This Thesis is dedicated to the memory of my father, Daniel Okunọla Ogunbanjọ

A. O. Ogunbanjọ

SULPHUR CONTAINING ANTIFATIGUE AGENT FOR RUBBER

by

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A. O. Ogunbanjọ

The work described in this Thesis has been carried out between April 1980 and November 1983. It has been carried out independently and submitted for no other degree.

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THE UNIVERSITY OF ASTON IN BIRMINGHAM

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Akinola Omotayo Ogunbanjo; Ph.D., November 1983

SUMMARY

A number of substituted phenolic sulphides, namely Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulphide; Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-disulphide; 3,5-di-tert-butyl-4-hydroxy-benzyl-dodecylthioglycolate and 3,5-di-tert-butyl-4-hydroxy-benzyl-dodecyl sulphide have been found to possess antifatigue and antioxidant activities. They showed marginal activity in sulphur vulcanisates but high activity in peroxide vulcanisates. Their initial oxidation products - sulphoxides - exhibited reduced antifatigue activity but increased thermal antioxidant action. Certain preprocessing conditions have been found to enhance the antifatigue activity of the substituted phenolic sulphides and 4-mercapto-acetamido-diphenylamine.

An examination of the transformation products formed from the substituted phenolic sulphides during fatiguing revealed that the following compounds were formed; 2,6-di-tert-butyl-1,4-hydroquinone, 2,6-di-tert-butyl-1,4 parabenzoquinone, 3,5-di-tert-butyl-4-hydroxy-benzaldehyde 3,5,3',5'-tetra-t-butyl-stilbenequinone 4,4'-dihydroxy-3,5,3',5'-tetra-tert-butyl-diphenyl-methane, 3,5-di-tert-butyl-4-hydroxy-benzyl-alcohol and sulphoxides. These transformation products showed varying degrees of antifatigue activities and are effective thermal antioxidants.

Key Words: Antifatigue agents; antiozonant; antioxidant; quinonoid products; mechano-oxidation and sulphur-acids.

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CHAPTER ONE

1. INTRODUCTION

Natural rubber (NR) is used in a wide variety of products, but over 70 per cent is consumed by the automotive industry.[1] These applications for natural rubber have been made possible by improved compound design and most especially by the development of more effective stabilisation systems against deterioration in service.

It is difficult to isolate any single factor as being solely responsible for failure of rubber goods as there is a random interplay of factors and conditions. Of the various modes of failure which are observed in rubber goods, a very important one involves the growth of cracks under dynamic loading conditions. This is termed fatigue failure and is quite distinct from ozone cracking as they occur only under dynamic loading conditions, while ozone attack can occur under both static and dynamic strains. However, ozone can accelerate fatigue failure by initiating crack formation which eventually leads to crack propagation and failure of the compound.

As a result of the demanding conditions under which rubber goods are used a variety of procedures are employed in the stabilisation of vulcanised rubbers. These involve the use of antioxidants, antiozonants, antifatigue agents, light stabilisers, protective waxes and protective coatings. Organo-sulphur compounds are known to function as antioxidants in technological media[2] but their potential as antifatigue agents is only now being assessed because there has been other well-established class of compounds as antifatigue agents, notably the para-phenylene-diamines, for example, N-isopropyl-N'-phenyl-p-phenylene-diamine (IPPD). These para-phenylene-diamines have the major problem of discoloration, especially in non-filled and white-filler filled stocks but this is less prominent in the organo-sulphur compounds, for example, hindered phenolic sulphur compounds. However, it is a known fact that sulphur cured rubbers have superior fatigue properties to those cured by other means. Recent studies have shown that the following factors are probably involved[3]:

i) the lability of the polysulphidic crosslinks which can break and reform under strain, thereby easing localised stress concentration and at the same time increase the strain energy required to cause chain rupture;

ii) the preferential oxidation of sulphur under mechanochemical conditions to give products which have a chemical antifatigue function[4, 5].

In contrast to IPPD, the exact role being played by organo-sulphur compounds in fatigue of rubber[6, 7] is still inconclusive, despite the known role of sulphur oxidation products as hydroperoxide decomposers.

1.2 OXIDATIVE DETERIORATION OF ELASTOMERS

A number of factors are known to contribute to the deterioration of natural and synthetic rubbers. Changes in mechanical properties on ageing are due primarily to the deteriorative effects of a combination of the following factors; heat, light, oxygen and ozone. Heat and light have considerable effects on the rate of rubber oxidation and oxygen in the form of O_2 and O_3 is the primary cause of polymer deterioration. This deterioration is a complex process but it is known to involve cross linking and main chain and/or crosslink scission reactions.

1.2.1 AUTOXIDATION REACTION IN RUBBERS

a) Unvulcanised Rubber

Unvulcanised rubbers undergo autocatalytic oxidation with oxygen with the formation of hydroperoxides as primary products. The hydroperoxides accumulate autocatalytically during the early stages of oxidation and then decompose to give free radicals which initiate the free radical chain reactions. This autocatalysis of the oxidation process by the hydroperoxides formed is termed autoxidation.

Model compounds with similar structures to rubbers have been used to explain the mechanism of autoxidation[8-10] in rubbers because there are certain fundamental reactions common to all these systems which are applicable to all hydrocarbon polymers.

The generally accepted mechanism of autoxidation was put forward by the British Rubber Producers' Research Association[8-10] (Scheme 1.1).

Scheme 1.1

Initiation:

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

$$2ROOH \xrightarrow{heat} RO^{\bullet} + ROO^{\bullet} + H_2O$$

Propagation:

$$ROO^{\bullet} + R'H \longrightarrow ROOH + R'^{\bullet}$$

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

Termination:

$$2R^{\bullet} \longrightarrow R\text{-}R$$

$$R'^{\bullet} + ROO^{\bullet} \longrightarrow ROOR'$$

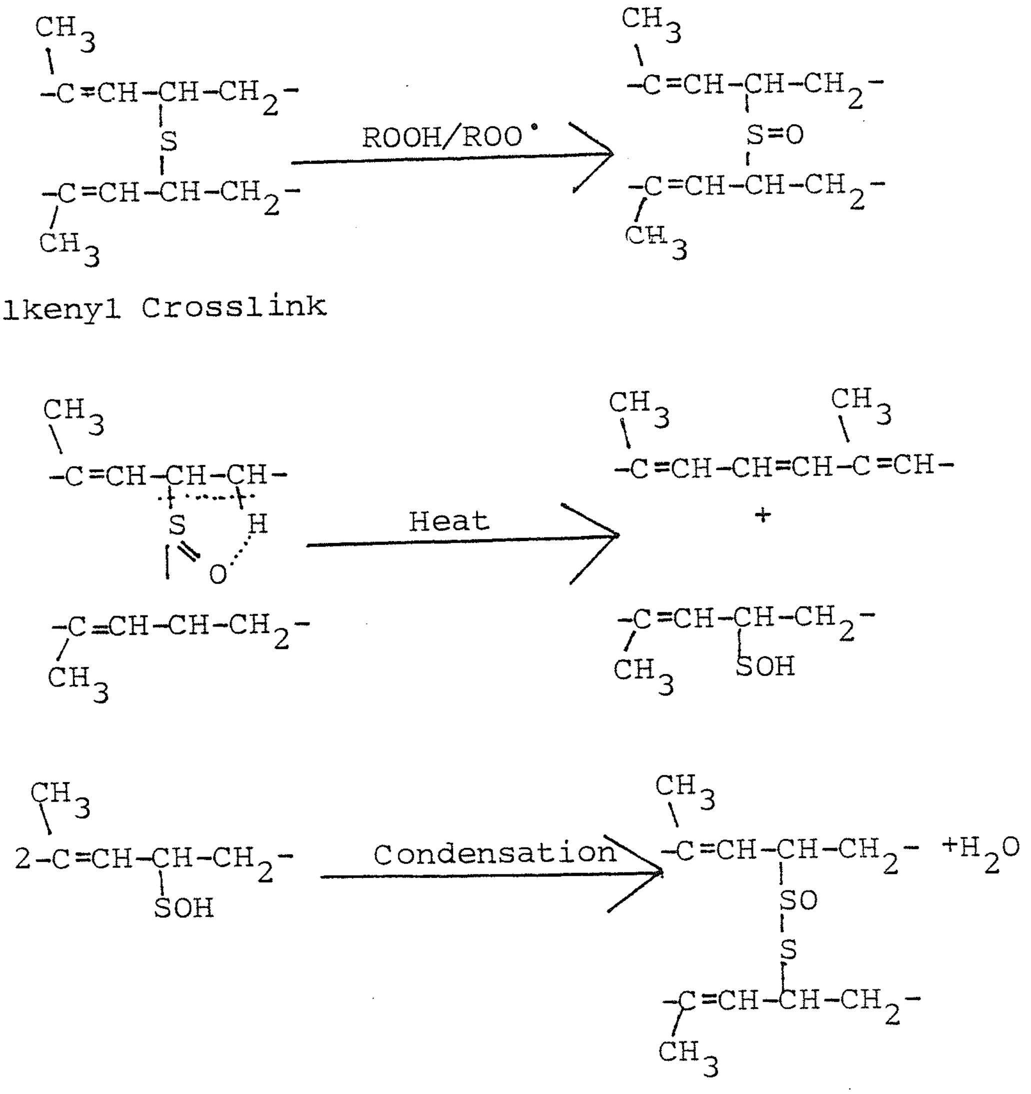
$$2ROO^{\bullet} \longrightarrow \text{Non-radical product} + O_2$$

b) Rubber Vulcanisate

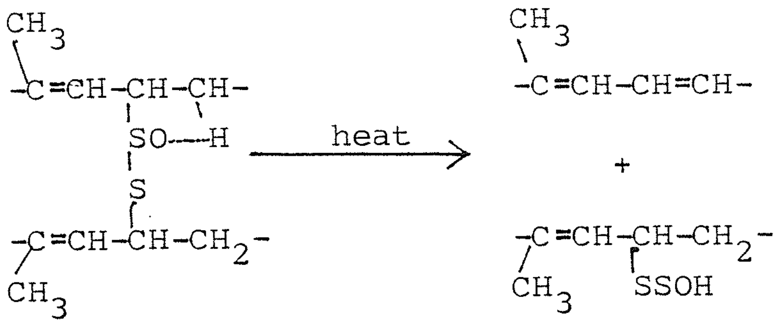
The ageing behaviour of sulphur vulcanised rubbers differs considerably from that of the raw rubbers or rubbers cured by other means such as peroxide and high energy irradiation. A feature of sulphur vulcanisates is their auto-retarding nature in contrast to the autocatalytic process occurring in raw rubbers and dehydrocrosslinked rubbers.

Investigations of the autoxidation of simple organic sulphides showed the occurrence of reactions which if simulated in vulcanisates would cause crosslink scission. This is in addition to the purely thermal scission of polysulphidic crosslinks via interchange reactions at higher temperatures. There is evidence that the oxidation reaction outlined in Scheme 1.2 can occur in vulcanised rubbers[11].

Scheme 1.2

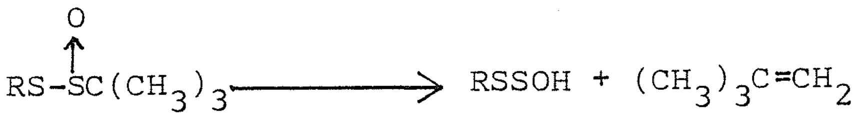


In addition, the thiosulphinate cross-link formed can undergo scission (reaction 1-1).



(1-1)

Shelton et al[12] put forward this mechanism, but for alkyl tertiary butyl thiosulphinate.



$$RS\overset{O}{\overset{\uparrow}{S}}C(CH_3)_3 \longrightarrow RSSOH + (CH_3)_3C{=}CH_2 \qquad (1\text{-}2)$$

In the oxidation of dissulphide cross-links, the thiosulphinate group is thermolabile and this will lead to interchange reaction resulting in creep and permanent set of the network when strain is applied[13].

$$R\text{-}SS\text{-}R \longrightarrow RSOSR \longrightarrow \tfrac{1}{2}RSO_2SR + \tfrac{1}{2}RSSR \qquad (1\text{-}3)$$

1.3 PROTECTION OF RUBBER VULCANISATES AGAINST OXIDATIVE DETERIORATION

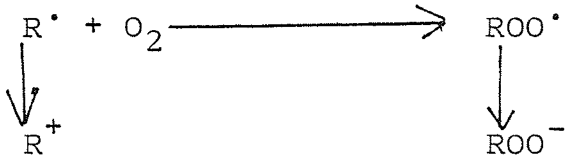
Oxidative ageing of vulcanisates is important because the absorption of as little as 1% of oxygen, by natural or synthetic rubber vulcanisates causes considerable changes in their physical properties[14]. Hence, antioxidants are of major importance to the polymer industry in that they extend the useful temperature range and service life of polymers. Antioxidants are therefore employed to interrupt the autoxidation chain process outlined in Scheme 1.1. These protective agents function in a number of ways which entails their grouping into two mechanistic classes, namely:-

i) the radical chain-breaking; and
ii) the preventive antioxidants.

1.3.1 RADICAL CHAIN-BREAKING ANTIOXIDANTS

This class of antioxidants operates by deactivating the two important species normally involved in the chain propagation step, the alkylperoxy and alkyl radicals. Alkyl radical deactivation involves an electron acceptor while alkylperoxy radical deactivation involves an electron donor. Hence two types of radical chain-breaking antioxidant have been distinguished according to Scheme 1.3[4].

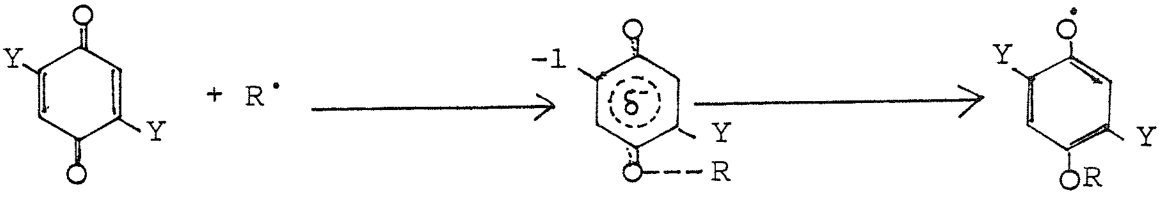
Scheme 1.3



Chain-breaking Acceptor (CB-A) Chain-breaking Donor (CB-D)

1.3.1.1 CHAIN-BREAKING ACCEPTOR ANTIOXIDANTS (CB-A)

Free radical traps are substances which are capable of removing an alkyl radical in the form of products that do not reinitiate the oxidation reaction in an autoxidising system[15]. Some of the known free radical traps include quinones, nitro compounds, nitrones and a variety of 'stable' radicals of which the phenoxyls and nitroxyls have been most studied. These compounds are oxidising agents. The molecular requirements for an effective CB-A antioxidant is shown in the transition state of a reaction of an alkyl radical with a quinone[2] (eqn 1-4).

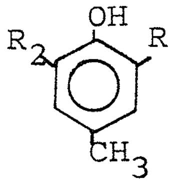


1-4

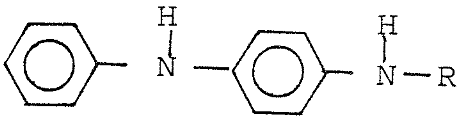
The transition state involves partial transfer of an electron to the aromatic bond and therefore making electron attracting and delocalising substituents to increase the antioxidant activity.

1.3.1.2 CHAIN-BREAKING DONOR (CB-D) ANTIOXIDANTS

The two best-known classes of commercial rubber antioxidants in this group are the hindered phenols (I) and aromatic amines (II).



I



II

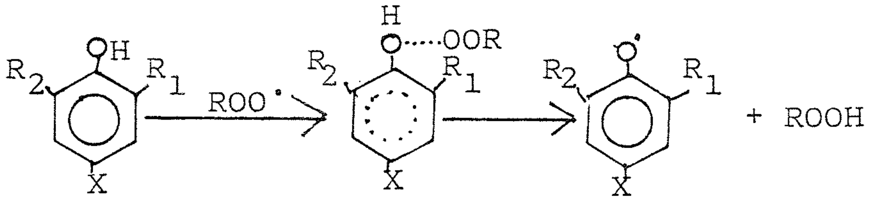
R_1 = CH_3, t-Butyl, phenyl
R_2 = t-Butyl, CH_3, phenyl

R = Isopropyl, Di-octyl

Both phenol and amine antioxidants interfere with the autoxidation process mainly by donating either a hydrogen atom or an electron to the most abundant chain propagating species, the alkylperoxy radical.

a) Phenolic Antioxidants

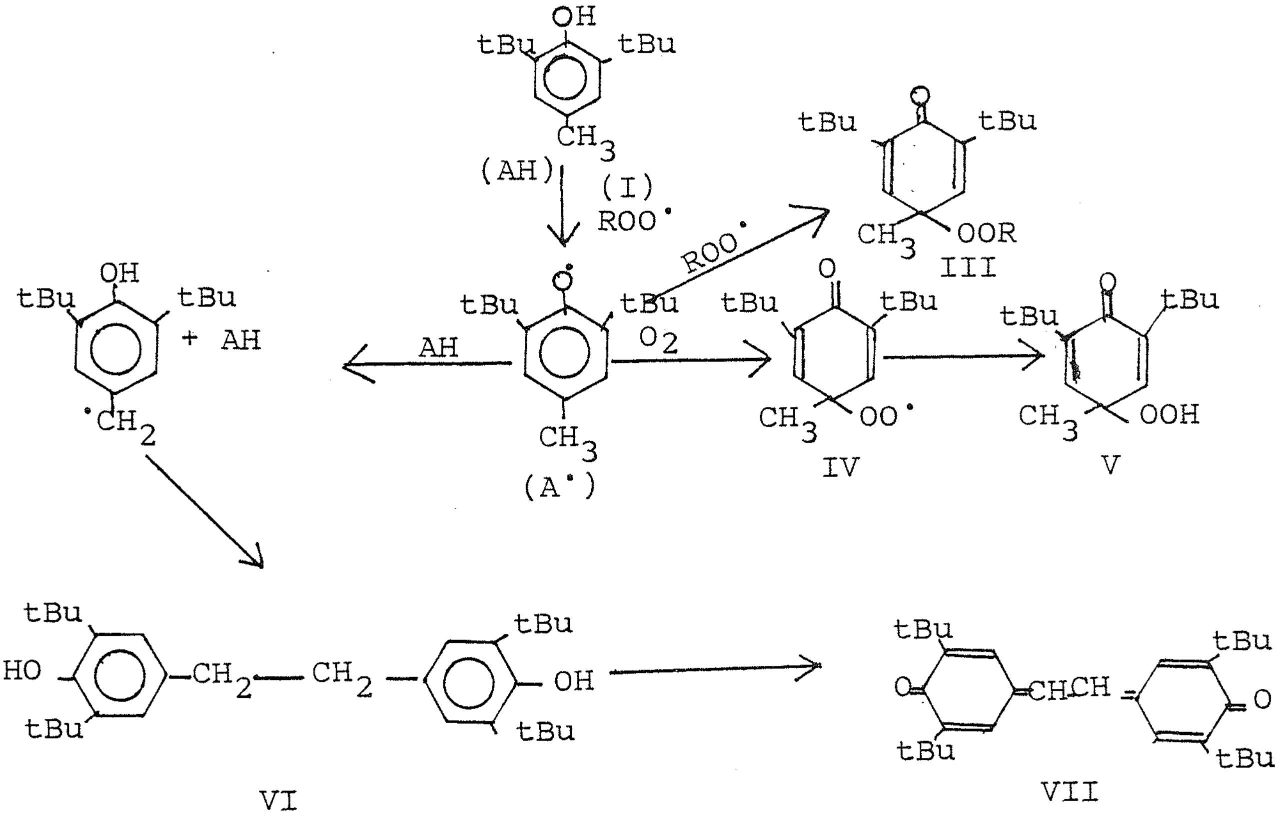
The activity of phenols depends on the substituents attached. It is known that electron-releasing and delocalising substituents in the ortho- and para-positions markedly increase the antioxidant activity by reducing the energy of the transition state[16]. Under autoxidation conditions the phenoxyl radical (eqn 1-5) has been shown[34] to be the initial primary product of the deactivation of alkylperoxy radical and which then react further to give series of products known to have antioxidant as well as pro-oxidant activity.



(1-5)

In extensive reviews[17-19] on the chemistry of phenoxy radicals, it is established that their chain-breaking reaction involves in general, a hydrogen abstraction step. A more recent review[4] on the oxidation of hindered phenol outlined the major reactions (Scheme 1.4)

Scheme 1.4 Oxidation product of a hindered phenol.

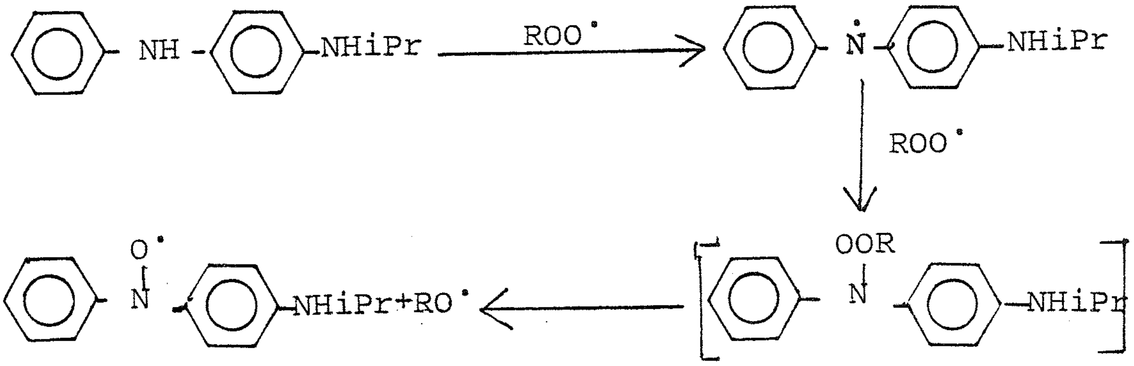


The ethylene bisphenol (VI) is known to be an effective antioxidant as the starting phenol (I) while the stilbenequinone (VII) is effective in oxygen deficient atmosphere. However, the peroxydienones (III and V) are said to be potential pro-oxidants especially at higher temperatures.

b) Aromatic Amine Antioxidants

Aromatic amines behave in a similar fashion to phenols. Some of the aryl and alkyl N- substituted p-phenylenediamines are particularly effective antioxidants in polymers. The step involved in the abstraction of the amine hydrogen is the rate determining inhibition process. Additionally the mechanism of radical formation by amine antioxidants is believed to be represented by Scheme 1.5[20].

Scheme 1.5



The diaryl-aminyl radicals are substantially less stable than the nitroxyl radicals, and they readily react with further alkylperoxy radical before disproportionating.

Nitroxyl radicals are not formed from primary and tertiary amines, while of all the secondary amines, diphenylamines are most effectively converted to nitroxyl radicals.

Hindered amines are known to be effective inhibitors[21] due to the fact that the nitroxyl radical formed is unable to initiate chain propagation owing to the steric hinderance and thus reacts with alkyl radical within the polymer. Also the secondary oxidation products from aromatic amines, the hydroxylamines, are known to be very powerful antioxidants. In rubbers, the secondary oxidation products, the nitroxyl radicals, are as important as the parent amine in conditions where mechano-chemical initiation is dominant[5] leading to appreciable alkyl radical concentration[22].

1.3.2 PREVENTIVE ANTIOXIDANTS

This group of antioxidants prevent the initiation of the free radical autoxidation chain mechanism by removal of hydroperoxides which are the principal sources of free radicals. Light, heat and metal ions are powerful catalysts for the decomposition of hydroperoxides. In relation to these catalysts, there are three main classes of preventive antioxidants, namely:

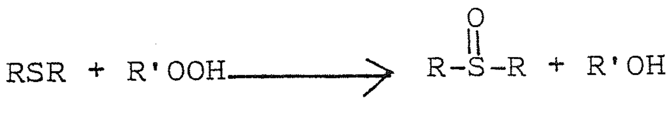
i) Metal deactivators,
ii) Light absorbers and,
iii) Peroxide decomposers.

Of the three classes of preventive antioxidants, the peroxide decomposition mechanism is found to be very important in rubber.

Ultraviolet light stabilisation is not normally very important in rubber vulcanisates because of the general presence of fillers, in particular carbon black, which are effective ultraviolet light screens.

There are a variety of organic compounds which either remove hydroperoxides in a process which does not involve free radical formation or protect hydroperoxides from decomposition and hence effectively inhibit oxidation. These compounds range from mercaptans, sulphides, sulphenic acids, metal dialkyl dithiocarbamates to phosphorus compounds. It is recognised over the years that a large number of sulphur compounds, for example, dialkylmonosulphides and zinc dialkylthiophosphates have the ability to inhibit autoxidation. Hitherto, it was assumed that these compounds function primarily by destroying chain-initiating hydroperoxides by a non-radical mechanism. It is, however, now recognised that organo-sulphur compounds have a complicated effect on hydrocarbon autoxidation because they can decompose hydroperoxides in a variety of ways. As a result, two main mechanistic groups of peroxide decomposers have been distinguished[23] - the stoichiometric peroxide decomposers and catalytic peroxide decomposers.

The stoichiometric reducing agents function mainly through a molecular reaction with hydroperoxides yielding alcohol without the substantial formation of free radicals (1-6).



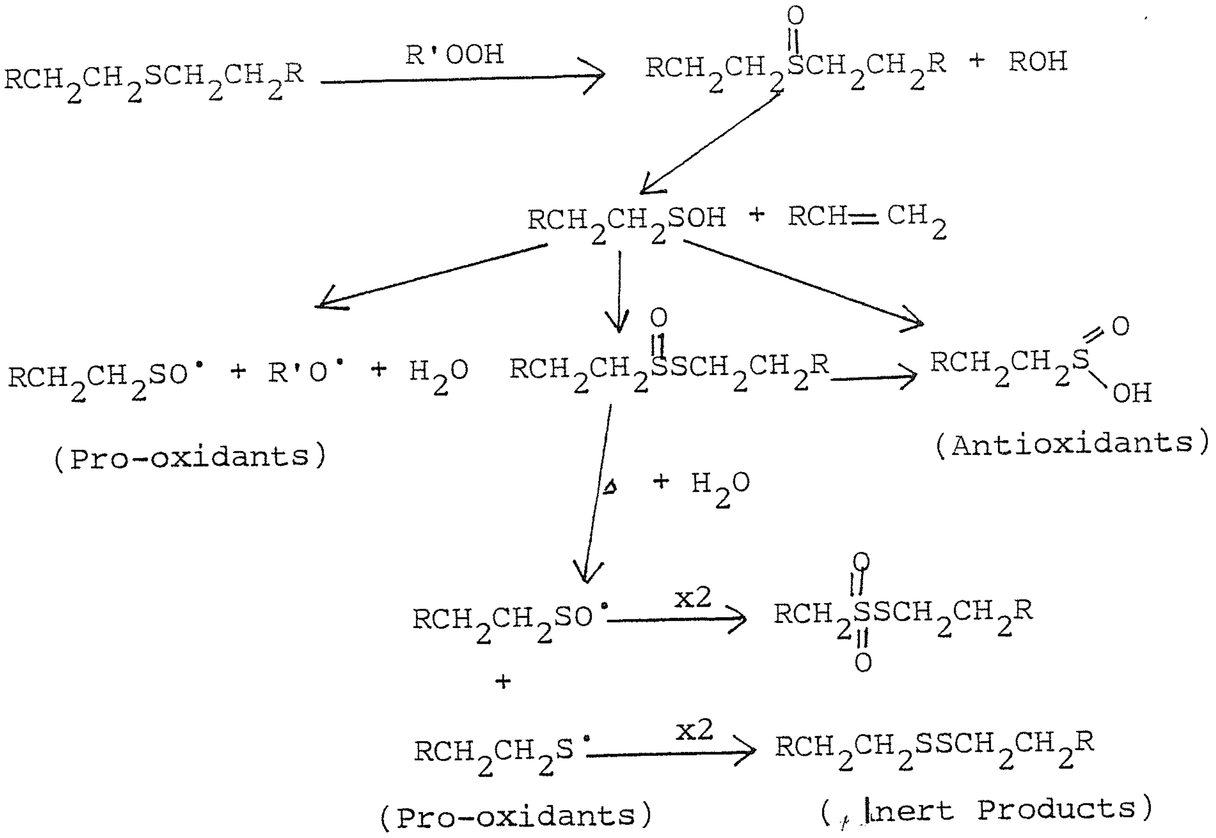
$$RSR + R'OOH \longrightarrow R-\overset{\overset{O}{\|}}{S}-R + R'OH \qquad (1-6)$$

A wide variety of sulphur compounds act as catalysts for peroxide decomposition. These compounds destroy hydroperoxides by forming acidic product but at the same time generate free radicals which account for the pro-oxidant stage associated with large numbers of organic sulphur compounds. In a review, Scott[24] pointed out that the importance of the pro-oxidant stage is related to the structure of the organic sulphur compound, hence the dithiocarbamates, dithiophosphates, mercaptobenzthiazolates and the mercaptobenzamidozolates exhibit insignificant pro-oxidant stage because of their inability to undergo redox reaction with hydroperoxides whereas those organic sulphur compounds which do, for example, the dialkyl sulphides, diarylsulphides and thiols, showed considerable initial pro-oxidant stages. Scott[25] suggested that radicals are produced by a bimolecular reaction between a sulphenic acid formed by thermal decomposition of a sulphoxide and a hydroperoxide.

$$\begin{array}{l} ROCOCH_2CH_2SOH + R'OOH \\ \qquad\qquad\qquad\quad \downarrow \\ ROCOCH_2CH_2SO^{\bullet} + RO^{\bullet} + H_2O \end{array} \qquad (1\text{-}7)$$

However, monosulphides have been studied in considerable detail[24,26] and their[23] behaviour during oxidation is outlined in Scheme 1.6. It is also known that di- and polysulphides link into Scheme 1.6 through their oxidation products, e.g. thiosulphinates, which readily undergo homolysis[27] to give free radicals which then dimerise to give stable end products.

Scheme 1.6



Also sulphur containing acids, for example sulphenic acids, formed by oxidation of organo-sulphur compounds function as catalyst for the ionic decomposition of hydroperoxide.

1.4 OZONE ATTACK ON ELASTOMERS

The attack of ozone on unsaturated rubbers is a well-known phenomenon. Ozone has been known as a specific agent for double bonds for many years and the importance of atmospheric ozone in the cracking of rubber articles exposed outdoors has been established by a number of investigators[28-34].

The early lack of recognition of the part played by ozone has been attributed to three unrelated factors. First is the existence of several types of cracking; second is that ultraviolet light can produce in-situ the very low concentration of ozone necessary for degradation. Finally the very low concentration of ozone involved made detection difficult and measurement very difficult.

It is now well established that physical process play a dominant role in ozone cracking. This is supported by the fact that there is a critical stress or critical deformation at which the rate of crack formation is maximum[33-37]. Smith and Gough[38] found that large cracks grow at the expense of small cracks and it is a means of easing surface strain since the stress at the bottom or at the ends of a deep crack is greater than that in a shallow crack. Braden and Gent[39-41] showed that rubber deterioration may be considered to occur in two stages - crack initiation and crack growth. They also showed that cut growth depends in an inverse manner upon the cross-link density of the network[42]. However, unless sufficient stress is applied a crack will not grow even in an atmosphere of ozone. This idea of a critical stress in ozone-cracking has been quantified for some different rubber vulcanisates and Braden and Gent[40] have suggested that the ultimately important quantity is the critical stored elastic energy which appears to be essentially similar for different rubbers. They concluded that the primary requirement for crack initiation is, of course, instability of the rubber molecule towards ozone.

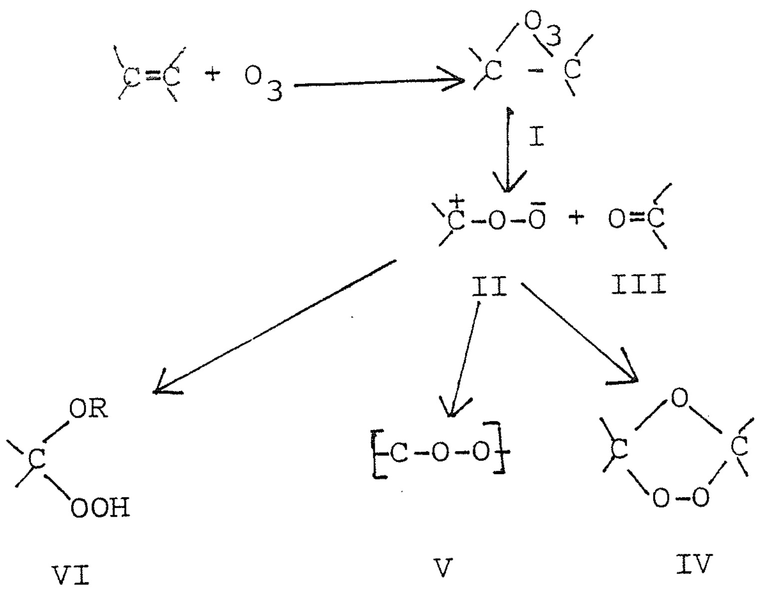
In addition to the physical process, Ossefort[43] outlined certain factors which affect the resistance of rubber products to ozone attack, namely;

i) Ozone concentration
ii) Static and dynamic stress
iii) The chemical nature of the base polymer
iv) Compounding variables:
    a) presence of chemical inhibitors
    b) type and quantity of filler
    c) plasticiser content
v) Temperature of exposure, and
vi) State of cure.

1.4.1 MECHANISM OF OZONE ATTACK

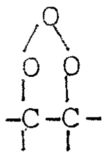
The reaction between olefins and ozone have been studied by various workers. In a review, Bailey[44] explained this reaction on the basis of the Zwitterion intermediate originally proposed by Criegee. According to this mechanism (Scheme 1.7) a molozonide, I, is formed by addition of ozone to the olefin. The structure of the molozonide is not fully known but Bailey, Thompson and Shoulders[45] supported the generally accepted five-membered ring structure. This compound is known to undergo a concerted decomposition to give a Zwitterion, II, and a carbonyl compound, III, the final products being formed by the subsequent reactions of these entities (II and III) as in Scheme 1.7.

Scheme 1.7



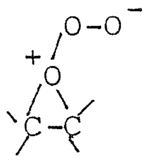
These final products are most commonly the normal ozonide IV, polymeric peroxide V, and when a compound containing active hydrogen such as an alcohol is present, a hydroperoxide VI.

This Scheme explains the observed products, however, more recent work has shown that it may not be completely adequate in explaining all of the experimental results. In particular, it does not appear to account for the observed effect of olefin geometry on product cis:trans ratio[46-49]. These recent results suggest that the Criegee mechanism provides one group of reaction pathways but that they are not exclusive and that other mechanisms may be operative in which the separation of the initial ozonide into fragments may not take place and thus some maintenance of configuration can occur. One possible suggestion advanced is that this initial ozonide in a configuration such as VII or VIII reacts directly



VII

or



VIII

with aldehyde or ketone to give an intermediate which produces ozonide via an elimination of a carbonyl compound[50,51]. This kind of pathway may be favourable in the case of cis olefins. It has been suggested[50,51] also that in some sterically hindered cis olefin, VIII may give ozonide directly with retention of olefin configuration.

1.4.2 PROTECTION AGAINST OZONE ATTACK

Waxes were first employed in protection against ozone attack and their mode of action has been investigated in detail and since well understood[52]. They function by blooming to the rubber surface thereby producing a coating of material inert towards ozone. As a result of this mode of action, there should be a suitable diffusion and solubility relationships existing between the wax and the rubber. Waxes provide good static protection at low extensions but are less useful at high elongations and under conditions of dynamic fatiguing because there is lack of elasticity of the bloomed wax film.

In contrast to wax protection, the mode of action of chemical antiozonants is not clearly understood, but a number of compounds[53] have been shown to provide a certain amount of protection. The first materials examined were the already well known antioxidants and a number of these were found to be partially effective in protecting against ozone. Four classes of materials are, however, known to provide good protection and they are: the N,N'-disubstituted p-phenyldiamines, the 1,2-dihydroquinolines, organo-metallic sulphur compounds and p-alkoxyl-N-alkyl-anilines. These compounds are all discolouring and staining and cannot therefore be used in non-black compounds or even in black compounds in contact with light coloured materials.

Delman, Ruff, Simms and Allison[54,55] in their study of the degradation of polymers in solution in the presence of antiozonants observed that the decrease in viscosity of the polymer solution is reduced by the antiozonants. This reduction was attributed to a probable reaction of antiozonant with ozone thus decreasing the amount of direct ozone attack on the polymer and also that the ozonides, carbonyl compounds or zwitterion formed by reaction of rubber with ozone may react with difunctional antiozonants to give a partial relinking of fragments hence minimising the viscosity decrease. There is no good evidence as to which of these reactions is of importance in protection but Stanley et al[55] have shown that reaction between ozone and antiozonants does occur.

In other studies, Lorenz and Parks[56] measured the consumption of antiozonant in a vulcanisate and found that about 45 per cent of the antiozonant was attached to the rubber (unextractable by acetone) and part of this recovered by hydrolysis. They[57] also noted that the antiozonants react rapidly with ozone, less rapidly with ozonides and aldehydes and slowly with polymeric peroxides formed in the ozonolysis experiments. Erickson and coworkers[58] in ozone uptake by relaxed rubber vulcanisates both protected and unprotected observed a rapid surface reaction of antiozonant with ozone leading to a protective inner layer. Similarly, McCool[59] found that the level of damage for a given ozone absorption depends largely upon the ozone concentration and being mostly severe in purified ozone.

Braden and Gent[41] looking at the effect of certain materials on critical stress and crack growth rate found that N,N'-dialkyl-p-phenylene diamines were the only compound to substantially increase the critical stress. This observed increase in critical stress was found to depend markedly upon ozone concentration, being greatly reduced at high ozone concentrations. The antiozonants examined reduced the rate of crack growth, so also did a number of carboxylic acids, diaryl amines and Zinc dithiocarbamates.

Invariably these experimental observations did not point out any one single mechanism which can fully explain antiozonant action. However, three prominent ones have been proposed as follows:

a) Scavenger Mechanism:

This is perhaps the first explanation advanced for antiozonant action. The ozone is said to react preferentially with antiozonant and thus the rubber remains undegraded. The question raised is that this mechanism requires the antiozonant to diffuse to the rubber surface sufficiently rapidly to replenish the loss by reaction with ozone but the measured diffusion rate has been shown[60] to be too low by a factor of 10^6 and also the period of ozone protection ought to be proportional to the amount of antiozonant as this will be depleted at a rate equal to the consumption of ozone at the surface but this is not observed. Even though this mechanism does not fully explain a number of experimental facts, the simple ozone-antiozonant reaction undoubtedly occurs at the surface of a protected rubber and hence is a part of an overall mechanism.

b) Protective Film Mechanism:

This also suffers from some of the same objections as the scavenger mechanism such as the need for a high diffusion rate, unrealistic stoichiometry and failure to account for unextractable nitrogen. It also requires the antiozonant to be far more reactive than rubber towards ozone and this is not, in general, found experimentally. Both mechanisms a) and b) implied that since there is direct reaction with ozone protection should increase with antiozonant concentration but an optimum concentration has been reported[61].

c) Relinking Mechanism:

The p-phenylene diamines are the most effective antiozonants and it has been suggested that their mode of action is to prevent chain scission or to link chain-ends. Lorenz and Parks[39] have shown that antiozonants react quite rapidly with aldehyde and thus suggested that the relinking of aldehydic end-groups might prove important. This mechanism again requires a high surface concentration of antiozonants as in the preceding mechanisms.

1.5 FATIGUE IN ELASTOMERS

As a result of their unique softness and toughness vulcanised rubbers find many uses in many components. However, if they are subjected to repeated flexing, their service life is considerably reduced. This phenomenon is referred to as fatigue and is characterised by gradual weakening of the rubber networks and eventual fracture. Two main causes have been identified as being responsible for such destructive changes. First is the alteration with time in the properties of the polymeric composition as a result of the action of either external agents such as oxygen, ozone, light and heat or of the components of vulcanisation mix, such as excess crosslinking components. The second is a mechanical effect and is a consequence of deformation stresses and the energy of deformations.

It has been shown that the mechanical activation of chemical reaction was the main cause of fatigue in vulcanised rubber[62] and is due to an acceleration of the normal oxidative processes. However, Slonimskii et al[63] found that mechanical fatigue differs from normal oxidative ageing in that its effect is anisotropic. Fatigued rubbers were found to have different physical properties in the direction of stress to those found at right angles to it. They concluded therefore, that not only does stress mechanically activate the oxidative processes occurring during fatigue, but that this will occur by scission of the polymer network structure resulting in the formation of alkyl free radicals which will not only accelerate autoxidative processes but may also lead to restructuring of the rubber network. On the other hand, Kuzminskii et al[64,65] demonstrated the connection between mastication and fatigue which is the development of mechanically activated chemical reactions, especially oxidative reaction.

Vulcanisation has been shown to accentuate local stresses because the polymer chains can no longer slip over one another freely. Lake and Lindley[64] have observed that in the absence of heat build-up, fatigue failure of rubber strips undergoing repeated extensions is due to the growth of small flaws which are initially present in the rubber. The growth of these flaws is primarily due to mechanical rupture of chains but is considerably enhanced by oxygen[67,68]. Furthermore, Lake and Lindley[69] established that there is a minimum tearing energy, T_o, above which mechano-oxidative cut growth can occur. At tearing energies less than T_o, cut growth has been attributed solely to chemical attack by ozone and is normally very much slower than mechano-oxidative cut growth. The physical interpretation of T_o, therefore, is that it is the minimum tearing energy at which the stress at the tip of a cut reaches the breaking value for the vulcanisates.

Investigating the effect of temperature and oxygen on the fatigue life of rubber vulcanisates, Kuzminskii and coworkers[62] showed that mechanically activated thermal degradation occurred. In an atmosphere of oxygen the service life of vulcanisates was found to fall sharply with increasing temperature while in nitrogen it increased. At room temperature in nitrogen the effect of mechanical stress became more evident. On raising the temperature, two trends were identified. First, there was an increase in the contribution made by heat energy during thermo-mechanical activated degradation. Second, the redistribution of mechanical strains was facilitated. The resultant effect of these opposing trends is the absence of temperature dependence of the service life of a vulcanisate in nitrogen. In addition, it was shown[70] that at low temperatures the contribution of mechanical stresses to the activation of chemical processes is decisive. As the temperature is raised the action of thermal energy is more manifested in the activation process. At high temperatures, the main role is already played by thermal activation while contribution of mechanical stress is small. The temperature limits within which different activation effects appear will differ depending upon the structure of the polymer, the medium and the intensity of the mechanical influences.

1.5.1 MECHANISM OF FATIGUE

The most vulnerable site for fatigue is not in the homogeneous polymer but at the interface of two different materials held together, for example, in rubber vulcanisate by cross linking. The action of mechanical forces may be divided into three types causing:

i) rupture of polymer chains to give macro-radicals
ii) mechanical activation of thermal reactions and,
iii) orientation of polymer molecules and filler particles in a wholly physical change.

Each of these components of fatiguing plays a primary or secondary role depending upon the specific properties of the ingredients of the polymeric composition, the activity of the surrounding atmosphere and the conditions of mechanical action.

Pike and Watson[71] first realised that mechanical degradation of natural rubber was a radical process and this was later confirmed by Electron Spin Resonance (ESR)[72]. However, Bresler et al[73] first discovered the formation of free radicals using ESR spectroscopy[73] and since then it has been established[71, 78] that mechanical treatment of polymers, such as fatiguing[72, 80] etc., causes chain scission and formation of mechano-radicals resulting in degradation of the polymers. Slominskii and coworkers[74], studying the effects of additives on the mechano-oxidation of natural and synthetic rubber vulcanisates believe that the nature of the free radical produced during mechanical scission of the rubber chain has a profound influence upon the subsequent processes which involve oxygen. Further evidence on the mechanical rupture of chemical bonds in rubber vulcanisates using ESR[71,73,74-79] have been provided. Potter and Scott[80] have also observed an initial chain scission during mechano-degradation of peroxide cured rubber vulcanisate.

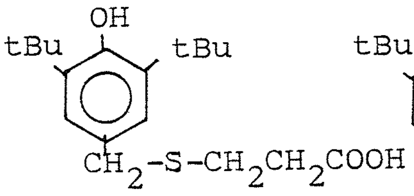
1.5.2 STABILISATION AGAINST FATIGUE

Chemical antifatigue agents are used to stabilise vulcanised rubber for service under fatigue conditions. In general, the known antifatigue agents are also effective antioxidants for polymers because of their ability to function both in an excess or deficiency of oxygen.

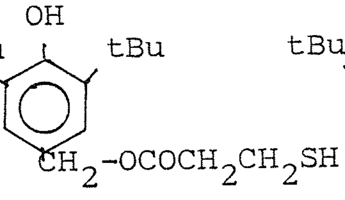
Russian workers were the first to put forward suggestion on mechanism of antifatigue agents. Kuzminskii et al[64] found that phenyl-B-naphthylamine (PBNA) was removed at a faster rate from stressed crosslinked rubber than from an unstressed one. Tarasova et-al studied[81] the effect of zinc diisopropyldithiophosphate, zinc diisopropyl dithiocarbamate and combinations of these with derivatives of phenols and p-phenylene diamine on the stabilisation of natural and synthetic rubber vulcanisates under thermal and thermal oxidative action in static and dynamic deformations and they found that compounds containing branched alkyl groups in the molecule, particularly the diisopropyl group have the best stabilising action against thermo-mechanical and thermo-oxidative processes which take place during fatigue of rubber vulcanisates. In addition they observed that the use of oxidative inhibitors together with substances which stabilise against thermal breakdown serves as an effective means of combating the fatigue of vulcanisates containing polysulphidic bonds at elevated temperature.

Thioderivatives of amines and phenols have also been assessed[82] in rubber vulcanisates under dynamic conditions and they proved to be more effective than the amines or phenols used alone. The improved antifatigue role of these thio-amines and phenols has been attributed to the ability of the oxidation products - nitroxyl radicals, sulphur-oxy products and hydroxylamines to scavenge alkyl radicals and decompose hydroperoxides which are known to be formed during fatiguing[5,82]

Phenolic sulphur compounds[5,6,74] have also been evaluated for antifatigue activity and they showed an improvement of activity over the corresponding phenolic compounds although not comparable to the p-phenylene diamine, such as IPPD. Katbab[5], showed that the higher fatigue resistance given by the hindered phenolic sulphur compounds I and II compared



I



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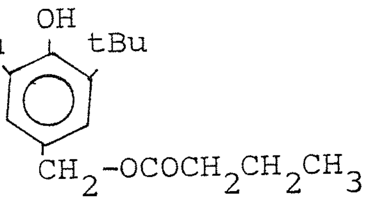


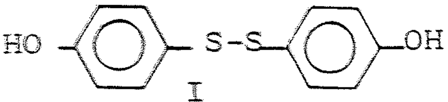
III

to the hindered phenolic compound III is due to the synergistic effects between the phenolic groups which act through electron donating chain-breaking (CB-D) mechanism while the sulphur moiety is involved in the destruction of hydroperoxides formed in the system.

In view of this observation, the present programme has been designed to give a broader view of the action of these phenolic sulphur compounds and their transformation products as they relate to fatiguing conditions.

1.6 NATURE OF RESEARCH PROGRAMME

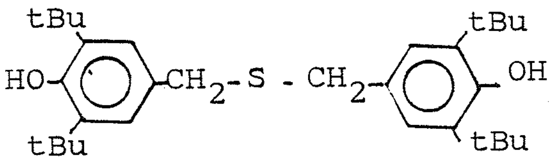
Sulphur cure rubbers have been recognised to have better fatigue properties than dehydro-crosslinked rubbers. The better fatigue properties has been attributed essentially to the physical role of the polysulphide crosslinks in relieving stress and the chemical role played by the sulphur crosslinks as antioxidants. Over the years, a variety of organo sulphur compounds have been employed mainly as antioxidants and some as antiozonants. These compounds range from metal dialkyldithiocarbamates, dithiophosphates, mercaptans and sulphides. However, Slonimskii et-al[74] showed that certain bisphenol sulphides, for example, I, are effective antifatigue agents particularly at low temperature.



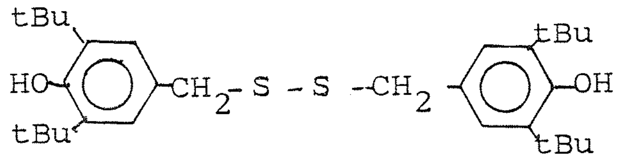
I

And more recently Katbab[5] and Suharto[6] have shown that certain hindered phenolic thioesters, mercaptan and sulphides, gave better fatigue resistance to rubber vulcanisates.

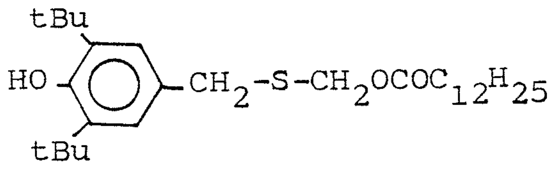
In view of these findings, this research programme was designed to evaluate the antifatigue/antiozonant activities of certain hindered phenolic sulphur compounds based on the bisphenol sulphide, I. The hindered phenolic sulphur compounds are;



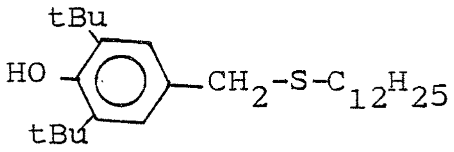
Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-monosulphide



Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-disulphide



3,5-Di-tert-butyl-4-hydroxybenzyl-dodecyl thioglycolate



3,5-Di-tert-butyl-4-hydroxybenzyl dodecyl sulphide

In addition, some of the corresponding sulphoxide will be assessed since it has been shown that the sulphides themselves are not the effective antioxidants but rather their oxidation products[83]. These compounds will be compared to a known antifatigue agent, IPPD, as well as a known peroxide decomposing antioxidant, DLTP. For a better understanding of their mode of action, their transformation products will be examined. Also certain hindered phenols will be evaluated for antifatigue activities and compared to the sulphides and sulphoxides.

CHAPTER TWO

2. EXPERIMENTAL TECHNIQUES AND PREPARATION OF TEST COMPOUNDS

2.1 MATERIALS

2.1.1 NATURAL RUBBER

The solid rubber used was SMR10 grade (Standard Malaysian Rubber Grade 10). The SMR10 rubber was first sheeted on a two-roll mill and then extracted with hot acetone under nitrogen and dried at 25°C under vacuum.

2.1.2 COMPOUNDING INGREDIENTS

Zinc Oxide	Amalgamated Zinc Ltd.
Stearic Acid	Imperial Chemical Industries
Sulphur	Anchor Chemicals Ltd.
N-(Cyclohexyl-2-benzothiazyl) Sulphenamide (CBS)	Monsanto Chemicals
Tetramethyl thiuram Disulphide (TMTD)	Monsanto Chemicals
Dicumyl Peroxide (DCP)	Hercules

2.1.3 ANTIOXIDANTS

Name	Source
N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD)	Imperial Chemical Industries

Dilauryl Thiodipropionate (DLTP)	Robinson Brothers Ltd.
4-methoxy-2,6-diphenyl phenol	Akzo Research
4-methoxy-2,6-di-tert-butyl phenol	Ethyl Corporation
2,6-di-tert-butyl-p-cresol (TBC)	Aldrich Chemicals
Galvinoxyl Free Radical	Aldrich Chemicals
4-mercaptoacetamido-diphenylamine (MADA)	Diamond Shamrock Europe
Di-pentamenthylene thiuram tetra-sulphide	Robinson Brothers

2.2 PREPARATION OF VULCANISATES

2.2.1 COMPOUNDING

The extracted natural rubber (SMR10) and compounding ingredients were mixed on a 12 inch, water cooled laboratory two-roll mill set at a friction ratio of 1:1. In formulation containing sulphur, this was added last so as to prevent prevulcanisation. Compounds for the three cure systems examined were based on the formulations:

Table 2.1 CBS-Sulphur Formulation

Natural rubber	100g
Zinc Oxide	5g
Stearic Acid	3g
CBS	0.6g
Sulphur	2.5g

Table 2.2 TMTD-Sulphurless Formulation

Natural Rubber	100g
Zinc Oxide	5g
Stearic Acid	3g
TMTD	3.5g

Table 2.3 Peroxide Formulation

Natural Rubber	100g
Dicumyl Peroxide (DCP)	3g

The cure characteristics of each formulation were determined from the Monsanto Rheometer data.

2.2.2 MONSANTO OSCILLATING DISC RHEOMETER

The Model 100 Monsanto Oscillating Disc Rheometer was used to determine the cure characteristics of each formulation containing the test compounds (antifatigue agents). This instrument quickly and precisely determines the cure and processing characteristics of elastomers. The compounded rubber sample is placed in a cylindrical cavity and into the sample is embedded a biconical rotor. The temperature of the cavity is set at the required vulcanisation temperature. The change in applied torque with time is then recorded on a potentiometric flat-bed recorder. A typical torque-time curve produced on the Monsanto Rheometer during curing of a rubber gum stock is shown in Fig. 2.1. There is an initial

decrease in viscosity of the sample due to the increasing temperature, which then flattens out until the onset of cross-linking when there is a sharp rise in viscosity and invariably in the torque exerted by the oscillating rotor embedded in the sample. The torque increases until cross-linking is complete. The curve may show a decrease in torque with time if chain scission takes place on prolonged heating (reversion) or a continuous increase if a slow cross-linking reaction occurs.

From the Monsanto rheograph, it is possible to obtain quantitative figures for 'scorch' time. This is based on an arbitrary number of units of torque increases above the minimum value (usually 5 units). Also the rate of cure can be assessed from the slope of the curve. However, there is a more accurate kinetic treatment[84,85]. It was assumed that crosslink formation is a first-order reaction after the end of the induction period, ti, and that the rate of crosslink formation is inversely proportional to the crosslink density. Since at maximum cure, the rate of formation of crosslinks is zero, then;

$$dv/_{dt} = k(V_{\infty} - V_t) \qquad (2\text{-}1)$$

where:

k is the overall first-order rate constant

V_{∞} is the maximum crosslink density and,

V_t is the crosslink density at any time t.

Thus, on integration:

$$\int_{V_o}^{V_t} {}^{d}V/V_{\infty} - V_t = k \int_{t_1}^{t} dt$$

Hence:

$$\text{In } V_{\infty} - V_t/V_{\infty} = k(t-t_1)$$

The torque developed (R) is a measure of the crosslink density, therefore equation 2-1 becomes

$$\text{In } \frac{R_{max} - R_t}{R_{max}} = k(t-t_1) \qquad (2\text{-}2)$$

or

$$\log(R_{max} - R_t) = \log R_{max} + {}^{k}/2.3(t-t_1) \qquad (2\text{-}3)$$

where:

R_{max} is the maximum torque attained,

R_t is the torque at any time t,

t_i is the induction time.

Hence a plot of $\log(R_{max} - R_t)$ against time would have a slope of ${}^{k}/2.3$ and an induction time of t_i. Typical first order plot is shown in Fig. 2.2.

Three parameters thus become evident in a vulcanising system and which are:

i) the overall first-order rate constant, k,

ii) the maximum torque developed, R_{max}, which is the crosslink density, and

iii) the induction time, t_i, which denotes the time before the formation of an active sulphurating agent and the reaction of this with the rubber to form the rubber-bound intermediate - a precursor to crosslink formation. For peroxide vulcanisation, t_i is a direct measure of the time for the peroxide to undergo homolysis and to abstract removable hydrogen from the main chain. This is due to the fact that peroxide vulcanisation is a free radical reaction, not involving the formation of a rubber-bound intermediate.

2.2.3 VULCANISATION OF TEST SAMPLES

2.2.3.1 VULCANISATION OF SAMPLES FOR OXYGEN ABSORPTION TEST

Vulcanisates for this test were prepared in a fully positive stainless steel mould of cavity dimensions of 13.5 x 13.5 x 0.018cm. so as to obtain vulcanised sheet of 0.018 - 0.023cm. thickness. The compounded rubber gum stock weighing 5g was first sheeted out on a mill and placed in the mould cavity. The mould was then placed between two platens of a steam heated press which have been previously set at the vulcanisation temperature. The press was momentarily closed and opened to release entrapped air. A pressure of 50 tons on an eight inch ram was applied and the vulcanisation temperature maintained for the length of cure. On completion of cure, the mould was removed and the vulcanisate quenched in cold water, dried and stored under vacuum prior to test.

2.2.3.2 VULCANISATION OF SAMPLES FOR OZONE AND STRESS RELAXATION MEASUREMENTS

The vulcanisation procedure is the same as for samples used in oxygen absorption test. However, a different mould is used which gives a rectangular sheet with a thickness of 0.7 - 0.8mm. 15g of the rubber gum stock is used.

2.2.3.3 VULCANISATION OF SAMPLES FOR FATIGUE TEST

Each test sample was moulded as rectangular sheet - (2.2 x 7.6 x 0.15cm) with a beaded edge. About 55 - 60g of the rubber gum stock is required. The samples were first sheeted out on a two-roll mill and placed in the cavity of the mould. The subsequent steps in the vulcanisation are the same as for samples used for oxygen absorption test.

2.3 OXYGEN ABSORPTION MEASUREMENT

The oxygen absorption test was carried out in a closed system using the modified pyrex test-tube of approximate volume of

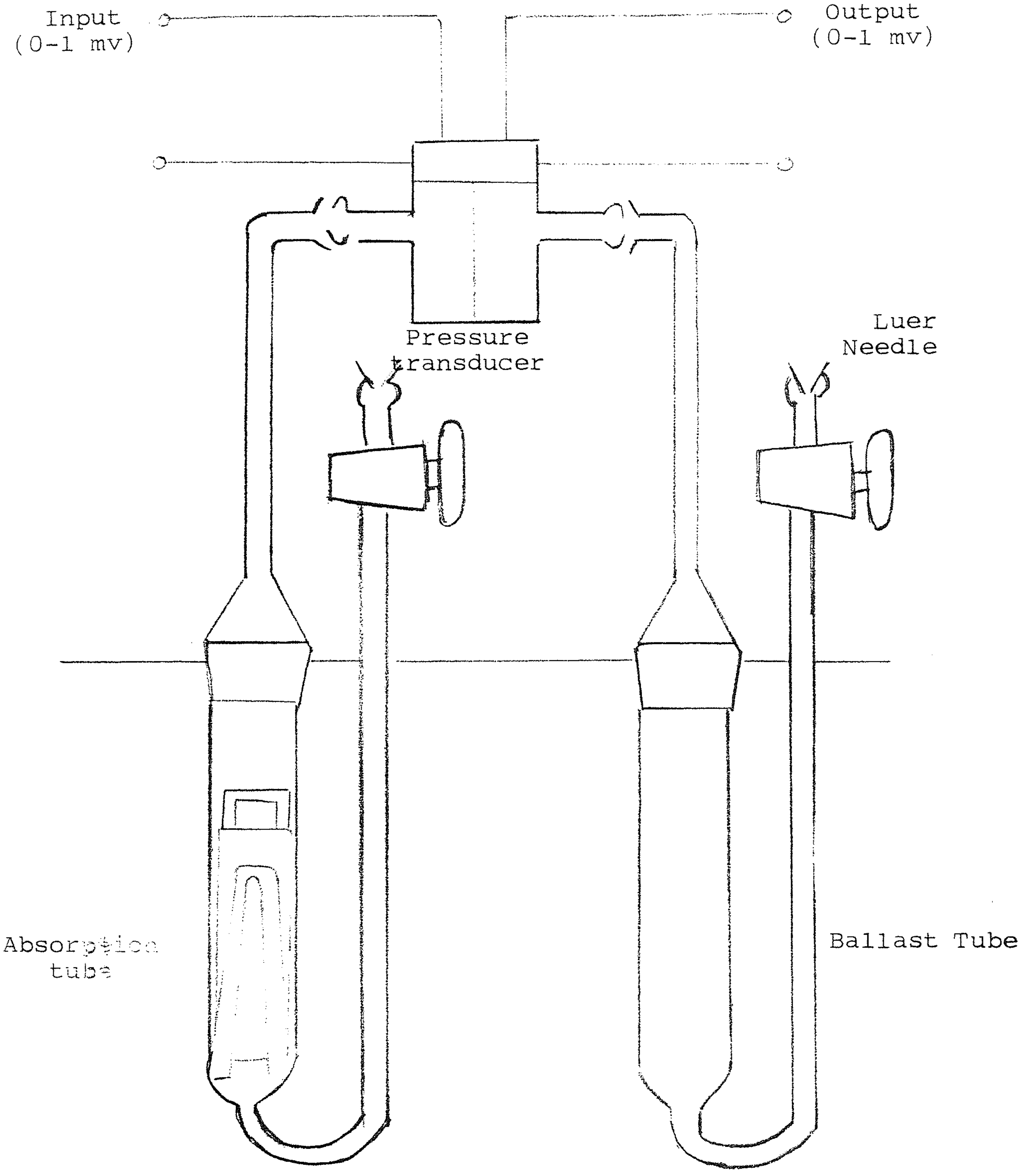


Fig. 2.3 : Apparatus for Oxygen Absorption of Vulcanisates

100ml with a B24 quickfit socket and cone attachment. The apparatus is shown diagramatically in Fig. 2.3. The arm fitted to the absorption vessel contains a Luer needle connected with epoxy resin at the opening. Through this needle, the flask can be purged with oxygen for calibration of the equipment. The absorption vessel is connected to the wet side of a pressure transducer with glass tubing via a ball and socket joint. The dry side of the pressure transducer is connected to a ballast vessel of similar dimensions to the absorption vessel. Both vessels are placed side-by-side in a thermostated oil bath. Capillary tubing is used for connections outside the oil bath and the distance is kept small so that the volume of the apparatus not thermostated is negligible to the total volume of the apparatus.

The transducer used is a strain guage type Pye Ether Model UP3 of 15 psi range. The size of the output voltage is proportional to the input voltage, so by varying the input voltage, the sensitivity of the transducer to pressure fluctuations can be varied. Any pressure difference between the reaction vessel and the ballast vessel is proportional to the voltage output of the transducer and this is recorded using a Speedomax W (Leeds and Northrup) multichannel millivolt recorder. In practice, the sensitivity of the transducer is selected so that a full-scale deflection on the recorder corresponds to about 2 per cent weight-by-weight of oxygen absorbed by a vulcanisate. Hence, as oxygen is absorbed by the sample in the absorption vessel, the pressure difference becomes greater and the voltage becomes correspondingly greater.

2.3.1 PROCEDURE

0.3g of test sample of maximum thickness 0.023cm was placed on glass support so that oxygen can diffuse freely onto both surfaces. The glass support with the sample was lowered into the absorption vessel and the apparatus assembled and small amount of silicone grease was applied to ensure a gas-tight seal. The absorption vessel was purged with oxygen for 5 minutes and placed in the thermostated oil bath at 100°C and connected to the transducer which already had the ballast vessel attached. The system was allowed to equilibrate for 5 minutes by venting both vessels to the atmosphere. The samples were then left to absorb oxygen.

The rate of oxygen absorption depends on the rate of oxygen diffusion into the rubber and the rate of reaction of oxygen with the rubber. To eliminate the oxygen diffusion variable, the sample used have the same weight and thickness[86-91].

2.4 STRESS RELAXATION MEASUREMENT

The continuous stress relaxation of vulcanised samples is followed automatically using a Wallace-Shawbury self-recording age tester in conjunction with a six-cell air ageing oven set to have a block temperature of 102°C. The cell temperature is about 2°C lower than the block temperature due to a 1 cubic foot per hour air flow. Each sample is clamped at both ends. The upper sample grip is supported on a horizontal beam which is mounted on and balanced about high grade miniature ball-bearings. The downward force exerted by the specimen is balanced by the upward force applied by a vertical helical stress spring. Movement triggers a small electric motor which adjusts the position of the stress spring upper anchorage to change the force applied by the spring until a condition of balance is restored to the beam. Attached to the spring anchorage mechanism is a lead pencil in contact with the chart paper. The change in the force applied by the spring is recorded in the form of a curve on the chart paper which is wrapped around a vertically mounted drum. This drum rotates through one revolution every 12 hours and is driven by a small electric motor. During the test, the force exerted by the spring equals that of the specimen. Any out of balance between the two forces will cause tilting of the beam in one direction or the other. Thus electrical contacts are closed and current is supplied to the servo-motor. This motor rotates and transmission is obtained through a gearbox which moves the vertical thread to restore a position of balance.

2.4.1 PROCEDURE

Samples were cut from vulcanised sheet using the MR 100 test cutter. Samples were examined for defects and those with defects were discarded. The samples each was mounted between two grips and clamped. The instrument was zeroed for the weight of the sample, after which the lower specimen grip was tightened around the sample. The sample was extended with the aid of a brass collar. The instrument was then placed in the air ageing oven which has been maintained at the ageing temperature and after allowing 5 minutes for expansion, the lead pencil was adjusted to 100 per cent stress and zero time on the chart. The sample was then allowed to relax in stress. The instrument recorded stress as a function of time on the chart.

2.5 OZONE RESISTANCE MEASUREMENT

The Hampden-Shawbury Ozone Test Cabinet was used to estimate the resistance of rubber vulcanisates to ozone cracking when exposed under static conditions to air containing a definite concentration of ozone at a given temperature. The test is made up of a closed dark test chamber with thermostatically controlled temperature. Purified and filtered air is ozonised at a constant temperature by exposure to ultraviolet light. The air is led into the chamber and recirculating into the cabinet by a lower unit. Test samples in the form of cut strips are stretched to the required degree in test piece holders and hung from a mobile test piece carrier inside the chamber which is moving at a constant speed to ensure that all test pieces are subjected to identical conditions of exposure.

The concentration of the ozone in the cabinet is measured by the use of an ozometer which is connected to the chamber. Ozonate Model OZT-2 is used. This instrument measures the ozone concentration in the range 0 - 140 pphm. The principle involves bubbling air containing ozone through a phosphate buffered solution of potassium iodide made up as follows:

Potassium iodide	1.500 ± 0.025g/litre
Sodium Monohydrogen Phosphate (Anhydrous)	1.500 ± 0.025g/litre
Potassium Dihydrogen Phosphate (Anhydrous)	1.400 ± 0.025g/litre

These solutions when mixed together should give a solution with pH 6.5 - 6.8.

The ozone oxidises the potassium iodide to iodine according to the following reaction (2-4).

$$2KI + O_3 + H_2O \longrightarrow 2KOH + I_2 + H_2O \qquad (2\text{-}4)$$

The iodine I_2 effectively conducts the current through the solution by being reduced to iodide I^- at the cathode and reoxidised back to iodine I_2 at the anode, i.e.

At the cathode

$$I_2 + 2e \longrightarrow 2I^- \qquad (2\text{-}5)$$

At the anode

$$2I^- - 2e \longrightarrow I_2 \qquad (2\text{-}6)$$

For this reaction system to measure continuously the iodine ion concentration and thus the amount of ozone passing through the solution, the iodine reformed at the anode must be prevented from recirculating and invariably the repetition of the reaction at the cathode which in effect would give a high reading. This is adequately prevented by employing a mercury anode which gives rise to insoluble mercurous iodide and thereby remove the unwanted iodine and enable the ozonate to measure within an accuracy of ± 5 per cent.

2.5.1 PROCEDURE

Rectangular pieces in form of rubber strips, dimension 7.0 x 1-1.2 x 0.025cm were cut from vulcanised sheets, section 2.2.3.2. Test pieces were stretched to the required extension and secured in test piece holders. The initial free length between the clamps on a holder was 5cm. The upper clamp was suspended from a hook in the test chamber roof and the cabinet closed. The test pieces were exposed to ozone at 25 pphm and 25°C. Test pieces were examined at intervals for the development of cracks using a magnifying lens - 5x according to BS 903[92] until the failure of the test pieces. The degree of cracking of samples with time was assessed by grading on the following basis:

Grade	Surface Appearance of the Samples
0	No cracks
1	Cracks just visible under 5x magnification
2	Cracks 0.005 - 0.01mm.
4	Cracks 0.01 - 0.20mm.
6	Cracks 0.2 - 0.3mm - cracks visible to the naked eye.
8	Cracks 0.3 - 0.45mm
10	Cracks 0.45mm.
12	Major cracks long enough to cause failure of sample.

2.6 FATIGUE RESISTANCE TEST

The Monsanto Fatigue to Failure Tester is employed for this assessment. The equipment has been developed to provide a simple reproducible method of determining the fatigue life or cut growth properties of cured stocks. The samples are subjected to a repeated rapid strain cycle. The fatigue cycle is made up of a single extension and a single relaxation of the sample. The sample being fatigued is extended for the first quarter of the cycle, relaxed over the next quarter and held at zero strain for the remaining half of the fatigue cycle. The number of cycles is recorded automatically. The maximum applied strain may be varied by changing the drive cams.

2.6.1 PROCEDURE

The samples were prepared as in Section 2.2.3.3. From the rectangular beaded sheets produced, individual dumbell samples were cut at right angles to the grain using a British Standard type 'E' dumbell cutter. Cut samples were mounted at zero strain, i.e. when the major axis of the drive cams in the horizontal position coincide with the horizontal line on the lower carriage. Each sample holder was adjusted with a 6cm long calibration rod so that zero strain was obtained when samples are mounted. The machine was run for 1000 cycles, the power then turned off and sample was adjusted for set by adjusting each upper shackle with the thumb nut so that when the lower shackle was raised a slight bow appeared in the sample. The machine was then switched on and fatigue life recorded as the number of cycles to failure. The drive cam used gave an extension ratio of 1.61 ± 0.04 (cam no. 4), equivalent to a 60 per cent extension. The samples were flexed at a frequency of 100 cycles per minute.

The Japanese Industrial Standard (JIS) average[93] was employed for the fatigue to failure results. The highest four readings from a sheet of 16 samples are taken and their average obtained using the JIS formula:

$$\text{JIS average} = 0.5A + 0.3B + 0.1C + 0.1D$$

where:

A, B, C, D are the fatigue lives in which $A > B > C > D$. The method is biased towards the high readings because any physical flaw on the test samples will drastically reduce the fatigue life thereby giving incorrect result.

2.7 PURIFICATION OF HYDROPEROXIDES[26]

a) Cumene Hydroperoxide (CHP)

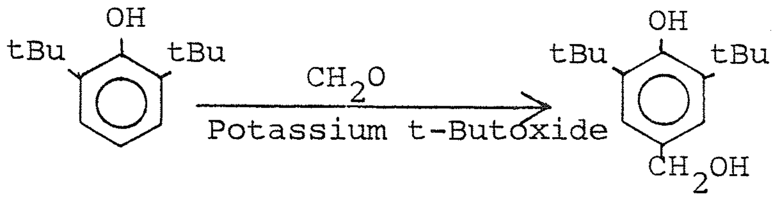
A solution of 200g cumene hydroperoxide and 200ml petroleum ether (40 - 60°C) in a 1000ml beaker was cooled to 0°C, and 160ml 25% aqueous NaOH was added with stirring. The beaker was placed in an ice-salt bath for 30 minutes. The sodium salt which precipitated was collected by vacuum filtration and washed several times with cold 25% NaOH solution. The precipitate was allowed to air dry, then suspended in petroleum ether. The free hydroperoxide was liberated by the use of acetic acid. The solution was filtered and washed several times with water then dried over anhydrous sodium sulphate (Na_2SO_4). The solvent was removed on a rotary evaporator and the remaining CHP distilled under vacuum at 83°C and 1.6 torr.

b) Tertiary-butyl Hydroperoxide (TBH)

The procedure described for CHP was also used for the purification of TBH.

2.8 PREPARATION AND CHARACTERISATION OF TEST COMPOUNDS

2.8.1. 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL ALCOHOL[94]



A reaction vessel fitted with stirring means and a thermometer was purged with nitrogen and in it were placed 50g of 2,6-di-tert-butyl phenol in 107ml tert-butanol, 8g paraformaldehyde in 100ml tert-butanol and 1.4g potassium tert-butoxide in 28ml tert-butanol, all solutions being cooled prior to mixing. The temperature of the mixture was maintained at 10°C by cooling in an ice bath. Stirring was continued for about 45 - 60 minutes until thick leaf-green oily liquid formed and immediately poured into ice water. The resulting mixture separated into an oily organic layer which promptly solidified and an aqueous layer. The solidified layer was filtered off, washed with water until neutral, then stirred with hexane and recrystallised from a mixture of hexane and chloroform to give a white crystalline solid.

Melting point 136 - 137°C (Literature 137°C)

Infra-Red Data

Phenolic OH	3620 cm^{-1}

NMR Data

Aromatic Proton	2.8τ	singlet
Phenolic Proton	4.8τ	singlet
Methylenic Proton	5.6τ	singlet
Tertiarybutyl Proton	8.5τ	singlet

2.8.2 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL CHLORIDE

The method used was that used by Ajiboye[95]. 2 moles of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol was stirred at room temperature in a flask containing 500g of toluene to give a slurry. 600g 30% hydrochloric acid was added and stirred at 25°C for 3 hours and by which time the slurry went into solution. The temperature was then raised to 45°C when two layers separated. The organic layer was separated, washed with water, then with 2% sodium hydrogen carbonate and finally with water. The organic layer was dried over anhydrous sodium sulphate. The solvent was distilled off under reduced pressure to give a yellowish red viscous product, about 90% in yield.

Infra-Red Data

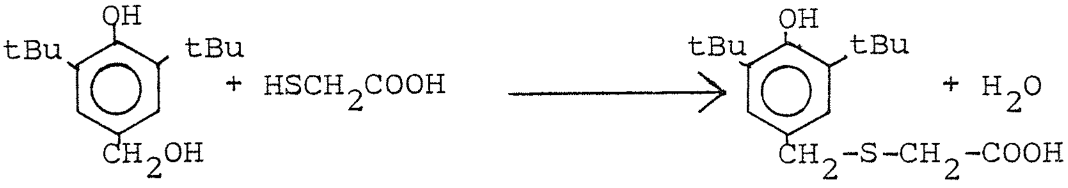
Phenolic OH	3620 cm^{-1}
CH_2Cl	1300 cm^{-1}

NMR Data

Aromatic Proton	3.0τ singlet
Phenolic Proton	5.0τ singlet

Methylenic (CH_2cl) Proton	6.4 τ multiplet
Tertiary Butyl Proton	8.6 τ singlet

2.8.3 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL THIOGLYCOLIC ACID[96]



To a toluene solution containing 47.2g of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol was added 15g of thioglycolic acid (3-mercapto acetic acid). The mixture was poured into a round-bottom flask fitted with a Dean and Stark glassware and a condenser. A drop of concentrated sulphuric acid was added and mixture allowed to reflux for 8 hours and then cooled. The organic phase was taken up in diethyl ether and excess acid removed by washing first with 2 per cent solution of sodium hydrogen carbonate and then water. The ether extract was dried over anhydrous magnesium sulphate, filtered and concentrated in a rotary evaporator. A brownish viscous product was obtained and which was washed with n-hexane to give a white solid powder.

Melting Point	106 - 108°C	(Literature 106-108°C)[96]

Infra-Red Data

Phenolic OH	3640 cm^{-1}
Acidic carbonyl	1700 cm^{-1}
C-S	700 cm^{-1}
Tetra substituted benzene ring	880 cm^{-1}
Tertiary-butyl group	1370 cm^{-1} and 1360 cm^{-1}

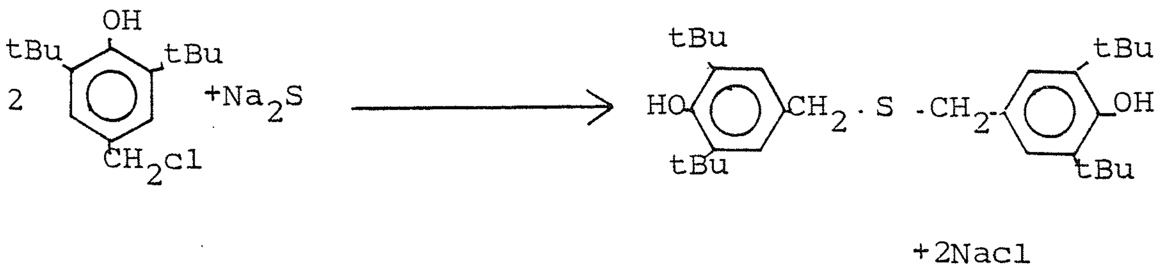
NMR Data

Aromatic Proton	2.85 τ singlet
Phenolic Proton	4.8 τ singlet
Methylenic Proton	6.25 τ and 6.9 τ singlet
Tertiary Butyl Proton	8.6 τ singlet
Carboxylic Proton	1.8 τ

Elemental Analysis

	%C	%H	%S
Calculated	65.81	8.39	10.32
Found	65.9	8.60	10.00

2.8.4 BIS-(3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL-) MONOSULPHIDE[53]



A mixture of 19.2g of sodium sulphide dissolved in 15ml of water, 120ml of isopropyl alcohol and 50g of 3,5-di-tert-butyl-4-hydroxybenzyl chloride was refluxed for 2 hours in a reaction vessel fitted with thermometer and means of stirring. The mixture was allowed to stand for 48 hours at room temperature. The solids were collected by filtration, washed with water and dried. The product then recrystallised from iso-octane and methanol to give a white crystalline product, a yield of 75%.

Melting Point 141 - 143°C (Literature 141 - 143°C)[5]

Infra-Red Data

Phenolic OH	$3640\ cm^{-1}$
Tertiary-butyl group	$1370\ cm^{-1}$ and $1360\ cm^{-1}$

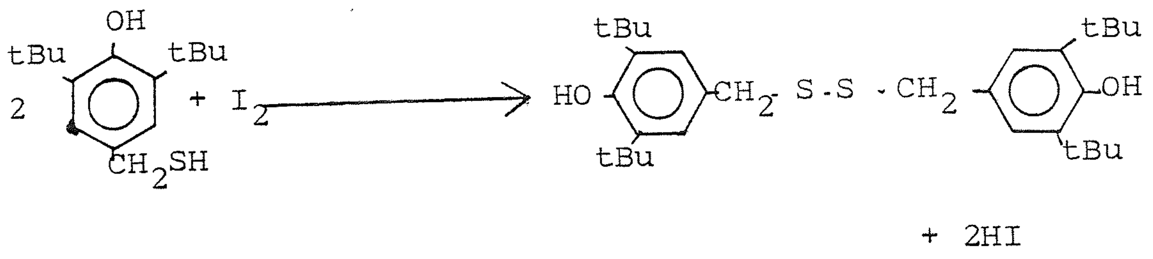
NMR Data

Aromatic Proton	2.9τ	singlet
Phenolic Proton	4.9τ	singlet
Methylenic Proton	6.4τ	singlet
Tertiary-butyl Proton	8.6τ	singlet

Elemental Analysis

	%C	%H	S%
Calculated	76.6	9.8	6.8
Literature[53]	74.4	10.2	6.95
Found	76.2	10.1	6.90

2.8.5 BIS-(3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL-) DISULPHIDE[53]



A mixture of 25.3gm 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (98% obtained from Diamond Shamrock Europe), 100ml benzene and 50ml water was stirred vigorously and a solution of 100ml benzene, 25ml ethanol and 25.4g iodine was added very slowly. When the stirred mixture showed a trace of iodine colour, the stirring and addition of iodine solution were stopped and the benzene layer was separated.

The organic layer was dried over anhydrous magnesium sulphate, filtered and concentrated. The disulphide was recrystallised from a benzene-petroleum ether solution to give a light coloured powder.

Melting Point	165 - 166°C	(Literature[53] 166-168°C)

Infra-Red Data

Phenolic OH	3620 cm^{-1}
Tertiary butyl group	1370 and 1360 cm^{-1}
-S-S-	525 cm^{-1}

NMR Data

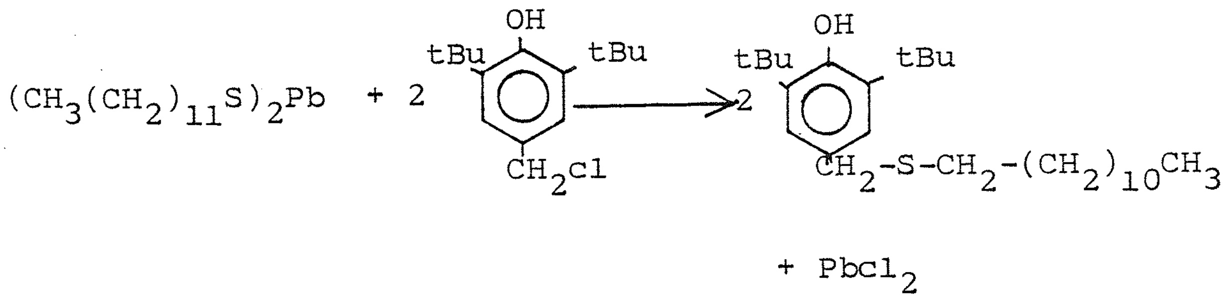
Aromatic Proton	2.9τ singlet
Phenolic Proton	4.85τ singlet
Methylenic Proton	6.35τ singlet
Tertiary-butyl Proton	8.6 τ singlet

Elemental Analysis

	%C	%H	%S
Calculated	71.6	9.2	12.8
Literature[53]	71.7	9.2	12.6
Found	72.8	9.3	13.1

2.8.6 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL-DODECYL SULPHIDE[53]

$$(CH_3COO)_2Pb + 2CH_3CH_2)_{11}SH \longrightarrow (CH_3(CH_2)_{11}S)_2Pb + 2CH_3COOH$$



40g n-dodecyl mercaptan in 125ml acetone was added to 38g lead acetate in 400ml of water. A yellow solid precipitate from the mixture was filtered off and washed with successive portions of water, ethanol and ether, then dried. 59g of the lead n-dodecyl mercaptide was put into 300ml of N,N'-dimethyl formamide and 45g 3,5-di-tert-butyl-4-hydroxybenzyl chloride in 100ml of hexane were added. White lead chloride precipitated out after slight agitation and was filtered off. The filtrate was allowed to stand at room temperature for 4 hours and was then poured into 300ml of ice water containing 50ml concentrated hydrochloric acid.

The water insoluble precipitate was taken up in diethyl ether and the ether solution dried over anhydrous magnesium sulphate and filtered. The ether was distilled from the filtrate under reduced pressure leaving a yellow viscous oily liquid.

Infra-Red Data

Phenolic OH	3640 cm^{-1}
Tertiary-butyl group	1370 and 1360 cm^{-1}

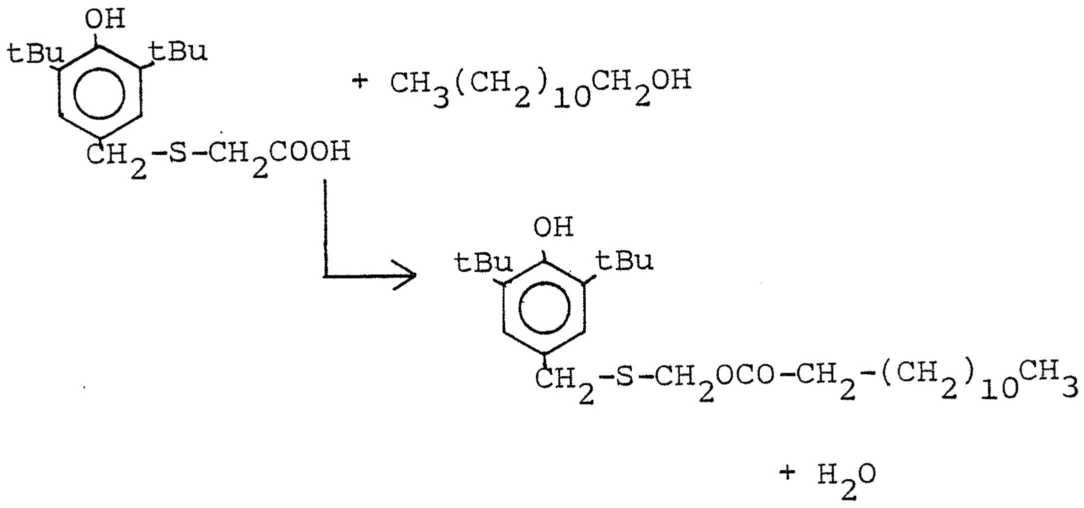
NMR Data

Aromatic Proton	2.95 τ	singlet
Phenolic Proton	4.9 τ	singlet
Methylenic Proton	6.4 τ	singlet
	5.0 τ	triplet
Tertiary-butyl Proton	8.6 τ	singlet
Methyl Proton	9.1 τ	singlet

Elemental Analysis

	%C	%H	%S
Calculated	77.1	11.4	7.6
Literature[53]	77.1	11.4	7.6
Found	77.1	11.39	7.8

2.8.7 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL DODECYL THIOGLYCOLATE



To 62g of 3,5-Di-tert-butyl-4-hydroxybenzyl thioglycolic acid in 200ml toluene was added 37.2g of dodecanol and the procedure for the condensation reaction is similar to that reported in Section 2.8.3. The product obtained is a light brown oily liquid.

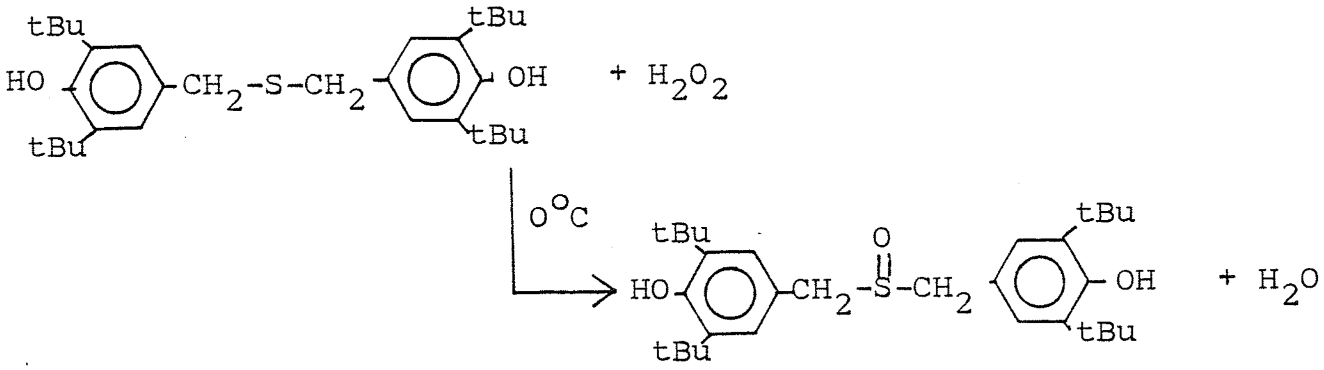
Infra-Red Data

Phenolic OH	3640 cm^{-1}
Ester carbonyl	1740 cm^{-1}
t-Butyl group	1370 and 1360 cm^{-1}

NMR Data

Aromatic Proton	2.9τ singlet
Phenolic Proton	4.85τ singlet
Methylenic Proton	6.4 τ singlet
	5.85τ triplet
Tertiary-butyl Proton	8.6 τ singlet
Methyl Proton	9.1 τ singlet

2.8.8 BIS-(3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL-) SULPHOXIDE



The method by Barnard et-al[97] and Armstrong[98] was employed. 5.64g (0.012 moles) of Bis-(3,5-di-tert-butyl-4-hydroxybenzyl-) monosulphide was dissolved in 20ml of AR grade acetone in a round bottom flask. The flask was placed in an ice bath and cooled to 0°C. 5ml 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. Acetone was removed using a rotary evaporator. The white solid residue was then recrystallised from a mixture of acetone and chloroform.

Melting Point 132 - 133^{6}

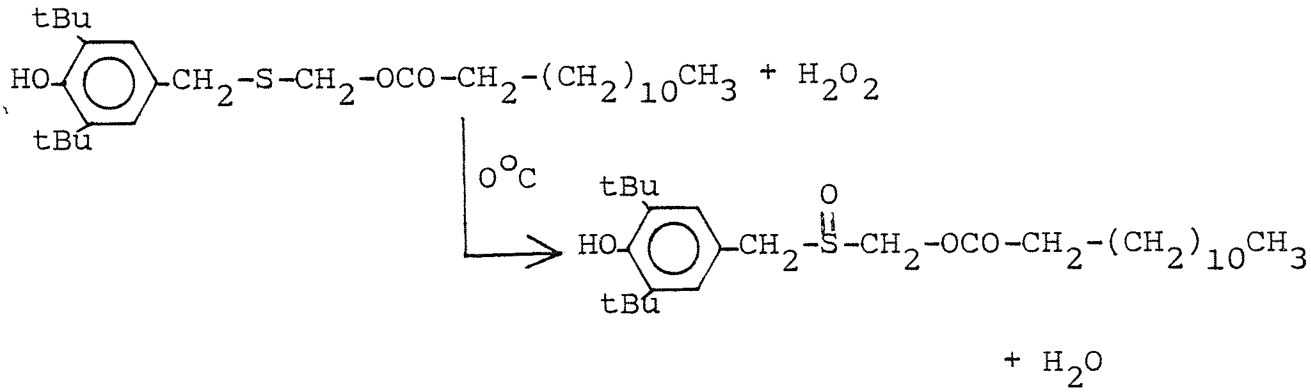
Infra-Red Data

Phenolic OH	3640 cm^{-1}
Sulphinyl (S=O)	980 cm^{-1}
Tertiary-butyl group	1375 and 1365 cm^{-1}

Elemental Analysis

	%C	%H	%S
Calculated	74.1	9.47	6.58
Found	73.9	9.35	6.60

2.8.9 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL-SULPHINYL DODECYL GLYCOLATE



The procedure described in Section 2.8.8 was adopted. In this case 5.74g (0.012 moles) of the light brown oily compound - 3,5-di-tertiary-butyl-4-hydroxybenzyl dodecylthioglycolate was oxidised with hydrogen peroxide. A light yellow oily liquid was obtained after the evaporation of the acetone. Thin layer chromatography was used to assess its purity and a single spot was obtained, different distance from the starting material.

Infra-Red Data

Phenolic OH	3640 cm^{-1}
Sulphinyl S=O	1020 cm^{-1}
Ester Carbonyl C=O	1720 cm^{-1}

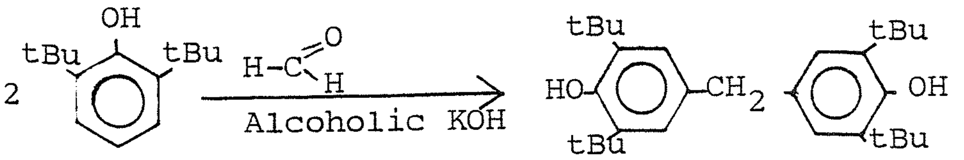
NMR Data

Aromatic Proton	2.85τ singlet
Phenolic Proton	4.8 τ singlet
Methylenic Proton	6.4$\tau$and 5.85τ singlet
Tertiary-butyl Proton	8.6 τ singlet
Methyl Proton	9.1 τ singlet

Elemental Analysis:

	%C	%H	%S
Calculated	78.4	11.3	7.2
Found	78.2	11.4	7.01

2.8.10 4,4'-DIHYDROXY-3,5,3',5'-TETRA-TERT-BUTYL DIPHENYLMETHANE[99]



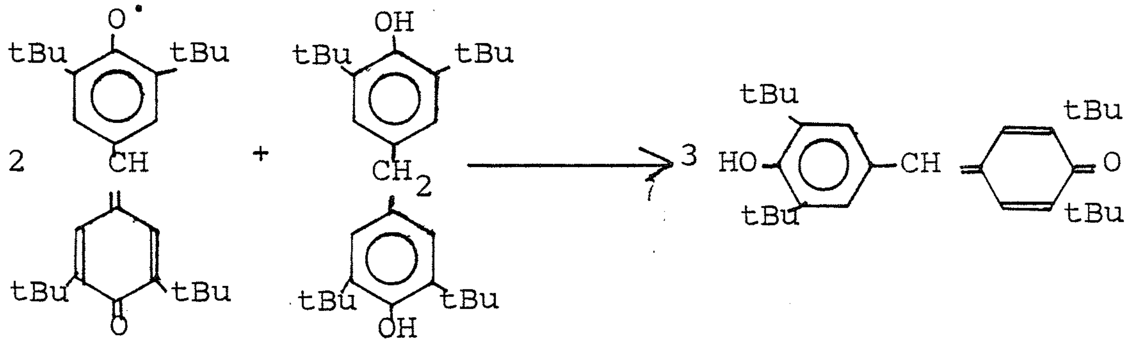
To 3.3g KOH in 200ml iso-propanal was added with stirring 103g 2,6-di-tert-butyl phenol under nitrogen. 22.7g of 37% formaldehyde solution was added dropwise at 30°C. The mixture was stirred for 1.5 hours at 60°C, cooled and the solid filtered off, washed twice with 200ml isopropanol containing 10ml of concentrated hydrochloric acid and dried.

Melting Point	155°C (Literature 154-5°C)[99]

Infra-Red Data

Phenolic OH	3640 cm^{-1}
Tertiary-butyl group	1370 and 1360 cm^{-1}

2.8.11 2,6,3,5-TETRA-TERT-BUTYL-4-HYDROXY-PHENYL-4-METHYLENE-2,5-CYCLOHEXA-DIENE-1-ONE - (HYDROGALVINOXY)[100]



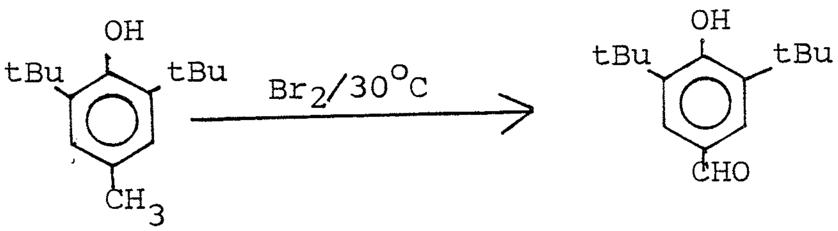
4.21g Galvinoxyl (2,6-di-tert-butyl- (3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy) and 2.12g of 4,4'-dihydroxy-3,5,3',5' tetra-tert-butyl-diphenyl methane were added to a small round bottom flask. To the mixture was added 300ml of freshly distilled and degassed ether. The solution had nitrogen gas passed through continuously for 48 hours in the dark until complete change of colour from violet to yellow was observed. The ether was removed under reduced pressure in a rotary evaporator. Two crystallisations of the yellow compound from equeous ethanol gave bright yellow crystalline product.

Melting Point	158-9°C (Literature 158°C)[100]

Infra-Red Data

Phenolic OH	3620 cm^{-1}
Quinonoid C=O	1680 cm^{-1}
Tertiary-butyl group	1380 and 1365 cm^{-1}

2.8.12 3,5-DI-TERT-BUTYL-4-HYDROXYBENZALDEHYDE[101]



10g of 2,6-di-t-butyl-p-cresol in 300ml of tert-butanol was treated with 14g of bromine at 30°C. The temperature rose to about 50°C due to the exothermic nature of the reaction.

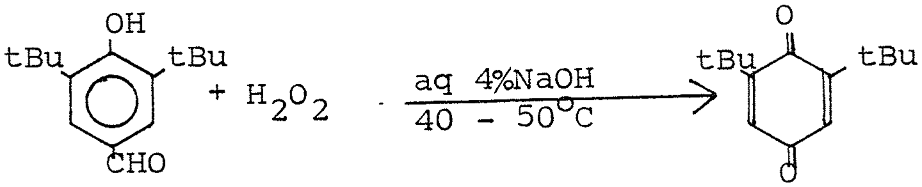
After one hour the crystalline product was filtered off, washed with sodium thiosulphate solution and recrystallised from methanol.

Melting Point	189°C (Literature 189°C)[101]

Infra-red Data

Phenolic OH	3620 cm^{-1}
Aldehydic C=O	1710 cm^{-1}
Tertiary-butyl group	1370 and 1360 cm^{-1}

2.8.13 2,6-DI-TERT-BUTYL-PARABENZOQUINONE[102]



57ml of 6% hydrogen peroxide (0.1m) were added to a solution of 23.4g (0.1m) of 3,5-di-tert-butyl-4-hydroxybenzaldehyde dissolved in 600ml of 4% aqueous sodium hydroxide maintained at 40-50°C. Air was blown through the reaction mixture and a yellow precipitate of 2,6-di-tert-butyl-parabenzoquinone was formed. The precipitate was washed several times with distilled water and dried. The dried product was recrystallised from methanol.

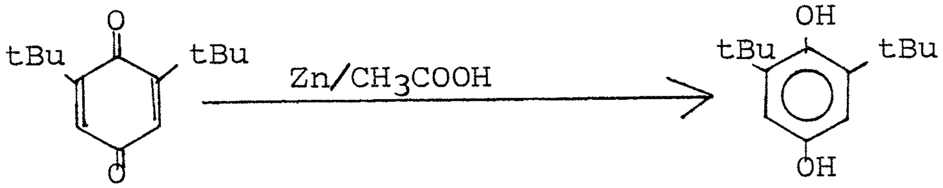
Melting Point 65-66°C

Infra-Red Data

Quinonoid C=O

Tertiary-butyl group

2.8.14 2,6-DI-TERT-BUTYL-HYDROQUINONE[102]



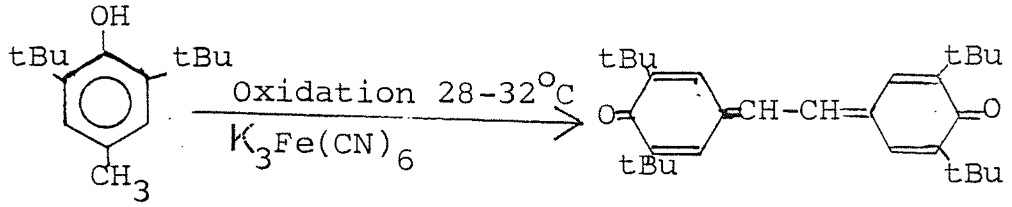
10g of 2,6-di-tert-butyl-parabenzoquinone dissolved in 100ml benzene were reduced with 4g zinc dust, 6ml glacial acetic acid and 4ml of water. The solution when colourless was poured on to crushed ice and the precipitated 2,6-di-tert-butyhydroquinone was filtered and recrystallised from petroleum ether.

Melting Point 114°C (Literature 114°C)[102]

Infra-Red Data

Phenolic OH	3620 cm^{-1}
Tertiary-butyl group	1370 and 1360 cm^{-1}

2.8.15 3,5,3',5'-TETRA-TERT-BUTYL-STILBENE-QUINONE[103]



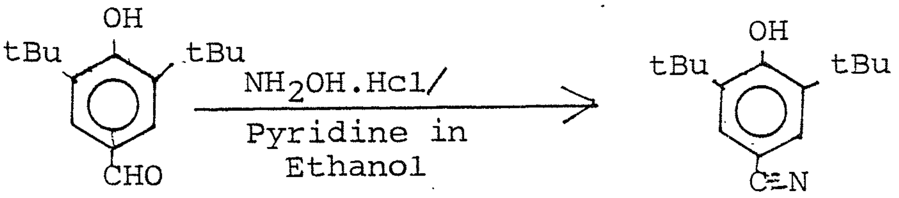
A solution consisting of 200ml of pentane and 25g of 2,6-di-tert-butyl-para-cresol was mixed with 100ml of 10% aqueous sodium hydroxide. This mixture was stirred continuously at 28-32°C while an aqueous solution consisting of 400ml of water and 104g of potassium ferricyanide was added over 20 minutes. A brick red compound was obtained. Crystallisation from glacial acetic acid gave crimson rods.

Melting Point	300°C (Literature 296°C[103], 300°C[104])

Infra-Red Data

Quinonoid C=O	1680 cm^{-1}

2.8.16 2,6-DI-TERT-BUTYL-4-CYANO PHENOL[105]



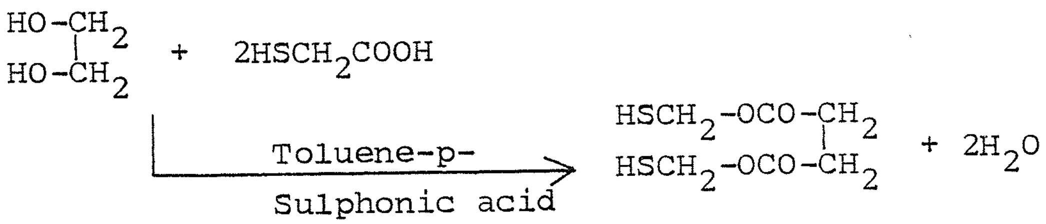
72g of 3,5-di-tert-butyl-4-hydroxybenzaldehyde was heated for 3 hours at 100°C with 42g hydroxylamine hydrochloride (NH_2OH Hcl), 96g pyridine (C_5H_5N) and 180ml ethanol and with occasional shaking. The mixture was then cooled and treated with water and a little diethyl ether. The upper phase was removed and heated for one hour at 100°C with 110ml acetic anhydride, then evaporated and the residue cooled, yielded 65% of the product. Crystallisation from glacial acetic acid gave white crystalline needles.

Melting Point 145°C (Literature 145°C)[105]

Infra-Red Data

Phenolic OH	3640 cm^{-1}
Cyano group	
Tertiary-butyl group	1370 and 1360 cm^{-1}

2.8.17 ETHYLENE GLYCOL BIS-THIOGLYCOLLATE (GLYCOL DIMERCAPTO ACETATE (GDMA))



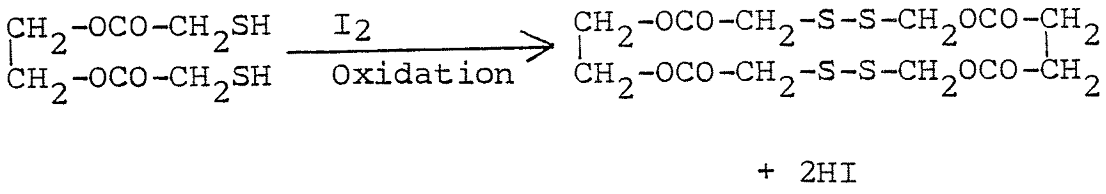
$$\begin{array}{l}HO\text{-}CH_2\\ \;\;\;\;\;|\\ HO\text{-}CH_2\end{array} + 2HSCH_2COOH \xrightarrow[\text{Sulphonic acid}]{\text{Toluene-p-}} \begin{array}{l}HSCH_2\text{-}OCO\text{-}CH_2\\ \;|\\ HSCH_2\text{-}OCO\text{-}CH_2\end{array} + 2H_2O$$

32g of ethylene glycol (1 mole) in 100ml benzene were placed in a round-bottom flask fitted with a Dean and Stark glassware and a condenser. Two moles, 184g of thioglycolic acid was added to the ethylene glycol. 0.3g of toluene-p-sulphonic acid was added and the mixture refluxed for 4 hours and then cooled. The organic phase was taken up in diethyl ether and excess acid removed by washing first with a 2 per cent solution of sodium hydrogen carbonate and then water. The ether extract was dried over anhydrous magnesium sulphate, filtered and solvent removed in a rotary evaporator. A pale yellow oily liquid was obtained.

Infra-Red Data

-SH group	2550 cm^{-1}
Ester C=O	1740 cm^{-1}
Aliphatic C-H	2965 cm^{-1}
Methylenic (CH_2)	1450 cm^{-1}

2.8.18 BIS-(GLYCOL DITHIODIGLYCOLLATE)



$$\begin{array}{l} CH_2\text{-}OCO\text{-}CH_2SH \\ | \\ CH_2\text{-}OCO\text{-}CH_2SH \end{array} \xrightarrow[\text{Oxidation}]{I_2} \begin{array}{l} CH_2\text{-}OCO\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2OCO\text{-}CH_2 \\ | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ CH_2\text{-}OCO\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2OCO\text{-}CH_2 \end{array} + 2HI$$

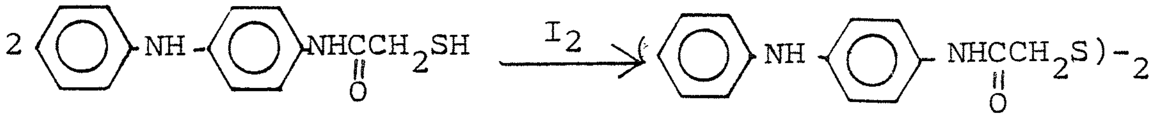
A mixture of 21.0g of glycol dimercapto acetate, 100ml benzene and 50ml water was stirred vigorously and a solution of 100ml benzene, 25ml ethanol and 25.4g iodine was added very slowly. When the stirred mixture showed a trace of iodine colour, the stirring and addition of iodine solution were stopped. The gel-like product that came out of solution during the course of addition of iodine and stirring was removed. Washed several times with petroleum ether to give a white gel-like material. This material was then dissolved in chloroform and precipitated with methanol. The chloroform/ methanol mixture was decanted and the traces of solvents left removed under vacuum to give a light pale gel-like compound.

This compound is insoluble in most solvents except chloroform.

Infra-Red Data

Ester C=O cyclic	1760 cm^{-1}
Aliphatic CH	2960 cm^{-1}
Methylenic (CH_2)	1450 cm^{-1}

2.8.19 BIS-(4-PHENYLAMINOPHENYL-THIOGLYCOLAMIDE)[106]



2g of 4-mercaptoacetamidodiphenylamine (MADA) in 150ml of methanol was put in a reaction flask and a solution of 0.48g

(0.0038 mole) of iodine in 20ml methanol was added slowly and stirred. When all the iodine solution had been added, the mixture was diluted with distilled water and the precipitate filtered. The grey precipitate was then recrystallised from methanol.

Melting Point	157-8°C (Literature 157°C)[5]

Infra-Red Data

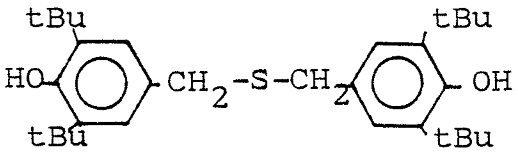
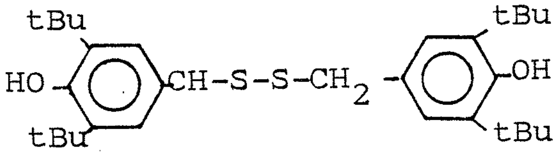
Secondary -NH group	3360 cm^{-1}
Amide -NH group	3260 cm^{-1}
Amide carbonyl	1650 cm^{-1}
Benzene ring	750 cm^{-1}

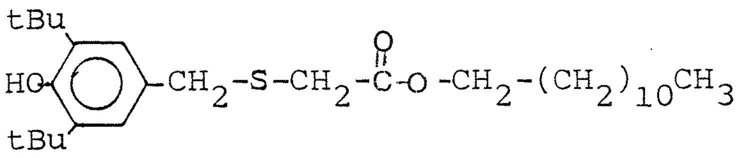
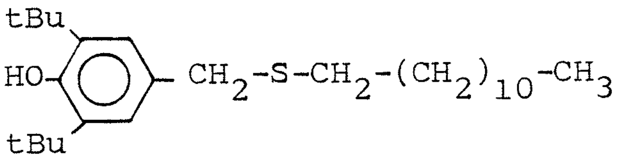
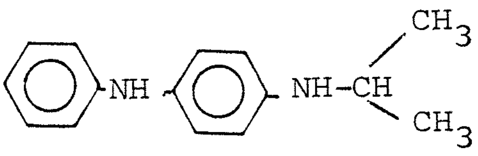
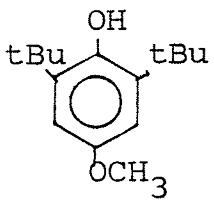
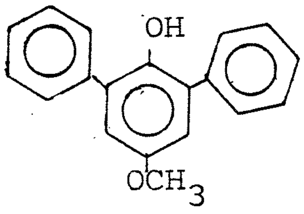
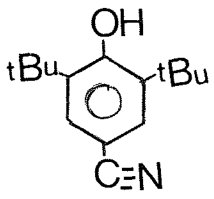
CHAPTER THREE

3. ASSESSMENT OF CURE AND AGEING CHARACTERISTICS OF SOME HINDERED PHENOLIC SULPHUR COMPOUNDS

A number of hindered phenolic sulphur compounds were evaluated for their effects on the cure and ageing behaviour of natural rubber gum stock. The cure and ageing characteristics of these test compounds in a vulcanised rubber gum stock are compared with those vulcanisates containing a conventional antioxidant such as N-isopropyl-N'-phenyl-para-phenylene diamine (Santoflex-IP (IPPD)) and which has been shown to be effective as a heat ageing antioxidant under both static and dynamic conditions. These test compounds were also compared with a known sulphur compound, dilauryl thiodipropionate (DLTP) and some hindered phenolic compounds.

The test compounds and their abbreviations are:

Chemical Structure	Name	Code
	Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-monosulphide	BDBS
	Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-disulphide	BDBDS

Chemical Structure	Name	Code
	3,5-Di-tert-butyl-4-hydroxybenzyl-dodecyl thioglycolate	DBDT
	3,5-Di-tert-butyl-4-hydroxybenzyl-dodecyl sulphide	DBDS
	N-isopropyl-N-phenyl-p-phenylene-diamine	IPPD
$(CH_3-(CH_2)_{10}CH_2-OCO-CH_2-CH_2-CH_2)_2S$	Dilauryl thio-dipropionate	DLTP
	4-methoxyl,2,6-ditert-butyl-phenol	MDBP
	4-methoxyl,2,6-di-phenyl-phenol	MDPP
	2,6Di-tert-butyl-4- cyano-Phenol	CBP

3.1 ASSESSMENT OF CURE CHARACTERISTICS

The rubber industry and the automobile industry owe their existence to the vulcanisation process whereby the properties - (weak, plastic, soluble and tacky) of raw rubber are modified to the end-use properties of the vulcanisate (strong, elastic, insoluble and non-tacky). Rubbers may be vulcanised by a number of cure systems and to varying degrees of crosslink density according to their intended end-use. However, the incorporation of any protective additive(s) demands that such additive(s) be first assessed for its effects on the vulcanisation parameters. The individual effects of the hindered phenolic sulphur compounds on the various cure systems employed have been assessed and in particular their effects on the modulus of the vulcanisates have been observed. The reason is that modulus has been shown[107] to be one of the factors which influence the fatigue life of a vulcanisate. The contributory effect of modulus was eliminated by milling the various natural rubber gum stocks to about the same Wallace Plastimeter number followed by curing to the same crosslink density.

3.1.1 PROCEDURE

The curing characteristics were assessed using the Monsanto Oscillating Disc Rheometer as described in Section 2.2.2. Compounding of the various natural rubber gum stocks was as set out in Section 2.2.1, using the formulations in Tables 3.1 - 3.3. The CBS-sulphur and TMTD-sulphurless gum stocks were cured at 140°C and the peroxide stocks cured at 160°C. All the hindered phenolic sulphur compounds and the control compounds (IPPD, DLTP, MDBP and MDPP) were used on an equimolar basis. The Monsanto rheographs obtained were then interpreted using the standard cure parameters namely, the induction time (t_i), the rate of vulcanisation, K, and the maximum torque (R_{max}). All the CBS-sulphur compounds were cured for 35 minutes, the TMTD-sulphurless stocks for 45 minutes and the various peroxide stocks at different cure times as described in Table 3.6.

Table 3.1. CBS-Sulphur Formulations

	Control	1	2	3	4	5	6	7	8
NR(SMR10)	100	100	100	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5	5	5	5
Stearic Acid	3	3	3	3	3	3	3	3	3
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
BDBS	-	0.94	-	-	-	-	-	-	-
BDBDS	-		1.00	-	-	-	-	-	-
DBDT	-	-	-	0.95	-	-	-	-	-
DBDS	-	-	-	-	0.84	-	-	-	-
IPPD	-	-	-	-	-	0.50	-	-	-
DLTP	-	-	-	-	-	-	1.02	-	-
MDBP	-	-	-	-	-	-	-	0.55	-
MDPP	-	-	-	-	-	-	-	-	0.47
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 3.2. TMTD-Sulphurless Formulations

	Control	1	2	3	4	5
NR(SMR10)	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5
Stearic Acid	3	3	3	3	3	3
BDBS	-	0.94	-	-	-	-
BDBDS	-	-	1.00	-	-	-
DBDT	-	-	-	0.95	-	-
DBDS	-	-	-	-	0.84	-
IPPD	-	-	-	-	-	0.50
TMTD	3.5	3.5	3.5	3.5	3.5	3.5

Table 3.3. Peroxide Formulations

	Control	1	2	3	4	5
NR(SMR10)	100	100	100	100	100	100
Dicumyl Peroxide (DCP)	3	3	3	3	3	3
BDBS	-	0.94				
BDBDS			1.00			
DBDT				0.95		
DBDS					0.84	
IPPD						0.50

Table 3.4. Cure Parameters of CBS-Sulphur Cure System Containing Test Compounds

Test Compounds	Concentration g/100g rubber	R_{max} x0.06 m-kg	$Kx10^{-1}min^{-1}$	t_i(min)
Control	-	58	2.8	10
BDBS	0.94 $1.99x10^{-3}$ mole	60	2.3	11.5
BDBDS	1.00 "	56	2.8	13
DBDT	0.95 "	59	2.3	10.5
DBDS	0.84 "	58	2.3	10
IPPD	0.50 "	60	2.3	9.5
DLTP	1.02 "	61	2.3	9
MDBP	0.55 "	60	2.7	9.5
MDPP	0.47 "	61	2.3	9

3.1.2 RESULTS

The cure characteristics of the protective additives are shown in Figs. 3.1 - 3.3 and their corresponding cure parameters in Tables 3.4 - 3.6 for the conventional CBS-sulphur, TMTD-sulphurless and peroxide cure systems respectively. In the CBS-sulphur cure (Table 3.4 and Fig. 3.1), almost all the additives have about the same induction time as the control, with the exception of BDBDS which had a slightly higher induction time of 13 minutes. All the additives have no effect on the rate of cure and the modulus at maximum cure is about the same although a slightly lower modulus is obtained in the case of BDBDS.

In the TMTD-sulphurless cure (Table 3.5), the induction times are about the same with the exception of BDBDS with a shorter time of 6 minutes. All the additives increased slightly the rate of cure over the control. There is a noticeable increase in the induction times of the additives in the peroxide cure as compared to the control (Table 3.6). The rate of cure is also noticeably reduced by the additives. The modulus at maximum cure is about the same for the control, BDBS, DBDT and DBDS but IPPD and BDBDS have lower moduli. The reduction in the modulus of the vulcanisate is most marked with BDBDS.

Table 3.5. Cure Parameters of TMTD-Sulphurless Cure System Containing Test Compounds

Test Compounds	Concentration g/100g rubber	R_{max} (m-kgx0.06)	$kx10^{-1}min^{-1}$	t_i(min)
Control	-	38	0.89	8.0
BDBS	$0.94=1.99x10^{-3}$ mole	35	0.99	8.5
BDBDS	1.00 "	39	1.19	6.0
DBDT	0.95 "	34	1.06	8.5
DBDS	0.84 "	32	1.15	9.0
IPPD	0.50 "	33	1.05	8.5

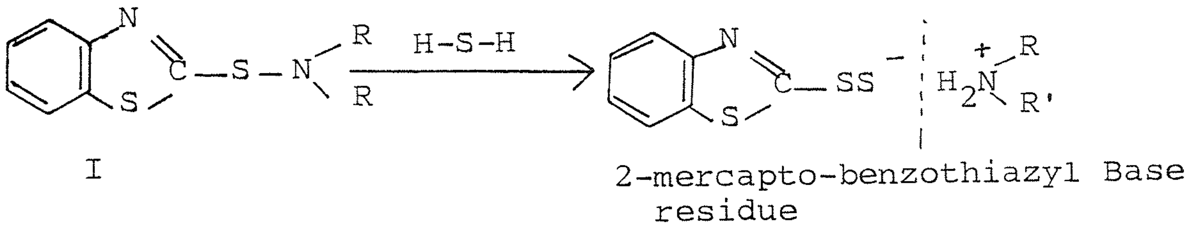
Table 3.6. Cure Parameters of Peroxide Cure System Containing Test Compounds

Test Compounds	Concentration g/100g rubber	R_t m-kgx0.06	$k\times10^{-1}$ min^{-1}	t_i (min)	Cure Time, t (min)
Control	-	55	1.38	1.5	14
BDBS	$0.94 = 1.99\times10^{-3}$ mole	55	0.92	3.5	16.5
BDBDS	1.00 "	55	1.02	3.5	21.5
DBDT	0.95 "	55	0.92	3	16
DBDS	0.84 "	55	0.92	3	18
IPPD	0.50 "	55	1.06	4	21

3.1.3 DISCUSSION

The chemical mechanism of accelerated sulphur vulcanisation is still a subject of dispute. There are extensive reviews[108-111] advocating both polar and radical mechanisms.

The delayed action of sulphenamides has been attributed to the fact that the molecule (I) splits to a 2-mercapto-benzothiazyl residue and a base only on attainment of the vulcanisation temperature by thermal, hydrolytic or reductive fission of the S-S or S-M bonds[112]. The base then activates the 2-mercapto-benzothiazyl residue, resulting in the high rate of vulcanisation typical of the CBS-sulphur cure system.



I

(3-1)

The TMTD-sulphurless cure system again suffers the same problem of disputed chemical mechanism as the accelerated sulphur vulcanisation and in the reviews by Hofmann[108] and Urabe[109], a mixed polar and radical mechanism is believed to be operative. The results in Fig. 3.2 and Table 3.5 showed the characteristic reduction in scorch time associated with a thiuram vulcanisation system and coupled with this, is the low rate of vulcanisation which is obtained when extremely low concentration of sulphur is involved in the cure. Invariably, at the level of incorporation, the test compounds do not interfere to any significant extent on the typical cure characteristics.

The peroxide cure system, unlike the conventional CBS-sulphur and TMTD-sulphurless cure systems is unequivocally 'free' radical in nature. As would be expected, the cross linking reaction is almost completely inhibited by hydroquinones and 1,1-diphenyl-2-picryl-hydrazyl (DPPH)[112]. The results in Fig. 3.3 and Table 3.6 showed that the test compounds interfered to varying extent but in a beneficial way with the cure characteristics. The increased 'scorch' time and slightly reduced rate of vulcanisation are due to the interaction of some of the transformation products of the hindered phenolic sulphur compounds, notably, hydroquinone, stilbenequinone with the alkoxyl radical thus reducing the number of the radicals involved in the actual cross linking process, (see Chapter 5). The lower modulus level produced by BDBDS and IPPD is due to their radical scavenging ability.

3.2 ASSESSMENT OF AGEING CHARACTERISTICS

3.2.1 STRESS RELAXATION MEASUREMENT

The oxidative stress relaxation method is a good indicator of the net effectiveness of an antioxidant to protect a rubber vulcanisate during service especially when considering such factors as, the rate of loss of antioxidant from the polymer and the mobility of the antioxidant within the polymer. In the stress relaxation method, a strip of rubber is stressed in tension to constant extension and the stress required to maintain this constant extension is monitored. The technique is based on the kinetic relationship between the force (or tension), F, exerted by a stretched rubber sample and the number, N, of stress-supporting network chains per Unit Volume[113] expressed as:

$$F = NkTA_o (\lambda - \lambda^{-2}) \qquad (3\text{-}2)$$

where:

k = Boltzmann's Constant

T = Absolute temperature

A_o = The Unstrained Cross-Section area

λ = The ratio of the stretched length to initial length of sample.

During the course of ageing, at time, t, the number of network chains supporting the stress will be reduced from No to N and the stress from F_o to F, however, N and F are always related as in equation (3.1), so that at constant extension ratio, λ , sectional area A_o, and temperature, the relationship is given by;

$$F/F_o = N/No \qquad (3\text{-}3)$$

Stress relaxation can be carried out continuously or intermittently. In continuous stress relaxation, the extension is maintained throughout the duration of the test and the resultant decay in stress at constant extension during ageing gives a measure of the network scission. In intermittent stress relaxation, the sample is only strained at such times as the stress is to be measured. It is held in the unstressed state for most of the time. In this case, most of any crosslinks are formed when the sample is at rest and these will contribute to the stress-supporting network. The difference in the results of the two types of stress relaxation provides a measure of the extent of cross linking during ageing.

The continuous stress relaxation mode was employed in this assessment and the hindered phenolic sulphur compounds were examined in three main types of network structure; $-C-S_x-C$; $C-S-C$; and $C-C$, that is, mainly polysulphide, monosulphide and carbon to carbon network structures respectively.

3.2.1.2 PROCEDURE

The vulcanisates used were prepared as described in Section 2.2.3.2. The test compounds were introduced as additives (Tables 3.1 - 3.3) during the compounding process and extracted SMR10 rubber was used. The continuous decay in stress was carried out at 100°C and according to the procedure set out in Section 2.4.1.

3.2.1.3 RESULTS

The continuous stress relaxation curves for the control and test compounds in CBS-sulphur vulcanisates are shown in Fig. 3.4. All test compounds showed delayed relaxation rates over the control but the degree varied. Among the sulphur compounds, DBDT gave the best overall improvement. However, in terms of 50% stress decay, F_{50}, DBDT, BDBS and DBDS have about the same time to F_{50} (Table 3.7). BDBDS gave the least improvement. The control compounds - IPPD, DLTP, MDBP and MDPP gave substantial improvement over the test compounds with MDPP giving the highest improvement in the rate of stress decay.

The stress relaxation curves for the sulphur compounds and IPPD in TMTD-sulphurless vulcanisates are shown in Fig. 3.5. All test compounds again reduced stress decay compared to the control. IPPD gave the highest reduction in rate of stress decay while BDBS was the best of the sulphur compounds.

Fig. 3.6 shows the stress relaxation curves for control and test compounds in peroxide vulcanisates. All test compounds, with the exception of BDBDS, gave substantial reduction in the rate of stress decay. The sulphur compounds except BDBDS, were equally as effective as IPPD.

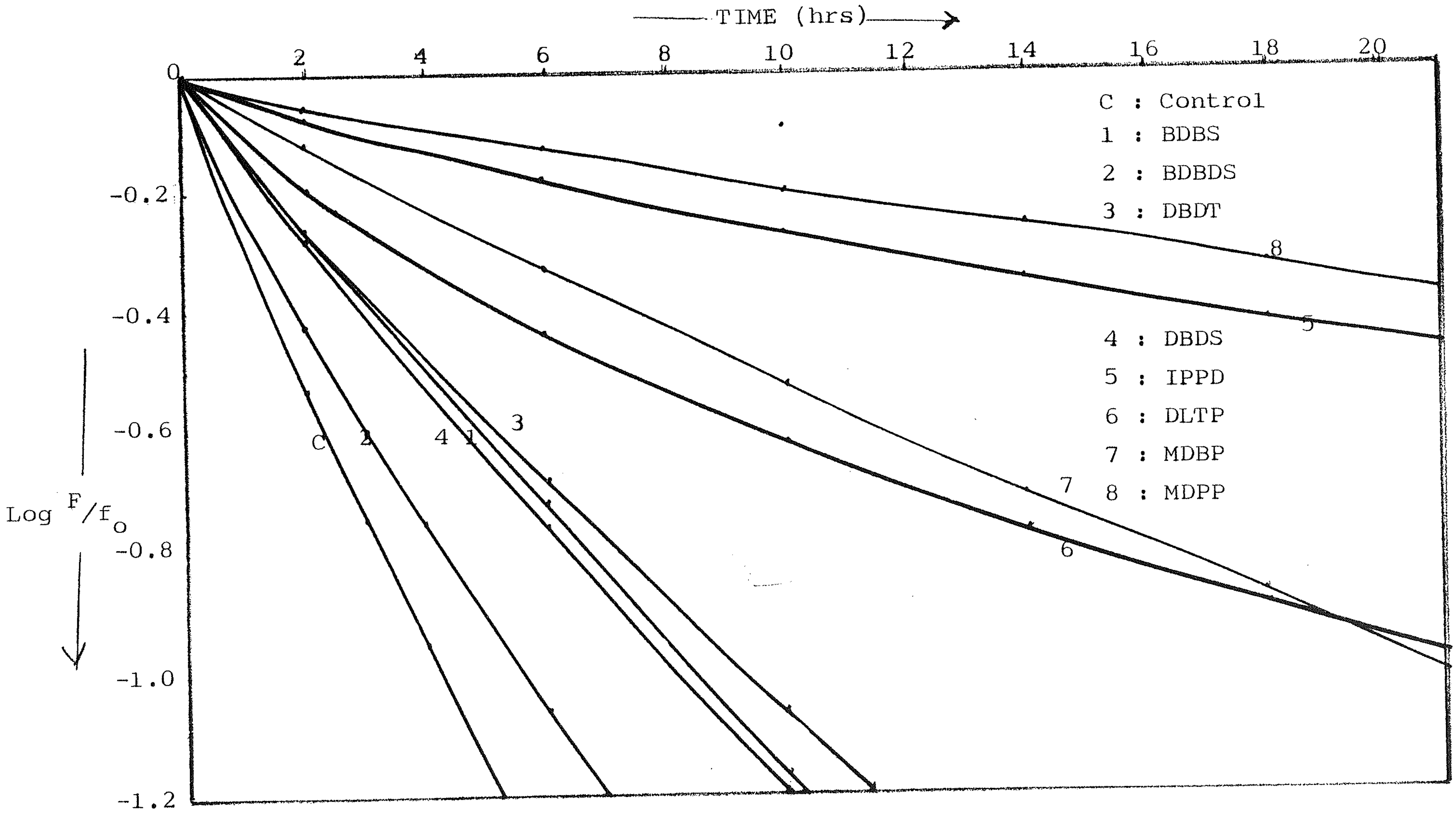


Fig. 3.4 : Continuous Stress Relaxation of CBS-Sulphur Vulcanisates Containing Test Compounds at 100^{o}C and 60% Extension

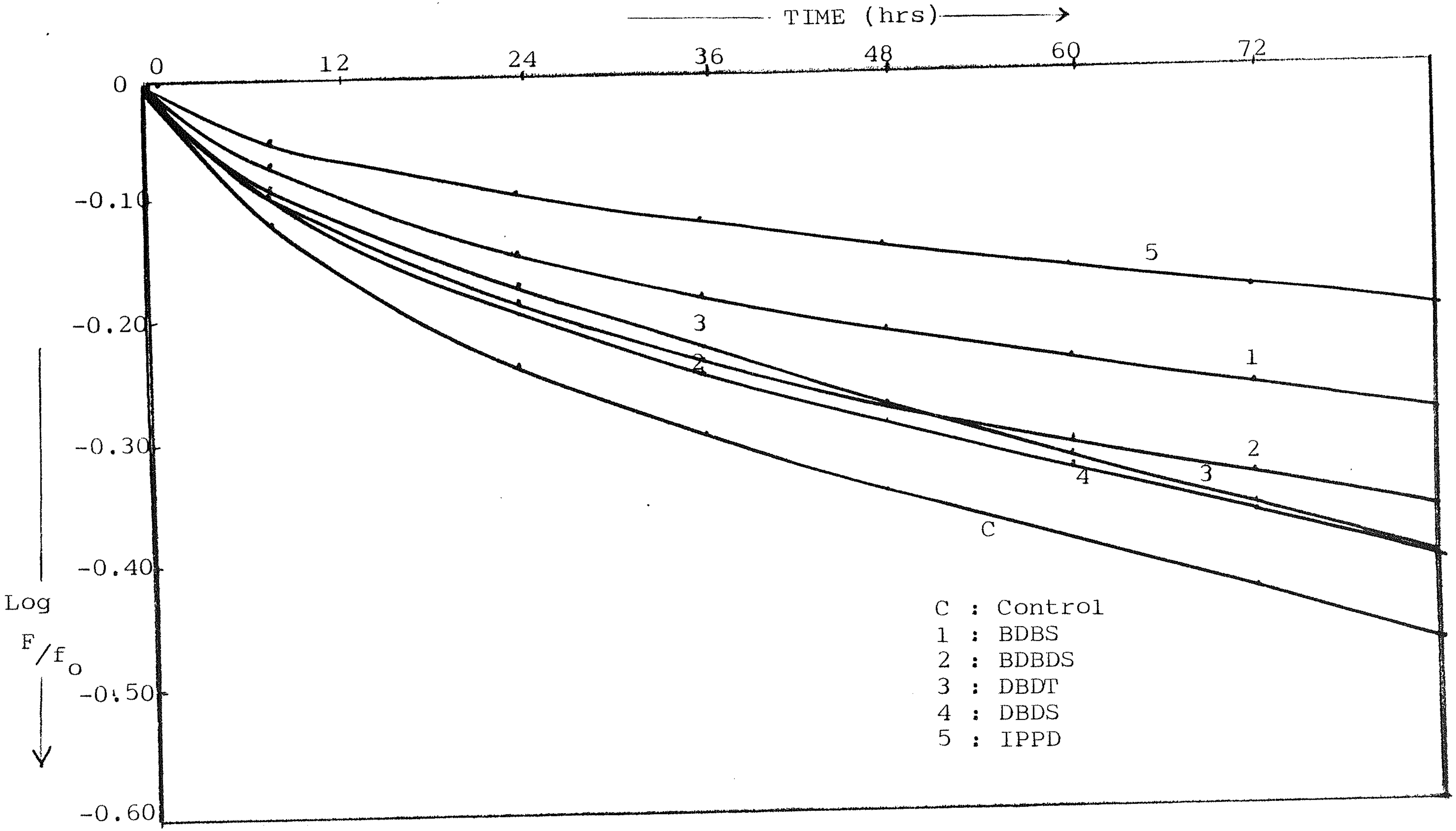


Fig. 3.5 : Continuous Stress Relaxation of TMTD-Sulphurless Vulcanisates Containing Test Compounds at 100^{o}C and 60% Extension

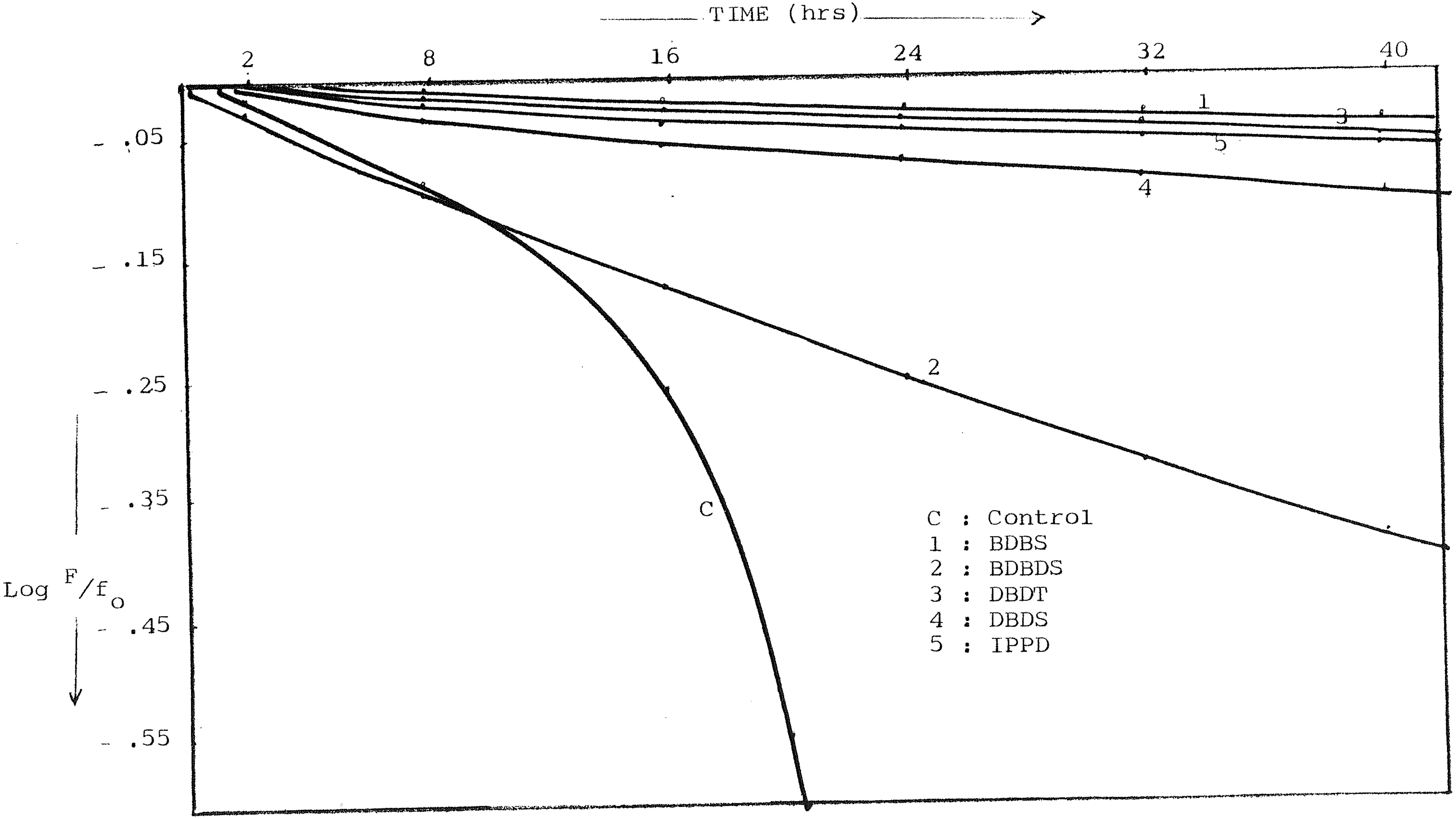


Fig 3.6 : Continuous Stress Relaxation of Peroxide Vulcanisates Containing Test Compounds at 100°C and 60% Extension

Table 3.7 Time to 50% Stress Decay (F_{50}) in Cure Systems

Test Compound	CBS-Sulphur	TMTD-Sulphurless	Peroxide
Control	1	39	18
- BDBS	2.25	98	180
- BDBDS	1.25	58	30
- DBDT	2.25	54	168
- DBDS	2	51	102
IPPD	11.5	140	150
DLTP	3.5	-	-
MDBP	5.0	-	-
MDPP	16.5	-	-

3.2.1.4 DISCUSSION

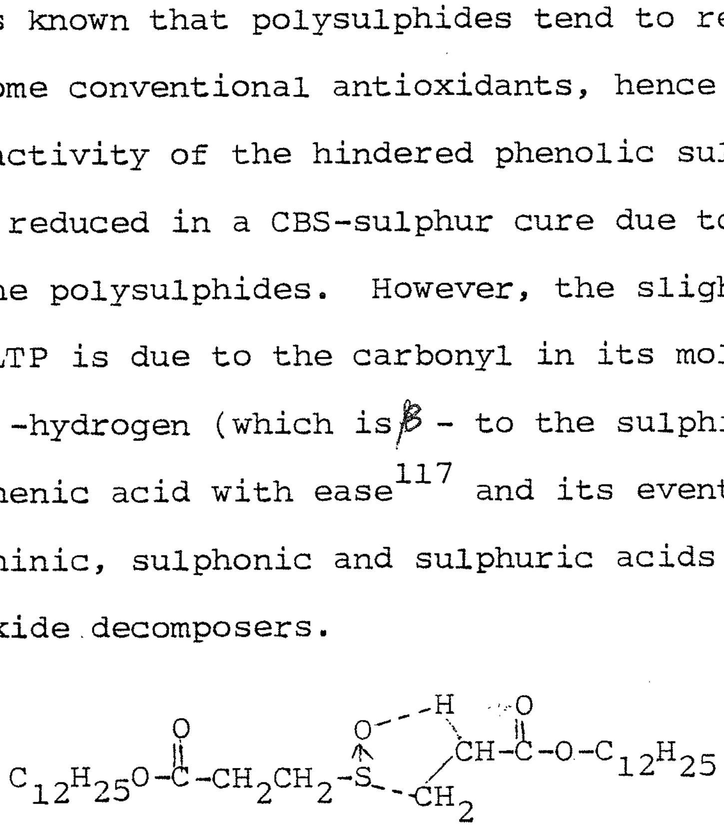
The three types of cure system employed produce network structures which respond differently to oxidative ageing. The CBS-sulphur cure is characterised by the presence of free sulphur, cyclic sulphides and polysulphides. These components are not present or are present to a very low level in the TMTD-sulphurless cure system and which gives mainly monosulphides while the CBS-sulphur cure gives mainly polysulphides. The peroxide cure gives mainly C-C crosslinks. These features have been shown to markedly affect their tendencies to self inhibition as shown by comparing the controls in Figs. 3.4 - 3.6.

The control in the peroxide cure (Fig. 3.6) relaxed autocatalytically, that in TMTD-sulphurless cure exhibited a very low rate of stress decay but was still autocatalytic, while in the CBS-sulphur cure, it was initially autocatalytic but then autoretarded. The different behaviour is characteristic of the type of cure system, and which in turn is related to the network structure and the extra network material.[114]

During thermal oxidative stress relaxation, hydroperoxides are being formed and these decompose to 'free' radicals which initiate the autoxidation reactions. The autocatalytic behaviour of the peroxide vulcanisate is due to its normal autoxidative behaviour and the resultant fast rate of stress decay.

The initial fast stress decay stage of the CBS-sulphur vulcanisate has been attributed to the instability of the polysulphide bonds to heat and the ability of the polysulphides to act as oxidation initiators[115]. In addition the presence of conjugated diene and triene groups which are formed alongside the cyclic sulphide groups[116] may contribute to the autocatalytic stage. The variety of oxidised organic sulphur groups (Scheme 1.2[11], Chapter 1) which later result from the reaction of the various mono-, di- and polysulphide groups with hydroperoxide are known to be responsible for the autoretardation stage. The low rate of stress decay of TMTD-sulphurless vulcanisate has been attributed to the zinc dimethyldithiocarbamate[114] formed during cure. This extra-network material has been shown to impart good thermal oxidative properties.

With this background on the characteristic behaviour of the control in the different types of cure employed, the hindered phenolic sulphur compounds have only given a marginal improvement on the relaxation rate when compared to the control compounds - IPPD, DLTP, MDBP and MDPP in the CBS-sulphur cure. It is known that polysulphides tend to reduce the efficiency of some conventional antioxidants, hence it is probable that the activity of the hindered phenolic sulphur compounds are much reduced in a CBS-sulphur cure due to antagonistic effects of the polysulphides. However, the slightly better activity of DLTP is due to the carbonyl in its molecule which activates the β-hydrogen (which is β- to the sulphinyl group) to form sulphenic acid with ease[117] and its eventual oxidation to sulphinic, sulphonic and sulphuric acids which are the effective peroxide decomposers.

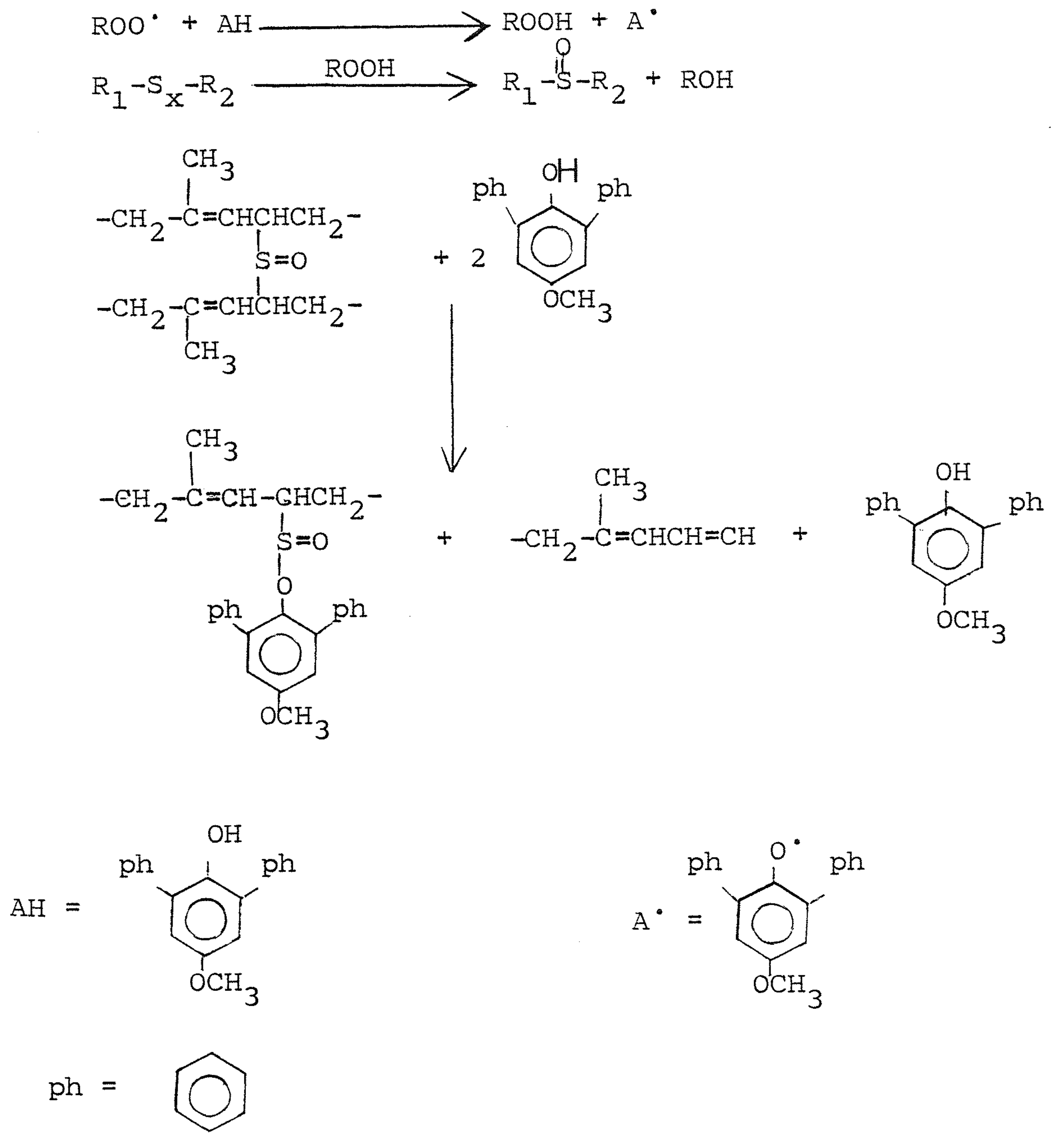


The hindered phenolic antioxidants MDBP and MDPP gave better protection to the CBS-sulphur vulcanisate against stress decay than the phenolic sulphur compounds. MDPP is particularly outstanding and has comparable activity to IPPD. In the sulphur crosslink vulcanisate, MDPP is likely acting in a synergistic fashion, with the polysulphide groups and other sulphide groups which tend to regenerate MDPP (Scheme 3.1) in contrast to the antagonistic effect observed with the phenolic sulphur compounds. MDPP has been reported to be continuously regenerated when used in conjunction with a thioester[118].

In the mainly monosulphidic crosslinked vulcanisate, the hindered phenolic sulphur compounds were able to improve the resistance to stress decay of the vulcanisate despite the presence of Zinc dithiocarbamate[119] which confers thermal oxidative stability to TMTD-sulphurless vulcanisate. This enhanced improvement must be due to the involvement of these sulphur compounds in hydroperoxide decomposition.

The hindered phenolic sulphur compounds manifest their protective ability in the peroxide vulcanisate and are comparable to IPPD with the exception of BDBDS. These sulphur compounds have effectively inhibited the characteristic autocatalytic stress decay to a significant extent. This is primarily due to their ability to destroy hydroperoxides which are the main sources of free radicals involved in autoxidation. The sulphur autosynergists are oxidised to their corresponding acidic species, which are capable of decomposing many molecules of hydroperoxides.[25,120,121-3] In addition, some of the transformation products such as stilbenequinone, hydroquinone and benzoquinone (see Chapter 5) formed during cure and ageing processes contribute to the reduction in rate of stress decay.

Scheme 3.1



3.2.2 OXYGEN ABSORPTION MEASUREMENTS

Stress relaxation described in the previous Section gives the resultant effects of intrinsic activity and loss of antioxidant by volatilisation. Oxygen absorption on the other hand gives the inherent activity of an antioxidant since it is normally carried out in a closed system.

3.2.2.1 PROCEDURE

The vulcanisates for this measurement were prepared as described in Section 2.2.3.1 using extracted SMR10. The test compounds were introduced as additives during the compounding process (Tables 3.1-3.3). The oxygen absorption measurements were carried out at 100°C and as outlined in Section 2.3.1.

3.2.2.2 RESULTS

The oxygen absorption curves for the hindered phenolic sulphur compounds and control compounds, IPPD and DLTP in CBS-sulphur, TMTD-sulphurless and peroxide vulcanisates are shown in Figs. 3.7, 3.8 and 3.9 respectively. The induction times and times to 1% oxygen absorption are set out in Tables 3.8 - 3.10. Of the hindered phenolic sulphur compounds in all three tests, BDBS gave the best protection but none of these compounds is comparable to IPPD at 1% level of oxygen absorption. In the CBS-sulphur vulcanisate where DLTP was used alone, the test compounds were comparable and they have higher induction times than DLTP. The control vulcanisates (Figs. 3.7 - 3.9) absorbed oxygen autocatalytically but the rate was much slower in the TMTD-sulphurless vulcanisate. All the test compounds showed an initial fast rate of oxygen absorption after the induction period followed by a slower rate of absorption.

Table 3.8 Induction Time and Time to 1% Oxygen Absorption of CBS-Sulphur Vulcanisates Containing Test Compounds at 100°C

Test Compound	Induction Time (hr)	Time to 1% O_2 Absorption (hr)
Control	1	5
BDBS	3	18
BDBDS	2	8
DBDT	2	11.5
DBDS	1.5	7
IPPD	9	44
DLTP	1	6

Table 3.9 Induction Time and Time to 1% Oxygen Absorption of TMTD-Sulphurless Vulcanisates Containing Test Compounds at 100°C

Test Compound	Induction Time (hr)	Time to 1% O_2 Absorption (hr)
Control	6	52
BDBS	35	153
BDBDS	15	109
DBDT	24	94
DBDS	18	82
IPPD	30	160

Table 3.10 Induction Time and Time to 1% Oxygen Absorption of Peroxide Vulcanisates Containing Test Compounds at 100°C

Test Compound	Induction Time (hr)	Time to 1% O_2 Absorption (hr)
Control	0.5	3
BDBS	18	101
BDBDS	18	38
DBDT	25.5	73
DBDS	24	53
IPPD	46.5	261

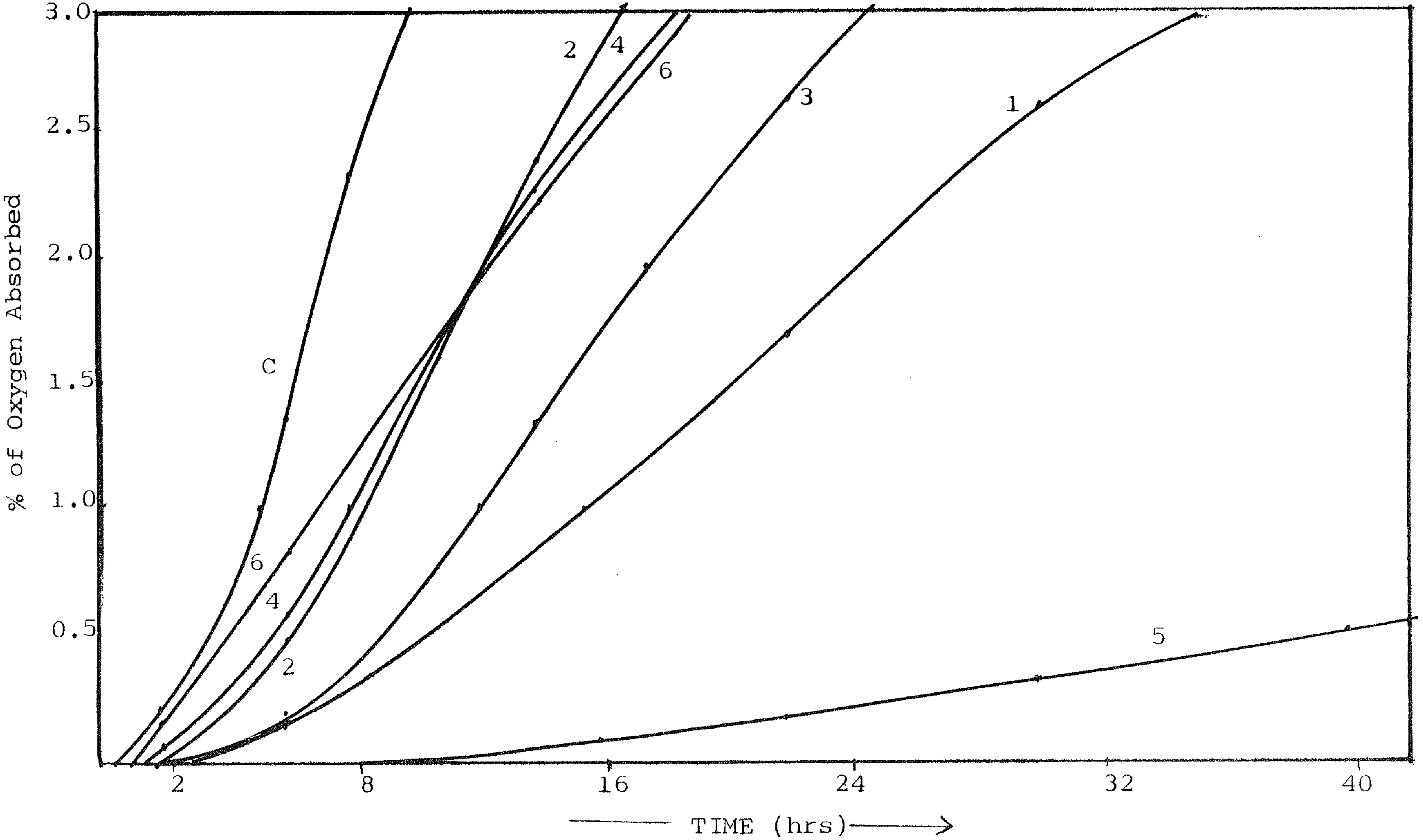


Fig. 3.7 : Amount of Oxygen Absorbed by CBS-Sulphur Vulcanisates Containing Test Compounds at 100°C

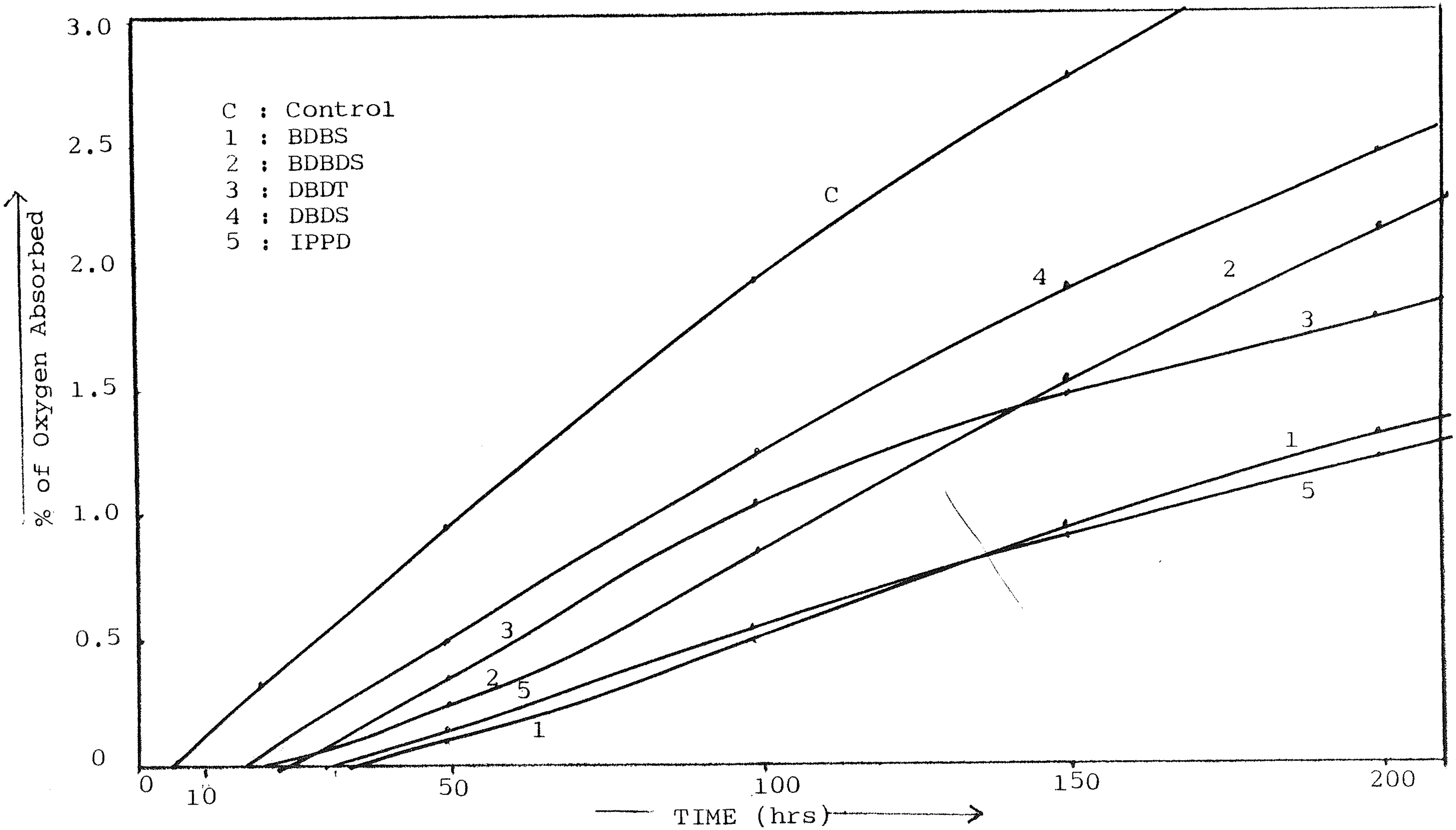


Fig. 3.8 : Amount of Oxygen Absorbed by TMTD-Sulphurless Vulcanisates Containing Test Compounds at 100°C

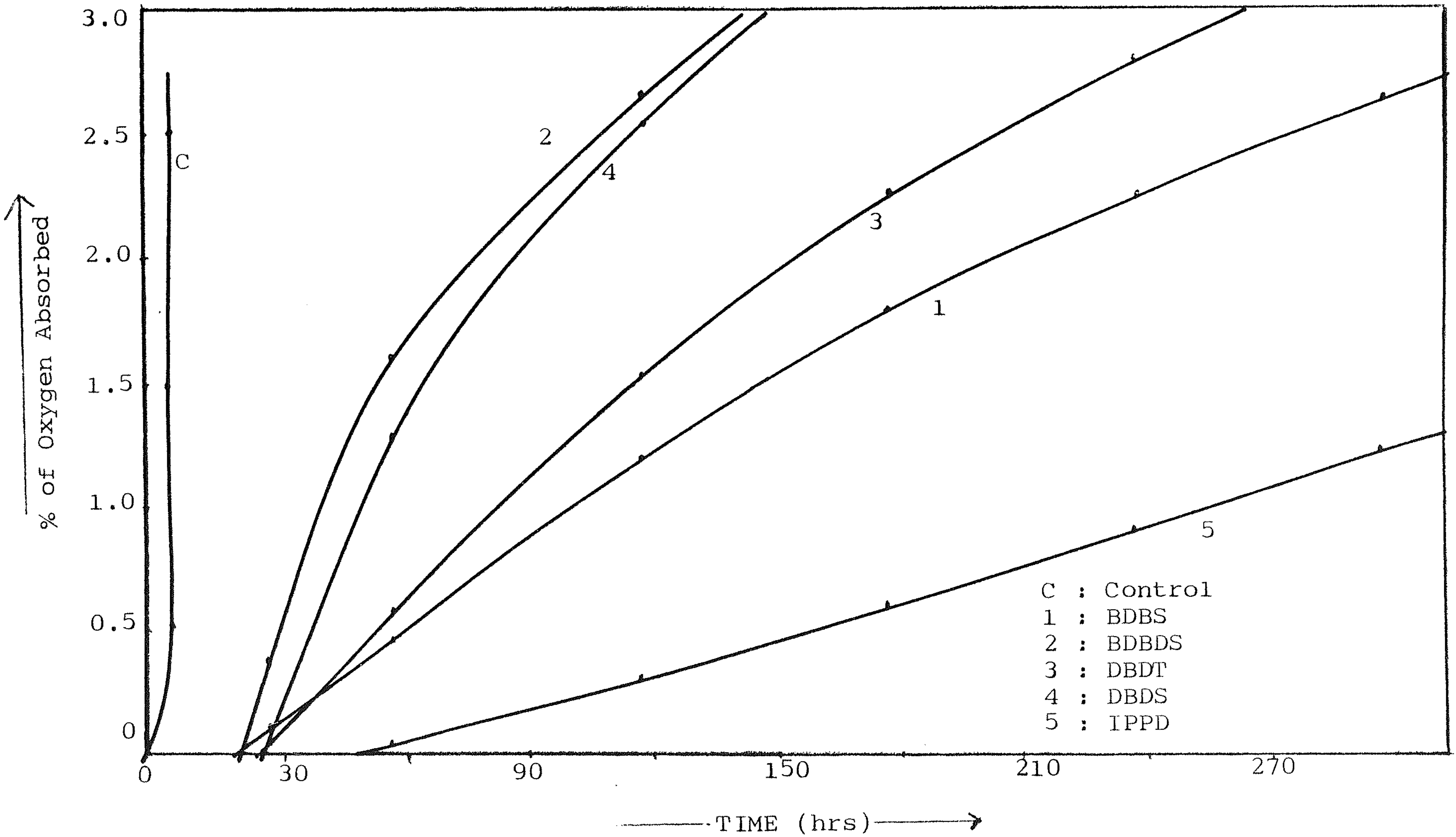


Fig. 3.9 : Amount of Oxygen Absorbed by Peroxide Vulcanisates Containing Test Compounds at 100^{o}C

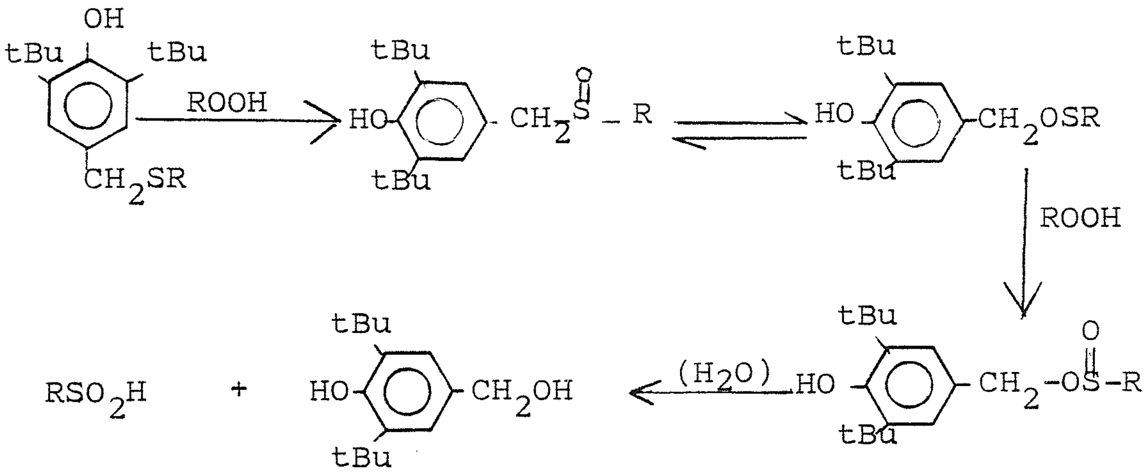
3.2.2.3 DISCUSSION

The pro-oxidant behaviours of the CBS-sulphur and TMTD-sulphurless are due to the reaction between sulphide groups in the vulcanisates with hydroperoxides formed during oxidative ageing[6]. These oxidised sulphide groups are known to exhibit antioxidant and pro-oxidant effects, hence the initial rapid rate of oxidation is attributable to the pro-oxidant state. In addition, the low rate of oxygen absorption by the TMTD-sulphurless vulcanisate is due to the presence of zinc dithiocarbamate formed during the curing process[119].

The variation in antioxidant activity of the hindered phenolic sulphur compounds is probably due to the relative ease with which they interact with hydroperoxide to form the active acidic species responsible for their antioxidant activity. The presence of polysulphide groups in the CBS-sulphur vulcanisates tend also to reduce the effectiveness of the organic sulphur compounds[115]. This is in contrast to the improved effectiveness of these organic sulphur compounds in other types of cure system (Figs. 3.8 and 3.9).

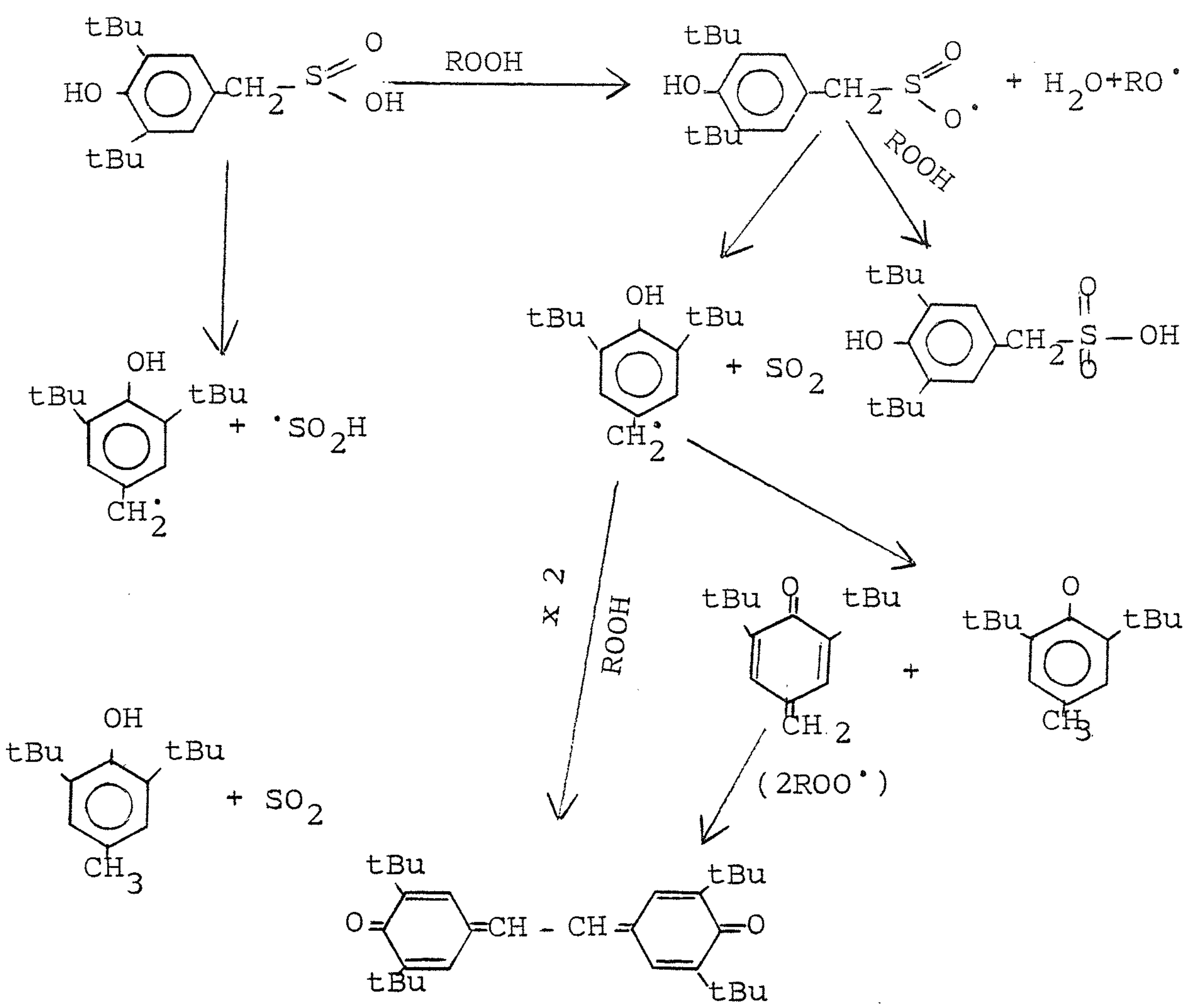
In related hindered phenolic sulphur compounds Scott and co-workers[25,120,121,124-5] showed that this class of sulphur compounds and dialkylthiodipropionate are effective antioxidants as a result of their ability to decompose hydroperoxides which is achieved through the formation first of sulphoxide or thiosulphinate and these then undergo thermolysis to give sulphur-oxy acids which are the active peroxide decomposing agents as outlined in Scheme 3.2[120,126]. Also it has been shown that a benzylic sulphide has twice the intrinsic activity of a simple phenol.

Scheme 3.2[120]

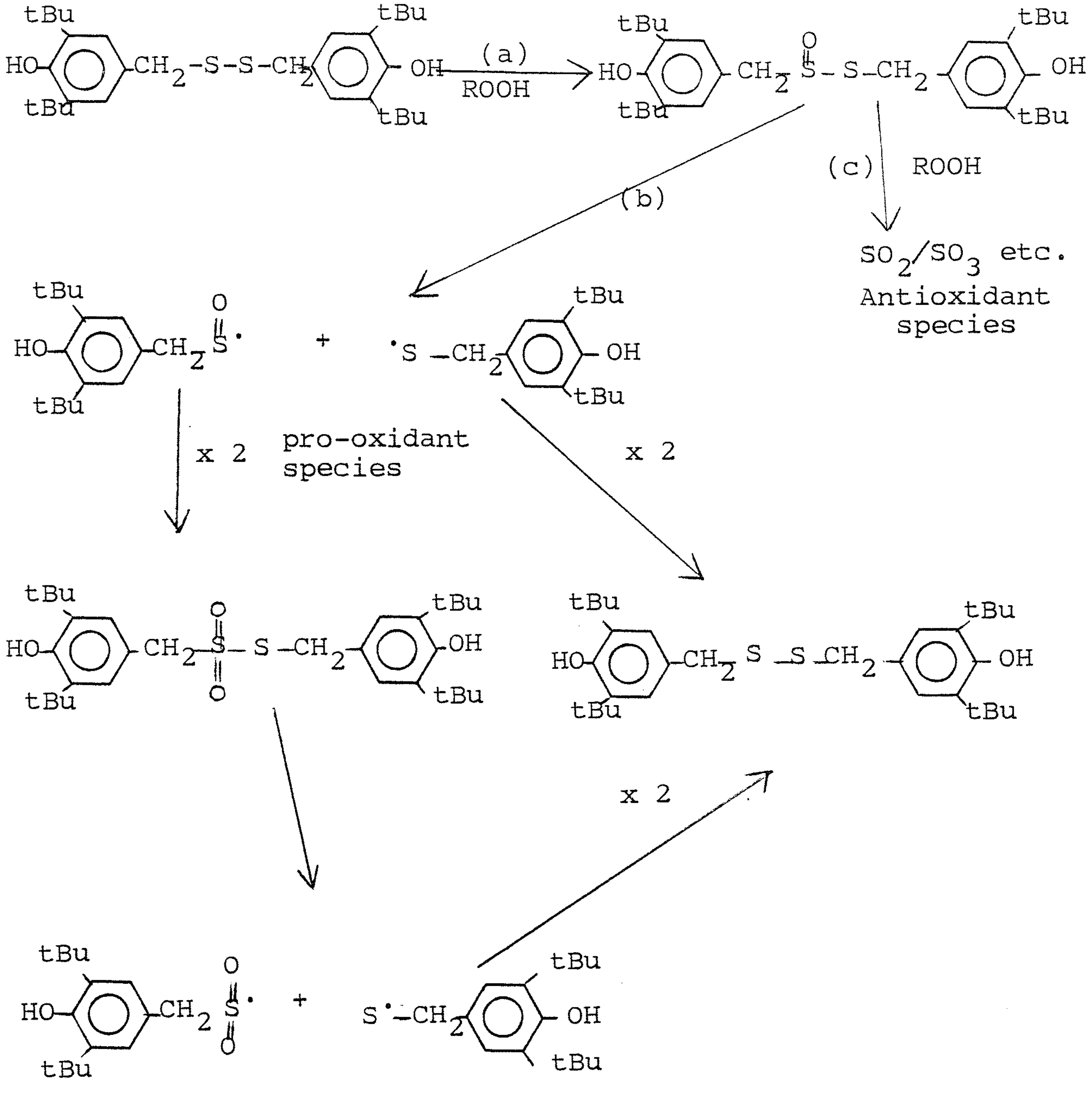


Where R is itself a benzyl residue as in BDBS, it has been shown[126] that there is complete elimination of the sulphur as in Scheme 3.3. This latter part of the reaction is the reason for the better activity of BDBS over the other organic sulphur compounds being examined. The lower performance of BDBDS can be explained on the basis of the continuous presence of pro-oxidant species alongside antioxidant ones (Scheme 3.4). Part of BDBDS is continually being reformed to produce both opposing species over again.

Scheme 3.3[126]



Scheme 3.4


tBu
HO
CH2-S-S-CH2
OH
tBu
(a)
ROOH
(b)
(c)
ROOH
SO2/SO3 etc.
Antioxidant species
pro-oxidant species
x 2
x 2
x 2
+
+

3.2.3 OZONE RESISTANCE MEASUREMENTS

3.2.3.1 PROCEDURE

The formulations used are set out in Tables 3.1 and 3.3. Compounding and curing were carried out as described in Section 2.2.3.2. The resistance to ozone of vulcanisates containing hindered phenolic sulphur compounds were compared to that of the control (without any protective additive) and IPPD and DLTP. Assessment of samples for ozone resistance was conducted at 25°C with ozone concentration of 25pphm at four extensions as outlined in Section 2.5.1.

3.2.3.2 RESULTS

Tables 3.11 - 3.14 give the induction time and time to failure for the CBS-sulphur vulcanisates while tables 3.15 - 3.18 give that for the peroxide vulcanisates. Figs. 3.10 and 3.11 show the relationship between the degree of cracking and time of ozone exposure at 20 and 30 per cent extensions for the CBS-sulphur vulcanisate and Figs. 3.12 and 3.13 for the peroxide vulcanisates.

In the CBS-sulphur vulcanisate, all the hindered phenolic sulphur compounds gave about the same degree of protection as shown by the induction and failure times. All samples had minimum time to failure at 20% extension. The IPPD sample had the best stability towards ozone cracking at all extensions. However, it showed an initial high rate of crack formation which then slowed down. The sulphur compounds gave marginally lower protection than DLTP.

The peroxide stock gave higher induction and failure times than the CBS-sulphur stock. All the sulphur compounds gave better protection against ozone cracking than the control and IPPD. The peroxide stocks had minimum failure time at 20% extension. A lower rate of crack propagation was evident in the peroxide than the CBS-sulphur stocks. DBDS gave the best stability at all extensions. In both the CBS-sulphur and peroxide stocks, BDBDS had the lowest rate of crack propagation up to the grading no. 6 at most extensions.

Above 20% extension there is slight increase in failure time for both the CBS-sulphur and peroxide stocks.

Table 3.11 Induction Time and Time to Failure at 5% Extension for CBS-Sulphur Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	1	22
BDBS	4	28
BDBDS	5	30
DBDT	3	29
DBDS	3	28
IPPD	1	45
DLTP	1	22.5

Table 3.12 Induction Time and Time to Failure at 10% Extension for CBS-Sulphur Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	1	20
BDBS	4	25
BDBDS	5	25
DBDT	2	27
DBDS	2	22.3
IPPD	1	40
DLTP	1	21

Table 3.13 Induction Time and Time to Failure at 20% Extension for CBS-Sulphur Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	1	18.5
BDBS	3	23.3
BDBDS	4	23.3
DBDT	2	24
DBDS	2	21
IPPD	1	35
DLTP	1	18.1

Table 3.14 Induction Time and Time to Failure at 30% Extension for CBS-Sulphur Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	1	31
BDBS	3	39
BDBDS	4	36
DBDT	2	52
DBDS	2	48.1
IPPD	1	50
DLTP	1	31

Table 3.15 Induction Time and Time to Failure at 5% Extension for Peroxide Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	10	142.9
BDBS	30	208.1
BDBDS	32	208.2
DBDT	38	165
DBDS	40	345
IPPD	8	165

Table 3.16 Induction Time and Time to Failure at 10% Extension for Peroxide Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	10	130
BDBS	30	205
BDBDS	35	200
DBDT	39	162
DBDS	40	336
IPPD	7	155

Table 3.17 Induction Time and Time to Failure at 20% Extension for Peroxide Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	10	121
BDBS	30	170
BDBDS	35	170
DBDT	42	156
DBDS	45	208
IPPD	8	150

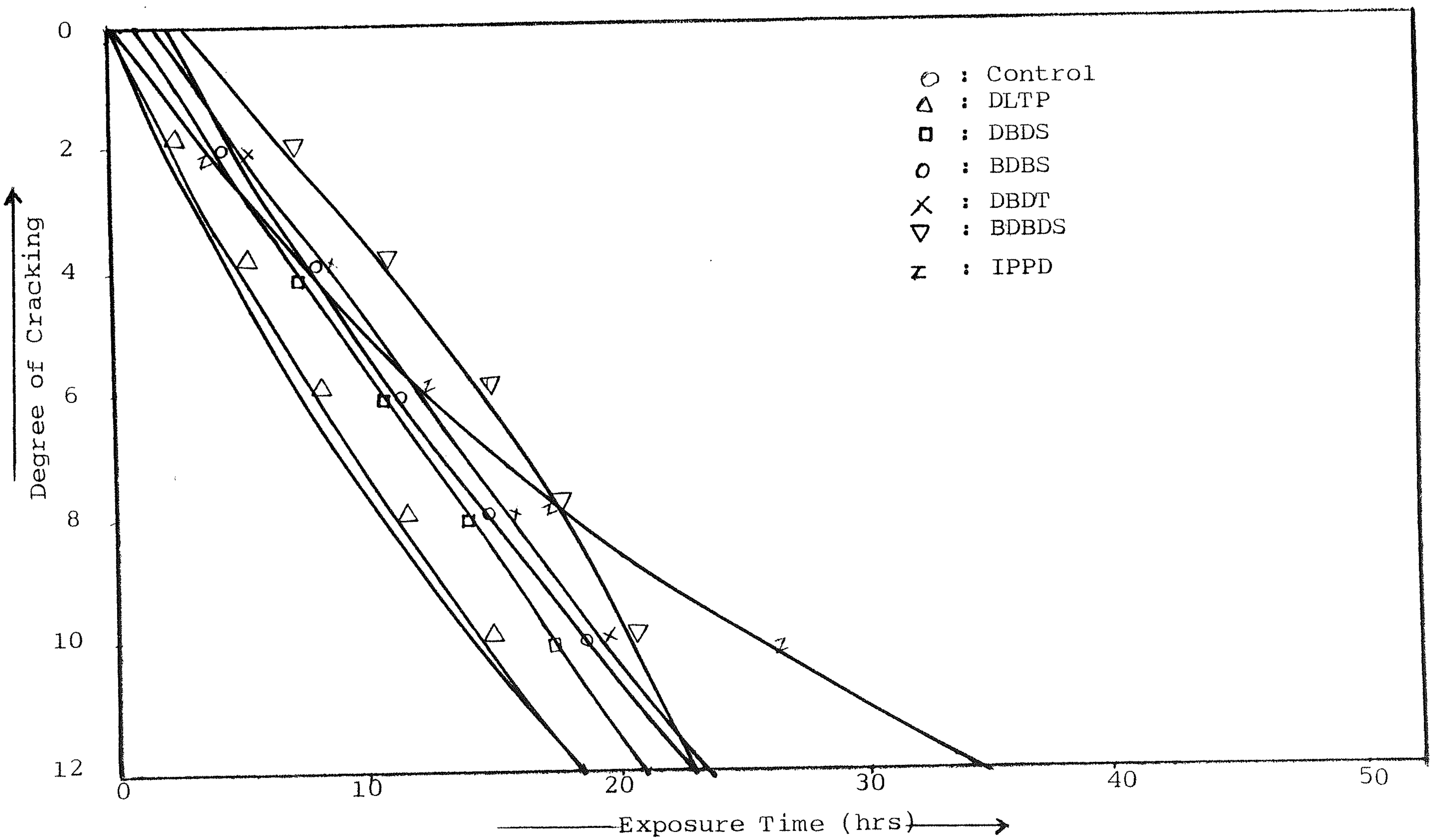


Fig. 3.10 : Relationship Between Exposure Time and Degree of Cracking in CBS-Sulphur Vulcanisates Containing Test Compounds at 20% Extension and 25^{o}C

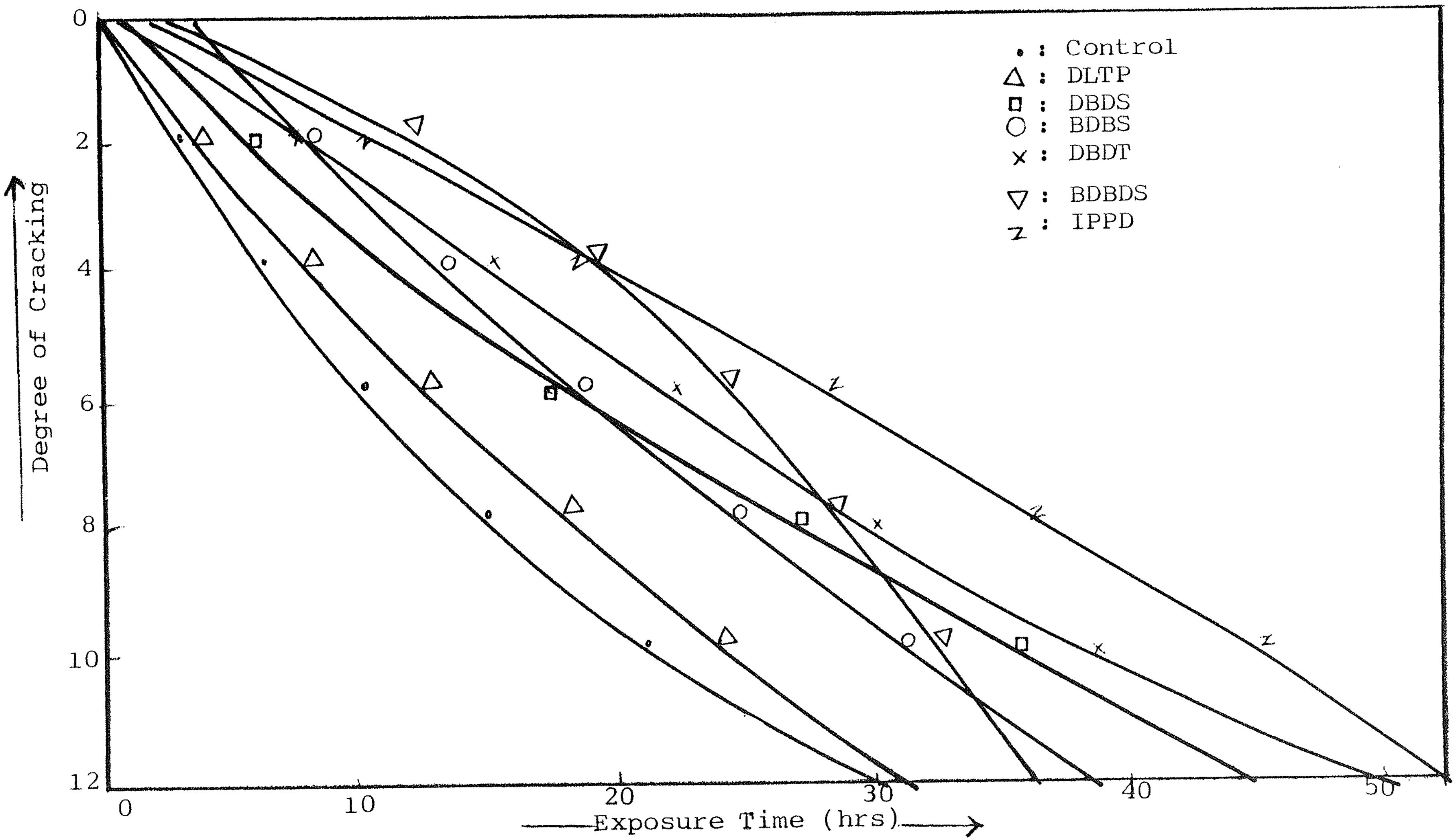


Fig. 3.11 : Relationship Between Exporsure Time and Degree of Cracking in CBS-Sulphur Vulcanisates Containing Test Compounds at 30% Extension and 25^{o}C

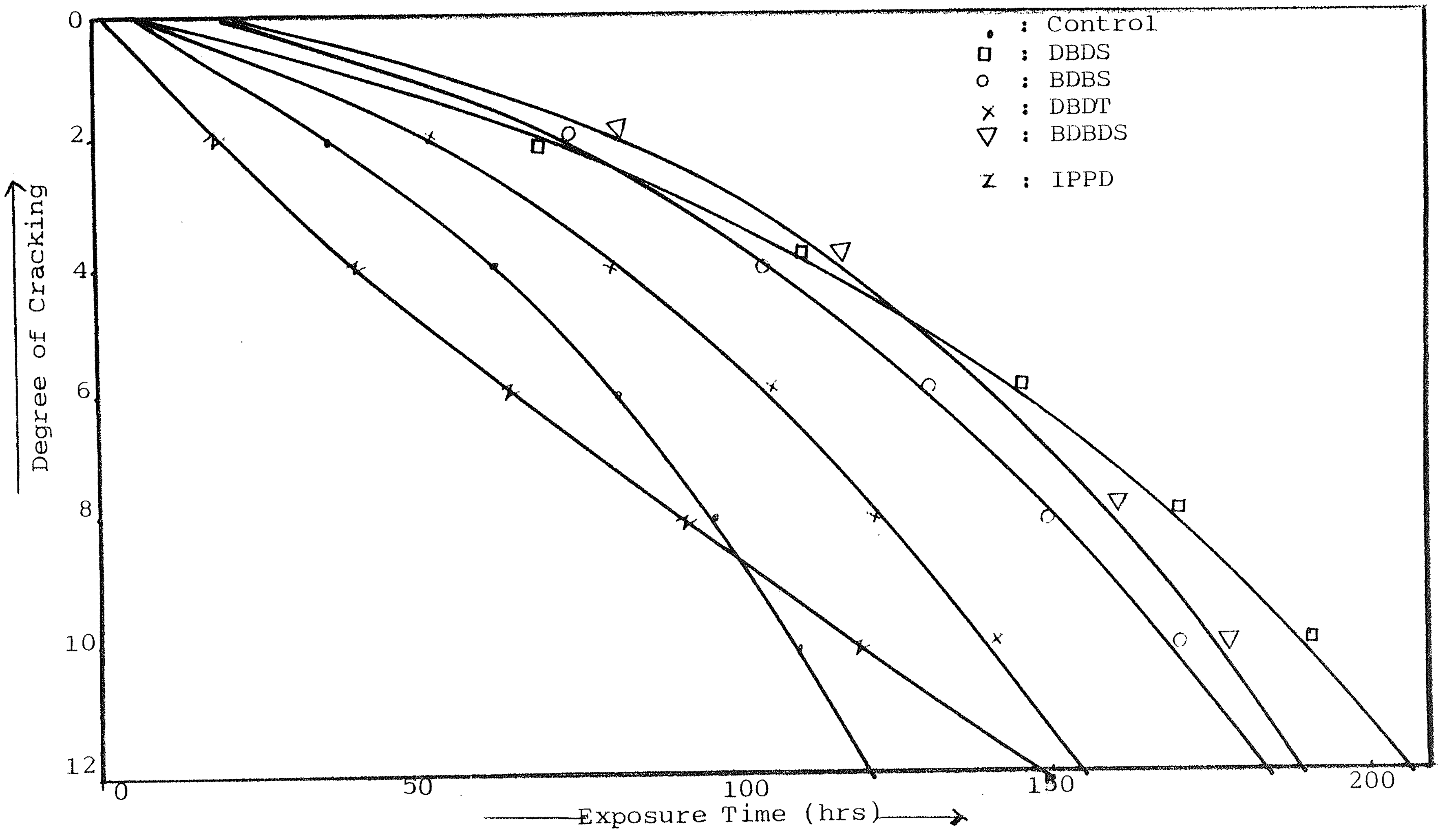


Fig. 3.12:Relationship between Exposure Time and Degree of Cracking in Peroxide Vulcanisates Containing Test Compounds at 20% Extension and 25°C

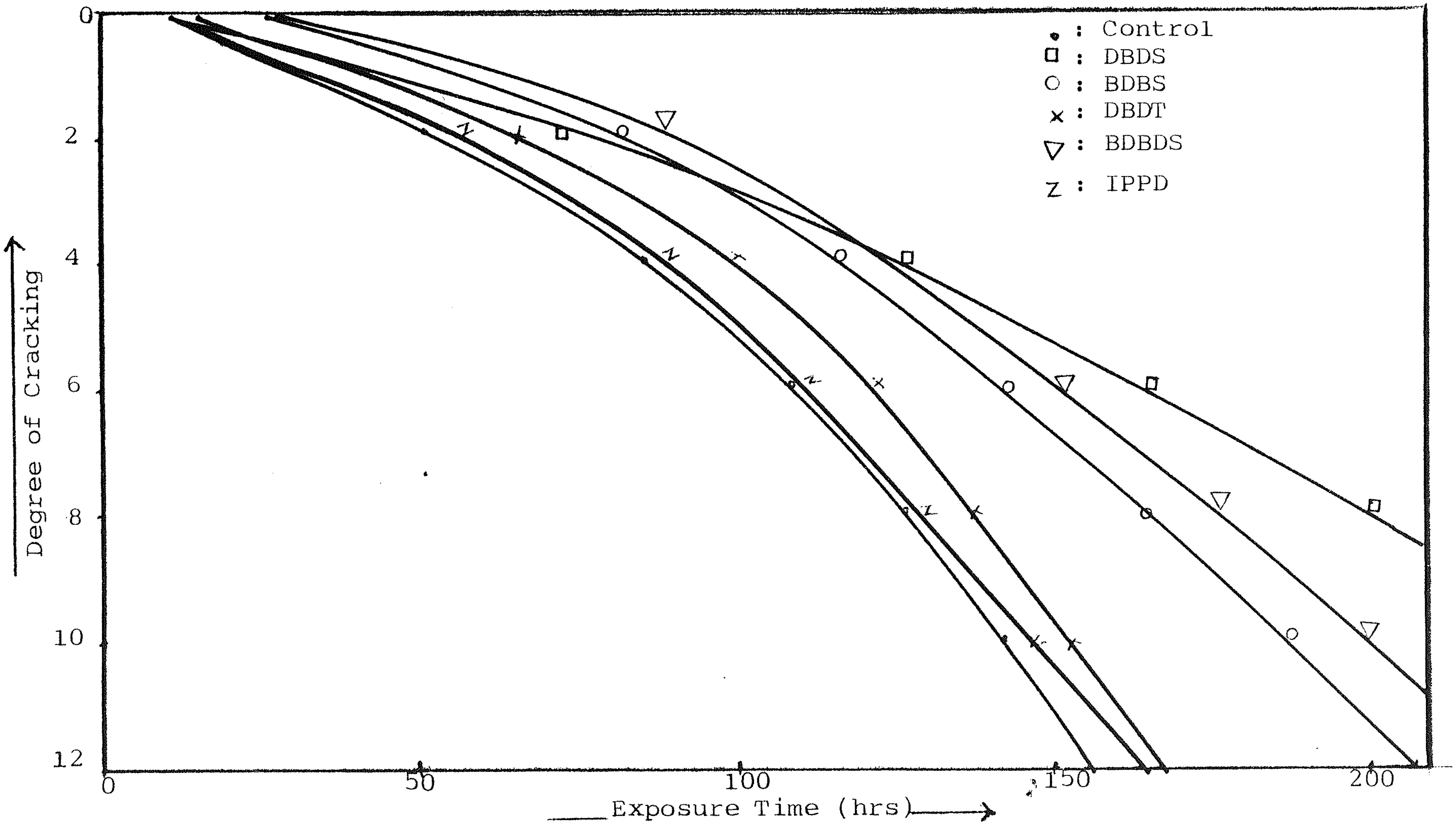


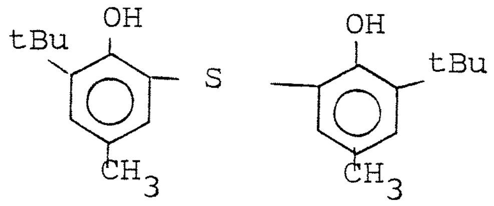
Fig. 3.13 : Relationship Between Exposure Time and Degree of Cracking in Peroxide Vulcanisates Containing Test Compounds at 30% Extension and 25° C

Table 3.18 Induction Time and Time to Failure at 30% Extension for Peroxide Vulcanisate

Test Compound	Induction Time (hr)	Time to Failure (hr)
Control	8	156
BDBS	25	210
BDBDS	28	220
DBDT	35	170
DBDS	37	360
IPPD	8	170

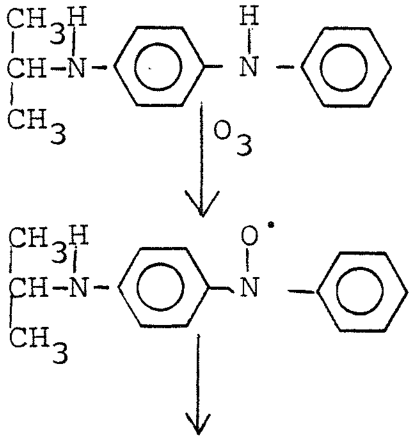
3.2.3.3 DISCUSSION

Ozone attack on rubber goods is a surface phenomenon, hence antiozonants are generally 'sacrificial' in their mode of action.[54, 127, 128] The better performance of IPPD in the CBS-sulphur vulcanisate over the hindered phenolic sulphur compounds is due to its high rate of reaction with ozone, 7×10^{-6} (litre $mol^{-1}s^{-1}$)[130]. The reactivity of the hindered phenolic sulphur compounds is probably very low when considering the reported reactivity of 0.5×10^{-6} (litre $mol^{-1}s^{-1}$)[131] for 2,2'thiobis(6-tert-butyl-4-methyl phenol).



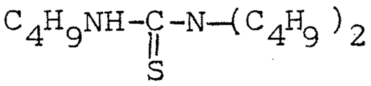
The NH groups of IPPD are the only ones attacked by ozone yielding nitroxyl radicals, aromatic nitrones, aliphatic nitrones and alkyl hydroxylamines (Scheme 3.5)[127,131].

Scheme 3.5



Ar-N=O Alk-N=O, $(CH_3)_2C=NOH$ and other products.

In general, the higher the rate constant of the reaction of antiozonants with ozone, the better the protection offered against ozone attack[130,131]. However, there is an exception to this rule, N-butyl-N-N'-dibutyl-thiourea with a lower rate constant



$$C_4H_9NH-\underset{\underset{S}{\|}}{C}-N-(C_4H_9)_2$$

2×10^{-6} (litre $mol^{-1}s^{-1}$)[130] than IPPD gave better protection to rubber during static ozone test. The reason being the tendency of this thiourea to accumulate on the rubber surface to a greater extent than other substances examined[132] and thus, more molecules are made available for reaction with ozone.

In both the CBS-sulphur and peroxide vulcanisates there was a critical strain at which the time to failure was minimal. Popov and Zaikov[133] found that the lowest durability and the greatest rate of crack propagation in the presence of ozone occur at small deformations termed 'critical' strain, ε_c, which for natural rubber under uniaxial stretching was 20% under constant deformation but 5% under constant load. The minimum time to failure was obtained in both CBS-sulphur and peroxide vulcanisates at 20% extension. However, above this extension, the test samples became more resistant toward ozone[37]. The reason advanced[133] was that as the applied strain on the vulcanisate is increased, two competing processes operate - first, is static fatigue which decreased the time to failure, and second, crystallisation which increased the strength of the vulcanisate in crack tip where maximum stress is set up, thereby raising the time to failure. This latter view may explain the physical process occurring during exposure of a strained vulcanisate to ozone, however, chemical processes are also important in the protective action of antiozonants.

3.2.4 FATIGUE RESISTANCE TEST

The dynamic conditions to which certain rubber articles are subjected have a profound, and in many instances, a decisive effect on their service life. This is because stress mechanically activates oxidative processes occurring during fatigue and in addition, the scission of the polymer network structure gives rise to alkyl- 'free' radicals, whose subsequent reactions, apart from accelerating autoxidation processes, leads to the restructuring of the rubber structure[63]. It is therefore essential that rubber articles employed in dynamic service conditions should be protected against fatigue. Generally, disubstituted aromatic amines are used, especially IPPD. However, a range of organo-sulphur compounds have come under scrutiny as a result of their autosynergistic role. Among this class of organic sulphur compounds are the hindered phenolic sulphur compounds which are being evaluated in the present study against a known commercial antifatigue agent - IPPD, and a known sulphur antioxidant, DLTP. This test is carried out with the aid of the Monsanto fatigue to failure tester. This machine provides a useful means of evaluating the resistance of a vulcanisate to repeated mechanical deformation and invariably the activity of the chemical compounds incorporated as antifatigue agents.

3.2.4.1 PROCEDURE

The formulation used are as in Tables 3.1 - 3.3. Compounding and preparation of vulcanisates are as described in Section 2.2.1 and 2.2.3.3. The fatigue resistance of the three types of vulcanisate was assessed as outlined in Section 2.6.1. In addition to normal compounding, test compounds were introduced by swelling.

Dumbell samples cut from the control of peroxide vulcanisate were hot acetone extracted for 60 hours under continuous stream of nitrogen to remove the breakdown products of the peroxide curing agent and then dried under vacuum at 25°C. The extracted samples were further extracted with cold benzene and dried to constant weight. The hindered phenolic sulphur compounds and IPPD were then swelled into the extracted dumbell-shaped samples.

One gram of each compound was introduced into 100g of extracted peroxide vulcanisate samples by swelling in dry benzene. 1g in 100ml dry benzene of each compound - BDBS, BDBDS, DBDT, DBDS and IPPD was prepared separately and extracted dumbell-shaped samples were placed in each of the five different solutions under a continuous stream of oxygen 'free' nitrogen for varying lengths of time to obtain 0.01g per gram rubber (i.e. 1g/100g rubber). It took about 2 hours for most of the compounds except DBDS which was 1.75 hours. The samples were then deswelled under vacuum at 25°C to constant weight and stored under vacuum before used for testing.

Samples were mounted on the Monsanto Fatigue-to-Failure Tester as described in Section 2.6.1 and the resistance of samples containing test compounds were compared to that of the control and IPPD at 60% extension.

Also a number of the dumbell-shaped samples from the different types of vulcanisate had a pin-hole introduced. A centre point in each sample was marked and a 0.3 mm mapping pin was used to introduce the pin-hole and the samples then fatigued.

3.2.4.2 RESULTS

Tables 3.19 - 3.21 show the fatigue lives based on the J.I.S. average. Table 3.22 shows the fatigue life of the peroxide vulcanisates in which the test compounds were swelled while Table 3.23 shows the improvement in fatigue life over the control expressed as percentage. In the CBS-sulphur vulcanisates the antifatigue activity of the hindered phenolic sulphur compounds are not comparable to the conventional antifatigue agent, IPPD, but are far better than DLTP and control. BDBS had the highest antifatigue activity among the organic sulphur compounds. The pattern shown is:

BDBS > DBDT > DBDS > BDBDS

The difference between the organic sulphur compounds and IPPD is as striking in the TMTD-sulphur cure system as in the CBS-sulphur. IPPD was always better than these sulphur compounds. The pattern of activity is similar to that obtained in the CBS-sulphur except that DBDT and DBDS have interchanged positions.

All the test compounds including IPPD showed remarkable activity in the peroxide cured system and the same pattern of activity as in CBS-sulphur cure being maintained. The peroxide vulcanisate without any additive as its counterparts in the CBS-sulphur and TMTD, had better fatigue life when cured to the same crosslink density.

In the swelled peroxide vulcanisates, a similar trend to that in the compounded peroxide vulcanisates was still evident.

The fatigue lives in the three types of cure system were drastically reduced after the introduction of a pin-hole. The peroxide vulcanisates had the poorest response followed by TMTD-sulphurless and then CBS-sulphur vulcanisates. With the pin-hole, IPPD stocks were only marginally better than the hindered phenolic sulphur compounds.

Table 3.19 Fatigue Life of CBS-Sulphur Vulcanisate Containing Test Compounds at 60% Extension

Test Compound	Fatigue Life (hr)	Fatigue Life of Sample with pin-hole (hr)
Control	23.5	16.2
BDBS	105.5	37.4
BDBDS	69.0	29.2
DBDT	98.8	34.1
DBDS	93.2	34.3
IPPD	232.1	40.8
DLTP	33.1	6.04
MDBP	33.7	12.1
MDPP	56.4	18.8

Table 3.20 Fatigue Life of TMTD-Sulphurless Vulcanisate Containing Test Compounds at 60% Extension

Test Compound	Fatigue Life (hr)	Fatigue Life of Sample with pin-hole (hr)
Control	18.7	13.5
BDBS	61.3	23.6
BDBDS	45.4	20.1
DBDT	51.0	22.4
DBDS	52.0	23.9
IPPD	112.2	26.5

Table 3.21 Fatigue Life of Peroxide Vulcanisate Containing Test Compounds at 60% Extension

Test Compound	Fatigue Life (hr)	Fatigue Life of Sample with pin-hole (hr)
Control	39.5	12.4
BDBS	280.6	26.5
DBDT	199.8	26.3
DBDS	154.1	32.1
IPPD	384.8	32.2

Table 3.22 Fatigue Life of Swelled Peroxide Vulcanisate at 60% Extension

Test Compound	Fatigue Life (hr)
Control	36.7
BDBS	161.2
BDBDS	96.4
DBDT	126.1
DBDS	104.9
IPPD	281.3

Table 3.23 Improvement in Fatigue Life Expressed as Per Cent of Control in the Cure Systems

Test Compound	-CBS Sulphur	-TMTD Sulphurless	Peroxide	Swelled Peroxide
Control	-	-	-	-
BDBS	349	228	372	208
BDBDS	194	143	151	84
DBDT	320	173	236	141
DBDS	297	178	159	101
IPPD	888	500	548	438
DLTP	41	-		
MDPT		-		
MDPP				

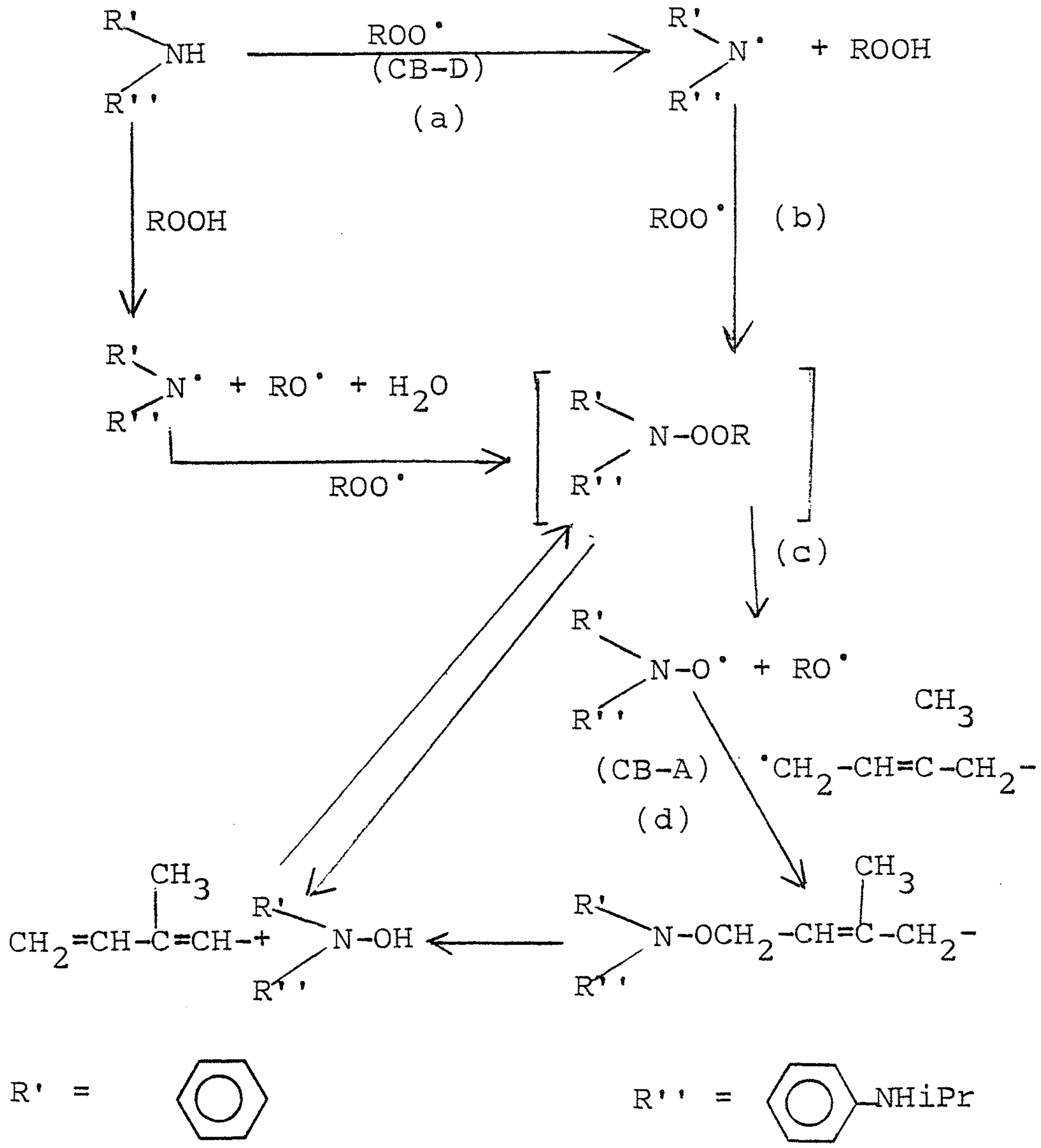
3.2.4.3 DISCUSSION

The different fatigue properties of the CBS-sulphur and TMTD-sulphurless vulcanisates is expected because of the difference in the composition of their network structure. The CBS-sulphur vulcanisate has a network structure of mainly polysulphide crosslinks and the higher fatigue life is attributed to the ability of the polysulphide crosslinks to release internal stresses as a result of crosslink mobility[134-5]. In contrast, the mainly monosulphidic crosslinks in TMTD-sulphurless vulcanisate are less likely to exchange or rearrange to relieve the highly localised stresses associated with the growth of flaws. Similarly, in dehydrocrosslinked vulcanisates (mainly C-C crosslinks), the application of repeated deformation should result in an uneven stress distribution with higher local stresses leading to chain rupture, macro-alkyl radical formation and alteration of the chemical structure which eventually lead to failure[135] at an early stage compared to the sulphurated vulcanisates. However, the result obtained in this assessment is the reverse of that expected. The main reason for this improved fatigue resistance is that the peroxide stock was cured to the same crosslink density as the CBS-sulphur vulcanisate for the purpose of comparison since modulus has been identified as one of the variables affecting fatigue life[107] of a vulcanisate. In addition, IPPD and BDBDS have a depressing effect on the final torque level of a peroxide vulcanisate (see Fig. 3.3), hence all other stocks had to be compared to this level. At the torque level of comparison - 3.3m-kg - the peroxide vulcanisate had improved hot tear strength and elasticity compared to that cured to the maximum torque level of 4.2-4.8m-kg normally attained by the peroxide cure. The increased elastic nature of the peroxide vulcanisate and reduction of main chain entanglement due to absence of main chain sulphur-modification facilitated the ease with which the rubber molecules re-orientate and thereby decrease the molecular stresses during repeated deformation with a resultant increase in fatigue life.

It is known that not all antioxidants are antifatigue agents. DLTP has only marginal antifatigue activity in a CBS-sulphur cure when compared to IPPD or the hindered phenolic sulphur compound. The distinguishing feature is that DLTP is not a CB-D antioxidant. There is a consensus of opinion that the oxidation products of the sulphides[25,82,117,122,136-7] are the active agents in hydroperoxide decomposition and during fatigue process hydroperoxides are eventually formed but macroalkyl radicals are also present and they further accelerate the rate of oxidation. The deactivation of macroalkyl radicals is one of the important functions of an antifatigue agent[63,138-39], hence any antioxidant which only decomposes hydroperoxides will be ineffective as an antifatigue agent since one of the root causes of the oxidative process (macro-alkyl radical formation) during fatigue is still operative. This is the main reason for the marginal antifatigue activity of DLTP compared to the hindered phenolic sulphur compounds and IPPD.

The diarylamines, for example, IPPD, are known to owe their effective antifatigue activity to their conversion to the corresponding nitroxyl radicals (alkyl radical scavengers) and hydroxylamines which scavenge alkylperoxy radicals with the eventual regeneration of the nitroxyl radicals. This continuous regeneration of the nitroxyl radicals in IPPD in a cyclical mechanism involving the hydroxylamine has been shown to be responsible for IPPD effectiveness as an antifatigue agent[139] (Scheme 3.6).

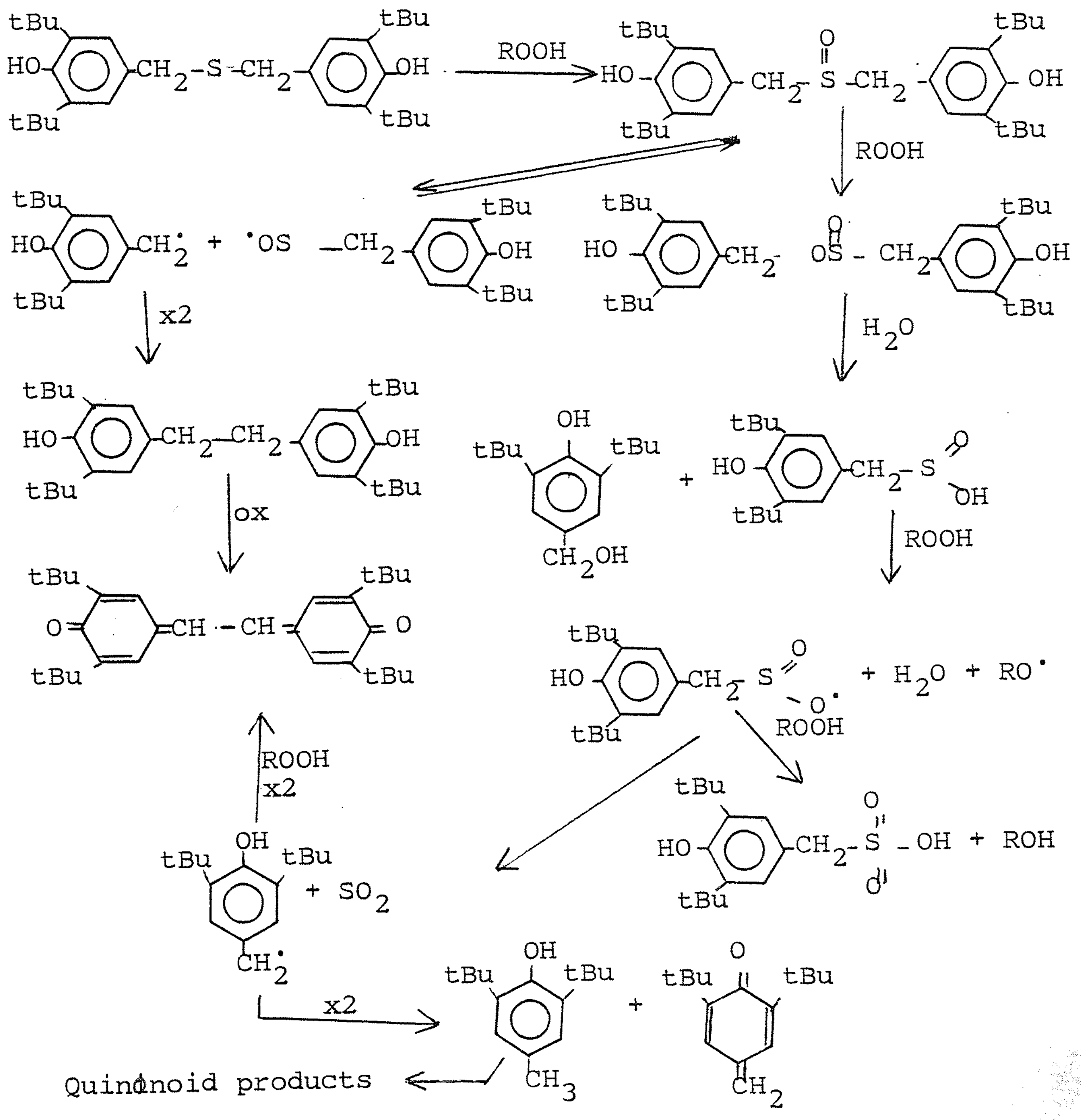
Scheme 3.6



The antifatigue activity of these hindered phenolic sulphur compounds may be viewed from three superimposed processes;

namely, the trapping of macro-alkyl radicals, the scavenging of alkylperoxy radicals and hydroperoxide decomposition. This approach stems from the work by Scott and co-workers[120,126] on the autosynergistic behaviour of sulphur containing phenols. Reaction Scheme 3.7 has been proposed to explain the reaction pathway of hindered phenolic sulphur compounds, for example, BDBS

Scheme 3.7



The oxidation products of the phenolic sulphur compounds (Scheme 3.7) - quinonoid products and sulphur-oxy acids - contribute to the antifatigue activity of the parent sulphides. The quinonoid products - stilbenequinone[78,140] and benzoquinone[141] have been shown to have high antifatigue activity as a result of their ability to trap alkyl radicals. The ethylene bisphenol is able to deactivate alkylperoxy radicals in a chain-breaking (donor) mechanism. Finally, the protonic acids will be involved in the catalytic decomposition of hydroperoxide to non-radical products.

Generally, it would be expected from the sum total of the effects outlined that the hindered phenolic sulphur compounds should exhibit a far greater antifatigue activity than IPPD but the results do not support this. The probable explanation must be that the effective components of the phenolic sulphur compounds occur at a much later stage of oxidation/decomposition whereas, the first oxidation product of IPPD is the nitroxyl radical which effectively scavenges the alkyl radicals during fatiguing and its continuous regeneration in a cyclical mechanism (Scheme 3.6) confers higher antifatigue activity to IPPD.

The BDBDS surprisingly had the lowest antifatigue activity among the hindered phenolic sulphur compounds assessed. The reason is that during fatigue process, the thiosulphinate produced will largely disproportionate yielding products which are pro-oxidant (Scheme 3.4, reaction b) and further homolytic processes occur. However, antifatigue species are produced such as stilbenequinone and benzoquinone and the sulphur-oxy acids which decompose hydroperoxide, all act together to produce the observed antifatigue activity of BDBDS.

As discussed earlier, the better fatigue activity of the peroxide stocks over the CBS-sulphur apart from the additives, must have been aided further by the level of cure employed which brought about noticeable improvement in the physical properties of the vulcanisates.

The introduction of a pin-hole into the test samples resulted in a significant reduction in the fatigue lives of the vulcanisates. This pinhole may be thought of as an enlargement of the first bond scission but more importantly, it focussed on the rate of crack growth rather than the induction time to crack growth and in turn reflects the ability of the additives to deactivate any resultant alkyl radicals. The differences in the fatigue lives after the introduction of pinholes reflected the ability of the additives to reduce the rate of crack growth. IPPD was still the best because of the involvement of nitroxyl radicals in a cyclical regeneration (Scheme 3.6). However, the hindered phenolic sulphur compounds were better than the hindered phenolic compounds in the CBS-sulphur cure system after the introduction of the pinhole.

The difference between these two groups of almost similar compounds probably reflects a synergistic role being played by the sulphur moiety in the regeneration[118] of quininoid products which are effective alkyl radical traps[86, 140]. The very poor response of DLTP is because none of its transformation products are effective CB-A antioxidants.

3.3 CONCLUSION

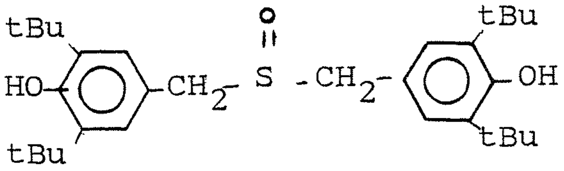
The hindered phenolic sulphur compounds act as antifatigue agents through their transformation products which function by CB-D, CB-A and PD-C mechanisms. CB-D and CB-A mechanisms are important for antifatigue activity but PD-C species enhance the activities of the CB antioxidants.

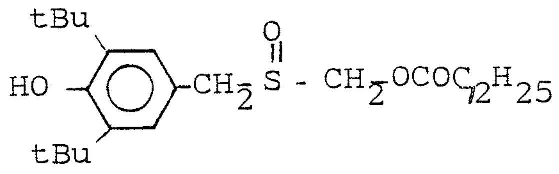
CHAPTER FOUR

4. STUDIES OF SOME OXIDATION PRODUCTS OF TWO HINDERED PHENOLIC SULPHUR COMPOUNDS

As was discussed in Chapter 3, there is agreement as to the antioxidant role of certain organic sulphur compounds and the evidence suggests that the sulphides themselves are not the effective antioxidants but rather their oxidation products formed in the reaction of the sulphides with hydroperoxides[25, 82,117,122,136-7]. The hindered phenolic sulphur compounds under review have shown varying degrees of antifatigue and antiozonant activities (Chapter 3). The tendency hitherto has been to relate the antifatigue activity of these organosulphur compounds to their oxidation products, particularly to sulphenic and sulphinic acids which are known to be readily converted to the corresponding sulphur-centred radicals by reaction with hydroperoxides[142]. These sulphur-centred radicals are said to be relatively stable and can effectively scavenge alkyl radicals which are the main initiating species of autoxidation during fatigue process. Hence sulphoxides of some of the hindered phenolic sulphur compounds are examined both for antifatigue and autoxidant activities.

The two sulphoxides to be examined are:

	Name	Code
	Bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulphoxide	BDBSO

	Name	Code
	3,5-Di-tert-butyl-4-hydroxybenzyl-sulphinyl-dodecyl-glycolate	DBSDG

4.1 ASSESSMENT OF SULPHOXIDE IN FATIGUE AND THERMAL OXIDATIVE AGEING TESTS

4.1.1 PROCEDURE

Vulcanisates were prepared as outlined in Section 2.2.1. The cure characteristics were obtained from the Monsanto Oscillating Disc Rheometer as described in Section 2.2.2. Samples for fatigue, stress relaxation and oxygen absorption tests were prepared according to the procedures described in Section 2.6.1, 2.4.1 and 2.3.1 respectively. The formulations used are set out in Table 4.1.

4.1.2 RESULTS

Fig. 4.1 shows the Monsanto Rheograph and Table 4.2, the cure characteristics. The sulphoxides have no significant effect on the induction time and the rate of vulcanisation (Table 4.2).

The fatigue results are shown in Table 4.3. The sulphoxides gave lower fatigue lives than IPPD and the parent sulphides but about the same as MDPP (Table 3.19).

The stress relaxation curves are shown in Fig. 4.2, and Table 4.4 shows the time to 50% stress decay. The sulphoxides gave a lower rate of stress decay than the parent sulphides (Fig. 3.4 and Table 3.7) but not better than IPPD.

The oxygen absorption curves are shown in Fig. 4.3 and the induction time and time to 1% oxygen absorption are outlined in Table 4.5. These sulphoxides were better than the parent compounds but not IPPD.

Table 4.1 CBS-Sulphur Formulations Containing Sulphoxides and IPPD

Compounding Ingredients	Control	BDBSO	DBSDG	IPPD
NR (SMR10)	100	100	100	100
Zinc Oxide	5	5	5	5
Stearic acid	3	3	3	3
CBS	0.6	0.6	0.6	0.6
BDBSO	-	0.97	-	-
DBSDG	-	-	0.98	-
IPPD	-	-	-	0.50
Sulphur	2.5	2.5	2.5	2.5

Table 4.2 Cure Parameters of CBS-Sulphur System Containing Sulphoxides at 140°C

Test Compound	Concentration g/100g rubber	R_{max} x0.06m-kg	kx10^{-1} min	t_i(min)	Cure Time (min)
Control	-	58	2.8	10	35
BDBSO	0.97 (1.99x10^{-3} mole)	57	2.3	11	35
DBSDG	0.98 "	57	2.3	11	35
IPPD	0.50 "	60	2.3	9.5	35

Table 4.3 Fatigue Life of CBS-Sulphur Vulcanisate Containing Sulphoxide at 60% Extension

Test Compound	Fatigue Life (hrs)	Fatigue Life of Sample with pin-hole
Control	23.5	16.2
BDBSO	48.1	19.5
DBSDG	35.7	18.2
IPPD	232.1	40.8

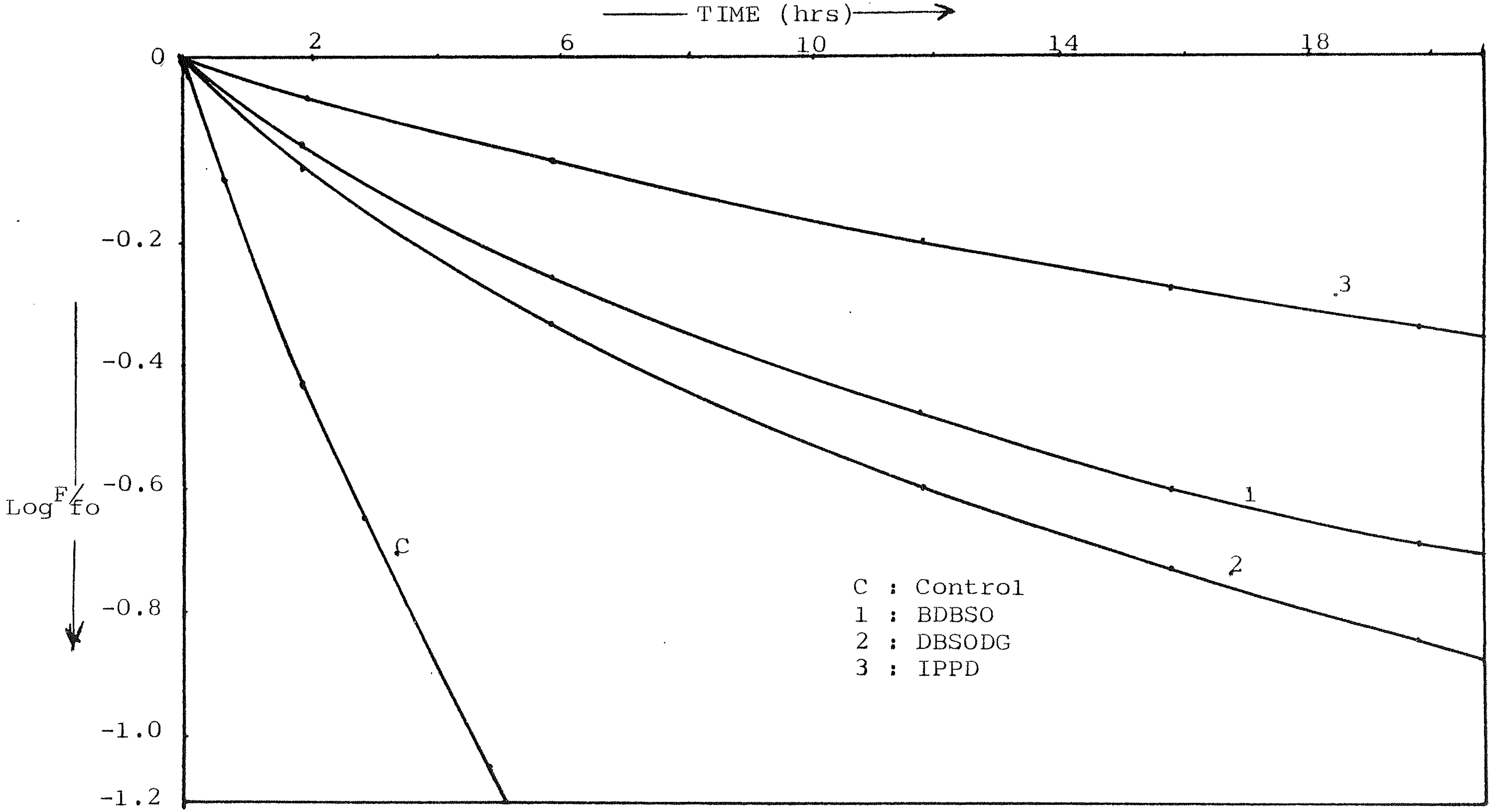


Fig. 4.2 : Continuous Stress Relaxation of CBS-Sulphur Vulcanisates Containing Sulphoxides and IPPD at 100°C and 60% Extension

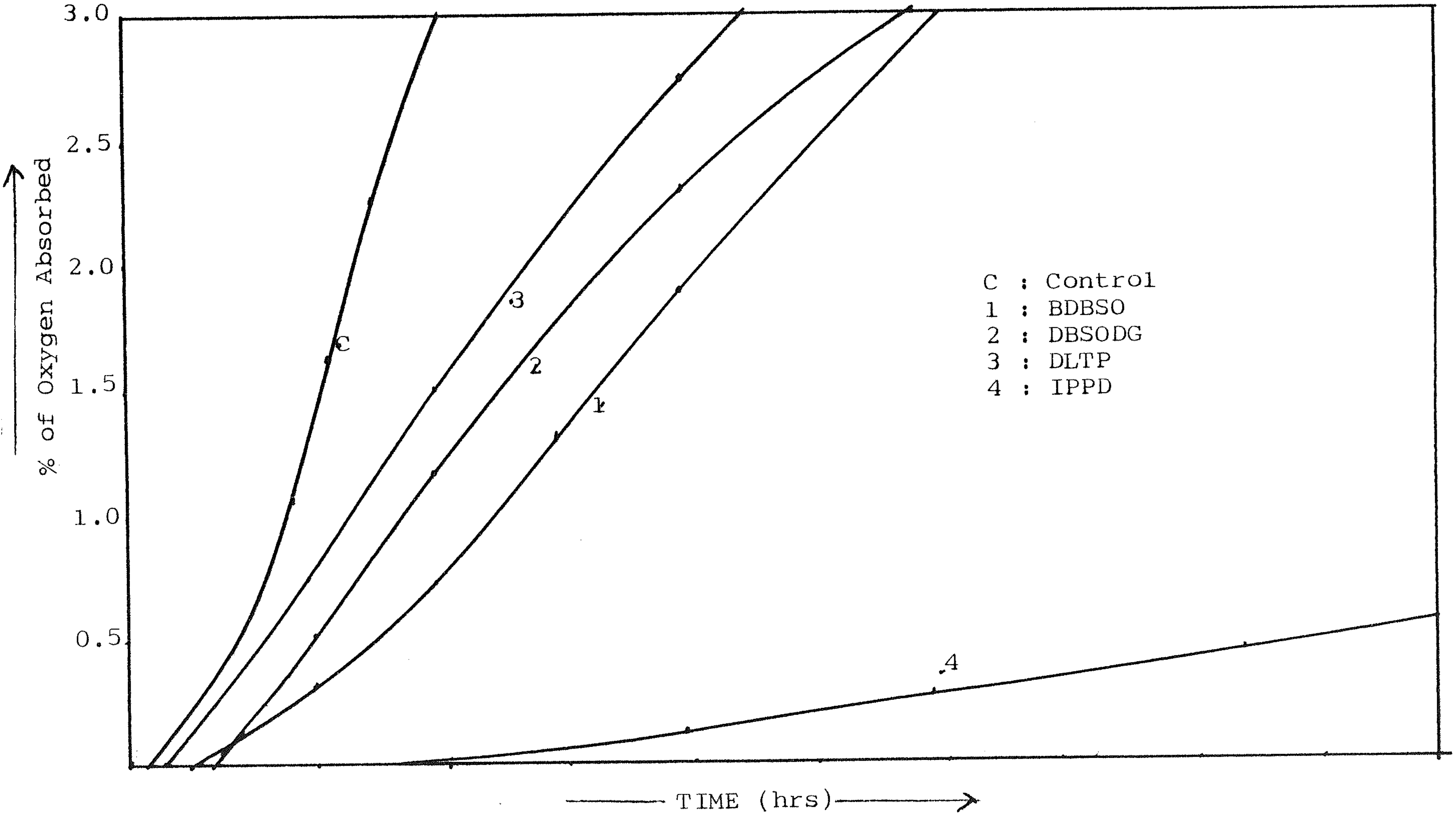


Fig. 4.3 : Amount of Oxygen Absorbed by CBS-Sulphur Vulcanisates Containing Sulphoxides, DLTP and IPPD at 100°C

Table 4.4 Time to 50% Stress Decay (F_{50}) of CBS-Sulphur Vulcanisate Containing Sulphoxide at 60% Extension and 100°C

Test Compound	Time to 50% Stress Decay (hrs)
Control	1
BDBSO	4.75
DBSDG	3.75
IPPD	11.5

Table 4.5 Induction Time and Time to 1% Oxygen Absorption of CBS-Sulphur Vulcanisate Containing Sulphoxide at 100°C

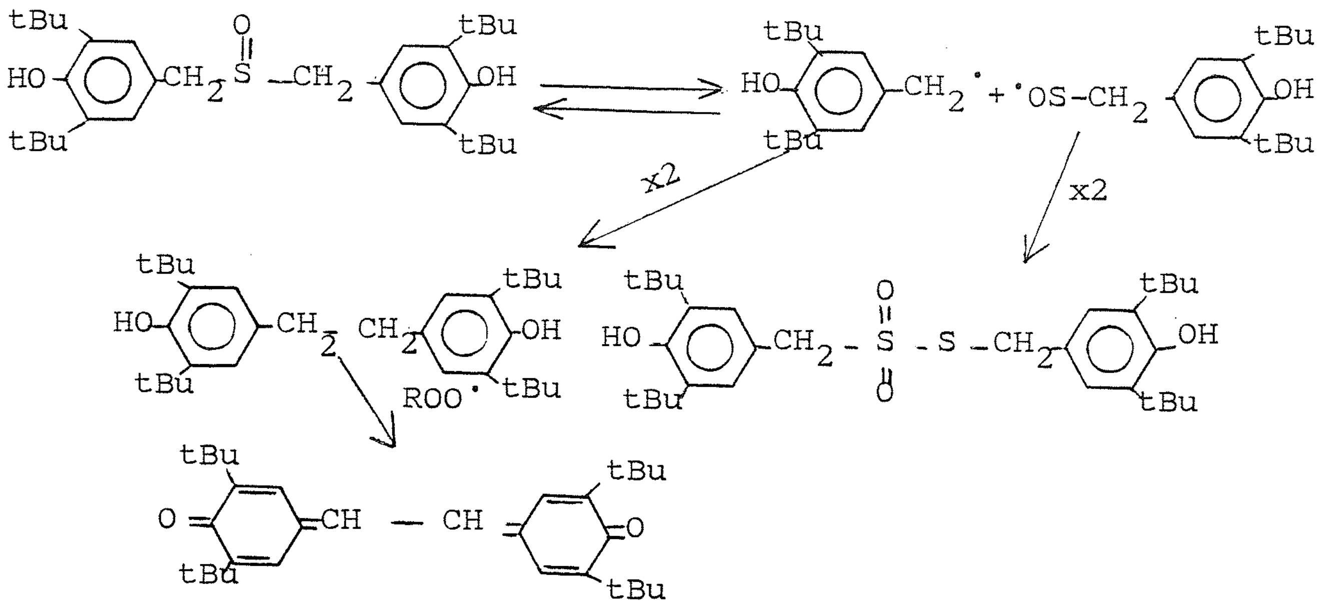
Test Compound	Induction Time (hrs)	Time to 1% Oxygen Absorbed (hrs)
Control	1	5
BDBSO	2	25
DBSDG	2	22
IPPD	9	44

4.1.3 DISCUSSION

The improved stress relaxation and oxygen absorption behaviour of the sulphoxides over the parent sulphides was expected and it tends to reinforce the established view that the oxidation products of the sulphides are the effective antioxidants. The decrease in the rates of both stress decay and oxygen absorption is due to the higher rate at which the sulphoxides could interact with hydroperoxides to produce the effective protonic acids (Schemes 3.2, 3.3). This view seems logical from the known behaviour of this class of hindered phenolic sulphur compounds during oxidation[27, 120]. In addition to the stabilization given by the subsequent protonic acids, certain phenolic transformation products namely, hydroquinone, benzoquinone and stilbenequinone (see Chapter 5), contribute to the overall picture of stabilisation. Evidence for this is that at the end of vulcanisation, colour formation was observed in the vulcanisates and this has been shown to be related to phenolic oxidation products[6].

The reduced fatigue lives of the sulphoxides when compared to the parent sulphides is surprising after considering the likely role of sulphenic and sulphinic acids in alkyl and alkylperoxy radicals trapping[142]. The observation of colour formation must have been brought about by the reactions in Scheme 4.1. Hence during fatigue, the only effective substance was stilbenequinone while the thiosulphenate is normally regarded as an inactive product making no contribution to the fatigue activity. As observed in Chapter 5, the phenolic transformation products in themselves in a peroxide vulcanisate gave lower fatigue lives than the hindered phenolic sulphur compounds.

Scheme 4.1



4.2 EFFECT OF CUMENE HYDROPEROXIDE TREATMENT OF CBS-SULPHUR VULCANISATES CONTAINING TEST COMPOUNDS ON FATIGUE LIFE

It is generally believed that during oxidative ageing of rubber vulcanisates hydroperoxides are formed. Similarly, during fatiguing, hydroperoxides are eventually formed, though to a lower extent. However, in sulphur cured rubber vulcanisates, oxidised sulphur crosslinks will result from the reaction of the various mono-, di- and polysulphide groups with hydroperoxides[14] and these are expected to enhance the service life of the vulcanisates. In this investigation, an external source of hydroperoxide is being introduced to generate the oxidised sulphur products within the rubber vulcanisate and thus avoid the transformation of the oxidised sulphur compounds which occurred during vulcanisation (see Section 4.1).

4.2.1 PROCEDURE

Compounds were prepared as described in Section 2.2.1 using the formulations in Table 3.1. Fatigue samples were obtained as outlined in Section 2.6.1. Eight dumbell-shaped samples from each compound were then treated with purified cumene hydroperoxide (Section 2.7a) for varying lengths of time and different concentrations as follows:

Treatment A: Using 100% CHP for 30 and 45 minutes.
Treatment B: Using two concentrations of CHP in 50 ml chloroform. (i) 1.99 x 10^{-3} mole and
(ii) 3.98 x 10^{-3} mole for two hours.

After each treatment, the samples were dried under vacuum at 25°C and tested for fatigue resistance using the Monsanto fatigue-to-failure tester (Section 2.6).

4.2.2 RESULTS

The fatigue lives of the different treatments are shown in Table 4.6 and the fatigue lives expressed as per cent of the untreated vulcanisates are given in Table 4.7. The control and disulphide-BDBDS showed improvements in the four different treatments. IPPD showed marginal improvement in the 100% CHP treatment both at 0.5 and 0.75 of an hour. BDBS, DBDT and DBDS showed no improvement. Apart from the control, the other samples had lower fatigue lives in chloroform solutions of CHP.

Table 4.6 Fatigue Lives of CBS-Sulphur Vulcanisates Containing Test Compounds Treated with CHP

Test Compound	100% CHP		$1.99x10^{-3}$ mole	$3.98x10^{-3}$ mole
	0.5 hr	0.75	2 hr	2 hr
Control	28.3	32.0	30.4	33.1
BDBS	70.9	60.4	87.5	91.1
BDBDS	95.6	102.2	80.8	82.8
DBDT	86.7	70.2	82.5	86.8
DBDS	89.5	62.6	73.6	86.2
IPPD	280	235	117.9	159.7

Table 4.7 Fatigue Lives of CHP-Treated CBS-Sulphur Vulcanisates Expressed as Per Cent change of Corresponding Untreated Vulcanisate

Test Compound	100% CHP		$1.99x10^{-3}$ mole	$3.98x10^{-3}$ mole
	0.5 hr	0.75	2 hr	2 hr
Control	20.5	36.3	29.5	40.9
BDBS	-32.8	-42.8	-17.0	-13.7
BDBDS	38.6	48.1	17.0	19.9
DBDT	-12.2	-29.00	-16.5	-12.1
DBDS	-4.0	-32.8	-21.0	-7.5
IPPD	20.6	1.3	-49.2	-31.2

4.2.3 DISCUSSION

In the undiluted CHP, there was mixed response due to the high concentration of hydroperoxide used. The improvement in fatigue life obtained with the control must have been due to the extensive oxidation of the extranetwork materials, excess sulphur, cyclic sulphides and sulphur crosslinks which limits the pro-oxidant stage[25, 121] normally associated with these groups of sulphur materials[115].

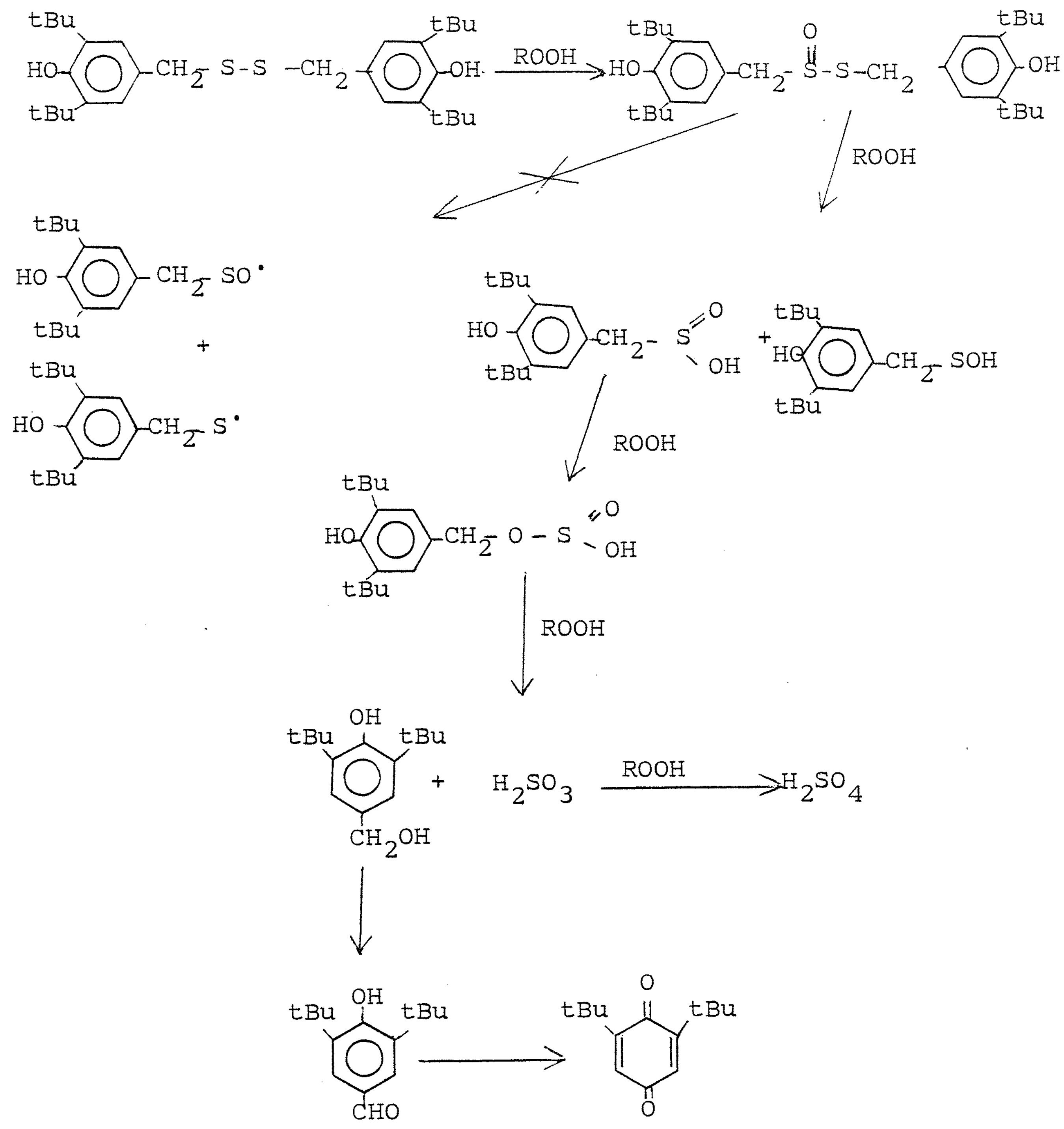
The improvement obtained in the diluted CHP can be ascribed to the physical leaching out of excess sulphur by chloroform as well as the oxidation of cyclic sulphides, extra-network materials and the sulphur crosslinks[143]. The improvement lends support to the pro-oxidant nature of excess sulphur and cyclic sulphides[144] in a CBS-sulphur vulcanisate.

BDBS, DBDT and DBDS all gave reduced fatigue lives compared to their respective untreated samples. In the undiluted CHP, the concentration of the hydroperoxide seems to be in excess of what the different additives can effectively decompose, hence the reduced fatigue lives. The lower concentrations of CHP also gave reduced fatigue lives due to physical leaching out of part of the parent sulphides and their oxidised forms by chloroform. Evidence for this, is the light yellow colouration of the chloroform during the swelling process.

IPPD gave a slight improvement in the undiluted CHP, probably as a result of the nitroxyl radicals which are formed prior to the fatiguing process. This is in addition to the oxidation of the excess sulphur and extra-network materials. These nitroxyl radicals are known[139] to decrease the rate of crack growth through their ability to deactivate alkyl radicals which are formed during fatiguing. In the dilute CHP, there was reduced fatigue life and the reason is as discussed earlier in similar treatment.

BDBDS alone (apart from the Control) gave improved fatigue lives in all treatments used. This is particularly striking in view of the mild response originally obtained with this compound (Chapter 3, Table 3.19). The mild response then was explained on the basis of Scheme 3.4 brought about by the high sulphide/hydroperoxide molar ratio which is inadequate to convert BDBDS into its active antioxidant species. However, with large excess of hydroperoxide, BDBDS will be oxidised to the sulphonic acid, then H_2SO_3, benzyl alcohol and eventually H_2SO_4 (Scheme 4.2). The benzyl alcohol can be oxidised further to give quininoid products which are known to have antifatigue activity (Chapter 5).

Scheme 4.2


tBu
HO
CH2- S-S -CH2
OH
ROOH
O
S-S-CH2
tBu
HO
CH2- SO•
+
CH2- S•
S=O
OH
SOH
O - S
H2SO3
H2SO4
CH2OH
CHO
O

4.3 EFFECT OF PREPROCESSING ON THE ANTIFATIGUE AND ANTIOXIDANT ACTIVITIES OF BDBS AND BDBDS

It is believed that during fabrication and service, stabilisers in polymers are transformed into antioxidant-active species. The preprocessing operation may be employed to generate these effective substances within the polymer prior to fabrication so as to enhance their activity. However, preprocessing has also been shown to slowly bind certain phenolic[145] and phenolic sulphur compounds[146-151] to polymer backbone under oxidation condition with improvement in their antioxidant effectiveness. During this process other transformation products are also formed which contribute to the overall antioxidant effectiveness.

In this investigation, the emphasis is not on binding of sulphur compounds to the polymer backbone during the mechanical shearing process, although it has been reported that this occurs to some extent[152] but rather on their performance in more traditional tests.

4.3.1 PROCEDURE

A number of preprocessing conditions were utilised and are outlined as follows:

a) Open Milling (OM)

100g of extracted natural rubber (NR) - SMR10 was first milled with the hindered phenolic sulphur compounds (Table 4.8) on a water-cooled laboratory two-roll mill with a frictional ratio of 1:1. A constant nip size was maintained for all subsequent milling operations. Four stocks were prepared from each of the test compounds on time basis of 2, 5, 10 and 15 minutes. After these initial preprocessing times, each stock was then compounded normally for eight minutes using the remaining compounding ingredients for a conventional CBS-sulphur cure system (Table 4.8).

b) Closed Torque Rheometer Processing (CT)

30g extracted SMR10 with equimolar concentration of the test compounds were processed using the proto-type RAPRA torque rheometer[153]. The rheometer has a small mixing chamber with mixing screws contra-rotating at different speeds[154]. All processings were carried out using the high speed which corresponds to 60 rev./min. The chamber temperature was set at 100°C. Four stocks were prepared for each of the test compounds as prepared in (a) above. Each stock was then compounded normally on a two-roll mill using the typical formulation in Table 4.9.

c) Closed Torque Rheometer Processing with Addition of 0.1ml TBH (CTP_1)

Procedure similar to (b) above with the exception of the presence of 0.1ml TBH.

d) Closed Torque Rheometer Processing with Addition of 0.5ml TBH (CTP_2)

Similar procedure as in (b) above with the addition of 0.5ml TBH.

Each of the compounded stocks in pretreatment a, b, c and d were vulcanised as outlined in Section 2.2.3.2. The cure characteristics were obtained from the Monsanto Oscillating Disc Rheometer (Section 2.2.2). Samples for fatigue and stress relaxation tests were prepared as described in Section 2.6.1 and 2.4.1 respectively.

Table 4.8 Typical Formulation for Open Milling

Premilled stock (NR + Additive (1.992×10^{-3})	100^{+} g
Zinc Oxide	5.0 g
Stearic Acid	3.0 g
CBS	0.6 g
Sulphur	2.5 g

Table 4.9 Typical Formulation for Closed Torque Rheometer Processing

Premilled stock (NR + Additive (1.992×10^{-3})	30^{+} g
NR (SMR10)	70 g
Zinc Oxide	5.0 g
Stearic Acid	3.0 g
CBS	0.6 g
Sulphur	2.5 g

4.3.2 RESULTS

a) Cure Characteristics for BDBS in CBS-Sulphur Cure System Under Different Preprocessing Conditions - Tables 4.10-13

Table 4.10 Open Milling (OM)

Preprocessing Time (min)	R_{max} x0.06 m-kg	kx10^{-1} min^{-1}	Induction time (t_i) (min)
2	58	2.3	11
5	57	2.3	12
10	58	2.3	13
15	56	2.3	13

Table 4.11 Closed Torque Rheometer (CT)

Preprocessing Time (min)	R_{max} x0.06 m-kg	kx10^{-1} min^{-1}	Induction time (t_i) (min)
2	58	2.3	12.5
5	57	2.3	15
10	57	2.3	14
15	56	2.3	13

Table 4.12 Closed Torque Rheometer in Presence of 0.1ml TBH (CTP$_1$)

Preprocessing Time (min)	R_{max} x0.06 m-kg	kx10^{-1} min^{-1}	Induction time (t_i) (min)
2	56	2.3	18.5
5	56	2.3	18.0
10	57	2.3	16.0
15	57	2.3	16.0

Table 4.13 Closed Torque Rheometer in Presence of 0.5ml TBH (CTP_2)

Preprocessing Time (min)	R_{max} x0.06 m-kg	$kx10^{-1}$ min^{-1}	Induction time (t_i) (min)
2	56	2.3	17.5
5	55	2.3	18
10	55	2.3	18
15	57	2.3	23

b) Cure Characteristics for BDBDS in CBS-Sulphur Cure System Under Different Preprocessing Conditions - Tables 4.14-17

Table 4.14 Open Milling (OM)

Preprocessing Time (min)	R_{max} x 0.06 m-kg	$kx10^{-1}$ min^{-1}	Induction time (t_i) (min)
2	57	2.3	11
5	55	2.3	11.5
10	55	2.3	12
15	55	2.3	13

Table 4.15 Closed Torque Rheometer (CT)

Preprocessing Time (min)	R_{max} x 0.06 m-kg	$kx10^{-1}$ min^{-1}	Induction time (t_i) (min)
2	57	2.3	14
5	56	2.3	14
10	56	2.3	17
15	55	2.3	16

Table 4.16 Closed Torque Rheometer in Presence of 0.1ml TBH (CTP_1)

Preprocessing Time (min)	R_{max} x0.06 m-kg	kx10^{-1} min^{-1}	Induction time (t_i) (min)
2	57	2.3	13.5
5	58	2.3	14
10	55	2.3	17.5
15	55	2.3	17

Table 4.17 Closed Torque Rheometer in Presence of 0.5ml TBH (CTP_2)

Preprocessing Time (min)	R_{max} x0.06 m-kg	kx10^{-1} min^{-1}	Induction time (t_i) (min)
2	57	2.3	15
5	55	2.3	15
10	55	2.3	16
15	55	2.3	15.5

Table 4.18 Fatigue Lives (hrs) of Preprocessed CBS-Sulphur Vulcanisates Containing BDBS

Preprocessing Time (min)	OM Open Milling	CT Closed Torque	CTP_1 Closed Torque + 0.1ml TBH	CTP_2 Closed Torque + 0.5ml TBH
2	111.5	100.6	78.8	87.3
5	104.5	76.6	90.7	82.8
10	91.4	74.9	75.2	78.3
15	64.9	69.2	73.5	73.4

Table 4.19 Fatigue Lives (hrs) of Preprocessed CBS-Sulphur Vulcanisates Containing BDBDS

Preprocessing Time (min)	OM Open Milling	CT Closed Torque	CTP$_1$ Closed Torque + 0.1ml TBH	CTP$_2$ Closed Torque + 0.5ml TBH
2	76.7	53.5	82.0	112.5
5	86.6	62.4	101.6	74.9
10	85.7	49.9	74.9	72.7
15	83.8	41.8	74.2	57.1

Table 4.20 Time (hrs) to 50% Stress Decay ($^{F}50$) of Preprocessed CBS-S Vulcanisates Containing BDBS

Preprocessing Time (min)	OM Open Milling	CT Closed Torque	CTP$_1$ Closed Torque + 0.1ml TBH	CTP$_2$ Closed Torque + 0.5ml TBH
2	12	14.5	11	8.5
5	20	12	12.5	10
10	16	10	15	6
15	14	12	16	12

Table 4.21 Time (hrs) to 50% Stress Decay ($^{F}50$) of Preprocessed CBS-S Vulcanisates Containing BDBDS

Preprocessing Time (min)	OM Open Milling	CT Closed Torque	CTP$_1$ Closed Torque + 0.1ml TBH	CTP$_2$ Closed Torque + 0.5ml TBH
2	6.5	8.5	9	7
5	6.5	6	8	8.25
10	8	5.5	8	6
15	6.5	5.5	7	4.5

4.3.2 RESULT

The cure characteristics under the different preprocessing conditions are given in Tables 4.10 - 17. The rate of cure remains the same for all conditions. The induction times for the OM and CT are about similar to the normally compounded stocks (Table 3.7), however, the stocks with TBH have slightly longer induction periods. The maximum modulus attained (R_{max}) vary between 3.3 and 3.48 m-kg.

The fatigue lives are outlined in Tables 4.18 and 4.19. The general trend is a gradual decrease from 2 to 15 minutes of processing time in almost all the different treatments containing BDBS except in the CTP_1, where there was an increase from 2 to 5 minutes and then decrease to 15 minutes. In BDBDS (Table 4.19), CT and CTP_1 showed an increasing trend from 2 to 5 minutes then decreased with increase preprocessing time. CTP_2 had the highest fatigue life at 2 minutes, then a drop to 15 minutes of preprocessing. In the OM, the 5 minutes had the highest fatigue life and a gradual drop to 15 minutes. However, with BDBDS, the 2 minutes in CTP_2 gave the highest fatigue life. This is comparable to the normally compounded BDBS CBS-sulphur stock (Table 3.19).

The continuous stress relaxation curves are shown in Figs. 4.4 to 4.11 while the times to 50% stress decay (${}^{F}50$) are given in Tables 4.20 and 4.21. In all the curves, the decay

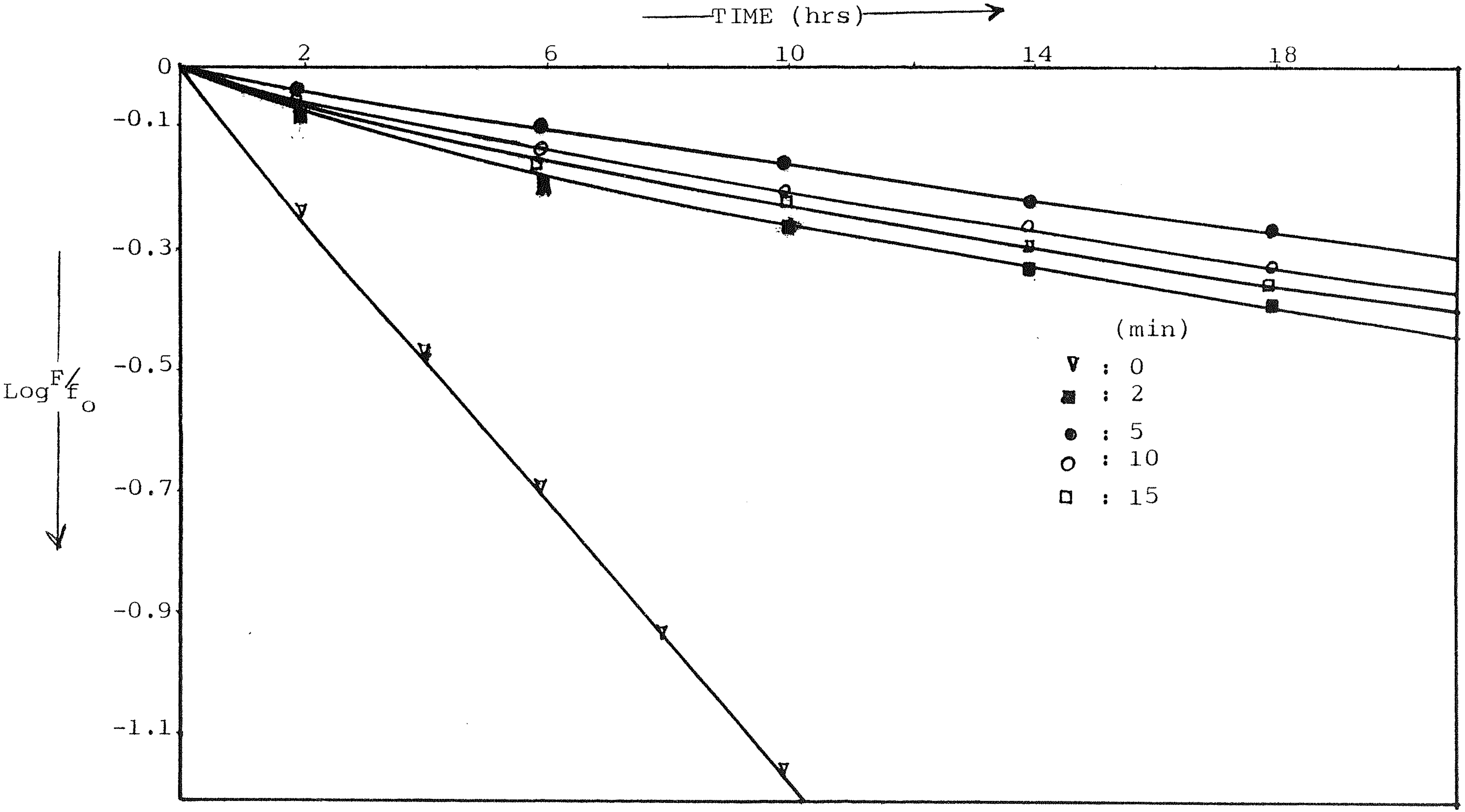


Fig. 4.4 : Continuous Stress Relaxation of Open Milling Preprocessing of BDBS in CBS-Sulphur Vulcanisates at 100°C and 60% Extension

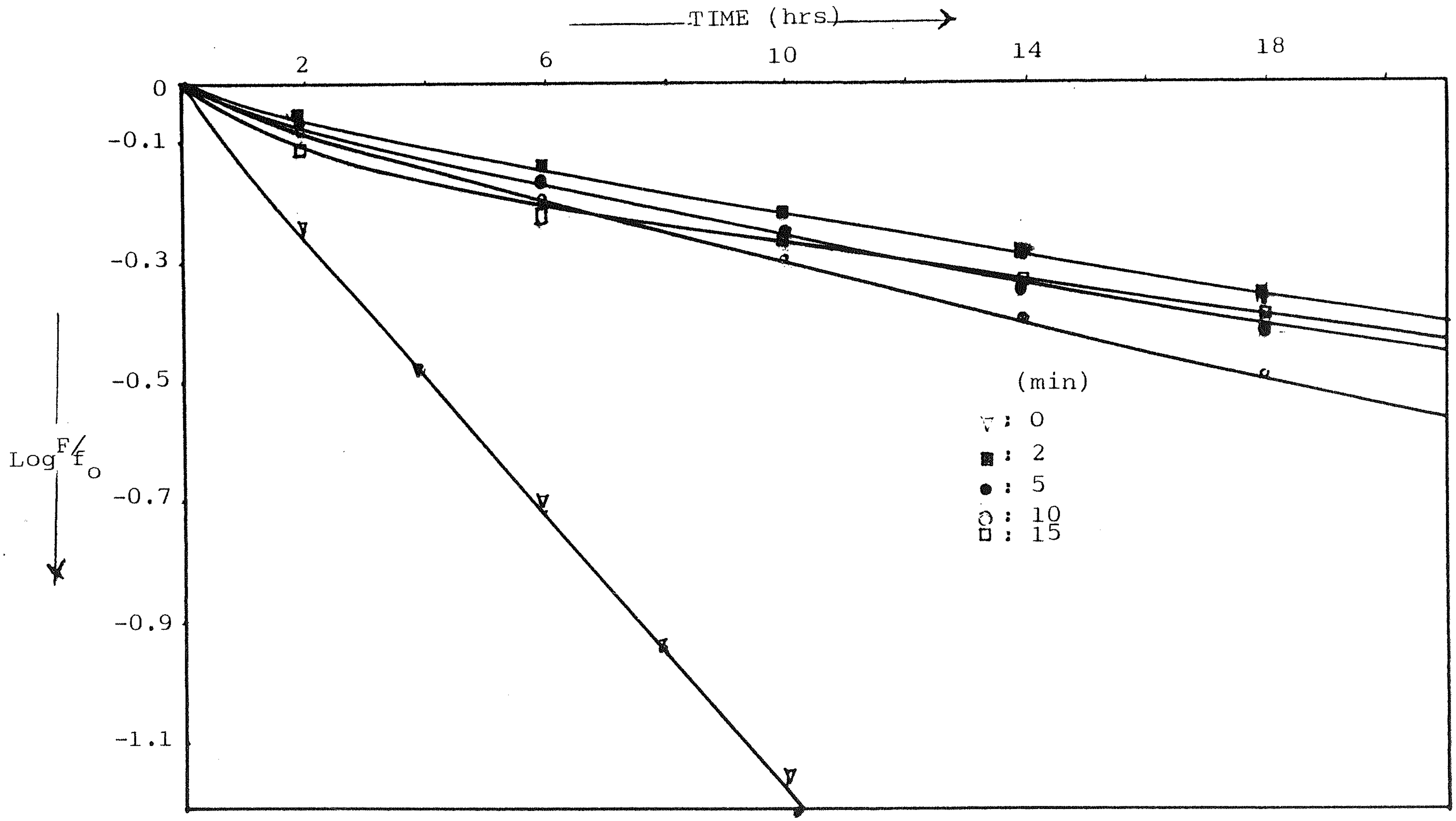


Fig. 4.5 : Continuous Stress Relaxation of Closed Torque Rheometer Preprocessing of BDBS in CBS-Sulphur Vulcanisates at 100^{o}C and 60% Extension

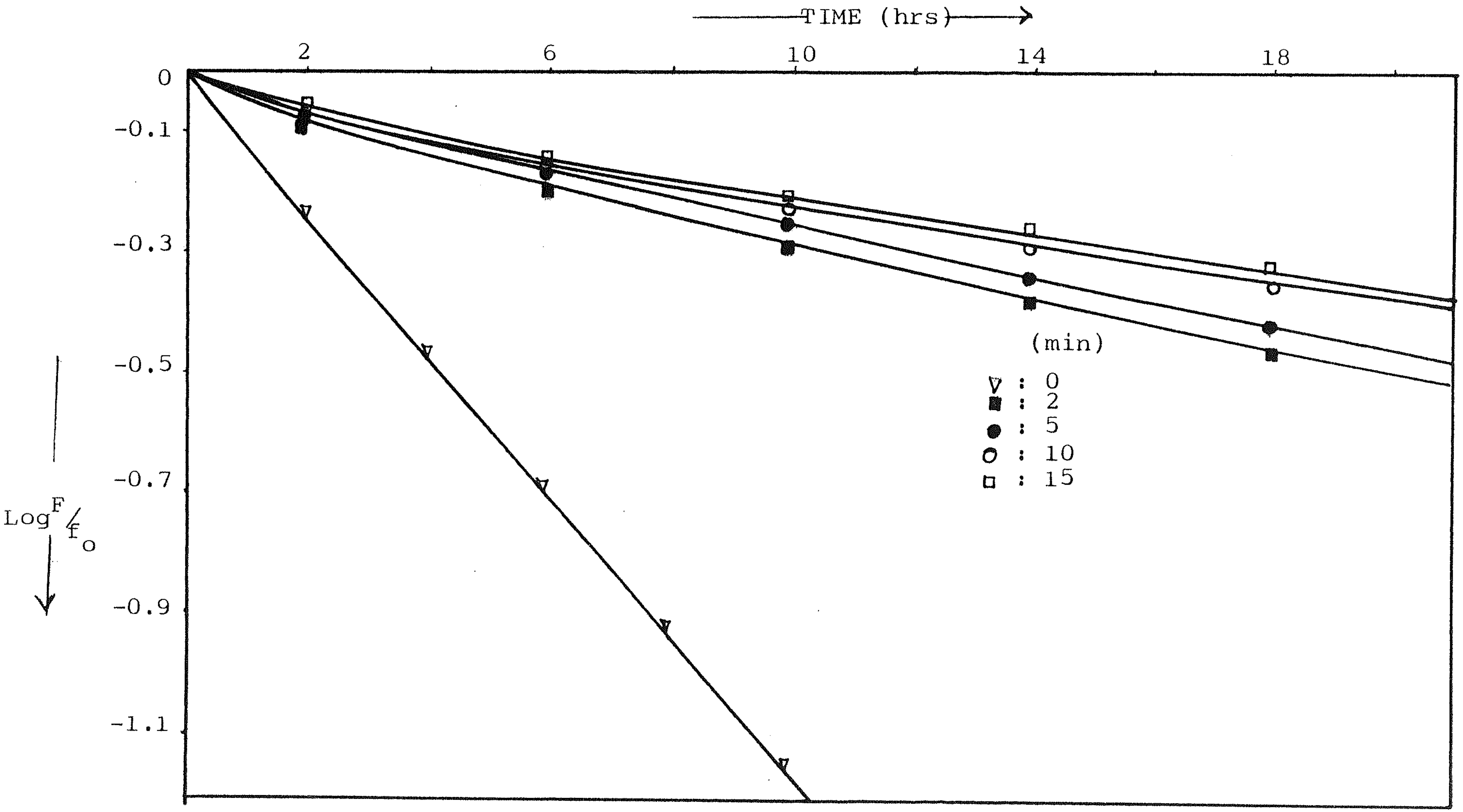


Fig. 4.6 : Continuous Stress Relaxation of Closed Torque Rheometer (plus 0.1ml TBH) Preprocessing of BDBS in CBS-Sulphur Vulcanisates at 100^{o}C and 60% Extension

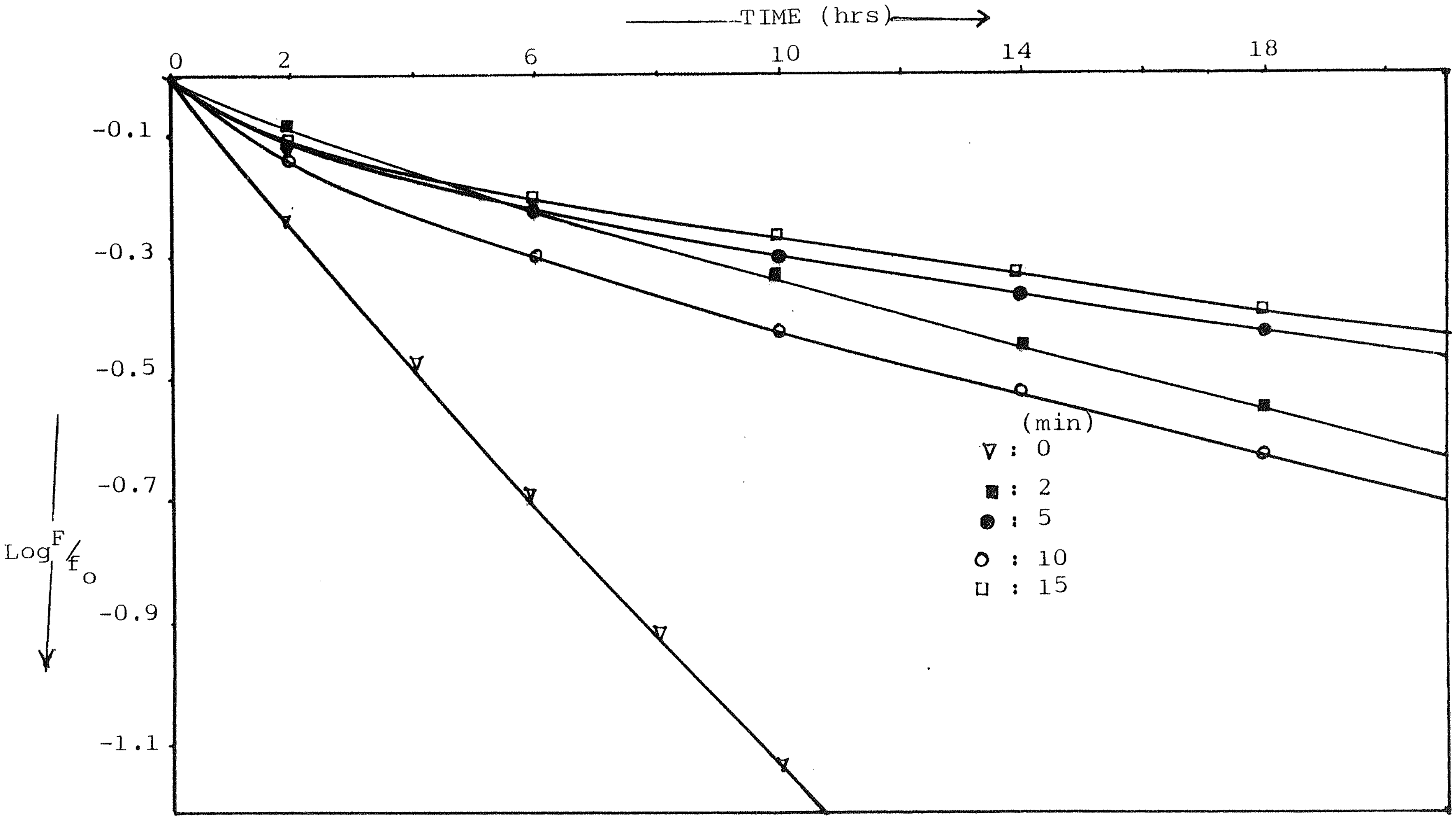


Fig. 4.7 : Continuous Stress Relaxation of Closed Torque Rheometer (plus 0.5ml TBH) Preprocessing of BDBS in CBS-Sulphur Vulcanisates at 100^{o}C and 60% Extension

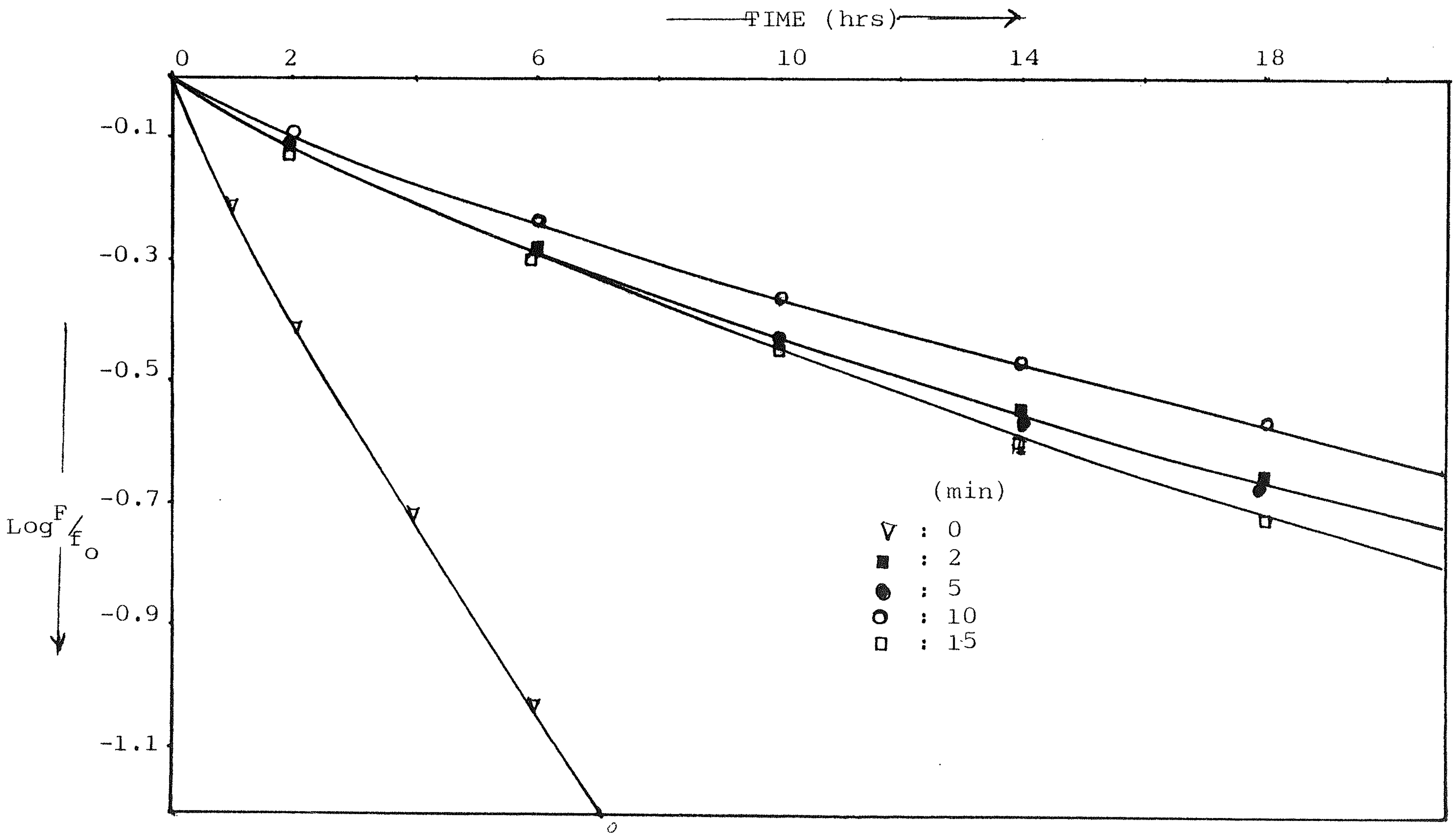


Fig. 4.8 : Continuous Stress Relaxation of Open Milling Preprocessing of BDBDS in CBS-Sulphur Vulcanisates at 100°C and 60% Extension

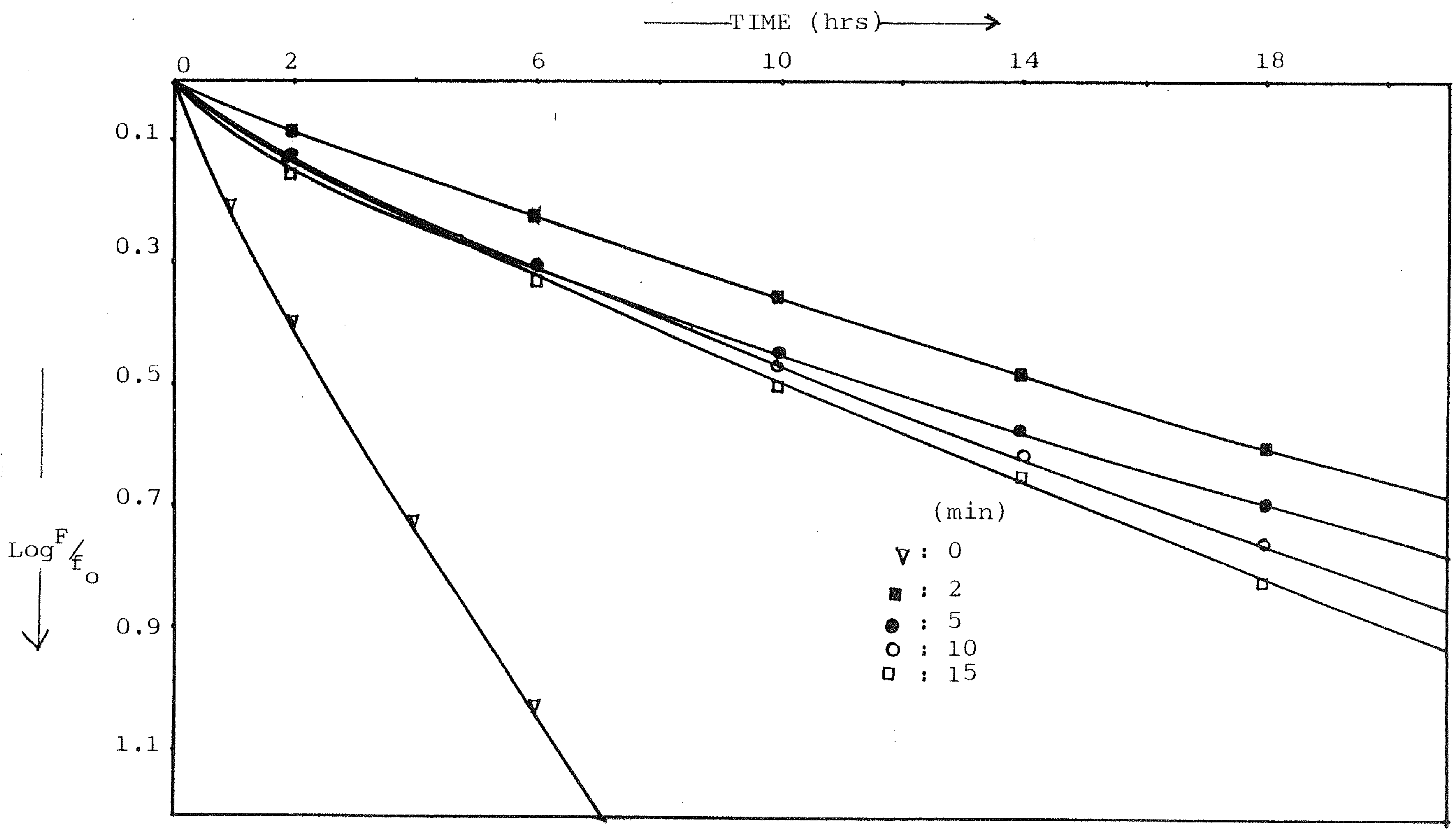


Fig. 4.9 : Continuous Stress Relaxation of Closed Torque Rheometer Preprocessing of BDBDS in CBS-Sulphur Vulcanisates at 100°C and 60% Extension

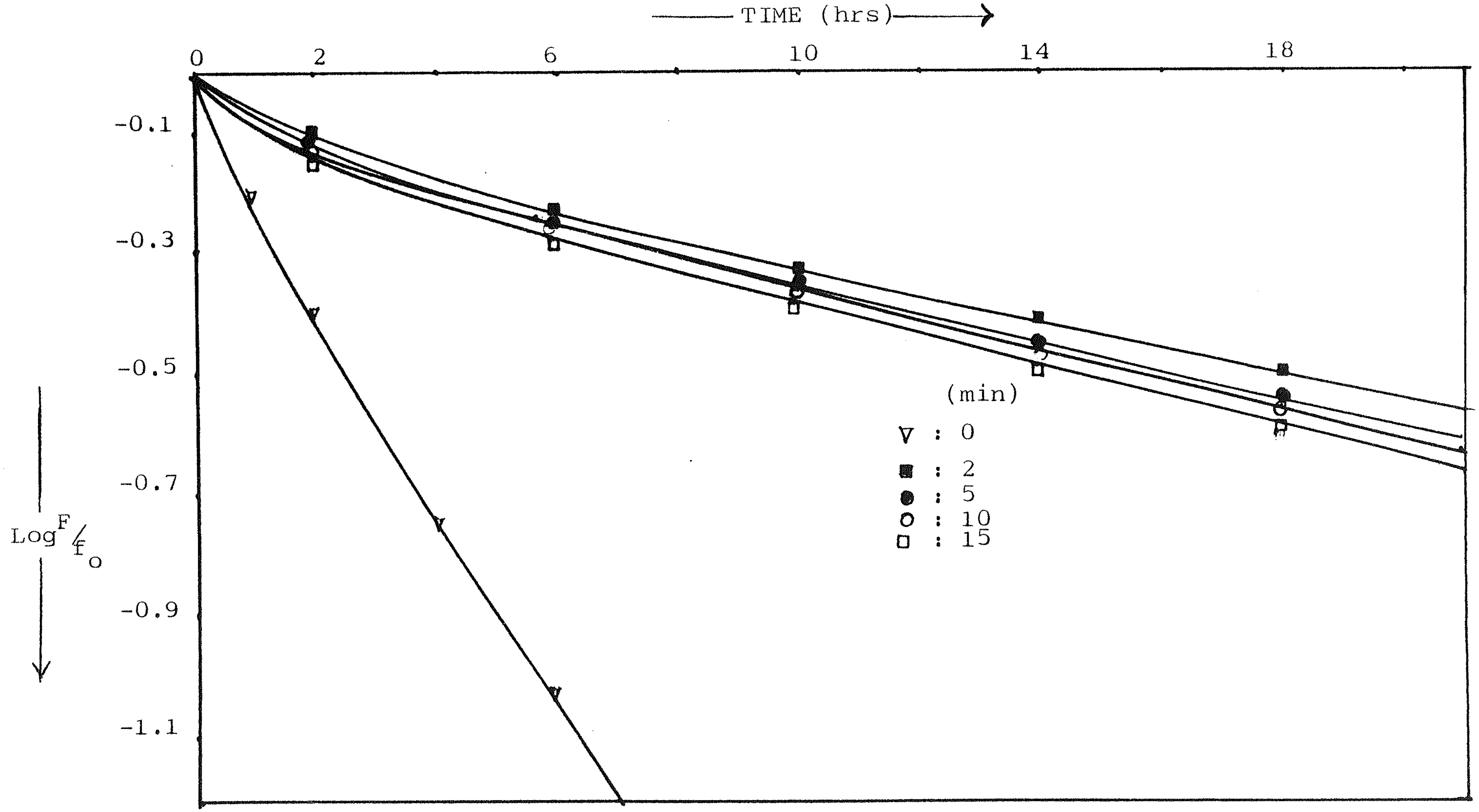


Fig. 4.10 : Continuous Stress Relaxation of Closed Torque Rheometer (plus 0.1ml TBH) Preprocessing of BDBDS in CBS-Sulphur Vulcanisates at 100°C and 60% Extension

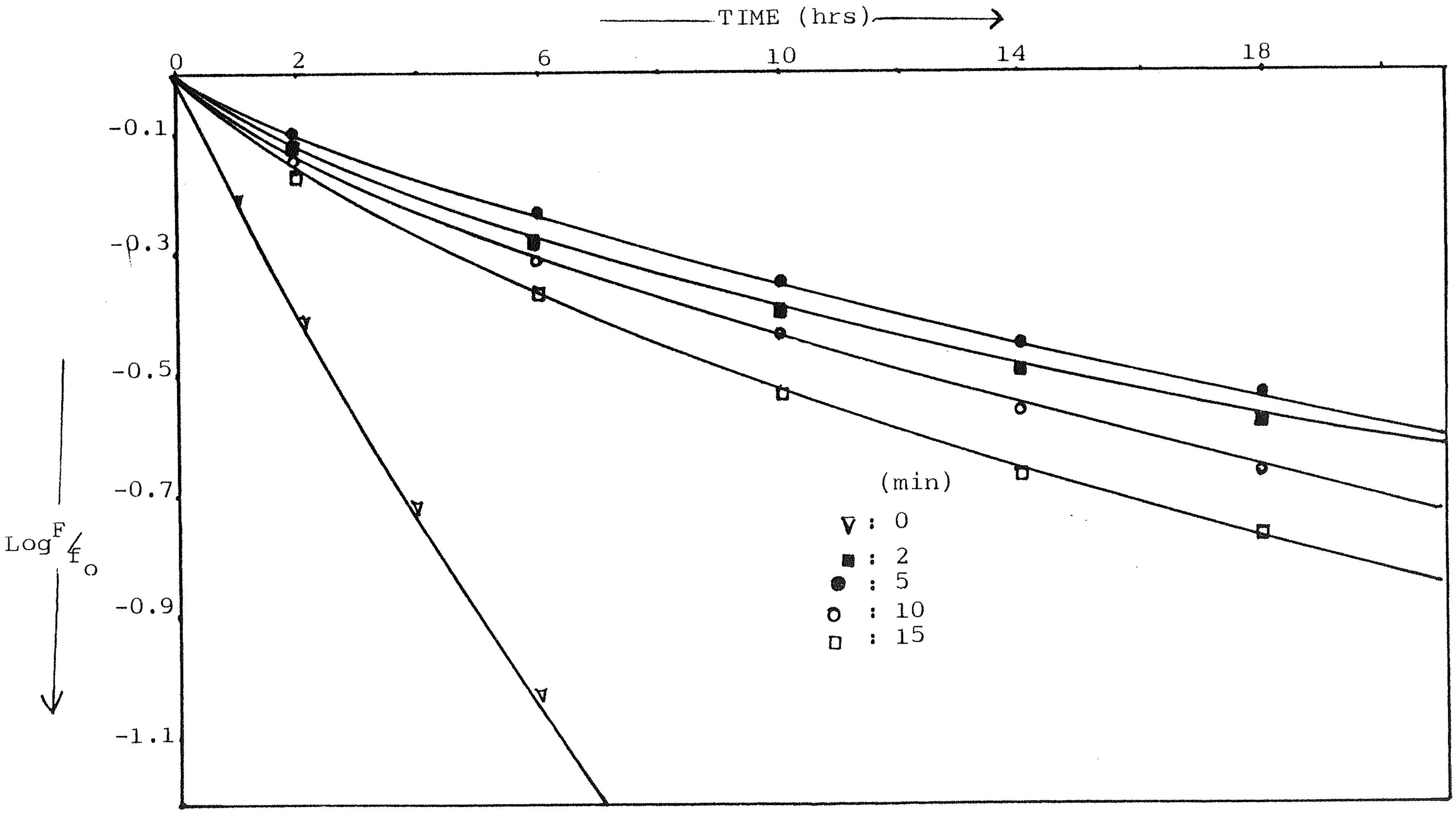


Fig. 4.11 : Continuous Stress Relaxation of Closed Torque Rheometer (plus 0.5ml TBH) Preprocessing of BDBDS in CBS-Sulphur Vulcanisates at 100°C and 60% Extension

was autoretarding. In BDBS, the OM treatment gave a generally better response to the reduction in the rate of stress decay while in BDBDS, the CTP_1 also gave a better response.

All results are reproducible within 5% limit of experimental error.

4.3.3 DISCUSSION

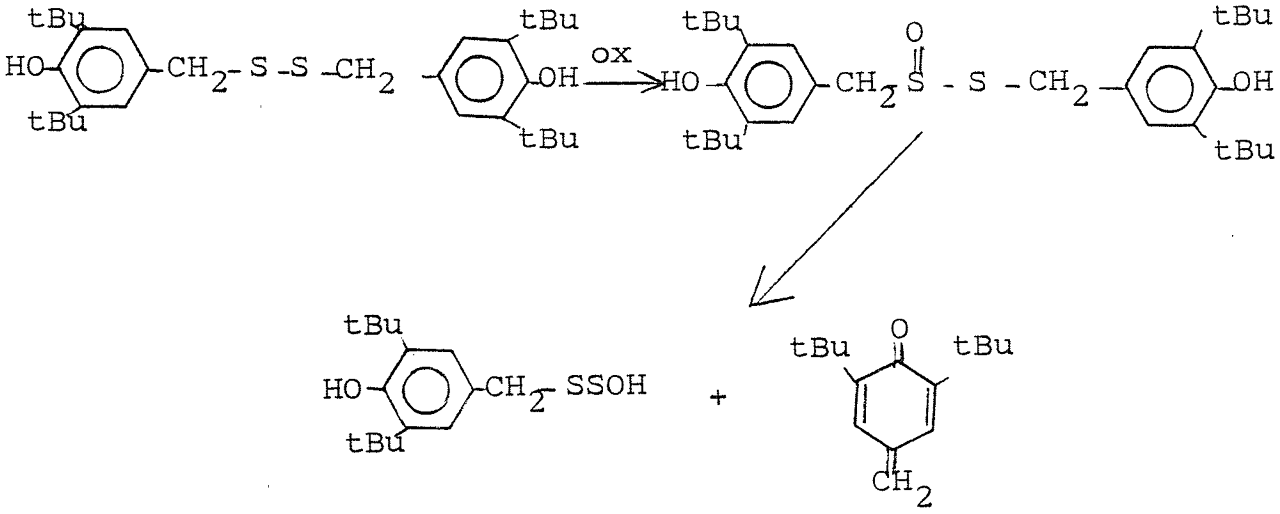
The increased vulcanisation induction periods obtained with treatments having TBH is due to the presence of the hydroperoxide (TBH) which is acidic and will normally cause a delay in the release of the active sulphurating agent[155-6] from the amine salt of the mercaptobenzothiazole (MBT) and until virtually all the sulphenamide accelerators have reacted crosslinking will not commence[157]. At maximum cure, the time to reversion was prolonged for all the various treatments compared to the normally compounded stocks (Chapter 3, Fig. 3.1). This improved heat stability is due to the transformation products of the hindered phenolic sulphur compounds, Scheme 3.3, during preprocessing. It has been shown that phenolic antioxidants in general are converted to higher molecular weight products[16,145,148,158-9] during their function as antioxidants and this explains why they become good heat stabilisers. This situation is also true with aromatic amine antioxidants.

The significant improvement in the rate of stress decay (Figs. 4.4-4.11) over the normally compounded stocks (Chapter 3,

Fig. 3.4) is due to the transformation products of the hindered phenolic sulphur compounds which enhanced the thermo-oxidative stability of the vulcanisates. During the preprocessing both BDBS and BDBDS are partially oxidised to the sulphur-oxy acids as well as to stilbenequinone, ethylene bisphenol and quinone. Ethylene bisphenol is an effective CB-D antioxidant while the sulphur-oxy acids act as peroxide decomposers - PD-C.

The OM treatment of BDBS gave the best overall improvement. The low temperature of the treatment (about 45°C) and the extensive oxidation of the additive may be responsible. However, in CTP, and CTP_2 treatments, the high temperature (100°C) of processing is likely to increase pro-oxidant species from the sulphur oxidation products (Schemes 3.4 and 4.1) hence the slightly lower improvement than in the OM treatment. In CT treatment the small amount of air dissolved in the polymer and air trapped within the mixing chamber, coupled with the high temperature of processing will favour a moderate oxidation of BDBS into effective products hence the slightly better performance than those treatments with TBH at 2 and 5 minutes processing.

In the case of BDBDS, there was a significant decrease in the rate of stress decay in view of its poor performance in the normally compounded stocks (Chapter 3, Fig. 3.4). This improvement is related to the severe treatment employed and which assisted in the oxidation of BDBDS into its effective oxidation products. CTP_1 treatment gave the best overall improvement because BDBDS was oxidised into its effective antioxidant components according to Scheme 4.2. The comparable improvement of the 2 minutes processing in CT treatment to CTP_1 is due to the oxidation of part of BDBDS by dissolved air in the rubber and air trapped within the mixing chamber to thiosulphinate. However, in the absence of further air or hydroperoxide, it has been shown that the thiosulphinate under heat treatment will be converted into thiosulphoxylic acid[160,161] - Eqn. 4-1.



(4-1)

With subsequent compounding and thermo-oxidative ageing, the thiosulphoxylic acid can be oxidised further to the sulphur acids which are the effective peroxide decomposing agents. The quinone methide, on the other hand, has been shown to be an effective radical trap, thus becoming bound to the polymer chain during preprocessing. In this form, the quinone methide still retains its stabilising action during the thermo-oxidative measurement[158].

The improvement obtained from OM treatment was due to the extensive oxidation of BDBDS and which increases with the time of preprocessing producing oxidation products (Scheme 4.2) which are the effective antioxidants.

BDBS had slightly reduced antifatigue activity with preprocessing compared to the normally compounded stock (Chapter 3, Table 3.19) but better than the control. The explanation lies in the complete loss of volatile sulphur compounds as in Scheme 3.3[126].

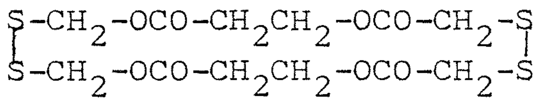
BDBDS, on the other hand, had improved antifatigue activity with the exception of CT treatment. In the CT treatment, the subsequent reaction of the thiosulphoxylic acid during fatiguing will produce sulphenic acid which gave rise to pro-oxidant species under the deficient oxygen and invariably low concentration of hydroperoxide associated with fatiguing. However, the presence of the quinone methide may account for the observed limited antifatigue activity in view of the ethylene bisphenol and stilbenequinone which are known to be formed from the methide[6,120,146,159,161-3] and they themselves have antifatigue activity. The antifatigue activity of these tert-butyl substituted benzoquinone and stilbenequinone (Chapter 5) are only moderate when compared to that of the unsubstituted benzoquinone[141].

In conclusion, both BDBS and BDBDS, their oxidation products were the effective antioxidants as well as antifatigue agents. Preprocessing is particularly effective in aiding the additives to be transformed into species which stabilised the rubber vulcanisate effectively.

4.4 OTHER GROUPS OF SULPHUR COMPOUNDS IN FATIGUE OF RUBBER VULCANISATE

4-mercaptoacetamido-diphenylamine, MADA, and Bis-(4-phenyl-aminophenyl-thioglycolamide), MADA-S, have been evaluated in a number of rubbers like natural rubber[5,6,149], SBR[6] and Nitrile rubber[150] for both antioxidant and antifatigue activities. The aim in this instance is to examine certain preprocessing conditions as earlier discussed (Section 4.3.1) on the antifatigue activity of MADA and MADA-S.

GDMA as a bifunctional dithiol is known[165] to cure NR and SBR but has also been effectively used for chlorobutyl rubber[166]. The possibility of GDMA being transformed into a biradical has prompted the use of this compound for anti-fatigue evaluation. Alongside GDMA is the derived disulphide - GDMA-S. Compound I was expected to be formed, however, a polymeric product, II, was obtained.



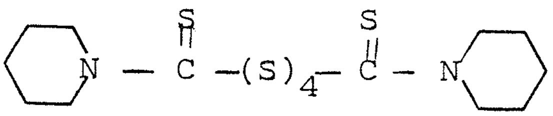
$$\begin{array}{l} S-CH_2-OCO-CH_2CH_2-OCO-CH_2-S \\ S-CH_2-OCO-CH_2CH_2-OCO-CH_2-S \end{array}$$

I

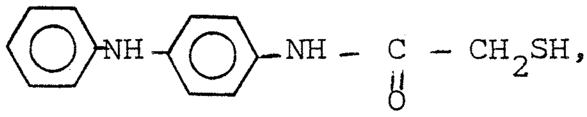
$$-(S-CH_2-OCOCH_2CH_2-OCO-CH_2-S)-_n \quad n \geq 2$$

II

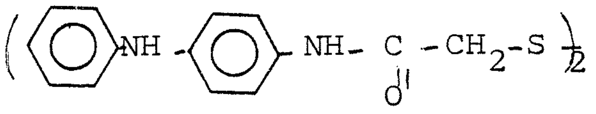
Di-pentamethylene thiuram tetrasulphide, MTTS, was also evaluated along with these two major groups of sulphur compound. MTTS as a thiuram is a sulphur donor/vulcanisation accelerator.



, MTTS



, MADA



4.4.1 PROCEDURE

Vulcanisates were prepared as set out in Section 2.2.1 using the formulations in Table 4.22. The curing characteristics were obtained using the Monsanto Rheometer (Section 2.2.2). Stress relaxation (for GDMA and GDMA-S) and fatigue tests were carried out as previously described in Sections 2.2.2.2

and 2.2.3.3 respectively. In the case of MADA and MADA-S, preprocessing was employed as earlier described in Section 4.3.1.

4.4.2 RESULT

Table 4.23 shows the cure characteristics of the normally compounded stocks while Tables 4.24 - 4.25 show those of the preprocessed MADA and MADA-S. All these compounds were 'scorchy'. They show lower modulus and rate of cure with the exception of MTTS with high modulus and fast rate of cure. The fatigue lives of the normally compounded stocks are shown in Table 4.26 while those of preprocessed MADA and MADA-S are shown in Tables 4.27. MADA-S has the highest antifatigue activity of the sulphur compounds, followed by MADA, GDMAS, GDMA and MTTS in that order.

In preprocessed MADA, Table 4.27, all treatments with the exception of CTP_2 at 15 minutes, showed improvement over the normally compounded additives. CTP_2 treatment showed an overall better improvement than CTP_1 and CT.

In the case of MADA-S, preprocessing seemed not to cause appreciable improvement except in CTP_1, at 2 and 10 minutes. These fatigue results are within 5% level of experimental error.

Fig. 4.12 shows the continuous stress relaxation curves for MTTS, GDMA and GDMA-S. All the sulphur compounds reduced the rate of stress decay better than the hindered phenolic sulphur compound and DLTP (see Fig. 3.4), but not as effective as IPPD.

Table 4.22 CBS-Sulphur Formulations

Ingredients	Control	1	2	3	4	5
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	3	3	3	3	3	3
CBS	0.6	0.6	0.6	0.6	0.6	0.6
MTTS	-	0.72	-	-	-	-
GDMA	-	-	0.42	-	-	-
GDMA-S	-	-	-	0.83	-	-
MADA	-	-	-	-	0.50	-
MADA-S	-	-	-	-	-	1.12
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 4.23 Cure Characteristics of the Normally Compounded CBS-Sulphur Stocks at 140°C

Test Compounds	Rmax (m-kg)	$kx10^{-1}$ min^{-1}	t_i(min)	Cure time (min)
Control	3.48	2.8	10	25
MTTS	4.2	6.08	6.5	8
GDMA	3.3	1.30	5	25
GDMA-S	3.3	1.30	5	25
MADA	3.06	1.08	5	25
MADA-S	3.06	1.08	6	25
IPPD	3.6	2.3	9.5	25

Table 4.24 Cure Characteristics of Preprocessed MADA in CBS-Sulphur Cure at 140^{o}C

Time	R_{max} (m-kg)			$kx10^{-1}$ min^{-1}			t_i (min)		
	CT	CTP_1	CTP_2	CT	CTP_1	CTP_2	CT	CTP_1	CTP_2
2	3.48	3.24	3.3	0.99	1.08	1.30	6.5	7.0	7.5
5	3.36	3.24	3.24	0.99	0.94	0.96	6	7.0	7.5
10	3.48	3.24	3.36	0.99	1.08	1.25	6	7.0	7.5
15	3.48	3.26	3.36	0.99	0.94	1.30	6	8.5	7.5

Table 4.25 Cure Characteristics of Preprocessed MADA-S in CBS-S Cure at 140^{o}C

Time	R_{max} (m-kg)			$kx10^{-1}$ min^{-1}			t_i (min)		
	CT	CTP_1	CTP_2	CT	CTP_1	CTP_2	CT	CTP_1	CTP_2
2	3.36	3.12	3.24	0.99	1.08	0.99	7	7	7.5
5	3.24	3.12	3.24	0.99	0.94	1.08	7	7	7
10	3.24	3.12	3.36	0.99	1.08	1.08	7	7	7
15	3.36	3.12	3.12	0.99	1.08	1.08	7	7	6.5

Table 4.26 Fatigue Lives of Normally Compounded CBS-S Stocks at 60% Extension

Test Compounds	Fatigue Life (hrs)
Control	23.6
MTTS	50.6
GDMA	58.6
GDMAS	61.4
MADA	105.6
MADA-S	143.1
IPPD	232.1

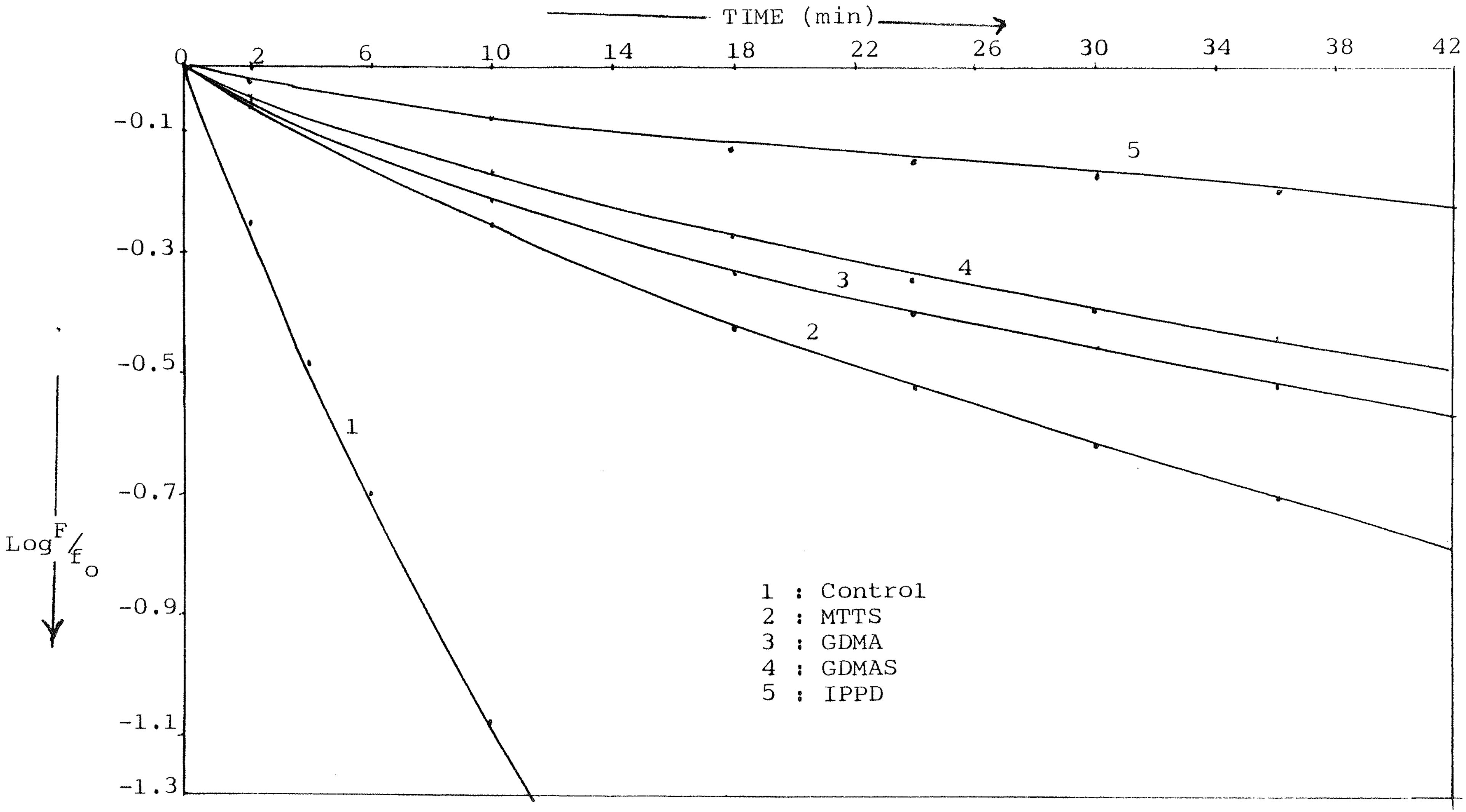


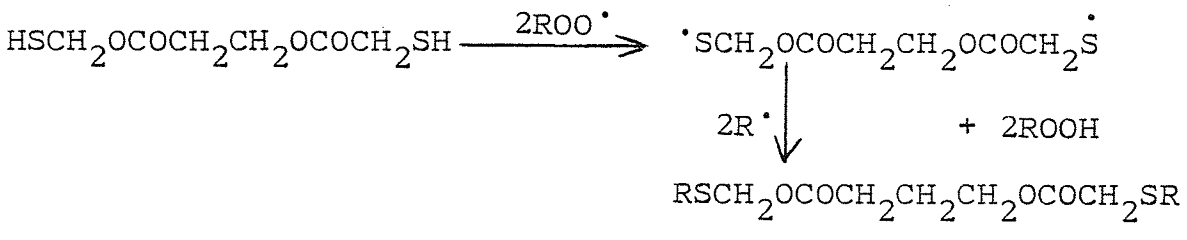
Fig. 4.12 : Continuous Stress Relaxation of GDMA/S and MTTS in CBS-S Vulcanisates at 100°C and 60% Extension

Table 4.27 Fatigue Lives of Preprocessed MADA in CBS-S Stocks at 60% Extension

	MADA Fatigue Life (hrs)			MADA-S Fatigue Life (hrs)		
Time	CT	CTP_1	CTP_2	CT	CTP_1	CTP_2
2	100	153.5	165.1	111.4	181.3	160.1
5	110	160.2	178	120.3	160.2	120
10	115	145	148.6	104.2	120.4	161.2
15	95	117	106.2	100.1	136.3	127.7

4.4.3 DISCUSSION

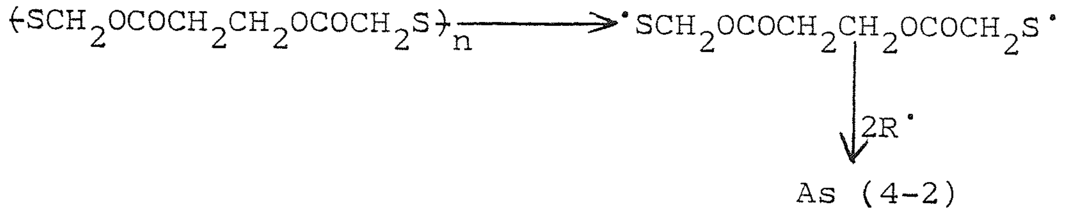
The antifatigue activity of MTTS, GDMA and GDMA-S is significant in view of the fact that these types of compounds will, like DLTP, have only PD-C activity. In the case of GDMA, the likelihood of diradicals being formed cannot be ruled out (4-2) and this may account for the observed antifatigue activity.



$$HSCH_2OCOCH_2CH_2OCOCH_2SH \xrightarrow{2ROO^{\bullet}} {}^{\bullet}SCH_2OCOCH_2CH_2OCOCH_2\dot{S} + 2ROOH \xrightarrow{2R^{\bullet}} RSCH_2OCOCH_2CH_2CH_2OCOCH_2SR$$

(4-2)

GDMA-S can similarly undergo cleavage at the S-S bond to form diradical which will interact with alkyl radical formed during fatiguing.



$$(\mathrm{SCH_2OCOCH_2CH_2OCOCH_2S})_n \longrightarrow {}^{\cdot}\mathrm{SCH_2OCOCH_2CH_2OCOCH_2S}^{\cdot} \xrightarrow{2\mathrm{R}^{\cdot}} \text{As (4-2)}$$

In addition, the thermal activity of MTTS, GDMA and GDMA-S is due to their PD-C role which is related to that of DLTP (Scheme 1). In the case of MTTS, the corresponding zinc complex is formed as in the case of TMTD to give enhanced thermal activity.

The antifatigue activity of MADA has been attributed[139] to the nitroxyl radicals formed during fatiguing and these are known to be efficient alkyl radical traps[163]. In addition, it has been observed[139] that the nitroxyl radicals are continuously regenerated in a cyclical mechanism (Scheme 3.7) involving the corresponding hydroxylamine. The effect of preprocessing is to introduce in-situ at an early stage transformation products of the parent thiolamide so as to enhance its activity. Table 4.27 indicates that the preprocessing treatment is important and under certain conditions higher levels of activity can be achieved.

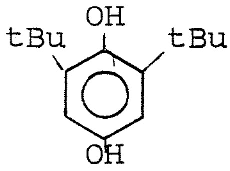
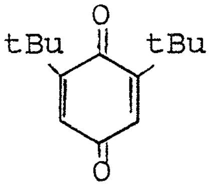
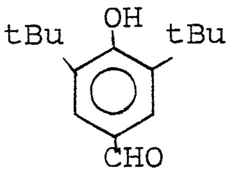
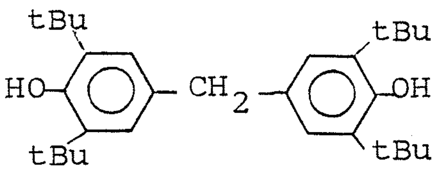
5. CHAPTER FIVE

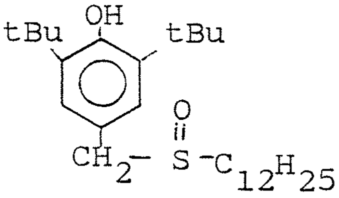
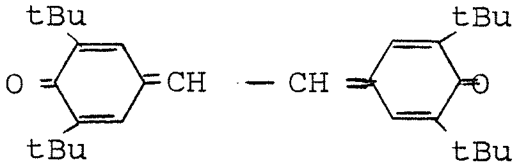
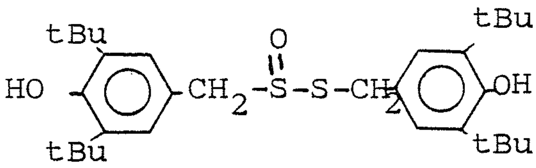
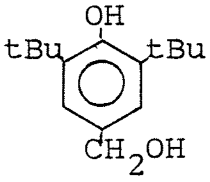
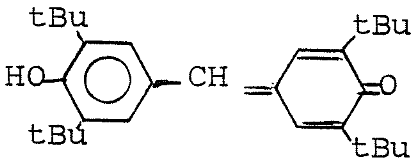
5.1 INVESTIGATION INTO TRANSFORMATION PRODUCTS FORMED FROM HINDERED PHENOLIC SULPHUR COMPOUNDS AFTER VULCANISATION AND DURING AND AFTER FATIGUE FAILURE

The hindered phenolic sulphur compounds[5,6,74] under review and also certain bisphenol sulphides[74] and aromatic thiolamides [6,139,163] have been found to exhibit antifatigue activities (Section 3.2.4). The antifatigue activities of these hindered phenolic sulphur compounds have been attributed to their transformation products, notably the sulphoxy-acids and quininoid products[5,6]. Katbab[5] found that in addition to these transformation products, galvinoxyl radicals are formed and these have been shown[5] to have antifatigue activity. On the other hand, in solution studies, Scott and Co-workers[120] found that these hindered phenolic sulphur compounds give rise to sulphoxy-acids, quinone, stilbenequinone and ethylene bisphenol. These quinonoid products and ethylenebisphenols are also known (Scheme 1-7)[4] to be formed during the oxidation of substituted phenols[101,104,162,164] and in the binding reaction of certain hindered phenols with solid rubber in the presence of free radical generators[145].

For simplicity, a peroxide cure system has been employed in this investigation in order to avoid the interaction from other sulphur compounds formed in the CBS-sulphur cure system. However, transformation products formed as a result of the vulcanisation process will be identified and compared to those formed in the swelled peroxide vulcanisate.

Compounds referred to in this Chapter are listed below along with their Codes. Other codes used have been listed in earlier Chapters.

Chemical Structure	Name	Code
	2,6-di-tert-butyl-1,4-hydroquinone	HQ
	2,6-di-tert-butyl-1,4, parabenzoquinone	BQ
	3,5-di-tert-butyl-4-hydroxy-benzaldehyde	BAL
	4,4'-dihydroxy-3,5,3'5'-tetra-tert-butyl-diphenyl-methane (trihydrogalvinoxy)	THG

Chemical Structure	Name	Code
	3,5-di-tert-butyl-4-hydroxybenzyl dodecyl sulphoxide	DBDSO
	3,5,3',5',tetra-tert-butyl-stilbene-4,4'-quinone	SB
	Bis-(3,5-di-tert-butyl-4-hydroxy-benzyl)-thiolsulphinate	BDBT
	3,5-di-tert-butyl-4-hydroxy-benzyl alcohol	BHBA
	2,6,3,5-tetra-tert-butyl-4-methylene-2,5-cyclohexadiene-1-one-(hydrogalvinoxy)	HG

5.1.1 PROCEDURE

Peroxide vulcanisates were prepared as outlined in Section 2.2. Samples for fatigue were prepared according to the procedure described in Section 2.6.1. The formulations used are set out in Table 3.3. Acetone extracts of vulcanisates were taken as follows:

i) After vulcanisation
ii) During fatigue, and
iii) After fatigue failure.

The different vulcanisate samples were extracted with cold spectrophotometric acetone in a conical flask using an electric shaker for 48 hours. The extracts were filtered and 1µl injected into the Gas Liquid Chromatographic (GLC) Column so as to separate the various fractions formed. For the GLC analysis, a Pye Unicam Model GCD Chromatograph, equipped with a servoscribe Recorder - RE 511.20 was used. The column employed was a 5ft. 4in. glass column packed with 3% SE30 on chromasorb W.HP. The GLC equipment was set at an initial temperature of 50°C, held for 3 minutes, then at 8°C rise per minute until a temperature of 250°C was attained. The carrier gas was nitrogen (N_2) and set at a flow rate of 30ml per minute and the chart speed was maintained at 600mm per hour. The flame ionisation detector was used and its temperature set at 270°C.

In order to eliminate the effect due to vulcanisation, additives were also swollen into extracted peroxide vulcanisates as described in Section 3.2.4.1. Swelled samples were then mounted on the Monsanto Fatigue-to-Failure Tester as set out in Section 2.6.1 and at 60% extension. Some of the fatigued samples were removed after 30 hours and the rest after fatigue failure. Each set of fatigued samples were acetone extracted and the filtered extracts injected into the GLC as earlier described for the compounded samples.

Infra-red spectrum of each set of samples extract was run in order to identify some of the newly formed functional groups.

The likely transformation products were prepared (Section 2.8.10 to 2.8.15) and used as reference compounds for the GLC analysis.

5.1.2 RESULT

Table 5.1 shows the transformation products of the hindered phenolic sulphur compounds identified after vulcanisation. The sulphoxides, BDBSO, DBSDG and DBDSO and thiosulphinate BDBT were only identified from the infra-red spectra. Common to all test compounds are HQ, BAL and THG. In addition, small traces of SB was found in BDBDS.

In BDBS, DBDT and DBDS, the predominant product was HQ followed by BAL and THG. This is supported by the strong to medium absorption at 3640cm^{-1} for the phenolic OH and a very weak C=O absorption at 1680cm^{-1} for BDBS and DBDS, but a strong ester C=O absorption at 1720cm^{-1} for DBDT. In BDBDS, BAL and SB were the major products, especially SB, the infra-red spectrum showed a weak phenolic OH absorption at 3620cm^{-1} and a strong quininoid C=O absorption at 1680cm^{-1}. Part of the starting DBDT and DBDS were also identified from the GLC.

The transformation products formed during and after fatigue are shown in Table 5.2. During fatigue, HQ, BQ, THG and BAL were common to all additives. Low level of SB was observed in BDBS and DBDT but not in BDBDS where it was one of the major products after vulcanisation. Benzyl alcohol was identified in BDBDS and DBDT while 1-dodecanol was identified in DBDT and DBDS.

After fatigue failure, BAL, BQ and THG were the predominant products in all test compounds. Traces of SB were found in BDBS, DBDT and DBDS but not in BDBDS. 1-dodecanol was still present in DBDT and DBDS.

Table 5.3 shows the transformation products formed from the swelled-in test compounds. During fatigue, substantial part of the starting parent sulphides were identified. BQ was the next major product followed by traces of SB. Benzyl alcohol was identified in BDBDS and DBDT while 1-dodecanol was found in DBDT and DBDS. After fatigue failure, the starting BDBS and DBDT were not present but were found in the case of BDBDS and DBDS. Traces of SB were also identified in all test compounds.

Table 5.1 Transformation Products Identified After Vulcanisation

Test Compounds	Infra-red Spectra	Compound Identified by GLC
BDBS	Phenolic OH 3640cm^{-1} (very strong) Quininoid C=O 1680cm^{-1} (very weak and broad) S=O 1025cm^{-1} (medium)	HQ BAL THG
BDBDS	Phenolic OH 3620cm^{-1} (weak) Quininoid C=O 1680cm^{-1} (very strong) S=O 1020cm^{-1} (small) Ester C=O 1720cm^{-1} (weak)	BQ SB HQ THG (traces) BAL (traces)
DBDT	Phenolic OH 3640cm^{-1} (strong) Ester C=O 1720cm^{-1} (strong) Quininoid C=O 1680cm^{-1} (absent) S=O 1025cm^{-} (small)	HQ BAL THG
DBDS	Quininoid C=O 1680cm^{-1} (weak broad) Phenolic OH 3640cm^{-1} (medium) Ester C=O 1720cm^{-1} (weak small)	HQ BAL THG DBDS

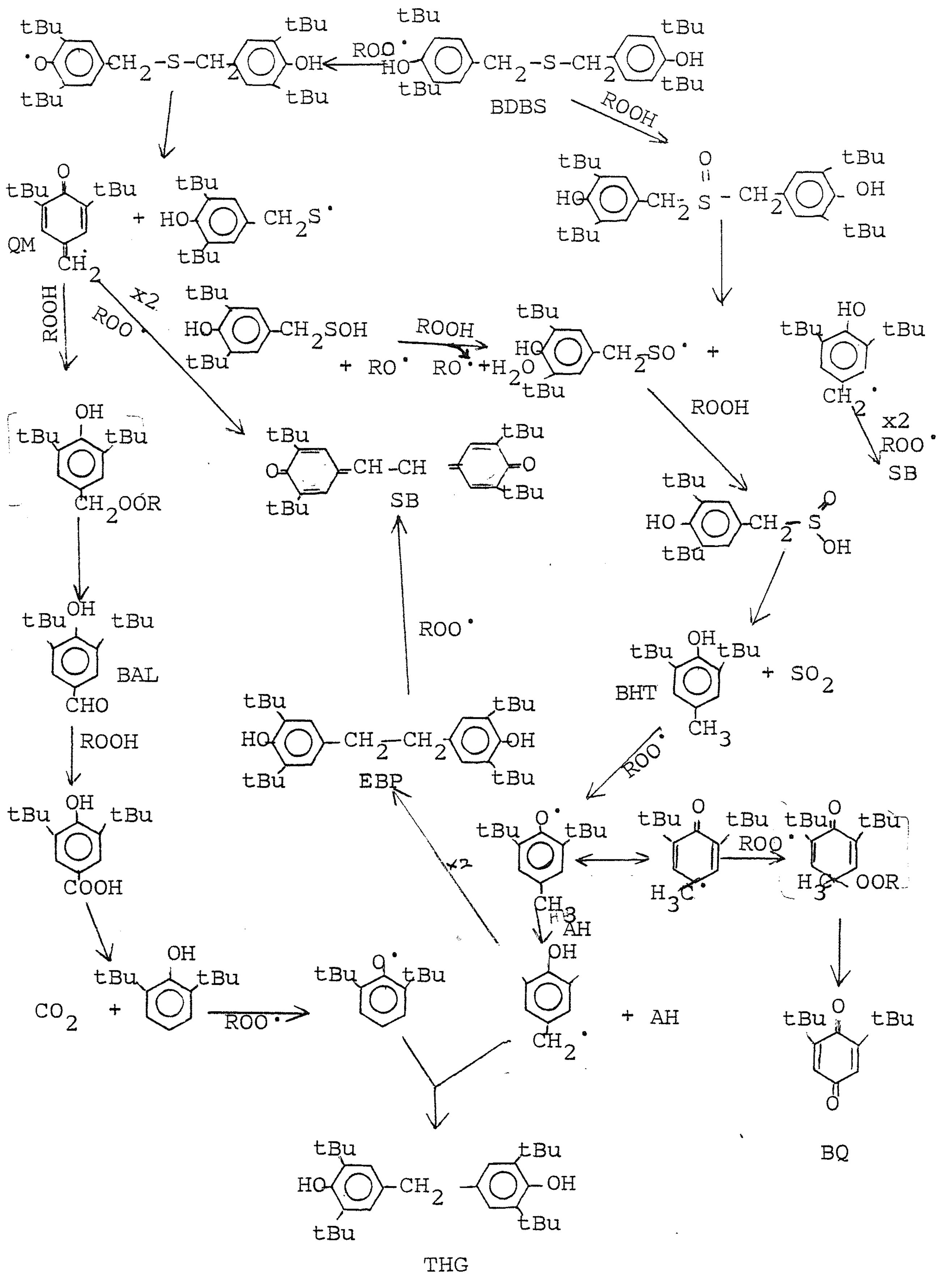
Table 5.2 Transformation Products Identified During and After Fatigue Failure by GLC

Test Compounds	During Fatigue (30 hrs)	After Fatigue Failure
BDBS	HQ, BQ, BAL, THG, SB (traces)	BAL, BQ, THG, SB (traces)
BDBDS	HQ, BQ, BAL, THG, BHBA	BAL, BQ, THG
DBDT	HQ, BQ, THG, BAL, SB (traces), BHBA, 1-dodecanol	BAL, BQ, THG, SB (traces), 1-dodecanol
DBDS	HQ, BQ, BAL, THG, 1-dodecanol	BAL, BQ, THG, SB (traces)

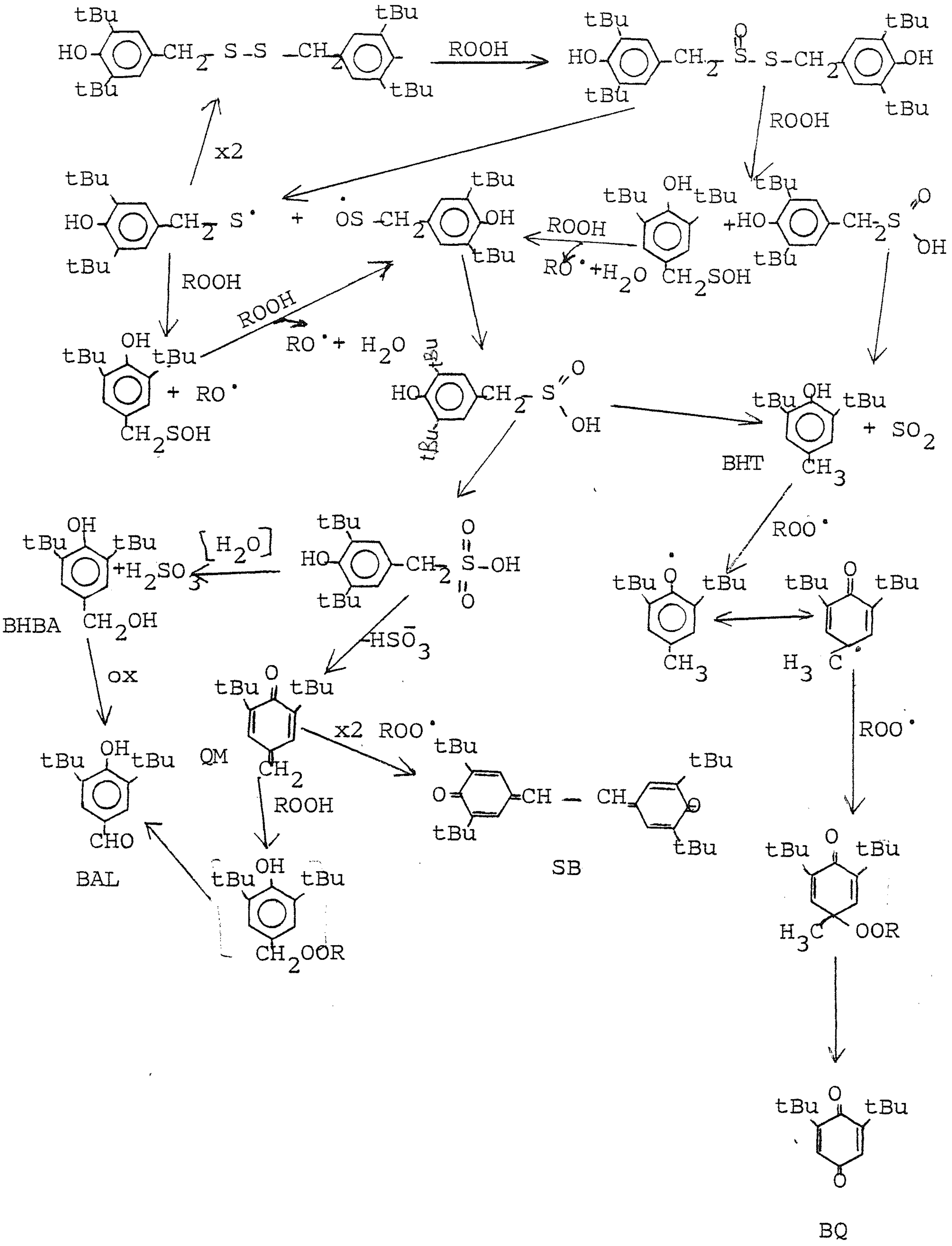
Table 5.3 Transformation Products Identified During and After Fatigue Failure of Swelled Peroxide Vulcanisates by GLC

Test Compounds	During Fatigue (30 hrs)	After Fatigue Failure
BDBS	BDBS, BQ, SB (traces)	BAL, BQ, THG, SB
BDBDS	BDBDS, BQ, SB, BHBA	BDBDS, BQ, SB, THG, BAL
DBDT	DBDT, BQ, SB, BHBA, 1-dodecanol	BQ, BAL, THG, SB, 1-dodecanol
DBDS	DBDS, BQ, SB, 1-dodecanol	DBDS, BAL, THG, SB, 1-dodecanol

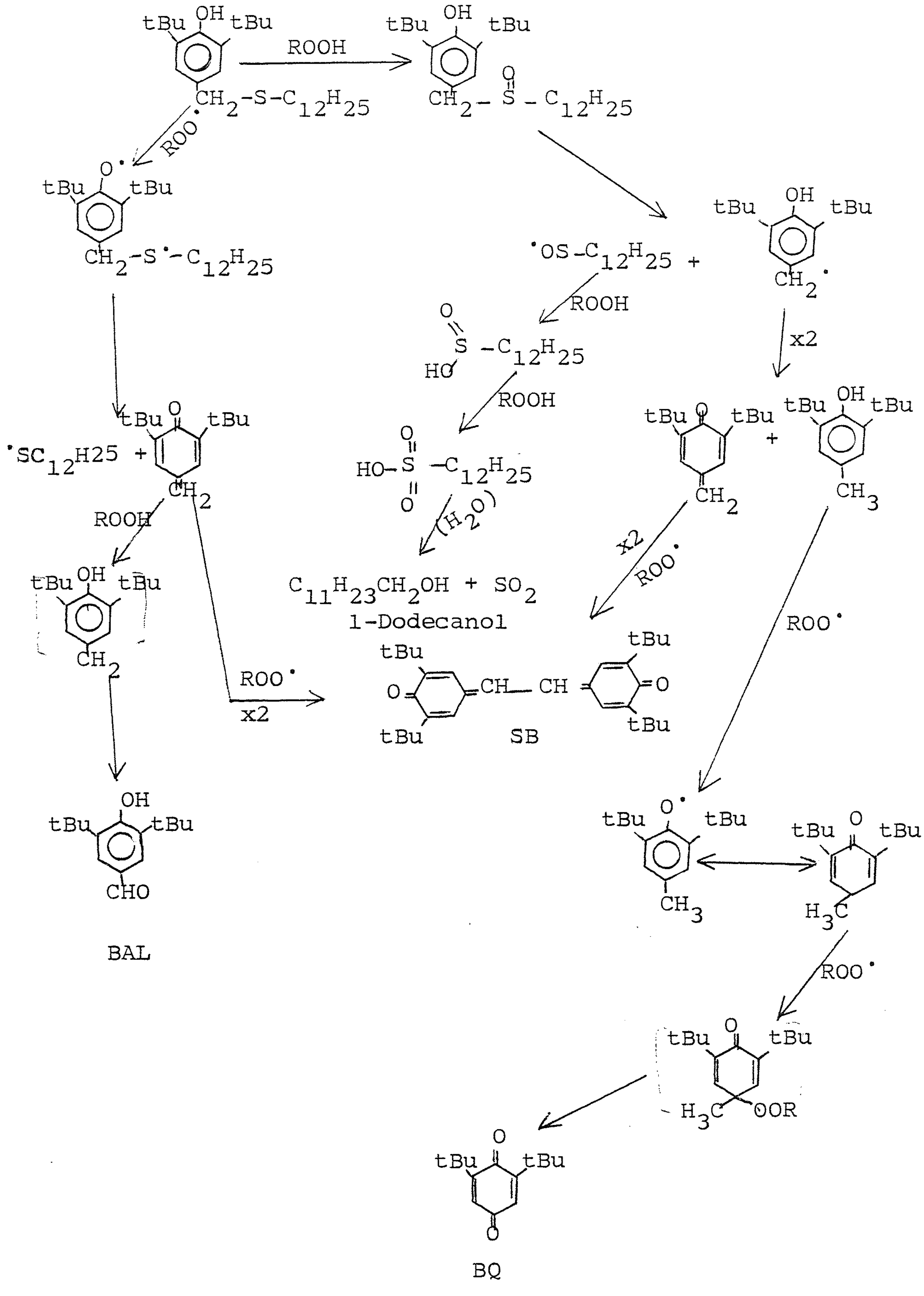
Scheme 5.1


tBu
CH$_2$-S-CH$_2$
OH
ROO$^\bullet$
HO
BDBS
ROOH
QM
O
CH$_2^\bullet$
HO
CH$_2$S$^\bullet$
ROOH
x2
ROO$^\bullet$
CH$_2$SOH
+ RO$^\bullet$
RO$^\bullet$ + H$_2$O
CH$_2$SO$^\bullet$
CH$_2$OOR
CH-CH
SB
x2
ROO$^\bullet$
CH$_2$ S OH
BAL
CHO
COOH
BHT
CH$_3$
+ SO$_2$
EBP
CH$_2$-CH$_2$
ROO$^\bullet$
AH
H$_3$C$^\bullet$
OOR
CO$_2$
+ AH
BQ
THG
CH$_2$

Scheme 5.2


ROOH
x2
ROOH
ROOH
ROOH
RO˙ + H$_2$O
+ RO˙
ROOH
RO˙ + H$_2$O
BHT
+ SO$_2$
ROO˙
[H$_2$O]
+H$_2$SO$_3$
BHBA
ox
-HSO$_3^-$
QM
x2 ROO˙
ROOH
ROO˙
BAL
SB
BQ

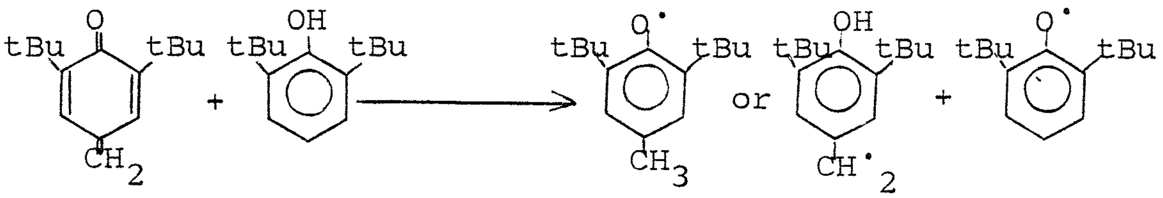
Scheme 5.3


tBu OH tBu
CH2-S-C12H25
ROOH
tBu OH tBu
CH2- S(=O) - C12H25
ROO•
tBu O• tBu
CH2-S•-C12H25
•OS-C12H25 +
tBu OH tBu
CH2•
ROOH
HO-S(=O)-C12H25
x2
ROOH
•SC12H25 +
tBu O tBu
CH2
HO-S(=O)(=O)-C12H25
(H2O)
tBu O tBu
CH2
+
tBu OH tBu
CH3
ROOH
tBu OH tBu
CH2
C11H23CH2OH + SO2
1-Dodecanol
x2
ROO•
ROO•
x2
tBu
O
CH — CH
O
tBu
tBu
tBu
SB
ROO•
OH
tBu tBu
CHO
BAL
tBu O• tBu
CH3
tBu O tBu
H3C
ROO•
tBu O tBu
H3C OOR
O
tBu tBu
O
BQ

5.1.3 DISCUSSION

Schemes 5.1-5.3 show the proposed reactions in which the hindered phenolic sulphur compounds are involved[6] and which invariably gave rise to the transformation products identified [5,6,120,161]. From the products identified, it is clear that there was an early loss of sulphur as SO_2 during the course of the antioxidant/antifatigue action of the sulphur compounds. It has been shown that in excess hydroperoxide (Section 4.3), the sulphur compounds are oxidised[6] to protonic acids like sulphinic, H_2SO_3 and H_2SO_4. However, during fatiguing, the more highly oxidised protonic acids may not be formed before the loss of the sulphur (as SO_2) component of the sulphur compounds due to the higher molar ratio of sulphur compound to hydroperoxide.

The presence of THG can be explained on the basis of the proposed reactions outlined in Scheme 5.1 and the redox reaction between the quinone methide and 2,6-di-tert-butyl-phenol (5-1)[162].



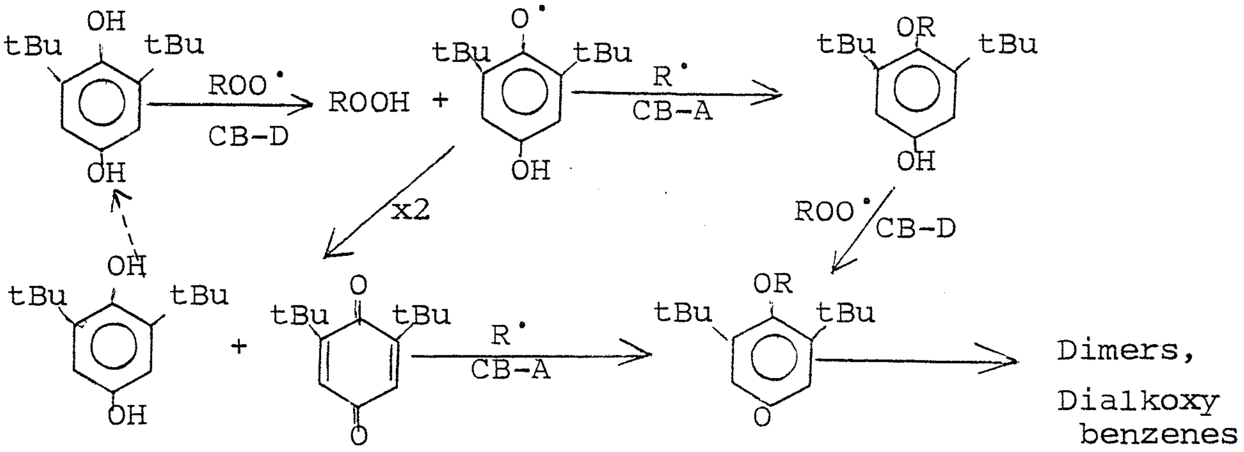
(5-1)

Reaction, 5-1, gives rise to the benzyl radical necessary in the coupling reaction to produce THG.

In the case of these sulphur compounds dissociation of the sulphoxides (Schemes 5.1 - 5.3) gives rise to a benzyl radical which can undergo the coupling reaction with aryloxy radical (Scheme 5.1).

In general, the hindered phenolic sulphur compounds undergo the typical reactions of any hindered phenolic compounds under oxidation condition (Scheme 1.6)[4,101,164,167,168,169] and in addition undergo those of sulphur compounds thus giving rise to quinonoid compounds aldehyde, sulphoxides and sulphoxy acids. The antifatigue activity of these sulphur compounds is probably due to their initial ability to interact with both hydroperoxides and alkyl-peroxy radicals prior to their transformation into HQ, BQ, and SB. BQ[86,149] and SB[140] are effective alkyl radical trap [170], hence the observed anti-fatigue activity of these sulphur compounds. HQ is also known[7] to act by complimentary mechanism involving redox reaction with its oxidation products (Scheme 5.4)[7].

Scheme 5.4[7]



The lower performance of the hindered phenolic sulphur compound compared to IPPD (Section 3.2.4) may be attributed to the pro-oxidant steps involved in Schemes 5.1 - 5.3. The more pro-oxidant stages there are, the lower will be the antifatigue activity; hence the unexpectedly poor performance of BDBDS. There are definitely other products formed as intermediates but only the stable ones can be easily identified under the analytical procedure used. At the same time there are considerable experimental problems involved in following reactions in rubber vulcanisates during fatigue due to the formation of polymer fragment-inhibitor molecule reaction products which cannot be easily extracted.

5.2 ASSESSMENT OF THE ANTIFATIGUE AND ANTIOXIDANT ACTIVITIES OF IDENTIFIED TRANSFORMATION PRODUCTS

In Section 5.1, a number of transformation products were identified. They range from BHBA, BAL, BQ, HQ, SB and benzylic sulphoxides. In Section 4.1, two sulphoxides were evaluated for both antifatigue and antioxidant activities. It is generally known[5,6,120] that these phenolic sulphides are transformed in the course of their action as polymer stabilisers to sulphur acids and phenolic products (Scheme 5.1). Individual evaluation of these transformation products will highlight the extent of the contribution made to the overall activity of the parent sulphide. In addition, these compounds are compared to other phenolic compounds (BHT and CPB) and also to known radical traps (Galvinoxyl).

5.2.1 PROCEDURE

The formulations in Table 5.4 were used. Peroxide gum stocks were prepared as set out in Section 2.2.1. The cure parameters were obtained using the Monsanto Rheometer (Section 2.2.2). Fatigue and stress relaxation samples were prepared according to the procedures in Section 2.2.3.3 and 2.2.2.2 respectively. Only fatigue samples for GLC analysis were treated as outlined earlier (Section 5.1.1). Continuous stress relaxation measurement was carried out as in Section 3.2.1.

Table 5.4 Peroxide Formulations

Ingredients	Control	1	2	3	4	5	6	7	8	9
NR (SMR10)	100	100	100	100	100	100	100	100	100	100
DCP	3	3	3	3	3	3	3	3	3	3
1 BQ	-	0.44	-	-	-	-	-	-	-	-
2 HQ	-	-	0.44	-	-	-	-	-	-	-
3 BAL	-	-	-	0.47	-	-	-	-	-	-
4 SB	-	-	-	-	0.86	-	-	-	-	-
5 THG	-	-	-	-	-	0.84	-	-	-	-
6 BHT	-	-	-	-	-	-	0.44	-	-	-
7 Galvinoxy	-	-	-	-	-	-	-	0.84	-	-
8 HG	-	-	-	-	-	-	-	-	0.84	-
9 CBP	-	-	-	-	-	-	-	-	-	0.46

5.2.2 RESULTS

The cure characteristics are shown in Table 5.5. BQ, HQ, SB and Galvinoxyl reduced both the rate of cure and modulus. The effect of HQ was most marked. The other compounds have no effect on the cure characteristics.

Table 5.6 shows the products identified from BQ, HQ, BAL, SB and BHT after vulcanisation. BAL, BQ and HQ showed no further products. SB had the starting material and BQ while BHT had been transformed into HQ and BAL.

Products identified during and after fatigue failure are shown in Table 5.7. BQ and HQ had the other in addition. BAL was transformed into BQ while an appreciable amount of the starting material was present. From SB were identified BQ, HQ, THG and the starting SB. BHT was partially transformed into BQ and BAL.

Table 5.8 shows both the fatigue lives of the compounded and swollen samples. In the compounded samples, SB was the most effective followed by Galvinoxyl, BQ, HQ, BHT, CBP, BAL, THG and HG in that order. Only SB, Galvinoxyl, BQ, HQ and BHT were better than the control.

In the swollen sample, Galvinoxyl became the best, followed by SB, BQ, HQ, CBP and BHT. They were all better than the control. All compounds with the exception of BHT showed increase in fatigue lives.

Table 5.5 Cure Characteristics of Peroxide Vulcanisate Containing Transformation Products

Test Compounds	Test R_{max} m-kg	Attained R_{max} m-kg	$k \times 10^{-1}$ min^{-1}	Cure Time (min)
Control	3.3	5.1	1.38	14
BQ	3.3	4.2	1.02	21
HQ	3.3	3.78	0.92	31
BAL	3.3	5.1	1.38	13.5
SB	3.3	4.2	1.02	21
THG	3.3	5.1	1.38	15.5
BHT	3.3	5.1	1.38	13.5
Galvinoxyl	3.3	4.2	1.02	21
HG	3.3	4.68	1.25	16.5
CBP	3.3	5.1	1.38	13.5

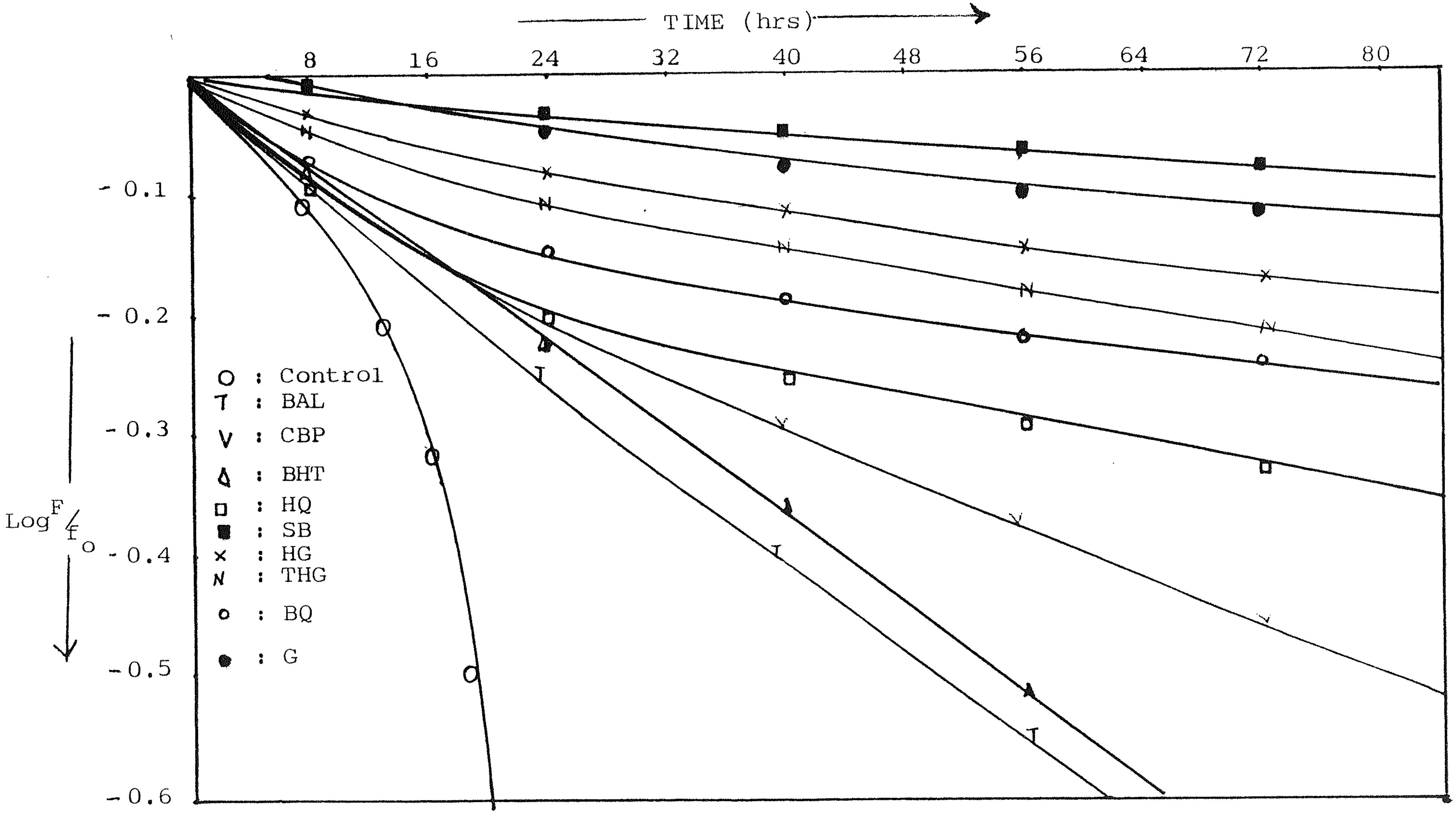


Fig. 5.1 : Continuous Stress Relaxation Curves of Identified Transformation Products and Control Compounds in Peroxide Vulcanisates at 100°C and 60% Extension

Table 5.6 Further Products Identified from the Transformation Products After Vulcanisation

Compound	Infra-red Spectra	Products Identified by GLC
BQ	Phenolic OH - (absent) Quininoid C=O 1680 (strong)	BQ
HQ	Phenolic OH 3640cm^{-1} (strong) Quininoid C=O (absent)	HQ
BAL	Phenolic OH 3620cm^{-1} (medium) Aldehydic C=O 1710	BAL
SB	Phenolic OH (absent) Quininoid C=O 1680^{-1} (strong)	BQ SB
BHT	Phenolic OH 3640cm^{-1} (medium) Carbonyl C=O 1680-1720cm^{-1} (broad and weak)	HQ BAL

Table 5.7 Further Products Identified from Transformation Products During and After Fatigue Failure

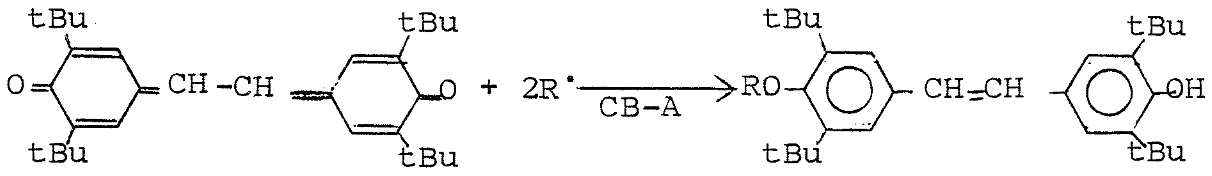
Compound	Products Identified During Fatigue (20 hrs)	Products Identified After Fatigue Failure
BQ	BQ, HQ	BQ, HQ
HQ	HQ, BQ	HQ, BQ
BAL	BAL	BHBA, BAL
SB	BQ, HQ, SB	BQ, HQ, THG, SB
BHT	BQ, BAL	BQ, BAL

Table 5.8 Fatigue Lives of Compounded and Swelled-in Peroxide Vulcanisates Containing Transformation Products at 60% Extension

Test Compound	Compounded (hrs)	Swelled (hrs)
Control	39.5	36.7
BQ	48.4	79.5
HQ	45.3	67.03
BAL	27.7	32.5
SB	56.2	84.6
THG	20.2	25.4
BHT	47.1	38.7
Galvinoxyl	50.4	101.2
HG	35.5	42.1
CBP	34.2	7.1

5.2.3 DISCUSSION

The relatively low antifatigue activity of galvinoxyl, SB, BQ and HQ in the compounded samples is due to radical scavenging by these compounds with a resultant reduction in their concentration. The radical scavenging activity is also seen in the reduction in the rate of cure[112] and lower crosslink density of the peroxide vulcanisate. In addition, the significant improvement in antifatigue activity of these compounds when swollen into the vulcanisate supports the view that a proportion of these compounds must have been used up during the compounding and curing processes thus reducing their activity as alkyl radical traps. SB and BQ act through a system of conjugated bonds present in their molecule, 5-2.



5-2

The activity of HQ can be explained on the basis of Scheme 5.4 whereby a complementary mechanism operates. The poor antifatigue of BAL, THG and BHT is because they are not chain-breaking acceptor antioxidants. However, THG showed significant reduction in the rate of stress decay while BHT and BAL had marginal activity. The activity of THG, BHT and HQ is related to their CB-D mode of action. The response given by SB, BQ and galvinoxyl in stress relaxation may seem surprising because of their CB-A mode of action. However, these compounds are transformed into species which have CB-D activity (Table 5.6).

CHAPTER SIX

6. CONCLUSION AND SUGGESTION FOR FURTHER WORK

6.1 CONCLUSION

The study reported in this Thesis focussed on the antifatigue activities of a number of organic sulphur compounds. However, their antioxidant activities were also examined since fatigue and oxidative processes occur together during service of rubber goods. The hindered phenolic sulphur compounds possess antifatigue activity but about half that exhibited by IPPD. On the other hand they have better antifatigue activity than the hindered phenolic compounds - MDPP and MDBP, suggesting autosynergism between PD-C and CB-A/CB-D functions. Further evidence of autosynergism was obtained from the transformation products identified during fatiguing and the subsequent evaluation of these products as antifatigue agents. The hindered phenolic sulphur compounds were found to be transformed into sulphur acids (PD-C), quinonoid products (CB-A), bisphenol and quinone methide (CB-D).

DLTP-related organic sulphur compounds - GDMA and GDMA-S - examined possessed antifatigue activity which was ascribed to their sulphur acids and derived diradicals.

From the mechanistic study, it was apparent that the oxidation products of the hindered phenolic sulphur compounds were responsible for the observed antifatigue activities, however their transformation in-situ enhances their performance. In this regard, some sulphoxides compounded normally into a CBS-sulphur stock, exhibited reduced antifatigue activity because of the early loss of sulphur as SO_2, thus leaving only the phenolic products which on their own are less efficient antifatigue agents. This finding was further strengthened by the result obtained in the preprocessing of BDBDS, BDBS, MADA and MADA-S where the transformation products were generated in-situ with a resultant improvement in antifatigue activities. Certain preprocessing conditions like CTP and CTP_2 gave the desired enhancement especially in the case of BDBDS which had the lowest antifatigue activity among the hindered phenolic sulphur compounds.

The hindered phenolic sulphur compounds had marginal ozone resistance in CBS-sulphur vulcanisate but were better than DLTP. In peroxide vulcanisate, they were far better than IPPD and DBDS, having outstanding antiozonant activity.

All the organic sulphur compounds examined showed marked reduction in the rate of stress decay and rate of oxygen absorption. Their PD-C and CB-D roles have been shown to be responsible for the observed activities. Again preprocessing of BDBS and BDBDS resulted in marked improvement in their thermal antioxidant activities which is linked to the early introduction of the transformation products in-situ.

6.2 SUGGESTION FOR FURTHER WORK

Stabilisation of rubber against fatigue failure has centred mainly on the deactivation of alkyl radicals thus preventing them from entering into further reactions with oxygen. In conjunction with this line of investigation, the antifatigue activities of these hindered phenolic sulphur compounds may be further improved by replacing the tertiary-butyl substituents at the ortho-position with electron withdrawing substituents.

Finally, it is worth evaluating GDMA and GDMA-S in polymer systems (especially in plastics) where DLTP is currently being utilised since it seems that they may synergise effectively with phenolic antioxidants.

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