Degradation and Stabilisation of Diisocyanate Cured Polybutadiene

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Doctor of Philosophy

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June 1992

Summary

Hydroxyl terminated polybutadiene (HTPB) has been used as a rocket propellant binder which is required to be stored for at least twenty years. It is found that the excellent stress-strain characteristics of this propellant can be totally lost, during this long storage, due to the deterioration of the polybutadiene chains. As a result, the propellant can not stand the service loads, which may lead to a catastrophe.

The study of the HTPB binder degradation, below 80°C, has been carried out by investigating the environmental factors and the changes which occur along the macromolecular chains.

Results have shown that oxygen is the main factor which causes the crosslinking and chain scission reactions. The former is the predominant reaction and proceeds rapidly under oxygen sufficient environment. The unsaturation of polymer chain, which provides the desired physical properties to the binder, was lost with the increase in crosslink density. At the same time hydroperoxides were found to form and decompose along the polymer chains. Therefore, the deterioration of the binder results from the oxidation of polymer chains. Since the oxidation reaction occurred at higher rate than oxygen diffusion rate and oxygen diffusion rate is inversely proportional to the crosslink density, the binder, below the surface layer in a thick section container, could be naturally protected under an oxygen deficient condition for a long time.

Investigation of the effectiveness of antioxidants in HTPB binder has shown that the efficiency of an antioxidant depends on its ability to scavenge radicals. Generally, aromatic amines are the most effective binder antioxidants. But when a peroxide decomposer is combined with an aromatic amine at the appropriate ratio, a synergistic effect is obtained, which gives the lowest binder gel increase rate.

Key words: HTPB binder, polybutadiene oxidation, oxygen diffusion in rubber, nmr of polybutadiene, antioxidants in polybutadiene, synergistic effect of antioxidants

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Acknowledgements

Declaration

The work described herein was carried out at Aston University between September 1988 and September 1991.

It has been done independently and submitted for no other degrees.

Wang Ting

List of Figures, Tables and Schemes

Chapter One

1.1. General Introduction

Composite propellants are highly filled rubbers with energetic fillers such as ammonium perchlorate and aluminium[1a]. The binder in current composite propellants is prepared from isocyanate cure of hydroxy terminated polybutadiene and it gives propellants with the rubbery properties required at low temperatures.

The reaction of isocyanate with primary alcohols occurs readily at $25°$-$50°C$[2,3]. Isocyanate, containing the highly reactive -N=C=O group, reacts with a host of compounds, and may also react with itself. Reaction can occur with almost any compound possessing a hydrogen atom that may be replaced by sodium[4]. The reaction proceeds by the attack of a nucleophilic centre upon the electrophilic carbon in the isocyanate group. The electronic structure of the isocyanate group indicates that it should have the following resonance possibilities:

$$R-\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}}-\overset{+}{C}=\overset{\cdot\cdot}{O}: \quad\longleftrightarrow\quad R-\overset{\cdot\cdot}{N}=C=\overset{\cdot\cdot}{O}: \quad\longleftrightarrow\quad R-\overset{\cdot\cdot}{N}=\overset{+}{C}-\overset{-}{\underset{\cdot}{O}}:$$
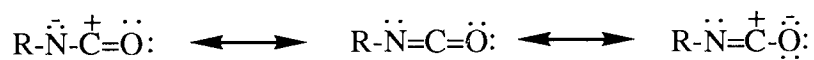
The normal reaction ultimately provides addition to the carbon-nitrogen double bond. In the reaction with those compounds having an " active hydrogen", the hydrogen becomes attached to the nitrogen of the isocyanate, and the remainder of the active hydrogen compound (A) becomes attached to the carbonyl carbon.

$$R-\overset{\cdot\cdot}{N}=C=\overset{\cdot\cdot}{O}: \quad + \quad H\text{-}A \quad\longrightarrow\quad \begin{array}{c} R\text{-}N\text{-}C\text{=}O \\ |\ \ | \\ H\ A \end{array}$$
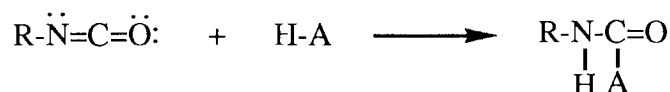
In this reaction the active hydrogen compound is acting as an electron donor and not as a hydrogen donor. In many cases the addition product is quite stable.

The crosslinking reaction occurs between the -NCO groups in the diisocyanate and the -OH groups in the polybutadiene when the functionality of -OH in the polybutadiene is more than two. A very important factor in the curing reaction is the ratio of -OH to -NCO, which is closely associated with the initial crosslink density of the product. Their relationship is shown in Fig.1-1, in which the crosslink densities are expressed by solubility values[5]. The initial crosslink density of the binder, therefore, is dependent on the amount of -NCO added as a curative. In practice, the theoretical ratio has to be modified because of any traces of water or other impurities in the system which contain groups like -OH or -NH.
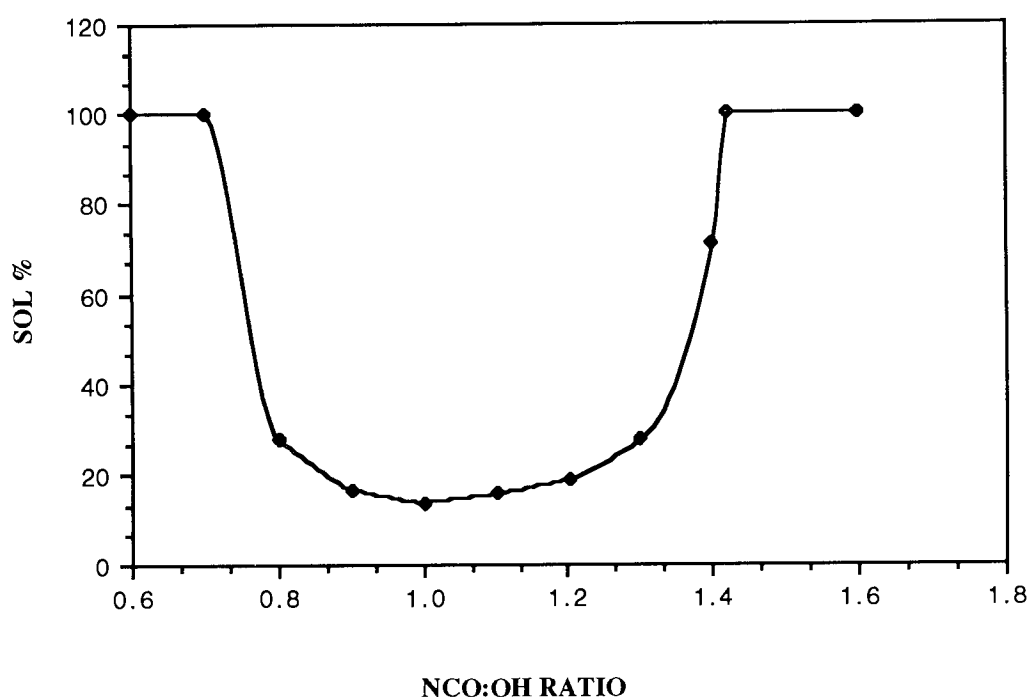
Fig.1-1 The relationship between initial solubility and NCO/OH ratio[5]

It is important to know that the reaction rates of isocyanates and active hydrogen compounds can be affected not only by the acidity of the mixture but can also be greatly modified by steric hindrance on the active hydrogen compound[2,4]. Steric hindered compounds, such as hindered phenols and hindered amines, will react with isocyanate at a much slower rate than unhindered alcohols and amines. Thus, it is possible to use chain-breaking antioxidants which are usually the most effective inhibitors to protect binders.

Usually solid propellant rocket motors are case-bonded, that is, the propellant is cast into a pressure vessel which is fabricated of high strength aluminium or steel(Fig.1-2)[1a,6]. After curing, a propellant storage time of twenty years is required[1b]. During this time it is subjected to two main loads [7,8]. One load results from the thermal strain that is generated as the rocket motor is cooled to a lower temperature than that for the cure. Significant stresses are created by thermal shrinkage and by the difference in the values of the thermal expansion coefficients for the polymer and the metal casing. The other load is caused by diurnal temperature cycling during storage. Besides the storage loads, a propellant must stand a higher stresses and strains caused by the acceleration when it is ignited. Because of these loads the stress capability at the binder/metal bondline and the strain capability at the inner bore are very important for a propellant to be able to perform reliably at a low ambient temperature.

The excellent stress-strain characteristics of a typical hydroxy-terminated polybutadiene/ammonium perchlorate propellant have been shown in a typical dynamic mechanical spectrum (Fig.1-3)[9]. G' is the dynamic storage modulus or the amount of energy stored elastically upon deformation and recovered per cycle. G" is the dynamic loss modulus or the amount of energy lost to viscous dissipation. As can be seen the elastic shear modulus (G') has a very high value at low temperatures and this value drops progressively as the temperature is raised. The major drop in the modulus occurs at about -83°C and this temperature is usually characterised by the peak in the loss modulus (G") curve. At temperatures lower than this peak the propellant is a hard low strain to failure material, above the peak the material is rubber-like with high failure strains. The low elastic shear modulus (G') of HTPB propellant in the rubbery region implies that the material possesses a high strain capability. These excellent stress-strain characteristics are the consequences of their molecular chain flexibility which comes from both C-C bonds free of hindrance from side groups, and C-C bonds adjacent to C=C bonds[10].

It has been shown that the unsaturation of the polybutadiene chain which is the reason for the good mechanical properties at low temperatures also makes the polybutadiene susceptable to atmosperic oxidation[1a]. There was a dramatic increase in the propellant's modulus (Fig.1-4) after ageing for 32 weeks at 60°C[9]. This change in modulus of over a decade at ambient temperature will be reflected in a loss of the material strain capability. As the rubbery-like properties of HTPB became a stiff material, it was unable to withstand the service loads[9].

The change in physical properties results from a change in the material structure. From the kinetic molecular theory of rubber-like elasticity [11, 12],

$$E_e = 3V_eKT \qquad (1)$$

where, E_e = rubbery modulus

V_e = effective network chain density

K = Boltzmann's constant

T = absolute temperature.

The rubbery modulus is related to the effective network chain density. The increase in the modulus comes from an increase in the material's crosslink density at a certain temperature.

As ageing causes deterioration of mechanical properties and could undermine the long shelf life required, antioxidants are used to alleviate the process. The antioxidant used in current propellants is 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) and it provides adequate protection against atmospheric oxidation. However, great economic benefit is to be achieved by finding an antioxidant which is more effective.

The purpose of this work is to identify an antioxidant which is not consumed in the isocyanate cure and which is more effective than 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) in protecting the polybutadiene binder from atmospheric oxidation.
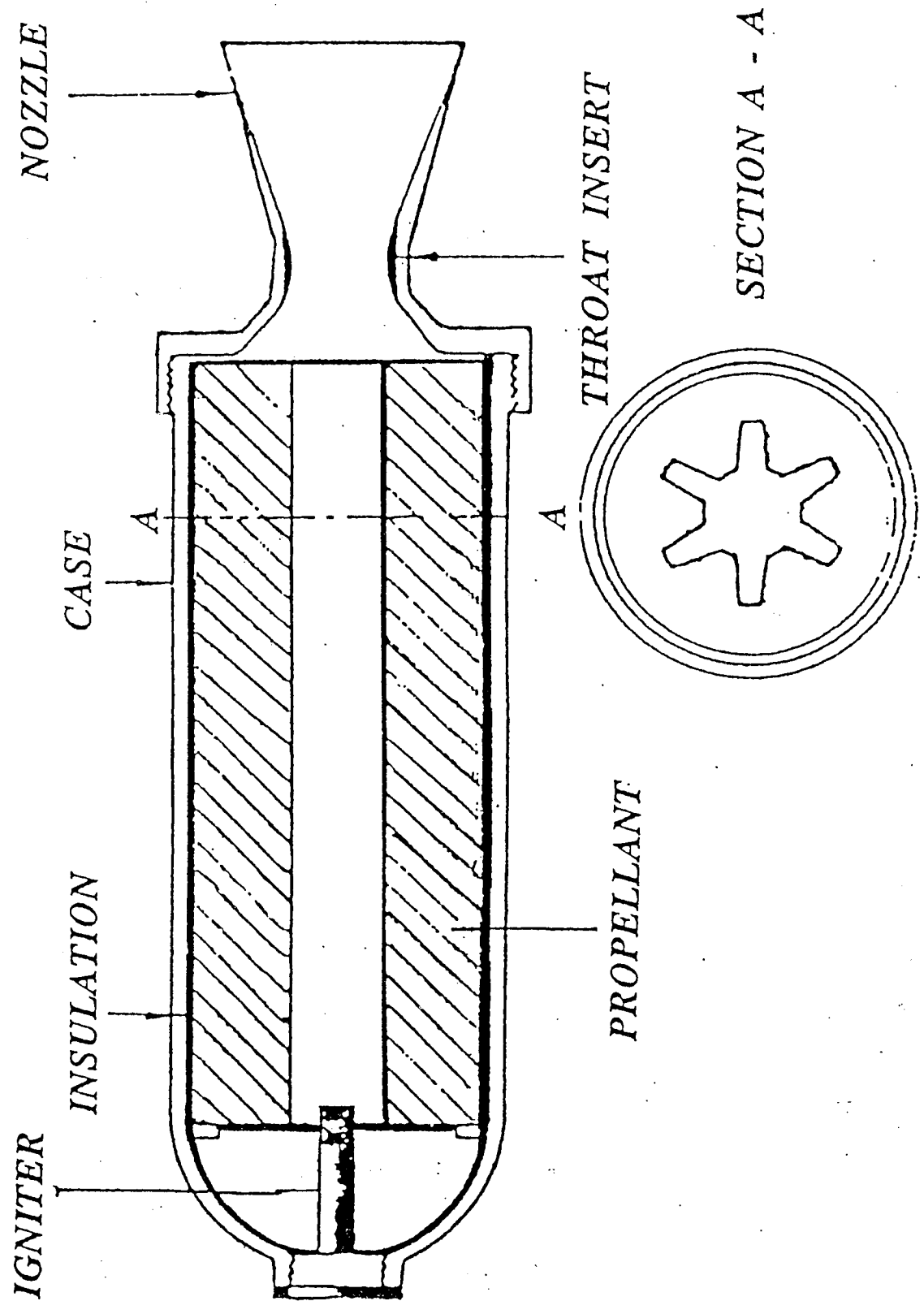
Fig. 1-2 The solid propellant rocket motor[1a]
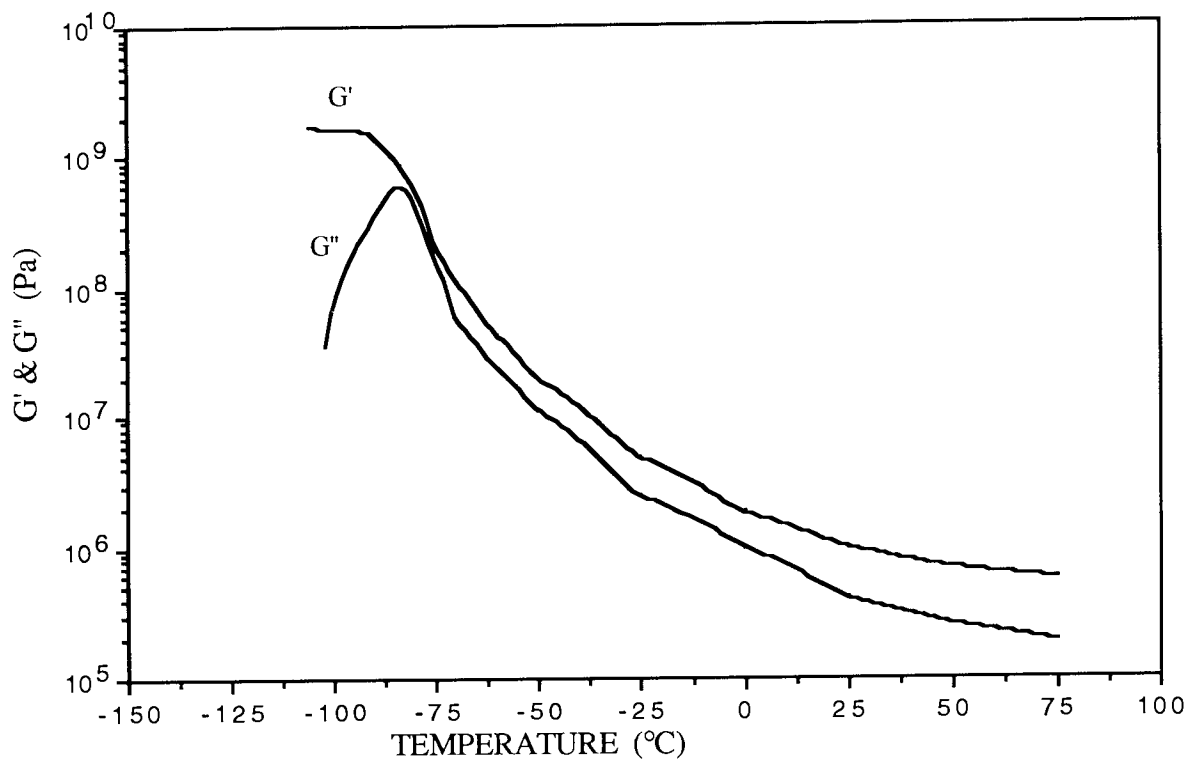
Fig.1-3 Dynamic mechanical spectrum of a typical hydroxy- terminated polybutadiene / ammonium perchlorate propellant[9]
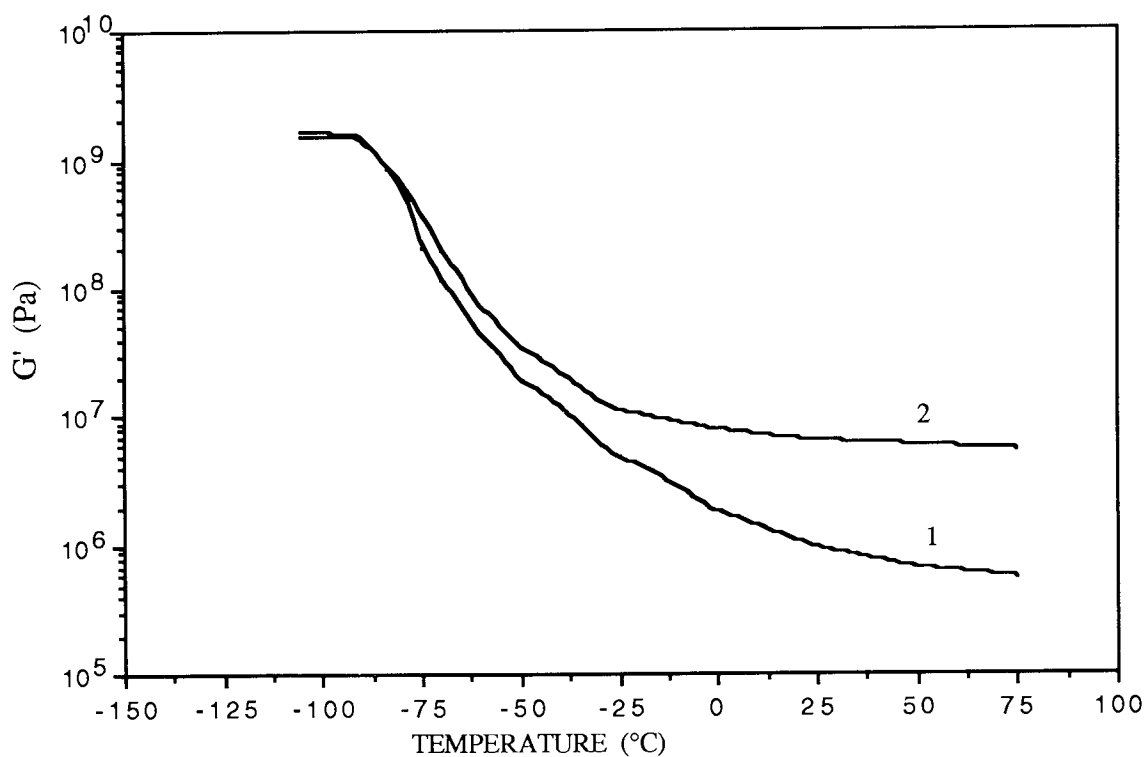
Fig. 1-4 The effect of ageing on HTPB propellant[9]

1: unaged; 2: aged for 32 weeks at 60°C.

1 4

1.2. Oxidation of Polybutadiene and Antioxidant Mechanisms

1.2.1. Chemical Structure of Polybutadiene

The hydroxyl terminated polybutadiene chains consist of trans-1,4, cis-1,4, and 1,2 polybutadiene:

| cis-1,4 | 1,2 vinyl | trans-1,4 |
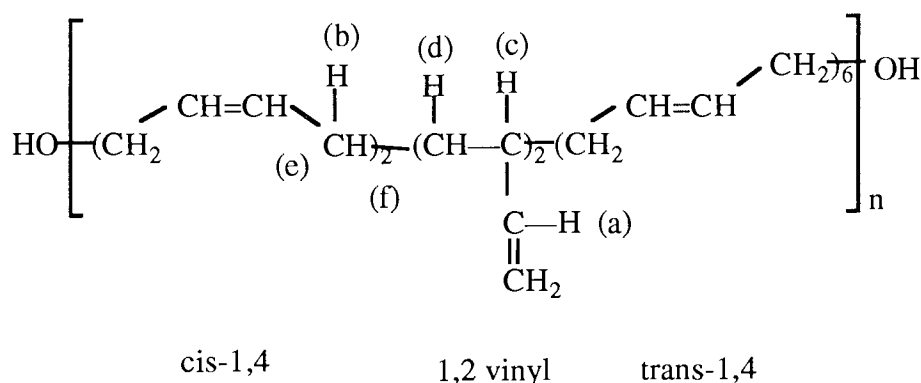
Four kinds of hydrogen-carbon bonds are involved along the chain: vinylic hydrogen(a), allylic hydrogen(b) bonded to a secondary carbon, allylic hydrogen(c) bonded to a tertiary carbon and non-allylic hydrogen(d) bonded to a secondary carbon.

Allylic hydrogens are the most reactive hydrogens since the formation of a resonance hybrid can stabilize the allyl radical after the allylic hydrogen is abstracted. Between the secondary allyl radical and the tertriary allyl radical, the latter may be more stable than the former, due to its further delocalization of electron cloud. Vinylic hydrogen-carbon bond is the most stable bond of the four. Its sp^2-s hybridization has a bond length of 1.103Å, which is shorter than that for allylic and non allylic hydrogen-carbon bonds of sp^3-s hybridization[13]. Therefore, the ease of hydrogen abstraction from hydrogen-carbon bonds decreases in this order:

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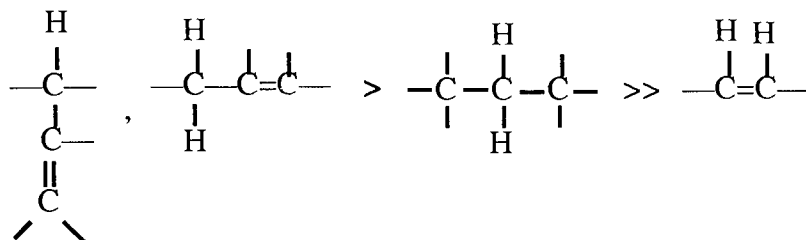
In HTPB there are three kinds of carbon-carbon double bonds presented in a ratio of trans/cis/vinyl = 6/2/2, having different reactivity due to steric effect and the delocalization of the π electron cloud. The measurements of the heats of hydrogenation and hyperconjugation energy[14](Table 1.1) show that the stability of the double bonds decrease in the order:

$$\text{trans-CH=CH-} > \text{cis-CH=CH-} \gg \text{-CH=CH}_2$$

Besides carbon-carbon double bonds, there are two kinds of carbon-carbon single bonds in the polymer chain. The carbon-carbon single bond(e) next to the carbon-carbon double bond is stronger than the carbon-carbon single bond(f) further away from the double bond because the sp^2-sp^3 bond is shorter than the sp^3-sp^3 bond. Thus the breaking of the backbone usually occurs at the sp^3-sp^3 hybridized bond rather than sp^2-sp^3 bond.

Table 1.1

Hyperconjugation energy of some olefins[14]

Olefin	Hyperconjugation energy (kcal)
$CH_2=CHCH_3$	2.7
$CH_3CH=CHCH_3$ cis	4.2
$CH_3CH=CHCH_3$ trans	5.2

It has been summaried[15] from the early oxidation work that both α-methylenic reaction and double bond addition were possible, depending on the nature of the polymer involved. The general oxidation of butadiene-like polymer is discussed in the following sections.

1.2.2.   General Oxidation of Polybutadiene

Polybutadiene is oxidized in an atmosphere containing oxygen leading to partial crosslinking and chain scission[16-18]. Gel content is formed and low mass products are evolved[17-19], and oxygenated compounds, such as, hydroperoxide, peroxide, carbonyl containing compounds, e.g., aldehyde, are formed along the rubber chain or at its ends[18-20].

The principal features of the oxidation are as follows:

1. Oxidation proceeds by a free radical chain process.

2. The reaction is autocatalytic.

3. The major initial product of the oxidation is a hydroperoxide and this is the principal material responsible for the autocatalysis.

For a pure polymer, the whole process is characterized by three steps: initiation, propagation and termination. During the initiation step oxygen absorption is at a very low rate and there is no obvious change in both chemical structure and physical properties. But this period is important because certain amounts of hydroperoxides are formed and accumulated. The decomposition of hydroperoxides is commonly recognized as the process responsible for the subsequent rapid autoxidation[14,21,22].

1.2.2.1. The Initiation Step

The formation of macroradicals is the necessary condition for an oxidation process. In this case, the initiation reaction may be induced by:

(1)   Physical factors such as stress and temperature,

(2)   Chemical factors such as catalysts(e.g. peroxides and metal ions), direct activity of oxygen, singlet oxygen and ozone.

1.2.2.1.1. Physical Factors

The formation of a macroradical depends on the dissociation energies of particular bonds in the polybutadiene. The environment in which a propellant is stored is not severe, but a propellant does stand loads caused by temperature change, as described in section 1.1.. The stress in a propellant is not uniform. On the surface layer the strength of the stress is higher than inside, because the surface layer experiences a much sharper temperature change (e.g. during a short period, temperature drops from curing temperature to the storage temperature), so that the polymer chains have less time to rearrange by chain-creeping to release the stress caused by thermal shrinkage. Furthermore diurnal temperature cycling adds a fatigue action to

those chains. When the stresses, probably in a defect region, are high enough to break the chemical bond in the polymer, free radicals are formed by physical force.

1.2.2.1.2. Chemical Agents

(1) *Initiation induced by molecular oxygen and peroxides*

The molecular oxygen O_2 found in nature is paramagnetic. This fact indicates that the spins of the two electrons are parallel and thus the molecule shows the characteristics of a bi-radical. The abstraction of a hydrogen atom from the polymer chain by an oxygen molecule (reaction 1.1) is considered to be quite difficult because it is an endothermic reaction to the extent of 30-45 kcal/mole (125.5-188.3 kJ/mole)[23,24]. Only molecules of polymer with energy which exceeds a certain critical value are capable of reacting with oxygen to give a primary peroxide[15]. It was reported[25] by Shimada and Kabuki that in the case of unsaturated polymer, it is possible to directly abstract hydrogen from acrylonitrile-butadiene-styrene copolymer (ABS) by oxygen. This was attributed to the fact that ABS resin contains some double bonds, and the C-H bond in the α-carbon position is particularly easy to oxidize.

$$\text{\textasciitilde CH}_2\text{-CH=CH-CH}_2\text{\textasciitilde} \quad + \quad O_2 \quad \longrightarrow \quad \text{\textasciitilde CH}_2\text{-CH=CH-}\overset{\overset{\textstyle OOH}{|}}{C}\text{H\textasciitilde} \qquad 1.1$$

It is recognized that, during the induction period, peroxides are accumulating which then decompose into two active radicals and catalyse the subsequent oxidation in an action as initiators. It has been found that oxidised polybutadiene is more unstable than unoxidised polybutadiene[16,19,26,27], due to the acceleration reaction of the hydroperoxide formed in the oxidation.

$$\text{\textasciitilde CH}_2\text{-CH=CH-}\overset{\overset{\textstyle OOH}{|}}{C}\text{H\textasciitilde} \quad \longrightarrow \quad \text{\textasciitilde CH}_2\text{-CH=CH-}\overset{\overset{\textstyle O\cdot}{|}}{C}\text{H\textasciitilde} \quad + \quad \cdot OH \qquad 1.2$$

It is important to know the role of peroxide in the polymer degradation because polymers are usually exposed to the atmosphere from the time when they are made.

(2) *Initiation induced by external initiators*

Even extremely pure polymer contains trace amounts of various impurities which act as initiators.

$$\text{initiator} \longrightarrow B\cdot$$

$$B\cdot + RH \longrightarrow R\cdot + BH$$

Radicals formed from external initiators may react with oxygen, producing highly active peroxyl radicals BOO·.

$$B\cdot + O_2 \longrightarrow BOO\cdot$$

These react with labile hydrogen (e.g. allylic hydrogen) in polymer to give an alkylradical.

$$\overset{\displaystyle H}{\underset{\displaystyle H}{\sim\!\!CH_2\text{-}CH\text{=}CH\text{-}\overset{|}{\underset{|}{C}}\!\!\sim}} + BOO\cdot \longrightarrow \sim\!\!CH_2\text{-}CH\text{=}CH\text{-}\overset{\cdot}{CH}\!\!\sim + BOOH \qquad 1.3$$
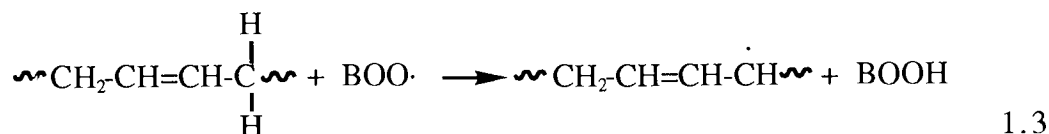
1.2.2.2. The Propagation Reaction

The macroradicals formed in the polymer undergo a free radical chain reaction under conditions where chain propagation is faster than chain termination so that the oxidation rate is dependent on initiation rate in the absence of antioxidants.

1.2.2.2.1. The Formation and Decomposition of Hydroperoxides

The macroradical formed during the initiation reaction reacts preferentially with oxygen molecules to produce peroxyl radicals.

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad 1.4$$
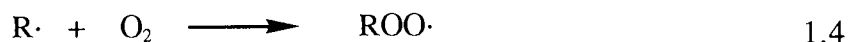
Research has shown[22,28-30] that the rate of oxygen addition to a radical also depends on its structure, with increasing radical stability the reaction rate decreases.

The peroxyl radical reacts with another macromolecule and abstracts a hydrogen atom to form a hydroperoxide.

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad 1.5$$

The rate of hydrogen abstraction reaction is associated with the stability of the free radical R·. In general, substituents which stabilise R· give rise to higher yields of the hydroperoxide[14,31-33].

In autoxidation of olefins, since the intermediate alkenyl radicals is stabilised by resonance, the hydrogen abstraction can take place efficiently. Peroxyl radicals, as a class, are relatively selective electrophilic species abstracting allylic and tertiary hydrogens in preference to secondary and primary. With a hydroperoxide forming, a new alkyl radical is produced, which may continue reacting in the same reaction cycle[14].

The relative values of oxidation rates are listed in Table 1.2[14,34], which are a measure of the ease of removal of the reactive methylenic hydrogen. It can be deducted from Table 1.2 that, on polybutadiene chains, the formation of hydroperoxides is much quicker in the region of 1,4 unsaturation than that of 1,2 unsaturation.

The double bond migration was observed during the oxidation of olefins[14,35,36].The driving force of this migration is a favoured alternative electron distribution in the intermediate free radical which leads to the attack of oxygen to give the most resonance stabilised hydroperoxide.

Table 1.2

The relative oxidation rates and the yields of hydroperoxides of olefins[34]

olefin	hydroperoxide yield (%)	temp. (°C)	relative oxidn. rate
$(CH_3)_2C=CHCH_2CH=C(CH_3)_2$	100	45	1210
$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOEt$	99	55	193
$[(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCH_2]_2$	93	55	34
$[(CH_3)_2C=CH(CH_2CH_2C(CH_3)=CH)_2CH_2]_2$	92	55	28
$CH_3(CH_2)_5CH=CH_2$	70	75	2.5

Normally the ease of formation of alkyl hydroperoxides is tertiary > seconary > primary. But when conjugative isomerisation can occur, this order is reversed. The favoured

hydroperoxide will be the one with the hydroperoxy group remote from the stabilising allyl or alkyl group. Therefore, for 1,2 vinyl group, the hydroperoxide should be formed more as structure I and less as II[37,38].

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle CH_2}{\underset{\parallel}{\underset{\displaystyle CH}{\mid}}}} & & \overset{\displaystyle OOH}{} \\
R-\overset{\mid}{\underset{\mid}{C}}-R \xrightarrow{\ O_2\ } & R-\underset{\mid}{\overset{\parallel}{C}}-R \ + \ R-\overset{\mid}{\underset{\mid}{C}}-R & \\
\end{array}
$$

R—C—R with CH, CH₂ side chain → R—C—R (C double bond CH, CHOOH) I + R—C—R (OOH, CH, CH₂ double bond) II
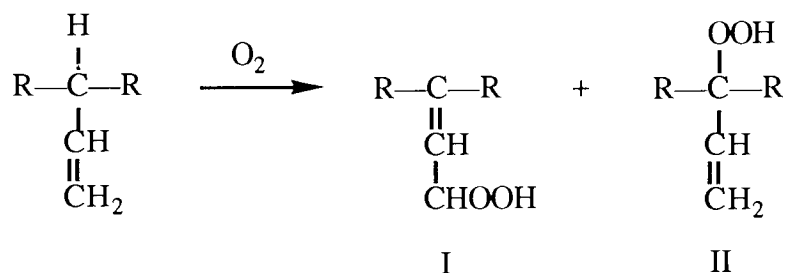
The bond dissociation energy of the oxygen-oxygen bond in hydroperoxide is about D(PO-OH)=40 kcal/mole (167.4 kJ/mole), depending on the hydroperoxide[14,36]. Since O-O bond is the weakest in the hydroperoxide group, its scission, due to thermal energy, UV radiation and catalysts, gives rise to the powerfully oxidising alkoxyl and hydroxyl radicals which play a vital role as initiators in the autoxidation chain mechanism.

$$ROOH \longrightarrow RO\cdot \ + \ HO\cdot \qquad\qquad 1.6$$

The decomposition of alkyl hydroperoxides can be induced by free radicals. It was observed that radical-induced decomposition of hydroperoxides occurs in both oxidative and reductive reactions(reactions 1.7 & 1.8).

$$ROOH \ + \ RO\cdot \ (HO\cdot) \longrightarrow ROO\cdot \ + \ ROH \ (H_2O) \qquad 1.7$$

$$
R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\underset{\mid}{\overset{\mid}{C}}}}-OOH \ + \ \cdot R' \longrightarrow R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\underset{\mid}{\overset{\mid}{C}}}}-O\cdot \ + \ R'OH \qquad 1.8
$$
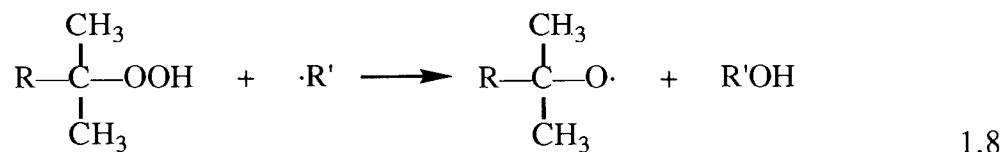
In general, it might be expected[14] that powerfully oxidising free radicals such as hydroxyl and alkoxyl will tend to induce hydroperoxide decomposition by an oxidative process,

$$RO\cdot \ + \ e \longrightarrow R\bar{O}$$
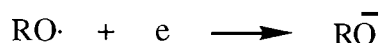
whereas resonance stabilised radicals such as tert-alkyl, will tend to be stabilised by reduction.

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$$R_1-\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{C}}\cdot \longrightarrow R_1-\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{C}}{}^{+} + e$$
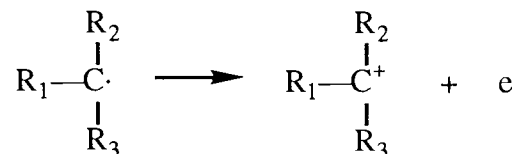
In a medium containning acetic acids, the decomposition of hydroperoxide is catalysed[39]. The function of acetic acid in this case seems to be as a reversible hydrogen donor[14].

$$RO\cdot + R'COOH \longrightarrow ROH + R'COO\cdot$$

$$R'COO\cdot + ROOH \longrightarrow R'COOH + ROO\cdot$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2$$
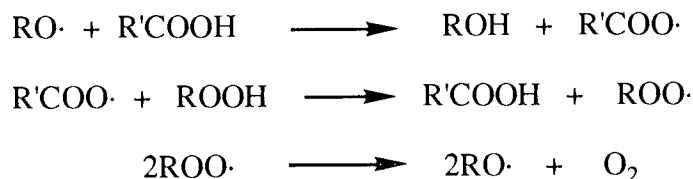
It was also observed that[40] the decomposition of hydroperoxide can be induced by the media.

$$R'H + ROOH \longrightarrow \begin{bmatrix} RO\cdot \\ R'\cdot \end{bmatrix} + H_2O \qquad 1.9$$
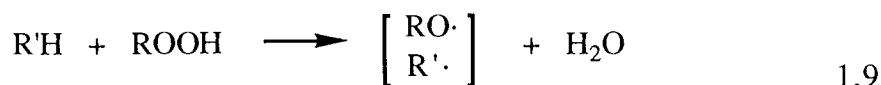
Further evidence was found in the fact that the more readily oxidisable media appear to increase the rate of hydroperoxide decomposition[14]. This is due to the decrease in the energy requirements of reaction1.9. For reaction 1.9, $\Delta H = D_{C-H} + D_{O-O} - D_{H-OH} = 94 + 40 - 120 = 14$ kcal (58.6 kJ) for interaction with a secondary carbon atom; for interaction of hydroperoxides with tertiary hydrocarbons the reaction is endothermic to the extent of about 10 kcal (41.8kJ) and for allylic compounds appears to be actually exothermic(=-13 kcal (-54.4kJ)).

The interaction of hydroperoxide with vinyl unsaturation gives rise to two new free radicals[41,42]. The mechanism of a hydrogen transfering to the vinyl group has been proposed by Walling and Chang[44] to account for the two initiating radicals.

$$ROOH + CH_2=CH-\langle\bigcirc\rangle \longrightarrow ROO\cdot + CH_3-\overset{\cdot}{C}H-\langle\bigcirc\rangle \qquad 1.10$$

The stabilities of alkyl hydroperoxides are dependent upon the nature of the medium. Not only are hydroperoxides subjected to radical induced decomposition but the order of their decomposition is often dependent upon their concentration. With increasing hydroperoxide

concentration, the pseudo first-order reaction is replaced by one which is second order in hydroperoxide[14]. Bateman and Hughes[43] suggested that this second order decomposition occurs in the associated state.

$$2ROOH \rightleftharpoons \begin{bmatrix} ROOH ---OOR \\ \quad\quad\quad | \\ \quad\quad\quad H \end{bmatrix} \longrightarrow ROO\cdot + H_2O + \cdot OR$$

$$1.11$$
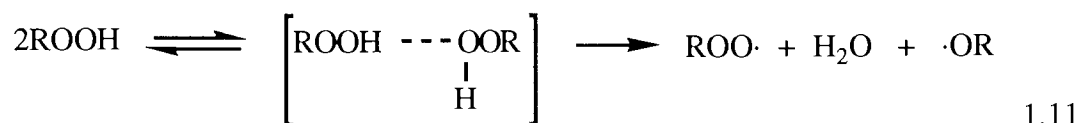
This hydrogen bonded interaction may also occur between a hydroperoxide and a peroxide, involving a similar complex to the bimolecular decomposition of hydroperoxides.

$$ROOH + R'OOH \rightleftharpoons \begin{bmatrix} RO----HOOR' \\ | \\ OR \end{bmatrix} \longrightarrow RO\cdot + ROH + ROO\cdot$$

$$1.12$$
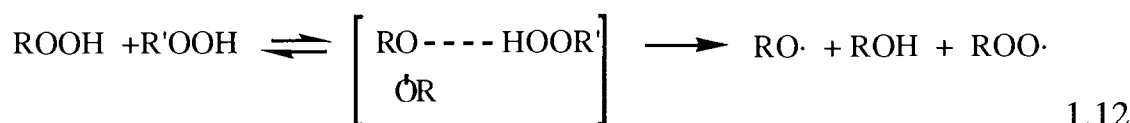
If a value for $D_{(ROO-H)}$ of 47 kcal [44,45] is used to calculate the energy changes involved in reactions 1.11 and 1.12, they are found to be exothermic to the extent of 33 kcal and 13 kcal respectively. A reasonably low activation energy might also be expected as a consequence of the hydrogen bonded transition state.

The radicals produced in the above decomposition reactions increase the rate of initiation reaction. But in special conditions the decomposition of hydroperoxides leads to non-radical products, which do not contribute to further oxidation[14].

(1) Acid catalysed decomposition

$$1.13$$

(2) Base catalysed decomposition

$$\underset{R_1\overset{\displaystyle R_2}{\underset{|}{C}}H\text{-OOH}}{} \xrightarrow{B^-} BH + \left[R_1\overset{\displaystyle R_2}{\underset{|}{C}}\text{-OOH}\right]^- \longrightarrow R_1\overset{\displaystyle R_2}{\underset{|}{C}}=O + \bar{O}H$$

$$\downarrow BH$$

$$B^- + H_2O \quad 1.14$$
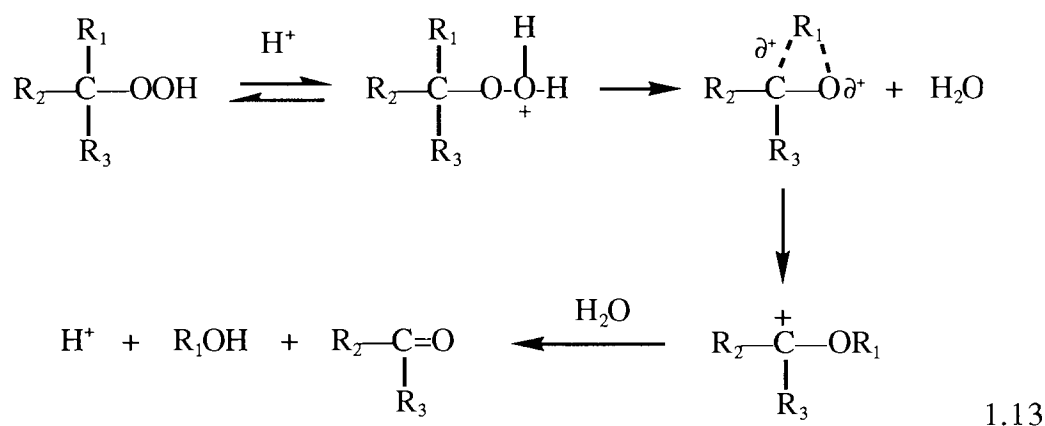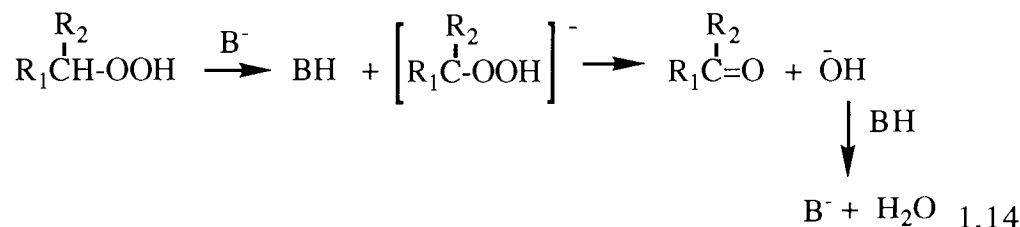
(3) The decomposition in a cage reaction

$$\underset{\text{—CH-CH-CH-CH}_2\text{—}}{R \quad \overset{\text{H}}{\overset{\text{O}}{\overset{|}{O}}} \quad R} \xrightarrow{\Delta H=42 \text{ Kcal/mol}} \left[\begin{array}{c} R \quad \overset{\dot{O}}{\underset{|}{}} \quad R \\ \text{—CH-CH-CH-CH}_2\text{—} \\ \text{HO·} \end{array}\right]$$

$$\underset{\begin{array}{c}+ \\ H_2O\end{array}}{\underset{\text{—CH-C-CH-CH}_2\text{—}}{R \quad \overset{O}{\overset{||}{}} \quad R}} \xleftarrow{\Delta H=-110\text{Kcal/mol}}$$

$$1.15$$
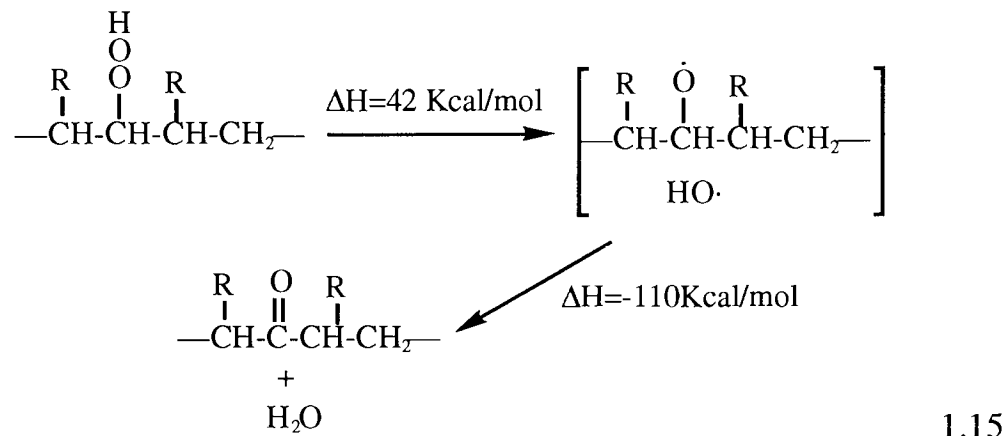
1.2.2.2.2. The Crosslinking Reaction

The fact that the increase in crosslink density is accompanied by the loss of unsaturation in polybutadiene has been observed by several workers[17,18,46-48]. This is attributed to the intermolecular addition of free radicals into the double bonds[14,15,17,18].

It was clearly reviewed by Scott [14] that the crosslinking reaction observed in the typical olefinic systems were related to the double bond arrangement. It seems that conjugation is a prerequisite for the formation of polymerise peroxide. Conjugated dienes can give rise to polymerise products from an early stage in their oxidation, whereas singly methylene interrupted dienes(III) give hydroperoxides initially but polymerise at an advanced stage of oxidation. Doubly methylene interrupted dienes(IV) on the other hand give rise only to hydroperoxides whose decomposition is associated with carbon-carbon bond scission.

$$\underset{\text{(III)}}{\text{—C=C—C—C=C—}} \longrightarrow \overset{\text{OOH}}{\underset{|}{\text{—C=C—C=C—C—}}} \longrightarrow \text{polymer}$$

$$\underset{\text{(IV)}}{\text{—C=C—C—C—C=C—}} \longrightarrow \overset{\text{OOH}}{\underset{|}{\text{—C=C—C—C=C—C—}}} \longrightarrow \text{chain scission products}$$

24
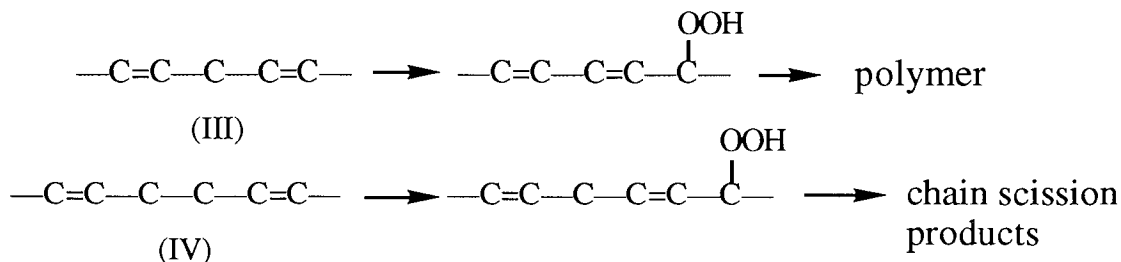
The conclusion drawn for doubly methylene interrupted dienes was derived from the pioneering work of Bolland and Hughes[49] on the thermal oxidation of squalene (a model for polyisoprene). Since gel was found as main oxidation product of polybutadiene, another doubly methylene interrupted diene, a mechanism which explains the formation of gel was proposed by Scott et.al.[17,18], which shows that the decomposition of hydroperoxides leads to crosslinking by addition of peroxyl or alkoxyl radicals to 1,2-vinyl groups and conjugated carbonyl formed by alkoxyl radical break-down (see Scheme 1-1).

$$
\begin{array}{ccc}
\sim CH_2\underset{\underset{CH=CH_2}{|}}{C}HCH_2\sim & \xrightarrow[\text{oxidation}]{(a)} & \sim CH_2\underset{\underset{CH=CH_2}{|}}{\overset{\overset{OOH}{|}}{C}}CH_2\sim \\
\end{array}
$$

(f) $\downarrow$ RO·

$\sim CH_2\underset{\underset{\cdot CH-CH_2OR}{|}}{C}HCH_2\sim$

(b) $\downarrow$ heat, hγ

$\sim CH_2\underset{\underset{CH=CH_2}{|}}{\overset{\overset{O\cdot}{|}}{C}}CH_2\sim$ (RO·)

(g) $\downarrow$ O_2/RH

$\sim CH_2\underset{\underset{\underset{HOO}{|}}{CH-CH_2OR}}{|}CHCH_2\sim$

cross-linked gel

(c) $\downarrow$

$\sim CH_2COCH=CH_2$ + ·$CH_2\sim$

(d) $\downarrow$ RO·/ROO·

$\sim CH_2CO\overset{\cdot}{C}H-CH_2O(O)R$

(e) $\downarrow$ O_2/kH

$\sim CH_2CO\underset{\underset{OOH}{|}}{C}H-CH_2O(O)R$

cross-linked gel
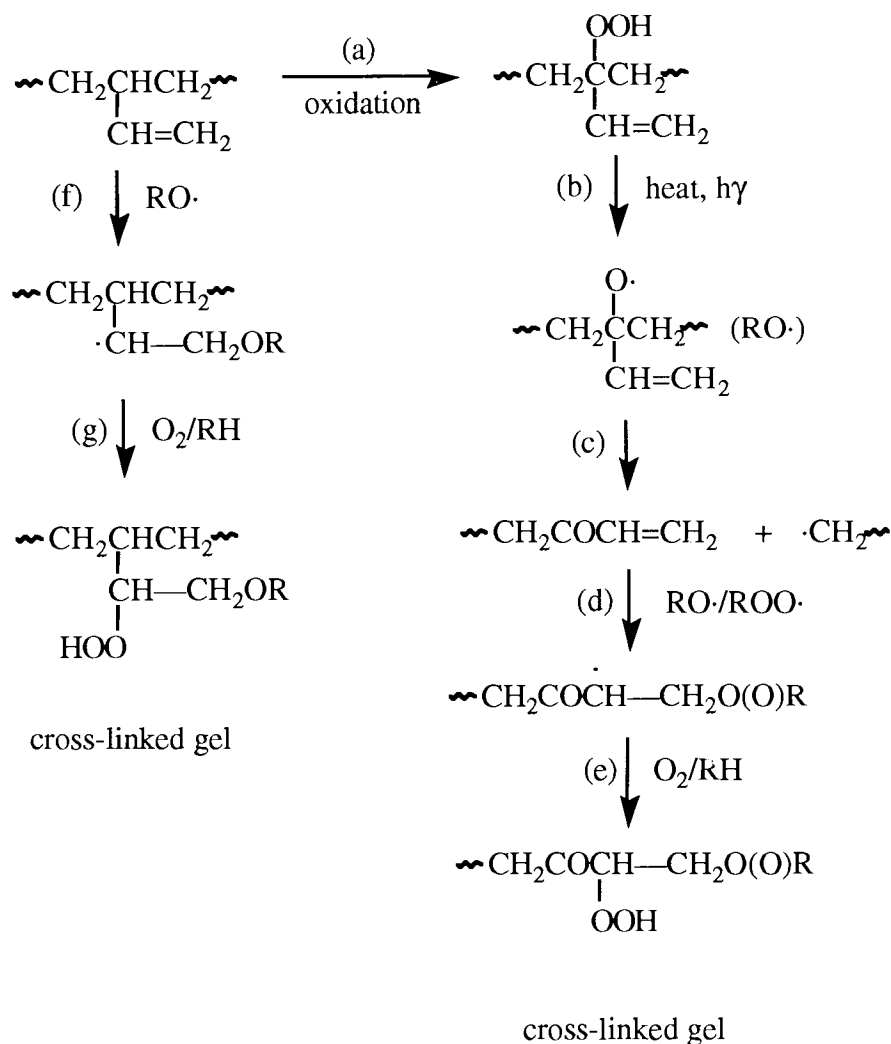
Scheme 1-1 The crosslinking reaction by addition to 1,2-vinyl group and conjugated carbonyl group

At very low oxygen pressures, carbon-carbon bond formation through conventional olefin polymerisation has been suggested and is theoretically possible during the polymerisation

25

stages of the reaction [14]. In cumyl peroxide vulcanizations of polyisoprene and polybutadiene [50-52], the crosslink efficiency is about unity for polyisoprene and 10 or more for polybutadiene. This implies that alkoxyl initiated polymeric chain reaction occurs in polybutadiene. Load [52] has found that the cumyloxyl radicals react largely by hydrogen abstraction while about 20% reacts in some other way. By infrared analysis, Van. Der. Hoff [50], has shown that polymer unsaturation disappears on curing to about the same extent as crosslinks are formed. Therefore, Load has expressed the reactions as in Scheme 1-2 [52].

$$ROOR \longrightarrow 2RO\cdot$$

$$RO\cdot + \underset{(B)}{-CH_2-CH=CH-CH_2-}$$

$$\begin{array}{l} OR \\ | \\ -CH_2-CH-CH-CH_2- \qquad (R_1\cdot) \end{array}$$

$$ROH + -\overset{\cdot}{C}H-CH=CH-CH_2- \qquad (R_2\cdot)$$

$$R_1\cdot + B$$

$$\begin{array}{l} OR \\ | \\ -CH_2-CH-CH-CH_2- \\ | \\ -CH_2-CH-CH-CH_2- \end{array} \qquad (R_3\cdot)$$

$$\begin{array}{l} OR \\ | \\ -CH_2-CH-CH_2-CH_2- \\ + \\ -\overset{\cdot}{C}H-CH=CH-CH_2- \end{array} \qquad (R_2\cdot)$$

$$2R_2\cdot \longrightarrow \begin{array}{l} -CH-CH=CH-CH_2- \\ | \\ -CH-CH=CH-CH_2- \end{array}$$
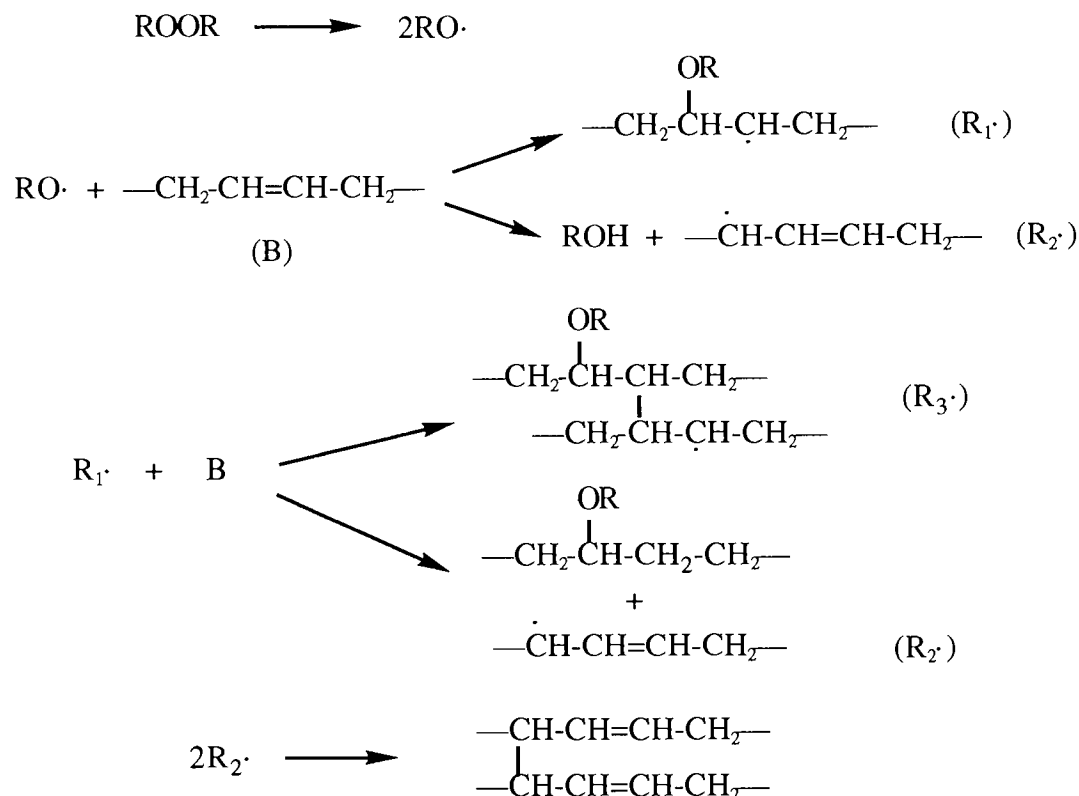
Scheme 1-2 The crosslinking reaction through the unsaturation of   polybutadiene in the peroxide vulcanization

Dunn has suggested[53] that the gelation of polybutadiene in oxidation would be precisely that which occurs in peroxide vulcanization[54]. However, it was found that, in polybutadiene, only a limited number of propagation steps occur consecutively without interruption by hydrogen transfer reaction. In oxidation the chain propagation would be also competed by reacting with oxygen.

The crosslinks formed during the oxidation of polybutadiene, therefore, would be carbon-carbon structure or peroxide bridge structure, depending on oxygen pressure.

1.2.2.2.3. The Chain Scission Reaction

One of important reactions involving alkoxyl radical is the alkyl elimination. By the ß-scission process, alkoxyl radicals can be split to produce aldehydes or ketones and alkyl radicals [14] (reaction 1.16). This reaction is of fundamental importance to the degradation which normally accompanies autoxidation. Alkoxyl radicals are formed by the hydroperoxide break-down. They have also been identified as products of a non-terminating reaction between peroxyl radicals [55] (reaction 1.17).

$$
\begin{array}{ccc}
& & \overset{O}{\underset{\parallel}{}} \\
\overset{\cdot O}{\underset{|}{}} & & \sim CH{=}CH{-}C{-}H \\
\sim CH{=}CH{-}CH{-}CH_2{-}CH{=}CH\sim & \longrightarrow & + \\
& & \cdot CH_2{-}CH{=}CH\sim \;\rightleftharpoons\; CH_2{=}CH{-}\overset{\cdot}{C}H\sim
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\cdot O}{\underset{|}{}} & & \overset{O}{\underset{\parallel}{}} \\
\sim CH_2{-}C{-}CH_2{-}CH{=}CH\sim & & \sim CH_2{-}C{-}CH{=}CH_2 \\
\underset{|}{} & \longrightarrow & + \\
CH{=}CH_2 & & \cdot CH_2{-}CH{=}CH\sim \;\rightleftharpoons\; CH_2{=}CH{-}\overset{\cdot}{C}H\sim \quad 1.16
\end{array}
$$

$$
ROO\cdot + ROO\cdot \longrightarrow ROOOOR \longrightarrow RO\cdot + O_2 + RO\cdot \qquad 1.17
$$
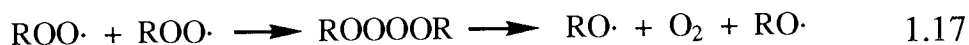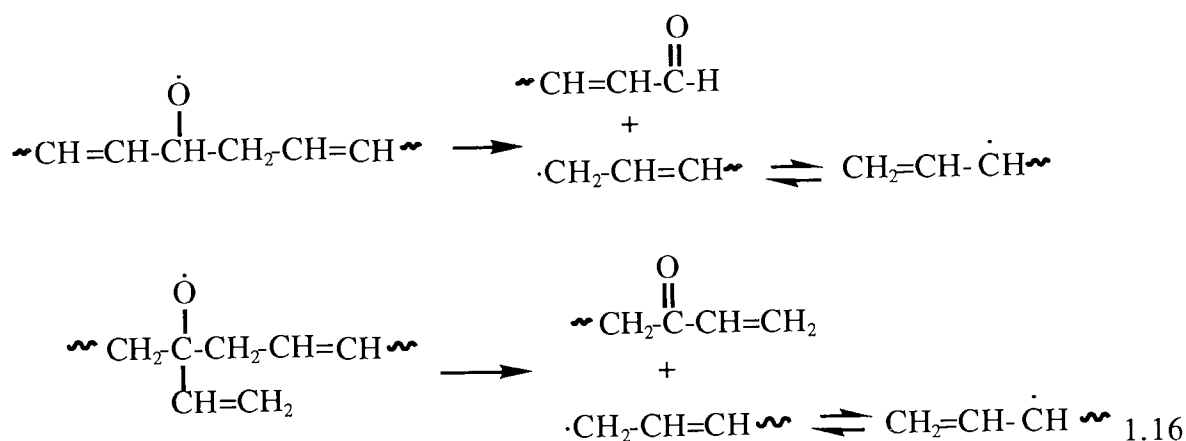
It was observed that the degree of carbon-carbon bond scission is a function not only of the C-C bond strength but of the temperature of the reaction and the hydrogen donation capacity of the medium [14].

The alkyl radicals formed in the scission are more likely to react with oxygen, but may also attack the neighbouring chains to abstract a hydrogen or to add to a double bond, forming a C-C crosslink.

1.2.2.3. The Termination Reaction

The termination of the chains is due to the reactions of free radicals with each other, in which inactive products are formed:

$$RCO\cdot \ + \ ROO\cdot$$ 1.18

$$ROO\cdot \ + \ R\cdot \quad \longrightarrow \quad \text{inactive products} \quad 1.19$$

$$R\cdot \ + \ R\cdot$$ 1.20
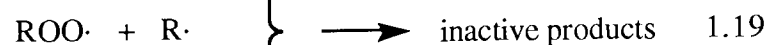
At atmospheric pressure and moderate temperatures, alkylperoxy radicals are by far the commonest radical species occurring in autoxidation, and chain termination occurs exclusively through their interaction (reaction 1.18). At low oxygen pressures, the concentration of alkyl radicals increases and chain ending takes place by reaction 1.20. For intermediate pressures all three chain ending steps are involved.

The relative contribution of the three termination steps at oxygen pressures from 0-760 mm have been calculated by Bateman and Morris [56 for a number of olefins and are found to be markedly dependent upon olefin structure. It is clear that crossed termination becomes increasingly important the more readily oxidisable the hydrocarbon, which is a function of the resonance stabilisation of the derived alkenyl radical [57].

1.2.2.4. The Effect of Temperature

The rates of most reactions increase as the temperature is raised, as more energy is supplied to the whole system.

The strength of the temperature dependence for both Arrhenius-like and non-Arrhenius-like reactions can be expressed by defining an activation energy as [58]:

$$E_a = RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_v$$ 1-1

This shows that the higher the activation energy, the stronger the temperature dependence on the rate constant.

Many workers have tried to predict the long-term ageing behaviour of a propellant at room temperature from the accelerated ageing results[47,59]. But this approach implies an assumption[7,60]: that only one chemical mechanism can be responsible for the observed ageing effect, or all mechanisms have the same activation energy. In practice, the temperature dependence of polymer degradation is composite since many reactions are involved in oxidation.

1.2.2.5. The Effect of Oxygen Pressure

1.2.2.5.1. The Influence on the Induction Period

The influence of oxygen pressure on polymer oxidation has been observed and studied [14,61-63]. Shelton and Cox [14,64] have shown that the oxidation of all the vulcanizates could be described by a generalised equation

$$K_2 = \alpha[1+(1+\beta P)^{-1}]+\gamma P \qquad 1\text{-}2$$

where, K_2 = the oxidation rate,

P = the oxygen pressure,

α, β and γ = constants

and have explained this in terms of the direct reaction of oxygen with the polymer. This applies primarily to the linear induction period before the autocytalytic reaction commences. With decreasing oxygen presure and with increasing sample thickness, the induction period increases [22,65].

1.2.2.5.2. The Diffusion of Oxygen in Polymer

The diffusion of oxygen in polymers is unaffected by any complication due to the concentration dependence of the diffusion constant [66]. The fundamental differential equation for the diffusion of oxygen into the polymer takes the form:

$$\frac{\partial [O_2]_f}{\partial t} = D\left(\frac{\partial^2 [O_2]}{\partial x^2} + \frac{\partial^2 [O_2]}{\partial y^2} + \frac{\partial^2 [O_2]}{\partial z^2}\right) \qquad \text{1-3}$$

Usually the diffusion occurs effectively in only one direction. If there is a gradient of concentration along the x-axis only, where x is the distance from the film surface, equ.1-3 reduced to:

$$\frac{\partial [O_2]_f}{\partial t} = D\frac{\partial^2 [O_2]}{\partial x^2} \qquad \text{1-4}$$

For autocatalytic oxidation in the presence of low concentrations of oxygen, the rate of oxygen uptake or hydroperoxide formation is given by:

$$\frac{\partial [O_2]_f}{\partial t} = k\,[O_2]_f\,[R\cdot]_f \qquad \text{1-5}$$

Substituting equs.1-4 in equation 1-5:

$$D\frac{\partial^2 [O_2]}{\partial x^2} = k\,[O_2]_f\,[R\cdot]_f \qquad \text{1-6}$$

It can be seen from equ.1-6 that the rate of oxidation in films depends on the relatively low rate of oxygen supply by diffusion, and is directly proportional to the concentration of oxygen. Wilson [67,68] and Bauman and Maron[69] show that it is possible to express the reaction rate as a function of film thickness, diffusion constant and solubility of oxygen in the film. When the thickness of the film is reduced to less than a certain value, the chemical reaction, and not the diffusion, becomes the controlling factor. The activation energy of the oxidation reaction amounts to 16-35 kcal mole^{-1}, or even more, whereas the activation energy of the diffusion of gases in polymer film [70] is of the order of only 10 kcal mole^{-1}. Control by diffusion is facilitated at higher temperatures by the decrease of oxygen solubility in the films.

Jellinek et al.[71-73] discussed the role of diffusion in the kinetics of polymer oxidative degradation. It should be ascertained in the investigation of the oxidation of polymer films whether the observed oxidation rate is actually due to the chemical oxidation reaction and that it is not influenced by the relatively slow diffusion of oxygen into the films.

Oxidation preferentially occurs at the surface of the films and little oxidation takes place in the bulk of the sample even on prolonged exposure. The dependence of the oxidation rate on sample thickness confirms this view[74,75]. The local concentrations of oxygen and of radicals, as well as the oxidation rate, are functions of the distance from the surface.

The rate of oxygen diffusion depends on the nature of the polymer and especially on:

1. The number and size distribution of pre-existing pores.

2. The ease of pore formation.

The former will depend on the degree of packing of the chains and the free volume and density. The ease of pore formation will depend on the mobility of chain segments, that is the chain stiffness and on the cohesive energy of the polymer. It has been found that with an increasing degree of crosslinking, the diffusion constant decreases. The activation energy of the diffusion increases with increasing crosslinking[76,77].

1.2.3. Antioxidant Mechanisms

It is commonly desirable to minimize autoxidation and in principle there are two mechanistically distinct classes of antioxidant which retard autoxidation by chemical means[78].

(1) By removing from the medium the two important species normally involved in the chain propagating step, the alkylperoxyl and alkyl radicals. Materials that function in this way are known as chain-breaking antioxidants which can capture free radical and stop chain propagation.

(2) By preventing the introduction of chain initiating radicals into the system. Materials that function in this way are known as preventive antioxidants which destroy hydroperoxides into a non radical products and thus reduce the rate of initiation .

1.2.3.1. Chain-Breaking Mechanism and Chain-Breaking Antioxidants

The chain-breaking antioxidants are the best known and the most frequently used class of polymer stabilisers. They have been classified by Scott [78,79] into two groups: chain-breaking donor antioxidants and chain-breaking accepter antioxidants. the latter may be radical species or conjugated molecules which scavenge R·. The former, in most cases, are inhibitors of the InH type, able to deactivate the propagating radical ROO· while giving rise to another more stable radical In· which does not take part in the chain transfer and reacts by a different sequence of reactions

1.2.3.1.1. General Reactions

Reactions with ROO·

Alkylperoxy radical is an electrophilic reagent. The general reaction of InH is to donate a hydrogen to an alkylperoxy radical.

$$ROO· + InH \longrightarrow ROOH + In· \qquad\qquad 1.21$$

32

If this reaction proceeds more quickly than reaction 1.5, InH can function as an oxidation retarder. Usually this is a key process in the action mechanism of InH in the system where ROO· is present in highest concentration.

The readiness with which the In-H bond is broken correlates with the energy of the transition state between the antioxidant and alkylperoxide radical. The more stable are the contributory structures such as II and III the lower will be the energy of the transition state. The substituent groups in the aromatic rings influence the energy of the transition state. It was shown that electron releasing groups in the aromatic ring increase the antioxidant activity whereas electron attracting groups decrease it [78].
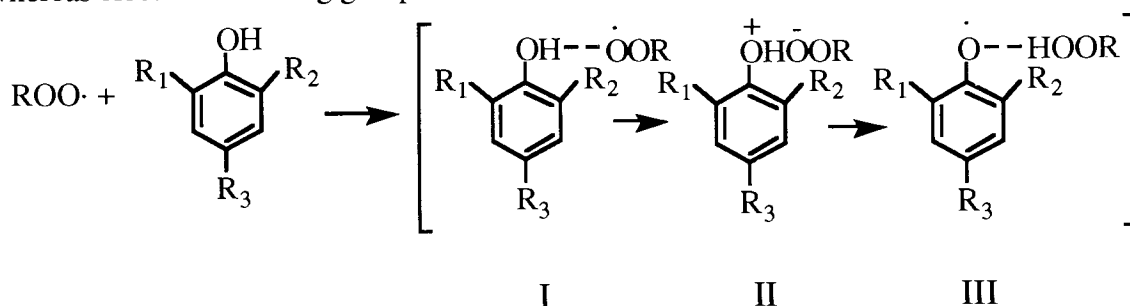
The In· formed in reaction 1.21 can further react with ROO· through the mesomeric forms of In·[78].

$$In'· + ROO· \longrightarrow ROO\text{-}In' \qquad\qquad 1.22$$

Reaction with RO·

Reaction 1.23 is competitive with reaction 1.21

$$RO· + InH \longrightarrow ROH + In· \qquad\qquad 1.23$$

Reaction with R·

Although, normally, the alkylperoxy radical is the commonest species present in an autoxidising system, under conditions of limited air supply, or in the case of highly reactive hydrocarbons, alkyl radicals may predominate. In this case, alkyl radicals can be captured by chain-breaking accepter inhibitors, e.g., quinones, which resultant resonance stabilised radicals are effectve scavengers for other alkyl radicals present.

1.24
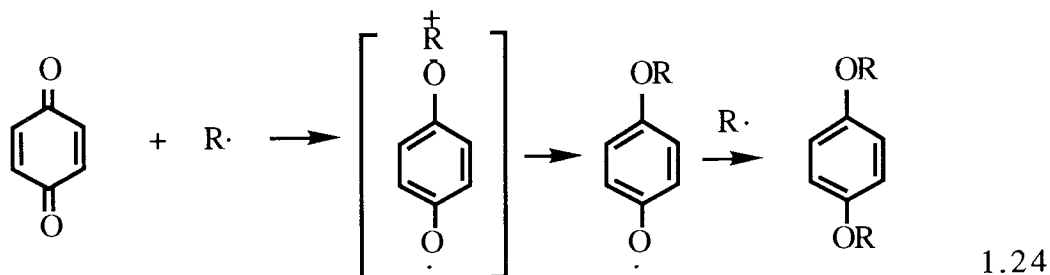
The effectiveness of a chain-breaking accepter inhibitor as an autoxidation retarder will depend on the efficiency with which it can compete with oxygen for the alkyl radical.

For InH type antioxidants, the alkyl radical trapping, reaction 1.25, becomes possible only in oxygen deficient environments (e.g. during fatiguing)[80].

Reaction with RH

Chain transfer reaction with the free radical derived from antioxidant, In·, is a highly undesirable reaction. These reactions reduce the degree of inhibition of antioxidant and depend upon the reactivity of the derived radical In· toward the substrate[78]. It has been shown that the bulky substituents on nitrogen of amines and *ortho* position of phenols can effectively retard or eliminate this reaction[78,81,82].

$$In \cdot \ + \ RH \ \longrightarrow \ InH \ + \ R \cdot \qquad\qquad 1.25$$

1.26
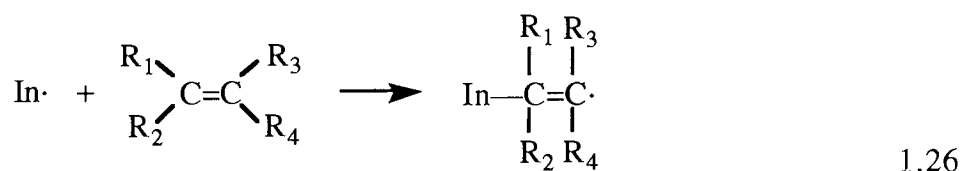
Reaction with O$_2$

Direct oxidation of InH with oxygen is another undesirable process:

$$O_2 \ + \ InH \ \longrightarrow \ HOO \cdot \ + \ In \cdot \qquad\qquad 1.27$$
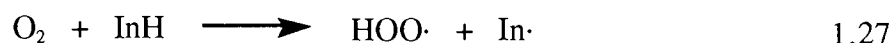
This reaction is regarded[81,83] as the main source of initiation in the early stages of inhibited oxidation. Its activation energy is very high and the reaction proceeds only at rather high temperatures, at high concentration of InH, and with the more reactive InH [81,84].

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1.2.3.1.2. Chain-Breaking Antioxidants

Aromatic Amines

Aromatic amines are the most important antioxidants used to stabilize unsaturated elastomers.

Their antioxidant efficiencies are generally higher than those of phenols. Among aromatic amines, N,N-disubstituted 1,4-phenyldiamines (PDs) are the most important ones and widely used in various technical products made from rubber.

The highest antioxidant efficiency of amines is reached in a system containing ROO· radicals as the main chain propagating species. Evidence for the formation of In· was obtained by continuous flow ESR in an inert medium[87]. The strength of the N-H bond plays an important role. Compounds with a high bond strength possess low antioxidant efficiency[86,87]. The activity of amine has been related with three structural factors by Scott[78], based on numerous experimental evidence. These are (a) effective delocalisation of the unpaired electron formally resident on the nitrogen, (b) high electron density on the nitrogen to facilitate electron transfer to the alkylperoxy radical, (c) sufficient steric protection of the nitrogen atom to reduce chain transfer by the arylamino radical.

The rate of reaction 1.21 is influenced by the substituents on either the aromatic ring or on nitrogen[78]. Electron releasing groups in the aromatic ring increase the antioxidant activity whereas electron attracting groups either in the nucleus or in the side chain effectively reduce antioxidant activity[88]. N-Phenyl groups and N-alkyl groups which is branched at α-position markedly increase the antioxidant activity, due to effectively delocalising the unpaired electron in the aminyl radical. It has been suggested[88,89] that bulkier substituents limit the undesired reactions of derived aminyls, In·. The fact that N,N-diaryl- and N-alkyl-N-aryl-1,4-PD are stronger antioxidants in rubber than N,N-dialkyl derivatives have been shown[90] and they even have a stronger retarding effect after the induction period. However, Pospisil pointed out that a generally valid formulation of the relationship between structure and activity

was not found. The influence of N,N-disubstitution is strongly dependent on the reactivity of the substrate and the parameters chosen for evaluation[86].

Hydrogen transfer leading to aminyl (In·) is the rate determining step in reaction 1.21 [86,91,92]. The possible involvement of a charge-transfer complex has also been proposed in the stabilization of NR vulcanisate with PD[86,93]. An acetone-soluble quinone diimide (BQDI) formed via reaction 1.28, route (a) and an EtOH / HCl insoluble rubber-bound species formed via reaction 1.28 route (c) (R: rubber residue, R'= phenyl) were identified. However it was reported that the reversible complexing of ROO· with the π-electrons of the amine is only an additional but not essential alternative process.

1.28
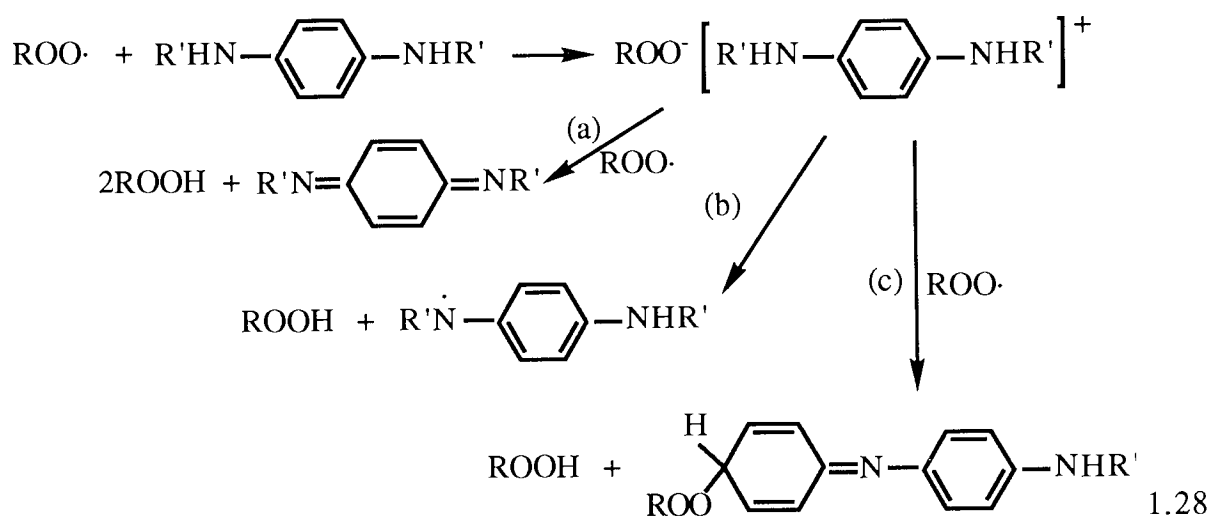
Direct oxidation by O_2 is operative in amines having low oxidation potentials. It was confirmed experimentally that BQDI and cation-radicals are formed from various PD compounds by air oxidation[86,94]. This may give pro-oxidant effect of aromatic amines when used at high concentration[83,95].

The aminyl formed from InH is the precursor of most amine transformation products. It participates in a series of reactions either as nitrogen-centred radical (In·) or in mesomeric iminocyclohexadienyl, as carbon-centred radical (In'·)[78,97]. In general, In· derived from monoamines is more reactive than that from PD due to the lower conjugation in the radical.

$$\text{In·} \qquad\qquad \text{In'·} \qquad\qquad 1.29$$
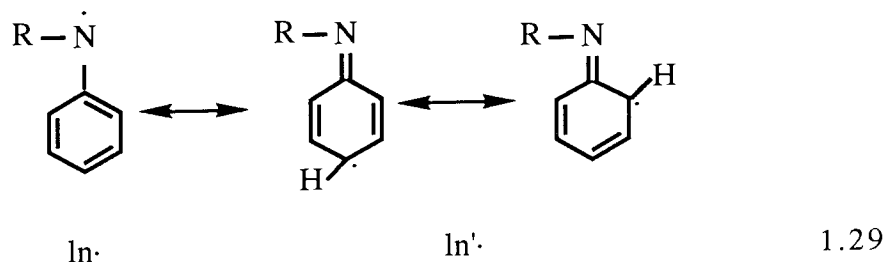
N-N, C-N and C-C coupled products have been shown to be formed from various amines[92,96-98].

Aminyl radicals are stable towards oxygen but they are weak oxidants, can oxidise PD, aniline, sterically hindered phenols and thiols[86].

BQDI should be considered to be the most important transformation product of the PD compounds[86]. Most PDs are transformed into BQDI at the end of the induction period to oxidation by reactions of In· with In·, ROO· and ROOH. BQDI are very reactive and are involved in hydrolytic, substitution and redox reactions[99]. Hydrolysis is catalysed by weak acids and trace amounts of adsorbed water. The process proceeds more easily with C=N-alkyl than C=N-aryl[100]. The aromatic amine moiety is hydrolytically split off and participates in nucleophilic attack on the quinoid nucleus. The retarding effect of BQDI in rubbers seems to be the result of a regenerative mechanism leading to PD (see Scheme 1-3)[86].

In Scheme 1-3, the reaction is initiated by the addition of one proton to I. The main reaction pathway is via V to give 1,2,4-trisanilinobenzene (VI), its disproportionation product DPPD (VII) and 2-anilin-N,N'-diphenyl-1,4-BQDI (VIII).

The antioxidant or retardant properties of BQDI has been explained as its alkyl radical scavenging activity[101,102]. It has also been suggested[103] that BQDI may be incorporated during this process into an unsaturated polymeric chain. Because of the bifunctionality of BQDI, cross-links may be formed.

Reaction of In· with alkylperoxyls are of importance (reaction 1.30). Evidence of the formation of InO· during inhibited oxidation has been found by means of ESR[104]. *tert -* Alkylperoxyls are more efficient reactants in reaction 1.30 than *sec* or *prim* alkylperoxyls.
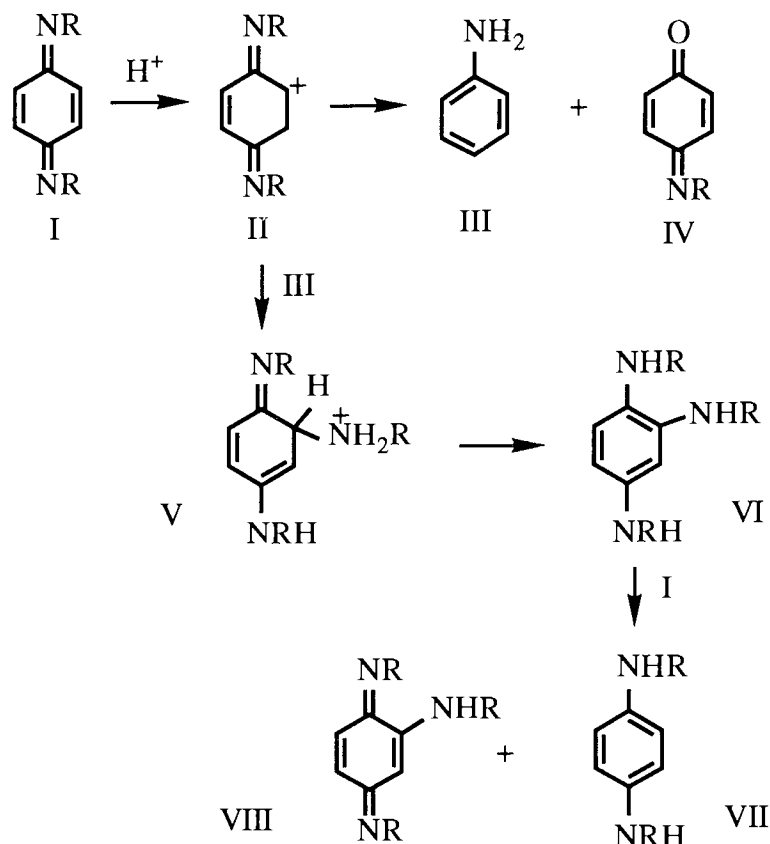
Scheme 1-3 Reactions of BQDI

$$In\cdot + ROO\cdot \longrightarrow InO\cdot + RO\cdot \qquad 1.30$$
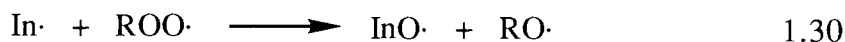
The importance of $InO\cdot$ for the mechanism of action of amine antioxidants is evident since aromatic nitroxyls have delocalised free electrons[105].

$$1.31$$
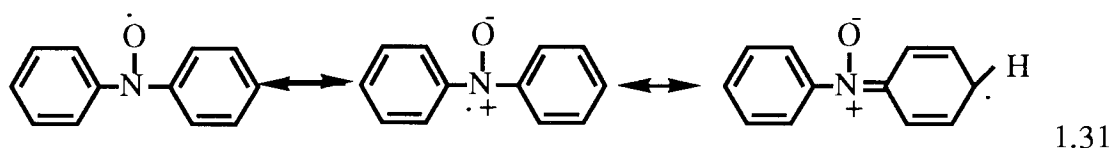
The reactivity of nitroxyls in dimerisation, disproportionation and fragmentation reactions is influenced by steric and polar effects; those derived from aromatic amines are less stable than those formed from the hindered aliphatic amines and their lifetimes do not exceed more than a few days due to dimerisation[86,105,106]. $InO\cdot$ compounds are efficient oxidants, able to transform PD into cation-radical or BQDI[105]. Hydrogen abstraction takes place with reactive C-H bonds of hydrocarbons[107] or with S-H bonds in thiols[108]. Addition to a C=C bond has also been observed[105].

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Aromatic nitroxyls are able to scavenge both alkyl and alkylperoxyl[109]. The former through the formation of alkylhydroxylamines and the latter by attack at the aromatic ring to give nitrones[110,111].

$$1.32$$
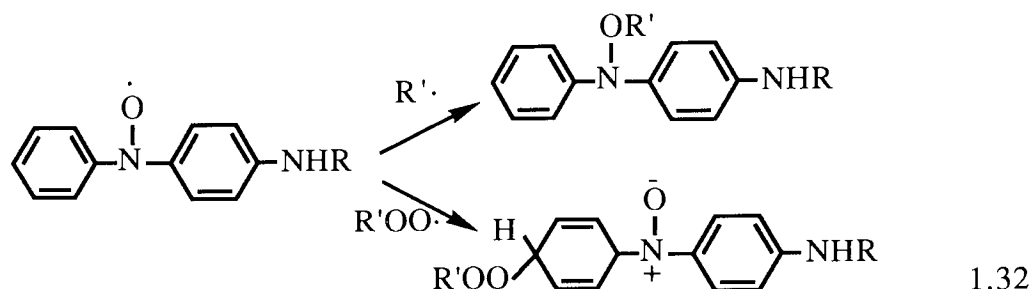
The alkylhydroxylamine, InOR, undergoes C-O homolysis to give corresponding olefin and hydroxylamine InOH which is, in turn, able to scavenge $RO_2\cdot$ with simultaneous regeneration of $InO\cdot$. The regenerative cycle proposed for rubber involves an alternating sequence of CB-D and CB-A steps and is outlined in Scheme 1-4[110,111].
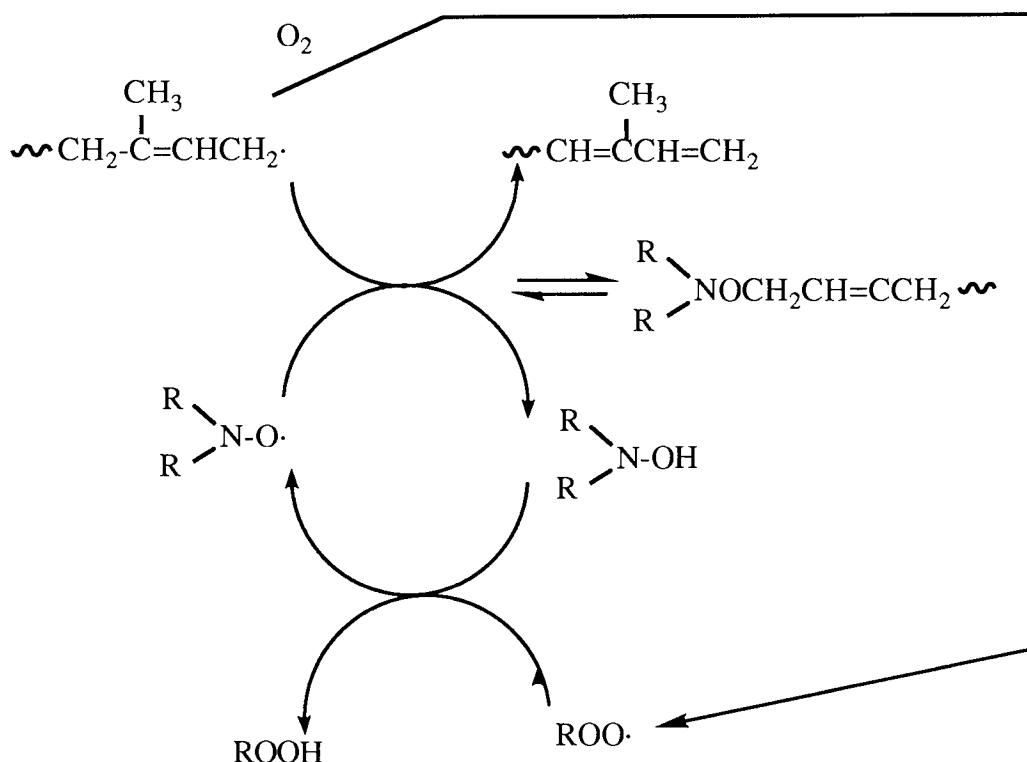
Scheme 1-4 The regenerative cycle of nitroxyls

Amine may be involved in ROOH homolysis resulting in a pro-oxidative effect due to the formation of $RO\cdot$[112]. The reactivity of aromatic amines with ROOH is generally lower than that of aliphatic amines[86,113].

39

The important reactions in the antidegradant mechanisms of amines are presented in a simplified cyclic mechanism in scheme 1-5.
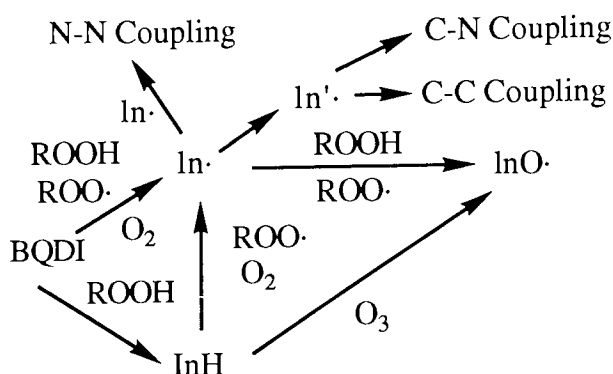
Scheme 1-5   General reactions involved in the antioxidant

mechanisms of aromatic amines

Hindered   Phenols

Hindered phenols are excellent inhibitors mainly for thermoplastics, elastomer modified plastics and elastomers. A substantial amount of hindered phenols has been used to stabilise polyolefins and styrene based plastics[114].

Phenols have been the focus of intensive industrial and academic research for several decades. There is a good deal of information on the relationship between the antioxidant activity of phenols and their structures[78]. The main conclusion has been summarised as follow[78].

(1) Electron releasing groups in the *ortho* and *para* positions markedly increase the antioxidant activity.

(2) Electron attracting groups decrease activity.

(3) α-Branched *ortho* alkyl groups considerably increase antioxidant activity whereas such groups in the *para* position decrease it.

Scheme 1-6 briefly describes the reactions involved in phenol inhibited oxidation by using a typical phenolic antioxidant (BHT).
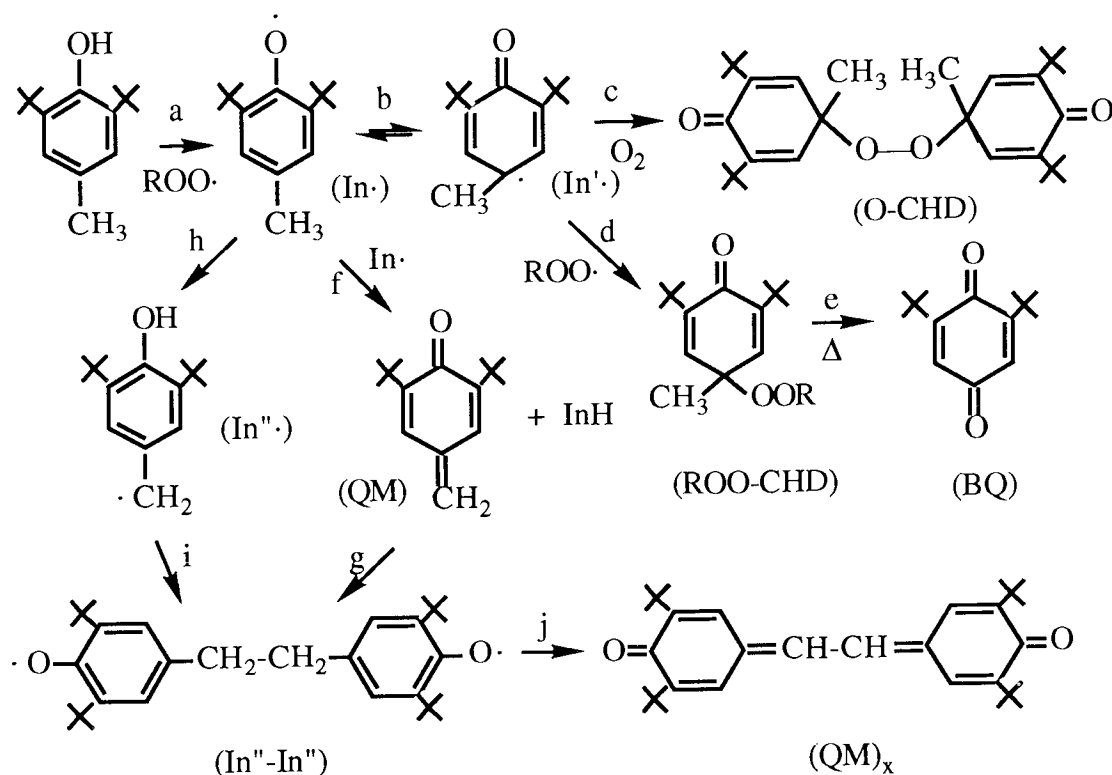
Scheme 1-6 General reactions involved in the antioxidant mechanism of BHT

Hindered phenoxyl radicals, formed by donating electrons to alkylperoxy and alkoxy radicals, are the primary oxidation products of phenols[78,81,115]. Because of electron delocalisation and steric effects, O-C or C-C couplings take place only through the mesomeric cyclohexadienonyl radical In'·, or by isomerisation to the benzyl radical In''· [78]. 2,6-disubstituted phenols give rise to biphenyldiols HIn-InH, which participate further in the inhibition process, leading to diphenoquinones.

The disproportionation of phenoxyl gives rise to the original InH and a quinone methide (QM). QM is highly reactive and readily undergoes further reactions.

At a sufficiently high ROO· concentration, the reaction d proceeds with In'· to give ROO-CHD. ROO-CHD is thermally and photo-chemically unstable owing to the presence of the O-O bond. It has been found that RO· radical is one of the break-down products of ROO-CHD[116]. To form benzoquinone, alkyl elimination from the associated alkoxy radical is probably occurred (reaction 1.33)[78]. The initiating activity of these radical intermediates has been observed[81,117,118].

41

$$1.33$$
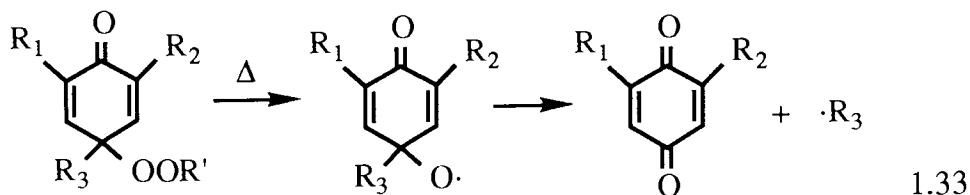
Benzoquinoid compounds (BQ) formed from phenolic antioxidants, may participate in further processes in a very complex manner. They are able to bind R· radicals through the system of π-bonds[81,19,120]. They act as oxidation and dehydrogenation agents[81,121], and oxidise both phenols and amines very readily.

Sterically Hindered Aliphatic Amine

Sterically hindered aliphatic amines used as polymer stabilisers are mainly related to piperidine derivatives. Comparing with aromatic amines and hindered phenols, piperidine can only be a very inefficient inhibitor[122-124]. The energy of the N-H bond in unsubstituted piperidine is 364 kJ /mol, considerably higher than 330 kJ /mol in aniline. Thus the removal of the hydrogen of piperidine analogues will be much slower and the free piperidyl radical more active. Continuation of the chain reaction is therefore more likely since the energy of the C-H bond in low molecular weight polymer models is 320-390 kJ /mol.

It was demonstrated that the stabilising effect of SHA results from their transformation into nitroxyl radicals during the induction period of thermo-oxidation[122,125]. SHA can be oxidised by tungsten peracid[126], hydrogen peroxide[127], hydroperoxides [128], peroxyl radicals[129] and other oxidants to produce stable nitroxyl radical (reaction 1.34 and 1.35). The hydrogen abstracting activity of nitroxyl is only slight since the energy of the O-H bond in the corresponding hydroxylamine is only 303kJ /mol[122].

$$1.34$$

$$1.35$$
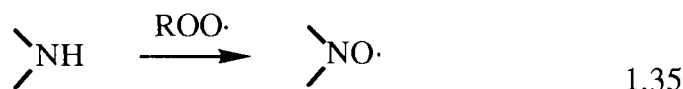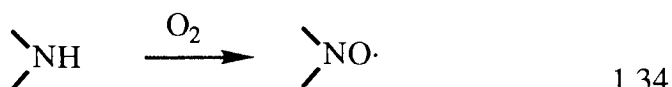
Nitroxyls containing a piperidine structural group are known to react only with alkyl radical[122,130-132]. The high efficiency of nitroxyl radicals in inhibiting the autoxidation of hydrocarbon substrates has been shown by Bolsman et.al.[133] and attributed to the

involvement of nitroxyl in a catalytic cycle[134]. The proposed cycle involves the alternating scavenging of alkyl and alkylperoxyl radicals. The alkyl radicals are scavenged by the nitroxyl to give an O-alkylhydroxylamine, which undergoes thermolysis to give the corresponding hydroxylamine and olefin. The hydroxylamine formed reduces an alkylperoxyl radical with simultaneous regeneration of nitroxyl (Scheme 1-7).
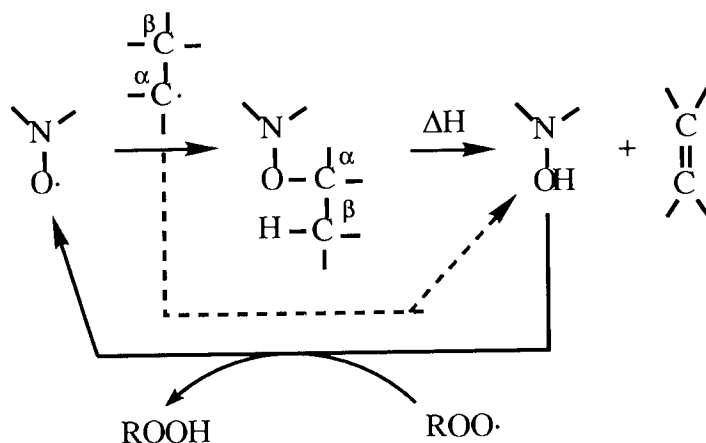
Scheme 1-7   The catalytic cycle of nitroxyl in the oxidation of hydrocarbons

This CB-A/CB-D catalytic cycle has been proved to operate in polymers stabilised with nitroxyl[132,135,136], under conditions where alkyl radicals play an important part. However, some modification to this mechanism, based on the experimental evidence in polymer work, has been contributed by Scott (Scheme 1-4).

In Bolsman's scheme, the reaction of nitroxyl radical with alkyl radical is predominantly by way of combination to form alkylhydroxylamine. The subsequent thermolysis of alkylhydroxylamine proceeds via homolysis of the O-alkyl bond followed by transfer of a β-hydrogen atom to produce hydroxylamine and olefin (reaction 1.36). This reaction is readily proceeded at elevated temperatures[133].
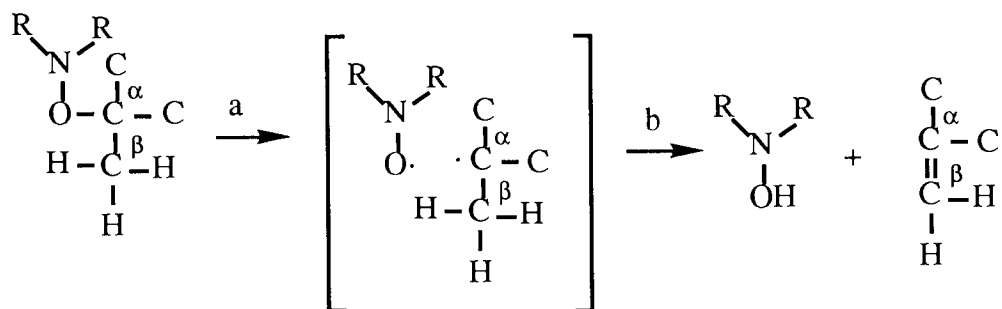
1.36

It was shown by Berger et.al. that the inhibition coefficient of nitroxyl depends strongly upon the structure of substrate (R) and temperature[133]. It seems that the formation of I in Scheme 1-8 is the key step in the antioxidation activity of nitroxyl.

$$\begin{array}{c} \diagdown \\ \diagup \end{array}\text{N-O}\cdot \;+\; \text{R}\cdot \;\rightleftharpoons\; \left[\begin{array}{c} \diagdown \\ \diagup \end{array}\text{N-O}\cdot\text{R}\cdot \right] \;\underset{k'_{-c}}{\overset{k'_{c}}{\rightleftharpoons}}\; \begin{array}{c} \diagdown \\ \diagup \end{array}\text{NOR}$$

$$(\text{I})$$

$$\Big\downarrow\; k'_{d}$$

$$\begin{array}{c} \diagdown \\ \diagup \end{array}\text{NOH} \;+\; \text{olefin}$$
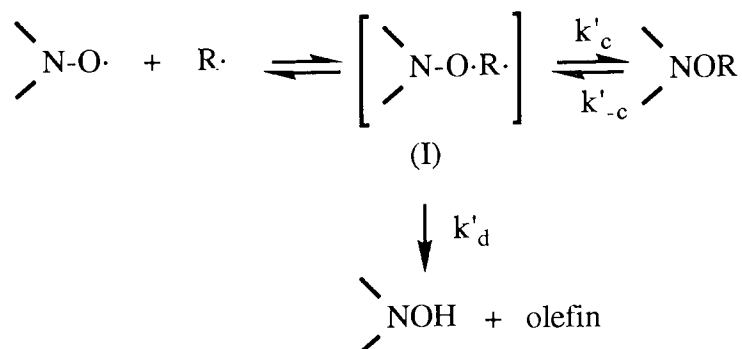
Scheme 1-8

The formation of alkylhydroxylamine, however, was reported to occur when oxygen is absent[137], and this process is readily reversed in the presence of oxygen[138,139]. The research carried out at Aston[136] showed that there are no alkylhydroxylamines formed either during the melt stabilisation of polypropylene by nitroxyls or from the reaction of nitroxyl with squalene in the presence and absence of oxygen. It seems likely that under these conditions ($\geq 180°$C for PP, $100°$C for squalene), macroalkyl radicals are primarily deactivated by direct oxidation by nitroxyl, leading to the irreversible formation of unsaturation[140]. The relative rates of forming olefin and hydroxylamine and forming alkylhydroxylamine in Scheme 1-4, at any temperature, depend both on the stability of the alkyl radicals formed in the shear initiated chain scission reaction and on the lability of the hydrogen atom removed by the nitroxyl. In the case of the radical formed by sicission of the cis-polyisoprene molecule, R·, not only is it stabilised by delocalisation but the δ-C-H bond is particularly weak due to the conjugation energy of the developing unsaturation. Therefore, the δ-hydrogen abstraction process may be the preferred reaction (reaction 1-37).

$$\overset{\displaystyle H\cdots \overset{\textstyle \cdot}{O}\text{-N}\diagup_{\diagdown}}{\underset{\underset{\textstyle CH_3}{|}}{\sim\!\!\sim CH\text{-}C\text{=}CH\text{-}CH_2\cdot}} \;\longrightarrow\; \underset{\underset{\textstyle CH_3}{|}}{\sim\!\!\sim CH\text{=}C\text{-}CH\text{=}CH_2} \;+\; H O\text{-N}\diagup_{\diagdown}$$

$$1.37$$
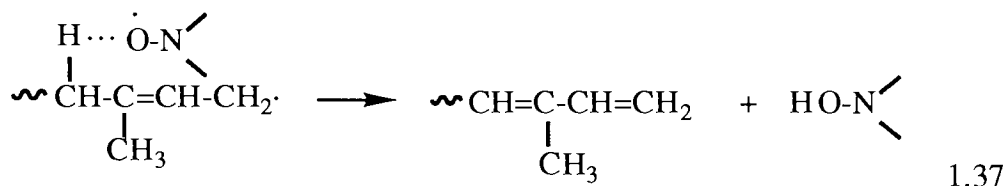
1.2.3.2. Peroxide Decomposition and Peroxide Decomposers

1.2.3.2.1. Peroxide Decomposition Mechanism

Peroxide decomposition mechanism is the most important preventive mechanism[79], since hydroperoxides which are the most potential radical generators, widely exist in the raw and processed polymer. The ionic mechanism of peroxide decomposition results in non radical products and thus retard autoxidation. Usually the initial inhibitors of this kind are not the efficient peroxide decomposers. After being oxidised by hydroperoxides to a series of species, they will carry out catalytic decomposition[141,142].

Like chain-breaking antioxidants, an undesireable side-reaction is also involved in the preventive process[141,142].

1.2.3.2.2. Peroxide Decomposers

Organic Sulphur Compounds

Several organic sulphur compounds, including alkyl and arylsulphides (I)[1443,144] and disulphides(II)[145], dialkyl dithiocarbamates(III)[146] and dialkyl dithiophosphates(IV) [146,147], were found to decompose hydroperoxides.

$$RSR \qquad\qquad RSSR$$

$$(I) \qquad\qquad\quad (II)$$

$$[R_2N\overset{\overset{\textstyle S}{\|}}{C}\text{-S-}]_2Zn \qquad [R_2\overset{\overset{\textstyle S}{\uparrow}}{P}\text{-S-}]_2Zn$$
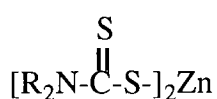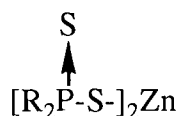
$$(III) \qquad\qquad\quad (IV)$$

The investigations of antioxidant mechanisms of these sulphur compounds have shown following features in common[141,142]:

(1) The effective antioxidant is not the parent sulphur compound but an oxidation product formed from it in the autoxidising medium[143,144];

(2) In all cases, the effective antioxidant is a catalyst for the ionic decomposition of hydroperoxides[143];

(3) The antioxidant stage is frequently preceded by a pro-oxidant stage which varies in intensity. Hence the oxidations are generally autoretarding[143].

When alkyl sulphides react with hydroperoxides, thermally unstable sulphoxides are produced (reaction 1.38).

$$RSR \xrightarrow{ROOH} R\overset{\overset{\displaystyle O}{\uparrow}}{S}R \qquad\qquad 1.38$$

Sulphoxides with one or more hydrogens on a ß carbon to the sulphinyl group undergo thermal decomposition at moderate temperatures to give sulphenic acids and olefins by a stereospecific cis-elimination reaction [148-152] (reaction 1.39).

$$(CH_3)_3C\overset{\overset{\displaystyle O}{\uparrow}}{S}C(CH_3)_3 \longrightarrow (CH_3)_3CSOH + (CH_3)_3C=CH_2 \qquad 1.39$$
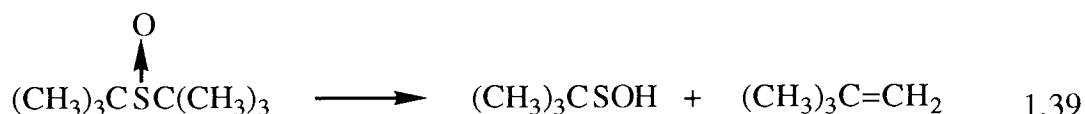
In the case of the sulphinyl dipropionate esters, this process (reaction 1.39) was found to be reversible and became first order in the presence of an oxidising agent which removed the corresponding sulphenic acid as it was formed[153]. When hydroperoxide was present in a low [ROOH]/[S] ratio, pro-oxidant effects have been observed and was explained as the formation of alkoxy radical in the reaction 1.40.

$$ROCOCH_2CH_2SOH + ROOH \longrightarrow RO\cdot + H_2O + ROCOCH_2CH_2SO\cdot \quad 1.40$$
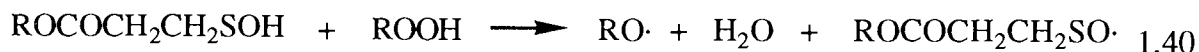
The oxidation product of sulphenic acid is sulphinic acid (RSO_2H) which is relatively stable at room temperature but rapidly disproportionated at 60°C to give sulphonic acid (RSO_3H)[154]. At high temperature sulphinic acid undergoes homolysis to produce sulphur dioxide (SO_2)[154].

All three sulphur compounds are powerful catalysts for the ionic decomposition of hydroperoxides. However, it was found that the inhibition activities of RSO_2H and SO_2 exhibited only at high [ROOH]/[S] ratios. An initial pro-oxidant effect was observed for lower [ROOH]/[S] ratios[154], which again was considered to be due to the redox reaction of sulphur acids with hydroperoxides (reaction 1.41)[141,142]. The catalytic peroxide decomposition activity at high ratios was attributed to a soluble strong acid which is almost

certainly SO3 formed by the alternative ionic break-down of the unstable peracid (reaction 1.42 (c))[153].

$$MeOCOCH_2CH_2SO_xH \; + \; ROOH$$

$$\longrightarrow \; MeOCOCH_2CH_2\dot{S}O_x \; + \; H_2O \; + \; RO\cdot \qquad 1.41$$

$$ROOH \; + \; SO_2 \; \xrightarrow{(a)} \; \left[RO\overset{OH}{\underset{|}{O}S}=O \right]$$

(b) ↙   ↘ (c)

$$RO\cdot \; + \; \cdot OS\overset{OH}{\underset{O}{\diagup}} \qquad ROH \; + \; SO_3$$

(Pro-oxidants)   (Antioxidants)   1.42
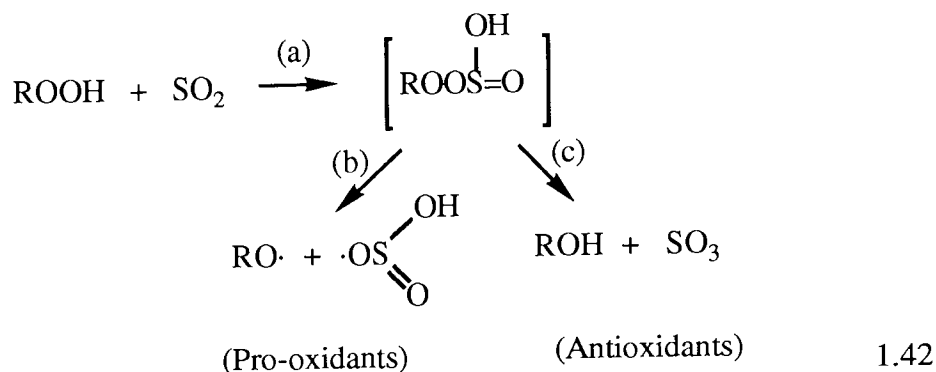
The presence of base will complex with any acid species to halt the ability of acids to decompose hydroperoxides. Only when sufficient acid is generated to exceed the ability of the base to effectively complex all of the acid, the free acid will catalyse the decomposition of hydroperoxide to non-radical products[148].

In addition to their activity as peroxide decomposers, RSO_2H, RSO_3H and SO_2 were all found to be powerful chain-breaking antioxidants (reaction 1.43)[154]. The presence of the acidic hydrogen is responsible for this activity [154,155]. The radical produced appears to be incapable of continuing the chain reaction[141,142].

$$RS_xH \; \xrightarrow{ROO\cdot} \; R\dot{S}O_x \; + \; ROOH \qquad\qquad 1.43$$

Organic Phosphorous Compounds

Organic phosphorus compounds, in particular phosphite ester, are used on a large scale as antioxidants for polymer. In a stoichiometric peroxide decomposition mechanism they reduce hydroperoxides to alcohols[78] (reaction 1.44).

$$(RO)_3P \; + \; ROOH \; \longrightarrow \; (RO)_3P=O \; + \; ROH \qquad 1.44$$

Cyclic phosphates are powerful Lewis acids and have the ability to destroy hydroperoxides in a cyclical regenerative mechanism (reaction 1.45) [156].

$$\text{CH}_3\text{-}\underset{|}{\overset{\text{CH}_3}{\text{C}}}\text{-OOH}$$

1.45
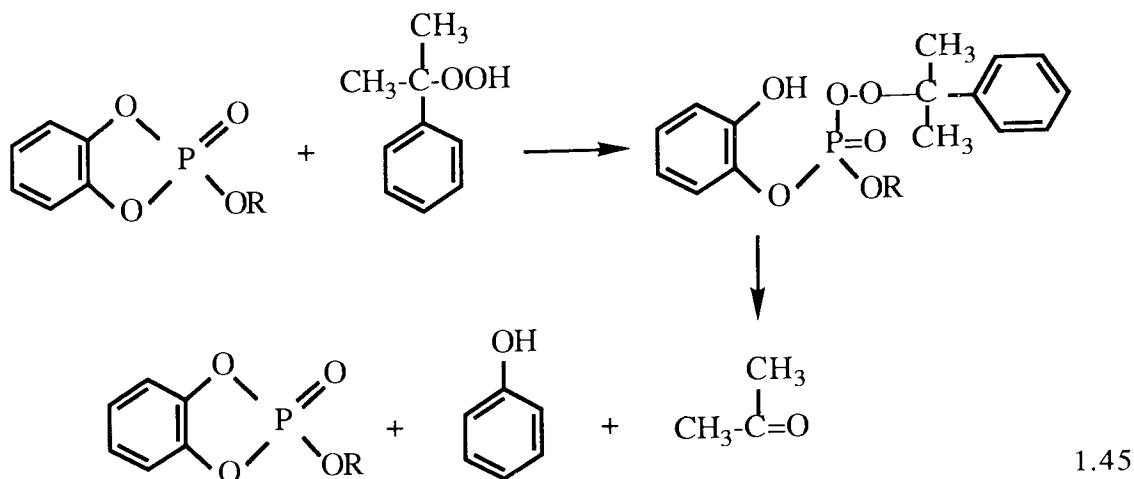
Phosphite esters can also be oxidised by alkylperoxide radicals and alkyloxyl radicals to give the corresponding phosphates and alkyloxyl radicals and alkyl radicals (reaction 1.46 and 1.47).

$$\text{ROO}\cdot + \text{P(OR')}_3 \longrightarrow \text{ROOP(OR')}_3 \longrightarrow \text{RO}\cdot + \text{O=P(OR')}_3 \qquad 1.46$$

$$\text{RO}\cdot + \text{P(OR')}_3 \longrightarrow \text{ROP(OR')}_3 \longrightarrow \text{R}\cdot + \text{O=P(OR')}_3 \qquad 1.47$$
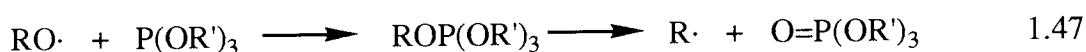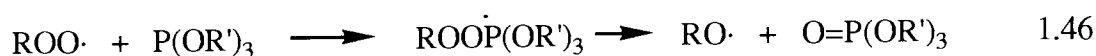
In the case of sterically hindered arylphosphites, the intermediate alkoxy-phosphoranylradical undergoes α scission (reaction 1.48) in addition to β-splitting (reaction 1.44).

$$\text{RO}\cdot + \text{=POAr} \longrightarrow \text{ROP-OAr} \longrightarrow \text{ROP=} + \text{ArO}\cdot \qquad 1.48$$
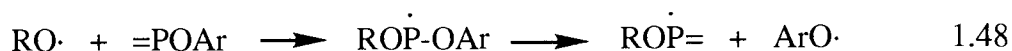
This sterically hindered aroxyl radical formed can act as a chain-breaking antioxidant to effectively trap alkylperoxide radical. Therefore the sterically hindered aryl phosphites can act as chain-breaking antioxidants. Their rate constants are two orders of magnitude lower than those of sterically hindered phenols .

1.2.3.3. Synergism

It has long been known that the combination between antioxidants can have a synergistic effect for polymer inhibition. Synergism exists if the overall effect of the two antioxidants is better than that which would be expected on the basis of a summation of the effects of each component alone[78]. This is particularly marked when the component antioxidants function by different mechanisms. Therefore stabiliser "packages", containing more than one

antioxidant species, are widely used in polymer stabilization technology.[78,157]. In some instances the reverse situation holds true and the combination is said to be antagonistic.

Homosynergism involves compounds of unequal activity which operate by the same mechanism[78]. This is often observed with combinations of two chain-breaking antioxidants [78,81,148]. The more reactive inhibitor will efficiently scavenge the chain-propagating peroxyl radicals and they will be regenerated by reaction with less reactive inhibitor which serves as a reservoir of available hydrogen. This mechanism extends the efficiency of the more reactive stabiliser over a longer period.

Heterosynergism involves two or more antioxidants acting by different mechanisms[78]. Combinations of preventive antioxidants which act by decomposing hydroperoxides to non-radical products with chain-breaking antioxidants which intercept chain propagating free radicals are the best known examples of heterosynergism.

The advantage of this combination is exhibited by overcoming the disadvantages in each mechanism. A chain-breaking antioxidant, reacting with a alkylperoxide radical, always produces a hydroperoxide which is a potential source of further initiation. The presence of peroxidelytic antioxidant is likely to remove it. Similarly, most peroxide decomposers, to varying degrees, give radicals as by-products of their antioxidant function. The presence of a chain-breaking antioxidant will trap the radicals and thus suppress the propagating.

On the other hand, if a peroxide decomposer destroys most of the hydroperoxide formed, few oxidation chains will be initiated and less of the chain-breaking antioxidant will be consumed. Similarly, if the kinetic chain length of the propagation reaction is shortened by efficient trapping of either R· or ROO· radicals, fewer hydroperoxide groups will form and less peroxide decomposer activity will be required[81,148].

In some cases, a single molecule may contain more than one antioxidant functions, a phenomenon known as autosynergism[157]. Autosynergism can have important advantages over conventional multicomponent synergists, particularly when the two functions are

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mechanistically inter-related. The co-operative reactions are carried out more efficiently. Thiobisphenol is one of this kind of antioxidants.

1.3. Objectives and Scope of Present Work

The first objective of this project is to find what causes the increase in crosslink density of HTPB. During the storage of a propellant, environmental factors, such as oxygen and thermal effects, will affect the polybutadiene chains. Earlier workers have demonstrated that the activity of polybutadiene towards oxygen and thermal effects is related to its double bond position[16-20,53,158-160]. However, a complete understanding of these processes has not been reached, especially for a solid bulk product where the oxygen diffusion factor plays an important role. Some researchers have tried to link physical changes of the propellant with its chemical changes[47,161,162]. This will reveal the nature of the deterioration in the propellant's mechanical properties. Although this work is still not sufficient, some methods have been established to predict the ageing behaviour of the propellant from its mechanical property tests[46,47,59,163,164]. But to effectively improve the shelf life of the propellant requires a better understanding of its deterioration process.

The second objective is to study the stabilization of polybutadiene by antioxidants, involving chain-breaking antioxidants and peroxide decomposers. Different antioxidants protect polymer through different mechanisms[78,79,165,166]. It is now well-recognised that the co-operation of two or more mechanisms is more effectively than using only one[157,166].

The overall aim of this project is to investigate the degradation mechanism of polybutadiene and to identify an antioxidant which is not consumed in the isocyanate cure and which is more effective than 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) in protecting the polybutadiene binder from atmospheric oxidation.

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Chapter Two

Experimental Work

2.1. Materials

2.1.1. Polymer

Hydroxyl Terminated Polybutadiene (HTPB) (R45M) This is a clear, colourless viscous liquid, free from visible impurities and suspended matter. The specification of HTPB are given in Table 2-1[167].

$$HO-(CH_2 \quad CH=CH \quad CH_2)_{\overline{2}}(CH_2\ CH)_{\overline{2}}(CH_2 \quad CH=CH \quad CH_2)_6\overline{]}_n OH$$
$$\underset{CH=CH_2}{|}$$
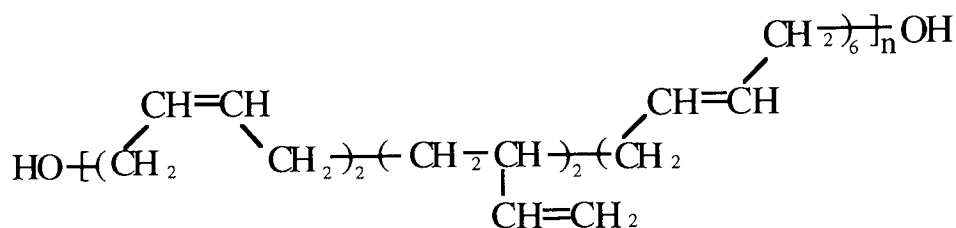
(HTPB)

2.1.2. Curing Agent

3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate (isophorone diisocyanate) (IPDI)

$$CH_2-N=C=O$$
$$N=C=O$$
$$CH_3$$
$$CH_3$$
$$CH_3$$
$$CH_3$$
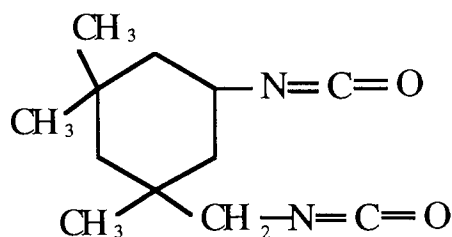
(IPDI)

IPDI is a colourless, low viscosity liquid which is miscible with many organic compounds like ketones, esters, ethers and hydrocarbons. It is practically insoluble in water, but it slowly react with it to form carbon dioxide.

As a cycloaliphatic diisocyanate, IPDI is subject to all typical isocyanate reactions; it is about as reactive as hexamethylene-diisocyanate.

Table 2-1

The Specification of HTPB

TEST	LIMIT	METHOD
Volatile matter	0.5 %Max	M898
Hydroxyl content	0.73±0.05 meq/g	M898
Viscosity at 30°C	5.0±1.0 Pas	M898
Water content	0.1 % Max	M898
Unsaturation type		
Trans	52 % Min	
	57 % Max	
Cis	22 % Min	
	27 % Max	
Vinyl	19 % Min	
	24 % Max	
Total peroxides as H_2O_2	500 ppm Max	M898
Trichlorethylene insolubles	0.2 % Max	M898
Relative density at 20°C	0.87 Min	BS 4522
Colour	50 Max	M898
Number average molecular mass	~ 3000	
Hydroxy Functionality	2.1~ 2.4	

As a bifunctional compound, IPDI can be used specifically for the preparation of high molecular weight plastics. Addition polymerisation with glycols yields polyurethanes. It is also used to crosslink low molecular weight resins through the reaction of the isocyanate groups with active hydrogen.

The physical specifications of IPDI are given in Table 2-2[168, 169].

2.1.3. Antioxidants

(1) Commercial antioxidants

A number of commercially available antioxidants have been used and are listed in Table 2-3.

(2) Synthesized antioxidants

Several nitroxyl-containing antioxidants have been synthesized and are listed in Table 2-4.

Table 2-2

The Physical Properties of IPDI

Refractive index n_D^{25}		1.4825
vapour pressure	at 20°C	0.0003 mmHg
	at 50°C	0.007 mmHg
Boiling point	at 10 mmHg	158°C
	at 20 mmHg	170°C
Density	at 15°C	$1.062 g / cm^3$
	at 20°C	$1.058 g / cm^3$
Viscosity	at -20°C	150 cps
	at -10°C	78 cps
	at 0°C	37 cps
	at 20°C	15 cps
Flash point (open cup) (according to DIN51584)		163°C
Ignition temperature (according to Din 51794)		430°C

Table 2-3

Commercially available antioxidants used in the project

chemical name	molecular structure	code
N-phenyl-N'-1,3-dimethylbutyl-para-phenylenediamine		6PPD
N-iso-propylene-N'-phenyl-para-phenylenediamine		IPPD
Octylated phenylamine		OD
4-Mercaptopropionamio-diphenylamine		MPDA
4,4-Dimethoxydiphenylamine Lancaster		DMDP
Poly(2,2,4-trimethyl-1,2-dihydroquindine)		Flecctol H
2,2'-methylenebis(4-methyl-6-tert-butylphenol)		2246
2,2'-Methylenebis((4-methyl-6-(1'-methyl-cyclohexyl)phenol))		WSP
2-Tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate		GM
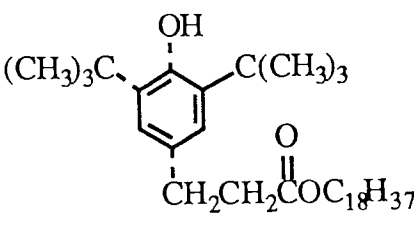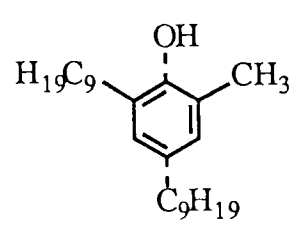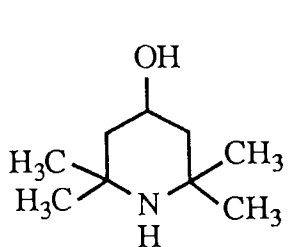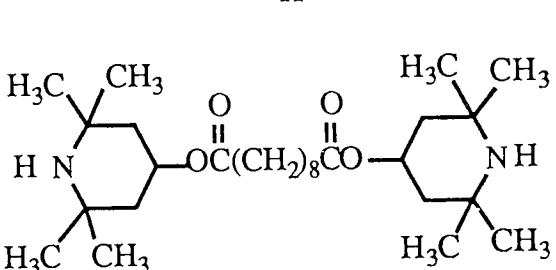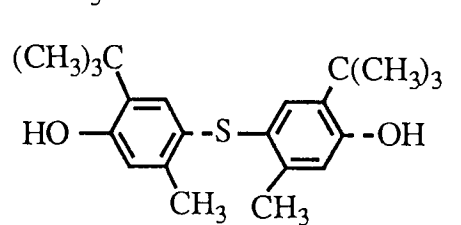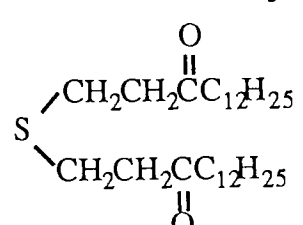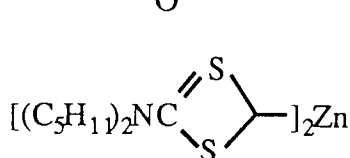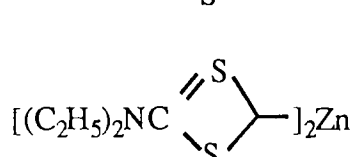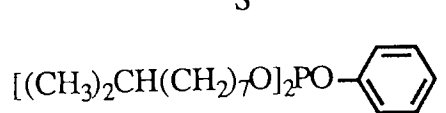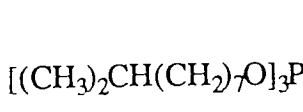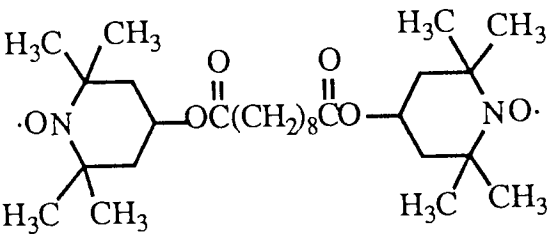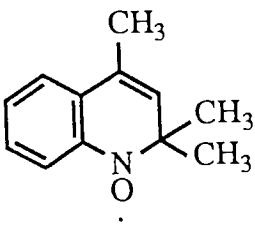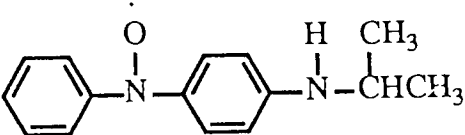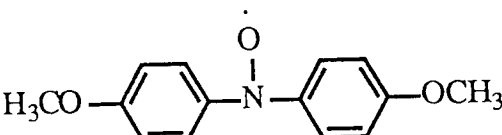
Name	Structure	Abbreviation
Octadecyl β-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate		1076
2-Methyl-4,6-dinonylphenol		Santowhite 54
2,2,6,6-Tetramethyl-4-hydroxypiperidine		TMP
Bis(2,2',6,6'-tetramethyl-piperidinyl)sebacate		770
4,4'-Thiobis(2-tert-butyl-5-methylphenol)		San. Cry.
Dilauryl thiodipropionate		DLTP
Zinc diamyl dithiocarbanate	$[(C_5H_{11})_2NC(=S)S-]_2Zn$	AZ
Zinc diethyldithiocarbamate	$[(C_2H_5)_2NC(=S)S-]_2Zn$	Ethasan
Diiso-decylphenylphosphite	$[(CH_3)_2CH(CH_2)_7O]_2PO-C_6H_5$	P310
Tridecylphosphite	$[(CH_3)_2CH(CH_2)_7O]_3P$	P210

55

Table 2-4

Synthesised antioxidants used in the project

chemical name	molecular structure	code
Bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)sebacate		770-NO
2,2,4-Trimethyl-1-oxyl-1,2-dihydroquinoline		Fle.H-NO
P-(N-isopropyl)diphenyl-nitroxyl		IPPD-NO
4,4'-Dimethoxydiphenyl-nitroxyl		DMDP-NO

2.2. Synthesis of antioxidants

2.2.1. Bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) sebacate (770-NO·)

CH₃ structure diagram of starting material (A) with m-chloroperbenzoic acid (B) and product.

(A)

(B)
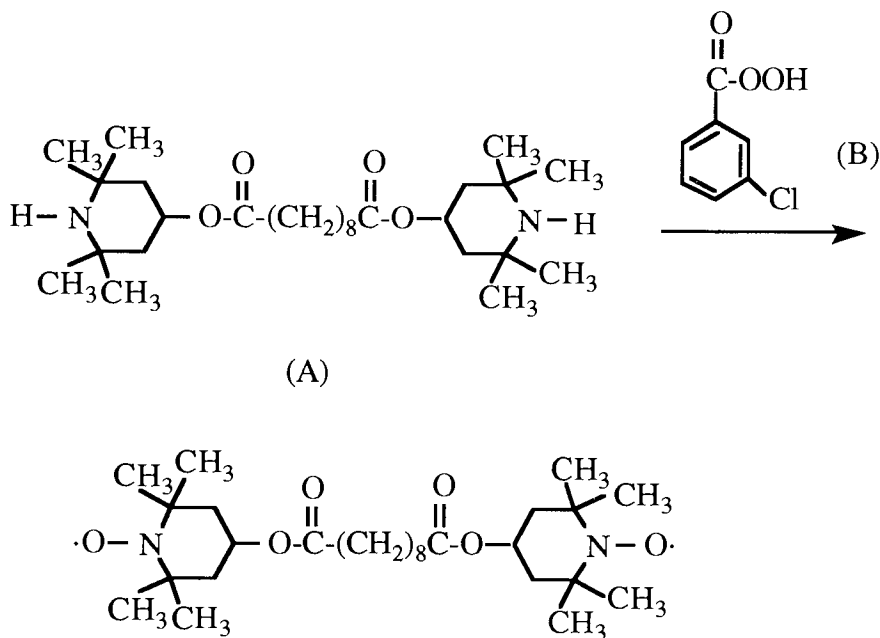
To a solution of 4.8g (0.01moles) of bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate(A) dissolved in 200ml ether, 8.1g (0.04 moles) m-chloroperbenzoic acid(B) was added in powder form with stirring over a period of 1 hour. The reaction solution was stirred magnetically for 24 hours at room temperature. At the end of this period the colour of the solution was deep red. The solution was then washed four times with 5% sodium bicarbonate solution (50ml each time) and the ether layer dried over anhydrous magnium sulphate. The ether was evaporated to dryness under reduced pressure and the orange red residue (powder, 770-NO·) was recrystallised from absolute ethanol. Orange crystals were formed. Yield: 3.8g (0.075 moles, 75% of theoretical). Melting point 99-101°C (lit.: 101°C)[170].

Infrared analysis: (KBr disc)

Band at 3600 cm^{-1} (N-H stretch) disappears. New absorption band appears at 1365 cm^{-1} (nitroxyl N-O· stretch).

2.2.2. 2,2,4-Trimethyl-1-oxyl-1,2-dihydroquinoline (Flectol H-NO·)
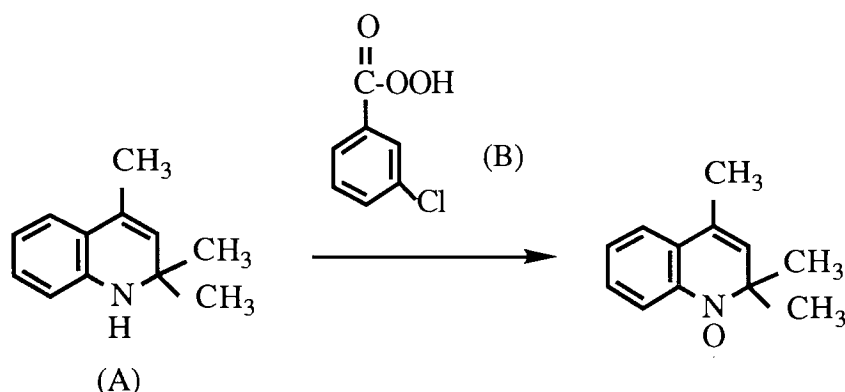
7.80g (0.045 mole) Flectol H(A) was dissolved completely in 300ml dichloromethane, then slowly over a period of 70 minutes 14.0g (0.09 mole) m-chloroperbenzoic acid(B) was added with continuous stirring. A dark red solution was obtained. This solution was allowed to stand overnight at room temperature. It was then extracted with 5% solution of sodium bicarbonate. The dichloromethane solution was dried over anhydrous magnesium sulphate and the solvent was removed by a rotary evaporator, under reduced pressure. Dark red crystals were deposited. Recrystalisation from ethanol gave red crystals. Yield: 2.4g (0.014mole, 31% of theoretical) Melting point 145°C (lit.: 144°C)[171].

Infrared analysis: (KBr disc)

Band at 3390 cm^{-1} (N-H stretch) disappears. New absorption band appears at 1370 cm^{-1} (N-O· stretch). Other bands are 2980 cm^{-1} (aliphatic C-H stretch), 1590 cm^{-1} (aromaticity), 3060 cm^{-1} (aromatic C-H stretch).

2.2.3. 4,4'-dimethoxy diphenyl nitroxyl (DMDP-NO·)
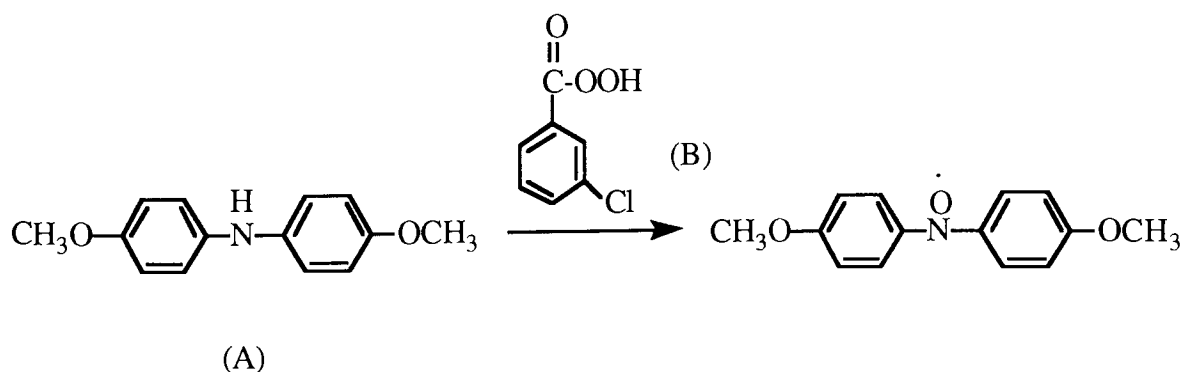
4g (0.017 mole) of 4,4'-dimethoxy dipenyl amine(A) was dissolved completely in 150ml of ether. Over a period of one hour 5.8g (0.034 mole) of m-chloroperbenzoic

acid(B) was added with continuous stirring. At the end of the reaction the red crystals formed were filtered off and then washed with 5% sodium bicarbonate solution followed by distilled water and dried. Recrystallisation from ethylacetate gave red needles.Yield: 2.8g (0.012 mole, 70% of theoretical) Melting point 150°C (Lit = 151°C)[172,173].

Infrared analysis: (KBr disc)

Band at 3420 cm^{-1} (N-H stretch) disappears. New band at 1350 cm^{-1} (N-O· stretch) appears. Other bands are 2960 cm^{-1} (asym. aliphatic C-H stretch), 2840 cm^{-1} (C-H stretch in CH$_3$-O-Aryl), 1250 cm^{-1} (C-O strong stretch) and 840 cm^{-1} (1,4-disubstituted ph-ring).

2.2.4. P-(N-isopropyl)-diphenyl nitroxyl (IPPD-NO·)

The same procedure in (DMDP-NO·) was followed. 6.78g (0.03 mole) IPPD, and 10.3g (0.06 mole) m-chloroperbenzoic acid was used. The product was recrystallised from benzene and pet-ether 40/60. Yield: 1.5g (0.007 mole, 22% of theoretical Melting point = 50°C(lit.: 54°C)[171].

(A)
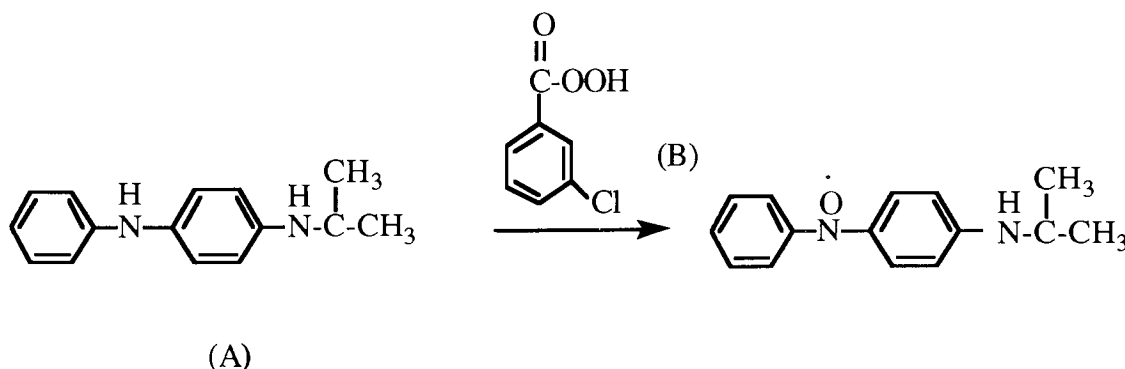
Infrared analysis: (KBr disc)

New band at 1115 cm^{-1} (N-O· stretch) appears. Other bands are 3370 cm^{-1} (sec. N-H stretch), 2960 cm^{-1} (aliphatic C-H stretch), 1595 cm^{-1} (aromaticity), 1380 cm^{-1} (-CH$_3$ sym. bending) and 1310 cm^{-1} (C-N stretch).

2.3. Outlines of the experimental work

Scheme 2-1 outlines the main work undertaken in this project.

Scheme 2-1 Schematic Presentation of Present Work

HO-(CH₂CH=CHCH₂)ₙ-OH

(HTPB)

+

(IPDI)

60°C ⇩ 7 days

(PURE BINDER)

Effect of Oxygen
samples aged under:
(1) oxygen sufficient condition,
(2) oxygen deficient condition,
(3) oxygen free condition.

Effect of Temperature
samples aged at 40°-80°C:
(1) in the presence of oxygen,
(2) in the absence of oxygen.

Relationship between
the permeability of oxygen
and the crosslink density.

The study on binder structure:
(1) the change of crosslink density,
(2) the change of mass and mass
     distribution of soluble binder,
(3) the change of hydroperoxide
     concentration,
(4) the formation of carbonyl
     groups,
(5) the loss of double bonds.

HTPB
+
IPDI
+
Antioxidants

60°C ⇩ 7 days

BINDER WITH ANTIOXIDANT

Antioxidant screening test

Amines and their nitroxyls

Synergism of the combination
of CB-D antioxidants and PD
antioxidant

2.4. Preparation of Binders

Binders were prepared by mixing hydroxyl terminated polybutadiene (HTPB) with

3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate (IPDI), and

antioxidants[174,175], followed by curing as described schematically in Scheme 2-2.

For pure binder tests no antioxidant were added.

Scheme 2-2 Schematic Presentation for Method of Preparation of Binder

```
                    ┌──────────────────────┐
                    │       dry HTPB       │
                    │  (vacuum, oil bath,  │
                    │    60°C, 2 hours)    │
                    └──────────────────────┘
                               ⇓
                    ┌──────────────────────┐
                    │         cool         │
                    │   (in a desiccator)  │
┌──────────────────┐└──────────────────────┘  ┌──────────────────┐
│      IPDI        │                           │   Antioxidant    │
│ (NCO/OH = 0.85)  │          (1)              │     (0.1%)       │
└──────────────────┘                           └──────────────────┘
          ⇓ (2)              ⇓                          ⇓ (3)
┌──────────────────────────────────────────────────────────────┐
│  a. mix (1) with (2) for pure binder                         │
│                                                              │
│  b. mix (1), (2) and (3) for the binder                      │
│     with antioxidant.                                        │
└──────────────────────────────────────────────────────────────┘
                               ⇓
                    ┌──────────────────────┐
                    │   pour into mould    │
                    │    (dish or tube)    │
                    └──────────────────────┘
                               ⇓
                    ┌──────────────────────┐
                    │        cure          │
                    │   (60°C, 7 days)     │
                    └──────────────────────┘
                               ↓
                    ┌──────────────────────┐
                    │     pure binder      │
                    │         or           │
                    │ binder with antioxidant │
                    └──────────────────────┘
```
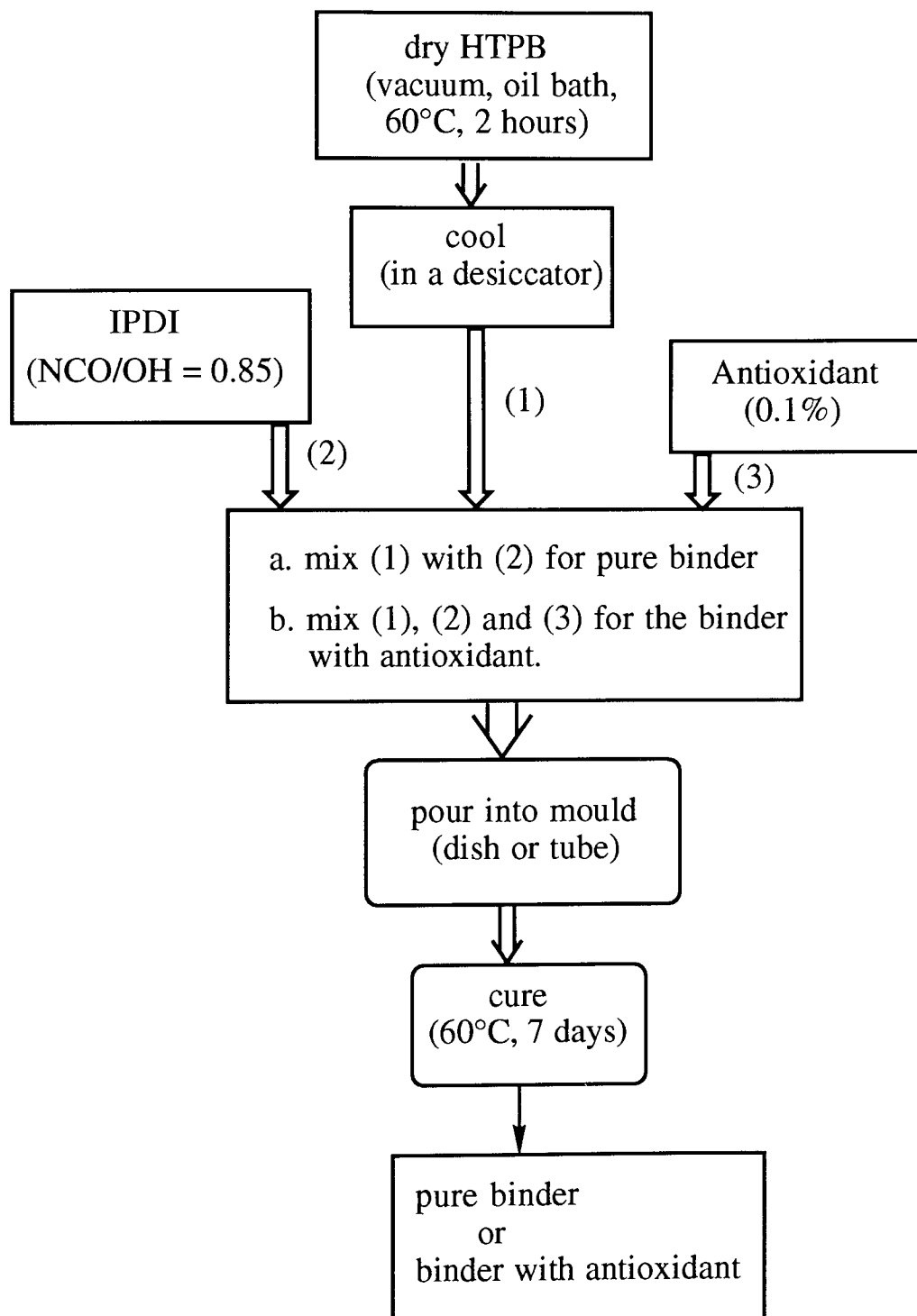
2.4.1. Method

The first step was to dry the HTPB in a vacuum rotary evaporator with an oil bath for 2 hours at 60°C, this was then left to cool to room temperature in a desiccator.

The appropriate amount of curing agent, IPDI, based on a OH / NCO = 0.85 and antioxidant(s) (0.1% of the weight of HTPB) were added into the dried HTPB, and mixed well. The mixture was then poured into the mould or container which was dry and was kept in a desiccator. The mould with uncured binder was covered untightly and placed in an oven at 60°C for 7 days.

Several kinds of moulds and containers were used according to the test requirements. Their sorts and sizes are listed in Table 2-5.

52 x 10 PS dish was used to make film binder. The amount of mixture (HTPB with IPDI) which was poured in the dish was calculated by 0.5 x 'area of dish'.

Table 2-5

Containers used for binders

container	material	size (mm)
		(D x L)
tube	glass	25.4 x 212.4
dish	PS	20 x 6
		52 x 10
		(L x W)
plate	glass	300 x 300

2.4.2. Calculation of NCO : OH Ratio

$$\text{The NCO: OH ratio} = \frac{\text{weight IPDI (g) x 2 x 1000}}{\text{weight HTPB (g) x hydroxy content (meq/g) x 222}}$$

IPDI has a molecular weight of 222 and contain 2 isocyanate groups per molecule. Hydroxyl content of HTPB is 0.73 meq / g (see Table 2-1). When a ratio of NCO / OH of 0.85 was chosen, the weight of IPDI can be calculated from:

$$\text{weight IPDI (g)} = 0.73 \times \frac{222}{2 \times 1000} \times 0.85 \times \text{weight HTPB (g)}$$

2.4.3. Preparation of Air Free Binder

Drying and mixing steps were the same as described in section 2.4.1.. The tube, containing the mixture, was connected to a vacuum line ($10^{-4} \sim 10^{-5}$ mmHg). The mixture was subjected to a freeze-thaw procedure. This operation was repeated for at least 5 times on the vacuum line before sealing the tube at the neck. Samples were cured in an oven at 60°C for 7 days.

2.5. Thermal-Oxidation

After curing, samples were oxidized in air ovens at temperatures of 40°C, 50°C, 60°C, 70°C, 80°C.

2.6. Testing

2.6.1. Sol / Gel Measurement.

A known weight of binder is added to a weighed alumina soxhlet extraction thimble. The sample was extracted for at least 16 hours in a Soxhlet apparatus using dichloromethane as a solvent. The thimble was dried and re-weighed. The sol fraction of the sample is equal to the loss in weight of the thimble divided by the weight of binder initially used[176].

Sampling

For 0.5mm film binder, sample was taken out of the PS dish mould and cut into small pieces.

For 5mm thick binder, sample was taken by cutting through the whole 5mm thickness and then cut into small pieces.

For tube binder, samples were taken from two parts of the tube: one from the bottom, another from the place which was 5mm from the top layer.

Apparatus

Soxhelt extraction apparatus.

Ceramic Soxhlet extraction thimbles.

Thermostatically controlled heater.

Extraction

The extraction and measurement were carried out in triplicates. The alumina extraction thimble was dried by heating in a vacuum oven for 3 hours at 60°C. This was left to cool for 1 hour to constant weight in a desiccator and was weighed accurately (W_1, g). 0.25±0.005 g of cut binder was added and reweighed accurately (W_2, g). This was extracted for at least 16 hours with 250 mls of dichloromethane in a Soxhlet apparatus. The extraction thimble was removed and placed in a fume-cupboard. The excess solvent was allowed to evaporate off by air-drying for 2 hours. Then the thimble was placed in a vacuum oven overnight at 60°C, followed by cooling in a desiccator. Then the thimble containing sample was reweighed (W_3, g).

Calculation

The sol fraction of the binder was calculated from equation 1[176].

$$\text{Sol fraction } \% = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad (1)$$

2.6.2. Crosslink Density

The crosslink density (CLD) of the binder was calculated from equation 2 using sol fraction[1a].

$$\text{Crosslink density} = \frac{(1-s)[2 - (s + s^{0.5})]}{s + s^{0.5}} \qquad (2)$$

where, s = sol fraction

2.6.3. Hydroperoxide Concentration Measurement

Chemicals:

a)   aged binders

b)   chloroform, as solvent.

c)   glacial acetic acid : isopropranol = 20 : 100 v/v solution.

d)   saturated sodium iodide isopropranol solution.

e)   approximate 0.001N sodium thiosulphate solution.

Method:

0.1g sample of binder was introduced into 25ml of chloroform in a conical flask and purged with nitrogen for half minute to replace the air inside the flask. The binder was then allowed to swell overnight in the dark. 15ml of a solution of acetic acid : isopropranol = 20 : 100 (v/v) and 10ml saturated sodium iodide isopropanol solution were added. The flask, containing the solution, was refluxed for 15 minutes under an atmosphere of nitrogen. 10ml distilled water was added and the solution was cooled in a dark place. The solution was titrated using 0.001N sodium thiosulphate till colourless. A blank test with no sample was carried out at the same time[177,178].

Standardisation of 0.1N thiosulphate solution[179]

0.8917g of potassium iodate previously dried at 180°C was weighed and dissolved in distilled water followed by dilution to 250ml using graduated flask. 25ml of this solution was transfered to a 250ml conical flask and 1g of potassium iodide and 5ml of 2N sulphuric acid were added. This was titrated with thiosulphate solution to a faint straw colour. Starch solution was added and the titration was continued to the end-point, blue to colourless.

2.6.4. Measurement of Molecular Mass and Molecular Mass Distribution

The molecular mass and molecular mass distribution of binder were measured using a standard GPC system at RAPRA Technology Ltd. Only soluble portion of the binder can be run.

The sample solutions were prepared by adding 10ml of chloroform to approx. 20mg of binder and leaving overnight to dissolve. The gel portion was filtered through a 5.0μm PTFE membrane and a 0.45μm polyamide membrane. The solutions were run using the following chromatographic conditions:

Columns:	P.L. gel	2 x mixed gel
		30 cm, 10 micron
Solvent:	chloroform (Analar)	
Flow-rate:	2.0 ml/min	
Temperature:	ambient	
Detector:	refractive index	

The system used was calibrated with polystyrene and all the results are expressed as the "polystyrene equivalent" molecular masses.

2.6.5. Microstructure Determination of Binder by NMR

Samples were prepared by dissolving the binder, aged for different times, in deuteratedchloroform. The 75.4-MHz ^{13}C NMR spectra and 300.13-MHz ^{1}H NMR spectra were obtained with a Bruker AC 300 spectrometer at ambient temperature. In performing quantitative ^{13}C NMR measurements via sequence distribution, one must take into account differences in nuclear Overhauser effects (NOE) and spin-lattice relaxation times (T_1)[180]. T_1 values have been measured with the use of the standard 180°-τ-90° inversion recovery pulse sequence, using nine values of τ of 0.1, 0.3, 0.7, 1.2, 2.0, 2.5, 4.0, 12 and 40 s. The T_1s were determined from a three-parameter fit to the peak intensities with the use of the program supplied with the spectrometer and found to be between 1 to 3 seconds. The technique of inverse-gated decoupling was used to produce a ^{13}C decoupled spectrum without the NOE. The area integral of a proton decoupled ^{13}C spectrum will accurately reflects ^{13}C intensities since the relaxation delay was properly defined (i.e. 5-10 time T_1)[181]. More than 2000 scans were accumulated with a digital resolution of 0.61Hz/point, corresponding to a spectral width of 10000 Hz and a data length of 32K.

2.6.6. FTIR Measurement

<u>Preparation of sample</u>

A neat liquid cell was used, which consists of two NaCl windows that are permanently mounted in a cell holder and separated by a Teflon spacer of known thickness. The clean, dry cell is filled by placing a drop or two of HTPB in one of the openings until the window is filled. The caps were inserted in both openings, and the cell was placed in an oven at 60°C and the spectra were run each day.

<u>IR spectra</u>

IR spectra were obtained on 1710 Perkin Elmer FTIR instrument.

2.6.7. Measurement of Oxygen Permeability

<u>Preparation of sample</u>

On a glass plate, binder was cast to a certain thickness of film, then placed in an oven to cure and age at 60°C. Before testing, binder was taken off from the glass plate.

<u>The apparatus</u>

The DAVENPORT Gas Permeability Measuring Apparatus (see Figures 2.1 to 2.4) is designed to measure directly the transmission rate of gases through films in general accordance with B.S. 2782, method 514A, procedure 2, ASTM D. 1434 and similar methods[182].

<u>Method</u>

A precision-bore capillary tube forming one arm of a manometer is partially filled with mercury. This tube is connected to a cell of accurately known volume, one wall of which is formed by the specimen under test.

The air in the test cell and manometer is pumped out and the test gas is fed to the upper surface of the sample under test, so that there is an effective pressure difference of one atmosphere between the two sides of the test specimen. The stop-cock connecting the apparatus to the vacuum pump is closed and the apparatus is allowed to remain in this condition.

The test gas flows through the test specimen under the pressure gradient thus set up, into the volum chamber, thus increasing the pressure therein. The mercury in the capillary tube therefore falls under the influence of the partial vacuum in the closed leg of the manometer assembly, as well as the space between the mercury reservoir and the stop-cock.

The rate of fall of the level of the mercury in the capillary is measured and, when this has become constant, i.e. when equal time intervals give equal change in the height of the mercury column, this rate is used to calculate the gas transmitted per unit area of specimen per unit interval of time per unit pressure differential.

Calculation of results

The gas transmission rate (T.R.) was calculated from the following equation:

$$T.R. = \frac{273 \times p \times V \times 1}{A \times T \times P \times 76} \quad \left(\frac{ml \cdot mm}{cm^2 \cdot sec \cdot cmHg}\right)$$

Where: T. R. is the gas transmission rate.

p is rate of pressure change in capillary in cm Hg per second.

V is the total volume in ml of the space between the lower surface of the sample and the top of the mercury column in the capillary.

This total volume is expressed as:

a) The volume of the lower cell cavity (i.e. 5,10,15 or 20 ml, depending on which insert is being used.)

b) The volume of the capillary above the mercury level half way through the test. As the area of cross-section of the capillary is 0.018 cm^2, this volume will be 0.018X, where X is the length in cm of the capillary above the mercury at the half-way point.

c) The "free-space"volume of the filter paper , For the filter paper used, this can be taken as 0.24 ml.

V will, therefore, be either:

$$(20 + 0.018X + 0.24) \text{ ml, or}$$

$$(15 + 0.018X + 0.24) \text{ ml, or}$$

$$(10 + 0.018X + 0.24) \text{ ml, or}$$

$$(5 + 0.018X + 0.24) \text{ ml.}$$

A is the area of specimen under test: 23.77 cm.

T is the test temperature in °K.

P is the pressure difference (cm Hg) across the sample. (can be taken as 76)

l is the thickness of sample.

2.6.8. Measurement of Antioxidants in the Binder After Curing

The binders which were stabilized by 2246, IPPD and Flectol H were extracted by solvent (dichloromethane). The extractes were sent to MOD for HPLC analysis to examine the level of antioxidants remained in the polymer after curing. The HPLC conditions used for different antioxidants are shown below:

<u>2246 antioxidant</u>

A normal phase silica column (Millipore Ltd.) with a hexane : dichloromethane elluant (13:7, 1ml/min.) was used.

<u>IPPD antioxidant</u>

A reverse phase Resolve C18 column with 5 micron particle size packing was used and the elluant was acetonnitrile : ethylene glycol : water (2:1:1).

<u>Flectol H antioxidant</u>

Conditions were the same as those used for the antioxidant 2246.

2.6.9. Reaction of Antioxidant with IPDI

Some antioxidants were mixed with IPDI and left in covered glass bottles at 60°C. After 7 days the mixtures were removed and run by FTIR.

Labels on figure:

Gas in

Gas out

Ground glass joint

PERMEABILITY CELL

Metal stand

Acrylic manometer support plate

High vacuum stopcock

Compression joint

Mercury reservoir

Capillary

Removable cover

MANOMETER UNIT

GAS PERMEABILITY APPARATUS

Fig 2-1

MERCURY RES:

Fig. 2-2

GAS

FILM

FILTER

VACUUM
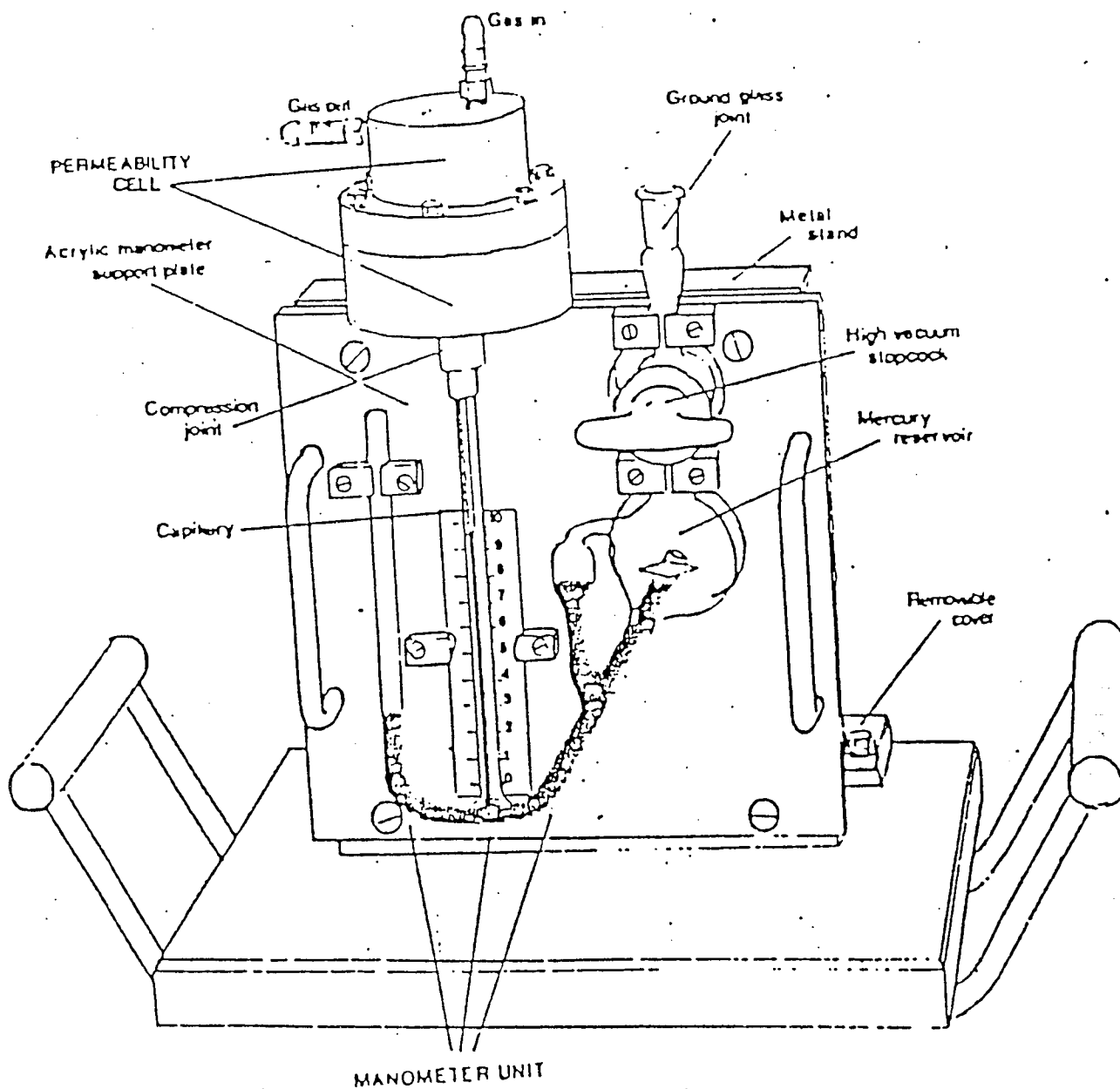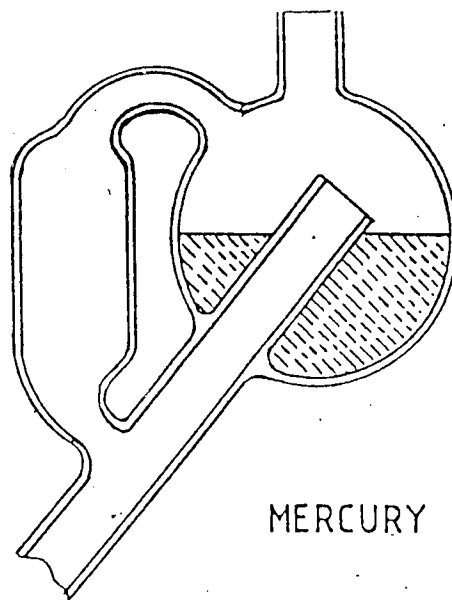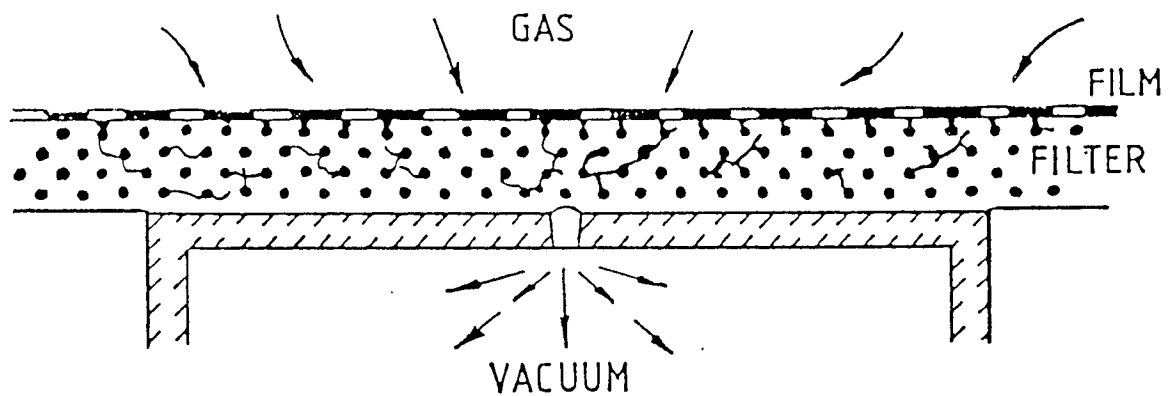
Section through Permeability Cell

Fig. 2-3

TEST GAS
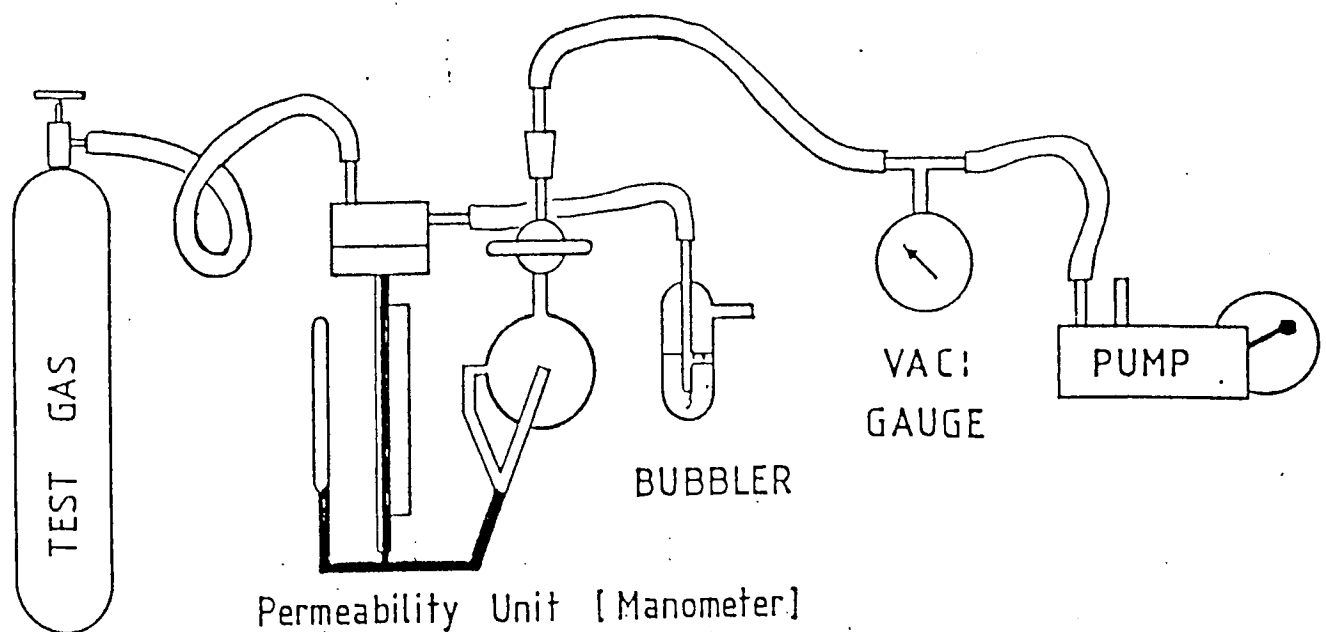
Permeability Unit [Manometer]

BUBBLER

VAC:
GAUGE

PUMP

Fig. 2-4

71

Chapter Three

Degradation of Diisocyanate Cured Polybutadiene

3.1. Object and Methodology

It has been observed[1a,9] that the binder, diisocyanate cured polybutadiene, loses its excellent stress-strain characteristics during long term storage due to the formation of high density network. Since the propellant is normally stored in the dark, at ambient temperature, the factors which may cause the degradation of the binder are chiefly oxygen and temperature. The effects of oxygen and temperature on binder were investigated in this chapter.

Considering the oxygen diffusion factor, the examination of the effect of oxygen on the binder was carried out by ageing the binder at 60°C in three different forms:

1. As a thin film in a 52 x10 mm dish, which represents the top of the bulk binder in an oxygen sufficient condition.

2. As a thick section bulk in a 25 x 212mm tube with one side open to the air, which is used to represent the real propellant.

3. As a thick section bulk in a vacuum sealed tube (15 x 150mm), which represents an oxygen free condition.

Since oxygen reacts with alkyl radical at a much faster rate than it is diffused into a solid polymer, the oxidation is controlled by the oxygen diffusion. Oxygen transmission rate in the binder was measured, and this is used for comparison with the rate of increase in gel content. This reveals the role of oxygen in the ageing of the binder.

The examination of the effect of temperature on the binder was carried out by ageing the binder at 40°-80°C under two conditions:

(1)   As a thin film in a 52 x 10mm dish, aged in the present of oxygen.

(2)   As a thick section bulk in a vaccum sealed tube(25 x 212), aged in the
absence of oxygen.

The extent of binder ageing is presented by measuring crosslink density which was
calculated from the sol fraction measurement (see section 2.6.2.). Investigation of the
changes in binder chain composition, during ageing, was carried out by measurements
such as hydroperoxide concentration, FTIR and n.m.r..

3.1.1. The Determination of Hydroperoxide Concentration

The hydroperoxide concentration in binder, during ageing, was measured by
traditional iodometric titration[179] (see section 2.6.3.), which has been proved by
Carlsson and Lacoste to be a highly reliable method for solid oxidized polyolefins[183].

3.1.2. The Measurement of Carbonyl Group

By using FTIR, the formation of carbonyl groups in HTPB, during ageing, was
analysed, but not quantitatively.

3.1.3. The Determination of the Composition of Unsaturation in Polybutadiene Chain.

The microstructure of polybutadiene used in binder consists of cis-1,4, trans-1,4 and
1,2-vinyl units. By using ^{1}H n.m.r., the change in total content of unsaturation can be
measured. But the determination of the ratio of these three base units is not possible due to
the poor resolution of the olefinic resonance in ^{1}H n.m.r. spectrum[180,184-187].

Infrared spectra of polybutadiene have been used in the determination of the
microstructure of polybutadienes[15-18]. But this method[180] relies on isomerically pure
polymers, each containing relatively high concentrations of one of the three kind of the
base units[15,16]. It has been found that using infrared spectra of HTPB to determine the
changes of three kind of double bonds is not accurate for two reasons. Firstly, the
characteristic peak for cis-1,4 double bond was not clear; secondly, although the peaks for
trans-1,4 and 1,2-vinyl double bonds are sharp, the quantitative calculation can not be

done because the thickness of sample changes with ageing time and it is not possible to find the reference peak which remains unchanged during the oxidation.

Geert van der Velden et.al.[180] have developed a new method for the microstructure determination of polybutadiene by ^{13}C n.m.r.. The olefinic resonances, based on the existing assignments[188,189], have been used (assuming Bernoullian statistics) to give the isomeric distribution along the polybutadiene chains.

Assignments

In ^{1}H spectrum, the resonance area between 5.21-5.47 ppm has been assigned to the main chain unsaturation, and the areas between 4.82-5.02 ppm and 5.47-5.63 ppm have been assigned to the side group unsaturation[190]. The area between 0.77-1.07 ppm belongs to the methyl groups in diisocyanate and is used as the reference area in the quantitative analysis.

In ^{13}C spectrum, the resonances at approximately 114 and 143 ppm have been assigned to the two different vinyl 1,2 carbon atoms, the methylene and methine, surrounded by neighbouring cis, trans and vinyl units. The complex resonance pattern between 127-133 ppm is due to compositional splittings of the two olefinic carbons in central cis or trans units, present in different combinations of homtriads (ccc and ttt), heterotriads (ccv, ttv, etc.) and symmetric and non-symmetric isolated triads (tct, vcv, tcv, vct, etc.)[188,189,191]. All assignments for the olefinic main-chain cis-1,4 and trans-1,4 carbon resonances have been depicted in Fig.3-1 and have been listed in Table 3-1.

Quantitative Analyses

The total unsaturation in the film binder can be quantitatively analysed from ^{1}H n.m.r. by using the ratio of area$_{(4.82-5.63)\ ppm}$ / area$_{(0.77-1.07)\ ppm}$.

The quantitative analysis of the composition of three kinds of double bonds is based on a least-squares fitting procedure between the experimentally observed and theoretically calculated areas of the main chain cis-1,4 and trans-1,4 olefinic resonances in ^{13}C spectra. Although the v-centered triads (at 114 and 143 ppm) have been excluded, the v ratio

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indirectly determines also to a certain extent the areas of the carbon resonances, e.g., triads like vtv, ctv, and ttv.

For the olefinic resonances of the central cis and trans carbons (127-133 ppm) occurring in the different kind of compositional triads, it is evident that a simple experimental discrimination between the cis- and trans-centred triads is not possible for two reasons: (a) overlapping resonances for the cis-1,4 and trans-1,4-centered triads (peaks 5 and 6, 8, 9, and 10, Fig.3-1) and (b) the resonance of two different carbon atoms of one triad at very different fields (e.g., peaks 3 and 18 for vcv).

Therefore, a somewhat more elaborate method must be followed which uses all 16-18 experimentally observed peak areas. For practical purposes, six peaks or combinations of peaks have been selected, namely 1, 2, 3-9, 10-12, 13-15, and 16-18.

The theoretically calculated peak areas denoted by A_1-A_6 can now be evaluated, taking into account Bernoullian statistics[191]. For matters of convenience, the parameters, c, t and v, are defined as the molar fractions of cis-1.4, trans-1,4, and vinyl-1,2 units present in the polymer chain. In such a description the homotriad ccc indicates three sequential cis-1,4 units, and the relative abundance in such a model will be given by c^3 and the abundance of other triads like ttv or tvt by vt^2. This Bernoullian model has been applied to polybutadienes. The six peak areas should fulfill the following relations:

$$A_1 = v^2 t \quad \text{peak 1}$$

$$A_2 = tv(1-v) \quad \text{peak 2}$$

$$A_3 = cv + (cv + 2t)(c + t) \quad \text{peaks 3-9} \quad (1)$$

$$A_4 = (2c - cv)(c + t) \quad \text{peaks 10-12}$$

$$A_5 = vt \quad \text{peaks 13-15}$$

$$A_6 = cv \quad \text{peaks 16-18}$$

The validity of eq(1) can be verified, realizing that the total area A_i (i = 1-6) necessarily equals two main-chain cis or trans olefinic carbon atoms, in other words

$$\sum_{i=1}^{6} A_i = 2(c+t) = 2(1-v) \quad (2)$$

7 5

Peak areas, normalized to unity, can be calculated as

$$B_i = A_i / \sum_{i=1}^{6} A_i$$

(3)

This leads to the following set of equations:

$$B_1 = 1/2 \, v^2 t (1-v)^{-1}$$

$$B_2 = 1/2 \, vt$$

$$B_3 = 1/2 cv(1-v)^{-1} + 1/2(cv + 2t)$$

(4)

$$B_4 = c(1 - 1/2 \, v)$$

$$B_5 = 1/2 \, vt(1-v)^{-1}$$

$$B_6 = 1/2 \, cv(1-v)^{-1}$$

The cis-1,4, trans-1,4 and vinyl-1,2 ratio of these polybutadienes can now be obtained from the experimentally determined areas B_i through a least-squares fitting program. This program estimates the c, t, and v ratios by minimizing the summed squared difference D between the six experimental areas and the calculated six areas obtained using eq (4)

$$D = \sum_{i=1}^{6} [B_i(calcd) - B_i(exptl)]^2$$

(5)

According to eq(4) this is a complicated nonlinear minimization problem. Fortunately, there are two constraints that simplify the problem:

$$c, t, v \geq 0$$

$$c + t + v = 1 \qquad (6)$$

The least-sqares fitting program (written in Basic) was run on an IBM computer and calculates the desired ratios.

The ratio of the three units in raw material, obtained by this method, shows good agreetment with the composition in the specification supplied by M.O.D..

3.2. Results

3.2.1. Results of the Effect of Oxygen

After curing, the binder is a colourless soft network material; but during ageing a yellow to brown colour appears. The film binder quickly loses its elasticity and becomes

brittle. The same effect occurs also on the surface of the tube binder. In spite of the colour change, the binder beneath the top layer in the open tube and the binder in a sealed tube remained soft throughout the ageing time.

3.2.1.1. The Crosslink Density

Figures 3-2 to 3-4 and Table 3-2 show the crosslink density of the three kinds of binders (film, open tube and sealed tube) aged at 60°C. The testing samples were taken from the levels of 5 mm and 60 mm from the surface of tube binders, respectively. The testing error was calculated for each sample, using the equation below.

$$\text{error} = \frac{\text{individual result - average result}}{\text{average result}} \times 100\%$$

The maximum error among each kind of test are listed in the Table.

3.2.1.2. The Molecular Mass and Mass Distribution

Figures 3-5 to 3-7 and Table 3-2 give the molecular mass and mass distributions of the binders aged at 60°C, including the film binder, the binder from the bottom of open tube and the binder from sealed tube. In Figure 3-5 the noise in the curve for the longest ageing time sample is due to the poor solubility of the sample.

3.2.1.3. The Hydroperoxide Concentration

Figures 3-8 to 3-10 and Table 3-2 show the hydroperoxide concentration in the three kind of binders aged at 60°C. The errors were calculated as the same as Section 3.2.1.1.. The big value of error for the tube sample was due to the low concentration of hydroperoxides and the relative high error of the testing method. For example, the testing results of [ROOH] for sealed tube binder which was aged for 133 days were: 0.6; 0.3; 1.2 (mol/g), then the maximum error for this sample is:

$$\frac{1.2 - (0.6 + 0.3 + 1.2)/3}{(0.6 + 0.3 + 1.2)/3} \times 100\% = 71\%$$

3.2.1.4. The Formation of Carbonyl Groups

Figure 3-11 is the FTIR spectrum of hydroxy terminated polybutadiene aged at 60°C. The increasing peaks at 1728 cm^{-1} and 1698 cm^{-1} are assigned to the carbonyl group of aldehyde and α-β-unsaturated carbonyl groups, respectively.

3.2.1.5. The Content and Composition of Unsaturation in Polybutadiene

Figure 3-13 is the ^1H n.m.r. spectrum of binder and Figure 3-12 is the ^{13}C n.m.r. spectrum of hydroxy terminated polybutadiene.

The change in total unsaturation, obtained by ^1H n.m.r. for the film binder aged at 60°C, is listed in Table 3-4 and shown in Figure 3-14. Table 3-5 lists the data analysis for the n.m.r. spectra, which is shown also in Figure 3-16.

3.2.1.6. Oxygen Permeability

Figure 3-17 shows the relationship beteen the oxygen permeability and crosslink density of film binder.

3.2.2. Results of the Effect of Temperature

Figure 3-20 and 3-21 and Table 3-6 give the crosslink density and hydroperoxide concentration of thin film binder aged at 40°C,50°C, 60°C and 80°C. Figures 3-22 and 3-23 show the crosslink density and hydroperoxide concentration of sealed binder aged at 40°C, 60°C and 80°C.

3.3. Discussion

3.3.1. The Effect of Oxygen

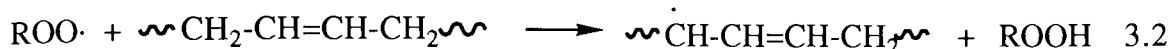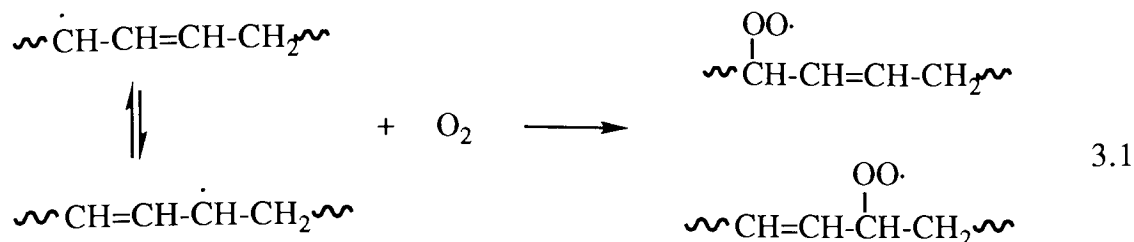It is shown by the sol fractions of three kinds of binders (Table 3-2) that under an oxygen sufficient condition, the crosslink density increased rapidly after a short induction period (Fig.3-2), whereas under oxygen deficient and oxygen free conditions, this increasing did not occur (Figs. 3-3 and 3-4). The fact that oxygen causes the crosslinking reaction in the binder was illustrated by comparison between Figs. 3-2 to 3-4. The

molecular mass measurement of the soluble portion of three kinds of binders (Table 3-3) shows the correspondent results to those of crosslink density, i.e. the decrease in molecular mass occured only under an oxygen sufficient condition whereas it remained almost unchanged under oxygen deficient and oxygen free conditions. Although the shift of molecular mass distribution in the direction of lower molecular mass (Fig.3-5) can be due to, in part, the relatively low probability of small molecular chains in the crosslinking reaction, it is obviously reflected in the longer ageing time samples that chain scission occurred also. It appears that chain scission accompanies the crosslinking during binder oxidation, but crosslinking is the predominant reaction. By comparison between Figs.3-2 to 3-4, and Figs.3-5 to 3-7, it is clear that oxygen plays an important role in the deterioration of polybutadiene. Without oxygen, neither crosslinking nor chain scission takes place.

The increase in the binder crosslink density and the decrease in the average molecular mass of non crosslinked chains are related to the reaction of polybutadiene with oxygen. The build up in hydroperoxide concentration is similar to that of the crosslink density (Table 3-2).

Under an oxygen sufficient condition, there is an induction period before the rapid formation of hydroperoxides (Fig.3-8). In the induction period, the reaction of the polymer chain with oxygen is an endothermic reaction, so the oxidation rate is slow. With the accumulation of ROOH, less endothermic decomposition of hydroperoxides occurs and free radicals are formed, which accelerates the oxidation and results in the autoxidation. The α-hydrogen in polybutadiene is the most reactive hydrogen and is prone to be abstracted by radicals. The new radical formed, which is stabilized by resonance effect from the adjacent double bond, may react with oxygen (see reaction 3.1). This is followed by the abstraction of a hydrogen to form another hydroperoxide and a new radical (see reaction 3.2). The reaction rate constants for propagation are high, so there is a rapid increase in hydroperoxide concentration. But after a certain period, the concentration of hydroperoxides begins to decrease. This phenomenon was also observed in HIPS, PP and PE[17,178,192,193]. It seems to be due to the minor products of

peroxide break-down (e.g., carbonyl compounds), which can act as retarders of the chain process.

$$\text{\textmu CH-CH=CH-CH}_2\text{\textmu} \qquad + \quad O_2 \quad \longrightarrow \qquad \begin{array}{c} OO\cdot \\ | \\ \text{\textmu CH-CH=CH-CH}_2\text{\textmu} \end{array}$$

$$\text{\textmu CH=CH-CH-CH}_2\text{\textmu} \qquad\qquad\qquad\qquad \begin{array}{c} OO\cdot \\ | \\ \text{\textmu CH=CH-CH-CH}_2\text{\textmu} \end{array} \qquad 3.1$$

$$ROO\cdot \; + \; \text{\textmu CH}_2\text{-CH=CH-CH}_2\text{\textmu} \quad \longrightarrow \quad \text{\textmu CH-CH=CH-CH}_2\text{\textmu} \; + \; ROOH \quad 3.2$$

The reaction of hydroperoxide with aldehyde has been discussed by Scott[14], which leads to an intramolecular bond rearrangement to give the final products without the intervention of free radicals. The mechanism proposed by Mosher and his co-workers is given in Scheme 3-1[194,195]. It was found[14] that the decomposition of n-butyl hydroperoxide gives rise to butyric acid and hydrogen as major products; very little butyraldehyde or butylalcohol, expected products on the basis of the conventional homolytic mechanism, were obtained. The reaction had an induction period which could be removed by the addition of butyraldehyde. α-Hydroxybutyl-n-butyl peroxide was prepared and was found to decompose at the same rate as the hydroperoxide after the induction period to give the same products.

$$RCH_2OOH \quad \longrightarrow \quad \begin{array}{c} RCH_2O\cdot \\ \cdot OH \end{array} \quad \longrightarrow \quad RCHO + H_2O$$

$$RCH_2OOH + RCHO \quad \longrightarrow \quad RCH_2OO\overset{\displaystyle OH}{\overset{|}{C}}HR$$

$$\begin{array}{c} \text{\Large R\.CH} \overset{H\cdots H}{\underset{O\cdots O}{\Large\diagup\diagdown}} \overset{OH}{\underset{}{\Large C\text{-R}}} \end{array} \quad \longrightarrow \quad RCHO + RCOOH + H_2$$
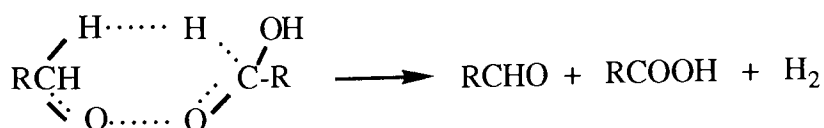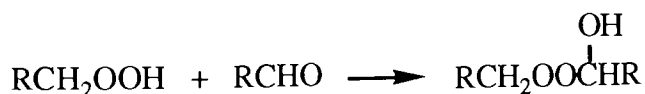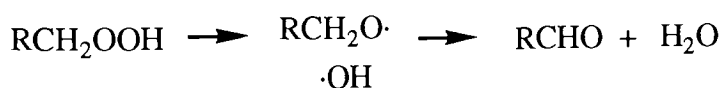
Scheme 3-1

The hydroperoxide concentration built in the cases of oxygen deficient binder (open tube binder) and the oxygen free binder (sealed tube binder) is low (Figs. 3-9 & 3-10). This may suggest that crosslinking and chain scission in polybutadiene result mainly from
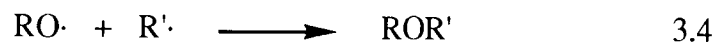
chain oxidation, that is the formation of hydroperoxides which, in turn, serve as initiators for new chains.

3.3.1.1. Chain Scission in Oxidation Reactions

The reactions of the radicals produced by the decomposition of hydroperoxides are not limited to hydrogen abstraction. They may undergo more reactions which lead to either crosslinking or chain scission. The alkoxy radicals can split by the β scission process which plays an important role in backbone scission and forms an alkyl radical and an aldehyde group at the end of chain[14,21]. The evidence for this reaction in polybutadiene is provided by the observation of the increase in the peaks at 1728 cm^{-1} and 1698 cm^{-1} in FTIR (Fig.3-11), which are assigned to the carbonyl group of aldehyde and α, β-unsaturated carbonyl group, respectively.

3.3.1.2. Crosslinking Reaction in Oxidation

The combination between radicals can form crosslinked products (reactions 3.3, 3.4, 3.5 and 3.6).

$$RO\cdot \ + \ R'O\cdot \ \longrightarrow \ ROOR' \qquad 3.3$$

$$RO\cdot \ + \ R'\cdot \ \longrightarrow \ ROR' \qquad 3.4$$

$$ROO\cdot \ + \ R'\cdot \ \longrightarrow \ ROOR' \qquad 3.5$$

$$R\cdot \ + \ R\cdot \ \longrightarrow \ R\text{-}R' \qquad 3.6$$

However, it is unlikely that the rapid increase in crosslink density and the stability of the crosslinks only result from these reactions. This may be, firstly, due to the fact that the probabilities of reactions 3.4 and 3.6 are low because of the low concentration of R$\cdot$ in polymer, and secondly, ROOR' is an unstable crosslink which may decompose again due to thermal energy, uv radiation or reaction with hydroperoxide (see reaction 1.12). Therefore, some other crosslinking reaction should be considered to take the main responsibility for the increase in the network density.
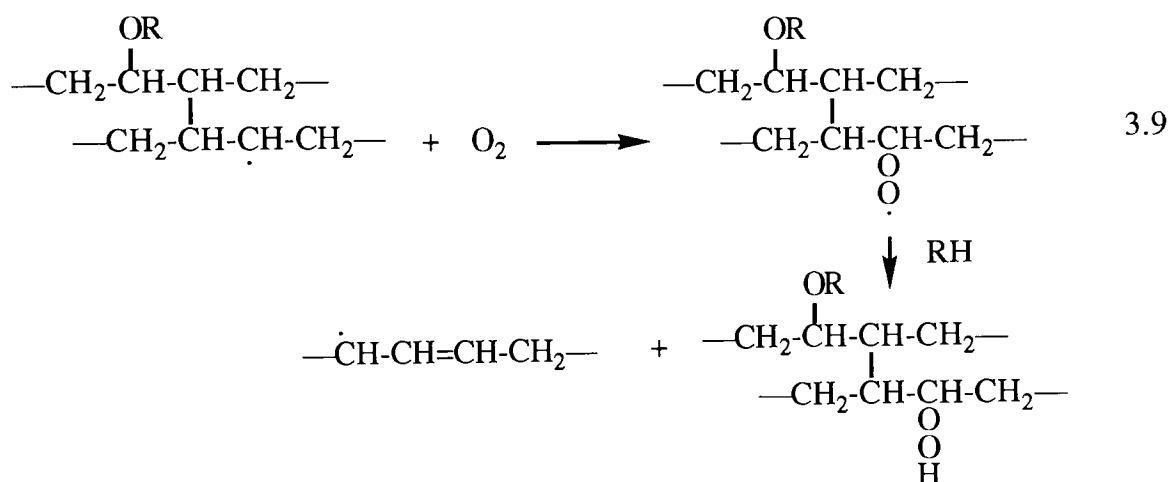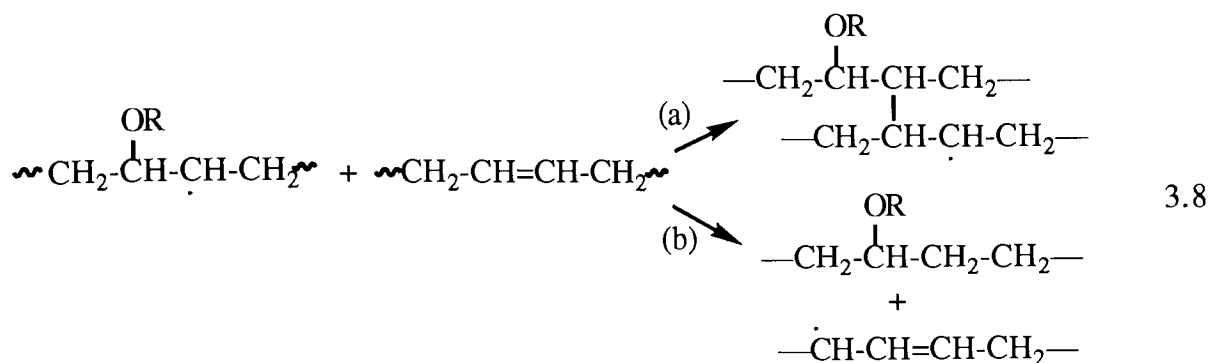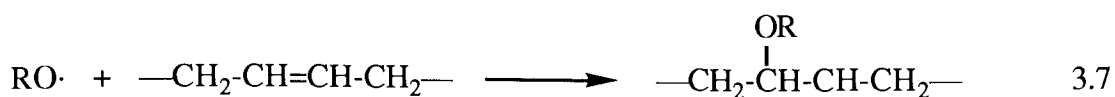
It has been observed from ^{1}H n.m.r. spectra that the content of double bonds decreases with the increase in the content of gel (Fig.3-14). The loss of double bonds is obviousely related to the crosslinking reaction.

The work, carried out by Scott and co-worker in 70's, on the photo-oxidative behaviour of some polybutadiene-based polyblends clearly revealed the mechanism of crosslinking reaction of polybutadiene under photo-oxidation condition[17,18]. The crosslinks are formed in two ways. One is by addition of peroxy or alkoxyl radicals to 1,2-vinyl groups, another is to conjugated carbonyl formed by alkoxyl radical break-down (see Scheme 1-1 in Chapter 1). It seems necessary in this mechanism that polymer chains contain 1,2-vinyl groups or form conjugated double bonds during the process.

In peroxide vulcanisation of polybutadiene, which was carried out under vacuum condition, it was observed that a radical chain reaction, initiated by alkoxyl radical, occurred, leading to form crosslinks[50-52]. It was reported that this reaction is regardless to the content of 1,2-vinyl groups[52]. In this case, the addition of RO· to the double bond gives rise to a secondary alkyl radical (reaction 3.7). Without resonance protection this secondary alkyl radical has a very short life time and thus is highly reactive. It is possible that this radical will react with nearby chains by either abstracting a hydrogen (reaction 3.8 (b)) or adding to another double bond (reaction 3.8 (a)). If reaction 3.8 (a) can get the chance to propagate, polymer network will be rapidly formed in the polymer. But hydrogen will act as chain transfer agents and intercept the chain propagation in several steps (reactions 3.9).

For a solid polybutadiene binder, ageing is a process resulted from the diffusion of oxygen into the polymer. Since the diffusion rate is much lower than oxidation rate, thus oxygen free situation may exist temporarily on the reaction site. Alkyl radicals differ from alkylperoxy radicals in that they tend to give up rather than gain an electron[14]. One consequence of their reducing character is their facile reaction with double bonds and this is particularly important for secondary and tertiary alkyl radicals which are relatively unreactive in the competing hydrogen abstraction reaction[196]. Thus, it is possible that when a secondary radical is formed by an RO· attacking a double bond, it propagates in a

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chain reaction, under the condition that oxygen is excluded, leading to crosslinking polymer chains effectively.

$$RO\cdot \ + \ \text{---CH}_2\text{-CH=CH-CH}_2\text{---} \ \longrightarrow \ \underset{\underset{\cdot}{|}}{\overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}}} \qquad 3.7$$

$$\underset{\underset{\cdot}{|}}{\overset{OR}{\underset{|}{\sim\!\!\!\text{CH}_2\text{-CH-CH-CH}_2\!\!\!\sim}}} \ + \ \sim\!\!\!\text{CH}_2\text{-CH=CH-CH}_2\!\!\!\sim$$

(a) ⟶

$$\overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}}$$
$$\underset{\cdot}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}$$

(b) ⟶

$$\overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH}_2\text{-CH}_2\text{---}}}$$
+
$$\underset{\cdot}{\text{---CH-CH=CH-CH}_2\text{---}}$$

3.8

$$\overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}}$$
$$\underset{\cdot}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}} \ + \ O_2 \ \longrightarrow$$

$$\overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}}$$
$$\underset{\underset{\underset{\cdot}{O}}{O}}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}$$

3.9

↓ RH

$$\underset{\cdot}{\text{---CH-CH=CH-CH}_2\text{---}} \ + \ \overset{OR}{\underset{|}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}}$$
$$\underset{\underset{\underset{H}{O}}{O}}{\text{---CH}_2\text{-CH-CH-CH}_2\text{---}}$$

The initiation action of alkoxyl radical is proved by the fact that a binder mixed with 0.1% phosphite ester showed a quicker increase in the crosslink density than pure binder aged under the same condition (Fig.3-15). Because the reaction of phosphite ester with ROO· can produce RO· radical (reaction 1.46).

On the outmost layer of the binder, this chain reaction will be easily stopped by the reaction of alkyl radicals with oxygen to give peroxyl radicals which form peroxidic crosslinks by preferentially attacking 1,2-vinyl groups which are the most active double bonds among three kinds. In Fig.3-16 the change in the composition of microstructure of film binder during thermal oxidation is shown, in which the side group unsaturation (1,2-vinyl) is lost more than main chain unsaturation (1,4-cis and trans). The 1,2-vinyl group shows a little higher reactivity than 1,4 unsaturation in which cis-1,4 is slightly more

reactive than trans-1,4. This is in agreement with Scott's work measured by infrared[18,19].

The difference between 1,2 and 1,4 double bonds is not as expected from their real reactivities. This may be due to the high viscosity of the substrate and the short life time of secondary alkyl radical. The crosslinking reaction was carried out in a small range with a low selectivity .

Oxygen, therefore, has dual roles in this chain crosslinking mechanism: forming initiator and intercepting the chain reaction. These two actions are the same in nature. Their difference is due to the occurrence of a chain reaction involving active alkyl radical in temporary oxygen free environment.

A rough calculation was carried out to see what sort of crosslink is more likely to be formed in the oxidation. The question to be asked is whether the C-C crosslink (as in reaction 3.8 (a)) or the C-O-O-C (or C-O-C) crosslink (as in Scheme 1-1 (f)) is mainly responsible for the crosslink build-up in the substrate.

Firstly, the amount of oxygen which was permeated into the binder was calculated approximately as below.

Extrapolating the curve in Fig.3-17 to the low crosslink density direction, the permeability of oxygen at CLD=0.73 (65% gel content) is 5.85×10^{-9} $cm^3 \cdot mm/cm^2 \cdot s \cdot cmHg$. This may be taken as if there is 5.85×10^{-9} ml oxygen permeated into 1 cm^2 area and 1 mm thick film per second under 1 cmHg pressure difference. This amount of gas is presumed as air, not oxygen. According to the ideal gas-law expression:

$$PV = nRT \qquad (8)$$

and Dalton's law of partial pressures:

$$P = P_1 + P_2 + P_3 + \cdots \qquad (9)$$

$$P_i V = n_i RT \qquad (10)$$

one can write :

$$P_{O_2} V = n_{O_2} RT$$

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since in atomosphere, $P_{O_2} = 1 / 5 \, P_{AIR}$

then $\qquad n_{O_2} = P_{AIR} V / 5RT \qquad\qquad$ (11)

For experimental film sample of 0.5 mm thickness, take:

$$P_{AIR} = 1 \text{ atm.,}$$

$$V = 5.85 \times 10^{-9} / 0.5 = 1.17 \times 10^{-8} \text{ ml}$$

$$R = 82.056 \text{ml} \cdot \text{atm} \cdot \text{K}^{-1} \text{mol}^{-1},$$

$$T = 287°K,$$

Substituting these values in Equ. (11),

$$n_{O_2} = 9.94 \times 10^{-14} \text{ mole}$$

This is the amount of oxygen permeated into 0.5 mm film binder of 65% gel content per cm^2 per second at 14°C.

Secondly, the amount of sol fraction which became gel in the oxidation was calculated in the presumptions: (1) the degradation mechanism of polybutadiene remains the same below 60°C; (2) the formation of gel is the reaction of uncrosslinked macromolecule (sol fraction) with network (gel).

From the slopes in Fig.3-18, the gel increase rates (k), at gel content of 65%, can be obtained for three temperatures. When these values for k are plotted against 1/T and the line is extended to the point for a temperature of 14°C(Fig.3-19), the corresponding $k(14°C) = 5.0 \times 10^{-6}$ (%/s) is obtained as the gel increase rate of the binder, of 65% gel content, aged at 14°C.

For the film binder of area=1 cm^2, thickness=0.5 mm and density about 0.93 g/cm^3, the amount of gel increased per second can be calculated as:

W = [gel increase rate (%/s)] x (amount of binder)

$\quad = 5.0 \times 10^{-6} \times 1.0 \times 0.05 \times 0.93$

$\quad = 2.3 \times 10^{-7} \text{ g/s}$

The average molecular mass of uncroslinked macromolecules (sol fraction) in the film binder of 65% gel content can be obtained from Table 3-4, which are Mn = 8,219; Mw =

23,621. Therefore, the mole of uncrosslinked macromolecules which were crosslinked onto network (gel) per second was calculated as below:

$$n_b' = W / Mn = 2.3 \times 10^{-7} / 8219 = 2.8 \times 10^{-11} \text{ mole/s, or}$$

$$n_b'' = W / Mw = 2.2 \times 10^{-7} / 23621 = 9.7 \times 10^{-12} \text{ mole/s}$$

This is a simplified crosslinking reaction. Actually, crosslinking reaction also takes place among linear molecular chains and gel polymer chains, but the latter does not contribute to the decrease in sol fraction. Furthermore, chain scission occurs at the same time as minor reaction in the system, which undermines the network. Thus the real chain crosslinking rate must take place more than n_b' or n_b''.

A comparison of 9.94×10^{-14} mole/s (the amount of oxygen diffused into the film binder per second) with 2.8×10^{-11} mole/s (the amount of uncrosslinked macromolecules (by number average molecular weight) which became part of network per second) or 9.7×10^{-12} mole/s (the amount of uncrosslinked macramolecules (by average weight molecular weight) which became part of network per second) indicates that the crosslinks formed are mainly C-C bonds. It is an oxygen initiated crosslinking reaction.

It can now be understood why binder, beneath the top layer in the tube with one side open to the air, remained almost unchanged after ageing for more than 200 days at 60°C. Because the oxygen diffused rapidly reacts with the binder on the top to form either crosslinks or initiator for the subsequent chain crosslinking reaction. As a result, a compact skin was formed on the binder surface, which in turn protects the binder beneath it by greatly reducing the oxygen permeability.

Denisov has described the oxidation of the polymer in the kinetic and diffusion controlled regimes[197] in the equation shown below:

$$r_{O_2} = \gamma P_{O_2} \cdot 2D_{O_2} / l^2 \qquad (13)$$

where r_{O_2} = oxidation rate

P_{O_2} = partial pressure of oxygen

D_{O_2} = diffusion coefficient of oxygen

l = thickness

γ = constant

According to this equation, the oxidation rate for the binder aged in a tube decreases along the tube, because of the increase in l and decrease in D_{O_2}.

3.3.1.3. Oxygen Permeability of Binder

The permeability (P) is the amount of substance passing through a polymer film of unit thickness per unit area, per second and at a unit pressure difference. Here units used will be mm as unit of length and cmHg as unit of pressure, so that the dimension of P becomes: $cm^3 \cdot mm/cm^2 \cdot s \cdot cmHg$.

The diffusion coefficient (D) is the amount of matter (m) passing per second through a unit area, under the influence of a unit gradient of concentration.

For simple gases a general relationship between the three main permeation properties P (permeability), S (solubility), D (diffusivity) is almost exactly valid:

$$P = S \cdot D \qquad\qquad (7)$$

This means that permeation is a sequential process, starting with solution of the gas on the outer surface of the polymer (where equilibrium nearly exists), followed by slow inward diffusion ('reaction with pre-established equilibrium')[198].

It is believed that oxygen diffuses through the amorphous phase[199], and crystalline regions obstruct the movement of the molecules and increase the average length of the paths they have to travel. The diffusion coefficient of oxygen in the amorphous phase, D_{am}, was found to depend on the nature of the polymer, the diameter of the oxygen molecule d_{O_2}, and the free volume in the amorphous phase v_f[197].

Since v_f varies with temperature and the intermolecular structure, the diffusion coefficient of oxygen in polybutadiene may depend on the same factors.

Increasing the temperature, on the one hand, reduces the energy needed to enable an oxygen molecule to jump from one 'hole' into another 'hole; on the other hand, it enlarges the size of the 'hole' due to increasing vf. So the diffusion coefficient of oxygen is greater at higher temperatures.

Figure 3-17 shows the decrease of oxygen permeability with increasing in crosslink density. This can also be accounted for by the change in v_f, which results in the reduction of the size of the 'hole'.

3.4. The Effect of Temperature

3.4.1. In the Presence of Oxygen

Temperature affects the oxidation of a solid polymer in two ways:

(1)   By reducing the activation energy of oxygen diffusion,

(2)   By increasing the oxidation reaction rate constants.

The role temperature plays in the oxidation of polybutadiene is mainly reflected in the length of the induction period (Fig.3-20). With an increase in the temperature, autoxidation starts earlier.

As previously discussed, there are more oxygen molecules permeated into the binder at a high temperature than at a low temperature. The reaction of oxygen with polybutadiene in the initiation is an endothermic reaction, increasing temperature will enhance the initiation rate. The steady state hydroperoxide concentration $[ROOH]_{max}$ depends only on the temperature and concentration of the hydrocarbon[14,200]. $[ROOH]_{max}$ varies with temperature according to the magnitude of $E_p - 0.5(E_i + E_t)$,

E_p — activation energy of reaction 1.5;

E_i — activation energy of initiation;

E_t — activation energy of termination 1.18

consequently when this value is appreciably negative, the steady state concentration of hydroperoxide will decrease rapidly with increasing temperature. The lower the maximum hydroperoxide concentration, the more rapidly is the steady state achieved[14]. This can be seen from Figure 3-21. Therefore, the length of the induction period becomes shorter for the sample aged at a higher temperature.

In the autoxidation period, the effect of temperature is not obvious, due to the low reactivity energy of the radical reactions.

3.4.2. In the Absence of Oxygen

The solely thermal ageing of elastomers in the complete absence of oxygen, may be regarded as commercially unimportant since storage temperatures are well below the decomposition temperature of the polymer backbone. The thermal effect on polybutadiene can be seen from the samples aged in a sealed glass tube (Figs.3-22 and 3-23). The crosslink densities of the samples, at three different temperatures, remained unchanged throughout the ageing period. This further proves that binder remains stable, without oxygen, at ambient temperatures below 80°C.
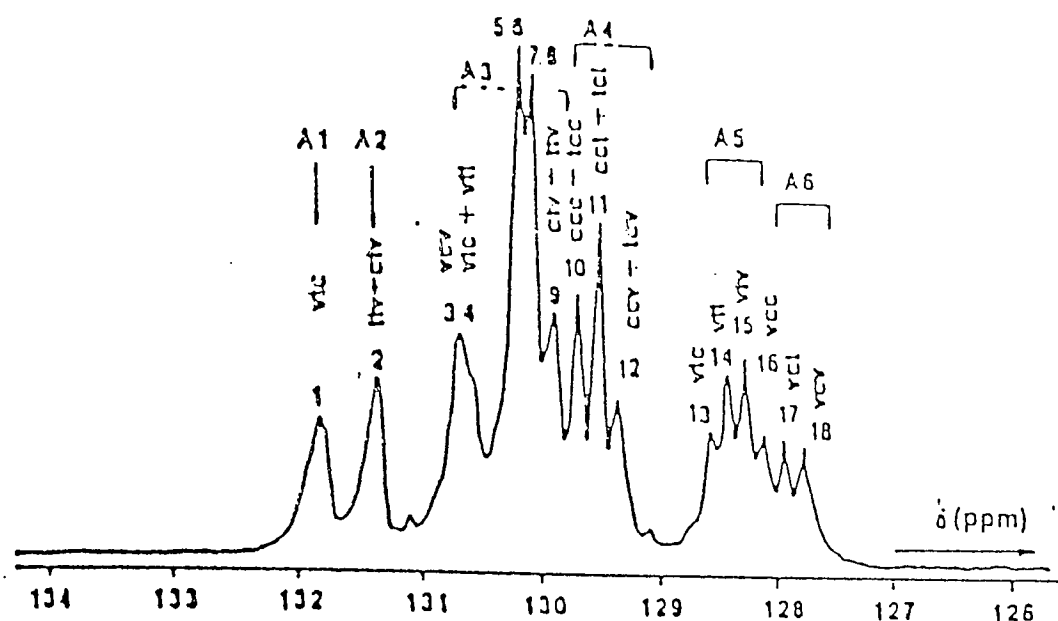
Fig. 3-1 Expanded ^{13}C n.m.r. spectrum of the olefinic main-chain cis-1,4 and trans-1,4 carbon resonances
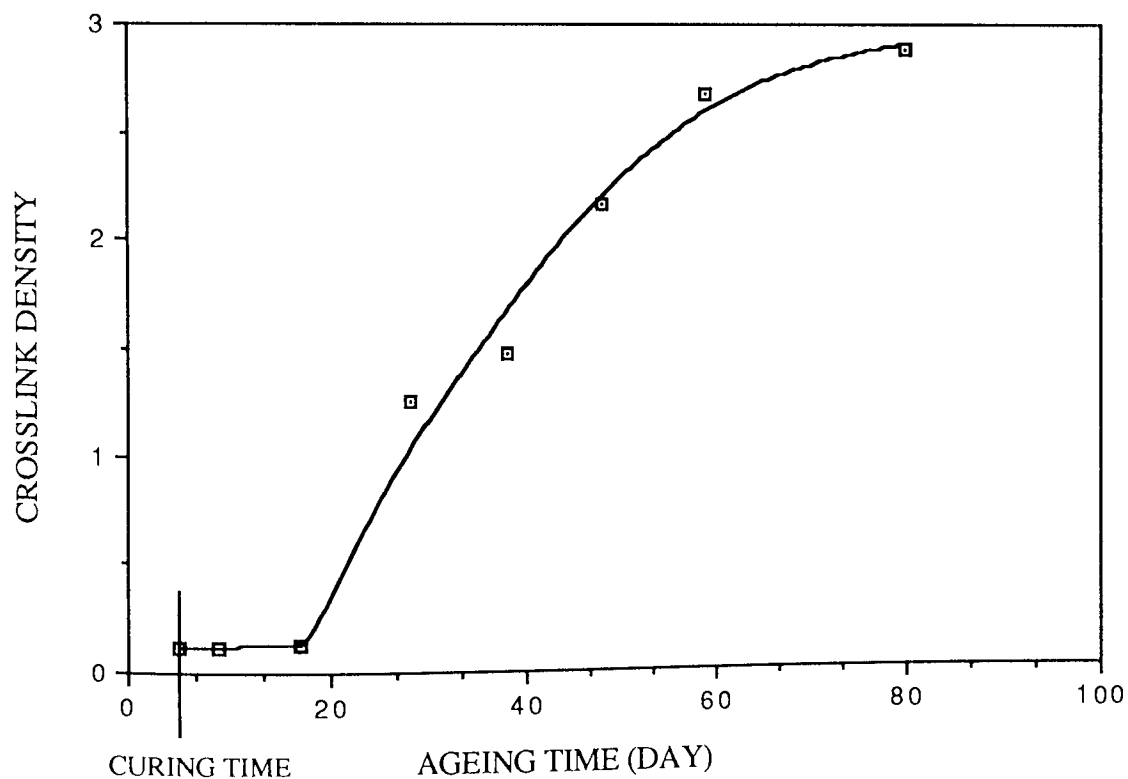

Fig.3-2 Crosslink density of diisocyanate cured polybutadiene aged at 60°C in 0.5mm

thick film

90

Table 3-1

Assignments for the ^{13}C n.m.r. Signals of the Olefinic Main-Chain Cis-1,4 and Trans-1,4 Carbons in Polybutadiene

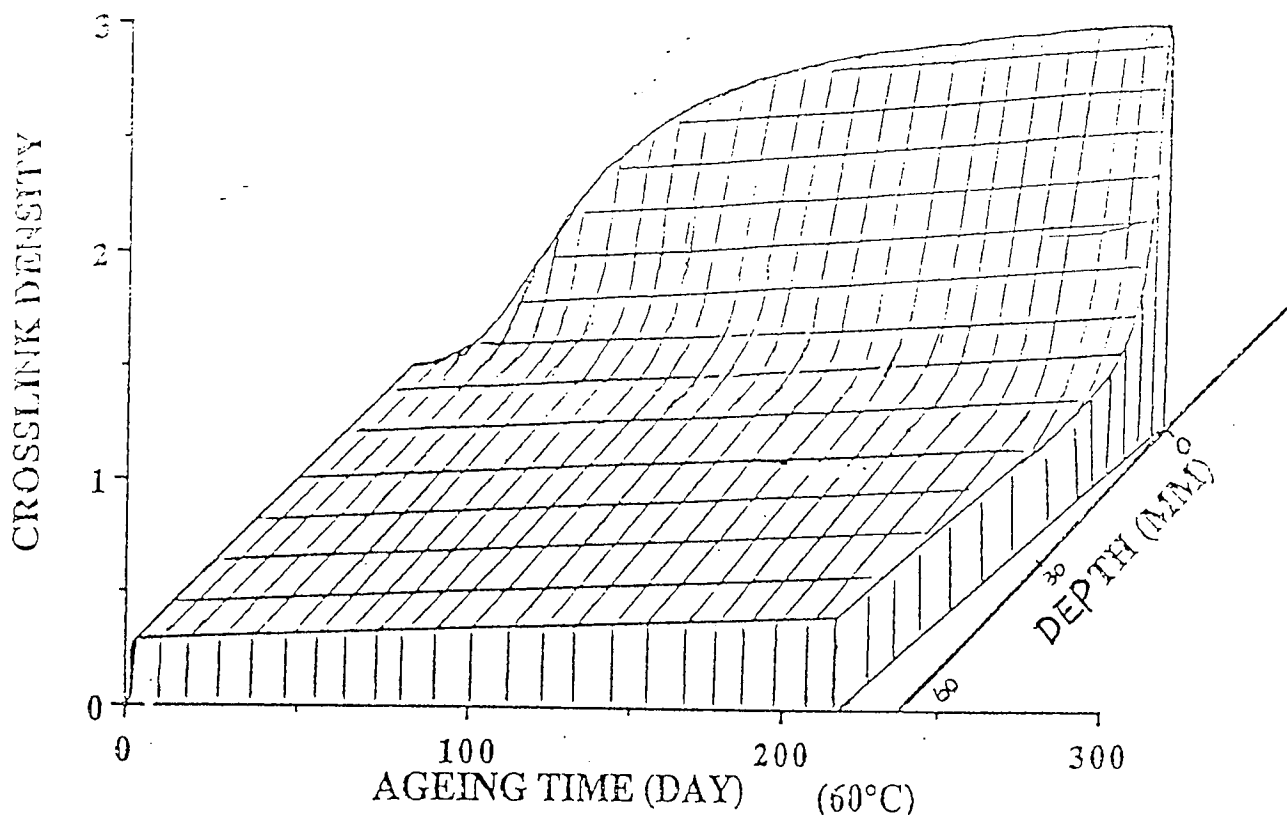| carbon atom	resonance	triad assignt	chem shift (ppm)
—C=C*—	1	vtv	131.79
	2	ctv,ttv	131.35
	3	vcv	130.69
	4	vtt,vtc	130.56
	5	ccv,tcv	130.24
	6	ctc,ctt	
	7	vcc,vct	130.08
	8	ttc,ttt	
—*C=C—	9	ctv,ttv	129.88
	10	ccc,tcc	129.67
	11	cct,tct	129.48
	12	ccv,tcv	129.34
	13	vtc	128.51
	14	vtt	128.37
	15	vtv	128.23
	16	vcc	128.08
	17	vct	127.90
	18	vcv	127.75

Fig.3-3 Crosslink density of diioscyanate cured polybutadiene aged at 60°C in the tube
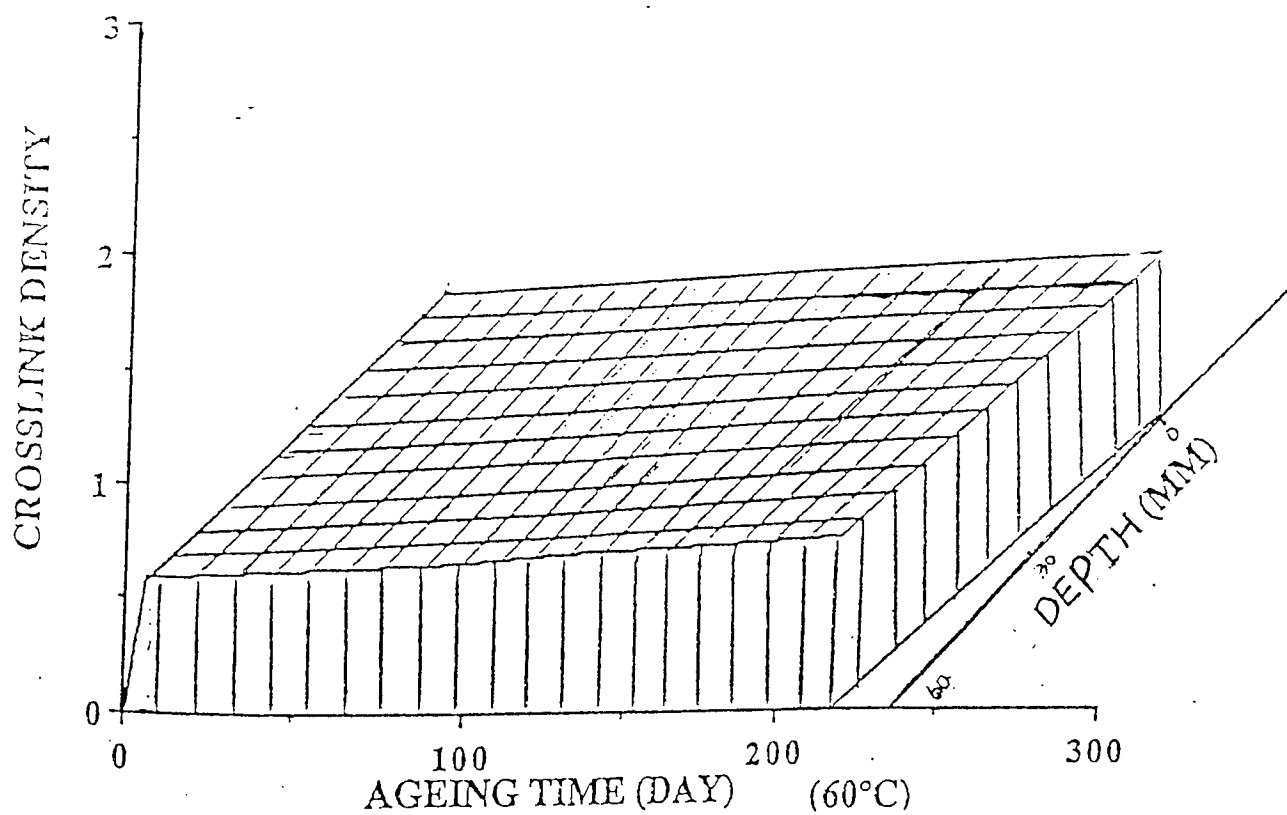
mould (diameter = 25mm)

Fig.3-4 Crosslink density of diisocyanate cured polybutadiene aged at 60°C in the sealed
tube mould (under vacuum)

Table 3-2

Oxidation of polybutadiene binder at 60°

ageing time (day)	sol %	CLD	[ROOH] x10^{-6} mol/g
film binder			
5	67	.11	8.4
9	66	.12	11.0
17	65	.13	17.2
28	25	1.25	73.2
38	22	1.48	33.3
48	16	2.16	28.5
59	13	2.68	31.6
80	12	2.89	
the maxmum error	4%		12%

open tube binder — _depth_ (from top, mm)

ageing time (day)	sol % 5	sol % 60	CLD 5	CLD 60	[ROOH] 5	[ROOH] 60
8	53	50	.28	.33	2.2	4.0
44	55	49	.25	.35	1.1	3.1
92	57	48	.22	.37	1.1	1.3
134	49	39	.35	.59	1.1	
176	48	48	.37	.37	1.5	1.6
251	50	50	.33	.33	2.2	1.7
the maxmum error	8%	2%			31%	37%

sealed tube binder

ageing time (day)	sol %	CLD	[ROOH]
7	39	.59	2.2
43	37	.66	0.9
91	38	.62	1.2
133	34	.77	0.7
175	35	.73	0.4
217	34	.77	1.0
tne maxmum error	6%		71%

Table 3-3

Molecular masses* and molecular mass distributions of three kinds of binders

aged at 60°C.

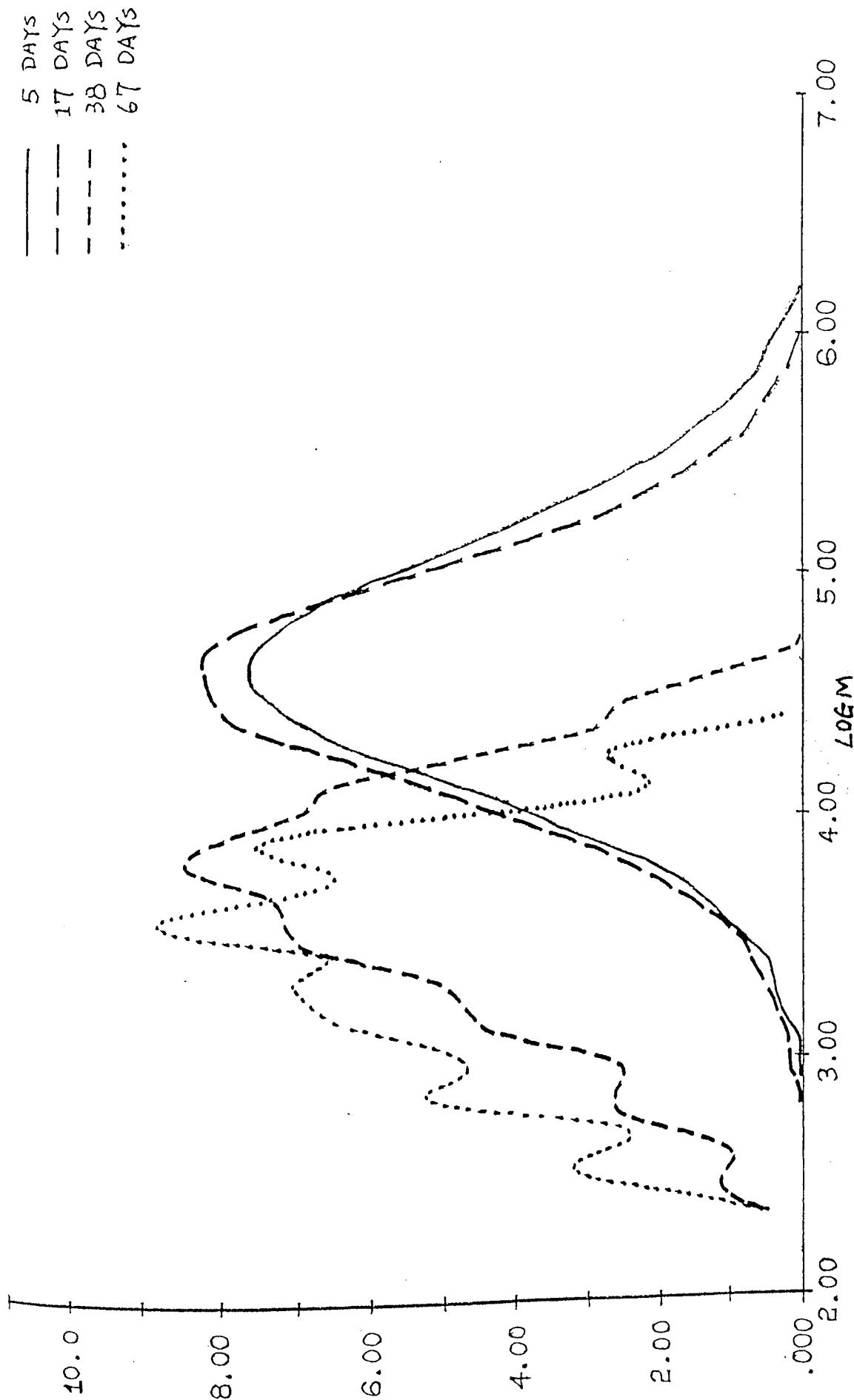| ageing time (day)	Mn	Mw	Mw/Mn
film binder			
5	15,660	71,203	4.55
17	14,815	42,063	2.84
38	1,623	5,178	3.19
67	1,401	2,700	1.93
open tube binder (bottom of tube)			
8	16,237	63,329	3.90
44	16,047	54,425	3.39
133	16,448	47,753	2.90
251	15,485	49,420	3.19
sealed tube binder			
7	15,360	37,256	2.43
44	14,629	33,420	2.28
133	17,151	36,417	2.12
217	14,424	30,910	2.14

*   polystyrene equivalent

Fig.3-5 Molecular mass distribution of diisocyanate cured polybutadiene aged at 60°C in the form of 0.5mm thick film (the time quoted above includes curing time) (see Fig.3-2 for CLD of this film)
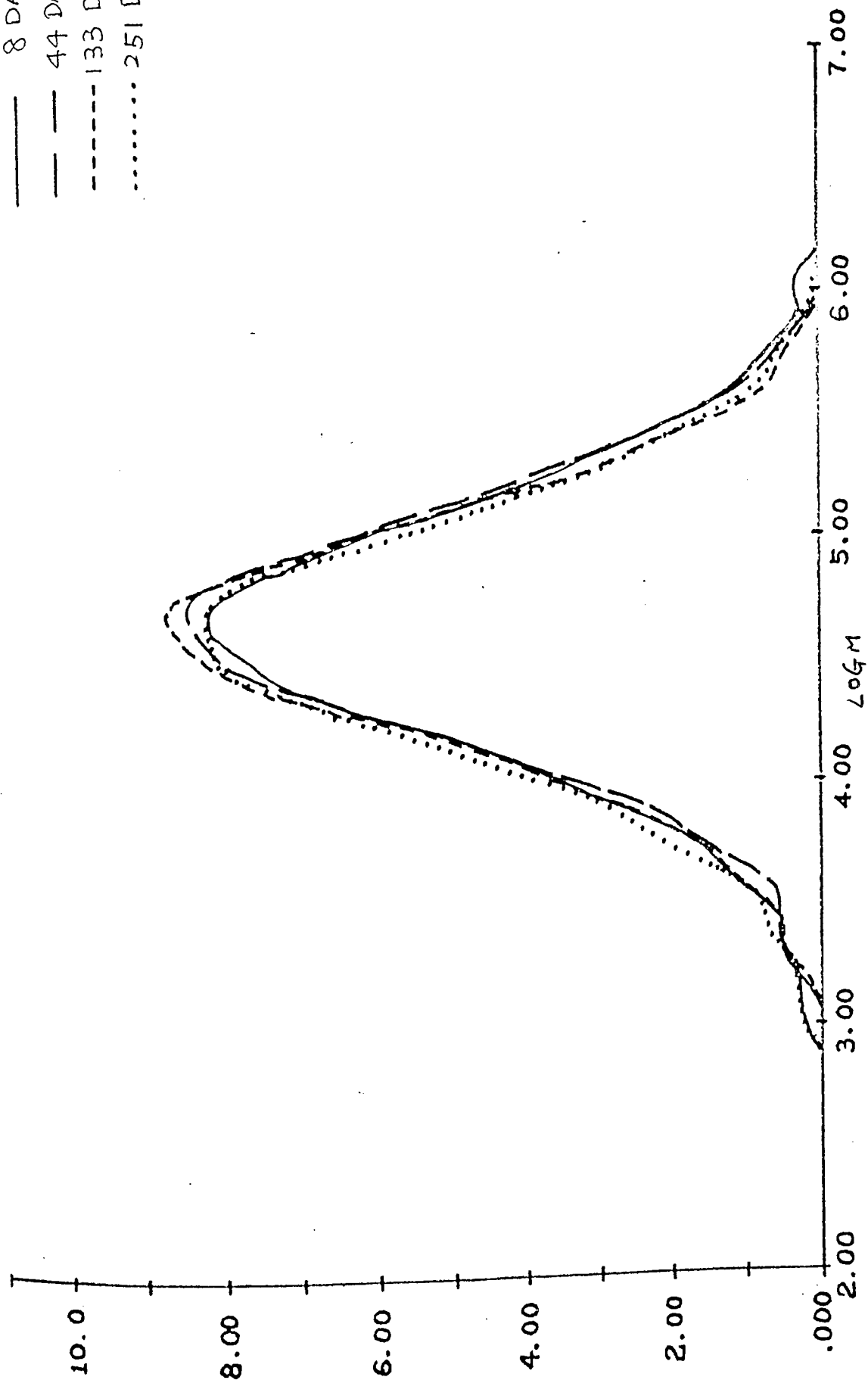
Fig.3-6 Molecular mass distribution of diiioscyanate cured polybutadiene aged at 60°C in the bottom of open tube mould (the time quoted above includes curing time)
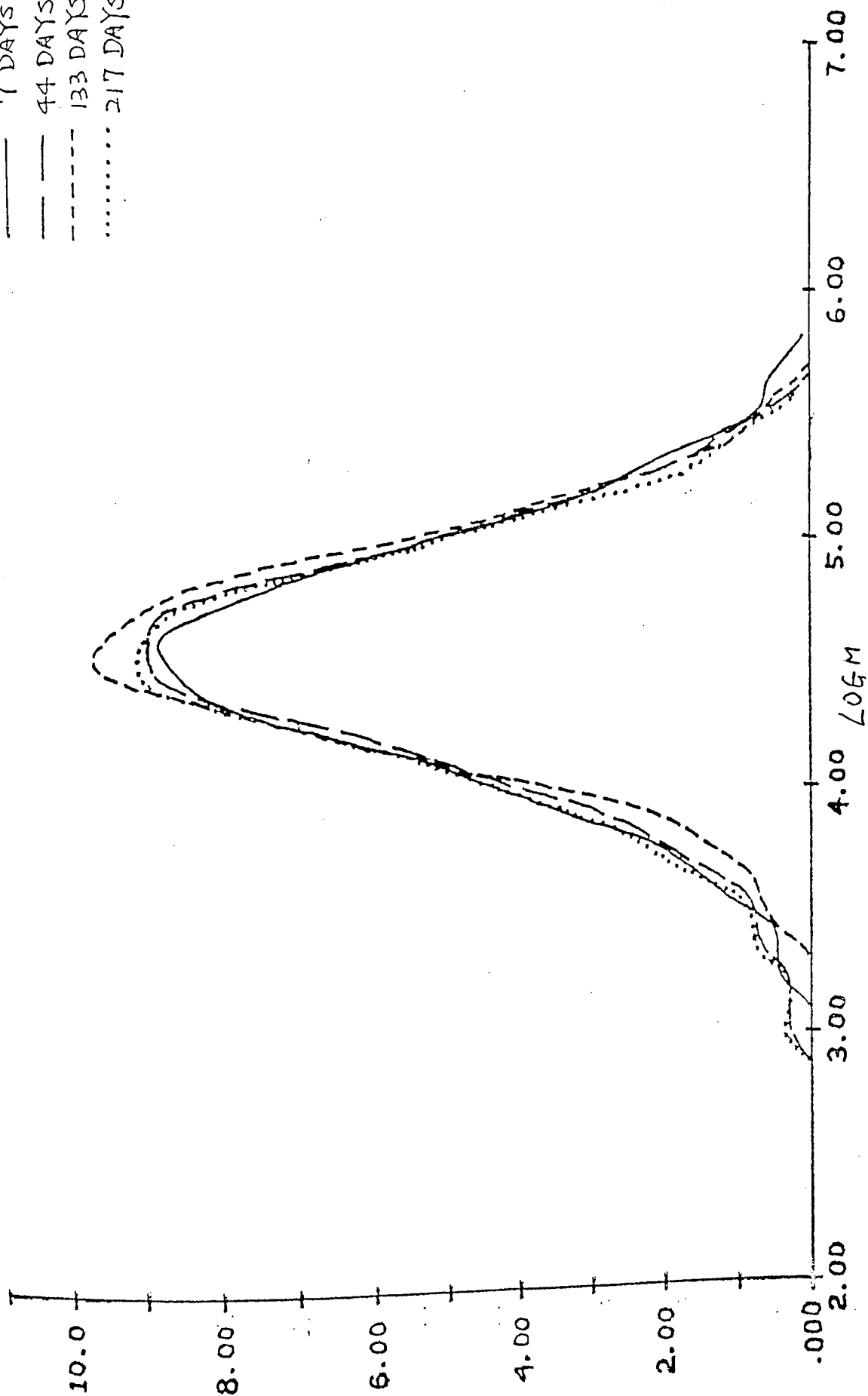(see Fig.3-3 for CLD of this film)

Fig.3-7 Molecular mass distribution of diisocyanate cured polybutadiene aged at 60°C in the sealed tube mould (the time quoted above includes curing time)
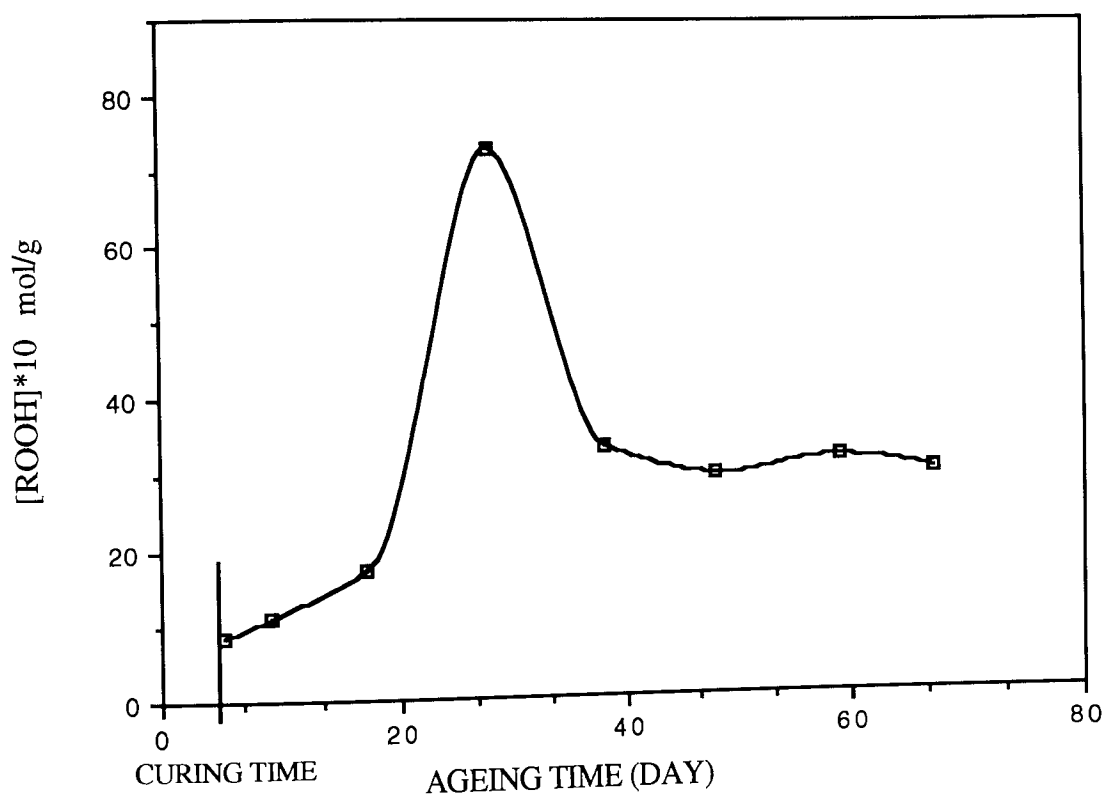(see Fig.3-4 for CLD of this film)

Wn (LogM) ×10⁻¹

97

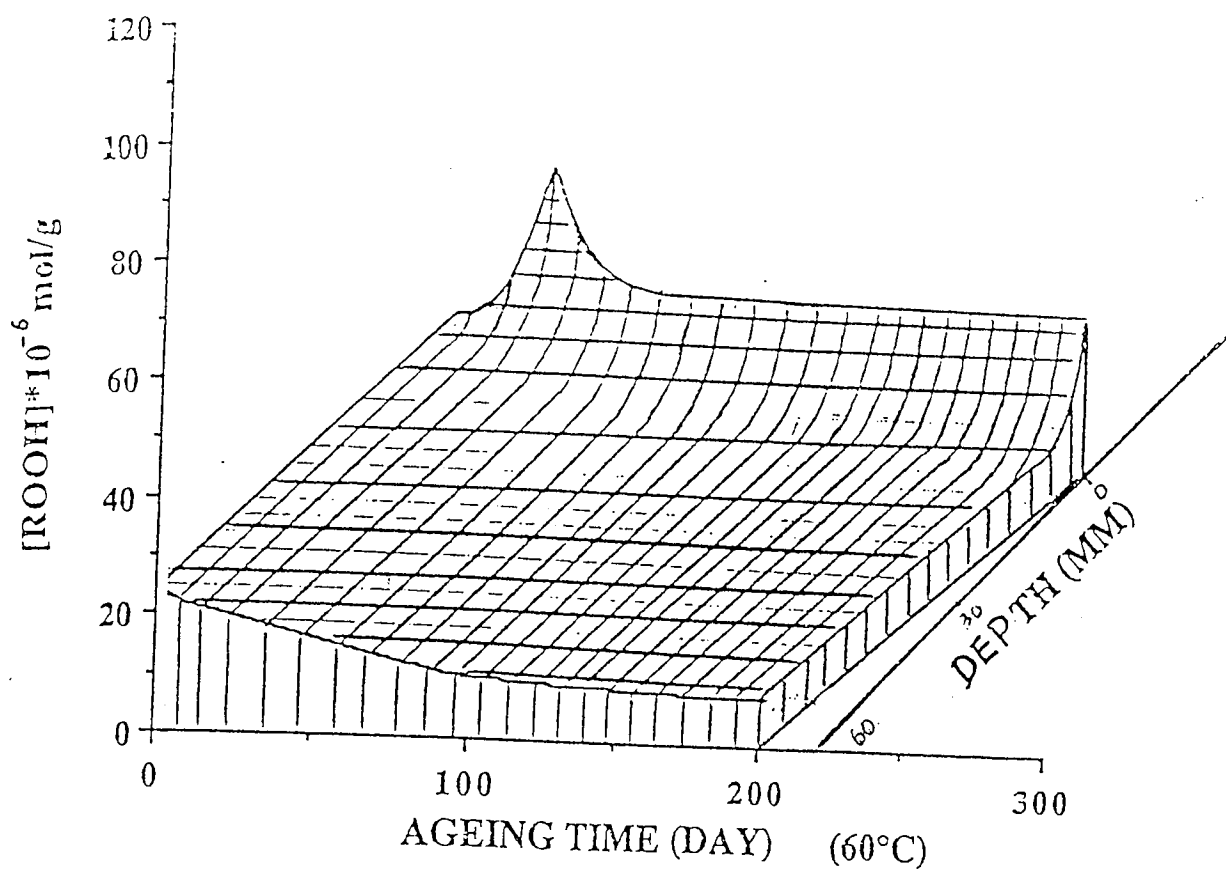**Fig.3-8**   Hydroperoxide concentration of 0.5mm thick film binder aged at 60°C

Fig.3-9 Hydroperoxide concentration of the tube binder aged at 60°C
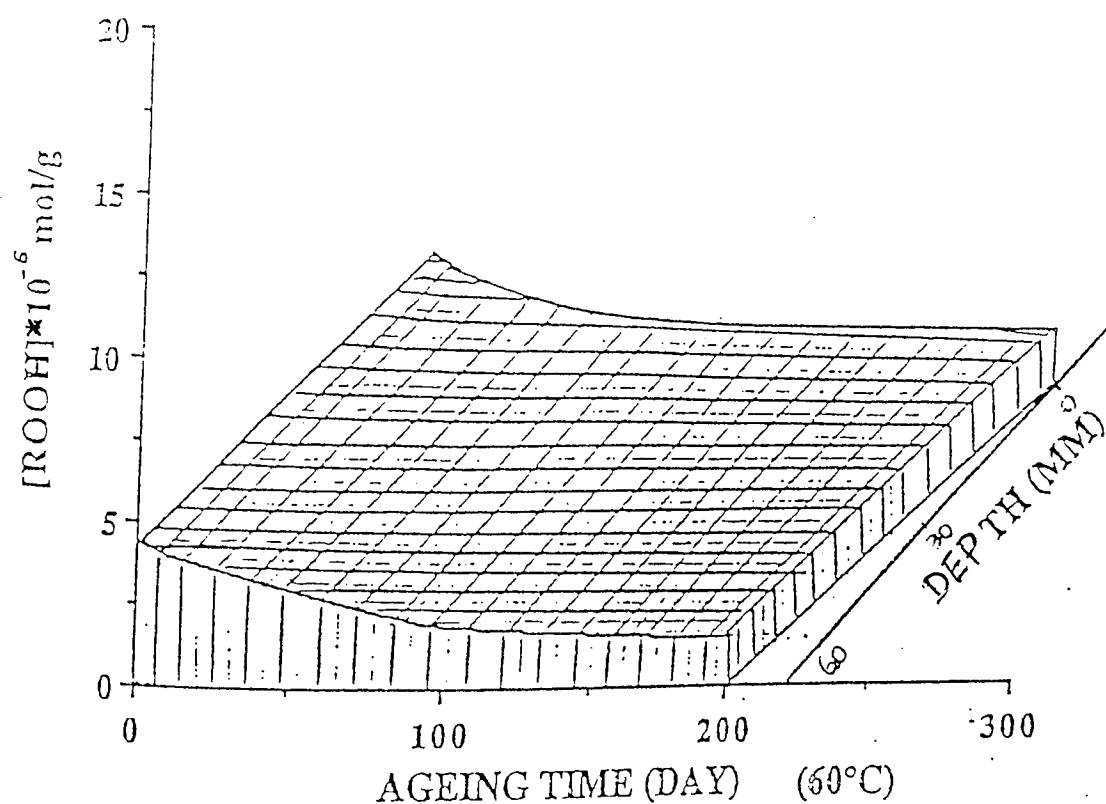

Fig.3-10 Hydroperoxide concentration of the sealed tube binder aged at 60°C
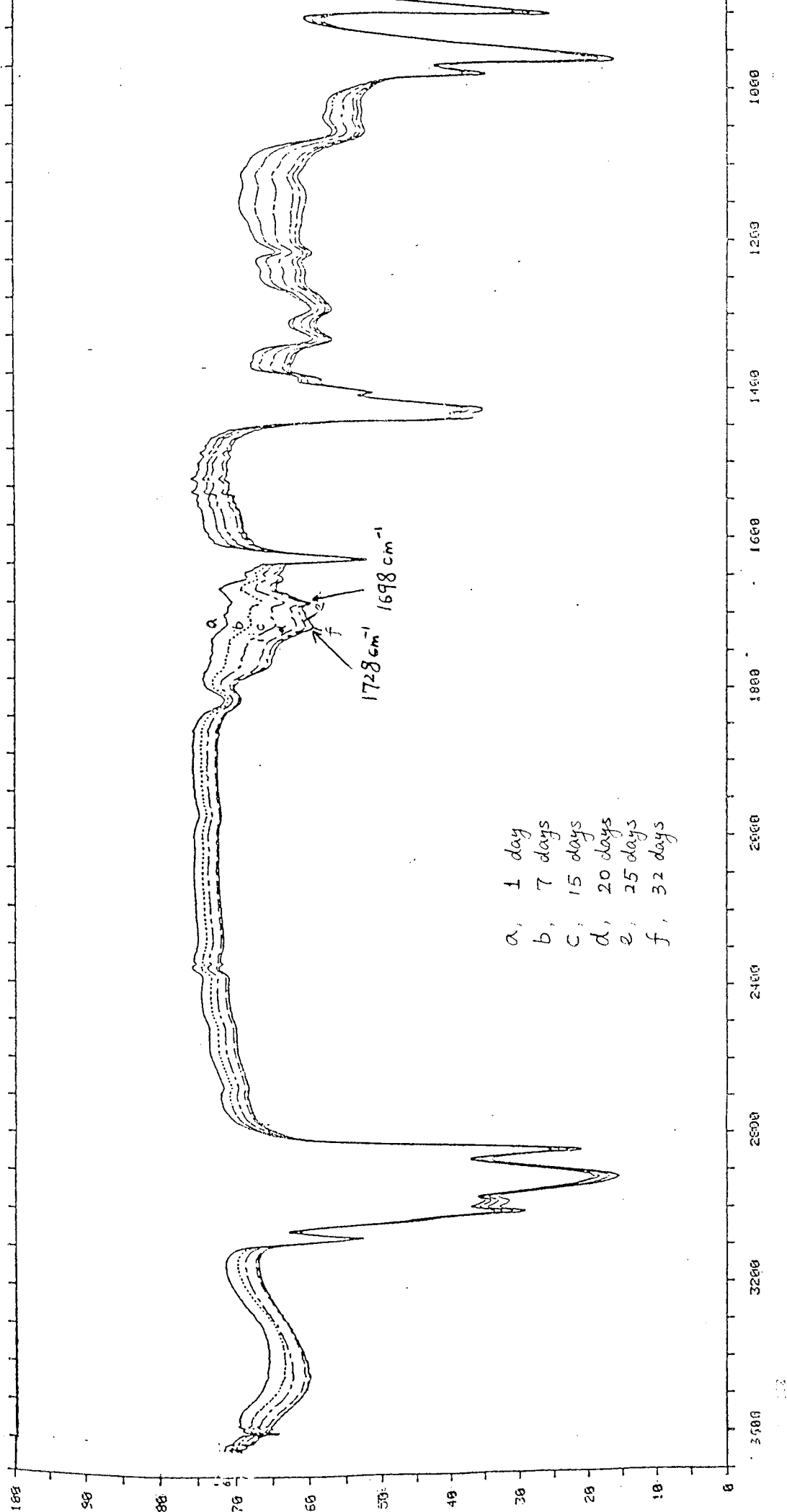
Fig.3-11 FTIR spectrum of HTPB film aged at 60°C

a, 1 day
b, 7 days
c, 15 days
d, 20 days
e, 25 days
f, 32 days

1728 cm⁻¹ 1698 cm⁻¹

100

Fig. 3-12 ^{13}C n.m.r. spectrum of HTPB

(SEE TABLE 3-1 AND FIGURE 3-1 FOR THE STRUCTURE ASSIGNMENTS)

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Fig. 3-13 ^{1}H n.m.r. spectrum of diisocyanate cured polybutadiene

Table 3-4

Unsaturation index (U.I.) obtained from ^{1}H n.m.r.of film binder aged at 60°C

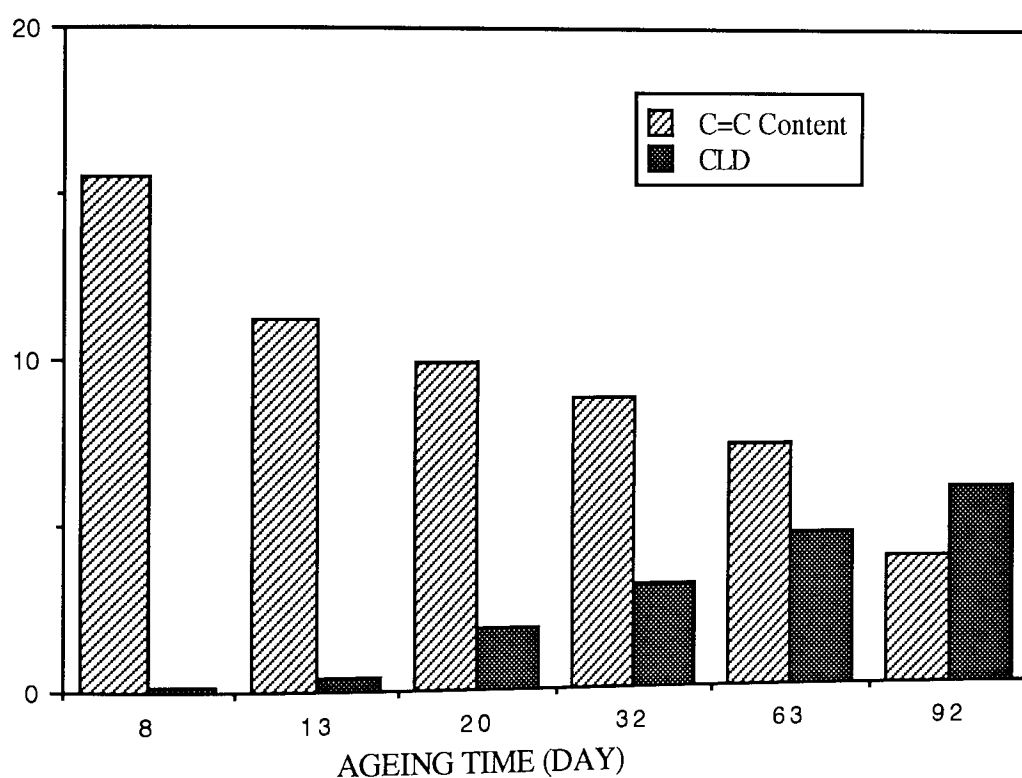| ageing time (day)	8	13	20	32	63	92
U.I.	15.53	11.24	9.84	8.74	7.79	3.87

Fig.3-14 The changes in double bond content measured from ^{1}H n.m.r. and crosslink density of a 0.5mm thick film binder aged at 60°C
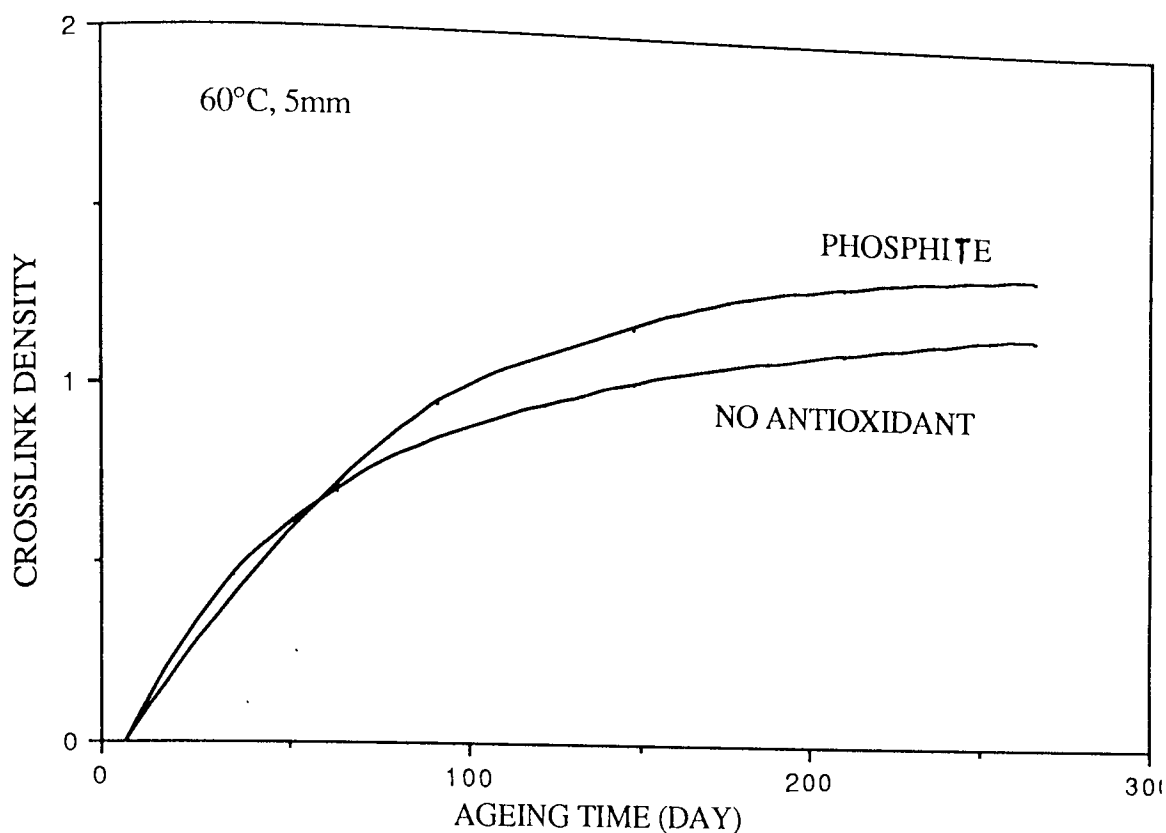
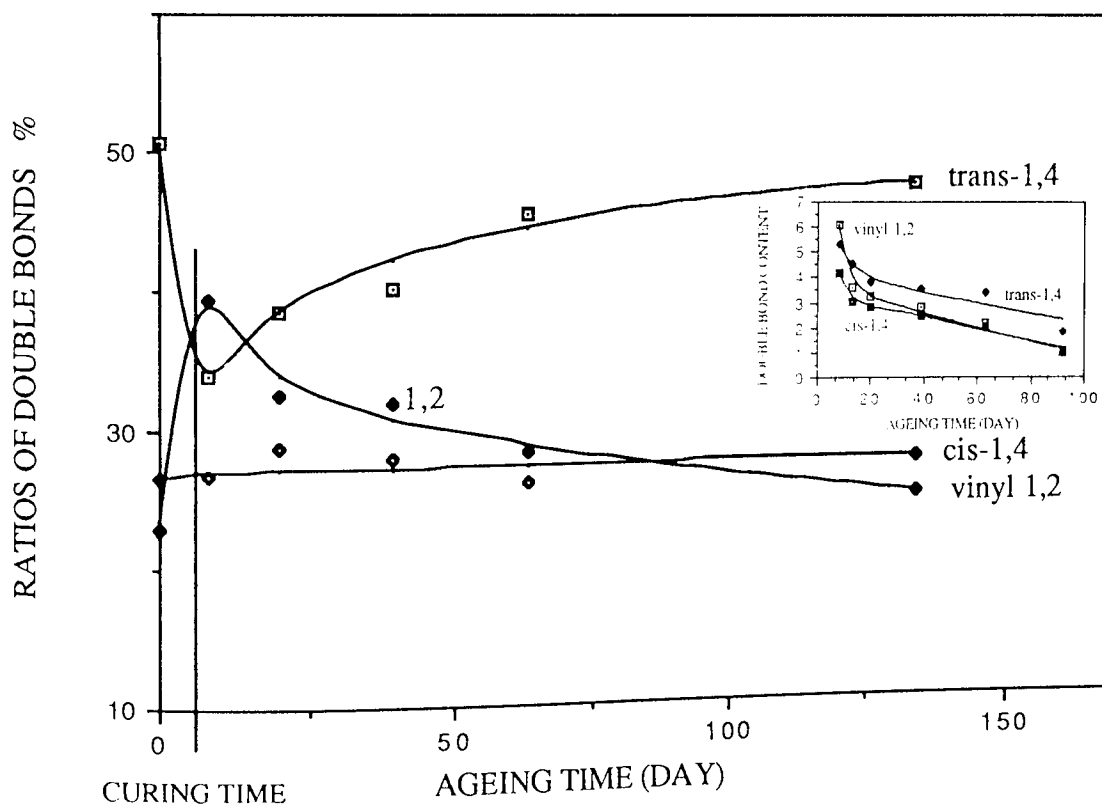**Fig. 3-15** The pro-oxidant effect of phosphite (P310, 0.1% w/w) on binder

Fig.3-16 The changes in three kinds of double bonds in the 0.5mm thick binder aged at 60°C measured by ^{13}C n.m.r.

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Table 3-5

Experimentally Observed and Theoretically Calculated Peak Areas A_i (i=1-6) and Best Fit Values for c, t, and v for HTPB Binder Aged at 60°C

| parameter	ageing time						
	0	8	13	20	39	63	134
A_1							
calcd	0.020	0.055	0.037	0.036	0.037	0.034	0.025
exptl	0.017	0.038	0.035	0.036	0.022	0.022	0.026
A_2							
calcd	0.063	0.076	0.072	0.070	0.072	0.075	0.068
exptl	0.059	0.085	0.077	0.070	0.073	0.080	0.055
A_3							
calcd	0.588	0.487	0.524	0.518	0.513	0.561	0.575
exptl	0.575	0.476	0.511	0.501	0.524	0.543	0.557
A_4							
calcd	0.212	0.174	0.199	0.207	0.199	0.177	0.199
exptl	0.234	0.211	0.227	0.240	0.231	0.221	0.237
A_5							
calcd	0.082	0.131	0.109	0.106	0.109	0.108	0.093
exptl	0.072	0.101	0.086	0.087	0.088	0.075	0.071
A_6							
calcd	0.038	0.080	0.062	0.065	0.062	0.047	0.043
exptl	0.042	0.089	0.064	0.066	0.072	0.058	0.054
v	0.229	0.394	0.324	0.325	0.319	0.283	0.249
t	0.506	0.339	0.403	0.387	0.403	0.456	0.477
c	0.265	0.267	0.273	0.288	0.278	0.261	0.274
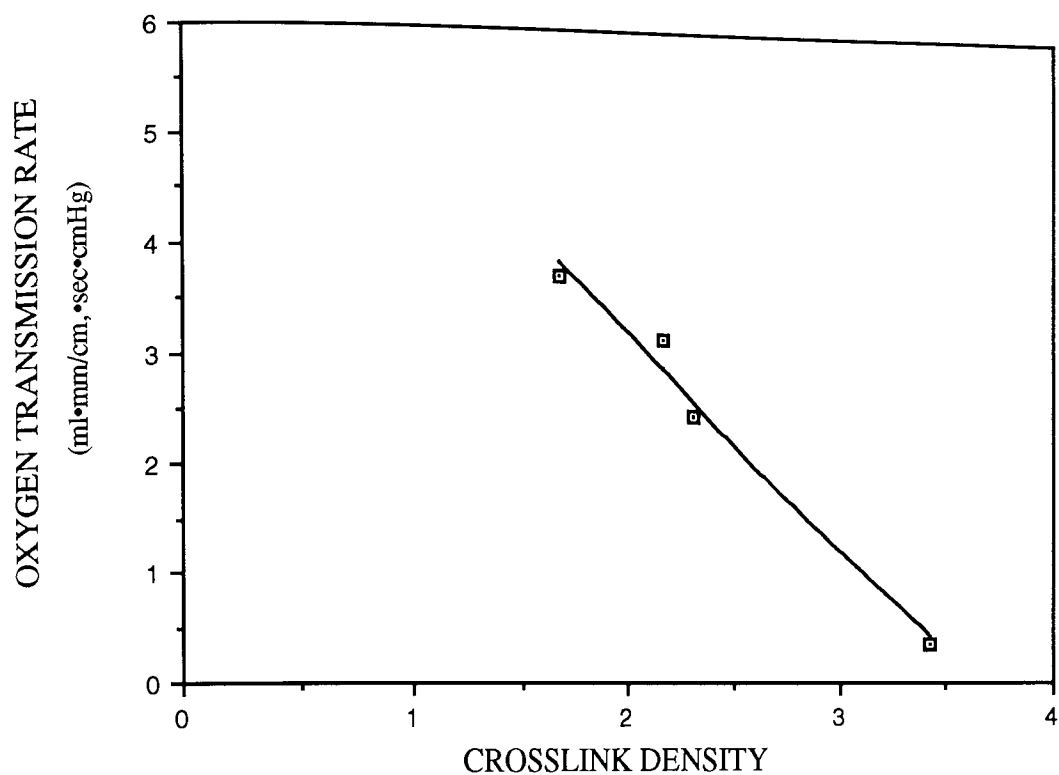
Fig.3-17 The relationship between oxygen permeability measured at 14°C and crosslink density of film sample

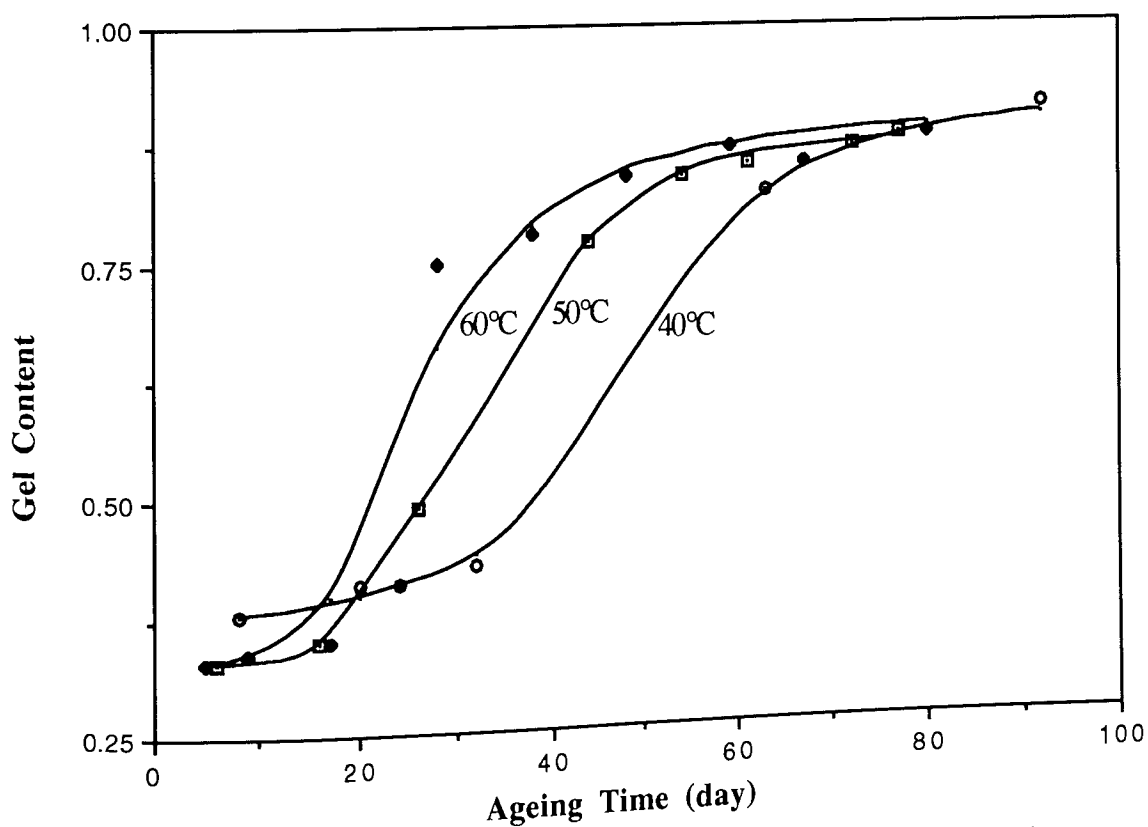**Fig.3-18** Gel contents of 0.5mm thick film binders aged at different temperatures
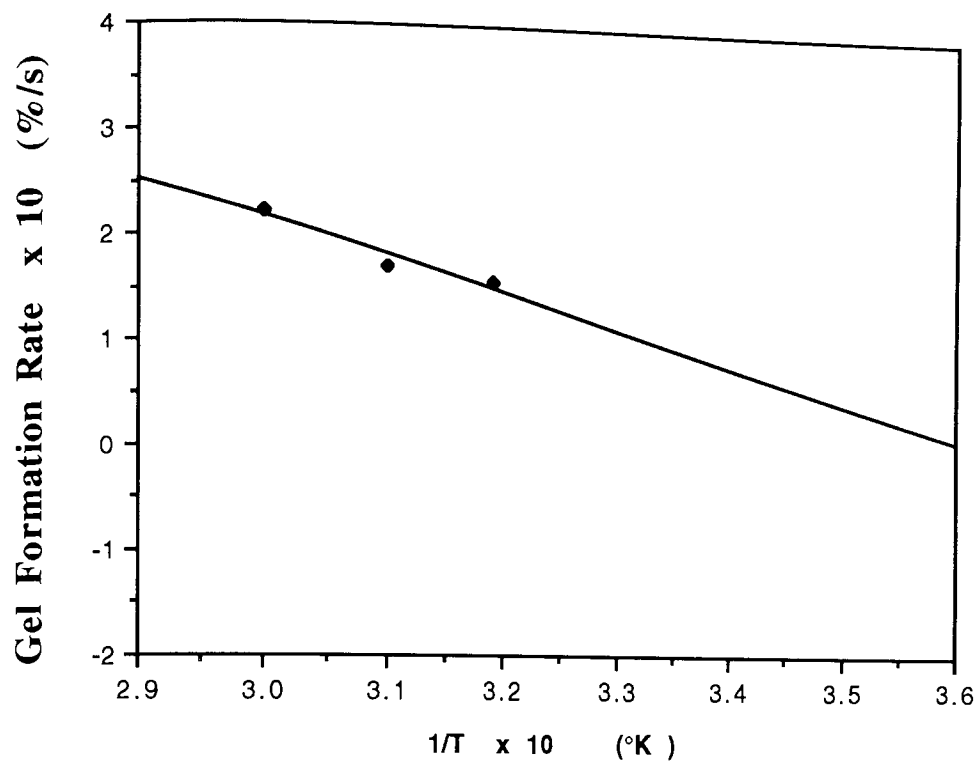
106

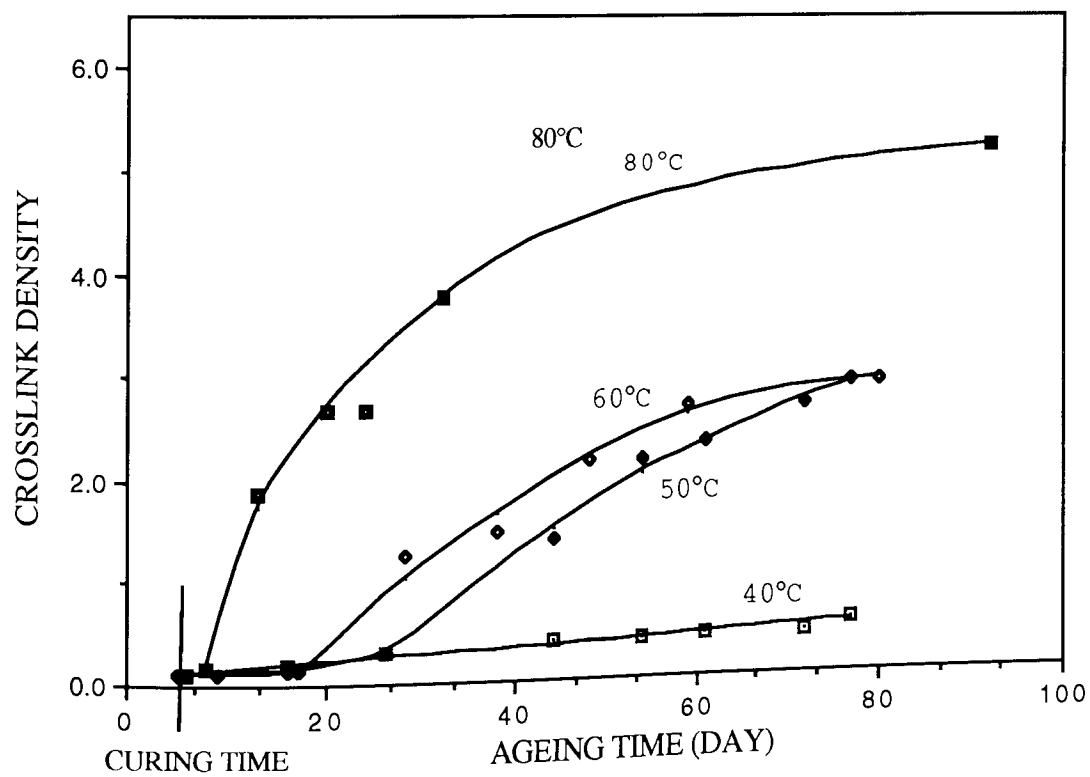**Fig.3-19** Gel formation rate as a function of temperature

Fig.3-20 The crosslink density of binders aged at different temperatures
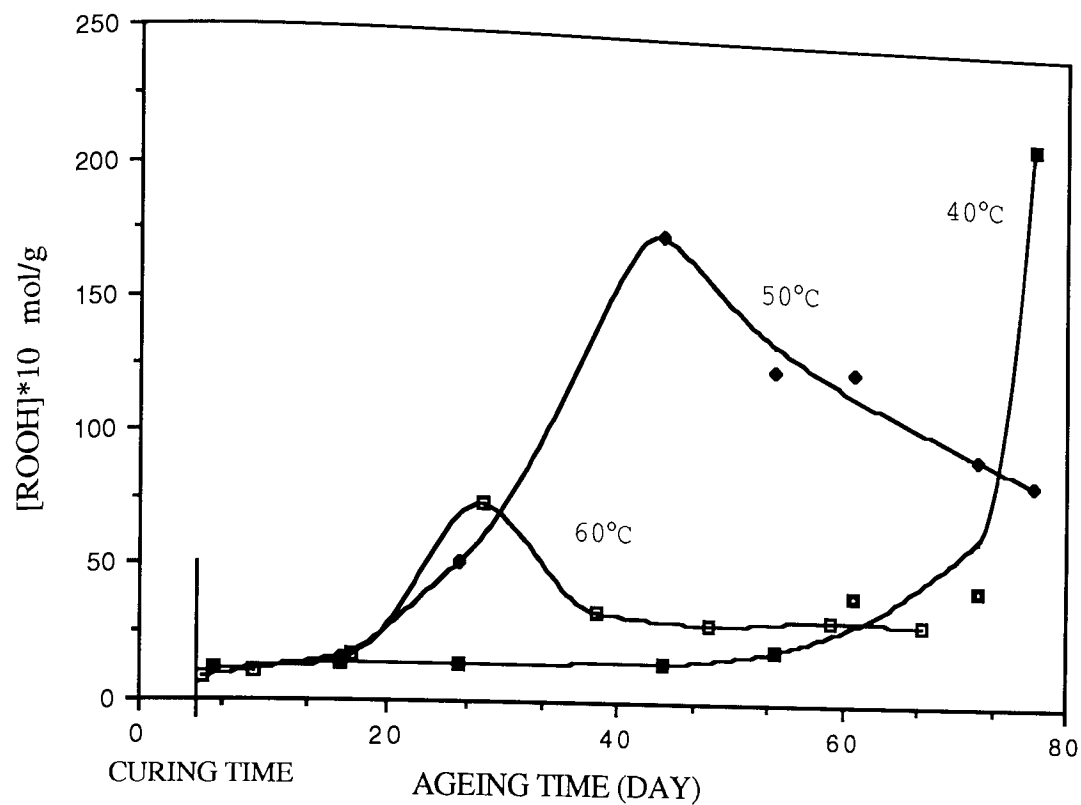
107

Fig.3-21 Hydroperoxide concentrations of film binders aged at different temperatures
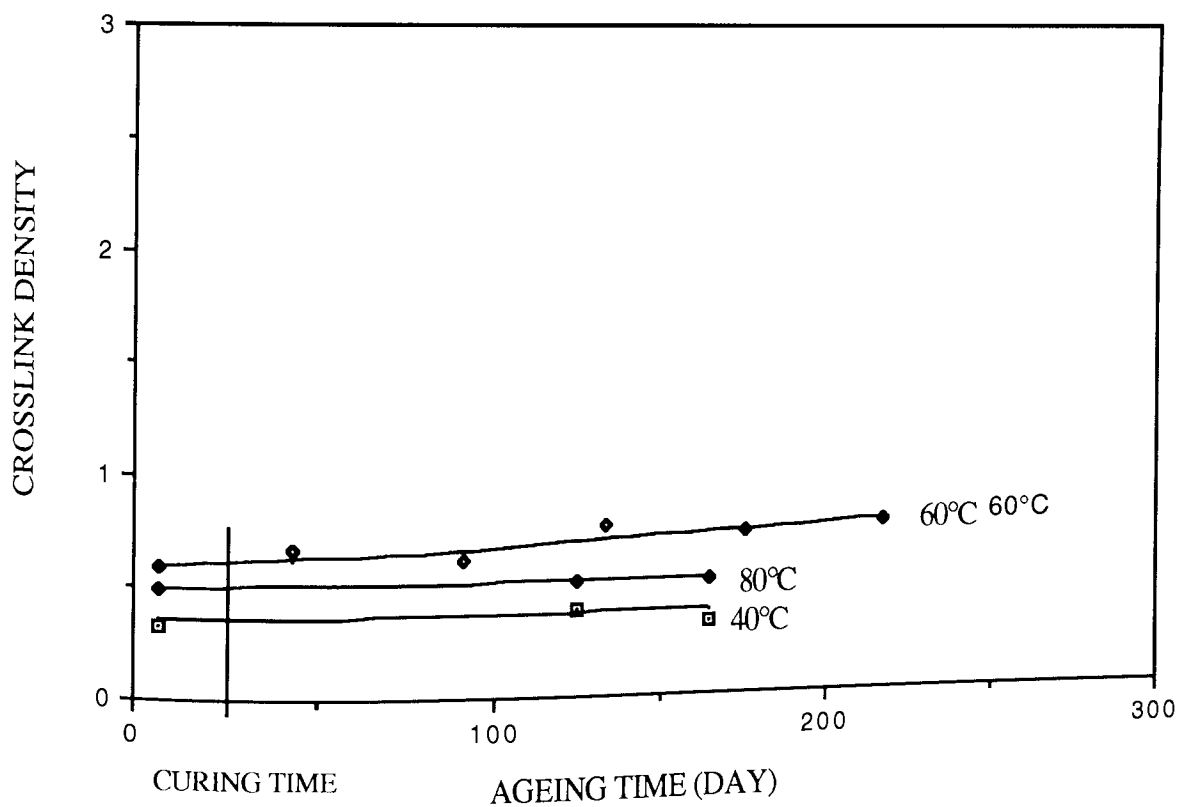

Fig.3-22 The crosslink density of sealed binders aged at different temperatures

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Table 3-6

Thermal oxidation of film binder aged at different temperatures

| ageing time(day)			sol %				CLD				[ROOH]*10^{-6} mol/g		
40°&50°C	60°C	80C	40°C	50°C	60°C	80°C	40°C	50°C	60°C	80°C	40°C	50°C	60°C
6	5	8	67	67	67	62	.11	.11	.11	.16	11.4	11.4	8.4
16	9	13	61	65	66	18	.19	.13	.12	1.89	13.4	15.5	11.0
26	17	20	58	51	65	13	.31	.31	.13	2.68	13.8	51.6	17.2
44	28	24	57	23	25	13	.37	1.40	1.25	2.68	14.5	176	73.2
54	38	32	57	16	22	9	.37	2.16	1.48	3.76	19.9	127	33.3
61	48	39	56	15	16	6	.41	2.31	2.16	5.22	41	127	29.5
72	59	63	56	13	13	5	.41	2.68	2.68	5.99	44	95	31.6
77	67	92	54	12	15	5	.53	2.89	2.31	5.99	215	85	30
	80				12				2.89				
The maxmum error			4%	7%	4%						11%	11%	12%

109
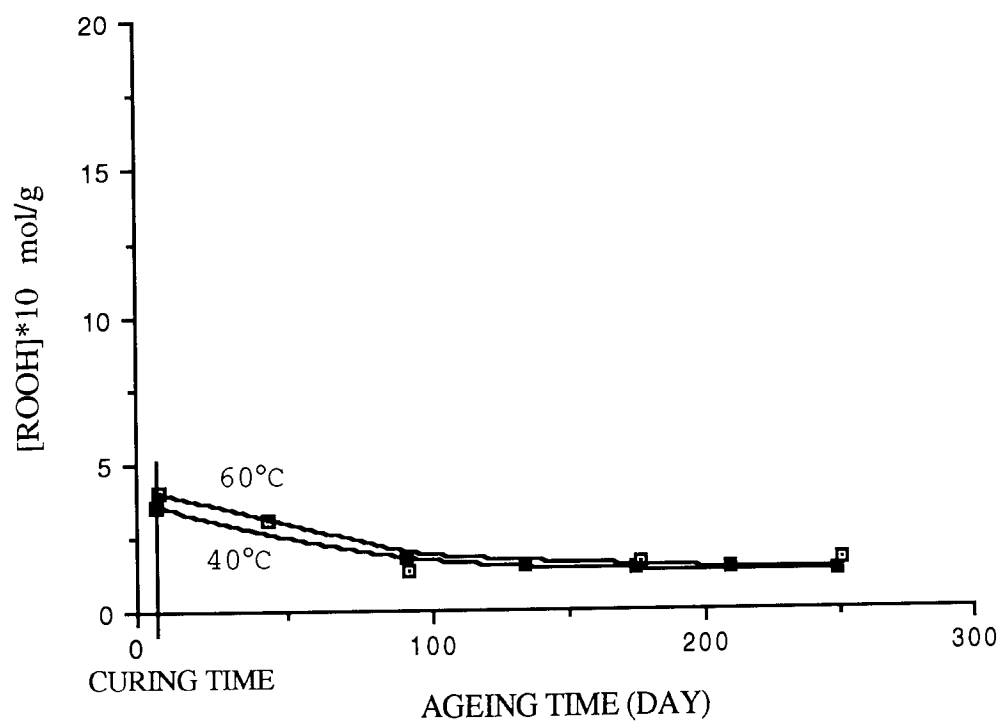
Fig.3-23 Hydroperoxide concentrations of the binders at the bottoms of tubes aged at 40° and 60°C

Chapter Four

The Stabilization of Diisocyanate Cured Polybutadiene

4.1. Object and Methodology

From the work described in Chapter 3, it is clear that the presence of unsaturation in polybutadiene makes it particularly susceptible to oxidation which leads to both crosslinking and chain scission.

The work described in this Chapter deals with the stabilization of polybutadiene under oxidative conditions. This has been carried out by investigating the behaviour of antioxidants, including chain-breaking antioxidants and peroxide decomposers. The measurement of changes in crosslink density is used to evaluate the efficiency of antioxidants. Although only one NCO/OH ratio was used to cure all samples, the initial crosslink densities of the binders with different antioxidants showed differing values. This difference may be due to several factors. Firstly, there is the probability of the reaction of diisocyanate with the antioxidants which will reduce the initial crosslink density of the binder. The reaction rate of isocyanate with primary hydroxyl in HTPB is much higher than that of isocyanate with -OH in hindered phenol or -NH in hindered amine, but the reaction does occur and has been measured by the loss of antioxidant in the binder with antioxidant 2246 after curing. Secondly, water is an active reactant for isocyanate group. Traces of water, even moisture in the atmosphere can reduce the initial crosslinks. So binders cured in different humidity conditions have different crosslink density. Thirdly, experimental errors exist from the processing to the testing. For the sake of checking, the initial crosslink densities have been given in the Tables in this Chapter, but for comparison of effects of antioxidants, the initial crosslink density was subtracted from the data used in the figures.

Experience on the effect of antioxidant in polymers shows that different polymers usually have their own selection of best antioxidants. Since numerous antioxidants exist, an antioxidant screening test was carried out first before the work focused on any

particular antioxidant. 2246, a bis-phenol antioxidant (see Table 2-4), employed by MOD, was used as a reference in the evaluation.

The high efficiency of amine antioxidants is partly attributed to their transformation products, nitroxyls, especially in the case of hindered amines. A specific investigation of the selected amines and their nitroxyls has been carried out in polybutadiene under two extreme conditions. 0.5 mm thick films represent the top layer of a bulk binder aged in an oxygen sufficient condition. Tube binder beneath the "skin" simulates the rest of the binder in a bulk, where oxygen is deficient. In the previous Chapter it was shown that the oxidation of the binder starts from the top layer and forms a hard "skin" which protects the binder beneath it by reducing the oxygen permeability. So the most important part in a binder which needs to be protected is the top layer. But, for practical reasons, the tube binder sample was also tested in this experiment. It has to be mentioned that samples in this experiment were aged at 60°C for 94 days and then ageing was continued in an 80°C oven for the rest of the ageing time. The purpose of this arrangement was to reduce the experimental time so that the work could be finished in time. It is important to point out that these results can only be compared with themselves and not with other samples described in this work.

The combination of two kinds of antioxidants or antioxidant functions in one polymer system is often used in order to seek a better inhibition in the polymer. The experiments of different combinations of antioxidants were carried out in a dish mould of 5 mm thickness.

4.2. Results

4.2.1. Screening of Antioxidants

4.2.1.1. Aromatic Amines

Fig.4-1 and Table 4-1 show the performance of several aromatic amines in the binder aged at 60°C in a 5mm dish mould. The good antioxidants in this group are Flectol H and IPPD.

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4.2.1.2. Hindered Phenols

Fig.4-2 and Table 4-2 give the results of several phenols under the same condition as for amines. Only WSP can compete with 2246.

4.2.1.3. Aliphatic Hindered Amines

Aliphatic hindered amines are usually used as light stabilizers in polymer. In this application their antioxidation activities can not compete with 2246 (Fig.4-3, Table 4-3).

4.2.1.4. Phosphites

Fig.4-4 and Table 4-4 show the effects of two phosphites on the binder. They can not be compared with 2246, even worse than non-antioxidant sample.

4.2.1.5. Sulphur Compounds

Three sulphur compounds have been used in binder. Similar to phosphites, they show pro-oxidant effects (Fig.4-5, Table 4-5).

4.2.2. Amines and their Nitroxyls

In Figs.4.6 to 4.9 and Tables 4-6 and 4-7, the results of three aromatic amines and their nitroxyls, and one hindered amine and its nitroxyl are shown.

4.2.3. Synergism and Antagonism of Antioxidants

Figure 4-10 and Table 4-8 show the performance of an two functional group antioxidant, Santowhite Crystals.

Figures 4-11 to 4-13 and Table 4-9 give the results of the combinations of two chain-breaking antioxidants.

Figures 4-14 to 4-17 and Table 4-10 show the effects of the combinations of chain-breaking antioxidant with peroxide decomposer.

4.2.4. Reactions of Antioxidants with IPDI

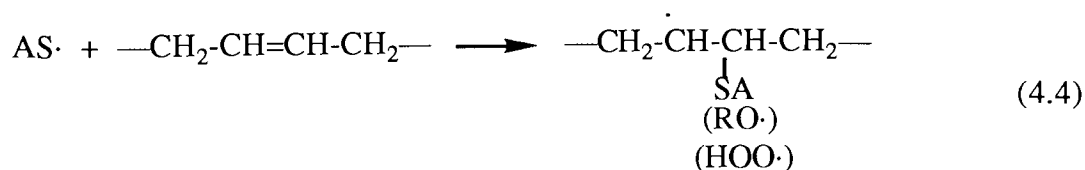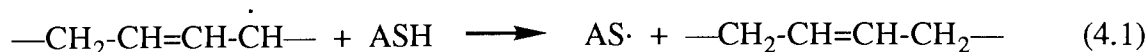Table 4-11 lists the results of antioxidant solubilities in the binder and their reaction with IPDI.

4.3. Discussion

4.3.1. The Screening of Antioxidants

The results of the screening test show that the suitable antioxidants for the binder are from the chain-breaking antioxidant class, mainly the aromatic amines. Peroxide decomposers, on the other hand, such as phosphite and sulphur containing compounds show pro-oxidant effects.

The high efficiency of aromatic amines, such as IPPD and Flectol H, is due to the low strength of their N-H bonds and the high activities of their derivatives. The reaction rate of amine with free radical is much higher than that of free radical abstracting a hydrogen from the molecular chain. So the concentration of free radicals remains at a very low level in the binder. The derivatives of amine, for example, quinone diimide and nitroxyl, also have the abilities to scavenge radicals (see section 1.2.3.1.2). The low efficiency of MPDA is most likely due to the formations of thiyl radical in the reaction (4.1), and other radicals in the reactions (4.2) and (4.3)[154,201,202]. These radicals may attack the double bond (reaction (4.4)) and initiate the chain crosslinking reaction.

Only bis-phenol, with a similar structure to 2246, from the phenols used can compete with aromatic amines in this high ROO· concentration system. Other phenols show a pro-oxidant effect. This must be due to the formation of radicals in their reactions.

$$—CH_2\text{-}CH\text{=}CH\text{-}\overset{\bullet}{C}H— + ASH \longrightarrow AS· + —CH_2\text{-}CH\text{=}CH\text{-}CH_2— \quad (4.1)$$

$$ASH + ROOH \longrightarrow AS· + RO· + H_2O \quad (4.2)$$

$$ASH + O_2 \longrightarrow AS· + HOO· \quad (4.3)$$

$$AS· + —CH_2\text{-}CH\text{=}CH\text{-}CH_2— \longrightarrow —CH_2\text{-}\overset{\bullet}{C}H\text{-}CH\text{-}CH_2—$$
$$\underset{\substack{(RO·)\\(HOO·)}}{\overset{|}{S}A} \quad (4.4)$$

Aliphatic hindered amines are not effective radical scavengers owing to the high energy of their N-H bond. But nitroxyl radicals, an oxidized product of hindered amines, can also react with free radicals. In the oxygen deficient system, this reaction can protect

binder to some extent. Furthermore, the known regenerative characteristics of nitroxyls[148,149] enhance their efficiency.

Generally speaking, both phosphites and sulphur containing compounds do not act primarily by scavenging radicals, but by decomposing hydroperoxides. Their pro-oxidant effects exhibited in the binder must be due to the redox reaction of their derivatives with hydroperoxides in which alkoxyl radicals are produced (see section1.2.3.2. 2).

Thus, peroxide decomposers are not suitable for use alone in the polybutadiene binder. Their effect as a secondary antioxidants is investigated later (section 4.3.3).

4.3.2. Amines and Their Nitroxyls

Aromatic amines, IPPD, Flectol H and DMDP, exhibit very good protection against binder crosslinking under both oxygen sufficient and deficient conditions(see Figures 4-6 to 4-8). But for nitroxyls, only DMDP-NO shows comparable activity under both ageing conditions(see Figure 4-8). IPPD-NO· and Flectol H-NO· show similar activity to their precursor amine samples in the tube binders, but in the film binders, Flectol H-NO· has a good performance at 60°C but loses it at 80°C, and IPPD-NO· soon shows no protection (see Figures 4-6 and 4-7).

It is clear from the study on the mechanism of polybutadiene oxidation (Chapter 3) that radicals, such as ROO·, RO· and R·, formed during the oxidation, are the most potential species in the crosslinking reaction. In the film binder, ROO· is present in a high concentration. The efficiency of a chain-breaking antioxidant, to some extent, is usually related to the capability of transfering hydrogen. For the aromatic amines this process proceeds rapidly and thus effectively retards the development of the radical concentration in the polymer.

In spite of conjugation, aminyl formed from aromatic amine may also participate in a series of reactions and forms various transformation products.

Nitroxyl is one of the most important species in transformation products. It performs by trapping alkyl radical and forming hydroxylamine which is an effective chain-breaking donor antioxidant (Scheme 4-1).

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It is reasonable to believe that the reaction of nitroxyl with alkyl radical is a relatively fast reaction in polybutadiene. Because the hydrogen abstracted is from the α-position and the conjugated polymer chain formed has a lower energy.

ROOH $\quad$ $\diagdown$NO· $\quad$ —CH=CH-CH-CH$_2$-CH=CH—

ROO· $\quad$ $\diagdown$NOH $\quad$ —CH=CH-CH=CH-CH=CH—
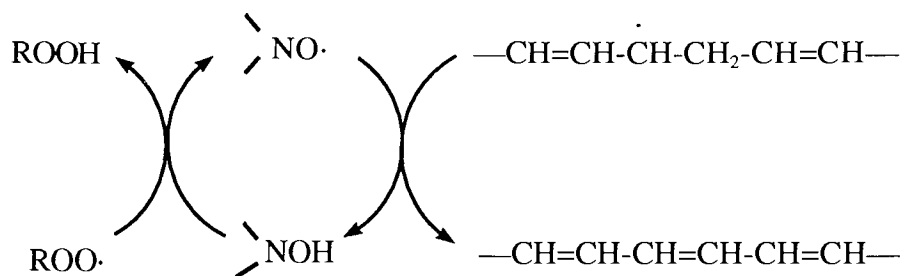
**Scheme 4-1** The regeneration of nitroxyl in polybutadiene

Increasing the temperature results in enhancing of all reaction rate constants; oxidation becomes more severe at higher temperature. But if the reaction rate constant, between antioxidant and radical, rises to the same degree as the oxidation rate constant does at a higher temperature, the antioxidant will keep the same activity. If the former can not match the later, for example, increases less, the inhibition of antioxidant will be reduced.

The poor performance of IPPD-NO· can be partially attributed to their poor solubility in the polybutadiene.

4.3.3. Synergism and Antagonism of Antioxidants in Binder

4.3.3.1. The Combination of Two Antioxidant Functions in One Molecule

4,4'-thiobis(2-tert-butyl-5-methylphenol) (I) has both phenols and sulphur in its structure.

$\qquad$ C(CH$_3$)$_3$ $\qquad\qquad$ C(CH$_3$)$_3$

HO— S —OH $\qquad$ (I)

$\qquad$ CH$_3$ $\quad$ CH$_3$
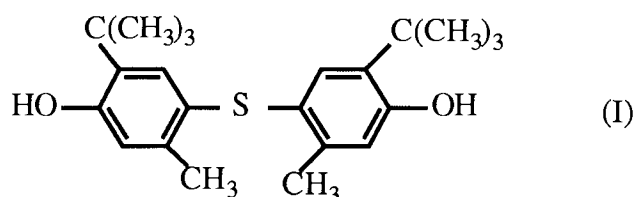
(Santowhite Crystals)

Phenol functions as a chain-breaking antioxidant whereas sulphur acts as a hydroperoxide decomposer. However, the effect of this antioxidant used alone in polybutadiene did not show any promising action (Fig.4-10). Considering the high radical concentration formed during polybutadiene oxidation, IPPD, a primary antioxidant, was

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added to increase the capability of radical scavenging. A synergism effect is shown in this combination system. It seems that the phenol group in Santowhite Crystals is not efficient enough in scavenging radicals formed in the binder. When an effective Chain-breaking antioxidant was added, the efficiency of this antioxidant system is exhibited not only by scavenging radicals effectively but also by the contribution of sulphur group in decomposing peroxides formed in the binder.

4.3.3.2. The Combination of Two Chain-Breaking Antioxidants

The usual combination of two antioxidants with the same mechanism involves unequal activity compounds. An unusual experiment was carried out by combining two similar activity antioxidants, IPPD with Flectol H, IPPD with 2246 and Flectol H with 2246. The results show that no better effect can be obtained from these three combination systems (Figs 4-11 to 4-13). This suggests that there is no co-operation between strong antioxidants.

4.3.3.3. The Combination of Chain-Breaking Antioxidant with Hydroperoxide Decomposer

Several chain-breaking antioxidants exhibit excellent antioxidant activity in polybutadiene by effectively suppressing free radicals and thus stopping the radical chain reaction. But as the main reaction product is hydroperoxide which is a potential oxidation species. The combination of a chain-breaking antioxidant with a hydroperoxide decomposer was considered as a way to improve the long term stability of polybutadiene.

Three different ratios of two kind of antioxidants have been used. A synergistic effect is observed in the ratio of IPPD/DLTP = 2 : 1. This is consistent with the result in section 4.3.3.1 where sulphur group in bifunctional antioxidant also shows a positive action in the presence of a high concentration of chain-breaking antioxidant.

It is known[141,142] that sulphur compounds are not themselves the active peroxide decomposer but their oxidation products are the main species which catalyse the decomposition of hydroperoxide to non-radical products. Its ability to destroy peroxide increases with the formation of more oxidized acid species. But at the beginning of the oxidation process when [ROOH]/[S] ratio is low, sulphur compound homolyses

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hydroperoxide by the redox reaction to give RO· radicals. Since RO· radicals accelerate the oxidation of polybutadiene, the sulphur compound alone shows a pro-oxidant effect in the binder(see section 4.3.1. and Figure 4-5). When chain-breaking antioxidant is present with sulphur-compound, it does not only scavenge the free radicals caused by the polymer oxidation, but also reduce or eliminate an initial pro-oxidant process involved in the oxidation of the sulphur compound to an effective antioxidant product[203]. Because chain-breaking and preventive antioxidants interfere at different points in the autoxidation process, they mutually reinforce one another, leading to an effect greater than the sum of the effects of each antioxidant alone. The co-operation of these two mechanisms must, therefore, provides the best protection for polybutadiene. To obtain such a good co-operation, the ratio of two antioxidants is very important. It is dependent on the polymer nature and the ageing condition. In this experimental condition, ratios of IPPD/DCTD = 2 : 1 and WSP/DCTP = 2 : 1 show synergistic effect, but ratios of 1 : 1 and 1 : 2 do not .

4.3.4. Reaction of Antioxidant with IPDI

Reaction of the curing agent, diisocyanate, with compounds containing active hydrogen such as hindered phenols and aromatic amines could affect the stabilizing role of these antioxidants. Two tests (sections 2.6.8. & 2.6.9.) were carried out in order to find out the effect of the isocyanate-antioxidant interaction. Results from HPLC showed that about 68% of 2246 antioxidant remained in the binder after curing, but neither IPPD nor FlectolH could be detected in the extracts.The extract of IPPD binder gave a peak with a retention time of 6.8 minutes whereas the IPPD standard showed a large single peak with a retention time of 21 minutes. Keeping the standard for four days in a solution of eluant, it gave a small peak at 12.6 minutes retention time.

The loss of 2246 is most likely due to the reaction of the phenol group with the isocyanate group even though the reaction rate is much slower than that for a primary hydroxy group with isocyanate. It is also possible that some of the 2246 was consumed by acting as an antioxidant during the curing period. The failure to detect IPPD and FlectolH in the extracts is attributed to two possibilities.One could be due to the possibility of the reaction between the secondary amines and isocyanate which means that the amine becomes part of the network. Another possibility is that the original IPPD and FlectolH

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have been transformed into other chemical structures which have also good antioxidant activity.

Table 4-1

The effects of aromatic amines on the binder of 5mm depth aged at 60°C

antioxidant	ageing time (day)				
	7	48	76	104	132
	sol %				
IPPD	47	42	42	38	37
Flectol H	66	54	51	49	45
6PPD	56	38	41	37	42
MPDA	61	32	37	36	33
OD	59	32	32	31	30

Table 4-2

The effects of hindered phenols on the binder of 5mm depth aged at 60°C

antioxidant	ageing time (day)				
	7	48	76	104	132
	sol %				
2246	56	47	43	43	42
WSP	61	54	51	50	47
1076	67	30	21	19	17
GM	62	26	29	24	17
S.W.54	59	27	27	27	22

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Table 4-3

The effects of aliphatic hindered amines on the binder of 5mm depth aged at 60°C

antioxidant	ageing time (day)				
	7	48	76	104	132
	sol %				
770	63	50	42	39	36
TMP	68	50	45	41	30

Table 4-4

The effects of phosphites on the binder of 5mm depth aged at 60°C

antioxidant	ageing time (day)				
	7	48	76	104	132
	sol %				
P310	52	33	33	29	25
P210	55	31	32	30	30

Table 4-5

The effects of sulphur compounds on the binder of 5mm depth aged at 60°C

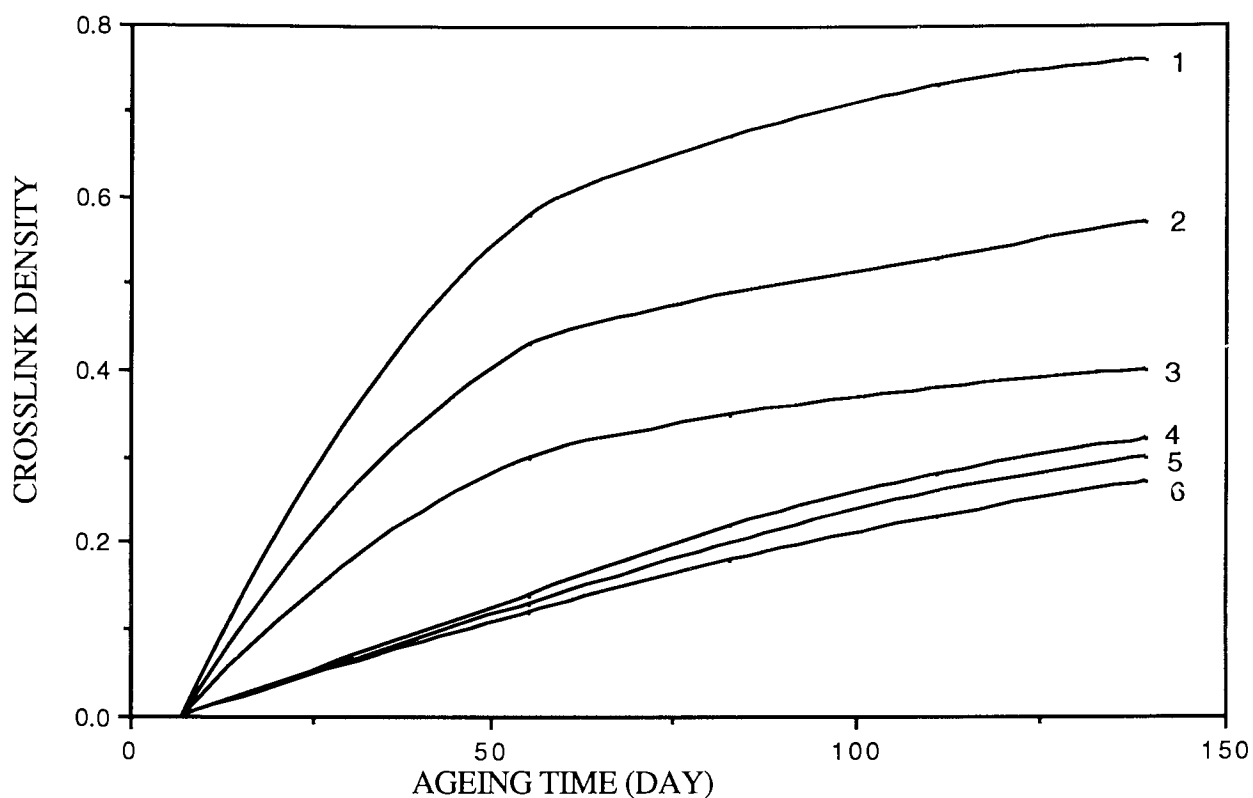| antioxidant	ageing time (day)				
	7	48	76	104	132
	sol %				
DLTP	53	32	32	26	28
Zinc D. D.	55	35	34	34	26
ETHASAN	53	32	30	26	26

Fig.4-1 The effects of aromatic amines (0.1%w/w) on the binder in 5mm dish mould aged at 60°C 1. OD, 2. MPDA, 3. 6PPD, 4. 2246, 5. Flectol H, 6. IPPD (see Table 2-4 for chemical structures)
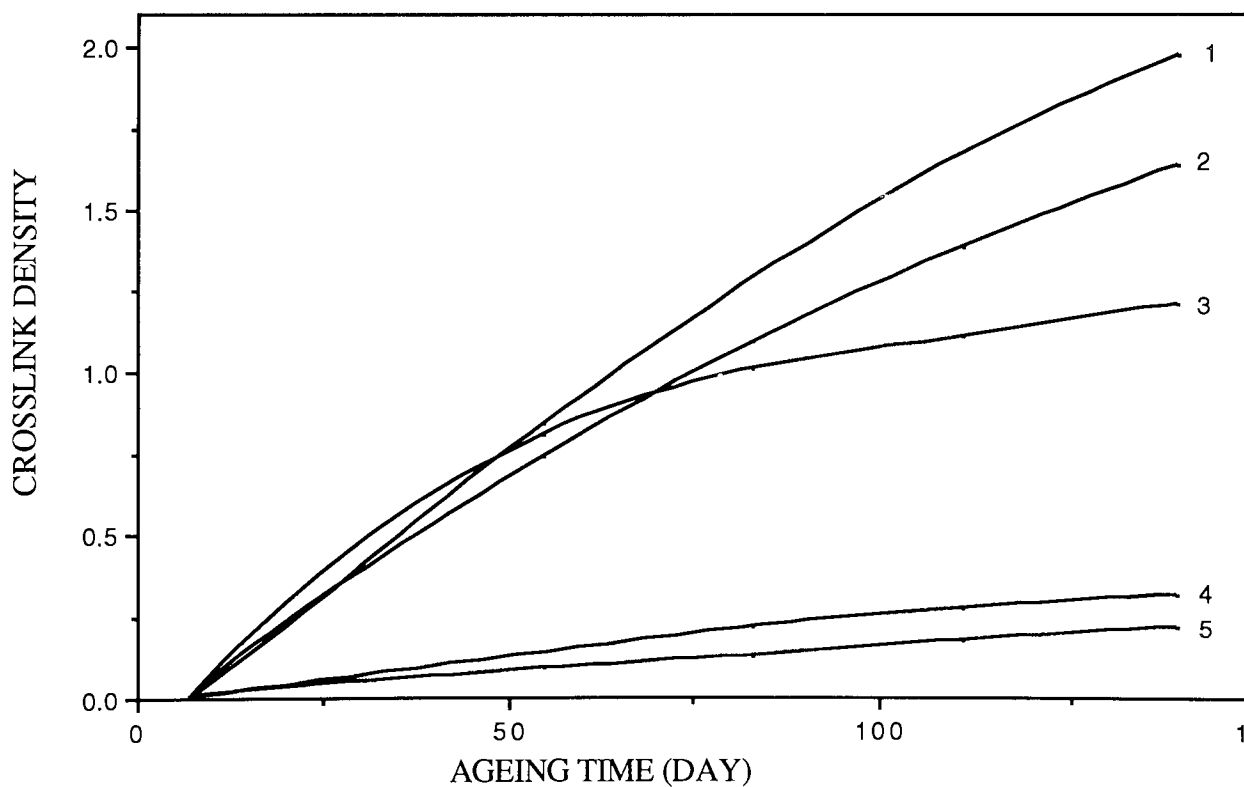

Fig.4-2 The effects of hindered phenols (0.1% w/w) on the binder in 5mm dish mould aged at 60°C 1. 1076, 2. GM, 3. Santowhite 54, 4. 2246, 5. WSP (see Table 2-4 for chemical structures)
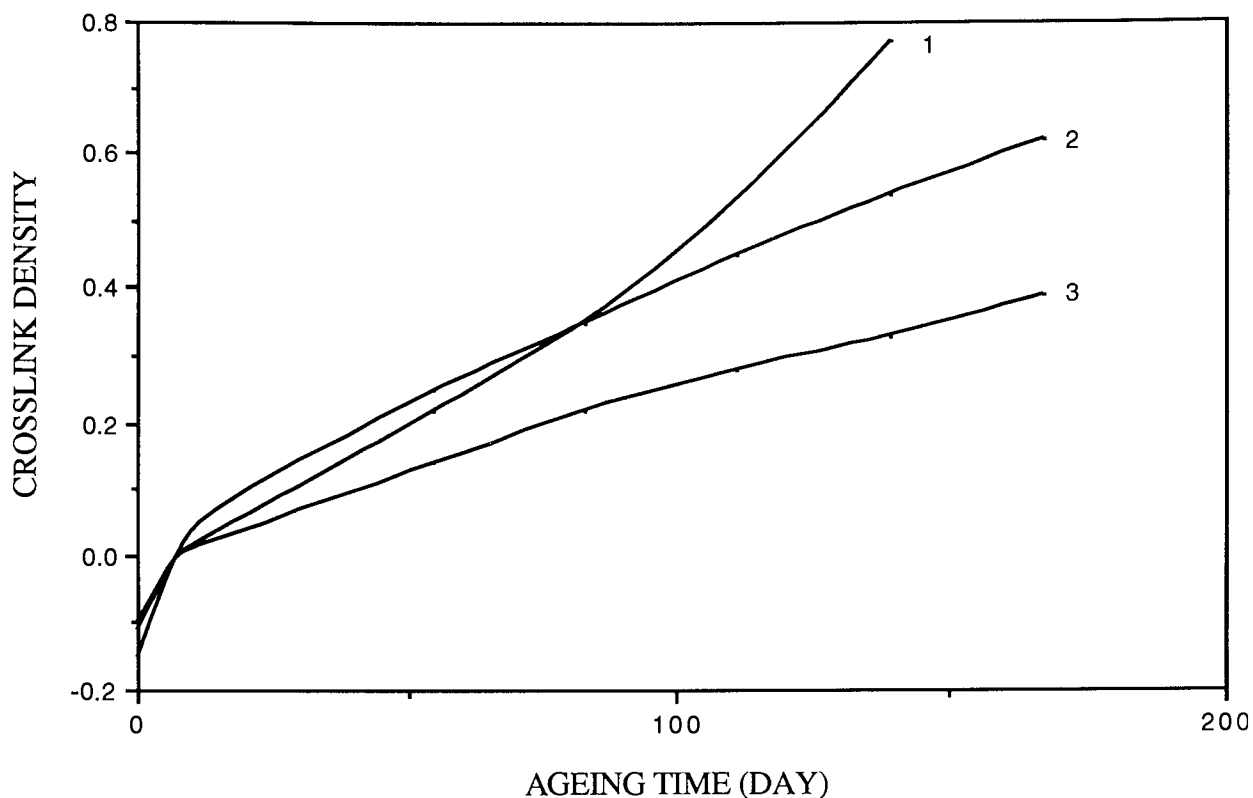
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Fig.4-3 The effects of aliphatic hindered amines (0.1% w/w) on the binder in 5mm dish mould aged at 60°C 1. TMP, 2. 770, 3. 2246 (see Table 2-3 for chemical structures)
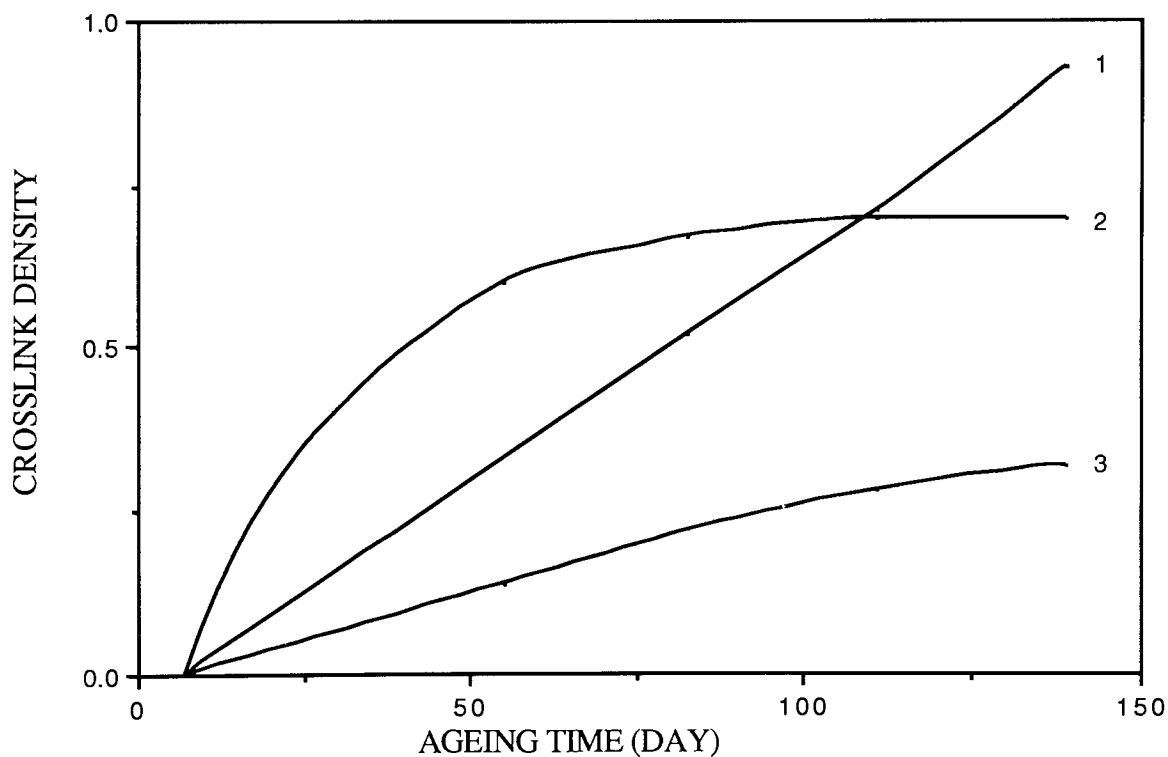

Fig.4-4 The effects of phosphites (0.1% w/w) on the binder in 5mm dish mould aged at 60°C 1. P310, 2. P210, 3. 2246 (see Table 2-3 for chemical structures)
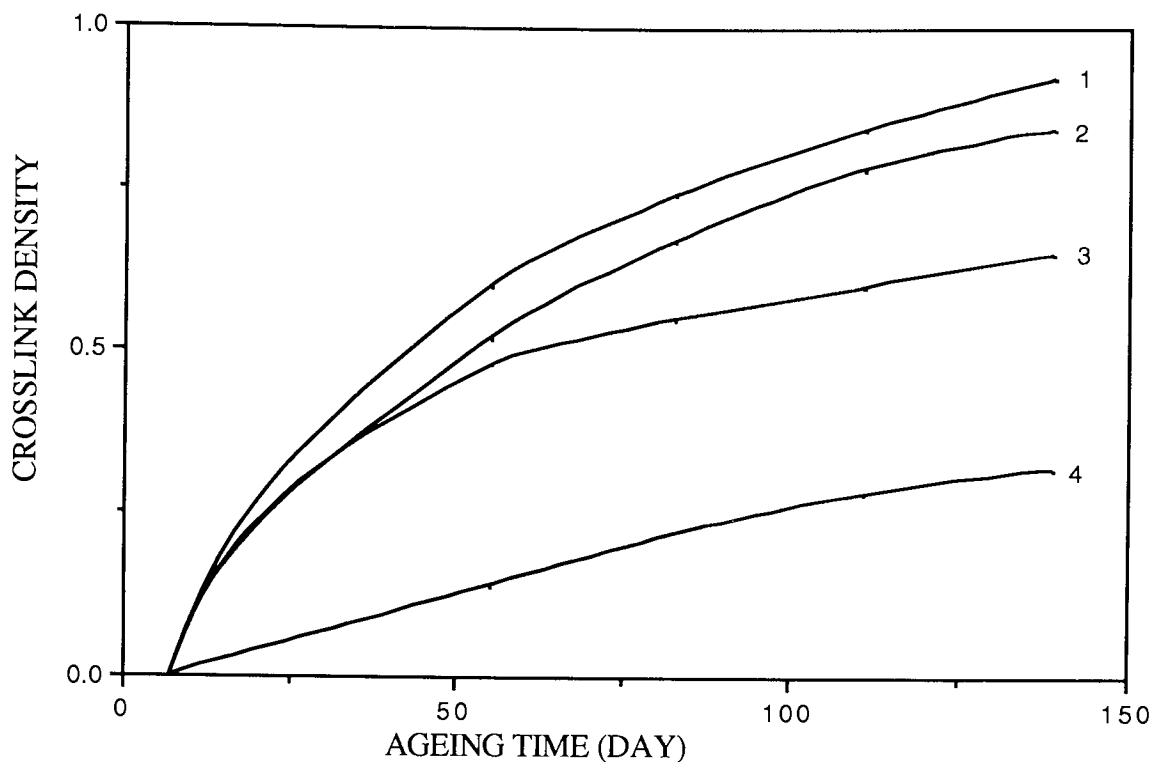
122

Fig.4-5 The effects of sulphur compounds (0.1% w/w) on the binder in 5mm dish mould aged at 60°C 1. Ethasan, 2. DLTP, 3. Zinc diamyl dithiocarbamate, 4. 2246

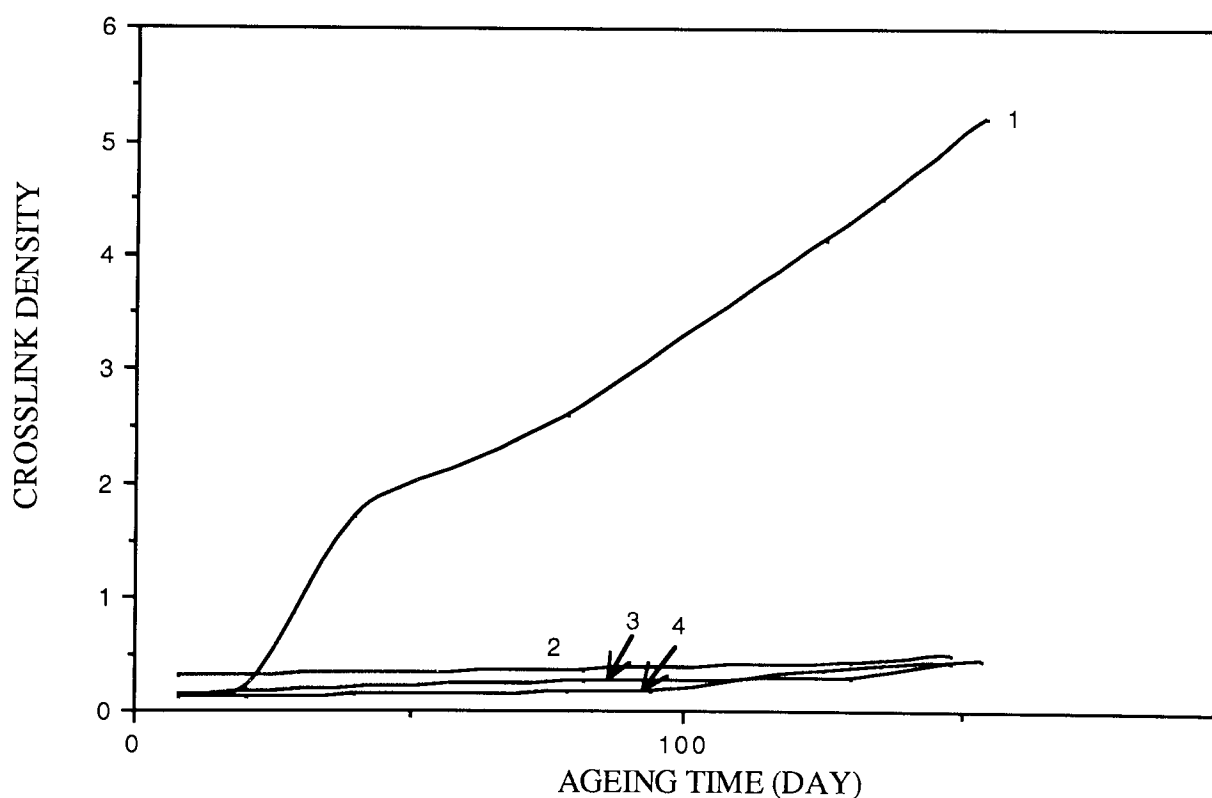(see Table 2-3 for chemical structures)

Fig.4-6 The effects of IPPD and its nitroxyl (0.1% w/w) on polybutadiene binder ageing (from 0 to 97 days: 60°C; from 98 to the end: 80°C) 1. IPPD-NO· in film binder, 2. IPPD-NO· in bottom of tube binder, 3. IPPD in film binder, 4. IPPD in bottom of tube binder (see Tables 2-3 and 2-4 for chemical structures)
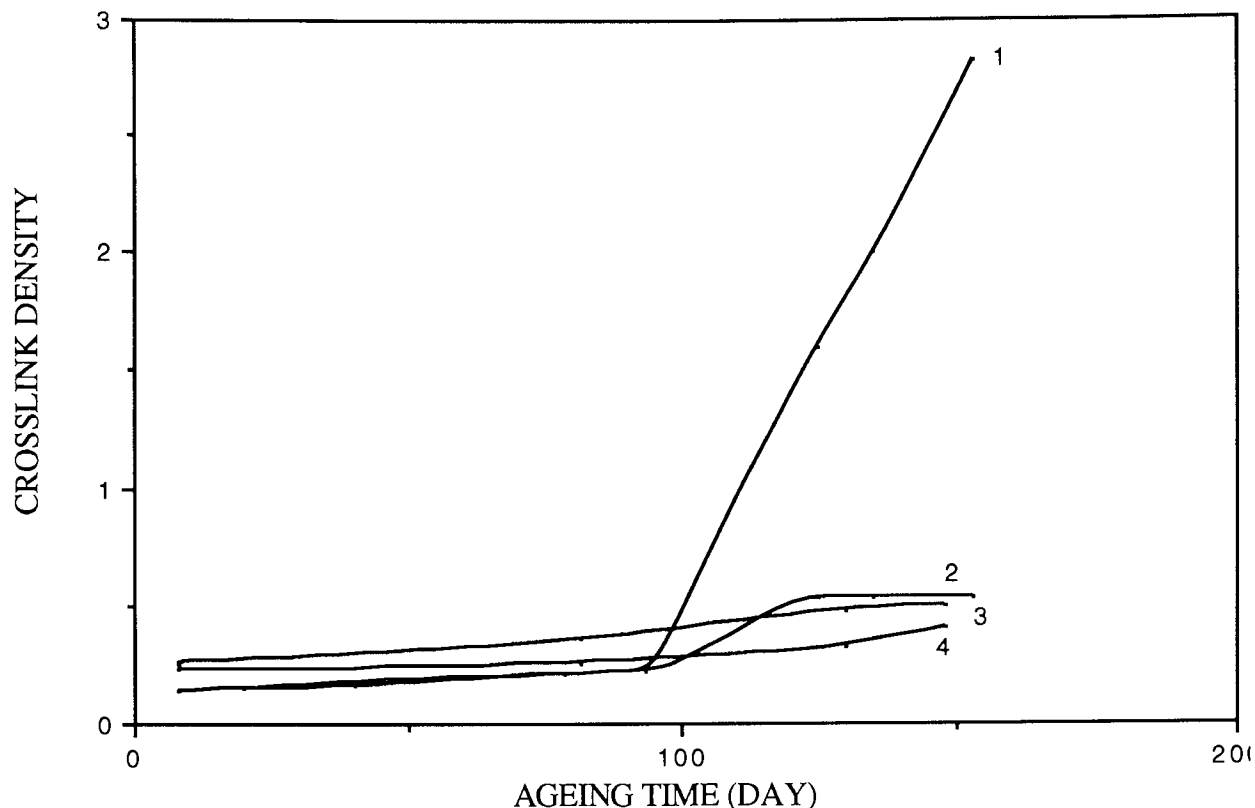
Fig.4-7 The effects of Flectol H and its nitroxyl (0.1% w/w) on polybutadiene binder ageing

(from 0 to 97 days: 60°C; from 98 to the end: 80°C) 1. Flectol H-NO· in film binder, 2. Flectol H in film binder, 3. Flectol H in bottom of tube binder, 4. Flectol H-NO· in bottom of tube binder (see Tables 2-3 and 2-4 for chemical structures)
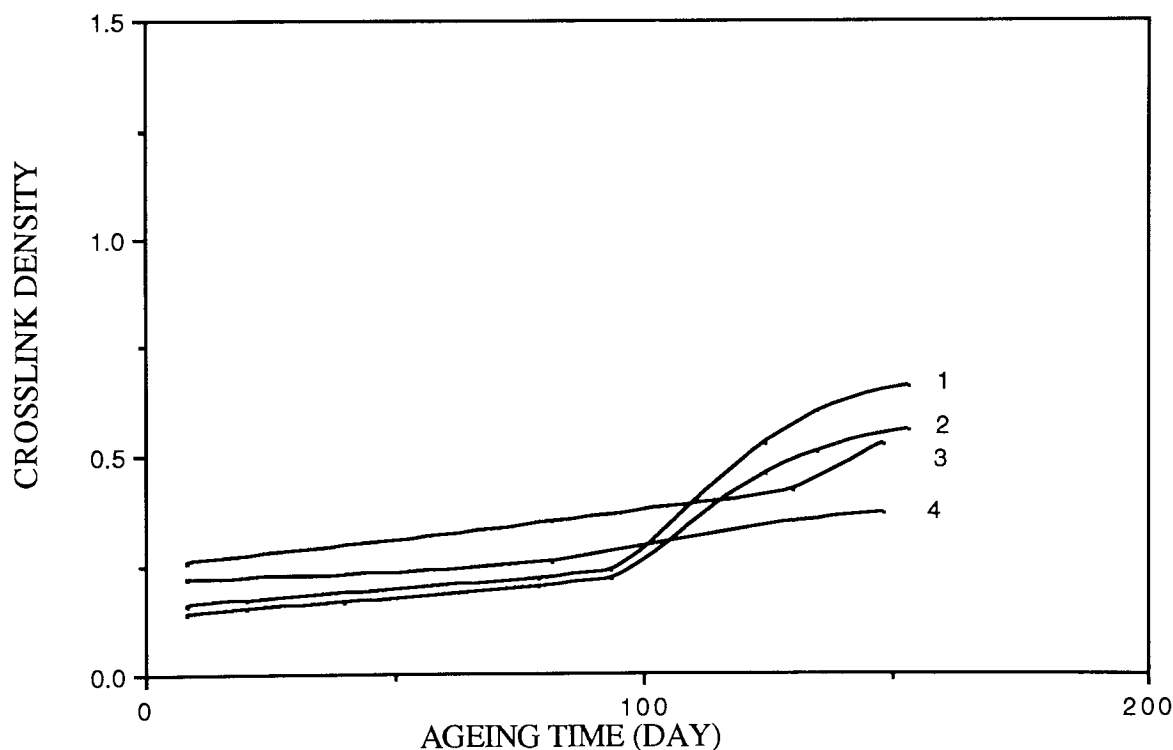

Fig.4-8 The effect of DMDP and its nitroxyl (0.1% w/w) on polybutadiene binder ageing

(from 0 to 97 days: 60°C; from 98 to the end: 80°C) 1. DMDP in film binder, 2. DMDP-NO· in film binder, 3. DMDP in bottom of tube binder, 4. DMDP-NO· in bottom of tube binder (see Tables 2-3 and 2-4 for chemical structures)

Fig.4-9 The effect of 770 and its nitroxyl (0.1% w/w) on polybutadiene binder ageing

(from 0 to 97 days: 60°C; from 98 to the end: 80°C)   1. 770 in film binder, 2. 770-NO· in film binder, 3. 770-NO· in bottom of tube binder, 4. 770 in bottom of tube binder (see Tables 2-3 and 2-4 for chemical structures)

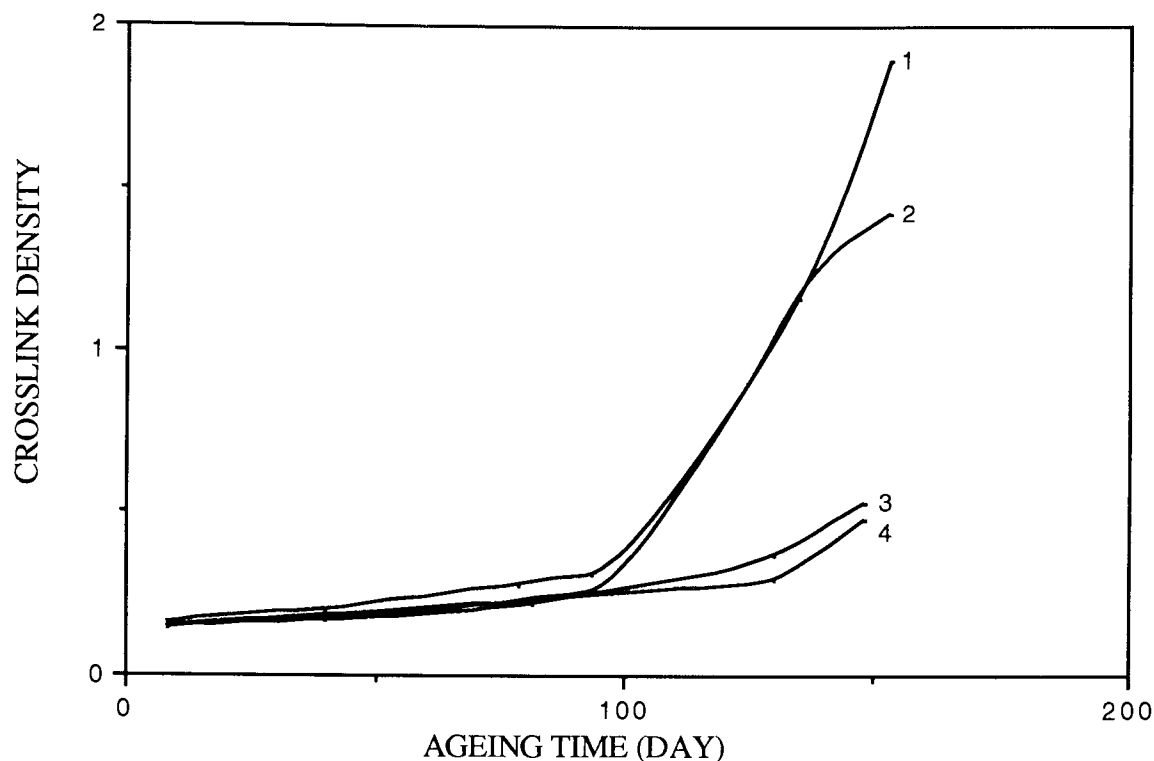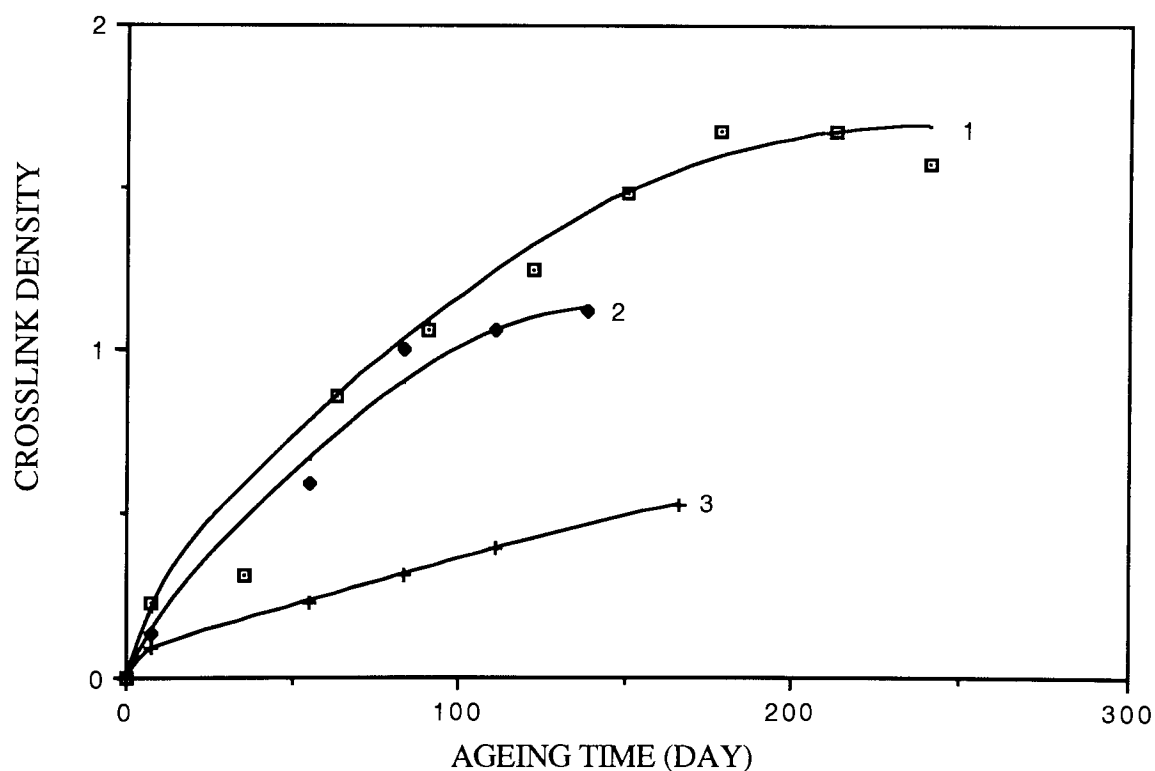**Fig. 4-10** The effect of Santowhite Crystals on polybutadiene binder in 5mm dish mould aged at 70°C 1. Santowhite Crystals, 2. IPPD, 3. Santowhite Crystals/IPPD = 1 : 1

(antioxidant(s) concentration: 0.1% w/w)

Table 4-6

The Effects of Amines and Their Nitroxyls on a Film Binder Aged at 60°C

antioxidant	ageing time (day)							
	8	20	40	79	94	125	135	153
	sol %							
DMDP	62	61	57	57	57	41	38	37
DMDP-NO·	64	63	61	58	59	44	42	40
Flectol H	63	64	60	57	58	41	41	42
Flectol H-NO·	62	65	62	57	58	20	18	12
IPPD	68	62	64	62	61	48	48	43
IPPD-NO·	66	60	18	14	17	8	8	6
770	62	62	57	51	52	29	28	18
770-NO·	64	64	60	54	56	31	26	23

Table 4-7

The Effects of Amines and Their Nitroxyls on a Tube Binder Aged at 60°C

antioxidant	ageing time (day)			
	8	82	130	148
	sol %			
DMDP	54	50	48	40
DMDP-NO·	59	54	49	48
Flectol H	54	42	43	42
Flectol H-NO·	56	56	50	46
IPPD	64	52	54	43
IPPD-NO·	51	48	45	42
770	57	56	52	43
770-NO·	55	56	48	41

Table 4-8

The effects of Santowhite Crystals on polybutadiene binder aged at 70°C

antioxidant	ageing time (day)						
	7	35	63	91	119	148	259
	sol %						
San. Cry.	56	51	32	28	25	22	18
IPPD	51	43	42	35	27	27	23
S.C./IPPD (1:1)	60	44	43	42	39	39	35

Table 4-9

The effects of the combinations of two strong chain-breaking antioxidants on polybutadiene binder aged at 60°C (5mm)

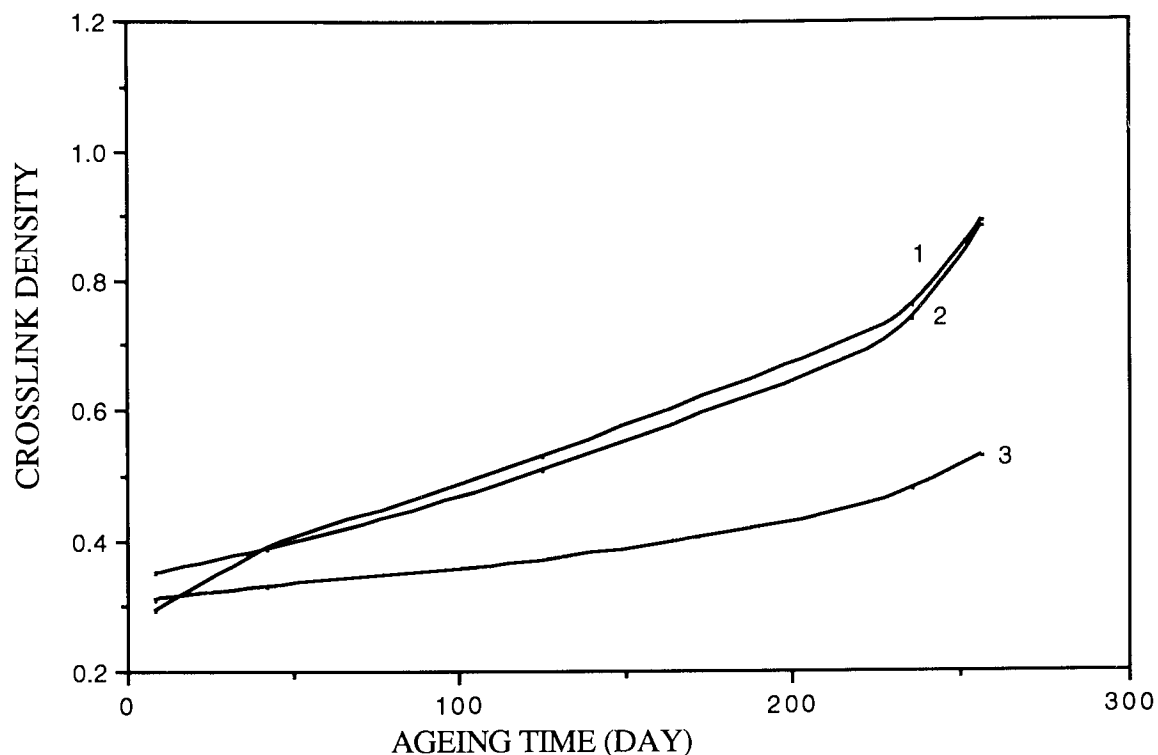| antioxidant	ageing time (day)				
	8	42	125	236	257
	sol %				
IPPD	51	49	48	43	41
Flectol H	52	46	45	41	38
2246	49		42	37	30
2246/Fle.H	53	43	42	34	35
IPPD/Fle. H	48	50	46	41	35
2246/IPPD (1 : 1)	52	45	41	38	34

Fig. 4-11 The effect of the combination of IPPD with Flectol H on polybutadiene binder in 5mm dish mould aged at 60°C 1. IPPD/Flectol H = 1 : 1, 2. Flectol H, 3. IPPD (antioxidant(s) concentration: 0.1% w/w)
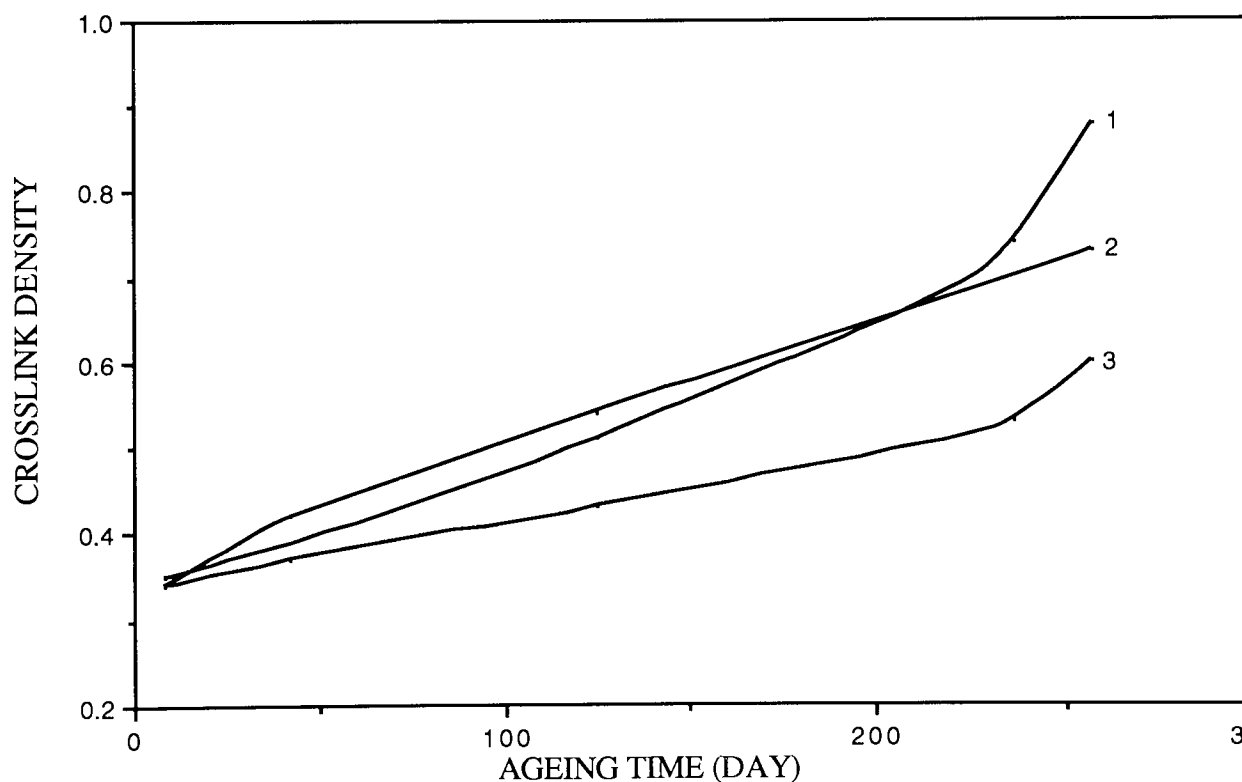

Fig.4-12 The effect of the combination of Flectol H with 2246 in polybutadiene binder in 5mm dish mould aged at 60°C 1. 2246, 2. Flectol H/ 2246 = 1 : 1, 3. Flectol H (antioxidant(s) concentration: 0.1% w/w)

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Fig.4-13 The effect of the combination of 2246 with IPPD in polybutadiene binder in 5mm dish mould aged at 60°C 1. 2246, 2.IPPD/2246 = 1 : 1, 3. IPPD (antioxidant(s) concentration: 0.1% w/w)

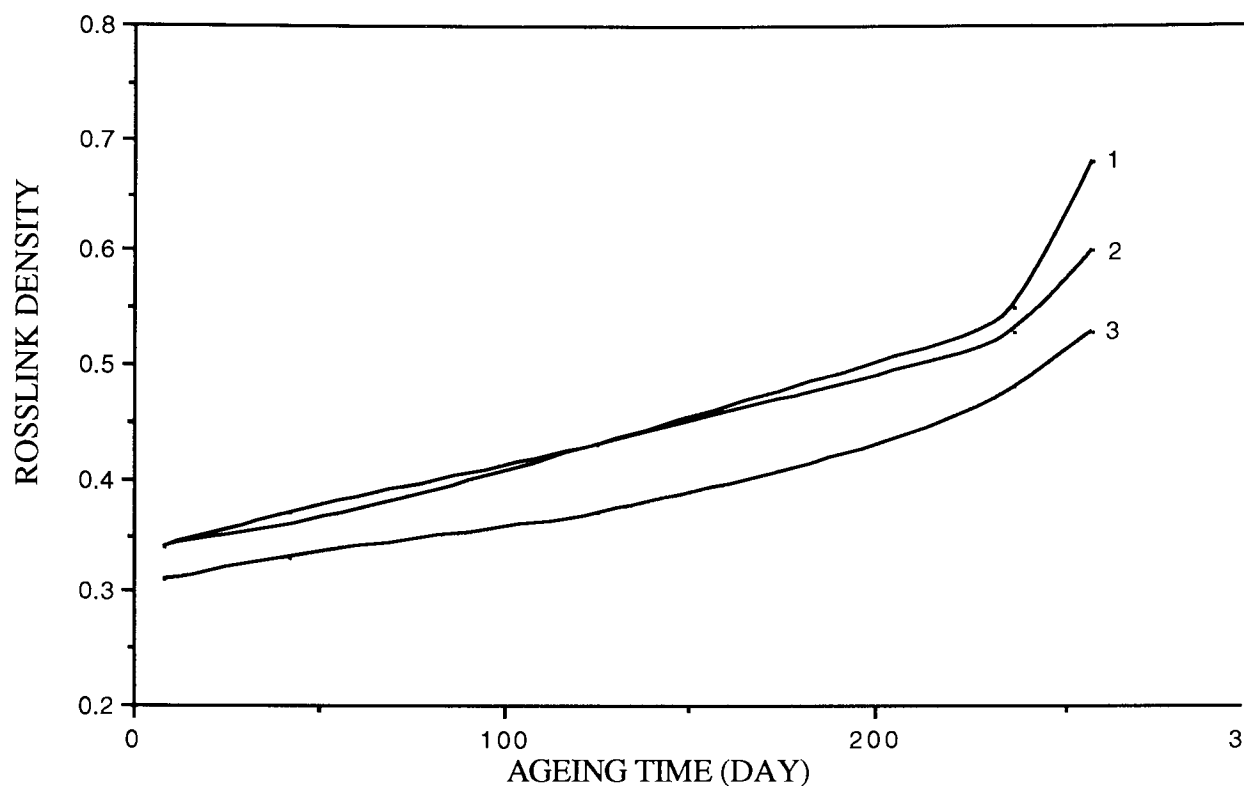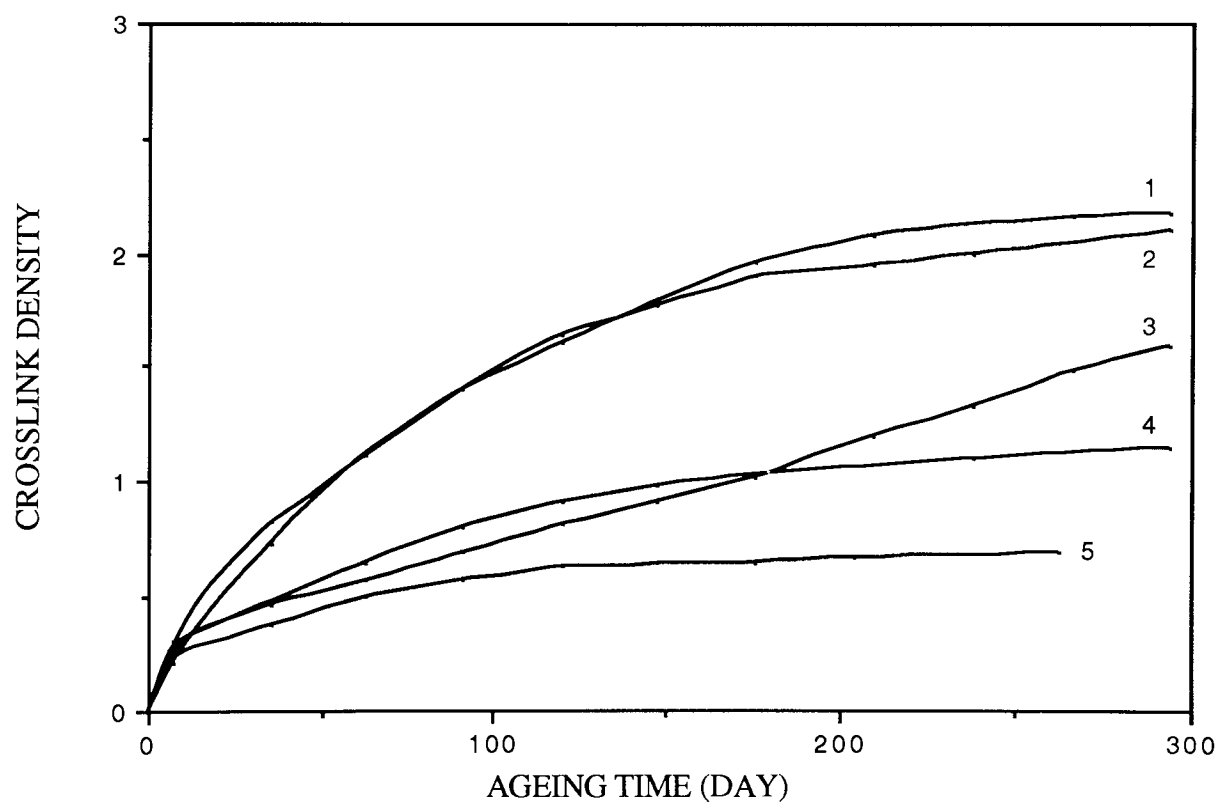**Fig.4-14** The effects of the combination of IPPD with DLTP in polybutadiene binder in 5mm dish mould aged at 70°C 1. IPPD/DLTP = 1 : 2, 2. DLTP, 3. IPPD/DLTP = 1 : 1, 4. IPPD, 5. IPPD/DLTP = 2 : 1 (antioxidant(s) concentration: 0.1% w/w)

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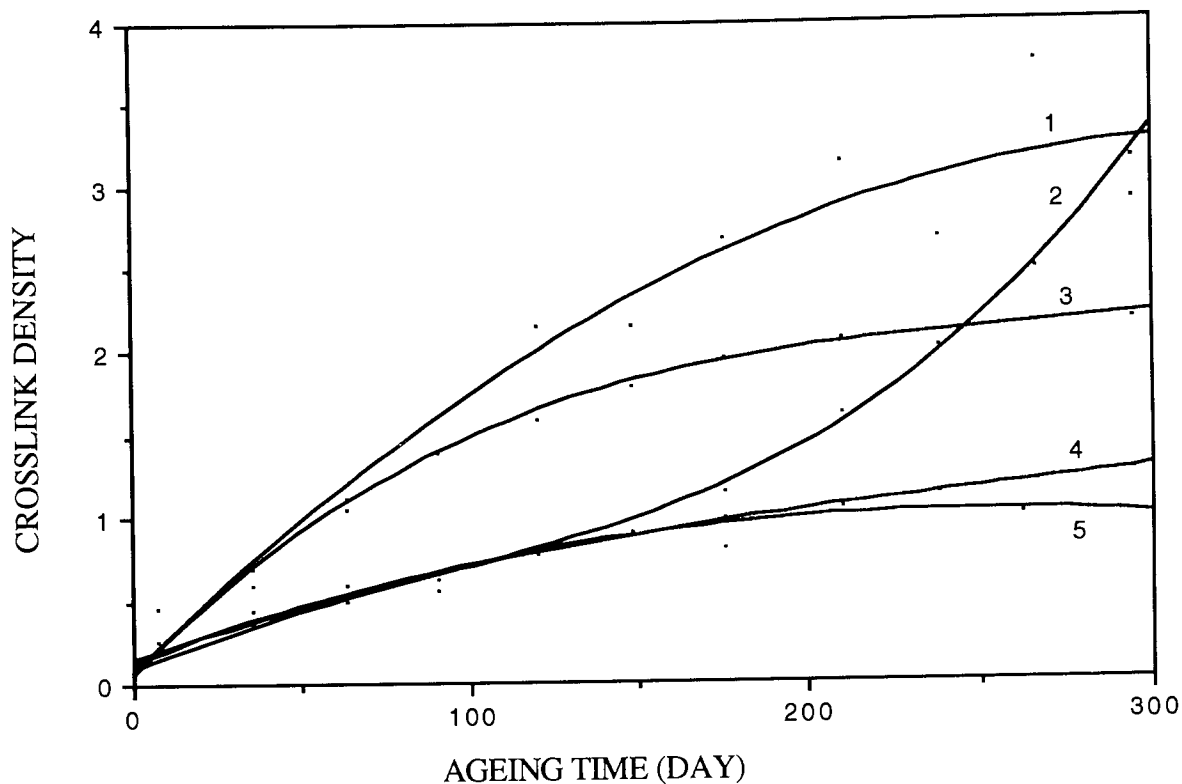
Fig.4-15 The effect of the combination of WSP with DLTP in polybutadiene binder in 5mm dish mould aged at 70°C 1. WSP/DLTP = 1 : 2, 2. WSP/DLTP = 1 : 1, 3. DLTP, 4. WSP, 5. WSP/DLTP = 2 : 1   (antioxidant(s) concentration: 0.1% w/w)
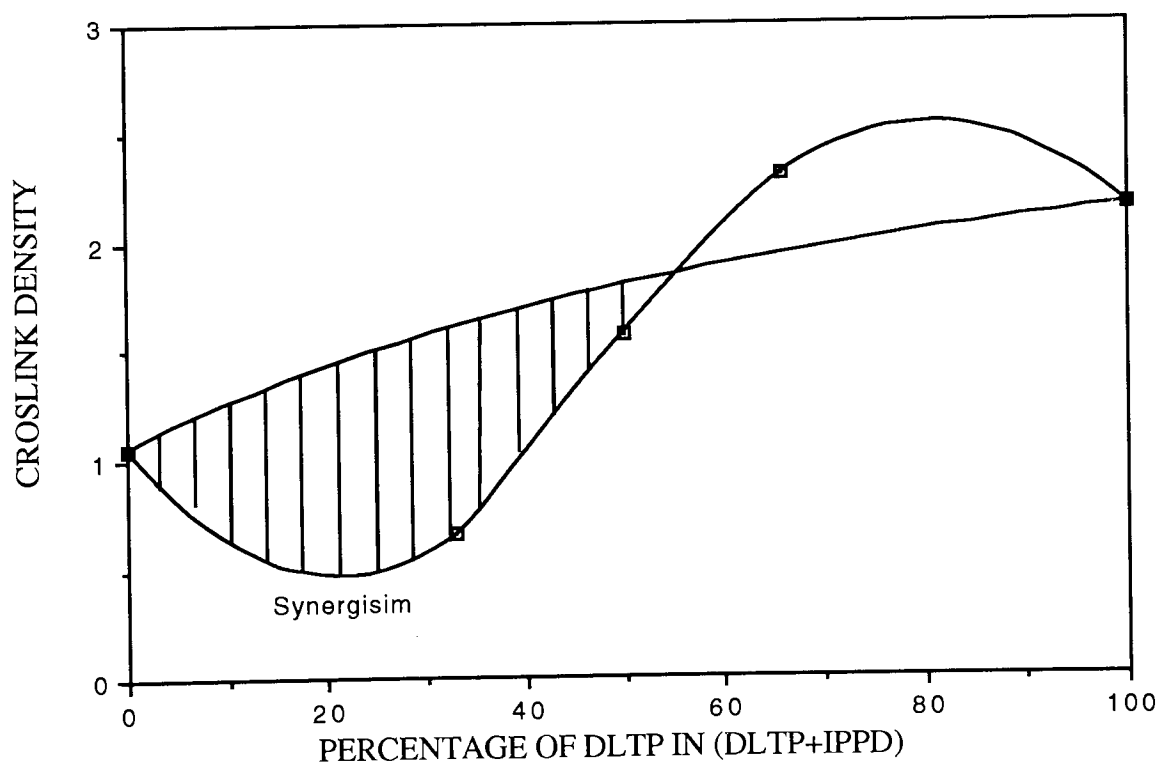
Fig.4-16 The crosslink density of polybutadiene binders with different antioxidant combination ratios after ageing for 266 days (antioxidant(s) concentration: 0.1% w/w)

130
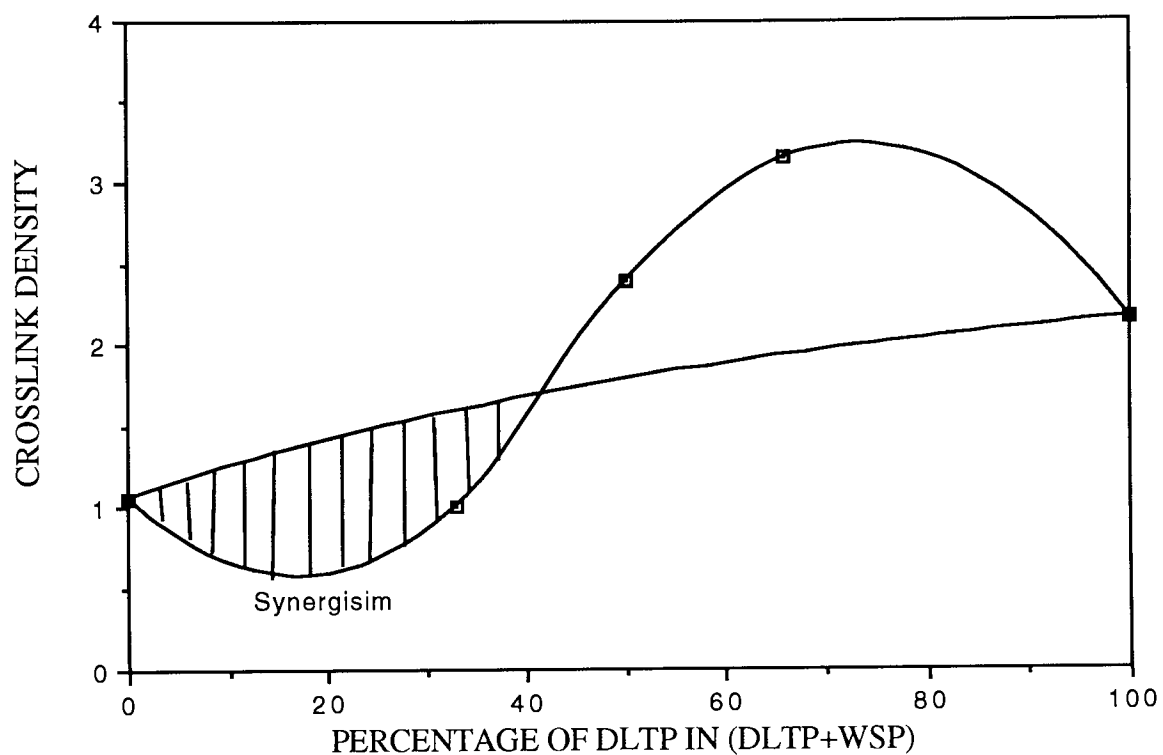
Fig.4-17 The crosslink density of polybutadiene binders with different antioxidant

combination ratios after ageing for 266 days

(antioxidant(s) concentration: 0.1% w/w)

Table 4-10

The effects of the combinations of chain-breaking antioxidant with peroxide decomposer on polybutadiene binder aged at 70°C (5mm)

| antioxidant	7	35	63	91	120	176	238	266
				ageing time (day)				
				sol %				
IPPD	51	43	42	35		31	30	28
WSP	57	51	40	42	32	31	28	28
DLTP	57	35	27	23	21	19		16
IPPD/DLTP								
1 : 1	53	42	42	36	33	32	26	21
1 : 2	52	30	30	23	19	15	15	14
2 : 1	55	49	37	41	38	38	38	37
WSP/DLTP								
1 : 1	54	44	41	37	34	26	19	14
1 : 2	44	36	28	23	16	13	13	12
2 : 1	57	39	39	40	33	33	29	29

Table 4-11

The Solubility and the Reaction of Some Antioxidants with IPDI

Antioxidant	Solubility* (0.1%, 60°C)	Stand at 60°C for 3 to 7 days C=O amide peak (1665 cm^{-1})
IPPD	soluble	strong
IPPD-NO·	insoluble	no
DMDP	soluble	weak
DMDP-NO·	soluble	no
Flectol H	soluble	strong
Flectol H-NO·	insoluble	no
770	soluble	no
770-NO·	slightly soluble	no
TMP	soluble	strong
TMOP	soluble	no
2246	soluble	weak

* The solubility was examined visually, i. e., no suspension antioxidant particles coulde be seen.

Chapter Five

Conclusion and Suggestions for Further Work

HTPB binder loses its excellent stress-strain characteristics during the normal storage, due to the crosslinking reaction between the polybutadiene chains.

5.1. Conclusions

The Study of the degradation of HTPB binder, below 80°C, showed that:

1. Oxygen is the main factor which causes binder deterioration. Under an oxygen sufficient condition, increasing temperature can reduce the length of induction period so that autoxidation starts earlier. Hydroperoxides and carbonyl groups are formed along the polymer chains, and, at the same time, the gel content increases and molecular mass of sol portion decreases. In contrast to this, all these changes did not occur in HTPB binder aged under a high vacuum condition.

2. Crosslinking reaction is the predominant reaction in oxidation of polybutadiene whereas chain scission is a minor reaction. Crosslinks can be formed by three kinds of reactions:

   (1) Alkylperoxyl radicals attack 1,2 vinyl double bonds to form dialkyl peroxide crosslinks;

   (2) Alkoxyl or alkylperoxide radicals attack conjugated double bonds to give ether or peroxide crosslinks;

   (3) Free radicals initiated chain reaction through opening double bonds, to form carbon-carbon crosslinks.

The first two reactions are more likely to occur under oxygen sufficient condition whereas the third reaction only takes place under oxygen deficient condition. Since, in binder, oxygen diffusion rate is much lower than the oxidation rate, an oxygen free

environment exists temporarily in the reaction site. Thus gel builds up rapidly due to the fast reaction (3).

3. The oxygen permeability is inversely proportional to crosslink density. For a bulk binder, the oxidation of polybutadiene is very fast on the surface and leads to the quick formation of a hard "skin". This high density layer protects the binder beneath it from further oxidation by greatly reducing the oxygen permeability.

The investigation of the efficiency of antioxidants in HTPB binder showed that:

1. Chain-breaking antioxidants are the most effective. Since the radicals, ROO·, RO· and R·, are the source of the chain crosslinking reaction, the efficiency of an antioxidant is dependent on the ability of the antioxidant to scavenge radicals. Generally, aromatic amines are the most effective antioxidants for HTPB binder. Only bis-phenols, like 2246 and WSP, can compete with aromatic amines, such as, IPPD, Flectol H and DMDP, DPPD.

2. In contrast to the nitroxyls of IPPD and Flectol H, DMDP-NO·, the nitroxyl of DMDP, shows a better performance than its precursor DMDP.

3. The lowest gel increase rate was obtained when not only the trapping of radicals was considered but also the destroying of the hydroperoxides formed during the binder oxidation. In reaching this aim, it was found that the ratio of chain-breaking antioxidant to peroxide decomposer is very important. The combination of IPPD with DLTP, in a ratio of 2:1, shows a synergistic effect, but in a ratio of 1:2, gives an antagonistic effect.

5.2. Suggestions for Further Work

The investigation results in this work suggest that the shelf time of HTPB composite propellant may be improved by considering the following:

(1) reducing the content of 1,2-vinyl group and the content of cis-1,4 double bond in HTPB molecular chain ;

(2) storing propellant in an inert gas environment, e.g., CO_2 or N_2;

(3) a better understanding of the effect of physical factors on antioxidant activity and examination of nature and role of antioxidant transformation products during curing and ageing should lead to developing better antioxidant systems.

The antioxidant solubility in polybutadiene needs to be considered. Both IPPD and Flectol H do not dissolve well in the binder at room temperature, but can be dissolved completely at a higher temperature. The advantage of DMDP and DMDP-NO· is that they are soluble in the binder. This means that they do not bloom at low temperature and can be used at a higher concentration. The synergistic effect of the combination of DMDP-NO· with other antioxidants seems possible and is worth exploring.

4,4'-thiobis(2-tert-butyl-5-methylphenol) has shown a synergistic effect when used in a combination with IPPD. This result gives the idea that it is worth investigating other antioxidants, e.g. 2.2'-thiobis(4-methyl-6-tert-butylphenol). It is likely that a better performance than 2246 can be achieved if it is used in a proper combinaton.

Since chain-breaking antioxidants are very effective in the binder, a system in which a chain-breaking antioxidant can be regenerated can be considered, for example, IPPD with 2,6-dialkylphenol. It was suggested that [86] in a mixture of a strong antioxidant and a weak one, a co-operative mechanism operates involving BQDI, the transformation products of IPPD, to regenerate IPPD (reaction 5.1).

5.1
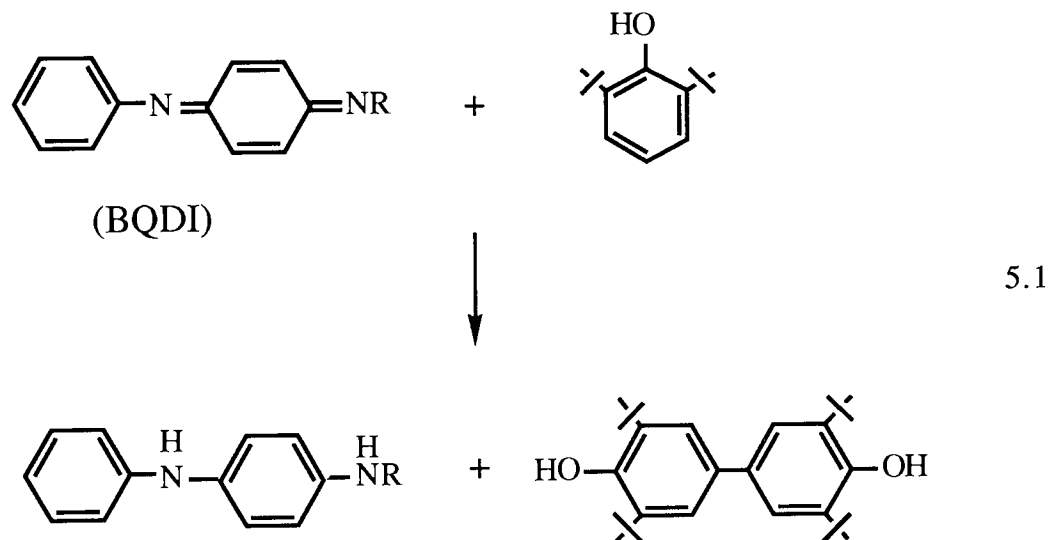
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Appendix

Calculation Programm for the Composition of Double Bonds

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10    READ A1, A2, A3, A4, A5, A6, V1, V2, T1, T2, D1
11    Y=A1+A2+A3+A4+A5+A6
12    Y1=A1/Y
13    Y2=A2/Y
14    Y3=A3/Y
15    Y4=A4/Y
16    Y5=A5/Y
17    Y6=A6/Y
18    PRINT Y1, Y2, Y3, Y4, Y5, Y6
20    FOR V=V1 TO V2 STEP .001
30    FOR T=T1 TO T2 STEP .001
40    C=1-V-T
50    B1=V^2/2*T/(1-V)
60    B2=V*T/2
70    B3=C/2*V/(1-V)+C*V/2+T
80    B4=C-V*C/2
90    B5=V/2*T/(1-V)
100   B6=C/2*V/(1-V)
110   D=(B1-Y1)^2+(B2-Y2)^2+(B3-Y3)^2+(B4-Y4)^2+(B5-Y5)^2+(B6-Y6)^2
120   IF D>D1 THEN 170
130   IF D<D1 THEN 140
140   D1=D
145   LPRINT D,V,T,C
146   PRINT D,V,T,C
150   IF D=D1 THEN 161
161   PRINT D,V,T,C
162   LPRINT D,V,T,C
170   NEXT T
180   NEXT V
210   B1=V^2/2*T/(1-V)
220   B2=V*T/2
```

```
230   B3=C/2*V/(1-V)+C*V/2+T

240   B4=C-V*C/2

250   B5=V/2*T/(1-V)

260   B6=C/2*V/(1-V)

270   PRINT B1, B2, B3, B4, B5, B6

280   LPRINT Y1, B1, Y2, B2, Y3, B3, Y4, B4, Y5, B5, Y6, B6

290   END

300   DATA
```