A STUDY OF POLYMER BOUND SULPHUR BASED ANTIOXIDANTS IN RUBBER

by

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SUMMARY

A commercially available hindered phenolic antioxidant, 2,6-Ditert-butyl phenol has been converted into a mercaptan derivative, viz. 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan and the latter has been successfully bound to natural rubber by a free radical process. Reaction parameters such as mode of initiation, initiator concentration, mercaptan concentration, time, temperature etc., have been investigated in rubber solution, in natural rubber latex, and in the polymer melt. A masterbatch technique has been developed to saturate a small quantity of rubber with a large amount of mercaptan and to use this concentrate to dilute untreated latex to obtain a desired level of stability. Infra-red spectroscopy has been used to estimate the concentration of adduct phenol, and accelerated ageing tests, viz. oxygen absorption and continuous stress relaxation were carried out to evaluate ageing behaviour. The effects of the presence of 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan on the vulcanization characteristics have been investigated in detail using a Monsanto Rheometer.

To investigate the mechanism of addition, a number of mercaptans and simple unsaturated model compounds have been used and the products have been analysed. The effect of the presence of antioxidant bound rubber on the oxidation of polypropylene was studied by a rapid flowing air oven test.

An attempt to add 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan to a saturated polymer, polythelene, was unsuccessful as theoretically expected.

Oxidation of an unsaturated compound, tetralin, was studied in the presence of monosulphides which are similar to those obtained by adding mercaptans to olefins.

The undersigned declares that the work in this thesis has not been carried out in collaboration with others. Neither has the work been submitted for any other award.

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CONTENTS

Page

CHAPTER 1 - Introduction

1.1. Autoxidation 1

1.1.1. Oxidation of Rubber 2

1.1.1.1. Oxidation of unvulcanized rubber 2

1.1.1.2. Oxidation of vulcanized rubber 4

1.1.1.2.1. Autoxidation of olefins 5

1.1.1.2.2. Oxidation of organic sulphides 6

1.1.1.2.3. Co-oxidation of sulphides and olefins 7

1.1.1.2.4. Oxidation of vulcanizates 13

1.2. Inhibition of Autoxidation 15

1.2.1. Antioxidants 15

1.2.1.1. Mechanisms of antioxidant action 16

1.2.1.1.1. Radical Chain Breaking Mechanism 16

1.2.1.1.2. Preventive Mechanism 19

1.3. Inhibition of rubber oxidation 21

1.3.1. Antioxidants in Rubber 21

1.3.1.1. Synergism 22

1.3.1.2. Volatilization and leaching of Antixidants 24

1.3.1.2.1. The use of high molecular weight antioxidants 26

Page

1.3.1.2.2. Copolymerization of Antioxidants 27

1.3.1.2.3. Binding of antioxidants during compounding or vulcanization 28

1.3.1.2.4. Binding of antioxidants into the base polymer before compounding 30

1.3.1.2.5. Chemical binding of antioxidants to a modified rubber 31

1.4. Objectives of the present work 32

CHAPTER 2 -

2.1. Introduction 36

2.2. Addition of mercaptans to simple olefins 36

2.3. Experimental 40

2.3.1. Photochemical addition of benzyl mercaptan to 2-methyl-but-2-ene 40

2.3.2. Addition of benzyl mercaptan to 2-methyl-pent-2-2ne 45

2.3.3. Addition of 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan to Oct-1-ene 49

2.3.4. Addition of 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan to 2-methyl-but-2-ene 55

CHAPTER 3 -

3.1. Introduction 61

3.2. The addition of Thiols to Polymers 61

Page

3.3. The Reaction of a Hindered Phenol containing a Mercaptan function with Natural Rubber 64

3.4. Experimental 66

3.4.1. Grafting in Solution 66

3.4.1.1. The effect of reaction time on addition 67

3.4.1.2. The effect of temperature on the addition reaction 69

3.4.1.3. The effect of thiol concentration on addition 72

3.4.1.4. The effect of Initiator concentration 74

3.4.1.5. Addition by photochemical initiation 76

3.4.2. Grafting to latex 74

3.4.2.1. The effect of mercaptan concentration 79

3.4.2.2. The effect of Initiator concentration 80

3.4.2.3. The effect of oxygen on the addition reaction 82

3.4.2.4. Addition reaction in steam 83

3.4.3. Attempted addition to a saturated polymer 85

3.4.4. Copolymerisation Reactions 86

3.4.4.1. Polymerisation of styrene in the presence of 3,5-Ditertiarybutyl-4-benzyl mercaptan 88

3.4.4.2. Inhibition effect 89

Page

3.4.5. Reaction Products 90

3.4.5.1. Products of grafting reaction 91

3.4.5.2. Reaction between Azobisisobutyronitrile and Natural Rubber 93

3.4.5.3. Reaction between Azobisisobutyronitrile and 3,5-Ditert-butyl-hydroxy benzyl mercaptan 94

CHAPTER 4

4.1. Assessment of Ageing Characteristics 96

4.1.1. Stress Relaxation 96

4.1.2. Oxygen absorption 99

4.2. Assessment of Vulcanization Characteristics 101

4.3. Investigations in the presence of 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan 105

4.3.1.1. Curing behaviour 107

4.3.1.2. Ageing behaviour 107

4.3.2. Addition of the antioxidant as a compounding ingredient 108

4.3.2.1. Curing behaviour 109

4.3.2.2. Ageing behaviour 111

4.3.2.2.1. Stress Relaxation 111

4.3.2.2.2. Oxygen absorption 113

Page

4.3.3. Intial thermal treatment of rubber in the presence of mercaptan 115

4.3.4. Conversion Products 116

4.3.5. Comparison of masterbatch technique and straight addition 121

4.3.6. Oxidation of polypropylene 125

4.3.7. Autosynergism and oxidation of tetralin 127

CHAPTER 5 Conclusions and Suggestions for further work

5.1. Conclusions 131

5.2. Suggestions for further work 133

REFERENCES

CHAPTER 1

INTRODUCTION

1.1. Autoxidation

The degradation of polymeric materials under processing conditions and during subsequent service results in a loss of desired properties and presents a serious problem to the polymer industry. An apparent variety of causes are responsible for this deterioration; viz. oxygen, heat, light, ozone, fatigue etc., of which oxygen is the underlying factor and the severity of the attack is accelerated by the presence of one or more of the others. Because of the vast economic importance of oxidative degradation much effort has been expended in solving the problem.

The oxygen attack under consideration is often autocatalytic in nature, and therefore a very small amount of oxygen can cause severe degradation. This type of autoxidation is found to be a chain reaction of a free radical nature and therefore, it is susceptible to very efficient prevention or control. Antioxidants are the substances used in inhibiting autoxidation, which are usually either aromatic amines or phenols. Although used in very small proportions the world consumption of antioxidants is very substantial which is an indication of their ever increasing importance (1). Antioxidants function either by destroying the hydroperoxides which are the free-radical precursors or by destroying the free-radicals themselves.

Antioxidants are usually added to polymers by a process of physical blending and they function effectively as long as they remain within the polymer matrix. But unfortunately these antioxidants are lost from the polymer during service, by leaching and volatilization and therefore the development of non-extractable antioxidant systems has become an important task in the field of polymer stabilization. This work represents one of the many attempts that have been made to increase the longevity of antioxidants by combining them chemically with the polymeric network itself. Natural rubber is the polymer under consideration and only its thermo-oxidative degradation will be dealt with in this study.

1.1.1. Oxidation of Rubber

The modes of oxidation of raw rubber and vulcanized rubbers differ considerably from one another and therefore it is necessary to consider the two systems separately. Raw rubber or rubber cured with peroxides or high energy radiation (without the use of sulphur) oxidise autocatalytically while sulphur vulcanized rubbers are always autoretarding (2). The mechanism of oxidation of raw rubber itself is very complex, and the introduction of sulphur links and many other main chain modifications by vulcanization, increases this complexity.

1.1.1.1. Oxidation of unvulcanised Rubber

The main result of the reaction between raw rubber and oxygen is a sharp decrease in the molecular weight of the polymer, which is accelerated by an increase in temperature. This decrease in molecular weight is accompanied by the formation of low molecular weight compounds, such as water, carbon dioxide, formic acid, acetic acid, levulinaldehyde etc.

Levulinaldehyde is considered as a primary product which can be further oxidized to carbon dioxide and acetic acid. Several attempts have been made to suggest a reaction scheme for the oxidation of rubber, and each suggestion includes a carbon -carbon bond cleavage in a peroxide intermediate. The initial attack on the rubber chain is by a free radical, presumed to be a peroxy radical, which can easily be formed as a result of technological processing conditions (3).

The usual methods of product isolation and analysis are unsuitable for rubber due to its high molecular nature. Therefore low molecular weight model compounds have been used extensively, and squalene is the most important among them as it closely resembles rubber chemically (4), (5). By this method Tobolsky and co-workers (6) predicted the formation of acetonyl acetone and Bevilacqua (7), (8) indicated the formation of levulinaldehyde during rubber oxidation. Although several other mechanisms also have been suggested by many workers (9) - (16), none of them is completely satisfactory as no single mechanism explains the formation of each and every product identified.

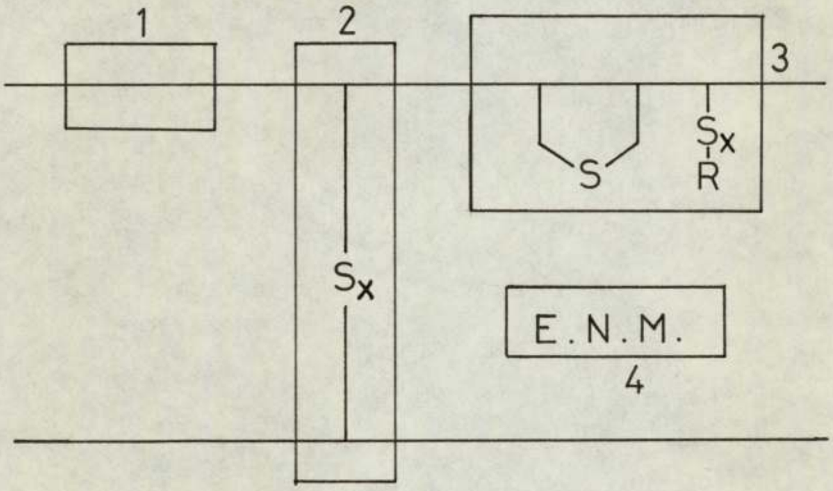
Most of the world's rubber production ends up in the vulcanized state and therefore it is more important to study the oxidation of vulcanized rubbers in detail than that of raw rubber. Furthermore, as the final aim of this project is to bind an antioxidant molecule into the rubber chain, through a sulphur bridge which closely resembles the sulphur links in a sulphur vulcanised rubber, it is essential to consider the oxidation of vulcanized rubbers and sulphides in depth.

1.1.1.2. Oxidation of vulcanized Rubber

A typical sulphur vulcanizate mainly consists of:

1. Unmodified raw rubber
2. Sulphidic crosslinks
3. Chain modifications, for e.g. cyclic sulphides, pendent sulphur containing groups etc. and
4. Extra network material.

A schematic representation of it is as follows:



Each of the above four constituents can have an effect upon the autoxidation process.

The most appropriate way to consider the oxidation of vulcanizates is to study a sequence of:

1. Autoxidation of olefins
2. Autoxidation of organic sulphides
3. Co-oxidation of olefins and organic sulphides and
4. Oxidation of vulcanizates.

Informative studies of the oxidation process include:-

1) The use of model compounds related to the rubber hydrocarbon
2) The analysis of low-molecular weight products
3) Network analysis
4) Oxygen absorption studies
5) Stress relaxation studies etc.

1.1.1.2.1. Autoxidation of olefins

The most significant contribution to understanding the mechanism of oxidation of olefins was made by Criegee and co-workers (17). They have shown that the primary product of the reaction between an olefin and oxygen is the formation of a hydroperoxide at the α-methylenic position, and not oxidation at the olefinic double bond to yield a cyclic peroxide. Later it was found that the reaction proceeds by a free-radical chain process (18). The autoxidation of olefins has been reviewed in detail by many workers (19) - (23), and the general mechanism can be given by the following scheme:-

a) Initiation - Production of free radicals due to heat, radiation or mechano-chemical reactions,

$$RH \longrightarrow R.$$

b) Propagation,

$$R. + O_2 \longrightarrow RO_2.$$

$$RO_2. + RH \longrightarrow ROOH + R.$$

c) Termination,

$$\left.\begin{array}{l} 2R. \\ RO_2.+R. \\ 2RO_2. \end{array}\right) \longrightarrow \text{Inactive products}$$

The decomposition of peroxide ROOH can take place in one or more of the following ways:-

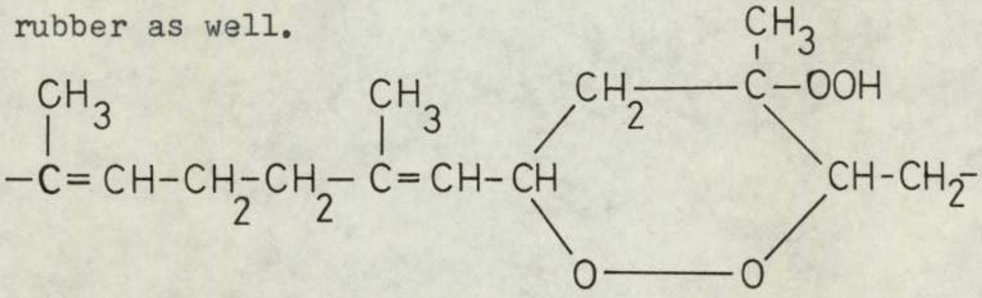
$ROOH \longrightarrow RO. + .OH$

$2\ ROOH \longrightarrow RO. + RO_2. + H_2O$

$RO. + RO_2. + ROOH \rightarrow$ Various products

$ROOH \longrightarrow$ Non radical products.

With squalene the primary product contains two molecules of oxygen for each hydroperoxide group formed, after an intramolecular cyclisation of the alkyl peroxy radical as shown below (4), (5). A similar type of reaction is believed to occur in rubber as well.



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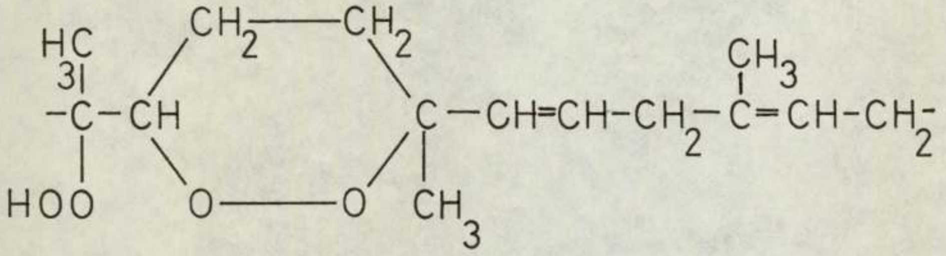


1.1.1.2.2. Oxidation of organic sulphides

Although the autoxidation of sulphides is decidedly more complex than that of olefins, certain features have been recognized by product analysis. Workers at N.R.P.R.A. (24) - (27) have studied this subject in detail and the most important features which emerge from their work are:

1. In the absence of a catalyst, saturated sulphides are inert towards oxygen.

2. Allylically unsaturated sulphides react rapidly initially with the formation of a α-methylenic hydroperoxide, and the reaction is insensitive to peroxide catalysis.
3. Carbon-sulphur bond scission occurs to a considerable extent,

and

4. The reaction is auto-inhibitive, in comparison to the auto-catalytic olefin oxidation.

1.1.1.2.3. Co-oxidation of sulphides and olefins

An excellent model system to study the oxidation of a sulphur vulcanizate is a mixture of squalene and sulphides. When squalene was co-oxidized with sulphides at comparable concentrations to those of vulcanized rubber, the following features were observed, (28), (29), (30):

(i) The autoxidation of the hydrocarbon is strongly retarded by dialkyl sulphides and alkyl alkenyl monosulphides. The retarding effect is more prominent after an initial absorption of oxygen.

(ii) The effects of dialkenyl monosulphides and disulphides are negligible.

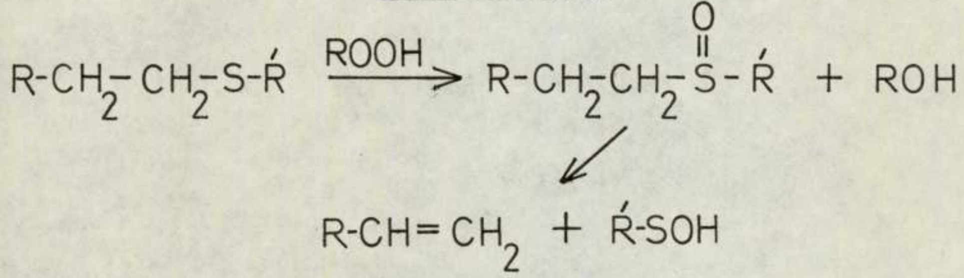
(iii) The addition of alkyl disulphides and dialkyl and dialkenyl polysulphides have moderate effects which increase with the length of the sulphur chain.

(iv) The effects of monosulphides, dialkyl disulphides and their oxidation products are the same as in a peroxide vulcanizate although less pronounced than in squalene.

An unaccelerated sulphur vulcanizate oxidises in the same way as squalene containing dialkyl sulphides and alkyl alkenyl monosulphides. After an initial period the rate of oxygen absorption falls, and this effect has been attributed to the inhibitive action of sulphoxides ($R.SO.R^1$) derived from sulphides, and thiosulphinates ($R.SO.S.R^1$) formed from sulphoxides (31). However, the above work done by N.R.P.R.A. does not explain the reason for the initial pro-oxidant behaviour of rubber networks. These studies were carried using uninitiated systems.

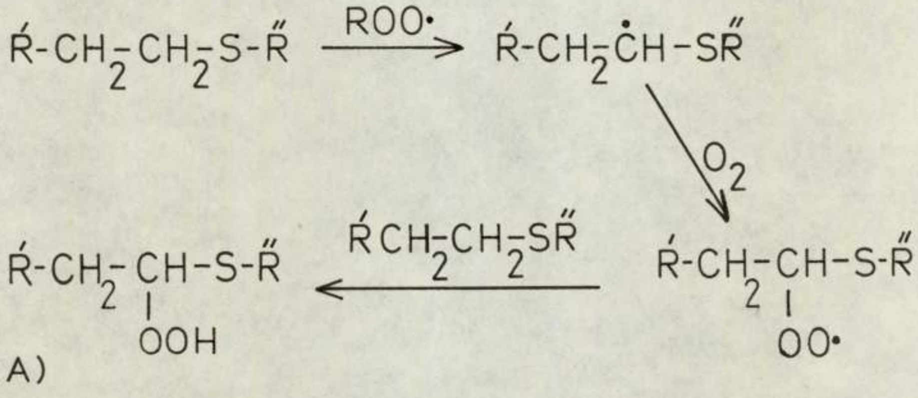
Scott and Armstrong (32) have shown that in the presence of hydroperoxides the initial pro-oxidant effect is due to the behaviour of sulphides and sulphoxides under these conditions. This is relevant to practice since hydroperoxides are always present in technologically processed rubbers (3). When cumene was oxidized in the presence of dimethylsulphenyldipropionate, initiated by cumene hydroperoxide the initial product formed was the sulphoxide which underwent further breakdown into the sulphenic acid.

Reaction (A)



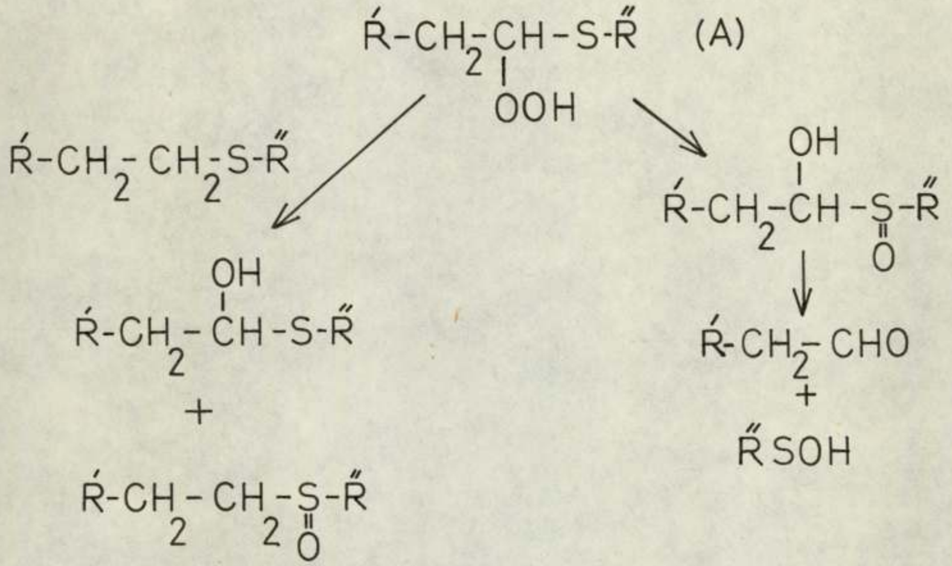
$$R\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R' \xrightarrow{ROOH} R\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{S}}\text{-}R' + ROH \longrightarrow R\text{-}CH{=}CH_2 + R'\text{-}SOH$$

When the substrate is a sulphide, an α-hydroperoxide (A) is formed which undergoes further oxidation by itself or with another molecule of the sulphide.

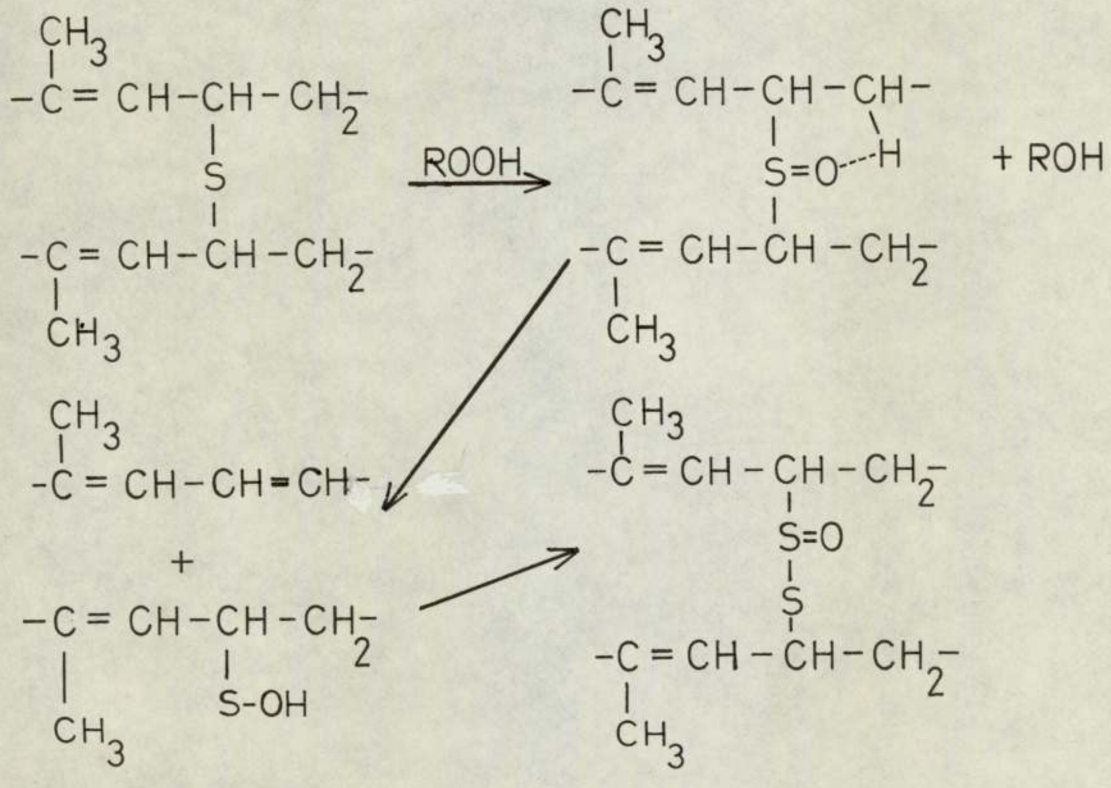


$$R'\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R'' \xrightarrow{ROO\cdot} R'\text{-}CH_2\text{-}\dot{C}H\text{-}SR'' \xrightarrow{O_2} R'\text{-}CH_2\text{-}\underset{OO\cdot}{\underset{|}{C}H}\text{-}S\text{-}R'' \xrightarrow{R'CH_2\text{-}CH_2\text{-}SR''} R'\text{-}CH_2\text{-}\underset{OOH}{\underset{|}{C}H}\text{-}S\text{-}R''$$

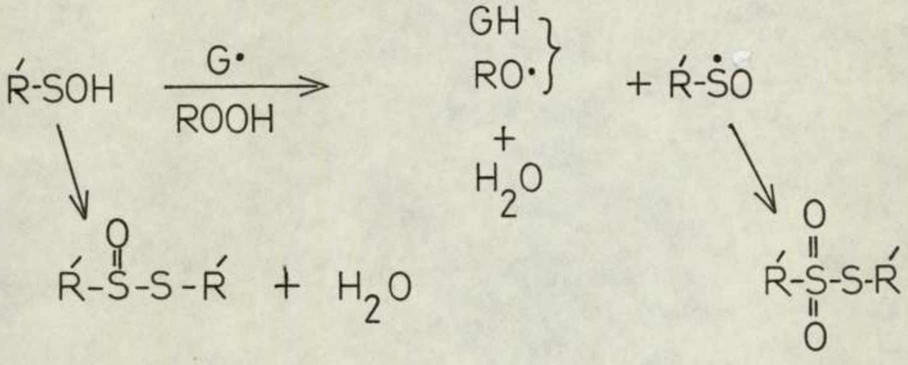
(A)

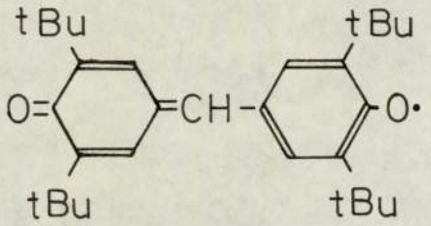


In both cases the product is an unstable alcohol which leads to a carbon-sulphur bond scission. A similar process is responsible for carbon-sulphur bond scissions in the oxidation of vulcanizates, and there are thus two ways in which crosslink scission can occur. But Cunneen has suggested (33) that in the absence of oxygen, two molecules of sulphenic acid can react together resulting in some sort of a partial repair of a broken crosslink.



Kinetic investigations of Armstrong and Scott (34) have shown that dimethylsulphenyldipropionate undergoes decomposition by a first order reaction only in the presence of oxidizing agents; which indicates the reversibility of reaction (A), shown above. The oxidizing agents used, viz; Galvinoxyl and cumene hydroperoxide removed the sulphenic acid irreversibly as follows:-





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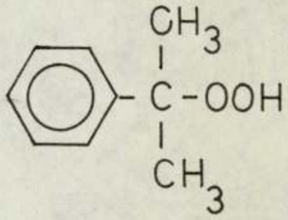
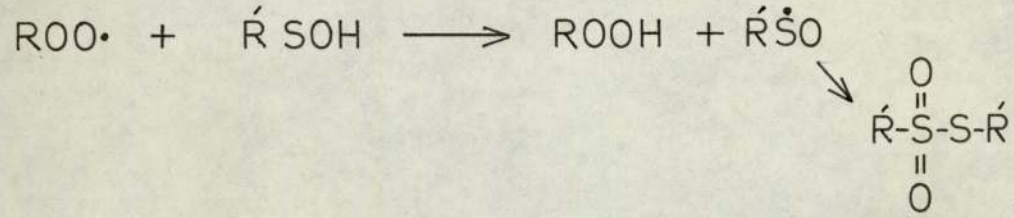


ROOH

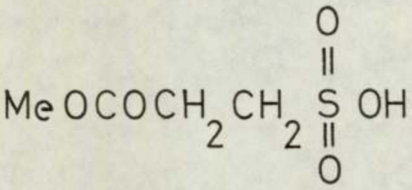
The redox reaction of hydroperoxide with sulphenic acid provides a satisfactory explanation for the pro-oxidant effect which is observed at hydroperoxide/sulphide molar ratios less than one. The overall antioxidant effect is optimal at this ratio and when the sulphoxide is added to autoxidizing cumene, oxidation ceases immediately. This has been proved not to be due to the destruction of hydroperoxide, by using azo-bis-isobutyronitrile as the initiator which generates alkyl radicals. Therefore it has been expected that the sulphenic acid acts as an effective kinetic chain breaking antioxidant.



$$ROO\cdot + R'SOH \longrightarrow ROOH + R'\dot{S}O \searrow R'-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-R'$$

The stable sulphenyl radical does not continue the kinetic chain reaction and is removed by dimerization. Therefore Scott and co-workers attribute the partial repair of crosslinks observed by Cunneen and co-workers, to the formation of thiosulphonate crosslinks. The inhibiting activity of sulphenic acids was also shown in polymerization reactions. 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 which is quite distinct from the powerful inhibition observed later. The formation of a powerful Lewis acid derived from the sulphenic acid is responsible for this.

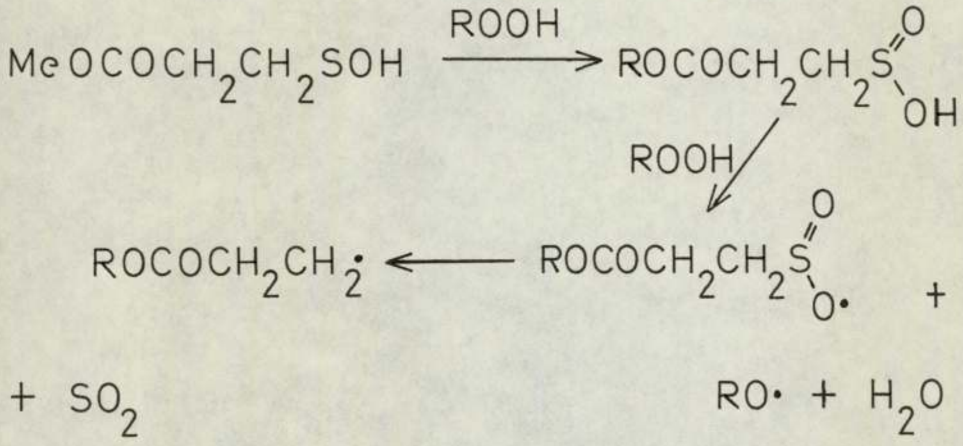
In the reaction between dimethylsulphenyldipropionate and hydroperoxides the strong acid methyl-β-sulphopropionate (B) is also formed,



$$MeOCOCH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OH$$

(B)

which is a very powerful antioxidant in cumene. But the rate of decomposition of cumene hydroperoxide in its presence does not account for the antioxidant behaviour of the sulphoxide. Therefore it seems likely that the Lewis acid is sulphur dioxide (or sulphur trioxide) which is known to be a powerful catalyst for hydroperoxide decomposition and a very powerful antioxidant. Sulphur dioxide can be most likely formed from the sulphenic acid as follows:-



Sulphur dioxide is much more reactive than dimethylsulphenyldipropionate as a catalyst for cumene hydroperoxide decomposition and kinetic studies have also indicated that sulphur dioxide is the active species.

Monosulphidic crosslinks are a source of instability in a vulcanizate although it is eventually converted to an antioxidant. The latter occurs only at unrealistically high ratios of hydroperoxide to sulphide, but the formation of such an antioxidant involves the breakdown of crosslinks. Thiodipropionates are very poor antioxidants in sulphur vulcanizates because the ratio of sulphide to hydroperoxide is already above the critical level required for good peroxide decomposing activity even in the absence of added antioxidant (35). According to recent work done by Scott and co-workers(36) there are three chemical reactions involved in the antioxidant behaviour of thiodipropionate esters:

1. A radical trapping process which involves the sulphenic acid formed by the breakdown of the sulphenyldiproprionate ester which is an oxidation product of the thiodipropionate.
2. A radical generating process which occurs as a result of a redox reaction between hydroperoxides and the sulphenic acid.
3. A Lewis acid catalyzed destruction of hydroperoxide by a further oxidation product of the sulphenic acid.

Only some of the requirements of the process are satisfied by sulphur dioxide and therefore it is possible that other products are also involved. The deactivation of hydroperoxide by complexing with sulphoxide does not appear to be involved.

1.1.1.2.4. Oxidation of vulcanizates

(a) Peroxide vulcanizates: Only carbon-carbon crosslinks are present in peroxide cured rubbers (e.g. rubber vulcanized with dicumyl peroxide) and their ageing behaviour is autocatalytic. This is demonstrated by oxygen absorption studies on such vulcanisates and model olefins and by the stress-relaxation behaviour of vulcanisates in air at elevated temperatures.(37).

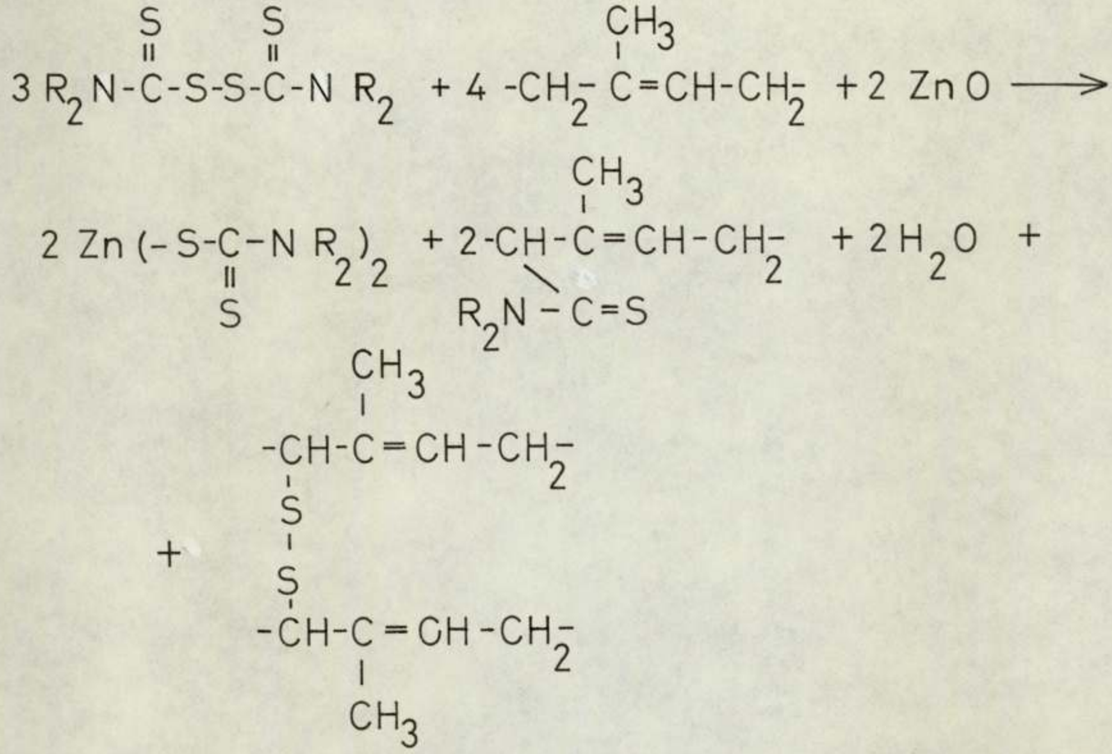
(b) Unaccelerated sulphur vulcanizates: These vulcanizates are shown to contain alkyl alkenyl mono, -di-, and polysulphides and a considerable amount of cyclic and pendent sulphides. The presence of a weak antioxidant in this system is apparent from stress-relaxation studies, and a similar observation is made when an alkyl alkenyl monosulphide is added to a peroxide vulcanizate. This similarity shows the ability of sulphides of the type present in the vulcanizate to function as "built in" antioxidants (38).

(c) Accelerated sulphur vulcanizates: These vulcanizates contain entirely dialkenyl sulphidic crosslinks, out of which a considerable proportion is polysulphidic. The oxidative ageing is rapid, and there is significant vacuum ageing. Because of the latter, the response to phenolic inhibitors is comparatively poor. As in the case of unaccelerated systems, the polysulphidic crosslinks are labile, whick break and reform at different points (38).

(d) T.M.T. sulphurless vulcanizates: Dialkenyl mono and disulphidic crosslinks are found in these vulcanizates and their autoxidation pattern is autocatalytic. As there are no polysulphidic links, thermal degradation in vacuum is insignificant and the response to phenolic inhibitors is good.

The excellent ageing behaviour of these vulcanizates is known to be due to the formation in situ of a dithiocarbamate which is removed by extraction (39).

Beilstein and Scheele (40) have put forward a reaction scheme for the formation of the dithiocarbamates.



As it is known that the accelerated vulcanizates too in general contain essentially the same type of unsaturation pattern at the crosslinks, it can be said that the extra network material is responsible for a large part of the differences in ageing behaviour of different vulcanizates.

1.2. Inhibition of Autoxidation

1.2.1. Antioxidants

The only instance where autoxidation is considered advantageous is in the mastication of rubber during which mechano-chemical degradation renders the polymer processable so that additives can be incorporated into it.

Antioxidants are usually added in small proportions, to control or inhibit autoxidation where it is harmful. A lot of interest has been shown in the development of suitable antioxidants for various applications and mechanisms of their action have been dealt with in detail by several authors (41) - (50).

1.2.1.1. Mechanisms of antioxidant action

There are two distinct ways by which antioxidants function. The first is called the radical chain breaking mechanism according to which, the alkyl and the alkylperoxy radicals, which are the most important species in the propagation step, are removed from the system. The second is the preventive mechanism by which the introduction of chain initiating radicals into the system is prevented. In certain cases, two different antioxidants each of which functions by one of the above two ways show a synergistic effect when used together., i.e. the total effect is larger than the two individual effects on the basis of additivity.

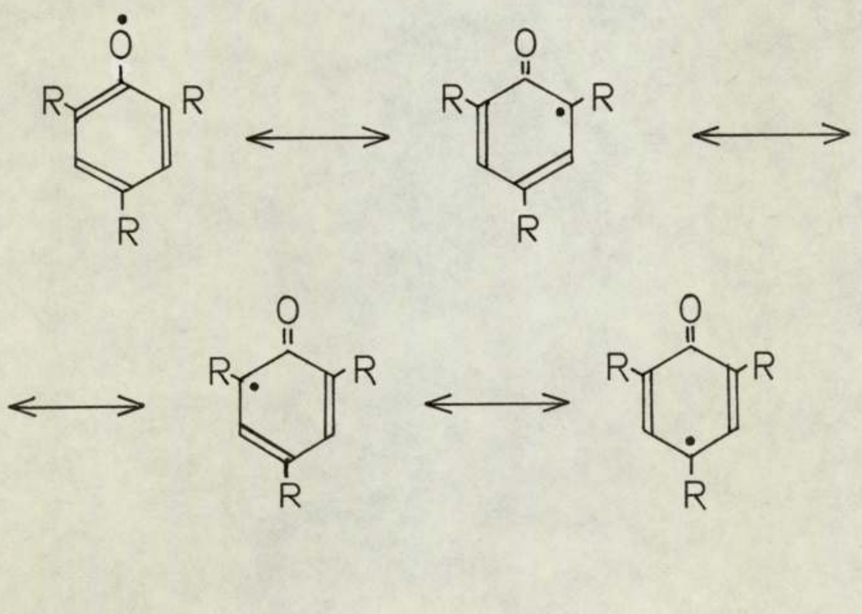
1.2.1.1.1. Radical Chain Breaking Mechanism

Aromatic amines and hindered phenols are the most important substances which act as antioxidants by this mechanism. The antioxidant competes with the hydrocarbon for the chain propagating radicals, and ends up as a stable radical which is not capable of propagating the chain reaction any further.

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

In the above equation, AH is the antioxidant from which a hydrogen atom is abstracted by the peroxy radical, and A. is the resulting stable radical.

The efficiency of monohydric phenols as antioxidants varies widely with the type and position of substituents in the benzene ring. Thus phenol itself which is almost inactive as an antioxidant is converted into very potent ones by the substitution of alkyl groups in the 2, 4 and 6 positions. The effect of increasing the number of substituents is more than that predicted on the basis of additivity (51), for e.g. the stabilization by 2, 4 dimethyl phenol is greater than the summation of that by ortho cresol and para cresol; the addition of a third methyl group to 2, 4 dimethyl phenol increases its activity to a greater extent than that observed with a mixture of xylenol and cresol. Bulky groups in the ortho positions to the hydroxyl, cause steric hindrance thus interfering with the normal functions of a phenolic hydroxyl group. This is also an important feature in phenolic antioxidants. In the case of hindered phenols, the stable A. radical referred to above is a phenoxy radical which is stabilized by the delocalization of the unpaired electron, by resonance. This can be represented by a series of structures as follows:-



The contribution of the quinoid form to the radical structure has been confirmed by various spectroscopic methods and quantum-mechanical calculations (52), (53).

In essence, to function as an antioxidant, the hindered phenol should be able to lose the phenolic hydrogen atom to a peroxy radical and the phenoxy radical thus formed should not be capable of propagating the chain reaction of autoxidation. Another important feature is that the phenol should not be directly attacked by oxygen.

$$AH + O_2 \longrightarrow A\cdot + HO_2$$

The disadvantage in the above reaction is that, not only a propagating radical is not removed, but also an additional radical is introduced into the system.

In general, amine antioxidant action is similar to that of hindered phenols. For an amine to function as a good antioxidant, (i) the unpaired electron on the nitrogen atom should be delocalized, (ii) the nitrogen atom should be sterically hindered and (iii) the amine should be able to react with the propagating peroxy radical. The presence of a hydrogen atom which was earlier thought to be necessary is now proved to be not a vital requirement (54), (55).

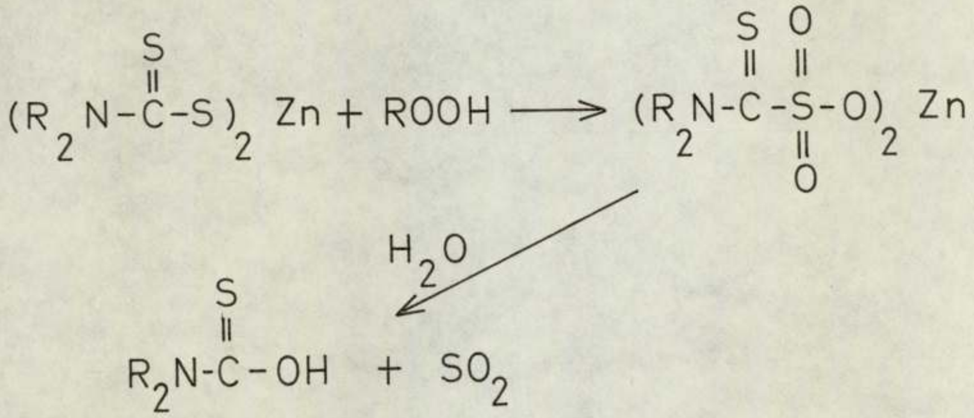
In a mechanism proposed to explain the reactivity of amines as antioxidants (56), it has been proposed that there is an initial complex formation with a first peroxy radical, followed by the reaction with another peroxy radical.

The second interaction takes place only with diamines. In contrast to phenols, substitution on the nitrogen atom, rather than in the ortho position increases the activity of amines.

1.2.1.1.2. <u>Preventive Mechanism</u>

Compounds such as zinc dialkyldithiocarbamates, zinc dialkyldithiophosphates and dialkylthiopropionates act as preventive antioxidants by reacting with the hydroperoxides to form stable non radical products. A predominantly non-radical mechanism has been proposed for their action, (57) - (61). Other than being chain initiation suppressors, dithiocarbamates and dithiophosphates act as chain breaking antioxidants as well, by an electron transfer mechanism (62) - (64).

Scott (58), (59) has established that there is an initial pro-oxidant stage during oxidation in the presence of dialkyl-dithiocarbamates and esters of thiodipropionic acid, which depends on the molar ratio of hydroperoxide to sulphur compound. In the case of dithiocarbamates the pro-oxidant stage is followed by the evolution of a gas which was identified as sulphur dioxide.



$$(R_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S)_2\,Zn + ROOH \longrightarrow (R_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}\text{-}O)_2\,Zn$$

$$\xrightarrow{H_2O} R_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}OH + SO_2$$

Sulphur dioxide is capable of functioning as a powerful peroxide decomposing antioxidant, (57), (60), (65). Certain sulphur compounds stoichiometrically decompose hydroperoxides and convert them to the corresponding alcohols (66), (67).

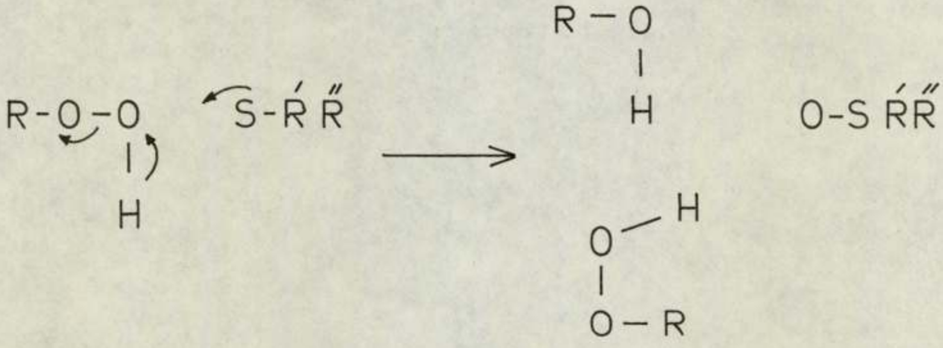
$$\mathrm{ROOH} + \mathrm{R'SR''} \longrightarrow \mathrm{RooH} + \mathrm{R'S(O)R''}$$

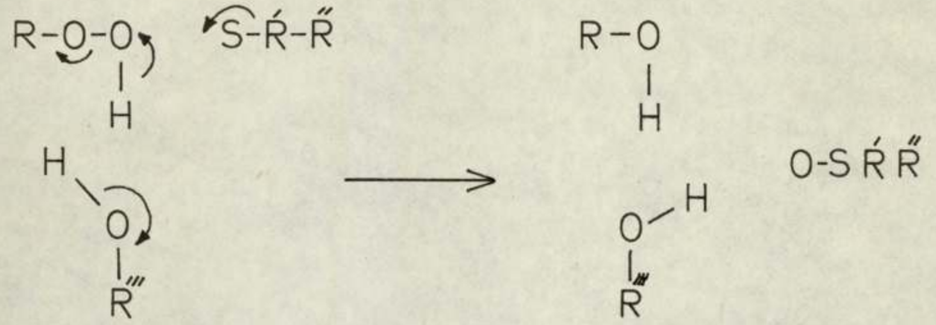
$$\mathrm{ROOH} + \mathrm{R'S(O)R''} \longrightarrow \mathrm{ROH} + \mathrm{R'S(O)_2R''}$$

Monosulphides containing at least one aliphatic or cycloaliphatic group attached to the sulphur atom are more effective antioxidants than mercaptans and disulphides, while diaryl sulphides and sulphones are inactive (67).

While many sulphides are fairly stable towards oxygen, both sulphoxides and sulphones autoxidize rapidly with the formation of sulphonic acids. Sulphonic acids which are almost always produced when sulphides are used as antioxidants are able to decompose further peroxide by a catalytic ionic rearrangement process (68), (69).

The decomposition of peroxides by sulphides is in fact more complex than shown above. In hydrocarbon solvents two molecules of hydroperoxide are involved, while in alcoholic solvents only one (70).





Other than peroxide decomposers, there are stabilizers which function by deactivating metal ions which catalyze the radical decomposition of peroxides (42), (71), (72).

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

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

Reducing agents react according to the former while oxidizing agents according to the latter reaction. With multivalent metals such as cobalt, copper and manganese which have two valency states, both the above reactions occur and therefore the presence of traces of such metals is drastic with respect to autoxidation. The inhibition of metal catalyzed autoxidation is reviewed by Scott (42), and Hawkins (45).

1.3. Inhibition of rubber oxidation

1.3.1. Antioxidants in Rubber

Although various antioxidant systems are used to control the deterioration of rubber due to many environmental and technological processing conditions only those used in the case of thermal oxidative ageing will be dealt with here.

Both hindered phenols and aromatic amines are used commercially in protecting vulcanized rubber. Aromatic amines show an optimum concentration which is fairly low, after which the improvement in stabilization is negligible. This effect has not been seen with hindered phenols (73). It has also been shown that arylamines and especially their condensation products with aldehydes and ketones are more effective heat ageing stabilizers than phenols (74). In the presence of carbon black, which is very extensively used in vulcanised rubbers, amines are more effective than phenols. Phenols with only one ortho position containing a bulky group and the other containing a normal alkyl group give the optimum stability to rubber. In the case of bisphenols the 2-2' derivative is more effective than the 4-4' analogue. When disulphide accelerators are used in low sulphur curing, the rubber possesses a better ageing resistance in a way similar to T.M.T. vulcanizates (75). At present there are a large number of commercially available antioxidants to be used with rubber to suit different end uses. Some are pure compounds while others are mixtures functioning synergistically. Although the further development of individual antioxidants has only limited scope there appears to be little doubt that the phenomenon of synergism has not been fully exploited.

1.3.1.1. Synergism

Probably the most effective synergistic mixtures of antioxidants are those in which one compound functions as a decomposer of peroxides and the other as an inhibitor of free radicals (49). The latter prevents the formation of long reaction chains although some hydroperoxide is nevertheless formed by the reaction.

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

If this hydroperoxide then reacts with a decomposer of peroxides, rather than by decomposing into free radicals, the two antioxidants act together to complement each other. The synergistic effects generally observed between the natural sulphur compounds and the polynuclear aromatics present in lubricating oils (76) have been attributed to the oxidation of the sulphur compounds to sulphonic acids followed by the acid catalyzed rearrangement of the aromatic hydroperoxides to phenolic inhibitors. The high efficiency of many antioxidants containing two or more functional groups (e.g. OH and NH, OH and S, etc.) is also undoubtedly connected with the occurrence of a different inhibiting reaction at each group. The synergistic effect of mercaptobenzimidazole with amines and phenols has been explained by two mechanisms, one chain breaking and the other peroxide decomposing (77), (78). Another explanation suggested for this effect is the metal inhibiting activity of M.B.I. (79). Synergistic mixtures of antioxidants for rubber have been well studied, using amines and phenols in the presence of metallic copper (79). Synergism where both components function by the same mechanism is also known (80).

Another important aspect of synergism is known as autosynergism where the two antioxidant components are associated in the same molecule. Kuzminskii et al. (81) have shown that all diarylamine antioxidants which are powerful copper inhibitors act by metal deactivating mechanism as well as by chain breaking. The activity of a bisphenol containing a sulphur bridge is much higher than that of a similar structure containing a methylene bridge which should be due to the thioether linkage (82). Thiols and sulphides which are inactive alone show powerful antioxidant activity in the presence of carbon black (82).

1.3.1.2. Volatilization and leaching of Antioxidants

The natural antioxidants, which are present in the natural rubber latex when it leaves the trees, are lost during coagulation, in the rubber serum, or they are destroyed during subsequent vulcanization. Antioxidants added during vulcanization are usually physically blended with the rubber, and they readily leach out when in contact with water and industrial solvents. A highly stable P.B.N. containing rubber vulcanizate can be converted into a stock as unstable as one containing no antioxidant by acetone extraction. Although such a drastic situation is rarely encountered under service conditions, there are many occasions where less severe leaching of antioxidant causes damage to the ageing properties of the rubber.

Garments which contain latex thread or foamed rubber, which have to be washed frequently, become useless after sometime due to the degradation of the rubber. There is a suggestion that the reduction of fatigue life and dynamic ozone resistance in tyres is also due to the loss of antioxidant by contact with water (83), (84).

In certain cases the volatility of antioxidants creates a similar problem. In many engineering applications as well as during processing, higher temperatures are experienced and therefore the volatility of antioxidants has to be considered important. Robinson and Dunn (85) have shown that, in styrene-butadiene-styrene block copolymers, 2,6-di-tert.butyl-4-methyl phenol and tris (nonyl phenyl) phosphite volatilized during milling at 160°C. Phenyl-β- naphthylamine, N N^1 -di-naphthyl-p phenylene diamine and N-phenyl - N^1 - isopropyl-p-phenylene diamine completely volatilized at 210°C, while $4,4^1$-methylene-bis (2,6-di-tert butyl phenol), tris (thiobisphenolphosphite), 2, 2^1 - thio - bis (4-methyl-6-tert butyl phenol) and $N{:}N^1$ -di-2-octyl-p-phenylene diamine showed partial volatilization at that temperature.

Spacht and co-authors (86) have investigated the oxygen absorption of pale-crepe vulcanisates containing 2,6-di-tert-butyl-4-methyl phenol and 2-benzyl-4-methyl-6-tert butyl phenol, before and after ageing in a circulating air oven at 100°C. Initially the sample containing the former was more resistant to oxidation than that containing the latter, while after ageing a reversed behaviour was seen. Both samples showed better ageing resistance when aged in a closed system. The observed results were in correlation with the volatilities of the two antioxidants, the former being very volatile compared to the latter.

Therefore the loss of antioxidants due to volatilization and leaching out happens to be a major problem in rubber stabilization. According to Dunn (87) the search for a solution to the problem of fugitive antioxidants represents the main thrust in rubber stabilization today.

The problem of volatilization and leaching out of antioxidants from polymers can be overcome by several methods. The most important of the latter at present are:

1. The use of high molecular weight antioxidants
2. The chemical binding of an antioxidant into the polymer by copolymerisation, during the polymerisation stage.
3. The chemical binding of an antioxidant to the polymer during compounding, or vulcanization.
4. The chemical binding of an antioxidant to the base polymer before compounding.
5. Chemical modification of the base polymer so that an antioxidant can be bound in,via a reactive functional group.

1.3.1.2.1. The use of high molecular weight antioxidants

Although it provides only a limited remedy as they are not unextractable, high molecular weight antioxidants can reduce the damage caused by leaching or volatilization of the antioxidant. This has been demonstrated by many workers with rubber using special recipes for vulcanization, (88), (89). According to Plant and Scott (90), an increase in antioxidant activity, and a decrease in loss due to volatility, are associated with an increase in the molecular weight of esters of 3,5-di-tert.butyl-4-hydroxy phenyl propionic acid, as antioxidants in polypropylene.

Scott (91) has observed that the behaviour of antioxidants in polymers varied markedly according to the test method. The performance of an antioxidant in a polymer was affected by its intrinsic activity, compatibility with the polymer, and its volatility. The ageing behaviour of polypropylene containing polyphenols of different molecular weights showed completely opposite trends when estimated by oxygen absorption and torsion braid test.

There are various examples of high molecular weight antioxidants which have been used wih minimized loss due to volatility, in different applications. Polymerized2, 2,4-trimethyl-1, 2-dihydroquinoline, condensates of hydroquinone and p-phenylene diamine (92), p-cresol and formaldehyde (93), are among them.

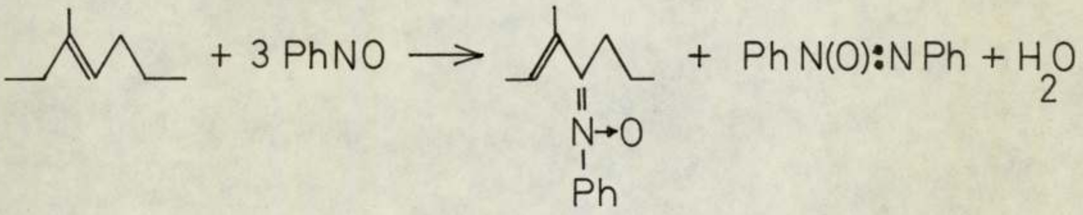
The leaching of antiozonants from the rubber due to rain water is also known and Latos and Sparks (94) have shown that, with the increase of molecular weight the amount of antiozonant extracted, decreased.

1.3.1.2.2. Copolymerization of Antioxidants

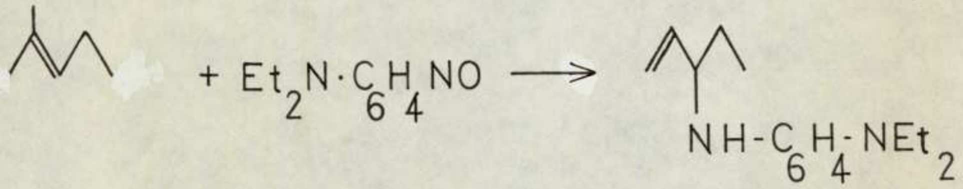
Very little work has been done so far in this field, but the results available are promising. Amine type antioxidants have been copolymerized with styrene-butadiene rubbers, and nitrile butadiene rubbers using emulsion systems (95), (96), and were found to be non-extractable thus causing little discolouration due to ageing.

1.3.1.2.3. Binding of antioxidants during compounding or vulcanization

Workers at NRPRA, who carried out some of the original work in this field have been successful in obtaining a rubber containing a chemically bound antioxidant by the addition of the precursor during curing in the conventional way. The reaction of nitroso benzene with rubber forms the basis for NRPRA work (97), (98).



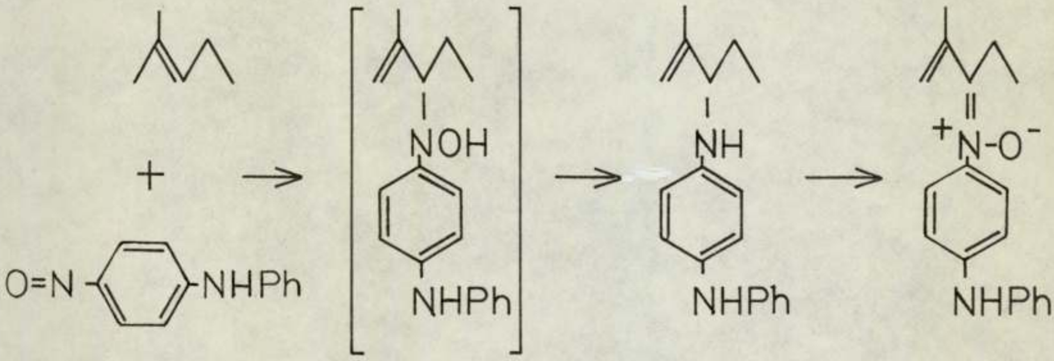
Cain and co-workers replaced the nitroso benzene in the above reaction with N, N-diethyl-p-nitrosoaniline and the product thus obtained was a rubber with an attached aromatic group which functions as the antioxidant, (99). By working with a suitable model compound (2-methyl-pent-2-ene) the above workers have put forward the following reaction path.



The reaction product N, N-diethyl-N-1-ethyl-2-methyl prop-2-enyl-p-phenylene diamine has been isolated as evidence for the reaction.

Cain and co-workers have again shown that (100)

4-nitrosoanilines and 4-nitrosophenols reacted with rubbers containing α-methylenic hydrogen during the vulcanization process:



The nitrosoanilines were more effective than the nitrosophenols in the same way as amines are generally more effective than phenols.

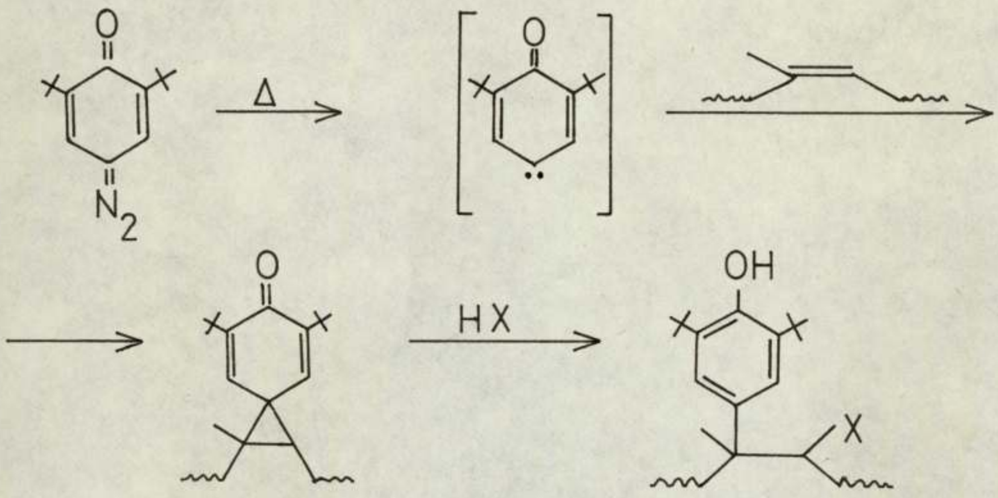
In 1964 Cunneen and Lee (101), found that the efficiency of a sulphur containing antioxidant was considerably reduced by chemical attachment to the vulcanizate network. Barnard et al, (102) have ascribed this effect to the reduced mobility of the antioxidant. But the recent work of Cain and Cunneen, (100), has compared the effects of 4-nitrosodiphenylamine (NDPA) with a conventional amine antioxidant N-isopropyl-N^1 -phenyl-p-phenylene diamine (IPPD) at 1% concentration in natural rubber, and it was found that, although NDPA was not as efficient as IPPD, its behaviour was good enough to dismiss all fear that a bound antioxidant would not be sufficiently mobile to act as an antioxidant. However, NDPA was not a commercial success because it was found to cause staining and to reduce scorch resistance.

Comparing the activities of N-phenyl-N^1 - isopropyl-p-phenylene diamine and polymer bound p-Nitrosodiphenyl amine, Fedorova and Kavun (103) have shown that, not only the low molecular weight inhibitor, but also the one attached to the molecular chain reduce the rate constant of degradation of the molecular chain, and do so practically to the same extent. They also conclude that, the high stabilizing effect of an antioxidant in the ageing of a vulcanizate under static conditions is not noticeably linked with the tendency to migration. In the case of antiozonants and anti-fatigue agents bound stabilizers are ineffective, where the capacity for migration is a criterion.

Yamamoto and co-workers, (104) have also found a route to bound antioxidants by grafting allyphenols to unmodified rubber during vulcanization.

1.3.1.2.4. Binding of antioxidants into the base polymer before compounding

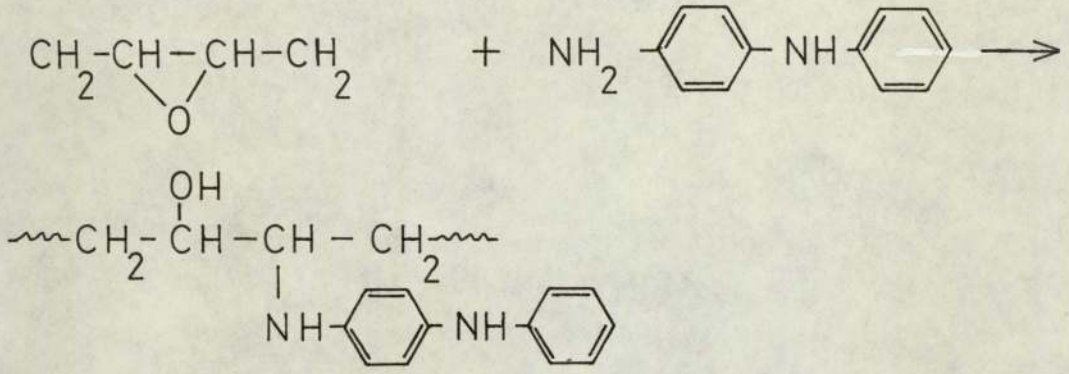
Investigations have been carried out to attach an antioxidant function to rubber with the use of carbene intermediates (105), (106). On heating or irradiation, 3, 5-di-t-butyl benzene-1, 4-diazoxide loses nitrogen forming a carbene, which reacts readily with natural rubber. The primary reaction product is a spirodienone which rearranges itself rapidly forming a hindered phenol bound rubber chain.



In the presence of free radical generators, antioxidants containing polymerizable vinyl groups as well as those containing no vinyl groups have been successfully grafted on to natural rubber latex. The non vinyl containing antioxidants were more effective than the corresponding vinyl antioxidants, and this behaviour was attributed to the fact that only a part of the vinyl antioxidants grafted on to the rubber backbone while the rest was oxidized or remained unchanged, (107).

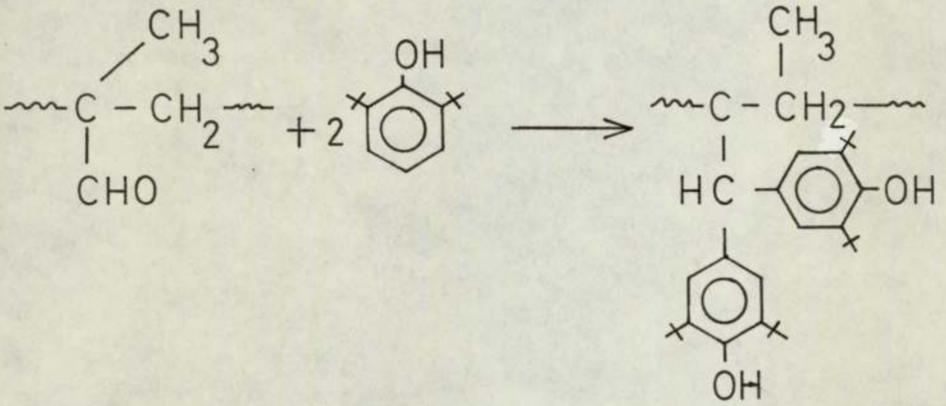
1.3.1.2.5. Chemical binding of antioxidants to a modified rubber

Epoxidized rubbers can be regarded as very promising in this respect, and work has already been done where, p-aminodiphenyl amine was attached to the rubber yielding a pendent N-alkyl-N^1-aryl-p-diphenyl amine which functions as a bound antioxidant, (108), (109).



The use of copolymers containing monomers such as glycidyl methacrylate (110), and copolymers of butadiene and methacrolein (111) has also been investigated.

The reaction of 2,6-ditert-butyl phenol with a copolymer of butadiene and methacrolein yields a bisphenol bound rubber network.



1.4. Objectives of the present work

The problem of oxidative deterioration of rubber and the leaching out of antioxidants which are added to prevent such deterioration have been discussed earlier. In principle therefore, the preparation of natural rubber networks containing bound antioxidants is of great practical importance.

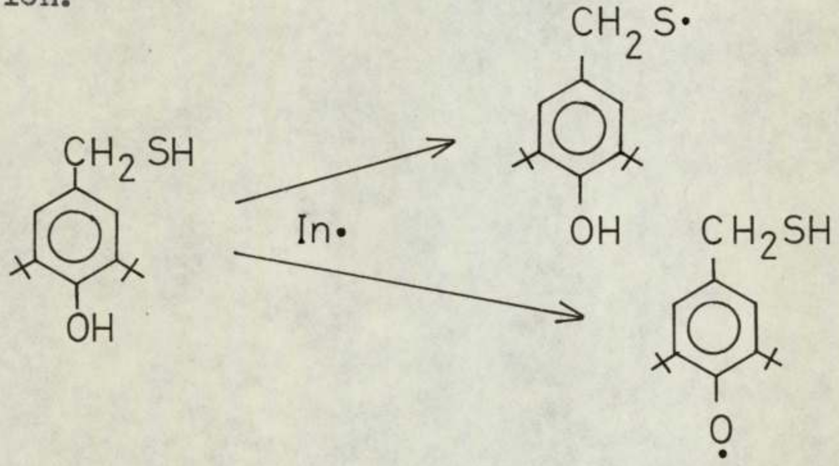
An essential requirement is an antioxidant containing a functional group, which will react chemically with the rubber. 2, 6-ditertiarybutyl phenol was selected as the antioxidant grouping as it is commercially available and possesses good antioxidant efficiency.

The addition of mercaptans to double bonds of conventionally prepared diene rubbers represents a very versatile reaction and the reaction can be carried out in latex form as well. The use of thioglycollic acid and like compounds (112) - (118) to confer specific polar groups to rubber, by the method of mercaptan-olefin double bond addition reactions has been reported. Simple alkyl mercaptans have been added to rubbers by Pierson and co-workers (119), and they report that at high extents of saturation, the products are very interesting from a commercial stand point. Good ageing resistance, low gas permeability, balance between low temperature properties and solvent resistance, heat resistance, and ozone resistance make these "mercaptan adduct rubbers" excellent candidates as competitors for the various speciality rubbers now available.

Thiols are known to add to double bonds by a free radical mechanism and thiols containing the hindered phenol structure seemed to offer one possible starting point for a bound antioxidant structure.

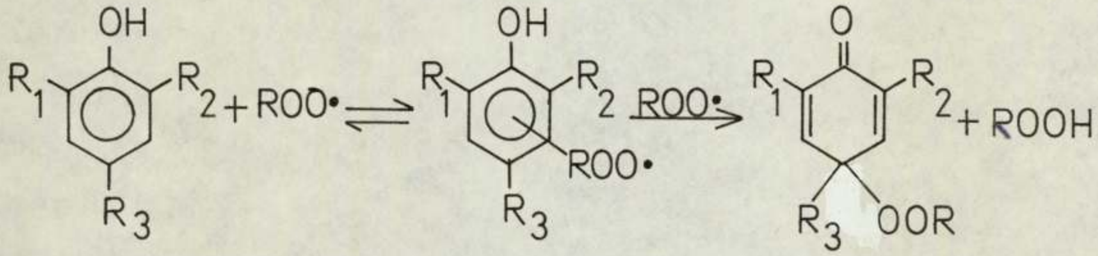
A further advantage of thiol addition over other possible means of forming a polymer antioxidant bond is that a large proportion of the double bonds present in the rubber can be saturated. This leads to the prospect of producing antioxidant latex concentrates which might be used as additives for conventional latices.

Although mercaptans are known to undergo addition to double bonds the presence of a benzene ring with bulky substituents, in the example chosen (3, 5-ditertiary butyl-4-hydroxy benzyl mercaptan) might interfere with the addition reaction. The phenolic hydroxyl group is also capable of transformation into a phenoxy radical by hydrogen abstraction, and there might be a possibility of addition at the phenolic end of the molecule competing with a thiol addition.



The abstraction of a hydrogen from the phenolic -OH group could be by an initiator radical or even by a polymer radical. The strength of SH bond in an aliphatic thiol is 88 KCal/mole while the strength of OH bond in a phenol with 2 ortho tertiarybutyl groups is 78 KCal/mole (120), (121). Therefore a bond energy consideration indicated that there is a possibility of the mercaptan being consumed at the phenolic end, which is undesirable according to the aim of this work. However, it is likely that the bulky substituents at the phenolic end of the molecule of 3, 5 ditert-butyl-4-hydroxy benzyl mercaptan will interfere with addition to the rubber network at the phenolic hydroxyl group.

The presence of oxygen can play an important role in the reaction of natural rubber with the above mercaptan. The alkyl radical formed on the rubber chain by the attack of a thiyl radical can be converted into an alkyl peroxy radical by oxygen. Although alkyl radicals do not react readily with the hydroxyl group in phenols, alkyl peroxy radicals do react (122), (123).



Therefore the presence of oxygen can cause the consumption of the mercaptan in ways besides the thiyl addition and should probably be avoided.

The aim of the present study therefore was to use the thiol group to attach antioxidants to rubber. The extent of this reaction and its mechanism were studied both in rubber and in model compounds and evidence for autosynergism between the phenolic part of the molecule and the sulphur atom was considered to be a potential advantage of this system.

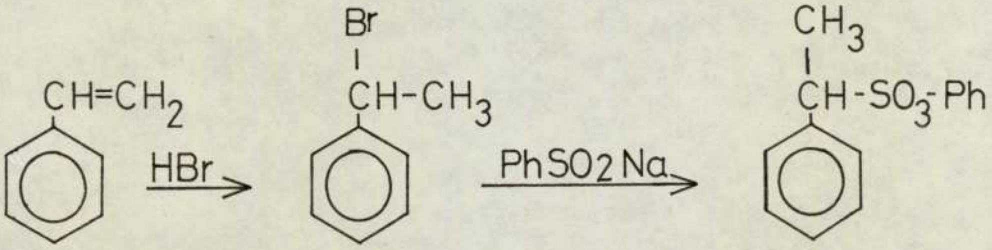
CHAPTER 2

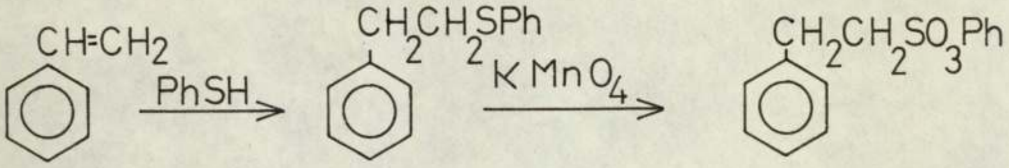
2.1. Introduction

In accordance with the widely accepted method of understanding chemical reactions of rubber, the use of model compounds is dealt with in this Chapter. A study of the addition of the antioxidant-containing thiol to simple olefins was studied in order to provide the necessary information on the mechanism of addition of the antioxidant-containing thiol to natural rubber. Oct-1-ene, 2-methyl but-2-ene and 2-methyl pent-2-ene which are model compounds for rubber were reacted with benzyl mercaptan and 3,5, di-tert-butyl -4- hydroxy benzyl mercaptan. Benzyl mercaptan represents the antioxidant containing mercaptan from which the sterially hindered phenolic hydroxyl group is removed.

2.2. Addition of mercaptans to simple olefins

One of the earliest addition reactions of mercaptans to double bonds was carried out by Posner (124), who investigated the addition of phenyl mercaptan to styrene, and observed a striking exception to the Markovnikoff rule. By oxidizing the addition product to the corresponding sulphone, it was proved that the reaction of phenyl mercaptan with styrene was in an opposite manner to that of hydrogen bromide with styrene.

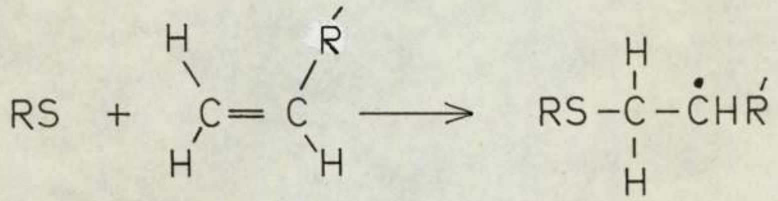




A possible mechanism to explain reactions of this type was proposed by Kharash and co-workers (125). They suggested that the reaction proceeds through a chain mechanism and also showed that oxygen and peroxides catalyse this reaction.

Burkhardt (126) also supported the idea of a chain mechanism and suggested that a PhS• radical in the system was the active species. According to the generally accepted reaction scheme, addition reactions of mercaptans to unsaturated compounds are initiated by the formation of thiyl radicals which add to an unsymmetrically substituted double bond, with the formation of the more stable of the two possible intermediate radicals. The reaction proceeds further through the abstraction of a hydrogen atom from the mercaptan, by the above intermediate, with the formation of a new thiyl radical.

$$RSH \longrightarrow RS\cdot$$



$$RS + H_2C{=}CHR' \longrightarrow RS{-}CH_2{-}\dot{C}HR'$$

$$RS\text{-}CH_2\text{-}\dot{C}HR' + RSH \longrightarrow RS\text{-}CH_2\text{-}CH_2\text{-}R' + RS\cdot$$

Kharash and his co-workers (127) have mentioned that anti-Markovnikoff olefin-mercaptan addition reactions involve three steps, and the formation of the free mercaptyl radical occurs via the attack of an oxidant (Ox) upon the mercaptan. This mechanism can be represented as follows:

$$RSH + Ox \longrightarrow OxH + RS\cdot$$

$$RS\cdot + R'CH{=}CH_2 \longrightarrow R'(RSCH_2)\dot{C}H$$

$$R'(RSCH_2)\dot{C}H + RSH \longrightarrow R'CH_2CH_2SR + RS\cdot$$

Kharash and co-workers established that the relative reaction rates of thiol addition to double bonds follow the order, $ArylSH > HO_2CCH_2SH > RCH_2SH > RR'CHSH > RR'R''CSH$ which is the same order observed for corresponding rates of mercaptan oxidation by a variety of oxidants.

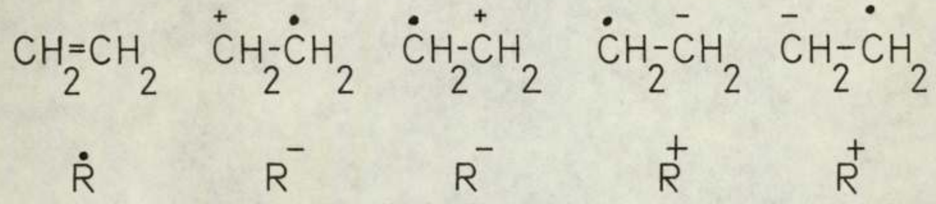
Investigating the photochemical addition of methyl mercaptan to unsaturated hydrocarbons in the gas phase, Sivertz and co-workers (128) predicted that the attack of a thiyl radical upon a double bond involves the reversible formation of a radical complex ($\dot{C}$), by the following mechanism:

$$RS\cdot + M \rightleftharpoons \dot{C}$$

$$\dot{C} + RSH \longrightarrow R\dot{S}MH + RS\cdot$$

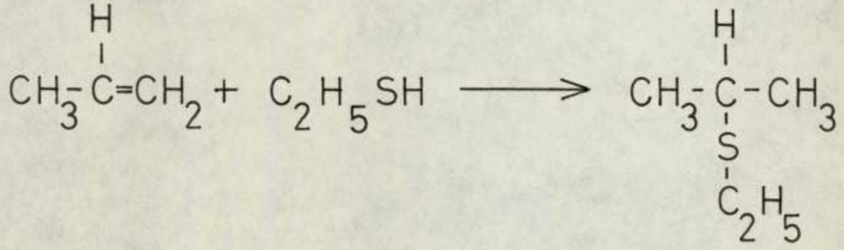
where M is the unsaturated hydrocarbon.

Sivertz and co-workers suggested the following canonical structures for the complex, which according to them, most probably involves the triplet stage of the double bond.

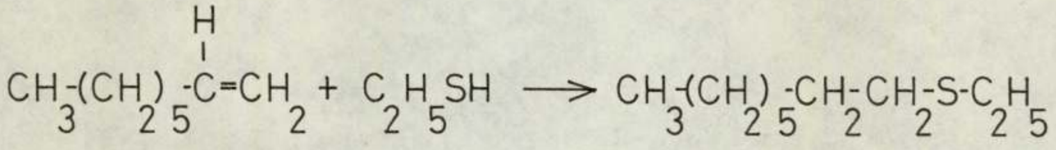


$$\underset{\dot{R}}{CH_2{=}CH_2}\qquad \underset{R^-}{\overset{+}{C}H_2-\dot{C}H_2}\qquad \underset{R^-}{\dot{C}H_2-\overset{+}{C}H_2}\qquad \underset{\overset{+}{R}}{\dot{C}H_2-\overset{-}{C}H_2}\qquad \underset{\overset{+}{R}}{\overset{-}{C}H_2-\dot{C}H_2}$$

Jones and Reid (129) observed that peroxides influence the mode of addition of mercaptan to unsaturated compounds in a similar way as they affect the addition of hydrogen bromide. By heating ethyl mercaptan with propylene, ethyl isopropyl sulphide was obtained while with octene the product was ethyl n-octyl sulphide.



$$CH_3-\overset{H}{\overset{|}{C}}{=}CH_2 + C_2H_5SH \longrightarrow CH_3-\underset{\underset{C_2H_5}{\underset{|}{S}}}{\overset{H}{\overset{|}{C}}}-CH_3$$



$$CH_3-(CH_2)_5-\overset{H}{\overset{|}{C}}{=}CH_2 + C_2H_5SH \longrightarrow CH_3-(CH_2)_5-CH_2-CH_2-S-C_2H_5$$

This anomality was explained by the fact that octene contained some peroxides due to storage in air, and it was confirmed when ethyl n-propyl sulphide was obtained by adding peroxides to the propylene system. The above authors have mentioned that even the addition of thiophenol to unsaturated compounds in an Anti-Markovnikoff's manner, could be reversed by completely excluding peroxides.

Cunneen (113) has also observed that thiophenol and isopentanethiol add readily to cyclohexene and 1-methylcyclohexene under peroxidic conditions. The fragments formed by the scission of S-H bonds in the thiols undergo addition at the double bond contrary to Markovnikoff's rule.

Therefore it can be concluded that the addition of mercaptans to olefins takes place in an Anti-Markovnikoff's manner due to the presence of peroxides on other similar reactive species, which initiates a radical chain mechanism.

The relative stability of simple alkyl radicals happens to be in the same order as that of the corresponding carbonium ions. A tertiary radical is more stable than a secondary which is more stable than a primary radical. This results from the decrease in stabilization by hyperconjugation in the series.

2.3. Experimental

2.3.1. Photochemical addition of benzyl mercaptan to 2-methyl-but-2-ene

Although 2-methyl-but-2-ene is an excellent model compound for natural rubber as it closely resembles the isoprene unit in a polyisoprene, a thermally initiated addition reaction is almost impossible to carry out due to its very high volatility. Therefore a photo-initiated reaction was carried out to investigate the mechanism and products of addition of benzyl mercaptan to 2-methyl-but-2-ene.

Materials

Benzyl mercaptan	B.D.H. Analar grade
2-methyl-but-2-ene	Aldrich Chemicals
Azobis isobutyronitrile	Recrystallized from ether

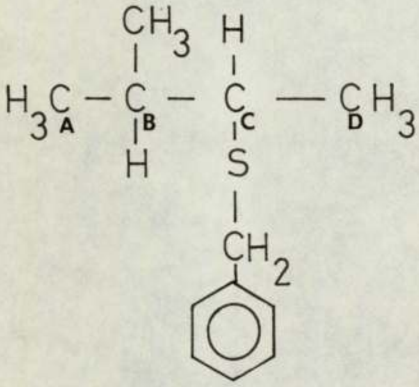
Procedure

0.01 mole (1.24 gms, 1.17 ml) of benzyl mercaptan, 0.1 mole (7.01 gms - 10.6 ml) of 2-methyl-but-2-ene and 0.05 gms of azobis isobutyronitrile were taken in a quartz tube, which was sealed under vacuum while keeping in a dry-ice acetone bath. Then the tube was kept rotating in an Ultra-Violet cabinet for a period of 72 hours.

After 72 hours the excess hydrocarbon was removed under vacuum and the resulting colourless liquid was vacuum distilled. A fraction boiling at 78 - 84°C under 0.08 - 0.1 mm mercury pressure was collected and was analyzed by infra-red, N.M.R. and Mass spectroscopy.

Analysis of spectra

The obtained spectra were analysed in detail to confirm the structure of the mercaptan-hydrocarbon adduct, which according to theoretical considerations should be as follows:

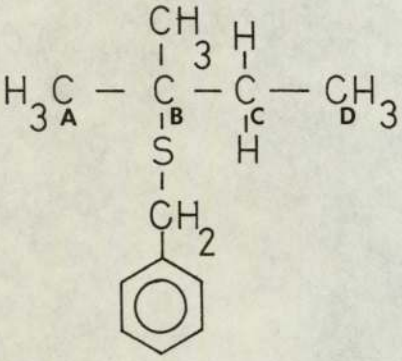


M. Wt. 194

Mass Spectrum (see fig.(1)).

The mass spectrum shows a clear molecular peak at 194 confirming that a 1:1 adduct is obtained. A loss of a methyl group is indicated by the peak at 179, which could be assigned to the D-methyl group in the above structure.

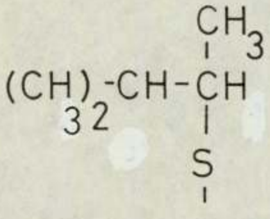
If the addition reaction took place in a Markovnikoff's manner the product should have been as follows:



In this case we should see a peak at 165 corresponding to the loss of the ethyl group at C and D positions. Such a peak is absent in the spectrum obtained.

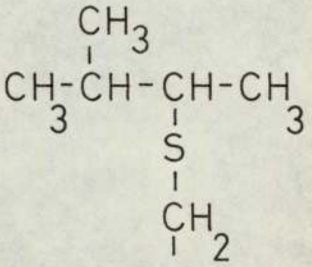
A peak appears at 123 showing the presence of benzyl mercaptyl group, and the peak at 91 corresponds to the loss of a sulphur atom from this group. In addition to this there are clear peaks at 77, 103, 117 and at 151 corresponding to the following fragments.

77



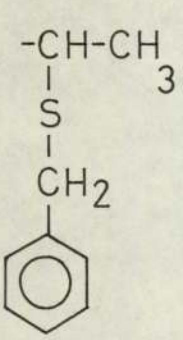
$(CH_3)_2\text{-}CH\text{-}CH(CH_3)\text{-}S\text{-}$

103



$CH_3\text{-}CH(CH_3)\text{-}CH(S\text{-}CH_2\text{-})\text{-}CH_3$

117



151

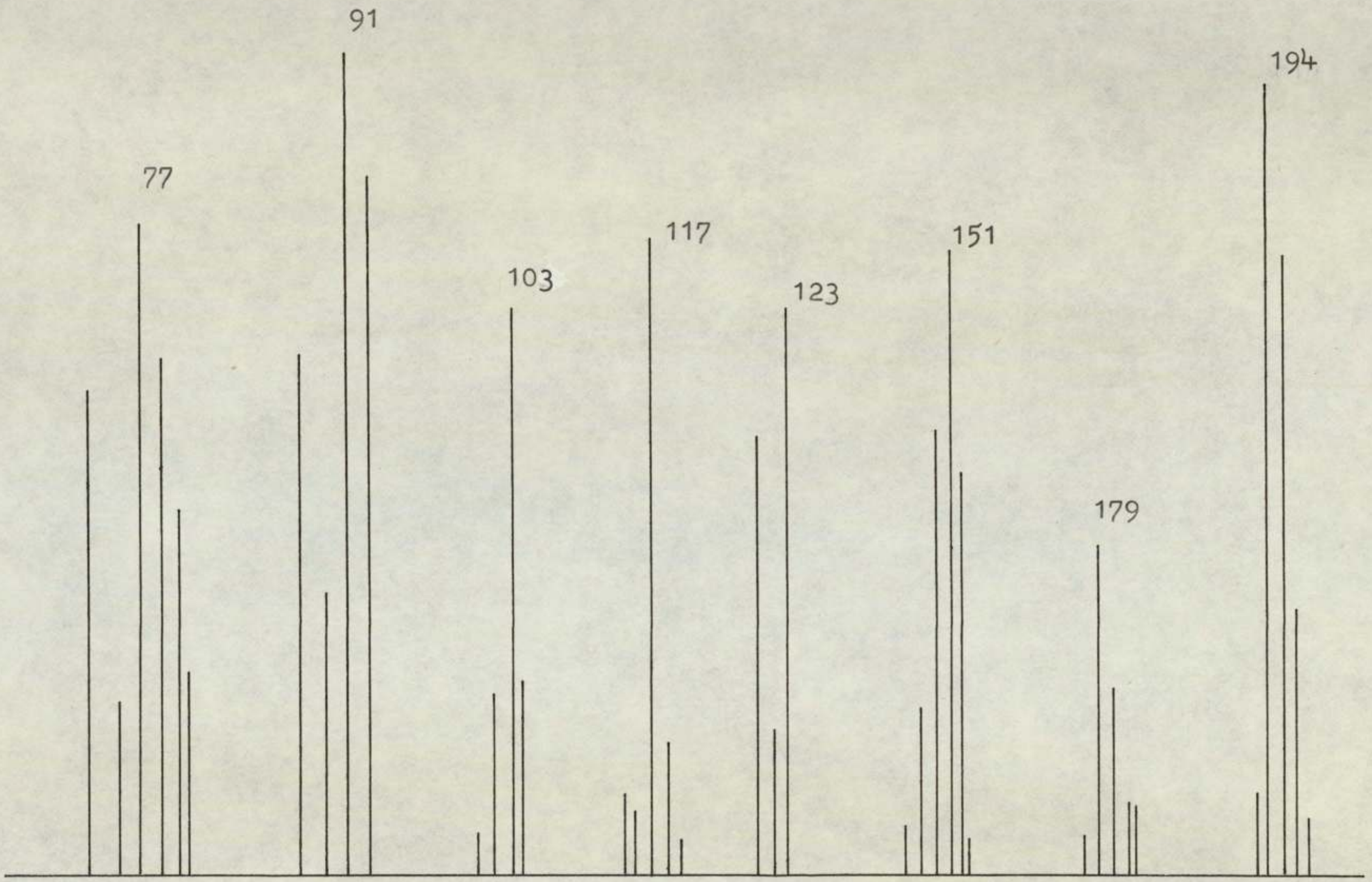
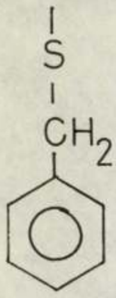
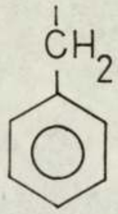


Fig. 1. Mass Spectrum of Benzyl mercaptan and 2-methyl-but-2-ene adduct.



123



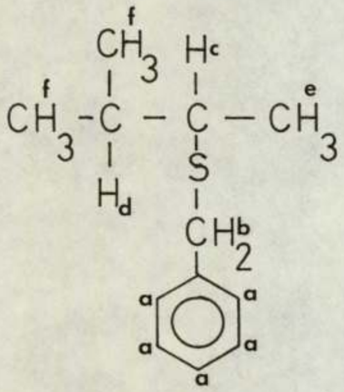
91

<u>Infra-red Spectrum</u> (see fig.(2)).

The absence of a band at 2550 cm^{-1} proves the absence of a thiol group showing that the reaction has taken place at the -SH end. A sharp peak at 1602 indicates the presence of an aromatic group in the compound. There is also no peak corresponding to olefinic unsaturation around 1660 cm^{-1}.

<u>N.M.R. Spectrum</u> (see fig.(3)).

The adduct structure was labelled as follows during the analysis of the N.M.R. spectrum.



According to the above structure the hydrogen atom ratios at different positions of the molecule should be as follows:

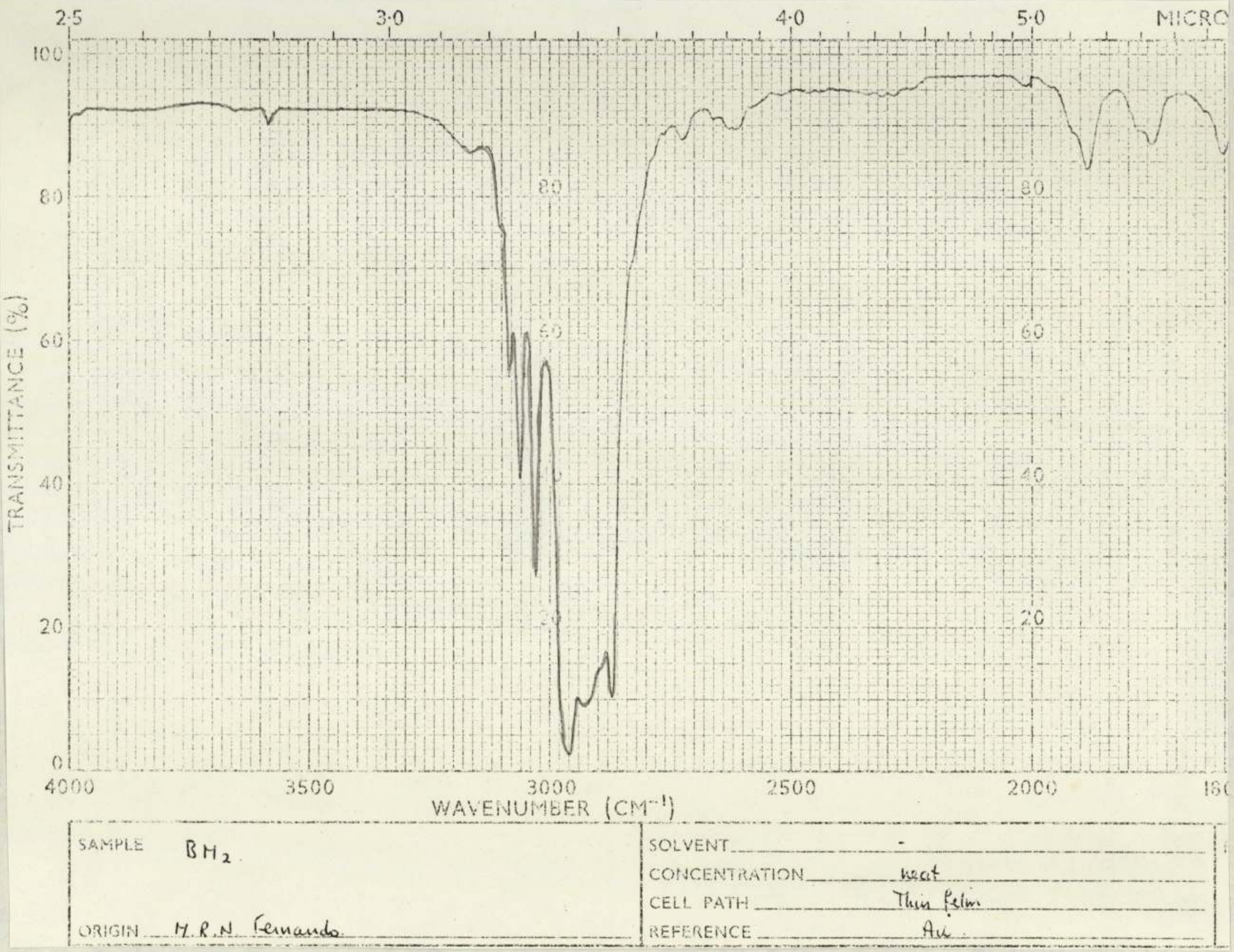
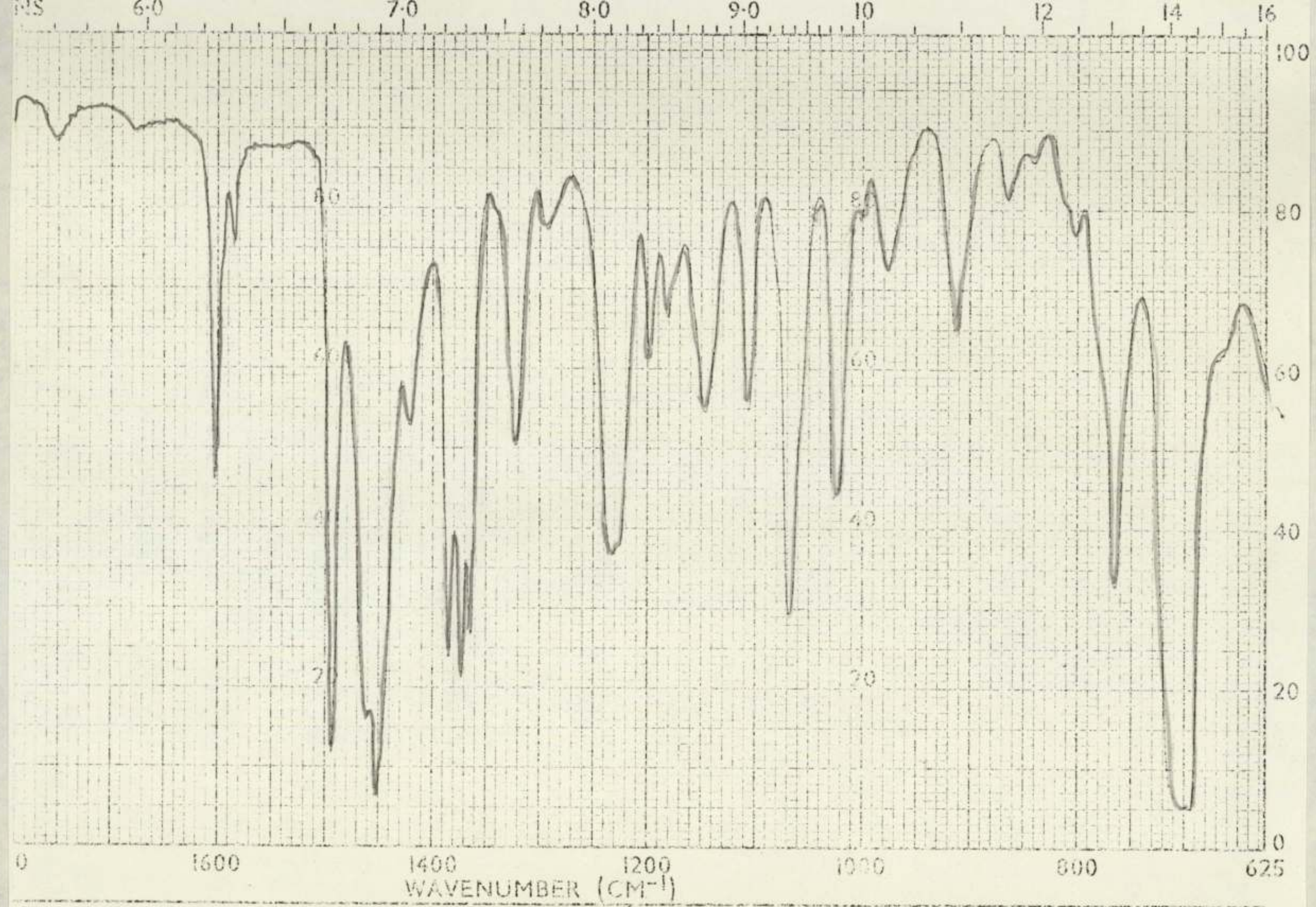


Fig. 2. I.R. spectrum of benzyl mercaptan and
2-methyl - but-2-ene adduct.



EMARKS

SCAN SPEED Slow.

SLIT Standard.

Intek
RPK/215/1001 472-5039

OPERATOR V M. Clenton

DATE 6th August 1974

REF. NO. 1741

Fig. 2 continued.

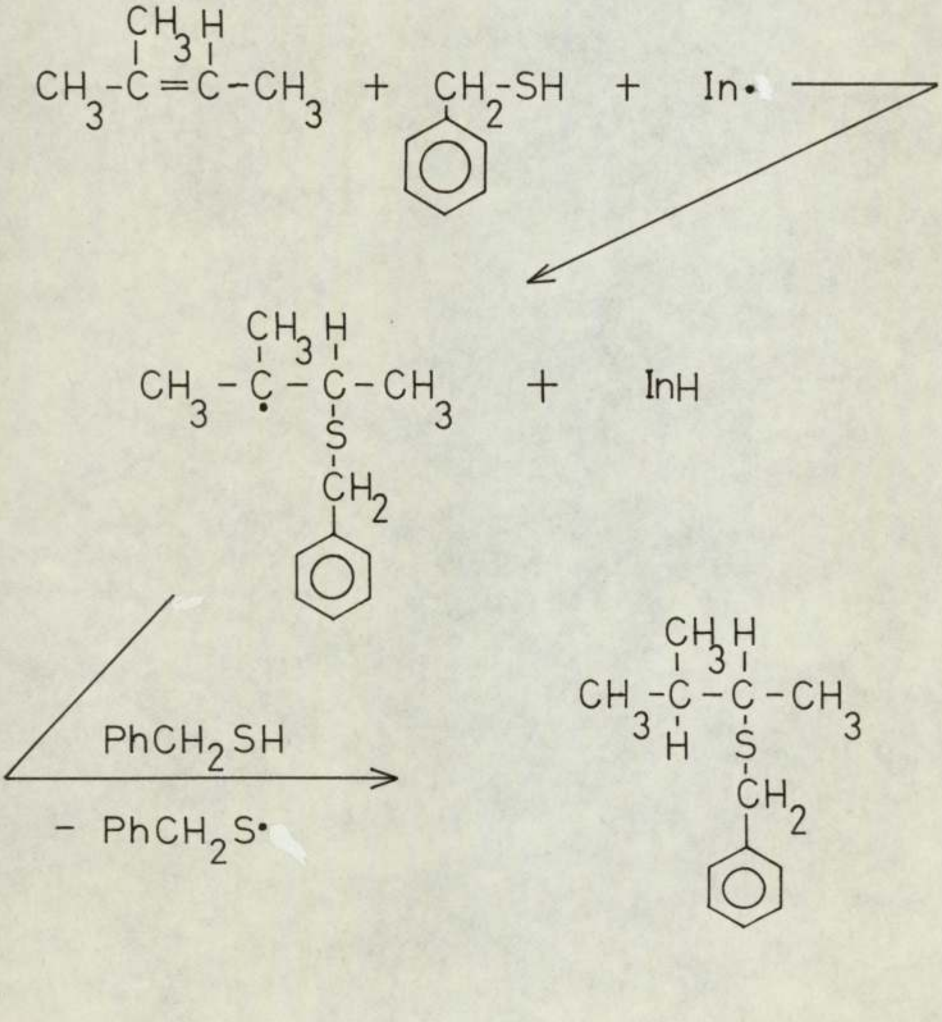
Fig. 3. N.M.R. spectrum of benzyl mercaptan and 2-methyl - but-2-ene adduct.

a : b : c : d : e : f
5 : 2 : 1 : 1 : 3 : 6

Such a ratio is more or less observed in the spectrum and the different bands are as follows:

Aromatic protons	a	2.9 τ (Singlet)
Methylenic protons	b	6.42 τ (Singlet)
Proton	c	7.6 τ (Multiple)
Proton	d	8.4 τ (Multiple)
Methyl protons	e	8.9 τ (Doublet)
Methyl protons	f	9.1 τ (Doublet)

Therefore the above spectroscopic data clearly confirms the structure of the adduct and the reaction path should be as follows which is in accordance with theoretical data.



2.3.2. Addition of benzyl mercaptan to 2-methyl-pent-2-ene

A free radical addition of benzyl mercaptan, a simplified model of 3, 5-di-tert-butyl-4 hydroxy benzyl mercaptan to 2-methyl pent-2-ene, which is a model compound for natural rubber was carried out.

Materials

Benzyl mercaptan	-	B.D.H. Analar grade
2-methyl pent-2-ene	-	Aldrich chemicals
Azo bis isobutyronitrile		Recrystallized from rubber

Method:

The addition reaction was carried out in a 100 ml 3 necked round-bottomed flask, fitted with a capillary tube, water cooled condenser and a rubber septum. An additional dry-ice acetone condenser was fitted on top of the water condenser. 0.1 mole (12.4 gms, 11.7 ml) of benzyl mercaptan and 0.1 mole (8.4 gms, 12.3 ml) of 2-methyl pent-2-ene were added to the reaction vessel which was followed by 0.25 gms of azo bis isobutyronitrile. Oxygen free nitrogen was passed through the capillary tube at the rate of 25 ml/min, and the flask was immersed in a digol bath at 50°C. With the help of a syringe, samples were taken from the reaction mixture at different intervals.

Infra-red spectra of these samples were obtained on a Perkin Elmer 457 spectrophotometer, using cells with sodium chloride windows.

Analysis of the spectra

Two characteristic bands were looked into in the spectra. They were, the band at 2564 cm^{-1} corresponding to the -SH of benzyl mercaptan, and the band at 1672 cm^{-1} of the carbon-carbon double bond of 2-methyl pent-2-ene. Another clear feature was the change in intensity of the band at 882 cm^{-1} which kept on reducing with time. This peak could also be attributed the -SH group of the mercaptan. The variation of intensity of the former two bands with time is shown in the following table.

Time hours	Intensity 2564 cm^{-1} -SH	Peak height m.m. 1672 cm^{-1} -C=C-
0	35.0	94.0
½	26.¼	92.0
1	26.0	93.0
2	29.3	93.0
4	29.2	91.0
8	29.0	63.2
11	25.2	35.1
24	20.1	3.0

According to the above table the concentration of unsaturation in the reaction mixture, due to 2-methylpent-2-ene, has completely disappeared accompanied by a reduction in -SH concentration, although there is still a residual amount of mercaptan groups. This provides evidence that the mercaptan is becoming attached to the double bond.

Volumetric analysis (130)

The method of volumetric analysis was also used to measure the concentrations of unsaturation and mercaptan function in the reaction mixture. Olefinic unsaturation was measured by the addition of mercuric acetate in methanol. One mole of methanol and one mole of mercuric acetate saturate one double bond, and a mole of acetic acid is formed at the same time, which is titrated with an alkali in methanol.

$$\% \ C{=}C = \frac{(S-b)(\text{normality})(24.02) \times 100\%}{\text{Wt. of sample in mg.}}$$

where S = ml of KOH for sample and

b = ml of KOH for blank.

The thiol function was quantitatively estimated by an oxidation with iodine in acid solution. The iodine was generated in situ using potassium iodate and potassium iodide in acetic acid.

$$\% \ SH = \frac{(\text{ml. of } KIO_3)(\text{normality})(33.074) \times 100\%}{\text{Wt. of sample in mg.}}$$

The original concentrations of thiol function and unsaturation function were taken as 100% and their variation with time were plotted (see fig.(4)).

It is clearly seen that the volumetric estimation gives a similar result as obtained by infra-red spectroscopic method. During the time when all the unsaturation disappeared from the reaction mixture, 50% of thiol function still remained.

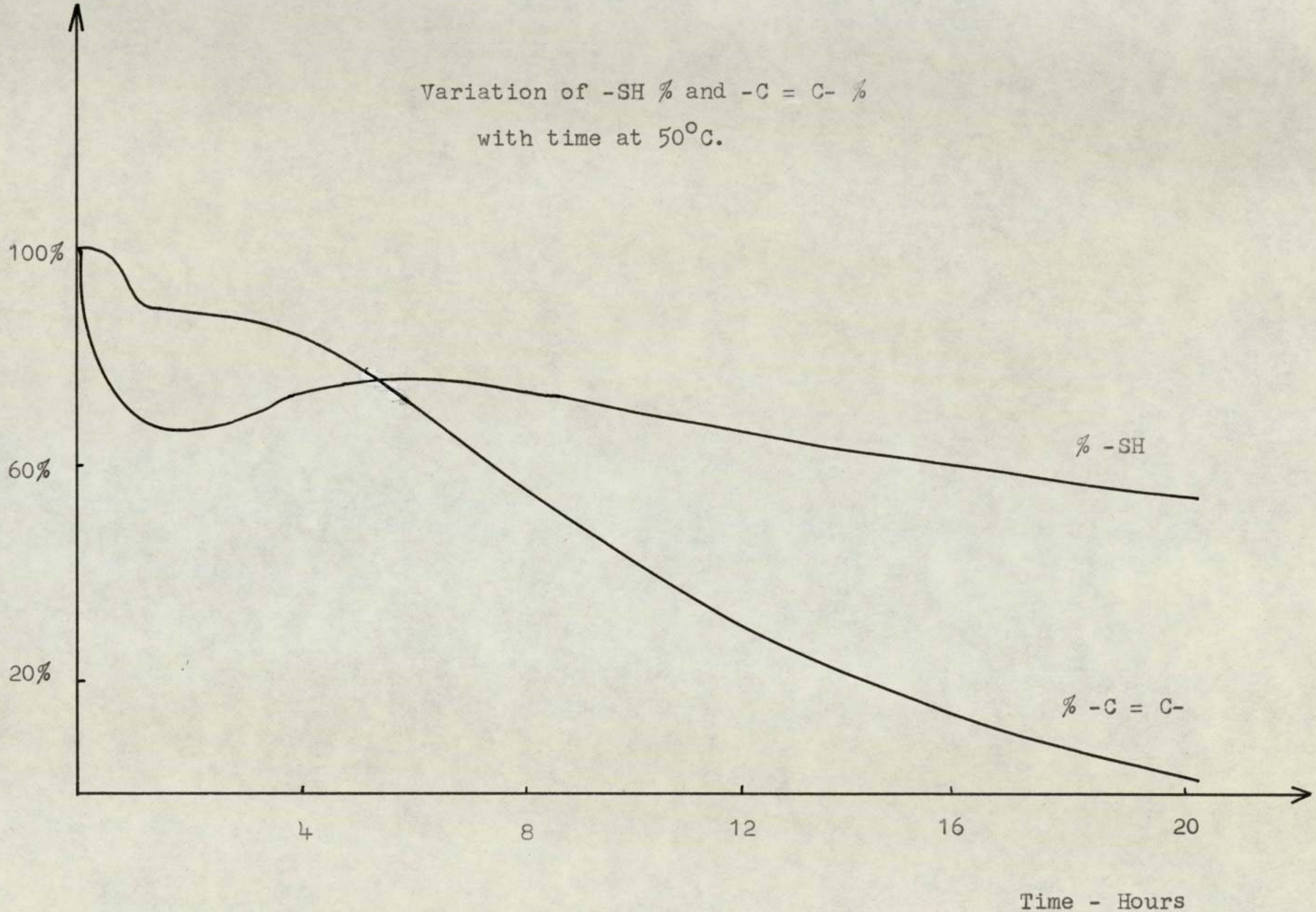
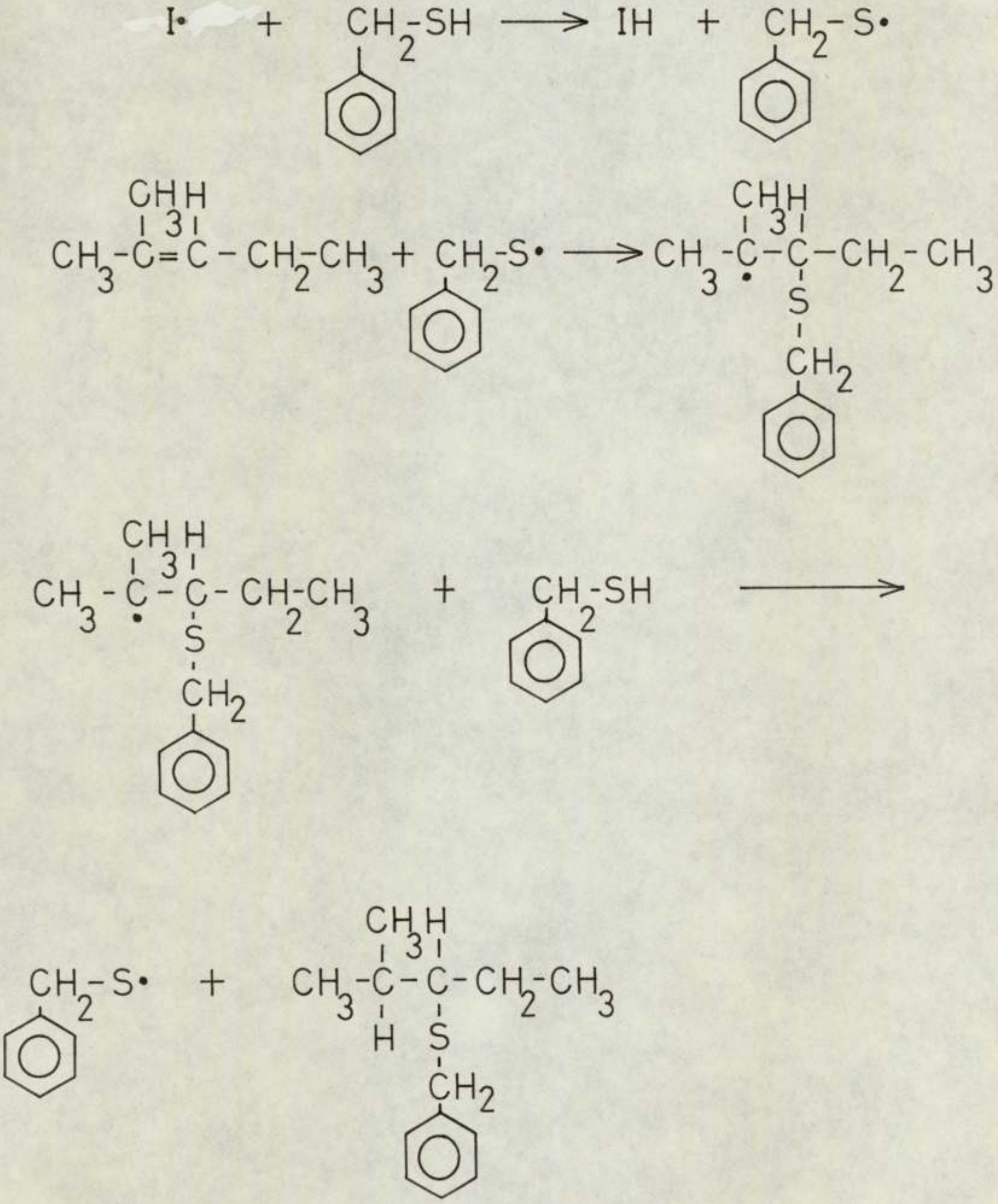

Variation of -SH % and -C = C- %
with time at 50°C.
100%
60%
20%
4
8
12
16
20
% -SH
% -C = C-
Time - Hours

Fig. 4.

Therefore it was concluded that the unsaturation function was also consumed by an additional reaction.

Attempts to further investigate the reaction products and mechanism were unsuccessful due to the hazardous nature of benzyl mercaptan. According to the theoretical evidence the following path of reaction could be predicted for free radical addition of benzyl mercaptan to 2-methyl pent-2-ene.



2.3.3. Addition of 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan to Oct-1-ene

Material

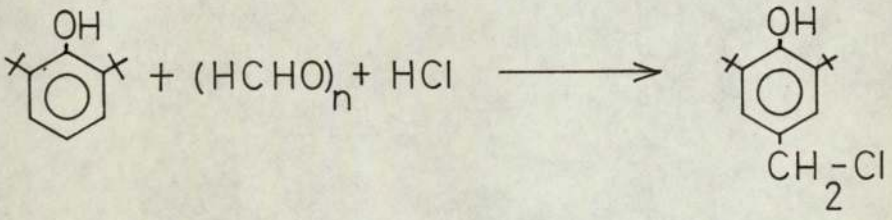
Oct-1-ene - B.D.H. Analar grade
3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan
Azo bis isobutyronitrile - Recrystallized from ether

Procedure

Preparation of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan

Commercially available 2,6-Ditertiarybutyl phenol was used as the starting material which was first chloromethylated in the following manner to yield the corresponding benzyl chloride.

3,5-Ditertiarybutyl-4-hydroxy benzyl chloride (131)

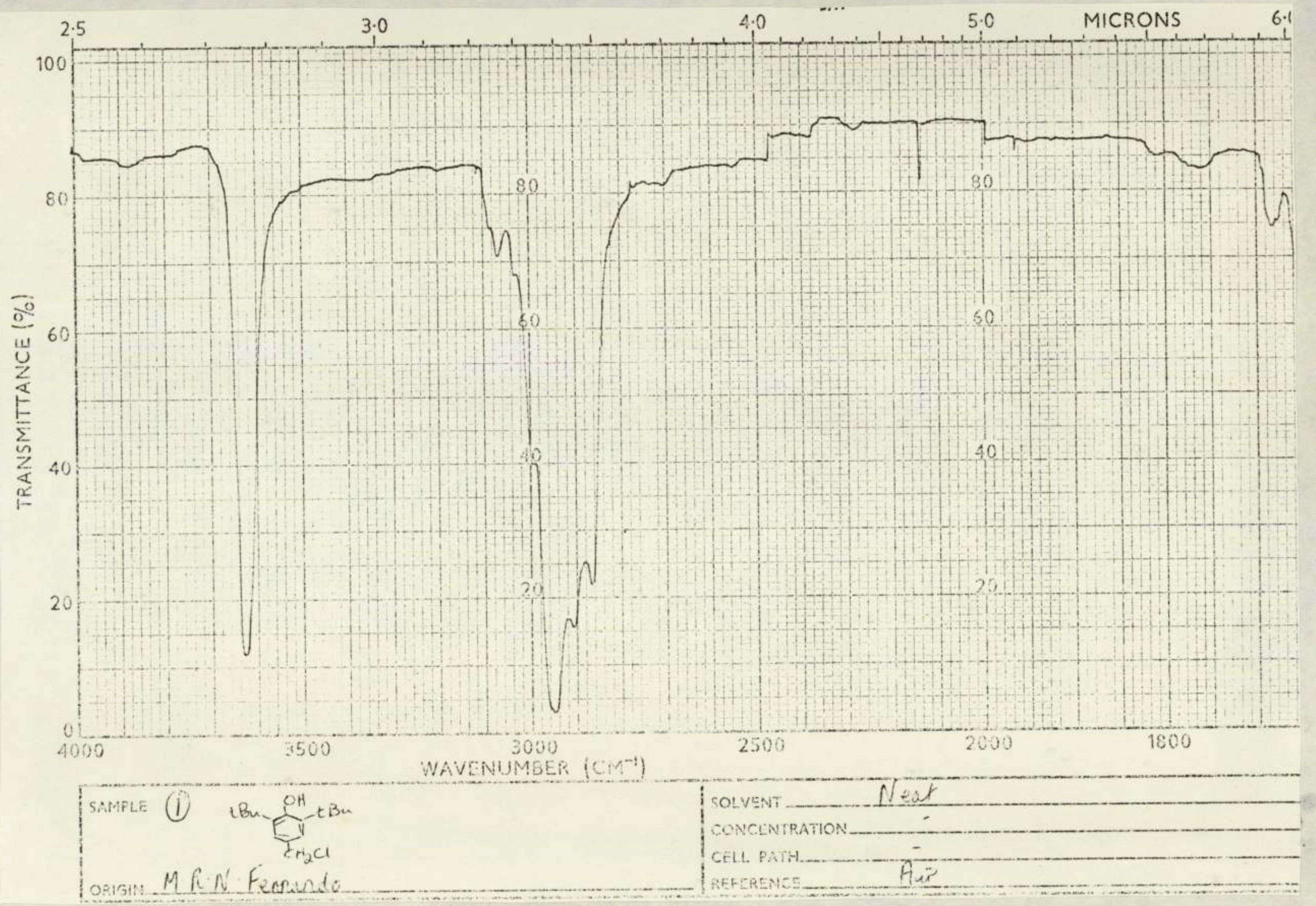


206.0 gms of 2,6-Ditertiarybutyl phenol was taken in a 1 litre round bottomed flask and 120 gms of paraformaldehyde was added to it. 500 ml of 35-36% hydrochloric acid was poured in and the mixture was stirred vigorously using a fast rotating electric motor. Dry hydrogen chloride gas from a cylinder was bubbled through the stirred mixture through a sintered dispersion tube for a period of 7 hours at such a rate so that the escape of unreacted hydrogen chloride gas was kept to a minimum. The reaction mixture became slightly warm and all the 2,6-Ditertiarybutyl phenol went into an emulsion in the hydrochloric acid. After 7 hours of passing hydrogen chloride gas, the reaction mixture intensified in colour, which was left for 5 hrs. After 15 hours of standing, hydrogen chloride gas was again bubbled through the mixture while stirring, for another two hours during which the mixture became almost orange in colour. When the stirring was stopped the reaction mixture separated into an oily layer and a water layer. The oily organic layer was separated using a separating funnel and was then repeatedly washed with distilled water. Ether and benzene was added to it and was again washed with 2% sodium bicarbonate and distilled water to remove any free hydrochloric acid present. Then the mixture was dried with anhydrous sodium sulphate and the solvents were removed on a rotary evaporator. The resulting liquid was oily and reddish orange. It was further purified by a a vacuum distillation and the fraction boiling at 128 - 130°C at 1.5-2.0 mm pressure was collected. A 70% yield of 3,5-Ditertiarybutyl-4-benzyl chloride was obtained by this manner.

The structure of the compound was confirmed by I.R., N.M.R. and Mass spectrometry.

<u>Infra-Red Analysis</u> (see fig.(5)).

2.74 Microns 3630 cm^{-1} ------ Phenolic OH
7.18 Microns 1395 cm^{-1} ------ t Butyl groups
7.43 Microns 1360 cm^{-1} ------ " "



SAMPLE ①

ORIGIN M.R.N. Fernando

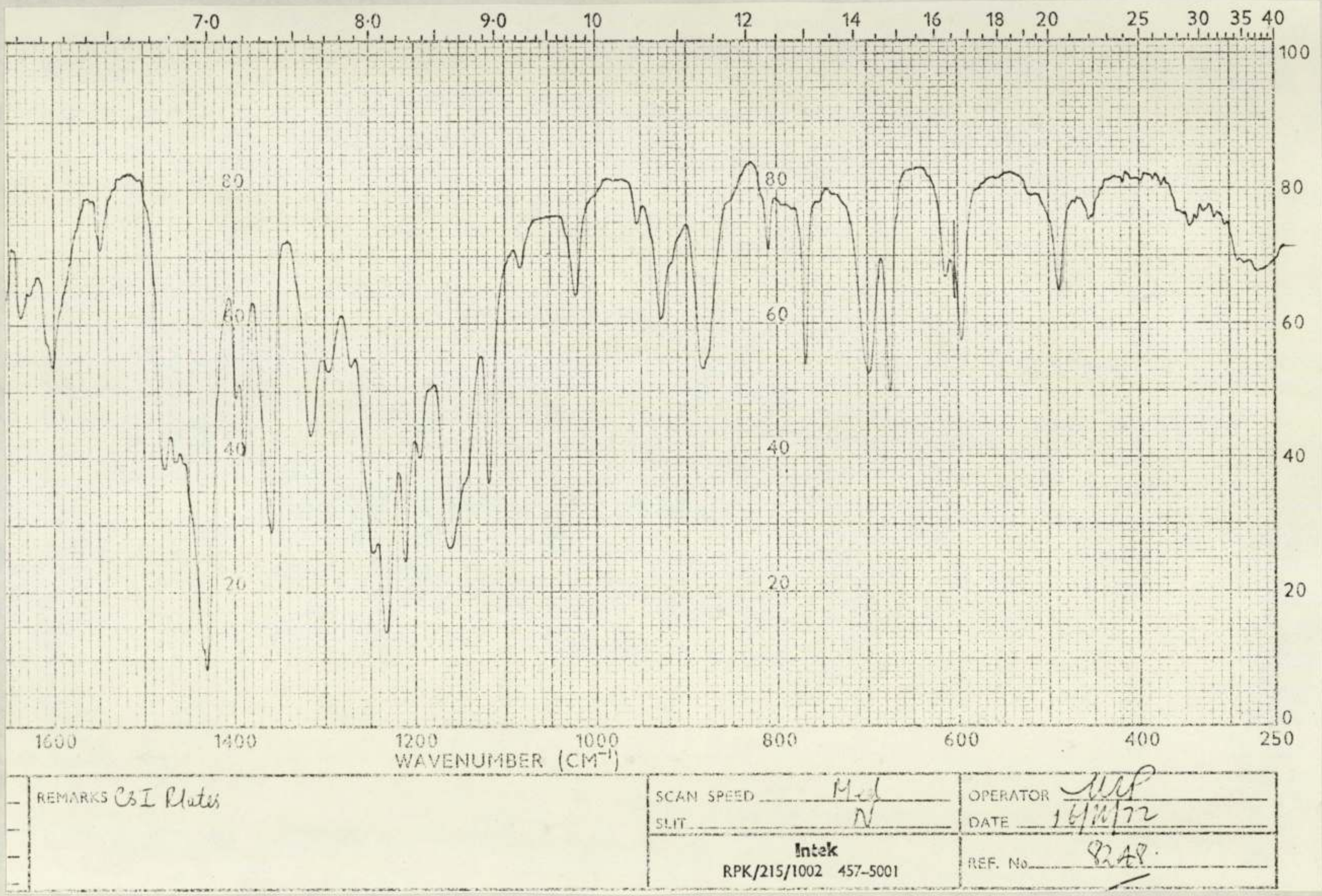
SOLVENT Neat

CONCENTRATION -

CELL PATH -

REFERENCE Air

Fig. 5. I.R. spectrum of 3,5-Ditertiarybutyl-4-hydroxy benzyl chloride.



REMARKS CsI Plates

SCAN SPEED Med

SLIT N

OPERATOR

DATE 16/11/72

REF. No. 8248.

Fig. 5 continued.

11.36 Microns 882 cm^{-1} ------ Benzene ring

14.5 Microns 700 cm^{-1} ------ Carbon chlorine

<u>N.M.R. Analysis</u> (CCl_4) (see fig.(6)).

		τ Value	Proton ratio
Aromatic Protons		3.0 Singlet	2
Hydroxyl Protons	-OH	5.03 Singlet	1
Methylenic Protons	$-CH_2-Cl$	6.35-6.45 Doublet	2
Tertiarybutyl Protons		8.6 Singlet	18

According to the mass spectrum obtained the breakdown of the compound shows a final peak at 254 which agrees with the molecular weight of the compound thus confirming its purity.

<u>3.5 -Ditertiarybutyl-4-hydroxy benzyl mercaptan</u> (132)

5.8 gms of magnesium hydroxide powder was taken in a 500 ml round bottomed flask and 200 ml of N,N Dimethyl formamide was added to it. The mixture was stirred on a magnetic stirrer and dry hydrogen sulphide gas was passed into the stirred mixture for a period of 30 minutes, during which a deep blue colour developed. 22.5 gms of 3,5-Ditertiarybutyl-4-hydroxy benzyl chloride was dissolved in 50 ml of technical grade hexane fraction and this solution was added to the mixture over a period of 15 minutes. As soon as the orange benzyl chloride solution reacts with the reaction mixture it turns white in colour and the addition of benzyl chloride was controlled so that the white colour remains. Faster addition of benzyl chloride solution

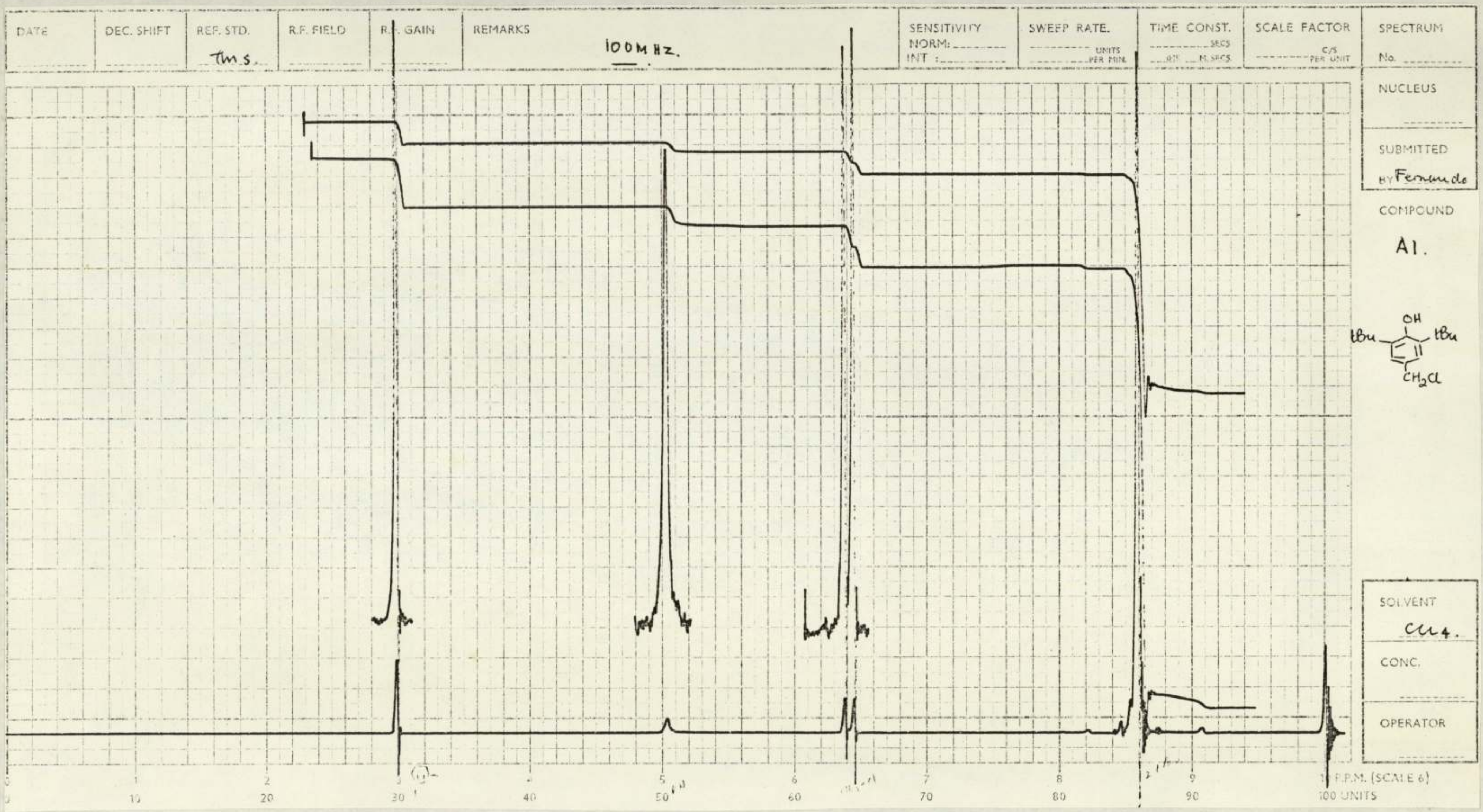


Fig.6. N.M.R. spectrum of 3,5-Ditertiarybutyl-4-hydroxy benzyl chloride.

makes the reaction mixture yellow in colour. This was found to be important to avoid any side reactions of disulphide or mono sulphide formation.

After 90 minutes the mixture was added to 500 ml of ice cooled water and the organic layer was extracted with diethyl ether. This solution was dried over anhydrous magnesium sulphate and the resulting solution was concentrated using a rotary evaporator. The product was vacuum distilled using a short air condenser and the fraction boiling between 128-135°C at 1.0-1.5 mm Hg pressure was collected. This colourless oily fraction after some time turned to white crystals with a melting point of 30-31°C. Yield 64.3%.

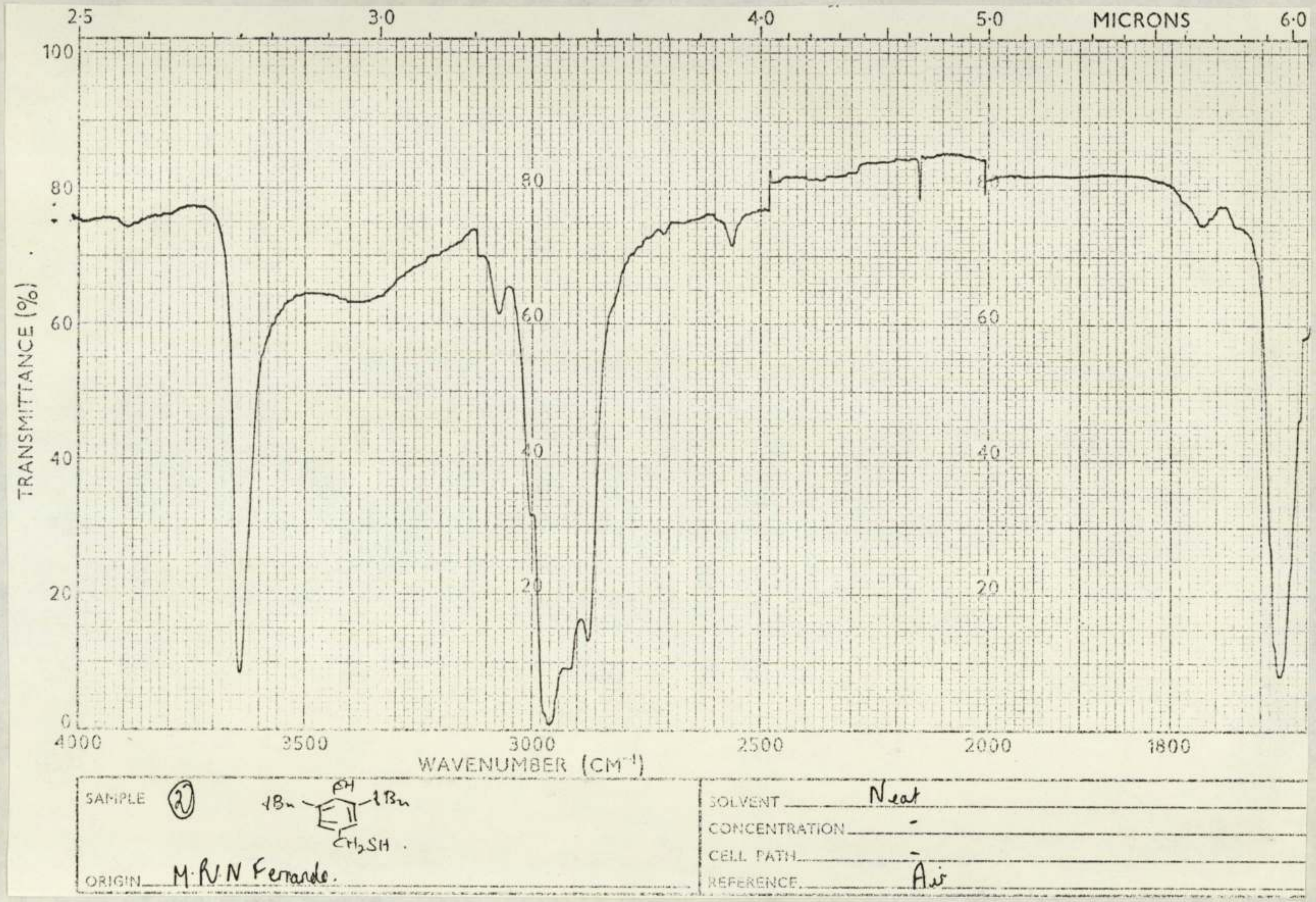
Analysis

Infra-Red Analysis (see fig.(7)).

2.75 Microns	3622 cm^{-1}	------ Phenolic OH
7.16 Microns	1393 cm^{-1}	------ t Butyl groups
7.34 Microns	1362 cm^{-1}	------ t Butyl groups
11.37 Microns	880 cm^{-1}	------ Benzene ring
3.88 Microns	2561 cm^{-1}	------ SH group

N.M.R. Analysis (see fig.(8)).

	τ Value		Proton Ratio
Aromatic Protons	2.96	Singlet	2
Hydroxyl Protons	4.98	Singlet	1
Methylenic Protons	6.3-6.4	Doublet	2
Tertiarybutyl Protons	8.54	Singlet	18



SAMPLE ②

ORIGIN M.R.N Ferando.

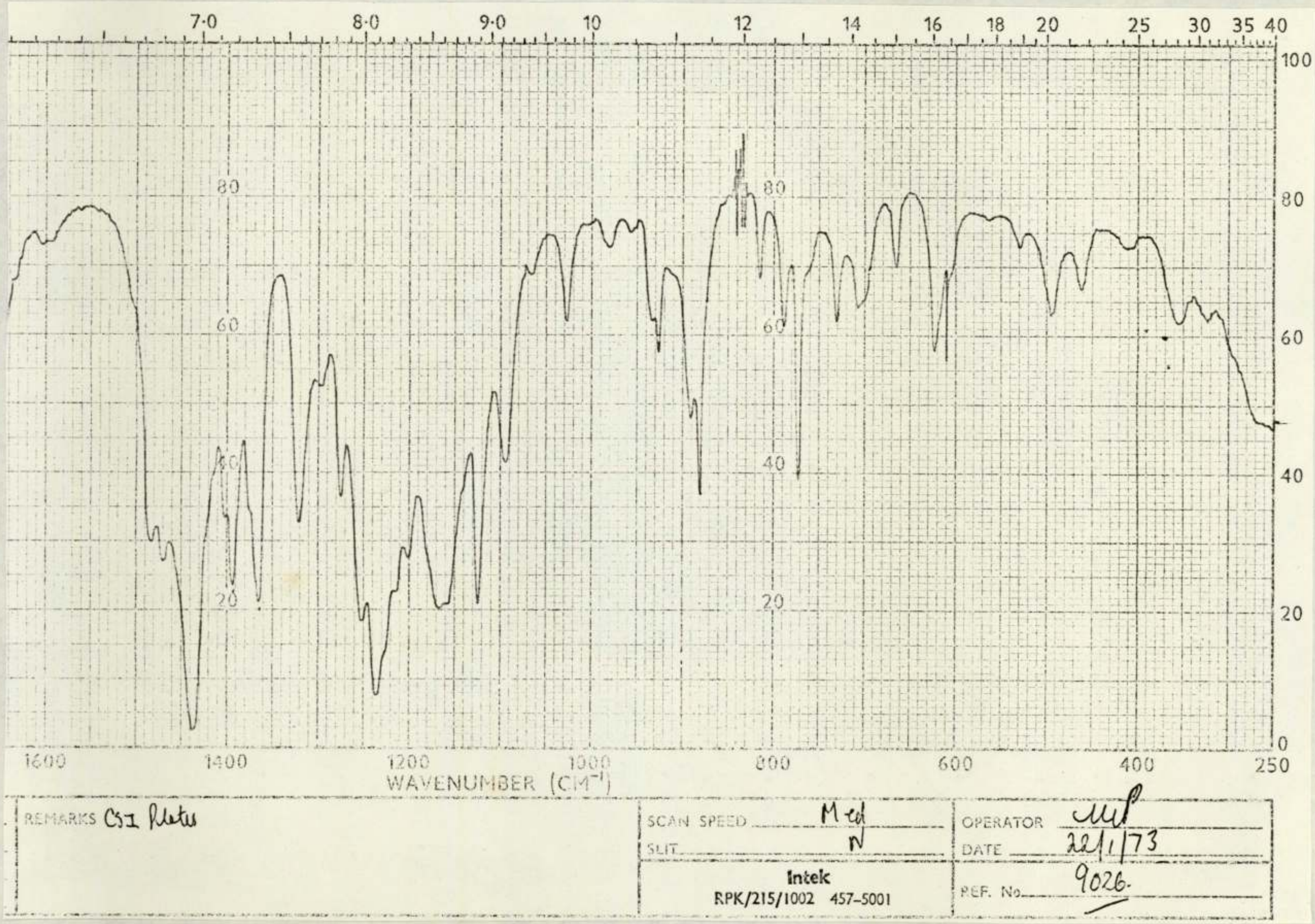
SOLVENT Neat

CONCENTRATION -

CELL PATH -

REFERENCE Air

Fig. 7. I.R. spectrum of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan.



REMARKS CsI Plates

SCAN SPEED Med

SLIT N

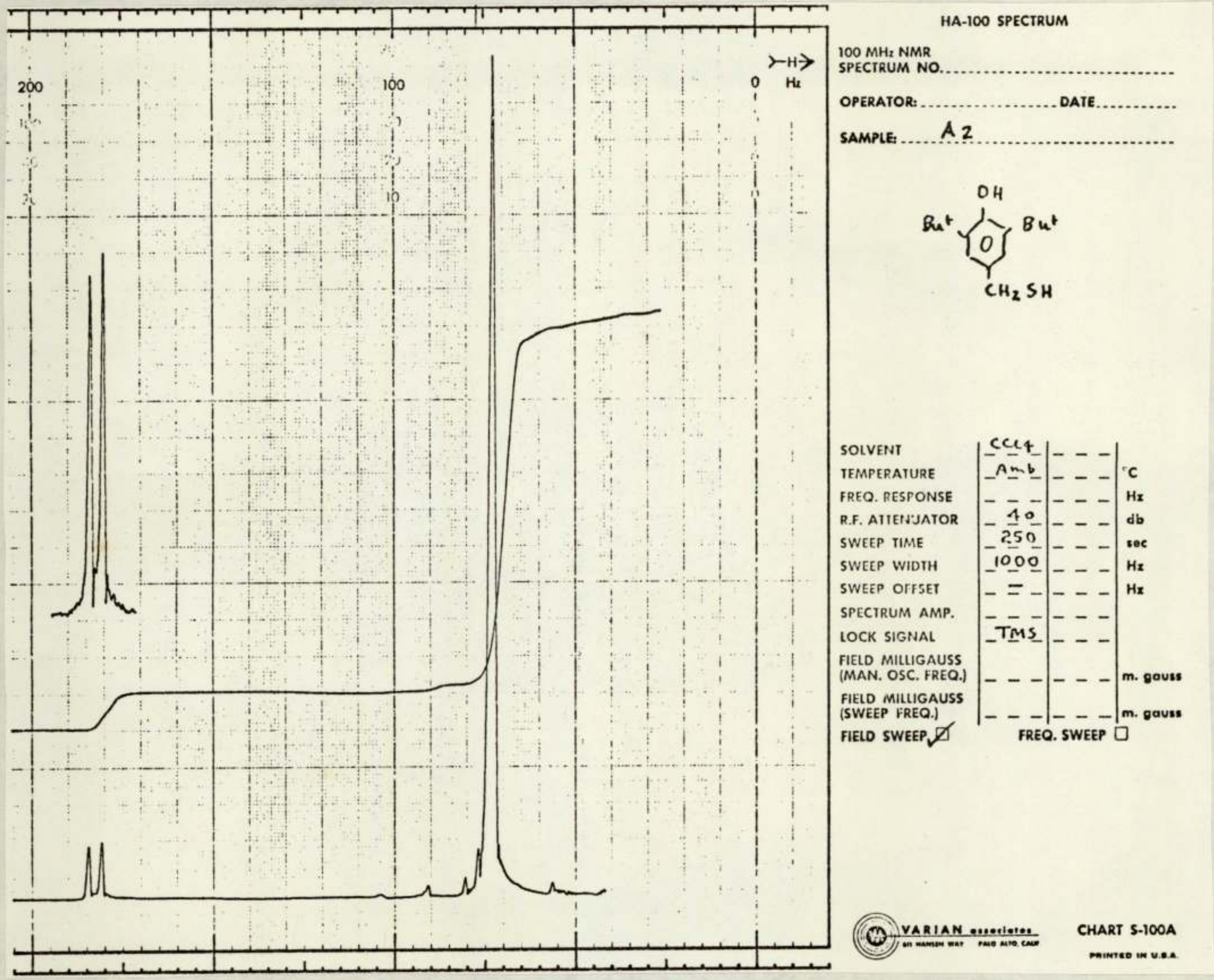
Intek
RPK/215/1002 457-5001

OPERATOR MP

DATE 22/1/73

REF. No. 9026.

Fig. 7 continued.



HA-100 SPECTRUM

100 MHz NMR SPECTRUM NO.

OPERATOR: DATE

SAMPLE: A 2

SOLVENT	CCl4		
TEMPERATURE	Amb		°C
FREQ. RESPONSE			Hz
R.F. ATTENUATOR	40		db
SWEEP TIME	250		sec
SWEEP WIDTH	1000		Hz
SWEEP OFFSET	–		Hz
SPECTRUM AMP.			
LOCK SIGNAL	TMS		
FIELD MILLIGAUSS (MAN. OSC. FREQ.)			m. gauss
FIELD MILLIGAUSS (SWEEP FREQ.)			m. gauss

FIELD SWEEP ☑ FREQ. SWEEP ☐

VARIAN associates
611 HANSEN WAY PALO ALTO, CALIF

CHART S-100A

PRINTED IN U.S.A.

Fig.8. N.M.R. spectrum of 3,5-Ditertiarybutyl-
-4- hydroxy benzyl mercaptan.

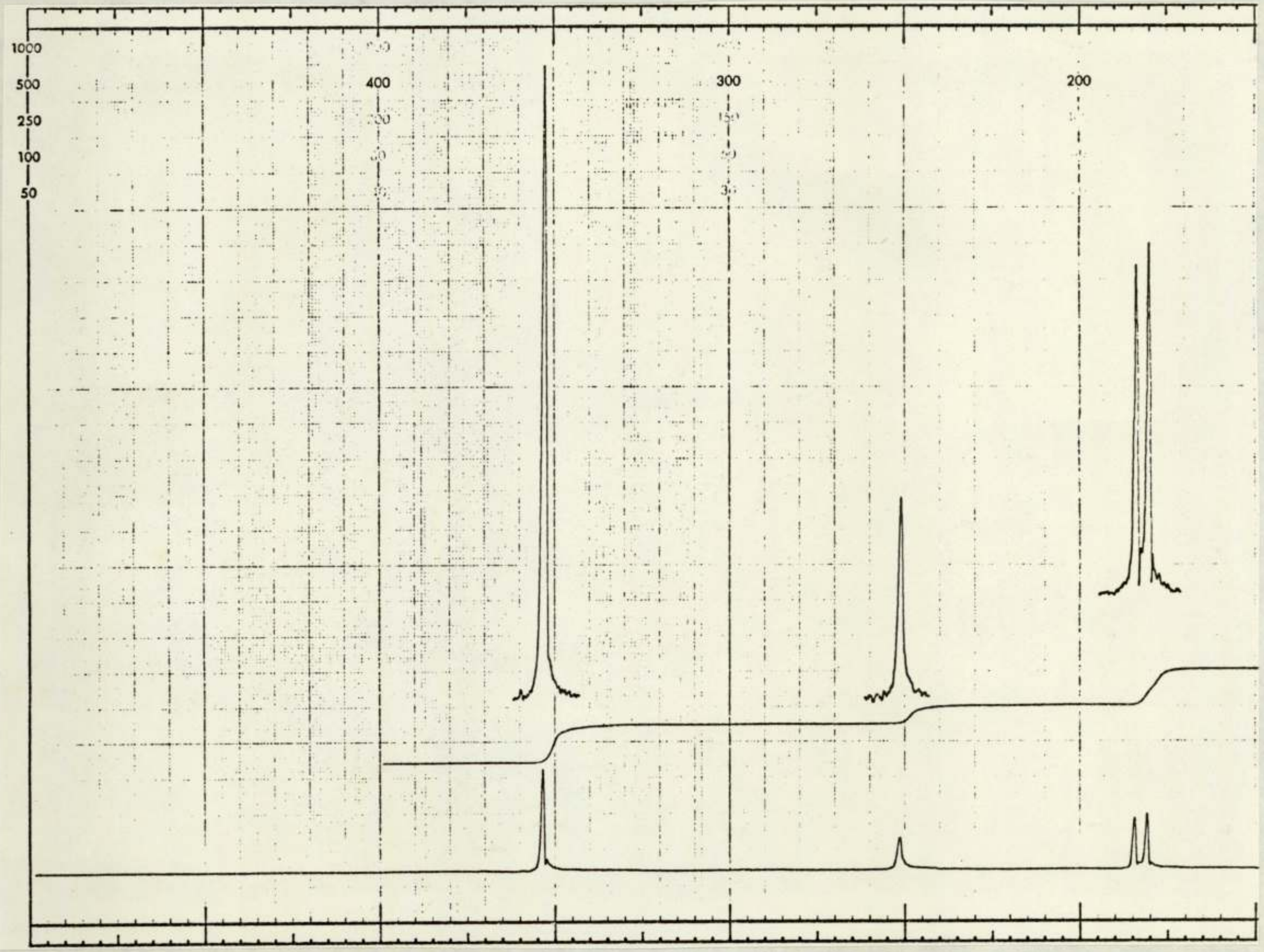


Fig. 8 continued.

The signal for SH group appears between 8.3-8.5 τ and is very weak.

The molecular weight of the compound obtained from the mass spectrum gives a value of 252 confirming the correctness of the structure.

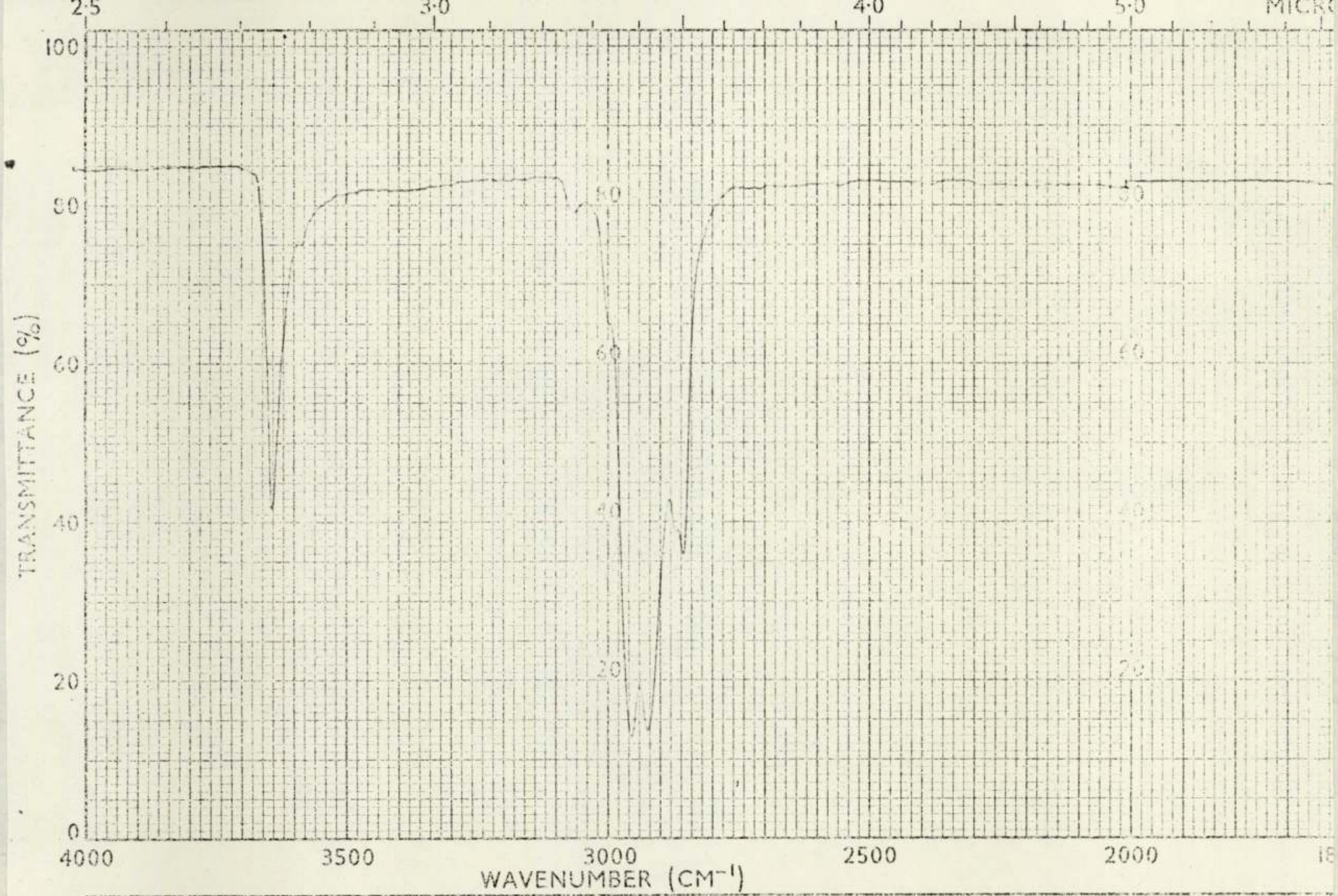
Addition

0.1 mole of oct-1-ene (11.22 gms, 15.7 ml) were taken in a 100 ml 3 necked round-bottomed flask and 0.01 mole (2.52 gms) of 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan and 0.05 gms of azo bis isobutyronitrile were added to it. A water cooled condenser was fitted to the reaction vessel and oxygen free nitrogen was bubbled through the reaction mixture at the rate of 20 ml per minute. The flask was kept in a digol bath at 60°C for a period of 24 hours while stirring with a magnetic follower.

Unreacted oct-ene was removed from the mixture by heating under vacuum and the resulting oily liquid was distilled under vacuum. A fraction of yellow colour boiling at 156-158°C at 0.2 ÷ 0.4 mm mercury was collected. This fraction was analysed by infra-red and N.M.R. spectroscopy (see fig. 9 and 10).

Analysis of the spectra

The infra-red spectrum shows the presence of a phenolic hydroxyl in the compound associated with the band appearing at 3642 cm^{-1}. The presence of tertiarybutyl groups is shown by bands at 1365 cm^{-1} and 1392 cm^{-1}. The absence of



SAMPLE Oct. 2.

ORIGIN M.R.N. Fernando

SOLVENT -

CONCENTRATION neat

CELL PATH Thin film

REFERENCE Air.

Fig.9. I.R. spectrum of oct-1-ene and mercaptan adduct.

REMARKS

SCAN SPEED Slow.

SLIT Standard.

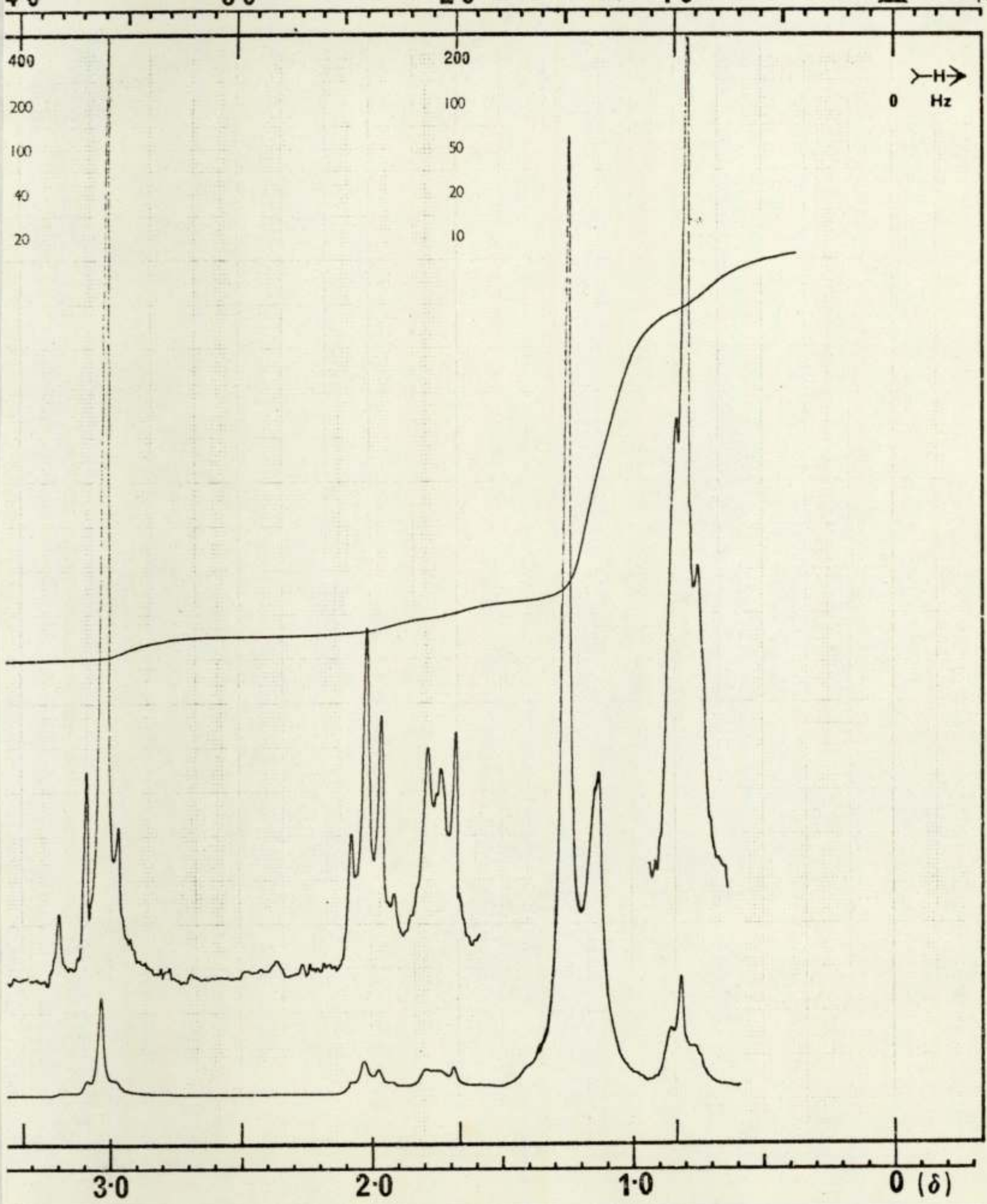
OPERATOR V.M. Clenton.

DATE 10th April 1974.

Intek
RPK/215/1001 472-5039

REF. NO. Ho58.

Fig. 9 continued.



SPECTRUM NO: ____

OPERATOR: ____ DATE: ____

SAMPLE NO: Oct 2

DONOR: M. Fernandes

100 MHz NMR SPECTRUM ☑ 60 MHz NMR SPECTRUM ☐

NUCLEI ^1H

SOLVENT	CCl_4		
TEMPERATURE	Amb		°C
FREQ. RESPONSE			Hz
R.F. ATTENUATOR	40		db
SWEEP TIME	250		sec
SWEEP WIDTH	1000		Hz
SWEEP OFFSET	—		Hz
SPECTRUM AMP.			
INTEGRAL AMP.			
LOCK SIGNAL	TMS		
FIELD MILLIGAUSS (MAN. OSC. FREQ.)			m. gauss
FIELD MILLIGAUSS (SWEEP FREQ.)			m. gauss

FIELD SWEEP ☑ FREQ. SWEEP ☐

NUCLEAR MAGNETIC RESONANCE LTD.

Fig.10. N.M.R. spectrum of oct-1-ene and mercaptan adduct.

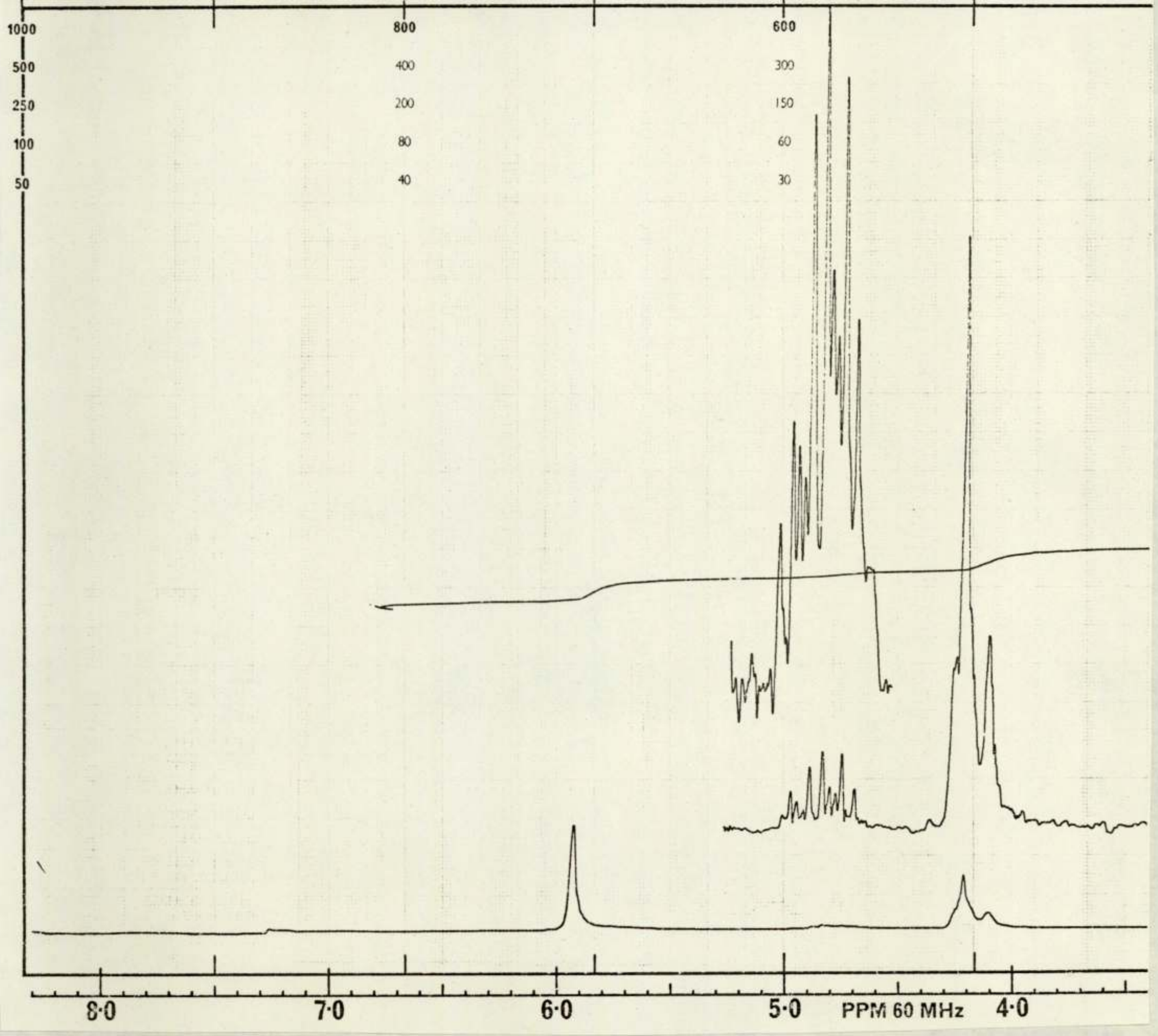
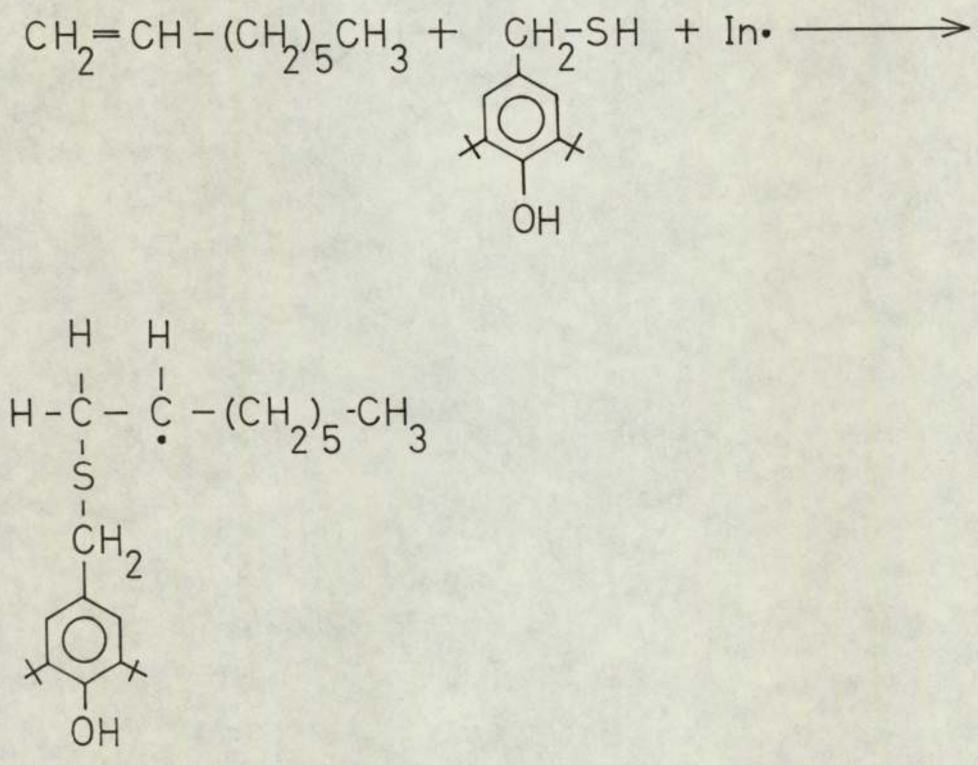


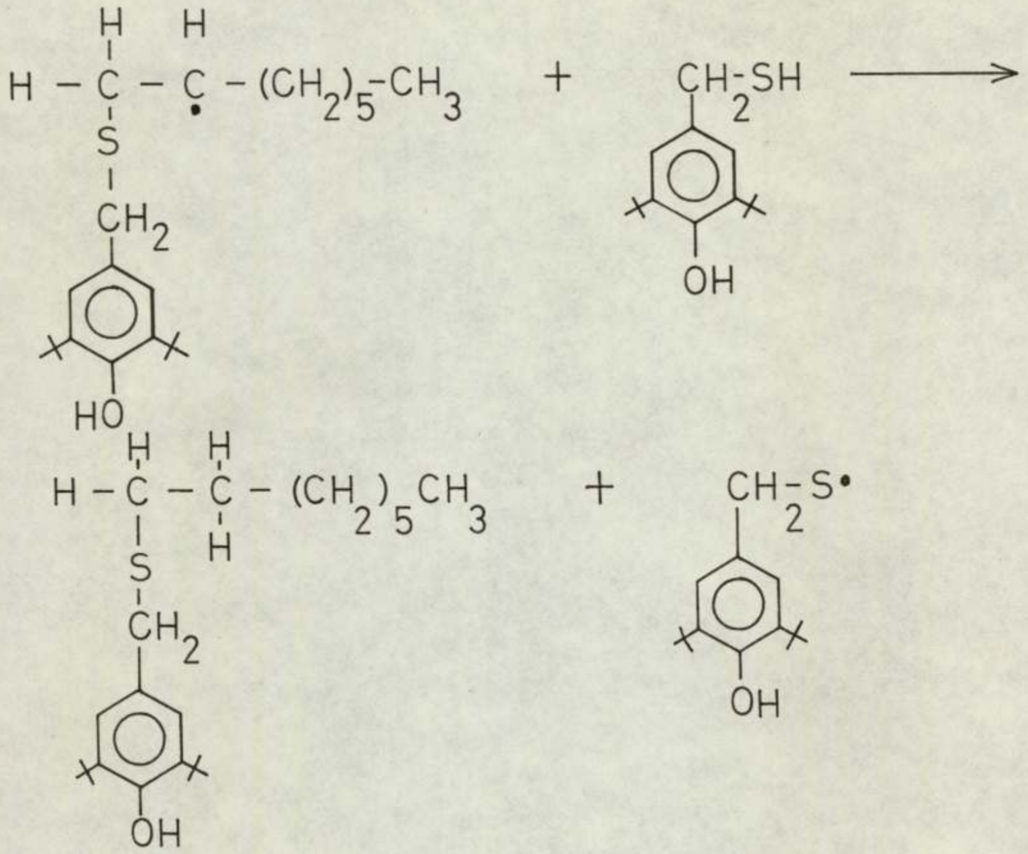
Fig. 10 continued.

any absorption at 1660 cm^{-1} clearly shows that there is no unsaturation left in the compound.

Although the N.M.R. spectrum of the adduct is complex, in comparison with that of pure 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan, there are additional bands corresponding to the oct-1-ene.

The following reaction path is suggested according to the known theoretical considerations.





2.3.4. Addition of 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan to 2-methyl-but-2-ene

The reaction of 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan with 2-methyl-but-2-ene, which is a model compound for natural rubber, by thermal treatment in the presence of azo bis isobutyronitrile was unsuccessful. The hydrocarbon was highly volatile (b.p.37.5°C) and the use of dry-ice condensers could not prevent the escape of the hydrocarbon at a temperature high enough to decompose the initiator into radicals. Therefore a photochemical method of initiation was used again in this experiment.

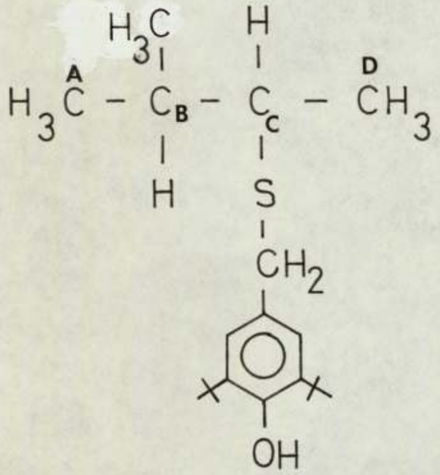
Procedure

0.1 mole (7.01 gms - 10.6 ml) of 2-methyl-but-2-ene, 0.01 mole (2.52 gms) of 3,5-ditertiarybutyl-4-hydroxy benzyl mercaptan, and 0.05 gms of azobis-isobutyronitrile were taken in a quartz tube, which was sealed under vacuum while keeping in a dry-ice acetone bath. Then the tube was kept rotating in an ultra-violet cabinet for a period of 48 hours.

After 48 hours the excess hydrocarbon was removed by vacuum and the resulting light yellow oily liquid was distilled under vacuum. A fraction boiling at 148-152°C under 0.2 - 0.4 mm mercury pressure was collected and was analysed by infra-red, N.M.R. and mass spectrometry.

Analysis of spectra

The obtained spectra were analyzed in detail to confirm the structure of the mercaptan-hydrocarbon adduct, which according to theoretical considerations should be as follows:

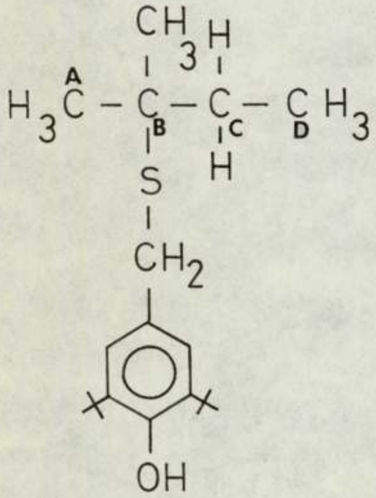


M.W. 322.

Mass spectrum (see fig.(11)).

The mass spectrum shows a clear molecular peak at 322 confirming that a 1:1 adduct is obtained. The peak at 321 (M-1) is more abundant than the (M+) 322 peak showing the loss of proton, most probably from the phenolic hydroxyl. A loss of a methyl group is indicated by the peak at 307, which could be assigned to the D-methyl group in the structure above.

If the addition reaction took place in a Markovnikoff's manner the product should have been as follows:



In this case we should see a peak at 293 corresponding to the loss of the C and D ethyl groups. Such a peak is not seen in the spectrum obtained.

A peak appears at 251 showing the presence of 2,5-ditertiarybutyl-4-hydroxy benzyl mercaptyl group, and the peak at 219 corresponds to the loss of a sulphur atom from this group.

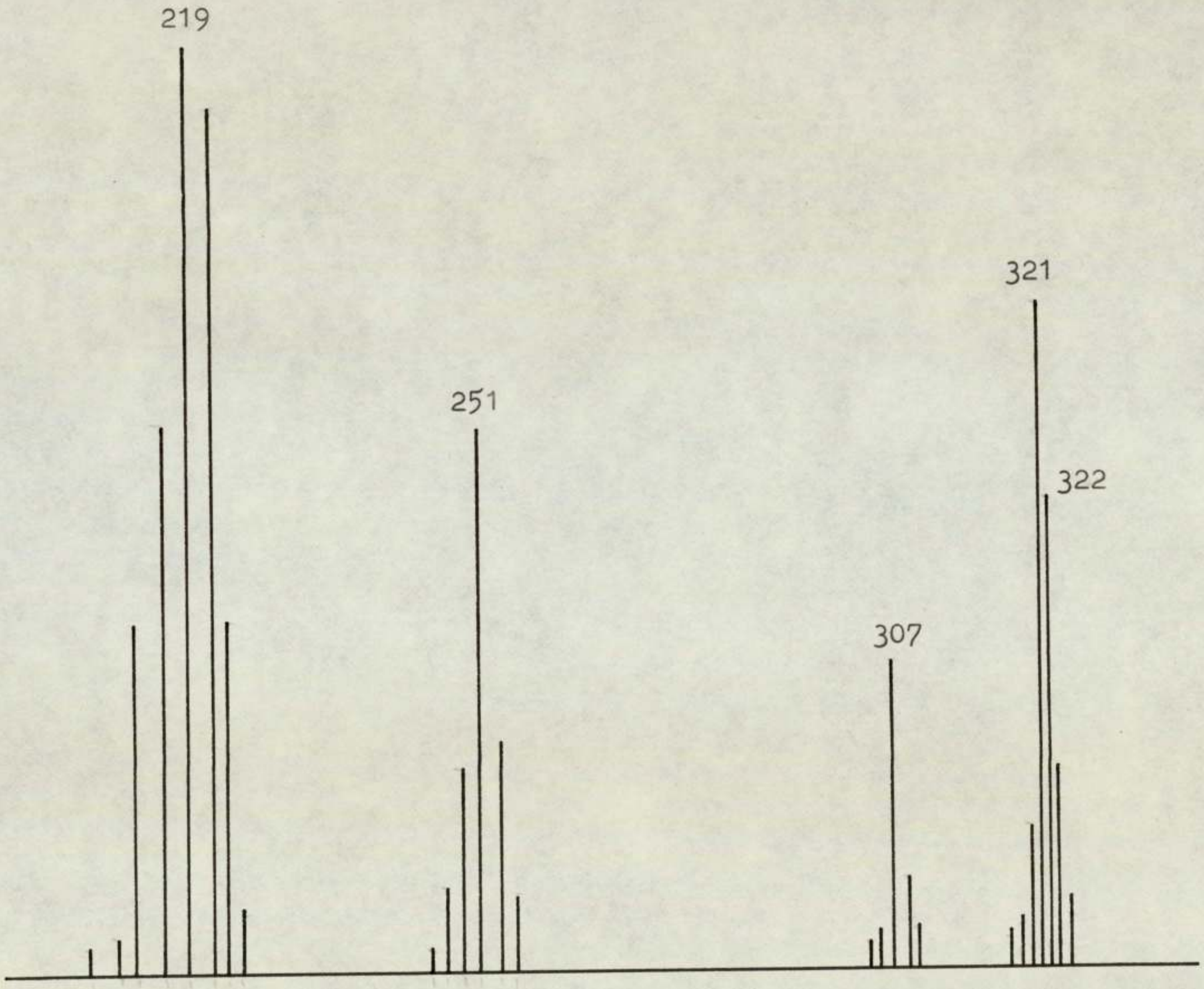


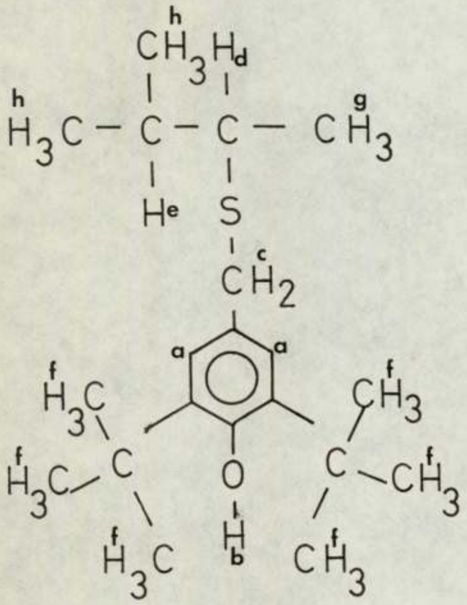
Fig. 11. Mass spectrum of 2-methyl-but-2-ene
and mercaptan adduct.

Infra-red spectrum (see fig.(12)).

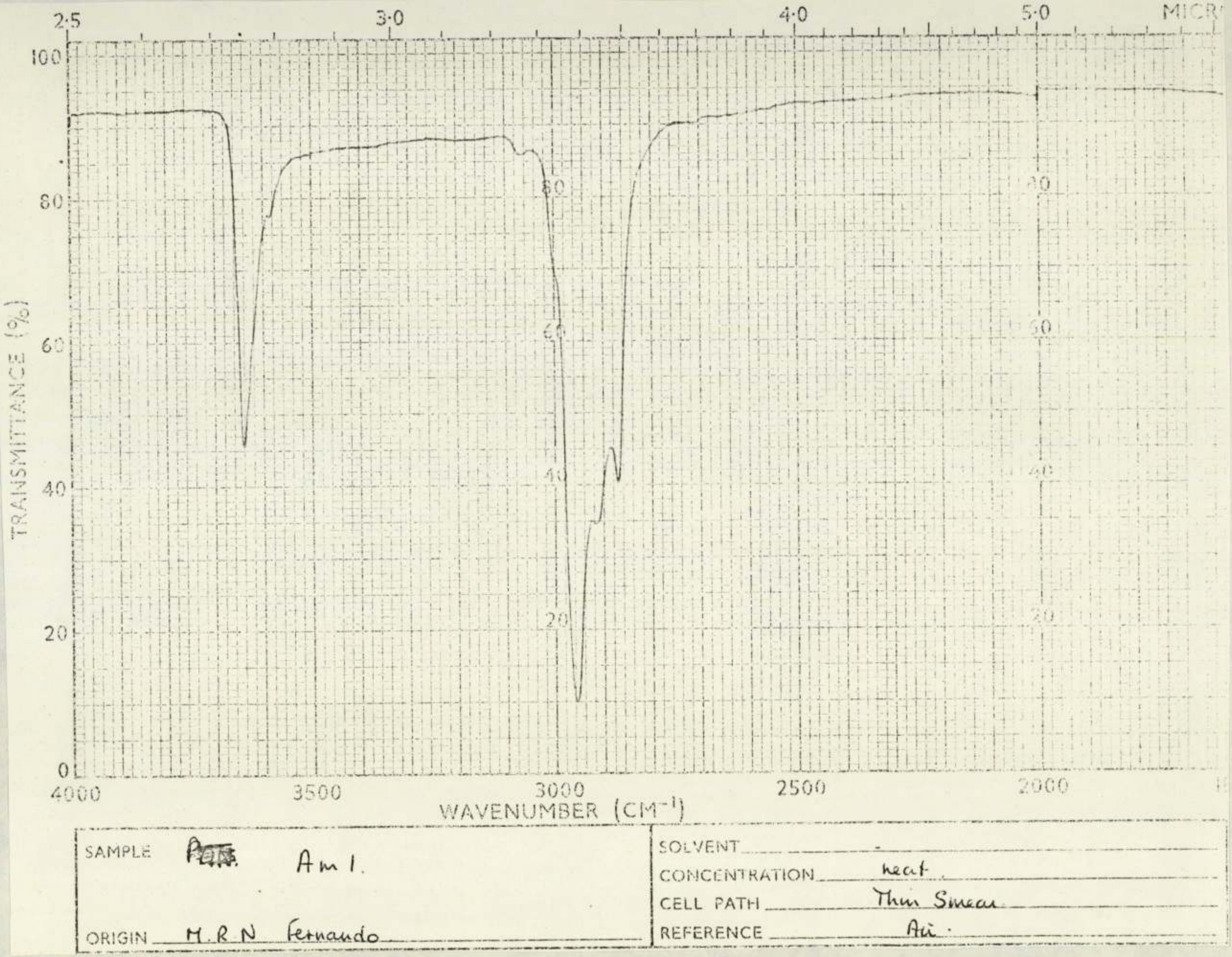
The band at 3640 cm^{-1} shows the presence of a phenolic hydroxyl group showing that the phenolic structure remains unchanged during the reaction. The absence of a band at 2550 cm^{-1} proves the absence of thiol group indicating that the reaction has taken place at the thiol group. The presence of tertiary butyl groups in the molecule is shown by the bands at 1363 cm^{-1} and 1390^{-1}.

N.M.R. spectrum (see fig.(13)).

The adduct structure was labelled as follows during the analysis of the N.M.R. spectrum:



According to the above structure hydrogen atom ratio



SAMPLE Am 1.

ORIGIN M.R.N Fernando

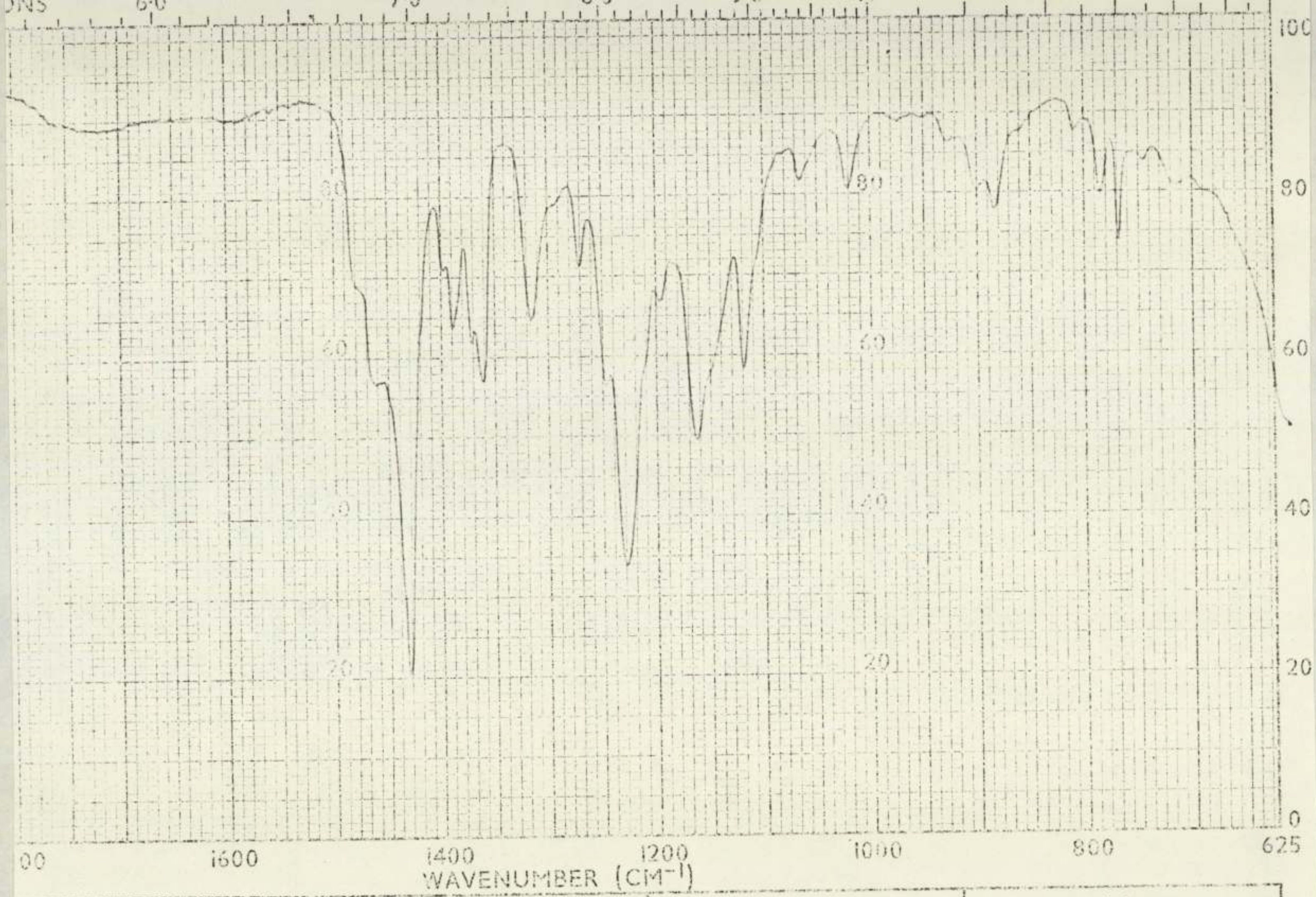
SOLVENT -

CONCENTRATION neat.

CELL PATH Thin Smear

REFERENCE Air.

Fig. 12. I.R. spectrum of 2-methyl-but-2-ene and mercaptan adduct.



REMARKS

SCAN SPEED Slow.

SLIT Standard.

Intek
RPK/215/1001 472-5089

OPERATOR V.M. Clenton.

DATE 27th June 1974

REF. NO. H428

Fig. 12 continued.

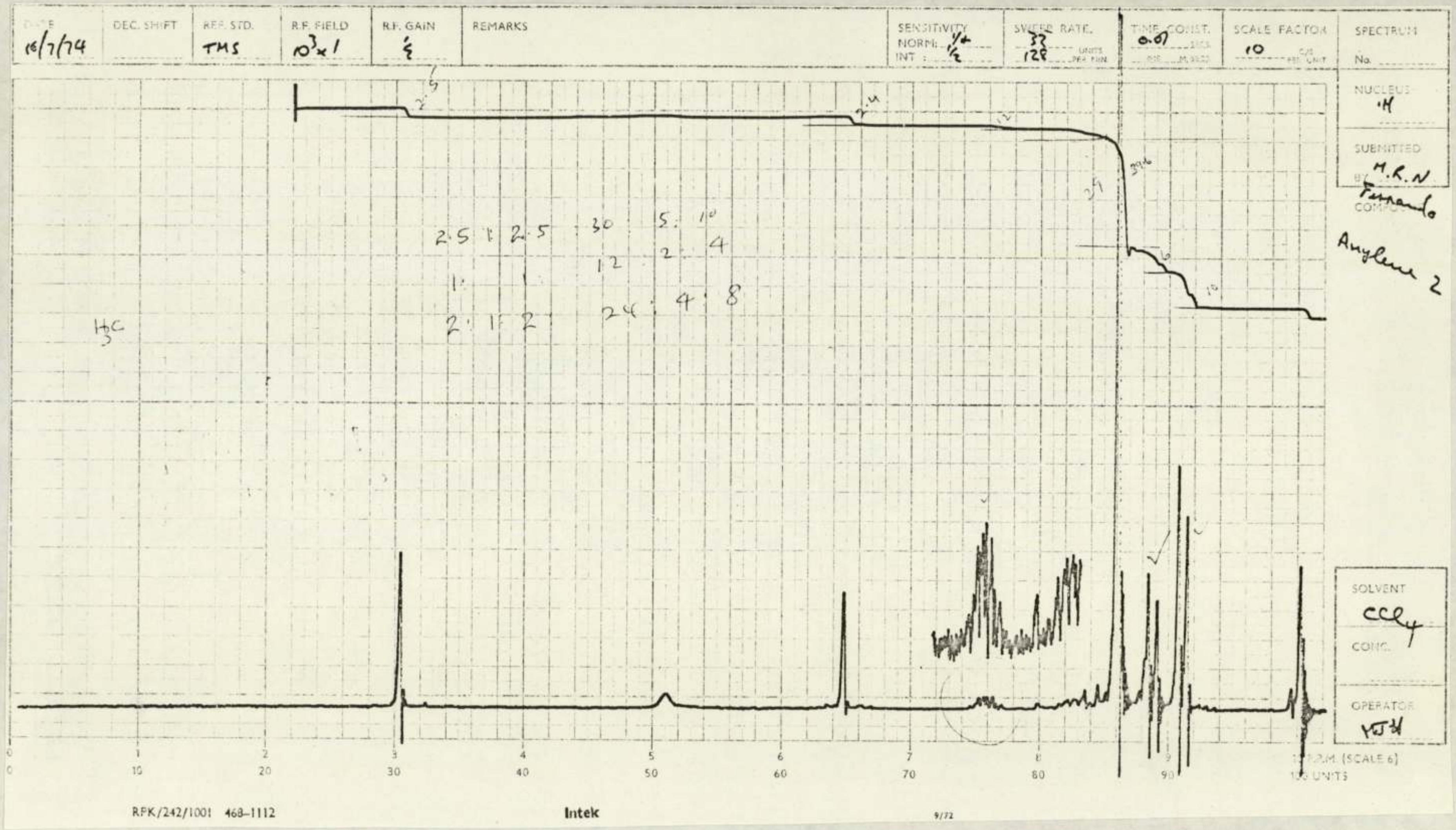


Fig. 13. N.M.R. spectrum of 2-methyl-but-2-ene and mercaptan adduct.

at different positions of the molecule should be as follows:

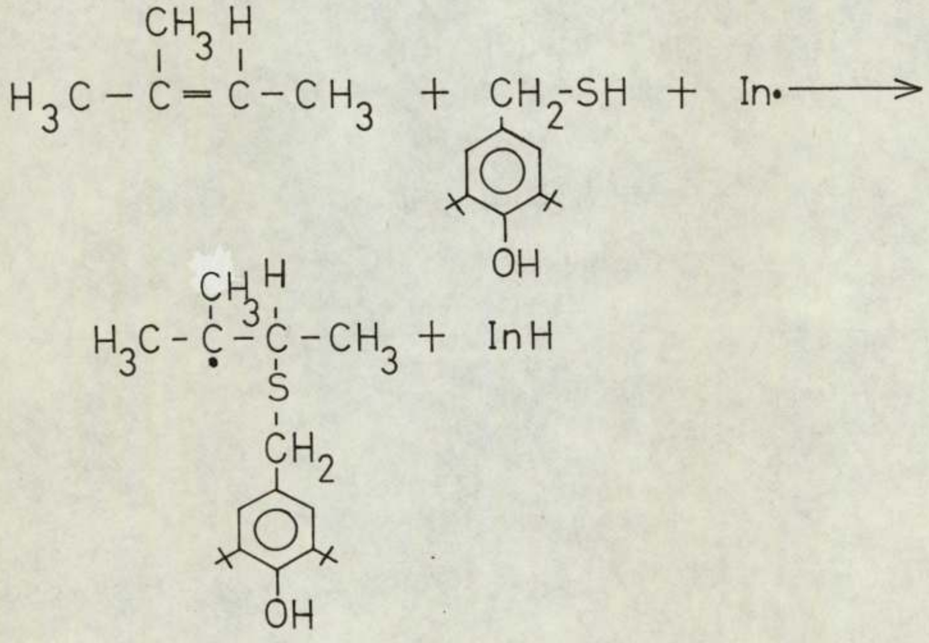
a : b : c : d : e : f : g : h

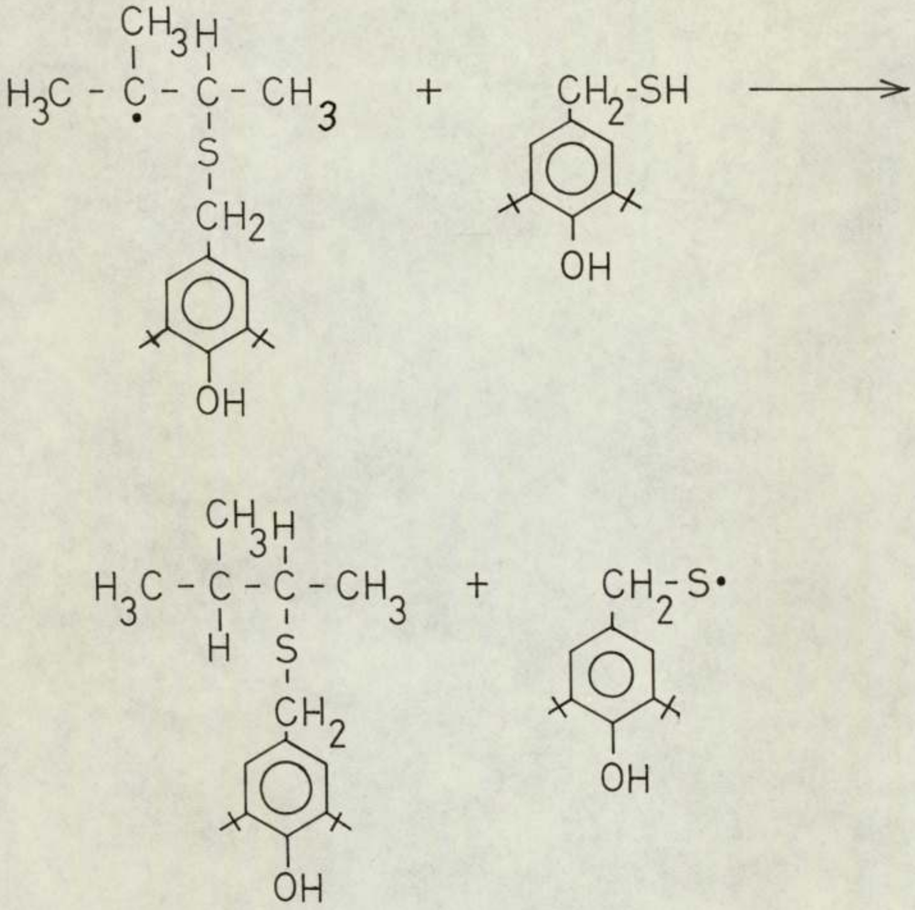
2 : 1 : 2 : 1 : 1 : 18 : 3 : 6

Such a ratio is more or less observed in the spectrum and the different bands are as follows:

Aromatic Protons	a	3.04 τ	(Singlet)
Phenolic Proton	b	5.05 τ	(Singlet)
Methylenic Protons	c	6.48 τ	(Singlet)
Proton	d	7.6 τ	(Multiplet)
Proton	e	8.4 τ	(Multiplet)
Tertiarybutyl Protons	f	8.6 τ	(Singlet)
Methyl Protons	g	8.9 τ	(Doublet)
Methyl Protons	h	9.1 τ	(Doublet)

Therefore the above spectroscope data clearly confirms the structure of the adduct, and the path of the reaction should be as follows which agrees with known theoretical data.





CHAPTER 3

The Addition of Thiols to Polymers

3.1. Introduction

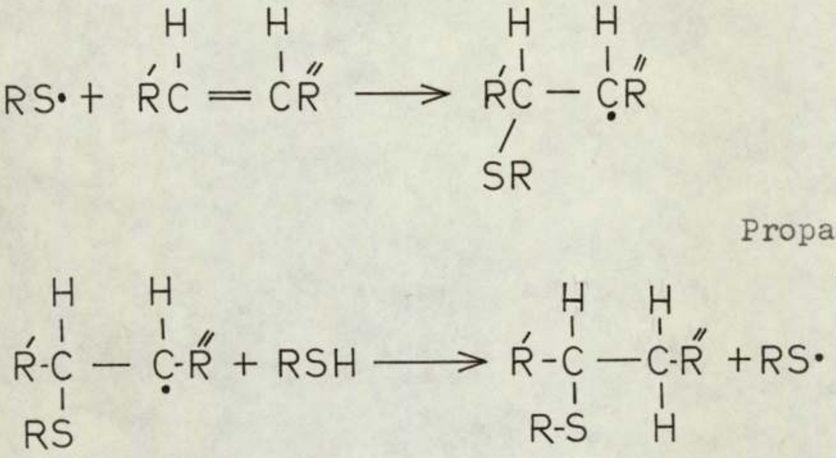
The mechanisms of addition of thiols to olefins as well as product isolation and identification have been fully dealt with in the previous Chapter. Particular attention was paid to olefinic model compounds for rubber and the antioxidant-containing thiol. The addition of 3,5-Ditert-butyl-4-hydroxy benzyl mercaptan to natural rubber is thoroughly investigated in the present Chapter to determine the kinetics of the reaction as well as the optimum conditions for the mercaptan - rubber interaction. Kinetic investigations are carried out with rubber solutions as well as with latex using thermal and photochemical methods initiation.

3.2. The Addition of Thiols to Polymers

The addition of mercaptans to polymers containing unsaturation proceeds by a free-radical mechanism, and standard emulsion polymerisation catalysts act as initiators in this reaction. The formation of a thiyl radical by the action of the initiator on the mercaptan, is the initiation step. This thiyl radical will then attack a double bond in the polymer chain, forming an adduct radical, and this radical in turn propagates the chain by abstracting a hydrogen atom from a molecule of the mercaptan, yielding a saturated product and a new thiyl radical. The above two steps of initiation and propagation can be represented as follows:

Initiation

$$I\cdot + RSH \longrightarrow RS\cdot + IH$$



$$RS\cdot + R'\overset{H}{C} = \overset{H}{C}R'' \longrightarrow R'\underset{SR}{\overset{H}{C}} - \underset{\bullet}{\overset{H}{C}}R''$$

Propagation

$$R'\text{-}\underset{RS}{\overset{H}{C}} - \underset{\bullet}{\overset{H}{C}}\text{-}R'' + RSH \longrightarrow R'\text{-}\underset{R\text{-}S}{\overset{H}{C}} - \underset{H}{\overset{H}{C}}\text{-}R'' + RS\cdot$$

where I. is the initiator radical, RSH is the mercaptan and $R' - \underset{H}{C} = \underset{H}{C} - R''$ represents an unsaturated polymer.

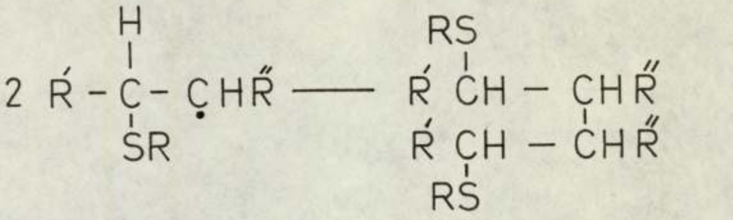
Oxygen plays an important role in this reaction. In the absence of an initiator, small quantities of oxygen can act as the free radical generator, while at higher levels it promotes chain-scission. With rather high levels of oxygen the reaction taking place will be a co-oxidation rather than an addition(133).

Termination of the reaction can occur in one or more of the three following possible ways:

1. $2\ RS\cdot \longrightarrow RSSR$

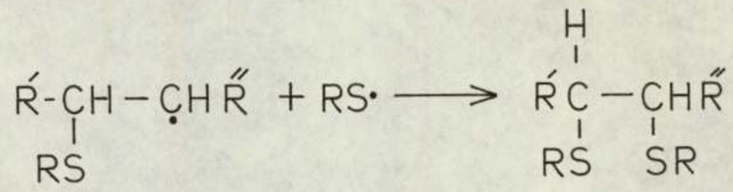
Termination

2.



$$2\,R'-\overset{H}{\underset{SR}{C}}-\dot{C}HR'' \longrightarrow \begin{array}{l} R'\overset{RS}{CH}-CHR'' \\ \quad\;\; | \\ R'\underset{RS}{CH}-CHR'' \end{array}$$

3.



$$R'-\underset{RS}{CH}-\dot{C}HR'' + RS\cdot \longrightarrow R'\overset{H}{\underset{RS}{C}}-\underset{SR}{C}HR''$$

The ultimate aim of this work is to produce a polymer network containing a bound antioxidant grouping, attached to the polymer via a sulphur link. Therefore the formation of the disulphide by the first of the termination reactions will be undesirable, as the disulphide which is formed at the expense of the mercaptan could be lost from the polymer by extraction. However, the disulphides are also good antioxidants and therefore they will serve a purpose as far as they remain within the polymer. In any case the smaller the amount of disulphide formed, the better will the efficiency of the addition reaction be.

The formation of two vicinal sulphur links at both ends of the double bond is also highly undesirable, because of its low stability under conditions of ageing (133).

Chain lenthening by the second of the termination reactions should lead to an increase in the gel content of the polymer.

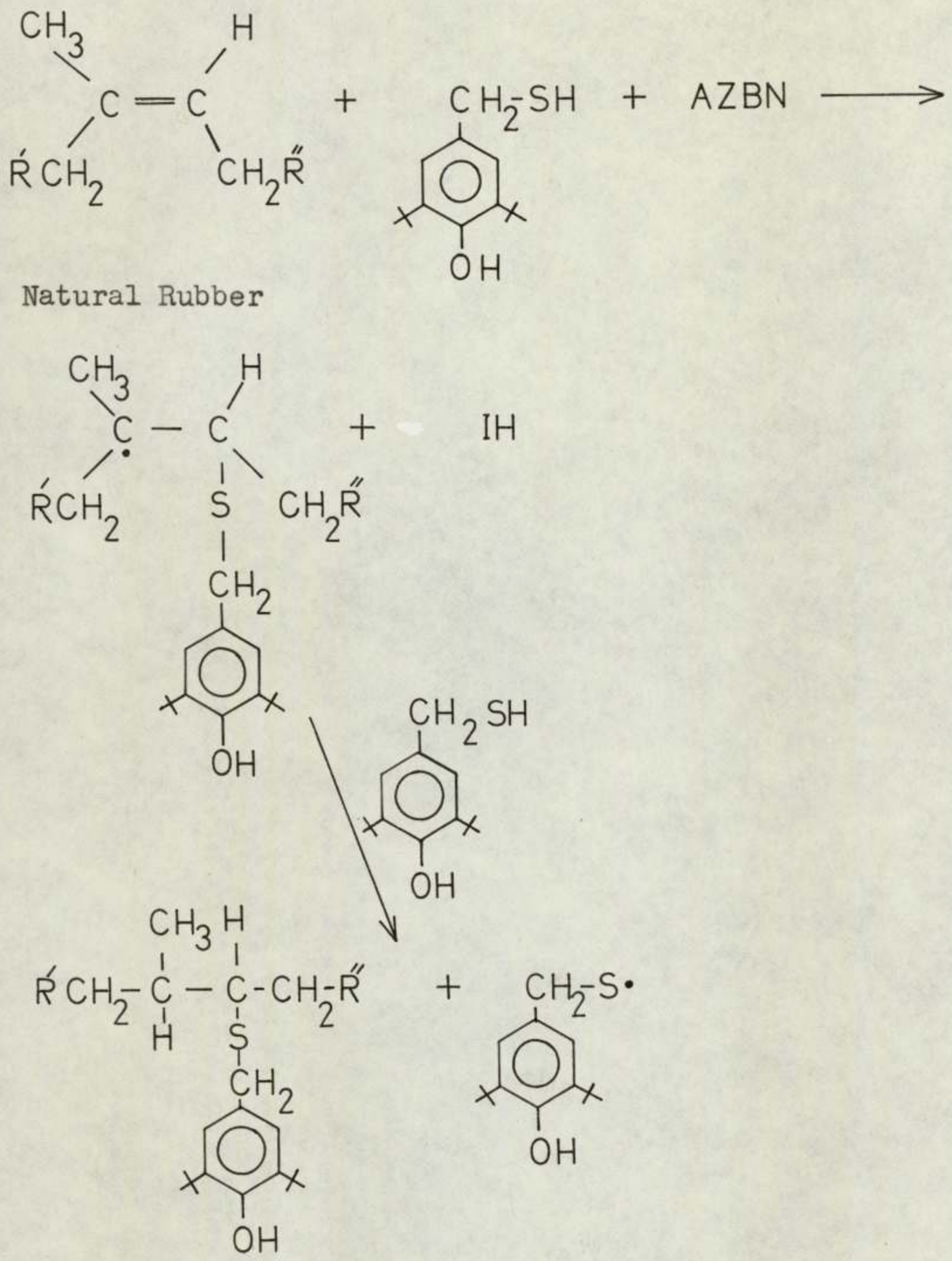
3.3. The Reaction of a Hindered Phenol containing a Mercaptan function with Natural Rubber

As mentioned earlier the mercaptan function adds readily to polymeric double bonds, and a high level of double bond saturation can be obtained. This feature of the reaction was made use of in this project and an antioxidant function has been successfully built into the natural rubber network through a mercaptan-double bond addition reaction.

The mercaptan used was a derivative of 2,6 Ditertiarybutyl phenol which itself is a commercially available antioxidant. 2,6 Ditertiarybutyl can be converted to 3,5 Ditertiarybutyl-4- hydroxy benzyl mercaptan by chloromethylation and subsequent reaction with magnesium hydroxide and hydrogen sulphide(See Chapter 2).

In the presence of a free radical initiator, 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan can add to the double bonds in the natural rubber network in the following way. Although there are two possible ways of addition across the double bond, the one depicted below is expected to occur because the adduct radical should be the more stable of the two alternatives.

The method of addition has been shown in model compound studies. (see Chapter 2).



The reaction should initiate and propagate as shown above until termination can occur by one or more of the ways already discussed(page 63).

If the 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan remains attached to the main rubber chain, both the phenolic grouping and the sulphide group can function as antioxidants which will remain within the rubber network. The presence of a methylene grouping between the phenol and the rubber chain may increase the mobility of the hindered phenolic segment thus increasing its efficiency as an antioxidant.

It also must be noted that, as the unsaturation content decreases in the rubber by the mercaptan addition, enough double bonds should remain in the polymers if it is to be vulcanised subsequently by a conventional sulphur vulcanisation.

3.4. Experimental

3.4.1. Grafting in Solution

The addition reactions of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan to rubber were carried out using Natural rubber (Pale Crepe), as well as synthetic polyisoprene (Natsyn). The rubbers were extracted in acetone for a period of 24 hours prior to the preparation of solutions. Extraction was carried out under nitrogen to avoid any oxidative breakdown.

The addition reactions in solution were carried out under vacuum to completely avoid the presence of oxygen.

3.4.1.1. The effect of reaction time on addition

Materials

4.0% Natural rubber solution in chlorobenzene

2.0% Mercaptan solution in chlorobenzene

AZBN - recrystallized from ether.

The experiment was carried out at 50°C which is adequate to form free radicals from the initiator. Although the usual initiator concentration used in this type of grafting reactions is in the range of 1.0 to 2.0% w/w on mercaptan, an excess concentration of 4.0% on mercaptan was used so that the initiator concentration does not act as a rate determining parameter. The ratio of mercaptan to rubber was 1:2.5 by weight which is approximately equivalent to a molar ratio of 1:0.67 as the molecular weights of an isoprene unit and 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan are 68 and 252 respectively.

Method

Six long necked 50 ml. round bottomed flasks were charged with 5.0 ml. of rubber solution, 25.0 ml. of mercaptan solution and 0.02 gm. of AZBN. The tubes were then completely degassed using glass cones fitted with taps and kept in a water bath at 50°C for different periods of time. The tubes were agitated regularly. After specific periods of time the contents in the tubes were transferred to beakers and coagulated with excess of isopropyl alcohol. The polymers thus obtained were extracted in acetone for 24 hours to remove any ungrafted mercaptan, dried under vacuum and 2.0% solutions were made using carbontetrachloride as the solvent. I.R. Spectra of these solutions were obtained using a Perkin-Elmer-577-Infrared Spectrophotometer fitted with sodium chloride windows. A typical spectrum of a mercaptan-rubber adduct is shown in fig. 14.

The samples were numbered as follows:

Sample No.	-	1	2	3	4	5	6
Reaction time (Hours)	-	2	4	8	12	16	24

Analysis of the Spectra

The band appearing at 3640 CM^{-1} in the I.R. Spectra is characteristic for the phenolic hydroxyl group in the antioxidant containing thiol. To carryout a quantitative estimation of level of grafting, a calibration curve was made use of, which was obtained using the spectra of rubber solutions containing predetermined quantities of the mercaptan in carbon tetrachloride.

Quantitative Estimation

Solutions

2.0% Rubber solution in carbon tetrachloride
2.0% Thiol solution in carbon tetrachloride

Procedure

0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 ml. quantities of the 2.0% mercaptan solution were added to 2.0 ml. samples of the 2.0% rubber solution and their I.R. Spectra were obtained. (See fig. 15). The heights of the phenolic


2·5
3·0
4·0
5·0
MICRONS
6·0
100
80
60
40
20
0
TRANSMITTANCE (%)
80
60
40
20
80
60
40
20
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM⁻¹)

Fig. 14.

Fig. 14 continued.

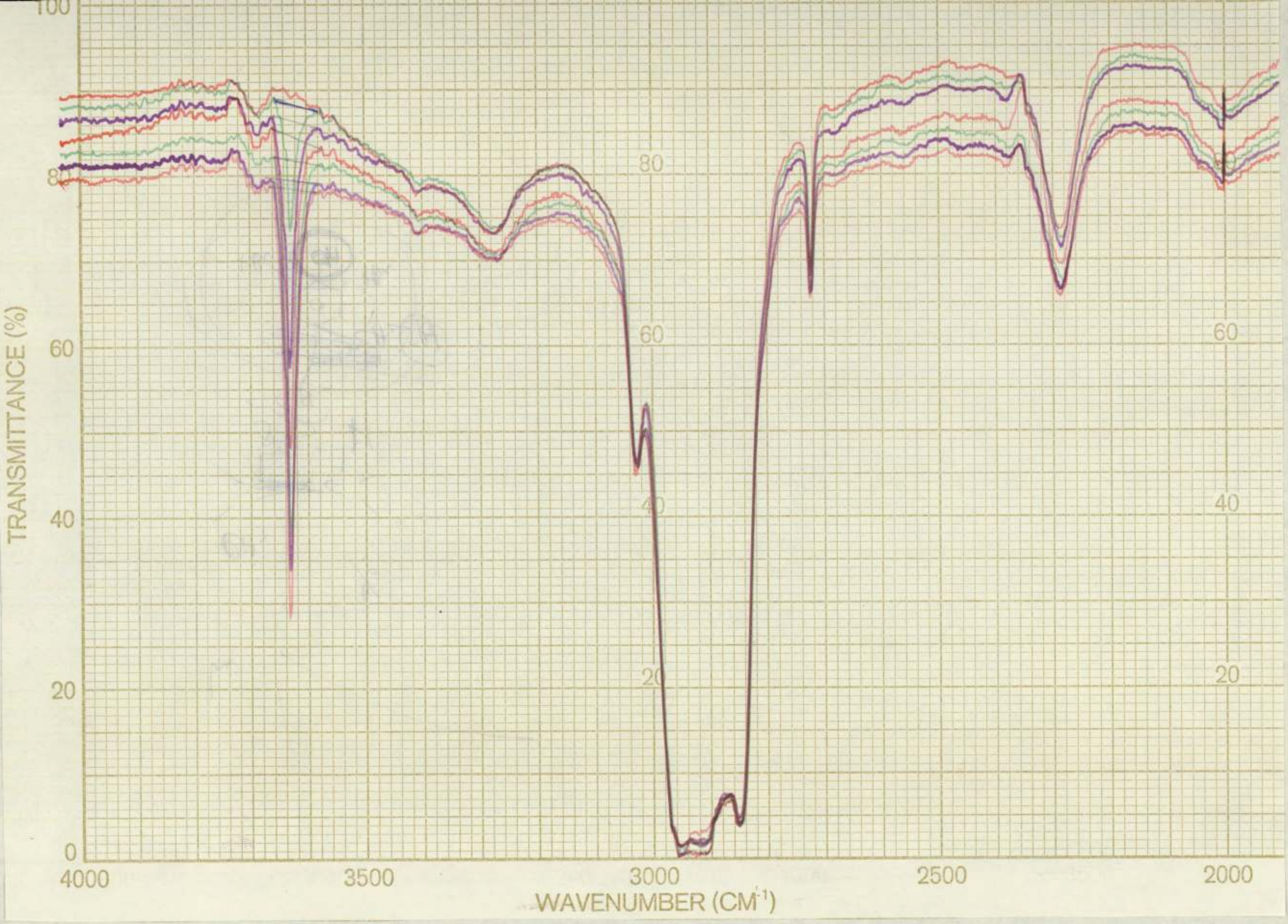

TRANSMITTANCE (%)
100
80
60
40
20
0
80
60
40
20
60
40
20
4000
3500
3000
2500
2000
WAVENUMBER (CM^{-1})

Fig. 15.

hydroxyl group were measured and after making the correction for dilution, these values were plotted against the mercaptan to rubber w/w ratio. (See fig. 16). From fig.16 it is clearly seen that the height of the hydroxyl peak increases with the increase in the thiol to rubber ratio. This calibration curve provides the mercaptan to rubber w/w ratio of a given sample once the height of the phenolic hydroxyl peak is known; and the obtained values for the above samples are given below:

Sample No.	-OH Peak (mm)	% Wt. Bound	Reaction Time (Hours)
1	1.0	0.25	2
2	2.5	0.5	4
3	49.5	11.25	8
4	58.2	13.75	12
5	62.5	15.25	16
6	65.0	16.00	24

A graph of % Wt. Bound mercaptan against reaction time was plotted and is shown in fig.17.

Discussion

It is seen from the above table and fig.17 that the reaction is almost complete within a period of 8 hours. The change in the extent of grafting at reaction times longer than 10 hours is comparatively low. At lower reaction times, i.e. for a period of upto 4 hours the extent of grafting is negligible.

3.4.1.2. The effect of temperature on the addition reaction

Azobisisobutyronitrile is active as a free-radical

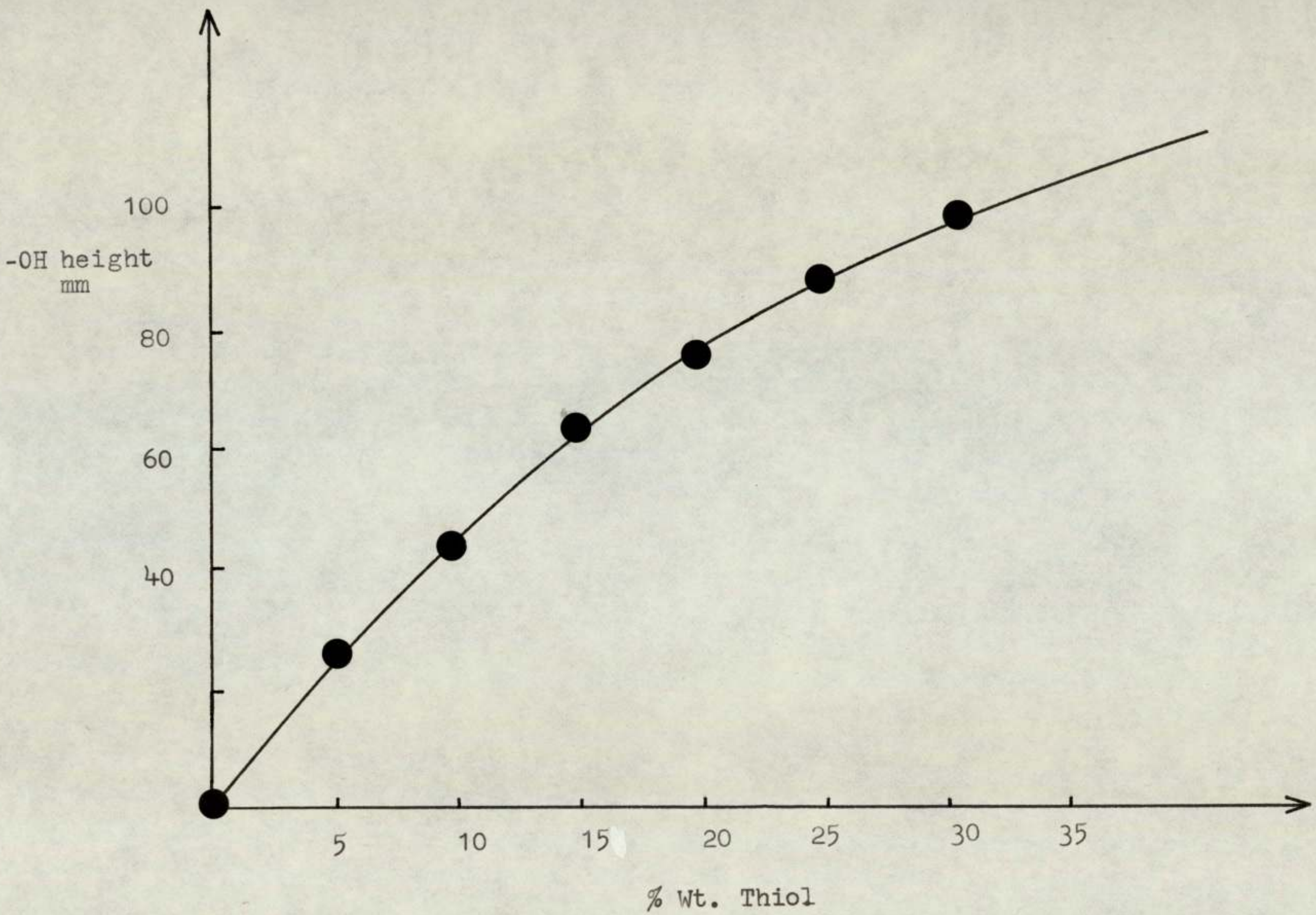


Fig. 16.

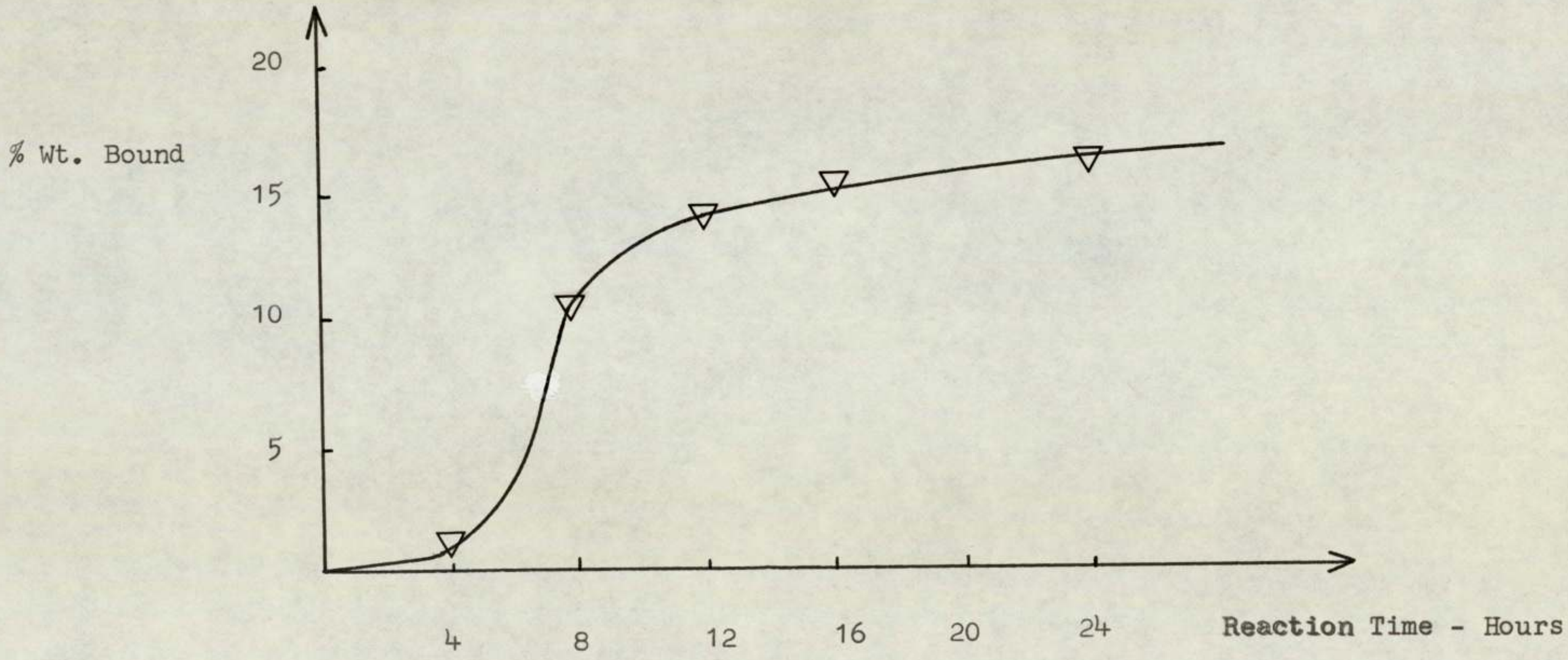


Fig. 17.

initiator at temperatures of 30 - 80°C. Therefore the effect of temperature on the extent of grafting was investigated at four temperatures, viz. 30°C, 40°C, 50°C and 60°C. Although chlorobenzene is a comparatively high boiling solvent, it cannot be used at temperatures higher than 60°C where the reaction tubes have to be degassed completely.

Materials

4.0% Rubber solution in chlorobenzene
2.0% Mercaptan solution in chlorobenzene
Azobisisobutyronitrile

Procedure

Sixteen reaction flasks were charged with 5.0 ml. of rubber solution, 25.0 ml. of mercaptan solution and 0.02 gms. of azobutyronitrile. After degassing they were kept in water baths at 30°C, 40°C, 50°C and 60°C for different periods of time. After the specific time of reaction, the contents of each tube were coagulated using isopropyl alcohol. The rubber thus obtained was extracted in acetone, dried under vacuum and then dissolved in carbon tetrachloride to prepare 2.0% solutions for I.R. Spectroscopy. From these spectra the height of the characteristic phenolic hydroxyl group was measured and the corresponding mercaptan to rubber w/w ratio was obtained as before, using the calibration graph. The calculated values are given below:

Temperature 30°C.

Sample No.	-OH Peak (mm)	% Wt. Bound	Reaction Time(Hours)
1	-	-	4
2	-	-	8
3	-	-	12
4	-	-	16

Temperature 40°C.

Sample No.	-OH Peak (mm)	% Wt. Bound	Reaction Time(Hours)
5	1.0	0.25	4
6	45.2	10.25	8
7	55.3	12.75	12
8	57.4	13.50	16

Temperature 50°C.

Sample No.	-OH Peak (mm)	% Wt. Bound	Reaction Time(Hours)
9	2.5	0.5	4
10	49.5	11.25	8
11	58.2	13.75	12
12	62.5	15.25	16

Temperature 60°C.

Sample No.	-OH Peak (mm)	% Wt. Bound	Reaction Time(Hours)
13	6.2	1.25	4
14	53.4	11.75	8
15	58.4	13,75	12
16	65.3	15.75	16

Using the above data the extent of grafting was plotted against the temperature for different reaction times and the graph thus obtained is shown in fig. 18.

Discussion

No grafting occurs at 30°C even with 16 hours of reaction time and this can be attributed to the stability of azobisisobutyronitrile at such a low temperature. At 40°C grafting occurs to a considerable extent and the increase in temperature from 40°C to 60°C does not produce a proportionately increased effect. The effect of increasing the reaction time is also clearly demonstrated by the same graph. At reaction times higher than 8 hours the extent of formation of the adduct does not increase proportionately. Therefore with a reaction time of 8 hours and at a temperature of 50°C the extent of addition of the mercaptan to natural rubber reaches more or less a steady level, which is followed by a plateau at higher temperatures and with longer reaction times.

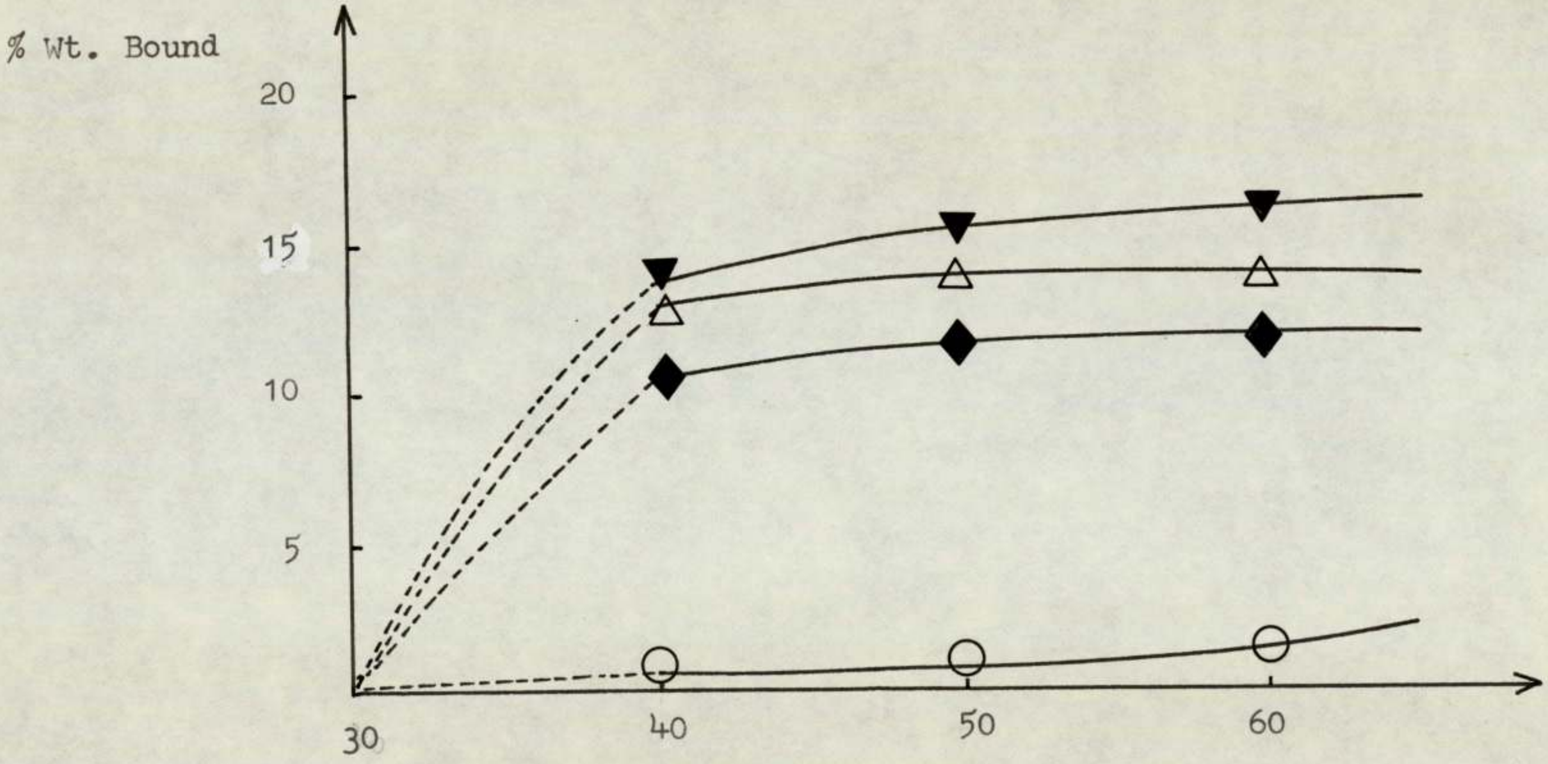
3.4.1.3. The effect of thiol concentration on addition

Materials

The same solutions of rubber and mercaptan were used in this investigation. The concentration of initiator was kept at a higher level to prevent it from being a limiting factor.

Procedure

Four reaction vessels were charged with the following quantities of polymer, antioxidant, and the initiator, and were degassed:



Temperature °C.

Fig. 18.

Sample No.	Rubber Solution (ml.)	Thiol Solution (ml.)	Initiator (gm.)
1	5	5	0.04
2	5	10	0.04
3	5	25	0.04
4	5	50	0.04

The reaction vessels were then kept in a water bath at 50°C for a period of 12 hours with regular stirring. Then the contents in the tubes were precipitated using isopropyl alcohol and after extraction in acetone the rubber samples were dried under vacuum. 2.0% solutions of these rubbers were prepared in pure carbon tetrachloride and their I.R. Spectra were obtained. From these the heights of the characteristic phenolic hydroxyl band were measured and the corresponding percentages of bound mercaptan were calculated using the calibration graph. The values obtained are given below:

Sample No.	-OH Peak Height (mm)	% Wt.Bound	% Wt.Added	Yield %
1	4.0	2.0	33.3	6.0
2	18.5	8.9	50.0	17.8
3	30.5	14.8	66.6	22.2
4	33.5	16.3	83.3	29.5

Using the above values a graph of extent of grafting was plotted against the mercaptan to rubber w/w ratio and is shown in fig. 19.

Discussion

Fig.19 shows that an increase in the initial amount of mercaptan added, at constant initiator concentration,

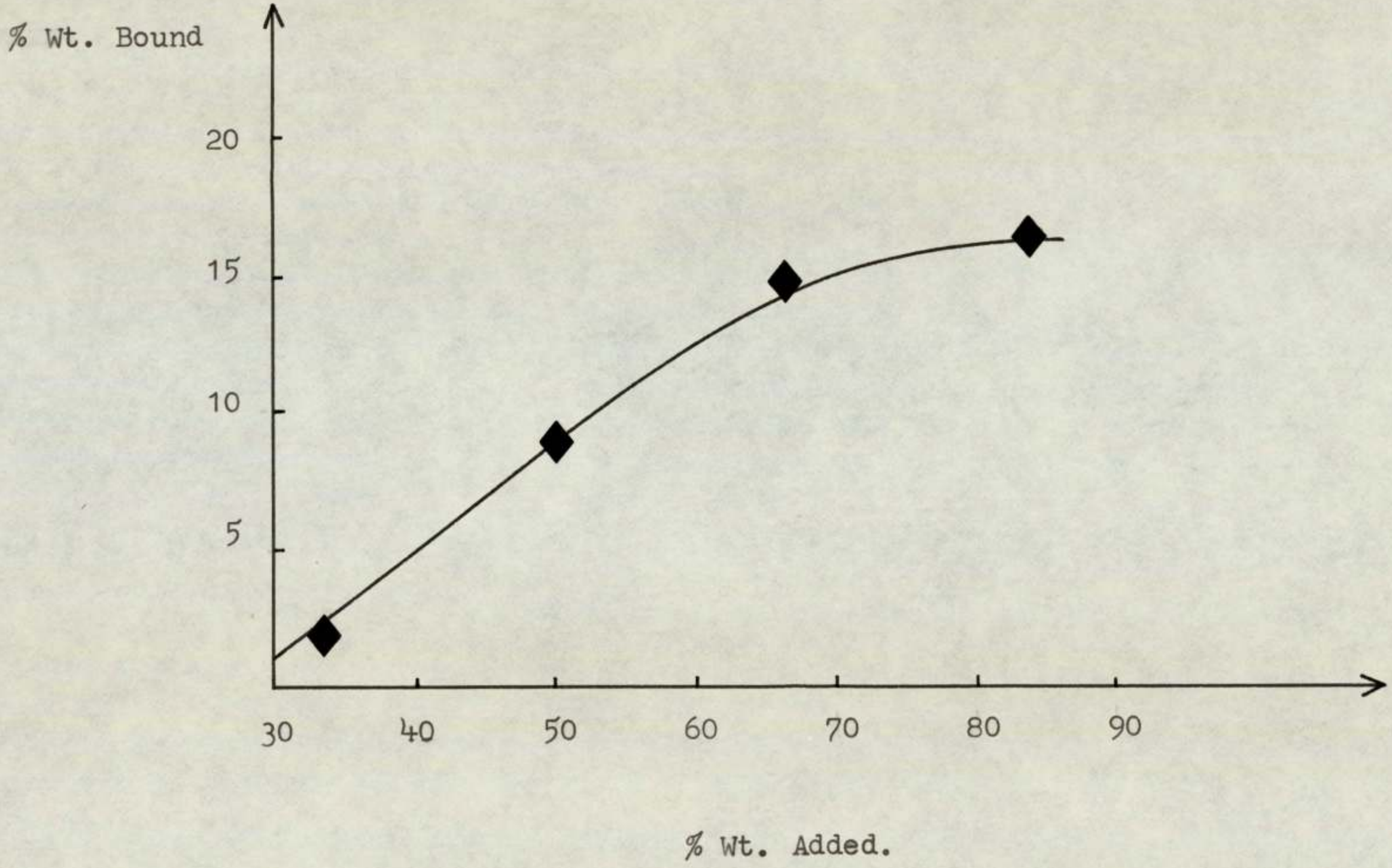


Fig. 19.

results in an increase in the quantity of rubber bound mercaptan formed. But this effect is significant only upto a certain maximum value of mercaptan to rubber w/w ratio. The change in the extent of grafting beyond this maximum is comparatively less. It is also evident that the yield of the reaction too does depend on this ratio of the initial quantity of mercaptan used in the grafting reaction.

3.4.1.4. The effect of Initiator concentration

In free radical reactions the concentration of the initiator used has an effect upon the reaction only upto a certain critical concentration beyond which the effect is not very significant. It is also known that increased initiator concentration causes increased termination reactions. To investigate this behaviour an experiment was carried out using the same rubber and mercaptan solutions with given proportions of initiator.

Method

The following quantities of reactants were added into five reaction tubes:

Sample No.	40% Rubber solution (ml.)	Mercaptan (gms.)	AZBN (gms.)
1	5	0.5	-
2	5	0.5	0.01
3	5	0.5	0.02
4	5	0.5	0.04
5	5	0.5	0.08

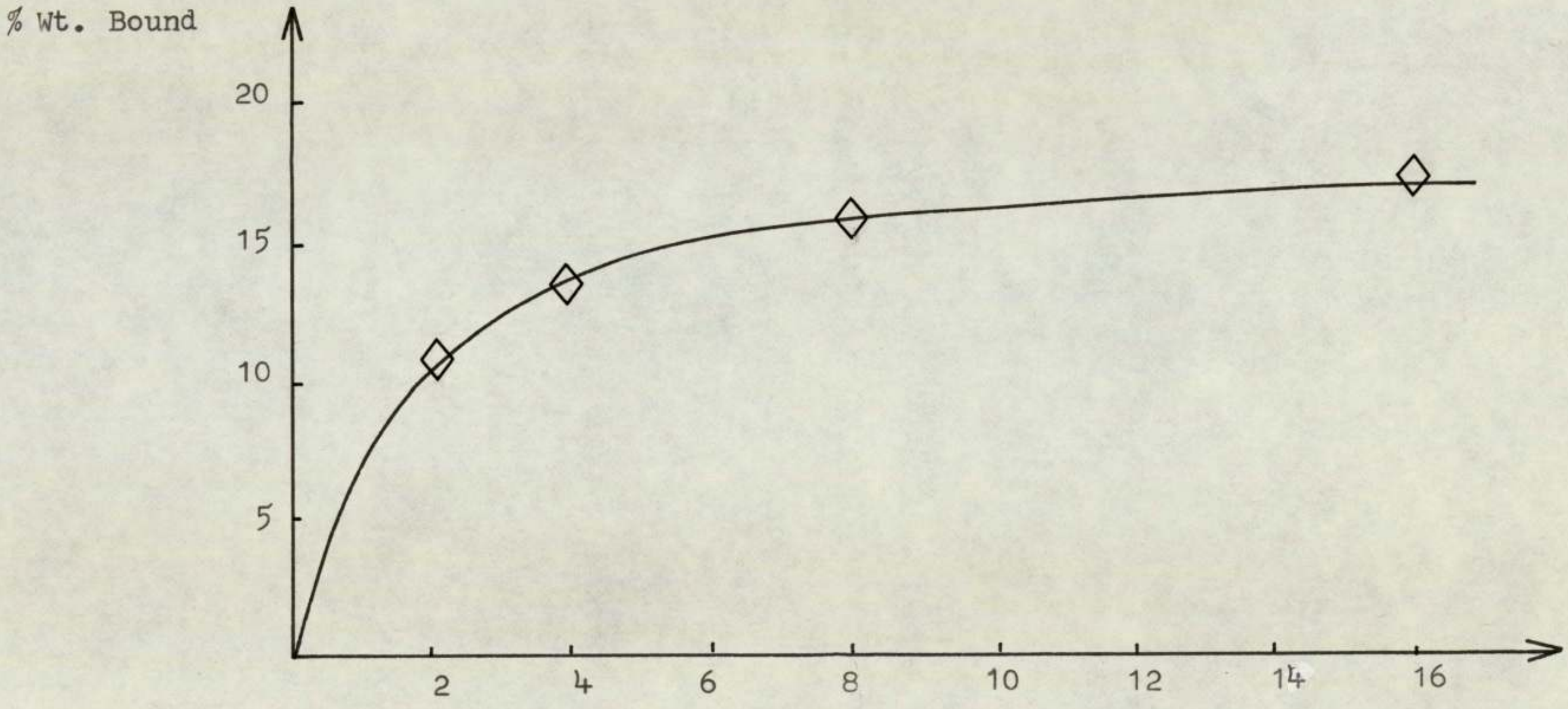
After degassing the tubes were kept at 50°C in a water bath for a period of 12 hours. Coagulation, extraction and drying were done as before. 2.0% solutions of the extracted dual dried samples were made in carbon tetrachloride for I.R. Spectroscopy. The heights of the phenolic hydroxyl bands were measured and the corresponding % wt. bound mercaptan values were obtained using the calibration curve. The results obtained are as follows:

Sample	-OH Peak height (mm)	% Wt. bound	% Wt. added	Initiator to mercaptan ratio	Yield %
1	-	-	-	-	-
2	46.1	10.3	71.4	2:100	14.4
3	57.2	13.5	71.4	4:100	18.9
4	64.1	15.5	71.4	8:100	21.7
5	67.4	16.7	71.4	16:100	23.4

The above values of % Wt. bound mercaptan are plotted against the initiator concentration and the graph obtained is shown in fig.20.

Discussion

Fig.20 shows that at higher concentration of initiator the quantity of mercaptan grafted on to the rubber is higher. With no initiator no grafting occurs proving that the presence of the free radical generator is essential for the initiation of the thiyl radical grafting reaction. At higher levels of initiator the effect is not proportionate, because the change in the extent of grafting when the initiator to mercaptan ratio is raised from 8:100 to 16:100 is not in the ratio of 1:2. This may be due to increased termination reactions.



Initiator:Mercaptan ratio w/w.

Fig. 20.

3.4.1.5. Addition by photochemical initiation

The addition reaction of the mercaptan to the rubber network starts by the decomposition of the free radical initiator, AZBN, giving two free radicals. It is well known that this initial breakdown of the initiator could be carried out thermally or by U.V. irradiation. Therefore a series of experiments were carried out using rubber in solution form in the presence of the mercaptan and the initiator under U.V. irradiation.

Materials

Natural Rubber	10 g in 500 ml of chlorobenzene
AZBN	1 g in 50 ml of chlorobenzene
Mercaptan	2 g in 100 ml of chlorobenzene

Four reaction tubes were charged with the above solutions with different amounts of mercaptan solution as shown below and were degassed.

	Rubber Solution (ml.)	AZBN Solution (ml.)	Mercaptan Solution (ml.)
UV 1	10	2	5
UV 2	10	2	10
UV 3	10	2	15
UV 4	10	2	20

The reaction tubes were then irradiated under U.V. light for a period of 70 hours, (temp. 30°C) and then the samples were coagulated washed, extracted, dried in the same manner as before. Infra red spectra of these samples were obtained in CCl_4 solution. As only minute quantities of polymer were recovered almost in the form of a powder, obtaining solutions of equal concentration was not successful. Therefore as seen from the fig.(21) a quantitative estimation of the phenolic content in the adduct was not carried out. But, the presence of the mercaptan in the rubber is clearly seen through the sharp phenolic -OH band, appearing at 3640 cm^{-1}.

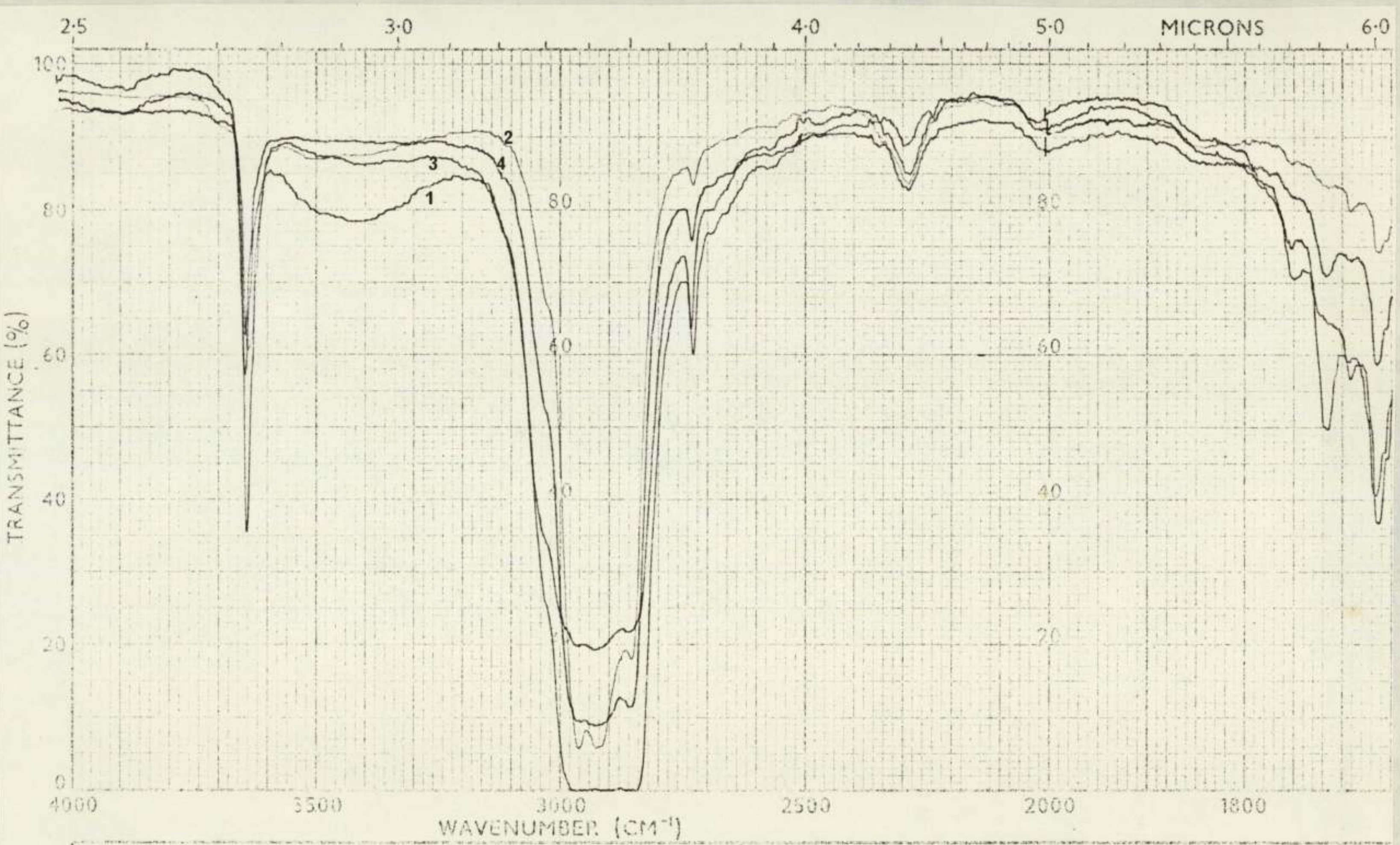
3.4.2. Grafting to latex

The preparation of antioxidant grafted rubber is of great practical importance as it provides a method of obtaining more durable elastomers. But the above studies were carried out in solution form where solvents have to be used which brings in severe limitations if the process is to be commercially applied. If the process of grafting can be successfully carried out in the latex form as well, the range of applicability of the process can be considerably widened. The latter is most important for the natural rubber producing countries where the elastomer is initially obtained in the latex form. Therefore experimental work was also carried out to investigate the process of grafting of the antioxidant containing thiol to natural rubber latex.

Procedure

Latex rubber

4500 ml of Qualitex A natural rubber latex (50% D.R.C.) stabilized with 0.5% ammonia were taken in a 5 litre beaker and were diluted with an equal amount of distilled water. Oxygen free nitrogen was bubbled through this latex at the



SAMPLE UV₁. — Green
UV₂. — Purple
UV₃. — Black
UV₄. — Red

ORIGIN

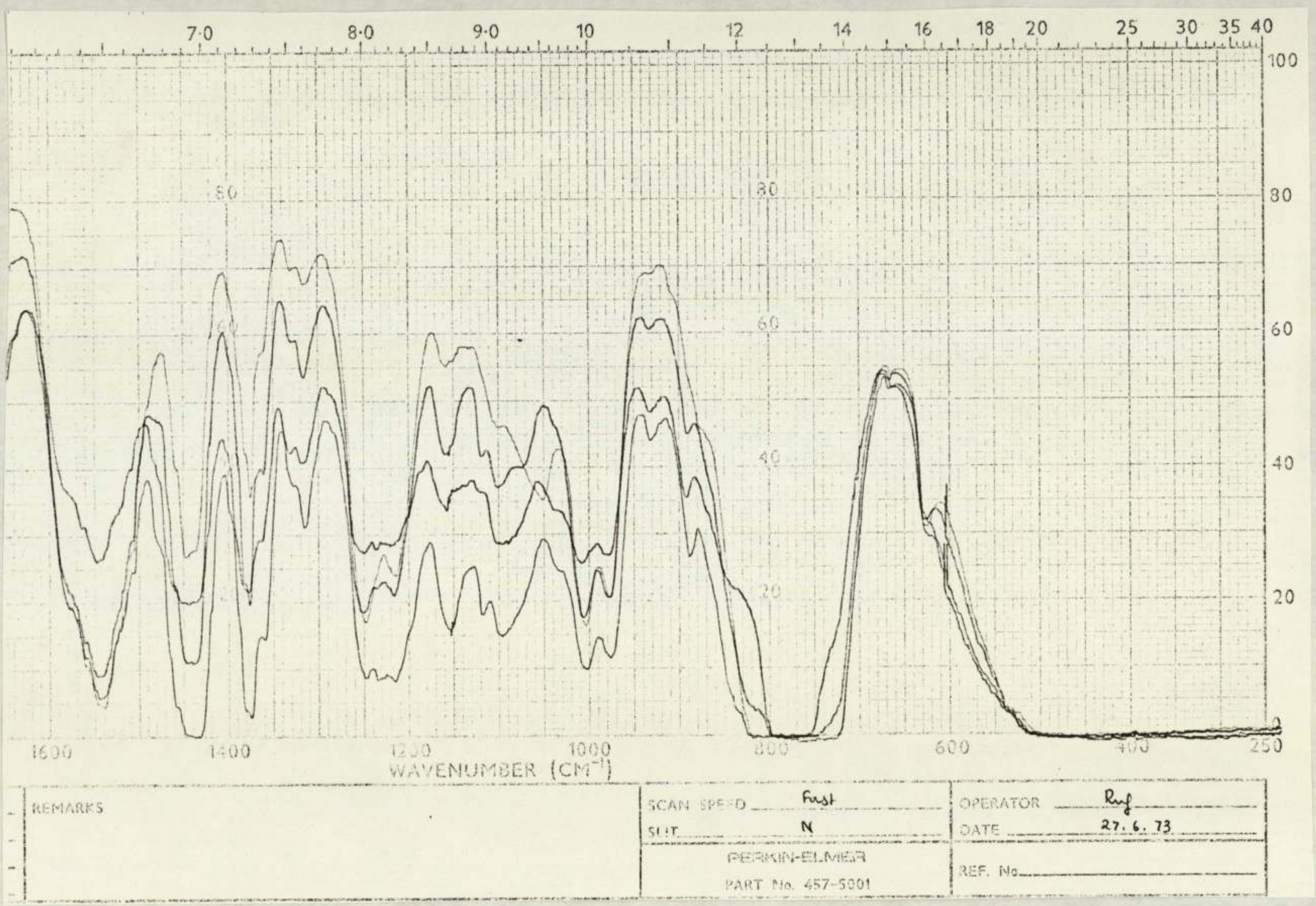
SOLVENT CCl_4

CONCENTRATION x various.

CELL PATH

REFERENCE NaCl cell

Fig. 21.



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REF. No.

Fig. 21 continued.

rate of 100 cc/min while stirring on a magnetic stirrer for a period of 48 hours. To the latex thus de-ammoniated, 15.0 gms (2% of the dry rubber content) of Vulcastab C paste (Sodium Oleyl Sulphate) was added, and stirring and nitrogen bubbling was continued for another 24 hours.

Vulcastab C was selected as the stabilizer because it is recommended as a dispersion stabilizer against heat, fillers and mechanical action. It is pale yellow or almost white in colour and therefore does not decolourize the latex. It was added by dissolving 15.0 g in 50 ml of distilled water after slight warming.

The latex thus obtained had a dry rubber content of approximately 25%, and was used in the grafting experiments.

Initiator

Azobisisobutyronitrile was again used as the initiator. It was purified by recrystallization from ether.

Grafting Experiments

Materials: 25% D.R.C. Latex (stabilized)
AZBN. 1.0 g in 50 ml of chlorobenzene
2.0 g of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan in 100 ml of chlorobenzene

The grafting experiments with small quantities of latex and additives were carried out in 100 ml pyrex boiling tubes with a hot water circulating heating jacket. The system is shown on page (95). The reactants were added into the inner tube A and the system was degassed through the tap C using a vacuum pump. Then hot water at the desired temperature from a thermostatic bath was circulated through the outer jacket B using a centrifugal pump, while stirring the whole system on a flask shaker.

3.4.2.1. The effect of mercaptan concentration

Two reaction systems were charged with 5.0 ml of 25% D.R.C. (stabilized) latex and 2 ml of 2% azobisisobutyronitrile in chlorobenzene. 10 ml of 2% 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan in chlorobenzene was added to one (L_1) and 20 ml of the same to the second (L_2). After degassing, hot water at 50°C from a thermostat was passed through the two systems while shaking for a period of 5 hours. After 5 hours the contents were poured into separate beakers and the latex mixture was coagulated with an excess of isopropyl alcohol. The coagulum was separated and dissolved in benzene and was again coagulated with isopropyl alcohol. This process was repeated three times and then the pieces of rubber thus obtained were extracted in thimbles on soxlet extractors with acetone for a period of 24 hours. After extraction the samples were dried in vacuum at 40° and then 2% solutions of them were made in pure carbon tetrachloride. A 2% carbon tetrachloride solution of an untreated sample of rubber (from latex) was also made for comparison, (Lo).

Infra-red spectra of these solutions were obtained using NaCl cells in a Perkin-Elmer 457 Infra red spectrophotometer and are shown in Fig.22.

The corresponding heights of the characteristic phenolic hydroxyl band were measured and with the use of the calibration curve, the bound mercaptan quantities (% Wt.) were calculated.

Sample No.	% Added	% Bound	Yield %
Lo	0	0	0
L1	13.7	4.85	35.4
L2	24.3	9.9	40.4

It is clearly seen from the above that, by increasing the quantity of mercaptan initially added to a given quantity of rubber, there is a marked change in the concentration of bound mercaptan in the extracted rubber although the conversion of the reaction does not vary considerably.

3.4.2.2. The effect of Initiator Concentration

Materials: 25 D.R.C. rubber latex
2.0 g of mercaptan in a 5 ml solution of chlorobenzene
1.0 g of AZBN in 50 ml of chlorobenzene

As in the previous experiment, two reaction systems were loaded with 5 ml of rubber latex and 2.5 ml of mercaptan solution. 2.0 ml of initiator solution was added to one (L_3) and 4.0 ml of the same to the second (L_4). After degassing, the reaction was carried out for

SAMPLE Red L_0
Black L_1
Green L_2

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

Fig. 22.

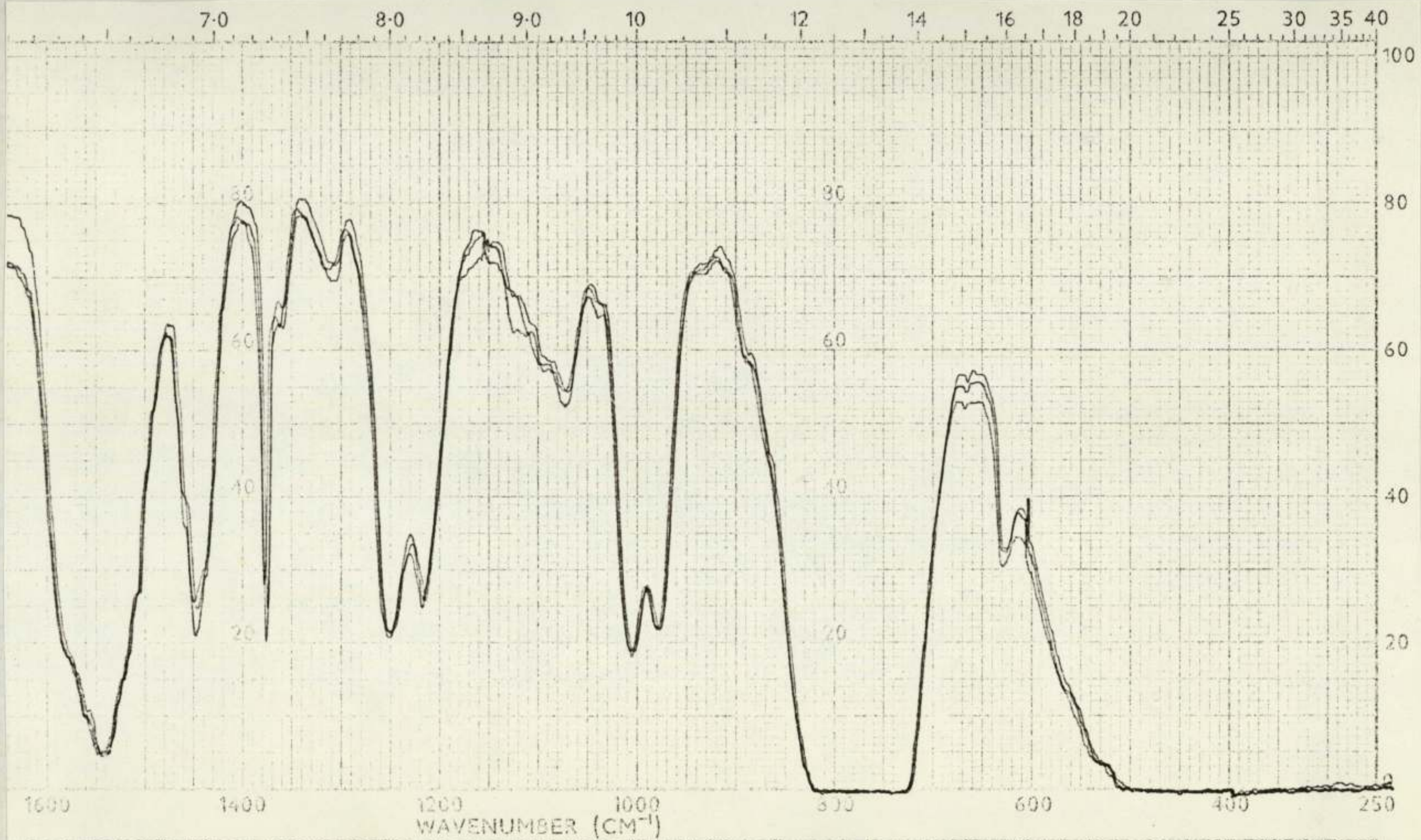

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Fig. 22 continued.

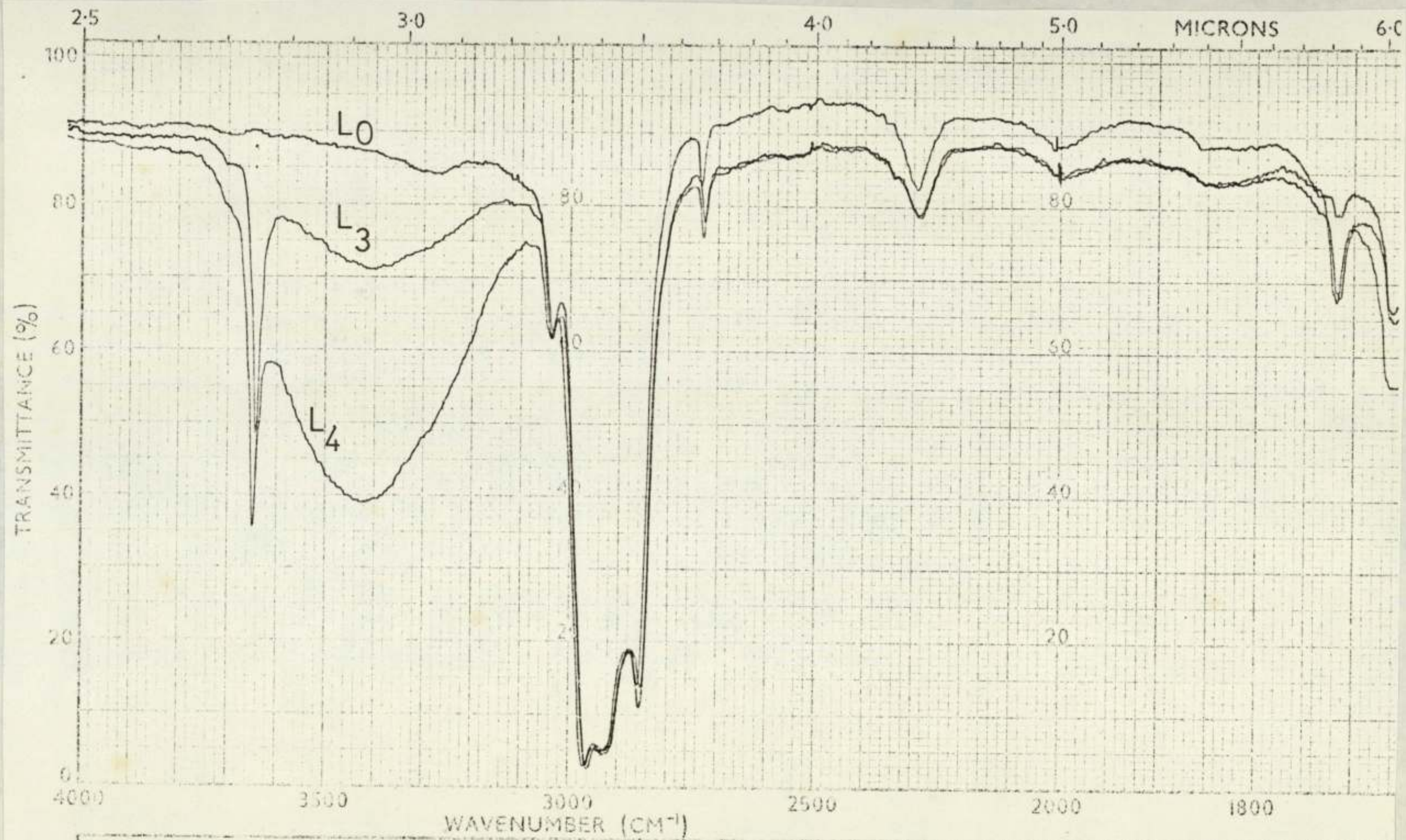
5 hours at 50°. Precipitation, extraction and drying were done as before. 2% CCl_4 solutions were made of the resulting samples and their Infra-red spectra were obtained. (See Fig.23).

Analysis of the spectra

The spectra of the solutions L_3 and L_4 with comparison to an untreated rubber solution L_o, clearly show the presence of the phenolic -OH group. There is also a marked change in the unsaturation content of the polyisoprene chain which can be seen from the peak at 1665 cm^{-1}. Characteristic absorption peaks of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan appear very clearly at 1434 cm^{-1}, 1392 cm^{-1}, 1362 cm^{-1}, 1320 cm^{-1}, 1170 cm^{-1}, and at 1120 cm^{-1}.

Sample No.	% Wt.Bound	% Wt.Added	Yield %	Initiator to mercaptan ratio (Wt.)
L_o	0	0	0	0
L_3	28.7	44.4	64.6	1:25
L_4	36.1	44.4	81.3	2:25

From the above table it is clearly seen that by increasing the initiator concentration a higher amount of mercaptan has been bound to the rubber with a given initial amount of the mercaptan. However, there should exist an optimum initiator concentration necessary to achieve a desired level of saturation of the double bonds, as there is a possibility for increased termination reactions with increased initiator concentrations.



SAMPLE Red L0
Black L3
Green L4

ORIGIN

SOLVENT CCl_4

CONCENTRATION 2%

CELL PATH

REFERENCE NaCl cell.

Fig. 23.

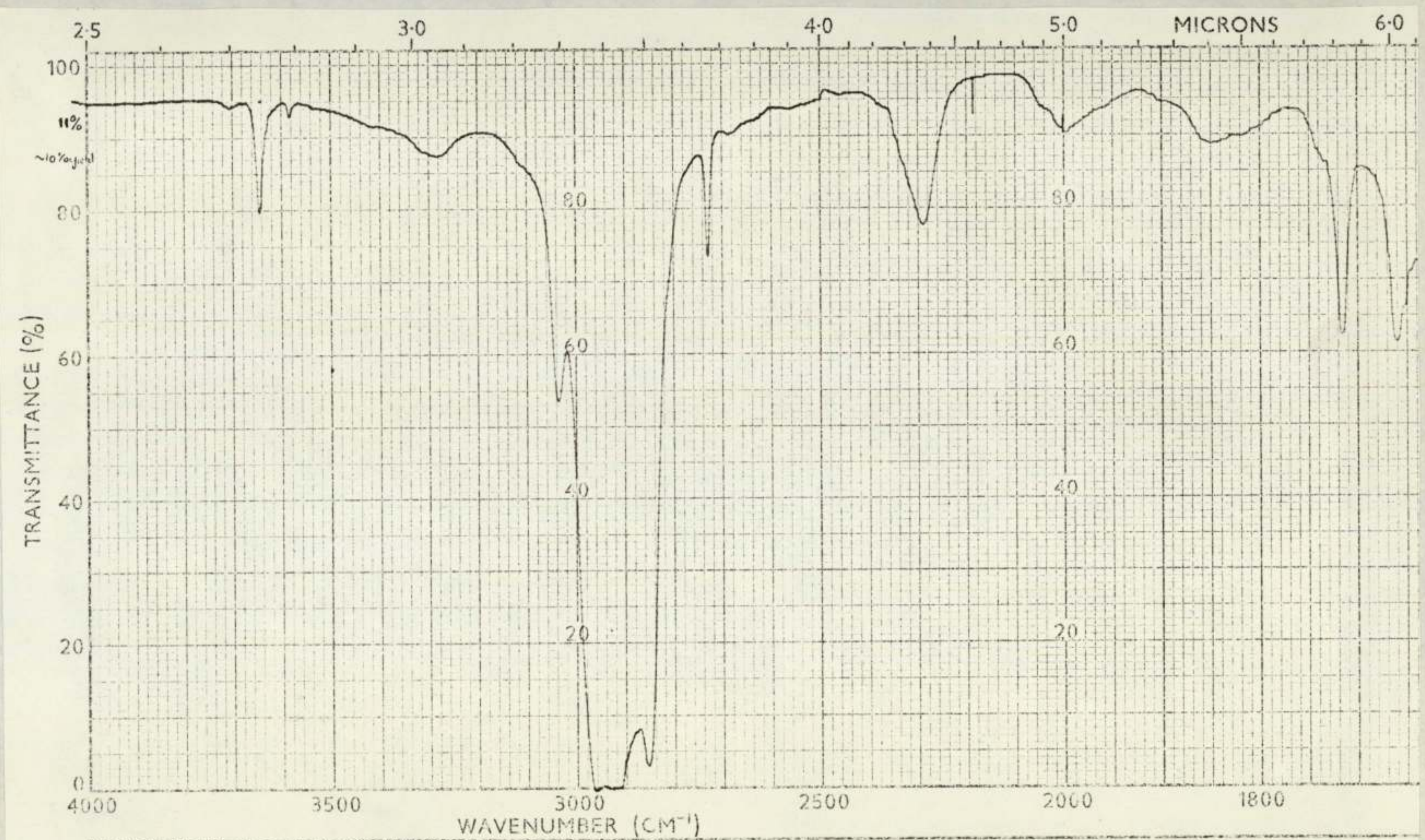
3.4.2.3. The effect of oxygen on the addition reaction

As mentioned earlier, the presence of oxygen plays a critical role in a radical addition reaction of mercaptan to an unsaturated compound. In the presence of considerable amounts of oxygen the reaction taking place will be a co-oxidation rather than addition.

As the previous addition reactions in this chapter were carried out in vacuo, there is a great necessity from a practical point of view to find out whether, the addition of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan to natural rubber latex could be carried out in air. Therefore the following experiment was carried out.

Experimental

Stabilized natural rubber latex was taken in a round bottomed flask and while stirring vigorously 125% molar of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan and 2% of azobisisobutyronitrile were added. The flask was kept open to the atmosphere and immersed in a water bath at 50°C. After a period of 24 hours the latex was coagulated using 2% formic acid and then the rubber was extracted for a period of 24 hours, in an azeotrope of acetone/methanol/1,1,1-trichloroethane. After drying in vacuum at 40°C a 2% solution was made in carbon tetrachloride and an infra-red spectrum of the solution was obtained using a sodium chloride cell. The infra-red spectrum is shown in Fig. 24.



SAMPLE N.R. latex stabilized
+ 125 molar percent of A
+ 2% J. in air
50°c 24 hours. 2% tannic acid; Ext, Dissolved with Ccl4

ORIGIN

SOLVENT Ccl4

CONCENTRATION 2%.

CELL PATH Nacl

REFERENCE

Fig. 24.

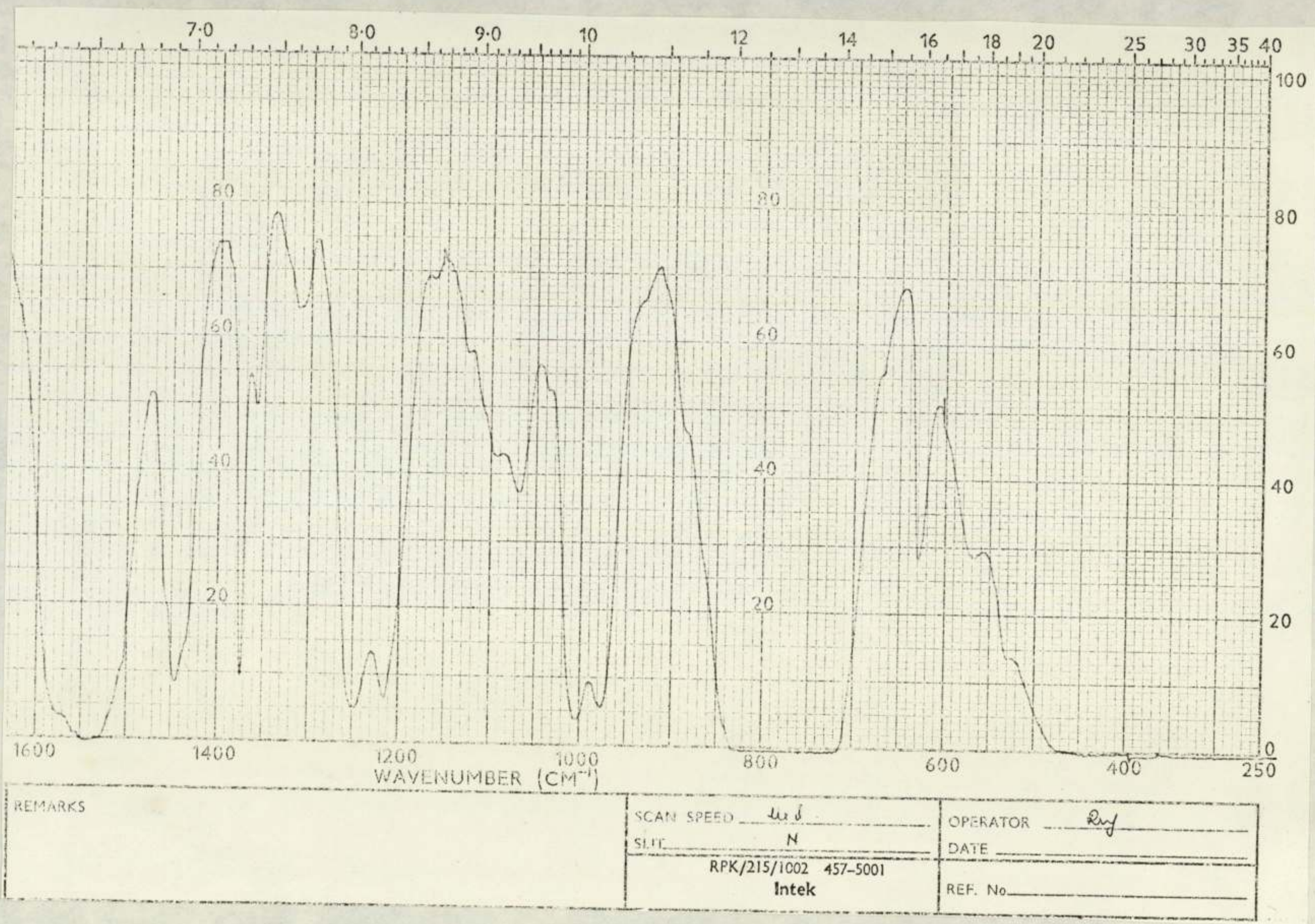


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Fig. 24 continued.

Analysis of the spectrum

The presence of the band at 3650 cm^{-1} clearly proves the presence of mercaptan containing phenol in the rubber thus indicating that addition has taken place. But as a higher proportion of mercaptan was initially added by comparison with the previous experiments, a higher yield of adduct would have been expected if carried out in the absence of oxygen.

According to the calibration curve, there is only 11% of adduct in the rubber and hence only a 10% conversion is obtained.

The presence of the band at 1665 cm^{-1} shows the presence of a considerable amount of residual unsaturation in the rubber.

Therefore this experiment shows that although the addition reaction can be carried out in air, the conversion to adduct is much lower than in the absence of oxygen. In the presence of oxygen, the mercaptan function may be oxidized to other species (e.g. monosulphide, disulphide etc.) which are incapable of free radical addition to double bonds. Another possibility is that the thiyl radical addition is inhibited by oxygen since the alkylperoxy radical can also be present.

3.4.2.4. Addition reaction in steam

As it is of practical importance to investigate the various possibilities in which the addition reaction can be carried out, the following experiment was done.

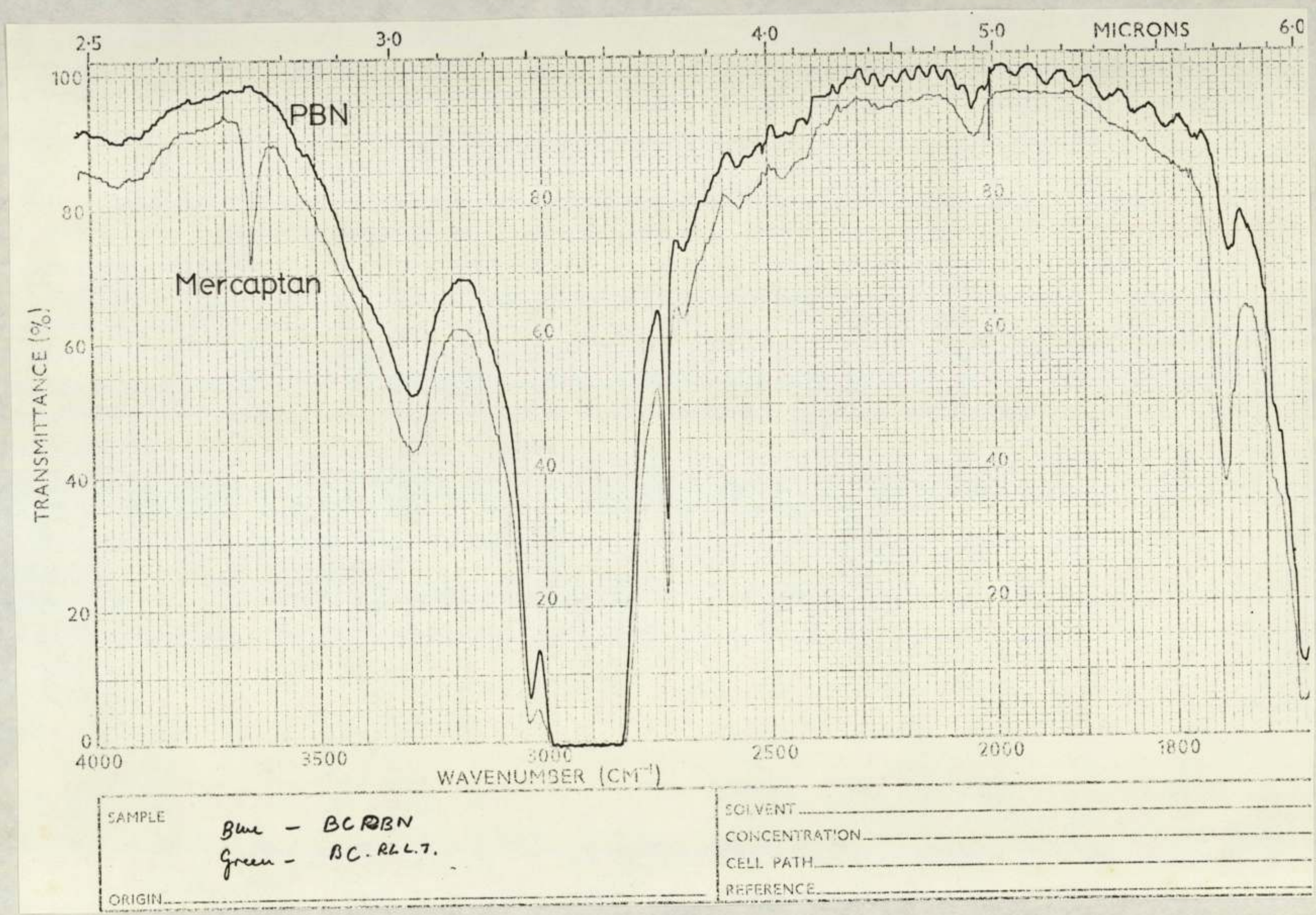
Experimental

50 ml of 25 D.R.C. natural rubber latex was taken in a round bottomed flask and was diluted with 100 ml of water. 15.0 ml of linseed oil was added as the emulsifying agent and the mixture was vigorously shaken so that the oil and the latex were almost in a homogeneous mixture. 10.0 gms. of 3,5 Ditertiarybutyl-4-hydroxybenzyl mercaptan and 0.05 gms of azobisisbutyronitrile were then added and the flask was immersed in a Digol bath at 100°C. This was an indirect way of generating steam within the reaction vessel and it was due to this that an excess of water was used at the beginning. After 24 hours the latex was coagulated using isopropyl alcohol and the rubber thus obtained was extracted and dried.

The rubber was then vulcanised using a C.B.S. Sulphur recipe and an infra-red spectrum of a sheet of thickness 1-2τ was obtained. The spectrum of a 2% P.B.N. stabilised rubber vulcanizate was also obtained in the same way. The spectra are shown in Fig. 25.

Analysis of the spectra

The band appearing at 3650 cm^{-1} clearly indicates the presence of the phenol adduct in the rubber which is unextractable. By comparison with the spectrum of the P.B.N. containing vulcanizate, the thiol containing vulcanizate shows the presence of a very strong carbonyl band appearing at 1745 cm^{-1}.



SAMPLE Blue – BC PBN
Green – BC. RLL.T.

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

Fig. 25.

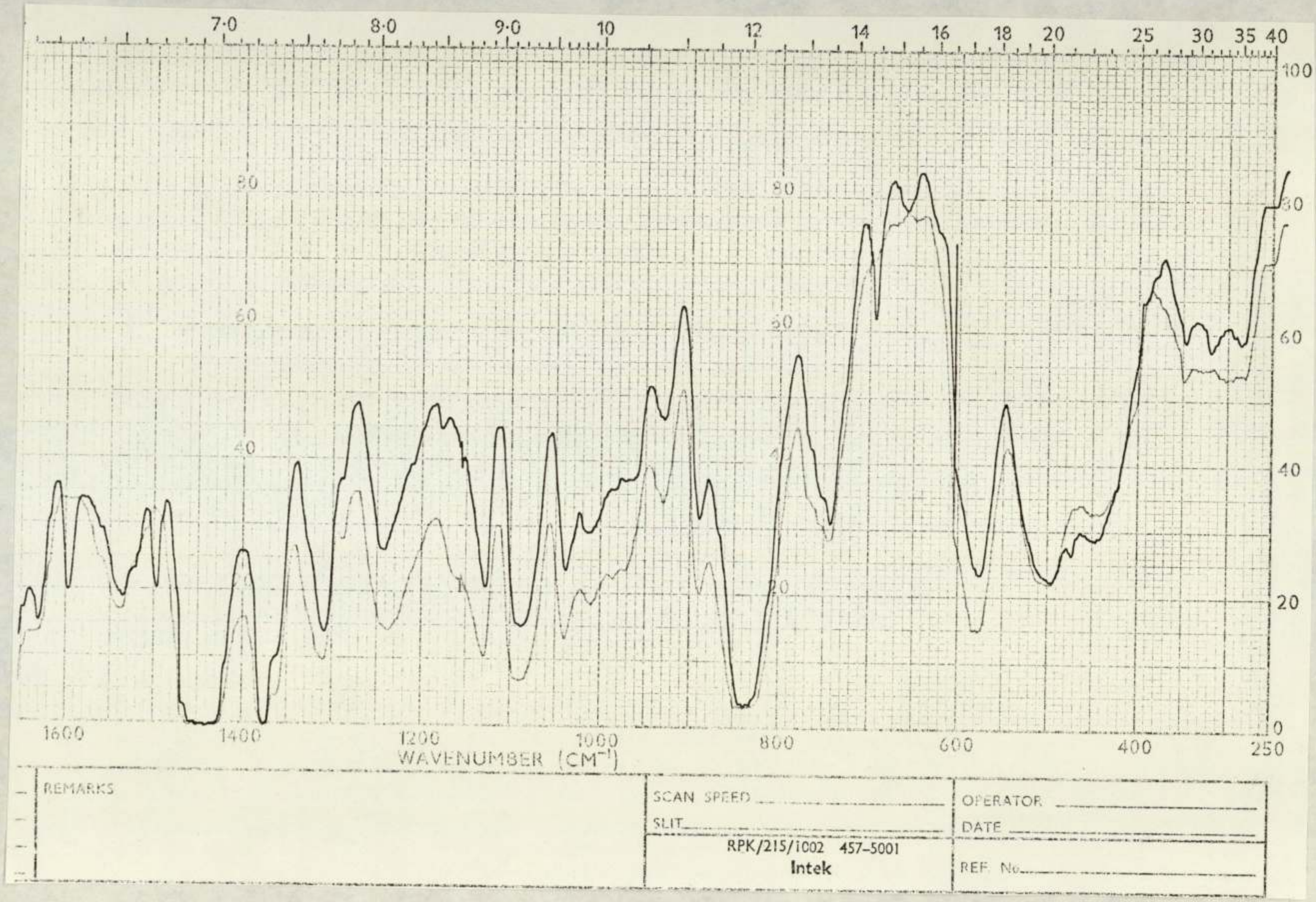


Fig. 25 continued.

This shows that although the addition reaction can be carried out in steam, extensive oxidation of the rubber occurs. This problem could be overcome by passing oxygen free nitrogen as well as steam through the system although it would not be practically favourable.

3.4.3. Attempted addition to a saturated polymer

As mercaptan addition to unsaturated compounds takes place by thiyl radicals attacking the double bonds, theoretically there should not be any addition to a saturated polymer. However commercial polyethylene contains small amounts of olefinic groups. To investigate this the following experiment was carried out.

Experimental

Materials

Low Density Polyethylene (ICI Alkathene)
3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan
Azo-bis-isobutyronitrile

Procedure

The following mixes of low density polyethylene, mercaptan, and azobisisobutyronitrile were made in the torque rheometer (R.A.P.R.A. Torque Rheometer Mark 3) at 160°C, by mixing for a period of 5 minutes with a ram pressure of 40 p.s.i.

Mix No.	Polymer gms.	Mercaptan gms.	Initiator gms.
1	35	0.0	0.0
2	35	1.8	0.0
3	35	1.8	0.036

Then the polymers were pressed into 7-8τsheets in a press for 2 minutes at 130°C (preheat 30 sec.) with subsequent cooling to 60°C for 1 minute, between two cellophane films and 2 stainless steel plates. Samples were cut from these sheets and their infra-red spectra were taken. The changes occurring in the polymer structure during oven-ageing at 100°C, and by extraction with acetone for 24 hours were investigated. See Fig.26-28.

Discussion

As seen from Fig.(27) the intensity of the band at 3650 cm^{-1} provides evidence for the fact that the mercaptan which is present in the polymer before extraction is completely lost by extraction.

Thermal ageing in air at 100° for a period of 2 hours is sufficient to volatalize away all the mercaptan from the polymer. The presence of a free radical generator has no effect on the reaction. Fig.(28).

This experiment clearly confirms that a mercaptan cannot be added to a saturated polymer by a free radical mechanism, by incorporation in the melt state.

3.4.4. Copolymerisation Reactions

The preparation of polymers containing hindered phenolic groupings linked via a sulphur bridge, which is the final aim of this work, can be carried out mainly in two distinct ways:

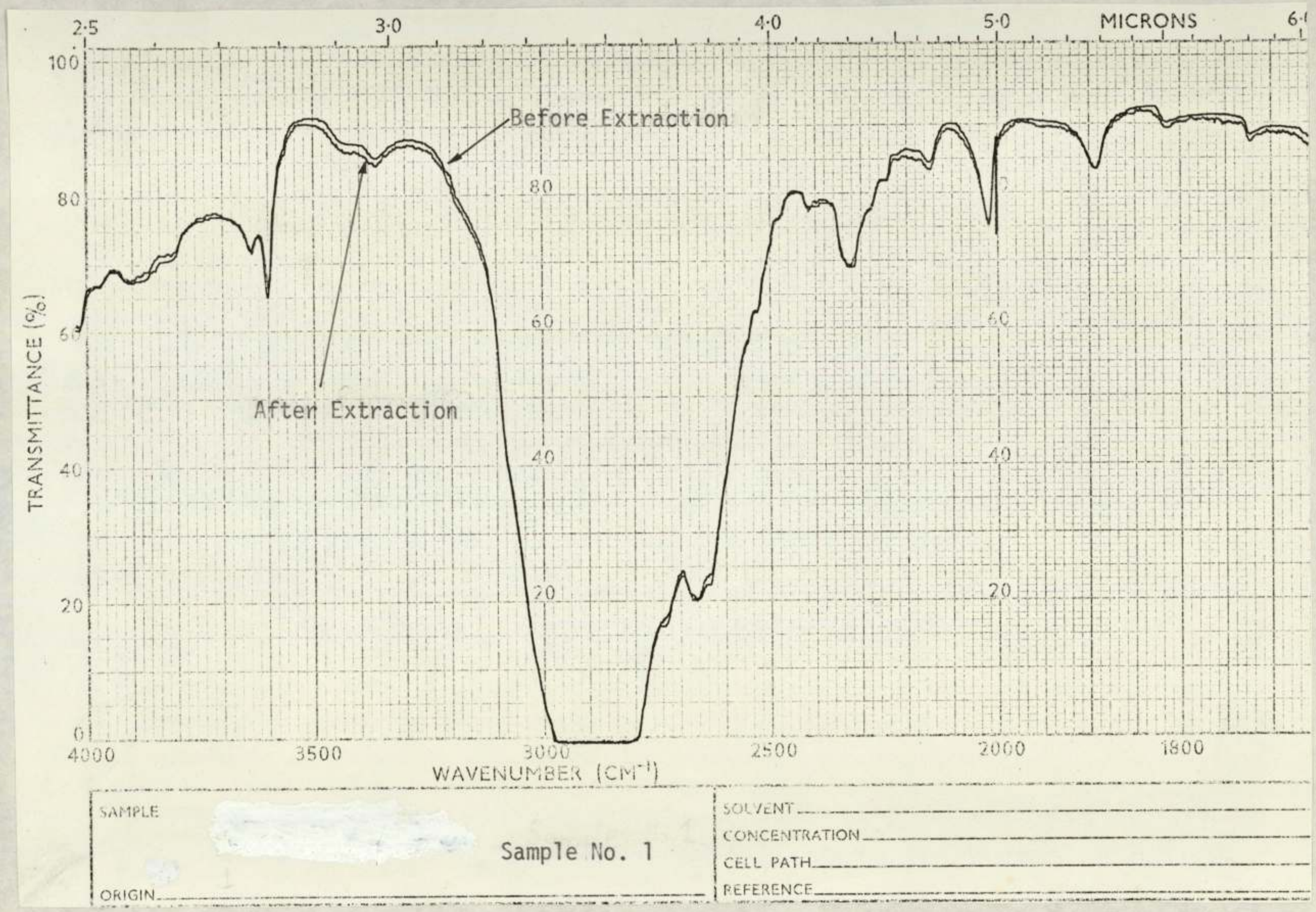

2·5
3·0
4·0
5·0
MICRONS
6·
100
80
60
40
20
0
TRANSMITTANCE (%)
Before Extraction
After Extraction
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM⁻¹)
SAMPLE
Sample No. 1
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

Fig. 26.

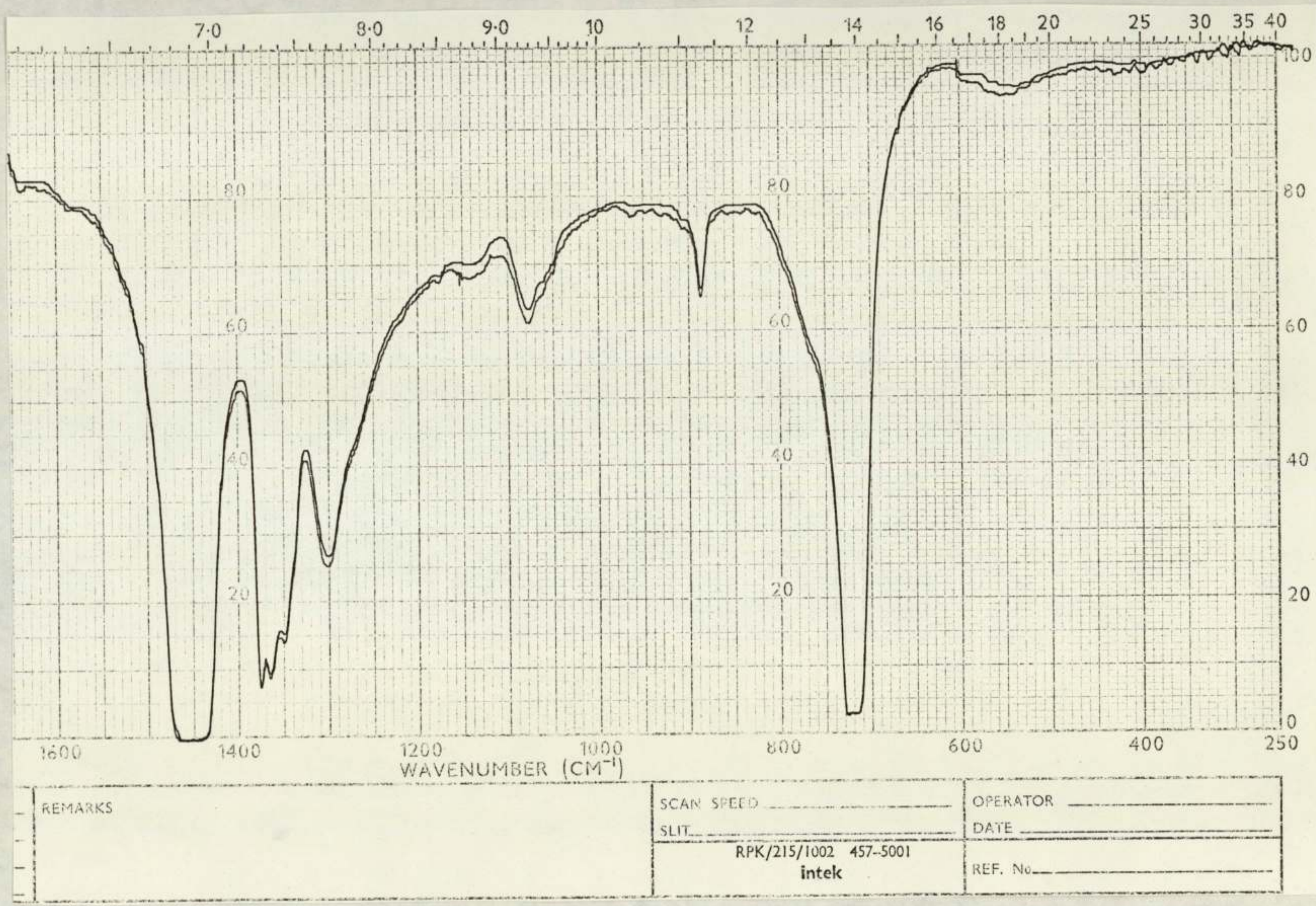


Fig. 26 continued.

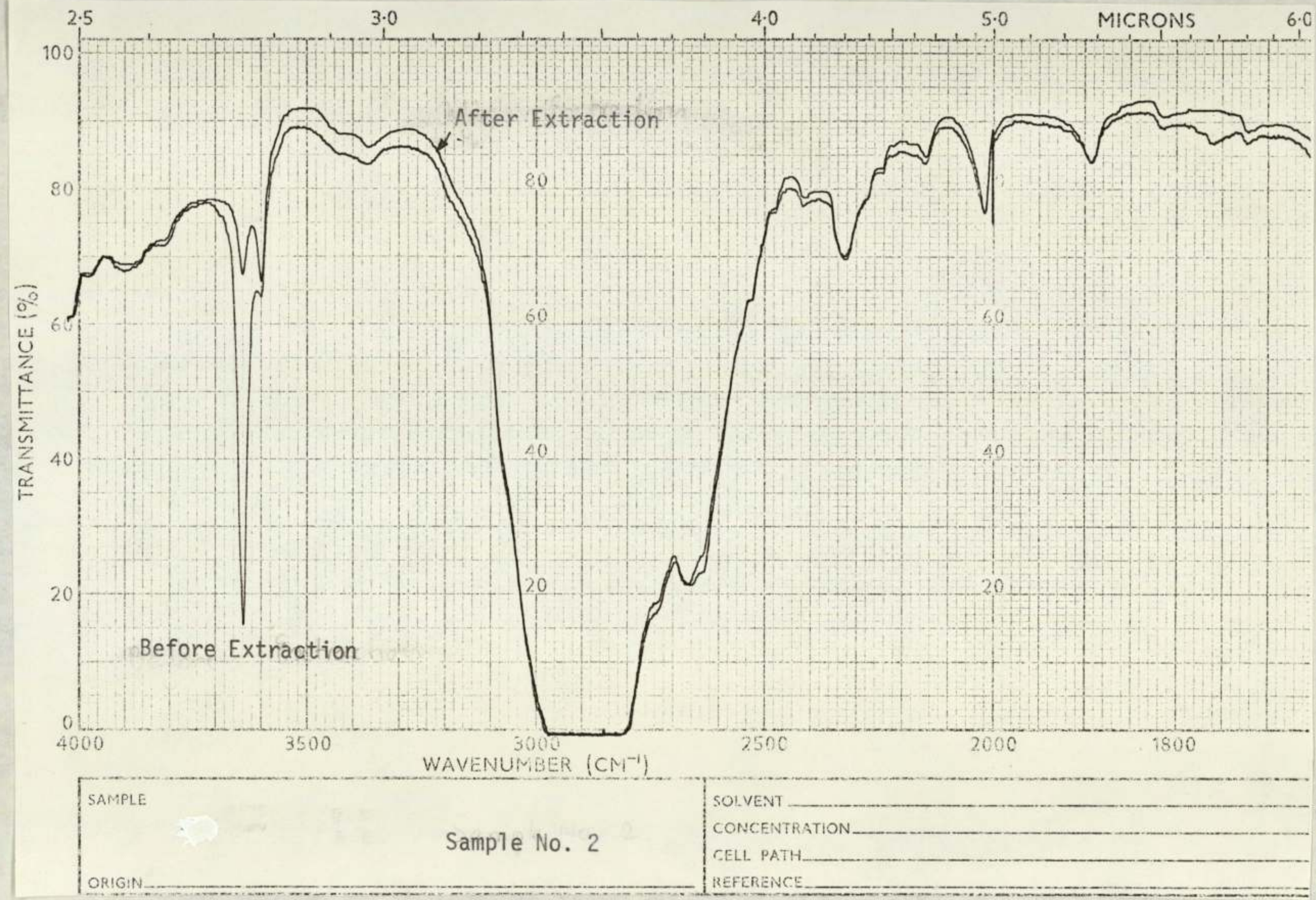

2·5
3·0
4·0
5·0
MICRONS
6·0
100
80
60
40
20
0
TRANSMITTANCE (%)
After Extraction
Before Extraction
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM⁻¹)
SAMPLE
Sample No. 2
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

Fig. 27.

Fig. 27 continued.

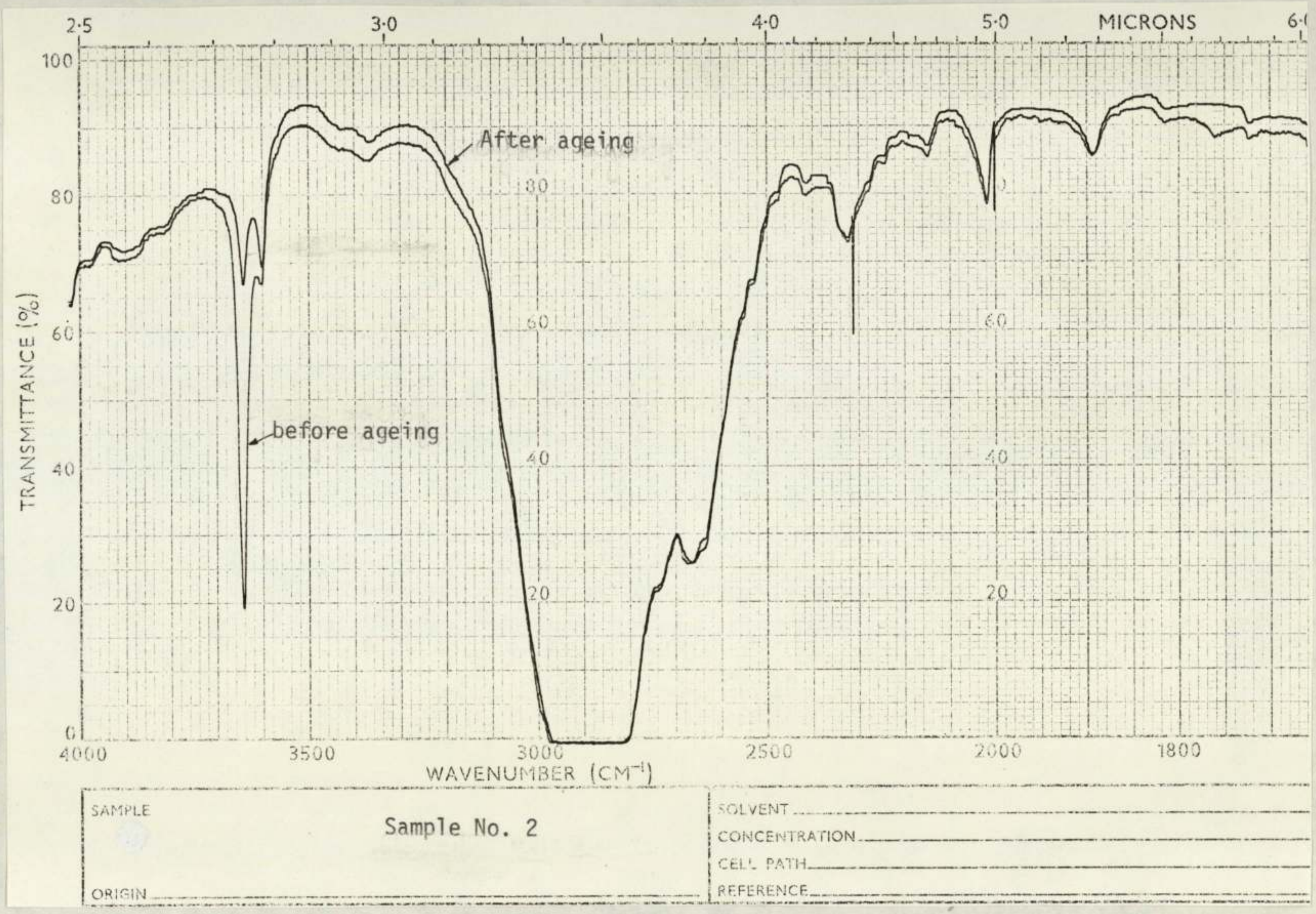

2·5
3·0
4·0
5·0
MICRONS
100
80
60
40
20
0
TRANSMITTANCE (%)
After ageing
before ageing
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM^{-1})
SAMPLE
Sample No. 2
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

Fig. 28.

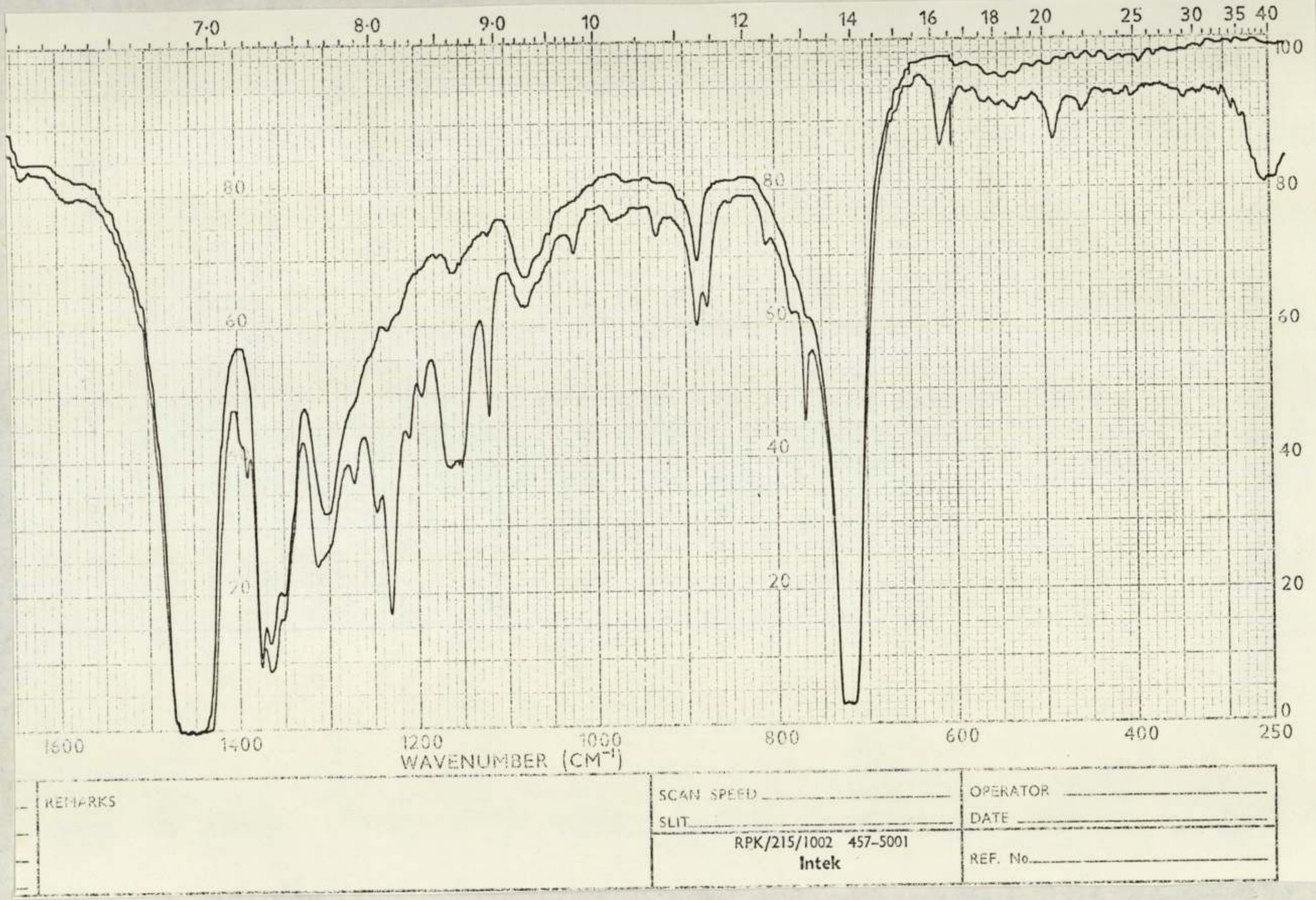


Fig. 28 continued.

1. Addition during polymerization
2. Addition in the polymer stage

Addition of mercaptans to polymers is dealt with in Chapter 3.

Thiols are used as transfer agents in industrial polymerisations and they have high transfer constants. A hydrogen abstraction from the -SH group is involved in the transfer process thus revealing thiyl radicals (134), (135), (136). Therefore in a free radical initiated polymerisation of a compound like styrene, thiyl radicals are capable of becoming attached to the polymer chain.

It has also been found that polymerisation of styrene and methylmethacrylate in the presence of N,N'-tetramethylthiuram disulphide, yielded polymers containing thiuram breakdown products (137).

The possibility exists therefore that if a free radical polymerization of styrene is carried out in the presence of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan, a polymer containing bound antioxidant groupings might be produced. This polystyrene could be used by itself as a stable polymer or could be blended with other polymers to attain a desired level of stability. It is also known that mercaptans retard or sometimes inhibit the polymerization process.

The following experiments were carried out to investigate (i) the addition of a mercaptan during polymerisation and (ii) the inhibition effect.

Experimental

Materials

Styrene B.D.H.
AZO bis isobutyronitrile
3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan

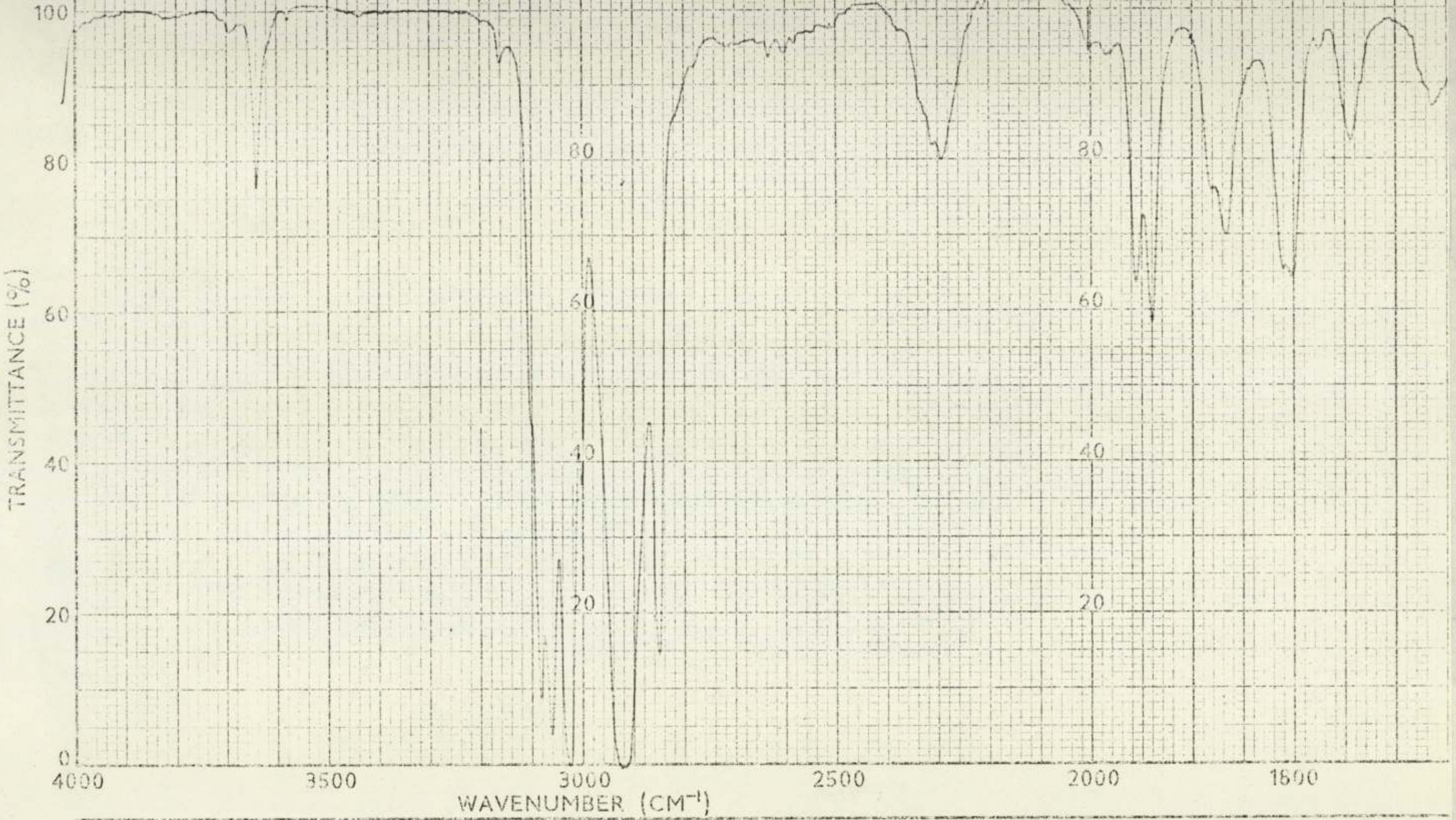
Styrene was purified by washing with 10% sodium hydroxide solution, and then with distilled water. After drying with calcium chloride, it was distilled in vacuum.

3.4.4.1. Polymerisation of styrene in the presence of 3,5-Ditertiarybutyl-4-benzyl mercaptan

5.0 ml of purified styrene were taken in a pyrex tube and 2.5 gms of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan and 0.1 gms of AZO bis butyronitrile were added to it. The tube was sealed under vacuum and kept in a water bath at 60°C for a period of 24 hours. Isolation of the polymer, and separation from unreacted additives was done by precipitations three times repeated from benzene solution with methanol. The sample thus obtained was dried in vacuum and an infra red spectrum of a 5% carbon tetrachloride solution was obtained. (Fig.(29).

Analysis of the spectrum and discussion

The band appearing at 3640 cm^{-1} clearly proves the presence of a phenol adduct in the polymer. The



SAMPLE 5.0 ml of styrene 2% I.
2.5 g A
60° 24 hours. in vacuum.

ORIGIN

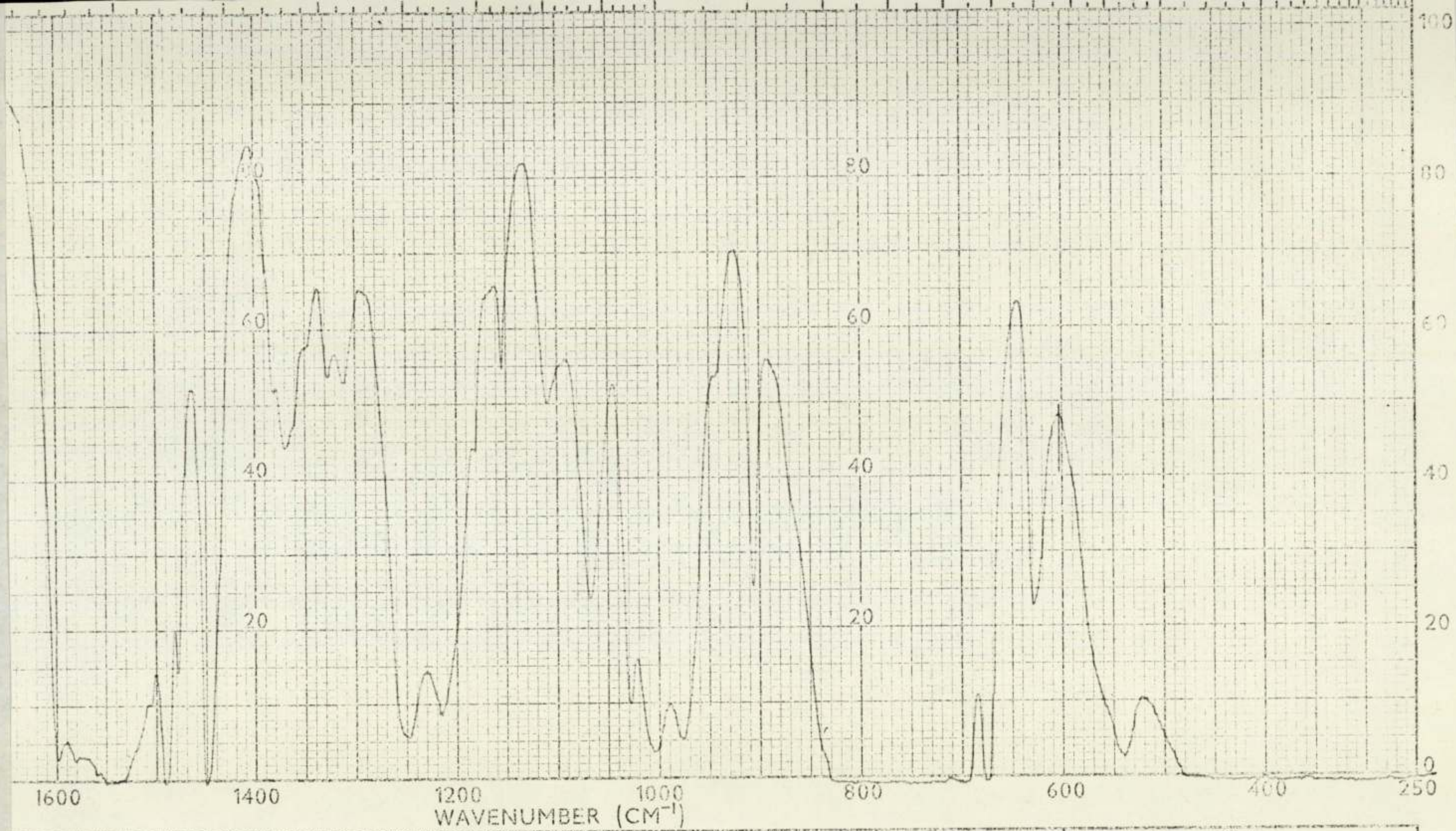
SOLVENT CCl_4

CONCENTRATION 5%

CELL PATH NaCl

REFERENCE —

Fig. 29.



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REF. No.

Fig. 29 continued.

intensity of this band was compared with calibration solutions of polystyrene to which different proportions of the mercaptan were added. Although a large proportions of the mercaptan was initially added to styrene, only 0.8% by weight of mercaptan remains in the polymer and therefore it can be said that copolymerisation does not represent any practically important method of binding a mercaptan into a polymer.

3.4.4.2. Inhibition effect

The inhibition effect of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan on the polymerisation of styrene was investigated by the method of dilatometry.

The densities of the monomer dm, and the polymer dp, are commonly used in dilatometric measurements and are known for the polymerisation of styrene (138). From these data the percentage volume contractions for 100% conversions are calculated according to the following formula:

$$\begin{array}{l}\%\text{ volume contraction}\\ \quad\text{for }100\%\text{ concentration}\end{array} = \left(\frac{{}^{1}/_{dm} - {}^{1}/_{dp}}{{}^{1}/_{dm}}\right) \times 100$$

When the temperature is kept constant, the density of the solid polymer is less than that of the polymer dissolved in the monomer or a solvent (139). The density of the polymer does not vary systematically with the concentration of the polymer (140), and the apparent specific volume of polystyrene does not vary with the degree of polymerisation, if the latter is sufficiently high (141).

Experimental

The following solutions were made using purified styrene:

0.5 gms of mercaptan in 5.0 ml of styrene

0.15 gms of A.Z.B.N. in 50 ml of styrene

5.0 ml of portions of styrene A.Z.B.N. mixture were kept in glass dilatometers in a water bath at 60°C, to which 0, 0.1, 0.2 and 0.5 ml quantities of mercaptan solution was added. The contraction was measured using a cathetometer and a graph of h against time was plotted. Fig. (30).

Discussion

The inhibitor effect of mercaptan on the polymerisation of styrene is clearly seen from Fig. (30), and inhibition could be a reason for the low extent of grafting.

3.4.5. Reaction Products

The grafting of 3,5-Ditertbutyl-4-hydroxy benzyl mercaptan to natural rubber in the presence of azobisisobutyronitrile has been successfully achieved. However, the extent of saturation of the double bonds in the polymer by the thiol varied from experiment to experiment by changing the conditions of reaction, and in no case was all the thiol initially added bound to the polymer. This showed that there were additional side reactions by which the thiol was consumed. Therefore it was essential to isolate and identify the byproducts of the grafting reaction. In addition, the products of reaction

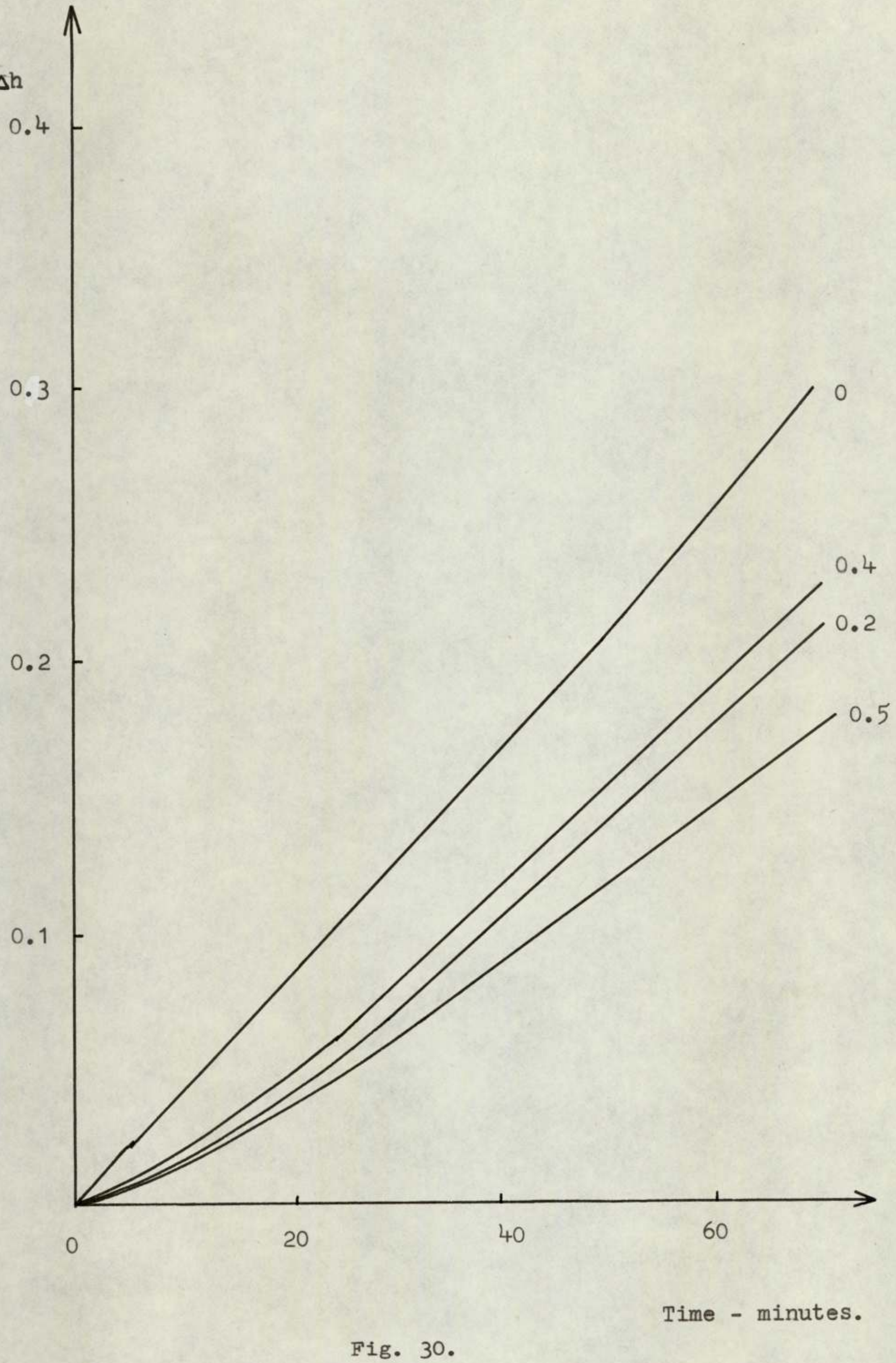


Fig. 30.

between the initiator and the thiol as well as between the initiator and the polymer were also investigated.

3.4.5.1. Products of grafting reaction

Materials

4.0% Natural rubber solution in chlorobenzene
2.0% Mercaptan solution in chlorobenzene
AZBN - recrystallized from ether

Experimental

A reaction tube was charged with 10.0 ml of 4.0% rubber solution, 10.0 ml of 2.0% 3,5-Ditertbutyl-4-hydroxy benzyl mercaptan and 0.005 gms of azobisisobutyronitrile. The tube was then completely degassed and kept in a water bath at 50°C. for a period of 16 hours with constant stirring. 16 hours was selected as the reaction time because the earlier experiments carried out showed that the reaction is complete within this period. The contents of the tube were then precipitated in a beaker using an excess of isopropyl alcohol and the rubber thus coagulated was separated. The remaining solution was then concentrated by evaporating all the solvents present under vacuum, and a light yellow oil was obtained. The latter was analyzed by Infra-red spectroscopy using a Perkin-Elmer 577 spectrophotometer with sodium chloride windows.

Results and discussion

Although the reactants were colourless substances a yellow colour appeared in the reaction tube with time, which intensified towards the end of the reaction. The I.R. spectrum of the yellow oily substance (see fig.31) has the following characteristic peaks:

2.75 Microns 3622 cm^{-1} ----- Phenolic OH
7.16 Microns 1394 cm^{-1} ----- t-Butyl groups
7.34 Microns 1358 cm^{-1} ----- t-Butyl groups
11.37 Microns 878 cm^{-1} ----- Benzene ring
3.88 Microns 2554 cm^{-1} ----- SH groups

The above spectrum shows very close similarity to that of the mercaptan (Fig.7) monosulphide (Fig.45) and the disulphide (Fig.47). The band characteristic for the mercaptan group appearing at 2554 cm^{-1} is very weak.

Therefore it can be said that the yellow oily product contains some unreacted thiol as well. The monosulphide and the disulphide are solids at room temperature and therefore the oily nature of the product should be due to the presence of the monosulphide and/or disulphide. Infra-red spectroscopy does not provide a method to differentiate a monosulphide and a disulphide. But an earlier experiment using the method of thin layer chromatography indicated the possibility of the presence of monosulphide as well (see page 120). The disulphide can be easily formed by the dimerization of thiyl radicals formed due to the hydrogen abstraction from the thiol by initiator radicals or propagating polymer-thiol

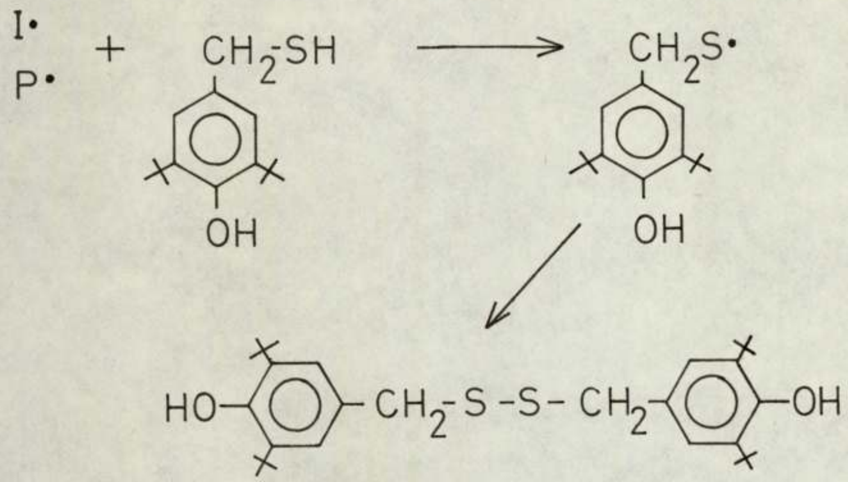
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM^{-1})
80
60
40
20
80
60
40
20

Fig. 31.

Distilled

Fig. 31 continued.

adduct radicals.



Any unreacted initiator or its reaction products if present do not interfere with the I.R. spectrum of the extract as they are purely of alkyl nature.

3.4.5.2. Reaction between Azobisisobutyronitrile and Natural Rubber

Materials

4.0% Natural rubber solution in chlorobenzene
Azobisisobutyronitrile

Experimental

10.0 ml of 4.0% rubber solution and 0.01 gm of AZBN were mixed in a reaction tube and the I.R. spectrum of the mixture was obtained. The reaction tube was then degassed and kept in a water bath at 50°C for a period of 24 hours. The I.R. spectrum of the mixture was again recorded and compared with the spectrum of the initial mixture.

Results and discussion

According to Fig.32 there is no significant difference between the two spectra, although a very weak additional peak appears in the spectrum of the reacted mixture at 1260 cm^{-1}. This is not a characteristic peak for any particular functional group and therefore was considered as negligible. Therefore it can be said that AZBN does not react with natural rubber under the given conditions. It is known that unlike peroxide type initiators AZBN does not hydrogen abstract from rubber and cause cross linking of the polymer (142). This behaviour was kept in mind during the selection of the initiator for the grafting experiments. The method of producing free radicals on the base polymer which is used in usual grafting reactions with rubber is not made use of in this study. In thiol grafting it is the thiyl radical which attacks the polymer chain and not vice-versa.

3.4.5.3. Reaction between Azobisisobutyronitrile and 3,5-Ditert-butyl-hydroxy benzyl mercaptan

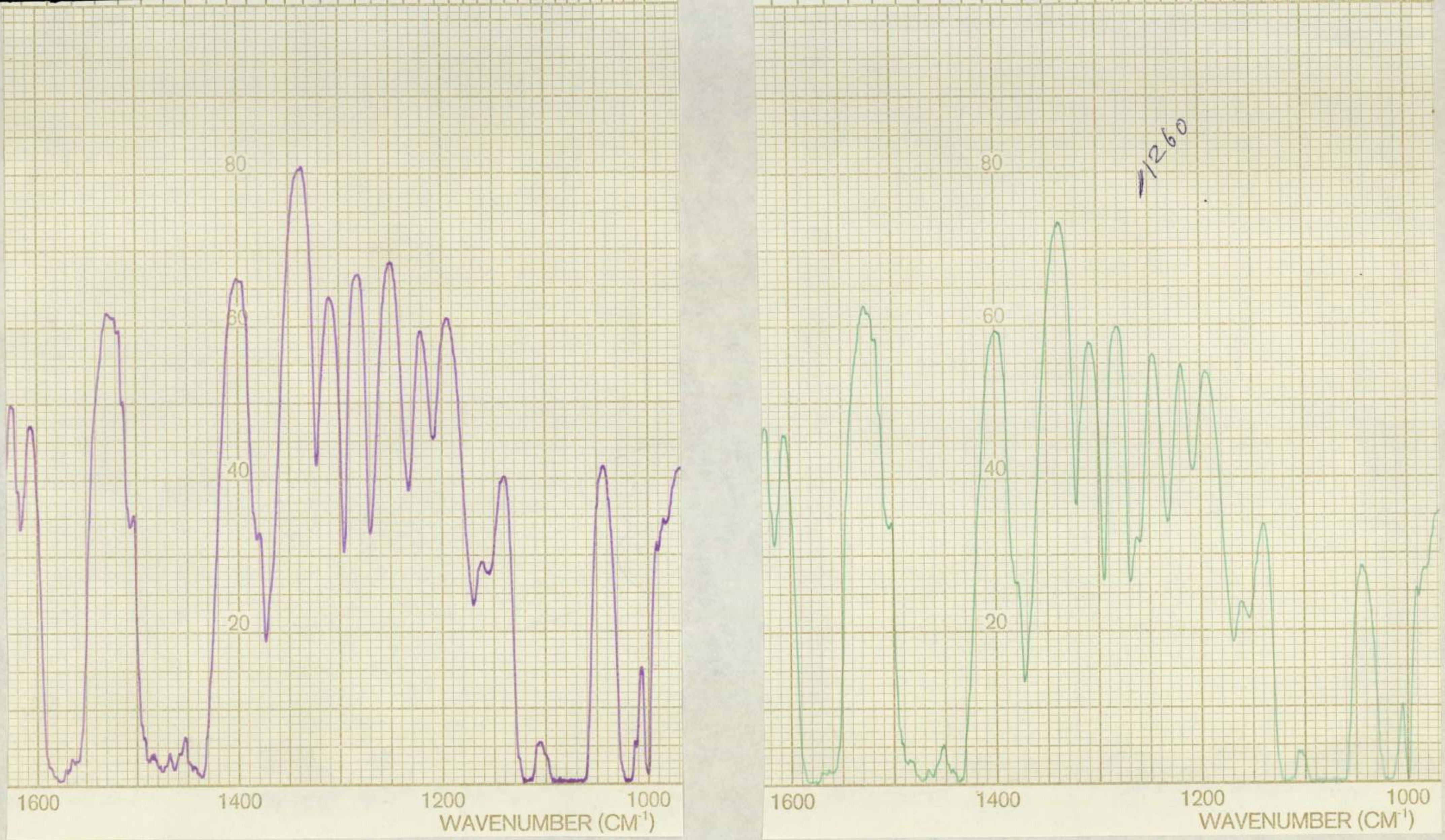
Materials

2.0% mercaptan solution in carbontetrachloride

Azobisisobutyronitrile

Experimental

10.0 ml of 2.0% mercaptan solution and 0.005 gms of AZBN were mixed in a reaction tube and the I.R. spectrum of the mixture was recorded. Then the reaction tube was degassed and kept in a water bath at 50°C for a period of 8 hours and again an I.R. spectrum was taken.



Before Reaction

After Reaction

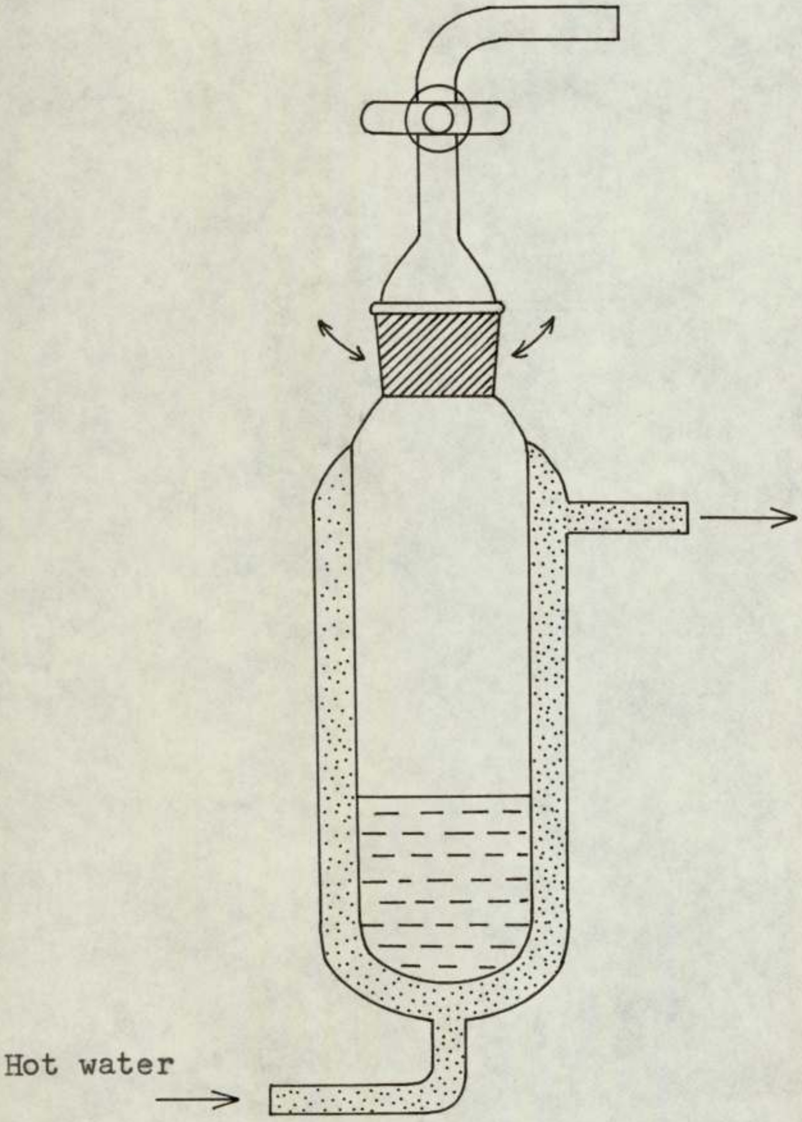
Fig. 32

Results and discussion

In the original Infra-red spectrum, the band corresponding to the thiol group appears very clearly at 2554 cm^{-1} while this band has lost its intensity in the final mixture.

During the course of the reaction the contents in the reaction tube developed a yellow colouration.

Therefore it can be said that a portion of the thiol undergoes dimerization to form the disulphide after being converted into thiyl radical by the action of the initiator.



Reaction Vessel for grafting experiments

CHAPTER 4

Assessment of Ageing and Curing Characteristics

The effects of the presence of 3,5-Ditertiary-butyl-4-hydroxy benzyl mercaptan in natural rubber on the ageing and curing characteristics of vulcanizates are dealt with. Vulcanizates containing bound mercaptan as well as free mercaptan (i.e. mercaptan added as a compounding ingredient) are considered.

During the grafting reactions carried out in the present work not all the intially added mercaptan is grafted and therefore a certain portion of it remains as free mercaptan. In practical applications there is no necessity to remove this free mercaptan by extraction as it can remain within the polymer and act as a conventional antioxidant. But its effect on ageing and curing behaviour of the vulcanizates have to be known and this fact justifies the attempt to investigate these characteristics using free mercaptan also.

4.1. Assessment of Ageing Characteristics

Two techniques have been used to assess the ageing characteristics of natural rubber vulcanizates containing 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan as the antioxidant; viz. continuous stress relaxation and oxygen absorption.

4.1.1. Stress Relaxation

Theoretical Aspects and Method

The dependence of stress of a stretched rubber like material upon time of application, when held at a constant temperature and elongation, provides valuable information about the material. Although stress relaxation employs simple apparatus, measurements of high degree of precision and reproducibility can be carried out. This method of accelerated ageing has been successfully used in the rubber industry to predict various reactions taking place during the thermal oxidation of vulcanised rubber.

There are two methods of stress relaxation, viz. continuous and intermittent. In the continuous method the rubber sample is kept stretched continously. In the intermittent method the sample is stretched only for a shorter period (2 minutes) and is maintained in the unstretched condition for a longer period (28 minutes), and the process is repeated. The intermittent method is closer to practice.

The interpretation of stress relaxation is based upon the kinetic theory of rubber elasticity, according to which the stress of an elongated sample is given by (143):

$$f = SkTA_o \frac{l}{lo} - (\frac{l_o}{l})2$$

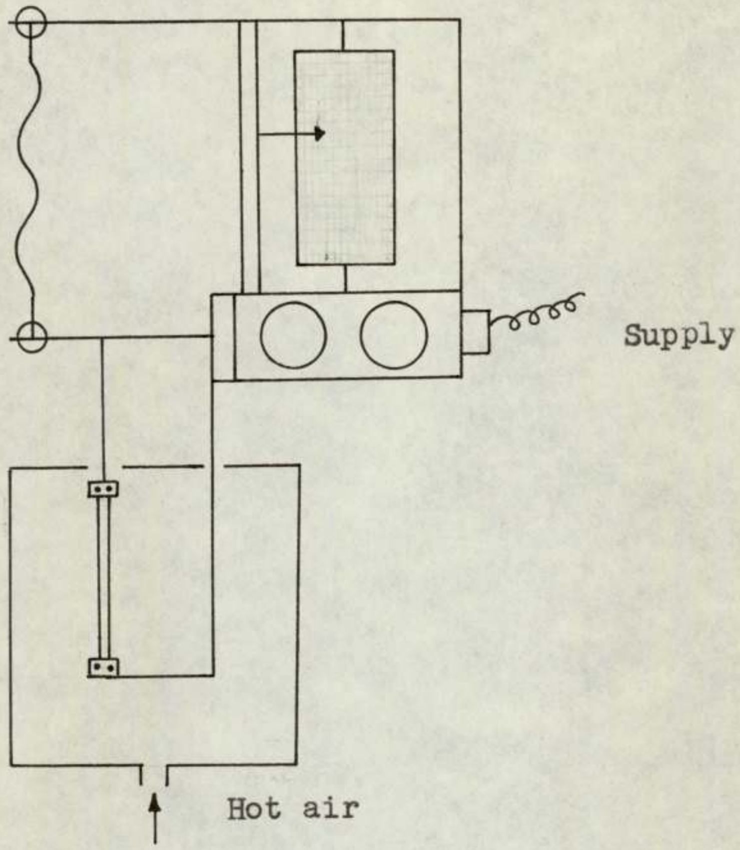
where f is the tension, s the number of chains per unit volume supporting the stress, k is Boltzmann's constant, T the absolute temperature, l/l_o the ratio of stretched to unstretched length (extension ratio), and A_o the unstrained cross sectional area.

Therefore if a sample of rubber can be maintained in extension at a constant length and constant temperature (i.e. keeping T and l/l_o constant) the value of stress f will be proportional only to s, the number of stress supporting chains.

$$f/f_o = S/S_o$$

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

A Wallace extension stress relaxometer was used in the following experiments where the sample of the vulcanised rubber was held in extension between two fixed points and fully submerged in a thermostatically controlled ageing oven (± 2°C) with a regular replacement of preheated air. The stress of the extended piece of rubber is balanced by a helical spring. If the tension in the strip falls, (as happens during continuous stress relaxation when the rubber degrades) a small servo motor reduces the length of the spring to decrease its tension so that this balance is maintained. This is automatically recorded. The stress at any particular instant can be directly read from the recorder chart. A diagrammatic view of the apparatus is shown below.



4.1.2. Oxygen absorption

Oxygen absorption provides very useful information on the oxidizability, or the inhibition, during accelerated ageing of a material in a closed system, saturated with oxygen. The rate at which a particular material absorbs oxygen, the time taken for the antioxidation to become autoaccelerating (the induction period) or the time needed to absorb a particular level of oxygen (usually 0.5% or 1.0%) by the sample are the parameters normally investigated by this technique.

Anyhow, all these parameters will have to be considered simultaneously because there exists a possibility that a specimen with a short induction period can have a slow rate of subsequent oxidation when compared to a specimen with a long induction period but followed by a rapid rate of oxidation. Oxygen absorption is carried out in a closed system, a loss of stabilizer due to volatilization does not occur. Therefore it has to be mentioned that the technique of stress relaxation is more relevant to practice where the polymer is oxidized in a changing stream of air.

Apparatus for oxygen absorption measurements

A continuous automatic system was used to follow the oxygen absorption of vulcanizate samples. A diagrammatic view of the system is shown in Fig. (33).

A 100 ml pyrex-boiling tube was used as the reaction vessel, fitted with a side arm containing a tap and a syringe needle. The mouth of the tube is connected to a pressure transducer system through capillary tubes. Any slight variations in temperature are compensated for by having a similar reference tube attached to the dry end of the transducer. The two tubes are immersed in a thermostatic oil bath. A constant input voltage is supplied to the transducer, and when a pressure difference occurs between the two reaction tubes on either side of the diaphragm of the transducer an output voltage is created which is proportional to the pressure difference and is automatically recorded on a chart recorder. The system is calibrated by taking out measured amounts of

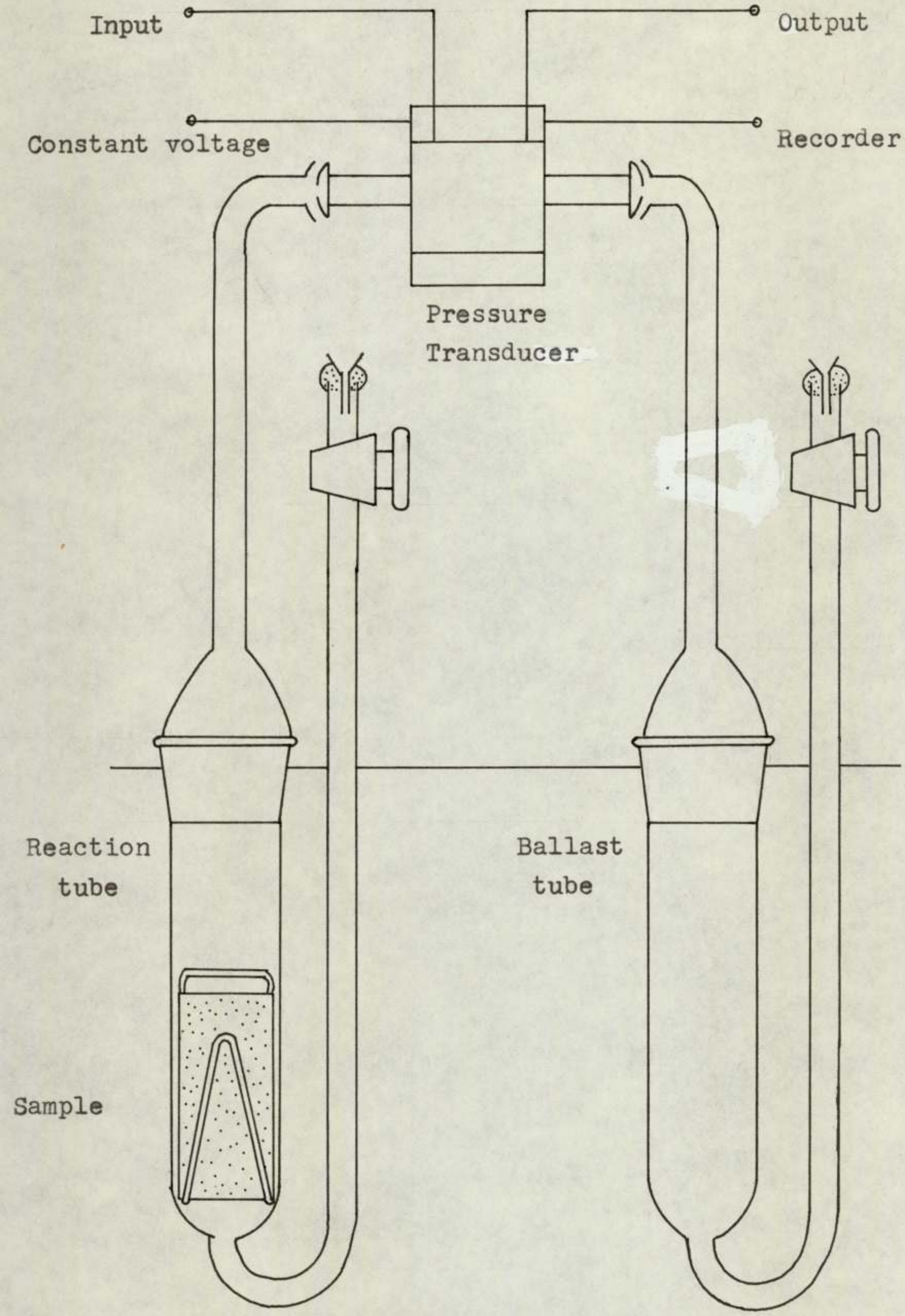


Fig. 33. Oxygen absorption system.

oxygen from the system by means of a syringe.

4.2. Assessment of Vulcanization Characteristics

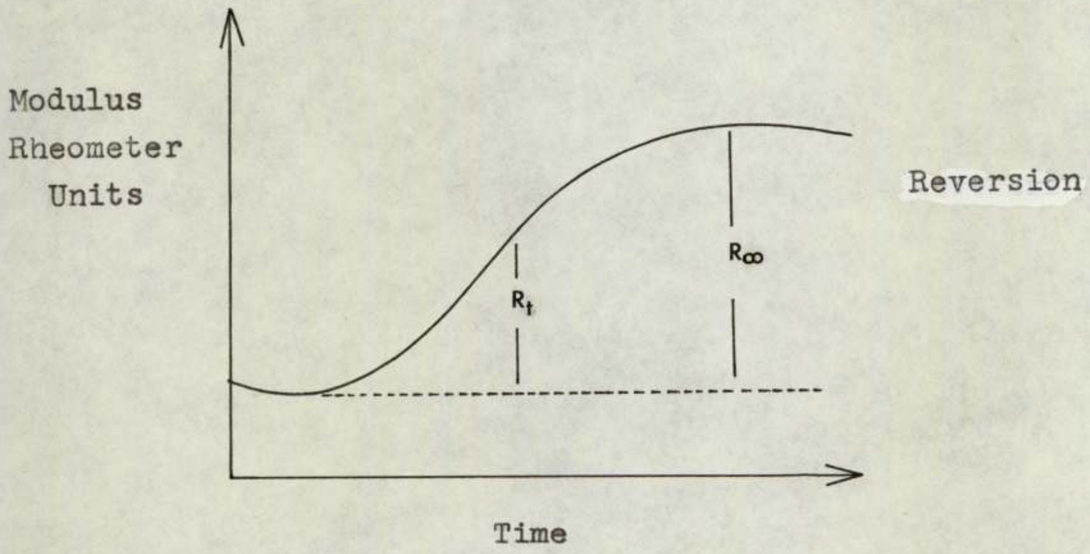
Rubber became an important industrial raw material only after it was found out that it could be vulcanized. Since then almost all the rubber used in the world is vulcanized to suit the desired applications. The presence of non-vulcanizing ingredients in the vulcanizing mixture may affects the subsequent curing behaviour of the rubber. Antioxidants for example may affect the induction period of the vulcanization process on the rate at which the vulcanization proceeds.

As the compounds investigated in this work are added to the rubber prior to vulcanization it is important to determine their effects on curing characteristics. At present several methods and instruments are available for this purpose. A Monsanto Rheometer has been used in this work to assess the curing characteristics of a natural rubber gum stock containing different antioxidants in various proportions. A curve obtained from a Monsanto Rheometer provides information regarding the curing behaviour and therefore it is necessary to mention briefly the theoretical aspects.

The Monsanto oscillating disc rheometer consists of a biconical disc surrounded by the compound specimen contained in a cavity. The temperature of the cavity, specimen and the disc is maintained at a desired level with an accuracy of ± 0.5°C by means of electrical heating.

The cavity is made up of two halves which open and close pneumatically. A motor-driven eccentric oscillates the shaft of the biconical disc sinusoidally. A torque transducer is connected to the shaft of the disc which indicates the force required to oscillate the disc or in other words to apply a shearing strain to the rubber specimen. The torque on the transducer is recorded on a chart. In a typical Monsanto rheograph for a natural rubber stock, there is an initial drop in torque due to the decrease in the viscosity of the rubber as its temperature rises. This is followed by an induction period after which the torque increases steadily showing that curing is taking place. After a certain period of time the torque reaches a maximum. In certain cases this maximum can further increase or decrease after sometime, indicating a secondary vulcanization or a reversion respectively. Reversion can be caused by the breaking down of cross links.

A typical Rheometer tracing obtained with a Monsanto oscillating disc Rheometer is shown below.



Coran (144) has provided a kinetic interpretation of a curve of this type. Cross link formation is assumed to be a first-order reaction after an induction period t_1, and is represented as below:

$$dVu/dt = k_2(Vu_\infty - Vut)$$

where

Vut = cross link density,
Vu_∞ = cross link density at infinite time,
t = the vulcanization time,
and k_2 = the overall first order rate constant.

It has been found that the increase in Rheometer torque readings R_t (at time t) are proportional to the cross link density as determined by swelling measurements (145).

By integrating the above equation,

$$\int_{V_{u_o}}^{V_{u_t}} \frac{dV_u}{V_{u_\infty} - V_{u_t}} = k_2 \int_{t_1}^{t} dt$$

Therefore,

$$\ln \left[V_{u_\infty} - V_{u_t} \right]_{V_{u_o}}^{V_{u_t}} = k_2 \left[t\right]_{t_1}^{t}$$

$$\ln \frac{V_{u_\infty} - V_{u_t}}{V_{u_\infty}} = k_2(t - t_1)$$

As said above, $V_{U_t} \propto R_t$

$$\text{Therefore, } V_{U_t} = k_2 R_t$$

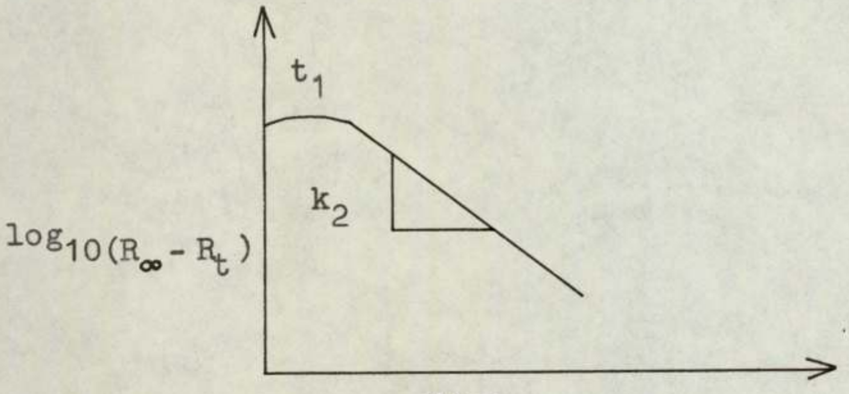
$$\text{and} \quad V_{U_\infty} = K_2 R_\infty$$

Substituting,

$$\ln \frac{R_\infty - R_t}{R_\infty} = K_2(t - t_1)$$

$$\log_{10} (R_\infty - R_t) = \log_{10} R_\infty + \frac{k_2(t - t_1)}{2.303}$$

If we plot $\log_{10} (R_\infty - R_t)$ against t, we obtain a curve similar to one shown below:



From the above plot two parameters of the kinetics of cross link formation can be obtained. They are the "delay time" or the induction period t_1, and the first order rate constant k_2, which is the negative slope of the straight line obtained after time t_1. It should be noted that the value R_∞ must be selected on the basis of closeness of fit, since reversion or even secondary crosslink formation can occur.

R_∞ gives a measure of the ultimate cross link density.

4.3. Investigations in the presence of 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan

An important conclusion that emerges from the series of addition reactions of antioxidant containing thiol to natural rubber is that, a rubber containing a large proportion of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan can be obtained by a free radical reaction, either in the latex or in organic solution. It follows that, such a rubber concentrate with a large concentration of bound antioxidant might be used to dilute untreated rubber, ending up with a polymer containing a desired amount of bound antioxidant. This is of great industrial importance because, it concerns the reaction of large quantities of rubber. However the probability exists, that there is an optimum concentration of the additive in the adduct because as the addition reaction consumes unsaturation in the main network, enough double bonds must be left in the rubber for subsequent vulcanisation. The following experiment was carried out to investigate this possibility.

To 50 cc of Qualitex A (0.5% ammonia stabilised) natural rubber latex with a dry rubber content of 25% (by adding an equal amount of water), 1% by weight of vulcastab C paste was added and the mixture was stirred at 80°C while bubbling nitrogen through it. 5.0 gms of

3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan and 0.1 gms of azobisisobutyronitrile were added, followed by 200 cc of distilled water. The reaction mixture was stirred for 24 hours at 80°C under nitrogen. Different quantities of this latex were added to untreated natural rubber latex and the mixtures were coagulated using 2% formic acid. The samples thus obtained were extracted with an azeotrope of acetone, methanol and 1,1,1, trichloroethane under nitrogen using a soxhlet apparatus. An undiluted latex sample was also coagulated and extracted. The samples were dried at 40°C under vacuum and 2% solutions were made in carbon tetrachloride for infra-red spectroscopy.

According to the infra-red spectrum of the undiluted sample and the calibration curve, there is 10% of mercaptan by weight bound to the rubber.

The initial weight of rubber used was 25.0 g
" " " " mercaptan " " 5.0 g

The amount of mercaptan bound to the rubber is:

$$25 \times \frac{10\ \%}{100} = 2.5 \text{ g}$$

The yield of the reaction is: $\frac{2.5}{5.0} \times 100\% = 50\%$

The amounts of concentrate added to 50 ml samples of 50% D.R.C. latex, and the height of the phenolic -OH band corresponding to each sample are shown below. (see Fig.34).

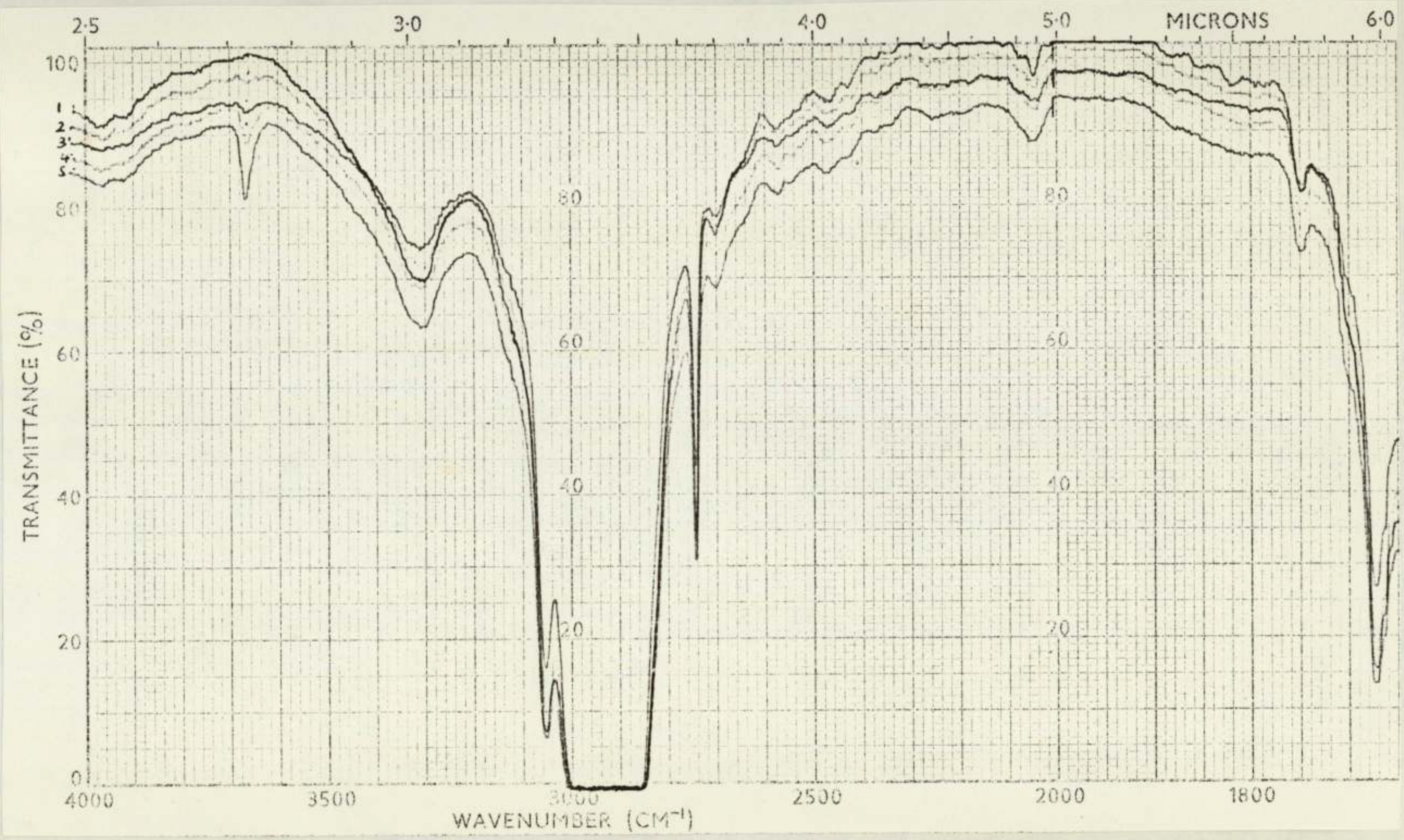

2·5
3·0
4·0
5·0
MICRONS
6·0
100
80
60
40
20
0
1
2
3
4
5
TRANSMITTANCE (%)
80
60
40
20
80
60
40
20
4000
3500
3000
2500
2000
1800
WAVENUMBER (CM⁻¹)

Fig. 34.

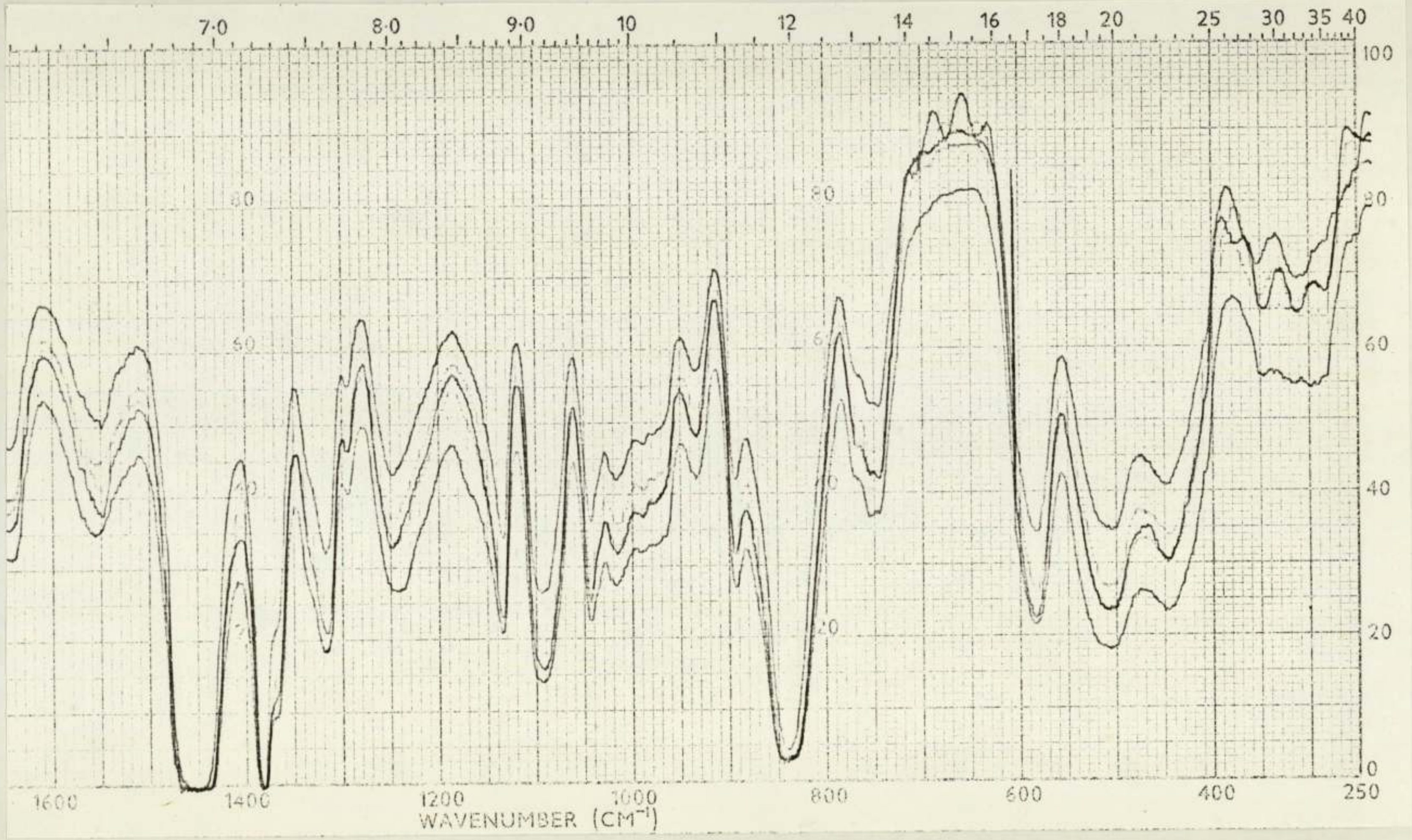


Fig. 34 continued.

Sample N-O	Concentrate ml.	-OH peak mm.	% Bound mercaptan by wt.
1	0	0	-
2	10	2.5	0.55%
3	25	6.2	1.2%
4	50	18.5	3.7%
5	100	34.0	7.5%

4.3.1.1. Curing behaviour

The dried samples were separately vulcanized into 8-10τsheets at 140°C for 30 minutes using the following formulation:

Rubber	100 g
Stearic acid	2.0 g
Zinc oxide	5.0 g
CBS	0.5 g
Sulphur	2.5 g

The curing characteristics of these samples were compared with those of an untreated rubber, using a Monsanto Rheograph. As seen from Fig.35 there appears to be no significant change in the scorch times (induction periods), or ultimate modulus in the vulcanizates due to the presence of the mercaptan.

The colour of the dried coagulate latex samples containing bound mercaptan was found to be remarkedly better when compared with that of an untreated rubber.

4.3.1.2. Ageing behaviour

The ageing characteristics of the above vulcanizates were followed by oxygen absorption at 80°C using the

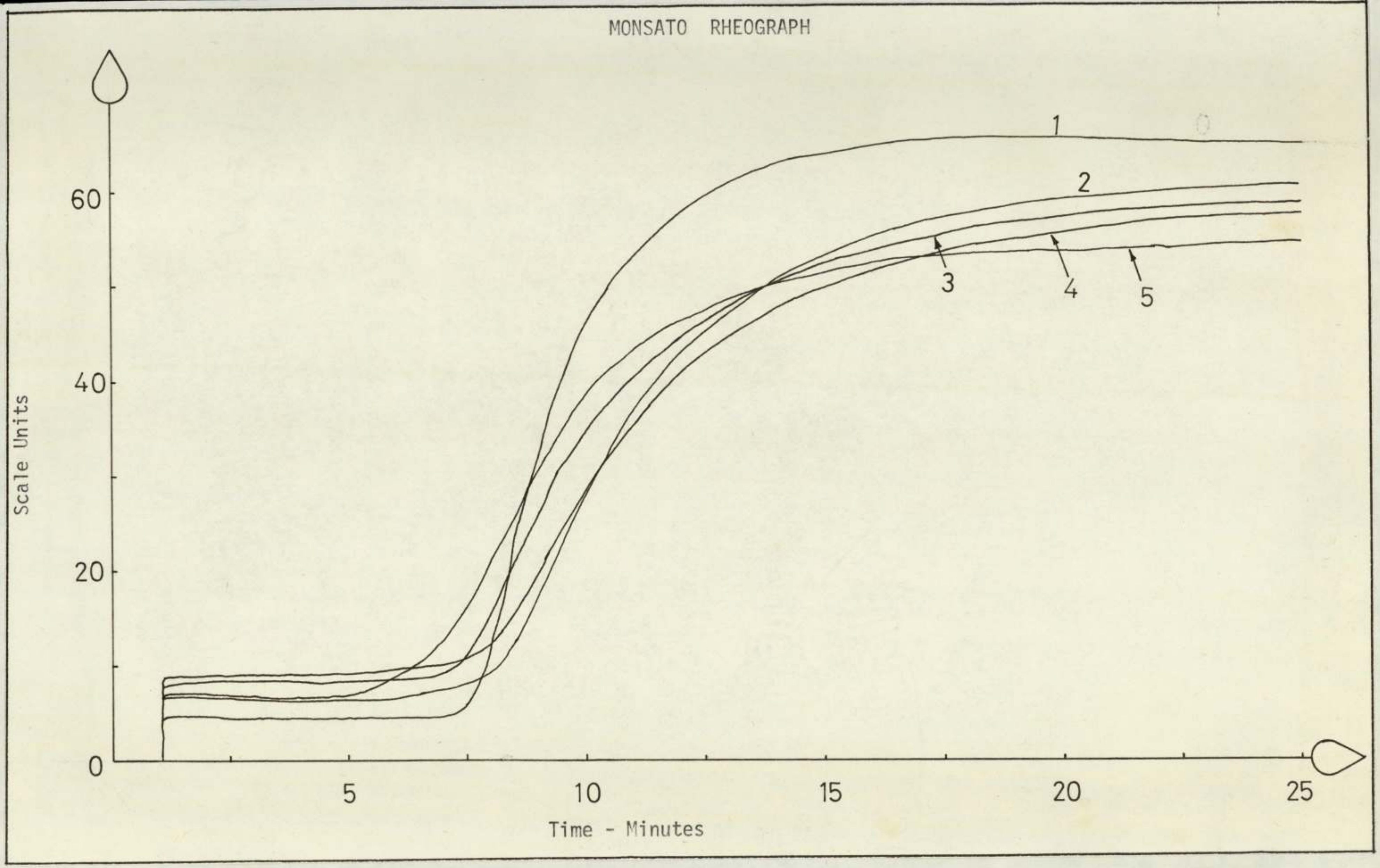

MONSATO RHEOGRAPH
Scale Units
0
20
40
60
Time - Minutes
5
10
15
20
25
1
2
3
4
5

Fig. 35.

system of pressure transducers.

The times necessary to absorb 0.5 and 1.0% by weight of O_2, and the amounts of bound mercaptan present in each sample calculated on the basis of the concentrate are shown in the following table:

Sample	Concentration mol %	Time in hours absorb O_2	
		0.5%	1.0%
1. No additive	0	17	25
2. 10 cc Antioxidant bound latex	0.125	24	36
3. 25 cc " " "	0.313	43	53
4. 50 cc " " "	0.625	60	125

There is a clear improvement in the ageing behaviour of rubber by the addition of the 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan, which is unextractable, although the efficiency of it as an antioxidant is not very remarkable although adequate. The lower efficiency may be attributed to the reduced mobility of the antioxidant groupings when they are fixed to particular places in the rubber network.

4.3.2. Addition of the antioxidant as a compounding ingredient

The ageing and curing characteristics of vulcanizates prepared by the addition of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan as a compounding ingredient are studied. The properties are compared with those of a vulcanizate containing a conventional antioxidant, viz. phenyl-β-naphthyl amine.

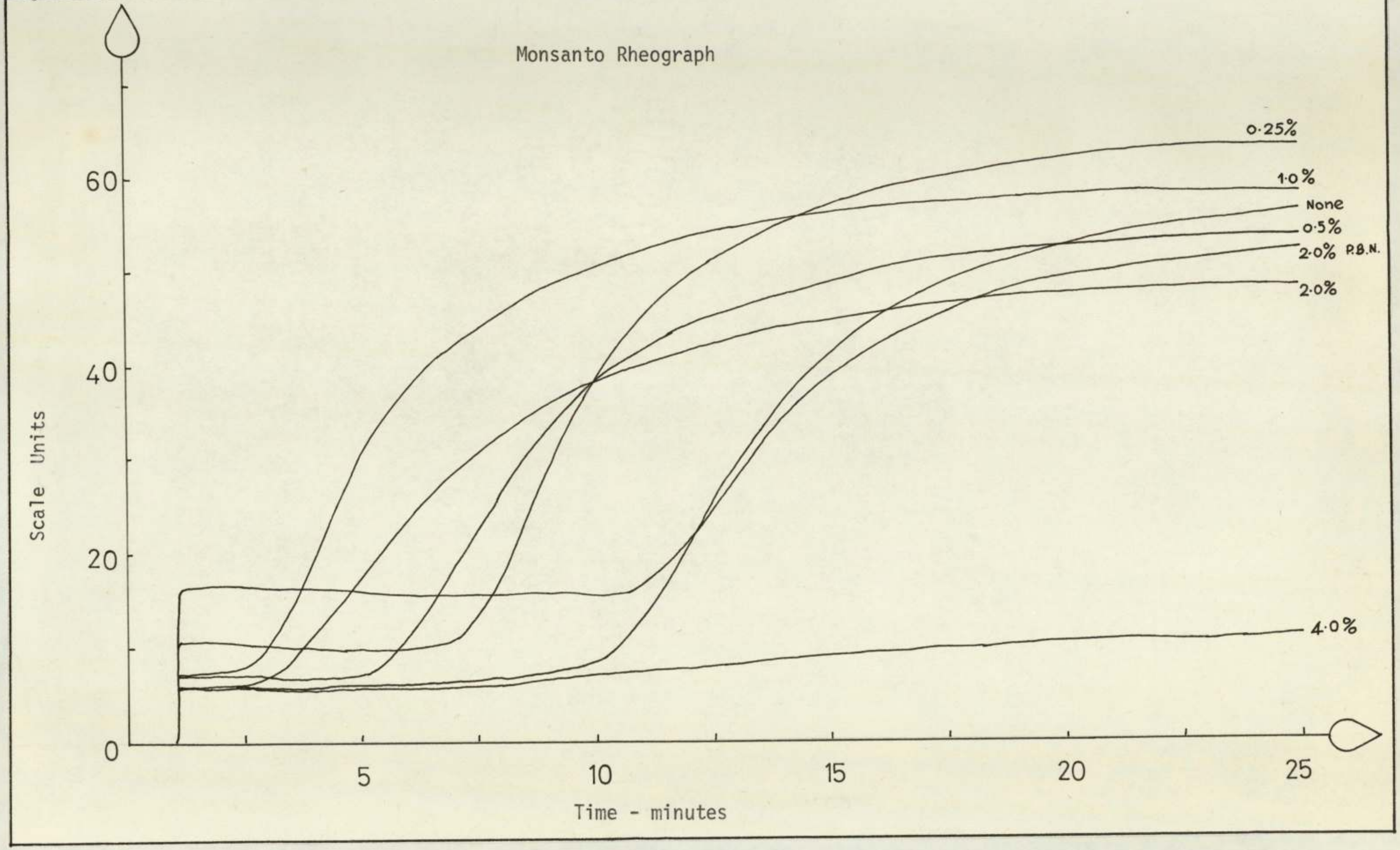
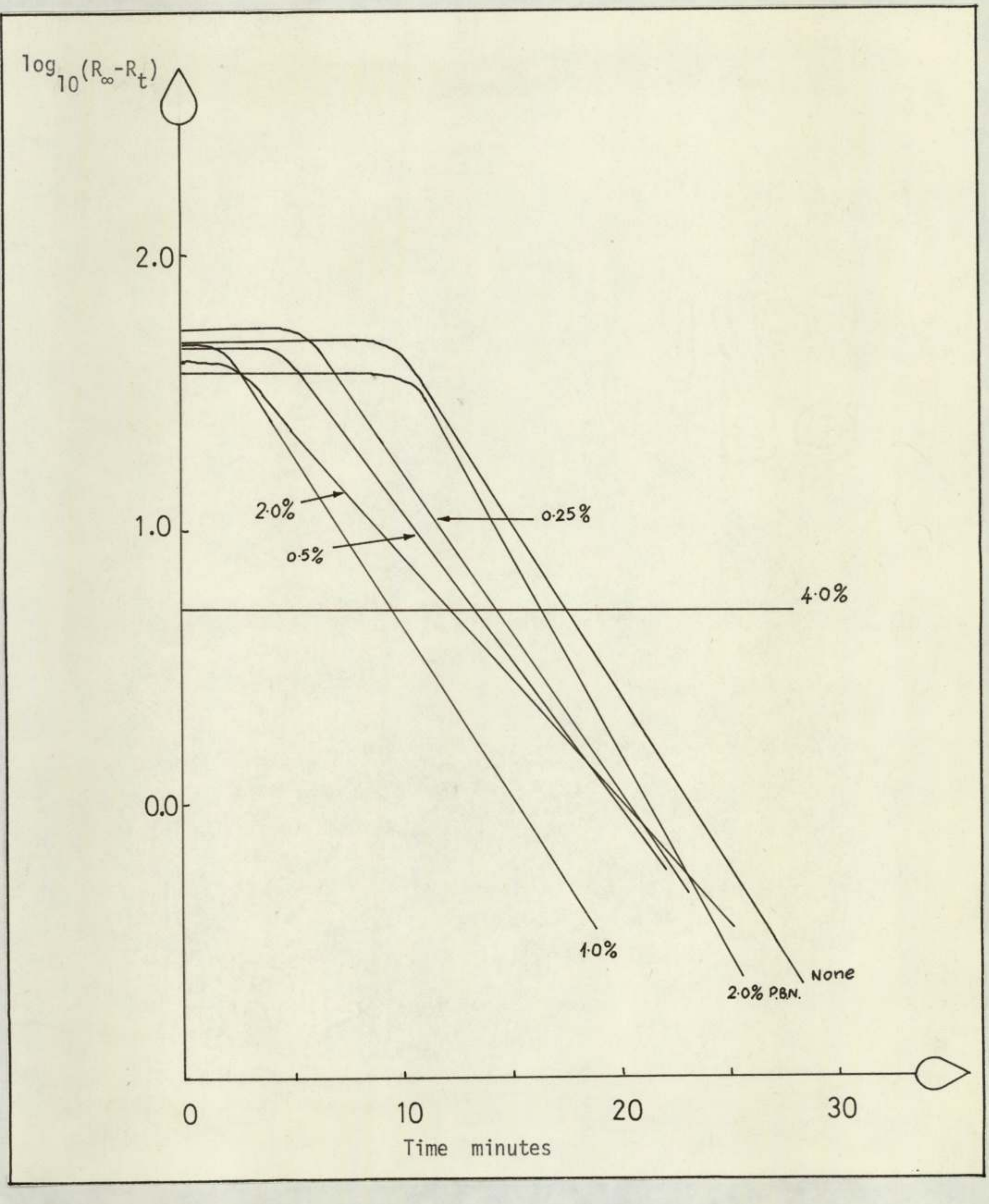
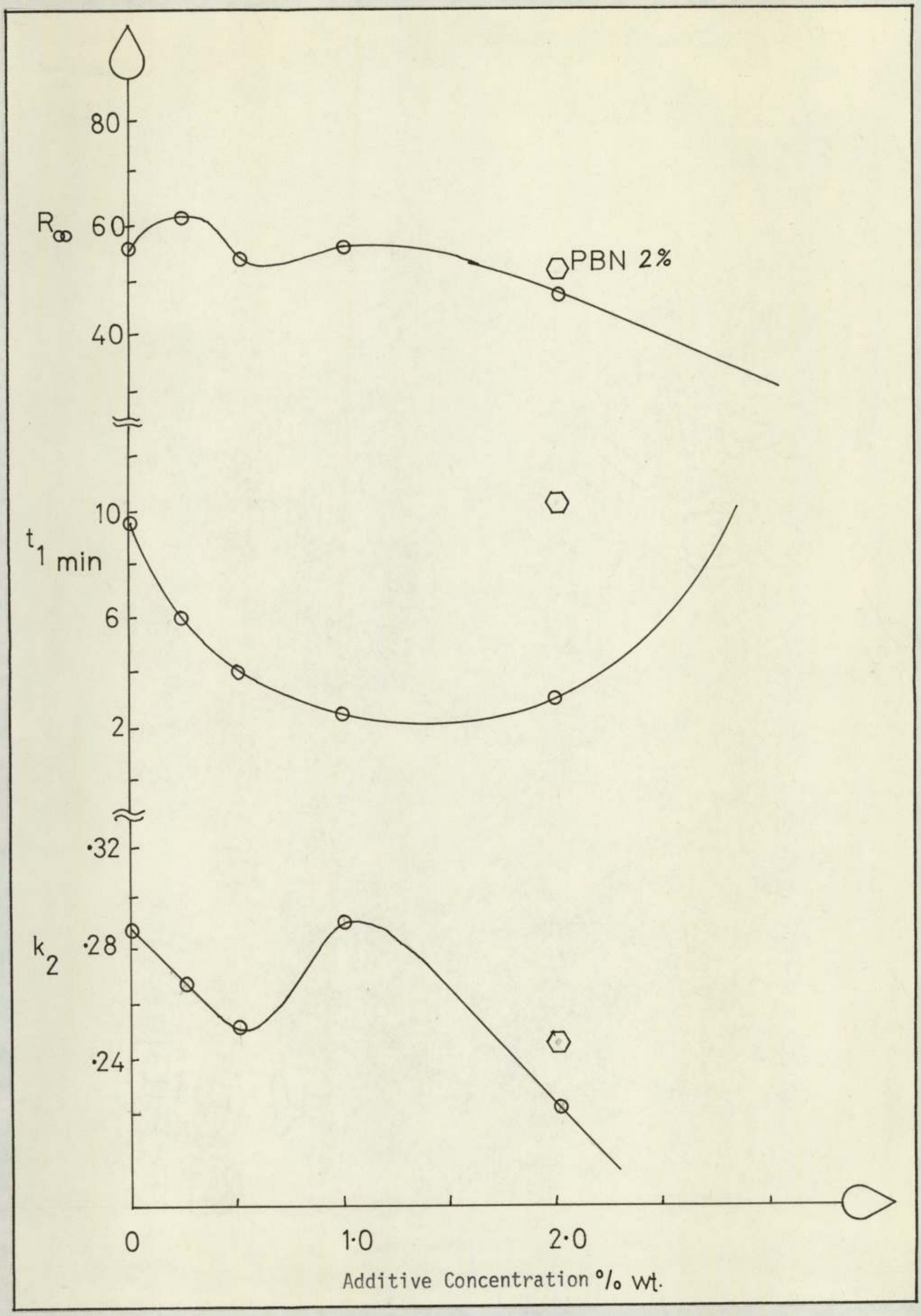

Monsanto Rheograph
Scale Units
0
20
40
60
5
10
15
20
25
Time - minutes
0·25%
1·0%
None
0·5%
2·0% P.B.N.
2·0%
4·0%

Fig. 36.



$\log_{10}(R_\infty - R_t)$
2.0
1.0
0.0
2·0%
0·5%
0·25%
4·0%
1·0%
2·0% P.B.N.
None
0
10
20
30
Time minutes

Fig. 37.



80
R∞ 60
40
10
$t_{1\ min}$
6
2
·32
k_2 ·28
·24
PBN 2%
0
1·0
2·0
Additive Concentration % wt.

Fig. 38.

4.3.2.1. Curing behaviour

The following basic formula was used in making the gumstocks:

Natural rubber	100 parts
Stearic acid	2.0 "
Zinc oxide	5.0 "
C.B.S.	0.5 "
Sulphur	2.5 "

Samples containing different proportions of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan as well as 2% P.B.N. were cured in the Monsanto Rheometer at 140°C for a period of 30 minutes (with a preheat time of 60 seconds).

The curves obtained are shown in Fig. (36).

The plot of log (R_∞ - R_t) against time is given in Fig. (37).

Analysis of the results

The parameters R_∞, k_2 and t_1 obtained from the Figures (36), (37) and (38) are given in the following table:

Stock	R_∞	k_2 min^{-1}	$t_{1\text{min.}}$
No additive	57.0	0.2872	9.75
0.25% Mercaptan	63.0	0.2700	5.63
0.5% "	54.0	0.2498	4.35
1.0% "	57.7	0.2898	2.5
2.0% "	48.0	0.2149	2.8
4.0% "	11.2	0	
2.0% P.B.N. (by weight)	52.9	0.3224	10.38

As clearly seen from the above table the presence of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan in the vulcanization recipe has a considerable effect on the induction period of cure. At lower concentrations (0.25 - 0.5%) the induction period is reduced significantly and at moderate concentrations (1.0 - 2.0%) the effect decreases. At a rather higher level (4.0%) the induction period reaches infinity; no vulcanization occurring even after 90 minutes.

Certain sulphur compounds are known to act as activators of premature vulcanization as well as inhibitors of vulcanization. The above experiment shows that at lower concentrations the scorchy effect is predominant while at higher concentrations the inhibiting effect becomes more significant. [redacted]

The ultimate torque R_{∞}, which is a measure of cross-link density, decreases steadily but slowly with the increase of mercaptan concentration. At 0.25%, R_{∞} achieves a maximum which is at a higher level than that containing no mercaptan which may be associated with the scorchiness at very low concentrations. At any rate, the difference in R_{∞} of stocks containing 2.0% of mercaptan and P.B.N. is negligible.

The shapes of the curves obtained for R_∞ , k_2 and t_1 clearly indicate that there are different modes of action which become predominant at particular concentrations, and the mechanisms of the chemical interactions of the gumstock with the mercaptan are of a complex nature.

As mentioned earlier, the mercaptan added by the masterbatch technique did not have any significant effect on vulcanization characteristics probably due to the absence of the free -SH group. But when the mercaptan is added as an ingredient during vulcanization the changes are significant.

4.3.2.2. Ageing behaviour

4.3.2.2.1. Stress Relaxation

Extracted natural rubber was vulcanized into sheets of 5 - 7 $\hat{\ell}$ thickness using a C.B.S. sulphur formulation containing different proportions of 3,5 Ditertiary-butyl-4-hydroxy benzyl mercaptan and P.B.N. according to the table given in the earlier part of this Chapter.

Long thin samples were cut using a die and their continuous relaxation curves were obtained at 100°C while passing air at the rate of 20 cc per minute. The same procedure was repeated with samples which were extracted with the azeotrope and then dried.

From the curves obtained, plots of log f/f_o against time were made and are shown in Fig.(39) and (40).

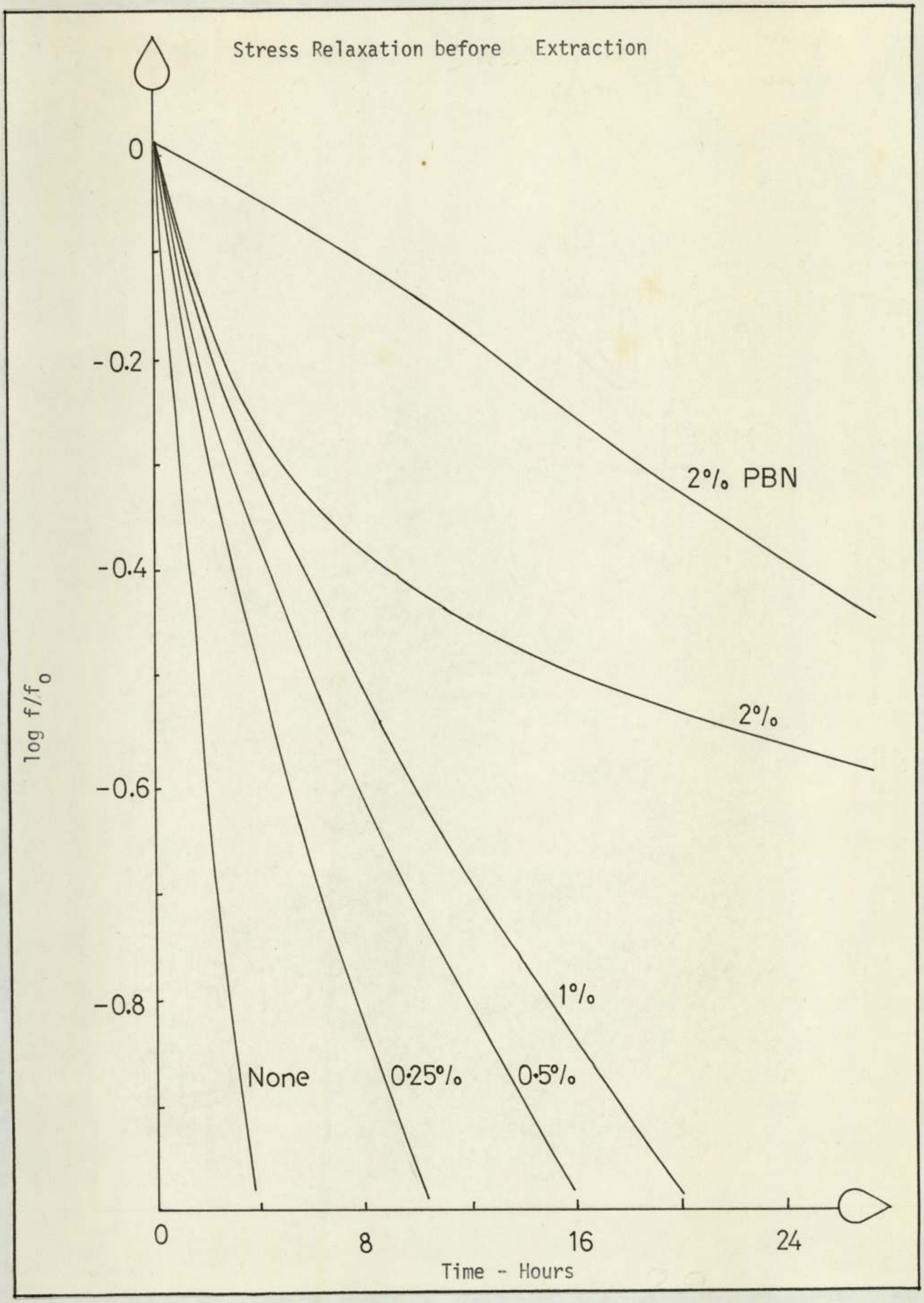

Stress Relaxation before Extraction
0
-0.2
-0.4
-0.6
-0.8
log f/f$_o$
2% PBN
2%
1%
None
0·25%
0·5%
0
8
16
24
Time - Hours

Fig. 39.

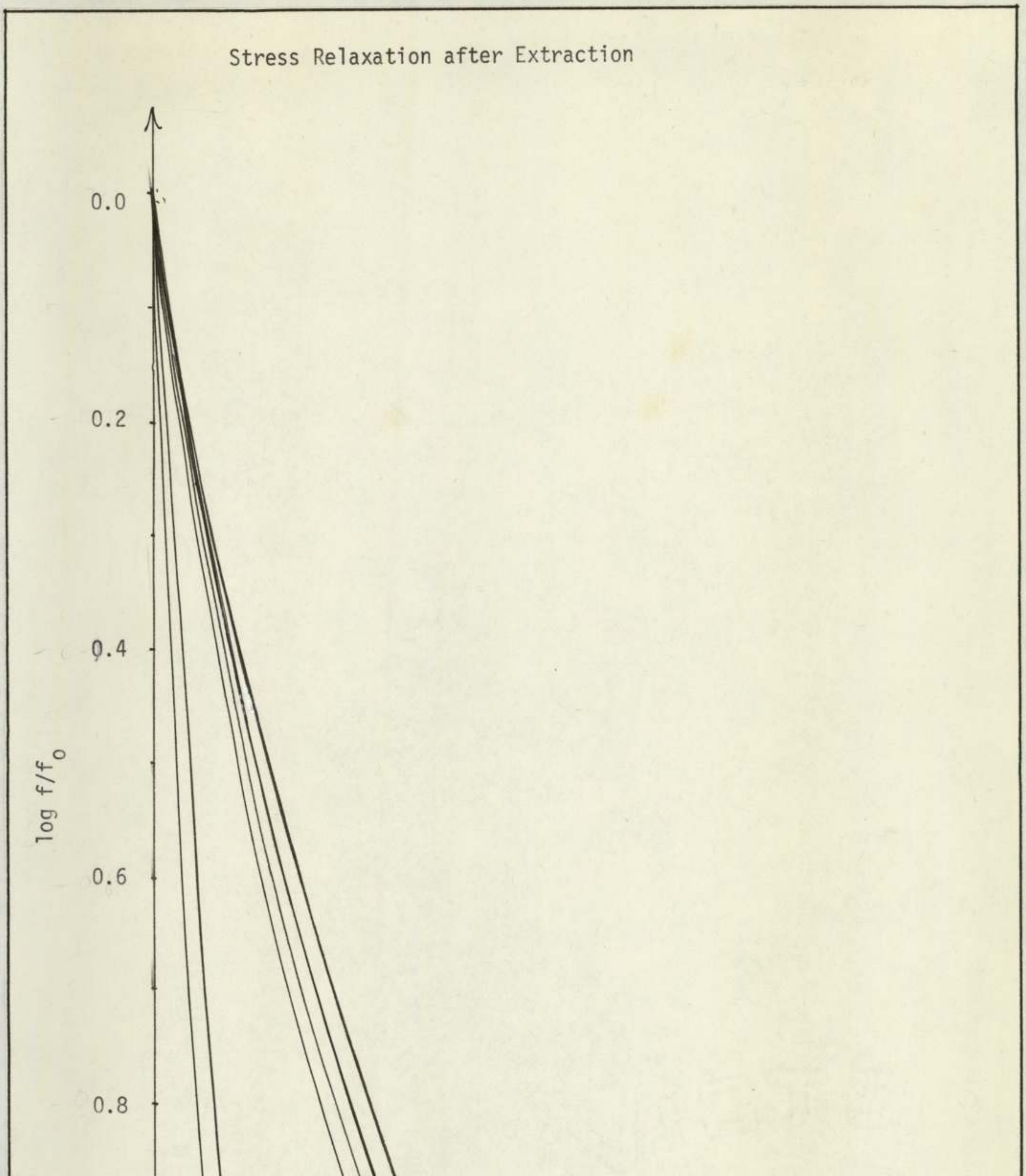

Stress Relaxation after Extraction
log f/f$_0$
0.0
0.2
0.4
0.6
0.8
0
8
16
24
Time - Hours
None
P.B.N. 2%
0·25%
0·5%
1%
2%

Fig. 40.

Analysis of the results

As clearly seen from Fig. (39) the stress of a rubber containing no antioxidant decays drastically within a very short period of time indicating its instability to thermal oxidation. The sample containing 2% P.B.N. is very stable in this respect although after extraction the sample is not much different from the one with no antioxidant. This clearly indicates the removal of the antioxidant during extraction.

The samples containing the mercaptan show interesting results with relation to its concentration. The presence of 0.25% of mercaptan shows a clear improvement in the decay of stress with comparison to the sample containing no antioxidant. The most important feature here is that, even after extraction the stability of the same sample is retained. The samples containing 0.5, 1.0 and 2.0% of the mercaptan show a clear trend in increasing stability, although after extraction the stability of all of them is reduced to almost the same level as that of the sample containing 0.25%.

Therefore it can be concluded that, when added as a compounding ingredient during vulcanization, small amounts of the mercaptan become chemically attached to the rubber network thus becoming unextractable. The stability of rubber samples containing higher proportions of mercaptan drops to a similar level after extraction. This indicates that there exists a maximum in the concentration of mercaptan which can be chemically bound to the rubber during vulcanization. The higher stability before extraction of samples containing larger amounts of mercaptan could be explained in two possible ways.

(1) Of the mercaptan initially added, only a small portion becomes attached to the rubber and the rest remains unreacted, the unreacted portion is removed by extraction.

(2) A certain proportion of the mercaptan becomes attached to the rubber, the rest is thermally converted into other species which possess antioxidant activity and they are later lost during extraction.

4.3.2.2.2. <u>Oxygen Absorption</u>

The oxygen absorption system was calibrated at 80°C. Small rectangular pieces were cut from the vulcanizates of thickness (5 - $\overset{\tau}{7}$), containing different proportions of mercaptan (0.25% - 2.0%) and 2% P.B.N. and were accurately weighed. The sample thickness of 5 - 7τ is small enough to avoid the process of oxidation being diffusion controlled.

The samples were then kept between the two arms of the holder to prevent adhesion to the tube wall and oxygen was purged through the system. Then the system was closed using the taps and the oxygen absorption was followed.

Results

Knowing the exact weight of a sample used, and with the help of the calibration curve and the recorder curve, graphs of Wt.% of oxygen absorbed against time were drawn and are shown in Fig. (41). The same procedure was repeated with extracted samples and the corresponding curves are shown in Fig. (42). Times to absorb 0.5% and 1.0% by weight of oxygen by each sample were calculated and are given in the following table:

Time to absorb

Sample	$0.5\%\ O_2$		$1.0\%\ O_2$	
	Unextracted	Extracted	Unextracted	Extracted
None	6.6	3.0	9.9	6.4
0.25% Mercaptan	7.4	6.9	13.3	12.5
0.5% "	8.6	7.1	16.7	13.3
1.0% "	14.7	7.6	26.0	13.7
2.0% "	23.0	8.0	-	14.2
2.0% P.B.N.	25.8	3.3	-	7.0

From the above table, the problem of leaching out of a physically mixed conventional antioxidant is clearly emphasized. The presence of 2% by weight of P.B.N. shows a period of 25.8 hours for 0.5% oxygen absorption, while after extraction the rubber becomes almost as unstable as a sample containing no antioxidant, in relation to 0.5% and 1.0% oxygen absorption. The presence of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan shows the same results as by stress relaxation. Only a small proportion of mercaptan remains attached to the rubber and the rest is extractable.

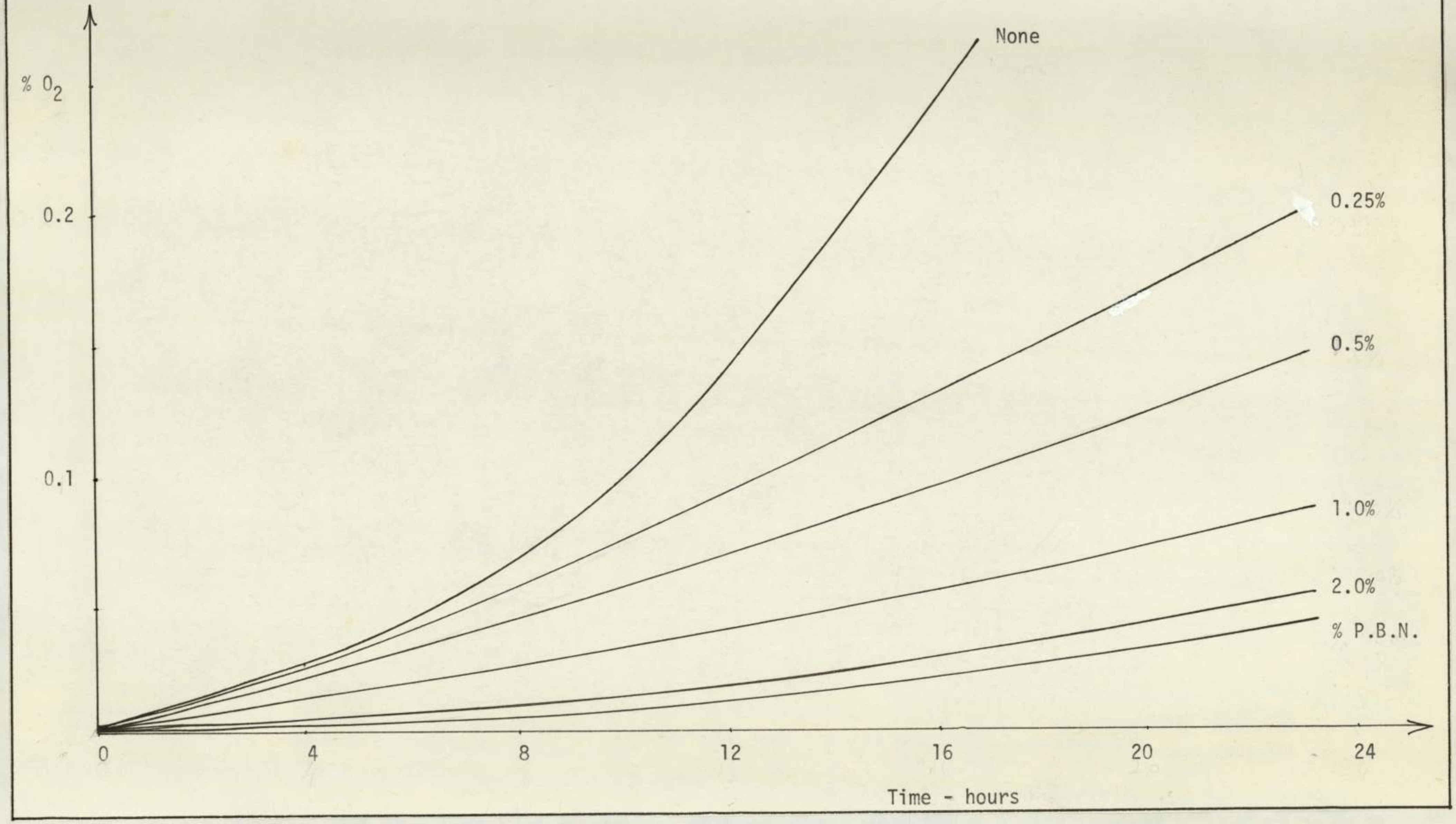


Fig. 41. Oxygen absorption - Before extraction.

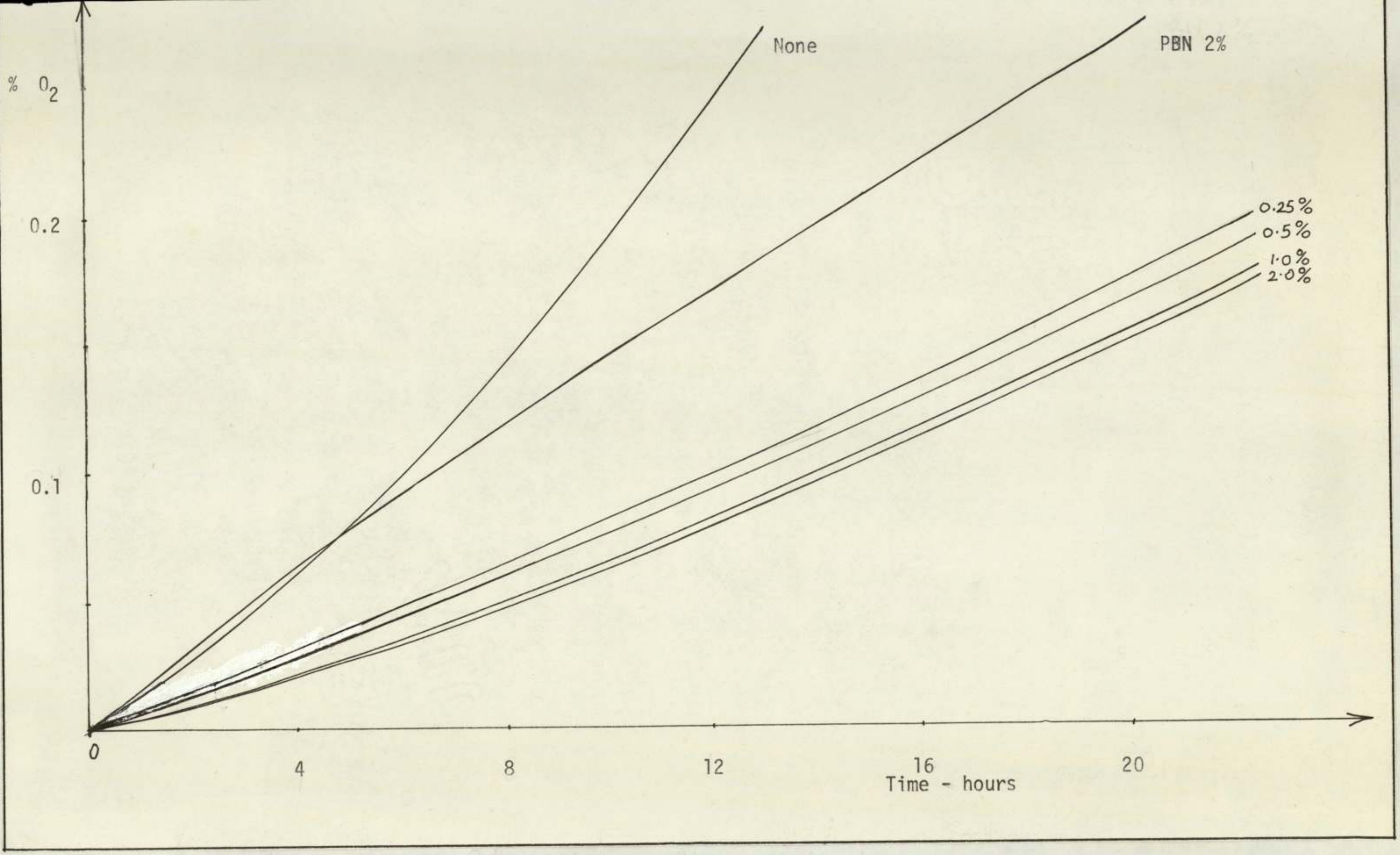


Fig. 42. Oxygen absorption - After extraction.

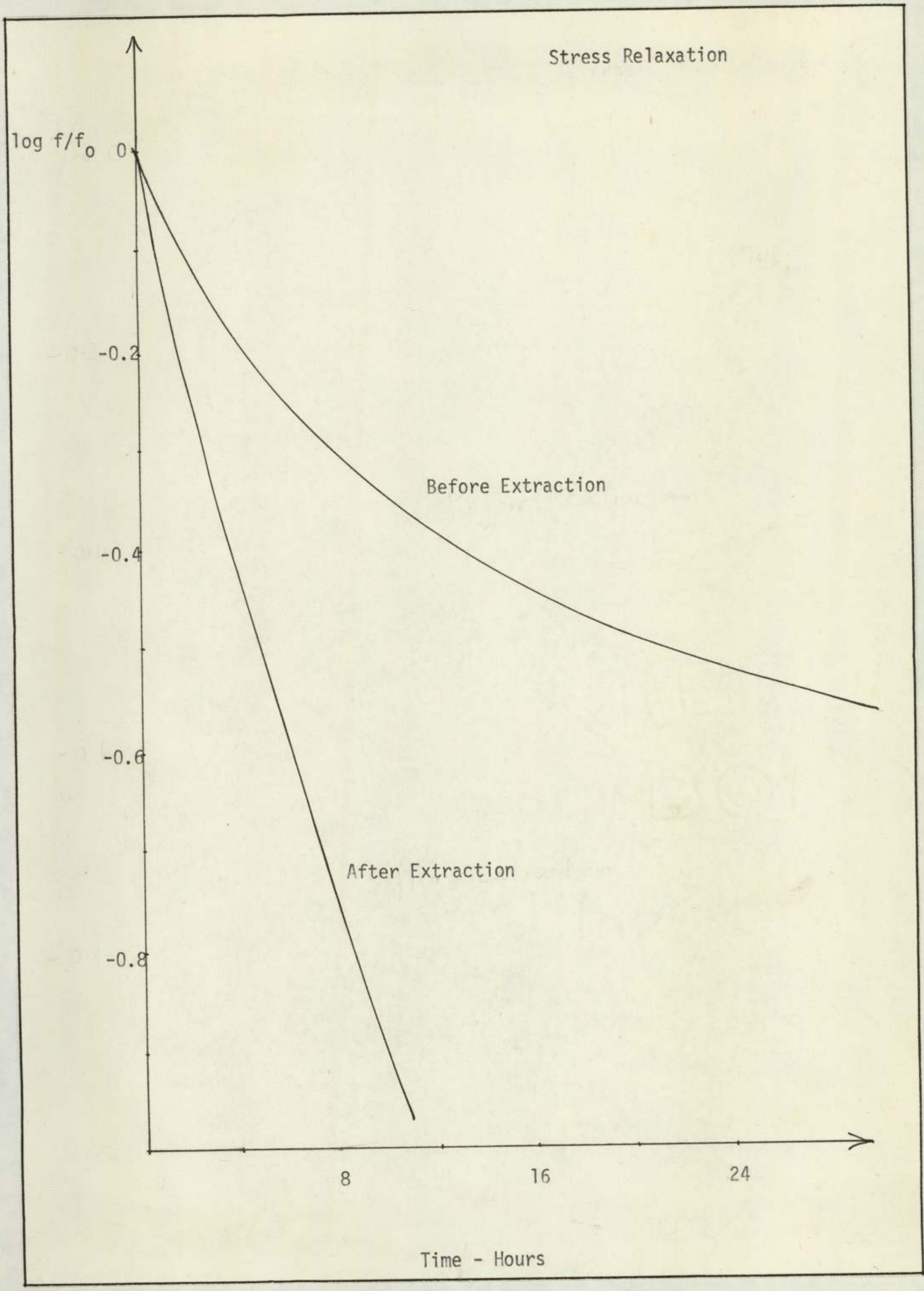
4.3.3. Initial thermal treatment of rubber in the presence of mercaptan

When the mercaptan is added to rubber as a vulcanizing ingredient, the chemical reaction between rubber and mercaptan, if any, occurs in the presence of all the vulcanizing ingredients and at vulcanization temperatures. The interaction between rubber and mercaptan alone by a thermal treatment in the solid phase might be expected to be different from the above and to investigate this, the following experiment was carried out.

Experimental

50.0 gms of extracted natural rubber were masticated on a water cooled two-roll mill and 1.0 gms of 3,5 Ditertiarybutyl-4-hydroxy benzyl mercaptan was incorporated into it. The rubber was taken out of the mill in the form of a thin sheet which was wrapped with aluminium foil and kept in an oven at 80°C for a period of 24 hours. The rubber appeared to be decolourized after the oven treatment.

25.0 g of this rubber were then vulcanized as before using the same C.B.S. sulphur recipe into a thin sheet. Half of the sheet was cut into test pieces and tested by stress relaxation and oxygen absorption. The other half was extracted with the azeotrope and dried as before and the same two ageing tests were carried out. The stress relaxation results are shown in Fig. (43) and oxygen absorption curves in Fig. (44).



Stress Relaxation
log f/f$_o$
0
-0.2
-0.4
-0.6
-0.8
Before Extraction
After Extraction
8
16
24
Time - Hours

Fig. 43.

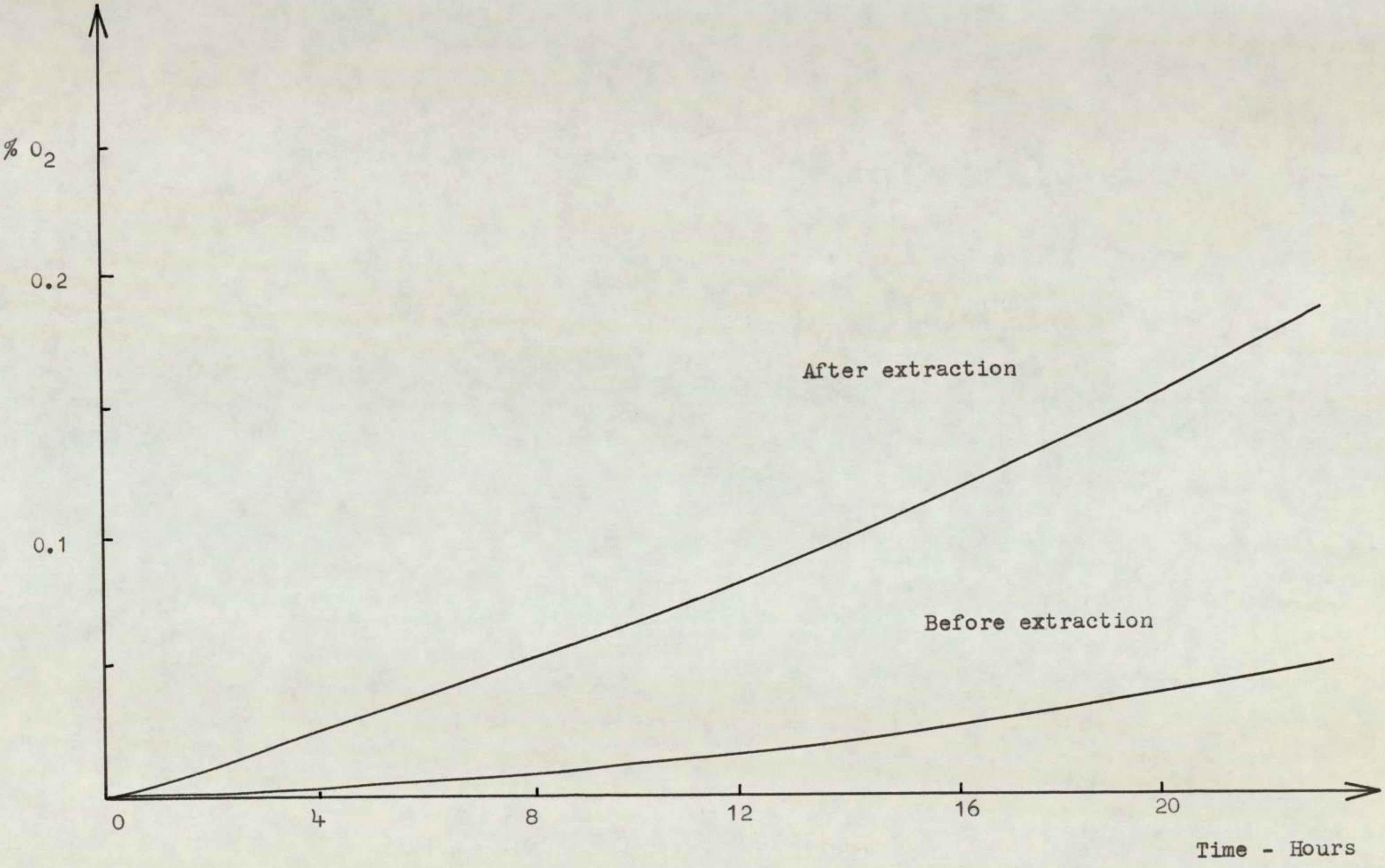


Fig. 44 - Oxygen absorption.

Discussion

The stress relaxation curves show that the initial stability of a thermally treated sample is slightly higher than that which was obtained by adding the mercaptan during vulcanization. But the reverse is seen after the extraction process. Oxygen absorption curves also show a similar behaviour.

The initial increase in stability can be explained by the fact that the milling treatment results in a better dispersion of the antioxidant. The stability of an extracted thermally treated sample is less than an extracted untreated sample indicating that it is not chemically bound. This could be because thermal treatment converts the mercaptan into other species which are active as antioxidants but are incapable of becoming bound to the main chain. The discolouration of the rubber during thermal treatment also provides evidence for this conversion of mercaptan into other species.

4.3.4. Conversion Products

If the process of thermal treatment or vulcanization converts the mercaptan into other antioxidant species, it might be expected that these secondary compounds may include either monosulphidic or polysulphidic dimers (146),or a mixture of them. According to the results obtained earlier these latter compounds should act as antioxidants in rubber but should be extractable. To clarify this bis (3, 5 Ditertiarybutyl-4-hydroxy benzyl) monosulphide and bis

(3,5 Ditert-butyl-4-hydroxy benzyl) disulphide were prepared and their effect on stabilizing rubber vulcanizates were investigated.

Synthesis of bis (3,5 Ditertiarybutyl-4-hydroxy benzyl) monosulphide (131)

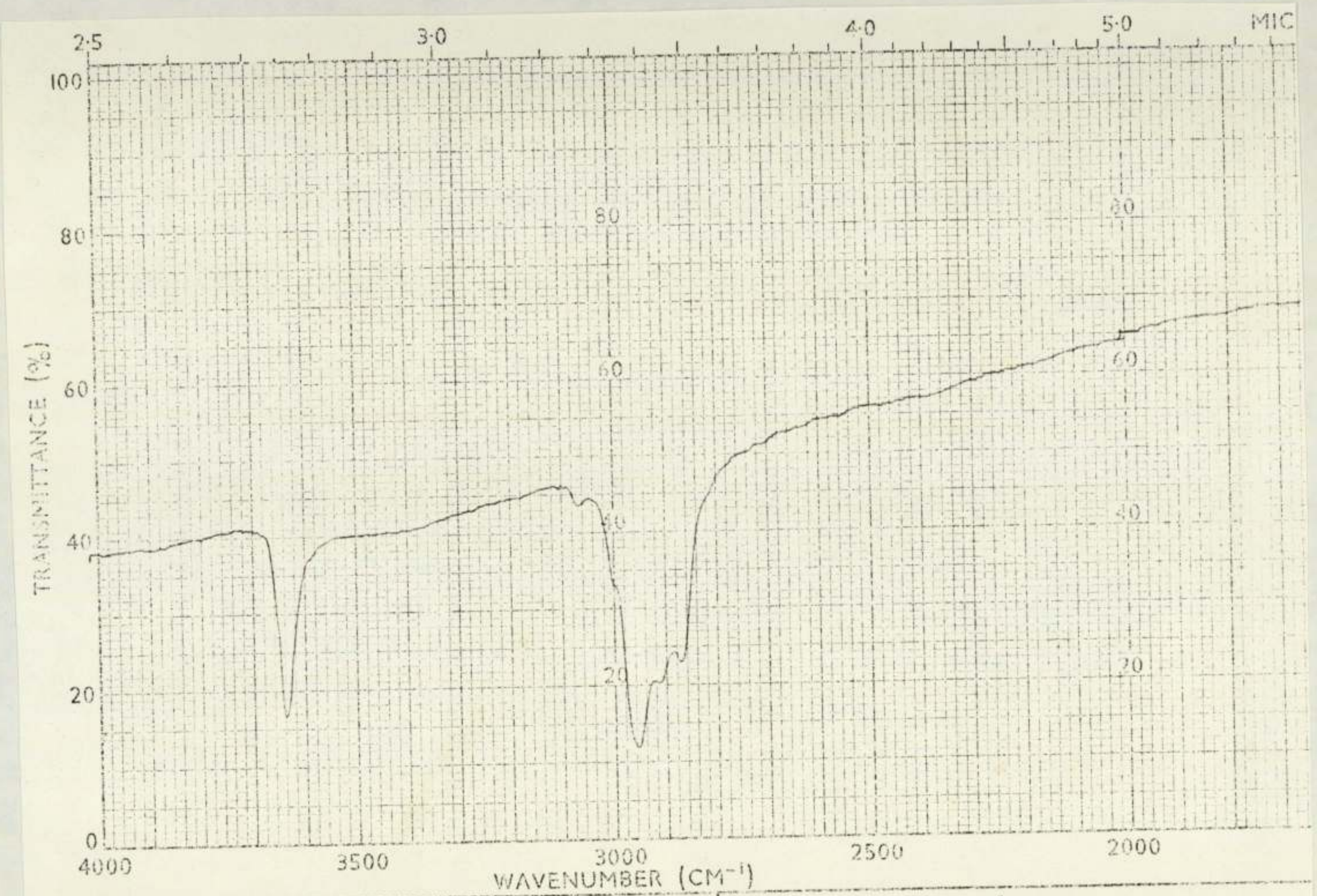
The starting material, 3,5 Ditertiarybutyl-4-hydroxy benzyl chloride was prepared as described in Chapter 2. In a reaction vessel equipped with a heater, thermometer, water cooled condenser and a means of stirring, a mixture of 19.2 gms of sodium sulphide dissolved in 15.0 ml of water, 120 ml of isopropyl alcohol, and 50 gms of 3,5 Ditertiarybutyl-4-hydroxy benzyl chloride was refluxed for a period of 2 hours. After cooling the mixture was kept standing for a period of 48 hours and then the solids were filtered, washed with water and dried. They were then recrystallized from a mixture of isooctane and methanol and a yellow crystalline compound was recovered. The monosulphide thus obtained had a melting point of 142°C and was also characterized by I.R., N.M.R. and Mass spectrometry.

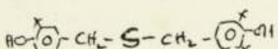
Infra-red Analysis Fig. (45).

Phenolic OH	2.75 microns	3640 cm^{-1}
Tertiary butyl groups	7.18 "	1390 cm^{-1}
	7.35 "	1360 cm^{-1}
Tetrasubstituted benzene ring	11.4 "	878 cm^{-1}

N.M.R. Analysis Fig. (46).

Tertiary butyl protons 8.6 τ (Singlet)

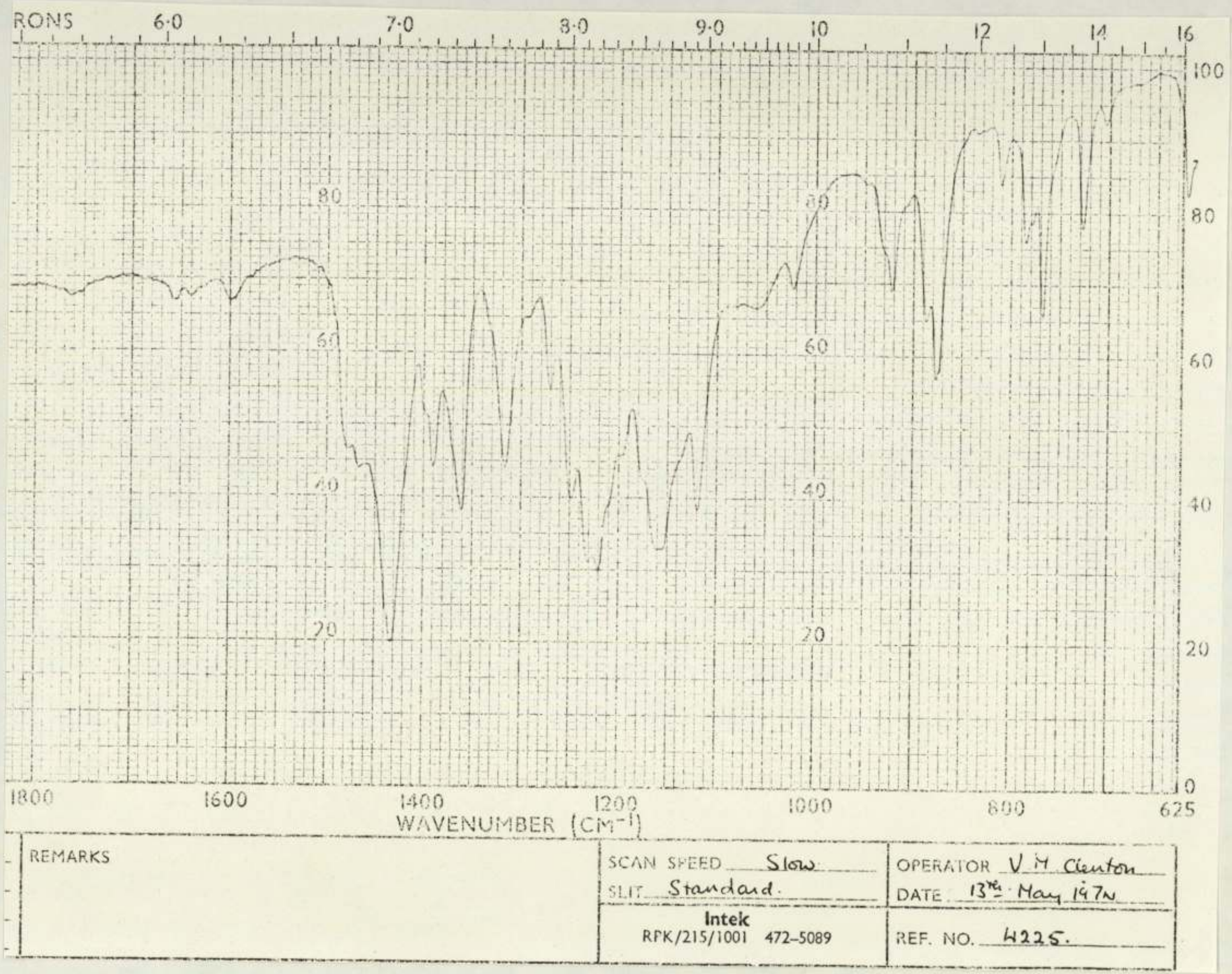


SAMPLE ⑥


ORIGIN M.R.N Fernando.

SOLVENT KBr
CONCENTRATION approx. 1.0%
CELL PATH 13.0 m/m. dia. disc
REFERENCE Air.

Fig. 45.



REMARKS

SCAN SPEED Slow

SLIT Standard.

Intek
RPK/215/1001 472-5089

OPERATOR V M Clenton

DATE 13th. May 1974

REF. NO. 4225.

Fig. 45 continued.

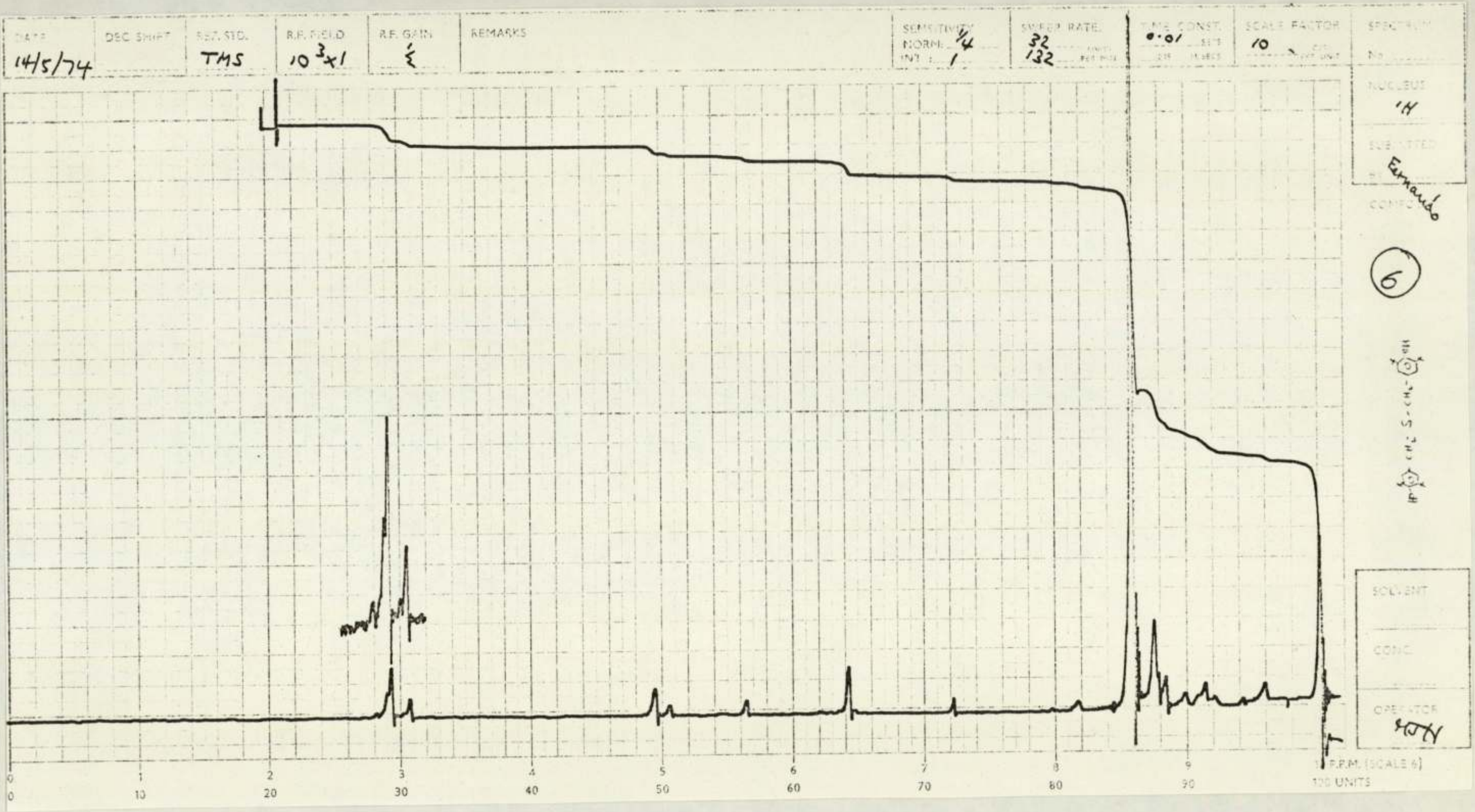

DATE
14/5/74
DEC. SHIFT
REF. STD.
TMS
R.F. FIELD
10^3x1
R.F. GAIN
REMARKS
SENSITIVITY
NORM. 1/4
INT. 1
SWEEP RATE
32
132
TIME CONST.
0.01
SCALE FACTOR
10
SPECTRUM No.
NUCLEUS
1H
SUBMITTED BY
Fernando
COMPOUND
6
SOLVENT
CONC.
OPERATOR
0 1 2 3 4 5 6 7 8 9 10 P.P.M. (SCALE 6)
0 10 20 30 40 50 60 70 80 90 100 UNITS

Fig. 46.

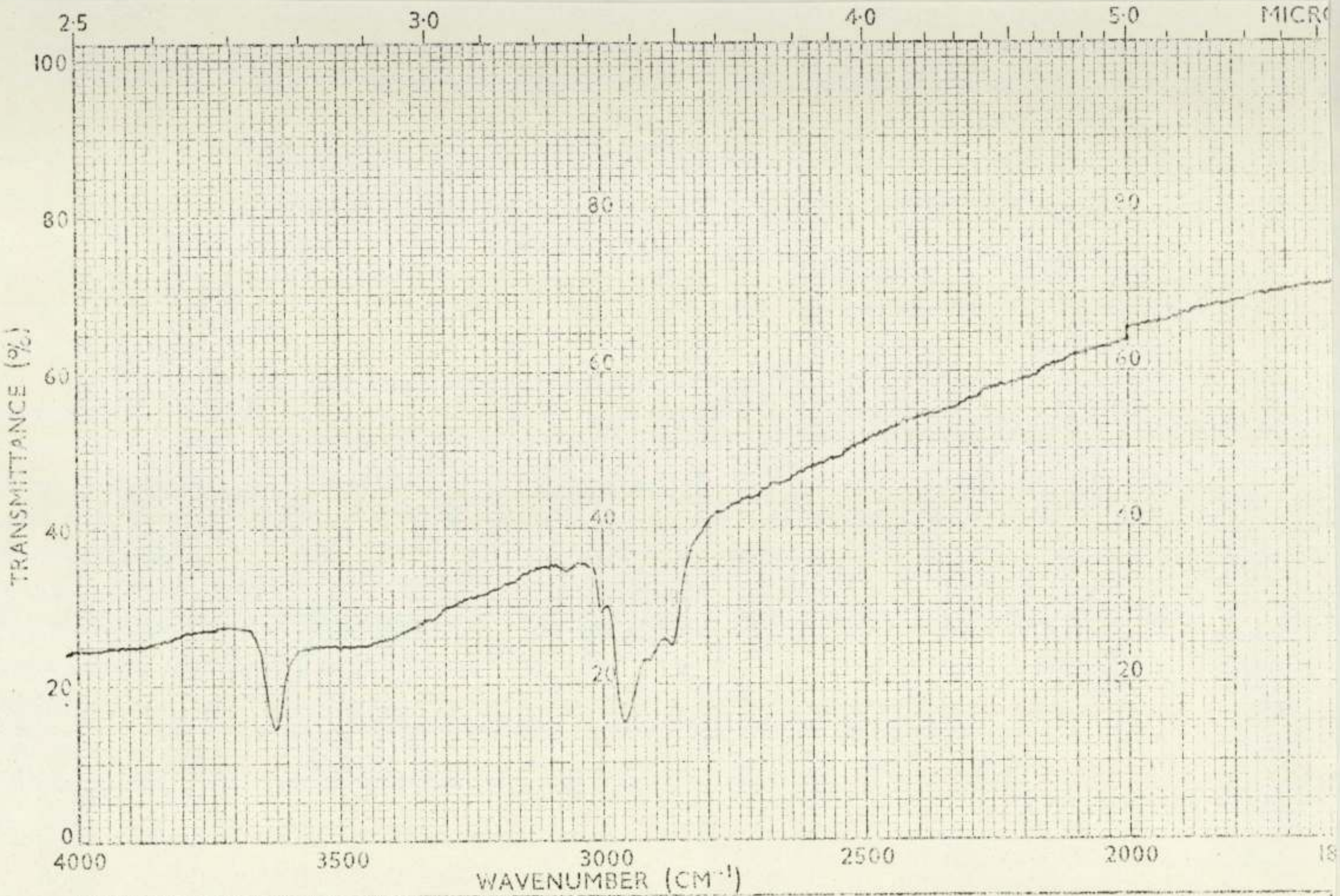
Phenolic protons	4.94 τ (Singlet)
Aromatic protons	2.91 τ (Singlet)
Methylenic protons	6.32 τ (Singlet)

Synthesis of bis (3,5 Ditertiarybutyl-4-hydroxy benzyl disulphide (132).

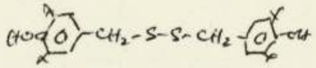
The starting material was prepared as mentioned in Chapter 2. A mixture of 25.3 gms of 3,5 Ditertiary-4-hydroxy benzyl mercaptan, 100 ml of benzene and 25 ml of water was shaken vigorously in a round-bottom flask and a solution of 25.4 gms of iodine, 100 ml of benzene and 25 ml of ethanol was slowly added from a dropping funnel. When the stirred mixture showed a slight brown colour the addition of iodine was stopped and the organic layer was separated, dried over magnesium sulphate, filtered and the solvents were removed on a rotary evaporator. The solid thus obtained was recrystallized from benzene and petroleum ether and a light yellow crystalline compound melting at 168°C was recovered. The disulphide was further characterized by I.R., N.M.R., and Mass spectrometry.

I.R. Analysis Fig.(47).

Phenolic OH	2.76 microns	3620 cm^{-1}
Tertiarybutyl groups	7.18 "	1390 cm^{-1}
	7.35 "	1360 cm^{-1}
Tetrasubstituted benzene ring	11.4 "	880 cm^{-1}



SAMPLE 9.



ORIGIN M.R.N. Fernando.

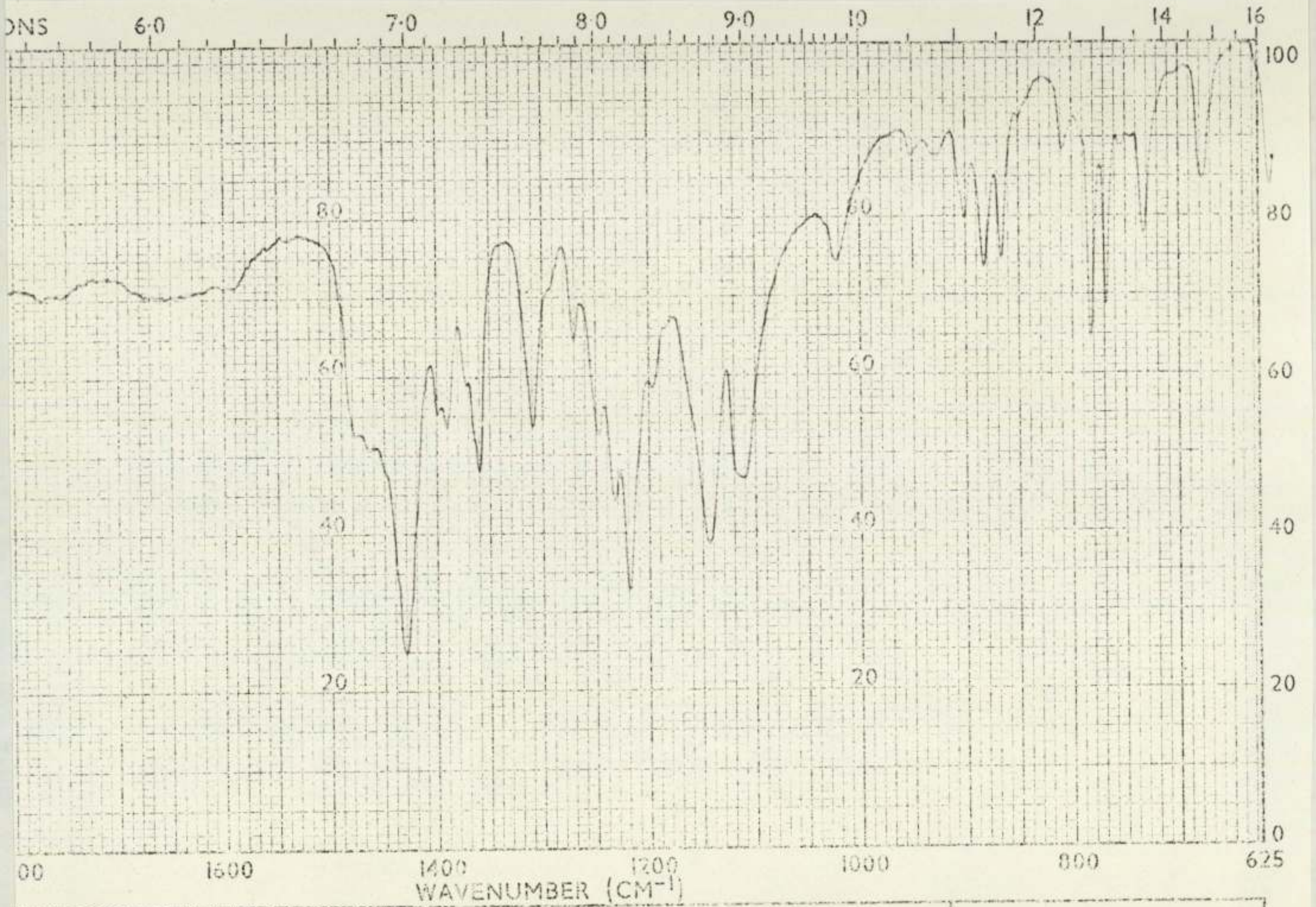
SOLVENT KBr.

CONCENTRATION approx 1.0%

CELL PATH 13.0 m/m. dia. disc

REFERENCE Air.

Fig. 47.



REMARKS

SCAN SPEED Slow.

SLIT Standard.

Intek
RPK/215/1001 472-5089

OPERATOR V.M. Clenton.

DATE 26th June 1974

REF. NO. 4424.

Fig. 47 continued.

N.M.R. Analysis Fig.(48).

Tertiarybutyl protons	8.56 τ (Singlet)
Phenolic protons	4.9 τ (Singlet)
Aromatic protons	2.93 τ (Singlet)
Methylenic protons	6.3 τ (Singlet)

The above two compounds, the monosulphide and the disulphide were added in 2.0% concentrations to rubber during vulcanization, and the ageing charateristics of the samples were obtained before and after extraction by oxygen absorption and stress relaxation. (Fig. (49) & (50).

Discussion

As clearly seen from Fig. (49) and (50) both the monosulphide and disulphide are good antioxidants for rubber, but they do not become bound to the rubber during vulcanization, since they are completely extractable.

Thin layer chromatography

The method of thin layer chromatography was used to find out the presence of the monosulphide and the disulphide in the extract of a rubber sample vulcanised in the presence of 3,5 Ditert-butyl-4- hydroxy benzyl mercaptan. The extraction was carried out with an acetone, methanol, trichloroethane azeotrope under nitrogen for a period of 24 hours. A vulcanizate containing no antioxidant was also extracted for comparison purposes. The extracts were concentrated on a rotary evaporator.

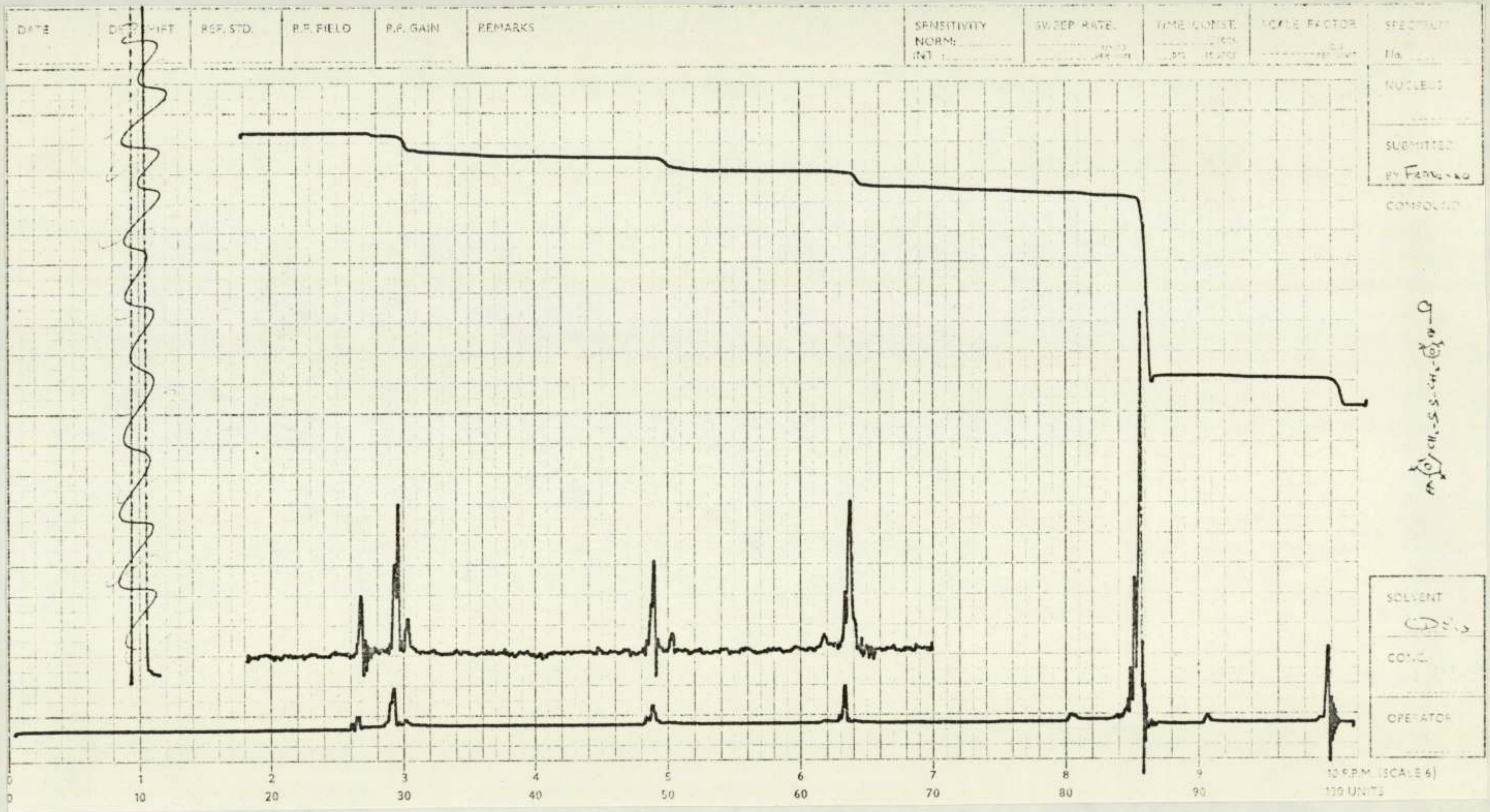

DATE
DRIFT
REF. STD.
R.F. FIELD
R.F. GAIN
REMARKS
SENSITIVITY
NORM:
INT
SWEEP RATE
TIME CONST.
SCALE FACTOR
SPECTRUM
No.
NUCLEUS
SUBMITTED
BY Fernando
COMPOUND
SOLVENT
CDCl3
CONC.
OPERATOR
0
1
2
3
4
5
6
7
8
9
10 P.P.M. (SCALE 6)
0
10
20
30
40
50
60
70
80
90
100 UNITS
CH2-S-S-CH2

Fig. 48.

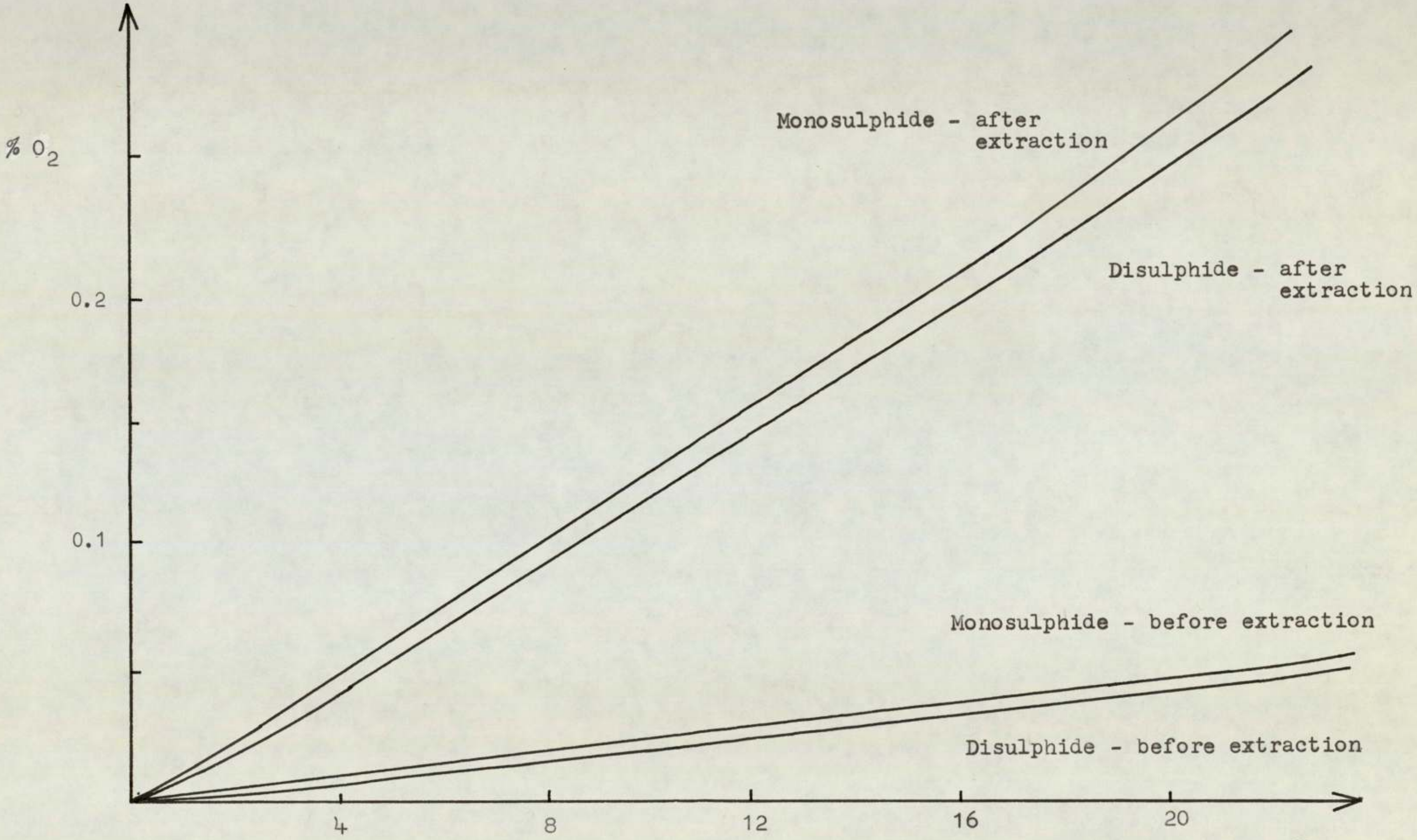


Fig. 49. Oxygen absorption.

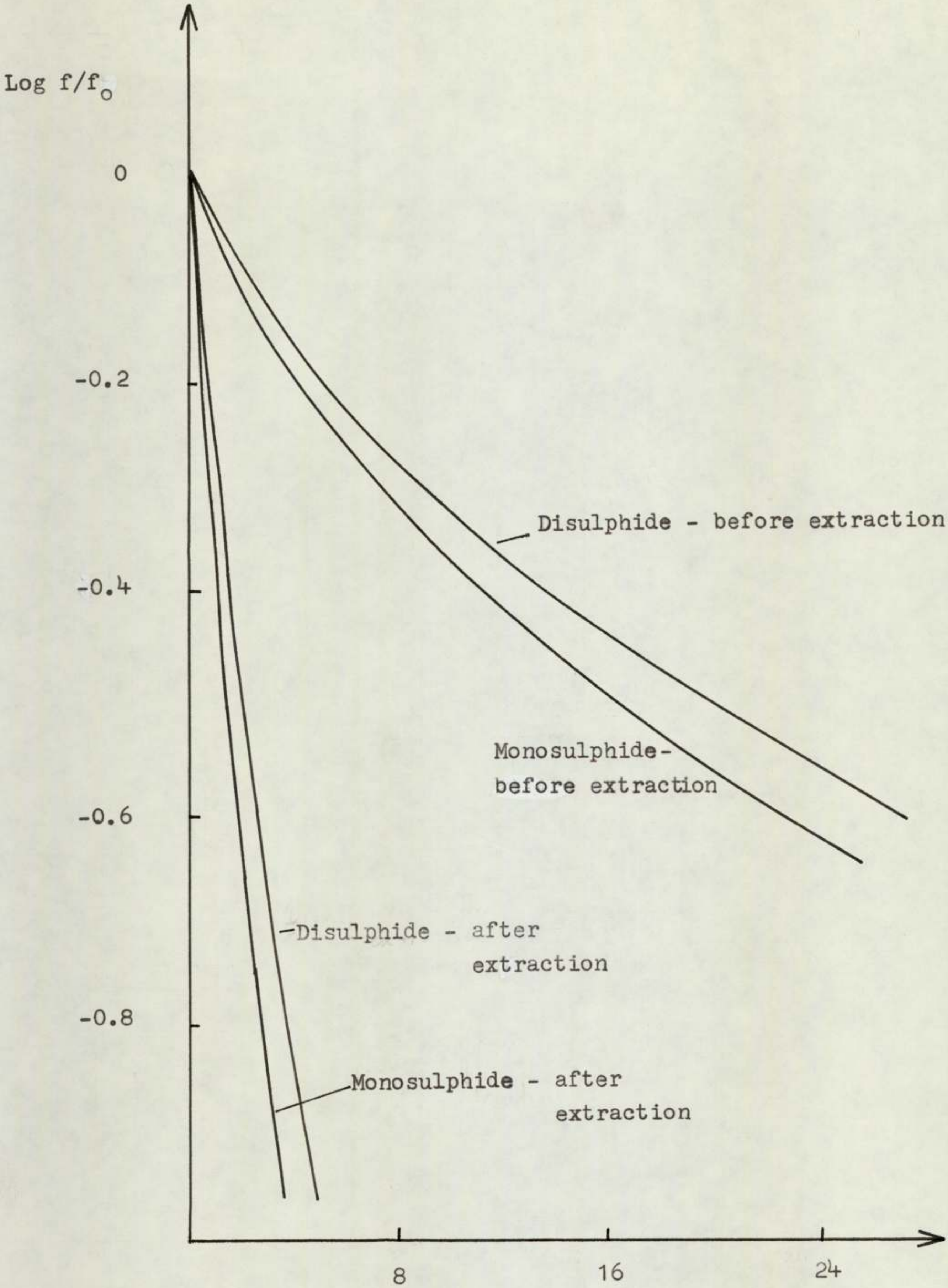
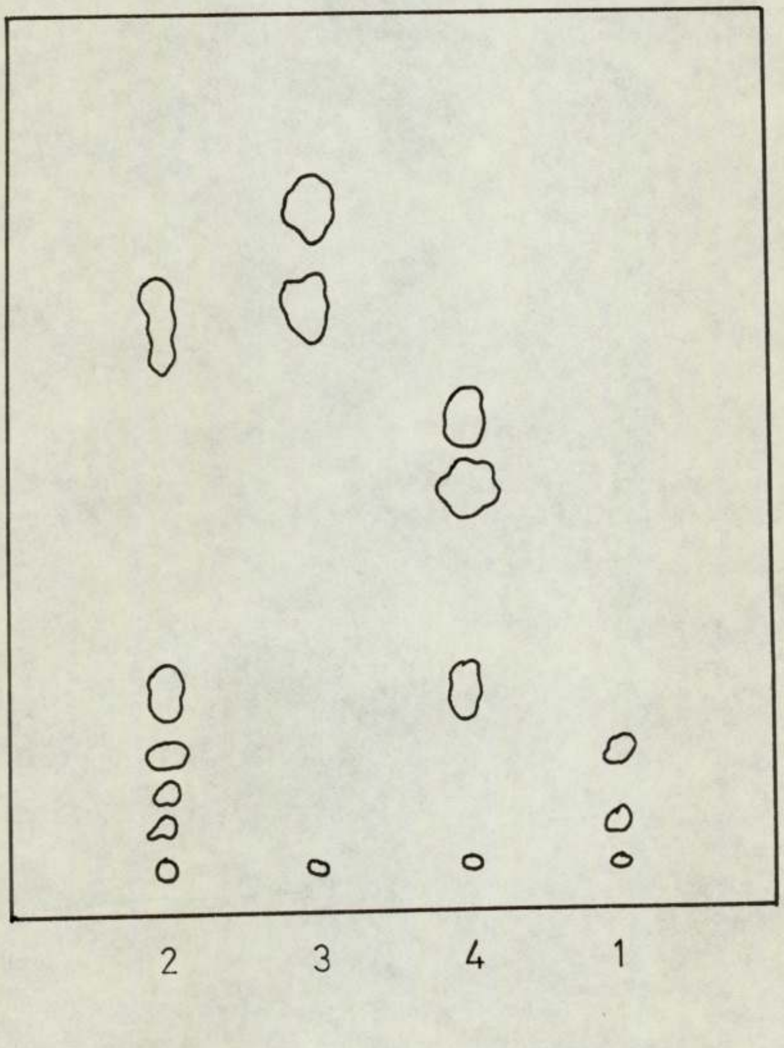


Fig.50. Stress Relaxation.

The method of Slonaker and Siebers (147) was used for the investigation. 4% methanol in cyclohexane was used as the solvent with silica gel plates and detection was done with 3% phosphomolybdic acid in ethanol followed by exposure to ammonia vapour. The following four substances were analyzed:

1. Extract of vulcanizate with no antioxidant
2. Extract of vulcanizate with 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan
3. bis (3,5 Ditert-butyl-4-hydroxy benzyl) monosulphide
4. bis (3,5 Ditert-butyl-4-hydroxy benzyl) disulphide

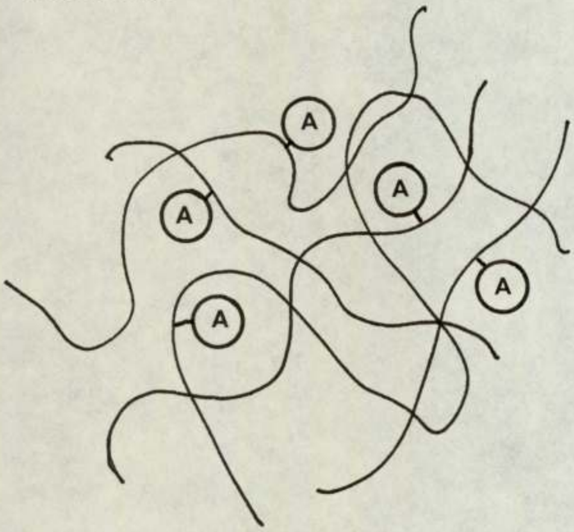
The chromatogram obtained is shown below:



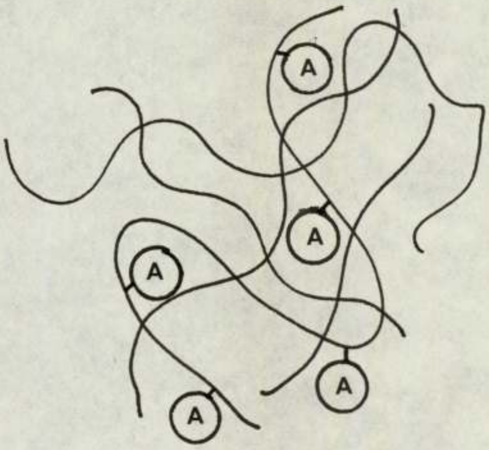
There are additional spots in the mercaptan vulcanizate by comparison to that of unstabilized vulcanizate. These additional spots should be due to the mercaptan or its transformation products. The two pure phenolic compounds also gave a number of spots and there are certain spots of them corresponding to the mercaptan vulcanizate extract. Therefore although the evidence is not conclusive, with the help of theoretical considerations, it could be said that the mercaptan might be converted into the monosulphide and disulphide during vulcanization.

4.3.5. Comparison of masterbatch technique and straight addition

It is well known that the mobility of a chemical compound is one of the main requirements for it to take part in chemical reactions. Antioxidants which are physically blended into polymers possess this mobility (within a certain range) and function satisfactorily unless they are removed by extraction or leaching out. But when an antioxidant molecule is bound to a polymer backbone its mobility is restricted and this may result in a decrease in its antioxidant efficiency. As mentioned in Chapter 3, when the masterbatch technique is used only a small proportion of the rubber chains are containing all the attached antioxidant molecules, and the major part of rubber chains have no bound antioxidant. Depending on the extent of addition of the masterbatch the ratio of antioxidant-containing rubber chains to no-antioxidant-containing rubber chains will vary in a given vulcanizate. For example if rubber samples are prepared by (a) addition of a given amount of antioxidant into the whole of the rubber and (b) by diluting a masterbatch containing a large amount of bound antioxidant to contain the same overall amount of antioxidant, the distribution of bound antioxidant groupings in the two samples will be different from one another. This can be schematically represented as follows:-



(a)



(b)

If mobility is of major importance with regard to antioxidant efficiency the above two samples can show different behaviours with respect to autoxidation. To investigate this phenomenon the following experiment was carried out:

Materials

Rubber containing 0.5% (wt) bound mercaptan
Rubber containing 2.0% (wt) bound mercaptan
Rubber containing 16.0% (wt) bound mercaptan
Chlorobenzene.

The above rubber samples were obtained from earlier experiments where the kinetics of the addition reaction were studied. (see page 73).

Experimental

2.0% solutions of the above rubber samples were made in chlorobenzene. Using a 2.0% solution of pure natural rubber in chlorobenzene, the 16% antioxidant containing rubber solution was diluted to obtain solutions with 0.5% and 2.0% of antioxidant. Using 10.0 ml quantities the oxygen absorption characteristics of these rubber solutions were studied in a capillary oxygen absorption system. (see Fig.51).

The capillary oxygen absorption system comprised of a 100 ml two necked round-bottomed flask, fitted with a long bent capillary tube and a syringe needle. The flask was kept in an accurately controlled thermostatic bath and the end of the capillary tube was dipped in mercury. A slight vacuum in the system was created initially by the use of a syringe and when a small pellet of mercury was sucked into the end of the capillary tube the mercury bath was removed. The height travelled by the mercury pellet was measured using the meter ruler attached to the capillary tube. When a rubber sample was tested the system was initially flushed with oxygen.

The system was calibrated by removing measured quantities of air from the system using a syringe and

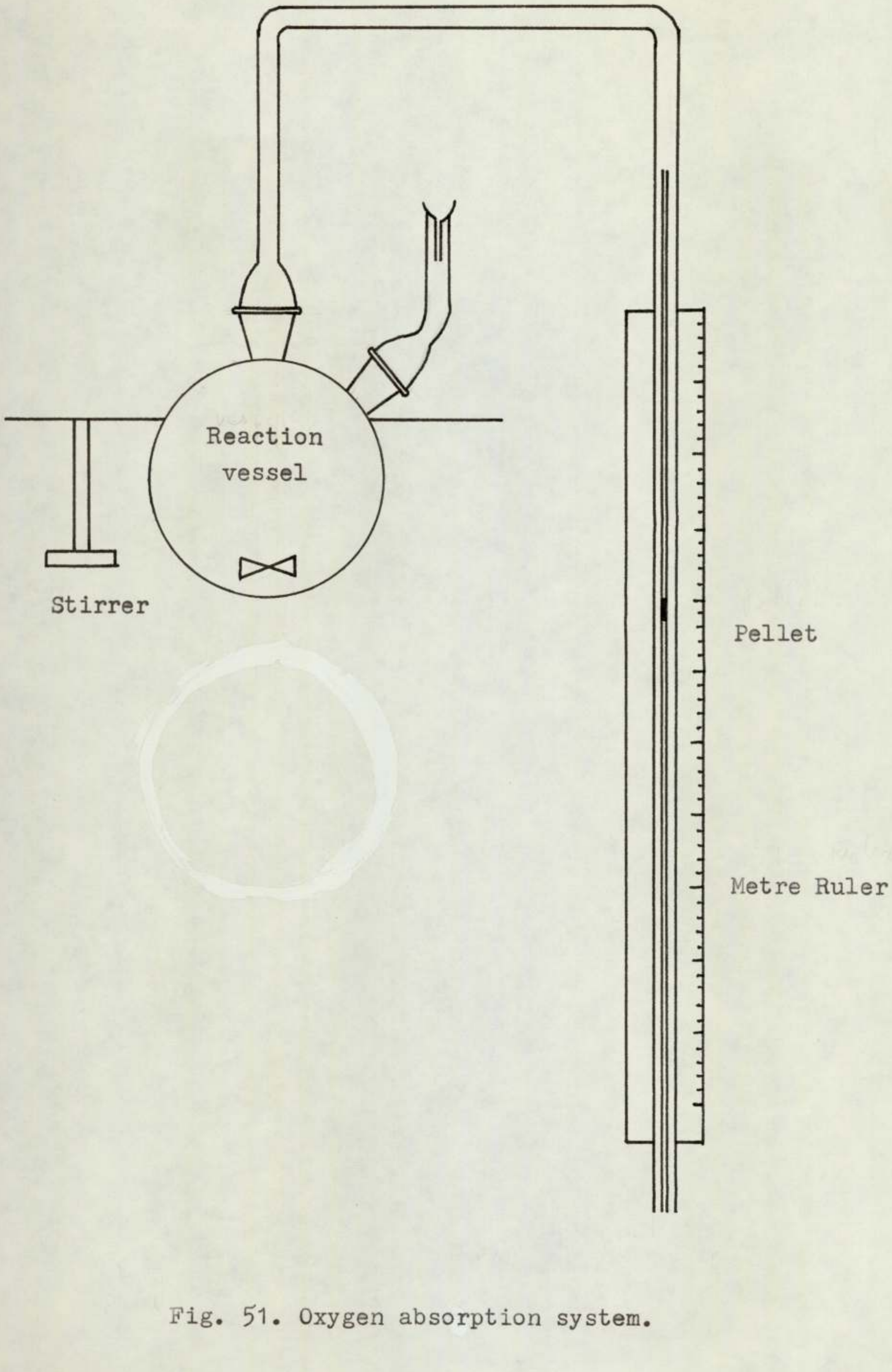


Fig. 51. Oxygen absorption system.

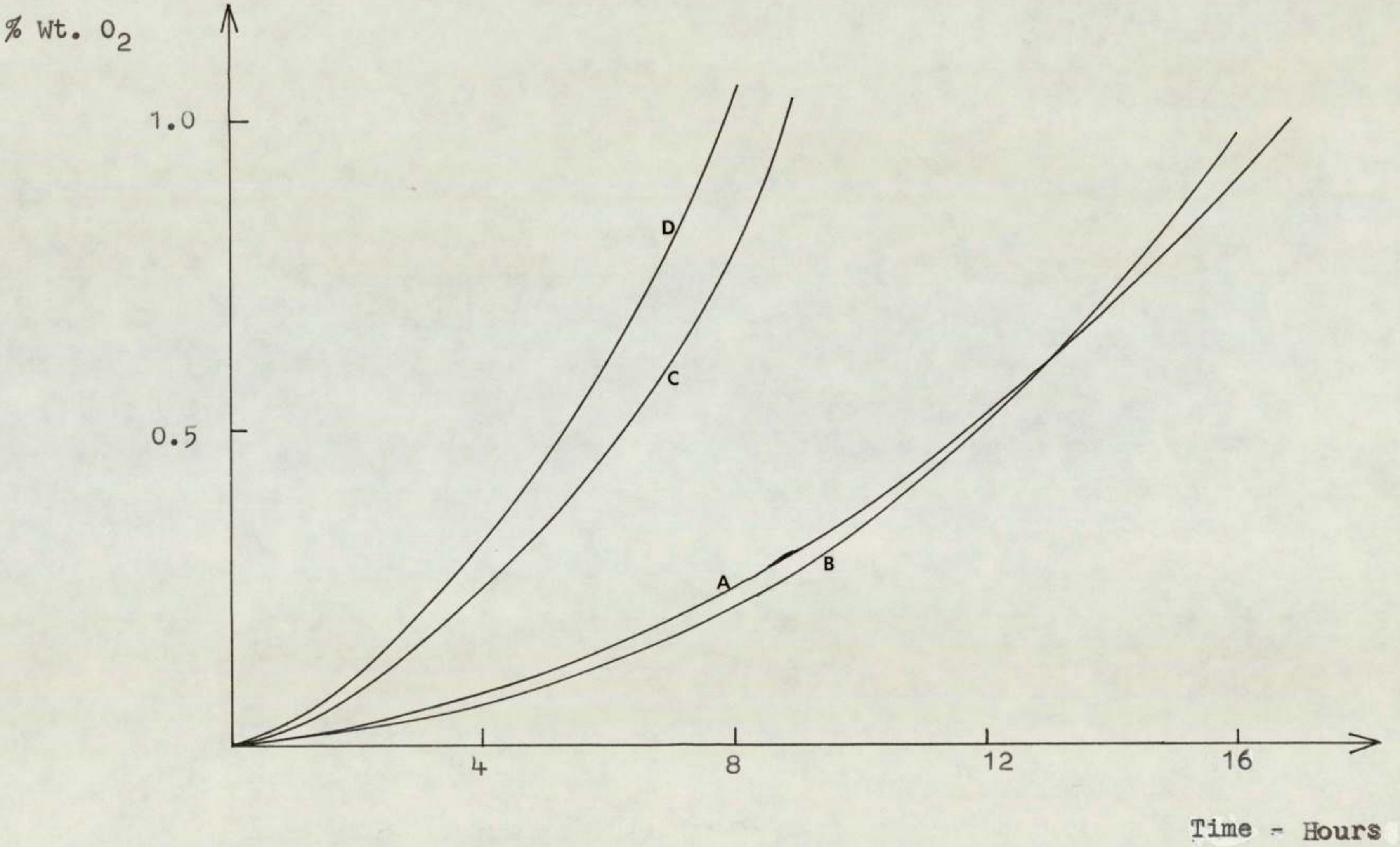


Fig. 52. Oxygen absorption.

measuring the height travelled by the mercury pellet. A reduction of 1 ml of air from the system corresponded to a 28.3 cm length travelled by the mercury pellet.

The oxygen absorption of the following solutions were studied:

(A). Rubber solution containing 2.0% of bound mercaptan obtained by straight addition.

(B). Rubber solution containing 2.0% of bound mercaptan obtained by diluting the 16.0% masterbatch.

(C). Rubber solution containing 0.5% of bound mercaptan obtained by straight addition.

(D). Rubber solution containing 0.5% of bound mercaptan obtained by diluting the 16.0% masterbatch.

The % wt. of oxygen absorbed by the above samples with time were plotted and are shown in Fig. (52).

Results and Discussion

According to Fig.(52) sample D oxidizes faster than sample C. The difference in oxidation curve of sample A and B is negligible. Although during the initial stages sample B has a better stability than sample A, the behaviour is reversed at later stages.

Therefore it can be said that the difference in ageing behaviour of rubbers containing bound antioxidant obtained by masterbatch and straight addition techniques is more prominent at lower antioxidant concentrations. The mobility of the antioxidant molecule should be the key factor determining these differences in the efficiency of stabilization. Although the masterbatch technique leads to a slightly reduced stability compared with the direct addition method the enormous advantages of using the masterbatch technique in commercial applications can compensate this slight disadvantage.

An explanation for the behaviour of samples A and B at later stages was not found.

4.3.6. Oxidation of polypropylene

The method of obtaining antioxidant bound rubber was successful according to Chapter 3, and therefore there exists a possibility of using this adduct rubber as a high molecular weight antioxidant in other polymers. The concentration of the adduct should play an important part in this, because the amount of rubber added to the polymer will affect the ageing behaviour of polymers.

The effects of a low adduct and a medium adduct with comparison to a very volatile and a conventional high molecular weight antioxidant on the ageing of polypropylene were studied by rapid flowing air oven ageing and Infra-red spectroscopy.

Materials

Unstabilized polypropylene powder	I.C.I.
Topanol OC	I.C.I.
Irganox 1076	Geigy

Rubber mercaptan adducts 2% and 10%.

Procedure

35.0 gm batches of polypropylene containing Topanol OC, Irganox 1076 2% and 10% 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan-rubber adducts, in the ratio of 10^{-3} mole of pure antioxidant to 100 gms of polymer, were mixed in a RAPRA Torque Rheometer Mark 3 for a period of 5 minutes at 180°C.

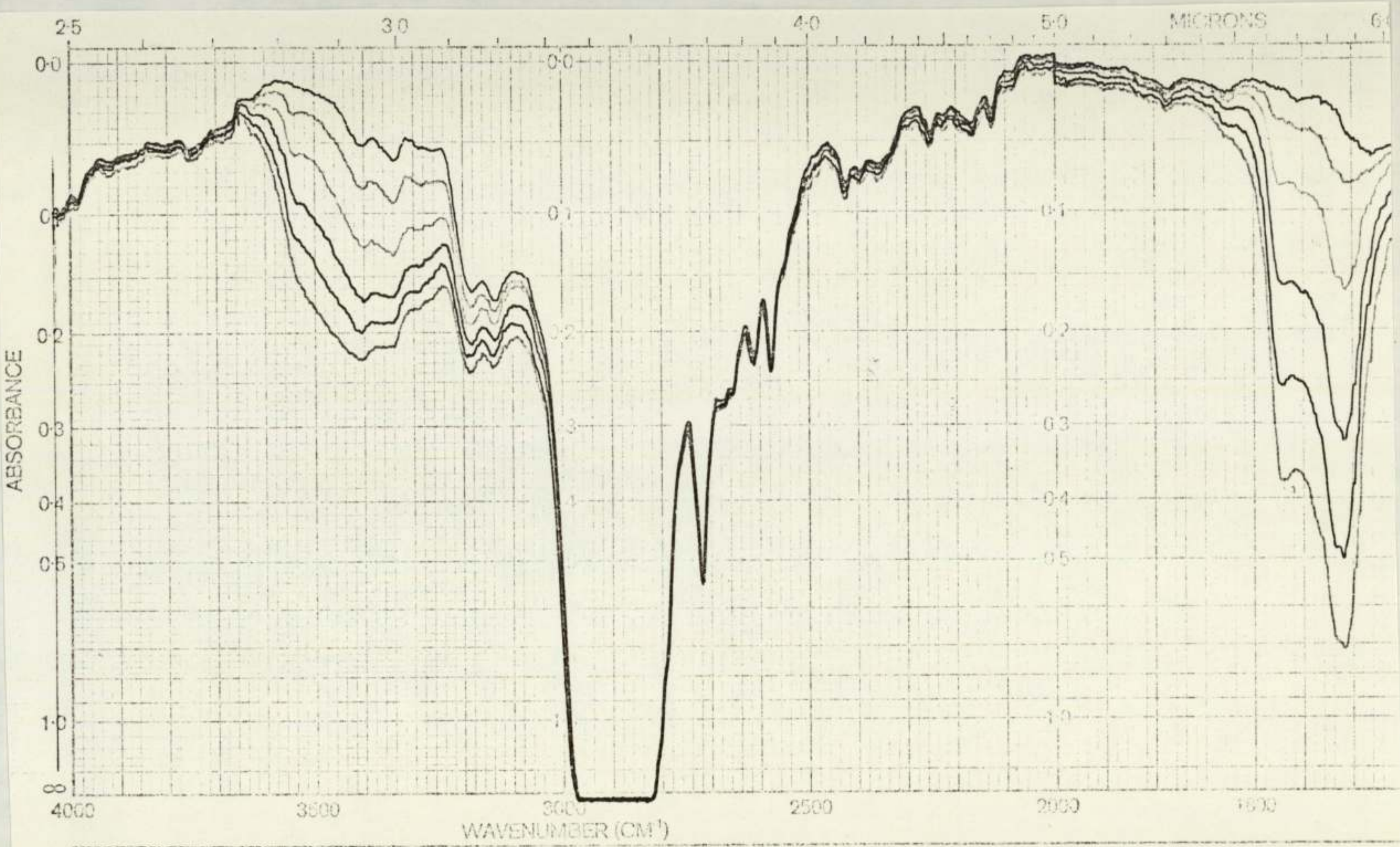
Thin films were pressed out of these samples using glazing plates and cellophane films in an electric press at 180°C, followed by rapid cooling. Strips of 5τ thickness were cut from the sheets and were aged in a Wallace oven at 140°C with an air circulation rate of 20 ml/min. Infra-red spectra of the samples were obtained at regular intervals using a Perkin Elmer 457 spectrophotometer. A typical spectrum of a sample containing no antioxidant is shown in Fig. (53).

The ageing characteristics were compared by an arbitrary carbonyl index which was the ratio of the intensity of the carbonyl band at 1710 cm^{-1} to that of the band at 2720 cm^{-1}.

A plot of carbonyl index against time for the samples is shown in Fig. (54).

Discussion

According to Fig. (54) it is seen that unstabilized polypropylene develops a carbonyl index very rapidly. The sample containing Topanol OC is fast ageing, almost



SAMPLE
1. 15 mnt.

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

Fig. 53.

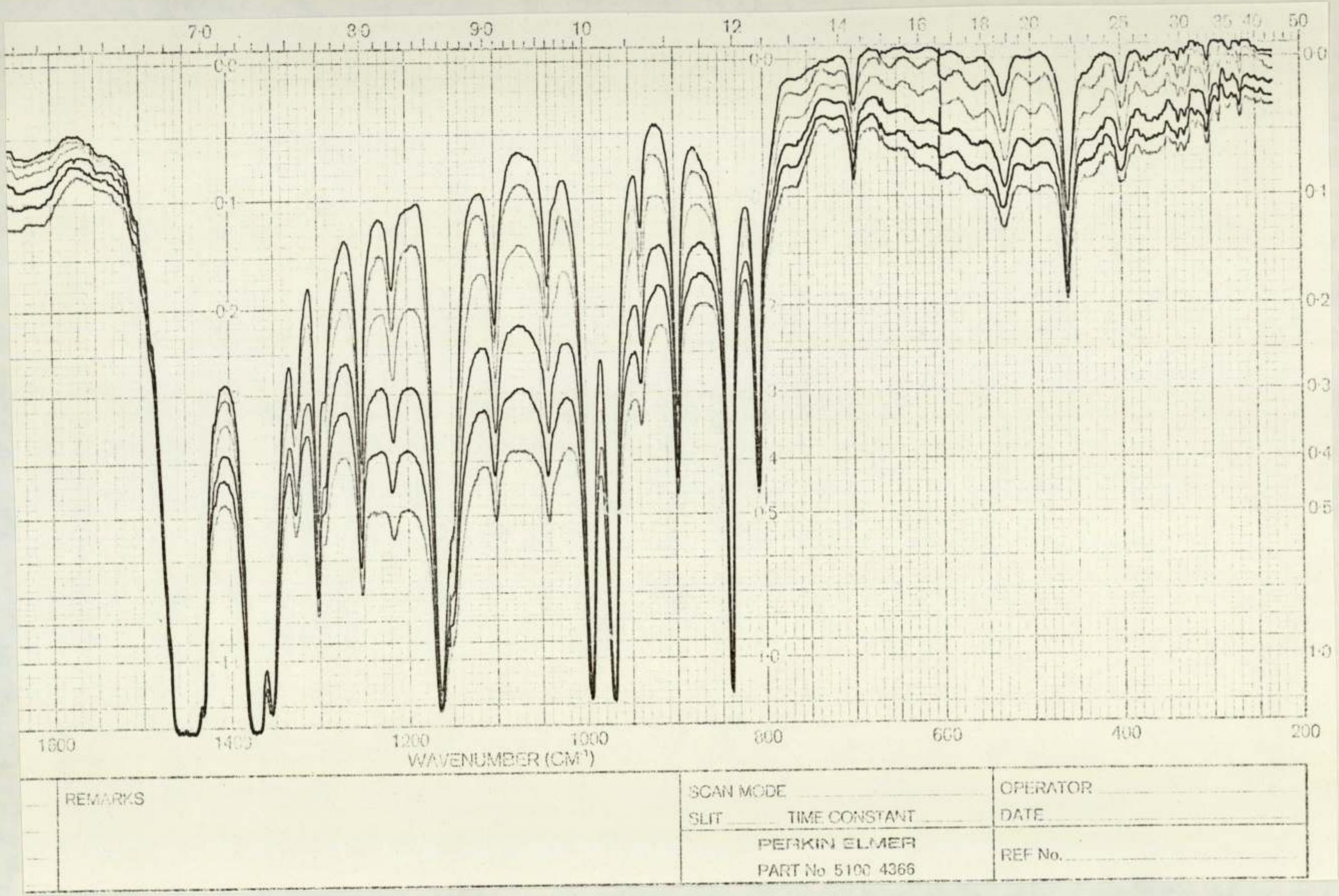


Fig. 53 continued.

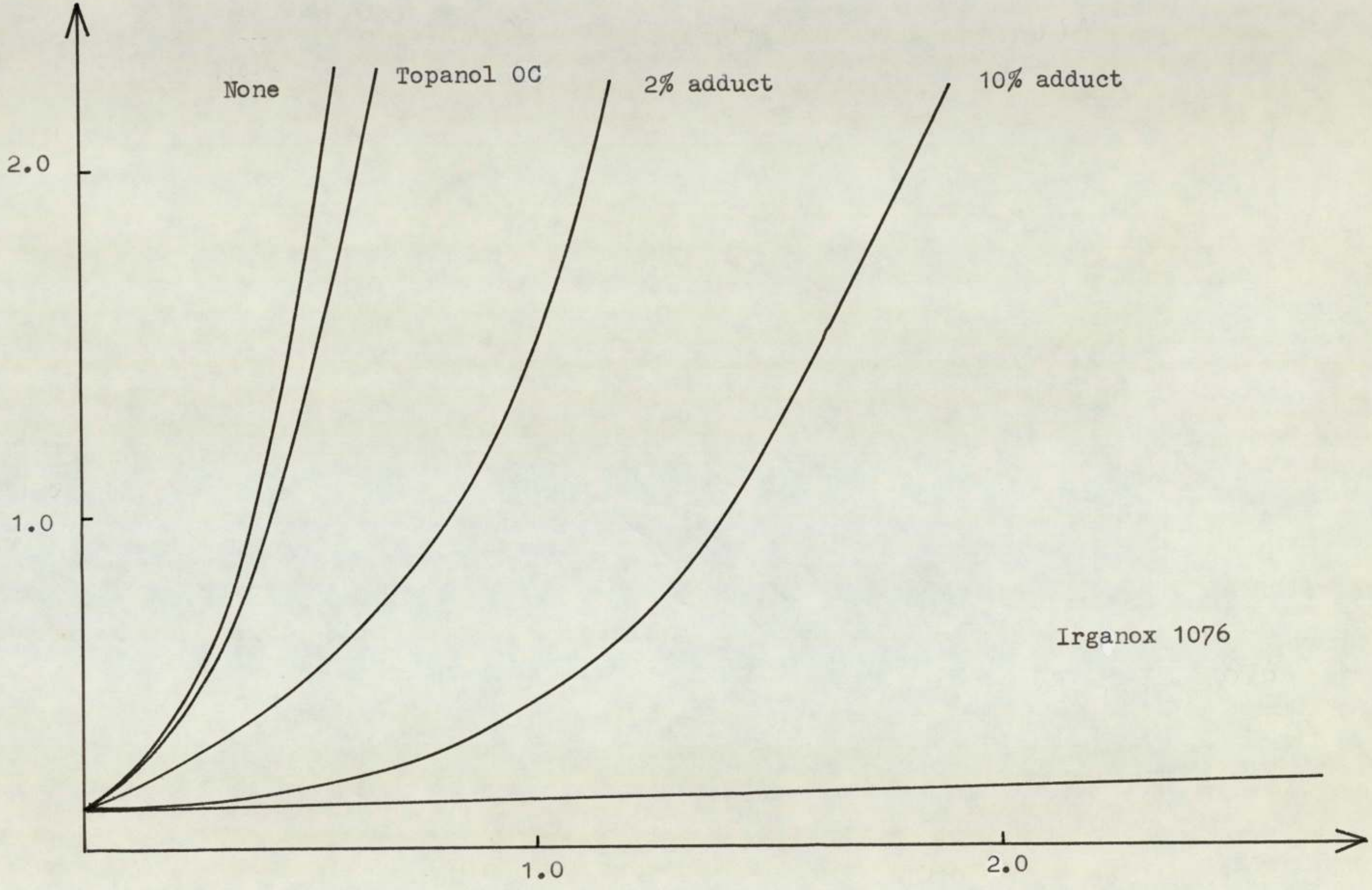

None
Topanol OC
2% adduct
10% adduct
Irganox 1076
2.0
1.0
1.0
2.0
Time - Hours

Fig. 54.

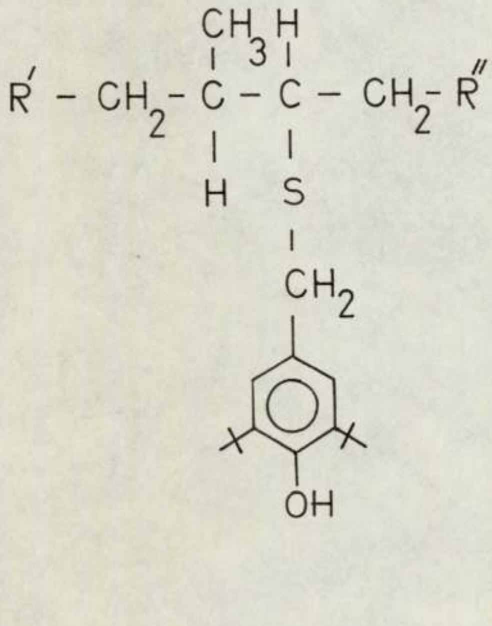
like the unstabilized sample which should be due to the high volatility of Topanol OC. Such a behaviour was also seen in the case of polyethylene (Chapter 3) even at 100°C.

The 2% adduct makes the polymer comparatively stable and the effect of the 10% adduct is even better. The sample containing Irganox 1076 ages very slowly.

Therefore it could be said that although a 10% adduct does not markedly inhibit the oxidation of polypropylene, a very high concentrated adduct should be much better. It is possible to obtain such high adducts according to Chapter 3.

4.3.7. Autosynergism and oxidation of tetralin

As mentioned in Chapter 1, two functions in the same molecule can act synergistically to inhibit antioxidation of an organic substrate. According to Chapter 3, the addition of 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan to natural rubber results in the formation of a monosulphidic structure which could be represented as follows:



In the above molecule the hindered phenolic group is expected to act as the antioxidant. But it is also known that sulphides also possess antioxidant activity. Therefore there is a possibility that the hindered phenolic group and the sulphidic group function synergistically.

To investigate such a behaviour it is necessary to have systems containing only one of the two functions, (the hindered phenolic function and the sulphidic function).

The addition products of 3,5 Ditert-butyl-4-hydroxy benzyl mercaptan to a simple olefin can be used for this purpose. The addition of the two mercaptans to 2-methyl-but-2-ene was carried out and the products were analysed in detail (Chapter 2) keeping in mind this purpose of using them to investigate the autosynergism.

Experimental

Tetralin was used as the organic substrate and the oxidation was studied by oxygen absorption at 80°C. The system is similar to that used in Chapter 4 for rubber samples, except that the reaction vessels were 250 ml round bottomed flasks. The solutions were stirred using magnetic followers Fig. (55).

Tetralin was purified by washing with 2-N sodium hydroxide solution followed by water. Then it was dried and distilled under vacuum.

The following two systems were oxidized in the above system saturated with oxygen:

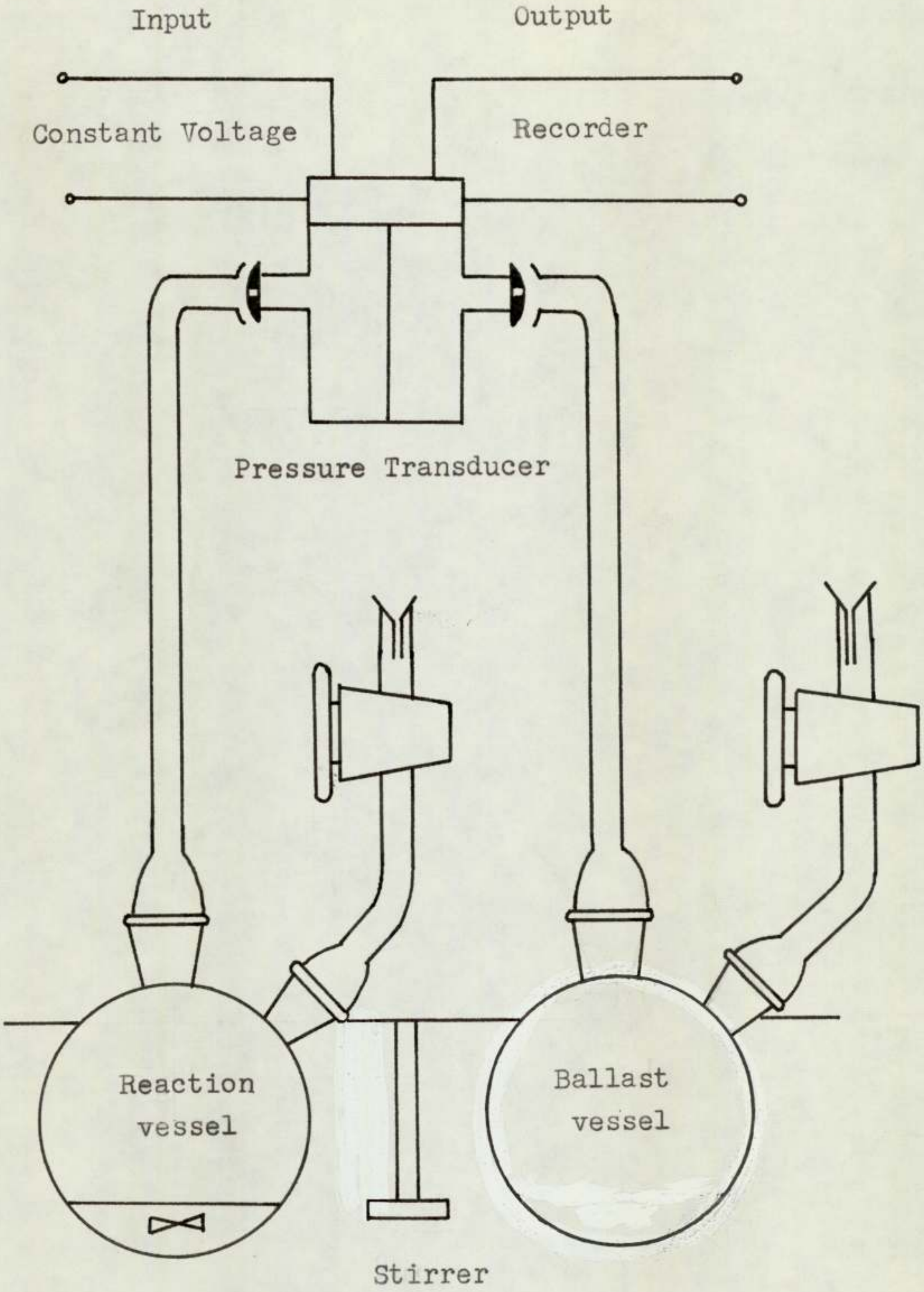


Fig. 55. Oxygen absorption apparatus.

A. 10.0 g (10.3 ml) of tetralin

10^{-4} mole (0.0322 g) of 2-methyl-but-2-ene, 3,5-ditert-butyl-4-hydroxy benzyl mercaptan adduct.

B. 10.0 g of tetralin

10^{-4} mole (0.0194 g) of 2-methyl-but-2-ene benzyl mercaptan adduct.

10^{-4} mole (0.022 g) of 2,6-ditertiarybutyl-4-methyl phenol.

The additives were measured using a microsyringe.

It is clear from the above that system A contains both the sulphidic and the phenolic function in the same molecule while in system B the two functions are contained individually.

Oxidation of pure tetralin was also followed.

The oxygen absorption system is described in Chapter 4.

Results

System A had an induction period of 226 hours while system B had 168 hours before autocatalytic oxidation occurred. Therefore it can be said that autosynergism exists in system A. It has to be mentioned that although system A had an induction period of 226 hours, the solution developed a light brown colour with the precipitation of a black powder, which was not seen in system B.

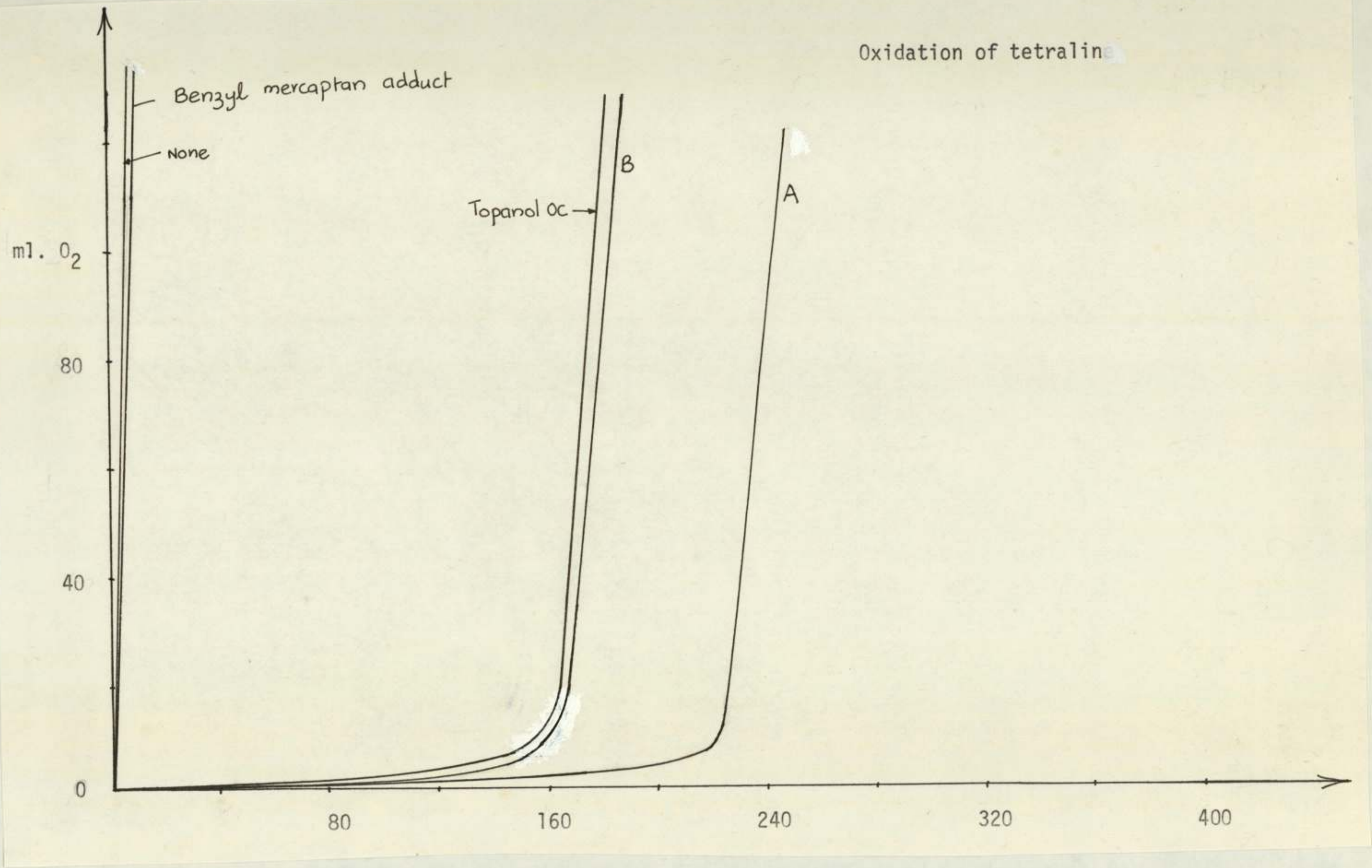

Oxidation of tetralin
Benzyl mercaptan adduct
None
Topanol OC
B
A
ml. O_2
80
40
0
80
160
240
320
400
Time - Hours

Fig. 56.

The effect of the presence of the benzyl mercaptan adduct and 2,6-ditert-butyl-4-methyl phenol individually on the oxidation of tetralin was also studied. The former had no induction period although the rate of oxidation was reduced. (4 hours to absorb 80 ml of oxygen with comparison to 15 minutes for pure tetralin). The latter had an induction period of 162 hours. (Fig.56).

The above results clearly show that the presence of both the phenolic group and the sulphur group in the same molecule provides a better stability to tetralin via autosynergism.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1. Conclusions

The work carried out clearly shows that an antioxidant function can be bound to Natural Rubber through a mercaptan function, by a free radical addition reaction. Thermal and Photochemical treatment in the presence of Azobisisobutyronitrile successfully initiate the addition reaction. 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan adds to rubber at 50°C and the reaction is complete within a period of 10 hours. The reaction can be carried out in both latex phase and in solution. If added as a compounding ingredient to solid rubber, the rubber is resistant to oxidation, but the mercaptan and its transformation products are extractable.

The presence of oxygen is disadvantageous in that the extent of addition is reduced. Under vacuum or in an inert atmosphere like nitrogen large amounts of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan can be added to rubber. Masterbatches of latex produced by this method can be successfully used to dilute untreated latex to obtain oxidation resistance. There is only a slight decrease in antioxidant efficiency when a sample is prepared by the masterbatch method with comparison to a straight addition.

The mercaptan containing antioxidant cannot be chemically bound to a saturated polymer in the melt stage by a free radical reaction. During a free radical polymerisation, a small proportion of 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan can be added to styrene. But the inhibition of polymerisation by the mercaptan is more prominent than the addition.

When 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan is bound to the rubber initially, there is no considerable effect on subsequent vulcanization. But when added during vulcanization as a compounding ingredient there is a clear scorchy effect at low concentrations and an inhibitive effect at higher concentrations. The mercaptan is converted into other extractable antioxidant species when added during vulcanization. An antioxidant bound rubber can be used to inhibit the oxidation of other polymers, and a high adduct is advantageous in this case to avoid any oxidation of the rubber itself.

The mechanism of the addition reaction has been conclusively shown by using a variety of model compounds. The addition takes place in an anti-Markovnikoff manner.

In 3,5-Ditertiarybutyl-4-hydroxy benzyl mercaptan, the phenolic function and the sulphide function act synergistically to inhibit oxidation, which has been shown using tetralin.

5.2. Suggestions for further work

As the mercaptan addition represents a very practical method of obtaining network bound antioxidants, various known antioxidants could be modified into mercaptan derivatives and these bound to polymers by free radical processes. Hindered phenols with different alky-substituents, aromatic amines, U.V. absorbers like benzophenone derivatives, phosphite and phosphate esters etc. could be used in the above way.

As the addition reactions were carried out in vacuum or oxygen free nitrogen, an investigation into other easier practical methods for the reaction will be of great importance. A study of methods of initiation other than the use of A.Z.B.N. will be useful.

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