REACTIONS OF HINDERED PHENOLS WITH UNSATURATED HYDROCARBONS IN THE PRESENCE OF FREE RADICALS

BY

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Submitted for the degree of Ph.D - 1977

The reaction of hindered phenolic antioxidants , notably 2,6-ditert-butyl-4-methyl-phenol (TBC) and 3,5-ditert-butyl-4-hydroxy-benzyl mercaptan (BHBM) with rubber has been investigated and the percentage of antioxidant bound under optimum conditions has been determined. The byproducts formed during the adduct formation and their effect on the binding reaction was also studied.

The reaction mechanism involved in both cases has been studied. It has been found that the BHBM adduct was formed by the addition of thiol to the rubber double bond and that of TBC by the attachment of the benzylic carbon atom to the allylic carbon atom of natural rubber.

Tensile measurments, oxygen absorption tests and stress relaxation measurements have been used to evaluate the antioxidant activity of the bound antioxidants. Comparison of their performances with commercial antioxidants has shown that the latter are completely removed under severe environmental conditions, whereas, rubber-bound antioxidants exhibit exceptional stability. A major advantage of the rubber-bound systems, which has emerged during the evaluation was their suitability for the preparation of bound antioxidant concentrates and the superior performances of rubbers prepared using concentrated masterbatches have been demonstrated under severe testing conditions.

Similar studies were carried out with nitrile-butadiene (NBR) latices and it has been found that NBR containing bound antioxidants, particularly, the BHBM adducts exhibit superior stability to conventionally added antioxidants, when used in applications where loss of antioxidants by volatilisation or leaching or by extraction may occur.

RUBBER
LATEX
BOUND-ANTIOXIDANTS
AGEING
PHENOLIC-THIOLS

The work described in this thesis was carried out between October 1974 and September 1977 at the University of Aston in Birmingham. It has been done independently and submitted for no other degree.

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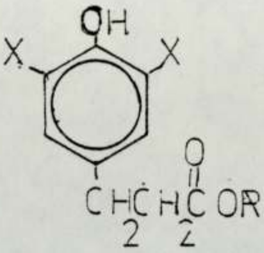
CHAPTER ONE

INTRODUCTION

The demands made on elastomers during service are continually increasing. Antioxidant formulations currently in use have been developed on an empirical basis and utilising a limited number of selection procedures. The conventional ageing test methods, such as , the oxygen absorption test or the oxygen bomb or air oven tests may be inadequate under the aggressive condition often experienced by rubbers in modern industrial and domestic environments. The ability of an antioxidant to protect rubbers under the high temperature condition of an automobile or aeroengine particulary in contact with lubrication oils depends not only its intrinsic activity, but its ability to remain in the rubber under these conditions. Similar arguments apply to rubbers, which are subjected to repeated cleansing operation suchas, detergent washing or solvent dry cleaning, particularly when they are in the form of articles with a high surface area to volume ratio, such as eg. latex threads or thin films eg. rubber gloves, garment interlining etc.

1.1.1 Volatilisation and leaching of antioxidants in polymers

The antioxidants used in polymer formulations are physically blended with polymers and they may be lost readily either by volatilisation or by leaching out in contact with water or industrial solvents. Plant and Scott[1] studied the volatilisation of high molecular weight, low volatile antioxidants (1) in thin polypropylene films at 140°C and the results are shown in table 1.1



(a) R = CH_3

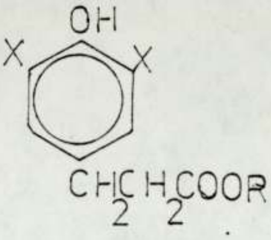
(b) R = C_6H_{13}

(c) R = $C_{12}H_{23}$

(d) R = $C_{18}H_{37}$

$X = (CH_3)_3C$

Table 1.1 - Activity of phenolic antioxidants in polypropylene at 140° C



		Induction period in polypropylene in hours		Antioxidant half life in N_2 stream
R	Mol-wt	Closed system	Moving air stream	
CH_3	292	95	2	0.28
$CH_3(CH_2)_5$	362	312	2	3.60
$CH_3(CH_2)_{11}$	446	420	2	83.00
$CH_3(CH_2)_{17}$	530	200	1.65	660.00
Tert-butyl p cresol (TBC)	220	140	2	0.10

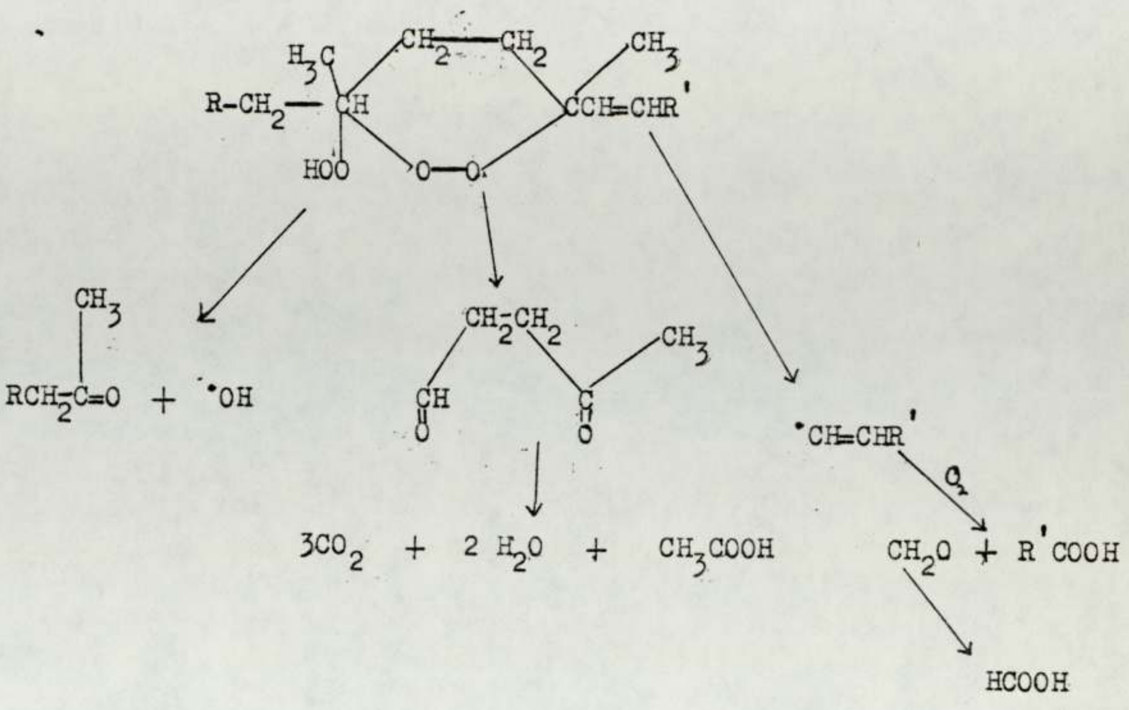
It is clear from the above table that volatility is a deciding factor in determining the effectiveness of antioxidants of polypropylene in an open system. Below a certain limiting molecular weight, this antioxidant structure is ineffective in a changing atmosphere due to loss by volatilization. Further, it shows that TBC which is one of the efficient antioxidant structures known is relatively ineffective in polypropylene in both closed system and in an open system. The work carried out by Spatch and co-workers[2] has shown that the loss of TBC is much more rapid than that of 2-benzyl-6-tert-butyl phenol and the effect was much predominant in thin samples than thick samples.

Robinson and Dunn[3] found that in styrene-butadiene copolymer, TBC and tris phosphite volatilized during milling at 160° C. There are evidences for the leaching out of antioxidants from finished articles. For instance, in tyre treads, where significant amounts of antioxidants are lost by leaching in contact with water causing considerable reduction in fatigue and ozone resistance[4-5].

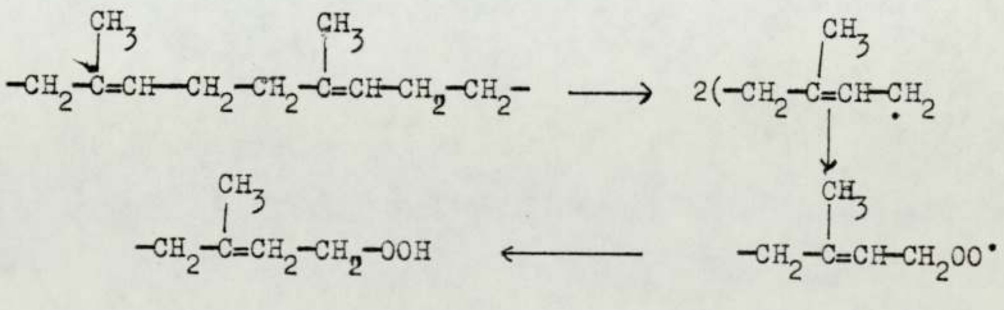
1.1.2 Degradation of polymers

The oxidisability of polymers depends on the chemical structure, composition, the presence of impurities and the external environment to which they are exposed. The presence of double bonds and of labile hydrogens in the polymer backbone, accelerate their oxidative degradation. For instance, cis-isoprene and natural rubber are highly susceptible for deterioration. Other than oxygen, the factors which influence the deterioration of polymers are heat, light, mechanical stress, contamination of metal ions and ozone. Oxidation of polymers may occur during the processing as well as in service life.

Bevilaqua[6-9] has extensively studied the reduction of molecular weight of raw rubber as a function of the absorption of oxygen and the formation of chemical entities such as carbon monoxide, carbon dioxide and carboxylic acids including formic, acetic and levulinic acid. He has proposed that the products were formed as a result of break down of rubber hydroperoxide, which was closely related to that proposed by Bollard and Hughes as an oxidation product of squalene.



It was clear from the studies of Stafford[11] that the effect of milling was much more important to the subseqent thermal and photochemical oxidation than was irradiation by weak day light. Oxidation in the absence of ultra violet light, was accelerated by milling due to the formation of free radicals by mechanical scission of the rubber molecule. These trapped radicals decay over a period of months due to disproportionation or recombination reactions. During the milling process, however, hydroperoxides are formed rapidly and their concentration will be related to milling time.



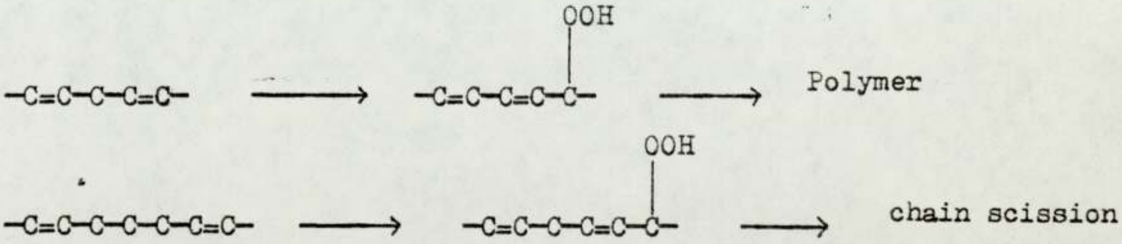
Under condition of U.V irridiation, these will act as photoactivators for the oxidation and since they will be an important source of free radicals, the oxidation rate depends only upon the total milling time.

Several workers[11-12] have studied the autoxidation of natural rubber and they explained it by the following scheme, where RH represents the hydrocarbon.

Initiation:

$$\begin{aligned} RH &\longrightarrow R^{\bullet} \\ R^{\bullet} + O_2 &\longrightarrow ROO^{\bullet} \\ ROO^{\bullet} + RH &\longrightarrow ROOH + R^{\bullet} \\ ROOH &\longrightarrow RO^{\bullet} + {}^{\bullet}OH \end{aligned}$$

The most noticable difference between the isoprene and butadiene containing rubbers is that in the former, chain scission is predominant and the benzene solubility remains high. In the latter rapid gelation occurs in the presence of oxygen with consequent insolubilisation[13]. Scott has explained that singly methylene interupted dienes give hydroperoxide initially and polymerised at an advance stage of oxidation. Doubly interupted methylene dienes on the other hand give rise to hydroperoxide, where decomposition is associated with carbon-carbon scission.



$$-C{=}C{-}C{-}C{=}C- \longrightarrow -C{=}C{-}C{=}C{-}\overset{\displaystyle OOH}{\overset{|}{C}}- \longrightarrow \text{Polymer}$$

$$-C{=}C{-}C{-}C{-}C{-}C{=}C- \longrightarrow -C{=}C{-}C{-}C{=}C{-}\overset{\displaystyle OOH}{\overset{|}{C}}- \longrightarrow \text{chain scission}$$

1.1.3 Mechanism of antioxidant action

It is obvious from the oxidation reactions of rubbers that the inhibition of rubber oxidation can be achieved by scavenging the reactive free radicals formed or by preventing the initiation of RH and can be achieved by decomposing the hydroperoxide to non radical products.

Hinderd phenols and secondary aryl amines are mainly included under the class of chain terminating antioxidants. These have ability to transfer their labile hydrogens to the propagating radicals(alkyl peroxy and alkyl radicals), thus terminating the reaction.

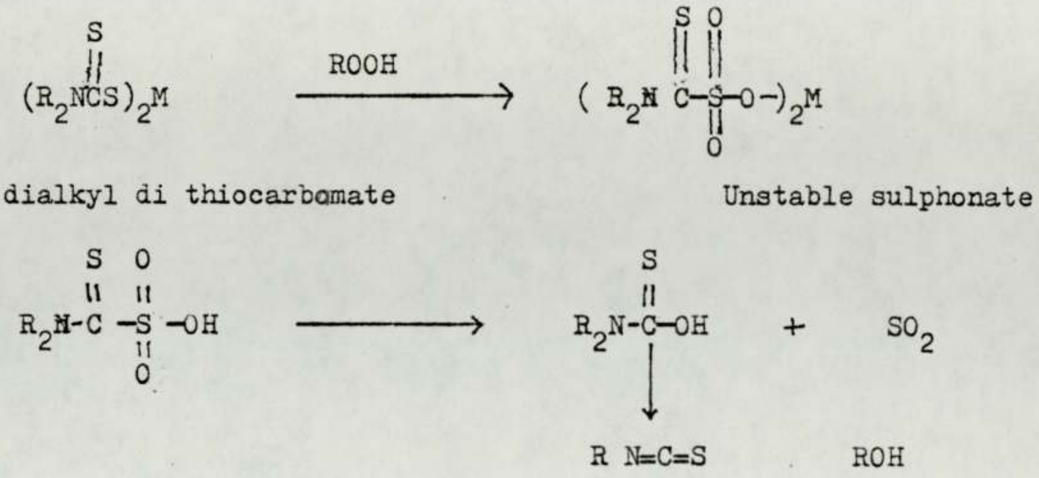
$$ROO^{\bullet} + AH \longrightarrow ROOH + A^{\bullet}$$

$$2A^{\bullet} \longrightarrow \text{Stable product}$$

The resulting phenoxy radical has a tendency to react with oxygen or polymer and the rate of the reaction depends on the steric environment of the aroxy radical. The ease of hydrogen abstraction by alkyl peroxy is increased by electron releasing in the phenolic or amine, but the same electronic characteristics favours the direct attack of oxygen on the phenolic hydrogen , which is potentialy a chain initiating reaction.

$$A{-}H + O_2 \longrightarrow A^{\bullet} + {}^{\bullet}OOH$$

The second antioxidant process is the preventive mechanism, which is concerned with the radical initiation process. Preventive antioxidants include mainly peroxide decomposers, metal deactivators and light absorbers. Some of the peroxide decomposers are sulphur containing compounds, such as thiodipropionate esters, metal complexes of the dithiocarbamic and phosphorus containing compounds. It is clear from the papers published by Scott and co-workers[14-16] that the mechanism of this class of antioxidants mainly metal complexes destroy hydroperoxide by an ionic mechanism , generally Lewis acid catalysed reactions. eg:

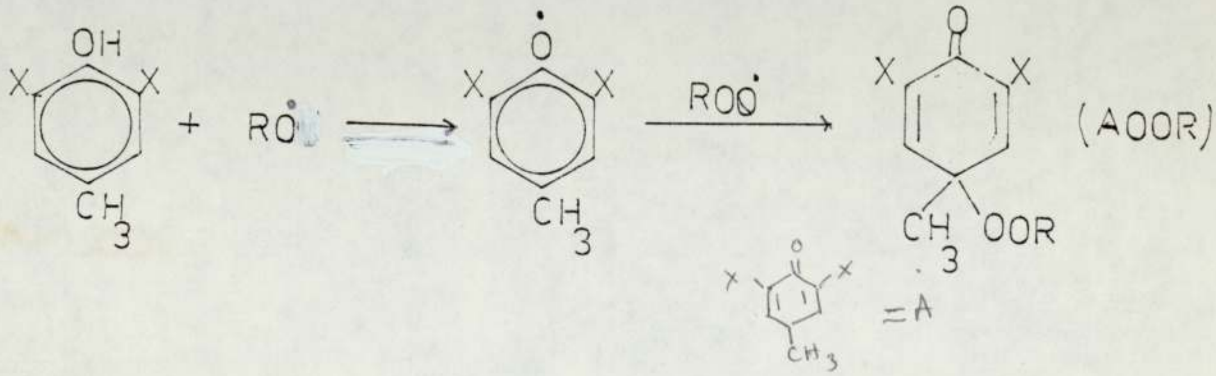


Sulphur oxides are effective ionic catalysts for the decomposition of hydroperoxide. Thus for example cumene hydroperoxide gives phenol and acetone.[14]

These two mechanisms interfere at two different positions in the autoxidation process, they mutually reinforce one another, leading to an effect greater than the sum of the effect of individual alone. This phenomenon is called synergism.

1.1.4 Oxidation of phenols under autoxidation condition

The products of the oxidation of hindered phenols under autoxidation condition has been shown to be due to the initial formation of a phenoxy radical followed by subsequent reaction with other free radicals, either the same or different, which may be present in the system. The work of Boozer[17] has shown that initialy formed phenoxy radicals react with hydroperoxy radicals and resulting in the following end product.



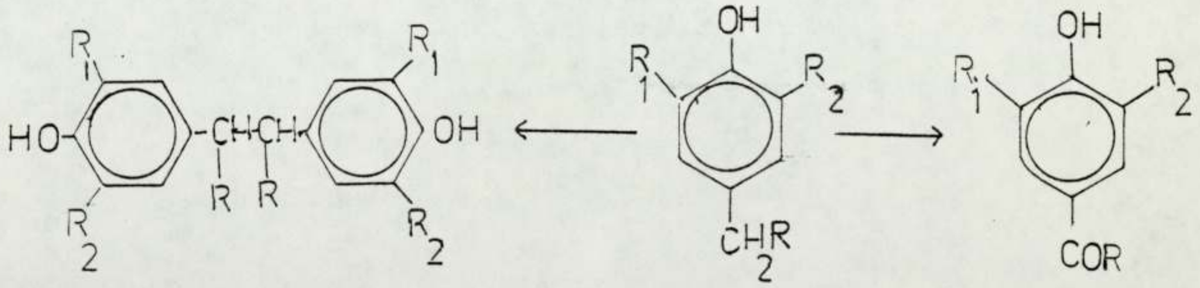
The most important function of phenolic antioxidants is to remove chain propagating alkyl peroxy radicals. According to above investigation a new type of peroxide is formed, which is fairly stable at low temperatures, but at high temperatures it homolyses , causing initiation.

$$AOOR \longrightarrow RO^{\bullet} + AO^{\bullet}$$

$$RO^{\bullet} + AH \longrightarrow ROH + A^{\bullet}$$

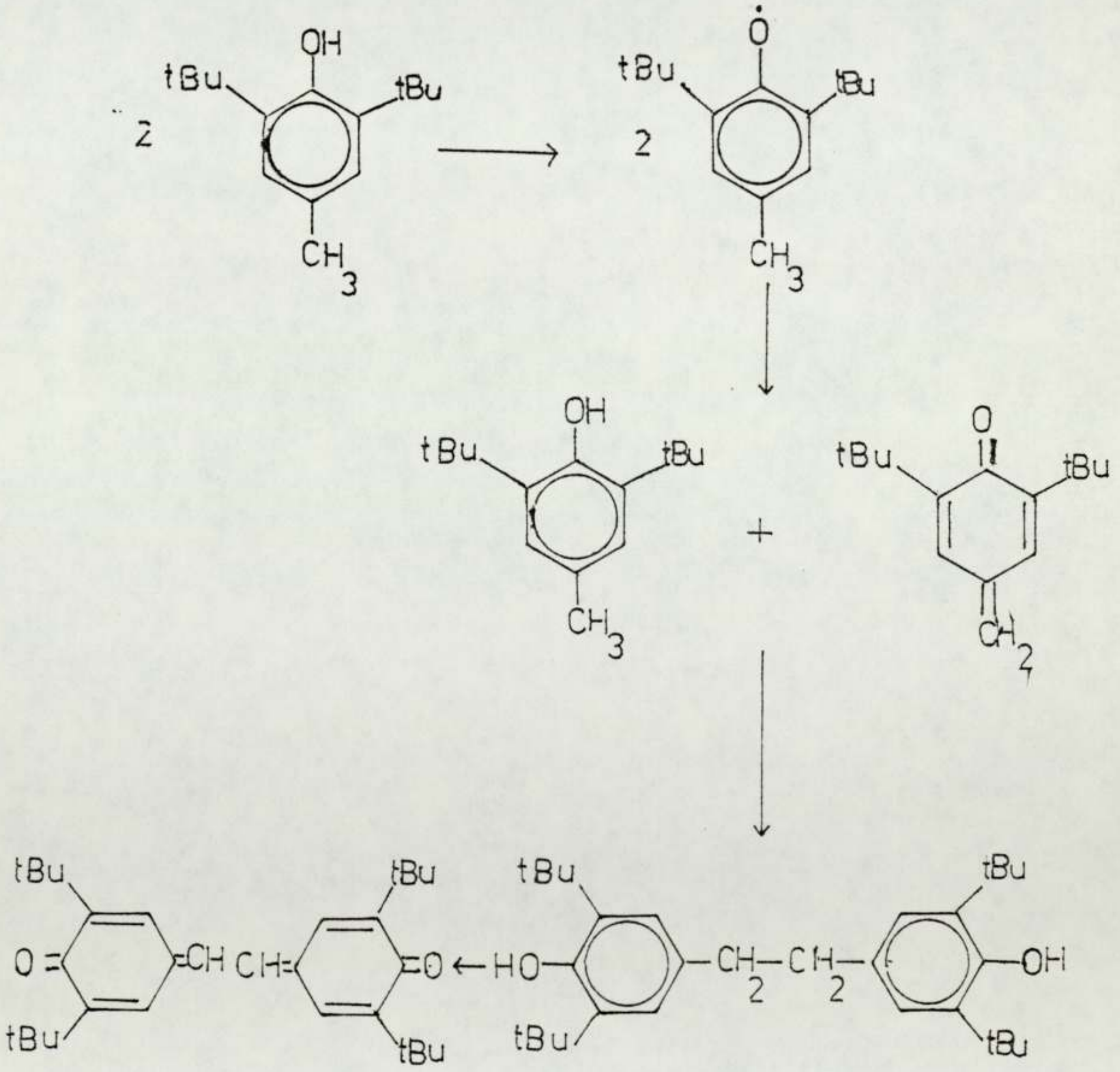
This may be one of the reasons why phenolic antioxidants are comparativly ineffective at high temperatures, whereas sulphides and other antioxidants are effective.

Waters and his co-workers[18-19] have examined the products of the oxidation of phenolic antioxidants by isolating them from the products of cumene oxidation at 80°-100° C, The two main classes of compounds identified were the dibenzyl derivative and the 4-hydroxy ketone.



It was observed by electron spin resonance studies that the primary product of the oxidation of phenol was an aryloxy radical. There was evidence that the ortho-tert-alkyl group has a marked stabilising effect upon the primary phenoxy radical in the absence of oxygen and on the subsequent electron transefer reaction involved dimerisation or disproportionation reaction.[21-22]

Waters[19] has pointed out that unlike the ortho and para positions in the benzene nucleus, the para - -methylenic position is not conjugated with the unpaired electron and he has proposed that the hydroxybenzyl radical must be an intermediate possibly by direct oxidation of the methyl group. Becconsal, et, al[21] have identified stilbene quinone as the major product of oxidation of (2-6-di-tert-butyl-4-methyl)phenol and have suggested that p-quinone methide is an intermediate. Filar[23] attempted to prepare quinone methide by the oxidation of tert-butyl cresol, but ended up with stilbene quinone.



1.2.1 The need for persistant antioxidant system

Three factors affect antioxidant performance in a polymer.[1, 24] The first is the intrinsic activity of the antioxidant functional group on molar basis. The second factor is the compatability or solubility and possibly the ease of migration of the antioxidant. The last factor is the rate of loss of antioxidant through the process of volatilisation, extraction etc.

As a result of rapid migration and volatility, physical loss of antioxidants may reduce the efficiency of the stabiliser system causing deterioration of the polymer. Under aggressive environments and particulary in high surface area to volume sample, these two factors decide the service life of the finished articles. Several approaches have been made during recent years to overcome this problem. Some of these are,

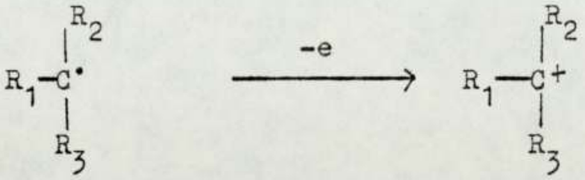
1. The use of high molecular weight antioxidants.
2. The chemical binding of an antioxidant to the base polymer during compounding or vulcanisation.
3. Chemical modification of the base polymer so that a suitable antioxidant can be bound through reactive fuctional group.
4. The chemical binding of an antioxidant to the base polymer before vulcanisation.

1.2.2 Macromolecular Antioxidant

In recent years, experiments have been carried out on polymeric antioxidants, mainly centered on vinyl based antioxidants. These antioxidants were incorporated in to the existing polymer by copolymerisation procedure using a suitable free radical initiator or by adding polymerised antioxidants.

Since chain breaking antioxidants function as free radical scavengers, they must be expected to prevent polymerisation by a free radical initiator. In fact initial attempts to co-polymerised monomers having antioxidant substituents failed. However, using highly purified monomeric antioxidants, fewer problems were encountered in free radical initiated polymerisation. Ladd[25] has reported that the co- polymerisation of phenolic substituted monomers in SBR system using 2-2'-azo-bis-isobutyro--nitrile (AIBN) as initiator. Kleiner[26] observed that some monomers, containing sterically hindered phenols, could be co- polymerised with free radical initiators, such as azo compounds and certain organic peroxides. The more commonly used initiators, such as hydroperoxide used in redox systems, benzoyl peroxide and tert-butyl peroxide, were reported not to initiate polymerisation, because the aryloxy and alkoxy radicals preferentially abstracted the hydrogen from the antioxidant substituents of the monomer, instead of initiating the polymerisation. The reactivity of azo compounds and unreactivity of some peroxides were explained by Scott[27], as follows.

Azo compounds on decomposition, form resonance stabilised radicals, which tend to be stabilised by oxidation.



$$R_1R_2R_3C^{\bullet} \xrightarrow{-e} R_1R_2R_3C^{+}$$

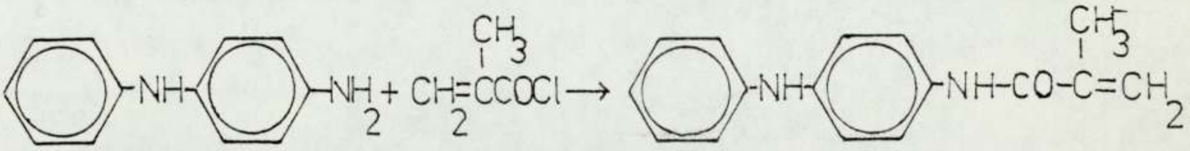
These radicals would therefore, initiate the polymerisation of monomers, rather than abstract a hydrogen from hindered phenols, The more powerfully oxidising free radicals such as , hydroxy, alkoxy, and benzoyloxy are stabilised by reductive processes.

$$RO^{\bullet} + e \longrightarrow RO^-$$

This principal accounts for the high reactivity of phenols and amines etc, as reducing agents towards alkoxy and alkyl peroxy radicals and of quinones, and nitro aromatic compounds etc, as oxidising agents for alkyl radicals.

Similar observations were made by Kato and co-workers[28] that 2-2'-a zobisisobutyronitrile (AIBN), but not cumene hydroperoxide could be used as an initiator to polymerise styrene, maleic anhydride or methylmethacrylate with a vinyl monomer chemically attached to hindered phenol.

The preparation of monomeric antioxidants was studied by Kliner and Miller[29]. Polymerisable antioxidants of the amine types were prepared by acylation of p-aminodiphenylamine and of p-hydroxidiphenylamine with chloride of - unsaturated acids. For example,



Unsaturated acid chlorides were also used to prepare polymerisable phenolic antioxidants by acylation of 2-6-ditert-butyl hydroquinone, 2-6-ditert-butyl-4-amino phenols, 3-5-di-tert-butyl-4 hydroxy phenyl alkenols and 3-5-ditert-butyl-4-hydroxyphenyl alkylamine.

The antioxidant activities of these compounds were determined by oxygen absorption tests and better ageing resistance was reported. The use of antioxidant monomers to build effective stabilisers with polymers, has particular significance to nitrile rubber. The commonly used antioxidants are readily removed from the nitrile rubber products, especialy oil seals by leaching, volatilisation, and other aggressive conditions. Meyer and co-workers[30] were able to co-polymerise butadiene acrylonitrile and 4-aminophenyl methacrylamide with tert-butyl hydroperoxide -ferrous sulphate initiator system. Differential thermal analysis (DTA) and oxygen absorption tests were used to study the stability of bound antioxidant polymers. It was observed by DTA that the antioxidant bound polymer did not change whether extracted or not, whereas, conventionally stabilised commercial nitrile-butadiene and specially stabilised heat resistance nitrile-butadiene polymer changed dramatically. This was furthur confirmed by oxygen absorption tests. It is clear from the following table , the NBR containing bound antioxidant is far superior to conventionally stabilised polymer.

Oxygen absorption of extracted and non-extracted NBR polymer

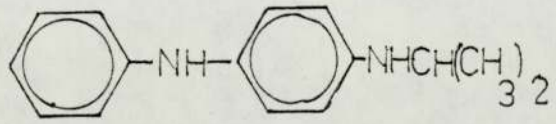
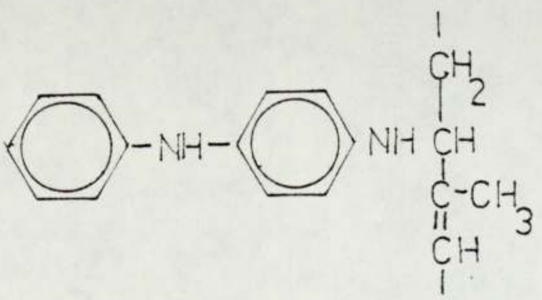
Sample	Non-extracted	Extracted
	Hours to absorbed to 1% O_2	Hours to absorbed 1% O_2
Medium NBR with conventional antioxidant (mixed alkylated diphenylamine)	250	10
Medium NBR with bound antioxidant	675	620

These workers have reported the antioxidant bound rubbers exhibit superior heat/aged resistance at much low level of antioxidant. This clearly distinguishes the advantage of chemically bound antioxidant with polymers.

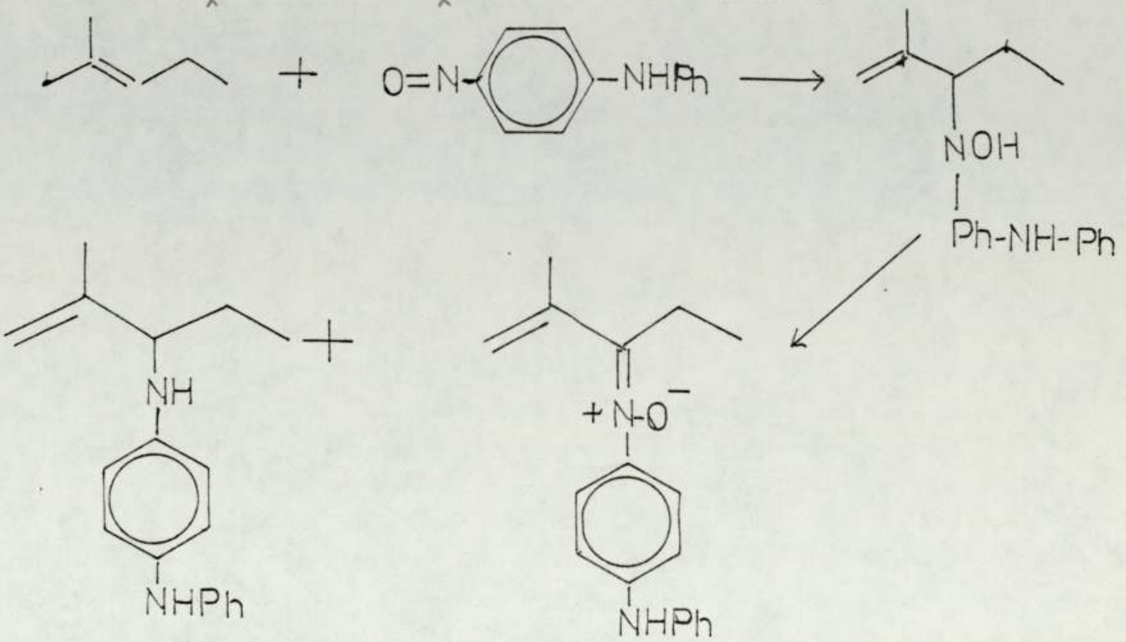
1.2.3 Rubber Bound Antioxidants

The logical approach to prevent loss of antioxidants from the rubber article by volatilisation, leaching and other aggressive environmental condition is to attach a suitable antioxidant to the rubber back bone at reactive positions. This could be achieved either by reacting at the latex stage or in solid phase , during compounding or vulcanisation Several attempts to attach antioxidants to rubbers during vulcanisation have been reported. Cain and co-workers[31] were successfull in attaching antioxidants to rubber through the reactive nitroso group. The activity of added conventional Sec-alkyldiphenylamines was lost during solvent extraction, whereas the activity of rubber bound antioxidant was relatively uneffected by solvent extraction. The results were confirmed by oxygen absorption tests.

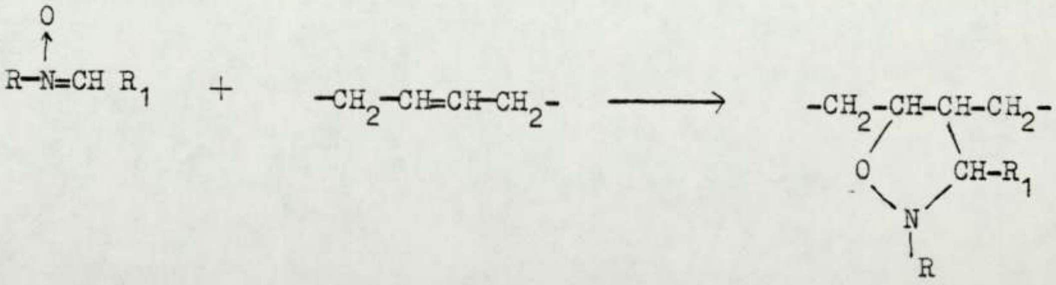
Activity of Sec-alkylaminodiphenyl amine antioxidants

Antioxidant structure	Time to absorb 1/ O_2 at 100°C in hours	
	Before extraction	After extraction
	47	4
	60	53·

The mechanism of the reaction of the nitroso compounds with natural rubber during the vulcanisation process has been studied in model compounds and the mechanism has been shown to be as follows.



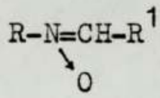
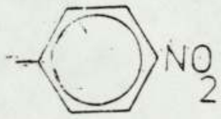
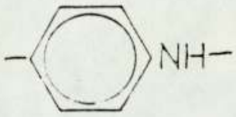
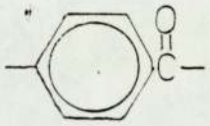
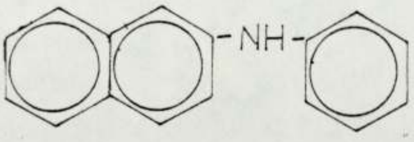
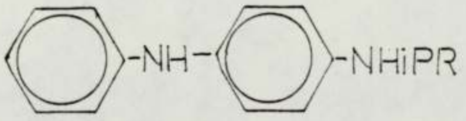
The 1,3cyclo-addition of nitrones to the double bonds in elastomers also provides a general technique for introducing an antioxidant group into rubber molecule. This technique has been successfully applied to cispolybutadiene and cis-polyisoprene during vulcanisation of variety of curing systems[32].



The antioxidant functions were introduced throug R and R_1 groups. The activity of the bound antioxidants were compared with commercial arylamine antioxidants before and after extraction.

Table 1.2

Comparison of nitro-amine bound antioxidants with commercial amine antioxidants (10^{-4}mol/gm) in cis-polyisoprene.

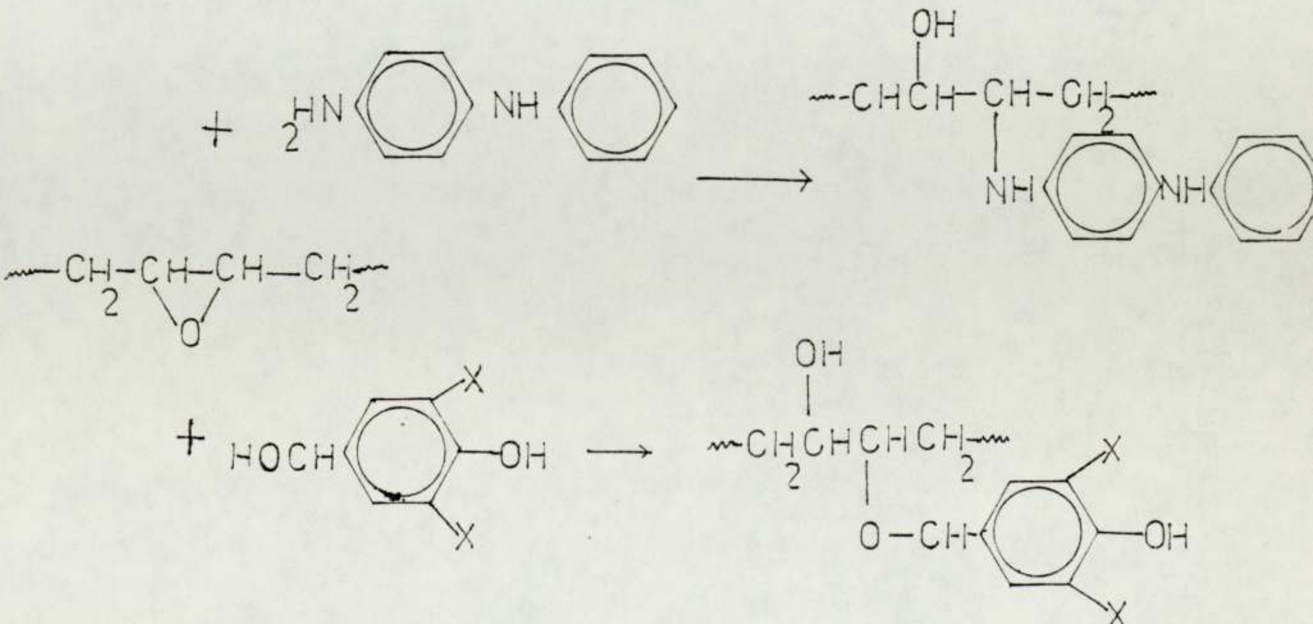
Nitrone  $R-\underset{\searrow O}{N}=CH-R^{1}$		Time to absorb 1/ O_2 at 100°C in hours	
		Unextracted	Extracted
Bound system			
R	R^1		
		30	7.0
		39	5.0
		73	14.0
Conventional antioxidant			
 PBN		63	0.8
		76	1.0
control (no antioxidant)		3.0	0.8

From the above results, it is clear that bound antioxidant systems retain their activity after extraction and show superior effect when compared to conventional antioxidants

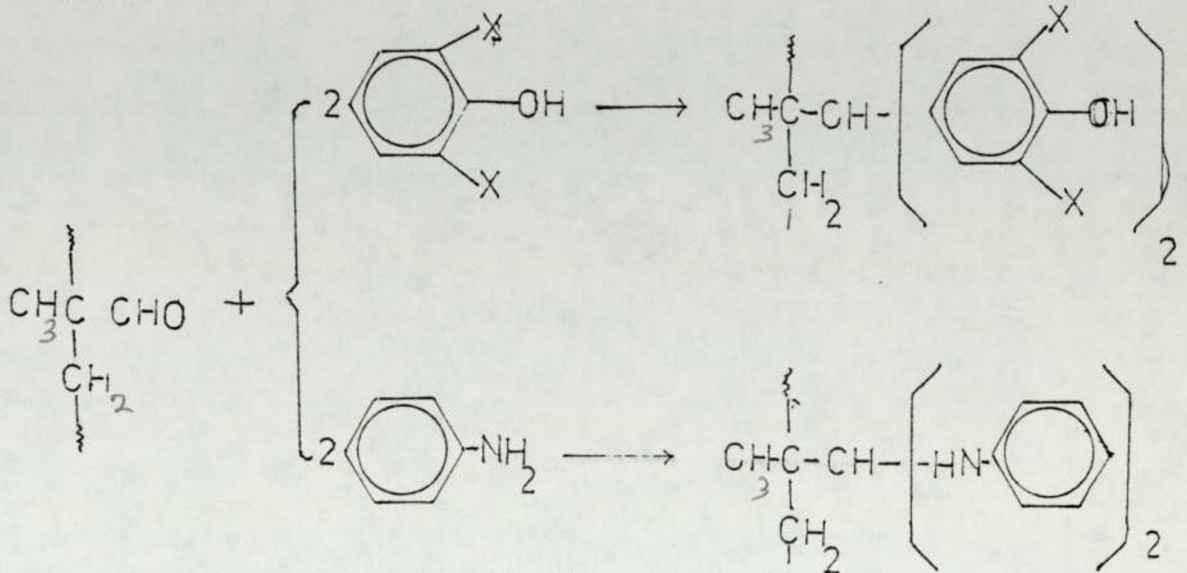
The main disadvantage of the arylamine type antioxidants is that the discolouration of the finished products and this limits its use to black rubber compounds. But hindered phenol nitrones were found to react with rubber during vulcanisation with lower level of discolouration, this again showed superior antioxidant activity to that of conventional antioxidant in isoprene rubber after extraction. Both antioxidant systems affected the vulcanisation characteristic of conventional cis-isoprene vulcanisates, cured with a typical delayed action accelerator, cyclohexylbenzyl sulphenamide (CBS) at 140° C.

1.2.4 Chemical Modification of polymers as a base for antioxidants

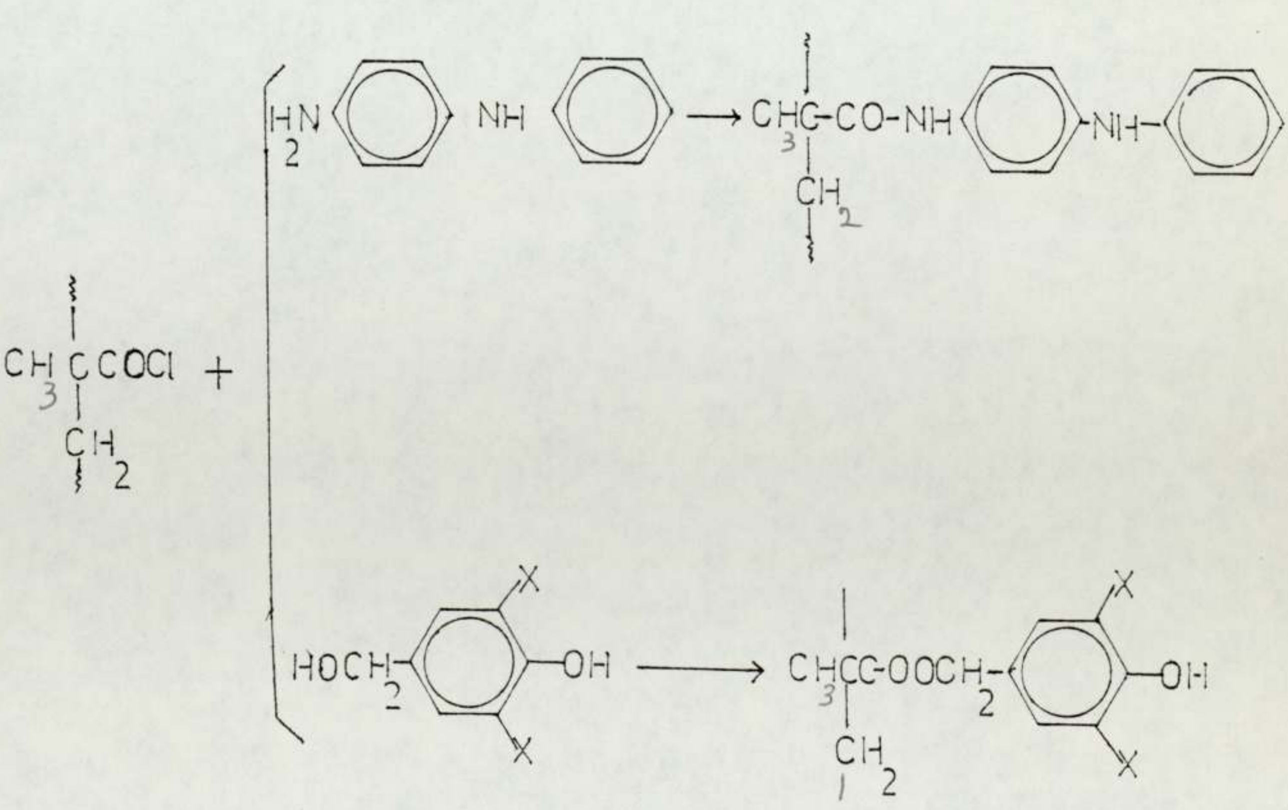
As an alternative method, reactive pendent groups were attached to rubber, sothat they were able to react with substituent groups of the antioxidant. For example, epoxy groups were introduced either by direct epoxidation or by co-polymerising a compound such as glycidyl methacrylate with the rubber. These were then reacted with amines such as p-aminodi-phenylamine or napthylamine and with phenols such as 2-6ditert-butyl-4-hydroxy methyl phenol[33-34].



A similar antioxidant function has been attached to a co-polymer of butadiene and methacrolein by reacting with aniline and 2-6-ditert-butyl phenol[34]



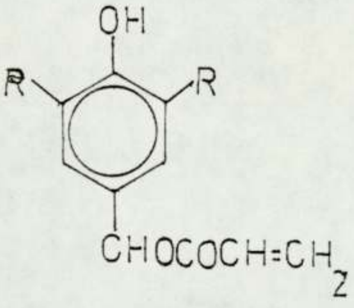
Polymers such as, butadiene/ acrylonitrile and methacrylic acid terpolymer chlorinated and then able to react with amine such as, p-aminodiphenylamine or with substituted phenols such as, 2-6-ditert-butyl -4-hydroximethyl phenol and following polymer bound antioxidants were obtained[35].



The disadvantage of this technique is that the involvement of sequence of reactions, which in fact, may change the physical and chemical properties of the original polymer. Such reaction procedures may be impossible to carry out without deteriorating the existing rubber molecule.

1.2.5 Antioxidant modification of rubber latices

Vinyl antioxidants of the type shown below can be successfullly grafted into the natural rubber molecule in the latex phase[35]. The principal involved is similar to that employed in the grafting of conventional monomers to natural rubber or polybutadiene and by the appropriate choice of redox system a high level of bound antioxidant activity can be acheived.



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

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

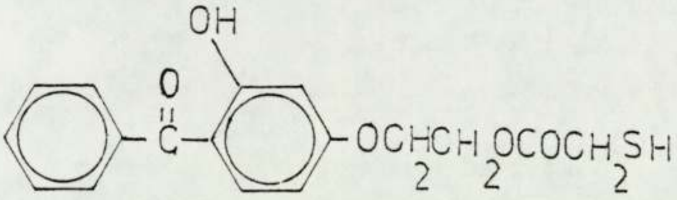
(c) $R_1= R_2=$Me

In ouer to demonstrate that the effect obtained was not due to the formation and binding of a homopolymer of the vinyl antioxidant, poly DBBA was incorporated as a conventional antioxidant. This was found to be relatively ineffective as bound antioxidant.

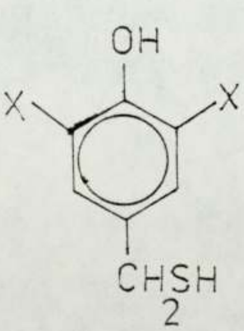
Further more, the oxygen absorption curves of vulcanised and extracted rubber containing known amount of bound DBBA was compared with that of vulcanised rubber containing DBBA as an additive but without extraction. The effectiveness of the two antioxidants was almost identical, indicating that the binding to the rubber back bone has no significant effect on antioxidant mobility . This led to conclusion that reduced mobility of the bound antioxidants does not significantly affect antioxidant behavior. It seems probable that the lateral movement of the polymer chain gives adequate mobility to the rubber bound antioxidant molecule.

Fernando[36] carried out a similar investigation with 3,5-ditert-butyl-4-hydroxybenzyl mercaptan (BHBM) with natural rubber using AZBN as initiator. The main disadvantage of the process developed by him was that chloro benzene used as solvent for AZBN, due to its incompatibility with water, limited its use in latex.

Recent work[37] on ABS bound stabilisers based on thiol (11) and a hydroxybenzophenone (111) U.V stabiliser given below, shows a remarkable effect when compared to conventional antioxidants and U.V stabilisers in ABS.



Hydroxy-benzophenone U.V stabiliser (111)



3,5-ditert-butyl-4phenoxy-benzyl-mercaptan (11)-

The table 1.2 illustrates the superior performances of the thiol adduct (11) and the bound U.V stabiliser (111).

Table 1.2

Comparison of bound stabilisers with conventional stabilisers

Stabiliser	Concentration (g 10^{-2}	U.V degradation(a)		Thermal oxidation (b)	
		Before extraction	After extraction	Before extraction	After extraction
Conventional additives					
Commercial ABS (phosphite stabiliser)	Unknown	26	x	175	x
UV 531	1.0	42	x	20	x
BHT + UV 531	1.5 1.0	66	26	170	40
Rubber bound					
11	1.5	52	50	850	850
111	1.5	56	48	45	30
11 + 111	1.0 1.0	110	108	650	545
11 + 111	1.5 1.0	143	140	850	850
Control (unstabilised ABS)	-	22	x	20	x

x stability essentially that of the unextracted control

(a) embrittlement time (hours)

(b) IP at 100°C in air (hours) {IP = Induction Period)

The superior effects of bound UV stabiliser are due not only to the auto-synergism between a chain breaking antioxidant (phenol) and a peroxide decomposer (sulphide), but that also due to the auto-synergistic effect of a UV absorber (benzophenone) and a peroxide decomposer (sulphide) (111), when present in the rubber molecule. Furthermore, it was shown that these polymers had much superior thermal stability to that of conventional thermally stabilised ABS.

1.3.1 Graft Co-polymers from natural rubber

During last few years research has been carried out to graft polymerised vinyl monomers with natural rubber latex. Successful polymerisations were reported by using water soluble catalysts such as , persulphates or organic hydroperoxide.[38] The grafting of acrylonitrile in natural rubber , with the object of preparing oil resistance rubber, was first investigated by Le Bras and co-workers[39]. They observed that tha polymerisation was retarded by ammonia. Much later this was overcome by using a different catalyst system normally a hydroperoxide activated by an activator such as , polyethylene polyamine[40].(PETA)

There are three main types of radical intermediates in the system of vinyl monomer, natural rubber latex co-polymerisation;

1). those derived from initiator ,denoted $I^{\bullet}$,

2). those produced by the polymerisation of monomer ,that is polymer radicle $M_n^{\bullet}$ and

3). those derived from the rubber molecule RH, H indicates a labile hydrogen atom.

Two ways of interaction can produce rubber radicals;

A. Addition of radical to the double bond in RH

$$I^{\bullet} + RH \longrightarrow I\text{-}\dot{R}H$$

$$M_n^{\bullet} + RH \longrightarrow M_n\text{-}\dot{R}H$$

B. Removal of hydrogen atom from RH

$$I^{\bullet} + RH \longrightarrow IH + R^{\bullet}$$

$$M_n^{\bullet} + RH \longrightarrow M_n\text{-}H + R^{\bullet}$$

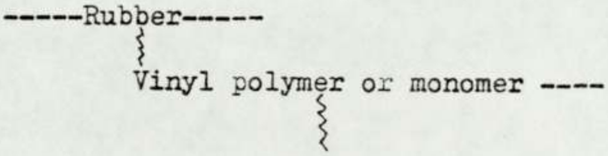
The newly formed free radical centers on the rubber molecule may react either with a monomer radical or with a polymer radical.

$$\text{I -}\dot{\text{R}}\text{H} \xrightarrow{\text{monomer or polymer radical}} \text{I-RH-M}_n$$

$$\text{M}_n\text{-}\dot{\text{R}}\text{H} \xrightarrow{\text{monomer}} \text{M}_n\text{-RH -M}_n$$

$$\text{R}^{\bullet} \xrightarrow{\text{polymer radical}} \text{R -M}_n$$

All these reactions lead finally to a compound in which the vinyl polymer chains are chemically bound to rubber. The basic structure may be represented as,



The properties of these grafted co-polymers depend on (a) the type of the monomer (b) the length of polymer chains (c) the number of polymer chains per rubber molecule.

Bacon and co-workers[41] have successfully co-polymerised common vinyl monomers with natural rubber latex, using tert-butyl hydroperoxide and polyamine activator. The hydroperoxide was dissolved in the monomer and was then added with stirring to a diluted latex containing stabiliser. The activator, polyamine ,usually polytetraethylene pentamine was added after completion of the dispersion, because it was necessary to allow monomer to diffuse into the rubber particles, The polymerisation was completed with in a few hours at room temperature.

Another technique developed by Sekhar[42] involved the use of catalyst formed in the rubber in situ, the latex was aerated by rotating a half filled container for few days , and the product found to be able to initiate polymerisation of a range of monomers, without the addition of hydroperoxide, but in the presence of small amount of ferrous ion or polyamine activator. He considered that the reactive sites were formed on the rubber molecules, probably being hydroperoxide in nature.

1.3.2 Redox initiators used in Emulsion Polymerisation

Redox initiators are mainly used in emulsion polymerisation of vinyl monomers. The essential feature of the components constituting redox pair for aqueous polymerisation is their stability in water and a fairly fast, steady liberation of active radicals in the aqueous phase. Redox initiators can be classified into five catogaries, a) Peroxide systems b) Peroxidisulphate systems c) Redox pair involving metal ions d. Miscellaneous redox systems e) Electrochemical initiation.

1.3.3 Peroxide systems

The simplest water soluble peroxide is hydrogen peroxide and classical redox pair containing this substance is Fentons Reagent[43-45] - This has been used by Bendal at al, in the polymerisation of methylmethacrylate, methyl acrylate and acrylonitrile. Usually an effective redox system contains a reducing agent, which cleaves the O-O bond of the peroxide into its radicals

$$M^{2+} + \text{R-O-O-H} \longrightarrow M^{3+} + RO^{\bullet} + OH^{-}$$

Other than metal ions, some polyamines are used as reducing activators to cleave the peroxide at lower temperatures. These amine activated peroxides are effective in polymerisation of monomers at low temperatures. It has been shown[46] that the essential features of polyamine activators are 1) the presence of amino groups of different degree of substitution in the amine molecule for example, primary and secondary amino groups or primary or tertiary amino groups, 2) separation of amino group by not more than two carbon atoms. The most common polyamine used in emulsion polymerisation of vinyl monomers is poly-tetra-ethylene-pentamine (PETA).

$$NH_2(CH_2-CH_2-NH-CH_2-CH_2-NH)_2$$

1.3.4 Peroxidisulphate system

Peroxydisulphates form powerfull redox initiators in combination with one of the metal ions such as , Ag^+, Fe^{2+}, Cu^{2+}, Ti^{3+},; complex ions such as, ferricyanides, cobalt complexes; various reducing agents such as hydrazine, hydroxylamine, hydrogen sulphide, thiols; salts of various oxy acids of sulphur and polyhydric phenols[49-52]. All the redox pairs of the above type probably first form a complex, either with monomers or other constituents and then breaks into its component initiating radicals. For instance, Cu^{2+} used in polymerisation of acrylonitrile, first involves reduction to Cu^+ by monomer, and then dissociating into its radical species[53].

$$Cu^+ + S_2O_8^{-2} \longrightarrow Cu^{2+} + SO_4^{-2} + {}^{\bullet}SO_4^-$$

A similar mechanism probably holds for other metal ions. Regarding the peroxidisulphate, oxyacids of sulphur combination[51], a good deal of attention has been directed to the redox pair $S_2O_8^{-2}$ and $S_2O_4^{-2}$. It was found by tracer technique that polytetrafloroethylene made using this initiator contains sulphur as a nonhydrolysable end group. Studies using a dye technique in the presence of methyl methacrylate as monomer ,showed the presence of both hydrolysable sulfate and non hydrolysable sulphonate end groups. The initiation mechanism proposed was similar to the Haber Weiss type reaction.

$$S_2O_8^{-2} + HSO_3^- \longrightarrow SO_4^{-2} + {}^\bullet SO_4^- + H\dot{S}O_3$$

In the case of peroxidisulphate alone complexing should be by water molecules, and this probably accounts for the extensive occurence of hydroxyl end groups in polymers in the presence of the catalyst.

$$S_2O_8^{-2} + H_2O \longrightarrow (S_2O_8^{-2}.\,H_2O) \longrightarrow HSO_3^- + {}^\bullet OH + {}^\bullet SO_4^-$$

1.3.5 Redox pair involving metal ions

The initiating radicals are formed only in the presence of suitable metal ions. One such example, is the polymerisation of acrylamide in the presence of ceric salts such as sulphate and nitrate in combination with alcohols, glycols, aldehyde or amine as reducing agents[54]. The suggested mechanism is given below.

$$Ce^{4+} + A \longrightarrow B \longrightarrow Ce^{3+} + {}^\bullet R + H^+ \xrightarrow{M} R\dot{M} \text{ etc}$$

Where A is the alcohol molecule, B an alcoholic ion complex, R the free radical formed and M is the monomer. Similary manganic (3+) pyrophosphate in conjuction with glycols, aldehyde , ketones, carboxylic acids and phenols[55] used as initiators in the polymerisation of vinyl monomers.

Coopers[56] studies showed that methyl methacrylate can be polymerised using diazonium compounds such as p-nitrobenzene diazonium p-chlorobenzene sulfonate and metal ions such as Fe^{2+}

$$RN_2^+ \quad + \quad Fe^{2+} \longrightarrow RN_2^{\bullet} \quad + \quad Fe^{3+}$$

$$\dot{R}N_2 \longrightarrow R^{\bullet} \quad + \quad N_2$$

$$\dot{R}N_2 \quad \text{or} \quad R^{\bullet} \quad + \quad M \longrightarrow \dot{R}N_2M \quad \text{or} \quad RM^{\bullet}$$

Where RN_2 is the diazonium salt and M is the monomer.
Menon and Kapur[56] were successful in polymerising methylmethacrylate in the presence of oxygen. The initiator used was Cu^{2+}-hydrazine hydrate. They suggested that the hydrazine was oxidised by Cu^{2+} to $\dot{N}_2H_3$ radical, which initiated the polymerisation and then the molecular oxygen reoxidised Cu^+ to Cu^{2+}

$$N_2H_4 \quad + \quad Cu^{2+} \longrightarrow \dot{N}_2H_3 \quad + \quad Cu^+ \quad + \quad H^+$$

1.3.6 Miscellaneous Redox systems

Enzymatic redox pair initiated aqueous polymerisation has been reported by Ferrano[58] and shown that xanthane oxidase (XO) in the presence of formaldehyde, initiated the polymerisation of methyl methacrylate (M). The reaction was completely inhibited by the traces of oxygen.

$$XO \quad + \quad CH_2(OH)_2 \longrightarrow XOH \quad + CH_2(OH)O^{\bullet}$$

$$XOH \quad + \quad M \longrightarrow XO \quad + \quad HM^{\bullet}$$

$$CH_2(OH)O^{\bullet} \quad + \quad M \longrightarrow HCOOH \quad + \quad HM^{\bullet}$$

Other complex system of initiators, which have been used are $NaClO_3$-Na_2SO_3 redox pair in acid[59], for the polymerisation of acrylonitrile and acrylamide, $KMnO_4$-oxalic acid redox pair for vinyl monomer polymerisation.

In the second system, end group analysis showed that the presence of carboxyl-ic end groups. The polymerisation took place even after the disappearance of Mn^{3+} ions, which was attributed to the formation of a fairly stable complex containing the oxalic acid radical that would act as a steady source of initiating radical.

1.3.7 Electrochemical Initiation

Kolthoff[60] polymerised acrylonitrile in poor yield by partial electrolytic reduction of $S_2O_8^{2-}$, hydrogen peroxide and cumene hydroperoxide, However, in the presence of Fe^{3+} ions, high yield of polymerisation taken place, possibly because of the generation of Fe^{2+} by electrolitic reduction, which then formed a redox pair with H_2O_2, $S_2O_8^{-2}$ or cumene hydroperoxide. Vinyl acetate, vinyl chloride and methyl methacrylate were polymerised at the anode by Smith at al,[61] using Kolbe,s process. They suggested the formation of initiating radicals such as methyl and acetoxy radicals during electrolysis. Initiation at the cathode is comparatively easier than at the anode due to the presence of oxygen at the anode particularly in aqueous medium.

Object and Scope of the present work

One of the main objectives of the polymer industry in recent years has been to establish better quality products with long service life. As discussed in the last chapter this can be achieved either by incorporating polymeric antioxidants or modification of the polymer to produce bound antioxidants.

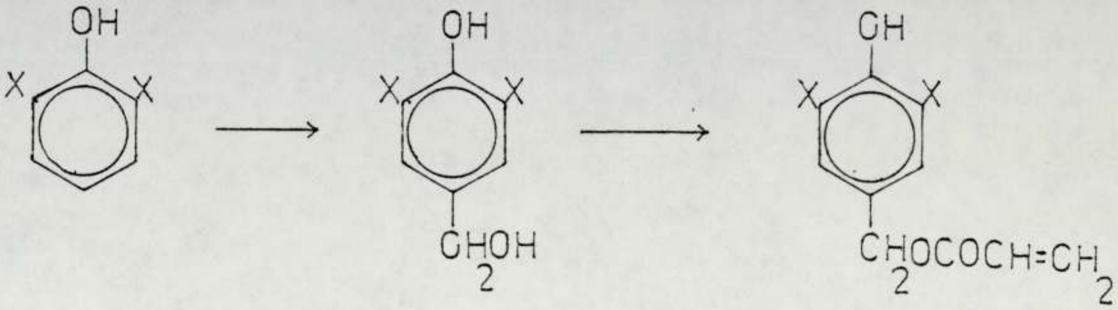
In the latex industry most of the rubber products lose their oxidative stability during their service life resulting in poor physical properties. The possibility of reacting an antioxidant with the preformed polymer in the latex stage is therefore of considerable practical interest to the producers and the users of rubber latex. Scott and co-workers were successfull in grafting antioxidants to natural rubber latex and the present work is a continuation of the work done by Amarapathy[35] and Fernando[36] on this topic. This study is concerned with the chemistry of the antioxidant binding process and with the antioxidant behavior of the rubber-bound antioxidants in technological systems.

The final object is to investigate the effect of similar bound antioxidants in synthetic rubber latex, such as, nitrile-butadiene rubber and styrene-butadiene latex. NBR latex is used for the production of dipped goods, rubber threads, foam rubber, binding of textile fibers in the production of non-woven fabric of all types requiring good resistance to ageing and solvents; It is also used in the binding of mineral fibers for example, asbestos in the production of seals, couplings and brake linings, impregnation , proofing and lamination of fabrics, production of can sealing components and oil seals. One of the main drawbacks of these products is their poor performances under the service ageing condition found in practice and this results in poor physical properties and short service life. Grafting a suitable antioxidant to NBR latices, should increase the service life of such finished products.

CHAPTER TWO

SYNTHESIS OF ANTIOXIDANTS

2.1.1 3,5 - Ditert - butyl - 4 - hydroxy - benzyl acrylate



The method used in the preparation was the one described by the Shell International Research(63-65)

53.3 mls (0.140 moles) of formaldehyde (7.5% solution of formaldehyde in tertiary-butyl alcohol), 50 mls (0.128 moles) of 2,6-ditertiary-butyl phenol (500 gms in 1000 mls of tertiary-butyl alcohol) and 14 mls of potassium tertiary-butoxide (50 gms in 1000 mls of tertiary-butyl alcohol) were mixed at 20° C and stirred under nitrogen atmosphere for twenty minutes.

The mixture was then poured into excess of ice-water and two layers were formed. The solid formed was filtered, stirred with n hexane and then filtered. The product was rewashed till the reddish colour disappeared and white crystalline solid was obtained if M. P 137°C.

I.R data

Free phenolic OH	3620 cm^{-1}
Hydrogen bonded OH	3500 cm^{-1}

N.M.R. data (Scl$_4$)

Aromatic protons	2.9 τ singlet
Phenolic protons	4.9 τ singlet
Methylene protons	6.4 τ singlet
Tert butyl protons	8.8 τ singlet

Mass Spectrum shows a parent peak at 236.

2.1.1.1 3,5 - Ditertiary - butyl - 4 - hydroxy benzyl alcohol with acrylic acid(60-63)

A mixture of 47.2 gms (0.2 mole) of 3,5 ditert butyl-4-hydroxy benzyl alcohol and 130 mls of acrylic acid was warmed gently in a steam bath until it was dissolved completely. Then 10 mls more of acrylic acid, containing a drop of conc. Sulphuric acid was added. The reaction was carried out for 6 hours and was then poured into water.

The organic phase was extracted with ether and the remaining acrylic acid was removed from the organic phase with aqueous sodium bicarbonate. The ether layer was dried over anhydrous magnesium sulphate, filtered and was then evaporated. The residue was recrystallised from 30°-40° petroleum ether gave yellow powder. M.P. 67-69°C.

Yield 18.0 gms

Mass Spectrum data - parent peak at 290

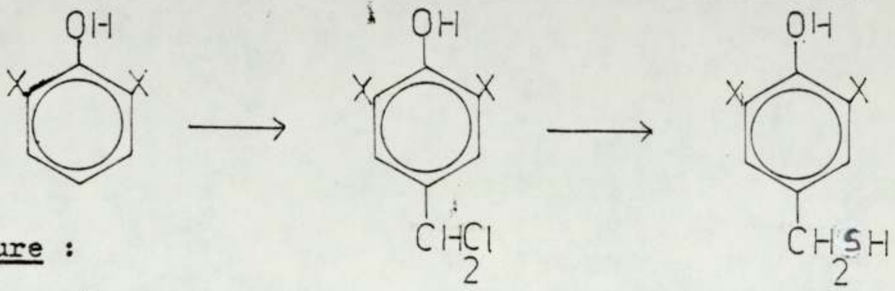
I.R data

Free phenolic OH	3620 cm^{-1}
Ester carbonyl	1710 cm^{-1}
Vinyl double bond	1640 cm^{-1}

N.M.R. data

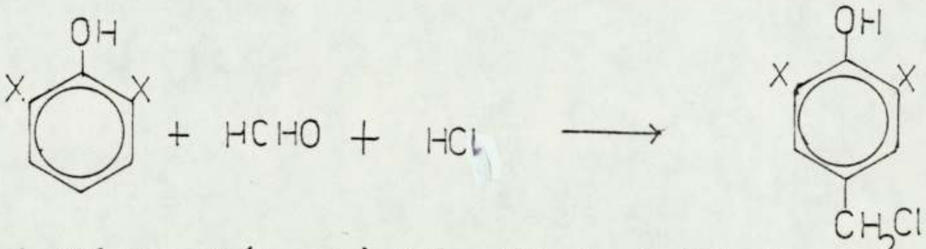
Aromatic protons	- 2.9	τ	singlet
Vinyl hydrogens	- 3.6 - 4.5	τ	multiplet
Phenolic protons	- 5.0	τ	singlet
Tertiary butyl protons	- 8.6	τ	singlet
Methylene protons	- 6.3	τ	singlet

2.1.2 3 - 5 Ditert - butyl, -4- hydroxy benzyl mercaptan



Procedure :

i) 3 - 5 - ditert - butyl - 4 - hydroxy benzyl chloride



206 gms of (1 mole) 2,6 - ditert - butyl phenol was taken in a 1 litre round bottom flask and 120 gms of paraformaldehyde was added to it. 500 ml of 35 - 36 % hydrochloric acid was poured in and the mixture was stirred vigorously using a fast rotating electric motor. Dry hydrogen chloride gas was bubbled into the mixture for a period of seven days at a rate so that the escape of unreacted HCl kept to a minimum. Then the reaction was left for 15 hours and HCl gas was again passed for another two hours. During this time the colour of the mixture became orange and was found to be carcinogen. The mixture was allowed to settle, the oily layer was seperated, and then repeatedly washed with distilled water. Ether was added to it and was again washed with 2% sodium bicarbonate followed by distilled water to remove free HCl acid. Then the mixture was dried over anhydrous sodium

sulphate and the solvents were removed on a rotatory evaporator. This was further purified by vacuum distillation and the fraction boiled, at 128 - 130°C at 1.5 - 2.0 mm pressure was collected.

Yield 70 % .

I. R. data

Phenolic OH	3620 cm^{-1}

Mass spectrum

peaks at 254 and 219

N.M.R. data

Aromatic protons	3.0 τ	singlet
Hydroxyl protons	5.03 τ	singlet
Methylinic proton (CH_2Cl)	6.40 τ	singlet
Tert butyl protons	8.6 τ	singlet

2.1.2.1 ii) 3 - 5 - ditert - butyl - 4 - hydroxy benzyl mercaptan

5.8 gms of magnesium hydroxide powder was taken in a 500 ml round bottomed flask and 200 ml of N,N dimethyl formamide was added to it. Hydrogen sulphide gas was passed into the mixture for 30 minutes while it was stirring. 22.5 gms of 3,5 ditert - butyl - 4 - hydroxy benzyl chloride was dissolved in 50 ml of technical grade hexane fraction and was added slowly to the mixture. At this stage the rate of addition was controlled to prevent yellow coloured sulphides. The mixture was allowed to stand for 90 minutes and was added into ice cooled water. The organic layer was separated by ether extraction , dried over magnesium sulphate and was then concentrated. The product was vacuum distilled and the fraction distilled at 128 - 131°C at 1.0 mm pressure was collected.

M. P. 28°C Yield 64.0 %

Spectral Analysis

I. R. data

Phenolic OH	3620 cm^{-1}
Thiol (SH)	2560 cm^{-1}

Mass Spectrum

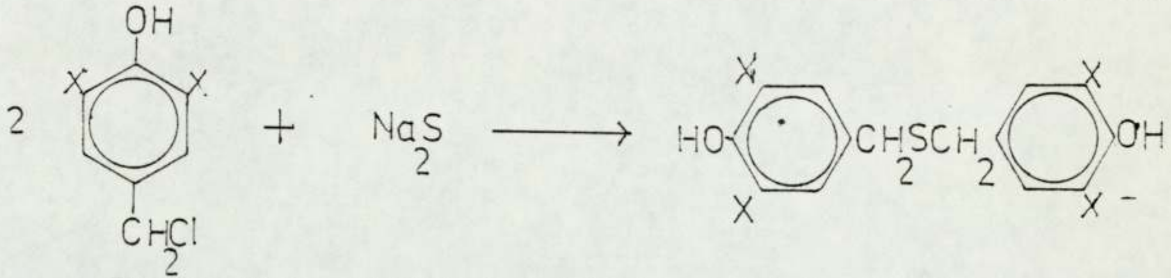
Parent peak appeared at 252 and 219

N.M.R. data

Aromatic protons	2.96 τ	singlet
Phenolic protons	4.9 τ	singlet
Methylenic protons	6.4 τ	doublet
Tert - butyl protons	8.6 τ	singlet

Peak for - S - H - interfere with Tert butyl protons

2.1.3 Bis (3,5 - Ditertiary - butyl -4- hydroxy benzyl monosulphides 68



The starting material 3,5 ditertiary butyl - 4 - hydroxy benzyl chloride was prepared as described in section 2·1·2. In a reaction vessel equipped with a heater, thermometer, water cooled condenser and a stirrer, a mixture of 19.2 gms of sodium sulphide was dissolved in 15.0 ml of water, 120 ml of isopropyl alcohol, and 50 gms of 3,5 ditert - butyl -4- hydroxy benzyl chloride was refluxed for a period of two hours. The mixture was allowed to stand for 48 hours, solids were filtered, washed with water and dried. The product was recrystallized with iso-octane and methanol and yellow product was obtained. M. P. 142°C -

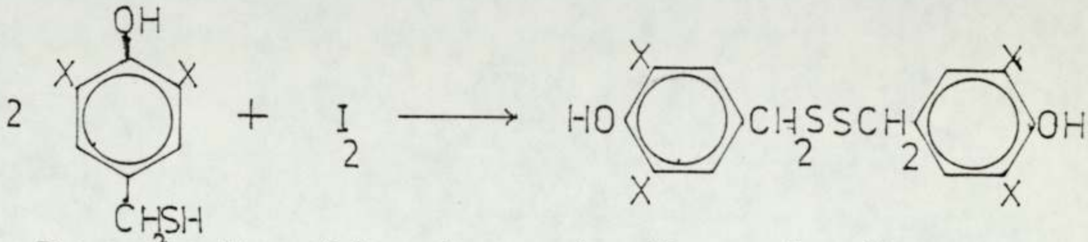
I. R. analysis

Phenolic OH	3640 cm^{-1}

N.M.R. analysis

Tert butyl protons	8.6 τ singlet
Phenolic protons	5.0 τ singlet
Aromatic protons	2.9 τ singlet
Methylinic protons	6.4 τ singlet

2.1.4 Synthesis of bis(3 , 5-ditert butyl - 4 - hydroxy benzyl di sulphide 69



The preparation of benzyl mercaptan discussed earlier . A mixture of 25.3 gms of 3,5-ditert - 4 - hydroxy benzyl mercaptan, 100 ml of benzene and 25 ml of water was shaken vigorously in a round bottomed flask and a solution of 25.4 gms of iodine, 100 mls of benzene and 25 mls of ethanol was slowly added from a dropping funnel. When the colour of the solution turned slight brown, addition of iodine was stopped, and the organic layer was separated, dried over magnesium sulphate and was then concentrated. The solid obtained was recrystallized with benzene and petroleum ether and light crystals of M.P. 168°C was obtained.

I.R. data

Phenolic OH	3620 cm^{-1}

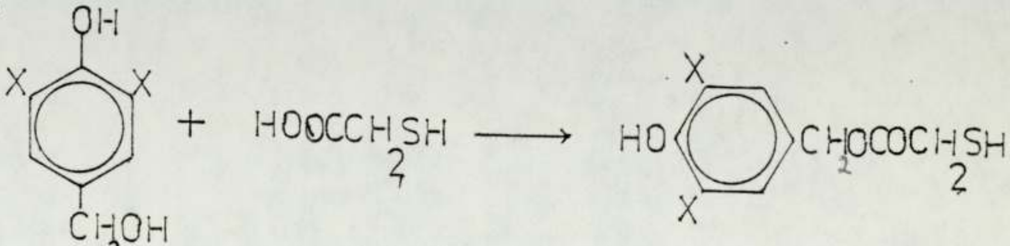
Mass spectram

peaks appeared at 502, 251, 219.

N.M.R. data

Tert-butyl protons	8.6	τ	singlet
Phenolic protons	5.0	τ	singlet
Aromatic protons	2.93	τ	singlet
Methlenic protons	6.4	τ	singlet

2.1.5 3, 5-ditert butyl - 4 - hydroxy benzyl - thiol glycolic ester



A mixture of 47.2 gms of (0.2M) of 3,5-ditert - butyl - 4 - hydroxy benzyl alcohol and 15 gms of (0.2M) of thiol glycolic acid was dissolved in toluene. The mixture was poured into a round bottomed flask, filled with a reflux condenser with a side tube to collect the water produced during the reaction. Temperature of the mixture was maintained at 100°C. To the above mixture, 5 ml of thiol glycolic acid containing one drop of concentrated sulphuric acid was added. The solution was allowed to reflux for 8 hours and was allowed to cool.

The organic phase was extracted with ether and the excess acid was removed by washing with distilled water followed by aqueous sodium bicarbonate solution. The organic phase was dried over anhydrous magnesium sulphate and the filtrate was evaporated. A white solid powder was obtained. M. P. 78°C Yield 95 % .

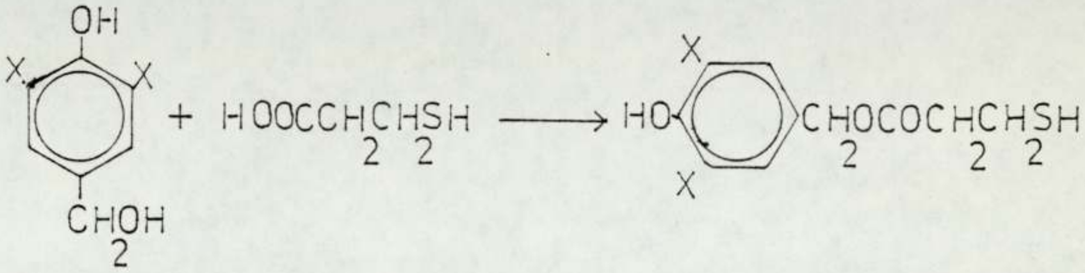
I. R. data

Phenolic OH	3620 cm^{-1}
Thiol - S - H	2560 cm^{-1}
Ester carbonyl	1710 cm^{-1}

N.M.R. data

Methylenic protons attached to ester function and thiol	6.2	τ	doublet
Methylenic protons	5.9	τ	singlet
Aromatic protons	2.9	τ	singlet
Phenolic protons	5.0	τ	singlet
Tert - butyl protons	8.7	τ	singlet

2.1.6 Synthesis of 3 , 5-ditert - butyl - 4 - hydroxy benzyl - thiol propionic ester



3 , 5 - ditert - butyl - 4 - hydroxy benzyl alcohol was used as an original reactant with thiol propionic ester. The rest of the procedure is very similar to the last experiment .

Yield obtained was 94 % - M. P. 89°C

I. R. data

Phenolic OH	3620 cm^{-1}
Thiol S - H	2570 cm^{-1}
Ester carbonyl	1700 cm^{-1}

N.M.R. data

Tert - butyl protons	8.7	τ	singlet
$-CH_2$ attached to SH	7.2	τ	multiplet
$-CH_2$ attached to C=O	6.8	τ	triplet
Methylenic protons attached to benzene ring	5.9	τ	singlet
Phenolic proton	5.2	τ	singlet
Aromatic proton	2.9	τ	singlet

2.2 Experimental Techniques

Materials :

Natural rubber latex -

The natural rubber latex used in the experiments were supplied by W. M. Symington and Sons Ltd. (Qualition A) Total solid content 60 % by weight and was preserved by 0.7 % of ammonia.

Prevulcanized latex -

60 % ammonia preserved prevulcanized latex was supplied by Reverton Ltd.

Perbunan N latex - (Nitrile - butadiene latex)

This was supplied by Bayer UK limited. Total solid contents 50 % by weight.

Perbunan N latex 3310 - without reactive group

Perbunan N latex 3415 - contains reactive group.

Monomerless - nitrile butadiene latex was supplied by Revertex Ltd . Solid content 50 % and contains a cross linking agent -

Compounding Ingredients and Antioxidants

N Cyclohexybenzylthiozole-2sulphenamide (CBS) Monsanto chemical Limited

Sulphur - Anchor chemical Limited

Zinc oxide - Amalgamated oxide limited

Dispersol LN - Imperial Chemical Industry

Tetra methyl thiuram disulphide (TMTD) supplied by Monsanto Chemicals

2,6 - ditertiary - butyl - 4 - methyl - phenol

Topand O.C and Nonox WSP - supplied by Imperial Chemical Industry.

Tert butyl hydroperoxide 70 % (Koch Light Laboratories Limited)

Tetra ethylene pentamine - BDH Technical grade

2.2.1 Preparation of Rubber Vulcanizates

The vulcanizates were prepared from antioxidant - bound natural rubber or from natural rubber itself. The latex reacted or unreacted was coagulated with 1 % formic acid and was thoroughly washed with water to remove acid. This was then sheeted in to a thin sheet and was washed again. The sample was dried and was wrapped with aluminium foil.

The sample was extracted continuously for 48 hours under nitrogen atmosphere to remove the unreacted antioxidants and the other organic biproducts. The azeotropic mixture used for extraction consists of 1,1,1 trichloroethane (60 ml), acetone (110ml) and methanol (42 ml) The temperature of extraction varied between 50°- 60° C. After the extraction the rubber was dried under vaccum dessicator at 20°C in the dark until required.

2.2.1.2 Compounding

The compounding ingredients were mixed with extracted natural rubber on a 12 inch water cooled laboratory 2 roll mill. A fraction - ratio of 1:1 was employed . If sulphur was included in the formation then this was added after all the other ingredients had been incorporated. Compounds were prepared according to the formation given in table 2.2.1, the total compounding time was 5 minutes.

Table 2.2.1 Compound formation

Natural rubber	100 gms
Zinc oxide	5 gms
Stearic acid	3 gms
Sulphur	2.5 gms
CBS	0.5 gms

2.2.1.3 Vulcanization of Compounds

Vulcanizates were prepared in a stainless steel mould of cavity dimensions 13.5 x 13.5 x 0.018 cm so as to produce a sheet of thickness 0.018 - 0.023 cm. A sample of compound (5 gms) was milled into a thin sheet and placed in the mould cavity. The mould was placed between two plates of a steam heated press, the temperature of which had been previously raised to the required temperature 140°C. A pressure of 50 tons on a 8 inch ram was applied to produce the required sheet thickness.

At the end of 1/2 an hour cure time, the mould was removed and quenched in cold water. The vulcanized sheet was removed, dried and was stored in a vaccum desicator. The sample was cut from the centre to eliminate edge effects.

Preparation of films from vulcanized latex will be discussed in a later chapter. These films were used in Tensile measurements, stress relaxation tests and oxygen absorption tests.

2.3 Technological Ageing Tests

The important factors, which determine the effectiveness of antioxidants in rubbers are,

a) Antioxidant activity
b) Rate of loss of antioxidants from polymer
c) The mobility of the antioxidant within the polymer

The assessment of antioxidant activity of bound and unbound antioxidants, were determined by oxygen absorption tests, on both extracted and unextracted samples so that the antioxidant ability of the bound antioxidant could be assessed. Stress relaxation measurements were carried out to assess the other two factors. The determination of Tensile properties of films at various states of oxidation can be carried out as an important test, which determines the effectiveness of bound - antioxidant systems and the retention of mechanical properties.

2.3.1 Oxygen absorption of Vulcanizates

Rate of oxygen absorption depends on the rate of which oxygen can diffuse into the rubber sample and the rate of reaction of oxygen with the polymer. To control the first factor ie. diffusion, samples were used with same thickness.

Oxygen absorption tests were carried out in a pyrex test tube of approximate total volume of 100 ml with a B 24 quickfit socket and a cone attachment. The apparatus has been described by previous workers

The reaction tube containing the sample was flushed with oxygen for several minutes and immersed in a thermostated oil bath. As oxygen was absorbed by the sample a pressure difference set up between the two tubes. The pressure variation was directly recorded as an oxidation curve on a Leeds and Northrop speedometer recorder.

The pressure variation was measured through a transducer Pye Ether model up 3, ± 5 PSI range. The experiments were carried out in a such a way that 1 ml of oxygen absorbed by the sample was equivalent to 20 division on the scale of the chart.

Procedure :

An accurately weighed specimen (0.3 gms) of thickness 0.023 cm was placed on the glass support, so that oxygen was able to diffuse to both sides freely. The glass support with the sample was inserted in to the absorption tube and was purged with oxygen. The apparatus was assembled in the thermostated bath at 70°C and was then connected to the transducer. The ballast tube was already positioned, and the system was allowed to equilibrate for 5 minutes so as to reach the temperature to 70°C. The samples were then left to absorb oxygen and the maximum value of oxygen that could be absorbed at this voltage {V} was, five mls, hence the required oxygen was added through Luer needle until desired pressure had been re - established.

The duration of the oxygen absorption measurements were dependent on the rate of oxygen absorption of the sample. At the end of the experiment , the sample was removed and weighed.

2.3.2 Stress Relaxation of Vulcanizates

Apparatus -

The continuous stress relaxation of vulcanizate was following automatically, using Wallace - Shawbury self - recording age - testers (Wallace Instruments Ltd), which consists with a six cell air ageing oven set. The cell temperature can be adjusted, and is approximately lower than 2°C than the adjusted temperature, due to 1 cubic - feet per hour air flow.

Procedure : Samples were cut from vulcanized sheet using the MR 100 apparatus test cutter. The samples were fixed between two fixed points and was then kept in extension inside the cell. The specimen was allowed to relax in stress at 100°C and with an air flow of 1 cubic - feet per hour. The results being recorded as the logarithm of the stress against time. Experiments were carried out with extracted and unextracted rubber samples.

2.3.4 Measurement of Tensile properties

The tensile properties of the rubber samples were measured using a Hounsfield E type Tensometer. There are five speed ranges, which are selected by the appropriate switch on the control panel. The speed of the crosshead is controlled by the varying the speed of the constant torque motor. Crosshead speed between 0.01"/minute to 4"/minute can be adjusted on lower speed setting and corresponding maximum pull is 2500 kg. On the upper speed setting speed varies from 0.1"/minute to 40"/minute , but the maximum pull limited to 1250 kg. There are two drum switches to control the upper setting and lower setting for the cross head

Four load cells are available with maximum load capacities of 2500kg, 1250 kg, 25 kg, and 2.5 kg respectively. The push button attenuator on the front pannel of the amlifier enables any one of seven load ranges to be selected. Five of these give full range on the recorder for 100 %, 50 %, 20 %, 10 % and 5 % of the load cell maximum load and any of these may be used for normal testing.

Extensometer : The three position marked extensometer F, F - R and Ext - Test is used in conjunction with an extensometer feeding through Extensometer Servo Control Unit on the rear which enable to measure the extension.

Procedure :

The 25 kg load cell was fixed in position and 10 kg load range was selected for testing. The recorder was set to zero with the upper chuck and chuck pin in place but no test pieces were inserted. The crosshead speed selected for natural rubber vulcanizate was 12"/ minute for nitrile rubber sample 3"/ minute. The lower drum switch was set to zero when the crosshead was in position, where the test piece could be easily fixed in the chucks. The upper drum switch was set to 35" reading, where the crosshead was likely to reach during the test, The test pieces were cut from 0.25 mm thickness vulcanizate using a die of width 3.5 mm width. Test specimen was fixed between the two chucks and the start button was pressed. As the test proceeded a stress - strain diagram was plotted on the chart paper. The chart speed was set to 2 in / minute. At the end of the break the cross head automatically move to the zero level.

For each sample, three test pieces were tested and average of the results were noted.

2.4 Estimation of the Concentration of bound antioxidants (70 - 71)

The concentration of bound antioxidant was determined by the Infra Red spectroscopy. The samples used were transparent and of thickness 0.0085 - 0.009 inch. In hindred phenolic antioxidants, it was possible to measure the absorbance of the phenolic -OH strething peak at 3620 cm^{-1}. To determine the exact concentration following method was carried out.

Calibration curve : 100 gm (D.R.C) in 166 mls of 30 % N. Rubber latex was coagulated, dried and was then extracted with azeotrope for 48 hours under nitrogen atmosphere. This was then dried under a vaccum to remove solvent and was stored in a desicator. 100 gms of the extracted natural rubber was mixed with known quantity of thephenolic antioxidant and with other vulcanizing ingredients. The sample was vulcanized, dried and I.R spectrum of the film was taken. Samples were prepared with different concentration of antioxidant varied from 0.5 %, 1% and 2 %.

The intensity of the phenolic -OH was proportional to the concentration of the added antioxidant and was measured as a function of peak area. To eliminate the errors due to thickness, a peak at 2720 cm^{-1} was taken as the reference peak. The concentration of the phenolic antioxidant could be interpreted as the ratio of peak area of phenolic OH at 3620 cm^{-1} to that of peak area of reference at 2720 cm^{-1}.

Curves were plotted of peak ratio versus the concentration of antioxidant added. The calibration curves for different antioxidants were illustrated in Fig 2.1 - 2.7. These curves were used to estimate the concentration of the bound antioxidants, which curve correspond to the ratio of the peak area of the bound antioxidant.

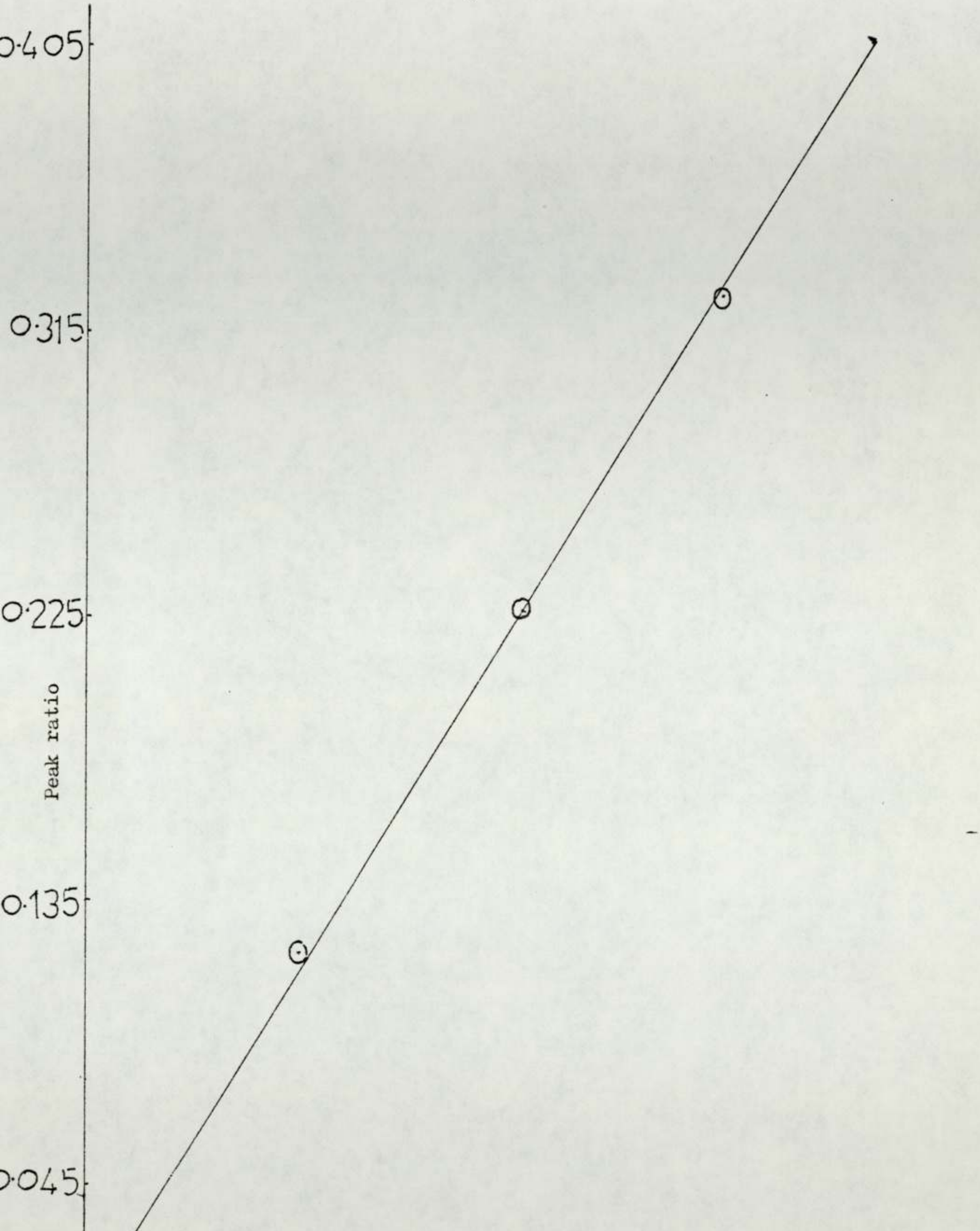
Similarly curves were plotted with prevulcanized latex. The composition of the prevulcanized latex given in table.

	Wet weight	Dry weight
60 % Natural rubber	166 gms	100 gms
50 % Zno (dipersion)	0.4 gms	0.2 gms
50 % Sulphur	0.6 gms	0.3 gms
50 % ZDC	0.8 gms	0.4 gms

The above data was supplied by Revetex Company.

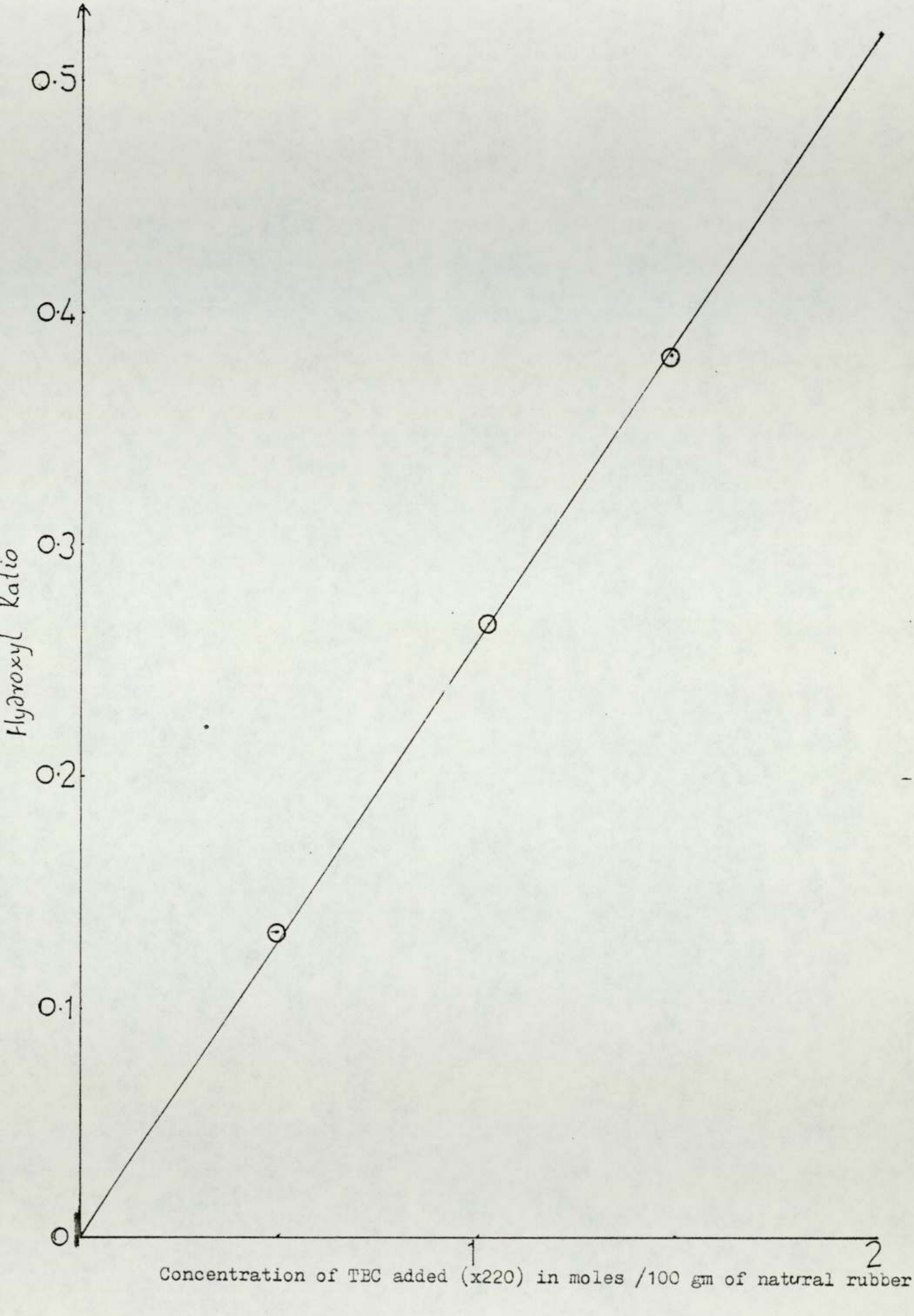
The known amount of 50 % antioxidant dispersion was added and films were cast over glass plates. Films were dried , and the I.R of the films were taken. The curves were plotted as in the last experiment.

Figure 2.1



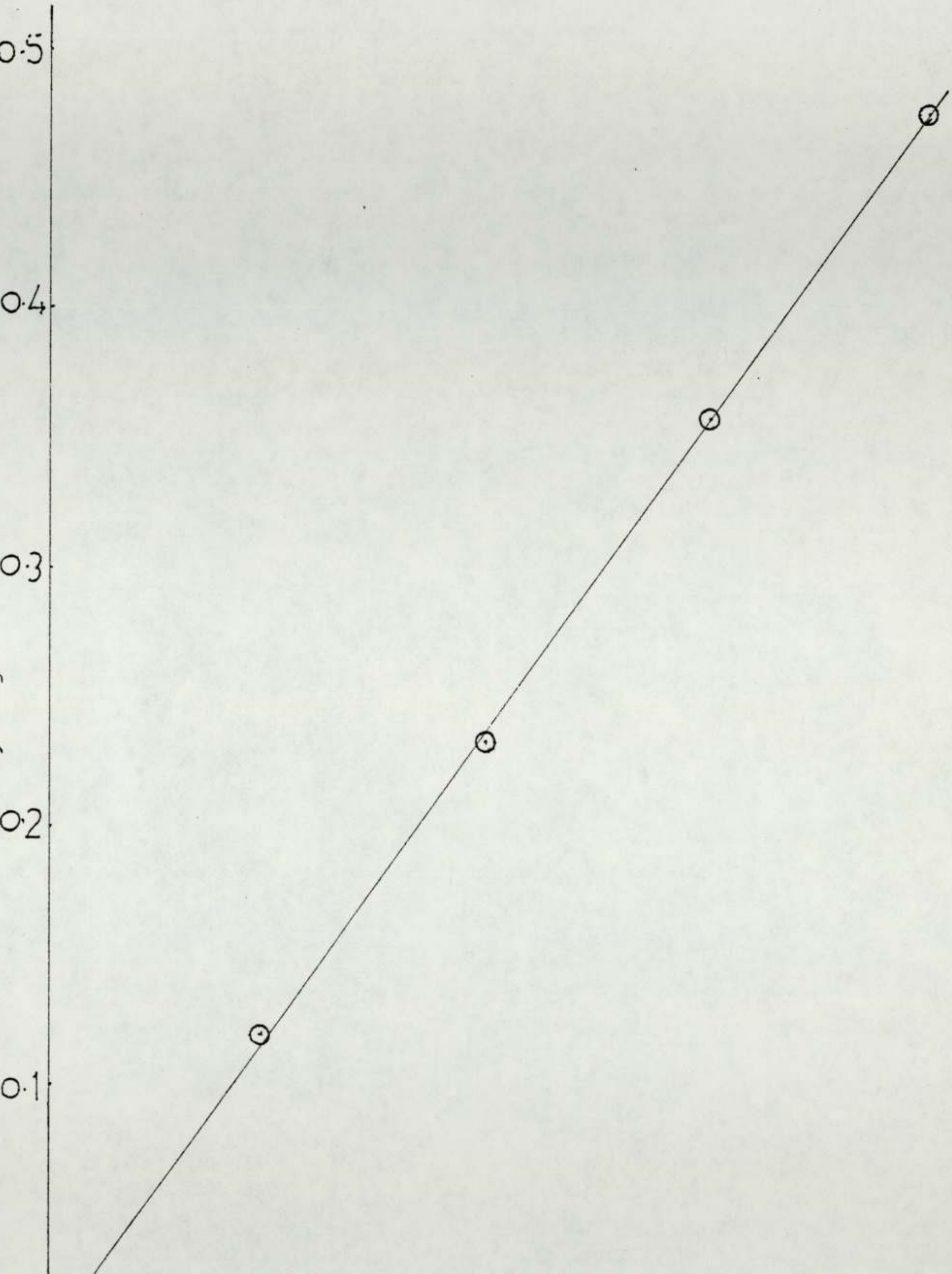
Infra-red calibration curve for TBC in natural rubber

Figure 2.2 - Infra-red calibration curve for TBC in prevulcanised latex



Concentration of TBC added (x220) in moles /100 gm of natural rubber

Figure 2.3 - Infra-red calibration for BHBM in natural rubber



Concentration of BHBM (x 252) in moles / 100 gm of natural rubber

Figure 2.4 - Infra-red calibration curve for BHBM in prevulcanised latex

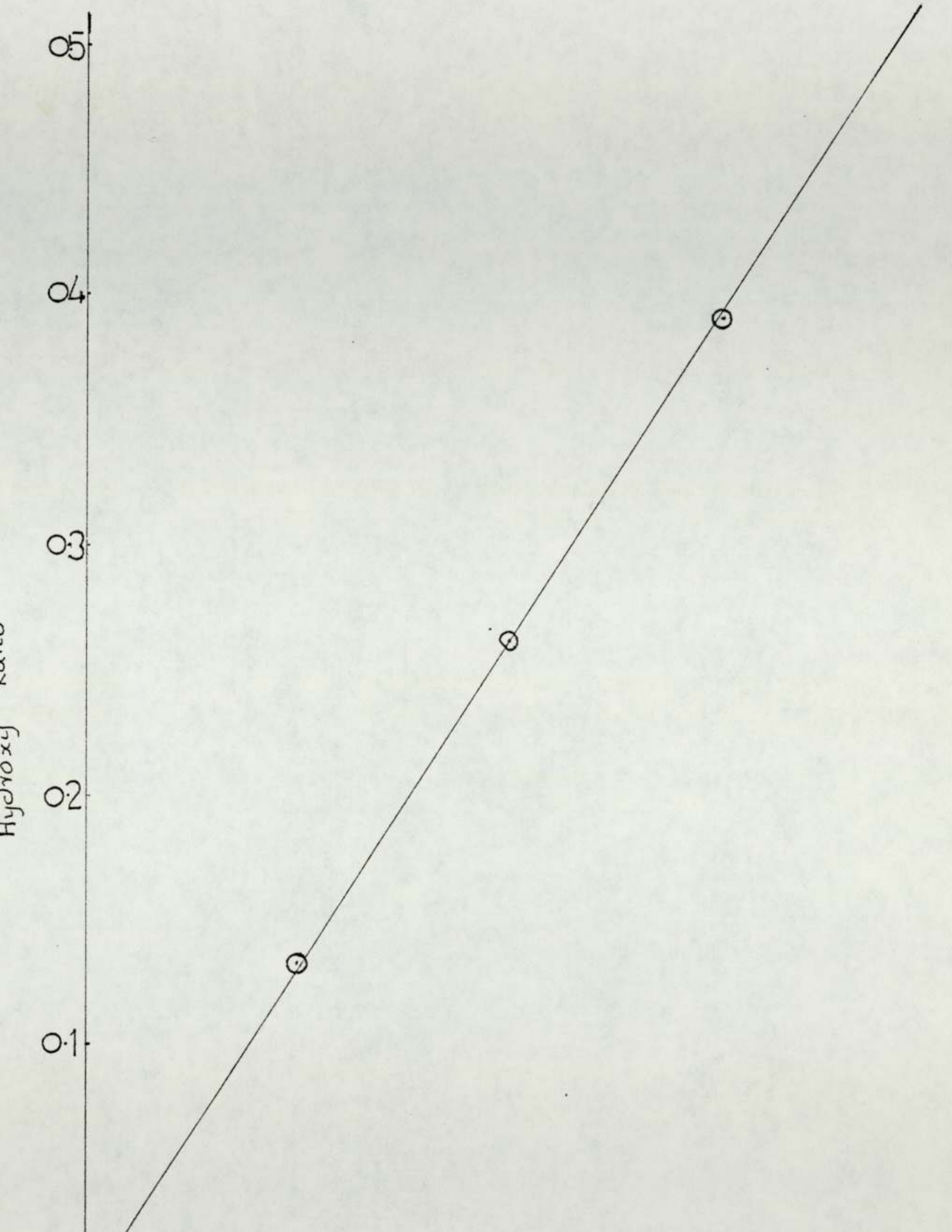


Figure 2.5 - Infra-red calibration for $RCH_2O\overset{O}{\overset{\|}{C}}-CH_2-CH_2-SH$ in rubber

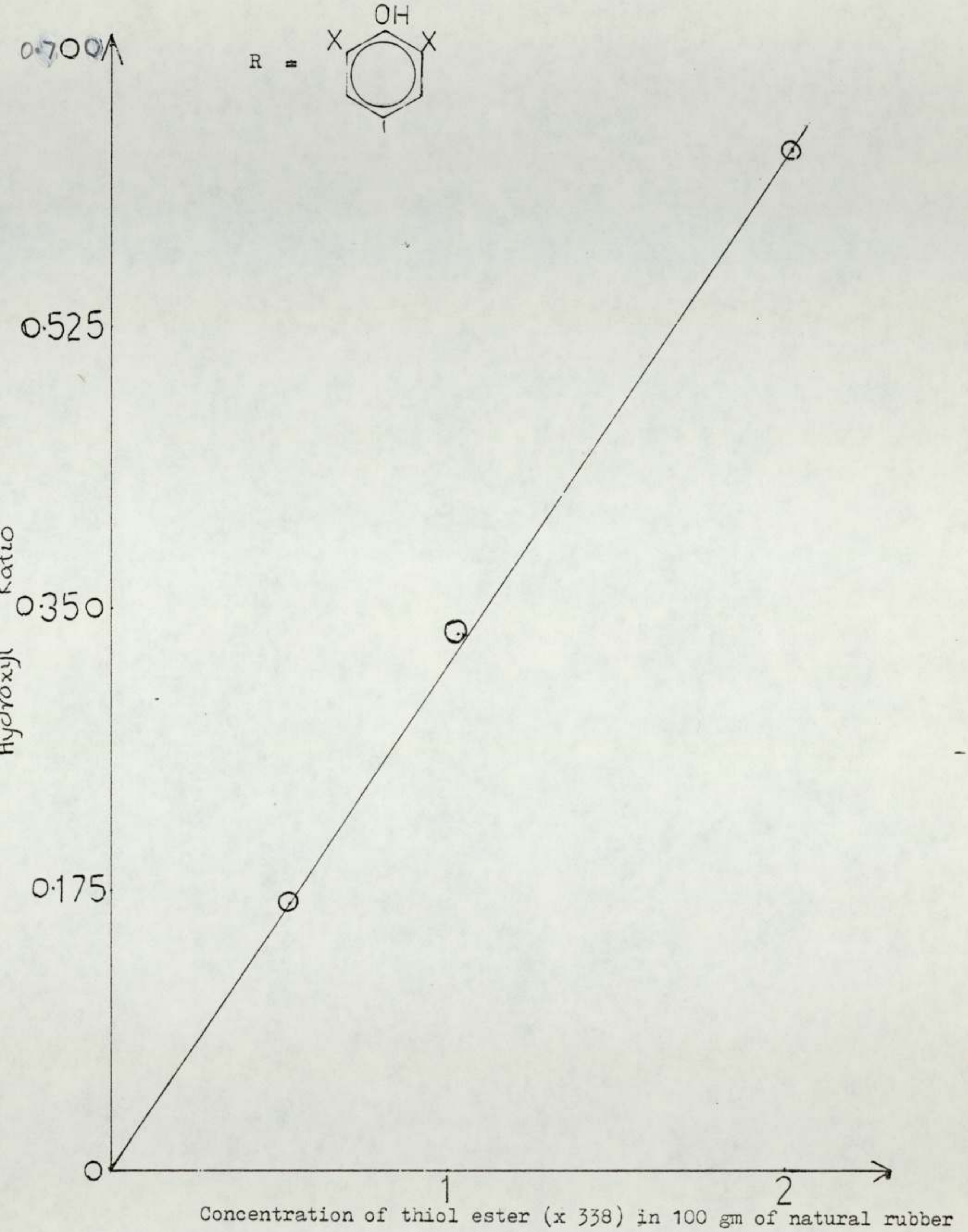


Figure 2.6 - Infra-red calibration for $\mathrm{RCH_2O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-CH_2-CH_2-SH}$ in rubber

Carbonyl curve

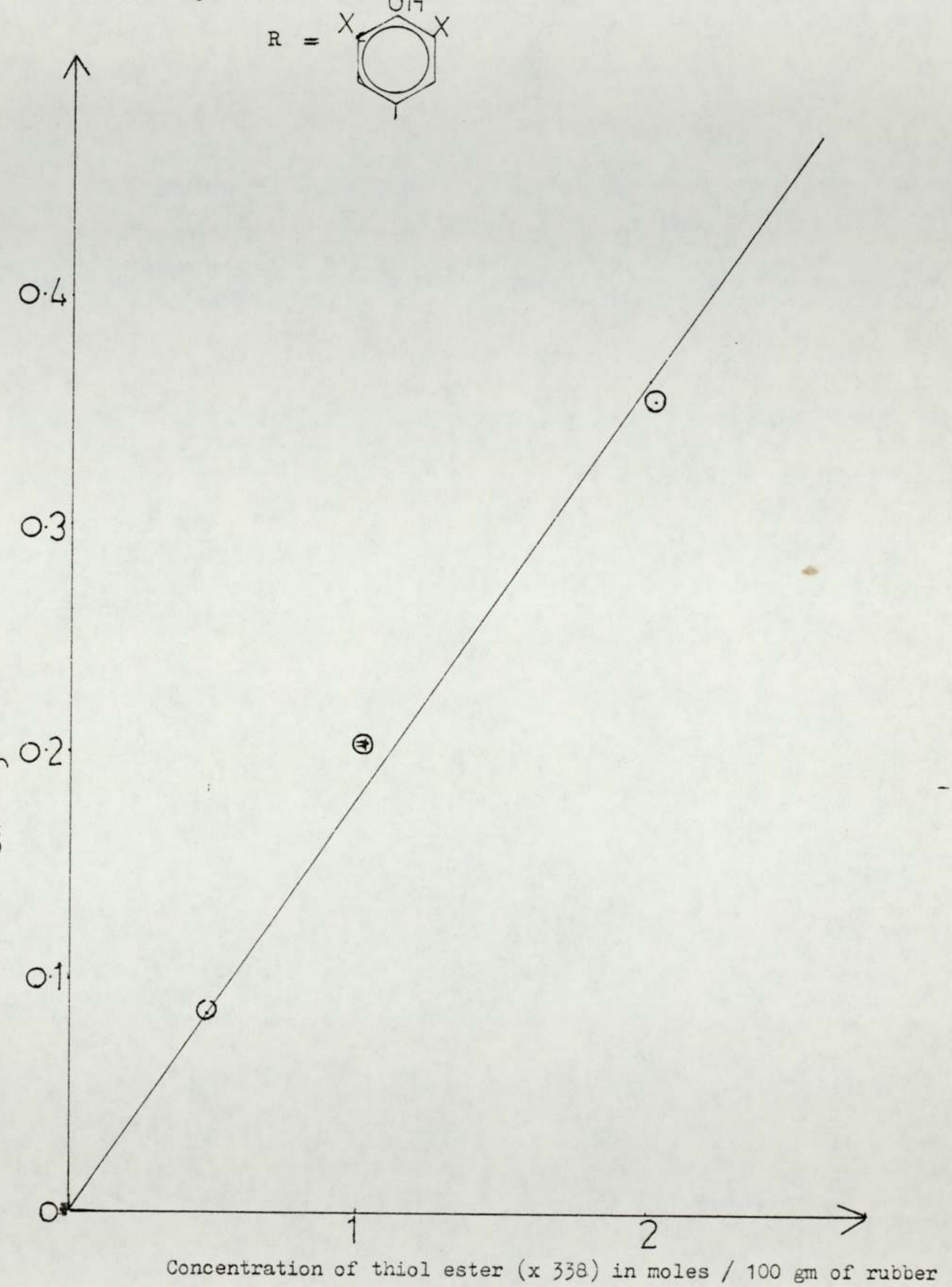
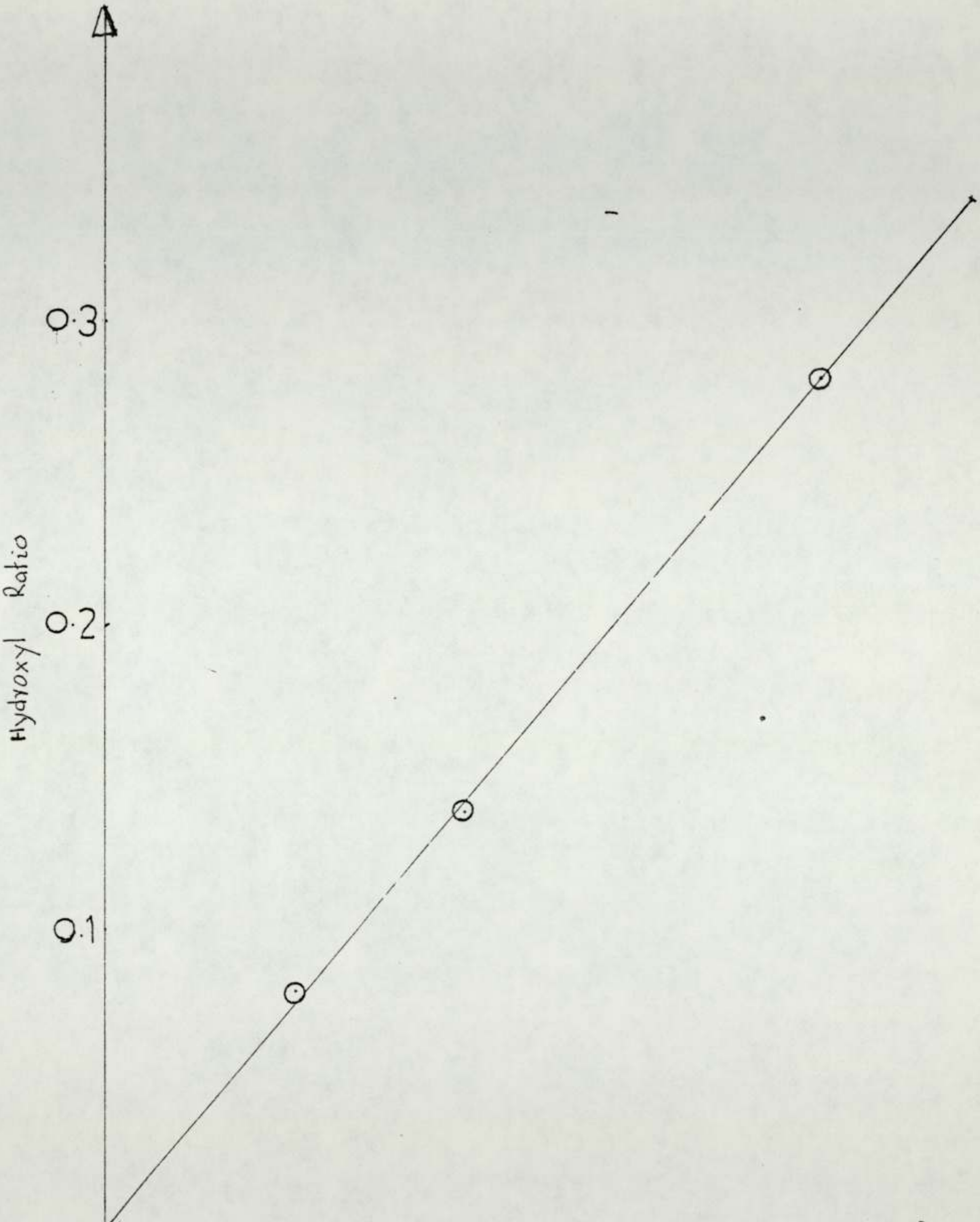
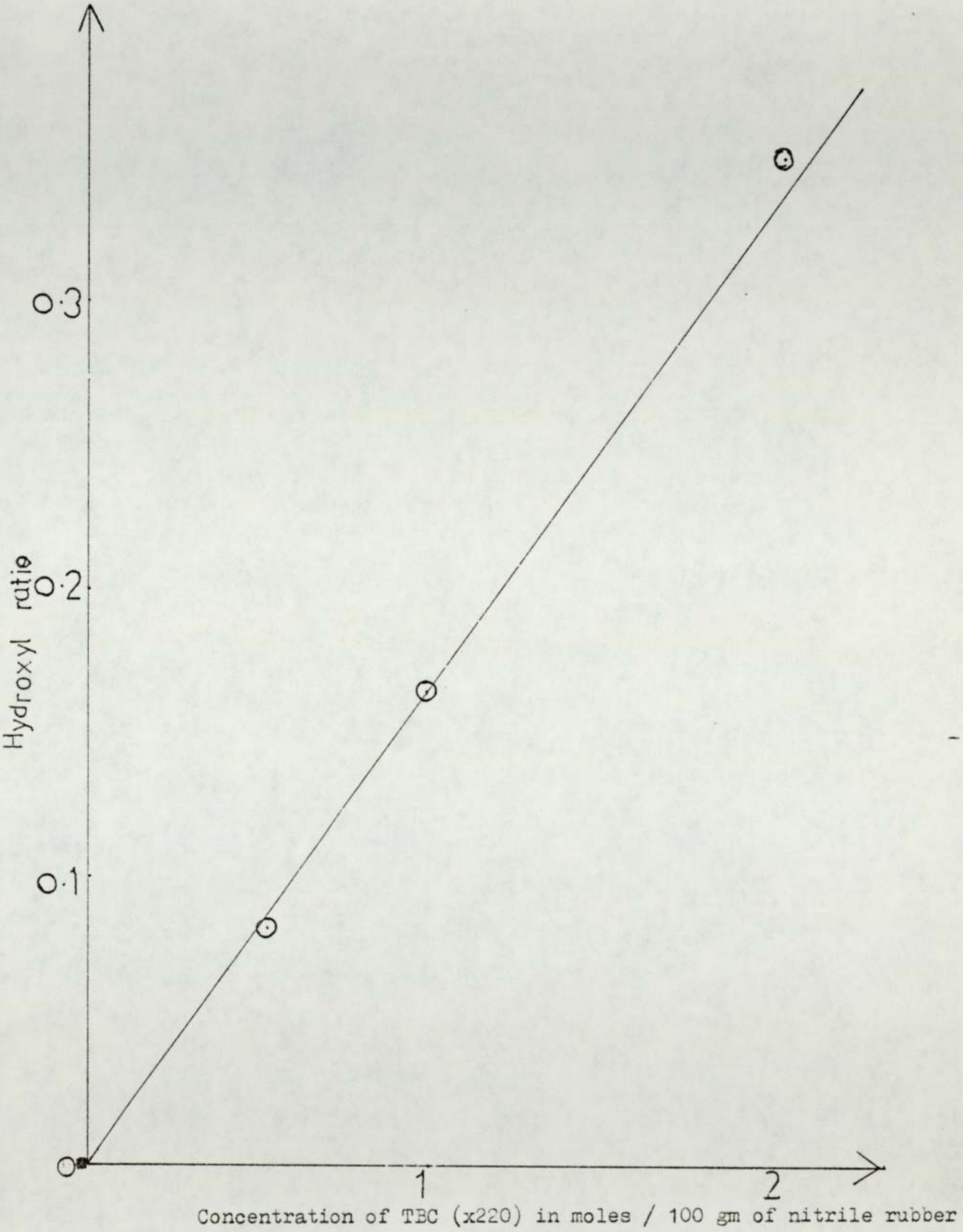


Figure 2. 7- Infra-red calibration curve for BHBM in nitrile rubber



Concentration of BHBM (x252) in moles / 100 gm of nitrile rubber

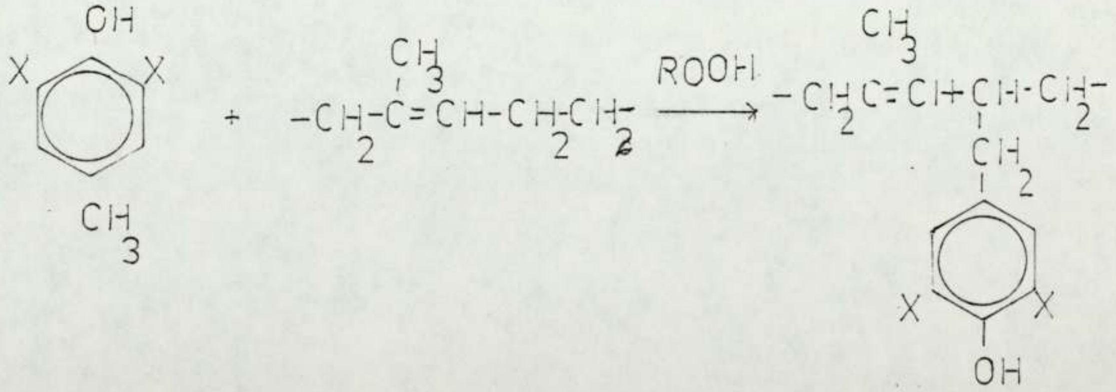
Figure 2.8 - Infra-red calibration curve for TBC in nitrile rubber



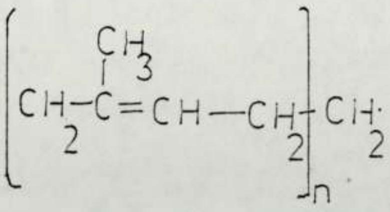
CHAPTER THREE

Reaction of hindered phenols with natural rubber latex

Scott and co-workers have shown that hindered phenols containing vinyl and thiol groups can be grafted to natural rubber in the latex stage using a suitable initiator. A furthur development from these studies was that many antioxidants which do not contain the above groups can also be bound to rubber in the latex form. One such example is 2,6-ditert-butyl-4-methyl phenol (TBC). The present objective is to study the reactions of this type of antioxidant with natural rubber in more details and also their effectivness as antioxidants, particularly in latex products such as, gloves , threads etc. According to model compound studies to be described in subsequent chapters, the reaction mechanism of TBC with natural rubber can be represented as follows.



Natural rubber latex is a two phase system consisting of a dispersed phase and dispersing medium. The dispersed medium consists of small rubber particles , normally less than 5µ in diameter, the molecule of which are polymeric in nature and comprise a basic unit which is repeated many times over. The disperse medium is the aqueous phase.



$$\left[CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right]_n CH_2\cdot$$

Compounding ingredients are added to latex either as aqueous solution, dispersion or emulsion according to their physical characteristic. The particle size of the dispersion and the droplet size of the emulsion are significant factors, which effect the physical properties of the finished products. Before adding compounding ingredients in the form of dispersions emulsion, or in solutions, the pH and the stability of the latex has to be considered.

3.1.1. Preparation of dispersions.

The dispersions were prepared in Szegvari attritor under a nitrogen atmosphere. The solid antioxidant was ground and was sieved through 200 mesh size sieve. 10 gms of the powdered antioxidant was placed in the container with 0.2 gm of Dispersol LN. Distilled water was added just to cover the surface of the balls and was stirred at a constant speed for 10 hours. The temperature of the container was kept low by passing water through the outlet. The dispersion was then discharged into a conical flask and was stored in a nitrogen atmosphere.

3.1.2 Preparation of emulsions

Emulsions can be prepared in two ways, either by adding liquid antioxidants to water containing emulsifing agent or by preparing soap in water.

Procedure 1 :

10 gms of the liquid antioxidant was added to 50gm of distilled water containing 0.5 gm of the emulsifing agent, vulcastab LS. The tightly stoppered container was shaken vigorously in a flask shaker for more than 24 hours under nitrogen atmosphere.

Procedure 2 :

0.42 gm of lauric acid and 0.08 gm of potassium hydroxide were dissolved in 50 ml of water. 10 gm of the liquid antioxidant to be emulsified was poured in and the flask was shaken vigourously for 24 hours under nitrogen atmosphere.

3.2. Determination of the optimum reaction condition for the reaction of 2,6-ditert-butyl-4methyl phenol (TBC) with natural rubber latex.

The experiments described below were carried out with 332 ml of 30% (100 gm of dry rubber) natural rubber latex which was partially deammoniated by passing nitrogen through diluted latex for about three hours with stirring. To prevent the coagulation of the latex, the pH of the deammoniated latex was maintained at 8.0-8.5.

The main factors which determine the rate of the reaction as well as the yield of the final product are temperature, reaction time, initiator and antioxidant concentrations. The following set of experiments were carried out to examine these parameters.

3.2.1. Initiator System

Amarapathy[35] has shown that the redox system tert-butyl hydroperoxide(TBC) and tetra-ethylene-pentamine(TEPA) as the best initiator for the grafting of DBBA with natural rubber latex. A set of experiments was carried out with natural rubber latex and different initiator systems including the above to find the best initiator system for the reaction of TBC with natural rubber and to throw light on the mechanism of the process.

Procedure :

Experiments were carried out in five necked flask. 100gms (D.R.C) of 30% natural rubber latex was placed in the flask and was immersed in a thermostatically controlled water bath at 55-60°C, because most of the initiators were reactive above 50°C . Then 2 gm of TBC dispersion was added and was stirred for about 1/2 an hour so as to swell into the latex. The following initiators were used for the reaction and were added slowly into the mixture.

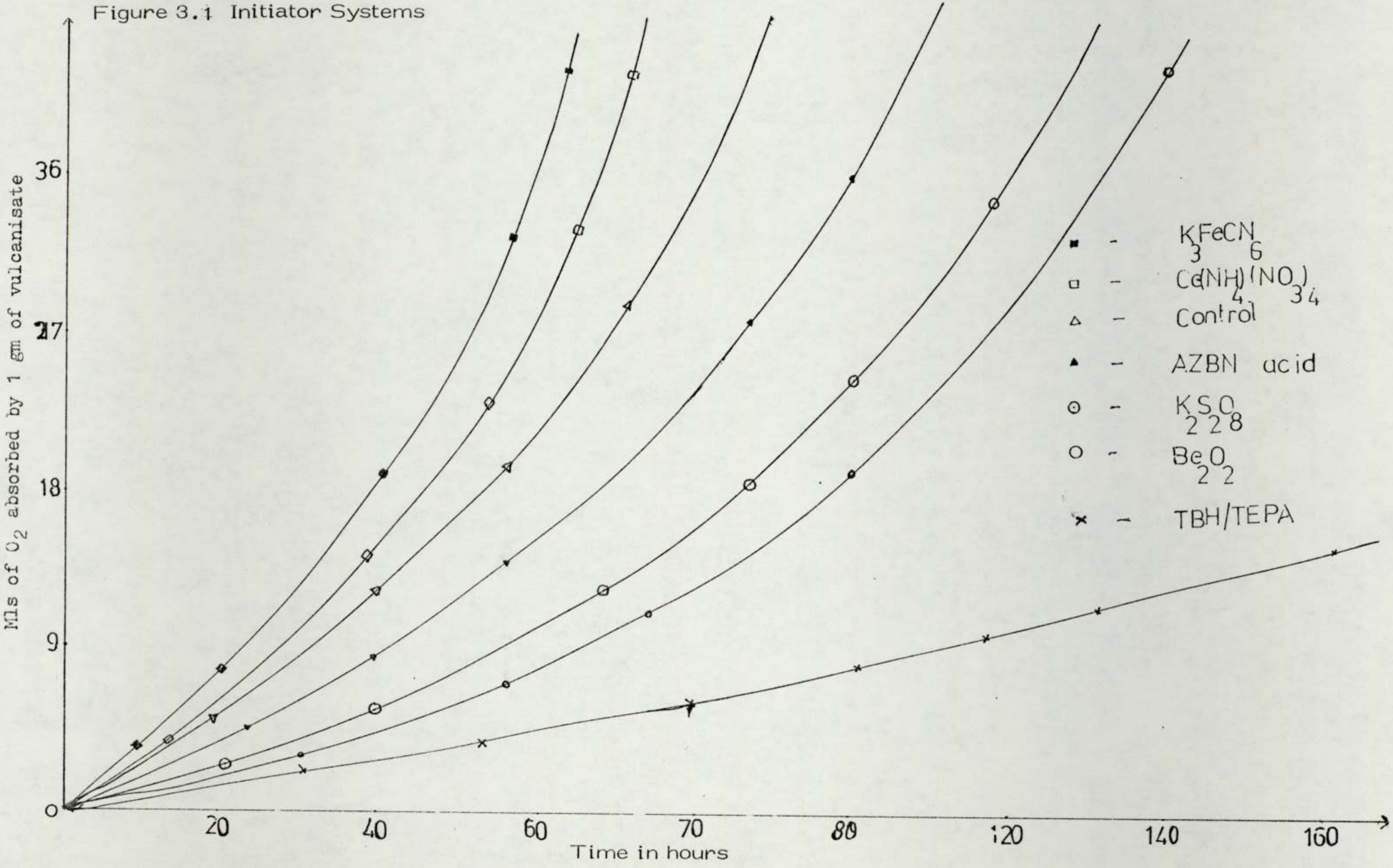
Table 3.1

Type of initiator	Initiator concentration in moles/100 gm N.R	TBC bound concentration /100 gm N.R	% of TBC bound	Time to absorbed 2% O_2
No initiator	-	*	-	27
Potassium persulphate /ferrous sulphate (A.R)	0.008	*	-	35
Benzoyl peroxide	0.008	*	-	45
4-4' azobis(4-cyano -valeric acid(AZBN acid) in Na_2CO_3	0.008	*	-	33
Ceric ammonium nitrate in alcohol (A.R)	0.008	*	-	22
Potassium ferricyanide (A.R) in alkaline solution	0.008	*	-	14
Tert-butyl hydroperoxide (TBH)/TEPA(4.5ml of 10% solution)	0.008	11.0	11	106

* No phenolic OH peak at 3620 cm^{-1}

The reaction was allowed to proceed for 20 hours and was then allowed to cool. The latex was coagulated by adding 1% formic acid, washed with distilled water and the coagulum was sheeted into thin sheet, rewashed dried , and was then extracted with azeotropic mixture for 48 hours under

Figure 3.1 Initiator Systems

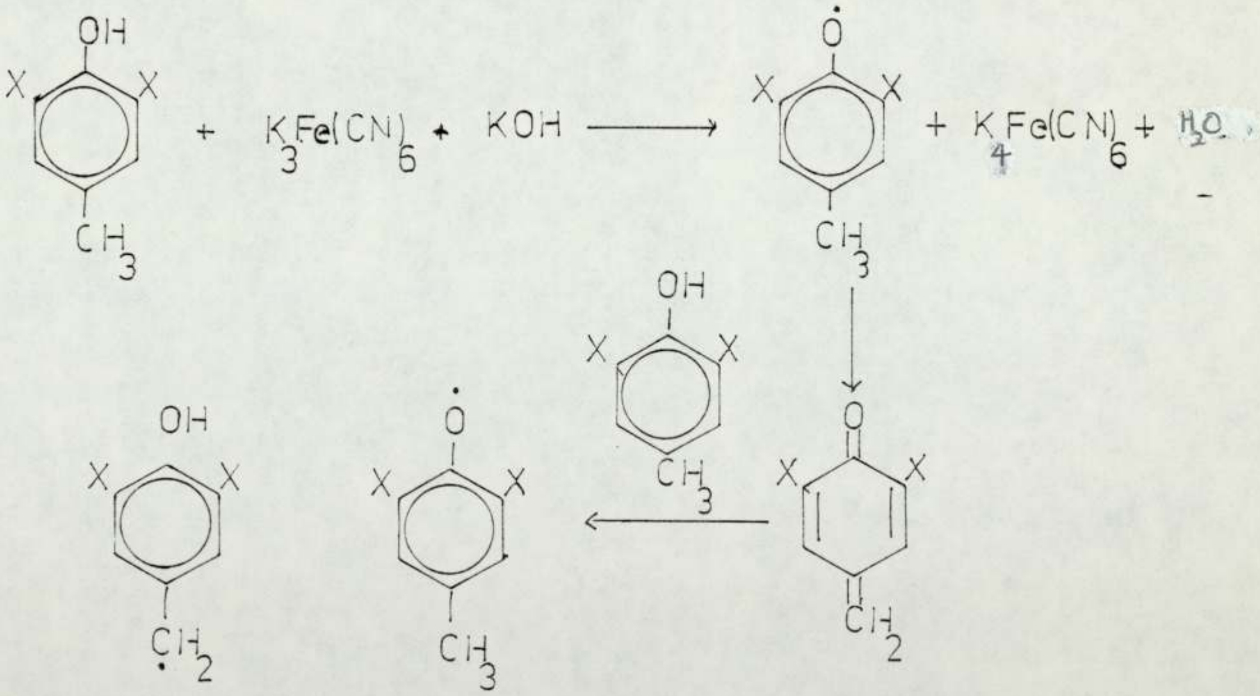


Oxygen absorption of the extracted vulcanisates at 70°C

N_2 atmosphere. The coagulum was dried and the vulcanizates were prepared as described in chapter 2. The amount of TBC bound was estimated by I.R technique and was further confirmed by oxygen absorption test shown in table 3.1 and curves in fig. 3.1

3.2.1 Discussion

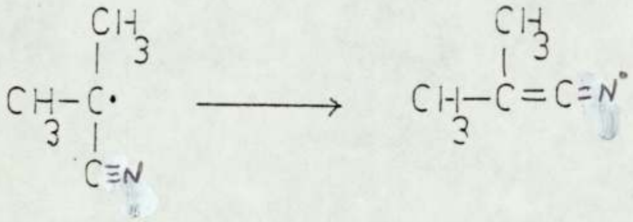
To obtained the required product, it is necessary to create radicals on both the TBC as wellas on the rubber molecule. But potassium ferricyanide is incapable of forming radicals on rubber molecules which results in no bound reaction with rubber. On the other hand ,Beconsall and co-workers[21] have studied the reaction of TBC with K_3FeCN_6 and have found that the benzyl radical and quinone methyde as intermediate. They suggested that these intermediates brought about the formation of all the byproducts.



Because of this,the formed potassium ferrocyanide reacts with K_3FeCN_6 resulting in the formation of green coloured complex, which causes the prooxidant effect of the vulcanizate prepared from it. (Fig.3.1)

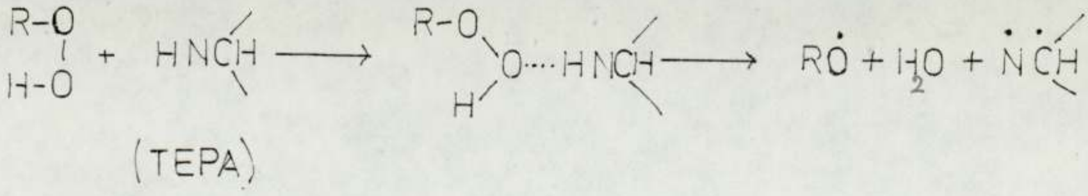
Persulphate initiators were , as explained in chapter 1, used for graft polymerisation of natural rubber with vinyl monomers. There is evidence that they are capable of forming radicals on the natural rubber molecule but this is retarded in the presence of ammonia.[71] Apart from this, the size of the persulphate radical inhibits the abstraction of hydrogen from sterically hindered phenols. These two factors can be considered as the reasons for the lower reactivity of TBC in the presence of this initiator.

As mentioned earlier, the alkyl radical formed from AZBN tends to stabilise itself by a reducing process.[27] Peroxides on the other hand are oxidising species. Because of this AZBN is incapable of abstracting hydrogen from the hindered phenols. Moreover, tert-alkyl radicals such as cyano iso-propyl are stable and cannot abstract hydrogen from the rubber. Hence no reaction was observed.



$$CH_3-\dot{C}(CH_3)-C\equiv N \longrightarrow CH_3-C(CH_3)=C=N^{\bullet}$$

Peroxides are capable of abstracting hydrogen from hindered phenols as well as from rubber molecules, thus creating the necessary intermediate for the desired final product by the radical process. The activity of tert-butyl hydroperoxide(TBH) is enhanced by the activator TEPA, which is water soluble and creates reactive species at lower temperatures than benzoyl peroxide. Huyser[72] has shown that the rapid decomposition of hydroperoxide is due to the hydrogen transfer from TEPA, which weaken the 0-0 bond resulting in the formation of free radicals.



$$R{-}O{-}O{-}H + HNCH \longrightarrow R{-}O(H)O\cdots HNCH \longrightarrow R\dot{O} + H_2O + \ddot{N}CH$$

Benzoyl peroxide forms radicals readily at high temperatures, but cannot be used in latex , since the latter tends to coagulate at these temperatures. It has been found that the performance of this initiator is poor even in the presence of activators such as ferrous sulphate. It is clear from the above results in table 3.1 that the best initiator system of those examined for the reaction of TBC with natural rubber is tert-butyl hydroperoxide/tetraethylpentamine.

With potassium ferricyanide, ceric ammonium nitrate discolouration in the latex was observed, whereas no such change was observed in the presence of persulphate, AZBN acid and TBH /TEPA. Benzoyl peroxide showed a slightly yellowish colouration probably due to the formation of stilbene quinone.[20]

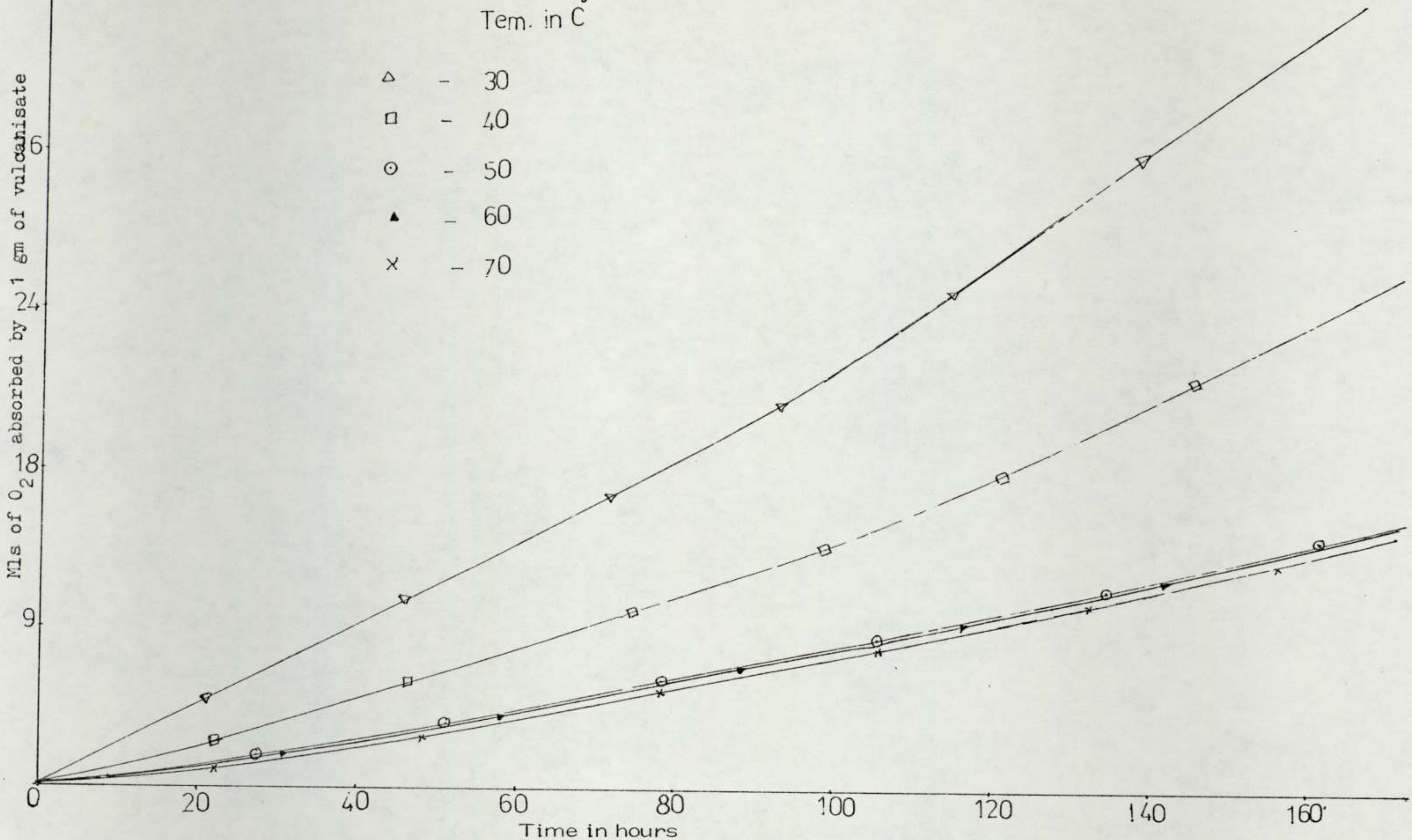
3.2.2 Effect of temperature

A set of experiments was carried out with 2gm of TBC and 100 gm (DRC) of 30% deammoniated latex, at temperatures 30, 40, 50, 60, and 70°C. TBH/TEPA was used as initiator and rest of the experiment procedure was the same as in the previous section. At the end of 20 hours, the latex was coagulated dried and was extracted. The amount of antioxidant bound in each sample was examined by I.R method and was furthur confirmed by oxygen absorption test and the curves are shown in Fig. 3.2

Table 3.2

Temperature in centigrade	Concentration of TBC bound/100 gm N.R	% of TBC bound	Time to absorb 1% oxygen
30	no OH peak	-	40
40	0.00046	5.1	58
50	0.0009	10.0	98
60	0.001	11.0	104
70	0.001	11.0	107

Figure 3.2 Reaction time



Oxygen absorption of the extracted vulcanisates at 70°C

If the temperature is raised above 60°C, the latex tends to coagulate, therefore to prevent this and for a satisfactory yield, temperature of the reaction must be maintained at 60°C.

3.2.3 Reaction time

A set of experiments was carried out at 60°C for varying lengths of time and rest of the experimental procedure was the same. The samples were taken out at 6 hours intervals of time, coagulated, dried and was then extracted. The I.R method was used to determine the concentration as described previously of the bound antioxidant and was correlated with oxygen absorption tests, curves shown in Fig 3.3

Concentration of TBC used - 2gm (0.009M)/100 gm N.R

Concentration of the initiator - 1.5 ml of TBH(0.018M)/100 gm N.R

Natural rubber (DRC) - 100gms

Table 3.3

Reaction time in hours	Concentration of TBC bound	% of TBC bound	Time to absorbed 2% oxygen
0	no OH peak	-	27
6	"	-	36
12	0.0005	5.0	52
18	0.0012	11.2	108
24	0.0011	11.0	104

It is obvious from the results that the rate of the reaction is very slow, and to obtain a reasonable yield, the reaction must be carried out at least for 18 hours. The incompatability of the TBC particle is a possible explanation for the slow rate, since the former is insoluble in latex. If the diameter of the TBC particles are greater than that of

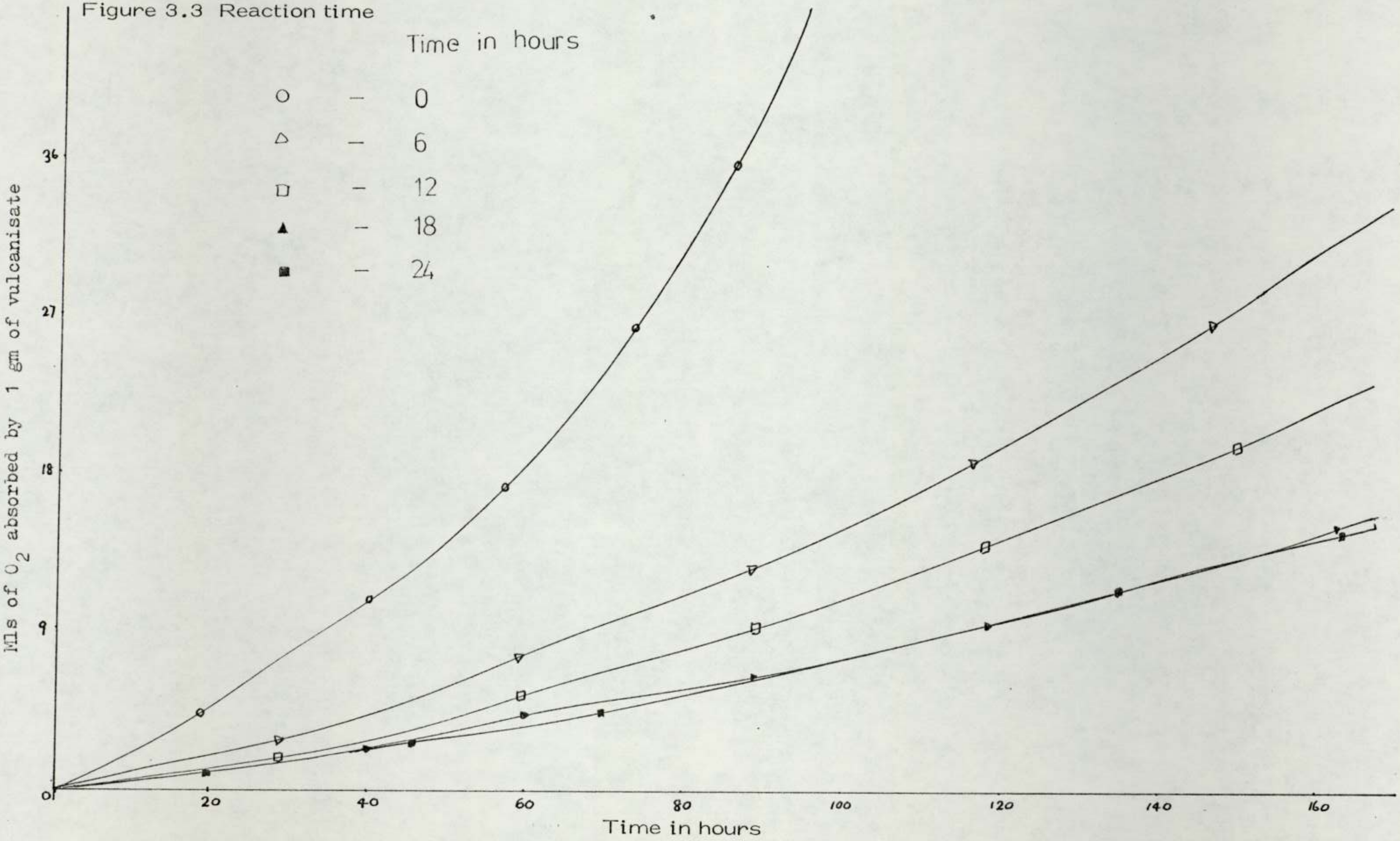


Figure 3.3 Reaction time

Oxygen absorption of the extracted vulcanisates at 70°C

rubber latices then the penetration or swelling of TBC is reduced, which affects the rate of the reaction.

3.2.4 Effect of initiator concentration

A set of experiments was carried out, similarly to that described above with different concentrations of initiator. The temperature of the reaction was maintained at 60°C in a nitrogen atmosphere.
Concentration of TBC used - 0.009 moles in 100 gm of natural rubber

Table 3.4

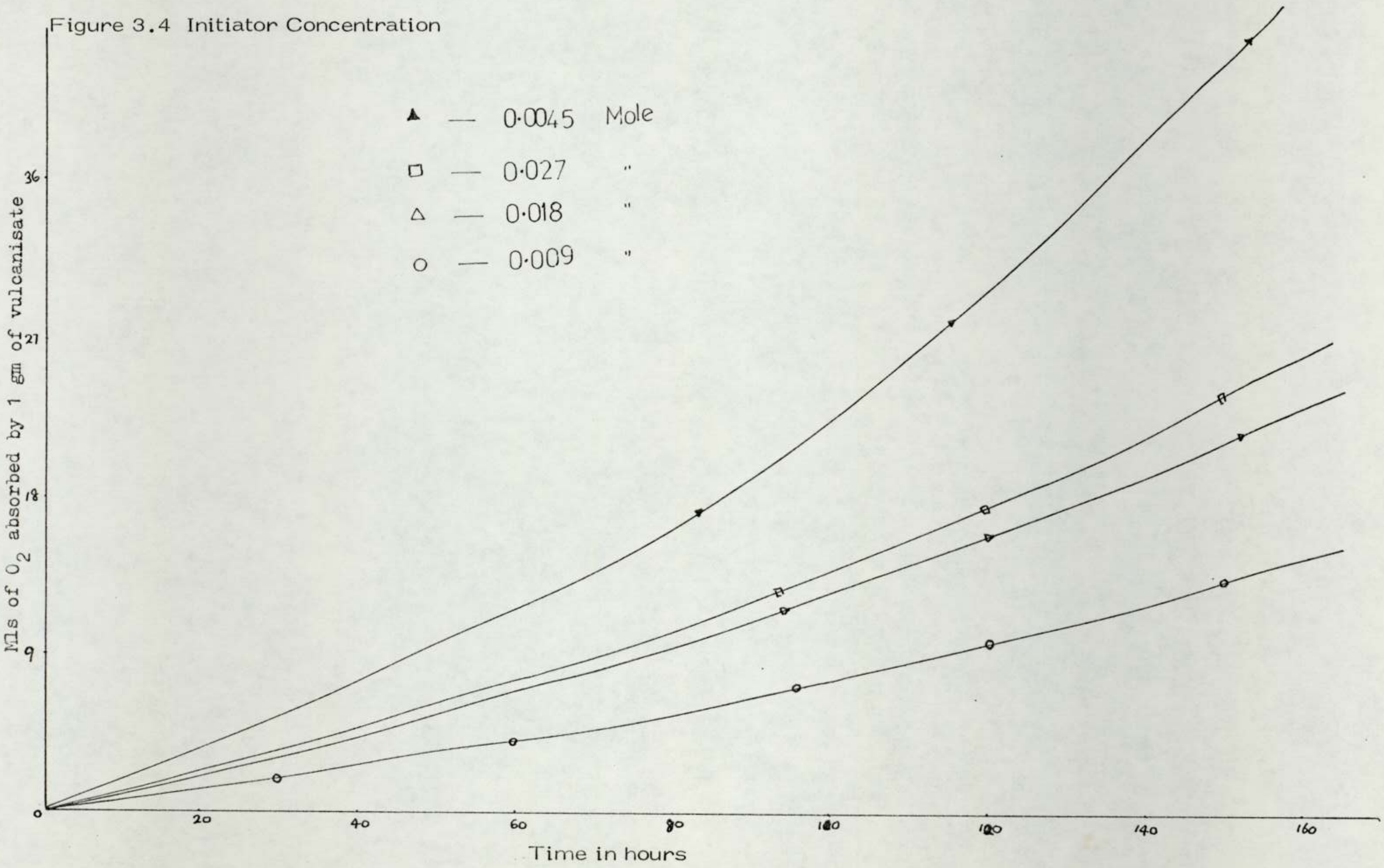
TBH concentration in moles /100 gm N.R	TEPA added in mls	% of TBC bound/100 gm N.R	Time to absorb 2% oxygen
0.0045 (0.4ml)	1.125 of10%	-	34
0.009 (0.8ml)	3.25 "	5.0	54
0.018 (1.6ml)	4.50 "	10.6	104
0.027 (2.4ml)	6.75 "	4.3	47

As the concentration of the initiator increased, the intensity of the colour as well as the crosslinking of the rubber molecule increased. The latter will be discussed in chapter 4. The discolouration of the latex which occurred at high concentration due to the formation of stilbene quinone.

3.2.5 Effect of swelling time

Experiments were carried out with 100gm(DRC) of 30% deammoniated latex and 2 gm of TBC dispersion. Initially the TBC dispersion was allowed to swell into rubber network for known lengths of time and then 1.6 ml of TBH/4.5 ml of 10% TEPA was added. The reaction was carried out for 18 hours at 60 °C. After the reaction , the coagulum obtained was

Figure 3.4 Initiator Concentration



Oxygen absorption of the extracted vulcanisates at 70°C

dried , extracted and the vulcanisates were prepared. Inthe usual way the amount bound was determined by I.R and was confirmed oxygen absorption,

Table 3.5

Swelling time in minute	% of TBC bound	Time to absorb 2% O_2 in hours
0	0	32
15	6.6	63
30	11.0	107
60	11.0	109

The reaction of TBC reaches to maximum, when the TBC is allowed to swell ½ an hour before the addition of the initiator. Probably the time of swelling could be reduced further, if the particle size of the TBC dispersion were lower than that of rubber latices, since the former could be more easily penetrated into latex and the rate would be increased.

3.2.6 Effect of TBC and initiator concentration on the reaction

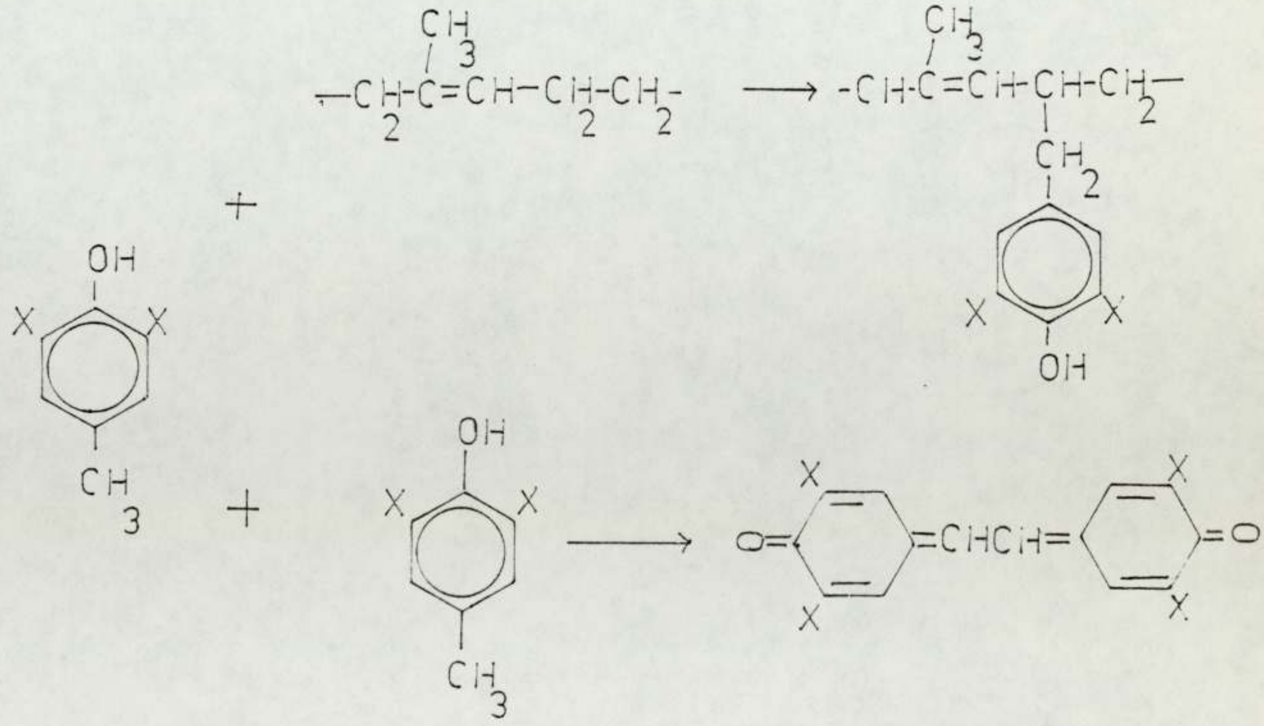
The reaction is found to be not catalytic with respect to the concentration of the initiator. According to the results in table 3.4 the yield is maximal , when one mole of antioxidant is reacted with two moles of initiator. Theoretically one mole of TBC consumes one mole of initiator, the other mole is for the abstraction of hydrogen from the rubber molecule. It follows that for a complete reaction the concentration of the initiator should be varied with that of TBC and rubber. To investigate this the following set of reactions were carried out with various concentration of TBC and respective concentration of the initiator.

Ml of 30% rubber latex used - 332 (100gm DRC)

Table 3.6

TBC concentration in moles/100gm N.R	TBH concentration in moles/100gm N.R	10% TEPA in mls	% of TBC bound	Time to absorb 2% O_2 in hours
0.0045 (1gm)	0.0135 (1.2ml)	1.4	18.2	88
0.009 (2gm)	0.018 (1.6ml)	4.5	11.0	106
0.018 (4gm)	0.027 (2.4ml)	6.75	6.8	126
0.036 (8gm)	0.045 (4.0ml)	11.25	5.4	192

As the concentrationsof the initiator and the TBC increased, the yellowish discoluration of the latex was increased, this is probably due to the formation of stilbene quinone. This behaviour was further substantiated by model compound studies, which will be discussed in subsequent chapters. All these results led to the conclusion that the reaction of TBC with natural rubber is favoured at low concentrations of TBC and to the formation of stilbene quinone at high concentrations.



In addition, the hydroperoxides are well known as crosslinking agents for rubber, which effects the reaction of TBC with natural rubber, this has been studied in full details and is discussed in a later chapter.

Aliquot system

A reaction was carried out with 8 gm of TBC and 100gm of latex (DRC), first the TBC dispersion was allowed to swell for ½ an hour before adding the initiator. Then four aliquots of initiator followed by the activator was added at a time interval of 2 hours and each aliquot was contained 1.0 ml of TBH and 2.8 ml of 10% TEPA. At the end of the experiment, the sample was coagulated , dried, extracted and the amount of TBC bound was estimated by I.R technique. It was found that 5.8% of the TBC remained bound to the network, this indicates that even the gradual release of the initiator by aliquot system would not make much difference to the final result and the colour of the latex. Again it may be due to the slow reaction rate of the TBC with natural rubber latex.

3.2. 7 Effect of oxygen on the reaction

2 gm of TBC and 100 gm(DRC) of latex were reacted in the absence of nitrogen to study the effect of atmospheric oxygen on the bound reaction. The reaction conditions similar to that described earlier. It was found by I.R examination that 9.8% of the original TBC remained bound to the rubber after the extraction. This difference, when compared to the 11% of the previous case in the presence of nitrogen, can be accounted for the oxidation of TBC by atmospheric oxygen.

3.2.8 Effect of solubility of the reactants on the reaction

The original reactants were selected, so that they were more soluble in organic phase than in aqueous phase. Instead of TBC dispersion, 2.0 gm of 2,4-ditert-butyl ,6-methyl phenol emulsion was reacted with 100gm (DRC) of latex in the presence of cumene hydroperoxide as an initiator, which is more soluble in organic phase than aqueous phase. After slow addition of the initiator, the activator was incorporated in aliquots, so as to release the initiating species gradually into the media. Five aliquots, each of 0.9 ml of 10% TEPA, were added in 2 hours interval and rest of the procedure was the same as in previous experiments. At the end of the reaction, the extracted sample was examined by I.R for the estimation of bound 2,4-ditert-butyl,6-methyl phenol (TBOC).

Similary a reaction was carried out with TBOC and TBH/TEPA and the amount of bound TBOC was determined by usual way.

Table 3.7

TBOC concentration in moles/100 gm N.R	TBC concentration in moles/100 gm N.R	CHP in moles/100 gm N.R	TBH in moles/100 gm N.R	% TBOC bound	% TBC bound
0.009	-	0.009	-	8.2	-
0.009	-	-	0.009	7.8	-
-	0.009	-	0.009	-	11

It is evident from the above results that the para position of the TBC is more reactive than the ortho position of the TBOC. This led to suggestion that the reaction of hindered phenols depends on the reactivity of the functional groups rather than the solubility. This is much more conclusive in BHBM/N.R reaction, because the former contains a more reactive thiol group. (see later)

3.3. Reaction of (3,5-ditert-butyl-4-hydroxy benzyl) mercaptan (BHBM) with natural rubber latex

It will be explained, as a result of model compound studies that the reactive function of BHBM is completely different from that of TBC. The well known addition reaction of mercaptans to unsaturated compounds[73-75] depends on the electron deficient sulphur atom of the mercaptan and it's susceptibility towards the double bonds. In view of this , Fernando[36] was successful in grafting BHBM to natural rubber using AZBN as an initiator, since chlorobenzene was used as a solvent for the latter, this limits its usefulness in latex. In an attempt to overcome the latter problem, the addition reaction of BHBM to natural rubber was studied in more detail . The following sets of experiments were carried to investigate, the best initiator system and the optimum reaction conditons.

3.3.1 Initiator system

A set of experiments was carried out with 2gm (0.008 mole) of BHBM with 100gm (DRC) of 30% deammoniated latex. The experimental procedure was the same as that of TBC/natural rubber reactions. Again the I.R method was used to estimate the bound antioxidant and was confirmed by oxygen absorption tests , curves given in Fig 3.5

Table 3.8

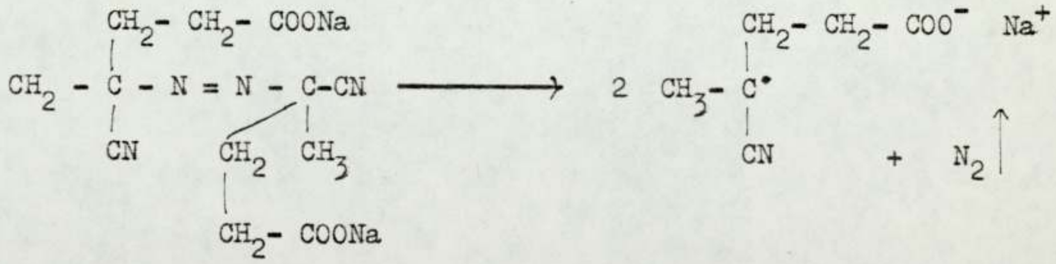
Type of initiator	Initiator concentration in moles/100 gm N.R	BHBM bound in gms/100gm N.R	% of BHBM bound
No initiator	0	*	-
4,4'-azobis(4-cyano valaric acid(AZBN acid) /sodium carbonate	0.008	0.38	19

Azobis-isobutyronitrile (AZBN)	0.008	*	-
TBH/ TEPA	0.008	0.74	37
Potassium persulphate /ferrous sulphate ($FeSO_4$)	0.008	*	-

* No visible peak at $3620\ cm^{-1}$

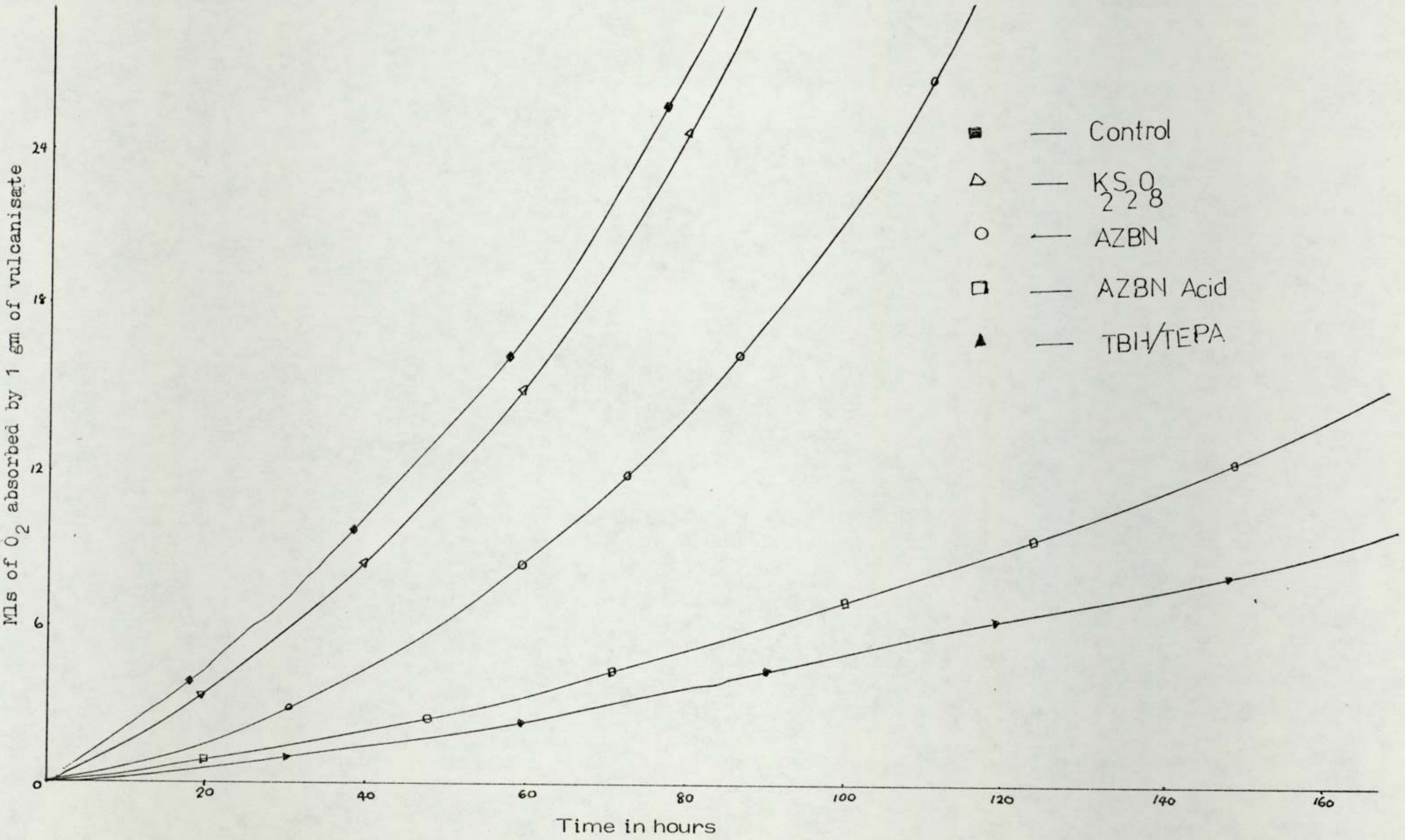
3.3.1.1 Discussion

The water soluble AZBN acid/Na_2CO_3 system forms free radicals itself, but is negatively charged in nature, which acts as a repulsive barrier towards latex, for because the latter is also negatively charged. This could be one of the reasons, the lower reactivity of BHBM with natural rubber latex in the presence of AZBN as an initiator.



AZBN alone as an initiator shows a different mode of reaction. The incompatibility of AZBN with latex reduces the extent of the reaction and instead causes a yellow mass on the surface of the latex.

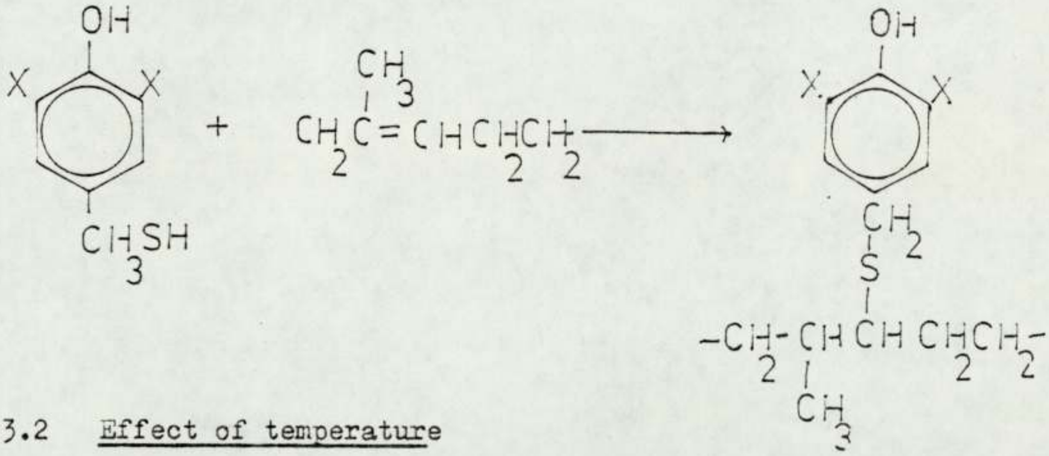
Figure 3.5 Initiator systems



Oxygen absorption of the extracted vulcanisates at 70°C

Again as in the earlier experiment (see page 52) that the reaction of BHBM with rubber latex in the presence of persulphate/ferrous sulphate as an initiator is retarded by the ammonia present in the latex.

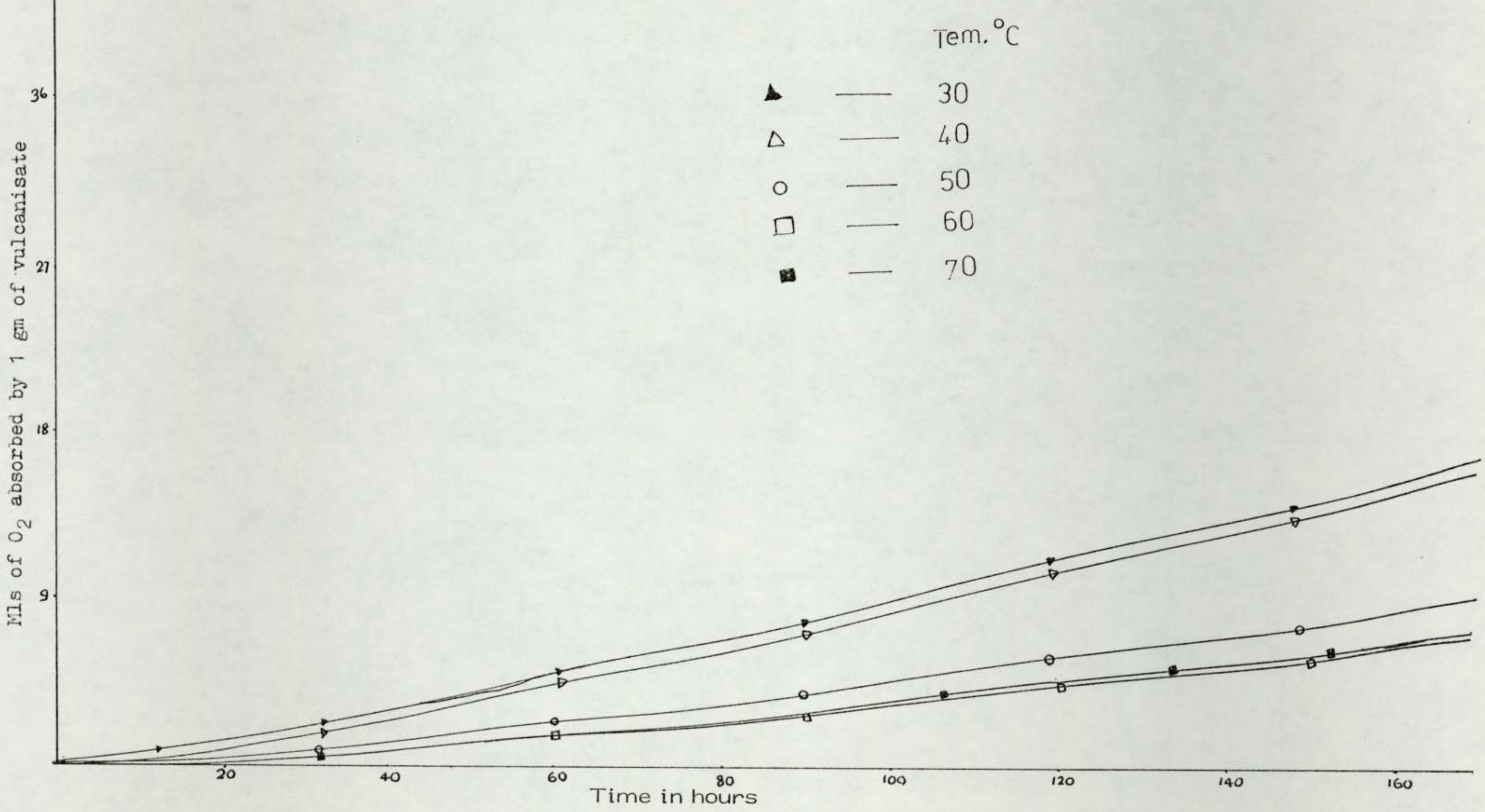
It is obvious from the results shown in table 3.8 that the most efficient initiator system for the reaction of BHBM with rubber latex is TBH/TEPA. The reaction mechanism of this will be discussed in subsequent chapters and it is observed that the thiyl radical as the reactive intermediate. The initiators examined above, do not show any discolouration of the latex. Though, thiols in the presence of powerful oxidising agents form yellowish disulphide, which was not observed in the latex, since the rate of addition of thiols is faster than the formation of disulphides.



3.3.2 Effect of temperature

A set of experiments was carried out at temperatures 30, 40, 50, 60 and 70°C. The experimental procedure was the same as in TBC with natural rubber latex (p.53) and the reactions were carried out for 18 hours in a nitrogen atmosphere. The concentrations of bound BHBM were determined by the I.R method and was confirmed by O_2 absorption tests shown in Fig 3.6

Figure 3.6 Effect of temperature on the reaction



Oxygen absorption of the extracted vulcanisates

Temperature in centigrade	Concentration of BHBM bound in gms/100 gm N.R	% of BHBM bound
30	0.68	34
40	0.74	37
50	1.22	62
60	1.41	70
70	1.42	71

concentration of BHBM used - 2 gm (0.008)/100 gm N.R

Weight of dry rubber content - 100 gm (332 ml of 30% latex)

TBH/TEPA - 1.6 ml/4.5 ml of 10% TEPA

The concentration of BHBM bound vs temperature was plotted and is shown in Fig. 3.7 and the yield is maximal when the temperature is 60°C.

3.2.3 Reaction time

The procedure was the same as in TBC/ natural rubber latex reaction (p.54) The samples were taken out at a time interval of 3 hours and then coagulated, dried and the vulcanisates were prepared for the determination of the BHBM bound.

Concentration of BHBM used - 2 gm (0.008moles)/100 gm N.R

Dry rubber content - 100 gm (332 ml of 30% latex)

TBH/TEPA - 1.6 ml/ 4.5ml of 10% TEPA

Reaction temperature - 60°C

The amount of BHBM bound was estimated by I.R technique and the the maximum bound antioxidant effectiveness was confirmed by oxygen absorption and the curves are shown in Fig 3.9.

Figure 3.7 Bound BHBM vs reaction temperature

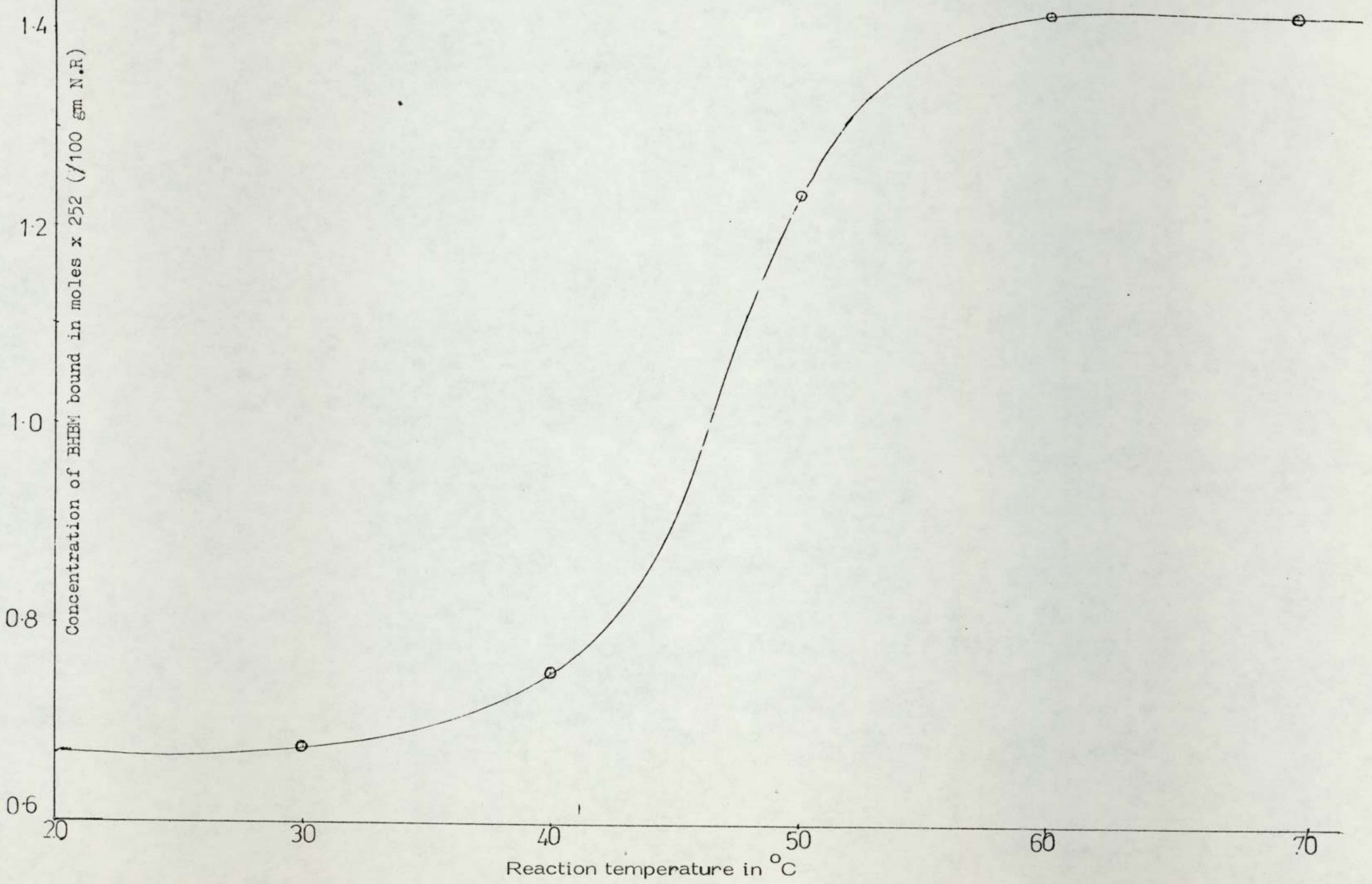


Table 3.10

Reaction time hours	Amount of BHBM bound in gms/	% of BHBM bound
0	*	-
3	0.76	38
6	1.16	58
9	1.40	70
12	1.41	70
15	1.40	70

The concentration of BHBM bound vs time was plotted and is shown in Fig. 3.8. The yield is maximal when the reaction is carried out for nine hours.

3.3.4 Effect of initiator concentration

The experimental procedure was the same as in TBC/N.R latex and the reactions were carried out at 60°C for 9 hours. (see p 55)

Dry rubber content - 100 gm (332 ml of 30% latex)

Concentration of BHBM used - 2 gm (0.008 moles)/100 gm N.R

Table 3.11

TBH concentration in moles/100gm N.R	10% TEPA in mls	Amount of BHBM bound in gms/100gm NR	% BHBM bound
0.004 (0.4 ml)	1.15	0.48	24
0.008 (0.75ml)	2.25	0.74	37
0.016 (1.5 ml)	4.50	1.40	70
0.032 (3.0 ml)	9.00	1.28	64

Figure 3.8 BHBM bound vs Reaction time

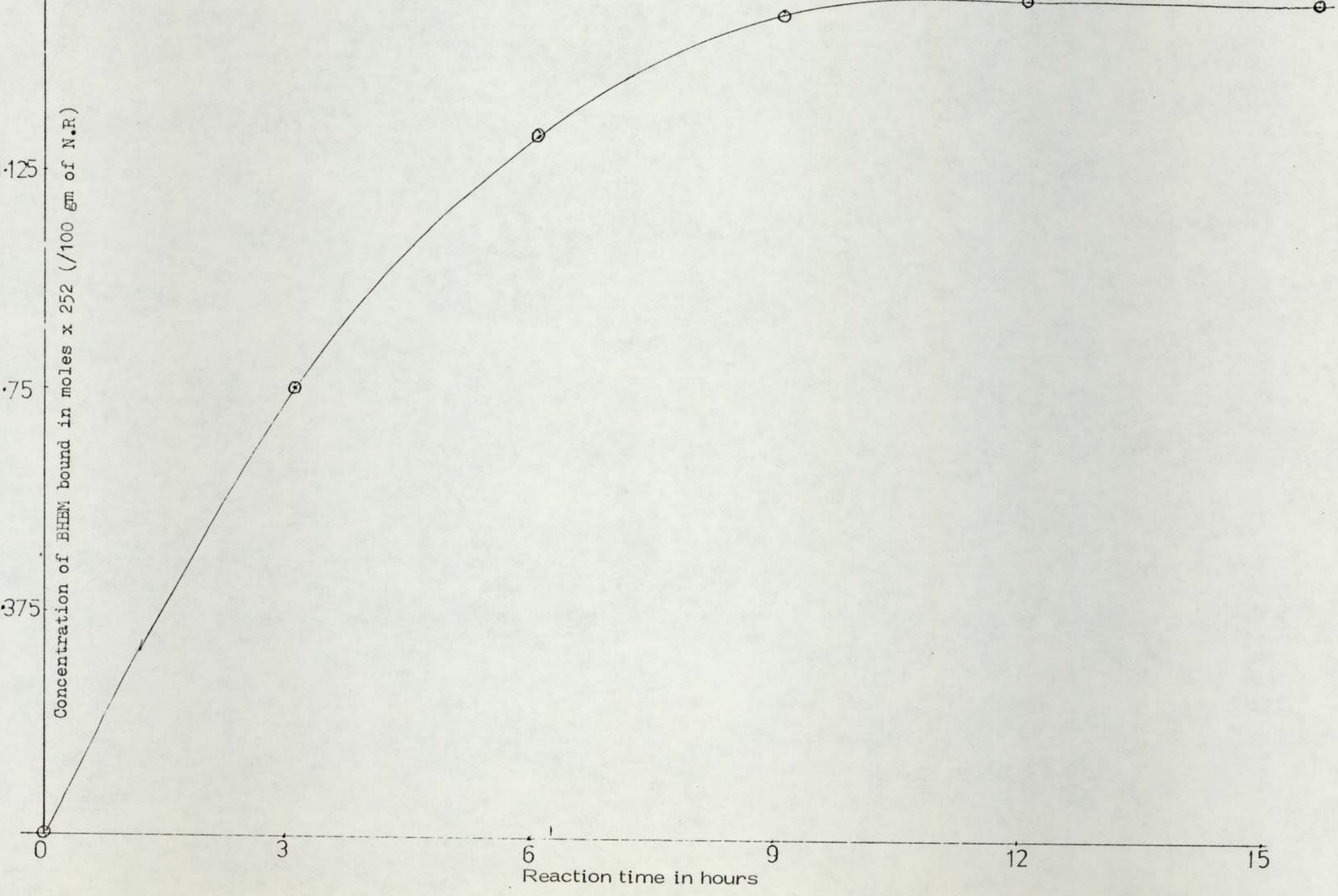
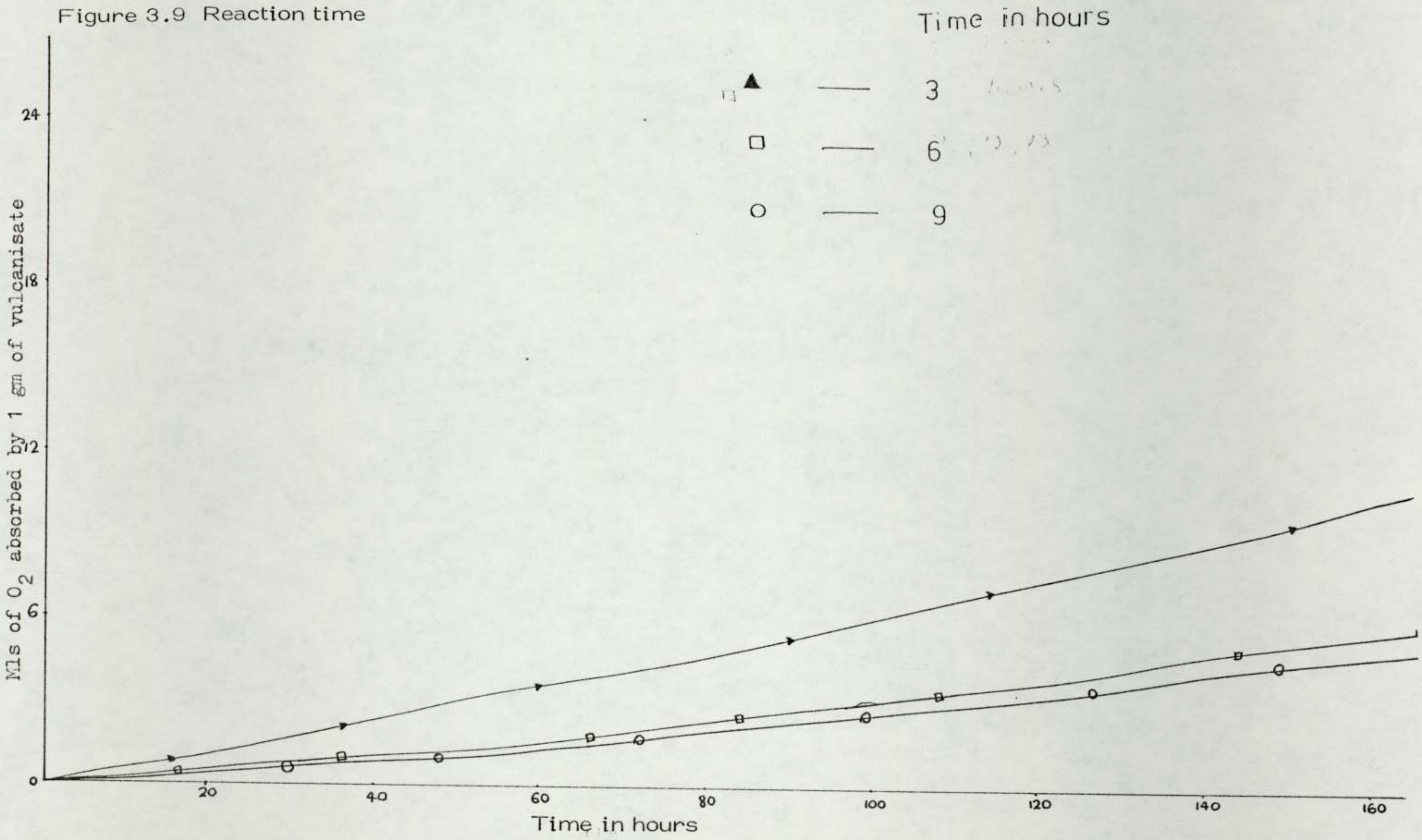


Figure 3.9 Reaction time



Oxygen absorption of the extracted vulcanisates at 70°C

The concentration of BHBM bound vs initiator concentration was plotted and is shown in Fig. 3.11. The oxygen absorption curves are given in Fig. 3.10 The conclusion, which emerges from these data is that the initiator concentration must be varied with respect to the concentration of BHBM in the ratio of 2:1 respectively.

3.3.5 Effect of swelling time

Three sets of experiments were carried out with 2 gm of BHBM and 332 mls of 30% N.R latex at 60°C for 9hours under nitrogen. Before adding the initiator, the BHBM was allowed to swell into natural rubbber latex for a known length of time. The rest of the experiment was the same as in TBC/N.R latex swelling experiments. (See p 55)

Concentration od TBH/TEPA - 1.5 ml/ 4.5 ml of 10% TEPA

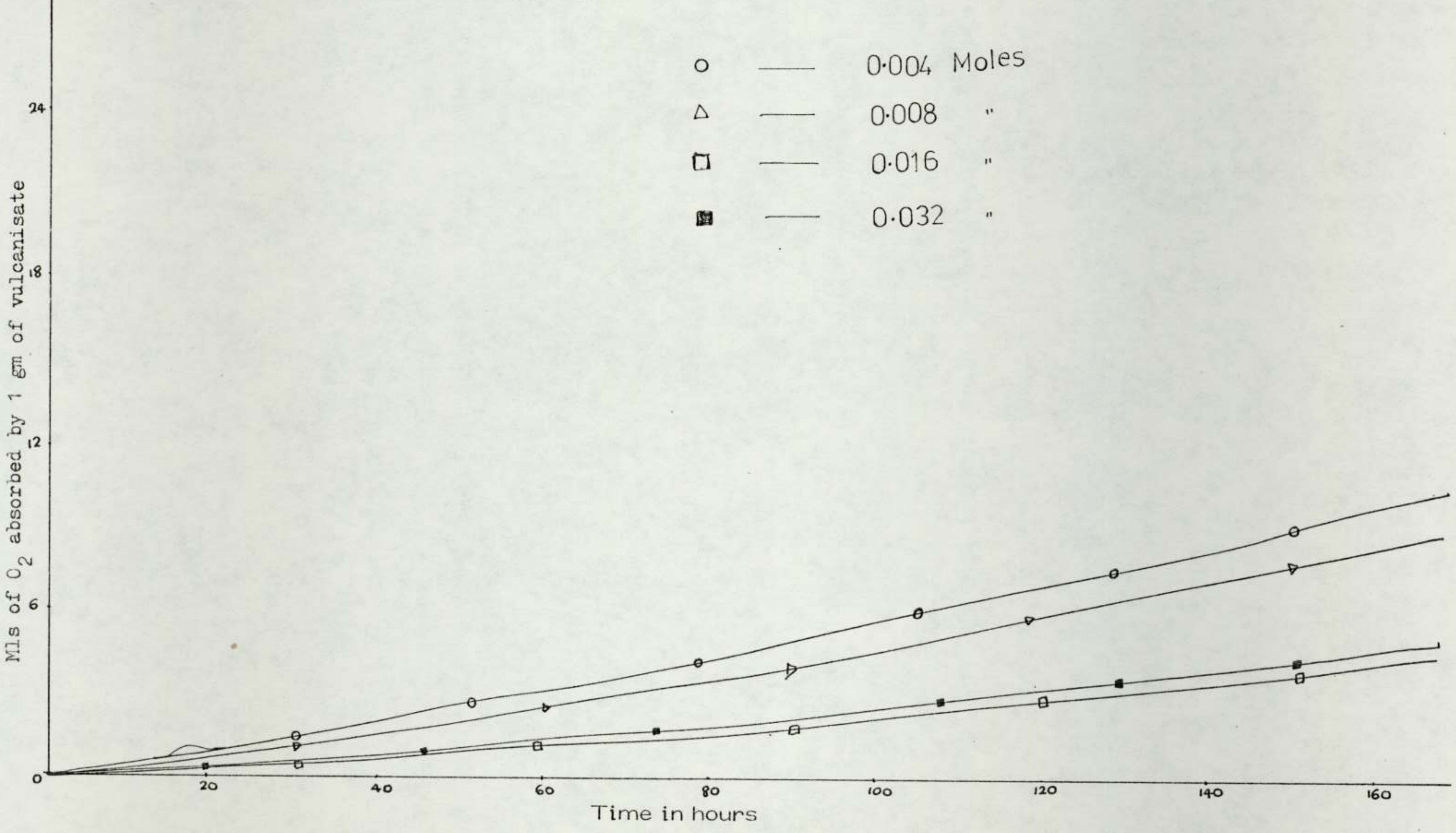
Table 3.12

Swelling time in minutes	Amount of BHBM bound in gms /100 gm N.R	% of BHBMbound
0	0.84	42
15	1.38	69
30	1.40	70

The required swelling time is less than 30 minutes, because the rate of addition of BHBM to natural rubber is faster than TBC and the particles are in emulsion form, which is easy to swell into the network.

The following set of experiments was carried out to study the reaction behaviour of BHBM with natural rubber latex with variation of the thiol concentrations under the above studied optimum reactiom

Figure 3.10 Effect of initiator concentration



Oxygen absorption of the extracted vulcanisates at 70°C

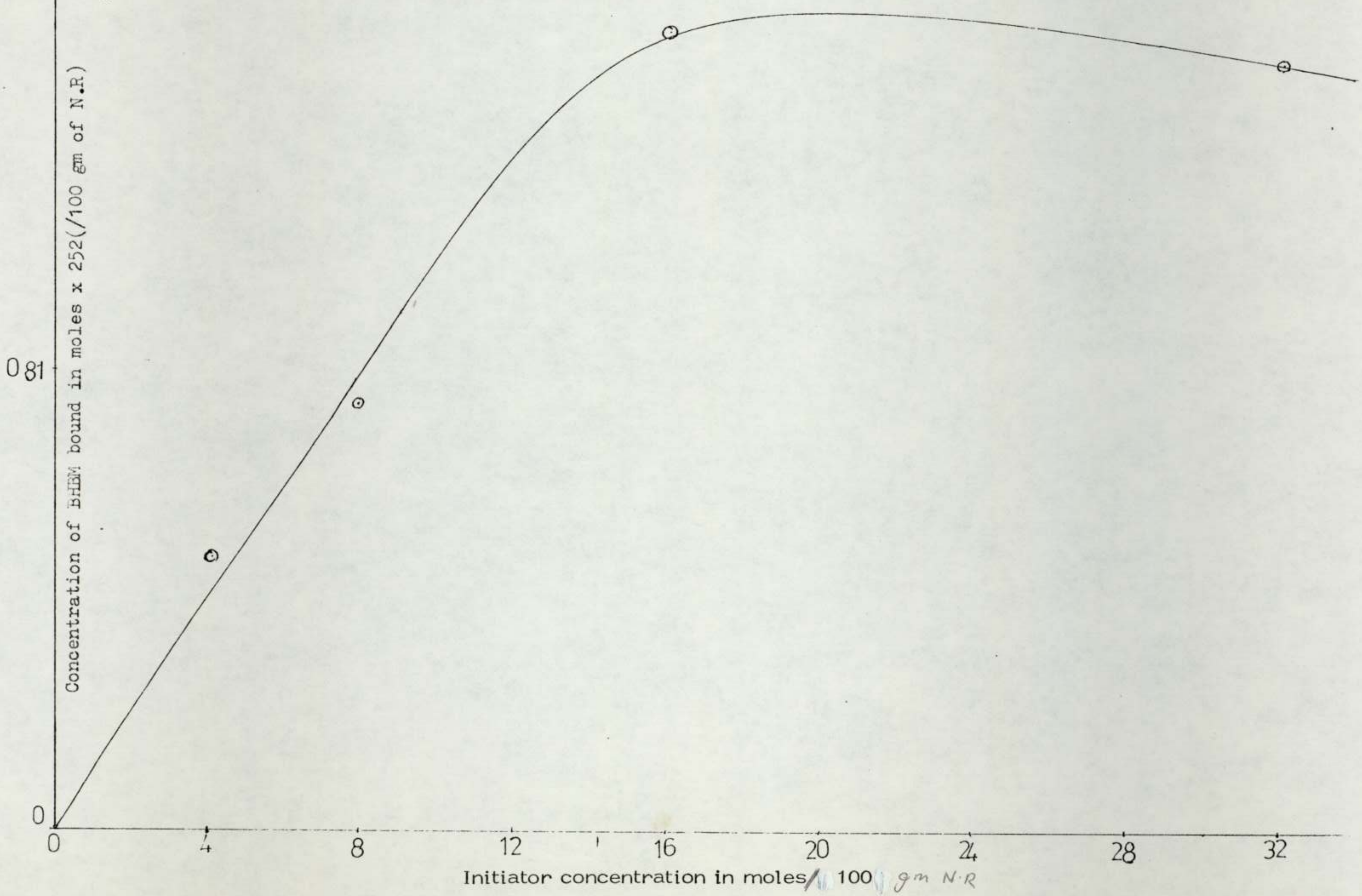


Figure 3.11 BHBM bound vs initiator concentration

conditions. The ratio of TEPA to hydroperoxide was kept constant.

Dry rubber content	-	100 gm (332 ml of 30% latex)
Reaction time	-	9 hours
Reaction temperature	-	60°C

Table 3.13

Concentration of BHBM in moles/100 gm N.R	Initiator concentration in moles/100 gm NR	Mls of 10% TEPA	% of BHBM bound
0.004 (1 gm)	0.012	3.6	72
0.008 (2 gm)	0.016	4.5	70
0.016 (4 gm)	0.024	6.7	67
0.032 (8 gm)	0.040	11.5	65

It is obvious from the above data that the concentration of the initiator must be increased proportionately with that of BHBM. Theoretically one mole of BHBM (252 gm) can be reacted with one isoprene unit of natural rubber, that is 68 gm. According to this, there is a possibility to react 370 gm of BHBM with 100 gm of natural rubber. The amount of BHBM bound is decreased gradually with the higher concentration of BHBM and the initiator, this is probably due to the formation of more oxidised products, such as disulphide , and monosulphide. (see p 56)

3.3.6 Effect of oxygen on the reaction of BHBM with natural rubber latex

A reaction was carried out with 2 gm of BHBM and 100 gm of rubber latex in the presence of air. The rest of the experiment procedure was the same as in previous experiments. At the end of the reaction the bound BHBM of the extracted sample was determined by I.R technique and it was found that 69% of the original BHBM remained bound to the rubber, which reflects that no effect on the reaction in the presence of oxygen or air. The conclusion emerges from this result is that addition reaction is faster than that of the oxidation reaction of BHBM by atmospheric oxygen.

3.3.7 Conclusion

The yield of bound antioxidant obtained in the BHBM reaction is high and it could be used as a polymeric antioxidant for the preservation of natural rubber against oxidation by using concentrates of bound antioxidants as additives in normal latex. (masterbatch technique) The adduct of thiol antioxidants with rubbers give rise to an auto-synergistic effect due to the presence of both a hydroperoxide decomposer (the monosulphide) and a chain breaking function (phenolic) in the same molecule and are in bound form. (structure A) It is not surprising that this structure is considerably more effective as a thermal antioxidant than either a phenol or a sulphide alone.

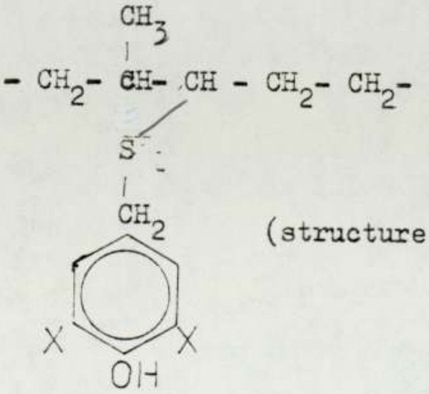
For a successful BHBM -natural rubber bound system, the following reaction conditions are essential.

a) Swelling time of BHBM in latex is more than 15 minutes

b) Reaction temperature ; 60°C

c) Reaction must be carried out for 9 hours

d) Initiator concentration must be increased proportionately to the concentration of BHBM (Ratio 2:1)



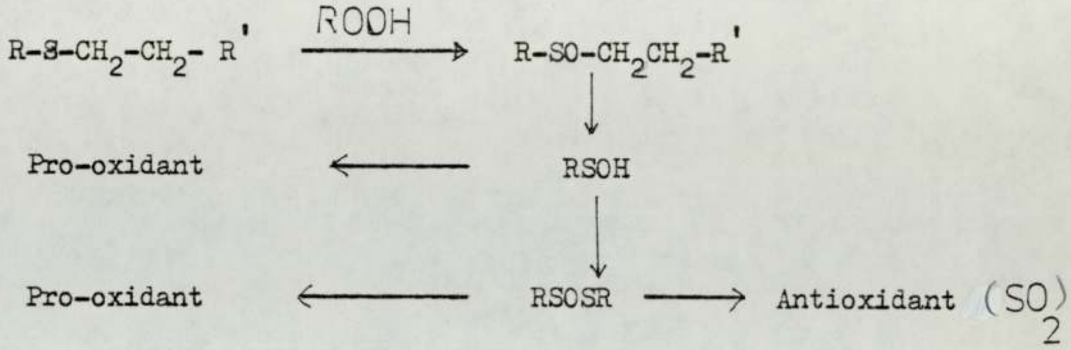
(structure A)

CHAPTER FOUR

4.1 Analysis of the byproducts formed during the reaction of hindered phenols with natural rubber latex.

The inhibition of polymer oxidation can be achieved at least in two ways, 1) by scavenging reactive free radicals, 2) by decomposing hydroperoxide to non radical products. During the inhibition process, the added antioxidants such as, hindered phenols act as radical trapping agents, mercaptans and the related sulphides as hydroperoxide decomposers. The resulting intermediate aryloxy radicals react with other component or rearrange in such a way as to give non radical products. For instance, TBC in the presence of peroxides, oxidise to non radical products such as, 3,5,3',5'-tetra-tert-butyl stilbene 4,4'quinone[18-19], 3,5 ditert-butyl4-hydroxy benzaldehyde[19], etc. The oxidised products of thiols, metal dithiocarbamates, disulphides and monosulphides in the presence of hydroperoxide were investigated by Scott at, al[76 - 78] and Hawkins.[78] They have suggested the following reaction sequence for the thiols, monosulphides and disulphides reactions.

$$\begin{tikzcd}
 & \text{R-SH} \arrow[r, dashed, "\text{ROOH}"] & \text{R-S-S-R} \arrow[d, "\text{ROOH}"] & \\
\text{Pro-oxidant} & & \text{R-S-O-S-R} \arrow[ll] \arrow[r] & \text{Antioxidant } (SO_2)
\end{tikzcd}$$



Stilbene quinones, aldehydes and benzyl alcohols have been identified as the major products during the grafting of DBBA with natural rubber latex.[35] The effect of some of these byproducts as antioxidants has been studied. Again the same byproducts have been observed in the present work by the study of the oxidative reaction of TBC with the model compound 2-methyl-2-pentene and this will be discussed furthur in a subsequent chapter. The data available from these studies is sufficient to explain the mechanism of these reactions with natural rubber and this will be not considered further here.

It is known from previous studies[73-75] that the reactive function of a mercaptan is the thiol group and therefore, the byproducts formed during the reaction with rubber are completely different from those from TBC.

Hydroperoxides such as , cumene hydroperoxide (CHP), and tert-butyl hydroperoxide (TBH) are well known as crosslinking agents for natural rubber[79-80]. As the rubber molecule becomes crosslinked, the molecular weight of the rubber is increased resulting a change in physical as well as chemical properties. The degree of crosslinking depends on the other constituents present and the rate of formation of byproducts.

The following experiments were carried out to study a) the byproducts formed during the reaction of BHBM with rubber latex b) the degree of crosslinking of natural rubber in the presence of the additives BHBM/TBH and TBC/TBH.

4.1.1 Analysis of byproducts during the reaction of BHBM with rubber latex

Thin layer chromotography [81] was employed to identified the products formed during the reaction. This was carried on Poly Gram plastic plates consisting of a 0.25 mm layer of silica gel. The products formed during the reaction of TBC with rubber were extracted from the rubber vulcanisates by using the pure azeotrophic mixture (see chapter 2) and was concentrated by evaporating the solvents. Then 1% solution of this in ether was applied to a 20 x 20 cm silica plate and allowed to dry. The development of the chromatogram was done by the ascending method and the solvent system used was a mixture of benzene, methanol and acetic acid in the ratio 45:8:4 respectively. The plates were then placed inside a solvent tank, which was already saturated with the solvent mixture. Then the solvent mixture was allowed to run till the solvent front reached to certain height and after marking the solvent front, the plates were dried. The separated spots were located by exposing the plates to an iodine atmosphere. To identified the byproducts, known probable compounds were run in parallel with the mixture. The R_f values of the authentic compounds and the mixture were noted.

$$R_f = \frac{\text{Distance moved by the component}}{\text{Distance moved by the solvent}}$$

The authentic samples used were

1. BHBM - preparation was given in chapter 2
2. Bis(3,5-ditert-butyl-4-hydroxy benzyl)monosulphide - Preparation given in chapter 2

3. Bis(-3,5-ditertbutyl-4-hydroxy benzyl) disulphide
(see chapter 2)
4. 3,5,3',5'-tetra tert-butyl stilbene 4,4'quinone
(see preparation below)
5. 3,5-ditert-butyl-4hydroxy benzaldehyde (see preparation below)
6. 3,5-ditert-butyl-benzyl alcohol (see chapter 2)

Preparation of reference compounds:

3,5-ditert-butyl-4-hydroxy benzaldehyde (82)

64 gms (0.4 moles) of bromine was added with stirring to 22.3 gm (0.1 mole) of 2,6-ditert-butyl-4methyl-phenol in 300 ml of tert-butyl alcohol at 25°C. The temperature was raised to 67°C and the stirring was continued for a furthur hour. The mixture was cooled and yellow crystalline product was filtered off. This was then washed with 10% sodium thiosulphate solution, followed by distilled water and was dried in vacuum. The off white crystalline product was obtained. M.P 189°C Yield 80%.

I.R data:

Phenolic OH at - 3620 cm^{-1}
Carbonyl peak at - 1670 cm^{-1}

N.M.R data:

Singlet at-o.2 τ - aldehyde proton
Singlet at 2.8 τ - aromatic proton
Singlet at 5.0 τ - phenolic proton
Singlet at 8.6 τ - tert-butyl proton

3,5,3',5'-tert-butyl stilbene 4,4'quinone (83)

2,6-ditert-butyl-4methyl phenol (11 gm, 0.05 mole) and benzoyl peroxide (12.1 gm) were refluxed in chloroform for 140 hours. The bright red solution was extracted with aqueous sodium hydrogen carbonate, the extract was acidified and benzoic acid was collected. The stilbene quinone was separated by evaporatinf the chloroform and was further purified by washing with ether. This was then recrystallised from glacial acetic acid to reddish needle shaped crystals , which decomposed to a black mass above 300°C.

I.R data:

Peak at 1680 cm^{-1} - congugated carbonyl

Peak at 1600 cm^{-1} - aromatic group

Results:

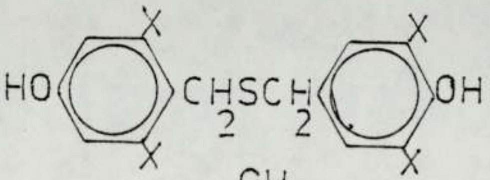
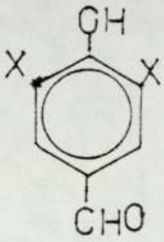
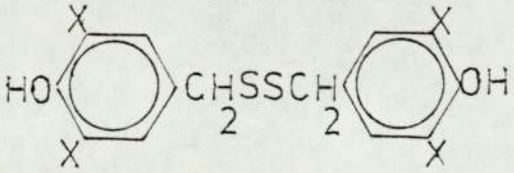
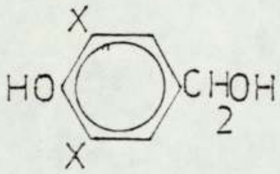
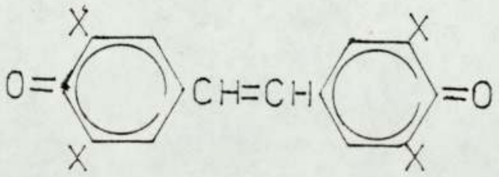
I.R data the concentrated mixture was as follows

Peak at 3620 cm^{-1} - phenolic OH

Peak at 1670 cm $^{-1}$ - aldehyde group

No peak was observed at 2550 cm^{-1} for -SH group

Comparison of the R_f values of the mixture with the reference compounds

R_f values of the reference compounds		R_f values of the mixture
Compound	R_f value	
BHBM	0.96	-
	0.81	0.80
	0.52	0.53
	0.94	0.94
	0.61	-
	0.90	-

I.R data of the mixture was as follows,

Phenolic OH at - $3620\ cm^{-1}$

Aldehyde group at - $1670\ cm^{-1}$

No peak at $2550\ cm^{-1}$ for thiol group (SH)

4.1.4 Results

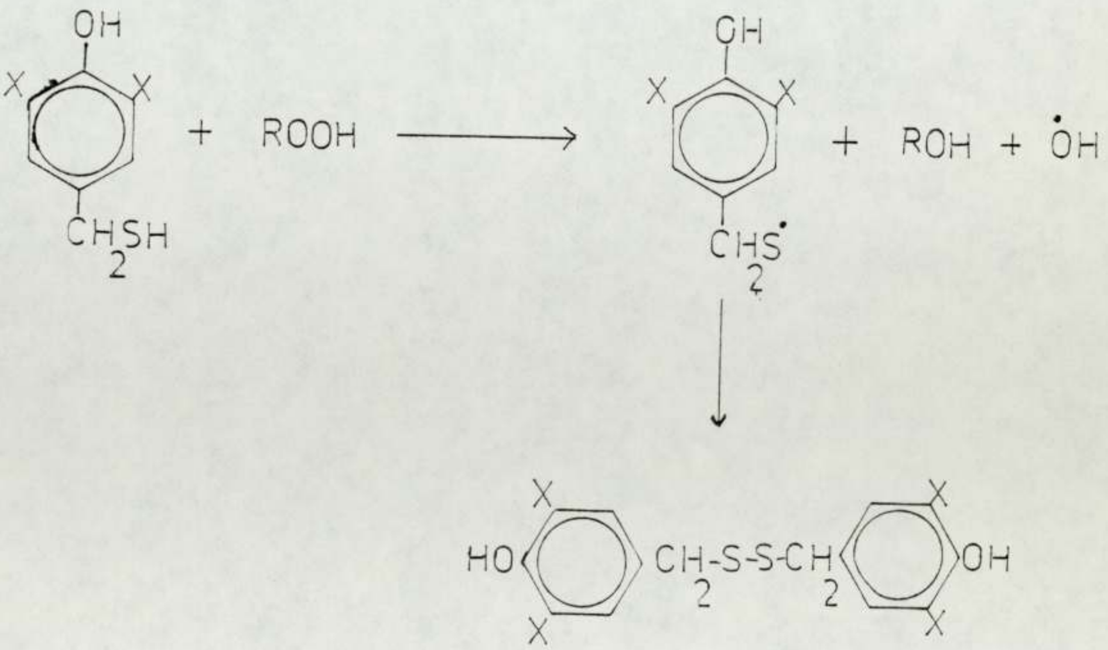
It is clear from the above data that the following compounds are formed during the reaction with rubber latex.

1. Bis (3,5-ditert-butyl-4-hydroxy-benzyl) monosulphide
2. Bis (3,5-ditert-butyl-4-hydroxy-benzyl) disulphide
3. 3,5-ditert-butyl-4-hydroxy-benzaldehyde

The absence of a peak at 2550cm^{-1} confirms that the BHBM had completly reacted and 70% of it has been bound to the rubber network, the remaining 30% for the formation of the above identified byproducts.

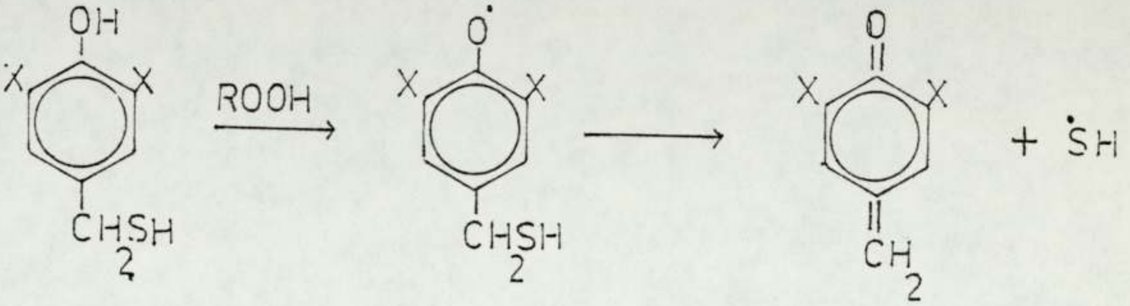
4.1.5 Discussion

Though the rate of formation of the desired adduct is faster than that of the byproducts during the reaction, nevertheless their formation is inevitable. It has been found that thiols are oxidised to disulphides through thiyl radical in the presence of powerful oxidising agents such as peroxides, iodine,[66] etc. Therefore it can be suggested that the thiyl radical is responsible for the formation of the yellowish disulphide and the reaction mechanism can be rationalised as follows.

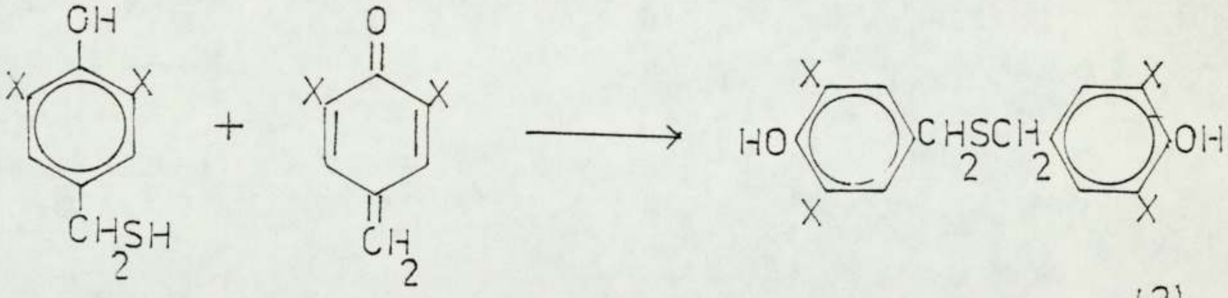


(1)

The order of decreasing intensity of the spots observed on the T.L.C plates was disulphide > aldehyde > monosulphide, which is relevant to the order of the yield of the byproducts. The last two products may be formed via the quinone methide intermediate which originates from the phenoxy radical and is favoured by the efficient elimination of the SH radical.

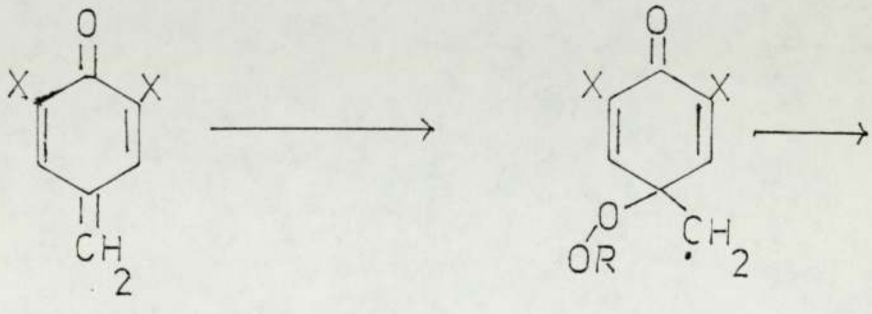


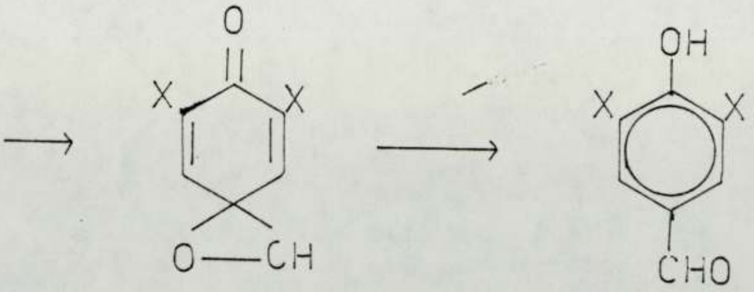
(2)



(3)

The formation of aldehyde again through the quinone methide intermediate, has been explained by Scott[84]





The intermediate thiol radical is more favoured than the phenoxy radical, resulting in high yield of BHBM being bound to natural rubber. According to the above reaction mechanism one can expect stilbene quinone as a byproduct formed from the quinone methide , this was not observed the quinone methide preferentially reacts with the reactive thiol group in BHBM resulting in the formation of monosulphide. (see reaction 3) It has been explained[76-77] that monosulphides and disulphides can undergo a furthur sequence of reactions in the presence of hydroperoxide. But these products such as sulphoxides were not observed as extra spots on the T.L.C plate or by I.R examination. This is probably due to the fact that hydroperoxide was used up in the reactions described above.

4.2 Effect of sulphides in the adduct process

The adduct reaction was carried out with bis(3,5-ditert-butyl-4-hydroxy-benzyl) monosulphide (BHBMS) and bis(3,5-ditert-butyl-4-hydroxy-benzyl) disulphide (BHBDS). These reactions were carried out in order to investigate the effect of these byproducts a) on the reaction b) as potential sources of bound intermediate during ageing of natural rubber.

4.2.1 Reaction of BHBMS with natural rubber latex

The reaction was carried out under following reaction conditions:

Initiator TBH/TEPA - 1.5 ml / 4.5 ml of 10% TEPA
Concentration of BHBMS - 0.008 moles/100 gm N.R
Reaction temperature - 60°C
Reaction time - 18 hours
Swelling time - 30 minutes

The experimental procedure was similar to that described in Chapter 3.

Discussion

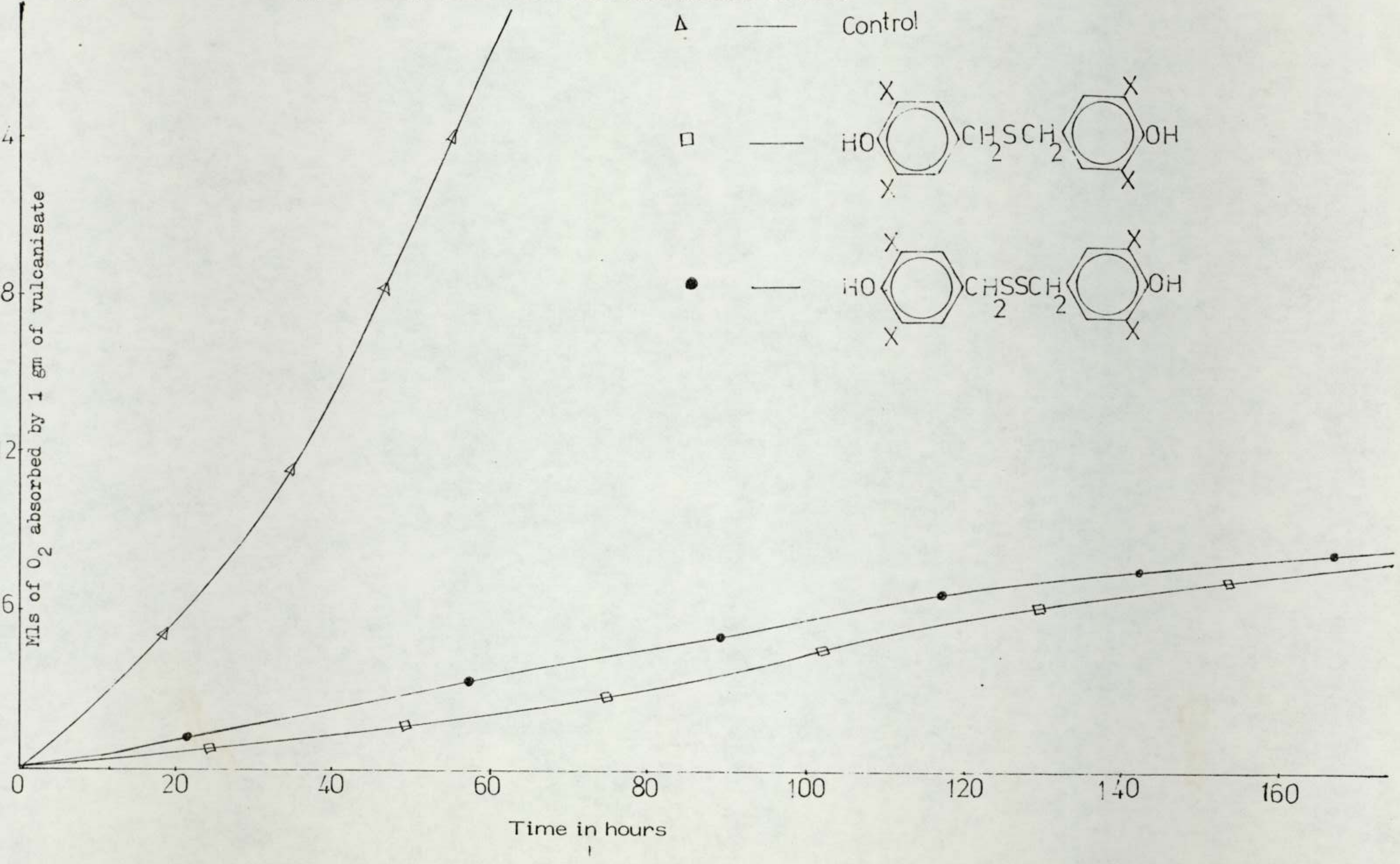
The I.R examination of the extracted vulcanisate shows a peak at 3620 cm^{-1}, which corresponds to the hydroxyl group of the BHBMS and confirms that it undergoes adduct reaction to natural rubber. The peak area of the OH in the I.R of the extracted vulcanisate shows that 25% of the BHBMS has become bound to the rubber. A major disadvantage of the system was the yellowish discolouration of the latex.

The oxygen absorption curves are given in Fig 4.1. The induction period observed substantiates the fact that the BHBMS can undergo the reaction with latex. It seems likely therefore that during the reaction of BHBM with natural rubber latex in the presence of excess TBH, the BHBMS formed as a byproduct can itself become bound to the rubber.

4.2.2 Reaction of BHBDS with natural rubber latex

The reaction conditions and the procedure were similar to that described in last experiment. 0.008 mole of BHBDS dispersion was reacted with 332 ml of 30% latex (100 gm DRC).

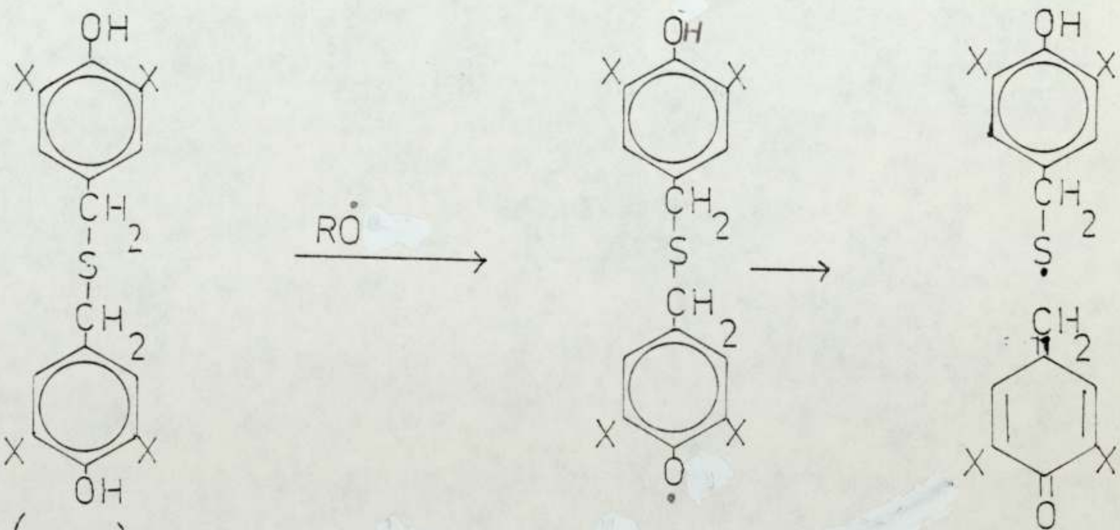
Figure 4.1 Rate of oxygen absorption of extracted vulcanisates at 70°C



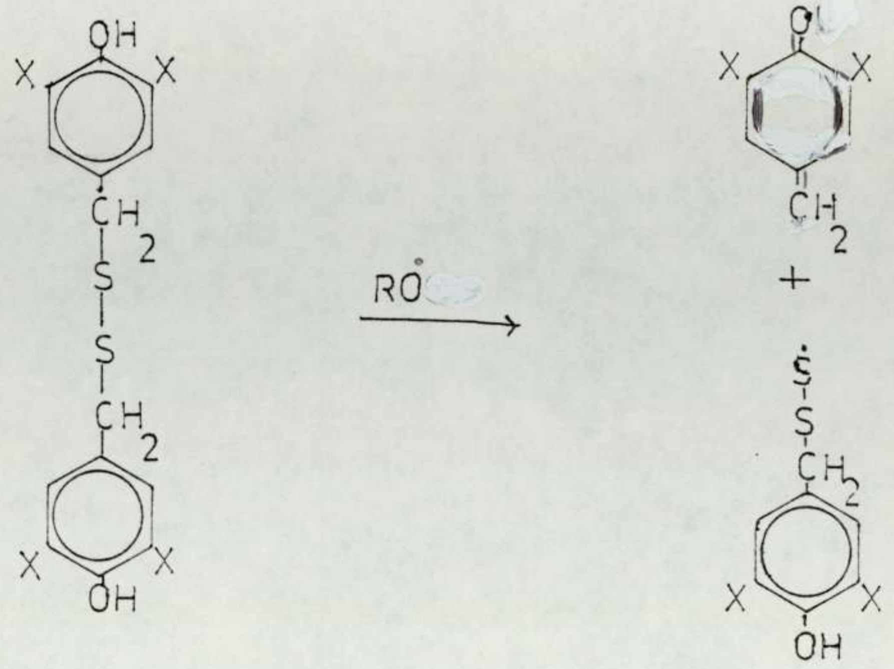
Discussion

I.R data obtained on the extracted vulcanisate shows a peak at 3620 cm^{-1} corresponding to the OH group of BHBDS. This is evidence, that not only the BHBMS but also the BHBDS may be bound to the rubber. However, the peak intensity of the OH peak of BHBDS is weaker than that of BHBMS and indicates that only 10-12% of the BHBDS become bound to the rubber network. Again the major drawback is the discolouration of the latex as in the previous case. The oxygen absorption curves given in Fig 5.1 substantiates the fact that the BHBDS also can react with latex.

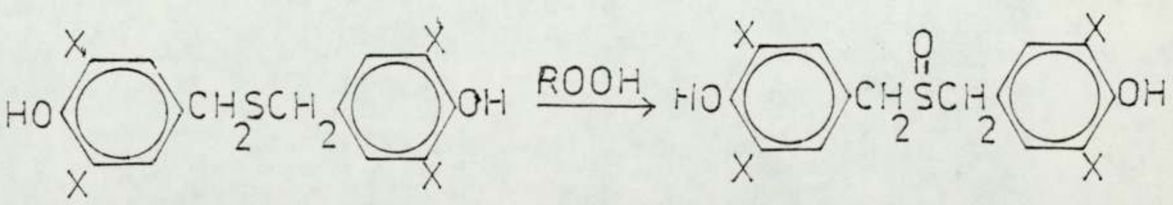
The data available is insufficient to put forward a clear picture for the formation of the adduct. It is obvious from the I.R data that the reactive intermediates of BHBMS are different from that of BHBDS. In the case of BHBMS/N.R both benzyl radicals and thiol radicals can be considered as the intermediates whereas that of BHBDS/N.R possible intermediates are disulphide and benzyl radicals.

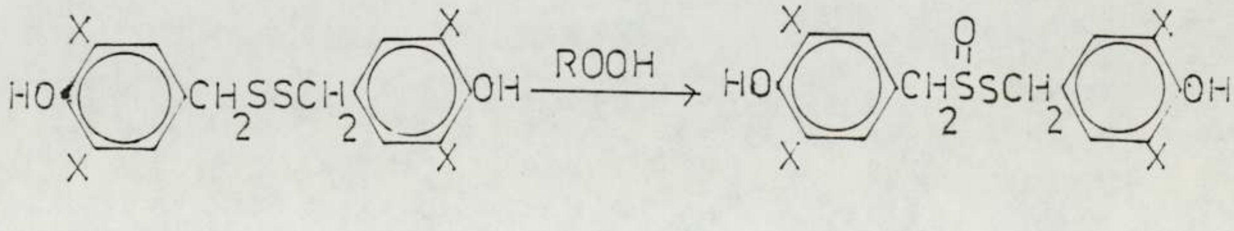


(R_1SR_1)



However, it has been found that[37] the decomposition of hydroperoxides by thiols, BHBMS, and BHBDS are in the same order. Scott and co-workers[76-77] have identified that sulphoxides are the initial byproduct formed during the decomposition reaction, which lead to the formation of other products with hydroperoxide.





4.3 Determination of degree of crosslinking

It is a known fact that hydroperoxides are used as crosslinking agents for rubbers. Therefore during the reaction , the formation of crosslinks are inevitable since the media contain the hydroperoxide as an initiator. The degree of crosslinking also depends on the other constituents present in the system and the rate of formation of the other products during the reaction. The following experiments were carried out to study the degree of crosslinks formed and it's effect on the adduct formation. The degree of crosslink density was determined by the solvent swelling method using the Flory- Rehner equation.[85]

$$-\left(\ln(1-V_r) + V_r + XV_r^2 \right) = pV_oM_c^{-1}\left(V_r^{\frac{1}{3}} - V_r/2 \right)$$

Where $V_r = v_R/(v_S - v_R) =$ Equilibrium swelling ratio

v_R - Volume of rubber

v_S - Volume of solvent absorbed

X - Polymer solvent interaction constant

p - Density of rubber

V_o - Molar volume of solvent

M_c - Inter crosslink molecular weight

The crosslink density is defined as the number of crosslinks per one gram molecule of rubber.

$$\text{Crosslink density} = 1/2M_c$$

4.3.1 Crosslink density of unvulcanised TBC bound natural rubber

A set of experiments was carried out with different concentrations of TBC and 332 ml of 30% deammoniated latex. The concentration of the initiator was varied with the concentration of TBC and the experiments were carried out under the following reaction conditions which had previously been determined (chapter 3).

Reaction temperature - 55°-60°C

Reaction time - 18 hours

Swelling time - 30 minutes

At the end of each experiment the latex was coagulated, dried and was then sheeted to a thin sheet of thickness 0.025 cm. The samples were rewashed to remove traces of formic acid, dried in vacuum and three specimens of dimension 3x3 mm were cut. The specimens were weighed accurately and immersed in hexane at 25°C until swollen to equilibrium at this temperature. (approximately 2 hours, untill a constant weight was reached). Samples were taken out, dried with a filter paper and were transfered to stoppered weighing bottles and were then reweighed. The samples were deswelled under vacuum at 50°C to a constant weight and the difference between swollen and deswollen weight was considered as the weight of hexane absorbed.

The Flory- Rehner equation was used to determined the cross-link density. The volume of the rubber (v_R) and the solvent(v_S) was calculated assuming the density of solvent hexane at 25°C is 0.659 gm/c.c

Density of the rubber - 0.9 gm /c.c

Value of X for natural rubber/hexane at 25°C - 0.513 gm/c.c

4.3.2 Results:

Crosslink density of natural rubber with different concentrations of TBC and initiator

TBC concentration in moles	TBH concentration in moles	% of TBC bound	Crosslink density
0	0	0	0
0	0.009	0	0.69×10^{-4}
0	0.018	0	0.20×10^{-3}
0.0045(1gm)	0.009	17.2	0.20×10^{-4}
0.009 (2gm)	0.018	10.1	0.98×10^{-4}
0.018 (4gm)	0.027	6.4	0.25×10^{-3}

The graphical interpretation of the crosslink density vs initiator in the presence of TBC and the absence of TBC are given in Fig 4.2

4.3.3 Discussion

The results show that as the initiator concentration increases, the percentage of the TBC bound decreases with the crosslink density of the rubber. There are three major competing reactions, which consume the tert-butyl hydroperoxide during the reaction. They are a) reaction of TBC with natural rubber b) the formation of the byproducts c) the crosslinking of the rubber molecules.

The crosslinking of natural rubber in the presence of peroxides such as , dicumyl peroxide and ditert-butyl peroxide have been extensively studied [86] and the following reaction mechanism has been put forward to explain the formation of crosslinks.

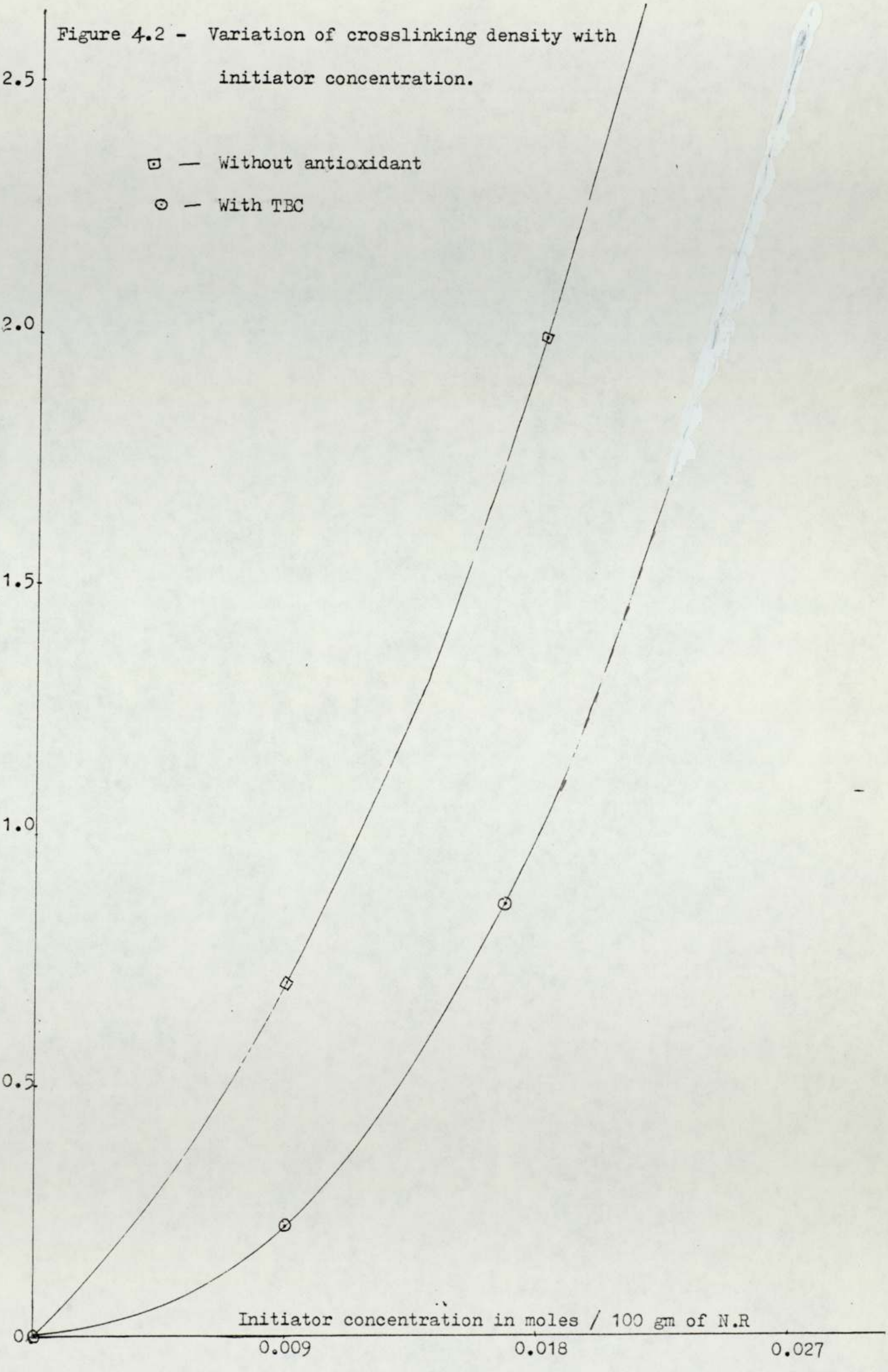
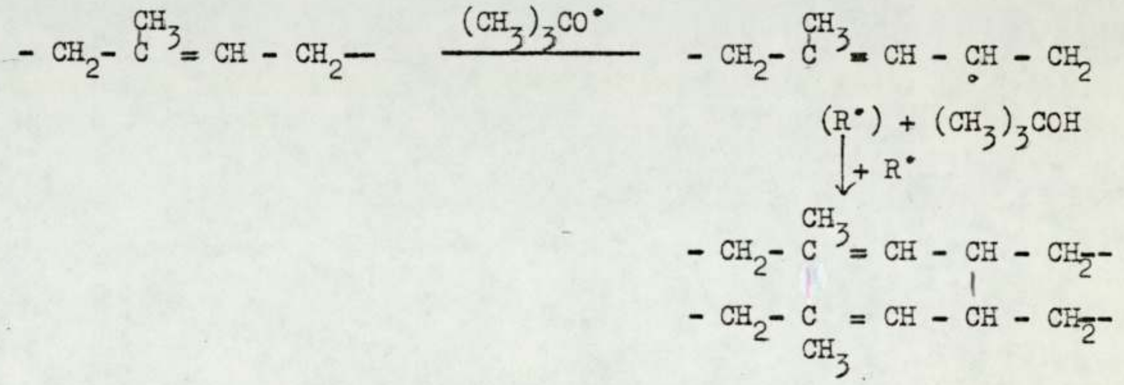


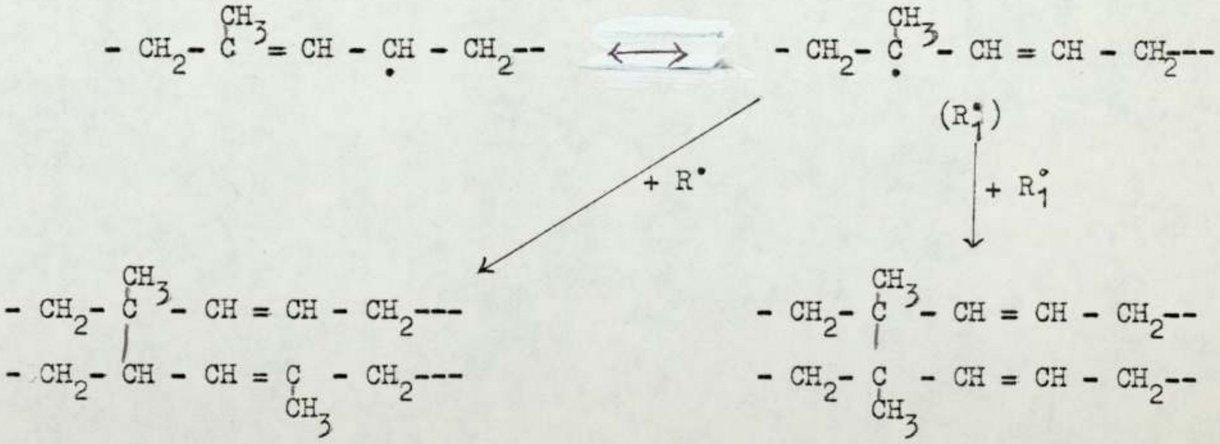
Figure 4.2 - Variation of crosslinking density with initiator concentration.

$$(CH_3)_3\text{-C-O-O-H} \xrightarrow{\Delta H} (CH_3)_3\text{-C-O}^{\bullet}$$

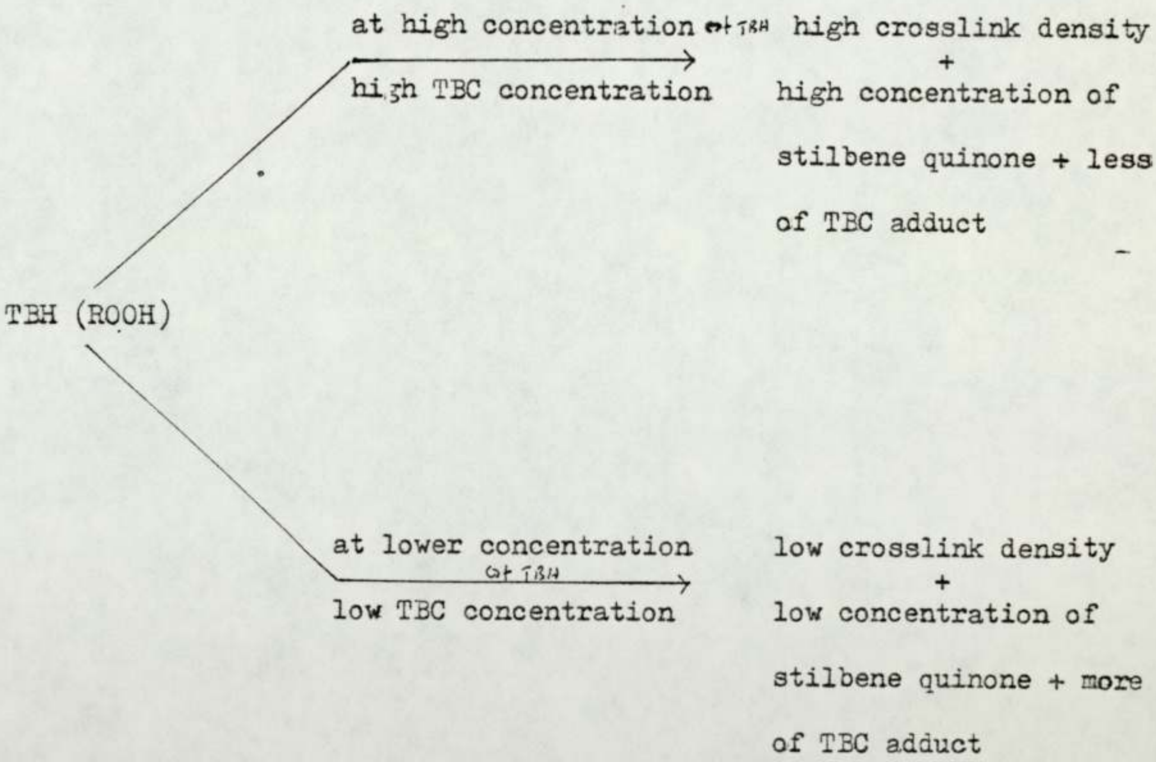
The tert-butoxy radical abstracts hydrogen from the allylic carbon atom, leaving alkenyl radical, which undergoes mutual combination and addition reactions.



or,



The same reaction mechanism holds for the crosslinking of natural rubber with tert-butyl hydroperoxide. The formation of crosslinks is a practical disadvantage in concentrated samples. However, it is obvious from the curves given in Fig. 5.2 that the rubbers without antioxidant (TBC) have been crosslinked to a higher degree than the rubbers with antioxidant (TBC). This clearly indicates that the hydroperoxide is used not only in crosslink formation but also in the reaction of TBC/N.R as well as the formation of byproducts. The schematic diagram given below illustrate the effect of initiator concentration on the reactions involved during the adduct formation of TBC with rubber.



4.3.3 Crosslink density of BHBM bound unvulcanised rubber

The experimental procedure was similar to the one described in last experiment and the reaction conditions were as follows.

Reaction temperature	-	60°C
Reaction time	-	9 hours
Swelling time	-	15 minutes

Three specimens were cut from each samples and crosslink density was determined by using the Flory equation. It was found that the BHBM bound rubber samples were completly dissolved in hexane.

Table 4.3

Crosslink density of BHBM bound rubber

BHBM concentration in moles/100 gm N.R	Initiator concentration in moles/100 gm N.R	% of BHBM bound	Crosslink density
0	0	0	0
0	0.008	0	0.6×10^{-4}
0	0.016	0	0.17×10^{-3}
0.004	0.008	71	0
0.008	0.016	70	0

Discussion:

The complete solubility of BHBM bound rubber in hexane confirms the absence of crosslinked molecule in the network. This clearly demonstrates that the tert-butyl hydroperoxide has been completely used up in BHBM bound reaction and in the formation of byproducts. It is evident from these results that the rate of formation of BHBM adduct is faster than that of the formation of crosslinks. The thiol radicals formed during the reaction immediately attack the double bond of N.R or the other free radical available in the system, which does not give an opportunity for the carbon radicals on the rubber molecule to crosslink with each other.

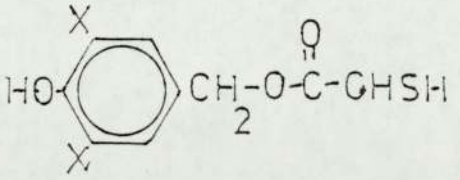
4.4 Determination of unreacted TBH after the bound reaction

At the end of the reaction , the rubber serum after coagulation was tested for unreacted tert- butyl hydroperoxide by the iodiometric method in the case of both TBC and BHBM. One gram of sodium iodide was added to the acidified serum and was heated for few minutes. It was found that the colour of the mixture remained colourless and is concluded that the TBH has been utilized in both reactions.

4.5 Reaction of thiol esters with natural rubber latex

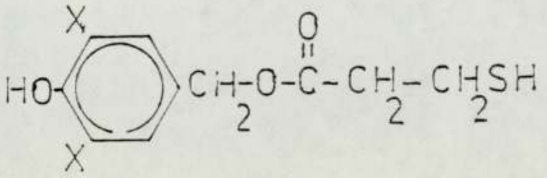
The reactions of following two thiol esters were carried out with natural rubber latex.

a). 3,5-ditert-butyl-4-hydroxy-benzyl-thio-glycolic ester



(BTGE)

b). 3,5-ditert-butyl-4-hydroxy-benzy-thio propionic ester



(BTPE)

The procedure was similar to that described in the BHBM/natural rubber reaction. 2 gm of the thiol ester dispersion was reacted with 332 ml of 30% latex at 60°C for 12 hours under a nitrogen atmosphere. The latex was then coagulated, dried and was extracted. The I.R technique was used to estimate the amount of ester bound and their effectiveness as antioxidants were studied by oxygen absorption test. Curves are shown in Fig 4.3

4.5.1 Results and discussion

The presence of the peak at 3620 cm^{-1} after extracting both the vulcanisates, confirms that the thiol esters can be bound to rubber under similar conditions to those used for BHBM. Measurement of the hydroxyl peak by I.R shows 57% of the adduct formation based on thiol (BTPE) whereas carbonyl indicates 20%. The disagreement between the results can be accounted for interms of masking of the carbonyl peak by other peaks, (see figure 4.4) leading ~~to~~ incorrect carbonyl estimation. The hydroxyl peak on the other hand, was clear and distinct (see figure 4.4), therefore the grafting of 57% is more acceptable and is in accord with the results obtained for BHBM. Oxygen absorption supports the idea that the propionic ester is more effective than ~~the~~ glycolic ester and by analogy of BHBM, the structure of the ester bound rubbers can be represented as follows.

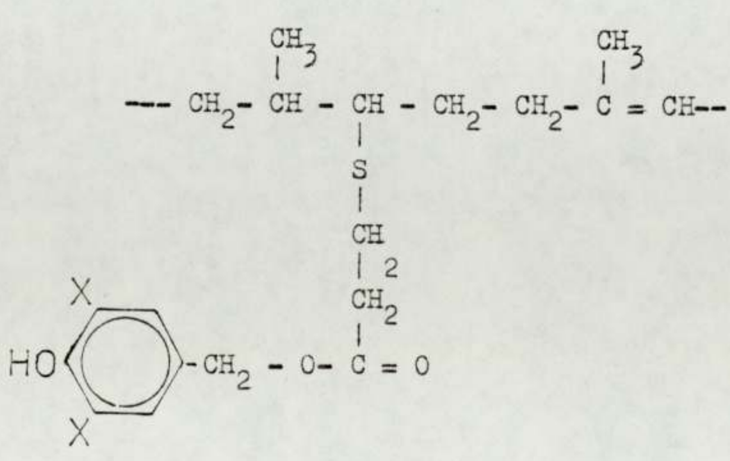
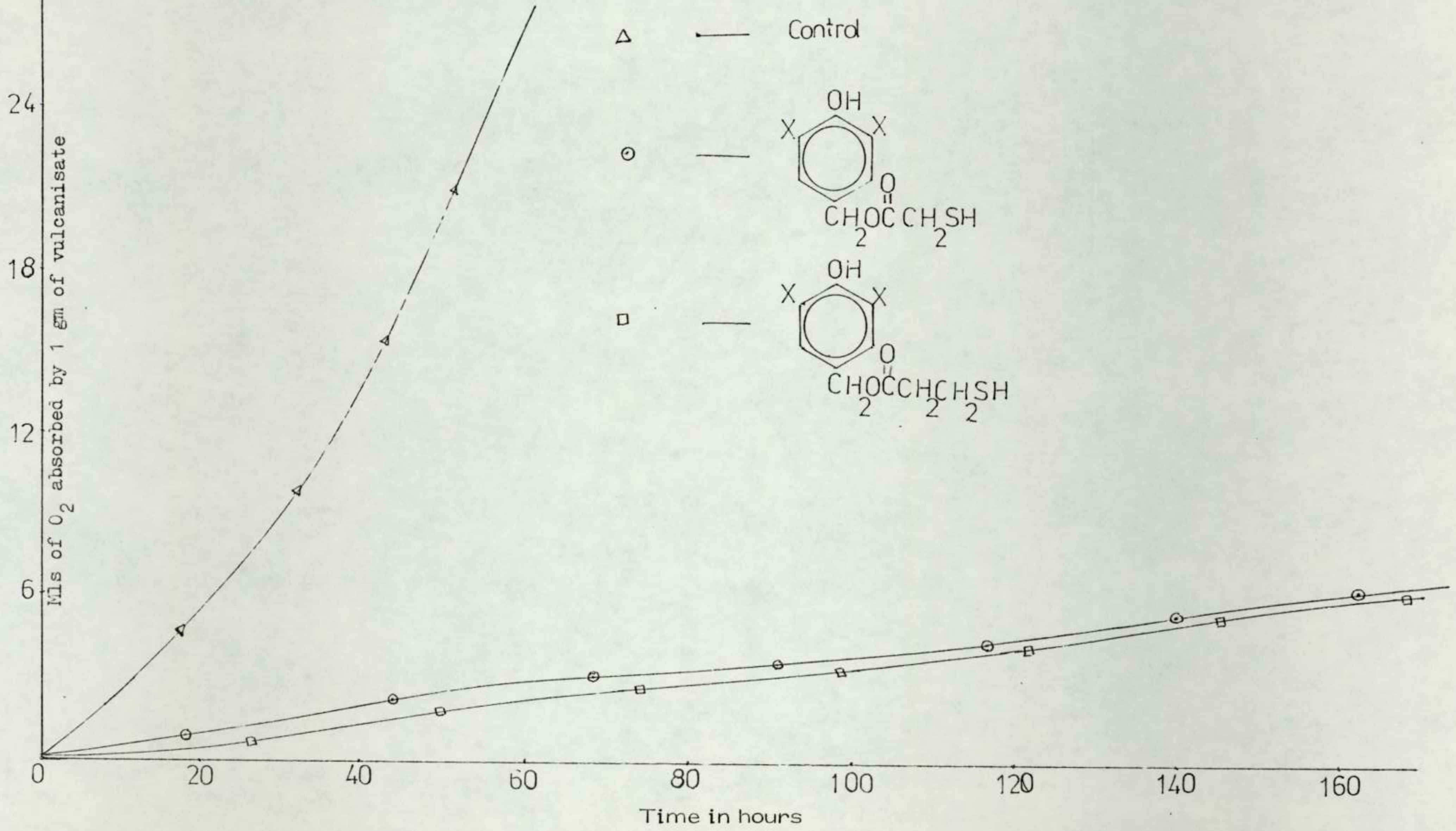
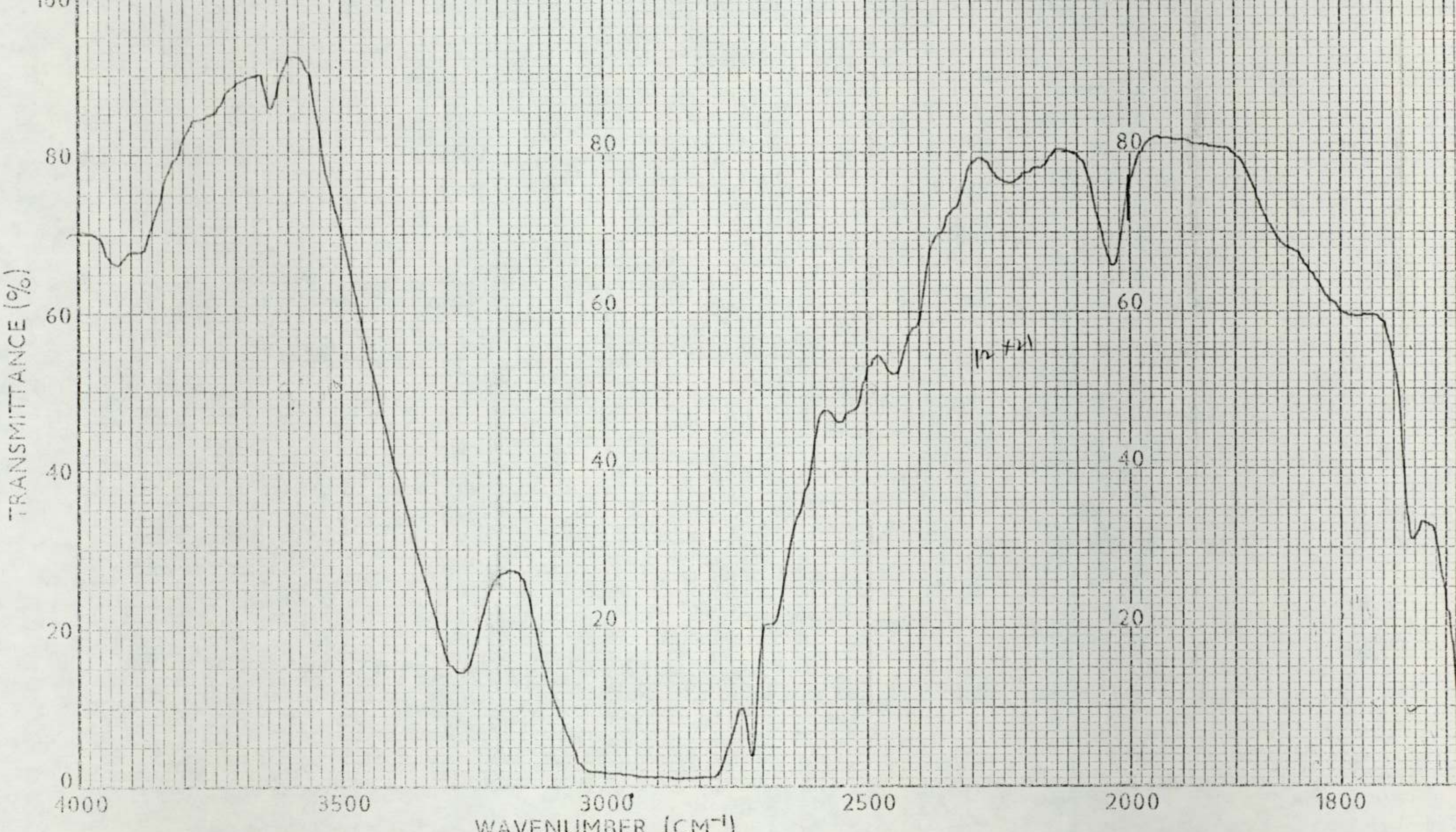


Figure 4.3 Rate of oxygen absorption of the extracted vulcanisates at 70°C





SAMPLE Extracted $RCH_2OCOCH_2CH_2SH$ {2/100} N.R
vulcanizate

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

There is evidence for the relative effectiveness of the thiol esters such as , thiodipropionic esters, when used alone as stabilisers in polymers. Recent research by Shearn[87] has shown that they are powerfully synergistic with phenolic antioxidants. The reason for this apparently low activity of the sulphide, when used alone is associated with initial pro-oxidant effect. In combination with phenolic antioxidants the pro-oxidant effect is reduced resulting in powerful synergistic behaviour.

CHAPTER FIVE

MODEL COMPOUND STUDIES

The difficulties involved in studing the mechanisms of chemical reaction in polymers are mainly related to the complexity of the polymer network. Consequently simple chemical or physical procedures cannot be used in evaluating the behavior of polymers during autoxidation. The study of analogous compounds of lower molecular weight is an obvious technique for overcoming these difficulties. Knowledge of the steps involved in the oxidation and degradation of high polymers has emerged from the model compound studies mainly from the work by Farmer, Bolland and their coworkers at NRPRA,[88] in the field of natural rubber and Green Cole, at al, and Shelton[89] in the field of synthetic rubber.

In general these studies include the determination of a) the major end products that are formed and b) the most probable mechanism by which they were formed. For instance, workers in NRPRA successfully studied the end products of the reaction of N,N-diethyl-p-nitrosoamine with 2-methyl-2 pentene to derive the mechanism for the same compound with natural rubber. Similar studies were carried out by Scott and coworkers to study the mechanism of the addition of hindered phenolic nitrones and amine nitrones to natural rubber.[32] Similarly model compound studies of BHBM with natural rubber has also been investigated.[36] The same technique was used in tetralin to study the antioxidant behavior of polypropylene antioxidants.[90]

In the present study, this technique has been used to investigate the mechanism of the following reactions.

a) Reaction of 2,6-ditert-butyl-4methyl phenol with natural rubber.

b) Reaction of (3,5-ditert-butyl-4hydroxy) benzyl acrylate with natural rubber to complement the work done by Amarapathy.[35]

c) Reaction of BHBM with natural rubber using tert-butylhydroperoxide as initiator.

5.1.1 Reaction of TBC with 2-Methyl-2-Pentene

Procedure:

2 gm (0.009 mole) 2,6-ditert-butyl-4-methyl phenol was dissolved in excess (10 gm) of 2-methyl-2-pentene (98%) in a three necked flask fitted with a reflux condenser, thermometer and a dropping funnel. The temperature of the mixture was maintained at 55°C- 60°C and then 1.6 ml of tert-butyl hydroperoxide was added slowly, followed by 4.5 ml of 10% tetraethylpentamine solution. The solution was refluxed for 24 hours under N_2 atmosphere.

At the end of the experiment, the lower boiling fraction at 100°C was collected by distillation and was identified by gas liquid chromatography. The results are shown below.

The remaining reddish product was washed with distilled water and was then dried under vacuum. Column chromatography was employed for the separation of the solid mixture. The polarity of the solvent system was varied gradually from redistilled pet-ether to methanol. Silica gel, which was previously washed with ether and dried was used as the separating medium of the column.

The reddish residue was dissolved in methanol and was then eluted through the packed silica gel column by varing the polarity of the solvents from pet-ether to methanol as eluent. Each 10 ml of the eluents were tested by thin layer chromatography for the pure components. By this method six major components were collected. The minor components observed on the T.L.C plates were insufficient for further analysis. The yield, melting point and spectroscopic data are listed below.

First Component:

White crystalline product -M. P. 67-68°C Yield 62%

I.R. Data:

Phenolic - OH at 3620 cm^{-1}

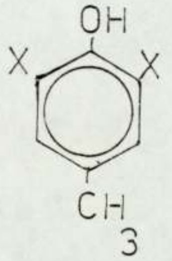
N.M.R. Data:

Singlet at 2.9 τ	aromatic protons
Singlet at 5.4 τ	phenolic proton
Singlet at 8.9 τ	tert-butyl protons
Singlet at 7.2 τ	methylenic protons

Mass Spectrum:

peaks appeared at 220, 219.

The probable structure is unreacted 2,6-ditert-butyl-4-methyl phenol



Second Component:

Lightly yellow crystalline product - M.P. 84°C, yield < 0.2 gm. (2%)

I.R. Data:

Phenolic - OH at 3620 cm^{-1}

Olefinic double bond at 1640 cm^{-1}

N.M.R. Data:

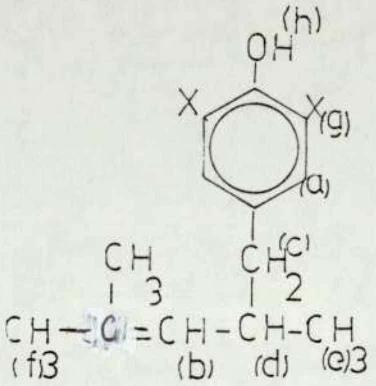
a,	Singlet at 3.0 - 3.1 τ	aromatic protons
b,	Doublet at 4.5 τ	olefinic proton
c,	Doublet at 7.8 - 7.9 τ	methylenic protons attached to aromatic ring.
d,	Multiplet at 8.3 - 8.4 τ	proton at allylic position

e, doublet at 9.0 τ	protons of [illegible] - CH_3 groups
f, doublet at 8.5 τ	2 - CH_3 groups attached to double bond.
g, Singlet at 8.8 τ	tert-butyl protons
h, Singlet at 5.4 τ	phenolic proton

Mass Spectrum:

Parent peaks appeared at 302,219,83

The probable structure is



Third Component:

Yellowish needle shaped crystals. On exposed to air gradually turned to reddish orange product. Melting point - decomposed > 300°C. Yield < 0.1 gm. This was preserved in a sealed tube to prevent oxidation.

I.R. Data:

Phenolic - OH at 3620 cm^{-1}

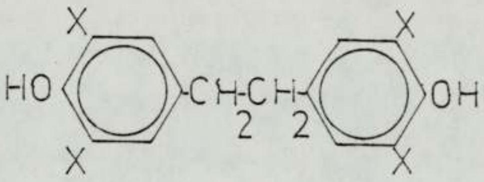
N.M.R. Data:

Singlet at 3.0 τ	aromatic protons
Singlet at 5.4 - 5.5 τ	phenolic proton
Singlet at 7.1 τ	methylenic protons
Singlet at 9.1 τ	tert-butyl protons

Mass Spectrum:

[illegible] peak appeared at 219.

The probable structure :



Fourth Component:

Sparkling white crystalline solid, M.P. 137°C, Yield < 0.1 gm.

I.R. Data:

Phenolic - OH at 3620 cm^{-1}

Hydrogen bonded - OH at 3500 cm^{-1}

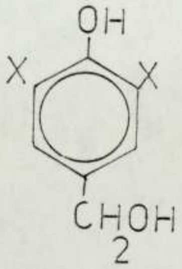
N.M.R. Data:

Singlet at 3.0 τ	aromatic protons
Singlet at 5.4 τ	phenolic proton
Singlet at 6.8 τ	methylenic protons
Singlet at 8.9 τ	tert-butyl protons
Singlet at 4.2 τ	hydroxyl proton

Mass Spectrum:

[illegible] peaks at 236,219 .

Probable Structure :



Fifth Component:

Off white crystalline product, M .P 189°C, yield o.26 gm.

I.R.Data:

Phenolic - OH at 3620 cm^{-1}

Carbonyl peak at 1670 cm^{-1}

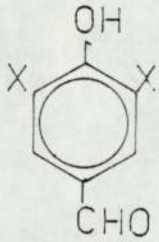
N.M.R.Data:

Singlet at 3.0 τ	aromatic protons
Singlet at 5.2 τ	phenolic proton
Singlet at 8.9 τ	tert-butyl protons
Singlet at -0.2 τ	aldehydic proton

Mass Spectrum:

[illegible] peak at 234.

The probable structure;



Sixth Component:

Reddish needle shaped crystals, yield 0.2 gm. Decomposed on heating to a black mass above 300°C.

I.R.Data:

Carbonyl peak at 1680 cm^{-1}

Conjugated aromatic peak at 1600 cm^{-1}

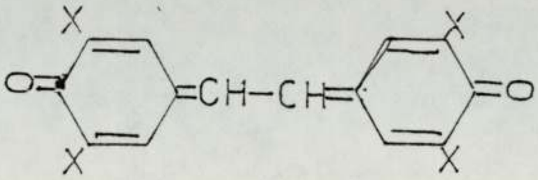
N.M.R.Data:

Multiplet at 2.0 - 3.5 τ	protons of aromatic conjugated system
Singlet at 8.5 τ	tert-butyl protons

Mass Spectrum:

[illegible] peaks at 434, 217.

The probable structure:

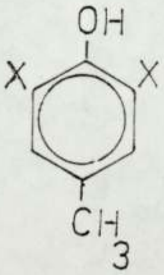


The low boiling products were identified by G.L.C. The retention times obtained from the mixture were the same as for the retention times of 2-methyl-2-pentene and tert-butyl alcohol.

Retention times of the mixture: 4.35, 4.25 minutes.

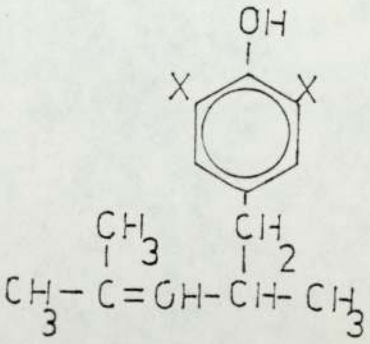
Retention times of pure redistilled 2-methyl-2-pentene and tert-butyl alcohol - 4.25 and 4.35 minutes respectively.

The following compounds were identified as the products of the reaction of 2-methyl-2-pentene with TBC.



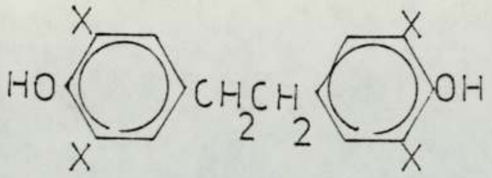
2-6-ditert-butyl-4-methyl phenol

Yield (%): 60



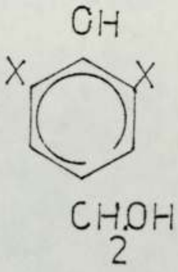
2,methyl-4-(benzyl-3'-5'ditert-butyl -4-hydroxy)-2-pentene

yield (%): < 10



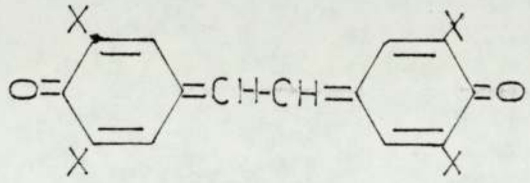
Bis-(2,6-ditert-butyl benzyl phenol)

Yield (%) : < 5



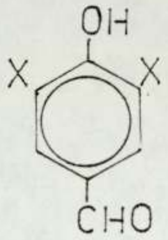
3,5-ditert-butyl-4-hydroxy

benzyl alcohol, yield (%): 5



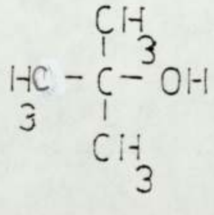
Stilbene quinone

Yield (%): 10



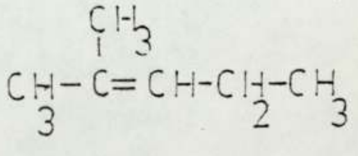
3,5-ditert-butyl-4-hydroxy

benzaldehyde, yield(%):13



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

Tert-butyl alcohol

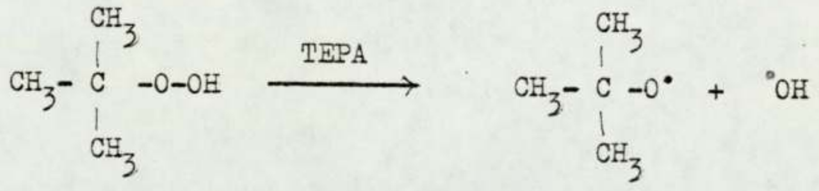


$$CH_3-\overset{CH_3}{C}=CH-CH_2-CH_3$$

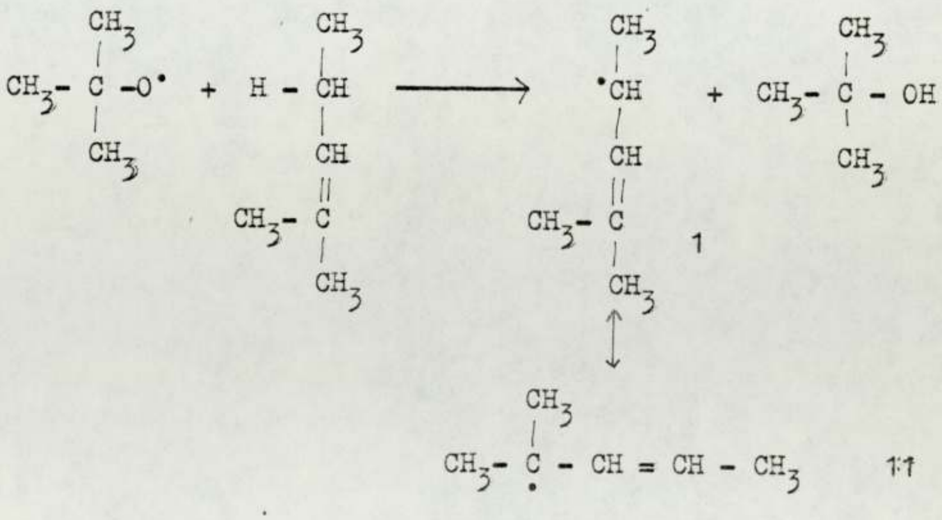
Unreacted 2-methyl-2-pentene

5.1.3 Discussion

At the end of the reaction, 60 % of TBC remained unreacted and only 10 % of the TBC reacted with 2-methyl-2-pentene. The results is in accord with the reaction of TBC with natural rubber. Therefore one can suggest that the rate of the reaction is slow, even in organic solvent medium. However, the second component throws light on the reaction mechanism of the formation of TBC bound rubber, as well as understanding the ageing behavior of the bound antioxidants. It is obvious from the data available that the reactive part of the 2-methyl-2-pentene is the allylic hydrogen. This is directly attached to the 4-methylenic position of TBC and is not formed by addition reaction of TBC to the double bond. According to the above identified compounds, the plausible reaction mechanism is as follows.



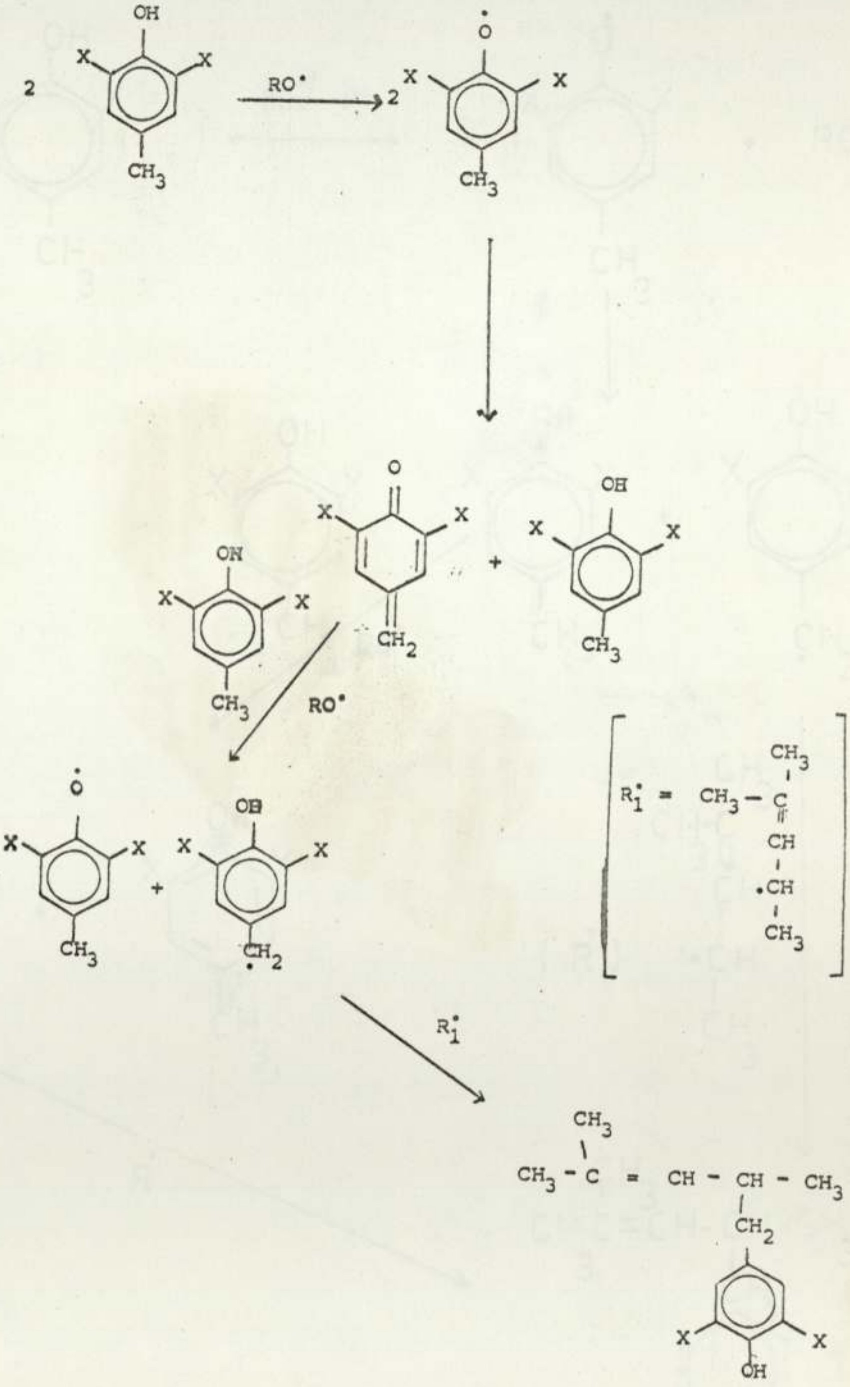
$$(CH_3)_3C{-}O{-}OH \xrightarrow{TEPA} (CH_3)_3C{-}O^{\bullet} + {}^{\bullet}OH \qquad -(1)$$



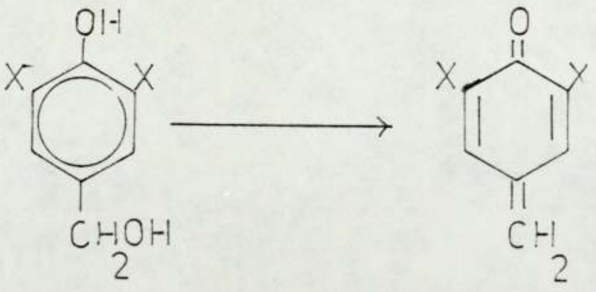
1

11

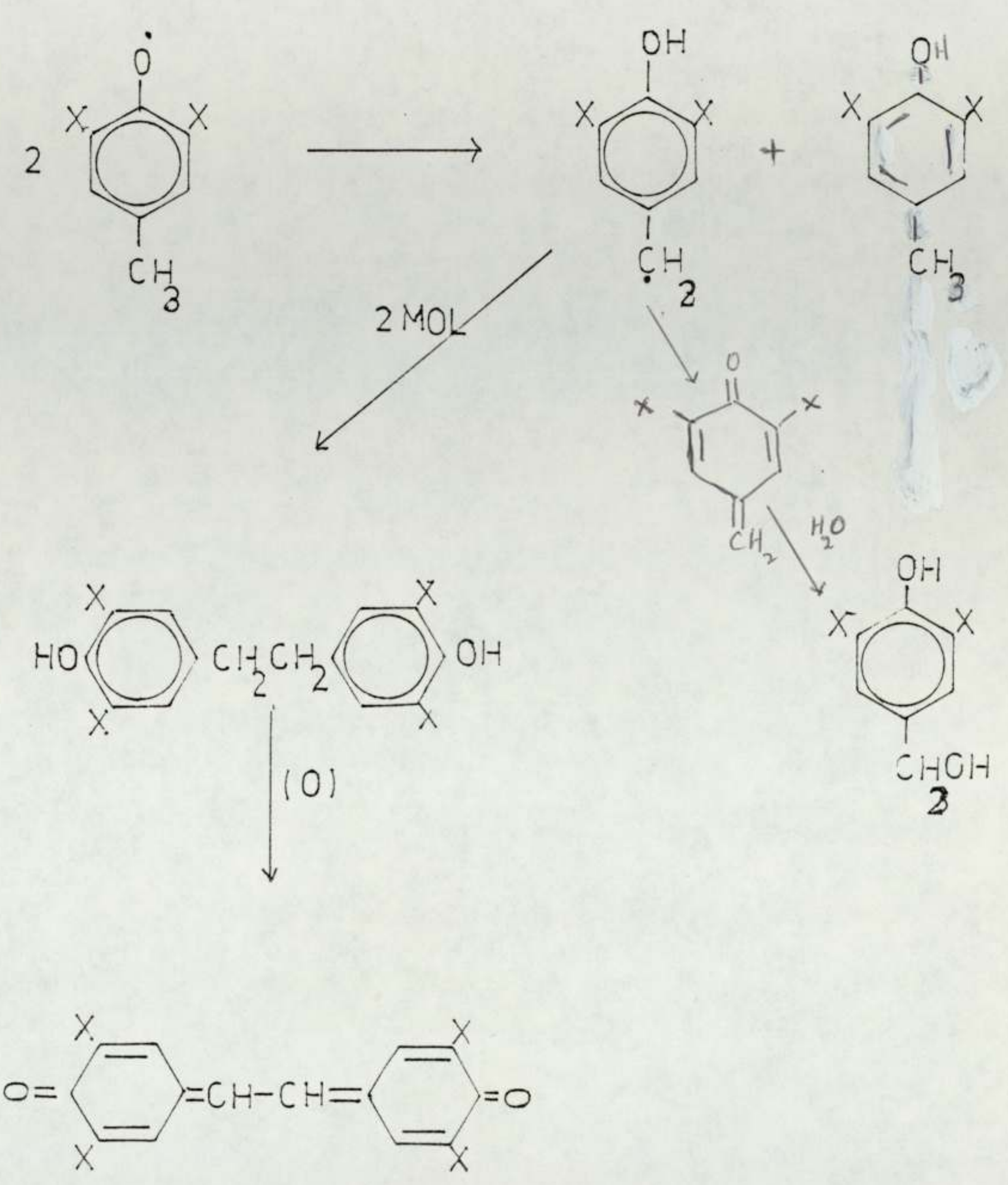
The formation of tert-butyl alcohol was identified by G.L.C. The structure (1) is stabilised by resonance as shown above, but the attachment of TBC to the stable (11) radical was not observed. This is probably due to the steric hinderance created at the carbon atom by the two methylenic groups, and the size of the TBC radical. The intermediate quinone methide may be responsible for the attachment of 4-methylinic group to the 2-methyl-2-pentene and can be represented as follows.



There is considerable evidence for the existence of the quinone methide intermediate as well as the intermediate benzyl radical. Filar and Winstein[23] have attempted to prepare the quinone methide by shaking a solution of TBC with lead dioxide or silver oxide. The resulting product formed was found to be stilbene quinone. This led them to suggest that the quinone intermediate formed during the reaction is so reactive that it immediately dimerised to stilbene quinone. The existence of quinone was further substantiated by the work of Beconsall et al,[21] using electron spin resonance. Waters[19] also suggested that the benzyl radical is responsible for the formation of stilbene quinone. Westfahl[91] has demonstrated the formation of quinone methide and benzyl radical in the presence of an oxidising agent. He proposed that the quinone methide can be prepared by the dehydration of the corresponding phenols, using a Lewis acid.

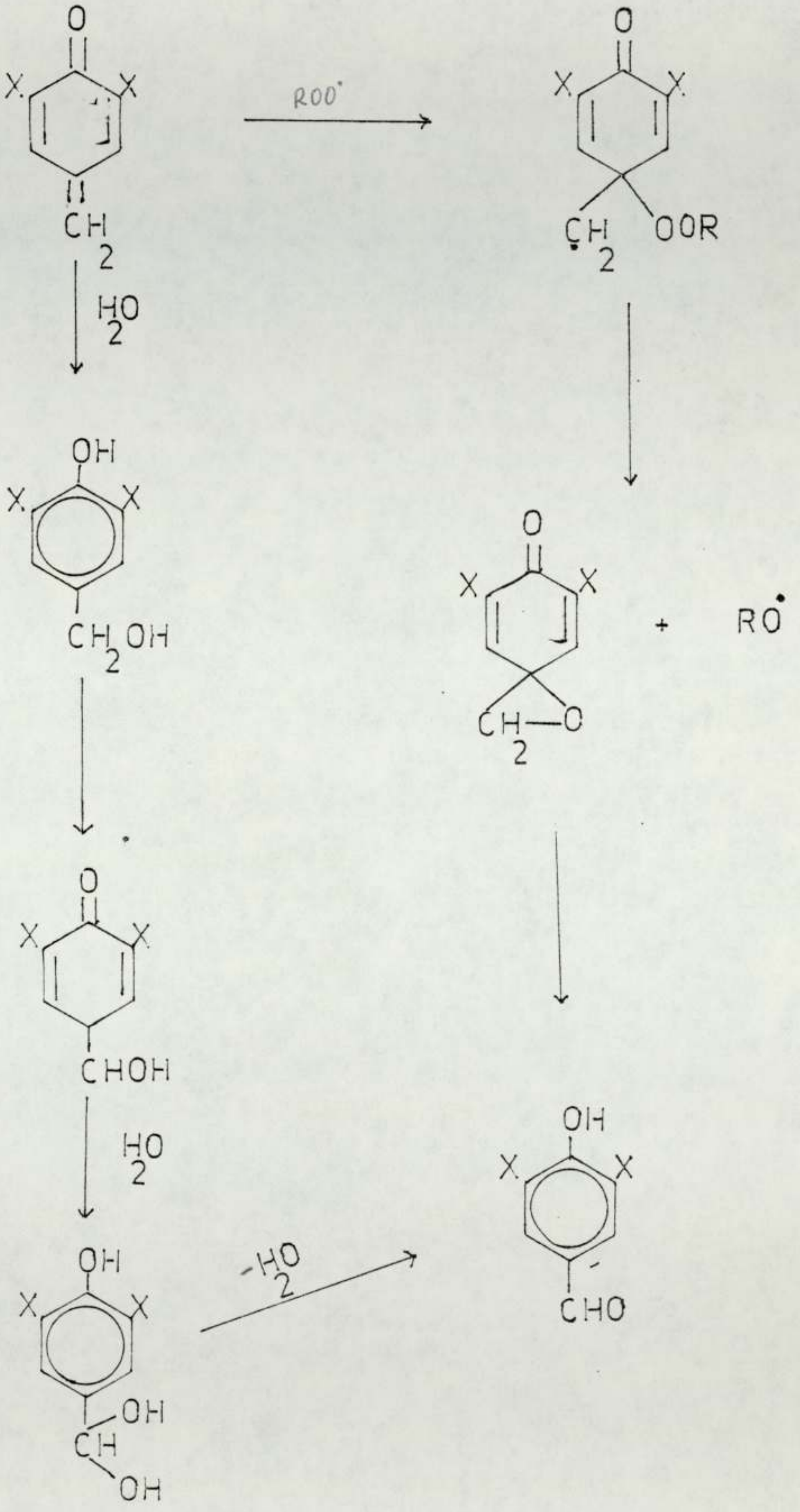


However, as already mentioned earlier, the quinone methide can be considered to be the main precursor, which is responsible for the formation of the identified products. The mechanism for benzyl alcohol and stilbene quinone can be derived as follows.



The conversion of the bis- benzyl phenol to the stilbene quinone was evidenced by its change in colour when on exposure to air. The yellowish colour changed first to the reddish orange stilbene quinone and on further heating decomposed at 300°C to a black semi-solid mass.

Aldehyde derivatives also can be derived through the quinone methide intermediate as explained by Scott[82] and Pospisil[93]


ROO˙
H_2O
H_2O
$-H_2O$
RO˙
OOR
X
X
X
X
X
X
X
X
X
X
X
X
O
OH
CH2OH
CHOH
CHO

5.1.4 Effect of TBC and initiator concentrations on the reaction of TBC with 2-Methyl-2-pentene

The procedure was the same as that described earlier for the reaction of TBC with 2-methyl-2-pentene. A set of experiments was carried out with different concentrations of TBC in excess of 2-methyl-2-pentene (20 gms, 0.24 moles). The concentration of the initiator (TBH/TEPA) was increased with respect to the concentration of TBC in the ratio 2:1. The resulting product 2-methyl-(-4'-benzyl3',5',4-hydroxy)-2-pentene (MBTHP) and the stilbene quinone were separated by column chromotography and the yield of the products were noted.

Results

Table 5.1

TBC concentration in moles/20 gms 2-Me-2pentene	TBH concentration in moles/20 gms	Stilbene quinone in moles/20gms	MBTHP conc^{n} in moles/20 gms
0.009	0.018	0.00003	0.00014
0.018	0.036	0.00023	0.00026
0.027	0.054	0.00035	0.00031
0.036	0.072	0.00055	0.00032
0.045	0.090	0.00090	0.00033

The variation of the concentration of MBTHP (model compound) and stilbene quinone with concentrations of TBC and initiator is shown in Fig.5.1

Discussion:

This set of experiments was carried to study, how the concentrations of TBC and initiator affect the yield of the product MBTHP and reddish stilbene-quinone, which causes the discolouration of the latex at high concentrations. It is clear from the curves shown in Fig. 5.1, that the

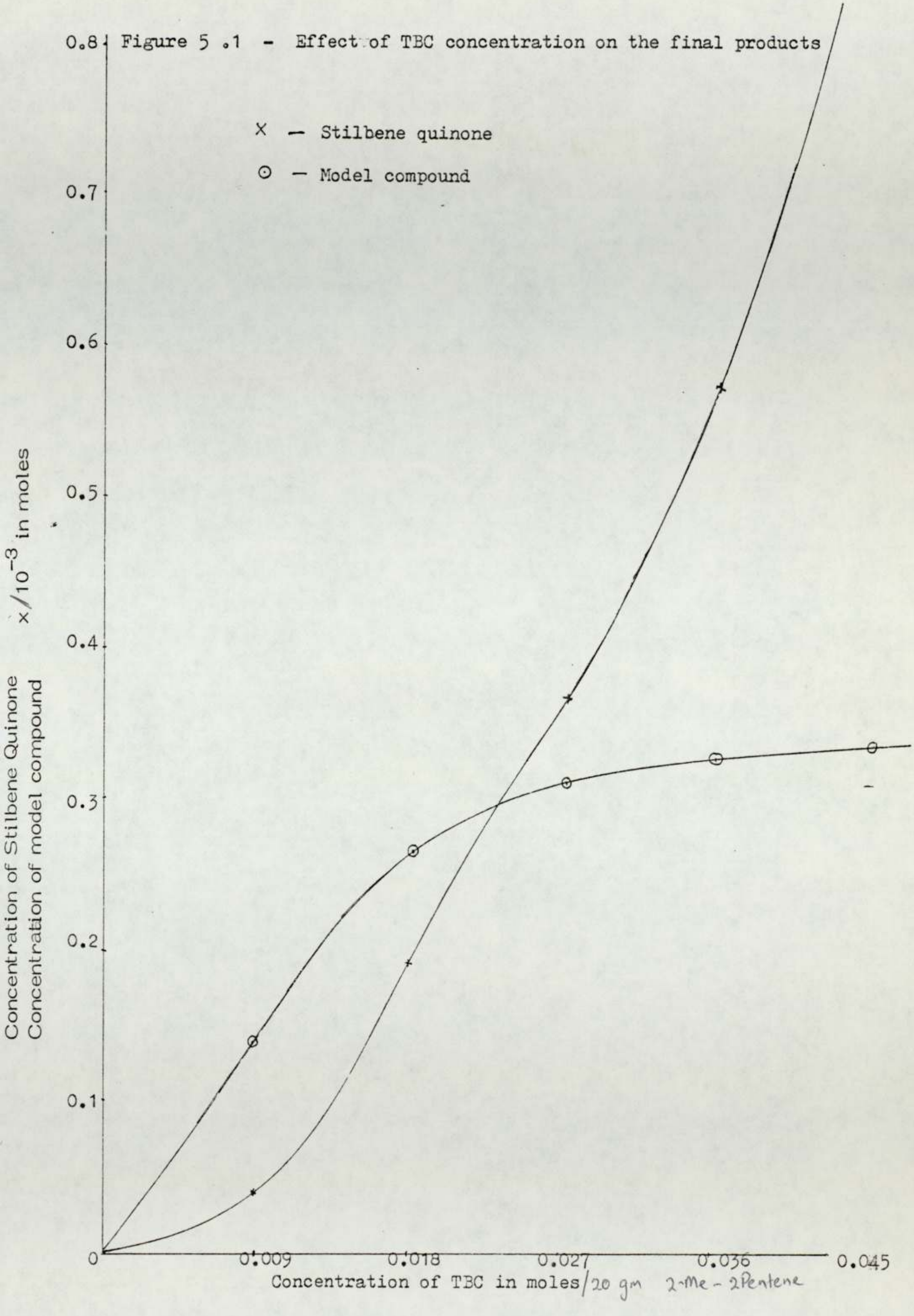


Figure 5 .1 - Effect of TBC concentration on the final products rate of formation of stilbene-quinone is faster at high concentrations of TBC and initiator. However, conversely a high yield of MBTHP was observed at lower concentration. Such similar trends were observed in TBC/natural rubber reaction. This appears to suggest that the formation of stilbene-quinone is unavoidable in both the aqueous as well as in the organic phase. Both systems (ie N.R/TBC, 2-methyl-2pentene/TBC) clearly distinguish that the yield of the stilbene-quinone is minimised at lower concentrations of TBC and initiator and in excess of natural rubber or 2-methyl-2- pentene.

5.2.1 Reaction of (3-5-ditert-butyl-4-hydroxy) benzyl acrylate (DBBA) with 2-methyl-2pentene.

The procedure was similar to that for TBC/2-methyl-2pentene - experiment. At the end of the experiment three fractions were seperated. The first fraction was a volatile mixture, which was collected at 130°C and the products were identified by gas liquid chromotography.

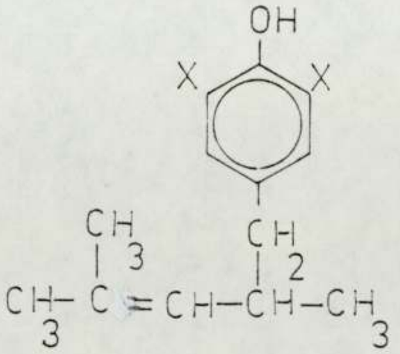
Retention times of the components of the mixture - 4.25, 4.35, 12 minutes.

Retention times of the pure (redistilled) tert-butyl alcohol, 2-methyl-2-pentene, and acrylic acid are 4.35, 4.25, 12 minutes respectively

The second fraction was a solid mixture, which was separated from the resinous phase by washing with ether and then with methanol. This was then concentrated and was dried. The mixture was separated into its components by column chromotography as in the last experiment and six major components were observed and were identified by spectral analysis.

Results:

The first component was a slightly yellowish crystalline compound - M.P 84°C, yield < 0.1gm. The N.M.R, I.R and mass spectra were the same as that of the second compound observed in TBC/2-methyl-2-pentene.



Second component:

Yellowish product M.P 69°C, yield 0.6 gm.

I.R data:

free phenolic at 3620 CM^{-1}

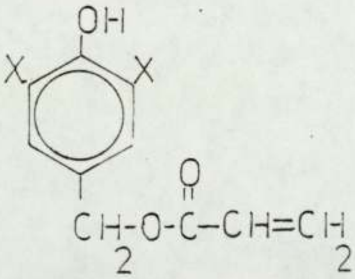
ester carbonyl at 1830 cm^{-1}

vinyl double bond at 1640 cm^{-1}

N.M.R data:

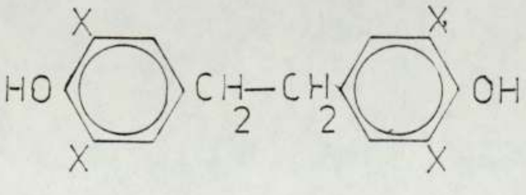
Singlet at 3.6 τ	aromatic protons
Multiplet at 4.3 - 4.5 τ	vinylic protons
Singlet at 5.4 τ	phenolic proton
Singlet at 8.9 τ	tert-butyl protons
Singlet at 5.8 τ	methylenic protons

The probable structure is unreacted (3,5-ditert-butyl-4-hydroxy)acrylate



Third component:

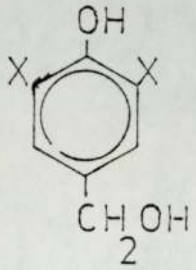
Yellow crystalline product, gradually turned to orange reddish product. Spectral data are similar to the third component of the TBC/2-Me-2pentene reaction.



Fourth component :

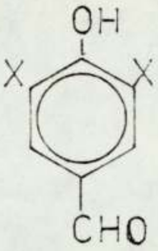
Sparkling white crystalline solid , M.P 137°C, yield 0.2gm.

Spectral data are similar to the fourth component of TBC/2Me-2pentene.



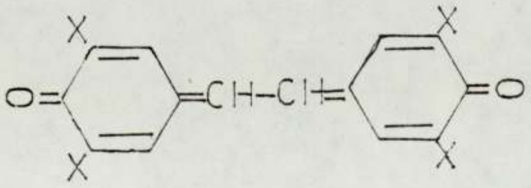
Fifth component:

White crystalline solid , M.P 189°C. Spectral data are similar to the fifth component of TBC/2Me-2pentene.



Sixth component:

Orange reddish needle shape crystals, decompose above 300°C to a black mass. Spectral data are similar to the stilbene- quinone of TBC/2-methyl-2-pentene.



Analysis of the resinous phase:

Yellowish resin ,

I.R data:

Ester carbonyl at 1830 cm^{1}

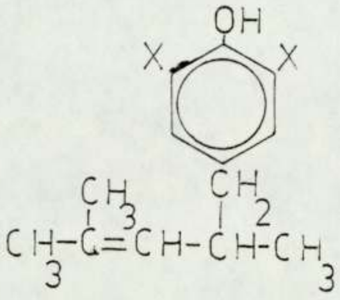
Weak vinyl peak at 1640 cm^{-1}

Sharp peak at 3620 cm^{-1} phenolic OH

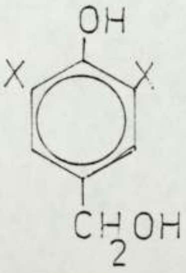
Broad peak between 3500 cm^{1} - 3300 cm^{-1}

Probably polymerised product of DBBA with 2-methyl-2-pentene, yield 30%

The following compounds were identified as the products of the reaction of DBBA with 2methyl-2-pentene.

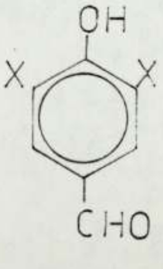


2-methyl-4(benzyl-3'-5'-ditert-butyl-4'-hydroxy)-2-pentene



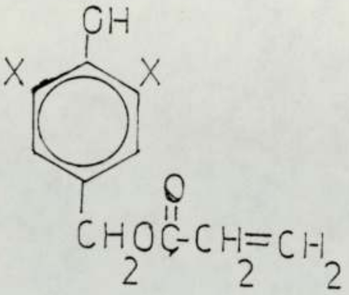
3,5-ditert-butyl-4-hydroxy

benzyl alcohol



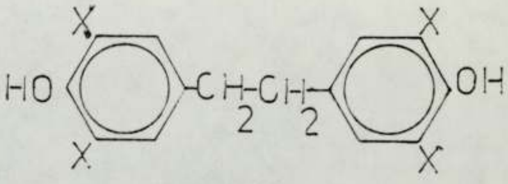
3,5-ditert-butyl-4-hydroxy

benzaldehyde

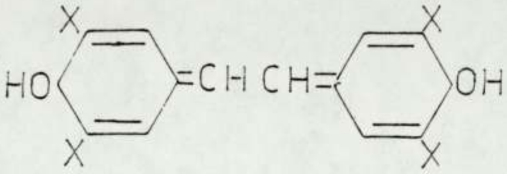


Unreacted 3,5-ditert-butyl4hydroxy

benzyl acrylate



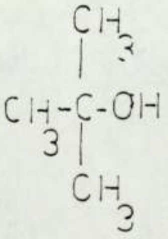
Bis(2,6-ditert-benzyl phenol)



Stilbene quinone

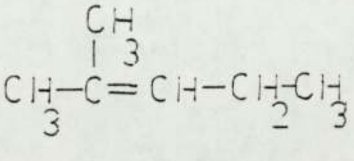
$CH_2=CHCOOH$

Acrylic acid



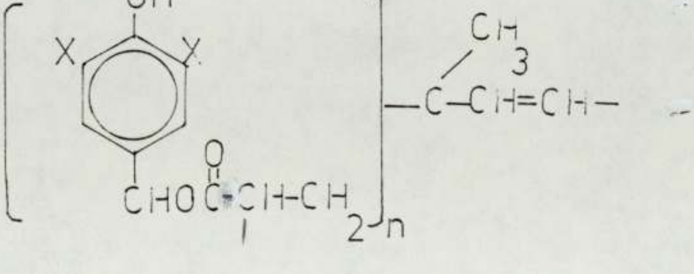
$$(CH_3)_3C\text{-}OH$$

Tert-butyl alcohol



$$CH_3\text{-}C(CH_3)=CH\text{-}CH_2\text{-}CH_3$$

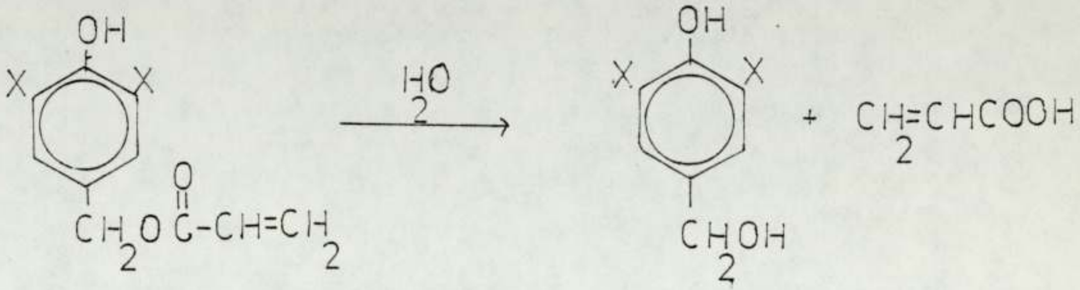
Unreacted 2-methyl-2-pentene



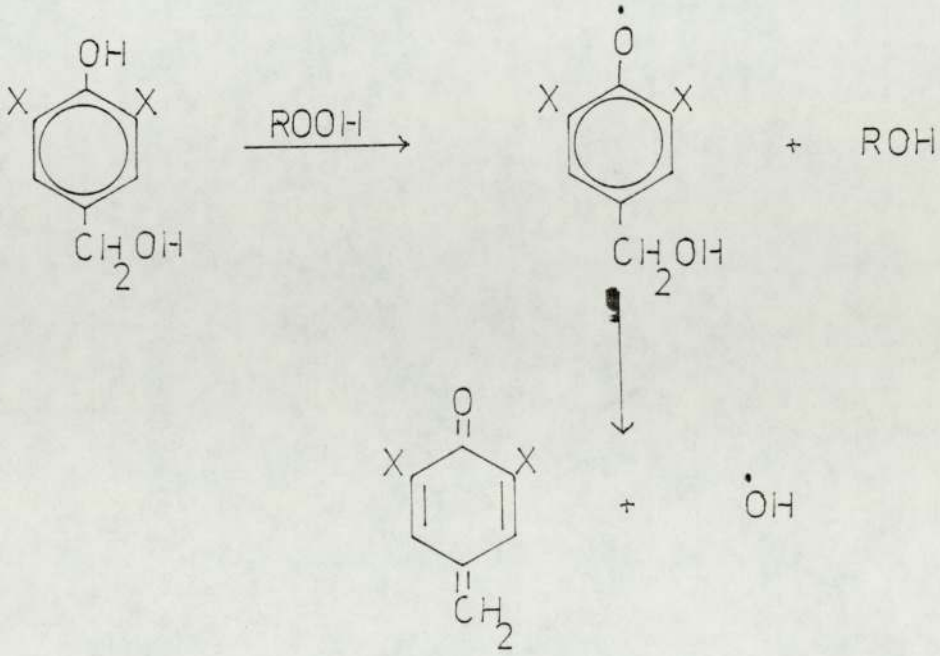
Probable structure of the resinous product

5.2.2 Discussion

Amongst the identified products benzyl alcohol and acrylic acid were found to be major products. Therefore it can be suggested that during the reaction the benzyl acrylate (DBBA) was hydrolised into its components due to water present in the 10% TEPA.



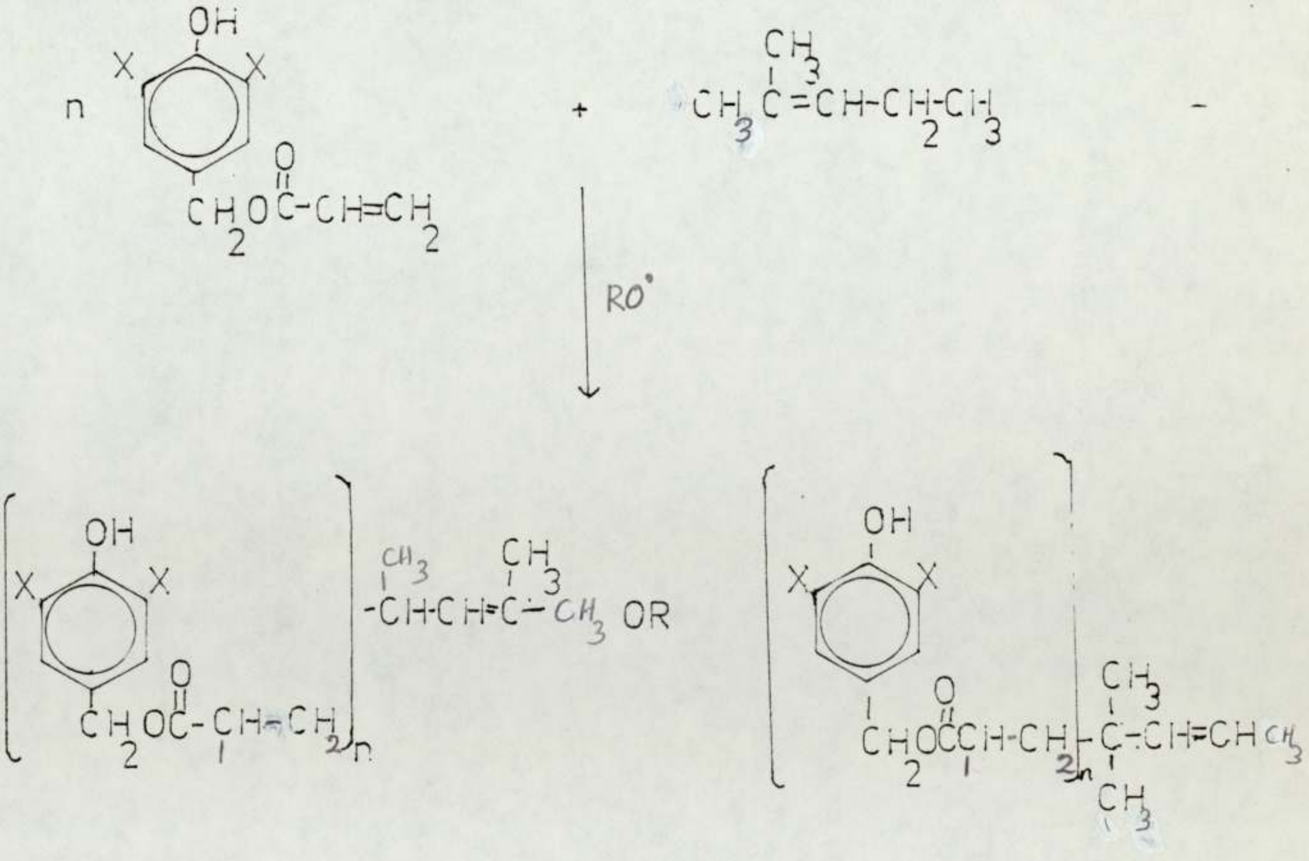
Amarapathy[35] has shown that benzyl alcohol can be reacted to natural rubber under similar conditions. Again as in the previous case the presence of the quinone methide intermediate is responsible for the formation of products during the reaction.



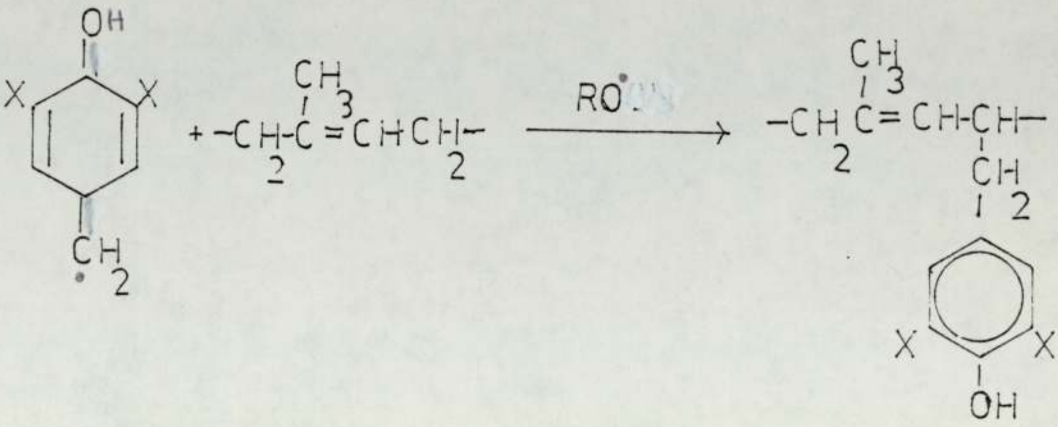
The rest of the reaction mechanism is similar to that described in TBC/2-methyl-2-pentene, in the formation of MBTHP, benzaldehyde, bis- benzyl phenol, and stilbene quinone.

During the reaction, acrylic acid was formed by hydrolysis of DBBA, which then co-polymerised with the benzyl acrylate resulting in the formation of resinous product. However, the presence of absorption at 1640 cm^{-1}, which corresponds to the double bond of 2-methyl-2-pentene, indicates that the latter is chemically attached to the resinous product, which contains phenolic OH as well as C=O and appear at 3620cm^{-1}, and 1830cm^{-1} respectivly. The conclusion that emerges from these studies is that DBBA grafts to natural rubber, but in addition direct bonding of benzyl alcohol to natural rubberoccurs via the quinone methide intermediate.

Co-polymerisation reaction



The reaction of benzyl alcohol with natural rubber is again via the quinone methide intermediate as described earlier. (see P 99)



This is in accord with the reaction of DBBA with natural rubber since it has been shown that the grafting of DBBA occurs partly through graft co-polymerisation In addition to that DBBA was found to be hydrolysed during the reaction and benzyl alcohol was observed as the major by-product. A discrepancy between the estimation of bound antioxidant by OH measurment and C=0 measurment has been revealed at different concentration of DBBA. At lower concentration, a relatively high level of reaction is achieved with DBBA and benzyl alcohol ,which is a hydrolysis product of DBBA, indicating high estimation in OH measurment. Where-as at high concentration the reverse is true due to the formation of stilbene quinone as in TBC/natural rubber reaction, and graft co-polymerisation of excess acrylic acid during the reaction , with natural rubber resulting in high estimation in C=0 measurment

5.3.1 Reaction of (3,5-ditert-butyl-4-phenol)benzyl mercaptan with 2-methyl-2-pentene.

The addition reaction was carried out in a three necked flask, fitted with a condenser, thermometer, and a dropping funnel. 0.008mole(2gm) of BHBM was dissolved in excess 2-methyl-2-pentene(10gm, 0.11 mole) followed by 0.008 moles of TBH. The temperature of the mixture was maintained at 55°-60°C. The reaction was carried out for 9 hours under nitrogen atmosphere.

The unreacted 2-methyl-2-pentene and low volatile fractions were removed by distillation and the resulting oily liquid was distilled under vacuum. A light yellow oily product was collected at 142°C at 0.05mm-0.1mm pressure. This fraction was identified by infra-red spectroscopy, N.M.R and mass spectroscopy.

I.R data:

Phenolic OH at 3620cm^{-1}

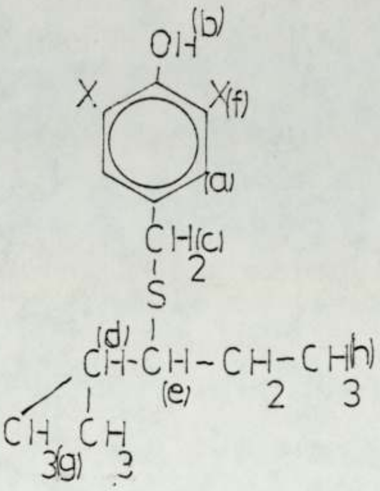
Absence of the peak at 1640cm^{-1} confirms that the compound is fully saturated.

N.M.R data:

Singlet at 3.0	a- aromatic protons
Singlet at 5.0	b- phenolic proton
Singlet at 6.48	c- methylenic protons
Multiplet at 8.4	d- methylenic protons
Multiplet at 7.6	e- methylenic protons
Singlet at 8.8	f- tert-butyl protons
Triplet at 9.0	h- methylenic protons
Doublet at 9.2	g- methylenic protons

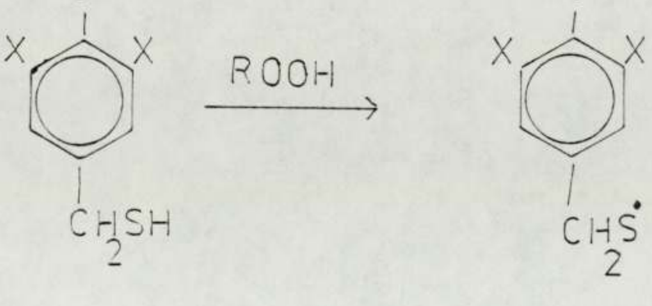
Mass spectrum shows peaks at 336, 251, 85.

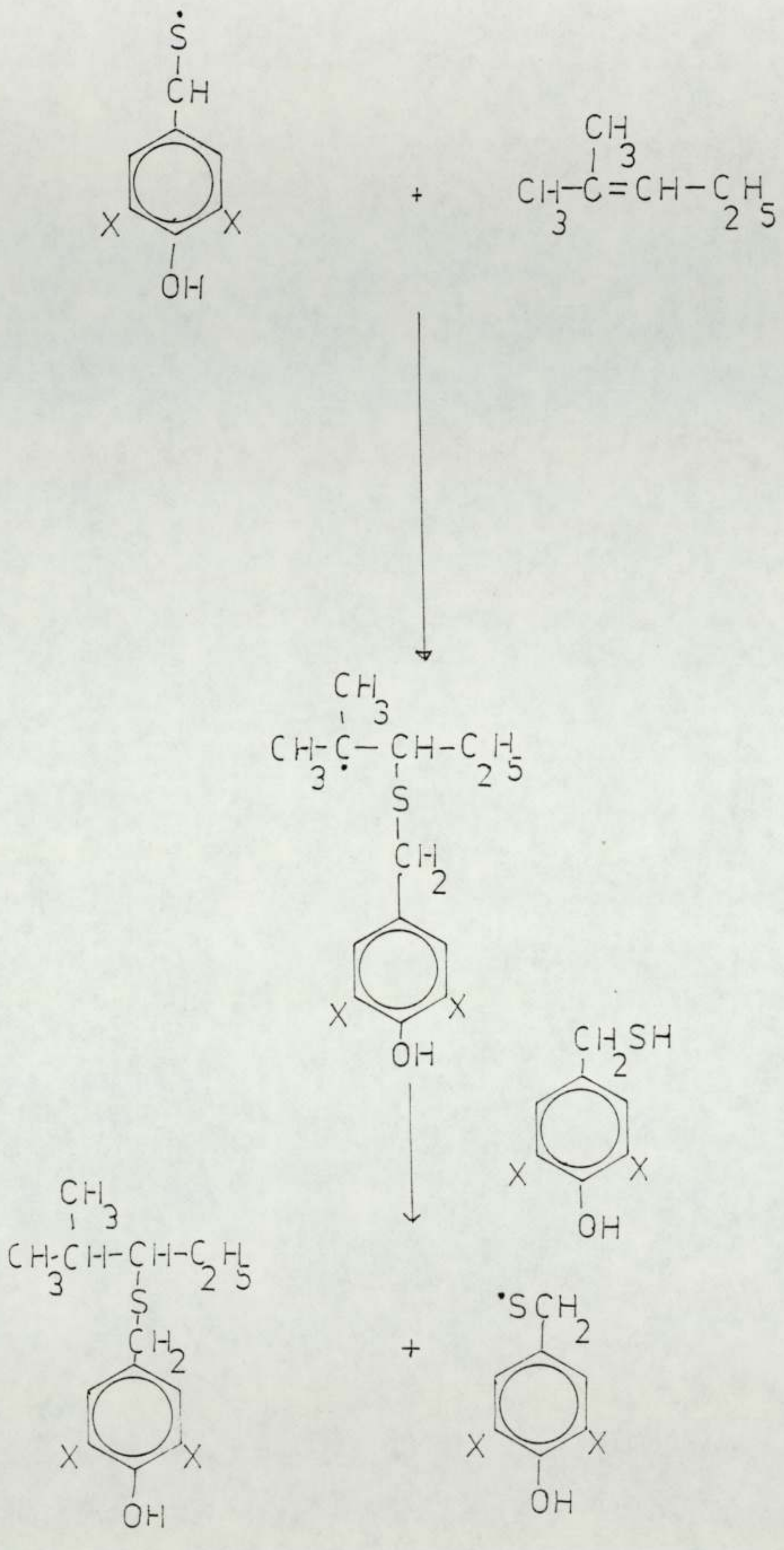
The probable structure is



Discussion :

The above result parallels the model compound studies of the reaction of 2-methyl-2-pentene with BHBM using AZBN as initiator.[36] Jones and Reid[95] have observed that the addition of thiols to unsaturated compounds in the presence of peroxide initiators follows the anti-Markovnikoff's addition. Similar studies were carried out with thiophenols and cyclohexene by Cunneen[75] and it was shown that the addition was again anti-Markovnikoff in nature. The possible reaction mechanism and the reaction path for the addition of mercaptan(BHBM)-to unsaturated hydrocarbons can be represented as follows.





The same mechanism almost certainly holds for the reaction of BHBM with natural rubber.

CHAPTER SIX

6.0 Technological ageing properties of bound antioxidants in latex derived vulcanisates

The most important properties of rubbers are their elasticity and strength. This is particularly true in applications such as , pneumatic tyres, where the rubber undergoes continuous stress and strain. The deterioration of these properties in service normally determines the useful life of the articles. The rate of loss of tensile strength of vulcanized rubber, even in the absence of added antioxidants, is much too slow at room temperature to be a practical technique for assessing the useful service life of rubbers. There are two ways, in which the rate of oxidations may be speeded up to give the decay of physical property of the order of days instead of years. These are (a) increasing the temperature of the oxidation (the air oven) and (b) increasing both the temperature as well as the partial oxygen pressure. (The air bomb and oxygen bomb) - Kohman[94] has shown that the absorption of a few tenths of 1% oxygen is sufficient to reduce the tensile strength of a rubber vulcanisate by 50%.

Deterioration is not necessarily uniform throughout the rubber, since the formation of cracks (flex or ozone cracks) seriously weaken the structure of any article under stress. This is particularly serious problem in rubber subject to both static and dynamic strains. For applications, where rubbers are not subjected to dynamic stress, strength may be less important than appearance. In light coloured rubber articles, the development of stain due either to agents added to assist in vulcanisation or from the antioxidants themselves, may be a serious disadvantage.

Ageing under condition of stress is much more rapid than is "shelf ageing" and is manifested particulary under dynamic conditions by the development of deep cracks, which rapidly weaken the rubber structure. Two methods are commonly used to assess the degradation of cracking in a rubber strip, after exposure to air at high temperatures. The first involves the measurment of the number and depth of the cracks in a given area, where the rubber subjected to standard strain. The second measurement assess cracking in terms of the stress relaxation or creep, which occurs in a stretched strip. This does not give an indication of the cracking pattern, which may be one of the most important factors which determines the useful life of the rubber article. (eg. a tyre sidewall)

The technique of oxygen absorption is a complementary procedure for measuring the oxidative behaviour of polymers. This technique provides particularly valuable information regarding the chemistry of the oxidative behaviour of rubbers and in combination with technological and physical techniques, provides information about the efficiency of oxygen in bringing about crosslinking or scission of the polymer chain.

The following chapter is concerned with the physical properties of antioxidant-bound rubber vulcanisates during ageing and with their effectiveness as antioxidants. Three techniques have been used in studying this ageing behaviour viz: (a) Tensile properties, which determines the effectiveness of bound antioxidants in the retention of mechanical properties. (b) Stress relaxation, which is a useful means of assessing the degree to which an antioxidant can protect a rubber vulcanisate in service and particularly in the case of vulcanisates having a high surface area to volume ratio, such as elastic fibers and films. Several changes in the network structure can occur during heat ageing; scission of the main chains and of the crosslinks, the formation of more crosslinks of the same type as those already present or of a different type, which may be immune to further scission. This technique provides information regarding the scission or crosslinking reaction of rubbers during ageing and the point of attack of oxygen in rubbers. This is found to produce a very satisfactory distinction between antioxidants. Finally, (c) Oxygen absorption test, assess as the intrisic activity of the bound antioxidants.

6.1 Tensile properties of rubber bound antioxidants in latex form

There has been increasing interest in recent years in high molecular weight antioxidants. The reason for this is essentially practical, since it has been shown that under certain conditions of antioxidant testing which are relevant to service condition, antioxidant loss from the polymer can be a dominating factor in determining their effectiveness.[1] This is particularly true in thin films such as, rubber threads, surgical gloves etc, which are routinely bathed in various media, which can remove the commonly added antioxidants , thereby reducing service life. The following experiments were carried out to investigate rubber bound antioxidants in thin films as antioxidants, under aggressive environmental conditions.

6.1.1 Experimental Procedure:

Preparation of 50% dispersions of vulcanising ingredients in water

Allthe dispersions were prepared in ball mills and were milled for 24-48 hours. The formulations of the dispersions of different vulcanising ingredients are given below.

50% sulphur dispersion:

Sulphur	-	1000.0 gm
Dispersol LN	-	40.0 gm
10% casein solution	-	200.0 gm
Water	-	760.0 gm

milled for 48 hours

50% zinc oxide dispersion:

Zinc oxide	-	1000.0 gm
Dispersol LN	-	40.0 gm
Water	-	960.0 gm

milled for 24 hours.

50% zinc dithiocarbamate dispersion:

ZDC	-	250.0 gm
10% Dispersol LN	-	50.0 gm
10% casein solution	-	50.0 gm
Water	-	150.0 gm

6.1.2 Preparation of thin latex films

Latex compounds of the composition given in table 6.1 were prepared, matured for two days by gently stirring and were then filtered through a wire gauze. Films were cast in glass moulds of cavity thickness 1mm, to produce a dried film of ½mm thickness. Half of each films were leached in distilled water at 60°C for 30 minutes, rinsed with distilled water and was then dried at low temperature.

All the films were then vulcanised for 30 minutes at 120°C in hot circulated air, only one type of film being vulcanised at a time in order that antioxidant migration or contamination [illegible] would not interfere with final test results. Set of films were then tested for normal modulus, tensile strength and elongation. (see chapter 2) Further set of films were then aged in hot circulated air at 70°C for 7 days; (b) boiled in 2% Tide for 1 hour, rinsed in distilled water, dried and aged for 3 days at 70°C in circulated air; (c) washed in 80:20 :: pet-ether:toluene, dried and aged for 3 days at 70°C as in (b). The usual modulus, tensile and elongation properties were retested after the various ageing procedures. The details of the testing procedure was supplied by GuthrisLtd.

Table 6.1

Ingredients	Wet weight in gm	dry weight in gm
60% natural rubber latex	165	100.0
50% ZnO	3	1.5
50% ZDC	2	1.0
50% sulphur	4	2.0
20% vulcastab LW	0.25	0.05

6.1.3 Behaviour of antioxidants as additives

A set of films was prepared as described earlier by incorporating 2gm of the antioxidants. Then tensile properties of unleached, leached and aged films were tested.

Table 6.2

Formulation	code	Unleached films T,S in Kgm/cm^2	Unleached films %elongation at break	Leached films T.S in Kgm/cm^2	Leached films %elongation at break
Without antioxidant	A	306	870	266	880
2gm of BHBM as an additive	B	284	890	281	890
2gm of TBC as an additive	C	298	880	274	865
2gm of Nonox WSP(conventional antioxidant)	D	285	880	277	880

Table 6.3

Tensile strength of aged films in Kgm/cm^2

Formulation code	Oven aged at 70°C for 7 daye	2% detergent washed/ aged 3 days at 70°C	Solvent washed/ aged 3 days at 70°C
A	143	143	176
B	188	159	168
C	174	197	142
D	179	220	150

Table 6.4

Percentage retention of tensile strength of the aged films

Formulation code	Initial T.S in Kgm/cm^2	Aged for 7 days	Detergent washed/ aged	Solvent washed/ aged
A	306	47	47	58
B	284	66	56	59
C	296	58	66	50
D	285	63	77	53

The poor performance of the added antioxidants us evident from the above results.

6.1.4 Behaviour of rubber bound antioxidants

A set of films was prepared from the bound antioxidant latices as described earlier. (p.119) The tensile properties of the unleached, leached and aged films were tested.

Table 6.5

Tensile properties of unleached and leached films

Formulation	code	Unleached films		Leached films	
		T.S in Kgm/cm^2	%elongation	T.S in Kgm/cm^2	%elongation
BHEM bound (2/100gm)	B$_1$	279	890	280	860
TBC bound (2/100gm)	C$_1$	283	850	279	850

Table 6.6

Tensile strength of aged films

Formulation code	Oven aged for 7 days at 70°C	2% detergent washed/ aged 3 days at 70°C	Solvent washed/ aged 3 days at 70°C
B_1	271	256	281
C_1	281	278	266

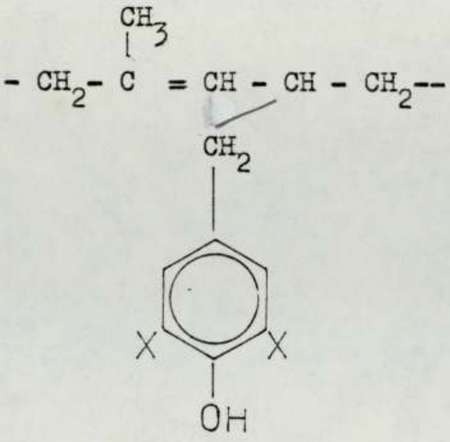
Table 6.7

Percentage retention of tensile strength of the bound antioxidant systems after ageing

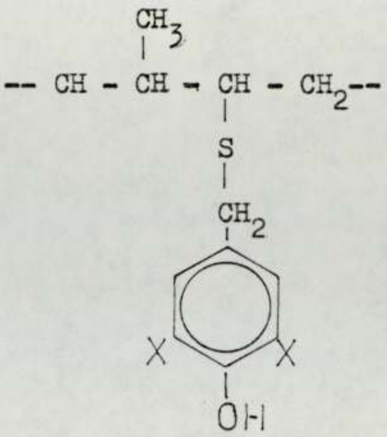
Formulation		Initial T.S in Kgm/cm^2	Air oven aged	Detergent washed/ aged	Solvent washed/aged
BHBM bound	B_1	279	97	92	100
TBC bound	C_1	283	99	97	98
Without antioxidant	A	306	47	47	58
Nonox WSP	D	285	63	77	53

6.1.5 Discussion

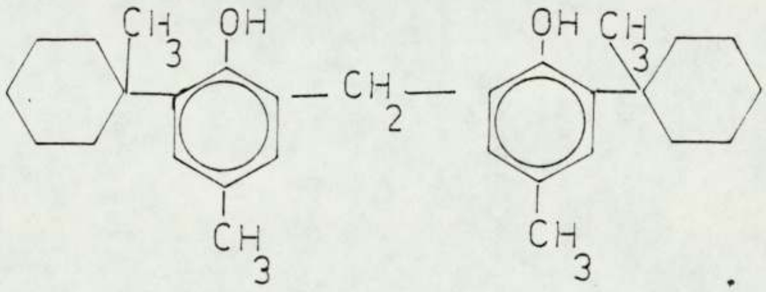
Tables 6.2-6.7 compare the modified latices containing bound TBC and bound BHBM with latex containing one of the most effective of the commercial bis phenols (Nonox WSP) as a conventional additive in latex formulations. It can be seen that when subjected to solvent or detergent washing followed by ageing these rubbers show almost complete retention of tensile strength under conditions where the conventionally stabilised rubber shows extensive degradation.



TBC bound rubber



BHBM bound rubber



Nonox WSP (conventionally added antioxidant)

Infra-red examination of the solvent-extracted rubbers shows that the bis-phenol is removed completely from natural rubber under these conditions, whereas 70% of the original BHBM and 10% of TBC remained bound to the network. What is much more surprising is that relative ineffectiveness of the bis-phenol in a conventional air oven test compared with the bound systems. This is consistent with the behaviour of the lower molecular weight bis-phenols in polypropylene described by Plant.[1] It demonstrates that under aggressive conditions in large surface area to volume samples, intrinsic activity is much less important than is molecular weight and hence volatility.

6.2 Reactions of hindered phenols with prevulcanised latex

Partily prevulcanised latices are prepared commercially by incorporating the vulcanising ingredients with rubber latex and then partially vulcanising by heating. This is therefore of cosiderable practical interest to the producers and the users of the rubber latex and the products are made directly from it, for instance, teats, rubber threads gloves etc,. The following experiments were carried out to examine the reaction of hindered phenols such as TBC, BHBM and their effectiveness as bound antioxidants in prevulcanised latices.

The prevulcanised latex was supplied by Revertex Ltd and was formulated as follows.

Ingredient	wet weight	dry weight
60% natural rubber latex	167 gm	100 gm
ZDC	-	0.4
sulphur	-	0.3
ZnO	-	0.2

This was diluted with equal amount of water to give 30% latex and the reactions of TBC, BHBM were carried out as described in chapter 3, under the following reaction conditions,

Initiator (TBH/TEPA) - 1.5 ml/ 4.5 ml of 10% TEPA
Reaction temperature - 60°C
Concentration of TBC or BHBM - 2 gm [0.009 moles]/100 gm of N.R
Reaction time for TBC - 18 hours
Reaction time for BHBM - 9 hours
D.R.C - 100 gm

At the end of the experiment, films were cast on glass plates as described earlier. Then the films were dried and cured in an air oven at 100°C for 30 minutes. The specimens were cut for tensile measurements and the tensile properties of the leached, unleached and the aged films were tested.

Table 6.8

Tensile properties of antioxidant-bound prevulcanised latices

Formulation	code	Unleached films T.S in Kgm/cm^2	Unleached films %elongation	Leached films T.S in Kgm/cm^2	Leached films %elongation
Prevulcanised latex without antioxidant	PA$_1$	260	865	257	877
BHBM bound prevulcanised latex(2/100)	PB$_1$	193	890	187	880
TBC bound prevulcanised latex(2/100)	PC$_1$	188	910	186	965
Nonox WSP in prevulcanised latex	D	285	880	277	880

Table 6.9

Tensile properties of aged antioxidant-bound prevulcanised films

Formulation code	Oven aged at 70°C for 7 days	2% detergent washed/ aged 3 days at 70°C	Solvent washed/ aged 3 days at70°C
PA$_1$	114	137	147
PB$_1$	119	148	146
PC$_1$	92	163	89
D	179	220	150

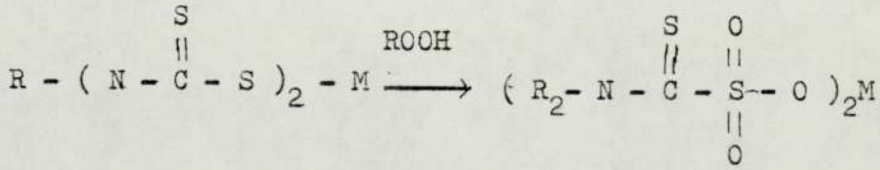
Table 6.10

Percentage retention of tensile strength of aged prevulcanised films

Formulation code	Initial T.S Kgm/cm^2	Air oven aged	Detergent washed/ aged	Solvent washed/aged
PA_1	266	44	52	56
PB_1	193	61	77	75
PC_1	188	49	76	47
D	285	63	77	53

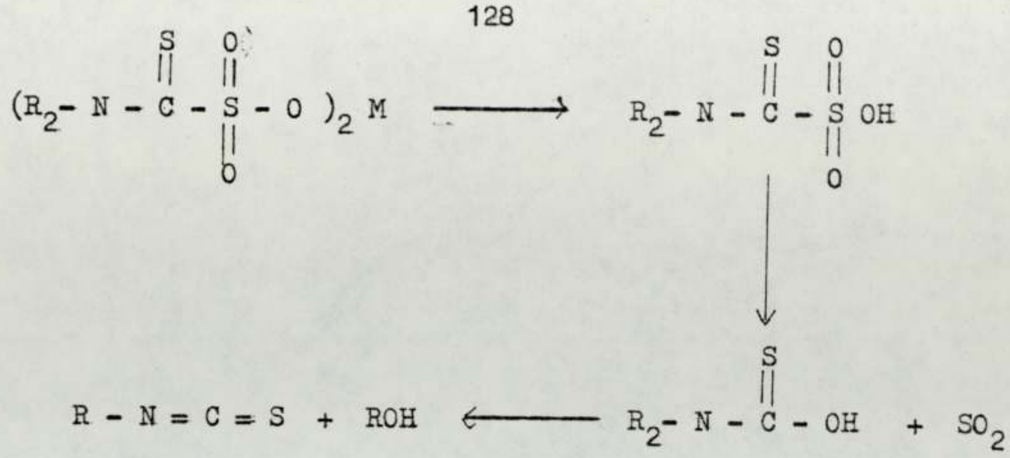
6.2.1 Discussion

The above tables 6.8- 6.10 illustrates the poor initial strength of the prevulcanised latices and their inferior performance during ageing. Infra-red examination of the solvent extracted films showed that 42% of the BHBM and a lower level of TBC remained bound. The lower level of reaction achieved may be due to the loss of hydroperoxide during the reaction. It is a known fact that the undercuring of latices reduces the tensile strength of the films by appreciable amount. There is literature evidence[90] for the decomposition of hydroperoxide by ZDC. Scott[77] has proposed the following reaction mechanism for the reaction of ZDC with hydroperoxide.



$$R-(N-\overset{S}{\overset{\|}{C}}-S)_2-M \xrightarrow{ROOH} (R_2-N-\overset{S}{\overset{\|}{C}}-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-O)_2M$$

unstable sulphonate



$$(R_2-N-\overset{\overset{S}{\|}}{C}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O)_2M \longrightarrow R_2-N-\overset{\overset{S}{\|}}{C}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}OH$$

$$\downarrow$$

$$R-N=C=S + ROH \longleftarrow R_2-N-\overset{\overset{S}{\|}}{C}-OH + SO_2$$

Therefore as a result of the above reaction, both hydroperoxide and ZDC decompose each other, resulting in a lower level of reaction of antioxidant with rubber and a lower level of cure. This accounts for the poor properties of prevulcanised latices. The effect of ZDC on the decomposition of hydroperoxide willbe discussed in a later section.

6.3 Masterbatch Technique

A major advantage of the thiol bound antioxidant systems is that they are potentially useful system for the preparation of concentrated latex masterbatches. Provided, there is a substantial concentration of the original double bonds present in such concentrations, co-vulcanisation of the modified and conventional rubber should occur readily by the addition of a relatively low concentration of masterbatch to unmodified latices. This is particularly convenient way of introducing bound antioxidants into prevulcanised latices without interfering with the subsequent vulcanisates.

Procedure:

(See p.56/57) 10 gm of the antioxidant was reacted with 100 gm of normal rubber latex and one part of this was then diluted with nine parts (90gm) and 19 parts (190gm) of normal rubber latex respectively, so that the concentration of antioxidant in the 100 gm of rubber was 1.0 gm and 0.5 gm respectively. Then the films were cast and vulcanised as described earlier.

Similar samples were prepared with prevulcanised latex such that 0.5 gm and 1.0 gm of antioxidant in 100 gm of latex. The concentrated samples were made in normal latex and were then diluted with prevulcanised latex. The tensile properties of the leached, unleached and aged films were tested and the reproducability of the results was checked.

Table 6.11

Tensile properties of the antioxidant-bound rubbers (masterbatch technique)

Initial tensile properties

Formulation	code	Tensile strength in Kgm/cm^2	% elongation
TBC masterbatch in normal latex (1/100)	MC_1	293	760
BHBM masterbatch in normal latex (1/100)	MT_1	304	710
TBC masterbatch in prevulcanised latex			
0.5/100 -	MPC_1	292	755
1.0/100 -	MPC_2	259	730
BHBM masterbatch in prevulcanised latex			
0.5/100 -	MPT_1	286	770
1/100 -	MPT_2	263	730
Nonox WSP (2/100) (conventional antioxidant)		285	880

see page 126

Table 6.12

Tensile strength of the aged films of the antioxidant bound rubbers

Formulation code	Oven aged for 7 days at 70°C	Solvent washed/aged for 3 days at 70°C	Detergent washed/ aged 3days at 70°C
MC_1	283	284	286
MT_1	268	273	269
MPC_1	226	239	252
MPC_2	241	225	242
MPT_1	265	266	257
MPT_2	257	262	271
WSP(2/100)	179	150	220

Table 6.13

Percentage retention of tensile strength of the aged films

Formulation code	Initial T.S in Kgm/cm^2	Air oven aged	Solvent washed/ aged	Detergent washed/ aged
Without antioxidant	260	44	57	53
MC_1(1/100)	293	89	87	92
MT_1(1/100)	304	91	88	97
MPC_1(0.5/100)	292	77	82	86
MPC_2(1/100)	259	93	87	93
MPT_1(0.5/100)	286	92	93	90
MPT_2(1/100)	263	98	96	99
Nonox WSP(2/100)	285	63	53	77

6.3.1 Discussion

The above tables 6.11- 6.13 illustrates the use of bound antioxidant latex masterbatches with normal latices and prevulcanised latices. The superiority of all the bound antioxidant masterbatches over the conventional antioxidant used at a higher concentration than that of bound antioxidant is very evident from table 6.13. In masterbatch form, the thiol based bound antioxidants are generally superior to the simple monophenolic due to the higher level of reaction achieved. However, in spite of this the durability of the masterbatches are very much superior to the best conventional antioxidants used as additive and this will be furthur elaborated in subsequent sections.

6.3.2 Effect of solvents on antioxidant bound rubbers.

The specimens of masterbatch latex films, which contained 2 gm of reacted antioxidant in 100 gm of latex, were boiled in a 2% solution of Tide for a known lengths of time. The samples were then taken out, rinsed with fresh distilled water, dried and the amount of antioxidant remained was determined by infra-red technique. (see chapter 2)

Similarly films were extracted by solvent, (pet-ether/toluene:: 80/20) at room temperature and then rewashed with pure solvent mixture. The samples were dried and examined by I.R to estimate the concentration of the antioxidant which remained bound to the rubber.

Initial concentration of the antioxidant - 2.0 gm/{0.009 moles}/100 gm of N.R

Results :

Table 6.14

Concentration of the antioxidant after detergent washing

Time in hours	BHBM remaining in gms	TBC remaining in gms	Nonox WSP remaining in gms
0.0	2.00	2.00	2.00
0.25	1.89	1.80	1.73
1.00	1.80	1.60	1.58
2.00	1.67	1.32	1.27
3.00	1.56	1.18	1.11
4.00	1.48	1.07	1.03
5.00	1.44	1.00	0.95

Table 6.15

Concentration of the antioxidant remained after solvent extraction

Time in hours	BHBM remaining in gms	TBC remaining in gms	Nonox WSP remaining in gms
0.00	2.00	2.00	2.00
0.25	1.73	0.65	0.44
1.00	1.48	0.22	0.00
2.00	1.31	0.16	0.00
3.00	1.30	0.16	0.00
4.00	1.30	0.16	0.00
5.00	1.30	0.16	0.00

The graphical interpretation of the remaining antioxidant concentration vs time is shown in Fig. 6.1

Figure 6.1.1 - Solvent extracted rubber vulcanisate

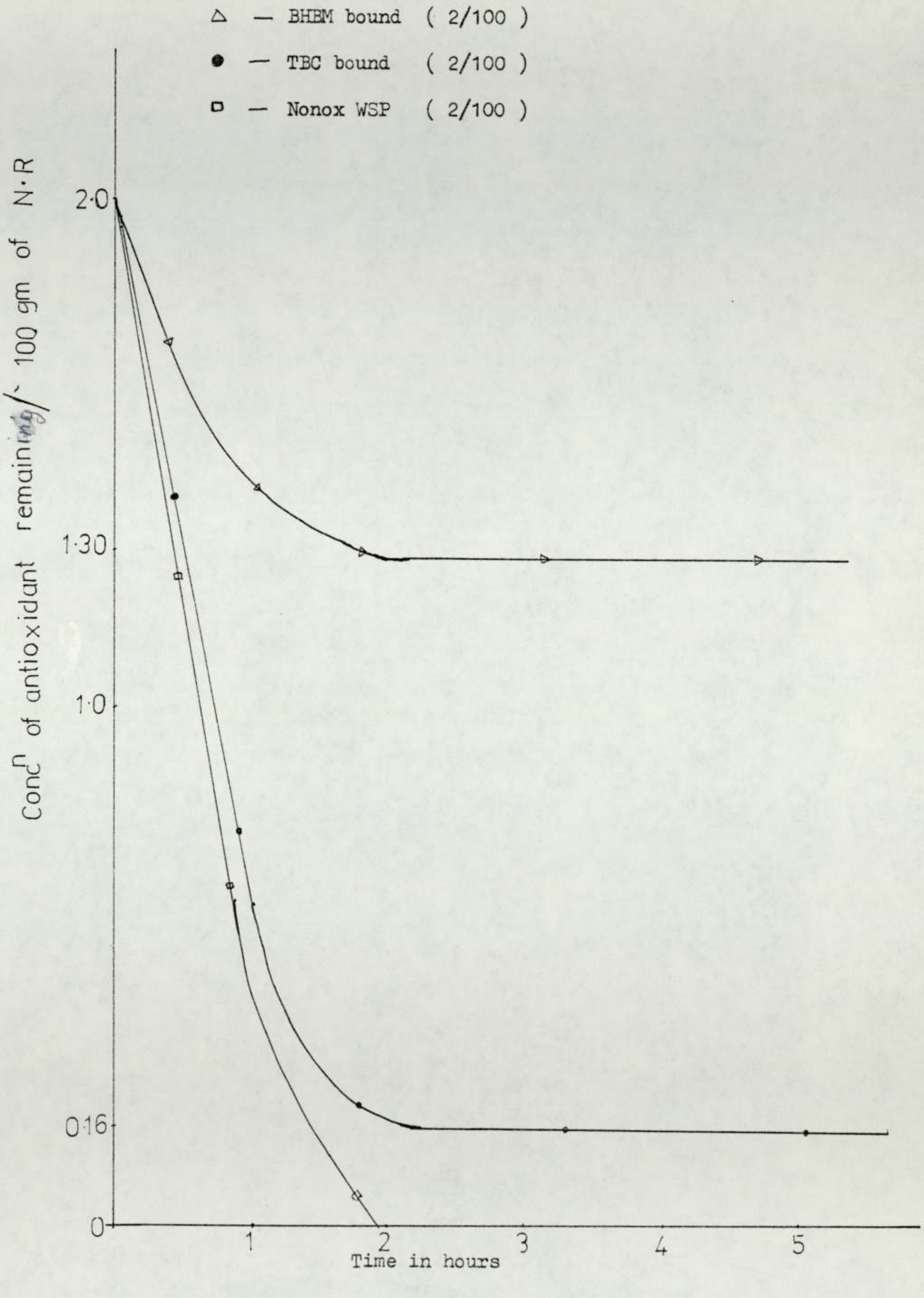
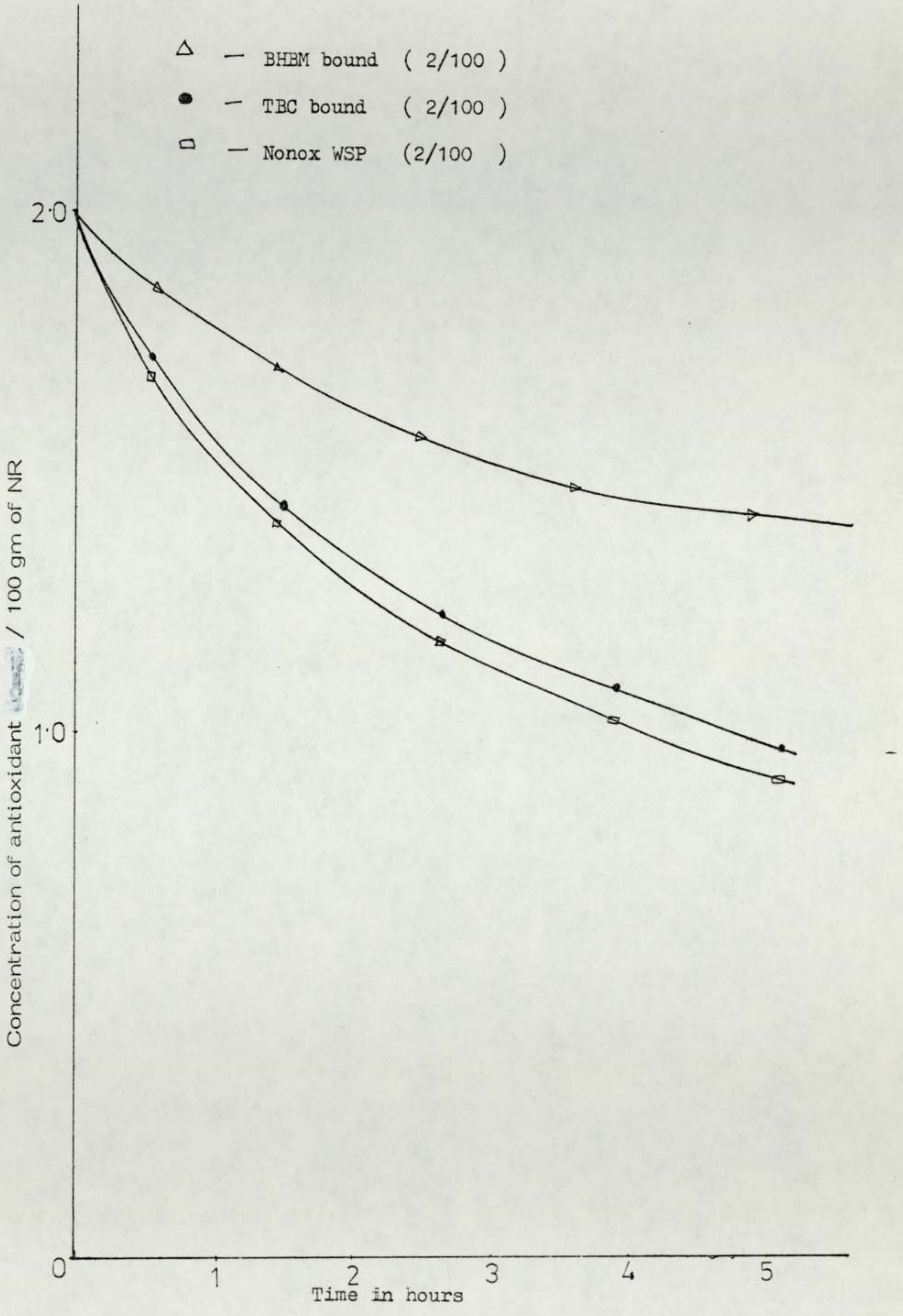


Figure 6.1.2 - Detergent extracted antioxidant bound rubber vulcanisate



Discussion:

It appears from the results and the curves shown in Fig.6.1, the bound antioxidants are much more resistant to solvent than that of conventionally added antioxidants. During the extraction in organic solvent, the Nonox WSP is completely removed from the films, whereas, 65% of theBHBM and 8% of the TBC remained bound to the rubber. Possibly this removal of conventionally added antioxidant is more prominent in high surface area to volume samples, such as thin samples. For instance, thin samples such as, latex threads, teats, surgical gloves. etc, loose their antioxidants very rapidly, when they are in contact with water or industrial solvents, during their service life. This leads to the shortening of the valuble service life of the articles. From the present studies it may be concluded that the extractability or leaching can be minimized using antioxidant bound rubbers.

6.3.3 Variation of tensile strength of the antioxidant bound rubbers with ageing time

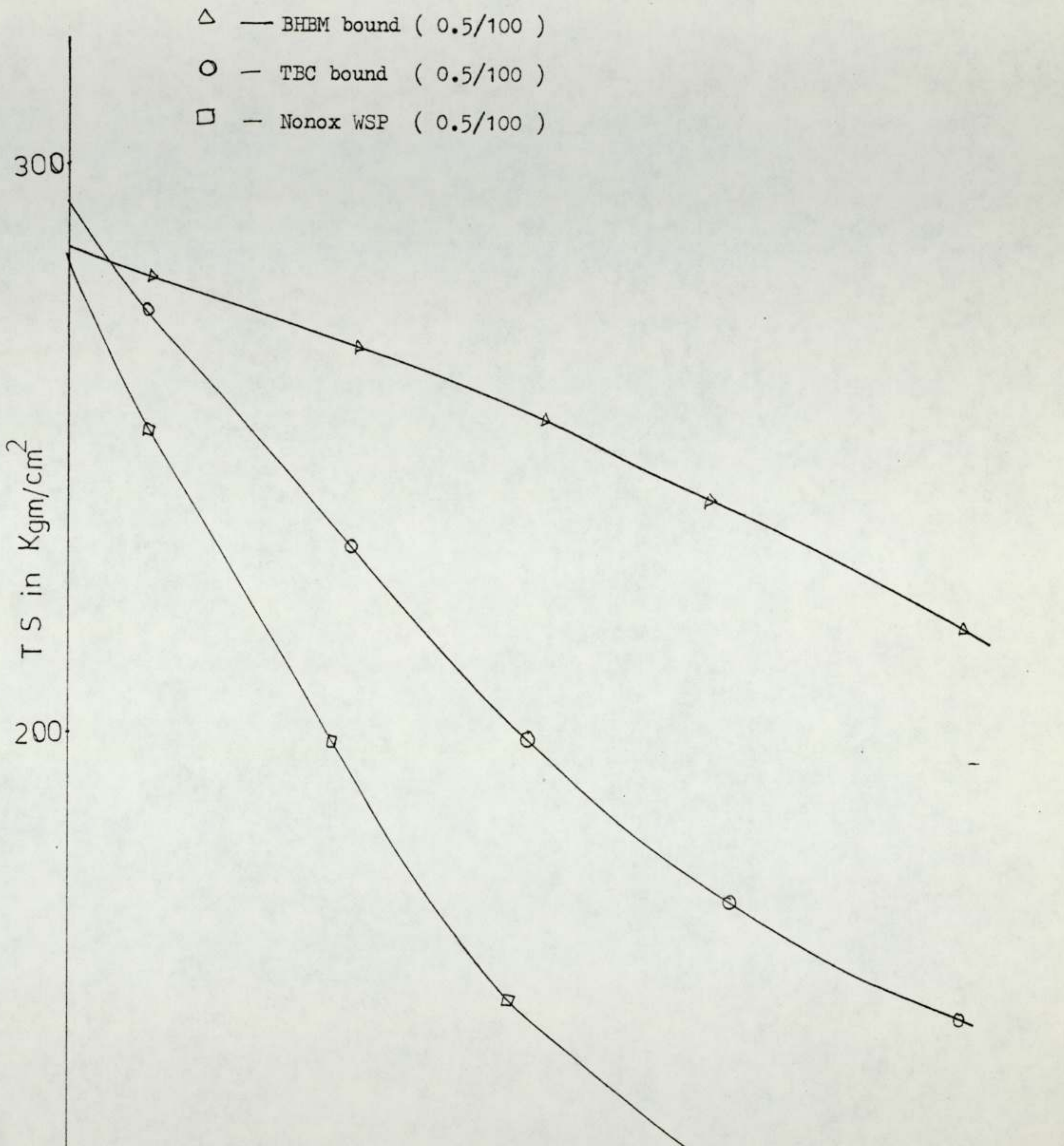
A set of films, which contained 0.5/100 of antioxidant (by masterbatch technique) was aged at 70°C for known lengths of time and then the tensile strength were tested.

Table 6.16

Tensile strength of the aged films in Kgm/cm^2

ageing time in days	BHBM bound 0.5/100	TBC bound 0.5/100	Nonox WSP 0.5/100
0	286	292	284
$3\frac{1}{2}$	277	267	237
7	265	226	180
10	256	196	152
14	244	173	125
20	227	150	104

Figure 6.2 - Variation of tensile strength with ageing time at 70°C



6.3.3 Discussion

Again the superior effect of the rubber bound antioxidant over the conventional antioxidant is very evident from the tables 6.16- and the curves in Fig. 6.2. The thiol-based bound antioxidants are generally superior to the simple monophenolic due to the higher level of reaction achieved. This again demonstrates that under aggressive conditions in large surface area to volume samples, intrinsic activity is much less important than is molecular weight and hence volatility.

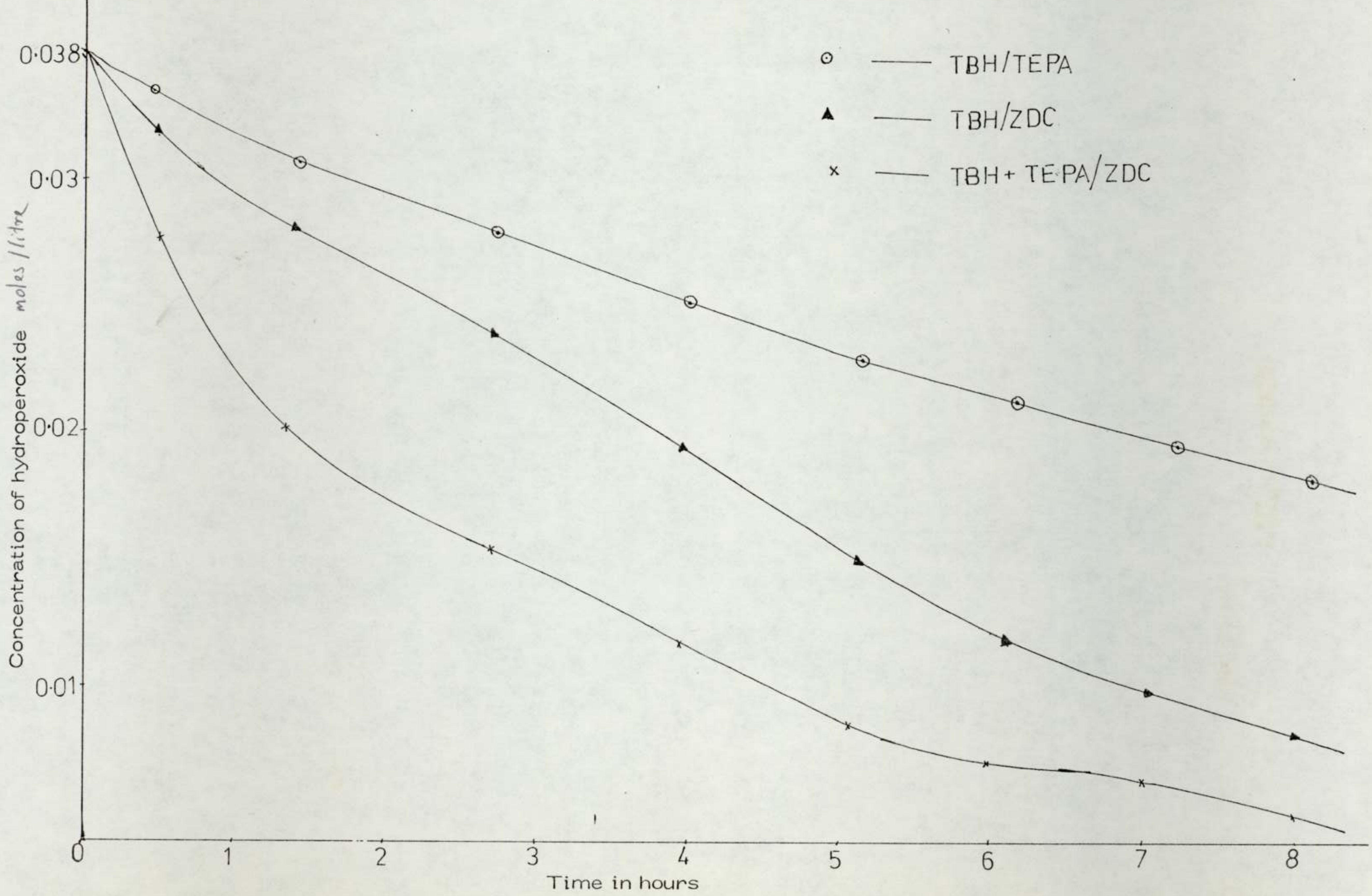
6.3.4 Decomposition of ZDC in prevulcanised latex by hydroperoxide

A set of experiments was carried out with 100 gm of prevulcanised latex, which contained 0.5 gm of ZDC and 1.5 ml (0.009 moles) of TBH/ 4.5 ml of 10% TEPA. The reaction temperature was maintained at 55^{o}-60^{o}C. 5 ml of the solution was taken out at known time interval and to this 0.5 gm of sodium iodide was added. Then the solution was acidified with a drop of concentrated sulphuric acid and the liberated iodine was titrated against standard 0.1 M solution of sodium thiosulphate solution. A graph of the concentration of the remaining hydroperoxide vs time was plotted. This is a direct indication of the rate of decomposition of ZDC by hydroperoxide.

To differentiate the decomposition of ZDC by TBH, another set of experiments were carried out in the absence of ZDC and TEPA respectively. The graphical interpretation of these curves are shown in Fig. 6.3

To study the effect of ZDC on vulcanisation, a masterbatch of 10/100 of bound antioxidant in prevulcanised was prepared with 900 gm of unreacted prevulcanised latex, so that 1/100g of antioxidant was

Figure 6.3 Decomposition of hydrpperoxide by ZDC, ZDC + TEDA, TEDA



present in the system. The ZDC added in the form of prevulcanised latex, was effected the curing of the films. This is clearly demonstrated, when the tensile properties of the masterbatches are compared with the undiluted samples.

Table 6.17

Tensile properties of the prevulcanised films

Formulation	T.S in Kgm/cm^2	%elongation
BHBM bound prevulcanised latex		
2/100	193	865
TBC bound prevulcanised latex		
2/100	188	910
Masterbatches		
BHBM bound prevulcanised latex		
1/100	299	730
TBC bound prevulcanised latex		
1/100	263	730

Discussion :

The data reveal (fig 6.3) that the rate of decomposition of hydroperoxide by ZDC is faster in the presence of TEPA than that of TBH/TEPA alone and TBH/ZDC. The concentrations of both the hydroperoxide and the ZDC are diminishing during the reaction at a similar rate as in the reaction of BHBM with latex (See chapter 2). Therefore part of the BHBM becomes bound to the rubber. But in the case of TBC, the rate is relatively slower than that of ZDC decomposition (see chapter 2) , resulting in very low yield of TBC being bound to the rubber.

The table 6.17 demonstrates the effect of added ZDC through prevulcanised latex, which causes a better cured system than the reacted prevulcanised alone, hence the tensile properties were improved. This is clearly shown in table 6.17 in which the tensile strength of the masterbatches are compared with the undiluted, reacted prevulcanised latices.

6.4 Stress Relaxation Test

This method simply involves the measurment of the decay in stress of a sample of rubber maintained in extension at constant length and temperature. The stress relaxation method based on the kinetic theory and is expressed as a relationship between tha tension f exerted by a stretched rubber sample and the number of stress supporting network chains N , In more simplified way the N can be defined as chain segments between junction points in the network per unit volume.

$$f = NKTA_o \; l/l_o - l_o^2/l$$

Where
T - Absolute temperature
A_o - Cross-sectional area
K - Boltzmann's constant
l/l_o - Stretched length/ unstretched length
N - Number of stress supporting chains

Therefore f (stress) is directly propotional to N, if the other parameters, such as , temperature and the length of the stretched sample are constant.

$$f/f_o = N/N_o$$

As chain scission occurs during thermal degradation of rubbers, the decay in stress is a direct measurement of the degradation of natural rubber.

The experimental procedure was given in chapter 2. A set of extracted and unextracted samples were tested and the curves are shown in figures 6.4-6.

6.4.1 Discussion

Figures 6.4-6.7 illustrate that the unextracted vulcanisates, particularly, the control and the antioxidant bound prevulcanisates decay drastically within a short period of time, whereas, the antioxidant bound samples show much more resistance to decay. Similar results were observed with extracted samples, except in nonox WSP, which decays more drastically than the rest.

When it comes to masterbatches, a similar behaviour was observed and again the extracted samples decay rapidly due to the loss of their unreacted antioxidants during the extraction. However, from these results it is clear that the antioxidant bound samples are much more resistant to oxidation even after the solvent extraction, whereas, conventionally added antioxidants are not. The thiol based antioxidants are generally superior to the simple monophenolic due to the high level of reaction achieved. Again the poor performance of the prevulcanisates were evident and probably related to the lower level of reaction achieved as well as the lower state of cure of the vulcanisates.

Figure 6.4 - Stress relaxation of unextracted vulcanisates at 100°c

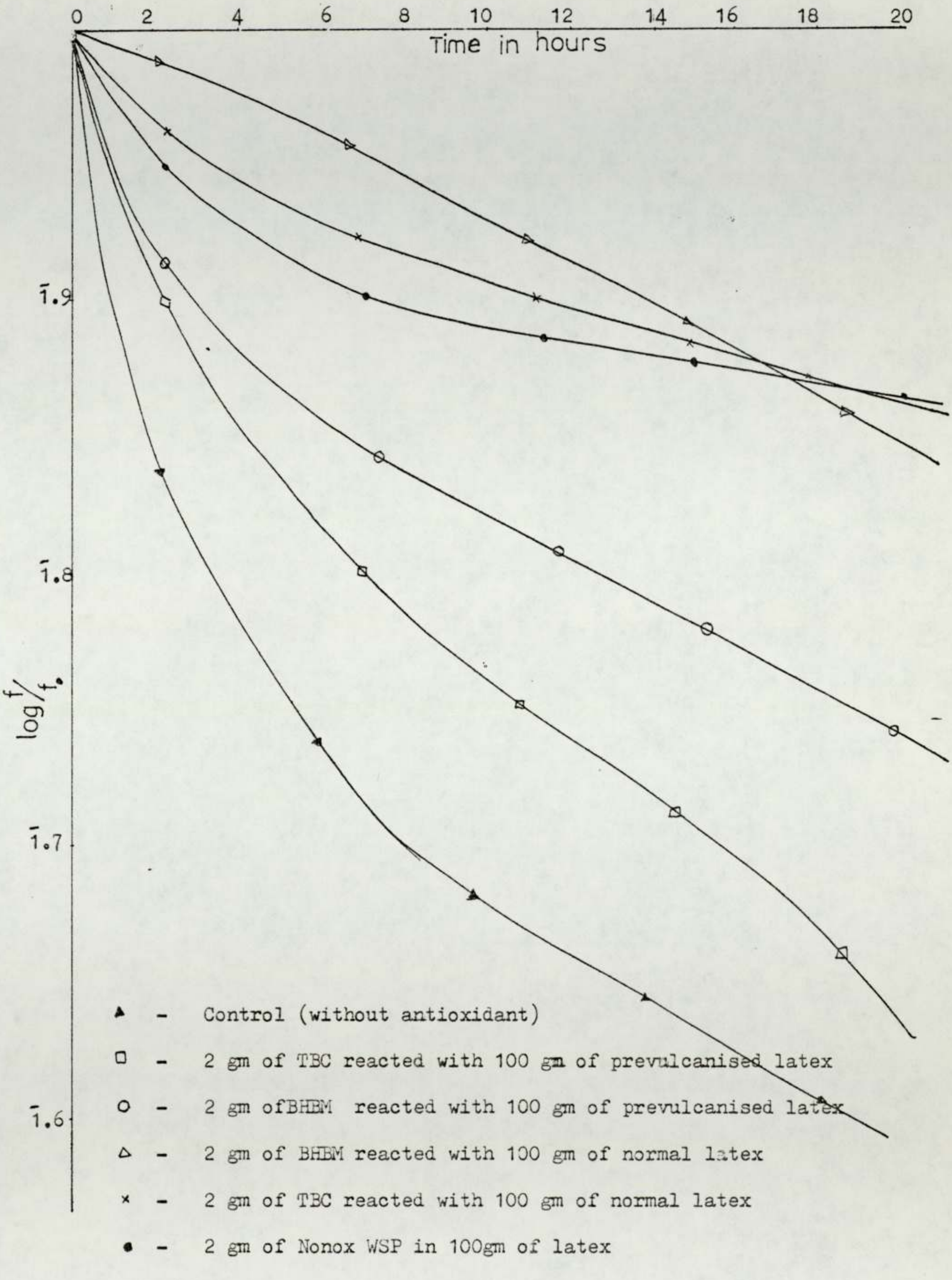


Figure 6.5 - Stress relaxation of extracted vulcanisates at 100°c

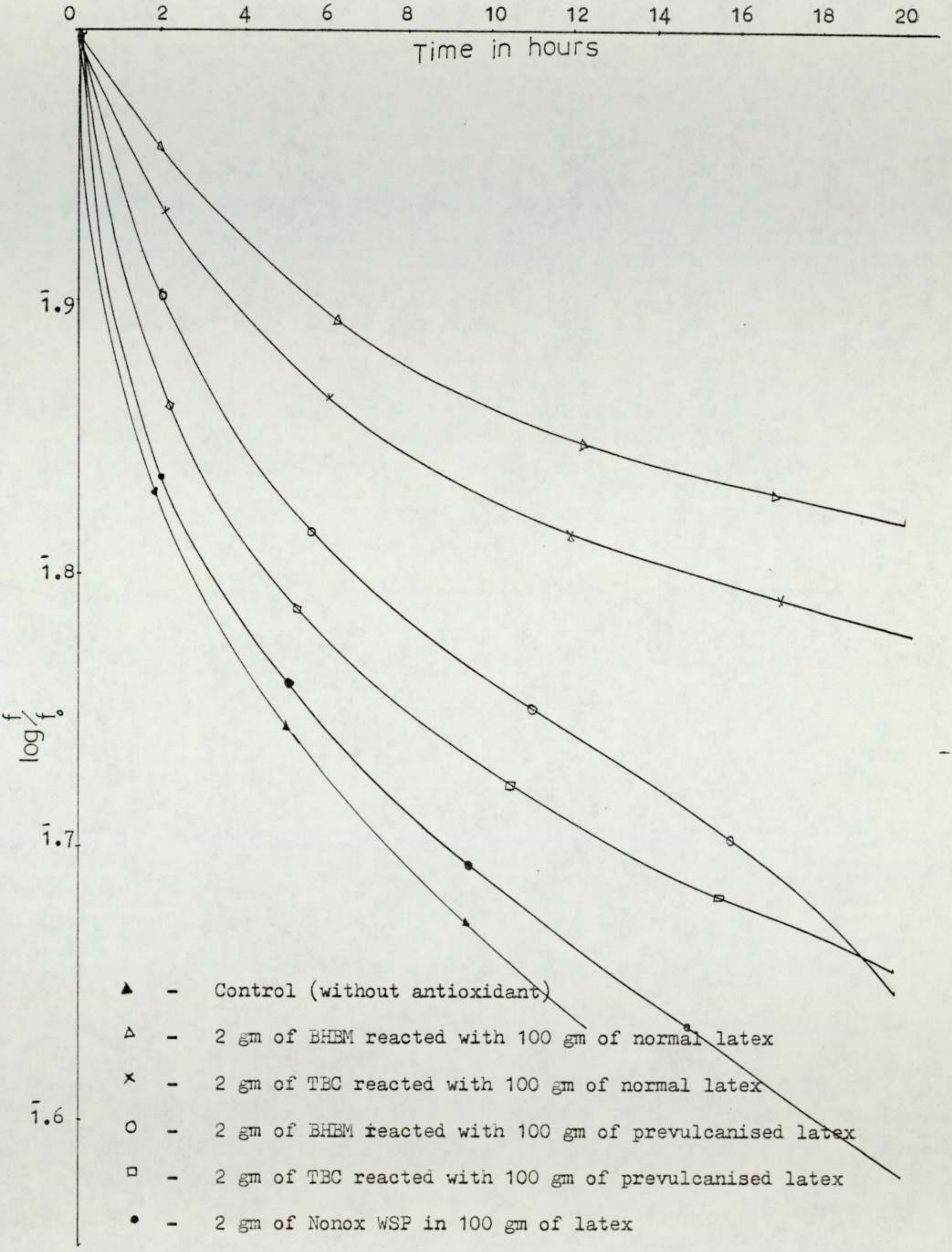


Figure 6.6 - Stress relaxation of unextracted masterbatch samples at 100°c

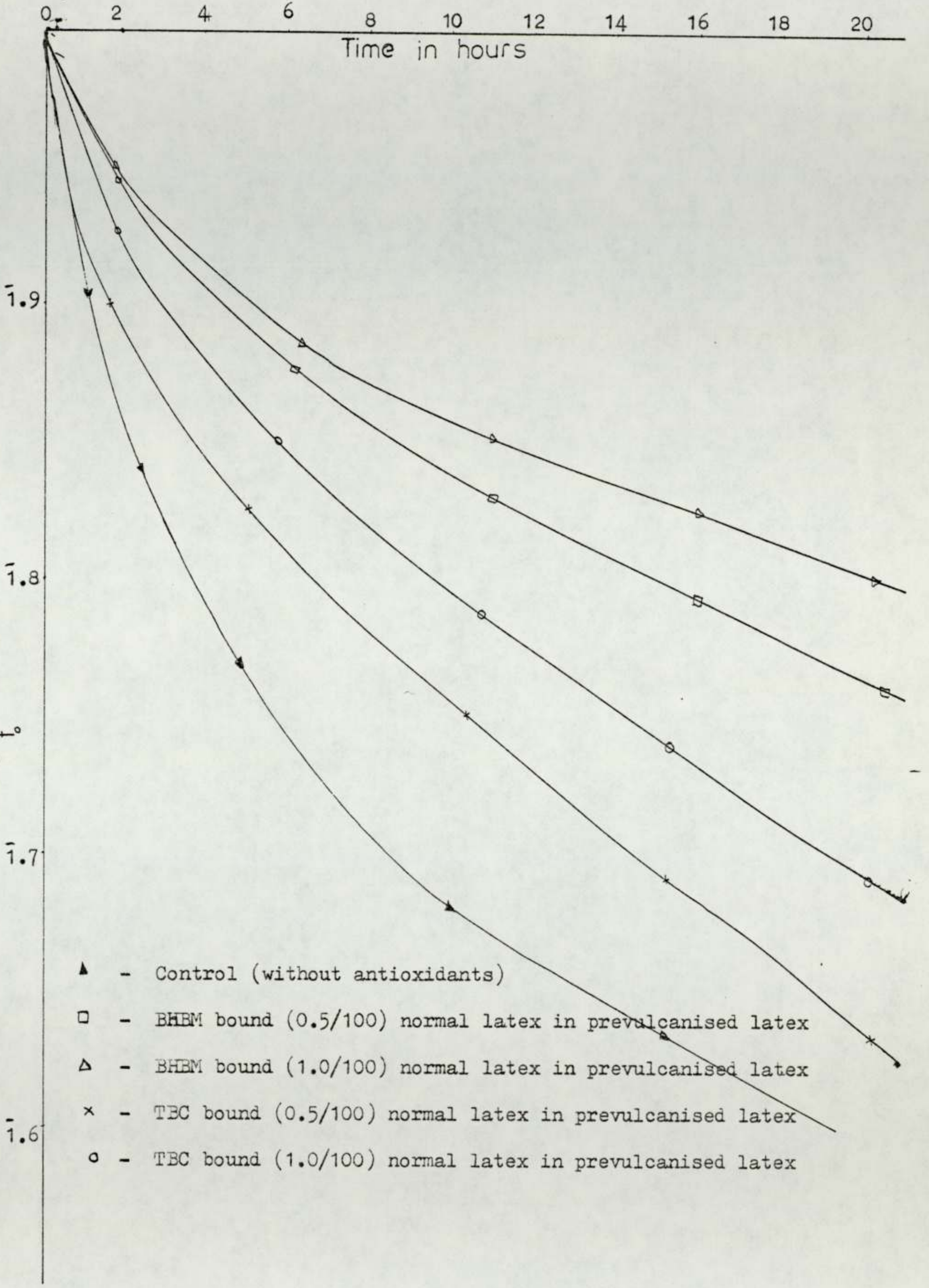
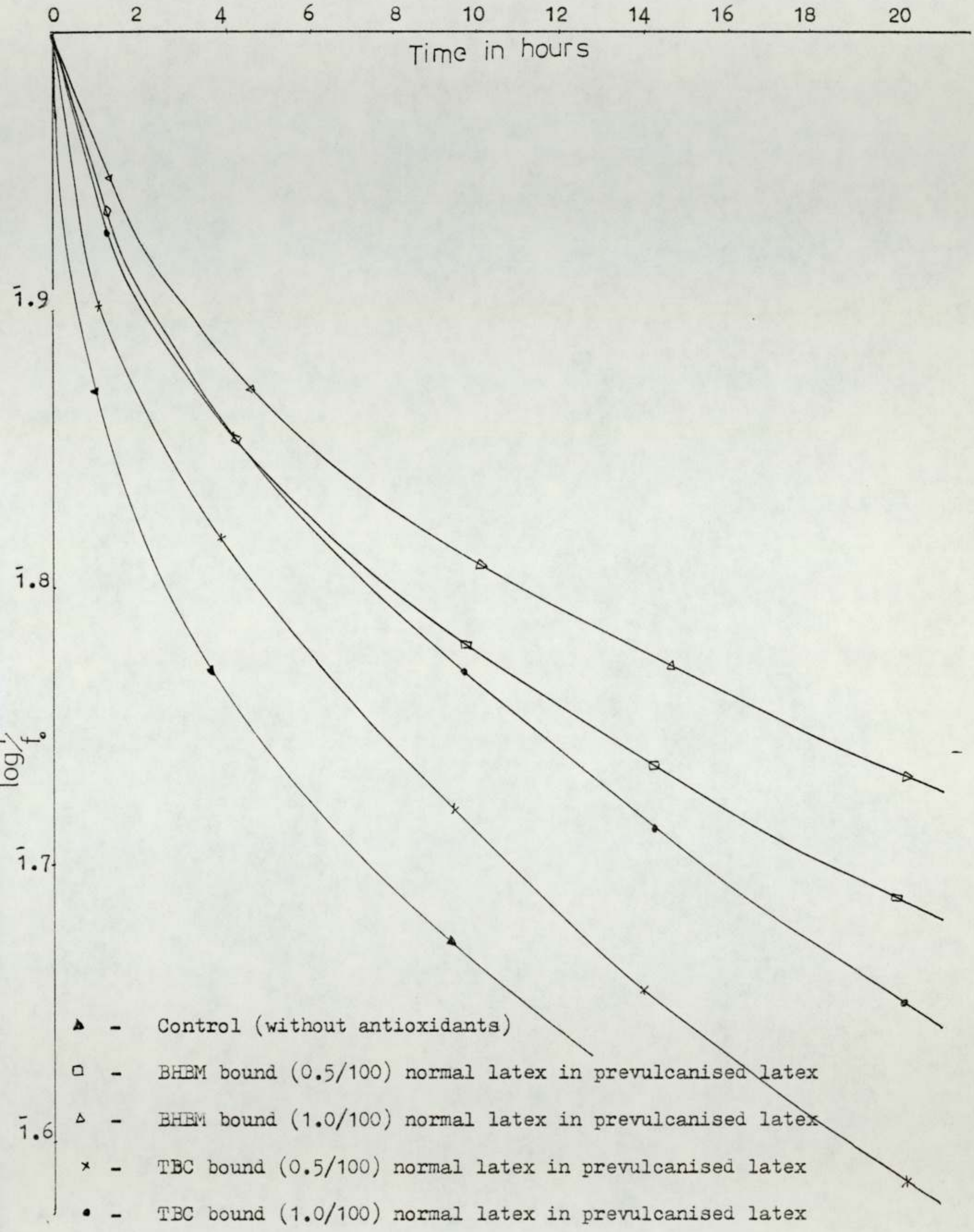
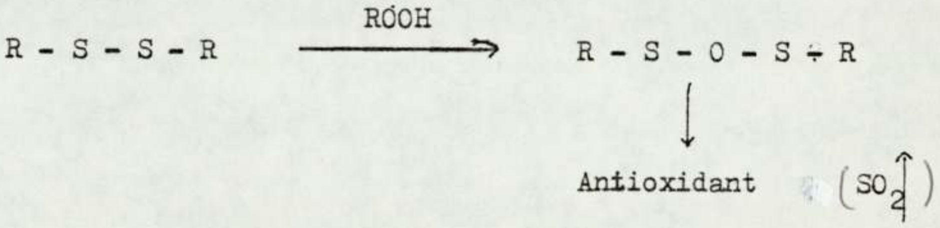


Figure 6.7 - Stress relaxation of extracted masterbatches at 100°C



6.5 Oxygen Absorption Test

The oxygen absorption curves for the extracted, unextracted and the masterbatch samples are shown in Fig. 6.8 - 6.10. The peculiar shape of the unextracted thiol bound vulcanisates, which was not evident in extracted samples is probably due to the liberation of sulphur dioxide by the reaction of disulphide and monosulphide with hydroperoxide formed during the experiment. In unextracted thiol vulcanisates disulphide and monosulphide are more mobile and hence more easily react with the hydroperoxide.



$$\begin{tikzcd} R-S-S-R \arrow[r, "R\acute{O}OH"] & R-S-O-S-R \arrow[d] \\ & \text{Antioxidant}\quad (SO_2\uparrow) \end{tikzcd}$$

Conclusion :

The evidence presented illustrate that the physical properties of aged films of antioxidant bound rubbers are much superior to the conventionally added antioxidants. Stress relaxation and oxygen absorption tests substantiate the superior performance of the rubber-bound antioxidants. All these results lead one to suggest that antioxidant volatility is at present the main factor limiting the usefulness of antioxidants and stabilisers. Simple antioxidant structures when combined chemically with rubbers become very much more effective even in conventionally accelerated tests but particularly in assessment techniques which simulate aggressive environments experienced by many rubbers under practical conditions.

Figure 6.8 Oxygen absorption of the unextracted vulcanisate

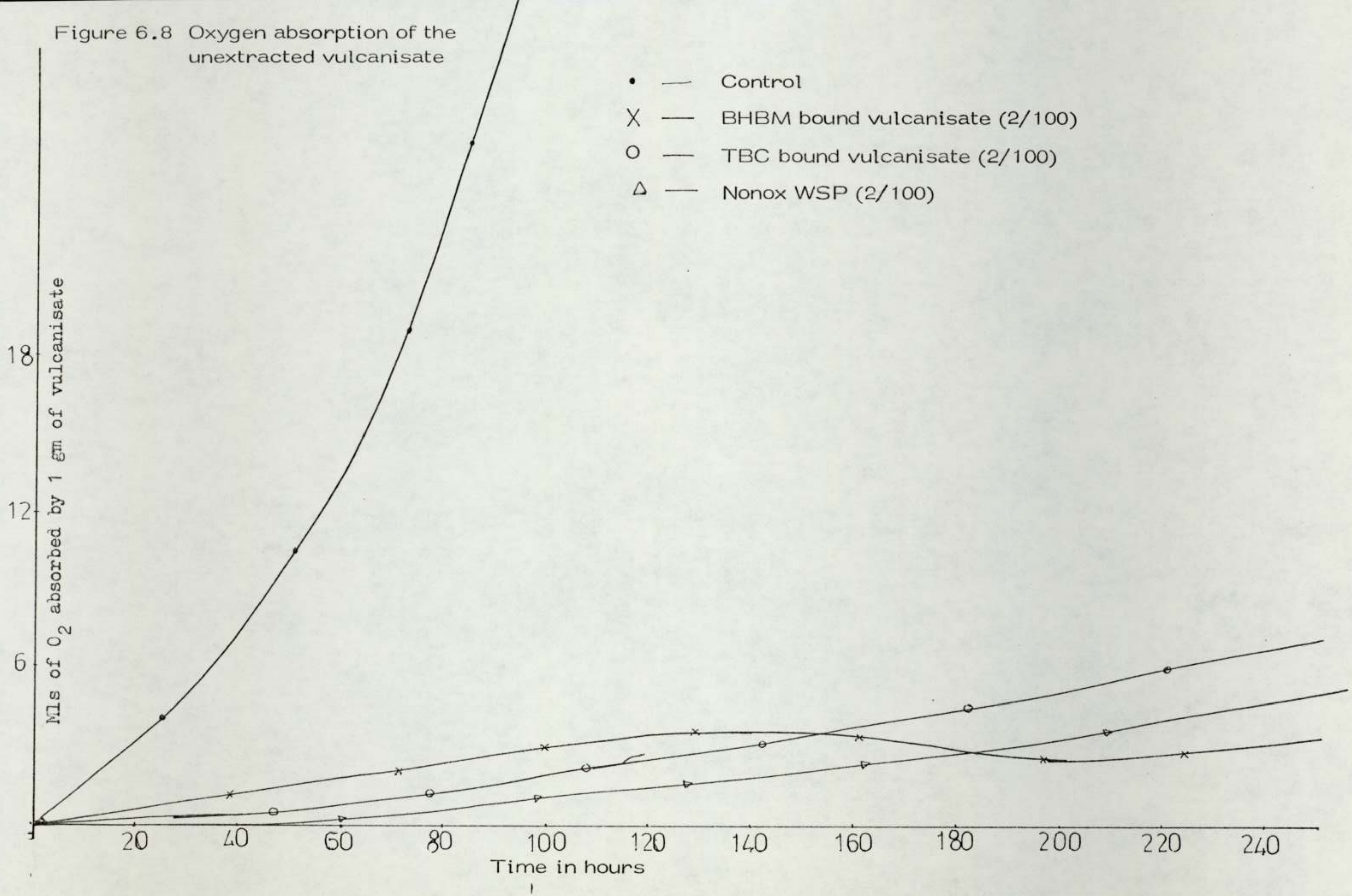


Figure 6.9 Oxygen absorption of the extracted antioxidant bound vulcanisate at 70°C

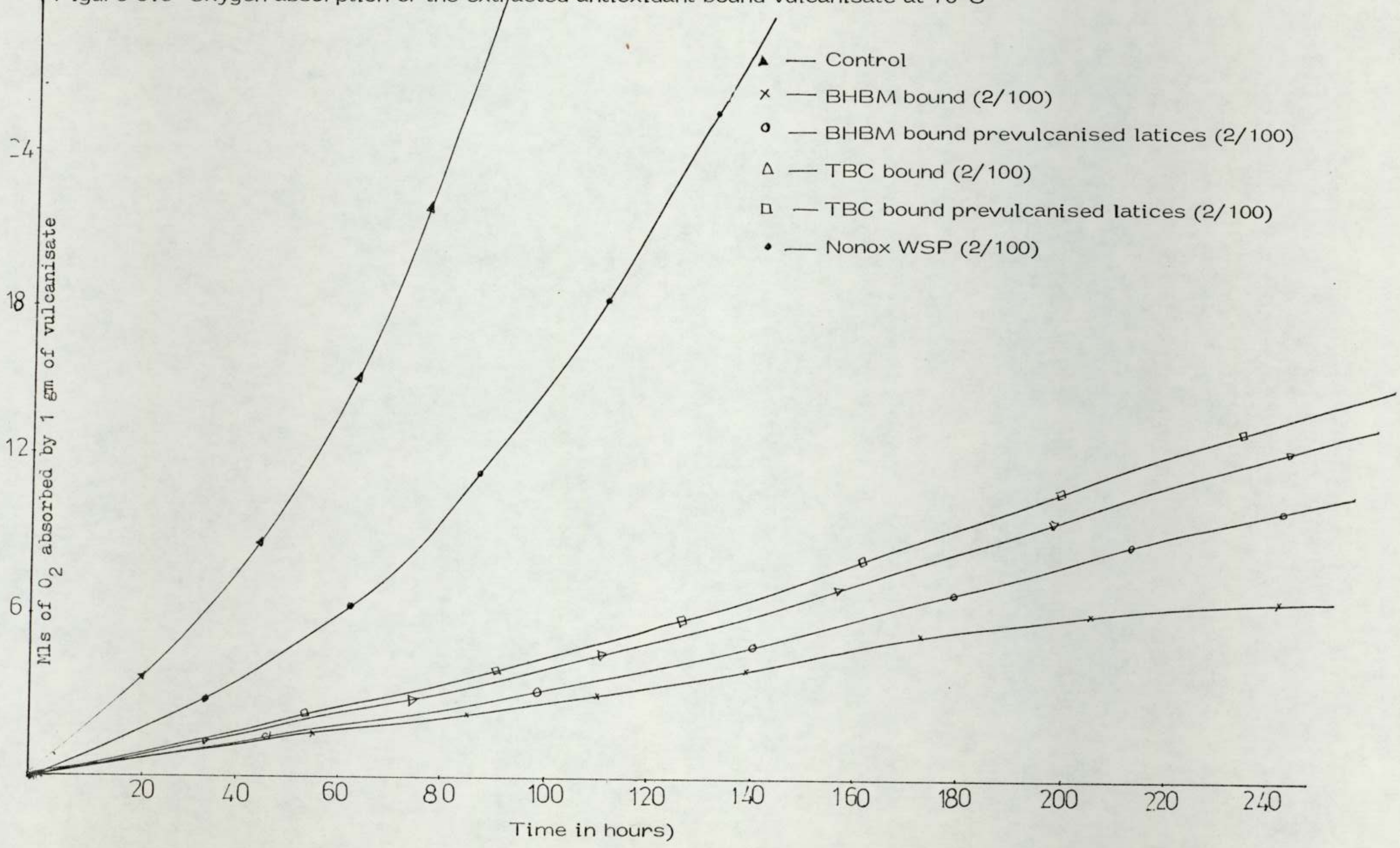
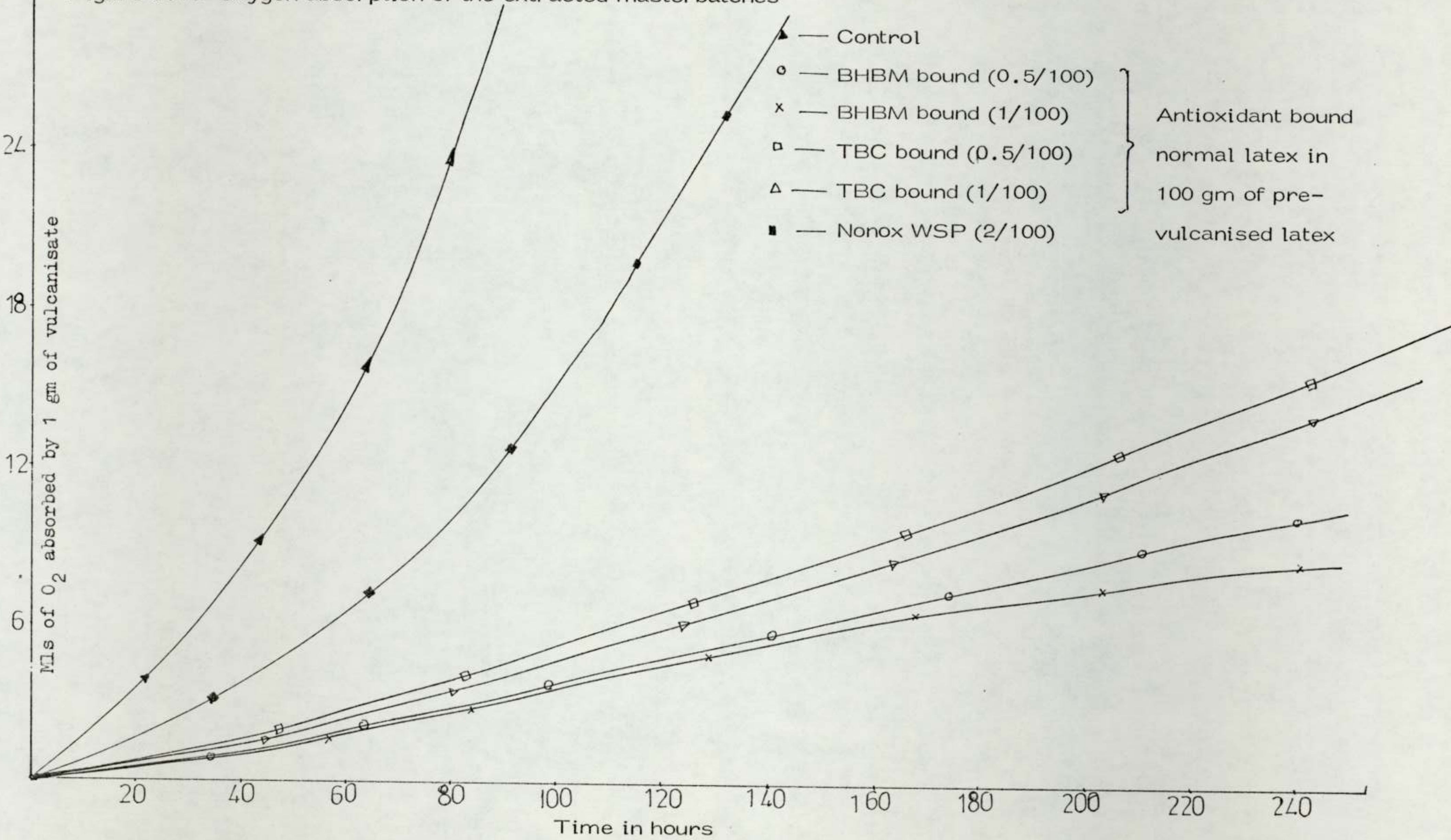


Figure 6.10 Oxygen absorption of the extracted masterbatches

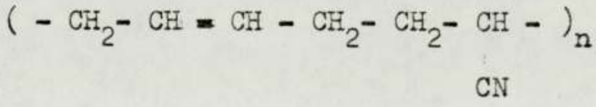


CHAPTER SEVEN

Reactions of hindered phenols with butadiene-acrylonitrile latices

Butadiene-acrylonitrile rubbers (NBR rubber) are well known speciality rubbers and are used in a variety of commercial applications, which involve direct or intermittent contact with oils and fuels. The combination of inherent oil resistance, processing ease, good physical properties and versality in compounding and curing has resulted in a substantial market for these polymers. The need for greater heat resistance and overall performance in the automobile industry has initiated a number of investigations designed to meet the more stringent performance requirments. NBR polymers are routinely bathed in various media , which can and do remove the commonly added antioxidants by extraction or by leaching, thereby reducing service life. One such example is NBR oil seals used in automobile industry. Dry heat alone is sometimes sufficient to volatilise the stabiliser and cause failure through embrittlement of the part.

Basically nitrile rubbers are manufactured by emulsion polymerisation of butadiene and acrylonitrile monomers. Theoretically , the polymer structure can be represented as the repeated units of butadiene and acrylonitrile.



$$(- CH_2 - CH = CH - CH_2 - CH_2 - \underset{CN}{CH} -)_n$$

The properties of the polymer depend on the ratio of butadiene to acrylonitrile. NBR rubbers used for oil seals contain 32% nitrile. Usually NBR latices are anionic and show similar behaviour to natural rubber latices. But the diameter of the NBR particles are generally smaller than that of natural rubber, being between 5 and 80 millimicrons according to the grade concerned. Owing to their small particle size, NBR latices are particularly suitable for impregnating and saturating fibres, because in order to penetrate fabrics, the rubber particles have to be smaller than the space between the fibres of the fabric.

This chapter is mainly concerned on the reactions of BHBM and TBC with medium nitrile rubber (32% nitrile content) and then to study the effect of NBR bound antioxidants in industrial applications such as, oil seals and as a binder for non-woven fabrics.

7.1 Reaction of BHBM with NBR latices

All the reactions were carried out with 50% NBR latex 3316, which was supplied by Bayer Ltd and consists of 32% nitrile. This was diluted to 30% and the unreacted monomers were removed by suction for 3 hours at room temperature. It has been found[37] that the monomers present in acrylonitrile-butadiene-styrene (ABS) latices inhibit the adduct formation of BHBM with the latices, and is prominent in the latices, which contain styrene monomers. The reaction parameters such as, reaction time , temperature, and initiator concentration were investigated as in the natural rubber latex reactions.

7.1.1 Reaction time

A set of experiments was carried out with 30% NBR latex and 2 gm of BHBM using 1.5 ml of TBH/TEPA as an initiator. The temperature was maintained at 55^{o}-60^{o}C and the samples were taken out at known time intervals. The films were cast on glass plates, dried and were then extracted with methanol for 24 hours, which was found to be sufficient to remove the unreacted BHBM and the other byproducts. The amount bound was estimated by the I.R technique described earlier.

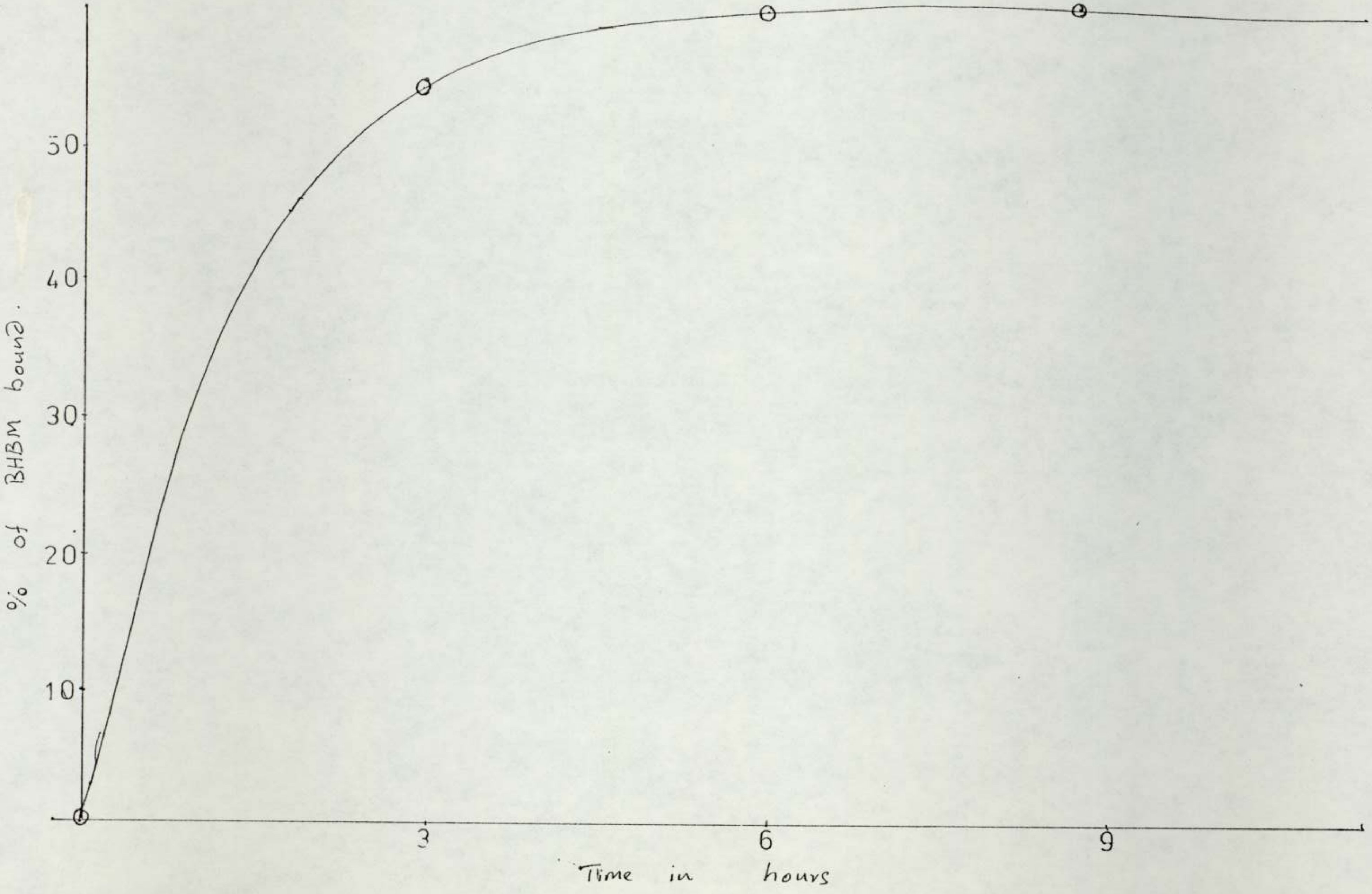
Table 7.1

Percentage of BHBM bound at various time intervals

Time in hours	Concentration of BHBM bound	% of BHBM bound
0	0	0
3	0.0042	52.5
6	0.0046	58.5
9	0.0047	59.5

The graphical interpretation of the concentration of the bound BHBM vs time is given in Fig. 7.1. This illustrates that the reaction is essentially completed within 6hours. The lower level of reactivity than that of natural rubber can be accounted for by the presence of monomers such as butadiene, particularly acrylonitrile,which inhibits the addition reaction,since the latter cannot be removed by suction at room temperature. The faster rate of the addition reaction than N.R may be due to the greater solubility of BHBM in the organic phase, which contains polar groups such as cyanide.

Figure 7-1 - Reaction



7.1.2 Effect of initiator concentration

A set of experiments was carried out with different concentrations of initiator with 0.008 moles of BHBM and 100 gm of NBR latex(DRC). The films were prepared, washed, dried and were then extracted with methanol. The concentration of the bound BHBM was determined by the I.R technique.

Table 7.2

Effect of the TBH concentration on the addition reaction of BHBM with NBR latices.

Concentration of BHBM used - 0.008 moles

Initiator concentration (TBH) in moles	Concentration of BHBM bound	% of BHBM bound
0	0	0
0.004	0.0009	11.1
0.008	0.0032	39.6
0.016	0.0045	56.5
0.032	0.0044	55.5

A graph of the concentration of BHBM bound vs concentration of the initiator is shown in Fig. 7.2. It is clear from the results that the concentration of the initiator to antioxidant is in the region of 2:1.

Conclusion :

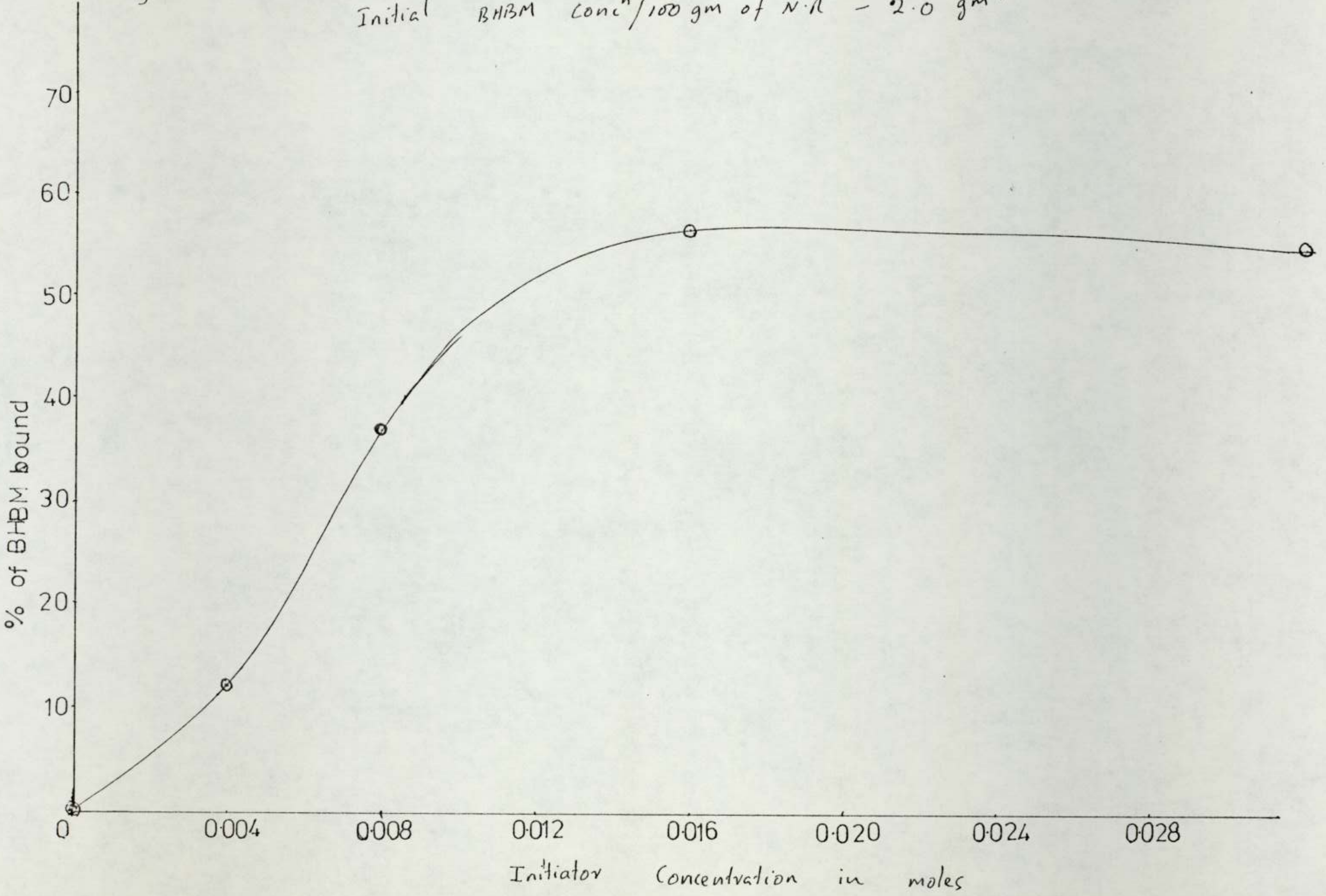
The following reaction conditions are necessary for the reaction of BHBM with NBR latices.

1. Reaction time 6 hours

2. Concentration of the initiator must be increased proportionately with respect to that of BHBM.

Figure 7·2 - Effect of Initiator

Initial BHBM conc^n/100 gm of N·R - 2·0 gm.



3. Reaction temperature ; 55°-60°C
4. Swelling time ; 15 minutes

7.1.3 Reaction of TBC with NBR latices

The reaction conditions were the same as that described in TBC/natural rubber in chapter 2. Again the unreacted monomers were removed by suction at room temperature for three hours.

1. Reaction time ; 18 hours
2. Reaction temperature ; 55°- 60°C
3. Swelling time; 30 minutes
4. Concentration of the initiator was increased propotionately with respect to the concentration of TBC

The concentration of the bound TBC was determined by I.R technique and was found to be 9.8%. The lower level of reaction acheived may be due to the presence of unreacted monomers, which inhibit the reaction and is oxidised to other products by the initiator.

7.2 Compatibility of antioxidant-bound NBR rubbers with service fluids

Preparation of vulcanised NBR :

The following formulation was used for the preparation of the test specimens.

Table 7.3

Compounding ingredients	Dry weight in gms
Nitrile rubber(extracted)	100.0
Zinc oxide	5.0
Stearic acid	0.5
Sulphur	0.5
Carbon black	60.0
Tetra-methyl thiuram disulphide	2.0
N-tert-butyl-2-benzathiazole sulfenamide	1.0
Di-octyl pthalate	5.0

Carbon black was incorporated first and was followed by pthalate during the mixing of ingredients. The rest of the mixing procedure was the same as described in chapter two for natural rubber. The samples were cured at 168°C for 10 minutes under 50 tons/sq,in pressure and the thickness of the specimens were 2.0 mm.

7.2.1 Testing procedure[95] (ASTM testing procedure)

Change in mass :

The dimensions of the test specimens were in the order of 25 x 50 x 2 mm. The specimens were weighed accurately in air and were then immersed in ASTM oil number 2 at 150°C for 72 hours and 168 hours respectively. At the end of the immersion periods, the specimens were taken out, washed with acetone and blotted lightly with filter papers. The samples were reweighed and the percentage change in mass was noted. Similary three specimens were tested.

$$\% \text{ change in mass} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Final weight}} \times 100$$

Change in volume :

This was carried out to determine the volume of oil that has been swollen into the NBR polymer network. Three specimens were weighed accurately in air and then the volume was determined by water displacement method. Similarly the weight and volume of the immersed samples at 150°C for 72 and 168 hours were determined. The change in volume is expressed as

$$\% \text{ change in volume} = \frac{\text{Final volume} - \text{Initial volume}}{\text{Initial volume}} \times 100$$

Change in tensile strength, elongation and hardness :

The tensile pieces were cut from the vulcanisate and the original tensile strengths, elongation and hardness were determined. Then the samples were immersed in ASTM oil No 2 at 150°C for known length of time and the final tensile strength, elongation, modulus at 100 % and 200 % elongation and hardness were determined.

7.2.2 Antioxidant-bound NBR rubbers for oil seals

Masterbatches were prepared with the antioxidant bound polymers so that 1.0 gm and 2.0 gm of the antioxidant were contained in 100 gm of NBR rubber. For this purpose, 10 gm of the antioxidant (TBC or BHBM) was reacted with 100 gm of NBR latices using 4.8 ml of TBH and 13.5 ml of TEPA as an initiator. The rest of the reaction procedure was the same as that described earlier. The dried films were then mixed up with nine and nineteen parts of unreacted, extracted NBR rubber.

Similary 100 gm of NBR latex was reacted with TBH/TEPA (1.5/4.5 ml of 10% TEPA) in the absence of the antioxidant. This was carried out to investigate the reaction of commercially added antioxidant during the processing, with NBR latices in the presence of the initiator. It was observed by the I.R technique that a phenolic compound was present in the latex, probably the added antioxidant during the processing of NBR latex. What was more surprising was the presence of the same phenolic group after the extraction of the reacted NBR rubber with the initiator, which was not observed in the extracted films of the unreacted NBR. The conclusion emerging from these data is that somehow the available phenolic compound in the latex was reacted with the NBR latices in the presence of TBH/TEPA initiator. This was furthur elaborated in the subsequent sections.

The vulcanised samples were prepared as described earlier and the physical properties of the specimens were testd. Then the samples were immersed in ASTM no 2 oil at 150°C for 3, 7 and 14 days respectively and the properties were retested. After the immersion, the change in volume, mass and the hardness were determined, which are direct indication of the amount of oil swelled into the network and is dependent on the original surface area as well as the resistance of the network.

Table 7.4

Initial tensile properties of antioxidant-bound rubber (for oil seals)

Formulation	Hardness	Modulus at 100% E	Modulus at 200% E	T.S in Kgm/cm^2	Elongation at break
Polymerised trimethyl hydroquinoline					
NBR$_1$ (2/100)	68	30	90	203	300
NBR latices reacted with TBH/TEPA (no antioxidant) NBR$_2$	71	35	105	187	210
Masterbatch samples					
BHBM bound masterbatches					
(1/100) - NBRT$_1$	73	36	-	179	180
(2/100) - NBRT$_2$	73	34	137	183	230
TBC bound masterbatches					
(1/100) - NBRC$_1$	74	27	73	173	310
(2/100) - NBRC$_2$	72.5	33	125	222	270

Table 7.5

Tensile properties of antioxidant-bound NBR rubbers (oil seals) after immersion in ASTM oil at 150°C for 3 days

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	T.S at break in Kgm/cm^2
NBR_1	20	66.6	210	120
NBR_2	19	58.0	260	109
$NBRT_1$	36.5	-	180	147
$NBRT_2$	34	125	220	156
$NBRC_1$	20	66.6	270	126
$NBRC_2$	33	116.6	220	179

Table 7.6

Percentage retention of tensile properties after 3 days immersion

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	T.S at break
NBR_1	63	62	70	59
NBR_2	55	55	123	58
$NBRT_1$	100	-	100	82
$NBRT_2$	100	96	96	86
$NBRC_1$	74	91	87	72
$NBRC_2$	100	93	81	80.6

Table 7.7

Tensile properties of antioxidant-bound NBR rubber after immersion in ASTM oil at 150°C for 7 days

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	T.S at break in Kgm/cm^2
NBR_1	20	66.6	210	108
NBR_2	27	97.0	210	101
$NBRT_1$	36.5	120.0	210	146
$NBRT_2$	37.7	131.0	230	159
$NBRC_1$	33.2	76.0	220	86
$NBRC_2$	37.0	127.8	220	152

Table 7.8

Percentage retention of tensile properties after 7 days immersion

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	T.S at break in Kgm/cm^2
NBR_1	66.6	74	70	53.0
NBR_2	77.0	92	100	53.0
BHBM masterbatches				
$NBRT_1$	100.0	-	113	81.5
$NBRT_2$	110.8	96	100	87.0
TBC masterbatches				
$NBRC_1$	118.5	104	71	49.7
$NBRC_2$	112.0	102	81	68.4

Table 7.9

Tensile properties of antioxidant-bound NBR rubber after immersion in ASTM oil at 150°C for 14 days

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	Tensile strength in Kgm/cm^2
NBR_1	29	-	190	93
Masterbatches				
$NBRT_2$	36	122	210	152
$NBRC_2$	29	-	180	88

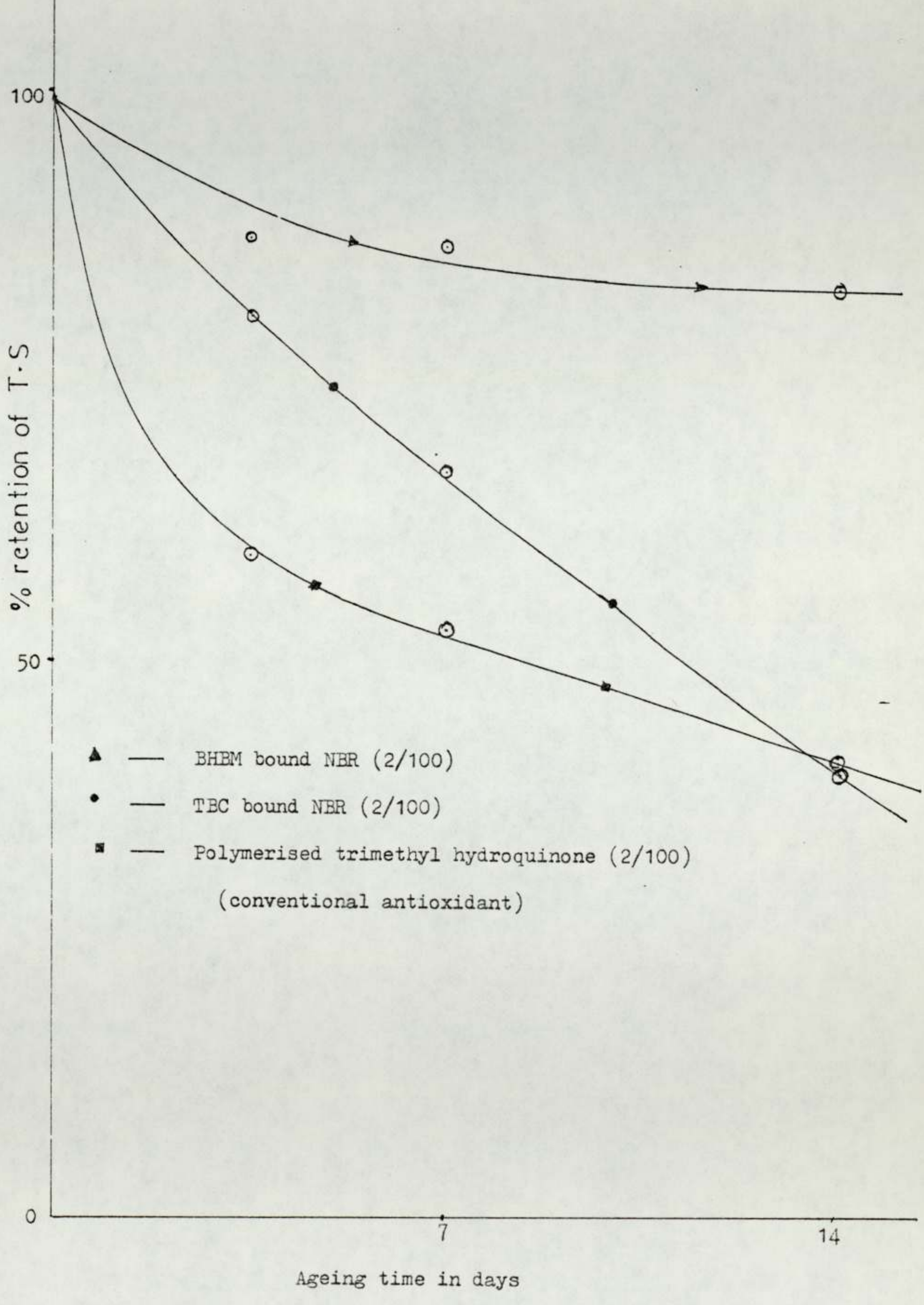
Table 7.10

Percentage retention of tensile properties after 14 days immersion

Formulation (code)	Modulus at 100% E	Modulus at 200% E	Elongation at break	Tensile strength in Kgm/cm^2
NBR_1	96	-	63	40.4
Masterbatches :				
$NBRT_2$	105	89.5	91	83.0
$NBRC_2$	87	-	66	39.6

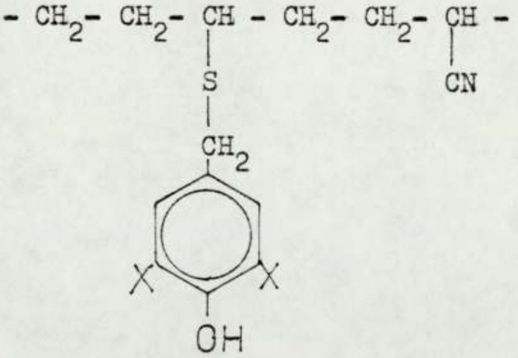
The graphical interpretation of the percentage retention of tensile strength vs ageing time was plotted and is shown in Fig. 7.3.

Figure 7.3- Retention of tensile strength of the antioxidant bound NBR rubbers at 150°C in ASTM No. 2 oil

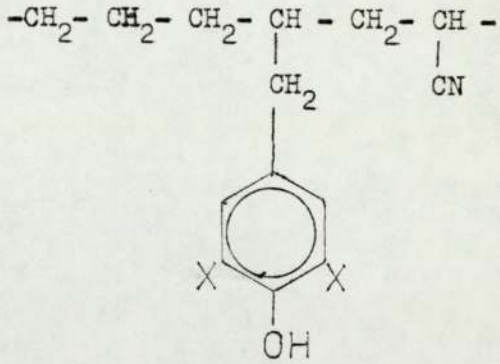


7.2.3 Discussion

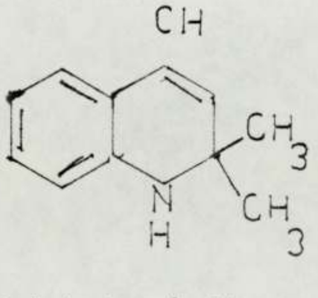
Tables 7.5 - 7.10 illustrate the superiority of the antioxidant-bound NBR polymers in an oil seal formulation. The poor performance of the conventionally added antioxidant is evident and is comparable with the reacted NBR latices with TBH/TEPA as initiators. This performance suggests that somehow the added antioxidant during the manufacturing has been chemically attached to the NBR latices in the presence of the TBH/TEPA initiator. The available data is insufficient to postulate a clear picture for the reaction mechanism of the unknown antioxidant in the NBR latex with TBH/TEPA. However, the far superior effect of the BHBM bound NBR polymer is evident from Fig 7.3. It has been found by I.R examination that 52% of the original BHBM remained bound to the NBR network, whereas, that of TBC was only 8%.



BHBM bound NBR (1)



TBC bound NBR (2)



Trimethyl hydroquinoline monomer

In masterbatch form, the BHBM based bound antioxidants are generally much superior to the simple monophenolic due to the higher level of reaction achieved. In addition, the adduct of thiol antioxidants with NBR rubbers gives rise to an auto-synergistic antioxidant effect due to the presence of both a hydroperoxide decomposer (the monosulphide) and a chain breaking function (phenolic B) in the same molecule (1). Therefore this structure is considerably more effective as a thermal antioxidant than either a phenol or sulphide alone.

The inferior properties of the heat-resistant stabiliser, polymerised trimethyl hydroquinoline is not surprising, because similar behaviour was observed with this antioxidant in NBR by Meyer and his co-workers They have reported that 43% retention of tensile strength of this antioxidant in NBR polymer after immersing in ASTM oil at 300°F (166°C) for 3 days and 76% retention after ageing in air oven at 300°F for 7 days. What emerges from these data is that the stability of the NBR polymer cannot be acheived under aggressive environmental condition by incorporating a polymeric antioxidant. The gradual loss of added antioxidant by volatilisation, leaching and extraction is unavoidable under the testing conditions carried out. These results illustrate that the chemical attachment of a simple thiol compound is a much better solution than the conventional additive procedure. In the masterbatch form, the modified latices and the unmodified latices are co-vulcanised in the presence of the vulcanising ingredients and the bound antioxidant acts as a part of the molecule, whereas in the conventionally added systems, it is present as an additive.

7.3.4 Effect of oil on the physical properties of antioxidant-bound NBR rubbers (oil seals)

Table 7.11

Percentage change in hardness, volume and mass of antioxidant bound NBR vulcanisates after immersing in ASTM oil at 150°C

Immersion period - 3 days

Formulation (code)	% change in hardness	% change in volume	% change in mass
NBR_1	6.7	12.1	9.8
NBR_2	6.9	12.3	10.1
BHBM masterbatches			
$NBRT_1$	6.8	11.6	9.5
$NBRT_2$	2.7	9.5	7.75
TBC masterbatches			
$NBRC_1$	6.7	11.8	9.5
$NBRC_2$	5.4	11.6	9.5

Table 7.12

Change in physical properties after 7 days immersion

Formulation (code)	% change in hardness	% change in volume	% change in mass
NBR_1	13.2	14.5	11.2
NBR_2	18.0	15.6	12.2
Masterbatches			
$NBRT_1$	9.5	12.3	9.9
$NBRT_2$	6.8	11.2	9.2
$NBRC_1$	9.8	13.8	11.8
$NBRC_2$	9.4	12.2	10.0

Discussion

The percentage change in hardness, volume and mass is a direct indication of the oil that has been swelled into the network. Again it is obvious that BHBM-bound NBR rubbers are more resistant to oil than that of the TBC bound and the conventionally added antioxidant. The swelling of the oil depends on the polarity and the crosslinked pattern of the network. The former is found to be the major governing factor. The higher resistance of BHBM bound rubbers may be due to two reasons, a) higher reaction achieved by BHBM, b) the additional polar groups, which have been introduced into the network through BHBM adduct, namely phenolic OH and monosulphide.

7.3 Antioxidant-bound NBR latices as a binder for textile fibers

It is a known fact that NBR latices are used to bind textile fibers in the production of non-woven fabrics of all types requiring good resistance to ageing and solvents. The following experiments were carried out to investigate these antioxidant-bound NBR latices as a binder for non-woven fabrics. Specialy prepared monomer-free NBR latex was used for the reactions, which was supplied by Revertex Limited and was contained an unknown crosslinking agent.

Procedure :

Masterbatches of the monomer-free, antioxidant-bound NBR latices (1/100) were prepared as described earlier with both TBC anf BHBM. Then the films of $\frac{1}{4}$ mm thickness were cast on glass plates, washed and was cured at 120°C for 20 minutes. The initial tensile properties of the films were tested and then extracted, aged and the final tensile properties were tested.

Table 7.13

Initial tensile properties of the films

Formulation	Modulus at 100% E	Elongation at break	Tensile strength in Kgm/cm^2
NBR without antioxidants			
NB	25	660	38
Masterbatches:			
BHBM bound NBR - NBT$_1$	20	680	51
TBC bound NBR - NBC$_1$	27	650	57

Table 7.14

Tensile properties of 2% detergent washed and aged films for 3 days at 70°C

Formulation (code)	Moudulus at 100% E	Elongation at break	Tensile strength in Kgm/cm^2
NB	26	680	38
NBT$_1$	24	820	93
NBC$_1$	27	730	58

Table 7.15

Tensile properties of solvent washed (pet-ether/ toluene :: 80 ; 20) for 5 minutes and aged films - 3 days at 70°C.

Formulation	Modulus at 100% E	Elon. at break	T.S in Kgm/cm^2
NB	24	660	36

NBT_1	26	690	97
NBC_1	26	700	60

Table 7.16

Percentage retention of tensile properties after ageing

Formulation (code)	Initial T.S in Kgm/cm^2	Detergent washed/ aged	Solvent wahed/ aged
NB	38	100	96
NBT_1	51	182	190
NBC_1	57	102	105

Discussion :

It is interesting to note that the higher percentage retention of tensile strength of all the samples and this may be due to the crosslinking of the monomers,dimers and high monomers by the added unknown crosslinking agent at high temperatures during the ageing. The superior effect of BHBM bound rubber can be accounted for the higher reaction level acheived.

7.3.1 Non-woven application test (see appendix)

A bath was prepared containing 20% NBR latex. 6 webs of each of dimension 6" x 10" were cut from the standard non-woven material, so that 10" was in the zero strength direction and then all were weighed accurately. One of the webs was placed between two wire gauze, thoroughly impregnated in the latex bath and was then passed through a wringer. The non-woven was peeled off from the wire gauze and was placed on the released paper, to minimize the direct handling. This procedure was repeated with the other five webs. These were then dried in a laboratory oven at 130°- 140°C for 20 minutes and were weighed accurately. Each web was cut into 9 strips of dimension 1" x 5", where 5" was in the non-stretched direction. The strips were then sorted out into 3 files of 18 each, in such a way that each contained 3 strips from the original webs. These were then stored in a desiccator and the strips were tested for,

a) dry tensile strength at break,

b) hot wash (2% tide at 60°C, soaked for 5 minutes and were tested while wet),

c) tensile strength, when is wet with solvent (soaked in tri-chloro-ethylene for 5 minutes)

Tensile strength were calculated as follows,

$$\text{\% wet retention of T.S} = \frac{\text{Wet tensile strength}}{\text{Dry tensile strength}} \times 100$$

$$\text{\% solvent retention of T.S} = \frac{\text{Solvent tensile strength}}{\text{Dry tensile strength}} \times 100$$

A correction factor of A was introduced, where A is the grams of dry latex picked by the total number of non-wovens, for comparison of different latices.

$$\text{Corrected solvent tensile strength} = \text{Measured solvent tensile strength} + A \times 0.04$$

$$\text{Dry tensile strength} = \frac{\text{Corrected solvent tensile strength}}{\text{\% solvent retention}} \times 100$$

$$\text{Wet tensile strength} = \frac{\text{Corrected dry T.S} \times \text{\% wet retention}}{100}$$

The masterbatches of BHBM and TBC (1/100) were prepared and were tested for non-woven fabrics as described earlier.

Results:

Table 7.17

Tensile strength of the impregnated webs

Formulation	Dry tensile strength in Kgm/cm^2	Solvent T.S in Kgm/cm^2	Wet tensile strength in Kgm/cm^2
NBR without antioxidants	3.6	3.3	1.19
Masterbatches			
BHBM (1/100)	3.7	3.3	1.38
TBC (1/100)	3.8	3.1	1.28

Discussion :

The performances of the antioxidant-bound rubbers and the control have not shown a significant difference in tensile properties. These tests do not represent any indication relevant to the ageing behaviour of rubbers, but they can be considered as tests, which determine the effectiveness of these latices as binders for the fabrics. Therefore, what-ever the antioxidant system, the poor performance is inevitable because the latices act as a weak binder for the fabrics.

CHAPTER EIGHT

Conclusion :

There has been increasing interest in recent years in high molecular weight antioxidants. The reason for this is essentially practical, since it has been shown that under certain conditions of antioxidant testing, which are relevant to service conditions, antioxidant loss from the polymer can be the dominating factor in determining its effectiveness. Three testing procedures have been developed, which give information concerning the antioxidants. These are,

a) Evaluation of intrinsic antioxidant activity in a sample model system by oxygen absorption,

b) Evaluation of antioxidant activity in a polymer by oxygen absorption test. Since the solubility of antioxidants in the polymer is an additional factor introduced into this test, but loss by volatilisation is not, this test gives information about compatibility and the mobility of the antioxidant in polymers, when taken in conjunction with the first test,

c) Evaluation of antioxidant activity in a polymer with a large surface area to volume ratio (eg. films or fibers) in a flowing air stream. This type of test (eg. stress relaxation test) measures the resultant of intrinsic antioxidant activity, polymer compatibility and volatility under the conditions of test and conditions can be chosen to accentuate the latter for certain applications.

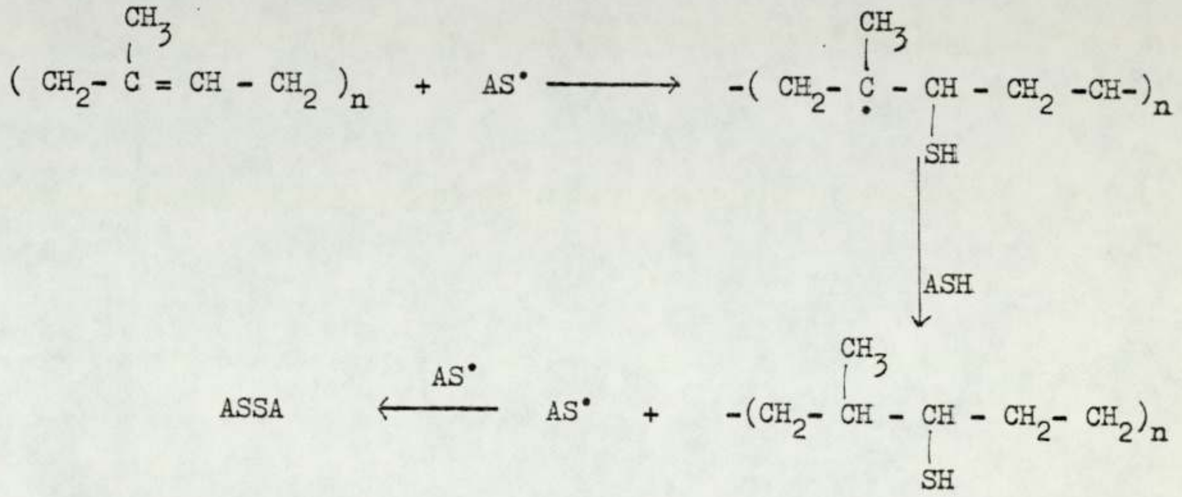
Another test which has relevance to certain conditions experienced in practice is solvent extraction or detergent leaching followed by ageing and then measuring the retention of tensile properties This is relevant to fibers subjected to dry-cleaning or washing or films subjected to weathering. The extraction test is more severe, for example it has been shown that some of the polymeric antioxidants and stabilisers will perform well in an oven test but may still be ineffective after solvent extraction.

The main theme of this research work was to investigate an antioxidant system, which is more effective than conventional system under the above mentioned testing conditions.

Reaction of hindered phenols with natural and synthetic latices

It has been found that the adduct reactions of hindered phenols such as , BHBM and TBC can be carried out successfully with natural and synthetic latices using TBH/TEPA as an initiator. Infra-red examination of the solvent extracted natural rubber samples showed 70% of the original BHBM and 11% of the TBC remained bound to the rubber. In the case of TBC, the concentration achievable is limited by side reactions such as, formation of stilbene quinone, aldehyde etc, a nd the crosslinking of the network.

A parallel behaviour was observed in NBR latices, with 57% of the original BHBM and 9% of TBC remained bound after extraction. The decrease in the percentage bound in NBR latices may be due to the inhibitory effect of the monomers, dimers present in the latex. However, BHBM can be reacted to a much higher conversion in both latices than the simple phenols, because the former undergoes a facile addition to the double bond of rubber in the presence of a free radical initiator. The reaction is a radical chain process as shown below and is terminated by reaction of thiyl radical (AS•) with other radicals in the system.



This type of reaction mechanism was confirmed by model compound studies and the analysis of the byproducts during the reaction. Further more, it has been found that byproducts such as, disulphides and monosulphides can be reacted with the rubber in the presence of the same initiator and not only that, thiol esters, which contain -SH function can be reacted to the same extent as that of BHBM with rubber latices.

In the case of TBC, it has been observed by model compound studies that the reactive position of natural rubber is the allylic carbon atom next to the double bond and is attached to the benzylic position of the TBC. In addition to this, the formation of stilbene quinone has been show to be a major byproduct during the reaction, which cause the discolouration of the latex.

Latex crepes containing bound antioxidants based on thiols show a considerably improved colour retention. This leads to the practically very important consequence that where guaranteed cleanliness and non-toxicity are important, for example in medical applications, thiol based antioxidants not only give better coloured products but are also completely safe, since they cannot be leached from the rubber during the use. It was evident from the results that latex products containing bound antioxidants exhibit exceptional stability, when used in applications where loss of antioxidants by volatilisation or by leaching may occur. The performance of BHBM adduct is very much superior in both natural and nitrile rubber latices than the TBC adduct and the conventional antioxidants. This is probably due to the higher level of reaction acheived by BHBM with rubbers.

A major advantage of the thiol based antioxidant system is that it can be used conveniently in the preparation of masterbatches. It was found in thiol system, when subjected to solvent or detergent leaching followed by ageing, these rubbers show almost complete retention of tensile strength under conditions where the conventionally stabilised rubber shows extensive degradation. It was very clear in antioxidant NBR bound rubbers that so long as the antioxidant remained bound to the network, what-ever the testing conditions, the performance is always much superior to the conventionally added antioxidants.

Suggestion for furthur work

The ability of disulphide (BHBDS) and monosulphide (BHBMS) to react with rubbers in the latex stage has been demonstrated, and the data available was insufficient to put forward a clear picture about the reaction mechanism. It would be therefore of interest to study the reaction mechanism of these sulphides with rubber using model compound studies, which would rationalize the different reactivity level of BHBDS and BHBMS with rubber.

It has been found that thiol esters can be reacted with rubber to the same extent as that of BHBM. The preparation of thiol esters are much more easier, safer and appears to be synergistically more powerful than BHBM. Therefore, it is of interest to investigate the effectiveness of the thiol ester bound rubbers under aggressive testing conditions.

The thiol-based bound antioxidants might be profitably extended as a method of producing high molecular weight antioxidants. Thiols could be reacted with unsaturated oils or oligomers to produce antioxidants for fuels or lubricating oils, where colour is considered to be an important factor.

Furthermore, this technique (thiol adduct formation) could be used to introduce more effective antioxidant or stabiliser functions in to the network in bound form. It may be possible to bind thiol based antioxidants by mechano-chemical reaction, so as to produce required radicals for the initiation.

Appendix

Revertex non-woven application test

A bath is prepared containing 20% solid latex. 6 webs each measuring 6" x 10" are cut from the standard non-woven meterial. The 10 inch dimension is in the zero strength direction. The six webs are all weighed together, reading to the first decimal place (A grams). Six papers of release paper are cut to a size approximately 7" x 12" One of the 6" x 10" pieces of non-woven is placed between two pieces of wire gauze, thoroughly impregnated in the latex bath and then passed through a wringer. The non-woven is then peeled off the gauze and placed directly on to the release. Direct handling of the web is thus kept to minimum. This procedure is repeated with other 5 webs. They are then dried together in a laboratory oven at 130- 140°C for 20 min. The weight of the six webs taken immediately on removal from the oven (B Gram). Each web is cut into nine strips each measuring 1" x 5", where 5" dimension is in the non-stretch direction. The strips are sorted into 3 piles of 18 each. The 18 in each pile contains 3 from each original web. The webs are stored at ambient for at least an hour before testing. Using a Hampden Tensometer with a 2lb beam and a speed of 4" per minute, the 18 strips are tested for;

a) Dry tensile strength at break;

b) Hot wash (2% Daz at 60°C, soak for 5 minutes and test while wet)

c) Solvent tensile when wet. (Soaked in tri-chloro-ethylene for 5 minutes)

Results are calculated as follows:

Latex pick is the number of grams dry latex picked up by the total number of non-wovens (B-A)

There are 18 scale reading for each tensile measurement. The highest and the lowest reading are neglected and the remaining 16 results averaged

$$\text{Tensile at break} = \frac{2 \times \text{Tensometer reading}}{100} \text{ lbs/in strip}$$

$$\text{\% wet retention} = \frac{\text{Wet tensile}}{\text{Dry tensile}} \times 100$$

$$\text{\% solvent retention} = \frac{\text{Solvent tensile}}{\text{Dry tensile}} \times 100$$

To allow for a comparison of different latices a constant pick-up (B-A) of 6 grams is aimed for. However slight variation are corrected as follows.

$$\text{Corrected solvent tensile} = \text{Measured solvent tensile} + (\ 6.0 \text{ measured pick-up }) \times 0.04$$

$$\text{Dry tensile strength} = \frac{\text{Corrected solvent tensile strength}}{\text{\% solvent retention}} \times 100$$

$$\text{Wet tensile} = \frac{\text{Corrected dry tensile} \times \text{\% wet retention}}{100}$$

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