a (hrs.)	b (hrs.)	a (hrs.)	b (hrs.)	a (hrs.)	b (hrs.)	a (hrs.)	b (hrs.)	a (hrs.)	b (hrs.)
Control	15	28	7	14	9	18	10	21	20	28
IPPD	9	34	6	25	6	30	12	35	24	48
HPPD	8	24	6	20	8	22	8	23	13	25
MPN	10	30	10	22	15	37	30	46	30	54
MHPBN	15	42	12	28	18	46	30	58	30	70
MHPPN	20	50	12	35	22	55	30	72	50	110

Notation
a = Time for appearance of cracks 0·5 mm long
b = Time to failure of test pieces (severage)

Table 7·7: Comparison of the antiozonant activities of typical efficient nitrones and other additives at various extensions ([additive] = 1 p.h.r.; premill time for nitrones = 2 minutes; conventional C.B.S. vulcanisate).

Static test; strain as shown; [ozone] = 25 ± 5 p.p.h.m ; temperature = 30°C					
Strain % / Additive	Rate of ozone cracking (arbitary units/hour)				
	5	10	15	20	25
Control	0·180	0·360	0·278	0·230	0·178
IPPD	0·150	0·200	0·166	0·142	0·125
HPPD	0·208	0·250	0·227	0·217	0·200
MPN	0·166	0·227	0·135	0·108	0·097
MHPBN	0·119	0·178	0·108	0·086	0·071
MHPPN	0·100	0·142	0·090	0·069	0·045

Table 7·8: Comparison of the rates of ozone cracking at different extensions conventional C.B.S. vulcanisates containing two typical nitrones and other agents ([additive] = 1 p.h.r. ; all nitrones premilled for 2 minutes).

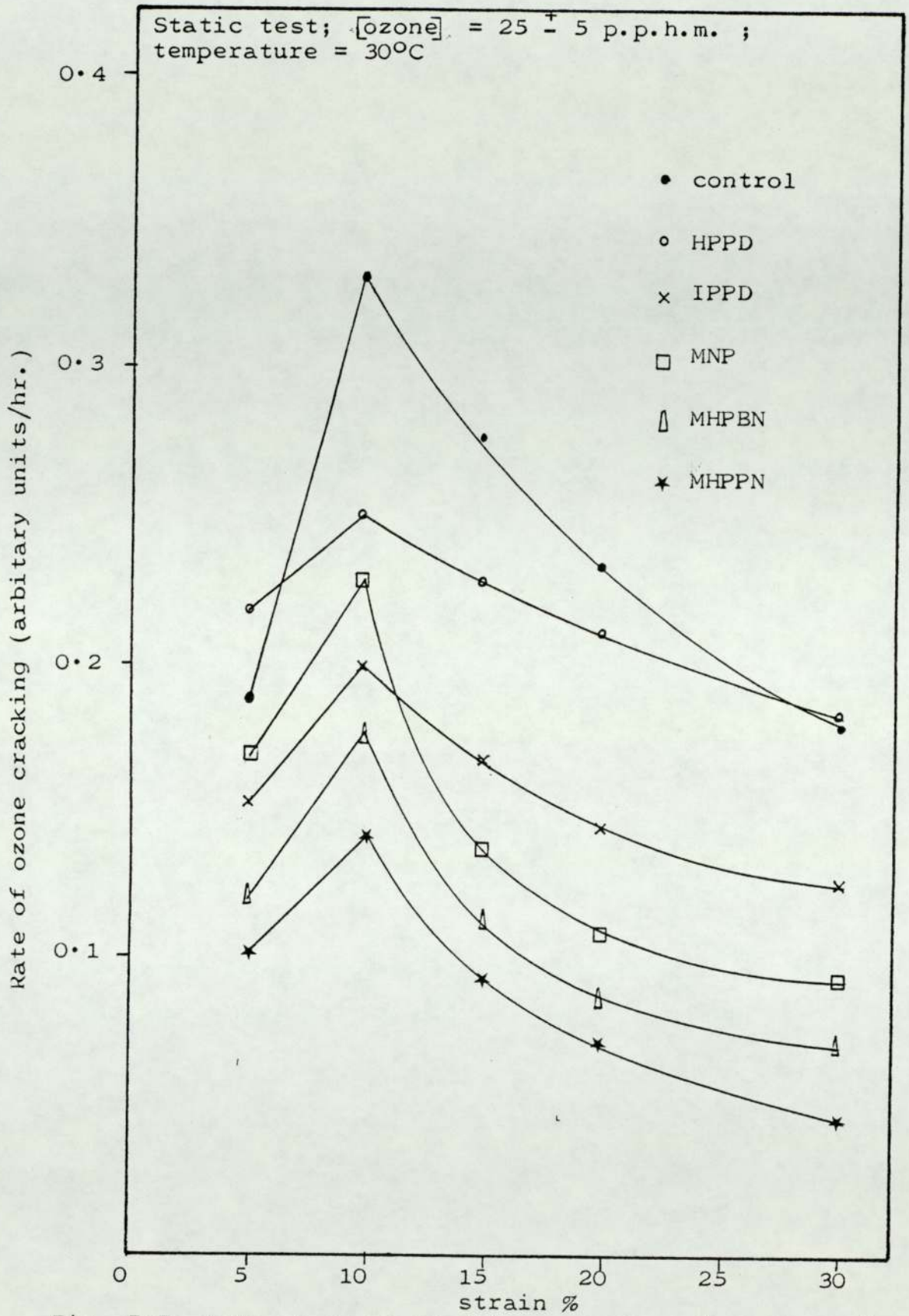


Fig. 7·7: Rate of ozone cracking as a function of strain for conventional C.B.S. vulcanisates protected by various additives

Fig. 7.8 Photographs comparing the cracks developed in conventional C.B.S. vulcanisates protected by IPPD and MHPBN respectively after 28 hours of static ozone exposure (additive = 1 p.h.r.; ozone = 25 p.p.h.m.; temperature = 30°C ; scale 5cm = 1cm)

Notation:

1. IPPD, 5% strain
2. IPPD, 10% strain
3. IPPD, 20% strain
4. MHPBN, 5% strain
5. MHPBN, 10% strain
6. MHPBN, 20% strain

```
Listing 7.1: Implementing a counting semaphore using a binary semaphore

/* Structure used to implement a counting semaphore */
typedef struct {
    int count;
    int wakeups;
    BinarySemaphore mutex;
    BinarySemaphore block;
} CountingSemaphore;

/* Initialize a counting semaphore */
void InitCountingSemaphore(CountingSemaphore *s, int initialCount)
{
    s->count = initialCount;
    s->wakeups = 0;
    InitBinarySemaphore(&s->mutex, 1);
    InitBinarySemaphore(&s->block, 0);
}

/* Wait operation for counting semaphore */
void CountingWait(CountingSemaphore *s)
{
    WaitBinarySemaphore(&s->mutex);
    s->count--;
    if (s->count < 0) {
        s->wakeups++;
        SignalBinarySemaphore(&s->mutex);
        WaitBinarySemaphore(&s->block);
    } else {
        SignalBinarySemaphore(&s->mutex);
    }
}

/* Signal operation for counting semaphore */
void CountingSignal(CountingSemaphore *s)
{
    WaitBinarySemaphore(&s->mutex);
    s->count++;
    if (s->wakeups > 0) {
        s->wakeups--;
        SignalBinarySemaphore(&s->block);
    }
    SignalBinarySemaphore(&s->mutex);
}
```

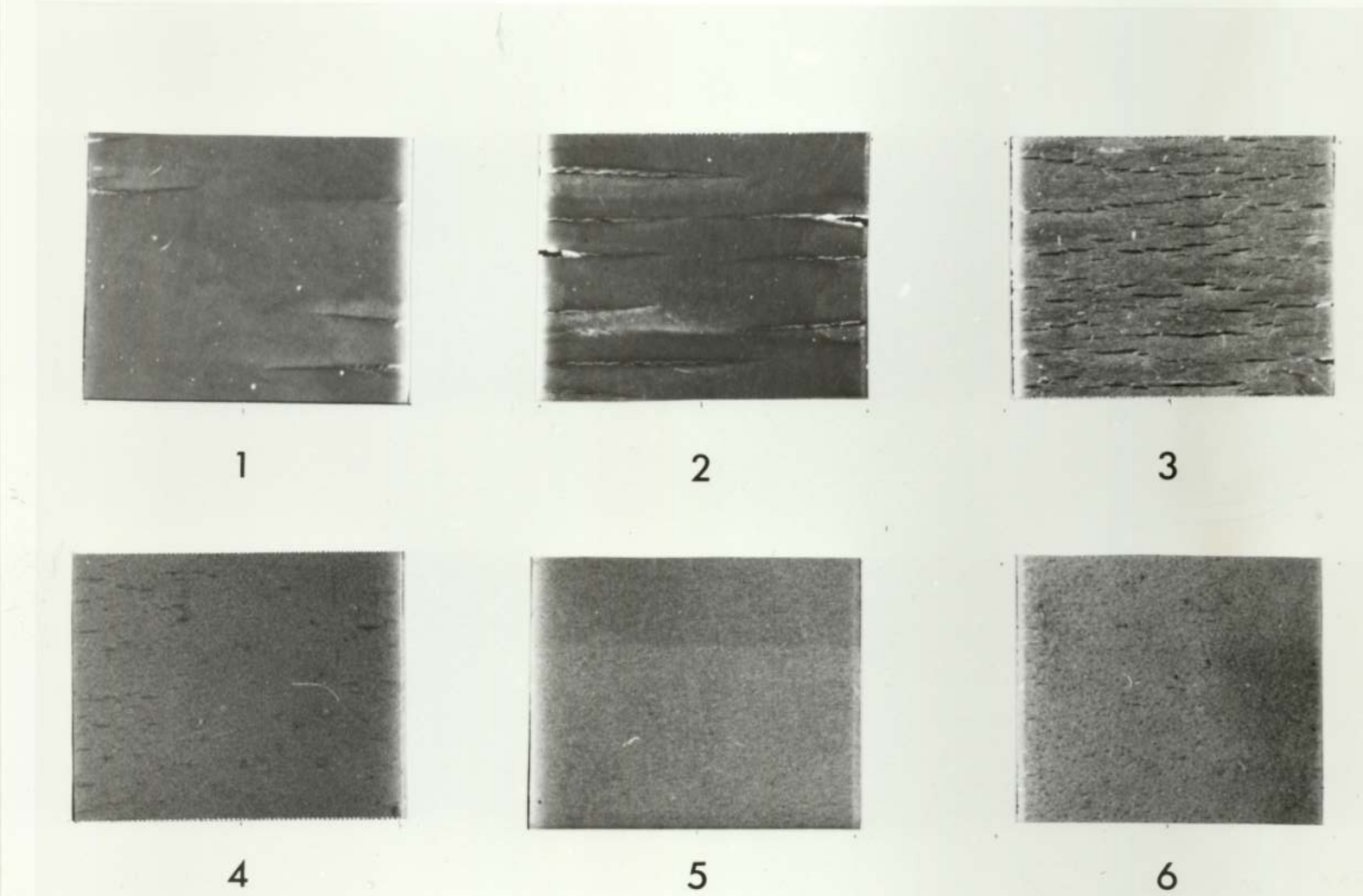


Fig. 7.8

when the test piece was strained by an extension of 10%. At all other extensions the rate of deterioration was slower. Furthermore above this peak strain the rate of ozone cracking decreased with increasing extension. Figure 7.7 shows the rate of ozone cracking as a function of strain and highlights this effect.

Figure 7.8 shows photographs of the extent of ozone cracking for rubber protected by a typical nitrone (MHPBN) and IPPD at test piece strains of 5, 10 and 20 percent respectively after 30 hours of ozone exposure. The photographs highlight the improved static antiozonant efficiency of the nitrones relative to the commercial material IPPD.

The photographs in figure 7.8 also show that the nature of the crakcs formed in the rubber protected by the nitrone is different to that protected by IPPD. In the case of the rubber protected by the IPPD the cracks were sharp and deep. However the cracks formed in the rubber protected by the nitrone were very fine and shallow. In contrast to the rubber protected by the IPPD however although the cracks were fine and shallow, their density per unit area of rubber surface was greater. The nature of the cracks formed for the other nitrones too were similar to that of MHPBN. For the control the cracks were sharp and deep like that for IPPD. Furthermore in

the case of the nitrones, upon exposure to ozone the texture of the rubber surface changed becoming matt and light coloured in appearance. This change in the rubber surface was not caused by bloom as it only occured when the strained rubber was exposed to ozone. When the rubber was strained without exposure to ozone no such change in the texture of the surface was observed. No bloom was observed either. This change in the texture of the rubber upon ozone exposure was not observed for the control nor for the rubber containing IPPD or HPPD.

7.A.4 Discussion

It is well known that N,N'-disubstituted-p-phenylenediamines, are effective antiozonants and are commercially used as such. The principle theories for their activity have been described in section 1.10. The first is the scavenger theory in which the ozone is believed to react preferentially with the antiozonant. Thus the protective agent competes with the double bonds in the rubber for the ozone. The second theory is the protective layer theory which suggests that the ozonised antiozonant products form a protective layer on the surface of the rubber so preventing further attack by the ozone on the rubber. The third is the relinking theory. This theory states that the antiozonant prevents scission of ozonised rubber by recombining with the severed double bonds. The

fourth mechanism is the self healing film theory which states that the antiozonant reacts with the zwitter ion to give a low molecular weight, inert, self healing film on the rubber surface. There is yet another theory which proposes that the antiozonant increases the critical strain energy of the rubber consequently reduces the rate of crack formation and propogation within the rubber.

The literature has presented a good case for each theory which makes it difficult to attach proper significance to any or all of them. In reality they may all contribute to some extent to the overall antiozonant protection activity. It has also been suggested that for efficient antiozonant activity, antiozonants must migrate to the surface of the rubber. This will depend to some extent on their compatibility with the rubber and relative rates of diffusion within the rubber vulcanisate. However recently[117] there has been evidence which casts some doubt on the necessity for the antiozonant to migrate to the surface for efficient activity.

Recently Lattimer et al[112,113] have used attenuated total reflectance(ATR) infrared spectroscopic techniques and scaning electron microscopy to study rubber surfaces of vulcanisates protected by N,N'-dialkyl-p-phenylenediamines. They suggested that the principal modes of antiozonant activity for these compounds are a combination

of the scavenger theory and the protective film mechanism. The evidence[112,113] for this was that only ozonised products of the antiozonant were detected on the rubber surface. Furthermore the ozonised products had formed a continous "elastic" film on the surface of the rubber beneath which there was unreacted rubber. No rubber--ozone products were detected on the surface or beneath the "skin" formed from the ozonised products of the antiozonant. The ozonised products forming the "skin" consisted mainly of amides, nitrones, nitroso-aryls, nitroso-alkyls and various conjugated aromatic species. They had been identified by gas liquid chromatography, mass spectrometry and micro-ATR techniques. Lattimer et al[112] have suggested that two principal mechanisms govern the ozonisation of the p-phenylediamines. The first is amine oxide formation and the second is oxidation of the side chains.

The first mechanism involves the formation of an amine-ozone adduct of the type:

$$R_3 - \overset{+}{N} - O - O - \overset{-}{O}$$

Subsequent dissociation of this adduct leads to the formation of nitroso and nitro compounds. The second mechanism, in which the side chains are oxidised, leads to the formation of a number of low molecular weight

components including some that contain an amide moiety. A minor pathway involving a nitroxyl radical intermediate leads to the formation of stable dinitrone species. Razamovskii et al[114] have reported similar results for rubber protected by IPPD.

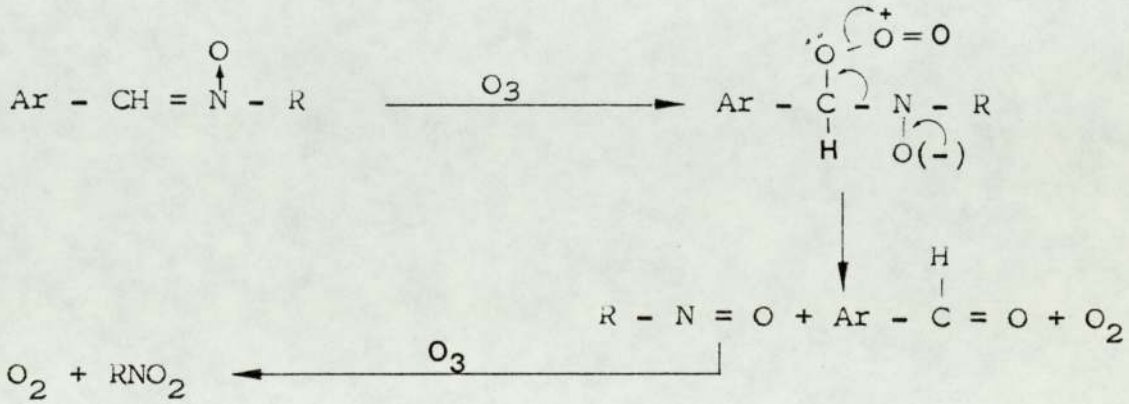
In the present work the hindered alicyclic amines, nitroxyl radicals and hydroxylamines were found not to possess any antiozonant activity relative to the control. The inactivity of these compounds was not entirely unexpected for although the amines and hydroxylamines are able to react with ozone to give the nitroxyl radicals, the protective action of the latter is very weak[34]. Further more the inactivity of these compounds could be due to the inability of the alicyclic nitroxyl radicals to terminate peroxidic species formed during secondary oxidative reactions involving decomposition of the ozonised rubber molecules[101].

Unlike the alicyclic series however, all the nitrones and the nitroso compound MNP were found to possess good antiozonant activity. Furthermore the activity of these compounds exceeded that of the commercial materials IPPD and HPPD.

HPPD was found to have very little antiozonant protective action in the rubber (table 7.2). This result was very surprising since HPPD is marketed as a static antiozonant under the trade name Santoflex 77. Infact the IPPD was considerably better than HPPD as a static antiozonant.

The high activity of the nitrones and PMN must be due to the known ability of these compounds to react with ozone. In addition they must be satisfying the other compatibility and migration criteria required for good antiozonant protection of rubbers.

Nitrones are known to be very reactive towards ozone. Riebel et al[207] have reported that solutions of nitrones in methylene chloride (PBN and α,N-di-phenylnitrone respectively) react very rapidly with ozone even at -78°C. The products were the aldehyde and the nitro compound which were obtained in very high yields. The mechanism of the reaction is outlines in scheme 7·1.



Scheme 7·1

Thus one nitrone molecule can scavenge two ozone molecules. The antiozonant activity of PMN too must be associated with its capacity to react with ozone.

All the nitrones except for MPPN and CPPN were found to exhibit good antiozonant activity. Except for CPPN and MPPN the variation of the substituents on the aryl group of the nitrone did not show a significant trend (table 7.1; PBN, HPBN, MHPBN and PMN, MHPMN, BHPMN). The slight differences in their activities may be due to compatibility and migration effects of the additives in the rubber.

The lack of activity of MPPN may be attributed to the electron donating capacity of the methoxy group situated on the phenyl ring para to the nitrone function. Riebel et al[207] have suggested that the ozonisation of the nitrone occurs by nucleophilic attack of ozone on the carbon atom of the carbon-nitrogen double bond. A decrease in the electrophilicity of this carbon atom will retard the rate of ozonisation of the nitrone. Electron donating substituents on the phenyl ring particularly para to the nitrone function will therefore retard the rate of ozonisation of the nitrone. Conversly electron withdrawing substituents (e.g.: Cl- as in CPPN) will have the opposite effect and will increase the rate of ozonisation of the

nitrone.

The small variations in activity found when the nature of the N-alkyl group was changed (table 7.2; MHPMN, MHPEN, MHPPN and MHPBN) may be due to the relative ease of the respective nitrones reacting with ozone and or compatibility/migration effects.

The scavenging of ozone by the nitrones is a stoichiometric process (scheme 7·1). Therefore this alone is not sufficient to explain the high antiozonant activity of the nitrones. In all the rubber test pieces containing the nitrones, without exception, the texture of the rubber test piece changed upon ozone, exposure. Moreover the colour of the rubber became lighter. These changes were not a result of bloom, as it was not formed in the absence of ozone. It probably is a layer of ozonised nitrone porduct and it may possibly function by protecting the rubber against further ozone attack. Furthermore the nature and density of the cracks formed in the rubber test pieces protected by the nitrones were different to that protected by IPPD, HPPD or in the rubber with no protection. This too is also an important factor in arguing the reason for the good antiozonant activity of the nitrones. Figure 7.8 shows photographs of rubber test pieces protected by IPPD and a typical efficient nitrone (MHPBN). In the case of the rubber protected by

MHPBN the cracks were very fine, small and shallow. The density of the cracks per unit area of rubber surface was also high. In contrast for the rubber protected by IPPD the cracks were sharp, deep, large and the density of cracks per unit area was low. Therefore in the case of the rubber protected by the nitrone because the cracks are fine, shallow and large in number per unit area of rubber surface, the total stress (tearing energy) at the tip of any crack will be much less than when the cracks are fewer and deeper. The reason for this is due to efficient stress distribution. Therefore in such a case the cracks will grow at a slower rate than when the cracks are few deep and large. This is indeed what was observed and is highlighted in figures 7.3 and 7.7. These figures compare the relative rates of crack growth for the rubber test pieces protected by the nitrones and the commercial agents.

The bis-nitrone (BMHPPN) was slightly more effective than its mono-nitrone counterpart (MHPEN). The improved efficiency may be due to better compatibility with the rubber and the presence of two nitrone functions in the molecule.

Upon extraction of the vulcanisates the antiozonant activity of the nitrones was lost (table 7.5). The protective efficiency of the commercial antiozonant (IPPD)

was lost also after extraction. The loss of protection was probably due to extraction of the protective agents from the rubber.

The loss of antiozonant activity upon long premilling of the nitrone (MHPBN) with the rubber on the two-roll open mill (table 7.5) may be associated with the interaction of some of the nitrone with peroxidic entities formed in the rubber during the premilling operations. Therefore less nitrone is available to function as an antiozonant.

The lack of antiozonant activity for WSP was not unexpected since phenolic antioxidants are known not to protect rubber against ozone attack[1,5,188]. For the combination of WSP with MHPPN there was a slight loss in the protective efficiency of the nitrone. The reason for this loss of activity of the nitrone is not known. It must be pointed out however that the effectiveness of the combination is still greater than that of IPPD.

Although the combination of NODP with MHPPN was not additive, the protection against ozone cracking is very good and is very much superior to that of IPPD (table 7.4). The antiozonant efficiency of the combination was slightly less than that of the nitrone alone (table 7.4).

The reason for this may be the destruction of some of the nitrone by interaction with nitric oxide radicals (•NO) liberated from the NODP during the compounding and vulcanising stages. N-nitroso compounds are known to release nitric oxide radicals during the curing of rubber[208-210].

Figure 7.7 shows that the rate of ozone cracking of the rubber test pieces was fastest at a strain level of 10%. At all other strains the rate of cracking was slower. The reasons for the existance of the peak strain has already been described in section 1.5.2. Raab and Rospesil[211] have suggested that it is due to strain induced orientation effects. Kuzminsky[34] has suggested that at high strains the double bonds become more single bond like in character and become increasingly so as the strain is increased. Therefore the rate of ozone attack on the rubber is correspondingly decreased.

7.B ASSESSMENT OF THE ANTIOXIDANT PROPERTIES BY STRESS RELAXATION STUDIES.

7.B.1 Introduction

Stress relaxation studies involve the monitoring of the decay in stress for a test piece held at constant

elongation. It can be done at any desired temperature. The technique was first developed by Tobolsky and co-workers[212-214] and was used to study the breakdown of rubber networks. Subsequently the technique has found wide usage in the evaluation of antioxidant performance during thermal oxidative ageing of rubbers, providing the same curing formulation is used in all cases[215]. The technique is very useful since it provides a quick assessment of the protection imparted to the rubber by the antioxidant since the decay in stress can be monitored automatically by the instrument.

Stress relaxation may be of two types, either continuous or intermittent. In continuous stress relaxation the rate of decay of stress in a rubber test piece is a direct measure of breakdown of the network. Any new cross-links formed during the ageing procedure are assumed to be in equilibrum with the breakdown of the rubber and do not contribute to the stress. In intermittent stress relaxation the test piece is unstretched for most of the time and is only extended for short intervals to measure the stress. In this case the new cross-links will contribute to the stress. In both cases the decay in stress is measured by the ratio τ / τ_0 where τ_0 is the original stress and τ is the stress after a given time interval. Intermittent stress relaxation is used

particularly for synthetic rubber vulcanisates (such as S.B.R. vulcanisates) where cross-linking occurs during thermal oxidative ageing. For natural rubber vulcanisates, where chain scission processes predominate during the ageing process, continuous stress relaxation is sufficient to provide information on the antioxidant performance in the rubber.

7.B.2 Experimental Procedure

The compounds described in section 2.1 were incorporated into the rubber as described in section 3.2, 4.2, 5.2 and 5.3.1. The vulcanisation was carried out as described in section 3.5.2. Test pieces were cut and conditioned as described in sections 3.7 and 3.8. Continuous stress relaxation was done using the Wallace Shawbury Self Recording Age Tester as described in section 3.11. The test pieces were strained by an elongation of 60% and the test was carried out at a temperature of 100 $\pm$ 2°C. The air inflow rate into the cell of the oven was 0·071 m^3 per hour. The results were treated in the manner described in section 3.11.3.

7.B.3 Results

Table 7.9 shows the times for the stress to decay to 50% of its original value (τ_{50} time) for the vulcanisates

Continuous stress relaxation strain = 60%; temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3
Control	2·8
TMP	1·3
TMOP	1·3
TMPD	1·3
TMMP	1·0
TMPS	1·6
TMOPS	1·3
TMPDS	1·0
TMOPX	1·6
TMOXPZ	1·6
BHTMOP	7·0

Table 7·9: τ_{50} times for continuous stress relaxation of conventional C.B.S. vulcanisates containing the hindered alicyclic nitroxyl radicals and precursors ([additive] = 1 p.h.r.)

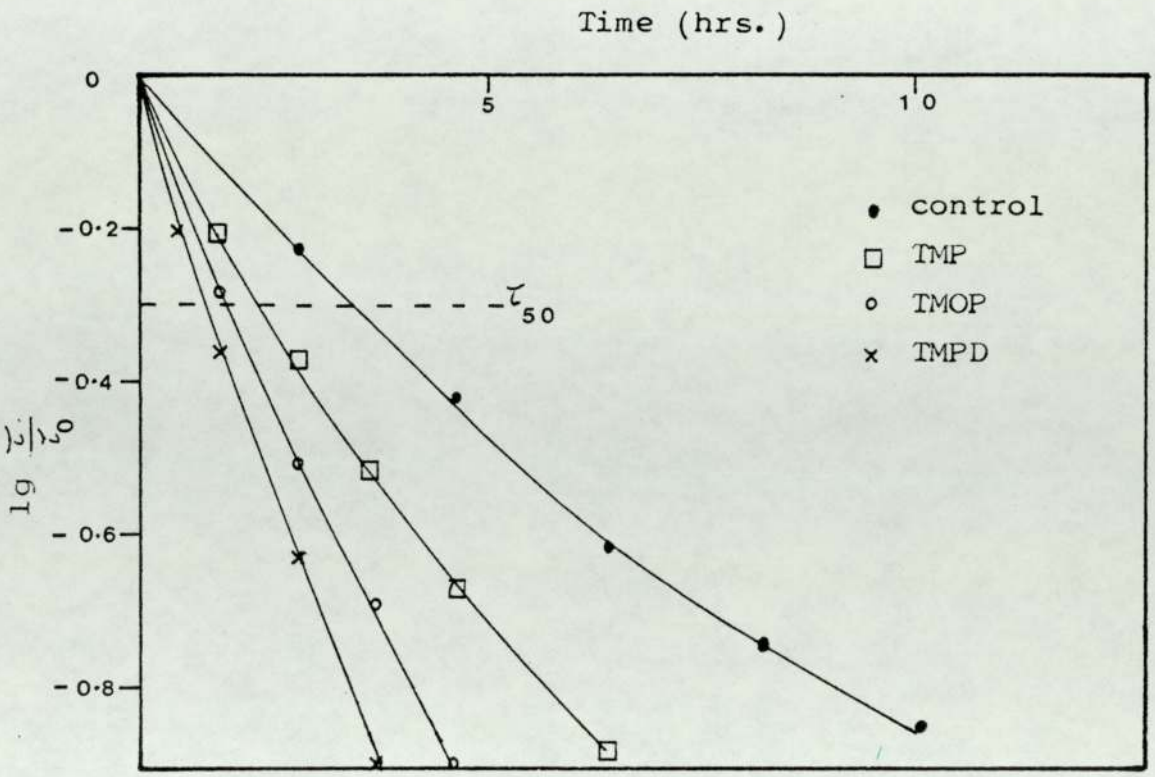


Fig. 7·9: Continuous stress relaxation for conventional C.B.S. vulcanisates protected by TMOP and its precursors (1 p.h.r. each; 60% strain; 100 ± 2°C)

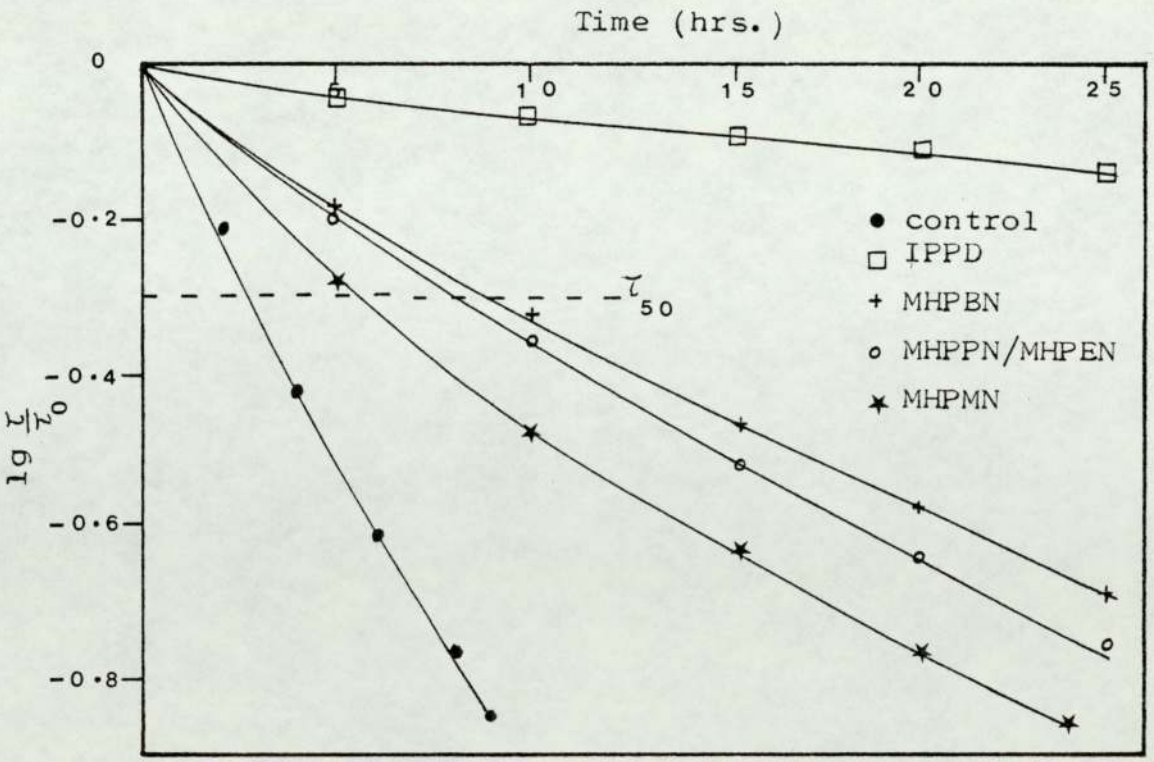


Fig. 7·10: Continuous stress relaxation for conventional C.B.S. vulcanisates protected by various nitrones (1 p.h.r. each; premill time = 2 min.; 60% strain; 100 ± 2°C)

containing the hindered alicyclic amines, nitroxyl radicals and hydroxylamines. In all cases except for BHTMOP, the compounds did not show any antioxidant activity. Infact they were found to act as pro-oxidants, as the vulcanisates containing these additives deteriorated faster than the control. Figure 7.9 shows typical stress relaxation curves for the amine, nitroxyl radical and hydroxylamine illustrating their pro-oxidant behaviour. BHTMOP on the other hand exhibited anti-oxidant activity (table 7.9).

There was no difference in the behaviour of the additives when unextracted rubber was used to make up the vulcanisates.

Table 7.10 shows the τ_{50} times for the all the nitrones, IPPD, MNP and MHB. It is clear that for the nitrones optimum antioxidant activity was observed only for those containing the "semi-hindered" phenolic antioxidant function (i.e. for MHPMN, MHPEN, MHPPN and MHPBN). Furthermore except for the N-methyl nitrone the nature of the N-alkyl group did not significantly affect the antioxidant efficiency.

Figure 7.11 shows the stress relaxation curves for the nitrones PMN, MHPMN and BHPMN. The figure illustrates

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3 *
Control	2·8
IPPD	50·0 ± 2
MHB	3·0
MNP	4·6
MHPBN	8·8
HPBN	8·6
PBN	2·6
PMN	2·6
BHPMN	3·2
MHPMN	6·3
MHPEN	8·0
MHPPN	8·5
MPPN	2·5
CPPN	3·8
BHPPN	9·0

* : except where otherwise indicated

Table 7·10: τ_{50} times for continuous stress relaxation of conventional C.B.S. vulcanisates containing the nitrones and other additives ([additive] = 1 p.h.r.; all nitrones premilled for 2 minutes).

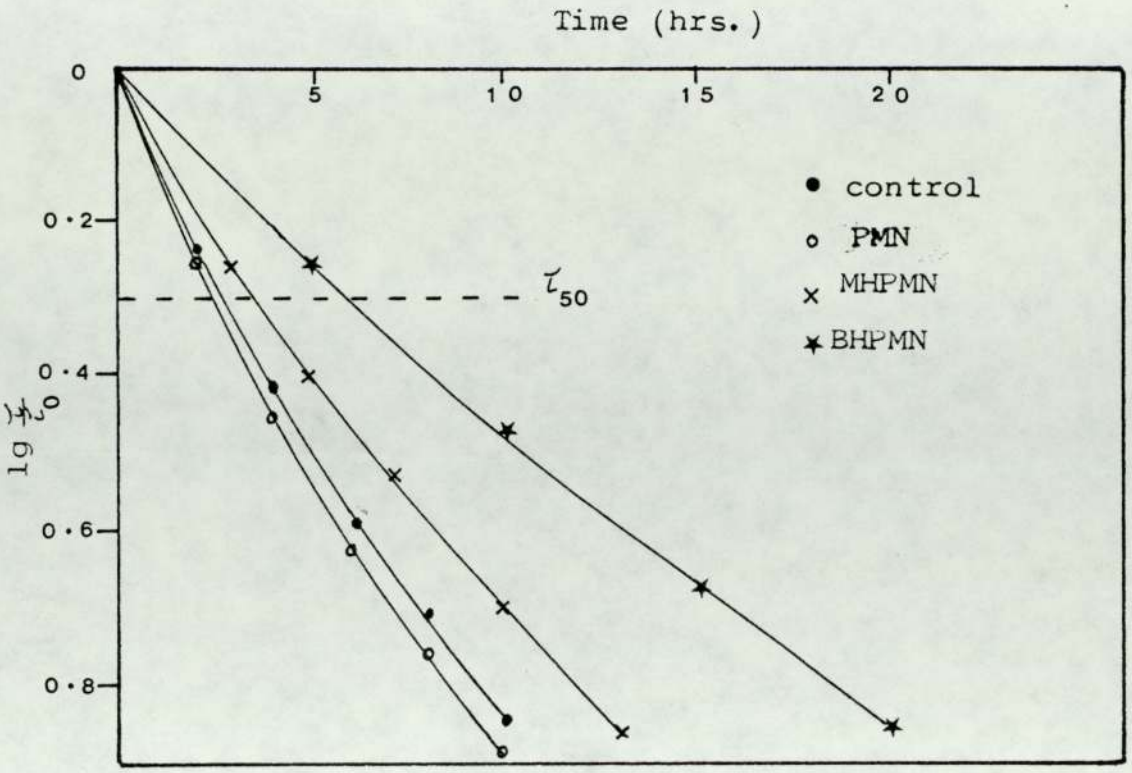


Fig. 7·11: Comparison of continuous stress relaxation curves for the N-methyl nitrones in conventional C.B.S. vulcanisates (1 p.h.r. each; premill time = 2 mins.)

the effect of the substituents on the phenyl ring. It is clear that increased steric hinderence of the groups ortho to the phenolic function decrease the antioxidant activity. A similar trend was observed for the N-tert--butylnitrones (see table 7.10 for τ_{50} times)

Table 7.10 shows that the optimum activity for the best nitrones (MHPPN & MHPBN) was a τ_{50} time of approximately ten hours. Moreover the antioxidant efficiency of the bis-nitrone (BMHPPN) in the rubber did not differ very much to its mono-nitrone counterpart (MHPEN).

The antioxidant activity for the nitrones was much less than that observed for IPPD (table 7.10) & WSP (table 7.11). Table 7.11 shows the τ_{50} times for the vulcanisates containing WSP, NODP and their respective combinations with MHPPN. The combination of WSP with MHPPN appears to be antagonistic with respect to the activity of WSP. However the combination of NODP with MHPPN is slightly less than additive.

Table 7.12 shows the effect of premilling MHPBN with the rubber prior to the compounding operations. It is evident that premilling decreases the antioxidant activity slightly.

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 1·0 *
Control	2·8 ± 0·3
IPPD	50·0
MHPPN	8·5 ± 0·3
WSP	34·0
MHPPN + WSP	30·0
NODP	42·0
NODP + MHPPN	48·0

* : except where otherwise indicated

Table 7·11: τ_{50} times for continuous stress relaxation of conventional C.B.S. vulcanisates containing combination of MHPPN with other antioxidants ([additive] = 1 p.h.r. each).

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Milling time (min)	Time to τ_{50} (hrs.) ± 0·3
0	11·0
2	8·8
4	8·8
6	9·5

Table 7·12: Effect of premilling time of MHPBN with rubber on the times to τ_{50} in conventional C.B.S. vulcanisates ([additive] = 1 p.h.r.)

Table 7.13 shows the τ_{50} times for the nitrones MHPMN, MHPEN, MHPPN and MHPBN incorporated into the rubber as a normal additive. It shows that there was no significant difference to the values obtained when the compounds were premilled with the rubber for two minutes prior to the compounding stage (cf. table 7.10).

A study of the antioxidant activities for the nitrones MHPMN, MHPEN, MHPPN and MHPBN in vulcanisates made up from unextracted rubber showed no difference to the activity when extracted rubber was used. Table 7.14 shows the results. Table 7.15 shows the τ_{50} times for the vulcanisates after acetone extraction prior to testing. It shows that after extraction much of the original antioxidant activity was lost.

7.B.4 Discussion

The results described in the previous section were not unexpected. None of the hindered alicyclic compounds except for BHTMOP were found to possess any antioxidant activity. Indeed they were all found to be pro-oxidants since they caused a faster deterioration of the rubber than the control.

The lack of stabilisation on the part of the alicyclic amines is due to its ready conversion to nitroxyl radicals

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3
Control	2·8
MHPBN	11·0
MHPPN	10·0
MHPEN	10·0
MHPMN	7·3

Table 7·13: τ_{50} times for continuous stress relaxation of conventional C.B.S. vulcanisates containing nitrones incorporated into the rubber as a normal additive without any prior premilling ([additive] = 1 p.h.r.)

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3 *
Control	3·0
IPPD	51·0 ± 2
MHPBN	9·0
MHPPN	9·0
MHPEN	8·5
MHPMN	7·0

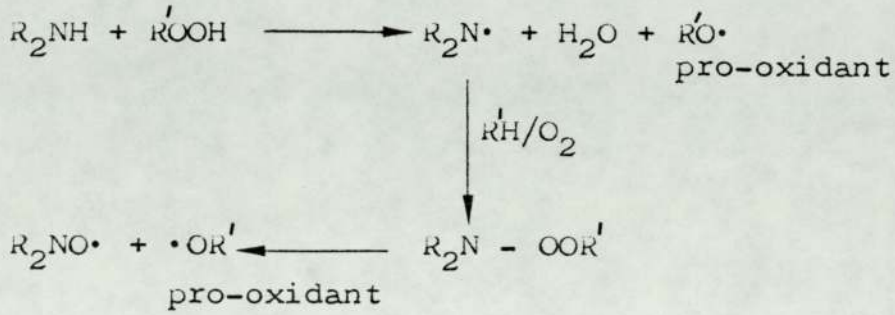
* : except where otherwise indicated

Table 7·14: τ_{50} times for the stress relaxation of conventional C.B.S. natural rubber vulcanisates made up from unextracted rubber containing nitrones. (all nitrones premilled for 2 minutes prior to compounding [additive] = 1 p.h.r.).

Continuous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3
Control	2·0
IPPD	6·0
MHPBN	3·5
MHPPN	3·6
MHPEN	3·5
MHPMN	3·2

Table 7·15: τ_{50} times for continuous stress relaxation of conventional C.B.S. vulcanisates containing nitrones and extracted prior to testing. (all nitrones premilled for 2 minutes; [additive] = 1 p.h.r.)

to its ready conversion to nitroxyl radicals by a stoichiometric interaction with hydroperoxides (scheme 7.2).



Scheme 7·2

The reaction involves the formation of pro-oxidant species ($R'O\cdot$) which contribute to the acceleration of the thermo-oxidative degredation of the polymer.

The nitroxyl radicals do not further interact with hydroperoxides. They may be destroyed[205] by interactions with thermolysis products of hydroperoxides or may become associated[204] with the hydroperoxides. However these reactions are not terminating steps especially at the elevated termperature used in the test.

Under thermal oxidative conditions hydroxylamines too are immediately converted to nitroxyl radicals[72,76]. They are known to exhibit some antioxidant effect during

the thermo-oxidative degredation of polymers. However this effect was not seen, probably due to subsequent antagonistic interactions of the nitroxyl radical with other antioxidant species formed in the sulphur cross-linked rubber.

It has been reported that alicyclic amines interfere antagonistically with the antioxidant activity of sulphur containing compounds[216]. Furthermore it is well known that alicyclic nitroxyl radicals interact with thiols, and disulphides giving rise to the amine plus pro-oxidant species[178,179]. These pro-oxidant species include thyl radicals and sulphenyl radicals[178,179].

It is well known[1] that thermal oxidation of a sulphur cross-linked rubber gives rise to oxidation of the cross-links. These oxidised sulphur cross-links are known to impart protection to the rubber although chain scission is normally associated with the formation of these antioxidant species. The oxygenated sulphur compounds function as antioxidants by the PD-C mechanism described in scheme 1.5. Additional protection to the rubber is given by the ZMBT and MBT which are formed during the vulcanisation stages in conventional C.B.S. vulcanisates[215]. In the presence of nitroxyl radicals the antioxidant efficiency of the sulphur cross-links the ZMBT and the MBT would be reduced due to competing interactions with

the nitroxyl radical itself. This is probably the reason why all the hindered alicyclic amines, nitroxyl radicals and hydroxylamines exhibited pro-oxidant behaviour relative to the control during the thermal oxidative stress relaxation of the rubber.

The antagonistic effects of the interactions of alicyclic nitroxyl radicals with sulphur containing compounds during thermal oxidation is exemplified by the enhanced pro-oxidant behaviour of the nitroxyl radicals containing the xanthogenato functional groups (TMOPX; TMOXPZ; table 7.9).

The antioxidant activity observed for the nitroxyl radical containing the hindered phenol antioxidant function (BHTMOP) must be due to the CB-D activity of the hindered phenol. Hindered phenols are well known stabilisers and are used widely to stabilise thermo-oxidative deterioration of rubbers and other polymers. They function by the CB-D mechanism described in section 1·8. In the literature[71] it has been reported that nitroxyl radicals are capable of undergoing hydrogen abstraction reactions with phenols. However in the case of BHTMOP, this reaction is unlikely due to steric hinderence around the nitroxyl and phenol functions respectively.

The thermo-oxidative stabilising activity of the nitrones (table 7·10) too was as expected. Nitrones are known to react with hydroperoxides[96]. Indeed nitrones containing phenolic antioxidant functions have been used as substantive antioxidants in cis-polyisoprene rubber[99]. None of the nitrones used in the present study were found to bind to the rubber (section 6.B.1). Table 7·10 shows that the structure-activity relationship for the nitrones containing the phenolic antioxidant function were the same as that reported in the literature[99]. Increased steric hinderence of the phenolic function decreased the overall antioxidant efficiency of the nitrone. (table 7.10; BHPMN, MHPMN, PMN; figure 7·11). The inverse of the normal structure-activity relationship is probably due to a combination of the electron withdrawing effects of the nitrone group para to the phenol site and auto-synergistic peroxide decomposition by the nitrone function.

A study of the antioxidant activity for the nitrones containing different N-alkyl groups (MHPMN, MHPEN, MHPPN and MHPBN; table 7·10) showed that except for the N-methyl nitrone (MHPMN) the nature of the N-alkyl group did not significantly affect their antioxidant activities. The reduced efficiency of the N-methyl nitrone may be related to the rates at which it reacts with the hydro-

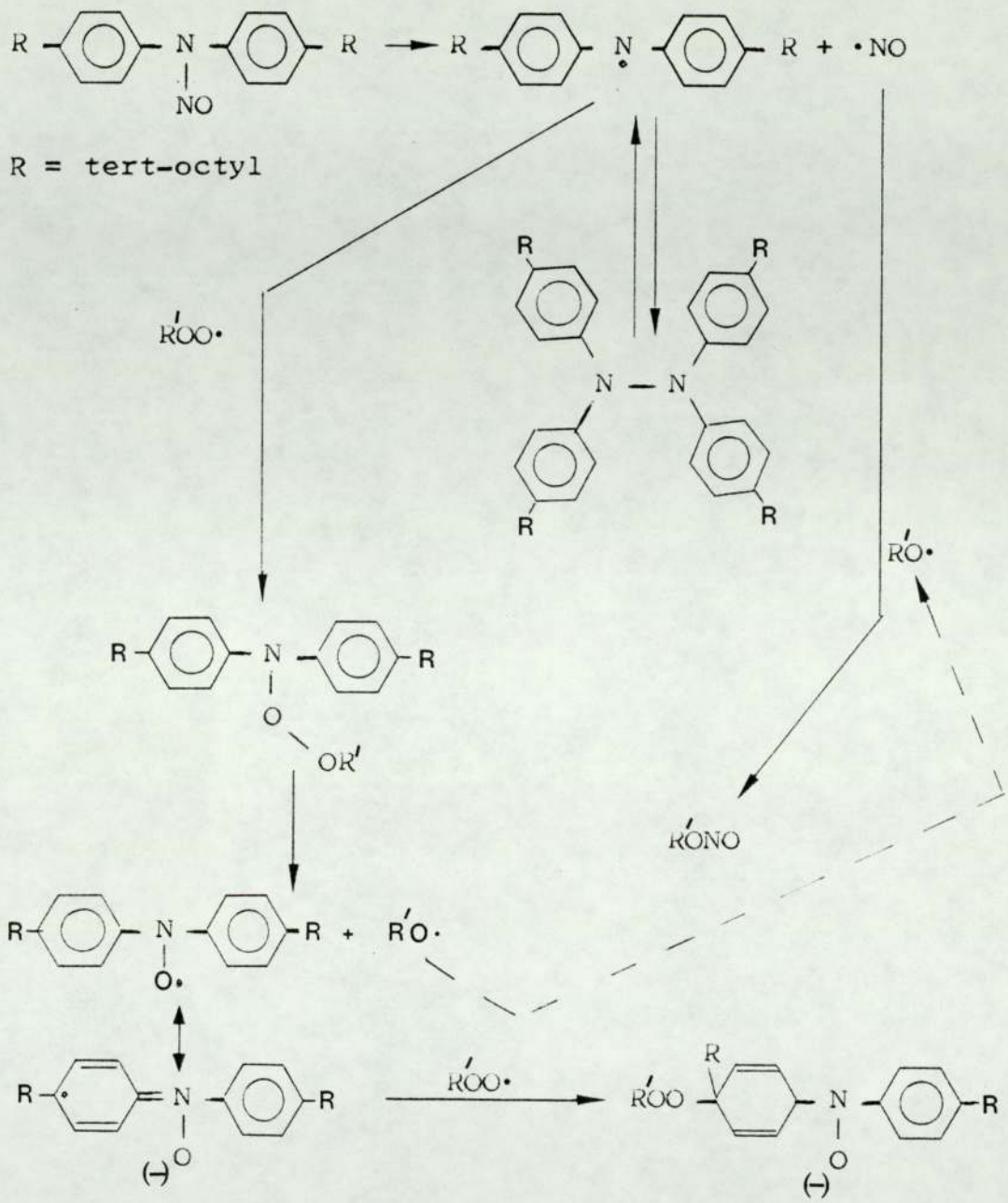
peroxides or loss of the antioxidant by volatility.

The antioxidant activity of the bis-nitrone(BMHPPN) did not differ very much to its mono-nitrone(MHPEN) counterpart (table 7·10). This was probably because in terms of functional molarity the amount of BMHPPN and MHPEN was the same. Furthermore it implies that antioxidant loss by volatility for the mono-nitrone MHPEN was not very significant. If antioxidant loss of MHPEN by volatility was occuring, then BMHPPN having a significantly higher molecular weight than its mono-nitrone counterpart should have had much better antioxidant activity during the stress relaxation of the vulcanisate.

The nitrones CPPN and MPPN (table 7·10) had little activity relative to MHPPN. However relative to the control CPPN was slightly better than MPPN. The difference in the antioxidant behaviour of the two compounds may be attributed to the electron withdrawing capacity of the chlorine atom in CPPN. Electron withdrawing substituents on the phenyl ring in the nitrone (particularly at the para-site) of reaction of the nitrone function with the hydroperoxides. Conversly electron donating substituents (e.g.MeO-) will retard the rate of reaction.

Table 7·13 shows that when the nitrones MHPMN, MHPEN, MHPPN and MHPBN were incorporated into the rubber as additives without any prior premilling, the antioxidant activities were slightly greater than that when the nitrones were premilled with the rubber for two minutes. (cf: table 7·9). Table 7·12 shows that within experimental error there was no significant effect on the τ_{50} times for the vulcanisates containing MHPBN premilled with the rubber for two, four and six minutes respectively. The result suggests that unlike the case of antifatigue and antiozonant activity (chapter 5 and chapter 7.A respectively) the best antioxidant activity was obtained when no premilling was done. The reason for this is probably due to destruction of some of the nitrone during the premilling operations.

The antioxidant protection imparted to the vulcanisates by the nitrones was small relative to the protection given by IPPD or WSP. The τ_{50} times for these two compounds were 50 and 34 hours respectively (table 7·11). In order to increase the antioxidant efficiency of the nitrone a 1:1 mixture of MHPPN and WSP (1 p.h.r. each) was studied. Table 7·11 shows that the τ_{50} time for this mixture was not additive. In fact the τ_{50} time was 30 hours. This is slightly antagonistic with respect to the activity of WSP alone. The slight antagonism may



Scheme 7·3

be due to competition between the nitrone and WSP for alkylperoxyl radicals. WSP alone is a very good antioxidant for rubber because of its efficient CB-D antioxidant activity and its lack of volatility due to its high molecular weight.

NODP has also been found to be an effective antioxidant for rubber under stress relaxation conditions[182]. The τ_{50} time for rubber protected by this agent is shown in table 7·11. Its good thermal antioxidant activity is attributed to its decomposition[182,208-210] to diphenylamino radicals and nitric oxide radicals and subsequent scavenging of alkylperoxyl and alkoxyl radicals by these species[182] (scheme 7·3).

The antioxidant activity for the combination of NODP with MHPPN (table 7·11) was slightly less than additive. They do not synergise, but more importantly from the technological point of view they do not antagonise.

Table 7·15 shows that after extraction most of the antioxidant activity of the nitrones was lost. Similarly for IPPD. The small antioxidant effect still observed must be due to traces of additive still left in the rubber after the extraction process. In section 6.B.1 it was shown that none of the nitrones were significantly bound during the vulcanisation process.

The decrease in the τ_{50} time for the control after extraction is due to the removal of ZMBT, MBT and other antioxidant species from the rubber.

Table 7·14 shows that extraction of the rubber prior to compounding has little effect on the antioxidant activity.

7.C ASSESSMENT OF THE DISCOLOURATION AND THE STAINING PROPERTIES

7.C.1 Introduction

It was pointed out in the introduction (section 1·13) that discolouration of the rubber and staining caused by the protective agent is aesthetically undesirable particularly for light coloured rubber products. For rubber products which are dark in colour further discolouration is not particularly important. However for light coloured rubber products it is imperative to use protective agents which do not cause the rubber to discolour or stain. Therefore it was considered important to test the discolouration and staining properties of all the compounds that were used in the work described in this thesis. In particular since some of the nitrones showed good antiozonant and

antifatigue properties it was worthwhile studying their discolouration and staining properties.

7.C.2 Experimental Procedure

The degree of discolouration and staining of the rubber by the compounds listed in table 2·1 were studied relative to the control and the commercial agents (IPPD and WSP respectively). The testing was done by the procedure described in section 3·12.

Initially the discolouration of the rubber containing the additives was assessed visually in diffused day light and graded on an arbitary numerical scale from 0 to 12. On this scale the control was denoted a value of 5. Test pieces which were darker than the control were given values greater than 5 and those that were lighter than the control were given value below 5.

For the technologically interesting compounds, in particular the nitrones MHPBN, MHPPN, MHPEN and MHPMN the degree of discolouration imparted to the rubber was also assessed after exposure to U.V. light in an artificial daylight cabinet (section 3·12). The degree of discolouration imparted to the rubber by these four nitrones was also assessed quantitatively by reflectance

spectroscopy using the Colour Master-V, spectrometer.

The staining properties of the vulcanisates containing MHPBN, MHPPN, MHPEN and MHPMN respectively were studied as described in section 3.12.2. The results were compared with that for IPPD, WSP and the control.

7.C.3 Results

Table 7·16 compares the discolouration imparted to conventional C.B.S. vulcanisates by the various protective agents used in the work described in this thesis. The assessment was done visually. The table also compares and shows the results for a typical non-discolouring commercial antioxidant (WSP) and for a strongly discolouring antidegradant (IPPD). It is clear that in relation to the control none of the alicyclic amines and derivatives nor the nitrones significantly discoloured the rubber. Indeed the alicyclic nitroxyl radicals and their hydroxylamines had a bleaching effect on the rubber. In relation to WSP none of the nitrones were significantly different.

Table 7·17(a) compares the visual assessment of the discolouration of the vulcanisates containing the technologically interesting nitrones, IPPD and WSP after

Additive	Discolouration rating *
Control	5
IPPD	8
HPPD	7
WSP	3
TMP	5
TMOP	2
TMPD	2
TMMP	4
TMPS	4
TMOPS	2
TMPDS	2
TMOPX	2
TMOPZ	2
BHTMOP	3
MHPBN	2
HPBN	2
PBN	5
PMN	5
BHPMN	4
MHPMN	5
MHPEN	6
MHPPN	5
CPPN	5
MPPN	5
BMHPPN	5
MNP	5

* : assessment made visually
Discolouration rating: 0, 1, 3, 4, 5, 6, 7, 8,
- increasing discolouration →

Table 7·16: Comparison of the discolouration properties of the additives in conventional C.B.S. vulcanisates ([additive] = 1 p.h.r.; all nitrones premilled for 2 minutes).

Additive	Time of exposure to U.V. light (hrs.)		
	0	25	50
	Discolouration rating *		
Control	5	5	5
IPPD	8	8	10
WSP	3	3	4
MHPBN	2	2-3	3
MHPPN	5	5-6	6
MHPEN	6	5	6
MHPMN	5	5	6

* : assessment made visually
rating as for table 7·16

Table 7·17 (a)

Additive	Time of exposure to U.V. light (hrs.)		
	0	25	50
	% reflected light *		
Control	10·9	11·0	11·0
IPPD	7·6	5·9	5·0
WSP	16·3	15·2	14·8
MHPBN	16·2	13·2	12·8
MHPPN	12·5	11·8	11·8
MHPEN	11·9	10·6	10·8
MHPMN	11·8	10·3	10·1

* as measured from the Colour Master-V
ratings 0 5 10 15
←—increased discolouration—

Table 7·17 (b)

Table 7·17: Comparison of the discolouration properties of nitrones in conventional C.B.S. vulcanisates after exposure to U.V. light. (a):assessed visually; (b): % reflected lights as measured from the Colour Master-V.

Additive	Time of exposure to U.V. light (hrs.)		
	0	25	50
	Discolouration rating **		
Control	5	5	5
IPPD	8	8	10
WSP	7	8	10
NODP *	5	6	6
MHPBN	5	5-6	6
WSP + MHPPN	5	5	6
NODP + MHPPN	6	7	7

* : reference 182

** : assessment made visually; rating as for table 7·16.

Table 7·18 : Comparison of discolouration properties of combinations of MHPPN with other non-discolouring antioxidants (1 p.h.r. each) in conventional C.B.S. vulcanisates.

Fig. 7.12: Photograph comparing the discolouration properties of the nitrones and commercial stabilisers (1 p.h.r. each) after 50 hours of U.V. light exposure.

Notation: 1. Control 2. MHPBN 3. MHPPN 4. MHPMN 5. MHPEN 6. WSP 7. IPPD

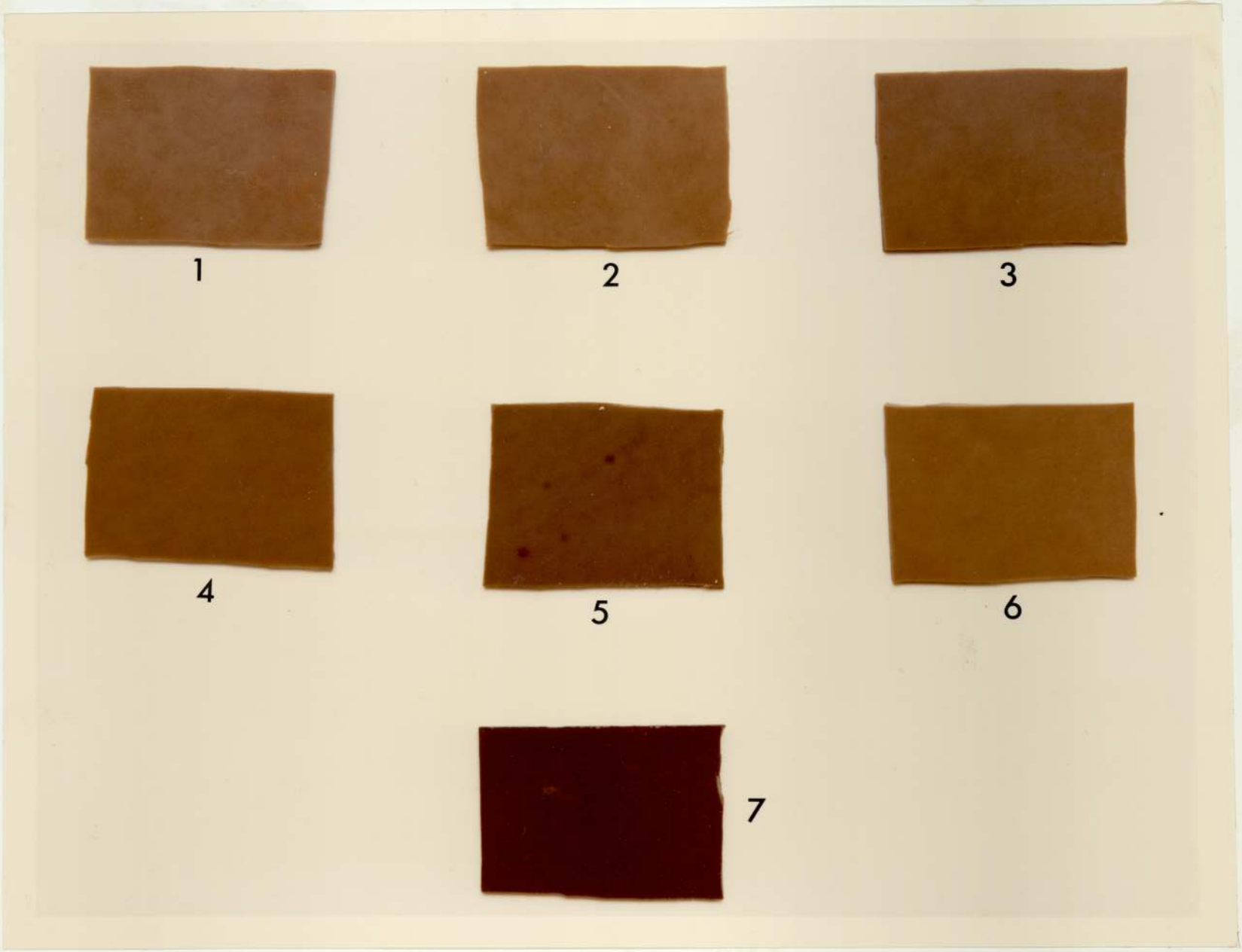


Fig. 7.12

exposure to U.V. light in the artificial daylight cabinet. It is clear that except for the test piece containing IPPD none of the other test pieces discoloured significantly upon U.V. exposure. Infact the test piece containing IPPD became darker. Table 7·17(b) shows the discolouration tendency of these compounds measured as a percentage of reflected light off the rubber surface. The results are similar to that described for the visual assessment.

Table 7·18 shows the relative discolouration properties for combinations of MHPPN with WSP and NODP before and after U.V. exposure, the assessment done visually. It is clear that relative to IPPD, the combinations are not particularly discolouring. However, in comparison to WSP the combinations were somewhat darker.

Figure 7·12 shows a photograph of the discolouration caused by the nitrones in relation to the commercial agents and the control after fifty hours exposure to U.V. light. It is evident that none of the nitrones were particularly discolouring.

Table 7·19 shows the degree of stain caused by migration of the additive from the rubber test piece onto a white metal panel before and after U.V. exposure of the panels.

Additive	after 24 hours ageing in oven at 70°C	after oven ageing + 50 hours U.V. exposure
	Discolouration rating *	
Blank	0	0
Control	1	0
IPPD	8	10
WSP	2	0
MHPBN	2	0
MHPPN	2	0
MHPEN	4	0
MHPMN	3	0
MHPPN + WSP	3	1
NODP	2	0
MHPPN + NODP	3	1

* assessed visually

0 white 2 tan 5 yellow/brown 8 brown 10 grey/brown

Table 7·19 (a)

Additive	after 24 hours agening in oven at 70°C	after oven ageing + 50 hours U.V. exposure
	% reflected light *	
Blanc	79	80
Control	74	79
IPPD	35	32
WSP	62	74
MHPBN	64	72
MHPPN	61	70
MHPEN	50	68
MHPMN	57	69

* from reflectance measurements of Colour Master-V.

Table 7·19 (b)

Table 7·19: Degree of migration - staining from conventional C.B.S. vulcanisates protected by nitrones and other commercial agents (1p.h.r. each; (a) assessed visually (b) assessed by reflectance spectroscopy.

Fig. 7.13: Photograph comparing the staining properties of the nitrones and commercial stabilisers after 24 hours of oven ageing at 70°C (additive = 1 p.h.r.; conventional C.B.S. vulcanisates)

Notation: 1. blank 2. control 3. MHPBN 4. MHPPN 5. MHPEN 6. MHPMN

7. WSP 8. IPPD

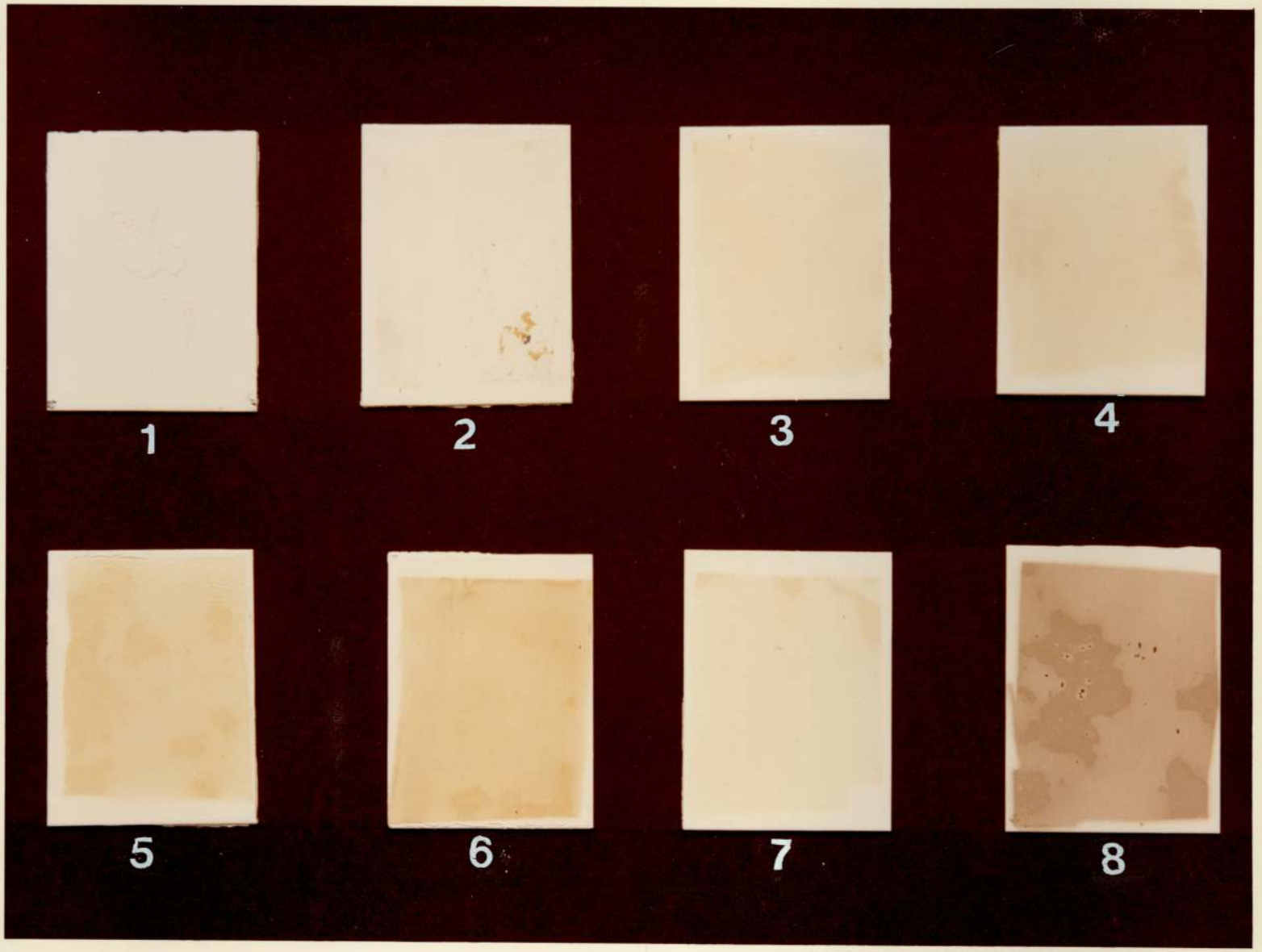


Fig. 7.13

Fig.7.14: Photograph comparing the staining properties of the nitrones and commercial stabilisers after 24 hours of oven ageing at 70°C + 50 hours of exposure to U.V. light (additive = 1 p.h.r. ; conventional C.B.S. vulcanisates)

Notation: 1. blank 2. control 3. MHPBN 4. MHPPN 5. MHPEN 6. MHPMN

7. WSP 8. IPPD

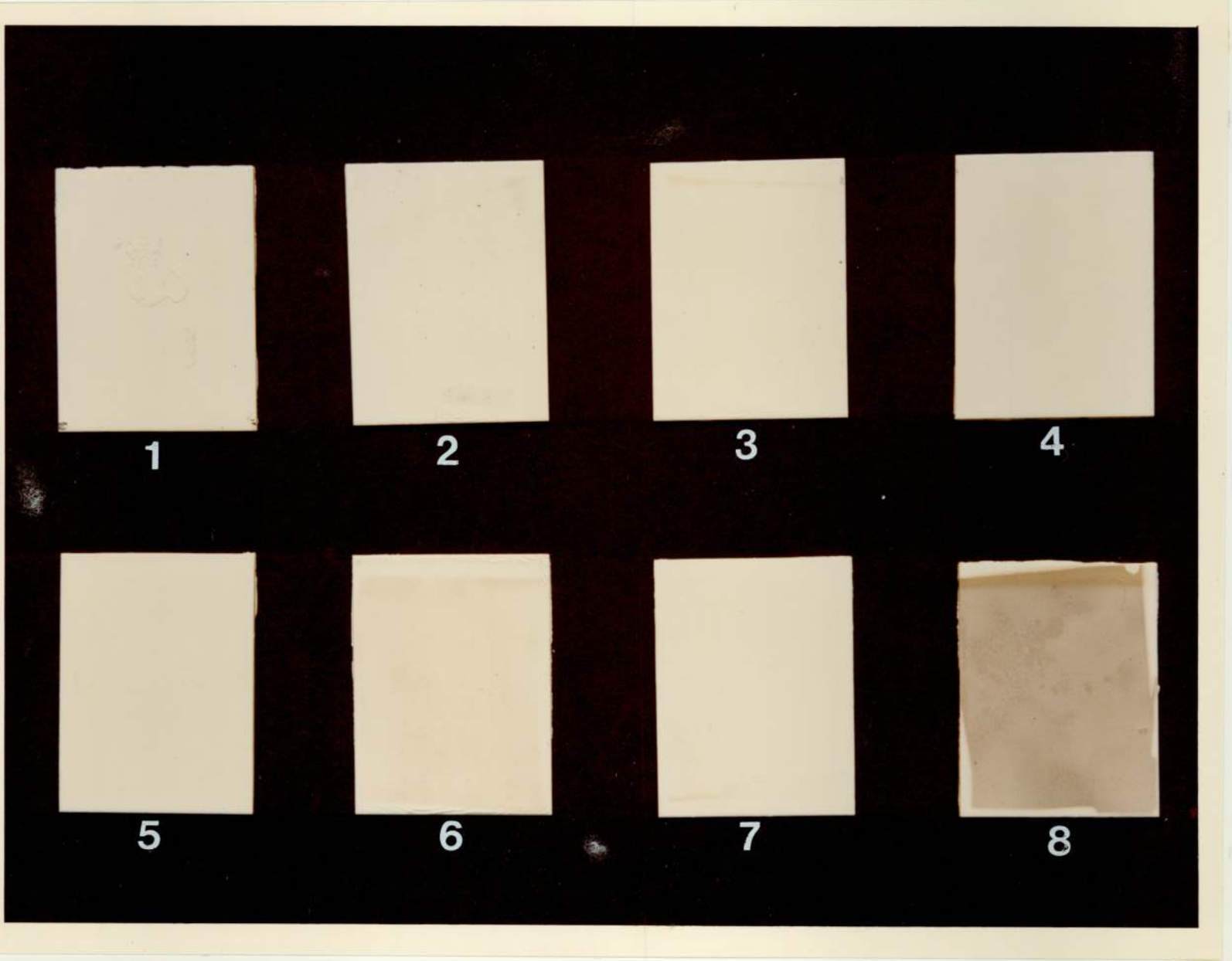


Fig. 7.14

It is clear that IPPD caused the most staining both before and after U.V. exposure. MHPBN and MHPPN were not significantly more staining than the commercial non-staining antioxidant WSP. However MHPEN and MHPPN were slightly more staining. After the stained metal plates were exposed to fifty hours of U.V. light, in all cases except IPPD the stain had disappeared. Infact the stain caused by IPPD became darker. Figures 7·13 and 7·14 respectively show photographs of the stain developed on the white panels before and after the U.V. light exposure. The staining properties of the combinations (WSP + MHPPN and NODP + MHPPN) were not very different to that of the nitrones alone (table 7·19(a)).

7.C.4 Discussion

The discolouration and staining properties of IPPD and other aromatic amines in rubber are well known[1]. It is caused by the formation of polyconjugated dimers and trimers[1] as described in section 1·12. These dimers and trimers being relatively insoluble in the rubber migrate to the surface and cause the discolouration and the staining.

WSP does not discolour the rubber or cause staining because it is not able to form heavily conjugated dimeric

and trimeric species. None of the alicyclic compounds were found to discolour the rubber. The nitrones too were found not to discolour the rubber significantly. The reason for this is probably due to the fact that none of these compounds are capable of forming heavily conjugated species. The nitrones were also found to be non-staining (figures 7·12, 7·13 and table 7·19). The reason for this is probably the same as that suggested for the non-discolouring property of these compounds.

CHAPTER EIGHT

THE TECHNOLOGICAL PERFORMANCE OF NITRONES CONTAINING PHENOLIC ANTIOXIDANT FUNCTIONS IN CARBON BLACK REINFORCED NATURAL RUBBER VULCANISATES

8·1 Introduction

In chapters 5 and 7 it was shown that when nitrones, particularly MHPBN, MHPPN, MHPEN, MHPMN and BMHPPN, were incorporated into conventional C.B.S. gum vulcanisates good antiozonant protection and acceptable antifatigue activity was conferred to the rubber. Furthermore these nitrones were relatively non staining and non discolouring.

In the rubber industry, over 60% of the rubber goods manufactured today contain carbon black. This is particularly so for the automotive, aircraft and building industries. Tyres account for the largest volume of carbon black used each year. Since the nitrones described in the preceeding paragraph were highly effective against ozone cracking in gum rubber vulcanisates it was decided to evaluate their technological ageing properties in natural rubber vulcanisates reinforced with carbon black as well.

Carbon black is used to reinforce the strength, hardness and abrasion resistance of rubbers[188]. It is also reported

to confer oxidation resistance to the rubber[1]. However this is achieved only at a cost of sacrificing[217] some flex crack resistance, heat dissipation and set properties of the vulcanisate. The reinforcing property of carbon black is due to the formation of "carbon-gel" within the rubber which effectively act as transient cross-links and strengthen the rubber tremendously. The dispersion, the particle size, the pH and its origin are critical to the reinforcing action of carbon blacks.

In the present study a typical level (40 p.h.r.) of high abrasion furnace carbon black (H.A.F. - Black) was used to reinforce the rubber, and the ageing characteristics of the nitrones were compared with the commercial material IPPD and the control.

8.2 Experimental Procedure

A 60 p.h.r. masterbatch (MB - 1) of H.A.F. - black with 5 p.h.r. aromatic oil (sunpar 2280; Robinson Brothers Ltd.) in unextracted natural rubber (S.M.R. grade 10) was made in a Banbury (Frarrel Bridge model BC; total capacity = 2000g). The ingredients were mixed into the rubber according to the following cycle:

Add all rubber (600g) at	0 min.
Masticate for 1 minute	
Add all oil (30g) at	1 min.
Mix for 2 minutes	
Add half the carbon-black loading (180g) at	3 min.
Mix for 2 minutes	
Add the rest of the carbon black (180g) at	5 min.
Mix for 2 minutes, and then for a further half minute	
Dump	6½ min.

The total cycle time in the Banbury was 6½ minutes. During the mixing cycle the temperature inside the chamber rose to 120°C.

The formulation for MB - 1 was

Natural rubber	100 parts
H.A.F. black	60 p.h.r.
Oil	5 p.h.r.

MB - 1 was then diluted to a masterbatch containing 40 p.h.r. carbon black (MB - 2) by appropriate dilution with fresh natural rubber. The dilution to MB - 2 was done on an open two roll laboratory mill heated at 60°C (to facilitate easy milling) using a nip size of 0.115 cm. To ensure thorough

mixing of the fresh rubber into MB - 1 the rubber was milled for 5 minutes. During this mixing procedure the temperature of the rubber rose to 90 - 100°C.

The formulation of MB - 2 was:

Natural Rubber	100 parts
H.A.F. - black	40 parts
Oil	3.3 parts

495g of MB - 1 was mixed with 150g of fresh rubber to give 545g of MB - 2.

MB - 2 was then compounded with the other vulcanisation ingredients for a conventional C.B.S. cure as described in section 3·2.

The formulation containing 40 p.h.r. carbon black is shown below:

Natural rubber (S.M.R. grade 10)	: 100 parts
Carbon black (H.A.F.)	: 40 parts
Oil (Sunpar 2280)	: 3·3 parts
Zinc oxide	: 5·0 parts
Stearic acid	: 3·0 parts
Antioxidant	: 1·0 parts
C.B.S.	: 0·6 parts
Sulphur	: 2·5 parts

Total compounding time = 15 minutes.

Nip size between the rolls on the mill = 0·045 cm.

100g of MB - 2 was used each time to make the stock. The nitrones were premilled with the MB - 2 before addition of the other compounding ingredients. After compounding, the Wallace Plasticity number of each stock was measured (section 3·3) to ensure that its value was 11-13 units.

The vulcanisation and technological ageing tests were done in the manner described for the gum stocks (sections 3·4 to 3·11).

8·3 Results

Figure 8·1 and table 8·1 compare the curing characteristics for conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. -black protected by the nitrones and IPPD respectively. The vulcanisation parameters for the stock containing IPPD do not differ from that of the control. In contrast the nitrones did affect the cure considerably. All the stocks containing the nitrones were scorchy, their rates of cure faster and their optimum torque were greater than the control. Furthermore relative to each other too the optimum torque and scorch differed for the nitrones (table 8·1). The scorch time for the

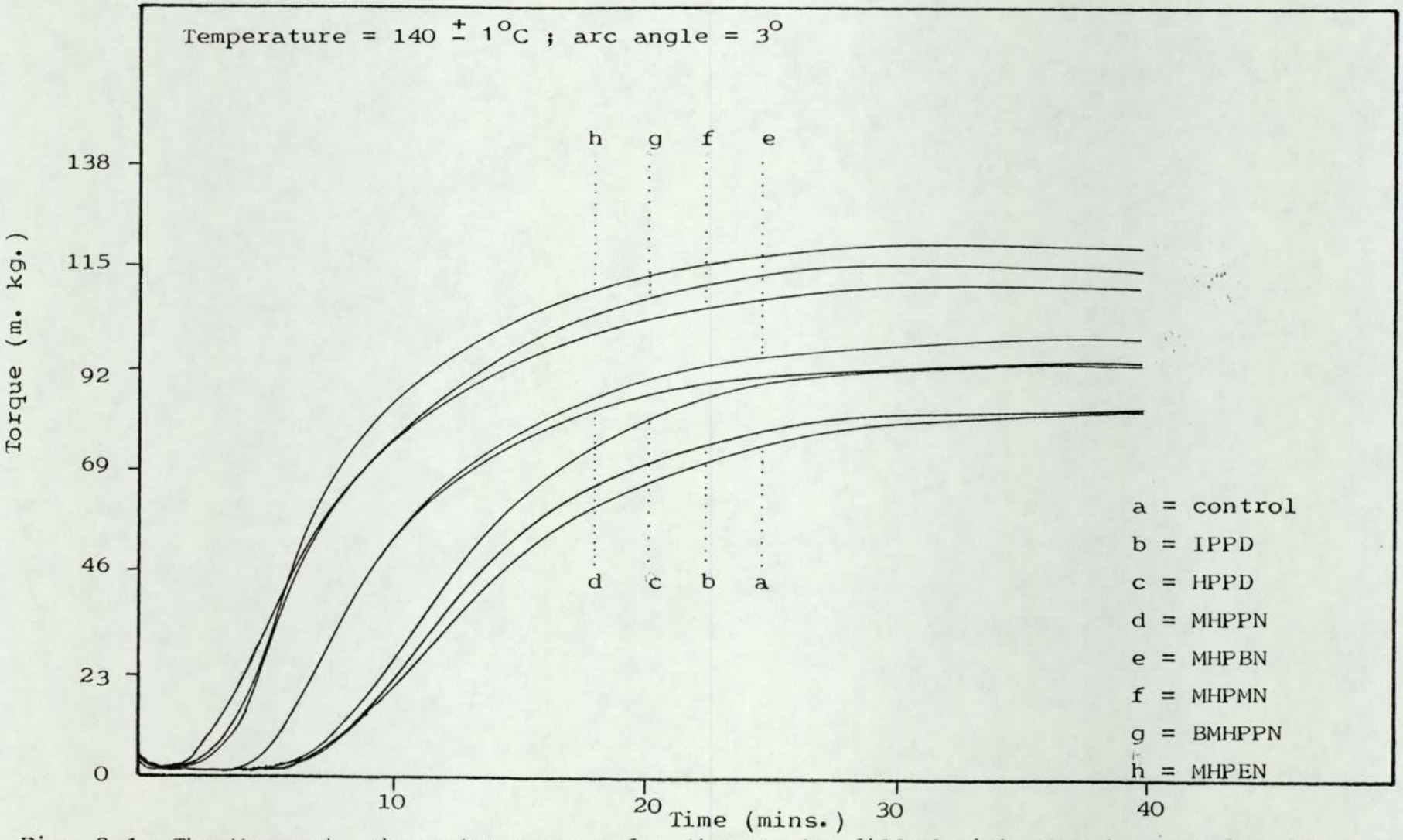


Fig. 8·1: The Monsanto rheometer curves for the stocks filled with 40 p.h.r. carbon black containing various protective agents

ADDITIVE	CURING CHARACTERISTICS				
	Optimum cure time (min.)	Scorch time (min.)	1st order rate constant $k(min.)^{-1} \pm 0{\cdot}01$	90% cure time (min.)	Optimum torque (m.kg.)
Control	35	8·0	0·15	30	0·82
IPPD	35	8·0	0·17	30	0·82
HPPD	40	7·0	0·16	30	0·93
MHPBN	35	5·0	0·18	30	0·99
MHPPN	35	5·0	0·18	28	0·93
MHPEN	35	3·0	0·18	28	1·2
MHPMN	35	3·0	0·18	28	1·1
BMHPPN	35	2·0	0·16	28	1·1

Table 8·1: The curing characteristics for the nitrones and IPPD in 40 p.h.r. H.A.F. carbon black filled stocks (all additives at 1 p.h.r. level)

N-isopropyl and N-tert-butyl nitrones were the same (5 minutes), and it was shorter (3 minutes) for the N-methyl and N-ethyl nitrones. The bis-nitrone (BMHPPN) was even more scorchy. No particular trend could be seen for the variation of the optimum torque with the nature of the N-alkyl group of the nitrone (table 8·1).

Figure 8·2 and table 8·2 compare the fatigue life of the vulcanisates containing the nitrones with that containing IPPD and no protective agent. Since the optimum torque (hence modulus) of all the vulcanisates differed from each other considerably (table 8·1) it was necessary to evaluate their fatigue life at the same strain energy input. This was done by the technique described in section 3·9·4.. The fatigue life for each vulcanisate was equated at the strain energy input that was calculated for the extension of the control by a strain of 60%.

Figure 8·2 shows that IPPD is by far the superior antifatigue agent, the vulcanisate protected by this compound having an improvement of over 700% relative to the control. In contrast the nitrones were much less effective as anti-fatigue agents. The percentage improvement of the best nitrone was approximately a third of that for IPPD. The structure-activity relationship for the nature of the N-alkyl group of the nitrone was similar to that observed

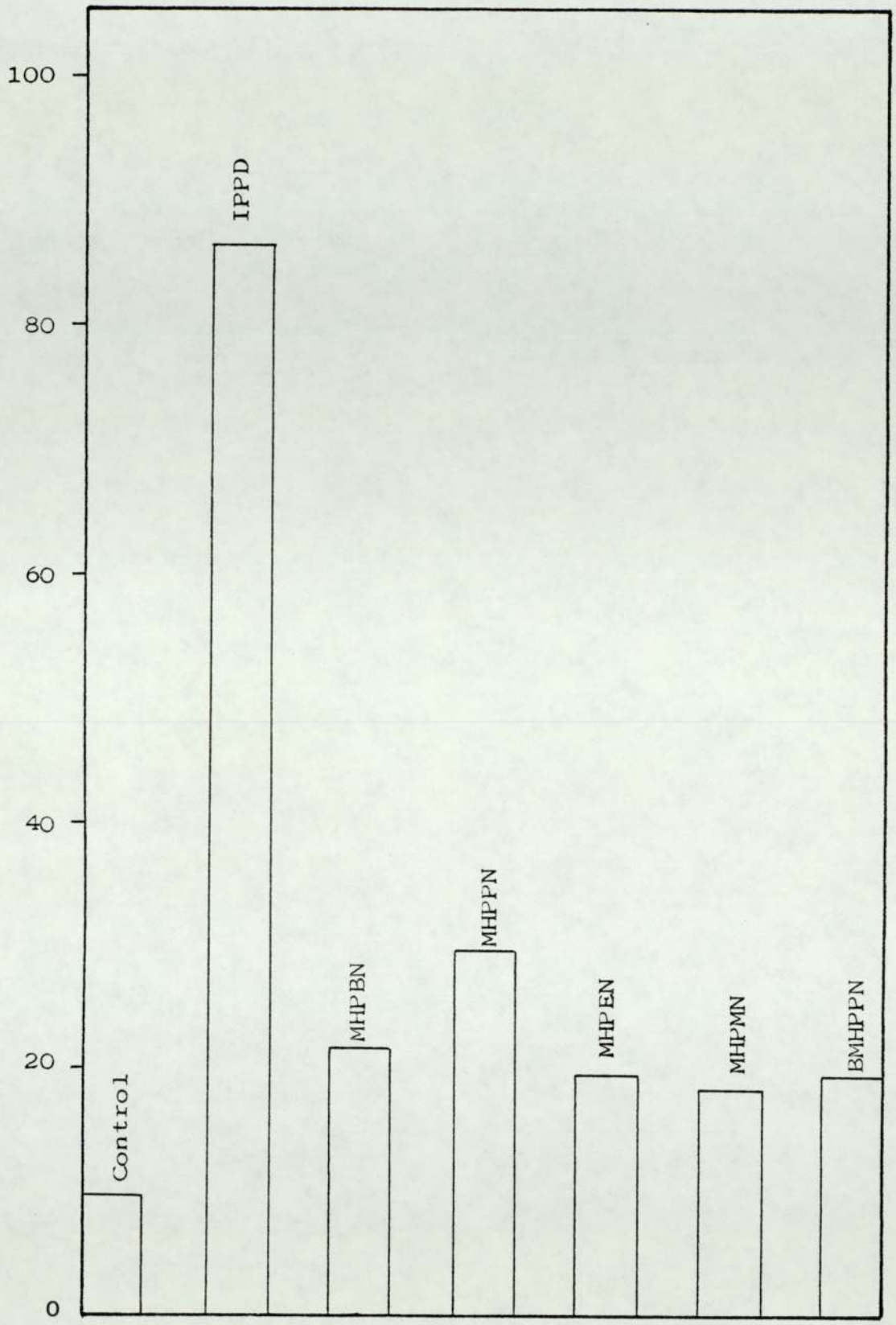


Fig. 8·2: A comparison of the fatigue life for conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black, protected by the nitrones and IPPD ([additive] = 1 p.h.r.; all nitrones premilled for 2 minutes)

	FATIGUE LIFE		
	corrected to equivalent strain energy input calculated for control at 61% maximum strain		
ADDITIVE	Number of cycles to failure x 10^{-2}	Number of hours to failure (hrs.)	Percent improvement over control
Control	598	10	-
IPPD	5220	87	770
MHPBN	1440	24	140
MHPPN	1800	30	200
MHPEN	1200	20	100
MHPMN	1140	19	90
BMHPPN	1200	20	100

Table 8·2: The fatigue life of conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black protected by nitrones and IPPD ([additive] = 1 p.h.r. ; all nitrones premilled for 2 minutes).

for the unfilled gum vulcanisates (chapter 5) MHPPN showed the best activity, then MHPBN followed by the other nitrones (figure 8·2, table 8·2).

Figure 8·3 and table 8·3 compare the static ozone protection of the vulcanisates by the nitrones and IPPD at a strain of 20%. It is clear that the antiozonant activity of the nitrones was superior to that of IPPD. HPPD was found not to have any antiozonant activity. Table 8·4 shows the relative protection imparted by the nitrones and IPPD at extensions of 5, 10, 15 and 20% respectively. Figure 8·4 and table 8·5 show the relative rates of ozone cracking at these extensions. Figure 8·4 shows that the rate of ozone cracking and deterioration is highest when the specimen was strained by an extension of 10%.

Table 8·6 compares the τ_{50} times of the vulcanisates under continous stress relaxation at 60% strain and 100°C. Only the vulcanisate containing IPPD imparted antioxidant protection to the rubber. None of the nitrones did, and infact figure 8·5 shows that there was no difference between the stress relaxation of the control and that of the vulcanisates containing the nitrones.

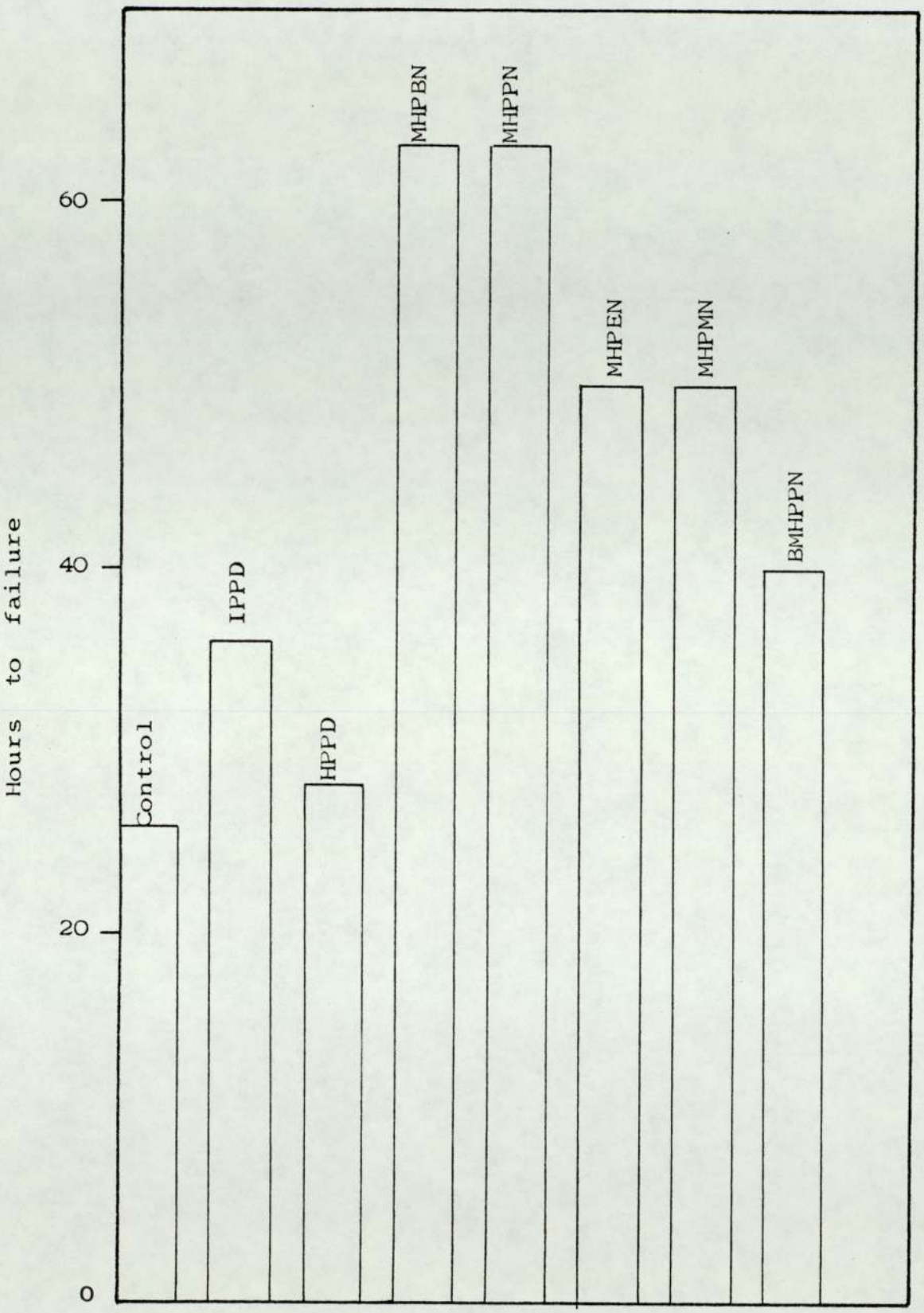


Fig. 8·3: A comparison of the ozone test results for the nitrones, IPPD and HPPD in conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black ([additives] = 1 p.h.r.; all nitrones premilled for 2 minutes)

Static test; strain = 20% [ozone] = 25 ± 5 p.p.h.m.; temperature = 30°C		
ADDITIVE	Time for appearance of cracks 0·5 mm long (hrs.) ± 1	Time for failure (severage) (hrs.) ± 2
Control	12	26
IPPD	10	36
HPPD	6	28
MHPBN	20	63
MHPPN	20	62
MHPEN	20	50
MHPMN	20	50
BMHPPN	15	40

Table 8·3: Comparison of ozone test results for the nitrones, IPPD and HPPD in conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black ([additive] = 1 p.h.r. all nitrones premilled for 2 minutes).

Static test; strain as shown; [ozone] = 25 ± 5 p.p.h.m.; temperature = 30°C								
Strain %	5		10		15		20	
ADDITIVE	a	b	a	b	a	b	a	b
Control	12	26	.5	20	8	24	12	28
IPPD	12	35	5	29	10	34	10	36
HPPD	6	23	6	20	6	22	6	24
MHPB	18	51	10	46	15	52	20	63
MHPPN	18	52	10	46	15	52	20	63
MHPEN	15	41	8	36	13	45	20	50
MHPMN	15	40	8	35	15	46	20	50

Notation:

a = Time for appearance of cracks 0·5 mm long.

b = Time for failure of test piece (severage).

Table 8·4: Comparison of the antiozonant activities for the nitrones and IPPD in conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black ([additive] = 1 p.h.r.; all nitrones premilled for 2 minutes).

Static test; strain as shown; [ozone] = 25 ± 5 p.p.h.m.				
Strain % ADDITIVE	5	10	15	20
Control	0·19	0·25	0·20	0·180
IPPD	0·14	0·17	0·15	0·14
MHPBN	0·22	0·25	0·23	0·21
MHPBN	0·09	0·11	0·096	0·08
MHPPN	0·10	0·11	0·10	0·08
MHPEN	0·12	0·14	0·11	0·1
MHPMN	0·13	0·14	0·11	0·1

Figure 8·5: Comparison of the rates of ozone cracking for conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black protected by the nitrones and IPPD ([additive] = 1 p.h.r. all nitrones premilled for 2 minutes).

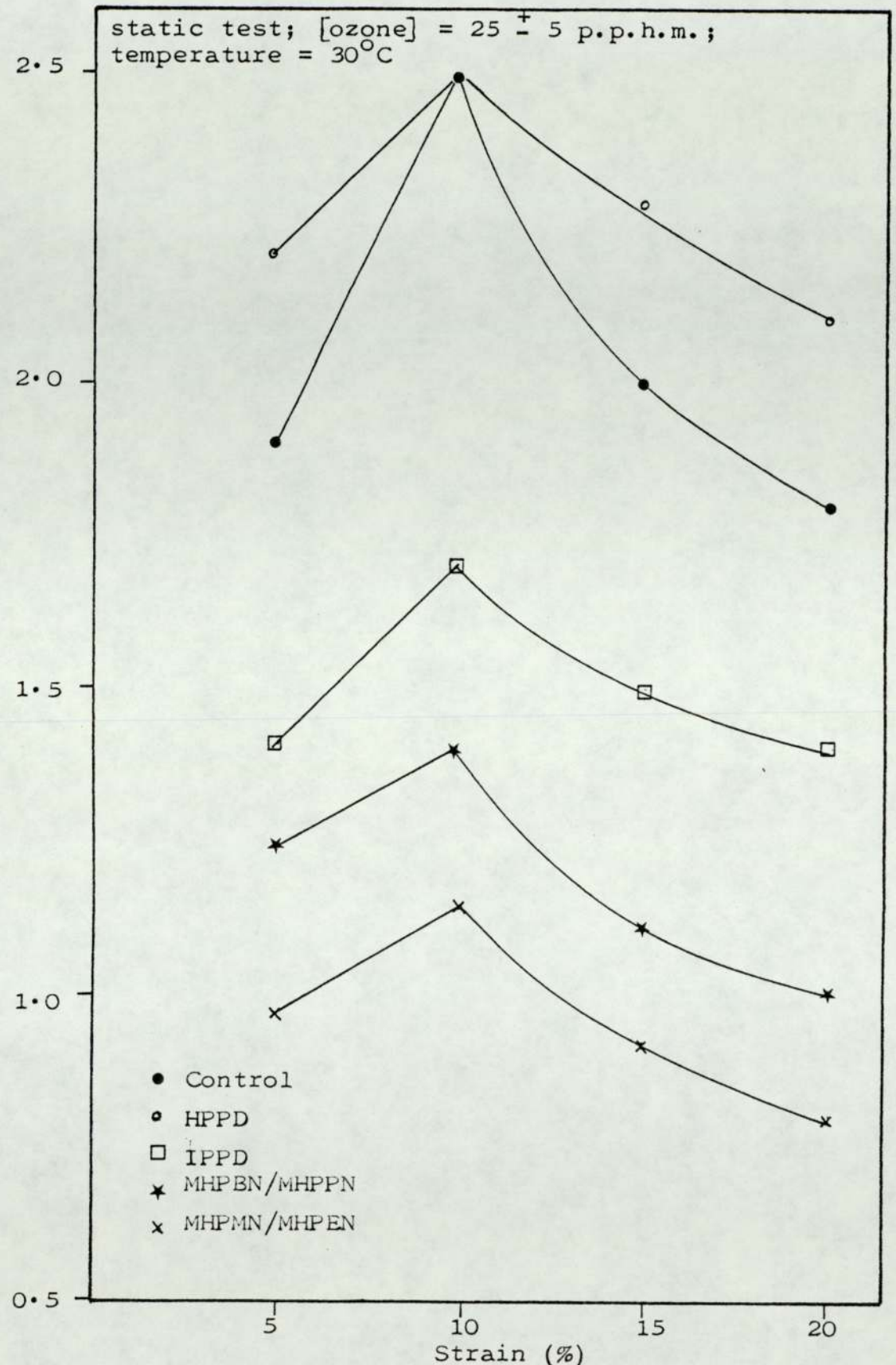


Fig. 8·4: Rate of ozone cracking as a function of strain for the conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black protected by various additives

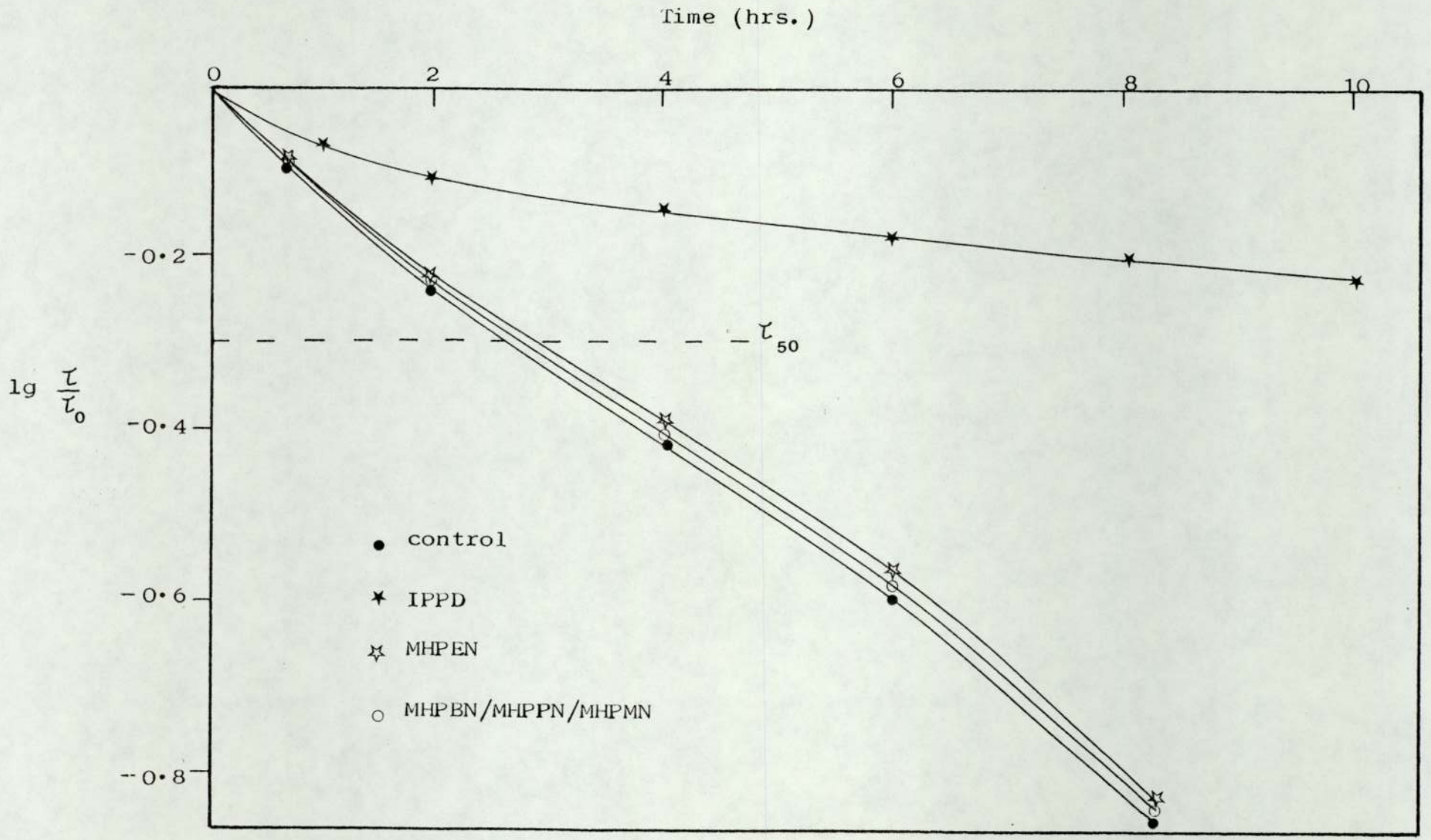


Fig. 8·5: Continous stress relaxation of conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black protected by the nitrones and IPPD ((additive = 1 p.h.r.); all nitrones premilled for 2 minutes)

Continous stress relaxation strain = 60% temperature = 100 ± 2°C	
Additive	Time to τ_{50} (hrs.) ± 0·3
Control	5
IPPD	18
MHPBN	5
MHPPN	5
MHPEN	5
MHPMN	5
BMHPPN	4

Table 8·6: τ_{50} times for the continous stress relaxation of conventional C.B.S. vulcanisates containing 40 p.h.r. H.A.F. black protected by the nitrones and IPPD ([additive] = 1 p.h.r.; all nitrones premilled for 2 minutes).

8·4 Discussion

The relative decrease in the scorch times for the filled rubbers containing the nitrones may be rationalised in the same terms as that explained for their scorchiness in the unfilled gum rubber stocks (chapter 5). The explanation centers around the formation of nitrone-accelerator adducts by ionic and/or free radical reactions, the relative stabilities of the adducts and their relative rates of formation (section 5.3). In contrast to the nitrones the scorch time for the stock containing the commercial material IPPD did not differ very much from the control.

A comparison of the scorch times shown in table 8·1 and table 5·2 show that for all stocks the scorch times were reduced in the presence of the carbon black. This effect is a consequence of the basicity of the carbon black that was used in the formulation. H.A.F. blacks are basic having a pH of 8-10[218].

The increased optimum torque for the filled vulcanisates (table 8·1) compared to the unfilled gum vulcanisates (table 5·2) is a consequence of the reinforcing effect of the carbon black. The variation in the optimum torque for the filled rubbers containing the nitrones (table 8·1) relative to the control and IPPD could be due to adsorption of the

nitrones or derived nitroxyl radicals on to the surface of the carbon black particles. As a consequence the reinforcing action of the carbon black will be affected. Additives, especially free radicals are known to be adsorbed on the surface of carbon black particles in the rubber[219-221].

The trend for the efficiency of fatigue protection of the nitrones is similar to that in the unfilled gum vulcanisates. The N-isopropyl nitrone was superior to the N-tert-butyl nitrone which in turn was better than the N-ethyl, the N-methyl nitrones or the bis-nitrone. The antifatigue activity of the nitrones may be rationalised in the same terms as described for the gum vulcanisates in chapter 5 and 6B. The structure-activity relationship of the nature of the N-alkyl group may also be explained in the same manner as described in chapter 5.

When compared to the gum vulcanisates (table 5·7) the fatigue lives of the carbon black filled rubbers were very much reduced. This is a modulus effect. The stress that can be borne by a high modulus vulcanisate is very much less than that borne by a low modulus more flexible rubber[26].

As in the gum vulcanisates (chapter 7A) the antiozonant activities for the nitrones were superior to that of IPPD

and HPPD did not have any antiozonant activity. The activity of the nitrones may be explained in the same terms as that described in section 7.A.4. Like the unfilled vulcanisates the nature of the cracks formed were different to that of the control or in the presence of IPPD. In the presence of the nitrones the cracks were always fine, small and shallow. In contrast the cracks formed in the control or in the presence of IPPD were sharp and deep. Figure 8·4 and table 8·5 show that the rate of ozone deterioration of the "filled" rubber was fastest when the test piece was extended by a strain of 10%. At the other strain at which the test pieces were tested the rate of cracking was slower. Similar results were obtained for the unfilled rubbers (figure 7·7) and the effect is explained in section 7·A·4.

The antioxidant activity for the carbon black filled rubbers, as determined by continous stress relaxation studies, showed that none of the nitrones were effective in protecting the rubber against thermo-oxidative deterioration. On the other hand IPPD was quite effective, although in relation to the unfilled rubber (table 7·10 and figure 7·9) its efficiency was considerably reduced. The lack of activity of the nitrones in the presence of carbon black is surprising because in the absence of filler they did show some activity. The apparent loss of activity

of the nitrones and the reduced activity of the IPPD compared to the unfilled vulcanisates must be due to adsorption and destruction of the protective agent by the carbon black particles. Shelton and co-workers[222] found that the protective efficiency of commercial antioxidants is reduced in the presence of carbon black. They suggested[222] that this was due to the faster rate of oxygen uptake by the rubber in the presence of the carbon black. However in view of the known antioxidant activity of carbon black Kuzminskiiet al[219] suggested that the reduction in the protective efficiency was due to some of the stabiliser being adsorbed on to the surface of the carbon black particles and therefore not being available to function as an antioxidant.

The antioxidant activity of carbon black is thought to be due to its ability to function as polyphenol-type antioxidants[223]. It does this by the temporary stabilisation of the broken rubber chain ends on the surface of the carbon black particles. In the present study the antioxidant activity of the carbon black is reflected in the times to τ_{50} during the stress relaxation of the controls for the unfilled and filled vulcanisates (tables 7·10 and 8·6 respectively).

The adsorption and probable destruction of IPPD and the nitrones by the carbon black is reflected in the antifatigue

and antiozonant results too. When the efficiency and the percentage inprovement over the control for these protective agents are compared with the corresponding results, for the unfilled vulcanisates (table 8·2, 8·3, 5·x and 7·2) it is clear that their effectiveness is reduced in the presence of the carbon black.

CHAPTER NINE

OVERALL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 Overall Conclusions

The work in this thesis clearly highlights the differences between deterioration of rubber by fatigue failure, thermal oxidation and ozone attack. It also demonstrates the different chemical requirements needed in a stabiliser to counteract each of these deterioration processes. The main differences between the three modes of deterioration and the different chemical requirements needed in a stabiliser to protect rubber against each of them are summarised in table 9.1. The different stabilising reactions of the various protective agents which have been used in this thesis are summarised in table 9.2.

It is apparent from table 9.1 that although alkyl radical trapping is a requirement for good antifatigue agents, during the early stages of fatigue alkylperoxyl radical trapping is also important. This is in fact reflected in the results obtained for the different protective agents used in this thesis.

IPPD is very effective because during fatiguing it is converted to the nitroxyl radical which is a powerful

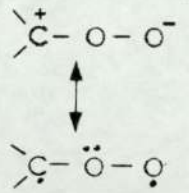
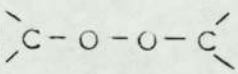
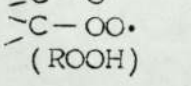
	INITIATION PROCESS	RADICAL SPECIES	INHIBITION REACTION
FATIGUE			
initially	shear	ROO·	CB-D
at equilibrium	shear	ROO· + R· (ROO· < R·)	CB-A/CB-D
Additional requirements for stabiliser: compatibility; migration to ozones of crack growth			
THERMAL OXIDATION			
initially	ROOH	ROO ·	CB-D/PD
at equilibrium	ROOH	ROO ·	CB-D/PD
		PD = PD-S or PD-C	
Additional requirements for stabiliser: Non volatility; compatibility			
OZONE ATTACK			
initially	stress ozone		Ozone scavenging CB-A/CB-D
at equilibrium		 (ROOH)	CB-D (PD-S/PD-C)
Additional requirements for stabiliser : surface protection; ozone impermeable layer; compatibility			

Table 9.1: Summary highlighting the differences between fatigue, thermal oxidation and ozone cracking of rubber and their different stabilisation requirements.

ADDITIVE	FATIGUE	THERMO-OXIDATION	OZONE CRACKING
alicyclic nitroxyl radical and precursors	Only CB-A no CB-D during early stages for $R_2NO\cdot$	no CB-D activity for the $R_2NO\cdot$	no ozone scavenging, no CB-D activity for $R_2NO\cdot$
alicyclic nitroxyl radicals attached to i) PD-C function (TMOXP)	only CB-A for $R_2NO\cdot$ and sulphenyl radical during early stages	PD-C effect not seen because of antagonism with $R_2NO\cdot$	CB-A; PD-C
ii) CB-D function (BPTMOP)	CB-A/CB-D from early stages	CB-D activity	no ozone scavenging; CB-A;CB-D
nitrone without semi-hindered phenol function	only CB-A	PD-S only	ozone scavenging;affects nature of surface and cracks formed;CB-A;no CB-D
nitrone with semi-hindered phenol function	CB-A;CB-D from early stages	PD-S and CB-D autosynergism	ozone scavenging;affects nature of surface and cracks formed;CB-A;CB-D
MNP	CB-A;CB-D but is pro-oxidant	CB-D activity but pro-oxidant	ozone scavenging; CB-A;CB-D
p-phenelenediamine. (IPPD)	CB-A;CB-D from early stages for derived $R_2NO\cdot$; compatibility and migration may be ideal	good CB-D	ozone scavenging;forms protective layer; CB-A;CB-D
WSP	CB-D	good CB-D	no ozone scavenging; CB-D; no CB-A

Table 9.2: Table comparing the different stabilising functions of the various classes of protective agents used in this thesis.

alkyl radical trap and terminates the macro-alkyl radicals that are formed in the rubber.[101] Its action involves a cyclical regeneration mechanism where both alkyl and alkylperoxyl radicals are removed from the system. Moreover the IPPD-nitroxyl radical is also able to trap alkylperoxyl radicals during the early stages of fatigue, by delocalising the unpaired electron onto the ring system Thus all the chemical requirements for good antifatigue activity are satisfied by the oxidised product of IPPD. Nitrones such as MHPPN and MHPBN are also good antifatigue agents because they are able to trap alkyl radicals at the nitrone function and alkylperoxyl radicals at the semi-hindered phenolic function; the latter mechanism being operative from the very begining of fatigue. Moreover their activity probably relies in part on a chain repair mechanism (chapter 6.B) where two alkyl radicals are trapped by one nitrone molecule. In contrast the nitrones without the semi-hindered phenolic antioxidant function are weak antifatigue agents. This is probably due to their inability to function by the CB-D mechanism during the early stages of fatigue. Similarly the alicyclic nitroxyl radicals are also very weak antifatigue agents probably due to the same reason. The hydroxylamine was slightly better because it can terminate alkylperoxyl radicals especially if it is present from the begining of fatigue. The parent amine,

however, is poorer because, although it can react with alkylperoxyl radicals, during its conversion to the nitroxyl radical pro-oxidant species are also produced (scheme 4.3) . The improved effectiveness of BPTMOP over the alicyclic nitroxyl radical TMOP is again a reflection of the CB-D mechanism operating from the very onset of fatigue together with the CB-A mechanism of the nitroxyl function. In contrast the relative ineffectiveness of TMOPX and TMOXPZ may be due to the formation of the sulphenyl radical derived from these compounds which again acts by the CB-A mechanism, therefore only complements the activity of the nitroxyl radical. The antifatigue structure-activity relationship for the amine, nitroxyl radical and hydroxylamine reflects the regeneration of the nitroxyl radical during their antifatigue activity. It was also shown in this thesis (chapter 6.A) that the formation of the O-alkylated hydroxylamine, if any, during the fatigue is probably a reversible process and alkyl radical termination may take place mainly by hydrogen abstraction by the nitroxyl radical from the carbon atom β to the alkyl (allyl) radical.

The differences between the various classes of stabilisers (namely arylamine, nitrones, alicyclics) may also in part be related to compatibility effects of the additives in the rubber.

Table 9.1 shows that for good thermal antioxidant activity CB-D or PD mechanisms are necessary in a stabiliser. Thus WSP and IPPD are very effective antioxidants because they function efficiently by the CB-D mechanism. Furthermore,their oxidised products are also capable of functioning similarly. The weak thermal antioxidant effect of the nitrones must be because they are only able to react with the hydroperoxides stoichiometrically Moreover,they are converted to non active oxidation products. The improved activity of the nitrones containing the semi-hindered phenolic antioxidant functions must be due to auto-synergism between the PD-S mechanism of the nitrone function and CB-D mechanism of the phenolic function. Loss of nitrone by volatility is probably low because the bis-nitrone (BMHPPN) has the same antioxidant activity as its mono-nitrone counterpart (MHPEN) at equivalent molar concentrations. The inactivity of the hindered alicyclic compounds is due to lack of CB-D activity for the derived nitroxyl radicals. The inactivity of the xanthogenato nitroxyl radicals (TMOXP and TMOPXZ) is probably due to antagonism between the xanthate group and the nitroxyl function. The improved activity of BPTMOP is due to the CB-D mechanism of the hindered phenol function in the molecule.

As shown in table 9.1 effective antiozonants must be able to

scavenge ozone, form a protective layer on the surface of the rubber which is impervious to ozone and also probably be able to function by the CB-A and CB-D mechanisms as well. The latter mechanisms may be useful to protect the rubber from secondary oxidative reactions after the initial ozone attack has occured. Certainly, physical factors such as the nature and density of cracks are also important, but these appear to be governed by the chemical efficiency of the antiozonant. Thus, p-phenelenediamines are effective antiozonants because they satisfy all these requirements. In contrast WSP is ineffective because it is unable to scavenge ozone. Similarly the hindered piperidines and derivatives have no activity because of the inactivity of the derived nitroxyl radicals to ozone. On the other hand the high efficiency of the nitrones as static antiozonants must be related to their rapid reaction with ozone[207], and also their interaction with radicals and hydroperoxidic species that are formed during the secondary oxidative reactions. Moreover, they could also be capable of relinking reactions by interacting with the radical from of the zwitterion which may be formed during the rearrangement of the molozonoid into the iso-ozonoid. The nitrones are also capable of decomposing any hydroperoxides that are formed in the system by the PD-S mechanism. Certainly ,the change in appearance of the

surface of the rubber containing the nitrones upon ozone exposure, and the high density of the small fine cracks that are formed,must also contribute greatly to the high antiozonant activities of the nitrones. The cracks formed in the control or in rubber protected by the p-phenelenediamines are much fewer, larger and deeper (chapter 7A). The role played by the oxidation products of antiozonants may also be significant because MNP (an oxidation product of MHPBN) was also quite effective as an antiozonant (chapter 7A).

The synergism observed for the antifatigue activity of the combination of MHPPN with WSP and the slight antagonism for the antioxidant and antiozonant activities is a reflection of the different needs required in stabilisers to counteract these modes of deterioration. The slight antagonism that was observed for the combination of MHPPN with NODP (a good antifatigue agent, antioxidant [182]) is probably due to destruction of the nitrone by the nitric oxide radicals produced from the NODP. These results probably reflect the need for judicious selection of antidegredants when they are to be used in combinations.

The dependence of the antifatigue activity of the nitrones with mild premilling on an open mill (2 mins. for

optimum activity) is probably related to the need for a certain amount of nitroxyl radical to be present for good antifatigue activity. However, longer premilling destroys the nitrone by interactions with hydroperoxides formed in the rubber. In contrast mild premilling did not appear to affect the antiozonant activity of the nitrones very much although long premilling did reduce their efficiencies slightly. For antioxidant activity, even mild premilling reduced the efficiency of the nitrone. These effects too are probably associated with destruction of the nitrone by the hydroperoxides.

The work done in this thesis has also demonstrated that most of the compounds did not greatly affect the vulcanisation process. However the alicyclic nitroxyl radicals did retard cure slightly and some of the nitrones, particularly the N-primary alkyl nitrones (MHPMN, MHPEN), were slightly scorchy. The bis-nitrone- was unacceptably scorchy. These effects were rationalised in terms of interaction of the protective agents with the intermediates of the vulcanisation system.

It was also demonstrated that the hindered piperidines and the nitrones were non-discolouring and non-staining. The effects were related to the inability of these compounds to form heavily conjugated dimers and trimers. Combinations of MHPPN with WSP and NODP respectively, were also relatively non-discolouring and non-staining.

Moreover, it was shown that the trend in activity for the nitrones, relative to the commercial agents, in carbon black filled rubbers were similar to that in the gum vulcanisates. However, the relative efficiencies of all the compounds were very much reduced.

Finally, besides highlighting the different chemical needs required to protect rubber against fatigue deterioration, thermal oxidation and ozone cracking, this thesis has demonstrated that the N-alkyl aldonitrones (in particular MHPBN and MHPPN) are very effective static antiozonants and are satisfactory antifatigue agents. Moreover they are non-discolouring and non-staining. The use of the p-phenelenediamines to protect light coloured rubbers is aesthetically undesirable due to their severe staining and discolouration properties. The nitrones do not have this disadvantage. Therefore, they represent a new class of compounds which can be potentially used to protect light coloured rubbers against fatigue deterioration and ozone attack. They can also be used in combination with other non-discolouring/non-staining protective agents without greatly impairing their effectiveness.

9.2 Suggestions For Further Work

In view of the results and conclusions reported in this

thesis the following suggestions are recomended for further work: -

1) During the antifatigue mechanism of amines and nitroxyl radicals, it was suggested that the role played by the O-alkylated hydroxylamine was small. This should be estabilished clearly by synthesising long chain O-alkylated hydroxylamines and assessing their behaviour and performance in rubber and in model compounds.

2) The antifatigue activity of the nitrones was at optimum when they were premilled with the rubber for two minutes on an open two roll mill. It would be of interest to mill the nitrones with the rubber in the R.A.P.R.A. torque rheometer (Closed Chamber) as well, and assess their antifatigue activities.

3) The nitrones were found to impart good ozone protection to the rubber. The precise mechanism for the antiozonant activity of these compounds should be studied both in rubber and in model compounds.

4) The bis-nitrone (BMHPPN) was found to impart better antiozonant protection to the rubber than the best of the mono-nitrones (MHPPN). However, because of its extreme scorchiness it is not considered to be commercially acceptable. It is suggested that the structure of the bis-nitrone

be modified in order to overcome its scorchiness. This could probably be done by increasing the steric hinderence around the carbon atoms which are directly attached to the nitrogens. Alternately, combinations of bis-nitrones with retarders could be studied.

5) Since the nitrones (particularly MHPPN and MHPBN) are good static antiozonants and satisfactory antifatigue agents it would be interesting to study their dynamic antiozonant behaviour.

6) In view of the commercial potential of the N-alkyl nitrones for use as stabilisers in light coloured rubbers it is suggested that a larger scale study of these compounds be made using real service life rubber components. Furthermore, the relative toxicity of these nitrones should also be studied.

REFERENCES

1. G. Scott, Atmospheric Oxidation and Antioxidants, Elsevier Publishing Company (1965).

2. J.M. Buist, I.R.I. Monograph on Ageing and Weathering of Rubber, Heffer & Sons Ltd (1956); Annual Report on the Progress of Rubber Technology p.56 (1954).

3. J.R. Shelton, Rubb. Chem. Tech., 30 125 (1957).

4. A.S. Kuzminskii, Polym. Sci. U.S.S.R. 19, 2509 (1977).

5. G.J. Lake and P.B. Lindley, in Use of Rubber in Engineering, (ed. P.W. Allen, P.B. Lindley and A.R. Payne), Maclaren and Sons Ltd (1969), ch.5.

6. Z.T. Ossefort, A.S.T.M. Special Publication 229, 38 (1958).

7. A. Neal and A.J. Northam, Ind. Eng. Chem., 23, 1449 (1931).

8. G. Scott, Chem. and Ind., 271 (1971).

9. J.L. Bolland, Quart. Rev. Chem. Soc., 3, 1 (1949).

10. L. Bateman, ibid, 8, 147 (1954).

11. J.F. Smith in The Applied Science of Rubber (ed. W.J.S. Naunton), Edward Arnold (Publishers) Ltd., (1961), ch. XIII pt.1.

12. A.V. Tobolsky and G.M. Brown, Rubb. Chem. Tech., 29, 1195 (1956).

13. A.V. Tobolsky and R.D. Andrews; J. Chem. Physics 13, 3 (1945).

14. A.V. Tobolsky, B. Prettyman, J.H. Dillon, Rubb. Chem. Tech., 17, 551 (1944).

15. A.V. Tobolsky and A. Mercurio, J. App. Polym. Sci. 2, 186 (1959).

16. J.R. Dunn, J. Scanlan and W.F. Watson, Trans. Farad. Soc., 54, 730 (1958).

17. T. Colclough, J.I. Cunneen, G.M.C. Higgins, J. App. Polym. Sci., 12, 195 (1968).

18. G. Scott, in Developments in Polymer Stabilisation-4, (ed. G. Scott), Applied Science Publishers (1981)ch.1.

19. C. Armstrong, F.A.A. Ingham, A.A. Pimblott, G. Scott and J.E. Stuckey, Proc. Int. Rubb. Conf., Brighton, (May 1972), F 2·1.

20. G.J. Lake, Rubb. Chem. Tech., 45, 309 (1972).

21. G.J. Lake, Rubber Age, 30, (Aug. 1972); ibid, 39, (Oct. 1972).

22. R.S. Rivlin and A.G. Thomas, J. Polym. Sci., 10, 291 (1953).

23. A.N. Gent and P.B. Lindley, J. App. Polym. Sci. 8, 455 (1964).

24. G.J. Lake and P.B. Lindley, ibid, 8, 707 (1964).

25. P.B. Lindley, Rubb. Chem. Tech., 47, 1253 (1974).

26. J.R. Beatty, ibid, 37, 1341 (1964).

27. P.B. Lindley, in Rubber in Engineering 1973, (ed. P.B. Lindley and H.G. Rodway), published by the N.R.P.R.A. (1973).

28. D.G. Young, E.N. Kresge, and A.J. Wallace, Rubb. Chem. Tech., 55, 428 (1982).

29. P.B. Lindley and A. Stevenson, ibid, 55, 337 (1982).

30. A.G. Thomas, J. Polym. Sci., 467 (1958).

31. H.W. Greensmith, J. App. Polym. Sci., 8, 1113 (1964).

32. W. Potter and G. Scott, Eu. Polym. J., 7, 489 (1971).

33. A.S. Kuzminskii and L.I. Lyubchanskaya, Rubb. Chem. Tech., 29, 770 (1956).

34. A.S. Kuzminsky in Developments in Polymer Stabilisation -4, (ed. G. Scott), Applied Science Publishers (1981), ch. 3.

35. M.K. Khromov and K.N. Lazareva, Int. Polym. Sci. Tech., 6, no 3, T/73 (1979).

36. M. Braden and A.N. Gent, J. App. Polym. Sci., 3, 100 (1953).

37. M. Braden and A.N. Gent, ibid, 3, 90 (1960),

38. G.J. Lake and P.B. Lindley, ibid, 9, 2031 (1965).

39. G.J. Lake and P.B. Lindley, ibid, 10, 343 (1966).

40. J.C. Amberlang, R.H. Kline, O.M. Lorenz, C.R. Parks, C.Wadelin and J.R. Shelton, Rubb. Chem. Tech., 37, 1497 (1963).

41. A.A. Popov, B.E. Krisyak, N.N. Blinov and G.E. Zaikov, Eu. Polym. J., 17, 169 (1981).

42. W. Cox, A.S.T.M. Special Publication 229, 57, (1958).

43. A.N. Gent, J. App. Polym. Sci., 6, 497 (1962).

44. J.M. Buist, Trans. Inst. Rubb. Ind., 29, 72 (1953).

45. J.M. Buist, and G.E. Williams, India Rubb. World, 124, 320 (1951); ibid, 124, 447 (1951); ibid, 124, 567 (1951).

46. E.T. Rainier and R.H. Gerke, Ind. Eng. Chem. (Anal. Edn.), 7, 368 (1935).

47. L.V. Cooper, ibid, 2, 391 (1930).

48. S. Eccher, Rubb. Chem. Tech . , 13, 566 (1940).

49. R.G. Newton, ibid, 18, 504 (1945).

50. J.A. Brydson, Rubber Chemistry, Applied Science Publishers (London) (1978), ch.9.

51. J.R. Shelton and W.M. Cox, Rubb. Chem. Tech . , 27, 671 (1954).

52. C.J. Pedersen, Ind. Eng. Chem., 41, 924 (1949).

53. Polymer Stablilisation, ed. W.L. Hawkins, Wiley Interscience (1972), ch. 2-4.

54. C. Armstrong, M.A. Plant and G. Scott, Eu. Polym. J., 11, 161 (1975).

55. C. Armstrong and G. Scott, J. Chem. Soc., 1741 (1971).

56. J.R. Shelton, Rubb. Chem. Tech., 47, 949 (1974).

57. C. Armstrong, M.J. Husbands and G. Scott, Eu. Polym. J., 15, 241 (1979).

58. M.J. Husbands and G. Scott, Eu. Polym. J., 15, 249 (1979).

59. M.J. Husbands, PhD. Thesis - Aston University (1977).

60. J.R. Shelton, in Developments in Polymer Stabilisation -4, (ed. G. Scott,) Applied Science Publishers, (1981), ch.2.

61. G. Scott, Pure and App. Chem., 52, 365 (1980).

62. T.J. Henman, in Developments in Polymer Stabilisation--1, (ed. G. Scott), Applied Science Publishers (1980), ch.2.

63. K.B. Chakraborty, R. Bagheri and G. Scott, Chem. Ind., 865 (1980).

64. O.L. Harle and J.R. Thomas, J. Am. Chem. Soc., 79, 2973 (1957).

65. J.R. Thomas, ibid, 82, 2955 (1960).

66. J.G. Baird and J.R. Thomas, J. Chem. Physics, 35, 1507 (1961).

67. A.T. Kovitskii and A.F. Lukovinkov, Dokl. Abad. Nauk. U.S.S.R., 147, 1126 (1962).

68. J.Q. Adams, S.W. Nicksi and J.R. Thomas, J. Chem. Physics, 45, 654 (1966).

69. I.T. Brownie and K.U. Ingold, Can. J. Chem., 45, 2419 (1967); ibid, 45, 2427 (1967).

70. E.G. Rozantsev, Free Nitroxide Radicals, Plenum Press (1970), (trans. H. Ulrich).

71. A.R. Forrester, J.M. Hay and R.H. Thomson, Organic Chemistry of Stable Free Radicals, Academic Press (1968), ch.5.

72. J.R. Thomas and C.A. Tolman, J. Am. Chem. Soc., 84, 2930 (1962).

73 E.G. Rozantsev and V.D. Sholle, Synthesis, 190 (1971); ibid, 401 (1971).

74. J.F.W. Keana, J. Am. Chem. Soc., 78, 37 (1978).

75. K. Adamic, D.F. Bowman, T. Gillan and K.U. Ingold, ibid, 93, 902 (1971); ibid, 93, 6551 (1971); ibid, 93, 6555 (1971).

76. T. Bolsman, A. Block and J. Frijins, Recl. Trav. Chem. Pays-Bas, 97, 310 (1978).

77. Y.Ya. Shlyapintokh, V.B. Ivanov, O.M. Khvostach, A.B. Shapiro and E.G. Rozantsev, Dolkady Phys. Chem., 1362 (1975).

78. J. Sedlar, J. Petruj, J. Pac and M. Navratil, Polymer, 21, 5 (1980).

79. D.W. Grattan, D.J. Carlsson and D.M. Wiles, Polym. Degrad. Stab. , 1, 69 (1979).

80. H.J. Heller and H.R. Blattmann, Pure and Appl. Chem., 36, 141 (1973).

81. N.S. Allen, J.F. McKellar and D. Wilson, Polym. Degrad. Stab. , 1, 205 (1979).

82. V. Ivanov, Y.Ya. Shlyapintokh, O.M. Khvostach and E.G. Rozantsev, Bull. Acad. Sci. U.S.S.R. (div. Chem. Sci.), 1845 (1974).

83. Y.Ya. Shlyapintokh, E. Bystritokaya, A.B. Shapiro, L.N. Smirnov and E.G. Rozantsev, ibid, 1870 (1973).

84. K.B. Chakraborty and G. Scott, Polym. Degrad. Stabl., 1, 37 (1979).

85. R. Bagheri, K.B. Chakraborty and G. Scott, ibid, 4, 1 (1982).

86. D.K.C. Hodgeman, J. Polym. Sci. (Polym. Chem. edn.) 18, 533 (1980).

87. D.M. Wiles, and D.J. Carlsson paper entitles "U.V. Stabilisation of Polyolefins by Hindered Amines", given at the conference on Stabilisation of Polyolefins, France (June 1982).

88. J.R. Thomas and C.A. Tolman, J. Am. Chem. Soc., 84, 2930 (1962).

89. M.V. Sudnik, M.F. Romantsev, A.B. Shapiro and E.G. Rozantsev, Bull. Acad. Sci. U.S.S.R. (div. Chem. Sci.), 2702 (1975); ibid, 35, (1977).

90. M.B. Nieman and E.G. Rozantsev, ibid , 1095 (1964).

91. J. Hammer and A. Macluso, Chem. Rev., 64, 473 (1964).

92. G. Tennet, in Comprehensive Organic Chemistry (ed. D. Barton and W.D. Ollis), vol. 2, Pergaman Press (1980), part 8, p.500.

93. M. Kamimori, H. Sakuragi, K. Sawatari, T. Suehiro, K. Tokumaru and M. Yoshida, Bull. Chem, Soc. Japan, 52, 2339 (1979).

94. J.S. Roberts, in Comprehensive Organic Chemistry, (ed. D. Barton and W.D. Ollis), vol. 2, Pergaman Press (1980), part 6·4.

95. E.G. Janzen and B.J. Blackburn, J. Am. Chem. Soc., 90, 5909 (1968); ibid, 91, 4481 (1969).

96. G. Scott and K.V. Smith, Eu. Polym. J., 14, 39 (1978).

97. K.V. Smith, Ph.D. Thesis, University of Aston in Birmingham (1976).

98. H. Yaghmour, personal communication, University of Aston in Birmingham (1982).

99. G. Scott and K.V. Smith, Eu. Polym. J., 14, 905 (1978); Rubb. Chem. Tech., 52, 949 (1979).

100. G. Scott, in Developments in Polymer Stabilisation-4, ed. G. Scott, Applied Science Publishers (1981), ch. 6.

101. A.A. Katbab and G. Scott, Chem. Ind., 573 (1980); Eu. Polym. J., 17, 559 (1981).

102. Cieba Geigy - Technical Information Bulletin - publication no.: 37327/2/e.

103. M. Cain, G.T. Knight, T.M. Lewis and B. Saville, Rubb. J., 150, vol.10, 22 (1968).

104. T.V. Fedorova and S.M. Kavun, Int. Polym. Sci. Technol. 2, no.1, T/85 (1975).

105. G. Scott, Plastics and Rubber Processing, 41 (June 1977); unpublished work.

106. A.A. Katbab, Ph.D. thesis, University of Aston in Birmingham (1980).

107. R. Suharto, Ph. D Thesis University of Aston in Birmingham (1982).

108. M. Coker, G. Scott and A.A. Sweiss, Polym. Degrad. Stab., 4, 333 (1982).

109. L.A. Walker, J.J. Luecken, Elastomerics, 112, 36 (May 1980).

110. D.A. Lederer and M.A. Fath, Rubb. Chem. Tech., 54, 415 (1981).

111. J.C. Andries, C.K. Rhee, R.W. Smith, D.B. Ross and H.E. Diem, ibid, 52, 823 (1979).

112. R.P. Lattimer, E.R. Hooser, H.E. Diem, R.W. Layer and C.K. Rhee, ibid, 53, 1170 (1980).

113. J.C. Andries, C.K. Rhee, R.P. Lattimer, H.E. Diem and R.W. Smith, paper entitled "Surface Studies of Antiozonant protection of polymers", - given at the International Conference on Advances in the Stabilisation and Controlled Degredation of Polymers, Luzern, Switzerland, (June 1981).

114. S.D. Razumovskii and L.S. Batashova, Rubb. Chem. Tech., 43, 1340 (1970).

115. W.J.E. Parr, J. Chem. Soc. Perkin I, 3002 (1981).

116. Rubber Developments, 34, no.3, 72 (1981).

117. A.A. Katbab and G. Scott, Polym. Degrad. Stab., 3, 221 (1981).

118. R.W. Layer, in Developments in Polymer Stabilisation--4, (ed.G. Scott), Applied Science Publishers (1981), ch.5.

119. P.P. Nicholas, A.M. Luxeder, L.A. Brooks and P.A. Hammes in Kirk-Othamer's Encyclopedia of Chemical Technology vol.3, Third edn., John Wiley and Sons (1978), p.128.

120. B.R. Meadows (Marketing Planning - Tyre Division, Dunlop Ltd.), personal communication.

121. I.U.P.A.C. Nomenclature of Organic Chemistry; sections A, B, C, D, E, F and H; prepared for publication by J. Rigaudy and S.P. Klesney, Pergamon Press (1979 edn.).

122. R. Briere, H. LeMaire and A. Rassat, Bull. Soc. Chem. de France, 3273 (1965).

123. M. Iwamura and N. Inamoto, Bull. Chem. Soc. Japan, 703 (1967).

124. E.T. Strom and A.L. Bluhm, Chem. Commun., 115 (1966).

125. A. Mackor, T.A.J.W. Wajer, T.J. De Boer and T.W. Van Voorst, Tetrahedron Letters, 22, 2115 (1966); ibid, 23, 4021 (1967); ibid, 23, 285 (1967); ibid, 24, 1623, (1968).

126. W.D. Blackley, J. Am. Chem. Soc., 88, 480 (1966).

127. R. Bonnet, R.F.C. Brown, V.M. Clark, I.O. Sutherland and A.J. Todd, J. Chem. Soc., 2094 (1959).

128. E. Bamberger, Ber., 27, 1548 (1894).

129. P.A.S. Smith, "Open Chain Nitrogen Compounds", vol.2, W.A. Benjermin Inc. (1966), ch.1 and 13.

130. M.A.T. Rogers, J. Chem. Soc., 769 (1955).

131. E.G. Rozantsev and V. Golubev, Bull. Acad. Sci. U.S.S.R. (div. Chem. Sci.), 852 (1966).

132. G. Zinner, Angewante Chemie, 71, 311 (1955).

133. V.D. Sholle, V.A. Golubev and E.G. Rozantsev, Doklady Chem., 196-201, 761 (1971).

134. V.A. Golubev and E.V. Kobylyanskii, J. Org. Chem. U.S.S.R., 8, 2657 (1972).

135. G.A. Kovtun, A.L. Aleksandrov and V.A. Golubev, Bull. Acad. Sci. U.S.S.R. (div. of Chem. Sci.), 23, 2115 (1974).

136. G.M. Whitesides and T.L. Newirth, J. Org. Chem., 40, 3449 (1975).

137. K. Murayama, S. Morimura and T. Yoshiko, Bull. Chem. Soc., Japan, 42, 1640 (1969).

138. J.A. Howard and T.C. Tait, J. Org. Chem., 43, 4279 (1978).

139. M. Iwamura and N. Inamoto, Bull. Chem. Soc. Japan, 40, 702 (1967).

140. W.R. Dunstan and E. Goulding, J. Chem. Soc. Trans. II, 75, 792 (1899).

141. R.F. Kleinschmidt and A.C. Cope, J. Am. Chem. Soc., 66, 1929 (1944).

142. J.M. Anderson and J.K. Kochi, ibid, 92, 1651 (1970).

143. F. Minisci, R. Bernardi, F. Bertini, R. Galli and M. Perchinummo, Tetrahedron, 27, 3575 (1971).

144. R.M. Silverstein, C.G. Bassler and T.C. Morril, "Spectrometric Identification of Organic Compounds", 3rd edn., John Wiley and Sons Inc., (1974), ch.3.

145. E.G. Rozantsev, V.A. Golubev, M.B. Neiman and Yu.V. Kokhanov, Bull. Acad. Sci. U.S.S.R. (div. Chem. Sci.), 559 (1965).

146. L.N. Kirchenko and A.A. Medzhikov, ibid, 2685 (1969).

147. G.A. Nikiforov, K.M. Dyumaev. A.A. Volodkin and V.V. Ershov, ibid, 1741 (1962).

148. J.C. Stowell, J. Org. Chem., 36, 3055 (1971).

149. F.D. Greene and J.F. Pazos, J. Org. Chem., 34, 2269 (1969).

150. H. Shindo and B. Umezawa, Chem. Pharm. Bull. (Tokyo) 10, 492 (1962); Chem. Abstr. 57, no.14, 598 (1962).

151. O.L. Brady, F.P. Dunn and R.F. Goldstein, J. Chem. Soc., 2386 (1926).

152. A. Hantzsch, B.E.R., 31, pt.2, 2065 (1898).

153. C. Kjellin, ibid, 30, 1891 (1897).

154. "Handbook of Chemistry and Physics", 60th edn. (ed: R.C. Weast); CRC Press Inc. (1980).

155. J.G. Pacifici and H.L. Browning, J. Am. Chem. Soc., 92, 5231 (1970).

156. L.M.K. Tillekeratne, personal communication.

157. P.W. Allen and G. Bloomfield in The Chemistry and Physics of Rubber Like Substances, (ed. L. Bateman) Maclaren and Sons Ltd. (1963), ch.1.

158. R.P. Brown, "Physical Testing of Rubbers", Applied Science Publishers (London), (1979).

159. Rubber Technology - edited by M. Morton, Van Nostrand Reinhold Company (1973).

160. A.Y. Coran, Rubb. Chem. Tech., 37, 689 (1964); ibid, 38, 1 (1965).

161. Monsanto Fatigue to Failure Tester Handbook.

162. J.W. Mellor, "Higher Mathematics for Students of Chemistry and Physics", Dover Publications Inc. (1955).

163. British Standards - no. 903, part A43 (1980) - "Determination of resistance to ozone cracking under static conditions".

164. K.T. Paul, R.A.P.R.A. Bull., 2, 29, (1972); R.A.P.R.A. Members J., p.273, Nov. (1963).

165. D.J. Angier and W.F. Watson, J. Polym. Sci., 18, 129 (1955).

166. G.M. Bristow and B. Westall, J. App. Polym. Sci., 9, 495 (1965); N.R.P.R.A. publication number 507.

167. M. Symons "Chemistry and Biochemistry Aspects of Electron Spin Resonance Spectroscopy", Van Nostrand Reinhold Publishers (1978).

168. JEOL - PE Electron Spin Resonance Spectrometer Handbook.

169. L. Bateman, C.G. Moore, M. Porter and B. Saville, in The Chemistry and Physics of Rubber Like Substances, (ed. L. Bateman), Maclaren and Sons Ltd. (1963), ch.15.

170. V. Duchacek, Angew.Makromol., 23, 21 (1972).

171. W. Scheele, Rubb. Chem. Tech . , 34, 1306 (1961).

172. E.M. Bevilacqua, ibid, 32, 721 (1959).

173. S.P. Manik and S. Banerjee, ibid, 43, 1294 (1970).

174. S. Urabe, Int. Polym. Sci. Technol., 7, no.2 T/102 (1980).

175. P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press, (1971).

176. J.R. Shelton and E.T. McDonel Rubb. Chem. Tech., 33, 342 (1960).

177. D. Craig, ibid, 29, 944 (1956).

178. R.I. Zhdanov, V.A. Golubev, V.M. Gida and E.G. Rozantsev, Bull. Acad. Sci. U.S.S.R., (div. Chem. Sci.) 21, 2258 (1970).

179. K. Murayama and T. Yoshioka, Bull. Chem. Soc. Japan, 42, 1942 (1969).

180. C.G. Moore and R.W. Saville, J. Chem. Soc., 2082 (1954).

181. W. Scheele, H.E. Toussaint and Y.K. Chai, Rubb. Chem. Tech., 33, 846 (1960).

182. H.S. Dweik, personal communication, University of Aston in Birmingham (1982).

183. P.D. Bartlett, E.F. Cox and R.E. Davies, J. Am. Chem. Soc., 83, 103 (1961).

184. P.D. Bartlett, A.K. Colter, R.E. Davies and W.R. Roderick, ibid, 83, 109 (1961).

185. H. Krebs, Rubb. Chem. Tech., 30, 962 (1957).

186. W.E. Hammer, J.D. Pratt and J.E. Such, Chemicals for the Rubber, Leather and Match-Making Industries, Pergamon Press (1966), chapter on Rubber Chemicals.

187. T.J. Watts, in "The Applied Science of Rubber", (ed. W.J.S. Naunton), Edward Arnold Publishers Ltd. (1961), ch. VI, pt.1.

188. Rubber Technology and Manufacture, edited by C.M. Blow, Butterworth and Co. Publishers Ltd. (1971).

189. J. Pospisil, in Developments in Polymer Stabilisation--1 (ed. G. Scott), Applied Science Publishers (1980), ch.1.

190. K.U. Ingold, J. Am. Chem. Soc., 90, 296 (1968).

191. O. Exner, Collection Czechoslov. Chem. Communs., 16, 258 (1951).

192. R. Grashey, R. Huisgen and H. Leitermann, Tetrahedron Letters, no.12, 9 (1960).

193. S. Nishita, J. Furakawa and S. Yamashita, Nippon Gomu Kyokaischi, 43, 307 (1970).

194. K. Adamic, D.F. Bowman, T. Gillan and K.U. Ingold, J. Am. Chem. Soc., 93, 902 (1971).

195. D.F. Bowman, J.L. Brokenshire, T. Gillan and K.U. Ingold, ibid, 93, 6551 (1971).

196. D.F. Bowman, T. Gillan and K.U. Ingold, ibid, 93, 6555 (1971).

197. R.M. Dupeyre and A. Rassat, ibid, 88, 3180 (1966).

198. P. Schmid and K.U. Ingold, ibid, 100, 2493 (1978).

199. D.W. Grattan, D.J. Carlsson, J.A. Howard and D.M. Wiles, Canad. J. Chem., 57, 2834, (1979).

200. R. Bagheri, Ph.D. thesis, University of Aston in Birmingham (1981).

201. V.Ya. Shlyapintokh and V.B. Ivanov, in Developments in Polymer Stabilisation-5, (ed. G. Scott), Applied Science Publishers Ltd. (1981) ch.3.

202. M. Hajian, Ph.D. thesis, University of Aston in Birmingham (1980).

203. K.B. Chakraborty and G. Scott, Polymer 21, 252 (1980).

204. D.W. Grattan, D.J. Carlsson and D.M. Wiles, in Developments in Polymer Stabilisation-1, (ed. G. Scott), Applied Science Publishers, (1980), ch.7.

205. S. Nigam, K.D. Asmus and R.L. Wilson, J. Chem. Soc. Faraday I, 2324 (1976).

206. S. Jantrawaratit, Ph.D. thesis, University of Aston in Birmingham (1980).

207. A.H. Riebel, R.E. Erickson, C.J. Abshire, P.S. Bailey, J. Am. Chem. Soc., 82, 1801 (1960).

208. B.A. Dogadkin, A.V. Dobromyslova and O.N. Belyatskaya, Rubb. Chem. Tech., 35, 501 (1962).

209. S.P. Lyakina, A.V. Dobromyslova, V.M. Kazakova, A.A. Dontsov and B.A. Dogadkin, J. Polym. Sci. U.S.S.R., 15, 3151 (1973).

210. W.A. Waters, The Chemistry of Free Radicals, Clarendon Press, (1946).

211. M. Rabb and J. Pospisil, Polym. Degrad. Stab., 4, 353 (1982).

212. A.V. Tobolsky, I.B. Prettyman and J.H. Sillon, J. App. Phys., 15, 380 (1944).

213. A.V. Tobolsky, R.D. Andrews and E.E. Hanson, ibid, 17, 352 (1944).

214. R. Menderson and A.V. Tobolsky, Polym. Sci., 2, 463 (1947).

215. L. Bateman, J.I. Cunneen C.G. Moore, L. Mullins and A.G. Thomas, in The Chemistry and Physics of Rubber Like Substances, (ed. L. Bateman), Maclaren and Sons Ltd. (1963), ch. 19.

216. K.B. Chakraborty and G. Scott, Chem. Ind., 237, (1978).

217. P.K. Pal, A.K. Bhowmick and S.K. De, Rubb. Chem. Tech., 55, 23 (1982).

218. C.H. Leigh-Dugmore, in "The Applied Science of Rubber" (ed, W.J.S Naunton), Edward Arnold Publishers Ltd. (1961), ch. VII pt.2.

219. A.S. Kuzminskii, L.I. Lyubchanskaya, N.G. Khitrova and S.I. Bass, Rubb. Chem. Tech., 26, 858 (1953).

220. G. Crauss and R.L. Collins, Rubb. World, 139, 219 (1958).

221. V.A. Garten and D.E. Weiss, Indust. Chemist, 525 (1959).

222. H. Winn, J.R. Shelton and D. Turnbull, Ind. Eng. Chem., 38, 1052 (1946).

223. V.A. Garten, K. Eppinger and D.E. Weiss, Aust. J. App. Sci., 7, 148 (1956).