To my parents, my wife and my son,Adrian.

THE ANTIOXIDANT FUNCTION OF DITHIOPHOSPHORYL COMPOUNDS IN RUBBERS

by

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DECLARATION

The work described in this thesis has been carried out between October 1980 and February 1984. It has been done independently and submitted for no other degree.

S Honggokusumo

July 1984

THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

A quantitative study of the reaction between 0,0-dialkyldithiophosphoric acids and natural rubber latex, showed that a moderate yield of adduct was obtained using low concentrations of the acids. High concentration of the acids caused coagulation of the latex due to their acidity. Attempts to bind the dithiophosphoryl compounds mechanochemically under shearing condition in the polymer melt resulted in a lower extent of binding. The adduct, however made, became unbound during vulcanization. All the dithiophosphoryl compounds examined were found to exhibit a pro-oxidant effect in conventional accelerated sulphur vulcanizates, but bis-(0,0-dibutyl)thiophosphoryl disulphide was shown to improve oxidation resistance in low sulphur (CBS-EV) and sulphurless (TMTD) vulcanizates.

Bis-(0,0-diisopropyl)thiophosphoryl disulphide and bis-(0,0-dibutyl)thiophosphoryl disulphide have been found to possess antifatigue activity in peroxide vulcanizate cured at 160°C. The activity increased considerably when the stocks were cured at 180°C. An infra-red examination of the reaction using squalene as a model compound revealed that a transformation product characterized as a sulphenic acid was formed. This compound is believed to be involved in the regenerative process during fatiguing and the corresponding sulphinyl radical acts as an alkyl radical trap. Ultraviolet spectroscopic analysis showed the formation of conjugated diene and triene supporting the above mechanism.

KEY WORDS
DITHIOPHOSPHORYL COMPOUNDS
MECHANOCHEMICAL
PRO-OXIDANT
ANTIFATIGUE AGENT
SULPHENIC ACID

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LIST OF ABBREVIATIONS

NAME	CODE
Ammonium O,O-dibutyldithiophosphate (Ammonium O,O-di-butylphosphorodithioate)	ABuTP
Bis-(O,O-dibutylthiophosphoryl) disulphide [Bis-(O,O-di-butylphosphorothioic) disulphide; O.O.O.O-Tetra-butyl thioperoxydiphosphate]	BuTPDS
Bis-(O,O-diisopropylthiophosphoryl) disulphide [Bis-(O,O-di-isopropylphosphorothioic) disulphide; O.O.O.O-Tetra-isopropyl thioperoxydiphosphate]	P^{i}TPDS
Bis-(O,O-diOctylthiophosphoryl) disulphide [Bis-(O,O-di-Octylphosphorothioic) disulphide: o,o,o,o-Tetra-Octyl thioperoxydiphosphate]	OcTPDS
Cumene hydroperoxide (1-Methyl-1-phenylethyl hydroperoxide)	CHP
N-Cyclohexylbenzthiazylsulphenamide	CBS
Dibenzthiazyl disulphide	MBTS
O,O-Dibutyldithiophosphoric acid (O,O-Di-butylphosphorothioic acid; O,O-Di-butyl hydrogendithiophosphate)	BuTPH
Dicumyl peroxide bis-(1-Methyl-1-phenylethyl) peroxide	DCP
O,O-Diisopropyldithiophosphoric acid (O,O-Di-isopropylphosphorodithioic acid; O,O-Di-isopropyl hydrogendithiophosphate)	P^{i}TPH
O,O-DiOctyldithiophosphoric acid (O,O-Di-Octylphosphorothioic acid; O,O-Di-Octyl hydrogendithiophosphate)	OcTPH
N-Isopropyl-N'-phenyl-p-phenylene diamine	IPPD
2-Mercaptobenzthiazole	MBT
Natural rubber	NR
Tetraethylene pentamine	TEPA
Tetramethylthiuram disulphide	TMTD
Tertiary-butyl hydroperoxide	TBH
Zinc O,O-dibutyldithiophosphate [Zinc bis-(O,O-di-butylphosphorodithioate)]	ZBuTP
Zinc dimethyldithiocarbamate	ZDMC

CHAPTER ONE

AN INTRODUCTION TO THE DETERIORATION AND STABILIZATION OF NATURAL RUBBER

1.1 Introduction

The desirable properties of rubber compounds are lost when those articles are affected by heat, ozone, radiation or mechanical action. Oxygen is known to be the major factor responsible for the deterioration of rubbers. The attack of oxygen on rubber compounds is activated by such factors as heat, light, metallic impurities and mechanical action such as fatigue(1-4).

Chemical research into natural rubber is directed at two main objectives; to improve the behaviour of natural rubber during the manufacture of the rubber articles, and to improve the performance in service of these articles. This includes research into the oxidative degradation of natural rubber and the mechanism by which antioxidants function to retard this process.

Antioxidants are often lost from the rubber during the service life of the rubber compounds by volatilization and leaching effects. If however, the antioxidants are chemically bound to the polymer(5-8), the loss of antioxidants can be minimised, and hence the service life of the rubber articles lengthened considerably. The concept and the advantages of network bound antioxidants which were initially ignored by rubber manufacturers, are now beginning to attract attention.

1.2 Autoxidation

The rubber hydrocarbon which contains double bonds and hence labile C-H bonds is highly sensitive towards atmospheric oxidation at moderate temperatures. A series of studies in the laboratories of Natural Rubber Producers' Research Association (NRPRA; now the Malaysian Rubber Producers' Association; MRPRA)(9-14) established the free-radical chain reaction mechanism which is now generally accepted. It applies not only to olefins for which it was originally developed but also to alkanes(12), saturated polymers and many other organic compounds(1,15-18). The reaction mechanism can be represented by the following sequence(19-21):

Initiation:

$$\mathrm{ROOH} \longrightarrow \mathrm{RO^{\cdot} + {}^{\cdot}OH} \tag{1.1}$$

$$\mathrm{2ROOH} \longrightarrow \mathrm{RO^{\cdot} + RO_2^{\cdot} + H_2O} \tag{1.2}$$

Propagation:

$$\mathrm{RO_2^{\cdot} + RH} \longrightarrow \mathrm{ROOH + R^{\cdot}} \tag{1.3}$$

$$\mathrm{R^{\cdot} + O_2} \longrightarrow \mathrm{RO_2^{\cdot}} \tag{1.4}$$

Termination:

$$\mathrm{2R^{\cdot}} \longrightarrow \mathrm{R\text{-}R} \tag{1.5}$$

$$\mathrm{R^{\cdot} + RO_2^{\cdot}} \longrightarrow \mathrm{RO_2R} \tag{1.6}$$

$$\mathrm{2RO_2^{\cdot}} \longrightarrow \text{Non radical products} + \mathrm{O_2} \tag{1.7}$$

According to the reaction scheme above, the primary product of oxidation, hydroperoxides (ROOH) are also the main initiator. During the initiation period of the oxidation process, hydroperoxides present at very low concentration are capable of decomposing to form radicals initiating free radical chain mechanism. It is for this reason that these reactions are commonly referred to as autoxidation; that is, an auto-catalytic process. The degradation of the hydroperoxides can be accelerated by light (1.1), heat and metal ion (1.2) (1,2,22,23). Free radicals are also capable of initiating the oxidation and may be produced from the substrate (RH) either by a bimolecular reaction with oxygen (1.8):

$$RH + O_2 \longrightarrow R^{\cdot} + HOO^{\cdot} \qquad (1.8)$$

$$R{-}R \longrightarrow 2R^{\cdot} \qquad (1.9)$$

or by mechanochemical chain scission of the rubber chain or by photolysis (1.9) (24,25).

The higher the concentration of peroxide, the more rapid is its rate of degradation. The chain reaction is normally terminated by combination of two radicals, predominantly by reaction 1.7.

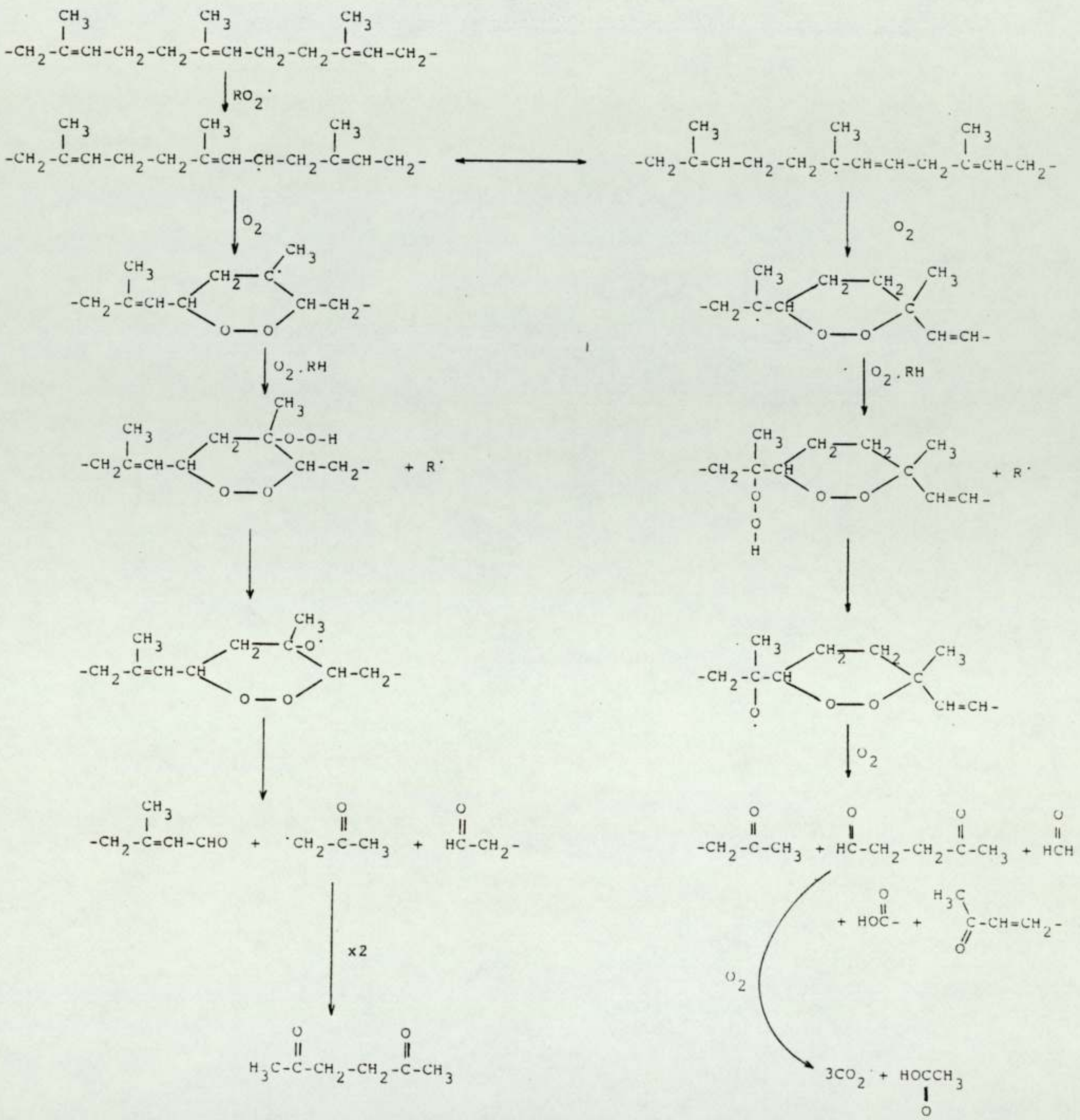
1.3 Oxidative Degradation of Raw Rubber

On the basis of analytical and chemical evidence from low molecular weight products related to autoxidizing natural rubber, a number of possible routes to scission in natural rubber have been postulated(26-37). The generally accepted routes are those which suggest that peroxy radicals formed in autoxidation are able to react intramolecularly by addition to an adjacent double bond to form cyclic peroxidic intermediates. It is likely that more than one cyclic structure is involved. The initial peroxy radical could remove an allylic hydrogen from the methylene group of an isoprene unit, and allylic rearrangements would further increase the number of possible structures for producing radicals(19,20,36,37). The oxidative scission of natural rubber is shown in Scheme 1.1.

1.4 Oxidative Degradation of Vulcanized Rubber

Oxidative degradation of vulcanized rubber differs substantially from that of the raw rubber from which they were prepared. The oxidation process is complicated by the presence of sulphur crosslinks which impart useful properties to the rubber components during service. There are two types of scission which can occur in a vulcanizate; main chain scission or crosslink scission(14,38-40). Their effects on the physical properties are different. Main chain scission in the early stages of oxidation will reduce physical properties about four times more than crosslink scission(39).

In rubber vulcanizates prepared by peroxide and high energy radiation crosslinking, in which the crosslinks are direct carbon-carbon links, thermal oxidation is autocatalytic



<u>Scheme 1.1</u> The possible mechanisms for the autoxidation of natural rubber

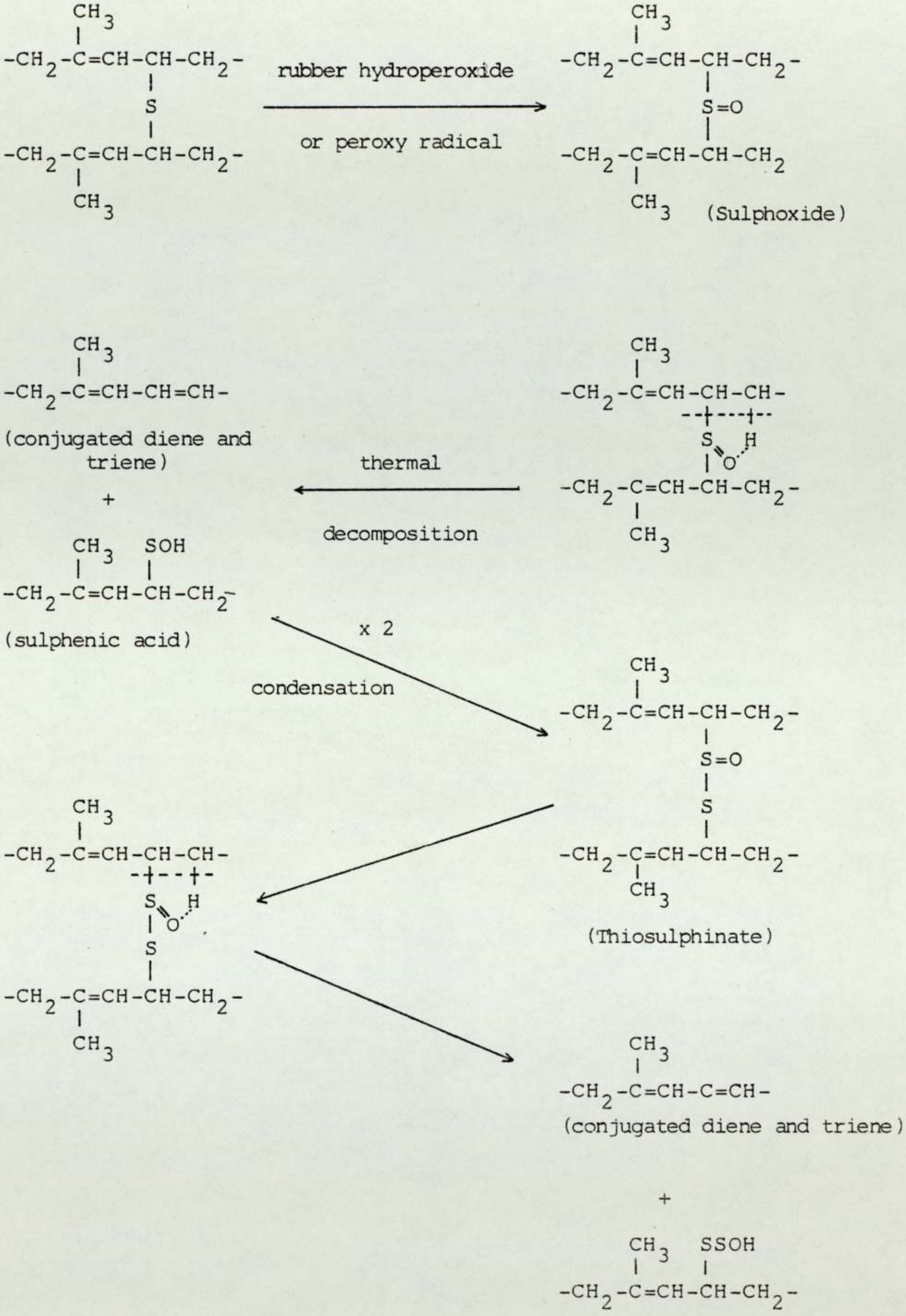
and degradation is due to main chain scission(42-45), which corresponds closely with that observed for raw rubber(46).

In the case of sulphurated crosslinks, apart from the main chain scission due to autoxidation, crosslinks are also oxidized(14,38,40,47-56). Vulcanizates which contain mainly monosulphidic crosslinks undergo oxidation by hydroperoxides or peroxy radicals to form sulphoxide which is thermally unstable(53), leading to decomposition with scission at the C-S bonds to give sulphenic acid intermediates. The sulphenic acids undergo condensation giving a thiosulphinate crosslink which may also undergo scission by a similar mechanism(47,55). Conjugated dienes, trienes and ketone groups are also formed along the main chain as a likely consequence of crosslink decomposition (14,47,55). The oxidation processes are illustrated in Scheme 1.2.

Disulphide crosslinks are thermolabile and susceptible to oxidation by hydroperoxide in a similar way to give thiosulphinate, which undergoes a free radical disproportionation in the presence of peroxy compounds (1.10)(47,54,55).

$$\text{RSSR} \longrightarrow \text{RSOSR} \longrightarrow \tfrac{1}{2}\text{RSO}_2\text{SR} + \tfrac{1}{2}\text{RSSR} \qquad (1.10)$$

Little is known about oxidation of polysulphide crosslinks, but it is believed that they will behave in a similar manner(55).



Scheme 1.2 Oxidation of monosulphidic crosslink

1.5 Fatigue Failure of Rubber Vulcanizates

A number of rubber components are subjected to repetitive stresses during service. The rubber is gradually weakening and eventually fracture occurs due to repeated deformation at energies much lower than the breaking strain. This failure is commonly termed "fatigue" failure. In the absence of heat build-up which may also occur in thick components(57-59), this failure arises from the development of a crack initiated by small flaws initially present in the rubber(57,60-62). The growth of the cracks is primarily due to mechanical rupture of the polymer molecules and accelerated by oxygen and ozone(1,63-67).

The pre-existing flaws are formed from a number of sources(58,68,69) such as; poorly dispersed compounding ingredients, polymer gel, dirt, grit particles, trapped air, areas of unequal cure, or accidental damage in service or on removal from the mould.

The roles played by oxygen and ozone are clearly distinct, although the combined effects of the two stimulants may be synergistic(1). Ozone effects the formation of deep cracks perpendicular to the direction of applied strain on the surface of rubber, whereas oxidation leads to a random development of shallow cracks. When mechanical rupture occurs under the influence of oxygen, the failure is termed as 'mechanico or mechano-oxidative' failure(1,57,58,70,71).

1.5.1 Mechanical Aspects of Crack Growth and Fatigue of Rubber

A satisfactory explanation of fatigue failure in rubber has been developed by workers at MRPRA(57,61,62,65-67,70,72-76). The crack growth characteristics of vulcanized rubber are based on the strain energy release rate concept originally proposed by Griffith(77), and the approach began with a study of tear behaviour by Rivlin and Thomas(72). This approach considered the energetics of crack propagation and the energy release rate has become known as the 'tearing energy'.

The fatigue life of a rubber specimen can be predicted mathematically from the crack growth behaviour, assuming that the crack growth is initiated at small flaws, and the tearing energy (T) is given in terms of the crack length. If a crack in a strained test piece grows by a small amount, thus producing an area dA of new surface, the amount of elastic strain energy (U) stored in the strained test is reduced by dU(Eq 1.1). The test piece is considered to

$$T = - \frac{dU}{dA} \quad l \qquad \text{(Eq 1.1)}$$

be held at constant length l, so that the external forces do not interfere.

If the tearing energy is known in terms of the crack length, the above expression can be integrated to give the fatigue life. The tearing energy of an edge crack in a simple extension strip is given by

$$T = 2KWc \qquad \text{(Eq 1.2)}$$

where K is a constant which varies as a function of extension and W is the strain energy density in the bulk of the test piece. c is the crack length in the unstrained rubber.

It has been found that the crack growth per cycle for a repeated stress through zero strain can be expressed by a power law relationship of the form(67,73)

$$\frac{dc}{dn} = BT^{\beta} \qquad \text{(Eq 1.3)}$$

where c is the crack length, n the number of cycles, B and β are constants for a given rubber. By integration, Equations 1.1 and 1.2 can be used to derive the Equation 1.4 for the fatigue life N.

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

where c_o is the effective length of initial flaws and its value is 2.5 x 10^{-3} cm for natural rubber.

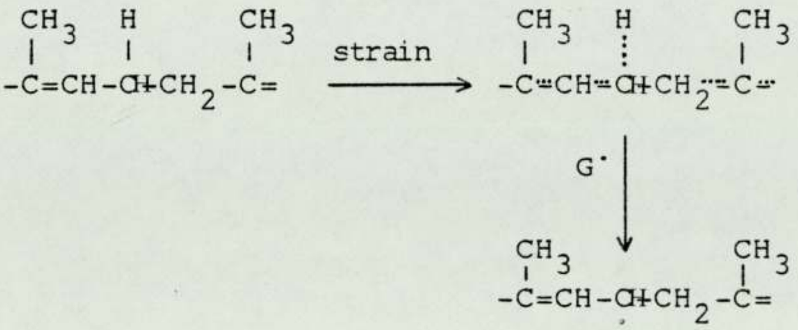
1.5.2 Factors Affecting Fatigue Life of Rubber Vulcanizates

1.5.2.1 Effect of Oxygen

Oxidative ageing in rubber is a fairly well understood process that leads to a general deterioration in strength and other physical properties. It has been known that oxygen also plays an important role in the fatigue behaviour of rubber(71,79). The process differs from oxidative ageing in that it can occur without changing its bulk properties such as modulus(74,80). Gent(79) reported that unprotected natural rubber vulcanizates show an increase in fatigue life if the fatigue tests were carried out in vacuo rather than air. He also stated that the effect of oxygen is more pronounced at low strains. However, the mechanism of this oxidative process has remained unclear. The possible processes that have been suggested are:

1) the macro alkyl radicals formed by mechanical rupture of polymer chain react with oxygen, since oxygen is known to be an efficient radical acceptor(1,71,78).
2) The very high mechanical energy in the vicinity of a crack tip acting somewhat similarly to high thermal energy in activating reaction with oxygen(57,74).

Porter and Scott(78) studied the formation of free radicals in stressed rubber using ESR spectroscopy and found that the rate of disappearance of stable aryloxy radical (galvinoxyl) in peroxide vulcanizate increased with stress applied. They concluded that double bonds and C-H bonds adjacent to the double bond are weakened by strain energy. This leads to addition of galvinoxyl (G˙) to the activated double bond or abstraction of the weaker hydrogen atom:



$$\overset{CH_3}{\overset{|}{-C}}=CH-\overset{H}{\overset{|}{C}}H-CH_2-\overset{CH_3}{\overset{|}{C}}= \xrightarrow{\text{strain}} \overset{CH_3}{\overset{|}{-C}}\cdots CH\cdots\overset{H}{\overset{\vdots}{C}}H-CH_2\cdots\overset{CH_3}{\overset{|}{C}}\cdots \xrightarrow{G^{\cdot}} \overset{CH_3}{\overset{|}{-C}}=CH-\underset{\cdot}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}}= \;+\; GH \qquad (1.11)$$

It seems likely that the activation of rubber to oxygen under stress is associated with the reaction of oxygen with rubber.

Using the tearing energy approach, Lake$^{(74)}$ explained that there is a minimum tearing energy (T_o) at which mechano-oxidative cut growth can occur. The presence of oxygen appears to lower the value of T_o.

1.5.2.2 Effect of Ozone

The effect of ozone on fatigue differs from that of oxygen in that it appears to be solely responsible for crack growth below $T_o$$^{(57,81)}$. In this region the rate of growth is proportional to the ozone concentration and is independent of tearing energy. Above T_o, its effect is negligible because the rate of growth due to mechano-oxidative effects is very much higher(82).

The reaction between ozone and double bond is believed to cause direct cleavage of that bond and hence of the polymer chain. As a result, crack growth can occur if the rubber is stressed, and this applies not only as a contributory factor in fatigue at low strain, but also under constant deformation.

1.5.2.3 Effect of Vulcanizing Systems and State of Cure

Fatigue strength is markedly dependent on the nature of the network structure and hence the vulcanization systems used(83). It has long been recognised that conventional sulphur cured natural rubber compounds exhibit good fatigue characteristics but poor thermal and oxidative ageing resistance. High sulphur - low accelerator ratio in this vulcanizing system produces a relatively high proportion of polysulphidic crosslinks which impart a high degree of flexibility, which are able to break and reform during fatiguing(51,74,84-86). Mullins(87) suggested that the slippage of weak crosslinks allows relief of localized high stresses at the tip of the crack so that they become more uniformly distributed around the crack.

Efficiently vulcanized (EV) systems(88-90) i.e., low sulphur - high accelerator ratios or replacement of free sulphur with sulphur donors, produce mainly monosulphide crosslinks. This thermally stable type of crosslink, unlike the polysulphidic type, cannot readily exchange or rearrange under high localised stresses, so that fracture of the linkage results in a site which is a potential source of further crack growth. Peroxide cures(91) promote the formation of carbon-carbon crosslinks which impart very good thermal stability. However, the fatigue life of those vulcanizates are generally poor.

The semi-EV systems(89,90) are characterized by the use of an intermediate sulphur to accelerator ratio or by partial replacement of sulphur with a sulphur donor. These systems produce networks intermediate in structure, thermal stability and fatigue characteristics between those of conventional and EV systems.

The fatigue characteristics of rubber vulcanizates are dependent on the state of cure and curing time(92). Increasing the degree of crosslinking decreases the fatigue resistance. This is presumably related to the capacity of the rubber molecules for orientation, and a decrease in the degree of orientation increases the molecular stresses(1). If the level of crosslinking is too low, it may also lower resistance to crack growth(93).

The fatigue characteristics of polysulphidic crosslinks are superior to that of monosulphidic and carbon-carbon crosslinks when the test pieces pass through a zero strain (completely relaxed). However, under non-relaxing conditions, vulcanizates produced by EV systems are as good or better than conventional vulcanizates(94). It has been confirmed that the strain cycle has a profound effect on the fatigue life of natural rubber vulcanizates(58,74,95-98) due to the ability of natural rubber to undergo strain-induced crystallization, resulting in an increase in T_o and a reduction in the rate of crack growth at higher tearing energy(74). The different properties of vulcanizates containing predominantly different types of crosslinks was suggested to be accounted for on the basis of other factors, including the distribution of network chains(99) and main chain modification(100).

1.5.2.4 Other Factors

Other factors which influence the fatigue life of rubber components that have been reported in the literature include strain energy, temperature, ingredients dispersion, fillers.

The energy involved in the deformation of rubber components has a significant effect on the fatigue life(58). Increasing energy input will decrease the fatigue life since the greater amount of work done, the faster failure occurs, providing the minimum strain is held constant.

Natural rubber shows a small decrease in fatigue life with temperatures up to 100°C. At temperatures relatively close to the glass transition temperature, the rate of crack growth is much reduced(65). These effects are mainly associated with changes in hyster sis behaviour at high strain(74).

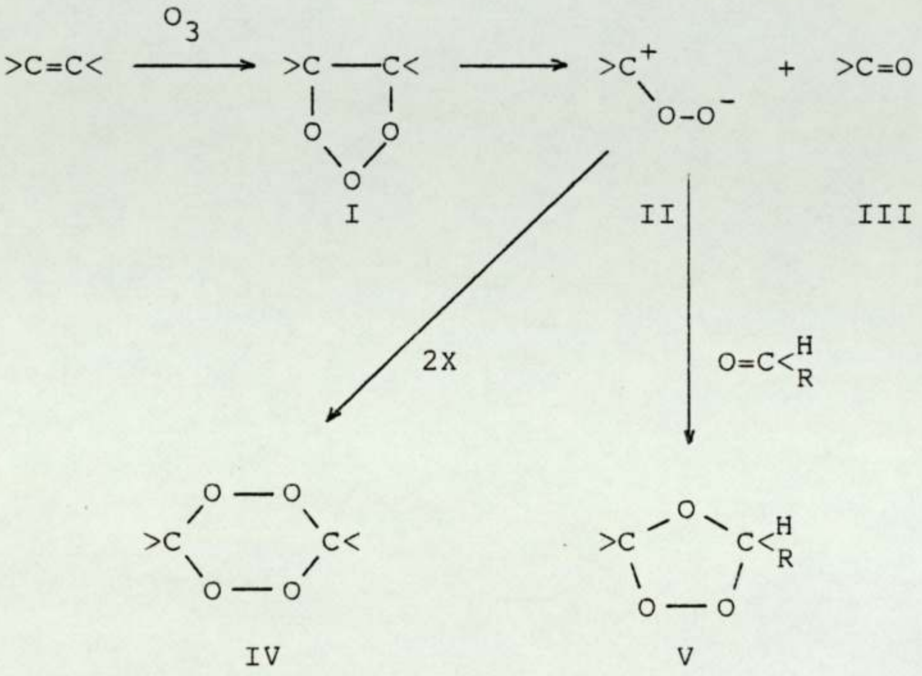
The dispersion of compounding ingredients also affects the fatigue properties, since the uniformity of the distribution of crosslinking sites will be affected. Small particle size fillers generally have little effect on fatigue life if comparisons are made on an equal energy basis(58).

1.6 Ozone Cracking of Rubber

The cracking of rubber due to ozone attack is a problem of considerable magnitude, although the concentration of ozone in the atmosphere is normally less than five parts per hundred million (pphm). Ozone reacts with double bonds available at the surface very rapidly and causes cracking if the rubber is stretched(101). The cracks are formed at right angles to the direction of applied stress(1,102-104). Ozone attack not only detracts from the surface appearance of rubber articles, it also causes loss of physical properties, especially in thin-walled articles. Much effort has been expended in the development of antiozonants which protect against ozone attack and in the study of the mechanism involved in ozone protection.

1.6.1 Mechanism of Ozone Attack

The currently accepted mechanism was originally put forward by Criegee* on the basis of a zwitterion intermediate (Scheme 1.3). Ozone may attack the nucleophilic carbon of the carbon-carbon double bond by an electrophilic process to give rise to a molozonide (I), which is unstable in nature.



Scheme 1.3 Mechamism of ozone attack on double bond

and undergoes decomposition involving a heterolytic cleavage of the oxygen-oxygen bond to give a zwitterion (II) and a carbonyl compound (III). The zwitterion is comparatively stable and in the absence of other reagents undergoes reaction with a similar species present to give polymeric or dimeric peroxides (IV) or with the carbonyl dissociation

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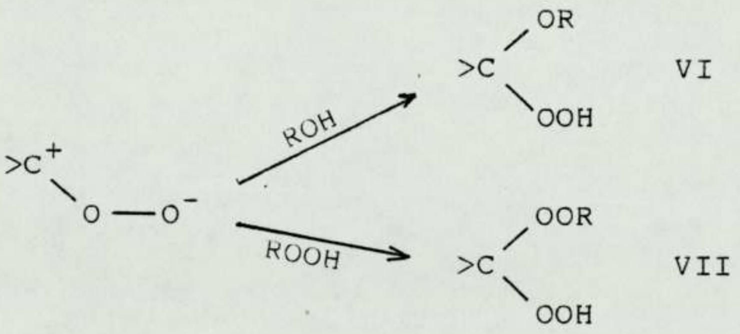
* See review by P S Bailey, Chem.Rev., 58, 925(1958)

products to give a more stable ozonide (V)$^{(1,102,105)}$. Other peroxidic products (VI and VII) may be formed when compounds containing active hydrogen such as alcohol or hydrogen peroxide are present$^{(106,107)}$.



The chemistry of double bond cleavage by ozone applies also to natural rubber. The cleavage does not seem to involve free radicals, but peroxides which are formed are detrimental to the rubber because they are able to initiate oxidative degradation.

1.6.2 Behaviour of Ozone Cracking

The reaction of ozone with double bonds in rubber occurs immediately on the surface, because the reaction is extremely fast. Chain scission causes crack formation provided the rubber is under stress. Cracks are oriented with their length perpendicular to the direction of the stress. Severed chain ends will then separate to form a new surface. The continual attack of ozone on the surfaces leads to the formation of deep cracks, and reduction in strength and fatigue life.

Braden and Gent(105,108-110) showed that the deterioration of rubber due to ozone may be considered to proceed in two stages; crack initiation and crack growth. They studied the growth of an isolated single crack and reported that the results can be readily expressed in terms of the tearing energy parameter, T, which reflects the strain at the tip of the crack. A critical T value is necessary for any growth to occur. Above this value the growth rate is substantially independent of T and the crack length,but proportional to the ozone concentration. The rate of cut growth is only slightly dependent on temperature but varies inversely with the crosslink density of the network(109).

If a bulky article is considered, such as a rubber spring or a bridge bearing used in compression, the growth of crack from the free surface is much slower than the single crack growth rate. The reduction may be several hundredfold, and it is probably due to the fact that multiple cracks open only slightly(104,111). At low strains near the fatigue limit, ozone resistance can be important in fatigue life since ozone can produce crack growth at a very low strain(112).

1.7 Antioxidants

Oxidative ageing of rubber vulcanizates causes an undesirable deterioration in their physical properties. Protection of the vulcanizates to this deterioration has received a good deal of attention over many years and a large number of antioxidants has been developed for this purpose.

Antioxidants have been classified by Scott(1) on the basis of their participation in inhibition of oxidation. Two main groups are distinguished: chain-breaking antioxidants which, by their reaction with alkyl and alkylperoxyl radicals, break the propagation cycle and thus lead to new chain termination reactions, and preventive antioxidants which inhibit or retard the formation of free radicals in the initiation step. By this means the overall oxidation process would be retarded.

1.7.1 Preventive Antioxidants

In the initiation step of the free radical chain mechanism of autoxidation, degradation of hydroperoxides to free radicals is accelerated by heat, light and metal ions(1,17,19,113,114) which can participate in electron transfer reactions. Stabilizers which are capable of retarding the initiation process may be termed as preventive antioxidants . Accordingly, these type of antioxidants can be divided into the following three groups: light absorbers, metal ion deactivators and hydroperoxide decomposers.

1.7.1.1 Light Absorbers

The damaging influence of ultraviolet light on unfilled vulcanizates is well known. It causes surface resinification, crazing and discolouration(17,115) of rubber components. Polymeric materials are subjected to photodegradation due to the presence of chromophoric groups which are either introduced during processing as adventitious impurities or as oxidation products such as carbonyl compounds. The function of light absorbers as preventive antioxidants is to reduce the effect of light on the degradation of the peroxide and to reduce the photo-excitation effect on the oxidation of rubbers; by absorbing the ultraviolet light to a minimal electron excitation level and transmitting the absorbed energy in the form of harmless low energy light quanta and thermal energy(19,116,117).

Ultraviolet stabilization in rubber vulcanizates is not very important due to presence of fillers, notably carbon black which is an effective light screen(19,113,115). Well known ultraviolet absorbers are nickel dibutyldithiocarbamate and o-hydroxybenzophenone derivatives(1).

1.7.1.2 Metal Ion Deactivators

The role of metal ion deactivators is to deactivate the catalytic effect of metal ion upon peroxide decomposition. Ions of transition metal are able to degrade the hydroperoxide to free radicals according to the following two redox reactions depending on their chemical character and oxidative state(17,19,114):

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

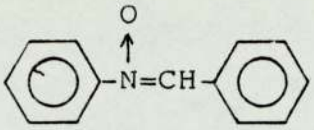
$$ROOH + M^{(n+1)+} \longrightarrow RO_2^{\cdot} + M^{n+} + H^{+}$$

Inhibition of metal ion catalysis can be achieved incorporating the metal ion in a complex, using chelating agents. Reactions which produce an insoluble compound can also deactivate the metal catalyst. Metal deactivators have not been found of use in rubber vulcanizates due to the deleterious effects of metals being alleviated by the vulcanization process. p-Phenylenediamines which are added as antioxidants, are also effective as metal deactivators. Iron is converted to insoluble FeS during the cure(115).

1.7.1.3 Peroxide Decomposers

The most important group of preventive anitoxidants consists of those which inhibit the chain initiation induced by the degradation of the hydroperoxide by degrading the hydroperoxide to stable non-radical products. Scott(113) classified this group of antioxidants into two main mechanistic classes: stoichiometric reducing agent for peroxide decomposition (PD-S) and catalysts for peroxide decomposition (PD-C)(118). Stoichiometric peroxide decomposers have the ability to destroy hydroperoxide to an alcohol(1.12) without the formation of free radicals. Phosphite esters such as trisnonylphenylphosphite (VIII) are commercially used as stabilizers for raw rubber(119). α,N-diphenylnitrone (IX) exhibits similar mechanism in reaction with

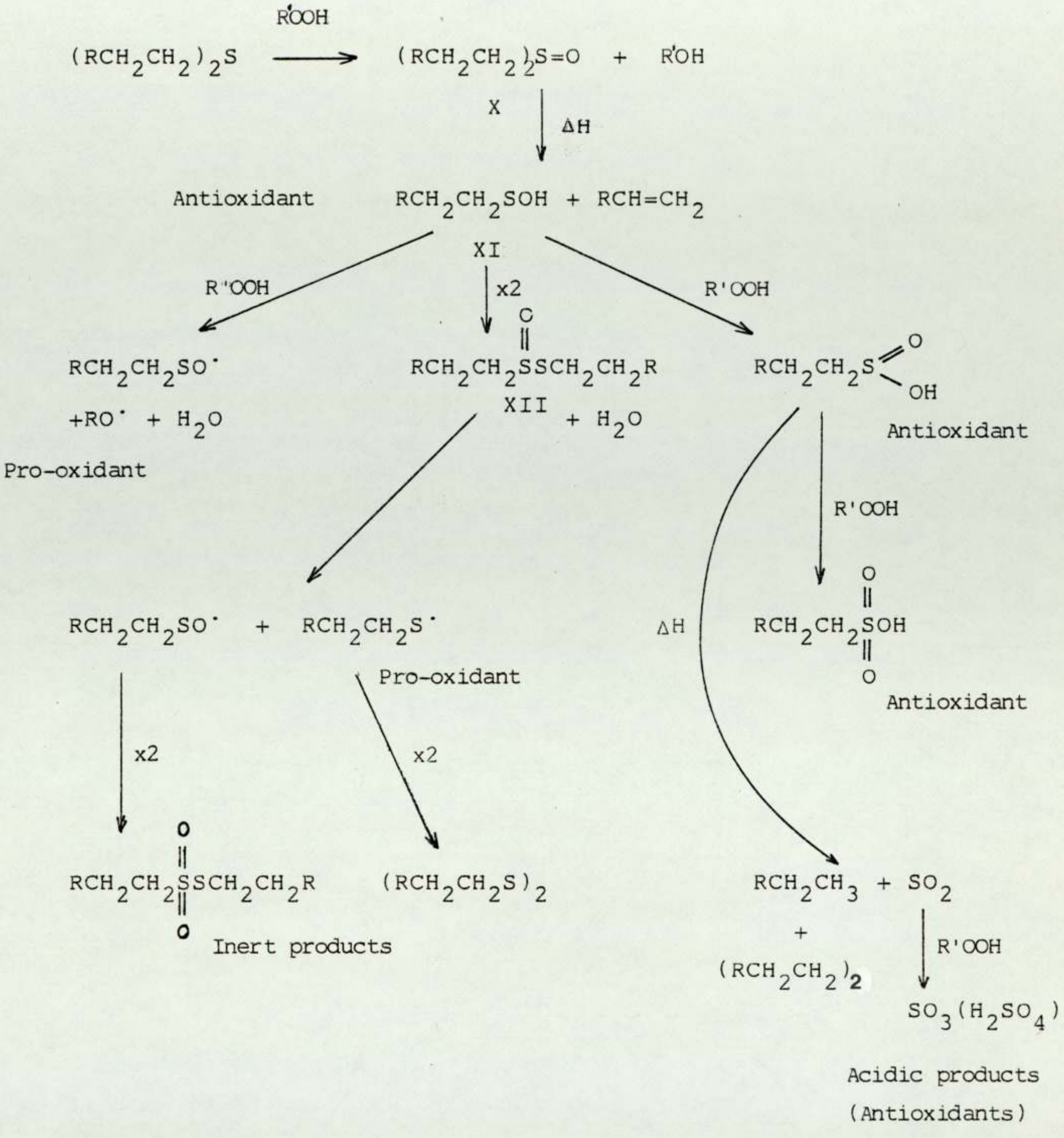
VIII (1.12)



IX

hydroperoxides. The stoichiometric reducing agent function of a wide variety of sulphur compounds occurs only at the initial stage of the reaction. Further reaction of the sulphur compounds with hydroperoxides will give rise to acidic products (Scheme 1.4).

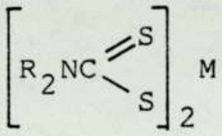
Compounds falling into catalytic peroxide decomposers are capable of degrading hydroperoxide through the formation of acidic products. A wide variety of organic sulphides and disulphides fall into this category due to production of oxygenated sulphur intermediates which then form sulphur dioxide and acids capable of destroying hydroperoxide catalytically. The antioxidant action of these compounds is typified by the chemical reaction sequence for dilaurythiodipropionate $[(C_{12}H_{25}OCOCH_2CH_2)_2S$: DLTP] shown in Scheme 1.4(113). The scheme shows that oxidized organic sulphur compounds are active as oxidative inhibitors only when hydroperoxide decomposition is involved in the autoxidation. Thermal instability of the sulphoxide (X) or

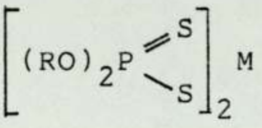


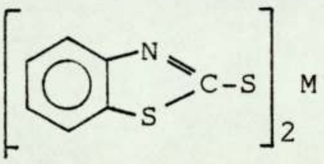
Scheme 1.4 Antioxidant and pro-oxidant behaviour during the oxidation of monosulphides

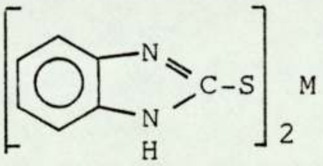
thiosulphinate (XII) was found to be an important requirement, and further oxidation gives rise to the formation of more reactive species (RSO_2H, RSO_3H, SO_2 and SO_3) for the non-radical decomposition of hydroperoxide.

The antioxidant function exhibits pro-oxidant stage originally proposed by Scott(120,121). However, the pro-oxidant effect is used to advantage in the chemical plasticisation of rubber during mastication, where thiols and disulphides are used as chemical plasticisers. Apart from the simple sulphides, derivatives of dithiocarbamic acid (XIII),


XIII


XIV


XV


XVI

dithiophosphoric acid (XIV), mercaptobenzthiozole (XV) and mercaptobenzamidazole (XVI) all act as PD-C antioxidants(113).

1.7.2 Chain-breaking Antioxidants

According to the autoxidation process, alkyl and alkylperoxyl radicals are responsible for the free radical chain reaction. Therefore, any substance which is capable of removing those radicals are potential chain breaking antioxidants and two types of chain-breaking process have been distinguished according to the redox process as illustrated in Scheme 1.5(113,122). The first involves oxidation of the

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

Electron accpetor
mechanism (CB-A)

Electron donor
mechanism (CB-D)

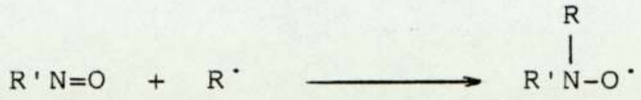
Scheme 1.5 Chain-breaking process during autoxidation

alkyl radical to give a carbonium ion or a derived product. This is known as the chain-breaking electron acceptor (CB-A) mechanism. The second involves the reduction of alkylperoxyl radical to give a hydroperoxide and this is known as the chain-breaking electron donor (CB-D) mechanism.

1.7.2.1 Chain-breaking Acceptor (CB-A) Antioxidants

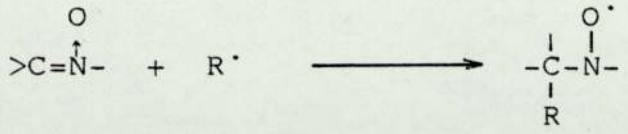
Macro-alkyl radicals are readily oxidized by electron acceptors due to their nucleophilic nature. Substances which are able to remove alkyl radicals from an autoxidizing system possess antioxidant activity(1,113). Quinones, nitro compounds, nitrones and stable free radicals such as nitroxyls and phenoxyls are the best known example of this class(113) (see reactions 1.13-1.16 and also Section 1.8).

(1.13)



$$R'N{=}O + R^{\cdot} \longrightarrow R'\overset{R}{\overset{|}{N}}{-}O^{\cdot}$$

(1.14)



$$>C{=}\overset{O}{\overset{\uparrow}{N}}{-} + R^{\cdot} \longrightarrow -\underset{R}{\underset{|}{\overset{|}{C}}}{-}\overset{O^{\cdot}}{\overset{|}{N}}{-}$$

(1.15)

$$R'_2N{-}O^{\cdot} + R^{\cdot} \longrightarrow R'_2N{-}OR \qquad (1.16)$$

1.7.2.2 Chain-breaking Donor (CB-D) Antioxidants

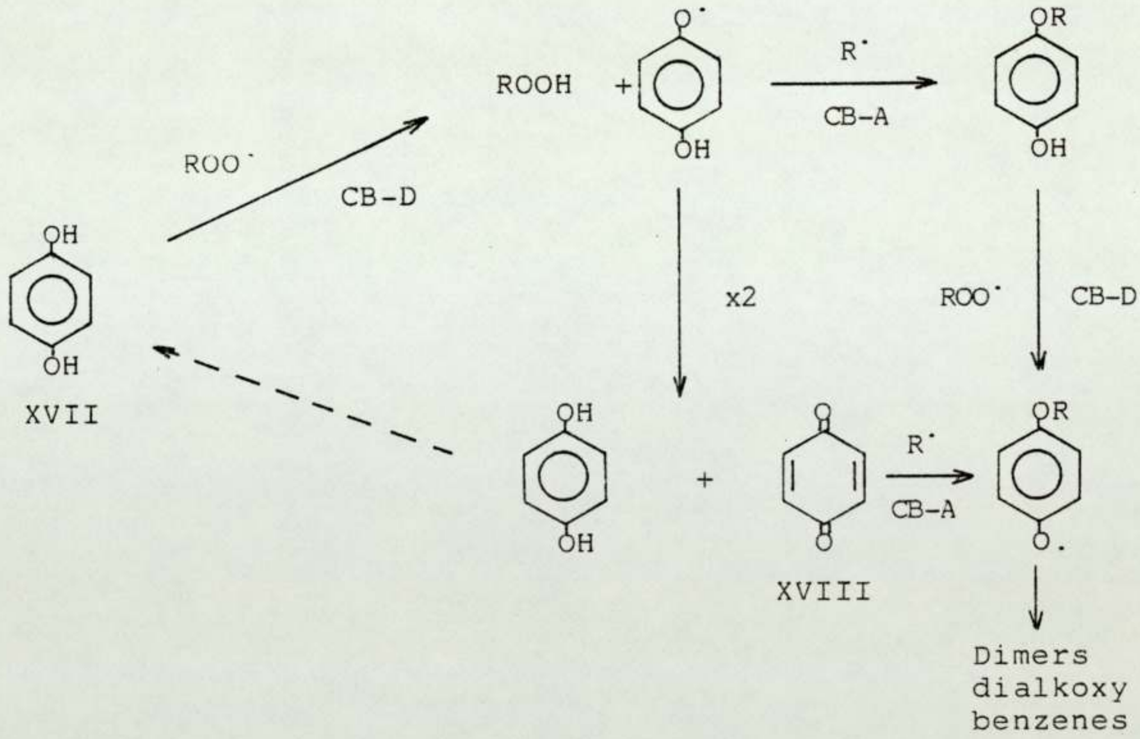
Alkylperoxyl radical removal by reduction is the most significant process occurring at ambient oxygen pressures during thermal oxidation. The CB-D antioxidants function by electron or hydrogen atom donation to an alkylperoxyl radical and thus terminate a kinetic chain. Hindered phenols and aromatic amines are typical of this category. Both fit very well into the inhibitor model described in Equation 1.17 for they possess labile H atoms and the radical desired from the antioxidant (denoted here by $A^{\cdot}$) is sufficiently resonance stabilized without abstracting hydrogen from the substrate. The antioxidant radical will then function as a radical trap and terminate a second kinetic chain(19) (see also Section 1.7.2.3).

$$ROO^{\cdot} + AH \longrightarrow [ROO...H...A] \longrightarrow ROOH + A^{\cdot} \qquad (1.17)$$

1.7.2.3 Complementary Antioxidant Mechanisms Involving Both CB-A and CB-D

In the presence of excess oxygen, the alkylperoxyl radical is the chain propagating species present in highest concentration in the system, thus, CB-D antioxidants ought to function most effectively. Conversely, the CB-A mechanism is effective in oxygen deficiency or at high initiation rates. Any antioxidant which is able to operate both kinds of mechanism simultaneously exhibits an advantage over those operating by a single mechanism, since in many oxidation processes both alkyl and alkylperoxyl radicals are present to some extent(113).

The best known antioxidant involving both mechanisms is hydroquinone (XVIII). Scheme 1.6 shows the complementary

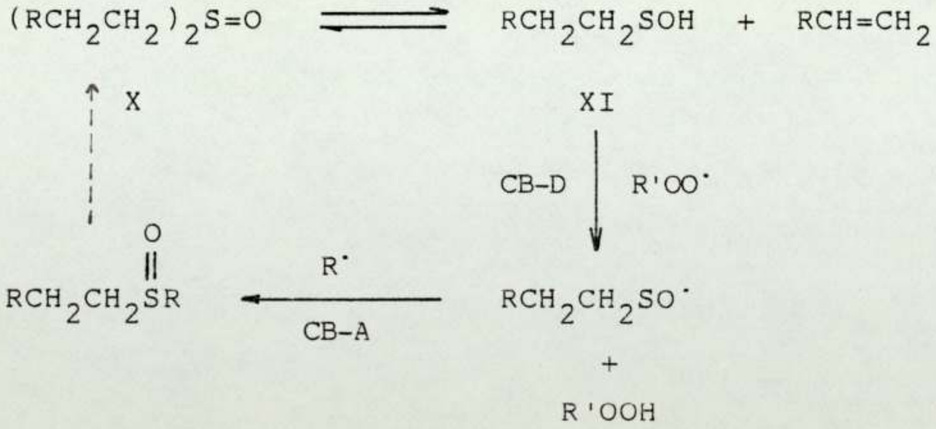


Scheme 1.6 Complementary mechanisms involving CB-D and CB-A in antioxidant functions of hydroquinone

mechanisms involving hydroquinone and its oxidation products. Hydroquinone is converted to benzoquinone (XVIII) by CB-D mechanism. However, benzoquinone is very reactive towards alkyl radicals and acts as an alkyl radical trap.

1.7.2.4 Regenerative Chain-breaking Antioxidants

An antioxidant may be more efficient when it is able to alternate between CB-A and CB-D reaction mechanisms since it may be involved in a regenerative cycle in which both alkyl and alkylperoxyl radicals are consumed(113,122). It has been shown in Section 1.7.1.3 that organic sulphides and disulphides are effective peroxide decomposers. Apart from this activity, the oxygenated products exhibit the ability to react with both alkyl and alkylperoxyl radicals. Therefore, they also act as chain-breaking antioxidants following the regenerative cycle as shown in Scheme 1.7 through the formation of sulphenic acid (XI)(122).



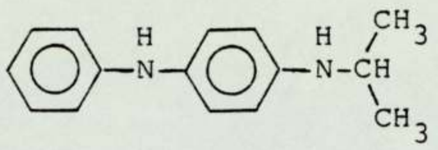
<u>Scheme 1.7</u> Regeneration of sulphenic acid

A similar regenerative process involving nitroxyl radicals has been shown to occur in the fatigue of vulcanizate rubber. Diarylamines owe their effective antifatigue activity to their conversion to the nitroxyl radical(113,123,124). The antifatigue and regenerative mechanism will be discussed in Section 1.8. Hindered piperidines(125-127) have been reported to display similar regenerative process in UV stabilization mechanisms through the effective nitroxyl ràdical. Some phenolic antioxidants behave in a similar regenerative reaction with stable phenoxyl radicals(113,127,128).

1.8 Antifatigue Agents

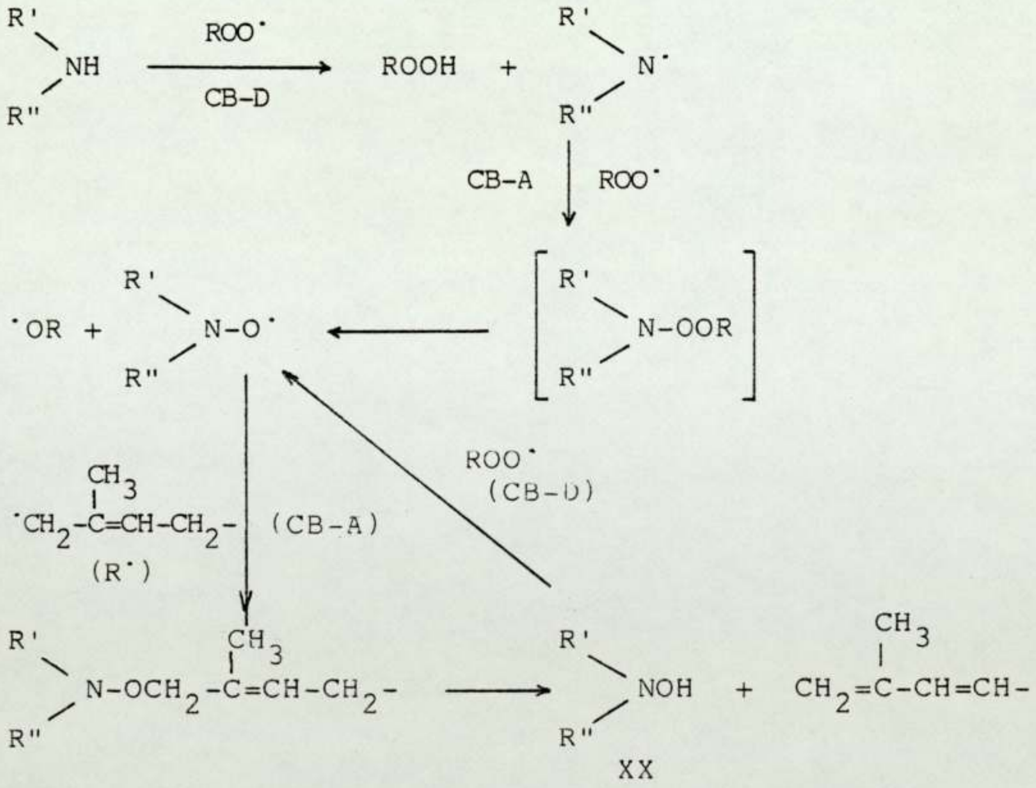
Fatigue of vulcanized rubber causes the activation of the rubber to oxygen by the generation of alkyl radicals and by activation of the double bond (see Section 1.5.2.1). Both processes can increase the rate of autoxidation by introducing mechanochemically formed radicals. The rate of alkyl radical formation in the fatiguing of rubber is much higher than that in thermal oxidation(1,71), and the oxygen concentration is limited by diffusion. A direct consequence of this is that both alkyl and alkylperoxyl radicals are involved in the fatiguing process.

The effective antifatigue agents are chain-breaking antioxidants having the capability of removing both alkyl and alkylperoxyl radicals from the system(71,113). Diarylamines are significantly more effective than other classes of antioxidants. The best known agent being N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD;XIX) commercially known as Santoflex 1P, Antioxidant-4010A or Nonox ZA. The anti-



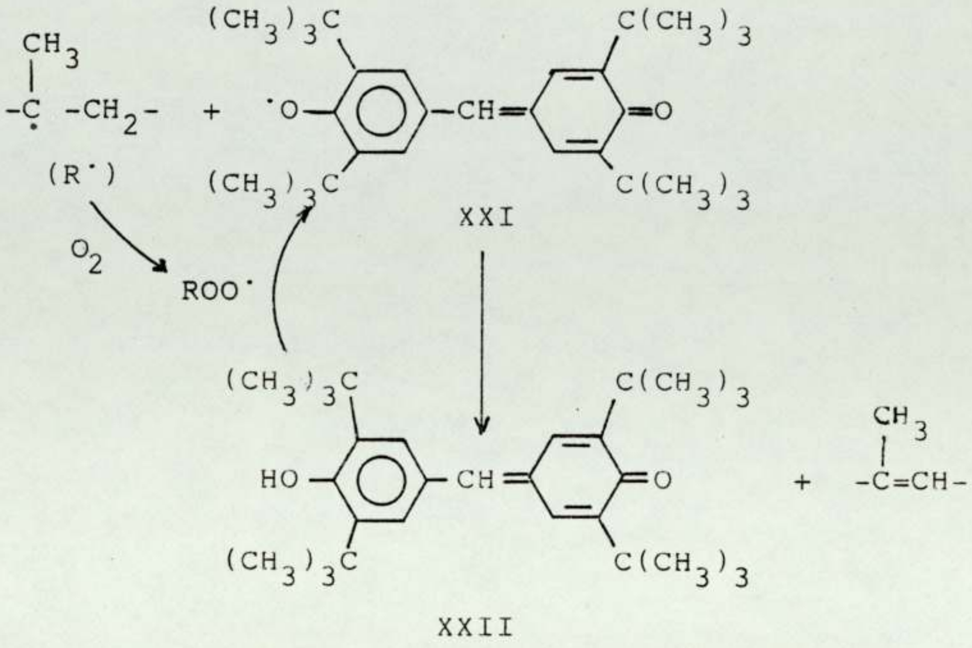
XIX

fatigue activity of the diarylamines has been shown to be due to the oxidation of these compounds to the corresponding nitroxyl radicals(129) which are able to scavenge both alkyl and alkylperoxyl radicals(113,124) (as they are both CB-A and CB-D antioxidants). The nitroxyl radicals are the key intermediates in a continual regenerative mechanism involving hydroxylamines (XX) as shown in Scheme 1.8(113,123).



Scheme 1.8 Regeneration of nitroxyl radical in fatiguing of rubber

Galvinoxyl (XXI) has also been reported to have antifatigue activity in rubber(113). It seems likely that a redox mechanism and regeneration are involved in the process. The stable galvinoxyl radical is converted to hydrogalvinoxyl (XXII, Scheme 1.9). Quinones, hydroquinones, benzoquinones,



Scheme 1.9

quinhydrones, nitrones and nitro compounds are also antifatigue agents in rubber(1). This is believed to be due to their ability to trap alkyl radicals through phenoxyl radicals (see also Section 1.7.2.1).

1.9 Protection Against Ozone Cracking

Waxes were first applied in protection against ozone attack(130). They function by blooming to the rubbers surface, thereby producing a thin layer inert towards ozone. Under dynamic services, waxes are less useful due to the lack of elasticity of the bloomed wax film. Therefore the use of chemical antiozonants is required under these conditions. The most effective protective agents against ozone cracking are N,N'-disubstituted-p-phenylenediamines(131). Among them, N-isopropyl-N'-phenyl-p-phenylenediamine (XIX) is commercially used as an antiozonant as well as antifatigue agent. When chemical antiozonants are used in combination with small amounts of waxes, the protection of ozone cracking is enhanced(1,63,71,103). The action of the wax is described as carrying the antiozonant to the surface of the rubber.

The precise protective mechanism of the para-phenylenediamines is not yet clear. Several different theories have been proposed.

1) The scavenger mechanism. This theory suggests that the antiozonant migrates to the surface of the rubber and reacts with ozone due to their greater reactivity towards ozone than that of the rubber double bond(132-135).

2) The protective film mechanism. The reaction of ozone with antiozonant forms a protective layer over the rubber surface(135-138). Andries and coworkers suggested a dual scavenger and protective layer mechanism.

3) The relinking mechanism. This theory states that antiozonant reacts with ozonization products such as aldehydic end groups leading to relinking of severed chain ends through an aldol condensation(137,139,140).

4) The self-healing mechanism. This theory explains that the antiozonant reacts with the zwitterion or ozonide to give a low molecular weight inert self-healing film on the rubber surface(102).

Recently, MRPRA(141-143) have developed a new class of antiozonants based on para-phenylenediamines bearing side chains containing one or two monoselenide linkages. The inclusion of a monoselenide linkage into the alkyl side chain of N-alkyl-N'-aryl-p-phenylenediamines has been reported to lead to enhancement of the static antiozonant and thermal antioxidant performance.

It has been reported(8,144) that bound formed 4-(mercaptoacetamido)diphenylamine (XXIII,MADA) was found to be more effective as an antiozonant than when present as a conventional compounding ingredient, and to be as effective as unextracted IPPD at the same molar concentration. This is

XXIII

not so in the case of nitroso based bound antioxidants$^{(5)}$ described in Section 1.10.2. This tendency appears to conflict with the need for an antiozonant to migrate to the surface to exert its effect. Further investigations are still in progress.

1.10 Rubber Bound Antioxidants

A great deal of the development work and concern in the antioxidant field in recent years has been concentrated around improving the permanence of the effect obtained. The purpose of this approach is to improve the performance of rubber products by reducing the loss of antioxidants by volatilization at high temperatures or under conditions of solvent or aqueous leaching processes, or steam distillation. The most important application of these materials are in engine seals, gaskets, car tyres, gloves etc.

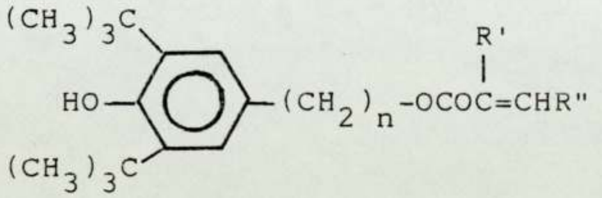
There are basically two ways of obtaining a substantial improvement in antioxidant performance in rubber: (i) selecting or creating high molecular weight antioxidant, and (ii) bonding the antioxidant chemically with rubber to produce a bound antioxidant.

An increase in molecular weight of antioxidant$^{(145-148)}$ can overcome the problem of physical loss due to volatilization. However, under conditions where antioxidants can be lost by solvent or water leaching, the above antioxidants are quite rapidly removed. The use of polymeric antioxidants made by reacting hydroquinone or p-benzoquinone with diamino(aromatic) amines has been reported to be effective in natural rubber(149).

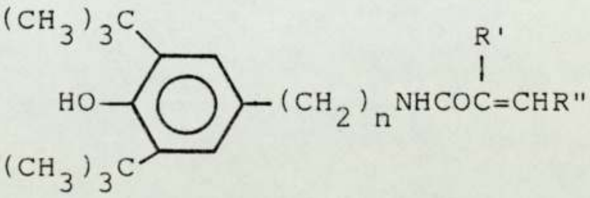
The best known method to overcome the serious disadvantages of conventional antioxidants in such conditions is to react the antioxidant chemically with rubber during manufacture by copolymerization of a vinyl antioxidant monomer(150-156), reaction during vulcanization(5,6,8,157-159), reaction of polymer latices with reactive antioxidants in a radical-initiated process(160-166) or by mechanochemical reaction of reactive antioxidant during processing(144,166-168).

1.10.1 Polymerizable Antioxidants

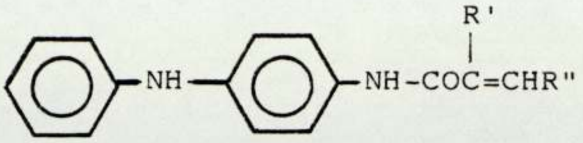
An alternative to this approach is copolymerization of compounds having both an antioxidant function and a polymerizable function in the same molecule. These compounds which include both phenolic and amine antioxidants (XXIV-XXVI)(151-153) were designed to be used as comonomer in the preparation of antioxidant-modified SBR's and NBR's. Antioxidant functional



XXIV



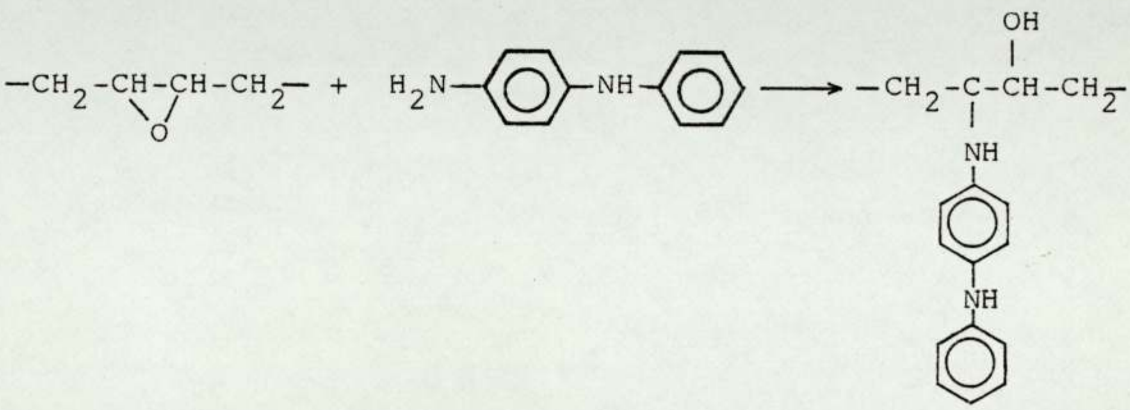
XXV



XXVI

styrenes have also been found to copolymerize in SBR and NBR formulations(154).

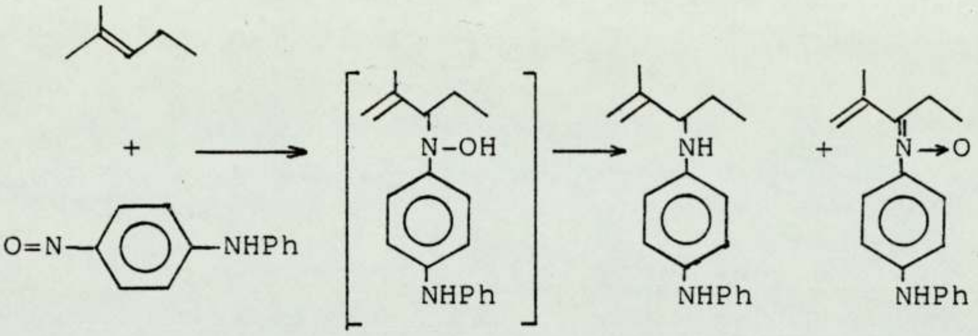
An alternative approach is to react antioxidants with polymers containing reactive functional groups such as epoxidized cis-1,4-polybutadiene (1.18)(155,156).



(1.18)

1.10.2 Binding Reaction During Vulcanization

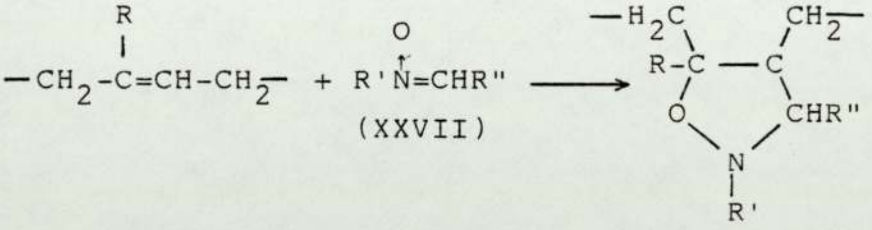
In this approach the antioxidant is bound to the rubber backbone during compounding and vulcanization. The best known method is perhaps that developed by workers at the MRPRA(157) involving the reaction of N-substituted-4-nitrosoanilines with rubber during vulcanization, leading to adducts formation which could not be removed by solvent extraction. The reaction sequence (Scheme 1.10) was proposed to account for the binding reaction⁽⁵⁾ on the basis of model compound studies. The resulting protection against heat ageing is



Scheme 1.10

comparable with that of lPPD and the effect resists exhaustive solvent extraction. Unfortunately, no protection against flexcracking or ozone is obtained.

MRPRA⁽¹⁵⁸⁾ have also shown that N,N'-disubstituted quinonediimines and N-substituted quinoneimines can react with rubber to give the corresponding p-phenylenediamine or p-aminophenol, together with a rubber bound entity. The nitrone group (XXVII) also has the ability to attack the functional group to rubber double bond through a 1,3-cyclo addition



(1.19)

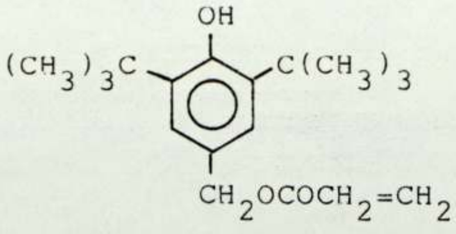
reaction (1.19)⁽¹⁶⁹⁻¹⁷¹⁾. Effective bound antioxidants can be produced, when either R' or R" contains an aromatic amine or a hindered phenol function⁽⁶,¹⁵⁹⁾.

Thiophosphoryl di- and polysulphides have been used as sulphur donors at 160°C in the presence of zinc oxide. The derived zinc dithiophosphate formed as an effective antioxidant analogous to the results observed with TMTD. In addition, however, the thiophosphoryl group becomes in part bound to cis-polyisoprene backbone during compounding and vulcanization(172-174).

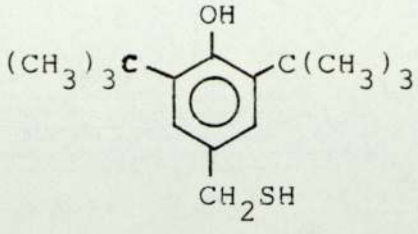
1.10.3 Reaction of Rubber Latices with Reactive Antioxidants

Binding of antioxidants to rubber in the latex has considerable practical interest. This is particularly important in the case of products which are directly made from rubber latex such as rubber gloves and latex threads, and in producing rubber bound antioxidant master-batches which are easily diluted with raw rubber to a desired concentration of antioxidant in rubber.

Antioxidants containing vinyl groups such as 3,5-di-tert-butyl-4-hydroxybenzylacrylate (XXVIII)(161) can be successfully bound with an appropriate redox initiating system. Amarapathy and Scott(161,175,176) demonstrated that phenol and amine containing p-methylene group can also be bound in this way. However, the extent of binding of antioxidants of the above type was not high enough to produce latex masterbatches suitable for commercial use.

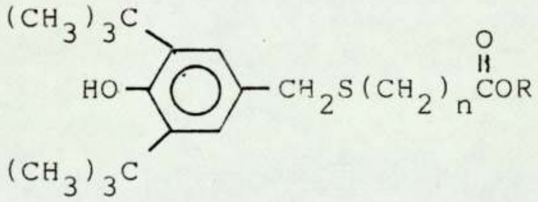


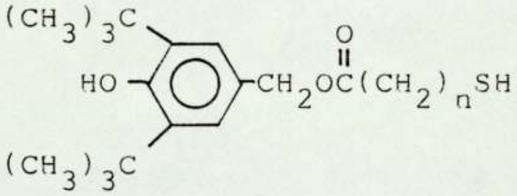
XXVIII



XXIX

Thiol containing antioxidant such as 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (XXIX;BHBM) are readily added to the double bond in natural rubber latex in the presence of azobisisobutyronitrile(162,177) and tert-butylhydroperoxide (TBH)(163,165,166,178) activated by tetraethylenepentamine (TEPA) as a redox system. The highest extent of binding can be achieved by using stripped styrene-butadiene-rubber(SBR) latex(166). It was suggested that non-rubber constituents preexisting in natural rubber latex is responsible for the interference of the binding reaction. Compounds such as MADA (XXIII)(123,124,167,168), derivatives of 3,5-di-tert-butyl-4-hydroxylcarboxy alkylsulphide (XXX,BTGA:XXXI,BTPA)





XXX : n=1,R=H

XXXI ; n=2,R=H

XXXII; n=1,R=C_4H_9

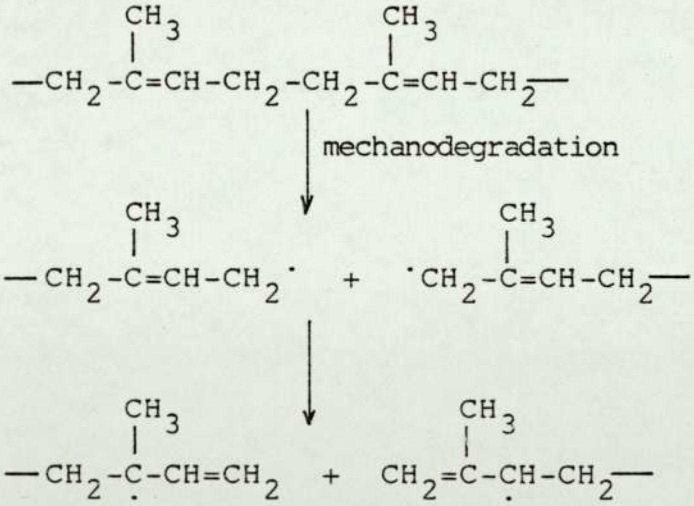
XXXIII; n=1

XXXIV ; n=2

and alkylthioglycollate (XXXII,BTBE) derivatives of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptoglycollate (XXXIII,BTGE) and mercaptopropionate (XXXIV.BTPE) have been reported to react with natural rubber latex in the presence of free radical generating system (TBH) producing rubber bound antioxidant(168).

1.10.4 Mechanochemical Binding of Antioxidants with Rubber

Mechanochemistry involves reactions for which the energy for initial radical formation is supplied mechanically. Mechanical forces acting on polymers are concentrated on separate positions of the chain as a result of non-uniform distribution of the internal stresses. This process leads to the formation of active terminal free radicals, which are very reactive towards oxygen. In the case of natural rubber, the most likely point of rupture is the $-CH_2-CH_2-$ bond since its dissociation energy is lowered by resonance of the alkenyl radical produced in the process (Scheme 1.11). The primary



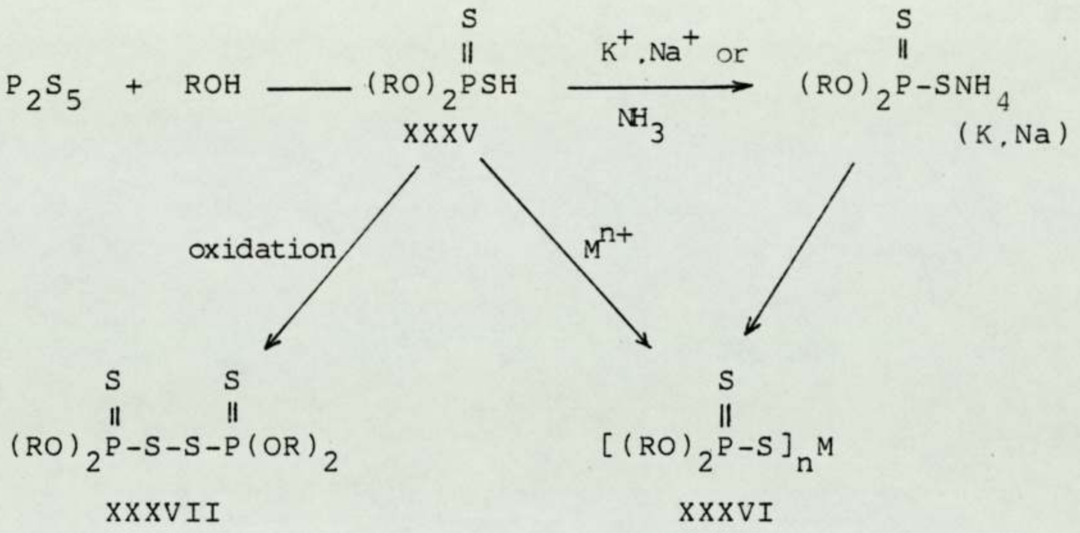
Scheme 1.11 Bond rupture of natural rubber during processing

radicals are resonance stabilized and reaction only occurs at the secondary or tertiary carbon atoms.

In subsequent studies in this area, Scott and his school(165,166,168 have found that some sulphur antioxidants such as BHBM, MADA, BTGA and BTPA can be mechanochemically reacted with both natural rubber and SBR. The processes were carried out in a RAPRA torque rheometer in the absence of oxygen. Masterbatch concentrates of bound antioxidant can be prepared containing up to 20% of bound antioxidant. About 20% of the total binding occurs during the vulcanization reaction. The extent of binding may be increased by reacting MADA with extracted rubbers in a Buss Ko Kneader(166). Further study and evaluation of these products is still in progress.

1.11 Dialkyldithiophosphoryl Compounds

Metal dialkyldithiophosphates (XXXVII), bis-(dialkyl)thiophosphoryl disulphides (XXXVI) and dialkyldithiophosphoric acids (XXXV) are common names referred to as metal dialkylphosphorodithioates, tetra-alkylthioperoxydiphosphates and dialkylhydrogendithiophosphates respectively. These compounds can be prepared by the reaction of phosphorus pentasulphide with alcohol corresponding to the desired alkyl group (R) producing the acid as shown in Scheme 1.12. Addition of metal salt or metal oxide to the acid or the ammonium or alkali metal salt, gives the metal complex where n is the valency of the metal. The corresponding disulphide can be obtained by oxidizing the acid or the ammonium or alkali metal salt.



Scheme 1.12 Preparation of metal dialkyldithiophosphate and the corresponding disulphide

The sulphides and metal complexes have been widely used in a variety of applications ranging from insecticides(179-182), corrosion inhibitors and lubrication oil antioxidants(183-192), extreme pressure additives(193-197) and applications for polymers such as antioxidants(198-207) and accelerators(88,146, 172-174,208-222).

1.11.1 Antioxidants

The metal dialkyldithiophosphate and bis(dialkyl)thiophosphoryl sulphides have been used as antioxidants in both polyolefin and elastomers. Di-, tri and tetrasulphides have been found to be equal or better than phenyl-β-naphthylamine (PBN) in stabilizing polyisobutylene against depolymerization(198). The disulphides have been used by Homberg and coworkers(199) to stabilize polyolefins against heat and oxidation and by Shell Research(200) to stabilize crystalline polyethylene and polypropylene against ultraviolet degradation.

Apart from the examples described above, the metal dialkyldithiophosphates have been reported to be antioxidants in rubbers. Dunn and Scanlan(201) showed that the zinc dialkyldithiophosphates retarded the stress decay of sulphurless rubber vulcanizates aged at 100°C. They also reported that nickel, zinc and lead diisopropyldithiophosphates were able to protect against oxidation under ultraviolet radiation, but were too short lived for practical application(41). Contrary to the above results, Tarasova et al(202) reported that zinc diisopropyldithiophosphate increased the resistance of sulphur vulcanizates to thermal-oxidative degradation but had practically no effect in the resistance of sulphur-free vulcanizates. Furthermore, they found that this compound improved markedly the fatigue life of vulcanizates containing polysulphidic crosslinks at elevated temperatures when it was used in combination with IPPD or bis(3-tert-butyl-5-methyl-2-hydroxyphenyl)methane (antioxidant 2246).

The metal complexes of dialkyldithiophosphate have also been used to stabilize polyvinylchlorides(203) and polyurethanes(204) against photooxidation, and to stabilize polyethylene against both photo and thermal oxidations$^{(205,206)}$. These complexes as well as the dialkyldithiophosphoric acids have been claimed to increase the storage life of butyl rubber without causing discolouring or other detrimental effects$^{(207)}$.

1.11.2 Accelerators and Sulphur-donors

The application of dithiophosphate in the vulcanization of rubber began with patent by Romieux$^{(213,214)}$, who claimed that bis-(0,0-diisopropyl)thiophosphoryl di-, tri and tetra-sulphides could be used as accelerators. Philpott$^{(215)}$ found in 1962 that combination of bis(dialkyl)thiophosphoryl disulphides with thiourea in a 1:1 mole ratio in latex compounding exhibits a considerable acceleration at 100°C. A combination of disulphide with another accelerator and activator were found to confer resistance to copper staining since the 'thiophosphoryl'-copper complex is not highly coloured and it possesses good heat resistance.

Scott and Williams$^{(216)}$ in 1962 patented bis(dialkyl)thiophosphoryl disulphides as activators or secondary accelerators to give improved antiozonant behaviour. Skinner and Watson$^{(88)}$ evaluated various efficient vulcanizing (EV) systems for natural rubber and concluded that bis(isopropyl) disulphide was a feeble sulphur donor and showed little or no synergism when used with MBTS, TMTD and MOR. The level of physical properties were low, none of the disulphide combination were evaluated technologically.

However, Kempermann(217) in 1967 found that addition of 1% thiourea to the disulphide produced a rapid acceleration in natural rubber. Stuckey et al(218) found a synergistic behaviour between bis(diisopropyl)thiophosphoryl disulphide and dimorpholyl disulphide (DMDS). At an optimum molar ratio of 1:1, a high degree of crosslinking was obtained without the production of bloom. Philpott reported again in 1969(219) that a mixture of the disulphide and sodium dialkyldithiophosphate was useful for latex vulcanization resistant to copper staining. The cure was activated by MBTS, thiourea and ZMBT.

The vulcanization of ethylene-propylene-termonomer (EPT) elastomers by Ashworth and Harper(220) has shown that the adidtion of bis(dialkyl)thiophosphoryl di-, tri- and tetrasulphides with MBT, TMTD and sulphur caused crosslinking of the elastomer to give a high level of physical properties and elimination of surface bloom. Furthermore, they vulcanized polyisoprene with bis(diisopropyl)thiophosphoryl trisulphide as a sulphur donor in combination with CBS(221). There is a similarity between this compound and a compound 'H56' described as a 'thiophosphoryl derivative' by Leyland et al(222,223). 'H56' was claimed to be a sulphur donor capable of being activated by CBS and sulphur. The vulcanizates from the trisulphides and 'H56' both exhibit good heat ageing which is lost on extraction.

Pimblott, Scott and Stuckey(172,173,224) reproted that bis-(diisopropyl)thiophosphoryl disulphide has been used as sulphur donor for vulcanizing cis-1,4-polyisoprene at 160°C. A predominantly monosulphidic network was formed which showed good thermal and thermal-oxidative ageing resistance due to formation of zinc diisopropyldithiophosphate in situ. The use of equimolar ratio of bis(O,O-diisopropyl)thiophosphoryl disulphide to DMDS and 0.5 phr of sulphur produced an accelerator blend which behaved as a delayed action system with a fast cure rate and the network structure associated with a semi-EV system. The vulcanizate possessed an outstanding thermal stability characteristic of a TMTD vulcanizate and a marked lack of reversion during cure at 160°C-180°C. They claimed that part of the thiophosphoryl compound became bound to rubber.

Russian workers(225) showed recently that in the sulphur vulcanization of nitrile rubber (NBR) a combination of zinc dialkyldithiophosphate and other accelerators such as MBTS or TMTD gives rise to a significantly increased rate of vulcanization but the scorch time is double that when only an individual accelerator is used.

1.11.3 Antioxidant Action of Dialkyldithiophosphates

The metal alkyldithiophosphates have been used as antioxidants for many years, the detailed mechanism of their activity is still unclear. However, it is well established that they or their transformation products are efficient peroxide decomposers. Therefore they are effective as inhibitors for hydrocarbon autoxidation(226,227). The reaction of zinc dialkyldithiophosphate with cumene hydroperoxide was first investigated by Kennerly and Patterson(226) in white mineral oil at 150°C. It was suggested that an ionic mechanism(228) of decomposition was involved, since phenol was observed as the main decomposition product. A similar explanation has been proposed(210,229) to account for the decomposition of various hydroperoxides by metal dialkyldithiophosphate.

Studies of the oxidation of squalene initiated by azobisisobutylonitrile at 60°C, Colclough and Cunneen(210) found that the rate of oxidation was also retarded by zinc dialkyldithiophosphate and the related xanthate and dithiocarbamate. They concluded that these salts also function as chain-breaking antioxidants, since hydroperoxide chain initiation is negligible under this condition.

Burn et al(230), Rossi and Imparato(231), Chien and Boss(232) and Ivanov et al(233,234) found that a three-step reaction occurred in the decomposition of hydroperoxide by metal dialkyldithiophosphate: (i) an initial rapid autoinhibited reaction, (ii) a very slow reaction described as an induction period when the rate of decomposition of the hydroperoxide is very slow, and (iii) a fast decomposition of the hydroperoxide.

The first step of the hydroperoxide decomposition is preceeded by co-ordination between the metal-containing chelate and the hydroperoxide leading to homolytic decomposition and formation of free radical products. During the retardation period the products formed in the first step, bis-(dialkyl)thiophosphoryl disulphide(231**), and basic zinc dithiophosphate(231,235) are oxidised to Lewis acids which catalyses the ionic decomposition of the hydroperoxide in the third step of the reaction. The formation of the disulphide strongly suggests that thiyl radicals of dialkyl dithiophosphate are produced in the decomposition reaction.

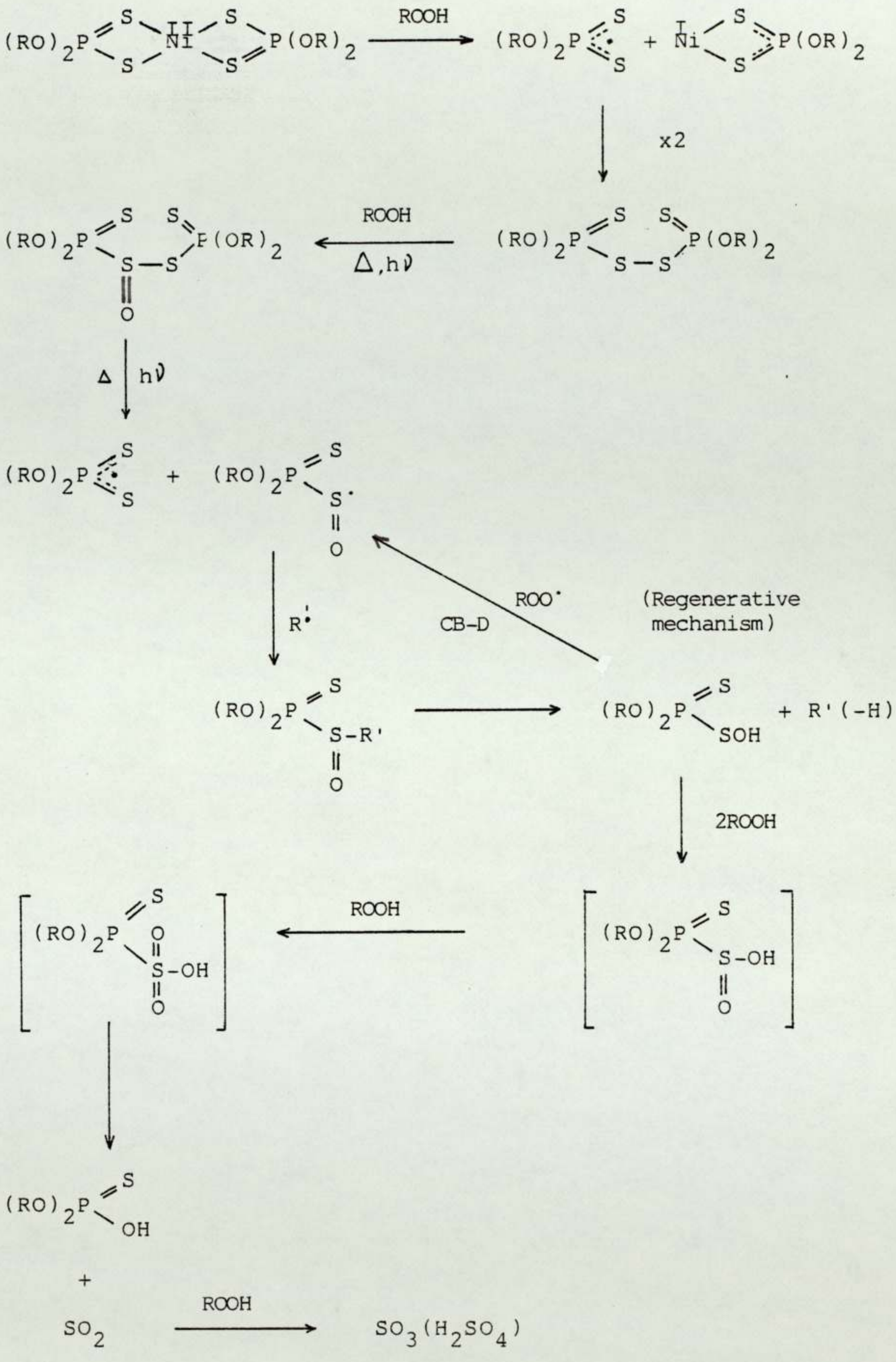
Although earlier work of Burn(212) showed that no antioxidant activity was found for the disulphide, Howard et al(236) have obtained evidence that zinc dialkyldithiophosphate reacts with hydroperoxides to form a more active antioxidant which reacts, at least partly, by an ionic mechanism. Grishina et al** have found that the disulphide decomposes hydroperoxide and it is possible that the disulphide breaks down to form a Lewis acid.

** See review by H S Laver,Ref.117,Ch.5.

Subsequent studies on the antioxidant action of those compounds have also been made by Al-Malaika and Scott(206,235-239). They found the three-stage mechanism as proposed by other workers(230-234). The mechanism involves two distinct catalytic processes in decomposing hydroperoxide in chlorobenzene at 110°C. The first invovles homolysis of hydroperoxide and the second results in ionic decomposition of hydroperoxide. It was proposed that the initial stage of the reaction leads to the formation of the corresponding disulphides. Disulphide-derived oxidation products such as sulphonic acid and thionophosphoric acid are formed during the induction period which is the middle step of the catalytic process. These oxidation intermediates undergo decomposition to produce sulphur acids which are responsible for the ionic catalytic decomposition of hydroperoxides. The proposed mechanisms are outlined in Scheme 1.13(237,238).

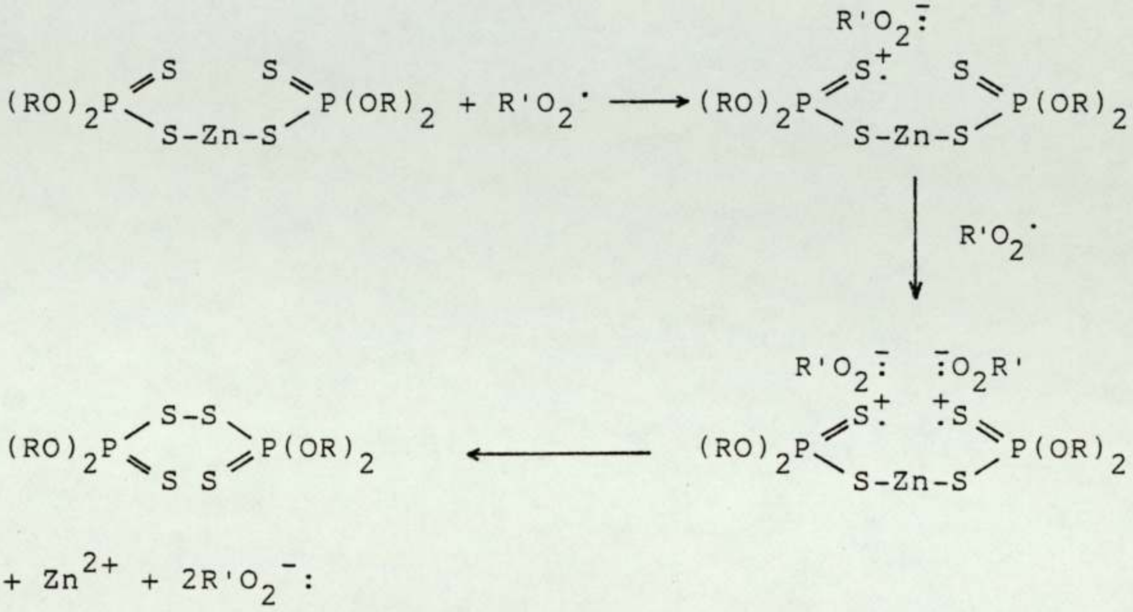
Furthermore, Al-Malaika(206) applied the metal dialkyldithiophosphate for heat and UV stabilization of polyethylene and polypropylene. She found that antioxidant residues became bound to the polymer during processing. It is suggested that a radical process is involved. The effectiveness of this class of stabilizer is believed to be due to their actions involving a cyclical regeneration in which sulphinyl radical is an alkyl radical trap.

Studies of the reaction of metal dialkyldithiophosphate with alkylperoxyl radicals have also been carried out by Burn(242),



<u>Scheme 1.13</u> Antioxidant mechanism of nickel dialkyldithiophosphate

Howard and co-workers(236,243-246) and Ivanov(234). In the course of the reaction, the thiophosphate chelate is destroyed and disulphide is formed(242). In order to account for this observation and the finding that disulphide is unreactive towards alkylperoxy radical, Burn has proposed an electron transfer mechanism (Scheme 1.14):



Scheme 1.14

Howard and co-workers(236) found that in the photolysis of zinc dialkyldithiophosphate or diisopropyldithiophosphoric acid, the dithiophosphate radical obtained has a doublet ESR spectrum and that the spin-spin splitting is very similar to that of the doublet spectrum observed by Liston et al(247). They have therefore suggested that the reaction of metal dialkyldithiophosphate with alkylperoxyl radical occurs at the metal centre by a mechanism that involves either an electron transfer reaction (1.20):

$$[(RO)_2PS_2]_2Zn + R'OO^{\cdot} \longrightarrow ROO^- + (RO)_2PS_2Zn^+ + (RO)_2PSS^{\cdot} \quad (1.20)$$

or an SH_2 reaction (1.21):

$$[(RO)_2PS_2]_2Zn + R'OO^{\cdot} \longrightarrow R'OOZnS_2P(OR)_2 + (RO)_2PSS^{\cdot} \quad (1.21)$$

They reported that dialkyldithiophsophoric acid was formed and was found to be a better inhibitor than the corresponding metal chelate(243). They also reported that the alkylperoxyl radical-metal dialkyldithiophosphate complex decomposes to give Lewis acid. The reaction products consisted of large amounts of α-methylstyrene and lesser amounts of benzophenone and cumyl alcohol. They suggested that the metal complex converts the alkylperoxyl radical to alkoxy radical, which then abstracts hydrogen from the ligands to form the alcohol. The Lewis acid which is formed from the oxidized metal complex is strong enough to dehydrate the alcohol to olefin.

Furthermore, Howard and co-workers(245) found that in the presence of excess of hydroperoxide, the cupric complex is converted to copper sulphate by reaction with the peroxyl radical. This sulphate is believed to be responsible for the heterogeneous ionic reaction, destroying cumene hydroperoxide (CHP) but not tert-butylhydroperoxide (TBH). A homolytic process was found to occur at low ratios of hydroperoxide to complex.

These observations were carried out in the very early stage of the course of the reaction, the results might be different when the reaction has reached a later stage.

Bridgewater and co-workers(248) have investigated the reactions of zinc dialkyl(aryl)dithiophosphate and related compounds with hydroperoxides at the temperature range 95°-125°C and reached the conclusions that: (i) the decomposition of CHP by a free radical reaction to form acetophenone is independent of the promoter used, (ii) the formation of the 2-phenylpropan-2-ol (α-cumyl alcohol) and 2-phenylpropene(α-methyl styrene) is due to ionic decomposition of the hydroperoxide and not by the free radical mechanism normally accepted, (iii) the ionic decomposition of CHP takes place by a cationic chain reaction, (iv) the catalyst formed from the promoters (zinc normal salts, zinc basic salts and disulphides) may be the dialkyldithiophosphoric acid. They emphasized that the ionic decomposition of hydroperoxide is solvent dependent. In protic solvents, the reaction is first-order with respect to the catalyst whereas in an aprotic solvent, the reaction is second order and not first order with respect to the hydroperoxide(232).

1.12 Scope and Objectives of the Present Study

It was shown in Section 1.7.1.3 that the activity of certain organic sulphides and disulphides comes from the oxidized products. It is believed that the active inhibitor may be the sulphinyl radical(113,122,172) which is formed either by elimination from the sulphoxides(121,249,250) or by thermolysis or hydrolysis, or even mechano-activated degradation of thiolsulphinate. The sulphinyl radical is known to be very reactive towards alkyl radicals and may trap macroalkyl radicals in the system. This may also raise the possibility of cyclical regenerative processes in which the radical is continuously regenerated in the system (Scheme 1.4) giving rise to very powerful antioxidant activity. A similar regenerative mechanism has been shown to operate for nitroxyl radicals in rubbers under fatigue conditions (Section 1.8).

Metal dialkyldithiophosphates and their corresponding disulphides have been shown to undergo a similar series of oxidation reaction and cyclical regenerative process (Section 1.11.3). It has been found that the derived sulphinyl radicals undergo chemical reaction with alkyl radical in polyolefins, giving rise to a chemically bound antioxidant (Scheme 1.13). Evidence was also gained for an active antioxidant being generated in the extracted vulcanizates during thermal oxidation, when bis(dialkyl)thiophosphoryl disulphide was used as a sulphur donor vulcanizing system for cis-1,4-polyisoprene (Section 1.11.2). These processes are related to the above and it seems likely that the role of dialkyldithiophosphate in the fatigue of rubber would be due to removal of alkyl radical. It is known that the addition of dialkyldithiophosphoric acids to olefin is similar to the addition of the thiol functional group to olefin through both normal and radical type addition(251,252). These facts suggested that it should be possible to react the acids with rubber double bond in latex and the disulphides with solid rubber using mechanochemical processes.

The purpose of the present study is to examine the above postulations in more detail, both in the polymer and in model systems and to devise improved antifatigue agents with possible antiozonant activity based on the dialkyldithiophosphate moiety which is chemically bonded to the rubber.

CHAPTER TWO

SYNTHESIS AND EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Natural Rubber Latex

Centrifuged natural rubber latex preserved with 0.7% ammonia was supplied by H W Syminton (Qualitex A; dry rubber content (DRC) 60%).

2.1.2 Natural Rubber

SMR-5L and SMR-10 were obtained from Dunlop. SMR-L was kindly supplied by MRPRA.

2.1.3 Compounding Ingredients and Antioxidants

These compounding ingredients were used without purification for vulcanization purposes. Listed are the suppliers of the chemicals used.

Chemical	Supplier
CBS (Santocure)	Monsanto Chemicals
DMDS (Sulfasan R)	"
TMTD (Thiurad Powder)	"
Zinc oxide	Amalgamated Oxides Ltd
Sulphur	Anchor Chemicals Ltd
Stearic acid	"
Dicumylperoxide	Hercules (it was crystallized from ethanol for model compound study)

IPPD (Santoflex IP)   Monsanto Chemicals

2.1.4 Other Chemicals

Unless it is stated otherwise, most of the solvents and reagents used were of standard laboratory grade without purification.

Acetone (ex Fisons)
Acetophenone (ex BDH)
Ammonia Gas (ex BDH)
Ammonium Cerium (IV) Sulphate (ex Aldrich)
n-Butanol (ex BDH)
Ether (ex Fisons)
n-Hexane (ex BDH) chromatographic grade
Iodobenzene (ex BDH)
Methanol (ex Fisons)
Methanoic Acid (formic acid; ex BDH)
n-Octanol (ex BDH)
Phenol (ex BDH)
2-Phenylpropan-2-ol (cumyl alcohol; ex BDH)
Phosphorus Pentasulphide (ex BDH)
Phosphoric Acid (ex BDH)
Potassium Oleate (ex Fisons)
Propan-2-ol (ex Koch-Light)
Silicagel MFC (ex Hopkin & Williams),100-200 mesh

TLC Plates; Kieselgel 60 F254 (ex Merck)

1,1,1-Trichloroethane (ex BDH)

Benzene (ex Fisons) was dried over a sodium wire, distilled, and stored over 4A molecular sieve.

Chlorobenzene (ex BDH) was fractionated from phosphorus pentoxide and the fraction boiling at 132°C was collected(253).

Hydrogen Peroxide 30% (ex BDH) was shaken well prior to use without further purification.

1-Methylcyclohexene (ex Aldrich) was fractionally distilled and the fraction boiling at 109-110°C was collected.

Squalene (ex Aldrich) was column chromatographed on alumina using benzene as the eluent.

Texofor FN 30 (alkylphenolethoxylate;ex IBM Chemicals) was kindly supplied by MRPRA.

2.1.5 Purification of Hydroperoxides

2.1.5.1 Tertiary-butyl Hydroperoxide (TBH) 70%

The peroxide (ex Aldrich) was placed in a flask which was then frozen in acetone-dry ice. The frozen solution was allowed to defrost and two layers were formed. The upper organic layer was taken out and dried with Na_2SO_4 over night and fractionally distilled under vacuum. The fraction boiling at 21°-23°C and at 1,70 torr was collected.

2.1.5.2 Cumene Hydroperoxide (CHP)

The peroxide was purified according to the following procedure(254): 200 g cumene hydroperoxide (ex BDH) and 200 ml petroleum ether (40-60°C) in a 1000 ml beaker was cooled to 0°C, and 160 ml 25% aqueous sodium hydroxide was added while 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 and then it was suspended in petroleum ether, and the free hydroperoxide liberated by adding acetic acid. The solution was filtered and washed three times with water and dried over Na_2SO_4. The solvent was removed in a rotary evaporator, and the remaining CHP was distilled under vacuum at 53°C (1 mm Hg). The resulting CHP was 99.3% pure as confirmed by iodometric titration.

2.2 Preparation of Dialkyldithiophosphoryl Compounds

2.2.1 Preparation of 0,0-Diisopropyldithiophosphoric Acid $(C_3H_7O)_2PSSH$

The 0,0-diisopropyldithiophosphoric acid was prepared by a known procedure described below(255). Phosphorus pentasulphide (111.2 g, 0.5 mol) was placed in a 3-neck round-bottom flask equipped with a nitrogen inlet tube, a condenser connected to cupric sulphate solution with a plastic hose to trap the liberated hydrogen sulphide, and a thermometer. The isopropanol (120.2 g, 2.0 mol) was added dropwise with stirring during 1½ hours under nitrogen and cooled in ice. The reaction mixture was stirred for 1½ hours, and the temperature was maintained below 10°C until the evolution of H_2S ceased. It was then heated at 60-80°C until the solution became clear yellow. The reaction product was filtered to remove unreacted matter. The crude acid was distilled in vacuo (as fast as possible to avoid decomposition) at 64-66°C/ 1.8 mm. The yield was 171 g; 80% (literature 71-72°C/2 mm(256), 71-72°C/3mm(257)).

Analytical Data

	Calculated (%)	Found(%)
Carbon	33.6	33.3
Hydrogen	7.0	6.6
Sulphur	29.9	29.3
Phosphorus	14.5	13.8

Infra-red Spectra Data

Infra-red spectra was obtained from neat liquid or KBr disc (solid compound) using Perkin Elmer 599B infra-red spectrophotometer.

Wave numbers	Assignment
2980s,2930s	C-H stretching
2500b	S-H stretching
doublets 1465s,1452s and 1385s,1372s	C-H bending,$C(CH_3)_2$ group

1170s,1143s,1104s,970b	(P)O-C stretching
895s,830s,758s	P-O(C) stretching
650vs	P=S stretching
520s,550s	P-S(H) stretching

NMR Data

The proton (^1H) NMR spectra were recorded on a Perkin Elmer R12 Spectrometer at 60 MHz using $CDCl_3$ containing tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are reported in ppm downfield from TMS, and coupling constants (J) are in Hz.

^{31}P NMR was carried out on a Jeol JNM FX90Q Fourier Transform NMR Spectrometer. The signals were recorded upfield from the centre of the spectral width and reported in ppm.

^1H: 1.33 and 1.44 (doublet,12H), $J(CH_3\text{-}CH)=9$
3.7 (singlet,1H)
4.3-5.2 (septuplet,2H), $J(CH\text{-}CH_3)=16$

^{31}P: -63.52

2.2.2 Preparation of O,O-Dibutyldithiophosphoric Acid $(C_4H_9O)_2PSSH$

The acid was prepared according to the method described in Section 2.2.1. The crude acid was distilled in vacuo at 121°C/3 mm (literature 120°C/0.8-1.0 torr)$^{(258)}$.

Analytical Data

	Calculated (%)	Found(%)
Carbon	39.6	40.2
Hydrogen	7.8	7.9
Sulphur	26.5	25.8
Phosphorus	12.8	12.0

Infra-red Spectra Data

Wave numbers	Assignment
2975s,2892s	C-H stretching
2485b	S-H stretching
1470s,1388s	C-H bending
1057w,1025w,977s	(P)O-C stretching
904m,860w,784m	P-O(C) stretching
663vs	P=S stretching
535m	P-S(H) stretching

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz.

^1H: 0.95 and 1.08 (doublet,6H), $J(CH_3-CH_2)=10$
1.28-1.85 (multiplet,8H), $J(CH_2-CH_2)=35$
3.16 (singlet,1H)
3.98-4.34 (multiplet,4H), $J(O-CH_2-CH_2)=20$

^{31}P: -59.79

2.2.3 Preparation of 0,0-Dioctyldithiophosphoric Acid

$(C_8H_{17}O)_2PSSH$

This acid was prepared according to the method described in Section 2.2.1. The crude acid was purified through the ammonium salt (Section 2.2.4). The salt was hydrolysed with excess of phosphoric acid, and the pure acid as the upper phase was separated from the immiscible liquid phases(259).

Analytical Data

	Calculated (%)	Found(%)
Carbon	54.2	49.6
Hydrogen	9.9	9.3
Sulphur	18.1	19.6
Phosphorus	8.7	8.4

Infra-red Spectra Data

Wave numbers	Assignment
2960m,2934s,2860s	C-H stretching - octyl group
2465b	S-H stretching
1470s,1382s	C-H bending
990w,956w,980m,995b	(P)-O-C stretching
930w,875b	P-O-(C) stretching
665vs	P=S stretching
550b	P-S(H) stretching

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz.

^1H: 0.94 and 1.03 (doublet, 3H), $J(CH_3-CH_2)=8$

1.37 and 1.80 (doublet, 12H), $J[(CH_2)_6-CH_2]=24.4$

3.27 (singlet, 1H)

3.99-4.49 (multiplet, 2H), $J[(CH_2-(CH_2)_6]=7$

^{31}P: -53.95

2.2.4 Preparation of Ammonium Salt of Dithiophosphoric Acids $NH_4S_2P(OR)_2$ (255)

The crude acids prepared above were diluted with 300-400 ml of dry benzene and a stream of anhydrous ammonia bubbled through the solution for 30 minutes. The ammonium salt precipitated was filtered. The bubbling of ammonia through the solution was repeated until no more precipitate was formed. The salt was washed with benzene and dried in vacuo.

2.2.5 Preparation of Bis-(O,O-dialkyl)thiophosphoryl Disulphides $[(RO)_2PS]_2S_2$

Three kinds of disulphide (the alkyl groups R being isopropyl, n-butyl and n-octyl) were synthesized by oxidizing the corresponding ammonium salt with iodine in potassium iodide solution(260). A solution of the ammonium salt (0.1 mole) in water (150 ml) was stirred at room temperature while iodine (0.05 mole) dissolved in potassium iodide solution (25 g in 100 ml water) was added dropwise. After completing the addition of the iodine solution, some ammonium salt was added when the colour of the solution turned brown due to the excess of iodine.

2.2.5.1 Bis-(0,0-diisopropyl)thiophosphoryl Disulphide $[(C_3H_7O)_2PS]_2S_2$

The resulting pale yellow solid from the preparation above was recrystallized from ether to yield bright yellow crystals (90.4%). Melting point 90-91°C (literature 90-91°C(173), 93.8-94.6°C(261)).

Analytical Data

	Calculated (%)	Found(%)
Carbon	33.8	32.3
Hydrogen	6.57	6.6
Sulphur	30.0	31.2
Phosphorus	14.5	15.4

Infra-red Data

Wave numbers	Assignment
2992s, 2938m	C-H stretching
doublets 1466w and 1451 w 1387s and 1375s	C-H bending. $C(CH_3)_2$

1179s,1143s,1102s,978vs	(P)-O-C stretching
908vs,780s,735	P-O-(C) stretching
638s	P=S stretching

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz

^1H: 1.26 , 1.37 (doublet,12H), $J(CH_3\text{-}CH)=10$
4.51-5.15 (septuplet,2H), $J(CH\text{-}CH_3)=20$

^{31}P: -63.52

2.2.5.2 Bis-(0,0-dibutyl)thiophosphoryl Disulphide
$[(C_4H_9O)_2PS]_2S_2$

The yellow oily substance obtained in preparation of the disulphide according to the method described in Section 2.2.5 was extracted from ether and washed with water several times and finally dried with $MgSO_4$ for 24 hours. The ether was evaporated under vacuum. Yield 91%.

Analytical Data

	Calculated (%)	Found (%)
Carbon	39.8	40.9
Hydrogen	7.4	7.8
Sulphur	26.5	27.3
Phosphorus	12.9	12.1

Infra-red Data

Wave numbers	Assignment
2900s,2770w,2370m	C-H stretching
1460m,1381m	C-H bending
1150w,1120w,1055w,1015-977vs(b)	(P)-O-C stretching
902s,858w,804m	P-O-(C) stretching
645	P=S stretching

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz

^1H: 0.97 and 1.08 (doublet,6H), J (CH_3-CH_2)=10
1.29-1.87 (multiplet,8H), J (CH_2-CH_2)=35
4.0-4.38 (multiplet,4H), J (CH_2-CH_2-O)=20

^{31}P: -59.76

2.2.5.3 Bis-(O,O-dioctyl)thiophosphoryl Disulphide

$[(C_8H_{17}O)_2PS]_2S_2$

The preparation methods in Sections 2.2.5 and 2.2.5.2 were adopted. Yield 83.3%.

Analytical Data

	Calculated(%)	Found(%)
Carbon	54.4	53.6

Hydrogen	9.6	9.4
Sulphur	18.1	19.8

Infra-red Data

Wave numbers	Assignment
2956w,2925vs,2852vs	C-H stretching
1465vs,1379s	C-H bending
1124w,985vs(b)	(P)-O-C stretching
929w,858s,805w,770w	P-O-(C) stretching
648vs	P=S stretching

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz.

^1H: 0.94 and 1.03 (doublet,3H), $J(CH_3-CH_2)=8$
1.37 and 1.80 (doublet,12H), $J[(CH_2)_6-CH_2]=24.4$
3.99-4.49 (multiplet,2H), $J[CH_2-(CH_2)_6]=7$

^{31}P: -53.90

2.2.6 Preparation of Zinc Bis-(0,0-dibutyl)dithiophosphate $[(C_4H_9O)_2PS_2]Zn$(262)

Aqueous solution of ammonium 0,0-dibutyldithiophosphate 2.59 g, 0.1 mole) and $ZnSO_4$ (9.6 g, 0.05 mole) were mixed with stirring at room temperature for 1 hour. The zinc complex was extracted into ether and separated from the aqueous layer, dried with $MgSO_4$ over night. The ether was removed under reduced pressure. Yellow liquid of the zinc complex was obtained (20.8 g, 76%).

Analytical Data

	Calculated(%)	Found(%)
Carbon	35.1	34.4
Hydrogen	6.6	6.6
Sulphur	23.4	23.1

Infra-red Data

Wave numbers	Assingment
2957vs,2935w,2874s	C-H stretching
1462vs,1430m,1381s	C-H bending
1057w,1016s,976s	(P)-O-C stretching
900vs,837s,795s	P-O-(C) stretching
664vs	PS_2 asymmetry
560s	PS_2 symmetry

NMR Data

Chemical shifts (δ) in ppm, coupling constant (J) in Hz.

^1H: 0.9,0.94,1.04 (triplet,3H),J =9
1.15-1.81 (multiplet,4H), J=35
3.98-4.35 (multiplet,2H), J=20

^{31}P: -39.57

2.3 Binding Reaction of Dialkyldithiophosphoryl Compounds with Natural Rubber Latex

2.3.1 Preparation of Dithiophosphoryl Compound Emulsion

40 ml distilled water was added into a 250 ml conical flask containing 1 g of dithiophosphoryl compound and 0.6 g 25% aqueous of Texofor FN30. After purging with nitrogen, the flask was stoppered tightly and was then shaken for 18 hours.

2.3.2 Binding Reaction(166)

The reactions were carried out in a 500 ml five-necked flask equipped with a stirrer, a thermometer and a nitrogen inlet tube, and it was immersed in an oil bath which was heated at 60-65°C. 166.6 ml of latex (100 g dry rubber) diluted with 125 ml distilled water was placed in the flask and stirred for 15 minutes under nitrogen. The additive emulsion was added and allowed to swell for 30 minutes. The initiator and the activator (separately dissolved in 3 ml of distilled water) were added alternately in three aliquots of 1 ml each at 30 minute intervals. The reaction was allowed to proceed under nitrogen for a determined period.

2.3.3 Extraction of Rubber Adduct

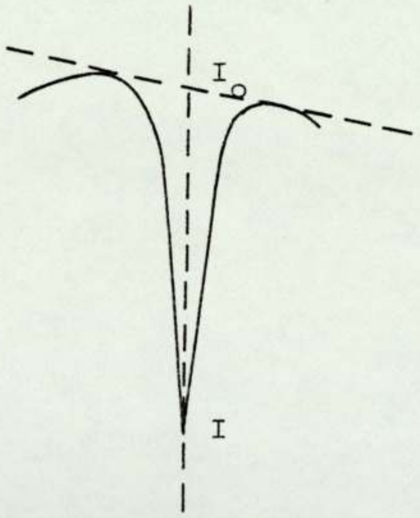
After the reaction was completed, the flask was cooled and the rubber was coagulated with 1% formic acid. The coagulum was washed under running water, sheeted on a two-roll mill, washed again and dried in a vacuum oven at 40°C. The dried rubber sheet was continuously extracted with hot acetone for 24 hours in a soxhlet, and the extent of bound additive was determined according to the method described in Section 2.3.4.2.

2.3.4 Estimation of Extent of Bound Additive(166)

2.3.4.1 Preparation of Rubber Samples Containing Different Amounts of Dithiophosphoric Acid for Calibration

Samples of extracted rubber (1 g) were placed in 100 ml conical flasks and dissolved in 35 ml chloroform. A stream of nitrogen was bubbled through the solution for 2 minutes. The flasks were then stoppered tightly and shaken for 24-48 hours to allow the rubber to dissolve completely. Known amounts of 0,0-diisopropyl-and dibutyl-dithiophosphoric acid (i.e., 0.25, 0.50, 0.75, 1 and 2%) were dissolved in 5 ml chloroform and added to the rubber solution. The mixtures were purged with nitrogen and the flasks were stoppered tightly, and shaken for a few minutes.

The rubber solution was deposited on a sodium chloride plate by allowing the solution to evaporate on the surface of the plate in a vacuum oven. Initially the pressure was reduced gradually to avoid the formation of bubbles in the rubber film. The film was then mounted between two salt plates and their infra-red spectra were obtained. The P=S peak at about 650 cm^{-1} was chosen as the sample peak, and the C-H stretching of rubber at 2720 cm^{-1} was chosen as the standard invariant peak to avoid the errors due to the film thickness. A suitable tangent baseline as shown in Figure 2.1 was constructed to measure the transmission values of I and Io, and the absorbance values (A) were calculated according to Equation 2.1 (264).



$$A=\log_{10}Io/I \qquad \text{Eq 2.1}$$

Figure 2.1 Tangent baseline

The P=S index for a given concentration of dithiophosphoryl compound, which is the ratio of the absorbance of P=S group to that of reference peak, was plotted as a function of concentration of additive on a graph. From the graph the concentration of bound additive can be determined.

2.3.4.2 Preparation of Rubber Adduct Film for Infra-red Measurement

2.3.4.2.1 Casting Method

The preparation of rubber film by the casting method in Section 2.3.4.1 was adopted for gel free rubber.

2.3.4.2.2 Compression Method

Extracted rubber adduct (2 g) was placed between two metal plates covered by cellophane. The plates were separated by a spacer (inner measurements: 8 cm x 8 cm, thickness 0.1 mm). The sample was preheated at 80-90°C (50-60°C for SMR-10 and processed rubber) for 1 minute and then pressed for 1 minute under 30 tons pressure per 8 inch ram. The film was separated from the cellophane, which was eventually moistened to facilitate the separation, and it was mounted on thick paper cardboard frames which were specially cut to fit the infra-red spectrophotometer sample holder. It was dried in a vacuum before determination of the absorption spectrum.

2.4 Mechanochemical Binding Reaction of Dithiophosphoryl Compounds with Natural Rubber

The mechanochemical reaction was carried out in a RAPRA torque rheometer. 30 g of acetone extracted rubber was mixed with 3 g (10 phr) of dithiophosphoryl compound on a 30 cm water-cooled laboratory two-roll mill, sheeted out and cut into small pieces. The rubber was processed for 10 minutes at various temperatures ranging from 25-140°C, in the chamber with a rotor speed of 60 r.p.m. On completion of processing, the rubber was rapidly removed and cooled. The mixture was diluted with extracted rubber to obtain 1 phr concentration of additive in the mixture. For determination of the amount of bound additive, the diluted rubber (5 g) was extracted in a soxhlet by boiling acetone under nitrogen for 24 hours, and dried in a vacuum for 24 hours.

2.5 Compounding and Vulcanization

2.5.1 Compounding

The vulcanization systems used in this work were varied from conventional, EV, sulphur donor and peroxide. Gum vulcanizates were used throughout the whole work. Table 2.1 lists the range of curing agents, accelerator and sulphur donor used in gum vulcanizates. The detailed formulation and curing time for various systems are listed in Chapter 4.

Extracted or unextracted natural rubber was masticated and mixed with compounding ingredients on a 30 cm water cooled

Vulcanization Systems	Curing agent and accelerator (phr)			
	Sulphur	CBS	TMTD	DCP
Conventional	2 -2.5	0.4-1	-	-
EV	0.3-1	2 -5	-	-
Sulphurless	-	-	3-7	-
Peroxide	-	-	-	1.5-4

Table 2.1 Concentration of curing agents and accelerators for different vulcanization systems in parts per hundred of rubber(89,90,265-267)

laboratory two-roll mill adjusted at 1:1 friction ratio. The clearance between rolls was set to 0.5 mm.

2.5.2 Assessment of Curing Characteristics

The curing characteristics of rubber stocks (11 g) were measured in a Monsanto Rheometer Model A-100(268). This instrument follows the resistance to motion of an oscillating rotor embedded in the test sample, held at a chosen temperature (140-180°C). Cure is followed from the initial phase through crosslinking to the fully cured stage. The resistance of oscillation through 3° arc is measured and recorded as a function of time to give a characteristic cure curve for the individual test sample (Figure 2.2).

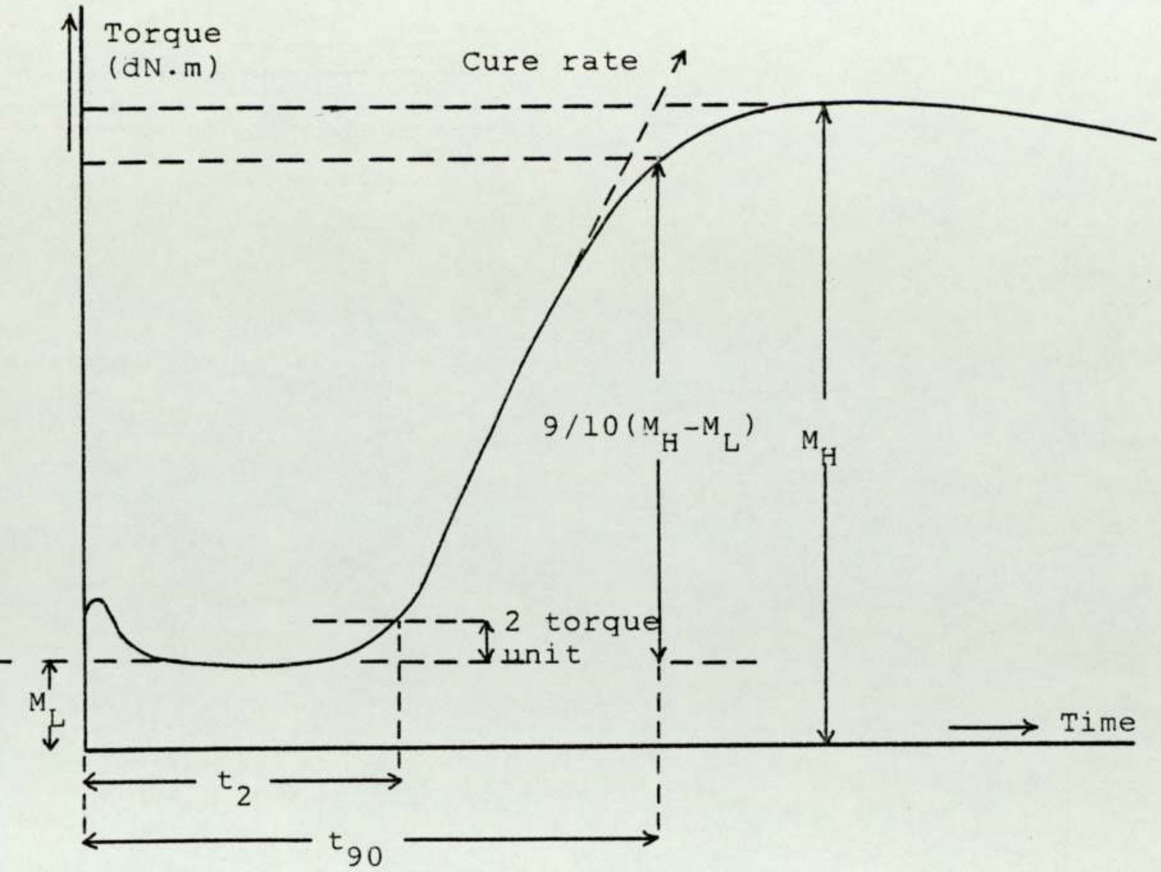


Figure 2.2 Rheometer curve

The cure curve (rheograph) can be analysed as follows(268-270):

M_L	Minimum torque, M_{LOW}; dN.m or kg.m
M_H	Maximum torque, M_{HIGH}; dN.m or kg.m
t_2	Scorch time; minutes. The time for the torque to rise 2dN.m above M_L.
t_{90}	Time to 90% cure; minutes. The time for the torque to rise to $9/10(M_H-M_L) + M_L$.
Cure rate	Slope of the rheograph curve in the steep region, i.e., $100/t_{90}-t_2$; minutes^{-1} (268). Or $t_{90}-t_2$; minutes (269,270).

Rheometric cure parameter reported in these studies are:

Torque, $T = M_H - M_L$ (kg.m)

Scorch time, t_2 (minutes)

Cure rate, $t_{90} - t_2$ (minutes) or

Rate constant, k (minute^{-1})

The rate constant k can be obtained by assuming that the crosslinking rate follows first order kinetics and using Equation 2.2$^{(271)}$.

$$\log_{10}(R_{max} - R_t) = \log_{10} R_{max} - \frac{k}{2.303}(t - t_i) \qquad \text{(Eq 2.2)}$$

when R_{max} is the maximum torque; R_t is the torque at time t, which is the time of cure, t_i is the scorch time, k is the rate of first order crosslinking. A plot of $\log(R_{max} - R_t)$ against t gives a straight line with slope of $\frac{k}{2.303}$ and an induction period of t_i (Figure 2.3).

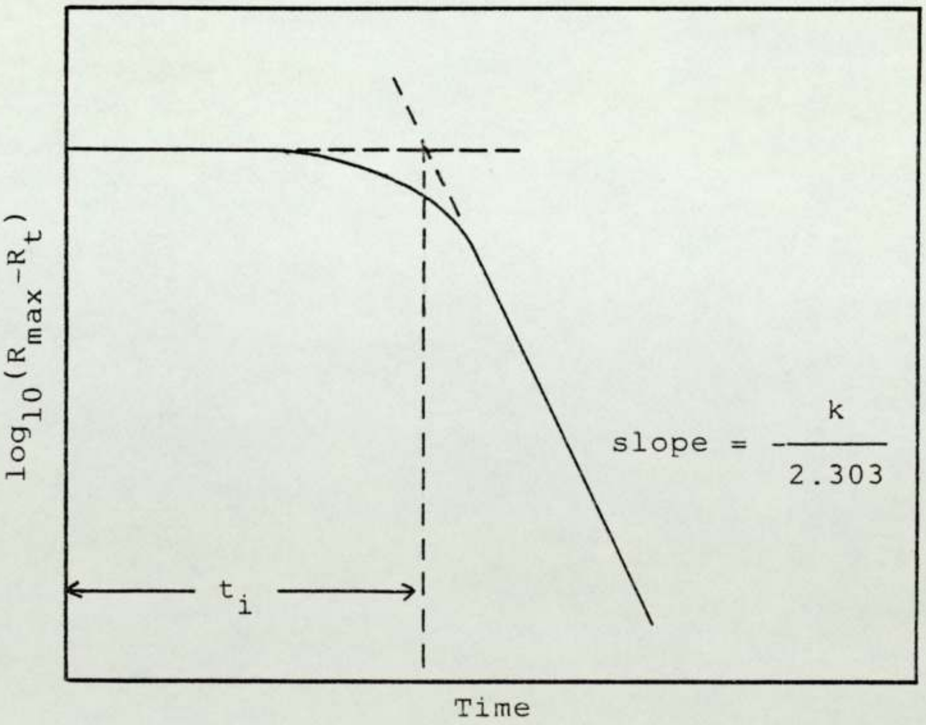


Figure 2.3 First order plot for the vulcanization of rubber according to the data obtained from the Monsanto Rheograph

2.5.3 Vulcanization

The rubber gum stocks were vulcanized under either steam or electrically heated press equipped with a thermocouple. The pressure was maintained at 30 tons per 8 inch ram for a determined cure time and temperature. The amount of stock for a particular mould of test sample are listed in Table 2.2. Samples were first sheeted out on a 30 cm water cooled laboratory two-roll mill to 3 mm thickness. and cured with the grain* direction along the length of the mould.

Test Sample	Amount of stock (g)
Infra-red	4.6
Ozone, Stress Relaxation	20
Fatigue	56

Table 2.2 Amount of gum stocks for different moulds

At the end of the cure time. except for the vulcanizate for infra-red spectroscopic analysis. the vulcanizates were quenched in cold water.

2.5.3.1 Vulcanizates for Infra-red Spectroscopic Analysis

A stainless steel mould having dimensions of 13.5 cm x 13.5 cm x 0.018 cm was used for this purpose. A sheet of

---

* Pattern of lines formed during milling and are perpendicular to the direction of the flow.

0.015 cm - 0.020 cm thickness can be obtained.

2.5.3.2 Vulcanizates for Fatigue Tests

The vulcanizates were prepared in a rectangular stainless steel mould having dimensions of 22.9 cm x 7.6 cm x 0.16 cm and beaded edges. Dumb-bell shaped test pieces were cut using a BS type E cutter. The test pieces were cut after alligning the cutter between marks on the beaded edges found on either side of the sheet. Samples with obvious flaws should be rejected.

2.5.3.3. Vulcanizates for Ozone and Stress Relaxation Tests

A stainless steel mould having dimensions of 24 cm x 15 cm x 0.068 cm was used. Strips of rubber 1 cm wide and 7 cm long were cut from the sheet for ozone exposure, and 0.4 cm wide and 7 cm long were cut for stress relaxation tests using the appropriate cutters.

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

2.5.3.4 Conditioning of the Test Pieces

As the properties of vulcanized rubber changes continuously with time, and since these changes are particularly rapid during the first 16 hours after vulcanization(272), no tests were carried out during this period. Samples were stored in the dark, in a dry atmosphere at room temperature for 24 hours before further storage in a vacuum desiccator or in a deep freeze at -20°C.

All test pieces were conditioned for 4 hours at room temperature prior to the test. For the static ozone tests, after mounting the test pieces on the jigs and straining to the required elongation, the stretched test pieces were conditioned for 24 hours at room temperature in the dark and dry atmosphere before being exposed to the ozone.

2.5.3.5 Extraction of Vulcanizates

The extraction of vulcanizates were carried out in a soxhlet extractor under a constant flow of nitrogen. The solvents used were an azeotropic mixture consisting of acetone, methanol, 1,1,1-trichloroethane in the proportion of 110 ml, 42 ml and 60 ml respectively. The conditioned test pieces were continuously extracted for at least 48 hours. After completion of the extraction, the test pieces were removed from the soxhlet, dried in a vacuum at 30°C for 24 hours and stored in a vacuum desiccator in the dark or in a deep freeze at -20°C.

2.6 Assessment of Durability of Vulcanizates

2.6.1 Fatigue Resistance of Vulcanizates (273,274)

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

Each sample holder was adjusted so that zero strain was obtained when the test piece was mounted. This was done by inserting a 6 cm long calibration metal rod between the upper and lower shackle and adjusting the thumb nut until a snug fit was obtained. Six test pieces for each stock were mounted in the sample holders. A cam 4 was used to obtain a single extension of 60% and cam 14 for 100% extension at a frequency of 100 cycles per minute.

After the machine has completed the run for 1000 cycles, the tester was turned off and the drive cams were set for zero extension by adjusting the thumb nut so that when the lower shackle was raised, a slight bow appeared in the sample.

The tester was then run again and fatigue life was recorded as the number of cycles to failure. The fatigue life was quoted as the Japanese Industrial Standard (JIS) average$^{(274)}$ obtained from the four highest test pieces tested using the formula:

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

where A, B, C and D are the fatigue lives with A>B>C>D.

The JIS average is biased towards the high readings. This standard is used because any small defect on the surface of the rubber test piece may cause premature failure on fatigue.

2.6.2 Ozone Resistance of Vulcanizates

2.6.2.1 Apparatus

Ozone resistance tests were carried out using a Hampden-Shawbury Ozone test cabinet. The ozone cabinet consists of a closed dark chamber, with thermostatically controlled temperature. The ozone is generated by exposing a stream of purified and filtered air to a single ultraviolet tube in conjunction with an electronic drive which gives precise control over the output of the tube. Manual over-ride of the automatic ozone control system is available at the turn of a switch. The concentration of ozone (0-140 pphm) is measured by the ozone analyser (Model OZT-2) which is connected to the chamber.

The principle of the operation of the ozone analyser relies on the reaction of ozone with a solution of potassium iodide to produce iodine, according to the following reaction:

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

The free iodine is reduced to iodide at the cathode and reformed to iodine at the anode. To enable a quantitative estimate of the free iodine reduced at the cathode to be made, it is necessary to prevent the iodine reformed at the anode from recirculating, and this was achieved by employing a silver on mercury anode. Silver on mercurous iodide is then formed at the anode which being insoluble, effectively removes the reformed iodine from solution.

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

Potassium iodide	1.500±0.025 g/l
Sodium monohydrogen phosphate(anhydrous)	1.500±0.025 g/l
Potassium dihydrogen phosphate(anhydrous)	1.400±0.025 g/l

2.6.2.2 Static Ozone Testing

The vulcanizate test strips were mounted on jigs and held in tension at 20% strain and conditioned in the manner described in Section 2.5.3.4. The ozone concentration in the chamber was set to 25 ± 5 pphm. The temperature inside the chamber was adjusted at 25°C, and the air flow was set at 150 l/hr.

The test pieces were then hung inside the chamber on the rotating test piece holder, exposed to the ozone, and the surface inspected for crack development at various time intervals. Examination of the test piece was carried out using a stand lens of x5 magnification according to BS903(275). The cracks were graded on an arbitrary scale as follows:

Grading	Surface appearance of the test piece
0	No crack
1	Cracks visible only when magnified x5
2	Fine cracks 1-2 mm long, visible to the naked eye
3	Cracks 2-5 mm long
4	Severe cracks penetrate through the test piece
5	Test piece broken

2.6.3 Stress Relaxation Measurement

2.6.3.1 Apparatus

The Wallace-Shawbury self-recording age tester was used for measuring the decay of stress in continuous relaxation providing a measure of the degradative reaction in the network of the vulcanizate. The test piece was subjected to accelerated oxidative ageing.

The tester consists of a balance beam, on which the tension exerted by a rubber strip is counter-balanced by that of a helical spring. By means of electrical contacts at the end of the beam, and a motor, the tension in the spring is automatically adjusted to balance the tension in the rubber. A lead pencil attached to the moving end of the spring records the stress in the test piece on a cylindrical chart revolving at a constant speed. The Wallace cell oven having 6 cells was used to provide an accurate temperature control.

2.6.3.2 Testing Procedure

The test pieces were mounted individually between 2 grips and clamped on the testers. Each instrument was zeroed for the weight of the test piece, after which the lower specimen grip was tightened. The test piece was extended with the aid of a brass collar providing an extension of 60%. The instruments were then placed in the air ageing oven which has been adjusted at $100^{o}+2^{o}C$ with an air inflow rate of 0.071 cubic meters per hour. After allowing 5 minutes for expansion, the lead pencil was adjusted to 100% stress and zero time on the chart. The test pieces were then allowed to relax in stress. The tester recorded stress as a function of time on the chart. The decay of the stress for each test piece was plotted against time, and the time to 50% (t_{50}) loss in stress was determined.

2.7 Model Compound Studies

Bis-(0,0-dibutyl)thiophosphoryl disulphide was purified for this purpose. It was column chromatographed on silica gel using benzene as the eluent.

2.7.1 Reaction of Bis-(0,0-dibutyl)thiophosphoryl disulphide (BuTPDS) with Dicumyl Peroxide (DCP) in Squalene

The reaction was carried out in a 50 ml 3-necked flask equipped with a condenser, nitrogen inlet tube, agitator and a thermometer. Squalene (25 ml) was poured into the flask and BuTPDS (0.375 g) was added. The mixture was heated in an oil bath at 160°C under nitrogen and DCP (0.937g) was added. Aliquot parts (1 ml) were taken from the solution at 5 minute intervals up to 30 minutes reaction, 15 minute intervals up to 60 minutes reaction and then 30 minute intervals up to 2 hours reaction. The solution taken was immediately placed in a stopped vial and cooled in acetone-dry ice mixture, then kept in a deep freeze until required. The solution was allowed to warm up and purged with nitrogen at room temperature prior to analysis.

2.7.1.1 Infra-red Spectroscopy Analysis

A Perkin Elmer 599B infra-red spectrophotometer was used to obtain the infrared spectra. This double-beam infra-red spectrophotometer provides the possibility of automatic elimination of the solvent absorption. A demountable NaCl cell was filled with reaction solution. Another cell was filled with unreacted solution used to compensate all the original's absorption in order to obtain the reaction product's absorption. The latter cell was placed on the reference beam. The reference cell containing only squalene was also necessary to monitor the decreasing of certain absorptions. The absorbance of specific absorptions were plotted as a function of reaction time. the graph being shown in Section 5.2.2.

2.7.1.2 Ultraviolet Spectroscopy Analysis

A Pye Unicam SP800B ultraviolet spectrophotometer was used for this purpose. The reaction solutions (0.05 ml) were diluted with hexane (12.5 ml). Hexane was used for the reference beam, the graphs being shown in Section 5.

CHAPTER THREE

BINDING OF DITHIOPHOSPHORYL COMPOUNDS WITH NATURAL RUBBER

3.1 Introduction

Polymer bound antioxidants are substantially less resistant to loss by volatilization at high temperature or extraction by solvent, detergents or hot oil. Recent research has shown that the addition of antioxidants containing thiol group to rubber in the presence of a radical generator produces high yields of adducts. Such thiol antioxidants as BHBM have been chemically bound to natural rubber latex in a hydroperoxide initiated reaction(161-166).

BHBM and MADA have also been bound to solid rubber by utilizing the macroalkyl radical produced mechanochemically in a shearing mixer(165-168). Masterbatch concentrates of thiol adducts can be obtained and diluted to the required concentration.

The following studies report an attempt to carry out a similar reaction with the dialkyldithiophosphoric acids and their derivatives.

3.2 Binding with Natural Rubber Latex

3.2.1 Natural Rubber Latex

Freshly tapped natural rubber (Hevea brasiliensis) latex consists of rubber hydrocarbon and a large number of non-rubber constituents present in relatively small amounts.

Many of these are dissolved in the aqueous serum of the latex, others are adsorbed on the surface of the rubber particles and some are constituents of non-rubber particles suspended in the latex.

Rubber hydrocarbon can be isolated by fractional centrifugation carried out in high speed separators e.g., De Laval and Westphalie centrifuges. The latex which has been stabilized with 0.2-0.4% ammonia is separated into two parts of approximately equal volume. The fraction of "cream" which is the lighter layer has a rubber content of approximately 60% and the fraction of "skim" contains mainly water and approximately 10% of the total solid of which 4-6% is rubber, the remainder consists of proteins, resinous substances, inorganic salts and carbohydrates. After centrifugation, additional preserving agents are needed e.g., gaseous ammonia or sodium pentachlorophenate(281,282). The total protein content in the fresh latex is 1%, of which 20% is adsorbed on the rubber particles. The adsorbed proteins, together with adsorbed phospholipids impart colloidal stability to the latex and remain associated with the rubber phase when the latex is coagulated during the manufacture of sheet or crumb rubber(283).

It has been reported that certain thiol based antioxidants can be reacted with natural rubber latex using tertiary-butyl hydroperoxide (TBH) as the initiator and tetraethylene pentamine (TEPA) as the activator[161-166]. This was found to be the only system that gave a good yield of bound antioxidant when the natural rubber latex containing ammonia was used.

3.2.2 Calibration Curves

The calibration curves for 0,0-diisopropyldithiophosphoryl and 0,0-dibutyldithiophosphoryl compounds were prepared based on the addition of a series of known weights of the corresponding acids to the rubber solution in chloroform. The preparation procedure is described in Section 2.3.3.1. The infra-red spectra was obtained from the film prepared by casting the rubber solution on NaCl plates. The P=S indexes were then plotted against the concentration of the additives in rubber. The curves are shown in Figure 3.1.

The rubber adducts obtained were extracted with hot acetone as described in Section 2.3.3 and then prepared as a film by compression moulding (Section 2.3.4.2) to obtain the infra-red spectra. The P=S indexes obtained from the spectra were used to deduce the amount of additives bound to rubber from the calibration curves.

3.2.3 Basic Reaction Condition for Binding Dialkyldithiophosphoric Acid and Its Derivatives to Natural Rubber Latex

The basic reaction conditions carried out in centrifuged

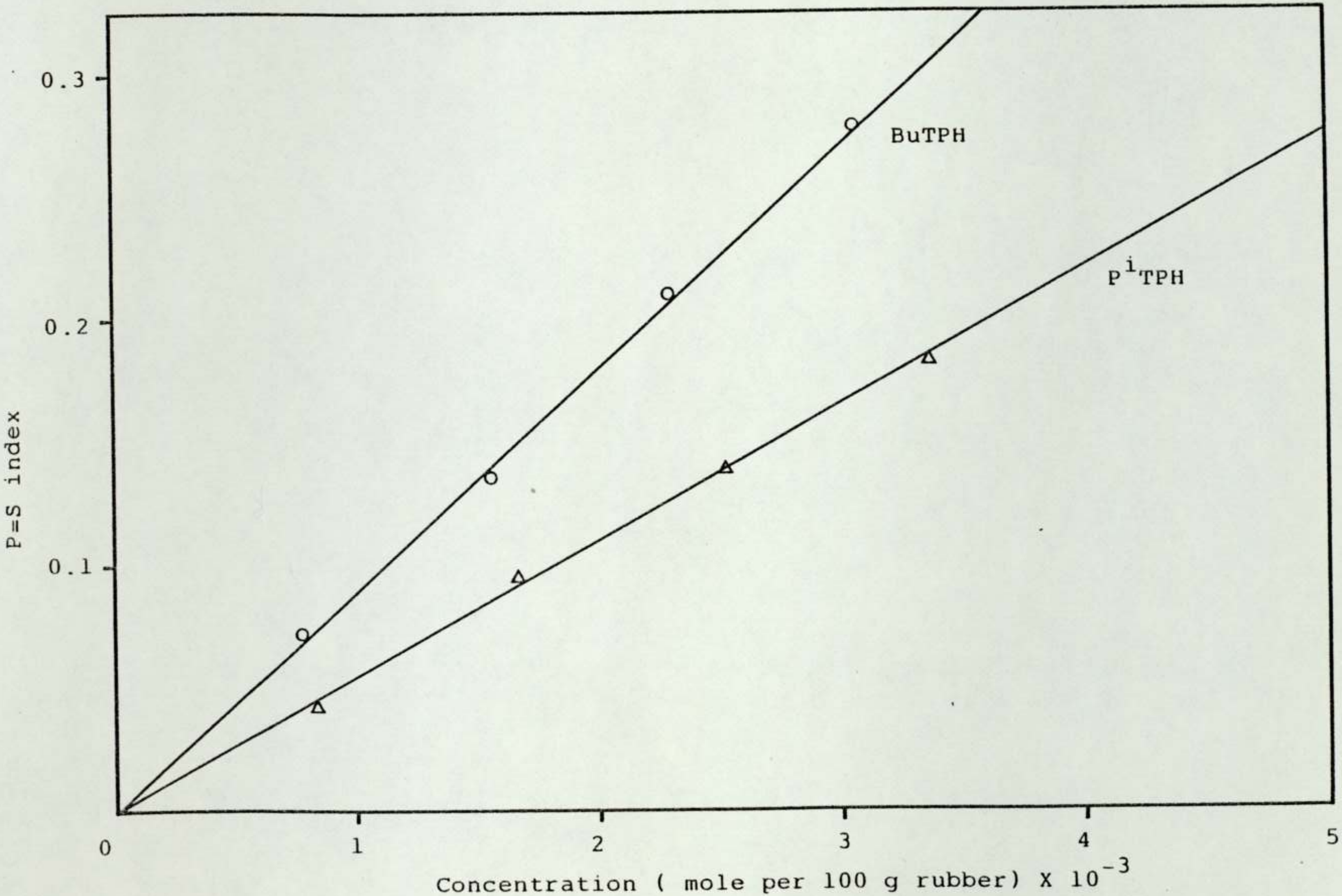


Figure 3.1 Infrared calibration curves for isopropyl and butyl derivatives dithiophosphoryl compounds.

natural rubber latex previously described in the literature(166) were adopted. The temperature for all reactions was 60°C and the soap used was 0.6 g of 25% Texofor FN30 per gram dithiophosphoryl compound added. The general procedures for preparing the emulsion of the additive and the binding reaction were described in Section 2.3.1 and 2.3.2.

3.2.4 Reaction of 0,0-Diisopropyldithiophosphoric Acid (P^iTPH) with Natural Rubber Latex

3.2.4.1 Effect of Initiator Concentration on the Amount of P^iTPH Bound to Rubber

The addition of TBH used as initiator at molar ratios of TBH to P^iTPH from 1:1 to 10:1 (0.42 g-4.2 g) were studied keeping the concentration of P^iTPH constant at 1 phr (4.67×10^{-3} M) and the reaction conditions described above were used. The reactions of centrifuged natural rubber latex (30% DRC) with P^iTPH were carried out for 8 hours (including swelling time). The results are shown in Table 3.1 and Figure 3.2.

[TBH/P^iTPH]	Yield (% bound)
1	11
2	26
3	37
4	36
5	35
7.5	28
10	22

Table 3.1 Effect of TBH concentration on the amount of P^iTHP bound to rubber

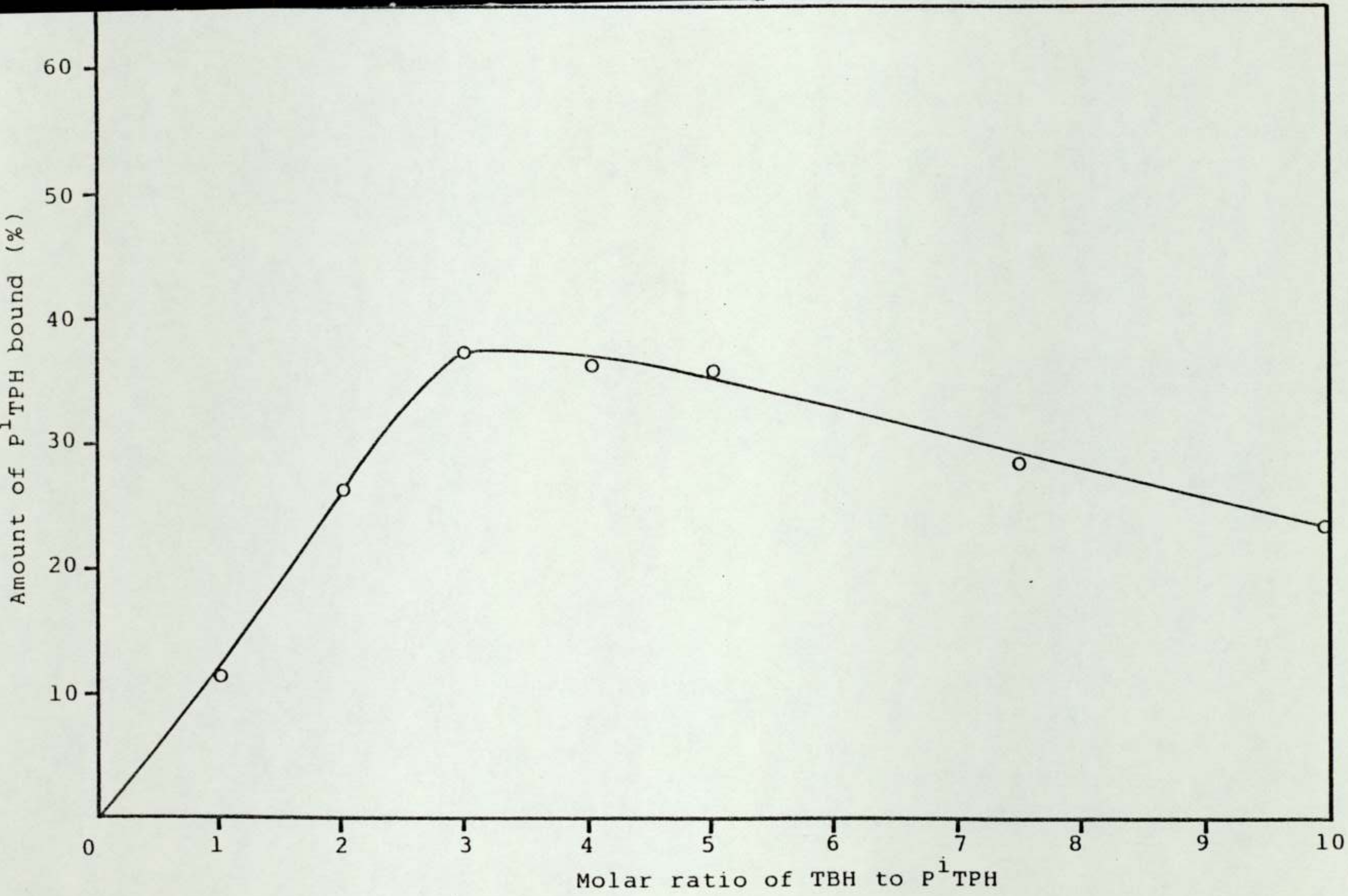


Figure 3.2 Amount of $P^{i}TPH$ bound to rubber at various molar ratio of TBH to $P^{i}TPH$ (1 phr. 4.67 X 10^{-3} mole) in casted film.

The above table shows that the maximum yield of bound P^iTPH is obtained at $[TBH]/[P^iTPH] = 3$. This is also shown in Figure 3.2.

3.2.4.2 Effect of Reaction Time

The optimum concentration of P^iTPH and TBH of the last experiment were employed in the binding reaction. The reaction conditions were kept constant except the reaction time was 28 hours with sampling time at 4 hourly intervals after completion of the swelling. The results are shown in the following Table.

Reaction time (hours)	Yield (% bound)
4	26
8	38.5
12	42
16	44
20	44
24	45
28	44.5

Table 3.2 Effect of reaction time on the amount of P^iTPH bound to rubber

Table 3.2 shows the amount of P^iTPH bound to rubber increases with time and reaches the optimum at about 24 hours. The effective time is about 12-16 hours (Figure 3.3).

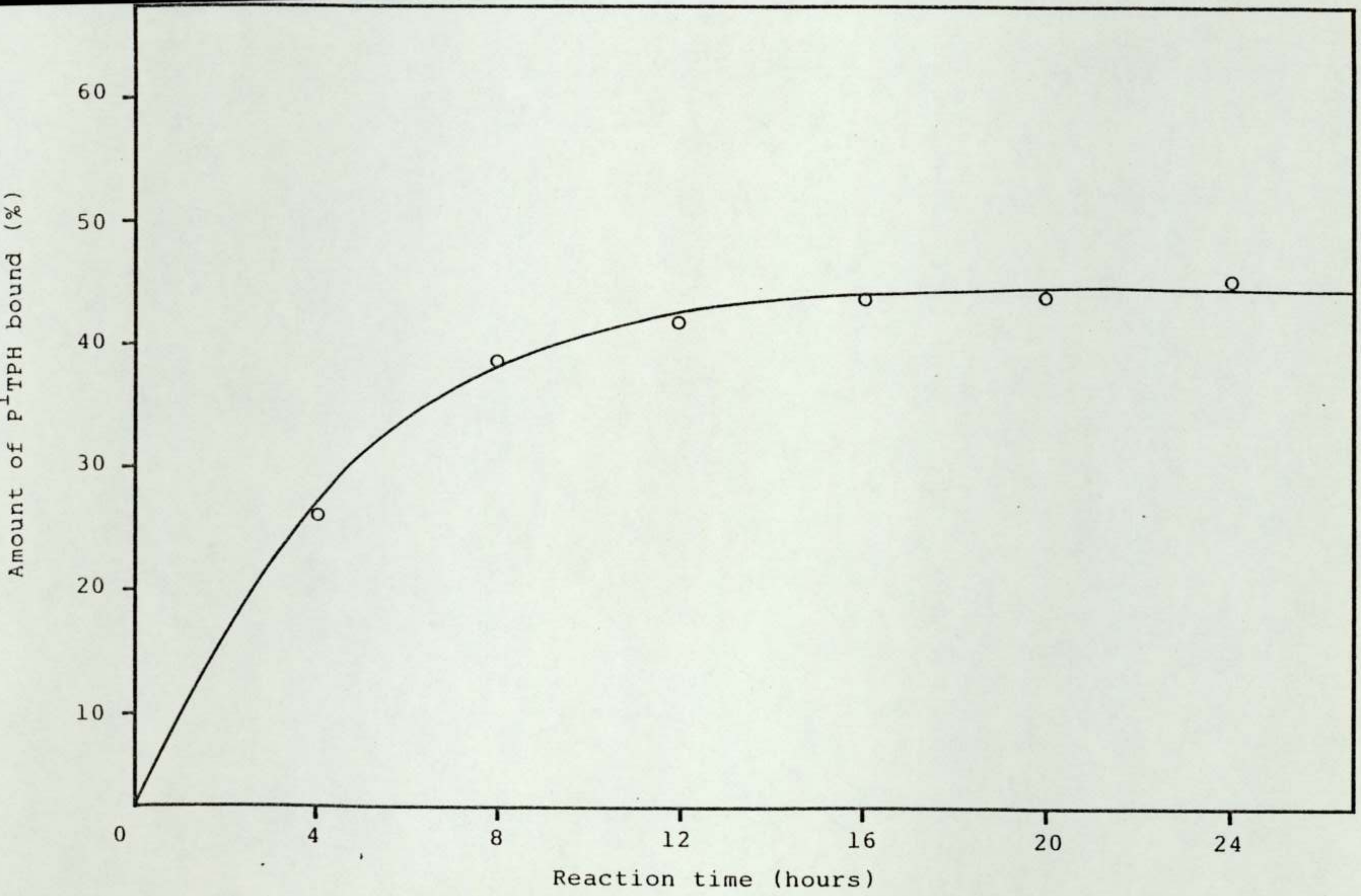


Figure 3.3 Effect of reaction time on the binding of P^1TPH to NR latex

3.2.4.3 Effect of Activators

Tetraethylene pentamine (TEPA) was used in conjunction with TBH in the binding reaction of thiol with natural rubber latex(161-166). The amount of TEPA used normally was about 0.5 g per 100 g rubber. In the production of prevulcanized polymer latex(292), 0.2-0.4% of sodium tungstate as activator has been used together with hydrogen peroxide. Thiyl radicals can be formed as primary intermediates in the oxidation of thiols in the reaction between thiols and Ce(IV)(293-295).

In the present study, reaction of P^iTPH (1 phr) with natural rubber latex initiated by TBH ($[TBH]:[P^iTPH] = 3$) was carried out under the reaction conditions described in Section 3.2.3 with the addition of activators. The activator was divided in 3 aliquots, which then were added to the latex immediately after the addition of initiator at half-hourly intervals as described in Section 2.3.2. After the addition of the last aliquot, the reaction was allowed to continue for a further 14 hours.

The types and amount of activators and the yield are listed in Table 3.3.

The results in Table 3.3 show that TEPA in that particular concentration reduces the amount of P^iTPH bound to rubber.

Activator (g per 100 g rubber)	Yield (% bound)
-	44
TEPA, 0.2	24
Na_2WO_4, 0.2	50
Na_2WO_4, 0.4	(coagulated)
$(NH_4)_2Ce(SO_4)_3$, 0.2	61
$(NH_4)_2Ce(SO_4)_3$, 0.4	74 (partly coagulated)

Table 3.3 Effect of activator on the amount of P^iTPH bound to rubber

The addition of 0.2 g of sodium tungstate increases the yield slightly. Double the concentration of the activator causes coagulation of the latex. Ammonium cerium sulphate increases the yield considerably. 74% of bound dithiophosphate on rubber can be achieved when the concentration of Ce(IV) is 0.4 g in 100 g rubber. However, a high concentration of the activator caused agglomeration of the latex.

3.2.4.4 Effect of P^iTPH Concentration

In order to study the preparation of latex additive masterbatches, the concentration of P^iTPH was varied considerably using reaction conditions previously obtained,as follows:

PiTPH concentration : 1, 2, 5, 10 phr
TBH concentration : [TBH]/[P^iTPH] = 3
Temperature : 60°C
Soap : 0.6 g 25% Texofor FN30 per g P^iTPH
Swelling time : 30 minutes
Reaction time : 16 hours

The preparation of emulsion of additive and the binding procedure were described in Section 2.3.1 and 2.3.2 respectively.

The results showed that the latex was coagulated when as low as 2 phr concentration of P^iTPH was added in the above example.

3.2.5 Binding Reaction of 0,0-Dibutyldithiophosphoric Acid (BuTPH) and Its Derivatives ($BuTP_S$) to Natural Rubber Latex

The failure of preparing masterbatch concentrates of P^iTPH adduct was due to the strong acidity of the P^iTPH, which caused coagulation of the latex at relatively low concentration of the acid. Atempts were made to react 0,0-dibutyldithiophosphoric acid (BuTPH), its ammonium salt (ABuTP) and the disulphide (BuTPDS) with centrifuged natural rubber latex and studied the optimal reaction conditions to obtain a maximum extent of binding and concentrated masterbatches.

3.2.5.1 Effect of Initiator Concentration

BuTPH, ABuTP and BuTPDS were reacted with natural rubber latex using various hydroperoxides such as TBH, cumene hydroperoxide (CHP) and hydrogen peroxide (H_2O_2). The concentration of 0,0-dibutyldithiophosphoric acid and its derivatives was 1 phr (4.13×10^{-3} M) and the concentration of hydroperoxides was varied based on the molar ratios of hydroperoxide to dithiophosphoryl compounds.

The reaction conditions were similar to that used in the binding of P^{i}TPH in Section 3.2.4.1, except that the reactions were carried out for 16 hours. The results are listed in Table 3.4 and drawn in Figure 3.4.

Molar ratios of hydroperoxides to additive	Amount of adducts formation (%) in the systems			
	BuTPH/TBH	BuTPH/CHP	BuTPH/H_2O_2	ABuTP/TBH
1	15.5	18	2	18
2	30.5	34	8	36.5
3	43	45	13	47
4	48	50	16	46
5	45	49	15	43
7.5	33	39	12	33
10	15	25	7	20

Table 3.4 Effect of initiator concentrations on the amount of dithiophosphoryl compounds bound to rubber

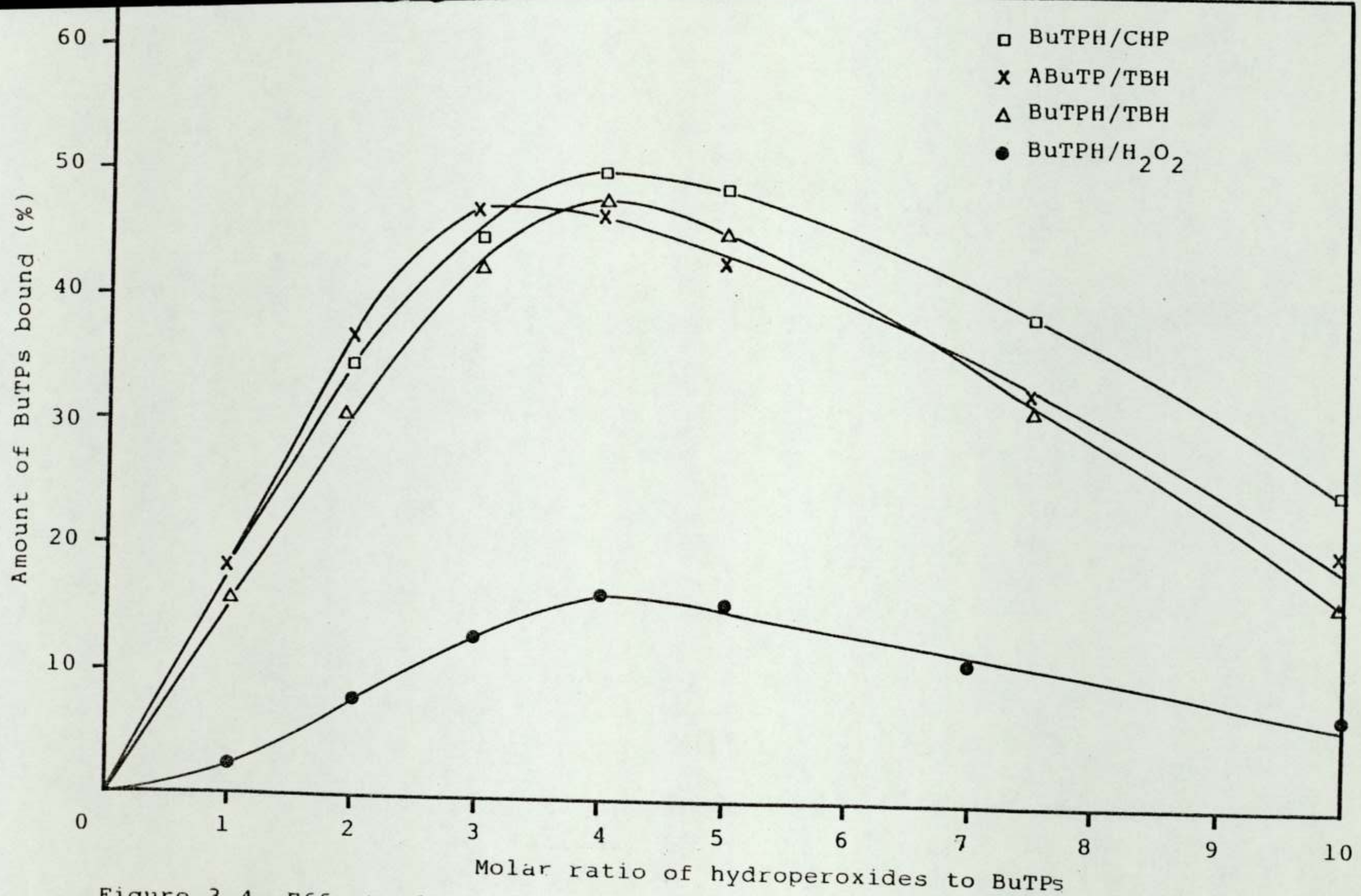


Figure 3.4 Effect of the concentration of hydroperoxides on the binding reaction of BuTPs to NR latex at 60°C for 16 hours. Points in the figure represent the molar ratio of hydroperoxides to BuTPs (1 phr) ranging from 1:1 to 10:1.

The results indicated that using various hydroperoxides, the maximum yield of BuTPH bound to rubber was at [TBH]/BuTPH]=4. Whereas ABuTP required a lower ratio of TBH to ABuTP to give maximum yield. When CHP was used as initiator, the amount of BuTPH bound to rubber (50%) was not significantly different from using TBH (48%). H_2O_2 gave rise to very low binding of BuTPH. BuTPDS did not bind using either TBH or CHP.

3.2.5.2 Effect of BuTPH and ABuTP Concentration

BuTPH and the ammonium salt were reacted with centrifuged natural rubber latex at concentrations of 5, 10, 15 and 20 phr. TBH was used as the initiator and the concentration was based on the molar ratios of 4:1 for BuTPH and 3:1 for ABuTP. The reaction conditions were kept constant. The results are shown in Table 3.5.

Additive (phr)		[TBH]/[BuTPs]	Yield(%bound)
BuTPH ,	5	4	47 (partly coagulated)
ABuTP ,	5	3	44
	10	3	37
	15	3	19
	20	3	(coagulated)
ABuTP ,	10	2	25

Table 3.5 Effect of concentration of BuTPs on the adducts formation

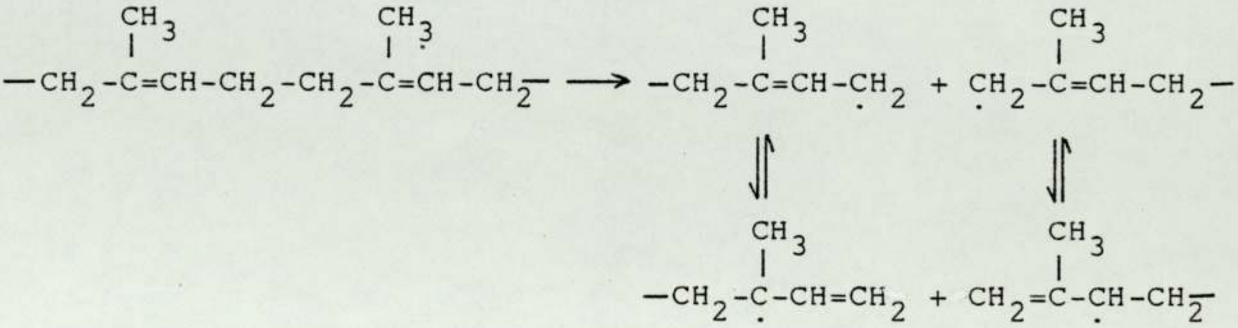
The results in Table 3.5 show that 5 phr of BuTPH yielded 47% binding. However it caused the latex to become unstable and it partly coagulated. It was found that using 5 phr of ABuTP, 44% binding was achieved. Increasing the concentration of ABuTP up to 10 phr caused a decrease in the amount of adduct to 37%. The latex tended to coagulate and the rubber was tacky when 15 phr ABuTP was added, and the yield of adduct was only 19%. 20% of ABuTP caused coagualtion of the latex. When 10 phr of ABuTP was reacted with natural rubber latex initiated by a molar ratio [TBH]/[ABuTP] of 2:1, only 25% adduct was obtained based on the amount added.

3.2.6 Mechanochemical Reaction of Dithiophosphoryl Compounds with Natural Rubber

3.2.6.1 Introduction

The polymer field for which reactions are induced by stress has often been referred to as mechanochemistry(284). The fundamental study of Pike and Watson(24,25) on the mastication of natural rubber leads to the study of the modification of rubbers such as synthesis of block and graft copolymers(285), and recently bound antioxidants(165-168) using mechanochemical reactions.

When sufficient energy is concentrated in a portion of the polymer chain, as a result of a new uniform distribution of internal stresses, the mechanical rupture of primary bonds results in the formation of macroradicals(286). A typical example is natural rubber mastication; which leads to the homolytic rupture of the weakest carbon bond in the backbone. The weakest bond is in the allyl position $(-CH_2-CH_2-)$ because of the resonance stabilization of the radicals formed as follows(24):



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\cdot}{C}H_2 + \underset{\cdot}{C}H_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

$$\Updownarrow \qquad\qquad \Updownarrow$$

$$-CH_2-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2 + CH_2=\overset{CH_3}{\overset{|}{C}}-\underset{\cdot}{C}H-CH_2-$$

In the absence of radical acceptors, the most prominent macroradical reactions are combination or disproportionation. The macroradicals may also react with the double bond or abstract α-methylenic hydrogen leading to the formation of branches and crosslinks. If a second polymer is present, block and graft copolymers can be formed(285,287). It has been demonstrated that antioxidants containing a thiol group can be readily reacted mechanochemically to rubber in the same manner(165-168).

3.2.6.2 Mechanochemical Reactions in the Torque Rheometer

In the present studies, mechanochemically induced free radicals were used to attach dithiophosphoryl compounds to extracted SMR-5L. The processes were carried out in a RAPRA Torque Rheometer Mk 3, which is essentially a small mixing chamber, containing mixing screws contrarotating at different speeds. It has good temperature control and a continuous readout is provided for both the melting temperature and the torque. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram.

The extracted rubber (30 g) was mixed with 3 g(10 phr) of BuTPH, BuTPDS and ABuTP individually on a two-roll mill. It was then sheeted out and cut into small pieces. The mechanochemical processes were carried out for 10 minutes at various temperatures ranging from 25° - 160°C in an open and closed chamber with a rotor speed of 60 rpm. Addition of tert-butyl peroxide (TBH) and dicumyl peroxide (DCP) at a concentration of 1:1 molar ratio to that of the additive was also carried out for particular conditions as shown in Table 3.5. The processed rubbers were diluted with unextracted rubber to obtain one phr concentration of additive in the mixtures. 5 g of diluted rubber was then extracted with boiling acetone as described in Section 2.4. The infra-red film was prepared by compression moulding (Section 2.3.4.2.2). The infra-red spectra from the extracted samples were obtained and the extent of binding was assessed by comparing the P=S index with the corresponding calibration curve (see Section 2.3.4, 3.2.2 and Figure 3.1). The results are shown in Table 3.6.

Compound	Processing temperature (^{o}C)	Extent of binding(%)			
		open chamber	closed chamber	closed chamber +	
				TBH	DCP
BuTPH	25	0	0	0	-
	40	0	0	0	-
	70	0	8	0	-
	110	7	15	17	-
	140	13	22	20	-
	160	(tacky)	(tacky)	17	-
BuTPDS	25-70	0	0	-	0
	110	0	12	-	14
	140	8.5	20	-	26
	160	(tacky)	(tacky)	-	22
ABuTP	25-70	0	0	-	-
	110	5	18	-	-
	140	12	23	-	-
	160	(tacky)	12	-	-

Table 3.6 The amount of dithiophosphoryl compounds bound to rubber processed in RAPRA torque rheometer at various temperatures

It is interesting to note that rubber processed with dithiophosphoryl compounds in the presence of peroxides at 140°C developed an unpleasant odour, which differed from the original odour of BuTPH, with the exception of BuTPDS without peroxide. The processed rubbers, except those containing ABuTP and peroxides, were tacky. The tackiness could be eliminated by diluting the processed rubbers with unprocessed rubber. However, when the processing temperature was increased to 160°C, the dilution gave no effect: the diluted rubbers were still tacky and could not be extracted and used to determine the extent of binding. In contrast, the processed rubber containing BuTPH + TBH, BuTPDS + DCP and ABuTP showed a tendency to brittleness and also developed an unpleasant odour.

Table 3.6 shows that the binding reaction of dithiophosphoryl compounds to rubber through the mechanochemical process gives rise to a very low extent of binding in the temperature range of 110°-160°C. It is shown that the extent of binding increases with processing temperature up to 140°C, but on further increasing the temperature to 160°C the extent of binding decreases. The mechanochemical process in a closed chamber in the presence of peroxide produces a higher extent of binding than that in a closed chamber without the addition of peroxide. Both processes produced higher adduct than that carried out in an open chamber.

Figures 3.5a-d show the changes of torque during processing of acetone extracted SMR-5L in a RAPRA torque rheometer in the presence of 10 phr dithiophosphoryl compounds at four

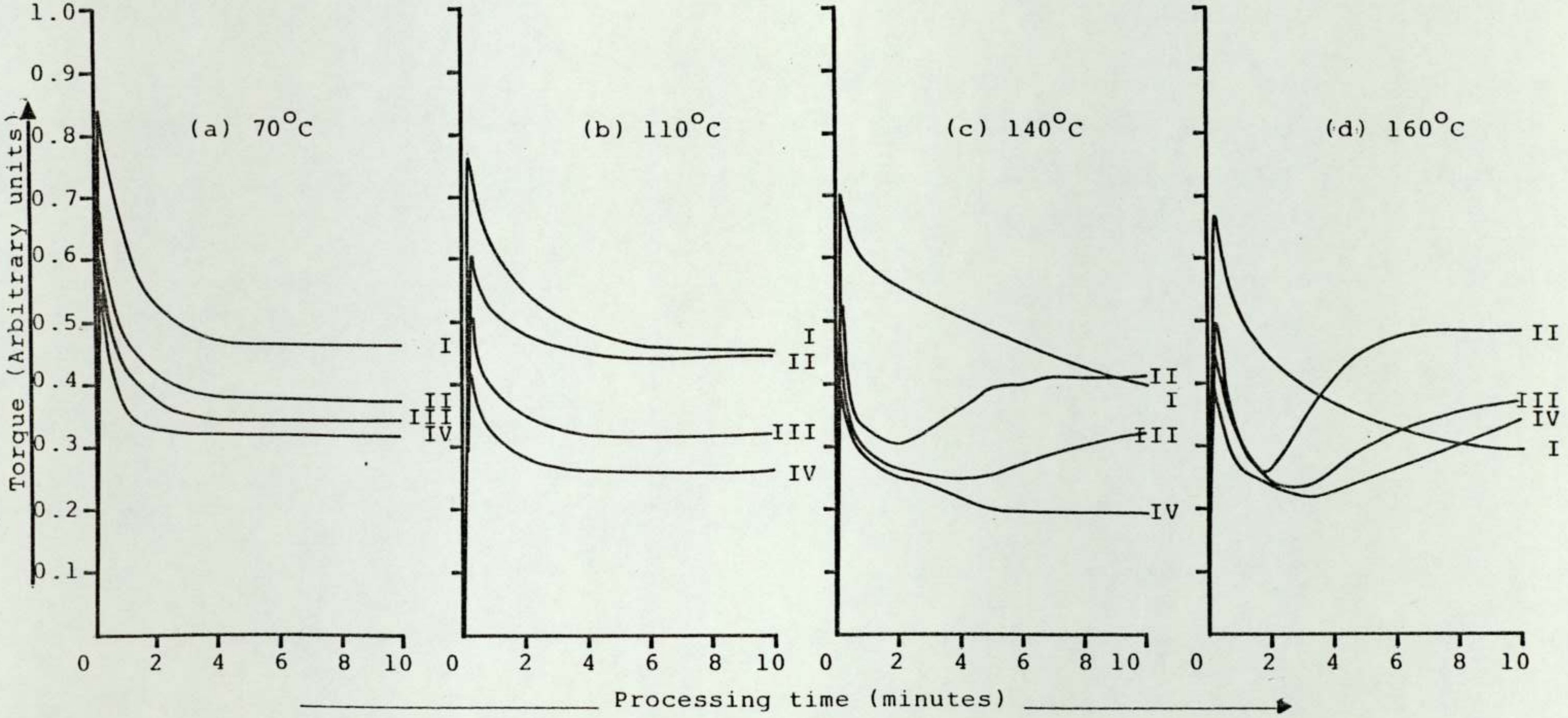


Figure 3.5 Change of torque with temperature. processing time and addition of dithiophosphoryl compounds (10%) during processing of extracted NR in RAPRA torque rheometer(closed chamber) for 10 minutes at 68 rpm. I No additive. II ABuTP III BuTPH and IV BuTPDS.

processing temperatures (70°, 110°, 140° and 160°C) for 10 minutes. Initially there is a sharp rise in the torque when the rubber is introduced into the processing chamber within the first minute of processing. After reaching a maximum (usually called fusion point), the torque decreases due to reduction in viscosity. The initial torque at all processing temperatures follows the order: control>ABuTP> BuTPH>BuTPDS, and the initial torque decreases with temperature.

At 70°C and 110°C (Figures 3.5a and 3.5b), the torque of all rubber samples drops sharply during the first 3 minutes and then reaches a plateau throughout the remainder of the processing time of 10 minutes. It should be noted that the torque level of BuTPH and BuTPDS during processing at 110°C is lower than that at 70°C, while the opposite is true for ABuTP. When ABuTP is processed at 140°C, the torque decreases sharply for the first 2 minutes and then starts to increase and reaches a plateau after 5 minutes (Figure 3.5c), the torque after 10 minutes is still lower than the initial torque. BuTPH follows the same pattern but the rate of torque decrease is slower and it starts to increase after 4 minutes. With BuTPDS on the other hand, the level of torque does not increase and shows the lowest torque among the entire processing temperature.

It is interesting to note that at 160°C, the level of torque of all the rubber samples containing dithiophosphoryl compounds increase after initially decreasing for the first 2-3 minutes. The torque of ABuTP after 10 minutes reaches the same level as the initial torque, while the final torque of BuTPH and BuTPDS is still lower than their initial torque, but the final torque of the processed rubber containing additive is higher than that of the control.

3.2.7 Permanency of Adducts During Vulcanization

Acetone extracted rubber containing known amounts of bound adducts were cured using a conventional system (S 2.5; CBS 0.6; ZnO 5; stearic acid 2), in a mould for preparing the infra-red film as described in Section 2.3.4.2. The films were then extracted continuously with an azeotropic solvent mixture as described in Section 2.5.3.5. The levels of binding were determined using the infra-red method described in Section 2.3.4. The results are tabulated in Table 3.7.

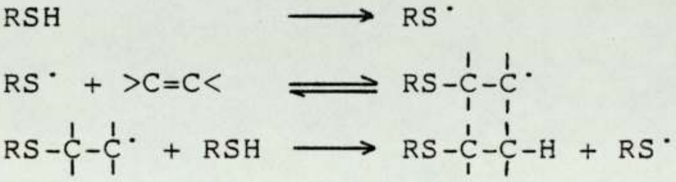
Adduct	Thiophosphoryl bound (%)	
	before vulcanization	after vulcanization
P^{i}TP	44	23
BuTP	48	21

Table 3.7 Binding level after vulcanization

The results above show that the adduct was partially eliminated during vulcanization, about half of it was lost after extraction.

3.3 Discussion

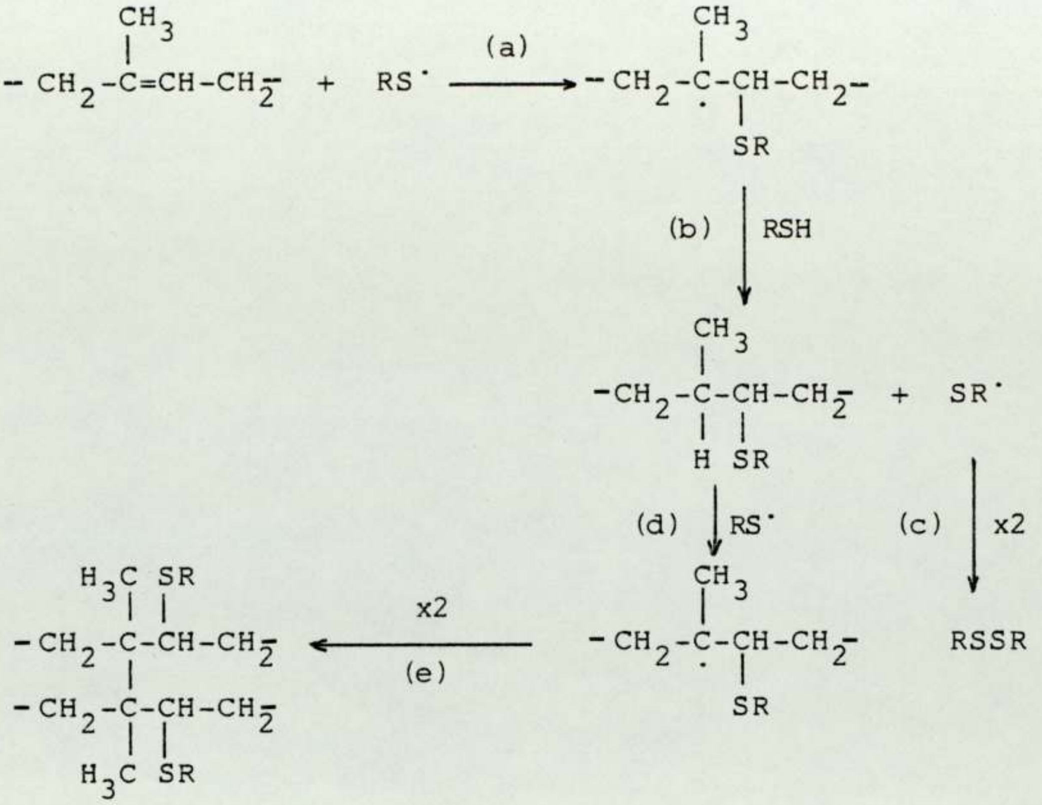
The free radical addition of thiols is a typical chain reaction, and is accordingly initiated by the addition of peroxides, azo compounds etc., or by exposure to other radiation. The anti-Markovnikov addition of thiols to unsaturated compounds, first studied by Kharasch et al(288,289), involves three essential steps(288):



$$\begin{aligned} &RSH \longrightarrow RS^{\cdot} \\ &RS^{\cdot} + {>}C{=}C{<} \rightleftharpoons RS{-}C{-}C^{\cdot} \\ &RS{-}C{-}C^{\cdot} + RSH \longrightarrow RS{-}C{-}C{-}H + RS^{\cdot} \end{aligned}$$

The initial products are thiyl radicals formed by hydrogen abstraction by free radical generators. The thiyl radicals subsequently add to the unsaturated substrate to form an alkyl radical, the latter is frequently reversible(290). The alkyl radical then reacts with a thiol molecule to give the saturated product and a new thiyl radical, thus propogating the radical chain.

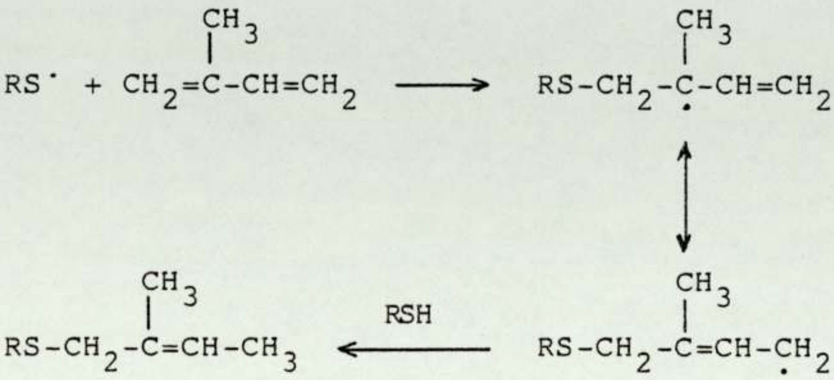
It has been demonstrated by Scott and his school(161-166) that similar reactions involve the hydroperoxide initiated free-radical addition of thiol based antioxidant to natural rubber according to Scheme 3.1 below(163).



Scheme 3.1 Adduct formation in natural rubber

The reaction scheme indicates that the other termination process in the free radical chain reaction is dimerization of the thiyl radical to form disulphide (Scheme 3.1c) and the formation of crosslinking (Scheme 3.1e)(291). However, BHBM inhibits the latter process even in the presence of a molar excess of radical generator(163).

0,0-dialkyldithiophosphoric acids are also readily added to a double bond in an anti-Markovnikov manner. Oswald et al(252) examined the addition of 0,0-diethyldithiophosphoric acid to dienes catalysed by cumene hydroperoxide and concluded that the course of the addition is similar to that of thiols. On addition to isoprene, the thiophosphoryl thiyl radical preferentially attacked the first carbon atom of the basic 1,3-butadiene skeleton in the first propagation step so as to give the more stable intermediate allylic radical, the latter in turn abstracted a hydrogen atom from the dithiophosphoric acid at the less highly substituted allylic carbon atom to yield the corresponding 1,4-monoadduct. The formation of this compound could be rationalized by the following mechanism:



$$RS^{\cdot} + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow RS{-}CH_2{-}\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2$$

$$\updownarrow$$

$$RS{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3 \xleftarrow{RSH} RS{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}\underset{\bullet}{C}H_2$$

It appears from present studies that thiophosphoryl compounds react with natural rubber latex in the presence of hydroperoxide, the reaction proceeds in a similar manner to that of other thiols. However, unlike BHBM, which requires a [TBH]/[antioxidant] ratio of 1.5:1 to maximise the binding to rubber, dithiophosphoryl compounds require a ratio of 4:1 to obtain a maximum of 50% bound to rubber (Section 3.2.4.1, 3.2.4.2 and 3.2.5.1). This suggests that apart from generating thiophosphoryl thiyl radicals, peroxides may be consumed by abstracting hydrogens from rubber molecules. The resultant alkyl radicals formed leads to the formation of crosslinks. As a matter of fact, gel was formed during the binding reaction.

It has been previously proposed(166,292,293) that a small portion of non-rubber constituents pre-existing in the latex interferes with the binding reaction initiated by the radical generator. Bloomfield and Swift(292) have reported low results in grafting methyl methacrylate with natural rubber latex using TBH or CHP as initiator. It was suggested that the addition of substantially higher proportions of initiator to monomer was necessary to offset the retarding effect of the unknown compound in natural rubber. Suharto(166) has also reported similar results during binding of BHBM to natural rubber latex and deproteinised natural rubber latex, but a higher binding level was obtained using SBR latex. It is believed that the retarding effect is due to resinous acetone extractable material pre-existing in latex and not the protein previously suspected(293).

Another possible factor responsible for the low binding level is chain termination due to dimerization of the thiophosphoryl thiyl radical to form the thiophosphoryl disulphide as occurs in the reaction of thiol with peroxyl radical(291), or oxidation of dithiophosphoric acid by hydroperoxide to form the disulphide (3.1)(248).

$$2(RO)_2PSSH + R'OOH \longrightarrow [(RO)_2PSS]_2 + R'OH + H_2O \qquad (3.1)$$

Similarly, the corresponding ammonium salt is readily oxidized to form disulphide under the reaction conditions reported in this study. However, disulphide was not oxidized to form the thiophosphoryl thiyl radical(294).

The concentrated masterbatches of the thiophosphoryl adduct cannot be prepared using the acids since these cause coagulation of the latex (Section 3.2.4.4 and 3.2.5.2), due to the strong acidity of 0,0-dialkyldithiophosphoric acid; the pKa of PiTPH and BuTPH are 1.82 and 1.83 respectively(295) (pKa acetic acid=4.75(296)). TEPA also seems to interfere with the binding reaction of the acid with the natural rubber latex. This is the reason for keeping the pH of the latex high in the present study. Reducing the pH of the latex down to 8.5-9 caused coagulation of the latex in the addition of 1 phr of dithiophosphoric acid. This can be avoided by using the corresponding ammonium salt, but the amount of ammonium salt added to the latex to make a high concentrate masterbatch was also limited (Section 3.2.5.2), since ions formed from the neutralisation also destabilized the latex.

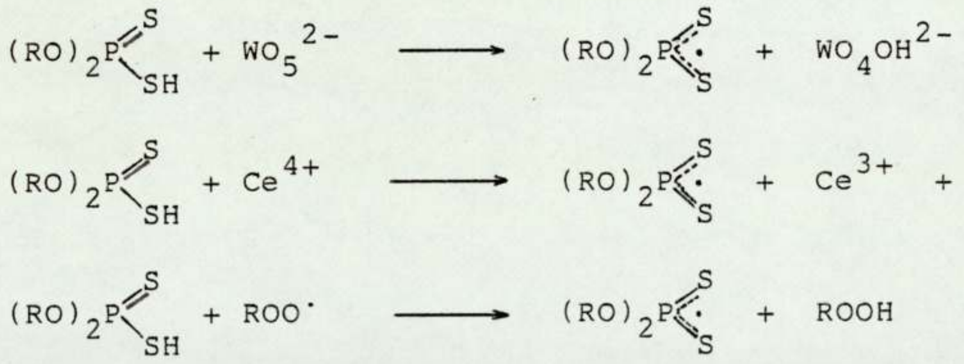
It was found that using TBH/WO_4^{2-} and TBH/Ce(IV) redox systems, the extent of binding were higher than that of TBH alone or TBH/TEPA (Section 3.2.4.3). It has been claimed that hydrogen peroxide together with sodium tungstate was used in the production of prevulcanized polymer latex(297). The reaction of cerium(IV) salt with a thiol involves direct oxidation of thiol to thiyl radical(291):

$$Ce^{4+} + RSH \longrightarrow RS^{\cdot} + H^{+} + Ce^{3+}$$

Gilbert et al(294) found that sulphinyl and sulphonyl radicals are also formed from thiols oxidized by cerium(IV), these radicals are derived from thiyl radicals. They suggested that cerium(IV) reacts rapidly with thiols to form thiyl radicals which, at least in the absence of a high concentration of the oxidant, dimerise. The resultant disulphides can be further oxidized if an excess of cerium (IV) is present, however, this is a much slower reaction with a half-life of several hours(294,299).

It appears that the redox reactions must also occur in the latex with TBH/WO_4^{2-} and TBH/Ce(IV):

$$WO_4^{2-} \xrightarrow{ROOH} WO_5^{2-}$$



As a result, the addition of sodium tungstate and ceric salt increased the extent of binding (Section 3.2.4.3). Since Ce(IV) might oxidize thiophosphoric acids directly to thiophosphoryl thiyl radicals, this activator may therefore give rise to a higher level of bound dithiophosphate. However, excess of ions present in the latex reduce the colloidal stability of latex which is believed to be due to a mixed film of protein and phospholipid on the surface of the rubber particles(283).

It was found that the optimum reaction time to obtain maximum extent of binding was about 24 hours. nevertheless. 12-16 hours reaction time yielded only 2-3% less than that of 24 hours (Figure 3.3). Therefore. the effective binding reaction time was 12-16 hours. Unfortunately. dithiophosphate bound to rubber became partially unbound during vulcanization (Section 3.7). the extent of bound dithiophosphate was reduced by about 50-55% after vulcanization and extraction.

Rubber bound antioxidants produced by chemical reaction with latex require rigid adherence to the formulation and conditions which mades the whole process longwinded. It would be of a great practical advantage if the binding reaction could be carried out in situ during mixing. prior to the compounding and vulcanization processes of solid rubber. The shearing forces developed by the mechanical process may produce free radicals which initiate the chain reaction of antioxidant binding to the rubber. In the present study however. the mechanochemical reaction of thiophosphoryl compounds with extracted rubber produced only a low level of binding (Table 3.6). This is due to the lubricating effect of thiophosphoryl compounds (Figure 3.5).

The compounds which reduce the shear force, and hence lead to a restriction in the formation of active radical species.

The adduct formation occurred at processing temperatures of 110°-160°C with maximum extent of binding at 140°C (Table 3.6). The level of binding decreased at 160°C with the development of an unpleasant odour, and the processed rubber containing 10% ABuTP, BuTPH with TBH and BuTPDS with DCP was brittle. This would suggest that ABuTP readily decomposes at 160°C and takes part in the formation of crosslinks, and the torque level increases during processing. Similarly, the rubber containing BuTPH with TBH and BuTPDS with DCP tends to crosslink. Although BuTPH and BuTPDS alone are able to promote crosslinks as shown by the increase in torque level during processing at 160°C(Figrue 3.5e), the degree of crosslinking was very low and the processed rubber was very tacky. The formation of crosslink leads to decrease in the adduct formation.

3.3 Conclusion

It appears that 0,0-diisopropyldithiophosphoric acid, 0,0-dibutyldithiophosphoric acid and its ammonium salt can be bound to natural rubber latex, producing a maximum yield of 50% in the presence of TBH or CHP. Cerium (IV) increases the amount bound considerably, but excess of ceric salt coagulates the latex. Concentrate masterbatch can only be prepared from ammonium salt of dithiophosphoric acid at maximum concentration of 15 phr. A slightly higher concentration of 0,0-dialkyldithiophosphoric acid causes coagulation of the latex. Binding of dithiophosphoryl compounds mechanochemically to an extracted rubber in a RAPRA torque rheometer gives rise to a low level of adduct formation.

CHAPTER FOUR

ASSESSMENT OF VULCANIZATION CHARACTERISTICS AND DURABILITY OF RUBBER VULCANIZATES CONTAINING DITHIOPHOSPHORYL COMPOUNDS

4.1 Introduction

A primary requirement for a rubber compound is that the vulcanization process must be possible to convert the relatively plastic polymer into a relatively elastic state with properties appropriate for adequate service life. This can be achieved by using an appropriate vulcanizing system and accurate parameters of vulcanization. Critical parameters related to the process of vulcanization are the time elapsed before onset (scorch time), the cure rate and the extent. There must be sufficient scorch resistance to permit mixing, forming the moulding, and a rapid formation of crosslinks. These parameters; scorch time, cure rate and modulus level can be simply measured by following the rheological changes in the rubber.

The technological properties of the vulcanizate are affected by the type of crosslink, the nature of polymer and the type and amount of compounding ingredients. They are primarily a function of the crosslink density. For example, fatigue life increases with small amounts of crosslink but is reduced with increasing crosslink formation(265). The rate of stress relaxation also depends on the degree of crosslinking(300), and for this reason comparison between different vulcanizates are made at approximately equal moduli(111).

It has been described in Section 1.9 that the aim of the present study is to evaluate the curing characteristics, fatigue life and ozone resistance of natural rubber vulcanizates containing dithiophosphoryl compounds. It is believed that sulphinyl radicals are formed during the processing of polyolefins containing dithiophosphoryl compounds. those radicals are capable of capturing alkyl radicals(206) which are known to be formed during fatiguing. In view of this finding, the antifatigue of activity of dithiophosphoryl compounds in the various vulcanization system such as conventional accelerated sulphur, EV, sulphurless and peroxide were evaluated. The curing characteristics, ozone resistance and oxidative ageing of those vulcanizates were also studied.

4.2 Assessment of Vulcanization Characteristics and Durability of Adduct Vulcanizates

4.2.1 Conventional Accelerated Sulphur Vulcanization Characteristics

The rubber adducts of 0,0-dialkyldithiophosphoric acids were prepared according to the procedure described in Sections 2.3.1 and 2.3.2. The process was carried out at 60°C for 16 hours. The initiator, activator used in the reactions and the level of binding are listed in the table below (Table 4.1).

The vulcanization characteristics of the above rubber adducts were assessed using the Monsanto Rheometer 100 as described

Compounds	[Acids]:[TBH]	Activator	% Bound
Adduct 1. P^iTPH	1:3	-	44
Adduct 2. P^iTPH	1:3	Ce(IV).0.4g	74
Adduct 3. BuTPH	1:4	-	50
Adduct 4. ABuTP*	1:3	-	40

* 10% concentrate masterbatch diluted 10x

Table 4.1 Rubber adduct of dithiophosphoryl compounds

in Section 2.5.2. The vulcanization system was a conventional accelerated sulphur tabulated in Table 4.2 and the gum stocks were cured at 140°C. Their curing characteristics

Substance	Parts by weight
Rubber	100
ZnO	5
Stearic acid	2
CBS	0.6
S	2.5

Table 4.2 Conventional accelerated sulphur formula

were compared with the rubber derived from centrifuged latex as a control and with the controls containing 1 phr each of IPPD and dithiophosphoryl compounds. The Monsanto rheographs obtained were then interpreted to obtain the following parameters; torque ΔT or $T_{max}-T_{min}$; scorch time, t_2; and cure rate $t_{90}-t_2$ as described in Section 2.5.2. The vulcanization characteristics of unextracted and acetone extracted rubber adducts together with the control and the rubber compounds containing different additives are listed in Table 4.3.

Results given in Table 4.3 show that all the adducts, extracted and unextracted, slightly reduce the scorch time but markedly reduce the cure rate compared to the control. Unextracted rubber adducts show a tendency to increase the modulus. The adducts produced by the binding reaction of P^{i}TPH with natural rubber latex catalysed by TBH/Ce(IV) did not effect changes in the modulus level over the control. There was no significant difference between the curing characteristics of the 0,0-diisopropyldithiophosphoryl adduct and that of 0,0-dibutyldithiophosphoryl adduct.

The addition of 1 phr of P^{i}TPH, BuTPH, BuTPDS and ABuTP drastically changed the curing characteristics over the control. All the above additives increased the modulus and there were noticeable decreases in the induction times and cure rates as compared to the control. The addition of ZBuTP had a less pronounced effect on the modulus, and reduced the induction time and cure rate considerably. An interesting feature from the rheographs was that all the unextracted adducts and stocks containing dithiophosphoryl

Stocks	T.Kg.m ($T_{max}-T_{min}$)		t_2.minutes (Scorch time)		$t_{90}-t_2$.minutes (cure rate)	
	Unext.(a)	Ext.(b)	Unext.	Ext.	Unext.	Ext.
Control (no additive)	3.42	3.36	13	12	16	14
Adduct 1.P^iTPH(c)	3.54	3.36	10.5	10.5	8.4	10
Adduct 2.P^iTPH/Ce(IV)	3.36	3.36	10.5	11	8.5	10
Adduct 3.BuTPH	3.72	3.48	10.5	10	9	10
Adduct 4.ABuTP	3.78	3.48	10.3	10.5	7.7	12
P^iTPH added	4.38	-	7	-	6.5	-
BuTPH added	4.26	-	7.5	-	5.5	-
BuTPDS added	4.2	-	11	-	8	-
ABuTP added	4.2	-	6.5	-	7	-
ZBuTP added	3.6	-	9.5	-	8.5	-
IPPD added	3.54	-	16	-	10	-

(a) Unextracted

(b) Extracted

(c) Codes used in this table are shown on page 17

Table 4.3 Curing characteristics of rubber adducts of dithiophosphoryl compounds and the controls at 140°C.

compounds added showed no reversion, whereas the extracted rubber containing adduct did.

IPPD delayed the induction time but accelerated the cure. The optimum modulus of the stock was about the same as that of the control. It was reported earlier (Section 3.2.7.) that the bound additives became partially unbound during vulcanization, while the dithiophosphoryl compounds added to rubber during compounding did not give rise to the formation of adduct (Table 4.3).

4.2.2 Discussion

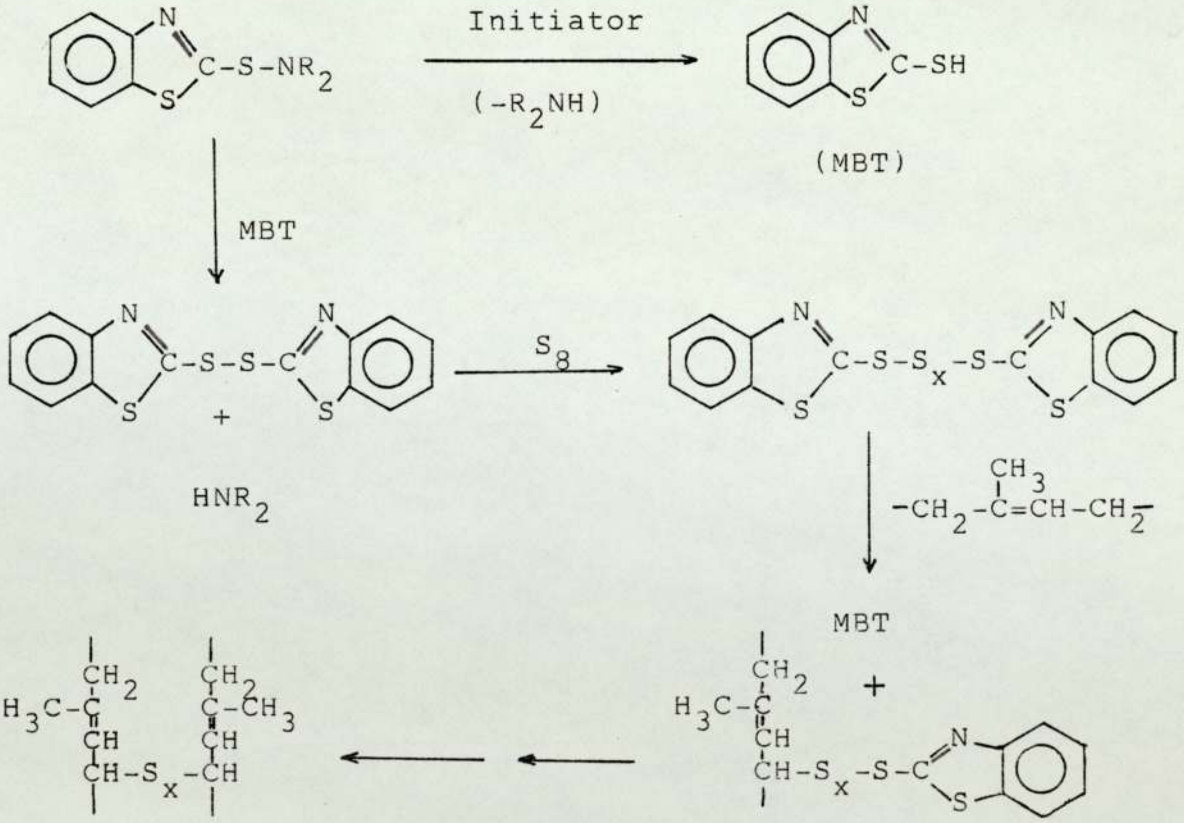
In recent years, there has been considerable debate concerning the mechanism of accelerated sulphur vulcanizations. It is still not understood whether the predominant reactions are free radical(303-306) or polar in nature(51,52,307-309). Several recent investigations provide evidence for a mixed radical and polar mechanism; these include kinetic(310,311) and Raman and ESR spectroscopic studies(312-314) of thiuram accelerated vulcanization.

Sulphur vulcanization accelerated by sulphenamides is thought to proceed by the steps shown in Scheme 4.1(315,316).

i. The accelerator reacts with sulphur to give monomeric polysulphide of the type $A_c-S_x-A_c$, where A_c is an organic fragment derived from the accelerator. Certain initiating species may be necessary to start the reaction, which then appears to be autocatalytic.

ii. The polysulphides can interact with rubber to give polymeric polysulphide of the type rubber-S_x-A_c. During this reaction, the formation of mercaptobenzthiazole (MBT) was observed.

iii. The rubber polysulphides then react either directly or through a reactive intermediate, to give crosslinking.



Scheme 4.1 Mechanism of sulphur vulcanization accelerated by sulphenamide

Crosslinking in the presence of a sulphenamide accelerator does not start until virtually all the sulphenamide has been consumed(317). Therefore the delayed action effect is largely associated with the disappearance of the accelerator, which becomes depleted in an autocatalytic fashion with the formation of 2-mercaptobenzothiozole (MBT)(318,319). The rate of depletion is almost proportional to the amount of MBT present. If MBT could be removed from the system as fast as it is formed, substantial improvement in processing safety would occur.

Tarasova et al(320) pointed out that when a dialkyldithiophosphoryl compound was used in a sulphur vulcanization accelerated by N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) at 143°C, there was a marked increase in the modulus and in crosslink density. However, the zinc complex did not accelerate the vulcanization. Furthermore, they found that the zinc complex of dithiophosphate reacted with CBS.

Bis(0,0-diisopropyl)thiophosphoryl disulphide has been studied(172-174) as a sulphur donor in the vulcanization of cis-polyisoprene, in the presence of 4,4'-dithiodimorpholine (DTDM or DMDS) and it was suggested that sulphur donation is due to the cleavage of the dithiophosphoryl disulphide bond promoted by the base, free sulphur being added for additional crosslinking.

In the present study, the addition of 1 phr of dithiophosphoryl compounds to natural rubber stocks cured in a conventional sulphur system accelerated by CBS at 140°C, increased the modulus level except for the stock containing zinc complex. All the additives, including the zinc complex reduced the scorch time and cure rate. These results are consistent with the results obtained by Tarasova et al$^{(320)}$ and suggest that, according to the mechanism of sulphur vulcanization accelerated by sulphenamide described in Scheme 4.1, dithiophosphoryl compounds act as catalysts for the formation of MBT and hence accelerate the cure and reduce the scorch time. It is thought that at the same time these compounds increase the efficiency of sulphur up-take by 2,2'-dibenzothiazyl disulphide (MBTS), thus leading to an increase in the crosslink density, or that they are taking part in the formation of additional crosslinks as pointed out by Pimblott et al$^{(172-174)}$.

Unextracted adducts slightly increased the modulus levels, this may be due to the presence of unreacted additive in the stocks, except for the adduct derived from $P^{i}TPH/Ce(IV)$ which contains a high proportion of $P^{i}TPH$ attached chemically to the rubber. The unreacted additives also caused a slight reduction in the induction time and cure rate.

Although the unreacted additives no longer exist in the rubber after extraction, the bound additives became partially unbound during vulcanization, and the curing characteristics were affected. The formation of intermediates $A_c-S_x-A_c$ (Scheme 4.1) is delayed due to the scavenging effect of IPPD.

4.2.3 Durability of Rubber Vulcanizates Containing Bound Dithiophosphoryl Compounds

The dithiophosphoryl adducts were vulcanized using the conventional sulphur system accelerated by CBS as described in Table 4.2. The fatigue resistance, ozone resistance and the stress relaxation were assessed and compared to the controls (i.e., the vulcanizates containing 1 phr of dithiophosphoryl compounds and a known commercial antioxidant, IPPD). All the gum stocks were cured at 140°C at the approximately equal modulus. The cure times to reach a torque level (ΔT) of 3.36 kg.m (56 dN.m) are tabulated in Table 4.4. The extent of binding in the adduct vulcanizates and other vulcanizates were evaluated after being extracted with azeotropic mixtures.

4.2.3.1 Stress Relaxation

The oxidative ageing of rubber vulcanizates by heat is a chemical process leading to the degradation of the polymer network, whereby a small amount of chemical changes has a profound effect upon the elastic properties of the material. It is, therefore, convenient to study ageing by following

Stock	Bound (%)		Curing time (minutes)
	Before Cure	After Cure	
Control	-	-	35
Adduct 1.P^{i}TPH	44	22.5	25
Adduct 2.P^{i}TPH/Ce(IV)	74	31	26
Adduct 3.BuTPH	50	23	22.5
Adduct 4.ABuTP	38	17	19.5
P^{i}TPH added	-	unbound	12
BuTPH added	-		11.5
BuTPDS added	-		17
ABuTP added	-		11
ZBuTP added	-		17.5
IPPD added	-		33

Table 4.4 Curing time for conventional accelerated sulphur vulcanizates to reach $\Delta T=3.36$ kg.m

the decrease of stress under constant elongation with time of ageing. Measurements of this type were first introduced by Tobolsky(302) in 1944, who pointed out that according to the kinetic theory of rubber elasticity, the stress F in a vulcanizate of cross-sectional area A_o stretched to an extension ratio λ is:

$$F = NkTA(\lambda-\lambda^2) \qquad \text{(Eq. 4.1)}$$

where k=Bolezman's constant

T=absolute temperature

N=the number of network chains supporting the stress per unit volume

During the course of ageing for any time t, the number of network chains supporting the stress will be reduced from N_o to N and the stress will also be reduced from F_o to F. N and F however, will always be related as in Equation 4.1, so that at constant extension ratio, λ, sectional A_o and temperature ,

$$F/F_o = N/N_o \qquad \text{(Eq. 4.2)}$$

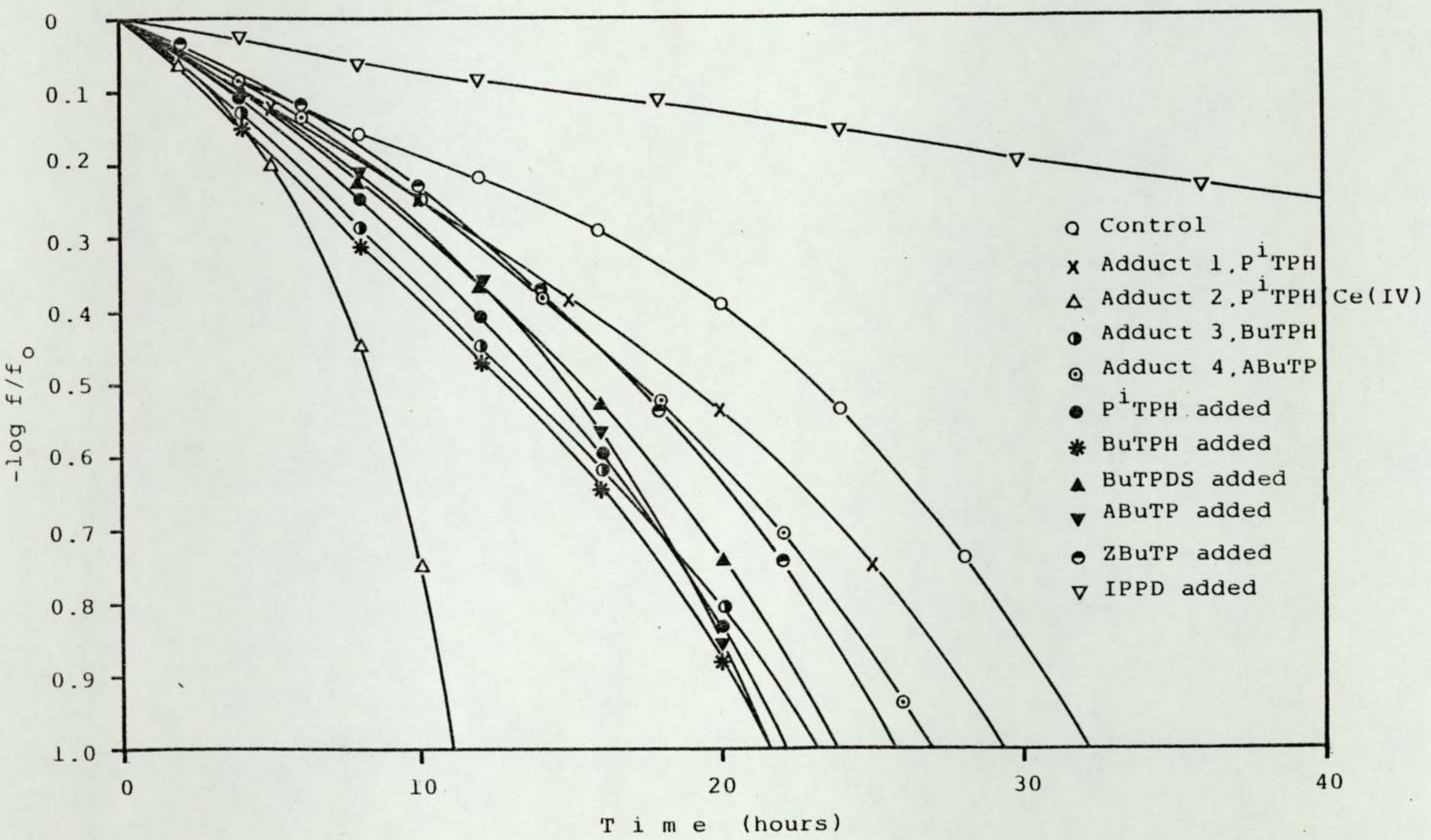
Stress relaxation can be carried out continuously or intermittently. In continuous stress relaxation, as carried out throughout this study, the extension is maintained constant during ageing, thus giving a measure of the network scission. In intermittent stress relaxation, the sample is only strained 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 the 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 rubber adducts of dithiophosphoryl compounds were examined in conventional sulphur vulcanizates and held at 40% extension at 100^{o}C. The apparatus and testing procedure were described in Section 2.6.3.1 and 2.6.3.2. The results are shown in Table 4.5, Figure 4.1 and 4.2.

4.2.3.2 Fatigue and Ozone Resistance Measurements

The conventional accelerated sulphur vulcanizates of dithiophosphoryl adducts were subjected to fatigue and evaluated against the known commercial antifatigue agent IPPD and dithiophosphoryl compounds added in 1 phr portions. The fatigue tests were carried out on the Monsanto Fatigue-to-Failure Tester at 60% extension as described in Section 2.6.1.

The ozone resistance of the above vulcanizates were also tested and the tests were carried out in a Hampden-Shawbury



<u>Figure 4.1</u> Continuous stress relaxation of unextracted conventional accelerated sulphur vulcanizates containing 1 phr of dithiophosphoryl compounds.

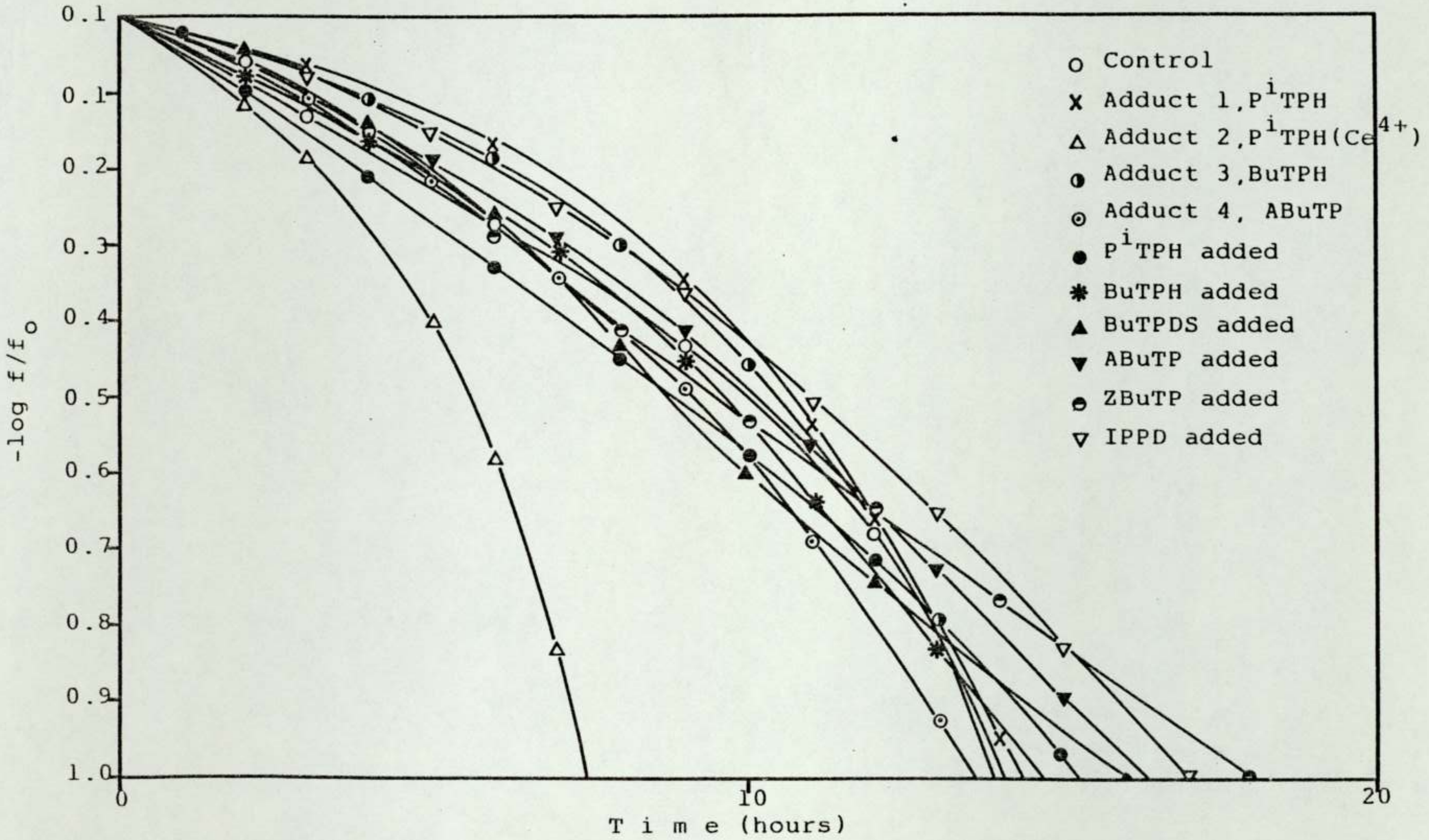


Figure 4.2 Continuous stress relaxation of extracted conventioal accelerated sulphur vulcanizate containing 1 phr of dithiophosphoryl compounds.

Ozone test cabinet at 20% extension in ozone concentration of 25 pphm as described in Section 2.6.2.1 and 2.6.2.2. The results were tabulated in Table 4.5 together with the results obtained from fatigue and stress relaxation tests.

Stock	Durability (hours)					
	Fatique life		**Ozone resistance**		$t_{50}^{(a)}$ (hrs)	
	Unext.	Ext.	Unext.	Ext.	Unext.	Ext.
Control	52	30	35	19	16.3	6.7
Adduct 1. P^iTPH	27	19	35	18	10.1	8.3
Adduct 2. $P^iTPH/Ce(IV)$	27	34	36	21	6.3	4.2
Adduct 3. BuTPH	29	23	34	18	8.3	7.8
Adduct 4. ABuTP	31	23	30	20	11.6	7.2
P^iTPH added	23	23	31	18	9.3	5.9
BuTPH added	29	21	30	19	7.7	6.7
BuTPDS added	28	24	33	17	10.3	6.3
ABuTP added	59	23	30	22	10.5	7.1
ZBuTP added	43	27	36	17	12	6.2
IPPD added	526	25	48	20	43.5	7.7

(a) t_{50} = Time to 50% stress decay

Table 4.5 The fatigue life, 50% stress decay and ozone resistance of conventional accelerated sulphur vulcanizates containing dithiophosphoryl compounds

4.2.3.3 Results

Incorporation of dithiophosphoryl compounds during normal compounding and vulcanization do not lead to rubber bound additives. Conversely, the amount of bound additives in the adduct vulcanizates were reduced during vulcanization (Table 4.4).

Table 4.5 shows that the vulcanizates containing both dithiophosphoryl adducts and dithiophosphoryl compounds introduced during compounding exhibit a lower fatigue life compared to the control, with the exception of vulcanizates containing ammonium 0,0-dibutyldithiophosphate (ABuTP) which improves the fatigue life slightly. Similar trends were observed with the extracted vulcanizates, with the exception of the adduct vulcanizate prepared by binding P^{i}TPH with latex in the presence of Ce(IV), and TBH which improved the fatigue life slightly. In the case of IPPD, the fatigue life is quite remarkably high. The extracted vulcanizates, however, have completely lost their fatigue resistance.

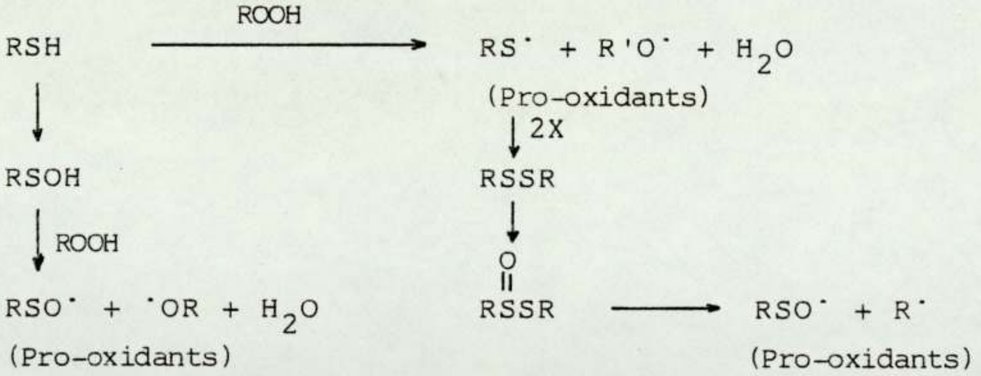
The ozone resistance of unextracted and extracted vulcanizates containing dithiophosphoryl compounds were not significantly different from that of the control. IPPD on the other hand, is a good antiozonant. The effect of IPPD as an antiozonant is lost after extraction.

Figures 4.1 and 4.2 compare the stress relaxation behaviour of the same vulcanizates at 100°C, and the times to 50%

decay are given in Table 4.5. All the curves except those for the unextracted vulcanizate containing IPPD are autocatalytic and fast. P^iTPH adduct prepared in the presence of Ce(IV) shows a very fast stress relaxation rate in both the unextracted and extracted vulcanizates. The unextracted vulcanizates containing dithiophosphoryl compounds showed a tendency towards an increased rate of stress relaxation over the control. IPPD showed retardation of stress decay (Figure 4.1) compared to the control. However, the IPPD vulcanizate lost its inhibition effect in the oxidative stress relaxation after extraction. Extracted vulcanizates containing dithiophosphoryl compounds showed no significant difference from the extracted control (Figure 4.2), except for the extracted vulcanizate prepared from the reaction of P^iTPH with natural rubber latex catalysed by Ce(IV) reported earlier, which shows a faster rate of stress decay.

4.2.3.4 Discussion

A review given by Kempermann(321) in the ageing of rubber and of the influence of stabilizers on the degradation reported that the peroxide decomposers based on sulphides or disulphides are equally ineffective in sulphur vulcanized rubber. It was suggested that the vulcanized rubber already contains sulphide and disulphide groups in excess; the addition of an extra sulphide such as dilaurylthiodipropionate can therefore produce no additional effects. Dunn and Scanlan(201) found that the metal complex of dithiophosphoryl compounds are ineffective in protecting accelerated sulphur vulcanizates against oxidative ageing. but they are potent retarders of stress decay in the sulphurless vulcanizates. In the present studies. the dithiophosphoryl compounds present in the sulphur vulcanizates are not only ineffective in the protection of the vulcanizates against oxidative ageing (see Table 4.5). but these compounds show a negative effect on ageing resistance. This would suggest that the dithiophosphoryl compounds exhibit a pro-oxidant effect under these conditions. It has been established that a wide variety of organic sulphur compounds can function as antioxidant. Despite their antioxidant activity. these compounds show an initial pro-oxidant effect(8,322) associated with the interaction of the sulphide and its derivatives with the limited hydroperoxides formed during the early stages of the oxidative ageing (Scheme 4.2)(8):

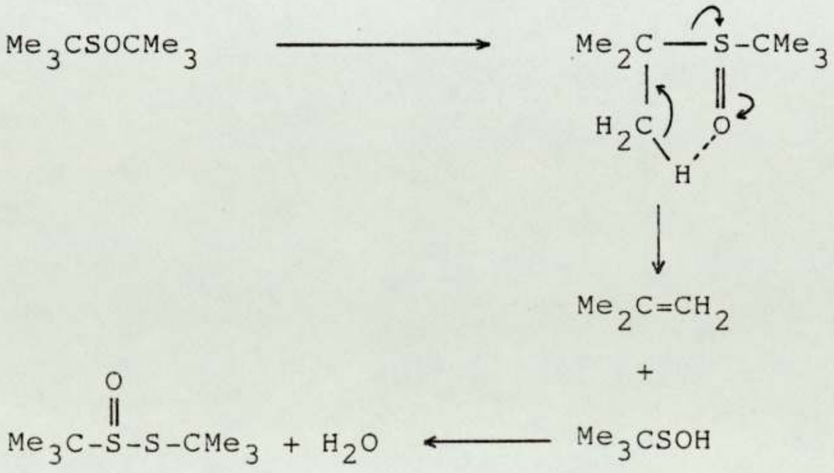


Scheme 4.2

These pro-oxidant species would be produced during vulcanization (further results in next section show that the formation of the antioxidant function is temperature dependent).

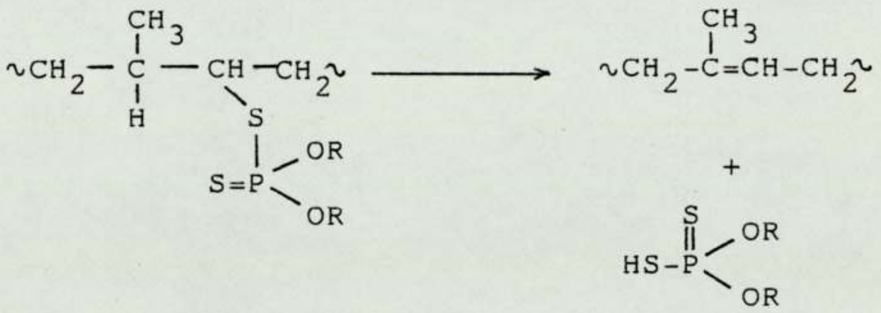
It has been shown in Section 3.2.6.2that ABuTP was degraded during processing in a torque rheometer at 140°C and above. This would suggest that the ammonium salt of 0.0-dibutyldithiophosphoric acid readily decomposes and this may also occur during vulcanization, giving rise to a CB-A activity during fatiguing and hence improves the fatigue life. However, there is no improvement in stress relaxation. The vulcanizates derived from rubber adduct prepared by the binding reaction of 0,0-diisopropyldithiophosphoric acid catalysed by Ce(IV) showed inferior fatigue and stress relaxation resistance with respect to other vulcanizates. This may be due to a trace amount of ceric salt being trapped in the rubber during coagulation of latex caused the oxidation of the vulcanizate.

It has been recognised that the thermal scission of monosulphdic crosslinks occurs at the C-S bond via an interchange reaction(54,55). The thermal decomposition (Scheme 4.3) occurs through a cyclic transition state, in which scission of the C-S bond is accompanied by a transfer of hydrogen from the β-carbon atom to the sulphinyl hydrogen proposed by Colclough and Cunneen(53):



Scheme 4.3

Unlike the interchange reaction above, the elimination of the adduct during vulcanization may be due to the cleavage of the dithiophosphoryl group initially bound to rubber (see Scheme 4.4):



Scheme 4.4

This thermolysis is probably the main reaction responsible for the pro-oxidant activity of the thiols, thiolates and disulphides in a reactive rubber substrate in the presence of oxygen during ageing (see Scheme 4.2)(8).

IPPD is known to owe its effective antifatigue activity to its conversion to the corresponding nitroxyl radical (Section 1.8) which is an alkyl radical scavenger. The continuous regeneration of the nitroxyl radicals in IPPD in a cyclical mechanism involving the hydroxylamine has been shown to be responsible for the effect of IPPD as an antifatigue agent(123).

4.3 Assessment of the Curing Characteristics and the Durability of Vulcanizates Containing Bis(0,0-dibutyl)thiophosphoryl Disulphide

4.3.1 Introduction

It has been established that, like the dialkyldithiocarbamates, the dialkyldithiophosphates are potent inhibitors of the ageing of sulphurless vulcanizates of natural rubber, although they are ineffective in an accelerated sulphur vulcanizate(201). Bis(0,0-diisopropyl)thiophosphoryl disulphide has been evaluated as a sulphur donor for cis-1,4-polyisoprene and found to be ineffective at 140°C. At 160°C the compound has good ageing behaviour(173). It has been found in the present studies that the dithiophosphoryl compounds are ineffective in accelerated sulphur systems to protect the vulcanizate from fatiguing,, stress relaxation and ozone exposure (Section 4.2.3.3).

In subsequent studies of antioxidant function of nickel dithiolates in polyolefin(237), a proposal has been put forward that the initial stage of the reaction leads to the formation of the corresponding disulphides, which then undergo further oxidation to sulphur acids which are able to decompose hydroperoxide catalytically. The oxidation product, thiosulphinates ,were found to be very effective antioxidants and the related sulphinyl radical produced during oxidation of the disulphide is thought to be a very effective alkyl radical trap(206). The disulphides appear to show a similar behaviour to that of the simple alkyl or aryl disulphides. which have been shown(327-329) to be ineffective themselves in inhibiting oxidation of organic substrates.

In the present studies therefore. bis(O.O-dialkyl)thiophosphoryl disulphides were added in various vulcanization systems such as EV. sulphurless and peroxide cure system at various temperatures and evaluated the fatigue, stress relaxation and ozone resistance.

4.3.2 Conventional Accelerated Sulphur. EV and Sulphurless Vulcanization

4.3.2.1 Curing Characteristics

The terms EV (efficient vulcanization) and inefficient. or conventional. represent two extremes. At one extreme. the EV uses a low or even zero level of elemental sulphur. a high concentration of accelerator and possibly a so-called "sulphurless" system can be used which includes a sulphur donor in place of elemental sulphur. At the other extreme. a conventional system uses a high concentration of elemental sulphur and a low concentration of accelerator.

In the present studies. natural rubber (SMR-10) was cured in the presence of 1 phr BuTPDS in various gum stocks using the formulations set out in Table 4.6. The accelerator used in the EV system was CBS and in the case of the sulphurless system, TMTD was used as a sulphur donor. The amount of sulphur and accelerators added was such that the modulus level of all the stocks was approximately the same, at a cure temperature of 140°C. The curing characteristics of the stocks were assessed using the Monsanto Rheometer 100 as described in Section 2.5.2. The rheographs obtained were then interpreted to obtain the parameters of vulcanization, namely: the torque ΔT or $T_{max}-T_{min}$: scorch time t_2 and cure rate $t_{90}-t_2$ as described in Section 2.5.2. The vulcanization parameters are listed in Table 4.6.

As described in Section 4.2.1, BuTPDS increased the modulus level and reduced the cure rate of conventional accelerated sulphur vulcanization at 140°C. At 160°C, a similar trend was observed. The addition of 1 phr of BuTPDS to EV system caused a slight decrease in scorch time and cure rate at 140°C and slightly reduced the scorch time at 160°C, but caused no significant change in modulus or cure rate at both temperatures. In the case of the sulphur donor system, the results in Table 4.6 show that the scorch times at 140°C and 160°C are longer in the presence of 1 phr BuTPDS, but the cure rate decreases at 140°C. The other curing characteristics are not affected by the presence of BuTPDS. EV and sulphurless systems gave flat curves of modulus at both temperatures, while conventional system gave reversion characteristics.

	Conventional		EV		Sulphurless	
Ingredients						
CBS	0.6	0.6	6	6	-	-
TMTD	-	-	-	-	7	7
BuTPDS	-	1	-	1	-	1
S	2.5	2.5	0.8	0.8	-	-
Curing Characteristics at 140^{o}C						
ΔT (kg.m)	3.39	3.75	3.48	3.51	3.54	3.54
t_2 (minutes)	8.7	8.5	9.3	8.8	6.2	6.8
$t_{90}-t_2$ (minutes)	10.3	4.2	11.7	10.7	51.3	44
Cure time to reach $\Delta T=3.36$ kg.m(minutes)	26	12.5	32.5	27	75	68
Curing Characteristics at 160^{o}C						
ΔT (kg.m)	3.15	3.7	3.66	3.54	3.48	3.42
t_2 (minutes)	3.2	3.3	5.2	4.8	2	2.5
$t_{90}-t_2$ (minutes)	3.5	0.8	2.8	3	11.5	11
Cure time to reach $\Delta T=3.36$ kg.m(minutes)	10**	4.3	8.5	10	19.5	19.5

* Conc. given in parts per 100 parts of rubber;ZnO 5, Stearic Acid 2. ** Cure to maximum torque.

Table 4.6 Compounding formulations* and the curing characteristics

4.3.2.2 Discussion

The curing characteristics of conventional accelerated sulphur vulcanization in the presence of dithiophosphoryl compounds have been discussed in Section 4.2.2. In the EV system (CBS 6, S 0.8), CBS is used as well as in the conventional accelerated sulphur system (CBS 0.6, S 2.5), therefore the effect of BuTPDS on the curing characteristics of EV system are similar to that of the latter system at 140°C as described in Section 4.2.2 with the exception of modulus level. The presence of BuTPDS in the EV system at 140°C and 160°C does not alter the modulus level considerably, it seems that BuTPDS does not effect the efficiency of the formation of crosslinks in the presence of high level of CBS and low level of sulphur as compared with the conventional accelerated sulphur system. At higher temperature, the slightly increased cure time may be due to the interaction of the transformation products of BuTPDS with accelerator, thus interferes with the formation of monomeric polysulphide of the type $A_c-S_x-A_c$ and hence reduces the cure rate.

The TMTD sulphurless cure system suffers the same problem of disputed chemical mechanism as the accelerated sulphur vulcanization, and in the reviews of Urabe(330), Wolfe(331), Manik and Banerjee(332) and Shelton et al(333), a mixed polar and radical mechanism is believed to be operative. The results in Table 4.6 show the characteristic of BuTPDS slightly delaying scorch time associated with TMTD-sulphurless system, this may be due to the transformation products acting as free radical scavengers leading to a delay in the formation of rubber-bound intermediate compound, which undergoes subsequent reaction to give crosslinks. As the cure proceeds, the transformation product disappears and forms another product which catalyses the reaction of $-SC(S)N(CH_3)_2$ with the sulphur produced on thermal decomposition of TMTD(52), accelerating the formation of $-S_xC(S)N(CH_3)_2$ and hence the cure rate.

4.3.2.3 Fatigue, Stress Relaxation and Ozone Resistance

SMR-10 was used in these studies. The compounding and vulcanization procedures are given in Section 2.5.1 and 2.5.3 respectively using the formulations in Table 4.6 and 4.7 for conventional accelerated sulphur, CBS-EV and TMTD sulphurless systems. BuTPDS (1 phr) was added during the compounding process and vulcanized at 140°C and 160°C for such periods (Table 4.6) that the modulus of all vulcanizates reached an equivalent level of 3.36 kg.m (56 lb.in).

The fatigue tests were carried out on the Monsanto Fatigue-to-Failure Tester at 60% extension as described in Section 2.6.1. The stress decay of the vulcanizates extended at 40% extension at 100°C in air was continuously recorded using the Wallace-Shawbury self-recording agetester as described in Section 2.6.3.1 and 2.6.3.2. The ozone resistance of the vulcanizates at 20% extension was tested in a Hampden-Shawbury ozone test cabinet at ozone concentration of 25 pphm at 25°C as described in Section 2.6.2.1 and 2.6.2.2. The results are listed in Table 4.7. and the stress relaxation curves are shown in Figure 4.3 and 4.4 for 140°C and 160°C respectively.

4.3.2.4 Results

The conventional accelerated sulphur was used in comparison with CBS-EV and TMTD-sulphurless system. the fatigue life. stress relaxation and ozone resistance of the former vulcanizates containing 1 phr BuTPDS were similar to the results obtained in Section 4.2.2.3. which show a pro-oxidant effect when cured at 140°C. At 160°C. BuTPDS did not significantly improve the fatigue life and ozone resistance. but improved the stress relaxation. Similarly. this compound improved the stress relaxation of CBS-EV and TMTD-sulphurless vulcanizates cured at 140°C. although the time to 50% stress decay at 140°C is longer than that at 160°C (Table 4.7). The results in Table 4.7 show that TMTD-sulphurless vulcanizates are more resistant to ozone exposure than other vulcanizates. It is interesting to note that a heavy bloom was shown on the surface of the TMTD-sulphurless vulcanizates.

Figure 4.3 shows continuous stress relaxation of conventional. CBS-EV and TMTD-sulphurless vulcanizates cured at 140°C.

Cure System Rubber 100, ZnO 5, Stearic Acid 2 (parts by weight)	Fatigue Life (hrs)		t_{50}: Time to 50% stress decay (hrs)		Ozone Failure (hrs)	
	140°C	160°C	140°C	160°C	140°C	160°C
<u>Conventional</u>: CBS 0.6, S 2.5	37	31	16.3	12	32	28
+ BuTPDS 1	30	27	15.6	19	27	29
<u>EV</u>: CBS 6, S 0.8	20	21	209	115	23	28
+ BuTPDS 1	24	24	252	188	25	31
<u>Sulphurless</u>: TMTD 7	22	23	77	61	88	91
+ BuTPDS 1	22	24	113	79	87	98

Table 4.7 The fatigue life, time to 50% stress decay and ozone failure of various vulcanizates containing 1 phr BuTPDS as normal additive

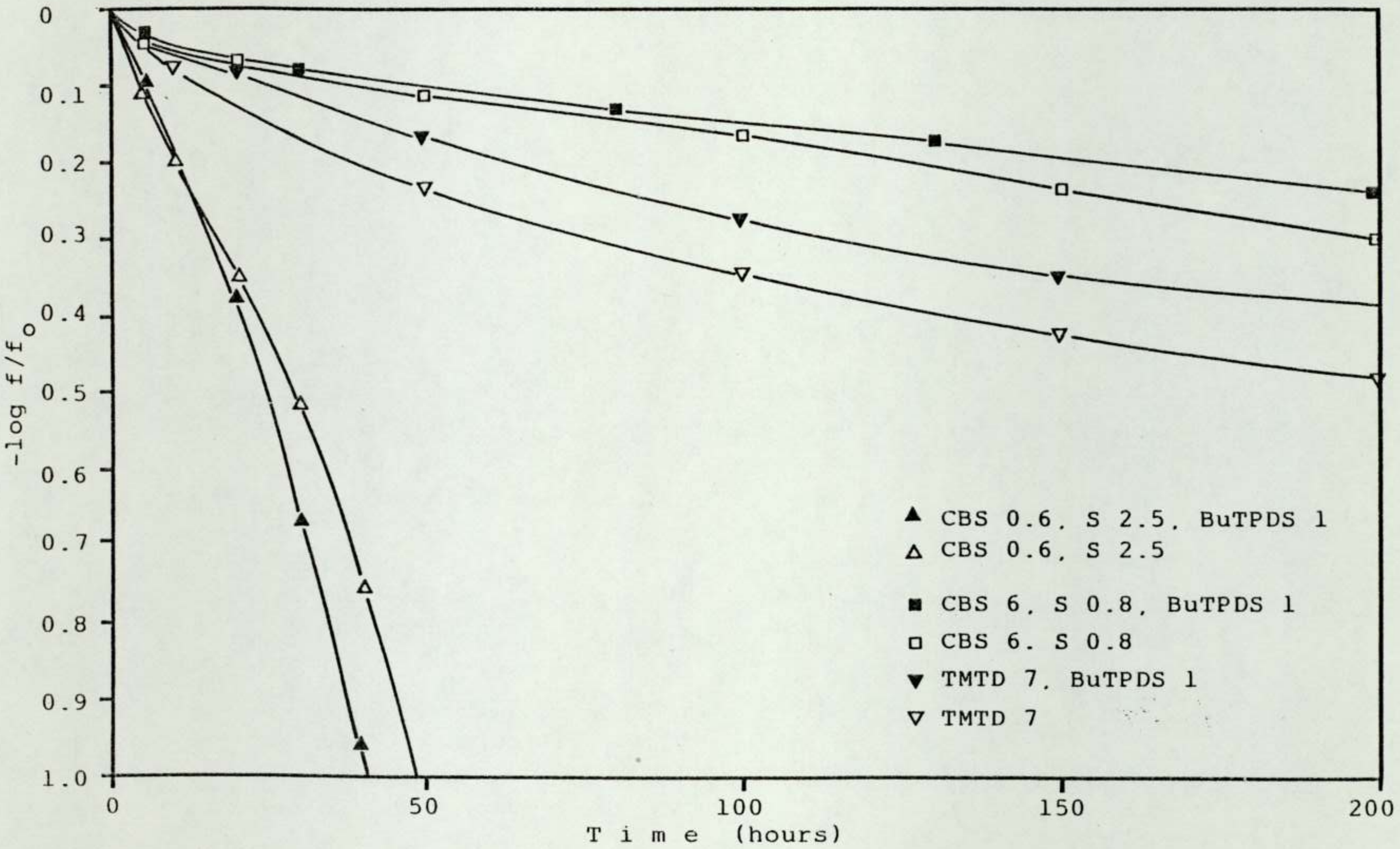


Figure 4.3 Continuous stress relaxation of various NR vulcanizates (cured at 140^{o}C) containing 1 phr of BuTPDS at 1000^{o}C in air.

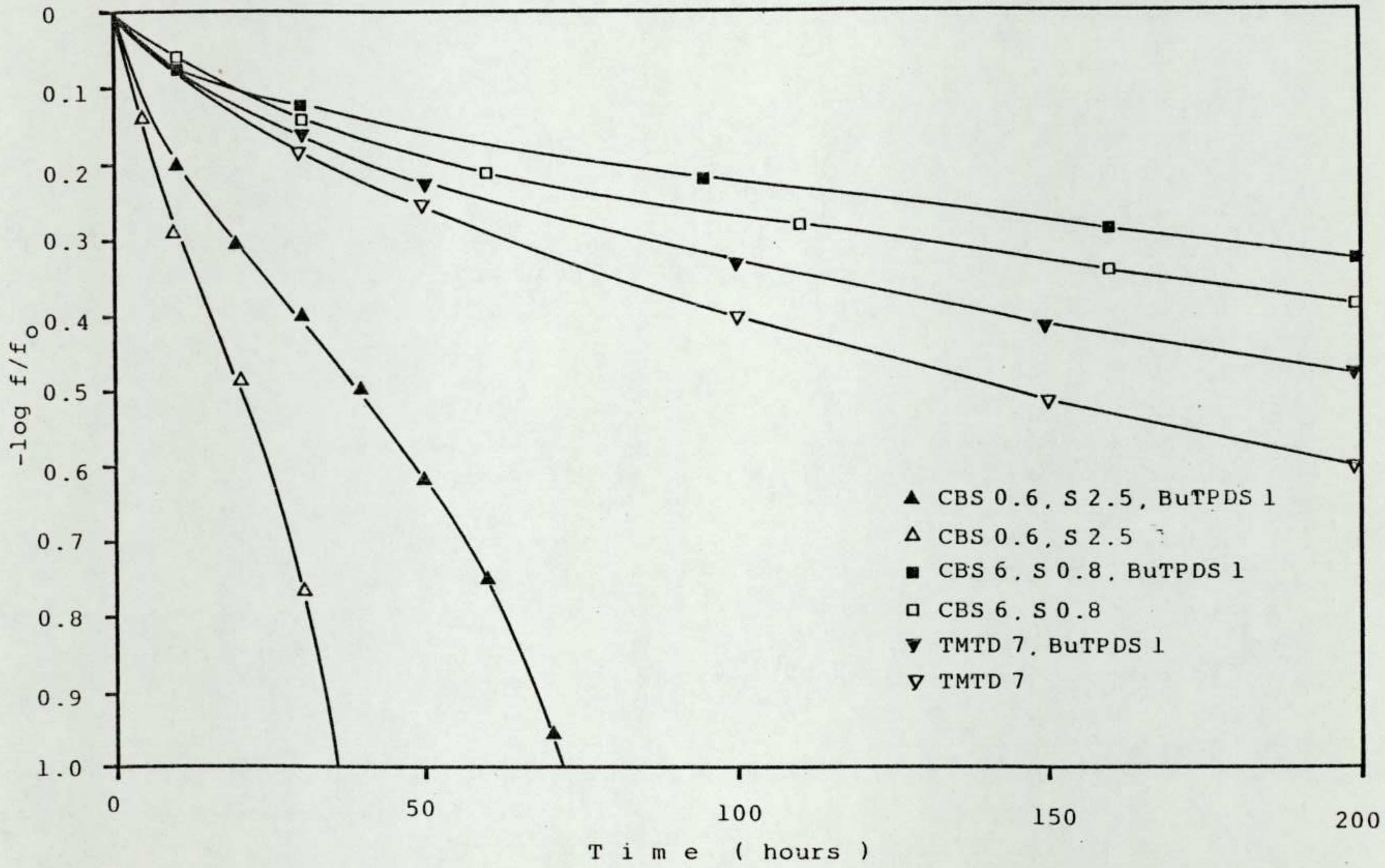


Figure 4.4 Continuous stress relaxation of various NR vulcanizates (cured at 160°C) containing 1 phr of BuTPDS at 100°C in air.

The conventional accelerated sulphur vulcanizate shows a fast autoacceleration of stress decay and BuTPDS increases the overall rate although it decreases the rate during the first 10 hours. EV and TMTD sulphurless vulcanizates show a superior heat ageing performance to the conventional accelerated sulphur vulcanizates. Both EV and TMTD-sulphurless show very slow autocatalytic stress decay. The presence of BuTPDS in the EV system (CBS 6, S 0.8) initially increases the rate of stress decay during the first 30 hours, and then gradually decreases the rate. Inhibition of thermal degradation by BuTPDS also occurs in the TMTD sulphurless vulcanizate cured at 140°C.

Figure 4.4 shows the stress relaxation characteristics of conventional accelerated sulphur, EV and sulphurless vulcanizates cured at 160°C. A similar pattern is obtained during 200 hours ageing of CBS-EV and TMTD-sulphurless vulcanizates cured at 140°C and 160°C, in which BuTPDS inhibits the thermal oxidation of the vulcanizates. However, the time to 50% stress decay of vulcanizates cured at 160°C are lower than for those cured at 140°C i.e., the stress decay at 160°C is faster than at 140°C. The addition of BuTPDS to conventional accelerated sulphur vulcanizates cured at 160°C also shows better resistance to thermal oxidative degradation compared to its control.

4.3.2.5 Discussion

The results show that CBS-EV and TMTD-sulphurless systems have inferior fatigue properties and superior ageing characteristics to that of conventional accelerated sulphur systems. It is well known that in the conventional accelerated sulphur system in which a high ratio of sulphur to accelerator is used, the crosslinks are predominantly polysulphidic, a small number are monosulphidic, rather more disulphidic and a large amount of main chain modification (307,334-336), whereas CBS-EV and TMTD-sulphurless systems give vulcanizates with essentially mono- and to a lesser extent disulphides and a small amount of main chain modification (88,334-336).

The high fatigue life has been attributed to a high concentration of polysulphidic crosslinks, which are able to exchange or rearrange to relieve the highly localized stresses associated with the crack growth. However, monosulphidic crosslinks are not able to rearrange under stress (82,84,85,89,335) (see Section 1.5.2.3). The absence of polysulphides in the CBS-EV and TMTD-sulphurless systems lead to marked improvement in ageing and a good reversion resistance, due to the stable nature of the monosulphide at high temperature and because monosulphide crosslinks cannot exchange with one another under conditions of heat or stress as can polysulphides. Furthermore, the accelerator residues, zinc mercaptobenzothiazole from CBS and zinc dithiocarbamate from TMTD, which are present in the rubber in fairly high concentration, function as antioxidant(88,337,338). The lower extent of main chain modification, such as conjugated diene and triene(323-325) groups which are very susceptible to oxidation(325,326), also contributes to the superior ageing properties of CBS-EV and TMTD-sulphurless systems compared with those given by conventional accelerated sulphur system.

The rate of relaxation of the vulcanizates prepared by CBS-EV and TMTD-sulphurless systems cured at 160°C is faster than that cured at 140°C, this is because the total concentration of monosulphidic crosslinks is reduced at elevated temperature, thus reducing the crosslinking efficiency(90,338).

The stress relaxation curves in Figures 4.3 and 4.4 indicate that BuTPDS addition increases the resistance of CBS-EV and TMTD-sulphurless systems cured at 140°C and 160°C and has practically no effect on the resistance of conventional accelerated sulphur system, although this additive slightly improves the latter vulcanizates cured at 160°C. This is in agreement with the observation that dialkyldithiophosphates(201) and dialkyldithiocarbamates(201,337) are potent inhibitors of the ageing of sulphurless vulcanizates, although they are ineffective in an accelerated sulphur vulcanizate. However, this is contrary to other published results obtained by Tarasova et al(320), who found that zinc diisopropyldithiophosphate increased the resistance of sulphur vulcanizates to thermooxidative degradation and has practically no effect in sulphurless vulcanizates.

The mechanism of dialkyldithiophosphates as antioxidants has been investigated by Al-Malaika and Scott(206) (see Section 1.11.3 and Scheme 1.13). It is believed that the thiophosphoryl disulphide-derived oxidation products such as sulphur oxides or acids, function as peroxide decomposers, a phenomenon related to the behaviour of the dialkyl or diaryl sulphides. These compounds have in common the ability to destroy hydroperoxides through the formation of an acidic product in a radical generating reaction involving the hydroperoxide which is also formed during fatiguing and ageing of rubber vulcanizates. In all cases the antioxidant function is preceeded by a pro-oxidant stage. In the case of dithiophosphoryl compound, a possible interpretation of the phenomena is that the pro-oxidant effect may be significant in the conventional accelerated sulphur system, while in the case of EV and sulphurless systems, the pro-oxidant effect may be transient and of no great significance.

As pointed out by Kemperman(321), vulcanized rubber contains sulphide and oligosulphide groups to excess, therefore the addition of an extra sulphide produces no additional effect. This may also depend on the thermal stability and oxidizability of the sulphide added and the influence of the accelerator on its stability and oxidizability.

Although BuTPDS or its oxidized products improve the oxidative ageing properties of CBS-EV and TMTD-sulphurless vulcanizates, only transient improvement was found in their fatigue life. The sulphinyl radical formed during the oxidation process,which is believed to be involved in a cyclical regeneration process,is an alkyl radical trap(239-241) (see Section 1.11.3 and Scheme 1.13). This may be due to the fact that the crosslinks are predominantly monosulphidic, whereas good fatigue resistance is given by polysulphidic crosslinks.

Braden and Gent(108) found that acetone soluble reaction product of TMTD (ZDMC) can reduce the rate of the cut growth process when it was added to the extracted rubber vulcanizate by swelling in a chloroform solution. A noticeable feature from the test was that a heavy bloomed material was found on the surface of the test samples. the low critical stress is considered to arise from the presence of flaws associated with surface finish. However, when a razor cut was made in the test piece, the value of critical stress was found to be similar to that for peroxide vulcanizate(108).

The superiority in ozone resistance of the TMTD-sulphurless system compared to the other systems may be due to the formation of zinc dimethyldithiocarbamate during vulcanization. It suggests that zinc dimethyldithiocarbamate migrates to the surface of the test piece and reacts with ozone or ozonide to produce a protective layer.

4.3.3 Curing Characteristics and Durability of Peroxide Vulcanizates Containing Dithiophosphoryl Compounds

4.3.3.1 Introduction

Organic peroxides have been used as crosslinking agents for rubber for decades. These compounds are capable of crosslinking rubbers to form a network having solely carbon-carbon crosslinks. With natural rubber and other common unsaturated polymers, the vulcanizates produced have strengths slightly inferior to those obtained with accelerated sulphur cures. However, they show lower compression set and better dynamic performance and also, if properly compounded, excellent resistance to ageing. The carbon-carbon crosslinks formed during peroxide vulcanization are thermally stable and hence lead to highly reversion-resistant networks(340). The factors which militate against the more widespred use of peroxide in natural rubber are the poor cure characteristics: scorchy and slow to cure, and the tendency to give sticky mould deposits.

The primary considerations in the selection of a peroxide for a specific application are processing safety, cure time and cure temperature requirement, volatility and the efficiency of crosslink formation(341). Those that have been considered for use with elastomers are diacyl, dialkyl, diaralkyl peroxides and peresters(340,341). Of these, dialkyl peroxides and t-butyl perbenzoate give efficient crosslink formation; di-t-butyl peroxide (TBH) and dicumyl peroxide(DCP) give good vulcanizates in compounds which contain reinforcing carbon blacks, but TBH is a volatile liquid and inconvenient to use, so that dicumyl peroxides(340) remain the generally useful peroxide for vulcanizing elastomers. However, vulcanizates cured with dicumyl peroxide have an unpleasant odour.

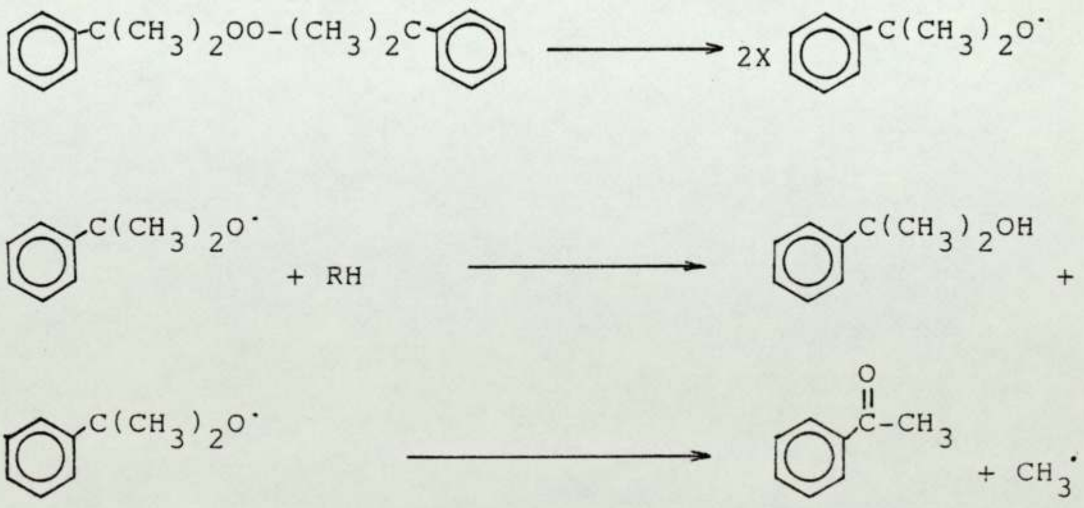
The basic mechanism of DCP vulcanization is well understood(341). The reaction involves:

i. free radical initiation by homolytic decomposition, and hydrogen abstraction from the polymer chain,

ii. propagation by chain transfer by hydrogen abstraction,

iii. termination by radical combination.

The detailed reactions are as follows(342):



$CH_3^{\cdot} + RH \longrightarrow CH_4 + R^{\cdot}$

$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6$

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

Where RH denotes a rubber molecule and $R^{\cdot}$ the rubber radical resulting from hydrogen abstraction. The fate of the polymer radical $R^{\cdot}$ depends on the polymer structure. In natural rubber there is evidence(343) that radical combination is the predominant reaction.

All peroxide cured compounds require the use of an effective antioxidant to obtain the superior vulcanizate properties associated with peroxide cures. Quinoline type and amine type.except p-phenylenediamine type. are the preferred antioxidants used in rubber. about 0.5 to 1.0 phr of one of these antioxidants gives optimum activity. Higher levels tend to retard the cure and reduce the efficiency of peroxides. p-Phenylenediamine type antioxidants are not effective in peroxide-cured compounds. These. being free radical scavengers. consume peroxide radicals. The net effect is a significant reduction in active levels of both the antioxidant and peroxide. Therefore. peroxide vulcanizates prepared in the presence of p-phenylenediamines are impractical(344).

4.3.3.2 Curing Characteristics of Peroxide Vulcanizates Containing Dithiophosphoryl Compounds

SMR-10 (100 g) was compounded on a 30 cm water cooled laboratory two-roll mill set at a friction ratio of 1:1. 0,0-dialkyldithiophosphoric acids and the corresponding disulphides were used ranging from 0.5 to 2 phr and dicumyl peroxide (DCP) used at standard level of 2.5 phr. the concentration was increased to increase the modulus level since dithiophosphoryl compounds reduce the efficiency of peroxides as crosslinking agents. Therefore. the level of peroxide in the control was lower. The peroxide was added last to prevent prevulcanization. The peroxide gum stocks were cured at 160^{o}C for 55 minutes and at 180^{o}C for 10 minutes. The curing characteristics of the stocks were assessed using a Monsanto Rheometer 100 as described in Section 2.5.2. The rheographs obtained were then interpreted to obtain the parameters of vulcanization. namely: the torque ΔT or $T_{max}-T_{min}$; scorch time t_2 and cure rate $t_{90}-t_2$.

The formulations and the effect of both the amount of dithiophosphoryl compounds and DCP on the curing characteristics are given in Tables 4.8, 4.9 and 4.10.

4.3.3.3 Results

The curing characteristics of peroxide vulcanizates (SMR-10 100, DCP 2.5) containing BuTPDS at various concentrations

Amount of BuTPDS	ΔT (kg.m)	t_2(min)	$t_{90}-t_2$(min)
-	3.48	1.5	19.5
0.5	2.22	1.7	15.8
1	1.74	2.2	18.3
1.5	1.62	2.8	20.2
2	1.5	3.3	17.7

Table 4.8 Curing characteristics of peroxide vulcanizates (SMR-10 100, DCP 2.5) containing BuTPDS at various concentrations (g/100 g rubber) cured at 160°C for 55 minutes

(g/100 g rubber) cure at 160°C are shown in Table 4.8. The addition of 0.5 phr of BuTPDS drastically reduces the modulus level and the cure rate, and increases the scorch time. When the amount of BuTPDS is further increased from 1 to 2 phr, the decrease of the modulus is less pronounced, while the scorch time further increases but has no significant effect on the rate of cure.

Table 4.9 shows the curing characteristics of peroxide vulcanizates containing various dithiophosphoryl compounds. The effect of the addition of these compounds on the curing characteristics is compared to the control which is cured with 1.5 phr DCP giving a modulus level approximately equal to those vulcanizates containing 1 phr dithiophosphoryl compound cured with 2.5 phr DCP. There are no significantly different effects between the curing characteristics of the dithiophosphoric acids and the corresponding disulphides, and between the alkyl constituent groups.

A markedly lower modulus and cure rate, and a slightly longer scorch time is obtained in the case of the zinc bis-dibutyl-dithiophosphate. When the amount of DCP is increased from 2.5 phr to 3.5 phr keeping the amount of BuTPDS constant at 1 phr, the modulus level increases from 1.74 kg.m (Table 4.8) to 2.22 kg.m (Table 4.9) and the cure rate decreases. When the amount of P^iTPDS is increased from 1 phr to 2 phr and the amount of DCP is kept constant, there is no significant change in the curing characteristics. A natural rubber gum mix with 1.5 phr of DCP without additive brings about a vulcanizate having the modulus level the same as that of gum stocks containing 2.5 phr of DCP and 1 phr of dithiophosphoryl compounds.

The curing characteristics of peroxide gum stocks containing various bis-thiophosphoryl disulphides at 180°C are given in Table 4.10. There is no significant difference in curing characteristics between the stocks containing 1 phr of BuTPDS and 1 phr of P^iTPDS cured with 2.5 phr DCP. At equal concentration (2.07×10^{-3} mole),OcTPDS, BuTPDS and P^iTPDS cured with 3.5 phr of DCP, OcTPDS shows a higher modulus level, while BuTPDS shows longer scorch time and cure rate. Increasing the temperature of cure from 160°C

Additive (phr)	DCP (phr)	ΔT (kg.m)	t_2 (min)	$t_{90}-t_2$ (min)
-	1.5	1.92	1.5	23.5
BuTPH, 1	2.5	1.95	2.5	22.5
BuTPDS, 1	3.5	2.22	2.5	19.5
ZBuTP, 1	2.5	1.41	2.7	16.8
P^iTPH, 1	2.5	1.95	2.5	22.5
P^iTPDS, 1	2.5	1.97	2.5	22.5
P^iTPDS, 2	2.5	1.92	2.7	21

Table 4.9 Curing characteristics of peroxide vulcanizates containing various additives cured at 160°C

Additive (phr)	DCP (phr)	ΔT (kg.m)	t_2 (min)	$t_{90}-t_2$ (min)
-	1.6	2.76	1	4.5
OcTPDS, 1.47	3.5	2.82	1.3	4.7
BuTPDS, 1	2.5	2.16	1	4.5
BuTPDS, 1	3.5	2.64	1.7	6.7
P^iTPDS, 1	2.5	2.16	1.3	4.3
P^iTPDS, 0.88	3.5	2.64	1.2	5.3

Table 4.10 Curing characteristics of peroxide vulcanizates containing various bis-thiophosphoryl disulphides at 180°C

(Table 4.9) causes an increase in the modulus level (Table 4.10) of corresponding stocks containing equal amounts of DCP and thiophosphoryl disulphide at 180°C. Increasing the amount of DCP and temperature of cure at the same time causes further increase in the modulus level. The rubber stock containing no additive cured with 1.6 phr of DCP at 180°C gives approximately equal modulus to stocks containing 2.07×10^{-3} mole of thiophosphoryl disulphides cured at the same temperature.

4.3.3.4 Discussion

It is very clear that dithiophosphoryl compounds reduce the efficiency of peroxide cure. The zinc complex reduces the efficiency of peroxide cure more than the disulphide does. This is indicated by lower modulus level obtained from the stock containing ZBuTP than that containing BuTPDS (Table 4.9). It seems that the zinc complex is more powerful a free radical scavenger than the disulphide, although a lower molecular level of ZBuTP was used (1 phr ZBuTP=1.83×10^{-3} mole, 1 phr BuTPDS=2.07×10^{-3} mole).

The interference with free radical reaction in the peroxide cure leads to a longer induction time and lower modulus level. However, when excess of disulphide was added in the peroxide cure (Table 4.8), the influence of the disulphide on the decrease of the modulus level was less pronounced although the addition of disulphide caused slightly further decrease of the modulus level. This is thought to be caused by the disulphide which takes part in the crosslinking of rubber as found by Manik and Banerjee(345) in the vulcanization of natural rubber with DCP in the presence of TMTD. It has also been shown in Section 3.2.6.2 that dithiophosphoric compounds promote crosslinking during processing of natural rubber in the RAPRA torque rheometer at 160°C as indicated by increasing the torque level without the addition of any other additive.

The vulcanization mechanism of natural rubber with DCP in the presence of dithiophosphoryl compounds at 160°C in the present study is uncertain. However, it is thought that vulcanization in the presence of dithiophosphoryl compound may occur in the same manner as in the presence of TMTD proposed by Manik and Banerjee(345). The crosslinks are exclusively produced by DCP in the absence of radical acceptor. In the presence of dithiophosphoryl compounds however, the vulcanization due to peroxy radicals and partial destruction of those radicals by the additives may proceed together. The nearly constant modulus level at higher disulphide concentration is probably due to the formation of sulphidic crosslinks leading to a poor ageing resistance (see Section 3.5.5.1).

Vulcanization at higher temperature (180°C) increases the modulus level of all the vulcanizates. This is in contrast to the conventional accelerated and EV systems in which the elevated cure temperature brings about a substantial drop in the degree of crosslinking due to desulphuration(338). In the case of peroxide cure in the presence of dithiophosphoryl compounds, higher cure temperatures increase the efficiency of peroxide cure. This is probably due to instability of dithiophosphoryl compounds at elevated temperature leading to lesser destruction of the cumyloxy radicals. Consequently, increasing the DCP concentration would cause further increase in modulus level (Table 4.10).

4.3.3.5 Durability of Peroxide Vulcanizates Containing Dithiophosphoryl Compounds

Natural rubber (SMR-10) was vulcanized with dicumyl peroxide (DCP) in the presence of dithiophosphoryl compounds at 160°C for 55 minutes and at 180°C for 10 minutes using the formulations given in Tables 4.8-4.10. The addition of dithiophosphoryl compounds was at the level of 0.5 to 2 phr and of equimolar amounts of BuTPDS at 1 phr (2.07×10^{-3} mole). The concentration of DCP used in the control was adjusted to obtain approximately equal modulus to that of the test samples.

The fatigue tests were carried out on the Monsanto Fatigue-to-Failure Tester at 60% extension as described in Section 2.6.1. The continuous stress relaxation characteristics were analysed using the Wallace-Shawbury self-recording agetester as described in Sections 2.6.3.1 and 2.6.3.2. The test samples were strained to 40% extension and aged at 100°C in air. The ozone resistance of the vulcanizates at 20% extension was tested in a Hampden-Shawbury ozone test cabinet at ozone concentration of 25 pphm at 25°C as described in Sections 2.6.2.1 and 2.6.2.2. All the samples were also extracted in hot azeotropic mixture before being subjected to the tests as described in Section 2.5.3.5.

The extent of binding of the isopropyl and butyl constituents of dithiophosphoryl compounds was determined by the procedures described earlier as follows: the infra-red film was prepared in a specially made infra-red mould producing a sheet of 0.015-0.020 cm thickness as described in Sections 2.5.3 and 2.5.3.1. The film was extracted under azeotropic mixtures (acetone:methanol:1,1,1-trichloroethane =110:42:60 ml) as described in Section 2.5.3.5. The infra-red spectra of the film was obtained from a Perkin Elmer 599B infra-red spectrophotometer. The P=S index, which is the ratio of the intensity of P=S peak at about 650 cm^{-1} to the intensity of a reference peak at 2720 cm^{-1}, was determined and the extent of binding was obtained using the calibration curves in Section 3.2.2.

The results are given in Tables 4.11 to 4.13 and in Figures 4.5 to 4.7 for the stress relaxation characteristics. The modulus level of each vulcanizate and the extent of binding for particular additives are included in the tables.

4.3.3.5.1 Effect of BuTPDS Concentration on the Durability of Peroxide Cured Vulcanizates at 160°C

Table 4.11 shows the durability of peroxide cured natural rubber vulcanizates containing BuTPDS in the range of 0.5 to 2 phr and cured with 2.5 phr of DCP at 160°C for 55 minutes. The fatigue life of the vulcanizates increased with increasing the concentration of BuTPDS before extraction, while t_{50} (the time to 50% stress decay) and the ozone resistance decrease. The results are not comparable to the control. On the other hand, the time to 50% stress decay and the ozone resistance are much lower. The vulcanizates lost their excellent fatigue life and the t_{50} and ozone resistance decrease considerably. The modulus levels of the vulcanizate cured with 2.5 phr DCP drop when BuTPDS is introduced to the stocks.

Figure 4.5 shows the continuous stress relaxation characteristics of the vulcanizates cured with 2.5 phr of DCP at 160°C for 55 minutes containing various concentrations of BuTPDS. The tests were carried out at 100°C in air. The vulcanizates containing 0.5 and 1 phr of BuTPDS (BuTPDS 0.5 and BuTPDS 1) before extraction show a slow autocatalytic stress decay at the first 10 hours followed by fast rate of relaxation. Their extracted samples have a similar pattern with faster rate of relaxation. The BuTPDS 1.5 and 2 before extraction initially show a fast stress decay followed by

Additive (g)	Fatigue Life (hrs)		Time to 50% stress decay T_{50} (hrs)		Ozone Failure (hrs)		ΔT (kg.m)	Bound (%)
	Unext	Ext	Unext	Ext	Unext	Ext		
-	34	23	-*	78.5	72	36	3.48	-
0.5	126	92	15.7	12.3	33	16	2.22	27.7
1	326	132	12	9.5	28	14	1.74	18
1.5	383	123	6.8	4.5	27	12	1.62	14.5
2	580	96	4.4	3	24	11	1.5	9

* unrecordable due to breakage of the samples after 25% stress decay at about 88 hours

Table 4.11 The fatigue life, time to 50% stress decay and ozone failure of peroxide (2.5 phr) vulcanizates containing various concentrations of BuTPDS cured at 160°C

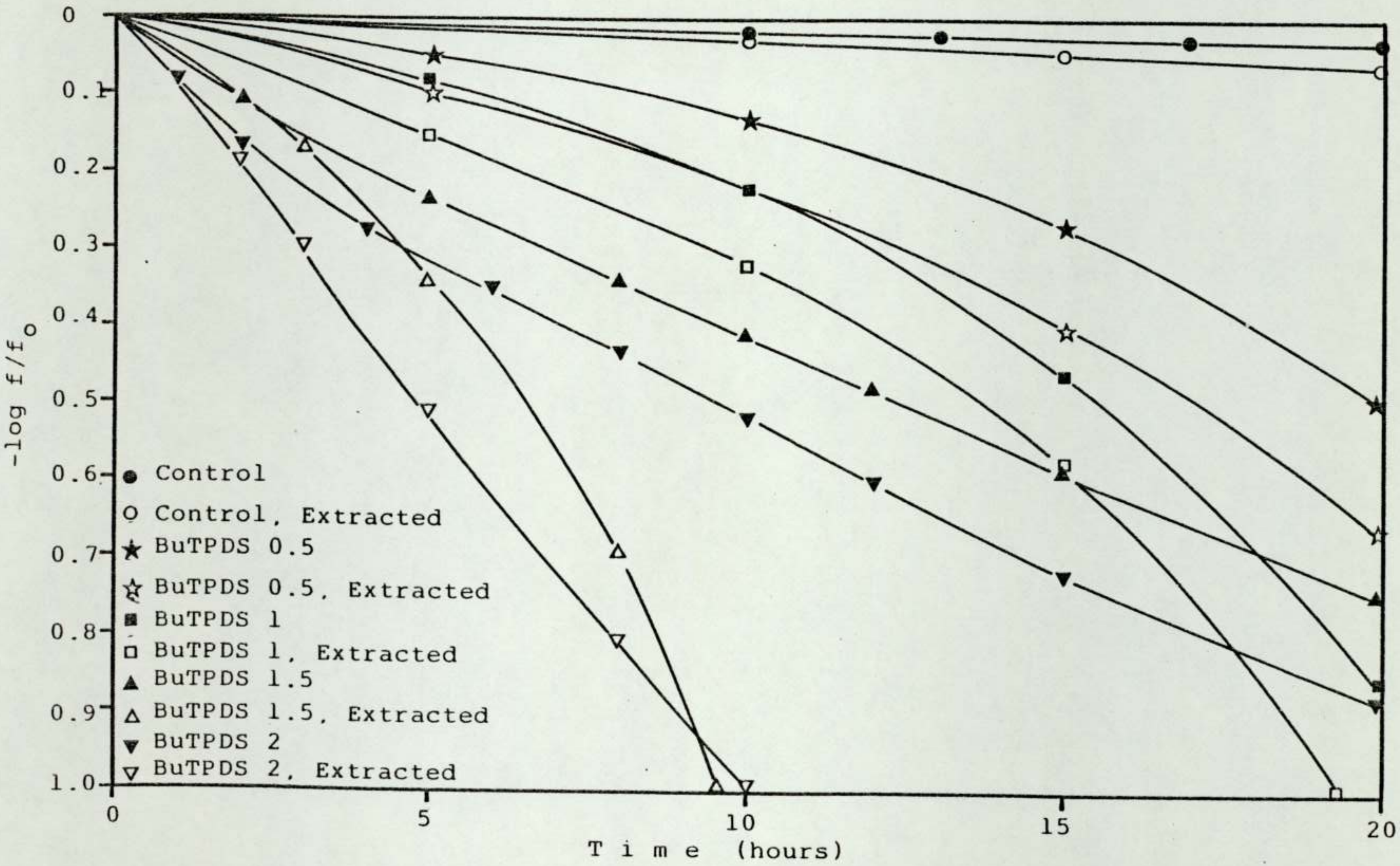


Figure 4.5 Continuous stress relaxation of peroxide vulcanizates (DCP 2.5 phr, cured at 160°C) containing various concentration of BuTPDS at 100°C in air

autoretardation. The extracted samples however, age very rapidly and show a much faster rate of degradation than that of BuTPDS 0.5 and 1. The thermal oxidative degradation of the control before and after extraction is autocatalytic, and shows an increase in degradation rate as ageing proceeds (Figure 4.5), although the rate of relaxation is far better than when in the presence of BuTPDS. Extracted control shows an increase in the relaxation rate.

4.3.3.5.2 Fatigue Life of Peroxide Vulcanizates Containing Various Dithiophosphoryl Compounds

The effect of the presence of various dithiophosphoryl compounds on the fatigue life of the peroxide vulcanizate cured with DCP at 160°C for 55 minutes and at 180°C for 10 minutes is given in the Tables 4.12 and 4.13 respectively. The modulus level of the vulcanizates and the extent of dithiophosphoryl compound bound to the vulcanizates are included in the tables.

The results shown in Table 4.12 indicate that the unextracted peroxide vulcanizates containing dithiophosphoryl compounds have superior fatigue lives relative to the control cured with 2.5 phr of DCP (Table 4.11). However, the improvement is less pronounced when they are compared with the control cured with 1.5 phr of DCP (Table 4.12) having approximately equal modulus.

Compound (phr)	DCP (phr)	Fatigue life (hrs)		ΔT (kg.m)	Bound (%)
		Unext	Ext		
Control, -	1.5	106	52	1.92	-
BuTPH, 1	2.5	247	102	1.95	11.3
BuTPDS, 1	2.5	326	132	1.74	19
BuTPDS, 1	3.5	213	113	2.22	17.5
ZBuTP, 1	2.5	179	113	1.41	21.5
P^{i}TPH, 1	2.5	272	110	1.95	17.4
P^{i}TPDS, 1	2.5	246	134	1.97	20.4
P^{i}TPDS, 2	2.5	421	99	1.92	10.5

Table 4.12 The fatigue life of peroxide vulcanizates containing dithiophosphoryl compounds cured at 160°C for 55 minutes

Compound (phr)	DCP (phr)	Fatigue life (hrs)		ΔT (kg.m)	Bound (%)
		Unext	Ext		
Control, -	1.5	136	45	2.66	-
OcTPDS,1.47	3.5	151	54	2.82	-
BuTPDS, 1	2.5	553	85	2.16	17
BuTPDS, 1	3.5	340	66	2.64	13.7
P^{i}TPDS, 1	2.5	543	66	2.16	25.4
P^{i}TPDS,0.88	3.5	527	76	2.64	33.3

Table 4.13 The fatigue life of peroxide vulcanizates containing dithiophosphoryl compounds cured at 180°C for 10 minutes

Extraction with azeotropic mixtures (acetone:methanol:1,1,1-trichloroethane = 110:42:60 ml) reduced the antifatigue activity although the fatigue lives of the extracted samples are still higher than that of the extracted control. Increasing the concentration of DCP from 2.5 to 3.5 phr in the vulcanizate containing 1 phr of BuTPDS decreased the fatigue life and increased the modulus level. Increasing the concentration of the additives from 1 phr to 2 phr at the constant amount of DCP (2.5 phr), increased the fatigue life. The zinc complex of dibutyldithiophosphate (ZBuTP) gives rise to the lowest fatigue resistance, and the corresponding disulphide shows the highest protection at 1 phr of the additives.

It is interesting to note that the fatigue lives of vulcanizates containing 1 phr of BuTPDS and P^iTPDS both cured with 2.5 phr of DCP at 180°C for 10 minutes (Table 4.13) are much higher than that of these compounds cured at 160°C (Table 4.12), although the modulus increases at 180°C. Increasing the modulus level by increasing the concentration of DCP from 2.5 to 3.5 phr, sharply decreased the fatigue life of the vulcanizate containing 1 phr of BuTPDS, but this is still higher than that of the same vulcanizate cured at 160°C. In the case of the vulcanizate containing 1 phr of P^iTPDS however, increasing the curing temperature from 160°C to 180°C at the same concentration of DCP (2.5 phr), almost doubled the fatigue life. Increasing the concentration of DCP from 2.5 to 3.5 phr, slightly decreased the fatigue life of the compound with lower concentration of P^iTPDS (0.88 phr) at higher modulus.

OcTPDS does not greatly affect the fatigue life relative to the control. P^iTPDS appears to be the best protective agent against fatigue at equimolar concentration cured with 3.5 phr of DCP. The fatigue resistance of all the vulcanizates were drastically reduced after extraction. The extracted vulcanizates cured at 180°C show lower fatigue life than that cured at 160°C.

4.3.3.5.3 Continuous Stress Relaxation Characteristics of Peroxide Vulcanizates Containing Various Dithiophosphoryl Compounds

The effect of various dithiophosphoryl compounds on the ageing properties of the peroxide vulcanizates as measured by the continuous stress relaxation characteristic is given in Figure 4.6 for the vulcanizates cured at 160°C and in Figure 4.7 for the vulcanizates cured at 180°C. The times to 50% stress decay (t_{50}) are tabulated in Table 4.14 and 4.15 together with the modulus level and the extent of dithiophosphoryl compound bound to the vulcanizates.

Dithiophosphoryl compounds were found to be bound to only a small extent to the rubber vulcanizates during vulcanization.

Compound (phr)	DCP (phr)	t_{50} (phr)		ΔT (kg.m)	Bound (%)
		Unext	Ext		
Control, -	1.5	57	42	1.92	-
BuTPH, 1	2.5	16.5	5	1.95	11.3
BuTPDS, 1	2.5	12	9.5	1.74	19
BuTPDS, 1	3.5	23.4	11.2	2.22	17.5
ZBuTP, 1	2.5	5	5.5	1.41	21.5
P^iTPH, 1	2.5	26	6.2	1.95	17.4
P^iTPDS, 1	2.5	46	11.2	1.97	20.4
P^iTPDS, 2	2.5	37	3.2	1.92	10.5

Table 4.14 The time to 50% stress decay (t_{50}) of peroxide vulcanizates containing dithiophosphoryl compound cured at 160°C

Compound (phr)	DCP (phr)	t_{50} (phr)		ΔT (kg.m)	Bound (%)
		Unext	Ext		
Control, -	1.5	101	30.3	2.66	-
OcTPDS,1.47	3.5	96	29.6	2.82	-
BuTPDS, 1	2.5	18	8.8	2.16	17
BuTPDS, 1	3.5	87	24.6	2.64	13.7
P^iTPDS, 1	2.5	50	21.2	2.16	25.4
P^iTPDS,0.88	3.5	59	18.3	2.64	33.3

Table 4.15 The time to 50% stress decay (t_{50}) of peroxide vulcanizates containing thiophosphoryl disulphides cured at 180°C

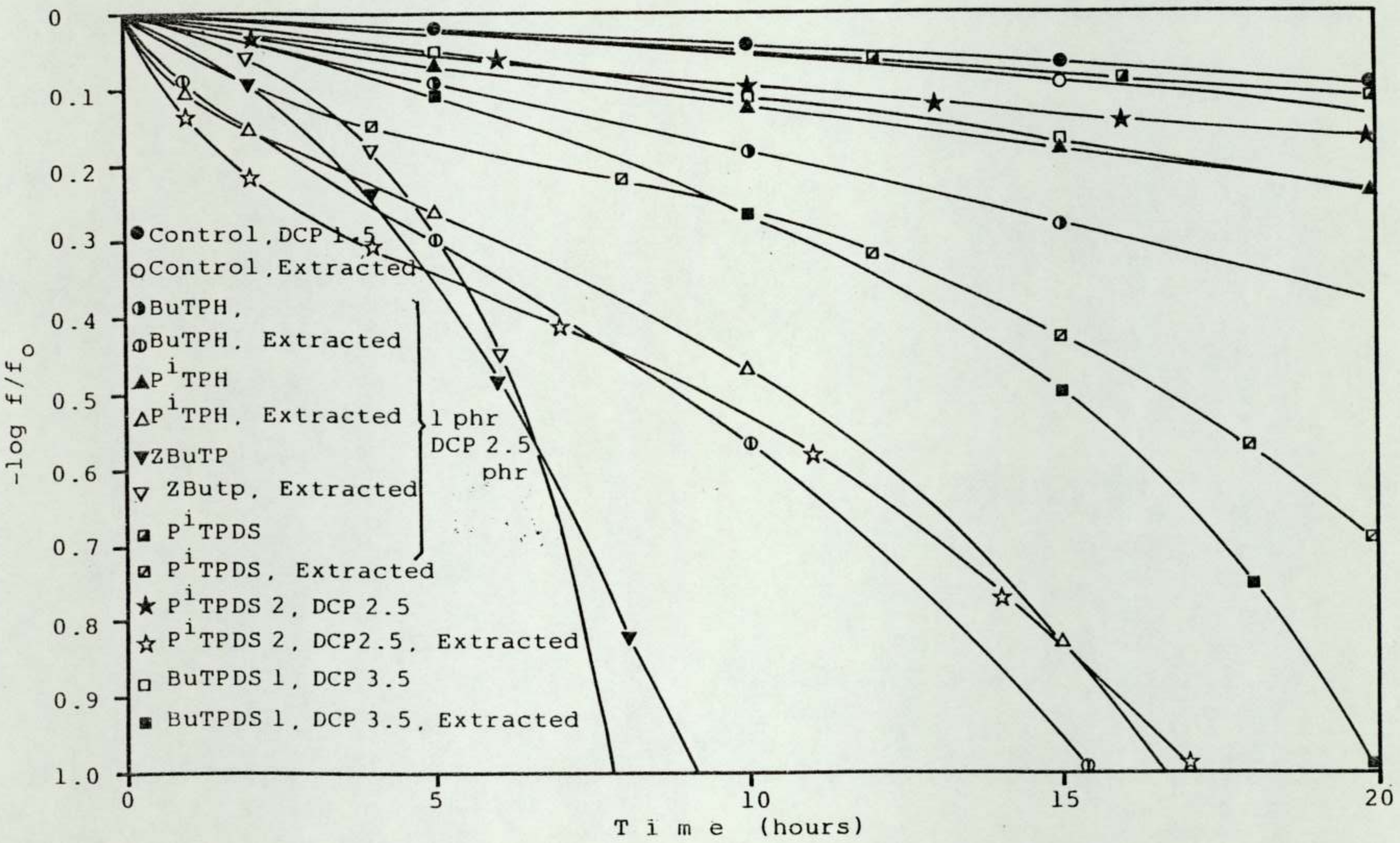


Figure 4.6 Continuous stress relaxation of peroxide vulcanizates (cured at 160°C) containing various additives at 100°C in air.

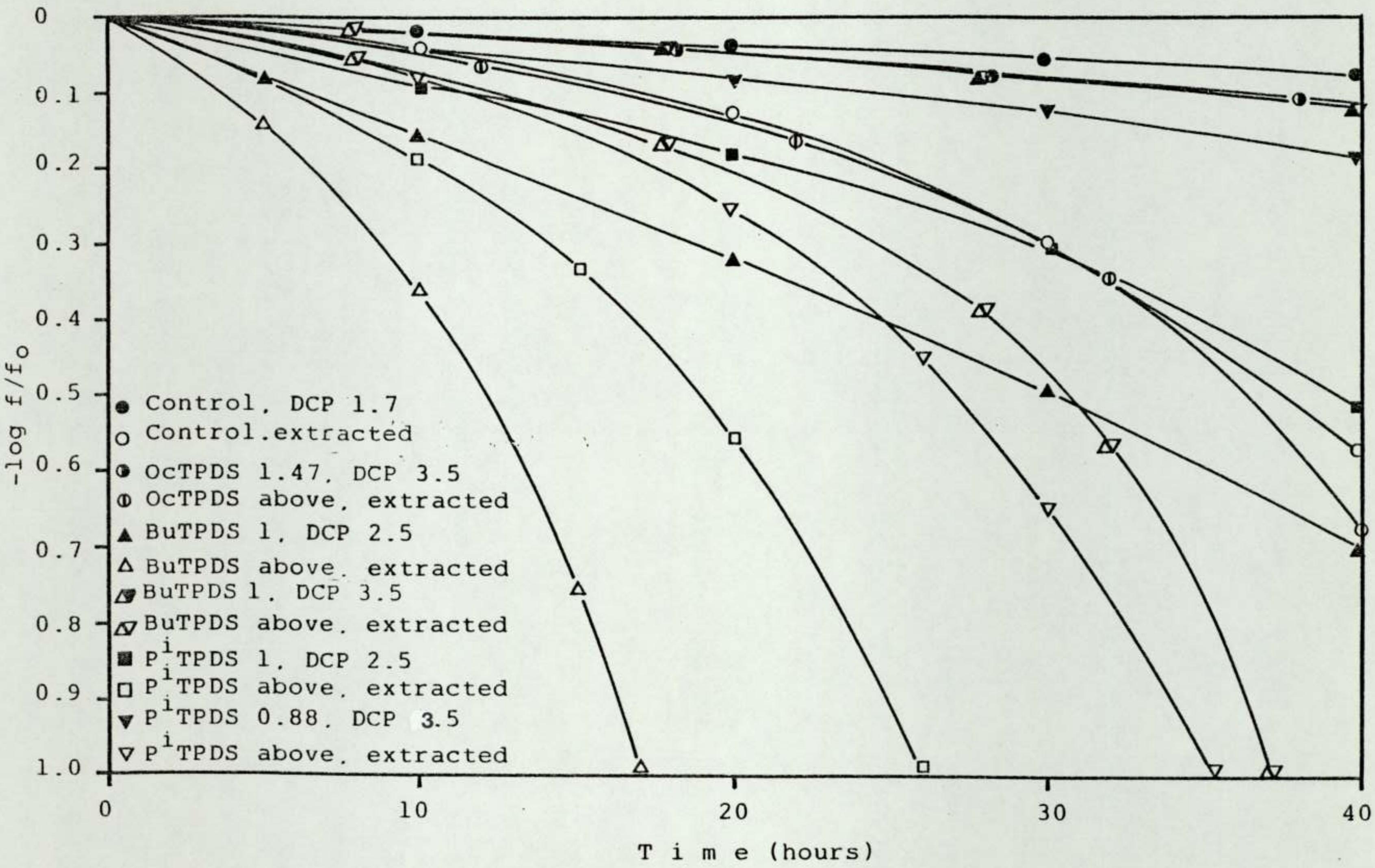


Figure 4.7 Continuous stress relaxation of peroxide vulcanizates (cured at 180°C) containing various additives at 100°C in air.

This has been proved by showing P=S peak remaining after azeotropic mixtures extraction (Tables 4.12, 4.13, 4.14 and 4.15).

The stress relaxation characteristics of peroxide vulcanizates containing various dithiophosphoryl compounds cured at 160°C for 55 minutes shown in Figure 4.6 and the t_{50} shown in Table 4.14 indicate that all the additives increase the rate of relaxation over the control. However, all the unextracted vulcanizates exhibit retardation of oxidation which is lost after extraction, with the exception of the vulcanizate containing ZBuTP which shows a very fast rate of relaxation both before and after extraction. The extracted vulcanizates, except that containing ZBuTP, show an autoretardation effect after a fast decay during the first 3 hours, although the rate of relaxation is faster than that for unextracted vulcanizates (Figure 4.6). Dithiophosphoryl compounds with isopropyl constituents show better antioxidant activity than the n-butyl compound. Increasing the concentration of P^{i}TPDS increases the rate of relaxation and decreases the modulus level.

The t_{50} in Table 4.15 indicate that unextracted and extracted peroxide vulcanizates containing thiophosphoryl disulphides cured at 180°C are more resistant to thermal oxidative ageing than those cured at 160°C, but less resistant compared to the control. The unextracted vulcanizates cured with 3.5 phr of DCP exhibit better resistance than those cured with 2.5 phr of DCP. The extracted vulcanizates containing BuTPDS showed reversion and were not significantly different from those containing P^iTPDS.

It is clear from Figure 4.7 that all the vulcanizates cured with 3.5 phr of DCP at 180°C give better protection against ageing than those cured with 2.5 phr of DCP having lower modulus. OcTPDS shows better resistance compared to BuTPDS and P^iTPDS at equimolar ratio. The extracted vulcanizates cured with 3.5 phr of DCP exhibit a slow autocatalytic action followed by autoacceleration. and vulcanizates cured with 2.5 phr of DCP exhibit only auto-acceleration.

4.3.3.5.4 Ozone Resistance of Peroxide Vulcanizates Containing Various Dithiophosphoryl Compounds

The effect of various dithiophosphoryl compounds on the ozone resistance of peroxide vulcanizate cured at 160°C and 180°C are given in Table 4.16 and 4.17 respectively.

All the unextracted and extracted vulcanizates cured at 160°C and 180°C show lower ozone resistance compared to the control. The vulcanizates cured at 180°C are more resistant to ozone exposure than those cured at 160°C. The vulcanizates containing ZBuTP cured at 160°C exhibit better resistance among

Compound (phr)	DCP (phr)	Ozone Failure (hrs)		ΔT (kg.m)
		Unext	Ext	
Control. -	2.5	45	19	1.92
BuTPH. 1	2.5	28	15	1.95
BuTPDS, 1	2.5	28	14	1.74
BuTPDS. 1	3.5	42	18	2.22
ZBuTP, 1	2.5	38	17	1.41
P^{i}TPH, 1	2.5	26	16	1.95
P^{i}TPDS. 1	2.5	27	15	1.97
P^{i}TPDS, 2	2.5	21	10	1.92

Table 4.16 Ozone failure of peroxide vulcanizates containing dithiophosphoryl compounds cured at 160°C

Compound (phr)	DCP (phr)	Ozone Failure (hrs)		ΔT (kg.m)
		Unext	Ext	
Control, -	1.5	78	38	2.66
OcTPDS,1.47	3.5	40	25	2.82
BuTPDS. 1	2.5	33	18	2.16
BuTPDS, 1	3.5	36	21	2.64
P^{i}TPDS. 1	2.5	32	23	2.16
P^{i}TPDS,0.88	3.5	35	19	2.64

Table 4.17 Ozone failure of peroxide vulcanizates containing thiophosphoryl disulphides cured at 180°C

other vulcanizates cured with 2.5 phr DCP. Increasing the concentration of peroxide from 2.5 to 3.5 phr for curing the stock containing 1 phr of BuTPDS increases the ozone resistance and the modulus.

4.3.3.5.5 Infra-red Spectroscopy of Peroxide Vulcanizate

SMR-10 (100 g) was mixed with BuTPDS (2 g) on a water cooled laboratory two-roll mill for 2 minutes. DCP (2.5 g) was then added to the mixtures and mixed on the two-roll mill for another 2 minutes. The compound (4.6 g) was cured in a mould designed for infra-red film (Sections 2.5.3 and 2.5.3.1) at 160°C for the determined period of time: 5, 10, 15, 20, 25, 35, 45, 60 and 75 minutes. The infra-red spectra of unextracted and azeotropic (Section 2.5.3.5) extracted films was obtained using a Perkin Elmer 599B infra-red spectrophotometer. The P=S index, which are the ratio of the intensity of P=S peak at about 650 cm^{-1} to the intensity of a reference peak at 2720 cm^{-1} was determined. The P=S indices obtained from extracted films represent the adduct, and the P=S indexes obtained from unextracted films represent the total thiophosphoryl disulphide remaining in the vulcanizates (bound and unbound). The corresponding concentrations were determined using the calibration curve shown in Section 3.2.2. The amount of thiophosphoryl disulphides remaining in the vulcanizate before and after extraction listed in Table 4.18

were plotted against curing time shown in Figure 4.8.

Curing Time (mins)	Amount of BuTPDS (%)	
	Unext	Ext
5	71.1	65
10	57.2	52.4
15	42.2	39
20	32.5	30.5
25	23.5	20
35	11.5	9.4
45	10.2	7.8
60	9.2	7.5
75	8.9	7.3

Table 4.18 Amount of BuTPDS remaining in the vulcanizate before and after extraction

Figure 4.8 shows the decrease of the BuTPDS content during vulcanization. This is demonstrated by the curve of unextracted film showing a rapid decrease of the BuTPDS content in the first 30 minutes then tending towards an almost stationary content of the compound.

The curve of the extracted films shows a similar pattern from about 5 minutes of vulcanization to the unextracted one, although the amount of dithiophosphoryl compound

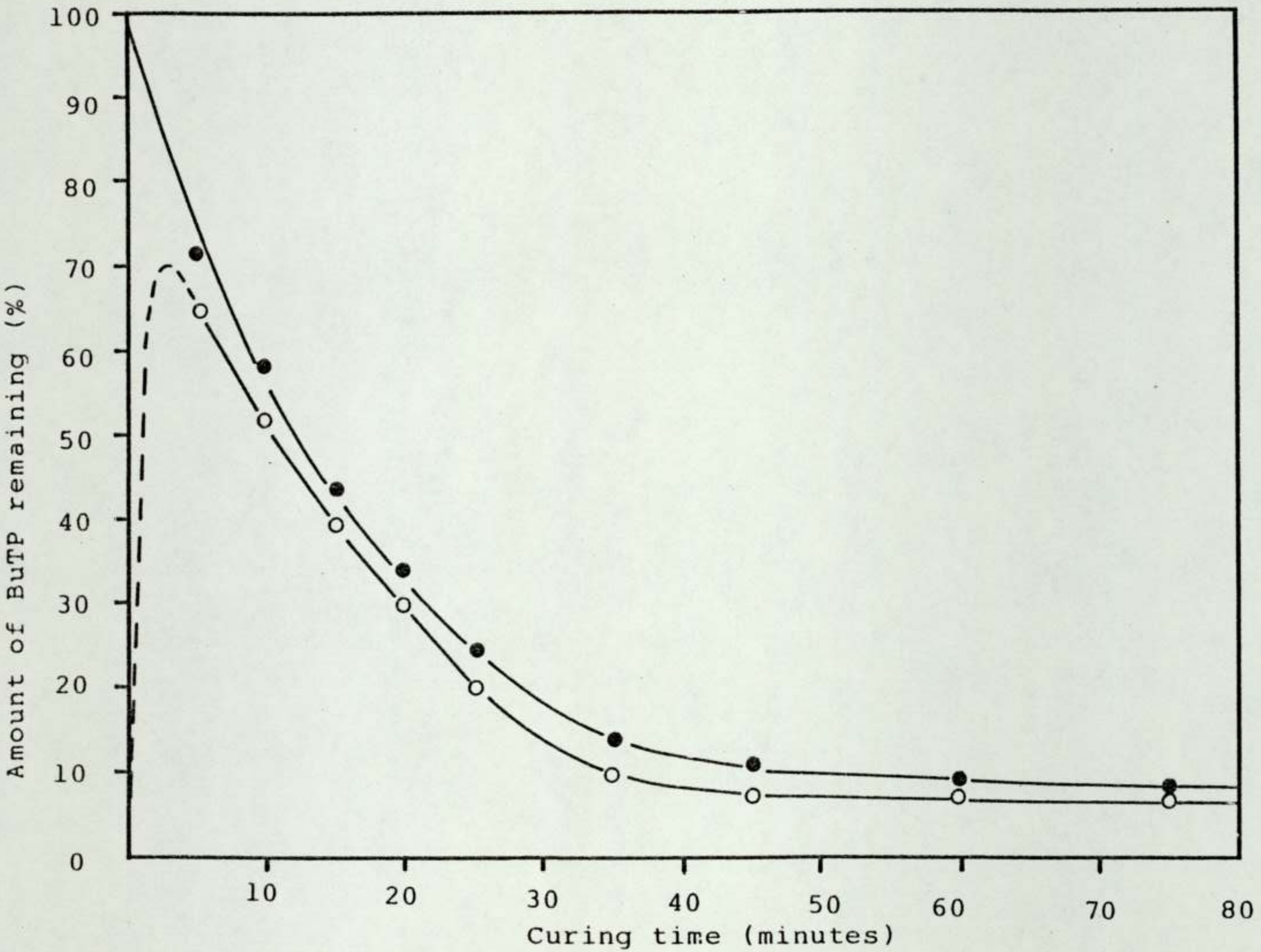


Figure 4.8 Amount of dibutyldithiophosphoryl compound remaining in the vulcanizate during vulcanization at 160°C.
● Unextracted, ○ Extracted, ---An extrapolation.

remaining in the former is slightly lower than in the latter. This indicates that the adduct is formed initially in the first few minutes and becomes unbound as vulcanization proceeds. Only 7.5% of the additive initially added remains in the film after 60 minutes vulcanization as detected by the infra-red method following the P=S indexes at the region of 600-700 cm^{-1}.

4.3.3.5.6 Discussion

Vulcanizates crosslinked with dicumyl peroxide (DCP) at 160°C in the presence of dithiophosphoryl compounds show superior resistance to fatigue. Increasing the concentration of the thiophosphoryl disulphide, increases the fatigue life of the vulcanizate but decreases the ageing resistance and the ozone resistance slightly (Table 4.11, Section 4.3.3.5.1). These characteristics are not only associated with crosslink density, which is decreased as the concentration of the additives increase, but they are also affected by active species produced during vulcanization.

It is clearly shown by addition of 2 phr of BuTPDS (Table 4.11) and of P^iTPDS (Table 4.12) to the peroxide (DCP 2.5 phr) vulcanizate, that there is considerable increase in the fatigue life and decrease in the modulus to approximately half that of the control. However, their ageing and ozone resistance are inferior to the control. The initially superior fatigue life decreases considerably after azeotropic mixture extraction, but remains higher compared to the extracted control. This suggests that there are four factors influencing the durability of the dicumyl peroxide vulcanizates:

i. The transformation product(s) derived from the dithiophosphoryl compounds produced during vulcanization which increase the fatigue life.

ii. The formation of main chain modification mainly conjugated diene and triene (this will be studied in Chapter V), and

iii. low modulus as a result of reducing the crosslink efficiency of peroxide by dithiophosphoryl compounds which increases susceptibility to oxidative degradation(14,47,300,323-325) but is conducive to good fatigue resistance(100).

iv. The temperature of vulcanization is responsible for the durability of DCP vulcanizates containing dithiophosphoryl compound. Increasing the temperature of vulcanization from 160°C to 180°C increases the fatigue life although the modulus also increases. The ageing and ozone resistance also increase considerably.

It is thought therefore, that main chain modification and low modulus become predominant in the stress relaxation and ozone resistance. The zinc complex (ZBuTP) appears to reduce dramatically the crosslink efficiency of DCP giving rise to a very low modulus. As a result, the vulcanizate suffers from inferior fatigue life and ageing resistance compared to other vulcanizates (Tables 4.12 and 4.14, Sections 4.3.3.5.2 and 4.3.3.5.3).

The fatigue life of the unextracted vulcanizates cured at 180°C is superior to those cured at 160°C, but the reverse is true for the extracted vulcanizates, suggesting that the transformation product(s) are responsible for the improvement in the fatigue life, and the formation of main chain modification being reduced during vulcanization at 180°C. These trends have also been demonstrated by the stress relaxation and ozone resistance.

The amount of dithiophosphoryl compound decreases during vulcanization as indicated by decreasing the P=S intensity detected by infra-red. This indicates that during vulcanization the compounds have been transformed to other product(s). The decrease of the P=S intensity proceeds initially by the formation of bound additive which becomes unbound during the course of vulcanization and may lead to the formation of double bonds, which cannot be identified in the vulcanized film due to the thickness of the films, which give rise to broad and strong absorptions of the infra-red spectra. Detailed studies of the formation of the double bonds and the deduction of the dithiophosphoryl compound during vulcanization in squalene are reported in Chapter Five.

The fast decay followed by the autoretardation effect on the stress (Figure 4.6) of extracted vulcanizates cured at 160°C is probably due to the residue of the dithiophosphoryl compounds attached to the rubber backbone. This effect is not shown in the case of vulcanizates cured at 180°C. Nevertheless, the extracted vulcanizates give rise to slow oxidation followed by autoacceleration.

The ozone resistance of peroxide vulcanizates seems to be dependent upon the crosslink density, which is related to the concentrations of dicumyl peroxide. Increasing the temperature of vulcanization and the concentrations of peroxide, increased the modulus and the ozone resistance. This is in agreement with the observation obtained by Braden and Gent(347) that the rate of cut growth due to ozone decreased as the degree of crosslinking increased from an impractically low level to a relatively high one. A similar trend is observed for the stress relaxation(300).

The fatigue life of the peroxide vulcanizates cured at 180°C is comparable to the conventional accelerated sulphur vulcanizates containing IPPD. These two different vulcanization systems cannot be compared at the same moduli.

This has been studied in the case of the tensile strength of radiation and peroxide crosslinked cures compared to that of accelerated sulphur cured$^{(348-350)}$. The maximum crosslink density to reach the optimal strength for accelerated sulphur cure is about twice that for peroxide and radiation cures.

4.3.3.5.7 Conclusion

Dithiophosphoryl compounds are ineffective antidegradants in a conventional accelerated sulphur system. Thiophosphoryl disulphides improve the oxidative ageing of EV and sulphurless vulcanizates.

Peroxide vulcanizates containing bis 0,0-di-n-butyl or -isopropylthiophosphoryl disulphides cured with dicumyl peroxide (3.5 phr) at 180°C exhibit excellent fatigue resistance. Although the extracted vulcanizates lose their protection against fatigue, their fatigue lives are still higher than the control after extraction. The fatigue life is comparable to the conventional accelerated sulphur vulcanizate containing IPPD (see Section 4.2.2.3). However, the peroxide vulcanizates suffer from scorchy, tacky [illegible] and give an unpleasant odour.

CHAPTER FIVE

ELUCIDATION OF THE REACTION MECHANISM OF BIS-(0,0-DIBUTYL)THIOPHOSPHORYL DISULPHIDE IN PEROXIDE VULCANIZATION FROM MODEL COMPOUND STUDIES

5.1 Introduction

It has been shown in Chapter Four that dithiophosphoryl compounds are effective antifatigue agents in a peroxide vulcanizate, but their thermal ageing resistance is very poor. The infra-red spectra of unextracted and extracted peroxide cured film (Section 4.3.3.5.5) indicated that the dithiophosphoryl radicals became bound to rubber at the early stages of vulcanization but became unbound as the course of the vulcanization proceeded. It is thought that there must be a relation between the cleavage of dithiophosphoryl radicals and the ageing properties of the vulcanizates, due to the fact that the degradation of vulcanizates during ageing was increased. The increase in fatigue life is probably associated with the low modulus of the vulcanizate but may also result from the products produced in the reaction of BuTPDS with DCP in the rubber during vulcanization (Section 4.3.3.5.1).

Infra-red analysis of the vulcanized film did not give satisfactory results due to the variability of the film thickness due to the overlap of characteristic frequencies. Therefore it seemed useful to examine the spectra of the reaction products in a related model compound in demountable fixed thickness cells. Squalene was used for the purpose providing the similarity in structure to polyisoprene and appropriately high boiling point. Ultraviolet spectroscopy has also been carried out to analyse the absorption of double bonds of the substrate and to study the formation of conjugated double bonds in the reaction product.

5.2 Infra-red Spectroscopy

5.2.1 Procedure

Squalene (25 ml), BuTPDS (0.375 g) and DCP (0.937 g) were reacted in a 3-necked flask under nitrogen equipped with a condenser, agitator and a thermometer at 160°C. Aliquot parts (1 ml) were taken from the solution at 5 minute intervals up to 30 minutes reaction, and every 15 minutes up to 60 minutes reaction. The solution taken was immediately placed in a stopped vial and cooled in acetone-dry ice mixture as described in Section 2.7.1.

The solution was placed in a demountable NaCl cell separated by a 0.25 mm spacer. Another cell was filled with unreacted solution as a reference in order to compensate all original's absorption and obtain the product's absorption. A reference cell containing only squalene was also necessary to monitor the decreasing of certain absorptions. The infra-red spectra of the solutions were obtained from a Perkin Elmer 599B infra-red spectrophotometer as described in Section 2.7.1.1. The absorbance of specific absorptions were plotted as a function of reaction time shown in Figure 5.1.

5.2.2 Results

The infra-red spectra compensated by the squalene as the reference is shown in Figure 5.1. The salient features are as follows. A decrease of the absorption band at 650 cm^{-1} due to the P=S absorption of the starting material BuTPDS was associated with a shift of this band to 660 cm^{-1} after 15 minutes. This absorbance increased during the first 5 minutes and then decreased again. Similarly, the absorbance of a very intense band at 700 cm^{-1} due to the monosubstituted aromatic ring of DCP decreased and was shifted to 706 cm^{-1} after 25 minutes and the intensity increased slowly followed by steady decreasing after 40 minutes. Figure 5.1 shows that the absorption of a band at 940 cm^{-1} due to (P)-O-C stretching decreases after 30 minutes.

The reaction products are obvious from the infra-red spectra substracted by the reference consisting all the starting material. A very intense band at 885 cm^{-1} assigned to vinylidene CH_2=C< group(350) was formed slowly at the first 20 minutes and then followed by a sharp increase throughout the reaction.

A very sharp band at 706 cm^{-1} assigned to monosubstituted aromatic was formed slowly during the first 15 minutes. The absorption of this band increased very quickly from 15 to 25 minutes of the reaction and thereafter increased

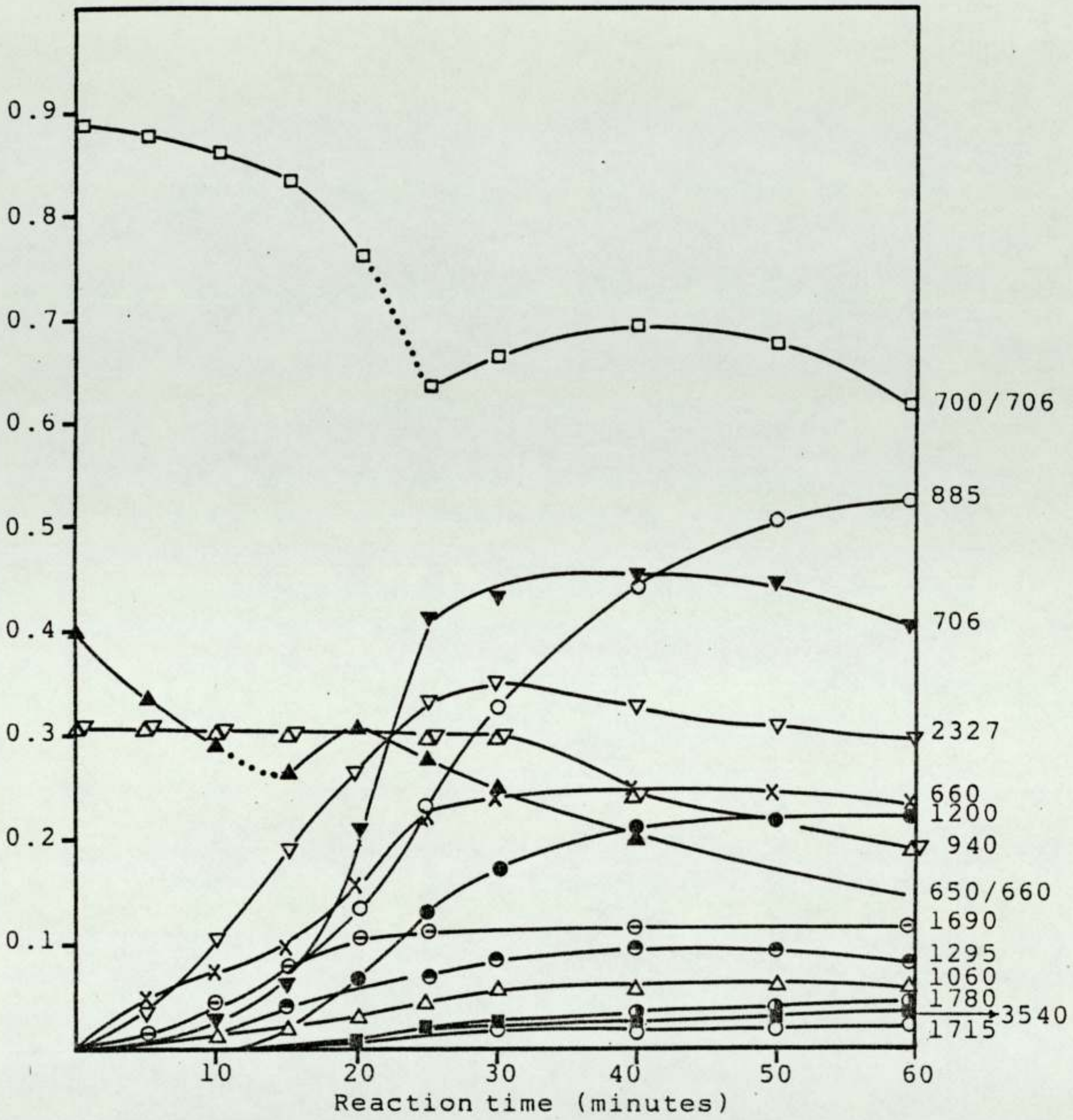
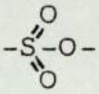
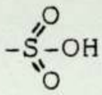
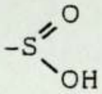
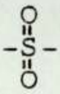
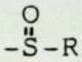


Figure 5.1 Absorbance of products (NaCl) after reaction of BuTPDS with DCP in squalene at 160°C. The numbers represent the absorption (cm^{-1}) of the products. 700/706 and 650/660 indicate the shifting of the absorption marked by doted line.

steadily but much more slowly and after 40 minutes started decreasing slowly. A band at 2327 cm^{-1} assigned to S-<u>O-H</u> stretching$^{(352)}$ was formed with a fast increase in the absorption up to 30 minutes and followed by a slow but steady decrease of the absorption. A similar pattern to the absorption curve of the band at 706 cm^{-1} shown in Figure 5.1 for the band at 660 cm^{-1} which is due to P=S bonds shifted from 650 cm^{-1} but the initial absorption is much faster.

It is very difficult to describe all of the new peaks in the range of 1400-800 cm^{-1}. Bands typical of  $-S(=O)_2-O-$  $-S(=O)_2-OH$  $-S(=O)-OH$  $-S(=O)_2-$ and  $-S(=O)-R$ are in that region. Figure 5.1 shows the absorption of bands at 1060, 1200 and 1295 cm^{-1}, all are at low intensity with the exception of the band at 1200 cm^{-1} which is broad and of medium intensity due to carbon-oxygen stretching mode of dicumyl alcohol. The bands at 1690 cm^{-1} indicates conjugation of a C=O with a C=C linkage probably due to acetophenone. The bands at 1715, 1780 and 3540 cm^{-1} are due to carbonyl group, cyclic ketone and phenol.$^{(351)}$ They appeared initially at 15 minutes of the reaction time and the absorptions increased slowly but steadily as the reaction proceeds. The bands at about 1600 cm^{-1} due to double bonds are difficult to identify. At least three new bands were formed in the range of 1660-1560 cm^{-1} and one of them shifted from 1630 cm^{-1} to 1640 cm^{-1} as shown in Figure 5.2. The characteristics of these double bonds will be examined by UV spectroscopy in Section 5.3.

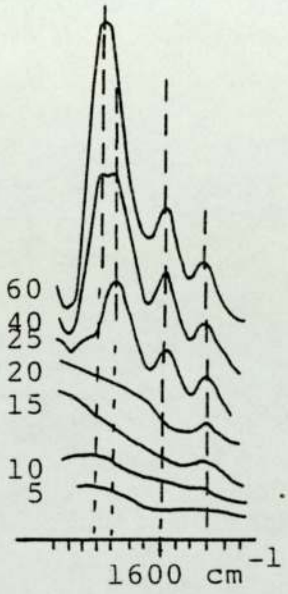


Figure 5.2 Infrared spectra (1660 - 1560 cm^{-1}) of products (NaCl) after reaction of BuTPDS with DCP in squalene at 160°C. The numbers represent the reaction time.

5.3 Ultraviolet Spectroscopy

5.3.1 Procedure

The reaction solutions (0.05 ml) were diluted with spectroscopic grade of hexane (12.5 ml). Hexane was used for the reference beam. The absorbance at a given wavelength in the range of 200 to 450 mμ was obtained from a Pye Unicam SP 800B ultraviolet spectrophotometer. The absorbance of particular wavelength was plotted as a function of reaction time shown in Figure 5.3.

5.3.2 Results

Three maxima were found from the ultraviolet spectrograph.

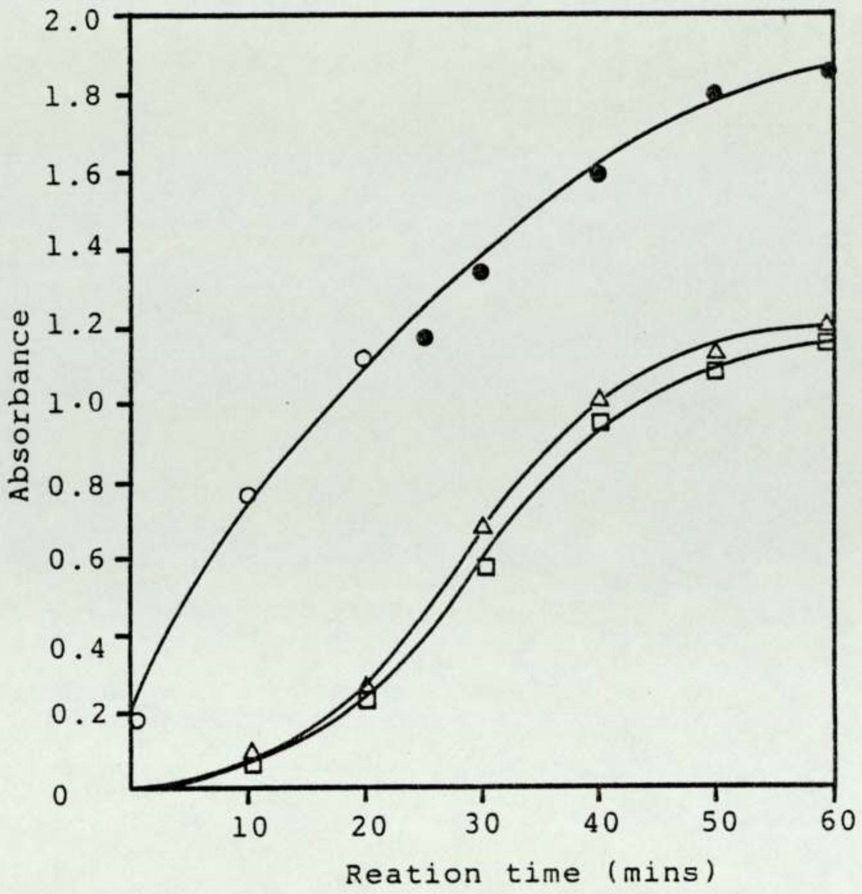


Figure 5.3 UV absorption (in hexane) of squalene after reaction with dicumyl peroxide an peroxide and BuTPDS at 160°C.

○ λ_{max} 225 mμ. ● λ_{max} 230 mμ

△ λ_{max} 273 mμ. □ λ_{max} 282 mμ

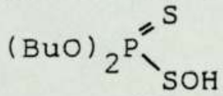
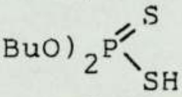
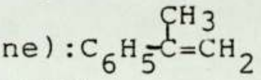
The first maximum was initially at 225 mμ and shifted to 230 mμafter 20 minutes. The absorption of this maximum increased very quickly from the beginning and the rate of increase was reduced after 50 minutes but still increased steadily. The other maximum (doublet) absorbed at 273 and 282 mμ. The absorption of both maxima shown in Figure 5.3 are identical: slow increase initially up to 20 minutes and followed by rapid increase to 40 minutes, then a steady increase at a much slower rate.

5.4 Discussion

Figure 5.1 shows that there are changes from the spectra of the starting material of bands at 650 cm^{-1} for the P=S bond, 700 cm^{-1} for mono- substituted aromatic ring and 940 cm^{-1} for (P)-O-C stretching vibration. It is obvious from the spectra that P=S bond of BuTPDS, monosubstituent of DCP and (P)-O-C bond of BuTPDS are modified or broken.

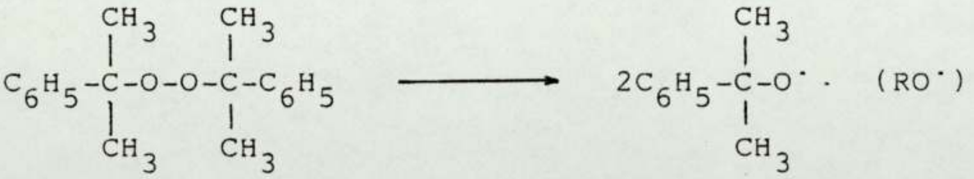
The decrease of the absorption of the spectra at 650 cm^{-1} due to P=S bond is followed by a shift to 660 cm^{-1}, where the known amount of squalene has been spectrally substracted from the mixture. From the spectra obtained by compensating with unreacted material, a new band at 660 cm^{-1} is observed indicating the thiophosphoryl disulphide has been modified. The modification of the disulphide is confirmed by the formation of a new band at 2327 cm^{-1} assigned to S-<u>O-H</u>(352).

At the same time, the absorption of the spectra at 700 cm^{-1} due to DCP decreases and shifts to 706 cm^{-1}. This is also accompanied by the formation of a related new band at 885 cm^{-1} assigned to $CH_2=C<$.

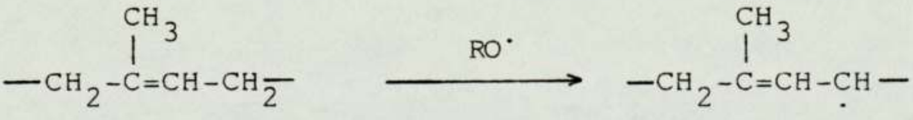
In the first case, the -SOH bond is probably due to  $(BuO)_2P(=S)SOH$. The P=S bond of  $(BuO)_2P(=S)SH$ also absorbs at about 660 cm^{-1}, but the -SH band at 2480 cm^{-1} was not found in the present work. In the second case, by observing the spectra of reaction products, one can observe the increase in the absorption band at 885 cm^{-1} of $CH_2=C<$ indicating the formation of the degradation products of dicumyl peroxide(353) which is due to α-methyl styrene (2-phenylpropene):  $C_6H_5-C(CH_3)=CH_2$ product by dehydration of cumyl alcohol(248,276-279) catalysed by sulphur acids. However, it is unlikely that sulphur oxides or acids are formed in the absence of oxygen during the reaction or during vulcanization. The low intensity of certain bands assigned to sulphur oxides or acids, phenol and acetone may be due to hydroperoxide initially present in the squalene at 3640 cm^{-1}. This suggests therefore, that the formation of α-methyl styrene due to dehydration by acids is unlikely to occur. Figure 5.1 shows a steady increase in the absorption band at 885 cm^{-1} due to vinylidene throughout the reaction, whereas the absorption of the band at 700 cm^{-1} due to monosubstituted aromatic ring decreases after 40 minutes. It is thought that other sources of vinylidene in the reaction mixtures, probably from the substrate, also gives rise to the absorption in that region.

The ultraviolet absorption spectra of the reaction mixtures in hexane shows the appearance of absorption bands at 230 mμ, 273 mμ and 282 mμ. Their intensity increases indicating the formation of conjugated double bonds as indicated by Colclough et al(47) during crosslink scission of monosulphidic networks. They found the appearance of absorption bands at 240 mμ and 284 mμ, the former being identified with a 1, 3, 6 partially conjugated triene as observed in the ocimenes (λ_{max}, 237 mμ) and the latter with a fully conjugated triene containing the same chromophore as allo-ocimene (λ_{max} 280 mμ dependent on geometrical isomer). The multiple absorption maxima characteristics of the allo-ocimenes were indicated in the vulcanizate spectra by inflextions at 270 mμ and 290 mμ.

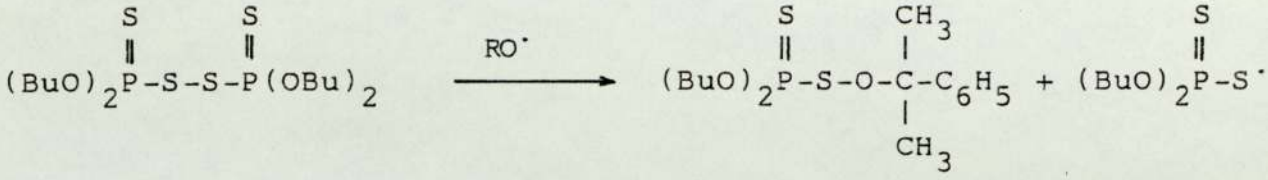
From the observation above, the possible reactions involved in the vulcanziation of natural rubber at 160°C using dicumyl peroxide as the curing agent in the presence of bis-(0,0-dibutyl)thiophosphoryl disulphide (BuTPDS) are proposed and outlined as follows:



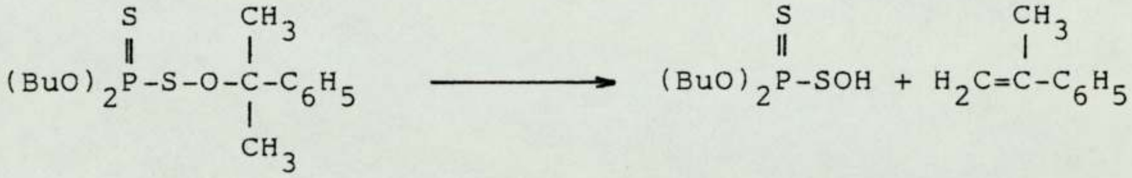
$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-O^{\cdot}\cdot \quad (RO^{\cdot}) \qquad (5.1)$$



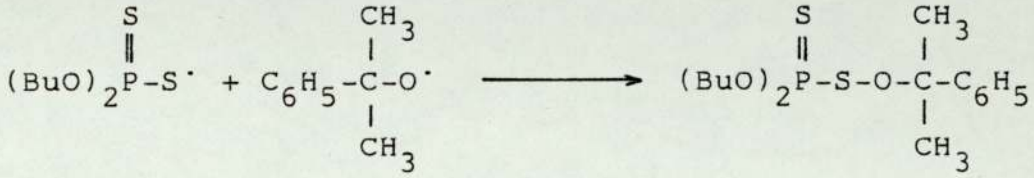
$$-CH_2-\overset{CH_3}{C}=CH-CH_2- \xrightarrow{RO^{\cdot}} -CH_2-\overset{CH_3}{C}=CH-\underset{\cdot}{CH}- \qquad (5.2)$$



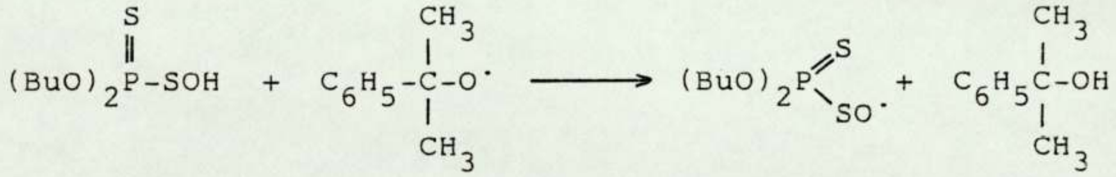
$$(BuO)_2\overset{S}{\overset{\|}{P}}-S-S-\overset{S}{\overset{\|}{P}}(OBu)_2 \xrightarrow{RO^{\cdot}} (BuO)_2\overset{S}{\overset{\|}{P}}-S-O-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 + (BuO)_2\overset{S}{\overset{\|}{P}}-S^{\cdot} \quad (5.3)$$



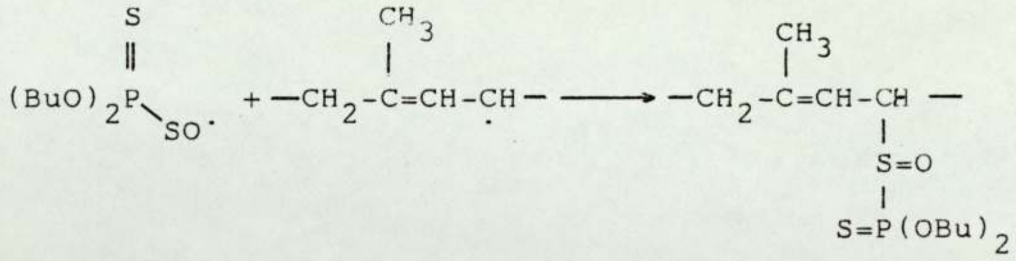
$$(BuO)_2\overset{S}{\overset{\|}{P}}-S-O-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 \longrightarrow (BuO)_2\overset{S}{\overset{\|}{P}}-SOH + H_2C=\overset{CH_3}{C}-C_6H_5 \quad (5.4)$$



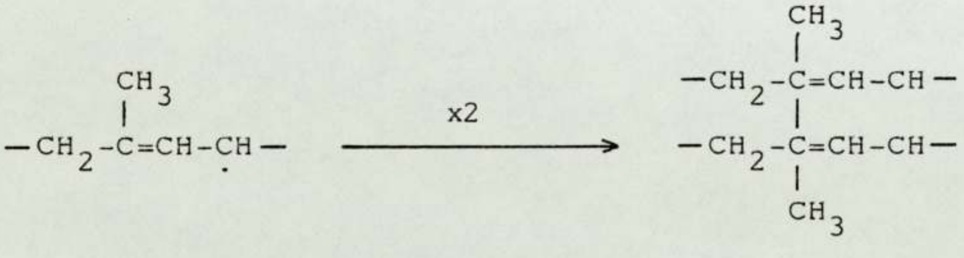
$$(BuO)_2\overset{S}{\overset{\|}{P}}-S^{\cdot} + C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-O^{\cdot} \longrightarrow (BuO)_2\overset{S}{\overset{\|}{P}}-S-O-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 \quad (5.5)$$



$$(BuO)_2\overset{S}{\overset{\|}{P}}-SOH + C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-O^{\cdot} \longrightarrow (BuO)_2P(=S)SO^{\cdot} + C_6H_5\underset{CH_3}{\overset{CH_3}{C}}-OH \quad (5.6)$$



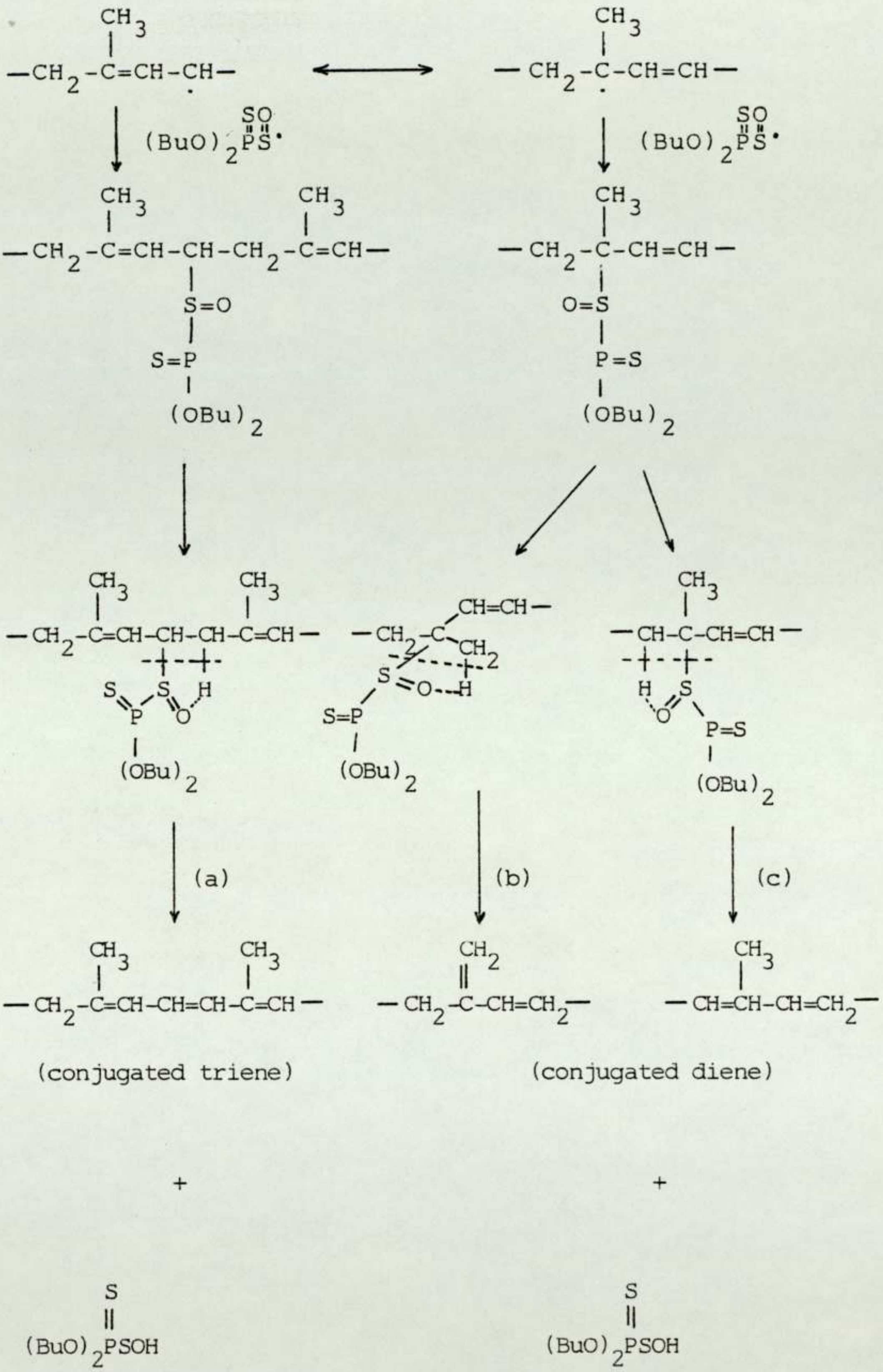
$$(BuO)_2\overset{S}{\overset{\|}{P}}SO^{\cdot} + -CH_2-\overset{CH_3}{C}=CH-\underset{\cdot}{CH}- \longrightarrow -CH_2-\overset{CH_3}{C}=CH-\underset{\underset{S=P(OBu)_2}{|}}{\underset{S=O}{\underset{|}{CH}}}- \quad (5.7)$$



$$-CH_2-\overset{CH_3}{C}=CH-\underset{\cdot}{CH}- \xrightarrow{x2} \begin{matrix} -CH_2-\overset{CH_3}{C}=CH-CH- \\ | \\ -CH_2-\underset{CH_3}{C}=CH-CH- \end{matrix} \quad (5.8)$$

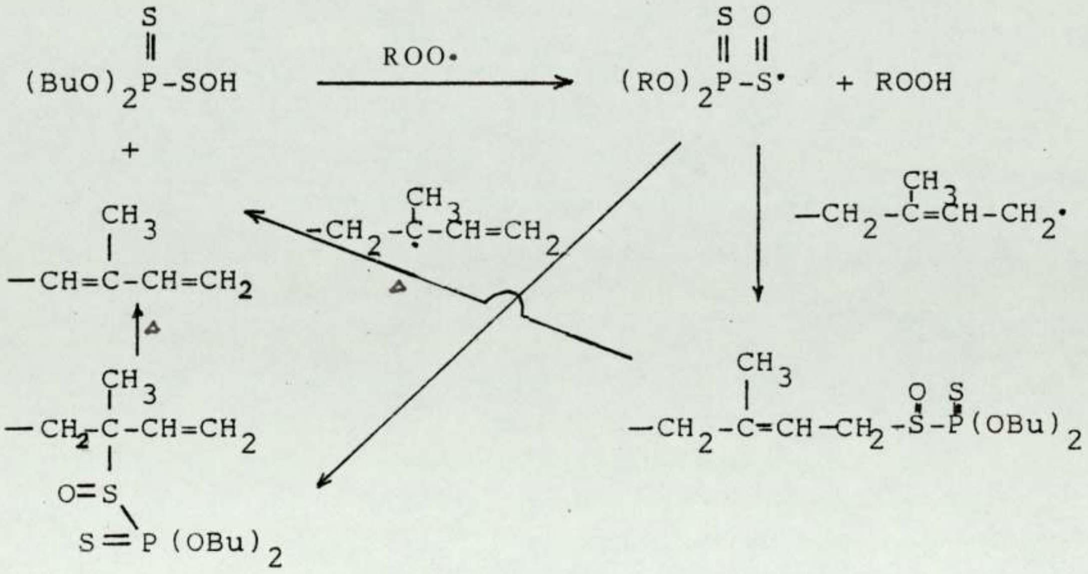
Reaction 5.1, 5.2 and 5.8 represent the normal course of dicumyl peroxide vulcanization leading to the formation of carbon to carbon crosslinks. The reactions 5.3 to 5.5 are considered to be responsible for the formation of the product having absorption at 2327 cm^{-1} and part of the vinylidene. In addition, the reaction 5.3 is thought to be responsible for the decrease of the efficiency of peroxide crosslink giving rise to the low modulus. The reactions 5.7 and 5.8 represent the formation of adduct during vulcanization which becomes unbound as the vulcanization proceeds. The scission of C-S bond probably occurs through a five-membered transition state similar to that proposed by Colclough et al(47) for the crosslink scission in monosulphidic crosslinks and results in conjugated diene and triene structures being introduced into the main polyisoprene chains as shown in Scheme 5.1.

The cleavage of sulphoxide via the alternative transition state involving β-hydrogen atom of the isoprenyl group in reaction (a) gives rise to the formation of conjugated triene. While reactions (b) and (c) give rise to conjugated diene. In addition, reaction (b) leads to the formation of vinylidene as well as conjugated diene. It may therefore be suggested that this contributes to the absorption band at 885 cm^{-1}. The sulphenic acid derived from dithiophosphoryl compound which is consumed (5.6 and 5.7) and reformed (5.3 to 5.5 and Scheme 5.1) during the course of vulcanization, is believed to be involved in a cyclical regenerative



Scheme 5.1

process during fatiguing of peroxide vulcanizate as shown in Scheme 5.2. The sulphinyl radicals are continuously regenerated in the system and react with alkyl radical formed during fatiguing. Evidence was gained for the



Scheme 5.2

antifatigue activity by showing an excellent fatigue life of the peroxide vulcanizate containing BuTPDS shown in Section 4.3.3.5.2. This is in agreement with the proposal put forward by Al-Malaika and Scott$^{(206)}$ (Section 1.11.3, Scheme 1.13).

The formation of conjugated diene and triene is believed to be contributory to the inferior ageing performance. Furthermore Figure 5.1 also explains the adduct formed in the early stages of peroxide vulcanization and became unbound as the vulcanization proceeded (Section 4.3.3.5.5, Figure 4.8).

5.5 Conclusion

The model compound study confirms the formation of a transformation product i.e., $(BuO)_2\overset{\overset{S}{\|}}{P}SOH$ (0.0-dibutylthiophosphoryl sulphenic acid) which acts as antifatigue agent via the corresponding sulphinyl radical $[(BuO)_2\overset{\overset{S}{\|}}{P}\dot{S}O]$ which traps the alkyl radical during fatiguing. Conjugated diene and triene introduced to the rubber molecules during vulcanization reduces the thermal ageing resistance.

CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusion

The study reported in this thesis describes the binding reaction of 0,0-diisopropyldithiophosphoric acid, 0,0-dibutyldithiophosphoric acid and its ammonium salt to natural rubber latex. The results indicate that compounds can be bound to rubber in the presence of hydroperoxides. There is no significant difference in the extent of binding using t-butyl peroxide and cumyl hydroperoxide. A maximum of 50% yield can be achieved using normal concentrations of the acids. High concentrations of the acids caused co-agulation of the latex due to their acidity. Cerium (IV) catalysed the formation of the adduct, but excess of ceric salt coagulated the latex. Concentrate masterbatch can only be prepared from ammonium salt of the dithiophosphoric acid at a maximum concentration of 15 phr, but the extent of binding was lower in this case.

Attempts to bind the dithiophosphoryl compounds mechano-chemically under shearing condition in the polymer melt in a RAPRA torque rheometer gave rise to a low level of adduct formation. This is due to the lubricating effect of the compounds at low to moderate processing temperatures, at higher processing temperatures crosslinking is promoted, especially in the case of the ammonium salt.

A study of the curing characteristic and the technological performance of the rubber containing the bound dithiophosphoryl compounds and of the compounds added as a normal additive during compounding vulcanized using conventional accelerated sulphur system showed that in general all the adducts reduced the scorch time, cure rate and increased the modulus compared to the control. The changes of the curing characteristics over the control were more pronounced in the stocks containing the compounds added as a normal additive. All the compounds examined which were introduced during compounding and binding were found to exhibit a pro-oxidant effect in the conventional accelerated sulphur vulcanizates. The adduct, however made, became unbound during vulcanization. Bis-(0,0-dibutyl)phosphoryl disulphide however, was shown to improve oxidation resistance in low sulphur (CBS-EV) and sulphurless (TMTD) vulcanizates.

Bis-(0,0-diisopropyl)thiophosphoryl disulphide and bis-(0,0-dibutyl)thiophosphoryl disulphide have been found to possess antifatigue activity in peroxide vulcanizate cured at 160°C. However, the oxidation resistance of the vulcanizates were poor, especially those containing high concentration of thiophosphoryl disulphides. The antifatigue activity increased considerably when the stocks were cured at 180°C, the oxidation resistance was also improved. The improvement of the durability is thought to be due to a transformation product produced during vulcanization.

An infra-red examination of a peroxide vulcanizate showed that the dithiophosphoryl adduct was formed in the early stages of the vulcanization and became unbound as the vulcanization proceeded. The infra-red examination of the reaction using squalene as the model compound showed that a transformation product characterized as a sulphenic acid was formed. This compound is believed to be involved in the regeneration process during fatiguing and the corresponding sulphinyl radicals produced are able to trap the alkyl radical. Ultraviolet spectroscopic analysis showed the formation of conjugated diene and triene along the squalene molecules supporting the above mechanism.

6.2 Suggestions for Further Work

The antifatigue activity of peroxide vulcanizates containing bis-(0,0-diisopropyl)thiophosphoryl disulphide and bis-(0,0-dibutyl)thiophosphoryl disulphide was improved by increasing the curing temperature and this was accompanied by an increase in the oxidation resistance. It would be of interest to study in more detail the correlation of the formation of the sulphenic acid, the conjugated diene and triene, and the durability of the vulcanizate cured at 180°C and above. It is necessary to study the network structure of the vulcanizates to evaluate the participation of the compound in the network structure and the fatigue and oxidation resistance.

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