To my mother and to the

memory of my father

Some aspects of the oxidative stability of cis-1,4-polyisoprene vulcanizates

by

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Summary

The oxygen absorption technique has been used to determine the thermal oxidative behaviour of vulcanizates prepared from unstabilized cis-1,4-polyisoprene. Initially the effect of specimen thickness was investigated to ensure that diffusion controlled oxidation did not occur during the course of the oxygen uptake measurements.

A comparison of several types of sulphur vulcanizates indicated that an efficiently cured system, other than that based on a sulphur donor-sulphurless system, possessed outstanding oxidative stability. This was found to be largely due to an extractable antioxidant formed in situ during the curing process. The antioxidant was identified and its modes of action were deduced by model oxygen absorption studies. The latter involved the oxidation of cumene, in the presence of the antioxidant, initiated by free radicals generated from $\alpha\alpha'$-azodi-isobutyronitrile and benzoyl peroxide and also by the addition of cumene hydroperoxide. Additional data obtained from analysis of the hydroperoxide decomposition products served to define the action of the antioxidant more precisely.

A comparison of the oxidative characteristics of solvent extracted vulcanizates showed that the efficiently cured network retained a superior degree of stability. The sequential pro- and antioxidant effects displayed by the more conventionally cured sulphur vulcanizates were absent and an induction period towards oxidation was noted. The feature responsible for this stability was examined.

Acknowledgements

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1. Introduction

The oxidative behaviour of rubber vulcanizates depends primarily on four factors:

(i) the type of rubber,

(ii) the type and extent of vulcanization,

(iii) the presence of antioxidants,

and (iv) the purification after cure.

The oxidative degradation of polyisoprene sulphur vulcanizates involves both main chain and cross-link scission,[1,2] the extent of the latter depending on the ease by which the main chain is oxidised.

1.1 Oxidative degradation of cis-1,4-polyisoprene

Autoxidations of non-conjugated olefins at moderate temperatures and to small extents of oxygen absorption have the following features:[3,4]

(a) hydroperoxides are the main products,

(b) the reaction is autocatalytic due to the formation of hydroperoxides,

(c) a free radical chain mechanism is generally accepted,

and (d) the rate of oxidation is largely independent of oxygen concentration and pressure above 50 mm. The rate of oxidation, however, depends on the structure of the olefin. The greater the lability of an alpha-methylenic atom the greater the rate.

The basic autoxidation scheme is shown below, (1.1)-(1.5). For polyisoprenes and 1,5-dienes at low extents of oxidation, the main product is a peroxide which contains both cyclic and hydroperoxide groups. Bolland and Hughes[5] have studied the thermal oxidation of squalene, (trans-hexaisoprene), and conclude that the product formed in the early stages of oxidation is a diperoxide, (I),

Initiation: production of R$\cdot$ (1.1)

$$2\ ROOH \longrightarrow RO_2\cdot + RO\cdot + H_2O \qquad (1.2)$$

Propagation:

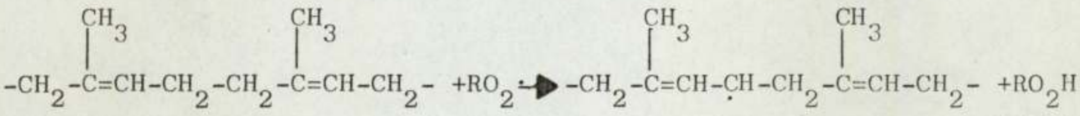
$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (1.3)$$

$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot \qquad (1.4)$$

Termination:

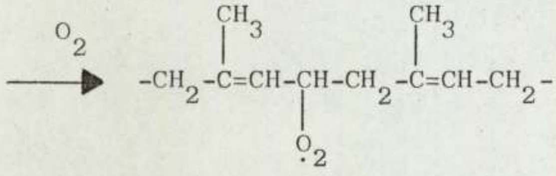
$$\left.\begin{array}{r} R\ + RO_2\cdot \\ 2RO_2\cdot \longrightarrow \\ 2R \end{array}\right\} \begin{array}{l} \\ \text{non-chain} \\ \text{carriers} \end{array} \qquad (1.5)$$

in which two atoms of oxygen are combined in a hydroperoxide group and two form an intramolecular peroxide ring according to the sequence (1.6)-(1.10).

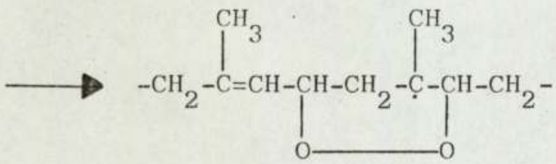


$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- + RO_2\cdot \longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- + RO_2H$$

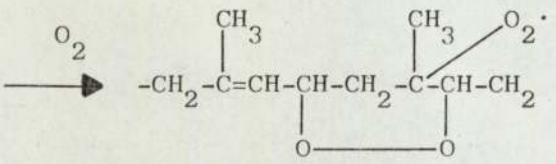
(1.6)



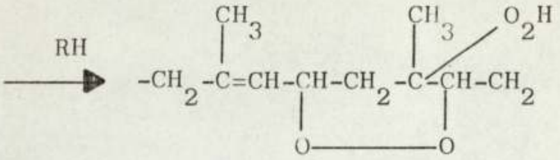
$$\xrightarrow{O_2} -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{\cdot O_2}{|}}{CH}-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \qquad (1.7)$$



$$\longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{O}{|}}{CH}-CH_2-\overset{CH_3}{\overset{|}{\dot{C}}}-\underset{\underset{O}{|}}{CH}-CH_2- \qquad (1.8)$$



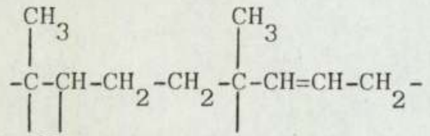
$$\xrightarrow{O_2} -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{O}{|}}{CH}-CH_2-\overset{CH_3\ \ O_2\cdot}{\overset{|\ \ /}{C}}-\underset{\underset{O}{|}}{CH}-CH_2 \qquad (1.9)$$



$$\xrightarrow{RH} -CH_2-\overset{CH_3}{C}=CH-\underset{O}{CH}-CH_2-\overset{CH_3}{C}-\overset{O_2H}{\underset{O}{CH}}-CH_2 \qquad (1.10)$$

I

The most noticeable feature of the effect of oxygen on natural rubber is the reduction in molecular weight. The exact nature of the chain scission reaction has not been conclusively identified however. Bevilacqua[6-14] has carried out a programme of work concerning the identification of volatile products and chemical entities produced from natural rubber oxidation. The primary products per scission event are one molecule of levulinaldehyde and two chain ends, one a ketone, the second an aldehyde. Bevilacqua proposed that the formation of these can be accounted for on the basis of breakdown of a hydroperoxide, (II), which is closely related to that proposed by Bolland and Hughes[5], formed by double bond rearrangement of the initially formed allylic radical, (1.6).

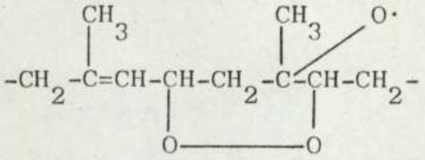


$$-\underset{O_2H}{\overset{CH_3}{C}}-\underset{O}{CH}-CH_2-CH_2-\underset{O}{\overset{CH_3}{C}}-CH=CH-CH_2-$$

II

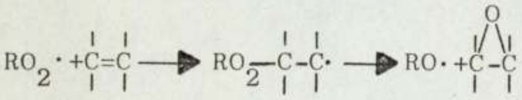
Tobolsky and Mercurio[15], however, have indicated that chain scission is unlikely to occur during the propagation stage of the autoxidation and instead favour a mechanism in which scission occurs during the termination step. The mechanism is based upon that proposed by Bolland and Hughes. First, alkoxy radicals are formed by breakdown of two alkyl peroxy radicals, (1.11), followed by breakdown of the alkoxy radicals, (III), resulting in chain scission.

$$2RO_2\cdot \longrightarrow 2RO\cdot + O_2 \qquad (1.11)$$



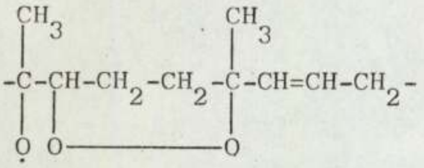
III

More recent investigations by Bell[16] support the view that scission occurs mainly in the propagation step of the reaction, scission during the termination step becoming important only in inhibited systems. The suggested propagation step leading to chain scission is similar to that proposed by Brill[17] in the autoxidation of mono-olefins, (1.12), and is supported by



$$RO_2\cdot + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow RO_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \longrightarrow RO\cdot + \overset{O}{\overbrace{\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}}} \qquad (1.12)$$

the identification of epoxides during the oxidation of model systems[2]. The alkoxy radicals, (IV), derived from this reaction breakdown by a series of reactions[2] to yield the observed scission products.



IV

1.2 The effect of vulcanizate structure on the oxidative stability of natural rubber (cis-1,4-polyisoprene) vulcanizates

The effects of oxidation on natural rubber vulcanizates have been studied by determining the changes in physical properties of test specimens, the method of stress relaxation[18-23], and by oxygen absorption measurements. Whilst the two former techniques are useful to the technologist a more fundamental understanding of the oxidation processes involved may be deduced from oxygen absorption data.

1.2.1 The oxygen absorption technique

The oxygen absorption method has become an acceptable means of evaluating the ageing characteristics of a rubber vulcanizate since a satisfactory correlation exists between the change in physical properties and the amount of oxygen absorbed. Shelton[24,25] has shown that the change in tensile strength and related physical properties of a high sulphur, low accelerator, black filled vulcanizate varies directly with the amount of oxygen absorbed. In addition, Pollack et al[26] have reported that the correlation between rates of oxygen absorption and the ~~detioration~~ deterioration of physical properties of natural and synthetic rubber vulcanizates is close enough to justify substitution of oxygen absorption measurements for standard ageing evaluation techniques. Providing that certain limitations are observed, particularly the effect of sample thickness[27], (section 3), informative data can be obtained. Three variations of the technique are available:

(a) gravimetric,

(b) manometric,

and (c) volumetric.

The first, the simple gravimetric technique involves the measurement of weight increase. This suffers from the disadvantage that small weight increases are difficult to measure accurately. The second measures the change in oxygen pressure at constant volume, whilst the volumetric technique involves a change in volume at constant pressure. Shelton[28] has stated that the volumetric technique is superior since the data obtained are more readily interpreted than with the manometric method. However, Duffraise[29] has pointed out that the manometric method, because of its simplicity and ease of operation, is extremely useful for routine comparative work. The limitation of pressure changes in the system may not be particularly restrictive if these are small since rates of oxidation are insensitive to changes of this magnitude[24,30-32]. Stafford[33] has carried out a series of oxygen absorption experiments on cured and uncured natural rubber. He reported that all sulphur vulcanizate networks can be described by a general three stage oxygen absorption curve consisting of an initial high absorption rate, an inflection rate, followed by a steady increasing rate of absorption. The magnitude and duration of each stage relative to the other two are greatly influenced by factors such as temperature of cure, degree of cure, and type of curing system. In other words, by the vulcanizate structure. Furthermore, McDonel and Shelton[34] proposed that the relative oxidation rates of natural rubber vulcanizates can be correlated qualitatively with the type of cross-link believed to be formed during the curing process. An advance in the understanding of this relationship was possible only after the structural characteristics of vulcanizates had been established.

1.2.2 The structural characteristics of natural rubber vulcanizates

The features present in natural rubber networks, particularly sulphurated systems, have been identified and estimated quantitatively where possible by workers at the Natural Rubber Producers Research Association, (NRPRA). A great deal of information has been acquired through studies involving model vulcanizate systems utilising 2-methylpent-2-ene and 2,6-dimethylocta-2,6-diene as models for cis-1,4-polyisoprene. The data ~~has~~ have been adequately reported elsewhere[35,36]. Whilst informative details may be obtained from such studies, a quantitative description of all the network features present in a vulcanizate, as suggested by the model studies, cannot be made at the present time. This applies in particular to specific main chain modifications such as cylic sulphides and conjugated unsaturation. The remaining features, i.e. monosulphidic cross-links, disulphidic cross-links, polysulphidic cross-links, pendent accelerator residues (mono, di and polysulphidic)[37-39] and the total combined sulphur[40-42] have been estimated quantitatively however. The type and concentrations of cross-links were estimated by determining the cross-link density of vulcanizate specimens[40,43-46] before and after treatment with chemical probes[40,47-49]. These are materials, soluble in the vulcanizate, that will cleave or modify specific types of cross-links.

The structural characteristics of the important types of natural rubber vulcanizates determined by these techniques are briefly discussed below and summarized in table 1.2. The corresponding vulcanizate recipes are given in table 1.1.

Table 1.1 Vulcanization recipes

Vulcanizate type	Natural rubber	Zinc oxide	Lauric acid	TMTD	CBS	S	DCP	Cure time (minutes)	Cure temp°C
Unaccelerated	100	5.0	-	-	-	10.0	-	420	140
TMTD sulphurless	100	5.0	1.5	4.0	-	-	-	420	140
EV	100	5.0	1.0	-	6.0	0.4	-	120	140
Semi EV	100	5.0	3.0	-	1.5	1.5	-	30	140
CBS Conventional	100	5.0	0.7	-	2.5	0.6	-	40	140
Peroxide cure	100	-	-	-	-	-	2.2	10*	100

TMTD - Tetramethyl thiaram disulphide

CBS - N-(cyclohexyl)-2-benzothiazyl sulphenamide

S - Sulphur

DCP - Dicumyl peroxide

EV - Efficient vulcanisation

* - Followed by 50 minutes at 150°C

Unaccelerated sulphur vulcanizates

Structurally these are very complex networks. The cross-links are mainly dialkenyl t-alkyl sulphides with long chains of sulphur atoms which progressively shorten to di and monosulphide as the cure time is extended. A large percentage, 75-95, of the combined sulphur is wasted as regards cross-linking by forming cyclic sulphide groups. Additional main chain modifications occur in the form of conjugated unsaturation. The efficiency of vulcanization, the number of sulphur atoms combined in the network per chemical cross-link formed, is of the order of forty to fifty[50].

TMTD sulphurless vulcanizates

Initially a complex network is formed which becomes simpler in structure as cross-linking proceeds. At the maximum cross-link level ninety per cent of the cross-links are monosulphidic, no polysulphidic cross-links are present and about two-thirds of the total combined sulphur is in main chain modifications, mainly as pendent accelerator groups[51]. Small amounts of cylic monosulphides and conjugated dienes and trienes are also present. As cross-linking proceeds the anti-oxidant zinc dimethyldithiocarbamate is formed.

EV vulcanizates

An efficiently vulcanized network, similar to that produced by the TMTD sulphurless system, can also be achieved from formulations involving synergistic combinations of accelerators or with low levels of elemental sulphur combined with high levels of accelerator[36,52,53]. In the fully cured network the majority of cross-links are monosulphidic and the efficiency of vulcanization at this stage is 3.9.

Semi-EV vulcanizates

Networks of improved vulcanization efficiency compared to the Conventional CBS systems can be obtained by use of equivalent concentrations of sulphur and accelerator, the so called Semi-EV systems. Unlike the EV networks a high proportion of polysulphide cross-links are present at the optimum cure level. On extended cure further monosulphidic and disulphidic cross-links are formed at the expense of a reduction in polysulphidic concentration. An efficiency of vulcanization at optimum cure of 5·8 has been reported[54].

CBS Conventional vulcanizates

Networks produced from conventionally accelerated systems are intermediate in complexity between TMTD sulphurless and unaccelerated sulphur vulcanizates. At the optimum cross-link level seventy per cent of cross-links are polysulphidic, the remainder being equal amounts of di and monosulphides. A significant amount of unsaturation is formed as main chain modifications and the efficiency of vulcanization is 13[36,55].

Peroxide vulcanizates

Peroxide cured networks are structurally the most simple type of vulcanizate. Vulcanization with dicumyl peroxide gives a network consisting of dialkenyl carbon-carbon cross-links and some cyclic structures[36].

The oxygen absorption characteristics of natural rubber vulcanizates have been investigated by Bell and Cunneen[56] and an attempt has been made to describe their behaviour in terms of corresponding network structure.

Table 1.2 Structural features of sulphurated networks[54,56].

Type of vulcanizate	Cure time $140^{o}C$, minutes	Combined % sulphur	Chemical cross-links, g moles per g of RHC x 10^{5}			Sulphur not as cross-links, g moles per g of RHC x 10^{5}	Efficiency of vulcanization, E
			S_1	S_2	S_x		
Unaccelerated sulphur	420	5.57	1.0	1.0	3.44	146.0	40-50
TMTD sulphurless	420	0.35	3.3	-	-	8.6	2.0
EV	120	0.70	4.2	0.35	-	12.4	3.9
Semi-EV	30	-	(11)	(24)	(65)*	-	5.8
CBS Conventional	40	2.08	0.85	0.82	3.6	21.7	13.0
High Modulus CBS	40	3.01	1.27	1.23	5.4	32.5	-

RHC - Rubber hydrocarbon.

* - The number of each type of cross-link expressed as a percentage of the total.

1.2.3 Oxygen absorption characteristics of natural rubber vulcanizates

Investigations at the NRPRA, utilizing a volumetric absorption apparatus, indicate that the shape of the oxygen absorption curves of natural rubber vulcanizates depends on the type of network present. All vulcanizates were prepared from highly purified natural rubber in which indigenous materials known to possess antioxidant activity[21,56,57] were absent. In addition, vulcanizates were extracted after cure with a methanol/acetone/chloroform mixture to remove extra network materials[58].

A peroxide vulcanizate exhibits autocatalytic behaviour similar to that found for olefins and 1.5-dienes, whereas Conventional CBS and TMTD sulphurless vulcanizates initially oxidise more rapidly. After the absorption of about half weight per cent of oxygen the CBS accelerated system is no longer autocatalytic, the rate of oxidation now being lower than the peroxide vulcanizate. The TMTD sulphurless system continues to oxidise at the initial rate[56].

The high initial rates of oxidation of the sulphurated systems have been attributed to the presence of conjugated dienes and trienes formed during vulcanization. Model studies have shown that conjugated trienes do act effectively as pro-oxidants during squalene and peroxide vulcanizate oxidation[59], presumably by increasing the lability of methylenic hydrogen atoms. However, the series of pro-oxidant and antioxidant reactions observed by Stafford[33] and displayed typically by the Conventional CBS network has also been observed in a saturated polyolefin-sulphide system, indicating that factors other than the effect of unsaturation may, in part at least, be responsible for the high initial rates of oxidation of sulphur vulcanizates. Scott and Shearn[60] reported that the extent of the initial pro-oxidant effect observed during polypropylene oxidation in the presence of dilaurylthiodipropionate, (DLTP), depends on the initial concentration of monosulphide. A more pronounced pro-oxidant effect occurs in systems containing greater concentrations of DLTP. Investigations of the cumene hydroperoxide initiated autoxidation of cumene in the presence of dimethylthiodipropionate[61], (DMTP), again indicate the occurrence of an initial pro-oxidant reaction, the extent of which depends on the concentration of sulphide or more precisely the ratio of sulphide to hydroperoxide.

It would appear therefore that the extent of the pro-oxidant behaviour observed during sulphur vulcanizate oxidation may be related to the concentration of combined sulphur, or the concentration of sulphidic features capable of taking part in the series of reactions leading to the radical generating step. Van Amerongen[62] and Shelton[63] in fact have shown that the rate of initial oxygen uptake of natural rubber vulcanizates increases as the sulphur content increases.

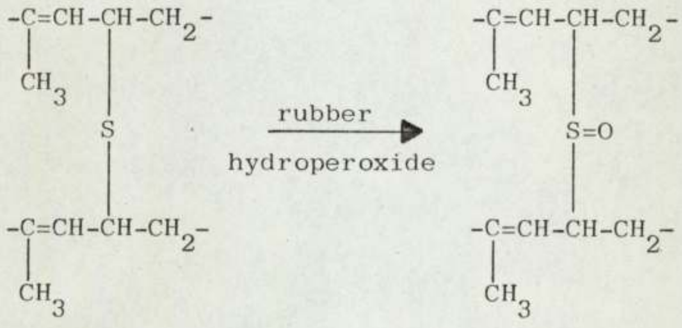
A redox reaction between sulphenic acid and hydroperoxide[64,65] has been suggested to account for the pro-oxidant behaviour of DMTP, the sulphenic acid being generated from decomposition of the sulphoxide[47,66-68], (1.13)-(1.15). The alkoxy radical can

$$(CH_3OCOCH_2CH_2)_2S + RO_2H \longrightarrow (CH_3OCOCH_2CH_2)_2SO + ROH \qquad (1.13)$$

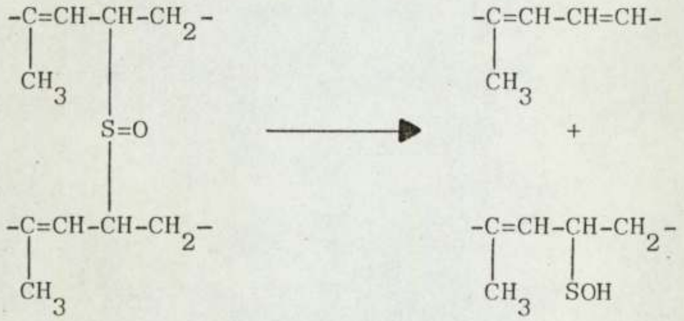
$$(CH_3OCOCH_2CH_2)_2SO \longrightarrow CH_3OCOCH_2CH_2SOH + CH_3OCOCH{=}CH_2 \qquad (1.14)$$

$$CH_3OCOCH_2CH_2SOH + RO_2H \longrightarrow CH_3OCOCH_2CH_2SO\cdot + RO\cdot + H_2O \qquad (1.15)$$

initiate oxidation whereas the more stable sulphinyl radical is removed by dimerization. An analogous series of reactions occurring in sulphur vulcanizates would account for their pro-oxidant behaviour. Colclough et al[47] reported that the oxidation of monosulphidic cross-linked, natural rubber networks involves the formation of sulphenic acid, further reactions leading to the formation of new cross-links containing two sulphur atoms, (1.16)-(1.19). A redox reaction between the sulphenic acid, (V),

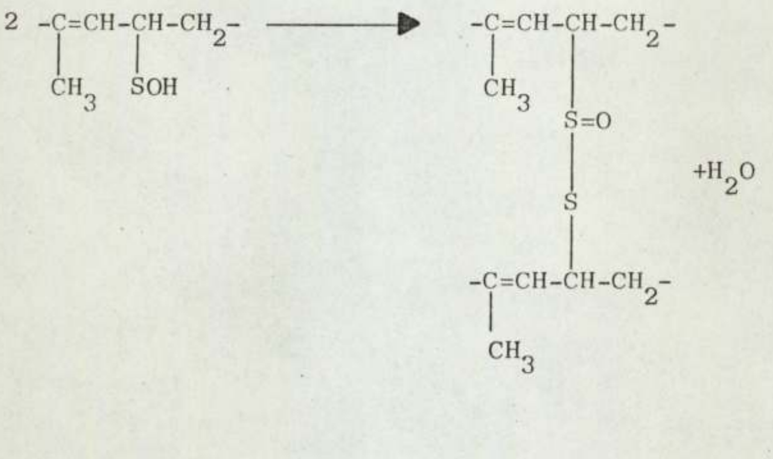


(1.16)

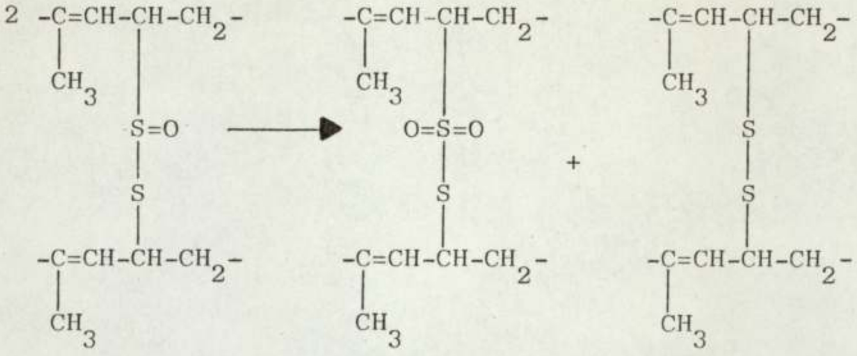


V

(1.17)



(1.18)



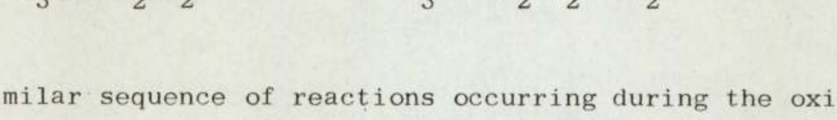
VI

(1.19)

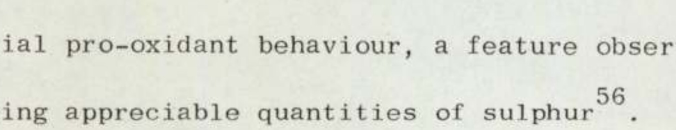
and rubber hydroperoxide would lead to the generation of initiating alkoxy radicals, the sulphinyl radicals giving thiolsulphonate cross-links, (VI), on dimerization.

The pro-oxidant effect observed during cumene autoxidation in the presence of DMTP is followed ultimately by strong autoinhibition resulting in the cessation of oxidation. It has been suggested that the effective peroxide decomposing antioxidant is sulphur dioxide or its further oxidation product sulphur trioxide, derived from desulphonylation of sulphonyl radical[61,65], (1.20)-(1.22).

$$CH_3OCOCH_2CH_2SOH + RO_2H \longrightarrow CH_3OCOCH_2CH_2\overset{\overset{O}{\|}}{S}\text{-}OH + ROH \qquad (1.20)$$



$$CH_3OCOCH_2CH_2\overset{\overset{O}{\|}}{S}\text{-}OH + RO_2H \longrightarrow CH_3OCOCH_2CH_2\overset{\overset{O}{\|}}{S}\text{-}O\cdot + RO\cdot + H_2O \qquad (1.21)$$



$$CH_3OCOCH_2CH_2\overset{\overset{O}{\|}}{S}\text{-}O\cdot \longrightarrow CH_3OCOCH_2CH_2\cdot + SO_2 \qquad (1.22)$$

A similar sequence of reactions occurring during the oxidation of sulphurated networks would result in marked inhibition following the initial pro-oxidant behaviour, a feature observed in networks containing appreciable quantities of sulphur[56].

Alternatively it has been suggested[56] that the inhibition is due to the sulphurated structures within the networks, particularly polysulphidic cross-links. These conclusions are based on data obtained from model studies involving the co-oxidation of organic sulphur compounds structurally related to cross-links and squalene, initiated thermally and by free radicals generated from αα'-azodi-isobutyronitrile, (AZBN)[69].

Dialkenyl and alkenyl alkyl monosulphides exert some inhibitory action in thermally initiated systems, the antioxidants being derived from oxidation of the monosulphides. Similarly dialkenyl and alkenyl alkyl disulphides possess some inhibitory power in thermally initiated systems. Organic polysulphides on the other hand exhibit chain terminating activity, confirmed by studies involving AZBN initiated systems.

Barnard et al[70] have studied the antioxidant activity of mono and disulphides and conclude that these function through the formation of their corresponding oxidation products, sulphoxide and thiosulphinate. In addition, the activity of the sulphur compounds was found to depend critically on the structure of the substituents. Bateman et al[71] extended the investigation and deduced that the antioxidant activity exhibited by sulphoxides and thiosulphinates was not due to a rapid reaction with hydroperoxide, but concluded that the primary source of inhibition was a result of molecular association between the sulphinyl compound and hydroperoxide. This feature, however, does not satisfactorily account for the observations that the most effective antioxidant promotes the decomposition of the hydroperoxide most readily and that high antioxidant activity is associated with thermal instability.

Armstrong and Scott[61,65] have investigated the effect of dimethylsulphinyldipropionate, (DMSD), on cumene hydroperoxide initiated autoxidations of cumene. In accordance with Bateman's findings involving squalene autoxidations, the addition of the sulphoxide to a system containing an equimolar or molar excess of hydroperoxide results in an immediate cessation of oxygen uptake. Even in the presence of an eighteen times molar excess of hydroperoxide the sulphoxide is effective. Thus, the suggestion that the mechanism of sulphoxide inhibition involves complex formation cannot be complete. Further spectral evidence[61] indicates that even in a system containing equimolar concentrations of sulphoxide and hydroperoxide there is sufficient free non-complexed hydroperoxide present to partake in initiating reactions.

It is not unlikely that the immediate cessation of oxidation in the presence of sulphoxide is associated with a kinetic chain breaking antioxidant derived from the sulphoxide since the addition of DMSD to cumene initiated by AZBN causes inhibition[61,65]. The behaviour of the sulphoxide differed from normal chain breaking antioxidants in that its effectiveness depended on the concentration added. These findings are contrary to those of Bateman[71] who indicated that di-t-butyl sulphoxide, an active sulphoxide, does not possess chain terminating activity. The chain terminating reaction suggested by Armstrong and Scott involves hydrogen atom abstraction from the sulphenic acid, (1.23), derived from the thermal decompostion of sulphoxide. Further

$$CH_3OCOCH_2CH_2SOH + RO_2\cdot \longrightarrow CH_3OCOCH_2CH_2SO\cdot + RO_2H \qquad (1.23)$$

supporting evidence was deduced from polymerization studies. Both the thermal and AZBN initiated polymerization of styrene is inhibited by DMSD[61,65].

The chain breaking antioxidant activity of organic polysulphides resembling sulphurated cross-links has recently been attributed to their reaction with chain propagating alkyl radicals[2], (1.24)-(1.25). The scheme is based on earlier work

$$R'S_3R' + R\cdot \rightarrow R'SR + R'S_2\cdot \qquad (1.24)$$

$$2R'S_2\cdot \rightarrow R'S_4R' \qquad (1.25)$$

R' - alkenyl

R - alkyl

produced by Pickering et al[72] involving a saturated trisulphide. The occurrence of reactions of this type in polysulphurated natural rubber networks is suggested as being responsible for the observed inhibition. However, the reaction of a hydrocarbon free radical, (R·), with oxygen is so fast relative to the additional propagation reactions, (1.7)-(1.10), that the concentration of R· is negligible, particularly in systems where diffusion of oxygen is not rate controlling. Thus it is difficult to reconcile the inhibiting behaviour of vulcanizates of higher sulphur content with this feature.

1.3 Antioxidants

Excellent texts and review articles are available that deal with the mechanisms of action of antioxidants in detail[73-82] and, therefore, only the essential features are described below.

1.3.1 Mechanisms of action of antioxidants

An examination of the basic autoxidation scheme, (1.1)-(1.5) reveals that an antioxidant may function via two distinct modes. First, by interfering with the initiation reaction (1.2) or secondly, by removal of the alkyl peroxy radicals that would otherwise continue the chain reaction. The latter mode of action has been investigated more thoroughly and a vast amount of data has been accumulated[73].

1.3.1.1 Suppression of the propagation reaction

The basic principle outlining the antioxidant activity of phenols is the removal of alkyl peroxy radicals from the system by a reaction analogous to the propagative reaction, (1.26). That is, the antioxidant, (AH), competes

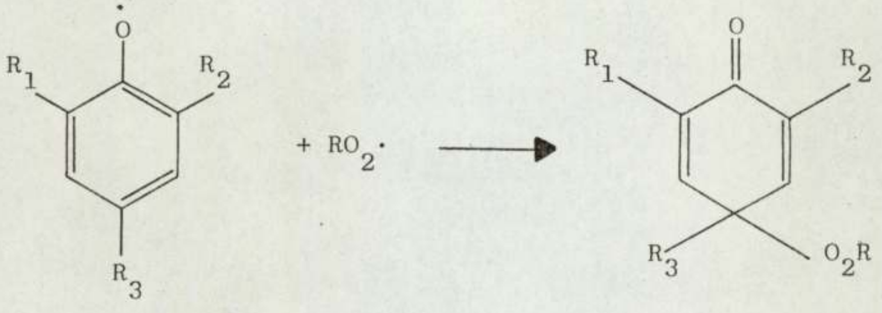
$$RO_2\cdot + AH \longrightarrow RO_2H + A\cdot \tag{1.26}$$

successfully with the substrate for alkyl peroxy radicals. An essential feature of the radical derived from the antioxidant is that it does not continue the chain sequence otherwise a retardation effect, not inhibition, would result. The stability of the phenoxy radical derived from a phenolic antioxidant[83] is increased to an optimum by the presence of bulky groups in the ortho position of the aromatic ring. This affords some protection to the phenoxy radical towards possible chain transfer with the substrate. In addition, electron releasing groups at the ortho and para positions increase the lability of the phenolic hydrogen atom and thus the antioxidant efficiency. Electron attracting groups on the other hand decrease activity. It is not surprising therefore that a correlation exists between a high antioxidant activity of phenols and a corresponding low oxidation-reduction potential[84]. A limiting factor of this dependence, however, is the direct attack on the phenolic hydrogen atom,[79] (1.27), which would

$$AH + O_2 \longrightarrow A\cdot + HO_2\cdot \tag{1.27}$$

result in destruction of the antioxidant not only by a non-inhibiting reaction but also by a potential chain initiating reaction.

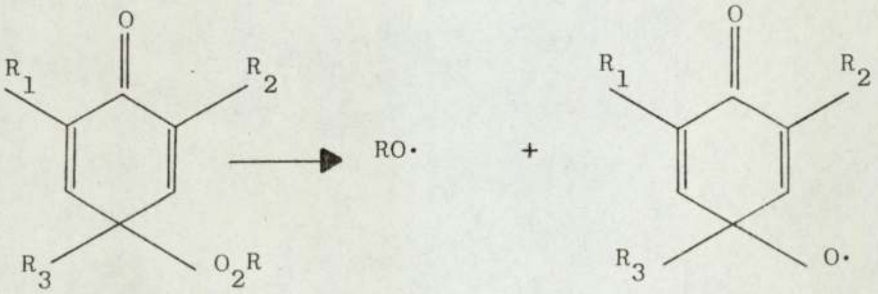
The phenoxy radical formed in reaction (1.26) may react further with an additional alkyl peroxy radical giving a peroxydienone, (VII), the extent of formation depending on the structure of the phenol[85], (1.28). At low temperatures



(1.28)

VII

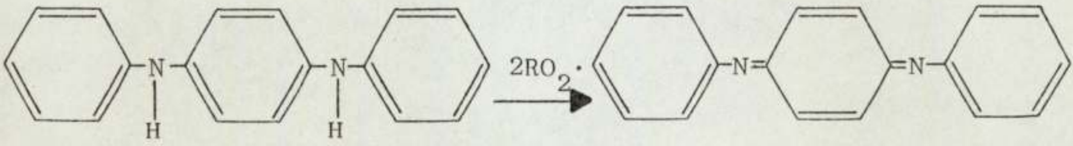
this is a fairly stable entity but at temperatures above 140°C decomposes rapidly to give radicals capable of initiating oxidation chains[79], (1.29). In addition, hydroperoxides



(1.29)

formed as indicated, (1.26), will dissociate and decrease further the effectiveness of the phenolic antioxidant at these elevated temperatures.

Secondary aromatic amines appear to function similarly to phenols. The product formed from N,N'-diphenyl-p-phenylene-diamine during inhibition of cumene oxidation was found to be consistent with the abstraction of both N-hydrogen atoms[86], (1.30).



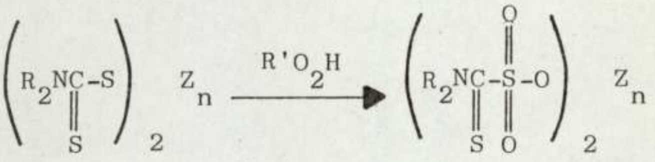
(1.30)

However, some t-amines have been shown to possess antioxidant activity[86,87] thereby illustrating that an N-hydrogen atom is not a necessary requirement. Thus, the prior formation of a complex between the inhibitor and a peroxy radical is envisaged followed by an interaction with a second peroxy radical to give stable products[73]. The relationship between structure and activity of amine antioxidants has not been investigated as thoroughly as phenolic compounds but in general the effects of substituents in the aromatic ring are similar. Electron releasing groups increase antioxidant activity whereas electron attracting groups reduce their effectiveness.

1.3.1.2 Suppression of the chain initiation reaction

Materials that promote the decomposition of hydroperoxides to form stable products rather than chain initiating free radicals may function as preventative antioxidants in polymers. Important antioxidants in this class are zinc dialkyldithiocarbamates, zinc dialkyldithiophosphates and dialkylthiodipropionates. Recent work had indicated that these are able to decompose hydroperoxides rapidly and catalytically by a predominantly non-radical mechanism[61,88-91]. In addition, zinc dibutyldithiocarbamate and zinc dialkyldithiophosphates have been shown to possess chain breaking antioxidant activity. Electron transfer mechanisms have been proposed to account for their behaviour[92-94].

The preventative mechanisms of antioxidant action have not been conclusively established but Scott has shown that dialkyldithiocarbamates and thiodipropionate esters exhibit an initial pro-oxidant effect during oxidation, the extent of which depends markedly on the molar ratio of hydroperoxide to sulphur compound[88,89]. At the end of the pro-oxidant stage a period of gas evolution occurs. In the case of the dithiocarbamate sulphur dioxide was identified as the major gaseous product. It was suggested that the reaction sequence involved the intermediate formation of an unstable sulphonate, (1.31), which is analogous to the formation of benzo-thiazole-2-sulphonic acid by oxidation of 2-mercaptobenzothiazole, and that like the latter it can break down thermally to give sulphur dioxide[88]. In addition, Chien and Boss[90] have indicated that the hydroperoxide decomposer formed from DLTP is gaseous or volatile, sulphur dioxide has been suggested. The latter is a powerful hydroperoxide decomposer functioning as a Lewis acid[61,90,95].



$$\left(R_2N\overset{}{C}(=S)-S\right)_2 Zn \xrightarrow{R'O_2H} \left(R_2NC(=S)-S(=O)_2-O\right)_2 Zn \qquad (1.31)$$

Burn[94] has suggested the formation of a co-ordination complex leading to non-radical hydroperoxide decomposition products to account for the preventative antioxidant action of dialkyldithiophosphates. More recently, Rossi and Imparata[96] have investigated the reaction between zinc di-isopropyldithiophosphate and cumene hydroperoxide and have established the formation of a basic zinc salt that undergoes further reaction to yield di-isopropylthiophosphoryl disulphide, di-isopropylphosphoryl disulphide, zinc sulphate and zinc oxide. The major oxidation product, di-isopropylthiophosphoryl disulphide, reacts further with cumene hydroperoxide via a radical mechanism giving the active hydroperoxide decomposer. The nature of the active antioxidant functioning by an ionic decomposition mechanism has not been established however.

In addition to antioxidants operating by the removal of hydroperoxides, a series of antidegradants are available that function by deactivating metal ions that would otherwise catalyse the free radical decomposition of hydroperoxides. The latter effect is well known and has been described in terms of a sequence of redox reactions[73,97,98], (1.32)-(1.33).

$$RO_2H + M^{n+} \longrightarrow RO\cdot + OH^- + M^{(n+1)+} \qquad (1.32)$$

$$RO_2H + M^{(n+1)+} \longrightarrow RO_2\cdot + H^+ + M^{n+} \qquad (1.33)$$

Strong reducing agents such as ferrous ion[99] will react according to (1.32), whereas strong oxidising agents such as ceric ion[100] will react according to (1.33). When the metal ion possesses two valency states of comparable stability such as cobalt, copper and manganese, then both reactions will occur and the effect of a trace quantity of the metal ion is to catalytically decompose the hydroperoxide[100,101]. The overall effect in an autoxidizing system is a more rapid rate of initiation compared to the uncatalysed bimolecular reaction (1.2).

The inhibition of metal catalysed autoxidations may be achieved by strongly complexing to the maximum co-ordination number or by stabilizing one valence state at the expense of others. This topic has been reviewed recently by Scott[73] and Hawkins[77].

1.3.2 Oxidation of conventionally stabilized natural rubber vulcanizates

A comparison of natural rubber vulcanizates freed from extra network materials, in the presence and absence of a conventional antioxidant, N-isopropyl-N'-phenyl-p-phenylenediamine, indicates that additional oxidative stability is conferred to all types of networks[56]. An additional prominent feature is the poor response towards the antioxidant in systems containing greater concentrations of combined sulphur. TMTD sulphurless, EV and Peroxide vulcanizates respond well to the antioxidant, whereas Unaccelerated sulphur and CBS Conventional networks do not. This behaviour has been attributed to an antagonistic effect of the sulphurated structures in the vulcanizates towards the anti-oxidant[56].

Evidence from oxygen absorption studies involving model compounds suggests that polysulphidic cross-links are mainly responsible for this effect. Dialkenyl trisulphides introduced into purified, natural rubber, Peroxide vulcanizates, in the presence and absence of conventional antioxidants, indicated a reduction in efficiency of the latter. Nevertheless, some degree of inhibition compared to control observations was observed in all cases. The effect therefore is not truly antagonistic but more precisely a reduction in efficiency of the antioxidant. Further evidence supporting the deleterious effect of polysulphidic cross-links was obtained from an investigation of conventionally stabilized vulcanizates varying in polysulphidic cross-link concentration but possessing very similar combined sulphur concentrations[1]. The system containing the greatest concentration of polysulphidic cross-links exhibited the poorest response to the antioxidant.

The mechanism of the effect has recently been associated with the homolytic scission of dialkenyl trisulphides[2,72] yielding chain initiating free radicals, (1.34). Whilst this

$$RS_3R \longrightarrow RS_3\cdot + R\cdot \qquad (1.34)$$

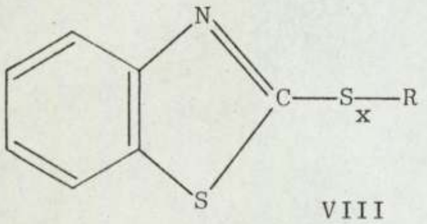
reaction does not provide a significant source of chain initiating alkenyl radicals in an uninhibited system, it does in a system in which the kinetic chain length of the autoxidation is short, that is, in the presence of an antioxidant. As a result the apparent efficiency of the antioxidant is reduced.

1.4 The effect of extra network materials on the oxidative stability of natural rubber vulcanizates

The oxidative characteristics of the vulcanizates discussed in section 1.2.3 concerned systems in which soluble vulcanization residues had been removed. Consequently the data obtained was related to the remaining sulphurated networks and not to other features in the vulcanization systems. The possibility of vulcanization residues modifying the oxidative stability of vulcanizates was pointed out by Shelton[34] and the most striking example of this behaviour is exhibited by the TMTD sulphurless system. The excellent thermal oxidative stability of the latter is drastically reduced following acetone extraction[102,103], that is, an effective antioxidant is removed. The main reaction product of TMTD was shown to be zinc dimethyldithiocarbamate,(ZDC), produced up to amounts of the order equivalent to seventy mole per cent of the original accelerator[51,104] at full cure. The formation of ZDC from TMTD vulcanization was first mentioned by Bedford and Sebrell[105] and its presence in natural rubber vulcanizates was substantiated by Clark et al[106] and Stiehler[107]. It has since been established that this compound is responsible for the thermal oxidative stability of the TMTD sulphurless vulcanizate[102,103].

More recently, it has been shown that the extractable extra network materials produced in cis-1,4-polyisoprene, sulphurless vulcanizates cured with di-isopropylthiophosphoryl disulphide impart thermal oxidative stability, the extent of which depends critically on the cure time[65,108]. An optimum effect is observed, the greatest stability corresponding to the maximum conversion of the accelerator to the active antioxidant zinc di-isopropyldithiophosphate.

The presence of specific accelerator residues in the more conventionally cured systems has been established by Clark et al[106] and Zeide[109]. Clark obtained X-ray diffraction data indicating the formation of dibenzothiazyl disulphide, (MBTS), and zinc benzothiazole-2-thiolate, (ZMBT), in systems accelerated with 2-mercaptobenzothiazole, (MBT). More recently Favre[110] also demonstrated the presence of zinc salts of MBT in vulcanizates accelerated with MBT. Two distinguishable zinc compounds were identified, one the normal zinc salt extracted with benzene and secondly, a basic salt formed by hydrolysis of the former. This was extracted with pyridine. Campbell and Wise[111] investigated the fate of the curing system during the vulcanization of natural rubber accelerated with derivatives of MBT. The extra network materials produced include MBT, MBTS, dibenzothiazyl polysulphide, a zinc salt of MBT and an extractable pendent group given the structure (VIII), where R is derived from the hydrocarbon backbone. Model compound studies[112] simulating vulcanization with a system comprising CBS, sulphur, zinc butyrate and diphenyl methane have established the formation of ZMBT, MBT and 2-(N-cyclohexylamino)-benzothiazole as some of the residues of vulcanization.



VIII

The effects of these accelerator residues on the thermal oxidative stability of vulcanizates has not been investigated but Shelton[63] has suggested that CBS, or its vulcanization products, possess antioxidant properties characterized by lower rates of oxygen uptake for systems cured with higher concentrations of accelerator. Furthermore, Baxter et al[113] noted that stocks cured with MBT gave superior thermal oxidative stability compared to diphenylguanidine and thiaram accelerated sulphur vulcanizates. Brooks[114] has suggested that this is due to the presence of a zinc salt of the accelerator since Montu[115] has reported that zinc salts of MBT are deactivating agents for peroxides, although no evidence appears to have been put forward to justify this claim.

1.5 Objectives of the present work

Initial observations in these laboratories[65] indicate that vulcanization residues play an important role in determining the oxidative behaviour of accelerated polyisoprene vulcanizates. In particular, efficiently vulcanized systems, (EV), other than that based on the sulphur donor-sulphurless system[52], exhibit high thermal oxidative stability. Even after removal of soluble extra network materials the EV vulcanizate retains a degree of stability far in excess of other sulphurated systems, so much so that the features discussed previously, (section 1.2), appear to be inadequate in explaining this behaviour.

Following an initial comparison of the oxidative stabilities of EV and other sulphurated, polyisoprene vulcanizates, the investigations described in this thesis were undertaken to establish the nature of the extractable antioxidant(s) formed in the EV system during the curing process. In addition, the oxidative behaviour of the solvent extracted EV network was examined to ascertain the feature(s) responsible for its excellent ageing.

2. Experimental methods

2.1 Materials

2.1.1 Cis-1,4-polyisprene

Cis-1.4-polyisoprene, (NATSYN 2200), was supplied by Goodyear Ltd. The polymer was manufactured by a Ziegler-Natta polymerization process giving a cis content of 96 per cent[116]. A technical specification of the material is shown in table 2.1. Prior to compounding all NATSYN was extracted with methanol to remove the phenolic antioxidant, (0.75%)[117]. Two hundred grammes of the polymer were sheeted out on a cold mill, rolled loosely in aluminium foil and placed in a soxhlet extractor. The polymer was continuously extracted with hot methanol under a nitrogen atmosphere for 24 hours, dried under vacuum and stored at -20°C until required.

Polymer type	Cis-1,4-polyisoprene
Specific gravity	0.91
Mooney viscosity, ML4' at 212°F	80-100
Antioxidant	Non-staining, non-discolouring
Ash content	0.35 per cent
Colour	Light
Storage stability	Excellent

Table 2.1 Raw polymer properties of NATSYN 2200

2.1.2 Normal zinc benzothiazole-2-thiolate, (ZMBT)

ZMBT was prepared according to the method of Spacu[118-120]. 4.6 grammes, (0.025 moles), of anhydrous zinc acetate, (previously dehydrated by refluxing in the presence of acetic anhydride), were dissolved in 35 mls of pyridine, (fractionally distilled and stored over potassium hydroxide). This solution was added whilst stirring to a solution of 2-mercaptobenzothiazole, 8.4 grammes (0.05 moles), in 15 mls of pyridine. Addition of 40-60 petroleum ether gave a yellow solid which was recrystallized from pyridine, washed with petroleum ether and dried under vacuum at 50°C. The yield of the dipyridine complex was 6.5 grammes, (47.5%). M.pt. 153-154°C (155-156°C)[119].

The pyridine complex was heated under vacuum at 120°C to constant weight giving the normal zinc salt. The weight loss on heating was 29%, (calculated for 2 moles of pyridine 28.4%).

Found: C,41.9; H,2.1; N,7.0; S,32.2

Calculated for $C_{14}H_8N_2S_4Zn$: C,42.3; H,2.0; N,7.0; S,32.2

The compound was stored in a desiccator and manipulated in a dry box.

2.1.3 Zinc oxide, (Amalgamated Oxides Ltd)

Zincola zinc oxide was used without further purification.

2.1.4 Sulphur, (Anchor Chemical Co)

Sulphur type D was used without further purification.

2.1.5 Lauric acid

Recrystallized from ethanol. M.pt. 42°C (44°C)[121].

2.1.6 Dicumyl peroxide, (Hercules Powder Co)

Recrystallized from ethanol. M.pt. 38.5-39.5°C (39°C)[122].

2.1.7 N-(cyclohexyl)-2-benzothiazyl sulphenamide, CBS, (Monsanto Chemicals Ltd)

Recrystallized from isopropanol. M.pt. 102°C (103-104°C)[123].

2.1.8 Tetramethyl thi~~a~~uram disulphide, TMTD, (Monsanto Chemicals Ltd)

Recrystallized from chloroform. M.pt. 149.5-150.5°C (151°C)[123].

2.1.9 2-Mercaptobenzothiazole, MBT, (Monsanto Chemicals Ltd)

Recrystallized from methanol. M.pt. 179°C (177-179°C)[124].

2.1.10 N-(t-butyl)-2-benzothiazyl sulphenamide, BBS, (Monsanto Chemicals Ltd)

Recrystallized from methanol. M.pt. 110°C (108)[125].

2.1.11 αα'-Azodi-isobutyronitrile, AZBN, (Koch-Light Ltd)

Recrystallized from ether. M.pt. 104°C (103-104°C)[126].

2.1.12 Cumene hydroperoxide, CHP, (Koch-Light Ltd)

Purified via the sodium salt according to the method of Kharash[127]. It was vacuum distilled and the fraction boiling at 52-55°C/0.01-0.1 mm collected. Iodometric titration[128] gave values of purity within 98-100%. (B.pt. 60°C/0.2 mm)[129].

2.1.13 Cumene

Technical grade cumene was washed four times each with concentrated sulphuric acid, water, 10% sodium carbonate solution, and finally water. The cumene was dried with magnesium sulphate, transferred to a round bottomed flask and fractionally distilled from phosphorus pentoxide. The fraction boiling at 151-152°C was collected, (152.39°C/760 mm)[130]. Fractionation was carried out under nitrogen previously passed through a column containing molecular sieves, (Linde type 5A). The collected fraction was passed through an activated alumina column to remove oxidation products and then stored in a well stoppered flask at -10°C.

2.1.14 Chlorobenzene

Fractionated from phosphorus pentoxide, the fraction boiling at 132°C was collected (131.7°C)[130].

2.1.15 Phenol

Fractionally distilled, the fraction boiling at 82°C was collected.

M.pt. 40-41°C (40.9°C)[130].

2.1.16 α,α-dimethylbenzyl alcohol

Fractionally distilled, the fraction boiling at 202°C was collected and recrystallized from 60-80 petroleum ether. M.pt. 33°C (36°C)[131].

2.1.17 α-methylstyrene

Fractionally distilled, the fraction boiling at 165°C was collected. (167-170°C)[124].

2.1.18 Acetophenone

Fractionally distilled, the fraction boiling at 202°C was collected. (202°C/760mm)[130].

2.1.19 Benzoyl peroxide

Dissolved in chloroform and precipitated by adding methanol. The precipitate was washed with methanol followed by petroleum ether. M.pt. 105-106°C (106-107°C)[132].

2.1.20 Analar reagents

The following reagents were used without further purification:

a) zinc sulphide
b) stannous chloride
c) ferrous ammonium sulphate
d) 1,1,1-trichloroethane
e) acetone
f) petroleum ether, (30-40) and (60-80)
g) benzene
h) chloroform
i) glacial acetic acid
j) n-heptane
k) iodobenzene.

All melting points are uncorrected.

2.2 Equipment and apparatus

2.2.1 Spectroscopy

Infra-red spectra were recorded using a Perkin-Elmer model 457 grating spectrophotometer, (4000-250 cm^{-1}). All crystalline solids were examined in the form of potassium bromide discs, solutions in potassium bromide cells with Teflon spacers, and vulcanizate films employing the magnetic sample holder attachment.

Visible and UV spectra were recorded using the Pye-Unicam model SP700 and Perkin-Elmer model 350 instruments. Matched quartz cells were used of path length 1 cm.

2.2.2 Gas-liquid chromatography, (g.l.c)

Analysis was carried out on a Perkin-Elmer model F-30 instrument. A flame ionisation detector was used and nitrogen was employed as the carrier gas at a flow rate of 30 mls per minute. The column was a 2 metre, stainless steel, $\frac{1}{8}$ inch O.D, packed with 10% ethylene glycol adipate on AW-DMCS Chromasorb W, (60-80 mesh).

2.2.3 Column chromatography

A glass column, 2 cms diameter x 38 cms long, was packed with aluminium oxide, 100-240 mesh, neutral CAMAG, supplied by Hopkin and Williams. The alumina was previously activated by heating at 200°C overnight.

The column was charged with a suspension of the alumina in 60-80 petroleum ether and allowed to settle, leaving a space of about 15 cms at the top of the column. A layer of ballotini beads, (No 15), was placed at the top of the column to prevent disturbance on addition of the sample and solvent.

2.24 Dry box

The manipulation of pure normal ZMBT was carried out in a two compartment, gloved dry box manufactured by SLEE (London). Trays of calcium chloride and phosphorus pentoxide were kept in both compartments. The phosphorus pentoxide was changed regularly.

2.2.5 The Monsanto oscillating disc rheometer

The mechanical portion of the rheometer consists of a biconical disc embedded in the compound specimen contained in a cavity. The cavity and sample are heated electrically and the temperature maintained to within ± $0.5^{o}C$. The dies which form the cavity are held together by the ram of a pneumatic cylinder. The disc oscillates sinusoidally through an amplitude of ± 1,3 or 5 degrees of arc. Oscillatory motion is accomplished by a motor driven eccentric. The shaft of the disc is connected to the eccentric by a torque transducer which registers the force required to oscillate the disc and thus apply a shearing strain to the rubber specimen.

The data is graphically presented on a flat bed recorder. The rheometer may be operated at a high or low frequency, 750 or 3 cycles per minute. The more popular method of recording the cure curve is when the rheometer operates at the higher frequency. In this case, continuous smooth curves are obtained, giving a measure of a dynamic shear modulus as a function of cure time. As vulcanization within the specimen takes place the shear modulus increases.

These curves enable the curing characteristics of a compound to be assessed quickly and easily, in particular, time to the desired extent of cure, time before the onset of cure, the rate of cure and the degree of cure.

2.2.6 Apparatus for oxygen absorption measurements of vulcanizates

The oxygen absorbed by vulcanizate samples was followed continuously and automatically using the apparatus shown diagrammatically in figures 2.1 and 2.2. The absorption flask was a modified pyrex test tube of approximate total volume 100 mls. with a B24 quickfit socket

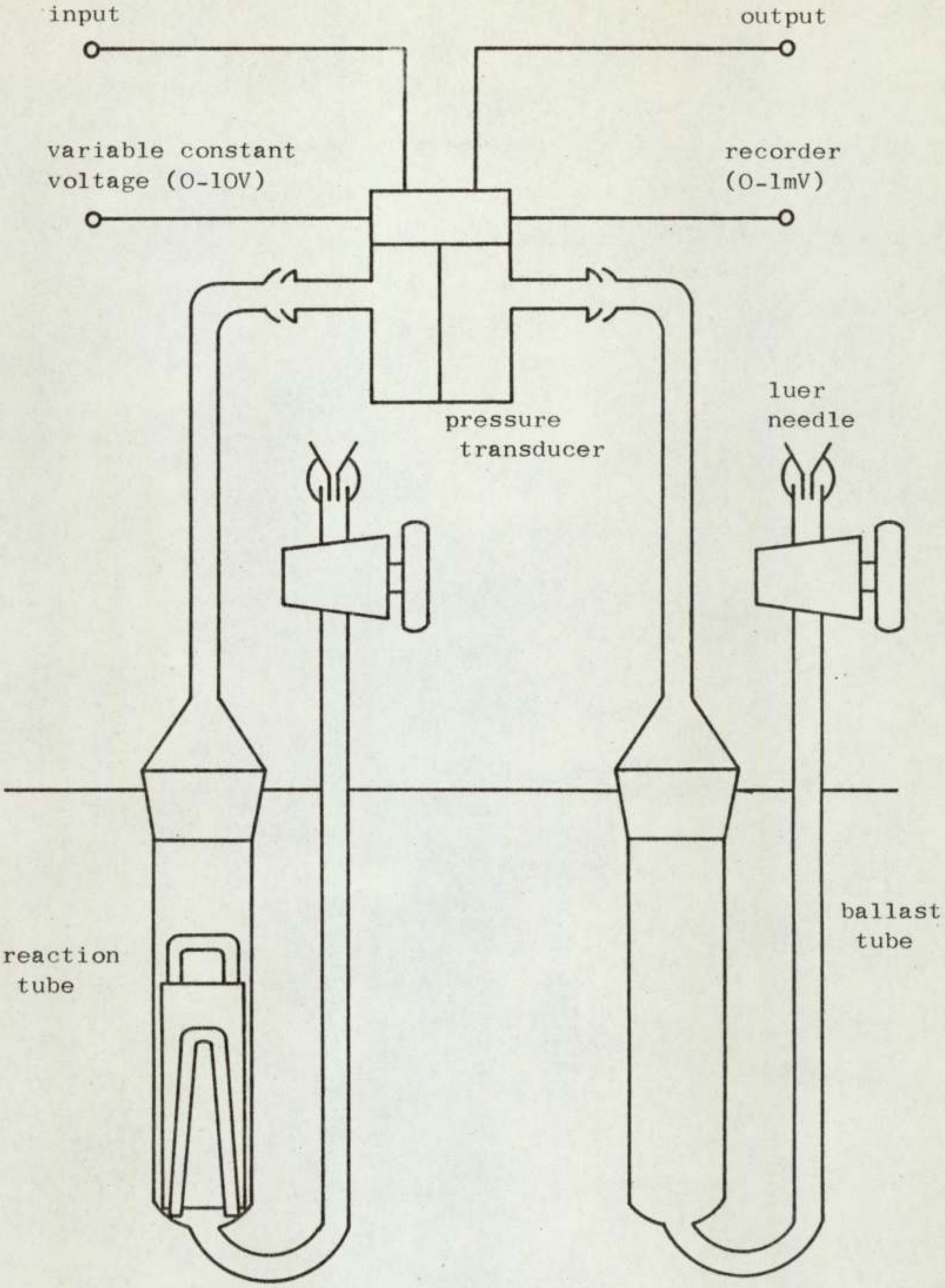


Figure 2.1
Vulcanizate absorption apparatus

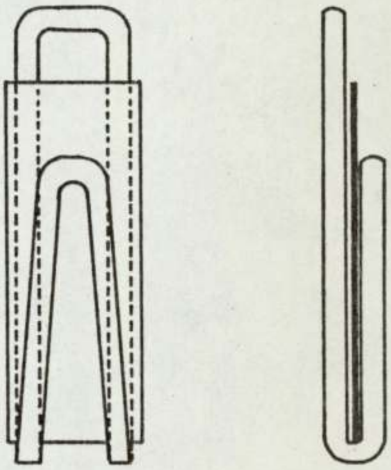


Figure 2.2 Front and side elevation of vulcanizate specimen and glass support

and cone attachment. The arm fitted to the test tube contains a luer needle cemented in at the opening. This allowed the flask to be purged with oxygen prior to absorption measurements and for calibration of the equipment. The absorption vessel was connected by glass tubing to the wet side of the pressure transducer via a ball and socket joint. The dry side of the transducer was connected to a ballast vessel of similar dimensions to the absorption vessel. Both vessels were placed side by side in a thermostatted oil bath, (± 0.05°C). Capillary tubing was used for connections outside the bath and the distance was kept small so that the total volume of the apparatus not thermostatted was negligible.

Any pressure difference between the reaction vessel and the ballast vessel is proportional to the output voltage of the transducer and this was monitored using a Perkin-Elmer model 165 millivolt recorder. Thus, as oxygen was absorbed by the contents of the reaction vessel the pressure difference between the two vessels became greater and the voltage output from the transducer was correspondingly greater. The transducer was a strain gauge type manufactured by Pye-Ether Ltd, model U.P.3., ± 5 p.s.i. range. The size of the output voltage is proportional to the input voltage, so by varying the input voltage the sensitivity of the transducer to pressure fluctuations can be varied. The magnitude of the input voltage and the quantity of specimen were optimized such that a one weight per cent absorption of oxygen by the latter produced almost a full scale deflection on the recorder. Under these conditions reproducibility between duplicate specimens was obtained, (section 2.4.1.1).

2.2.7 Apparatus for oxygen absorption measurements of cumene solutions[61]

The reaction vessel was a 50 mls, three necked, quickfit round bottomed flask fitted with a luer needle/tap attachment. The apparatus is shown diagrammatically in figure 2.3. To one neck of the flask a tube crushing device is fixed, (figure 2.4), and this allows the additive to be introduced at will to an autoxidizing solution. The solution was stirred with a magnetic follower sheathed in glass. The quantity of oxygen absorbed by the autoxidizing solution was monitored automatically as described in section 2.2.6.

2.3 Preparation of vulcanizates

All vulcanizates were prepared from the same bale of NATSYN 2200.

2.3.1 Compounding

Purified NATSYN and compounding ingredients were mixed on a 12 inch, water cooled, laboratory mill. A friction ratio of 1:1 was employed. If sulphur was included in the compound formulation then this was added after all other ingredients had been successfully incorporated. Compounds were prepared according to the formulations given in table 2.2. The total compounding time for each system was five minutes. The vulcanization characteristics of the compound were determined using the Monsanto oscillating disc rheometer, (section 2.2.5), operated according to the following conditions:

a) amplitude of oscillation	3^{o}
b) frequency of oscillation	750 cycles per minute
c) pre-heat time	60 seconds
d) torque range	0-100 in.lb.

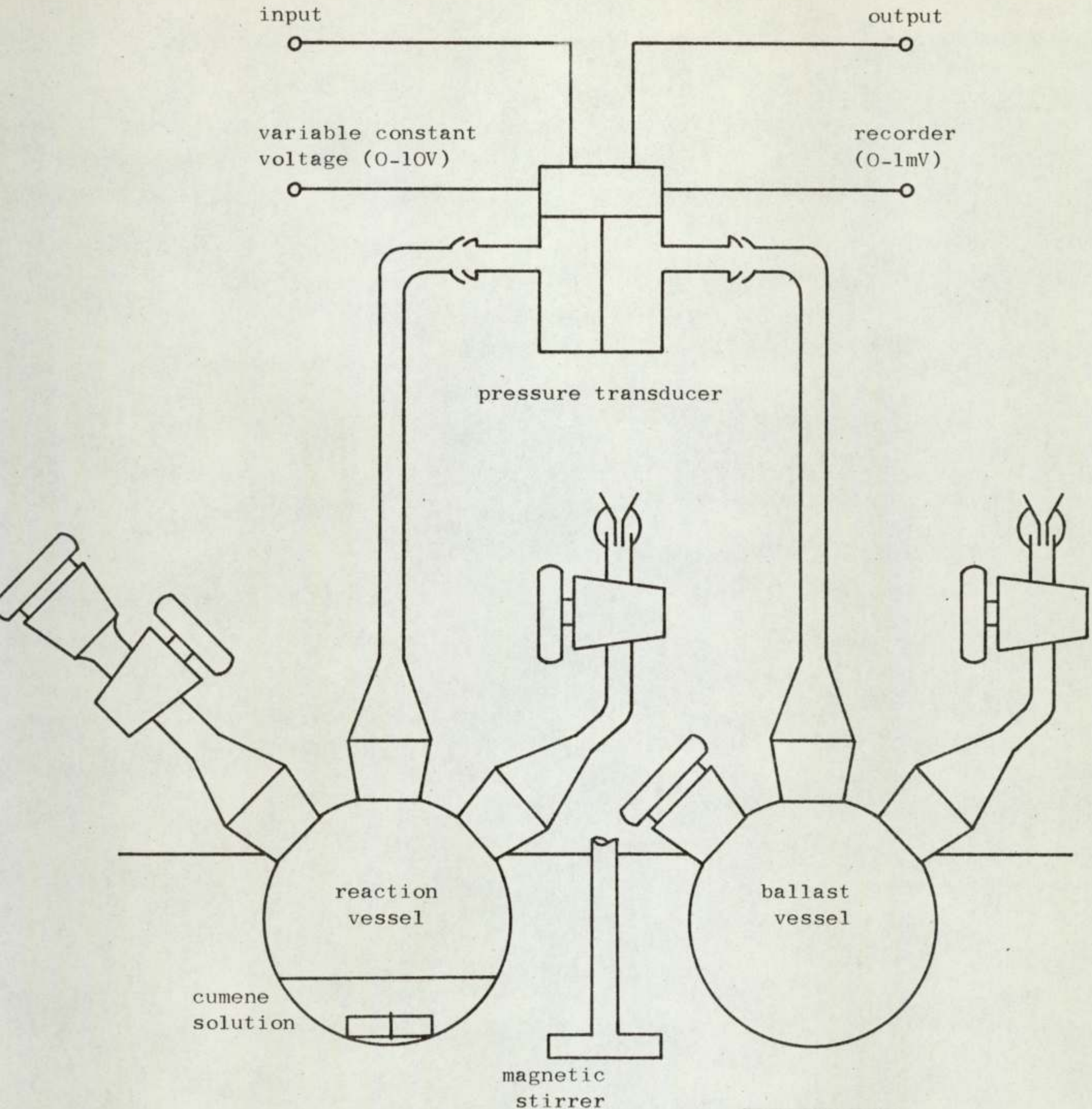


Figure 2.3 Cumene solution absorption apparatus

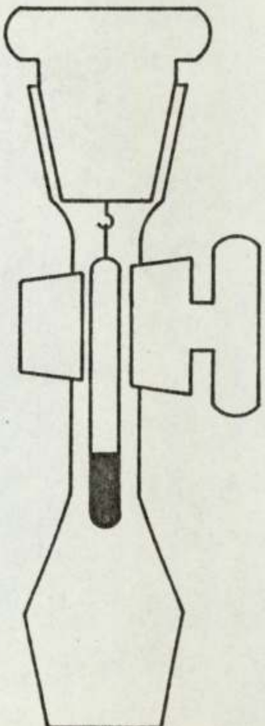


Figure 2.4 Tube crushing apparatus

Vulcanizate type	Extracted NATSYN	Zinc oxide	Zinc Sulphide	Lauric acid	Stearic acid	TMTD	CBS	S	DCP	Cure temp ^{o}C	Cure time minutes
A, Peroxide	100	-	-	-	-	-	-	-	3.0	160	45
B, Peroxide/ZnO	100	3.0	-	-	-	-	-	-	3.0	160	45
C, Peroxide/ZnS	100	-	3.0	-	-	-	-	-	3.0	160	45
D, High Modulus CBS	100	5.0	-	1.0	-	-	0.9	3.7	-	140	40
E, Conventional CBS	100	5.0	-	0.7	-	-	0.6	2.5	-	140	40
F, Conventional CBS	100	5.0	-	-	1.0	-	0.6	2.5	-	140	40
G, Semi EV	100	5.0	-	3.0	-	-	1.5	1.5	-	140	30
H, EV	100	5.0	-	1.0	-	-	6.0	0.4	-	140	120
I, TMTD Sulphurless	100	5.0	-	1.5	-	4.0	-	-	-	140	420
J, TMTD Sulphurless	100	4.0	-	-	1.0	4.0	-	-	-	160	85

TABLE 2.2 Vulcanization recipes

The cure curves are displayed in figures 2.5-2.8. From these data the times to the desired extent of cure of the compounds were estimated, (table 2.2), bearing in mind that the vulcanization characteristics of press cured compounds will differ slightly because of a difference in mould thickness.

2.3.2 Vulcanization

Vulcanizates were prepared normally in a fully positive stainless steel mould of cavity dimensions 13.5 x 13.5 x 0.018 cms. This gave vulcanizates of thickness 0.018-0.023 cms.

The compound was sheeted out through a tight nip on a water cooled mill and sufficient quantity, about 3.5 grammes, was placed in the clean cavity of the pre-heated mould. The mould was returned to the steam heated press, held at the required temperature, and 50 tons force was applied through an 8 inch diameter ram for a period corresponding to the cure time required. At the end of this period the mould was released from the press and quenched in cold water. The mould was opened and the vulcanizate sheet was immersed in cold water. After cooling, a 1 cm border was cut from each edge of the sheet to discard any inhomogeneity due to edge effects. The bloom was wiped from the surface of the vulcanizate with tissue soaked in chloroform prior to storing under vacuum, ($<$ 0.1 mm), at -10°C.

For vulcanizate sheets of thickness other than 0.023 cms, (section 3), a mould comprising two stainless steel photographic glazing plates and stainless steel shim as spacers between the plates was employed. Larger steel backing plates were placed above and beneath the mould to prevent damage to the glazing plates arising from irregularities on the press platens. The thickness of vulcanizates obtained from this type of mould depended on the thickness of steel shim employed. For example,

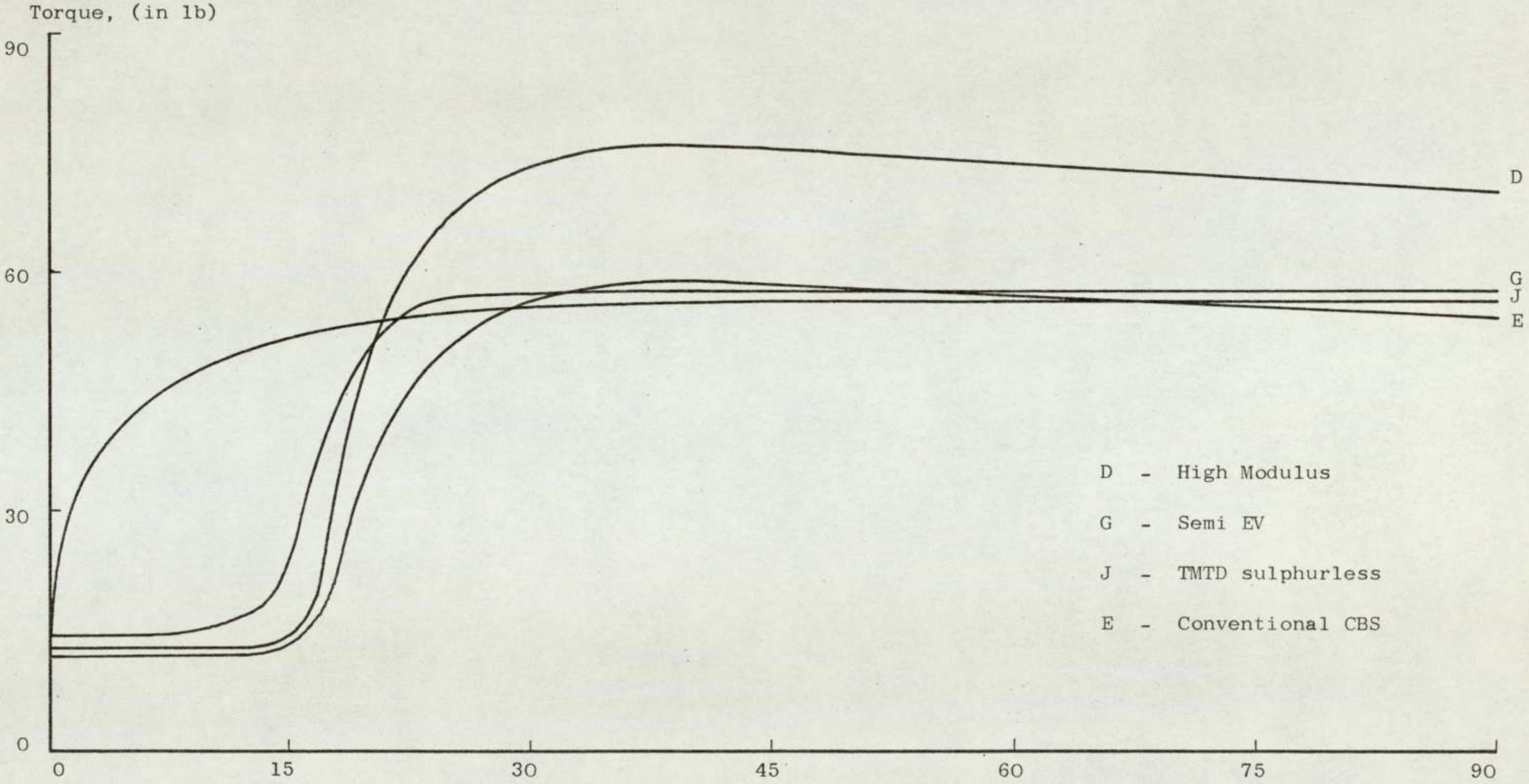


Figure 2.5 Rheometer cure curves

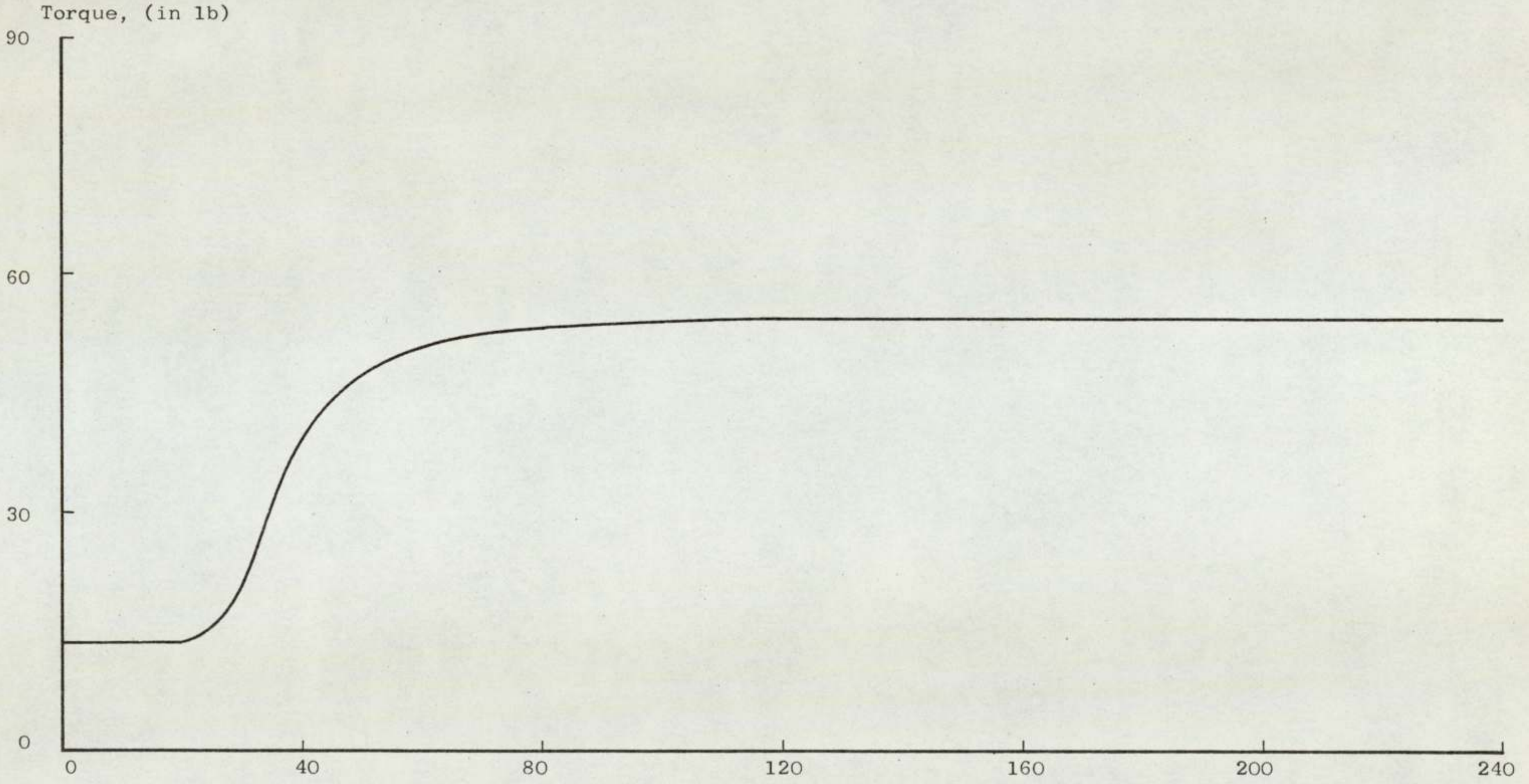


Figure 2.6 Rheometer cure curve for EV compound, (H)

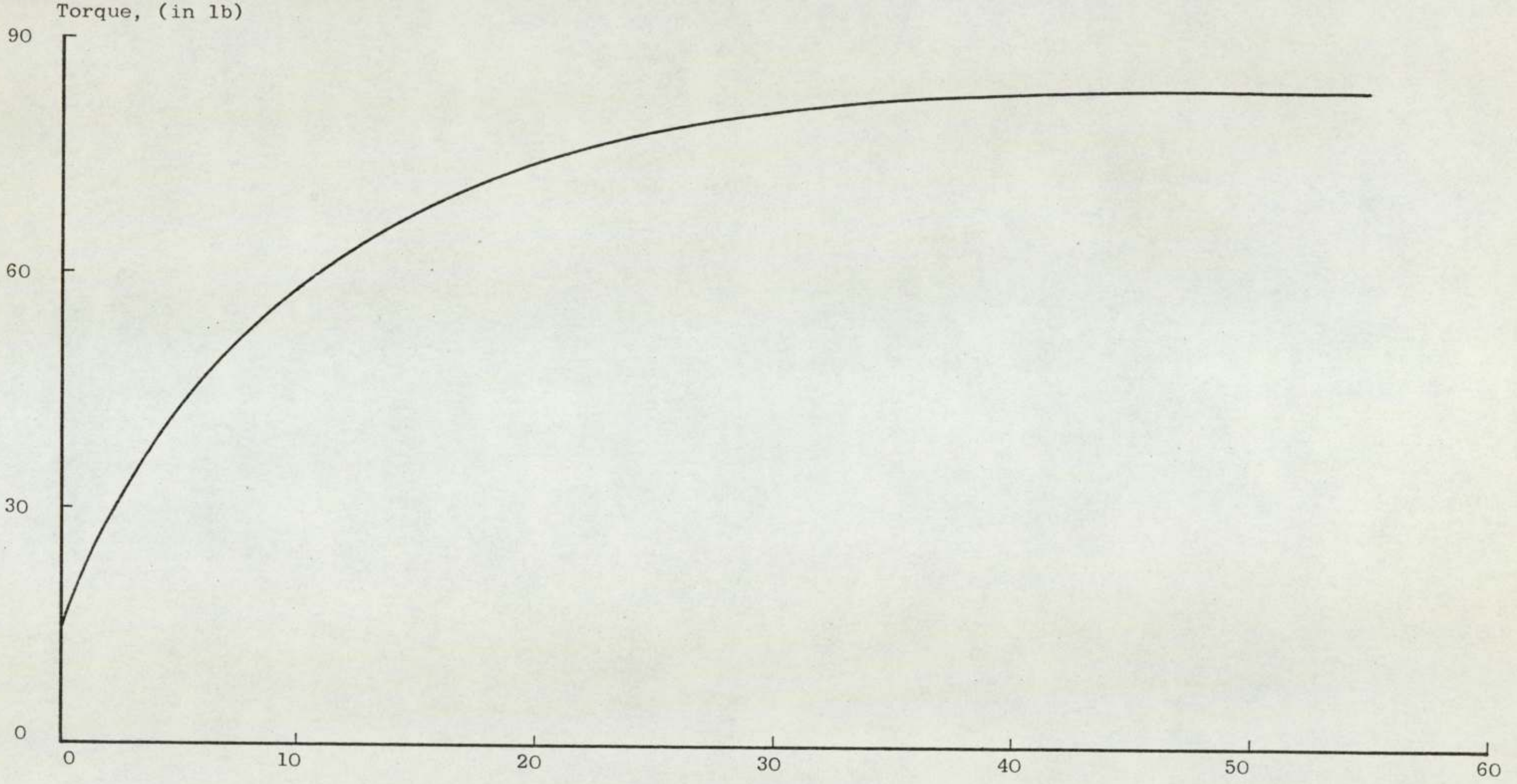


Figure 2.7 Rheometer cure curve for Peroxide compound, (A)

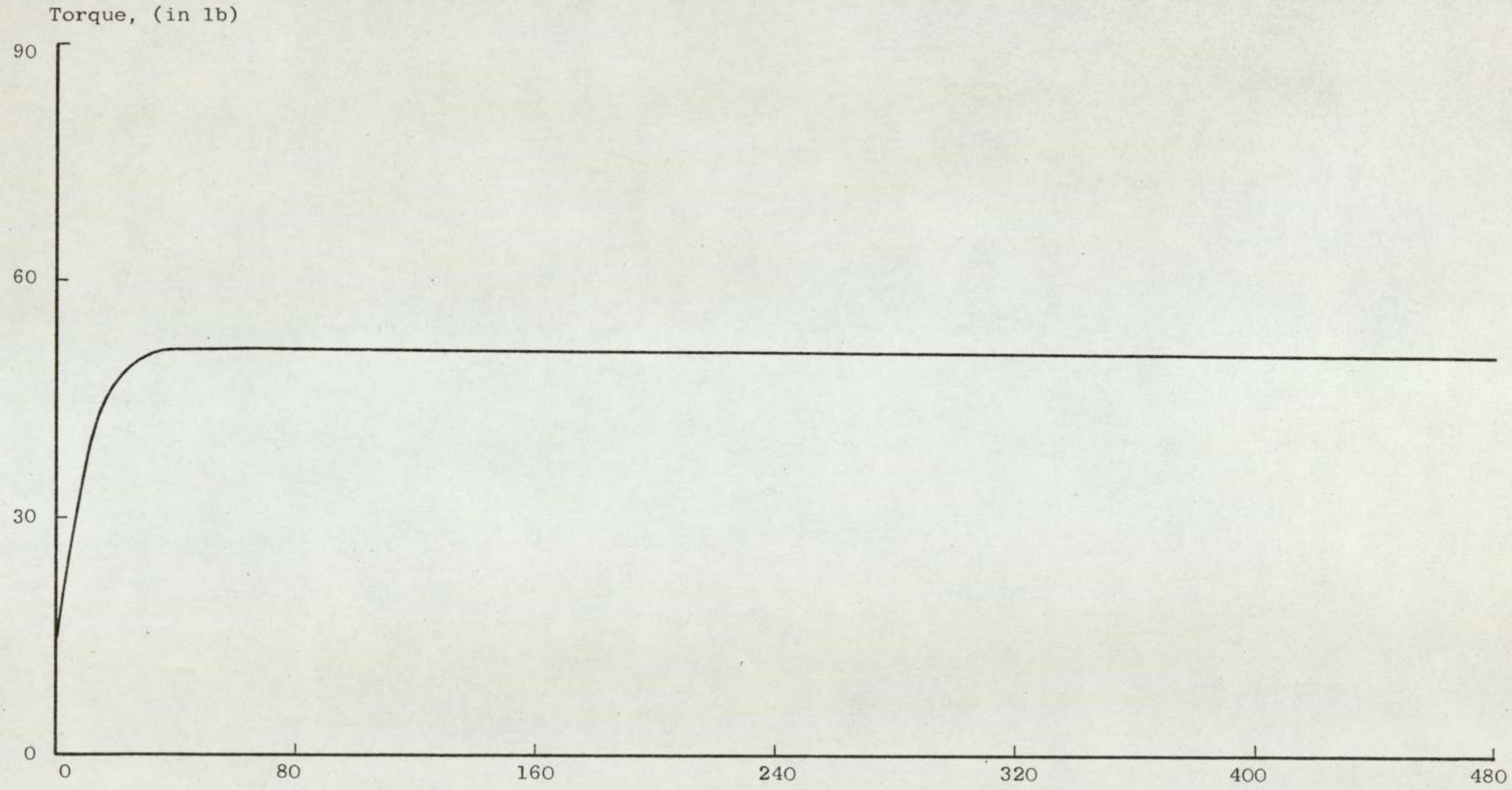


Figure 2.8 Rheometer cure curve for TMTD sulphurless compound, (I)

shim of thickness 0.01 cms gave vulcanizate films of thickness 0.012 cms.

A similar procedure was adopted for the preparation of vulcanizates as that described previously.

2.3.3 Extraction of vulcanizates

If required, the extra network materials were removed from vulcanizate sheets by continuous extraction with a solvent mixture in a soxhlet apparatus, (40 mls). Extraction was carried out under a steady stream of nitrogen in subdued light. The extraction medium, to be known as solvent mixture and the procedure as solvent extraction, was composed of acetone, methanol and 1,1,1-trichloroethane in the proportions described in table 2.3. This is not a true azeotrope but distills with reasonably constant composition at around 57°C[133]. An extraction period of 24 hours was found to be sufficient, (section 3), the temperature of extraction varying between 45-50°C. Following extraction the vulcanizates were dried under vacuum to constant weight then stored under vacuum, ($<$0.1 mm), at -10°C.

Component	Parts by volume
Acetone	110
Methanol	42
1,1,1-trichloroethane	60

Table 2.3 The solvent mixture

2.4 Techniques

2.4.1 Oxygen absorption measurements of vulcanizates

An accurately weighed vulcanizate specimen, (0.2-0.3 grammes), of maximum thickness 0.023 cms, (section 3), was placed on the sample support as shown in figure 2.2 so that oxygen was able to diffuse freely into both faces. The support and contents were transferred to the absorption flask and the apparatus assembled. After purging with oxygen through the luer needle for approximately 10 minutes, the apparatus was placed in the thermostatted bath and connected to the transducer. The ballast vessel was already positioned. After an initial period of 6 minutes, expansion was complete and the pressure in the absorption vessel was equilibrated to that of the ballast vessel by venting both through the luer needle attachments. The vulcanizate was allowed to absorb oxygen. The maximum pressure change which was allowed to occur between the two vessels was of the order of .5 per cent. If oxygen was still required to be absorbed, this was added through the luer needle attachment until atmospheric pressure had been re-established. The reaction is therefore carried out, to all intents and purposes, at constant pressure. Providing that diffusion control does not occur, (section 3), the rate of oxidation is independent of pressure fluctuations of this magnitude[30-32].

To determine the amount of oxygen absorbed by the specimen a syringe was fitted to the luer needle of the absorption vessel, known volumes of oxygen were withdrawn and the corresponding deflections on the recorder noted. In practice a calibration check was made at intervals following several absorption experiments.

Following the completion of a particular experiment, the absorption vessel was dismantled, the sample removed and the apparatus washed with acetone then water and dried prior to the commencement of another determination.

2.4.1.1 Results and reproducibility

Pyrex glass vessels were used and it was found that an ageing period was required before reproducible results were obtained. The vessels were heated at 80^{o}C in air for several days prior to their use for oxygen absorption determinations. Providing that this ageing period was observed, acceptable reproducibility was obtained between duplicate absorption measurements. Typical results are summarized in table 2.4.

Type of vulcanizate, (extracted after cure)	Time to 1 weight per cent absorption of oxygen, minutes (i)	(ii)
A, Peroxide	113	121
F, Conventional CBS	291	309
G, Semi EV	202	222
I, TMTD sulphurless	144	151

Table 2.4 Reproducibility between duplicate determinations

All subsequent data are reported graphically in terms of weight per cent of oxygen absorbed at 80^{o}C based on the initial weight of the specimen. All determinations were carried out in duplicate although only representative curves are reported.

2.4.2 Oxygen absorption measurements of cumene solutions

The solution of cumene and initiator, (AZBN, benzoyl peroxide or cumene hydroperoxide), was pipetted, (5 mls), into the reaction vessel shown in figure 2.3. The additive, ZMBT, hydrolyses readily in solution[134] and hence was handled in a dry box. A pre-weighed, drawn out tube was charged with ZMBT, stoppered, reweighed and finally sealed placing a hook on the end of the tube. This small glass ampoule was then suspended on the apparatus as shown in figure 2.4. The reaction flask was purged with oxygen whilst the solution was stirred. After 10 minutes the apparatus was transferred to the thermostatted bath and connected to the transducer. The ballast vessel was already attached and after an expansion period of 5 minutes the taps on both vessels were opened to the atmosphere then closed. The oxygen absorbed by the cumene solution was recorded continuously. When a constant rate of absorption was apparent, the additive was introduced by crushing the glass ampoule on rotating the tap and thereby dropping the contents into the vessel.

The maximum pressure change which was allowed to occur between the reaction and ballast vessels was 5 per cent. The rate of oxidation of cumene at 90°C is independent of oxygen pressure above 260 mm[135]. The apparatus was calibrated after each determination according to the procedure previously described in section 2.4.1.

2.4.2.1 Results and reproducibility

Again it was found necessary to pre-age the reaction vessels to obtain reproducible data. The flasks complete with glass stirrer were filled with a solution of cumene hydroperoxide in cumene and left open to the atmosphere at 80°C for several days. After this treatment the rate of oxidation of a stock solution of cumene hydroperoxide in cumene was reproducible within ± 8%. The systems initiated with AZBN or benzoyl peroxide were reproducible within ± 3%. Results are quoted graphically in terms of moles of oxygen absorbed per 5 mls of solution.

2.4.3 Quantitative analysis of MBT - (A)

Normal and basic zinc salts of MBT, present in vulcanizates as extra network materials, were estimated quantitatively as MBT by U.V. absorption spectroscopy based on the method proposed by Lorenz and Echte[136] and used successfully by Campbell and Wise[111]. Zinc salts of MBT are readily reduced to MBT by acids. The normal zinc salt is soluble in normal organic solvents, whereas the basic salt is insoluble but can be removed from vulcanizates in the form of MBT by a solvent/acetic acid, (5% v/v), mixture.

An aliquot of suitable volume of vulcanizate extract, or other solution to be analyzed, was evaporated to dryness on a rotary evaporator. 3 mls of benzene, 0.5 mls of acetic acid and 0.05 mls of water were added. The mixture was shaken vigorously and transferred to a 10 mls volumetric flask. The aliquot vessel was washed out twice with benzene and the washings transferred to the volumetric flask which was then made up to volume with benzene. The U.V. absorbance of the solution was recorded from 250-350 mμ in matched quartz cells, the reference cell containing a blank solution. A baseline was constructed from 290-350 mμ and the absorbance of the solution at λ_{max} 329 mμ was noted. The concentration of MBT present in the solution was obtained from a calibration curve constructed from MBT solutions of known concentration, see figure 2.9.

2.4.4 Quantitative analysis of MBT - (B)

Dibenzothiazyl disulphide, (MBTS), and higher sulphides are reduced to MBT by the action of a stannous chloride/hydrochloric acid reagent[136] whereas the former is unchanged in the presence of acetic acid. Thus, this procedure affords a quantitative determination of MBTS when used in conjunction with method (A).

An aliquot of suitable volume of the vulcanizate extract was evaporated to dryness then dissolved/suspended in 5 mls of acetone. 1 ml of stannous chloride solution, (5%), and 1 ml of 2.5N hydrochloric acid were added. The mixture was heated to boiling for 5 minutes giving a clear solution. The acetone was removed completely on the rotary evaporator leaving an aqueous acidic suspension of MBT. The MBT was extracted from the aqueous layer with 3 x 5 mls portions of benzene. A 5 mls aliquot of the combined benzene extracts was transferred to a 10 mls volumetric flask, 0.5 mls of acetic acid and 0.05 mls of water

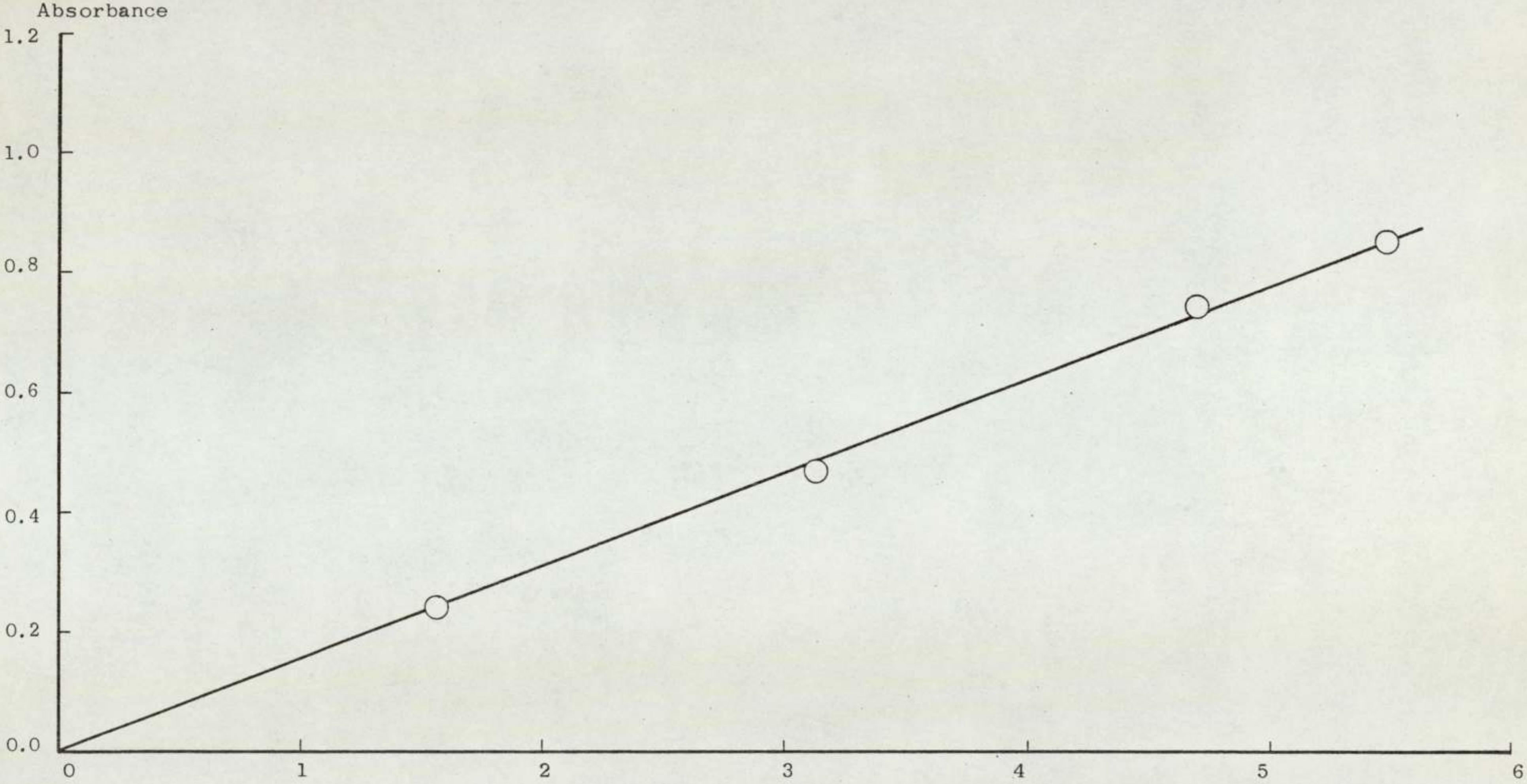


Figure 2.9 UV absorbance at 329 mµ (baseline 290-350 mµ) Vs concentration of MBT

Concentration of MBT, (10^{-3} grammes per litre) were added and the concentration of MBT determined by U.V. analysis as described in section 2.4.3.

2.4.5 Equilibrium swelling measurement determinations

2.4.5.1 Theory

The extent of swelling of a rubber vulcanizate in a given solvent is determined by the solvent power of the liquid and the cross-link density of the network. For a given solvent, the higher the cross-link density of the rubber the lower is the extent of swelling. This relationship is expressed quantitatively by the Flory-Rehner equation,[137] (2.1).

$$-\left(\ln(1-\nu_r)+\nu_r+\chi\nu_r^2\right) = \rho V_o M_c^{-1}\left(\nu_r^{\frac{1}{3}} - \frac{\nu_r}{2}\right) \qquad (2.1)$$

ν_r is the equilibrium volume fraction of the rubber in the swollen gell, (2.2);

$$\nu_r = \frac{\text{Vol. of rubber in swollen sample}}{\text{Vol. of rubber in swollen sample + Vol. of swelling solvent in swollen sample}} \qquad (2.2)$$

ρ, the density of the dry rubber;

χ, an interaction constant characteristic of the rubber and swelling liquid;

V_o, the molar volume of the swelling liquid;

M_c, the number average molecular weight of the network chains, (ie between cross-links).

Since each cross-link will terminate 4 network chains the number of network chains will be twice the number of cross-links, assuming that the network is free from chain ends. Thus, the cross-link density is expressed as $\frac{1}{2M_c}$ and the Flory-Rehner expression becomes:

$$\frac{1}{2M_c} = \text{cross-link density} = \frac{-\left(\ln(1-\nu_r) + \nu_r + \chi\nu_r^2\right)}{2\rho V_o\left(\nu_r^{\frac{1}{3}} - \frac{\nu_r}{2}\right)} \qquad (2.3)$$

Thus, provided the value of χ is known for the particular system, the cross-link density of the vulcanizate can be calculated from experimental measurements of ν_r and ρ. Certain limitations must be recognized however.

Since any real network is formed from molecules of finite length, some of the network chains will be terminated by a cross-link at only one end and these network chains will not be elastically effective. Therefore, a chain end correction must be applied to experimentally determined values of $\frac{1}{2M_c}$[138,139]. In addition, when cross-link density is estimated by a physical method such as swelling measurements, entanglements in the network may act as cross-links and hence lead to a high estimate. A corrected expression for M_c obtained from experimental measurements has been derived by Mullins[43] and Moore[45]. Finally, swollen vulcanizates only conform to the elastic behaviour predicted by the statistical theory of elasticity when highly swollen.

Semi-quantitative data can be obtained more speedily by considering the equilibrium weight swelling ratio:

$$SR = \frac{\text{Weight of swollen network}}{\text{Weight of dry deswollen network}} \qquad (2.4)$$

As the cross-link density decreases then the swelling ratio increases. Measurements of this type are useful in detecting any change in cross-link density of a network and does not necessitate the value of χ to be known. This technique has been adopted in the work presented in this thesis since quantitative estimations of cross-link density were not required.

2.4.5.2 Procedure

Specimens of dimensions 1 x 1 x 0.023 cms and approximate weight 0.015 grammes were carefully cut from the vulcanizate sheet with a scalpel, ensuring that no frayed edges resulted. Characteristic markings were cut on each specimen to facilitate recognition. The specimens were transferred to a 50 mls stoppered flask containing the swelling liquid held at a constant temperature, usually 25°C ± 0.05°C. If a higher temperature was employed, (section 3.2), then nitrogen was bubbled through the solvent and maintained at the top of the vessel to minimize oxidation of the vulcanizate specimens. The specimens were removed after swelling to equilibrium, or extended periods (section 3.2), and excess solvent was removed by gently pressing between filter papers prior to transferring into tared, stoppered, weighing bottles. The weight of each swollen specimen was obtained. Specimens were dried under vacuum to constant weight and their dry weights recorded. From the data equilibrium swelling ratios were calculated according to equation (2.4). All measurements were recorded in triplicate and reproducibility between samples was ± 2%.

2.4.6 Decomposition of cumene hydroperoxide by ZMBT

2.4.6.1 Quantitative analysis of cumene hydroperoxide, (CHP)

The method is based upon that of Bocek[140] and has been used successfully by Armstrong[61].

A volume of the solution to be analyzed, containing a maximum of 6 x 10^{-7} moles of hydroperoxide, was transferred into a 25 mls volumetric flask. 10 mls of benzene was added followed by 0.5 mls of a 0.004M solution of phosphoric acid in methanol. 5 mls of a standard solution of ferrous ammonium sulphate, (0.0005M), in methanol was added and washed down with benzene. The volumetric flask and contents were allowed to stand for 15 minutes before adding 1 ml of a 0.5% (v/v) solution of o-phenanthraline in benzene and finally making up to the 25 mls mark with benzene. The sample was left to stand for 30 minutes and then analyzed in the SP700 spectrophotometer between 490 and 520 mμ. A blank sample was prepared in the same way with pure benzene in place of the specimen. The difference between the absorbance maximum, (506 mμ), of the blank sample and the analytical sample gave the quantity of divalent ion that had been oxidized by the hydroperoxide. Using a fixed volume of solution and varying the concentration of hydroperoxide (w/w), a calibration of the difference in absorbance against hydroperoxide concentration was constructed[141].

2.4.6.2 Determination of the rate of decomposition of CHP by ZMBT

The reaction vessel employed is shown in figure 2.10. This was weighed clean and dry prior to the introduction of reactant solutions. A solution of CHP in chlorobenzene, about 2.5 grammes, was pipetted into one arm of the vessel and the vessel reweighed. A saturated solution of ZMBT in chlorobenzene, about 2.5 grammes, was introduced into the second arm of the vessel and once again the vessel was reweighed. The vessel was designed so that pipettes could be introduced into the arms of the vessel through the taps. The vacuum taps were re-sealed prior to weighing the apparatus. Finally, a rubber septum was secured over the sampling end.

The experimental preparation was carried out in a dry box to exclude moisture from the inside of the apparatus. The saturated solution of ZMBT in chlorobenzene was estimated as discussed in section 2.4.3, giving a figure of 1.34×10^{-6} gramme moles ZMBT per gramme of solution, (1.47×10^{-3} gramme moles ZMBT per litre).

The vessel was transferred to a thermostatted oil bath at $80^{\circ}C \pm 0.05^{\circ}C$

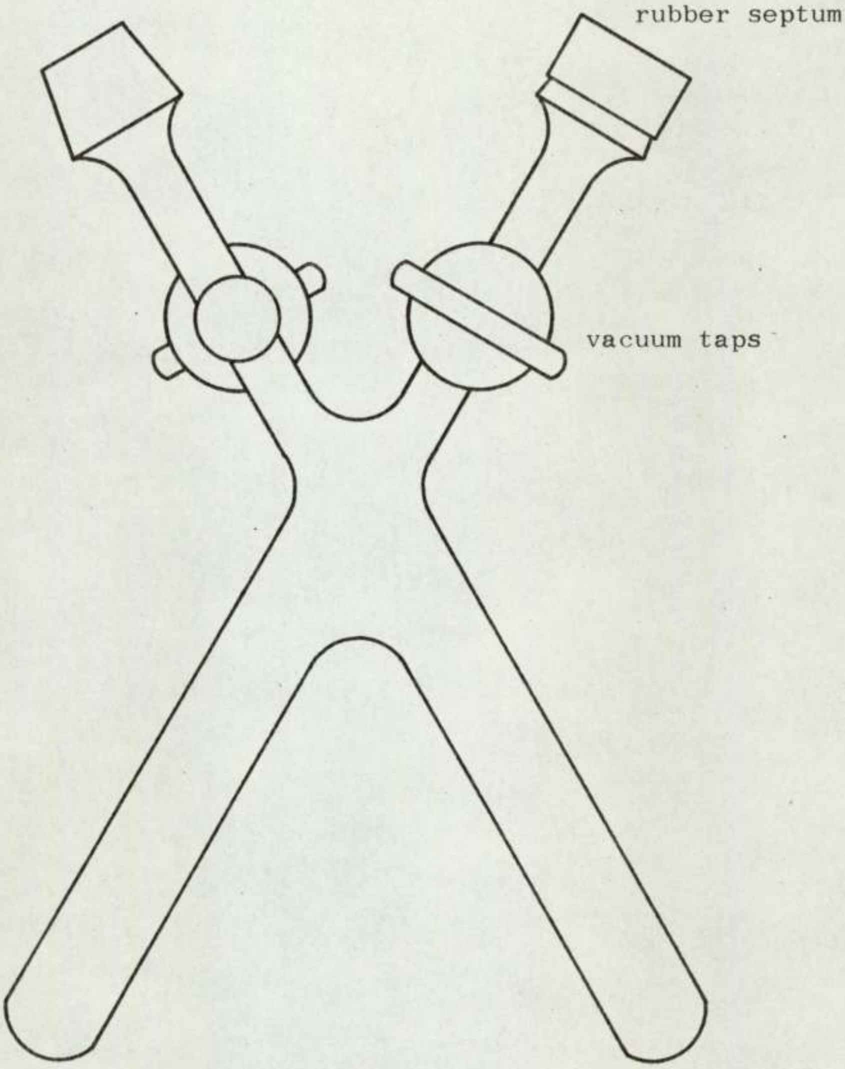


Figure 2.10 Reaction vessel employed in the study of the decomposition of cumene hydroperoxide

and the solutions were allowed to equilibrate for 10 minutes. At time t=0 the solutions were mixed by tipping from one arm to the other. Samples of solution were withdrawn at intervals via the rubber septum with a syringe fitted with a 6 inch needle. The analytical sample was transferred to a 25 mls volumetric flask and the amount of hydroperoxide present determined by the method described in section 2.4.6.1.

The concentration of the CHP/chlorobenzene solution was 2.717×10^{-4} gramme moles CHP per gramme of solution. A 5 μl syringe was employed to withdraw 4μl of solution, (0.0041 grammes). Thus, the weight of hydroperoxide analyzed initially was 5.6×10^{-7} moles.

2.4.7 Quantitative determination of acetone, phenol, α-methylstyrene, α,α-dimethylbenzyl alcohol, and acetophenone

The above products of the decomposition of cumene hydroperoxide were quantitatively analyzed using g.l.c. Details of the instrument and column are given in section 2.2.2. The method required that the column be operated according to the following programme:

a) 85°C for 5 minutes,

b) an increase of 10°C per minute up to 150°C,

and c) constant temperature of 150°C for 12 minutes.

Injection temperature, 250°C.

Detection temperature, 200°C.

Under these conditions the retention times displayed in table 2.5 were observed.

Calibration graphs for the individual products were constructed according to the following procedure[141]. Chlorobenzene solutions of various amounts of the decomposition products, but a fixed weight of iodobenzene (internal standard), were chromatogrammed according to the schedule described above. The peak height of the products and internal standard were measured

Component	Retention time, (minutes)
Acetone	0.6
α-methylstyrene	7.5
Iodobenzene	10.4
Acetophenone	13.3
α,α-dimethylbenzyl alcohol	15.2
Phenol	19.5

Table 2.5 Retention times of CHP decomposition products and internal standard

and plots were constructed of the ratio of peak heights of product to iodobenzene against their corresponding weight ratios. In all cases the calibration plots were linear.

For the analysis, a known weight of internal standard was added to a known weight of the solution of CHP decomposition products. The resulting solution was analyzed and the peak heights were measured. The amounts of the products in the solution were then determined from the calibration data.

3 Initial investigations into the effects of sample thickness and solvent extraction of vulcanizate specimens employed in oxygen absorption measurements

3.1 Introduction

Two processes are involved in the oxidation of a rubber vulcanizate. The first is the diffusion of oxygen into the rubber and the second, the reaction of oxygen with the polymer. For any rubber of practical dimensions the rate of oxidation is so slow at room temperature that it becomes the rate determining step. At higher temperatures, however, the rate of diffusion of oxygen may become rate determining depending on the thickness of the vulcanizate. Therefore, to obtain implicit data with respect to the rate of oxidation of vulcanizates it is necessary to determine the thickness of sample at which diffusion control does not occur, at a particular temperature.

Blum et al[27] have reported limiting dimensions of various types of vulcanizates throughout a series of temperatures. For a natural rubber, black filled vulcanizate in the absence of antioxidant, the limiting thickness was estimated at 0.040 inches at temperatures from 80°C to 100°C. In the presence of antioxidant the permitted thickness was increased to 0.075 inches. The effect of the added antioxidant is to reduce the rate of reaction of oxygen thereby increasing the maximum allowable thickness. Workers at the NRPRA have employed oxygen absorption specimens of thickness 0.03 cms, (0.012 inches). These were placed on smooth aluminium foil prior to insertion into the apparatus. As a result oxygen has access to one side of the specimens only thereby increasing the effective sample thickness by a factor of two. Absorption measurements were determined at 100°C and atmospheric pressure with no evidence of diffusion control[56,142]. This technique was later modified by supporting the vulcanizate specimens on a stainless steel gauze, in effect halving the apparent thickness[2]. A limiting sample thickness of 0.025 cms has been proposed by Lee and Morrell[143] during oxidation studies of nitrile vulcanizates. Results were reported for temperatures of oxidation up to 150°C in the presence and absence of added antioxidant. Finally, Parks et al[39] have reported oxygen absorption data for stabilized, polyisoprene, sulphur vulcanizates of thickness 0.05 cms. Measurements were determined at 80°C. A portion of the work presented in this section deals with an examination of the thickness of vulcanizate specimens at which diffusion control does not occur. This was undertaken because of the lack of consistency amongst the literature.

In addition to the specimen thickness other factors may lead to ambiguous interpretation of oxygen absorption data, particularly the presence of extra network materials, (section 1.4). In the past an azeotrope consisting of a mixture of acetone, methanol and chloroform was used successfully to remove the soluble vulcanization residues[56,58,108,142]. Extractions were carried out for periods up to 96 hours at room temperature. This low temperature bestows the advantage of minimal network disturbance during the extraction procedure. Unfortunately, because of the hazard associated with the handling of solvent mixtures containing acetone in the presence of chloroform[144] an alternative solvent system had to be utilized. Details of the solvent mixture are given in table 2.3. The effectiveness of the removal of soluble extra network materials from vulcanizates by this solvent mixture was investigated.

3.2 Experimental procedure

A series of vulcanizates, (A, F and J, table 2.2), of thicknesses 0.012 and 0.023 cms were examined with respect to their oxygen absorption characteristics, (section 2.4.1), at 100, 90 and 80°C.

Initial investigations were carried out on Conventional CBS vulcanizate specimens only. Final conclusions were derived from oxygen absorption data of the vulcanizates extracted after cure with solvent mixture for 24 hours, (section 2.3.3).

In addition, the oxidative stabilities of vulcanizate specimens of thickness 0.023 cms, extracted for 24 and 48 hours with solvent mixture were determined and any network degradation that had occurred during the extraction procedure was assessed from equilibrium swelling measurements at 50°C (section 2.4.5). A comparison with results obtained for the acetone/methanol/chloroform azeotrope at 25°C was made. Details of the latter are given in table 3.1.

Component	Parts by volume
Acetone	352
Methanol	274
Chloroform	291

Table 3.1

3.3 Results and discussion

Oxygen absorption measurements determined at 100°C on unextracted, Conventional CBS vulcanizate specimens indicate that diffusion control occurs - figure 3.1. The specimen of thickness 0.012 cms oxidizes more rapidly than that of 0.023 cms. Although the vulcanizates were not freed from extra network materials, the same conclusion would be anticipated for corresponding extracted systems since the latter oxidise at a greater rate, (section 4). These results, therefore, appear to conflict with those reported by Bell and Cunneen[56] for specimens of thickness 0.03 cms. The apparent thickness of these specimens was in fact 0.06 cms due to the technique employed.

The problem of diffusion control can be overcome either by reducing the thickness of specimens or by decreasing the reaction temperature and consequently the rate of oxidation. The preparation of vulcanizates of reduced thickness was impracticable and hence a solution was sought by consideration of the latter. A reduction of absorption temperature to 90°C again produced results indicating diffusion control - figure 3.2. Vulcanizate specimens in this case were extracted after cure. A further reduction of temperature to 80°C gave data consistent with the absence of diffusion control and, therefore, a true measure of oxidizability at that temperature - figure 3.3. Additional evidence is presented in figures 3.4 and 3.5 for TMTD sulphurless and Peroxide vulcanizates, both extracted after cure. Again diffusion control is absent.

The findings indicate that previous estimates of limiting sample thickness may lead to spurious results, particularly if measurements concerning unstabilized systems are obtained in which high rates of oxidation are observed. As a result, all subsequent absorption measurements reported in this thesis were determined on specimens of thickness 0.023 cms or less, at 80°C.

A period of 24 hours continuous extraction with the solvent mixture was sufficient to remove vulcanization residues from a TMTD sulphurless vulcanizate - figure 3.6. Reproducible absorption curves were obtained after extraction for 24 and 48 hours. Furthermore, similar results were obtained for the Conventional CBS and peroxide vulcanizates - figures 3.7 and 3.8 respectively. Again extraction for 24 hours was adequate to remove extra network materials from the sulphurated network that provided some oxidative stability. In the latter case, however, the removal of extra network materials gave rise to an increase in oxidative stability. That is a pro-oxidant was removed during extraction. This is most likely to be residual dicumyl peroxide[145] yielding initiating radicals under oxygen absorption conditions. The pro-oxidant was effectively removed after extraction for 24 hours.

Additional data has indicated that unlike the acetone/ methanol/ chloroform azeotrope, the solvent mixture was ineffective in removing extra network materials at ambient temperature. Utilization at the elevated temperature was therefore unavoidable and although extractions were carried out under nitrogen it was of interest to determine the extent of network degradation, if any, that occurred during the extraction procedure. Equilibrium swelling measurements of Conventional CBS vulcanizate specimens, in the presence of the solvent mixture at 50°C, indicate the development of a more highly swollen network compared to the acetone/methanol/chloroform azeotrope - figure 3.9. No additional network degradation occurred, although a slight redistribution of polysulphidic cross-links may have taken place giving rise to some additional cross-links of lower sulphur rank and cyclic structures. This effect has been noted previously during hot acetone extraction of unaccelerated sulphur vulcanizates[48].

Summarizing, it has been established that vulcanizate specimens of thickness less than or equal to 0.023 cms do not give rise to diffusion controlled oxidation at 80°C. Furthermore, a period of extraction of 24 hours with hot solvent mixture is sufficient to remove soluble extra network materials from the vulcanizates. This extraction procedure does not give rise to any significant amount of network degradation even in systems containing polysulphidic features.

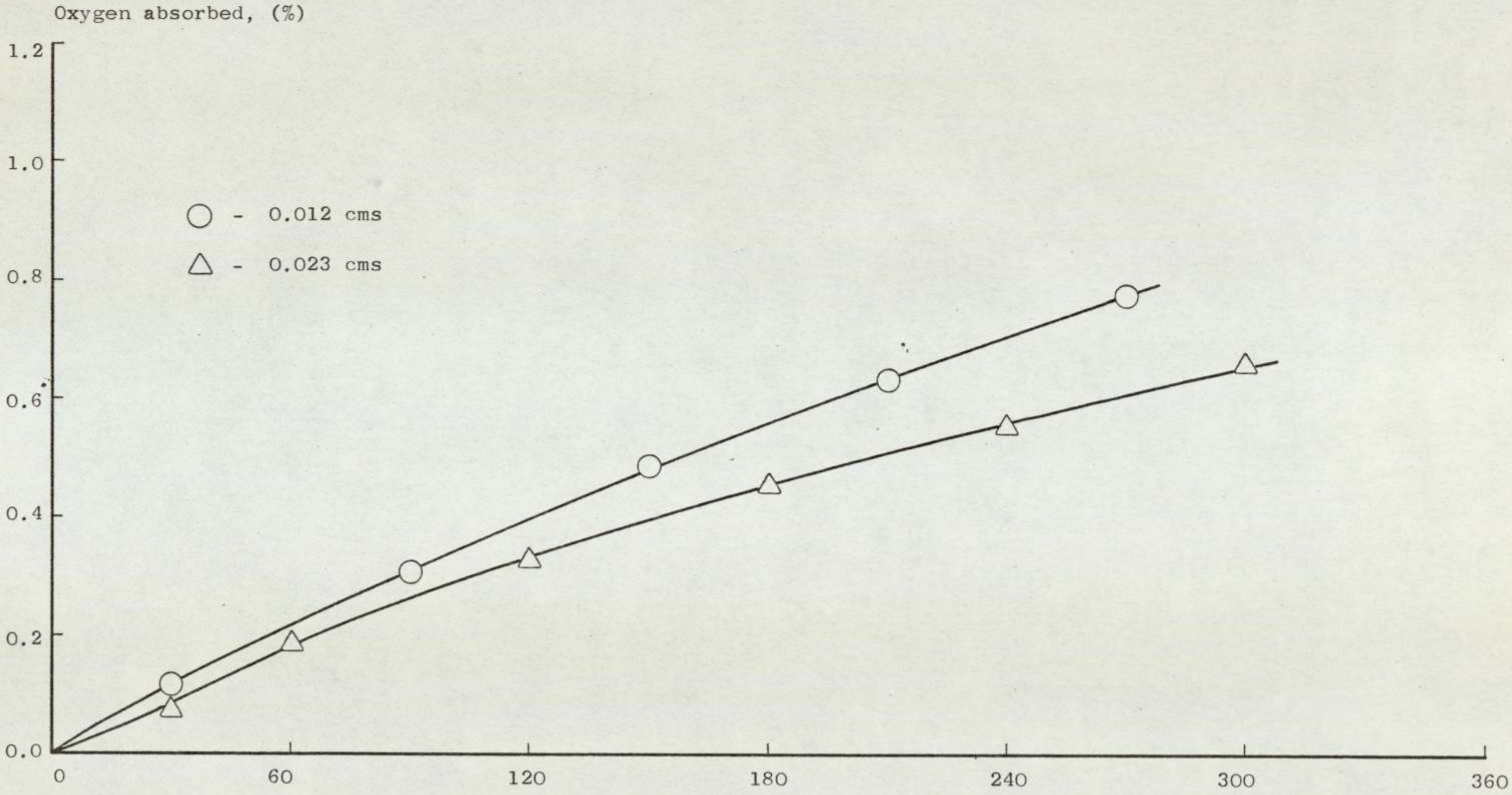


Figure 3.1 Oxygen absorption of unextracted Conventional CBS vulcanizates at 100°C. Effect of thickness

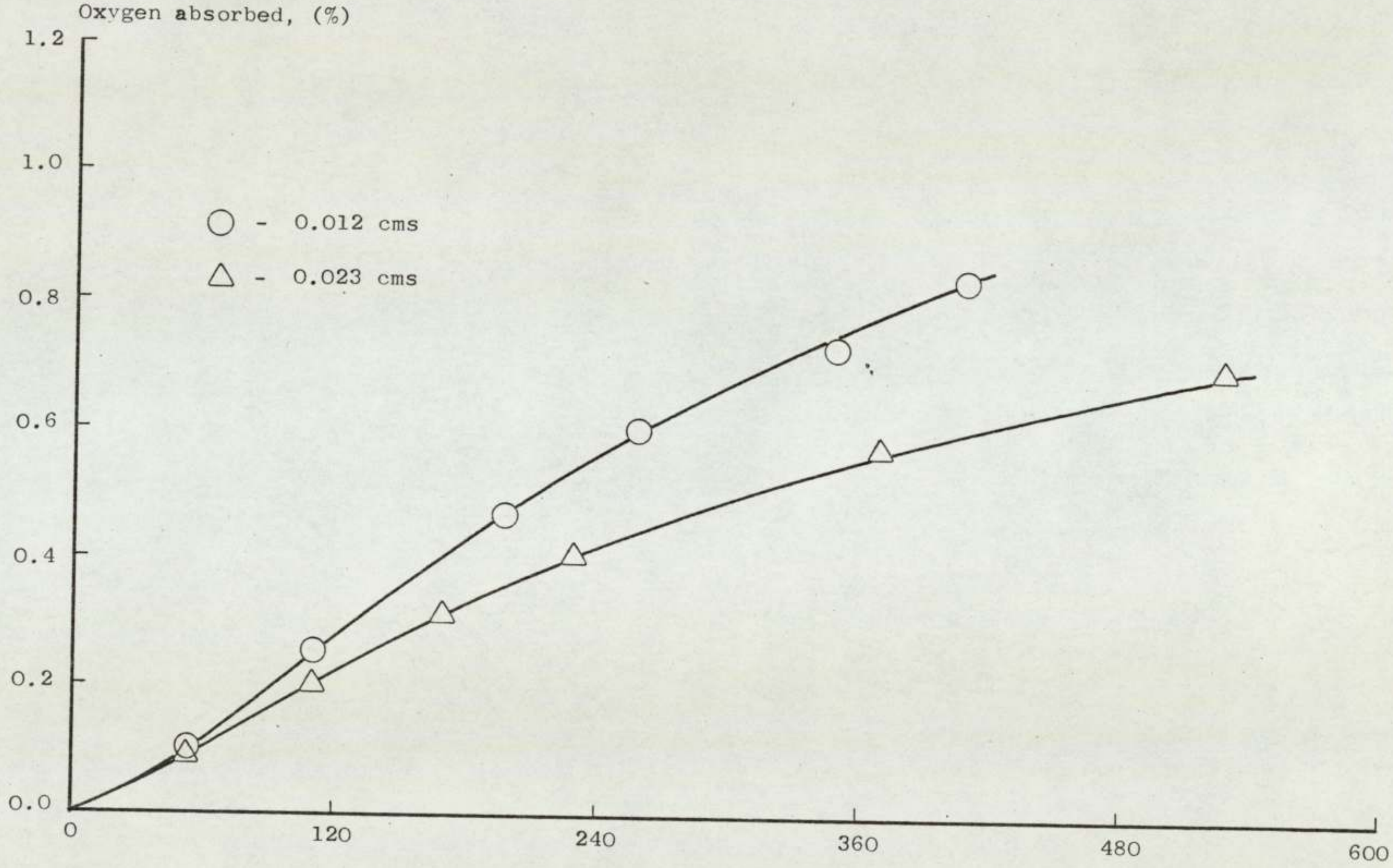


Figure 3.2 Oxygen absorption of solvent extracted Conventional CBS vulcanizates at 90°C. Effect of thickness

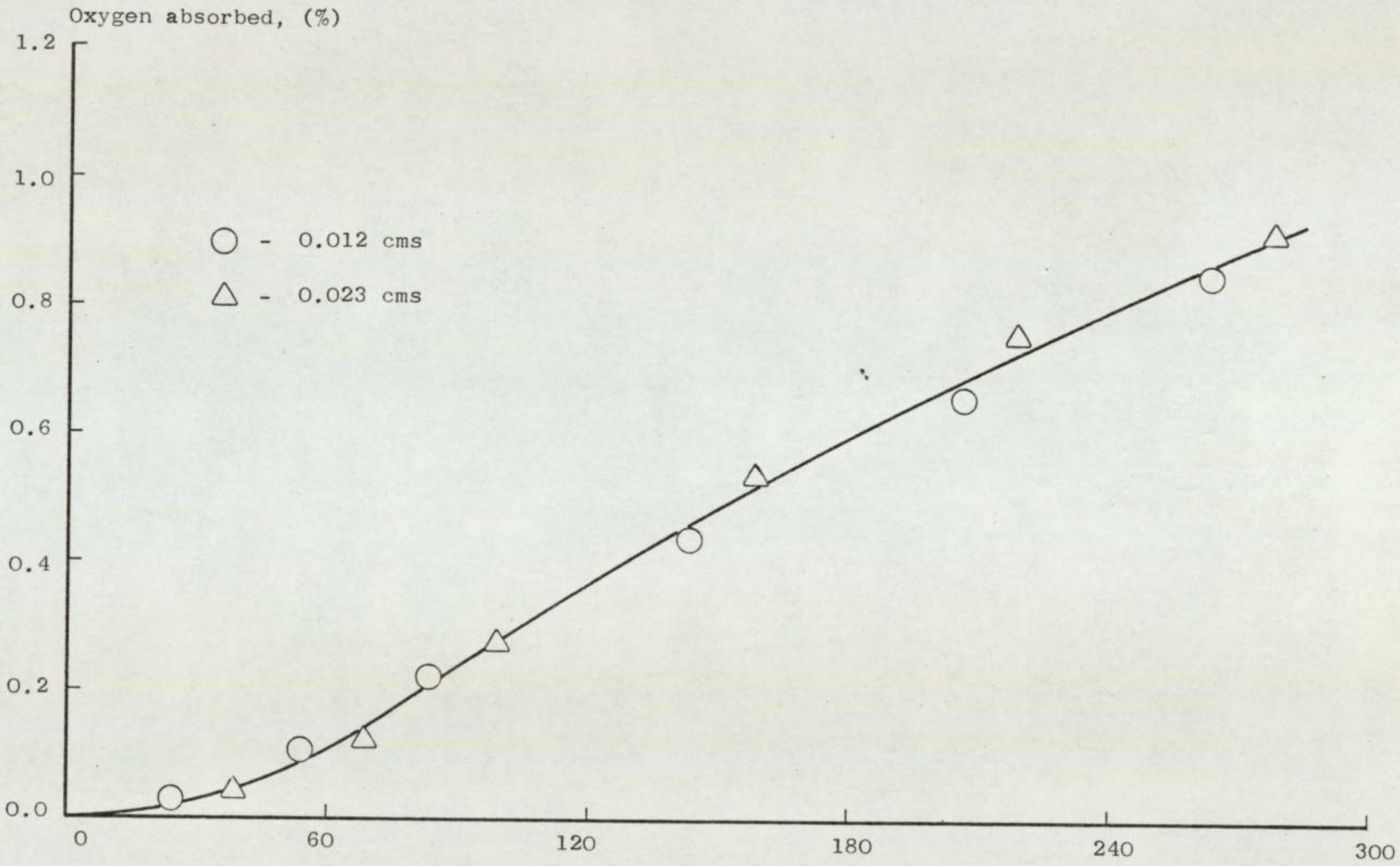


Figure 3.3 Oxygen absorption of solvent extracted Conventional CBS vulcanizates at 80°C. Effect of thickness

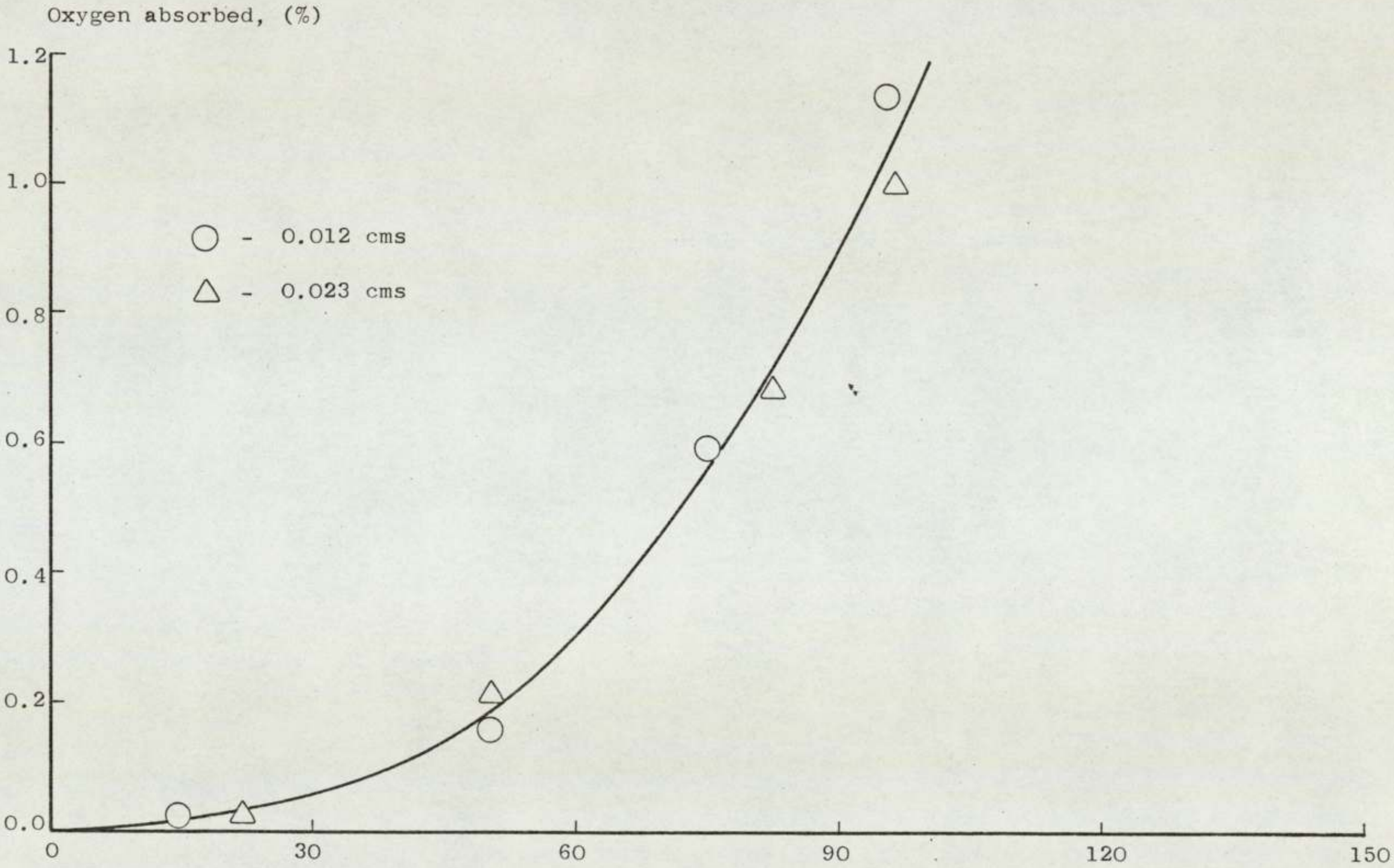


Figure 3.4 Oxygen absorption of solvent extracted TMTD sulphurless vulcanizates at 80°C. Effect of thickness

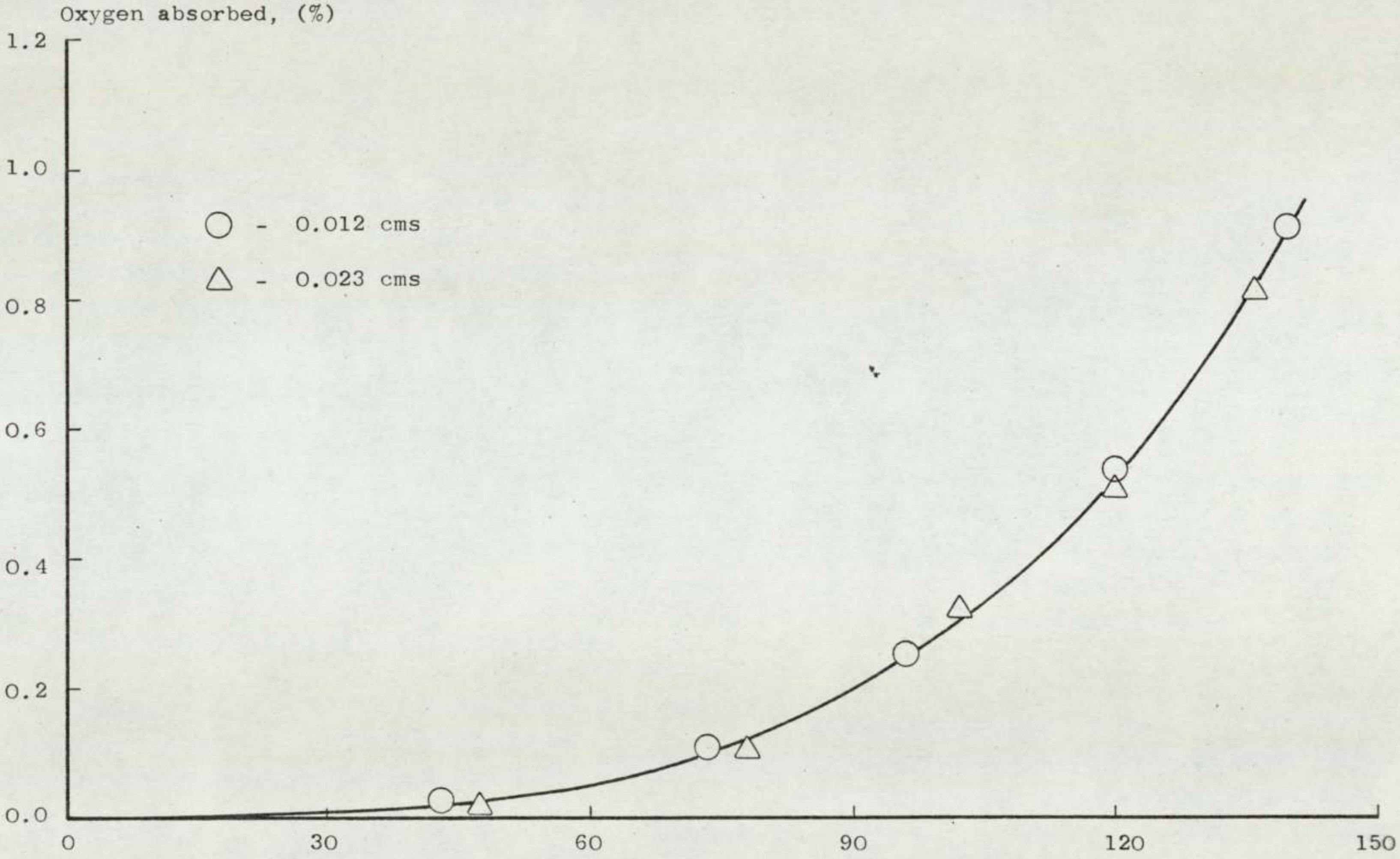


Figure 3.5 Oxygen absorption of solvent extracted Peroxide vulcanizates at 80°C. Effect of thickness

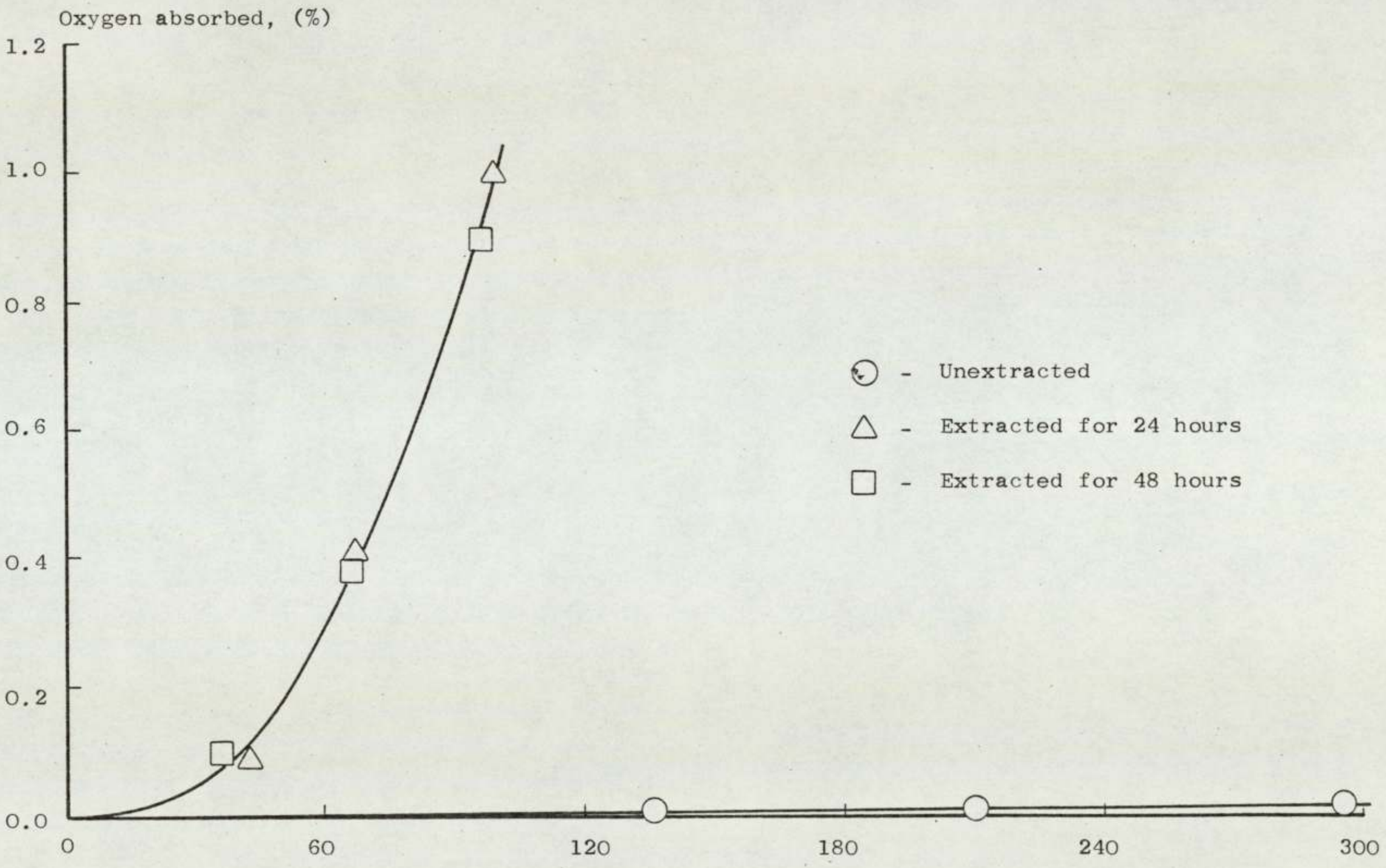


Figure 3.6 Oxygen absorption of TMTD sulphurless vulcanizates at 80°C before and after solvent extraction

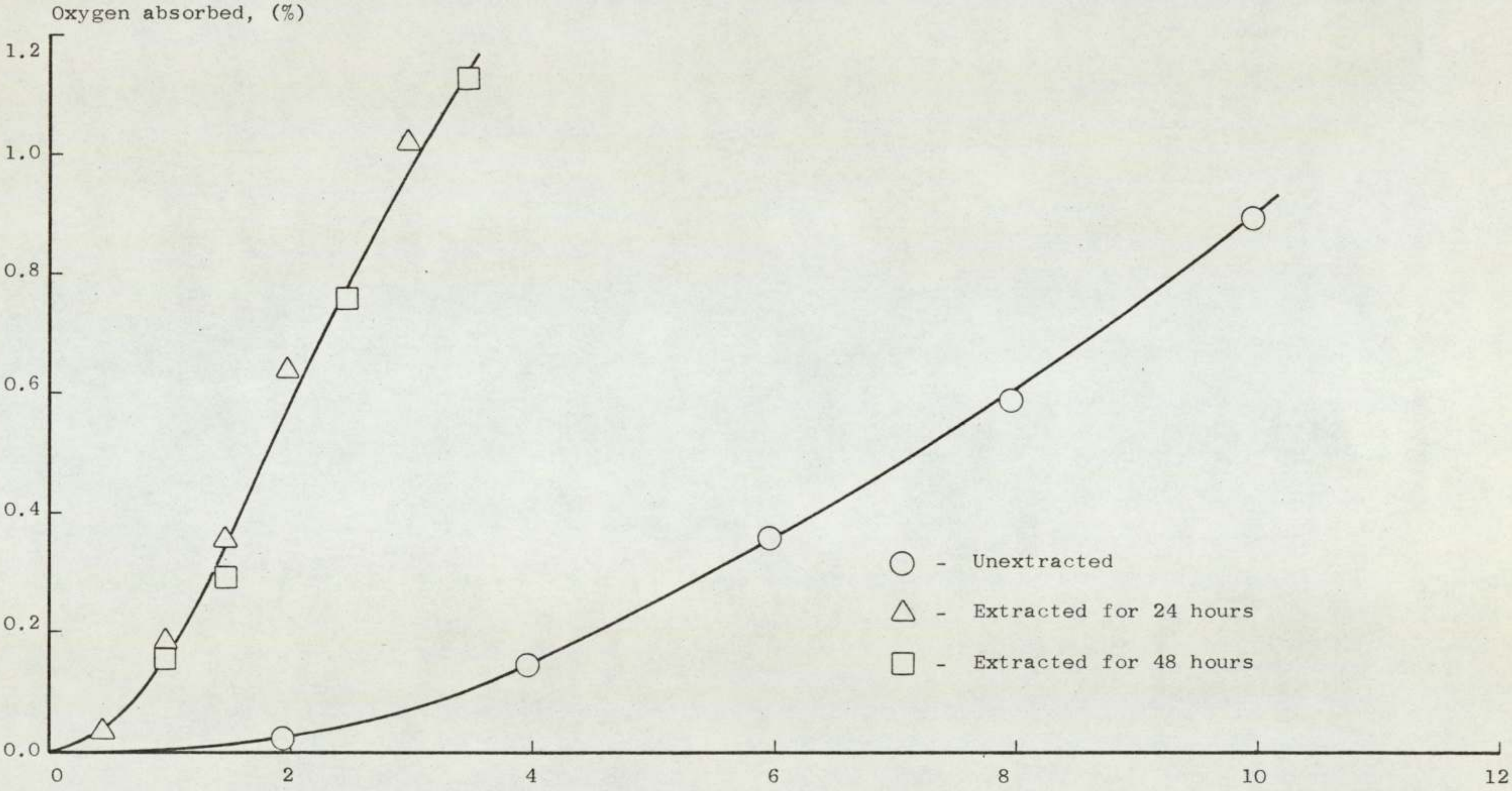


Figure 3.7 Oxygen absorption of Conventional CBS vulcanizates at 80°C before and after solvent extraction

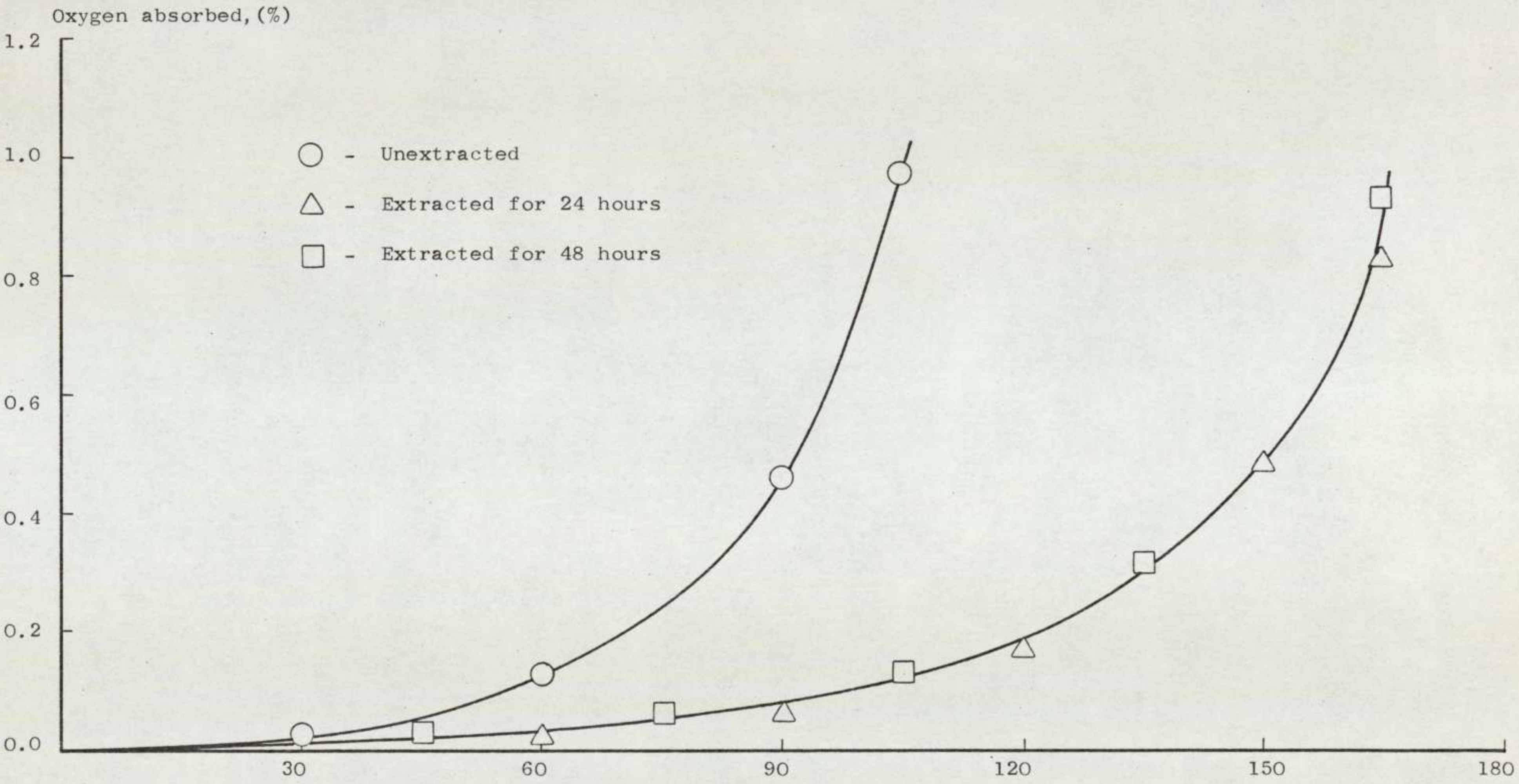


Figure 3.8 Oxygen absorption of Peroxide vulcanizates at 80°C before and after solvent extraction

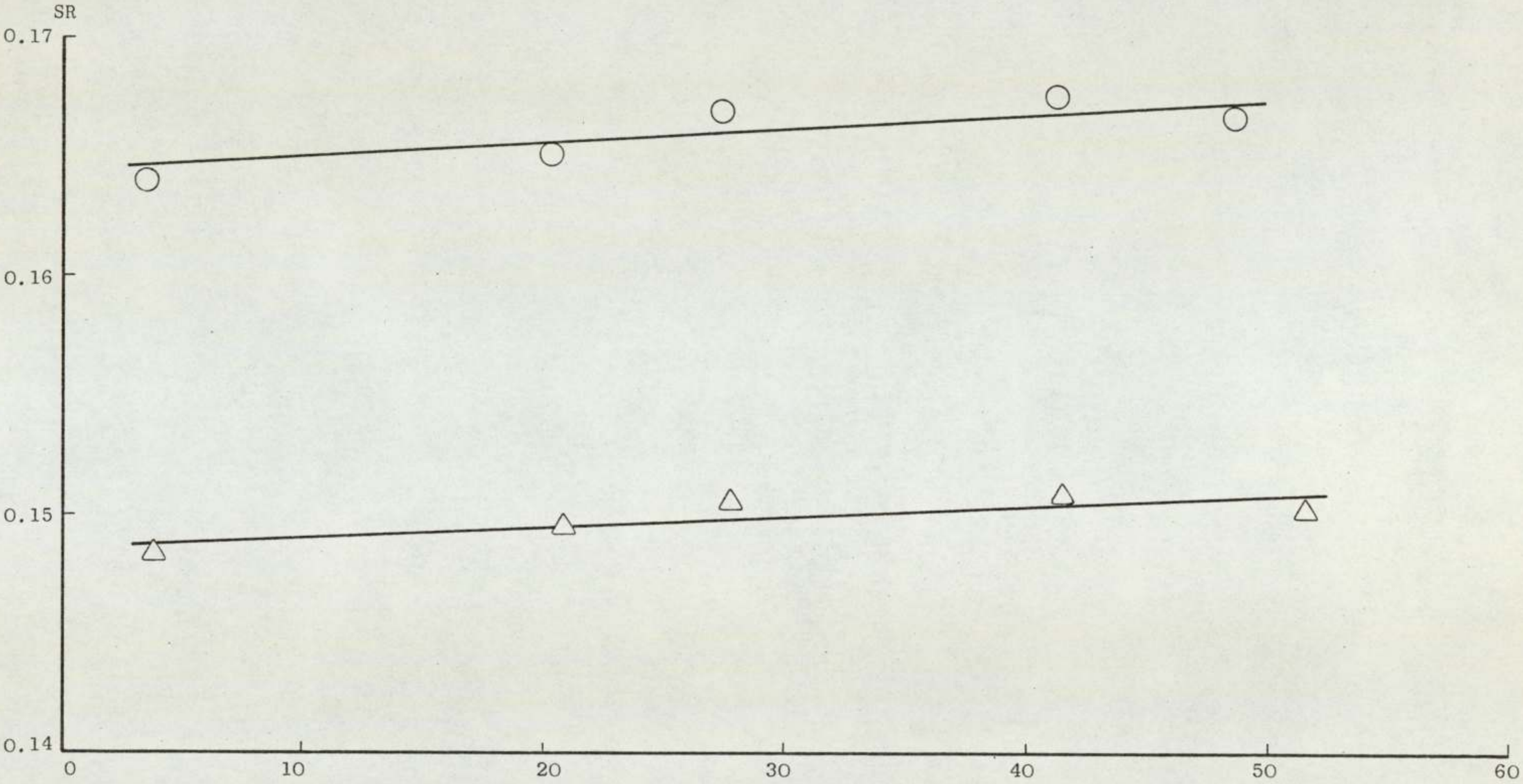


Figure 3.9 Equilibrium weight swelling ratio (SR) of Conventional CBS vulcanizates as a function of extraction time. (○)-solvent mixture at 50°C, (△)-acetone/methanol/chloroform azeotrope at 25°C

4. A comparison of the oxygen absorption characteristics of vulcanizates before and after solvent extraction

4.1 Introduction

The oxidation of peroxide cured and sulphurated vulcanizates of natural rubber have previously been reported and discussed fully in section 1.2. The ageing behaviour of efficient vulcanizates, (EV), of natural rubber have similarly been reported[1]. In this case vulcanizates were prepared from unpurified natural rubber and therefore contain indigenous materials. In addition, EV networks have been examined in the presence of added antioxidants[1,39]. However, the thermal oxidative behaviour of an EV network prepared from an unstabilized stock has not been reported.

The purpose of the work presented in this section is to compare the thermal oxidative behaviour of an EV vulcanizate with other sulphurated networks manufactured from extracted NATSYN. By doing this the presence of indigenous materials or purposely added antioxidants is avoided.

4.2 Experimental procedure and details

The series of vulcanizates, (table 2.2):

A, Peroxide;

D, High modulus CBS;

E, Conventional CBS;

G, Semi EV;

H, EV;

and I, TMTD sulphurless,

were prepared according to the procedure detailed in section 2.3. Oxygen absorption measurements were determined on specimens of the vulcanizates, (section 2.4.1), before and after solvent extraction, (section 2.3.3).

4.3 Results

Oxygen absorption data obtained for the unextracted vulcanizates are presented in figure 4.1. The initial oxygen uptake of the High modulus CBS and Conventional CBS systems was comparable with the peroxide cured vulcanizate. The remaining sulphurated systems possessed improved oxidative stability. In particular, the EV and to a lesser extent the TMTD sulphurless vulcanizate exhibited excellent thermal oxidative stability - figure 4.2.

Following extraction a reduction in stability in all cases was observed and pro-oxidant effects, high initial rates of oxygen absorption compared to the peroxide cured system, were apparent with the exception of the EV network - figure 4.3. After the absorption of approximately 0.5 weight per cent of oxygen the High modulus, Conventional and Semi EV extracted networks became autoinhibiting whereas the TMTD sulphurless vulcanizate continued its high rate of oxygen uptake. Ultimately the autoinhibition gave way to constant rates of oxygen absorption and the EV network began to oxidize at an appreciable rate - figure 4.4.

The thermal oxidative stability of the EV vulcanizate is outstanding, both before and after extraction with solvent mixture for 24 hours. Even after a period of extraction of 110 hours its characteristics are almost unchanged - figure 4.5.

4.4 Discussion During the course of this discussion reference is made to the network analysis data, reported in table 1.2, with respect to the NATSYN vulcanizates described in this section. It is recognized that this is not strictly valid since unpurified natural rubber contains a substantial portion of non-rubber constituents, natural fatty acids, resin acids and nitrogenous materials which

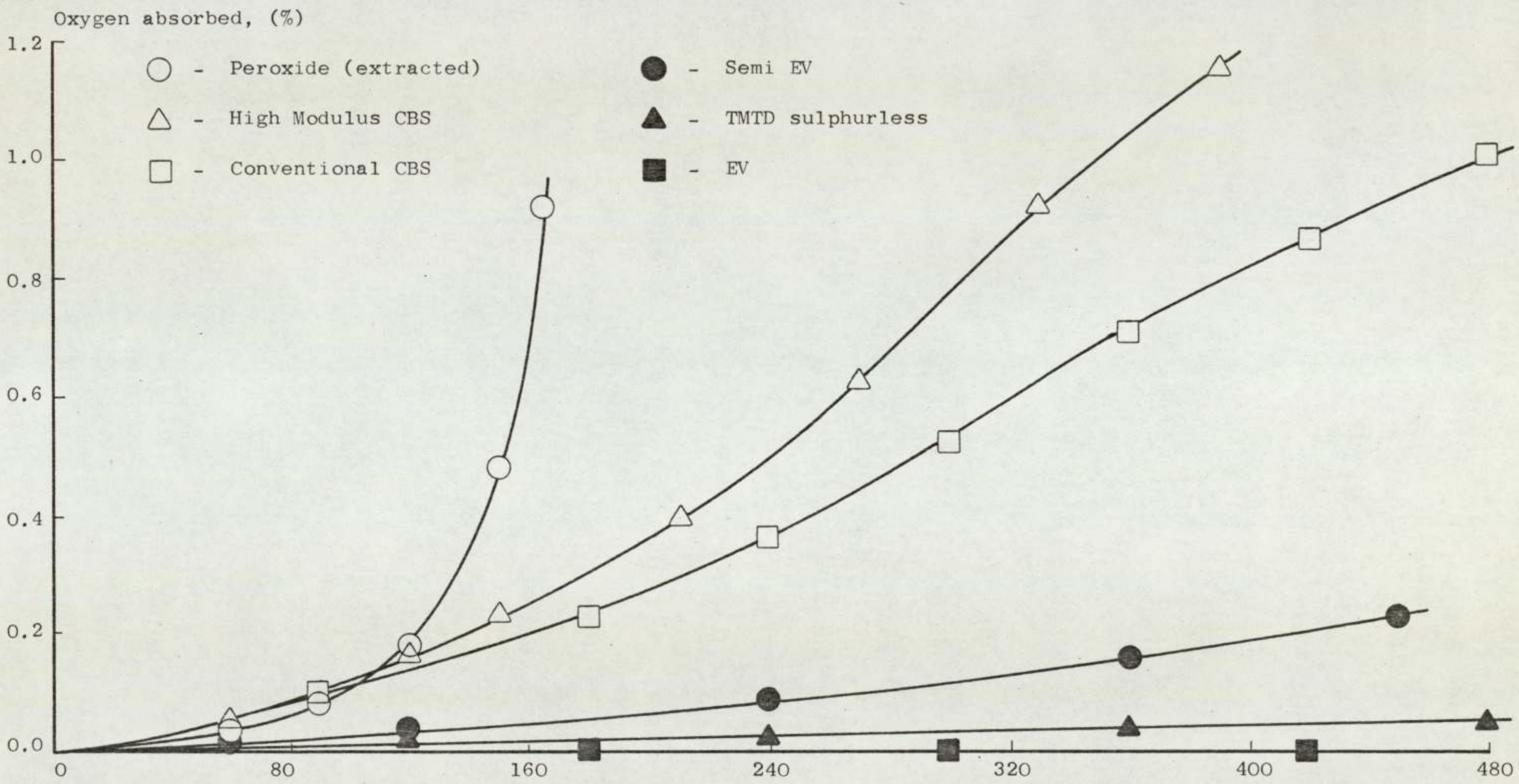


Figure 4.1 Oxygen absorption of unextracted vulcanizates at 80°C

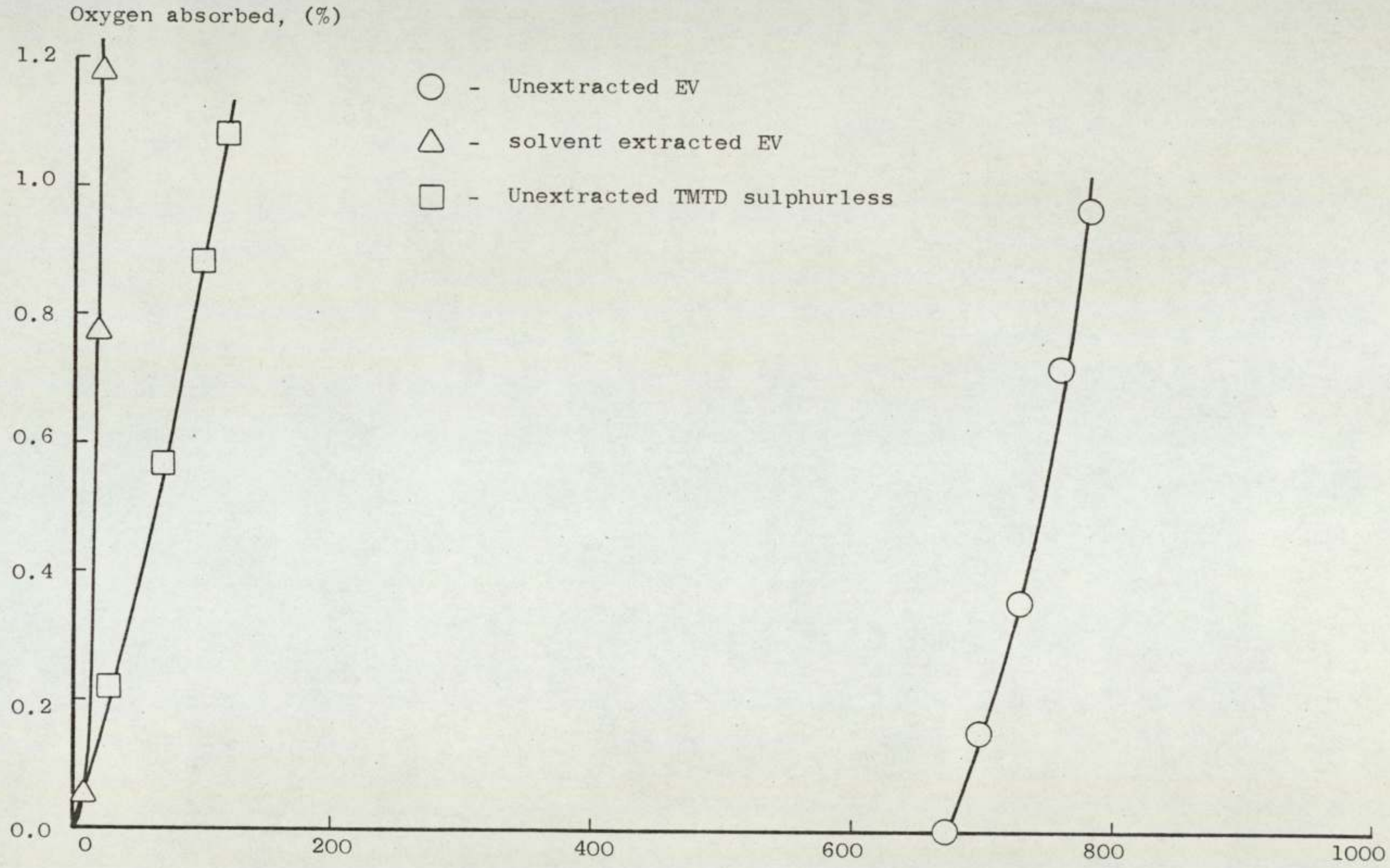


Figure 4.2 Oxygen absorption of EV and TMTD sulphurless vulcanizates at 80°C

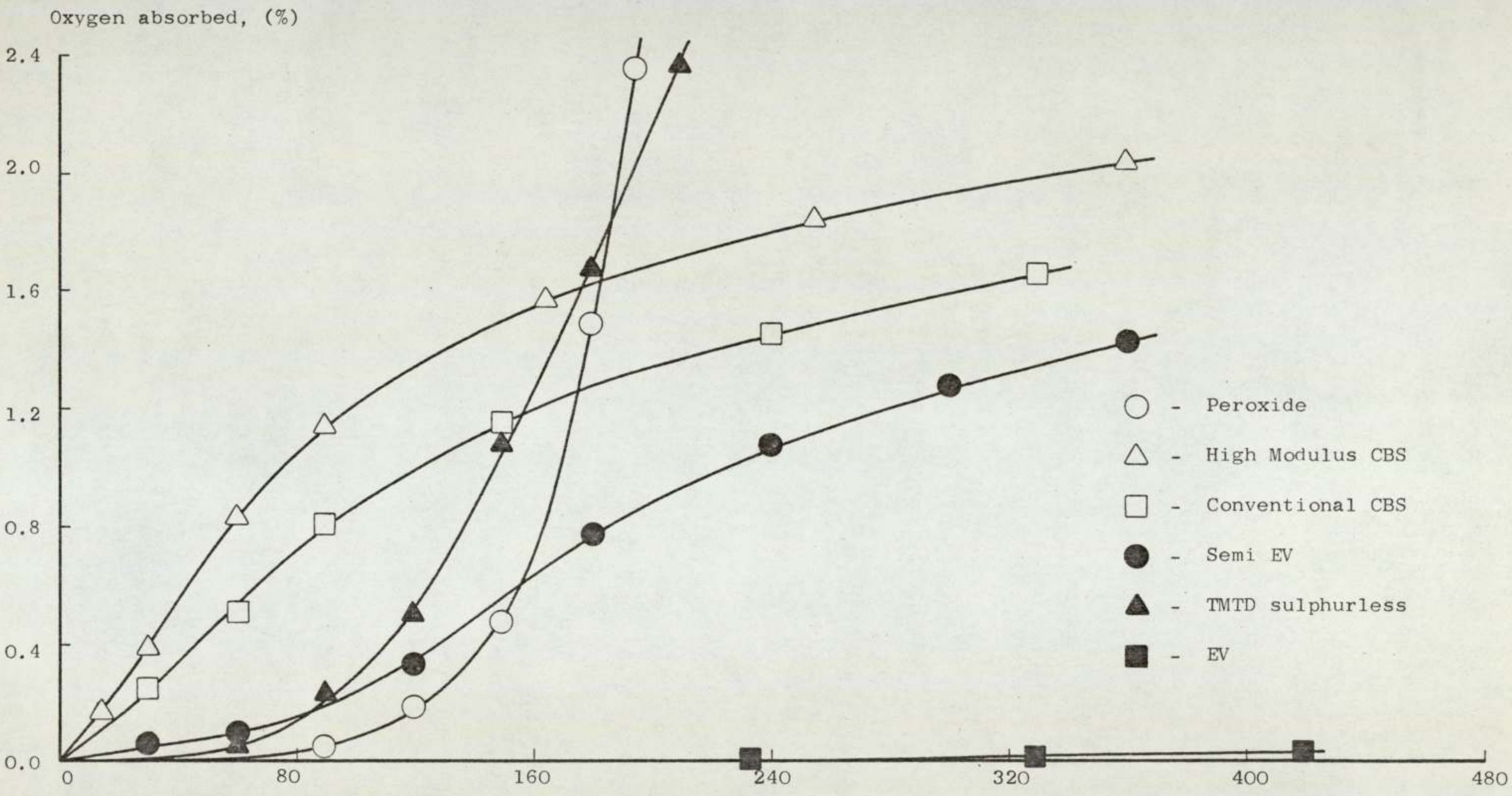


Figure 4.3 Oxygen absorption of solvent extracted vulcanizates at 80°C

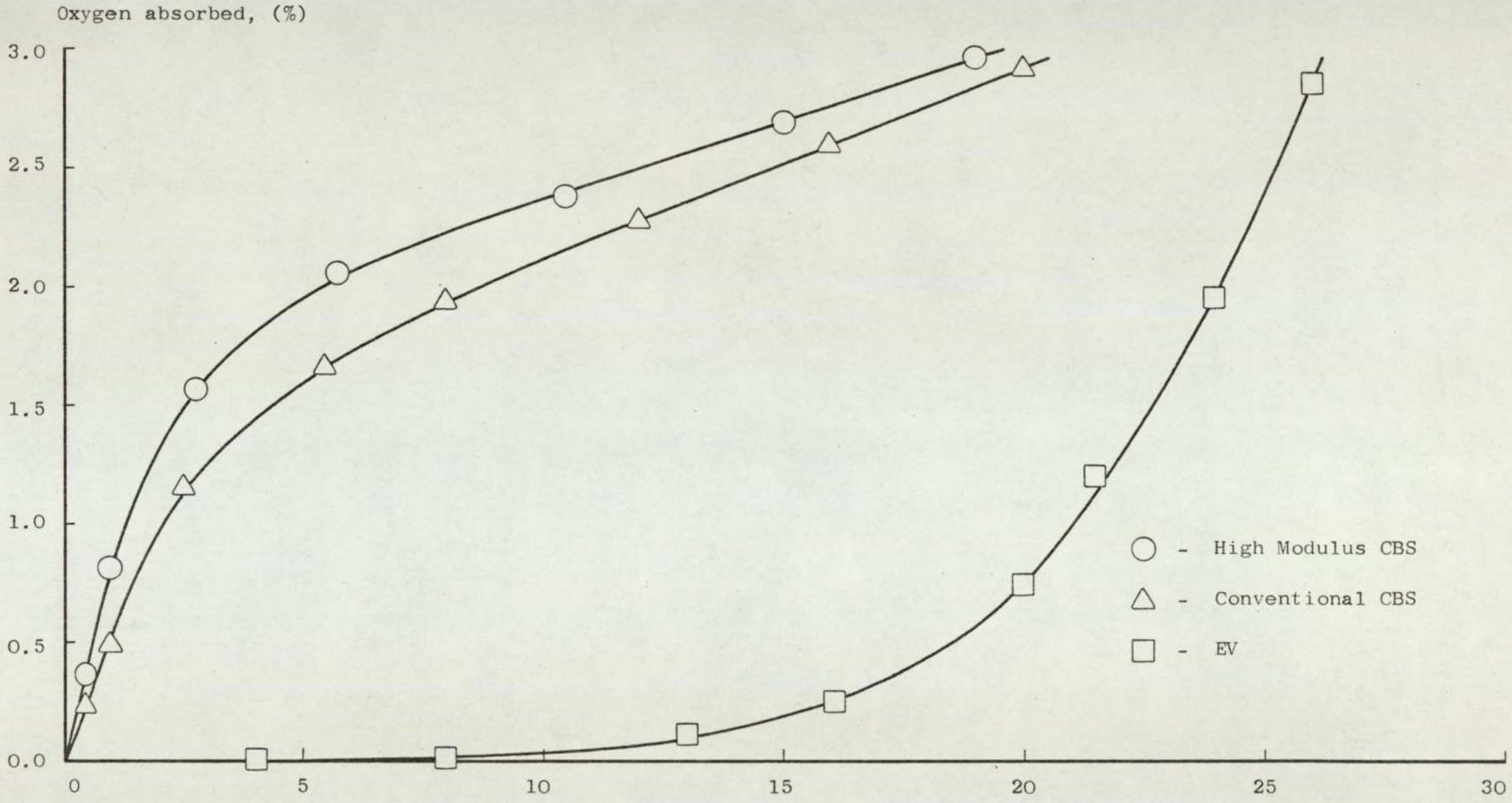


Figure 4.4 Oxygen absorption of solvent extracted vulcanizates at 80°C

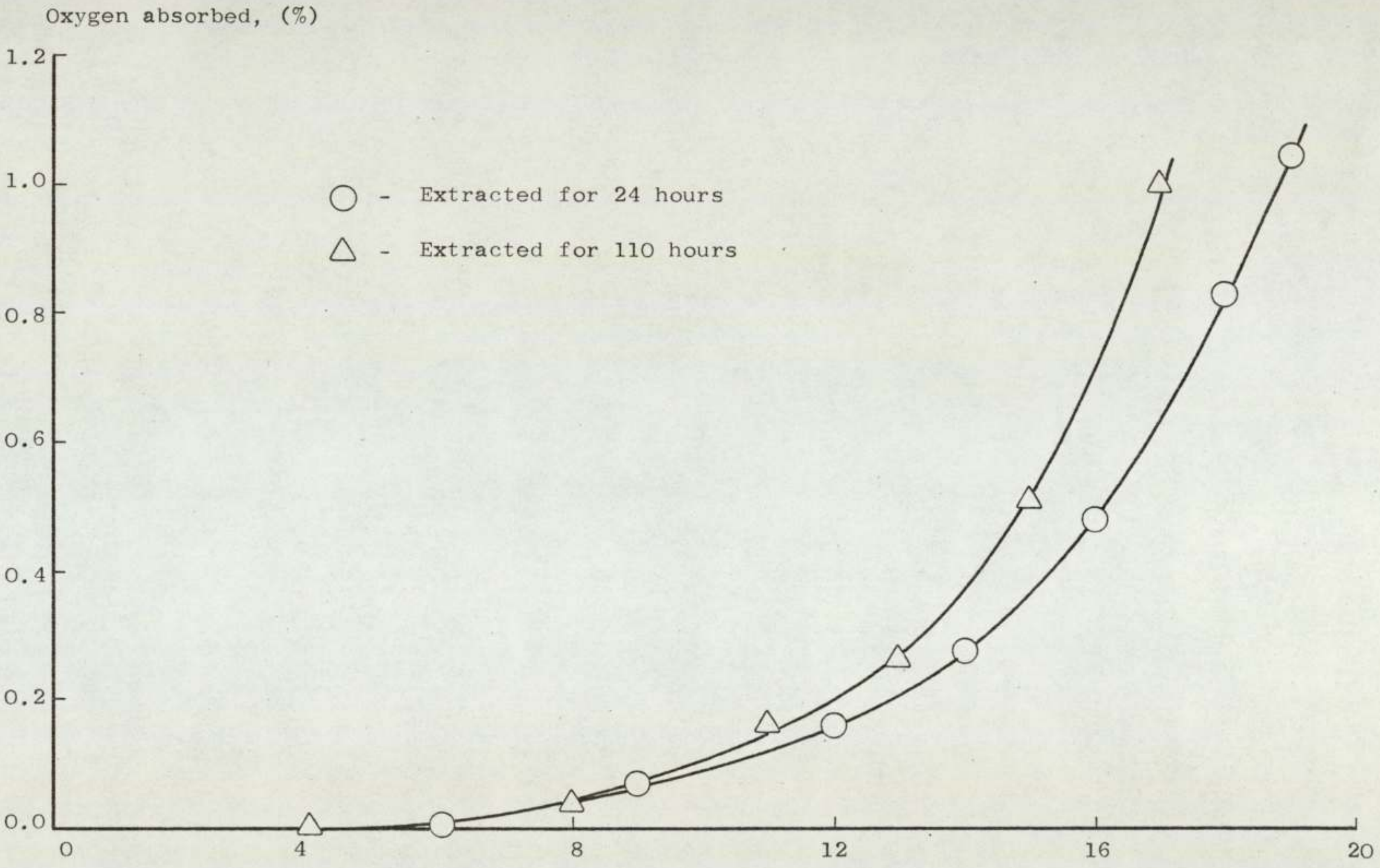


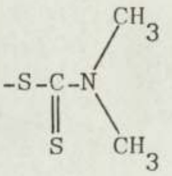
Figure 4.5 Oxygen absorption of solvent extracted EV vulcanizates at 80°C

will exert activating effects during the process of vulcanization[35]. Since these constituents are absent in synthetic polyisoprene, the network structures of vulcanizates manufactured from this and natural rubber will differ slightly. These differences are not so severe as to impede the use of these figures in describing, semi quantitatively, the network structures of NATSYN vulcanizates. Porter et al[55] have shown that the major features of a Conventional CBS vulcanizate prepared from natural rubber were retained in a system manufactured from synthetic polyisoprene. The synthetic polymer cross-linked more slowly than natural rubber and yielded a slightly more complex network. The reversion characteristics were identical with those of the natural rubber vulcanizate and the total sulphur combined in the two systems was similar. A slightly lower cross-link level was observed for the vulcanizate prepared from the synthetic material.
All unextracted sulphur vulcanizates examined possess improved thermal oxidative stability compared to the corresponding extracted systems - figures 4.1 and 4.3. This is particularly evident for the TMTD sulphurless and EV vulcanizates. In the case of the former this is known to be due to the presence and antioxidant activity of solvent extractable zinc dimethyldithiocarbamate formed during vulcanization. Similarly, an extractable antioxidant formed during vulcanization gives rise to the outstanding stability of the unextracted EV system - figure 4.2. This same antioxidant is probably responsible for the improved thermal oxidative stabilities of the High modulus CBS, Conventional CBS and semi EV vulcanizates compared to their extracted counterparts. Although considerable stability is observed during the early stages of oxidation the antioxidant effects appear trivial compared to that observed in the EV system. This is

due possibly to reduced concentrations of the antioxidant, particularly if the latter is derived from the accelerator CBS since the concentration of this compounding ingredient is far greater in the EV system, (table 2.2). In addition, the efficiency of the antioxidant will be reduced in the presence of polysulphidic features present in the higher sulphurated vulcanizates, (table 1.2), whereas the predominantly monosulphidic network of the EV vulcanizate will be highly sensitive to the protective action of an antioxidant.

The oxygen uptake data presented in figure 4.3 are essentially similar to those reported by Bell and Cunneen[56] for the oxidation of purified natural rubber vulcanizates at 100°C. These have been discussed fully in section 1.2.3. The oxygen uptake of the High modulus CBS and Semi EV vulcanizates, previously unreported, possess similar characteristics to those of the Conventional CBS system. Initial pro-oxidant effects are observed followed by autoinhibition and ultimately, linear rates of oxygen uptake - figure 4.4. The extents of pro-oxidation of the High modulus CBS and semi EV vulcanizates differ from that observed for the Conventional CBS system, a more pronounced effect being observed in the system containing a larger proportion of combined sulphur.

The prominent feature emerging from the present study is the superior ageing of the solvent extracted EV vulcanizate. No pro-oxidant effect is apparent, in fact an induction period towards oxidation is observed characteristic of a conventional antioxidant. Even after a prolonged period of extraction the antioxidant appears to remain locked in the network. An inspection of figure 4.3 and table 1.2 reveals that the remarkable difference in oxidative stabilities of the EV and TMTD sulphurless extracted vulcanizates occurs even though the two systems possess similar network structures. Both systems contain predominantly monosulphidic cross-links, the major difference is the type and extent of main chain modifications present. The non-crosslinked sulphur in the TMTD sulphurless network is largely in the form of pendent groups, (IX, X, XI), very few cyclic structures are present[51]. The chief main chain modifications of the EV vulcanizate are cyclic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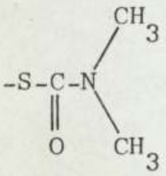
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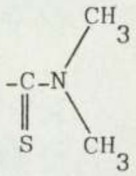
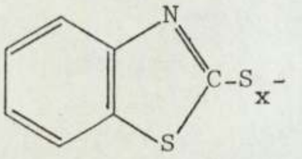

XI

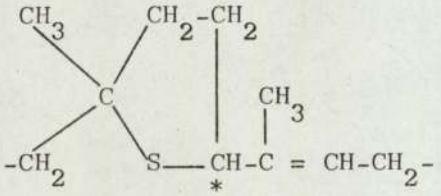
monosulphidic structures and pendent accelerator groups, (XII).


$x=1,2,>2$.

XII

Porter[146] has suggested that the concentration of cylic structures cannot be high since the efficiency of vulcanization is low, the significant main chain modifications being the pendent accelerator residues. Subsequent work[37,38] has indeed confirmed that pendent groups are an important feature of the EV network. Campbell has estimated the pendent group concentration as a function of cure time for a natural rubber vulcanizate and has concluded that an initial high concentration of di- and polysulphidic groups is reduced in number and sulphur rank as the network develops. In the fully cured network, 120 minutes, all pendent groups are monosulphidic, the concentration of which was estimated as equivalent to 3×10^{-5} gramme moles MBT per gramme of network, (section 6). However, this alone cannot account for the non-crosslinked sulphur in the EV network and, therefore, contrary to Porter's suggestion cyclic structures must be present in substantial concentration.

Parks et al have investigated the effects of cylic sulphides[147] and pendent accelerator groups[39] on the thermal oxidative stability of conventionally stabilized cis-polyisoprene networks. Both cyclic structures and pendent accelerator groups increased the rates of oxygen uptake of vulcanizates compared to control systems. Parks has suggested[147] that the pro-oxidant effect of unsaturated cylic sulphides is associated with the activation of a hydrogen at a tertiary carbon atom by an adjacent sulphur atom as well as by a double bond, (XIII). In direct conflict with these results Bell et al[1,48] have reported that cyclic sulphides possess mild antioxidant properties. Investigations were carried out in model systems in the absence of conventional antioxidants. In any event, it is extremely unlikely that cyclic sulphide structures are responsible for the remarkable thermal oxidative stability of extracted EV vulcanizates since these are present in other sulphurated networks also. The effect of pendent accelerator groups in an unstabilized vulcanizate has not been reported but the present investigations suggest that this is not the feature responsible for the stability of the EV network, (section 6). An additional contrasting feature between the TMTD sulphurless and EV systems concerns the extra network materials produced during



XIII

vulcanization. The notable forms of extra network materials in the two systems are zinc dimethyldithiocarbamate and ZMBT, the latter accounting for 56 per cent of MBT originally present as the accelerator CBS in the EV system, (section 5). The residues can be removed from both systems by extraction with solvent mixture. A minor proportion of ZMBT will be hydrolysed during vulcanization however, producing an insoluble basic salt that will effectively remain in the vulcanizate. The subsequent effect on the thermal oxidative stability of the system has not been reported.

5. The identification of the extractable antioxidant in the EV vulcanizate

5.1 Introduction

Although the extra network materials formed during cure with MBT and its derivatives appear to be well documented, (section 1.4), that responsible for the superior thermal oxidative stability of the unextracted EV vulcanizate has not been recognized. The purpose of the work presented here is to ascertain that part of the EV system responsible for its stability.

5.2 Experimental procedure

The solvent extract from an EV vulcanizate was swollen into peroxide cured networks in the presence and absence of inorganic extra network materials likely to be found in sulphur vulcanizates. The latter were compounded into the stocks prior to curing. This was undertaken to determine if the antioxidant was effective once extracted from the vulcanizate.

The extract was analyzed qualitatively and quantitatively, in particular for the major component. An authentic sample of the latter was introduced into a peroxide cured vulcanizate to examine its antioxidant activity.

5.3 Experimental details

5.3.1 Swelling of EV extract into Peroxide, Peroxide/ZnO and Peroxide/ZnS vulcanizates

6.5 grammes of a fully cured, (120 minutes), EV vulcanizate, wiped free of bloom, was extracted with 200 mls of solvent mixture. The extract, plus a small amount of precipitate, was reduced in volume by partial evaporation to give a final volume of about 60 mls. At this stage the solution was dark brown in appearance. Any further reduction in volume resulted in the formation of a large amount of precipitate. Two specimens each of Peroxide, Peroxide/ZnO and Peroxide/ZnS vulcanizates, (table 2.2), previously extracted with solvent mixture, were allowed to swell in the EV vulcanizate extract solution under nitrogen, in the dark for 24 hours. Duplicate control specimens were allowed to swell in 60 mls of solvent mixture under similar conditions. All specimens were dried under vacuum and their oxygen absorption characteristics were determined.

5.3.2 Analysis of the EV vulcanizate extract

About 3 grammes of the fully cured vulcanizate was accurately weighed then extracted with 200 mls of solvent mixture for 24 hours. The vulcanizate was dried to constant weight and the extract, containing a small amount of solid material, was retained.

The solid material was filtered off, washed with a small amount of 30-40 petroleum ether then dried. An infra-red spectrum of the material was recorded. The remaining extract solution was evaporated off on a rotary system and after the removal of the majority of the solvent a precipitate plus an oily solution remained. The complete removal of solvent gave rise to re-dissolution of the precipitate in the oil. This residue was dissolved in benzene and a U.V. spectrum was recorded from 190-390 mμ.

The benzene solution was reduced in volume until precipitation occurred. The precipitate was separated from the oil solution and washed with a small amount of acetone followed by 30-40 petroleum ether. The precipitate was dried under vacuum and an infra-red spectrum was recorded.

The solvent was completely removed from the oil solution leaving a viscous oil. This was dissolved in 30 mls of carbon tetrachloride and suspended on an alumina chromatographic column, (section 2.2.3).

The oil was eluted through the column with 150 mls of benzene. The benzene was removed from the eluate giving a brown viscous oil. An infra-red spectrum was recorded.

5.3.3 Estimation of MBT in the EV vulcanizate extract

5.3.3.1 Acetic acid as reducing agent

About 0.5 grammes of an unextracted EV vulcanizate was accurately weighed and extracted with 200 mls of solvent mixture for 24 hours. The extract was acidified with 12.5 mls of glacial acetic acid to dissolve the small amount of precipitate that had formed. The solution was transferred to a 250 mls volumetric flask and made up to volume with solvent mixture. The concentration of MBT in this solution was determined on a 1 ml aliquot as described in section 2.4.3.

5.3.3.2 Stannous chloride/hydrochloric acid as reducing agent

A 5 mls aliquot of the extract solution prepared as described in section 5.3.3.1 was analyzed for MBT according to the procedure described in section 2.4.4.

5.3.4 The thermal oxidative stability of a Peroxide vulcanizate containing normal ZMBT

5.3.4.1 Introduction of ZMBT into vulcanizate specimens

A saturated solution of pure normal ZMBT in benzene was prepared in a dry box. The benzene was previously dried with molecular sieves, type 5A. Six specimens of a solvent extracted Peroxide vulcanizate, each of approximate weight 0.2 grammes, were swollen in the ZMBT solution for 24 hours. An atmosphere of dry nitrogen was maintained above the solution. Three control specimens were swollen in dry benzene under similar conditions. The specimens were dried under vacuum and stored under vacuum at -10°C.

5.3.4.2 Estimation of ZMBT swollen into vulcanizate specimens

Three of the vulcanizate specimens containing ZMBT, prepared as

described in section 5.3.4.1, were swollen in three separate 50 mls portions of benzene/acetic acid, (5%), solution for 48 hours. This was repeated three times, each time transferring the extract from each specimen into a corresponding 200 mls volumetric flask. The flasks were made up to volume with benzene/acetic acid solution.
A 20 mls aliquot was removed from each extract solution and the concentration of MBT present, and thus the concentration of ZMBT present in the corresponding vulcanizate specimen, was determined as described in section 2.4.3.

5.3.4.3 Oxygen absorption measurements

Oxygen absorption measurements were determined on the remaining specimens prepared in section 5.3.4.1, (section 2.4.1). Furthermore, the effect of heating under vacuum at 100°C for 18 hours was investigated by determining oxygen uptake measurements on heat treated specimens that had been swollen in a saturated solution of commercial ZMBT in benzene. The commercial ZMBT had been previously freed from MBT by extraction with ethanol[149]. Control specimens were prepared and examined under identical conditions

5.3.5 The thermal oxidative stability of Peroxide and Peroxide/ZnO vulcanizates containing MBT

5.3.5.1 Introduction of MBT into vulcanizate specimens

Specimens of solvent extracted Peroxide and Peroxide/ZnO vulcanizates, of approximate weight 0.2 grammes, were swollen in an MBT/chloroform solution containing 0.407 grammes per litre of MBT. After swelling under a nitrogen atmosphere for 24 hours the specimens were dried under vacuum to constant weight. Control specimens were prepared by swelling in chloroform under identical conditions.

5.3.5.2 Estimation of MBT introduced into vulcanizate specimens

The concentration of MBT swollen into the specimens was estimated in a similar manner to that described in section 5.3.4.2.

The oxygen absorption characteristics of the remaining vulcanizate specimens were determined.

5.4 Results

The presence of an active antioxidant in the EV vulcanizate extract is demonstrated in figure 5.1. Marked increases in induction period are observed following the introduction of the antioxidant into vulcanizates in the presence and absence of zinc oxide and zinc sulphide, (3 p.h.r.). Superior ageing is observed in the Peroxide/ZnO system in which synergism occurs between the zinc oxide and a component of the extract. This becomes apparent on inspection of the absorption characteristics of the control specimens. These indicate that whilst zinc oxide imparts a small antioxidant effect alone, its combined effect in the presence of the extractable, EV vulcanizate residues is greater than the summation of the two distinct antioxidant effects. In contrast, zinc sulphide produces a reduction in efficiency of the extractable antioxidant.

The U.V. spectrum of the extract residues dissolved in benzene is shown in figure 5.2. The infra-red spectra of the various components of the extract are presented in figures 5.3, 5.4 and 5.5. Figure 5.3, the insoluble material found in the extract solution; figure 5.4, the major precipitate obtained from the extract; and figure 5.5, the oil residue after complete separation from the other components. A determination of the percentage weight lost on extraction of the EV vulcanizate with solvent mixture gave figures of 6.31% and 6.54%.

The concentrations of MBT recovered in the extract after reduction by the two analytical reagents are shown in table 5.1. Excellent reproducibility is observed. The major component of the extract was shown to be the normal zinc salt of MBT. The effect of an authentic

Reducing agent	Concentration of MBT, gramme moles per gramme of unextracted vulcanizate
Acetic acid	(i) 11.27×10^{-5}
	(ii) 11.30×10^{-5}
Stannous chloride/ hydrochloric acid	(i) 11.30×10^{-5}
	(ii) 11.22×10^{-5}

Table 5.1

sample of this compound on the oxygen absorption characteristics of a Peroxide vulcanizate is displayed in figure 5.6. The antioxidant activity of this compound is demonstrated. The concentration of ZMBT introduced into the Peroxide vulcanizate specimens was estimated as MBT. Results are shown in table 5.2. A greatly improved antioxidant effect is observed after heat treating specimens under vacuum at 100°C prior to oxygen absorption measurements. An increase in the induction period of oxidation of a control specimen is also noted, although in this case somewhat less marked - figure 5.7. MBT also exhibits antioxidant activity but it is not as effective in completely reducing oxygen absorption as its zinc salt. In the presence of zinc oxide, however, an induction period characteristic of ZMBT is observed - figure 5.8. The concentration of MBT introduced

Concentration of MBT, gramme moles per gramme of vulcanizate
(i) 0.41×10^{-5}
(ii) 0.38×10^{-5}
(iii) 0.39×10^{-5}

Table 5.2

into the Peroxide/Zno vulcanizate specimens was estimated in triplicate, results are illustrated in table 5.3.

Additional supporting spectra are shown in figures 5.9-5.12 inclusive.

Concentration of MBT, gramme moles per gramme of vulcanizate
(i) 0.47×10^{-5}
(ii) 0.48×10^{-5}
(iii) 0.48×10^{-5}

Table 5.3

5.5 Discussion

An antioxidant removed from the EV vulcanizate by solvent extraction has been shown to retain its activity when swollen into a Peroxide vulcanizate in the presence and absence of zinc oxide and zinc sulphide. The concentration of these inorganic zinc salts added intentionally to the Peroxide networks was 3 p.h.r. In reality the concentration of zinc sulphide in an EV vulcanizate is likely to be far smaller. Skinner and Watson[52] have measured the amount of sulphur as zinc sulphide in EV vulcanizates prepared from natural rubber and have reported a figure equivalent to 0.4 weight per cent. The compound was cured for 360 minutes at 140°C. The concentration of residual zinc oxide in EV systems has not been determined but a semi-quantitative figure can be deduced by considering the data presented in this present work.

The initial concentration of zinc oxide introduced into the EV compound was 5 p.h.r., this is equivalent to 5.47×10^{-4} gramme atoms of zinc per gramme of compound. The concentration of zinc present in the form of ZMBT after vulcanization was estimated at 0.564×10^{-4} gramme atoms

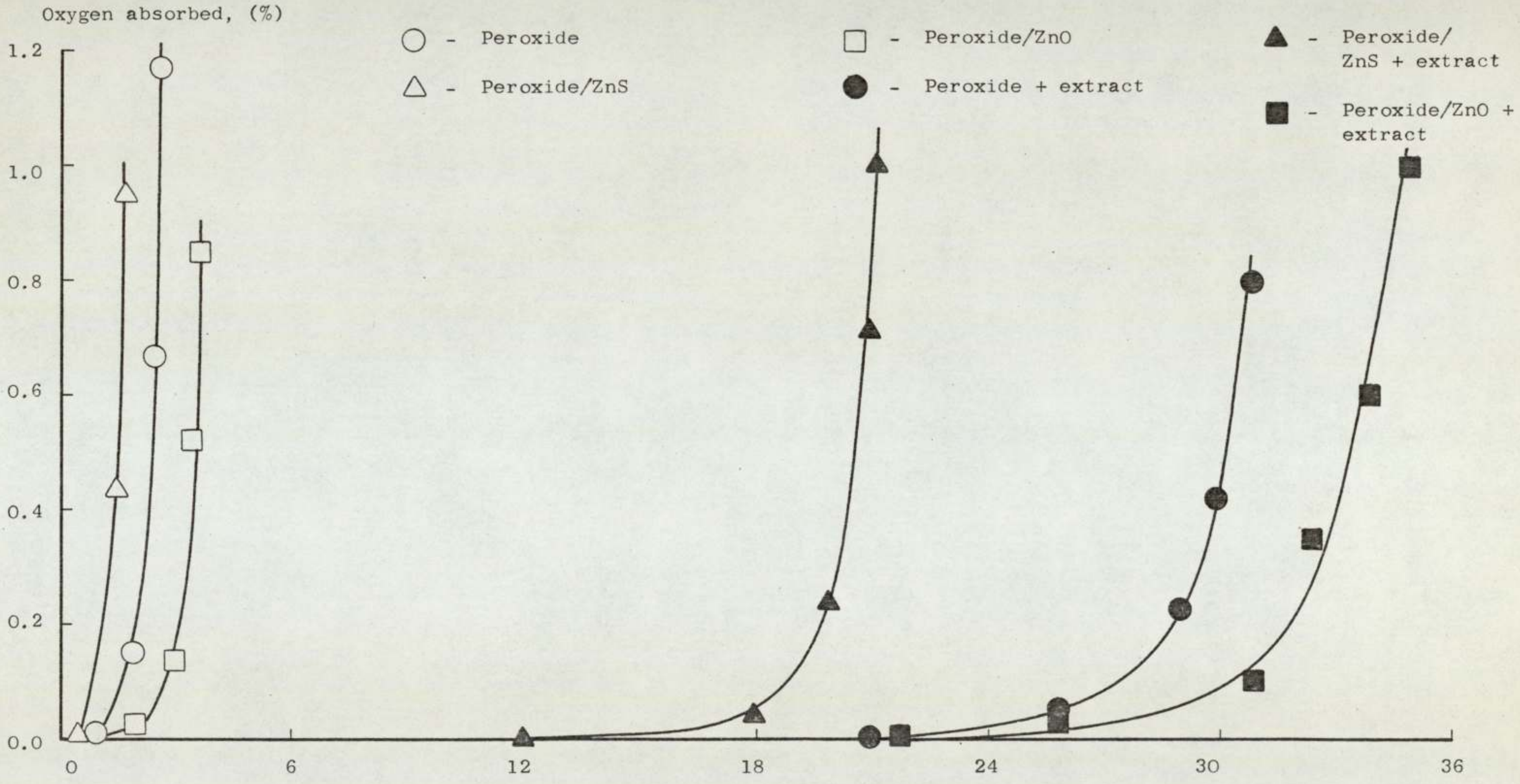


Figure 5.1 Oxygen absorption of Peroxide vulcanizates at 80°C in the presence and absence of EV vulcanizate extract residues

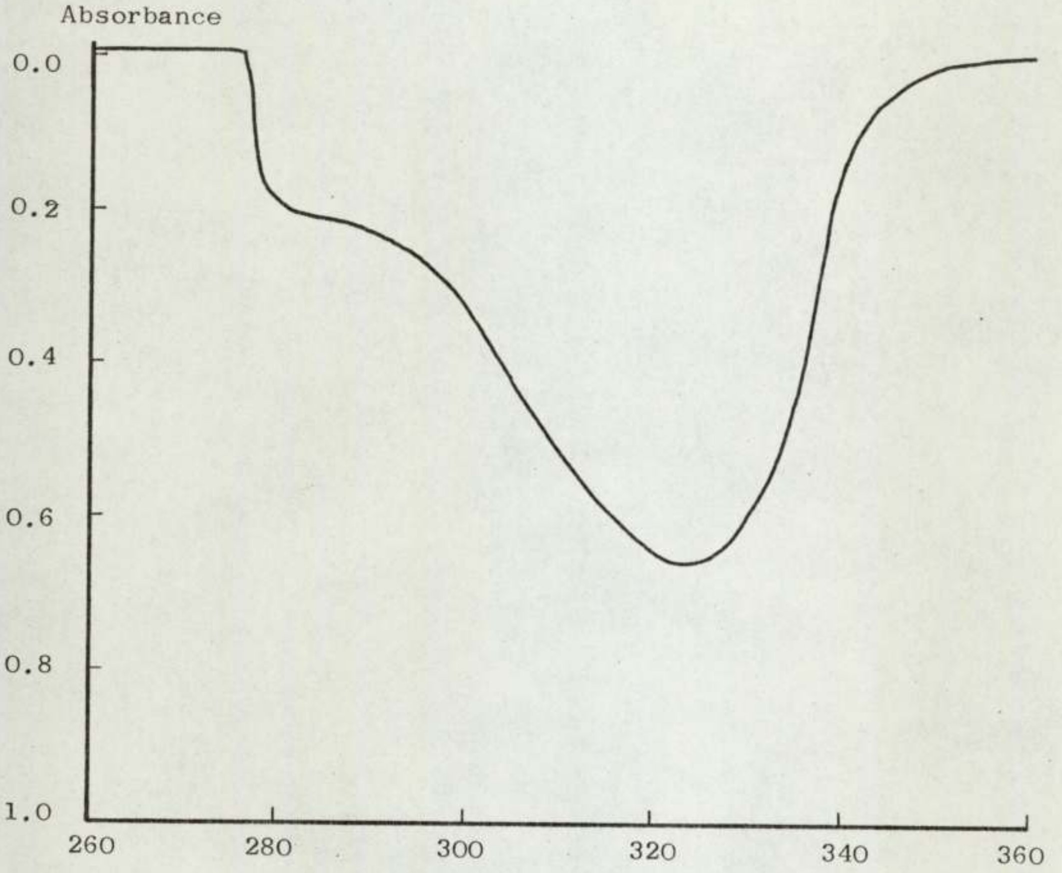


Figure 5.2 UV spectrum of EV vulcanizate extract solution

Wavelength, (mμ)

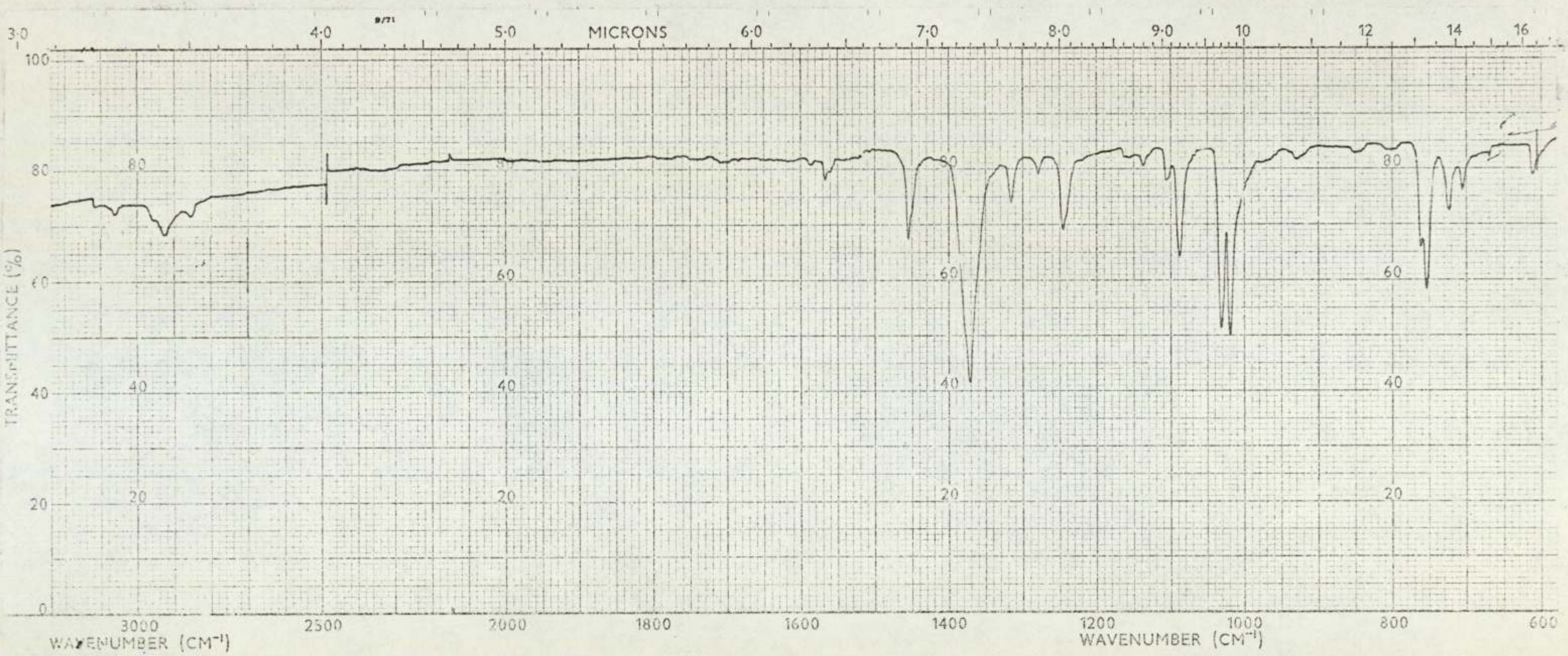


Figure 5.3 Infra-red spectrum of the insoluble material found in the extract solution

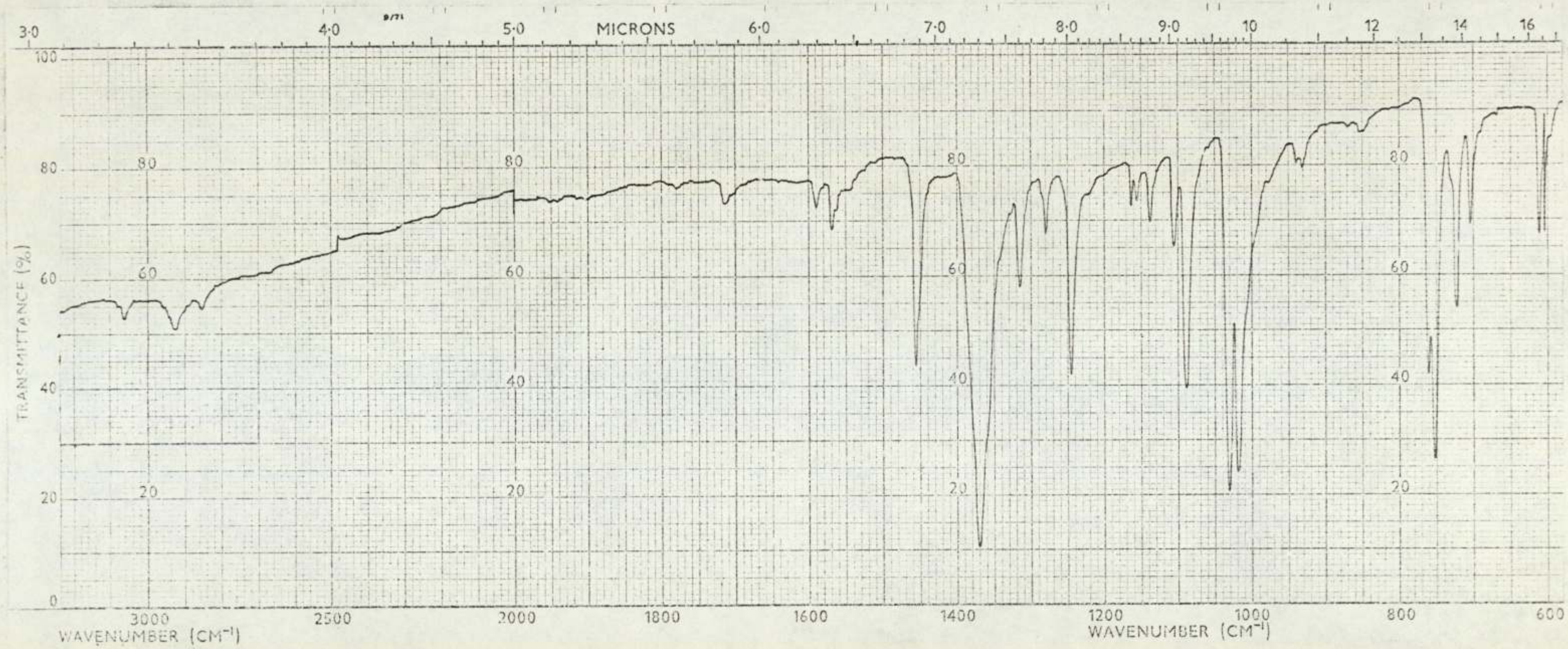


Figure 5.4 Infra-red spectrum of the major precipitate obtained from the extract solution

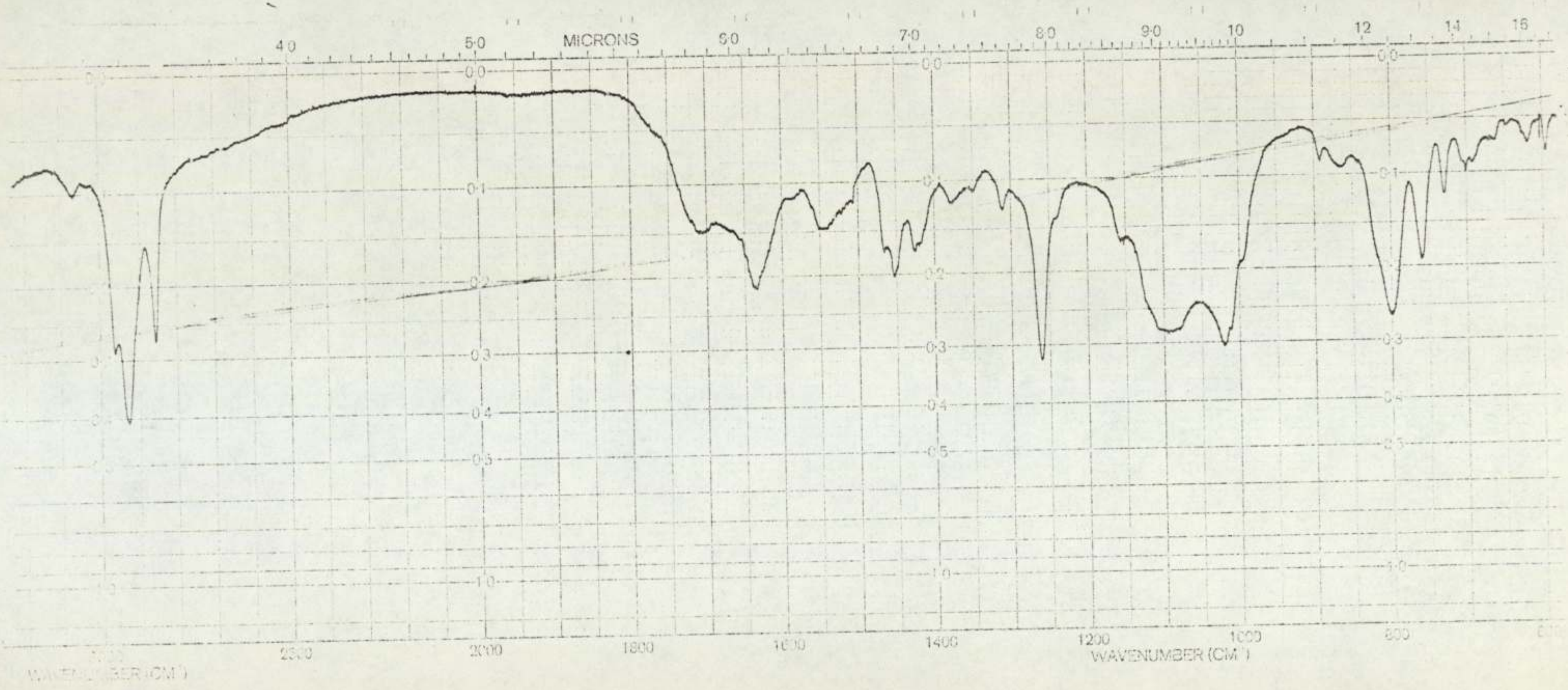


Figure 5.5 Infra-red spectrum of the oil residue from the extract solution

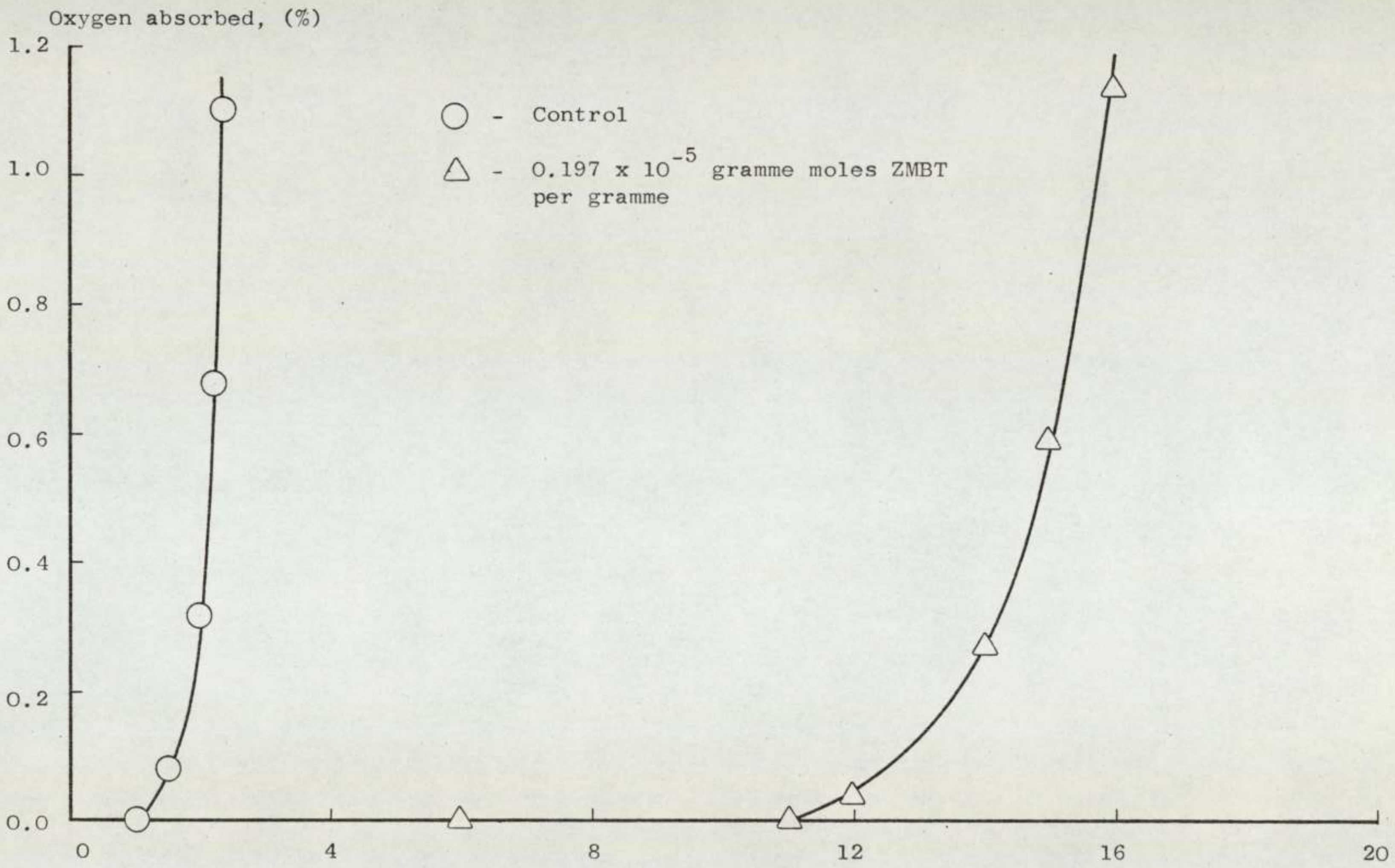


Figure 5.6 Oxygen absorption of Peroxide vulcanizates at 80°C in the presence and absence of ZMBT

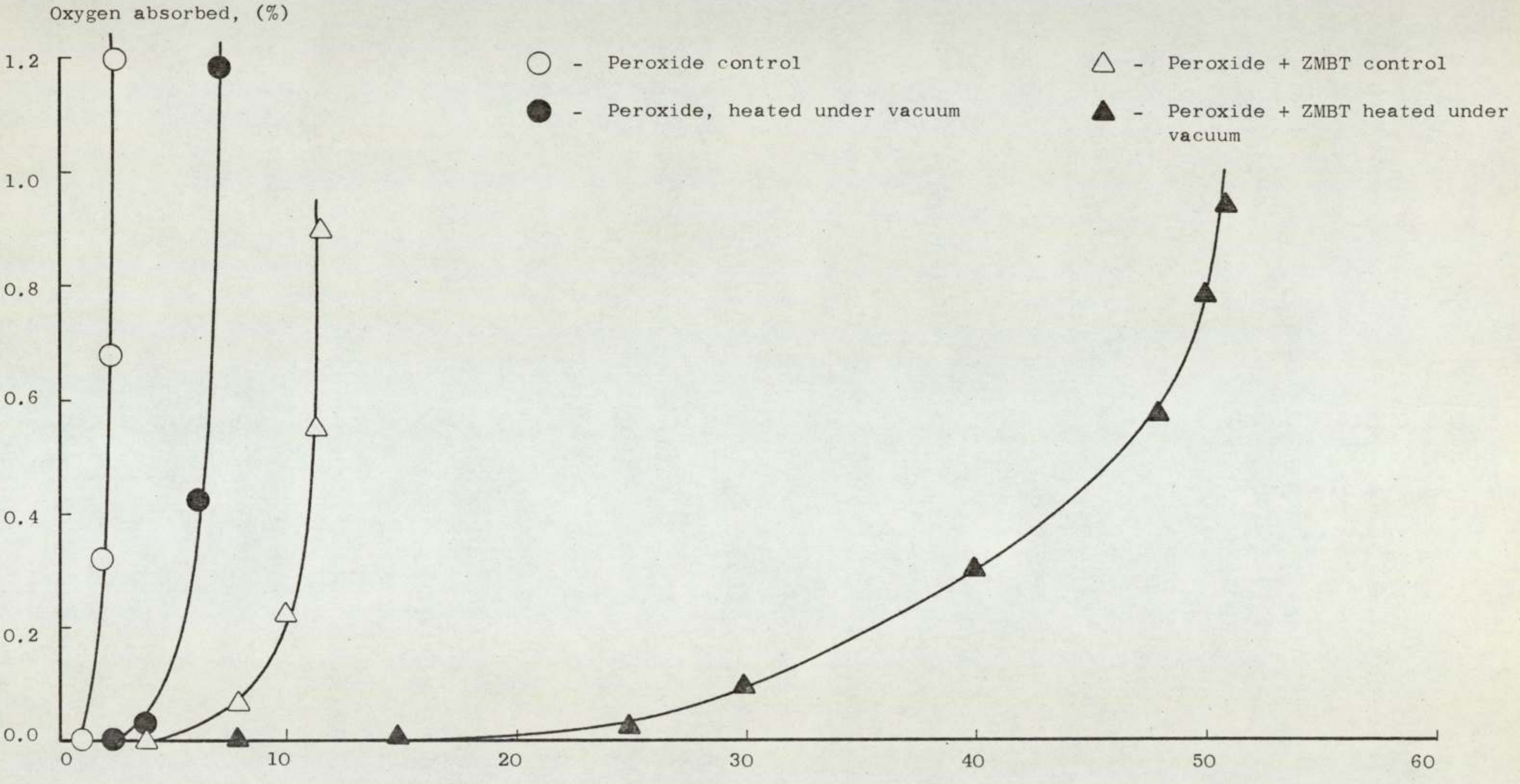


Figure 5.7 Oxygen absorption of Peroxide vulcanizates at 80°C in the presence and absence of ZMBT

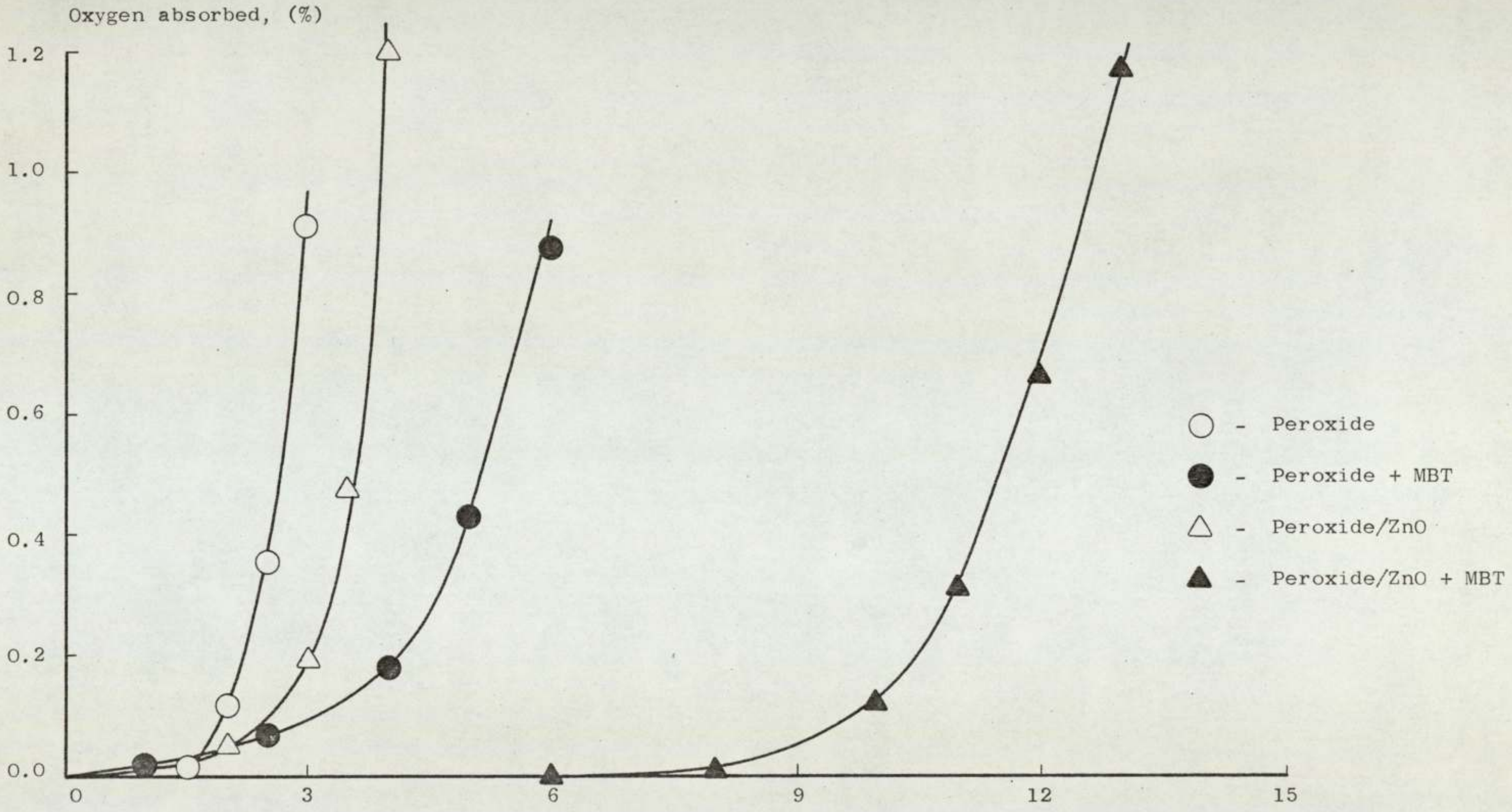


Figure 5.8 Oxygen absorption of Peroxide and Peroxide/ZnO vulcanizates at 80°C in the presence and absence of MBT

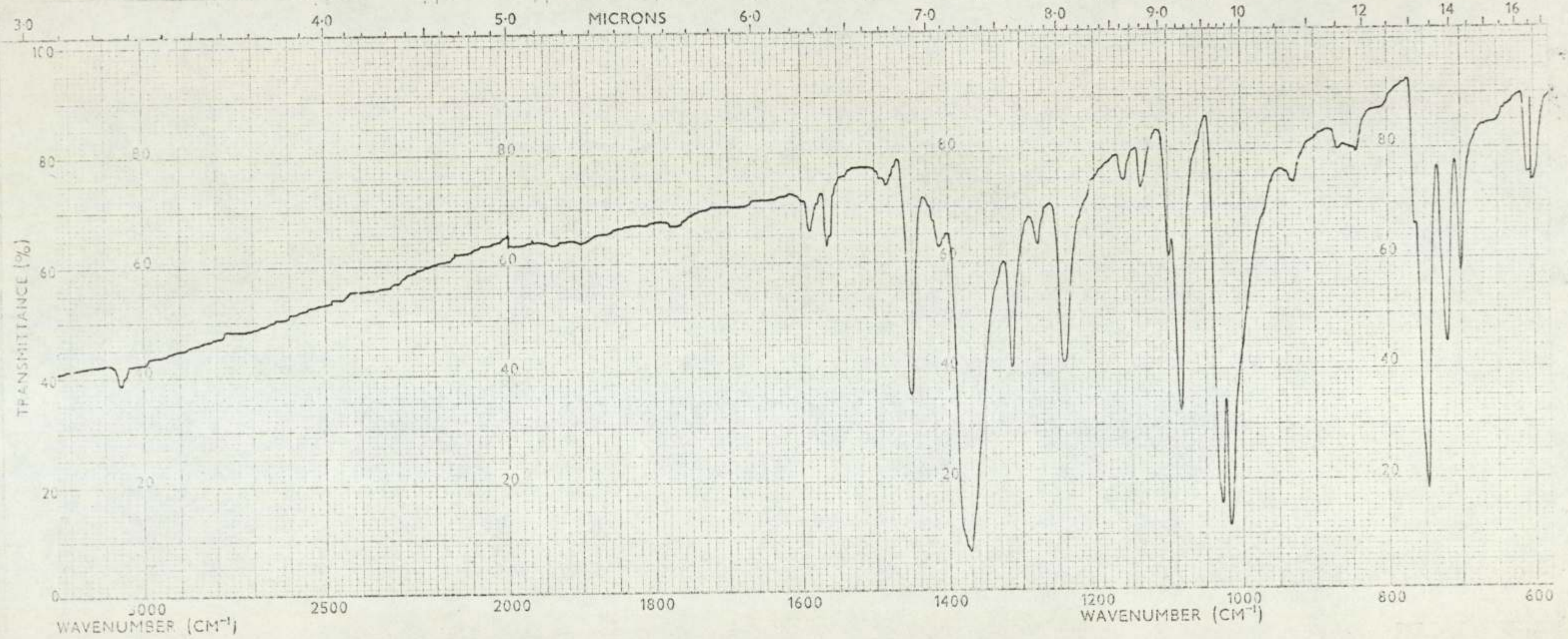


Figure 5.9 Infra-red spectrum of normal ZMBT

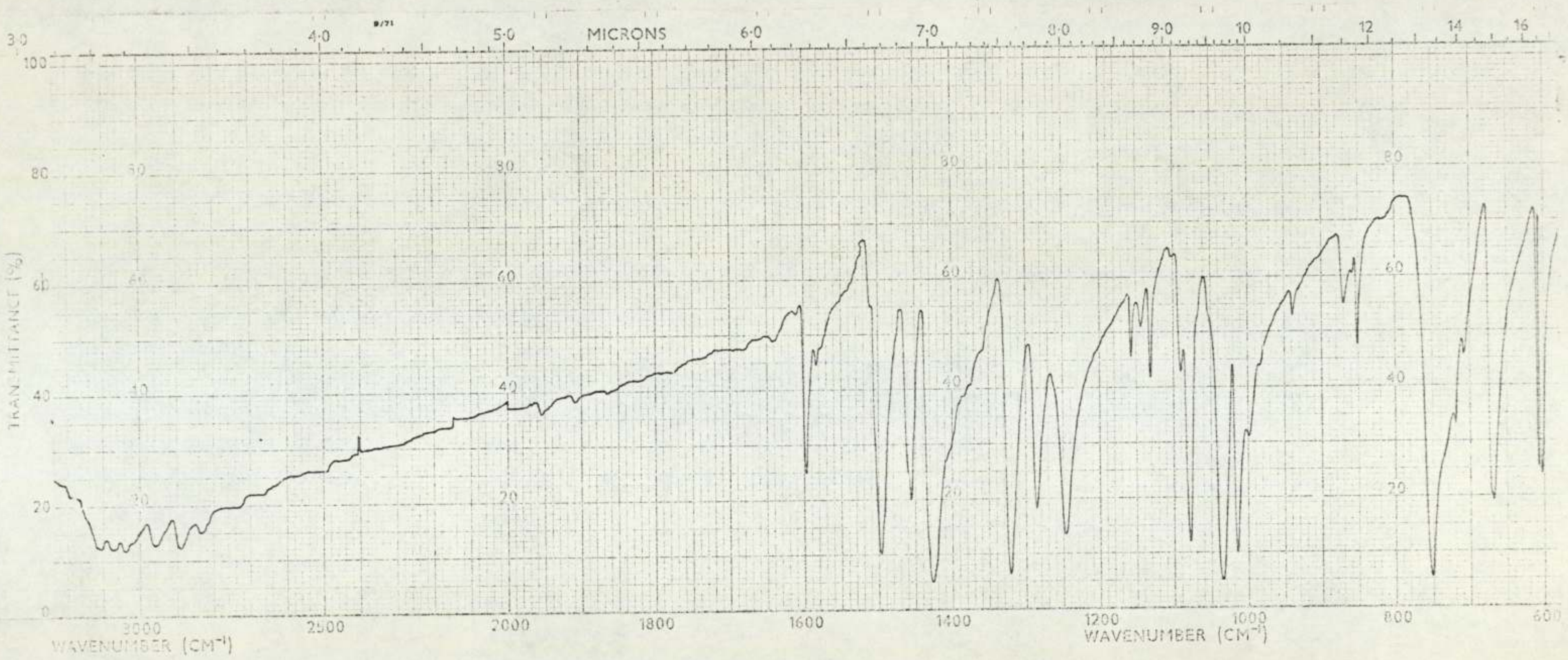


Figure 5.10 Infra-red spectrum of MBT

Figure 5.11 Infra-red spectrum of MBTS

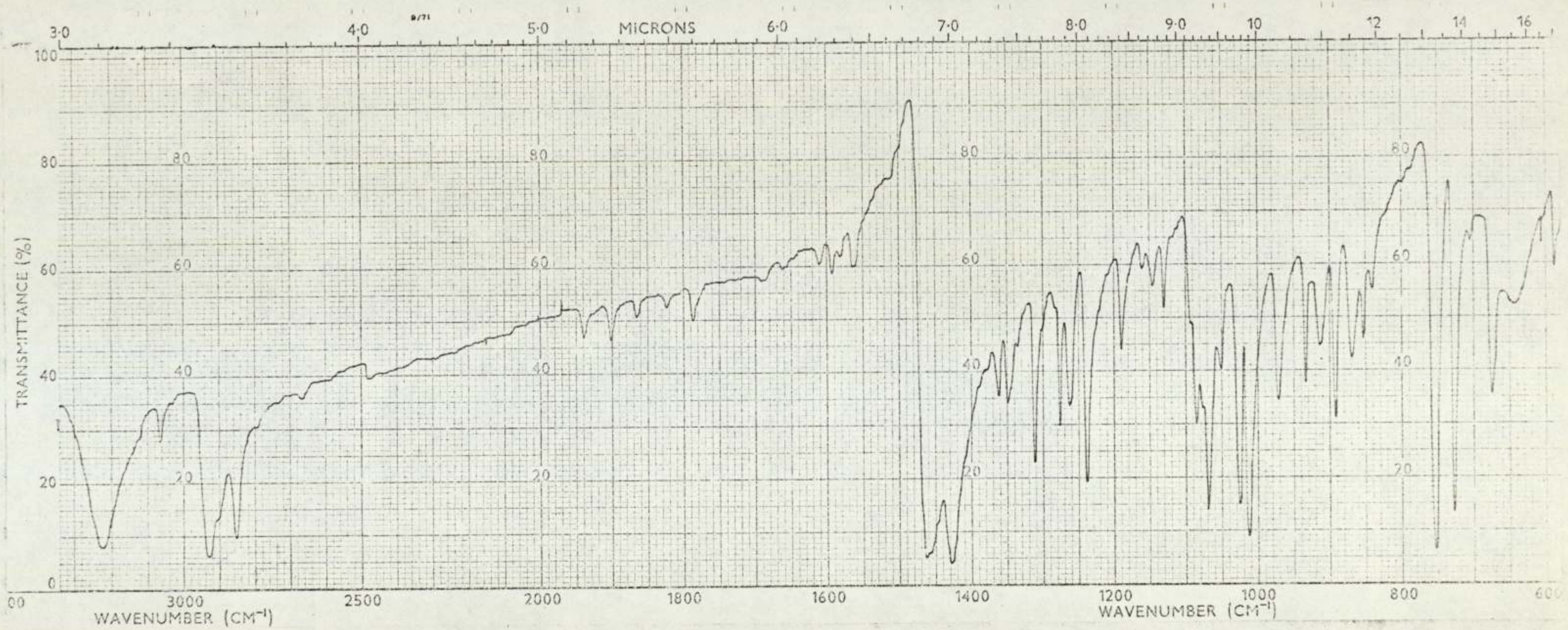


Figure 5.12 Infra-red spectrum of CBS

of zinc per gramme of vulcanizate. If it is assumed that the concentration of zinc sulphide present in the vulcanizate is of the order of that estimated by Skinner and Watson, that is 0.41×10^{-4} gramme atoms of zinc per gramme of vulcanizate, (0.4 wt.%), then an excess of zinc remains in the vulcanizate equal to 4.5×10^{-4} gramme atoms of zinc per gramme of vulcanizate. This will be present in the form of the laurate and residual zinc oxide. Since the zinc oxide originally present was in great excess compared to lauric acid, (12:1 moles), then the majority of the remaining zinc must be present as residual zinc oxide of the order of 4×10^{-4} moles of zinc oxide per gramme of vulcanizate. This is equivalent to 3.2 weight per cent. These figures are borne out by the additional weight loss observed on further treatment of the solvent extracted EV vulcanizate with 5% acetic acid/solvent mixture, (section 6). This removes a further 3 weight per cent of extra network material from the vulcanizate in addition to the 6.4 weight per cent removed by the initial extraction. Zinc sulphide has been shown to be insensitive to the acid extraction whilst zinc oxide is efficiently removed. In addition, the basic zinc salt of MBT is removed by the acid treatment but the concentration removed is insignificant as far as the total weight loss is concerned. Thus, a figure of the order of 3 p.h.r. of residual zinc oxide present in the EV vulcanizate is not unreasonable.

The data in figure 5.1 indicate that zinc sulphide itself is a mild pro-oxidant at a concentration of 3 p.h.r., whereas zinc oxide acts as an antioxidant in a system devoid of sulphurated features. The reason for the pro-oxidant nature of the sulphide is not clear but the antioxidant activity of zinc oxide has been noted previously in peroxide cured, ethylene propylene elastomers[150]. The elastomer was found to contain 140 p.p.m. of vanadium, residues from the vanadium tetrachloride polymerization catalyst. Addition of 5 p.h.r. of zinc oxide gave rise to improved ageing of vulcanizates as measured by percentage retention of tensile strength after oven ageing. On removal of the vanadium in the absence of zinc oxide improved ageing was also observed. Addition of zinc oxide to the purified system resulted in no additional improvement. Thus, zinc oxide suppresses the pro-oxidation caused by the metal residues originally present in the polymer.

The NATSYN used in the present study was prepared by a Ziegler-Natta polymerization process utilizing titanium tetrachloride in the catalyst system[116]. Furthermore, the technical specification of the material, (table 2.1), suggests that metallic residues are present in significant concentration. The catalytic effect of transition metal salts on the autoxidation of hydrocarbons is well known and has been discussed briefly in section 1.3. Angert et al[151] have studied the effect of titanium tetrastearate on the thermal oxidative stability of purified cis-polyisoprene. At all the concentrations investigated, (0.0004-0.02 weight per cent), pro-oxidant effects were observed as determined by oxygen uptake measurements. The reduction in oxidative stability was attributed to the catalytic decomposition of hydroperoxides into chain initiating peroxy radicals, (1.33). More recently Cicchetti et al[152] have investigated the effect of Ti^{IV} compounds on the autoxidation of polypropylene and related model compounds. At a low concentration of the order of 2×10^{-3} moles of titanium tetrastearate per litre, (2,4,6,8-tetramethylnonane), a pro-oxidant effect was noted. Above a critical concentration, however, an antioxidant effect resulted. An overall mechanism of autoxidation has been proposed and a sequence of radical generating reactions arising from the catalytic decomposition of hydroperoxides is included based on that previously described, (1.32)-(1.33). In addition, a primary initiation reaction has been postulated involving the formation of a metal-hydroperoxide complex which subsequently reacts with oxygen to yield an alkyl peroxy radical, (5.1)-(5.2). This is essentially equivalent

$$Ti^{IV} + RH \longrightarrow (Ti^{IV} \ldots\ldots RH) \qquad (5.1)$$

$$(Ti^{IV} \ldots\ldots RH) + O_2 \longrightarrow RO_2\cdot + H^+ + Ti^{III} \qquad (5.2)$$

to the decomposition of hydroperoxide and has been suggested previously by Bawn and Chaudri[153] for the manganese catalysed autoxidation of polypropylene in the liquid phase and by Stivala et al[154] for the cobalt catalysed autoxidation of polypropylene in the solid phase. The mechanism of suppression of the pro-oxidant effect on addition of zinc oxide to the Peroxide vulcanizate is not clear at the present time.

In the presence of the antioxidant introduced into the Peroxide, Peroxide/ZnS, and Peroxide/ZnO networks from the EV vulcanizate extract, all show improved oxidative stability. Zinc sulphide, however, reduces the efficiency of the antioxidant under these conditions. This effect is likely to be less severe in an EV vulcanizate since the concentration of zinc sulphide present in this system is of the order of 0.4 weight per cent. The reactions involved in this effect are not clear. Zinc oxide on the other hand exhibits what appears to be a mild synergistic effect. This is possibly due to a trace of MBT present in the extract derived from hydrolysis of ZMBT during the course of the extraction. In the presence of excess zinc oxide ZMBT will be formed under oxygen absorption conditions, or more likely the basic salt because of liberated water, thereby increasing the oxidative stability of the system. This effect is illustrated in figure 5.8. The MBT introduced into the Peroxide/ZnO system, 0.48 x 10^{-5} gramme moles of MBT per gramme of vulcanizate, bestows a greater oxidative stability compared to a Peroxide vulcanizate containing MBT introduced via the same swelling solution.

The infra-red spectrum of the precipitate isolated from the extract after partial removal of solvent, (figure 5.4), indicates that the major component is ZMBT on inspection of the spectrum of an authentic sample (figure 5.9). Further inspection of the infra-red spectra of MBT and dibenzothiazyl disulphide, (MBTS), figures 5.10 and 5.11 respectively, indicate that these are not present in detectable concentrations. That is, intense bands associated with MBT, (1495 cm^{-1}), and MBTS, (1430 cm^{-1}), are absent.

The infra-red spectrum of the insoluble solid found in the extract solution prior to the removal of solvent is also consistent with that of ZMBT, (figure 5.3). It is more likely that this solid material is the basic zinc salt of MBT since this is insoluble in normal organic solvents. The basic salt will be formed from the normal salt by hydrolysis during the extraction procedure. The infra-red spectrum of a mixture of the basic and normal zinc salts of MBT, commercial ZMBT with MBT removed by ethanol extraction[149], resembles that of the pure normal salt[114].

Since a small amount of the basic salt of MBT is present in the EV vulcanizate extract one would anticipate a corresponding quantity of MBT to be present also, a product of the hydrolysis reaction (5.3)[134]. Infra-red data did not confirm this however, either because the MBT

$$\text{normal ZMBT} \longrightarrow \text{basic zinc salt of MBT + MBT} \qquad (5.3)$$

was not precipitated from the extract solution or since the MBT was not present in a detectable quantity. More informative data was obtained from the U.V. spectrum of the extract in benzene solution, (figure 5.2). This shows an absorption maximum at 323 mμ. The U.V. spectra of MBT and ZMBT in benzene have absorption maxima of 329 mμ and 312 mμ respectively. A maximum at 323 mμ indicates a mixture of ZMBT and MBT[110,134], the concentration of MBT being small.

The infra-red spectrum of the oil isolated from the extract after chromatographic separation, (figure 5.5), exhibits intense bands at 2860 cm^{-1}, 2930 cm^{-1} and 2962 cm^{-1}. The former bands are attributed to the $-CH_2-$ stretching vibrations and the latter to a $-CH_3$ stretching vibration. In addition, a weaker band at 3060 cm^{-1} is attributed to the aromatic =C-H stretching vibration present also in the spectra of ZMBT and CBS, figures 5.9 and 5.12 respectively. Furthermore, the aromatic feature of the oil is supported by a band at 760 cm^{-1} attributed to the out of plane aromatic -C-H deformation present as strong bands in the spectra of ZMBT, MBT and CBS at 750 cm^{-1}. The data suggests the isolation of an extractable pendent group previously reported by Campbell and Wise[111] for MBT, MBTS and 2-(4-morpholinothio) benzothiazole accelerated sulphur vulcanizates. This was of a polysulphidic nature and was reduced by the stannous chloride/hydrochloric acid reagent to yield MBT. It is unlikely that the extractable pendent group associated with the EV vulcanizate is polysulphidic, more likely monosulphidic in parallel with the other sulphurated features of the network[37].

Thus, the EV vulcanizate extract consists essentially of:

a) ZMBT as the major constituent;

b) insoluble basic zinc salt of MBT;

c) MBT;

and d) an extractable pendent group.

It is not possible to show conclusively that MBT is absent in the fully cured vulcanizate and that the MBT present in the extract arises solely from hydrolysis of the extracted ZMBT. However, a minor amount of MBT present in the extract can be reconciled with the formation of some insoluble basic zinc salt of MBT. In addition, zinc oxide is present initially in a 2.7 molar excess compared to accelerator and the stoichiometry of normal ZMBT formation requires 2 moles of MBT per mole of zinc oxide. This 2:1 stoichiometry will be reduced slightly towards unity by the formation of a small quantity of basic zinc salt of MBT in the vulcanizate during cure, (section 6). Thus, any free MBT will be converted into the zinc salt in the presence of the excess zinc oxide. Favre[110] has also suggested that MBT is unlikely to be present in an optimum cured MBT accelerated vulcanizate.

The extractable ZMBT in the EV vulcanizate, recovered in the form of normal ZMBT, basic zinc salt of MBT and MBT, was estimated by reducing the former compounds with acetic acid to MBT followed by U.V. analysis. The figures of 11.27×10^{-5} and 11.30×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate show excellent reproducibility. The stannous chloride/hydrochloric acid reagent produced figures of 11.30×10^{-5} and 11.22×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate, giving good agreement with the previous data. The stannous chloride reagent will cleave disulphides whereas the acetic acid reagent will not. Thus, these results dismiss the possibility of MBTS being present in the extract confirming previous infra-red data. Since the extractable pendent groups are monosulphidic they will not be reduced by either of the analytical reagents and, therefore, they will not be included in the estimation of MBT. Thus, the figures ranging from 11.22×10^{-5} to 11.30×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate give a reliable estimate of the ZMBT extracted from the EV system.

The theoretical concentration of the MBT function originally present in the EV compound is 20.18×10^{-5} gramme moles of MBT per gramme of compound. Therefore the extractable ZMBT accounts for 56 per cent of the MBT originally present in the form of CBS. Additional MBT function is combined in the form of extractable pendent groups, the remaining portion being present in the unextracted vulcanizate largely as attached pendent groups. A minor quantity of the MBT function is present in the bloom of the unextracted vulcanizate and has been shown to consist essentially of ZMBT. A more detailed discussion concerning the recovery of MBT is given in section 6.5.

Since the major component of the extract was shown to be ZMBT its antioxidant activity was examined in a Peroxide network. The data are shown graphically in figure 5.6. A significant increase in induction period is obtained on introduction of ZMBT into the system. The concentration of ZMBT was estimated as equivalent to 0.39×10^{-5} gramme moles of MBT per gramme of vulcanizate, 0.197×10^{-5} gramme moles of ZMBT per gramme of vulcanizate.

The unextracted EV vulcanizate exhibits an induction period of 670 hours, (figure 4.2), and this is known to contain extractable ZMBT equivalent to 11.27×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate. On a linear proportional basis one would have anticipated an induction period of the order of 400 hours by comparison with the data obtained for ZMBT introduced into the Peroxide vulcanizate. There are several possible reasons for this discrepancy.

The first is that the concentration effect is not linear. Radical deactivating antioxidants, that is conventional phenolics and amines, give an induction period proportional to the concentration of the inhibitor[73], whereas peroxide decomposing antioxidants exhibit greater than direct proportional dependence. Kennerly and Patterson[91] have shown for a variety of sulphur containing compounds known to be effective peroxide decomposers, that the induction periods of autoxidations in white oil are proportional to the square of the inhibitor concentration. The exact nature of the concentration dependence of ZMBT in polyisoprene vulcanizates is not known but the kinetics are likely to be complex because of the two distinct modes of antioxidant activity exhibited by ZMBT, (section 7). Secondly, the basic network structures of the two systems, the Peroxide vulcanizate and the EV vulcanizate, are dissimilar. Certain structural constituents in the networks, particularly sulphurated features in the EV system, may affect the efficiency of ZMBT as an antioxidant. Thirdly, hydroperoxide groups present in a Peroxide vulcanizate prior to the commencement of oxygen absorption measurements will modify its subsequent oxidative stability. The structures of hydroperoxides present in polyisoprene systems have been described in section 1.1. These will be present in the peroxide cured system due to oxidation during compounding and possibly during vulcanization if oxygen is not completely excluded. The hydroperoxides will act as chain initiators thereby reducing the induction period of the autoxidation. The EV system on the other hand will be free from hydroperoxides because of the formation of ZMBT, a hydroperoxide decomposer (section 7), during vulcanization. As a result a direct comparison of the antioxidant efficiency of ZMBT in Peroxide and EV vulcanizates is not strictly valid.

The importance of initial hydroperoxide concentration with respect to ZMBT antioxidant efficiency is illustrated in figure 5.7 where Peroxide vulcanizates were heated under vacuum at 100°C for 18 hours, thus destroying the hydroperoxide groups[2]. Consequently an increase in the induction period of the autoxidation would be expected. This is observed, the oxidation of the vulcanizate containing ZMBT increasing in induction period by a factor of four. The ZMBT introduced into the peroxide cured network was the commercial grade and is known to contain the basic zinc salt of MBT and MBT[149]. Extraction of this material removes MBT leaving the normal and basic zinc salts. Since the latter is insoluble in benzene only the normal ZMBT will be effectively swollen into the vulcanizate.

In essence, ZMBT has been shown to be a major extractable material in the EV vulcanizate. Its presence in the system imparts good thermal oxidative stability illustrated by introduction of an authentic sample into a peroxide cured network. The modes of antioxidant action of ZMBT in model systems are reported in section 7.

6. A determination of the antioxidant in the solvent extracted EV vulcanizate

6.1 Introduction

A comparison of the thermal oxidative stabilities of TMTD sulphurless and EV vulcanizates, both extracted after cure with solvent mixture, indicates a remarkable stability of the latter, (figure 4.3). The reason for this difference between the two systems has been discussed in section 4.4. It was the purpose of the work presented in this section to establish the relative importance, with respect to thermal oxidative stability, of pendent accelerator groups and the basic zinc salt of MBT present in the solvent extracted EV vulcanizate.

6.2 Experimental procedure

The effect of cure time on the thermal oxidative stability of solvent extracted EV vulcanizates was investigated. An effort was made to estimate the concentration of pendent groups throughout the range of cure times. The fully cured vulcanizate, (120 minutes), was extracted further, but not continuously, with a solution comprising 5% acetic acid, (v/v), in solvent mixture. This extraction system, to be known as the acid extraction mixture and the procedure as acid extraction, removes the basic zinc salt of MBT from the vulcanizate[37]. The consequent effect on oxygen absorption was determined. The basic salt removed from the vulcanizate by acid extraction was estimated in the form of MBT and the possibility of network degradation occurring during the treatment was assessed from equilibrium swelling data.

6.3 Experimental details

6.3.1 Preparation of vulcanizates

EV vulcanizates were prepared of varying cure times, 40, 45, 60, 120 and 240 minutes, according to the technique described in section 2.3. The vulcanizates were extracted with solvent mixture in the usual manner for 24 hours. Oxygen absorption measurements were carried out, (section 2.4.1).

6.3.2 Estimation of the MBT function in solvent extracted vulcanizates

The major contribution derives from attached pendent accelerator groups whereas a smaller quantity is attributable to the insoluble basic zinc salt of MBT.

The transmission infra-red spectrum between 700-800 cm^{-1} was recorded for a selected specimen of required thickness, (0.0085 - 0.0090 inches), of each vulcanizate. The height of the band at 750 cm^{-1}, due to the ortho-disubstituted aromatic structure in the MBT group, was measured with reference to a baseline constructed from 710 cm^{-1} to 770 cm^{-1}. An extracted Peroxide vulcanizate specimen of corresponding dimensions was placed in the reference path of the spectrometer.

A calibration curve was constructed by swelling accurately weighed specimens in duplicate, of a fully cured, solvent extracted, EV vulcanizate in solutions of MBT/acetone of increasing concentrations. Smaller vulcanizate specimens intended for infra-red analysis were swollen in corresponding solutions. After drying under vacuum the concentrations of MBT introduced into the duplicate series of vulcanizate specimens were determined by reweighing accurately. Control experiments were also carried out. The infra-red spectra of the smaller specimens were recorded in the region of 700 cm^{-1} to 800 cm^{-1}, a control vulcanizate specimen was placed in the reference path of the spectrometer. The peak heights of the spectra at 750 cm^{-1} were measured and the calibration curve was produced by plotting peak heights against concentrations of MBT, the latter being obtained from the swelling data. The gain and balance of the spectrometer were checked regularly.

6.3.3 The removal of the basic zinc salt of MBT from EV vulcanizates

Ten specimens of a solvent extracted, fully cured, EV vulcanizate were further extracted in 100 mls of the acid extraction mixture under nitrogen for increasing periods up to 96 hours. At intervals of approximately 24 hours two specimens were removed, continuously extracted for 4 hours with solvent mixture to remove acetic acid, then dried under vacuum. Oxygen absorption measurements were determined on the specimens, each of approximately 0.2 grammes, in the usual manner. The acid extraction mixture was changed every 24 hours to ensure complete removal of the basic zinc salt.

Oxygen absorption measurements were also obtained for Peroxide vulcanizate specimens after treatment with the acid extraction mixture. Furthermore, equilibrium swelling measurements were determined in n-heptane at 25°C on specimens of Peroxide and EV vulcanizates following the acid treatment for increasing periods. These experiments were designed to estimate the extent of any network degradation that may have occurred during the course of the acid extraction.

6.3.4 Estimation of the basic zinc salt of MBT retained in the solvent extracted, EV vulcanizate

The basic salt was removed from the fully cured vulcanizate by the acid extraction and estimated in the form of MBT.

About 3 grammes of the unextracted vulcanizate was wiped free of bloom and weighed accurately, extracted with solvent mixture, dried and reweighed. The specimen was extracted further in 100 mls of the acid extraction mixture for approximately 24 hours. The extract was transferred to a 500 mls volumetric flask, washing down the sides of the extraction flask with a small volume of acetone. An additional 100 mls of acid mixture was added to the flask and the extraction procedure was repeated. The extraction cycle was repeated four times, each time transferring the 100 mls extracts into the volumetric flask. The vulcanizate specimen was finally continuously extracted with solvent mixture for 4 hours, dried under vacuum and reweighed. The volumetric flask was made up to volume with acetone.

A 10 mls aliquot of the extract solution was withdrawn and the concentration of MBT estimated, (section 2.4.3.1).

6.4 Results

The effect of cure time on the oxygen uptake characteristics of solvent extracted, EV vulcanizates is displayed in figure 6.1. Increased thermal oxidative stability is observed up to a cure time of 60 minutes after which the experimental data all fall on the same curve. The corresponding infra-red spectra are shown in figure 6.2 and summarized graphically in figure 6.3. A plateau stage is reached after an initial period of about 80 minutes. After this point a constant level of the MBT function is present in the vulcanizates in the forms of attached pendent groups and the basic zinc salt of MBT. The effect of further extraction in the acid mixture for a period of 24 hours is indicated for specimens cured for 40 and 120 minutes.

The infra-red calibration curve is shown in figure 6.4, this was constructed from the data listed in tables 6.1 - 6.3 inclusive.

Swelling solution	Concentration of MBT, grammes per litre of acetone
A	113.50
B	69.94
C	31.96
D	15.58

Table 6.1

Specimen	Swelling solution	Absorbance at 750 cm^{-1} (corrected peak height)
a	A	0.302
b	B	0.204
c	C	0.151
d	D	0.056

Table 6.2 Infra-red data

In addition to a small loss in intensity of the 750 cm^{-1} band, the acid extraction leads to a drastic reduction in oxidative stability of the solvent extracted, fully cured vulcanizate - figure 6.5. A fall in induction period is observed with increasing time of extraction. No further reduction is noted after a period of 70.5 hours. The acetic acid cannot be directly responsible for the degradative effect since the data shown in figure 6.6 indicates that an insignificant reduction in induction period occurs after treating a Peroxide vulcanizate with the acid extraction mixture. Furthermore, the network degradation occurring in the EV and Peroxide vulcanizates, determined from equilibrium swelling measurements, is negligible over a period of 96 hours treatment with the acid system - figure 6.7. The total loss in weight observed after extraction of the EV vulcanizate with solvent mixture followed by the acid mixture amounts to 9.44 per cent. Details are given in table 6.4. The percentage weight loss due to solvent extraction, (section 5.4), is 6.46 per cent. Therefore, the weight loss due to the acid extraction is 2.98 per cent.

Table 6.3 Swelling data

Specimen	Swelling solution	Weight of specimen prior to swelling, (grammes)	Weight of specimen after swelling, (grammes)*	Increase in weight, (grammes)	Concentration of MBT swollen in, (gramme moles per gramme)**	Average
A_1	A	0.4240	0.4319	0.0079	1.093×10^{-4}	1.127×10^{-4}
A_2	A	0.4845	0.4941	0.0096	1.162×10^{-4}	
B_1	B	0.4022	0.4076	0.0054	0.792×10^{-4}	0.786×10^{-4}
B_2	B	0.4382	0.4440	0.0058	0.781×10^{-4}	
C_1	C	0.3615	0.3647	0.0032	0.526×10^{-4}	0.526×10^{-4}
C_2	D	-	-	-	-	
D_1	D	0.4806	0.4823	0.0017	0.211×10^{-4}	0.23×10^{-4}
D_2	D	0.4546	0.4565	0.0019	0.249×10^{-4}	
Control	Acetone	0.5253	0.5251	-(0.0002)	-	

** - Based on the final dry weight after swelling in MBT

* - Corrected figures

	(i)	(ii)
Initial weight of unextracted vulcanizate, grammes	3.2905	3.0044
Weight after solvent mixture and acid mixture extraction, grammes	2.9882	2.7126
Weight loss, grammes	0.3023	0.2918
Percentage weight loss*	9.18	9.71
Average percentage weight loss	9.44	

* - Based on the initial weight of the unextracted vulcanizate

Table 6.4

The MBT removed from the EV vulcanizate by the acid extraction was estimated in duplicate and figures of 0.25×10^{-5} and 0.27×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate were obtained, giving an average figure of 0.26×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate.

6.5 Discussion

An increase in the thermal oxidative stability of solvent extracted EV vulcanizates has been shown to occur on increasing cure times up to a period of 60 minutes, after which no further increase is recorded - figure 6.1. The estimated MBT function in the extracted networks, in the forms of pendent accelerator groups and the basic zinc salt of MBT, exhibits a parallel effect - figure 6.3. In the fully cured vulcanizate, 120 minutes, an infra-red absorbance of 0.122 is observed and this figure is, according to the calibration data, equivalent to a concentration of 0.452×10^{-4} gramme moles of MBT per gramme of extracted vulcanizate. This is slightly reduced when stated in terms of unextracted vulcanizate, that is 0.423×10^{-4} gramme moles of MBT per gramme of unextracted vulcanizate. The concentration of MBT removed from the fully cured, solvent extracted network by the acid mixture is 0.26×10^{-5} gramme moles of MBT per gramme of unextracted

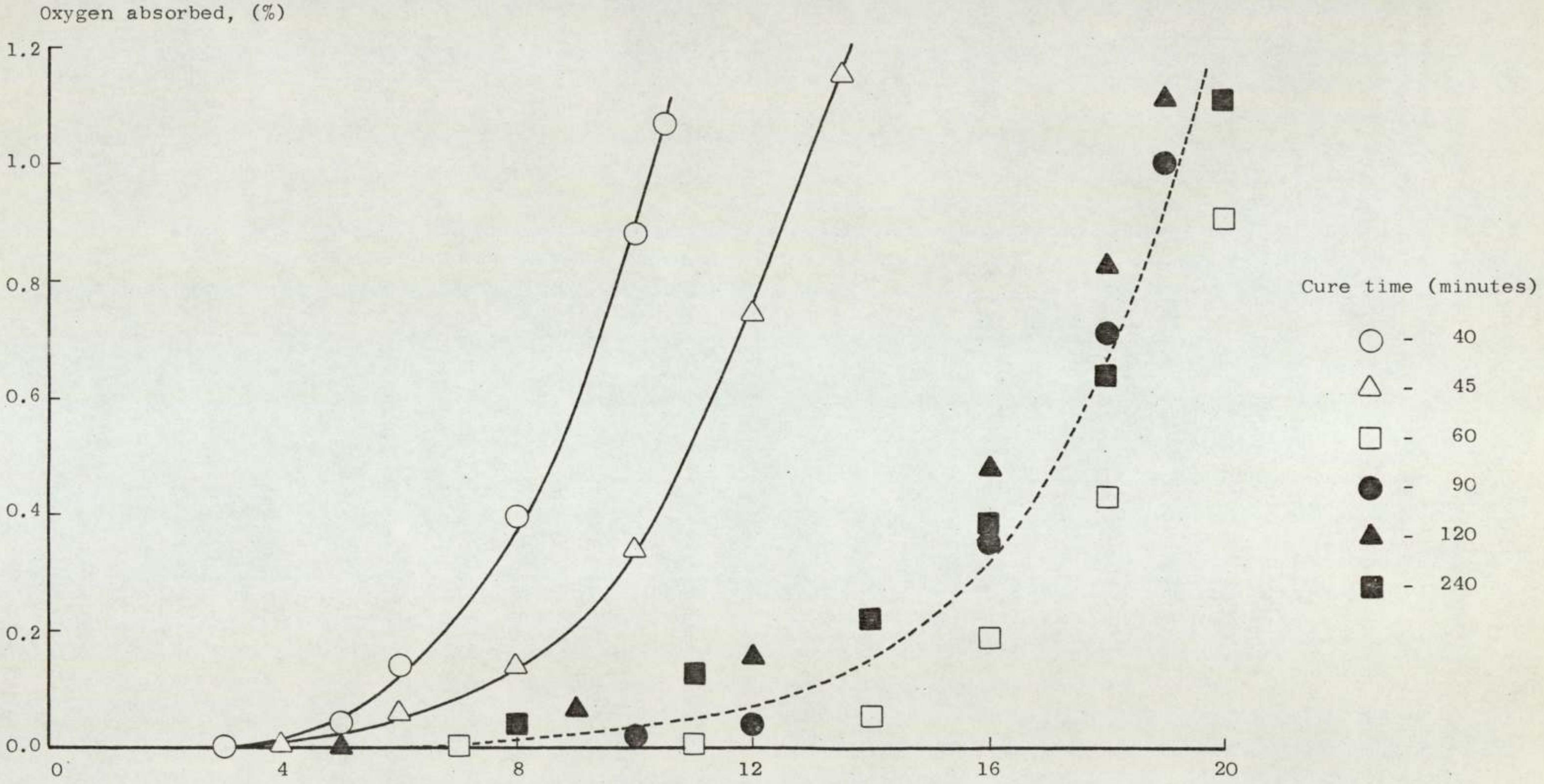


Figure 6.1 Oxygen absorption at 80°C of solvent extracted EV vulcanizates of varying cure time

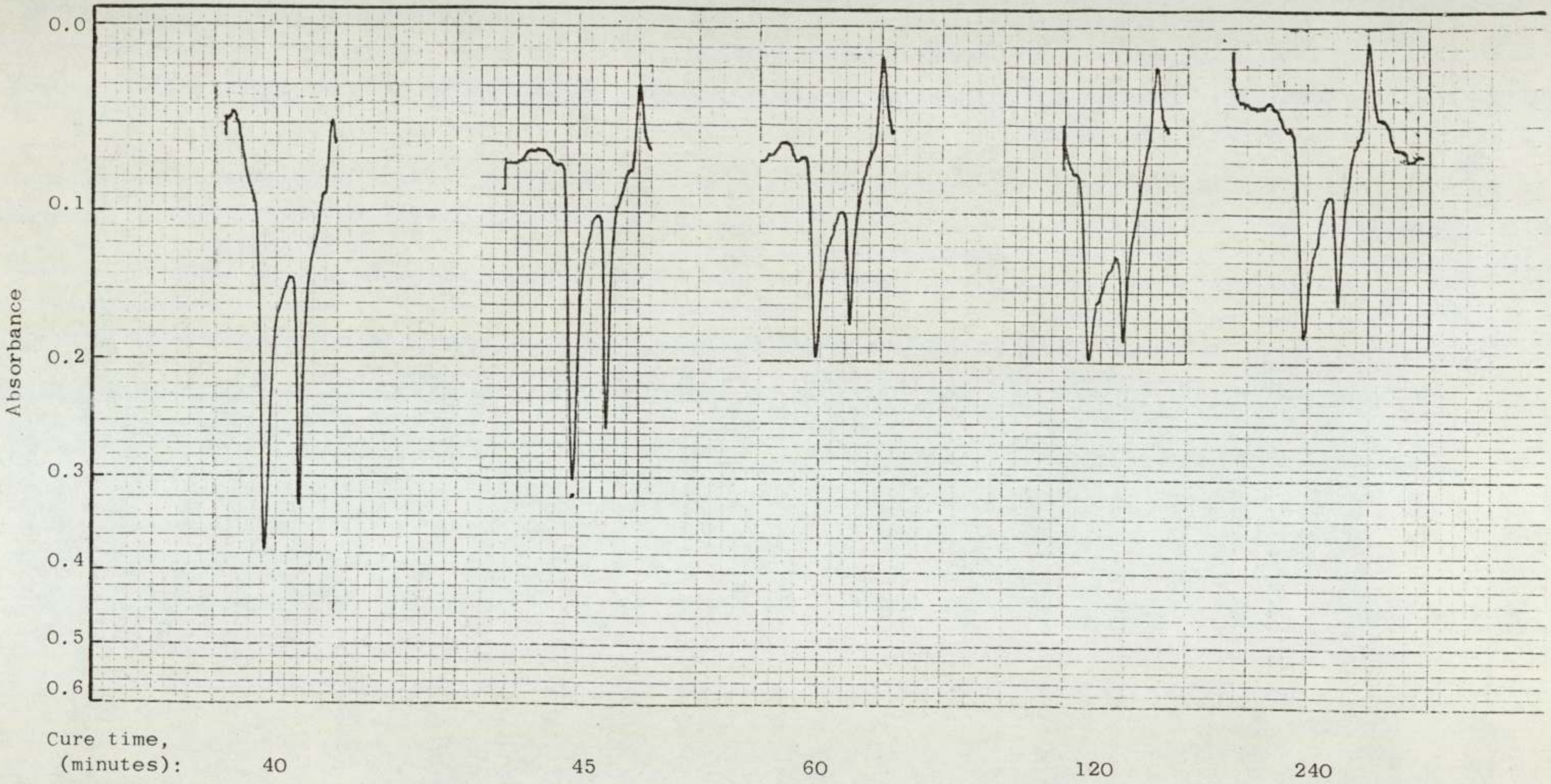


Figure 6.2 Infra-red absorption spectra, (700-800 cm^{-1}), of extracted EV vulcanizates as a function of cure time

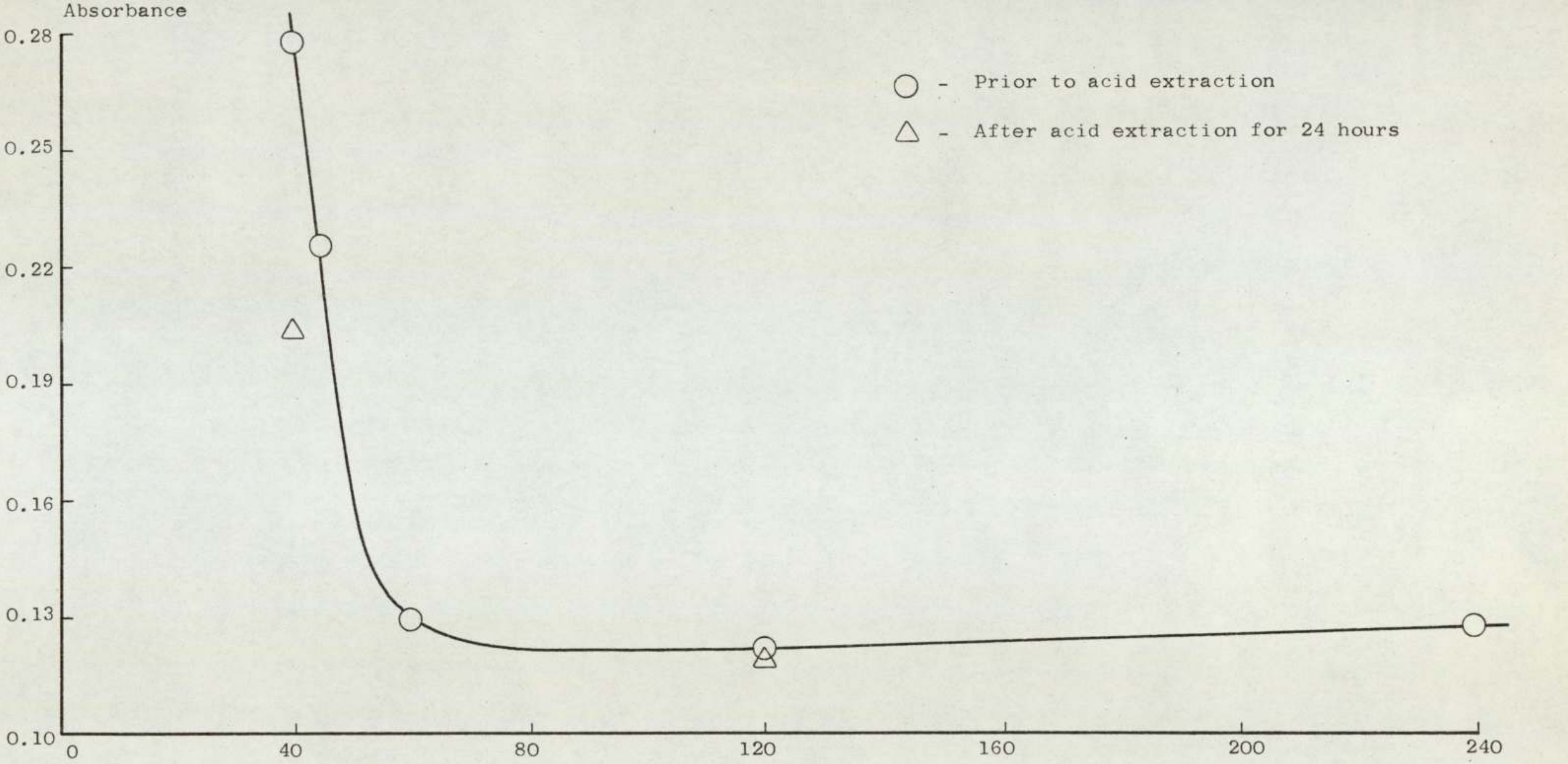


Figure 6.3 Infra-red absorbance at 750 cm^{-1} (corrected peak height) of solvent extracted, EV vulcanizates as a function of cure time

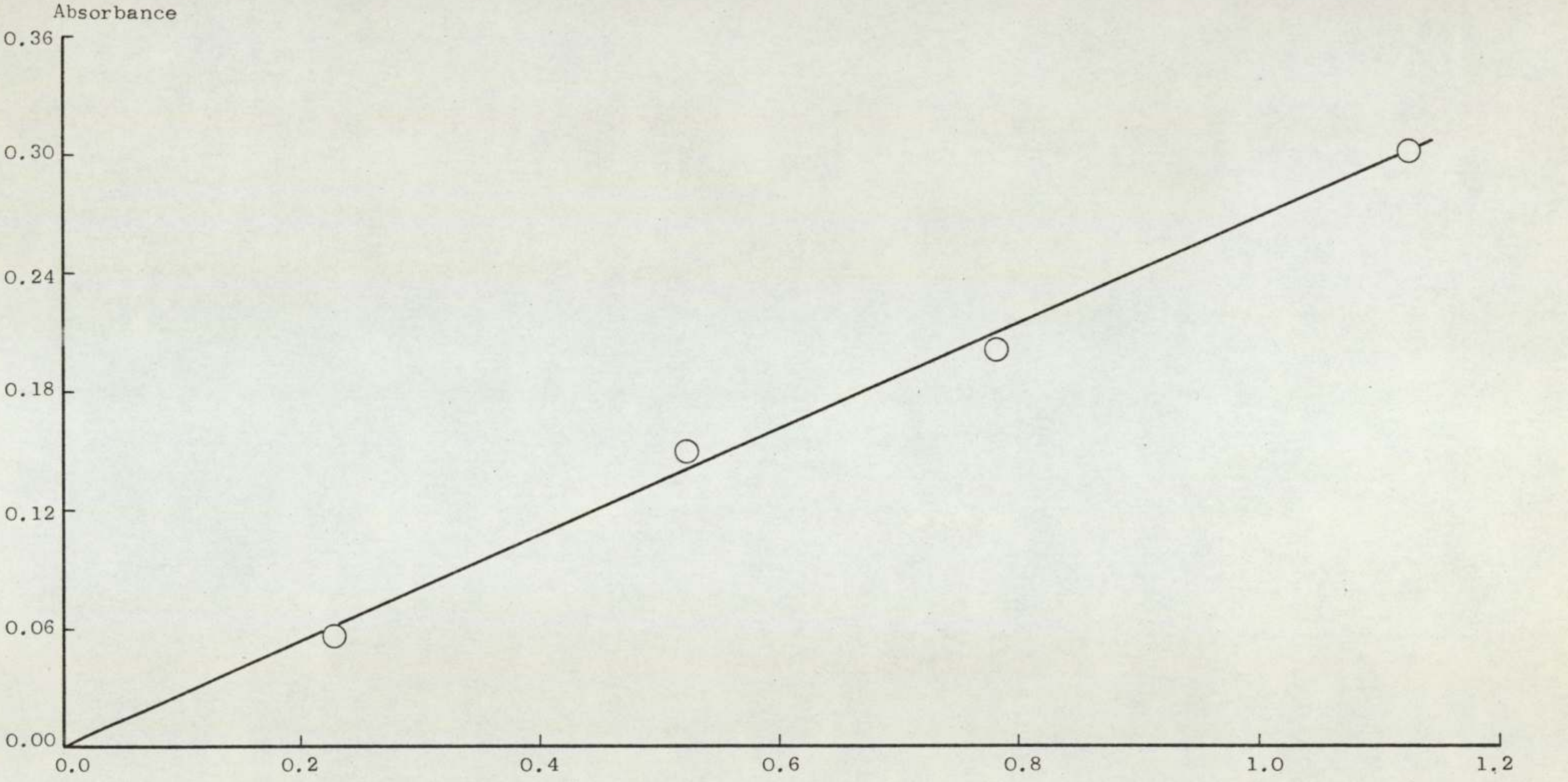


Figure 6.4 Infra-red absorbance at 750 cm^{-1} (corrected peak height) Vs concentration of MBT swollen into EV vulcanizates

Concentration of MBT, (10^{-4} gramme moles per gramme of vulcanizate)

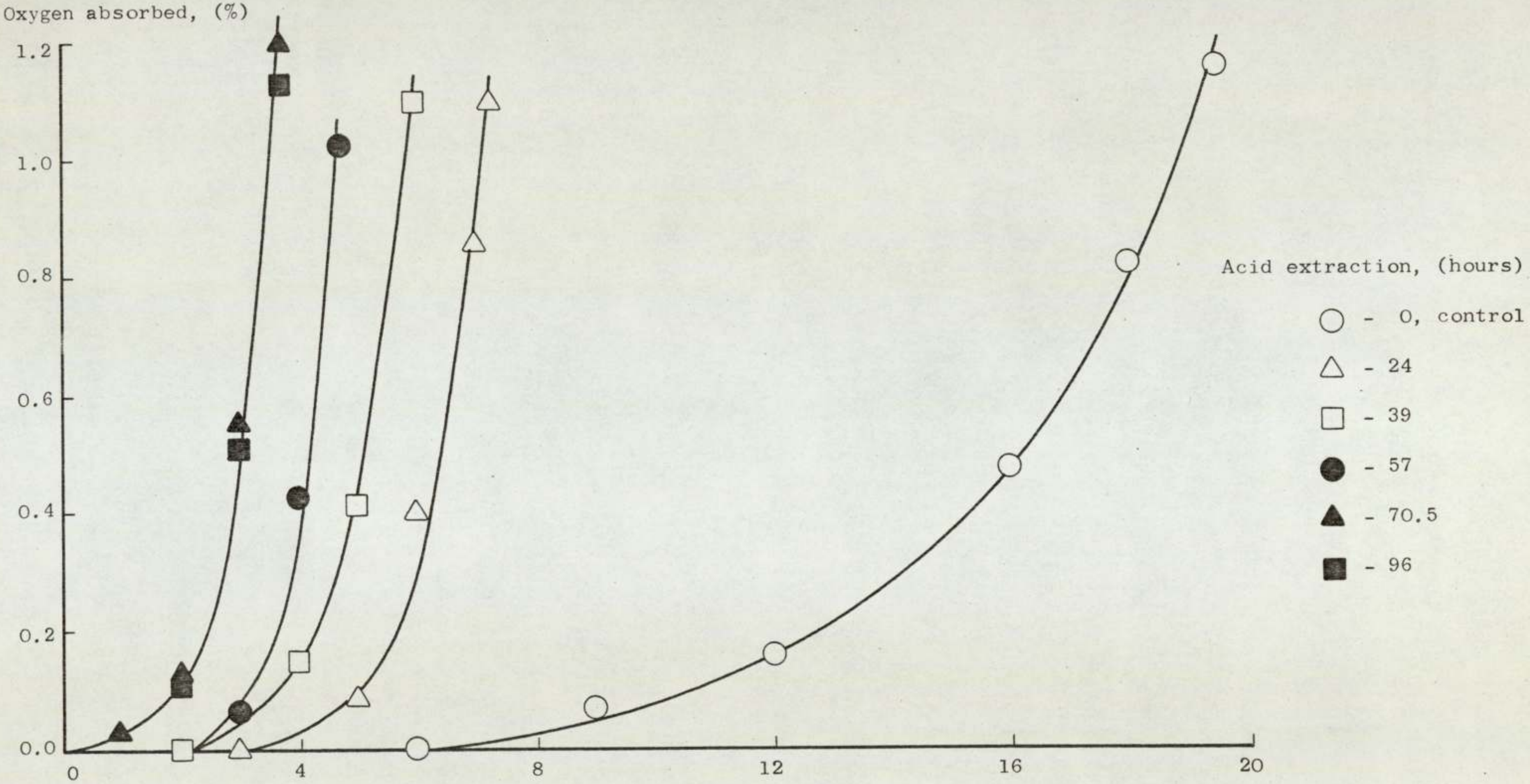


Figure 6.5 Oxygen absorption of solvent extracted, fully cured, EV vulcanizates. Effect of further acid extraction for increasing periods

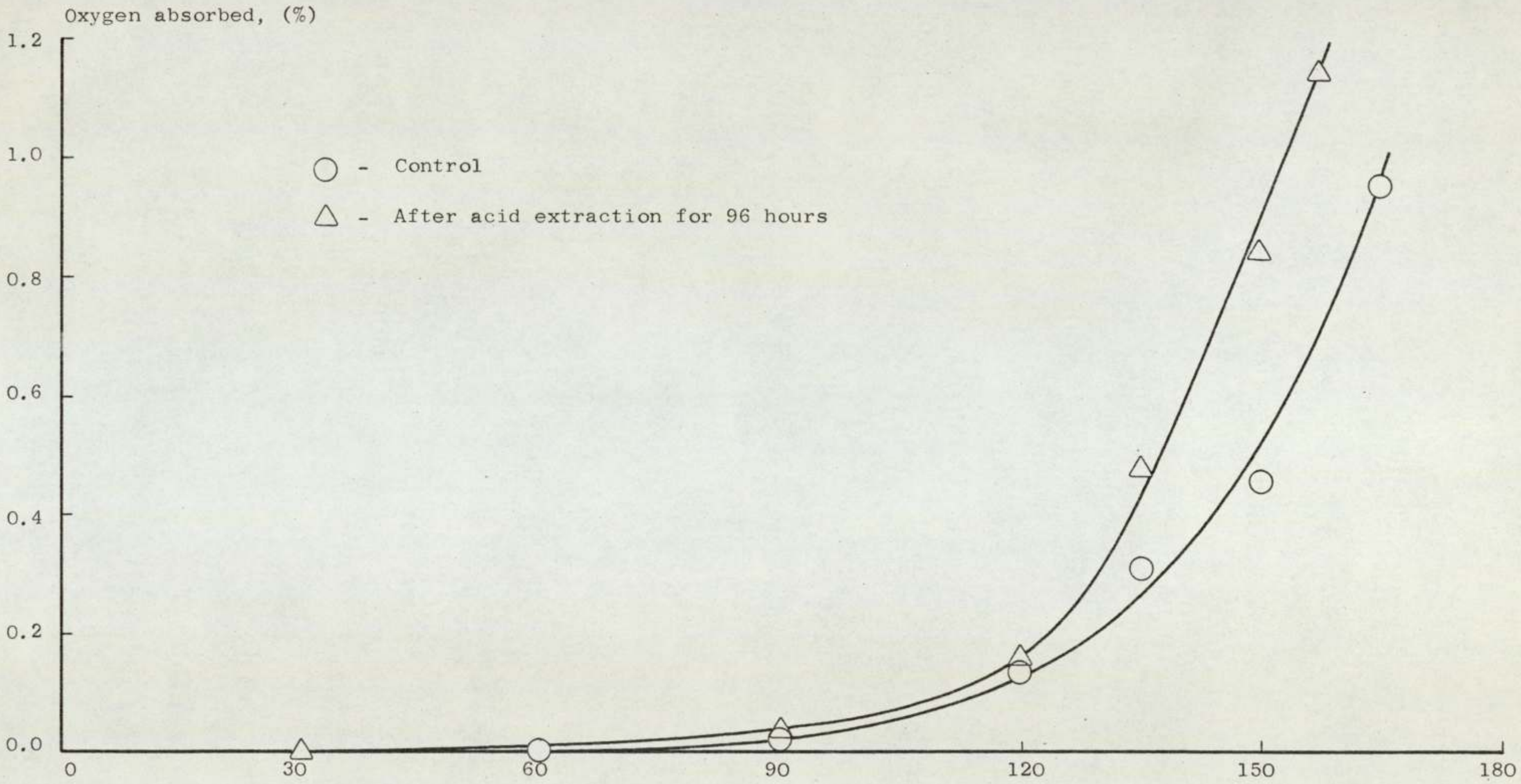


Figure 6.6 Oxygen absorption of solvent extracted Peroxide vulcanizates at 80°C

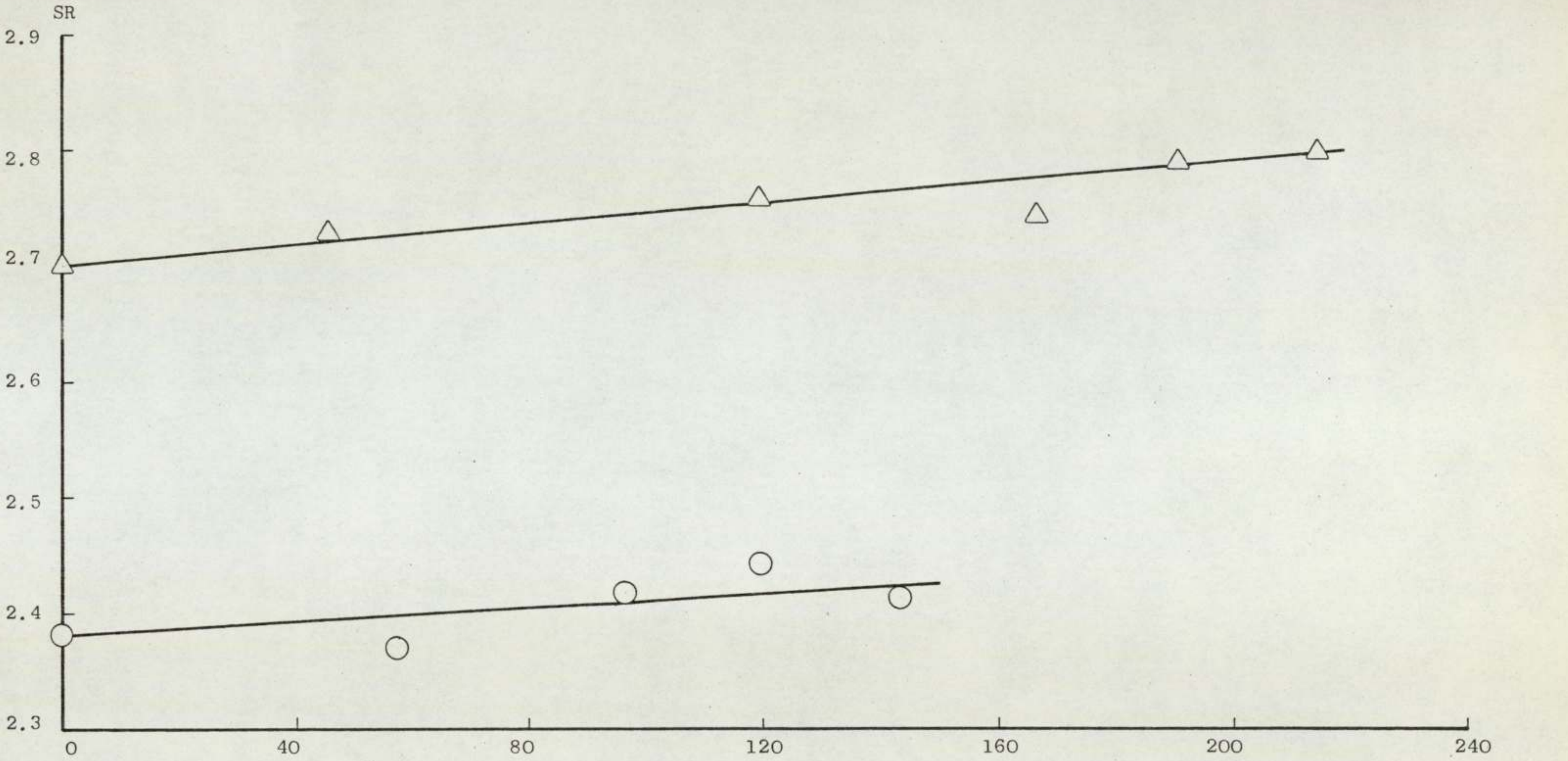


Figure 6.7 Equilibrium weight swelling ratio (SR) of Peroxide (○) and EV (△) vulcanizates in n-heptane at 25°C as a function of time of acid extraction

vulcanizate. Therefore, the MBT present in the form of pendent groups is 3.97×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate. The basic zinc salt of MBT present in the fully cured system is likely to be a maximum since the formation of ZMBT parallels the cure curve and reaches a maximum with maximum cross-linking[111]. Therefore, at early stages of cure the large infra-red absorption of the MBT function will be almost entirely due to pendent accelerator groups and not the basic salt. This is difficult to demonstrate conclusively because of the instability of the sulphurated network towards the acid extraction mixture at early stages of cure[37]. That is, polysulphidic cross-links and polysulphidic pendent groups are cleaved by the acid reagent.

The oxidative stability of solvent extracted vulcanizates of increasing cure times also parallels the cure curve for the EV compound - figure 2.6. As optimum cure is approached no further increase in oxidative stability is observed. This indicates that the stability of the EV vulcanizates is attributable, at least in part, to the residual basic zinc salt of MBT remaining in the networks after solvent extraction.

As the cure time is increased the thermal oxidative stability improves because of the build-up of the basic zinc salt in the system. In addition, other factors may influence the oxygen uptake characteristics of the vulcanizates, particularly at low cure levels. At this stage a significant proportion of disulphidic as well as a smaller concentration of polysulphidic cross-links are present[37]. Nevertheless the importance of the basic zinc salt of MBT with respect to the thermal oxidative stability of the fully cured system is established by the data shown in figure 6.5. After removal of the basic zinc salt from the solvent extracted network a reduction in induction period occurs. After 70.5 hours of acid extraction no further decrease is observed.

The corresponding infra-red data indicates that after treatment of the vulcanizate for 24 hours with the acid reagent a small reduction in absorbance occurs, corresponding to a loss of MBT function of the order of 0.12×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate. This figure is consistent with that for complete removal of MBT in the form of the basic salt, that is 0.26×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate. The latter figure was obtained from U.V. analysis of the acid extract. A greater reduction in absorbance is observed following the treatment of an under cured, (40 minutes), EV vulcanizate with the acid reagent for 24 hours. However, this does not give a true measure of extractable MBT in the form of the basic zinc salt since polysulphidic pendent groups, present in the undercured network, are susceptible to cleavage by the acetic acid[37]. Mono and disulphidic pendent groups are stable under these conditions.

Grant and Tipper[155] have shown that acids, including acetic acid, will inhibit the autoxidation of hydrocarbons in solution by heterolytically decomposing hydroperoxides. Certain acids, however, display pro-oxidant effect during the early stages of oxidation. Tipper[156] has suggested that this initial pro-oxidant effect is due to a fast chain transfer reaction shown in the sequence (6.1) - (6.2) for the case of benzoic acid during the oxidation of diphenyl methane. The effect of the acetic acid extraction mixture on a Peroxide vulcanizate with

$$\emptyset_2CHO_2\cdot + \emptyset CO_2H \rightarrow \emptyset_2CHO_2H + \emptyset CO_2\cdot \qquad (6.1)$$

$$\emptyset CO_2\cdot + \emptyset_2CH_2 \rightarrow \emptyset CO_2H + \emptyset_2CH\cdot \qquad (6.2)$$

respect to oxygen uptake is shown in figure 6.6. A small reduction of induction period is observed suggesting that only a minor amount of oxidation had occurred during the extraction procedure. This is insignificant compared to the fall in induction period of the fully cured EV vulcanizate. Therefore, the possibility of the acetic acid acting as a pro-oxidant during the extraction can be dismissed. Furthermore, negligible network deterioration occurred during the acid treatment - figure 6.7.

A weight loss amounting to 3 per cent occurred following acid extraction of the EV vulcanizate. This is in addition to the 6.46 per cent lost during the initial solvent extraction. The former was accompanied by an increase in transparency of the vulcanizate. Thus, the majority of the acid extractable material is residual zinc oxide, an authentic sample of which was shown to be extracted from a Peroxide vulcanizate. Zinc sulphide on the other hand remains in the network.

The important feature of the fully cured, solvent extracted, EV vulcanizate in determining its thermal oxidative stability is the basic zinc salt of MBT acting as an antioxidant. This is present as solvent insoluble material due to the hydrolysis of the normal zinc salt formed during the course of the curing process. If this basic salt is removed by the additional acid extraction, a drastic reduction in thermal oxidative stability of the vulcanizate is observed and the oxygen uptake characteristics resemble those of the solvent extracted, TMTD sulphurless system - figure 4.3. The monosulphidic pendent groups, not affected by the acid treatment, remain in the EV network and appear to play an insignificant role in the ageing behaviour of the system.

Parks et al[39] have investigated the effect of pendent accelerator groups in conventionally stabilized, cis-polyisoprene, sulphur vulcanizates and have shown that these enhance the rate of oxygen uptake when present in large concentration.

The analysis of the MBT function in the unextracted, fully cured, EV vulcanizate is summarized in table 6.5.

Component containing the MBT function	Concentration, gramme moles of MBT per gramme of unextracted vulcanizate
Solvent extractable ZMBT,MBT	11.27×10^{-5}
Basic zinc salt of MBT	0.26×10^{-5}
Bound pendent groups	3.97×10^{-5}
Bloom	0.36×10^{-5}

Table 6.5 Distribution of the MBT function in the unextracted fully cured EV vulcanizate

In addition to the MBT estimated in the forms of ZMBT, basic zinc salt of MBT and bound pendent groups, a further quantity is present as bloom on the surfaces of the vulcanizate and mould. This was shown to consist essentially of ZMBT, probably a mixture of the normal and basic salts. The bloom was removed from the vulcanizate and mould surfaces and estimated for MBT yielding a figure of 0.36×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate.

The total MBT recovered is 15.86×10^{-5} gramme moles of MBT per gramme of unextracted vulcanizate and this compares with a concentration of 20.18×10^{-5} gramme moles of MBT per gramme of compound initially in the form of the accelerator CBS. Therefore, assuming that one gramme of vulcanizate is equivalent to one gramme of compound, the percentage recovery of MBT is 78.6 per cent. Any sizeable error in the figure obtained for the extractable ZMBT will drastically effect the overall MBT recovery. However, the series of results obtained, (table 5.1), exhibit excellent reproducibility. In addition, the analytical reagents employed have been shown to be reliable, the stannous chloride reagent giving 97 per cent recovery of MBT in mixtures of ZMBT, MBTS and MBT[111]. Even large errors in the basic zinc salt of MBT and bloom estimations will not significantly affect the overall percentage recovery of MBT, although duplicate determinations did not indicate that this was the case. The infra-red data on the other hand must be viewed with some caution. In estimating the attached pendent groups in the EV network it is assumed that the extinction coefficient associated with the 750 cm^{-1} band in the MBT spectrum is equal to that for the pendent group. An examination of equimolar solutions of MBT, CBS and N-(t-butyl)-benzothiazyl sulphenamide, under standard conditions of 0.15 M and path length 0.023 cms, indicated that the intensity of the 750 cm^{-1} band in the MBT spectrum is of the order of 12 per cent lower than is observed for the remaining compounds. Since the extinction coefficient of the attached pendent group is not known errors of around 12 per cent cannot be dismissed.

Even allowing for errors of this magnitude all the MBT function in the unextracted EV vulcanizate cannot be accounted for. This loss is at least in part attributable to the extractable pendent groups analyzed qualitatively but not quantitatively, (section 5.5).

7. An investigation into the mode of antioxidant action of normal ZMBT

7.1 Introduction

ZMBT has been shown to possess antioxidant characteristics in sulphurated and non-sulphurated vulcanizate networks. To obtain informative data concerning its mode of antioxidant action it is necessary to resort to model compound investigations. The studies presented in this section describe:

a) model compound oxygen absorption studies involving cumene;

b) hydroperoxide decomposition studies;

and c) product analysis details from the ZMBT/cumene hydroperoxide reaction.

Oxygen absorption measurements provide a useful means of classifying the mechanism by which an antioxidant functions. This is achieved by studying the effect of an antioxidant on the oxygen absorption of a substrate whose mode of initiation is controlled. If a chain terminating antioxidant is added to a substrate whose oxidation has been initiated by added hydroperoxide or a free radical initiator such as AZBN, then the rate of oxidation in both cases will be reduced to a value determined by the effectiveness with which the antioxidant scavenges the propagating radicals. However, if a peroxide decomposing antioxidant is added to an oxidizing substrate whose autocatalysis by hydroperoxide initiation is rendered trivial by addition of a free radical initiator, the rate of oxidation is unaltered. In the case where the peroxide decomposer is added to the hydroperoxide initiated oxidation, the oxidation becomes autoinhibiting.

In addition to the oxygen absorption studies the kinetics of decomposition of cumene hydroperoxide by ZMBT in an inert solvent have been investigated. ZMBT has been previously described as a deactivating agent for peroxides[115] and Brooks[114] has also suggested that ZMBT reacts with and destroys hydroperoxides.

The modes of decomposition of cumene hydroperoxide, (CHP), have been extensively studied[99,129,131,157-160]. The products of CHP decomposition occurring by an ionic mechanism are acetone and phenol, whilst α-methylstyrene, α,α-dimethylbenzyl alcohol and acetophenone are the main products of the free radical decomposition. These products can be easily and rapidly analyzed quantitatively and so provide a means of estimating the basic decomposition mechanism involved.

7.2 Experimental procedure and details

7.2.1 Oxygen absorption of cumene hydroperoxide initiated cumene autoxidation

The technique is described fully in section 2.4.2. The stock solution of cumene was initiated with CHP at a concentration of 50×10^{-3} moles of CHP per litre at 80°C. ZMBT was added at two initial concentrations, 0.904×10^{-4} and 8.220×10^{-4} moles of ZMBT per litre of autoxidizing solution. These gave initial CHP:ZMBT molar ratios of 553.1 and 60.8 respectively.

7.2.2 Oxygen absorption of the free radical initiated autoxidation of cumene

7.2.2.1 AZBN initiation

Cumene was initiated with AZBN at a concentration of 1.18×10^{-4} moles of AZBN per litre at 80°C. ZMBT was added at two initial concentrations of 0.894×10^{-4} and 7.830×10^{-4} moles of ZMBT per litre of autoxidizing solution.

7.2.2.2 Benzoyl peroxide initiation

Cumene initiated with 1.31×10^{-3} moles of benzoyl peroxide per litre at 80°C was employed. This gave a comparable rate of initial oxidation to the AZBN initiated system. The effect of the addition of ZMBT at an initial concentration of 7.630×10^{-4} moles of ZMBT per litre of autoxidizing solution was investigated.

7.2.3 The decomposition of CHP by ZMBT

The technique is described fully in section 2.4.6. Details of a typical determination are given below.

Concentration of CHP/chlorobenzene solution: 2.717×10^{-4} gramme moles of CHP per gramme of solution.

Concentration of ZMBT/chlorobenzene solution: 1.34×10^{-6} gramme moles of ZMBT per gramme of solution.

Weight of CHP solution transferred into reaction vessel: 2.4693 g.

Weight of ZMBT solution transferred into reaction vessel: 2.4517 g.

Initial molar ratio of CHP:ZMBT : 204.2

The data obtained were plotted according to a first order rate expression. That is, log $\left([\mathrm{CHP}]_o / [\mathrm{CHP}]_t \right)$ against the time t, where $[\mathrm{CHP}]_o$ is the initial concentration of hydroperoxide and $[\mathrm{CHP}]_t$ is the concentration of time t.

7.2.4 Product analysis of the CHP/ZMBT reaction

During the initial stages of the reaction a small amount of a pale precipitate developed. This was collected in greater amount by heating 10 mls of the ZMBT/chlorobenzene solution with 10 mls of the CHP/chlorobenzene solution in a closed vessel at 80°C for 45 minutes. The pale precipitate that formed was filtered off, washed with 30-40 petroleum ether and dried under vacuum. The infra-red absorption spectrum of the solid was obtained.

A portion of the CHP decomposition product solution described in section 7.2.3 was weighed into a sample bottle, (4.6428 grammes). A known weight of iodobenzene was added, (0.1433 grammes), and the solution was analyzed quantitatively for acetone, phenol, α-methylstyrene, α,α-dimethylbenzyl alcohol and acetophenone by g.l.c. Iodobenzene was employed as the internal standard. The technique is described in section 2.4.7.

7.3 Results

The oxygen absorption data are summarized graphically in figures 7.1 - 7.3. Addition of ZMBT to the hydroperoxide initiated systems resulted in an immediate reduction in the rate of oxidation followed by autoinhibition. Even at an initial molar ratio CHP:ZMBT of 553 ZMBT exhibits a powerful antioxidant effect. On addition of ZMBT to systems initiated by free radicals generated from AZBN an antioxidant effect resulted. This differed from that observed in hydroperoxide initiated systems in that autoinhibition did not occur. Following the initial induction period the rate of oxygen uptake increased towards a rate comparable with that prior to the addition of the antioxidant. Confirmatory evidence of the chain breaking antioxidant activity of ZMBT is presented in figure 7.3. The cumene oxidation was initiated by free radicals generated from benzoyl peroxide and once again the characteristic induction period was observed on introduction of the antioxidant into the oxidizing system.

The first order rate plot of hydroperoxide decomposition by ZMBT is shown in figure 7.4. After an initial period of approximately 60 minutes first order kinetics were observed. Duplicate determinations gave identical kinetic features. The pseudo first order rate constants obtained from the data were:

(i) $10^4K = 3.81$ sec.$^{-1}$,

and (ii) $10^4K = 3.66$ sec.$^{-1}$.

The initial concentration of ZMBT in both cases was 0.667×10^{-6} gramme moles of ZMBT per gramme of reactant solution.

The precipitate formed during the initial period of the reaction gave the infra-red absorption spectrum displayed in figure 7.5. The spectrum is consistent with the major component being the metal sulphate. The spectrum of an authentic sample is shown in figure 7.6.

The g.l.c. analysis of the hydroperoxide decomposition products gave the information presented in table 7.1. The initial amount of hydroperoxide present in the sample was 6.33×10^{-4} gramme moles. On a mass balance 82 per cent of the original CHP is accounted for by these products. Phenol and acetone are shown to be the major products. The chromatogram is shown in figure 7.7.

Product	Molar quantity	Percentage molar yield
acetone	3.558×10^{-4}	56.20
phenol	4.555×10^{-4}	71.96
α-methylstyrene	0.755×10^{-4}	11.92
α,α-dimethylbenzyl alcohol	0.273×10^{-4}	4.31
acetophenone	0.237×10^{-4}	3.74

Initial molar ratio CHP:ZMBT = 204.2

Table 7.1 Analysis of CHP decomposition products

7.4 Discussion

The technique of determining the mode of action of an antioxidant has been successfully employed previously[61,71,88,92]. Scott[88] has

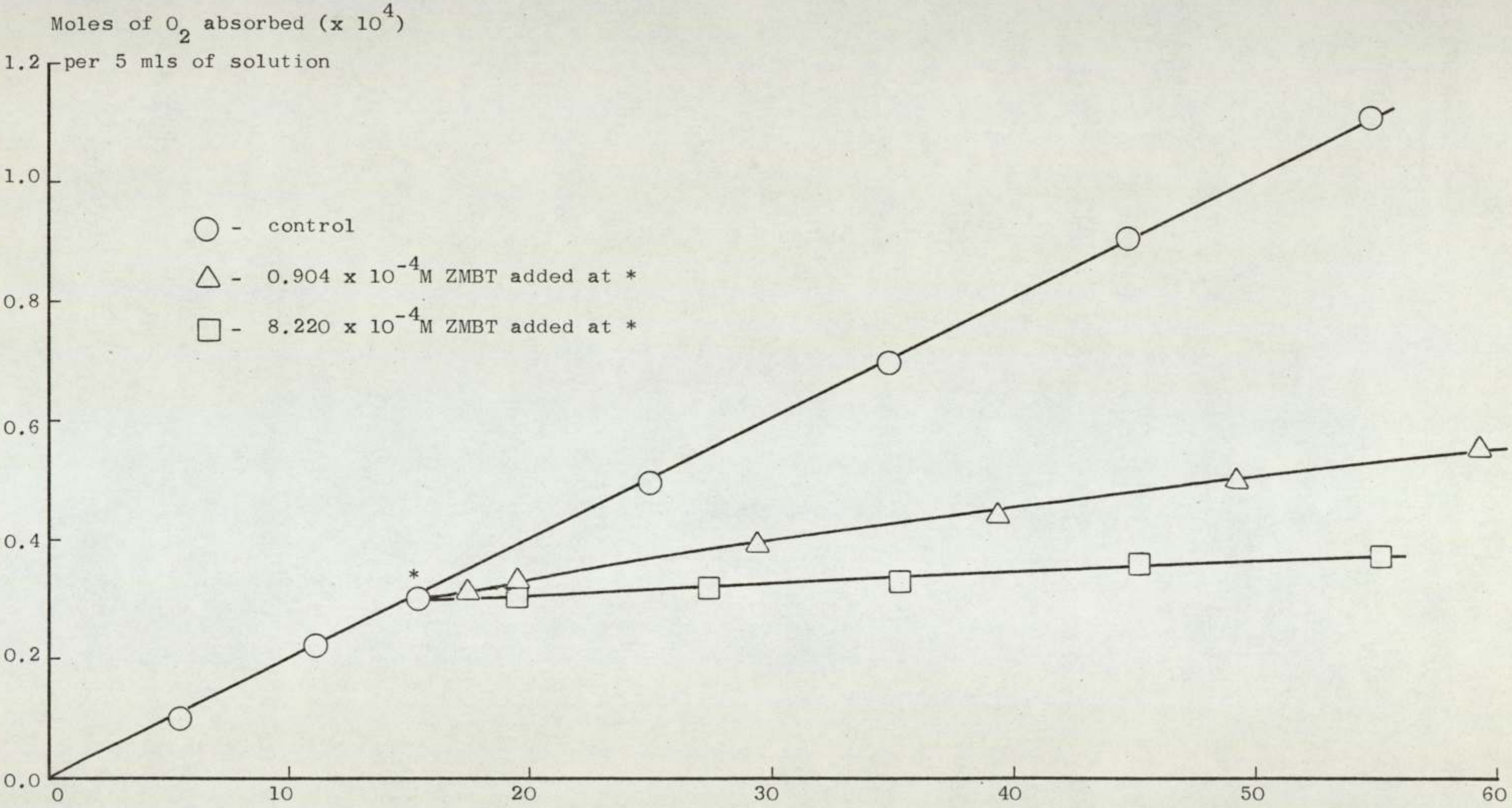


Figure 7.1 Oxidation of cumene at 80°C initiated with cumene hydroperoxide, (50 x 10^{-3}M)

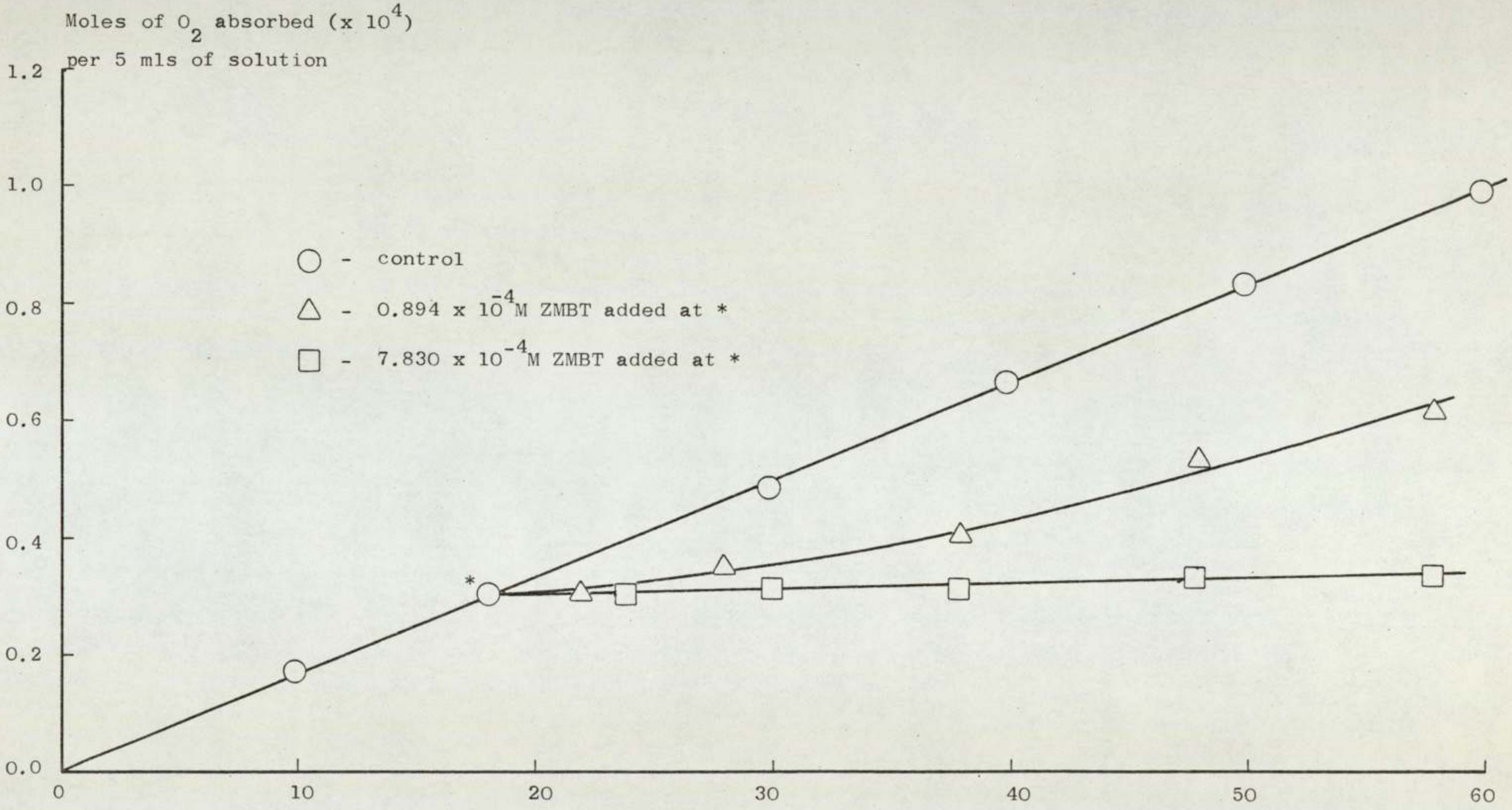


Figure 7.2 Oxidation of cumene at 80°C initiated with AZBN, (1.18×10^{-4}M)

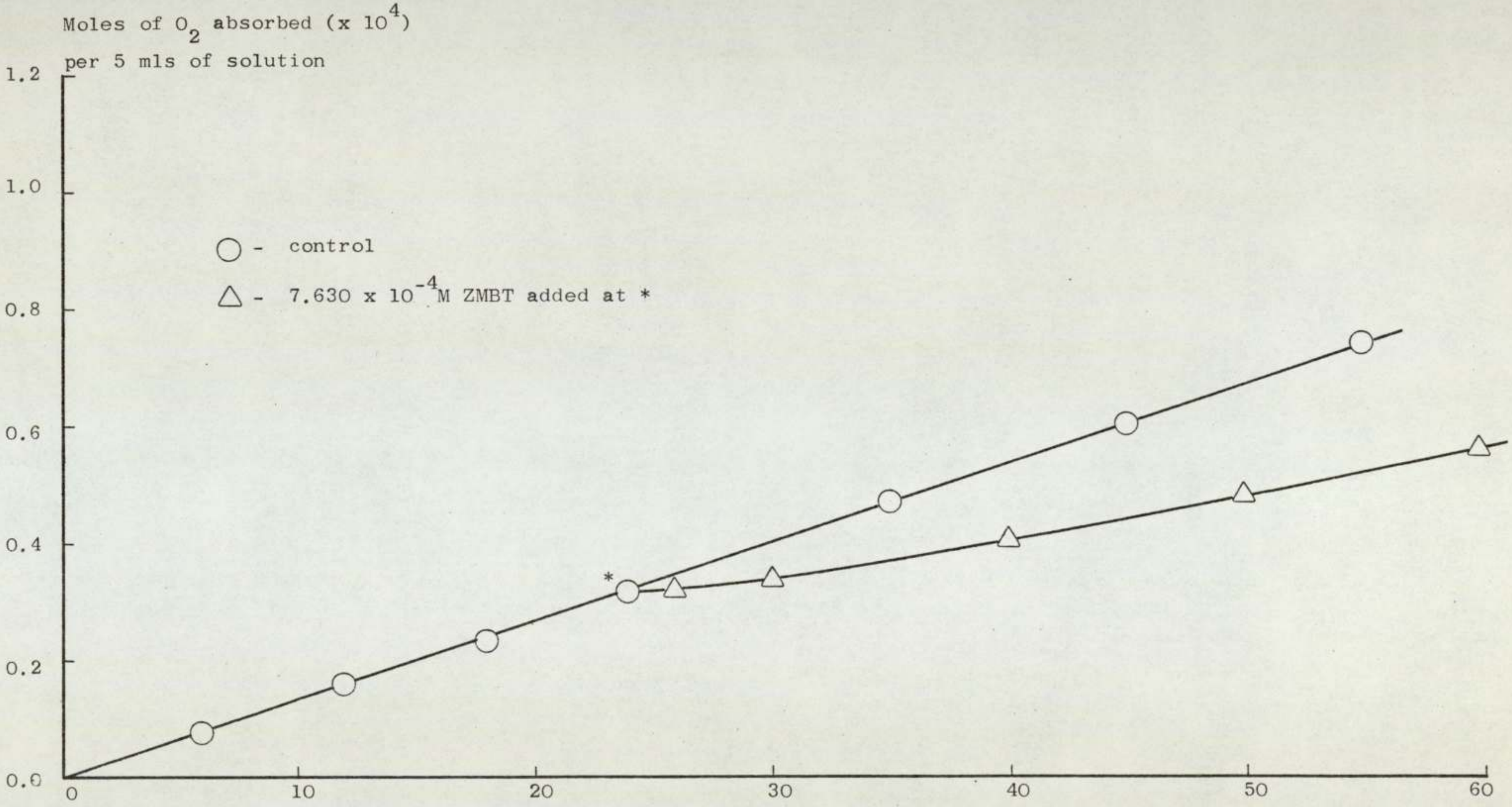


Figure 7.3 Oxidation of cumene at 80°C initiated with benzoyl peroxide, (1.31×10^{-3}M)

Time, (minutes)

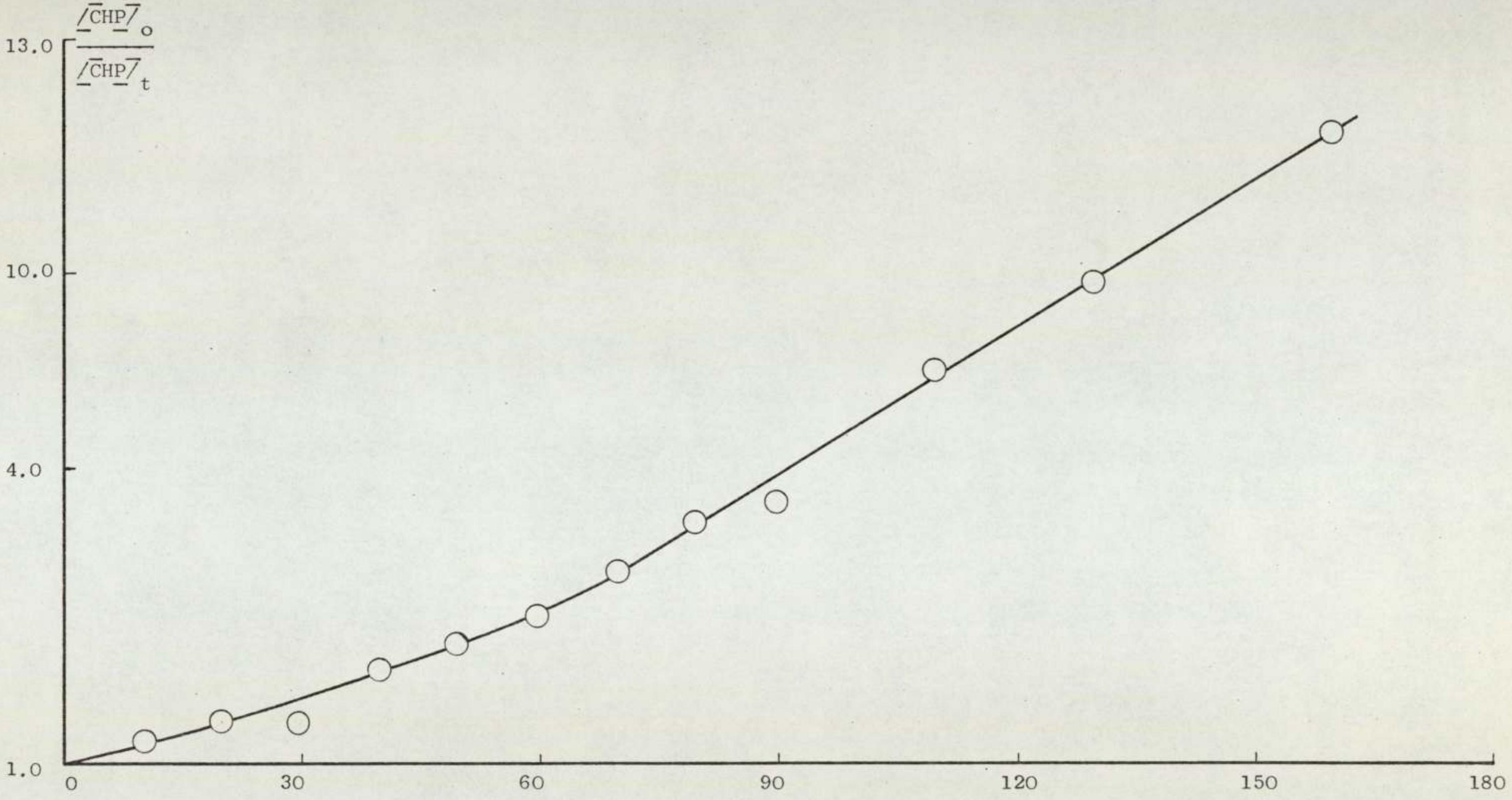


Figure 7.4 First order rate plot of the decomposition of CHP by ZMBT in chlorobenzene at 80°C. Initial molar ratio CHP:ZMBT 204.2

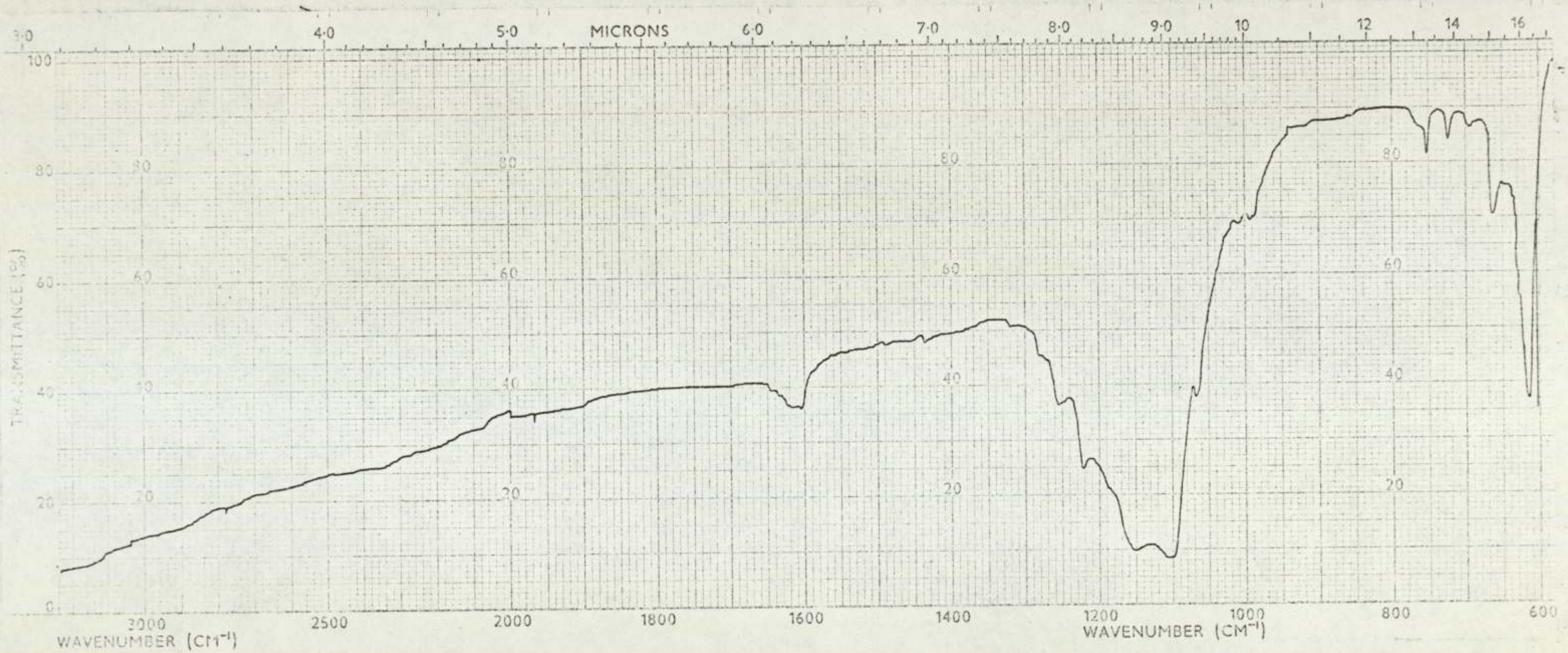


Figure 7.5 Infra-red spectrum of the solid precipitate from the CHP/ZMBT reaction

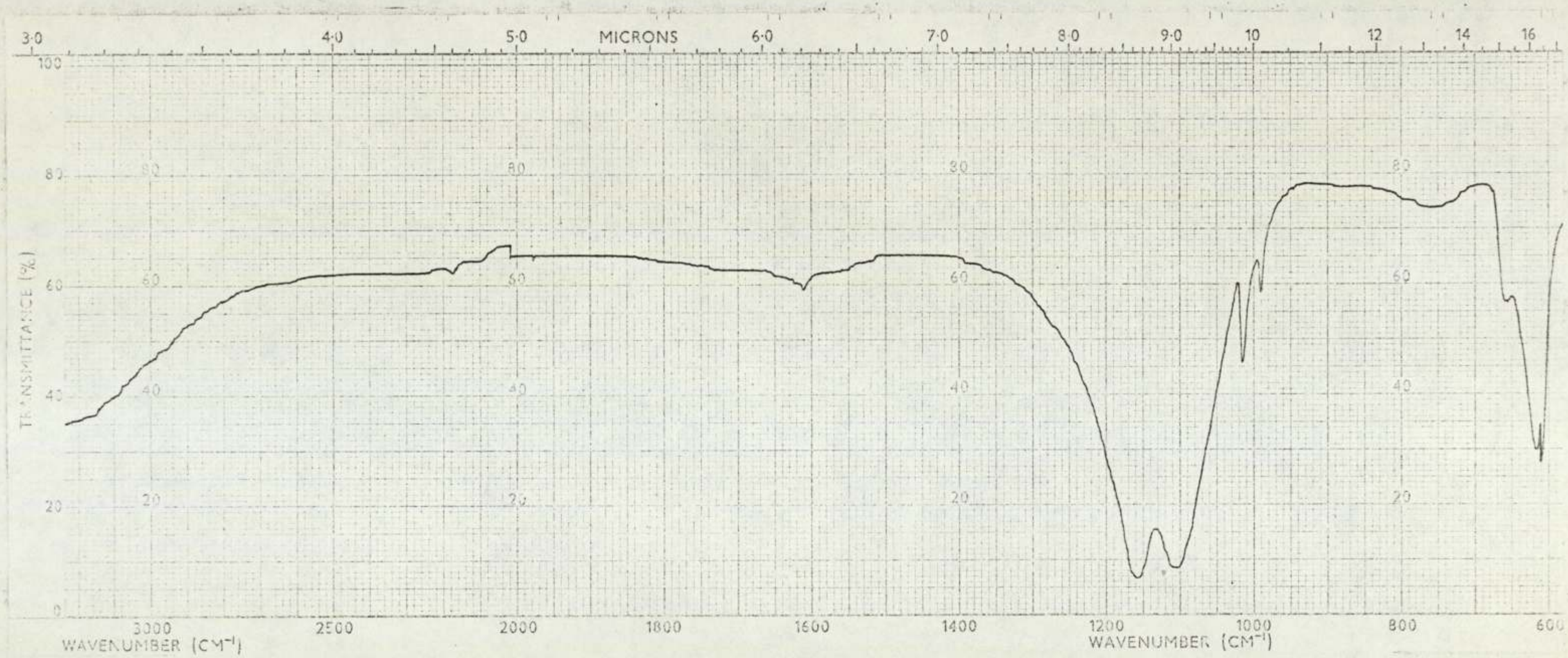
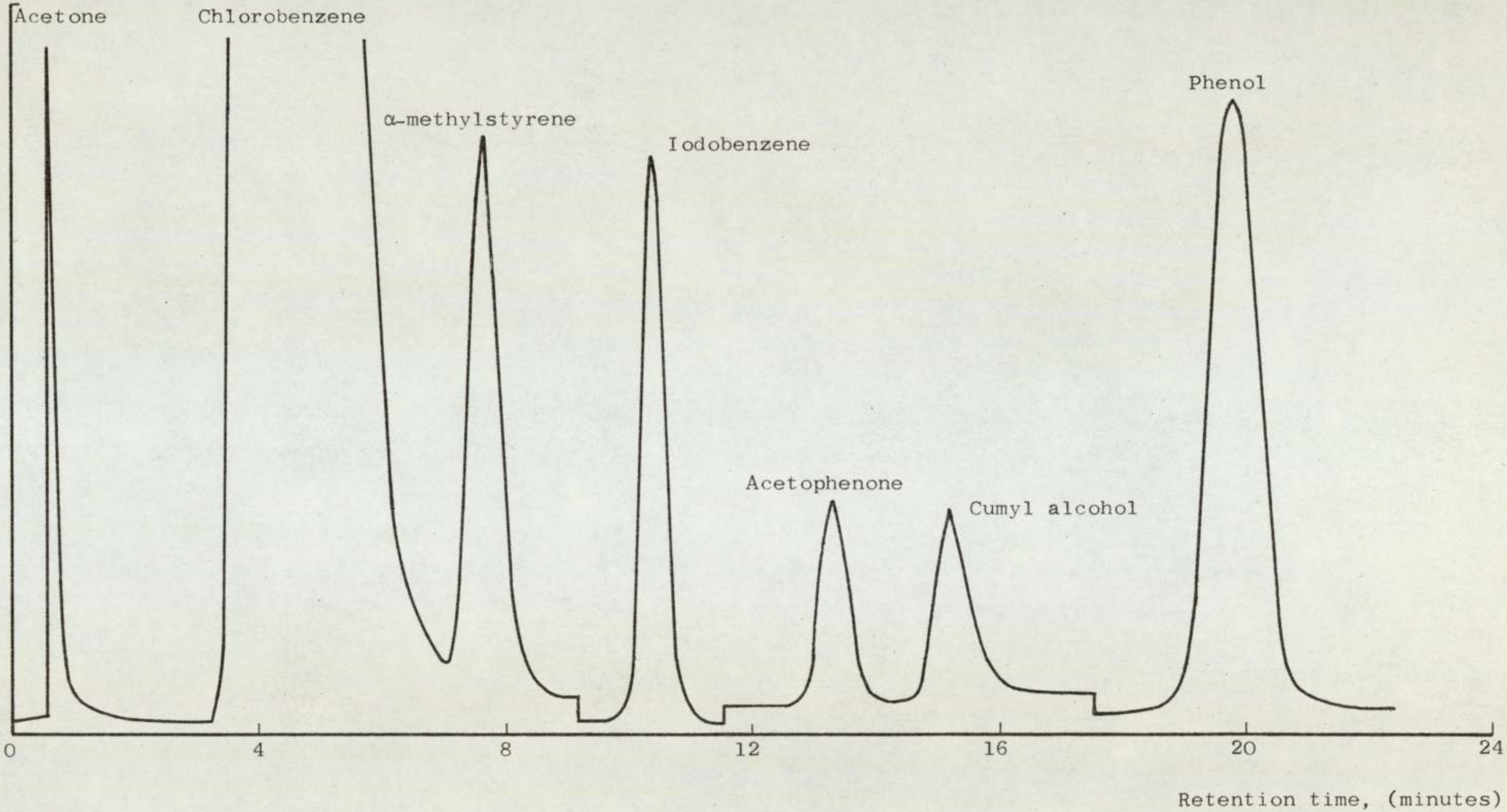


Figure 7.6 Infra-red spectrum of zinc sulphate

Figure 7.7 Chromatogram of cumene hydroperoxide decomposition products



(4 x 100) (1 x 100) (8 x 100) (8 x 10) (2 x 100) Attenuation

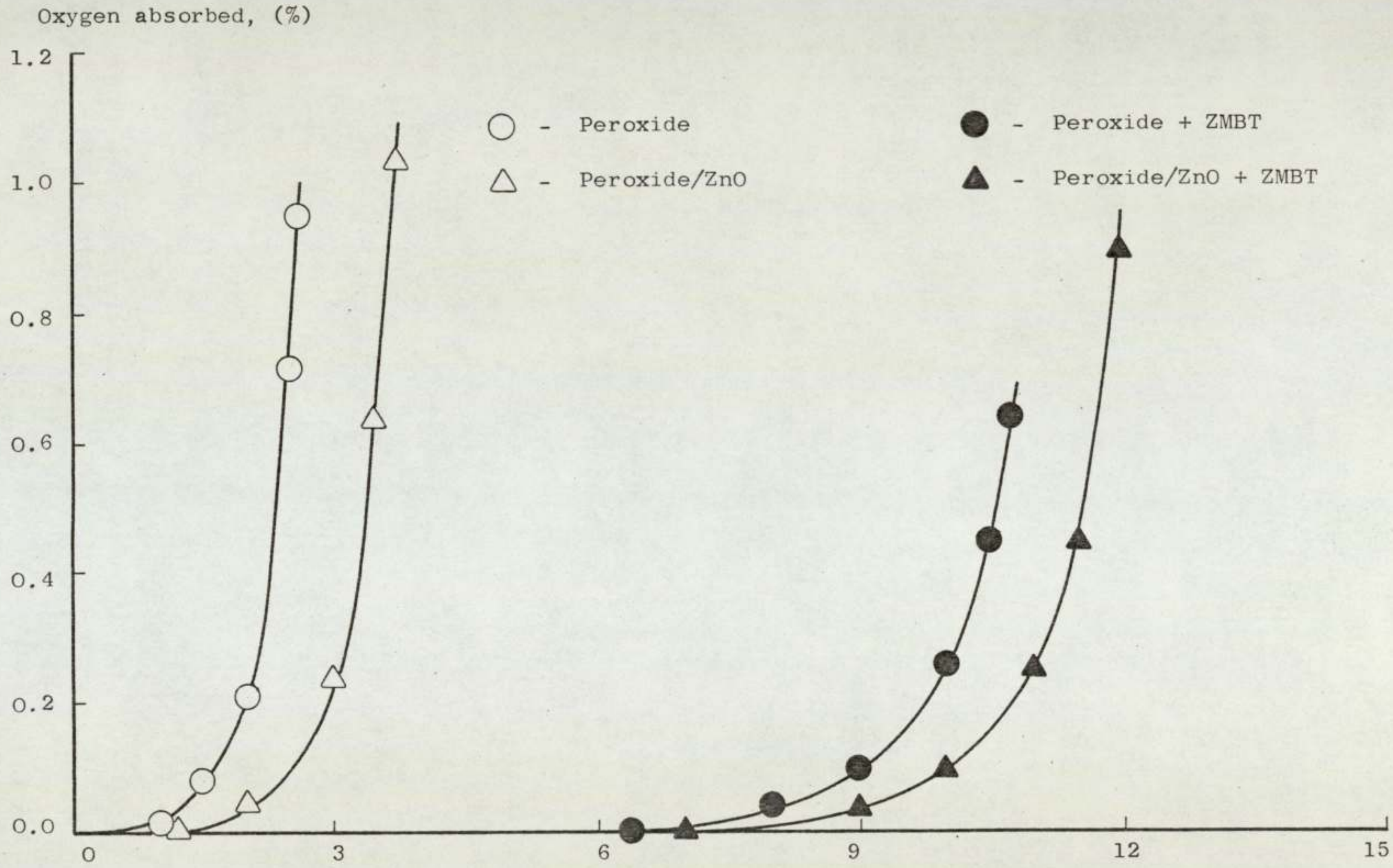
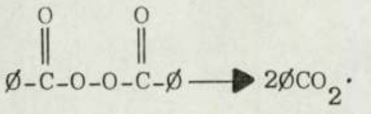


Figure 7.8 Oxygen absorption of Peroxide and Peroxide/ZnO vulcanizates in the presence and absence of ZMBT

shown that phenolic antioxidants, exhibiting the chain breaking mode of action, give a characteristic induction period in tetralin oxidation initiated with AZBN. Zinc diethyldithiocarbamate on the other hand was found to be almost ineffective in this system but displayed autoinhibiting characteristics in the presence of tetralin hydroperoxide. Bateman et al[71] produced evidence showing that t-butyl sulphoxide, an effective antioxidant, did not possess chain terminating activity, whereas Armstrong[61] has shown that under certain conditions active monosulphides can act effectively as chain terminating antioxidants. Colclough and Cunneen[92] investigated the antioxidant activity of a series of sulphur containing antioxidants. Phenothiazine, zinc isopropylxanthate, zinc di-isopropyldithiophosphate, and zinc dibutyldithiocarbamate were found to possess both chain breaking and hydroperoxide decomposing capabilities during the oxidation of squalene. The radical chain breaking effect was small, however, for the dithiocarbamate and isopropylxanthate.

The results presented in section 7.3 indicate that ZMBT acts as a chain breaking and hydroperoxide decomposing antioxidant during the autoxidation of cumene. In contrast to the free radical initiated systems, in which the rate of oxygen uptake reverts to that initially observed after an initial induction period, the hydroperoxide initiated systems exhibit autoinhibition. Even at the molar ratio CHP:ZMBT of 553 considerable autoinhibition occurs, whereas the antioxidant effect arising from the chain breaking mode appears to be significant only in systems containing a molar excess of ZMBT compared to initiator. Thus, the hydroperoxide decomposing ability of ZMBT is the prominent feature as far as antioxidant activity is concerned. Armstrong[61] has pointed out that AZBN may be removed from an autoxidizing system in the presence of dimethylsulphinyldipropionate, (DMSD), by a reaction other than that involving decomposition into free radicals. The addition of the sulphenic acid across the azo group of the initiator has been suggested as a possible mode of apparent inhibition observed in the AZBN initiated CHP/DMSD system. A similar type of reaction occurring in the presence of ZMBT appears unlikely since the data obtained from the benzoyl peroxide initiated autoxidation of cumene confirms the radical chain breaking activity of ZMBT, (figure 7.3). The initiating species derived from benzoyl peroxide are benzoyloxy and phenyl radicals, (7.1) - (7.2). Induced decomposition of benzoyl peroxide can occur but amounts to only a



$$\O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-O-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\O \longrightarrow 2\O CO_2\cdot \qquad (7.1)$$

$$2\O CO_2\cdot \longrightarrow 2\O\cdot + 2CO_2 \qquad (7.2)$$

few per cent of the total decomposition rate at 0.01M concentration and 80°C[161]. The mechanism of the chain breaking mode of antioxidant activity characteristic of phenolic antioxidants was described in section 1.3. Obviously this cannot apply to the effect observed with ZMBT. Colclough and Cunneen[92] have reported chain breaking activity associated with some sulphur containing antioxidants including dithiocarbamates. This was attributed to electron transfer from the electron rich sulphur atoms to the peroxy radical, thereby deactivating the latter forming the anion, (7.3). It is possible that a similar process accounts for the effect observed with ZMBT.

$$(R_2NCS_2)_2Zn + RO_2\cdot \longrightarrow RO_2^- \; (R_2NCS_2)^+ZnS_2CNR_2 \qquad (7.3)$$

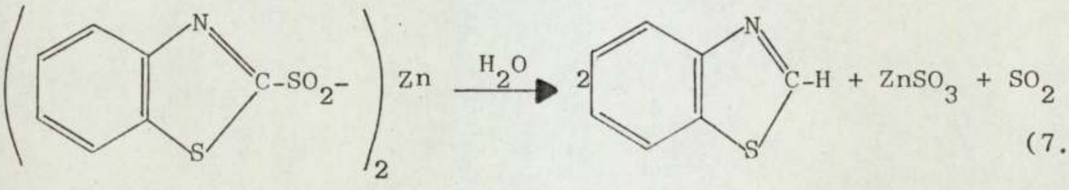
The decomposition of cumene hydroperoxide in chlorobenzene at 80°C

becomes first order, with respect to hydroperoxide, after an initial period of 60 minutes during which the rate of hydroperoxide decomposition is slower, (figure 7.4). The kinetic features indicate the production of a catalytic hydroperoxide decomposer from ZMBT during the initial stage of the reaction. Following this induction period a steady state concentration of the catalytic species has been attained and first order (pseudo) decomposition is observed. The precipitation of zinc sulphate during the induction period indicates that the ZMBT itself is unlikely to be the effective antioxidant.
The empiricial rate equation is:

$$-\frac{d[CHP]}{dt} = K[CHP] \qquad (7.4)$$

and the pseudo first order rate constant, K, for the reaction was estimated in duplicate as 3.81×10^{-4} and 3.66×10^{-4} sec^{-1}. After a period of 160 minutes 95 per cent of the CHP was decomposed, corresponding to 194.7 moles of CHP per mole of ZMBT present initially.

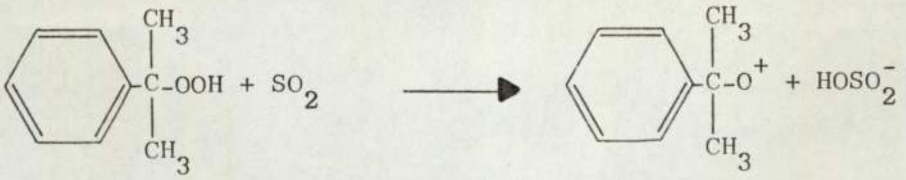
The major products of CHP decomposition, phenol and acetone, indicate that decomposition occurs via a non-radical mechanism and this implies that the catalytic decomposer is an acid species[99,131,162]. Brooks[114] has shown that the product resulting from the reaction of ZMBT with hydroperoxide is the sulphinate and further, this decomposes slowly to yield benzothiazole, sulphur dioxide and zinc sulphite, (7.5).



(7.5)

Scott[88] has studied the antioxidant activity of dithiocarbamates and has shown that cumene hydroperoxide is catalytically decomposed by a series of dithiocarbamates following an initial slower period that terminates with the precipitation of the metal sulphate. The hydroperoxide decomposition was attributed to the formation of sulphur dioxide, (section 1.3.1.2). Scott and Armstrong[61] have investigated the antioxidant action of thiodipropionic esters and have suggested that the actual hydroperoxide decomposer is sulphur dioxide or sulphur trioxide. Furthermore, Chien and Boss[90] have proposed that the hydroperoxide decomposer formed from dilaurylthiodipropionate is sulphur dioxide. Therefore, in light of the previous investigations concerning sulphur containing antioxidants, it does not appear unreasonable to suggest that the hydroperoxide decomposing activity of ZMBT is due to the formation of sulphur dioxide or its further oxidation product sulphur trioxide. The sulphur dioxide is formed following the initial oxidation of ZMBT by the hydroperoxide as suggested by the kinetics of the ZMBT/CHP reaction. The initial oxidation reaction may be of the form suggested by Brooks, sulphur dioxide being a product of the hydrolysis of the sulphinate. In addition, zinc sulphate is formed, a product noted during these present investigations. On the other hand, a series of reactions analogous to those for dithiocarbamates as proposed by Scott may be responsible for the antioxidant action of ZMBT. In both cases the hydroperoxide decomposition is a result of the formation of sulphur dioxide.

Several workers[61,90,95] have shown that sulphur dioxide is a powerful catalyst for the ionic decomposition of hydroperoxides. Its activity is due to its ability to function as a Lewis acid[95,131], (7.6) - (7.8). The products of the hydroperoxide decomposition are phenol and acetone. The commercial production of phenol and acetone from cumene by the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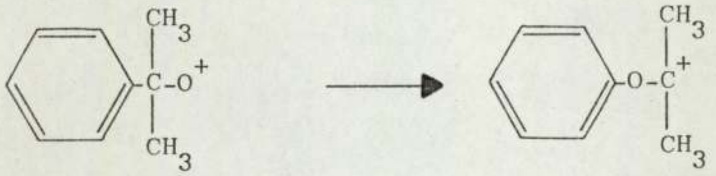
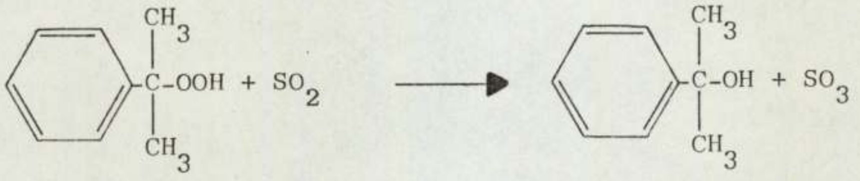
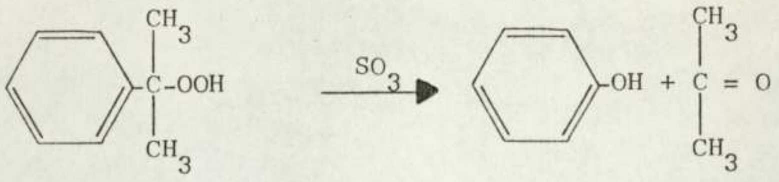

(7.7)


(7.8)

reaction of sulphur dioxide with CHP has been patented[163] and is described by Fortuin and Waterman[164].

The major products of the CHP decomposition during the reaction with ZMBT have been shown to be phenol and acetone consistent with the catalytic ionic decomposition reaction. In addition, α-methylstyrene is formed in a significant quantity. De Jong[165] has shown by the addition of sulphur trioxide acceptors such as pyridine, that the reaction of cumene hydroperoxide with sulphur dioxide proceeds according to the sequence (7.9) - (7.10). Approximately 5 mole


(7.9)



(7.10)

per cent of the CHP is converted according to reaction (7.9). and approximately 95 mole per cent according to reaction (7.10) if the initial concentration of the hydroperoxide is not less than 0.1 moles per litre. With lower hydroperoxide concentrations the percentage of CHP converted according to reaction (7.9) increases as the hydroperoxide concentration decreases. If equimolar amounts of sulphur dioxide, CHP and pyridine are reacted it is possible to obtain near quantitative yields of α,α-dimethylbenzyl alcohol. This reaction of sulphur dioxide with CHP would explain the presence of α-methylstyrene in the CHP/ZMBT product mixture, the unsaturated compound being produced by dehydration of the α,α-dimethylbenzyl alcohol which is catalyzed by sulphur dioxide[166]. More recently Husbands[141] has shown that the actual catalyst is in fact sulphur trioxide.

The presence of free radicals during the reaction of hydroperoxides with sulphur dioxide has been demonstrated in electron spin resonance, (ESR), studies[167] and by the use of free radical acceptors[168]. The ESR studies involved excess and equimolar quantities of sulphur dioxide to hydroperoxide and were carried out below 20°C. The results were interpreted in terms of the reactions (7.11) - (7.13). In addition, this system is capable of initiating the free

$$RO_2H + SO_2 \longrightarrow RO\cdot + HO\dot{S}O_2 \qquad (7.11)$$

$$RO_2H + SO_2 \longrightarrow HO\cdot + RO\dot{S}O_2 \qquad (7.12)$$

$$HO\cdot + SO_2 \longrightarrow HO\dot{S}O_2 \qquad (7.13)$$

radical polymerization of vinyl monomers[168,169]. If free radical intermediates are present in the sulphur dioxide/hydroperoxide system then an induced free radical decomposition of the hydroperoxide will also take place producing, in the case of CHP, quantities of α,α-dimethylbenzyl alcohol, α-methylstyrene and acetophenone[99]. Thus, the products of CHP decomposition during the CHP/ZMBT reaction, under the conditions studied, can be satisfactorily accounted for on the basis of the reactions discussed. The presence of a minor quantity of acetophenone suggests the insignificance of the free radical induced decomposition as an important feature of the removal of hydroperoxide from the autoxidizing system.

Brooks[114] has suggested that in a rubber vulcanizate ZMBT reacts in a stoichiometric manner with respect to its antioxidant action, four moles of hydroperoxide converting one mole of ZMBT to the sulphinate. Further hydroperoxide oxidizes the decomposition products of the sulphinate, namely zinc sulphite and sulphur dioxide, to sulphate and trioxide. Therefore, one mole of ZMBT decomposes six moles of hydroperoxide. It is suggested that sulphur dioxide, or trioxide, may not behave as a catalytic hydroperoxide decomposer because of the presence of zinc oxide in the vulcanizate, thereby converting the potential catalyst to a stable zinc salt. The present investigations involving model compounds have indicated that ZMBT produces a catalytic hydroperoxide decomposer, possibly sulphur dioxide or trioxide, which decomposes hydroperoxides via an ionic mechanism. Additional data obtained from vulcanizate studies, (figure 5.1), suggests that zinc oxide does not suppress the antioxidant activity of ZMBT. More convincing evidence is shown in figure 7.8. Peroxide and Peroxide/ZnO vulcanizates were swollen in a saturated solution of ZMBT, (commercial ZMBT freed from MBT), and subsequently analyzed for oxygen absorption. The presence of zinc oxide does not decrease the effectiveness of the antioxidant.

8. Conclusions and suggestions for further work

8.1 Conclusions

Oxygen absorption measurements of vulcanizates were determined on specimens of thickness less than or equal to 0.023 cms at 80°C. Under these conditions diffusion of oxygen into the vulcanizates was not rate controlling.

The outstanding oxidative stability of the EV vulcanizate was shown to be due to the solvent extractable antioxidant ZMBT formed during the curing process. This antioxidant accounts for 56 per cent of the MBT originally present as the accelerator CBS and confers a stability far in excess of the TMTD sulphurless system in which the antioxidant ZDC is similarly formed during vulcanization. Model studies have shown that ZMBT possesses both chain breaking and hydroperoxide decomposing antioxidant capabilities. The former becomes significant only in systems containing a molar excess of antioxidant to initiating species and it has been suggested that this mode of action is due to an electron transfer process previously proposed for other sulphur containing antioxidants. The hydroperoxide decomposing ability of ZMBT is effective even in systems containing a molar excess of hydroperoxide of 550. This is due to the production of a catalytic decomposer following initial reaction between ZMBT and hydroperoxide. The catalytic species has not been identified but it has been suggested that it is sulphur dioxide or sulphur trioxide derived from breakdown of the oxidation product of ZMBT, functioning by an ionic deactivating mechanism.

The solvent extraction procedure removed soluble vulcanization residues over a period of 24 hours and the elevated temperature of extraction did not give rise to any substantial network degradation or further cross-linking. The extracted vulcanizates of higher sulphur content exhibited oxidative characteristics previously reported for natural rubber systems, ie pro-oxidant and antioxidant effects were observed. An alternative suggestion has been offered, as opposed to the effect of conjugated unsaturation and polysulphidic cross-links, to account for the oxidative behaviour of these systems. The pro-oxidant effect results from a redox reaction between sulphenic acid and hydroperoxide and the antioxidant effect is due to the ultimate formation of sulphur dioxide or sulphur trioxide. However, these reactions occurring in a rubber vulcanizate have not been conclusively established.

The superior stability of the solvent extracted EV system compared to the other extracted sulphur vulcanizates was shown to be due to the presence and antioxidant action of the basic zinc salt of MBT. This is formed during the curing process by hydrolysis of normal ZMBT. The basic salt is removed from the system by acid extraction, the oxidative behaviour of the resulting network then resembling that of the solvent extracted, TMTD sulphurless vulcanizate. Pendent accelerator groups present in the EV network do not appear to play an important part in determining its oxidative stability.

8.2 Suggestions for further work

It has been suggested that the autoinhibition exhibited by extracted vulcanizates of higher sulphur content may be due to the production of an antioxidant derived from a series of reactions involving the formation of sulphenic and sulphinic acids. On the other hand, this feature has previously been attributed to the presence of polysulphidic cross-links exerting a stabilizing influence. This disparity may be resolved by investigating the oxidative characteristics of a sulphurated network devoid of polysulphidic features but possessing a combined sulphur concentration of the order of a conventionally cured system. It has been suggested that such a system is the High Modulus EV network[1] in which no polysulphidic cross-links are present but contains 2.0 per cent of combined sulphur. Details of the compound formulation are presented in table 8.1.

Component	p.h.r
Natural rubber	100
Zinc oxide	10.0
Lauric acid	2.0
Sulphur	1.6
CBS	24.0
Cure temp., °C	140
Cure time, minutes	120

Table 8.1 Compound formulation of the High Modulus EV system

A significant proportion of the combined sulphur may in fact be due to the presence of unextracted basic zinc salt of MBT since a high concentration of accelerator is utilized. This must be completely removed from the vulcanizate and then the sulphur combined in the network estimated prior to the determination of oxygen absorption data.

The catalytic hydroperoxide decomposer formed from ZMBT has not been identified, a more detailed investigation of the CHP/ZMBT reaction is therefore required, particularly during the early stages. Zinc sulphate has been found to be a final product of the reaction but the fate of the MBT function has not been determined.

Appendix

Abbreviations used in the text

NRPRA - Natural Rubber Producers Research Association

TMTD - Tetramethyl thiaram disulphide

CBS - N-(cyclohexyl)-2-benzothiazyl sulphenamide

S - Sulphur

DCP - Dicumyl peroxide

EV - Efficient vulcanization

RHC - Rubber hydrocarbon

DLTP - Dilaurylthiodipropionate

DMTP - Dimethylthiodipropionate

AZBN - $\alpha\alpha'$-azodi-isobutyronitrile

ZDC - Zinc dimethyldithiocarbamate

MBTS - Dibenzothiazyl disulphide

ZMBT - Zinc benzothiazole-2-thiolate

MBT - 2-mercaptobenzothiazole

NATSYN - Cis-1,4-polyisoprene, (Goodyear Ltd.)

BBS - N-(t-butyl)-2-benzothiazyl sulphenamide

CHP - Cumene hydroperoxide

SR - Equilibrium weight swelling ratio

DMSD - Dimethylsulphinyldipropionate

ESR - Electron spin resonance

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MECHANISM OF THE OXIDATION AND STABILIZATION OF VULCANIZED RUBBERS

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A study of the mechanism of oxidation of sulphur compounds related to the rubber crosslink has shown that they display a dual role. During the early stages of oxidation they act as pro-oxidants but eventually they become antioxidants. This stage is reached too late to be of technical value in simple vulcanizates and it is argued that the only way in which the sulphur crosslink can be protected against oxidation is by incorporating a reducing agent which will effectively compete with it for hydroperoxide. EV curing systems show considerable promise in that very powerful antioxidant activity appears to be associated with non-cross-link network bound sulphur compounds and developments based on EV curing systems are discussed.

It is surprising that although sulphur-vulcanized rubber is the oldest technologically important polymer, less is known about the mechanism of oxidation of rubber vulcanizates than almost any other polymeric material. It is well known that the introduction of sulphur into the rubber molecule changes its mode of oxidation. Whereas unvulcanized rubber or rubbers cured without the use of sulphur (peroxide or high energy irradiation) oxidise autocatalytically, sulphur-vulcanized rubbers always show auto-retarding characteristics.(1) The autoxidation of some typical cis-polyisoprene vulcanizates is shown in Fig. 1 (the formulations and curing conditions are listed in Table I). It can be seen that although the peroxide cure initially oxidises very slowly it rapidly auto-accelerates whereas all the sulphur vulcanizates, including the conventionally cured CBS system autoretard and ultimately oxidise more slowly.

In order to study the effect of bound sulphur it is, however, necessary to extract extra-network material and a comparison of the ageing properties of the same vulcanizates after extraction is illustrated in Fig. 2. The effect of extraction is strikingly different for a TMTD sulphurless and CBS EV cure. The former loses almost all its oxidation resistance whereas the latter is almost unchanged suggesting that the antioxidant in this case has been built into the network. However this cannot be in the form of crosslinks since the composition and concentration of the crosslinks are not very dissimilar in the two cases (see Table II). The difference must lie in the non-crosslink-bound sulphur which is a quite considerable proportion of the total bound sulphur (TBS) in the two cases.

It is known that TMTD sulphurless vulcanizates contain relatively little cyclic sulphides whereas the EV network contains both cyclic and pendant accelerator-polysulphide residues. It seems likely that the good oxidation resistance is associated in some way with the latter since Parks and Lorenz have shown(2) that polysulphides are pro-oxidants, and further studies of this are in progress. However the most important fact emerging from the oxidation of the extracted vulcanizates is that all the sulphur networks rapidly auto-retard to oxidise more slowly than the peroxide crosslinked rubber and at extended oxidation times, the CBS vulcanizates oxidise at a slower rate than the EV vulcanizate (see Fig. 3). It will be noted from Table II that the total combined sulphur in the CBS vulcanizates is 2.3% compared with 0.7% for the EV system and this behaviour is very similar to the effect of the sulphide antioxidant dilauryl thiodipropionate (DLTP) in polypropylene.(3) This is shown in Fig. 4 from which it can be seen that the change in melt flow index (which is a technological measure of the degree of oxidative degradation of polypropylene) is initially higher but ultimately lower the higher the concentration of the sulphide. Studies in model hydrocarbons have shown that the behaviour of DLTP (I) is typical of dialkylmonosulphides in general. The first product to be formed is

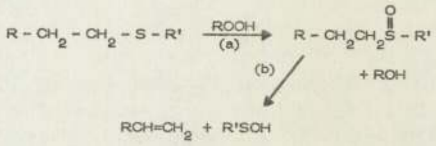
$(ROCOCH_2CH_2)_2S$ I

$(ROCOCH_2CH_2)_2S{=}O$ II

the derived sulphoxide (II) which gives rise to a powerful antioxidant. Extensive studies by the Natural Rubber Producers Research Association(4) have shown that this is generally true of dialkylsulphides, disulphides, sulphoxides and thiolsulphonates, all of which can be formed either during oxidation of sulphur vulcanizates or during their vulcanization. However, these studies have not explained the reason for the early pro-oxidant behaviour of rubber networks. Previous studies have largely been carried out in uninitiated systems but the evidence suggests that there are always hydroperoxides present in rubbers which have been subjected to technological processing conditions and in the presence of hydroperoxides both sulphides and sulphoxides do behave initially as pro-oxidants under certain conditions.(5)

When dimethylsulphinyldipropionate (DMSD)(II, R=Me) is added to oxidising cumene initiated by cumene hydroperoxide, there is an immediate pro-oxidant effect over a wide range of ratios of cumene hydroperoxide (CHP) to sulphide. In Fig. 5 the curves were obtained by holding CHP concentration constant and increasing the sulphide concentration from [CHP]/[S] = 17 to [CHP]/[S] = 0.5.

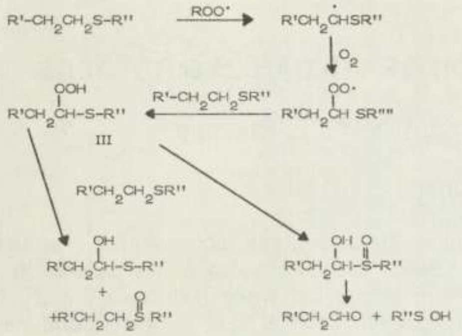
It is known that the initial breakdown products of sulphoxides (II) which contain a β-hydrogen atom are sulphenic acids.(6)



$$R-CH_2-CH_2-S-R' \xrightarrow[(a)]{ROOH} R-CH_2CH_2\overset{O}{\overset{\|}{S}}-R' + ROH$$
$$\xrightarrow{(b)} RCH{=}CH_2 + R'SOH$$

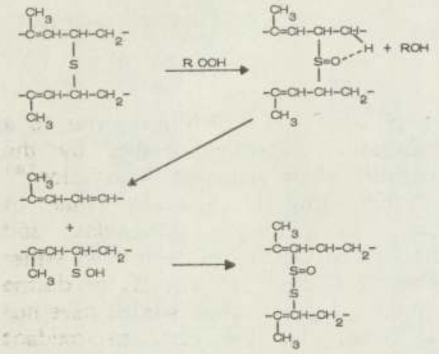
[1]

When the substrate is a sulphide, the first product formed on oxidation is the α-hydroperoxide of the thioether (III).



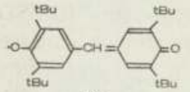
[2]

which may oxidise either itself or another molecule of sulphide. In either event the alcohol produced is unstable and leads to breaking of the sulphur-carbon bond. When this forms part of a polymer (e.g. a sulphur crosslink) then breakdown occurs. There are thus two ways in which crosslink scission can occur although Cunneen has adduced evidence which suggests that partial repair of broken crosslinks can occur in the absence of oxygen by reaction together of two molecules of sulphenic acid;(7)

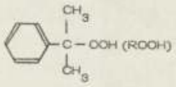


[3]

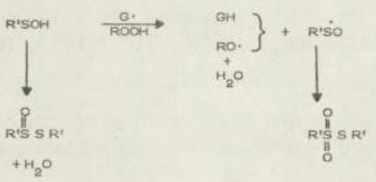
Kinetic evidence has shown (see Fig. 6)(8) that although in the presence of oxidising agents the decomposition of DMSD (II, R=Me) is first order, in the absence of oxidising agents it is not, indicating reversibility of reaction [1]. The oxidising agents, Galvinoxyl (IV) and cumene hydroperoxide (V) remove the sulphenic acid irreversibly as follows [4]



IV

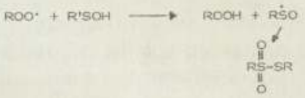


V



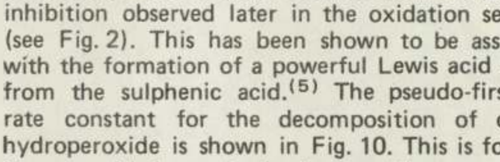
[4]

Confirmation for these competing reactions is found that in the absence of oxidising agent the yield of water is theoretical whereas in the presence of galvinoxyl it is not formed at all. The redox reaction of hydroperoxide with sulphenic acid gives a satisfactory explanation for the pro-oxidant effect which is observed (see Fig. 5) at hydroperoxide/sulphide molar ratios less than 1. Moreover the overall antioxidant effect appears to be optimal at this ratio and is characterized by an almost immediate cessation of oxidation when the sulphoxide is added to autoxidising cumene. This can not be due to destruction of hydroperoxide and the addition of DMSD to cumene initiated by azo-bis-isobutyronitrile (AZBN), which generates alkyl radicals without the intervention of hydroperoxide, again causes rapid inhibition (see Fig. 7) indicating that the sulphenic acid, as might be expected from the reactions described above, is an effective kinetic chain breaking antioxidant.



[5]

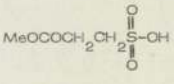
The sulphinyl radical is very stable and cannot continue the kinetic chain reaction and is removed by dimerization. It seems likely then that formation of thiolsulphonate crosslinks (which would be relatively stable, are probably mainly responsible for the new crosslink formation during the degradation of sulphur crosslinks observed by Cunneen and his co-workers.(7) Further evidence for the inhibiting ability of sulphenic acids comes from a study of their intervention in the polymerization of styrene. Fig. 8 shows that both the uninitiated and AZBN initiated polymerization of styrene is inhibited by DMSD. This occurs both in the presence and absence of oxygen. However, in the cumene hydroperoxide initiated polymerization (see Fig. 9), the behaviour is more complex. At high hydroperoxide to sulphoxide ratios, polymerization is inhibited. This is maximal at about 1:1 molar ratio but increases rapidly as the hydroperoxide to sulphoxide ratio is decreased further. Competing initiating and inhibiting processes are again involved.



[6]

The kinetic chain-breaking activity of the sulphenic acid is probably responsible for the initial induction period observed in the oxidation of most rubber vulcanizates and is quite distinct from the powerful inhibition observed later in the oxidation sequence (see Fig. 2). This has been shown to be associated with the formation of a powerful Lewis acid derived from the sulphenic acid.(5) The pseudo-first-order rate constant for the decomposition of cumene hydroperoxide is shown in Fig. 10. This is found to increase with increasing hydroperoxide concentration but does not increase further above a molar ratio of 8:1 (see Fig. 11). This is in accord with the observed high inhibitory activity of sulphoxides in the presence of excess hydroperoxide.

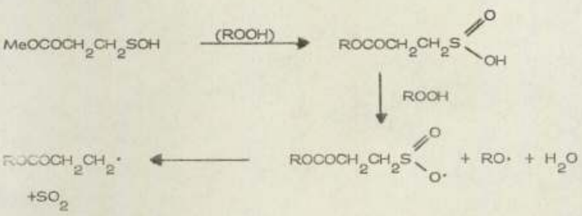
One of the products formed in the reaction between DMSD and hydroperoxides is the strong acid methyl-β-sulphopropionate (VI)(4)



$\mathrm{MeOCOCH_2CH_2S(=O)_2{-}OH}$

VI

which is indeed found to be a very powerful antioxidant in cumene. However, the rate of decomposition of cumene hydroperoxide in its presence is not fast enough to account for the antioxidant behaviour of the sulphoxide and it seems likely that the Lewis acid is SO_2 (or possibly its further oxidation product SO_3) which has previously been shown to be a very effective catalyst for the destruction of hydroperoxides at ambient temperatures and is a very powerful antioxidant. Its most likely mode of formation is from the sulphenic acid;

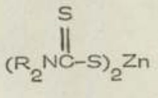


Sulphur dioxide is more than ten times more reactive as a catalyst for cumene hydroperoxide decomposition at 75°C than DMSD and calculation shows that the kinetic results obtained in these studies are consistent with SO_2 being the active species.

It will be evident from the evidence which has been discussed that the monosulphide crosslink must always be a source of oxidative instability in a vulcanizate since although it is eventually converted to an antioxidant, this is only favoured at unrealistically high ratios of hydroperoxide to sulphide and in any case, the formation of such an antioxidant invloves the destruction of crosslinks. Thiodipropionate esters have been found to be very poor antioxidants in sulphur vulcanizates[9] since the sulphide:hydroperoxide even in the absence of added antioxidant is already above the critical level required for good peroxide decomposing activity.

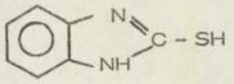
An alternative approach which theoretically should lead to a practically useful system is to remove hydroperoxide by extra crosslink sulphur compounds in a reaction which is faster than the rate of reaction of hydroperoxide with the sulphur crosslink and which will therefore lead to protection of the vulcanizate structure.

Four classes of compound have been extensively studied which act by decomposing hydroperoxides.[10] These are the zinc dialkyldithiocarbamates (IX), the zinc dialkyl dithiophosphates (X), mercaptobenzimidazole (XI) and the phosphite esters (XII).

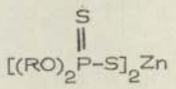


$(R_2N\overset{S}{\overset{\|}{C}}{-}S)_2Zn$

IX



XI



$[(RO)_2\overset{S}{\overset{\|}{P}}{-}S]_2Zn$

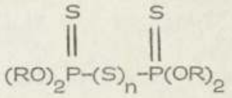
X

(RO)$_3$P

XII

The phosphite esters react rapidly with sulphur at vulcanization temperatures and the products do not seem to be antioxidants. The dialkyldithiocarbamates are powerful catalysts for hydroperoxide decomposition even at room temperature.[11] The higher alkyl compounds have less effect on cure and when used at concentrations of 1-2% are quite effective antioxidants.[12] However, the normal way of introducing the zinc dialkyldithiocarbamates is through the TMTD-sulphurless curing system. The effectiveness of the resulting dithiocarbamate salts has been shown by extracting the complex with acetone and comparing the ageing behaviour of the extracted vulcanizate with the original in stress relaxation.[13]

An unfortunate feature of the TMTD-sulphurless curing system is its poor scorch characteristics and the low level of physical properties that can be achieved. It has been found[14] that similar age-resisting vulcanizates can be obtained using di-isoalkyldithiophosphoryl di- and polysulphides (XIII) in the place of the thiurams.



$(RO)_2\overset{S}{\overset{\|}{P}}{-}(S)_n{-}\overset{S}{\overset{\|}{P}}(OR)_2$

XIII

Di-isopropylthiophosphoryl disulphide (DIPDIS, XII, R = iso-Pr, n = 2) has been studied as a typical sulphurless additive. At 6 phr it gives very similar good ageing behaviour to TMTD at 3 phr (see Fig. 12) in continuous stress relaxation and very much better than a typical CBS/S vulcanizate. Extraction destroys the good ageing behaviour. However, unlike a TMTD-sulphurless vulcanizate, DIPDIS-sulphurless vulcanizates show a very marked dependence on curing time. This is shown in Fig. 13 and in Fig. 14 both ageing performance and the extractable zinc di-isopropyldithiophosphate (ZDP) are plotted against cure time. It is clear that optimum ageing behaviour occurs at maximum conversion of the curing system to ZDP. The evidence suggests that the zinc salt is converted at least in part back to the disulphide during extended cure.

EV systems based on DIPDIS have proved to be much more practically interesting. Fig. 15 shows a comparison of an EV cure based on DIPDIS and dimorpholine disulphide (DMDS) with a TMTD-sulphurless and a CBS-sulphur vulcanizate. The notable features are the good level of physical properties obtained, the long induction period and the thermal stability of the vulcanizate.

Stress relaxation of the unextracted vulcanizates shows (Fig. 16) that the DIPDIS/EV cure is of similar oxidative stability to a TMT-sulphurless cure and is much superior to a conventional CBS vulcanizate. The EV system is remarkably stable to reversion at 160°C (see Fig. 17). In spite of the fact that the sulphur distribution in the network changes (see Table III) the stress relaxation curves of these two vulcanizates are almost identical, indicating that the extra- network material has a dominating influence in the ageing behaviour and in this case the zinc salt is not destroyed.

It is possible to build the sulphur donor into the thiophosphoryl compound. In the case of XIII when n = 3 or 4, 6 parts of the tetrasulphide gives a very rapid curing system at 160° although the scorch time is rather inferior to the donor system (see Fig. 18).

The vulcanizate, as might be expected contains no polysulphide and again the extent of cure at 160° has a relatively minor effect on ageing properties.

It seems clear then that the future for highly oxidatively stable rubbers lies in the development of systems like this which build the sulphur component of the antioxidant into the vulcanizate either as network bound or extra-network material during curing. The systems discussed also show synergism with conventional amines and phenols and also with certain transition metal ions (e.g. Cu). An advantage of the thiophosphoryl antioxidant is that unlike the dithiocarbamates it does not cause "copper straining", and Philpott has reported(15) that the antioxidant system formed from a DIPDIS-EV vulcanizate is much more resistant to solvent and detergent extraction than is ZDC.

A final advantage of the phosphorus based EV's that will not go unnoticed by the technologist is that the phosphorus curing agents are potentially much cheaper than the thiurams.

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Table I. Composition of Natsyn Vulcanizates

		Extracted Natsyn	ZnO	Stearic acid	Lauric acid	TMTD	CBS	S	DCP	Cure time (min/deg C)
A	TMTD Sulphurless	100	4	1	–	4	–	–	–	85/160
B	TMTD Sulphurless	100	5	–	1.5	4	–	–	–	420/140
C	High modulus CBS	100	5	–	1.0	–	0.9	3.7	–	40/140
D	Conventional CBS	100	5	–	0.7	–	0.6	2.5	–	40/140
E	Semi EV	100	5	–	3.0	–	1.5	1.5	–	30/140
F	EV	100	5	–	1.0	–	6.0	0.4	–	120/140
P	Peroxide	100	–	–	–	–	–	–	3.0	45/160

Table II. Network Analysis of Vulcanizates

	Vulcanizate	Total combined sulphur-TCS (%)	Chemical cross-links (% of TCS)			Sulphur not as cross-links (% of TCS)
			S_1	S_2	S_x	
B	TMTD Sulphurless (85 min at 160°C)	0.35	27.7	–	–	72.3
C	High modulus CBS	3.01	3.1	3.1	13.3	80.5
D	Conventional CBS	2.08	3.2	3.1	13.4	80.3
F	EV	0.70	23.8	2.1	–	73.1

Table III. Characteristics of a DIPDIS-EV System Cured at 160°C

Cure time (min)	C.L.D. × 10^{-4}	X	Hardness	Density	Network structure Poly-	Di- (%)	Mono-
12	0.97	0.407	57.4	0.958	34	30	36
80	0.92	0.405	55.2	0.958	3	18	79

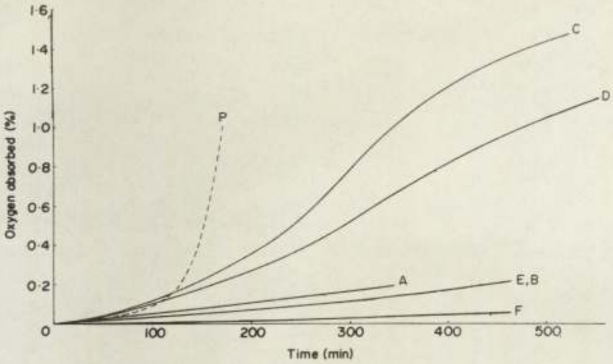


Fig. 1. Oxygen absorption of unextracted sulphur vulcanizates. A, TMTD sulphurless (85 min at 160°C); B, TMTD sulphurless (7 h at 140°C); C, high modulus CBS; D, conventional CBS; E, semi EV; F, EV; P, dicumyl peroxide.

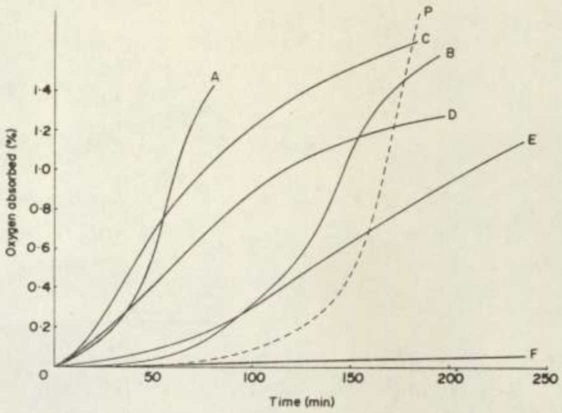


Fig. 2. Oxygen absorption of extracted sulphur vulcanizates at 80°C. Legend as for Fig. 1.

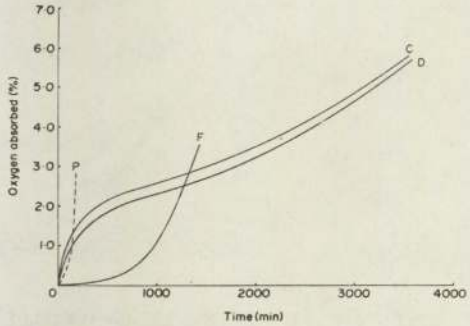


Fig. 3. Extended oxygen absorption of extracted sulphur vulcanizates at 80°C. C, high modulus CBS; D, conventional CBS; F, EV; P, dicumyl peroxide cure.

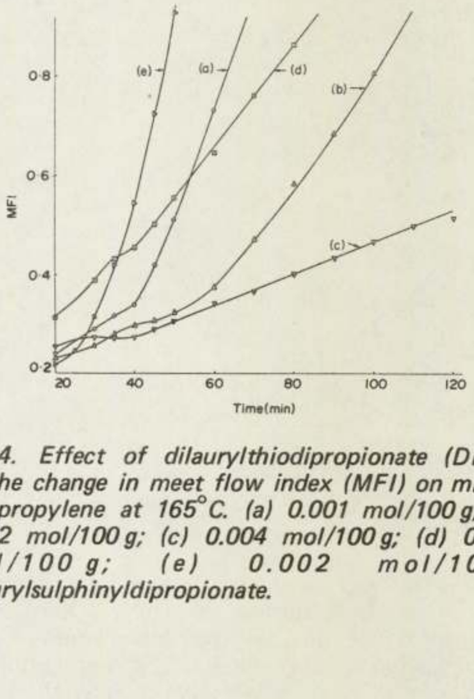


Fig. 4. Effect of dilaurylthiodipropionate (DLTP) on the change in meet flow index (MFI) on milling polypropylene at 165°C. (a) 0.001 mol/100 g; (b) 0.002 mol/100 g; (c) 0.004 mol/100 g; (d) 0.006 mol/100 g; (e) 0.002 mol/100 g dilaurylsulphinyldipropionate.

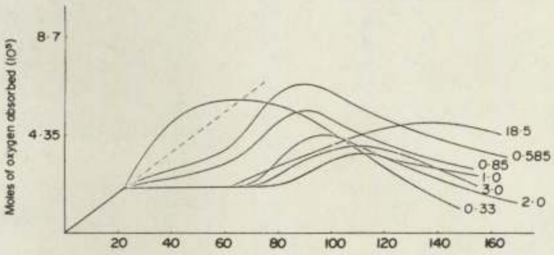


Fig. 5. The effect of dimethylsulphinyldipropionate on the oxidation of cumene initiated by α-cumene hydroperoxide (0.05 mol/l). Temperature 75°C. No. on curve is the ratio [cumene hydroperoxide] /DMSD.

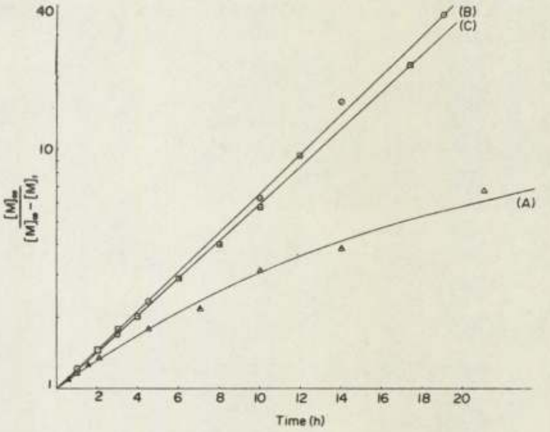


Fig. 6. Decomposition of dimethylsulphinyldipropionate (0.04 M) in dioxan at 75°C. A, no Galvinoxyl; B, 0.0815 mol Galvinoxyl/l; C, 0.09 mol cumene hydroperoxide/l.

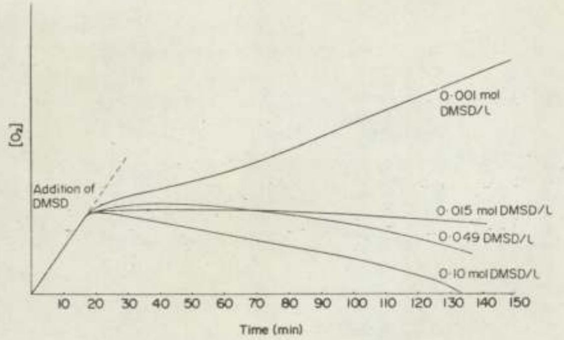


Fig. 7. The effect of dimethylsulphinyldipropionate on the oxidation of cumene initiated with AZBN (0.00042 M) at 75°C.

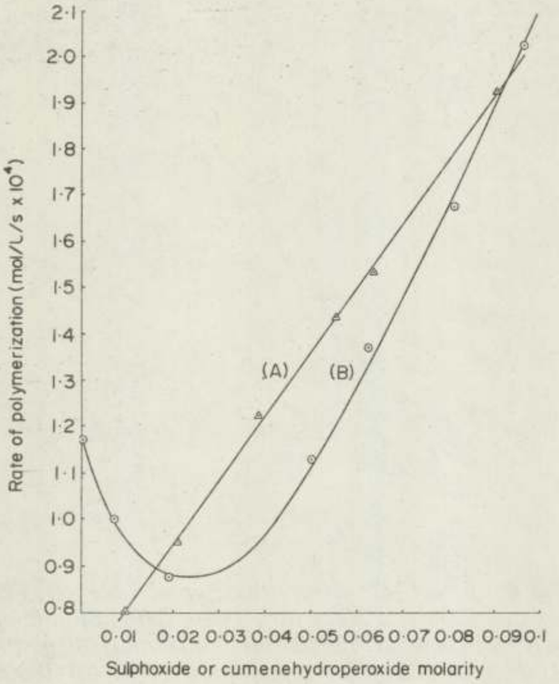


Fig. 9. The rate of polymerization of styrene at 75°C in vacuo. A, styrene containing 0.055 mol/l in the presence of varying concentrations of dimethylsulphinyldipropionate; B, styrene containing 0.055 mol dimethylsulphinyldipropionate/l in the presence of varying concentrations of cumene hydroperoxide.

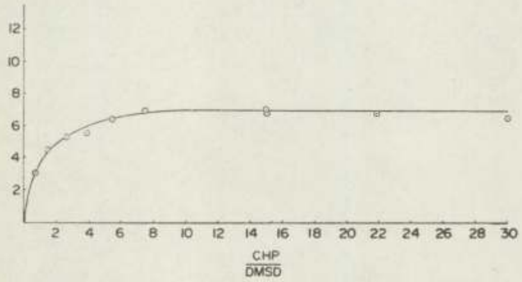


Fig. 11. Rate constants for reaction between dimethylsulphinyldipropionate (DMSD) and cumene hydroperoxide (CHP). Constant peroxide concn = 0.15 mol/l.

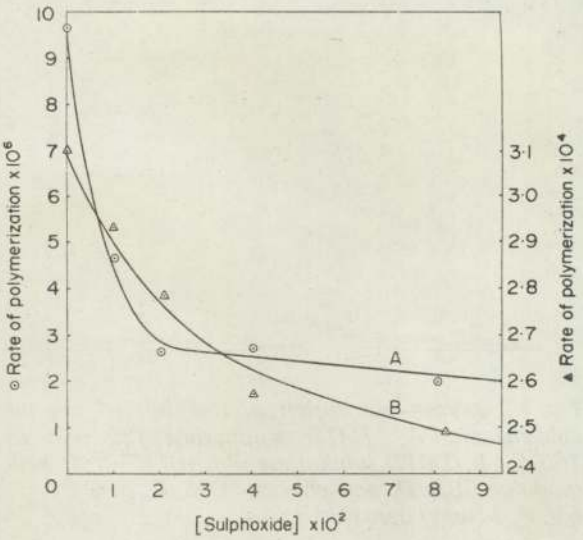


Fig. 8. Effect of dimethylsulphinyldipropionate concentration on the rate of polymerization of styrene at 75°C in nitrogen. A, uninitiated; B, initiated by 0.01 mol/l.

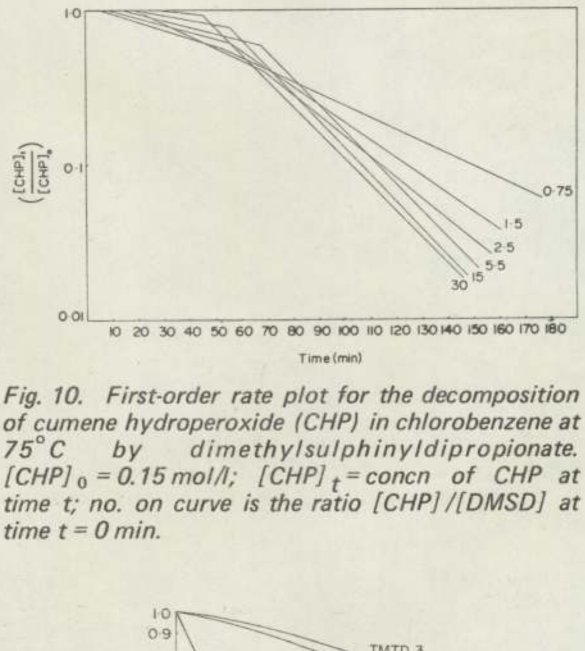


Fig. 10. First-order rate plot for the decomposition of cumene hydroperoxide (CHP) in chlorobenzene at 75°C by dimethylsulphinyldipropionate. $[CHP]_0 = 0.15$ mol/l; $[CHP]_t$ = concn of CHP at time t; no. on curve is the ratio [CHP]/[DMSD] at time t = 0 min.

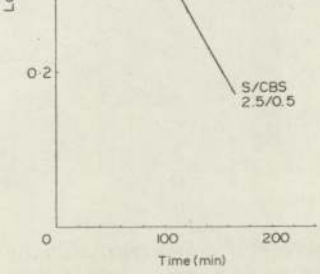


Fig. 12. Thermal oxidative continuous stress relaxation of sulphurless cures at 120°C.

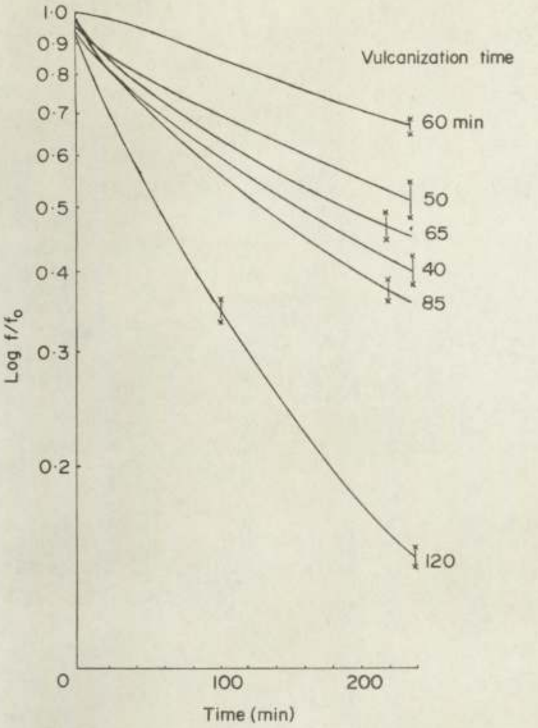
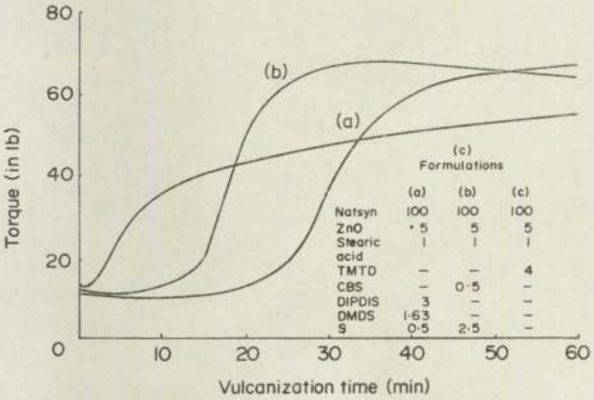


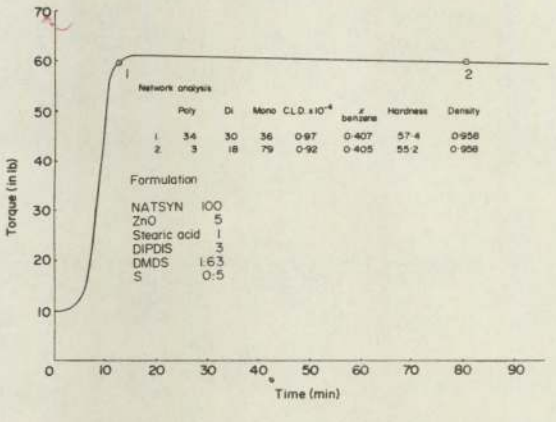
Fig. 13. Thermal oxidative continuous stress relaxation of DIPDIS sulphurless cure at 120° C.



Formulations

	(a)	(b)	(c)
Natsyn	100	100	100
ZnO	5	5	5
Stearic acid	1	1	1
TMTD	–	–	4
CBS	–	0·5	–
DIPDIS	3	–	–
DMDS	1·63	–	–
S	0·5	2·5	–

Fig. 15. Comparison of DIPDIS-EV curing system with other standards cured at 140° C.



Network analysis

	Poly	Di	Mono	C.L.D. x10^{-4}	χ benzene	Hardness	Density
1.	34	30	36	0·97	0·407	57·4	0·958
2.	3	18	79	0·92	0·405	55·2	0·958

Formulation

NATSYN	100
ZnO	5
Stearic acid	1
DIPDIS	3
DMDS	1·63
S	0·5

Fig. 17. Rheograph of DIPDIS-EV cure at 160° C.

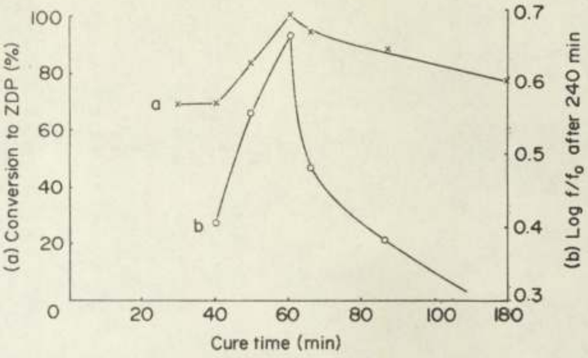
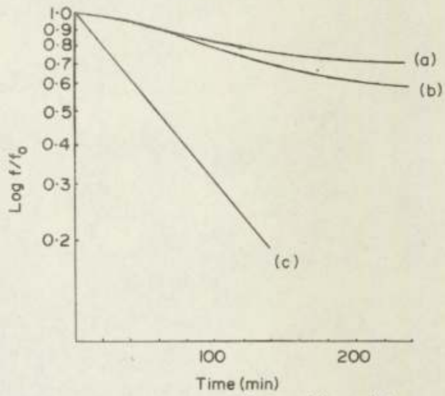
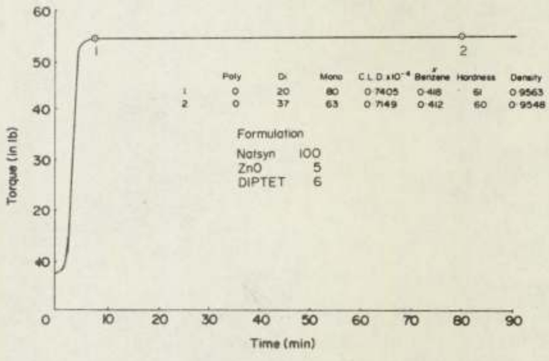


Fig. 14. Relationship between ZDP formation and thermal oxidative ageing at 120° C.



	(a)	(b)	(c)
NATSYN	100	100	100
Zinc Oxide	5	5	5
Stearic acid	1	1	1
TMTD	3	–	–
CBS	–	–	0·5
DIPDIS	–	3	–
DMDS	–	1·63	–
S	–	0·5	2·5
Cure (min)	90	100	45

Fig. 16. Thermal oxidative continuous stress relaxation at 120° C.



	Poly	Di	Mono	C.L.D. x10^{-4}	χ Benzene	Hardness	Density
1	0	20	80	0·7405	0·418	61	0·9563
2	0	37	63	0·7149	0·412	60	0·9548

Formulation

Natsyn	100
ZnO	5
DIPTET	6

Fig. 18. Rheograph of DIPTET-sulphurless cure at 160° C.