To my Father, my Brother Alireza
and to the memory of my Mother

SYNTHESIS AND EVALUATION OF BOUND THIOL ANTIOXIDANTS

by

SEYED - MEHDI TAVAKOLI

Submitted for the

Degree of Doctor of Philosophy

of the

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The work described in this thesis was carried out between May 1977 and May 1980. It has been done independently and submitted for no other degree.

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SUMMARY

The reactions of hindered phenolic antioxidants with NR latex in the presence of a free radical generating system have been studied. 3,5-Di-tert-butyl-4-hydroxybenzyl carboxy methyl (BTGA), and ethyl (BTPA) sulphides and 3,5-di-tert-butyl-4-hydroxybenzyl mercaptoglycollate (BTGE) have been found to react with NR in the presence of tert-butyl hydroperoxide (TBH) and tetraethylenepentamine (TEPA). The concentrations of bound antioxidants were estimated by an infra-red technique after exhaustive extraction.

The reactions of 4-mercaptoacetamidodiphenyl amine (MADPA) and 3,5,-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM) with natural and styrene-butadiene rubbers have also been investigated by a mechanochemical process in a torque rheometer. Masterbatch concentrates containing high levels of bound antioxidants in natural and styrene-butadiene rubbers, have been used as additives for untreated rubbers to obtain rubbers with high levels of oxidative stability. Oxygen absorption and stress relaxation techniques were used to evaluate the effectiveness of the bound antioxidants. The performances of bound antioxidants produced both by latex and mechanochemical binding have been found to be superior to conventionally added Nonox WSP, which is almost completely removed during extraction. A major advantage of the bound antioxidant concentrates studied in this work has been found to be their suitability for the preparation of solid masterbatches.

The effects of various rubber-bound systems on the curing characteristics of NR and SBR rubbers have been assessed using the Monsanto rheometer. In the case of MADPA and BHBM these effects have been found to be insignificant particularly in the extracted rubbers.

KEYWORDS

Polymer-bound antioxidants
Mechanochemistry
Rubber
Oxidative degradation
Masterbatch concentrates

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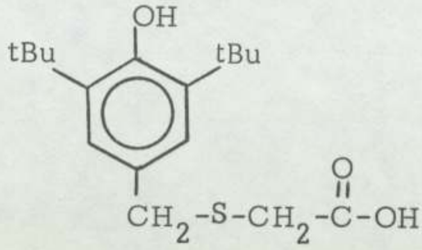
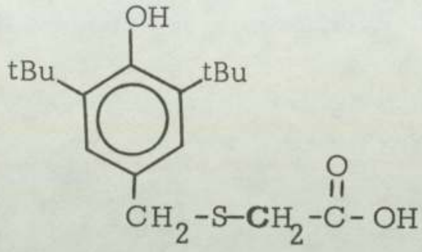
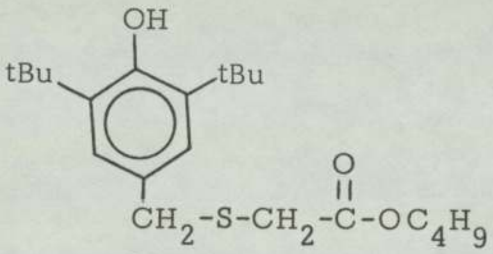
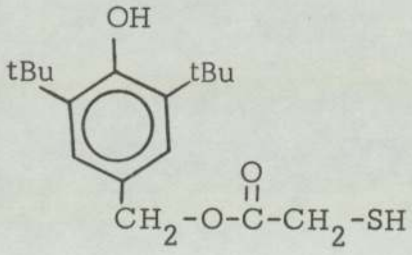
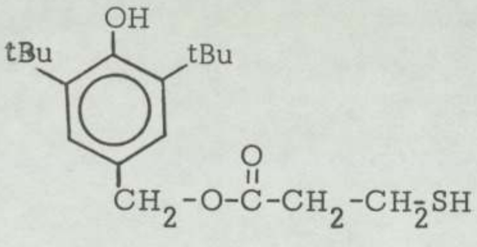
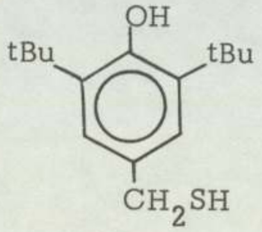
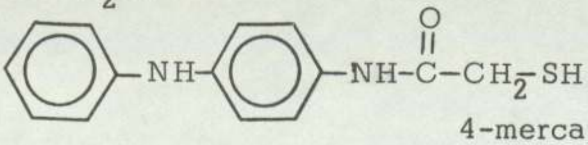
LIST OF ABBREVIATIONS

Chemical Structure	Name	Abbreviation
	3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-methyl sulphide	BTGA
	3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-ethyl sulphide	BTPA
	3,5-di-tert-butyl-4-hydroxybenzyl-butyl thioglycollate	BTBE
	3,5-di-tert-butyl-4-hydroxybenzyl mercaptoglycollate	BTGE
	3,5-di-tert-butyl-4-hydroxybenzyl mercaptopropionate	BTPE
	3,5-di-tert-butyl-4-hydroxybenzyl mercaptan	BHBM
	4-mercaptoacetamido-diphenylamine	MADPA

CHAPTER ONE

INTRODUCTION

1.1. Degradation of Polymers

Both natural and synthetic polymers deteriorate as a result of conditions encountered during service. The changes in structure and composition result in the loss of useful properties and finally to failure of the polymer. Typical examples of polymer degradation are, cracking of rubber, embrittlement of plastics and yellowing of cotton fabrics. Although many factors may be responsible for deterioration of polymers, oxygen is by far the most important factor involved. The failure of a vast majority of polymers under extreme conditions (i.e. at combustion temperatures), and at much lower temperatures during service life is known to be the consequence of their reaction with oxygen. The effects of water and light come next after oxygen. The effect of water in a polymeric environment can, for instance, lead to hydrolysis of condensation polymers or stabilizers containing ester groups. The absorption of light can also result in the loss of useful properties by initiating or accelerating some of the chemical reactions occurring during autoxidation. Apart from factors mentioned so far, the other important environmental agents which are deleterious to polymer stability are heat, contamination by metal ions and mechanical deformation. The chemical structure of the polymer itself is also important in determining its ease of degradation by oxidative attack. For instance, the presence of labile tertiary hydrogen in polypropylene or unsaturation and allylic hydrogen in cis-polyisoprene and polybutadiene can be considered to be responsible for their relative vulnerability to thermal as well as photoxidation.

1.2. Degradation of Rubber

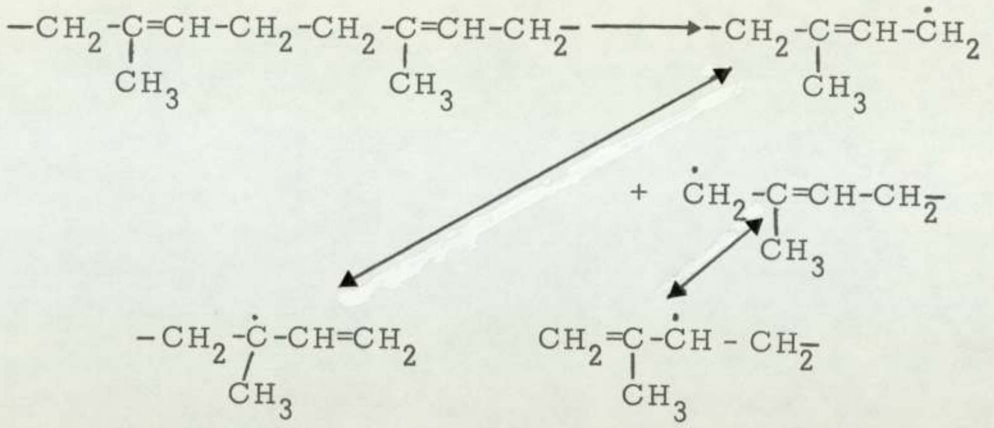
In the middle of the nineteenth Century Hofmann(1) and Spiller(2) showed that the degradation of rubber by oxygen was the cause of failure of rubber goods in service. Natural and synthetic rubbers are attacked by oxygen even at room temperature and the reaction is accelerated by heat, light and certain metallic impurities. Therefore, the protection of elastomers appears to be particularly important due to their unsaturation which makes them susceptible to unfavourable reactions such as oxygen absorption, chain scission and cross-linking. Deterioration may result in considerable changes in physical and chemical properties such as tensile strength, hardness, elongation, colour, tack, Mooney viscosity and processibility, etc. The modes of oxidation of raw and vulcanized rubber differ considerably from one another in detail and hence, it is important to consider the two cases separately.

1.2.1. Oxidation of Raw Rubber

Both synthetic and natural elastomers in unvulcanized form are susceptible to oxidation during the periods of shipping and storage, and also compounding and fabrication. Oxidation in the first period may occur when rubber is in the latex form. It has been shown that NR latex can absorb oxygen resulting on its hardening. Sekhar (3) has shown that carboxy end groups on hydrocarbon chains in NR latex are responsible for this effect. The increase in viscosity of rubber at this stage has also been correlated to their cross-linking with oxygen. Hydroperoxides formed during oxidation can initiate vinyl polymerisation or decompose and result in hardening of the latex. The oxidation of rubber during compounding and fabrication will be dealt with in some detail due to their relative importance to the present work.

1.2.1.1. Mechano-Chemical Degradation of Rubber

Mechano-degradation of rubber is not always undesirable. Mastication, the mechanical deformation of rubber in the presence of oxygen or an added chemical plasticiser is generally used in rubber technology to plasticize the elastomer before the addition of compounding ingredients. The same process in fabricated products may result in a reduction in the useful life of the rubber. The mastication of natural rubber is well documented and shows a distinctive behaviour. Mastication at room temperature in nitrogen produces no appreciable change in molecular weight. In oxygen, however, degradation is immediate and rapid. In nitrogen the radicals formed by shear forces recombine with eachother, whereas they recombine preferentially with oxygen when this is present. The macroradical in rubber must be relatively stable and unreactive in nitrogen. This seems quite possible in natural rubber since the weakest bonds are between isoprene units which leads to two radicals which are highly stabilised with resonsance. Therefore, by stabilisation of alkyl radicals and the associated weakening of $-CH_2-CH_2-$ bond the initial rupture in rubber may be shown as follows:

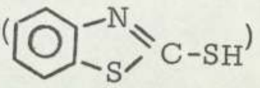


The formation of free radicals by mechanical scission of the rubber chain is particularly evident from the work of Watson (4) and his co-investigators. In the presence of oxygen, two types of radicals are produced. Alkyl radicals formed due to shear forces can react with oxygen to form $R\dot{O}$ and $ROO^{\cdot}$ radicals. Since these radicals cannot recombine, this should lead to a reduction in molecular weight. ESR studies (5) have shown that these radicals are very unstable since their spectra fade rapidly with time. A large number of other materials are also known which compete with oxygen and stablilize the ruptured radicals. As Scott (6) has pointed out, thiols for instance, can readily produce thiyl radicals by reaction with hydroperoxide and then react with alkyl radicals :

$$RSH \xrightarrow{ROOH} RS^{\cdot} + R\dot{O} + H_2O$$

The formation of alkyl thiyl radicals may also result from their reaction with oxygen :

$$RSH + O_2 \longrightarrow RS^{\cdot} + \dot{O}OH$$

Dogadkin (7) et al., have shown that in the case of MBT() thiyl radicals formed in this way can react with alkyl radicals. It is known (6) that in mastication of rubber in air and in the presence of a mercaptan the following reactions can occur :

$$\dot{R} + O_2 \longrightarrow ROO^{\cdot}$$

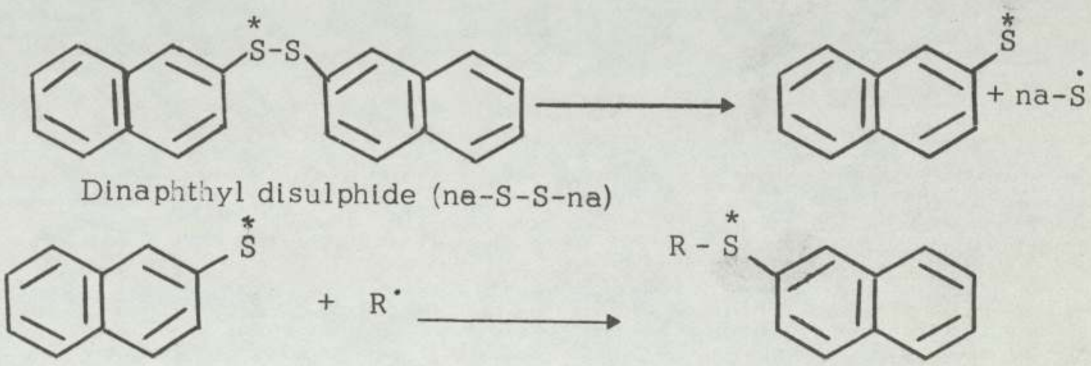
$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

$$RS^{\cdot} + RH \longrightarrow RSH + R^{\cdot}$$

$$RS^{\cdot} + RS^{\cdot} \longrightarrow RSSR$$

$$RS^{\cdot} + R^{\cdot} \longrightarrow RSR$$

Termination of alkyl thiyl radicals can occur by recombination or reaction with another radical. Aromatic disulphides are known as another type of radical acceptors which can cleave at S-S bonds and then react with alkyl radicals:



Dinaphthyl disulphide (na-S-S-na)

Ayrey et al., (8) have shown that the above reaction takes place when rubber is masticated in an inert atmosphere. The radioactively labelled sulphur atom was found combined with rubber after extraction of the unreacted disulphide. However, homolytic cleavage of disulphides does not appear to occur at room temperature. Therefore, the formation of alkyl thiyl radicals may be initiated by alkyl radicals :

$$R_1SSR_2 + R_3^{\bullet} \longrightarrow R_1S^{\bullet} + R_2SR_3$$

The effect of temperature on mechanical degradation is of fundamental importance. In the case of natural rubber mastication efficiency passes through a minimum (9) at about 115°C (curve a in Fig. 1.1). Further decrease in temperature results in mechano-oxidative degradation (4) (curve b). As a result of increase in the temperature of mastication the solubility of oxygen in the rubber, viscosity and the rate of breakdown decreases. The important difference between shear and oxidative breakdown is that, in the former mechanical forces initiate scission and oxygen may stabilize the chain ends, whereas in the latter the molecules cleave at peroxide sites originally formed by oxidation of the main chain. These two processes are generally termed as cold and hot mastication occurring at temperatures below 100°C and above approximately 130°C respectively.

However, the effect of shear forces on the reduction of molecular weight of the rubber is limited. The investigators at NRPRA (now MRPRA) (8,10) have found that there is a limiting molecular weight below which the breakdown virtually stops. This was found to be around 70000 for natural rubber.

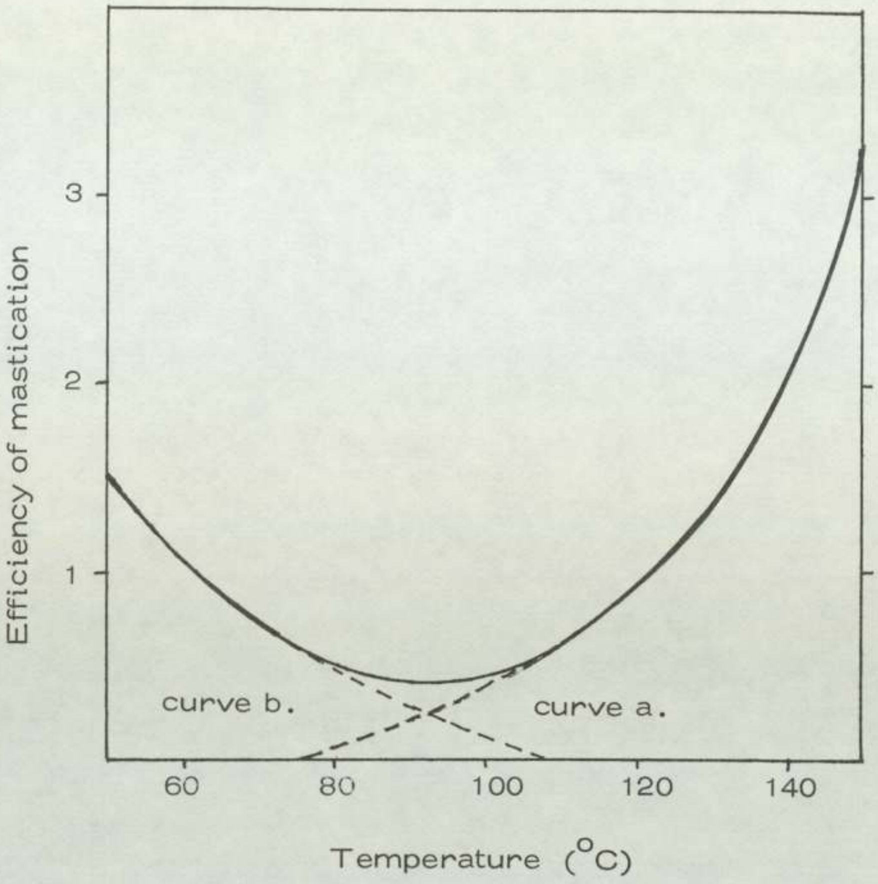


Fig.1.1. Efficiency of mastication of natural rubber at different temperatures.(4)

1.2.2. Oxidation of Vulcanised Rubber

The ageing behaviour of rubber vulcanisates differs considerably from the raw rubber and depends strongly upon the curing system used. Vulcanisates containing elemental sulphur oxidize faster than others (11). A simple representation of a sulphur cross-link is shown in Fig. 1.2.

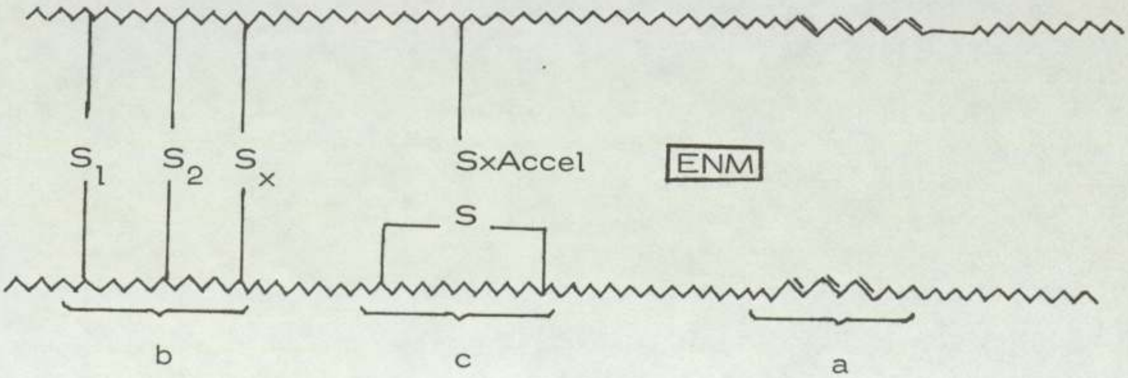


Fig. 1.2 Structural features of a vulcanisate

Extra Network Material (ENM)

(a) Unmodified polymer.

(b) Cross-links.

(c) Pendant and cyclic groups.

All the above factors can affect the autoxidative behaviour of a vulcanizate. However, due to the complex structure of the vulcanizate, information about their oxidative behaviour is usually obtained by studying the autoxidation of simple systems. The simplified systems include model olefins particularly those which structurally resemble polyisoprene, simple organic sulphur compounds similar to the cross-links and cyclic groups and mixture of olefins and sulphur compounds. The amount of the latter being such that the sulphur content is very similar to that of an accelerated sulphur vulcanisate.

1.2.2.1. Oxidation of Olefins

The reaction of oxygen and unsaturated hydrocarbons to produce hydroperoxides has long been recognized but the resolution of the course and mechanism of these reactions only started to be understood when Criegee (12) and co-workers showed that the autoxidation of cyclohexene produces cyclohex-3-enyl hydroperoxide as the main product. They have also shown that oxygen reacts at a CH_2 group adjacent to the double bond, not at the double bond itself. The autoxidation of olefins has been investigated by many workers (13-16). As a result of chemical identification of the products and kinetic studies the following well-known reaction stages have been suggested when RH represents the hydrocarbon.

1. Initiation: Production of free radicals

$$RH + O_2 \longrightarrow R^{\bullet} + \dot{O}OH$$

$$ROOH \longrightarrow RO^{\bullet} + HO^{\bullet}$$

2. Propagation :

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R\cdot$$

3. Termination :

$$R + R^{\bullet} \longrightarrow R\text{-}R$$

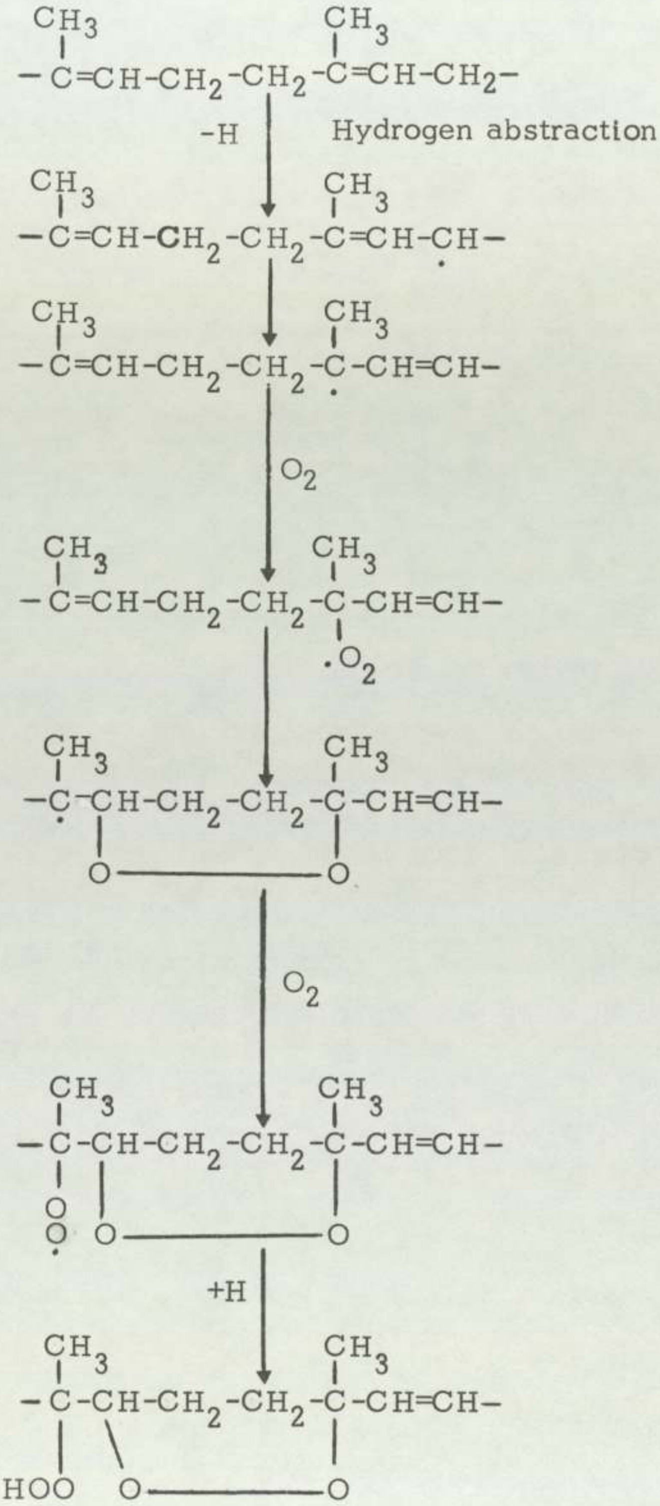
$$R^{\bullet} + RO_2^{\bullet} \longrightarrow ROOR$$

$$2RO_2^{\bullet} \longrightarrow \text{non-radical products.}$$

Certain important features of this system are to be noted :

1. The reaction is autocatalytic
2. Hydroperoxides are the main products initially
3. Oxidation proceeds by free radical chain process
4. The rate of oxidation is mainly dependent upon the structure of the hydrocarbon and increases as the lability of α-methylenic C-H bond increases.

However, in the case of natural rubber the hydroperoxide formation is known (17) to occur by the following reaction sequences. The special hydroperoxide has tertiary structure which is external to the peroxide ring :



1.2.2.2. Oxidation of Sulphides

The ageing behaviour of organic sulphides differs from that of raw rubber and is particularly dependent upon their detailed structure. The relative reactivities for different types of sulphides are as follows :

$$(-S-) > (-S-S-) > (-S-S-S-S-)$$

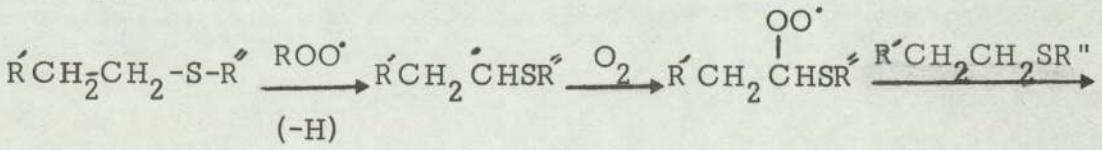
Investigators at NRPRA [(18-21)] (now MRPRA) have studied this subject in some detail and the most important features which may be concluded from their work are as follows :

a. The reaction is autoinhibitive in comparison to the autocatalytic olefin autoxidation.

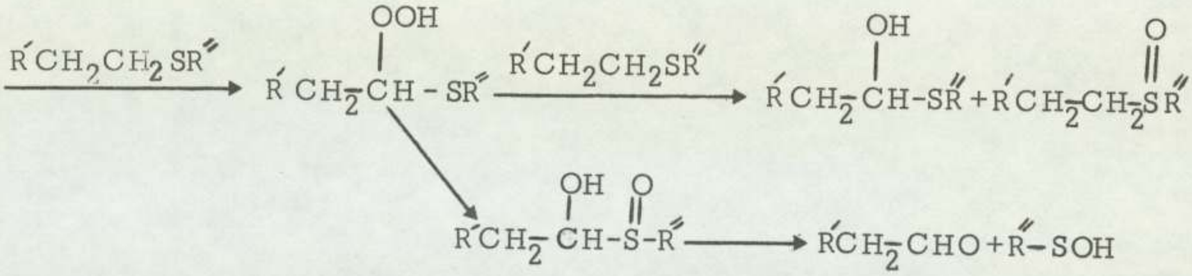
b. Saturated sulphides are inert towards oxygen when there is no catalyst present in the system.

c. Allylically unsaturated sulphides react rapidly with oxygen in initial stages to form α-methylenic hydroperoxide and the reaction is insensitive to peroxide catalysis.

When the substrate is a sulphide an α-hydroperoxide is formed which undergoes further oxidation by itself or with another molecule of the sulphide:



$$R'CH_2CH_2\text{-}S\text{-}R'' \xrightarrow[(-H)]{ROO^{\cdot}} R'CH_2\dot{C}HSR'' \xrightarrow{O_2} R'CH_2\overset{OO^{\cdot}}{\overset{|}{C}}HSR'' \xrightarrow{R'CH_2CH_2SR''}$$



However, due to the relative importance of the mechanism of sulphide autoxidation to the present work this will be discussed in further detail in forthcoming sections.

1.2.2.3. Co-oxidation of Olefin-organic Sulphide Systems

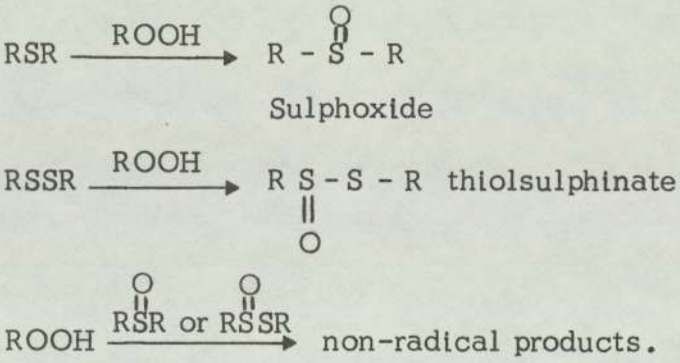
Studies of the autoxidation of a mixture of squalene and simple organic sulphides can give information about the ageing behaviour of a sulphur vulcanisate.(22,23) Simple organic sulphur compounds were used with concentration similar to the sulphur content in an accelerated sulphur vulcanisate. Some of the important features emerged from these investigations are as follows:

1. Most monosulphides are without appreciable effect but inhibitory activity was found where one substituent in t-alkyl and the other either t-alkyl or allyl group alkylated at the 1- and 3- positions. A phenyl group usually behaves similarly to a simple allyl substituent.

2. Monosulphides with keto substituentsin one alkyl side chain are not active except when the carbonyl group is in a γ-position to the sulphur atom, i.e. to form grouping $-SCH_2CH_2CO$. More branched alkyl groups enhance the activity.

3. Simple alkyl disulphides in comparison to monosulphides give a considerable inhibition effect, which diminishes on passing to more complex aryl and alkyl analogues.

Many alkyl, aryl monosulphides and disulphides may inhibit polymer oxidation. The inhibitory action of these materials is only evident after a certain amount of oxygen has been absorbed. This suggests that sulphides themselves are not the effective inhibitor but rather their oxygenated products. Investigators at MRPRA(24-26) have reported that the reactions of hydroperoxide with mono and disulphides result in the formation of corresponding sulphoxide and thiolsulphinate respectively.



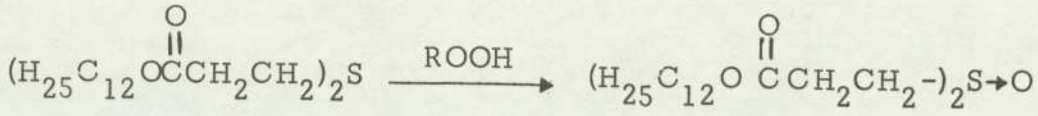
$$RSR \xrightarrow{ROOH} R - \overset{O}{\overset{\|}{S}} - R$$

Sulphoxide

$$RSSR \xrightarrow{ROOH} R\,\underset{O}{\underset{\|}{S}} - S - R \quad \text{thiolsulphinate}$$

$$ROOH \xrightarrow{R\overset{O}{\overset{\|}{S}}R \text{ or } R\overset{O}{\overset{\|}{S}}SR} \text{non-radical products.}$$

Direct addition of sulphoxide or thiolsulphinate immediately inhibits the oxidation of squalene as compared to the delayed inhibition observed with the corresponding sulphides. Marshall(27) investigated the decomposition of hydroperoxides in the presence of dilauryl thiodipropionate (DLTDP). An induction period was observed at temperatures 30-90°C consistent with oxidation of the sulphide to the corresponding sulphoxide :

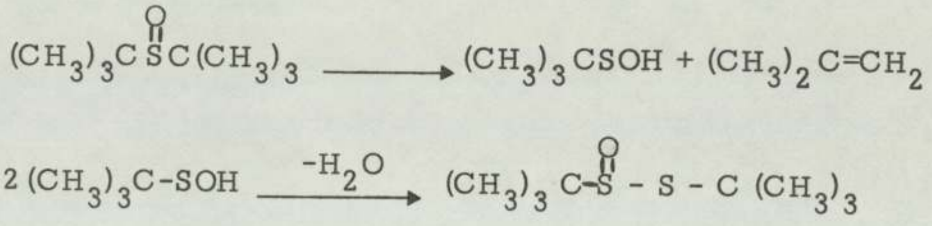


$$(H_{25}C_{12}O\overset{O}{\overset{\|}{C}}CH_2CH_2)_2S \xrightarrow{ROOH} (H_{25}C_{12}O\overset{O}{\overset{\|}{C}}CH_2CH_2-)_2S\rightarrow O$$

(DLTDP)

Several workers (28-30) have attempted to identify further oxidation products of the sulphoxide. They have shown that sulphoxides with one or more hydrogen atoms β to the sulphur atom can decompose at moderate temperatures to produce olefin.

Colclough and Cunneen(25) have found that di-tert-butyl sulphoxide under thermolysis at 75°C can produce olefin and sulphenic acid. They have also found that sulphenic acid formed can result in the formation of thiolsulphinate.

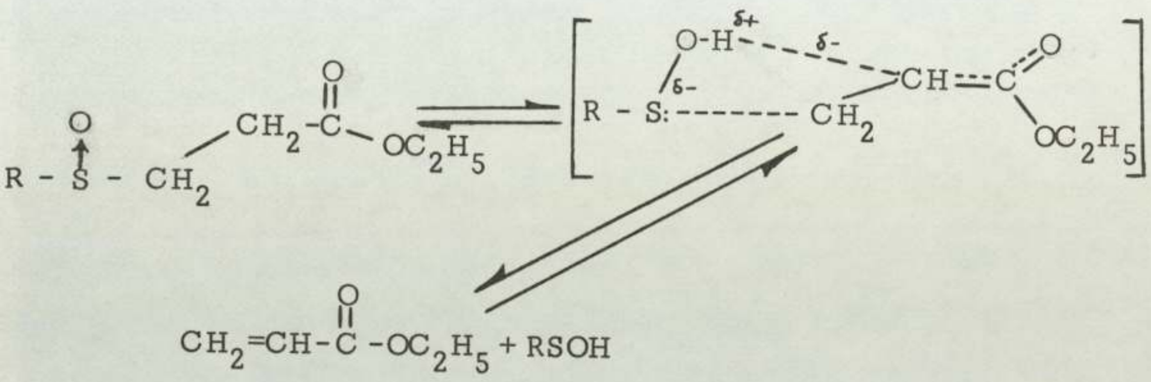


$$(CH_3)_3C\overset{O}{\overset{\|}{S}}C(CH_3)_3 \longrightarrow (CH_3)_3CSOH + (CH_3)_2C{=}CH_2$$

$$2(CH_3)_3C-SOH \xrightarrow{-H_2O} (CH_3)_3C-\overset{O}{\overset{\|}{S}}-S-C(CH_3)_3$$

t-Butanesulphenic acid   t-Butyl t-butanethiolsulphinate

The relative ease of the decomposition of sulphoxides and thus the antioxidant effectiveness are facilitated by bulky end groups (e.g. t-butyl) and presence of hydrogen near to the sulphoxide group. For instance, the rate of decomposition of di-t-butyl sulphoxide is 93 times faster than that of methyl-t-butyl sulphoxide. In the case of β-sulphinylpropionate even greater reactivity has been found. For comparison, the rate of decomposition of β-sulphinylproprionate is 15000 times faster than di-n-propyl sulphoxide. This higher reactivity is due to the activating effect of the carbonyl in stabilising the developing carbanion in the transition state as the hydrogen on the adjacent carbon is being transferred to the sulphinyl oxygen:



It has also been found (31) that electron-attracting substituents attached to the benzene ring in phenyl-t-butyl sulphoxide increase the ease of decomposition of sulphoxide while electron releasing groups tend to reduce the decomposition.

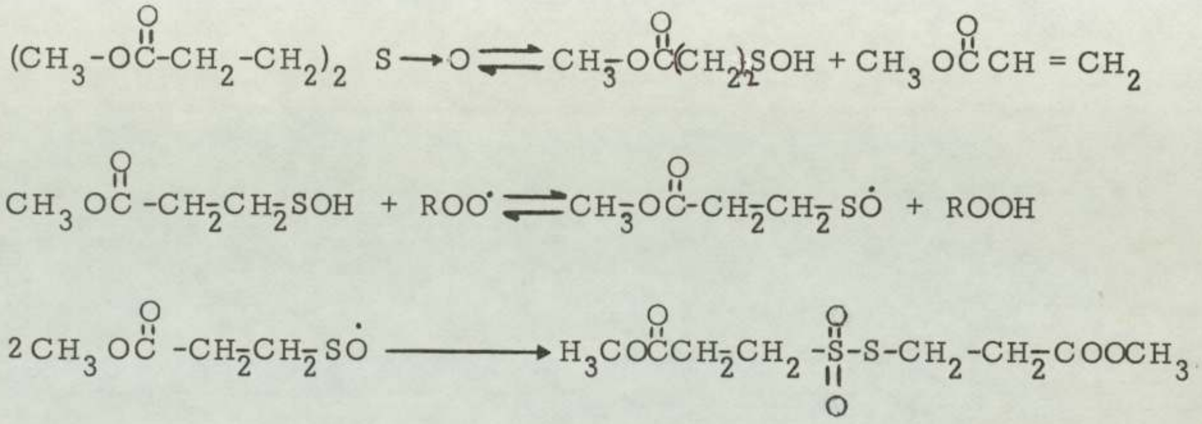
Recent investigation by Armstrong, Plant and Scott (32-33) on thiodipropionate esters has led to a better understanding of the mechanism of sulphur compounds. They have shown that there are three distinctive mechanisms which could account for the antioxidant behaviour of thiodipropionate;

1. A radical trapping reaction involving sulphenic acid formed by the breakdown of the sulphenyl dipropionate ester (oxidation product of thiodipropionate)

2. A radical generating reaction occurring as a result of a redox reaction between hydroperoxide and sulphenic acid.

3. A Lewis acid catalysed destruction of hydroperoxide by a further oxidation product of sulphenic acid.

The first mechanism can be shown by the following reaction scheme :

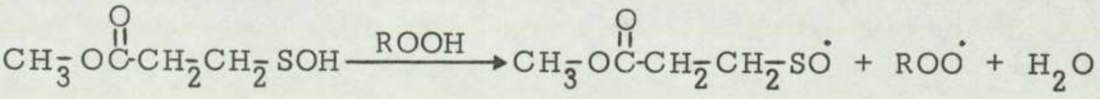


$$(CH_3-O\overset{O}{\overset{\|}{C}}-CH_2-CH_2)_2\ S\rightarrow O \rightleftharpoons CH_3-O\overset{O}{\overset{\|}{C}}(CH_2)_2SOH + CH_3O\overset{O}{\overset{\|}{C}}CH=CH_2$$

$$CH_3O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-SOH + ROO^{\bullet} \rightleftharpoons CH_3-O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S\dot{O} + ROOH$$

$$2CH_3O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S\dot{O} \longrightarrow H_3CO\overset{O}{\overset{\|}{C}}CH_2-CH_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-S-CH_2-CH_2-COOCH_3$$

It was shown that the sulphenic acid formed can perform in a similar manner as a chain breaking antioxidant by donating its labile hydrogen to alkyl peroxy radical to stop the kinetic chain. Armstrong and Scott (32-34) in an earlier investigation showed that the initial pro-oxidant stage exhibited by most sulphide antioxidants was due to the free radical generating reaction between hydroperoxide and sulphenic acid:



$$CH_3-O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-SOH \xrightarrow{ROOH} CH_3-O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S\dot{O} + RO\dot{O} + H_2O$$

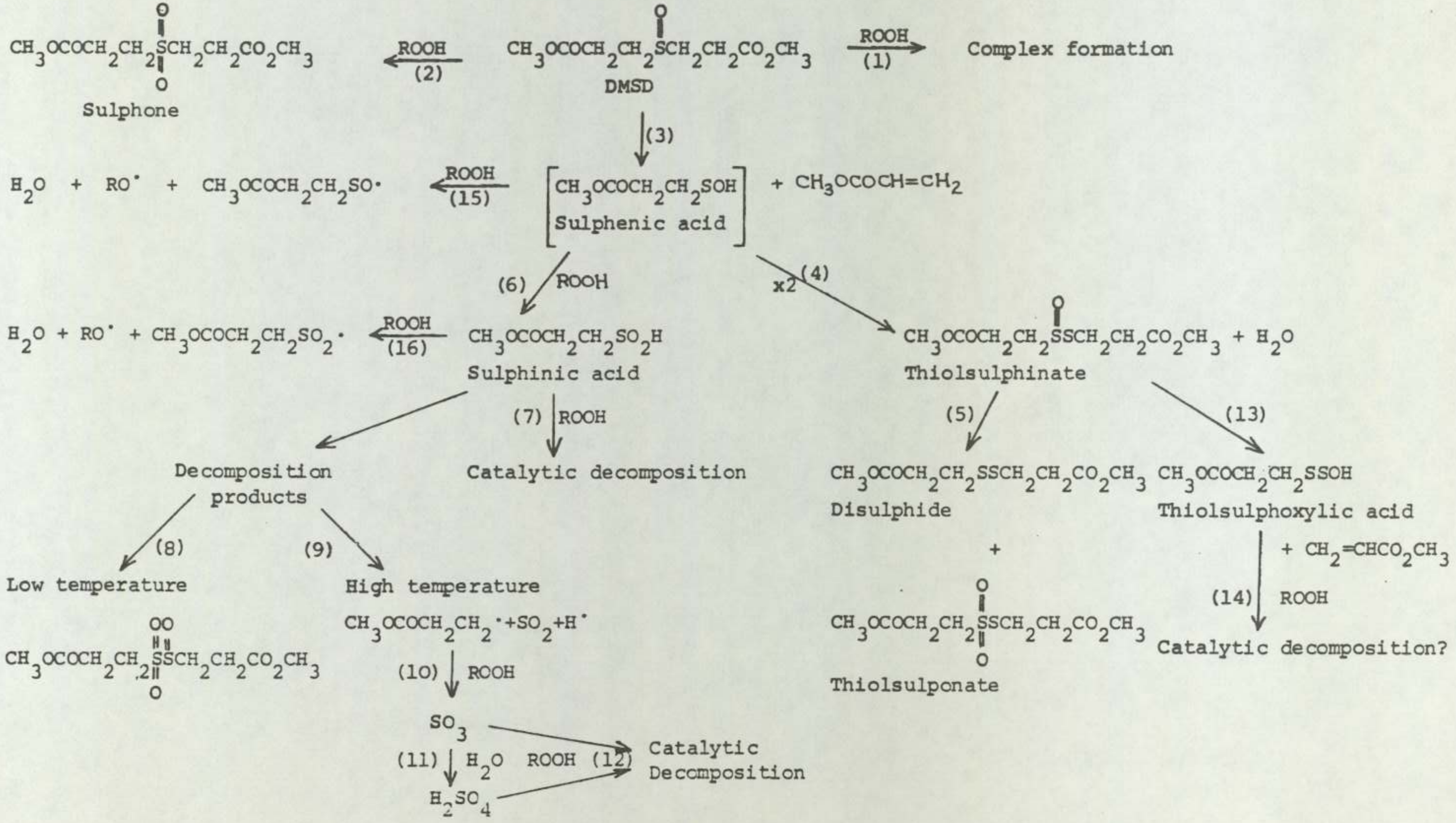
A recent investigation by Husbands (36) and Scott (37,38) has thrown more light on the understanding of the behaviour of sulphur compounds in autoxidizing systems. The reaction of dimethyl sulphinyl dipropionate (DMSD) with hydroperoxides has been investigated in some detail. DMSD(II) is known (39) to be the primary product formed from the corresponding sulphide (I).

$(CH_3OCOCH_2CH)_2S$ (I)

$(CH_3OCOCH_2CH)_2S=O$ (II)

The reaction of DMSD and its oxidation products with hydroperoxides has been proposed to occur as shown in Scheme 1. Reaction(1) involves direct antioxidant activity by DMSD to deactivate hydroperoxide by complex formation. Reaction (2) which represents intrinsic antioxidant activity of the DMSD molecule is the oxidation by the production of sulphone in an ionic reaction. Reaction (3) is the thermal decomposition of DMSD to produce methyl acrylate and sulphenic acid. Reaction (4) is the bimolecular production of thiosulphinate with the elimination of water. This is followed by reaction (5) where thiolsulphonate and disulphide are formed. Reaction (6) is the direct oxidation of sulphenic acid to the sulphinic acid. The latter acid is capable of catalytic hydroperoxide decomposition (7). At low temperatures this decomposition is thought to involve the formation of sulphinyl sulphone (Reaction 8). At elevated temperatures the decomposition of sulphinic acid has been shown to occur by a homolytic process producing sulphur dioxide. (Reaction 9) which is the precursor to an even more powerful catalytic hydroperoxide decomposer than the sulphinic acid. It is also concluded

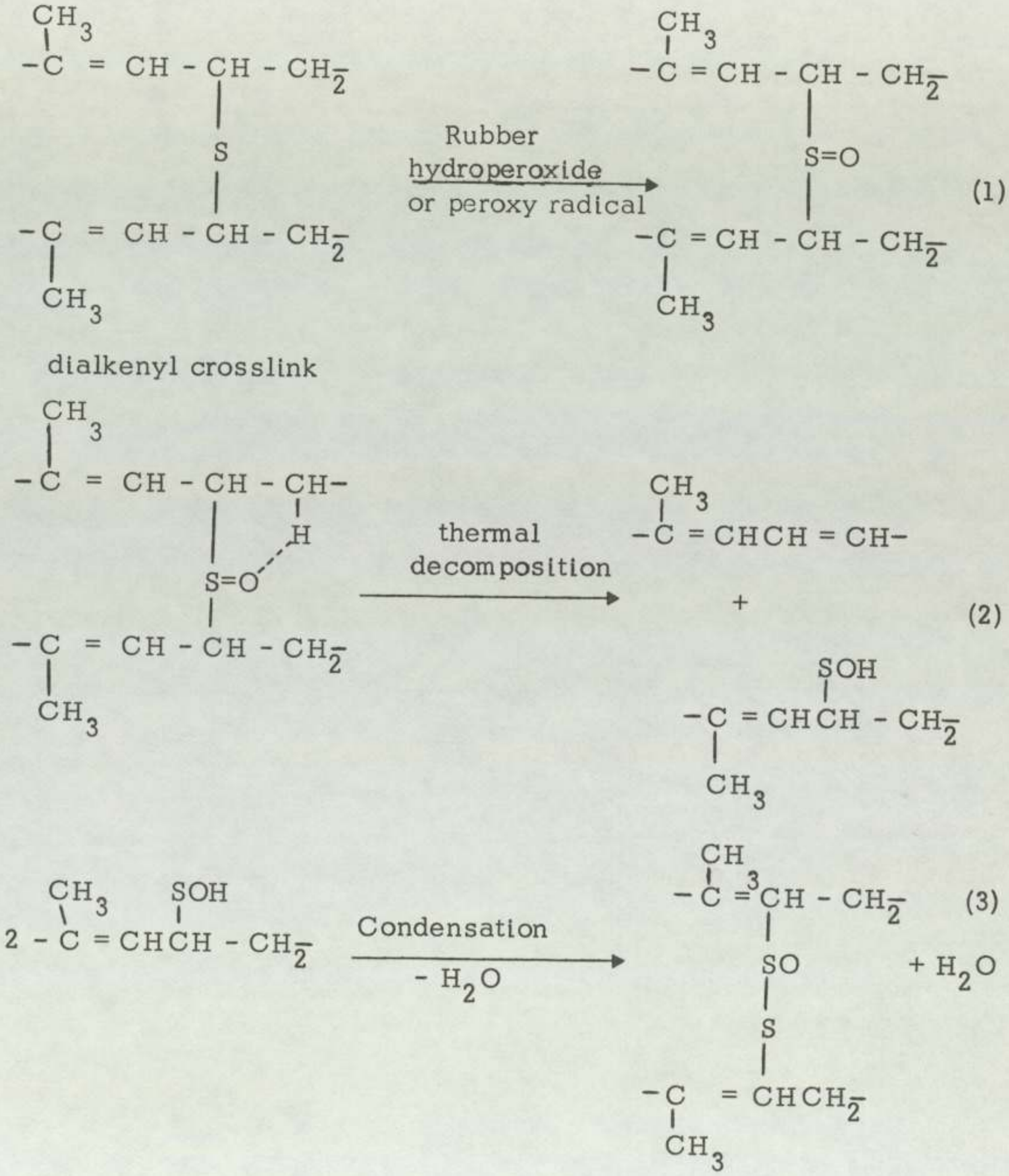
Scheme 1. The reaction between DMSD and hydroperoxide (from Dr. Husband's work, reference 36)



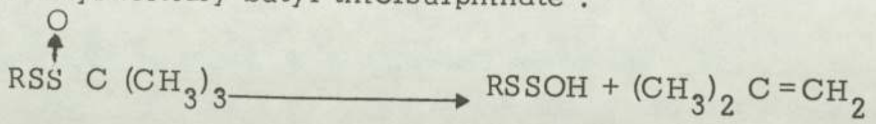
that this activity is associated with the oxidation of sulphur dioxide to sulphur trioxide (10), followed by reaction with water to produce sulphuric acid (11). The active catalyst for the decomposition here is either sulphur trioxide or sulphuric acid or more likely a combination of the two. The experimental evidence suggests that sulphur dioxide is only involved in the stoichiometric reaction with hydroperoxide. The catalytic process is shown as reaction (12). The formation of secondary acidic species derived from thermal decomposition of the thiosulphinate (13) was suggested to account for the unusually high activity of thermally decomposed solution of DMSD. The production of methyl acrylate in the decomposition products of thiolsulphinate both at high and low temperatures suggests that the acidic species is the thiosulphoxylic acid and that this is in fact the catalytic species involved in the decomposition of hydroperoxide by reaction (14). Reactions (15) and (16) account for pro-oxidant effects.

1.2.2.4. Oxidation of a Sulphur Crosslink

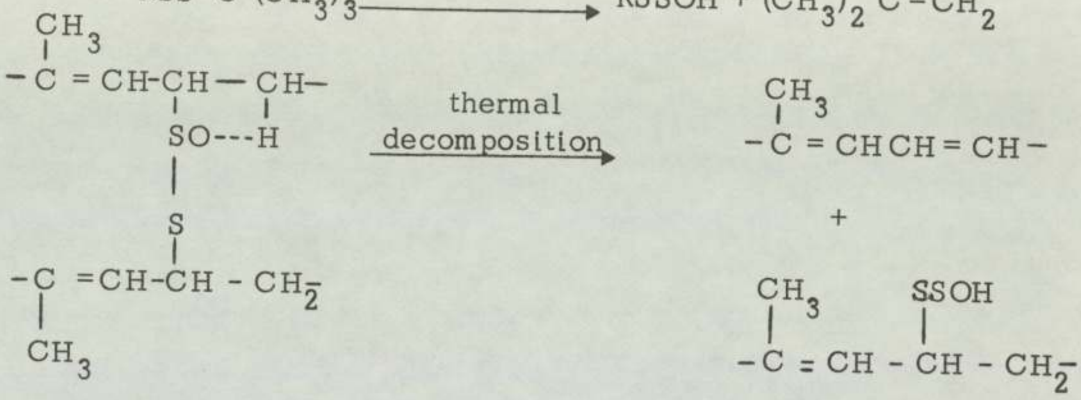
Vulcanisation of natural and synthetic rubber with sulphur and accelerator would result in a network structure consisting of various types of crosslinks. These are mono, di and polysulphide crosslinks as well as cyclic and pendant groups containing sulphur (40). The reactions of these sulphur groups with hydroperoxide formed during compounding or ageing of vulcanised rubber produces a variety of oxidised sulphur compounds. These oxidised structures would be expected to exhibit similar antioxidant and pro-oxidant effects to those already described for organic sulphur compounds. As a result of ageing of vulcanised rubber, main chain scission occurs. If sulphoxide and its decomposition products oxidize in a similar manner as already described (36), (Scheme 1), then the following reactions would occur in a dialkenyl monosulphidic crosslink present in a natural rubber vulcanisate prepared from a sulphurless or accelerated sulphur recipe :(44)



In the above reactions the rubber hydroperoxide or peroxy radical oxidizes the sulphur atom in dialkenyl crosslink which then decomposes with cleavage at the C-S bond forming a sulphenic acid. Two molecules of sulphenic acid can then react together to form a new crosslink containing two sulphur atoms. The new thiolsulphinate crosslink formed can also undergo scission by a similar mechanism as has been shown for the case of alkyl tertiary butyl thiolsulphinate : (45,46)



$$R\overset{\overset{O}{\uparrow}}{S}S\,C\,(CH_3)_3 \longrightarrow RSSOH + (CH_3)_2\,C{=}CH_2$$



A disulphide crosslink in a vulcanized rubber can react with hydroperoxide to form a similar type of thiolsulphinate structure shown above. However, in the case of polysulphide crosslinks Lal (47) reports that when they were removed by reaction with triphenylphosphine, lower rates of oxygen absorption of the vulcanisate at 100°C were observed. This reduction in the rate of oxidation on removal of essentially all polysulphidic sulphur suggests that polysulphidic structues in the original vulcanisate act as oxidation initiators. In the case of unsaturated cyclic sulphur crosslinks it has been found (40) that the crosslink density of vulcanisates containing a large amount of such crosslinks increases on ageing. The oxidation of cyclic sulphide may take place in a similar manner to that described for monosulphide crosslinks in reactions (1 - 3). This can result in the opening of the cyclic sulphide rings with the formation of new crosslinks. The sulphenic acid (RSOH) and thiosulphoxylic acid (RSSOH) formed during oxidation of vulcanisate can react further with hydroperoxide to produce sulphinic (RSO_2H), sulphonic (RSO_3H) and thiosulphuric ($RSSO_3H$) acids. All of these can function as hydroperoxide decomposers in a sulphur vulcanisate.

1.3. Mechanism of Antioxidant Action

Antioxidants may be divided into two fundamental groups according to the mechanism by which they function, preventive and chain-breaking. Preventive antioxidants such as organic sulphides and phosphites interfere with the initiation step and inhibit or retard the formation of free radicals. Chain-breaking antioxidants interfere with the propagation step and terminate the kinetic chains by removing radicals, e.g. alkyl and alkyl peroxy radicals. Typical examples of the second class are hindered phenols and aromatic amines. A mixture of two antioxidants from these groups leads to synergistic behaviour where the overall effect is greater than two individual effects. Scott(48) distinguishes two mechanistically distinct types of synergistic behaviour. First, homosynergism arises from two similar antioxidants with unequal activity. The second, heterosynergism where the co-operative effect derives from the mixture of antioxidants acting by different mechanisms.

1.3.1. Chain-breaking Antioxidants

This type of antioxidant competes with hydrocarbon to react with alkyl peroxy radicals, thus interfering with the kinetic chain:(49)

$$R^{\cdot} + O_2 \longrightarrow RO\dot{O} \qquad (1)$$

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \qquad (2a)$$

$$ROO^{\cdot} + AH \longrightarrow ROOH + A^{\cdot} \qquad (2b)$$

$$A^{\cdot} + ROO^{\cdot} \longrightarrow RO_2A$$

$$A^{\cdot} \longrightarrow \text{Inert products}$$

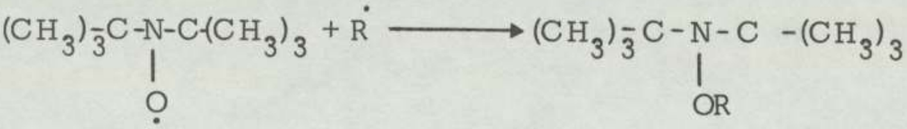
Where RH is hydrocarbon and AH is antioxidant. The antioxidant radical produced ($A^{\cdot}$) is stable and does not result in further propagation of the kinetic chain. Hawkins (50) has previously classified the chain-breaking antioxidants into three groups. These were free radical traps, electron donors and hydrogen donors. However, a more recent and advanced classification of chain-breaking antioxidants by Scott (51) shows this can be reduced into two groups. Scott points out that the removal of alkyl and alkyl peroxy radicals are potential chain-breaking processes. The former involves an electron acceptor (oxidizing agent) and the latter an electron donor (reducing agent) as follows :

$$\begin{tikzcd}
R^{\cdot} + O_2 \arrow[r] \arrow[d, "-e"] & RO\dot{O} \arrow[d, "+e"] \\
R^{+} & ROO^{-}
\end{tikzcd}$$

Chain-breaking (acceptor mechanism) (CB - A)

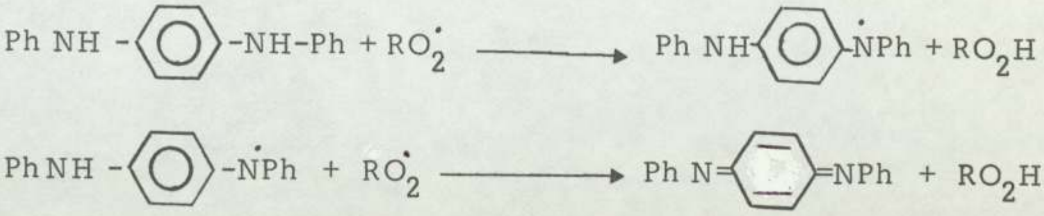
Chain-breaking (donor mechanism) (CB - D)

polymer alkyl radicals, unlike alkyl peroxy radicals are not powerful oxidizing agents but they are themselves readily oxidized. A variety of oxidizing agents (52) are capable of removing alkyl radicals from an oxidizing system and functioning by (CB-A) mechanism. These include nitrones, nitro-compounds, quinones and a variety of 'stable' radicals of which the phenoxyls and nitroxyls have been most studied. Di-t-butyl nitroxide, for instance, can trap alkyl radicals by the acceptor mechanism to form stable molecular product: (53)



$$(CH_3)_3C-\underset{\substack{|\\ \dot{O}}}{N}-C(CH_3)_3 + \dot{R} \longrightarrow (CH_3)_3C-\underset{\substack{|\\ OR}}{N}-C-(CH_3)_3$$

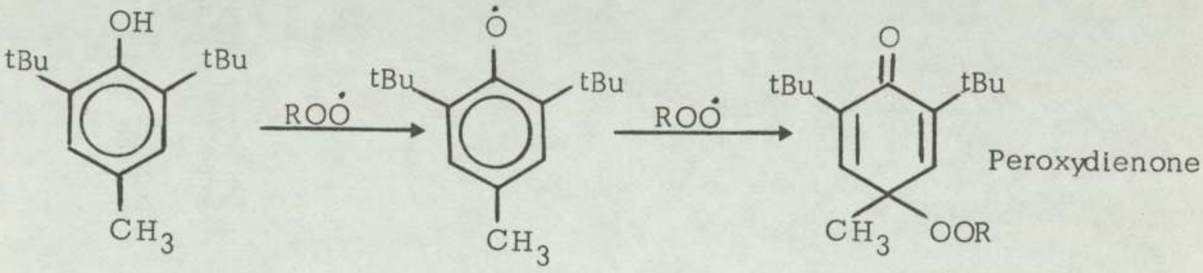
However, in the case of antioxidants functioning by the chain-breaking donor mechanism (CB-D), single electron donors or compounds which, after donation of a labile hydrogen, give rise to a stable radical ($A^{\cdot}$) can be considered (2b). Phenols and aromatic amines which are able to transfer a hydrogen readily to alkyl peroxy radicals with the formation of a resonance stabilized radical are effective as (CB-D) antioxidants. N,N'-diphenyl-p-phenylene diamine, for instance can make both its N-hydrogens available as follows :(54)



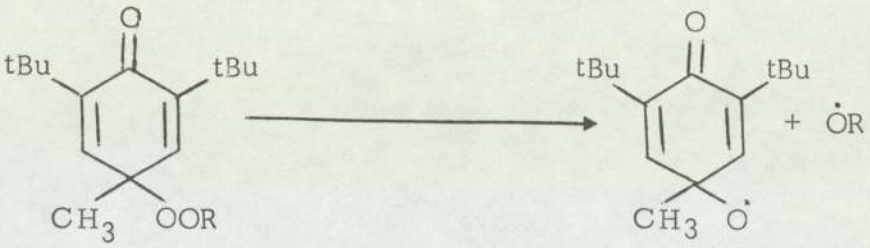
Replacement of hydrogen in N-H or O-H by an alkyl group reduces the antioxidant efficiency. Ease of hydrogen abstraction by alkyl peroxy radical is increased by substituting electron releasing groups in aromatic ring. However, the same electronic characteristics favours the direct attack of oxygen on the phenolic hydrogen which is a potential chain-initiating reaction :

$$AH + O_2 \longrightarrow A^{\bullet} + \dot{O}H$$

In general phenolic antioxidants contain the seeds of their own destruction as the following reaction indicates :(55)



At temperature above 140°C, the peroxy dienone decomposes rapidly to give new initiating free radicals which makes phenolic antioxidantsless effective at high temperatures (52):



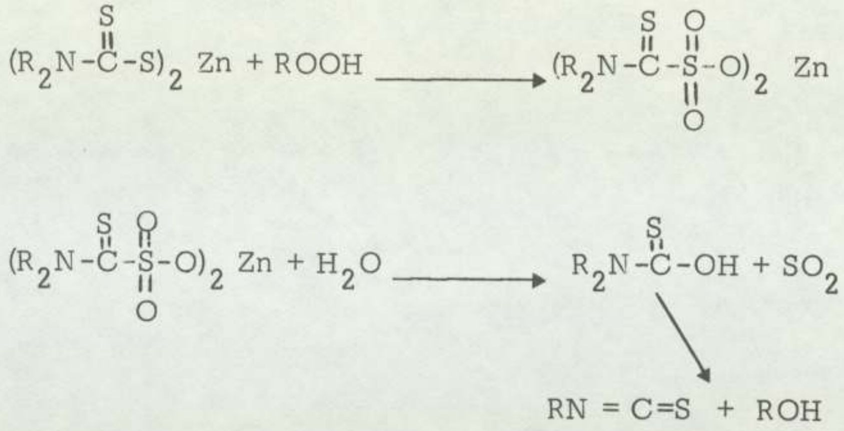
Despite this inefficiency phenolic antioxidants are commonly used as heat stabilizers for polymers especially in synergistic mixture with a peroxide decomposer.

1.3.2. Preventive Antioxidants

Preventive antioxidants inhibit or retard the formation of free radicals in the initiation step of autoxidation. Hydroperoxides are formed during initiation to produce active initiating free radicals:

$$\text{nROOH} \longrightarrow \text{RO}^{\cdot}\text{, }\dot{\text{O}}\text{H, }\text{R}\dot{\text{O}}_2\text{, }\text{H}_2\text{O}$$

Therefore, hydroperoxide decomposers which react with hydroperoxides and produce stable non-radical products function by the preventive mechanism. Since hydroperoxide decomposition can be accelerated by light and metal ions, materials which absorb the light or deactivate the metal ions can also be regarded as preventive antioxidants. Numerous papers have been published by Scott and co-workers (49,56-60) describing mechanism of various types of hydroperoxide decomposers. Metal dialkyl dithiocarbamates for instance, have been found to destroy hydroperoxides. Zinc dialkyl dithiocarbamates react with hydroperoxide to form sulphur di or trioxide and isothiocyanate (56,61) through the formation of an unstable sulphonate intermediate:

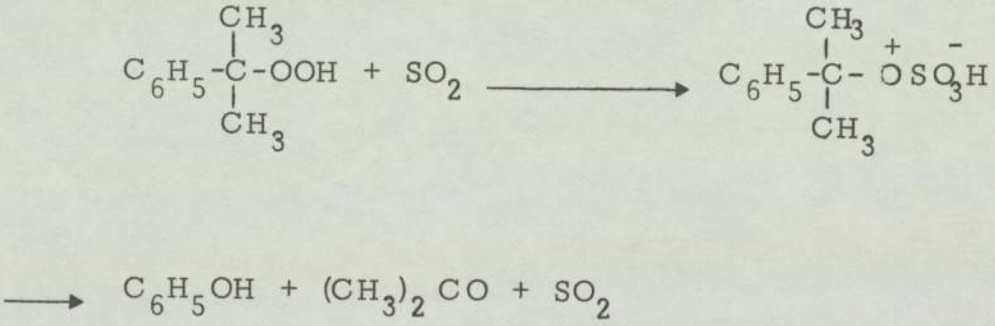


$$(R_2N-\overset{\overset{S}{\|}}{C}-S)_2\,Zn + ROOH \longrightarrow (R_2N-\overset{\overset{S}{\|}}{C}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O)_2\,Zn$$

$$(R_2N-\overset{\overset{S}{\|}}{C}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O)_2\,Zn + H_2O \longrightarrow R_2N-\overset{\overset{S}{\|}}{C}-OH + SO_2$$

$$\searrow\ RN = C=S + ROH$$

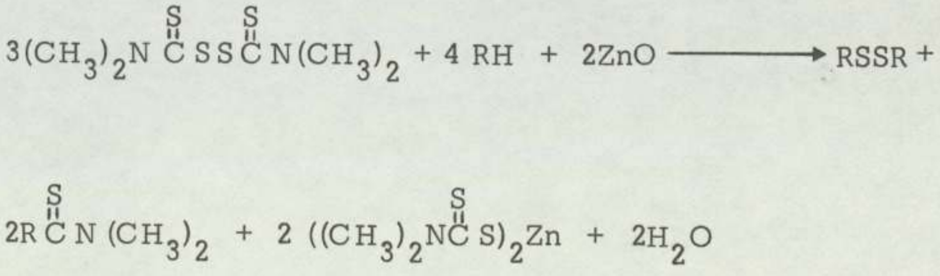
Recent investigation by Husbands(36) indicates that sulphur di or trioxide are effective catalysts for the decomposition of cumene hydroperoxide to give phenol and acetone :



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-OOH + SO_2 \longrightarrow C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{O}S\overset{-}{O_3}H$$

$$\longrightarrow C_6H_5OH + (CH_3)_2CO + SO_2$$

Zinc dimethyl dithiocarbamate (ZDC) is formed during the vulcanisation of rubber with TMTD (tetramethylthiuramdisulphide) in the presence of ZnO(62):



$$3(CH_3)_2N\overset{\overset{S}{\|}}{C}SS\overset{\overset{S}{\|}}{C}N(CH_3)_2 + 4\,RH + 2ZnO \longrightarrow RSSR +$$

$$2R\overset{\overset{S}{\|}}{C}N(CH_3)_2 + 2\,((CH_3)_2N\overset{\overset{S}{\|}}{C}S)_2Zn + 2H_2O$$

(Where RH is rubber hydrocarbon).

Therefore, the good ageing resistance of TMTD cured vulcanisates has been suggested to be due to the formation of ZDC because the acetone extraction of fully cured vulcanisates completely destroys its resistance to oxidation (63). The inhibition effect of certain sulphur compounds and their mechanism of action has already been discussed (see Section 1.2.2.3). Metal deactivators are also regarded as preventive antioxidants since metal ions decompose hydroperoxides to radical species (60, 61):

$$RO_2H + M^{n+} \longrightarrow RO^{\cdot} + M^{(n+1)+} + \bar{O}H \qquad (1)$$

$$RO_2H + M^{(n+1)+} \longrightarrow RO_2^{\cdot} + M^{n+} + H^{+} \qquad (2)$$

The significance of the above reaction depends upon the reducing and oxidizing strength of the metal ions. For instance, ferrous ion as a reducing agent will react to form alkoxy radicals (1) whereas, lead stearate as an oxidising agent will form alkyl peroxide radicals as shown in the second reaction (2). However, it appears that the above reactions may only be stopped, by complexing the metal ions to their maximum co-ordination number or by stabilizing one valence state at the expense of the other. The reaction resulting in the formation of an insoluble product (such as FeS in rubber vulcanised by sulphur) may also deactivate the metal ions. This subject has been extensively reviewed by Scott (66) and Hawkins (50).

1.4. Loss of Antioxidants due to Volatilization and Leaching

The effectiveness of antioxidant is usually determined by the following three major factors depending on the service conditions :

1. The intrinsic activity of the antioxidant which is primarily dependent upon its chemical structure.
2. The solubility or compatibility of antioxidant in the polymer and the ease of migration from the polymer matrix.
3. The rate of loss of antioxidant from the polymer due to volatilisation or extraction.

Improvements in effectiveness of antioxidants due to their chemical structure appears to be sufficient to impose enough service life to polymeric materials under normal but not extreme conditions. The incompatibility of antioxidants with polymers is a problem due to their migration towards the surface, where they can be easily lost by volatilisation or extraction. The ability of an antioxidant to protect rubber under the high temperature conditions in an automobile or aero engine, particularly in contact with lubricating oils depends not on its intrinsic activity but its ability to remain in the rubber under these conditions. Similar arguments apply to rubbers which are subjected to repeated cleaning operations such as detergent washing or solvent dry cleaning, particularly when they are in the form of articles with a high surface area to volume ratio such as latex threads or rubber gloves and garment interlinings. Robinson and Dunn (67) have shown that volatility of antioxidants is a problem in rubbers exposed to high temperatures during processing or service. They found that antioxidants such as 2,6 di-t-butyl-4-methyl phenol and tris (nonyl phenyl) phosphite volatilized during milling at 160°C. Phenyl-β-naphthylamine, N,N'-di-β-napthyl-p-phenylenediamine and N-phenyl-N'-iospropyl-p-phenylenediamine all volatilized at 210°C, whereas, 2,2'-thio bis-(4-methyl-6-tert butyl phenol) and N:N' di-2-octyl-p-phenylenediamine showed some stabilizing effect at this temperature. Temchin (68) and Burmistrov studied the volatilisation of a number of antioxidants and light stabilizers and concluded that the dominating factors involved in determining their volatility were their ability to form hydrogen bonds, their molecular weight and their dipole moments. It might be expected that volatility of antioxidants would reduce as the intermolecular forces increases. However, in contrast an increase in steric hindrance, which is known to increase antioxidant effectiveness will reduce the possibility of intermolecular interaction. Therefore, in general, the greater the effectiveness, the higher the volatility. However, in antioxidants with almost the same steric hindrance an increase in molecular weight considerably reduces the volatility.

Plant and Scott (69,70) have shown that the volatility and compatibility are not only dependent upon molecular weight but also on intra and inter molecular hydrogen bonding. Intra molecular hydrogen bonding in antioxidants used in high temperature applications, increases volatility and reduces compatibility. This is suggested to be due to lower intermolecular hydrogen bonding which can increase the volatility. The extraction of antioxidants in tyre threads (71) by water has been shown to have deleterious effect upon their fatigue and dynamic ozone resistances. Lloyd and Payne (72) have shown that paraphenylene diamine antiozonants (78) can be extracted from NR and SBR stocks by water as shown by a decrease in ozoneresistance and by chemical analysis. Therefore, it appears that the loss of antioxidants due to volatilisation and leaching is a major problem in the stabilization of rubber. In order to overcome these problems the following techniques have been developed:

1. The use of high molecular weight antioxidants.
2. The chemical binding of antioxidants to a modified rubber.
3. The chemical binding of antioxidants to rubber latices.
4. The chemical attachment of antioxidant to the polymer before compounding.
5. The chemical binding of antioxidants to the polymer during compounding and vulcanisation.

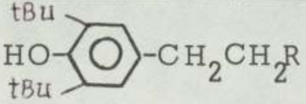
1.4.1. The Use of High Molecular Weight Antioxidants

1.4.1.1. High Molecular Weight Monomolecular Antioxidants

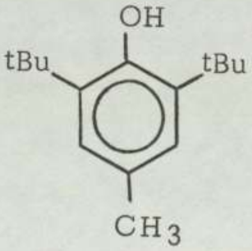
An increase in molecular weight of antioxidants is used to reduce their loss due to volatilisation. This has been investigated by many workers (69, 74, 75). Spacht et al., (76) studied the effect of molecular weight on volatility of 2,6 di-t-butyl-4-methyl phenol and 2-benzyl-4-methyl-6-t-butyl phenol during curing of natural rubber.

They found that the former with lower molecular weight was lost much faster than the latter. They have also shown (77) increase in sample thickness reduces the loss of antioxidant due to volatilisation. The effect of a number of phenolic and sulphur antioxidants were investigated by Plant and Scott (69) in polypropylene. The volatility of the antioxidants was determined by direct weight loss measurements at different temperatures in an inert atmosphere. The behaviour of the antioxidants was studied by measuring the induction periods derived from the torsional braid test at 100°C in air. The antioxidants used are shown in Table 1.1.

TABLE 1.1.(69)

Antioxidant	Side group	Molecular weight	Induction period (h)
$(ROCOCH_2CH_2)_2S$	Methyl	206	25
	Hexyl	346	30
	Lauryl	514	65
	Stearyl	702	130
	Methyl	292	25
	Hexyl	362	40
	Lauryl	446	75
	Stearyl	530	9800

The results in the above table indicate that the effectiveness of antioxidants (as measured by induction period) in both series increases as the molecular weight is increased. It also appears that at very low volatility (where R = stearyl) the induction period for phenolic antioxidant is considerably higher than that of high molecular weight sulphides. This was proposed to be due to the fact that the efficiency of sulphide antioxidants depends on their oxidative breakdown products such as sulphur dioxide (57, 78, 79) and trioxide (36) which are much more prone to volatilisation. Furthermore, the oxidation products of phenols are known in most cases to be higher molecular compounds which still have some antioxidant activity (80, 81). They concluded that in polymers with high surface area to volume ratio, volatility of antioxidant becomes more important than intrinsic activity in determining the efficiency. James and Widmer (82) have also studied the effect of volatility on a variety of phenolic and amine antioxidants. They have shown that certain phenolic antioxidants such as ;



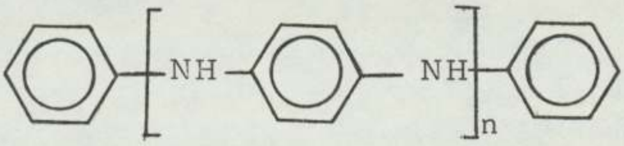
(BHT) MW = 220

2,6 di-tert butyl-4-methyl phenol

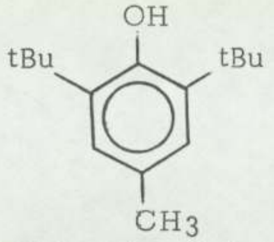
were highly effective when assessed in a closed system but had quite poor performances in a circulating air oven as compared with higher molecular weight phenols. They have also demonstrated that although N,N' diphenyl-p-phenylene diamine (DPPD) has approximately the same molecular weight (260) as BHT, the former is 3100 times less volatile than the latter. This was suggested to be due to the formation of intermolecular hydrogen bonds in DPPD resulting in lower volatility.

1.4.1.2. Polymeric Antioxidants

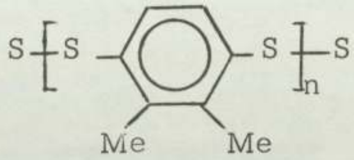
Further improvements in minimising the loss of antioxidants due to volatilisation have been achieved by the development of polymeric antioxidants. The idea was to retain high activity and reduce losses due to both volatility and extraction as well as reducing the skin sensitisation which arises from less volatile materials. For instance, in rubber thread preparation where latex is forced in a fine stream into an acid bath for coagulation and washing, it has been found that polymeric hindered phenols are quite useful(82). Since curing and drying of latex thread is usually carried out at above 130°C in the form of small denier thread, it has been found that only polymeric antioxidants are effective as compared with high molecular weight monomolecular antioxidants. Phillips, Thomas and Wright (83) have synthesized a polymeric antioxidant by reacting hydroquinone with p-phenylenediamine.



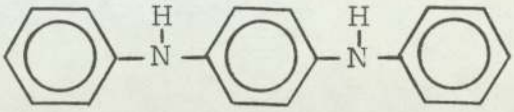
This was particularly designed for thermally stable high temperature rubber, (e.g. in EPDM at 150°C). Hawkins <u>et al.,</u> (84) studied the efficiencies of a number of phenolic and amine antioxidants at high temperatures and compared them with polymeric xylene disulphide. The following were typical examples :



2,6 di-tert butyl-4-methyl phenol

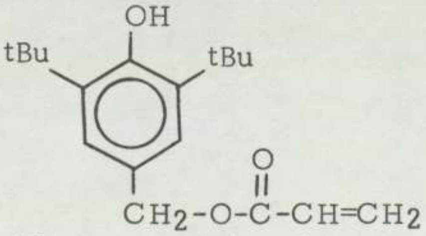


polymer xylene disulphide
(ThioKol polymer)



N,N'-diphenyl-p-phenylene
diamine (DPPD)

A comparison was made before and after evaporation or extraction using low density polyethylene as a base polymer. They have shown that the polymeric antioxidant is highly effective when compared with DPPD and Ionol. Evans and Scott (85) have also carried out a systematic study on mono molecular and polymeric antioxidants using mono and poly 3,5 di-tert-butyl-4-hydroxy benzyl acrylate (DBBA).



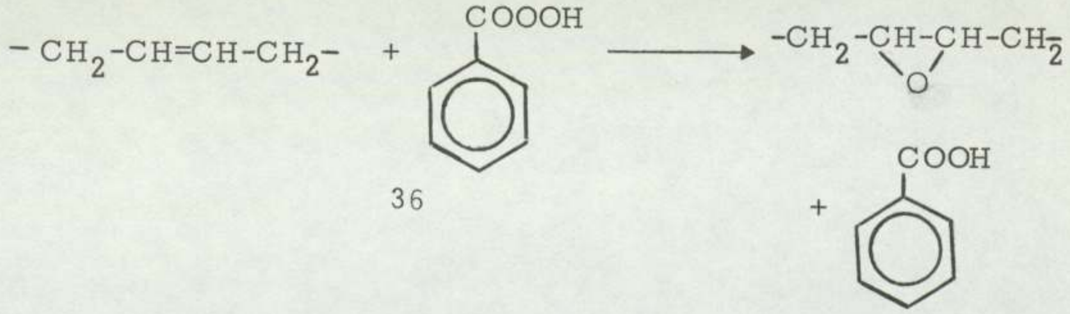
(DBBA)

These two antioxidants were incorporated into polypropylene using a conventional melt technique. Surprisingly it was found that the polymeric antioxidant does not reflect its non-volatility under conditions where loss of antioxidant due to volatilisation can occur.

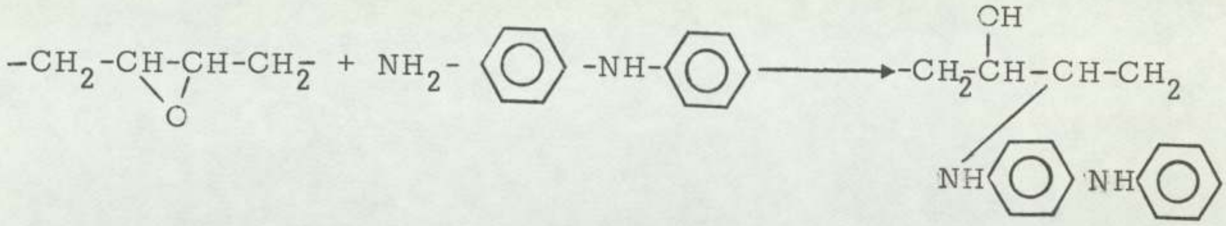
Although the reason was not very clear, it was proposed that it may be due to complete lack of solubility or incompatibility of the polymeric antioxidant in the polymer under the conditions of melt incorporation. The important feature concluded in this investigation was that high molecular weight is not the only factor determining the efficiency of antioxidant under aggressive environment. Other factors such as solubility, melting, point and compatibility should also be taken into account. This was further confirmed by the work of Amarapathy (86) who carried out oxygen absorption tests on the same antioxidant in natural rubber and found that mono DBBA is more efficient than polymeric DBBA.

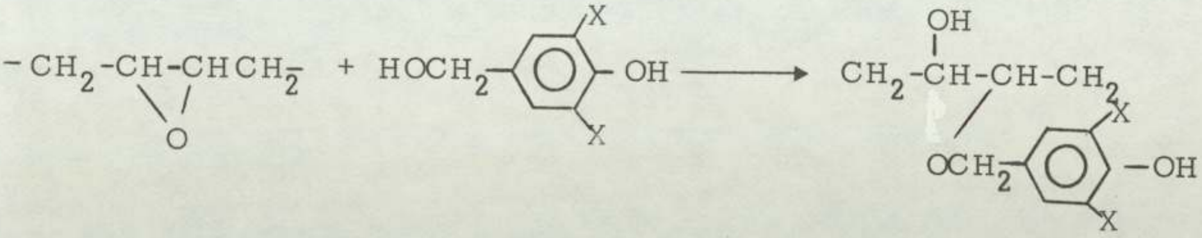
1.4.2. Chemical Binding of Antioxidants to a Modified Rubber

Binding of an antioxidant to rubber backbone can be achieved by reacting a rubber containing a reactive pendant group with an antioxidant containing a substituent group capable of reacting with the one attached to the rubber. For instance, rubber containing epoxy groups, which have been introduced either by direct epoxidation or by using a compound such as glycidyl methacrylate as a comonomer, has been shown to react with amines such as p-aminodiphenylamine or β-naphthylamine (87,88) and also phenols such as 3,5-di-t-butyl-4-hydroxy benzyl alcohol (89). The direct epoxidation was achieved by reaction of rubber (polybutadiene) with a perbenzoic acid according to the following equation :

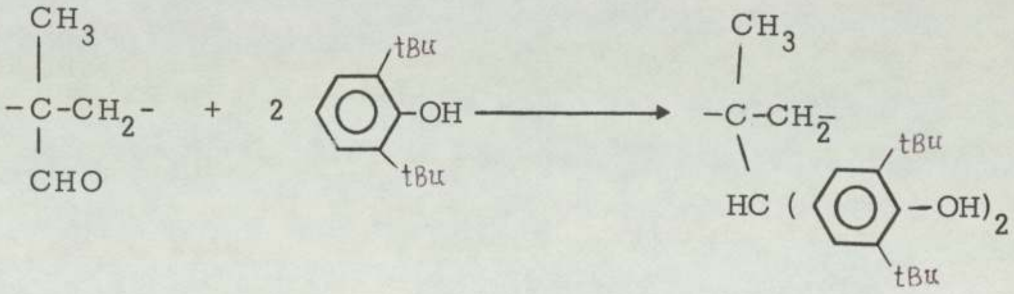


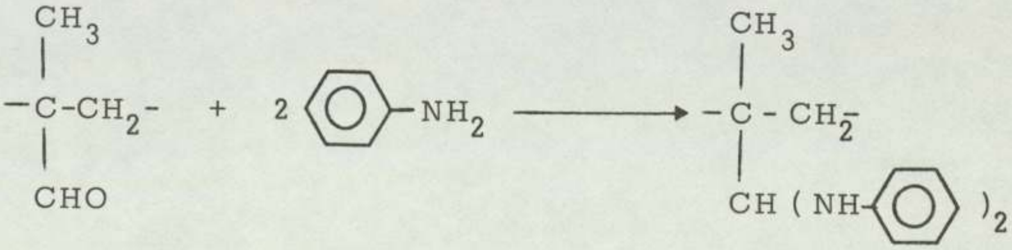
The modified rubber was then reacted with paramino diphenylamine or 2,6-di-tert butyl phenol to produce a rubber bound antioxidant :



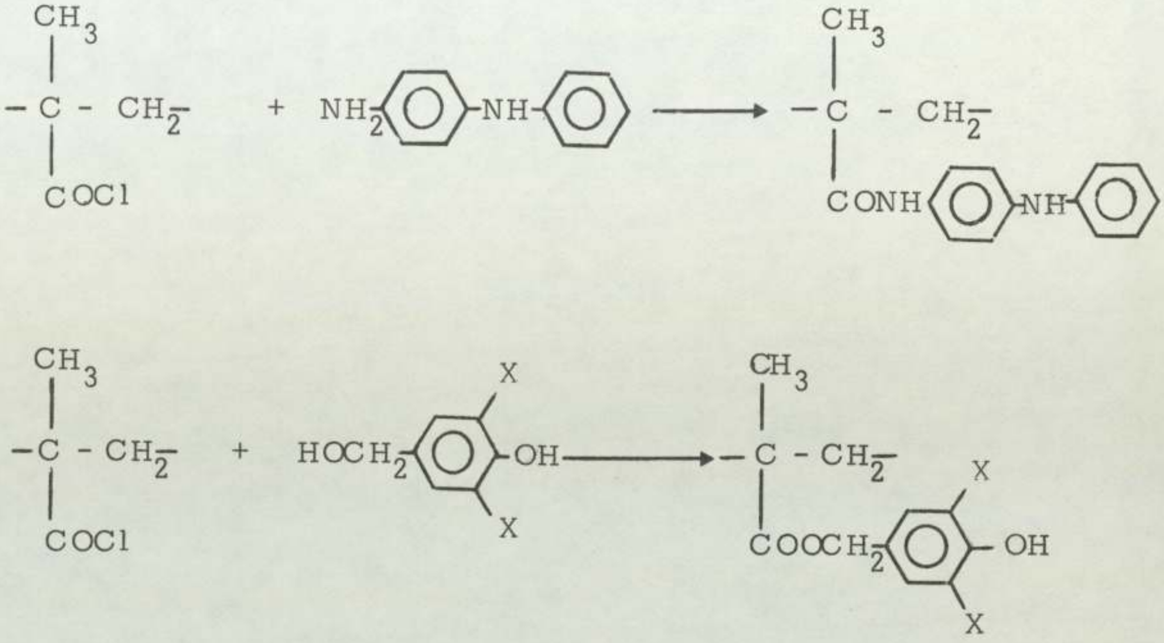


The formation of rubber bound antioxidant was confirmed by ir and U.V. techniques. Russian investigators (90) have also shown that a copolymer of butadiene and methacrolein can be reacted with aniline and with 2,6-di-tert-butyl phenol. The reaction was suggested to proceed as follows :



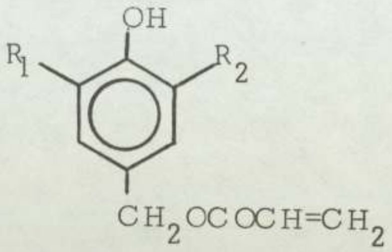


Blatz and Maloney (91) modified rubber with a carboxylic acid halide and then reacted with para amino diphenylamine and 3,5-di-t-butyl-4-hydroxy benzyl alcohol to produce the corresponding bound antioxidant :



1.4.3. Chemical Binding of Antioxidants to Rubber Latices

Chemical binding of antioxidants having reactive groups to NR latices would result in many advantages. This is due to the fact that incorporation of antioxidants into rubber molecule during manufacture is inconvenient and expensive, hence the possibility of reacting them with a preformed rubber in the latex has considerable practical interest to the producer and user of NR rubber latex. This is particularly important in the case of products which are directly made from NR latex such as rubber gloves and latex threads. Amarapathy (86) has shown that vinyl antioxidants such as shown below can be successfully bound into natural rubber molecule in the latex. The principle involved is similar to that employed in the grafting of conventional monomers to NR and polybutadiene and by appropriate choice of a redox system a high level of bound antioxidant can be achieved.



(a) $R_1 = R_2 = tBu$ (DBBA)

(b) $R_1 = tBu$ $R_2 = Me$

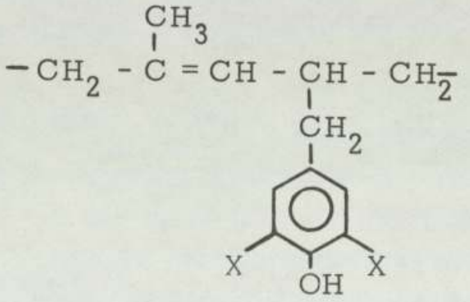
(c) $R_1 = R_2 = Me$

The reaction variables such as swelling time, pH, reaction time, soap concentration and type and concentration of initiator were established in order to maximize the yield of bound antioxidant formed. Various types of initiators were used for the reaction of DBBA with natural rubber latex and it was found that a redox system consisting of tertiary butyl hydroperoxide (TBH) and tetraethylene pentamine (TEPA) gave the best results. This is shown in Table 1.2 where it can be seen that the time to absorb 3% oxygen for redox system is longer as compared with other types of initiators used.

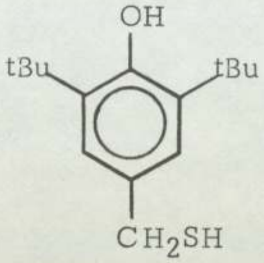
TABLE 1.2.(86)

Type of initiator	Amount added %	Time to absorb 3% O2 (h)
No initiator	0	-
Potassium persulphate	1.5 g	64
AZBN	0.5 g	41
Benzoyl Peroxide	0.5 g	48
TBH/TEPA (10%)	1.5/4ml	130

However, in order to demonstrate that the effect obtained is not due to the formation and binding of the homopolymer of DBBA, Amarapathy (86) incorporated polymeric DBBA into the rubber and found that the latter was relatively ineffective as a bound antioxidant. The oxygen absorption of vulcanised-extracted rubber with known amounts of bound DBBA have also been compared with that of a vulcanised rubber containing DBBA as additive but without extraction. The effectiveness of the two antioxidants were found to be almost the same, indicating that the binding of antioxidant which reduces its mobility has no important effect on its activity. A further improvement in this field was the discovery that many antioxidants which do not contain a vinyl group can also be grafted to natural rubber latex. Amarapathy and Scott (92-94) have shown that phenols containing a 4-methylene group can also be bound to natural rubber backbone in latex to produce rubber bound antioxidant with the following structure:

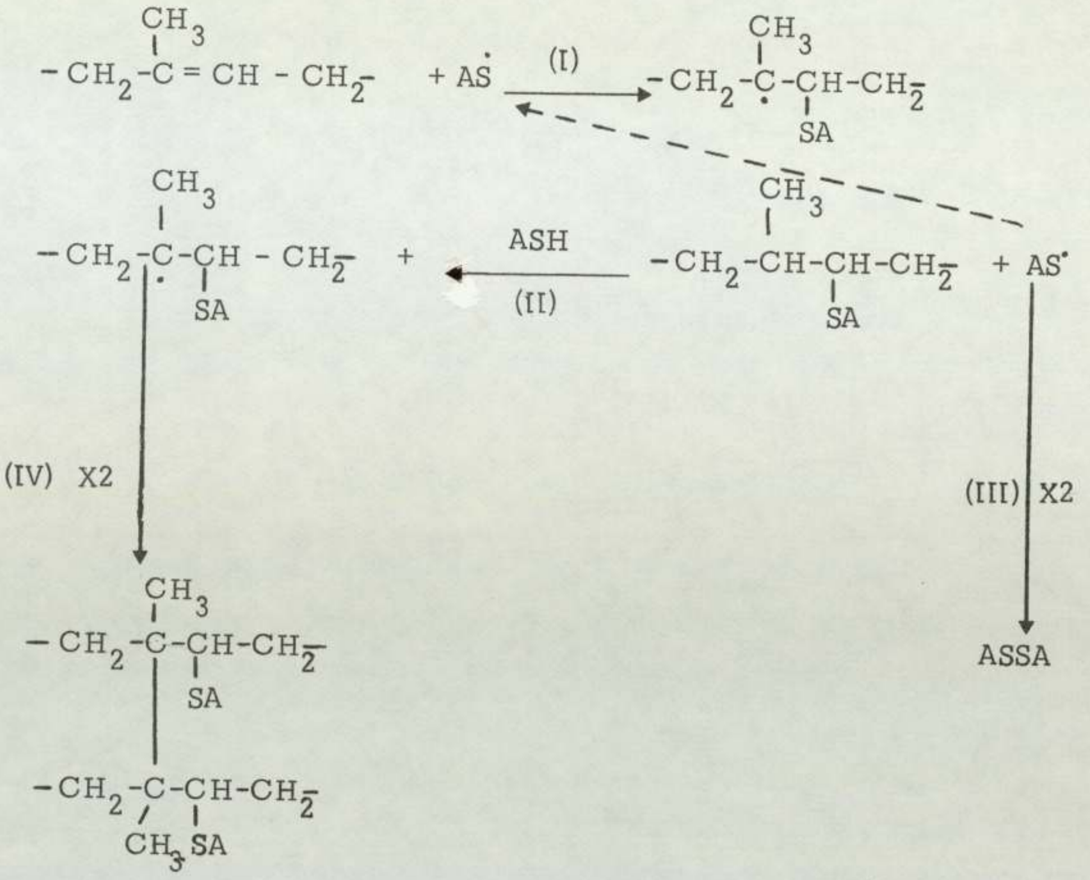


Using oxygen absorption technique, it was shown that maximum effectiveness from the rubber bound antioxidant with the above structure could be obtained when R_1 = t Bu and R_2 = Me which was similar to that found for dialkyl phenols containing vinyl substituent (86). However, the yield of bound antioxidant obtained from simple phenols was shown not to be high enough to make preparation of latex masterbatches commercially suitable. In a subsequent investigation, Fernando (95) has shown that thiol containing antioxidants such as 3,5-di-tert butyl-4-hydroxy benzyl mercaptan can also be reacted with natural rubber latex using AZBN as initiator.



(BHBM)

Antioxidant and AZBN were separately dissolved in chlorobenzene prior to grafting reaction to NR latex. The main disadvantage of this technique was that chlorobenzene used as solvent for BHBM and AZBN due to its incompatibility with water limited its use in latex. Kularatne (96) using the same antioxidant has shown that, under maximised conditions high yields of bound antioxidant can be obtained (70%) as compared to the corresponding phenols (maximum 20%). The higher level of BHBM bound-rubber than that of TBC (2,6-di-tert butyl-4-methyl phenol) was shown to be due to facile addition of the former to the double bond in the presence of free radicals (97-98). As Scott (99) pointed out the reaction of BHBM with natural rubber is a chain process and is terminated by reaction of thiyl radicals ($A\dot{S}$) with other radicals in the system as follows :



In these studies it was shown that natural rubber latex containing bound BHBM and TBC gave superior stability as compared with that containing a conventional antioxidant (Nonox WSP) under aggressive conditions.[(100,101)] Table 1.3 gives a comparison of treated latex having bound BHBM and TBC with that of a conventionally added Nonox WSP in a special rubber glove formulation. It can be seen that when rubbers containing these antioxidants are subjected to solvent and detergent washing followed by oven ageing the ones containing bound BHBM and

TBC are much more efficient than that of the control or rubber containing conventional antioxidant.

TABLE 1.3. Retained tensile properties of aged films of antioxidant bound NR rubber latex (99)

Formulation	Initial tensile (a) Strength	RETAINED TENSILE STRENGTH Air-oven aged (b)	Detergent washed (c) and aged (d)	Solvent extracted (e) and aged (f)
	Kgf/cm^2	%	%	%
Control (no antioxidant)	306	47	47	48
TBC-bound (2g/100 g)	283	99	97	98
BHBM-bound (2g/100 g)	279	97	92	100
Nonox WSP as additive (2g/100 g)	285	63	77	53

(a) unextracted, unaged

(b) 7 days/70°C

(c) 2% Tide; 1 h at 100°C

(d) 1 day/70°C

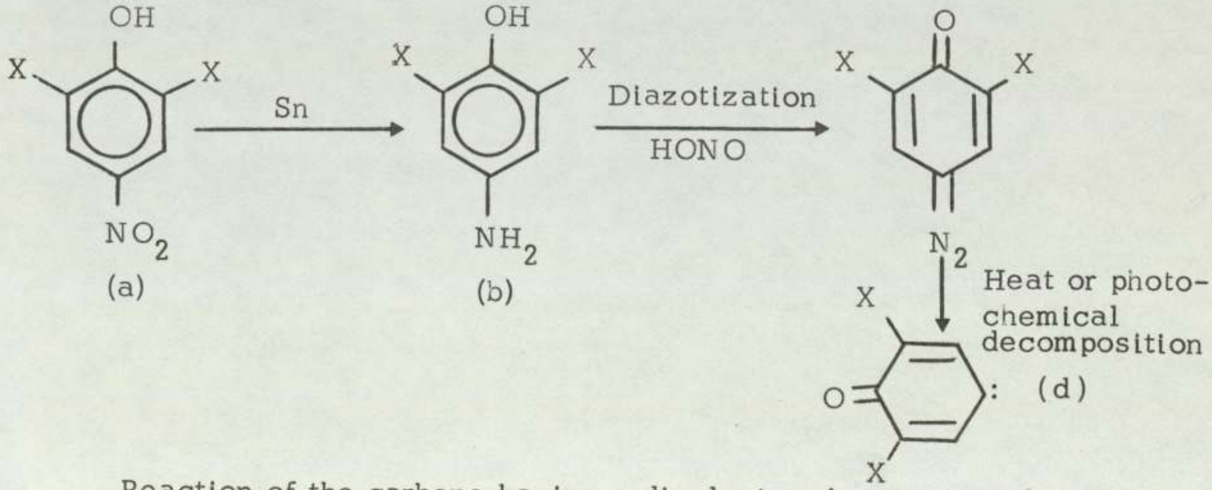
(e) Pet ether/toluene; 5 min.

(f) 3 days/70°C

Furthermore, it was shown that (101) mono and disulphide of BHBM could also be bound to natural rubber latex under similar conditions but to a lesser extent than that of BHBM (BHBM monosulphide ~ 25% and BHBM disulphide ~ 12%).

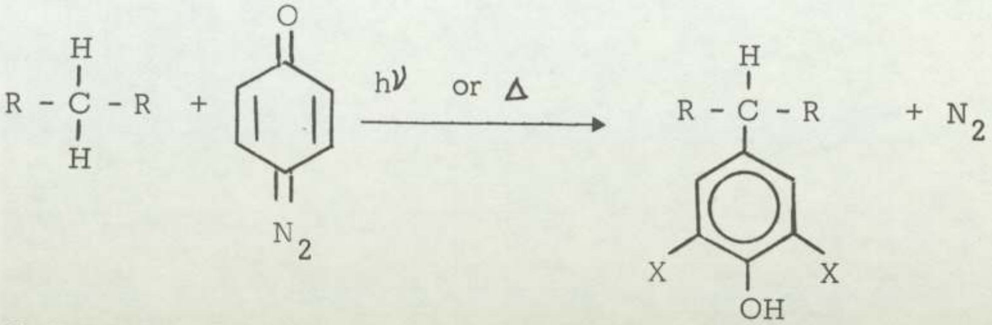
1.4.4. Chemical Binding of Antioxidants to the Base Polymer Before Compounding

It has been shown (102,103) that carbenes can insert themselves into C-H bond in a hydrocarbon. This process has been utilized to produce polymer bound antioxidants. Kaplan *et al.*, (104,105) have shown that polymers such as low and high density polyethylene, polypropylene and polyoxymethylene can be modified by binding of a phenol to polymer backbone. As shown below, this technique involves in reduction of a nitrophenol (a) with tin and hydrochloric acid to form aminophenol (b). This is followed by diazotization of the latter with nitrous acid to give p-diazooxide (c). Photochemical or thermal decomposition of p-diazooxide results in loss of nitrogen molecule and formation of carbene **(d)** :

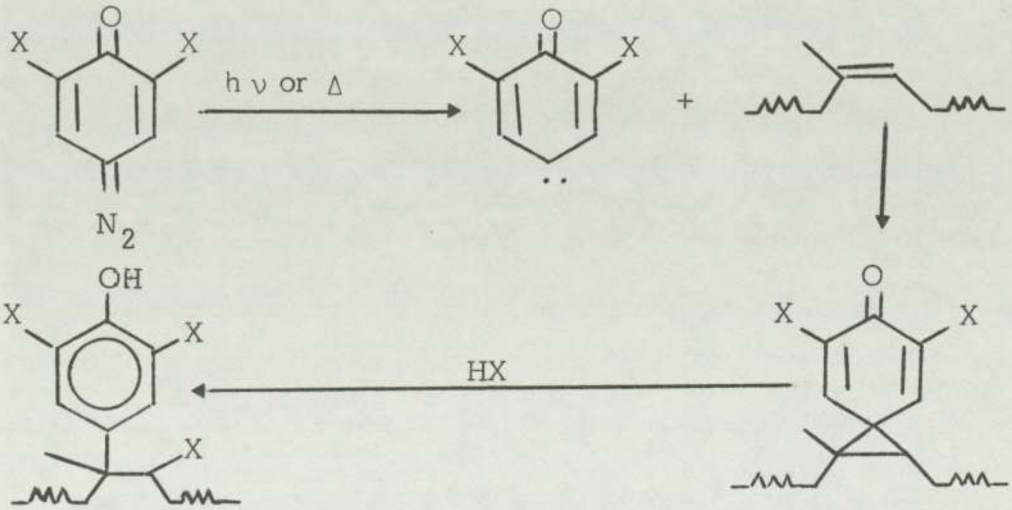


Reaction of the carbene having a divalent carbon atom with a

C-H group from a polymer result in the formation of phenol bound antioxidant :

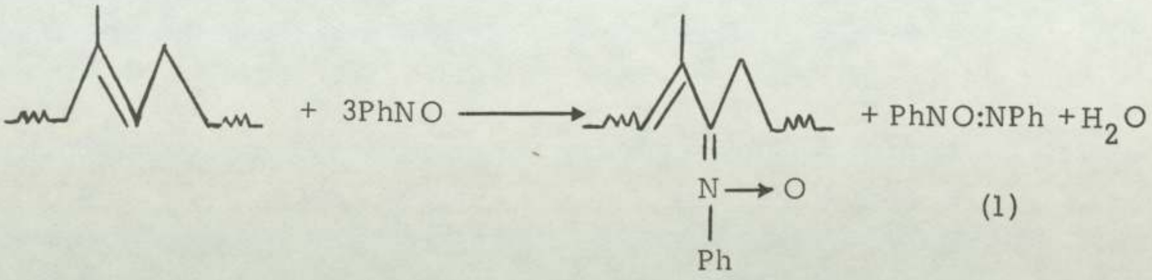


Using oxygen absorption technique they have shown that the polymer bound antioxidant so obtained is superior to conventionally added antioxidant after soxhlet extraction. A similar reaction (103) of p-diazooxide can also occur with natural rubber on heating or irradiation to produce a hindered phenol bound rubber.



1.4.5. Reaction of Rubber with Antioxidant during Compounding and Vulcanisation

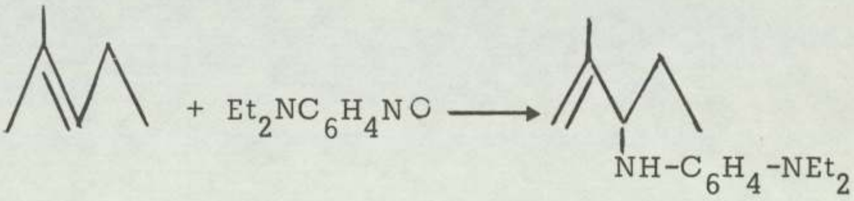
Investigations at MRPRA (106-111) have shown that by reacting antioxidants containing a reactive nitroso group with rubbers during vulcanisation, a rubber bound antioxidant can be obtained. The basis for their work was related to the previous findings (112,113) that the reaction of nitrosobenzene with rubber in benzene solution would produce an iso-rubber nitrone as follows :



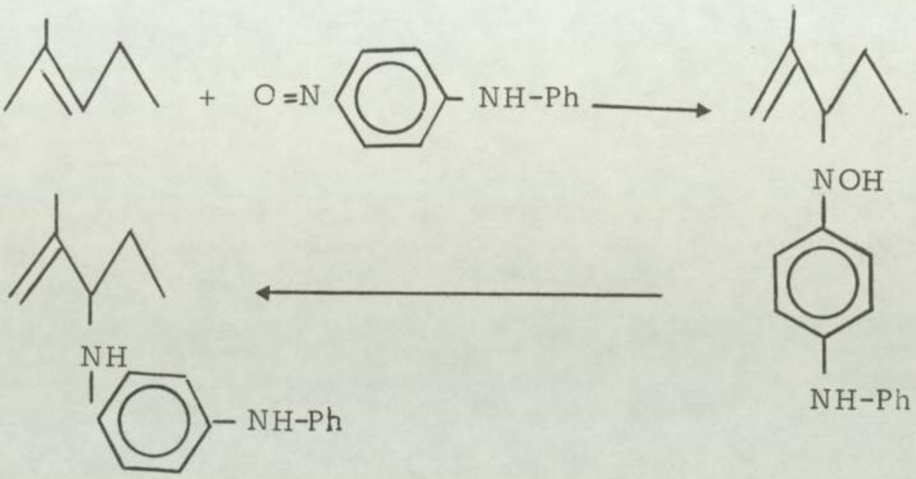
(1)

Instead of nitrosobenzene Cain and co-workers (106) have used N,N-di-alkyl-p-nitrosoanilines and have shown that the latter compounds can be bound to rubbers containing α-methylene hydrogen to give vulcanisates with improved oxidation resistance even after solvent extraction. Using 2-methyl-pent-2-ene as a model compound for natural rubber they have proposed that, N,N-di-ethyl-p-nitrosoaniline (DENA) for instance, can react with natural rubber in a similar manner during vulcanisation :

(2)

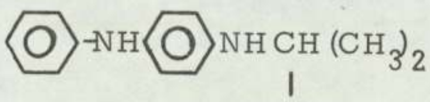
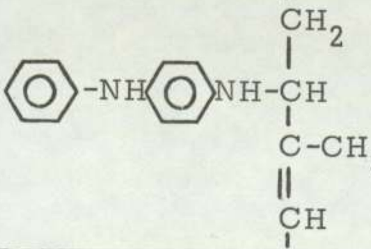


They have isolated N,N-diethyl-N'-(ethyl-2-methyl-prop-2-enyl)-p-phenylenediamine as evidence for the above reaction (2). In a subsequent investigation (108), they have also demonstrated that 4-nitrosoanilines and 4-nitrosophenols can react with diene rubbers during vulcanisation to produce rubber bound antioxidants. In the case of nitrosoamine the bound antioxidant produced had essentially the same structure as sec-alkyl aminodiphenylamine :

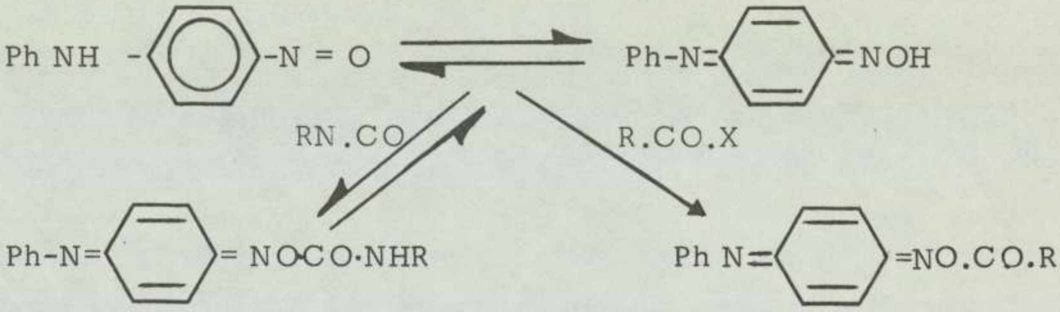


The rubber bound antioxidant obtained was compared with N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD) using an oxygen absorption technique. As shown in Table 1.4 the activity of conventional antioxidant is considerably reduced after solvent extraction, whereas, the activity of rubber bound antioxidant is almost unaffected.

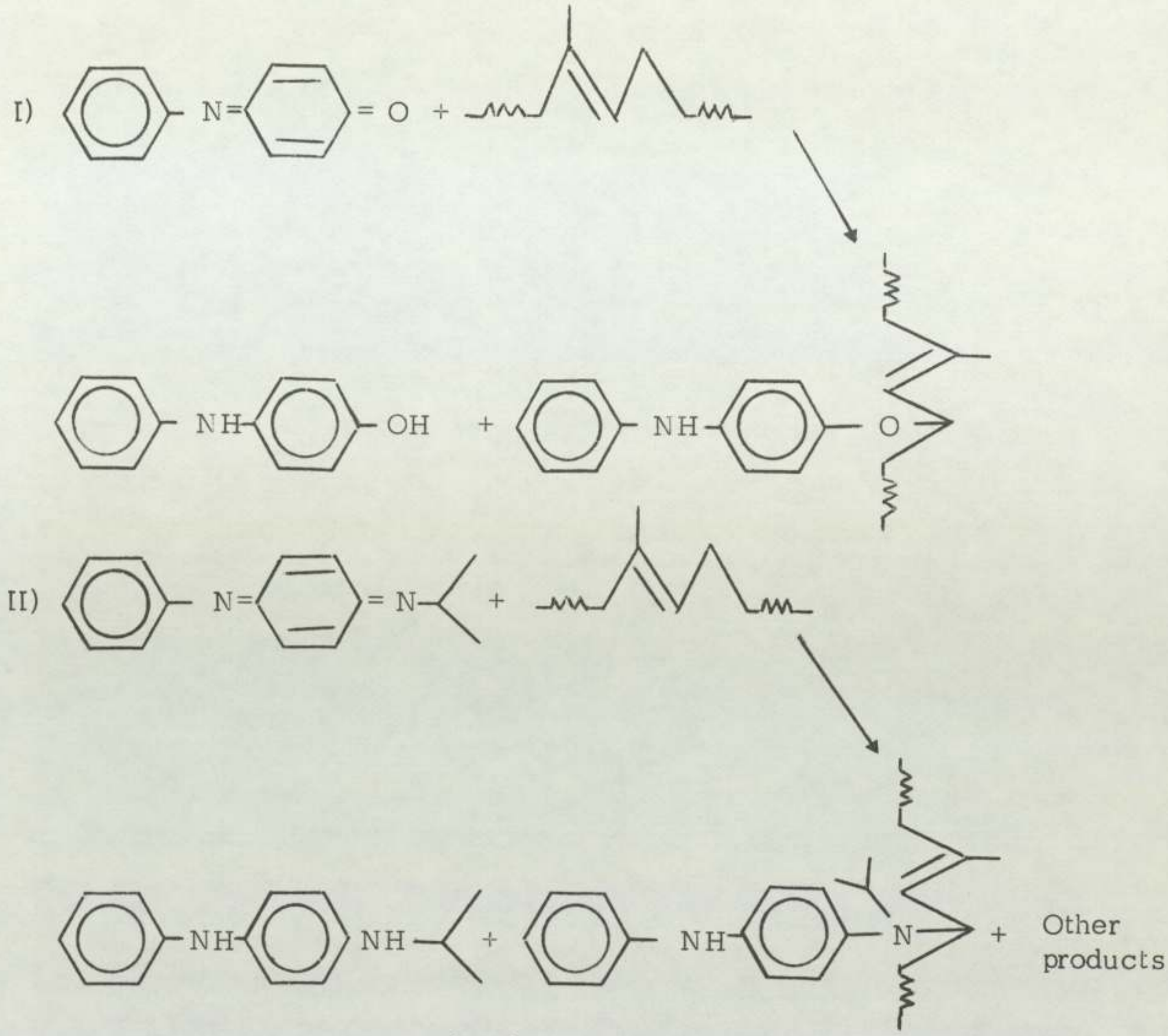
TABLE 1.4. Activity of sec-alkylaminodiphenylamine antioxidants (99)

Structure of antioxidant	Time to absorb 1% 0_2 at 100° C (h)	
	Before extraction	After extraction
	47	4
	60	53

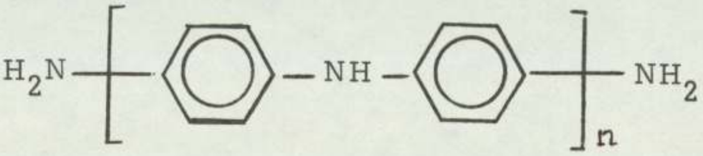
In comparative studies they found that nitroanilines were more effective than nitrosophenols just as amines are generally more effective than phenols. This technique of producing bound antioxidants presented its own problems. Scorch resistance was considerably reduced by the presence of nitrosoaniline and it was necessary to react the 4-nitrosodiphenylamine (NDPA) with isocyanate,(108,113) or an acylating (113) agent in order to improve the processing safety without loss of protection :



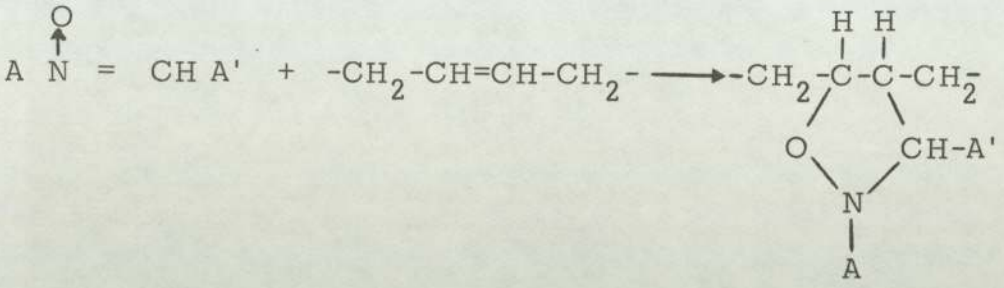
However, NDPA was not a commercial success since it was found to cause staining as well as reducing the scorch resistance. Another method of introducing rubber-bound antioxidant involving free radical mechanisms has been described by Gelling and Knight (114, 115). In this case N-substituted quinone imines and N,N' disubstituted quinone diimines were found, using 2-methyl pent-2-ene as a model compound, to add on at the α-methylene position :



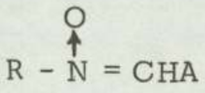
Yamamoto and co-workers (116) have also shown that allyl phenols can react with rubber during vulcanisation to produce rubber bound antioxidant. They found that the reactivities of triallyphenols were higher than mono and diallyl compounds. Kay, Wright and Thomas (117) examined the effect of adding compounds such as;



to fluorohydrocarbon during vulcanisation by diamines. The antioxidant Produced could not be removed from fluorohydrocarbon vulcanisates by extraction and protected them at temperatures up to 200°C. Recently Smith (118) and Scott (119-121) have shown that 1,3-cyclo-addition of nitrones to the double bonds in elastomers can provide a general technique for introducing an antioxidant group into a rubber molecule :



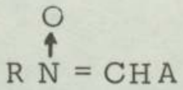
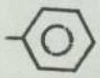
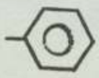
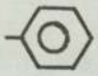
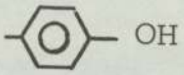
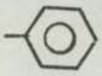
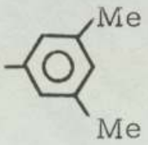
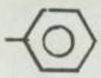
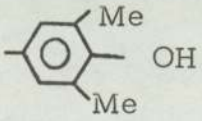
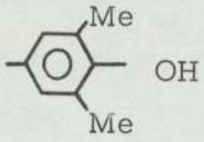
The reactive antioxidant component may be built in either at A or A' and can be either amine or phenolic in nature. This technique has been successfully applied to cis-1,4-polyisoprene and cis-1,4-polybutadiene during vulcanisation using a variety of curing systems. Phenolic and amine nitrones as bound antioxidants were both found to retain their activities after extraction and showed superior resistance to oxidation when compared to conventional antioxidants. In these studies it has also been shown that a major disadvantage of the arylamine group of antioxidants is their tendency to discolour which limits their use to black filled rubbers. In contrast phenolic nitrones (a) which were also found to react with rubber during vulcanisation, gave much lower level of discoloration.



$$R - \overset{\overset{O}{\uparrow}}{N} = CHA$$ (a)

The effectiveness of some phenolic nitrones before and after extraction are shown in the following table which indicates the superiority of the bound antioxidants under extreme conditions.

TABLE 1.5- Effectiveness of nitrone-phenol bound antioxidants (10^{-4} mol g^{-1}) with and without solvent extraction (118,119)

Nitrone  $R\overset{O}{\overset{\uparrow}{N}}=CHA$			Time to 1% oxygen absorption at 100°C	
R	A	% bound	Unextracted (h)	Extracted (h)
		62	25	5
		48	59	9
		71	35	10
		70	37	11
Me		Not bound	44	1.5
Control (no antioxidant)		–	3	0.8

A practical disadvantage of the most reactive antioxidants is that they tend to interfere with the Vulcanisation Process . Both phenolic and amine nitrones were found to affect the scorch time and also vulcanisation rate of a conventionally cured cis-polyisoprene-CBS system at 140°C.

1.4.6. Object and Scope of the Present Work

A major drawback of natural rubber is its susceptibility to oxidation even at room temperature. In order to prevent or retard the process of autoxidation and therefore to improve the performance of natural rubber, a wide variety of antioxidants and stabilizers have been developed. Conventional antioxidants, physically blended with rubber along with the additives prior to vulcanisation, may be readily lost by volatilisation, or by leaching by detergents or industrial solvents. This is a major problem particularly in latex threads, rubber gloves, under-water equipment, and rubber used for medical purposes, which items are frequently subjected to washing and sterilization. One possible way of overcoming this problem is to chemically attach the antioxidant to the rubber. Scott and co-workers (92-101,120,121) have been successful in grafting a variety of antioxidants to natural and synthetic rubber latices in the presence of radical generators and by the use of nitrones during vulcanisation. The present work is a continuation of the work done by Amarapathy(86), Fernando,(95) Kularatne(96) and Smith(118). This study is concerned with the synthesis of the phenolic and amine antioxidants, containing sulphur and thiol functional groups, the investigation of their reactions with natural and styrene-butadiene rubbers, and the evaluation of their effectiveness.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

2.1. Materials

2.1.1. Natural Rubber Latex

The natural rubber latex used in the present work was supplied by W. M. Symington and Sons Limited (QualitexA). The total solid content was 61.5% by weight and it was preserved by 0.7% of ammonia.

2.1.2. Styrene-Butadiene Rubber Latex

The styrene-butadiene latex used in most of the experiments was obtained from SBR International Synthetic Rubber Company (ISR) having the following specifications:

Total solid content	40%
pH	9-10
Particle size	650-750 Å
Soap average	40%
Styrene/Butadiene	25/75
Soap type	K, oleate
Residue styrene	normally $<$0.1%
Antioxidant	none
Sodium diethyldithiocarbamate and sodium polysulphide	very small amount

2.1.3. Compounding Ingredients and Antioxidants

Nonox WSP - Supplied by Imperial Chemical Industries.

N-(Cyclo hexyl)-2-benzothiazyl sulphenamide (CBS) was supplied by Monsanto Chemicals and used without further purification.

Zinc oxide - Amalgamated Oxides Limited

Sulphur-Anchor Chemicals

Dispersol LN- Imperial Chemical Industries.

2.1.4. Other Chemicals

Tert-butyl hydroperoxide 70% - BDH Chemicals, used without further purification.

Lauric acid - Aldrich Chemicals

Thioglycollic acid - Aldrich Chemicals

3-Mercapto propionic acid - BDH Chemicals

3,5-Di-tert-butyl -4-hydroxy benzyl phenol- Aldrich Chemicals

Paraformaldehyde - Koch Light Laboratories Limited

Potassium -tert-butoxide - Koch Light Laboratories Limited

Hydrogen peroxide - BDH Chemicals

Tetraethylene pentamine - Aldrich Chemicals

Para amino diphenyl amine - Aldrich Chemicals

2.1.5. Stripping and Coagulation of SBR Latex

The SBR latex was stripped, coagulated and extracted as follows in order to remove residual styrene monomer and other non-rubber constituents which are known to interfere with the grafting reaction(143).

600 ml SBR latex was poured into a one neck, two-litre flask connected to a vacuum pump, via a set of two liquid nitrogen traps. The flask was placed in a water bath and the temperature was raised slowly within an hour to around 60°C and kept constant for a period of 4 hours. The latex was magnetically stirred throughout the whole period of stripping. After the above period the flask was allowed to cool and SBR latex was coagulated with 10% sulphuric acid. The coagulated rubber soaked in distilled water, washed several times and eventually dried under vacuum. The dried SBR was sheeted on a 12" laboratory two-roll mill, washed with distilled water and dried again. The styrene-butadiene rubber obtained was extracted with acetone for 48 hours in a Soxhlet apparatus under nitrogen, dried and then stored in a vacuum desiccator until required.

2.2. Preparation of Vulcanisates

Most of the work was carried out with Symington natural rubber latex (Qualitex A). The latex reacted or unreacted was coagulated with 1% formic acid and then washed sufficiently with distilled water to remove the acid. The solid mass was dried, sheeted into a thin sheet, and was rewashed again with distilled water to remove any excess acid contaminated with rubber. The rubber was then dried in a vacuum oven at 25°C. The sheeted dried rubber was then wrapped in aluminium foil (to prevent oxidation due to sunlight) and continuously extracted with an azeotropic mixture for at least 48 hours to remove any extra network materials such as naturally occurring, or unreacted antioxidants and also other organic by-products which were either present in the latex or formed during the grafting reaction. The extraction of uncured samples were carried out in a Soxhlet extractor under a constant flow of nitrogen. The extraction of vulcanisates was carried out for at least 120 hours. The solvents used in extraction were usually an azeotropic mixture consisting of acetone, methanol and 1,1,1-trichloroethane in the proportion given in the following table.

TABLE 2.1.

Solvent	Amount in ml
Methanol	42
Acetone	110
1,1,1 trichloroethane	60

Samples after extraction were removed from the Soxhlet, dried in a vacuum oven at 25°C and stored in a vacuum desiccator at 20°C until required.

2.2.1. Compounding

Extracted or unextracted natural rubber (reacted or unreacted) was mixed with compounding ingredients on a 12 inch laboratory two-roll mill. The friction ratio employed during compounding was 1:1. Compounding of samples were carried out using the formulation given in the following table :

NR	100 g
Zno	5
Stearic acid	3
S	2.5
CBS	1

The addition of sulphur was carried out after all the other ingredients had been incorporated. The total compounding time usually was five minutes but was varied in the case of binding of antioxidants during milling and vulcanisation which will be mentioned in the relative section. Styrene-butadiene rubber which was mainly used was obtained by stripping and extraction of SBR derived from the latex (see Section 2.1.5). Compounding of SBR stocks were carried out in a similar manner as described for NR except that the amount of sulphur used was 2 g/100 g of SBR and time taken for compounding was 10 minutes.

2.2.2. Vulcanisation of Rubber

The vulcanisation of the compounded samples were carried out in a stainless-steel mould of cavity dimensions 13.5 x 13.5 x 0.018 cm in order to produce a vulcanised film of 0.018 - 0.023 cm thickness. The compounded rubber was first passed through a tight nip on a 12 inch laboratory two-roll mill to make a thin sheet and about 5g was placed in the clean cavity of the pre-heated mould. The mould was placed between 2 plates of a steam heated press. The press was momentarily closed and opened to release any entrapped air. A pressure of 50 tons on an eight inch ram was applied and the temperature of the press was maintained at 140°C throughout the process of vulcanisation. A curing time of 30 minutes was allowed and then the mould was taken out from the press and cooled down. The vulcanised film was removed from the mould and wrapped in aluminium paper and stored in a vacuum desiccator until required. The samples used in oxygen absorption and stress relaxation studies were cut from the centre of the vulcanised film to eliminate the edge effect. The compounded SBR samples were vulcanized in a similar manner as NR, except the time taken for curing was 45 minutes.

2.3. Estimation of the Concentration of Bound Antioxidants

2.3.1. Estimation of the Concentration of Antioxidants Reacted with NR Latex

Infra-red spectroscopy was used to determine the amount of antioxidant bound to the NR latex. This technique has been previously used (118,122, 123) by several workers for estimation of the amount of bound antioxidant containing hydroxyl or carbonyl groups. Since these groups are present in antioxidants under present investigation, this method was employed to determine the amount of bound antioxidant.

The infra-red spectra of the transparent vulcanised films with thickness of 7-9 τ were obtained and the following procedure was used to determine the amount of bound antioxidant.

2.3.1.1. Calibration Curve

A solution of NR latex containing 100 g dry rubber was coagulated with 1% formic acid and washed with distilled water. The coagulum was sheeted into a thin sheet and rewashed again. The rubber was then dried under vacuum and extracted with azeotropic mixture for at least 48 hours to remove all the non-rubber constituents from the rubber network. The extracted rubber was dried in a vacuum oven and stored in a vacuum desiccator 100 g of extracted rubber was mixed with a known amount of phenolic antioxidant (i.e. 1,2,3%) and also with other vulcanising ingredients on a 12 inch laboratory two-roll mill. The samples were vulcanised into a transparent thin film and their infrared spectra were obtained. The intensity of the phenolic OH peak was proportional to the amount of added antioxidant and was measured as a function of the peak height. To overcome the errors due to sample thickness an invariant peak at 2720 cm^{-1} which is a characteristic of NR was selected as standard peak. The absorbance due to the functional group and the absorbance due to the invariant group (peak at 2720 cm^{-1}) were calculated using the base line technique (86,122). It was then possible to determine the hydroxyl ratio for a given concentration of antioxidant which is the ratio of absorbance of the OH group (at 3640 cm^{-1}) to that of the reference peak (at 2720 cm^{-1}) :

$$\text{Hydroxy group ratio} = \frac{\text{Absorbance of the OH group}}{\text{Absorbance of the reference peak}}$$

The hydroxyl ratio obtained could then be plotted as a function of concentration of antioxidant added. The calibration curves obtained by this method were used to determine the concentration of antioxidant bound to the NR latex. The calibration curve for antioxidants such as BTGA, BTPA and BTGE are shown in Figs. 2.1 - 2.3. However, carbonyl groups were not used for calibration curves since it has been already shown (86) that their absorbance depended on the extent to which rubber had been oxidized during compounding.

2.3.2. Estimation of the Amount of Antioxidants Bound during Processing in the Torque Rheometer

In the case of 4-mercaptoacetamidodiphenyl amine (MADPA) bound to NR during processing the intensities of the aromatic peak at 1595 cm^{-1} due to the antioxidant and that of the reference peak at 2720 cm^{-1} due to NR were measured using base line technique (86,122).

$$\text{Aromatic ratio} = \frac{\text{Absorbance of the aromatic peak}}{\text{Absorbance of the reference peak}}$$

The calibration curve was then obtained by plotting aromatic ratios versus concentrations of MADPA (Fig . 2.4). In binding MADPA to SBR the intensities of the peaks due to secondary amide (-CONH-) at 3260 cm^{-1} and that of the reference at 1940 cm^{-1} were considered in calculating the amide ratio and obtaining the corresponding calibration curve

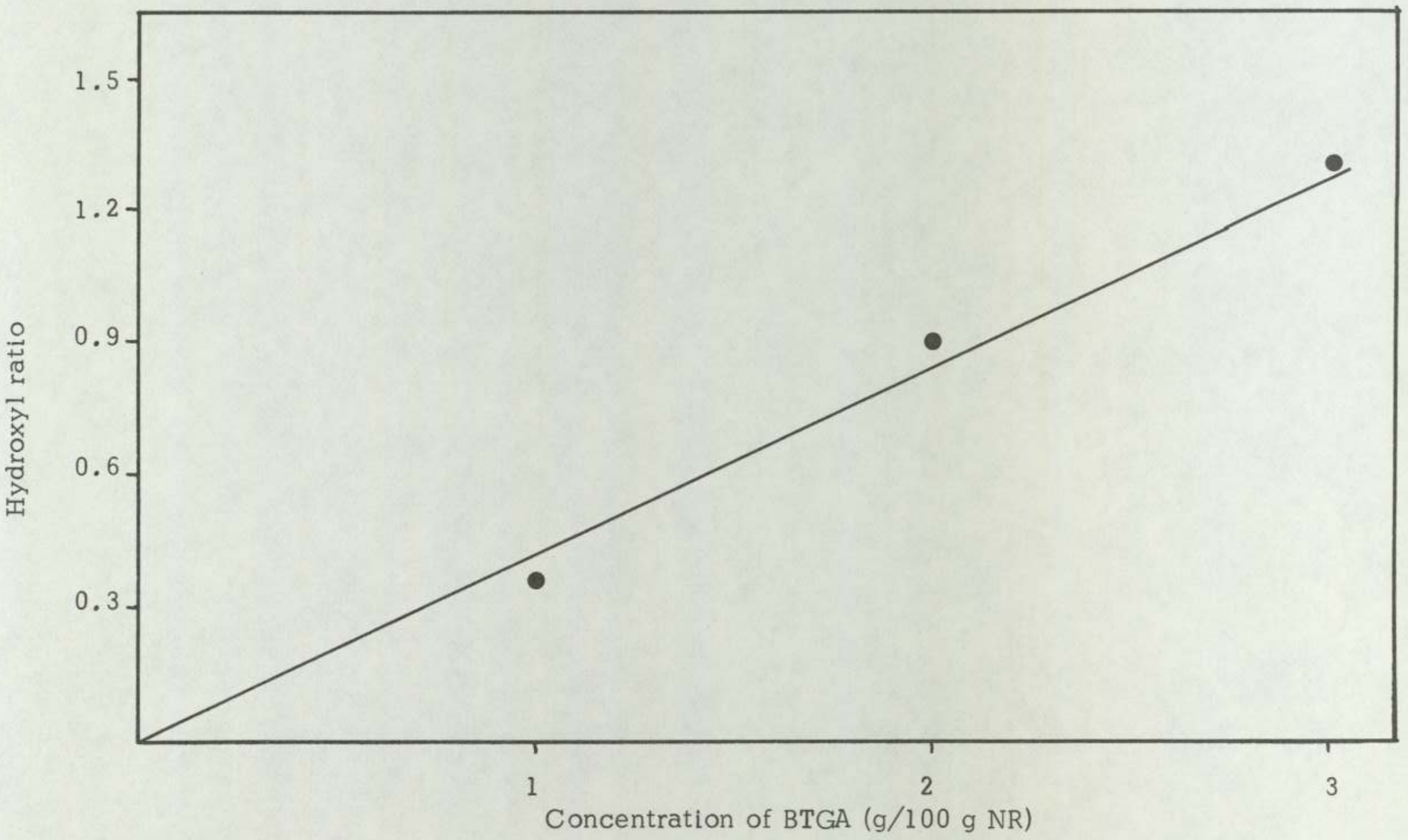


Fig. 2.1. Infra-red calibration curve for BTGA in natural rubber

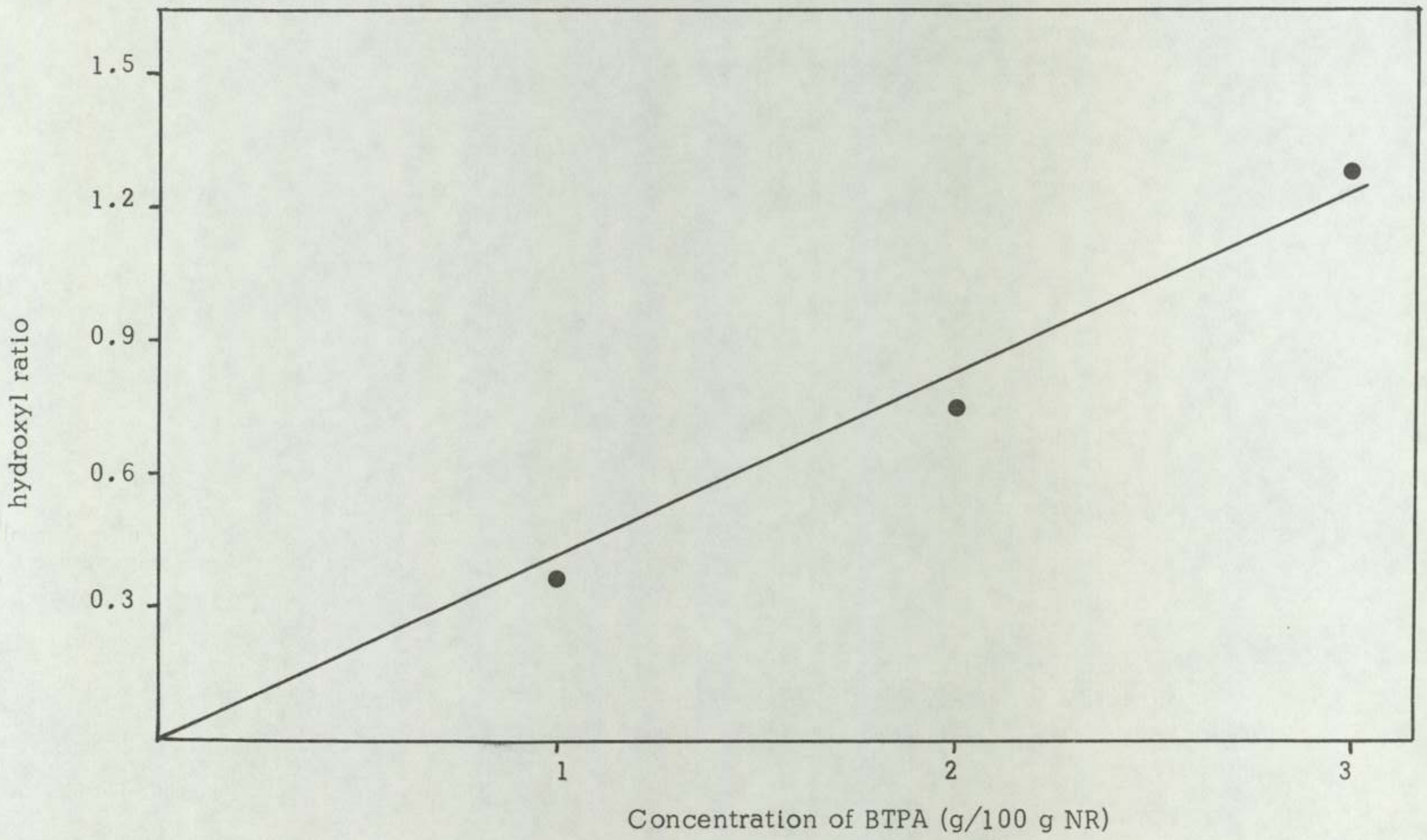


Fig. 2.2 Infra-red calibration curve for BTPA in NR

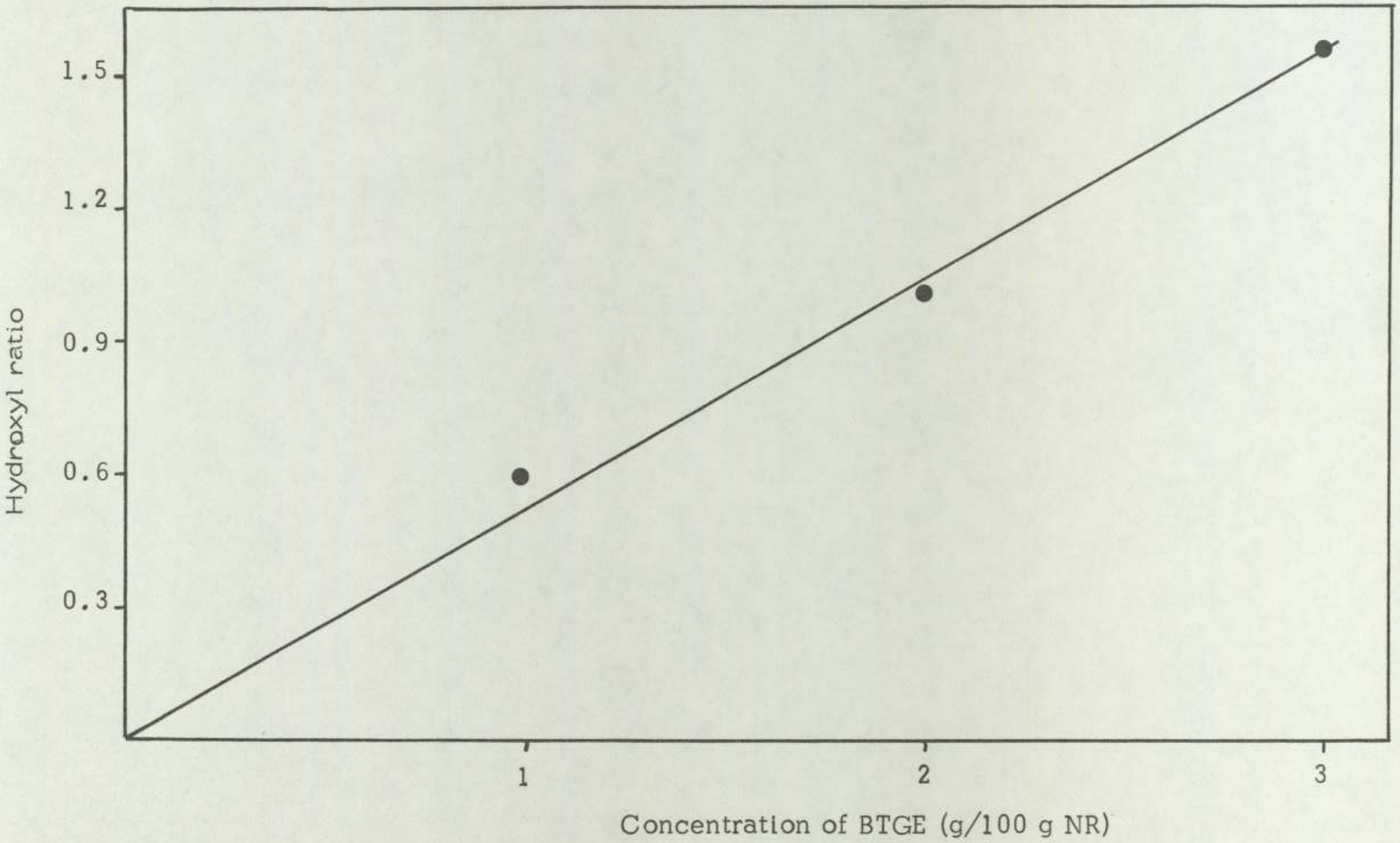


Fig. 2.3 Infra-red calibration curve for BTGE in natural rubber

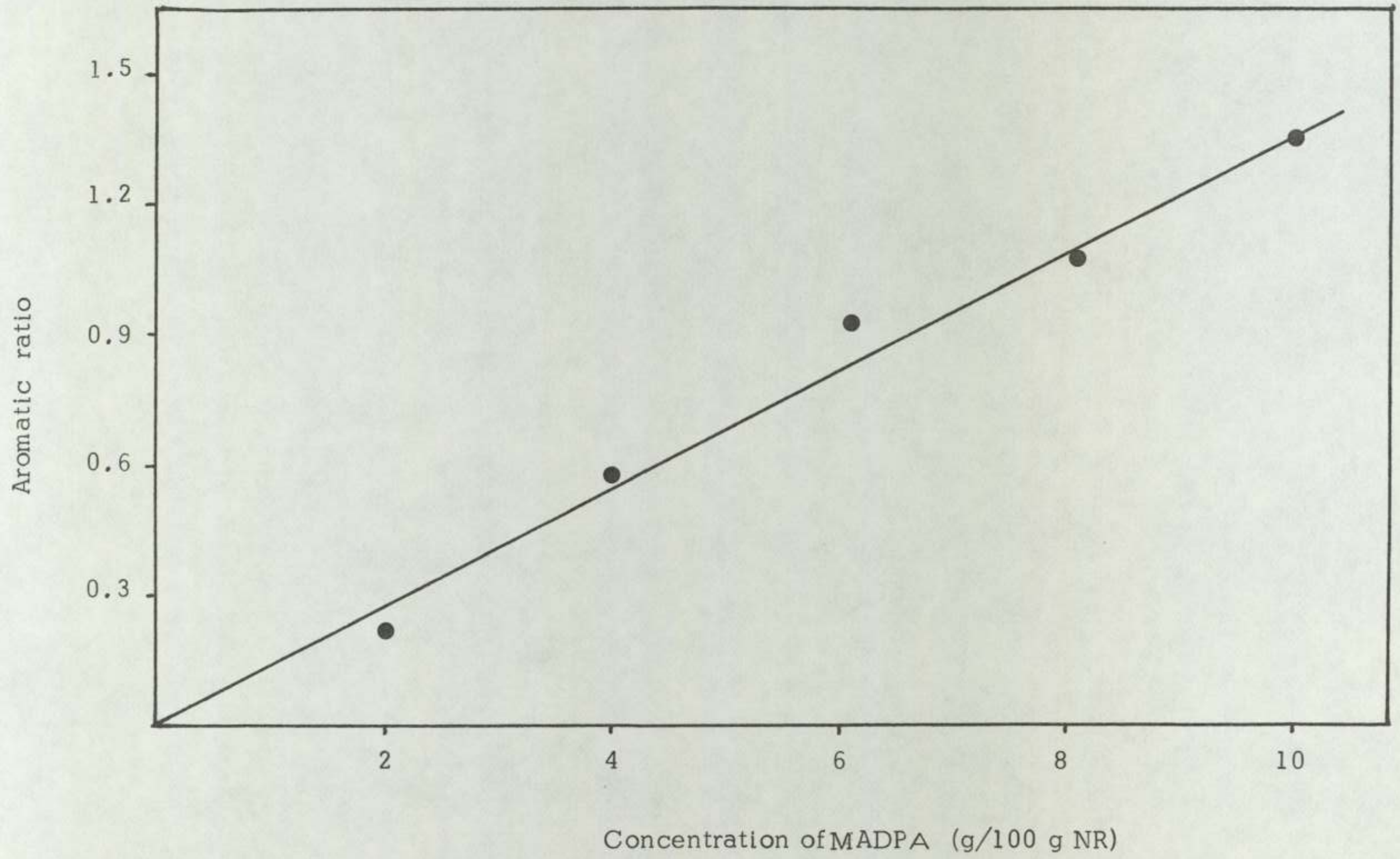


Fig. 2.4. Infra-red calibration curve for MADPA in natural rubber

(Fig. 2.5). However, the amount of BHBM bound to SBR during processing in the torque rheometer was estimated by determining the hydroxyl ratios and plotting the corresponding calibration curve (Fig. 2.6). The hydroxyl ratio in this case was the ratio of the absorbance of hydroxyl peak at 3640 cm^{-1} to that of the reference peak at 1940 cm^{-1}. For instance, the amount of MADPA bound during processing in the torque rheometer to NR was determined using the following procedure.

2.3.2.1. Calibration Curve

30 g of extracted natural rubber with a known quantity of MADPA (i.e. 2,4,6,10%) was mixed for 10 minutes in the torque rheometer. The processed rubber was then passed through a 12 inch laboratory two-roll mill to make a thin sheet. The films of the processed rubber and antioxidants were preparedon a stainless-steel plate at 50°C. A small quantity of the processed rubber was placed between two sheets of a cellophane paper and then between two stainless-steel plates. The plates were placed between two platens of an electric hand press. After a period of one minute, the film obtained was cooled down and removed from cellophane paper and mounted on a specially prepared frame for infra-red analysis. The infra-red spectra of the films obtained and aromatic ratios were determined for different concentrations of MADPA in NR. The calibration curve was obtained by plotting the aromatic ratios versus concentration of MADPA and is shown in Fig.2.4. The calibration curves for determining the amount of MADPA and also

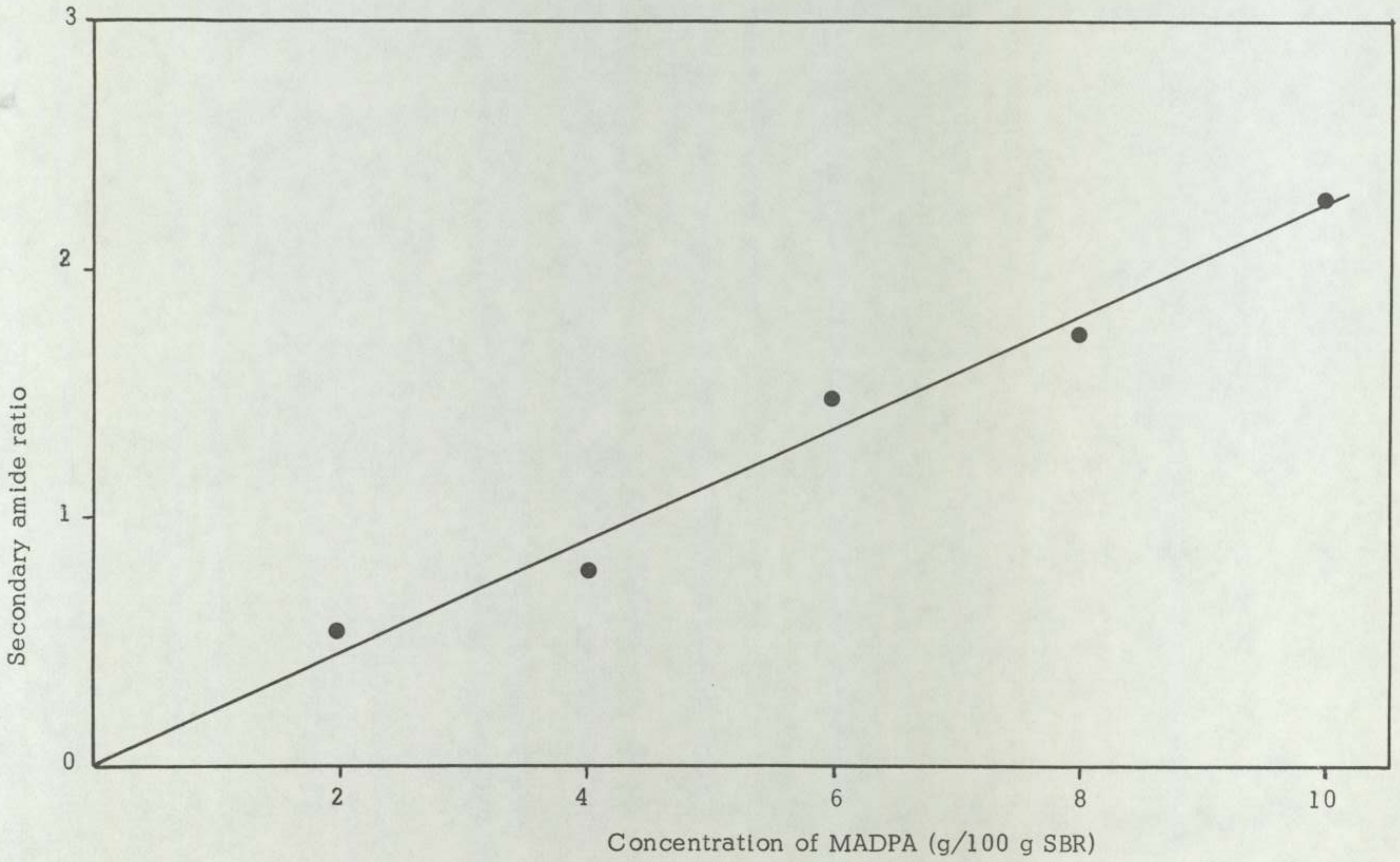


Fig. 2.5. Infra-red calibration curve for MADPA in SBR

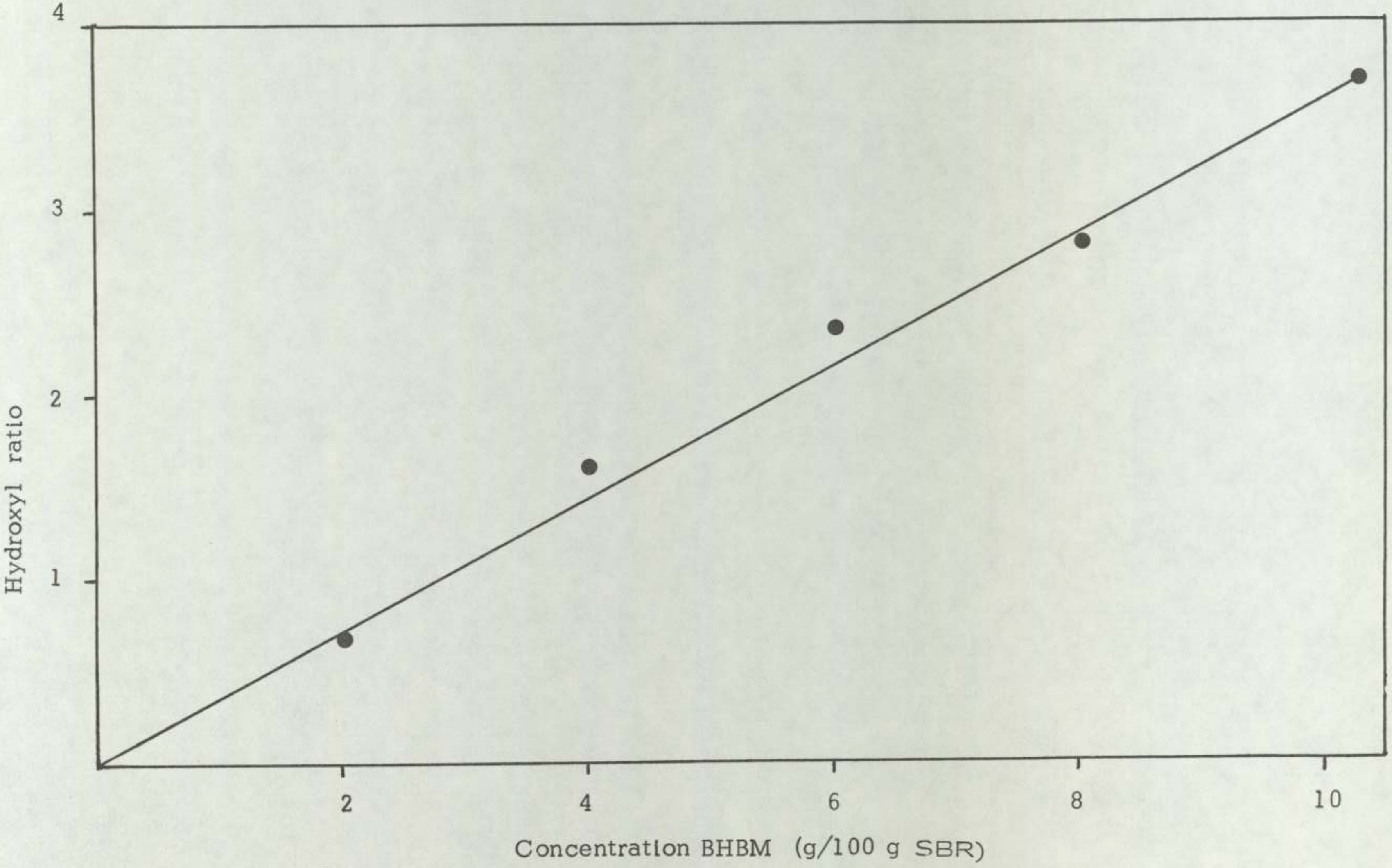


Fig. 2.6 Infra-red calibration curve for βHBM in SBR

BHBM bound to styrene-butadiene rubber were also determined using an almost similar procedure, except the SBR used was that obtained by stripping, coagulation and extraction of the SBR latex (see Section 2.1.5). These calibration curves are shown in Figs. 2.5 - 2.6.

2.3.3. Determination of the Percentage of Antioxidant Bound during Vulcanisation

Infra-red spectroscopy was used to determine the percentage and concentration of antioxidant bound during vulcanisation. This method has been previously used by other workers to determine (118) the extent of the binding of phenolic and nitrone antioxidants to the rubber during vulcanisation. The amount of antioxidant bound during cure was determined on vulcanisates with thickness of 7-9 τ. The infra-red spectra of the vulcanisates both before and after azeotropic extraction containing a known amount of antioxidant were run on the same chart paper using the same instrument settings each time. The absorbances of a certain functional group, such as hydroxyl for phenolic antioxidants, and aromatic or secondary amide groups for MADPA, to that of the reference peak (at 2720 cm^{-1} for NR and at 1940 or 1870 cm^{-1} for SBR) were determined using base line technique (86, 122) as described in previous section (see Section 2.3.1.1). The functional group ratios of the unextracted and extracted vulcanisates were compared and the amount of the antioxidant bound to NR or SBR vulcanisates were determined.

2.4. Monsanto Oscillating Disc Rheometer

Vulcanisation is a process which converts plastic rubber into cross-linked elastic rubber. The presence of a non-vulcanising ingredient in a vulcanising system may have a considerable effect on subsequent curing behaviour of vulcanised rubber. It is well known that antioxidants added or bound to the rubber can cause significant effect on vulcanisation characteristics of the rubber. They may for instance, cause a drastic effect on scorch time (i.e. induction period) or the rate of cure. Since a number of antioxidants were used in this work either as additive or bound antioxidant it was thought it was necessary to evaluate their vulcanisation characteristics, especially at required concentration, i.e. 0.25 - 2%. For this purpose the Monsanto rheometer was used to assess the curing behaviour of natural rubber gum stock containing various antioxidants in different proportions. A curve can be obtained from Monsanto rheometer which provides information about the curing behaviour of compounded rubber and for this reason, a brief discussion on the theoretical aspects of this instrument will be given. This instrument consists of a biconical disc surrounded by the polymer specimen confined in a die cavity located in large electrically heated platens. The temperature of the platens and dies are maintained to within ± 5°C by electric heaters. The cavity is formed by a fixed lower die and movable upper die and is kept closed during the tests by a pneumatic ram. Standard air pressure on the ram is 50 psi which provides approximately 700 psi pressure within the cavity. The oscillating disc system is schematically shown in Fig. 2.7. A motor driven eccentric oscillates the shaft of the biconical disc sinusoidially. The disc is oscillated through a small arc of ± 1, 3, 5 degrees.

The reciprocal motion is transmitted from the eccentric through a connecting link. The force required to oscillate the disc and therefore apply a shearing strain to the rubber specimen is measured electronically by the torque arm transducer. The torque arm transducer consists of a semi-conductor strain gauge bonded to each side of the torque arm. The strain gauges are excited by a direct current power supply located in the recorder cabinet, The torque applied to the disc produces a voltage proportional to the stiffness of the polymer to be developed across the strain gauge bridge. The resulting direct current signal is recorded to produce a continuous cure curve of elastic modulus versus cure time on a chart. The recorder is equipped with a range of selectors that provide full scale chart papers of 25, 50, 100 and 200 inch-lbs, of torque. There is also an automatic pen-return which returns the pen to the zero time position on the chart whenever the pen reaches the end of the chart or the cavity is opened. A typical Monsanto curve obtained during cure of a rubber stock is shown in Fig. 2.8.

As it is shown in Fig. 2.8 , there is an initial drop in torque due to the decrease in the viscosity of the rubber as its temperature rises. This drop then flattens out until the start of cross-linking (i.e. induction period). This is then followed by an increase in viscosity indicating that curing is taking place. After a certain period of time the viscosity reaches its maximum. In some cases this maximum can further increase or decrease indicating a secondary vulcanisation or reversion respectively. Reversion is due to the breaking down of the cross-links. Scorch time

Fig. 2.7. Oscillating Disc System

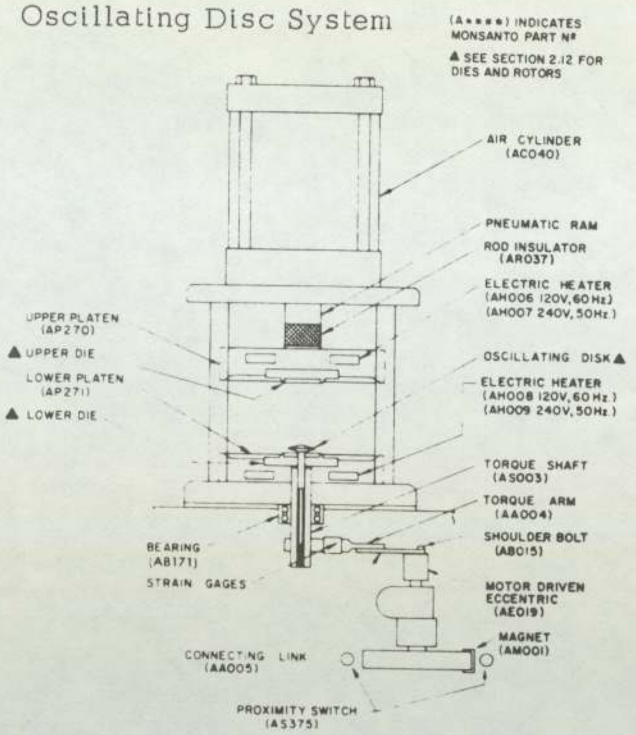
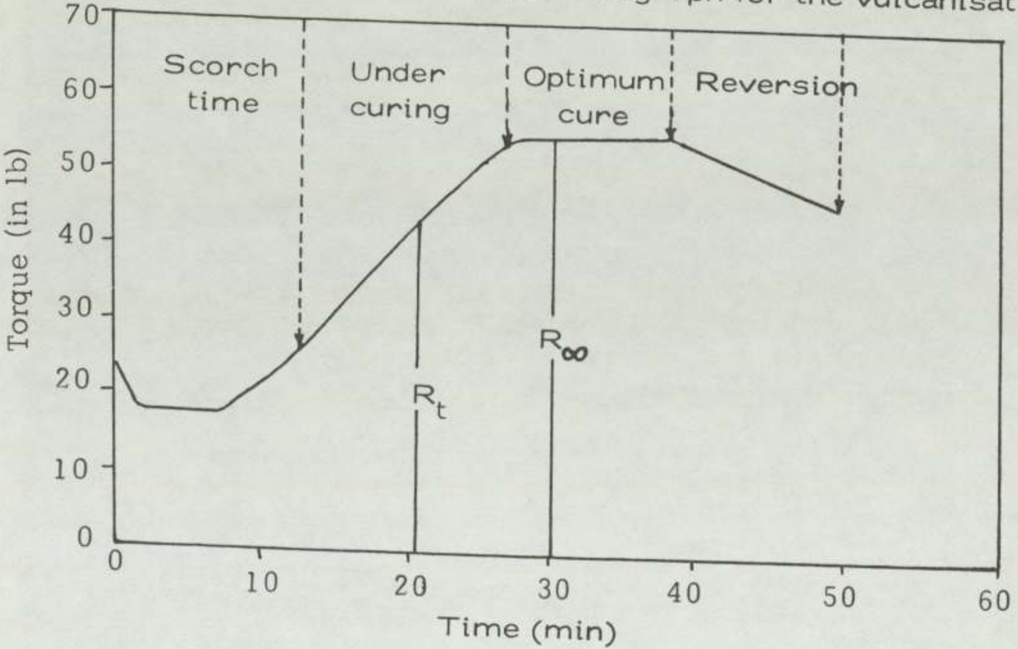


Fig.2.8. Typical Monsanto rheograph for the vulcanisation of rubber



may be obtained based on arbitary number of units of torque above the minimum viscosity. The kinetic treatment of Monsanto rheograph and curing characteristics of some of the antioxidants used in this work are given in Chapter 6.

2.5. Technological Ageing Tests

2.5.1. Oxygen Absorption Test

Oxygen absorption studies of rubber vulcanisates provide very useful data on inhibition and oxidizability of the material during accelerated ageing test in a closed system. Information that may be obtained from the oxygen absorption test includes the following :

i. The induction period which is the time taken for autoxidation to become autoaccelerating.

ii. The rate at which a particular material absorbs oxygen.

iii. The time required to absorb a certain amount of oxygen by the sample, which is commonly reported as 0.5%, 1% and 2%.

These factors are usually affected by factors such as the type of antioxidant used, the curing system, the temperature of the test, the pressure and concentration of oxygen and etc. These factors are usually varied for a particular sample, e.g. a sample may give a long induction period and absorb oxygen at a high rate, or with a short induction period and a slow rate of absorption of oxygen. The absorption of oxygen by rubber vulcanisates is usually controlled by two processes. Firstly, the rate of diffusion of oxygen into the specimen, secondly the rate of reaction of oxygen with the sample. At high temperatures the rate of oxidation may become controlled by the rate of diffusion of oxygen into the sample depending upon the thickness of the sample used.

The effects of diffusion of oxygen and sample thickness on oxidation of rubber vulcanisates have been investigated by a number of (124-128) workers. It has been shown that for black-filled vulcanised rubber in the absence of antioxidant the limiting thickness is 0.040 inches at temperatures ranging from 80° - 100°C, whereas in the presence of antioxidant this was shown to be 0.075 inches (125). It has also been found that the diffusion control did not operate with specimen of 0.012 inches (0.03) thick. Parks *et al.,* (128) have found that a thicker sample of polyisoprene vulcanisates (0.05 cm) could be used in the presence of antioxidant at 80°C as compared with nitrile rubber (127), (0.025 cm). Ingham (124) has recently shown that in the case of peroxide or sulphur cured vulcanisates of polyisoprene, a sample with thickness of 0.018 - 0.023 cm or less could be used. The oxygen absorption studies in the present investigation were also carried out with vulcanised films of 0.018 - 0.023 cm thick.

2.5.1.1. Apparatus for Oxygen Absorption Measurements of Vulcanisates

The rate of oxygen absorption by vulcanised films was followed automatically and continuously using apparatus shown in Fig. 2.9. The specimen was placed in a modified pyrex-test tube of 100 ml volume with B24 socket and cone attachment. The arm fitted to the tube was connected to a luer needle fixed in with epoxy resin at the opening. The absorption vessel was connected by a glass tubing to the wet side of the pressure transducer via a ball and socket joint. The dry side of

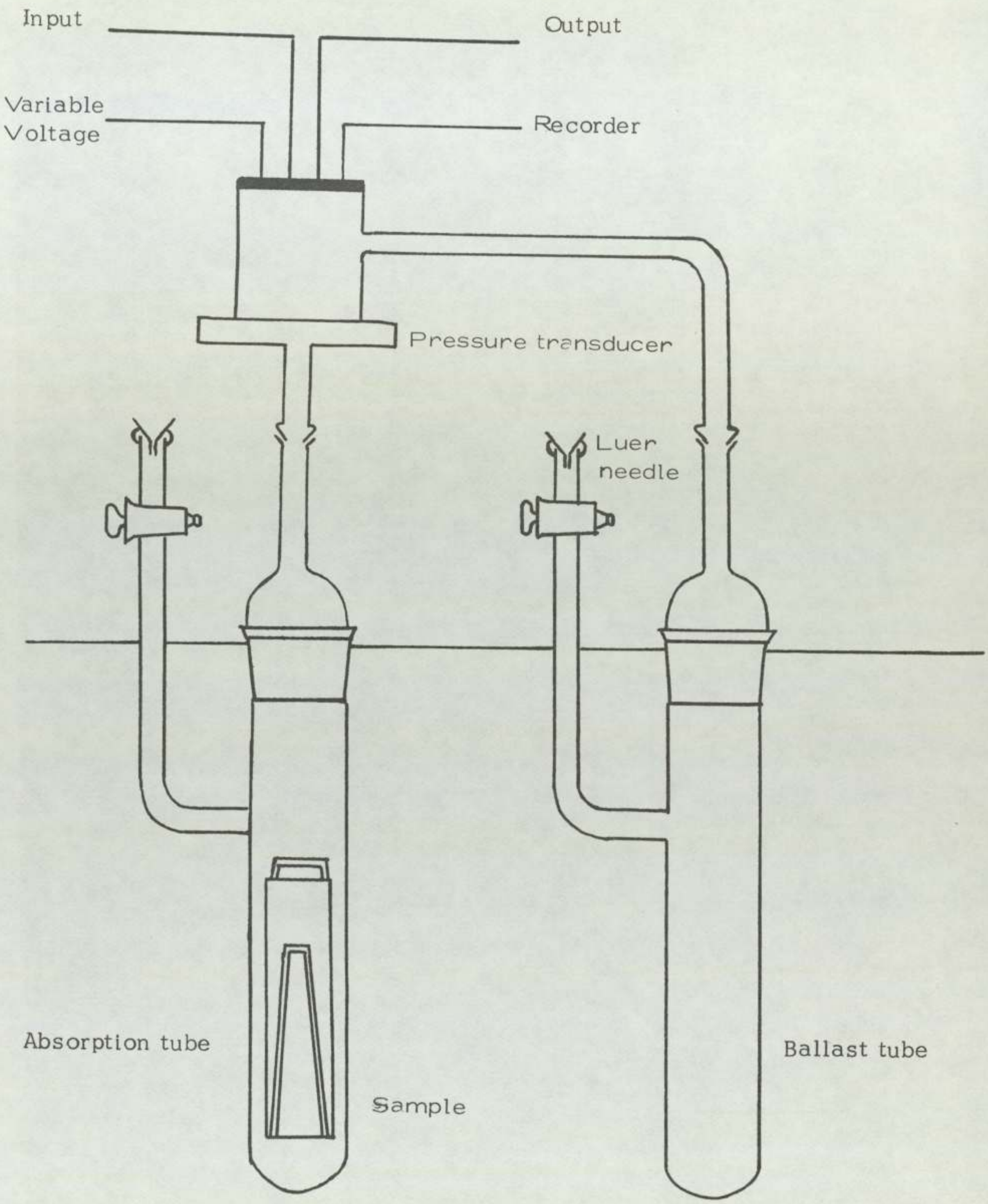


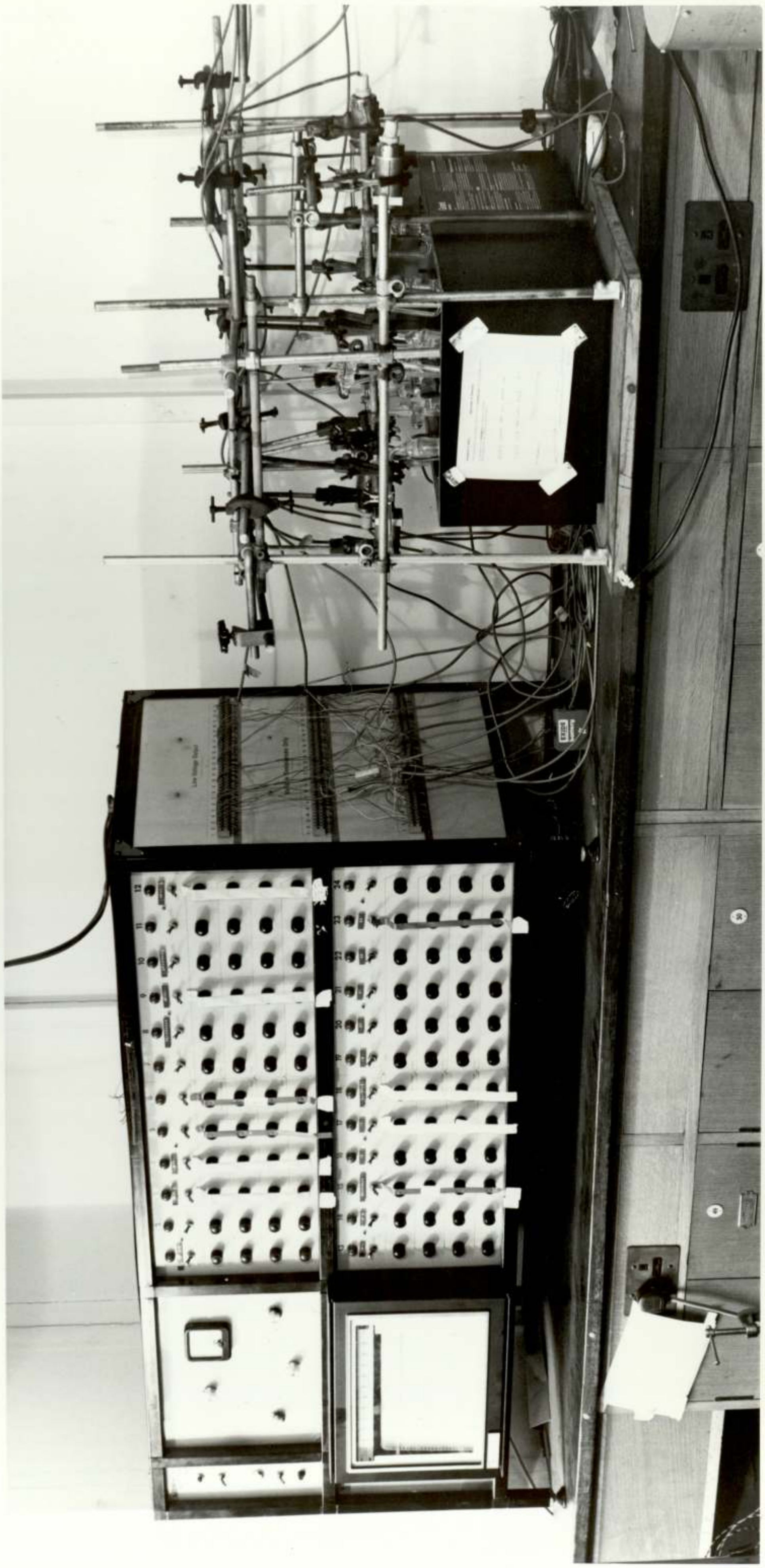
Fig. 2.9 Apparatus for oxygen absorption of vulcanisates

the pressure transducer was attached to a ballast vessel with a similar dimension to the absorption vessel. These two tubes were placed side by side in a thermostated oil bath (± 0.5°C). The tubes outside the oil bath were made up of short capillary tubes in order to minimize the effect of varying ambient temperature on the oxygen absorption of the samples. The transducer used was a strain gauge type manufactured by Pye-Ether Limited, model UP $3^{\pm}5$ psi. The size of output voltage is proportional to the input voltage, so by varying the input voltage the sensitivity of the transducer to pressure fluctuations could be varied. In the present investigation, the input voltage was usually maintained in a way that 2ml of oxygen could be absorbed for each 20 divisions on the scale of the chart paper. As the vulcanisate starts to absorb oxygen, a pressure difference is set up between two vessels. The pressure difference between the reaction vessel and the ballast tube is proportional to the output voltage of the transducer which was recorded automatically as an oxidation curve on a Leeds and Northrup speedomax recorder.

2.5.1.2. Procedure

An accurately weighed sample (0.3 g) of maximum thickness 0.023 cm was placed on the glass support as shown in Fig. 2. 9 , so that oxygen could be absorbed on both sides of the sample freely. The glass support with the sample was then placed in the absorption vessel. The reaction vessel was purged with oxygen for 15 minutes and assembled in the thermostatic bath at 30°C. A gas tight seal was obtained using

Plate 1. Oxygen Absorption Apparatus



a certain amount of vacuum grease. The reaction vessel was connected to the transducer having the other tube already attached. After a period of 10 minutes, for allowing the system to equilibrate so as to reach the temperature of 70°C the samples were left to absorb oxygen. If further oxygen was needed it was passed in through the luer needle until atmospheric pressure was re-stabilised. To measure the amount of oxygen absorbed by the sample the transducer was calibrated. This was done by withdrawing a known volume of oxygen using a syringe fitted to the luer needle. The amount of deflection was recorded on the chart paper. The duration of oxygen absorption studies was dependent upon the rate of oxidation by the sample under the test. At the end of each experiment the reaction vessel was disconnected and the sample removed. The apparatus was washed with acetone and dried before further use.

2.6. Stress Relaxation Technique

In oxygen absorption tests the loss of antioxidant due to volatility does not occur due to the fact that the test is carried out in a closed system. Therefore, the technique of stress relaxation is known to be more relevant to practice where the vulcanisate is oxidised in a stream of air. This test is particularly useful in the case of samples with high surface area to volume ratio, such as elastic fibres or vulcanisates under present investigation.. The information obtained from the oxygen absorption technique is mainly on the inherent activity of the antioxidant whereas in thin vulcanised films the factors such as volatility or ease of extraction of antioxidant by solvent is more important than the inherent activity of the antioxidant. There are two types of stress relaxation; intermittent and continuous. In intermittent stress relaxation the sample is only stretched for a short period of time and then maintained in an unstretched position for a longer period of time and the process is repeated. In an unstretched condition the new cross-links are formed which will contribute to the stress when the sample is stretched again. In continuous stress relaxation such as that used in the present work, the sample is stretched continuously at a given extension. The method of stress relaxation is based upon the kinetic theory of rubber elasticity. According to this theory the stress of an extended sample is given by the following equation:

$$f = N.K.T.A_o. (\lambda - \lambda^{-2})$$

where

$\lambda = \frac{l}{l_o}$, f is the force exerted by an extended rubber specimen, and N is the number of stress-supporting network chains or chain segments between junction points in the network for unit volume. The K is the Boltzmann's constant, T is the absolute temperature, A_o is the unstretched cross-sectional area and λ is the ratio of the stretched to the unstretched length of the specimen (extension ratio). If parameters such as T, A_o and λ are kept constant, then the stress is proportional to the N, the number of stress supporting network chains N, and if, during degradation, a number (N_o -N) of the original N_o chains present are broken, the ratio of the final tension f to initial tension f_o is :

$$\frac{f}{f_o} = \frac{N}{N_o}$$

Therefore, during thermal degradation of vulcanised rubber, as the chain scission occurs, the decay in stress is a direct measure of the degradation of the vulcanised network. Although stress relaxation employs simple equipment, a high degree of precision and reproducibility can be achieved. This technique has been extensively used in rubber industry in order to evaluate network changes taking place during the oxidation of the vulcanised rubber.

2.6.1. Procedure

The continuous stress relaxation of the vulcanisates was followed using the Wallace-Shawbury self recording age-testers (Wallace Instrument Limited). This equipment consists of six cell air ageing oven set. The cell temperature can be adjusted at 100± 2°C due to 1 cu. ft. per hour air flow.

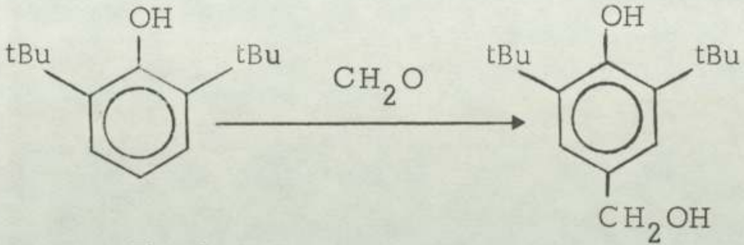
Samples were cut from a vulcanised sheet using the MR100 apparatus test cutter. The sample was first fixed to upper specimen grip and attached to the beam. The equipment was then zeroed for the weight of the sample and lower specimen grip was tightened around the sample. The apparatus was then placed in a thermostatically ageing oven at 100±2°C with 1 cu. ft/hour air flow. The specimen was extended and the pencil lead was adjusted to 100% stress and zero time on the chart. The sample was then allowed to relax and the instrument automatically recorded the decay in stress during the degradation of vulcanised rubber as a function of time on a chart paper.

CHAPTER THREE

SYNTHESIS AND CHARACTERISATIONS OF ANTIOXIDANTS

3.1. Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl Alcohol

3,5-di-tert-butyl-4-hydroxybenzyl alcohol was prepared according to the following scheme : (129-131)



The 2,6-di-tert-butyl phenol was used as obtained from Aldrich Chemical Limited.

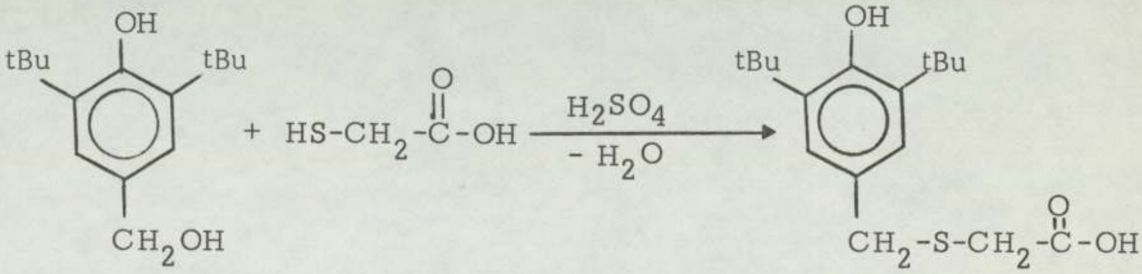
53.3 ml (0.140 moles) of a 7.5% solution of formaldehyde in tertiary butyl alcohol, 50 ml of a 500 g/lit solution of 2,6-di-tertiary-butyl phenol in anhydrous tert-butyl alcohol (0.128 moles of 2,6-di-tert-butyl phenol) and 14 ml of potassium-tert-butoxide solution (50 g in 1000 mls of anhydrous tert-butyl alcohol) were mixed at 16°C and stirred with a mechanical stirrer under a continuous stream of N_2 for 25 minutes. The reaction mixture was then poured into an excess of ice water and left in the refrigerator for 24 hours. Two layers were formed, the upper oily organic layer solidified on standing. The solid was filtered and washed with distilled water. This was followed by washing with n-hexane while stirring. The solid product was repeatedly rewashed with n-hexane and filtered till the reddish colour disappeared. The resulting white crystalline product was air dried having a melting point of 137°C. The infra-red spectrum is shown in Fig. 3.1.

IR data	
Free phenolic OH	3560 cm^{-1}
Hydrogen bonded OH	-3500 cm^{-1}

NMR	τ	
Aromatic protons	2.9	(singlet)
Phenolic protons	4.9	(singlet)
Methylenic protons	5.5	(singlet)
Tertiarybutyl protons	8.6	(singlet)

3.2. Synthesis of 3,5-di-tert-butyl-4-hydroxy benzyl-carboxy-methyl sulphide (BTGA)

This preparation was carried out according to the following scheme:(96)



47·2 g of (0.2 moles) of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol and 15 g (0.16 moles) of thioglycollic acid were dissolved in dry toluene. The mixture was poured into a round-bottomed flask, fitted with a reflux condenser having a side tube in order to collect the water formed during the reaction.

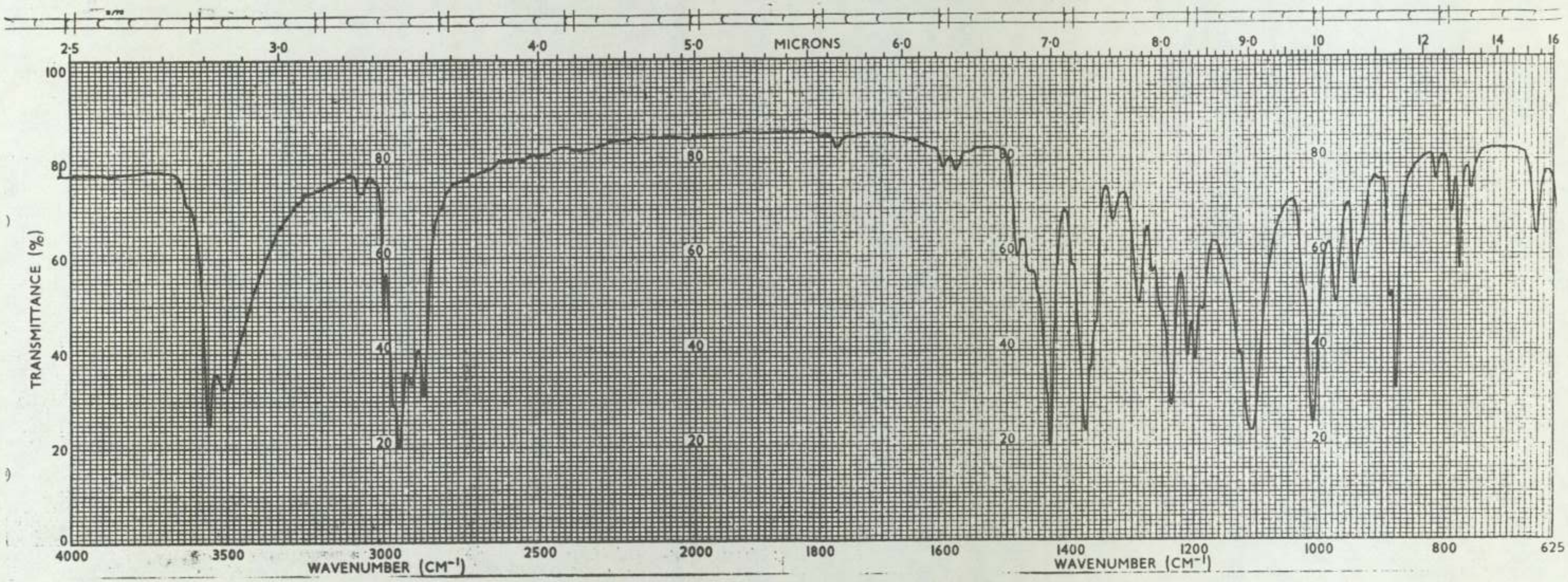


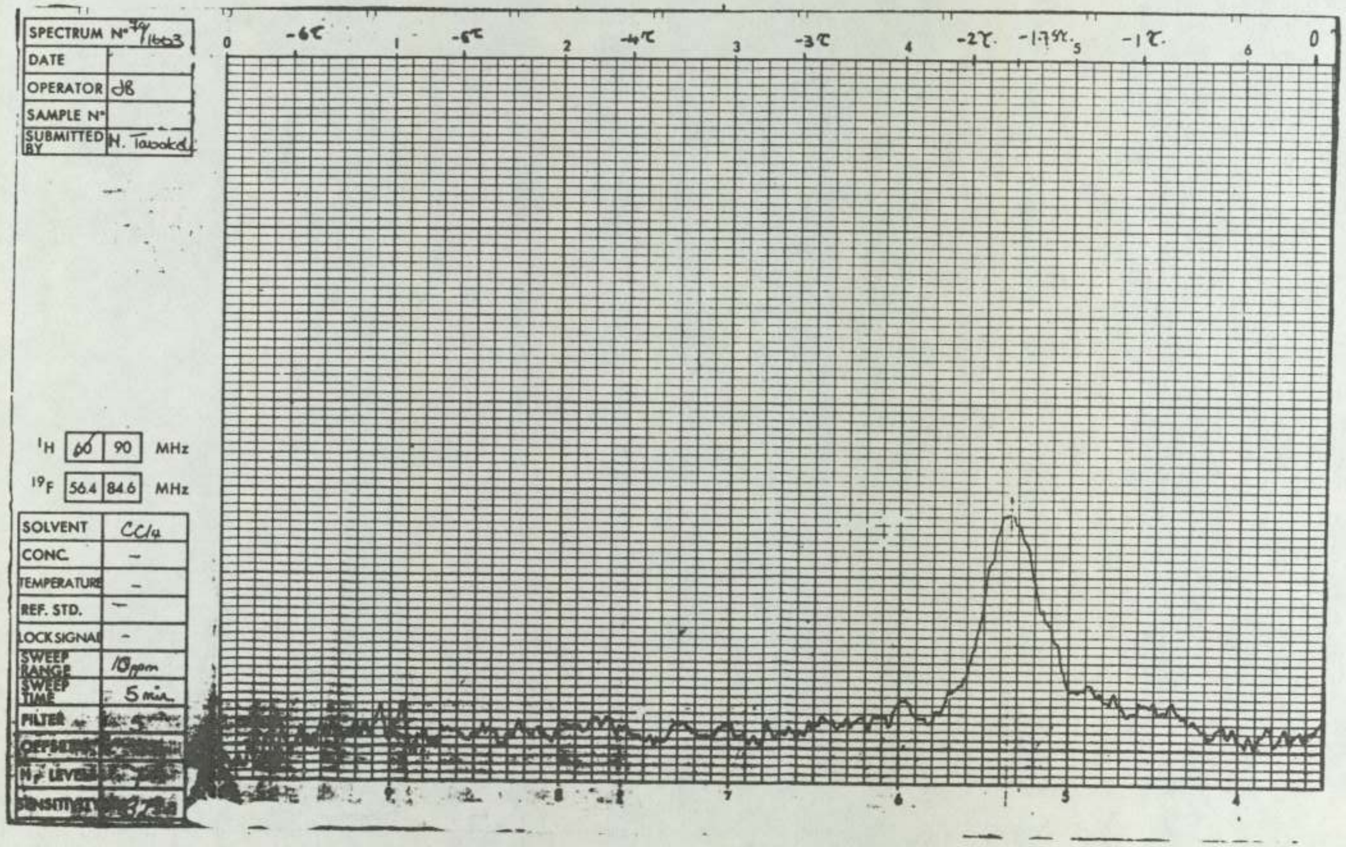
Fig. 3.1. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol

The flask was placed in an oil bath where the temperature was maintained at 115°C. To this mixture 5 ml of excess thioglycollic acid and 2-3 drops of concentrated sulphuric acid were added. The reaction was carried out for a period of 9 hours and then allowed to cool. The mixture was washed with water in order to remove any unreacted thioglycollic acid left. The solution was then dried in $MgSO_4$ and filtered. The organic layer was separated and toluene was removed on a rotatory evaporator. The product was recrystallised with n-hexane and dried. The melting point obtained was 99°C. This compound was identified by IR, NMR and elemental analysis. The IR and NMR spectra are shown in Figs. 3.2 and 3.3. respectively.

IR data	
Phenolic OH	3640 cm^{-1}
Acidic carbonyl	1700 cm^{-1}
Acidic hydroxyl	2540 and 2650 cm^{-1}
OH of carboxyl group	930 cm^{-1}

NMR data	τ	
Acidic proton	-1.75	(singlet)
Aromatic protons	2.9	(singlet)
Phenolic protons	5.	(singlet)
Methylenic protons ($-CH_2-S$)	6.29	(singlet)
Methylenic protons ($-CH_2-COOH$)	7	(singlet)
Tertiary butyl protons	8.6	(singlet)

Fig. 3.2. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-methyl sulphide (BTGA)



SPECTRUM N° 79/1663
DATE
OPERATOR JB
SAMPLE N°
SUBMITTED BY N. Tawakol

^{1}H	~~60~~	90	MHz
^{19}F	56.4	84.6	MHz

SOLVENT CCl_4
CONC. –
TEMPERATURE –
REF. STD. –
LOCK SIGNAL –
SWEEP RANGE 10 ppm
SWEEP TIME 5 min
FILTER [illegible]
OFFSET [illegible]
N_F LEVEL [illegible]
SENSITIVITY [illegible]

Fig. 3.3. NMR spectrum of 3,5 di-tert-butyl-4-hydroxybenzyl-carboxy-methyl sulphide (BTGA)

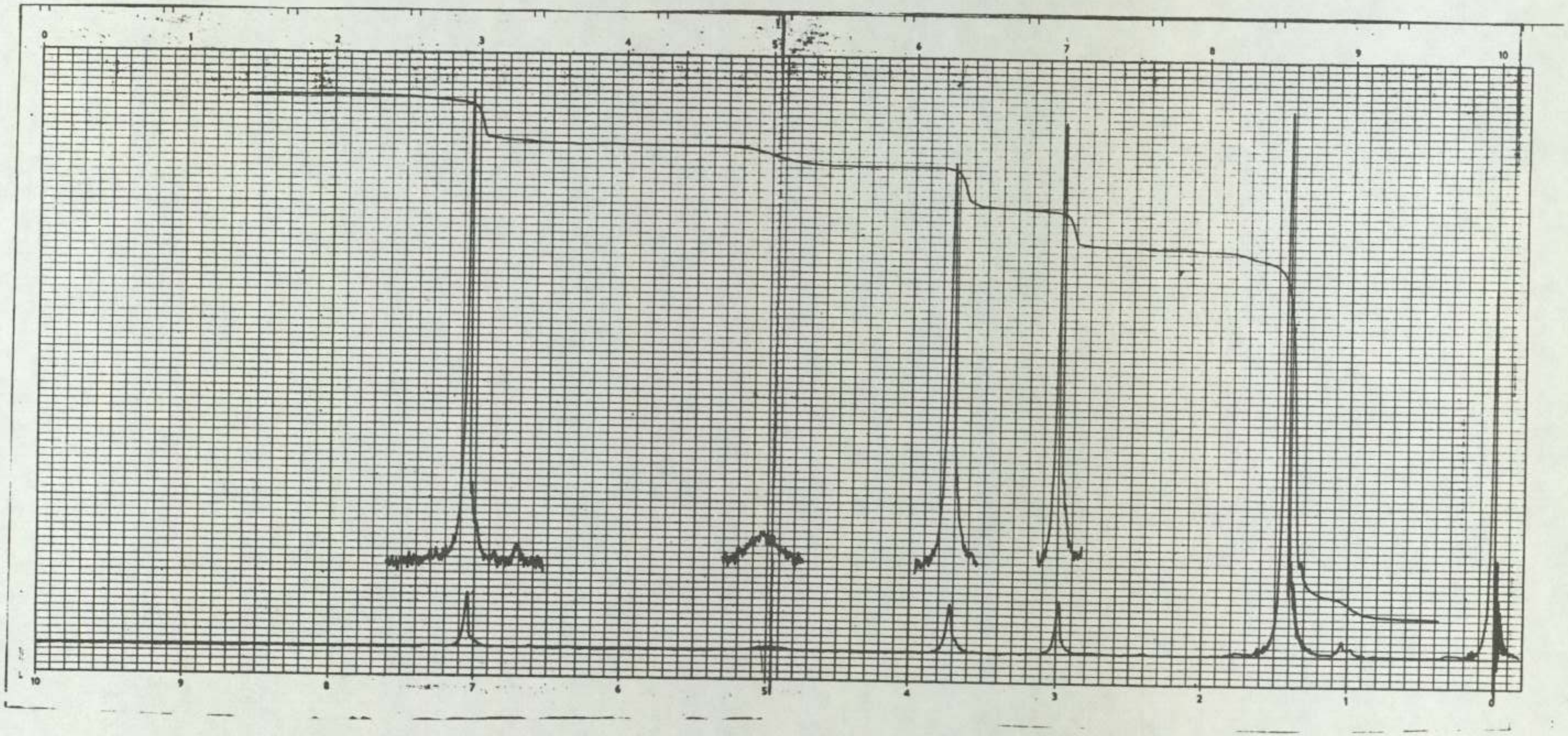


Fig. 3.3. continued.......

3.3. Preparation of 3,5-di-tertiary butyl-4-hydroxybenzyl-carboxyethyl sulphide (BTPA)

23.6 g of 3,5-ditertiarybutyl-4-hydroxybenzyl alcohol (0.1 moles) was dissolved in 250 ml of dry toluene and poured into a 500 ml three-necked round-bottomed flask equipped with a Dean and Stark apparatus. 0.15 moles (15.9g) of 3-mercaptopropionic acid was then added to this mixture. Three drops of sulphuric acid was also added and the flask was placed in an oil bath. The temperature was maintained at 115°C. The reaction was carried out for a period of 9 hours after which no further water could be collected in the side tube of the Dean and Stark apparatus. The mixture was allowed to cool and then washed with distilled water to remove any unreacted mercaptopropionic acid left. The solution was then dried in $MgSO_4$ and toluene removed on a rotatory evaporator. Recrystallisation was carried out in n-hexane and the white solid obtained had a melting point of 95-96°C. The product was characterised by elemental analysis, IR and NMR. The IR and NMR spectra are shown in Figs. 3.4 and 3.5. respectively.

IR data

Free phenolic OH	3600
Acidic hydroxyl	2540 and 2650 cm^{-1}
Acidic carbonyl	1700 cm^{-1}
OH of carboxyl group	930 cm^{-1}

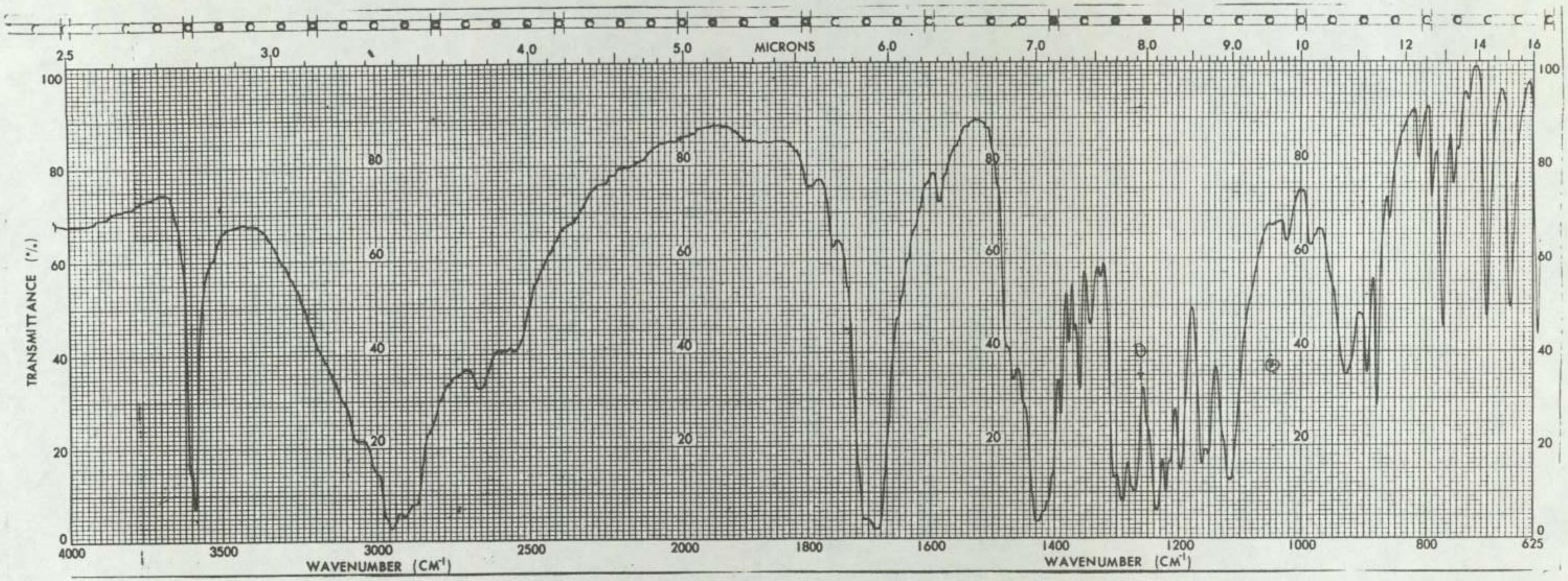


Fig. 3.4. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-ethyl sulphide (BTPA)

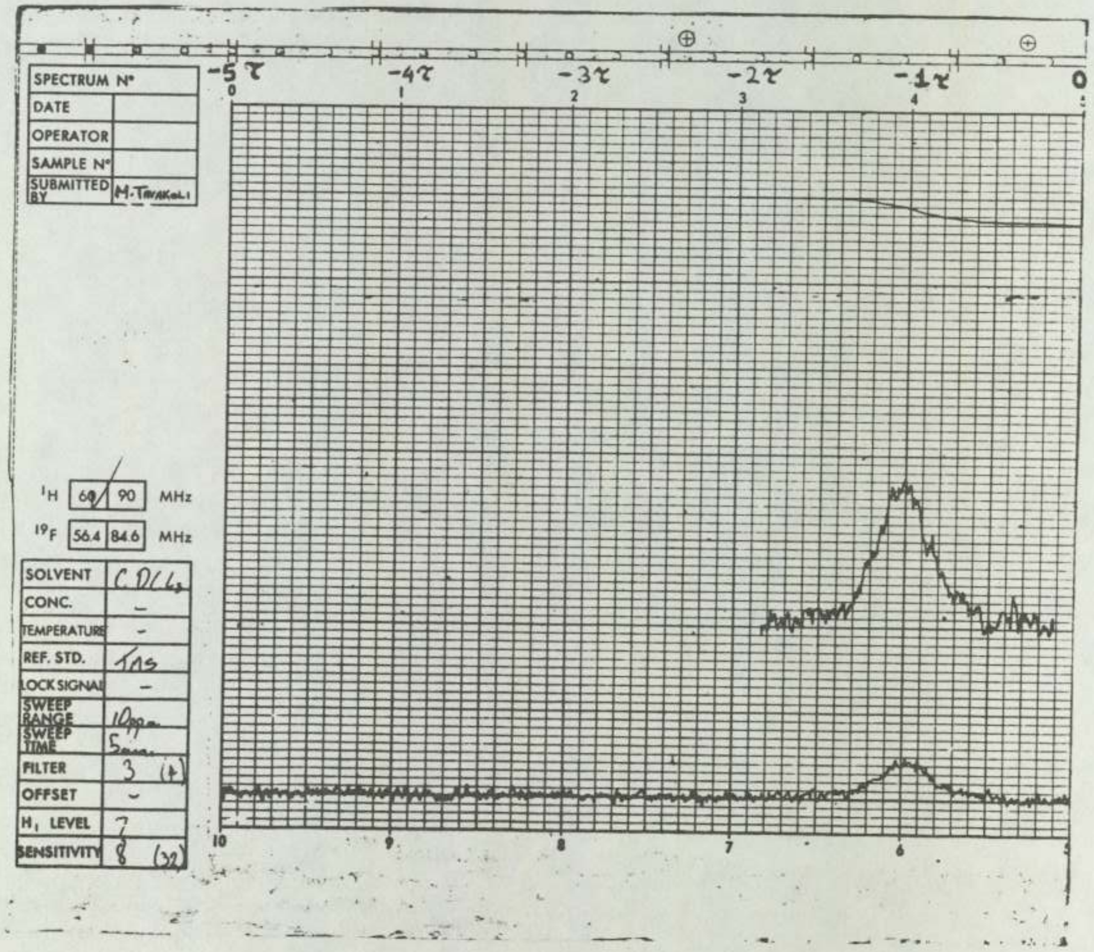


Fig. 3.5. NMR spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-ethyl sulphide (BTPA)

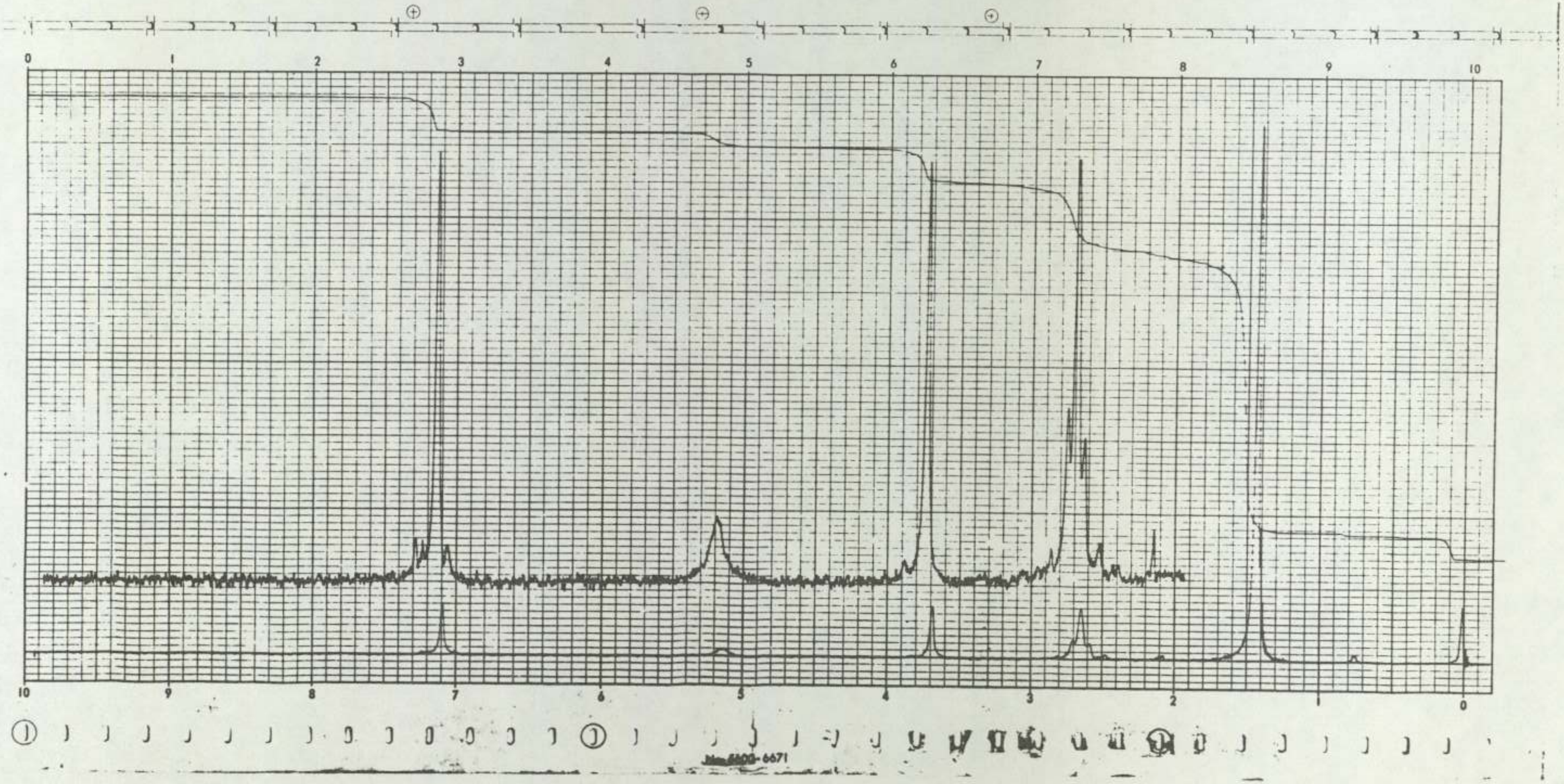
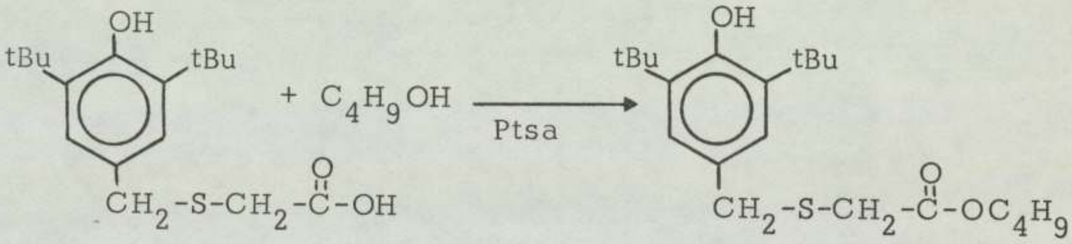


Fig. 3.5. continued.....

NMR data	τ	
Acidic protons	-1	(singlet)
Aromatic protons	2.85	(singlet)
Phenolic protons	4.81	(singlet)
Methylenic protons ($-CH_2-S$)	6.27	(singlet)
Methylenic protons ($-S-CH_2-CH_2$)	7.3	(triplet)
Tertiarybutyl protons	8.6	(singlet)

3.4. Preparation of 3,5-di-tertiary butyl-4-hydroxybenzyl-butylthioglycollate (BTBE)

This reaction was carried out according to the following scheme:(132)



2 g (0.06 moles) of 3,5-di-tertiary butyl-4-hydroxy benzyl-carboxy-methyl sulphide was dissolved in 50 ml of dried toluene. This solution poured into a 100 ml round-bottomed flask equipped with a Dean and Stark apparatus and a condenser to collect water formed during the esterification reaction. To this solution 4.05 g (0.05 moles) of dry butanol was added. Paratoluenesulphonic acid (Ptsa) was used as a catalyst (0.05 g). A slow stream of N_2 was bubbled through the reaction. After a period of 5 hours the reaction product was allowed to cool and washed with 500 ml of distilled water. The solution was dried over magnesium sulphate and toluene was removed on a rotatory evaporator. The light yellow solid obtained had a

melting point of 62-63°C. The infra-red spectrum of this compound is shown in Fig. 3.6.

IR data

Phenolic OH	3640 cm^{-1}
Ester carbonyl	1735 cm^{-1}

3.5. Preparation of 3,5-di-tertiarybutyl-4-hydroxybenzyl-mercapto glycollate (BTGE)

23.6 g of 3,5-di-tertiary-4-hydroxybenzyl alcohol (0.10 moles) in 200 ml of dry toluene. 9.3 g (0.10 moles) of thioglycollic acid was added to the above solution in a 500 ml round-bottomed flask. The flask was equipped with a Dean and Stark apparatus and a condenser in order to remove water formed during the reaction. The flask was immersed in an oil bath. The reaction mixture was refluxed for a period of 12 hours while stirring. A slow stream of nitrogen was passed through the reaction in order to inhibit oxidation of the product formed. At the end of the above period the reaction was stopped and allowed to cool. The solution was repeatedly washed with 1.5 litre of distilled water while shaking in order to remove any unreacted thioglycollic acid left. The mixture was then dried in $MgSO_4$ and toluene removed on a rotatory evaporator. The white greasy solid obtained was dissolved in dry-cold n-hexane. The thiol compound was soluble in hexane but the unreacted 3,5-di-tert-butyl-4-hydroxybenzyl alcohol precipitated. The hexane solution was filtered and the solvent was removed on a rotatory evaporator. The white viscous

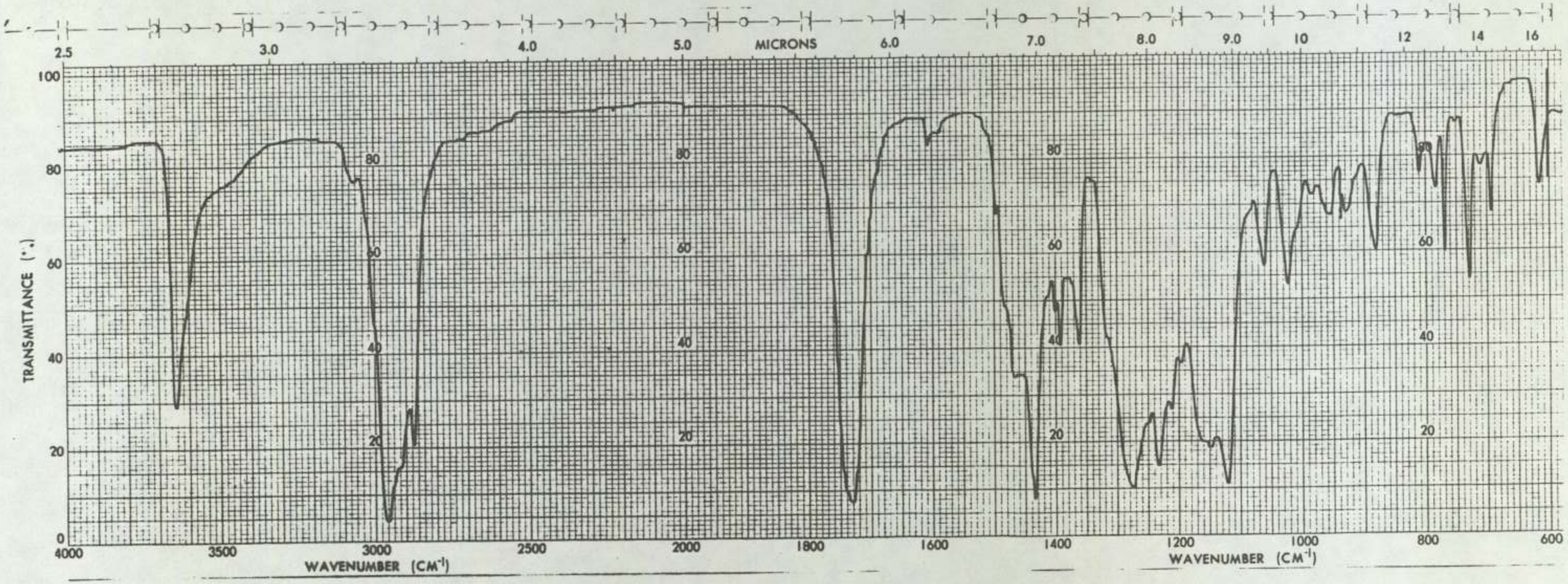


Fig. 3.6. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl-butyl thioglycollate (BTBE)

oily compound obtained was analysed by iodine titration, IR and elemental analysis. The infra-red spectrum of this compound is shown in Fig. 3.7. yield 40%.

IR data

Phenolic OH	3615 cm^{-1}
-SH group	2560 cm^{-1}
Ester carbonyl	1730 cm^{-1}

3.6. Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl-mercapto propionate

11.8 g of 3,5-di-tertiarybutyl-4-hydroxybenzyl alcohol (0.005 moles) was dissolved in 200 ml of dry toluene and poured into a 500 ml round-bottomed flask connected to a Dean and Stark apparatus and water cooled condenser. 5.3 g (0.05 moles) of mercaptopropionic acid (0.05 moles) was then added to the flask. The mixture was heated to reflux for a period of 11 hours while stirring. A slow stream of nitrogen was passed through during the reaction. At the end of 11 hours the mixture was allowed to cool and then frequently washed with approximately one litre of distilled water. The organic phase was separated and dried over $MgSO_4$. After removal of solvent the white greasy solid obtained was dissolved in n-hexane where unreacted alcohol was precipitated. After filtration, hexane was removed on a rotatory evaporator and a white waxy solid obtained which was identified by IR and iodine test. The yield of this reaction was very low (approximately 20%). The infra-red spectrum

Fig. 3.7. Infra-red spectrum of 3,5 di-tert-butyl-4-hydroxybenzyl-mercaptoglycollate (BTGE)

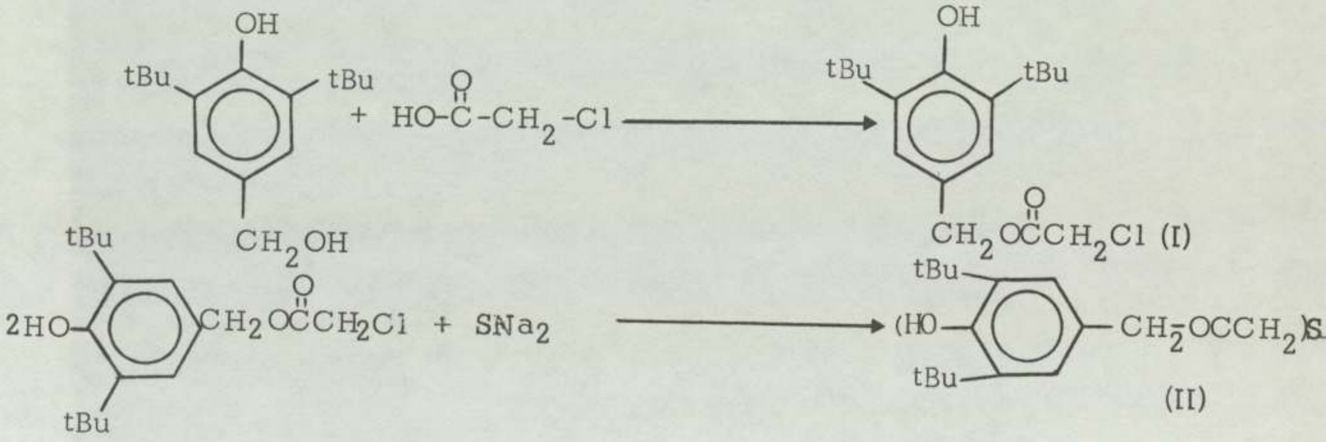
is shown in Fig. 3.8.

IR data

Phenolic OH	3600 cm^{-1}
-SH group	2565 cm^{-1}
Ester carbonyl	1730 cm^{-1}

3.7. Preparation of Bis(3,5-di-tert-butyl-4-hydroxybenzyl-methyl acetate) monosulphide

The preparation of BTGE monosulphide was carried out according to the following two steps scheme :



3.7.1. Synthesis of 3,5-di-tert-butyl-4-hydroxybenzyl monochloro acetate (I)

23.6 g of 3,5-di-tertbutyl-4-hydroxybenzyl alcohol (0.1 moles) and 14.2 g (0.15 moles) of monochloroacetic acid were separately dissolved in toluene and poured into a three-necked round-bottomed flask. A Dean and Stark apparatus was placed between the flask and the condenser to collect water formed in the reaction. The mixture was then refluxed

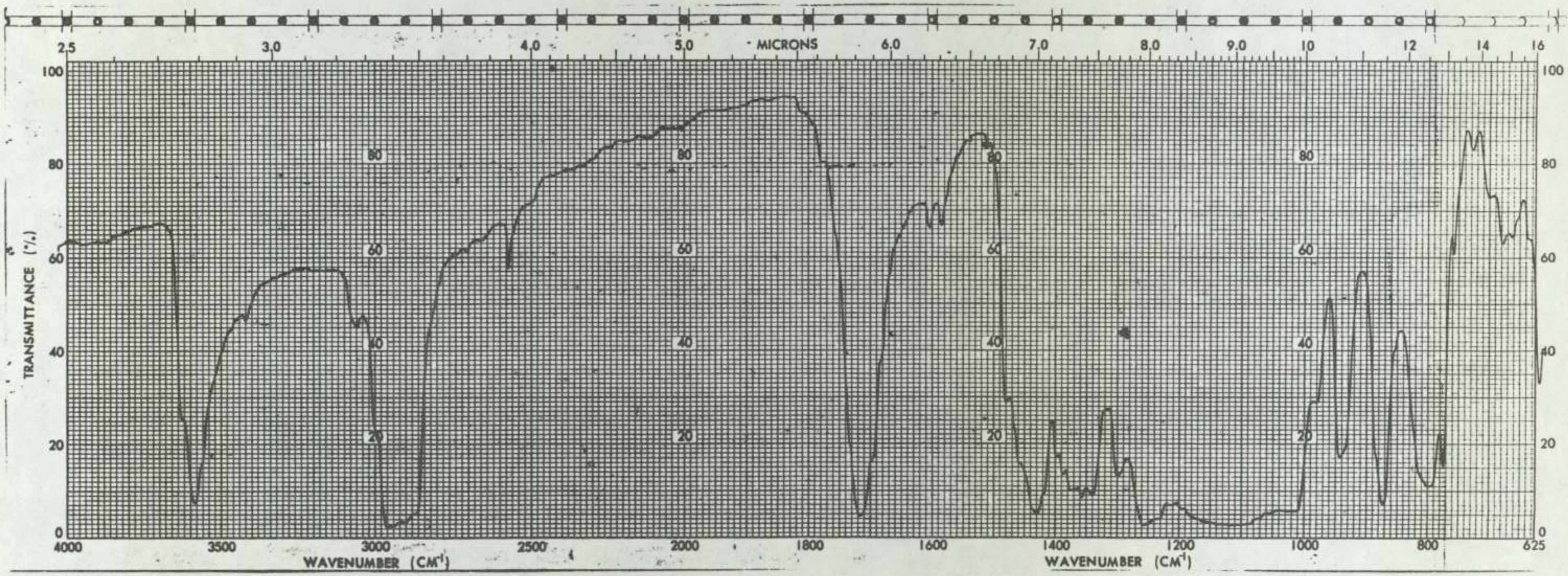


Fig. 3.8. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl-mercaptopropionate (BTPE)

for a period of 8 hours under a slow stream of nitrogen. After this period the mixture was allowed to cool and then washed with dilute sodium bicarbonate solution followed by distilled water. The organic phase was separated and dried over magesium sulphate. The solvent was evaporated on a rotatory evaporator and the orange waxy product obtained was characterised by elemental analysis and infra-red spectroscopy. The infrared spectrum is shown in Fig. 3.9.

IR data

Phenolic OH	3640 cm^{-1}
Ester carbonyl	1760 cm^{-1}

3.7.2. Preparation of Bis(3,5-di-tert-butyl-4-hydroxybenzyl-methyl-acetate) monosulphide (II)

3.1.g of 3,5-di-tert-butyl-4-hydroxybenzyl monochloroacetate (0.01 moles) was dissolved in 40 ml of isopropanol and poured into a round-bottomed flask equipped with a heater, thermometer, water cooled condenser and stirrer. 0.96 g of (0.012 moles) sodium sulphide was dissolved in 5 ml of water and added to the flask. The mixture was refluxed for a period of four hours under nitrogen. After this period the mixture was allowed to cool and diluted with toluene. The organic phase was washed with distilled water and dried over $MgSO_4$. The solvent removed on a rotatory evaporator and a brown waxy compound obtained was analysed by elemental analysis and infra-red spectroscopy. The infra-red spectrum is shown in Fig. 3.10.

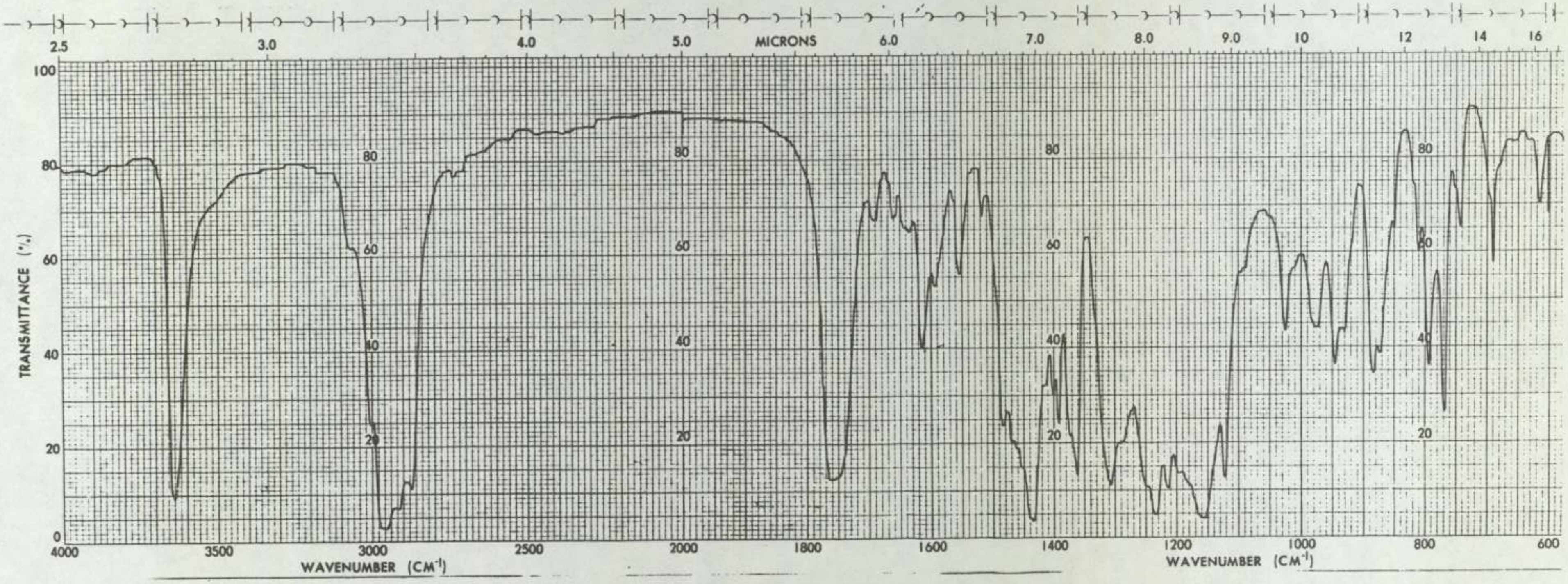


Fig. 3.9. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl monochloro acetate

Fig. 3.10. Infra-red spectrum of bis(3,5-di-tert-butyl-4-hydroxybenzyl-methyl-acetate)monosulphide

However, characterisation by elemental analysis showed that there were some impurities present and hence, further purification of this compound is recommended.

IR data

Phenolic OH	3640 cm^{-1}
Ester carbonyl	1735 cm^{-1}
$-CH_2-S$	1440

3.8. Preparation of Bis (3,5-di-tert – butyl-4-hydroxybenzyl-methyl acetate) disulphide (135)

2 g of 3,5-di-tert-butyl-4-hydroxybenzyl thioglycollic ester (0.006 moles) was dissolved in 10 ml of benzene, poured into a round-bottomed flask, and 2.5 ml of water was added. 1.6 g of iodine (0.013 moles) was separately dissolved in 10 ml of benzene and 2.5 ml of ethanol. The solution of thiolester was stirred vigorously and the iodine solution was added slowly through a dropping funnel. The addition of iodine solution was stopped when the solution turned to slight yellow. The mixture was then washed with distilled water. The organic layer was separated, dried over magnesium sulphate and solvent was removed on a rotatory evaporator. The white waxy product obtained was elemental

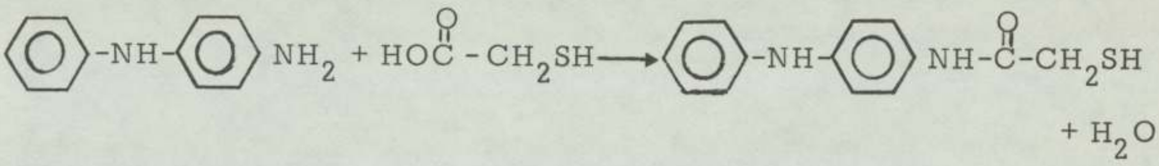
analysed and its infra-red spectra is shown in Fig. 3.11.

<u>IR data</u>

Phenolic OH	3615 cm^{-1}
Ester carbonyl	1730 cm^{-1}

3.9. Preparation of 4-mercaptoacetamidodiphenylamine (MADPA)

The preparation of 4-mercaptoacetamidodiphenylamine was carried out according to the following scheme : (133)



The starting materials, p-amidodiphenylamine and thioglycollic acid were obtained from Aldrich Chemicals and used without further purification. 18.4 g (0.10 moles) of p-aminodiphenylamine poured into a 500 ml round-bottomed flask and 300 ml of xylene was added. The flask was vigorously shaken until all the amine was dissolved. 13.8 g (0.15 moles) of thioglycollic acid was then added to this solution. The excess of thioglycollic acid was used in order to shift the reaction to the right in the above scheme. The flask was fitted with a Dean and Stark apparatus and a water cooled condenser. A slow stream of nitrogen was bubbled through during the reaction. The mixture was heated in an oil bath in order to reach the refluxing temperature. The reaction was carried out for a period of 10 hours while stirring. At the end of this period the flask was

Fig. 3.11. Infra-red spectrum of bis(3,5-di-tert-butyl-4-hydroxybenzyl-methyl acetate) disulphide

allowed to cool, the mixture was diluted with n-hexane and left to stand for 24 hours under nitrogen. The mixture was filtered, the precipitate was washed with dilute sodium bicarbonate solution followed by distilled water, and dried. The product obtained was recrystallised from a mixture of toluene and methanol (4/1 V/V) resulting in a white needle crystals. The white solid product melted at 131-133°C (135-136°C(133)) and was characterised by elemental analysis, IR and NMR yield = 70%. The infrared spectrum of this compound is shown in Fig. 3.12.

IR data

Secondary -NH	3360 cm^{-1}
Secondary amide-NH	3260 cm^{-1}
-SH group	2515 cm^{-1}
Secondary amid C=O	1650 cm^{-1}

NMR data	τ	
Secondary amide -NH	1.5	(singlet)
Aromatic protons	2.4-3.3	(multiplet))
Secondary amine	4.5	(singlet)
Methylenic protons	6.8	(doublet)
Thiol proton	7.8-9.2	(triplet)

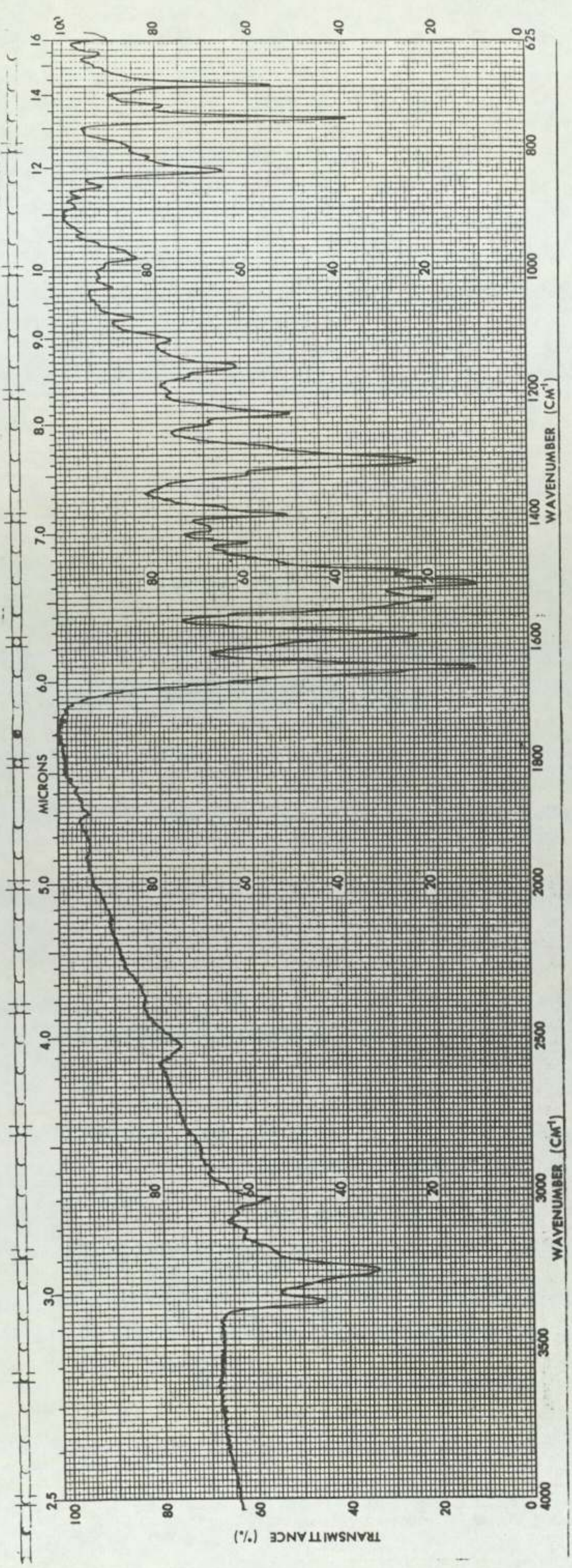
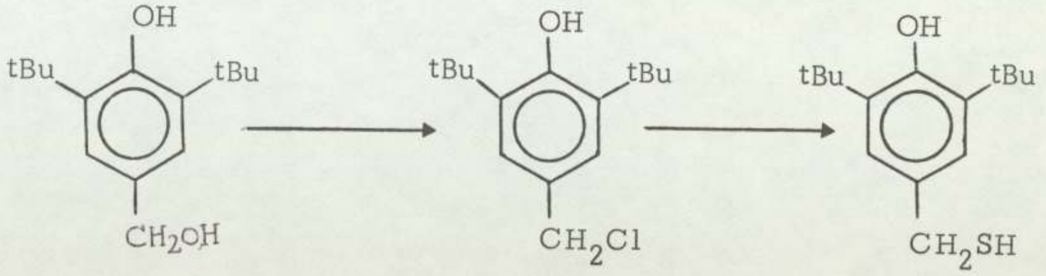


Fig. 3.12. Infra-red spectrum of 4-mercaptoacetamidodiphenylamine (MADPA)

3.10 Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan(BHBM)

This compound was prepared according to the following scheme(134):



3.10.1 Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl chloride (132,135)

20 g of 3,5-di-tertiarybutyl-4-hydroxybenzyl alcohol was stirred at room temperature in 100 ml of toluene (slurry). 27.2 ml of 30% HCl was then added to this solution and the mixture was stirred for a period of 3½ hours at 25°C. During this period the 3,5-di-tertiarybutyl-4-hydroxybenzyl alcohol gradually went into the solution and reacted with hydrogen chloride. Reaction was completed by warming the mixture to 45°C and stirring for a further 90 minutes. The stirring was then stopped and two layers were formed. The organic layer was separated from water layer using a separating funnel. The organic layer was repeatedly washed with distilled water until reaching neutrality. The solution was then dried in $CaCl_2$ and toluene removed on a rotatory evaporator. The resulting product was oily and reddish-orange which was further purified by vacuum distillation at reduced pressure (0.5-1 mmHg) and at 129-133°C. The infra-red spectrum of this compound is shown in Fig. 3.13.

IR data

Phenolic OH	3620 cm^{-1}

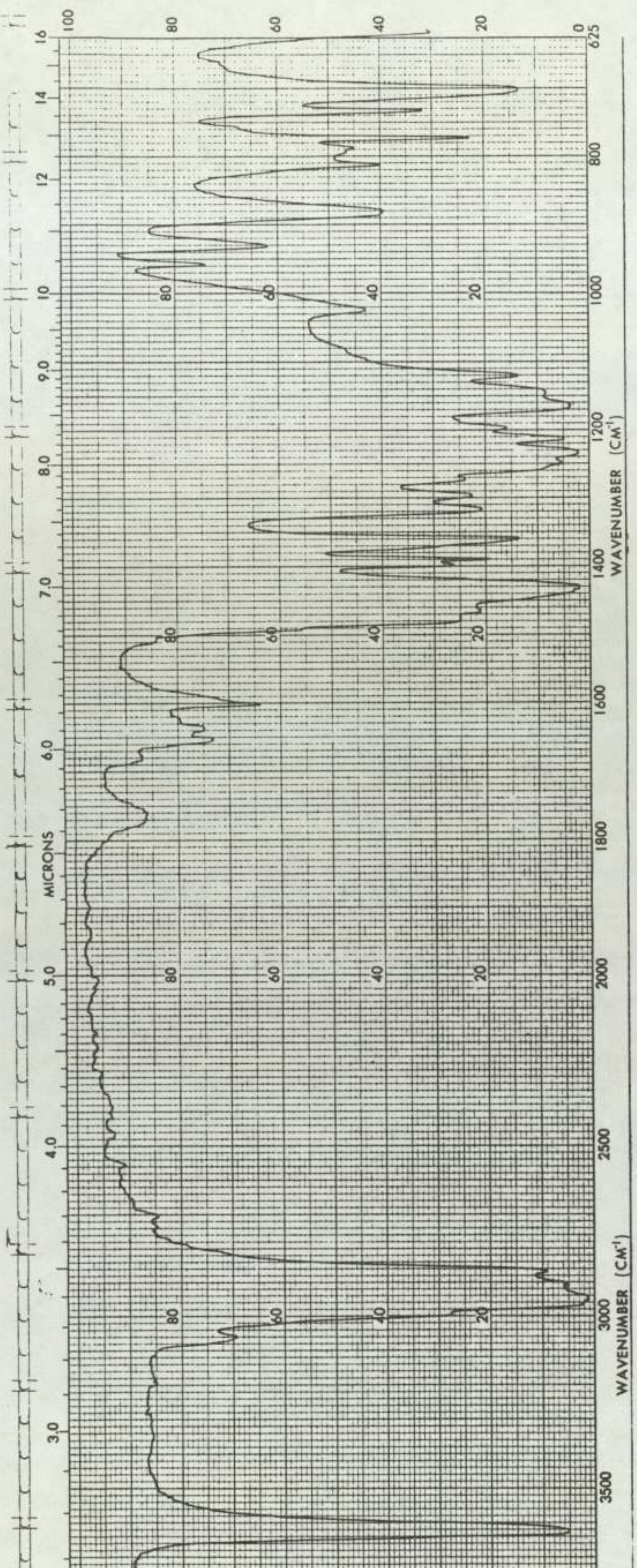


Fig. 3.13. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl chloride

IR data (continued)

Tertiarybutyl group	1360 cm^{-1} and 1390 cm^{-1}
Carbon-chlorine	700 cm^{-1}

NMR data	τ	
Aromatic protons	2.9	(singlet)
Hydroxyl protons	5	(singlet)
Methylenic protons $-CH_2-Cl$	6.35	(singlet)
Tertiarybutyl protons	8.6	(singlet)

3.10.2. Reaction of 3,5-di-tert-butyl-4-hydroxybenzyl chloride and hydrogen sulphide (134)

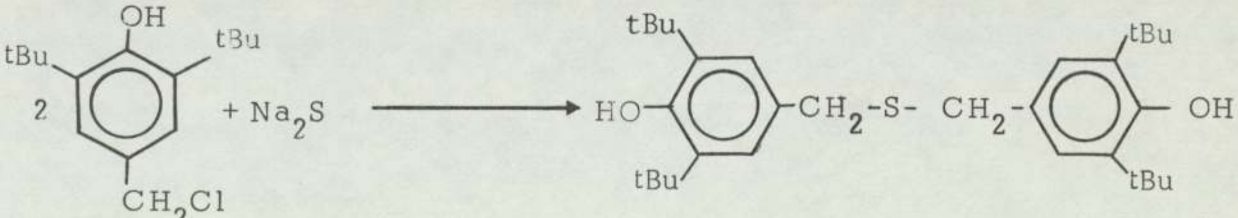
5.8 g of magnesium hydroxide powder was poured into a 500 ml round-bottomed flask and 200 ml of N,N-di-methyl formamide was added. The mixture was stirred using a magnetic stirrer. 22.5 g of 3,5-di-tertiary-butyl-4-hydroxybenzyl chloride was dissolved in 50 ml of hexane and added dropwise to the mixture. The addition was carried out in such a way that not to allow the reaction mixture to turn bright yellow in order to prevent the formation of yellow-coloured sulphides. The reaction mixture was allowed to stand for a further one and a half hours while stirring and was then added to an ice-water mixture. The organic layer was separated by ether extraction and dried over magnesium sulphate. The solvent was removed on a rotatory evaporator. The product was vacuum distilled at 128-130°C and at approximately 0.5 mm pressure. The 3,5-di-tertiarybutyl-4-hydroxybenzyl mercaptan was obtained as a white liquid which after solidifying melted at 27-28°C (28°C (134)). The infra-red spectrum of this product is given in Fig. 3.14.

IR data	
Phenolic OH	3640 cm^{-1}
-SH group	2550 cm^{-1}

NMR data	τ	
Aromatic protons	2.95	(singlet)
Phenolic protons	5	(singlet)
Methylenic protons	6.3	(doublet)
Tertiarybutyl protons	8.6	(singlet)

3.11 Preparation of Bis (3,5-di-tertbutyl-4-hydroxybenzyl) monosulphide

The preparation of bis(3,5-di-tertbutyl-4-hydroxybenzyl) monosulphide was carried out according to the following scheme (135) :



The starting material, 3,5-di-tertbutyl-4-hydroxybenzyl chloride was prepared as described in Section 3.10.1. In a 50 ml round-bottomed flask equipped

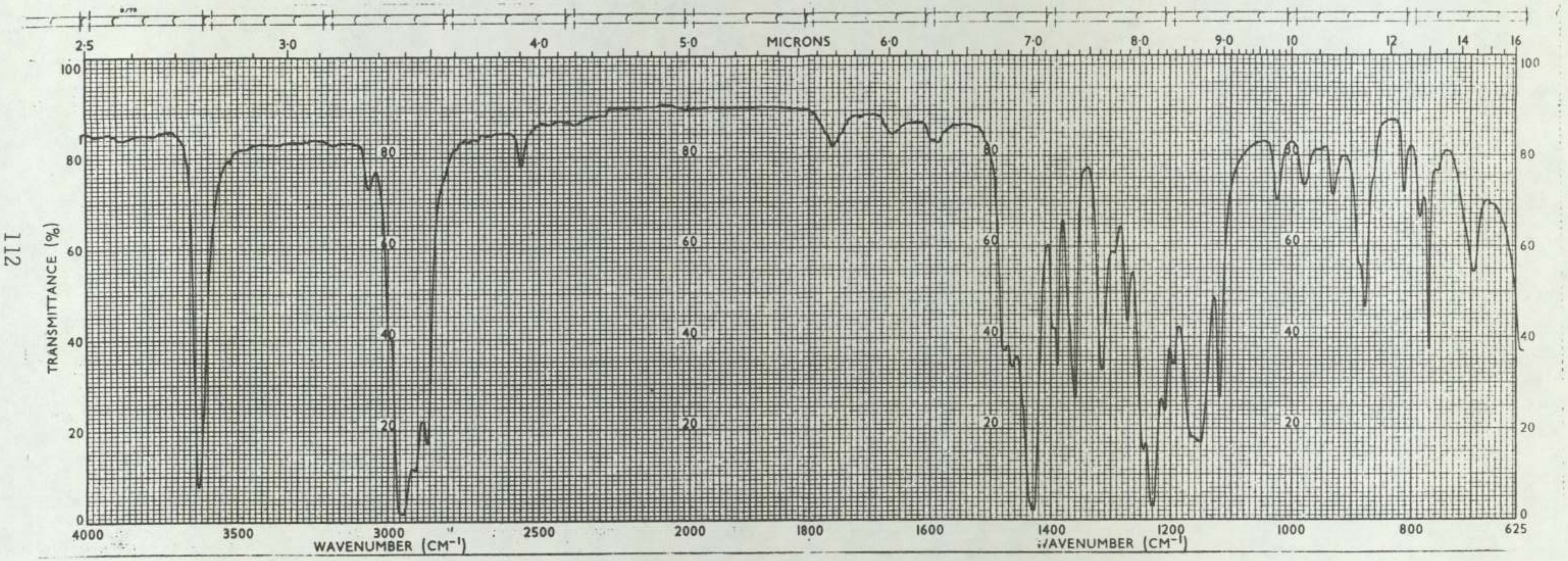


Fig. 3.14. Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM)

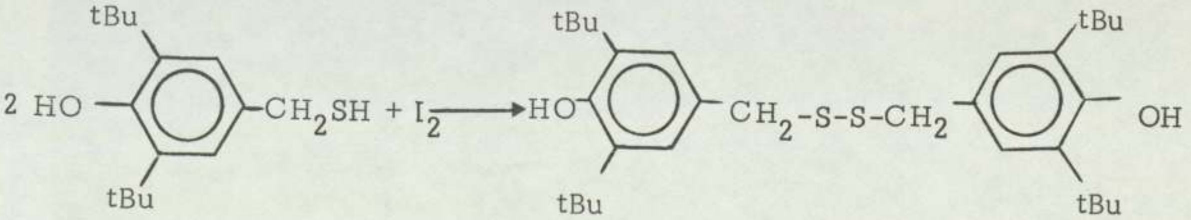
with a heater, thermometer, water cooled condenser and a stirrer, a mixture of 3.84 g (0.05 moles) of sodium sulphide in 3 ml of water, 24 ml of iso-propyl alcohol and 10 g (0.04 moles) of di-tert-butyl-4-hydroxybenzyl chloride was refluxed for a period of two hours. The mixture was allowed to cool and left for two days and then filtered. The precipitate was washed with distilled water and dried under vacuum. The yellow solid was recrystallised with a mixture of iso-octane and methanol and dried. The product melted at 139-141°C (143°C (135)) and the infra-red spectrum is shown in Fig. 3.15.

IR data

Phenolic OH	3640 cm^{-1}
Tertiarybutyl groups	1320 cm^{-1} and 1360 cm^{-1}
Tetrasubstituted benzene ring	880 cm^{-1}

3.12 Preparation of Bis (3,5-di-tert-butyl-4-hydroxybenzyl)disulphide (134)

The 3,5-di-tert-4-hydroxybenzylmercaptan prepared as described earlier was used as the starting material :



To a vigorously stirred mixture containing 2 g (0.008 moles) of 3,5-di-tert-butyl-4-hydroxybenzylmercaptan 30 ml of benzene and 7.5 ml of water,

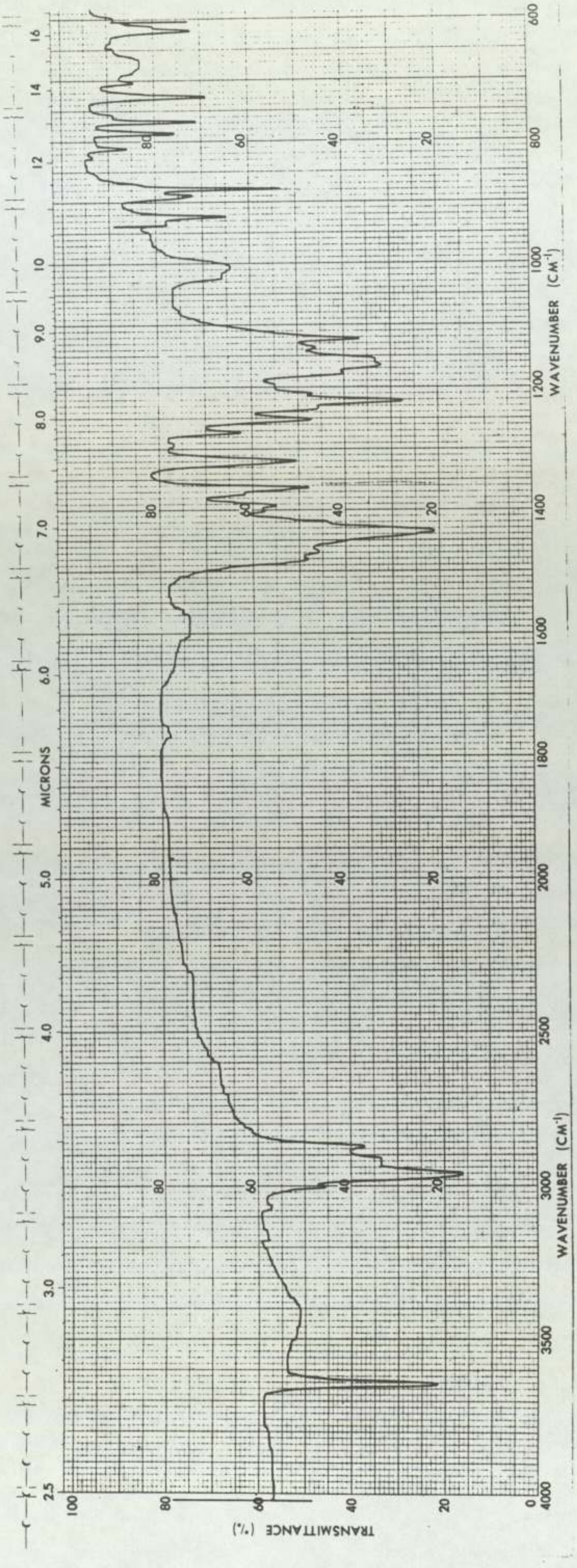


Fig. 3.15. Infra-red spectrum of bis(3,5-di-tert-butyl-4-hydroxybenzyl) monosulphide

a solution of 2.1 g of iodine in 10 ml of benzene and 2.5 ml of ethanol was slowly added through a dropping funnel. When the thiol solution showed a trace of iodine colour the stirring and the addition of the iodine were stopped. The organic layer was then separated, dried over magnesium sulphate and the benzene was removed on a rotatory evaporator. The disulphide was recrystallised from a solution of petroleum ether-benzene. The white crystals obtained had a melting point of 165-166°C. (167-168°C (134)). The infra-red spectrum of the bis(3,5-di-tert-butyl-4-hydroxybenzyl) disulphide is shown in Fig. 3.16.

IR data

Phenolic OH	3600 cm^{-1}
Tertiarybutyl groups	1310 cm^{-1} and 1360 cm^{-1}
Tetra substituted benzene ring	870 cm^{-1}

3.13 Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-methyl sulphoxide

The procedure used in this preparation was the method applied by Barnard et al.,(136) and Armstrong (35). 4 g (0.012 moles) of 3,5-di-tertiary-butyl-4-hydroxybenzyl-carboxy methyl sulphide was dissolved in 20 ml of AR grade acetone (15.6 g) and poured into a 50 ml round-bottomed flask. The flask was placed in an ice bath and cooled to 0°C. 3 ml of 30% hydrogen peroxide was then added dropwise over a period of four hours while stirring. The mixture was then left at room temperature for 48 hours.

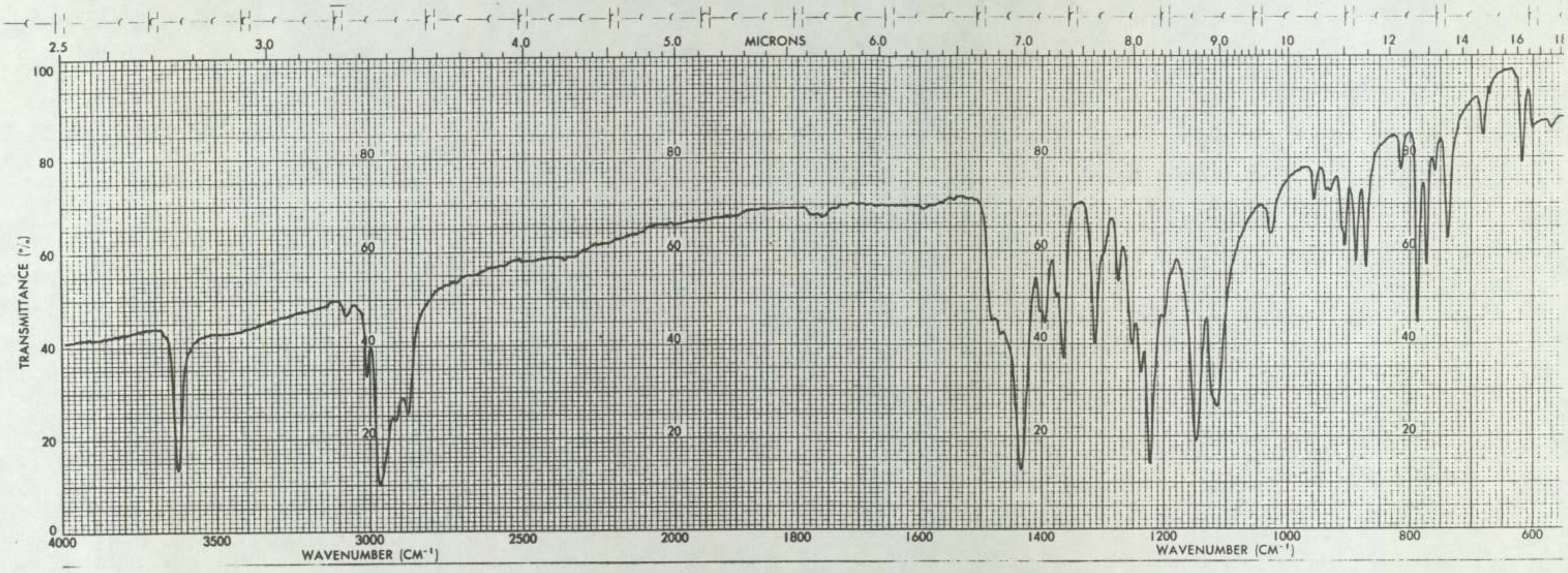


Fig. 3.16. Infra-red spectrum of bis(3,5-di-tert-butyl-4-hydroxybenzyl) disulphide

Acetone was removed on a rotatory evaporator. The white solid obtained was recrystallised from benzene and dried under vacuum. The product melted at 132-133°C, yield 84%. The compound was characterised by elemental analysis and infra-red spectroscopy. The infra-red spectrum is shown in Fig. 3.17.

<u>IR data</u>

Phenolic OH	3510 cm^{-1}
Acidic carbonyl	1720 cm^{-1}
Acidic hydroxyl	2520 and 2600 cm^{-1}
Sulphoxide group	1000 cm^{-1}

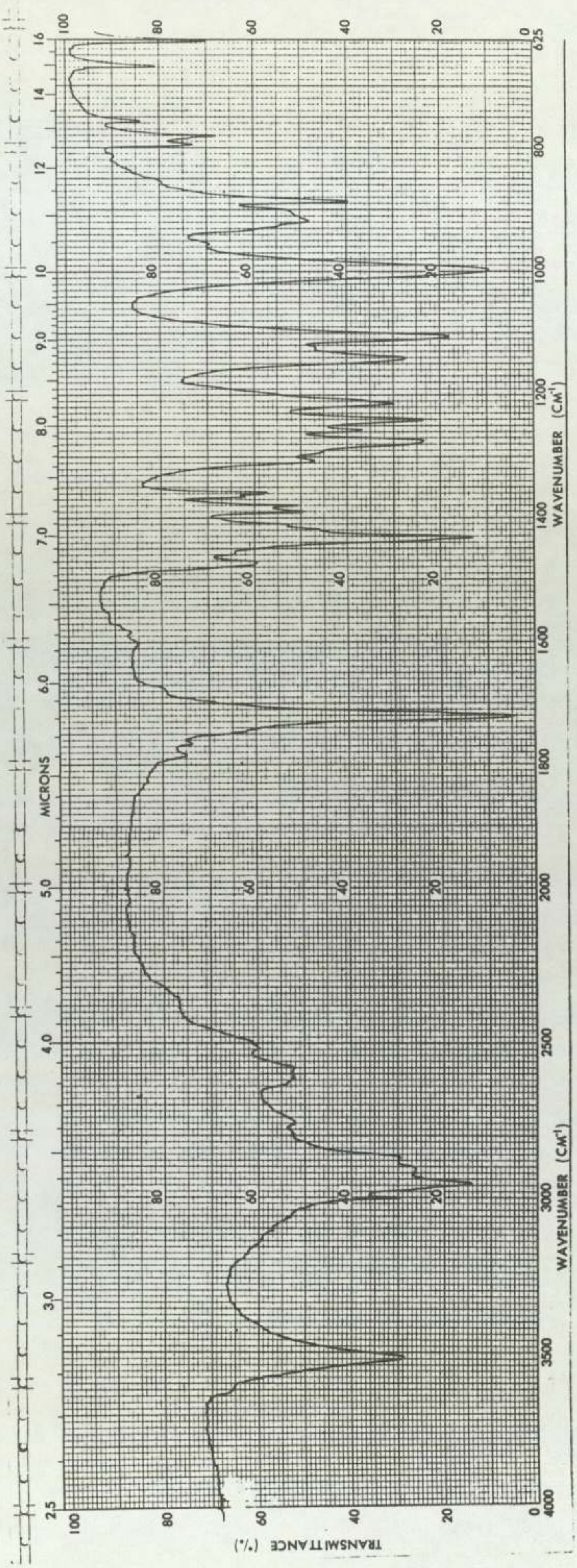


Fig. 3.17. Infra-red spectrum of 3,5 di-tert-butyl-4-hydroxybenzyl-carboxy methyl sulphoxide

CHAPTER FOUR

REACTION OF ANTIOXIDANTS WITH NATURAL RUBBER LATEX

4.1. Introduction

Natural rubber latex is basically a three-phase system; the rubber particles, which account for some 35% of the latex by weight; the aqueous phase, which is approximately 55% by weight of the whole, and the lutoid phase which accounts for most of the remaining 10%. Rubber particles are normally less than 5 μ in diameter, the molecules of which are polymeric in nature. Grafting of antioxidants to natural rubber latex has been extensively studied by Scott and(97,100,101) co-workers who have shown that hindered phenols containing vinyl and thiol groups can be bound to natural rubber using a suitable initiator. The same investigators have also shown that many antioxidants which do not contain the above groups can also be grafted to rubber in the latex form. Typical examples of this type of antioxidant are 2,6,-di-tertiarybutyl-4-methyl phenol (TBC) and 3,5-di-tertiarybutyl-4-hydroxybenzyl mercaptan (BHBM). The purpose of this work is to study the reactions of some of the sulphur and thiol-containing antioxidants with natural rubber in latex form using tertiarybutyl-hydroperoxide (TBH) and tetra-ethylene penta-mine (TEPA) as initiators.

4.1.1. Preparation of Dispersion

Dispersions of solid antioxidants were prepared in a Syegvari attritor under a nitrogen atmosphere. This apparatus consists of a cylindrical container half full of small solid glass balls (Ballotini) of 4 mm in diameter. The speed of the metal stirrer can be varied (see Fig. 4.1). The solid antioxidant was in the form of a fine powder. 10 g of powdered antioxidant was poured into the container and 0.2 g of Dispersol LN was then added; distilled water was added until the balls were just covered. A constant speed of stirring was selected and the dispersion was carried out for a period of 14 hours under the atmosphere of nitrogen. During this period the temperature of the container was kept low by passing cold water through the outlet. After grinding, the dispersion was discharged into a flask and the balls were washed with distilled water until the washings became clear. The antioxidant dispersion was kept under a nitrogen atmosphere in a refrigerator.

4.1.2. Preparation of Emulsion

Antioxidant to be emulsified (2 g) was first dissolved in 10 ml of hexane. 0.42 g of lauric acid and 0.08 g of potassium hydroxide were also dissolved in 40 ml of distilled water. These two solutions were added together in a conical flask. The air was removed from the flask by passing nitrogen through. The flask was stopped tightly and then vigorously shaken for a period of 18 hours.

4.2. Determination of Some of the Variables in the Reaction of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy-methyl sulphide (BTGA) with Natural Rubber Latex

4.2.1. Effect of Swelling Time

Three experiments were carried out in order to assess the effect

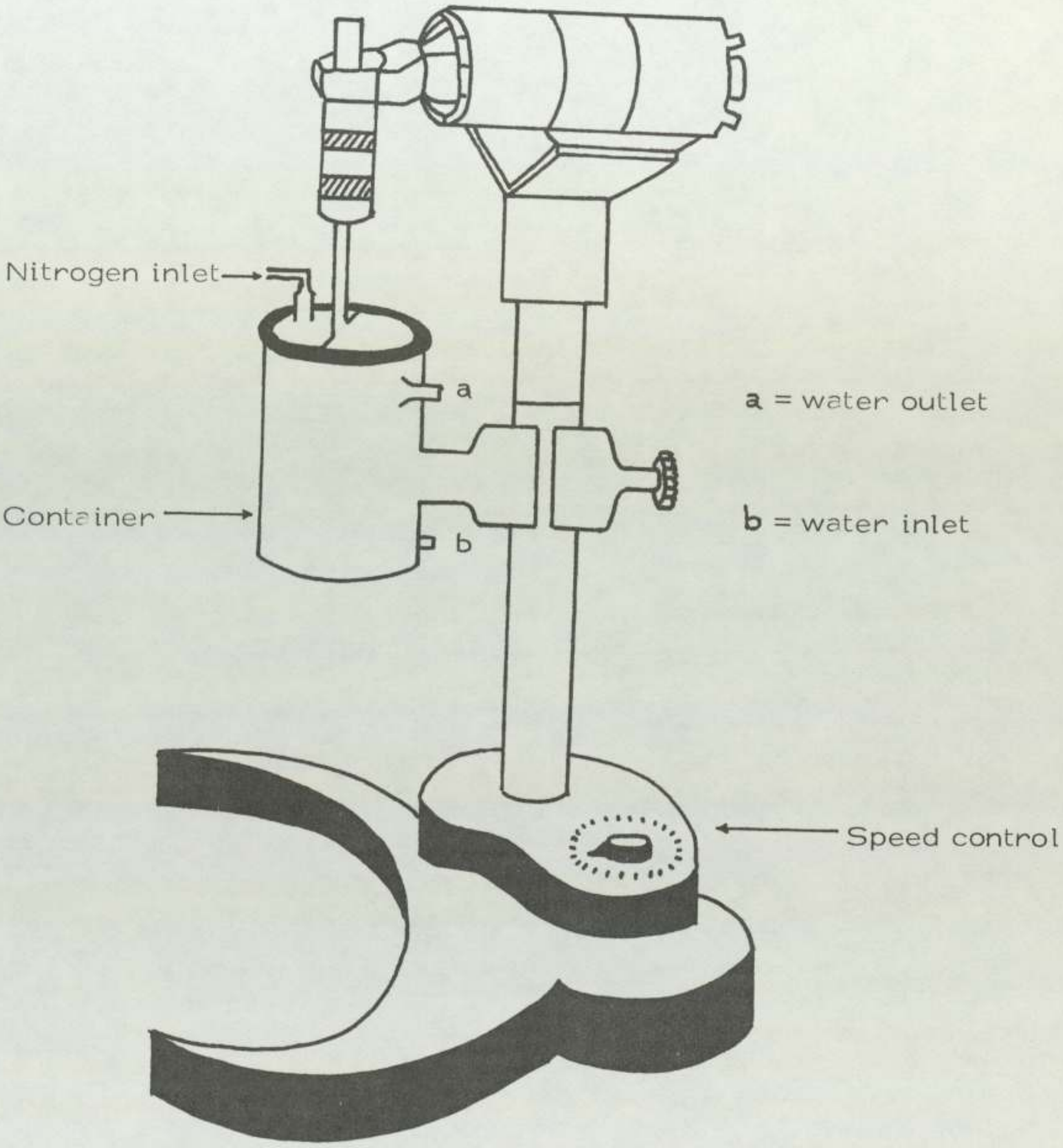


Fig. 4.1. Zigvaree Attritor used to prepare dispersion of solid antioxidants.

of swelling time on the reaction of BTGA with natural rubber latex. The reactions were done in a five necked round-bottomed flask fitted with a stirrer and a thermometer. To maintain the reaction at 60°C the flask was immersed in a thermostatically controlled water bath. Diluted NR latex (30%) was first deammoniated using white spot nitrogen to pH=8-8.5. Nitrogen was also bubbled through during the reaction to prevent any oxidation. The deammoniated latex was poured into the flask while stirring. The BTGA dispersion was then added and allowed to swell for a known period of time before adding the initiator system. The initiators (TBH/TEPA) were added during the first half of the reaction. The other variables were kept constant as follows :

Reaction time	7 hours
TBH	1.5 ml (of 70%)
TEPA	4.5 ml (of 10%)
NR latex	100 g Dry Rubber Content (D.R.C)
Reaction temperature	60°C
BTGA	2 g (0.006 moles)/100 g NR

After the reaction the flask was allowed to cool and the rubber was coagulated with 1% formic acid. The coagulum obtained was washed with distilled water and dried in a vacuum oven at 25°C. The dried rubber was sheeted out and washed further with distilled water to remove any acid left. The dried rubber was extracted with the azeotropic mixture and dried again (see Section 2.2). The vulcanisates were prepared and the amount of bound antioxidant was determined using the calibration curve given in Fig. 2.1. The results are given in the following Table.

TABLE 4.1

Swelling Time	BTGA bound		
(h)	g/100 g NR	moles/100 g NR	% bound
15	0.3	9.7×10^{-4}	15
30	0.7	2.3×10^{-3}	35
45	0.68	2.2×10^{-3}	34

As it can be seen in the above Table the yield of bound-BTGA with NR reaches to a maximum after 30 minutes swelling.

4.2.2. Effect of pH

Three grafting reactions were carried out at various pH conditions in order to evaluate the effect of pH on the reaction of 3,5-di-tertiary-butyl-4-hydroxybenzyl-carboxy-methyl sulphide (BTGA) with NR latex. The other reaction conditions were kept constant as follows :

Reaction temperature	60°C
Swelling time	30 minutes
Reaction time	12 hours
Initiator system	(TBH/TEPA) 1.5/4.5 ml

The reacted rubber was coagulated, extracted and vulcanised as described before and the amount of bound antioxidant was calculated. The results are shown in the following table.

TABLE 4.2

pH	BTGA bound		
	g/100 g NR	moles/100 gNR	% bound
8	0.92	3×10^{-3}	46
9	0.88	2.8×10^{-3}	44
12	0.6	1.9×10^{-3}	30

The results in the above table indicate that the extent of binding is not significantly affected between pH=8-9 but there is a considerable reduction in the amount of bound antioxidant at about pH = 12. The effect of pH on the concentration of BTGA is shown in Fig. 4.2.

4.2.3 Effect of Time

A set of reactions were carried out for a known length of time and the reacted rubber with antioxidant at different periods of time were coagulated, dried, extracted and vulcanised as it has been described previously (Chapter 2). The amount of bound antioxidant was determined using the IR technique (see Section 2.3.1). The results of these experiments are shown in Table 4.3. The other reaction conditions were kept constant as follows :

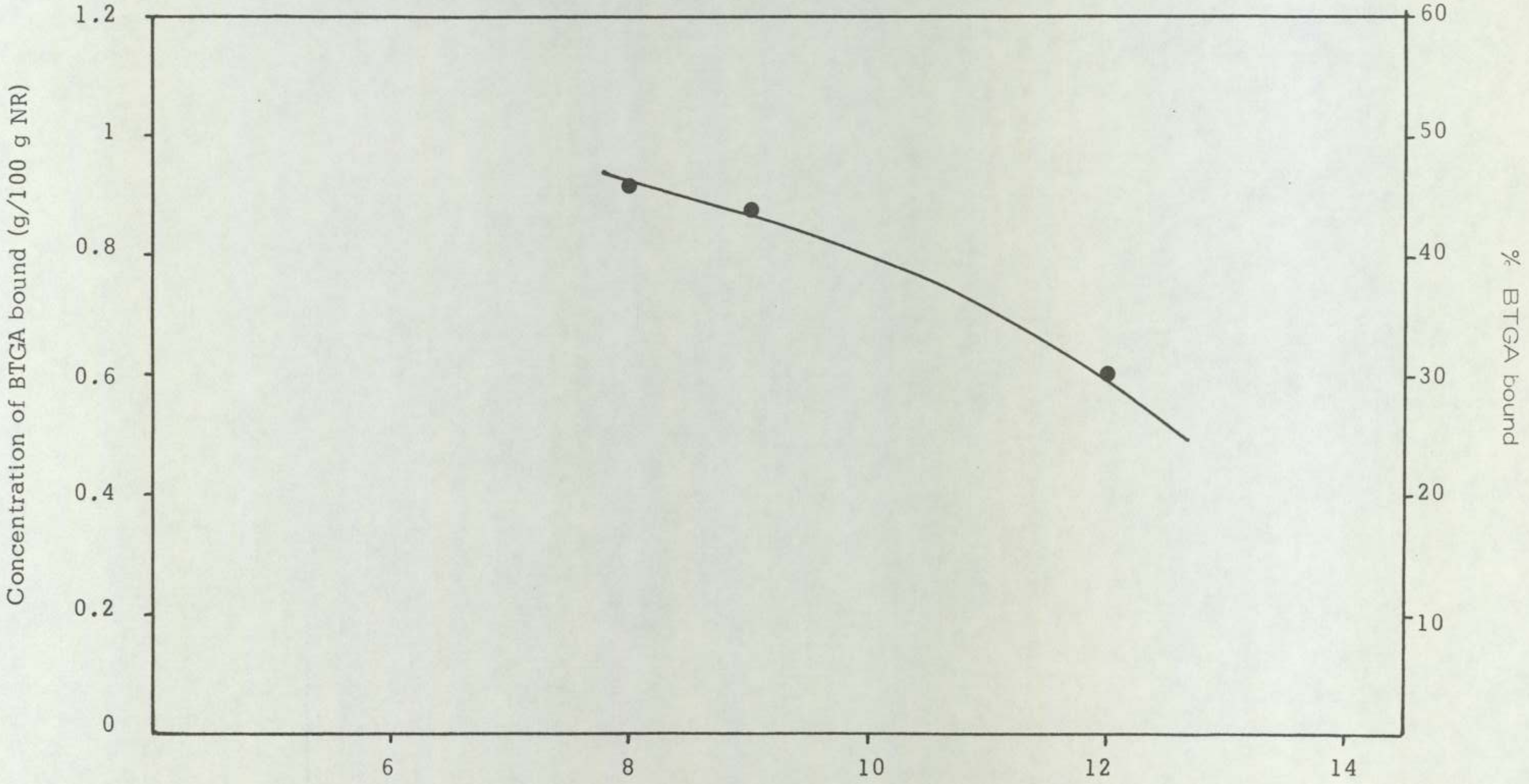


Fig. 4.2. Effect of pH on the reaction of BTGA with NR latex

Reaction temperature	60°C
Initiator	(TBH/TEPA) 1.5/4.5 ml
Swelling time	30 minutes
Concentration of BTGA	2 g (0.006 moles)/100 g NR
pH	8 - 8.5

The results are shown in the following table.

TABLE 4.3

Reaction time	BTGA bound		
(h)	g/100 g NR	moles/100 g NR	% bound
7	0.7	2.2×10^{-3}	35
12	0.92	3×10^{-3}	46
18	0.94	3×10^{-3}	47
24	0.92	3×10^{-3}	46

As it is seen in the above table the maximum yield of bound antioxidant is obtained after 12 hours reaction of BTGA with NR latex. This is also shown in Fig. 4.3. The infra-red spectrum of the grafted-extracted NR reacted with BTGA is shown in Fig. 4.4.

4.2.4. Effect of Gradual Addition of BTGA Dispersion

The antioxidant dispersion is usually added at the beginning of

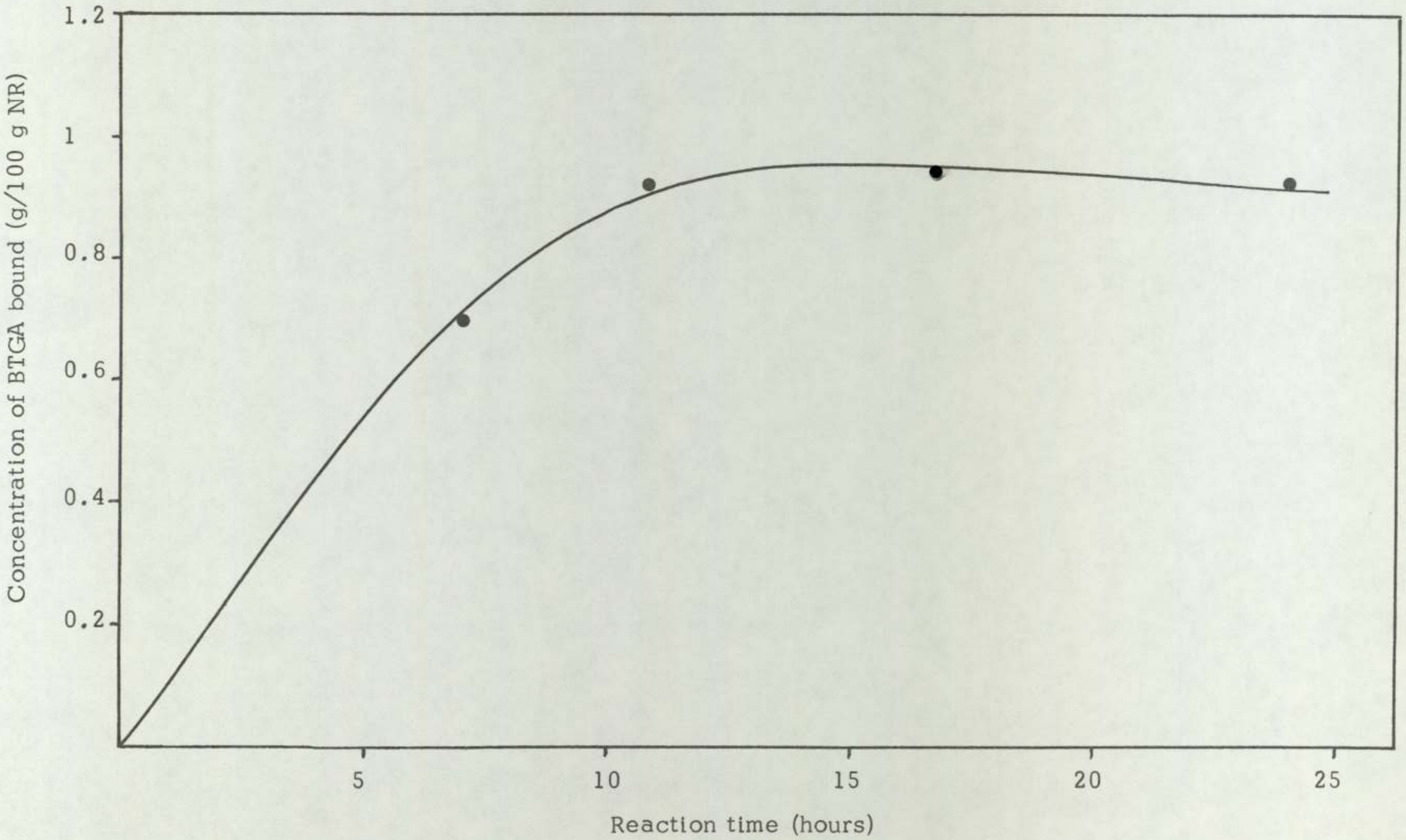


Fig. 4.3. Effect of time on the reaction of BTGA with NR latex

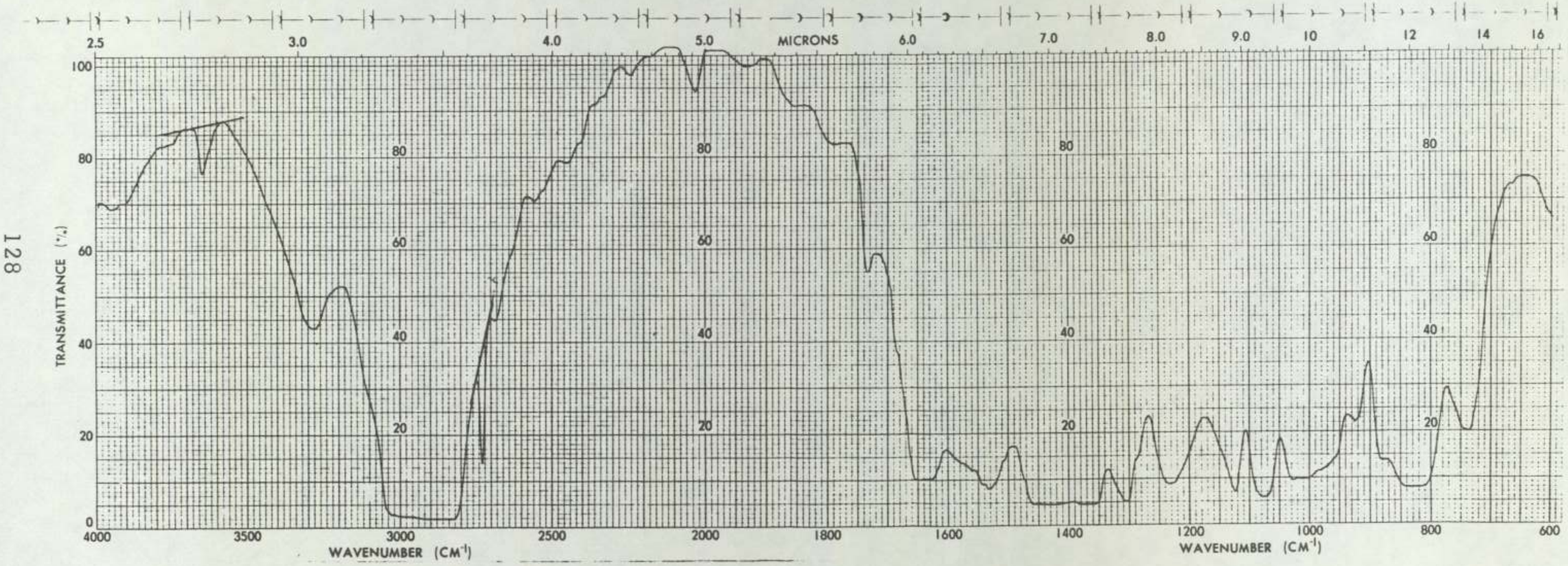


Fig. 4.4. Infra-red spectrum of the grafted-extracted NR vulcanisate reacted with BTGA (2g/100 g NR latex)

the reaction. It was thought this may cause an early termination of the radicals produced hence reducing the yield of the adduct formed. For this reason, a reaction of BTGA with natural rubber latex was carried out by adding antioxidant dispersion slowly in several stages of the reaction. The antioxidant dispersion containing 2 g (0.006 moles)/100g NR was added in several equal proportions at first 7 hours of the reaction. The reaction conditions used were as follows :

Reaction temperature	60°C
Swelling time	30 minutes
Initiator	(TBH/TEPA) 1.5/4.5 ml
Reaction time	9 hours

After the reaction, the rubber was coagulated, dried, extracted and vulcanised and the amount of bound antioxidant was determined as described before. It was found only 20% of the BTGA became bound to the rubber. This result indicates that the initial swelling of the antioxidant is a predominant factor in obtaining higher yield of bound antioxidant.

4.2.5. Effect of Concentration

A set of experiments was carried out to study the effect of the concentration of BTGA on the formation of rubber-bound antioxidant. Natural rubber latex was deammoniated to pH = 8-8.5. The other reaction conditions were as follows :

Reaction temperature	60°C
Reaction time	12 hours
NR latex	100 g D.R.C. (of 30%)
Initiator concentration	(TBH/TEPA) 1.5/4.5 ml
Swelling time	30 minutes

At the end of the reaction the reacted rubber was coagulated, dried and extracted. After extraction with azeotropic mixture vulcanisates were prepared as described in previous chapters (see Section 2.2) and the amount of bound antioxidant was determined using the IR technique. The results of these experiments are shown in the following table.

TABLE 4.4.

Concentration of antioxidant added	BTGA bound		
moles/100 g NR	g/100 g NR	moles/100 g NR	% bound
0.003 (1 g)	0.44	0.0014	44
0.006 (2 g)	0.94	0.003	47
0.009 (3 g)	1.47	0.0047	49
0.012 (4 g)	2.2	0.0071	55

The results in the above table clearly indicate that the amount of BTGA bound to the natural rubber increased as the concentration of initially added BTGA was increased. When the concentration of BTGA was increased to 10% level the natural rubber tended to coagulate after a short period of adding BTGA dispersion. Several attempts were also made to stabilize the latex with an ionic salt such as potassium oleate at various concentrations (w/w of NR) but coagulation of rubber again interfered with grafting reaction at high concentration of BTGA.

4.3. Reaction of 3,5-di-tert-butyl-4-hydroxybenzyl-carboxy ethyl sulphide (BTPA) with Natural Rubber Latex

3,5-di-tertiarybutyl-4-hydroxybenzyl-carboxy-ethyl sulphide (BTPA) was also reacted with natural rubber latex at the optimum conditions which has already been found for BTGA. 2 g of BTPA (0.006 moles) was reacted with 100g of deammoniated natural rubber latex at 60°C. The rest of the reaction conditions used were as follows:

Reaction time	12 hours
Initiator	(TBH/TEPA) 1.5/4.5 ml
Swelling time	30 minutes
pH	8-8.5

After the reaction the rubber was coagulated, dried and extracted. The extracted rubber was dried, a vulcanisate was prepared and the amount of BTPA bound was determined using the corresponding calibration curve (Fig. 2.2). The result is given below.

BTPA bound		
g/100 g NR	moles/100 g NR	%
1.1	0.035	55

The result indicates that BTPA can also become bound to natural rubber latex under similar conditions as BTGA and a yield of 55% bound antioxidant can be obtained. The infra-red spectrum of the grafted-extracted NR with BTPA is shown in Fig. 4.5.

4.4. Reaction of 3,5-di-tert-butyl-4-hydroxybenzyl-butyl-thio-glycollate (BTBE) with Natural Rubber Latex

3,5-di-tert-butyl-4-hydroxybenzyl-butyl-thio-glycollate was also reacted with natural rubber latex in order to compare the extent of binding with that of BTGA. The reaction conditions used were as follows :

Reaction temperature	$60^{\circ}C$
Reaction time	7 - 9 hours
Initiator concentration	(TBH/TEPA) 1.5/4.5 ml
Concentration of BTBE used	2 g (0.006 moles)/100 g NR
NR latex	100 g (D.R.C)
Swelling time	30 minutes
pH	8 - 8.5

This grafting reaction was carried out for a period of 9 hours but a sample was also taken after 7 hours. The grafted NR latex was coagulated, dried, extracted and vulcanised in a similar manner as described in previous sections. The results obtained are given in Table 4.5.

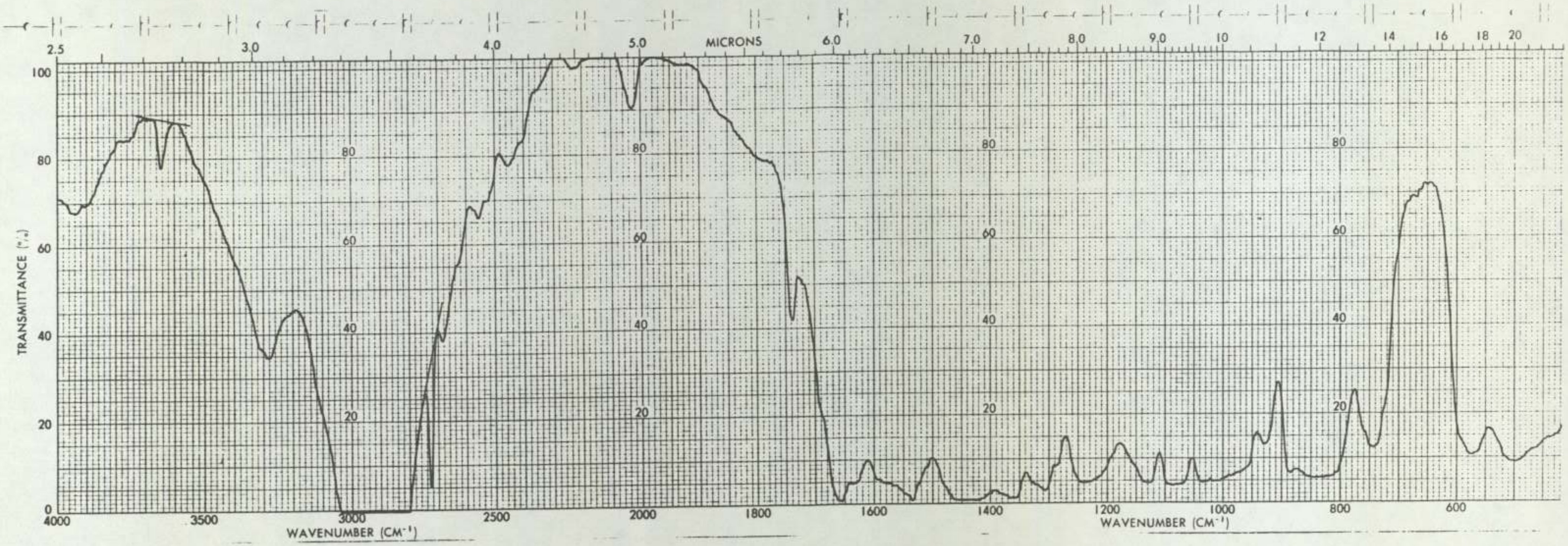


Fig. 4.5. Infra-red spectrum of the grafted-extracted NR vulcanisate reacted with BTPA (2g/100 g NR latex)

TABLE 4.5

Reaction time	BTBE bound		
(h)	g/100 g NR	moles/100 g NR	% bound
7	0.37	0.001	19
9	0.39	0.0011	20

As is seen from the result in the above table, 20% of initially added BTBE became bound to the rubber. Continuation of the reaction from 7 to 9 hours shows that a higher yield of bound antioxidant could not be obtained by increasing the reaction time. Comparison of the results obtained in the above table with that of BTGA (see Section 4.2.3) shows that the amount of bound antioxidant is almost 15% less than that of BTGA.

4.5. Reaction of 3,5-di-tert-butyl-4-hydroxybenzyl-mercapto glycollate with Natural Rubber Latex

4.5.1. Determination of Optimum Conditions

4.5.1.1. Effect of Swelling Time

Four sets of experiments were carried out with 2 g (0.006 moles) of BTGE reacted with 100 g of NR rubber latex (diluted to 30%). The BTGE emulsion was first allowed to swell into the natural rubber latex for a given period of time and then the initiators were added during the first half of the reaction. These reactions were done at 60°C for 7 hours. The rest of the reaction conditions used were as follows :

Concentration of BTGE	2 g (0.006 moles)/100 g NR
Initiator	(TBH/TEPA) 1.5/4.5 ml
pH	8 - 8.5

The grafted rubber was coagulated, extracted, vulcanised and the amount of bound antioxidant was determined using the corresponding calibration curve as described previously (see Section 2.3). The results of these sets of experiments are given in Table 4.6.

TABLE 4.6

Swelling time	BTGE bound		
(min)	g/100 g NR	moles/100 g NR	% bound
0	0.44	1.4×10^{-3}	22
15	0.71	2.3×10^{-3}	36
30	0.88	2.8×10^{-3}	44
45	0.82	2.6×10^{-3}	42

The results in Table 4.6 show that maximum yield of bound antioxidant is obtained when a swelling time of 30 minutes is allowed.

4.5.1.2. Effect of pH

Three sets of reactions of BTGE with NR latex were carried out at various pH conditions in order to determine the effect of pH on the formation of bound antioxidant. These experiments were done under the following reaction conditions :

Reaction time	7 hours
Reaction temperature	60°C
Concentration of BTGE	2 g (0.006 moles)/100 g NR
Initiator	(TBH/TEPA) 1.5/4.5 ml
Swelling time	30 minutes
NR latex	100 g D.R.C. (diluted to 30%)

The reacted rubber at a given pH was given similar treatment to that described in previous experiments and the amount of bound antioxidant was determined using the IR technique. The results obtained are given in the following table.

TABLE 4.7

pH	BTGE bound		
	g/100 g NR	moles/100 g	% bound
8	0.88	2.8×10^{-3}	44
9.5	0.69	2.2×10^{-3}	34
12	0.19	6.1×10^{-4}	9

The results in Table 4.7 indicate that at high concentration of ammonia i.e. high pH, a considerable amount of antioxidant is being consumed in reactions such as hydrolysis rather than adduct formation. However, it was not possible to reduce the pH below 8 since this was found to lead to coagulation of the latex during the grafting reaction. The effect of pH on the reaction of BTGE with natural rubber is shown in Fig. 4.6.

4.5.1.3. Effect of Reaction Time

A set of reactions w carried out at 60°C for various periods of time. Samples reacted for a given time were coagulated, dried, extracted and vulcanisates were prepared as described previously. The IR method was used to determine the concentration of BTGE bound. The reaction conditions used in these experiments were as follows :

Swelling time	30 minutes
Initiator	(TBH/TEPA) 1.5/4.5 ml
pH	8-8.5
NR latex	100 g D.R.C. (diluted to 30%)
BTGE	2 g (0.006 moles)/100 g NR

The results obtained are given in the following table :

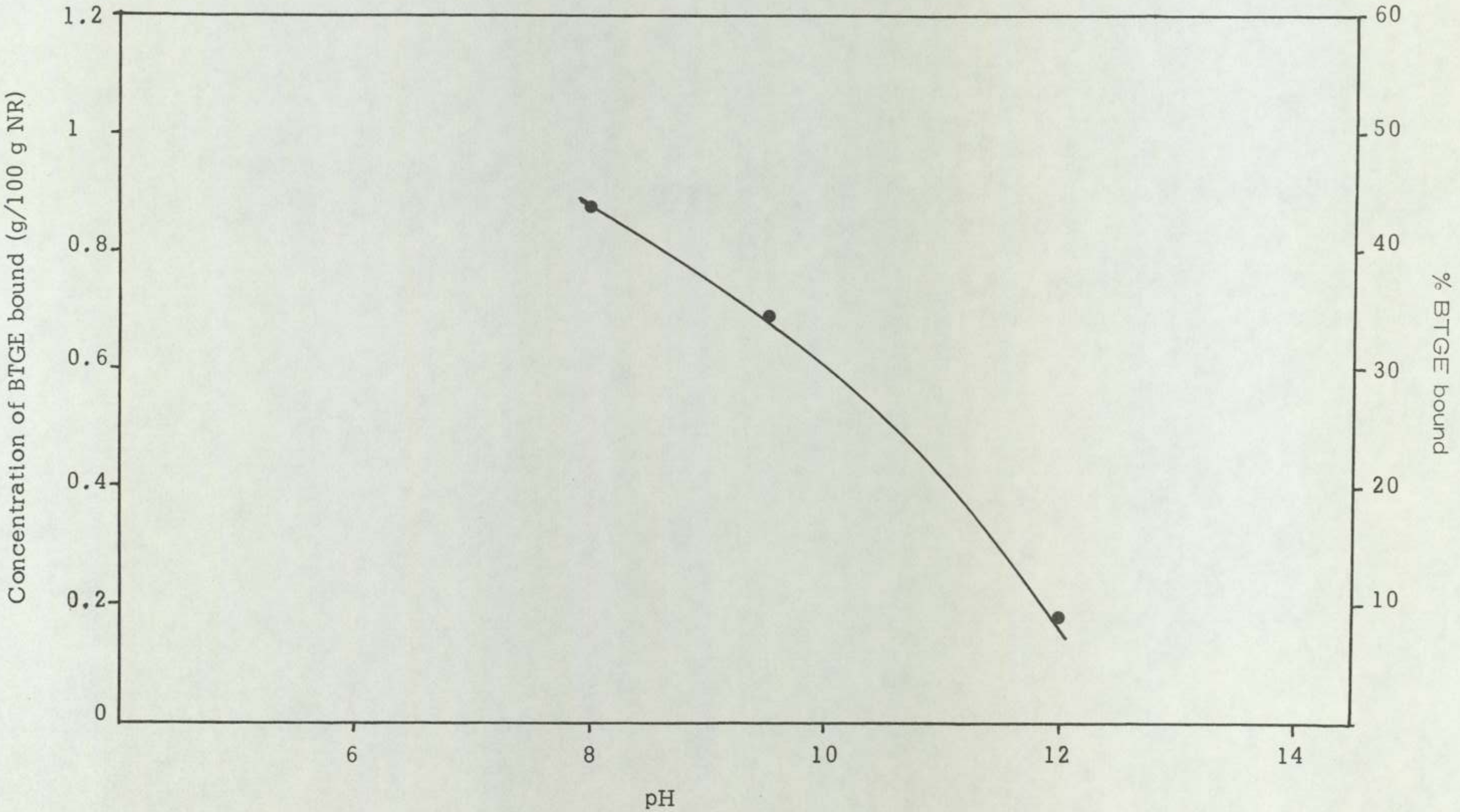


Fig. 4.6. Effect of pH on the reaction of BTGE with natural rubber latex

TABLE 4.8

Reaction Time	BTGE bound		
(h)	g/100 g NR	moles/100 g NR	% bound
5	0.76	2.45×10^{-3}	38
7	0.88	2.8×10^{-3}	44
12	0.8	2.58×10^{-3}	40
18	0.76	2.45×10^{-3}	38
24	0.71	2.29×10^{-3}	36

As it can be seen from the results in Table 4.8 maximum yield of BTGE bound is formed with a reaction time of 7 hours. A comparison of these results with that for BTGA (see Section 4.2.3.) indicates that the rate of addition of BTGE to natural rubber is much faster than that of BTGA. The effect of time on the reaction of BTGE with natural rubber is shown in Fig. 4.7. The infra-red spectrum of the grafted-extracted NR reacted with BTGE is shown in Fig. 4.8.

4.5.1.4. Effect of Initiator Concentration

In order to evaluate the effect of initiator concentration on the reaction of BTGE with natural rubber latex, a set of experiments was carried out at various $\frac{\text{TBH}}{\text{TEPA}}$ and $\frac{[\text{RSH}]}{[\text{TBH}]}$ concentrations. The reactions were done under the following conditions:

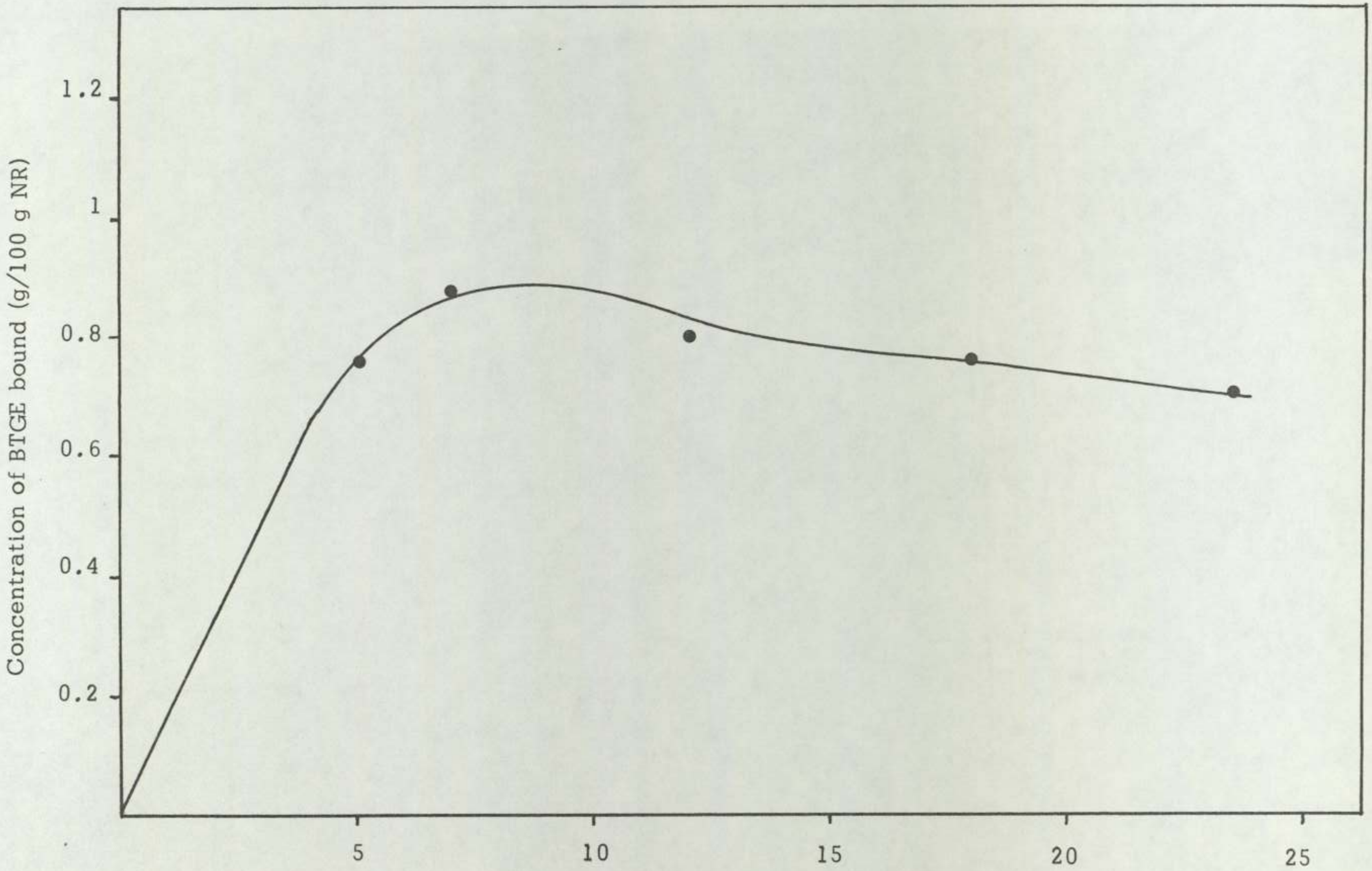


Fig. 4.7. Effect of time on the reaction of BTGE with NR latex

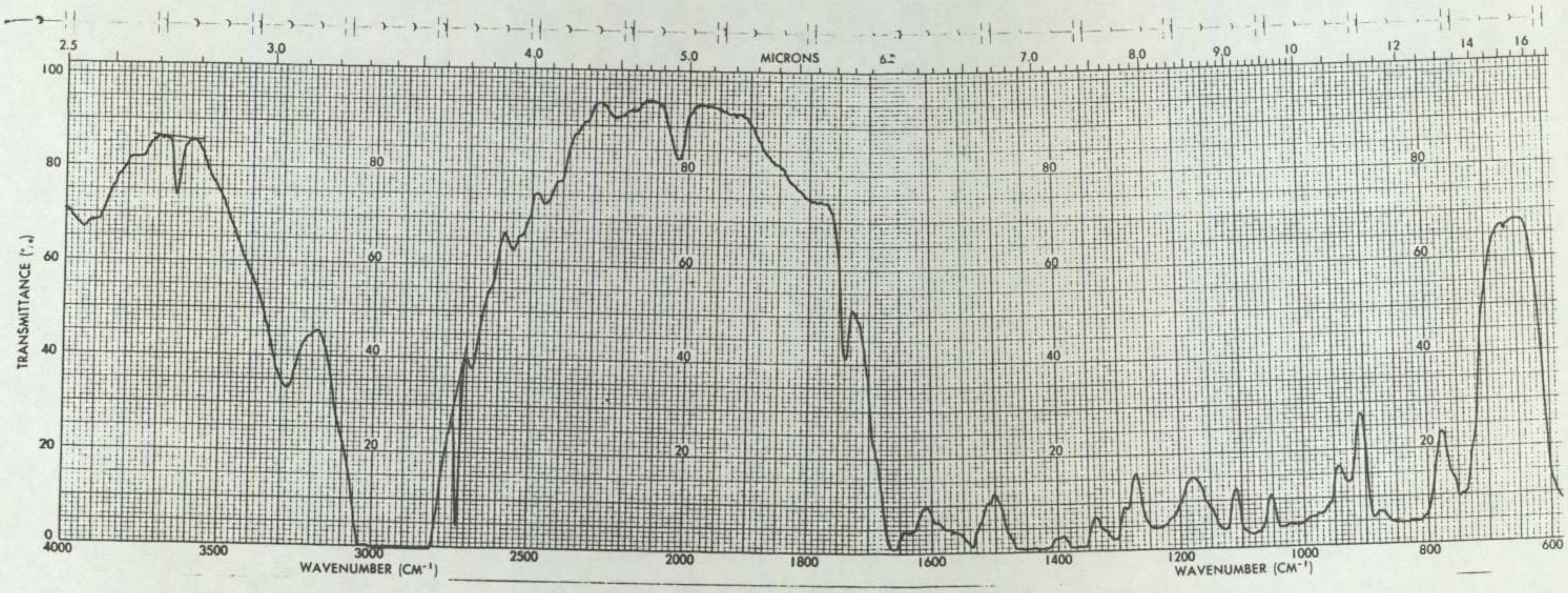


Fig. 4.8. Infra-red spectrum of the grafted-extracted NR vulcanisate reacted with BTGE (2g/100 g NR latex)

Reaction time	7 hours
Reaction temperature	$60^{\circ}C$
Swelling time	30 minutes
pH	8 - 8.5
NR latex	100 g D.R.C. (of 30%)
Concentration of BTGE used	2 g (0.006 moles)100 g NR

After the reactions the same procedure was followed to determine the degree of binding as described in previous experiments. The results are shown in Table 4.9.

TABLE 4.9

$\frac{\text{TBH}}{\text{TEPA}}$	$\frac{[\text{RSH}]}{[\text{TBH}]}$	BTGE bound	
(ml)	(molar ratios)	g/100 g NR	%
0.5	0.5	0.62	31
0.33	0.5	0.56	28
0.23	0.6	0.88	44
0.33	0.8	0.49	24
0.25	2	0.24	12
0.5	2	0.19	9.5
0.33	1	0.15	7.5

The results in Table 4.9 indicate that maximum yield of bound antioxidant is obtained when a molar ratio of $\frac{[RSH]}{[TBH]} = 0.6$ is used. It is also seen that variation in the ratio of $\frac{TBH}{TEPA}$ does not have a significant effect on adduct formation.

4.6. Analysis of By-products Formed during the Reaction of BTGE with Natural Rubber Latex

Thin layer chromatography was employed to identify the by-products formed during the reaction of BTGE with natural rubber latex. The reacted rubber was extracted with azeotropic mixture and solvent removed on a rotatory evaporator. 2 μl of 1% solution of brown-oily product obtained in ether was applied to a 15 x 20 cm silica gel precoated plastic plate. The spots on the plate were allowed to be dried. The development of the chromatogram was carried out by the ascending method, that is, by allowing a solvent mixture to move up an almost vertical plane by capillary action. In order to saturate the tank atmosphere as much as possible, the sides were lined with thick chromatography papers. The loaded plate was placed in the solvent tank consisting of benzene, methanol and acetic acid (45, 8, 4 ml) and run to a line (solvent front) from a fixed distance from the base line. The plate was then removed from the tank and dried in air. In order to observe the separated components a location reagent was necessary. For this purpose a 1% phosphomolybdic acid in ethanol was sprayed over the plates using an aerosol spray and the plates were then placed in another tank saturated with ammonia solution. The compounds were identified and characterised by the R_f

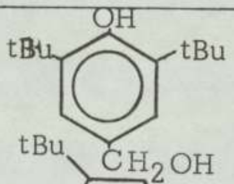
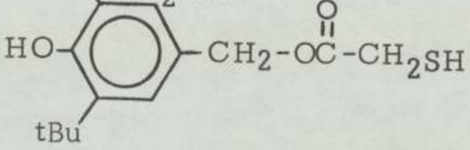
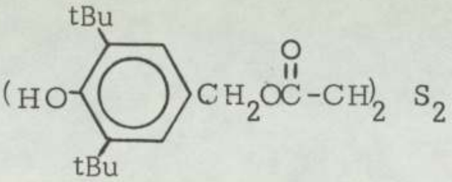
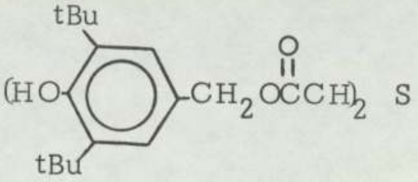
value which is defined as follows ;

$$R_f = \frac{\text{Distance of compound from origin}}{\text{Distance of solvent from origin}}$$

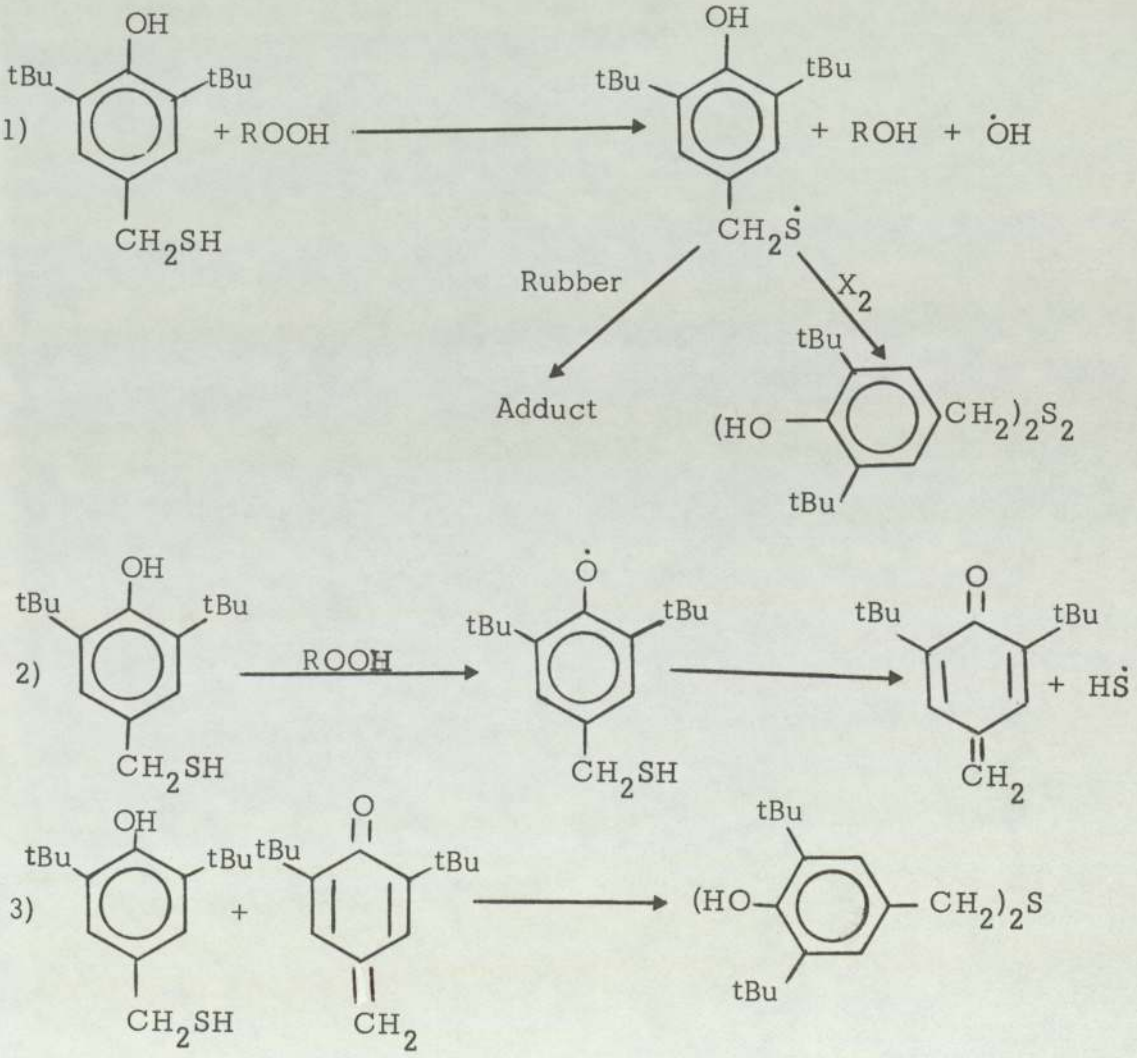
4.6.1. Results and Discussion

To identify the by-products formed it was necessary to use the probable products formed during the reaction as reference compounds. According to the R_f values obtained, the conclusions were as follows;

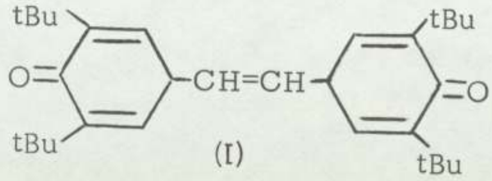
TABLE 4.10

Compound	Colour	R_f value x 100
	Pink	68
	Blue	58
	Green	33
	Brown	48
Unknown	Orange	76

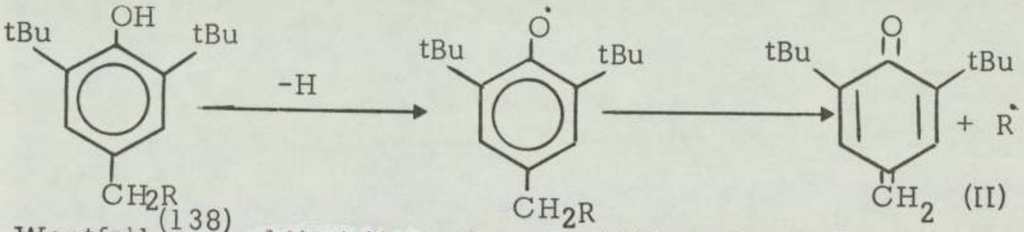
The presence of 3,5-di-tertiarybutyl-4-hydroxybenzyl alcohol may suggest that part of BTGE hydrolys during the reaction. It also can be seen that part of BTGE remain unreacted suggesting that the amount of thiol which could become bound to the rubber is limited possibly due to the presence of protein or its hydrolysis products in NR. The Presence of BTGE mono, and disulphides in extract also shows that Part of the BTGE is oxidized during the reaction. Scott <u>et al.,</u>(100,101) have shown that in the case of BHBM its mono and disulphide derivatives are formed during a reaction with natural rubber latex as follows :



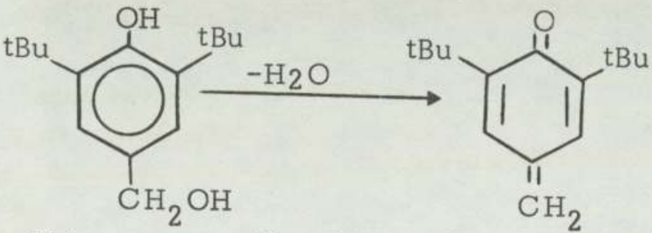
A similar reaction can take place during the reaction of BTGE with natural rubber latex. The unknown spot was not identified but could be due to the formation of 3,5-3',5'-tetra-butyl-stilbene 4,4' quinone (I).


(I)

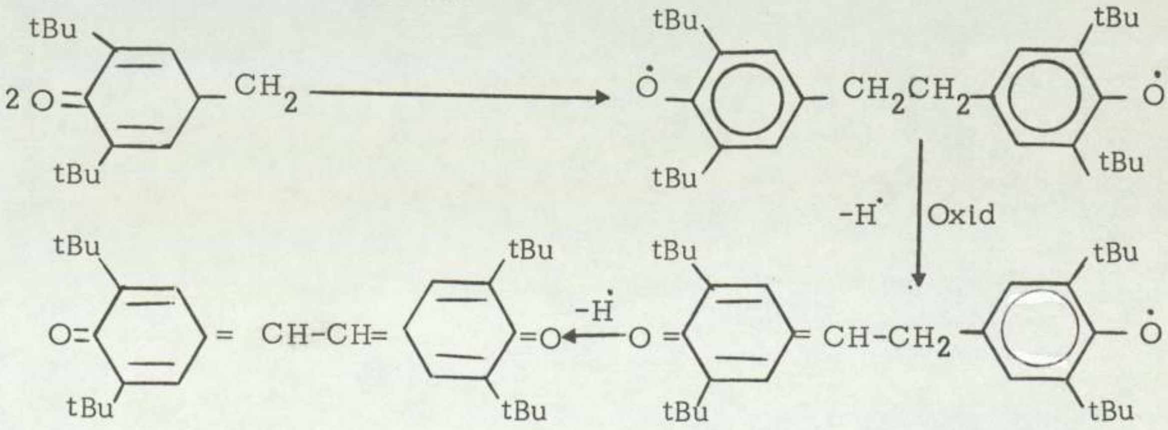
Westfahl (137,138) has evaluated the oxidation products from antioxidants containing the 3,5-di-tert-butyl-4-hydroxybenzyl group. He concluded that the group or atom attached to the 3,5-di-tert-butyl-4-hydroxybenzyl group can be removed to give the very unstable hydroquinone methide (II).



Westfahl (138) showed that the quinone methide not only formed in the presence of an oxidizing agent but also can be prepared by the dehydration of the corresponding alcohol using a Lewis acid.



This very reactive intermediate can undergo to (I) by dimerisation or disproportionation as follows: (137,138)



4.7. Reaction of Bis(3,5-di-tert-butyl-4-hydroxybenzyl-methyl acetate) disulphide with Natural Rubber Latex

The reaction of bis(3,5-di-tert-butyl 4-hydroxybenzyl-methyl acetate) disulphide with natural rubber was carried out under the following conditions.

Initiator concentration	(TBH/TEPA) 1.5/4.5 ml
Concentration of BTGE disulphide	2 g (0.003 moles)/100 g NR
Reaction temperature	$60^{\circ}C$
Reaction time	9 hours
Swelling time	30 minutes

The rubber was coagulated after the reaction and extracted. The estimation of bound antioxidant showed that 26-28% of the BTGE disulphide became bound to the rubber.

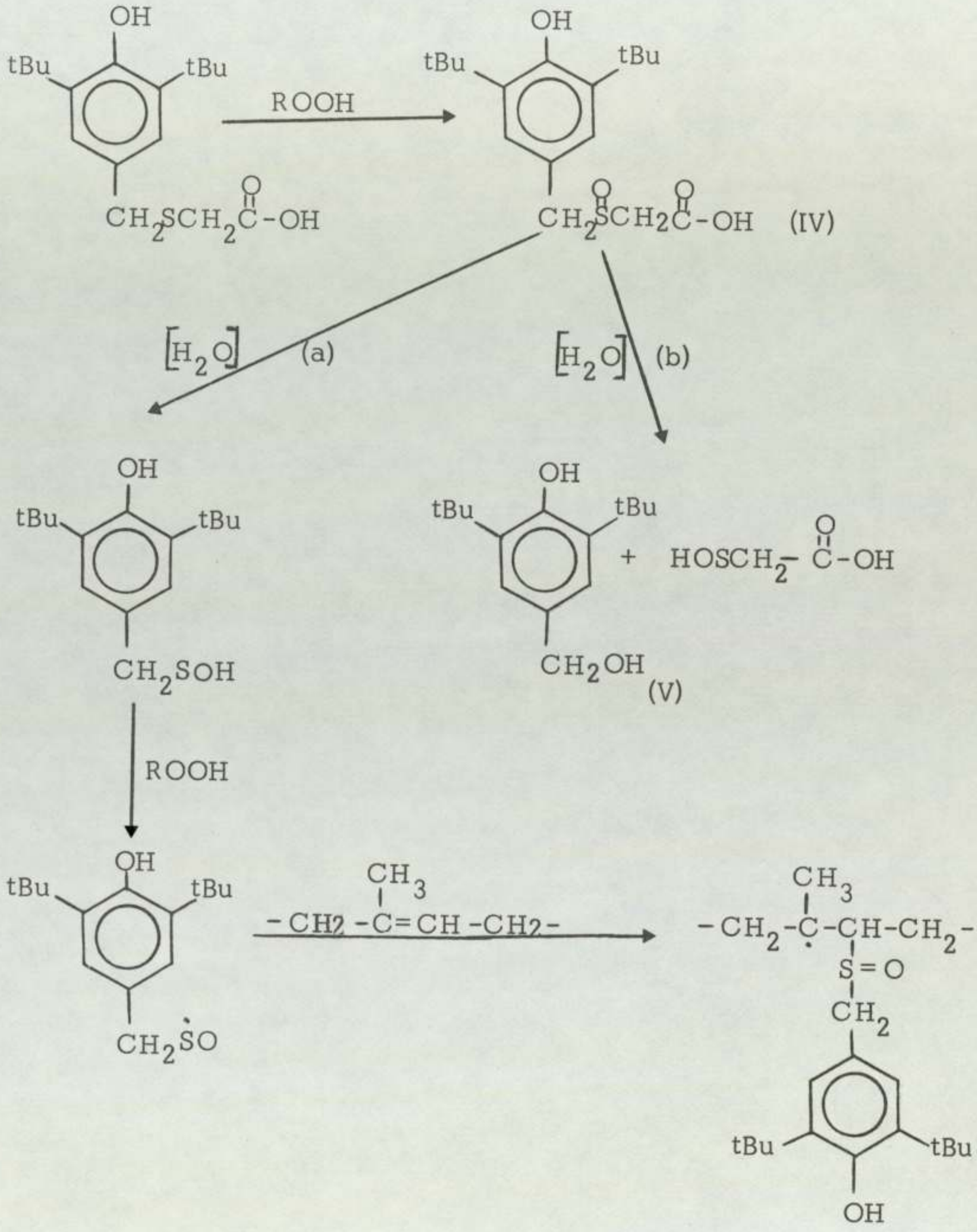
4.8. Discussion

The effect of pH on the reaction of BTGA with natural rubber latex (see Table 4.2. and Fig. 4.2) showed that from pH=8 to 12 the amount of bound antioxidant formed reduces from 46 to 30%. In contrast, it was found that the inhibitory effect of ammonia on the yield of bound antioxidant formed from BTGE is more significant. As shown in Table 4.7 and Fig. 4.6 the amount of rubber-bound antioxidant is considerably reduced from pH 8 - 12 suggesting that hydrolysis is certainly occurring in the latter case, this was also confirmed by thin layer chromatography on the extract, (see Table 4.10). The effect of time on the reaction of BTGA with natural rubber (see Table 4.3. Fig. 4.3) showed that the maximum yield of bound antioxidant is formed at a reaction time of 12 hours. Percentage of bound antioxidant remained almost constant when the reaction time was further increased. Reaction of BTGE with natural rubber for various lengths of time showed that a shorter period is required in order to reach the maximum yield of adduct. As shown in Table 4.8 and Fig. 4.7, a period of 7 hours was sufficient for BTGE to give the maximum amount of bound antioxidant. Further increase in reaction time was found to give a slight reduction in the yield of adduct formed. This also could be explained due to the hydrolysis of bound-BTGE on further reaction time. The effect of concentration of BTGA on the yield of bound antioxidant is shown in Section 4.2.5. Increase in concentration of BTGA from 1 to 4% gave rise to higher yield of bound antioxidant from 44 to 55% (see Table 4.4). The concentration of the initiator $\frac{\mathrm{TBH}}{\mathrm{TEPA}}$ and other variables were kept constant. Increase in the yield of bound antioxidant at higher concentrations of BTGA could be explained considering the previous investigations of Scott and co-workers (32,33,29) who have shown that dimethyldithiopropionate can react with hydroperoxides to produce the corresponding sulphoxide and sulphenic acid.The acid formed (III), particularly when it is in excess, can react with hydroperoxide in a redox radical-generating reaction as follows;

$$\mathrm{Me\,OCOCH_2CH_2SOH + ROOH \longrightarrow Me\,OCOCH_2CH_2\dot{S}O + R\dot{O} + H_2O}$$

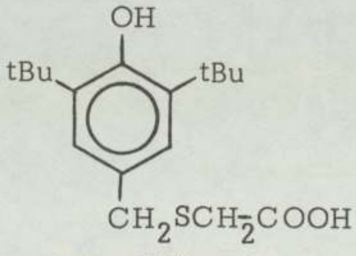
(III)

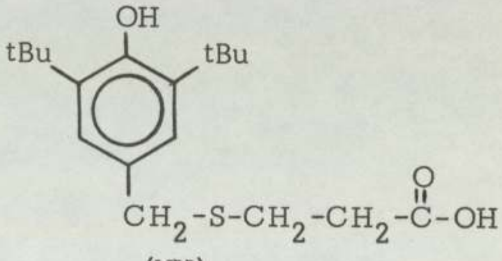
It seems that a similar reaction may take place when BTGA is used in excess of hydroperoxide leading to a higher degree of binding. Therefore, the reaction of BTGA with natural rubber may occur in a similar manner as follows :



Application of thin layer chromatography on products formed during the reaction of BTGE with NR showed that benzyl alcohol (V) can be formed, suggesting that hydrolysis of the sulphoxide may also occur according to the reaction (b).

Reaction of 3,5-di-tertiarybutyl-4-hydroxybenzyl-carboxy-ethyl sulphide (BTPA) with natural rubber latex was also carried out under the optimum conditions found for BTGA. The efficiency of binding of BTPA was found to be greater (55%) than BTGA (46%). This could be due to the fact discussed earlier in Chapter 1 (see Section 1.2.2.3) that, sulphoxide with one or more hydrogens on carbon β to the sulphinyl group was found to decompose readily(25) by an elimination reaction to give sulphenic acid. Unlike BTGA (VI), there is a β-hydrogen present in BTPA (VII) hence, the formation of sulphenic acid in the later case and its reaction with NR through sulphinyl radical can occur at higher rate.


(VI)


(VII)

3,5-Di-tertiarybutyl-4-hydroxybenzyl mercapto glycollate (BTGE) was also reacted with NR at the latex stage using various $\frac{TBH}{TEPA}$ ($^{v}/_{v}$) ratios. As shown in Table 4.9 the extent of binding reaches to a maximum at a ratio of $\frac{TBH}{TEPA} = 0.23$ and a molar ratio of $\frac{[RSH]}{[TBH]} = 0.6$. Resu given in this Table also show that variation in the ratio of $\frac{TBH}{TEPA}$ does not have a significant effect on the yield of BTGE bound. Recent investigation by Scott and Suharto (139) also shown that variation in the ratio of $\frac{TBH}{TEPA}$ does not have a significant effect on the efficiency of binding of BHBM to natural rubber latex.

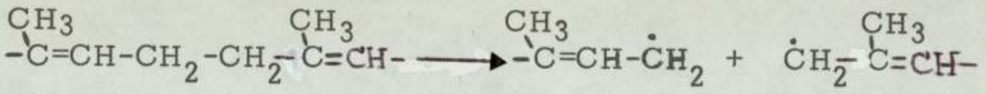
CHAPTER FIVE

MECHANO-CHEMICAL REACTIONS OF ANTIOXIDANTS DURING PROCESSING AND VULCANISATION WITH NATURAL AND SYNTHETIC RUBBERS

5.1. Reaction of Antioxidants with Natural and Styrene-Butadiene Rubbers during processing in the Torque Rheometer

5.1.1. Introduction

Mechanochemistry involves reactions for which the energy for initial radical formation is supplied mechanically. When sufficient energy is concentrated in a portion of the polymer chain, as a result of new uniform distribution of internal stresses, the mechanical rupture of primary bonds results in the formation of macroradicals (140). In the case of NR the bond which is most likely to be ruptured is the $-CH_2-CH_2-$ bond since its dissociation is lowered by the resonance energy of the alkenyl radical produced in the process :



$$-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH- \longrightarrow -\overset{CH_3}{C}=CH-\dot{C}H_2 + \dot{C}H_2-\overset{CH_3}{C}=CH-$$

Similar sites of scission are present in other 1,5-dienes including the polymers and copolymers of butadiene and chloroprene. Free radicals produced as a result of chain scission can attack polymer chains and will do so in the absence of reagents or structures which are capable of stabilizing them, resulting in branching or crosslinking. Polymeric radicals produced by mastication may also be utilized for other chemical reactions. (141) An especially interesting case is their utilization to initiate the polymerisation of a monomer (M) admixed in the polymer:

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

In the present studies mechanically induced free-radicals were used to produce rubber-bound antioxidants during pre-mixing and vulcanisation stages with natural and styrene-butadiene rubbers. Rubber-bound antioxidants produced by reacting antioxidants with natural and synthetic rubber latices, although useful for polymer manufacturers, may not have the flexibility required by polymer users. This is due to the fact that bound antioxidants in this case could mainly be used in latex-derived products whereas those obtained during pre-mixing could be used in a variety of rubber articles using the solid masterbatching technique. Therefore, there could be a considerable advantage of carrying out the adduct formation during preliminary processing. The driving force in this process could be due to the formation of free radicals by shear which may then initiate the chain reactions involved. In the present work the possibilities of adduct formation between a number of antioxidants and solid natural and styrene-butadiene rubbers in the RAPRA torque rheometer (142) were studied. The rheometer is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds. It has a good temperature control and a continuous readout is provided of both melt temperature and the torque required for mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. In the present studies, the processing of antioxidants with NR and SBR was carried out with closed chamber and a full charge of 30 g. On completion of processing the polymer sample was rapidly removed and quenched in cold water to prevent further thermal degradation.

5.1.2. Reaction of 4-mercaptoacetamidodiphenylamine (MADPA) with Styrene-Butadiene Rubber during Processing in the Torque Rheometer

The mechano-chemical reaction between MADPA and styrene-butadiene rubber was carried out in the RAPRA torque rheometer. The stripped-extracted SBR (see Section 2.1.5) derived from latex was sheeted out to approximately 1-2 mm thickness on a 12" water-cooled laboratory two-roll mill. The antioxidant was spread over the sheeted SBR and rolled in and then the rubber cut into small pieces. The rubber plus antioxidant was processed for 10 minutes at various temperatures ranging from 25-90°C. The MADPA was incorporated at a level of 10 p.h.r. and the processing was carried out in a closed chamber with a rotor speed of 68 r.p.m. The processed rubber was sheeted and mounted on a specially prepared frame for infra-red analysis. The infra-red spectra of the extracted and unextracted samples were obtained and the degree of binding was assessed by comparing the intensities of the peaks due to antioxidant before and after extraction and also the corresponding calibration curve (see Section 2.3.2.). The results are shown in the following Table.

TABLE 5.1

Temperature	MADPA bound	
°C	g/100 g SBR	% Bound
25	5.2	52
70	5.8	58
90	5	50

5.1.3. Binding of 3,5-ditertiarybutyl-4-hydroxybenzyl-mercaptan (BHBM) with Styrene-Butadiene Rubber during Processing in the Torque Rheometer

Grafting of 3,5-ditertiarybutyl-4-hydroxybenzyl mercaptan (BHBM) with styrene-butadiene rubber was also studied in the torque rheomter. BHBM (3 g) was spread over 30 g sheeted SBR (stripped-extracted), folded, and then cut in small pieces. The processing was carried out at three different temperatures, i.e. 25°C, 70°C and 90°C, for a period of 10 minutes. The rubber was quenched in cold water after processing and dried. The infra-red spectra of the extracted and unextracted SBR films were obtained and the hydroxyl ratios were measured and compared with the calibration curve. The amount of bound antioxidant was determined (see Section 2.3.2.). The results obtained are given in the following table :

TABLE 5.2

Temperature	BHBM Bound	
°C	g/100 g SBR	% Bound
25	4.3	43
70	4	40
90	3.6	36

Attempts were also made to bind BHBM onto the commercial grades of SBR (unextracted-unstripped). SBR Intol 1500 and 1502 (from ISR)(143) were used and processed with BHBM at 10 p.h.r. level. The temperature was maintained at 70°C and the processing time was 10 minutes. The amount of bound antioxidant was determined by the IR technique described previously (see Section 2.3.2.). The results are shown in Table 5.3.

TABLE 5.3

Grade of SBR	BHBM Bound	
	g/100 g SBR	% Bound
Intol 1500	1.2	12
Intol 1502	2.6	26
SBR derived from latex	4.3	43

5.1.4. Binding of 4-mercapto acetamidodiphenylamine (MADPA) with Natural Rubber during Processing in the Torque Rheometer

Mechano-chemical reaction between MADPA and natural rubber was also carried out in the torque rheometer. Natural rubber was coagulated from latex, dried and extracted with the azeotropic mixture under nitrogen in a soxhlet for 48 hours. The extracted rubber was dried again under vacuum at 25°C and sheeted out to approximately 15 thou thickness on a 12" water-cooled laboratory two-roll mill. 30 g of dried rubber was used and the amount of antioxidant added was varied between 10-20%. The temperature of the torque rheometer was kept constant at 70°C and a processing time of 10 minutes was allowed. At the end of this period the rubber was quenched in cold water to stop further oxidation and dried. The infra-red spectra of the extracted and unextracted samples were obtained and the amount of bound antioxidant was determined using the corresponding calibration curve (see Section 2.3.2, and Fig. 2.4). The result obtained are shown in the following table.

TABLE 5.4

Initial concentration of MADPA	MADPA Bound	
g/100 g NR	g/100 g NR	% Bound
10	5	50
20	8.8	44

The amount of rubber used in the torque rheometer was also varied from 10 to 30 g. keeping the initial amount of antioxidant at 10% level. The results obtained in these two cases are compared in Table 5.5.

TABLE 5.5

NR used	MADPA Bound	
g	g / 100 g NR	% Bound
10	3.3	33
30	5	50

5.1.5. Discussion

Mechano-chemical degradation of rubber is by no means always undesirable; mastication, the mechanical working of rubber in the presence of an added chemical plasticizer is universally used in rubber technology to plasticize the elastomer before the addition of compounding ingredients. Shear forces applied during the mastication of rubber give rise to polymeric radicals :

$$R - R \xrightarrow{\text{shear}} \dot{R} + \dot{R} \qquad (1)$$

In the presence of oxygen the free radicals react to give alkenyl peroxy radicals :

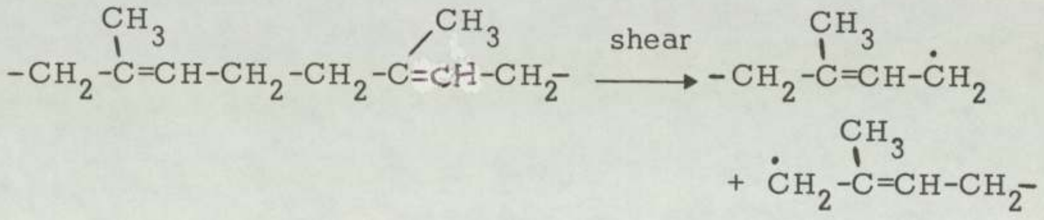
$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \qquad (2)$$

These radicals are also capable of hydrogen abstraction from either rubber molecules or other non-rubber constituents (140):

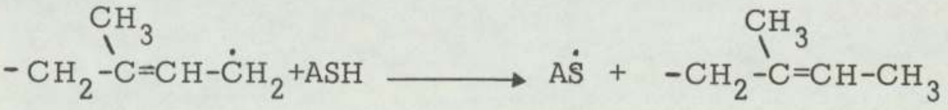
$$R\dot{O}_2 + RH \longrightarrow RO_2H + \dot{R} \qquad (3)$$

$$R\dot{O}_2 + HX \longrightarrow RO_2H + \dot{X} \qquad (4)$$

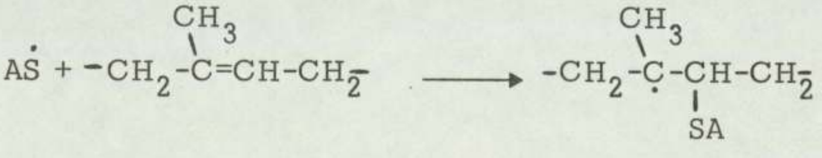
Hydroperoxides are known to be present in rubbers after mastication in (140) air giving rise to the formation of alkoxy (RO) and alkylperoxy (RO_2) radicals. In the case of natural rubber and in the presence of a thiol compound, the alkyl peroxy radical formed can abstract ∝-methylenic hydrogen from the rubber backbone and also from thiol-containing antioxidant in order to generate alkenyl and thiyl radicals respectively. The thiyl radicals may then add to the double bond of the rubber chain or react with alkenyl radicals :



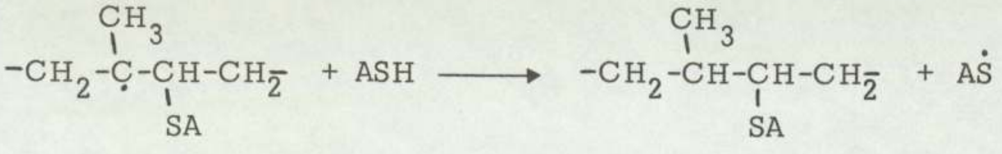
$$-CH_2-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH-CH_2- \xrightarrow{shear} -CH_2-\overset{CH_3}{C}=CH-\dot{C}H_2 + \dot{C}H_2-\overset{CH_3}{C}=CH-CH_2- \qquad (6)$$



$$-CH_2-\overset{CH_3}{C}=CH-\dot{C}H_2+ASH \longrightarrow A\dot{S} + -CH_2-\overset{CH_3}{C}=CH-CH_3 \qquad (7)$$

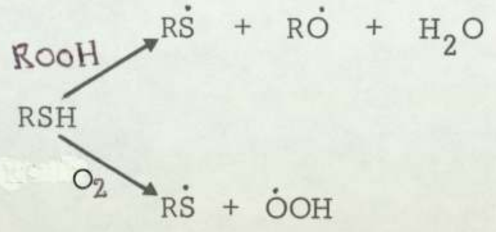


$$A\dot{S} + -CH_2-\overset{CH_3}{C}=CH-CH_2- \longrightarrow -CH_2-\overset{CH_3}{\dot{C}}-\underset{SA}{C}H-CH_2- \qquad (8)$$



$$-CH_2-\overset{CH_3}{\dot{C}}-\underset{SA}{C}H-CH_2- + ASH \longrightarrow -CH_2-\overset{CH_3}{C}H-\underset{SA}{C}H-CH_2- + A\dot{S} \qquad (9)$$

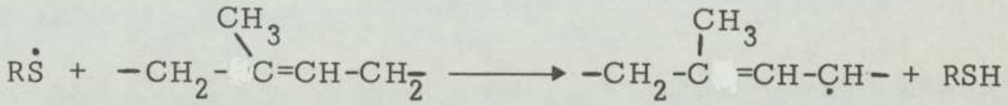
Scott $^{(6)}$ has pointed out that thiyl radicals can also be readily formed by reaction of thiols with hydroperoxides or oxygen as follows :



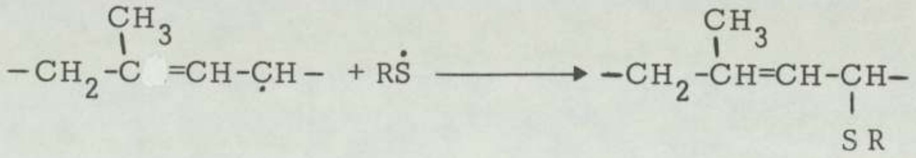
$$RSH \xrightarrow{RooH} R\dot{S} + R\dot{O} + H_2O \qquad 10\ (a)$$

$$RSH \xrightarrow{O_2} R\dot{S} + \dot{O}OH \qquad 10\ (b)$$

Thiyl radicals may also abstract α-methylenic hydrogen and produce alkyl radicals regenerating the thiol (11). The reaction of thiyl radicals with alkenyl radicals could also result in the formation of bound antioxidant (12).



$$R\dot{S} + -CH_2-\overset{CH_3}{C}=CH-CH_2- \longrightarrow -CH_2-\overset{CH_3}{C}=CH-\underset{\bullet}{C}H- + RSH \qquad (11)$$



$$-CH_2-\overset{CH_3}{C}=CH-\underset{\bullet}{C}H- + R\dot{S} \longrightarrow -CH_2-\overset{CH_3}{C}H=CH-\underset{SR}{C}H- \qquad (12)$$

It seems likely that the thiyl radicals eventually combine either with each other (13) or with another free radical ($X^{\bullet}$) present in the system (14).

$$R\dot{S} + R\dot{S} \longrightarrow RSSR \qquad (13)$$

$$R\dot{S} + \dot{X} \longrightarrow RSX \qquad (14)$$

Factors which may affect the mechano-chemical binding of antioxidants to the rubber are temperature, plasticity, rate of shear, initial molecular weight, compatibility of the antioxidant and the presence or absence of O_2.The results in Table 5.1 indicate that the maximum yield of bound antioxidant is obtained at 70°C. In contrast,the reaction of BHBM with styrene-butadiene rubber is highest at 25°C (see Table 5.2). This suggests that in the case of SBR + MADPA heat and shear forces are both responsible for optimum binding. For SBR + BHBM heat is not an important criterion. The reason for this could be the differences in the melting points of these two antioxidants. BHBM melts at 28°C, whereas MADPA melts at 133°C. The shearing of BHBM + rubber is accompanied by a certain amount of heat build up which would be sufficient to melt all the BHBM. When all the BHBM has melted it may act as a lubricant thus reducing the shear forces. At an elevated temperature, the rubber tends to soften and this together with the lubricating effect, reduces the shear forces even further. It is probably for this reason that optimum binding of BHBM to SBR is achieved at 25°C. MADPA gives a higher binding value at 70°C than at 25°C (see Table 5.1). This may be due to less efficient mixing of rubber with MADPA at lower temperatures. At 90°C, the softening effect of the rubber reduces the shear forces and hence, less shear induced active radical species are formed. The results in Table 5.3 show that the extent of binding is affected by the presence of the non-rubber constituents, that is the purer the rubber the higher is the yield of adduct formed. This has also been reported (144) to occur in binding of stabilizers to acrylonitrile-butadiene-styrene (ABS) copolymers. The SBR 1500 and 1502 both were expected to contain some non-rubber constituents since they were used without further purification. The SBR derived from the latex after stripping and extraction gave the highest efficiency in binding of BHBM during processing (see Table 5.3). This is believed to be due to the removal of the styrene monomer by stripping and other non-rubber constituents by acetone extraction.

However, Table 5.4 shows that increase in the amount of initially added MADPA in NR slightly reduces the degree of binding. This could be due to lower shear caused by softening or lubrication effect of the higher amounts of mercaptan used. It is shown in Table 5.5 that when the amount of NR used in the torque rheometer was reduced from 30 to 10 g the amount of antioxidant bound dropped significantly. This may be due to lower activation by shear or the effect of O_2 as the amount of rubber reduced. Various attempts were also made to bind phenolic antioxidants containing thiol and sulphur functional groups (BHBM, BTGE and BTGA, BTPA) with natural rubber during processing in the torque rheometer and under different conditions but were not successful.

5.2. Chemical Binding of Antioxidants to Natural and Styrene-Butadiene Rubbers during Vulcanisation

5.2.1. Introduction

Competition with newer chemically resistant polymers, higher operating temperatures, stricter test specifications and perhaps a more discriminating consuming public have all contributed to the present demand for natural and synthetic rubber components with high resistance to degradation. For satisfactory performance, antioxidants must not only be designed for high intrinsic activity, but must also be resistant to physical loss from the articles by evaporation or extraction. Chemical attachment of antioxidants to the rubber backbone during vulcanisation has been studied by many investigators (106,111,118). Cain and co-workers (108-111) have shown that antioxidants with a reactive nitroso group can become bound to rubber containing α-methylenic hydrogen during compounding and vulcanisation. They have also shown that reduced mobility was not a barrier to the activity of highly efficient bound antioxidants. In the present work the reaction of antioxidants with NR and SBR was studied at various conditions in order to investigate the possibility of adduct formation during vulcanisation. The amount of antioxidant becoming bound to the rubber was assessed by comparing the infra-red spectra of the vulcanisate before and after azeotropic extraction and measuring the intensities of the characteristic peaks due to antioxidant (see Section 2.3.3.).

5.2.2. Reactions of BTGA and BTPA with Natural Rubber during Milling and Vulcanisation

10 g of dried extracted rubber was milled with known quantities of BTGA and BTPA (1-3%) on a 12" laboratory two-roll mill with a nip size of 4 thou. The other vulcanising ingredients were added for a

further period of 3 minutes and the compounded rubber was vulcanised as described previously (see Section 2.2.2). The results are shown in the following table.

TABLE 5.6

Antioxidant	Initial concentration of antioxidant	Antioxidant Bound	
	g/100 g NR	g / 100 g NR	% bound
BTGA	1	0.04	4
	2	0.26	13
	3	0.63	21
BTPA	1	0.13	13
	2	0.45	22
	3	1.05	35

These antioxidants did not become bound to NR prior to vulcanisation.

5.2.3. Reactionsof BHBM and BTGE with Natural Rubber during Milling and Vulcanisation

Reactions of 3,5-ditertiarybutyl-4-hydroxybenzyl mercaptan (BHBM) and 3,5-ditertiarybutyl-4-hydroxybenzyl mercapto glycollate (BTGE) during vulcanisation were studied. BHBM and BTGE were added to the extracted natural rubber and compounded in a similar manner to those described in previous sections. The vulcanisation was carried out in the usual way (see Section 2.2.2) and vulcanised films were subjected to exhaustive extraction with an azeotropic mixture and the amounts of bound antioxidants were determined using the base-line technique (see Section 2.3.3). The results are given in the following table.

TABLE 5.7

Antioxidant	Initial concentration of antioxidant	Antioxidant Bound	
	g/100 g NR	g/100 g NR	% bound
BHBM	1	0.21	21
	2	0.59	29
	3	0.95	32
BTGE	1	0.22	22
	2	0.57	28
	3	1.14	38

5.2.4. Reactions of BTGA and BTPA with Natural Rubber during Processing in the Torque Rheometer and Subsequent Vulcanisation

Since it was found that most of the antioxidants used in the present work can readily become bound during pre-mixing and vulcanisation it was important to assess the effect of pre-mixing of antioxidants with the rubber in an internal mixer where the processing conditions could be accurately controlled. The RAPRA torque rheometer was used for this purpose.

5.2.4.1. Effect of Concentration

10 g of extracted natural rubber was sheeted out, BTGA or BTPA (2-4%) in the form of fine powder was spread over the sheet. The rubber was then rolled in and cut into small pieces. The mixing was carried out at 70°C for a period of 10 minutes with the chamber of the torque being closed. The rubber after processing was quenched in cold water and dried. The other vulcanising ingredients were added on a 12" laboratory two-roll mill and vulcanisation was carried out in a similar manner as described previously, (see Section 2.2.2). The vulcanised films were extracted and the amount of antioxidant bound was determined (see Section 2.3.3). The following table represents the results obtained.

TABLE 5.8

Antioxidant	Initial concentration of antioxidant	Antioxidant Bound	
	g/100 g NR	g/100 gNR	% bound
	2	0.53	26
BTGA	3	1.14	38
	4	1.61	40

Continued...

TABLE 5.8 (continued....)

Antioxidant	Initial concentration of antioxidant	Antioxidant	Bound
	g/100 g NR	g/100 g NR	% bound
BTPA	2	0.63	31
	3	1.17	39
	4	1.90	47

5.2.4.2. Effect of the Amount of Rubber

For optimizing the yield of adduct formed during vulcanisation it was important to study the variation in the amount of rubber used during processing. The concentrations of BTGA and BTPA were kept constant at 2 g/100 g of natural rubber. The other variables such as time and temperature of processing were also kept constant at 10 minutes and 70°C respectively. The processed samples were vulcanised and the amounts of bound antioxidants were determined as described previously. The results of these studies are shown in the following table.

TABLE 5.9

Antioxidant	NR used (g)	Antioxidant bound g / 100 g NR	Antioxidant bound % bound
BTGA	10	0.53	26
	20	1	50
	30	1.16	58
BTPA	10	0.63	31
	20	0.96	48
	30	1.09	55

5.2.4.3. Effect of Processing Temperature

The effect of processing temperature on the yield of bound antioxidant formed from BTGA and natural rubber during vulcanisation was studied. 30 g of extracted natural rubber was processed with 0.6 g of BTGA (2 g / 100 g NR) in the torque rheometer at temperatures of 50, 70, and 90°C. The processing was carried out for 10 minutes and processed samples were vulcanised and extracted. The amount of bound antioxidant for each vulcanisate was determined as described previously (see section 2.3.3). The results are given in the following table.

TABLE 5.10

Processing Temperature	BTGA Bound	
°C	g/100 g NR	% Bound
50	0.98	49
70	1.16	58
90	0.96	42

5.2.4.4. Effect of Processing Time

Variation in processing time on the extent of binding of BTGA with natural rubber during vulcanisation was evaluated. BTGA (0.6 g) was processed with 30 g of extracted natural rubber for 5, 10, and 15 minutes at 70°C. The amount of bound antioxidant was determined for vulcanisates processed at various times and the results are shown in the following table.

TABLE 5.11

Processing Time	BTGA Bound	
minutes	g/100 g NR	% Bound
5	0.98	49
10	1.16	58
15	0.96	44

5.2.5. Reactions of BHBM and BTGE with Natural Rubber during Processing in the Torque Rheometer and Subsequent Vulcanisation

5.2.5.1. Effect of Concentration

Phenolic antioxidants containing thiol functional groups such as BTGE and BHBM were processed with 10 g natural rubber in the RAPRA torque rheometer at various concentrations. The processing temperature was kept at 70°C, and 10 minutes of processing was allowed. The procedure of compounding, vulcanisation and determination of the amount of bound antioxidant was similar to that described previously. The results are shown in the following table.

TABLE 5.12

Antioxidant	Initial concentration of antioxidant	Antioxidant Bound	
	g/100 g NR	g/100 g NR	% Bound
	2	0.49	24
BHBM	3	1.41	37
	4	2.13	53
	2	0.8	40
BTGE	3	1.38	45
	4	1.97	49

5.2.5.2. Effect of the Amount of Rubber

Attempts were made to optimize the efficiency of binding of BHBM and BTGE to natural rubber during vulcanisation by varying the amount of rubber used during processing in the torque rheometer. Extracted natural rubber in quantities of 10, 20 and 30 g were processed with BHBM and BTGE at 2% (2g/100 gNR) level. The time and temperature of processing were kept constant at 10 minutes and 70°C respectively. The amount of bound antioxidant was determined and the results are shown in the following table.

TABLE 5.13

NR Used	BHBM Bound		BTGE Bound	
g	g/100 g NR	% bound	g/100g NR	% bound
10	0.49	24	0.92	41
20	0.77	38	1	50
30	0.99	49	1.08	54

5.2.5.3. Effect of Processing Temperature

In order to find the best processing temperature for binding BHBM to NR during vulcanisation a set of experiments was carried out in which the temperature was varied but all other parameters were kept constant. 30 g of NR was processed with 0.6 g of BHBM (2g/100 g NR) at the temperatures of 50, 70, and 90°C in the torque rheometer for a period of 10 minutes. The processed samples were compounded, vulcanised and continuously hot extracted with the azeotropic mixture. The amount of BHBM bound to the rubber was determined for each sample using the IR technique (see Sections 2.2.2. and 2.3.3). The results are given in the following table.

TABLE 5.14

Processing Temperature	BHBM Bound	
°C	g/100 g NR	% Bound
50	0.78	39
70	0.99	49
90	0.66	33

5.2.5.4. Effect of Processing Time

Attempts were made to investigate the effect of processing time on the yield of adduct formed from BHBM with natural rubber during vulcanisation. 30 g of extracted natural rubber and 0.6 g BHBM were processed for 5, 10 and 15 minutes at 70°C. The processed samples were compounded, vulcanised, extracted and the amount of bound antioxidant was determined in a similar manner as described previously.

Table 5.15 shows the results obtained.

TABLE 5.15

Processing Time	BHBM Bound	
(minutes)	g/100 g NR	% Bound
5	0.8	40
10	0.99	49
15	0.76	38

5.2.6. Reactions of Derivatives of Antioxidants with Natural Rubber during Processing and Vulcanisation

A set of experiments was carried out in order to evaluate the possibility of reacting antioxidant derivatives with natural rubber during vulcanisation. 0.6 g of BHBM and BTGE mono- disulphides, BTBE and also 3,5-ditertiarybutyl-4-hydroxybenzyl alcohol were processed in the torque rheometer with 30 g of extracted natural rubber at 70°C for a period of 10 minutes. The processed samples were compounded, vulcanised, extracted and the amount of bound antioxidant was determined for each vulcanisate. The results are shown in Table 5.16.

TABLE 5.16

Antioxidant	Antioxidant Bound	
	g / 100 g NR	% Bound
BHBM monosulphide	0.091	6
BHBM disulphide	0.9	45
BTGE disulphide	0.97	48
BTBE	0.26	6
Benzyl alcohol	None	None

5.2.7. Reactionsof Antioxidants with Styrene-Butadiene Rubber during Processing and Vulcanisation

Phenolic antioxidants containing thiol functional groups (BHBM and BTGE) and also phenolic sulphides (BTGA and BTPA) were reacted with styrene-butadiene rubber during vulcanisation. 30 g of stripped-extracted SBR was processed with 0.6 g of the corresponding antioxidants at 70°C for a period of 10 minutes in the torque rheometer. The amount of bound antioxidant was determined by camparing the hydroxyl ratios of the extracted and unextracted vulcanisates in their infra-red spectra (see Section 2.3.3.). The results are given in the following table.

TABLE 5.17

Antioxidant	Antioxidant Bound	
	g/100 g SBR	% Bound
BTGA	1.12	55
BTPA	0.83	46
BHBM	1.33	57
BTGE	0.96	44

5.2.8. Attempts to Improve the Yield of Bound Antioxidant on Natural and Styrene-Butadiene Rubbers Processed with MADPA in the Torque Rheometer

Since it was found that some antioxidants which did not bind to NR during pre-mixing could be readily bound during vulcanisation, it was decided to vulcanise the pre-mixed rubber stocks containing bound and unbound MADPA in an attempt to improve the overall degree of binding. Unextracted-grafted NR and SBR were used for preparation of solid masterbatches. NR and SBR processed in the torque rheometer containing MADPA (10 g/100 g NR) were added to the extracted NR and extracted-stripped SBR as a conventional additive on a 12" water-cooled two-roll mill. Rubbers containing various concentrations of MADPA (0.25, 0.5, 1 and 2%) were prepared. NR and SBR stocks were then compounded and vulcanised as described in Section 2.2.1. and 2.2.2. respectively. The vulcanisates were extracted and the amounts of bound antioxidants were determined on vulcanisates containing 2% MADPA. The results are shown in Table 5.18.

TABLE 5.18

Type of Rubber	MADPA Bound Before Vulcanisation		After Vulcanisation	
	g/100 g	% bound	g/100 g	% bound
NR	1	50	1.36	68
SBR	1.16	58	1.48	74

5.2.9. Attempts to Improve the Yield of Bound Antioxidant in SBR Processed with BHBM in the Torque Rheometer

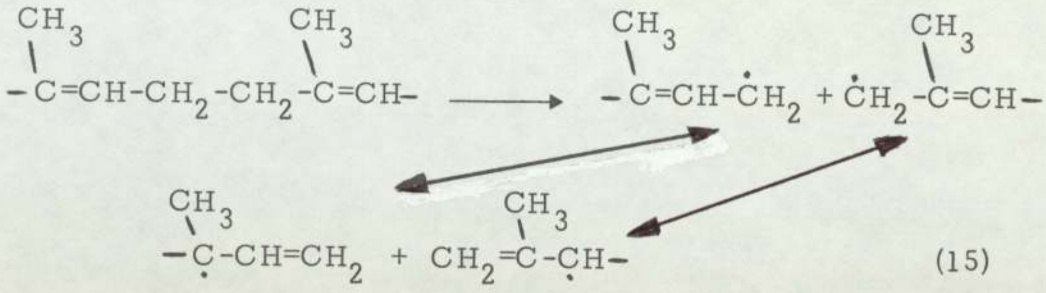
SBR processed with BHBM in the torque rheometer (see Section 5.1.3) was used to prepare solid masterbatches. Unextracted-processed SBR containing bound and unbound BHBM was added to stripped-extracted SBR on a 12" water-cooled two-roll mill in order to prepare rubber containing various concentrations of BHBM (0.25, 0.5, 1 and 2%). The masterbatches were then compounded, vulcanised and extracted. The hydroxyl ratios of the extracted and unextracted vulcanisates were compared and the amounts of bound antioxidants were determined. The results are shown in the following table.

TABLE 5.19

Initial concentration of BHBM	BHBM Bound Before Vulcanisation		After Vulcanisation	
g / 100 g SBR	g/100 g SBR	% bound	g/100 g SBR	% bound
0.25	0.11	43	0.15	60
0.5	0.21	"	0.31	62
1	0.43	"	0.56	56
2	0.86	"	1.16	58

5.2.10. Discussion

Plasticization of rubber by mastication has been a basic operation since its discovery in the early days of the rubber industry. The dependence of plasticizing efficiency on variables such as oxygen concentration, temperature and design of masticator has now been well established $^{(145)}$. It has been generally recognised that the plasticization of rubber results from the shortening of the long molecular chains. The shearing forces acting on rubber during cold mastication are mainly used to overcome intermolecular forces in bulk deformation of the rubber. These forces can cause breaking down of primary bonds in polyisoprene chain, producing two free radicals :

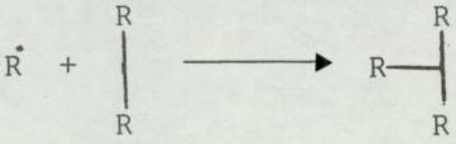


$$-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH- \longrightarrow -\overset{CH_3}{C}=CH-\dot{C}H_2 + \dot{C}H_2-\overset{CH_3}{C}=CH-$$

$$-\overset{CH_3}{\underset{\bullet}{C}}-CH=CH_2 + CH_2=\overset{CH_3}{C}-\underset{\bullet}{C}H- \qquad (15)$$

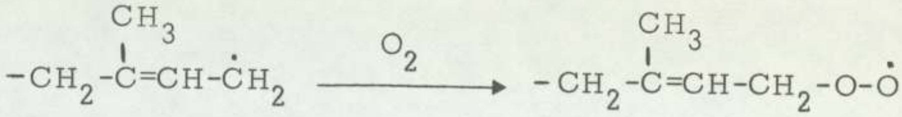
The rate of scission to radicals depends upon both the distribution of shearing forces and the nature of the polymer; and therefore, it is a function of several variables, e.g. viscosity and temperature of the polymer, geometry and performance of the plasticizing apparatus, and the strength of the primary chemical bonds in the polymer chain. In the presence of nitrogen and in the absence of radical acceptors recombination will be the normal fate of the radicals. Branching or crosslinking may also occur if a radical reacts with another polymer molecule :

$$\dot{R} + \dot{R} \longrightarrow R-R \qquad (16) \text{ recombination}$$

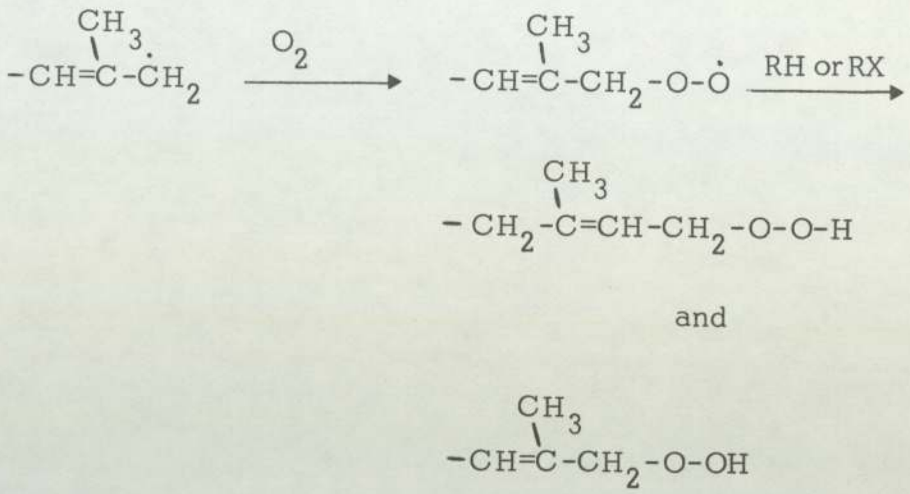


$$\dot{R} + \overset{R}{\underset{R}{|}} \longrightarrow R\!-\!\overset{R}{\underset{R}{|}} \qquad (17) \text{ branching}$$

If oxygen is present during mastication it reacts readily with macroradicals to form peroxy radicals which are deactivated by hydrogen abstraction from other rubber molecules or from non-rubber constituents:(145-148)



$$\mathrm{-CH_2-\overset{CH_3}{C}=CH-\dot{C}H_2 \xrightarrow{O_2} -CH_2-\overset{CH_3}{C}=CH-CH_2-O-\dot{O}} \tag{18}$$

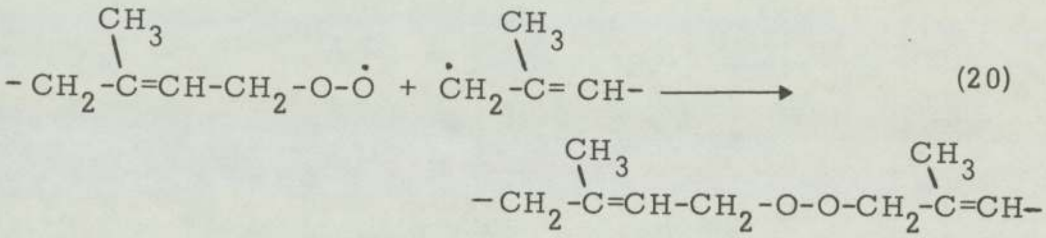


$$\mathrm{-CH=\overset{CH_3}{C}-\dot{C}H_2 \xrightarrow{O_2} -CH=\overset{CH_3}{C}-CH_2-O-\dot{O} \xrightarrow{RH\ or\ RX} -CH_2-\overset{CH_3}{C}=CH-CH_2-O-O-H} \tag{19}$$

and

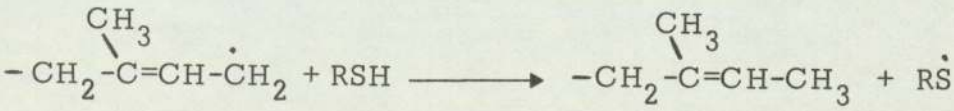
$$\mathrm{-CH=\overset{CH_3}{C}-CH_2-O-OH}$$

Peroxy radicals can also react with rubber macroradicals :

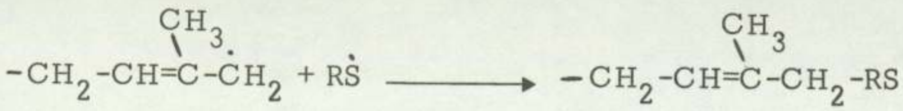


$$\mathrm{-CH_2-\overset{CH_3}{C}=CH-CH_2-O-\dot{O} + \dot{C}H_2-\overset{CH_3}{C}=CH- \longrightarrow -CH_2-\overset{CH_3}{C}=CH-CH_2-O-O-CH_2-\overset{CH_3}{C}=CH-} \tag{20}$$

Such oxidized rubber has been used as an initiator for block copolymer synthesis.(149) In the presence of free radical acceptors, under nitrogen, the macroradicals from mechanical scission are terminated by hydrogen transfer or by combination with radical acceptors :



$$\mathrm{-CH_2-\overset{CH_3}{C}=CH-\dot{C}H_2 + RSH \longrightarrow -CH_2-\overset{CH_3}{C}=CH-CH_3 + R\dot{S}} \tag{21}$$



$$\mathrm{-CH_2-CH=\overset{CH_3}{C}-\dot{C}H_2 + R\dot{S} \longrightarrow -CH_2-CH=\overset{CH_3}{C}-CH_2-RS} \tag{22}$$

Aromatic thiols are well known as "transfer catalysts" for autoxidation, and one of their main functions in the chemical plasticization of rubber at temperatures above 100°C is to reduce the activation enery of the autoxidation chain reaction (6):

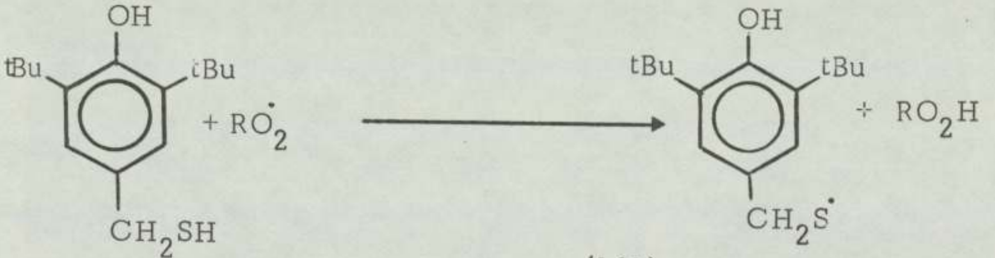
$$R\dot{O}_2 + ArSH \longrightarrow ROOH + Ar\dot{S} \qquad (23)$$

$$Ar\dot{S} + RH \longrightarrow ArSH + \dot{R} \qquad (24)$$

Aromatic disulphides are also known (8) to act as efficient radical acceptors during the mastication of natural and styrene-butadiene rubbers. They react with free radicals by cleavage of the S-S bond and produce thiyl radicals :

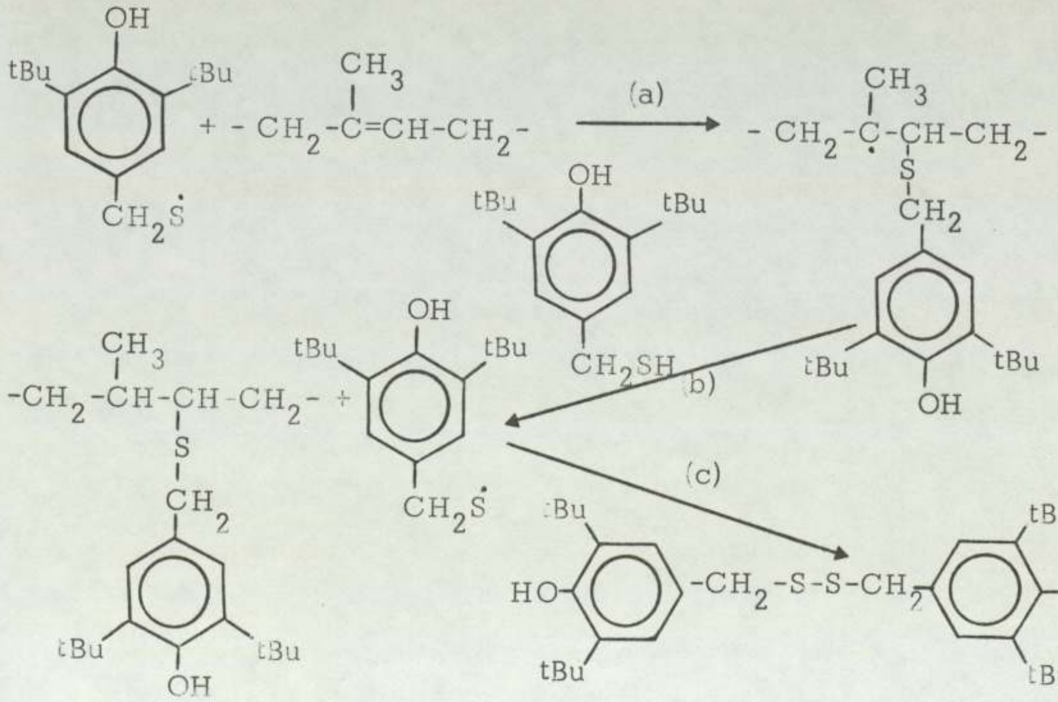
$$Ar - S\text{-}S\text{-}Ar + \dot{R} \longrightarrow RSAr + Ar\dot{S} \qquad (25)$$

In the present work sulphur-containing phenolic antioxidants and also MADPA were found to react readily with natural and styrene-butadiene rubbers during vulcanisation. As shown in Table 5.6 BTGA and BTPA can react with natural rubber after milling and during vulcanisation. Results in this table clearly indicate that as the concentration of antioxidant increases there is an increase in the amount of rubber-bound antioxidant. BHBM and BTGE were also reacted with NR under similar conditions (see Table 5.7). The extent of binding at the same concentration were found to be higher in the case of thiols than BTGA and BTPA. Results in Table 5.8 and 5.12 show that higher binding of the sulphur containing phenolic antioxidants can be achieved if the premixing is carried out in the torque rheometer rather than on a two-roll mill. This is evident when the results in Table 5.8 and 5.12 are compared with those of Table 5.6 and 5.7. Alkenyl radicals formed during milling or processing in the torque rheometer due to shear forces, can react with oxygen to produce alkenyl peroxy radicals (reaction, 18 and 19). These radicals would then readily react with, for instance, thiols such as BHBM to produce benzylthiyl radical :



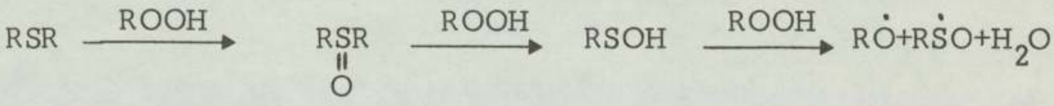
(26)

The benzyl thiyl radicals have been shown(101) to undergo facile addition to the double bond in natural rubber as follows :



(27)

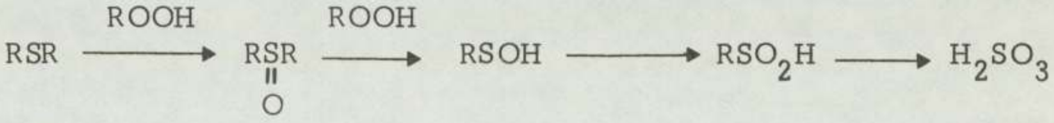
The reaction is a radical chain process mainly terminated by dimerization of the thiyl radicals(27c). During milling of BHBM and NR in air the concentration of peroxy radicals is expected to be higher than that produced during mixing in the torque rheometer. This will lead to higher concentration of hydroperoxide formed. Scott(32-39) *et al.,* have shown that the behaviour of sulphur-containing antioxidants in the presence of hydroperoxides is dependent upon their respective molar ratios. At molar ratios of $\frac{ROOH}{RSR} < 1$ there was found to be a pro-oxidant effect due to the redox radical-generating reaction between sulphenic acid and hydroperoxide :



$$RSR \xrightarrow{ROOH} \underset{\overset{\|}{O}}{RSR} \xrightarrow{ROOH} RSOH \xrightarrow{ROOH} R\dot{O} + R\dot{S}O + H_2O$$

(28)

They have shown that at molar ratios of $\frac{ROOH}{RSR} > 1$ Lewis acid antioxidant species are formed :



$$RSR \xrightarrow{ROOH} \underset{\overset{\|}{O}}{RSR} \xrightarrow{ROOH} RSOH \longrightarrow RSO_2H \longrightarrow H_2SO_3$$

(29)

Therefore, it is reasonable to suggest that higher yields of binding in vulcanisates which had been pre-mixed with antioxidants in the torque rheometer could be due to reaction (28) occurring as a result of the limited oxygen available in the system. This is further confirmed by increase in binding efficiency of the phenolic antioxidants as the concentration of initially added antioxidant is increased (i.e. $\frac{ROOH}{RSR} < 1$ see Tables 5.6, 5.7, 5.8 and 5.12). Variation in the amount of rubber used during processing was found to have a significant effect on the yield of bound antioxidant formed during vulcanisation. Results given in Table 5.9 indicate that an increase in the amount of rubber used during processing from 10 to 30 g (full chamber) can result in a considerable improvement in the yield of rubber-bound antioxidant. This could be due to two reasons :

1. There is less hydroperoxide formed since the amount of air was reduced by increasing the amount of rubber.

2. There will be more shear forces and hence, more active free radicals are formed for initiating the grafting reaction.

The effectsof processing temperature on binding of phenolic sulphides (BTGA and BTPA) and thiols (BHBM and BTGE) during vulcanisation are shown in Table 5.10 and 5.14. It appears that maximum yield of bound antioxidant can be obtained when the pre-mixing operations are carried out at 70°C. This may suggest that apart from the effect of shear and air, some solubility is required to insure better dispersion and compatibility of the antioxidant with the rubber. Attempts were further made to optimize the yield of bound antioxidant obtained by varying the processing time. The results given in Tables 5.11 and 5.15 show that the maximum yield can be obtained after a period of 10 minutes processing. However, reaction of the antioxidant derivatives with natural rubber was also found to be possible after pre-treatment and during the subsequent vulcanisation. The results obtained are shown in Table 5.16. It is evident that the disulphides of BHBM and BTGE can also react with natural rubber during vulcanisation giving rise to a higher degree of binding. The mechanism of binding of disulphides to NR could involve the formation of the thiyl radicals (reaction 25) and their addition to the double bond (reactions 27a and 27b). Phenolic antioxidants containing sulphur and thiol groups were also found to bind with SBR during vulcanisation. This is shown in Table 5.17. Since it was found that most of the antioxidants incorporated into NR and SBR during pre-mixing can react with them during vulcanisation, it appeared possible to use the same process in order to improve the yield of bound antioxidant on rubber already containing some bound and unbound MADPA (see Table 5.1, 5.4 and 5.18). As shown in Table 5.18, the extent of binding of MADPA pre-mixed with NR and SBR in the torque rheometer can be further increased by about 16-18% during the vulcanisation. Similarly, vulcanisation of SBR containing bound and unbound BHBM was found to improve the degree of binding by approximately 15-19% (see Table 5.2 and 5.19).

However, addition of phenolic antioxidants by normal compounding and without pre-treatment did not give any binding. This was particularly noticeable in the case of BHBM which was also previously reported by Fernando (95) and Lankro (132).

CHAPTER SIX

EVALUATION OF THE AGEING AND CURING PROPERTIES OF RUBBER-BOUND ANTIOXIDANTS

6.1 Oxygen Absorption Studies of Antioxidants Bound to Natural Rubber Latex

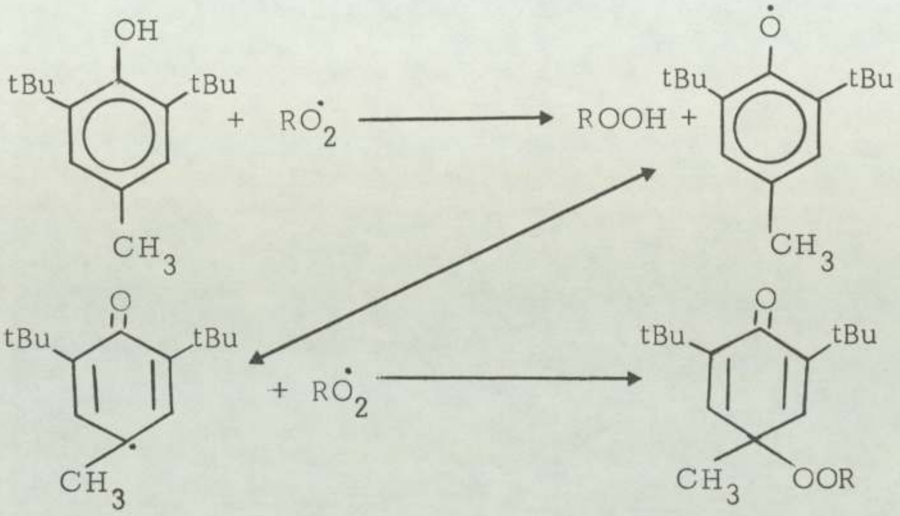
6.1.1. Introduction

The oxygen absorption technique has been in use for a (150, 151) long time. Oxygen attack on rubber is one of the main factors responsible for its ageing or degradation. Therefore it is logical to use the oxygen absorption technique in order to evaluate the ageing characteristics of rubber components. This technique has been increasingly used as a quick method for the comparison and assessment of chemical compounds used as antioxidants for rubber. Under certain conditions the results obtained from the oxygen absorption method correlate well with those obtained by the conventional technological method, in which the degradation of physical properties is measured after ageing in an oxygen bomb. In so far as this correlation exists, the oxygen absorption technique can be a simple replacement (from the technological point of view) of the conventional bomb ageing method of assessing relative antioxidant effectiveness. Under conditions where antioxidant loss from the polymer is not efficiency determining (oxygen absorption in a closed system) other factors become controlling. The most important of these factors appears to be the compatibility of antioxidant with the polymer (66). It has also been shown that there is (97) a relationship between the physical properties of antioxidants particularly solubility in the rubber and their relative effectiveness in an oxygen absorption test. In general, oxygen absorption studies involving model compounds and antioxidants gives information about the intrinsic antioxidant activity of the chemical structure, whereas polymer oxygen absorption tests emphasize solubility/compatibility aspects, and a flowing air test emphasizes additive volatility. The latter is of primary importance in polymer samples with a high surface area to volume ratio which are exposed to high temperatures, or flowing air atmospheres, or are subjected to detergent or solvent leaching operations.

6.1.2. Results and Discussion

In the present work the degree to which vulcanisates are protected by antioxidants bound to natural rubber latex was assessed by extracting unbound antioxidant from the grafted-uncured natural rubber with an azeotropic mixture (as described in Section 2.2) and measuring the absorption of oxygen by such vulcanisates with reference to a similarly treated control sample. These results along with those described in previous chapters, in which the amount of initially added antioxidant was assessed from infra-red studies, could then be used to give an indication of the effectiveness of the bound antioxidant involved. The procedure used for oxygen absorption was as described previously (see Section 2.5.1.2).

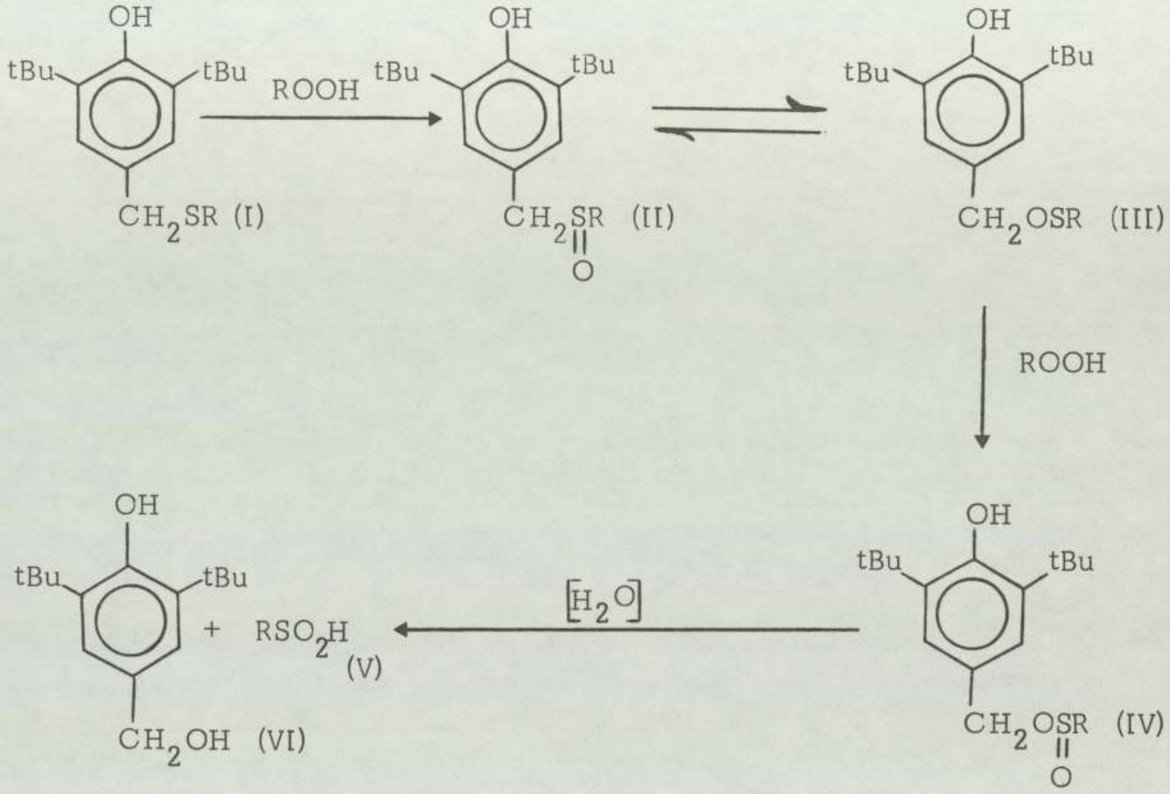
The inhibition of autoxidation has been widely studied for a number of inhibitors and substrates (152). In the case of hindered phenols the mechanism of inhibition has been established. These antioxidants have been shown to react in a stoichiometric manner and deactivate at least two peroxy radicals per molecule of antioxidant. The reaction of 2,6 di-tert-butyl-4-methylphenol (TBC) with peroxy radicals has been shown (49,53) to proceed as follows :



Phenoxy radicals are generally stabilized by resonance and are not capable of abstracting hydrogen atoms from the substrate. Denison and Condit (153) were the earliest workers to study the nature of the autoretardation which occurred with dialkyl and alkyl aryl monosulphides in lubricating oils. They concluded that the effect was probably the result of a stoichiometric reaction with hydroperoxide, thus removing from the system the main initiator of oxidation.

$$ROOH + R'SR' \longrightarrow ROH + R'SOR'$$

Scott and co-workers (33-39, 154) have shown that the powerful antioxidant activity of some phenolic compounds such as 3,5-di-tert-butyl-4-hydroxybenzyl sulphide is due to generation of a Lewis acid catalyst which can destroy a large number of moles of hydroperoxides per mole of sulphur compound. They have shown (154) that benzyl alkyl sulphide (I) can react with hydroperoxide to produce an unstable sulphoxide (II) which subsequently undergoes thermolysis to give sulphur oxy acids as follows :



When R is an alkyl group, the sulphinic acid (V) behaves as a powerful peroxide decomposing antioxidant eliminating SO_2 at high temperatures (36) :

$$RSO_2H \longrightarrow RH + SO_2 \xrightarrow{ROOH} SO_3$$

Figures 6.1 and 6.2 show the oxygen absorption of the extracted and unextracted BTGA and BTPA bound to NR latex (see Sections 4.2.3. and 4.3) respectively. The oxygen absorption of the vulcanisates containing BTGE and BTBE before and after extraction are shown in Figs. 6.3

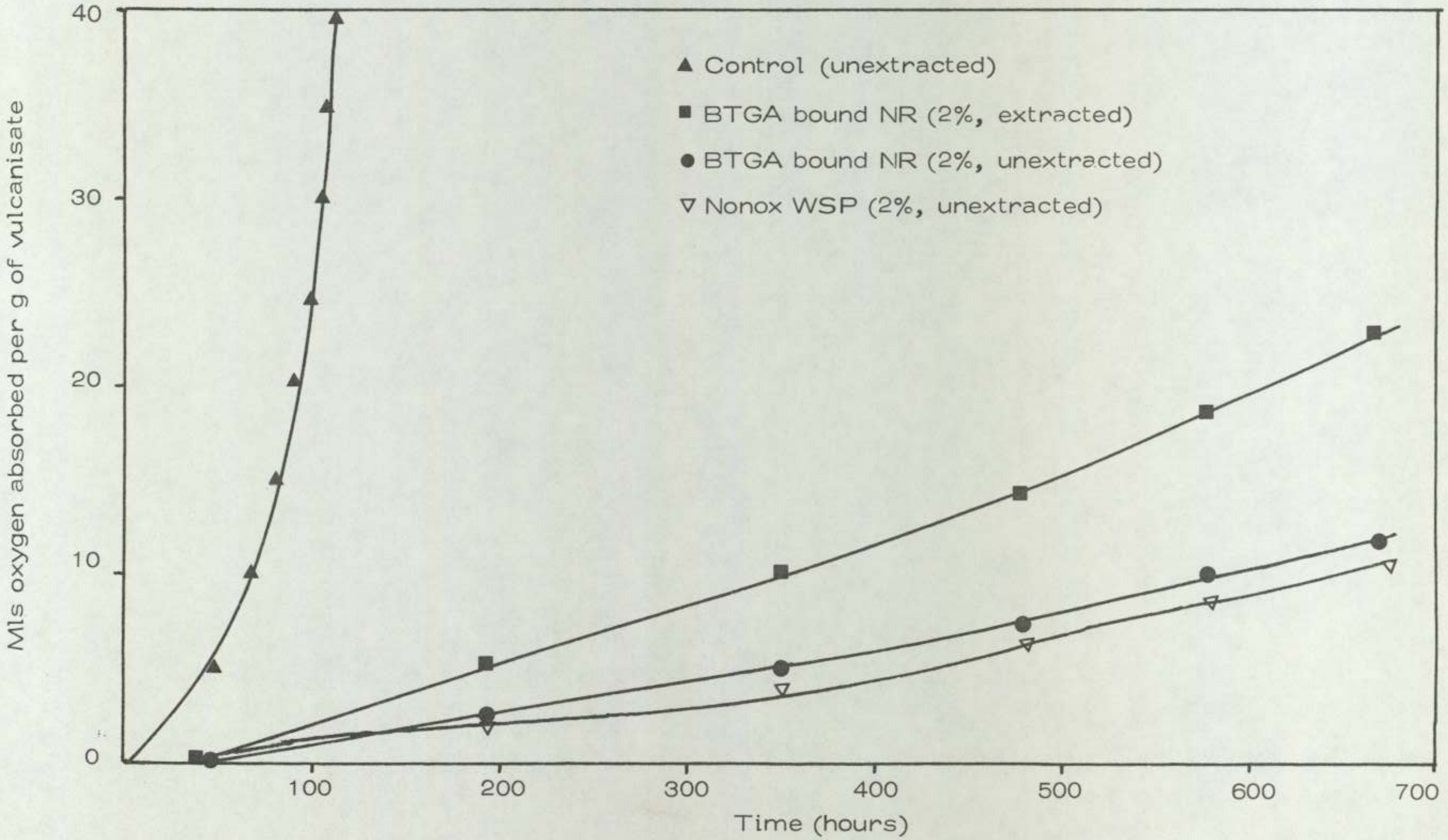


Fig. 6.1. Oxygen absorption of extracted and unextracted NR vulcanisates containing bound BTGA at 70°C.

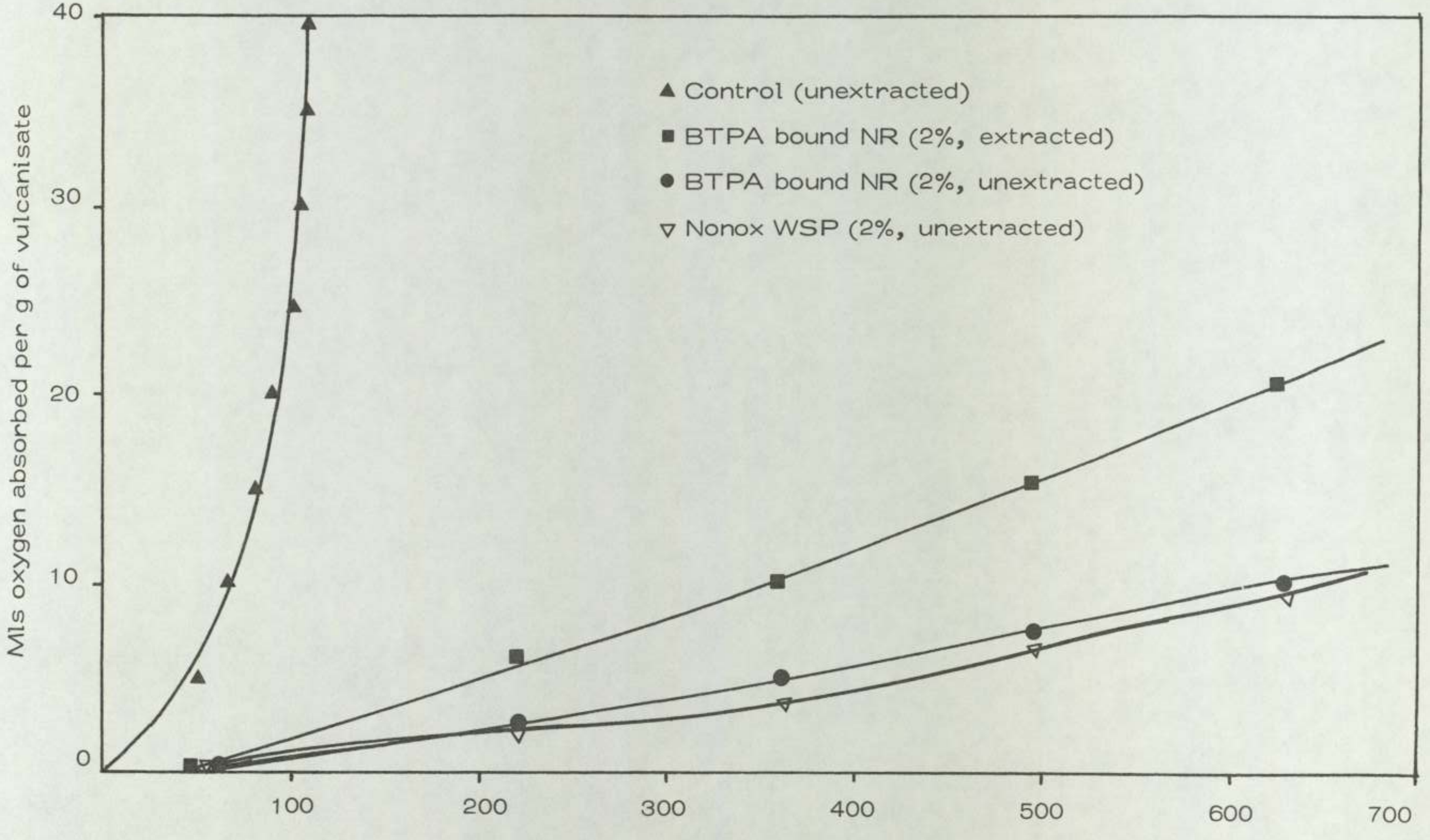


Fig. 6.2. Oxygen absorption of extracted and unextracted vulcanisates containing bound BTPA at 70°C. 70°C.

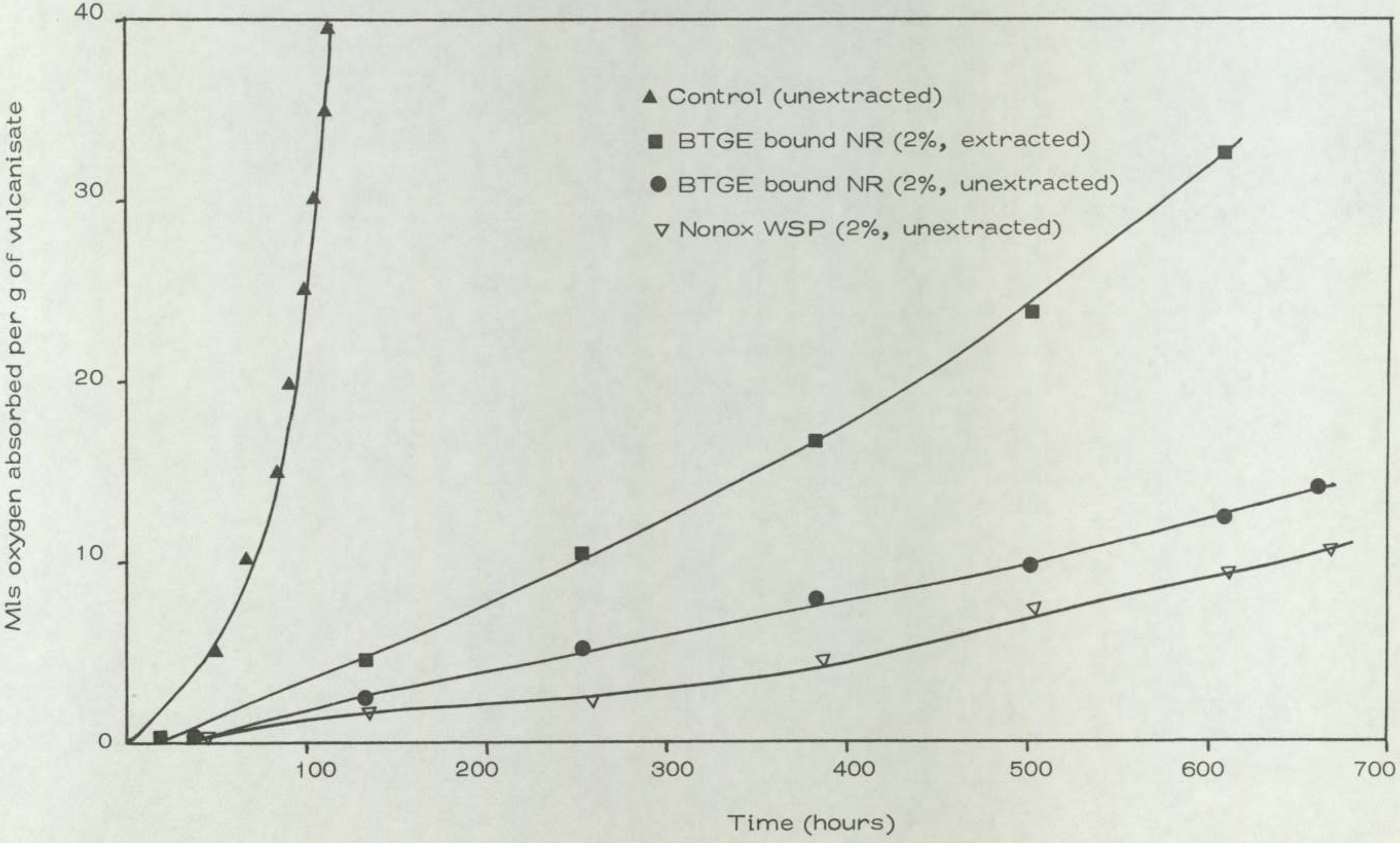


Fig. 6.3. Oxygen absorption of extracted and unextracted NR vulcanisates containing bound BTGE at 70°C.

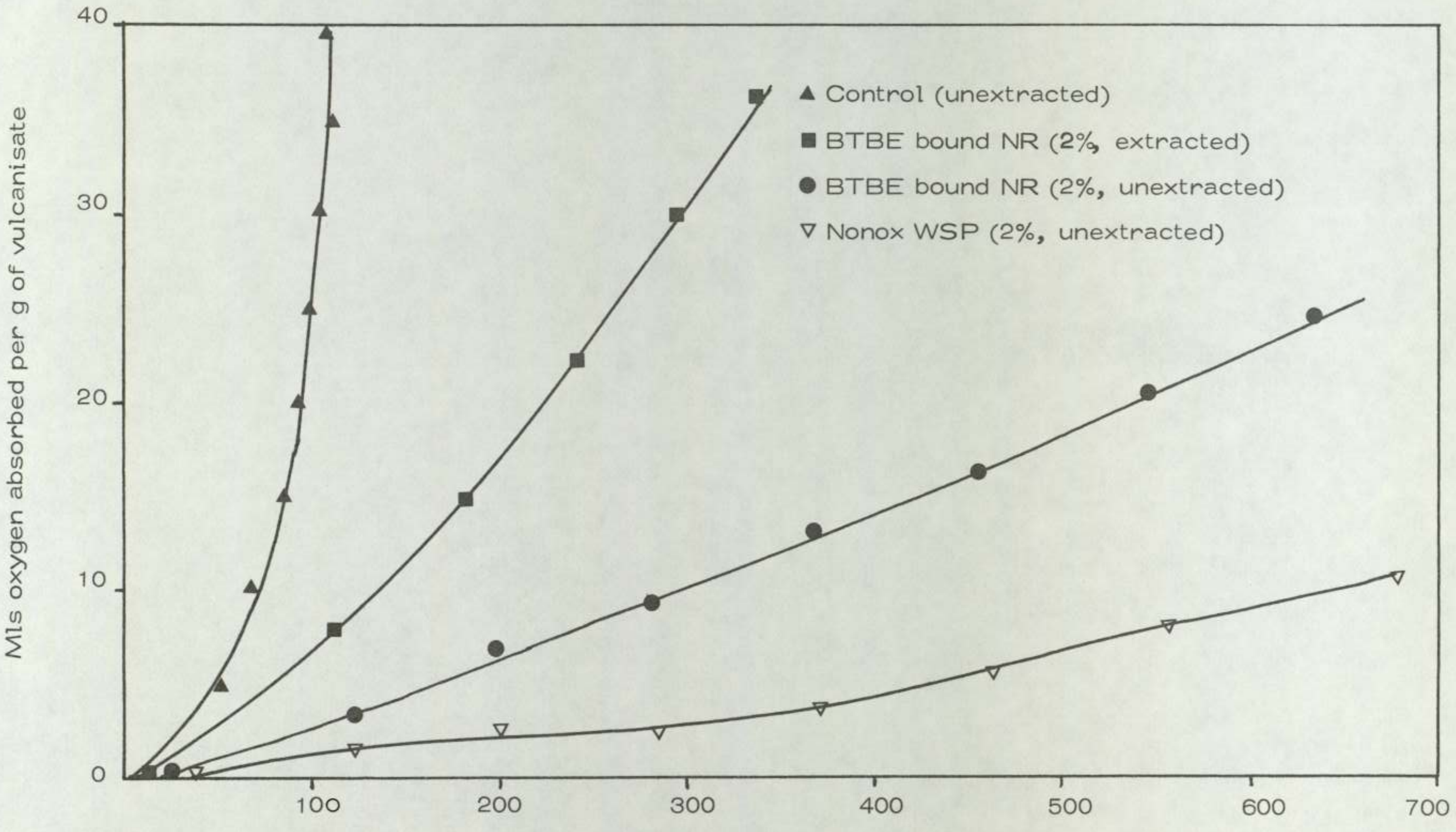


Fig. 6.4. Oxygen absorption of extracted and unextracted NR vulcanisates containing bound BTBE at 70°C

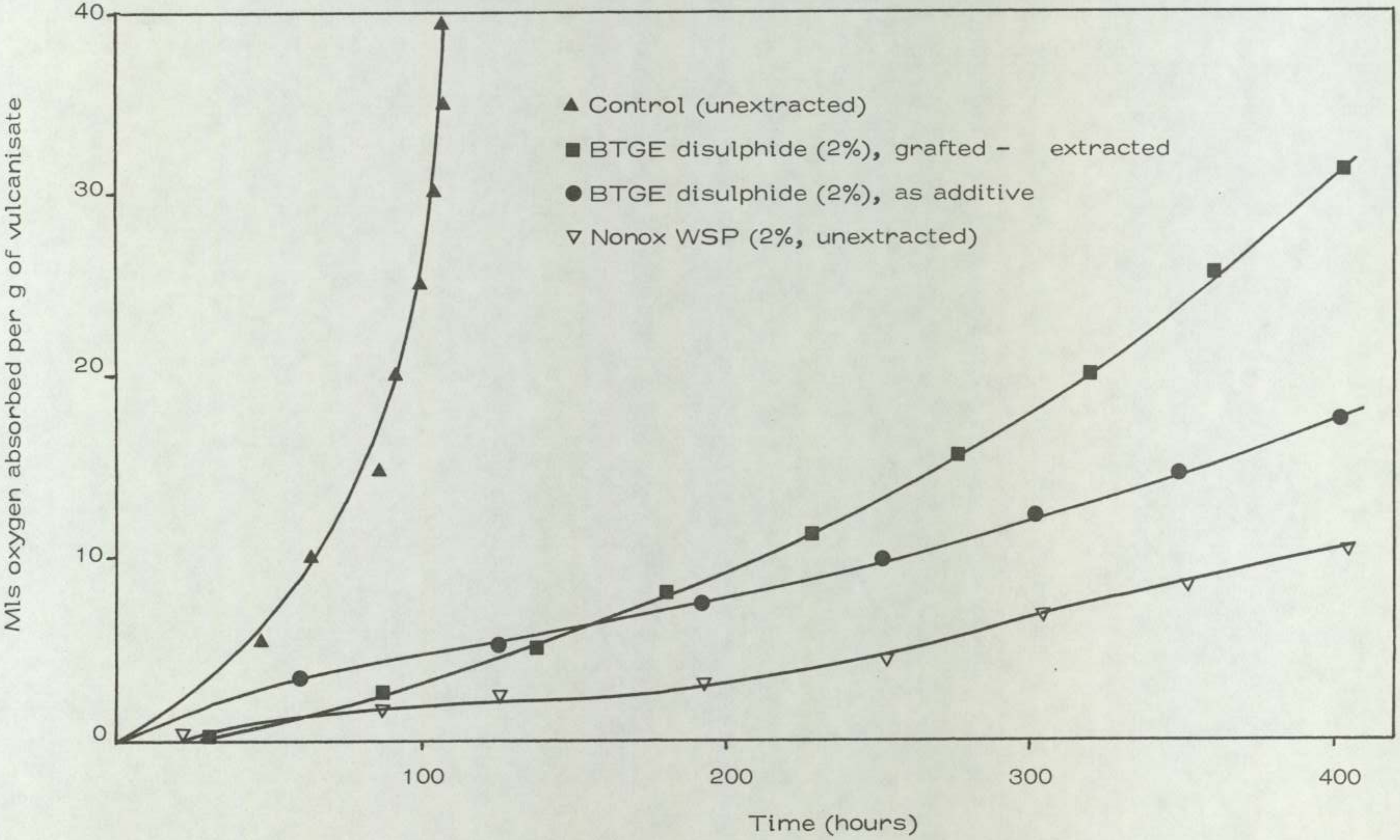


Fig. 6.5. Oxygen absorption of NR vulcanisates containing BTGE disulphide as additive and also as grafted–extracted at 70°C

and 6.4. BTGE disulphide reacted with NR latex (see Section 4.7) was also found to exhibit antioxidant activity both as grafted-extracted and as an additive. This is shown in Fig. 6.5. Grafted-extracted and unextracted NR reacted with BTGA at 4% level (see Section 4.2.5) was used for preparation of masterbatches. This was done by adding a given amount of grafted-extracted and unextracted rubber to fresh extracted NR on a 12" laboratory two-roll mill to prepare rubber stocks containing various concentrations of BTGA (0.5%, 1% and 2%). The diluted samples were compounded and vulcanised as described in Sections 2.2.1 and 2.2.2. The oxygen absorption curves for the extracted and unextracted vulcanisates are shown in Figs. 6.6 and 6.7. The results of these studies are summarised in Tables 6.1 and 6.2 so that the relative activity of each antioxidant could be compared.

Table 6.1. Antioxidant Activities of Vulcanisates Containing Bound Antioxidant Derived From NR Latex

Stock	% Bound	Induction Period (h)		Time to 1% oxygen absorption (h)	
		Unextracted	Extracted	Unextracted	Extracted
Control	-	4	0	52	9
BTGA	46	38	33	410	241
BTPA	55	41	35	422	248
BTGE	44	22	18	351	166
BTGE disulphide	26	-	14	-	164
BTBE	20	14	9	192	100
Nonox WSP 2% added	-	33	9	523	19

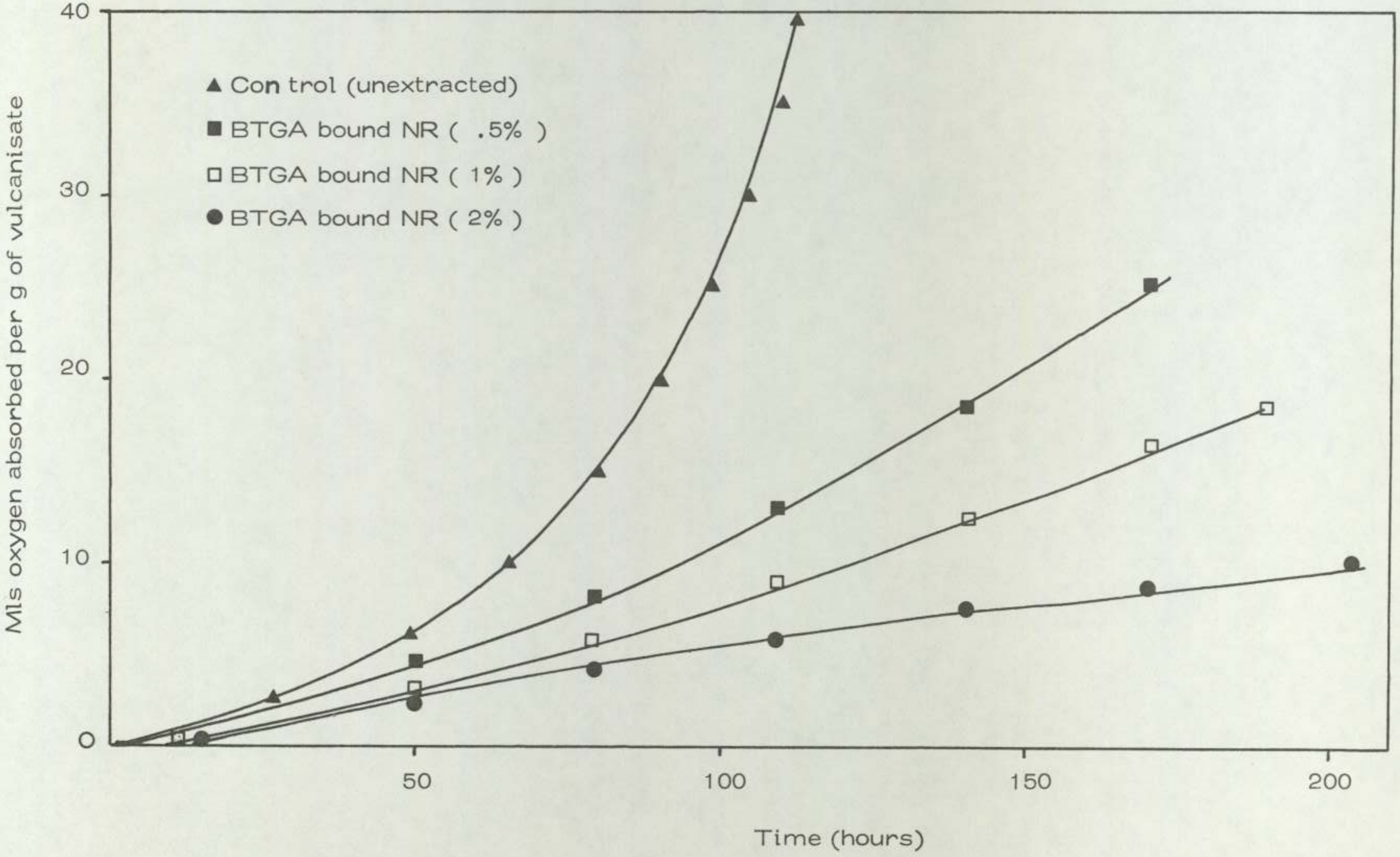


Fig. 6.6. Oxygen absorption of extracted masterbatches of BTGA bound to NR latex, at 70°C.

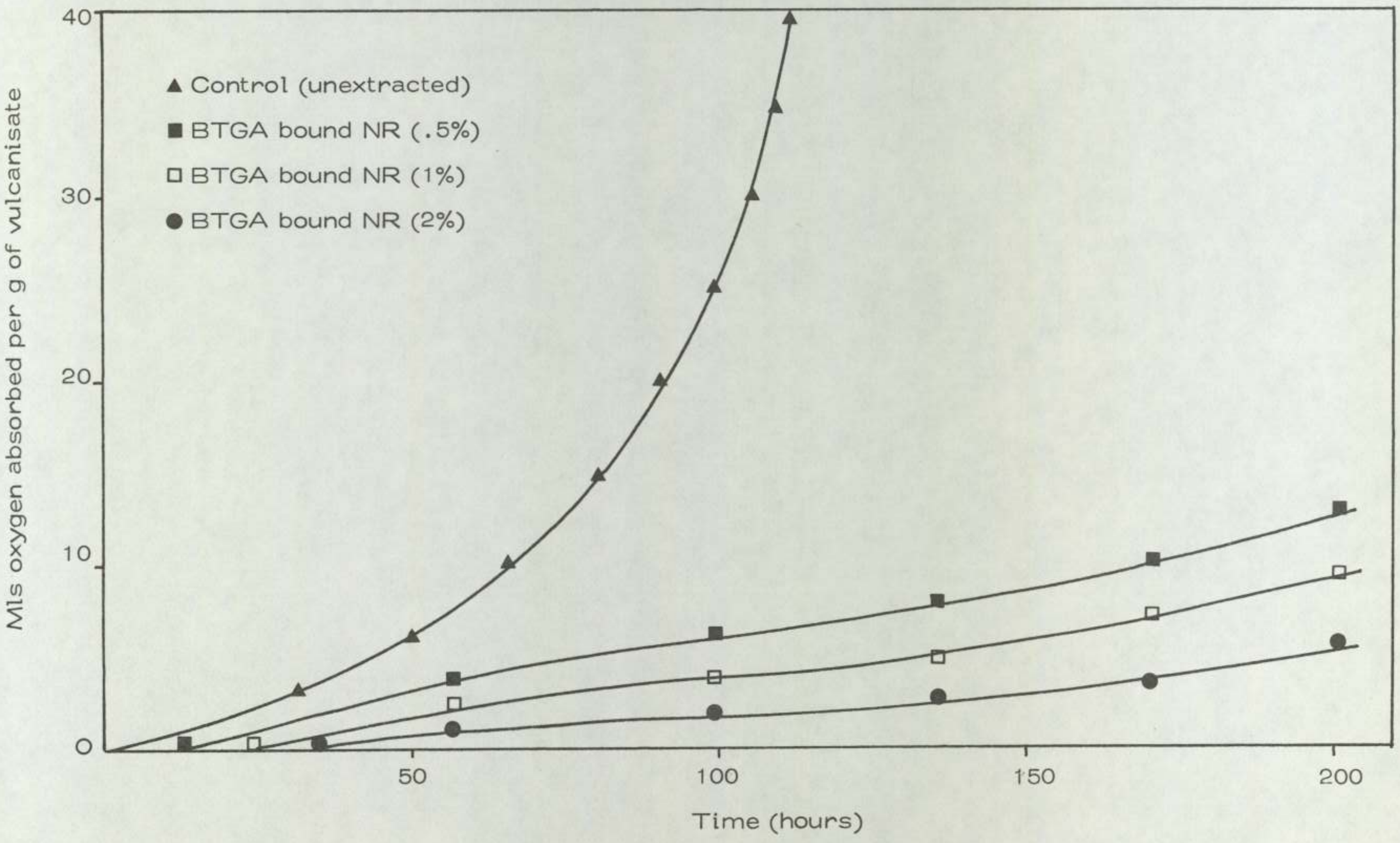


Fig. 6.7. Oxygen absorption of unextracted masterbatches of BTGA bound to NR latex, at 70°C.

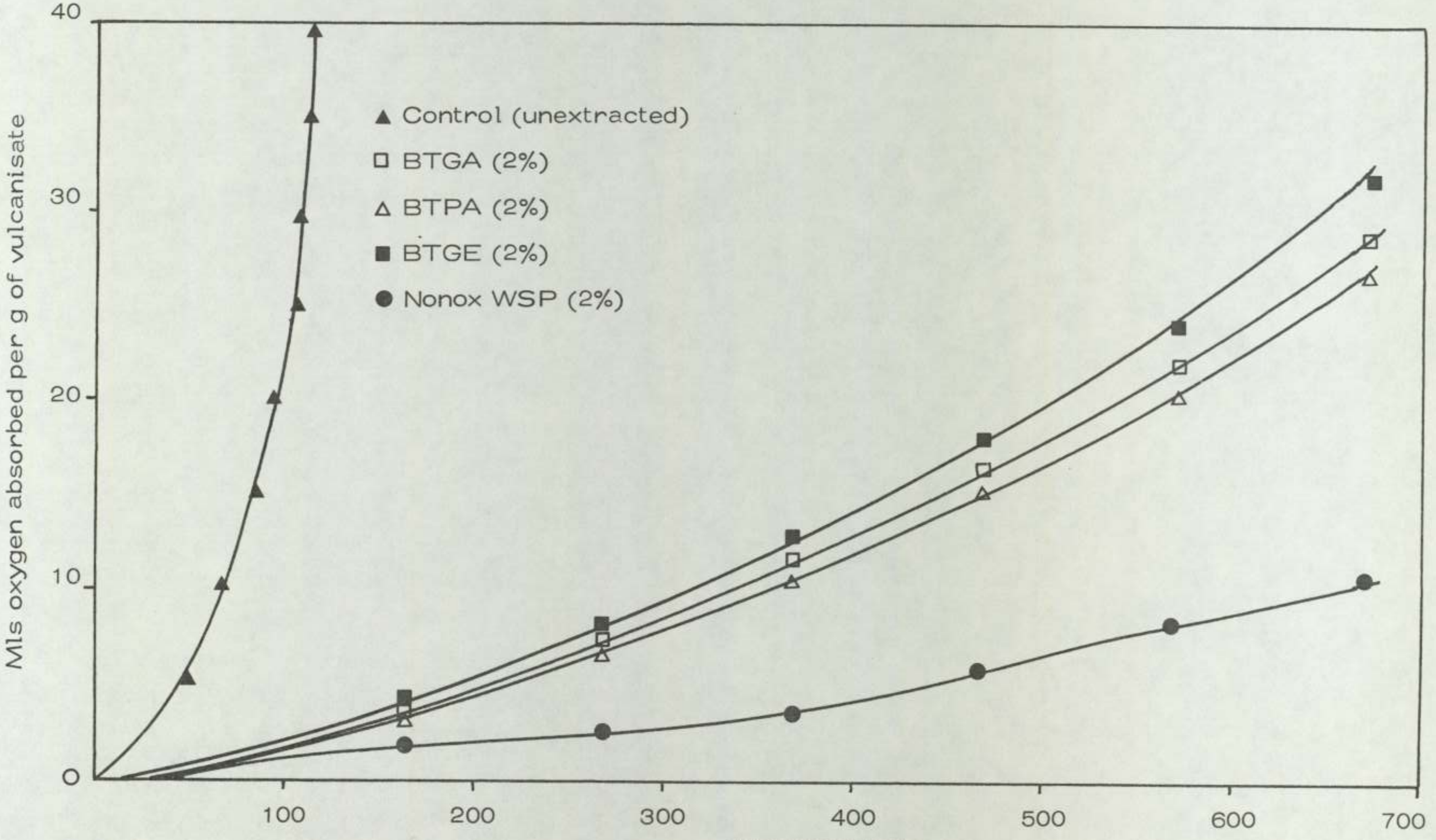


Fig. 6.8. Oxygen absorption of unextracted vulcanisates containing various antioxidants as additives at 70°C

TABLE 6.2. Antioxidant Activities of Masterbatches of BTGA with NR

BTGA Concentration (g/100 g NR)	Induction Period (h)		Time to absorb 1% oxygen absorption (h)	
	Unextracted	Extracted	Unextracted	Extracted
0.5	12	5	112	74
1	24	10	164	95
2	32	14	240	130

The oxygen absorption curves of vulcanisates containing 2% of BTGA, BTPA, BTGE and Nonox WSP as additives are shown in Fig. 6.8. The induction period and time to absorb 1% oxygen by these vulcanisates are given in Table 6.3.

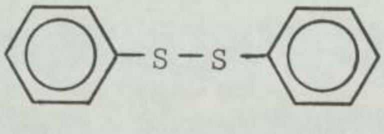
TABLE 6.3. Antioxidant Activities of Various Antioxidants as Additives

Antioxidant	Induction Period (h)	Time to absorb 1% oxygen (h)
BTGA	32	246
BTPA	37	250
BTGE	26	244
Nonox WSP	33	523
BTGE disulphide	None	179

Results in Table 6.1 indicate that BTPA bound to NR is very effective both before and after extraction. It can also be seen that the induction period and time to 1% oxygen absorption is longer for BTGA than BTGE. In the case of BTBE although only 20% (see Section 4.4) of the originally added 2 g became bound to NR (100 g) latex, the oxidation resistance is much superior than the similarly treated control (see also Fig. 6.4). The disulphide of BTGE reacted with NR latex also appears to be effective as a bound antioxidant. The effectiveness of Nonox WSP before extraction is better than any other phenolic antioxidant used but this was almost completely lost after extraction becoming similar to the extracted control. The effectiveness of Nonox WSP after extraction was found to be somewhat better than extracted control. This suggests that there might be a very small amount becoming bound to the rubber which could not be detected by infra-red spectroscopy.

Results in Table 6.2 show that BTGA added as masterbatch even at 0.5% concentration protects the vulcanisates against autoxidation compared with both the unextracted or extracted control. The antioxidant activity of a BTGA masterbatch was found to improve as the concentration was increased.

Results in Table 6.3 and Fig. 6.8 show that some of the above antioxidants incorporated as additives are also capable of producing high resistance to oxidation at 70°C. BTGE disulphide did not give any induction period (see also Fig. 6.5) suggesting that the antioxidant species are formed after an initial uptake of oxygen. Blundell and Scott (155) have shown that radical-generating and antioxidant-generating reactions are more complex in the case of the disulphides than in the case of the monosulphides and are very sensitive to temperature, peroxide/sulphide ratio and substrate, as well as to the chemical structure of the disulphide. This is confirmed by the work of Bateman <u>et al.,</u> (22) who have shown that unlike di-tert-butyl monosulphide and the derived sulphoxide which are both powerful antioxidants in uninitiated squalene, di-tert-butyl disulphide and diphenyl disulphide (VII) are almost ineffective as antioxidants, whereas the derived thiolsulphinate (VIII) are very powerful antioxidants under the same conditions.



(VII)

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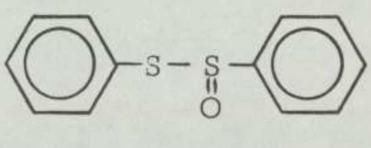


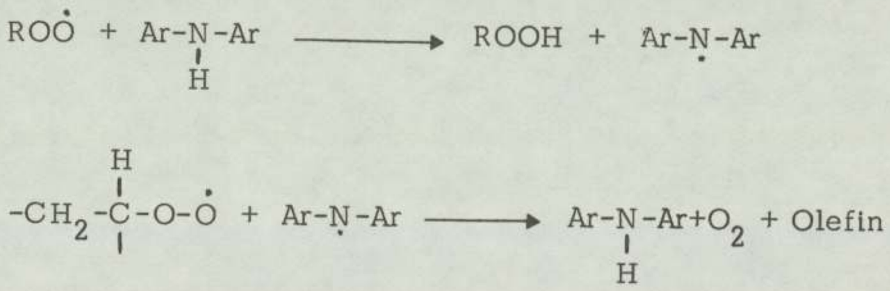
(VIII)

6.2 Oxygen Absorption Studies of Vulcanisates Containing BHBM and MADPA, Bound to NR and SBR during pre-mixing and Vulcanisation

The oxygen absorption technique was also used to assess the effectiveness of antioxidants bound to NR and SBR in the torque rheometer and during subsequent vulcanisation. Grafted-unextracted NR processed with 10% and 20% MADPA (g/100 g NR) in the torque rheometer containing maximum yield of bound antioxidant (see Section 5.1.4) was added to fresh extracted NR on a 12" water cooled two-roll mill to prepare the masterbatches containing various concentrations of MADPA (0.25, 0.5, 1, 2%). The rubber gum stocks were then compounded and vulcanised (see Sections 2.2.1. and 2.2.2). The oxygen absorption test was carried out on vulcanisates as described previously (see Section 2.5.1.2).

Grafted-unextracted SBR processed with MADPA and BHBM at 10% level were also used for preparation of the corresponding solid masterbatches. The procedure used was similar to that described for NR, except dilution was carried out on stripped-extracted SBR (see Section 2.1.5). SBR stocks containing various concentrations of MADPA and BHBM were compounded and vulcanised as described in Sections 2.2.1 and 2.2.2. The oxygen absorption of SBR vulcanisates was carried out at 100°C using a similar procedure as described for NR (see Section 2.5.1.2). In order to assess the effect of bound antioxidants alone, obtained during processing in the torque rheometer, part of the reacted rubber was extracted prior to vulcanisation, vulcanised masterbatches were prepared and studied by the oxygen absorption technique. This technique was also used to study vulcanised masterbatches extracted (see Section 2.2) only after the process of vulcanisation. This was carried out in order to evaluate the effects of further binding during vulcanisation, removal of extra-network materials and unbound antioxidant.

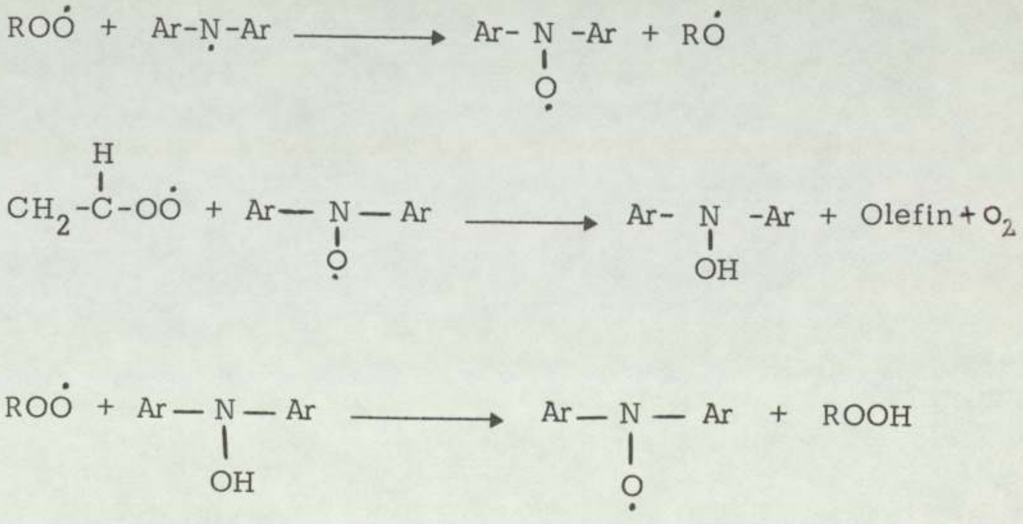
It is known that aromatic amines, like the hindered phenol antioxidants are effective electron donor chain-breaking antioxidants (CB-D), due to their capability to transfer a hydrogen atom to the alkyl peroxy radical(156). The aromatic amines are readily further oxidized to give nitroxyl radicals which can act as electron acceptor chain-breaking antioxidants (CB-A) by trapping alkyl radicals (157-159). Aromatic amines are also shown to be superior during thermal oxidation. This was suggested (158-159) to be due to this dual functionality and cyclical regenerative process, in which there is an alternating sequence of CB-D and CB-A mechanisms. Different mechanisms have recently been suggested for the catalytic scavenging of radicals in autoxidizing hydrocarbons by secondary arylamines and derived nitroxyl and hydroxyl amines. Varlamov (160) and co-workers suggested the following two alternative mechanisms :



$$RO\dot{O} + Ar\text{-}\underset{H}{N}\text{-}Ar \longrightarrow ROOH + Ar\text{-}\underset{\bullet}{N}\text{-}Ar$$

$$-CH_2\text{-}\overset{H}{\underset{|}{C}}\text{-}O\text{-}\dot{O} + Ar\text{-}\underset{\bullet}{N}\text{-}Ar \longrightarrow Ar\text{-}\underset{H}{N}\text{-}Ar + O_2 + \text{Olefin}$$

or

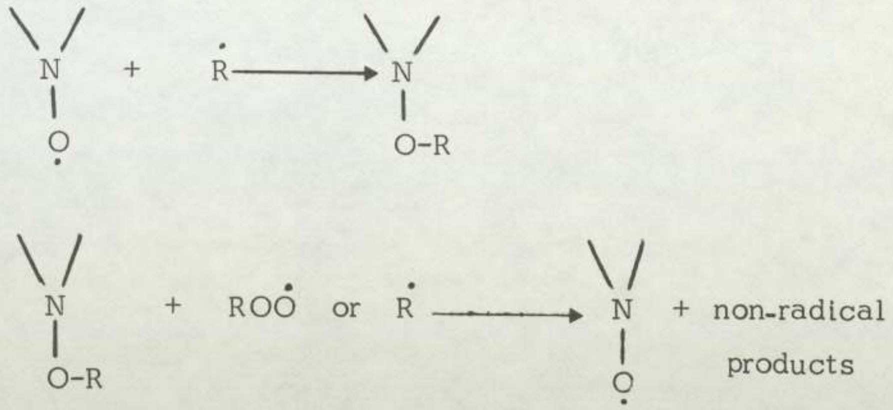


$$RO\dot{O} + Ar\text{-}\underset{\bullet}{N}\text{-}Ar \longrightarrow Ar\text{-}\underset{\underset{\bullet}{O}}{N}\text{-}Ar + R\dot{O}$$

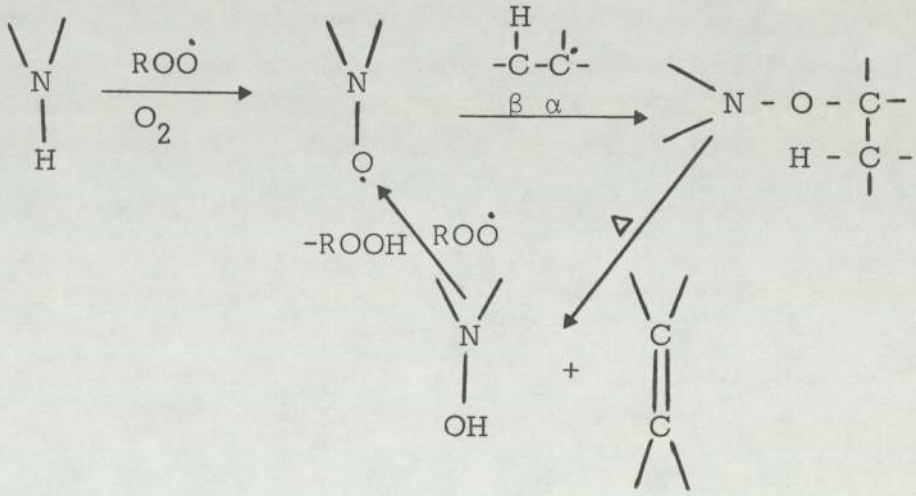
$$CH_2\text{-}\overset{H}{C}\text{-}O\dot{O} + Ar - \underset{\underset{\bullet}{O}}{N} - Ar \longrightarrow Ar\text{-}\underset{OH}{N}\text{-}Ar + \text{Olefin} + O_2$$

$$RO\dot{O} + Ar - \underset{OH}{N} - Ar \longrightarrow Ar - \underset{\underset{\bullet}{O}}{N} - Ar + ROOH$$

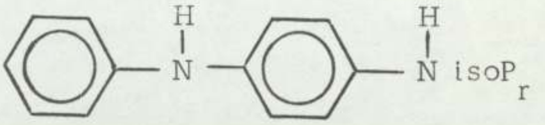
Sudnik and co-workers (161) studied the inhibition of radiation-induced autoxidation of n-octane at 100°C in the presence of some bisnitroxyl radicals and proposed the following mechanism :



More recently, Bolsman et al., (162) proposed the following mechanism for the catalytic inhibition of autoxidation of hydrocarbons by secondary amines, and demonstrated that diarylnitroxyls react both with alkyl and peroxy radicals as follows :

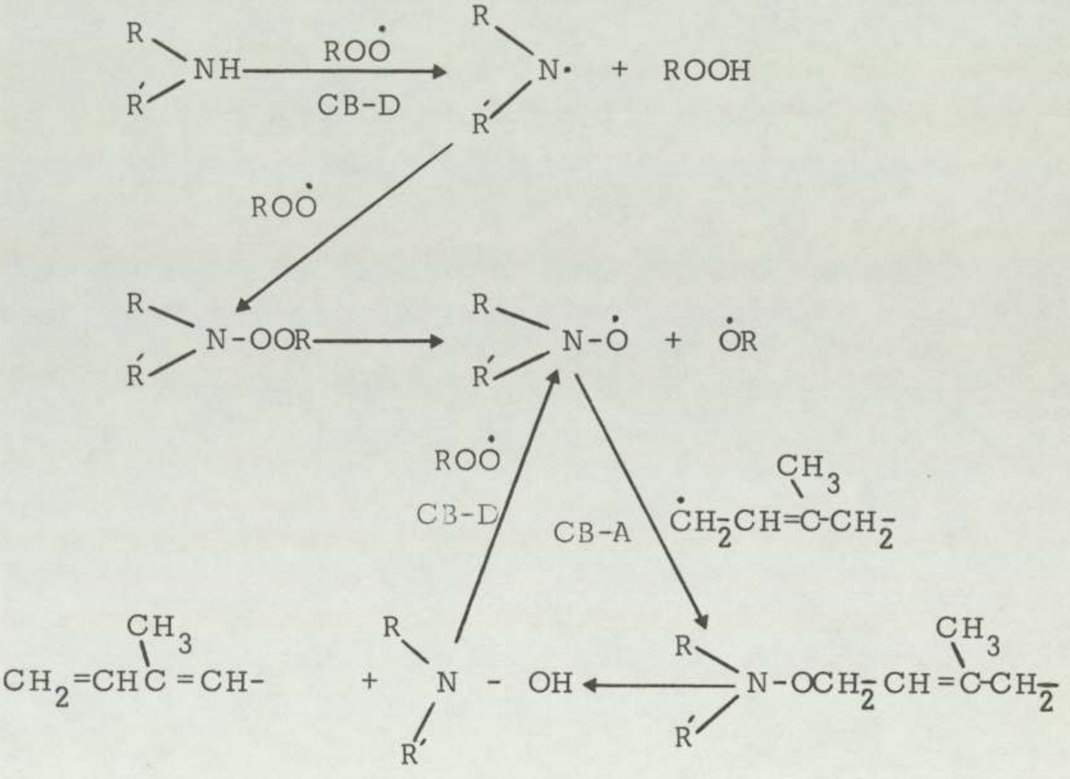


The most recent investigations by Scott and co-workers (163,164) on the mechanism of antifatigue action of IPPD (IX) have shown that the corresponding nitroxyl radical is formed during dynamic flexing of the rubber and this radical is continuously regenerated in a cyclical process involving the corresponding hydroxyl amine.

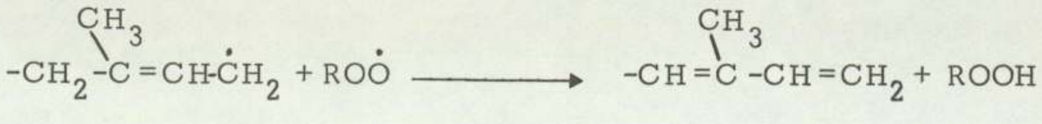

(IX)

N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD)

The mechanism proposed is similar to that suggested by Bolsman et al.,(162) to explain the behaviour of nitroxyl radicals during the thermal oxidation of hydrocarbons :

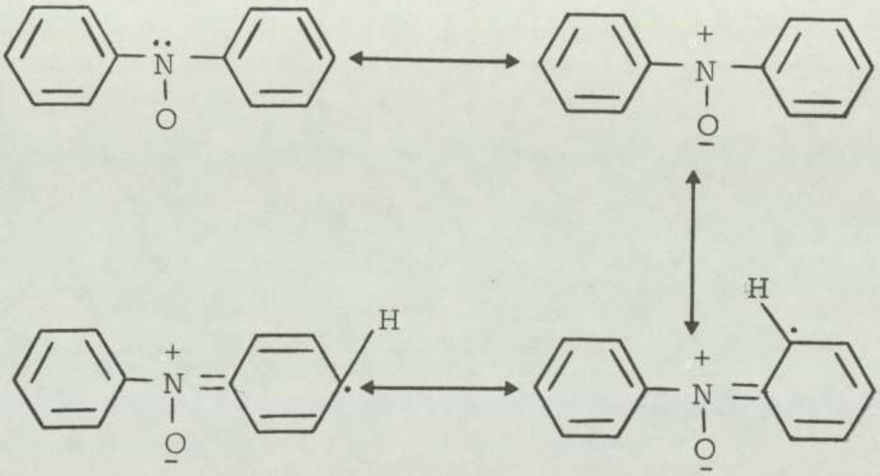


overall reaction



$$-CH_2-\overset{CH_3}{C}=CH\dot{C}H_2 + RO\dot{O} \longrightarrow -CH=\overset{CH_3}{C}-CH=CH_2 + ROOH$$

Furthermore, Neiman and Rozantzev (165) have shown that diarylnitroxides could also function as inhibitors during thermal oxidation. The addition of peroxy radicals was suggested to occur at the para- position. The delocalization of the unpaired electron on nitroxy radical may increase the number of active sites in the molecule thus allowing more alkyl peroxy radicals to be trapped.



The oxygen absorption of vulcanisates containing various concentrations of MADPA diluted from 10% reacted NR in the torque rheometer are shown in Figs. 6.9 - 6.11. These figures represent the oxygen absorption of unextracted and extracted (both before and after vulcanisation) vulcanised masterbatches. Vulcanisates containing various concentrations of MADPA diluted from 20% MADPA reacted with NR were also evaluated by the oxygen absorption technique and the results are shown in Figs. 6.12 and 6.13. The results of these figures in terms of induction period and time to 1% O_2 absorption are summarised in Tables 6.4 and 6.5. The extent of binding for these vulcanisates is given in

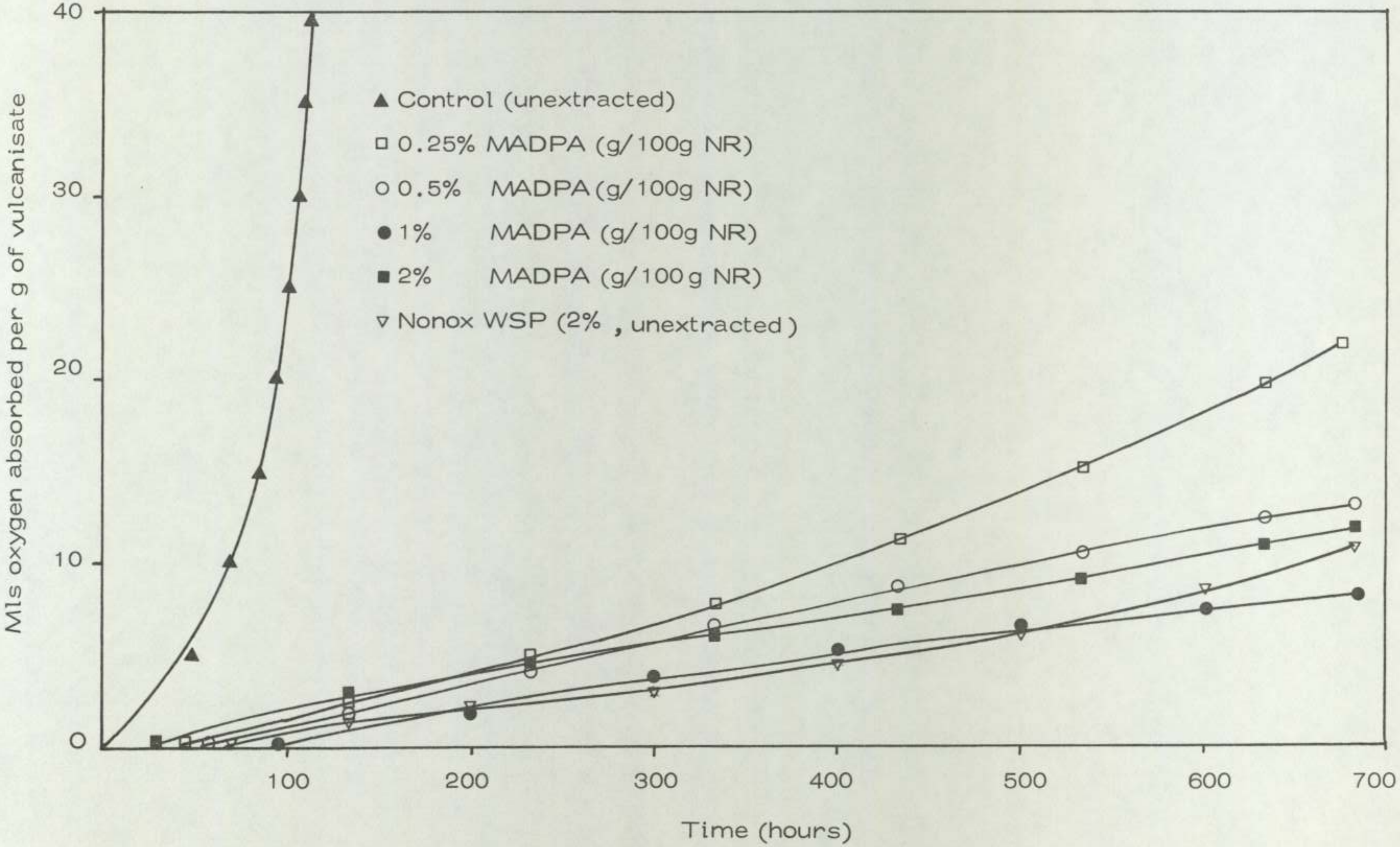


Fig. 6.9. Oxygen absorption of unextracted NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) at 70°C.

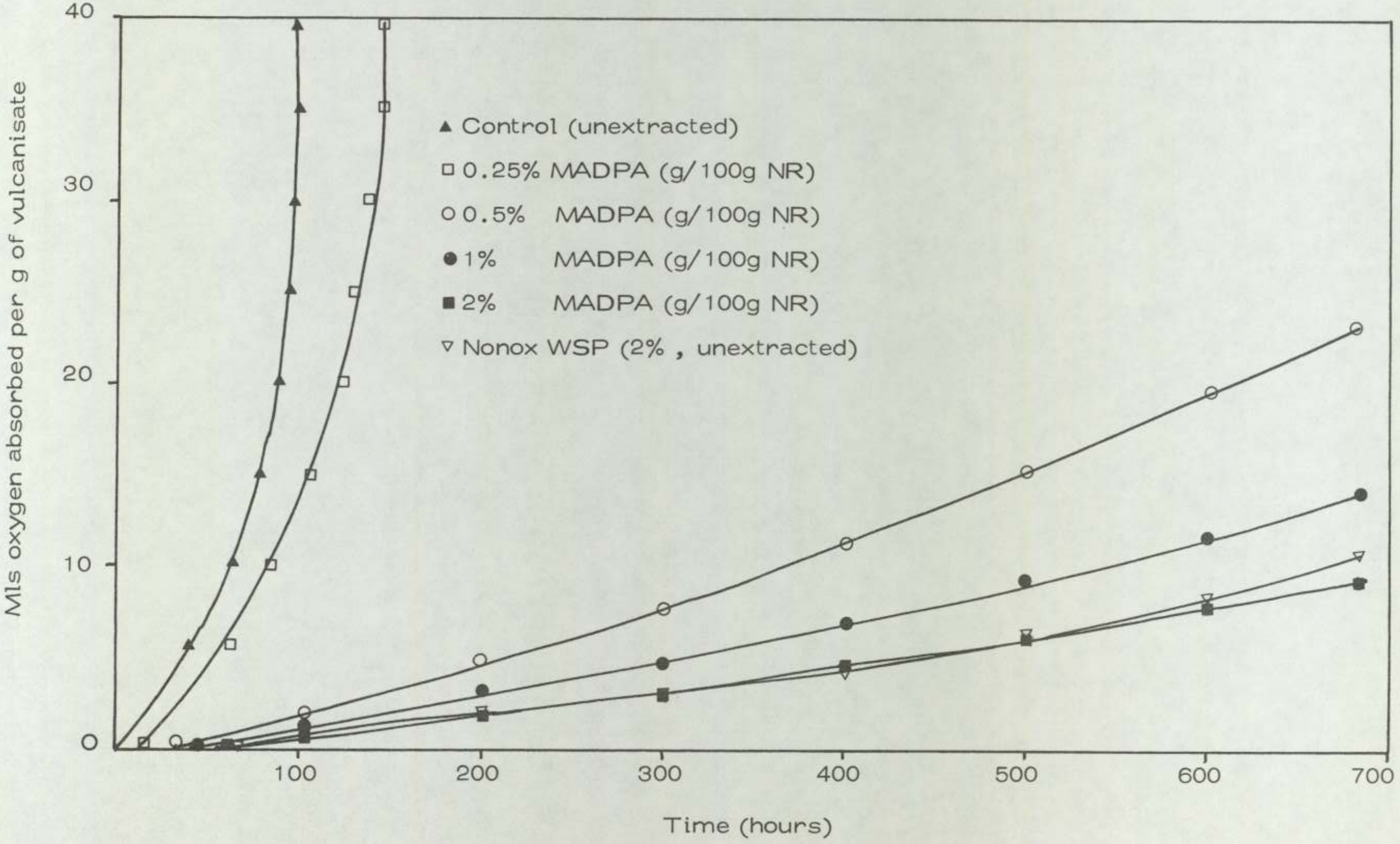


Fig. 6.10. Oxygen absorption of NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted prior to vulcanisation, at 70°C.

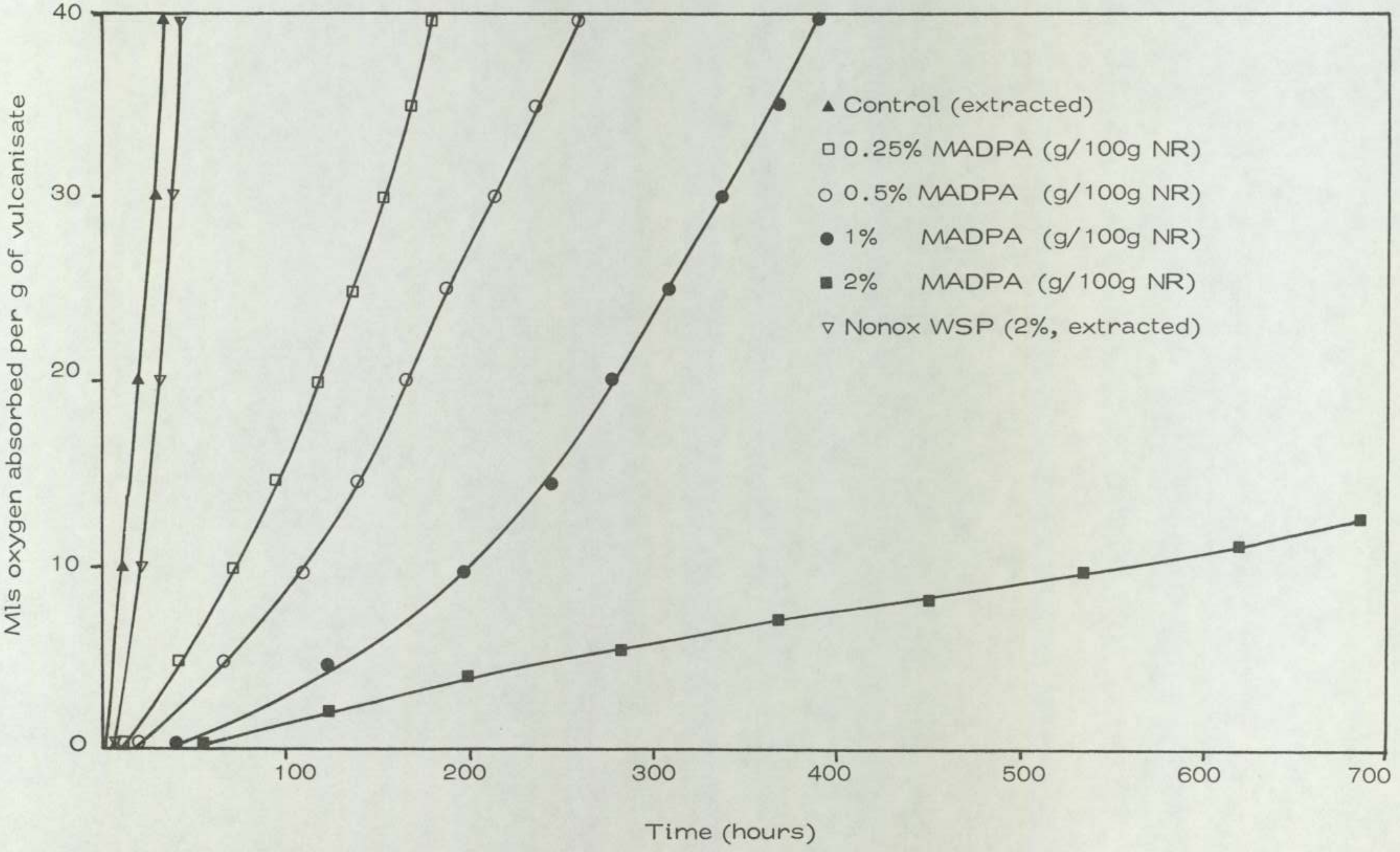


Fig. 6.11. Oxygen absorption of NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted after vulcanisation.

Tables 5.4 and 5.18.

TABLE 6.4

Antioxidant activity of MADPA in NR at 70°C (masterbatches from 10%)

Treatment	Initial Concentration of MADPA	Induction period	Time to 1% O_2 absorption
	(g/100 g NR)	(h)	(h)
Unextracted-Vulcanised-Unextracted	0.25	35	310
	0.5	44	350
	1	99	546
	2	26	401
Extracted-Vulcanised-Unextracted	0.25	7	76
	0.5	24	282
	1	40	405
	2	44	533
Unextracted-Vulcanised-Extracted	0.25	10	52
	0.5	16	79
	1	18	154
	2	48	345
Control			
Unextracted	None	4	52
Extracted	None	0	9
Nonox WSP (2g/100g NR)			
Unextracted		33	523
Extracted		9	19

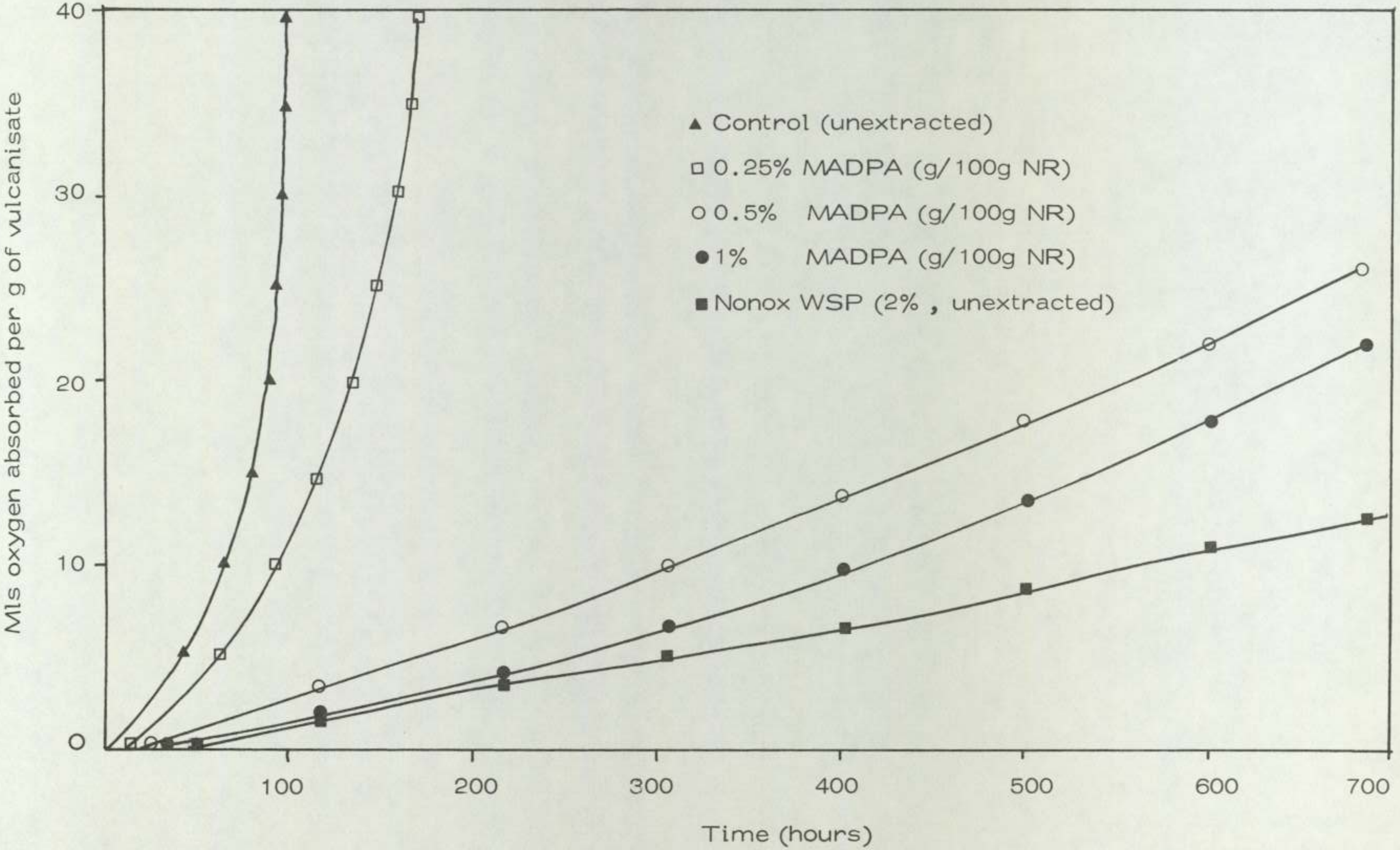


Fig. 6.12. Oxygen absorption of NR vulcanisates containing various concentrations of MADPA (masterbatches from 20%) extracted prior to vulcanisation, at 70°C.

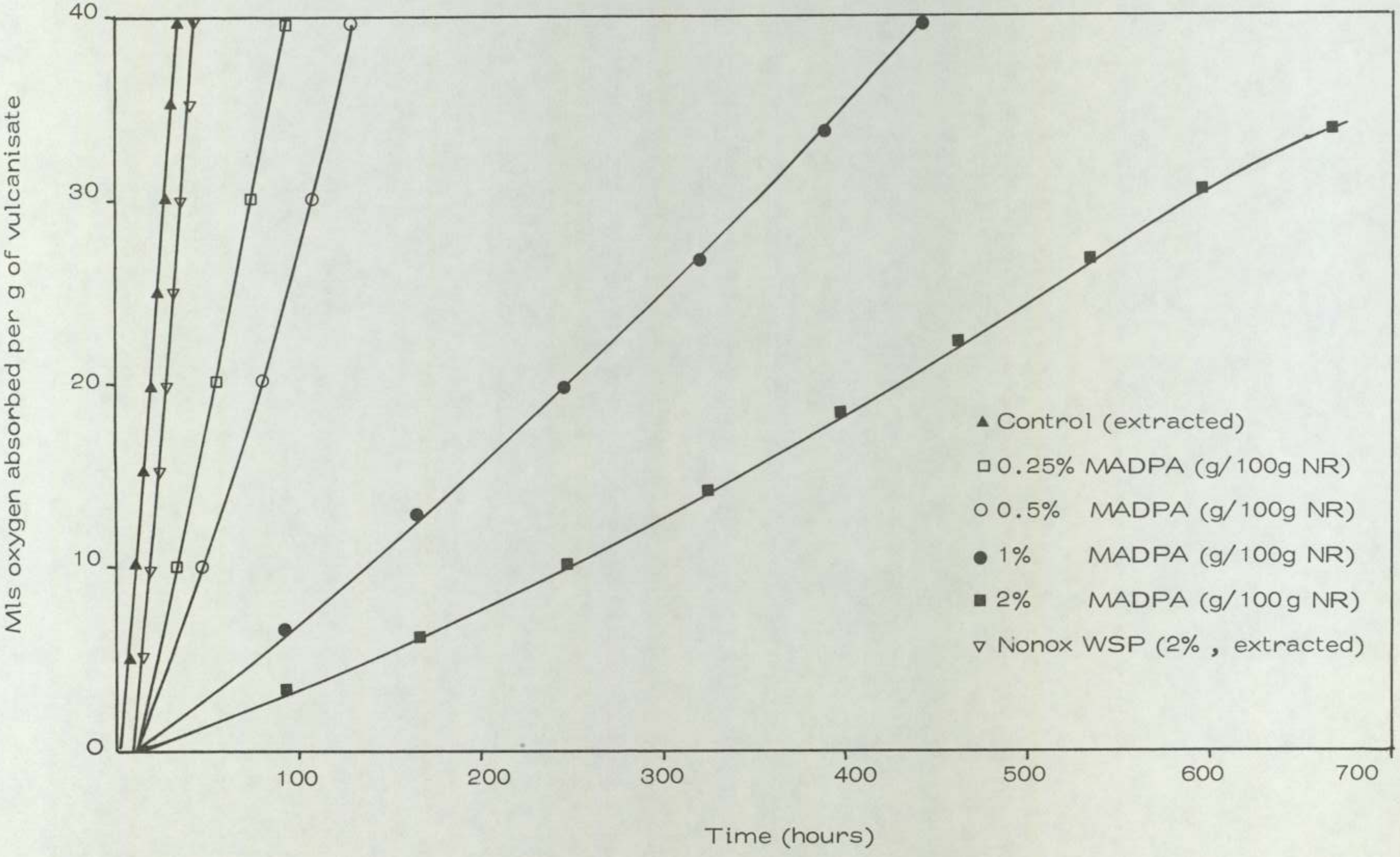


Fig. 6.13. Oxygen absorption of NR vulcanisates containing various concentrations of MADPA (masterbatches from 20%) extracted after vulcanisation, at 70°C.

TABLE 6.5

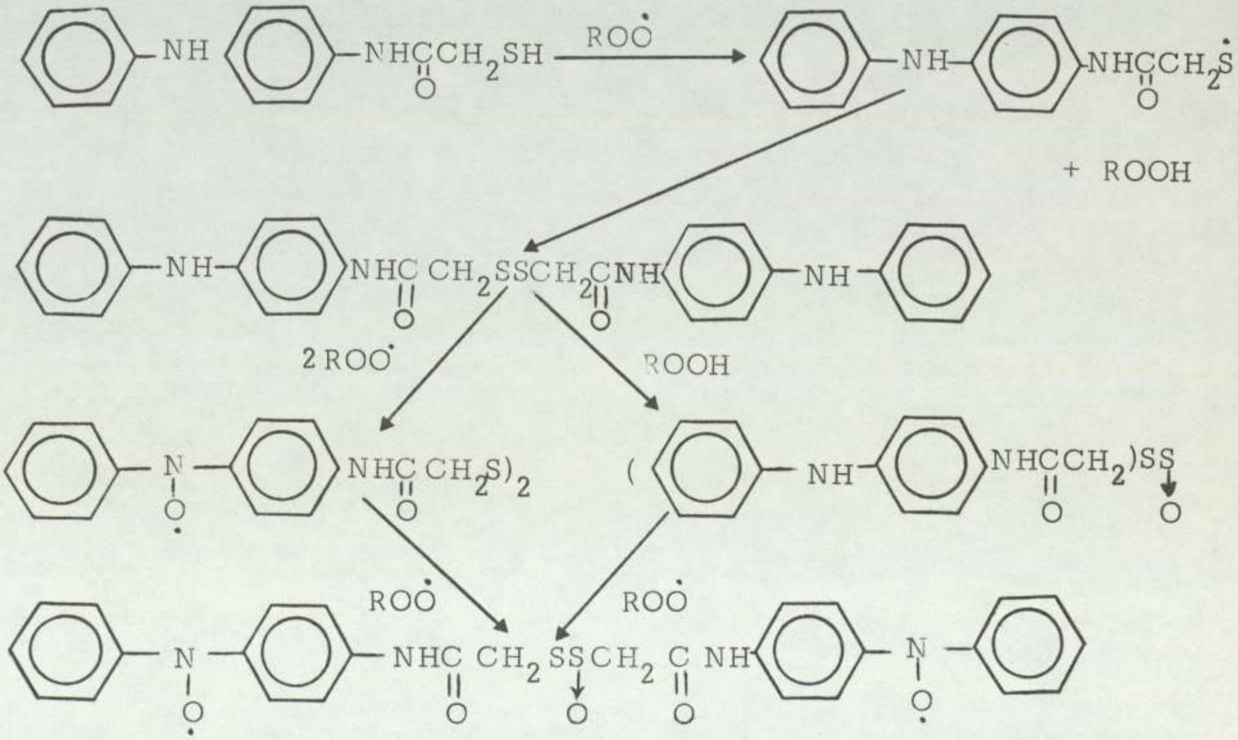
Antioxidant activity of MADPA in NR at 70°C (Masterbatches from 20%)

Treatment	Initial Concentration of MADPA	Induction period	Time to 1% O_2 absorption
	(g/100 g NR)	(h)	(h)
Extracted-Vulcanised-Unextracted	0.25	13	70
	0.5	20	222
	1	32	302
	2	39	385
Unextracted-Vulcanised-Extracted	0.25	7	26
	0.5	9	38
	1	18	102
	2	20	174
Control			
Unextracted	None	4	52
Extracted	None	0	9
Nonox WSP (2g/100g NR)			
Unextracted		33	523
Extracted		9	19

As it is seen in Table 6.4 maximum resistance to autoxidation is obtained with the unextracted vulcanisate containing 1% of MADPA. Further increase in antioxidant concentration to 2% was found to reduce the induction period and time for 1% O_2 absorption. This could be due to interference of MADPA at this concentration with the curing properties of NR vulcanisates resulting in a reduction of scorch time and lowering the state of cure (see Section 6.4.3 Table 6.9) and consequently reducing the oxidative stability of such a vulcanisate. Direct reaction of O_2 with antioxidant at concentration higher than optimum can also give rise to a pro-oxidant effect

$$AH + O_2 \longrightarrow \dot{A} + HO_2 \qquad (a)$$

Kennerly and Patterson (166) studied the inhibition effect of a number of antioxidants on mineral oil by the oxygen absorption technique and showed that there is an increase in induction period with increase in antioxidant concentration up to a certain point. They concluded that at the higher inhibitor concentration, the oxygen inhibitor reaction predominates and the effectiveness of the inhibitor reduces. Shelton (167, 168) investigated the effect of optimum concentration of some amine antioxidants in NR and synthetic rubber and reported that there is a pro-oxidant effect when the optimum concentration of antioxidant is exceeded. He has also shown that direct oxygen attack on amine antioxidant produces radicals which may initiate autoxidation. The results in Table 6.4 also show that the unextracted vulcanisate containing 1% MADPA gives superior resistance to oxidation than the vulcanisate having 2% Nonox WSP as conventional antioxidant. The higher effectiveness of MADPA than conventional phenolic antioxidant may be explaineddue to multi-functional antioxidant activity of the forme and also undergoing cyclical regenerative reactions as discussed earlier in this section. MADPA can act as chain-breaking antioxidant due to the diphenylamine group which according to the proposed mechanisms can interact with peroxy radicals and produce diphenylnitroxyl radicals and also diphenylhydroxylamines. The hydroxylamine further reacts with peroxy radicals formed during oxidation of rubber. MADPA can also function as a powerful hydroperoxide decomposer due to the presence of sulphur in the same molecule as was already discussed for other sulphur containing antioxidants in Chapter One. This does not occur in the case of Nonox WSP. Katbab (169) proposed that MADPA can react with alkyl peroxy radicals during oxidation of rubber producing thiyl radicals which can undergo dimerisation to give the corresponding disulphide. The subsequent reaction of the disulphide with hydroperoxide and alkyl peroxy radicals can give rise to a very powerful antioxidant activity according to the following Schemes: (169)



Results in Table 6.4 and Fig. 6.10 show that although removal of unbound MADPA prior to vulcanisation by extraction reduces their effectiveness in comparison to unextracted samples, the stability obtained still much superior to that of the unextracted control. In this set of vulcanisates effectiveness was found to improve from 0.25% to 2% suggesting that in the absence of free thiol the direct oxygen attack on antioxidant does not occur. In this case the vulcanisate containing 2% MADPA showed better stability than unextracted Nonox WSP. Protected NR vulcanisates extracted after vulcanisation in order to remove unbound antioxidant and also extra-network materials were also found to possess antioxidant activities. It can be seen (see Table 6.4 and Fig. 6.11) that all vulcanisates in this case show superior antioxidant activity than the control or extracted vulcanisate containing 2% Nonox WSP. Results in Table 6.5 show that masterbatches obtained on dilution of 20% MADPA reacted with NR also give better antioxidant activity than the corresponding control or extracted vulcanisates containing conventional antioxidant. The extracted WSP appears to give better resistance to autoxidation than the extracted control indicating that there might be a small proportion of this antioxidant becoming bound to the vulcanisate which was not detectable by infra-red spectroscopy. Such behaviour may also be rationalised in view of the known activity of such bisphenols as metal complexing agents (170), giving rise to the formation of a metal complex, insoluble in the azeotropic solvent.

However, it is known that (111) most efficient amine antioxidants, the disubstituted p-phenylenediamines, are only used for dark-coloured articles since they discolour badly during ageing and exposure to light.

Furthermore, even in dark-coloured articles they cannot be used in contact with light-coloured components since the antioxidant will migrate on to the surface of the light component and discolour it. For these reasons the less efficient phenolic antioxidants are normally preferred for light-coloured articles, especially those produced from rubber latex. In the present studies it was observed that vulcanisates containing MADPA initially have a light colour in comparison to those containing Nonox WSP. In unextracted vulcanisates containing MADPA it was found that unbound antioxidant tended to discolour the article during storage although less than Nonox WSP. However, extracted vulcanisates containing bound MADPA were found to maintain the initial light colour which were superior in performance to those containing Nonox WSP.

SBR processed with MADPA and BHBM (10%) in the torque rheometer at optimum conditions (see Sections 5.1.2 and 5.1.3) were also used as masterbatches. The oxygen absorption of the unextracted SBR vulcanisates containing 0.25 - 2% MADPA is shown in Fig. 6.14. Figures 6.15 and 6.16 show the oxygen absorption of SBR masterbatches extracted both before and after vulcanisation respectively. Part of the grafted SBR with MADPA was extracted in the uncured state, diluted with stripped-extracted (see Section 2.1.5) and vulcanisates were prepared containing various concentrations (0.25-2%) of this antioxidant. These vulcanisates were further subjected to exhaustive extraction (see Section 2.2) in order to remove the extra-network materials, hence leaving only the SBR-bound antioxidant. The oxygen absorption of these vulcanisates is shown in Fig. 6.17. Masterbatches prepared from SBR reacted with BHBM were

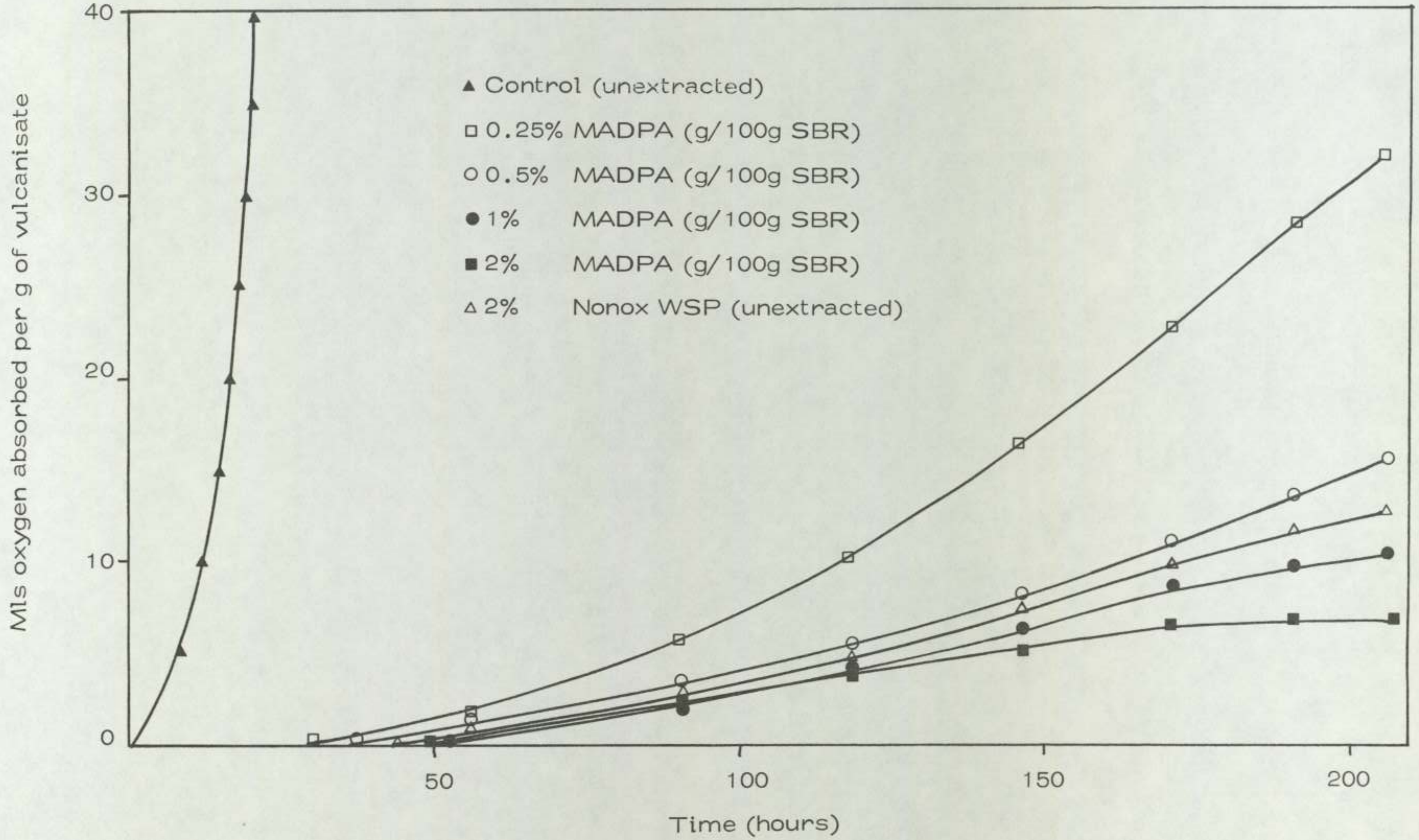


Fig. 6.14. Oxygen absorption of unextracted SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) at 100°C.

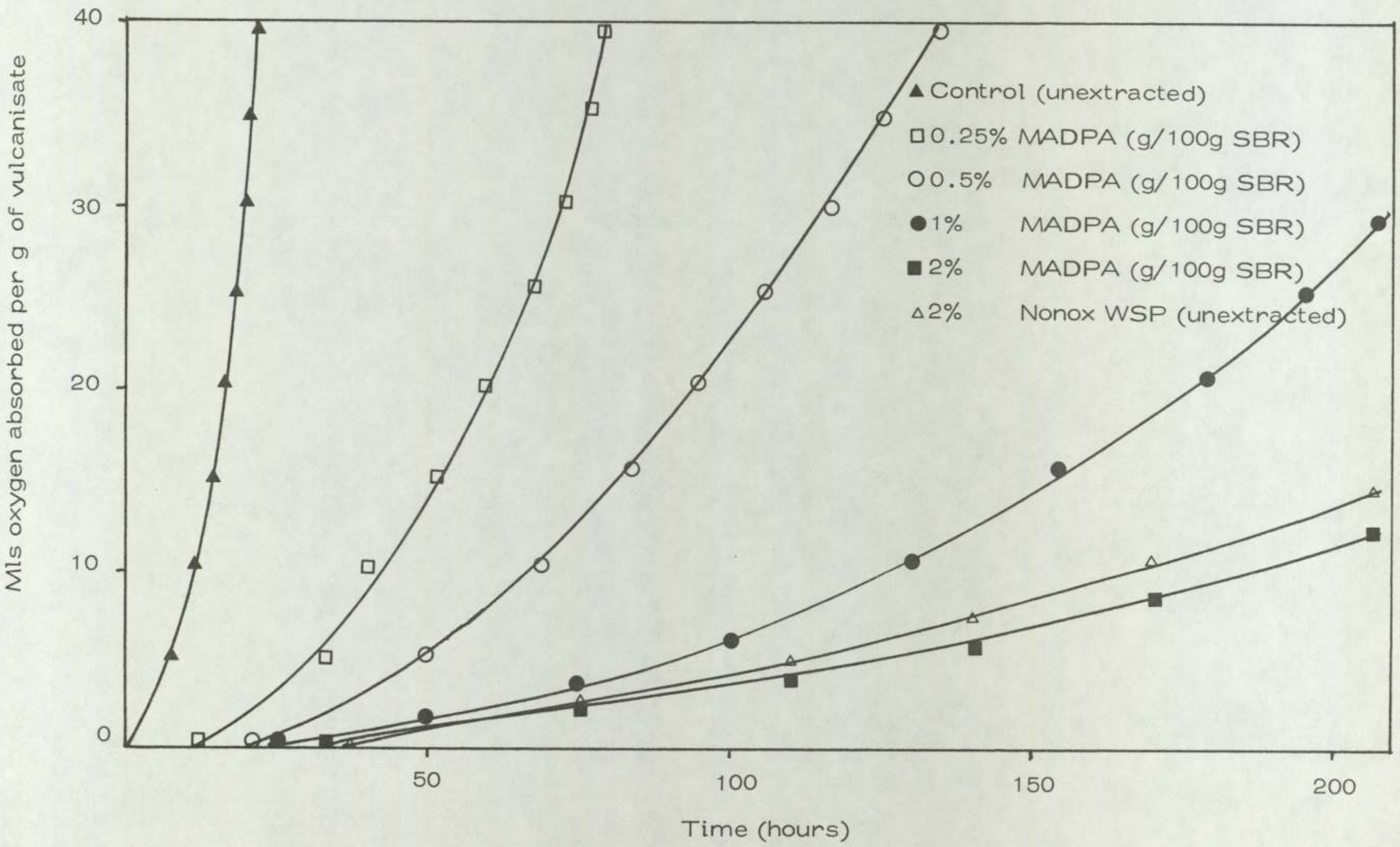


Fig. 6.15. Oxygen absorption of SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%), extracted prior to vulcanisation at 100°C.

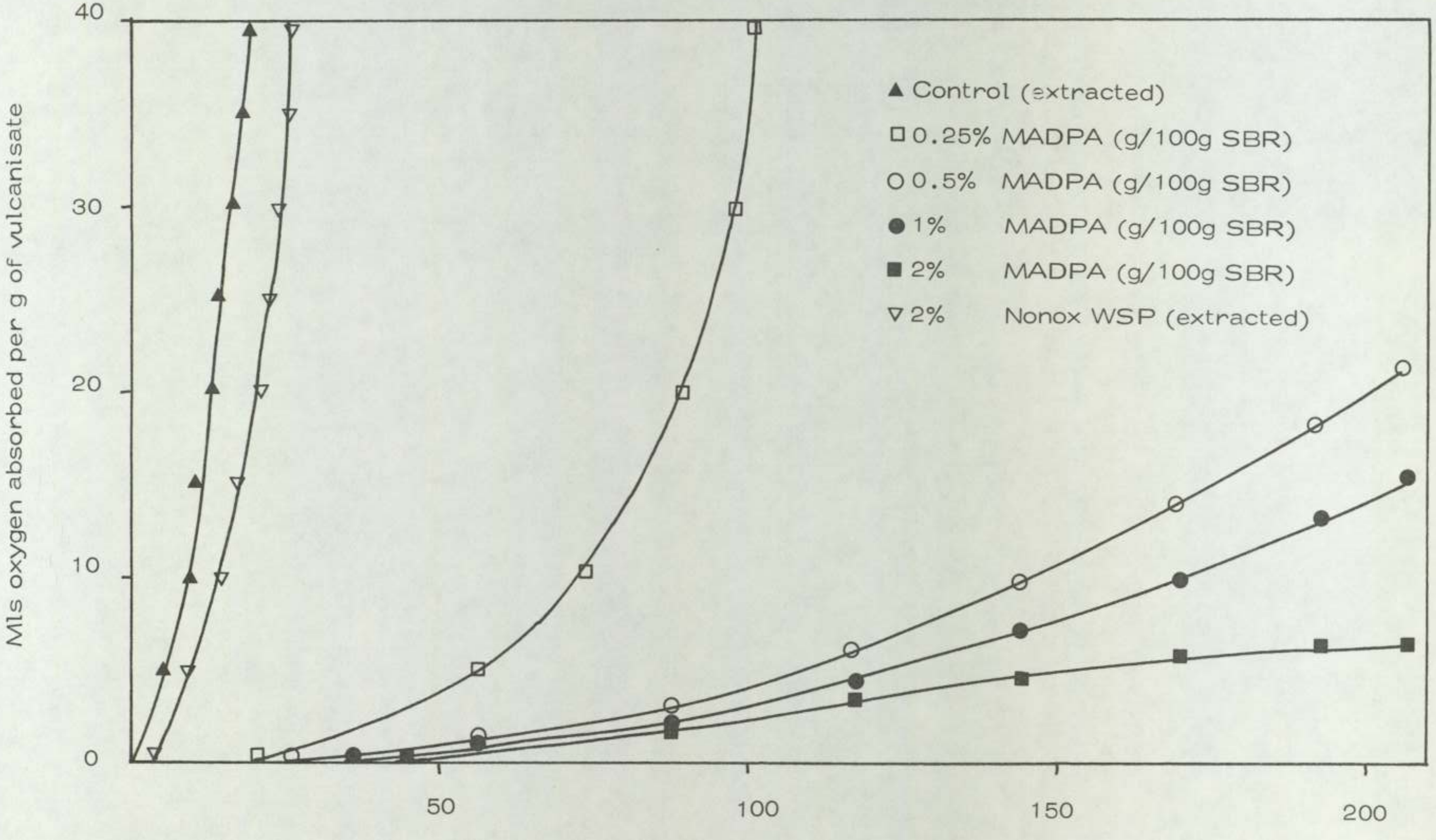


Fig. 6.16. Oxygen absorption of SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%), extracted after vulcanisation at 100^{o}C.

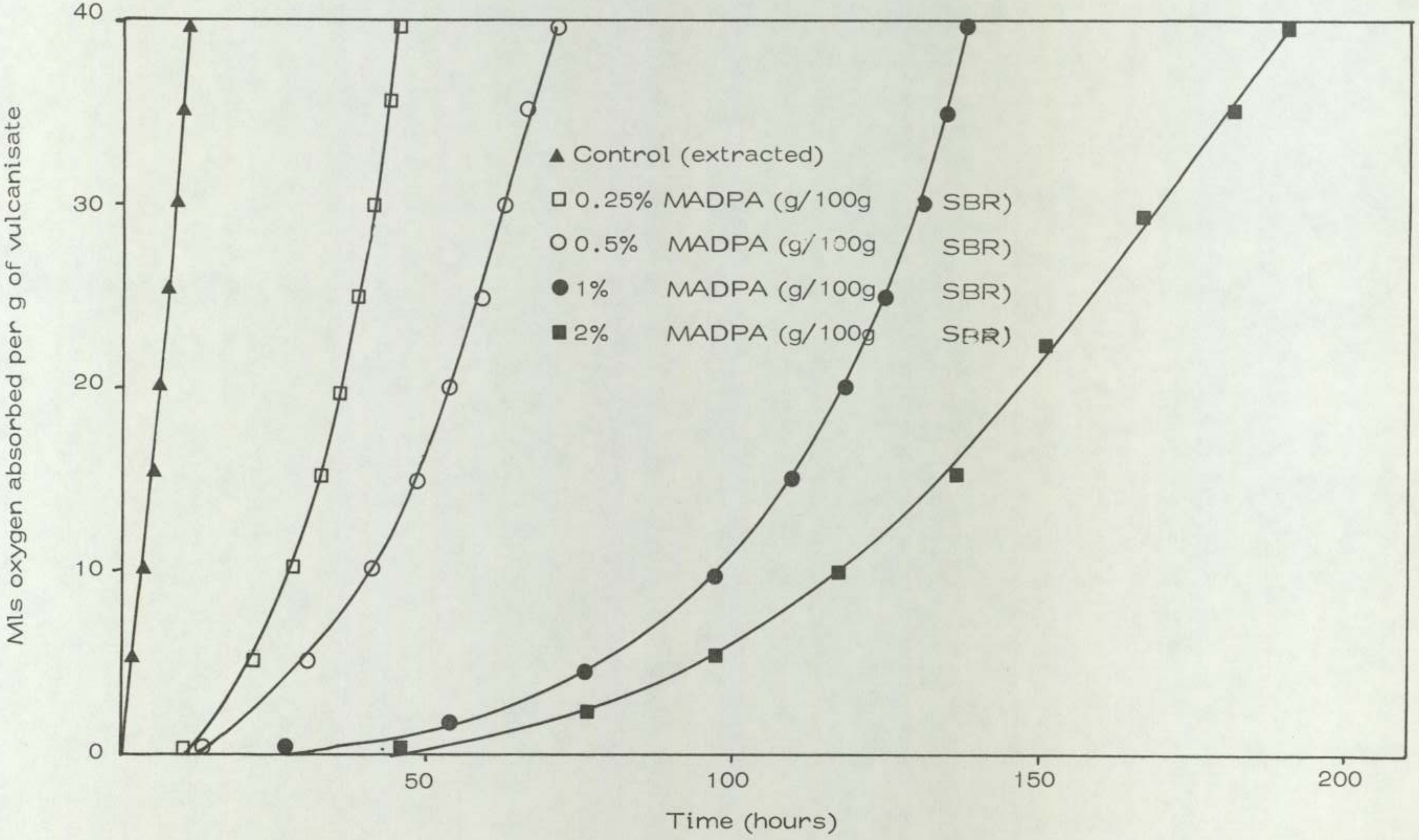


Fig. 6.17. Oxygen absorption of SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted both before and after vulcanisation at 100°C.

similarly assessed by oxygen absorption technique and the results are shown in Figs. 6.18-6.20. Induction periods and also time to absorb 1% O_2 derived from these figures are given in Tables 6.6 and 6.7.

TABLE 6.6 Antioxidant Activities of MADPA in SBR at 100°C

Treatment	Initial concentration of MADPA (g/100 g SBR)	Induction Period (h)	Time to 1% O_2 absorption (h)
Unextracted-Vulcanised-Unextracted	0.25	29	101
	0.5	34	128
	1	37	142
	2	30	196
Extracted-Vulcanised-Unextracted	0.25	11	37
	0.5	20	57
	1	25	107
	2	29	143
Unextracted-Vulcanised-Extracted	0.25	20	68
	0.5	25	120
	1	36	135
	2	45	189
Extracted-Vulcanised-Extracted	0.25	9	25
	0.5	13	38
	1	25	89
	2	42	108
Control (No antioxidant)			
Unextracted	-	1	9.5
Extracted	-	0	7
Nonox WSP (2g/100g SBR)			
Unextracted		32	132
Extracted		4	13

Results given in Table 6.6 (see also Fig. 6.14) indicate that all the unextracted SBR vulcanisates containing 0.25 - 2% MADPA show superior resistance to oxidation than that of the control. In this case, unlike NR (Table 6.4), an increase in concentration of antioxidant from 1 to 2% does not reduce the time to 1% O_2 absorption, although the induction period slightly drops. Shorter induction period in vulcanisate containing 2% MADPA than 1% may be due to the direct O_2 attack on antioxidant (Reaction a) in the former case. This gives rise to a pro-oxidant effect as discussed earlier in this section for a similar case of NR + MADPA. Furthermore, examination of curing characteristics of NR stocks containing 2% MADPA (see Sections 6.4.3, Table 6.9) reveals that optimum modulus, scorch time, and the rate of cure are significantly lower than that containing 1% MADPA. This may suggest that part of MADPA is involved in the vulcanisation process, leading to a lower concentration of antioxidant available to take part in the inhibition process. Therefore, the decrease in the effectiveness of 2% MADPA in NR as compared to 1% may be due to the combination of the optimum concentration effect and consumption of the antioxidant during vulcanisation. In the case of masterbatches of MADPA in SBR there is no significant decrease in curing properties (see Section 6.4.3, Table 6.11) at 1 and 2% levels. This may explain the decrease in effectiveness of MADPA at the higher concentration in NR but not in SBR.

Unextracted vulcanisates containing 1 - 2% MADPA were found to be more effective than the unextracted Nonox WSP. This again could be explained due to multi-functional antioxidant activities of MADPA, functioning both as a chain-breaking and hydroperoxide-decomposing antioxidant and its regeneration according to the cyclical mechanism proposed (158,159,162) and discussed previously.

SBR masterbatches subjected to extraction prior to vulcanisation although less effective (see Table 6.6 and Fig. 6.15) than the corresponding unextracted samples, still showed superior oxidative stability than the unextracted control. In this case, vulcanisate containing 2% MADPA exhibits superior resistance to thermal oxidation than even the unextracted Nonox WSP vulcanisate.

SBR masterbatches containing 0.25-2% MADPA extracted after vulcanisation were also assessed by oxygen absorption technique (see Table 6.6 and Fig. 6.16). It is important to note that oxidative resistance of these vulcanisates was almost the same as those before extraction. This is particularly evident when induction periods and time to 1% O_2 absorption of vulcanisates containing 0.25-2% MADPA are compared together (see Table 6.6). However, the observation made on discolouration of the SBR vulcanisates by MADPA and Nonox WSP was similar to that described earlier for NR.

However, Shelton et al., (171) have compared the oxidative behaviour of unextracted and acetone extracted sulphenamide-sulphur cured NR vulcanisates and concluded that at least part of the oxidative resistance of this type of vulcanisate must be due to the antioxidant derived from the accelerator. This was further confirmed by Pederson (172) and Begunovskoya (173) who studied the effect of sulphur-accelerator ratio on oxidation of MBT vulcanisates and found that as the amount of sulphur increases there is a significant drop in oxidative stability of this type of vulcanisate. The oxygen absorption studies on NR CBS/S cured vulcanisates in the present work further confirm this, when the induction periods and time to 1% O_2 absorption of the unextracted and extracted NR vulcanisates are compared (see Table 6.1). In contrast, in SBR vulcanisates the accelerator residue does not appear to function as an antioxidant. This is evident from the small difference between the oxidative stability of the unextracted and extracted SBR vulcanisates containing no antioxidant (see Table 6.6). SBR vulcanisates extracted both before and after vulcanisation also show superior oxidative stability than the control (see Fig. 6.17 and Table 6.6). This confirms the binding of MADPA to SBR during pre-mixing in the torque rheometer and demonstrates the high thermal stability of the rubber-bound antioxidant obtained in the absence of any other additive.

Antioxidant activities of SBR plus BHBM masterbatches in terms of induction period and time to 1% O_2 absorption derived from Figs. 6.18, 6.19 and 6.20 are summarised in Table 6.7.

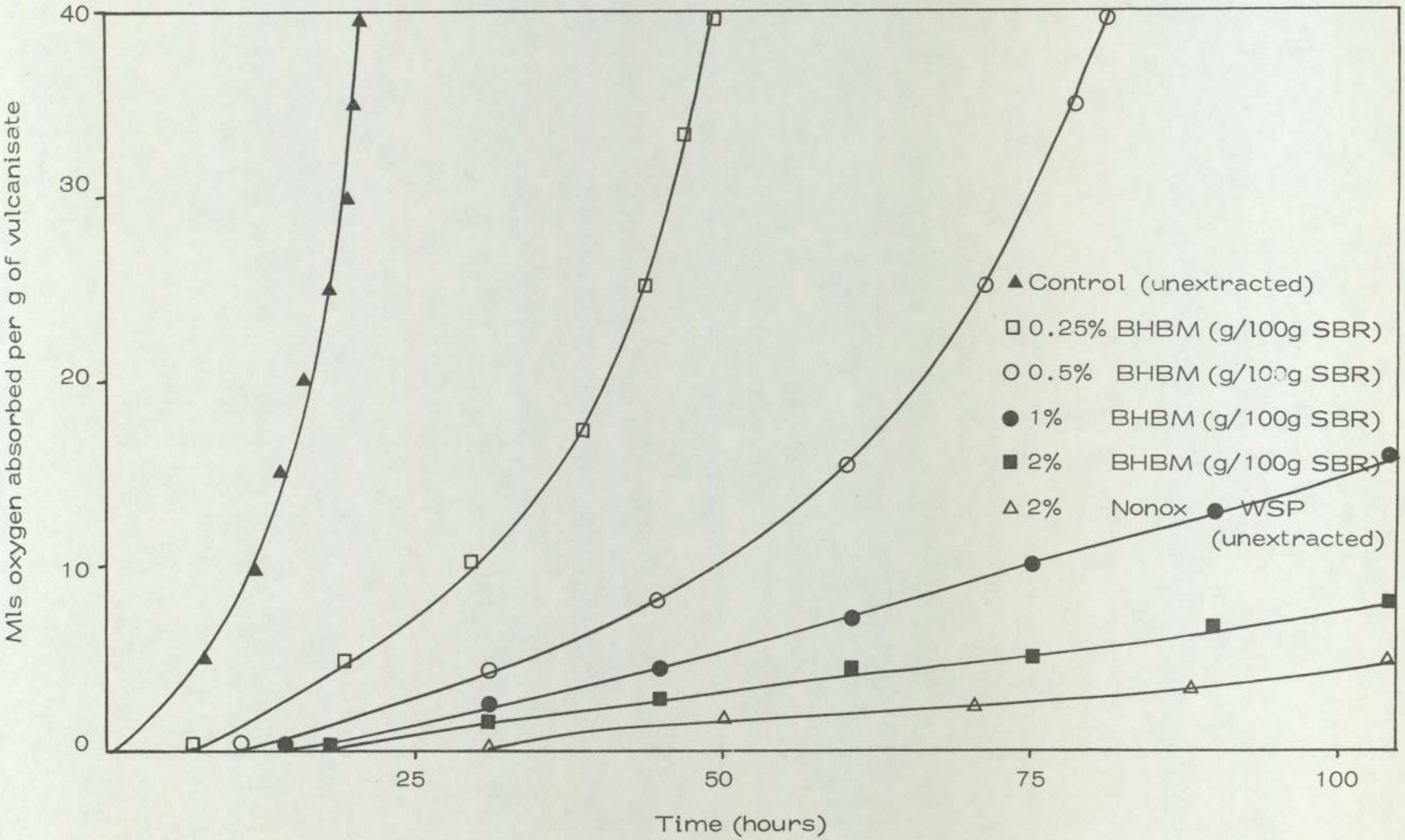


Fig. 6.18. Oxygen absorption of unextracted SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%) at 100°C.

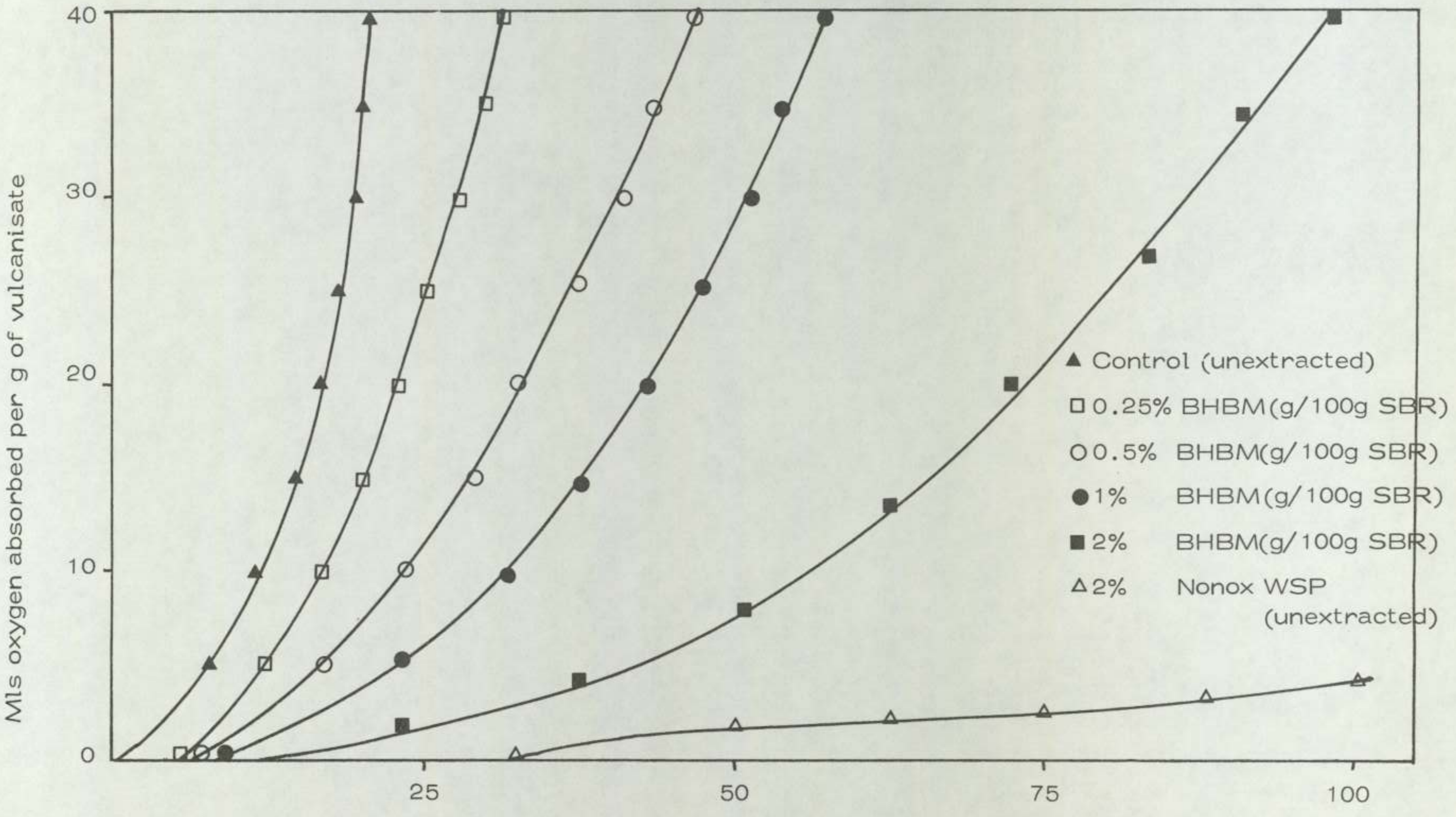


Fig. 6.19. Oxygen absorption of SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%)extracted before vulcanisation at 100°C.

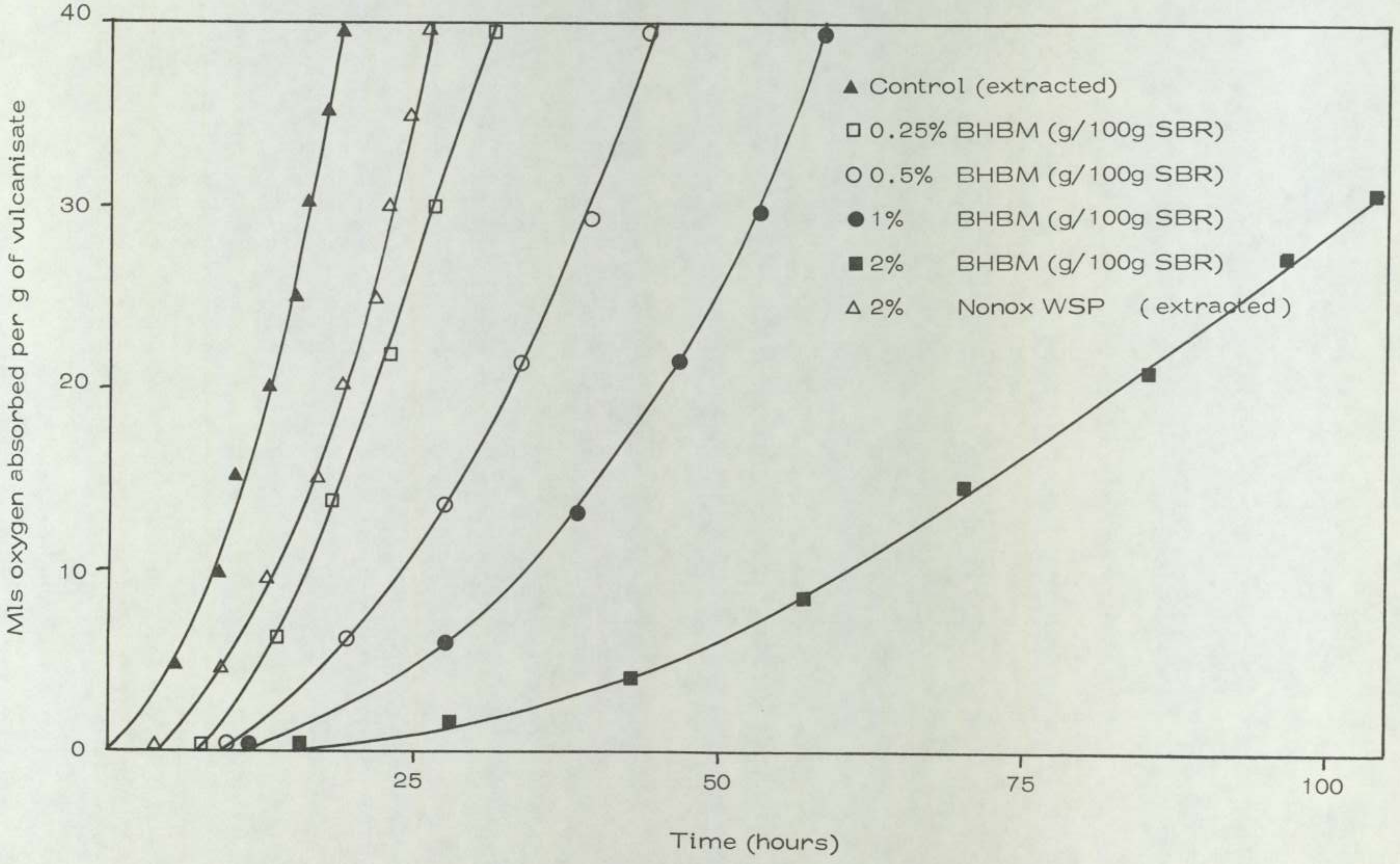


Fig. 6.20 Oxygen absorption of SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%) extracted after vulcanisation at 100°C.

TABLE 6.7 Antioxidant Activities of BHBM in SBR at 100°C

Treatment	Initial concentration of BHBM	Induction Period	Time to 1% O_2 absorption
	g/100 g SBR	(h)	(h)
Extracted Vulcanised Unextracted	0.25	7	26
	0.5	9	43
	1	14	59
	2	18	120
Extracted Vulcanised Unextracted	0.25	5	14
	0.5	6	19
	1	8	27
	2	11	48
Unextracted Vulcanised Extracted	0.25	7	15
	0.5	8	20
	1	11	29
	2	13	53
Control (No antioxidant)			
Unextracted	None	1	9.5
Extracted	None	0	7
Nonox WSP			
Unextracted	2	32	132
Extracted		4	13

Vulcanisates containing 0.25 - 2% BHBM show a steady improvement in effectiveness as the concentration of antioxidant in the vulcanisate increases. Results in Table 6.7 and Fig. 6.18 indicate that the unextracted vulcanisate containing 2% Nonox WSP provides better protection during thermal oxidation than that containing 2% BHBM. However, this protection is almost completely lost after extraction giving rise to a superior performance by the extracted vulcanisates containing various concentrations of BHBM (0.25-2%).

6.3 Stress Relaxation Studies of NR and SBR Vulcanisates Containing Bound Antioxidants

6.3.1. Introduction

The measurement of stress relaxation as a function of time has been shown by Tobolsky (174) to be a useful tool in investigating chemical degradation. By varying the temperature and the time of experiment the viscoelastic behaviour can also be studied. Such studies were termed chemorheology(175,176). It has been shown(177) that in the temperature range of 100 to 150°C natural and synthetic vulcanised rubbers show a fairly rapid decay to zero stress at constant extention. Since in principle, a cross-linked rubber network in the rubbery range of behaviour showed little stress relaxation and certainly no decay to zero stress, the phenomenon was attributed to a chemical rupture of the rubber network. In these studies it is essential to ensure that the rubber samples used are thin enough to permit steady state conditions of oxygen diffusion; otherwise the rate of chemical stress relaxation may become diffusion controlled (178, 179). In vulcanisates having a high surface area to volume ratio, such as elastic fibres and films, the stress relaxation test has technological advantages over the technique of oxygen absorption. Although the oxygen absorption test is performed in a closed system and some volatility of ingredients out of the vulcanisate into the oxygen atmosphere is to be expected, the test is more indicative of inherent activity of the antioxidant involved. In rubber articles with high surface area to volume ratio, factors such as the volatility and ease of removal of antioxidants by solvent extraction are more important than inherent antioxidant activity (69).

In the present work, the ageing resistance of various vulcanisates was assessed by the use of continuous stress relaxation at 100°C in air (see also Section 2.6). NR and SBR reacted with MADPA and BHBM during processing in the torque rheometer containing maximum amount of bound antioxidant (see Sections 5.1.2 and 5.1.3), were used in the masterbatch technique for preparation of vulcanisates containing various concentrations of these antioxidants (0.25-2%) as described previously (see Section 6.2). Compounding, vulcanisation and the procedure used for the measurement of the continuous stress relaxation were also described in previous chapters (see Sections 2.2.1., 2.2.2 and 2.6.1).

6.3.2. Results and Discussion

The effect of MADPA on the continuous stress relaxation of vulcanised NR masterbatches (from 10%) at 100°C in air before and after extraction are shown in Figs. 6.21-6.23. Vulcanised masterbatches prepared from 20% MADPA reacted with NR (see Section 5.1.4) were also assessed by stress relaxation technique and the results obtained are shown in Figs. 6.24 and 6.25. Styrene-butadiene rubber reacted with MADPA and BHBM at 10% level, diluted with stripped-extracted SBR on a 12" water-cooled 2-roll mill to prepare the corresponding masterbatches (see Section 6.2). The continuous stress relaxations of these vulcanisates were also studied using the procedure given previously (see Section 2.6.1). The results obtained are shown in Figs. 6.26-6.31.

Stress relaxation of the unextracted vulcanisates of NR plus MADPA shown in Fig. 6.21, indicates that this antioxidant under various concentrations used can protect the NR vulcanisates against oxidation relative to the unextracted control. In this case resistance to thermal oxidative degradation given by conventionally added Nonox WSP (2%) appears to be higher than the other vulcanisates. The rate of decay of stress for vulcanisate containing 2% Nonox WSP does not differ significantly from that containing 1% MADPA. This may be attributed to partial volatilisation of the unbound antioxidant since it has lower molecular weight than the Nonox WSP. In common with oxygen absorption results (Section 6.2., Table 6.4) vulcanisate containing 1% MADPA show a clear improvement in the decay of stress in comparison with other vulcanisates except Nonox WSP. NR vulcanisates extracted prior to vulcanisation in order to remove unbound MADPA were also studied by the stress relaxation technique. The

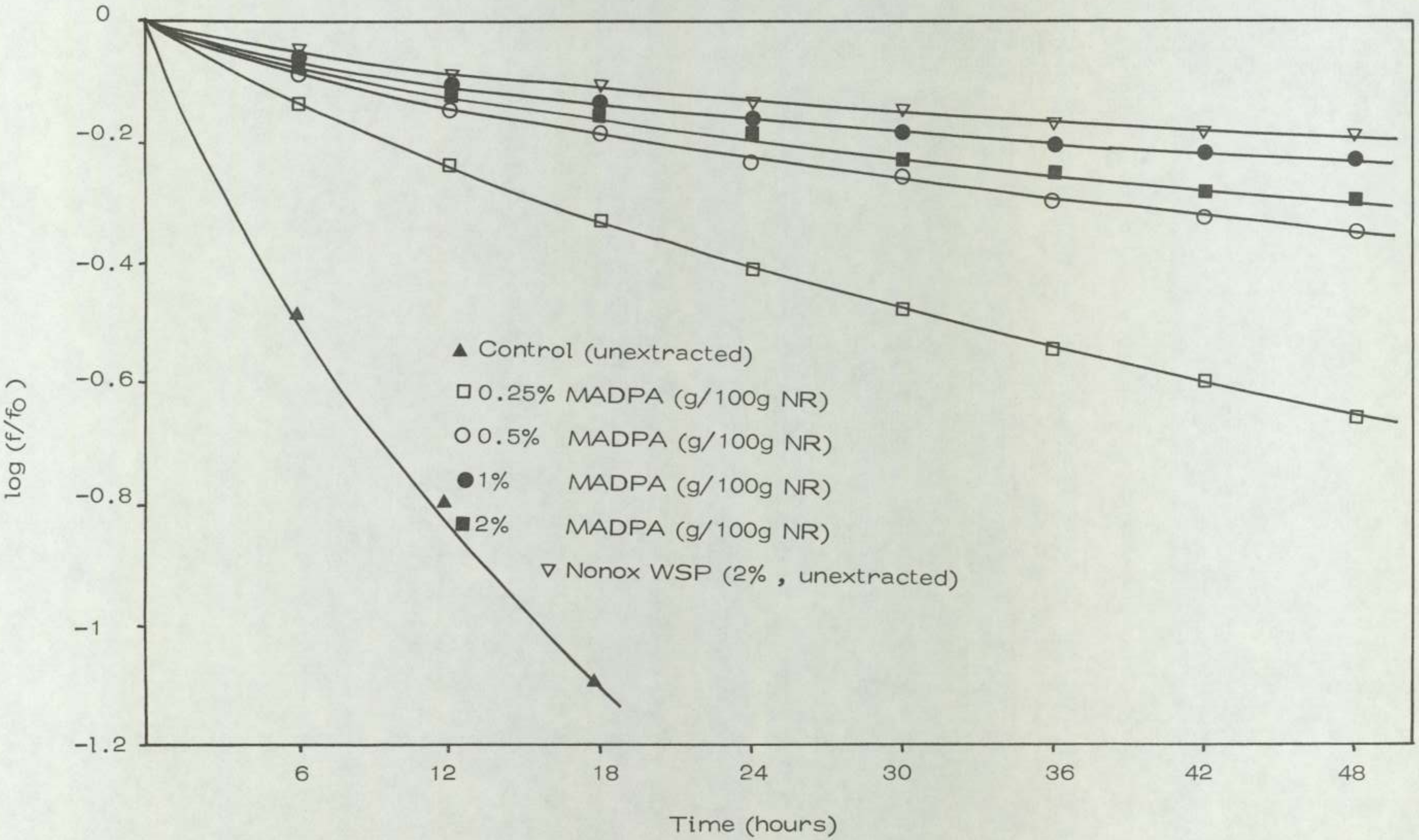


Fig. 6.21 Continuous stress relaxation of unextracted NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) at 100^{o}C in air.

relaxation curves for these vulcanisates are shown in Fig. 6.22. It is seen that these vulcanisates containing bound MADPA, obtained during processing with NR at 10% level in the torque rheometer (see Section 5.1.3) all show superior oxidative stability than the control containing no antioxidant. The shapes of the relaxation curves are similar to those of the unextracted samples (Fig. 6.21), except that maximum stability to decay in stress is given by vulcanisate containing 2% of MADPA. This vulcanisate shows even better resitance to stress decay than that of the unextracted Nonox WSP. This may suggest that in the absence of unbound MADPA volatilisation does not occur and bound antioxidant present can provide superior oxidative stability than that of the unextracted Nonox WSP.

However, since it was found that further binding of MADPA can be achieved during vulcanisation (see Section 5.2.8), unextracted MADPA masterbatches were vulcanised, subjected to exhaustive extraction (see Section 2.2) and their continuous stress relaxation was studied as described previously (see Section 2.6.1). The relaxation curves for these vulcanisates are shown in Fig. 6.23. Removal of unbound antioxidant and accelerator residues reduces the stability to stress decay and this is particularly evident in the control sample and also in the extracted vulcanisate containing Nonox WSP. The extracted vulcanisates containing bound MADPA all show superior oxidative stability towards decay in stress as compared with that of the extracted Nonox WSP and the control. Furthermore, it

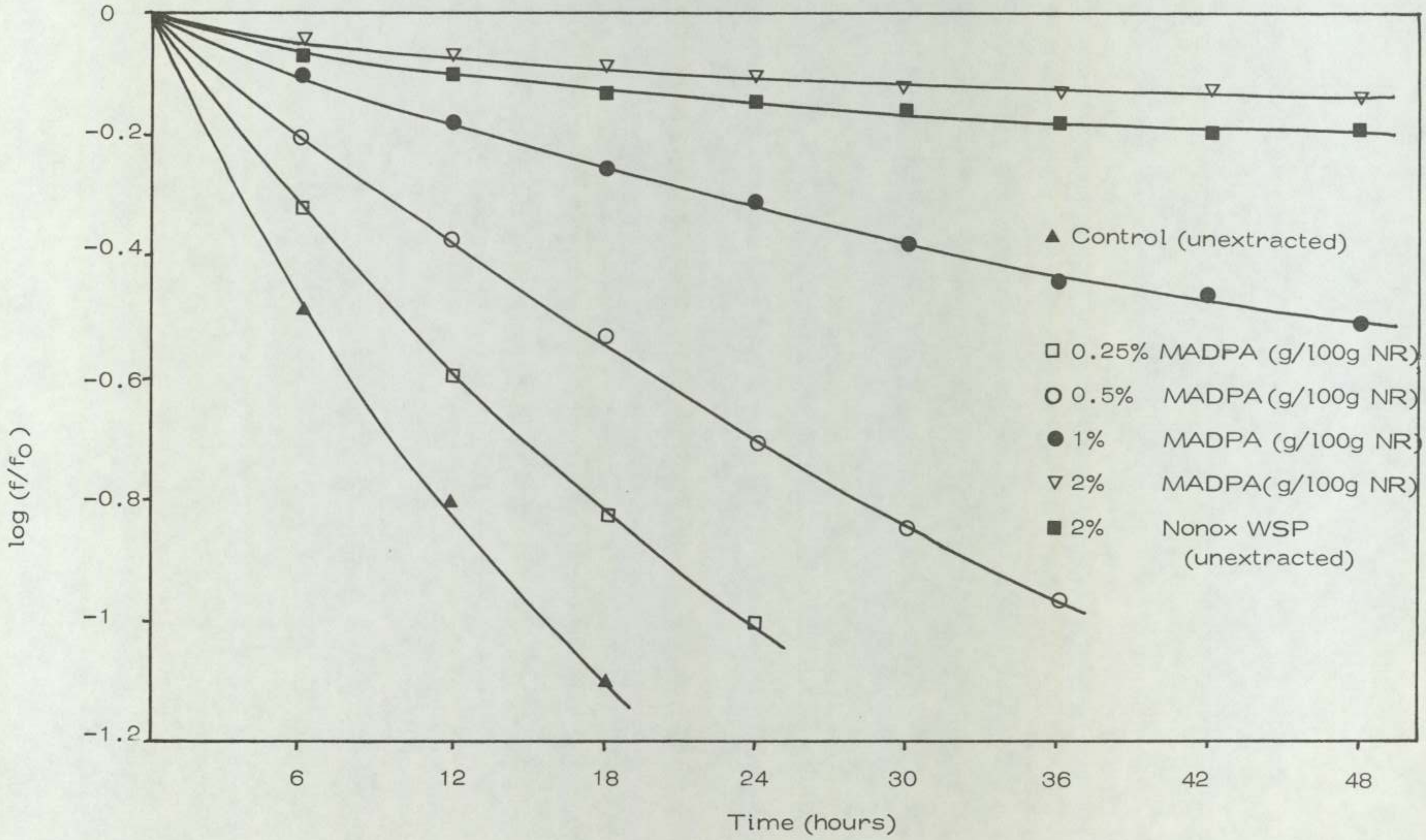


Fig. 6.22. Continuous stress relaxation of NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted before vulcanisation at 100°C in air.

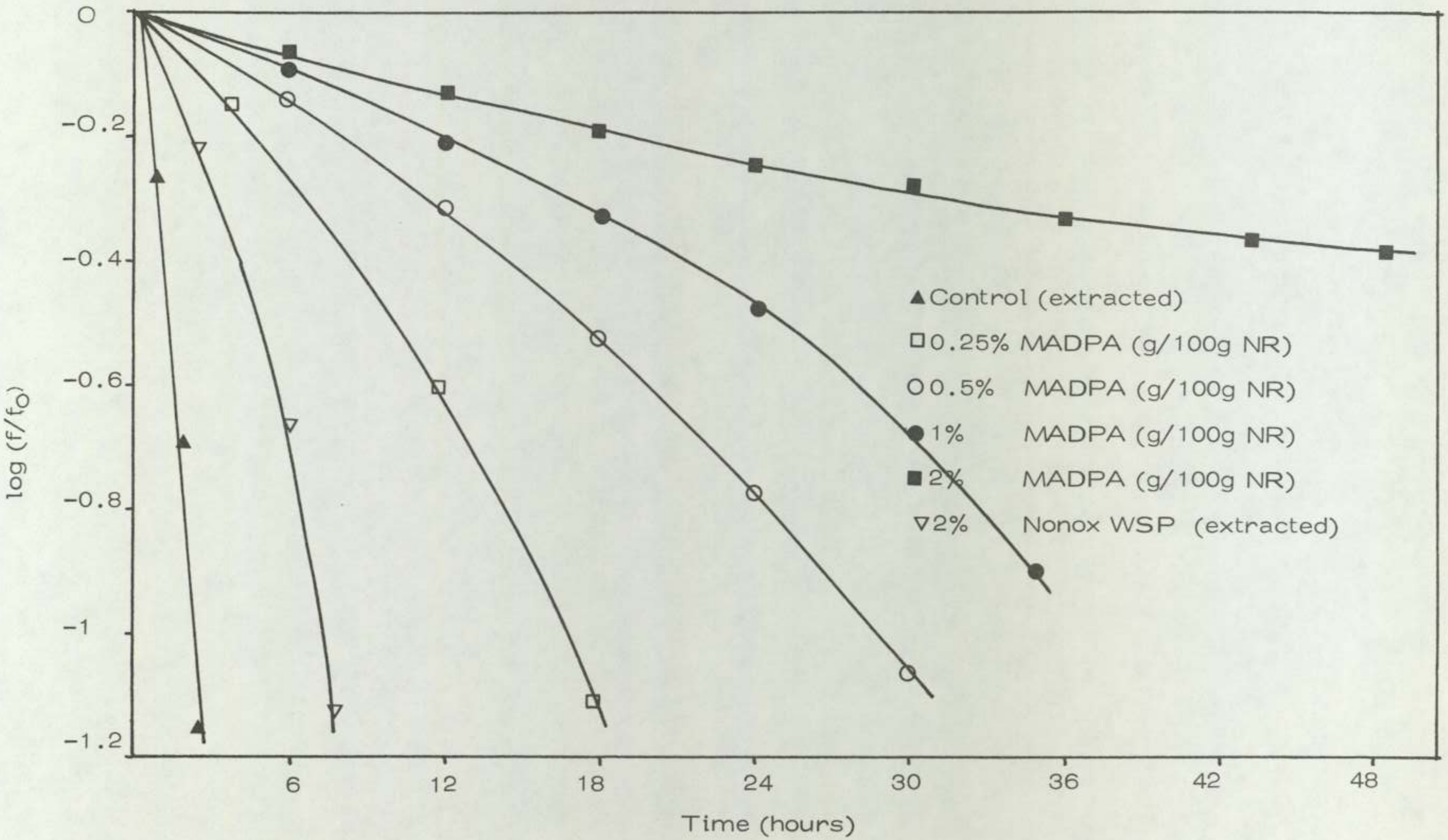


Fig. 6.23. Continuous stress relaxation of NR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted after vulcanisation at 100°C in air.

is evident that the rate of decay of stress in the extracted vulcanisate containing Nonox WSP is lower than that of the control. This is consistent with the oxygen absorption results (see Table 6.4), suggesting that a small amount of the conventional antioxidant may become bound to NR during vulcanisation and hence, resulting in a small improvement with respect to the extracted control. Figure 6.23 also shows that the decays of stresses for various vulcanisates are initially slow, becoming faster as oxidation proceeds. Furthermore, there is a steady increase in the drop of stress with time from vulcanisates containing 2% MADPA to 0.25% and from that to the extracted Nonox WSP and the control. This is in accord with the oxygen absorption results (see Fig. 6.11 and Table 6.4). Figures 6.24 and 6.25 represents the stress relaxation curves for vulcanisates prepared, from 20% MADPA (g/100 g NR) masterbatches. The unextracted Nonox WSP again was found to be slightly more stable than the vulcanisate containing 2% MADPA extracted prior to vulcanisation (Fig. 6.24). However, the loss of Nonox WSP after extraction is quite evident by rapid decay of stress as compared to any other protected vulcanisates with MADPA as shown in Fig. 6.25.

Masterbatches prepared from SBR reacted with MADPA and BHBM in the torque rheometer (see Sections 5.1.2. and 5.1.3) were also assessed by continuous stress relaxation. The relaxation curves of these vulcanisates are shown in Figs. 6.26-6.31. Figure 6.26 indicates that the unextracted SBR vulcanisates containing various

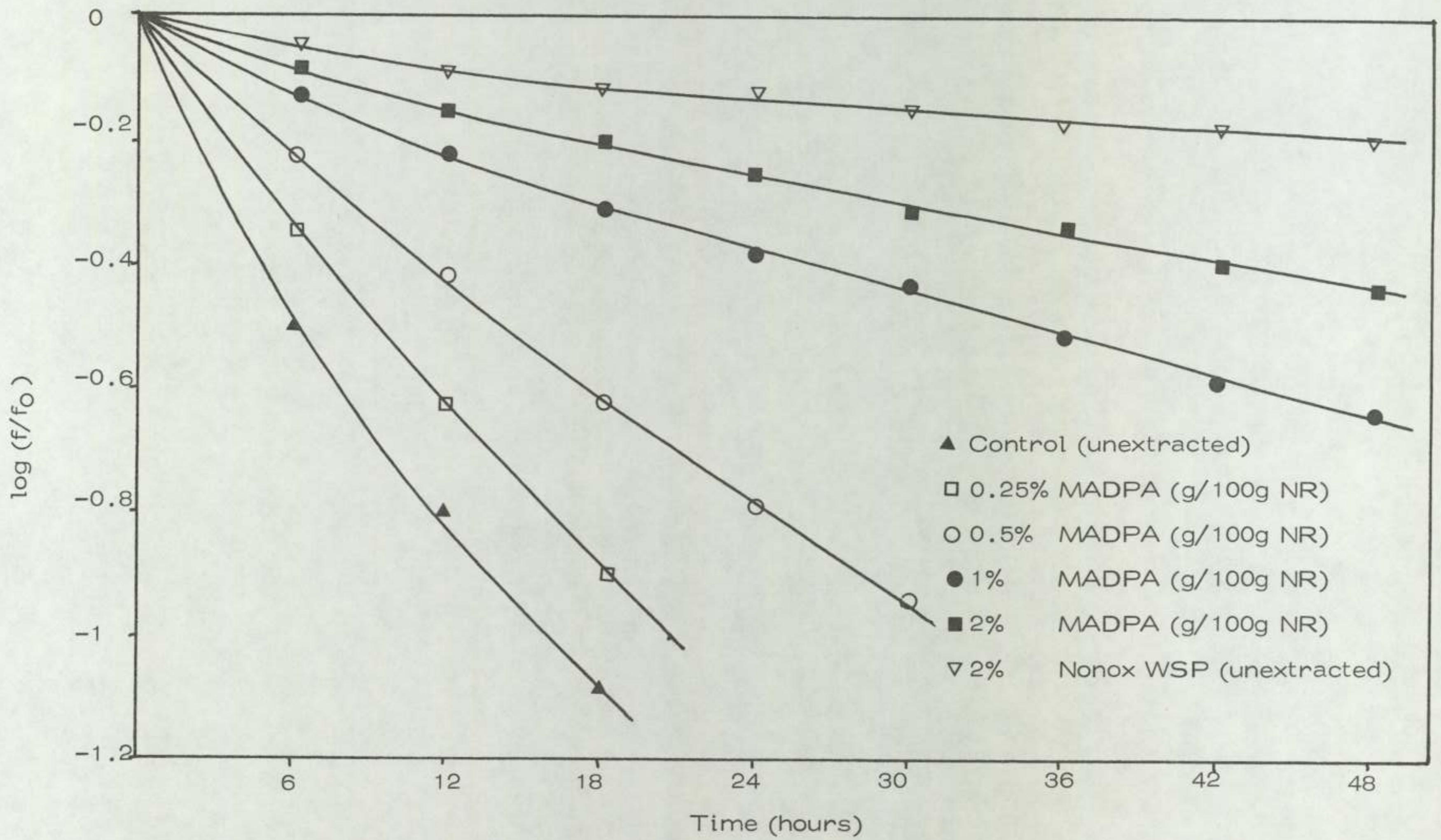


Fig. 6.24. Continuous stress relaxation of NR vulcanisates containing various concentrations of MADPA (masterbatches from 20%) extracted before vulcanisation at 100^{o}C in air.

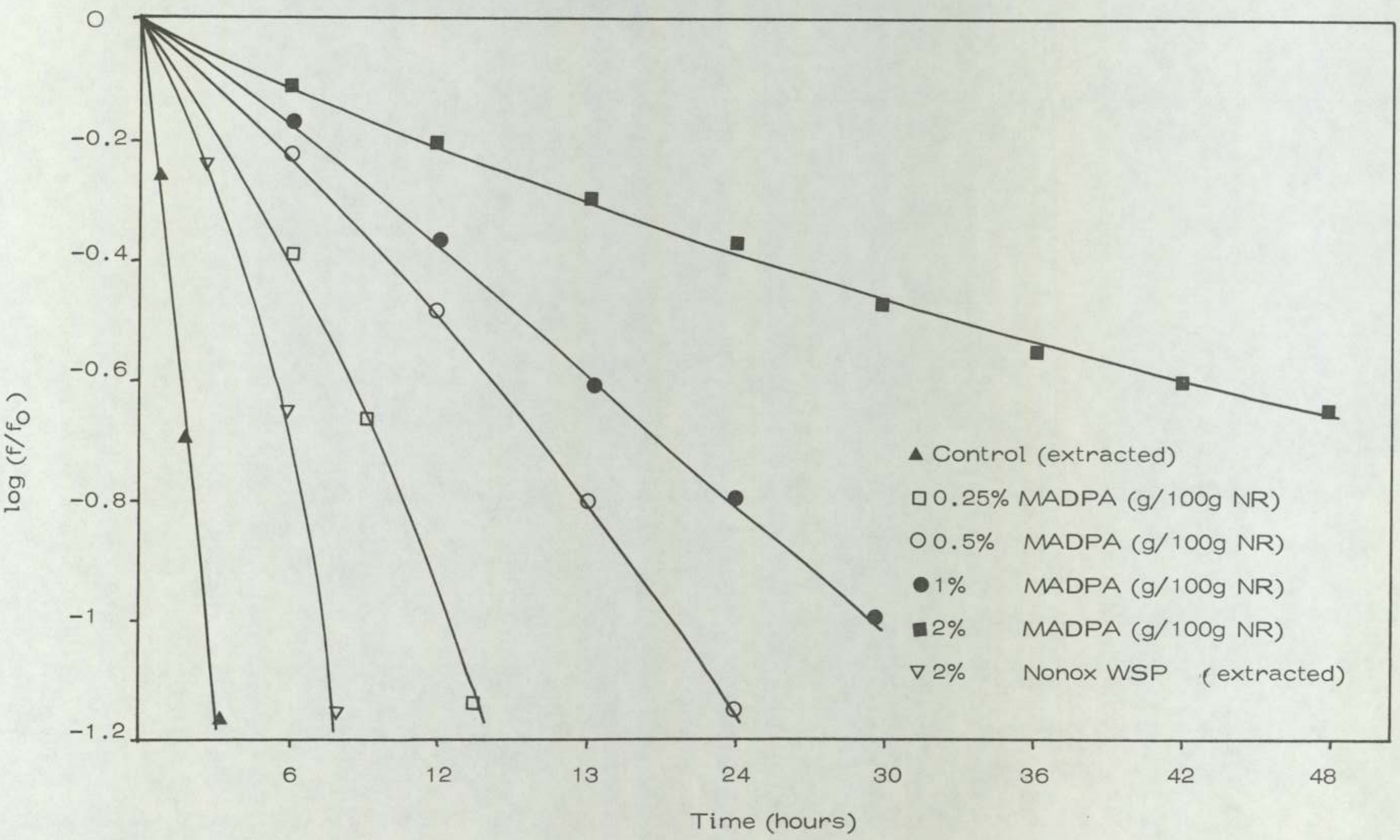


Fig. 6.25. Continuous stress relaxation of NR vulcanisates containing various concentrations of MADPA (masterbatches from 20%) extracted after vulcanisation at 100°C in air.

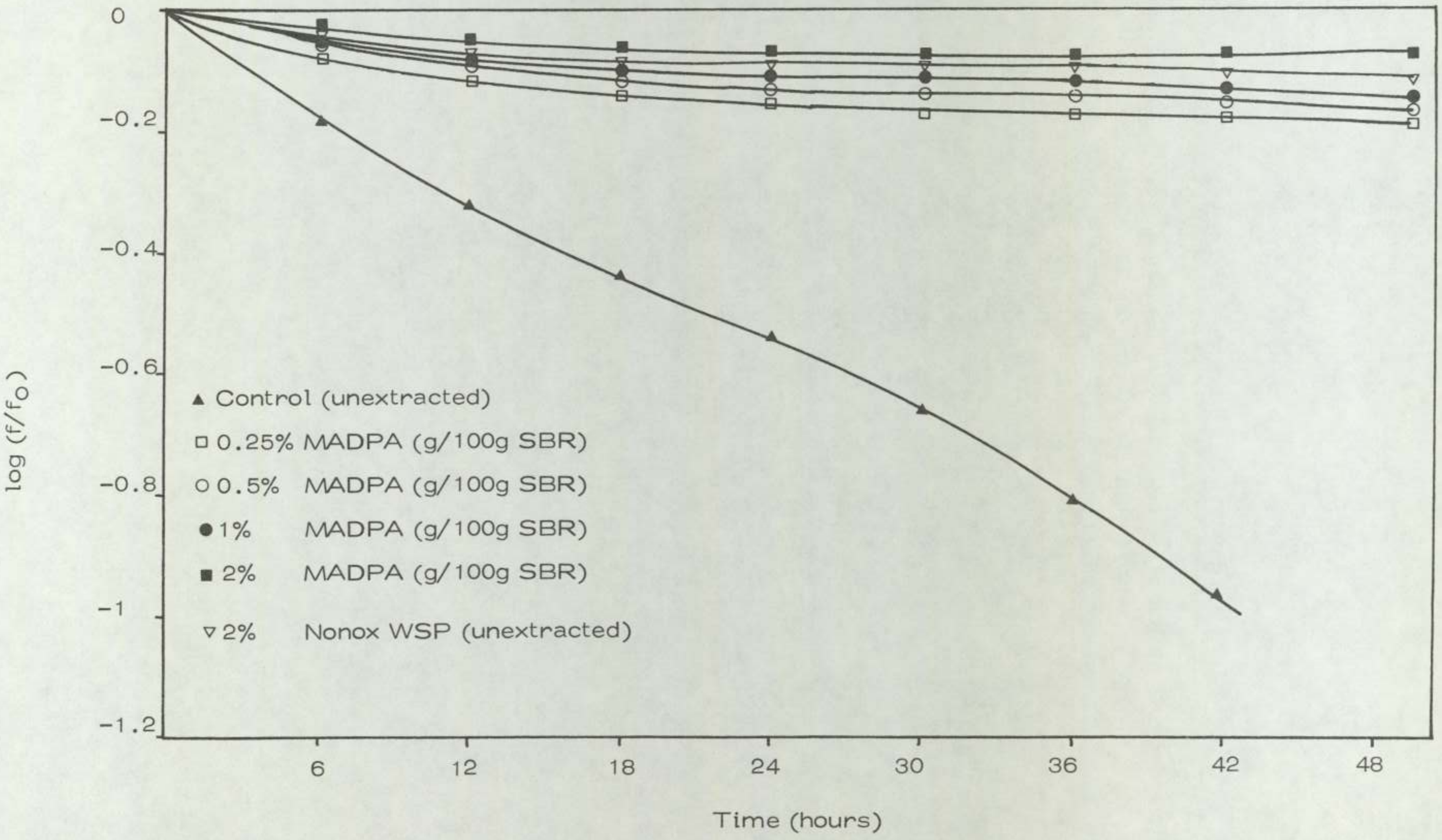


Fig.6.26. Continuous stress relaxation of unextracted SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) at 100°C in air.

concentrations of MADPA all show superior resistance to decay of stress than the unextracted control. It is also seen that the unextracted vulcanisate containing 2% MADPA shows the highest oxidative stability towards the decay of stress and even better stability than the unextracted vulcanisate containing Nonox WSP. This is in agreement with the oxygen absorption studies of these two vulcanisates (see Fig. 6.14 and Table 6.6). Unlike the oxygen absorption results, the vulcanisate containing conventional Nonox WSP was found to be slightly more stable during stress relaxation studies than the vulcanisate containing 1% MADPA. This could be again attributed to partial volatilisation of the unbound MADPA or its derived oxidation products. Figure 6.27 shows that removal of unbound MADPA prior to vulcanisation does not significantly affect the oxidative stability of the corresponding vulcanisate. It may also be seen in this figure that the vulcanisate containing 2% MADPA gives better stability towards the decay of stress than the unextracted Nonox WSP.

Figure 6.28 indicates that after removal of accelerator residue, unbound antioxidant and other extra-network materials, SBR vulcanisates containing various concentrations of MADPA do not lose their oxidative stability. This figure further shows that the vulcanisate containing Nonox WSP after extraction relaxes much faster than before extraction and reaches to that of the extracted control. This result proves that the effectiveness given by the conventional antioxidant to the vulcanisate will be lost when it is subjected to aggressive conditions such as solvent extraction and volatilisation at high temperatures.

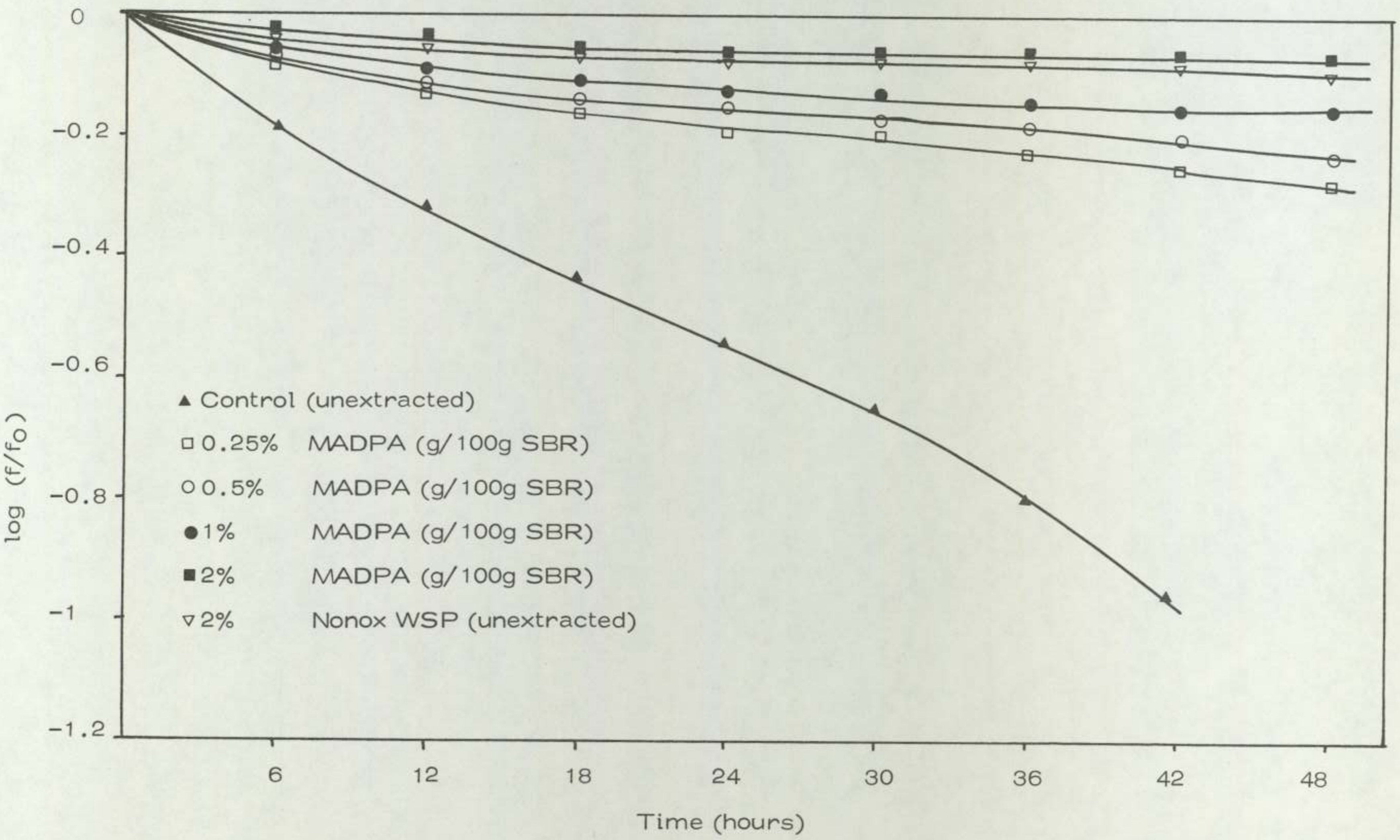


Fig. 6.27. Continuous stress relaxation of SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted prior to vulcanisation at 100°C in air.

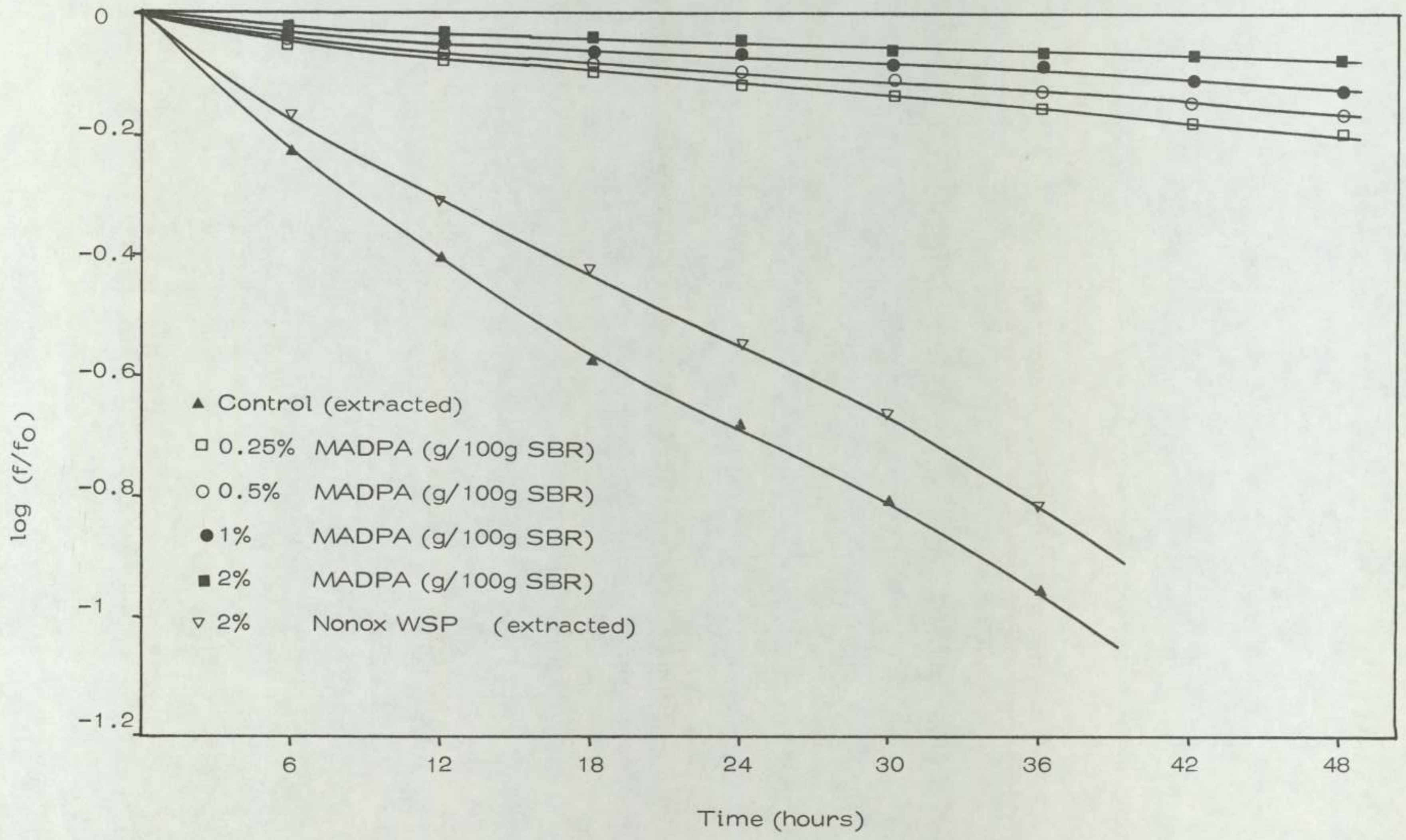


Fig. 6.28. Continuous stress relaxation of SBR vulcanisates containing various concentrations of MADPA (masterbatches from 10%) extracted after vulcanisation at 100°C in air.

However, the protection imparted to the vulcanisate by bound antioxidant is almost completely maintained even after such operations. In common with the oxygen absorption results (Table 6.6) oxidative stability of the extracted SBR masterbatches do not differ significantly from the unextracted samples (see Figs. 6.26 and 6.28). This may indicate that, unlike NR, extra network materials do not function as antioxidant in SBR.

SBR + BHBM masterbatches were also studied by stress relaxation technique. The relaxation curves for these vulcanisates are shown in Figs. 6.29 - 6.31. The unextracted SBR vulcanisate containing Nonox WSP appears to show better resistance to stress relaxation than other vulcanisates (Fig. 6.29), but this resistance disappears after extraction (Fig. 6.31). The shapes of relaxation curves for the unextracted vulcanisates containing 0.5 - 2% BHBM (Fig. 6.29) are quite similar to that of the unextracted Nonox WSP. The unextracted vulcanisate containing 0.25% of BHBM shows an initial slow rate of decay in stress which becomes faster at later stages of oxidation. The decay of stress in BHBM masterbatches extracted after vulcanisation (Fig. 6.31) is faster than those before extraction. This may be explained as due to the loss of unbound BHBM during extraction after vulcanisation. However, BHBM masterbatches extracted after vulcanisation all show superior oxidative stability to relaxation of stress than the extracted control and the

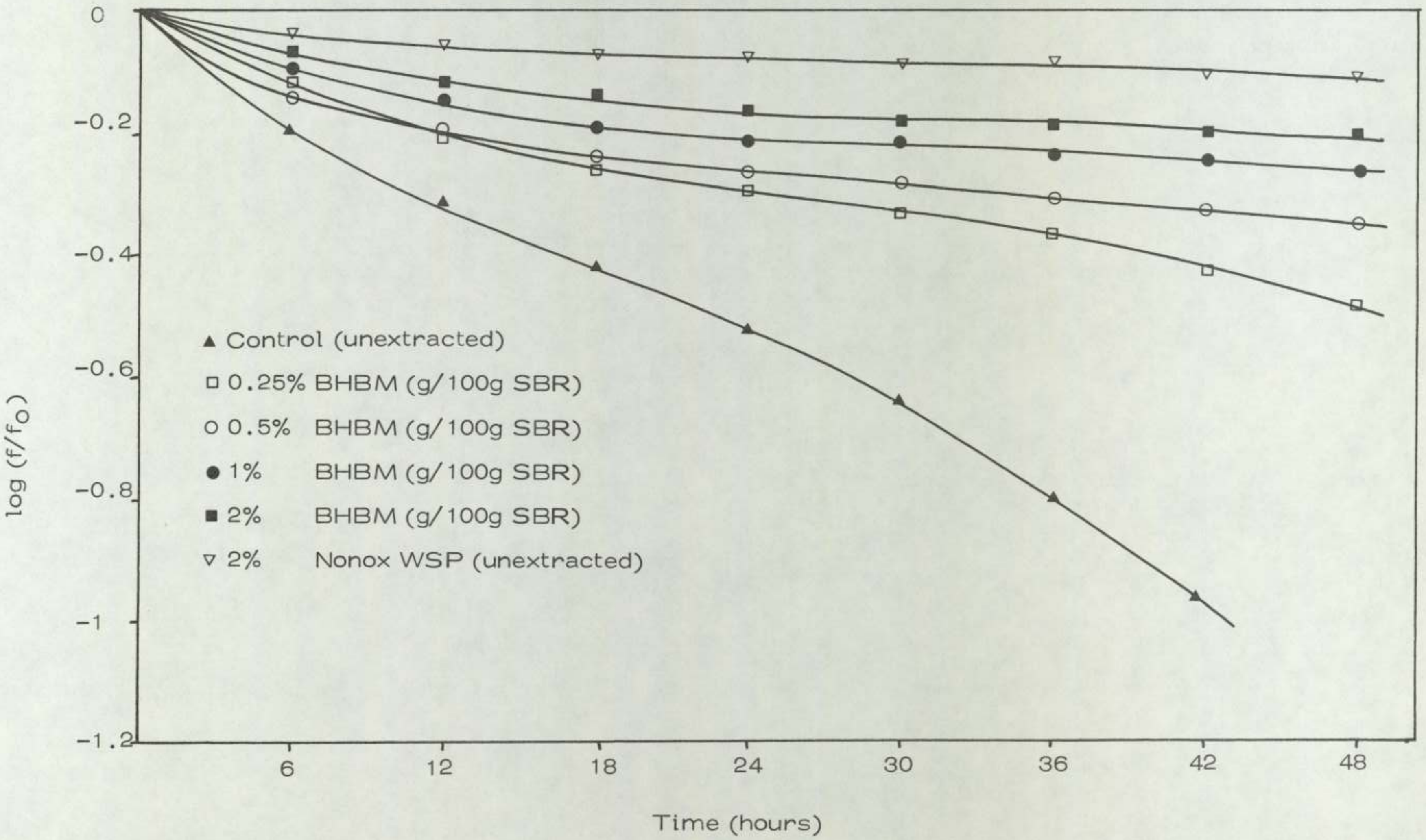


Fig. 6.29. Continuous stress relaxation of unextracted SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%) at 100°C in air.

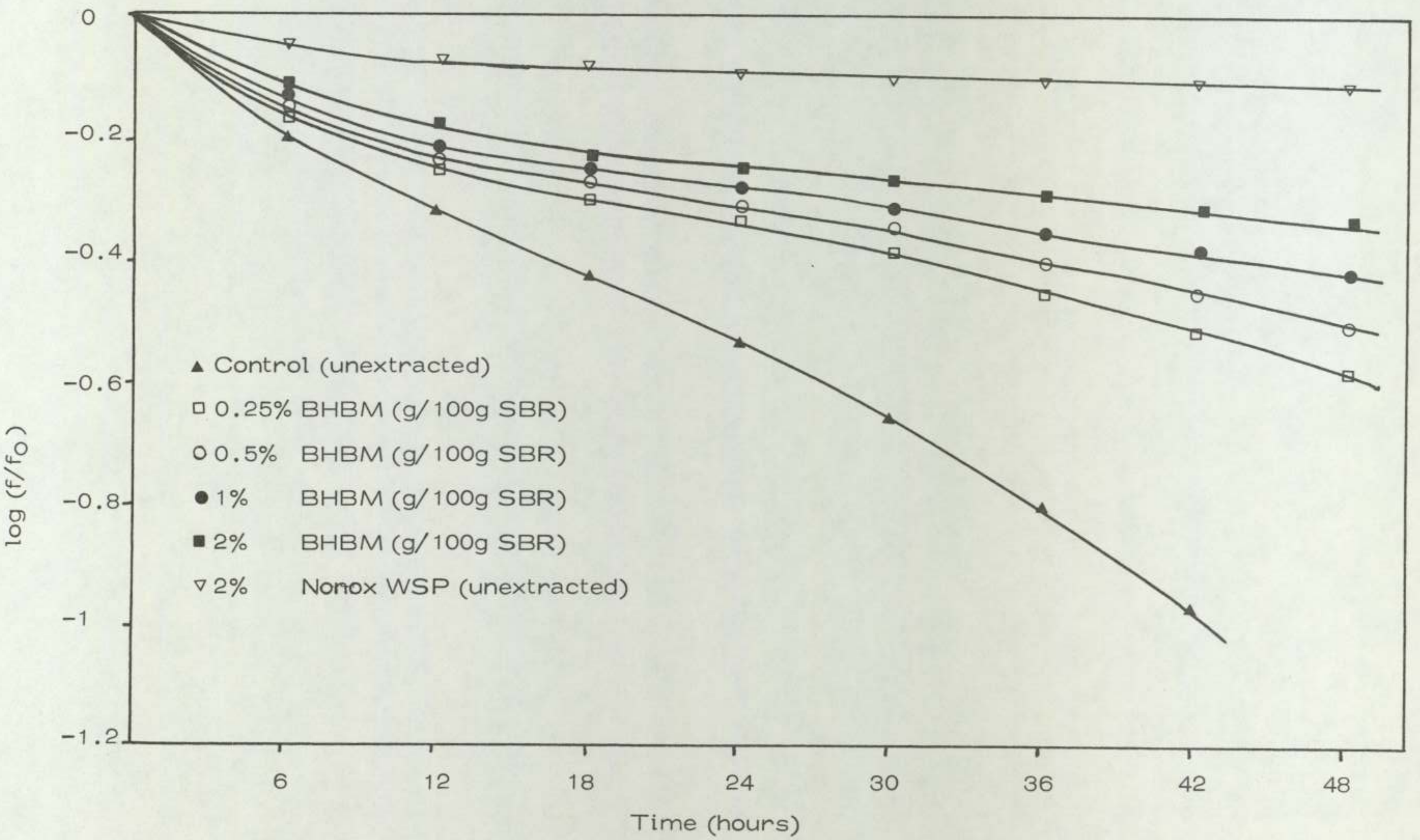


Fig. 6.30. Continuous stress relaxation of SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%) extracted before vulcanisation at 100°C in air.

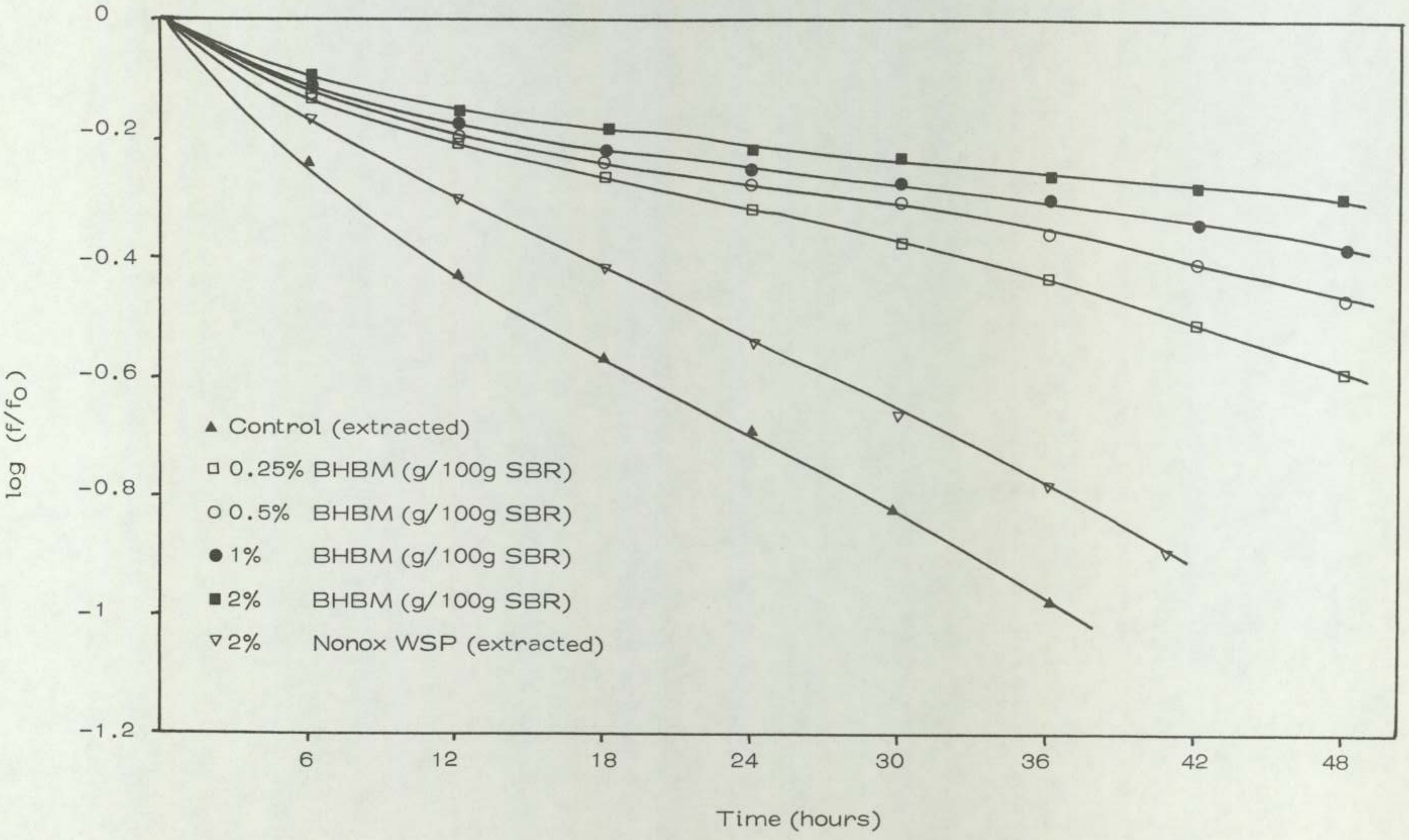


Fig. 6.31. Continuous stress relaxation of SBR vulcanisates containing various concentrations of BHBM (masterbatches from 10%) extracted after vulcanisation at 100°C in air.

extracted Nonox WSP.

6.4 Assessment of Vulcanisation Characteristics

6.4.1. Introduction

Vulcanisation is the process whereby the long chains of the rubber molecules become cross-linked to form three-dimensional structures. This reaction transforms the soft weak plastic-like material into a strong elastic product. The rubber loses its tackiness and becomes insoluble in solvents and is more resistant to deterioration normally caused by heat, light and ageing processes. The presence of non-vulcanising ingredients in the vulcanising mixture may affect the subsequent curing behaviour of the rubber. Antioxidants for example may affect the induction period of the vulcanisation process or the rate at which the vulcanisation proceeds. In the present work, the vulcanisation characteristics of the grafted - extracted and unextracted NR and SBR gum stocks reacted with different antioxidants at various proportions were studied using the Monsanto Rheometer. Details of the instrument and mode of operation have been previously described (see Section 2.4).

6.4.2. Kinetic Treatment of the Monsanto Rheograph

A typical rheometer curve obtained with the Monsanto disc rheometer is described in Section 2.4. The kinetic interpretation of this curve suggested by Coran(180,181) is as follows. If it is assumed that crosslink formation is a first order reaction after an induction period of ti, the rate of formation of crosslinks is inversely proportional to the crosslink density. Since at maximum cure the rate of formation of crosslinks is zero, then:

$$\frac{dv}{dt} = - k \quad (V_\infty - V_t). \qquad (6.1)$$

where:

k = overall first order rate constant.

V_t = the crosslink density at time t.

V_∞ = the maximum crosslink density.

t = the time in minutes.

ti = the induction time in minutes.

By integrating the above equation :

$$\int_{V_O}^{Vt} \frac{dv}{V_\infty - V_t} = - k \int_{ti}^{t} dt$$

Therefore:

$$\ln \left[V_\infty - V_t \right]_{V_o}^{V_t} = - k \left[t \right]_{ti}^{t}$$

or

$$\ln \frac{V_\infty - V_t}{V_\infty} = - k \quad (t-ti) \qquad (6.2)$$

Since the torque developed (R) is a direct measure of crosslink density, equation 6.2 can be rewritten as follows :

$$\ln \frac{R_{max}-R_t}{R_{max}} = -k\ (t - ti)$$

or

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

Therefore, if we plot log $(R_{max}-R_t)$ against time there would be a slope of $-\frac{k}{2.303}$ and an induction period of the ti, the time necessary for the reaction to become first-order A typical first order plot would then be as shown in Fig. 6.32.

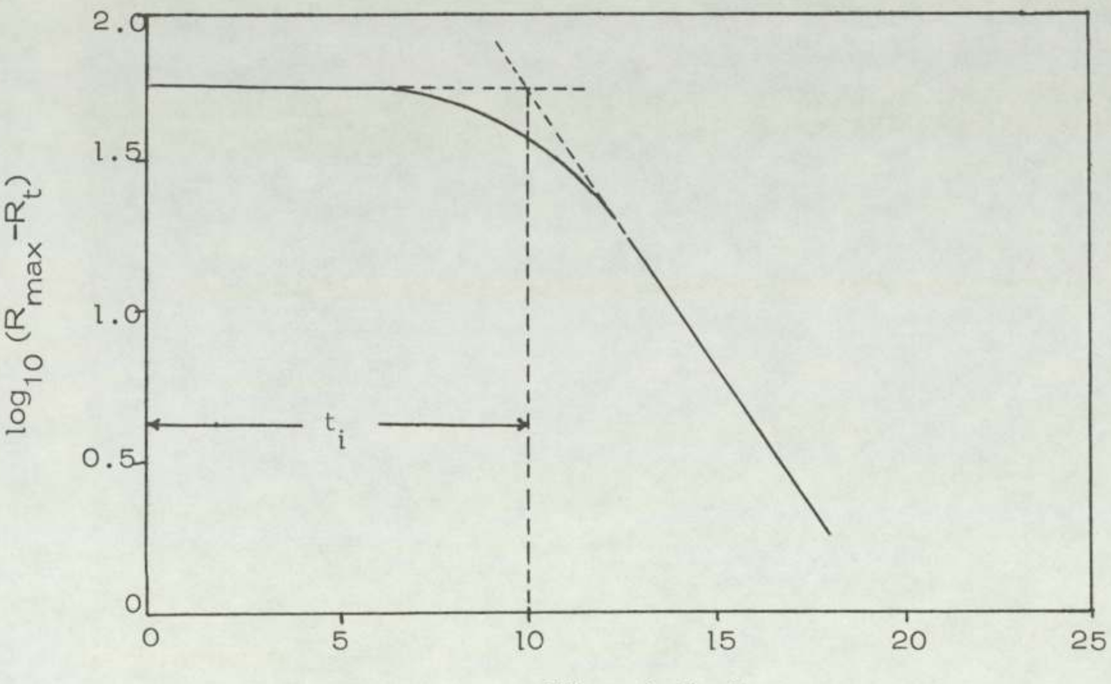


Fig. 6.32. Typical first order plot for the vulcanisation of rubber according to kinetic treatment of Coran (180, 181).

The vulcanising system therefore becomes characterised by three parameters. Firstly, the maximum torque developed R_{max}, which is a measure of crosslink density, secondly, the overall first-order rate constant k, and thirdly, the induction period t_i which is a measure of the time for formation of an active sulphurating species and the reaction of this with the hydrocarbon to form a rubber-bound intermediate, the precursor to crosslink formation.

6.4.3. Results

The curing characteristics of the grafted-unextracted and extracted BTGA and BTGE reacted at 2% level with NR latex containing maximum amount of bound antioxidant (see Sections 4.2.3 and 4.5.1.3) were studied using the Monsanto rheometer and the information obtained from rheographs was used for plotting $\log_{10} (R_{max}-R_t)$ versus time. The vulcanisation parameters derived from these plots are summarised and compared with that of the control (no antioxidant) in Table 6.8.

TABLE 6.8 Cure Parameters of the Antioxidants Reacted with NR Latex, at 140°C

Stock	Concentration of antioxidant (g/100 g NR)	R_{max} (in. lb)	ti (min)	k (min^{-1})
Control	-	67	9.5	0.26
Bound-extracted (BTGA)	0.92	60	7	0.22
Bound-unextracted (BTGA)	2	63	5	0.24
Bound-extracted (BTGE)	0.88	62	8	0.27

Continued.

TABLE 6.8 (Continued...)

Stock	Concentration of antioxidant (g/100 g NR)	R_{max} (in. lb)	ti (min)	k (min^{-1})
Bound-unextracted (BTGE)	2	58	6	0.23
Rubber containing BTGA as additive	2	61	4	0.18
Rubber containing BTGE as additive	2	59	3.5	0.17

The curing characteristics of the masterbatches of NR and SBR reacted with MADPA at 10 % level (see Sections 5.1.2 and 5.1.4) and SBR + BHBM (Section 5.1.3) were also studied. The curing parameters were determined for various masterbatches containing different proportions of the antioxidants using the procedure described earlier in this section. The curing parameters of unextracted and extracted masterbatches of NR + MADPA are given in Tables 6.9 and 6.10 respectively. The vulcanisation characteristics of the unextracted and extracted masterbatches of SBR + MADPA and SBR + BHBM were also determined and are summarised in Tables 6.11 - 6.14.

TABLE 6.9 Cure Parameters of the Unextracted Masterbatches of NR + MADPA (from 10%) at 140°C

Stock	R_{max} (in. lb)	t_i (min)	k (min^{-1})
Control	67	9.5	0.26
0.25% MADPA	63	6	0.28

Continued..

TABLE 6.9 (continued...)

Stock	R_{max} (in. lb)	ti (min)	k (min^{-1})
0.5% MADPA	60	4.5	0.27
1% MADPA	58	4	0.25
2% MADPA	44	3	0.17

TABLE 6.10 Cure Parameters of the Extracted Masterbatches of NR + MADPA (from 10%) at 140°C

Stock	R_{max} (in. lb)	ti (min)	k (min^{-1})
Control	67	9.5	0.26
0.25% MADPA	65	8.5	0.28
0.5% MADPA	63	8	0.25
1% MADPA	63	7.5	0.24
2% MADPA	61	6	0.22

TABLE 6.11 Cure Parameters of the Unextracted Masterbatches of SBR + MADPA (from 10%) at 140°C

Stock	R_{max} (in. lb)	ti (min)	K (min^{-1})
Control	72	9	0.22
0.25% MADPA	67	7.5	0.20
0.5% MADPA	64	7	0.19
1% MADPA	63	6	0.18
2% MADPA	60	4.5	0.17

TABLE 6.12 Cure Parameters of the Extracted Masterbatches (from 10%) of SBR + MADPA at 140°C

Stock	R_{max} (in. lb)	ti (min)	k (min^{-1})
Control	72	9	0.22
0.25% MADPA	69	9	0.21
0.5% MADPA	68	8.5	0.20
1% MADPA	67	8	0.18
2% MADPA:	65	7.5	0.18

TABLE 6.13 Cure Parameters of the Unextracted Masterbatches (from 10%) of SBR + BHBM at 140°C

Stock	R_{max} (in. lb)	ti (min)	k (min^{-1})
Control	72	9	0.22
0.25% BHBM	65	7.5	0.20
0.5% BHBM	64	7	0.19
1% BHBM	63	5.5	0.18
2% BHBM	56	3.5	0.17

TABLE 6.14 Cure Parameters of the Extracted Masterbatches (from 10%) of SBR + BHBM at 140°C

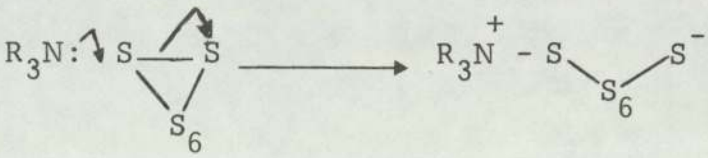
Stock	R_{max} (in. lb)	ti (min)	k (min^{-1})
Control	72	9	0.22
0.25% BHBM	69	8	0.21
0.5% BHBM	68	7.5	0.22
1% BHBM	66	8	0.20
2% BHBM	61	7	0.18

6.4.4. Discussion

Over the past two decades, there has been considerable debate concerning the mechanism of accelerated sulphur vulcanisation. During the 1950's investigators such as Craig(182) Scheele(183), Bevilacqua(184), Blokh(185) and Dogadkin(186), proposed free radical mechanisms for the accelerated sulphur vulcanisation of unsaturated elastomers. Later, however, the British BRPRA, later NRPRA (now MRPRA) group advanced (40,187) a polar mechanism for the accelerated sulphur vulcanisation

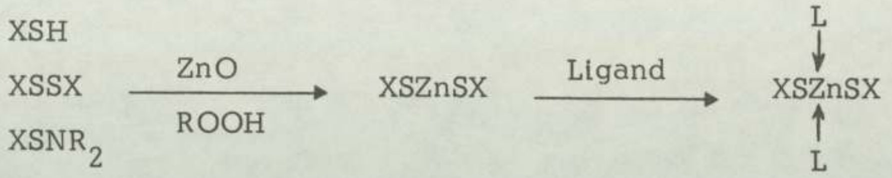
as an extension of their work on unaccelerated sulphur vulcanisation. There are still many unanswered questions and there is reason to believe that both free radical and ionic reactions are taking place simultaneously with one or the other predominating at different stages of the overall vulcanisation reaction depending on the vulcanisation system.

Krebs(189) studied the reaction of sulphur with amine accelerators and the sulphide ion. He concluded that the S_8 ring undergoes rapid ionic cleavage at relatively low temperatures in the presence of amines or sulphide ion:



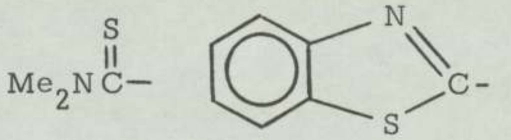
Krebs noted that the accelerating properties of amines were a function of the base strength and suggested that amines accelerate sulphur vulcanisation by ring-opening of sulphur. In conjunction with ideas advanced by Krebs(188) and co-workers(189), the most widely accepted mechanism for accelerated sulphur vulcanisation was suggested by the NRPRA (40,187) group which can be summarised as shown in Scheme A.

Reaction Scheme A Reaction of accelerator and activator



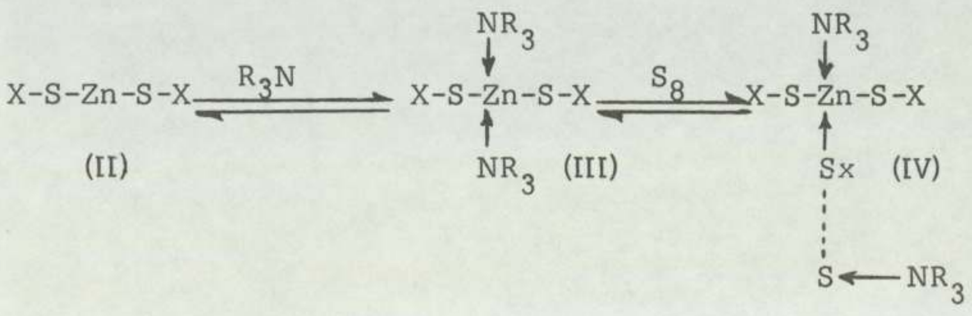
(I)

Where L = amine and X =



etc.

The reaction of the accelerator with the activators (ZnO, fatty acids, amines) leads to complex (I) which is in accord with the suggestion of Krebs(189) et al., who have shown that ZnO can participate in the formation of complexes and postulated that complexes such as zinc dimethyl dithiocarbamate (ZMDC) and zinc mercaptobenzthiazole (ZMBT) react with amines and sulphur as follows :

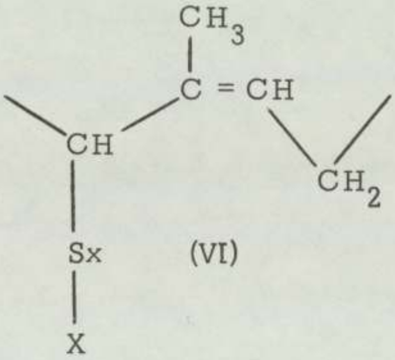


Reaction Scheme B Reaction of the zinc-accelerator complex with sulphur

$$XSZnSX + S_8 \longrightarrow XSS_xZnS_xSX$$

(V)

This reaction shows a departure from the suggestion of Krebs, who postulated complex (IV). The persulphurated zinc salt (V) has never been isolated. It is now generally accepted that the precursor to the formation of crosslinks in accelerated sulphur vulcanisation is the rubber-bound intermediate (VI).



(VI)

X = An accelerator fragment

Evidence for the formation (VI) is most definitive for the TMTD sulphurless vulcanising system. Moore and Watson(190) have shown that in the vulcanisation of cis-1,4-polyisoprene by the TMTD-ZnO system high amounts of nitrogen and sulphur are combined with the rubber after a short cure time but these are both reduced to limiting values as crosslinking reaches to a maximum. Further evidence for the formation of rubber-bound intermediate comes from the fact that when an under-cured vulcanisate (which has had all the extra-network materials except ZnO and ZnS removed) is reheated new crosslinks are shown (190, 191) to be formed. According to the NRPRA mechanism,(40,187) the zinc per thiomercaptides (V) are considered to be the actual sulphurating species. They proposed the possibility of homolysis of the zinc perthiomercaptide complex (V) to yield persulphenyl radicals which could then react with the rubber to form the rubber-bound intermediate (VI) as illustrated in reaction Scheme C.

Reaction Scheme C

$$XSS_xZnS_ySX \longrightarrow XS\dot{S}_x + ZnS + X\dot{S}_y$$

$$X\dot{S}_y + RH \longrightarrow \dot{R} + XS_yH$$

$$\dot{R} + XS\dot{S}_x \longrightarrow RS_xSX$$

$$\dot{R} + XSS_xZnS_ySX \longrightarrow RS_xX + ZnS + XS\dot{S}_y$$

Furthermore, there are many free radical mechanisms which have been suggested (182-186) for accelerated sulphur vulcanisation (particularly those involving TMTD, MBT, MBTS, and CBS) and the "sulphurless" TMTD-ZnO system prior to the development of NRPRA polar mechanism. These free radical schemes are basically very similar and the initial stages are shown in Scheme D. A marked similarity between this Scheme and that presented in Scheme C for the possible homolysis of the zinc perthiomercaptide complex may also be noted.

Reaction Scheme D

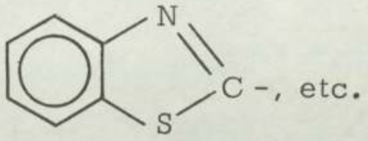
$$XSSX \longrightarrow 2\,XS^{\bullet}$$

$$XS^{\bullet} + RH \longrightarrow XSH + R^{\bullet}$$

$$R^{\bullet} + S_8 \longrightarrow RS_8^{\bullet}$$

$$R^{\bullet} + XSSX \longrightarrow RSX + XS^{\bullet}$$

$X = Me_2NC(=S)-$,



Recently there has been a tendency to consider accelerated sulphur vulcanisation in terms of a mixed free radical and polar mechanism. The studies of Shelton (192) and McDonel and later, Manik (193) and Banerjee, indicated that a mixed polar and free radical mechanism is involved. The dominant mechanism was shown (192) to be dependent upon a number of variables such as the type and concentration of the accelerator, the concentration and stability of the zinc complexes, etc.

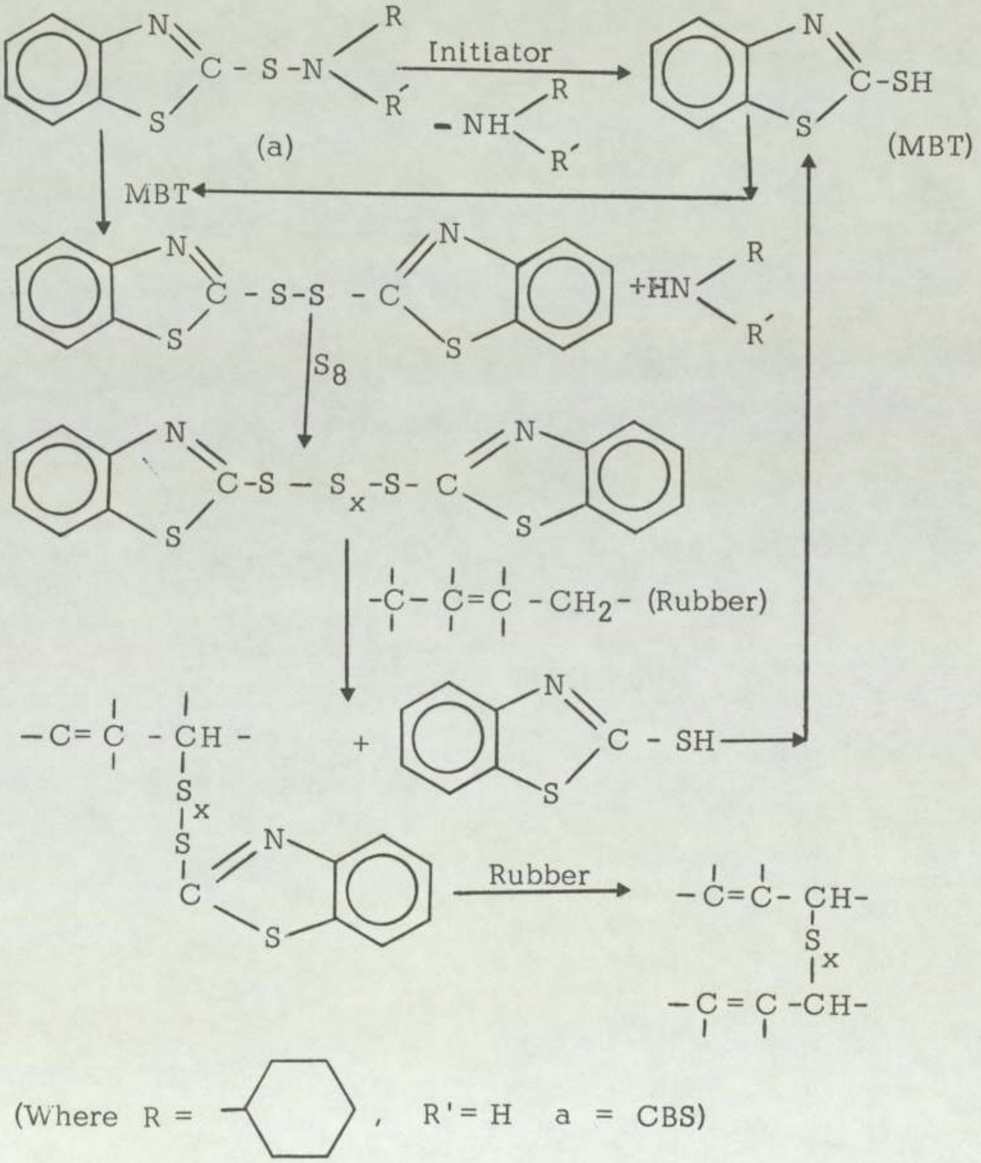
However, the accelerated sulphur vulcanisation in the case of sulphur/sulphenamide system has been suggested (194) to proceed by the following steps which are also shown in Scheme E.

i. Sulphur reacts with the accelerator to give monomeric polysulphides (A_c-S_x-A_c) where A_c is an organic component derived from the accelerator.

ii. The rubber can then react with the monomeric polysulphide to give polymeric polysulphide (rubber-S_x-A_c). During this process mercaptobenzothiazole (MBT) has been shown(195) to form when an accelerator derived from MBT is used.

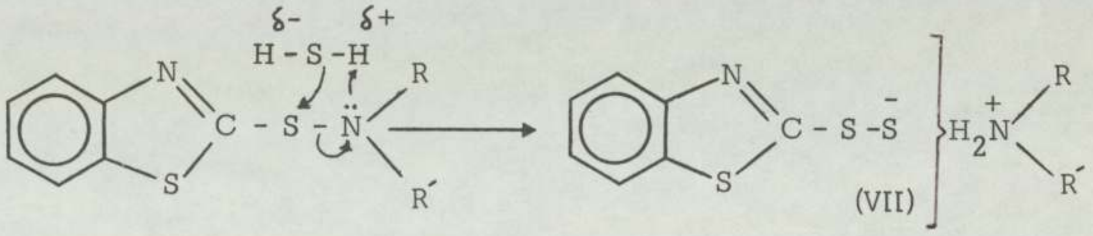
iii. The rubber polysulphides then react either directly or through a reactive intermediate, to give crosslinks or rubber polysulphide of the type rubber-S_x-rubber.

Reaction Scheme E



(Where R = , R' = H a = CBS)

The main technological importance of these MBT derivatives lies in their delayed action; that is, they do not exert full accelerative action until the technologically desirable vulcanisation temperature is reached and thus "scorch" and related disadvantageous forms of premature vulcanisation during processing are greatly reduced. It has been shown (195, 196) that the delayed-action effect results from the fact that the actual accelerator precursor, MBT, or in the case of sulphenamides the amine salt of MBT (VII), is only released effectively at the vulcanising temperature by the thermal, hydrolytic, or reductive fission of the S-S or S-N bonds. Furthermore, it has been shown (197) that hydrogen sulphide formed by the reaction of sulphur with natural nitrogenous bases (in NR), or the amine moiety of the sulphenamide can act as important reducing agent leading to the formation of amine salt of MBT (VII).



Scheele <u>et al.,</u> (198) have suggested that the amine salt of MBT is the first product of sulphenamides in the vulcanising system. This salt (VII) will then react rapidly with zinc soap to give persulphenyl Z-MBT which will be the active accelerator leading to activation of elemental sulphur.

Results given in Table 6.8 show that BTGA in grafted-extracted or unextracted vulcanisates causes a reduction in scorch time, but the effect on the rate of cure or modulus is not significant. Similar changes are also observed with vulcanisates containing BTGE before and after extraction. It also appears that when BTGA or BTGE are added as additives the interference with the vulcanisation process is more significant.

The curing parameters of the unextracted masterbatches of NR plus MADPA are given in Table 6.9. The results in this Table show that there is a drop in modulus as the amount of the antioxidant increased. This is particularly evident in vulcanisate containing 2% MADPA. The rate of cure for samples containing various concentrations of 0.25 - 1% of MADPA did not change significantly but the induction period was found to reduce continuously as the amount of antioxidant increased. In Contrast the vulcanisate with 2% MADPA showed a considerable drop in all curing parameters studied. This may be generally explained as being due to the presence of 4-acyl aminodiphenylamine groups which are expected not only to function as reducing agents for the cleavage of the S-N bond of the accelerator and the formation of the amine salt (VII) through their aminic groups, but they may also be involved in the formation of complex (I) or (IV) which accelerate the formation of persulphurated zinc salt and subsequent reaction of this salt with the rubber chains. Results given in Table 6.10 suggest that removal of unbound MADPA prior to vulcanisation reduces its interference with the vulcanisation process. It is shown in this Table that the reduction in modulus or induction period and the rate of cure are not very significant. The more pronounced accelerating effects in the unextracted masterbatches (Table 6.9) could be further explained as being due to the presence of free thiol groups(-SH) acting in a similar manner to hydrogen sulphide (197) by functioning as reducing agents for the cleavage of the S-N bond of the CBS and the formation of the amine salt (VII).

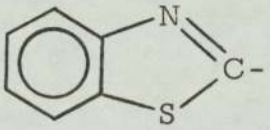
The curing characteristics of the unextracted masterbatches of MADPA in SBR are given in Table 6.11. The reduction in modulus and induction period can also be noted in this case. The rate of cure of different vulcanisates containing various proportions of MADPA, again was found not to change considerably as the concentration of antioxidant increased, except at 2%. However, the reduction in maximum torque (R_{max}) for the unextracted SBR vulcanisate containing 2% MADPA is less than that of the NR vulcanisate containing the same amount of MADPA (Table 6.9). Moreover, the curing characteristics of the extracted masterbatches given in Table 6.12 further support the suggestion that in the absence of unbound MADPA there will be less interference with the curing behaviour of the compounded rubber involved.

The curing characteristics of the masterbatches prepared from BHBM in SBR are given in Tables 6.13 and 6.14. The reduction in modulus and induction period also appears for the unextracted samples in this case (Table 6.13). In contrast, the extracted BHBM masterbatches do not show a significant variation in all the curing parameters studied. In general, the decrease in the rate of vulcanisation, particularly in unextracted samples, may be rationalised in terms of formation of free radicals derived from antioxidants during the process of vulcanisation. These free radicals may function as free radical traps for the other radicals from the homolysis of CBS in a similar manner to that described by Coleman _et al.,_ (199) for MBT or bis(2-benzothiazolyl), di or poly sulphides as shown below :

$$XSH \longrightarrow XS^{\bullet} + H^{\bullet}$$

$$XS_xX \longrightarrow XS^{\bullet} + XS^{\bullet}_{x-1}$$

Where $x \geqslant 2$, X =



Such radicals may then be trapped by thiyl or nitroxyl radicals derived from MADPA or BHBM during the process of vulcanisation.

CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1. Conclusions

The work described in this thesis has demonstrated that 3,5-di-tert-butyl-4-hydroxybenzyl carboxy methyl (BTGA) and ethyl (BTPA) sulphides, 3,5-di-tert-butyl-4-hydroxybenzyl-mercaptoglycollate (BTGE) and BTGE disulphide can be chemically bound into natural rubber in the form of latex and in the presence of a free radical generating redox system such as TBH and TEPA. In the case of BTGE it was found that hydrolysis may take place during the grafting to NR latex, reducing the yield of BTGE adduct formed. Deammoniation of the NR rubber latex to reduce the pH was found to minimise hydrolysis.

It was also found that MADPA and BHBM can be chemically attached to SBR and NR during mechanochemical reactions in the torque rheometer. Further improvement in the yield of adduct obtained from these antioxidants after processing in the torque rheometer, was achieved during subsequent vulcanisation. A major advantage of the bound antioxidant produced during processing was that it could be conveniently used in the preparation of masterbatch concentrates. It was found that vulcanised NR or SBR masterbatches containing various concentrations of BHBM or MADPA diluted in normal rubbers all show superior performances after extraction relative to an extracted vulcanisate containing Nonox WSP. Furthermore, the unextracted NR vulcanisate containing 1% MADPA

(diluted from 10%) showed higher resistance to oxidation than an unextracted vulcanisate containing 2% Nonox WSP. A similar observation was made in the case of masterbatches of MADPA in SBR, where vulcanisates with 1 and 2% MADPA both showed superior oxidative stability to an unextracted vulcanisate containing 2% Nonox WSP. Furthermore, SBR masterbatches containing 0.5, 1, 2% of MADPA, subjected to exhaustive extraction after vulcanisation, showed almost complete retention of oxidative stability whereas conventionally stabilised rubber showed extensive degradation. Vulcanised masterbatches containing bound antioxidants based on thiols, particularly at low concentrations showed a significantly improved colour retention.

Although BTGA, BTPA, BHBM and BTGE did not bind to NR during processing in the torque rheometer, they were found to produce the corresponding bound antioxidant during vulcanisation. The extent of binding of these antioxidants to NR and SBR was found to be dependent upon the premixing conditions and could be optimised by variation of processing time and temperature. The disulphides of BHBM and BTGE were also found to give bound antioxidants during vulcanisation.

The effects of various antioxidants at different concentrations bound to NR at the latex stage, or to NR or SBR during processing in the torque rheometer, were studied using the Monsanto rheometer. The cure parameters of vulcanisates containing bound BTGA and BTGE were not significantly different from those of the control. These antioxidants when used as additiveswere found to cause a significant reduction in the scorch time and the rate of cure. However, in unextracted masterbatches of MADPA in NR, particularly at lower concentrations, there was found to be a little change in the rate of cure, although the scorch time was slightly reduced as compared to the control. This interference with vulcanisation was further minimised when these masterbatches were extracted prior to vulcanisation to remove unbound antioxidant. The effects of this antioxidant at 0.25- 1% concentrations in SBR masterbatches, on all the cure parameters, both in extracted and unextracted stocks were insignificant. However, the effects of BHBM on vulcanisation of SBR masterbatches were found to be similar to those of MADPA in NR.

7.2. Suggestions for Further Work

The reactions of hindered-phenolic sulphides, such as BTGA and BTPA with natural rubber in the latex form or during vulcanisation have been demonstrated, but the data available were insufficient to put forward a clear picture about the reaction mechanism. Therefore, it would be valuable to study the reaction mechanisms of these sulphides with rubber using model compounds in order to determine the structure of the adduct and the nature of by-products formed. An investigation on the role of non-rubber constituents in NR latex such as protein and its hydrolysis products on the efficiency of binding of these antioxidants may lead to further improvement in the yield of bound antioxidant formed.

Mechanochemically initiated reactions of antioxidants with natural and synthetic rubbers to produce rubber-bound systems could be very useful to the rubber industry. This may also be achieved on the large industrial scale, under the appropriate conditions using various types of internal mixers. The rubber-bound antioxidants produced in this manner could be used in stabilisation of a variety of rubber products by solid masterbatching techniques. A study of the nature of the free radicals formed using the electron spin resonance (e.s.r.) and characterisation of the type of by-products produced should disentangle the chemistry involved. Finally, due to a general demand for polymeric-bound antioxidants in plastics and rubbers, this process could be further extended to other types of stabilisers and polymers.

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