GRAFT POLYMERISATION OF ANTIOXIDANTS INTO NATURAL RUBBER

by

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SUMMARY

Antioxidants containing polymerisable vinyl groups have been successfully bound to natural rubber in the presence of suitable free radical generators. Reaction parameters such as the mode of initiation, initiator system, reaction time, pH of the reaction medium, swelling time have been investigated in natural rubber latex. Of the free radical generating systems examined the redox system consisted of tertiary butyl hydroperoxide and tetra ethylene pentamine (TBHP/TEP) appeared to be most effective in natural rubber latex.

Infra-red spectroscopy has been used to estimate the concentration of the bound antioxidants and ageing behaviour was assessed by oxygen absorption and continuous stress relaxation. The curing characteristics of the grafted rubber samples were studied in detail using the Monsanto rheometer.

It was found that antioxidants which do not contain vinyl groups also react under the same conditions with natural rubber latex. Some of these appeared to be marginally more effective than the corresponding vinyl antioxidants. It was observed that in the case of the vinyl antioxidants only a part of the added antioxidant grafted into the rubber and the rest remained unchanged or was oxidised to coloured products. The by-products formed during the process of grafting were identified and analysed.

A masterbatch technique has been developed to produce concentrates of bound antioxidants in rubber latex and these have been used as additives to untreated latex to obtain grafted rubber latices with a known level of oxidative stability.

It was found that irrespective of the presence or absence of vinyl group in the antioxidants phenols containing one tertiary butyl and one methyl group in ortho position were most effective. Followed by phenols with two tertiary butyl groups. This is the order of activity previously observed for rubber antioxidants. The effectiveness of these antioxidant structures appears to be similar when present in a rubber bound form to that of the free antioxidant.

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January 1975

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CHAPTER 1

Introduction

1.1 Scope and object

The principal drawback of natural rubber is its succeptability to oxidation, even at room temperature. The most serious change that takes place is a change in physical properties which is associated with the decrease of molecular weight. In order to retard this process of autoxidation and to improve the performance of natural rubber, a wide variety of antioxidants and stabilisers have been developed. These antioxidants are now used not only in the rubber industry but also with fats, lubricating oils, petroleum and foodstuffs.

Raw rubber shows a remarkable stability towards oxidation compared with vulcanised rubber due to the presence of natural antioxidants such as phenolics and amines. During the process of vulcanisation these are either destroyed or rendered ineffective. This necessitates the availability of commercial antioxidants for the rubber industry. In practice antioxidants are added with the other additives to the rubber prior to vulcanisation. Normally these added antioxidants tend to be extracted to a greater or lesser extent by water, detergents or chemicals, depending on the nature of the fabricated rubber article. This is a particular problem in tyres, latex thread, gloves, underwater equipment and rubber used for medical purposes. This loss of antioxidants is particularly severe in the latex thread products because latex thread is a delicate product great care must be exercised in the preparation of compounding ingredient dispersion.

Coarse particles may result in serious defects either in the product itself or in the mixes by settlement at the bottom of the tanks. One possible way of obviating these difficulties is to chemically combine the antioxidant with the rubber.

However, if the antioxidant molecule is grafted to the molecular network, it looses some of its mobility. As a result, the grafted antioxidant may not be as effective as a free antioxidant molecule in the rubber. Due to lack of information in this field it is rather difficult to come to definite conclusions on the effect of mobility on antioxidant activity in rubber. Workers at NRPRA have observed (21) that the attachment of the protective group to the rubber molecule does not effect its antioxidant activity but reduces its effectiveness when migration to the surface is required. (eg in protection against ozone.) This project is concerned with an attempt to attach phenolic and amine antioxidants to rubber at the latex stage and to study the effectiveness of the bound antioxidants so obtained.

1.2 Degradation of natural rubber

A reduction of molecular weight due to oxidation or an increase of molecular weight due to cross-linking takes place when a polymer is exposed to the atmosphere. Also it has been found that a trace of oxygen is capable of destroying the characteristic macromolecular structure of natural rubber. The perishing and surface cracking of rubber, the yellowing of cotton and synthetic fibres and the embrittlement of plastics are typical examples of polymer deterioration.

Although the structure of natural rubber has been known for many years, the nature of the chain scission reaction in the process of oxidation has proved to be difficult to characterise. Bevilaqua has extensively investigated the possible mechanism of the oxidation of the raw rubber. His conclusions were based on the ultimate products of oxidation. The use of model compounds by Bolland and Hughes as well as the use of molecular probes by Bateman and Cuneen have thrown considerable light on the understanding of the phenomena involved.

The first detectable product of oxidation was found to be rubber hydroperoxide. The ultimate products were carbon monoxide, carbon dioxide, carboxyl ic acids including formic, acetic and levulinic acids.

Usually the initial formation of hydroperoxide involves the attack of the polymer by a free radical. The free radicals are formed in the rubber during the process of compounding, processing and fabrication. These processes involve the application of heat, exposure to direct sunlight, contamination by metal ions and subjection of the rubber to irregular stresses and strains.

The energy necessary for the formation of free radicals during the compounding is supplied directly as mechanical energy(1). The molecules being ruptured by the shearing forces imposed during the deformation of the bulk rubber. According to Kauzman and Eyring(2) C–C bonds of the polymer back bone break directly into free radicals

$$R - R \xrightarrow[\text{Energy}]{\text{Mechanical}} 2R^{O}$$

When rubber is masticated with another polymer in the absence of radical acceptors one or both maybe mechanically ruptured$^{(3)}$.

$$R - R \longrightarrow 2R^{O}$$

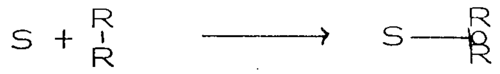
$$S - S \longrightarrow 2S^{O}$$

The radicals R^{O} and S^{O} may then undergo further reactions exemplified by

$R^{O} + S^{O} \longrightarrow R — S$ block rubber

$$R^{O} + \overset{S}{\underset{S}{|}} \longrightarrow R — \overset{S}{\underset{S}{|}}\,o$$

graft rubber

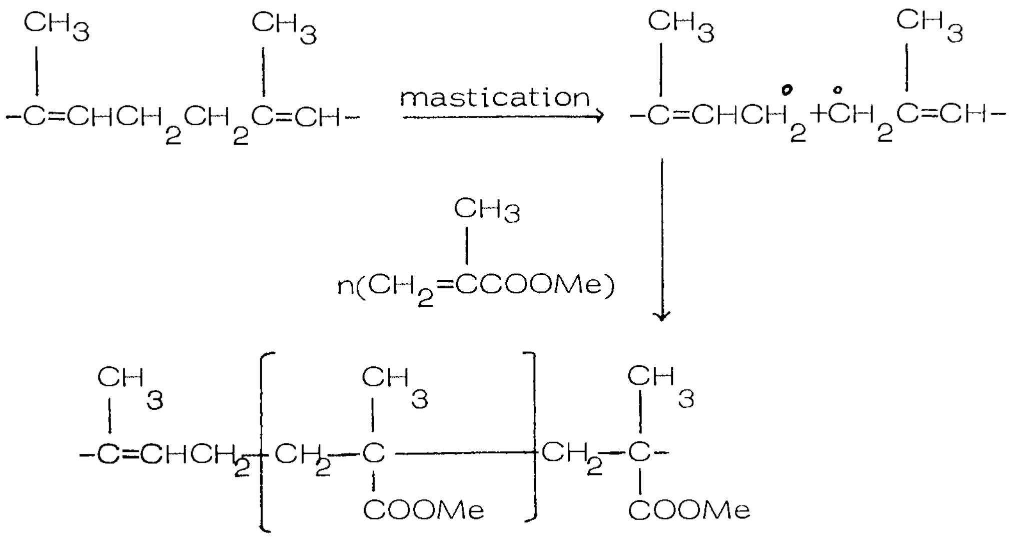


$$S + \overset{R}{\underset{R}{|}} \longrightarrow S — \overset{R}{\underset{R}{o}}$$

graft rubber

If mastication is carried out in the absence of oxygen, the free radicals produced react by addition to the double bonds of the rubber structure. As a result, these free radicals either destroy by disproportionation or dimerisation.

In the presence of an efficient radical acceptor, on the other hand, there are two possibilities. Firstly, if the addition product is another reactive free radical, then a chain reaction may occur involving the radical acceptor. Thus when rubbers or similar polymers$^{(4)}$ such as polystyrene, polymethylmethacrylate, cellulose acetate or PVC are masticated in the presence of vinyl monomers such as methylmethacrylate, graft polymerisation and gel formation occurs(5).



Several workers (6-14) have studied the autooxidation of natural rubber and they have explained it by the following scheme where RH represent the hydrocarbon.

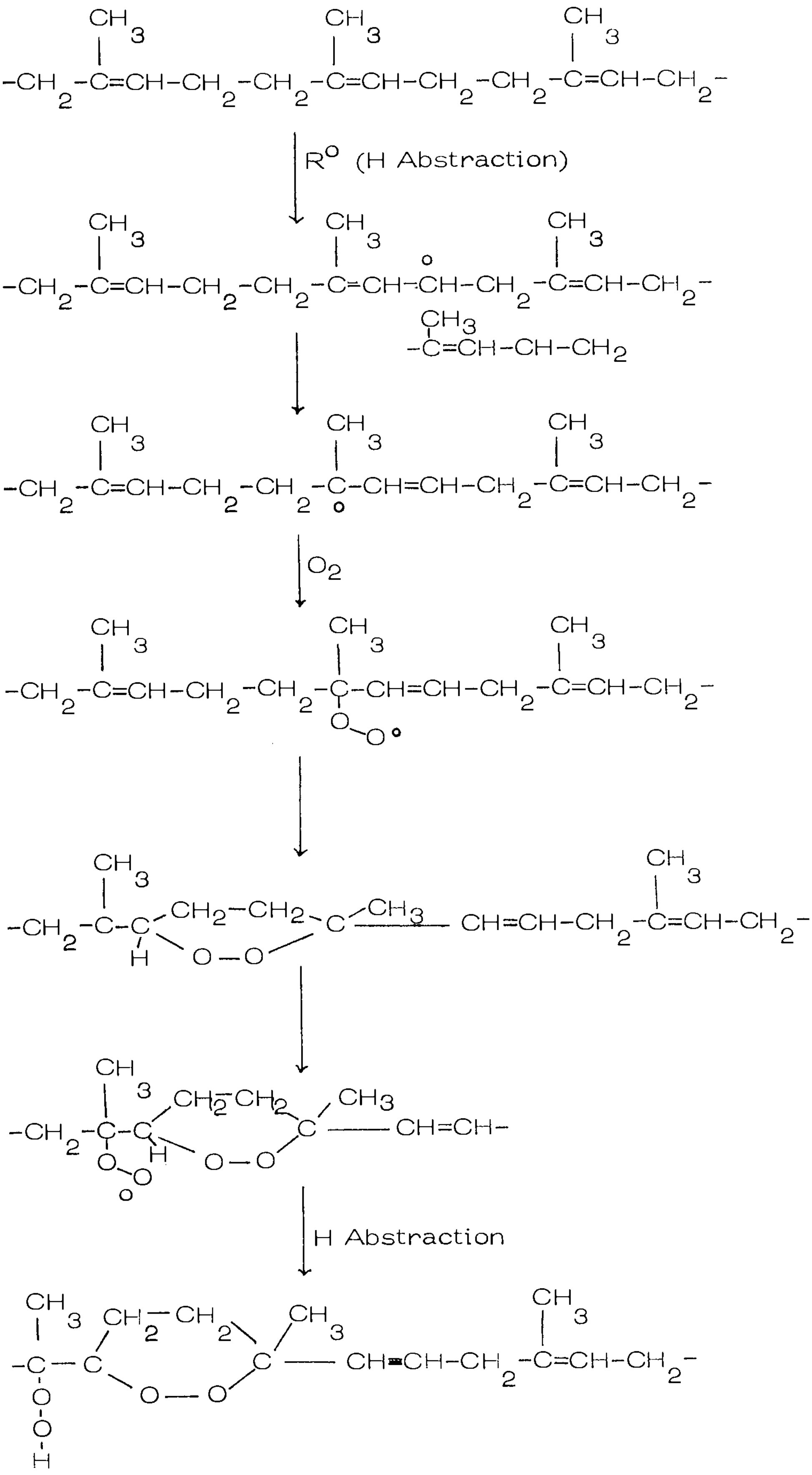
Initiation $RH + O_2 \longrightarrow R^{o}$ 1

Propagation $R^{o} + O_2 \longrightarrow ROO^{o}$ 2

$ROO^{o} + RH \rightarrow ROOH + R^{o}$ 2b

$ROOH \longrightarrow RO^{o} + OH^{o}$ 3

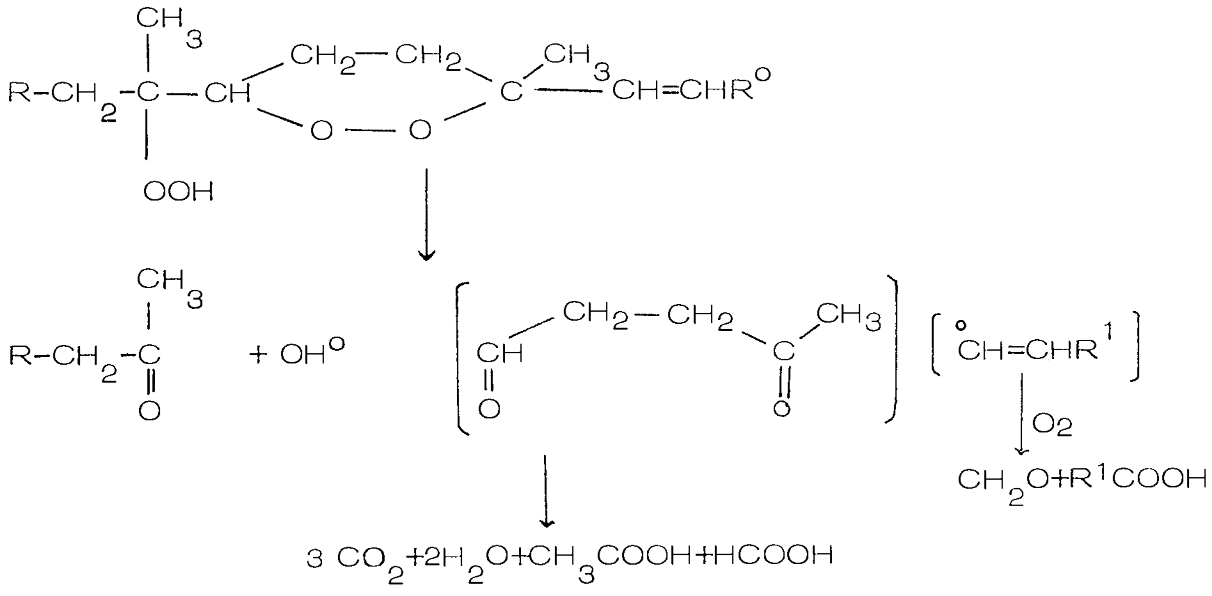
The chemical structure of the molecules in natural rubber makes it particularly susceptible to free radical attack. The polymeric free radicals so formed are stabilised by the conjugation due to the participation of other adjacent double bonds. This stabilisation can be illustrated in the following manner.



Hydroperoxide

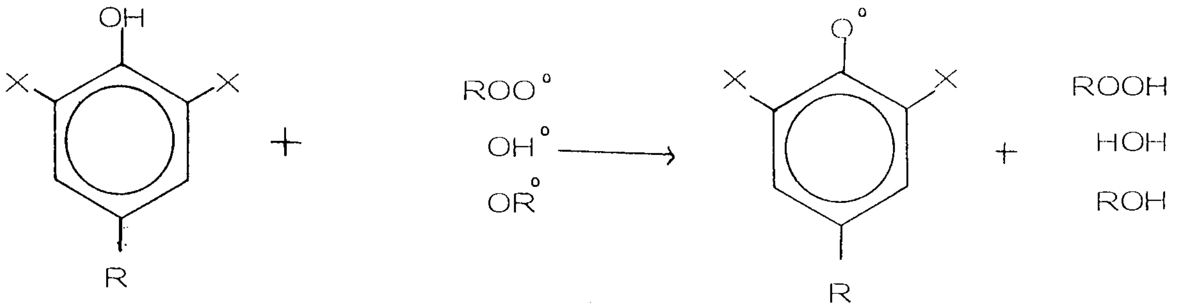
Bevilaqua(12) has proposed a mechanism for the break down of hydroperoxide.

According to this the ultimate products and ratios are:



The chain reactions illustrated by the reaction (2) and (2b)can be prevented by using free radical acceptors only. The most common free radical acceptors used in the natural rubber industry are of the phenolic and amine type. Both of these antioxidant types interfere with the process of autoxidation primarily by transferring either a hydrogen atom or an electron to the most abundant chain propagating species, the alkyl peroxy radical.

In the case of phenolic type, the resulting phenoxy radical resonance stabilised and does not react further with the polymeric back bone. This can be represented as follows:



(4)

(A)

This is the principle behind the use of phenols and amines as antioxidants. These materials possess labile hydrogen atoms and compete with the hydrocarbon for alkyl peroxy radicals.

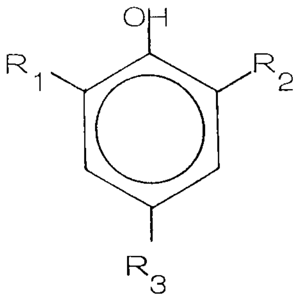
In the absence of a source of free radical the oxidation curve of a pure hydrocarbon is in most cases autocatalytic. The reason for this phenonemon is that in the absence of an added radical generator, hydroperoxide is the major source of chain initiating radicals by reaction (3) above and as their concentration builds up to a constant value where their rate of formation is equal to their rate of decomposition, so the rate of oxidation approaches a maximum(15) and remains constant there after.

1.3 Relation between antioxidant activity and structure

Antioxidant activity is a resultant, firstly, of the ability of the material to deactivate alkylperoxy radicals and, secondly, of the tendency of the antioxidant radical to continue the kinetic chain(16).

The relationship between the antioxidant activity of phenols and their structure has been thoroughly studied in petrol. A few examples are presented in the table below to show the effect of 2,4,6 substituted phenols in a variety of substrates.

Effect of substituent variation in 2,4 and 6 positions on the antioxidant activity of phenols



R_1	R_2	R_3	Antioxidant Activity in Petrol
H	H	NO_2	–
H	H	H	1
Me	H	H	14
H	H	Me	10
Me	Me	H	32
Me	H	Me	47
Me	Me	Me	120
Me	Me	tBu	20
tBu	Me	Me	170
tBu	Me	tBu	48
tBu	tBu	Me	100
tBu	tBu	tBu	46
tBu	tBu	OMe	200

The following generalisations can be made on the basis of the above table.

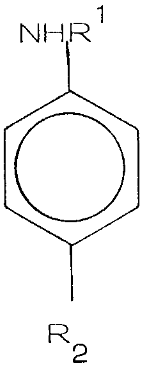
(1) Electron releasing group (eg methyl, t- butyl and methoxy) markedly increase antioxidant activity.

(2) Electron attracting groups (eg nitro, carboxy and hologen) decreases efficiency.

(3) α-branched ortho-alkyl groups considerably increases antioxidant activity whereas such groups in the para position decreases activity.

Beckel and Kooyman(17) have measured the efficiency of a number of amines in dihydroanthracene and it can be seen from the table below that considering these as derivatives of aniline, substitution of an N-hydrogen by methyl has a relatively minor effect on antioxidant efficiency. On the other hand substitution by phenyl markedly improves activity. As in the case of phenols, electron releasing nuclear substituents have a powerful activating effect.

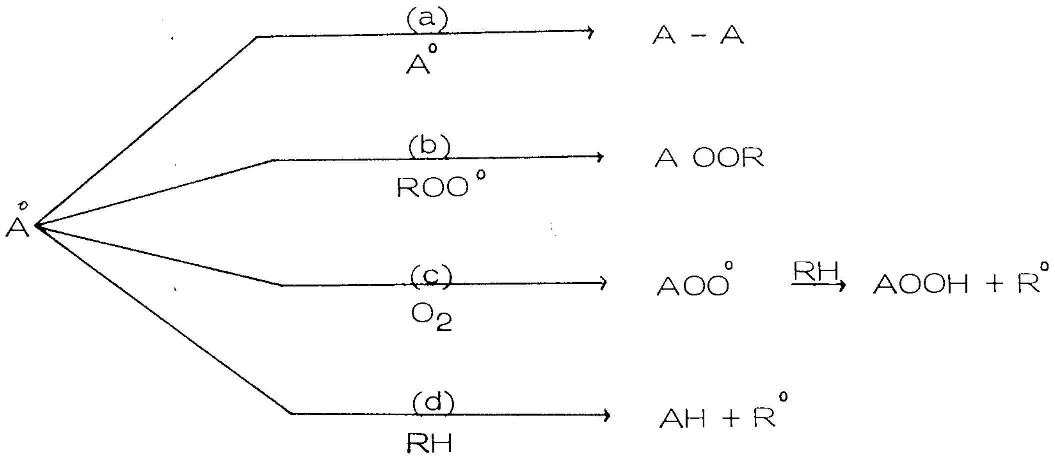
Efficiency of amine antioxidants in dihydroanthracene



R_1	R_2	Antioxidant Efficiency
H	H	40
Me	H	15
α-Naph	H	104
β-Naph	H	80
S-Bu	NHsBu	10000

The effectiveness of a chain breaking antioxidant depends not only upon its rate of interaction with alkylperoxy radicals but also upon the fate of the phenoxy radical (A) which is formed in reaction (1).

The possible reactions of hindered phenoxy radical (A) are as follows:



It is quite clear that (a) anb (b) are terminating in that radicals are removed from the system. (c) and (d), on the other hand, are chain transfer steps since they lead to the continuation of the chain and (c) may in some cases be chain branching as a result of peroxide decomposition. Substituents in the antioxidant affect its activity by

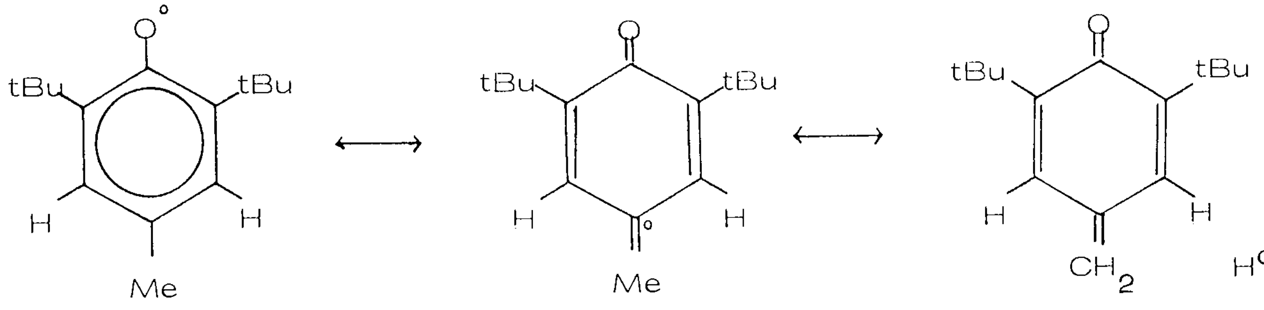
1 increasing or decreasing the rate of reaction of the alkylperoxy radical with the phenol, or

2 changing the ratio of chain transfer to termination.

Three factors have been found to be important.

(a) Aryloxy radical stability

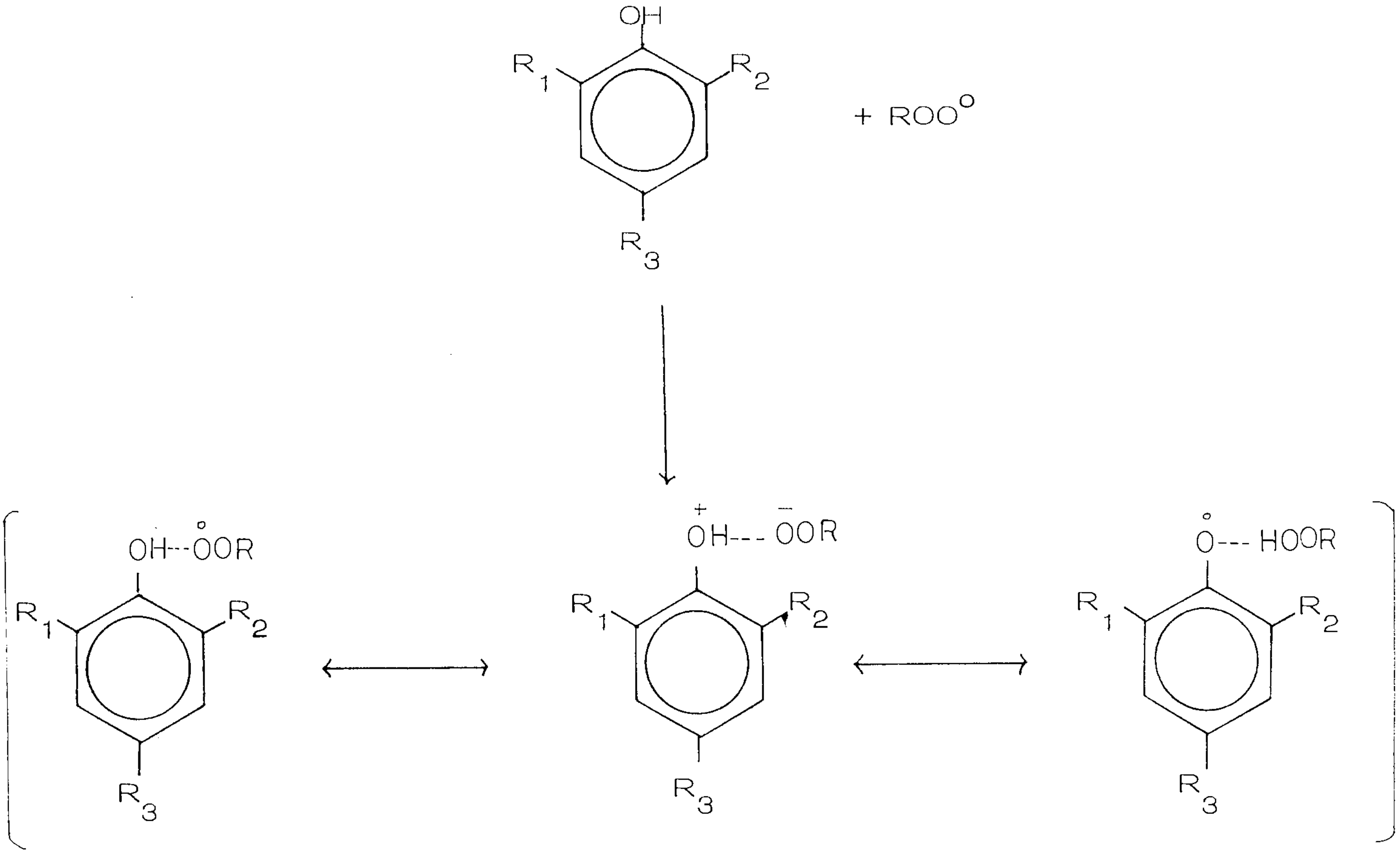
For example, 2,6-di-tert- -methyl phenol on oxidation in organic solution with lead dioxide gives a well defined spectrum which can be interpreted in terms of a major interaction of the unpaired electron (formally on the oxygen) with three hydrogens and a minor interaction with two. The former accords with the hyper conjugation structure (Ic) in which the three hydrogens are equivalent and the latter is due to the presence of a negative spin density in the meta position of the benzene ring.

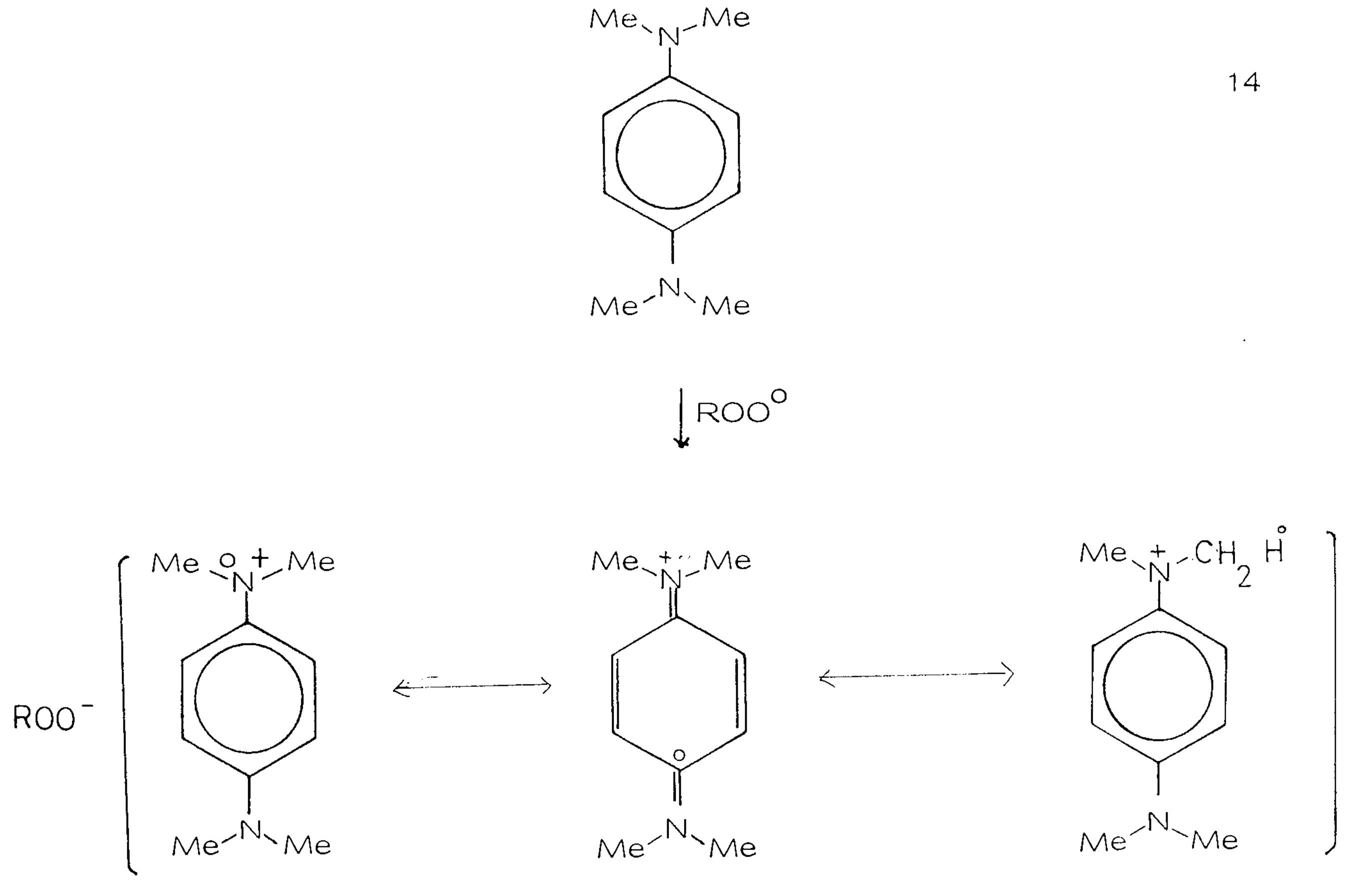


Ia Ib Ic

(b) The ease of electron release from the oxygen atom

The alkylperoxy radical (ROO°) is an electrophilic reagent. Consequently, substituents in a phenol which favour electron release increase the stability of the electron transfer component of the transition state.





IIa IIb IIc

Electron attracting groups decreases the ease of oxidation and electron releasing groups powerfully increase it.

(c) <u>Steric stabilisation of the aryloxy radical</u>

Bickel and Kooyman(17) have shown that the less sterically hindered phenoxy radicals continue the autoxidation chain reaction (d) instead of terminating by reactions (a) and (b). The only stable phenoxy radicals are those which contain two bulky ortho substituents. Maximum antioxidant activity occurs at a high degree of substitution and minimum hydrogen bonding with the most highly substituted member of the series 2,6-di-tert-butyl-p-cresol.

According to the kinetic studies the electron transfer complex formation is more important for aryl amine antioxidant than it is for phenols. The antioxidant activity of aromatic amines unlike that of phenols, is not destroyed by complete N-alkylation.

Tetra methyl-p-phenylene diamine can act as an effective antioxidant and the resulting würster radical ion II can be identified as a product of the oxidation under autoxidation conditions(18).

1.4 Stabilisation of natural rubber

The stabilisation of natural rubber involves the incorporation of antioxidants into the polymer. There are a number of ways of doing this in practice(19).

(a) Solid rubber and the antioxidants are dissolved together in a mutual solvent which is subsequently removed.

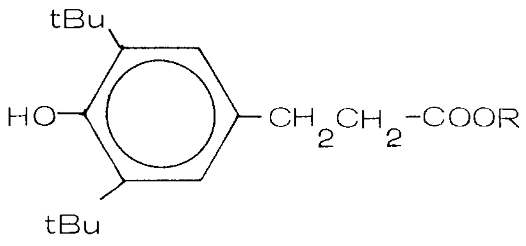
(b) Solid rubber and antioxidants are mixed on a mill or in an internal mixer.

(c) Rubber and antioxidants are mixed and co-agulant added to precipitate both together.

Of these the first is of little practical interest owing to the high solvent cost, but the remaining two have been extensively used in the industry. The second method is widely used where solid rubber is employed in manufacturing rubber goods. The third method is widely used in industry where latex is employed. This method generally gives a more uniform mixture.

Studies of Plant and Scott(20) have shown that the volatility decreased with increasing molecular weight. Further they observed an increase of antioxidant activity in polypropylene as the molecular weight increases. These studies were based on the following homologous series

R - Methyl
Hexyl
Lauryl
Stearyl

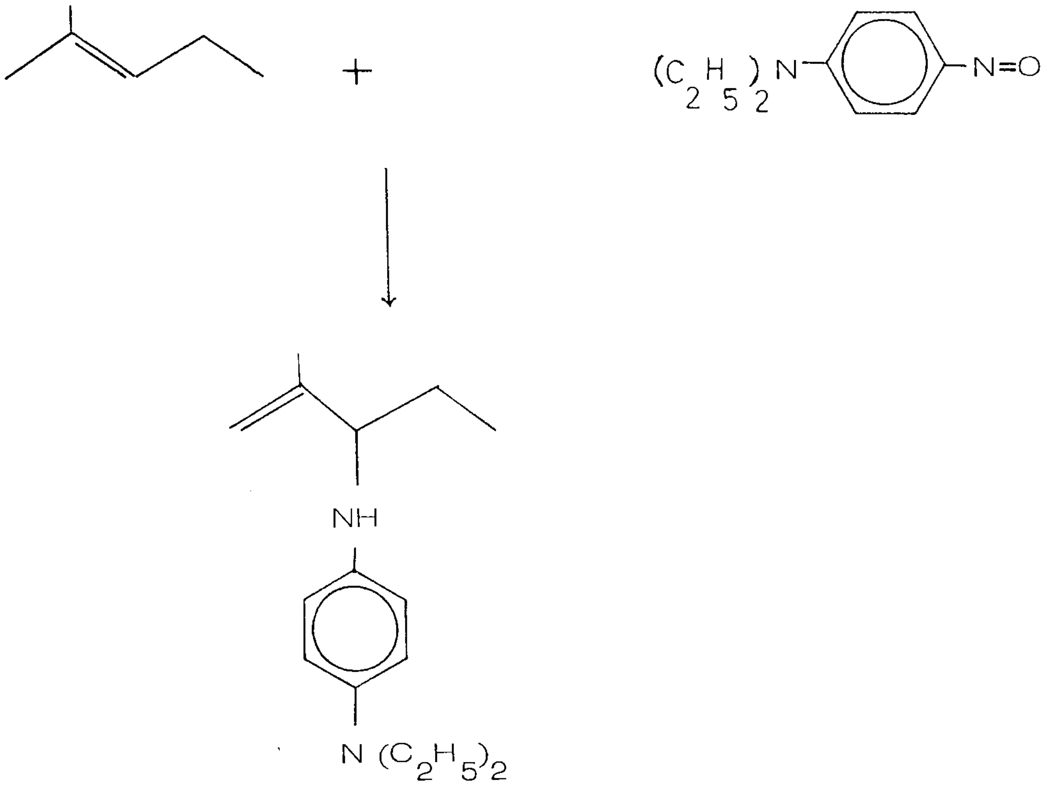


Antioxidant	R	Molecular weight	Induction period - hours 2×10^{-4} mol/100 g
R	Methyl	292	25
	Hexyl	362	40
	Lauryl	446	75
	Stiaryl	9800	9800

Although there are several methods of incorporating antioxidants into natural rubber, in principle the most successful method should be to graft the antioxidants into the polymer back bone. This solves the problem of antioxidant loss by volatility and extractability. It also ensures the presence of antioxidant group throughout the life time of the article.

The workers at the NRPRA(21) have reported the incorporation of network bound antioxidants into natural rubber. The mechanism was studied using a model compound, 2-methyl-2-pentene and reacting this with N,N-di-ethyl-p-nitroso aniline at elevated temperature.

This reaction can be represented as:



Subsequently, they incorporate 4-nitroso anilines and 4-nitroso phenols into natural and synthetic rubbers in an internal mixer and obtained a rubber bound antioxidant which was completely resistant to extraction by water or organic solvents.

1.5 Graft Polymerisation of Natural Rubber

Graft co-polymerisation of natural rubber has been carried out in bulk, for example, on a mill in solution and in the latex. Some of the earliest work on the reaction of vinyl monomers and rubber involved maleic anhydride. Since the latter is capable of co-polymerisation but not homo polymerisation it is not possible to add more than one monomer unit for each site of the attack on the rubber molecule. The literature contains numerous references to the polymerisation of various vinyl monomers dispersed in natural rubber latex.

1.5.1 Chemical grafting of vinyl compounds to NR

In order to graft vinyl compounds to natural rubber in a latex system, it is clearly necessary that the monomer is absorbed by the rubber particles, and that polymerisation should take place within the swollen globules(19,22). Hence a low proportion of a surface-active stabiliser is used in practice and adequate time is allowed for diffusion of the monomer into the rubber particles. Otherwise there is a considerable probability that polymerisation will take place in an emulsified monomer phase without involving the rubber, resulting in an intimate rubber-polymer mixture rather than a rubber-monomer compound. However, in the presence of a large amount of dispersing agent much of the monomer tends to polymerise independently of the rubber(23) as discussed earlier.

Refinements of the technique consists of deammoniating the latex when using systems which are sensitive to free ammonia or to ammonium ions, adjustment of PH to suit specific initiators, flushing with an inert gas in systems sensitive to inhibition by oxygen. In order to produce a graft co polymer by chain transfer mechanism it is obviously necessary to have three components present in the system.

(a) A polymerisable monomer

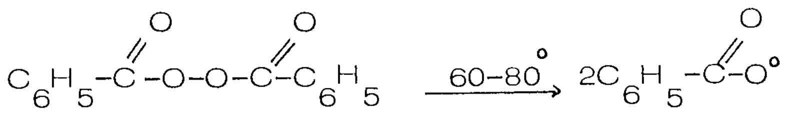
(b) A polymer chain upon which it is desired to graft

(c) A free radical source or a catalyst which is capable of abstracting an atom of the polymer to initiate the chain reaction

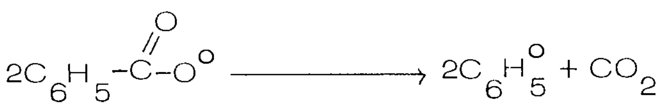
The success of the chain transfer method in producing graft co-polymer is directly dependent upon the structures of the monomer, the polymer and the catalyst.

Hevea latex is a hydrosol in which the dispersed rubber particles are strongly protected by a complex film containing protein and phospholipids. The stability of this suspension is strongly governed by the PH and the temperature of the latex. When excess acid is poured into ammonia preserved natural rubber latex a coagulum is formed which separates from the aqueous phase.

Graft polymerisation usually involves reactions in which the chain initiator is an oxidising free radical. This is usually formed by the decomposition of a relatively unstable initiator which when heated undergoes homolytic fission of the weakest chemical bond resulting in the formation of an oxygen radical.



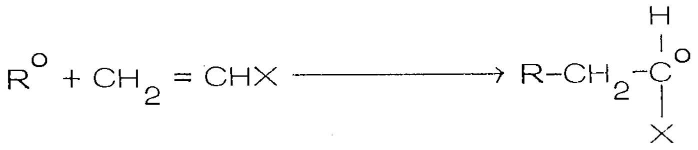
$$C_6H_5-\overset{O}{\overset{/\!/}{C}}-O-O-\overset{O}{\overset{/\!/}{C}}-C_6H_5 \xrightarrow{60-80^{\circ}} 2C_6H_5-\overset{O}{\overset{/\!/}{C}}-O^{\circ}$$



$$2C_6H_5\text{-}\overset{\overset{O}{/\!/}}{C}\text{-}O^{o} \longrightarrow 2C_6H_5^{o} + CO_2$$

When free radicals are generated in the presence of vinyl monomers, the radical adds to the double bond with the generation of another radical. If the radical formed by the decomposition of the initiator I is designated R^{o}.

$$I \longrightarrow 2R^{o}$$

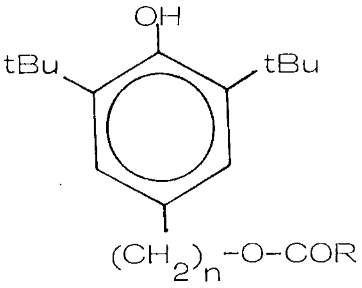


$$R^{o} + CH_2 = CHX \longrightarrow R\text{-}CH_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}{}^{o}$$

Thermal decomposition of an initiator has a disadvantage in that the rate of generation of free radicals cannot be changed rapidly because of the heat capacity of the system. Photo-initiated polymerisation, on the other hand, can be controlled with high precision since the generation of radicals can be made to vary instantaneously by controlling the intensity of the initiating light(24).

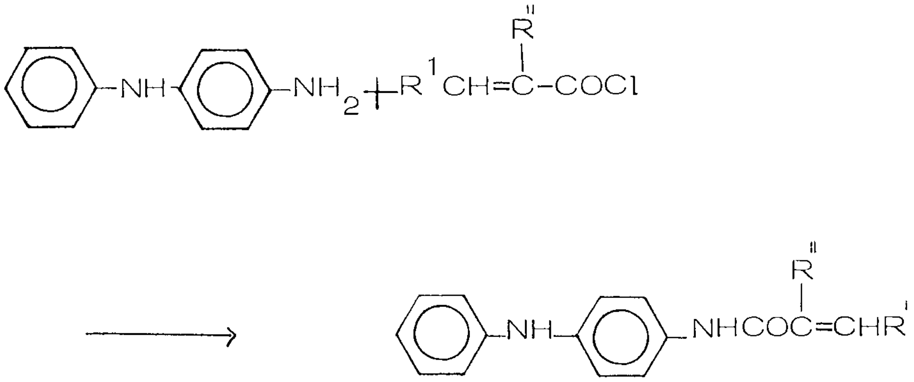
Grafting a vinyl compound into natural rubber back bone has been described in the literature(25-31).

Kleiner(32) studied a series of vinyl hindered phenols of the ester type (1) including acrylates, methacrylates, fumarates, maleates, etc. He homo polymerised the hindered vinyl phenols using high molecular weight peroxides such as lauroyl and decanoyl peroxides, and obtained a polymeric stabiliser. This he blended with the oxidisable polymers and studied the rate of oxidation. A remarkable antioxidant effect of the polymerised vinyl phenols was obtained.



Kline and Miller(33) attempted to prepare polymerisable antioxidants for emulsion rubbers. Although they have not grafted any of the antioxidants to a polymeric back bone they did manage to prepare several possible polymerisable antioxidants. This was achieved by introducing a reactive pendent group to p'-aminediphenylamines and to stearically hindered phenols.

Polymerisable antioxidants of the amine type were prepared by acylation of p-aminodiphenylamine and of p-hydroxydiphenylamine with chlorides of α-β unsaturated acids.



α-b unsaturated acid chlorides were also used by them to prepare polymerisable phenolic antioxidants by acylation of the hydroxy phenyl alkanols, hydroquinones or the amino phenols.

The antioxidant activity of these compounds were determined by oxygen absorption tests. Samples were prepared by adding one part of antioxidant in benzene solution to 100 parts of isopropanol coagulated SBR-1006, also in benzene solution. The solutions were poured into alluminium foil trays and allowed to evaporate. The trays with the residual film attached were rolled into cylinders and placed in an oxygen absorption apparatus.

By these experiments they observed a remarkable antioxidant activity with the amino type as well as with the phenolic type. According to these results the most important factor affecting antioxidant activity is the number of carbon atoms separating the aromatic ring from the hetero atom. In both the amide and the ester series, activity is at a minimum when $n = 1$. When $n = 0$ the amides are superior to the esters but this difference disappears when $n > 1$.

Meyer and Co workers(34) attempted to co-polymerise the monomeric antioxidants, proposed by Kline, with styrene-butadiene rubber (SBR) and with acrylonitrile-butadiene rubber (NBR). Ladd(35) reported the co-polymerisation of phenolic-substituted monomers in an SBR system using 2,3-azobisisobutyronitrile (AZBN) as the initiator. Kato and Nakano(36,37) were able to polymerise styrene, maleic anhydride or methylmethacrylate with a vinyl monomer chemically attached to a hindered phenol. They found that AZBN, but not cumine hydroperoxide, could be used as initiator. Meyer and Co workers have conducted their emulsion polymerisation of SBR and NBR with antioxidants in the presence of p-methane hydroperoxide.

It has been shown by them that compounds containing dual functionality (therefore bearing antioxidant and polymerisable functions) can be co-polymerised with numerous monomers in emulsion systems. The only incompatible initiator-monomer combinations found are those of persulphate and benzoyl peroxide with amine antioxidants. Further they observed that dual functional monomers retain their normal antioxidant characteristics in the co-polymerised form and are not removed by solvent extraction nor by vulcanisation except under conditions that destroy the polymer. Also they found that the amine antioxidants provide antioxidant protection equivalent to high quality conventional amine antioxidants.

Although numerous review articles have been written, together with several excellent books, on vinyl graft co-polymers very little work has been carried out attempting to graft co-polymerised vinyl compounds with natural rubber latex. Most of the work has been carried out with rubber solutions rather than with rubber latex.

Persulphates, perborates, hydrogen peroxide, alkyl hydroperoxides, diazoamino benzene, benzoyl peroxide, reduction-activated organic hydroperoxides, diazo thioethers and diazonium salts have all been used to initiate the graft polymerisation of vinyl monomers into natural rubber.

Attempts to graft co-polymerise styrene, nitriles, acrylic esters and methyl methacrylate into natural rubber latex indicated the difficulties attending the use of a peroxide as a catalyst(38). During polymerisation, the opalascent emulsion changes into a white, mobile, milky fluid rather similar in appearance to normal rubber latex. When polymerisation was slow or the emulsifying agent inefficient, a portion of the product appeared as a glossy or jelly like clot instead or as a latex.

But such losses were not usually serious with triethanolamine lauryl sulphate. In order to use benzoylperoxide it was necessary to

(a) deammoniate the latex

(b) work at temperatures not much below 80°C

(c) add substantial proportions of non ionic stabiliser to prevent coagulation

More successful polymerisations were later effected by using water soluble catalyst such as persulphate or organic hydroperoxide(27).

The graft co-polymerisation of acrylonitrite into natural rubber latex was first investigated by Le Bras and his co-workers(39). They observed, as did others, that ammonia retarded polymerisation even in the presence of persulphate as an initiator. But persulphate initiation was less sensitive to ammonia than was benzoyl peroxide.

Thus the preferred initiator for the graft co-polymerisation of common vinyl monomers into natural rubber latex should not be affected by the ammonia present in the latex. The practical reason for this is that in the field, it is essential to add a small amount of ammonia into latex as soon as it is obtained from the tree, otherwise within a few hours it may coagulate. If the activity of the initiator is affected by ammonia present in the latex it will be necessary to deammoniate the latex prior to carrying out any grafting reaction.

A successful method developed by Whitby(40) is based on a hydroperoxide activated by a polyamine. This system was especially interesting and useful as it does not require deammoniation of the latex nor was it particularly sensitive to inhibition by oxygen.

The products of graft polymerisation of methyl methacrylate into natural rubber utilising the above system were separated into free rubber graft co-polymer and polymethyl methacrylate. Some workers have found that a trace of soluble iron increases the amount of the co-polymer formation. Whitby and co workers(40) have studied the polyamine activated polymerisation using cumene hydroperoxide and various polyamines. According to their results many amines have the ability to decompose organic peroxides, but in peroxide-catalysed emulsion polymerisation only a limited number of amines have an activating effect so powerful that it is possible, by adding them to the system, to bring about rapid polymerisation at a low temperature. They have compared the effectivenss of polyamines of the series polyethylene polyamines, from diethylenetriamine to non aethylene decamine. They have found that the activity of these polyamines reaches a maximum in tetra ethylene-pentamine and pentaethylene hexamine and then gradually decreases in the higher numbers.

$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

Tetra ethylenepentamine (TEPA)

A less usual method of polymerising monomers into rubber latex is the hydrazine/cupric ion system(41). Probably the initiating species here is the hydrazyl radical formed by the oxidation of hydrazine by cupric ion.

$$N_2H_4 + Cu^{++} \longrightarrow N_2\overset{\circ}{H}_3 + Cu^{+} + H^{+}$$

In the presence of oxygen, the primary process must presumably be the same since a direct reaction between hydrazine and oxygen is considered improbable.

Duke and co workers(42) have shown that Ceric salts in the presence of amines or alcohols have a capacity to initiate graft polymerisation via free radicals. The complex form by the reaction between ceric ion and the alcohol/amine disproportionate to give free radicals.

$$Ce^{4+} + RCH_2OH \overset{K}{\rightleftharpoons} \beta_{complex} \xrightarrow{\quad\quad} K_d \rightarrow Ce^{3+} + H^{+}$$

$$\underbrace{R\overset{\circ}{C}HOH \text{ or } RCH_2\overset{\circ}{O}}_{\text{free radicals}}$$

The remarkable feature of this system is the oxidation of Ce^{4+} via a single electron transfer mechanism with the formation of a free radical on the reducing agent. If the reducing agent is a polymeric molecule such as natural rubber, the free radical formed on the rubber back bone will initiate polymerisation to produce a graft. Pure grafted rubber may be obtained with this system as free radicals are formed exclusively on the polymer back bone.

1.5.2 Grafting by high energy radiation

Recently considerable interest has been aroused in the preparation of graft polymers from a wide range of monomers and polymers using high energy radiation such as ultra violet and X-rays(43-45). Oster has reported the grafting of acrylamide on to natural rubber using ultra violet light(46). In this case he has placed an aqueous solution of the monomer over a solid film of rubber containing photosensitiser. Again in 1958 W Cooper and M Fielden(47) reported that it is possible to graft-polymerise monomers, such as methyl methacrylate and styrene, with natural rubber in emulsion using visible and ultra violet light in spite of the fact that a natural rubber latex is very opaque. Further they have observed that 50% of the light is reflected from the surface of a high concentration latex and the penetration for 90% absorption of light is less than 0.1 mm. Because of this they concluded that it was necessary to include a photosenisitiser with latex in the case of photo-initiated grafting. Although they used 1-chlo anthraquinone Menon and Kapur(48) have used water soluble photosensitisers, also, such as ferric ion pair $Fe^{3+}Cl^-$ and $Fe^{3+}OH^-$ in a nitrogen atmosphere in order to obtain a graft polymer from methyl methacrylate and natural rubber latex.

Evans(49) and Co workers studied the mechanism of photo-chemically initiated polymerisation of vinyl compounds in aqueous solution. The photo-chemically active species they studied was an ion pair complex of the formula $Fe^{3+}X^-$ ($X^- = OH^-$, Cl^-, N_3^- etc).

According to their theory, the light absorption by the ion pair leads to an electron transfer causing reduction of the cation and oxidation of the anion to an atom or free radical $\overset{o}{X}$. The latter leads to the initiation of polymerisation in accordance with

$$\overset{o}{X} + CH_2{=}CHR \longrightarrow X\ CH_2 \text{———} \overset{o}{C}HR$$

They put forward a complete mechanism, both with regard to the formation of free radicals and the polymerisation reaction.

(1) Light absorption

$$Fe^{3+}X^{-} \longrightarrow Fe^{2+} X$$

(2) Primary dark back reaction

$$Fe^{2+} X \longrightarrow Fe^{3+} X^{-}$$

(3) Initiation of polymerisation by the primary product

$$Fe^{2+} X$$

(M = vinyl monomer)

$$Fe^{2+} X + M \longrightarrow Fe^{2+} + X - M -$$

(4) Separation of the primary product

$$Fe^{2+} X \longrightarrow Fe^{2+} + X^{\circ}$$

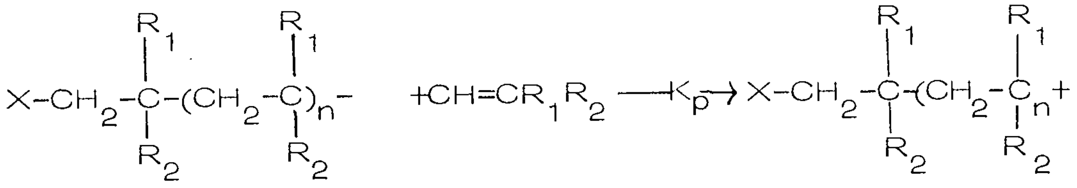
(5) Secondary dark back reaction

$$Fe^{2+} + X^{\circ} \longrightarrow Fe^{3+} + X^{-}$$

(6) Free radical initiation of polymerisation

$$X^{\circ} + M \longrightarrow X - M^{\circ}$$

(7) Propogation of polymerisation



$$X\text{-}CH_2\text{-}\underset{R_2}{\overset{R_1}{C}}\text{-}(CH_2\text{-}\underset{R_2}{\overset{R_1}{C}})_n\text{-} + CH{=}CR_1R_2 \xrightarrow{K_p} X\text{-}CH_2\text{-}\underset{R_2}{\overset{R_1}{C}}\text{-}(CH_2\text{-}\underset{R_2}{\overset{R_1}{C}})_{n+}$$

(8) Termination polymerisation

(a) by free radicals

$$X - M_p - + X \longrightarrow X - M_p - X$$

(b) by recombination of active endings

$$X - M_p . + -M_q - X \xrightarrow{K_t} X - M_p - M_q - X$$

W Cooper(50) and Co workers have studied the influence of monomer concentration, temperature, radiation intensity, and, in the case of photo-initiation, photo sensitiser concentration on polymerisation rates and molecular weights. They observed a high proportion of graft polymer initially but this falls with conversion and with increase in monomer concentration. Further they have reported that the photo-initiated grafting depends on the photo sensitiser and on temperature, but with γ-initiation the fraction grafted is independent of temperature.

1.6 Mechanistic aspect of graft polymerisation by chain transfer

It is well known that during graft polymerisation, the free radicals may remove an atom from a pre formed polymeric chain with the formation of a radical site where initiates the polymerisation of monomer. If it is a branched polymer the points of attack may also be located on the lateral groups of the chain.

The initial free radicals usually derive by the decomposition of an initiator.

According to G.Natta and Co workers the scheme of the reactions of initiation and propagation is as follows.

$$R_2 \longrightarrow 2R^{o} \qquad - 1$$

$$R^{o} + M \longrightarrow RM^{o} \qquad - 2$$

$$RM^{o} + nM \longrightarrow R\,M_nM^{o} \qquad - 3$$

$$R^{o} + SH \longrightarrow RH + S^{o} \qquad - 4$$

$$\overset{o}{RM_n} + SH \longrightarrow RM_nH + \overset{o}{S} \qquad - 5$$

$$\overset{o}{S} + nM \longrightarrow SM_{n-1}\overset{o}{M} \qquad - 6$$

R - initiator

M - monomer

SH - main polymeric chain

Reactions 1, 2 and 3 respectively correspond to the decomposition of the initiator with the formation of primary radicals, to the addition of a first monomeric unit to these primary radicals and to the growth of the homopolymeric chain by subsequent addition of the monomer molecules.

In reaction 4,a H atom of the main polymeric chain is removed by the action of a primary radical $\overset{o}{R}$.

In reaction 5 the hydrogen atom is removed from the polymeric chain by a growing molecule $\overset{o}{RM_n}$.

Finally, reaction 6 represents the addition of the monomer to the active centre and the formation of a graft co-polymer.

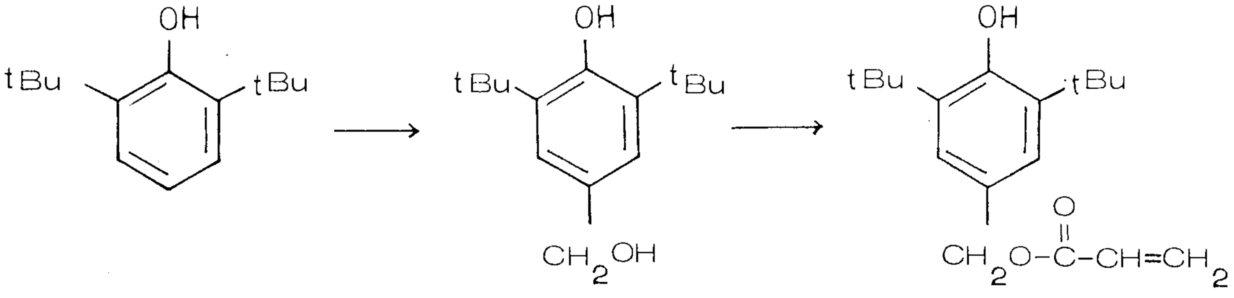
At an early stage of research it was concluded that the reaction of the primary radicals with a vinyl monomer (reaction 2) was easier than the removal of hydrogen atom from a macromolecule (4). (Chain transfer polymer.) This hypothesis was supported by the fact that the activation energy for a chain transfer reaction is higher than for the addition of a monomer. However, recent work has shown that the reaction 4 cannot be excluded on the basis of activation energy data. For some polymer-monomer systems the ability to graft totally depends on the nature of the initiator. A typical example is the polymerisation of methyl methacrylate in the presence of polystyrene. An appreciable yield of graft co-polmer was obtained with benzoyl peroxide as an initiator. With α-α^1 azo-iso-butyronitrile (AZBN) or with di-tert-butyl peroxide (DTBP) the grafting was negligible. Although the reactivity between methyl methacrylate and polystyrene was dependant on the type of initiator, the reactivity of vinyl acetate with methyl methacrylate did not depend on the type of initiator. Usually, the chain branching and grafting increases with increasing both temperature and polymer concentration. It was found that the chain transfer reaction, 4, depended on the reactivity of the polymer to be grafted.

CHAPTER 2

Synthesis and characterisation of vinyl substituted compounds for use as bound stabilisers as antioxidants

2.1 Synthesis of 3,5 - ditertiary butyl 4-hydroxy benzyl acrylate

This was prepared according to the following scheme.



DBBA

2.1.1 Preparation of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol

The 2,6-ditertiary butyl phenol was used as obtained from CIBA-GIGEY Ltd. without further purification.

The method used for the preparation was the one described by the Shell international research(51-53).

53.3 ml of a 7.5% solution of formaldehyde in tertiary butyl alcohol (0.140 mole CH_2O), 50 ml of a 500 g/l solution of 2,6-di-tertiary-butyl phenol in anhydrous tert-butyl alcohol (0.128 mole 2,6-di-tert-butyl phenol) and 14 ml of a 50 g/l solution of Potassium tert-butoxide in anhydrous tert-butyl alcohol (0.006 mole) were mixed at 20°C and stirred under nitrogen (white spot grade) for twenty minutes.

The reaction mixture was then poured in to excess of ice-water and two layers were formed. The upper oily organic layer promptly solidified. The recovered solids were freed of water, rewashed, stirred with n hexane, then filtered and washed with more n hexane then air dried.

The resulting product was a sparkling white crystalline solid, melted at 137°C.

I R data

free phenolic OH – 3580 cm^{-1}

hydrogen bonded OH – 3500 cm^{-1}

N M R (CCl 4)

aromatic protons – 2.9 (singlet)

phenolic protons – 4.9 (singlet)

methylene protons – 5.5 (singlet)

tertiary butyl protons – 8.6 (singlet)

N M R (Benzene)

solvent shift showing aliphatic alcoholic proton at 8.5 (singlet) also.

2.1.2 Reaction of 3,5-di tertiary butyl-4-hydroxy benzyl alcohol with acrylic acid

The method was followed directly as described by Shell International Research.(51-53)

A mixture of 47.2 g (0.2 M) of 3,5-di-tert-butyl-4-hydroxy benzyl alcohol and 130 ml acrylic acid was warmed gently on a steam bath until complete solution was achieved. To this was added about 10 ml more of acrylic acid, containing about a drop of conc sulphuric acid.

The mixture was allowed to stand at room temperature for six hours and then poured into water.

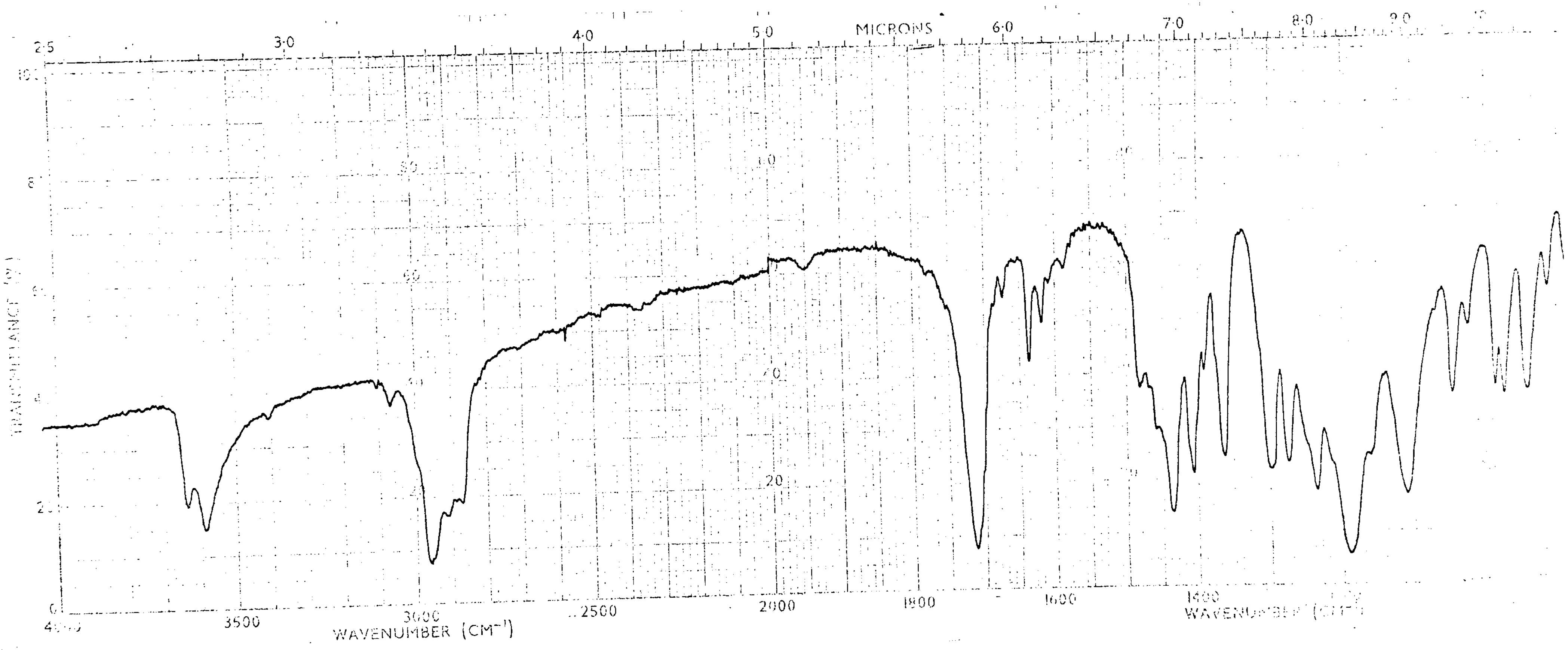
The organic phase was then extracted with ether and the excess acrylic acid extracted from the organic phase with aqueous sodium bi carbonate. The ether phase was then dried over anhydrous magnesium sulphate, filtered and the filtrate was evaporated. The residue was recrystallised from 30–40°C petroleum ether to give 19.9 g of 3,5 di tertiary butyl-4-hydroxy benzyl acrylate, melting at 67.5 - 69°C.

I R data

free phenolic OH	- 3640 cm^{-1}
ester carbonyl	- 1830 cm^{-1}
vinyl double bond	- 1640 cm^{-1}

N M R (CCl_4)

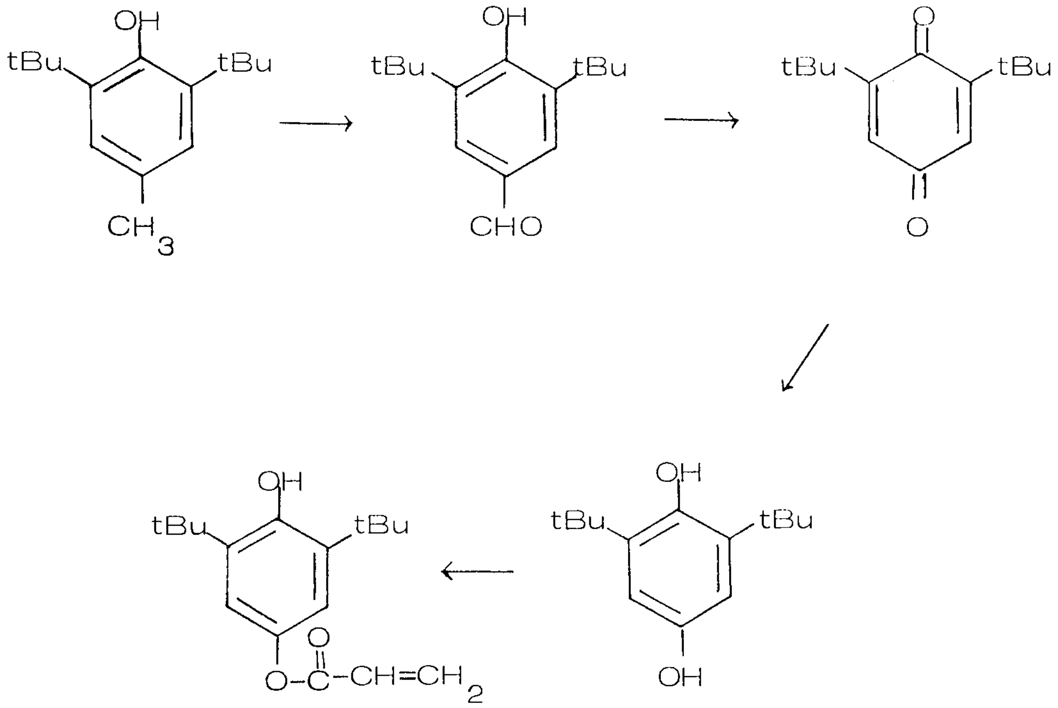
aromatic protons	- 2.9 (singlet)
vinylinic protons	- 3.6 - 4.5 (multiplet)
phenolic protons	- 4.8 (singlet)
methylene protons	- 5.0 (singlet)
tertiary butyl protons	- 8.6 (singlet)



Infra-red spectrum of the 3,5-di-tert-butyl-hydroxy benzyl acrylate

2.2 Synthesis of 3,5-ditertiary butyl-4-hydroxy phenyl acrylate

This was prepared according to the following scheme of reactions.



2.2.1 Preparation of 3,5-ditertiary butyl-4-hydroxy benzaldehyde

This was prepared by following a procedure similar to that described by Campbell.(54)

64 g (0.4 mole) of bromine was added with stirring to 22.3 g (0.1 mole) of 2,6-di-tertiary butyl-4-methyl phenol in 300 ml of t butyl alcohol at 25°C. The temperature rose to about 67°C, after the addition of bromine, stirring was continued for a further hour. The mixture was cooled and the yellow crystalline product

filtered off. This material was washed with 10% sodium thio-sulphate solution, then with distilled water and dried in a vacuum desicator. The product was an off-white crystalline solid, melting at 189°C. The total yield of 3,5-di-t-butyl-4-hydroxy benzaldehyde was 21.5 g. (91%).

<u>I R data</u>

Phenolic OH	- 3450 cm^{-1}
Carbonyl	- 1670 cm^{-1}

<u>N M R</u> (CCl_4)

alderhydic protons	- 0.2	(singlet)
aromatic protons	- 2.3	(singlet)
phenolic protons	- 4.3	(singlet)
tertiary butyl protons	- 8.6	(singlet)

2.2.2 Preparation of 2,6-di-tertiary butyl benzoquinone

The aldehyde (30 g) was dissolved in 5% caustic soda solution (640 ml) and 91 ml of 6% hydrogen peroxide solution added dropwise over one hour. The temperature was maintained at 50-60°C, and throughout the addition air was bubbled through the mixture. A deep yellow crystalline solid was precipitated. This was filtered, dried and re-crystallised from methanol as yellow-orange prisms (10.5 g) melting at 65.5°C

I R data

C – H aromatic – 3010 cm^{-1}

C – H aliphatic – 2900 cm^{-1}

carbonyl – 1660 cm^{-1}

N M R (CCl 4)

aromatic protons – 3.5 (singlet)

tertiary butyl protons – 8.6 (singlet)

2.2.3 Preparation of 2,6-di-tertiary butyl-4-hydroxy phenol (55)

25 g of 2,6-di-t-butyl benzo quinone was dissolved in 250 ml isoproponal and 25 ml of concentrated hydrochloric acid, to give a yellow solution. Excess of zinc dust was added and a rapid effervescence occurred. When the solution was colourless, sodium bi carbonate was added to neutralise any excess acid, and the solids were filtered off. The isopropanol solution was rotary evaporated to yield a white solid. This was re-crystallised from 30–40°C petroleum ether, and a white crystalline solid was obtained melting at 101°C.

I R data

free phenolic OH – 3640 cm^{-1}

hydrogen bonded OH – 3500 – 3100 cm^{-1}

N M R (CCl 4)

aromatic protons – 3.3 (singlet)

phenolic protons – 5.4 (singlet)

tertiary butyl protons – 8.6 (singlet)

2.2.4 Reaction of 2,6-di-tertiary butyl-4-hydroxy phenol with acrylolyl chloride(56,57)

22.2 g (0.1 mole) of 2,6-di-tert-butyl hydroquinone, 20.2 g (0.2 mole) of triethylamine and 150 ml of dried tetra hydro furan are stirred under nitrogen until a clear solution is obtained. Over a period of about 10 minutes, 9.1 g (0.1 mole) of acrylolyl chloride is added and stirring is continued for one additional hour. The tri ethylamine hydrochloride was filtered, and the filtrate poured in to 500 ml of water containing 25 mole of conc hydrochloric acid to give an oil which slowly solidified to form an orange solid.

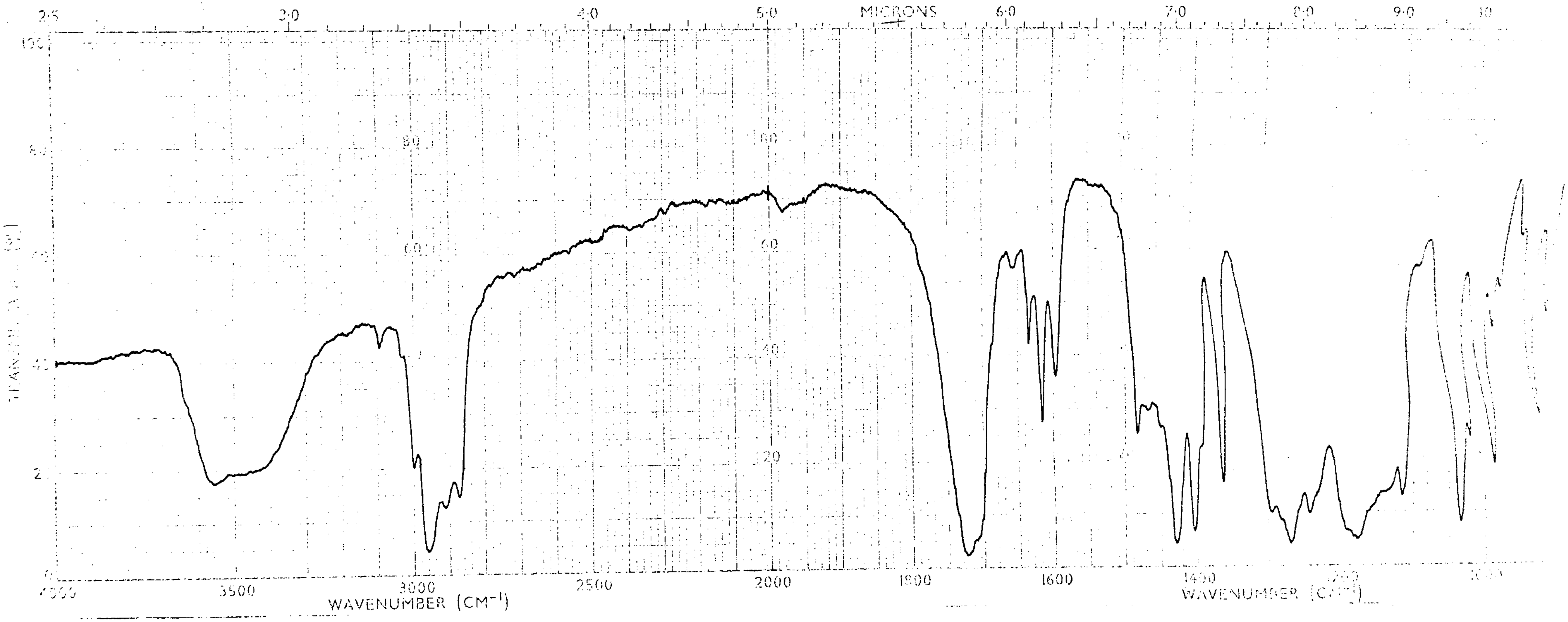
After several re-crystallizations from ethanol a white solid, 4-acryloyloxy-2,6-di tert butyl phenol, is obtained melting at 102-103°C.

I R data

phenolic OH	- 3500 cm^{-1}
ester carbonyl	- 1730 cm^{-1}
vinyl double bond	- 1650 cm^{-1}

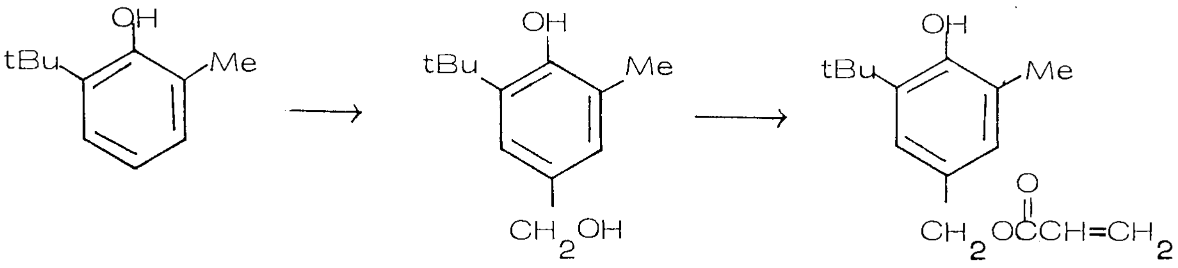
N M R ($CDCl_3$)

aromatic protons	- 3.2 (singlet)
vinyl protons	- 2.4 - 4.2 (multiplet)
phenolic protons	- 5.0 (singlet)
tertiary butyl protons	- 8.6 (singlet)



Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxy phenyl acrylate

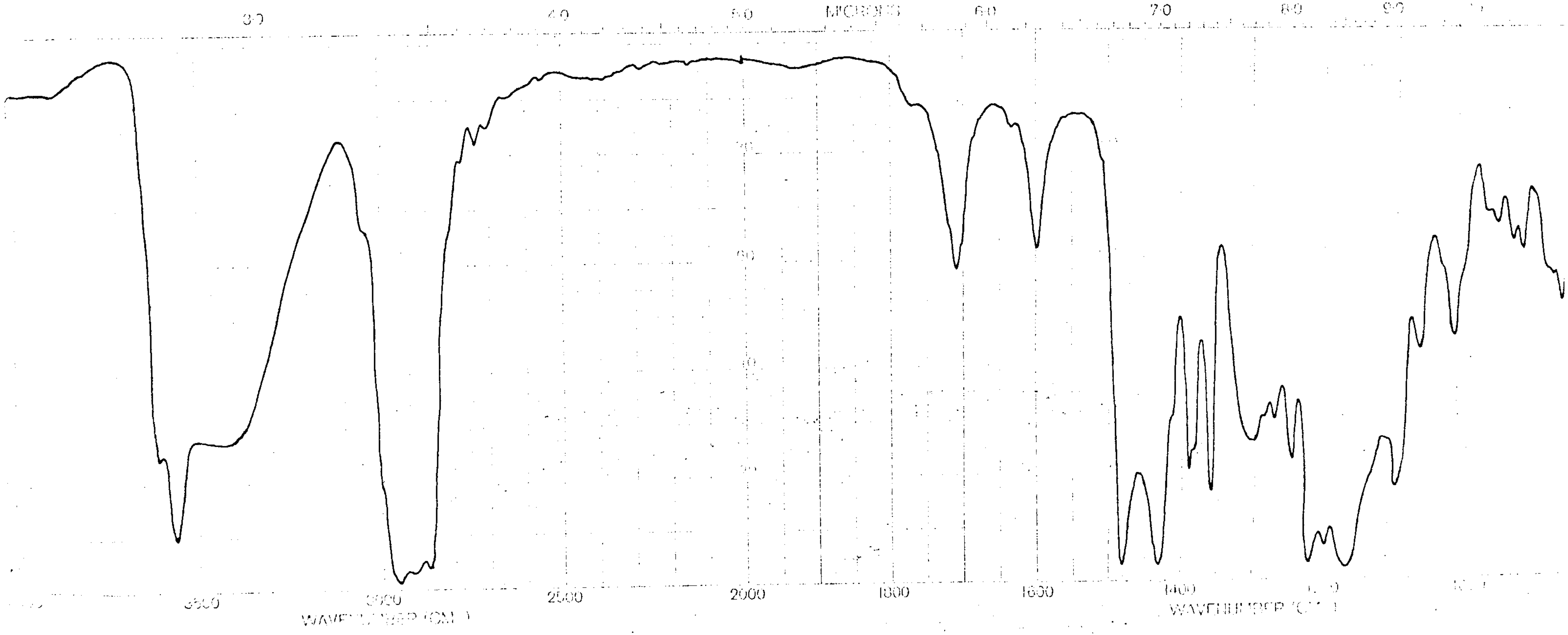
2.3 Synthesis of 3-tertiary butyl 5-methyl 4-hydroxy benzyl acrylate



2.3.1 Preparation of 3-tertiary butyl 5-methyl 4-hydroxy benzyl alcohol(51)

To a flask purged with nitrogen were added 18.3 g (0.15 mole) 2-t-butyl 6-methyl phenol, 42 g (0.2 mole) 14.3% w.formalc lehyde in tert butyl alcohol, and 15 ml (0.005 mole) 2.4% w potassium hydroxide in tert butyl alcohol. The phenol : formaldhyde : KOH molar ratios were therefore 1:1.33:0.033.

The mixture was allowed to stand overnight at about 20°C under nitrogen. To it was then added enough water to make a total of 500 ml, the mixture acidified with hydrochloric acid, and the organic phase was taken up in methylene chloride. The aqueous phase was extracted with two successive portions of methylene chloride, and the methylene chloride fractions combined. The methylene chloride was then stipped off in vacuo at 35°C and the 3-tert-butyl 5-methyl



Infra-red spectrum of 3-methyl 5-tert-butyl-4-hydroxy benzyl acrylate

4-hydroxy benzyl alcohol was vacuum distilled.

I R data

free phenolic OH	- 3580 cm^{-1}
C - H aliphatic	- 2900 cm^{-1}
H - bonded OH	- 3100 - 3500 cm^{-1}

2.3.2 Reaction of 3-tert butyl 5-methyl 4-hydroxy benzyl alcohol with acrylic acid

The same procedure was followed as for the preparation of 3,5-di-tert-butyl benzyl alcohol.

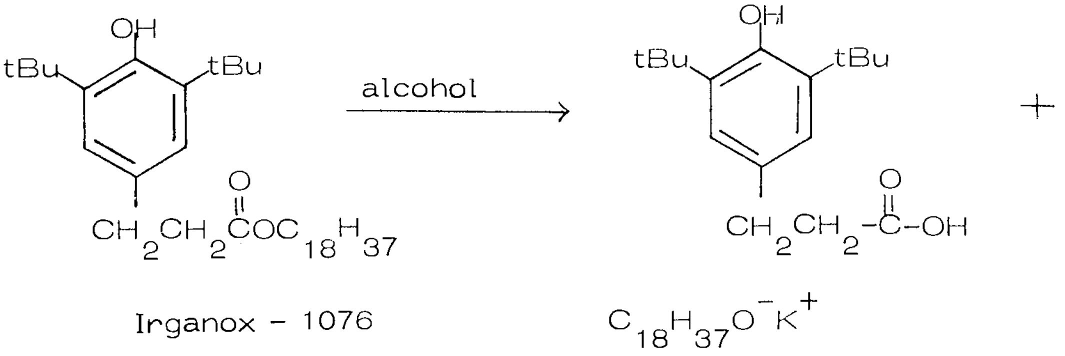
I R data

free phenolic OH	- 3610 cm^{-1}
H - bonded OH	- 3580 - 4300 cm^{-1}
ester carbonyl	- 1720 cm^{-1}
vinyl double bond	- 1610 cm^{-1}

2.4 Preparation of β-(3,5-di-tert-butyl-4-hydroxy phenyl)-propionic vinyl ester

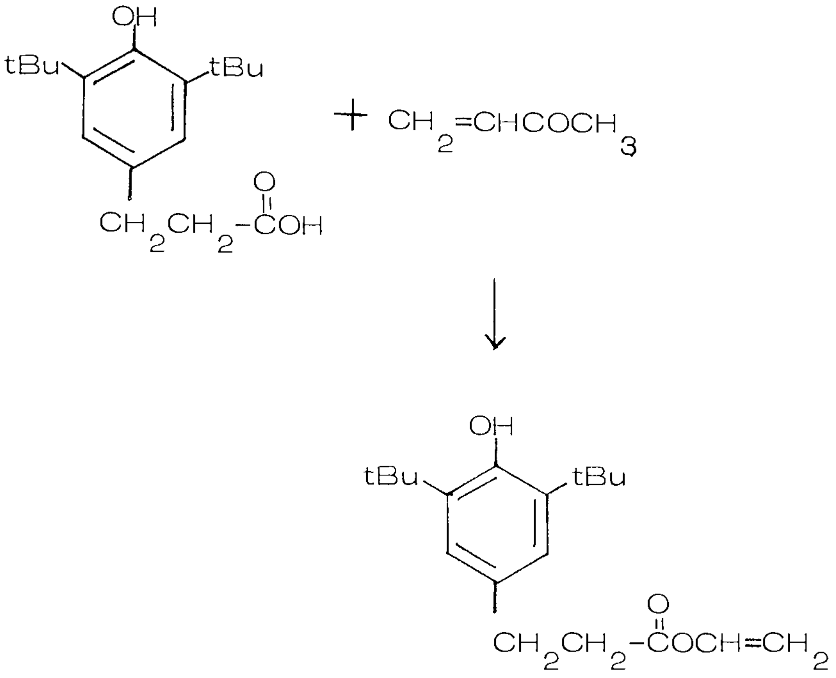
This was prepared according to the following scheme.

(a)



Irganox - 1076

(b)



2.4.1 Hydrolysis of β-(3,5-di-tert-butyl-4-hydroxy phenyl) proprionic octa decyl esters (Irganox 1076)

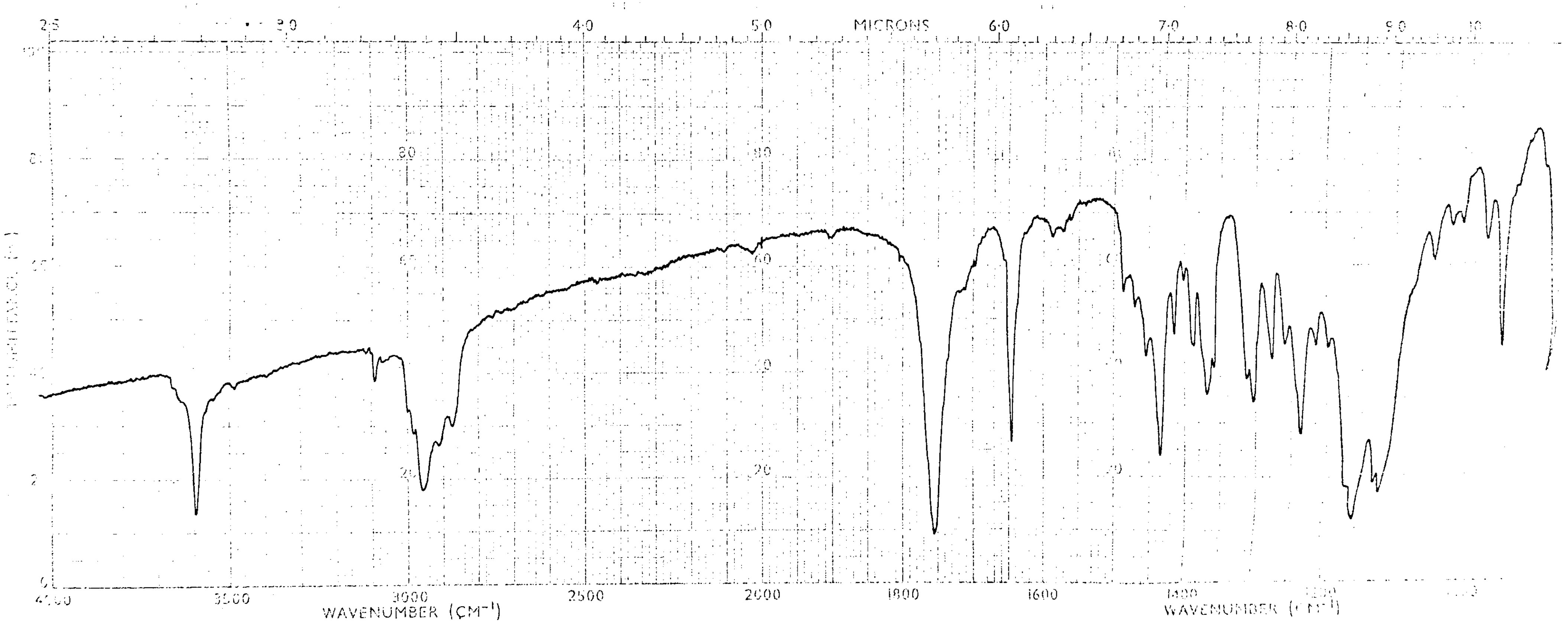
30 g of the ester, 30 g of potassium hydroxide in 400 ml of ethyl alcohol and 200 ml of water were refluxed for 30 minutes. Allowed it to cool and diluted it with 500 ml of cold water, and acidified with dil Hcl. The smoky white precipitate which was obtained was filtered, washed with warm water and dried under a vacuum dessicator. The β (3,5-di-tert-butyl-4-hydroxy phenol propionic acid) was re-crystallised with methanol in to colourless needles melted at 172^{o}C.

I R data

phenolic OH	- 3630 cm^{-1}
carbonyl	- 1720 cm^{-1}

2.4.2 Reaction of β(3,5-di-tert-butyl-4-hydroxy phenyl) propionic acid and vinyl acetate

To a mixture of 25.8 g (6 mole) of vinyl acetate and 13.9 g (1 mole)



Infra-red spectrum of the vinyl ester of 3,5-di-tert-butyl-4-hydroxy propionic acid of propionic acid there was added, to form the catalyst, 1.6% (0.203 g) of mercuric acetate based on the benzoic acid and sulphuric acid equivalent to the mercuric acetate (0.203 g). The reaction mixture was heated for three hours at 70°C, then 2 grams of sodium acetate was added to neutralise the sulphuric acid. The excess vinyl acetate was recovered by distillation at atmospheric pressure (vapour temperature about 70–80°C) until the flask temperature reached 125°C. The distillation was completed at 10 mm and collected about 9 gms of fairly pure vinyl ester as a colourless solid which melted at 63°C at atmospheric pressure.

I R data

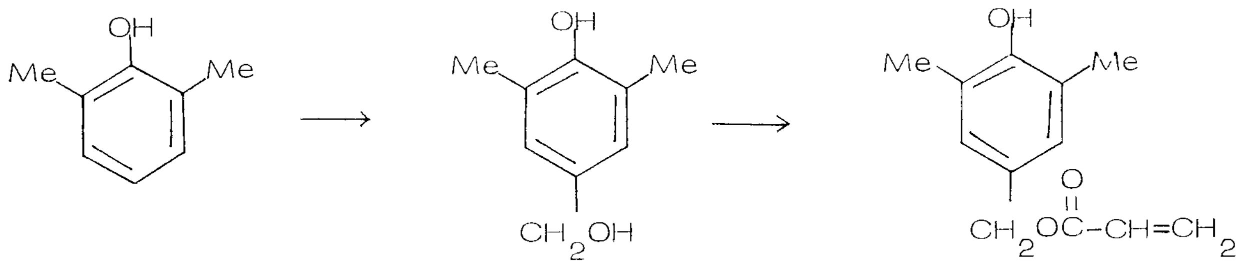
phenolic OH – 3600 cm^{-1}

ester carbonyl – 1760 cm^{-1}

vinyl double bond – 1650 cm^{-1}

2.5 Synthesis of 3,5-di-methyl-4-hydroxy benzyl acrylate

This was prepared according to the following scheme:



2.5.1 Preparation of 3,5-di-methyl-4-hydroxy benzyl alcohol(51)

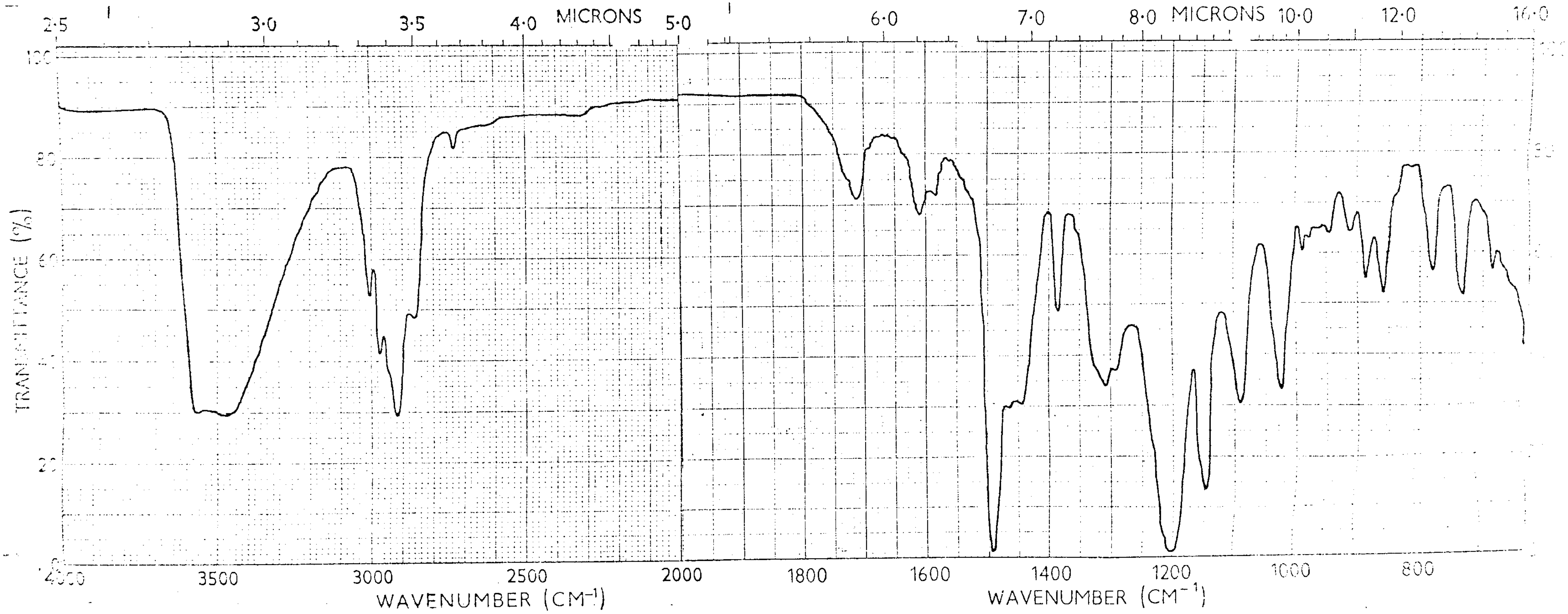
To a flask purged with nitrogen were added 18.3 g (0.15 mole) 2,6-di-methyl phenol, 42 g (0.2 mole) 14.2% w formaldehyde in tert butyl alcohol, and 15 ml (0.005 mole) 2.4% w potassium hydroxide in tert-butyl alcohol. The phenol : formaldehyde : potassium hydroxide molar ratios were therefore 1 : 1.33 : 0.033.

This mixture was allowed to stand over night at about 20°C under nitrogen. To it was then added enough water to make a total of 500 ml, the mixture acidified with hydrochloric acid, and the organic phase taken up in methylene chloride. The aqueous phase was extracted with two successive portions of methylene chloride, and the methylene chloride fractions combined. The methylene chloride was then stripped off in vacuo at 35°C, and the residue extracted with isopentane to leave an insoluble powdery white residue. Additional powdery white product was precipitated from the aqueous phase by further acidification. This was washed with isopentane.

The yield based on the starting phenol was about 82%. Melting point of the product was 95°C.

I R data

phenolic OH - broad 3300-3550 cm^{-1}



Infra-red spectrum of 3,5-di-methyl-4-hydroxy benzyl acrylate

2.5.2 Reaction of 3,5-di-methyl-4-hydroxy benzyl alcohol with acrylic acid

40 g of 3,5-di-methyl-4-hydroxy benzyl alcohol and 130 ml acrylic acid was warmed gently on a steam bath until complete solution was achieved. To this was added about 10 ml more of acrylic acid, containing about a drop of conc sulphuric acid.

The mixture was allowed to stand for 12 hours at room temperature and then poured in to water.

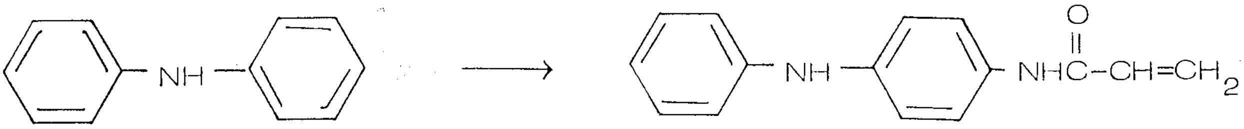
The organic phase (with the powdery substance) was then extracted with ether and the excess acrylic acid extracted from the organic phase with aqueous sodium bi carbonate. The ether phase was then dried over anhydrous magnesium sulphate, filtered and the filtrate was evaporated.

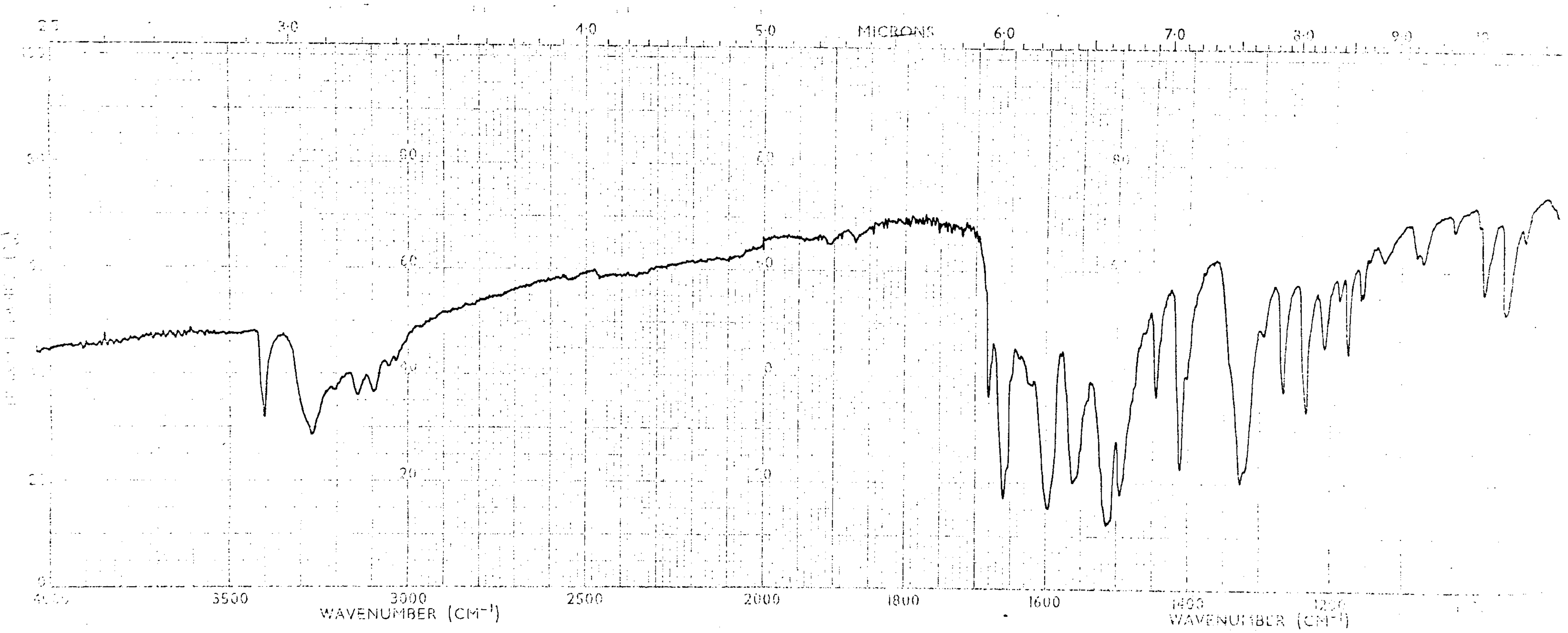
The melting point of the product was °C.

I R data

free phenolic OH	- 3500-3530 cm^{-1}
ester carbonyl	- 1720 cm^{-1}
vinyl double bond	- 1620 cm^{-1}

2.6 Synthesis of N-(4-anilinophenyl) acrylamide(56)





Infra-red spectrum of N-(4-anilinophenyl) acrylamide

16 grams (0.15 mole) of sodium carbonate was added to a solution of 36.8 g (0.2 mole) of p-aminodiphenylamine in 200 ml benzene. A solution of 22.6 g (0.25 mole) of acrylolyl chloride in 100 ml benzene was added dropuise in 30 minutes, beginning at room temperature. The mixture was stirred for 2 hours and the solid which precipitated during the reaction was filtered off. The filter cake was suspended in water and the mixture was stirred vigorously, then filtered. The crude product, which weighed 39 g, was re-crystallised from benzene.

The melting point of the product was 150°C.

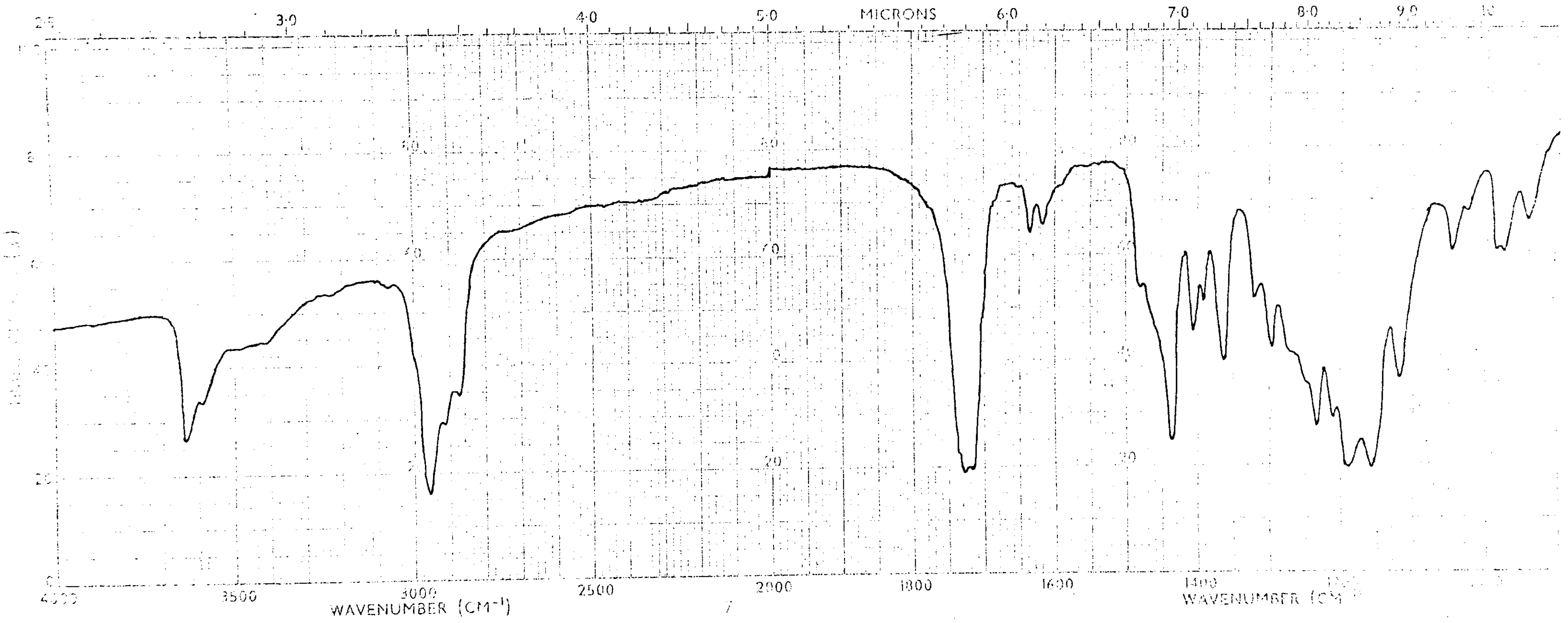
I R data

NH free	- 3400 cm^{-1}
NH_2 bonded	- 3200-3300 cm^{-1}
carbonyl	- 1660 cm^{-1}
vinyl double bond	- 1600 cm^{-1}

2.7 Polymerisation of the synthesised vinyl compounds

2.7.1 Preparation of poly-(3,5-di-tertiary butyl-4-hydroxy benzyl acrylate

2.9 g (0.01 m) of 3,5-di-tert butyl-4-hydroxy benzyl acrylate were dissolved in 20 ml of benzene and 0.03 g (0.002 m) azobisisobutyronitrile added as initiator. The whole was refluxed with stirring under nitrogen (white spot). After 8 hours a further 0.015 g initiator was added and the reaction left for further 16 hours. The



Infra-red spectrum of the Poly (3,5-di-tert-butyl-4-hydroxy benzyl acrylate) product was rotary evaporated to yield a white solid.

Polymerisation was confirmed by an infra-red spectrum showing disappearance of the vinylic absorption of the monomer.

I R data

broad phenolic OH – 3640 cm^{-1}
ester carbonyl – 1830 cm^{-1}
vinyl double bond – absent

N M R ($CDCl_3$)

aromatic protons – 2.8 (broad singlet)
phenolic protons – 4.8 (broad singlet)
methylene protons – 5.0 (broad singlet)
$CH - CH_2$ protons – 7.4–8.4 (broad multiplet)

2.7.2 Preparation of poly-(3,5-di-tertiary butyl-4-hydroxy phenyl acrylate)

Polymerisation of this monomer was carried out as described above and a white solid was obtained.

Polymerisation was confirmed by an infra-red spectrum showing disappearance of the vinylic absorption of the monomer. The N M R spectrum became broader, and additional peaks appeared at 7.6–8.4 τ typical of $CH - CH_2$ aliphatic resonance, with a corresponding decrease at 3.4–4.2τ.

CHAPTER 3

General experimental techniques

3.1 Materials

3.1.1 Natural rubber

The natural rubber latex used in all the experiments was supplied by W M Symington and Sons Limited under the trade name of Qualitex A. This is a kind of centrifuged latex stabilised with ammonia.

A typical analysis of Qualitex A is

	%
Total solid content	61.5
Dry rubber content	60.19
Non rubber solids	1.5
Ammonia % by weight	0.7
% on water phase	2.1
Mechanical stability	700–900 sec
K O H number Ca	0.6

3.1.2 Zinc oxide (Amalgamated Oxides Limited)

Zincola zinc oxide was used without further purification.

3.1.3 Sulphur (Anchor Chemicals Limited)

Sulphur, type D, was used without further purification.

3.1.4 N-(cyclo hexyl)-2-benzothiazyl sulphenamide CBS (Monsanto Chemicals)

Used without further purification.

3.1.5 Dispersol L N

Supplied by Imperial Chemical Industry.

3.1.6 Acrylic acid (B D H)

Stabilised with 0.05% p-methoxy phenol.

3.1.7 $\alpha \alpha^1$ -azo di-isobutyronitrile (A Z B N)

Koch Light Limited.

Re-crystallised from ether MP 104°C (103-104°C).

3.1.8 t Butyl hydroperoxide 70% (Kock Light Laboratories Limited)

Used without further purification.

3.1.9 Benzoyl peroxide

Dissolved in chloroform and precipitated by adding methanol. The precipitate was washed with methanol followed by pet ether.(58)

M Pt 105-106°C (106-107°C)

3.1.10 Potassium per sulphate

3.1.11 Lauric acid

(Re-crystallised from ethanol M P 42°C).

Other Chemicals

Topanol OC

Topanol A

2,6 di-tert-butyl phenol

2-tert butyl 6-Methyl phenol - Aldrich Chemical Company

2,6-di-methyl phenol - Ralph Emmanuel Limited

4-amino-di-phenyl amene - B D H

Nonox WSP

Nonox WSL

Tetra Ethyl Pentamine - B D H Technical grade

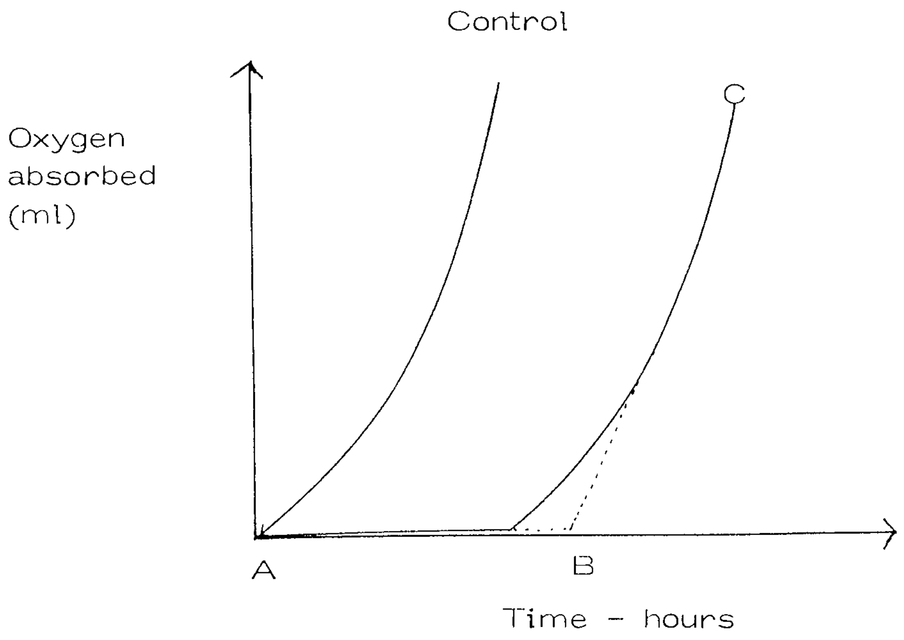
Bromine (Fissons)

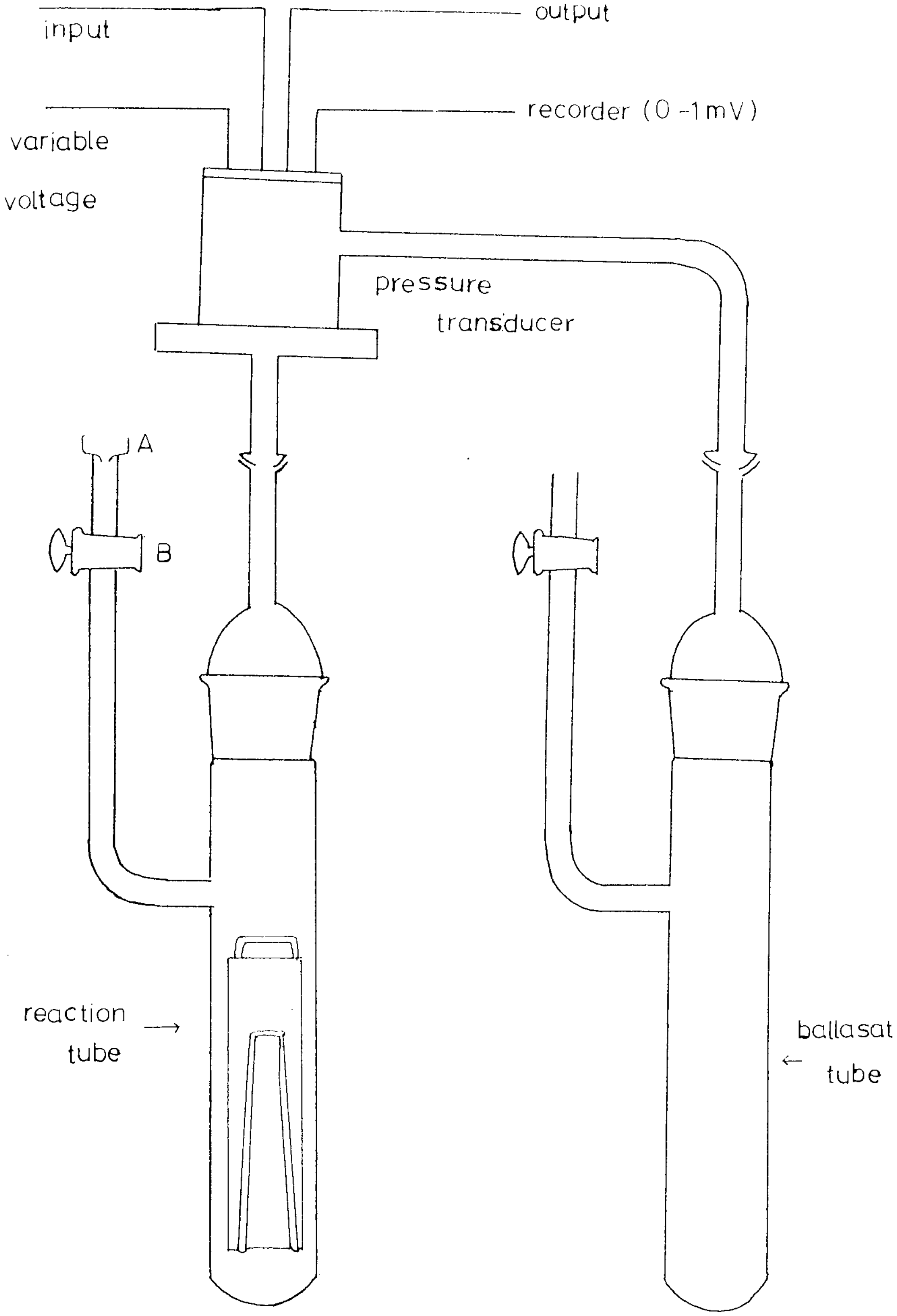
Acryloyl chloride - (Koch-Light Laboratories Limited)

3.2 Evaluation of antioxidant activity

The effectiveness of the sythesised monomers and polymers as antioxidants was determined using the technique of oxygen absorption. As many other polymers, in the absence of added antioxidants, natural rubber also show an autocatalytic oxidation process at elevated temperatures as illustrated in figure 1.

When an antioxidant is incorporated in to natural rubber prior to vulcanisation, the process of auto oxidation is retarded up to different extent depending on the effectiveness of the antioxidant used. During the first few hours or days there will be a very small or no oxygen absorption takes place by the sample even at high temperature in an oxygen atmosphere. This period is referred to as the 'induction period' as defined between A and B.





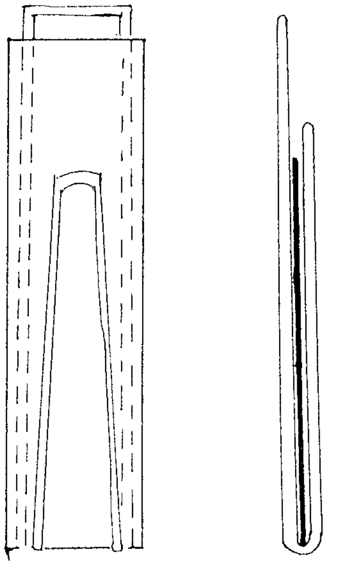


FIGURE 1

Apparatus used for the measurement of oxygen abosrption

Once the stabiliser has been exhausted during the induction period, the oxidation proceeds at a similar rate as for the unstabilised rubber, or the polymer, giving a curve BC. Hence the induction period is a measure of the relative activity of the antioxidant.

The magnitude and the duration of each stage profoundly influenced by such factors as the temperature of oxidation, the nature of curing system the presence of antioxidants on their effectiveness towards oxidation.

For a typical black natural rubber vulcanisate, that the tensil strength falls to half the original value with the absorption of about 2% oxygen (10 ml / g = 1.4%).

3.2.1 Preparation of vulcanisates

All the vulcanisates were prepared either from natural rubber itself or from natural rubber grafted with a prepared antioxidant. The rubber was grafted with various antioxidants using different initiator systems under different conditions. (Chapter 4)

Once the latex is reacted with the antioxidant it was coagulated with 1% Formic acid. This was done by the dropwise addition of formic acid in to the latex with rapid stirring. The solid mass of rubber was washed with oxygen free water and sheeted in to a thin crepe of the thickness of 2 mm. This was washed again with distilled water to remove any excess acid contaminated with the rubber and dried in a vacuum oven at 25^{o}C in the presence of self indicating silica gel.

Once it was completely dried the crepe was wrapped with aluminium foil to prevent the exposure to sunlight, which can accelerate the oxidation process at room temperature. In order to remove the naturally occurring extra network materials and the ungrafted antioxidants from the rubber, a continuous extraction of the grafted rubber was carried out in a Soxhlet apparatus (250 ml) with a solvent mixture. This was carried out under a steady stream of nitrogen. The extraction medium, to be known as solvent mixture, was composed of acetone, methanol and 1.1.1, - tri chloro ethane in the proportion described in the table below.

Really this is not a true azeotrope but distills with reasonably constant composition at around 57°C.

COMPONENT	PARTS BY VOLUME
Acetone	110
Methanol	42
1.1.1, - Tri chloro ethane	60

The rubber was extracted for about 48 hours. The temperature of extraction varied between 40-50°C. After the extraction the rubber was dried under a vacuum until it was free from any solvents.

3.2.2 Compounding

Extracted natural rubber (grafted or ungrafted) and compounding ingredients were mixed on a 12 inch, water cooled laboratory 2 roll mill. During the process of milling a friction ratio of 1:1 was employed. Compounds were prepared according to the formulation given in the table below.

Natural rubber	- 100 gms
Zinc oxide	- 5 g
Stearic acid	- 3 g
Sulphur	- 2.5 g
C B S	- 0.5 g

The total compounding time for each system was 5 minutes. Sulphur was added during mixing, after all the other ingredients had been successfully incorporated.

3.2.3 Vulcanisation

Vulcanisation of the samples were carriedout at 140°C under a pressure of 50 tons/sq inch. Samples were prepared in a fully positive stainless steel mould of cavity dimensions 13 × 13 cm.

This gave a vulcanisate of thickness 0.018 - 0.023 cm. The compound was sheeted out through a tight nip on a water cooled mill and about 5 gms was placed in the clean cavity of the pre-heated mould. The mould was placed between 2 plates of a steam heated press. The temperature of the plates was maintained at

140°C throughout the process of vulcanisation. 50 tons force was applied through an 8 inch diameter ram for 30 minutes. At the end of this period the mould was taken out from the press and quenched in cold water. The mould was opened and the vulcanisate sheet was immersed in cold water. The bloom was wiped from the surface of the vulcanisate with a tissue soaked in chloroform. A one centimetre border was cut from each edge of the sheet to discard any inhomogeniety due to edge effect. These were stored at 10°C.

3.2.4 Apparatus for oxygen absorption measurements of vulcanisates

The rate of oxygen absorption by the vulcanised samples was followed continuously and automatically using the apparatus shown in figure 1. The samples to be studies were placed in a modified test tube with a B24 socket and cone attachment as shown. A luer needle was connected to the opening of the axis fitted to the bottom of the test tube. The absorption tube was connected by a glass tubing to the wet side of the pressure transducer via a ball and socket joint. The dry side of the transducer was connected to a ballast tube of similar dimensions to the absorption tube. Both tubes were placed side by side in a thermostated oil bath (± 0.5°C). The tubes outside the oil bath were made up of capillaries and the distance was kept small in order to minimise the effect of change of room temperature on the system.

The reaction tube containing the sample was flushed with oxygen for several minutes and immersed in a thermostated oil bath. As oxygen was absorbed by the sample a pressure difference set up between the tubes. This pressure difference between the tubes is proportional to the output voltage of the transducer and this was automatically recorded as an oxidation curve on a Leeds and Northrup 'speedomax' recorder.

The transducer was a strain guage type manufactured by Pye-Ether Limited, model UP 3,±5 psi range. The size of the output voltage is proportional to the input voltage, so by varying the input voltage the sensitivity of the transducer pressure fluctuations could be varied. Throughout these experiments the input voltage was maintained in such a way that 1 ml oxygen absorb by the sample to be equivalent to 20 divisions on the scale of the chart.

An accurately weighed vulcanisate specimen (0.3 g) of maximum thickness 0.02 cm was placed on the sample support as shown in figure 1B so that the oxygen was able to diffuse freely in to both faces of the film. The support with the sample was inserted into the absorption tube and it was purged with oxygen through the luer needle for 15 minutes and the apparatus was assembled in the thermostated bath at 70°C and connected to the transducer. The ballast tube was already positioned. About 10 minutes was allowed to reach a temperature equilibrium between the air inside the tube and the oil bath and the tap was closed. The sample was allowed to absorb oxygen at 70°C. The maximum volume of oxygen that could be absorbed by this system at this voltage without damaging the transducer is 5 ml. Oxygen was still required to be absorbed and this was introduced into the system through the luer needle attachment.

To determine the amount of oxygen absorbed by the specimen the transducer was calibrated, and a calibrated curve of the change of pressure in the tube Vsthe deflection was plotted. This was done by fitting a syringe to the luer needle of the absorption tube, and a known volume of oxygen was withdrawn. The deflection on the recorder was noted. The duration of the oxygen absorption measurements were dependent on the rate of oxidation (rate of oxygen absorption) of the sample. After each experiment the absoption tube was dismantled, the sample removed and the apparatus washed with acetone then water and dried prior to the commencement of another determination.

3.3 Assessment of vulcanisation characteristics

This will be discussed in Chapter 10.

CHAPTER 4

Graft polymerisation of synthesised vinyl compounds with natural rubber latex

4.1 The preparation of aqueous dispersions

In an effective grafting system it is essential to carry out the grafting reaction in a one phase rather than in two phases. For this reason, it was necessary to emulsify or disperse all the polymers and monomers which are insoluble in water, with a suitable emulsifying agent or a dispersing agent before mixing with natural rubber latex to carry out any reaction. All dispersions added to the latex were prepared with distilled water.

The treatment required to produce high-quality dispersions of water insoluble solids and liquids depends on the physical nature of the materials. The solids which have been prepared by drying from a colloidal state do not usually require prolonged milling. Their primary particles are small and can be redispersed merely by stirring with water containing a dispersing agent. Other materials (solids), however, require actual grinding of the particles. The duration of the grinding or ball milling depends upon the size of the particles.

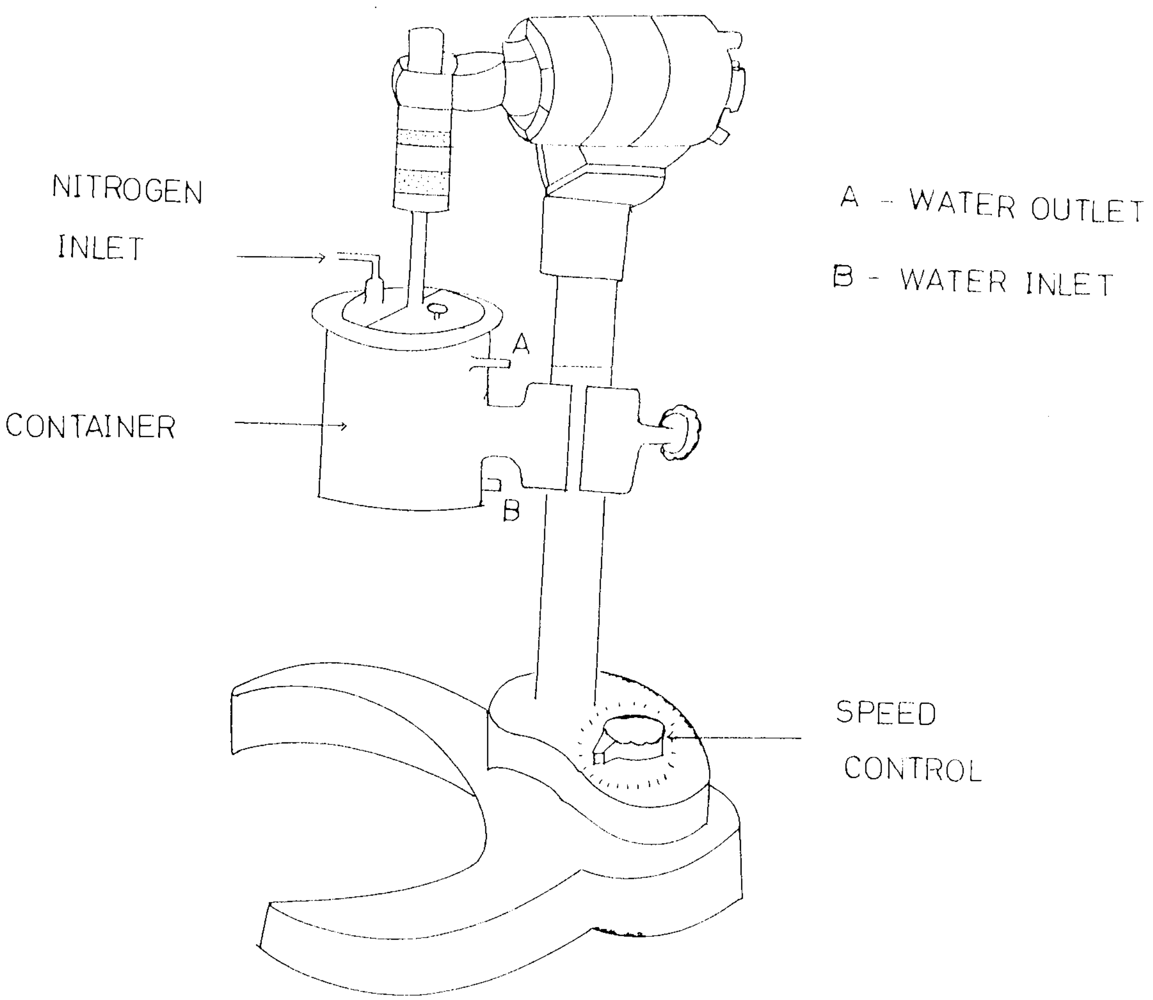
4.1.1 Dispersions of solids

This was done in a Szegvari attritor (type B) under a nitrogen atmosphere. This consists essentially of a cylindrical container half to two third full of small metal balls of 2 mm in diameter. The metal stirrer rotates vertically at such a speed that the charge is tumbled. The speed of the stirrer can be varied. The inner surface of the container is similar in hardness to the grinding charge and it is chemically inert to the materials introduced. The mill was (fig 2) charged with the antioxidant (solid) to be dispersed, distilled water and dispersing agent until the balls are just covered with water. The function of the dispersing agent is to wet the powder, to prevent or reduce frothing and to obviate re-aggregation of the particles. For all the preparations dispersal LN was used as the dispersing agent.

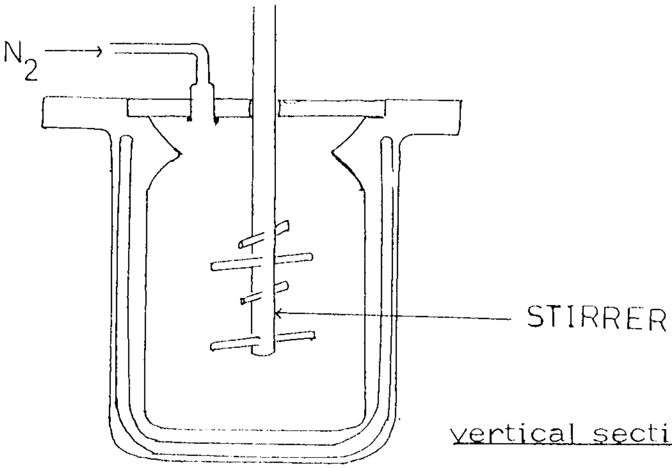
It was found that the ratio of water to solid matters in the dispersion should be such as to render the contents sufficiently fluid to tumble as it stirs. The rate of grinding by the mill is related to the speed of stirring.

In order to make a dispersion of prepared antioxidants(58) 10 gms of it was charged into the container with 0.2 gms of dispersol LN and distilled water was added (about 100 ml) until the balls are just covered. The charge was stirred at a constant speed for 10 hours. Throughout the stirring nitrogen was passed through the inlet tube into the container as shown in figure 2 to prevent any increase of temperature due to friction.

After grinding, the dispersion was discharged into a conical flask by covering the outlet with a piece of metal gauze to retain the grinding charge in the container. The metal balls were repeatedly washed with distilled water until the washings were clear. All the



Apparatus used to prepare dispersions of solids



vertical section of the container

FIGURE 2

washings were mixed and stored under a nitrogen blanket in a conical flask at 0°C. It was found that in a good suspension the solid particles are not sedimenting down on standing for any length of time.

4.1.2 Emulsification of liquids

To use a liquid monomer in latex, it was found to be essential that the water insoluble liquid should be emulsified in water. A general method for preparing emulsions is to shake the liquid with water in the presence of an emulsifying agent. With more viscous liquids, emulsions were prepared by dissolving a fatty acid in the liquid to be emulsified followed by pouring it, with stirring, into water containing an alkali so that a soap is formed in situ.

10 gms of the liquid to be emulsified was poured into a 250 ml conical flask and 0.42 gms of lauric acid was dissolved in it. 0.08 gms of potassium hydroxide in 50 ml of distilled water was poured into the conical flask while it is shaking. The air was purged out with nitrogen and stoppered tightly, and was shaken vigorously in a flask shaker for more than 24 hours until a milky emulsion was obtained.

4.2 Determination of optimum conditions for the graft polymerisation of rubber with DBBA

The average dry rubber content in the rubber latex obtained from the tree is about 30% by weight. For this reason the centrifuged latex containing 61% dry rubber was diluted with an equal volume of water before each experiment. The diluted latex was partially deammoniated prior to carrying out any grafting reaction. This was done by bubbling nitrogen through the diluted latex for about 3 hours with stirring. It was found that it is not advisable to get rid of all the ammonia present in the latex as the rubber then tends to get coagulated. But it was possible to deammoniate completely by adding 1% solution of vulcastab LW in water to the latex before passing nitrogen. Few grafting reactions were carried out with completely deammoniated latex (stabilised with vulcastab LW). Some reactions were carried out in the presence of a trace of ammonia without adding any stabilisers such as vulcastab LW.

It was necessary to determine the optimum conditions for the reaction before carrying out any detailed study of grafting with different vinyl antioxidants. The parameters involved are:

(a) the best initiator system
(b) the temperature at which the initiator system is most efficient
(c) the duration of the reaction
(d) the effect of ammonia on the grafting reaction
(e) the effect of oxygen on the rate of grafting
(f) effect of latex stabilisers
(g) duration of the swelling time

4.2.1 Determination of the best initiator system

Grafting reactions were carried out in a flask as shown in figure 3.

Apparatus used for grafting reaction

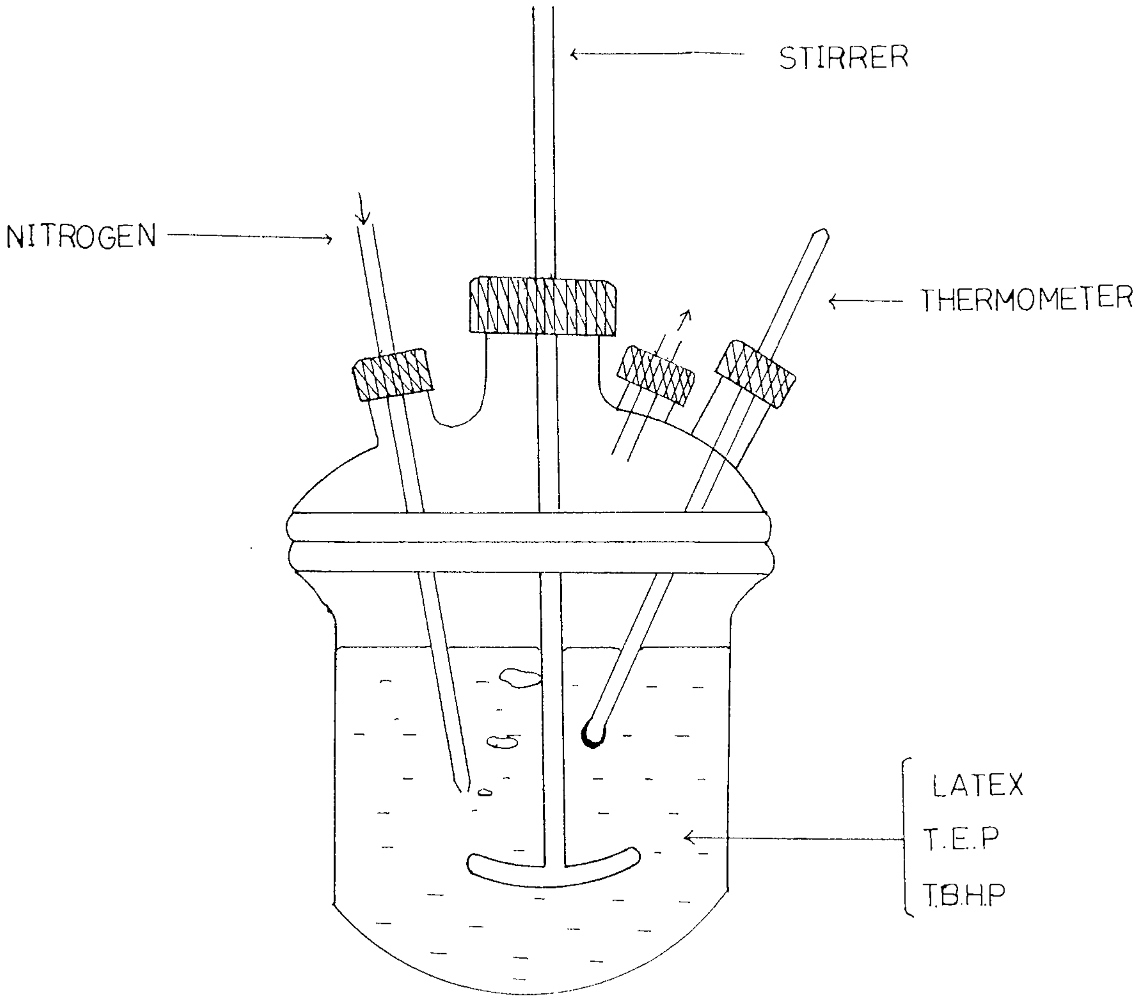


FIGURE 3

To maintain the temperature of the reaction system the flask was immersed in a thermostatically controlled water bath. Throughout the reaction, nitrogen was bubbled through the reaction mixture. In all the experiments a calculated amount of the antioxidant was added to the latex in the form of a dispersion.

166 ml of distilled water was added to 166 ml of centrifuged latex containing 60% rubber (w/w) in a flask. This was immersed in the thermostatically controlled water bath at a pre set temperature. The latex was partially deammoniated by passing white spot nitrogen through a glass tube going to the bottom of the flask for 2 hours while it was stirred. As the ammonia content decreased in the latex PH was decreased and DBBA dispersion containing 2 gms was added into the latex at PH 8-10. Stirring was continued until a uniform dispersion was obtained. After 5 minutes the initiator system was added into the latex. For this purpose 4 initiators were selected based on earlier work.

The concentration of each initiator added for each reaction for the above mentioned experiment were as follows:

	Type of initiator	Amount added%
a	No initiator	
b	Potassium per sulphate	1.5 g
c	Azo-iso-butyronitrile (1% solution in chlorobenzene)	0.5 g
d	Benzoyl peroxide	0 5 g
e	Tertiary butyl hydroperoxide/Tetra ethylene pentamine (10% solution in water)	1.5/4 ml

After the first 15 minutes the nitrogen flow was reduced to a few bubbles per second. The reaction was allowed to take place for a further 20 hours and the latex was poured into a beaker. The latex was coagulated by the dropwise addition of 1% formic acid. The coagulum was washed with oxygen free water and sheeted into a thin pale crepe of a thickness of 3-4 mm and was dried over a silica gel under a vacuum at 25°C. Once it was completely dry, the crepe was extracted continuously with the azeotrope in a soxhlet apparatus under nitrogen as described in Chapter 3.4. The vulcanisates were prepared exactly under the same conditions as described in Chapter 3.

Two sets of reactions were carried out with all the initiator systems at two different temperatures, 30°C and 50°C. The oxygen absorption results of these samples are illustrated in the figures 4 and 5.

4.2.2 Effect of stabilisers on grafting reaction

A set of grafting reactions was carried out under the same conditions as described above, with all the initiators and with the same concentration (2 g) of DBBA but using completely deammoniated latex stabilised with vulcastab LW.

The grafted rubber was extracted with the azeotrope and vulcanisates were prepared. Figures 6 and 7 illustrate the rate of oxygen absorption of these samples.

The rate of oxygen absorption of vulcanisates at 70°C

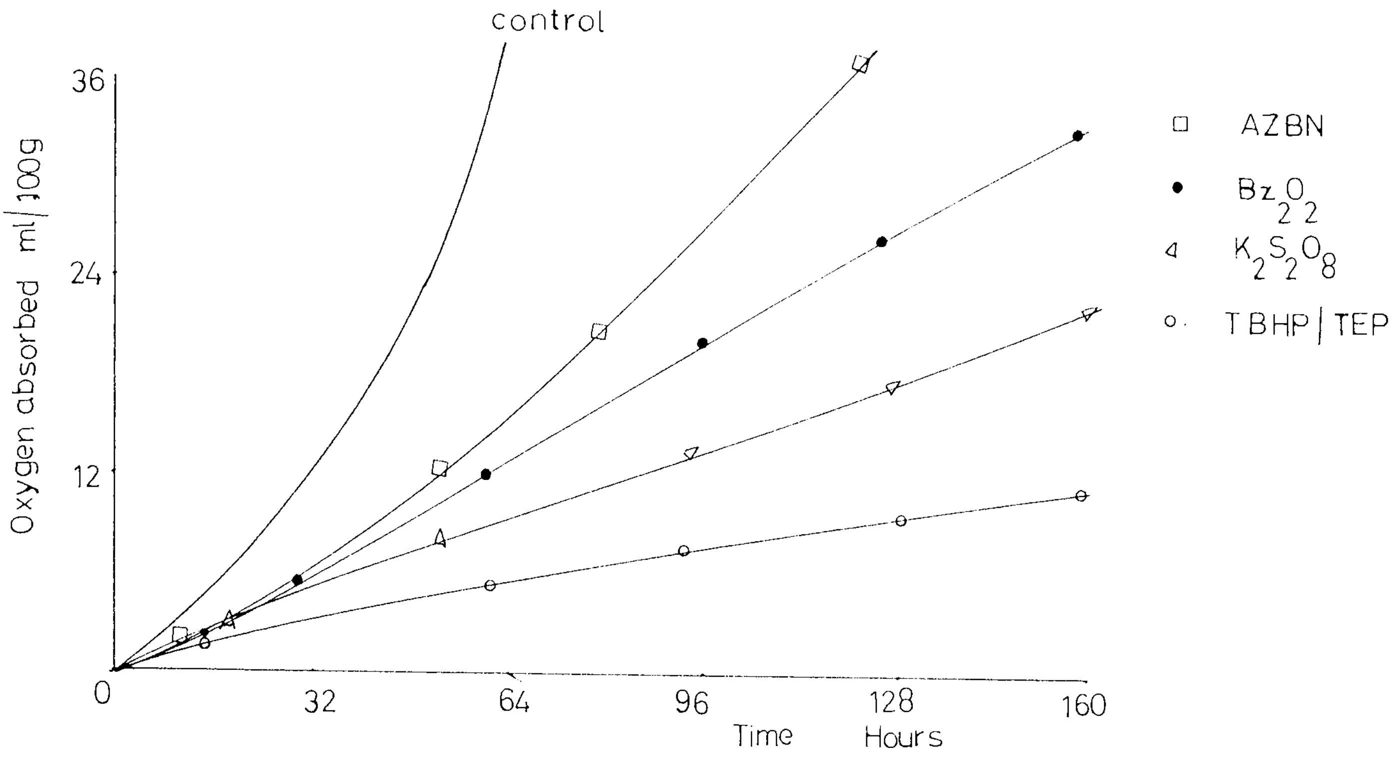


FIGURE 4

2g% of DBBA grafted with different initiators at 50°C using latex with 0.1% NH_3

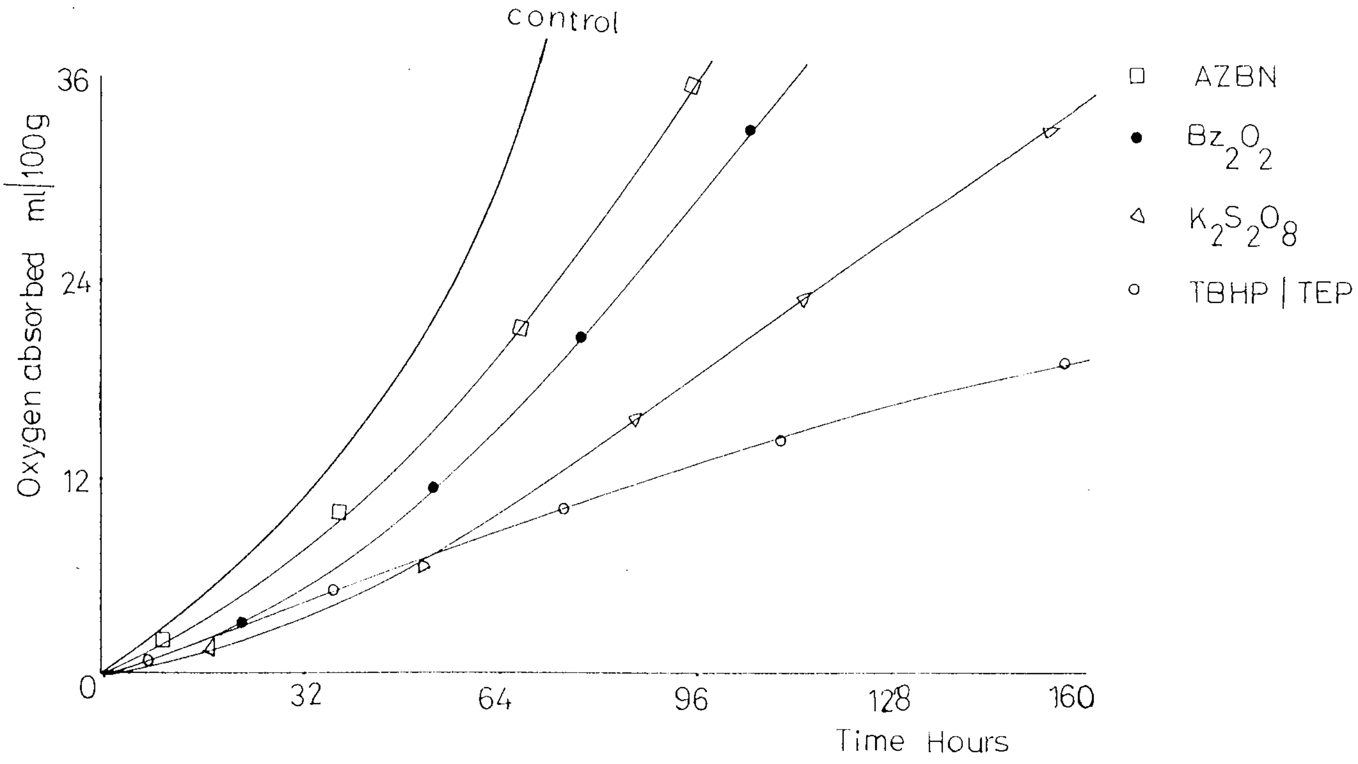


FIGURE 5

2g% of DBBA grafted with different initiators at 30°C using latex with 0.1% NH_3

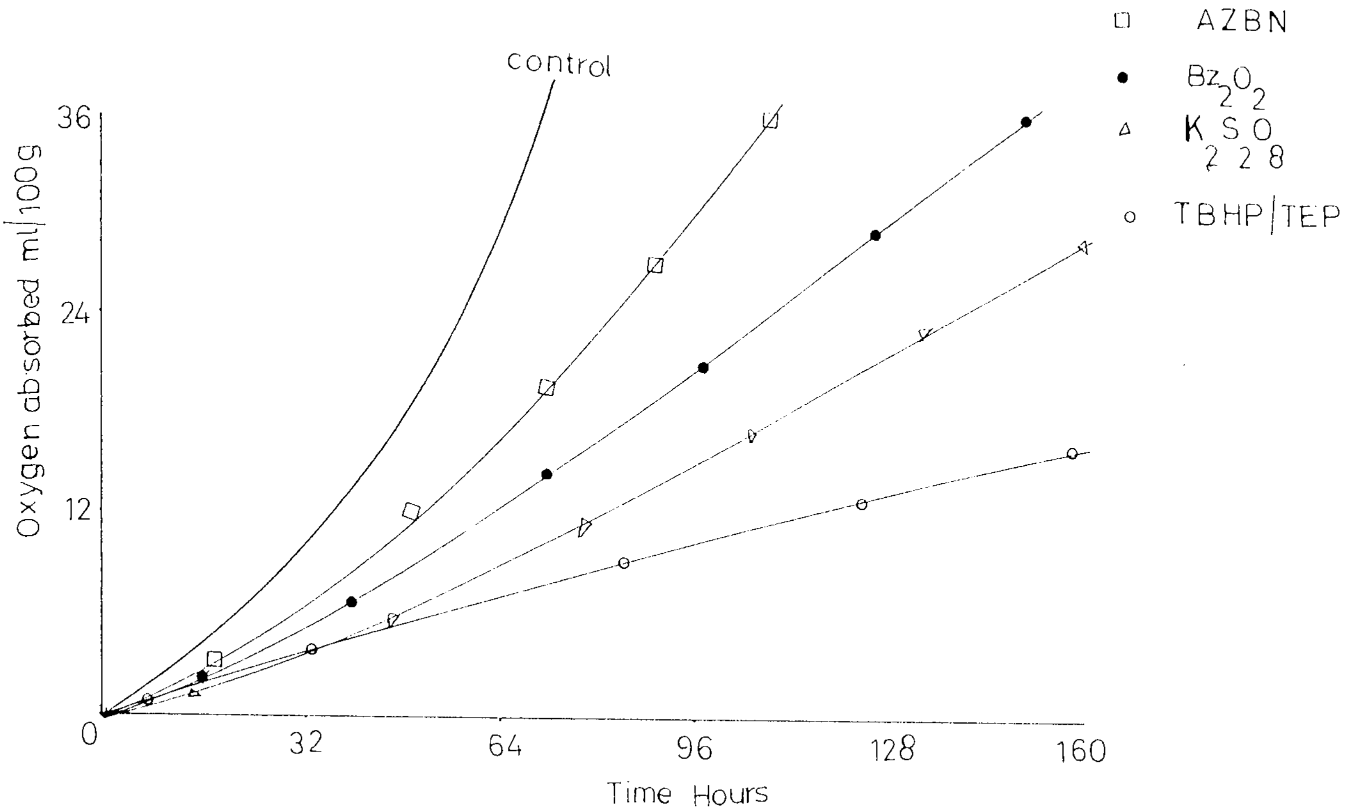


FIGURE 6

2g% of DBBA grafted to stabilised latex with vulcastab LW at 50°C

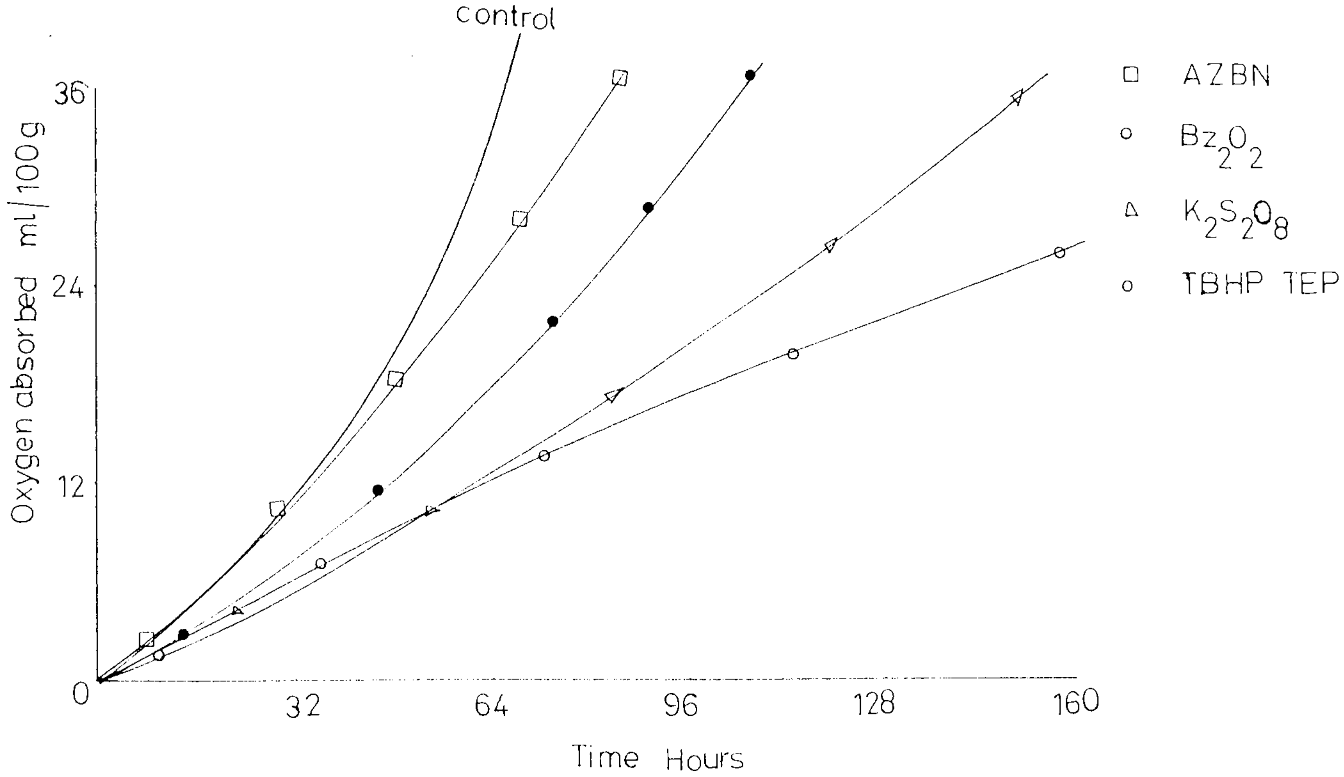


FIGURE 7

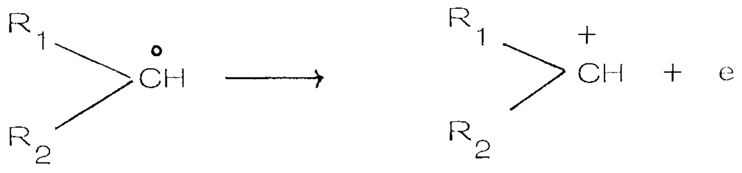
2g% of DBBA grafted to stabilised latex with vulcastab LW at 30°C

4.2.3 Effect of high concentration of ammonia

For this set of experiments the latex was used without deammoniation at all, but by diluting the centrifuged latex to obtain a dry rubber concentration of 30% w/w. The grafting reaction was carried out in exactly the same way as described previously using the initiator systems at 30°C and 50°C. The vulcanisates were prepared after extraction with the azeotrope. The rate of oxygen absorption is illustrated in figures 8 and 9.

4.2.4 Results and discussion

Although the hindered phenols are efficient antioxidants, the above results show that these phenols do not inhibit the graft polymerisation. The reason for this is probably associated with the differing reactivities of alkyl and alkylperoxy radicals towards phenols. In the presence of oxygen the alkylperoxy radical is the species present in the highest concentration in an autoxidising system. But in the absence of oxygen and in the presence of a free radical generator, alkyl radicals predominate. Alkyl radicals differ from alkylperoxy radicals in that they tend to give up rather than gain an electron.



$$ROO^{\circ} + e \longrightarrow ROO^{-}$$

Because of this reducing character of alkyl radicals it is unreactive in the hydrogen abstracting reaction. It is thus

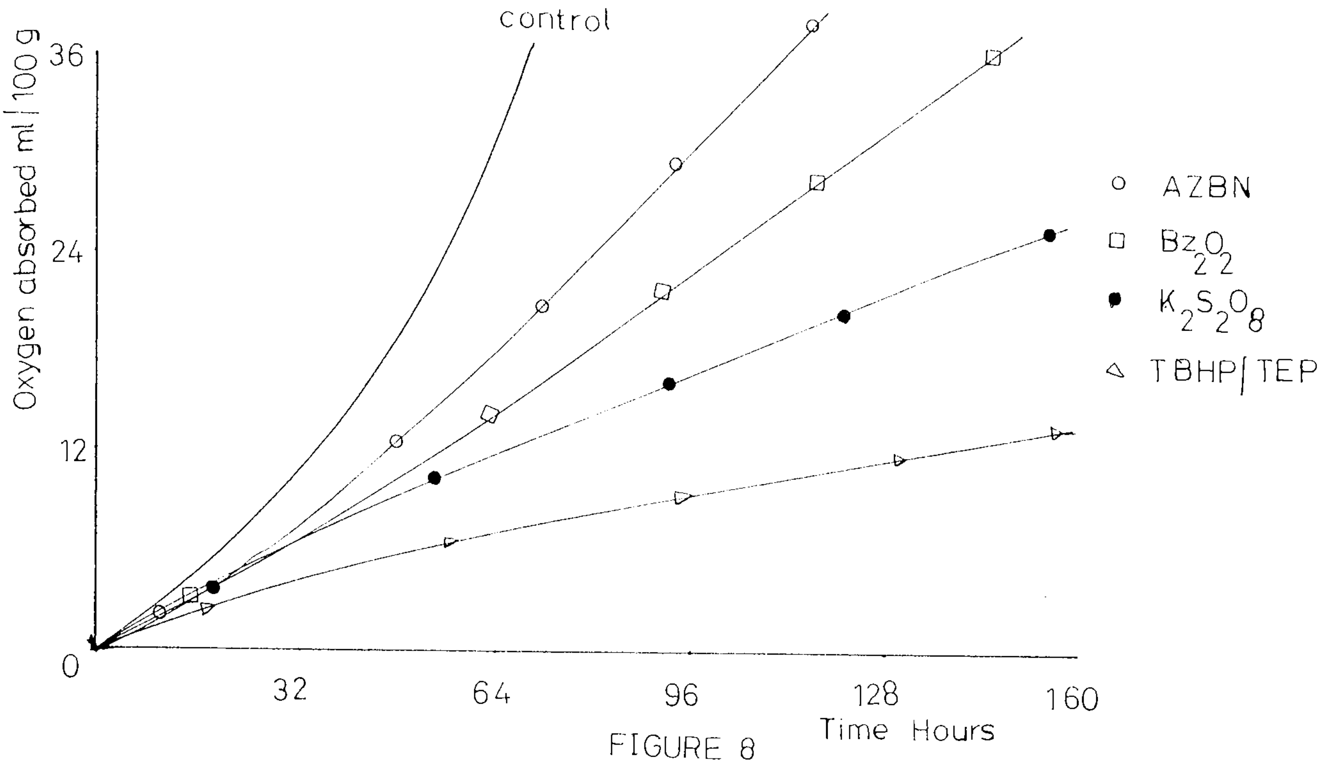


FIGURE 8

2g% DBBA grafted to 0.35% ammoniated latex at 50°C

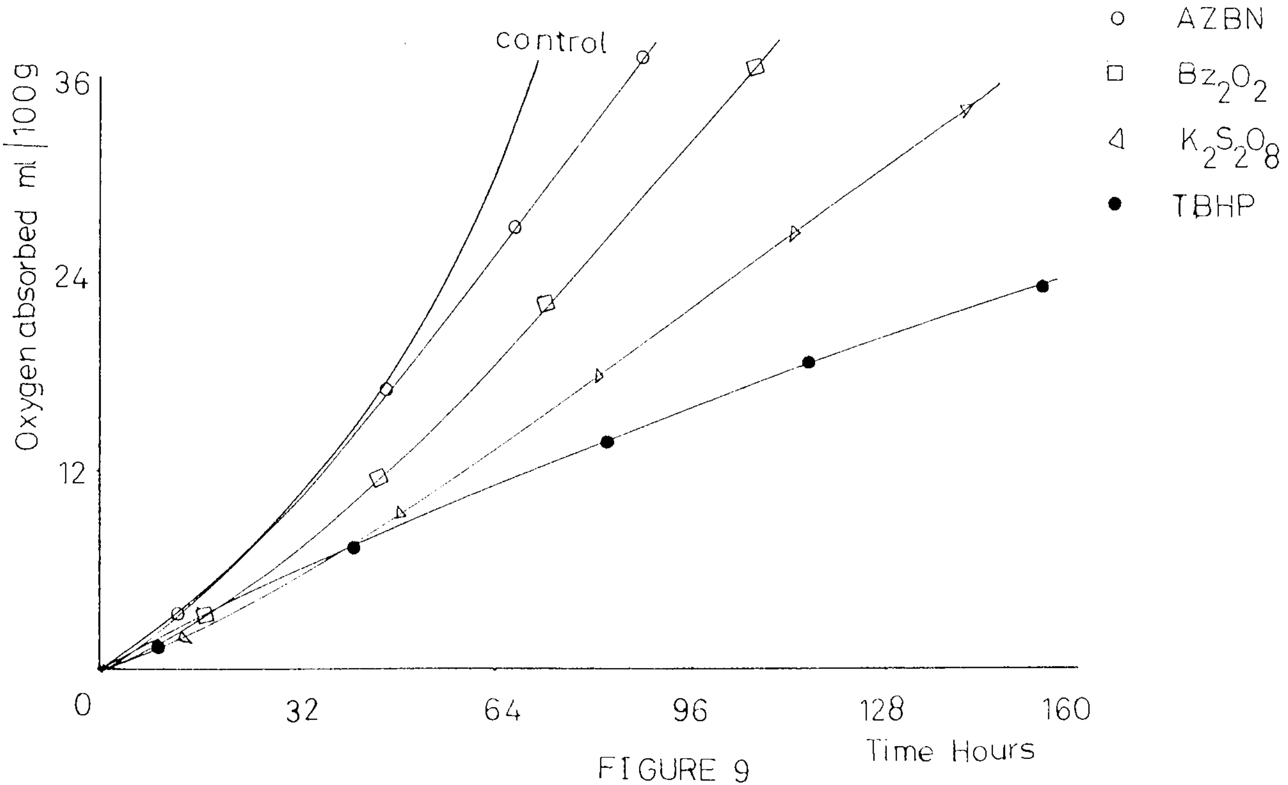


FIGURE 9

2g% DBBA grafted to 0.35% ammoniated latex at 30°C possible to polymerise vinyl monomers quite effectively in the presence of powerful phenolic antioxidants so long as oxygen is excluded.

The second conclusion emerging from the above series of experiments is that activated tertiary butyl hydroperoxide is the best initiator for grafting vinyl antioxidants with natural rubber latex. The other obvious conclusion is whatever the initiator, grafting is less effective in the presence of ammonia and in the presence of added emulsifiers or stabilisers.

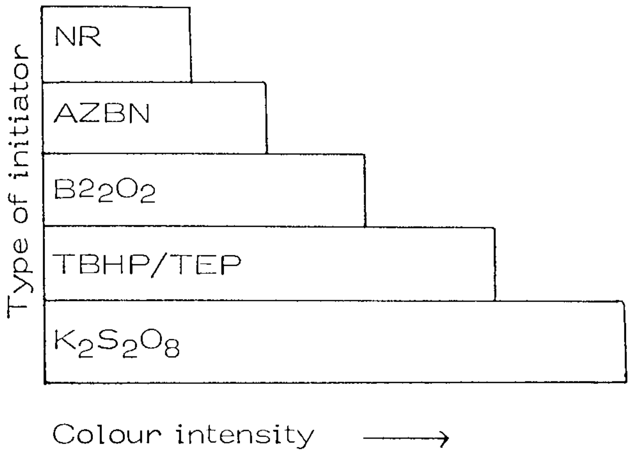
Jones and co workers(59) have successfully grafted acrylonitrile styrene and butadiene to natural rubber latex using potassium per sulphate and have obtained a light coloured tacky material. Also, according to their results, the efficiency of potassium per sulphate is very dependent on the ammonia concentration in the latex unlike TBHP. Several workers have shown that polyethylene polyamine activated hydroperoxides are relatively insensitive to oxygen and ammonia. This is true for DBBA and latex systems as well.

Type of initiator	0.35% ammoniated latex	Fully deammoniated, with vulcastob LW	Partially deammoniated 0.1% NH_3
TBHP/TEP	96 hrs	80 hrs	130 hrs
$K_2S_2O_8$	48 hrs	62 hrs	64 hrs
BZ_2O_2	42 hrs	46 hrs	48 hrs
AZBN	38 hrs	39 hrs	41 hrs

Time taken to absorb 3% oxygen by the vulcanisates at 70°C.

2% DBBA grafted at 50°C

An important feature of the ultimate product (grafted rubber) was the colour. It was found that the colour depended on the type of initiator used and the ammonia concentration in the rubber latex.



The rubber obtained with potassium persulphate was intensely yellow in colour. Also, if the ammonia concentration of the latex was too high, the colour of the product was very intense. This colour was shown to be due to the formation of different types of quinones. The identification of these will be discussed in a later chapter.

Persulphate initiators appeared to be less sensitive to ammonia than benzoyl peroxide. This has been described in the patent literature(60). Japanese workers(61) have succeeded in showing that some vinyl monomers (including acrylonitrile, methyl methacrylate and styrene) could be co-polymerised after their addition to rubber latex although ammonia was again observed to have a retarding action.

Taking advantage of conclusions reached on the previous experiments, the latex was diluted and partially deammoniated prior to carrying out the reactions, to determine optimum conditions for grafting with the TBHP/TEP initiator system.

4.2.5 Determination of optimum temperature for the reaction

2.6 di-tert-butyl-4-hydroxy benzyl acrylate was selected as the antioxidant and tertiary butyl hydroperoxide (TBHP) - tetra ethylene pentamine (TEP) was selected as the initiator since the initiator efficiency is not much dependent on the concentration of ammonia present in the latex. The reaction was carried out by using 166 ml (100 g DRC) of partially deammoniated latex with 2g DBBA.

The reactions were carried out under exactly the same conditions as described on page 61. The selected temperatures for the reactions were 25, 30, 40, 50, 60 and 70 degrees centigrade. The water bath maintained at the required temperature (± 2°C). The reaction was allowed to take place for 24 hours and the coagulation was obtained by acidification of the treated latex. The vulcanisates were prepared from the extracted rubber and oxygen absorption studies were done at 70°C. Figures 10 and 11.

4.2.6 Determination of the optimum duration of the reaction

A set of reactions were carried out at 55°C for known lengths of time. Every 4 hours a sample of the reaction mixture was taken out, coagulated, dried, extracted and the vulcanisates were prepared. The oxygen absorption studies are illustrated in figure 12.

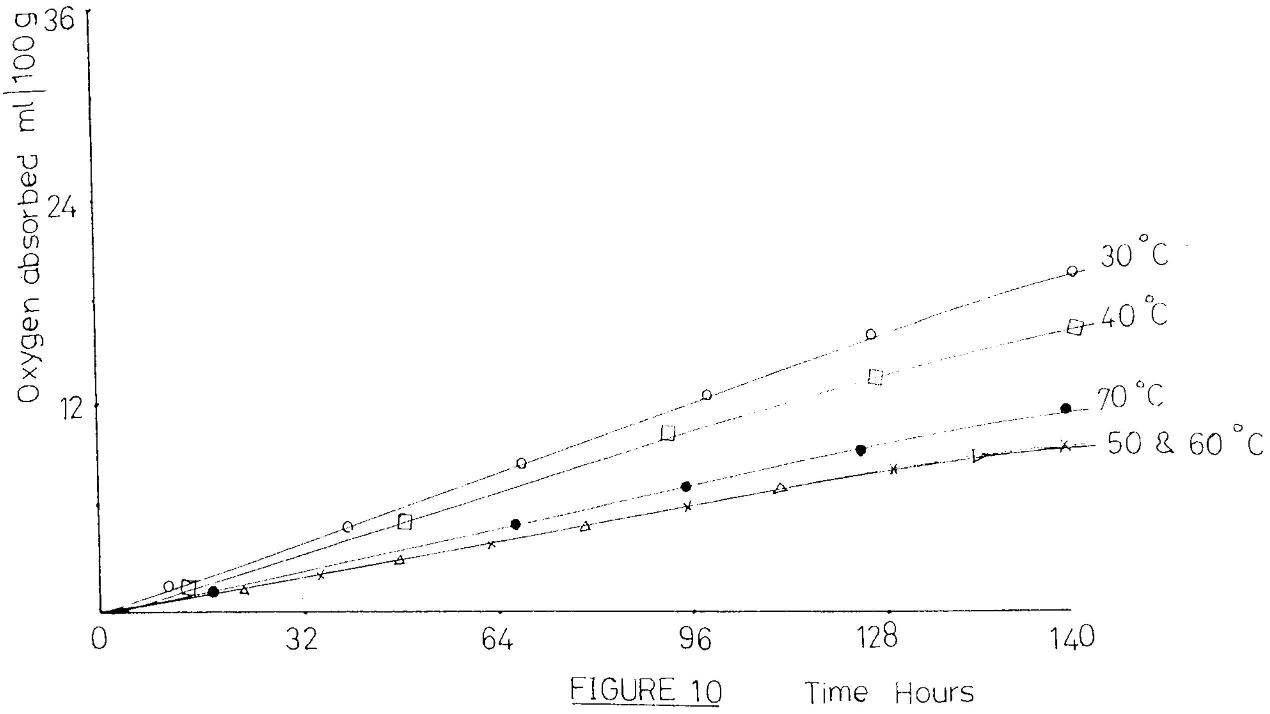


FIGURE 10

2g% DBBA grafted at different temperatures with TBHP/TEP

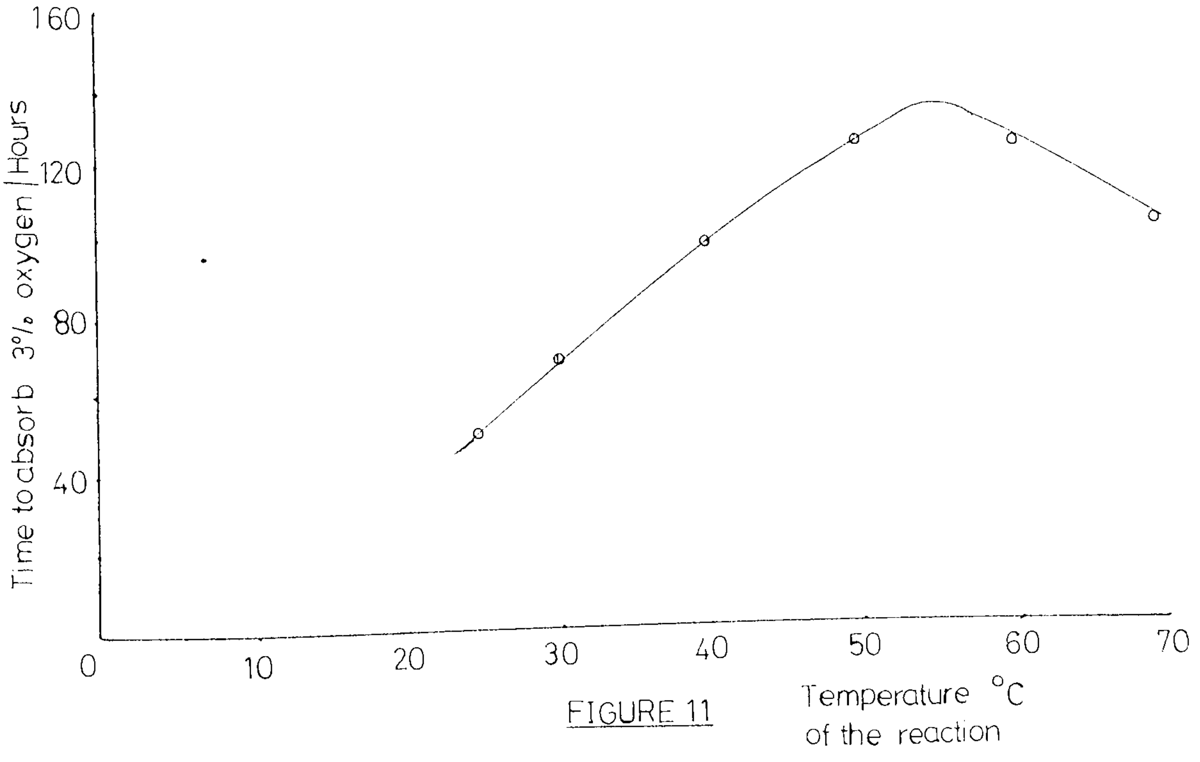
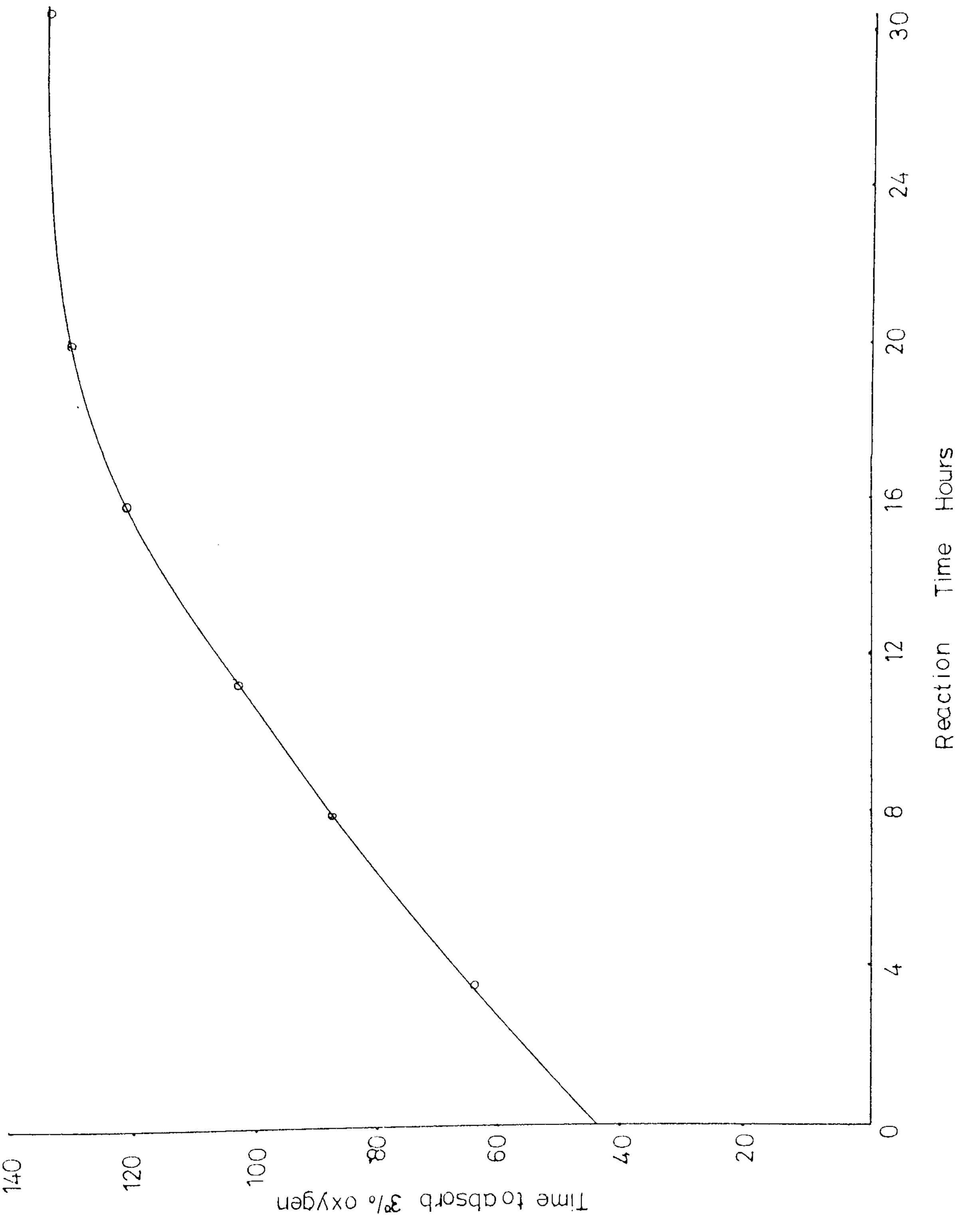


FIGURE 11

The effect of temperature on grafting reaction

FIGURE 12

The effect of the duration of the reaction on grafting



Three sets of experiments were carried out to determine whether to add the initiator to latex, or to the antioxidant dispersion or to a mixture of both to obtain maximum amount of grafting.

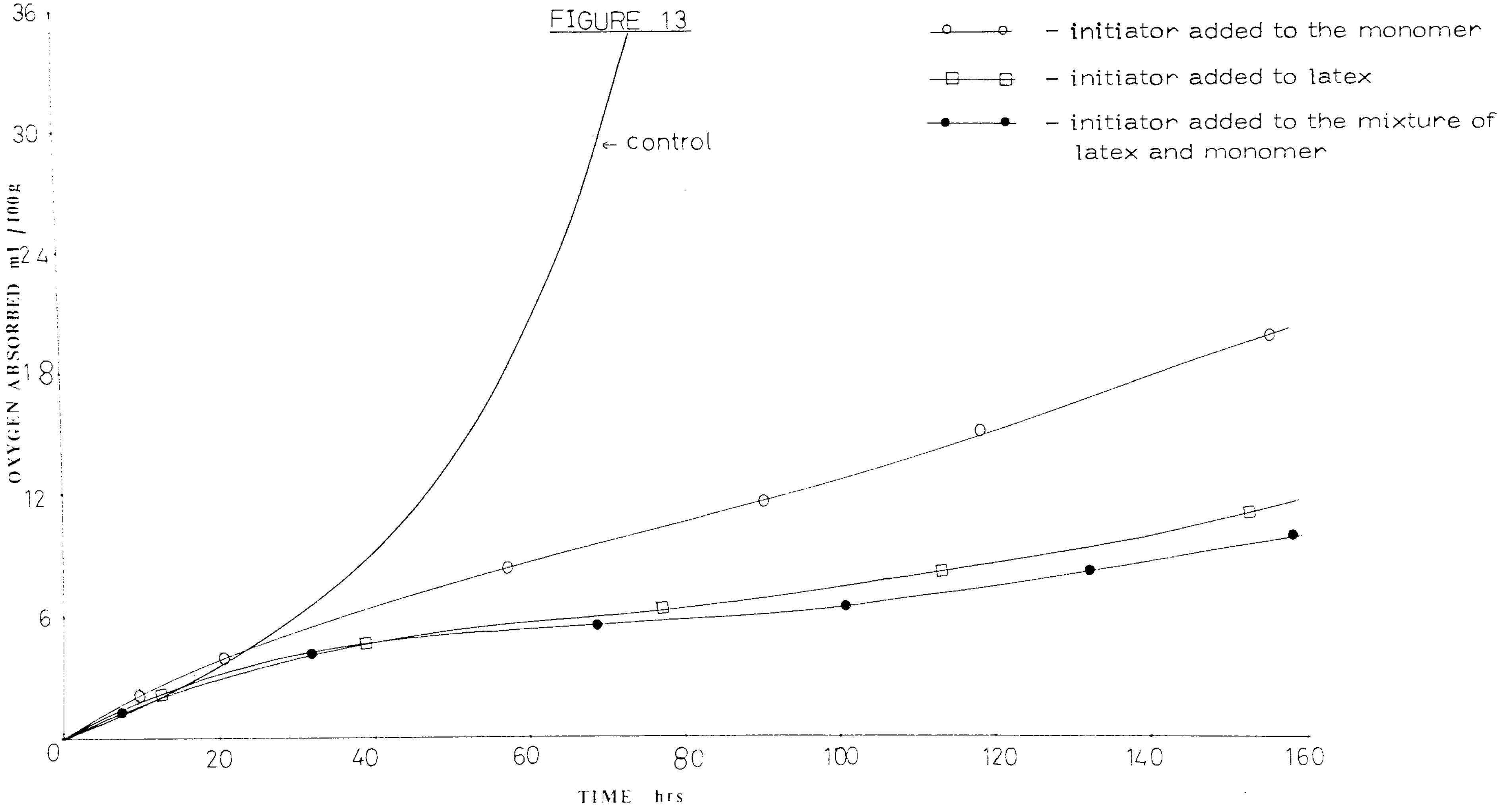
(a) Initiator system (1.5 ml TBHP and 4 ml of 10% solution of tetra ethylene pentamine in water) was added to 166 ml of (100 g of DRC) of partially deammoniated latex and diluted with another 166 ml of distilled water. Stirred thoroughly and allowed to stand for 15 minutes under nitrogen at 55°C. A dispersion containing 2 gms of DBBA was added to the latex after 15 minutes. The reaction was allowed to take place at 55°C under nitrogen at 55°C for 20 hours.

The grafted rubber was obtained by acidification and vulcanisates were prepared as previously described.

(b) The same amount of initiator (TBHP/TEP) was added to a dispersion containing 2 gms of DBBA at 55°C and allowed to stand. After 15 minutes, this was poured into a flask containing 166 ml (100 g DRC) at 55°C. Diluted with another 166 ml of distilled water and the reaction was allowed to take place at 55°C under nitrogen for 20 hours.

(c) The diluted latex containing 100 gms of rubber was mixed with a dispersion containing 6 gms of DBBA and allowed to stand at 55°C under nitrogen. After 15 minutes of swelling time the initiators were added and the reaction was allowed to take place under nitrogen at 55°C for 20 hours.

FIGURE 13



The rate of oxygen absorption of vulcanisates at 70°C

The results of the above experiment (figure 13) clearly indicate that the most successful grafting reaction takes place when the antioxidant is swelled into the rubber particles.

4.2.7 Effect of swelling time

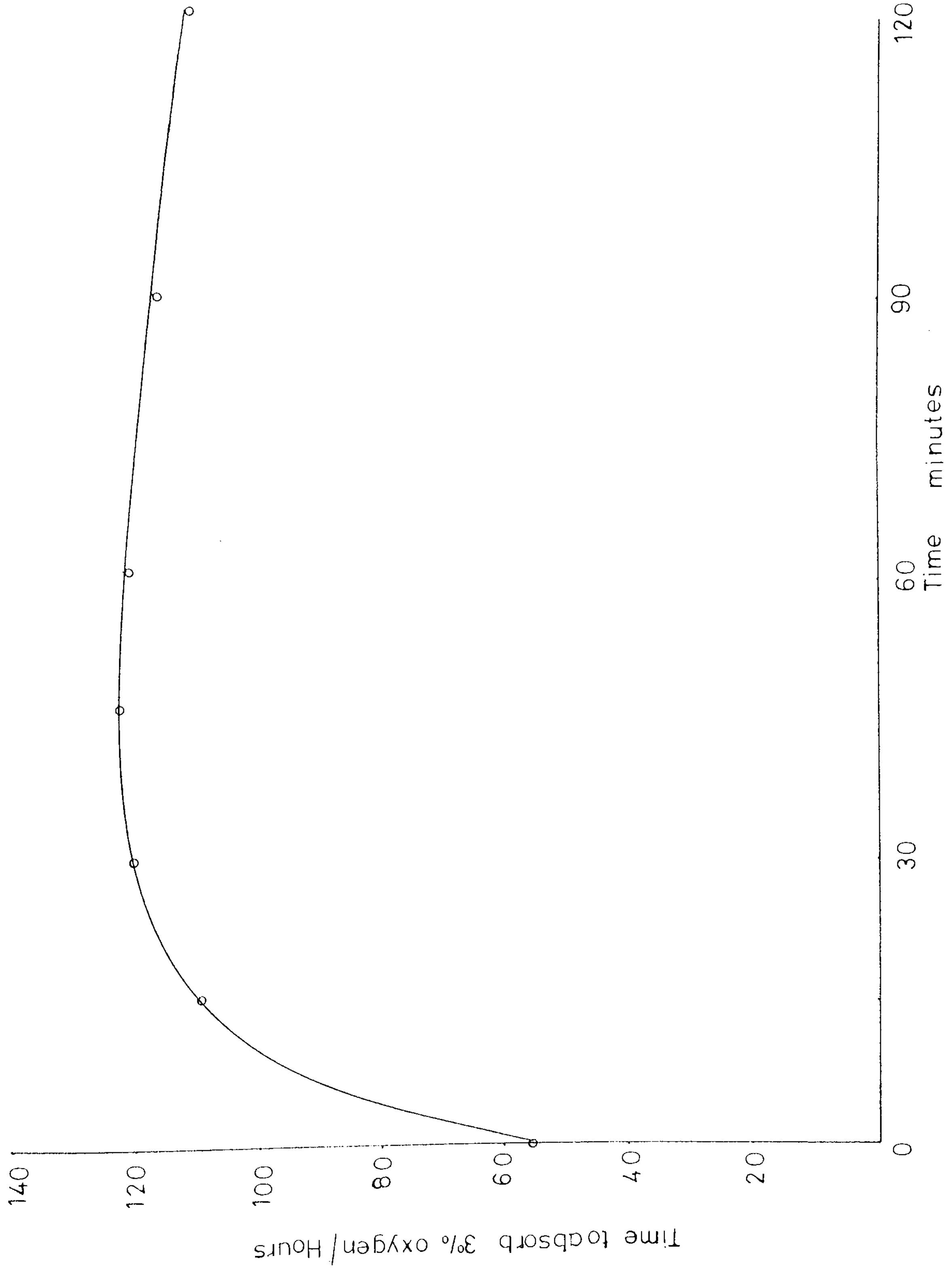
166 ml (100 g DRC) of partially deammoniated latex was diluted with an equal volume of distilled water and mixed with a dispersion of 2 g of DBBA. This was allowed to stand for a known length of time. The reaction was initiated by adding 1.5 ml TBHP and 4 ml of TEP. After the reaction the coagulation was obtained by acidification, dried, extracted and vulcanisates were prepared. The rate of oxygen absorption of these samples at 70°C are illustrated in figure 14.

4.3 Results and discussion

It was found that the amine activated TBHP shows its maximum initiator capacity around 55°C for this particular system. Usually other initiators such as azo-bis-iso-butyronitrile (AZBN), benzoyl peroxide (BZ_2O_2) are active at higher temperatures. One of the major drawbacks of the other initiator systems in working with latex is the high temperatures at which these show their optimum activity. With natural rubber latex it was difficult to work above 70°C as the water phase in the latex tends to evaporate. Another side effect, which can be accelerated by high temperatures, is the oxidation of added antioxidants in the latex and the rubber network by the traces of oxygen present in nitrogen. The other disadvantage

FIGURE 14

The effect of swelling time on grafting



of working at high temperatures is the hydrolysis of DBBA. The ammonium hydroperoxide in the rubber latex hydrolyses the acrylic esters into the corresponding alcohol which can be readily oxidised to the intensely yellow coloured quinone. This will be discussed in Chapter 7.

The optimum grafting time was about 18 hours. The conclusion which emerges from the above series of experiments is that the initiation should take place within the swelled rubber particle, therefore it is essential that the rubber particles should absorb as much of the monomer as possible before the polymerisation is started. This condition can be satisfied and no great difficulty is experienced in practice with hydrophobic monomers. The important factors are to use very good dispersions of monomers and diffuse into the rubber particles before initiating polymerisation. According to the above experiments carried out with DBBA and rubber latex it is necessary to allow this mixture to stand for about 30 minutes prior to the addition of initiators.

Figures 10 and 11 illustrate the increase of grafting of DBBA as the temperature is increased. This is due to the increase of free radical formation and transfer reactions, taking place in the rubber and the monomer, as the temperature is increased. The The decrease of the extent of grafting above 60°C may be due to the fact that the rate of hydrolysis of acrylate is more favourable at higher temperatures.

As far as the pH of the reaction medium is concerned, it was found that it was impossible to carry out a reaction with latex at pH below 7 as the rubber is coagulated. At high pH the hydrolysis of the acrylate was faster. Because of this, the colour of the ultimate rubber grafted at high pH was intense yellow.

CHAPTER 5

Estimation of the concentration of bound antioxidants

Infra red spectroscopy was employed to determine the amount of antioxidant grafted into the rubber. This has been previously used by several workers(32) to estimate the carboxy and hydroxyl groups in solutions and in films. Since both hydroxyl and carboxyl groups are present in the antioxidant it was thought that it may be possible to see infra red absorption peaks for these functional groups, for the solutions of grafted rubbers. For this purpose the Perkin-Elmer 257 spectrophotometer was used.

A 3% solution of grafted extracted rubber in spectrograde carbon tetrachloride was used for the measurement of carboxyl and hydroxyl absorbance in 0.5 mm sodium chloride cells with carbon tetrachloride in 0.45 mm cells, to compensate for solvent absorption. The hydroxyl and the carboxyl peaks of the grafted monomer should have been appeared in 3640 cm^{-1} and 1740 cm^{-1} respectively. It was not possible to see any absorption peaks by this method. This is because the concentration was so small.

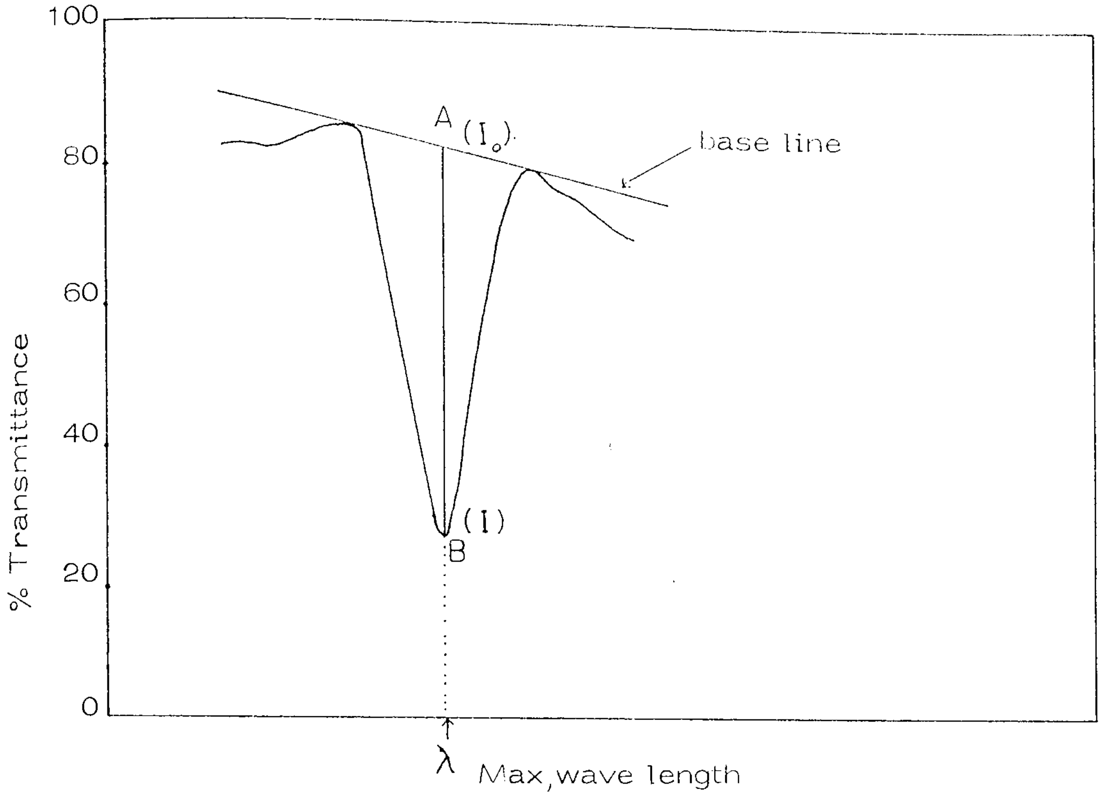
To overcome this problem, infra red spectra of the vulcanisates of 0.008 were obtained. The vulcanisate was solvent extracted with the azeotrope for 48 hours in order to remove all the non rubber constituents from the rubber network. After extraction this was dried in a vacuum dessicator and spectra measured. For quantitative purposes, all spectra of the extracted vulcanisate samples were scanned on the transmittance paper rather than on a logarithamic scale. The use of the former minimised any intensity loss due to reflection at outer and inner sample surfaces(63). Relative amounts of hydroxyl and carboxyl groups in rubber were determined by the measurement of the 'functional group ratio' of the different samples. This is a ratio of functional group transmittance to the transmittance of an invariant group chosen as the standard. Reasonably accurate values of functional group ratios could be obtained only when the (reference) standard peak is of medium intensity. The peak at 2720 cm^{-1} characteristic of rubber itself was used as a reference peak to minimise errors due to variation in sample thickness.

$$\text{Functional group ratio} = \frac{\text{Transmittance of the functional group}}{\text{Transmittance of the reference peak}}$$

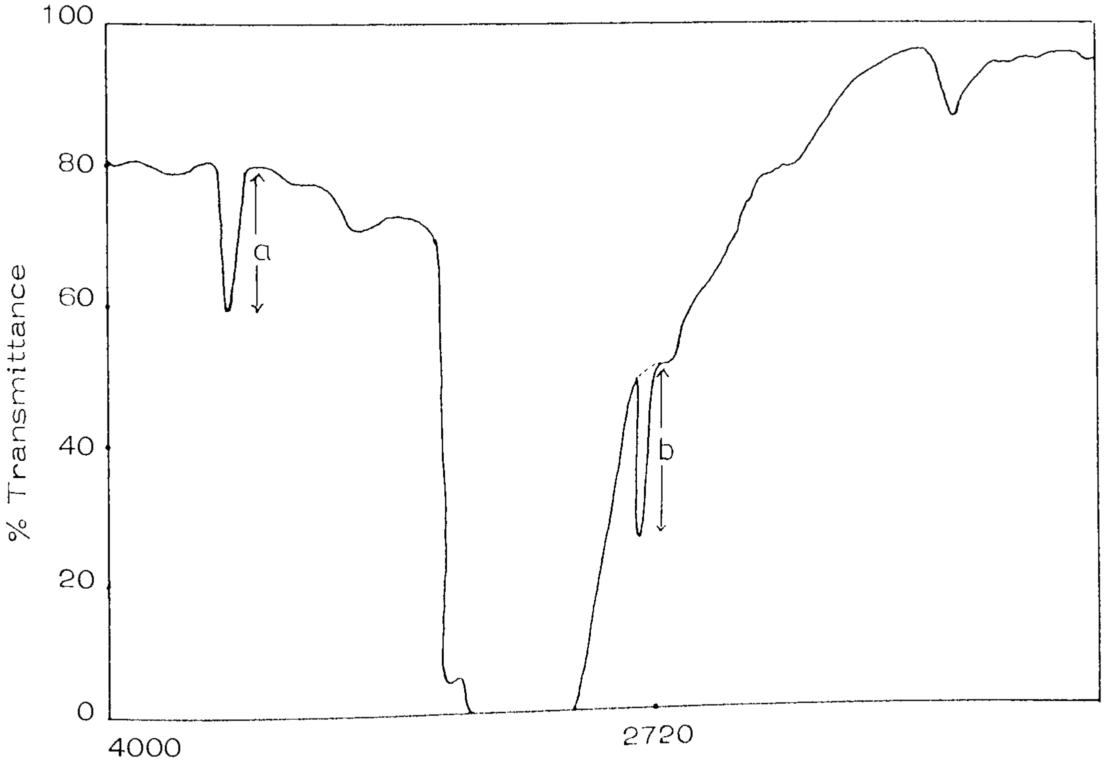
$$= \frac{T_s}{T_{ref}}$$

The transmittance due to functional group and the transmittance due to invariant group (reference peak) at their respective wave length was calculated using the base line technique. This was done as shown in figure 15 by drawing a straight line (base line) tangential to the adjacent transmittance minima then erecting a perpendicular through the analytical wave length until it intersected the base line.

FIGURE 15



100
80
60
40
20
0
% Transmittance
A (I_0)
base line
(I)
B
λ
Max, wave length



100
80
60
40
20
0
% Transmittance
a
b
4000
2720

For example, at A the concentration of hydroxyl group to be determined is zero and at B there appears an absorption peak whose height serves to calculate the concentration.

Therefore the hydroxyl ratio $= \frac{T_s}{T_{ref}} = \frac{a}{b}$

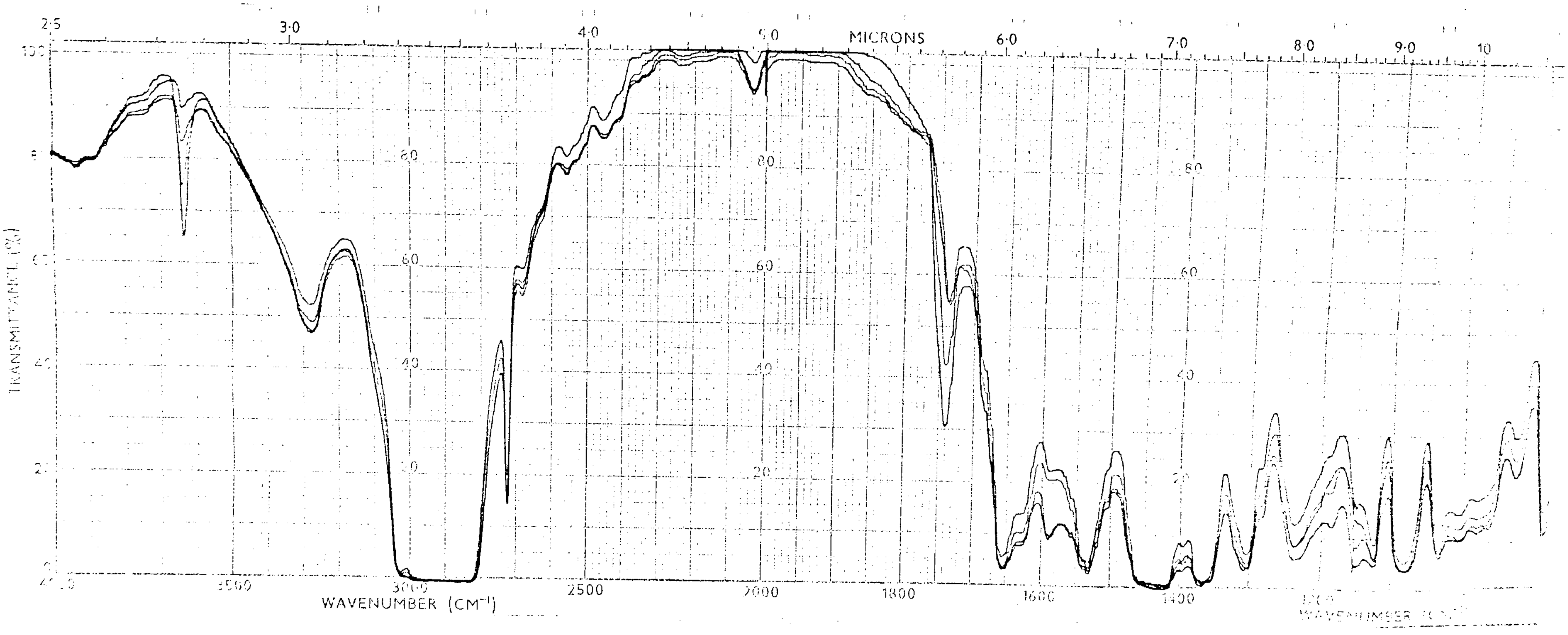
To determine the exact amount of concentration of chemically bonded antioxidant to rubber it was necessary to plot a callibrated curve for DBBA in rubber. This was performed as follows.

Deammoniated rubber latex was coagulated by adding 1% formic acid, dried and extracted with the azeotrope in a soxhlet apparatus for 48 hours under nitrogen to get rid of all the naturally occurring non rubber constituents. This was taken out and dried in a vacuum dessicator until it was completely free from the solvent. 100 gms of this extracted rubber was mixed with a known quantity of 2.6-di-tert-bityl-4-hydroxy benzyl acrylate and with other additives in a water cooled two roll mill. The vulcanisation was carried out at 140°C for 30 minutes.

Vulcanised samples were prepared with 0.5%, 1%, 2%, 3% of DBPA and DBBA. The infra red spectrum of these samples were obtained (figures 16 and 17) and the hydroxyl and carboxyl ratios were calculated. Curves were plotted functional group ratio verses concentration of DBBA in rubber, figures 18 and 19.

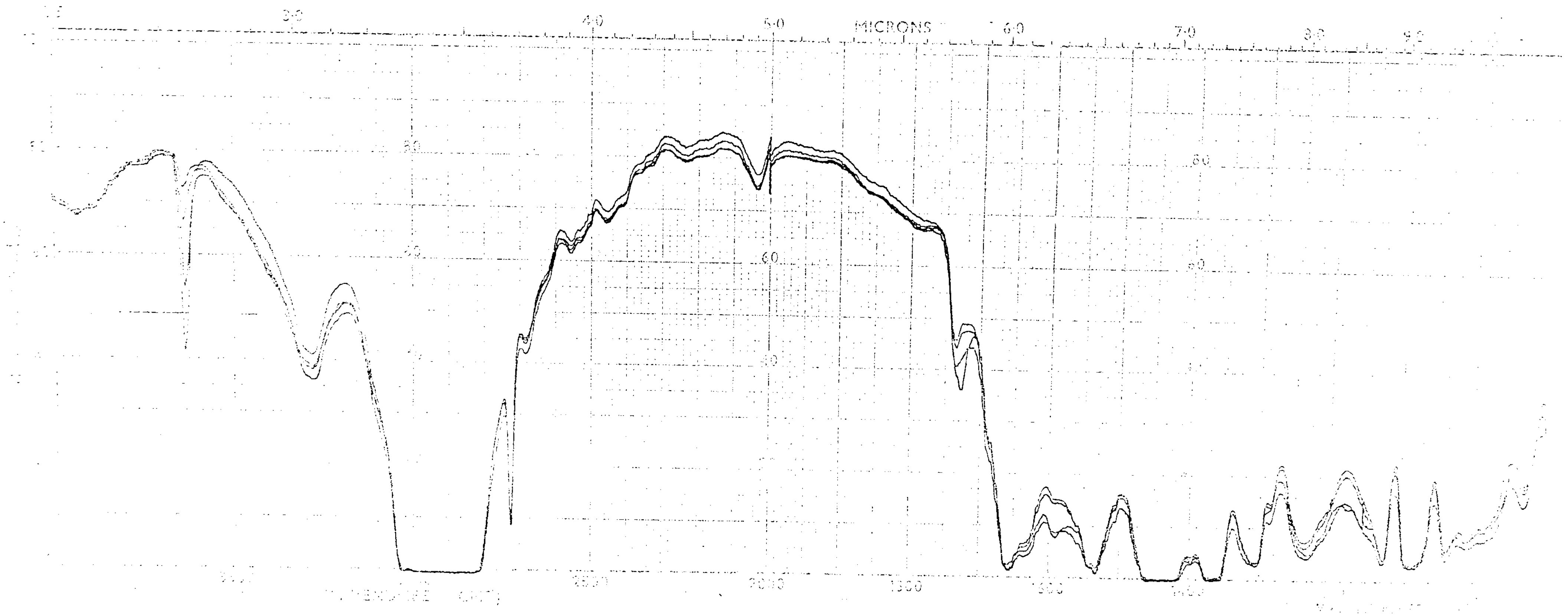
The callibration curve with the hydroxyl ratio gave a more reasonable and accurate estimation of the antioxidant present in the

Figure 16



Infra red spectra of vulcanisates containing 0.5, 1, 2 and 3% DBPA

Figure 17



Infra-red spectra of vulcanisates containing 0.5, 1, 2 and 3 g% DBPA

FIGURE 18

Infra-red calibration curve for DBPA in natural rubber

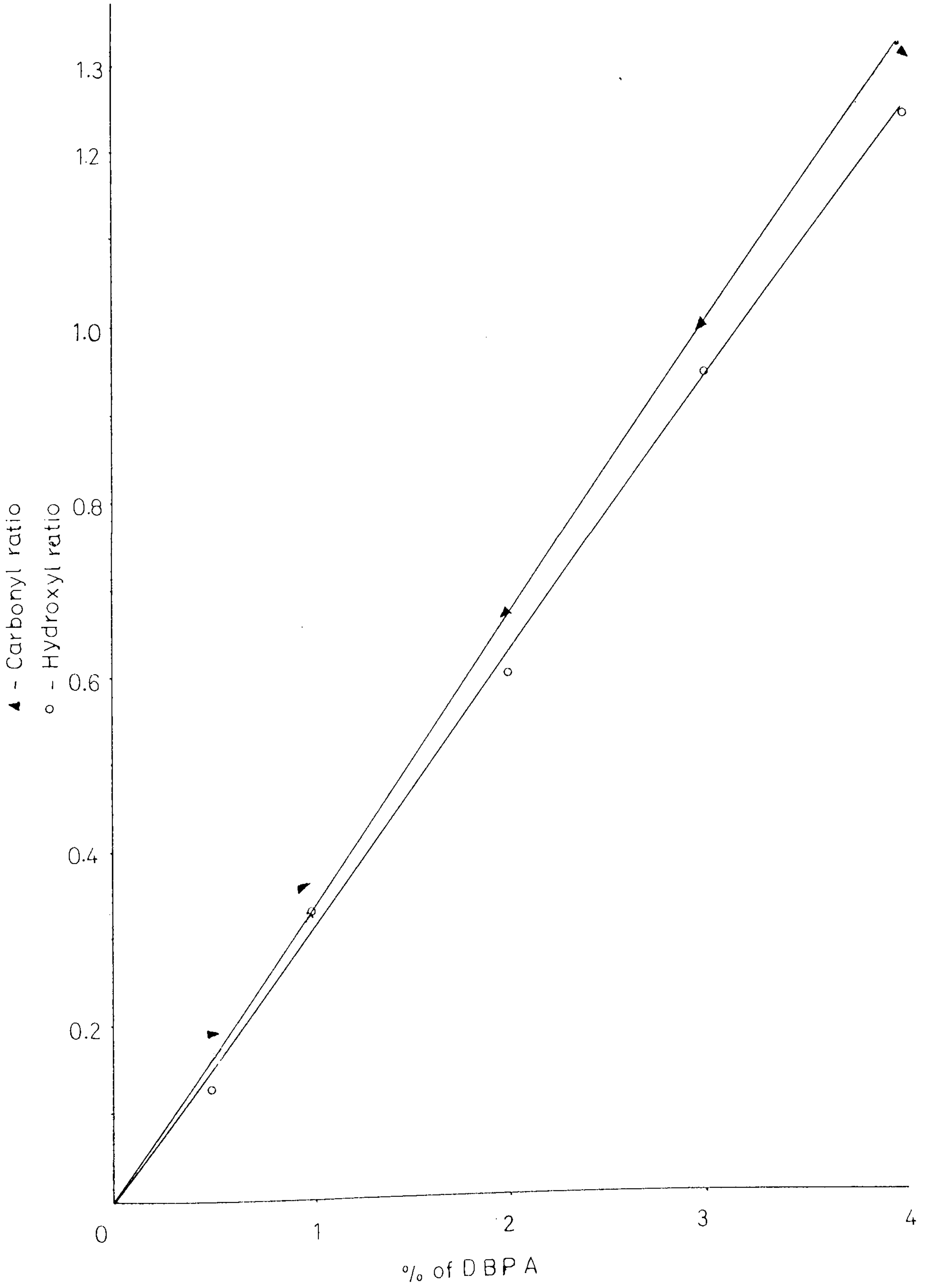
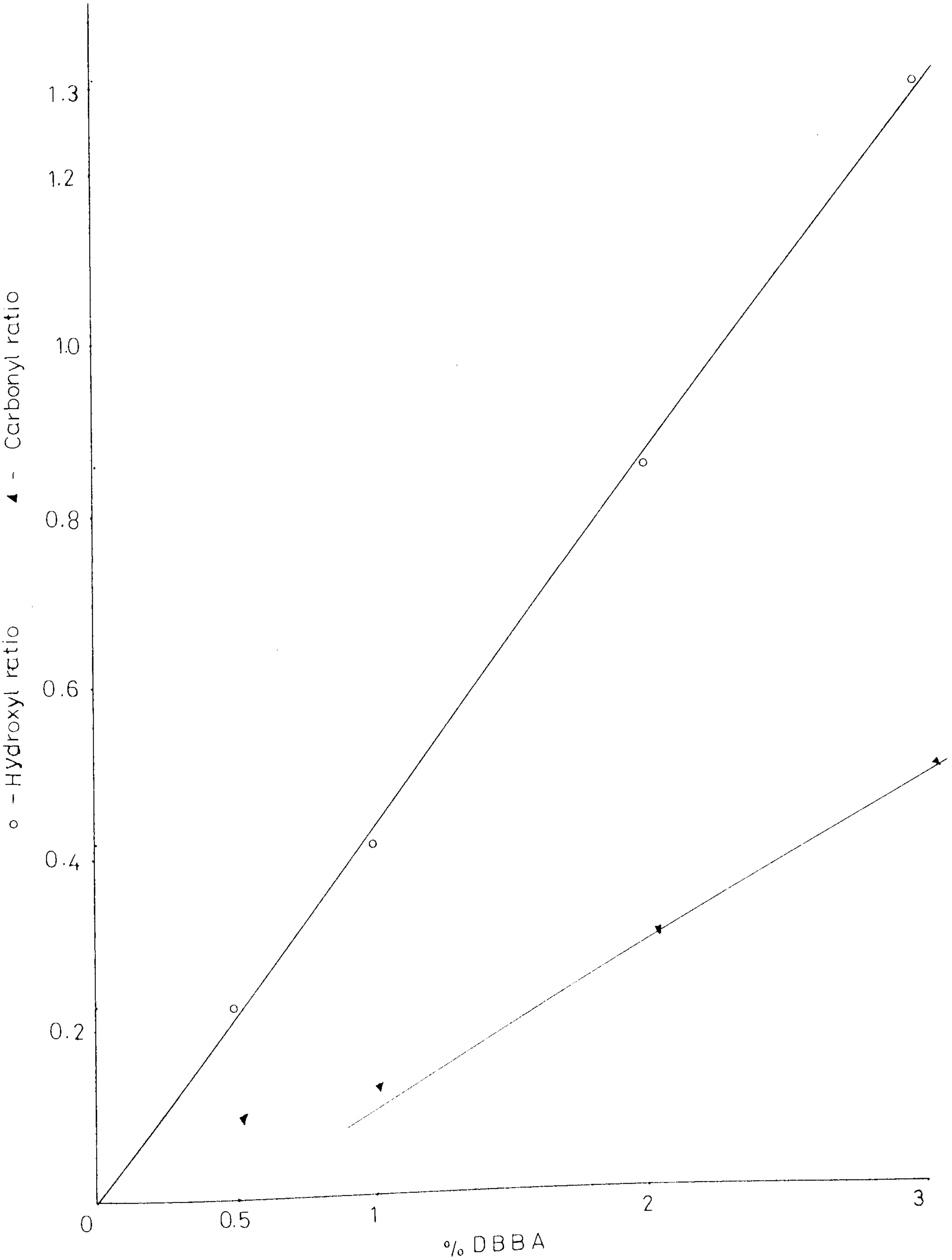


FIGURE 19

Infra-red calibration curve for DBBA in natural rubber



rubber than with that of the carboxyl ratio. This is because the carboxyl absorbance depends on the extent to which the rubber has oxidised during compounding.

The hydroxyl ratio calibration curve was used to estimate bound antioxidant concentration after grafting, milling and vulcanisation processes.

% of added DBBA	Hydroxyl ratio	Carbonyl ratio
0.5	0.23	0.14
1	0.42	0.15
2	0.86	0.27
3	1.31	0.48

% of added DBPA	Hydroxyl ratio	Carbonyl ratio
0.5	0.13	0.19
1	0.33	0.37
2	0.6	0.66
3	0.95	1.1
4	1.25	1.35

Results and Discussion

The remarkable feature of figures 18 and 19 is the difference between the carbonyl ratio curves. In the case of DBPA the change of hydroxyl ratio is more or less proportional to the change of carbonyl ratio. This is true only after a certain concentration of antioxidant (about 1%), but in DBBA samples it is not.

To study the variation in hydroxyl ratio with respect to the carbonyl ratio a graph of $\frac{\text{OH ratio}}{\text{CO ratio}}$ verses the concentration of the antioxidant was plotted. If the structure of the antioxidant molecule does not change during the process of milling and vulcanisation, a straight line graph parallel to the horizontal axis should be obtained. The plot of $\frac{\text{OH ratio}}{\text{CO ratio}}$ verses the concentration of DBPA (Figure 18a) shows a straight line with a very small negative gradient, which would mean that there has not been much structural change of DBPA molecule during the processing operation.

In the case of DBBA (Figure 19a) the concentration of carbonyl in the vulcanised sample does not increase with respect to the hydroxyl concentration. This indicates a change in structure of the DBBA molecule during the process of milling and vulcanisation.

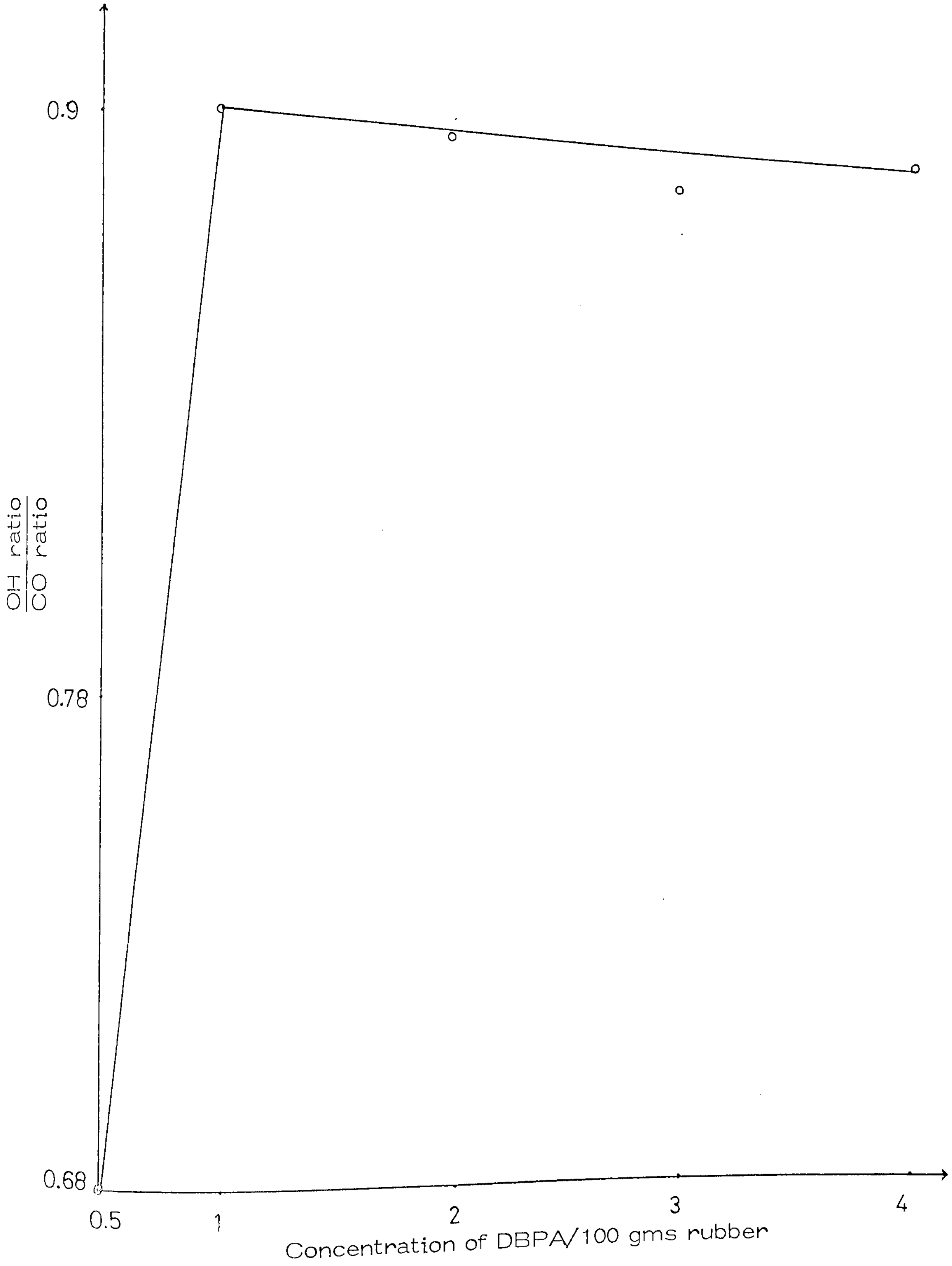
A possible change that may take place in DBBA is the oxidation of the added monomer, to quinones at the temperatures used. As the concentration of DBBA increases the concentration of carbonyl groups in the sample increases more than the hydroxyl. As a result $\frac{\text{OH ratio}}{\text{CO ratio}}$ decreases with the concentration of DBBA added. Initial low values of $\frac{\text{OH ratio}}{\text{CO ratio}}$ at lower concentrations of DBBA and DBPA were due to the presence of carbonyl groups formed by the oxidation of rubber and due to the decrease of OH groups by reacting with the free radicals formed in the rubber.

To find out the relationship between the hydroxyl and carbonyl groups in the grafted, extracted, vulcanised rubber, a graph of $\frac{\text{OH ratio}}{\text{CO ratio}}$ verses the actual concentration of bound antioxidants was plotted (Figure 19b).

According to this graph the rate of increase of concentration of hydroxyl groups in the grafted rubber is greater than that of the carbonyl groups. Hence it is possible to come to the conclusion that there is another way of grafting the monomer to the rubber chain other than via the vinyl group.

For example, DBBA can hydrolyse to give 3,5-di-tert-butyl-4-hydroxy benzyl alcohol which could in turn graft into the rubber. This will be discussed in Chapter 9.

Figure 18a


0.9
0.78
0.68
OH ratio / CO ratio
0.5
1
2
3
4
Concentration of DBPA/100 gms rubber

Figure

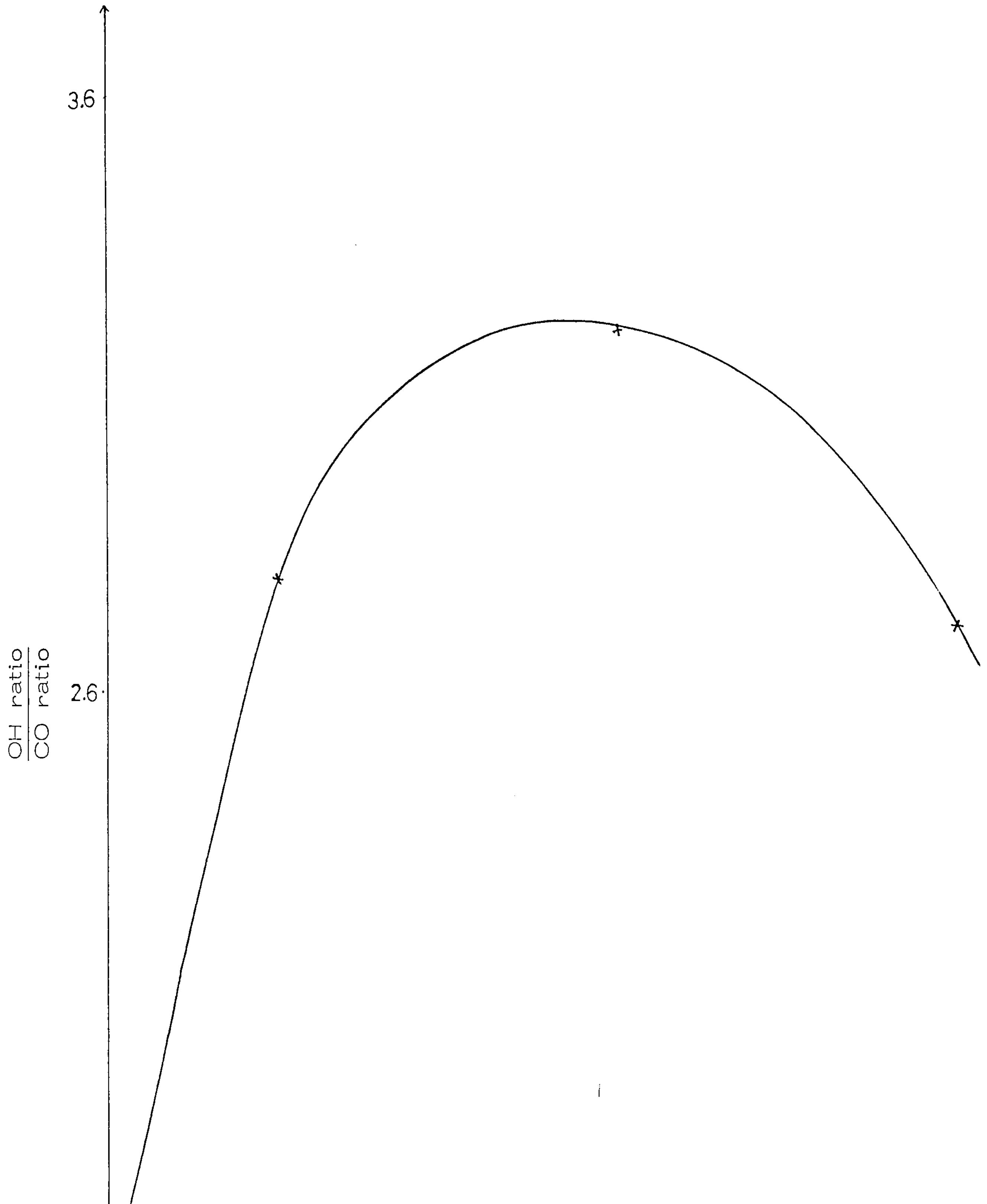
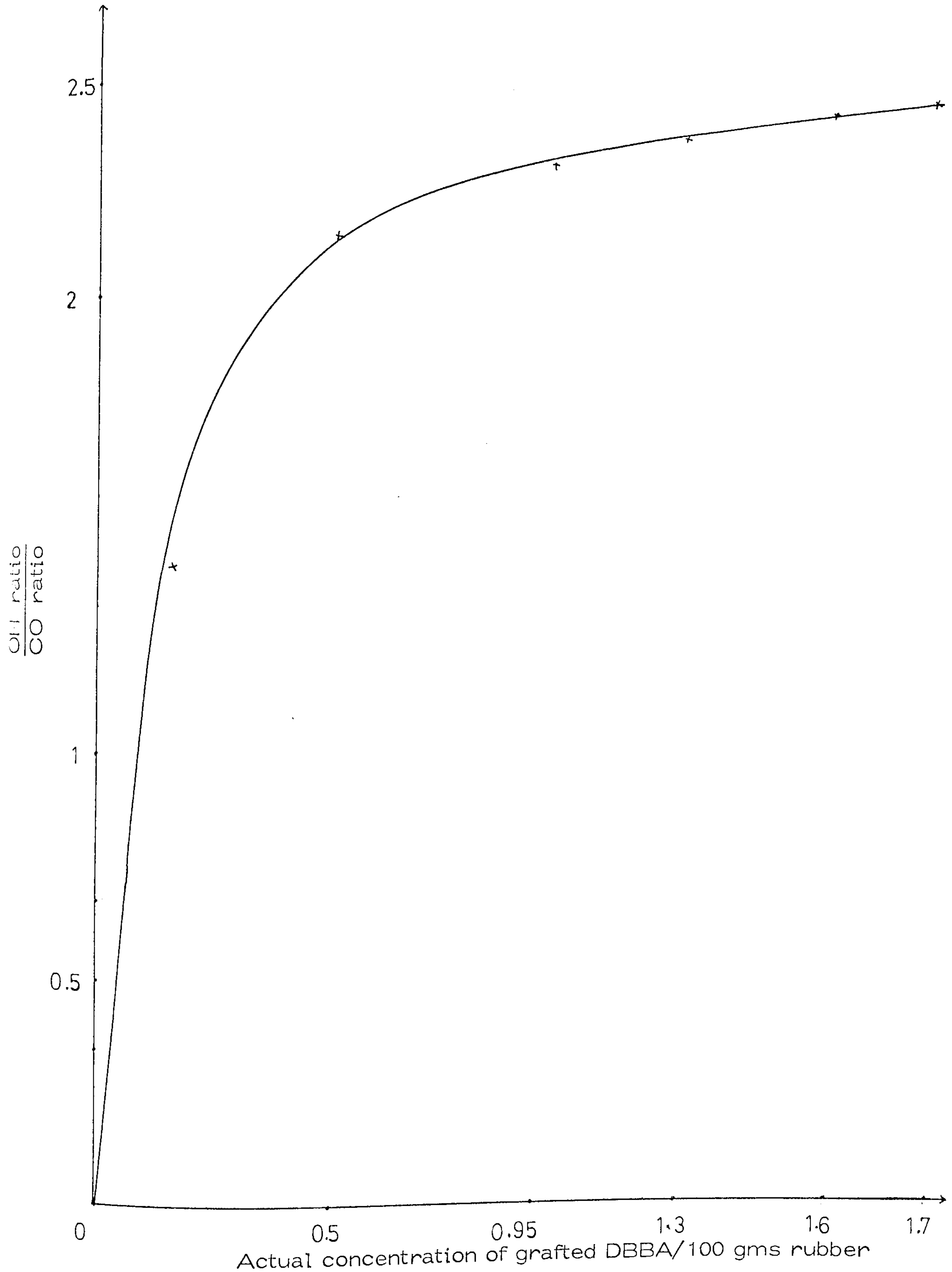

3.6
2.6
1.6
OH ratio / CO ratio
0.5
1
2
3
Concentration of DBBA/100 gms rubber

Figure 19b



Actual concentration of grafted DBBA/100 gms rubber

CHAPTER 6

6.1 Variation of ratio of initiator to monomer

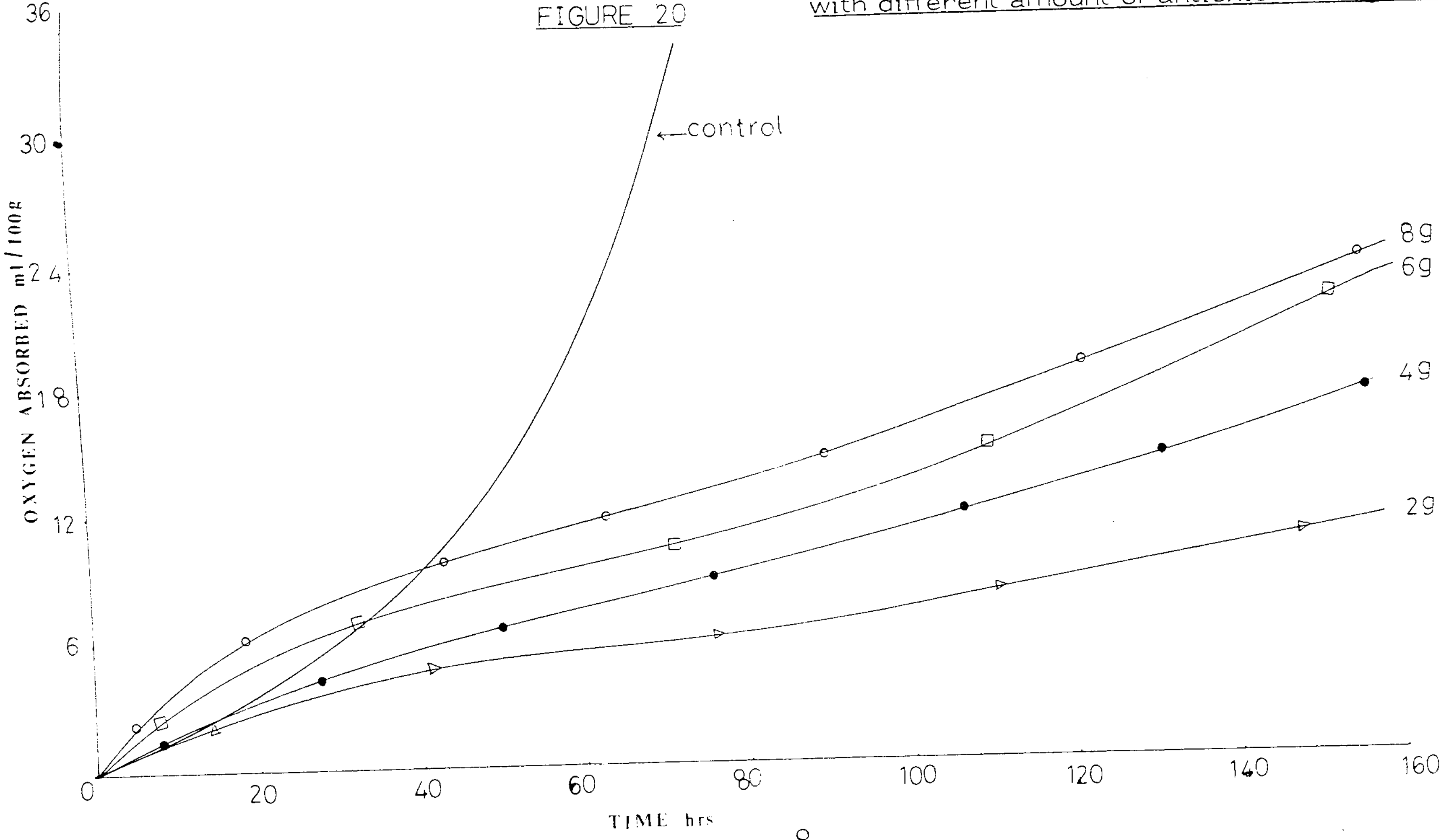
In the work described so far, all the reactions were carried out with 1.5 ml TBHP and 4 ml of a 10% solution of TEP in water with 100 gms of rubber and 2 gms of DBBA. To find out whether there is an optimum initiator to monomer concentration ratio, a series of reactions were carried out with the same amount of initiator but increasing the concentration of monomer in the rubber. All the reactions were carried out at 55°C in a nitrogen atmosphere with 166 ml of centrifuged latex (100 gms DRC) in the presence of the standard initiator system. The reaction was allowed to take place for 18 hours. The latex was coagulated by the addition of formic acid. The vulcanisates were prepared after the extraction of samples with the azeotrope.

The oxygen absorption studies were carried out at 70°C, figure 20.

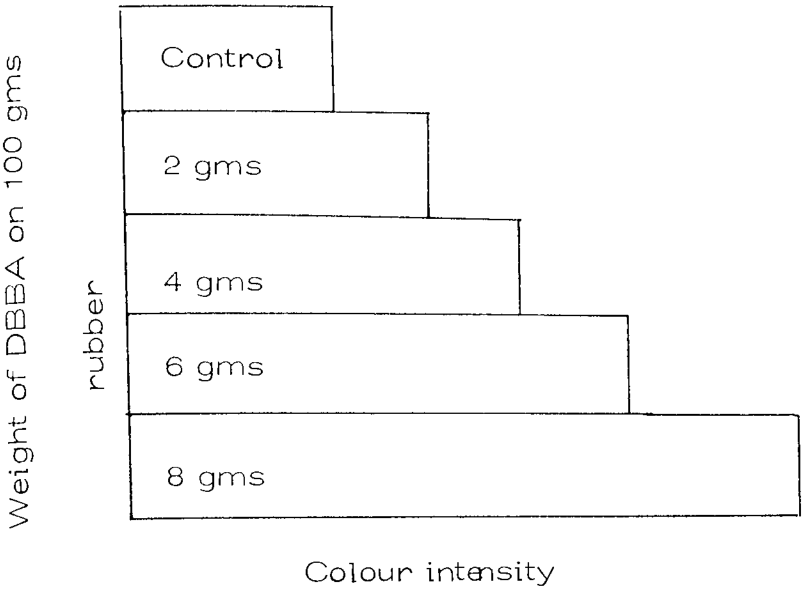
Concentration of added DBBA/100 g rubber	TBHP concentration ml	TEP solution ml	Time to absorb 3% oxygen hrs	Time to absorb 5% oxygen hrs
Natural rubber	-	-	32	42
2 g	1.5	4	132	200
4 g	1.5	4	87	138
6 g	1.5	4	62	113
8 g	1.5	4	40	95

FIGURE 20

The effect of the same concentration of initiator with different amount of antioxidant on grafting reaction



The rate of oxygen absorption of vulcanisates at 70°C



According to the results it is obvious that the initiator concentration should vary with the monomer concentration. By carrying out a series of experiments it was found that to obtain maximum grafting the following concentrations of initiator must be used with the respective concentrations of monomer.

Monomer DBBA gms	TBHP ml	TEP ml	Time to absorb 3% oxygen hrs	Concentration of bound monomer gms
2	1.5	0	60	-
2	1.5	4	130	0.95
4	2	6	172	1.3
6	3	8	201	1.6
8	4.0	12	229	1.58
10	4.0	12	240	1.71
12	4.0	12	252	1.8

It was noticed that the molecular weight of the rubber decreased when the reaction was carried out with excess of tertiary butyl hydroperoxide.

Monomer DBBA gms	Monomer DBBA moles	TBHP ml	TBHP moles	TBHP/DBBA moles	Conc^{n} of bound monomer/100g rubber
2	.007	1.5	.017	2.42	0.95
4	.014	2.0	.022	1.57	1.3
6	.021	3.0	.033	1.57	1.6
8	.028	4.0	.044	1.57	1.58
10	.035	4.0	.049	1.25	1.71
12	.042	4.0	.044	1.048	1.8

In order to find the relationship between the initiator (TBHP) and the DBBA the above optimum concentrations were expressed in terms of moles. It was found that to obtain the maximum amount of grafting, the initiator to monomer concentration ratio should be around 1 : 1.5 moles up to the monomer concentration of 8 g/100 g of rubber. However, above this phenol concentration it appears that the ratio optimum of 1 : 1.5 does not hold. From this it could be concluded that all the radicals formed do not react with DBBA. Also there is no possibility for a graft length of more than 1 molecule of DBBA.

The conclusions that emerge from these results are:

(a) tetraethylene pentamine plays a very important role in the grafting reaction.

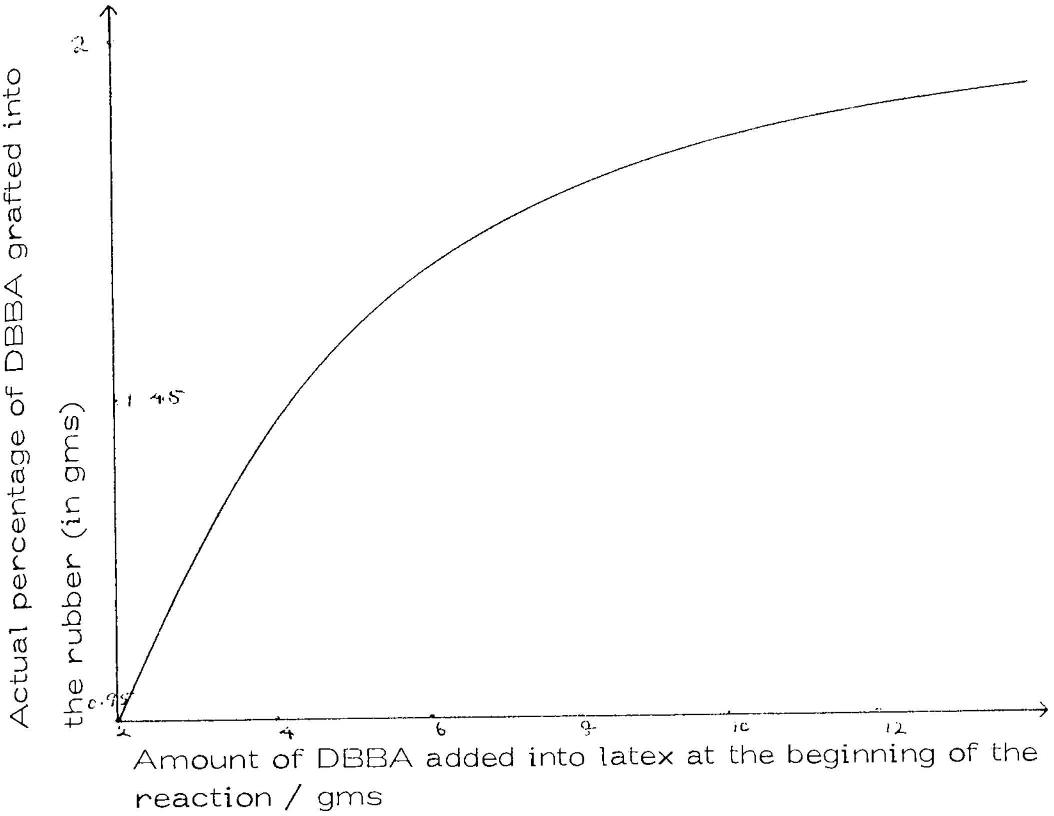
(b) the concentration of initiators used for the reaction should vary with the monomer concentration.

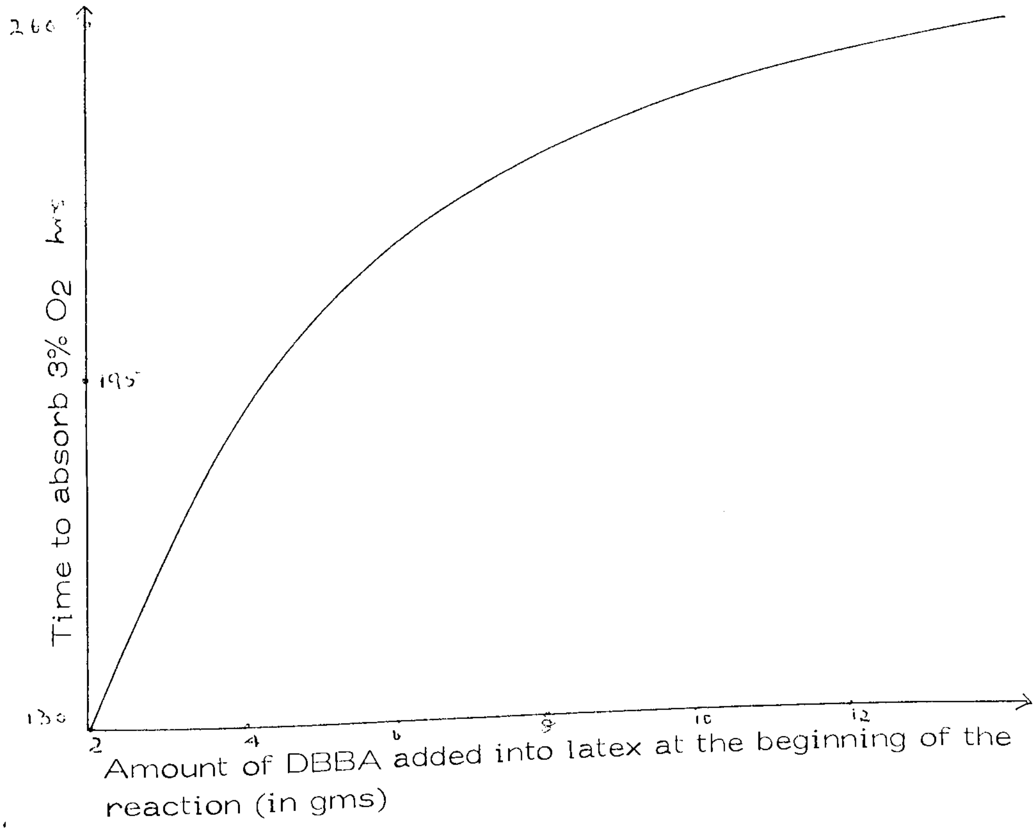
Kropacheva and co workers(64) have shown that, polyamine systems used for radical polymerisation initiation was not directly connected with the oxidation-reduction step. The primary product was a substance which dissociated into radicals at lower temperatures than the original hydroperoxide. These polyamine systems were very effective for emulsion polymerisation even at 5°C.

In polyamine activated systems, the hydroperoxide and the polyamine first formed an intermediate with an unstable C-O-N bond which cleaved to the free radical of the amine and the RO radical of the hydroperoxide.

Because of this kind of unstable intermediate formation between the amine and the hydroperoxide it was found that it is necessary to change the TEP concentration with that of the TBHP in this latex grafting system.

Subsequent experiments were carried out to see how much antioxidant could be bound into the rubber. It was found that it is difficult to graft above a certain limiting concentration under any circumstances. This could be proved by oxygen absorption studies and by the quantitative infra red spectroscopy.


Actual percentage of DBBA grafted into the rubber (in gms)
2
1.45
0.95
2
4
6
8
10
12
Amount of DBBA added into latex at the beginning of the reaction / gms


Time to absorb 3% O2 hrs
260
195
130
2
4
6
8
10
12
Amount of DBBA added into latex at the beginning of the reaction (in gms)

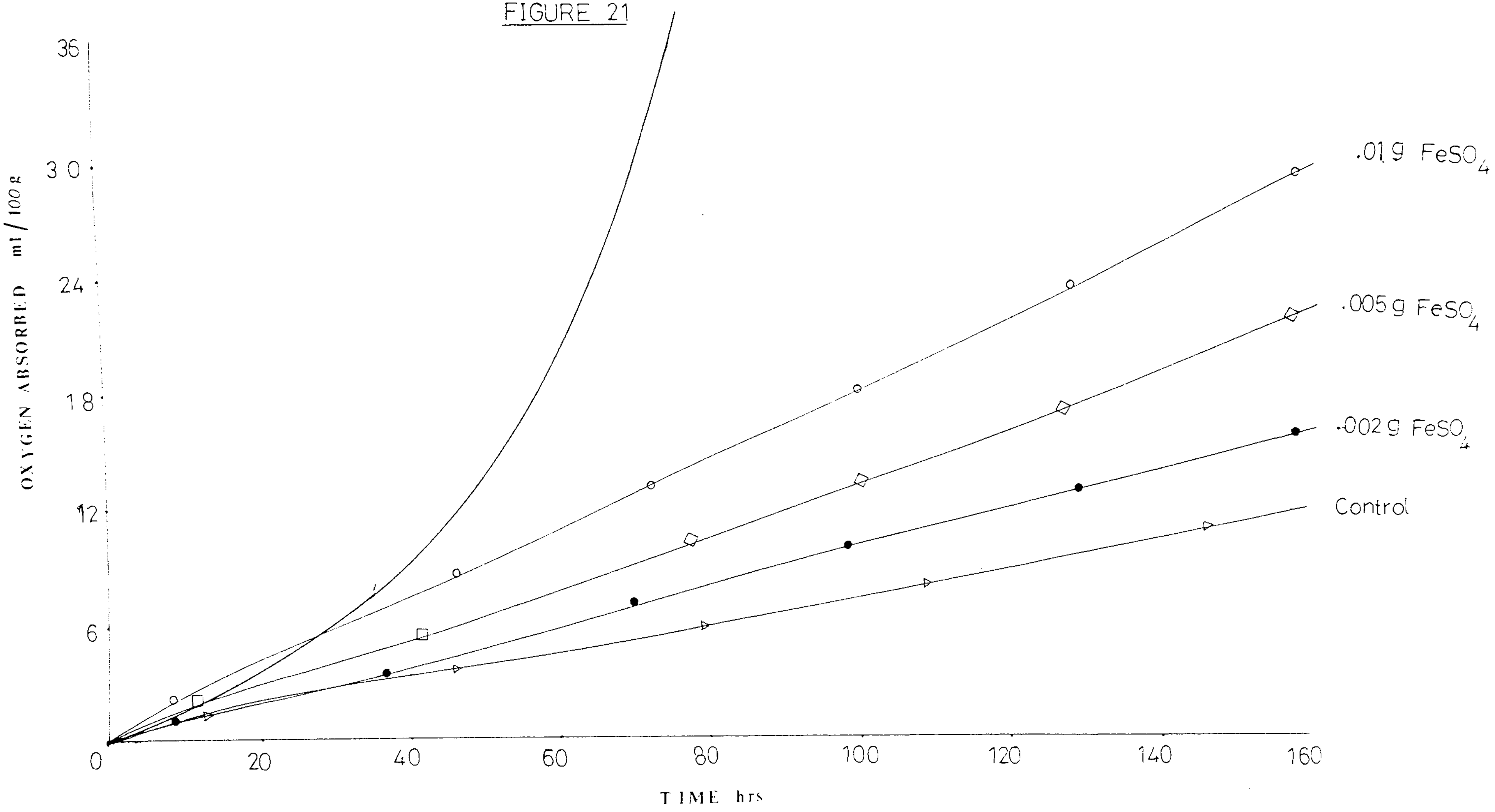
According to the literature, the initiating capacity of polyamine activated initiator systems, increases with the addition of a trace of ferrous sulphate. To study the effect on latex grafting systems, a few reactions were carried out in the presence of ferrous sulphate under the previously determined optimum conditions.

166 ml of distilled water was added to 166 ml of centrifuged latex containing 100 g of dry rubber and was partially deammoniated. It was allowed to stand with a dispersion of 2 g of DBBA for 15 minutes and a known amount of ferrous sulphate was added. (0.005 g, 0.01 g and 0.015 g.) The initiation of the reaction was carried out by the addition of the standard TBHP/TEP initiator. The reaction was allowed to take place for 18 hours at 55°C. The grafted rubber was isolated as described in earlier experiments and vulcanisates were prepared. Figure 21 illustrates the rate of oxygen absorption by these samples.

6.2 Masterbatch technique

It has been established in the above series of experiments that the amount of antioxidant bound into the rubber is proportional to the amount of antioxidant used at the beginning of the experiment up to a certain limit. It follows that such a rubber with a higher than normal concentration of bound antioxidant might be diluted with untreated rubber, giving a polymer containing a desired amount of bound antioxidant which should subsequently co-vulcanise. This is of

FIGURE 21



The effect of ferrous sulphate on grafting reaction great potential industrial importance because it might avoid the reaction with large quantities of rubber, the amount of antioxidant in the final rubber being controlled by varying the amount of masterbatch added.

Experimentally, the treated rubber latex was diluted with untreated latex on the basis of the known concentration of antioxidant in the concentrate.

Two grafting reactions were carried out with 8 gms (4 ml TBHP/12 ml TEP 10% solution) and 2 gms (1.5 ml TBHP/2ml TEP 10% solution) of DBBA with 100 gms of rubber and the former was diluted with known amounts of untreated rubber latex to obtain a rubber with known amounts of bound antioxidants. Each sample of latex was coagulated independently by adding 1% formic acid and prepared vulcanisates as usual.

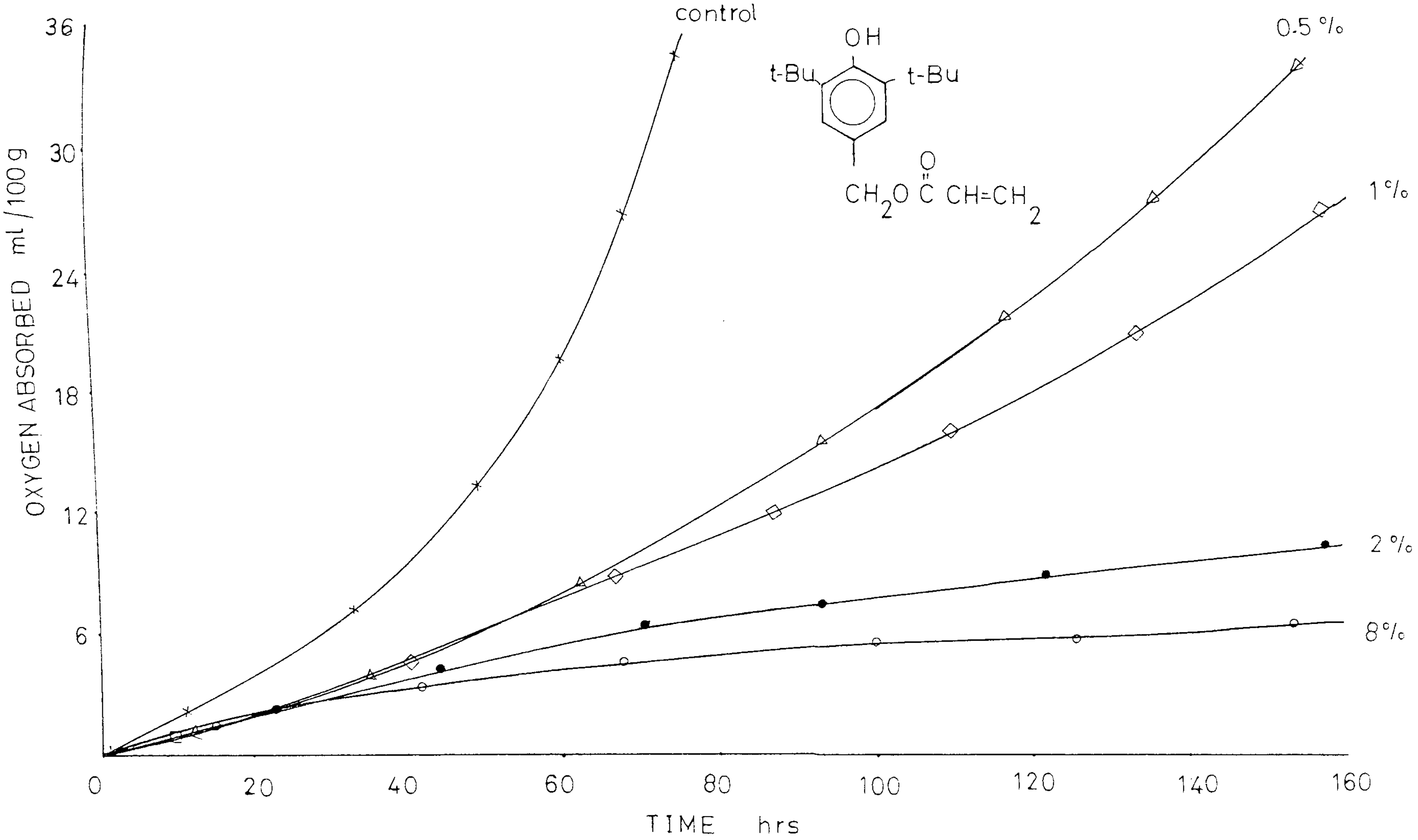
The oxygen absorption experiments were carried out at 70°C using the prepared vulcanisates samples, figures 22 and 23.

Results

1% of DBBA in rubber	Time to absorb 3% O_2. hrs	Time to absorb 5% O_2. hrs
2 gms	138	202
1 gms	68	106
0.5 gms	63	87
0.25 gms	53	70

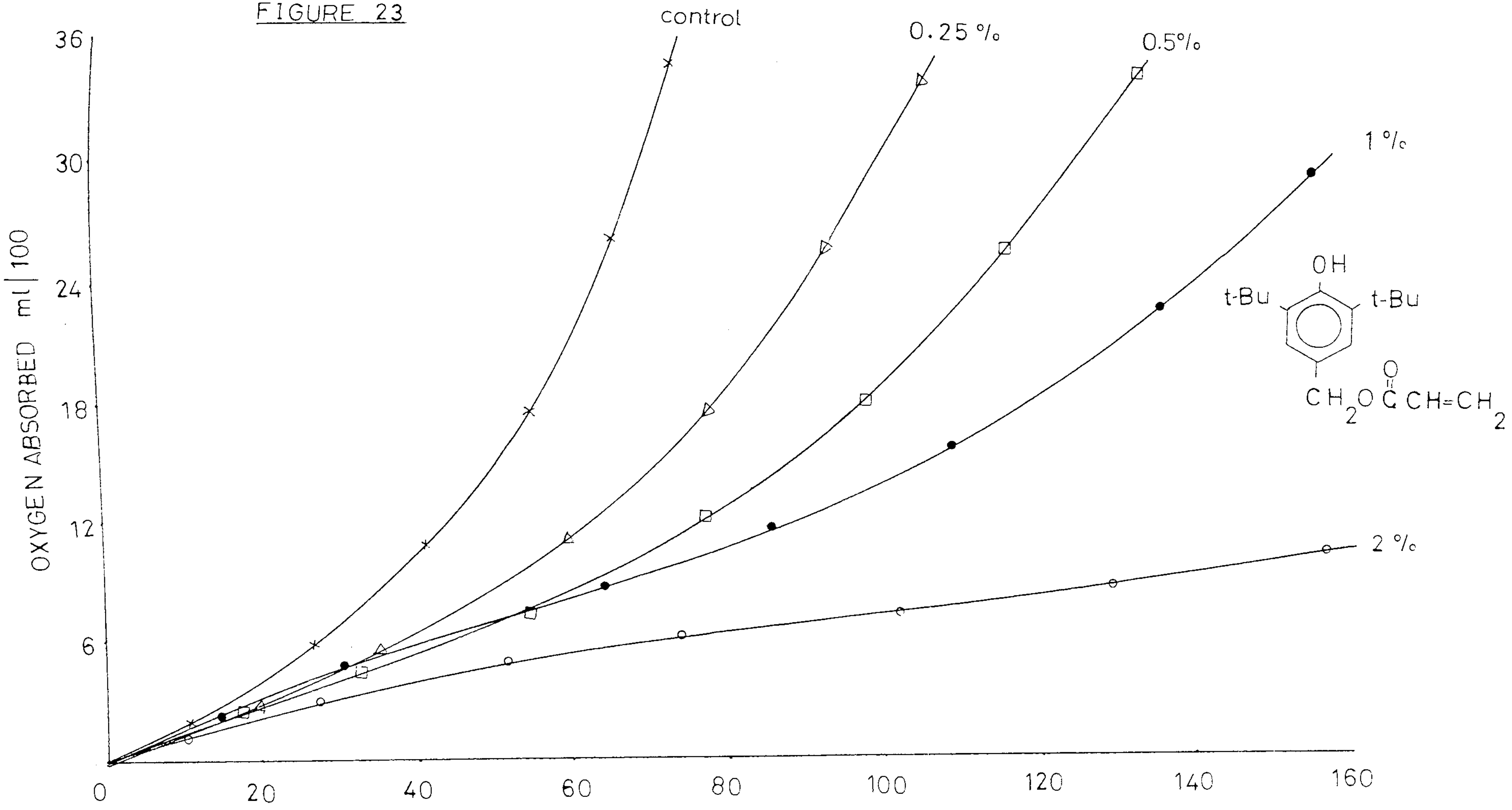
% of DBBA in rubber	Time to absorb 3% O_2	Time to absorb 5% O_2
8 gms	240	328
2	123	200
1	68	105
0.5	65	91

FIGURE 22



The rate of oxygen absorption at 70°C (Master batch technique)

FIGURE 23



The rate of oxygen absorption at 70°C (Master batch technique)

CHAPTER 7

Analysis of by-products formed during grafting

According to the experiments that have been carried out so far it may be concluded that DBBA is a very efficient bound antioxidant which can survive vigorous exhaustive extraction. However, the amount of hindered phenol actually grafted to the rubber is very small. The main disadvantage of the process from a commercial point of view is the intense yellow colour of the grafted rubber. It was noticed, however, that the compounds responsible for the colour is completely soluble in the azeotrope and the rubber was colourless after extraction. Several efforts were made to overcome this colour problem but none was successful.

7.1 Identification of the oxidised products

Thin layer chromotography was employed to identify the coloured products formed during the process of grafting.

This was carried out on 'POLYGRAM' plastic sheets with a layer of 0.25 mm silica gel. The grafted rubber was extracted with the azeotrope and by evaporation of this a yellow product was obtained.

2μl of a 1% solution of this in methanol was applied on to a 20 x 20 cm silica plate and the methanol was allowed to evaporate after application. The development of the chromotogram was done by the ascending method, that is, by allowing a solvent mixture to move up an almost vertical plane by capillary action. In order to saturate the tank atmosphere as fully as possible the sides were lined with thick chromotography papers. The loaded plates were placed in the solvent tank and the plates were run to a line drawn from a fixed distance from the origin (loading point). The plates were dried in air for a few minutes. To observe the separated constituents a location reagent was necessary. For this purpose a 1% phosphomolybdicacid in ethanol was sprayed over the plates using an aerosol spray and the plates were heated in an oven at 120^{o}C for one minute.

The compounds were identified and characterised by the R_f values.

$$R_f = \frac{\text{Distance moved from origin by the compound}}{\text{Distance moved from origin by solvent front}}$$

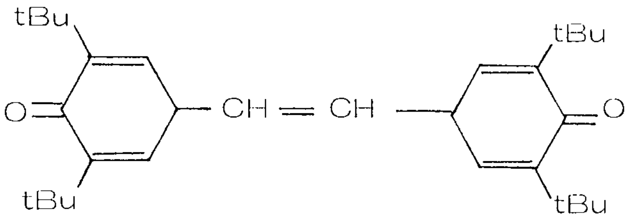
To identify the oxidation products of DBBA and DBPA, it was necessary to prepare the probable oxidation products.

Sugita (65) has carried out a reaction between 2.6.di-tert-butyl-4-hydroxy benzyl alcohol and nickel peroxide in benzene below 40^{o}C. He has reported that he obtained 3 5, 3^{1} 5^{1}-tetra-tertiary-butyl stilbene 4-4^{1} quinone VI, 35, 3^{1} 5^{1}-tetra-tert-butyl 4-4^{1}-bipheno quinone V, $[3,5,4\text{-tert-(butyl)}_2(OH)_2C_6H_2CH_2]_2$, 2,2-di-tert-butyl-4-hydroxy benzaldehyde I.

Hence to identify the products formed during the process of grafting, it was essential to obtain the R_f values of the most probable compounds.

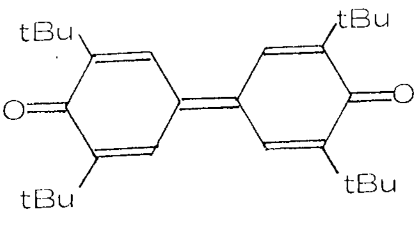
7.2 Synthesis of authentic samples

7.2.1 3,5,3^{1},5^{1}-tetra-tert-butyl stilbene 4 4^{1} quinone (66)



4-methyl 2,6-di-tert-butyl phenol (11 g, 0.05 mol) and benzoyl peroxide (12.1 g) were refluxed in purified chloroform (150 ml) for 140 hours. The bright red solution was then extracted with aqueous sodium hydrogen carbonate, the extracts were acidified, and benzoic acid was collected. Evaporation of the dried chloroform gave a bright red gum from which by rubbing with ether (30 ml) insoluble 3,5,3^{1},5^{1}-tetra-tert-butyl stilbene-4,4^{1}-quinone was removed by filtration. This crystallised from glacial acetic acid in crimson rods mp 300^{o}C.

7.2.2 3,3^{1},5,5^{1}-tetra-tert-butyl 4-4^{1}-bipheno quinone (67)



PAGE 85

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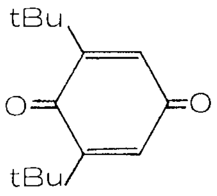
A mixture of 10 g (mole) of 2,6-di-tert-butyl phenol and 500 ml of water was heated to refluxing and emulsified by vigorous stirring. A solution of 20 g (0.07 mole) of ferric chloride hexahydrate in 50 ml of water was added dropwise over a 0.5 hour period and the refluxing mixture heated and stirred for 5 hours. After cooling, the organic material was removed by ether extraction. The ether extract was dried over sodium sulphate and evaporated. The residue was crystallised twice from ethanol to yield 3.5 g (38%) of 3,3^1,5,5^1-tetra-tert-butyl-4-4^1-bipheno quinone.

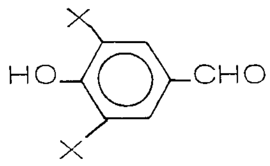
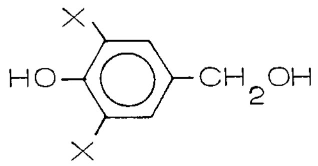
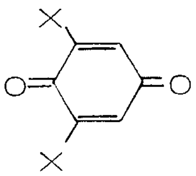
Melting point - 246^{o}C$^{(68)}$.

7.2.3 2,6-di-tert-butyl-p-benzoquinone

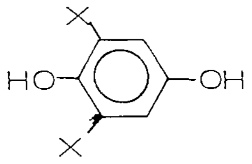
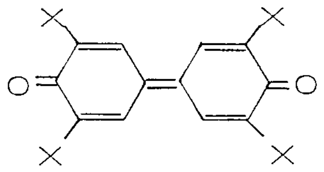
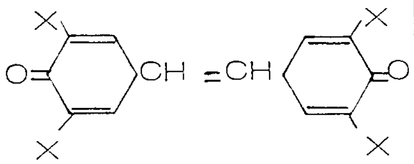


The synthesis of this compound is given on page 37.

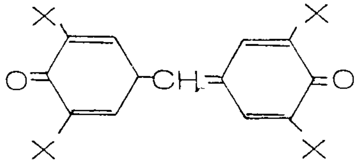
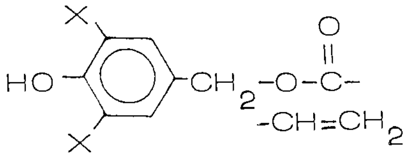
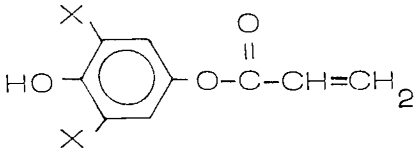
R_f × 100 values of authentic compounds on silica gel

	Sample	C_6H_6:EtoAc HoAc 90:5:5	C_6H_6:MeOH: HoAc 45:8:4	Colour with location reagent	Spots with DBBA extract	Spots with DBPA extract
I		73	88	Pink		
II		41	57	Pink	++	
III		81	91	Blue	+	++

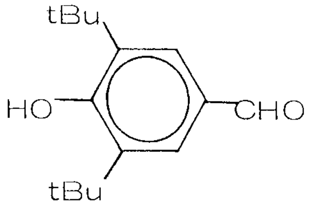
R_f × 100 values of authentic compounds on silica gel

	Sample	C_6H_6:EtoAc: HoAc 90:5:5	C_6H_6:MeOH HoAc 45:8:4	Colour with location reagent	Spots with DBBA extract	Spots with DBPA extract
IV		60	59	Blue		+
V		89	92	Yellow	+	+++
VI		90	92	Pink	++	

R_f × 100 values of authentic compounds on silica gel

Sample	C_6H_6:EtoAc: HoAc 90:5:5	C_6H_6:MeOH: HoAc 45:8:4	Colour with location reagent	Spots with DBBA extract	Spots with DBPA extract
			Pink	+	
	83	90	Pink	+++	
	90	96	Blue		+++

7.2.4 3,5-di-tert-butyl-4-hydroxy benzaldehyde



The synthesis of this compound is described on page .

7.3 Results and discussion

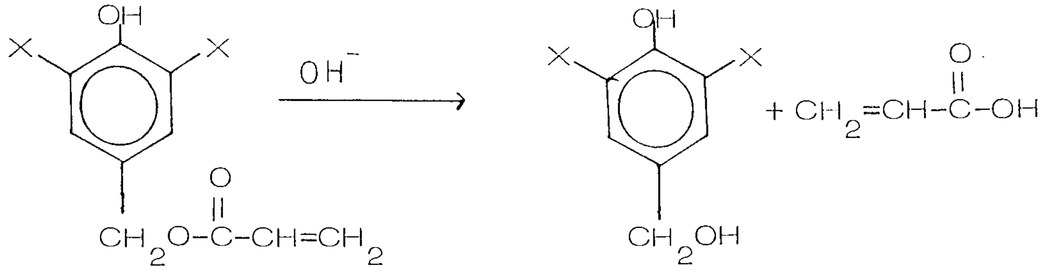
According to the R_f values of the oxidised products in the extracts of the 2.6-di-tert-butyl 4-hydroxy benzyl acrylate (DBBA) grafted samples the conclusions are as follows:

(a) A considerable quantity of DBBA is not grafted to the rubber network but is present in the rubber network as unoxidised monomer.

(b) Major proportion of the oxidised product is 3,5,3^1,5^1-tetra-tert-butyl stilbene 4,4^1-quinone (VI). This is an intense yellow coloured compound.

(c) Small proportions of 3,5^1,5,5^1-tetra-tert-butyl 4,4^1-bipheno quinone V and 2,2-di-tert-butyl-p-benzoquinone III were present in the oxidised products.

(d) A small amount of 2,6-di-tert-butyl-4-hydroxy benzyl alcohol II was present in the extract. Most probably, this must have formed by the hydrolysis of the acrylate.



From the values of the oxidised products in the extracts of the 2,6-di-tert-butyl-4-hydroxy phenyl acrylate (DBPA) grafted samples the following conclusions are possible:

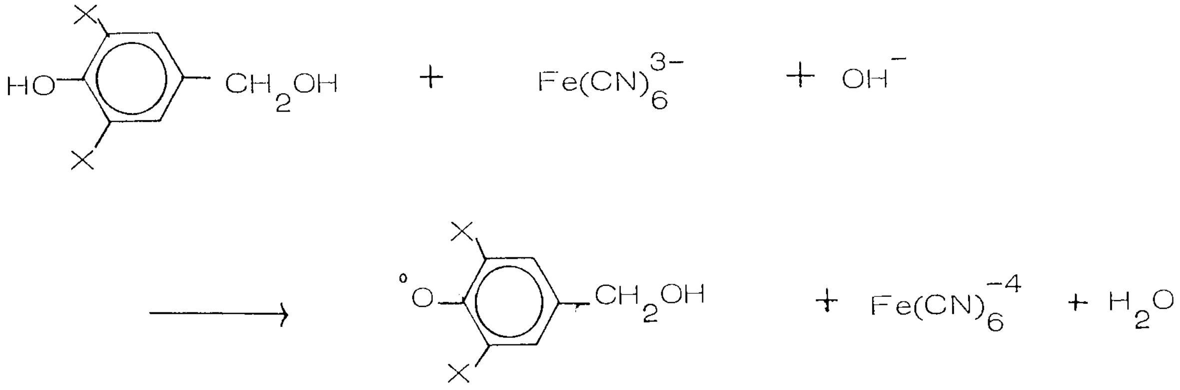
(a) A considerable quantity of DBPA is not grafted to the rubber network but is present in the rubber network as an unoxidised DBPA.

(b) A major proportion of the oxidised products were $3,3^1,5,5^1$-tetra-tert-butyl-4-4^1-biphenoquinone V. This is an intense yellow compound.

(c) A small proportion of 2,2-di-tert-butyl-p-benzoquinone III was present in the oxidised products.

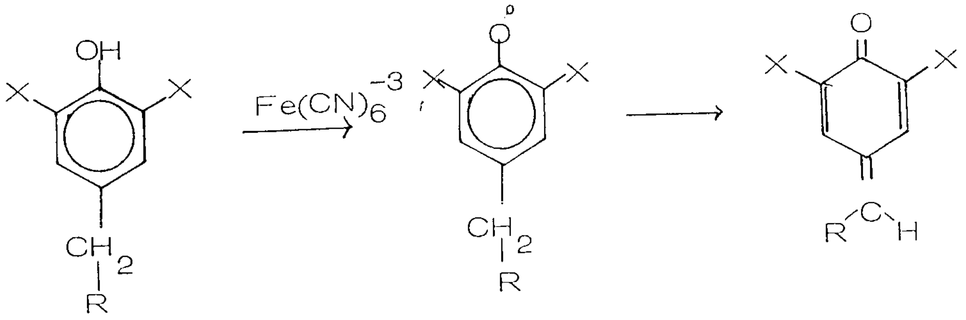
(d) A small amount of 2,6-di-tert-butyl-4-hydroxy phenol IV was present in the extract. Most probably this must have formed by the hydrolysis of the phenyl acrylate.

Westfahl[69,70] has studied the oxidation products from antioxidants containing the 3,5-di-tert-butyl-4-hydroxy benzyl group. He produced free radicals by single electron oxidation using the ferricyanide ion as the oxidising agent.



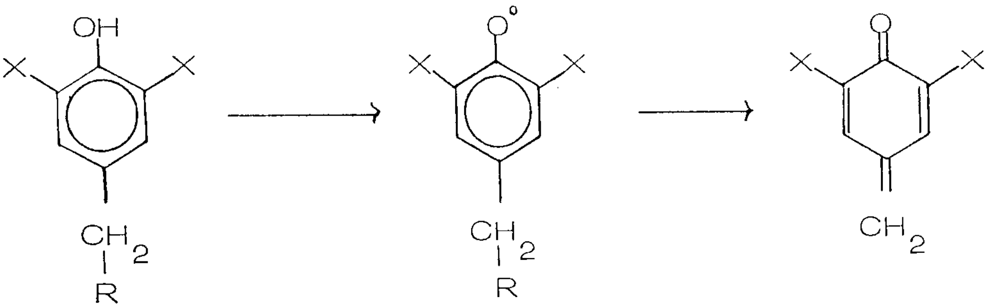
The reaction was carried out by rapid mixing of di-methyl sulfoxide solutions of the compounds to be oxidised and the oxidant. According to the results of the experiments, Westfahl came to the conclusion that the group or atom attached to the 3,5-di-tert-butyl-4-hydroxy benzyl group can be removed to give the very unstable 2,6-di-tert-buty- hydroquinone methide XI.

If the bond between the benzyl group and the rest of the molecule is strong, a phenoxy radical IX of considerable stability will form. The radical will disproportionate slowly to give mono substituted quinone methide X. No further radical products are observed.



IX X

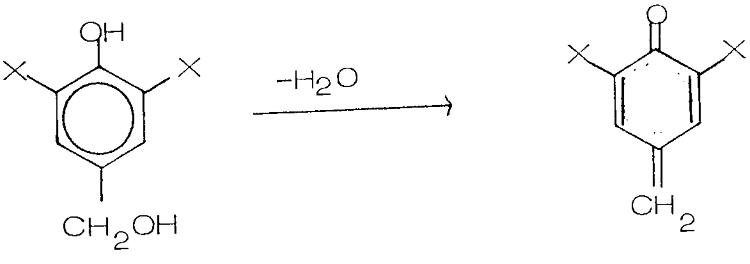
If the bond connecting the benzyl group to R is weak, a loss of R either by an ionic or free radical process to give the very unstable 2,6-di-tert-butyl quinone methide XI.

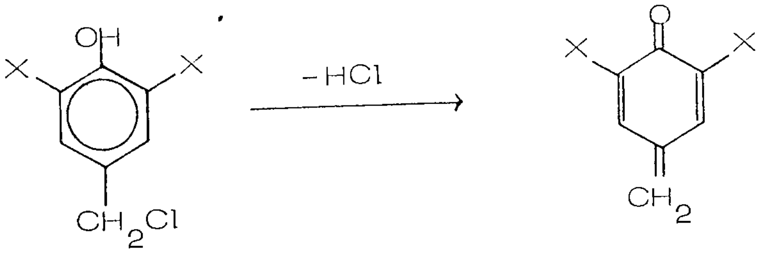


IX

XI

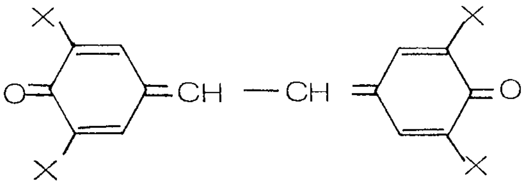
Although Westfahl has demonstrated the formation of quinone methide in the presence of an oxidising agent, it is also possible to prepare quinone methide by the dehydration or dehydrochlorination of the corresponding phenols, using Lewis acids.





The formation of quinone methide from other phenols will be dealt with in Chapter 9 .

This very reactive intermediate undergoes a dimensation and disproportionation to give VI.



VI

Therefore there is a possibility of formation of different types of quinones from the original esters through the hydroxy methyl compounds.

CHAPTER 8

Other possible methods of grafting vinyl compounds to natural rubber

8.1 Mechano-thermal initiated polymerisation

It has been shown that vinyl monomers can graft to natural rubber in the presence of free radical initiators. As discussed in Chapter 1, the free radicals can form in the rubber network by the molecular break down which occurs when rubber is milled or masticated. These free radicals behave towards radical acceptors in the same way as comparable free radicals formed in conventional liquid systems.

$$R\text{-}R \xrightarrow[\text{rupture}]{\text{Mechanical}} R^{o} + R^{o}$$

$$\begin{tikzcd} R^{o} + \underset{(M)}{\text{vinyl monomer}} \arrow[r] & RM^{o} \arrow[d, "M_{n-1}"] \\ & R\text{-}M_{n} \text{ (block co polymer)} \end{tikzcd}$$

The essential conditions here is that the monomer should itself be a radical acceptor.

Free radical formation in both the rubber network and in the vinyl monomer may take place at high temperature. Therefore, during the process of vulcanisation (at 140°C for 30 minutes) there is a possibility of vinyl monomers grafting into the rubber network if a vinyl monomer is included to the formulation.

To find out whether a grafting between natural rubber and vinyl monomer takes place during the process of milling and vulcanisation, a series of reactions carried out with solid rubber and DBBA.

The natural rubber latex was coagulated by adding 1% formic acid and dried at room temperature and after drying the rubber it was extracted with the azeotrope in an soxhlet extractor under nitrogen for 48 hours in order to remove all the non rubber constituents.

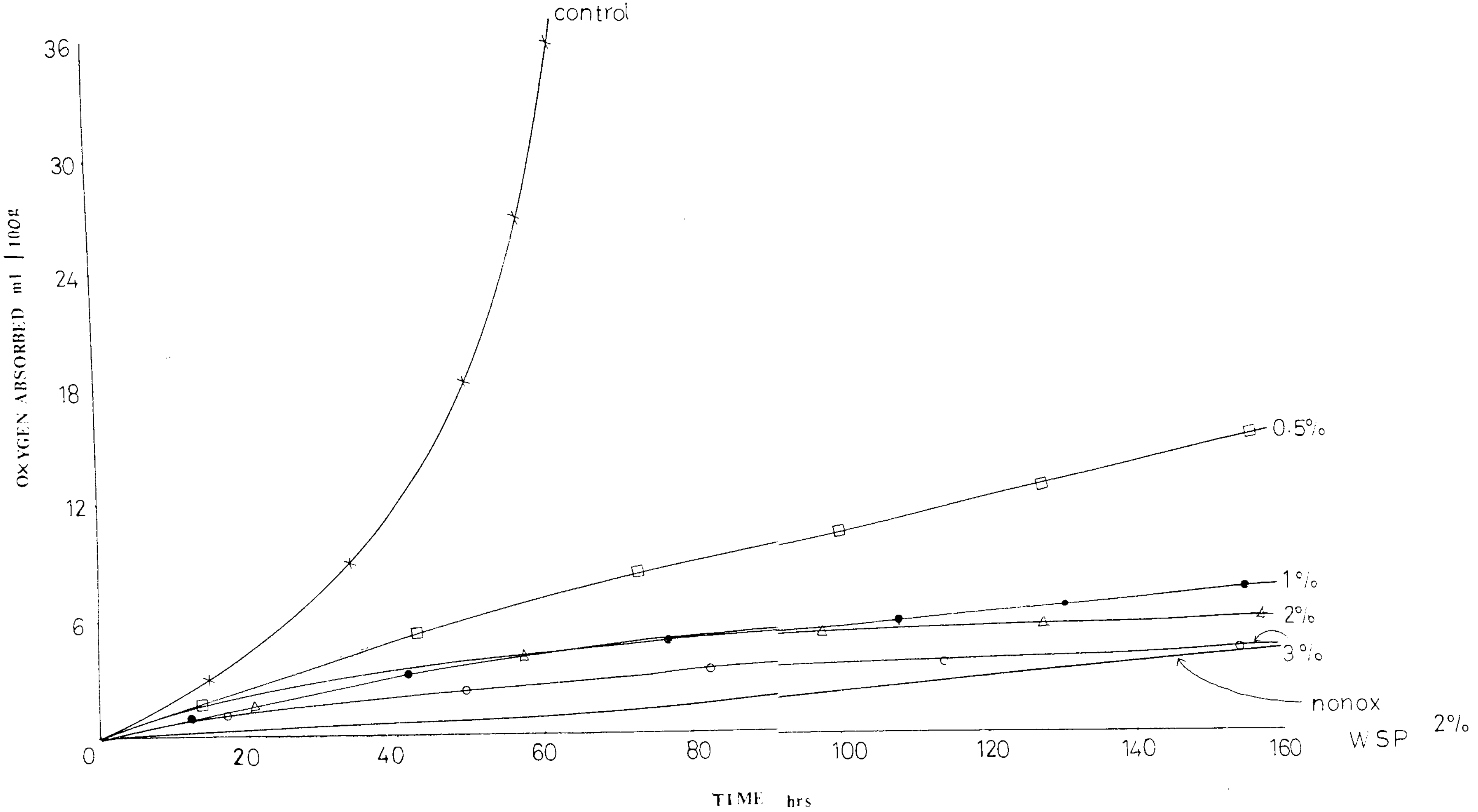
100 gms of extracted rubber was mixed with a known quantity of DBBA in a water cooled 2 roll mill and this was compounded with zinc oxide, stearic acid, sulphur and CBS, according to the formulation given on page 53. The vulcanisation was carried out at 140°C for 30 minutes. The samples were prepared with 0.5, 1, 2, and 3 gms of DBBA per 100 g of rubber. The rate of oxygen absorption of these samples were carried out to determine the effectiveness of the total amount DBBA on rubber towards oxidation, without extracting.

The vulcanisates were extracted for 48 hours with azotrope and oxygen absorption was carried out to study the effect of bound antioxidants (during the process of milling and vulcanisation).

In order to compare the effect of DBBA with a conventional antioxidant, vulcanisates were prepared with known quantities of Nonox WSP. The rate of oxygen absorption of these samples were measured before (figure 24) and after extraction with the azeotrope (figure 25).

FIGURE 24

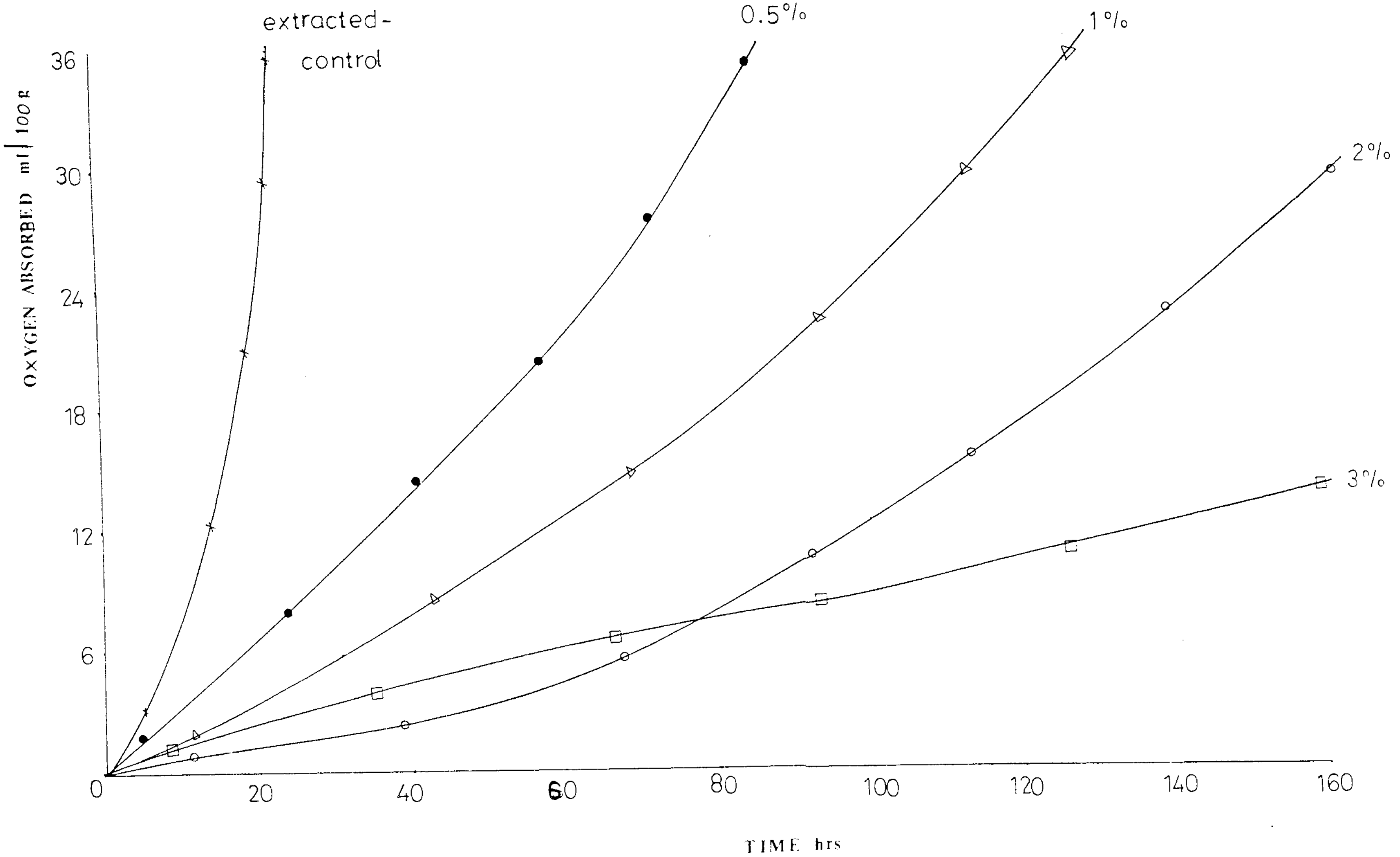
Vulcanisates prepared with different amounts of DBBA



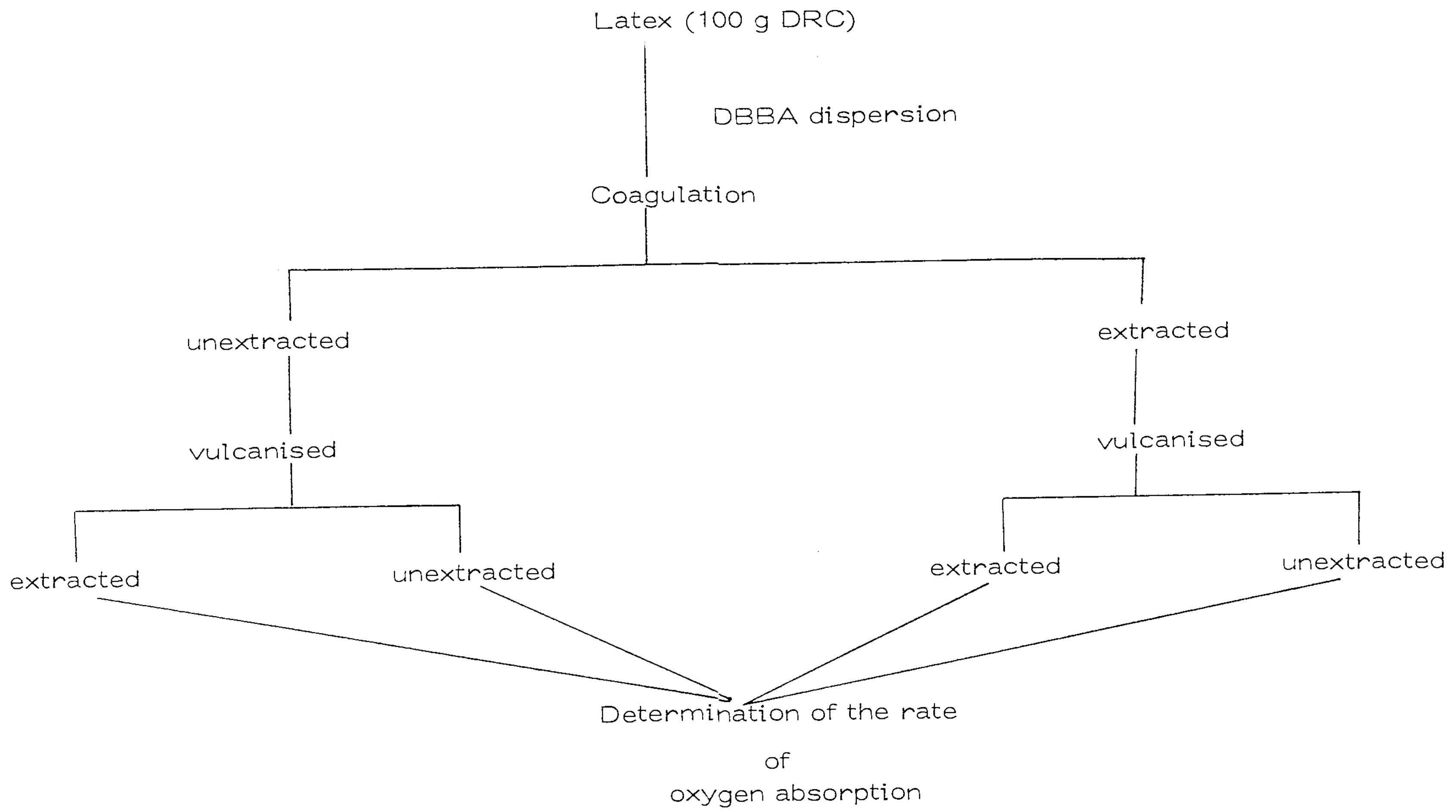
The rate of oxygen absorption at 70°C (UNEXTRACTED)

FIGURE 25

Vulcanisates prepared with different amounts of DBBA



The rate of oxygen absorption at 70°C (EXTRACTED)


Latex (100 g DRC)
DBBA dispersion
Coagulation
unextracted
extracted
vulcanised
vulcanised
extracted
unextracted
extracted
unextracted
Determination of the rate
of
oxygen absorption

8.2 Grafting of DBBA with natural rubber latex using UV radiation

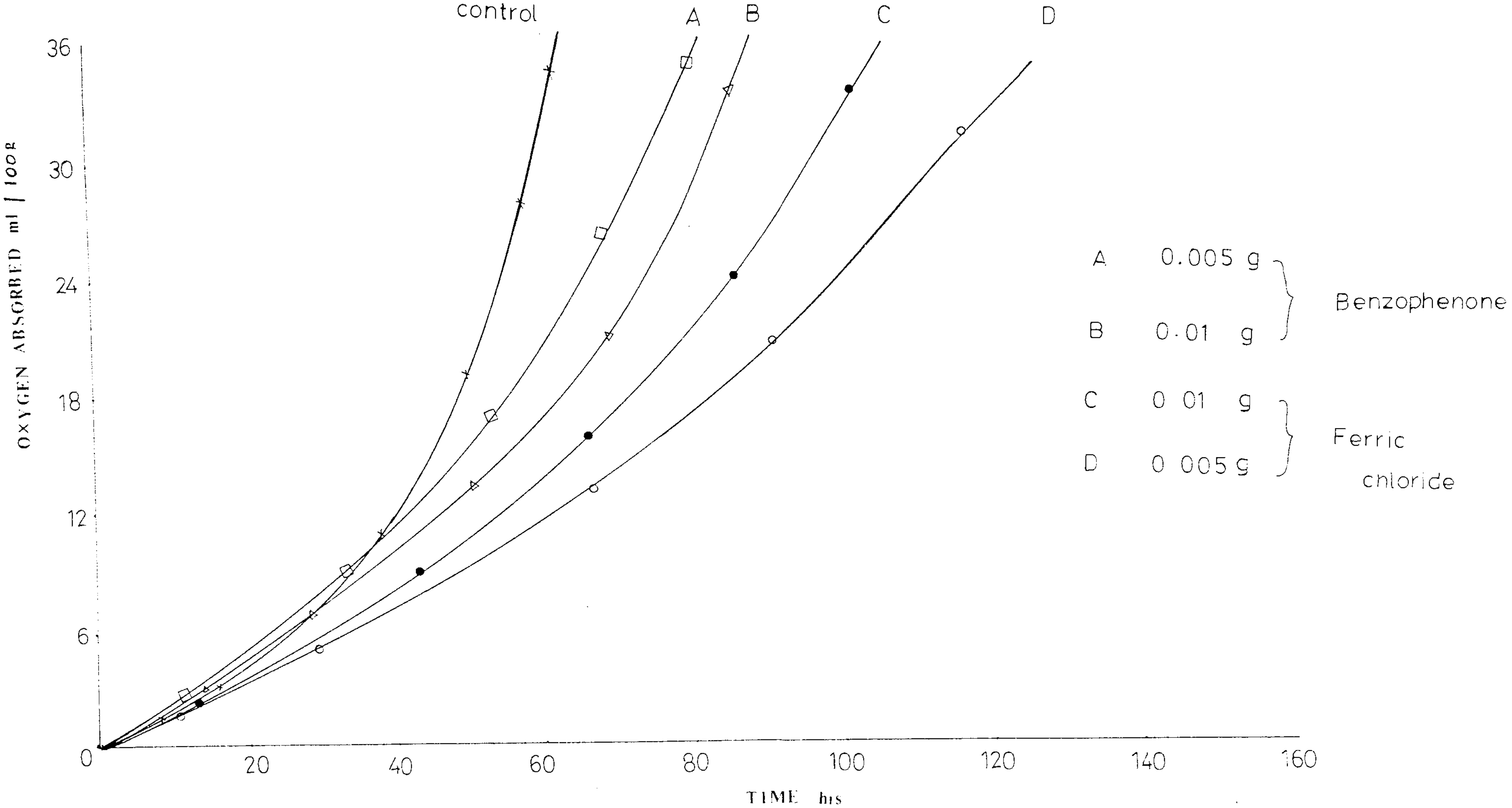
41 ml of natural rubber latex containers 25 gms of rubber was poured into a 500 ml conical flask and it was mixed with a dispersion of known quantity of DBBA. A known amount of photo-initiator was added to the conical flask containing the latex and the flask was completely filled with distilled water. The flask was placed about 4 inches away from an ATLAS 175 W mercury vapour lamp. The content of the flask was continuously stirred using a magnetic stirrer. The reaction was allowed to take place for 72 hours under ultra violet light and it was coagulated, dried, extracted and prepared vulcanisates. The rate of oxygen absorption by these samples are as illustrated in figure 26.

Conc^n of DBBA	Conc^n of $FeCl_3$ gms	Conc^n of Benzophenone gms	Time to absorb 5% oxygen hrs
-	-	-	42
2	0.01	-	57
2	0.005	-	65
2		0.01	50
2		0.005	43

8.3 Results and discussion

According to the results obtained from the grafting reactions discussed so far it is clear that a certain amount of DBBA (vinyl monomer) in the monomeric or polymeric form is grafted into the rubber to give very good resistance towards the oxidation. But there are two other possibilities.

FIGURE 26



The rate of oxygen absorption at 70°C

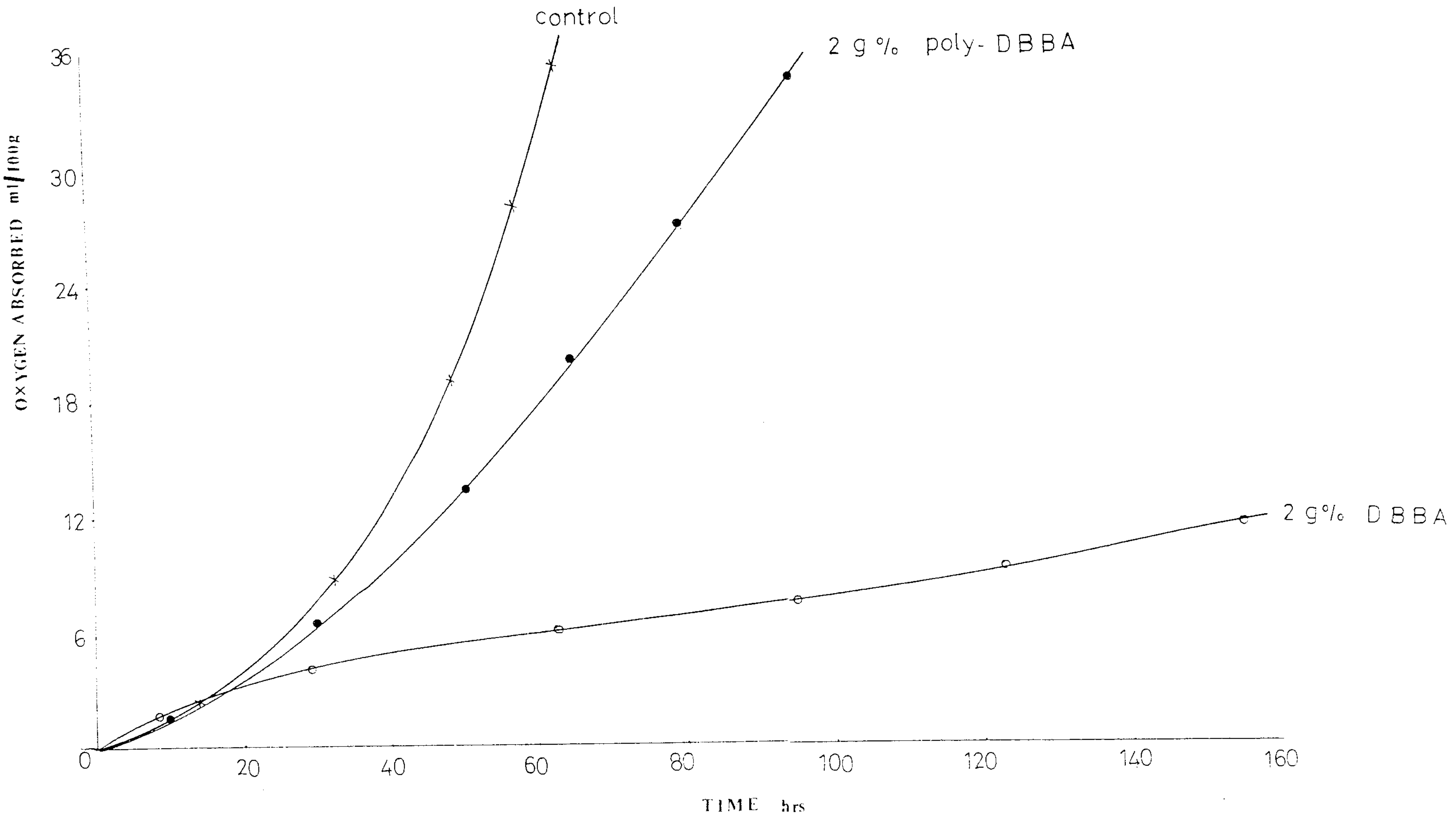
2% DBPA grafted to rubber with UV radiation in the presence of photo-initiators

Firstly, the DBBA can self-polymerise in the presence of the initiators and subsequently the polymers may bind into the rubber. To check this possibility, a grafting reaction was carried out with latex containing 100 gms of dry rubber centent exactly under the predetermined optimum conditions as described on page 68 with 2 gms of poly-2,5-di-tert-butyl-4-hydroxy benzyl acrylate. The vulcanisates were prepared from the grafted, extracted rubber and the rate of oxygen absorption was determined, figure 27.

The second possibility is that the added monomer (DBBA) can homopolymerise in the presence of initiators and poly DBBA can trap within the rubber network without coming out during the process of extraction. To find out whether this is possible in a latex system, a dispersion of 2 g of poly DBBA was mixed thoroughly with natural rubber latex containing 100 gms of rubber and coagulated it by adding 1% formic acid, dried, extracted and vulcanisates were prepared. The oxygen absorptions were carried out and the results are illustrated in figure 28.

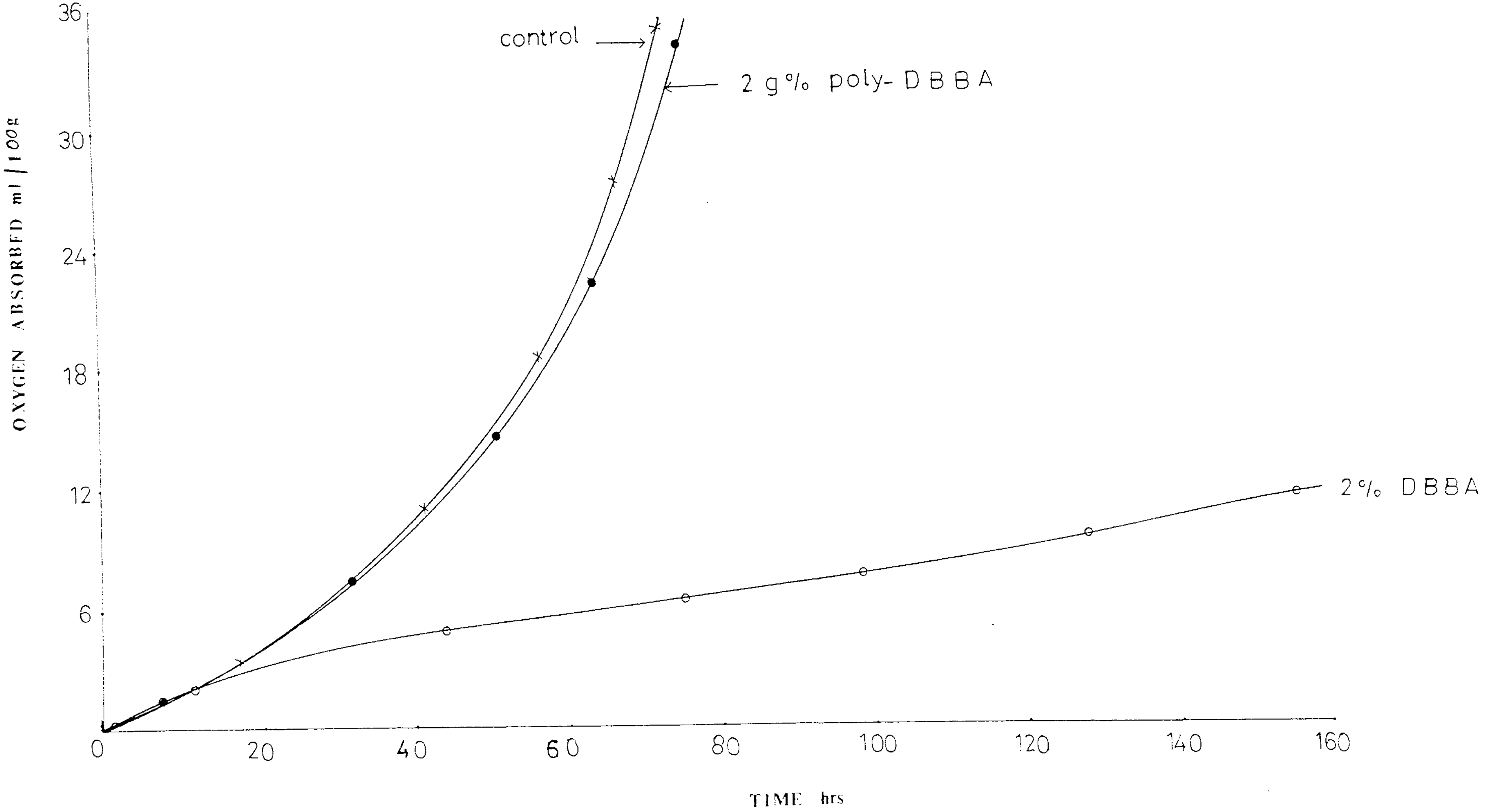
The results of the above experiments indicate that the samples prepared are slightly better than an ordinary ungrafted rubber vulcanisate towards oxidation. But it is not as good as the DBBA grafted samples. According to Bloomfield (9) high proportions of surface-active stabilisers favour polymerisation of the vinyl monomer independently of the rubber phase to give a rubber-polymer mixture rather than a rubber-monomer adduct. Here, in these grafting reactions, the chances of getting homopolymerisation is so small due to the lack of a stabiliser in the latex other than the dispersol LN which is used to prepare the emulsion of the monomer.

FIGURE 27



The rate of oxygen absorption at 70°C by the samples prepared by grafting poly-DBBA

FIGURE 28



The rate of oxygen absorption at 70°C by the samples prepared by mixing a dispersion of poly-DBBA

CHAPTER 9

9.1 Variation of the effectiveness of grafted antioxidant with structure

To study the effect of substituents on the benzene ring towards antioxidant activity a series of grafting reactions were carried out with different types of vinyl compounds.

All the reactions were done under the pre-determined optimum conditions listed below. The reactions were carried out under the standard conditions described in Chapter 4 using 30% partially deammoniated latex.

Initiation system - TBHP/TEP

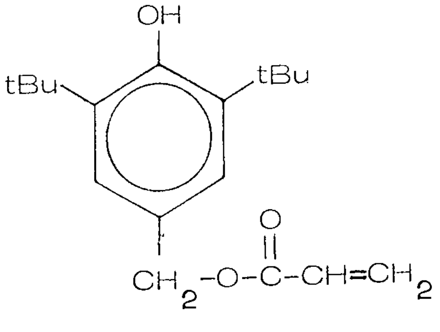
Swelling time - 30-45 minutes

Temperature of the reaction - 55-60°C

Duration of the reaction - 18 hours

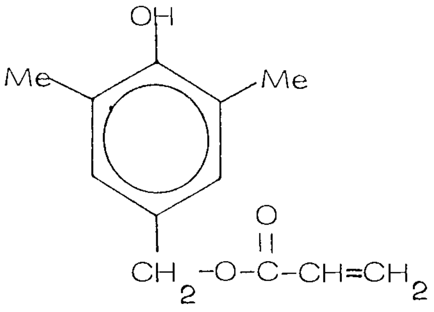
The following vinyl compounds were selected for the grafting reactions.

(a) 3,5-di-tert-butyl-4-hydroxy benzyl acrylate



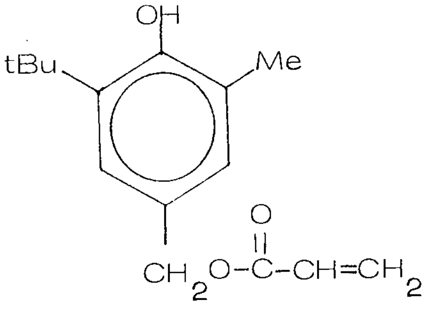
DBBA

(b) 3,5-di-methyl-4-hydroxy benzyl acrylate



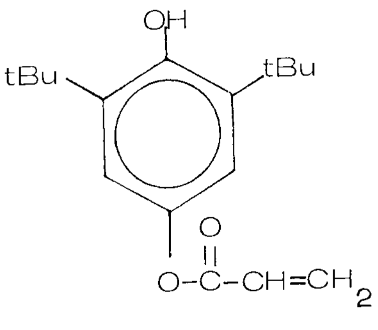
DHBA

(c) 3-tert-butyl-5-methyl-4-hydroxy benzyl acrylate



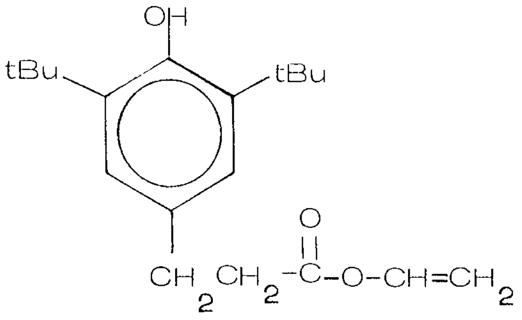
DMBA

(d) 3,5-di-tert-butyl-4-hydroxy phenyl acrylate

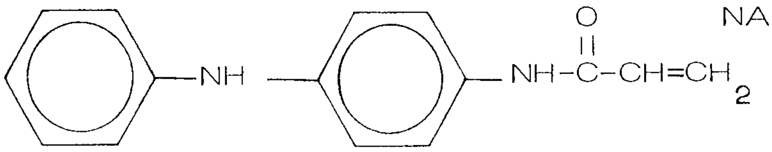


DBPA

(e) Vinyl β 3,5-di-tert-butyl-4-hydroxy phenyl propionate


VBPP

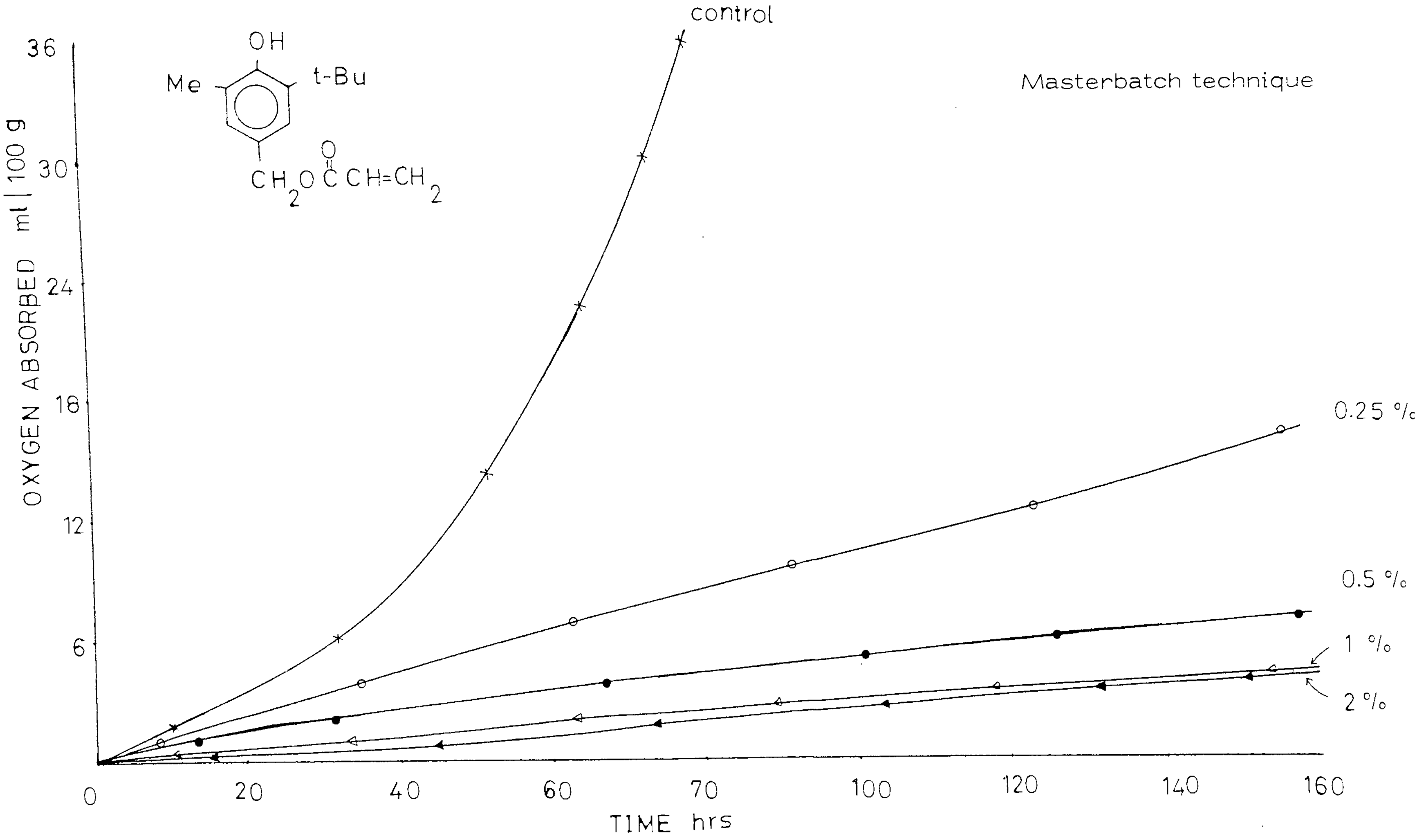
(f) N-(4-anilinophenyl) acrylamide


NAPA

The masterbatch technique described on page 79 was carried out with some of these vinyl compounds which were seen to be effective antioxidants.

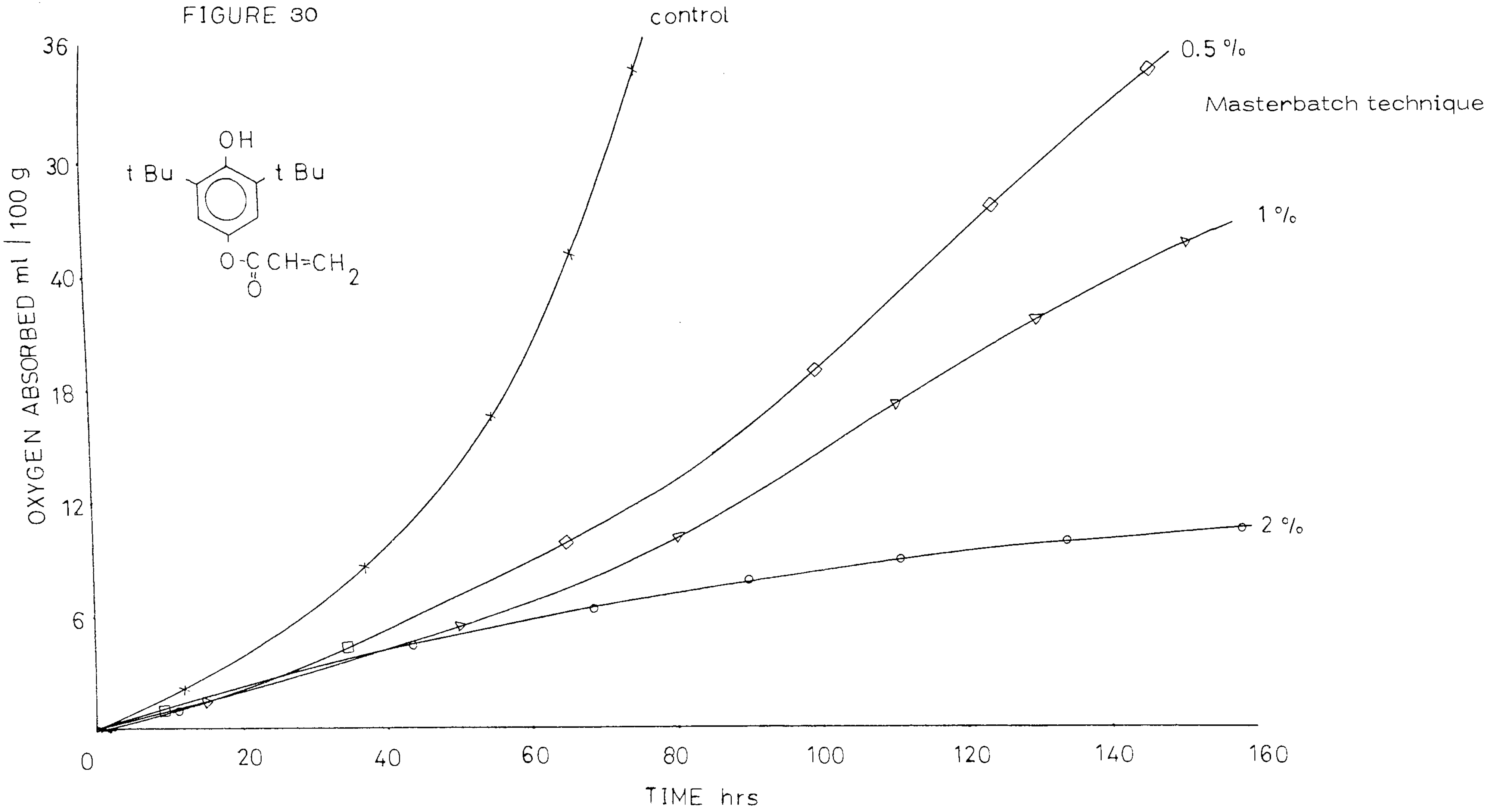
Figures 22, 23, 29-34 and the table below illustrate the oxidative stability of the antioxidant modified vulcanisates prepared by grafting the above mentioned vinyl compounds.

FIGURE 29



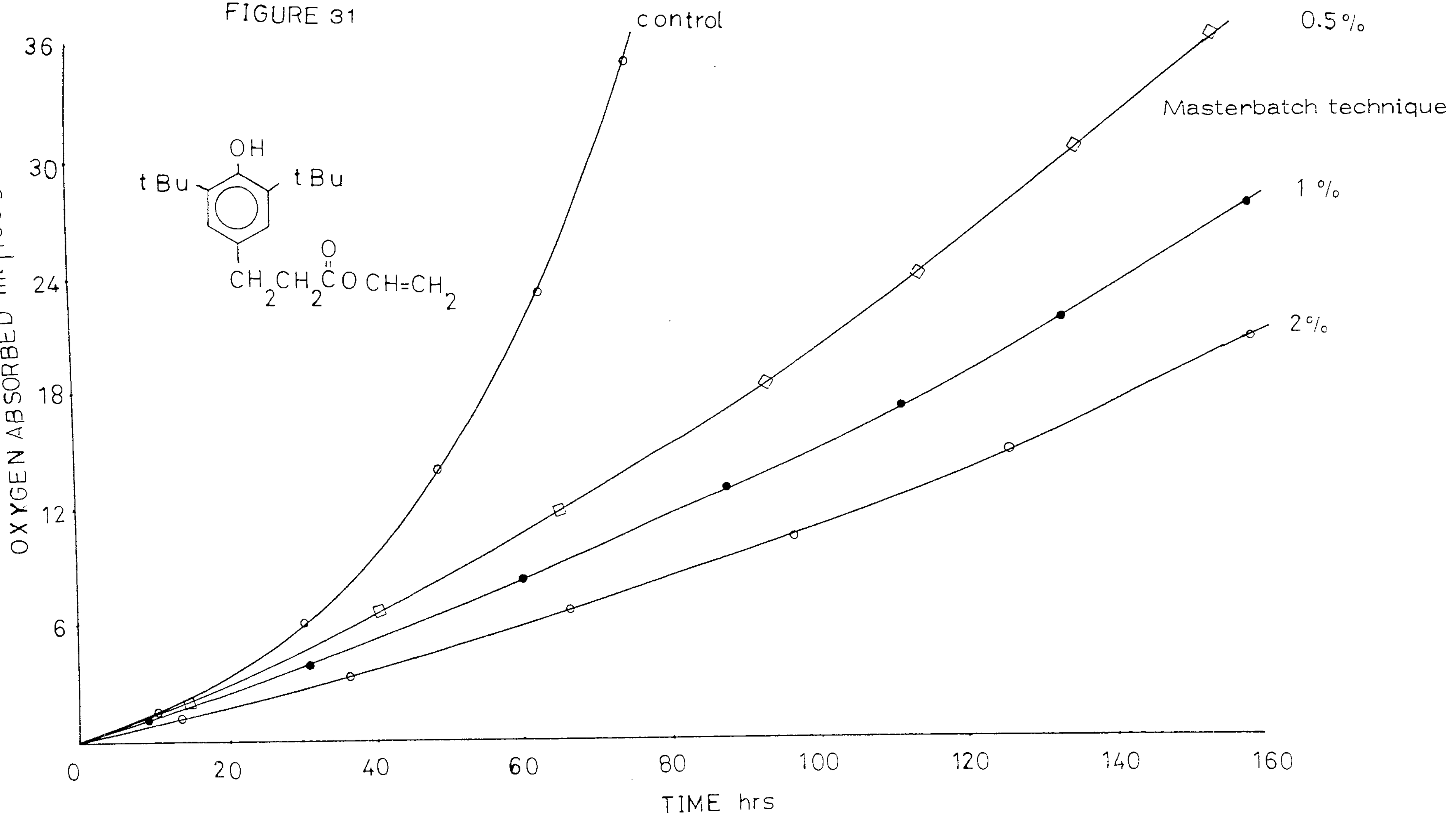
The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 30



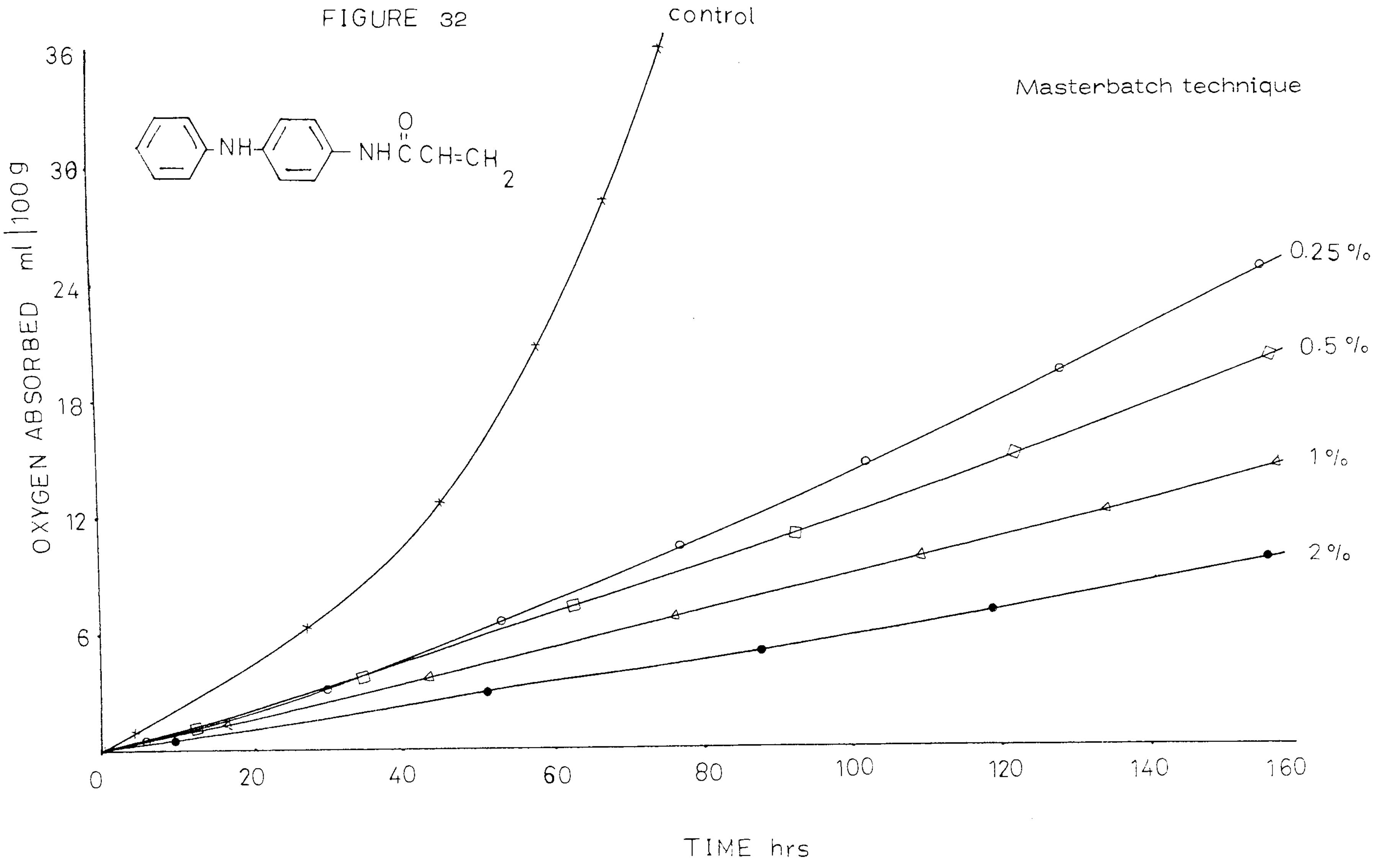
The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 31



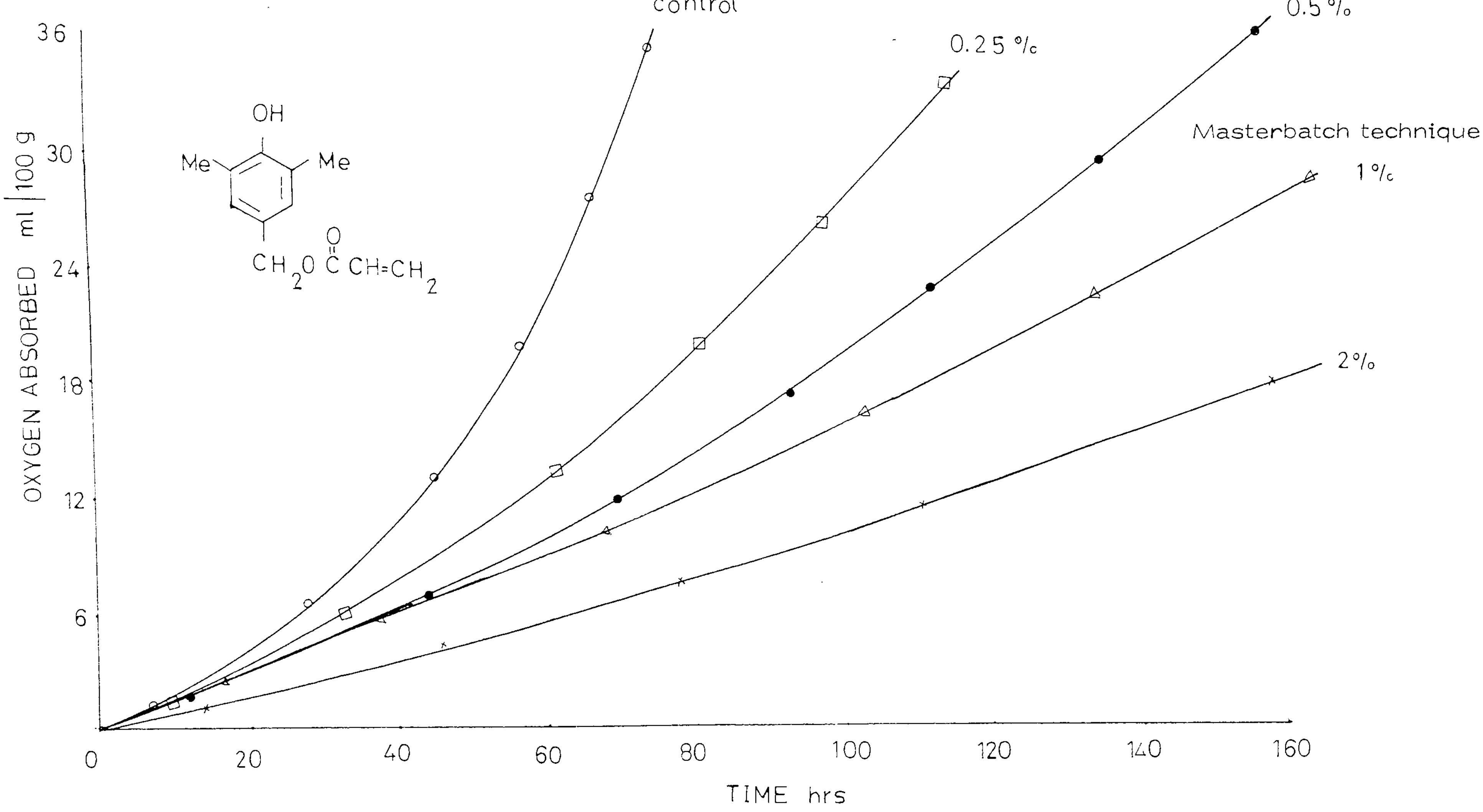
The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 32



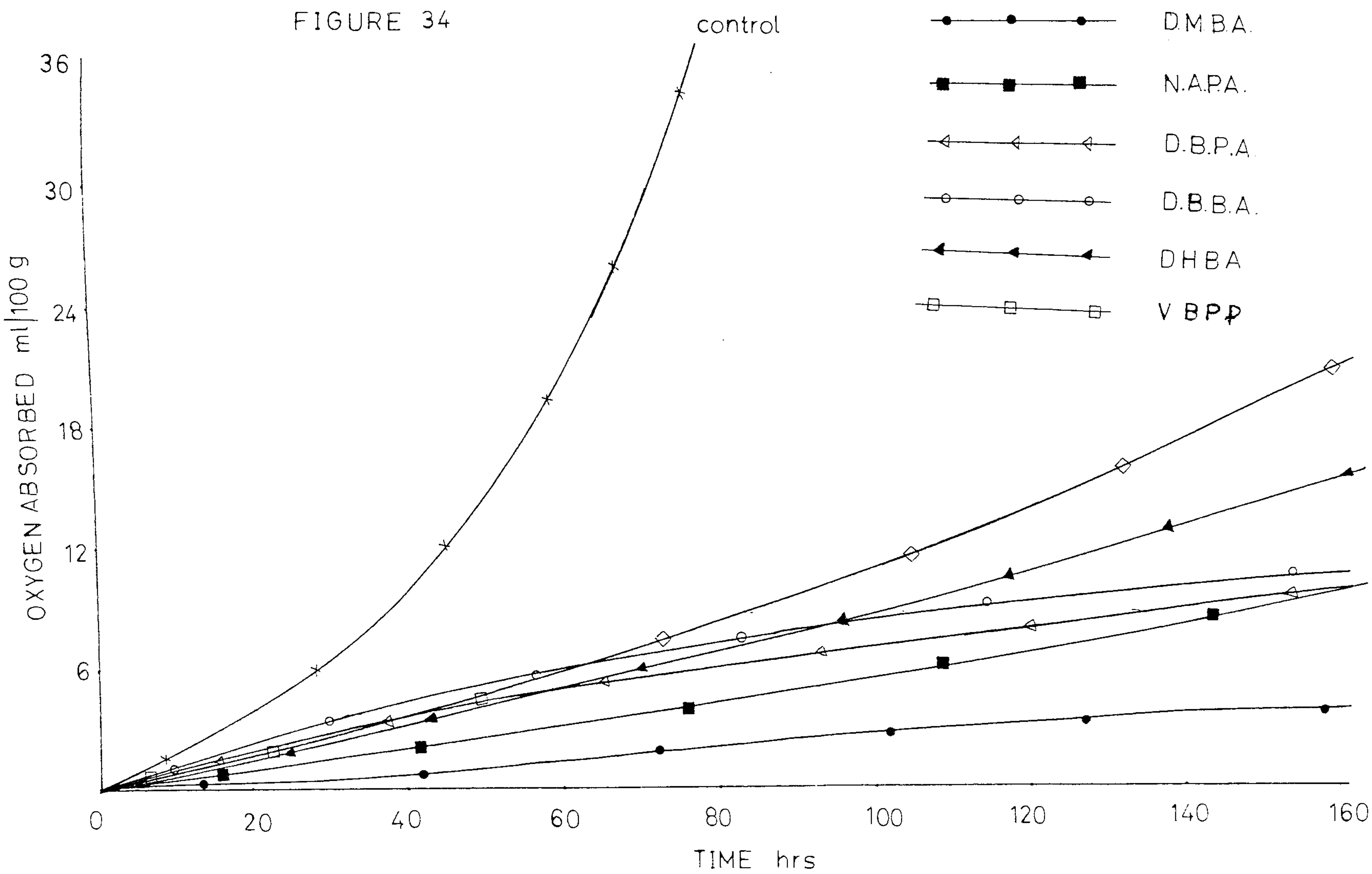
The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 33



The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 34



The rate of oxygen absorption of vulcanisates containing vinyl antioxidants at 70°C

2 g added to 100 g rubber

Type of antioxidant	Added amount for 100 gms of rubber	Time to absorb 3% oxygen hours
–	–	40
DBBA	2	103
DMBA	2	310
DHBA	2	87
DBPA	2	132
VBPP	2	83

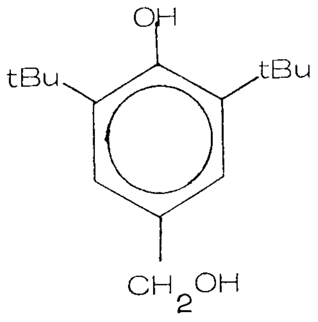
According to the oxygen absorption studies it was found that the most effective bound antioxidant is DMBA. The other antioxidants such as DBBA and DBPA also showed a remarkable antioxidant activity but all three antioxidants gave a light yellow colour to the ultimate grafted rubber. With NAPA a dark grey product was obtained which also confers a very good oxidative resistance. The grafted rubber obtained with the vinyl ester of 2,6-di-tert-butyl-4-hydroxy propionic acid (VBPP) showed very little colour change and it was found that a relatively small amount has been grafted into the rubber network and this is probably the reason for the lower stability of the grafted rubber. However, the dispersion obtained with this compound was poor. Several attempts were made to obtain a good dispersion by varying the time and rate of mixing, the concentration of dispersol LN and the water content.

In the reactions with DBBA and DMBA during the first few minutes an intense yellow colour was obtained in the latex but gradually the colour intensity decreased. Because of this peculiar colour change it was thought that the disappearence of the colour might be due to the grafting of quinones or other intermediate compounds to the rubber network.

In order to check this, initially a grafting reaction was carried out with 2,6-di-tert-butyl benzoquinone using the standard TBHP/TEP initiator system. The reaction was carried out under exactly the same conditions described on page 61.

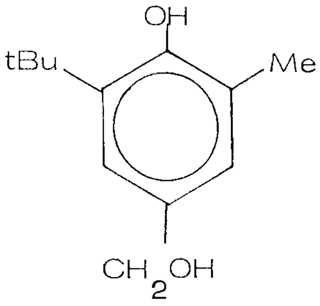
The grafted rubber obtained was intensely yellow in colour and also it did not show any sign of grafting or antioxidant activity. Following the identification of the other components of the grafting system by hydrolysis of the vinyl compounds (see Chapter 7) the grafting reactions were extended to hydroxy methyl phenols and to other conventional antioxidants. The compounds selected for this purpose were.

(a) 3,5-di-tert-butyl-4-hydroxy benzyl alcohol



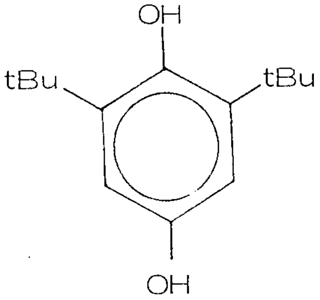
DTBA

(b) 3-tert-butyl, 5-methyl-4-hydroxy benzyl alcohol



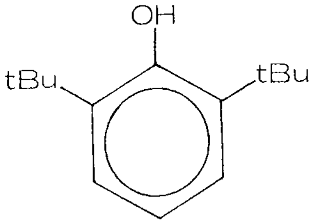
DTMA

(c) 2,6-di-tert-butyl hydroquinone



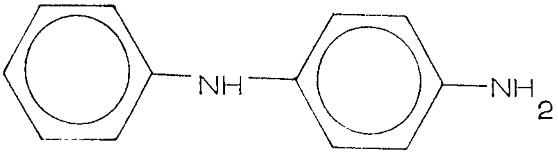
DTH

(d) 2,6-di-tert-butyl phenol



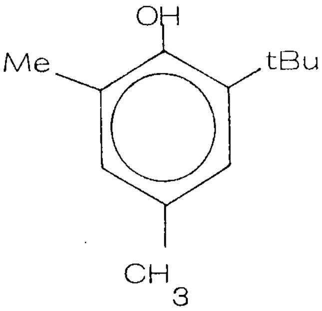
DTP

(e) 4-amino p-phenylene diamine

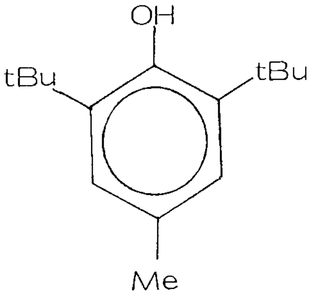


APD

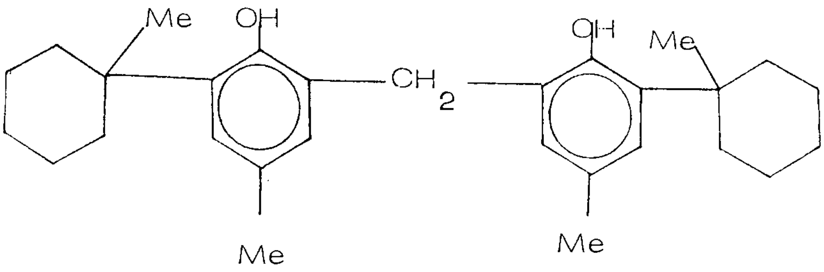
(f) Topanol A



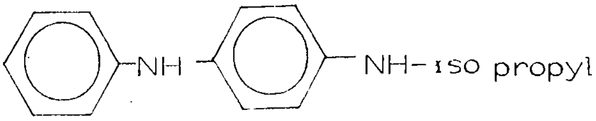
(g) Topanol OC



(h) Nonox WSP

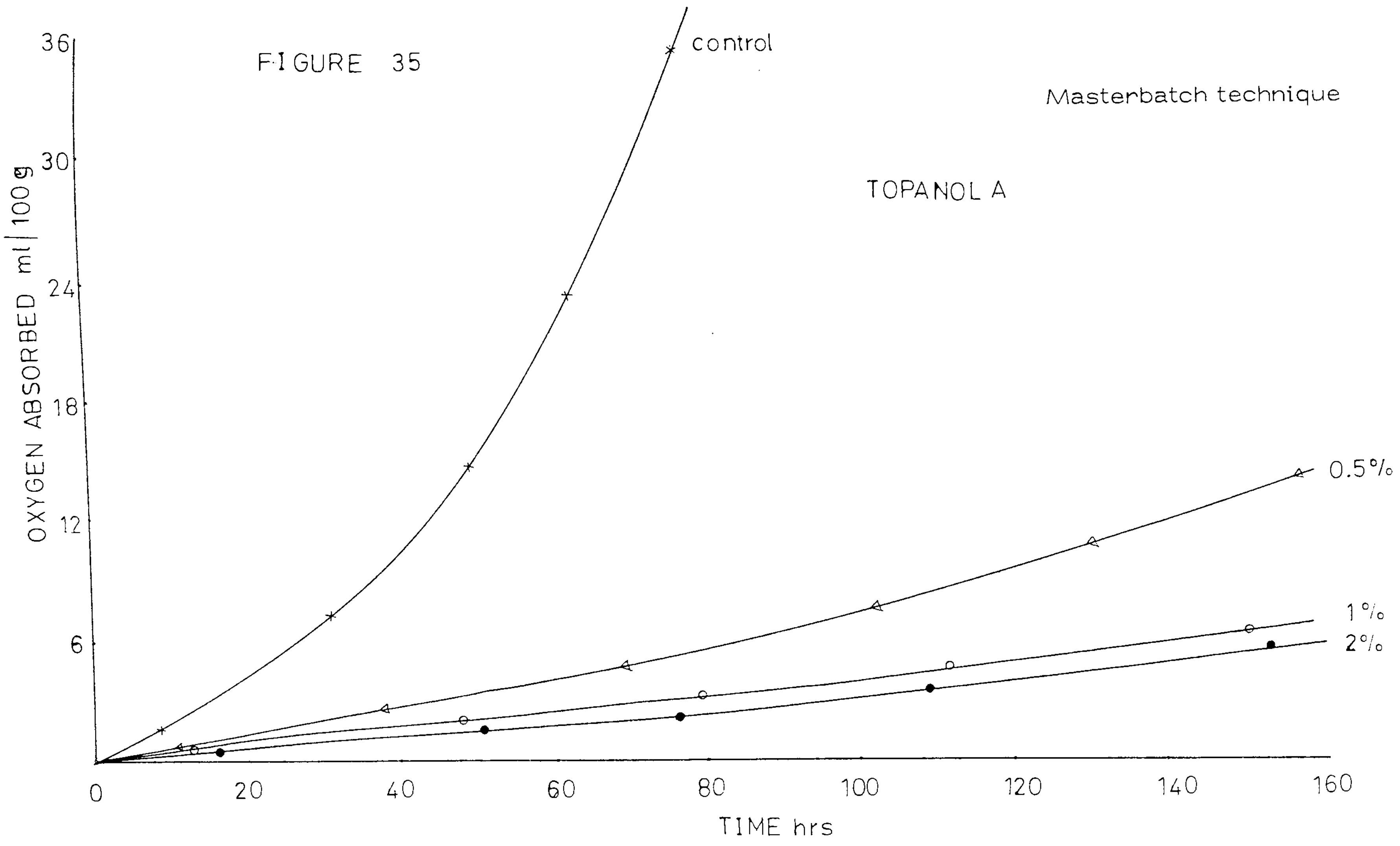


(i) Nonox ZA



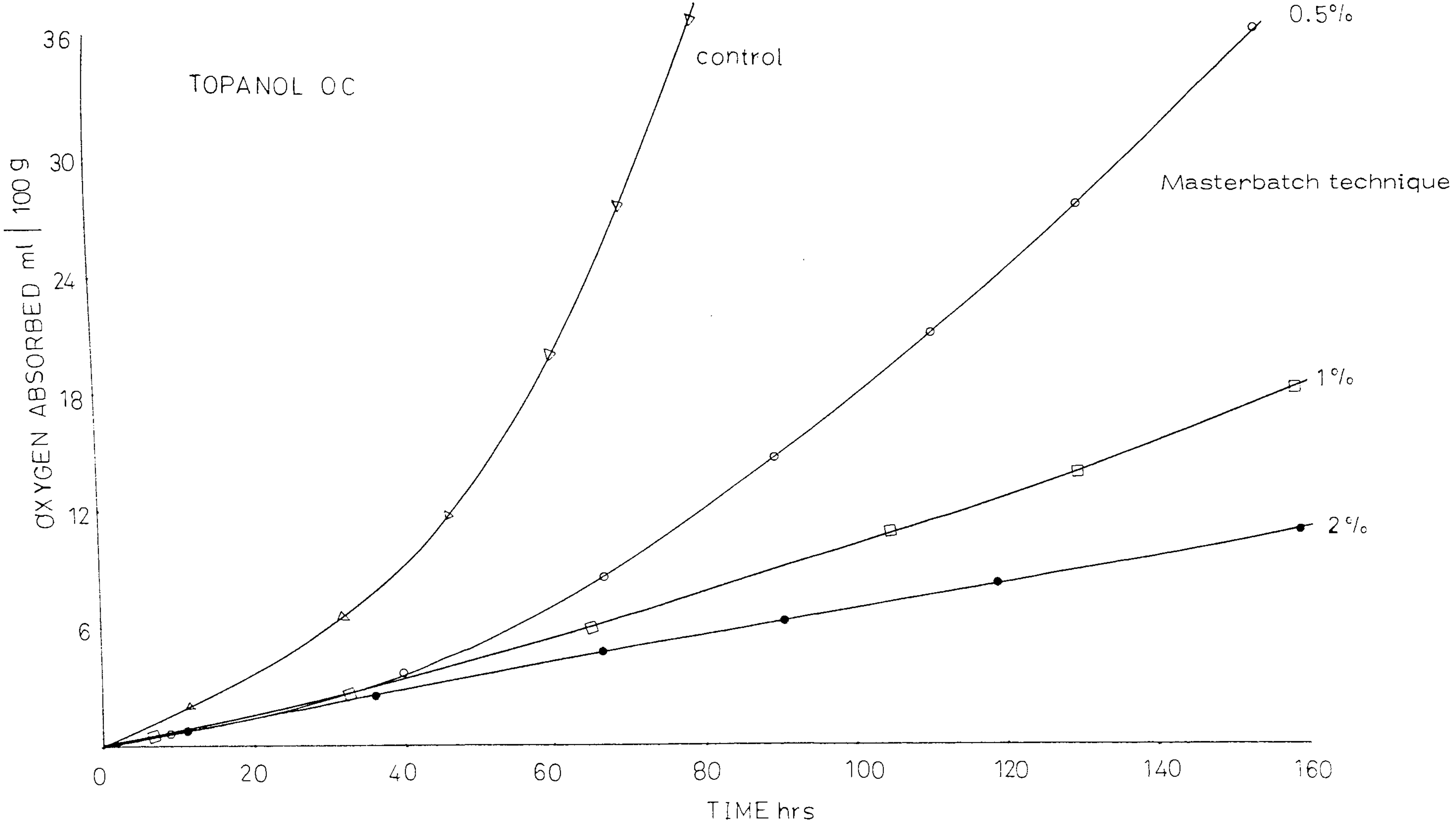
All the compounds listed above were reacted with rubber latex either in the form of a dispersion or in emulsion. The grafting reactions were carried out under exactly the same predetermined optimum conditions under a nitrogen atmosphere. The treated latex was coagulated, dried and extracted with the azeotrope prior to vulcanisation. Oxygen absorption tests were carried out with the vulcanisates at 70°C. The results are illustrated in figures 35-37.

FIGURE 35



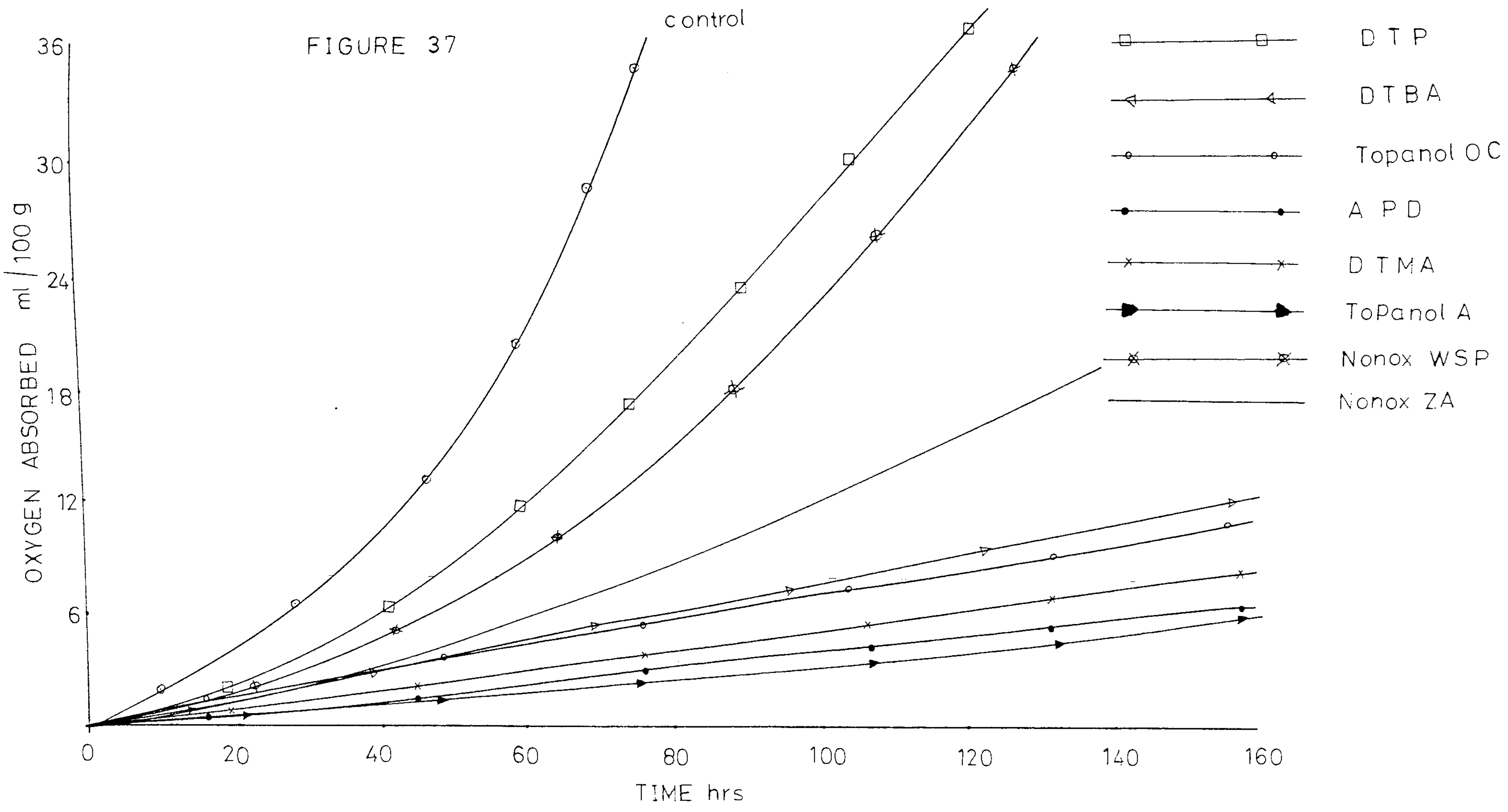
The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 36



The rate of oxygen absorption by the vulcanisates at 70°C

FIGURE 37



The rate of oxygen absorption of the vulcanisates containing commercial antioxidants at 70°C

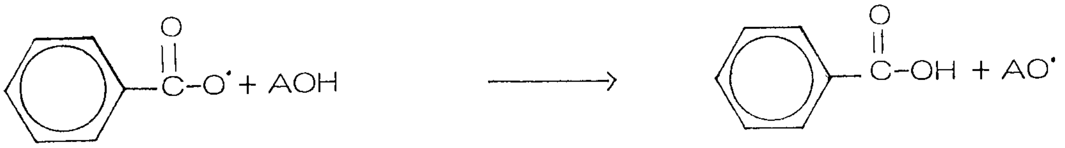
2 g added to 100 g rubber

9.2 Results and discussion

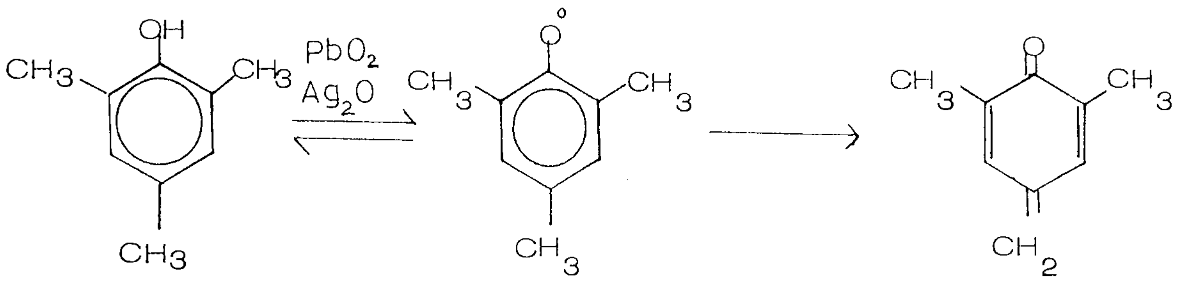
Outstanding stability was observed in the samples grafted with Topanol A, DTMA and Topanol OC.

There are some suggestions from the above results that a p-methyl or methylene group in the 4 position may be important and to understand the nature of the linkage with the polymer it is essential to understand the reaction of these phenols with the free radical generators.

Westfahl and Co workers have carried out thermal decomposition of benzoyl peroxide at 80°C in the presence of the phenolic antioxidant (70) and they observed that when a phenolic antioxidant is present, the very reactive benzoyloxy and phenyl radicals abstract a hydrogen atom from the hydroxyl group of the antioxidant to form benzoic acid or benzene and the much more stable phenoxyl radicals.



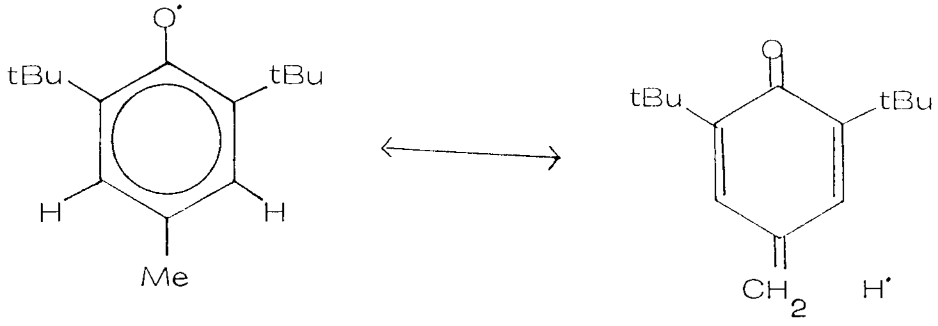
Filar and Winstein have demonstrated the formation of a quinone methide by shaking a solution of mesitol with silver oxide or lead dioxide[71].



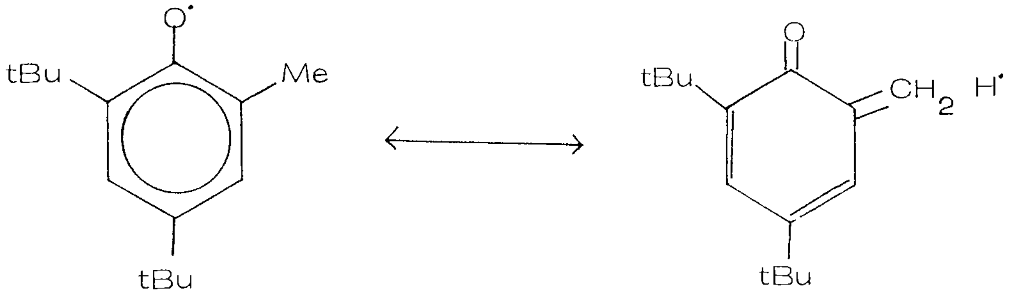
They have suggested that the formation of quinone methides proceed through the corresponding aryloxy radicals.

Cosgrove and Waters[72] obtained 4,4-di-hydroxy-3,3^1,5,5^1-tetra methyl-diphenyl methane among the products of the oxidation of mesitol with Fenton's reagent and more recently, the aryloxy radical has been identified by electron magnetic resonance as a stable and product of the oxidation of 2,6-di-tert-butyl-4-methyl phenol[73].

Reactive phenoxy radicals have been studied by Becconsall and Co workers using electron spin resonance[73]. They obtained four-triplet spectra from the radicals I and II, indicating a major interaction of the unpaired electron with the three hydrogens of the methyl groups and a minor interaction with the meta hydrogens.



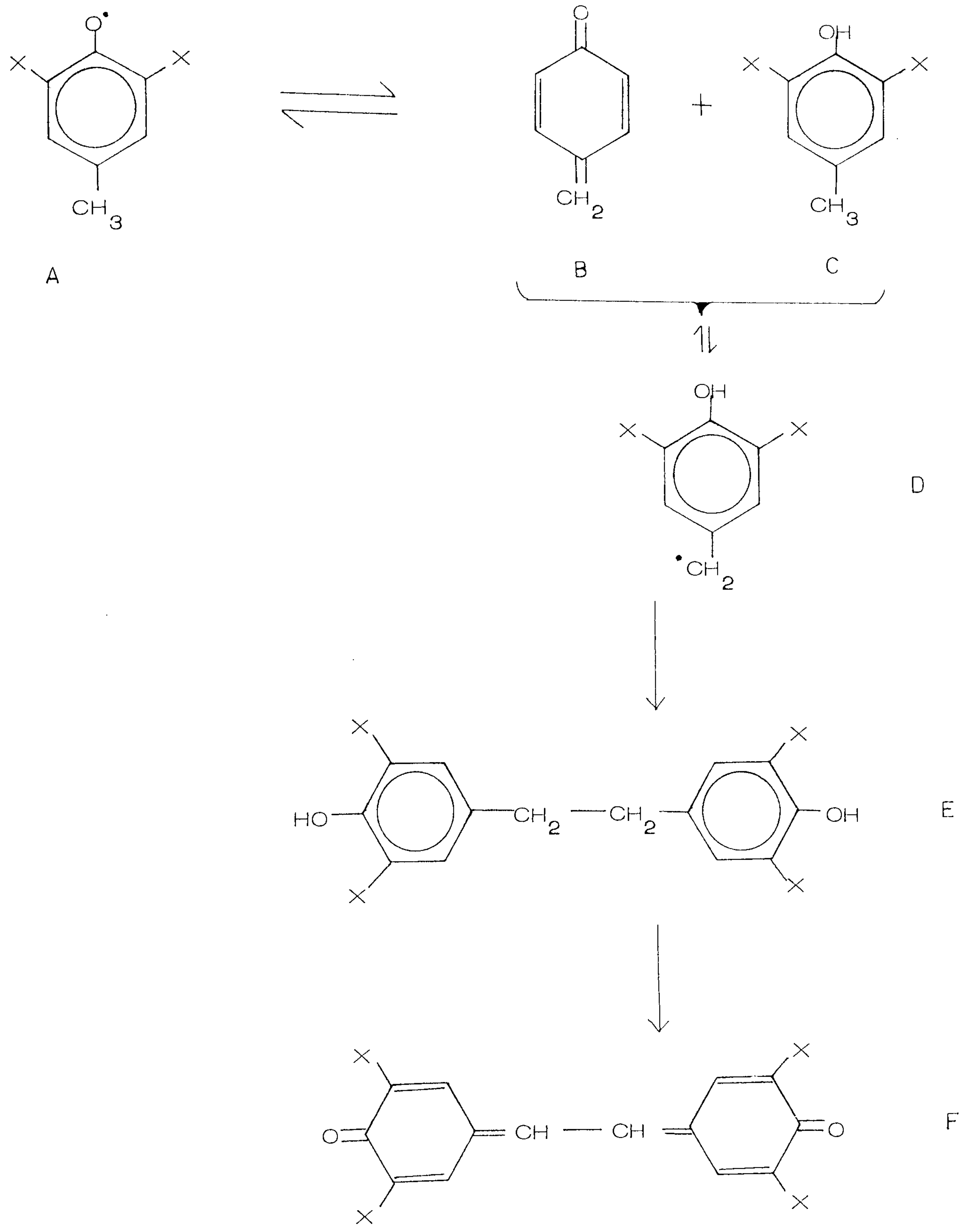
Ia Ib



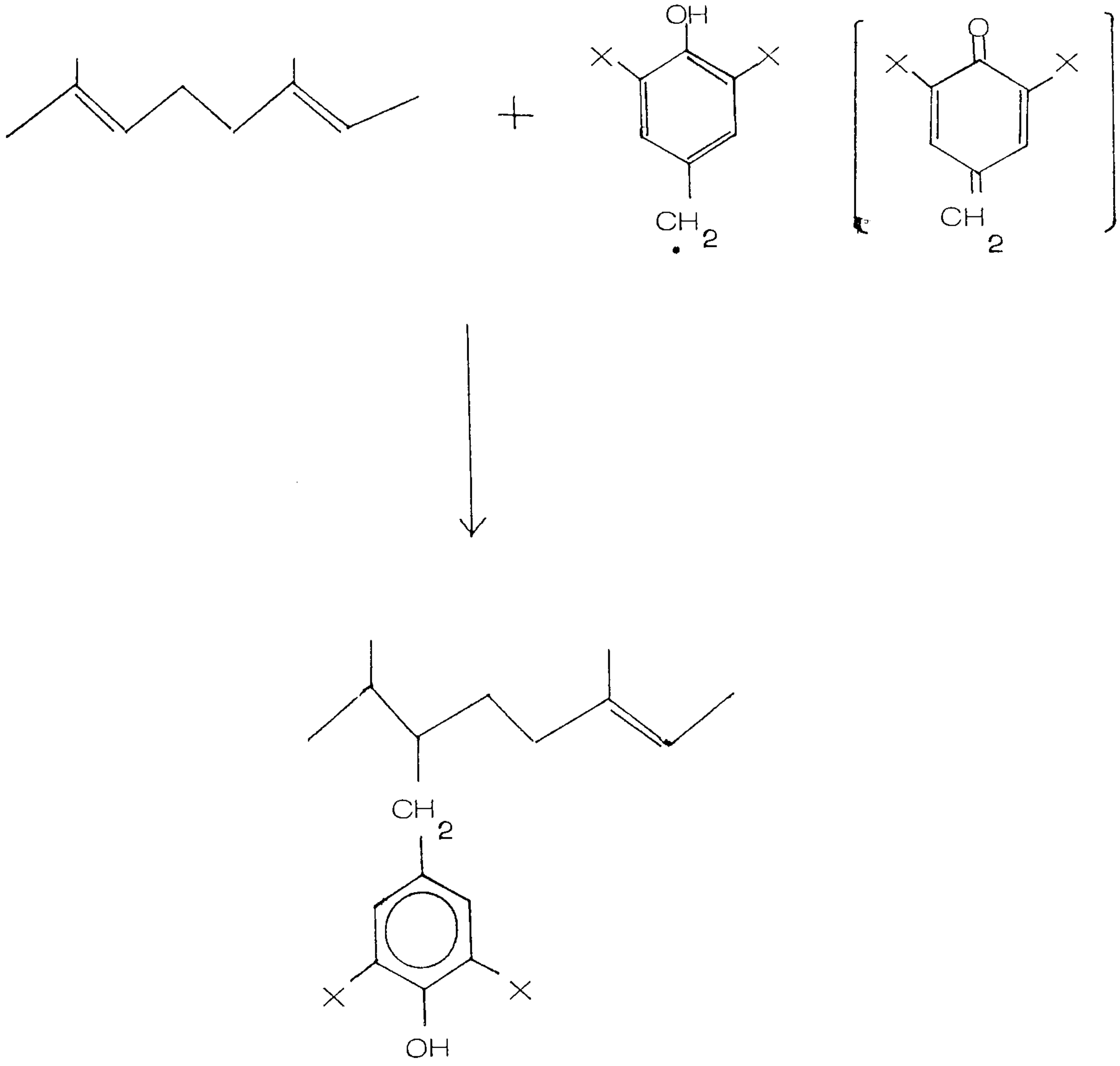
IIa IIb

Quinone methides formed from Topanol A or Topanol OC could possibly react with the rubber chain by addition to the double bond. However, recent studies by K Smith[77] have indicated that quinone methides appear to react with rubber only at high temperatures.

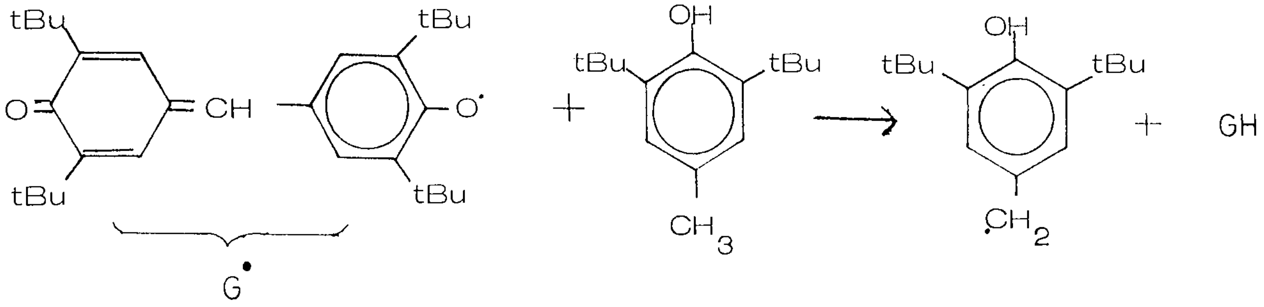
The aryloxy radical is in reversible equilibrium between structures A, B and C.

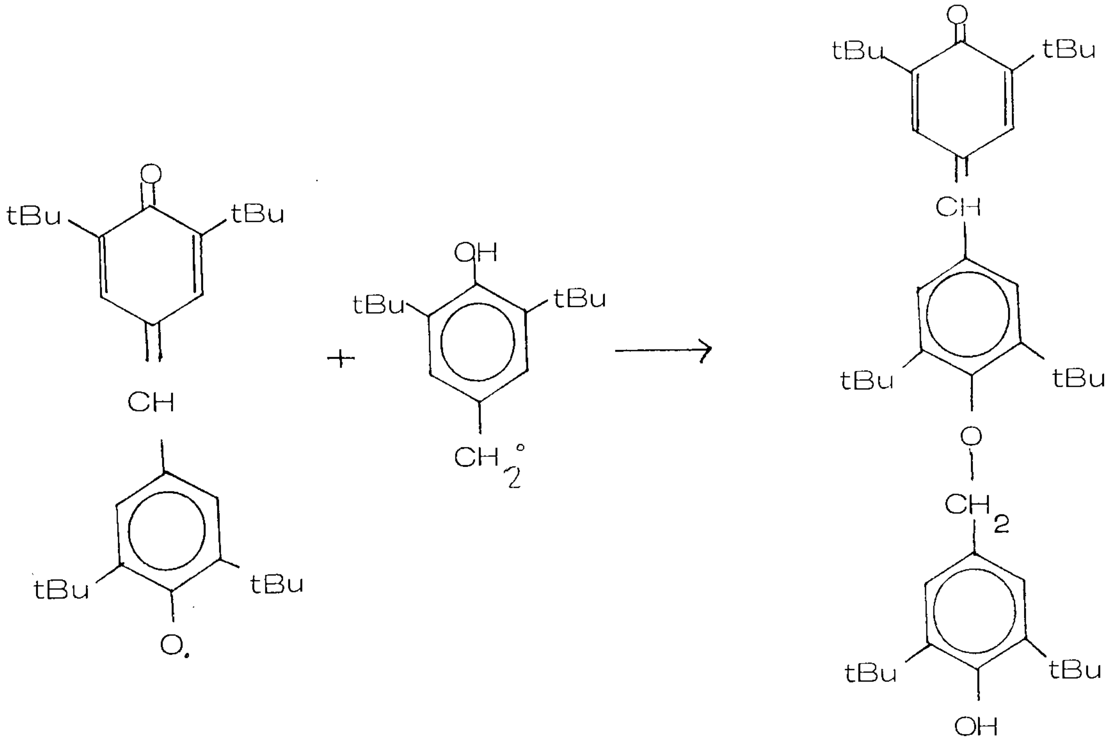

A
B
C
D
E
F
O•
X
CH3
O
CH2
OH
•CH2
HO
CH2
CH
+

If the benzyl radical D exist in the medium without attacking the polymer chain it should dimerise to give E, and it should get oxidised to F which is intense yellow. But there was not a serious colour change. This confirms the idea of a reaction between rubber and the benzyl radical.



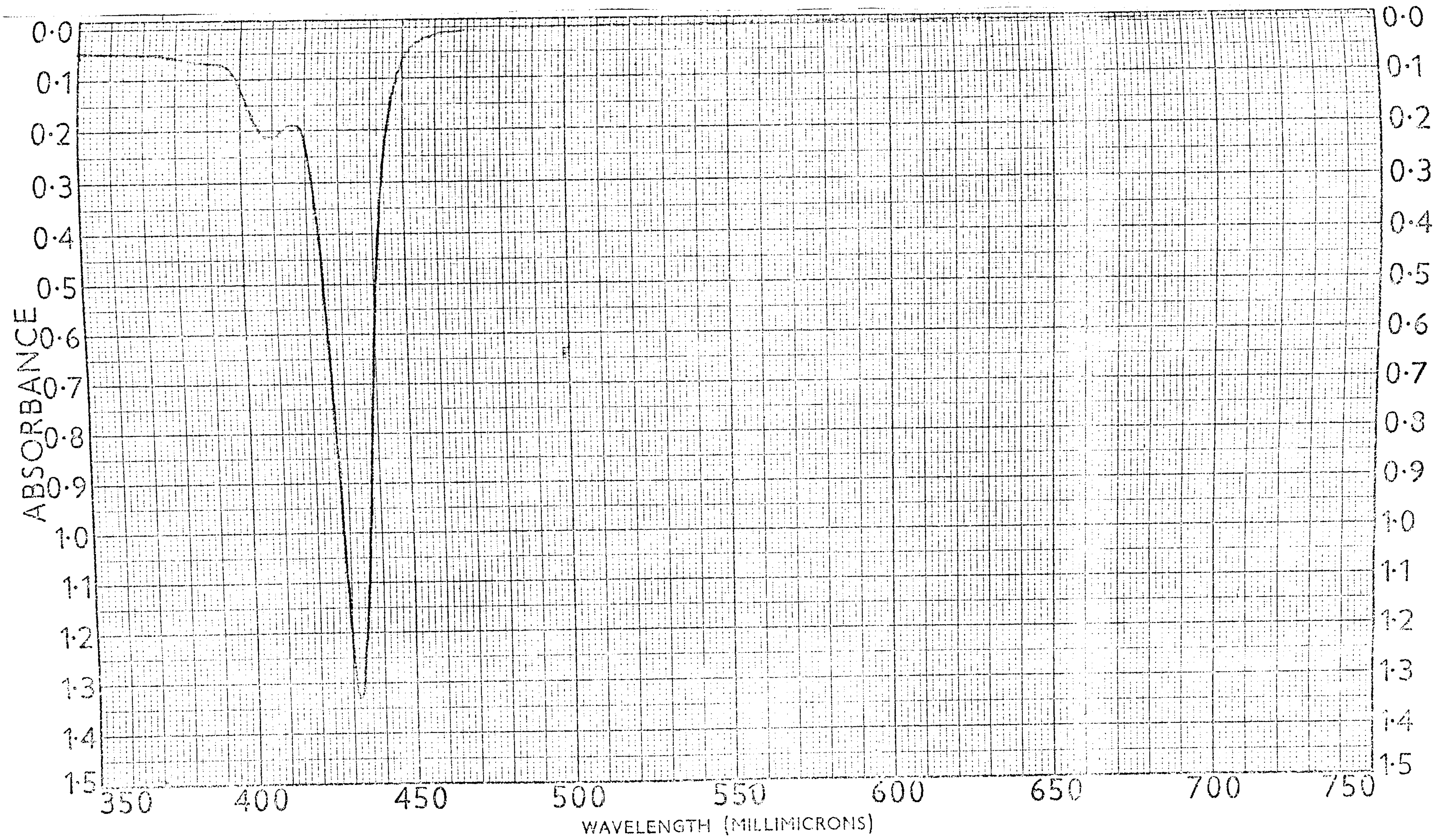
On the other hand, if benzyl radicals form during the reaction, it should be able to trap these by Galvinoxyl. As a result, the colour of the Galvinoxyl should disappear. The possible reactions are as follows.



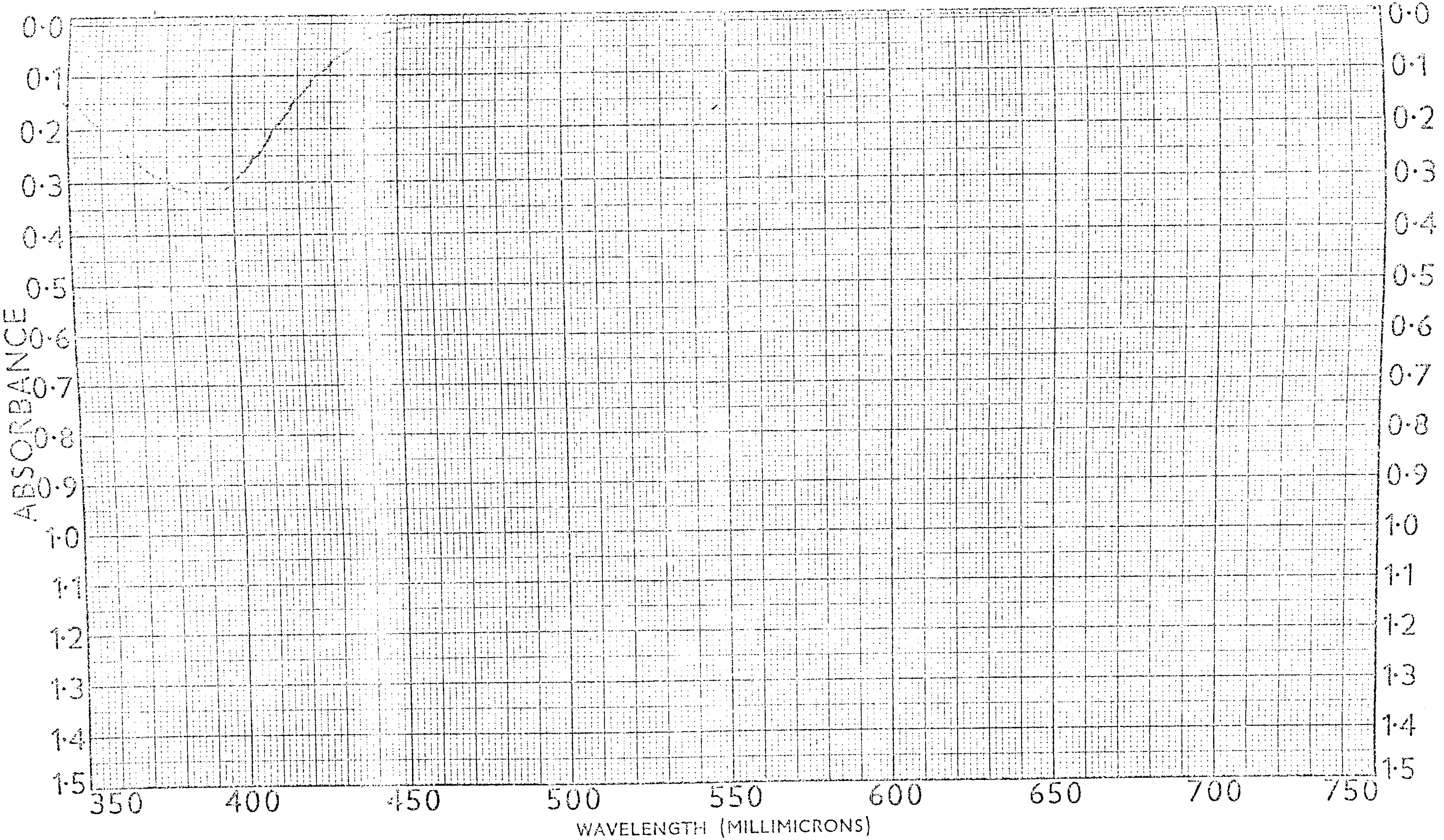


A reaction was carried out with 2 moles of Galvinoxyl and 1 mole of Topanol A in carbon tetrachloride.

The initial dark colour was gradually changed into orange and then to colourless. The reaction was followed by the visible



Visible spectrum of Galvinoxyl



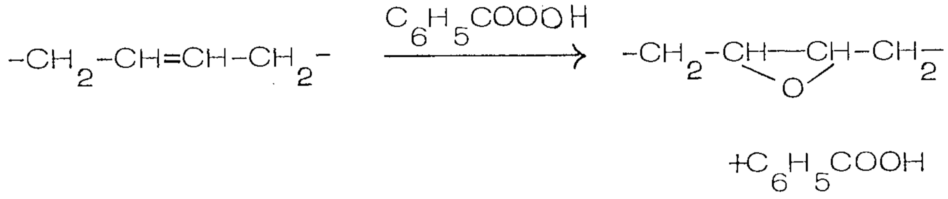
Visible spectrum of a mixture of Galvinoxyl and Topanol A in CCl_4.
2 minutes after mixing the two solutions

spectroscopy. It shows a disappearence of a one peak and appearence of a new peak.

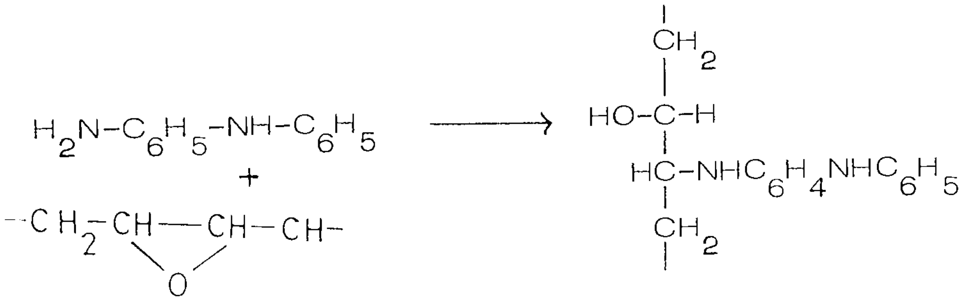
The above observations may prove the idea of a reaction between Topanol A and rubber via a benzyl intermediate.

Another feature observed with the vulcanisate was the remarkable stability of the p-amine diphenyl amine grafted samples. It is very unlikely to graft APD with a rubber molecule without any intermediate stage. Kirpicher and Yakubchik have grafted APD to epoxy polybutadiene[75] in toluene in the presence of a phenol. They have carried out the epoxidation of polybutadiene with benzoyl hydroperoxide.

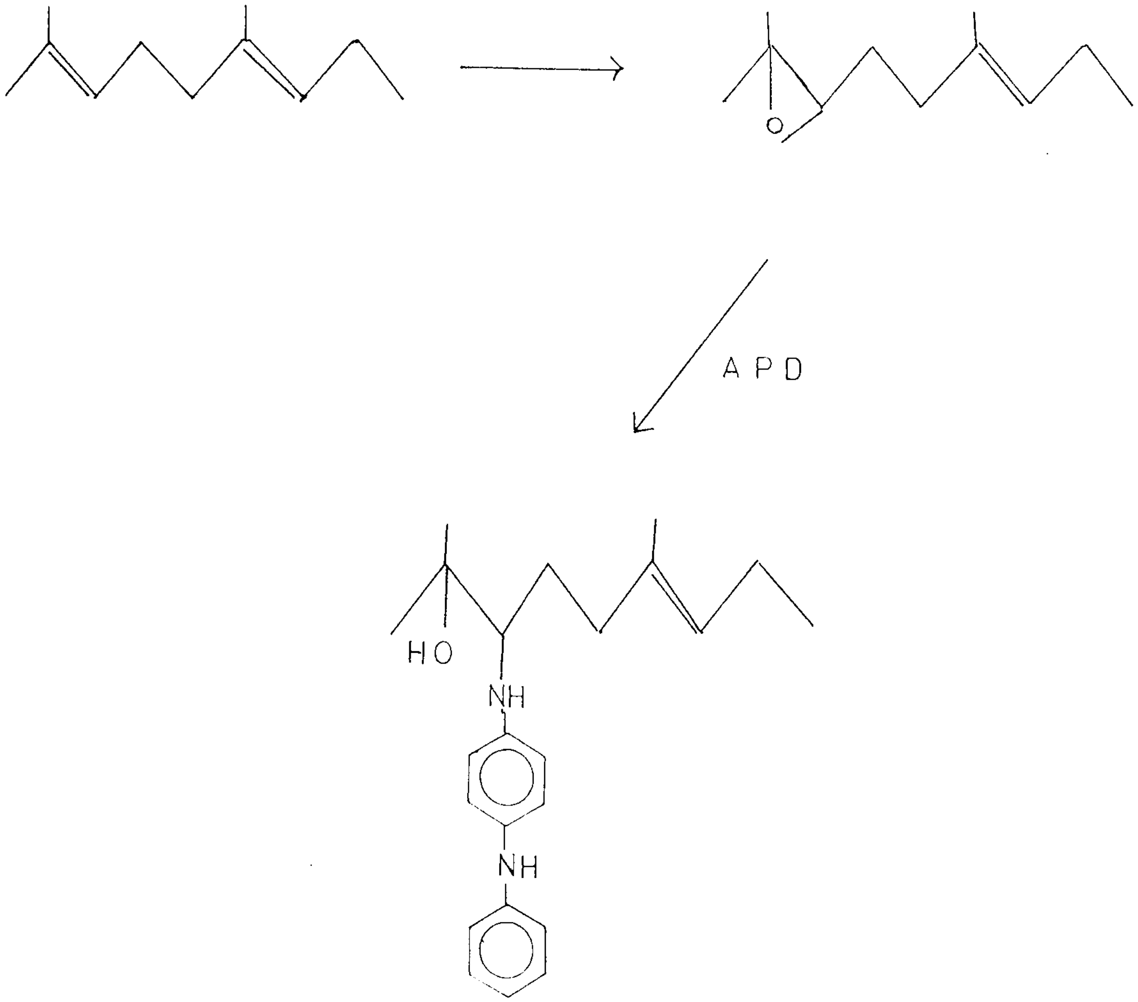
a)



b)



Therefore this kind of reaction is possible with the rubber molecule as well, in the presence of a hydroperoxide.



In all these experiments there is a possibility to trap the added antioxidant (Topanol A, Topanol OC, APD etc) within the rubber network instead of binding into the rubber chain. To eliminate this possibility dispersions of antioxidants were mixed with the rubber latex, coagulated, dried and extracted with the azeotrope. The vulcanisates were prepared and carried out the oxygen absorption test. As the samples did not show the expected stability towards oxidation it must be concluded that the added antioxidants are chemically bound to the rubber in the presence of free radical generators.

Type of antioxidant	Time to absorb 1% oxygen hrs	Time to absorb 3% oxygen hrs
Natural rubber (control)	18	–
Topanol A	95	205
APD	78	198
DTMA	62	143
Topanol OC	42	110
DBTA	41	100
Nonox WSP	30	55
DTP	25	47

One of the important conclusions emerges out from the above results is the relation between the structure and the efficiency of antioxidants. It is a known fact that the 2,6-di-tert-butyl substituted phenols are the most effective in polyolefins, but in rubber 2-methyl, 6-tert-butyl substituted phenol are most efficient.

The above results obtained from the grafted rubber confirms the theory of relative efficiency of antioxidants in rubber.

Another experiment was carried out to find out whether grafting reduces the mobility and hence antioxidant activity of the molecule. This was carried out as follows.

A sample of vulcanisate was prepared out of a DBBA grafted rubber latex and measured the actual percentage of DBBA grafted into the rubber network using infra-red spectroscopy technique. The same quantity of DBBA was mixed with 100 gms of extracted dry rubber and vulcanisate was prepared. Both vulcanisates, where one having DBBA in the form of grafting and the other having the same amount of DBBA in free form, were subjected into the oxygen absorption test and compared the rate of oxygen absorption by the samples. Figure 48 shows that there is a little difference between the effectiveness of the bound and unbound antioxidants when present in the rubber at the same concentration. This suggests that the bound antioxidant has adequate mobility in an elastomeric network to perform its function adequately.

CHAPTER 10

10.1 Assessment of vulcanisation characteristics

Vulcanisation is the process by which mainly plastic rubber is converted into the elastic-rubber or hard rubber state. The properties of the latter are decisively influenced by the course of vulcanisation. In particular, the modulus, hardness, elastic properties, resistance to swelling etc are considerably modified during the process of vulcanisation Other propoerties, such as tensile strength, gas permeability, low temperature flexibility and electrical resistance changes less with the degree of vulcanisation Almost all the rubber used in the world is vulcanised by various techniques depending on the requirements of the fabricated article

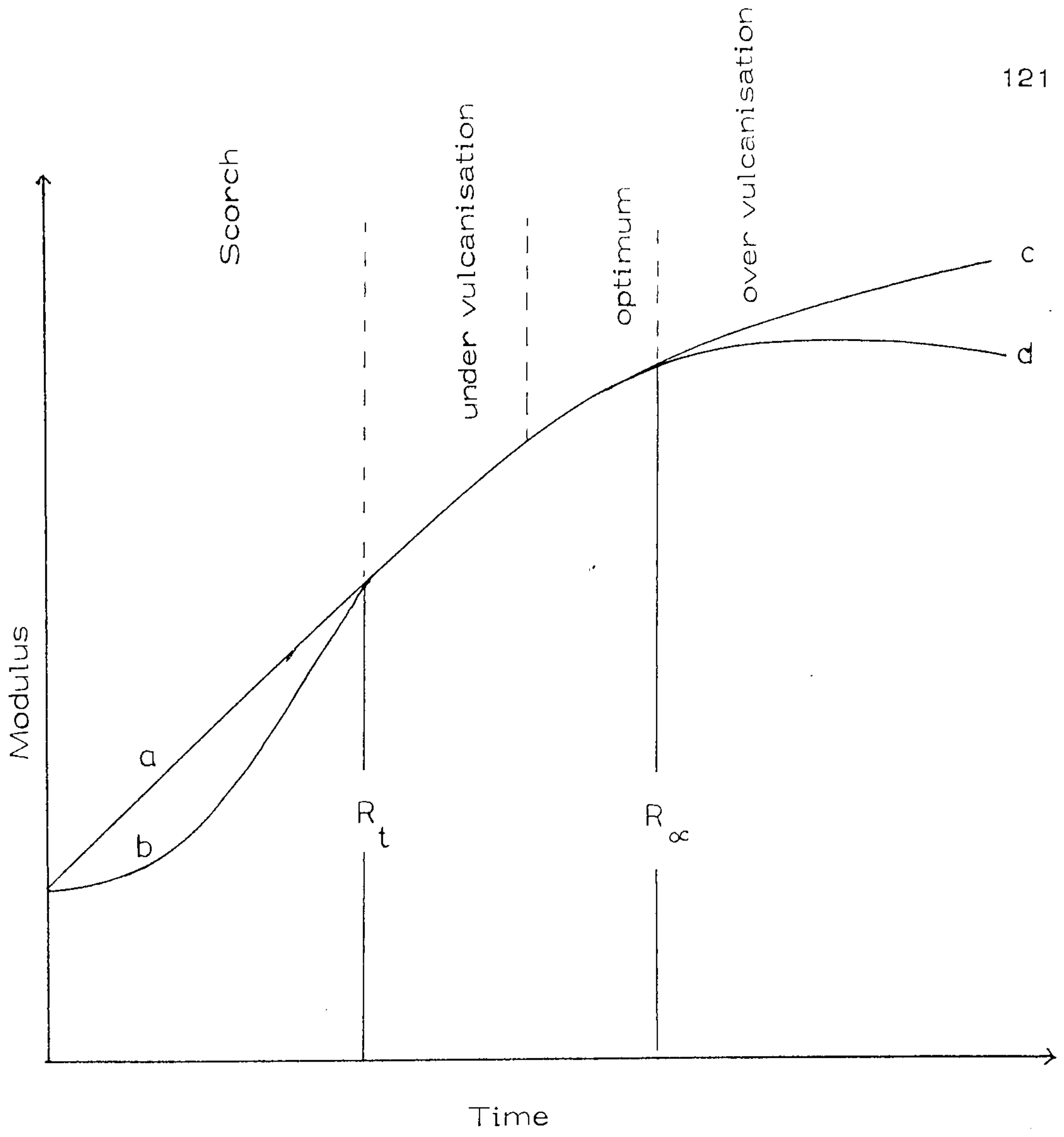
In this work the vulcanisation characteristics of grafted rubber was determined using the Monsanto Oscillating Disc Rheometer operated according to the following conditions:

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

A curve obtained from a Monsanto Rheometer provides information regarding the time to desired extent of cure time before the onset of cure, the rate of cure and the degree of cure. Therefore, it is worthwhile to mention briefly the theoretical aspects of this procedure.

The Monsanto oscillating disc rheometer consists of a bi conical disc surrounded by the compound specimen, contained in a cavity. The temperature of the sample, cavity and the disc was maintained at a desired temperature (± 0.5°C) by means of electrical heating. The cavity is made up of 2 discs which held together by the ram of a p eumatic cylinder. The disc oscillated sinusoidally. The shaft of the disc is connected to a torque transducer which indicate the force required to oscillate the disc and thus 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 vulcanisate, there is an initial drop in torque which indicates the melting of the rubber or its drop in viscosity. This is followed by an induction period after which the torque increased steadily showing that curing is taking place. After a certain period of time the torque reaches its maximum. In certain cases this maximum can increase or decrease, after some time, indicating over-vulcanisation or reversion respectively. Reversion is due to breaking down of cross-links.

A typical rheometer curve obtained with Monsanto disc rheometer is shown below:



(a) Compounds with rapid onset of vulcanisation

(b) Compounds with delayed onset of vulcanisation

(c) Compounds with rising modulus

(d) Compounds with reversion tendencies

A more accurate kinetic interpretation of this curve suggested by Coran[76] is as follows.

Assuming that cross-link formation is a first-order reaction after an induction period t_2.

$$\frac{dv}{dt} = K\,(V_{\infty} - V_t)$$

where

K = the overall first-order rate constant

V_t = the cross-link density at time t

V_{∞} = the maximum cross-link density

t = the time in minutes

t_i = the induction time in minutes

on integration the above equation

$$\int_{V_o}^{V_t} \frac{dv}{V_{\infty} - V_t} = K \int_{t_i}^{t} dt$$

$$\text{Therefore } \ln \left[V_{\infty} - V_t\right]_{V_o}^{V_t} = K[t]_{t_i}^{t}$$

$$\ln\left[\frac{V_{\infty} - V_t}{V_{\infty}}\right] = K(t - t_i) \text{ -------(1)}$$

It has been shown that $V_t \alpha R_t$ when R_t = the torque developed at time t.

Therefore, $V_t = KR_t$

and similarly $V_{\infty} \alpha R_{max}$

$$V_{\infty} = KR_{max}$$

where, R_{max} = the maximum torque developed and is taken as a direct reading from the rheographs.

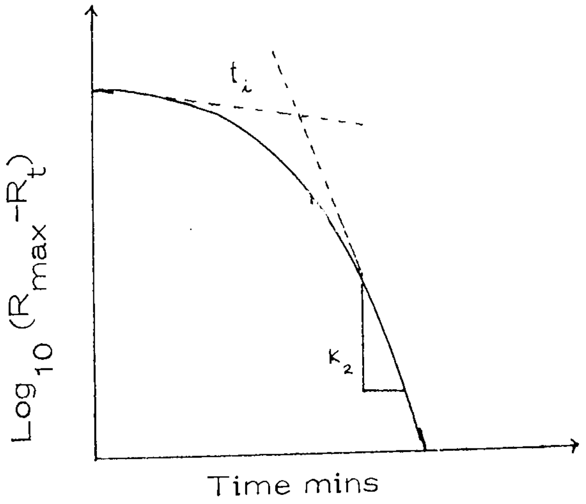
Substituting these values in equation (1) we have

$$\ln \frac{R_{max} - R_t}{R_{max}} = K\,(t-t_i)$$

$$\log_{10} (R_{max}-R_t) = \log_{10} R_{max} + \frac{K(t-t_i)}{2.303}$$

R_t and R_{max} can be directly read from the rheometer curve.

To obtain K, values of $\log_{10} (R_{max} - R_t)$ can be plotted against time (minutes).



$$\text{Slope} = \frac{K}{2.303}$$

$$K = \text{slope} \times 2.303 \text{ min}^{-1}$$

t_i is the time necessary for the reaction to become first-order. Therefore, the vulcanisation system becomes characterised by three parameters.

t_i - the induction period which is a measure of the time for the formation of an active sulphurating agent and the reaction of this with the hydrocarbon to form a rubber bound intermediate which is the precursor to cross-link formation.

K - the overall first order rate constant.

R_{max} - the maximum torque developed during the vulcanisation process which is a measure of the cross-link density.

Experimental

The following basic formula was used in making the gumstocks.

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

The compounds prepared from grafted rubber were cured in the Monsanto rheometer at 140°C for a period of 30 minutes (with a preheat time 60 seconds).

The curves obtained are shown in figures 38, 40 and 42.

The plot of $\log_{10}(R_{max}-R_t)$ against time is given in figures 39, 41 and 43.

FIGURE 38

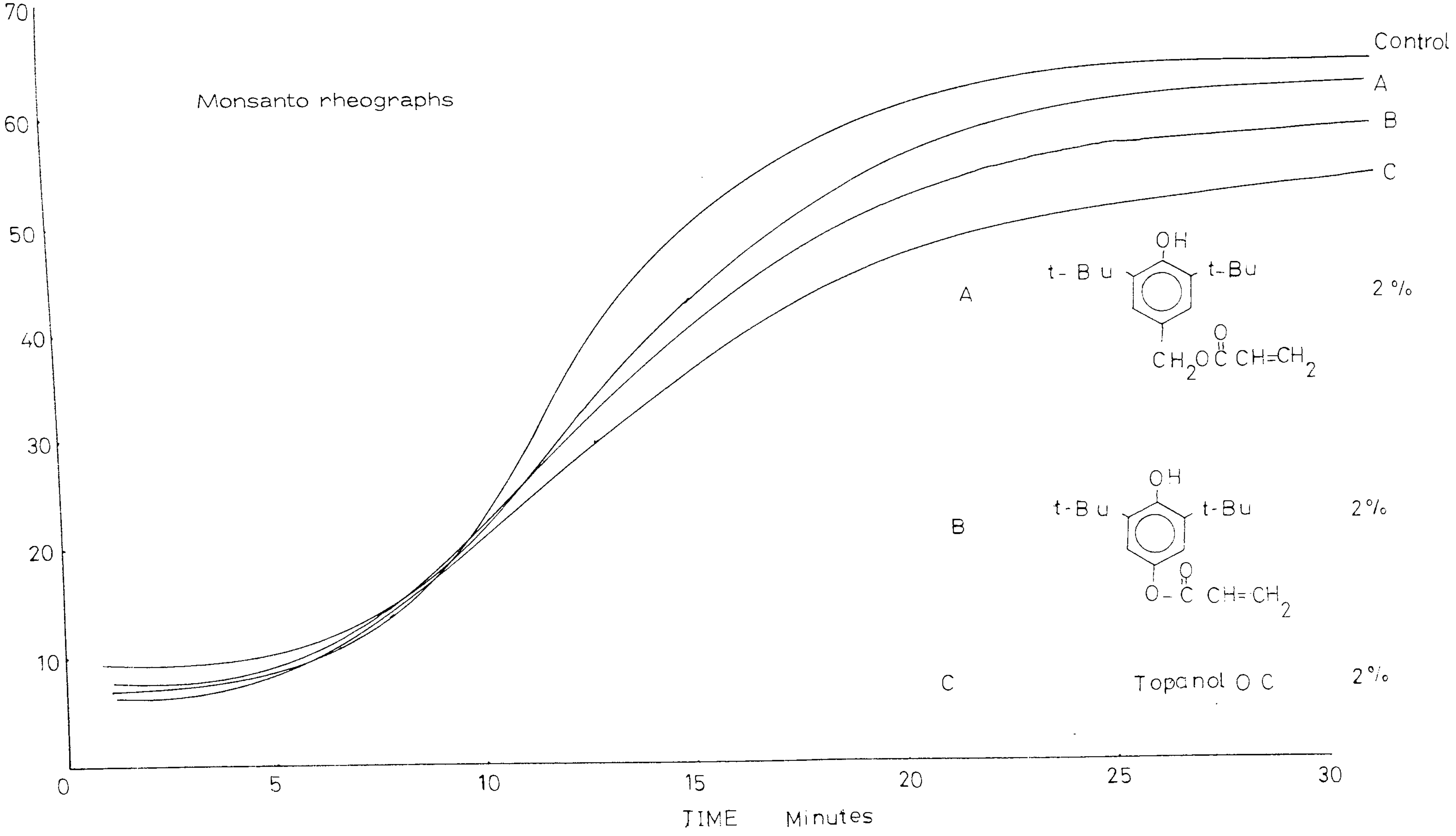

Monsanto rheographs
70
60
50
40
30
20
10
0
5
10
15
20
25
30
TIME Minutes
Control
A
B
C
A
t-Bu
OH
t-Bu
CH2OC(O)CH=CH2
2%
B
t-Bu
OH
t-Bu
O-C(O) CH=CH2
2%
C
Topanol O C
2%

FIGURE 39

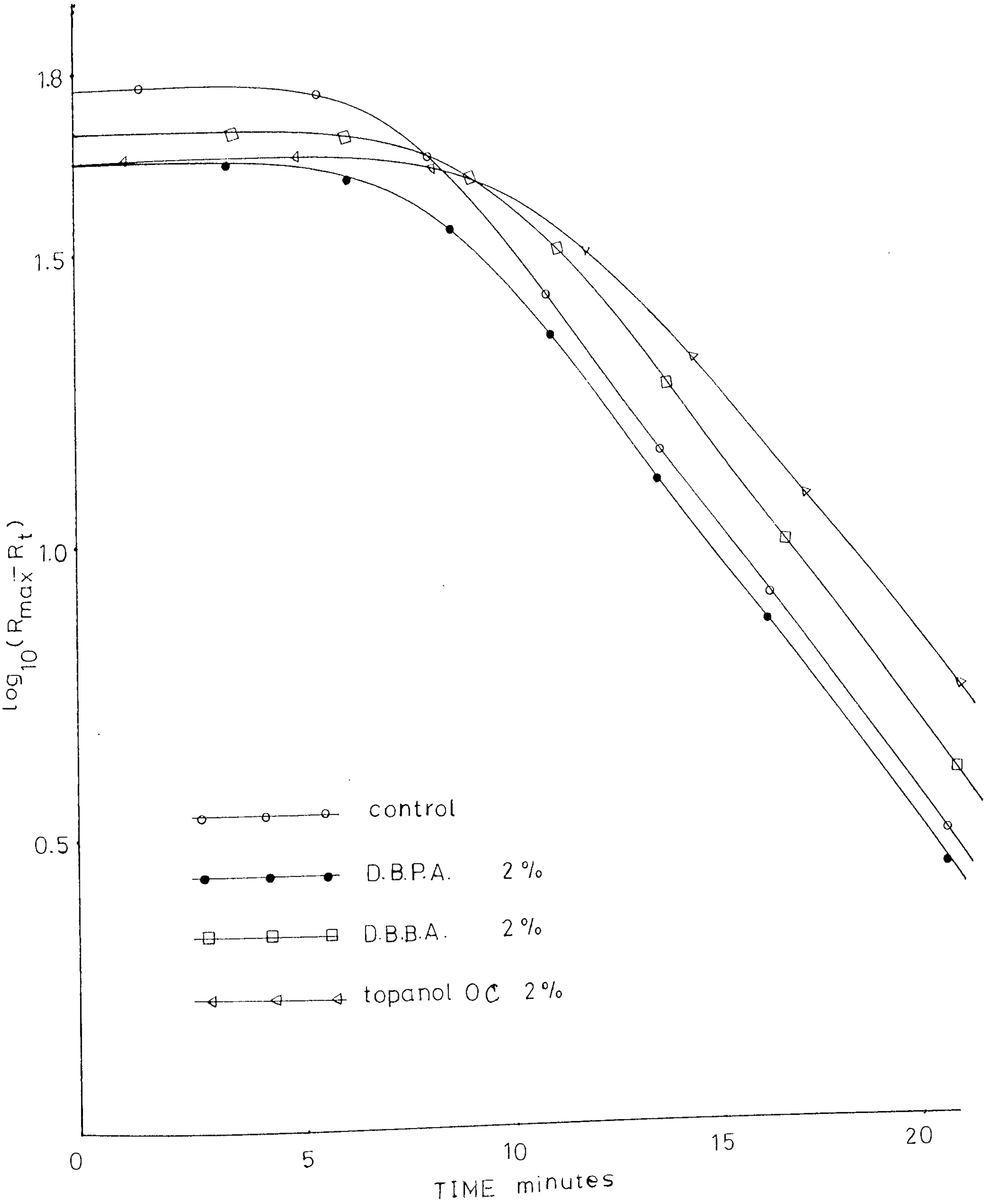

1.8
1.5
1.0
0.5
$\log_{10}(R_{max} - R_t)$
0
5
10
15
20
TIME minutes
control
D.B.P.A. 2 %
D.B.B.A. 2 %
topanol OC 2 %

FIGURE 40

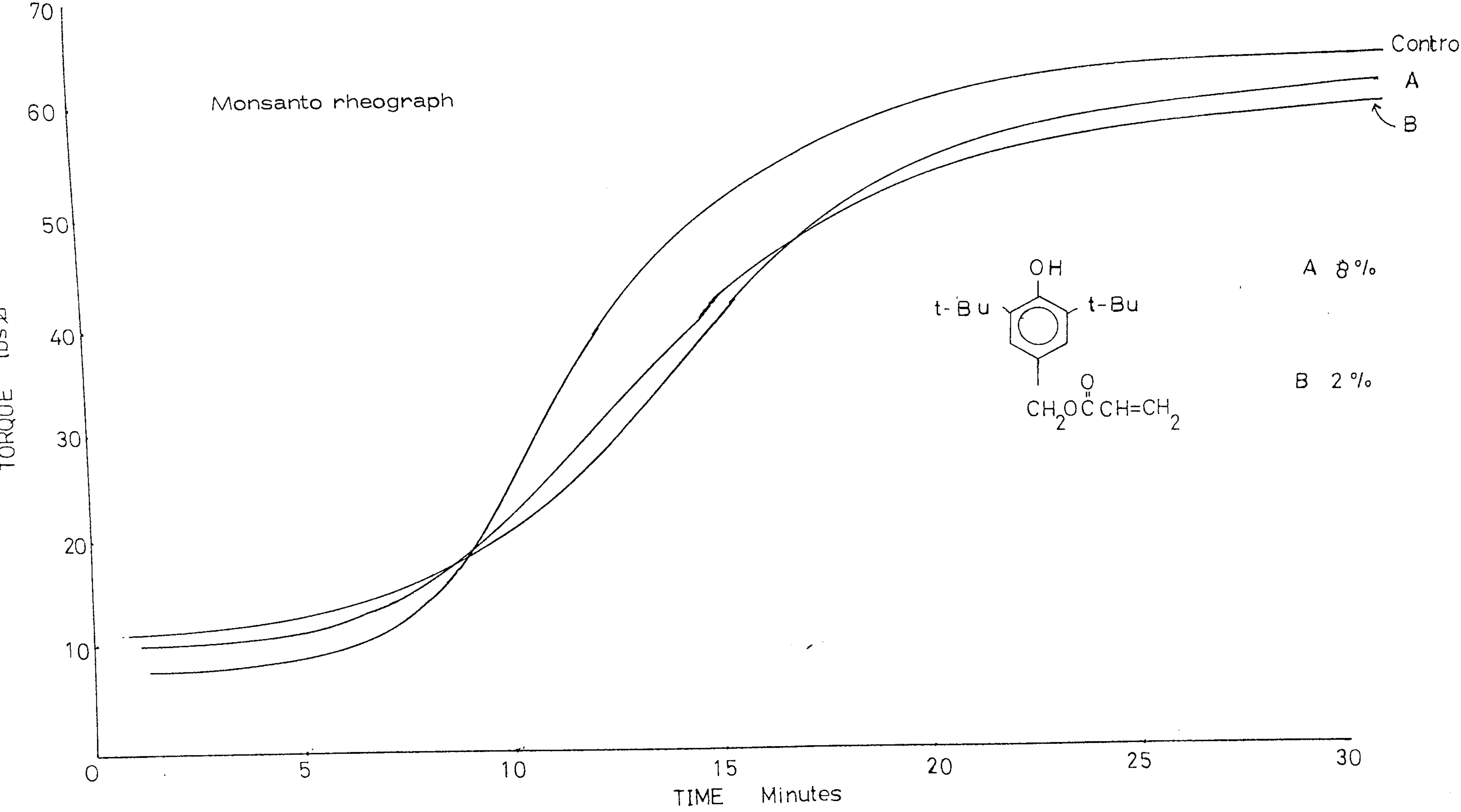

Monsanto rheograph
Control
A
B
A 8%
B 2%
OH
t-Bu
t-Bu
$CH_2O\overset{O}{\overset{\|}{C}}CH=CH_2$
TORQUE lbs
70
60
50
40
30
20
10
0
5
10
15
20
25
30
TIME Minutes

FIGURE 41

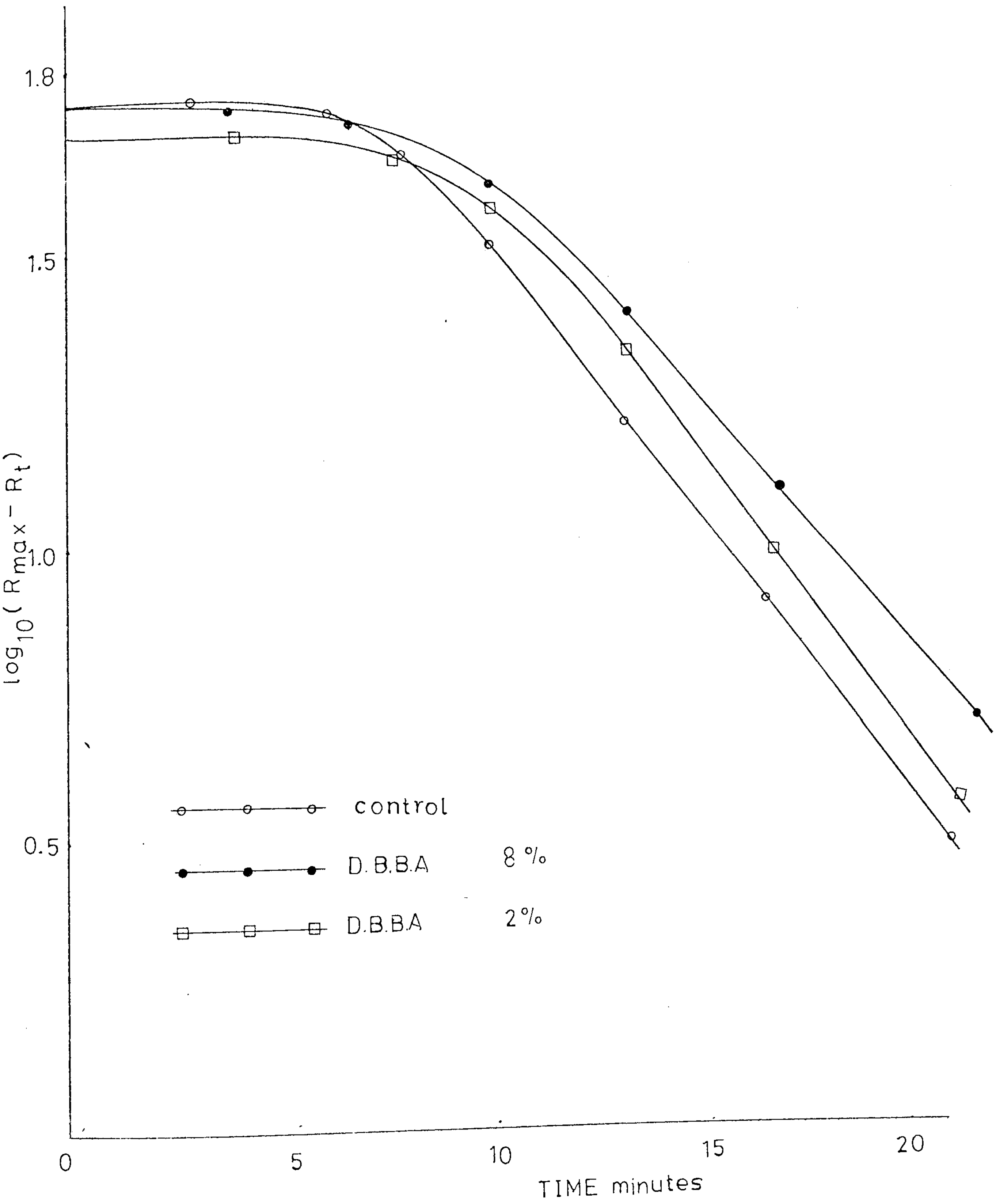

1.8
1.5
1.0
0.5
$\log_{10}(R_{max} - R_t)$
0
5
10
15
20
TIME minutes
control
D.B.B.A 8 %
D.B.B.A 2 %

FIGURE 42

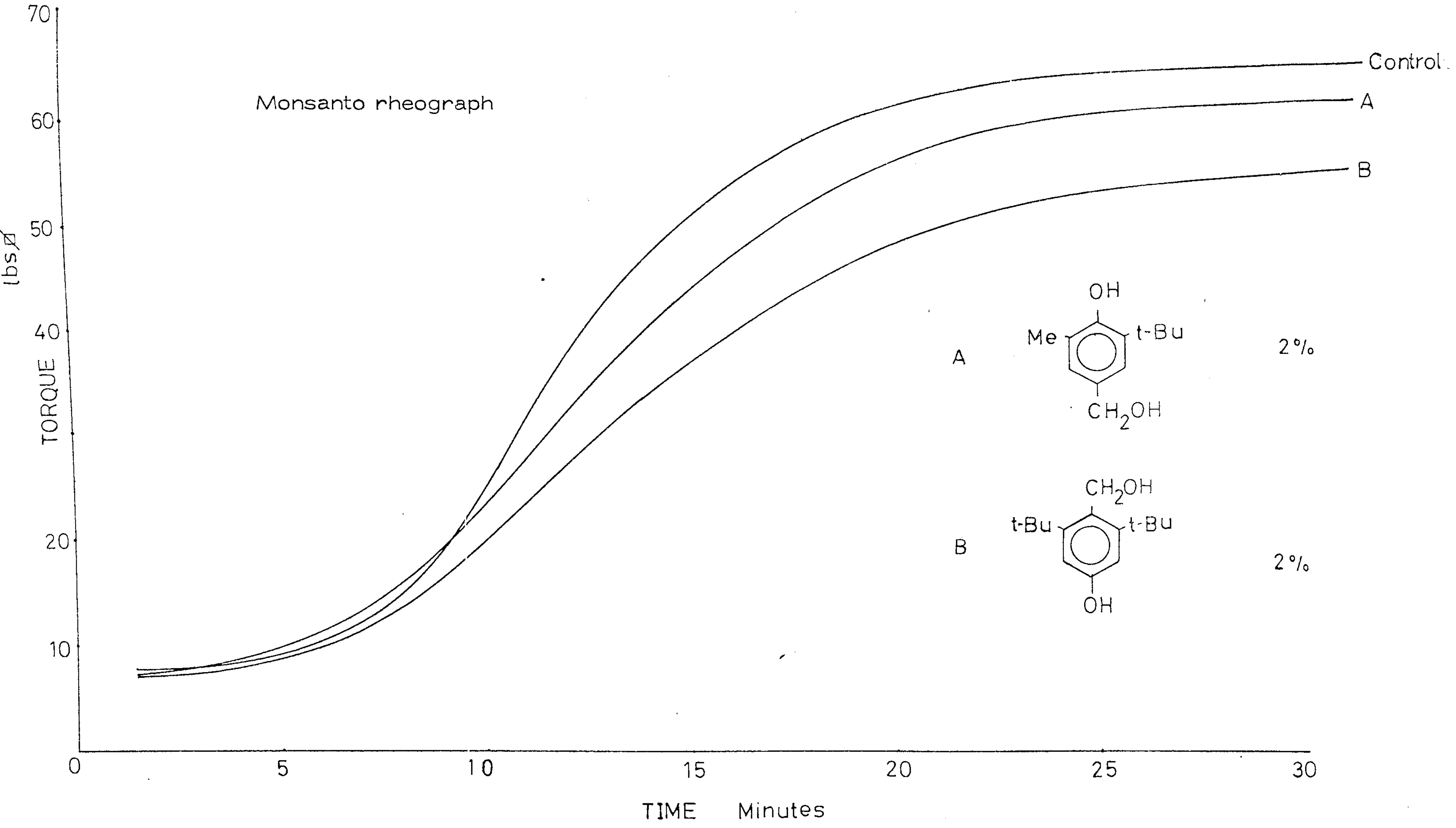
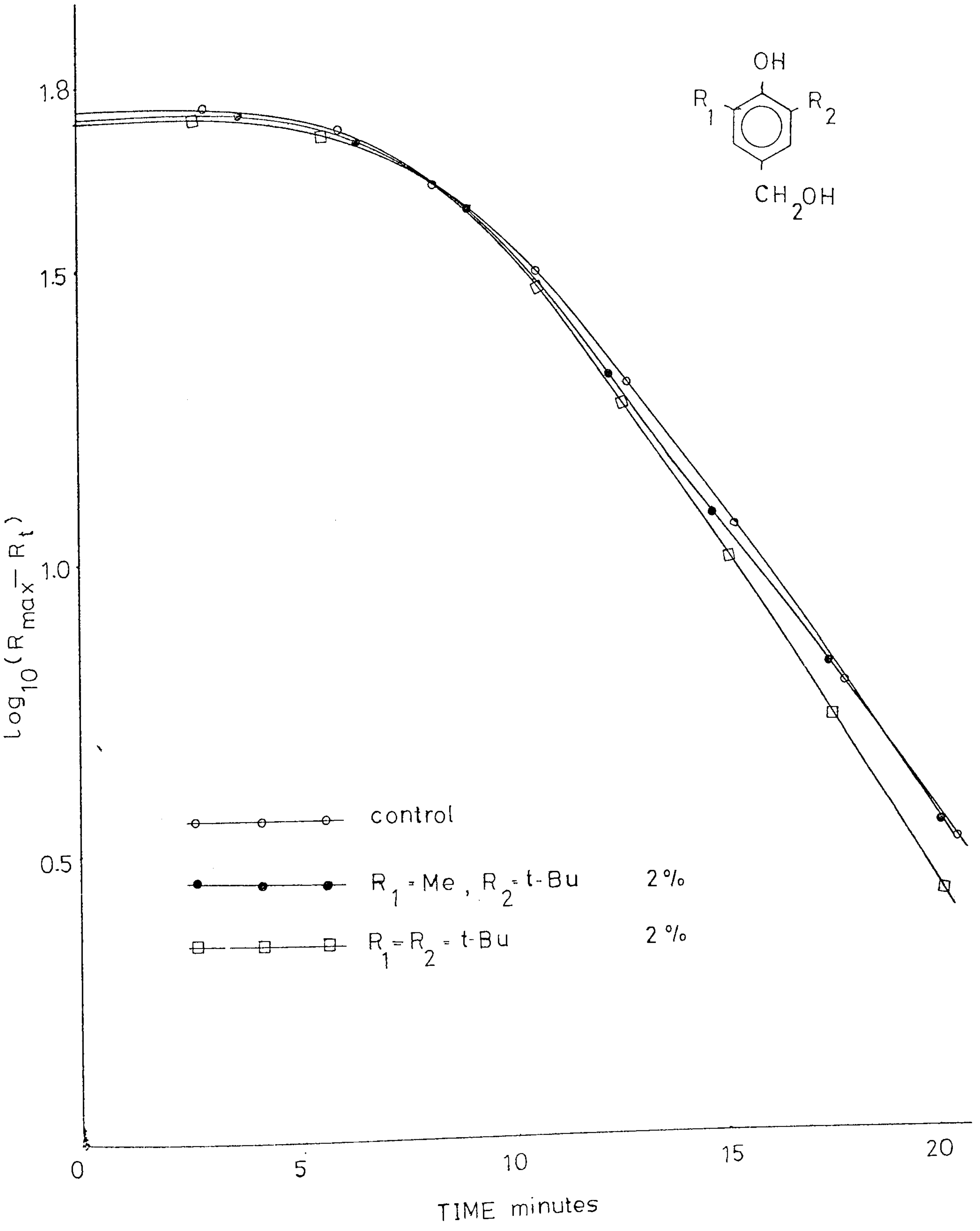
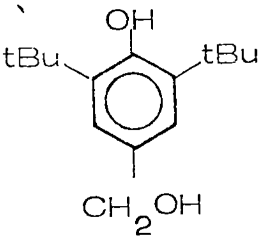
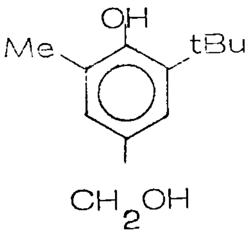

Monsanto rheograph
TORQUE
lbs
70
60
50
40
20
10
0
5
10
15
20
25
30
TIME Minutes
Control
A
B
A
OH
Me
t-Bu
CH2OH
2%
B
CH2OH
t-Bu
t-Bu
OH
2%

FIGURE 43


OH
R1
R2
CH2OH
1.8
1.5
1.0
0.5
Log10(Rmax − Rt)
control
R1 = Me , R2 = t-Bu 2 %
R1 = R2 = t-Bu 2 %
0
5
10
15
20
TIME minutes

10.1.1 Analysis of the results

The parameter R_{max}, K and t, obtained from figures 39, 41 and 43 are given in the table below.

Stock	R_{max}	K $minutes^{-1}$	t, minutes
Natural rubber 2% (control)	65	0.230	9.2
2% DBBA	63	0.219	10.2
2% DBPA	55	0.284	7.8
2% Topanol OC	54	0.207	11.0
8% DBBA	65	0.191	10.3
2% 	65	0.205	7.9
2% 	63	0.204	9.3

As clearly seen from the above table the grafting of the above mentioned vinyl compounds into natural rubber has not as much effect on the induction period of cure.

The ultimate torque R_{max}, which is a measure of cross-link density, is almost the same in all the samples except with Topanol OC and 2,6-di-tert-butyl-4-hydroxy phenyl acrylate.

The rate constant for cross-link formation K is minimum with 8% DBBA sample and it is highest with 2% DBPA sample.

10.2 Assessment of ageing characteristics

Two techniques have been used to assess ageing characteristics of grafted rubber vulcanisates.

(a) The rate of oxygen absorption, and

(b) Continuous stress relaxation.

The former was discussed in detail in Chapter 3.2.4.

10.2.1 Stress relaxation

Theoretical aspect

This method simply involves the measure of the decay in stress of a sample of rubber maintained in extension at a constant length and constant temperature. The stress relaxation method is based upon the kinetic theory relationship between the tension f exerted by a streched rubber sample and the number of, N, stress-supporting network chains, ie chain segments between junction points in the network, per unit volume.

$$f = NKTA_o \frac{l}{l_o} - \frac{l_o}{l}^2$$

where T is the absolute temperature, A_o is the unstrained cross-sectional area, K is the Boltzmann's constant $\frac{l}{l_o}$ is the ratio of streched to unstreched length (extension ratio).

Therefore, if a sample of rubber can be maintained in extension at a constant length and constant temperature (ie keeping T and $\frac{l}{l_o}$ constant) the value of stress f will be proportional to S only, the number of stress supporting chains.

$$\frac{f}{f_o} = \frac{S}{S_o}$$

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

Experimental technique

Wallace extension stress relaxometer was used in all the experiments where a sample of vulcanisate was held in extension between two fixed points and fully submerged in a thermostatically controlled ageing oven with a regular replacement of air. The stress at any particular instant can be directly read from the recorder chart.

Grafted natural rubber was extracted with the azeotrope and vulcanised into sheets of 2 mm thickness using the formulation given on page 53 .

Long thin samples were cut using a die and their relaxation curves were obtained at 100°C while passing air at the rate of

20 – 30 cc per minute.

From the curves obtained, plots of log $\frac{f}{f_o}$ against time were made and are shown in figures 44-47.

10.2.2 Results and discussion

As clearly seen from the figures the stress of a natural rubber vulcanisate (control) containing no antioxidant decays drastically within a very short period of time. This indicates its instability to thermal oxidation.

The samples containing the DBBA (grafted) show interesting results with relation to its concentration. The presence of 8% of DBBA in the reaction mixture (latex) shows a clear improvement in the decay of stress with comparison to the sample containing 2% of DBBA, figure 44.

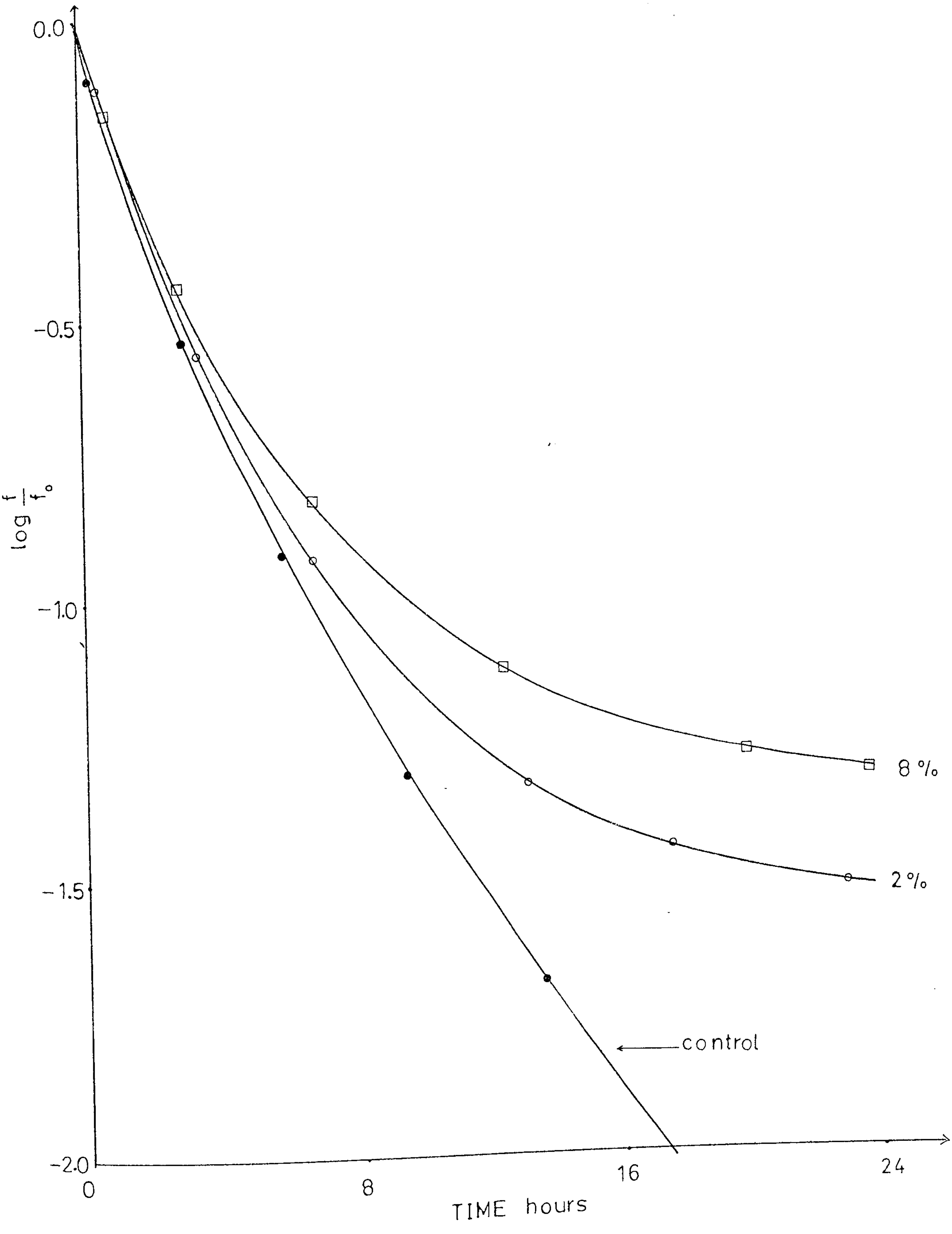
Figure 45 illustrates that the 2-methyl, 6-tert-butyl-4-hydroxy benzyl alcohol is a better bound antioxidant than the 2,6-tert-butyl-4-hydroxy benzyl alcohol.

The stability of the rubber samples containing different types of grafted antioxidant is illustrated in figure 46.

This clearly indicates that the Topanol A is the most efficient bound antioxidant in rubbers as far as the stress relaxation is concerned. Because of this a grafted latex masterbatch was prepared with 8% Topanol A. This was diluted with untreated rubber latex to obtain 4% and 2% Topanol A in rubber. These were coagulated dried, extracted and vulcanisates were prepared. Hence the vulcanisates contained only the grafted Topanol A.

Figure 47 illustrates the stress relaxation curves.

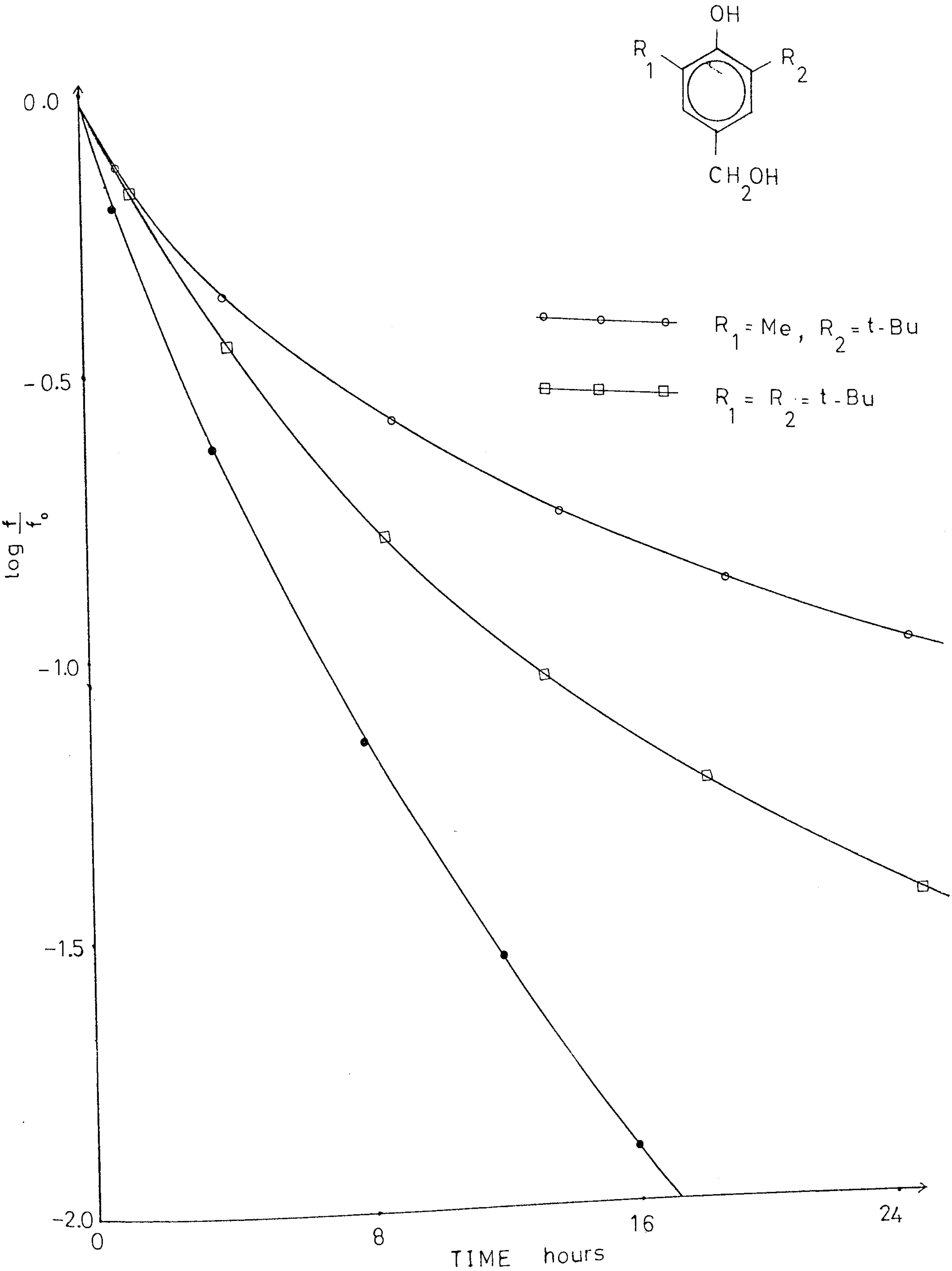
FIGURE 44



Stress relaxation

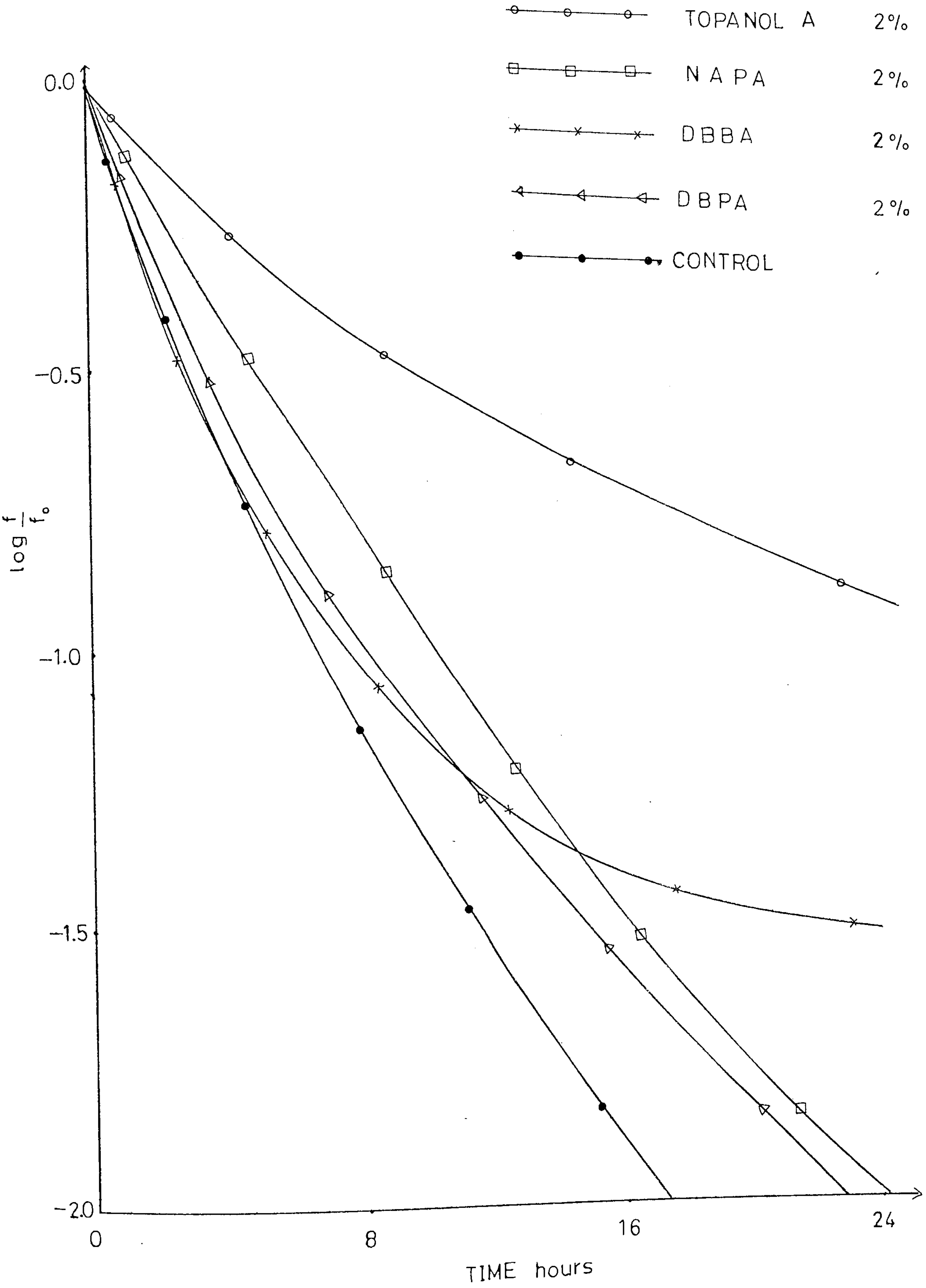
2% and 8% DBBA grafted

FIGURE 45



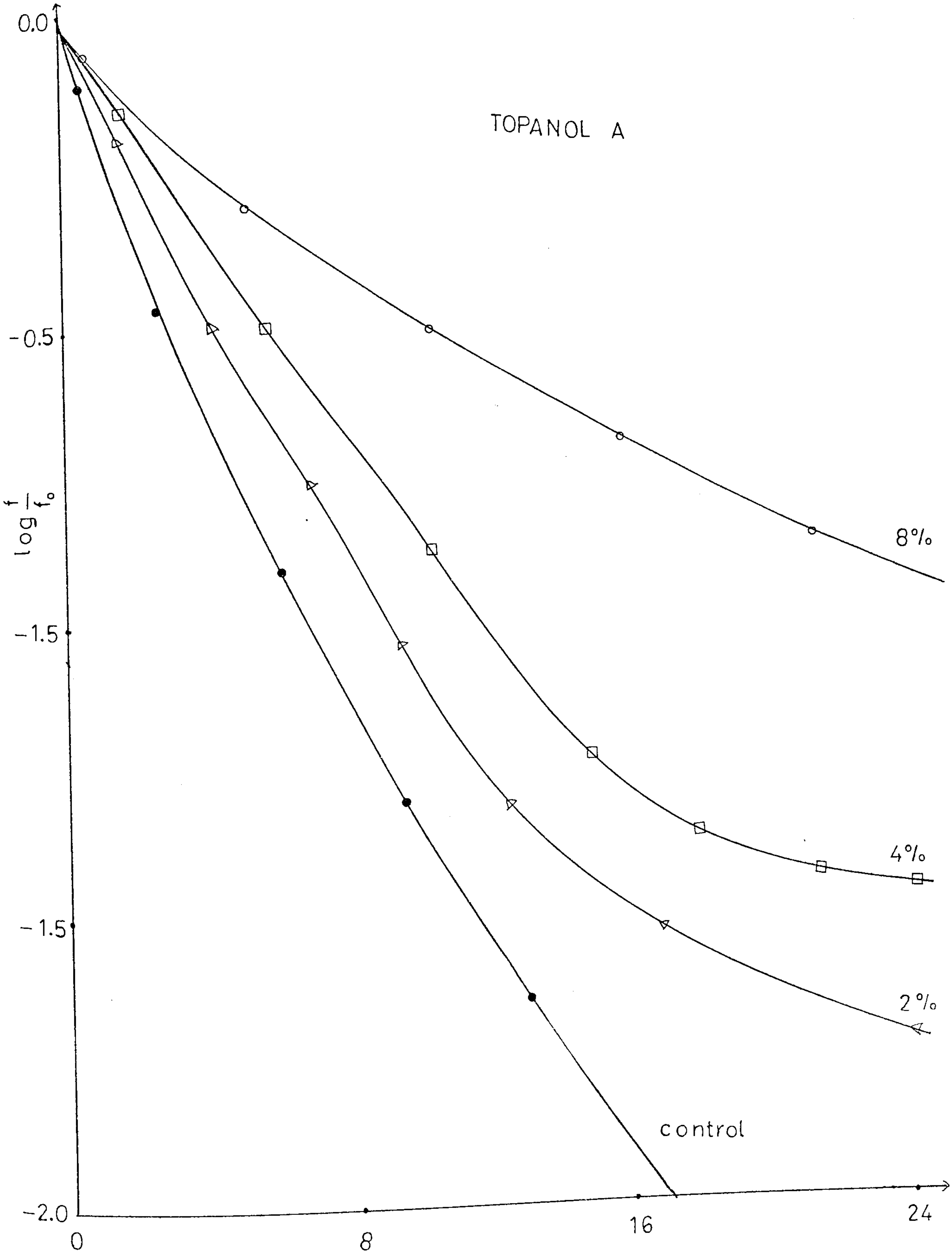
Stress relaxation

FIGURE 46



Stress relaxation

FIGURE 47



Stress relaxation

(Master batch technique)

Conclusions and suggestions for further work

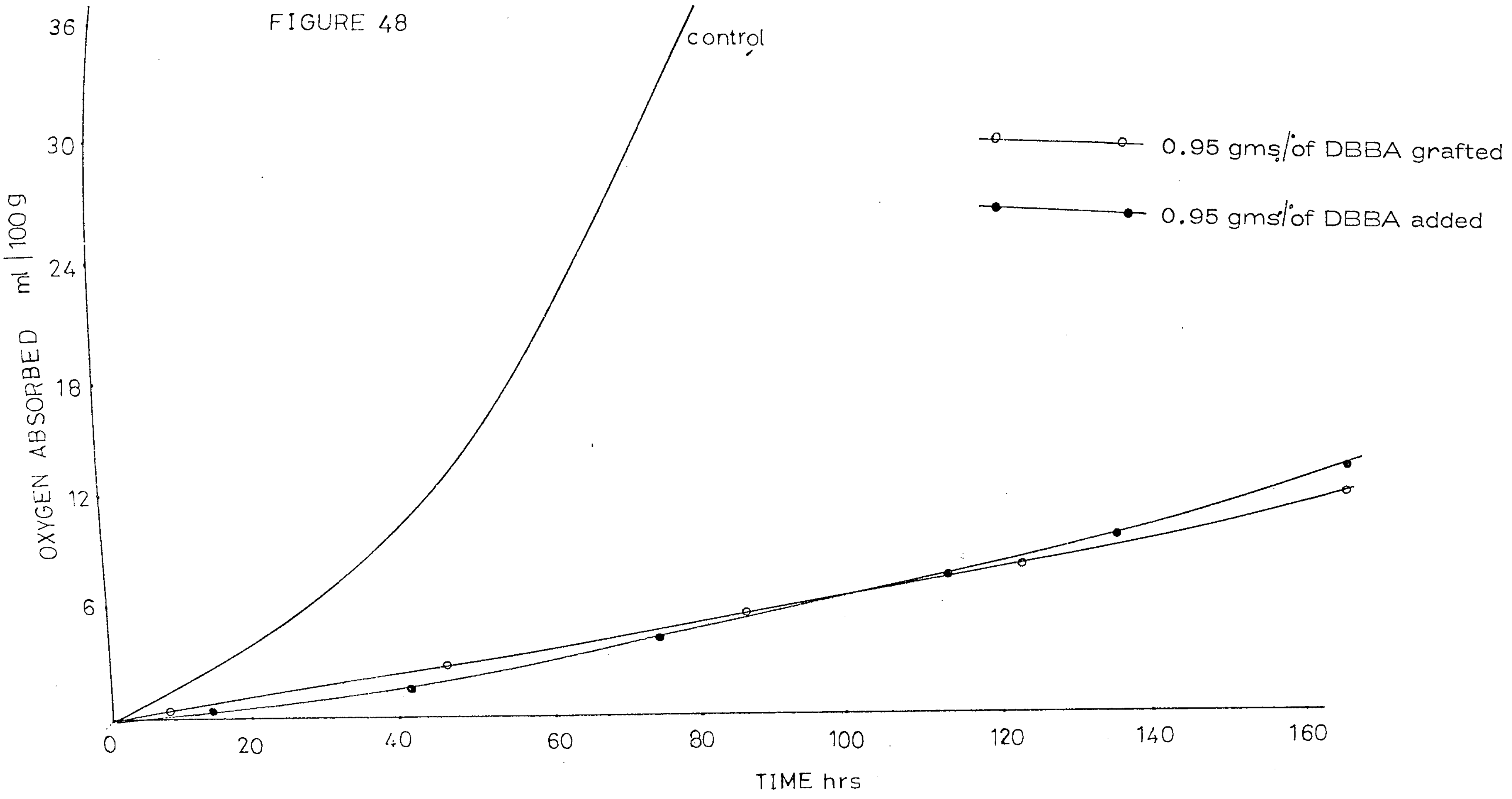
The grafting of natural rubber in the form of latex with vinyl antioxidants has produced a bonded antioxidant / rubber system. It was found that the grafted antioxidants are non attractable. The important feature of the grafting process was the ratio of the monomer to the initiator since optimum conditions were achieved for oxidation stability by varying this ratio in the initial reaction mixture. The optimum reaction conditions to obtain a successful grafting system were investigated. Of the free radical generating systems examined the redox system consisted of TBHP/TEP appeared to be most effective in natural rubber latex.

It is worthwhile to determine the exact point of grafting into the rubber chain. This may be able to find out by reacting vinyl compounds with the model compounds. On the other hand, a suitable method for determining the chain length of the grafted monomer would be useful.

It was found that the antioxidants which do not contain vinyl groups also react under the same conditions with natural rubber latex. According to the results of the brief study carried out on the mechanism of this grafting process, Topanol A, Topanol OC can graft into the rubber chain via a benzyl or quinone methide intermediates. It would be very useful to study this in detail.

A masterbatch technique has been developed to produce concentrates of bound antioxidants in rubber latex and these have been used as additives to untreated latex to obtain grafted rubber latices with a known level of oxidative stability. Further, it was found that the grafting of antioxidants into rubber has not much effect on subsequent vulcanisation.

FIGURE 48


36
30
24
18
12
6
0
OXYGEN ABSORBED ml | 100 g
20
40
60
80
100
120
140
160
TIME hrs
control
0.95 gms% of DBBA grafted
0.95 gms% of DBBA added

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