THE STABILIZATION OF ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMERS AGAINST HEAT AND LIGHT

BY

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The thermal and photo-oxidative stability of acrylonitrile-butadiene-styrene copolymer (ABS) has been investigated in the presence of various stabilizers representative of two different mechanisms of antioxidant action; chain breaking and preventive. When present in the polymer as additives bis (3,5 ditert butyl 4 hydroxybenzyl) monosulphide and 4-benzoyl 3 hydroxyphenyl o-ethyl thioacid esters were more effective thermal and UV stabilizers than any commercially available stabilizers. Furthermore, they showed synergistic behaviour as photo-stabilizers.

Stabilizers containing the above functional groups have been bound to ABS through the thiol group by free radical addition to the double bond. The antioxidant 3,5 ditert-butyl-4-hydroxy-benzyl-mercaptan was found to inhibit adduct formation in the presence of residual monomer (styrene) remaining from the polymer manufacture. This has been overcome by (a) removing the monomer before reaction, (b) by using a water soluble azo-type initiator. The mechanism of the inhibition process has been shown to be due to the oxidiation products derived from the antioxidant.

The adducts were effective both thermal and photo-oxidative stabilizers for ABS and their effectiveness was not modified by solvent extraction of the polymer. Furthermore, ABS obtained by mixing latices containing the antioxidant and UV stabilizer adducts showed synergistic behaviour towards photo-oxidation.

It was found that latex-bound antioxidants could be produced in concentrated form and that these, when diluted to normal concentration with unstabilized ABS latices were as effective as those obtained by reacting with total latices at lower concentrations.

ABS
LATEX
BOUND-ANTIOXIDANT
UV STABILIZER
SYNERGISM

The work described herein was carried out at the University of Aston in Birmingham between October 1974 and May 1977.

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

May 1977

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CHAPTER ONE - INTRODUCTION

The acrylonitrile butadiene-styrene (ABS) group of polymers is an example of a general class of two phase polymers consisting of a dispersion of soft rubber (elastomer phase) in a hard and usually brittle matrix (styrene-acrylonitrile copolymer SAN). In general elastomer phase contributes toughness to the polymer while the matrix gives hardness, ease of processing, tensile and flexural strength.

The development of this general class of polymers dates back almost 100 years, to the discovery of polystyrene (PS). The popularity and growth of PS has been due to its low cost, ease of processing, useful physical properties such as hardness, rigidity, high refractive index, good electrical properties and resistance to water. The chief defect of PS is brittleness manifested as low resistance to impact. Attempts to overcome this deficiency have culminated in the development of so called high impact polystyrene (HIPS) wherein an elastomer is incorporated in the polymerised styrene to improve greatly the resistance to shattering of plastic.[1]

Initially these materials were made by mechanically blending bulk rubber with PS on a two roll mill or in a Banbury mixer.[2] Though blending of two polymers by mechanical mastication would appear to be a very simple process, two elastomer blends of natural rubber (NR) and styrene butadiene rubber (SBR) blended to a homogeneous mixture showed microscopic heterogeneity[3]. ABS polymers made by mechanical blending of

a) SAN copolymer and butadiene acrylonitrile rubber

b) SAN copolymer and a graft styrene and acrylonitrile with polybutadiene (PBN)

had good impact properties but lower tensile and flexural strength, hardness and thermal properties[4] .

Graft copolymerisation of all monomers onto a preformed substrate such as PBD was able to rectify all the deficiencies of mechanical blending[5]. Graft copolymerised HIPS was not introduced until the late-forties and was soon followed by ABS.

The mechanism of reinforcement in rubber modified PS and SAN copolymers remains a subject of complexity. A mechanical mixture of PS and a high diene elastomer has much lower impact resistance than a conventional HIPS indicating the importance of grafting[6]. The theories so far proposed as explanation of rubber toughening have been classified into 4 categories by Boyer and Keskkula[7].

a. Energy absorbtion by rubber particles.

b. Craze initiation by rubber particles.

c. Rubber particles acting as reinforcement and craze terminators.

d. Rubber particles acting as obstacles to crack propagation.

The following Table (1) summarise the variables which could effect the final properties of ABS type of graft copolymers[8].

TABLE 1 VARIABLES WHICH EFFECT PROPERTIES

PHENOMENOLOGICAL VARIABLES	STRUCTURAL VARIABLES
Matrix properties	(1) Chemical Structure
	(2) Average Molecular Weight
	(3) Molecular Wt. Distribution
Dispersed phase	(4) Chemical Structure of Rubber
	(5) Volume of rubber
	(6) Volume fraction of the dispersed phase
	(7) Average particle size
	(8) Particle size distribution

TABLE 1 - VARIABLES WHICH EFFECT PROPERTIES (Cont'd

PHENOMENOLOGICAL VARIABLES	STRUCTURAL VARIABLES
	(9) Degree of cross-linking
Interfacial adhesion	(10) Degree and Structure of rubber matrix grafting.

1.1. STRUCTURE OF GRAFT COPOLYMERISED ABS

The two phased nature of HIPS was first suggested by Buchdahl and Nielson[9], on the basis of dynamic mechanical properties obtained with torsion pendulum. The existence of separate damping peaks for rubber and PS led to this conclusion. Microscopy provided the positive proof for the existence of the rubber as discrete dispersed phase in both HIPS and ABS.

Moore, Moyer and Frazer[10] put forward a general procedure to determine the chemical composition and major structural features for two-phase polymers and carried out the analysis of ABS graft copolymer.

The major steps of a typical procedure are

(i) IR analysis for its composition

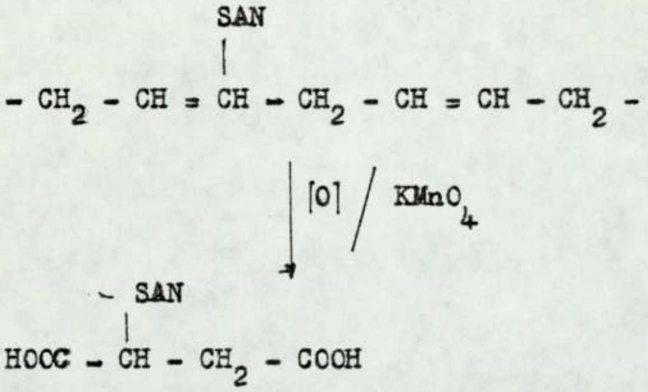
(ii) Centrifugation to separate the graft polymer from the ungrafted copolymer or homopolymer and non-polymeric ingredients

(iii) Ozonolysis of the graft phase under selected conditions to remove the graft polymer from the unsaturated substrate without alteration of the graft copolymer

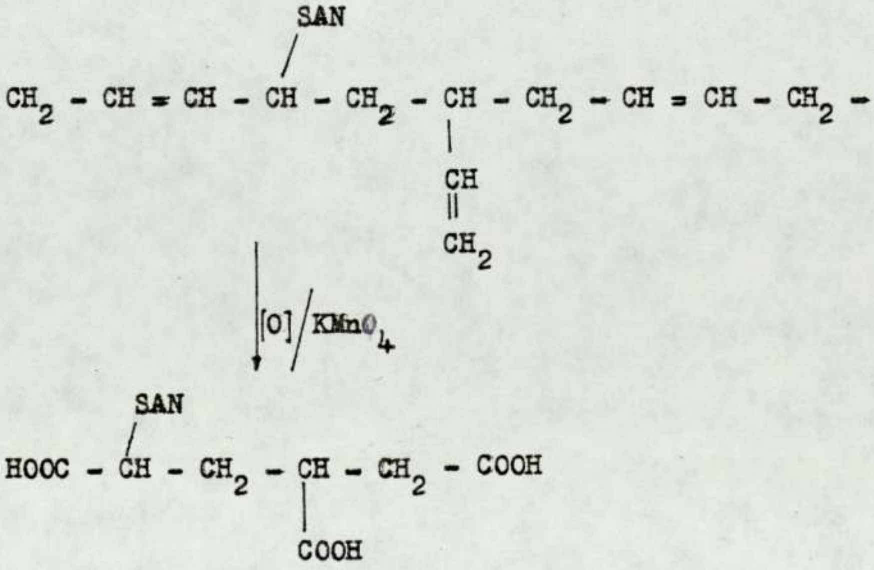
(iv) Analysis of the graft polymer, non-graft polymer and non-polymeric ingredients.

The analysis of the graft phase gave information of the addition sequence of polybutadiene, and it was found to be 1,4 and 1,2 and not 1,2 1,2 blocking. They were able to determine the degree of branching and cross-linking of the graft copolymer. The major drawback of this method was the succeptibility of C≡N group to hydrolysis.

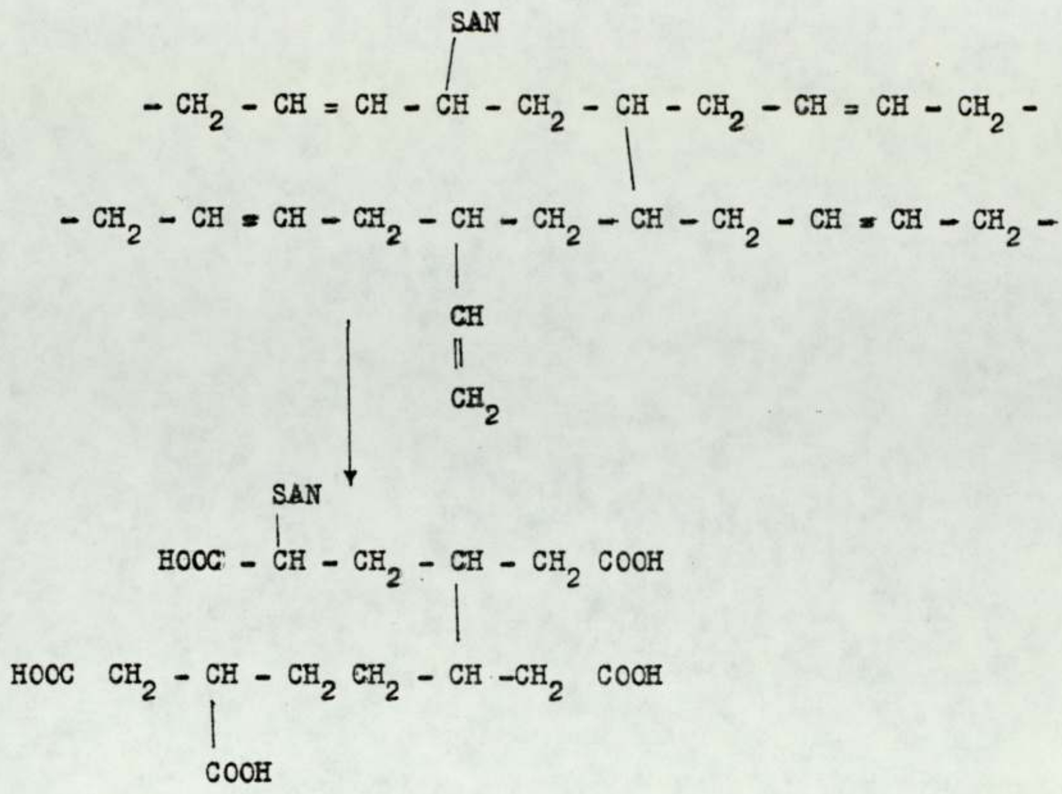
Schuster, Hoffmann and Dinges[11] showed that SAN copolymer grafted to polybutadiene can be isolated from the oxidation residue by a $KMnO_4$ oxidation. The different structural features of the graft copolymer, such as the graft positions, crosslink positions were identified by the increased content of COCH groups of the SAN copolymer obtained after the $KMnO_4$ oxidation of the polybutadiene graft.



$$\mathrm{-CH_2-CH=\overset{\overset{SAN}{|}}{CH}-CH_2-CH=CH-CH_2-}\;\xrightarrow{[O]\,/\,KMnO_4}\;\mathrm{HOOC-\overset{\overset{SAN}{|}}{CH}-CH_2-COOH}$$



$$\mathrm{CH_2-CH=CH-\overset{\overset{SAN}{/}}{CH}-CH_2-\underset{\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}}{CH}-CH_2-CH=CH-CH_2-}\;\xrightarrow{[O]\,/\,KMnO_4}\;\mathrm{HOOC-\overset{\overset{SAN}{/}}{CH}-CH_2-\underset{\underset{COOH}{|}}{CH}-CH_2-COOH}$$



Kranz, Dinges and Wendling[12], claim that polybutadiene graft polymers can be characterised by first degrading under mild conditions with tertiary butyl-hydroperoxide and OsO_4 at 110°C for 30 minutes in p-dichlorobenzene, and then degrading it in a second step with periodic-acid at room temperature. This was found to give very good results and did not effect the chain length of the grafted SAN copolymer chain.

The following information regarding the structure of graft co-polymerised ABS is now available:

(1) The two-phase nature of the polymer.

(2) Of the two phases the matrix which is made by SAN copolymer is soluble in most of the solvent and hence, can be separated from the insoluble graft polymer by centrifugation.

(3) The addition sequence of the substrate polymer, poly-butadiene is exclusively 14 and 12 and not 12, 12.

(4) Tertiary allylic H and vinylic double bonds are common in the graft copolymer.

(5) The appreciable number of cross-links in the graft copolymer are randomly distributed.

(6) The graft centre is usually a carbon atom containing 2 allylic hydrogen atoms. The C atoms allylic to vinylic double bonds remains usually ungrafted.

1.2. STRUCTURE PROPERTY RELATIONSHIPS IN ABS

When a rigid thermoplastic is subjected to an increasing strain as in a tensile test, two types of behaviour are observed as illustrated in the Figure 1. Several common thermoplastics which are normally described as brittle fall in the category of organic glasses vis PS, SAN copolymer, polymethylmethacrylate (PMMA). The organic glass is brittle because the formation and propagation of a crack overtake the process of deformation. The development of a crack in an organic glass may be described by Griffith-Irwing equation[13],

$$\text{Yield Stress } \sigma_B = \sqrt{\frac{G_c E}{\pi a}}$$

where the testpiece is a plate with a crack depth of 2a at one side. The equation provides for fracture stress on G_C, the energy required to extend the crack, E, the Youngs modulus and the crack length 2a.

The introduction of rubber reduces the short time (Hookean) modulus, as a result of incorporation of low modulus component effecting the overall modulus. When a Hookean elastic body is broken under tension the energy absorbed will be proportional to $\frac{\sigma_B^2}{E}$ so that the reduction in modulus provided it is not accompanied by an appreciable change in ∇_B will lead to an increase in energy uptake of glass.

The primary function of the rubber component is to impart ductility to the polymer. In order to get the maximum effect it is necessary to graft a portion of monomer onto the rubber in a controlled manner. The graft structure is influenced by the rubbers,

(i) average particle size
(ii) composition
(iii) cross-link density
(iv) cross-link structure.

The final balance of polymer properties is strongly dependent on the graft structure[14]. In general a decrease in styrene concentration in ABS increases the heat distortion temperature, elongation, impact strength, but decrease flow hardness and tensile strength. A decrease in butadiene content increase flow, hardness and tensile strength, decreases impact strength, heat distortion temperature, but elongation is relatively unaffected[14], as illustrated in the figures 2, 3, 4 and 5.

The increase in the impact strength of HIPS with the rubber content is accompanied by a fall in the yield strength Fig. 5 The loss of yield strength can be minimised by incorporation as a second monomer with styrene, acrylonitrile as in ABS polymer Fig. 6 The result is a superior product in rigidity and impact strength compared to HIPS. In general, a decrease in acrylonitrile content increases flow and tensile strength but decreases heat distortion temperature, elongation and impact strength[15].

Figure I

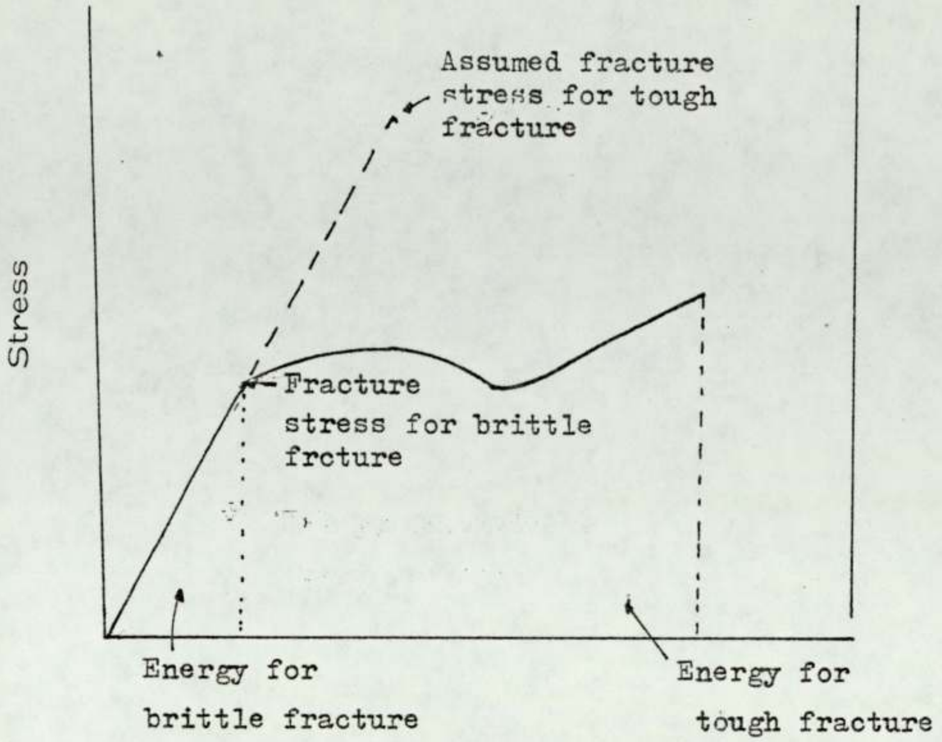


Figure 2

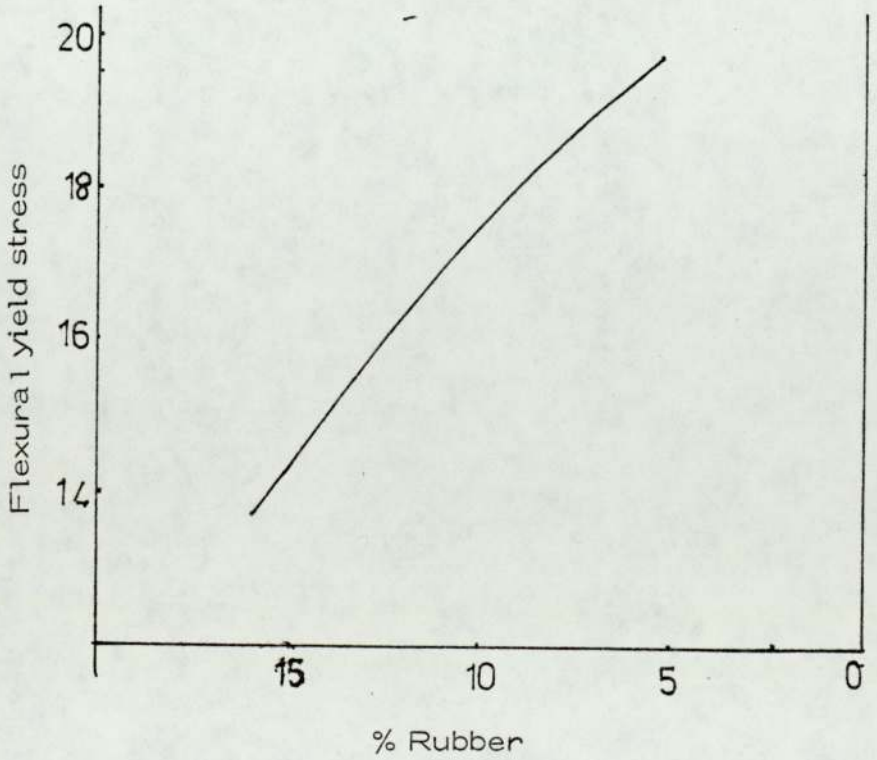


Figure 3. Effect of rubber on Izod impact strength.

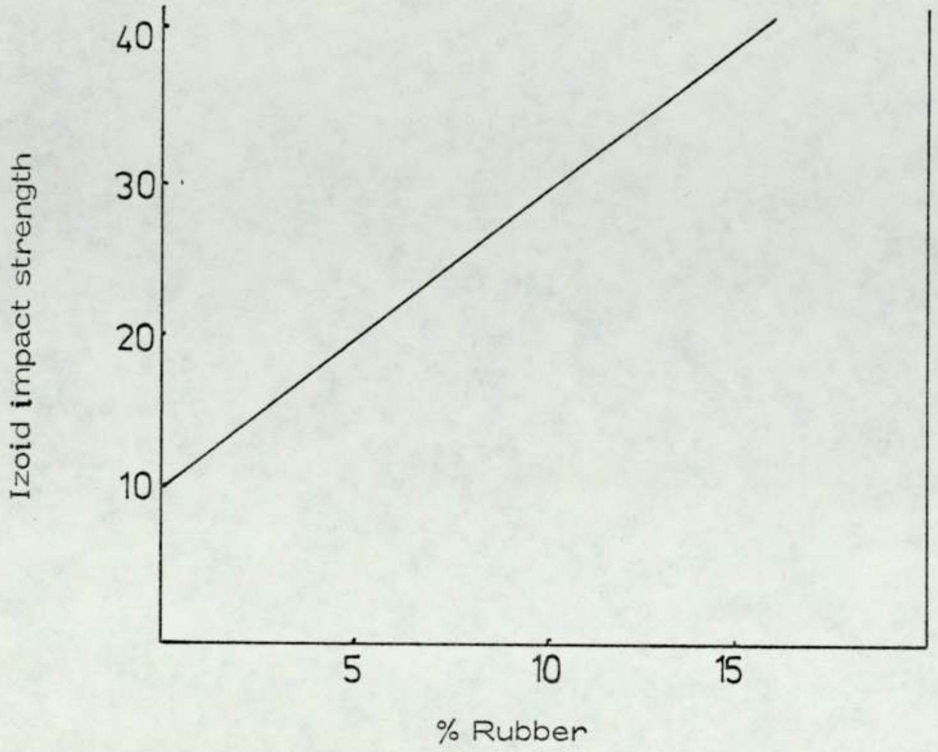


Figure 4. Effect of rubber on heat distortion temperature.

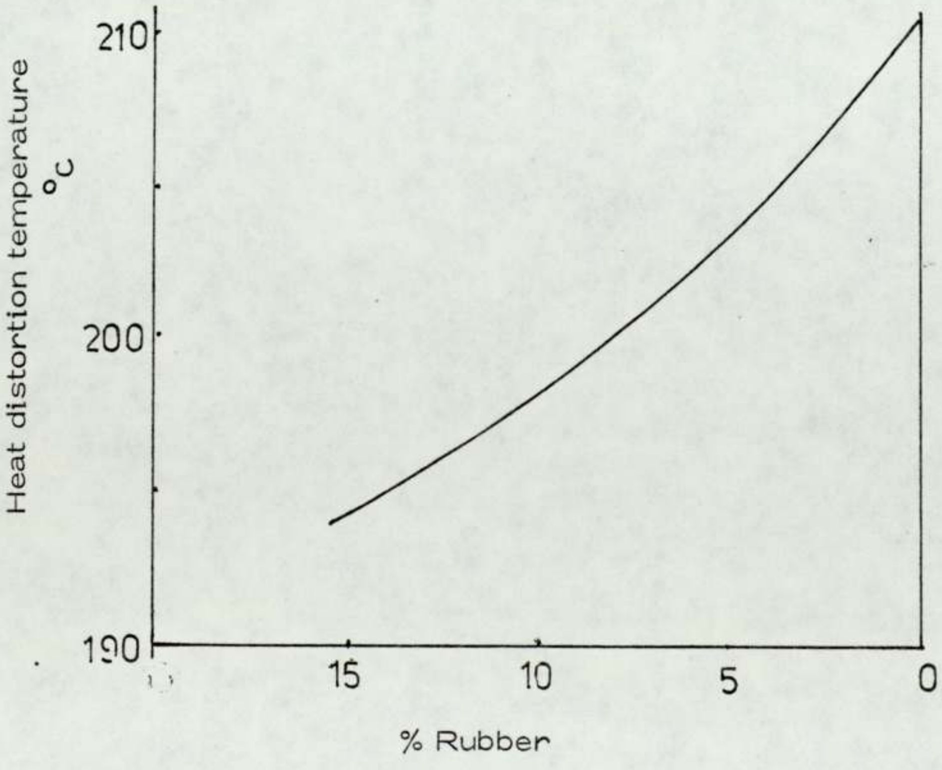


Figure 5. Effect of rubber content on yield and impact strength.

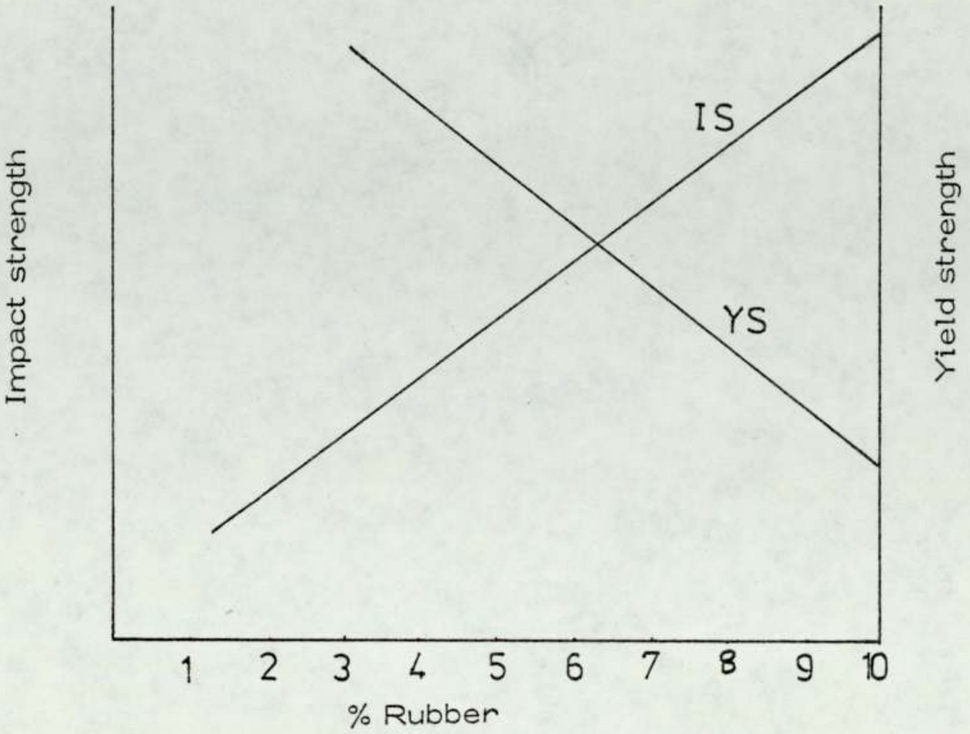
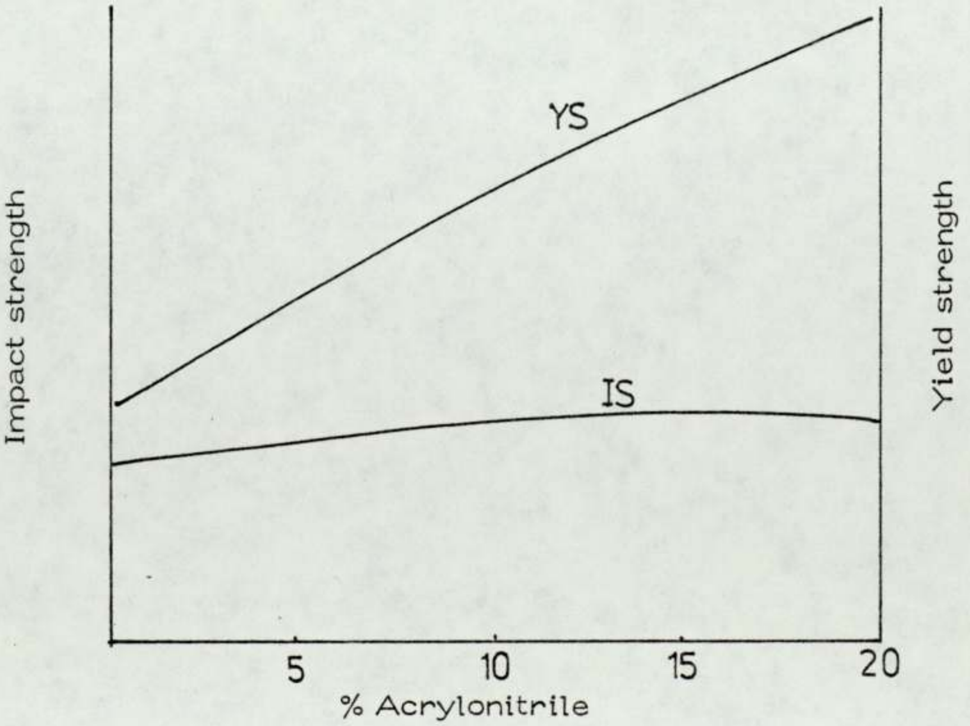


Figure 6. Effect of co-polymerisation of acrylonitrile on the properties of PS/PBD systems.



1.3. GENERAL MECHANISM OF OXIDATIVE DEGRADATION OF POLYMERS

Exposure of a polymer to oxygen is characterised by an induction period during which the polymer does not show any obvious changes. There is no evidence of oxygen absorption[16]. During this period hydroperoxides are formed and initiate the subsequent rapid autoxidation of the polymer. As a rule, an increase in temperature reduces the induction period and accelerates the autoxidation. In some cases, when the polymer contains trace amounts of peroxide impurities or catalysts such as metallic salts, the induction period is not observed at all and the process of catalytic oxidation begins immediately. The decomposition of hydroperoxides is commonly regarded as the process responsible for further rapid oxidation. This being a free radical mechanism, the following stages can be recognised during autoxidation of a polymer :

(1) Initiation
(2) Propagation
(3) Termination.

1.3.a. INITIATION

Initiation of oxidative degredation of a polymer, is by the detachment of a loosely attached hydrogen atom to form a macroradical for peroxidation. This is influenced by[17],

(a) the purity of the polymer
(b) the presence and the absence of
  (i) antioxidants
  (ii) stabilizers
  (iii) oxidative agents

(iv) materials capable of peroxidation

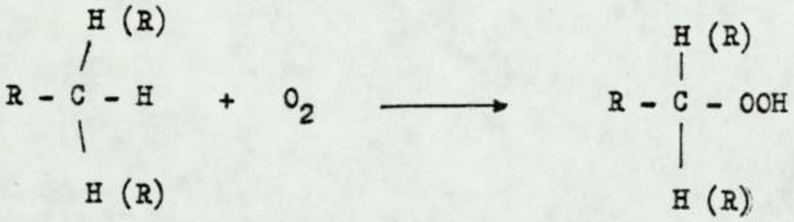
(v) residues of unoxidised materials

(vi) peroxides

(vii) metal salts

(viii) electromagnetic radiation (UV light perticularly)

The activation of a C-H bond which forms the hydroperoxide is dependent on the substitution of the same carbon atom. These substituents can decrease the bond energy of the C-H bond. The magnitude of the resonance energy liberated on the formation of the macroradical is one of the vital factors in promoting the peroxidation of the material. The listed substituents cover the most important groups that activate C-H bond with respect to attack of O_2, and fascilitate the formation of hydroperoxide.



$$R-\overset{H\,(R)}{\underset{H\,(R)}{C}}-H \;+\; O_2 \longrightarrow R-\overset{H\,(R)}{\underset{H\,(R)}{C}}-OOH$$

R = $-CH_3$

$-C_6H_5$ and other aryl

$-CH=CH$

$-OR$

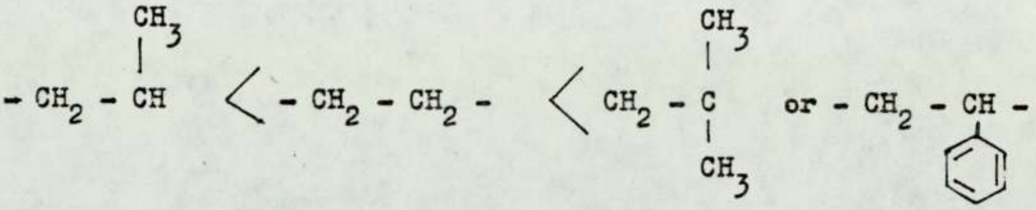
$-C=O$

$-NHR_2$

$-NHCOR_2$

$-Cl$

PS, contrary to the above, shows an anamolous behaviour. In the following series, the oxidative resistance increase from left to right.



It has been proposed that the stability of PS arises partly from the shielding effects of the phenyl groups[18], and perhaps, partly from loss in resonance energy caused by unfavourable orientation of crowded phenyl groups attached to the main chain[19]. Oxidative stability of polymers have been shown to decrease abruptly with an increase in the numbers of methylene groups separating the phenyl groups from the main chain.

The polymer hydroperoxides can decompose homolytically due to thermal energy, UV irradiation and catalysts such as transition metal ions.

$$\mathrm{ROOH} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{OH^{\bullet}} \qquad (1)$$

Bateman and Hughes[20] found that in the case of oxidation of polyolefins, the decomposition of hydroperoxides, initially a first order process (1) but as oxidation progresses, the bimolecular reaction (2) assumes greater importance.

$$2\,\mathrm{ROOH} \longrightarrow \mathrm{R\dot{O}} + \mathrm{RO\dot{O}} + \mathrm{H_2O} \qquad (2)$$

1.3.b. PROPAGATION

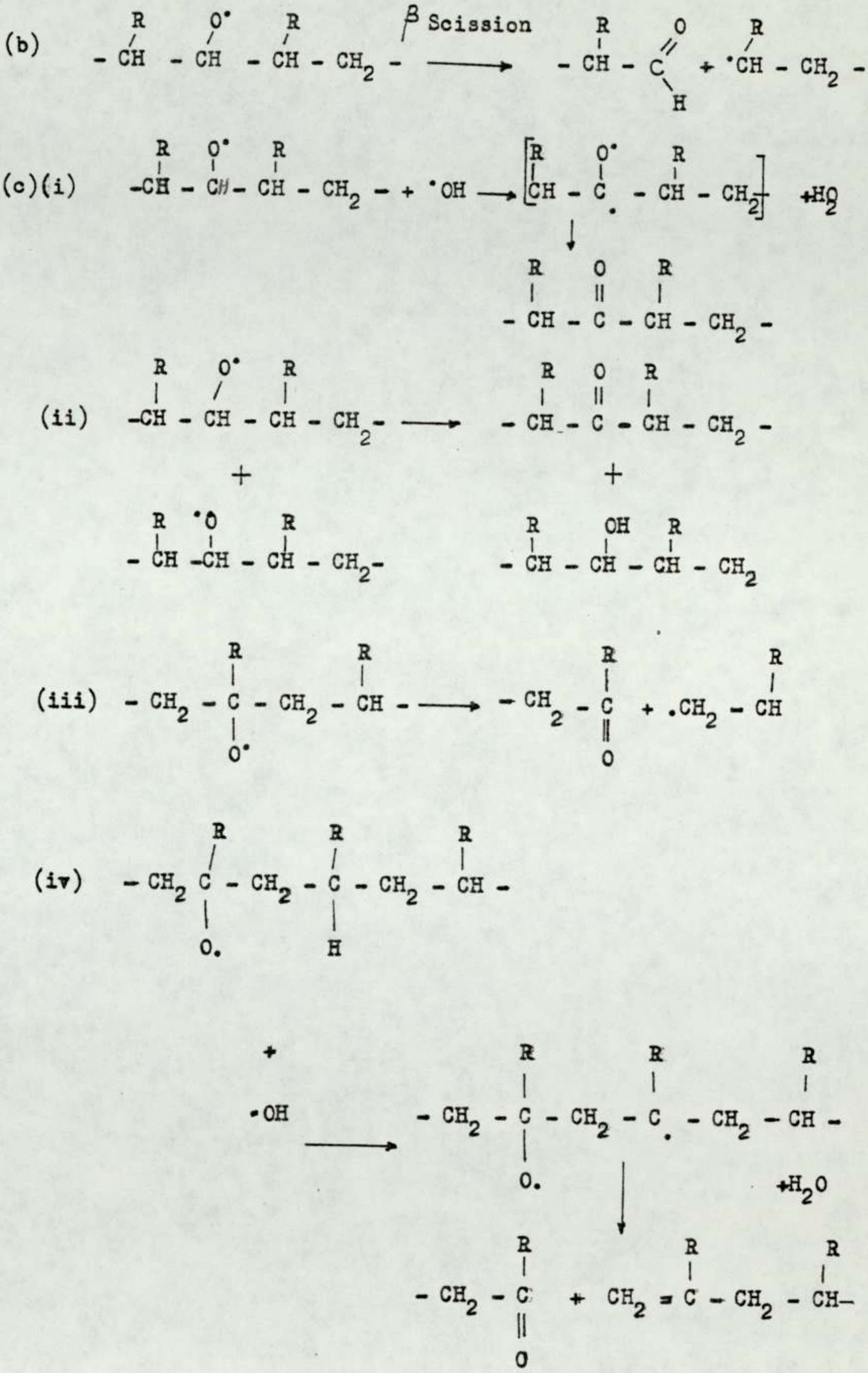
The alkoxy radicals formed after the decomposition of hydroperoxides can form[21];

(a) hydroxyl groups in polymers by the abstraction of H from other molecules

(b) aldehyde groups by β- scission

(c) ketonic C = O groups, the formation of which could be explained by 4 different mechanisms.

(a) $RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$



1.3.c. TERMINATION

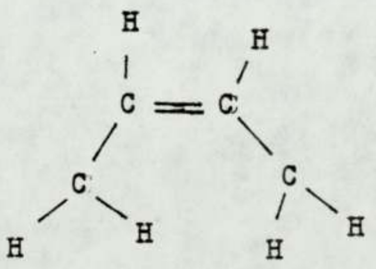
The termination of the chains is due to the reactions of free radicals with each other, in which inactive products are formed.

$ROO^{\cdot} + ROO^{\cdot}$) (3)
$ROO^{\cdot} + R^{\cdot}$) inactive products (4)
$R^{\cdot} + R'$) (5)

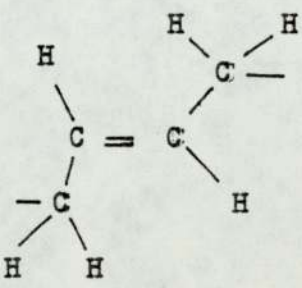
When oxygen pressure is high, the termination reaction is almost exclusively that of (3). Secondary effects of cross-linking and chain scission occurs in the oxidation process; scission may turn a solid polymer into a thin liquid; cross-linking may create a brittle network. Both these effects may occur in the same polymer.

1.4. MECHANISM OF OXIDATIVE DEGRADATION OF PBD

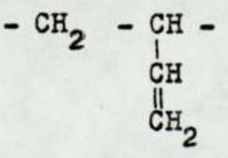
Polybutadiene used to manufacture ABS contain three different types of structural units of unsaturation, namely CIS 1,4, trans 1,4 and 1,2 vinyl, usually in a ratio of 4.5:4.5:1. These olefinic unsaturation decreases the bond disociation energies of allylic C-H bonds, facilitating the formation of macroradicals and also stabilise it by resonance.



Cis 14 unit



trans 1.4 unit



$$-CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{|}{CH}}-$$

1,2 vinyl unit

The oxidative degradation of PBD has been the subject of investigation by three independent groups[22, 23, 24, 25], with the identification of several intermediates in the autoxidation chain, but arriving at different conclusions. Work to date has shown that the two causes of polymer degradation (thermal and photo) leads to similar products and the mechanism may well be the same. The volatile products, 12 in number and identical were formed in each case on oxidation of polybutadiene, differing only in their relative concentrations[22] Table III.

TABLE III

VPC Analysis of Volatile Products Of PBD on Degradation

			Retention Time
Methane	6	2	70
Ethane or Ethylene	20	6	110
Propane	-	-	140
Allene	-	3	195
Isotontane	100	15	322
2 Mepropene	-	-	374
Butene or 13 Butadiene			
-	31	4	520
-	105	8	741
- (Water)	4	1	1300
Hexanl	8	2	1713
Crotonaldehyde	-	-	2120

Beavan and Phillips[22] observed the following changes in the IR spectrum on thermal oxidation of PBD films.

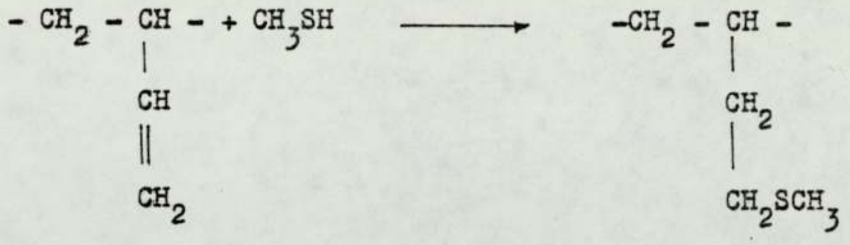
(i) Formation of carbonyl absorbtion at 1685 cm^{-1} (α-β unsaturated ketones), 1699 cm^{-1} (α - β unsaturated aldehyde), 1704 cm^{-1} (COOH), 1720 cm^{-} (saturated ketone), 1731 cm^{-1} (saturated aldehyde), 1739 cm^{-1} (ester group).

(ii) Formation of an absorbtion band at 2720 cm^{-1} due to the C-H stretching of an aldehyde.

(iii) Formation of a band at 3450 cm^{-1} due to CH stretching of alcohol.

The decrease in the relative concentration of α - β unsaturated C=O during photoxidation as opposed to thermal oxidation confirmed by IR and phospho emission spectra, led to their conclusion that these unsaturated carbonyl are responsible for observed final products, and proper photostabilization can only be achieved by quenching the excited states of these species.

According to Scott [25], 1,2 vinyl bonds are initially consumed faster than cis or trans unsaturated units during PBD photoxidation. Meyer et al[26], observed a large decrease in thermal oxidative degradation (by O_2 absorbtion) with the first 20% saturation of PBD by the addition of methylmercaptan and attributed this to faster saturation of vinyl double bonds in the system; thereby increasing the bond dissociation energy of the tertiary C-H bond. Fig. 8. Scott also observed the formation of hydroperoxides prior to the development of carbonyls or hydroxyls during photodegration and concludes hydroperoxides and not carbonyl are responsible for oxidative degradation of PBD.



$$-CH_2-CH(CH{=}CH_2)- + CH_3SH \longrightarrow -CH_2-CH(CH_2CH_2SCH_3)-$$

Shelton et al[23] studied thermal oxidation of cis PBD at 25°C and 60°C by Fourier transform infra red spectroscopy (FTIR). Cis PBD was selected because it has been the subject of a complete normal co-ordinate analysis. They observed loss of α- methylinic protons and a development of C-O grouping before the appearance of C=O, or OH absorbtion bands at 25°C, but at higher temperatures, there was no time lag. Furthermore, they did not observe the formation of a band at 1685 cm^{-1} due to unsaturated ketones; but observed the development of bands at 1700 cm^{-1} and 1725 cm^{-1} corresponding to α-β-unsaturated aldehyde and saturated carbonyl. Scheme 1.

The formation of carbonyl during degradation of 1,2-vinyl unit invariably involves chain scission, and hence a reduction in molecular weight andits dispersion,if the main chain is involved. The formation of ethylene as a degradation product can be explained by the following reaction pathway. Scheme 2.

Figure 7. Schematic diagram of latent degradation producing peroxide development and degradation[16].

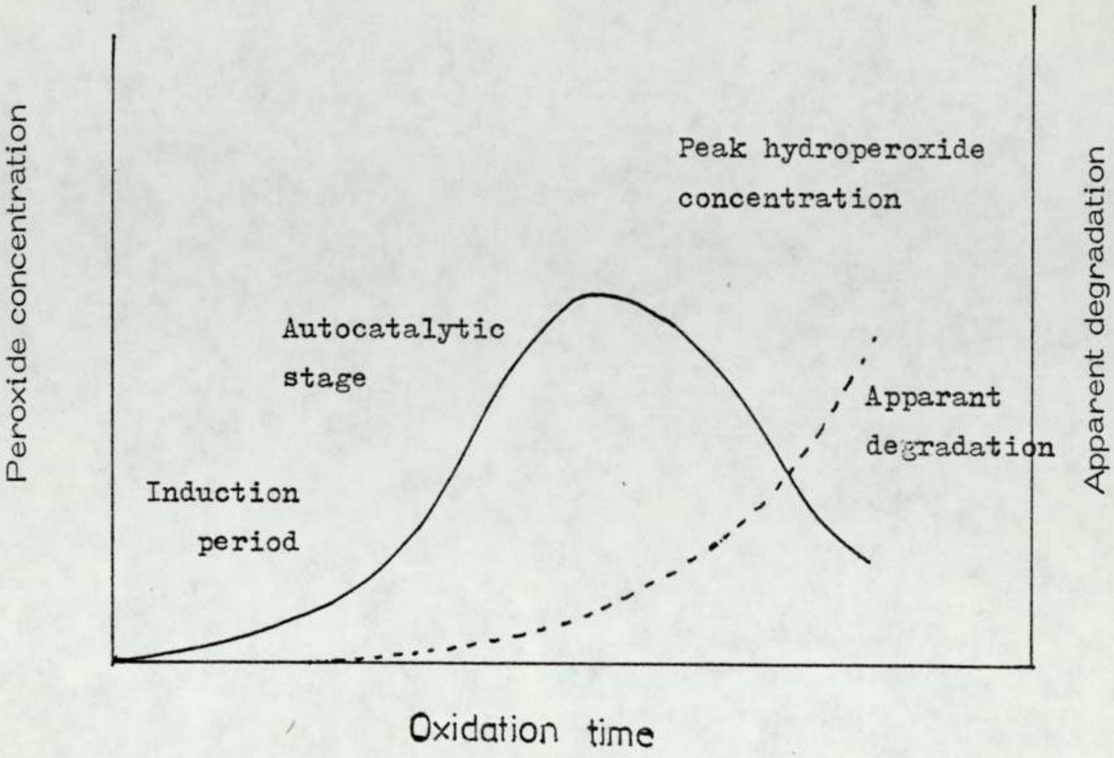
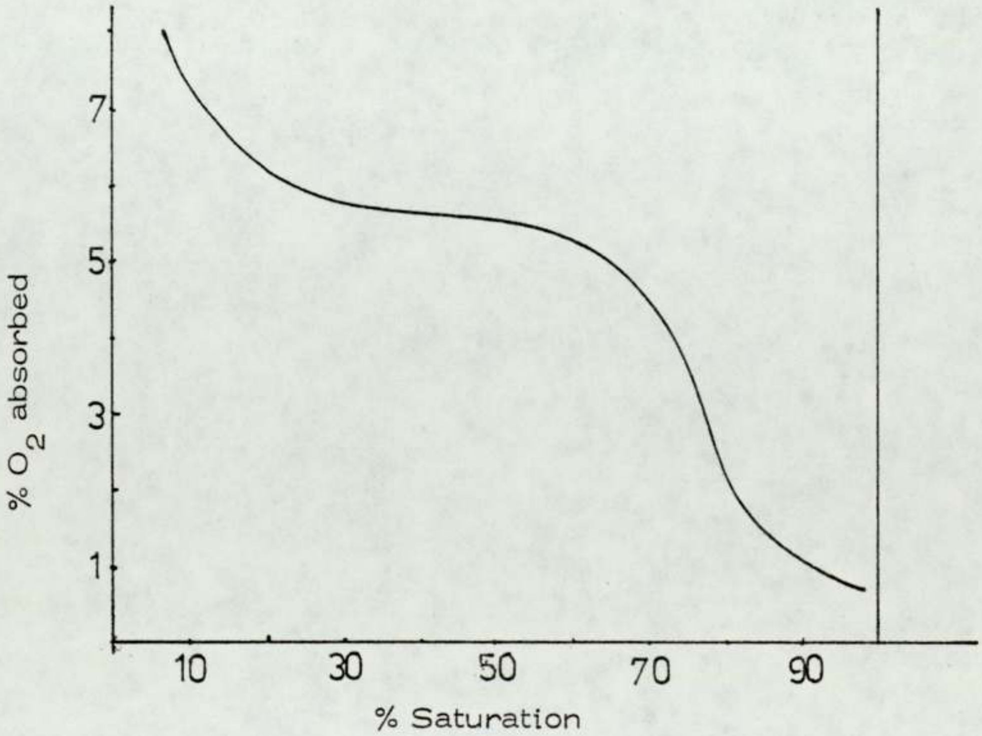
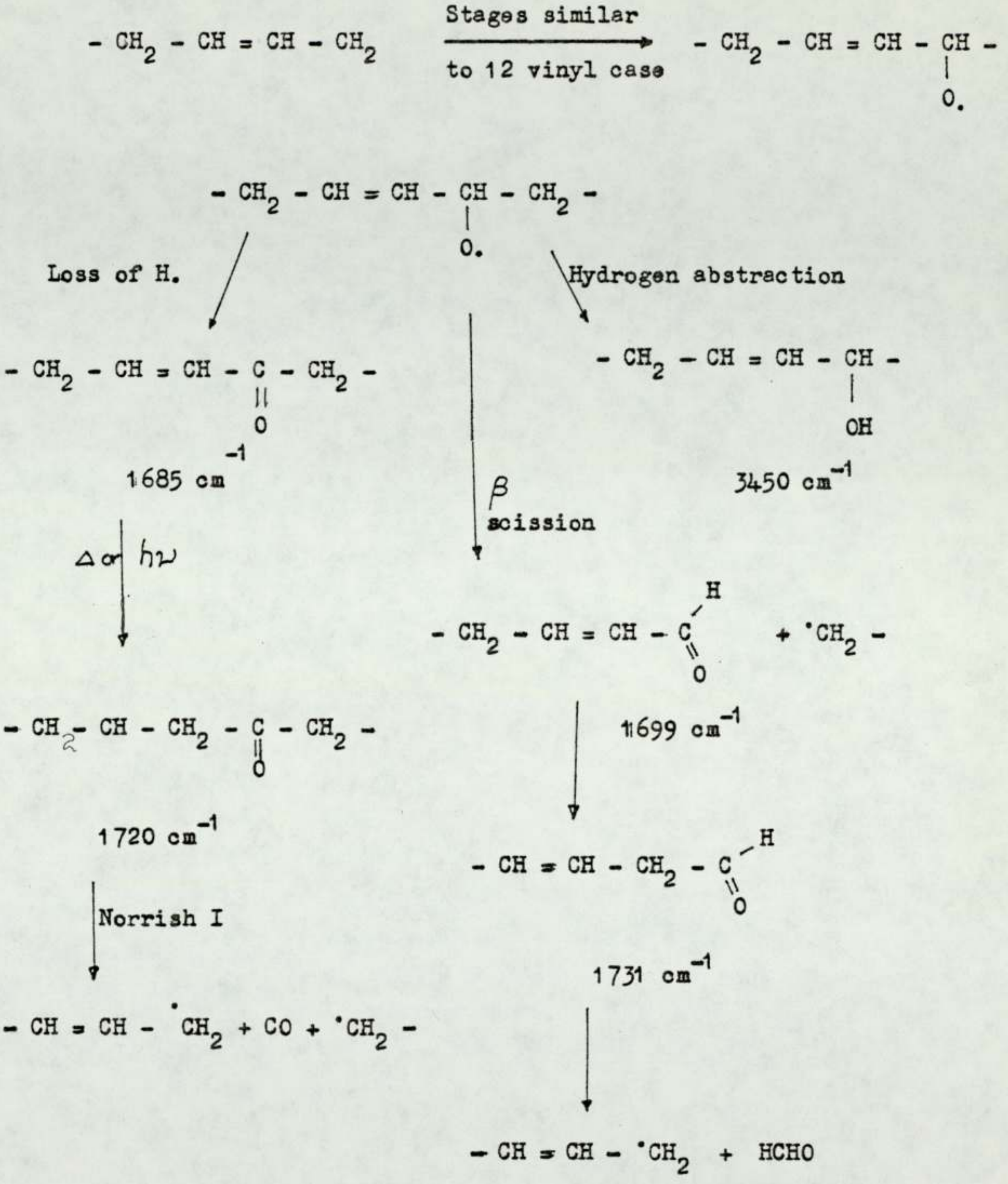


Figure 8. Oxygen absorbed after 140 hours vs percentage saturation of PBD-CH_3SH elastomers.



Scheme 1. Mechanism of Oxidation of Cis and trans 14 Units of PBD.



Scheme 2. Mechanism of oxidation of I,2 vinyl units of PBD.

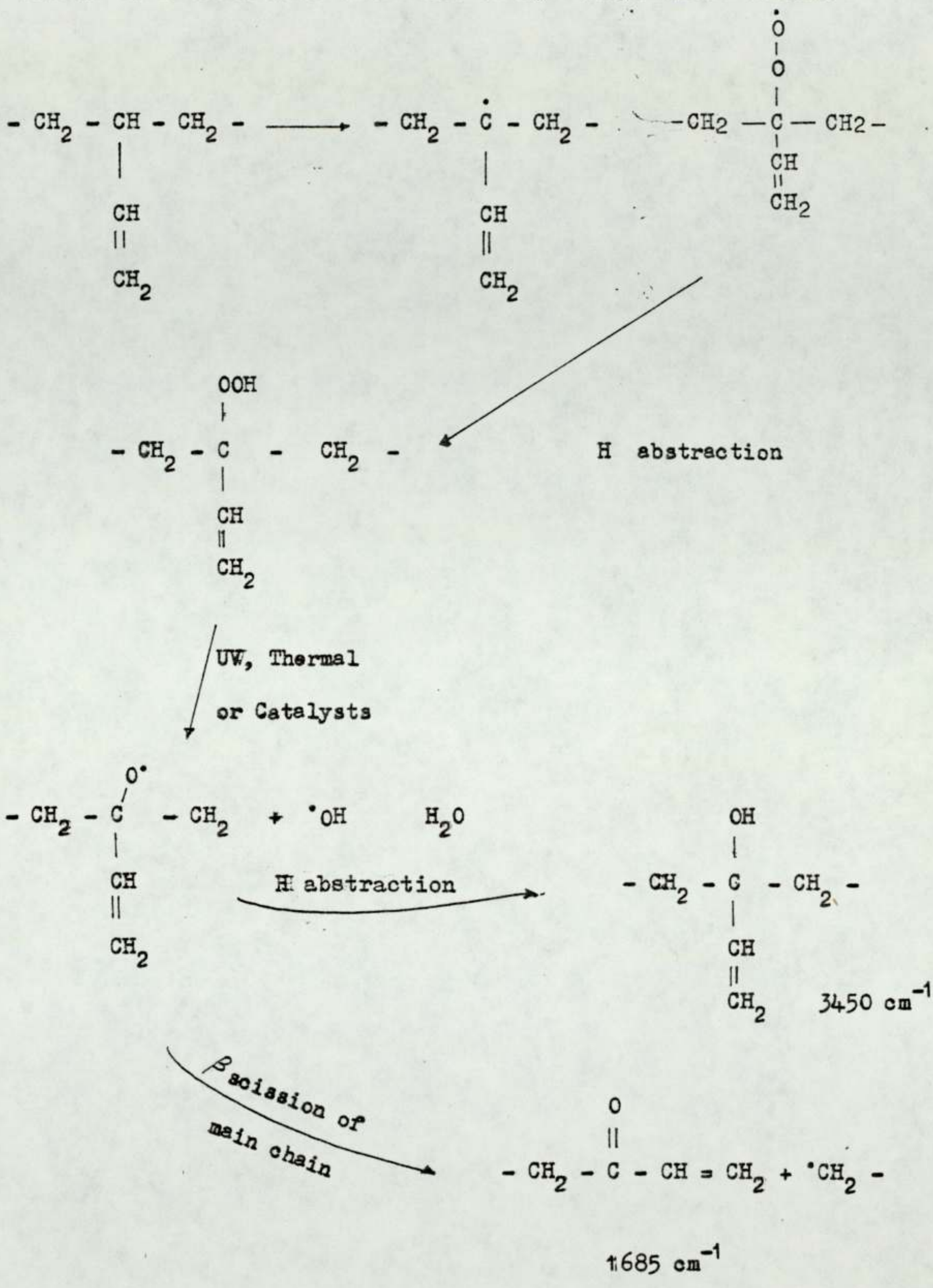
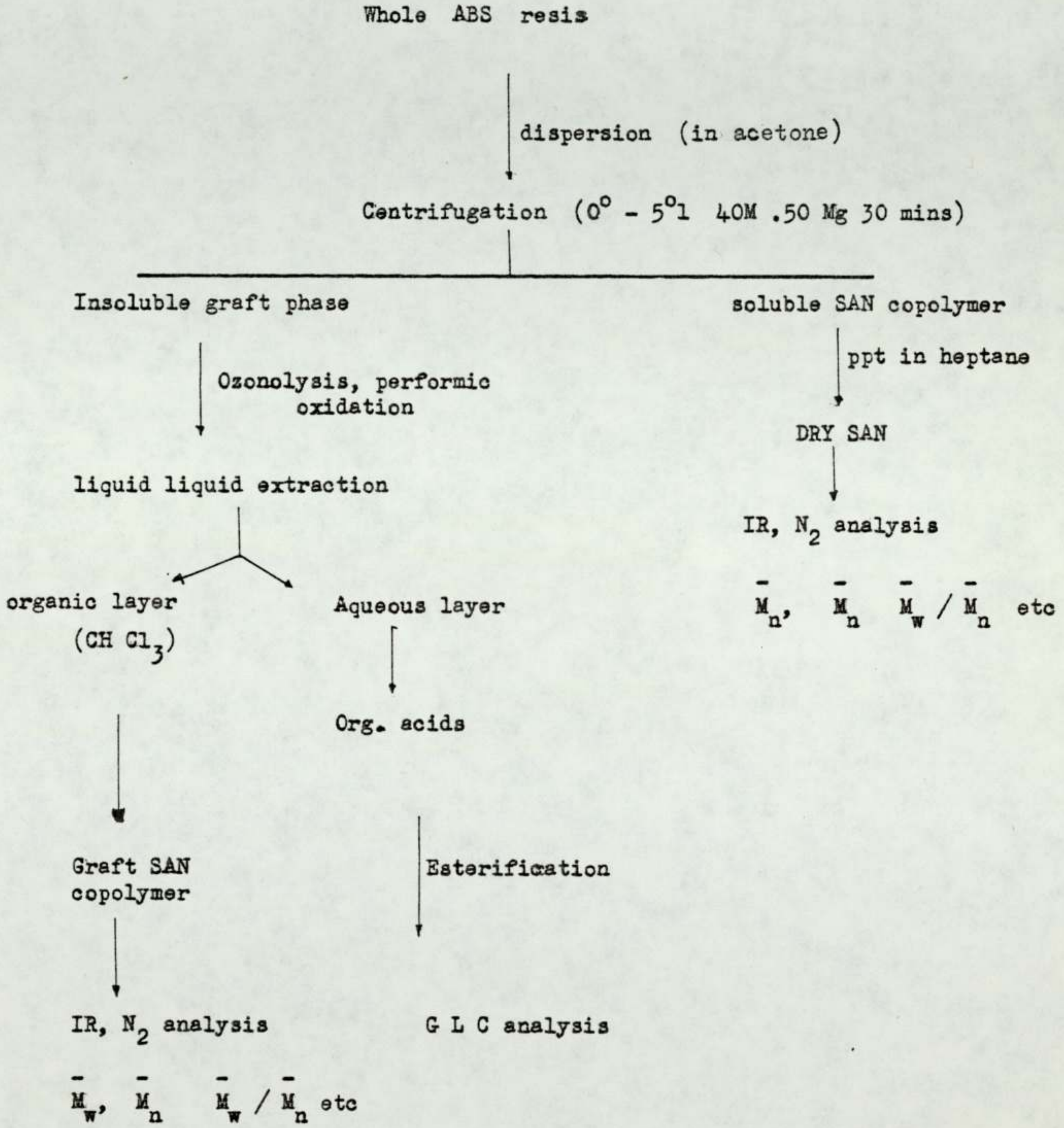


TABLE II


Whole ABS resis
dispersion (in acetone)
Centrifugation (0^o - 5^o1 40M .50 Mg 30 mins)
Insoluble graft phase
soluble SAN copolymer
Ozonolysis, performic oxidation
ppt in heptane
DRY SAN
liquid liquid extraction
IR, N_2 analysis
organic layer ($CH\ Cl_3$)
Aqueous layer
$\bar{M}_n$, $\bar{M}_n$ $\bar{M}_w$ / $\bar{M}_n$ etc
Org. acids
Graft SAN copolymer
Esterification
IR, N_2 analysis
G L C analysis
$\bar{M}_w$, $\bar{M}_n$ $\bar{M}_w$ / $\bar{M}_n$ etc

OBJECTIVES OF THE PRESENT WORK

ABS polymers are becoming increasingly useful in applications where high impact strength and toughness of the material is an essential requirement. However, it will become clear that the presence of PBD in these resins adversely effect their ultra violet light stability and hence the servicable outdoor life time. The majority of articles made from diene rubbers such as PBD and its copolymers SBR, NBR are available as black compounds, containing sufficient carbon black to cut off the harmful effects of solar radiation. Such a protection in ABS is limited to a smaller percentage of the articles made. From the volume of patents published claiming the efficiency of various types of stabilizers and their synergistic combinations, on the light stability of ABS, the magnitude of the problem of proper stabilization of this material could be judged.

The primary objective of the present investigation was to find a suitable stabilizer or a combination of stabilizers to give a better protection than that used commercially at the moment. A proper understanding of the mechanism of oxidative degredation (both thermal and photo) was found to be essential for this purpose.

To prevent the loss of these stabilizers by volatilization, leaching and for better dispersion, attempts will be made to chemically bind these with suitable functional groups to polymer backbone.

CHAPTER TWO - EXPERIMENTAL

2.1. MATERIALS

The following samples were supplied by Borg Warner Corporation, Holland.

'ABS' Unstabilized latex

'ABS' Factory stabilized latex

(33% W/V solids)

Polybutadiene latex Unstabilized.

'ABS' resin contains

54% W/W Styrene

30% W/W Acrylonitrile

15% W/W Butadiene

Traces of residual monomer, Emulsifier.

The following compounds were donated by ICI Limited.

2,6-di*tert*-butyl-4-methylphenol 'Toponol OC'

2,6-di*tert*-butyl phenol.

The following compounds were donated by Ciha-Geigy and Cyanamid Corporation.

Irganox 1076

Cyasorb UV531

2,4-dihydroxy benzophenone, thioglycollic acid and thio propionic acid were obtained from Aldrich Chemicals Limited.

2.2. SAMPLE PREPARATION

The sample films for analysis (Infra red, oxygen absorbtion studies, oven ageing, falling dart, impact testing etc.) were made by compression moulding 0.5g of processed ABS (in a torque rheometer, see below) between two polished steel plates at 190°C for 3 minutes ($1\frac{1}{2}$ minutes pre-heating time). Films of thickness $^1/_{12}$ m.m. were obtained by this method.

2.3. TORQUE RHEOMETER

A charge of 33g of powdered polymer was used in the chamber exposed to air (ram withdrawn) of the variable torque rheometer[27]. The samples were processed in a closed chamber (ram down) for 3 minutes at 190°C, at high shear rate (72 rpm). The hot melt was chilled rapidly in water on removal from the chamber to avoid uncontrolled thermal oxidation.

2.4. MEASUREMENT OF CARBONYL, HYDROXYL AND 14 TRANS POLYBUTADIENE ABSORBANCE BY INFRA RED SPECTROSCOPY.

Studies were made by using Perkin Elmer Model 457 IR Spectrometer. For quantitative analysis log chart paper Perkin Elmer Part No. 5100 - 4366 was used. Selected peaks were recorded on continuous chart paper and the peak 2220 cm^{-1} corresponding to C≡N was used as the reference. The indices were defined as the ratio of the absorbance of growing or decaying peak to that of the reference.

2.5. IMPACT STUDIES

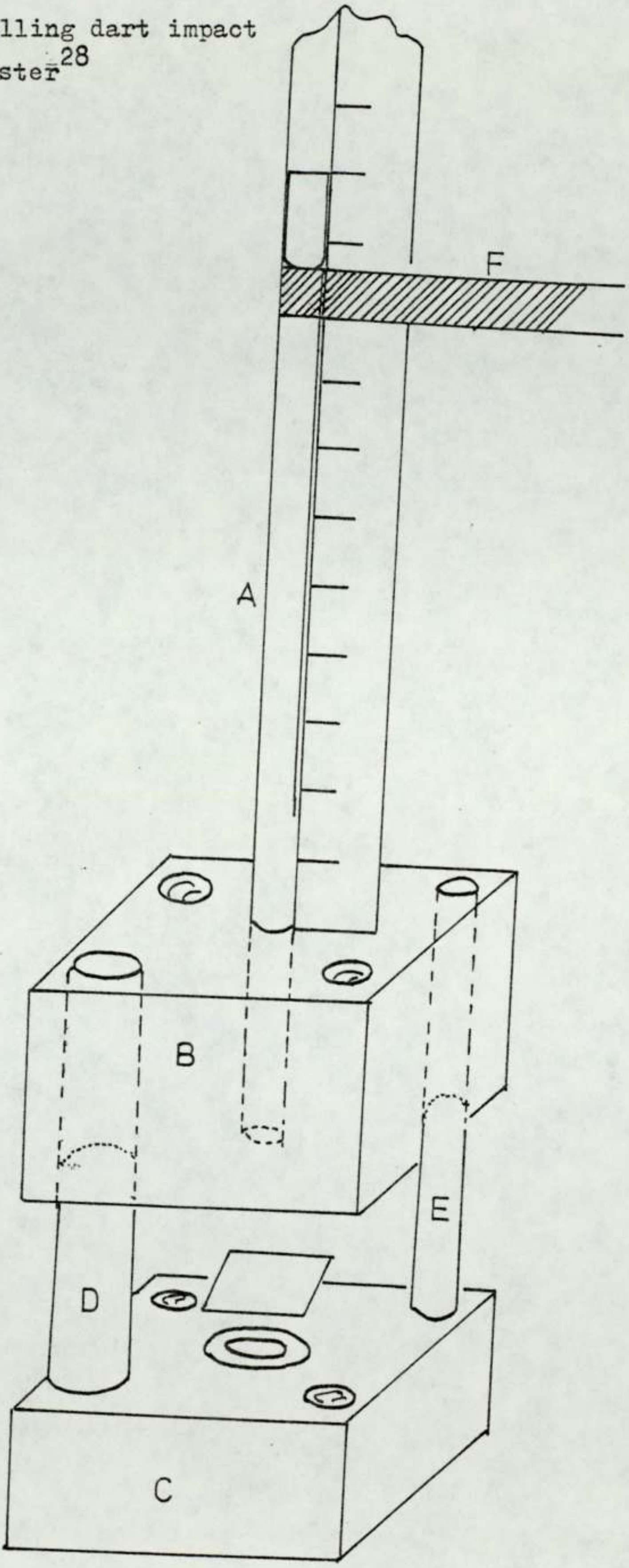
The impact strength of the ABS films were compared using a small falling weight impact tester[28]. This consisted of a metallic tube (A) fixed to a square steel block (B) which was clamped to another square steel block (C) by means of two pins (D and E). The sample was inserted between B and C and a dart like weight was released onto it, by withdrawing the retaining pin (F), Figure 9.

The energy to break the samples was measured at intervals of time during ageing. Samples of only 2.4-2.5 cm^2 were used for a single test. Twenty specimens were tested for every exposure time and the average was presented in the results.

2.6. OXYGEN ABSORBTION STUDIES

The change in volume of oxygen, absorbed by ABS samples during thermal oxidative ageing at 100°C, and hence the pressure was recorded on a chart via a pressure transducer maintained at 2.0 volts (Pye ether type UP 3TC). Two identical sets of tubes were connected to either ends of the transducer and were immersed in a silicone bath maintained at 100°C. The atmosphere of the cavity (116 cm^{-3}) containing the sample was purged with oxygen. The system was allowed to come to equilibrium and closed to the atmosphere. Calibration of the chart recorder was done by extracting known volumes of gas at the temperature of operation, from the sample vessel and reading the corresponding value on the recorder.

Figure 9. Falling dart impact tester[28]



2.7. UV CABINET

Indoor weathering of ABS films were conducted in a UV cabinet. The equipment supplied by Ciba-Geigy Limited, consisted of a cylindrical metal cabinet with thirty 20 watt lamps mounted around the periphery. The lamps were alternating equal numbers of fluorescent sunlamps and black-lamps, the spectral characteristics approximately that of sunlight. In order to maintain a constant spectral intensity the lamps were changed in strict rotation, one lamp being replaced every three days. The samples were placed vertically facing the lamps on a rotating sample holder.

2.8. OVEN AGEING

Films of ABS were mounted on cardboard frames (frames made to fit in the IR holder) and suspended in the cavities of a Wallace Oven, about 10 inches from the top. These were aged in air at 100°C flowing at $\frac{1}{2}$ cu.ft. per hour. The oxidative degradation was measured by infra red spectroscopy (refer 2-4).

2.9. EXTRACTION OF ABS

Hexane was employed to extract ABS in the form of powder, as well as films. Whatman paper thimbles were used to place the powder in the soxlet. Extraction was usually carried out for at least 48 hours, allowing 7 - 8 minute intervals for each filling of the soxlet with condensed hexane.

2.10. CHEMICAL DETERMINATION OF HYDROPEROXIDES

The polymer hydroperoxides of ABS were determined quantitatively by iodometry[29, 25]. Approximately (1 g) of ABS was measured accurately and dissolved in chloroform under N_2. (Best results were obtained when left overnight under N_2). 40 ml of freshly distilled isopropyl alcohol, 2 ml of glacial acetic acid and 10 ml of isopropyl alcohol saturated with sodium iodide, were added and the solution was magnetically stirred for about an hour, in a dark place under nitrogen. The solution was titrated with a standardised solution of 0.01 N sodium thiosulfate to the disappearance of yellow colour of liberated iodine.

$$2I^- \longrightarrow I_2 + 2e$$

$$ROOH + 2H^+ + 2e \longrightarrow H_2O + ROH$$

$$ROOH + 2I^- + 2H^+ \longrightarrow I_2 + H_2O + ROH$$

therefore

$$2I^- \equiv [I_2] \equiv [ROOH]$$

2.11. QUANTITATIVE DETERMINATION OF 2-HYDROXY BENZOPHENONE DERIVATIVES

2-Hydroxy benzophenone derivatives in chloroform solution show an absorption maxima in the region of 300 - 350 mm. The intensity of absorbtion was made use in the estimation of these derivatives. Hexane extracts of ABS were evaporated and the residue was dissolved in benzene, and any residual polymer was removed by adding absolute alcohol. The solution was filtered and the filtrate was used to obtain a UV spectrum using benzene/absolute alcohol as the blank. The concentration of the stabilizer was read off using a calibration curve.

2.12. CHEMICAL DETERMINATION OF HINDERED PHENOL ANTIXOIDANTS

Metcalf and Tomlinson's method of colorimetric determination of phenolic antioxidants was used in these estimations [30]. This procedure involves oxidation of antioxidants (A) under controlled conditions with ferric ions, followed by the reaction

$$\text{A reduced} + Fe^{+3} \longrightarrow \text{A oxidised} + Fe^{+2}$$

of Fe^{+2} ions produced, with 22' bipyridyl to form a coloured complex the intensity of which is proportional to the concentration of the antioxidant.

2.12a REAGENTS

Hexane Analar

Toluene Analar redistilled

Ethanol Absolute

22' bipyridyl (0.5% solution in absolute ethanol)

$FeCl_3$ 0.2% solution of $FeCl_3.6H_2O$ in absolute alcohol

(stored in the dark in an amber glass vessel).

2.12.b. PROCEDURE

10g of ABS (containing approximately 1 phr of antioxidant) was thoroughly extracted with 150 ml of analar hexane. The extract was rotary evaporated and the residue was dissolved in 25 ml of analar toluene. 25 - 30 ml of absolute ethanol was added to precipitate any residual polymer etc. The solution was filtered and the filtrate made up to 100 ml with absolute ethanol.

Two dry 10 ml volumetric flasks painted with several layers of black paint were immersed and clamped in a thermostatted (25 ± 0.5°C) water bath. 10 ml of the filtrate was pippetted to one, and 10 ml of 25/75 (V/V) toluene/EtoH solution to the other. 0.5 ml of dipyridyl solution and 1.0 ml of $FeCl_3$/EtoH solution were added to the two flasks and were allowed to stand at 25°C for about an hour. The optical density of the solution was measured against the blank using spectrophotometer cells, using wave length 520 mμ.

2.12.c. CALIBRATION

Weighed out accurately 0.03g of the hindered phenol into a 100 ml volumetric flask. The solution was made up to 100 ml by adding

25/75 (V/V) toluene/EtOH. Varying amounts of this solution was then diluted to 100 ml with toluene/EtOH (25/75) solution and the optical densities for the corresponding antioxidant concentration were determined. A calibration curve was plotted optical density vs the corresponding weight of the hindered phenol.

2.13. COAGULATION AND DRYING OF ABS

Coagulant was made by adding 1.5 parts of conc H_2SO_4, for every 100 parts of ABS, to 500 ml of distilled water. Steam was injected and the temperature of the solution was raised to 65°C. ABS latex was added slowly with stirring to give crumbs of coagulum. The solution was cooled by adding water and filtered. The crumb was dried in the laboratory in a vacuum oven at 55°C for a constant weight. Factory made samples were dried by fludised bed drying at 60°C for about 30 minutes.

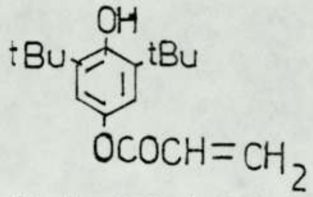
2.13.1. PREPARATION OF 'ABS' RESIN

ABS latex was prepared using the formulation and the method described in the US Patent 3,238, 275[31]. The amount of PBD latex, styrene and acrylonitrile used in the preparation of 'ABS' is mentioned below. (In parts by weight).

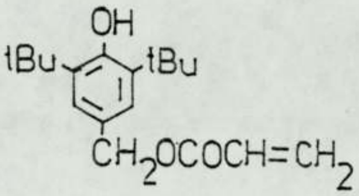
Styrene	54.0
Acrylonitrile	30.0
Polybutadiene/in latex	15.7

2.14. SYNTHESIS AND CHARACTERISATION OF VINYL SUBSTITUTED COMPOUNDS

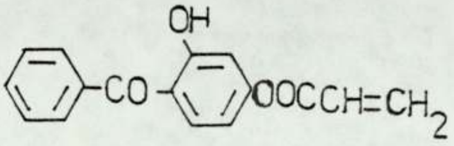
The following compounds were synthesised to determine their potential as bonded stabilize in ABS.



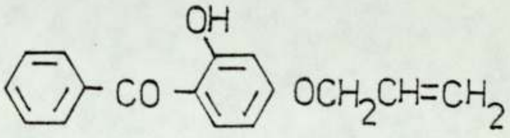
3,5 di-*tert*-butyl 4 hydroxy phenylacrylate.(DBPA)



3,5 di-*tert*-butyl 4 hydroxy benzylacrylate.(DBBA)



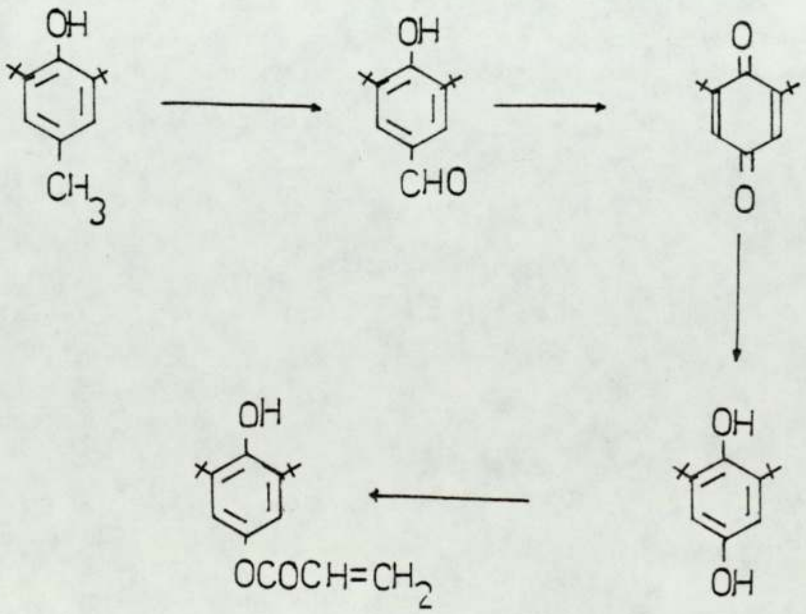
4-benzoyl 3 hydroxy phenyl-acrylate.(BHBA)



4-benzoyl 3 hydroxy phenyl allylether (BHAA)

2.14.a. SYNTHESIS OF 3,5-DITERTIARY-BUTYL-4-PHENYLACRYLATE

The following reaction scheme was used;[32]



2.14a.1. PREPARATION OF 26 DITERTIARY BUTYL BENZO-QUINONE.[33]

128g (0.8M) of bromine was added dropwise to a stirred solution of 44.6g (0.2M) of 26 ditertiary butyl-4 methyl pehnol (TOPONOL OC., ICI Limited) in 600 ml of tertiary butyl alcohol at 25°C. The temperature rose, and after the addition of bromine stirring was continued for a further hour. The mixture was cooled and the yellow crystalline product filtered off. This was washed with 10% sodium thiosulfate solution, then with distilled water and dried in a vacuum desiccator. The product was an off white crystalline solid, melting at 189°C. The yield was 42g (90%) of 3,5 ditertiary butyl 4 hydroxy benzaldehyde. The aldehyde was characterised by IR, and NMR spectroscopy.

IR data.

Phenolic	OH	3640 cm^{-1}
Carbonyl		1670 cm^{-1}

NMR (CCl_4)

Aldehydic proton	0.2T	(singlet)
Aromatic proton	2.3T	(singlet)
Phenolic proton	4.3T	(singlet)
Tertiary butyl protons	8.6T	(singlet).

The aldehyde (30g) was dissolved in 5% caustic soda solution (640 ml) and 91 ml of 6% H_2O_2 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 recrystallised from methanol as yellow-orange prisms (10.5g) melting at 65.5°C.

IR data

C-H Aromatic	$3010\ cm^{-1}$
C-H Aliphatic	$2900\ cm^{-1}$
Carbonyl	$1660\ cm^{-1}$

NMR (CCl_4)

Aromatic protons	3.5τ	(singlet)
Tertiaryl butyl protons	8.6τ	(singlet)

2.14.a2. PREPARATION OF 2,6 DITERTIARY BUTYL 4 HYDROXY PHENOL[33].

2,6 ditertiary butyl benzoquinone was dissolved in propanol and concHcl acid to give a yellow solution. Zn-dust was added, when the effervescence ceased sodium bicarbonate solution (10% W/W) was added to decompose the excess acids and the solids filtered off. The iso-propanol solution was rotary evaporated to yield a white solid. This was re-crystallised from pet ether and a white crystalline solid was obtained melting at 100°C.

IR Data.

Free phenolic OH	3640 cm^{-1}
hydrogen bonded OH	3500 - 3100 cm^{-1}

NMR (CCl_4)

Aromatic proton	3.3 τ (singlet)
Phenolic proton	5.4 τ (singlet)
Tertiary butyl proton	8.6 τ (singlet)

2.14.a.3. PREPARATION OF 3,5-DITERTIARYBUTYL-4-HYDROXY PHENYL ACRYLATE[34].

22.2g (0.1M) of 2,6 ditertiary butyl 4 hydroxy phenol and 20.2g (0.2M) of triethyl amine were dissolved in 150 ml of tetrahydrofuran, under nitrogen, and stirred with cooling in ice until a clear solution was obtained. 9.1g (0.1M) of acryloyl chloride (Aldrich Chemicals) was added over a period of ten minutes and stirring continued for one hour. The triethyl amine hydrochloride was filtered off and the filtrate poured into an excess of water to give an oil. This oil slowly solidified on standing to an orange solid. This was recrystallised, from ethanol, to a white solid melting at 102-103°C.

IR Data

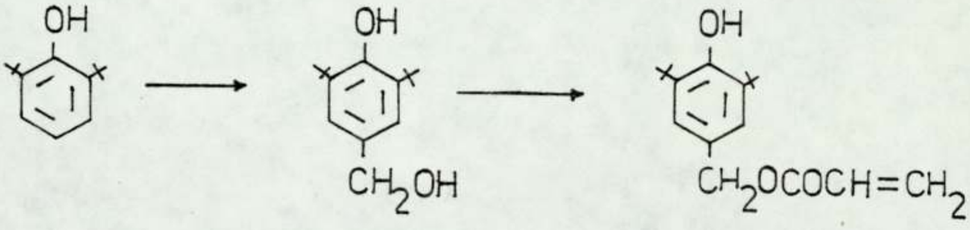
Phenolic OH	3640 cm^{-1}
Ester carbonyl	1730 cm^{-1}
Vinyl double bond	1650 cm^{-1}

NMR ($CDCl_3$)

Aromatic proton	3.2 τ (singlet)
Vinyl protons	3.4-4.2 τ (multiplet)
Phenolic protons	5.0 τ (singlet)
Tertiary butyl protons	8.6 τ (singlet)

2.14.b. SYNTHESIS OF 3,5 DITERTIARY BUTYL 4 HYDROXY BENZYL ACRYLATE

This was prepared according to the following scheme.



2.14.b.1. PREPARATION OF 3,5, DITERTIARY BUTYL 4 HYDROXY BENZYL ALCOHOL[35]

The 2,6 ditertiary butyl phenol was obtained from ICI Limited and used without further purification.

53.5 parts by volume of a 75% solution of formaldehyde in tertiary butyl alcohol 50 parts of a 500g/litre solution of 2,6 ditertiary butyl alcohol and 14 parts of a 50g/litre solution of potassium tertiary butoxide in the same solvent were mixed at 20°C and stirred under N_2, for thirty minutes. The mixture was then poured into ice water and two layers formed the upper organic layer solidifying. The solids were washed with water stirred with hexane filtered and air dried. A crystalline white solid of 3,5 ditertiary butyl 4 hydroxy benzyl-alcohol was obtained melting at 137°C.

IR Data

Free phenolic OH	3600 cm^{-1}
H-bonded OH	3500 - 3300 cm^{-1}

NMR (CCl_4)

Aromatic protons	2.9τ	(singlet)
Phenolic proton	4.9τ	(singlet)
Methylene protons	5.5τ	(singlet)
Tertiary butyl protons	8.6τ	(singlet)

2.14.b2. REACTION OF 3,5 DITERTIARY BUTYL 4 HYDROXY BENZYL ALCOHOL WITH ACRYLIC ACID.[36]

A mixture of 47.2g (0.2M) of 3,5 ditertiary butyl 4 hydroxy, benzyl alcohol and 130 ml of acrylic acid was warmed gently until a clear solution was obtained. A further 10 ml of acrylic acid containing one drop of concentrated H_2SO_4 acid was added and the solution allowed to remain at room temperature for six hours. The solution was washed with water and the organic layer was extracted with ether. The ether layer was washed with aqueous sodium bicarbonate to remove excess acrylic acid. The ether phase was dried over anhydrous $MgSO_4$ filtered and evaporated. The residue was recrystallised from pet ether to give

3,5 ditertiary butyl 4 hydroxy benzyl acrylate melting at 68° - 69°C in 90% yield.

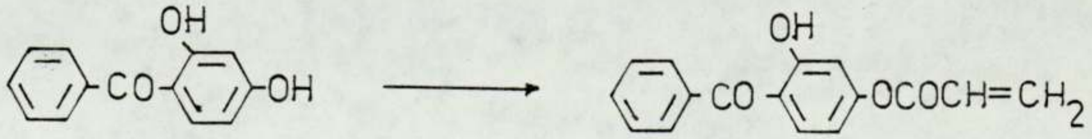
IR Data

Free phenolic OH	3640 cm^{-1}
Ester carbonyl	1820 cm^{-1}
Vinyl double bend	1640 cm^{-1}

NMR Data

Aromatic pretons	2.9τ	(singlet)
Vinylic protons	$3.6 - 4.5\tau$	(multiplet)
Phenolic proton	4.8τ	(singlet)
Methylene protons	5.0τ	(singlet)
Tertiary butyl protons	8.6τ	(singlet)

2.14.c. PREPARATION OF 4 BENZOYL-3-HYDROXYPHENYL ACRYLATE [37].



The 2,4 dihydroxy benzophenone was used as received from Aldrich Chemicals without further purification.

21.4 parts of 2,4 dihydroxy benzophenone were dissolved in a mixture of 4 parts of NaOH and 65 parts of methanol. The solvent was removed by rotary evaporation, and monosodium compound was dried and suspended in 125 parts of absolute benzene. Acryloyl chloride (9 parts) was added dropwise with stirring and cooling, and the mixture stirred for a further hour. The sodium chloride was removed and the benzene distilled off under vacuum. The ester was recrystallised from aqueous ethanol to give a pale yellow solid melting at 80°C in 70% yield.

IR Data.

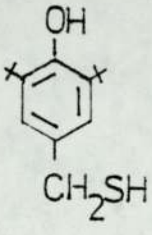
Phenolic OH	3400 cm^{-1}
Ketone carbonyl	1640 cm^{-1}
Ester carbonyl	1750 cm^{-1}

NMR Data

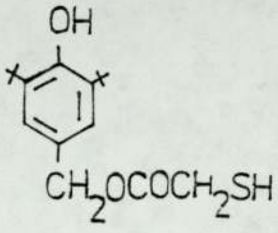
5 Aromatic protons	2.3 - 2.6 τ	(multiplet)
3 Aromatic protons	3.2 - 3.7 τ	(multiplet)
Phenolic proton	-2.2 τ	(singlet)
Vinyl protons	3.I - 4.0 τ	(singlet)

2.15 SYNTHESIS AND CHARACTERISATION OF MERCAPTO COMPOUNDS

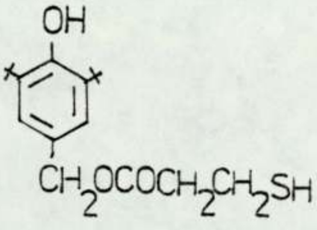
The following compounds were synthesised to determine their potential as adducts in ABS.



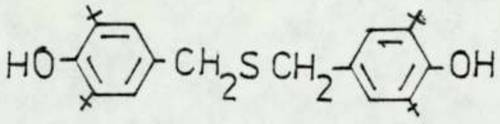
3,5 di-tert. butyl 4 hydroxy benzylmercaptan (BHBM)



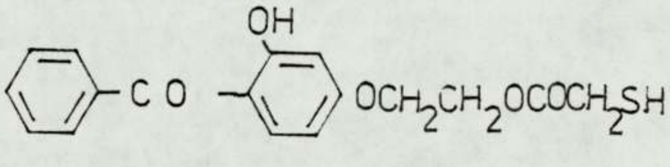
3,5 di-tert. butyl 4 hydroxy benzylthioglycollate (BHBT)



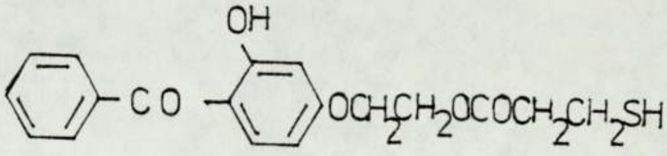
3,5 di-tert. butyl 4 hydroxy benzylthiopropionate (BHBP)



Bis(3,5 di-tert. butyl 4 hydroxy benzyl)monosulphide (TBMP)



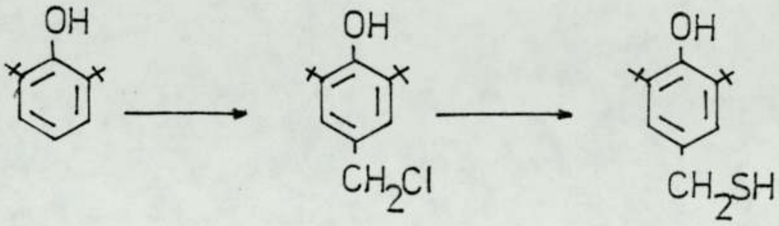
4 benzoyl 3 hydroxyphenyl o-ethyl thioglycollate (EBHPT)



4 benzoyl 3 hydroxyphenyl o-ethyl thiopropionate (EBHPP)

2.15.a. SYNTHESIS 35 DITERTIARYBUTYL 4 HYDROXY BENZYL MERCAPTAN

The following two step scheme was adopted [38].



2.15.a.1. PREPARATION 3,5 DITERTIARYBUTYL 4 HYDROXY BENZYLCHLORIDE

The 2,6 ditertiary butyl phenol was used as received from ICI Limited without any further purification.

205 g of 26 ditertiary butyl phenol was placed in a 3 necked flask with a sintered gas inlet, stirrer. 105 g of paraformaldehyde and 500 ml of concentrated hydrochloric acid were added and stirred. Hcl gas was passed into the mixture taking care that minimum would escape. Stirring was continued for 7 hours and the reaction mixture was allowed to stand for a further 15 hours. Hcl gas was again passed into the solution for a further 2 hours with stirring. The mixture separates into two layers, the bottom aqueous layer was discarded. The organic layer was extracted with ether and washed neutral with sodium bicarbonate solution followed by distilled water. The extract was dried with anhydrous $MgSO_4$ ether distilled off by rotary evaporation. The 35 ditertiarybutyl 4 hydroxy benzyl chloride was collected by vacuum distillation at 140°C as a red liquid.

(It was observed that catalytic amount of ferric chloride 0.5g increase the yield of the benzylchloride).

IR Data.

Phenolic	OH	3640 cm^{-1}

NMR Data.

Aromatic protons	3.0 τ (singlet)
Methylenic protons	6.2 τ (singlet)
Tertiary butyl protons	8.7 τ (singlet)
Phenolic protons	− 2.1 τ (singlet)

2.15.a.2. PREPARATION OF 3,5 DITERTIARY BUTYL 4 HYDROXY BENZYLMERCAPTAN

5.8g of $Mg(OH)_2$ was added to 125 ml of dimethylformamide solution. Hydrogen sulfide gas was passed through this mixture for about half an hour. The mixture turns green during this process. A solution of 29.0 g of 3,5 di*tert*butyl 4 hydroxy benzylchloridein 50.0 ml of hexane was added dropwise to this mixture while stirring. The addition was controlled in such a way not to allow the reaction mixture to turn bright yellow. (To prevent the formation of sulfides). The reaction mixture was allowed to stand for a further half hour with stirring and was added to an ice-water mixture. The mercaptan was extracted with ether dried with anhydrous sodium sulfate. The ether was rotary evaporated and the mercaptan was obtained by vacuum distillation at 128 - 131°C (0.5 mm of Hg) 3,5 ditert.butyl 4 hydroxy benzylmercaptan was obtained as a liquid solidifying at 27°C to a white solid.

IR Data

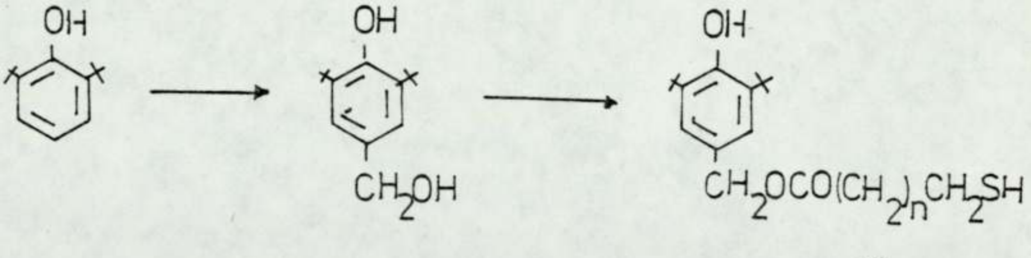
Phenolic OH	3640 cm^{-1}

NMR Data

Aromatic protons	3.0τ	(singlet)
Methylenic protons	6.0τ	(singlet)
Thiol proton	7.2τ	(singlet)

2.15.b. SYNTHESIS OF 3.5 DITERTIARY BUTYL 4 HYDROXY BENZYL THIO ACID ESTERS.

The following reaction scheme was used in the preparation of the two thio acid esters 3,5 ditertiary butyl 4 hydroxy benzyl thio glycollate and thio propionate.



The 35 ditertiary butyl 4 hydroxy benzyl alcohol was prepared using the procedure described under 14.b.1.

23.6 g of 3,5 ditertiarybutyl 4 hydroxy benzyl alcohol was dissolved in 200 ml of toluene, 3 drops of concentrated sulfuric acid and 0.15M of thio acid added to this solution. A Dean and Stark apparatus was placed between the flask and the condensor to collect the water formed in the reaction. The solution was refluxed and theoritical was collected in 5 - 6 hours. The solution was washed with sodium bicarbonate solution, followed by distilled water, and then dried with $MgSO_4$. The ester crystallises out from tolulene solution on standing. Further recrystallisation was carried out from benzene.

Thioglycollate ester pale yellow	MPt $98^\circ - 99^\circ C$
Thio propionate ester white	MPt $80^\circ - 81^\circ C$

Spectroscopic data for 35 ditertiary butyl 4 hydroxy benzyl thio glycollate.

IR Data

Phenolic OH	$3640\ cm^{-1}$
Ester carbonyl	$1725\ cm^{-1}$
Thio group S-H	$2550 ccm^{-1}$

NMR Data

Aromatic protons	2.9τ	(singlet)
Thiol proton	7.2τ	
Tertiary butyl protons	8.6τ	(singlet)
$-O-CH_2-$ protons	5.6τ	(singlet)
$-CH_2-S$ protons	6.0τ	(multiplet)

Spectroscopic data for 3,5 ditertiary butyl 4 hydroxy benzyl thio propionate.

IR Data

Phenolic OH	3640 cm^{-1}
Ester carbonyl	1720 cm^{-1}
Thiol group S-H	2550 cm^{-1}

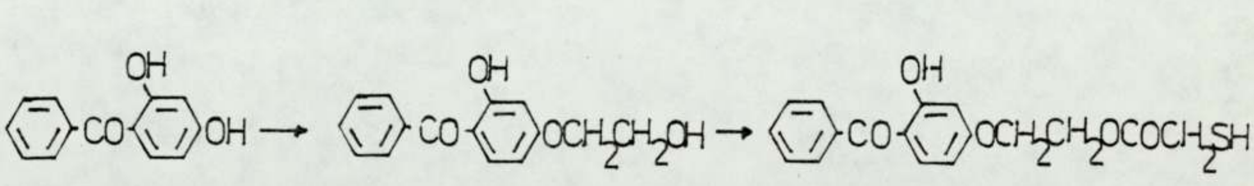
NMR Data

Aromatic protons	2.9τ	(Singlet)
Thiol protons	7.2τ	(Triplet)
Tertiary butyl protons	8.6τ	(Singlet)
$O-CH_2-$ protons	5.6τ	(Singlet)
$-CH_2-CH_2-S-$ protons	6.0-6.2τ	(Multiplet)

Both compounds were confirmed by Mass-spectrometry and elemental analysis.

2.15.c. SYNTHESIS OF 4 BENZOYL 3 HYDROXY PHENYL O-ETHYL THIOGLYCOLLATE.

The following two-stage process was used in the synthesis of this compound.



2.15.c.1. PREPARATION OF 2 HYDROXY 4(β- HYDROXY ETHOXY) BENZOPHENONE[39]

21.4 g (0.1 M) of 24 dihydroxybenzophenone and 4.0 g (0.1 M) of sodium hydroxyde were dissolved in 125 ml of distilled water 8.1 g (0.1 M) of ethylene chlorohydrin were added all at once to the above solution and the mixture was stirred at 90° - 95°C for 4 hours, and allowed to stand overnight at room temperature. The tacky solid obtained was recrystallised from acetonitrile to give white crystals. MPt 92° - 93°C.

IR Data

Phenolic hydroxyl and alcoholic hydroxy	3500 - 3100 cm^{-1}
Benzophenone carbonyl	1630 cm^{-1}
Aliphatic CH_2	2920 cm^{-1}

NMR Data

Aromatic protons	2.3 - 2.5τ	(Multiplet)
Phenolic proton	- 2.2τ	(Singlet)
Alcoholic hydroxyl proton	4.0τ	
Methylinic protons	6.5 - 6.7τ	(Multiplet)

The compound was confirmed by mass spectrometry.

2.15.c.2. PREPARATION OF 4 BENZOYL 3 HYDROXY PHENOXY ETHYLTHIOGLYCOLLATE.

25.8g (0.1M) of 2 hydroxy 4(β- hydroxy ethoxy) benzophenone and 10.0g (0.109 M) of thioglycollic acid were dissolved in 200 ml of toluene. 0.5 ml of concentration sulfuric acid was added to this solution. The flask was fitted with a Dean's stark and a condensor and the solution was refluxed till the theoritical amount of water was removed, (5 - 6 hours). The solution was washed neutral with sodium bicarbonate solution, distilled water and dried with anhydrous $MgSO_4$.

Toluene was removed by rotary evaporation to give a red liquid which gives a yellow solid on standing MPt $53^{\circ} - 54^{\circ}$C.

IR Data

H-Bonded Phenolic OH	3400 - 3200 cm^{-1}
Ester carbonyl	I720 cm^{-1}
Thiol group SH	2550 cm^{-1}

NMR Data (CCl_4)

Aromatic proton	2.3 - 2.6 τ
Methylenic protons	6.2 - 6.5 τ
Phenolic proton	- 2.2 τ
Thiol proton	7.2 τ
3 Aromatic protons	3.2 - 3.7 τ

The compound was confirmed by mass spectrometry.

The same procedure was adopted to make 4 benzoyl 3-hydroxyphenoxy ethylthiopropionate using II.5_{g} to thiopropionic acid.

IR Data

4-bonded Phenolic OH	3400 - 3200 cm^{-1}
Ester carbonyl	I720 cm^{-1}
Thiol group (SH)	2550 cm^{-1}
Aromatic carbonyl	I630 cm^{-1}

NMR Data (CCl_4)

5 Aromatic protons	2.3 - 2.6τ
3 Aromatic protons	3.2 - 3.7τ
Phenolic protons	- 2.2τ
Thiol proton	7.2τ
Methylene protons	
$OC-CH_2-CH_2-S$	6.2 - 6.4τ (multiple)
$O-CH_2-CH_2-O$	6.5 - 6.7τ (multiple)

This compound was confirmed by mass spectroscopy.

2.16. PREPARATION OF BIS (3,5 DITERTBUTYL 4 HYDROXY BENZYL) MONOSULFIDE [40].

19.2g of sodium sulfide (Na_2S) in 15 ml of water, 120 ml of isopropyl alcohol and 50g of 3,5 di*tert* butyl 4 hydroxy bensylchloride were refluxed for 2 hours. The solid obtained was filtered, washed with water, dried and recrystallisedffrom isooctane solution. The pale yellow solid after recrystallisation had a melting point of 142 - 143°C.

IR Data

Phenolic OH	3640 cm^{-1}

NMR Data

Aromatic protons	2.9τ	(singlet)
Tert butyl protons	8.6τ	(singlet)
Phenolic proton	4.8τ	(singlet)

Methylenic protons 5.6 τ (singlet)

The compound was confirmed by mass spectroscopy.

2.17. SYNTHESIS OF 35, 3',5' TRETRA TERT. BUTYL STILBENE-4 4'-QUINONE[41].

26 di*tert*-butyl 4 methyl phenol (11 g, 0.05 M) 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 $NaHCl_3$. Evaporation of dried chloroform solution gave a bright red gum. By repeated extractions with ether unsoluble 35,3'5 tetra tert butyl stilbene 44' quinone was purified. This material was recrystallised from glacial acetic acid in crimson needles.

MPt 300°C

IR Data

Quinone carbonyl 1634 cm^{-1}

NMR Data (Acetic acid)

Olefinic protons 6 - 7 τ (multiplet)

2.18a. ALTERNATIVE METHOD FOR THE PREPARATION OF 35 DITERTIARY BUTYL 4 HYDROXY BENZYLMERCAPTAN.

The following two-step procedure was adopted for the preparation of the thiol derivative mentioned above; using

3,5 di*tert* butyl 4 hydroxy toluene instead of 2,6 di*tert*. butyl phenol as in 2.15.a.

2.18.a.1. PREPARATION OF 35 DITERTIARYBUTYL 4 HYDROXY BENZYLBROMIDE.

The 3,5 di*tert* butyl 4 hydroxy toluene was used as received from ICI Limited, without any further purification.

22.0g (0.1M) of 35 di*tert* butyl 4 hydroxy toluene, 20.0g (0.1M) of N-bromosuccinamide and 0.3g of azobis isobutronitrile (AZBN) in 200 ml of carbon tetrachloride were refluxed for 3 - 4 hours. The succinimide floats to the surface after reaction. The solid was removed by filtration and CCl_4 was removed by rotary evaporation. The 3 5 ditertiary butyl 4 hydroxy benzylbromide distils off at 135°C on vacuum distillation at 0.5 m.m. of Hg pressure.

2.18.a.2. PREPARATION OF 3,5 DITERTIARYBUTYL 4 HYDROXY BENZYLMERCAPTAN (BHBM).

4.0g (0.1M) of NaOH was dissolved in 125 ml of ethanol. H_2S gas was allowed to pass through the solution till the w ight was increased by 1.6 gms. 29.9g of 35 di*tert*. butyl 4 hydroxy benzylbromide in 50 ml of ethanol was added dropwise over a period of 30 minutes to the above solution, with nigowrons stirring. The mixture so obtained was filtered to remove sodiumbromide separated during the reaction. Ethanol was removed by rotary evaporation and 3,5 ditertiary butyl 4 hydroxy benzylmercaptan was obtained by vacuum-distillation of the residue at 128-131°C (0.5 m.m. of Hg pressure). The liquid obtained solidified to a white solid having a melting point of 27-28°C.

The compound was identified by IR, NMR mass spectroscopy, and elemental analysis, (Section 15.a. this chapter).

2.19. PREPARATION OF EMULSIONS

Stabilizer emulsions were prepared by the following method described for Irganox 1076 in its technical bulletin[42], but using stearic acid in place of 10g of antioxidant was melted with 1g of stearic acid at 70-75°C and slowly added with vigorous stirring to 50 ml of water (70 - 75°) containing stoichiometric amound (0.135g of 98.8%) of NaOH. Stirring was continued for 1 - 2 minutes and the resulting emulsion was quickly cooled to room temperature in a cooling bath. The solution was diluted before use by stirring hot water to the required amount.

CHAPTER THREE - MECHANISM OF OXIDATIVE DEGRADATION OF ABS

3.1 RESULTS

3.1.a. Infra red spectra of unoxidised ABS

The following absorptions in the infra red spectra of ABS were assigned with the help of data published in three references [43, 44, 45].

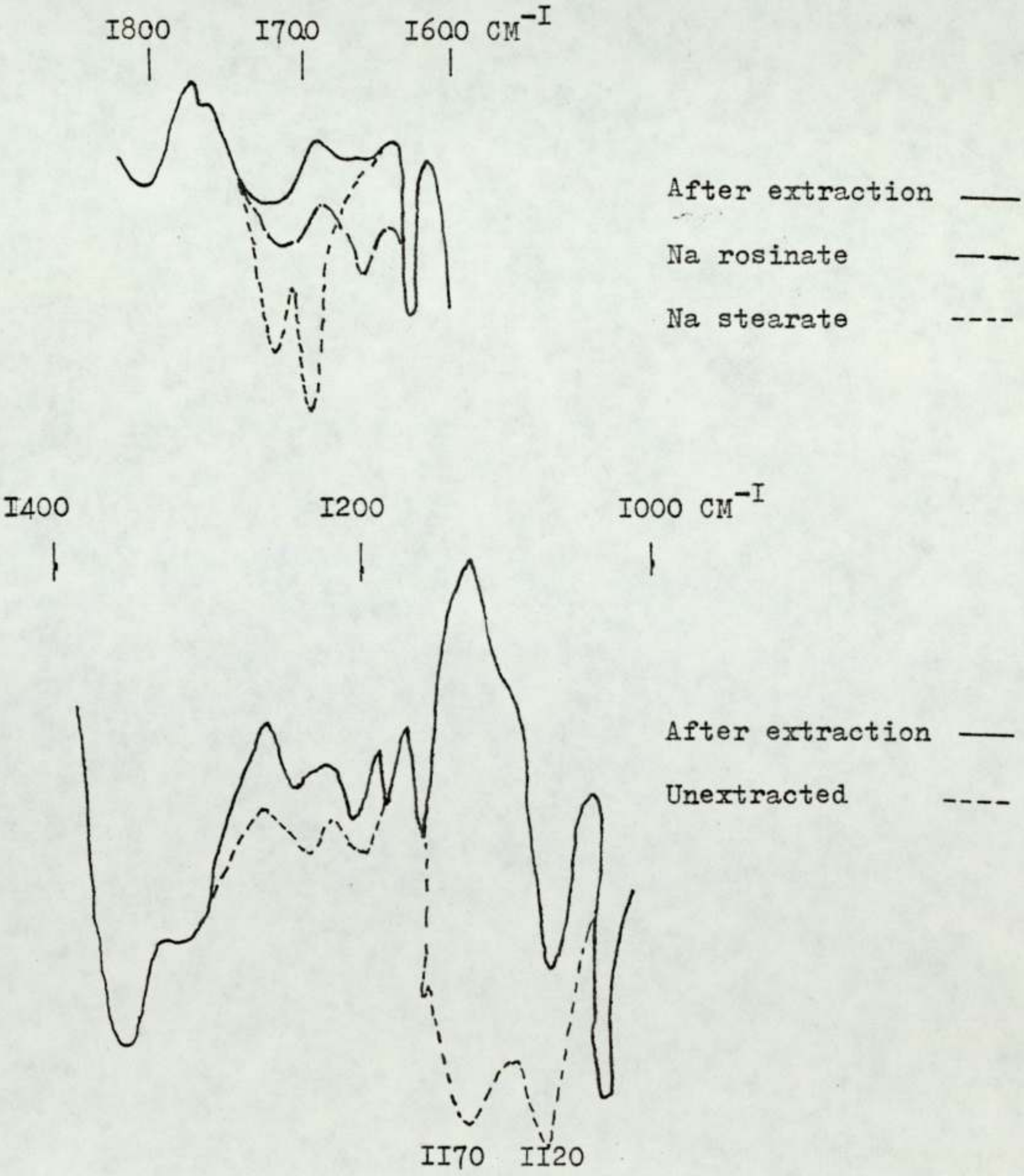
TABLE 4. IR GROUP FREQUENCIES IN ABS

ABSORBTION BAND cm^{-1}	ASSIGNMENT
3060	C-H stretching of phenyl group
3015	C-H stretching
2920	CH_2
2850	CH_2
2220	CN
1950, 1870, 1810 (3 peaks)	Phenyl group monosubstituted
1637	Cis 14 C=C polybutadiene
1600, 1580	phenyl group
1490	
1450	CH_2 and phenyl group
1350, 1315, 1240, 1210, 1180, 1160	CH_2 and phenyl group
1070, 1030	phenyl group
965	trans 14 C=C polybutadiene
912	1,2 vinyl and phenyl group
760, 700	phenyl group monosubstituted

3.1.b. Infra red spectra of extracted unoxidised ABS

The extraction of ABS polymer removes carbonyl absorbtion and two strong peaks at 1120 cm^{-1} and 1170 cm^{-1} respectively. The carbonyl removed differs with the emulsifier used in the preparation of ABS, Fig. 10.

Figure IO.



3.1.c. Photoxidation of Unstabilized ABS

Compression moulded unstabilized ABS films were exposed to UV irradiation at ambient temperature and the changes in the concentration of functional groups were monitored by IR. Typical IR spectrum of photoxidised ABS is shown in the Fig. II. The development of carbonyl and hydroxyl centred around 1720 cm^{-1} and 3450 cm^{-1} and the decay of trans 14 absorption are shown in Fig. 12. Both functional groups, carbonyl and hydroxyl show an induction period of 3 and 2 hours respectively. Trans 14 PBD absorbtion showed an initial slow decay leading to a faster linear depletion after about $3\frac{1}{2}$ hours of UV exposure. Oxygen absorption too, showed an induction period of about 3 hours followed by rapid absorption, similar to the build-up of carbonyl, Fig. 12. Impact strength fell very rapidly in a linear manner after only 3 hours of exposure to ultra violet radiation. The lowest value was reached in 11 hours, though at this stage, only 12% of the trans double bond had disappeared (by infra red) Fig. 13.

The complex band in the carbonyl region is centred around 1720 cm^{-1}. The shoulders are assigned as follows:-

1670 - 1685 cm^{-1}	unsaturated ketone
1690 cm^{-1}	unsaturated aldehyde
1705 - 1700 cm^{-1}	carboxylic acid group
1720 cm^{-1}	saturated C=O group
1735 cm^{-1}	Ester C=O group

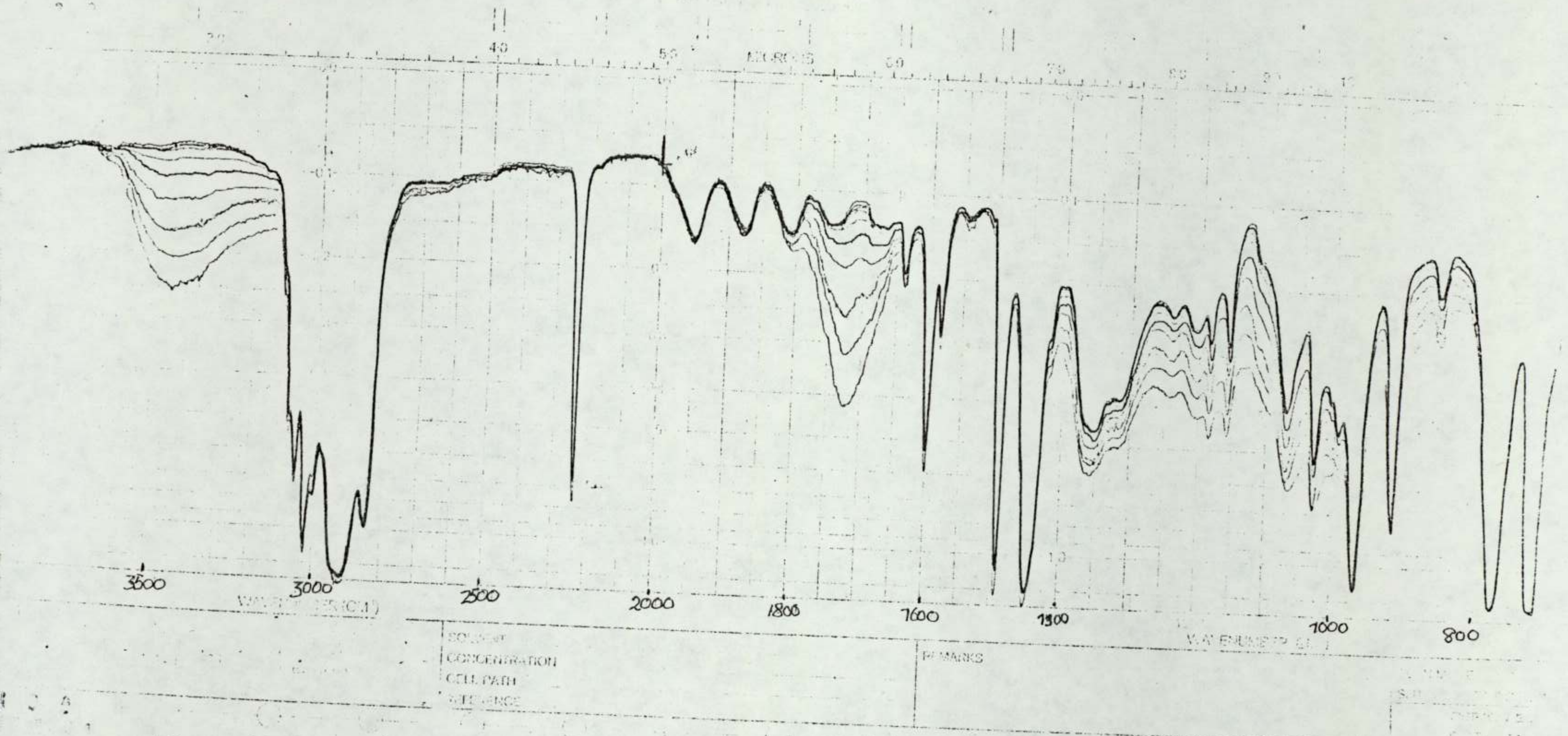


Figure 11 Changes in the IR spectrum of freshly prepared unstabilized ABS (S_2O_8/S_2O_5) on photo-oxidation for 20 hours

Figure 12 Changes in the functional group indices on uv exposure of unstabilized [redacted] ABS films

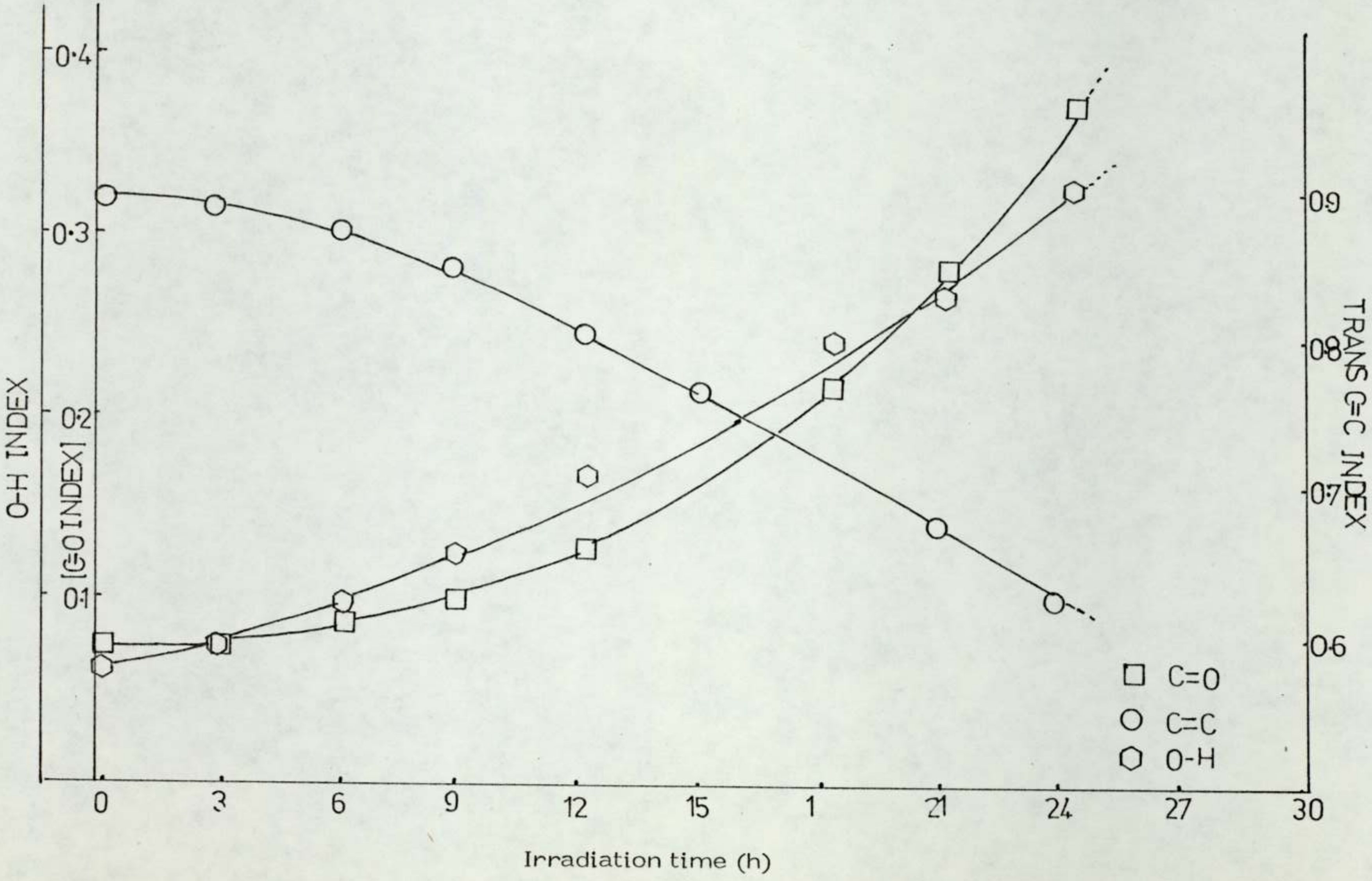
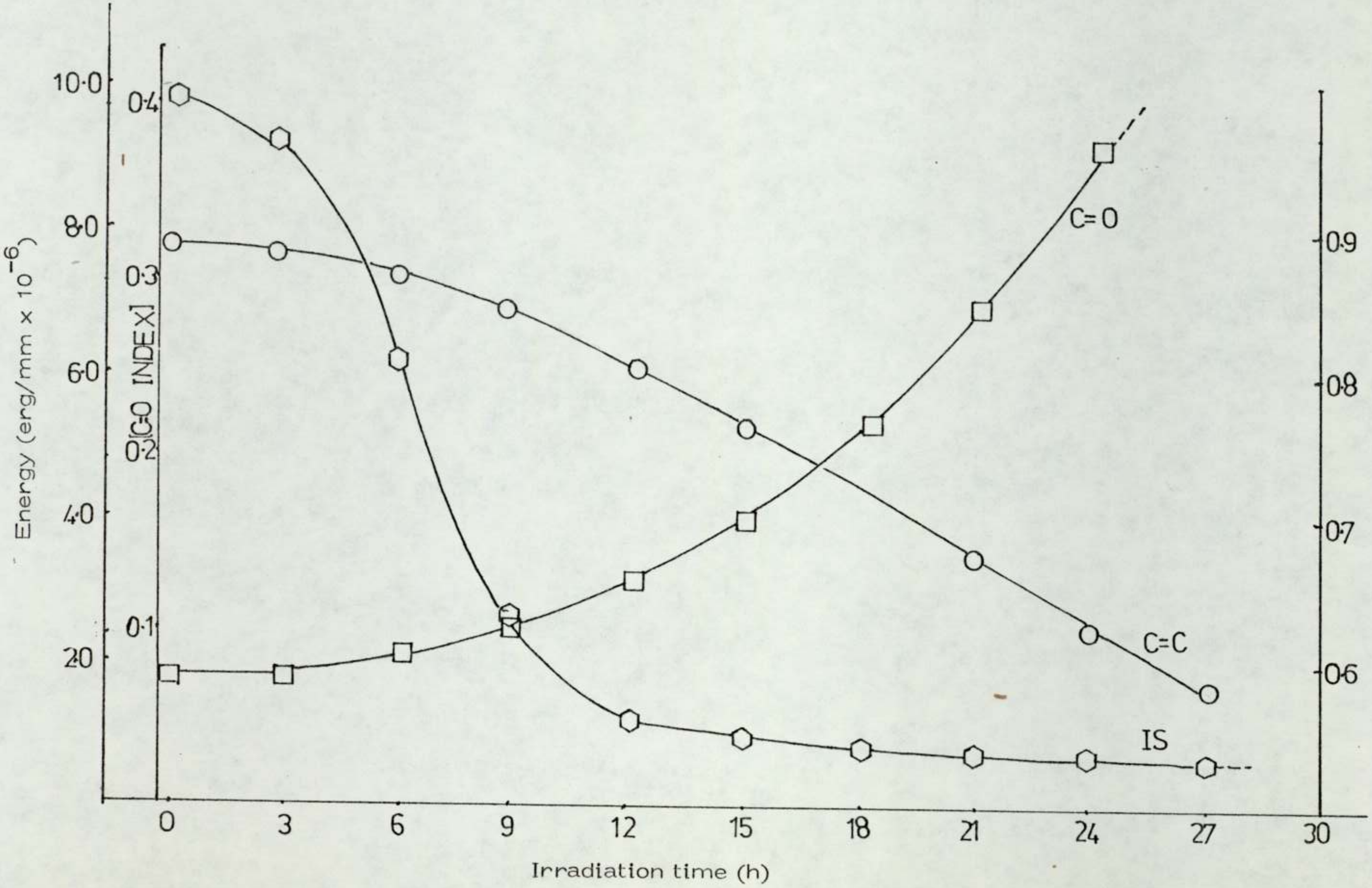


Figure 13 Changes in the impact strength, C=O and trans-1,4 C=C of unstabilized 'ABS' [redacted]
[redacted] photo-oxidation



The vinyl absorbtion at 912 cm^{-1} was not taken into account in the quantitative analysis by infra red, due to the fact that it overlaps with an absorbtion of the phenyl group. No change in the nitrile or phenyl absorbtions was observed.

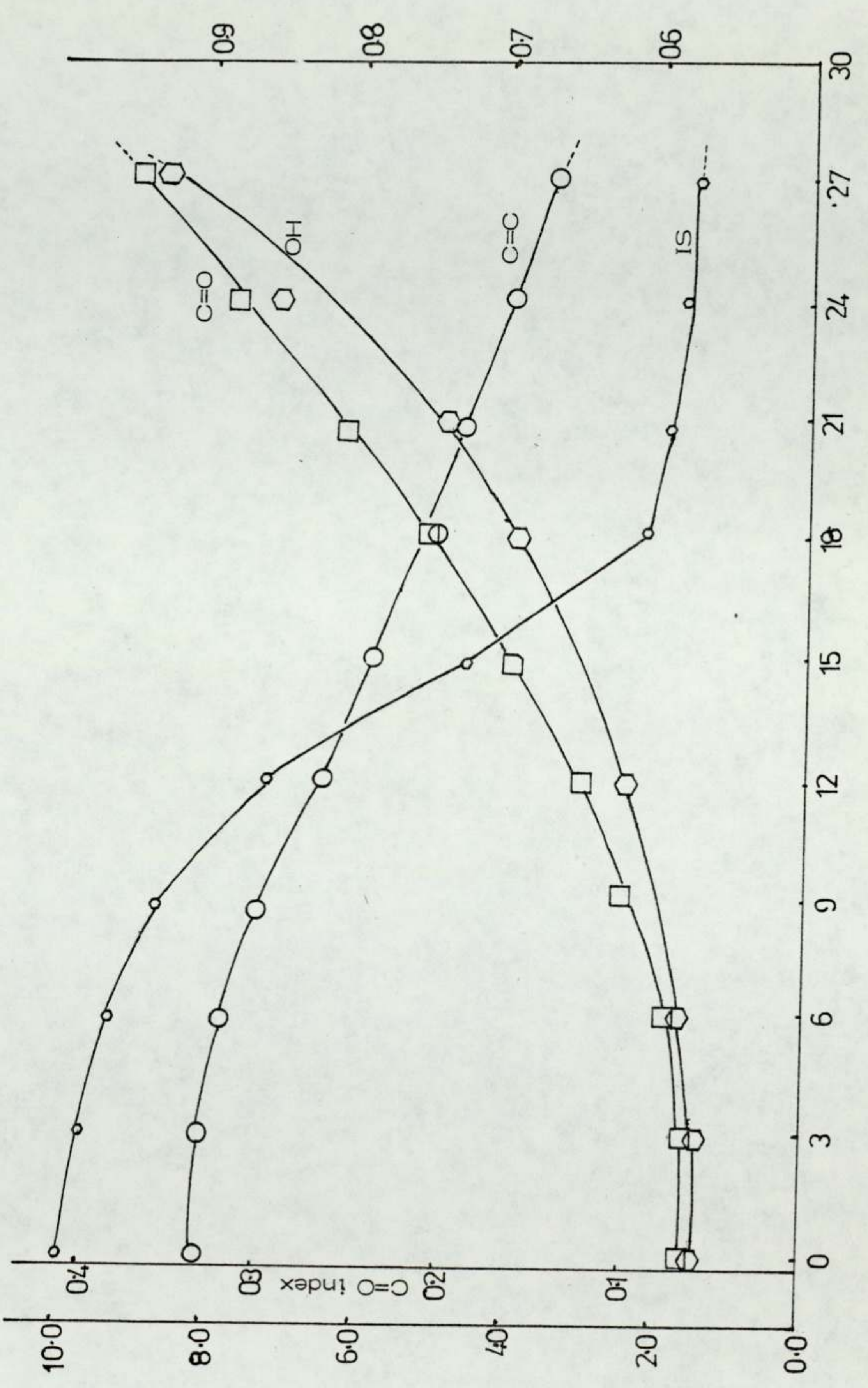
3.1.d. Thermal oxidative degradation of unstabilized ABS.

Compression moulded unstabilised ABS film was overnaged at 100°C in air and the changes in the concentration of functional groups were monitored by infra red spectroscopy.

The carbonyl and hydroxyl groups showed an induction period of 4 and 5 hours respectively at this temperature. The rapid development of these, after the induction period was quite similar to that observed on photoxidation. The decay of trans 14 polybutadiene absorbtion also showed an induction period of about 2 hours. The shorter induction period observed here could be due to both surfaces being exposed to ageing during thermal oxidation, as opposed to UV irradiation.

The falling dart impact data showed a smooth fall, and the lowest value was reached after 17 hours of ageing, when 40% of the trans 1,4 absorbtion had disappeared. Fig.14 . No changes in the absorbtion bond of nitrile and phenyl group frequencies were observed during this period of ageing.

Figure 14 Changes in the functional group indicies (by IR spectroscopy) and falling dart impact strength of unstabilized ABS films on oven ageing at 100°C in air



3.2. DISCUSSION

3.2.a. Photoxidation of unstabilized ABS

These studies show that during the first 20 hours of exposure to UV irradiation of unstabilized ABS films, only the unsaturation due to PBD is effected. This is accompanied by a rapid loss of physical properties such as impact strength of the polymer. Decrease in relative proportions of acrylonitrile, styrene, and butadiene components were determined by Priebe and co workers,[47], as a function of depth on outdoor exposure of ABS samples, 3.mm in thickness by infra red spectroscopy. Table 5 and 6. The weathered plaques after six months showed complete disappearance of trans 1,4 and 1,2 vinyl double bonds up to a depth of 30 μm. At around 50 μm material contained only one-third of the original C=C double bonds. The formation of hydroxyl corresponded to the disappearance of double bond absorbtions. Fig. 15. Similar exposure of SAN copolymer showed very little change even after eighteen months of ageing. Table 6 . These results, therefore, show the susceptibility of the PBD moiety in ABS to oxidative degradation.

Similar changes of the PBD component were observed by Scott et. al.[46] in HIPS. This observation eliminates the possibility of any unforeseen influence of acrylonitrile component on the photodegradation of ABS. Electronmicroscopy has also been used in these studies. Weathering has been shown to decrease the contrast of rubber particles

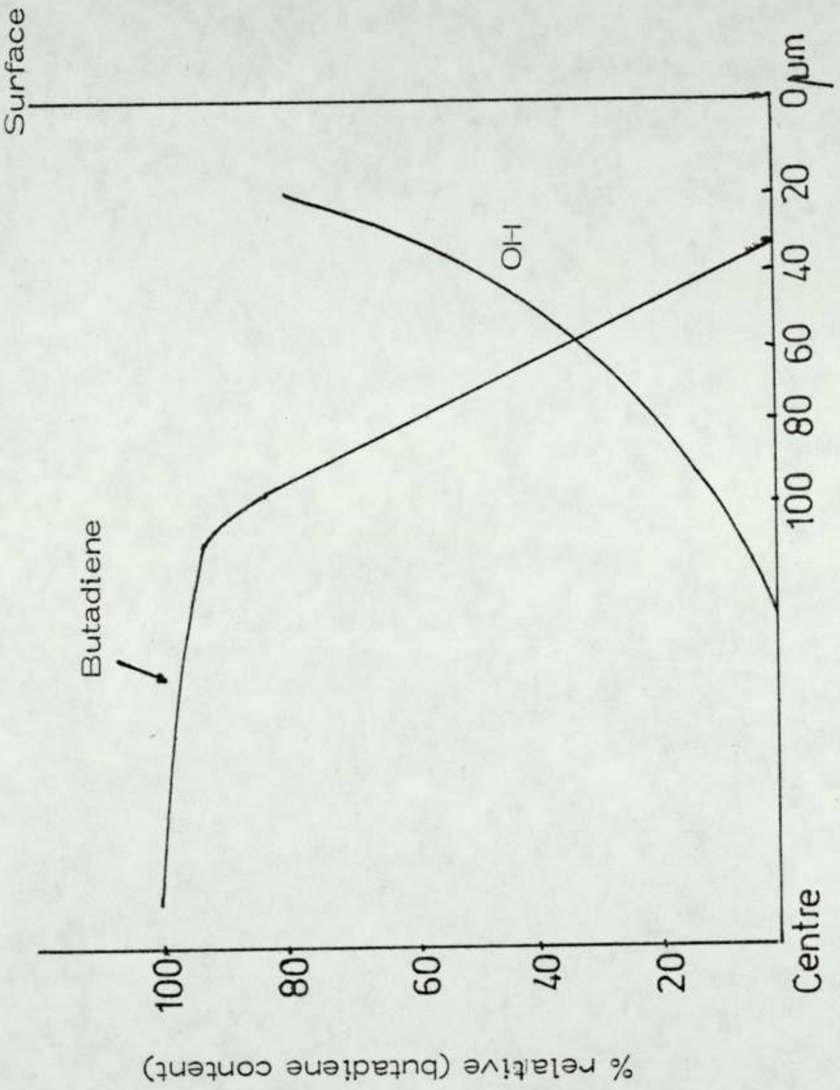
TABLE 5 COMPOSITION OF ABS SPECIMEN AFTER EXPOSURE FOR 6 MONTHS, AS A FUNCTION OF DEPTH

DEPTH OF SPECIMEN	ACN % rel	St % rel	But % rel	$E/_d$ OH
Centre around I500 µm	I00	I00	I00	I0
I00 µm deep	I00	I00	94	I8
50 µm deep	92	96	3I2	44
30 µm deep	96	I00	0	95
Surface	-	-	0	I60
Reverse side	I00	99	5	70

TABLE 6 COMPOSITION OF SAN SPECIMEN AFTER EXPOSURE 6 & I8 MONTHS RESPECTIVELY, AS A FUNCTION OF DEPTH.

DEPTH OF SPECIMEN			
Centre (~ 2000 µm)	35.4	65.0	0
30 µm deep	35.0	65.0	0
Surface	33.3	65.0	I0
Reverse side	34.2	65.5	0
AFTER I8 MONTHS			
Centre (~2000 µm)	35.0	66.0	0
I00 µm	33.0	68.0	I6
30 µm	34.0	68.0	24
Surface	26.0	59.0	42
Reverse side	34.0	68.5	2I

Figure 15 Increase and decrease of OH and butadiene content of weathered specimen after 6 months respectively as a function of depth(46)



to the matrix component, of the surface of the sample compared to the centre. This was atributed to the faster loss of double bonds at the surface, which takes up OsO_4 the staining agent used in preparation of samples[48].

Zelniger and Wolfova[49], found that ABS loses toughness much faster than acrylonitrile-styrene butylacrylate graft copolymer (ASA), but in contrast to ASA, ABS does not regain its initial toughness after the removal of the surface layer. This is said to be due to the PBD rubber being oxidised to greater depths. Dynamic mechanical properties of these polymers show a change in Tg of ABS on ageing. Similar changes were not observed for ASA, Figs. 16 & 17. Similarly notched impact strength, bending strength indicate the greater susceptibility of ABS to oxidative degradation than ASA due to the more vulnerable PBD moiety.

The damping peak, of HIPS was found by other workers[46] to decrease in a similar manner. Parallel changes have been recorded for carbonyl, and hydroxyl groups by infra red spectroscopy.

Scott and Tahan[28], observed that ABS with 30% more polybutadiene degrades faster on exposure to outdoor weathering. The rapid fall in the impact strength after few hours of exposure is probably due to photolysis of methylene bonds in the polybutadiene moiety. This has been shown to be the weakest bond in ABS and polybutadiene, having a bond energy of 38 Kcals, within reach of incident solar radiation.[43,50]. The following scheme 3, for the mechanism of photoxidation was put forward

Elastic materials convert mech work to pot energy, it is recoverable. If deformed by a stress stores energy & uses it to recover its original shape

$E^y \longrightarrow \Delta$ - [illegible]

Figure I6. Dependance of mechanical damping tan δ on the temperature (T) for ABS.

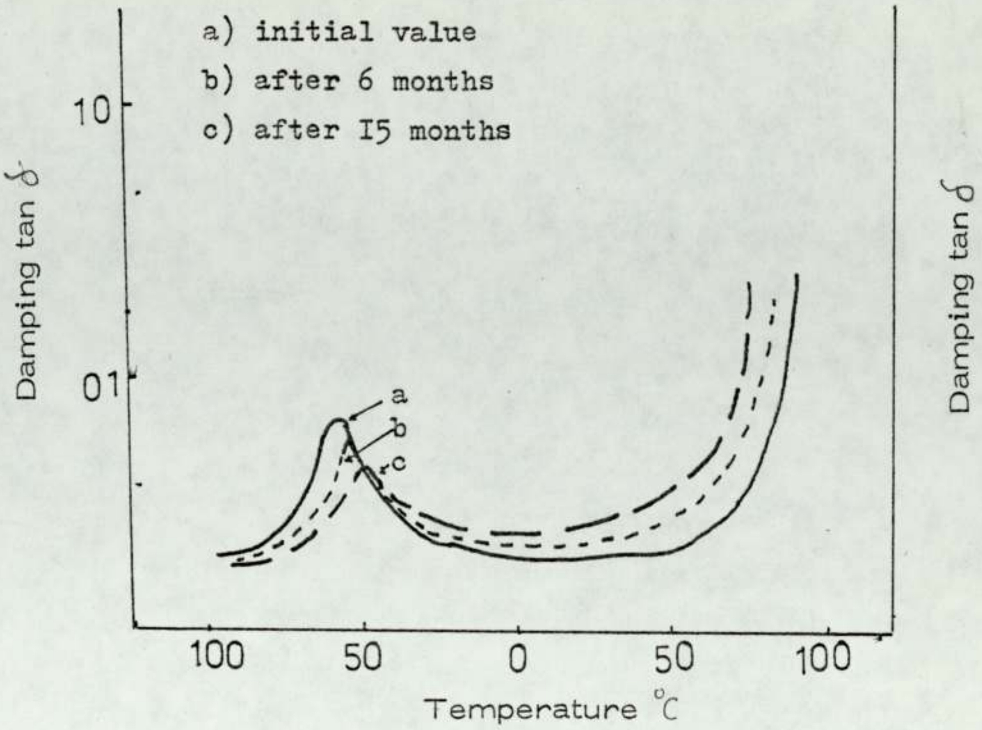
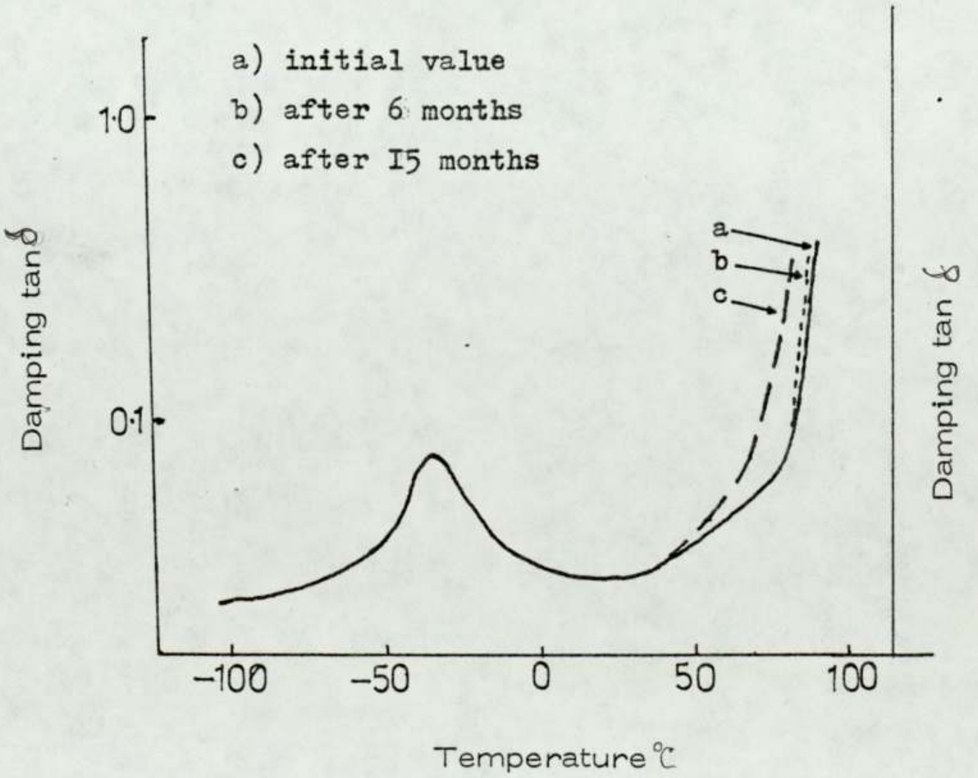
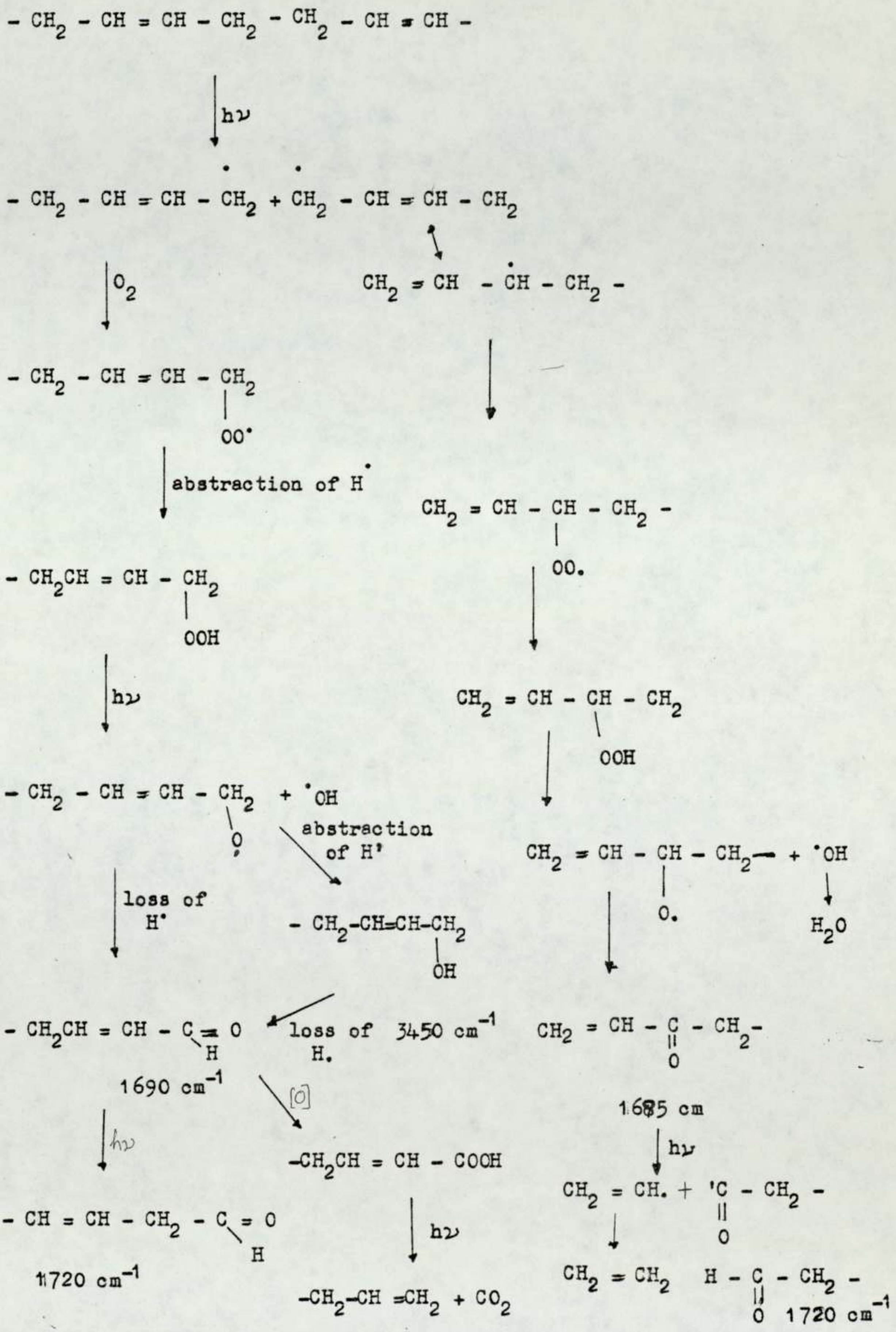


Figure I7. Dependance of mechanical damping tan δ on the temperature (T) for ASA.



SCHEME 3 - MECHANISM OF PHOTOXIDATION OF ABS



with the help of supporting references, to explain the infra red and impact data observed, on photoxidation of unstabilized ABS films.

3.2.b. Thermal oxidation of unstabilized ABS

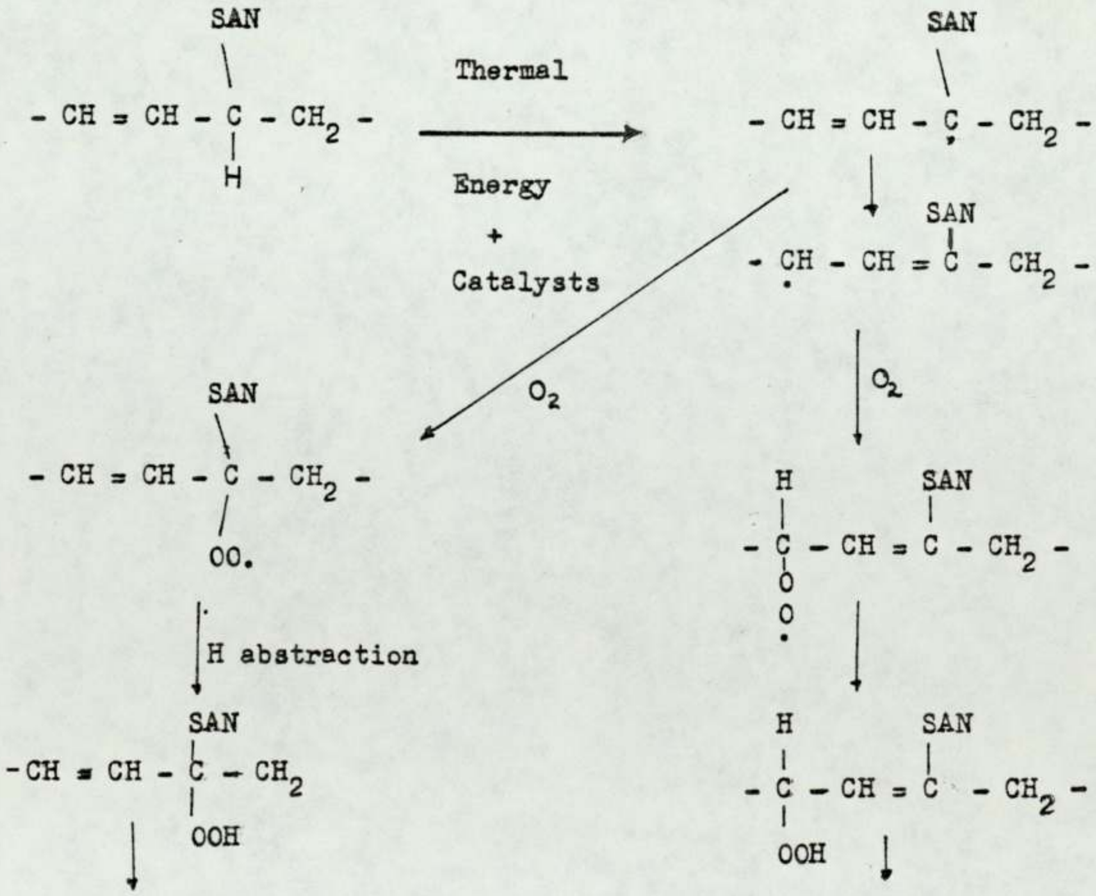
The structural units of unsaturation in the PBD component of ABS are similar to pure PBD, namely cis 14, trans 14 and 1,2 vinyl. The analysis of graft copolymerised ABS has shown, that, this method of manufacture increases the number of tertiary allylic hydrogens in the system. As a result the formation of carbonyl functional groups on oxidative degradation increases the possibility of C-C bond rupture than for pure PBD, effecting the molecular weight and its distribution much faster and hence the physical properties to which the polymer is tailor-made. In the absence of higher energetic reactions, the chances of methylene bond rupture in thermal oxidative ageing are lower than for photoxidation. This is manifested in the impact strength data Fig. I4. The loss in the impact strength is smoother and slower even though both surfaces are exposed to ageing. Therefore, it is possible to conclude that formation of allylic peroxides plays a major role in the mechanism of thermal oxidative degradation of ABS.

Shimada & Kabuki[43], were able to distinguish two parts to the oxidation reaction involving,

a. the formation of hydroperoxides, followed by

b. the decomposition of these hydroperoxides which induce chain propagation reactions. The formation of hydroperoxides in HIPS were determined iodometrically by Scott et al[46], on oven ageing. They found that the initial concentration of hydroperoxides increased very rapidly in a linear manner displaying no induction period. With the decay of hydroperoxides, after attaining a maximum concentration, the other functional groups, OH, and carbonyl begins to develop rapidly, Fig. 18. This development of hydroperoxides in the initial stages of thermal oxidative degradation in cis PBD was observed by Shelton and co-workers. The following reaction scheme 4, where initiation takes place with the loss of tertiary allylic hydrogen is therefore proposed to explain the experimental observations.

SCHEME 4 - THE MECHANISM OF THERMAL OXIDATIVE DEGRADATION OF ABS



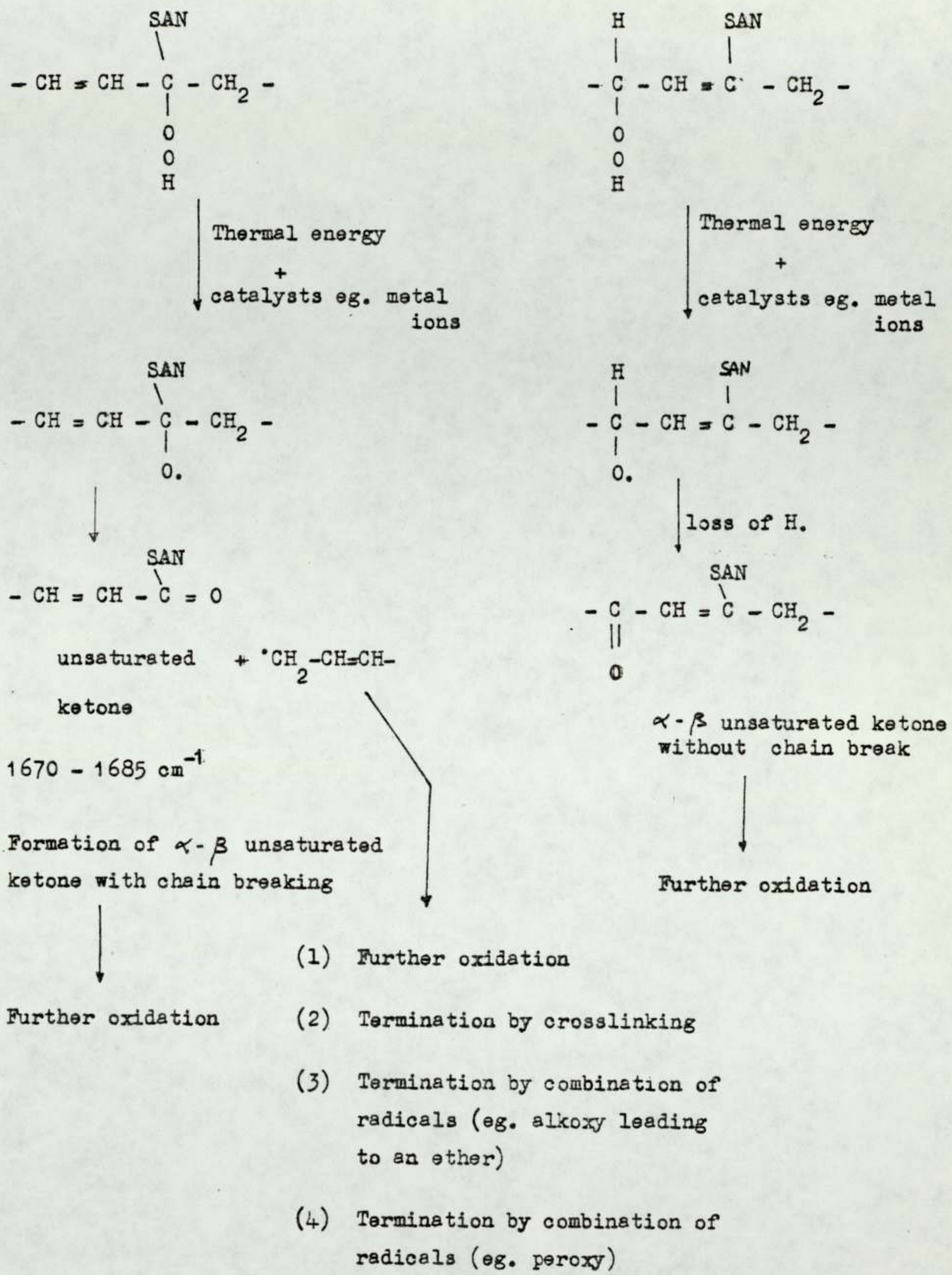

SAN
- CH = CH - C - CH2 -
O
O
H
Thermal energy + catalysts eg. metal ions
SAN
- CH = CH - C - CH2 -
O.
SAN
- CH = CH - C = O
unsaturated ketone
+ ·CH2-CH=CH-
1670 - 1685 cm-1
Formation of α-β unsaturated ketone with chain breaking
Further oxidation
H
SAN
- C - CH = C· - CH2 -
O
O
H
Thermal energy + catalysts eg. metal ions
H
SAN
- C - CH = C - CH2 -
O.
loss of H.
SAN
- C - CH = C - CH2 -
O
α-β unsaturated ketone without chain break
Further oxidation
(1) Further oxidation
(2) Termination by crosslinking
(3) Termination by combination of radicals (eg. alkoxy leading to an ether)
(4) Termination by combination of radicals (eg. peroxy)

Figure I8. Changes in concentration of functional groups in unstabilised HIPS extruded film (50 μm) on oven ageing at 98°C in air.

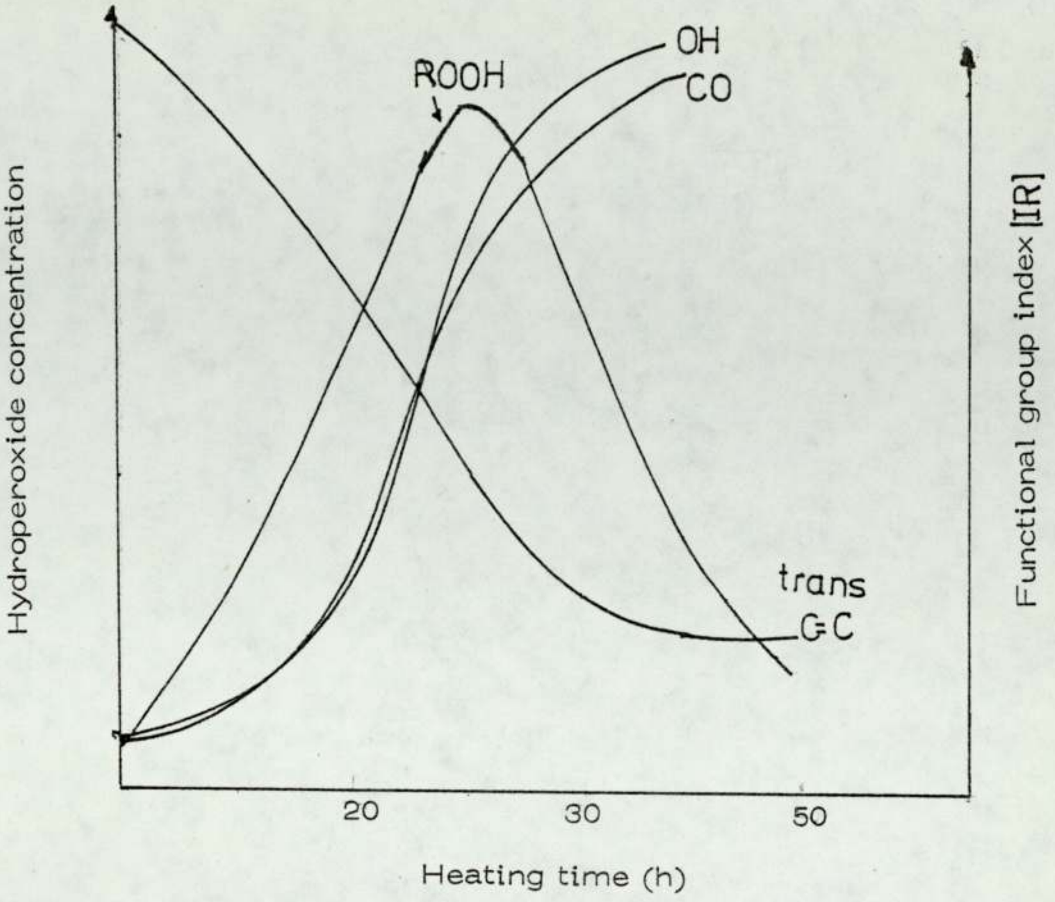
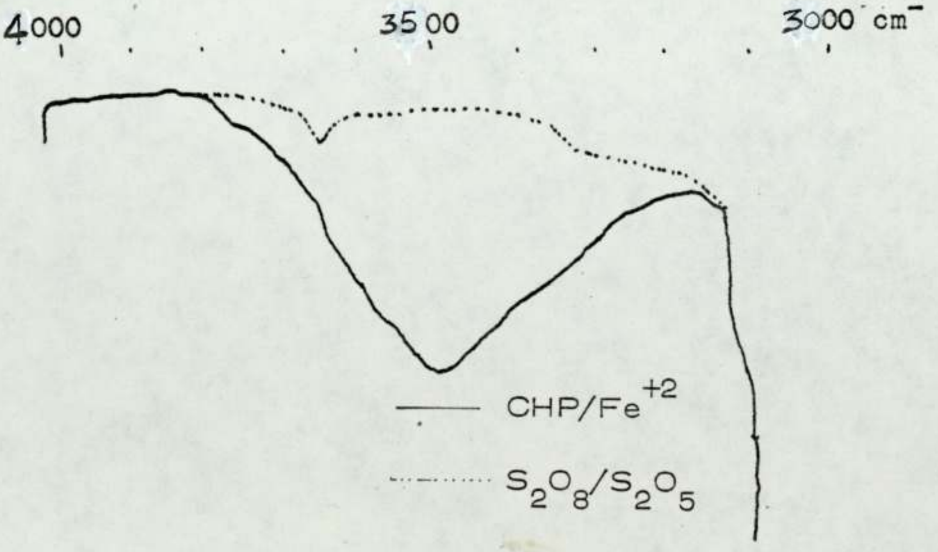
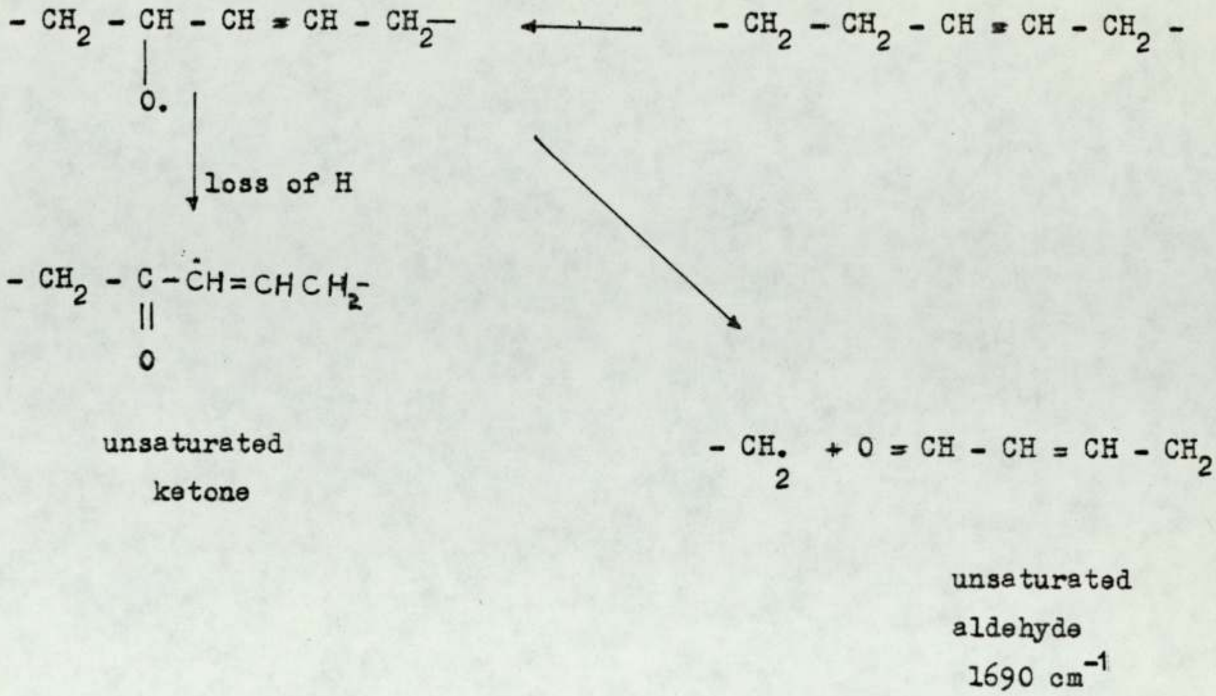
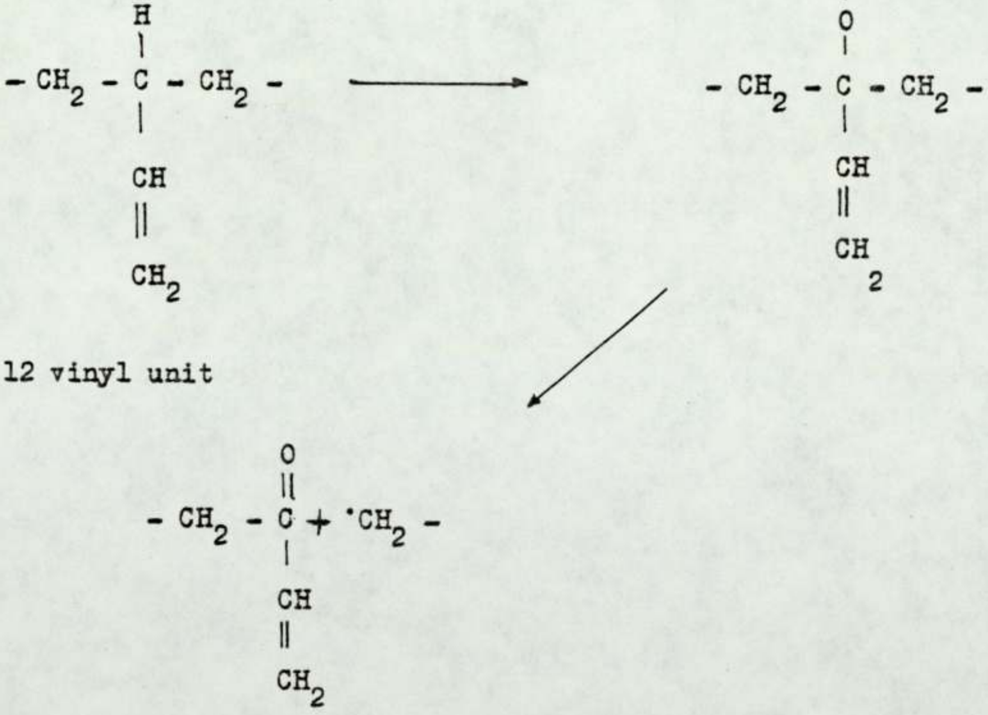


Figure I9. IR spectrum of ABS in the hydroxyl region.



Alkoxy radicals derived from allylic methylenic sites and 12 vinyl units can give rise to the carbonyl products mentioned.





3.3. EFFECT OF POSSIBLE PRODEGRADANTS IN THE COMMERCIAL FORMULATION ON THE STABILITY OF UNSTABILIZED ABS.

The most important manufacturing process for ABS employs the emulsion polymerisation procedure which gives an aqueous dispersion of colloid sized polymer particles ranging from 1000 to 5000 A in diameter. Polybutadiene is polymerised first as a seed latex and monomers acrylonitrile and styrene are subsequently added to continue polymerisation with the seed particles. The key process lies in the grafting of a significant portion of growing SAN random copolymer groups onto the allylic positions of the elastomeric component. The grafting between the plastic and the elastomer components lends compatibility to the system, resulting in a favourable state of dispersion and also bond the phases together.

The following components in the commercial formulation described in Chapter 2, section I3.I, may potentially act as pro-oxidants in the oxidative degradation of ABS.

(i) Fe^{+2} and Fe^{+3} ions -

A number of possibilities for the reactions of transition metal ions, leading to the formation of free radicals have been described by Rabek[51]. The reactions IV and V are of the redox types and hence, contribute more towards oxidative degradation of a polymer than the rest.

(i) $M^{(m+1)+} + RH \longrightarrow M^{m+} + R^{\cdot} + H^{+}$

(ii) $M^{(m+1)+} + RCH_2OH \longrightarrow M^{m+} + R\text{-}\dot{C}H\text{-}OH + H^{+}$

(iii) $M^{(n+1)+} + RCHO \longrightarrow M^{m+1} + R\text{-}\underset{\bullet}{C} = O + H^{+}$

(iv) $M^{m+} + ROOH \longrightarrow M^{(m+1)+} + RO^{\cdot} + OH^{-}$

(v) $M^{(m+1)+} + ROOH \longrightarrow M^{m+} + RO_2^{\cdot} + M^{+}$

By direct interaction with oxygen -

(iv) $M^{n+} + O_2 \longrightarrow M^{(m+1)+} + \bar{O}_2^{\cdot}$

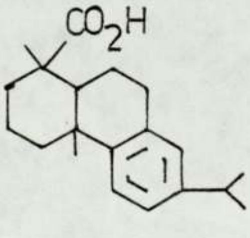
$\bar{O}_2^{\cdot} + H^{+} \longrightarrow HO_2^{\cdot}$

$\bar{O}_2^{\cdot} + RH \longrightarrow RO^{\cdot} + OH^{-}$

(Where R polymer segment)

Furthermore, Kelleher[52], found that Fe^{+2} and Fe^{+3} stearates reduce the induction period for thermal oxidation of unstabilized ABS to zero hours at 140°C from 3.7 hours observed for calcium stearate.

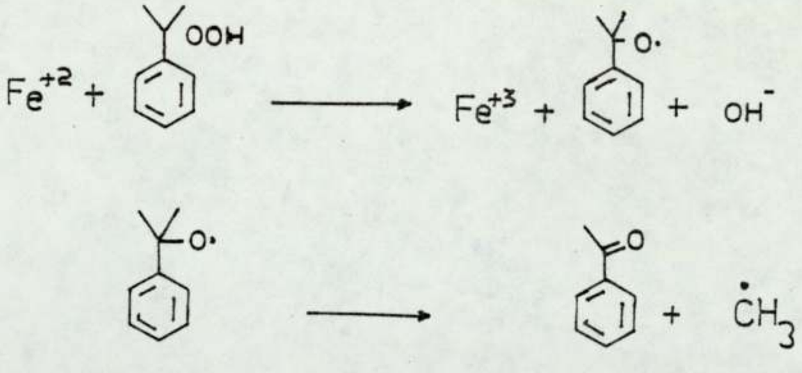
(ii) Rosin acids - The disproportionated rosin acids of wood rosin used in the commercial formulation as the emulsifier contain 50% dehydroabietic acid (I) among other acids.[53]



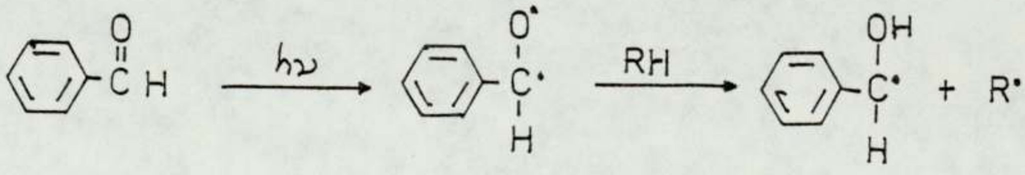
I

Low molecular weight polymers of acrylonitrile containing dehydro abietic acid have been prepared by copolymerisation in emulsion. This possibility of incorporation of rosin acids to the polymer in ABS cannot be excluded during graft copolymerisation. Hence, tertiary benzylic hydrogens similar to cumene can be introduced this way, thereby increasing the susceptibility of the polymer to oxidation .

(iii) Cumene hydroperoxide :- It has been established, the decomposition of cumene hydroperoxide by radical mechanism results in photosensitizers such as acetophenone, benzaldehyde.



These compounds are known to accelerate photoxidation of cumene[25] containing allylic hydrogen atoms.



To examine the possibility of such pro-degradants contributing to the degradation of unstabilized ABS, an attempt was made to use a completely inorganic initiator system, in the presence of sodium stearate or dodecyl benzene sulfonate sodium salt as the emulsifier.

3.13.a. Formulations excluding the predegredants, $K_2S_2O_8/Na_2S_2O_8$ system.

Formulations illustrated in Table 7 were tried out in the laboratory, detailed experimental procedure is similar to that discussed for Borg-Warner system in Chapter 2 Section I3.

Here the two phases are :-

Styrene
Acrylonitrile
$Na_2S_2O_5$-/100 ml H_2O
Dodecyl mercaptan
) Flowing phase.

PBD latex
Emulsifier solution
$K_2S_2O_8$
) Steady phase.

Since $Na_2S_2O_5$ was used in the flowing phase an extra dropping funnel was fixed to the apparatus. Best results were obtained when the chain transfer agent (mercaptan) was dissolved in the monomers.

TABLE 7

ALTERNATIVE FORMULATIONS FOR THE PREPARATION OF ABS IN THE LABORATORY

	I	II	III	IV	V
PBD Latex	92ml	92	92	92	92
Styrene	103ml	103	103	103	103
Acrylonitrile	64ml	64	64	64	64
Sodium rosinate (CHP/Fe^{+2})	50ml	-	-	-	-
Sodium Stearate	-	-	1.5g	5g	5g
Dodecyl benzene sulfonate Sodium salt	-	3.0g	-	-	-
$K_2S_2O_8$/50 ml H_2O	0.7g	0.5g	0.5g	1.0g	1.0g
Tert. Dodecyl mercaptan	0.5g	0.5g	0.25g	0.5g	0.7g
$Na_2S_2O_5$/100 ml H_2O	0.7g	0.5g	0.5g	0.75g	0.75g
Water	200ml	200	200	200	200
Time in hours	3	3	3	3	3
Temp °C	58	58	58	58	58
Yield of ABS (%)	65	95	95	95	95

3.13.b. Results and Discussion

The low yield of ABS in the presence of sodium rosinate (~ 65% Table 7 Column I) could be due to the sensitivity of the radicals from S_2O_8/S_2O_5 redox system, to benzylic hydrogens of dehydroabietic acids of emulsifier. Though high yields were obtained from the formulation in Table 7, columns II, III, IV (95%), the flow properties were poor, probably due to high molecular weights of ABS obtained, giving thick films on compression moulding.

This was eliminated by using a higher level of chain transfer agent (mercaptan) as in Table 7, column V. The flow properties of the resultant ABS were comparable to commercial ABS, as films of similar thickness were obtained by compression moulding as described in Chapter 2,; Section 2 .

The infra red spectrum of ABS made by this procedure showed no difference, except for the absence of peaks at 3450 cm^{-1}, due to OH; 1670 cm^{-1} due to an α-β unsaturated C=O group, and a broad band at 1130 cm^{-1} corresponding to C-O vibration (probably from C-OH group). Figs.19, 20. & 21.

Quantitative analysis for hydroperoxides by iodometry indicated a lower amount (0.5×10 moles^{-6}/g) compared to ABS made in the laboratory by the commercial formulation (2.5×10 moles $^{-6}$/g). The absence of OH peak in the infra red appear to relate to the lower level of hydroperoxide.

Figure 20. IR spectrum of ABS in the carbonyl region.

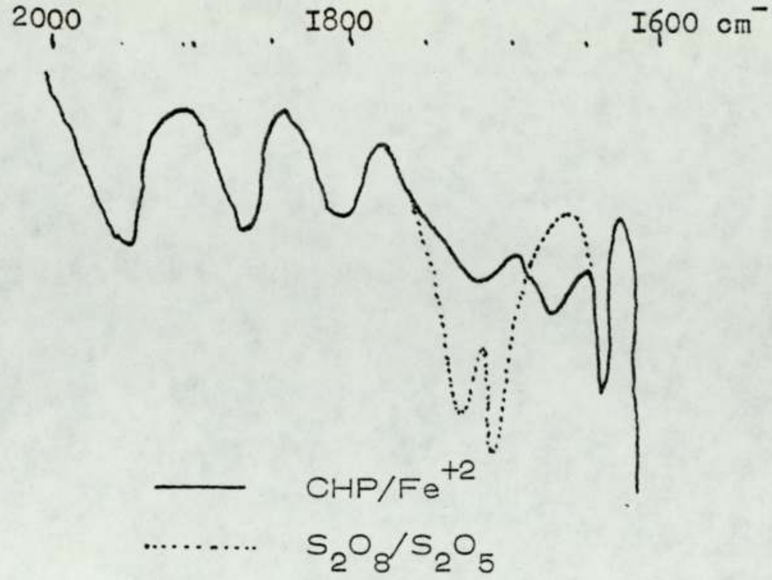
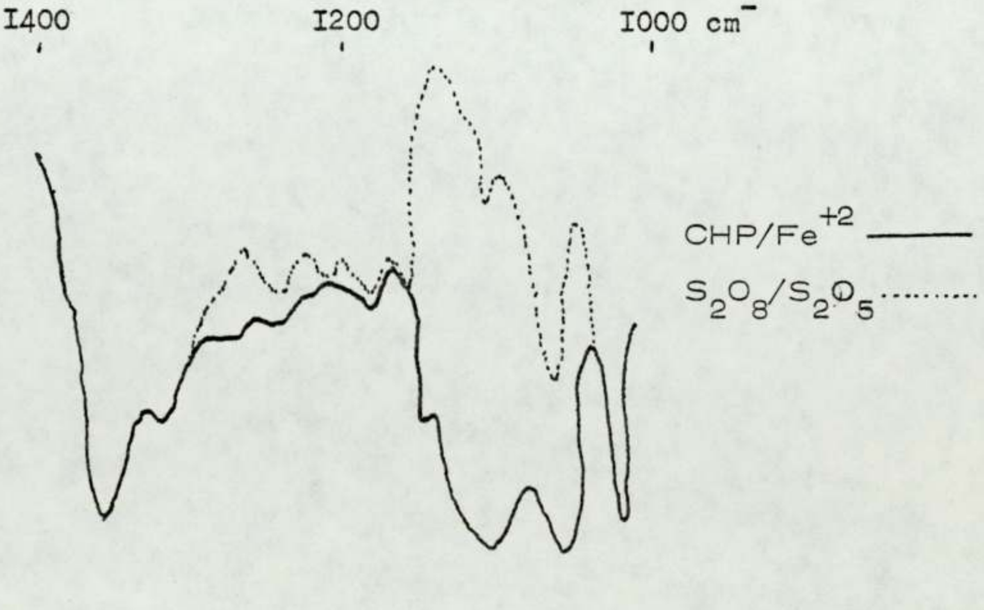


Figure 2I. IR spectrum of ABS in I400 - I000 cm$^-$ region.



The photoxidation of compression moulded ABS films were studied by IR, following the changes of carbonyl and trans 1,4-PBD. It was anticipated that ABS made by the S_2O_8/S_2O_5 method would show improved resistance to oxidation due to

a. Low hydroperoxide (polymeric) concentration in the polymer

b. The absence of transition metal ions Fe^{+2}/Fe^{+3} from the formulation.

c. The absence of possible photosensitizers such as benzaldehyde and acetophenone (decomposition products of cumenehydroperoxide).

The figures 22 and 23, show very little improvement in the stability of the ABS towards irradiation. This rapid carbonyl build up and trans 1,4 PBD decay comparable to commercial ABS was confirmed by oxygen absorbtion, at 100°C on thermal oxidation, showing no improvement towards oxidation of this material at this temperature. Fig. 22. Therefore, it is possible to conclude that the photo and thermal sensitive sites such as tertiary allylic hydrogens, in the polymer are so susceptible to oxidation, that the introduction of external sensitizers have very little or no effect at all in the initiation as well as in the propagation reactions of the unstabilized ABS.

Figure 22 Loss of trans-1,4 double bond (967 cm^{-1}) absorption on oven ageing of unstabilized ABS films at 100^{o}C and oxygen absorption at the same temperature

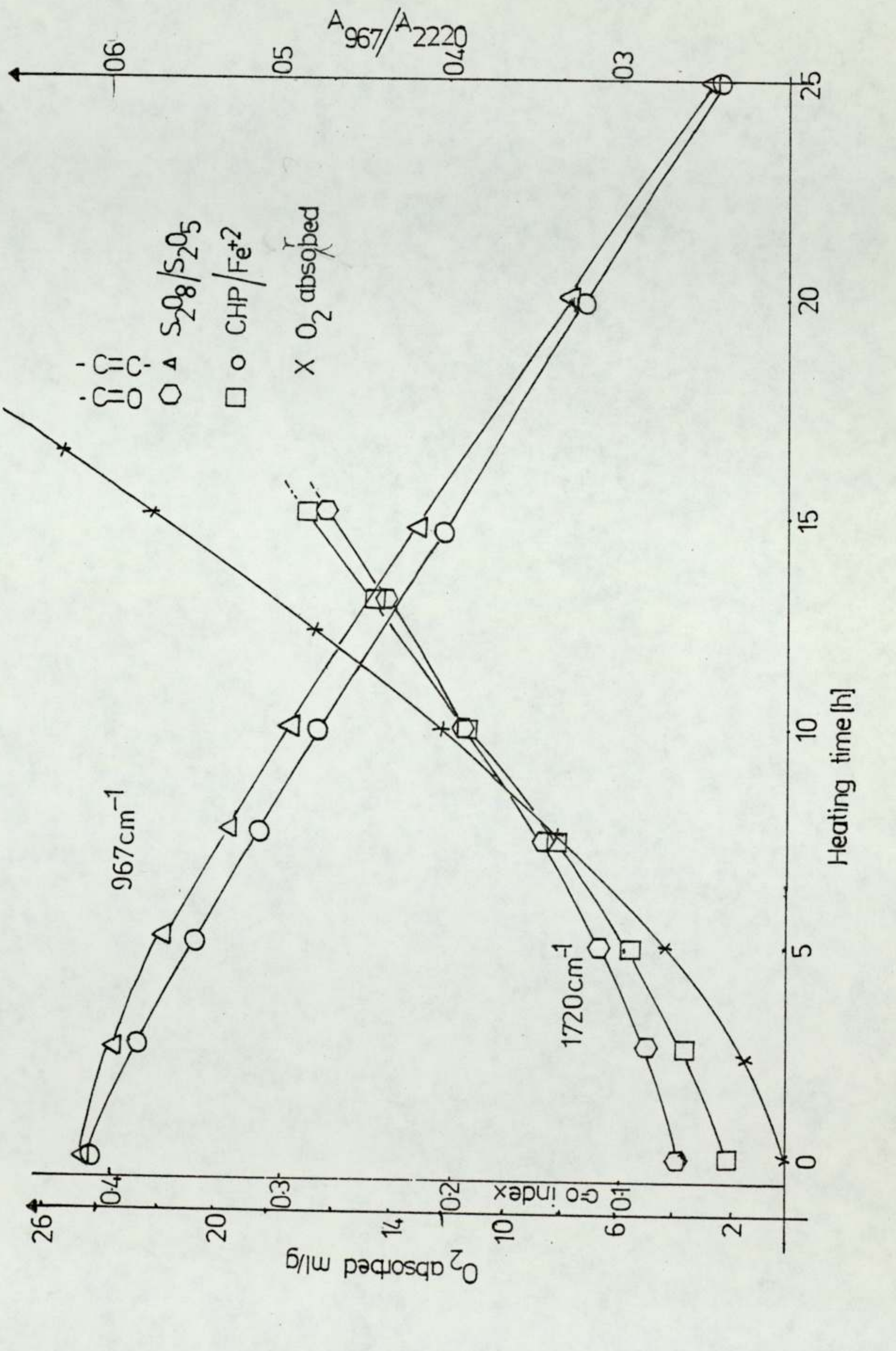
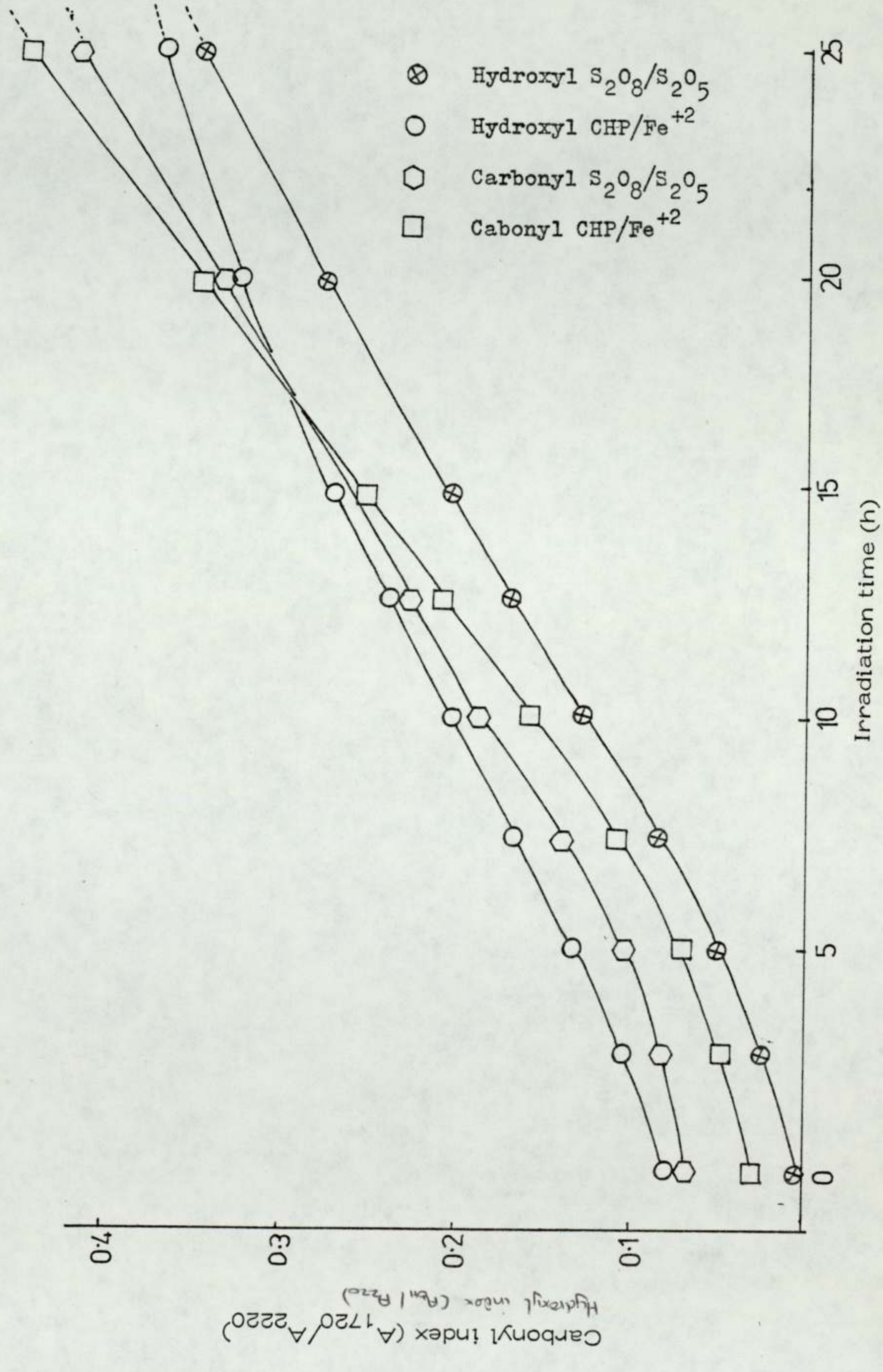


Figure 23. Development of hydroxyl and carbonyl functional groups on photo oxidation of unstabilised ABS films.



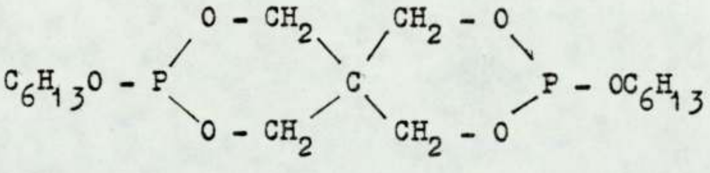
CHAPTER 4 - OXIDATIVE DEGRADATION OF ABS IN THE PRESENCE OF STABILIZERS AS ADDITIVES

4.1.a. PREVENTATIVE ANTIOXIDANTS

4.1.a.1 THE EFFECTS OF METAL DITHIOCARBAMATES, PHOSPHITES, AND THIODIPROPIONATES, ON PHOTO-OXIDATIVE DEGRADATION

The following stabilizers, all typical peroxide decomposers, were incorporated, by processing in the torque rheometer at 1 W/W % concentration.

Nickel dibutyl dithiocarbomate	(NiDBTC)
Zinc dibutyl dithiocarbomate	(Zn DBTC)
Weston 618 phosphite	(618)
Dilauryl thiodipropionate	(DLTP)

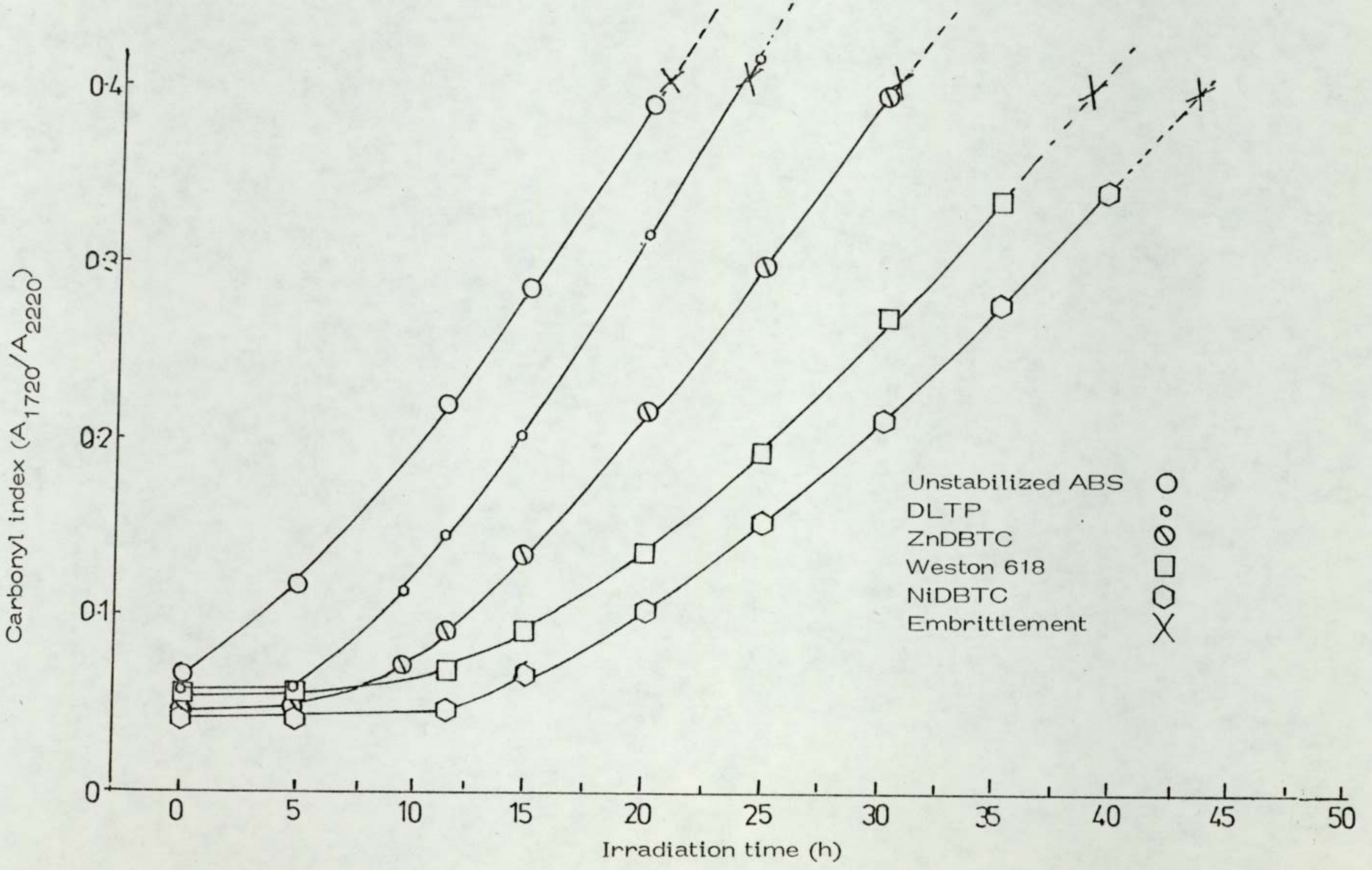


Weston 618 phosphite

The development of carbonyl group absorbtion on photo-oxidation of ABS films is shown in Figure 24. The induction periods and the embrittlement times are given in the accompanying Table 9.

The increased stability observed for the NiDBTC stabilizer is accompanied by a green colouration, which is typical of this transition metal complex. The colour fades slightly during photo-oxidation of the film but embrittlement sets in, before a significant loss of colour

Figure 24 Development of carbonyl functional group on photo-oxidation of ABS films containing peroxide decomposers (1% w/w)



has occurred. The other stabilizers tested did not impart any colour to ABS during processing operations or on subsequent photo-oxidation of the polymer.

STABILIZER	CONCENTRATION % W/W	INDUCTION PERIOD IN HOURS	EMBRITTLEMENT TIME IN HOURS
None	-	2 - 3	22
NiDBTC	1	12	44
ZnDBTC	1	6 - 7	30
Weston 618	1	10	40
DLTP	1	$4\frac{1}{2}$-5	25

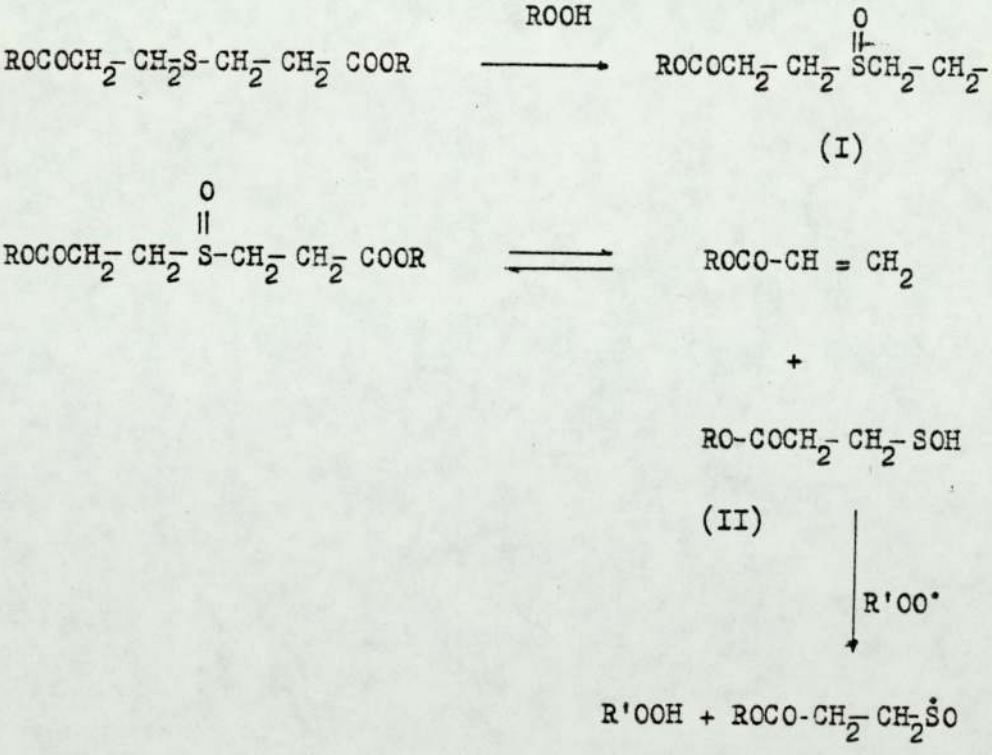
TABLE 9 - INDUCTION PERIODS AND EMBRITTLEMENT TIMES FOR ABS FILMS CONTAINING PEROXIDE DECOMPOSERS AS STABILIZERS

4.1.a.2. DISCUSSION

The ABS samples containing the above peroxide decomposing stabilizers, after a short induction period, offered very little resistance towards photo-oxidation. This was probably due to the destruction of the original stabilizer during the induction period. The resistance to oxidation after the induction period, therefore, probably depend on the antioxidant efficiency of the products formed and in this instance, such products from the stabilizers are in the following order of effectiveness in ABS.

NiDBTC > Weston 618 > ZnDBTC > DLTP

It has been suggested that monosulfides (such as DLTP) behave as antioxidants by conversion initially to sulfoxides (I) [54]. Three distinct mechanisms for the chemical reactions involved in the antioxidant behaviours of the derived sulfoxides have been identified by Armstrong, Plant and Scott[55]. The first is a radical trapping process involving the sulfenic acid (II) formed by the breakdown of sulfenyl dipropionate ester (I) which is an oxidation product of thiodipropionate.[1]



$$ROCOCH_2-CH_2-S-CH_2-CH_2-COOR \xrightarrow{ROOH} ROCOCH_2-CH_2-\overset{O}{\overset{\|}{S}}CH_2-CH_2-COOR \quad (I)$$

$$ROCOCH_2-CH_2-\overset{O}{\overset{\|}{S}}-CH_2-CH_2-COOR \rightleftharpoons ROCO-CH=CH_2 + RO-COCH_2-CH_2-SOH \; (II)$$

$$RO-COCH_2-CH_2-SOH \xrightarrow{R'OO^{\cdot}} R'OOH + ROCO-CH_2-CH_2\dot{S}O \qquad (1)$$

The second is a radical generating reaction resulting from a redox reaction between hydroperoxides and the sulfenic acid. (2). The sulfenyl radical (III) formed in both instances is inert and dimerizes readily[56].

$$ROCO\text{-}CH_2\text{-}\ CH_2\text{-}\ SOH \ + \ R'OOH \longrightarrow$$

$$ROCOCH_2\text{-}\ CH_2\dot{S}O + R'\dot{O} + H_2O \qquad - \quad (2)$$

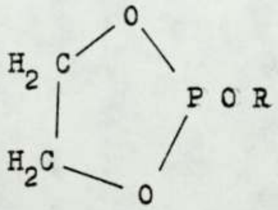
(III)

The third is a Lewis acid catalyst destruction of hydroperoxide by a further oxidation product of the sulfenic acid, thought to be sulfur-dioxide.(3) and (4)

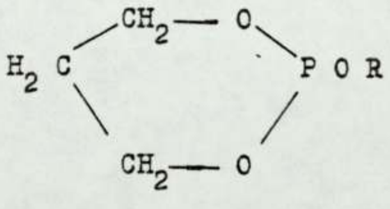
$$ROCO\text{-}CH_2\text{-}\ CH_2\text{-}\ SOH \xrightarrow{R'OOH} ROCOCH_2\text{-}\ CH_2\text{-}\ SO_2H \qquad - (3)$$

$$ROCOCH_2\text{-}\ CH_2\text{-}\ SO_2H \longrightarrow ROCOCH = CH_2 + H_2SO_3 \quad - (4)$$

According to Humphris and Scott[57, 58], for cyclic phosphites of the type IV and V, known to be catalysts for hydroperoxide decomposition, the course of the reactions can be divided into two consecutive phases. The first is the stoichiometric oxidation to phosphate as in monosulfides discussed above (5).

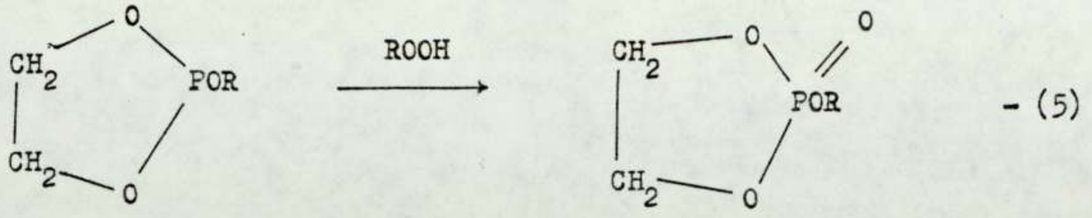


(IV)

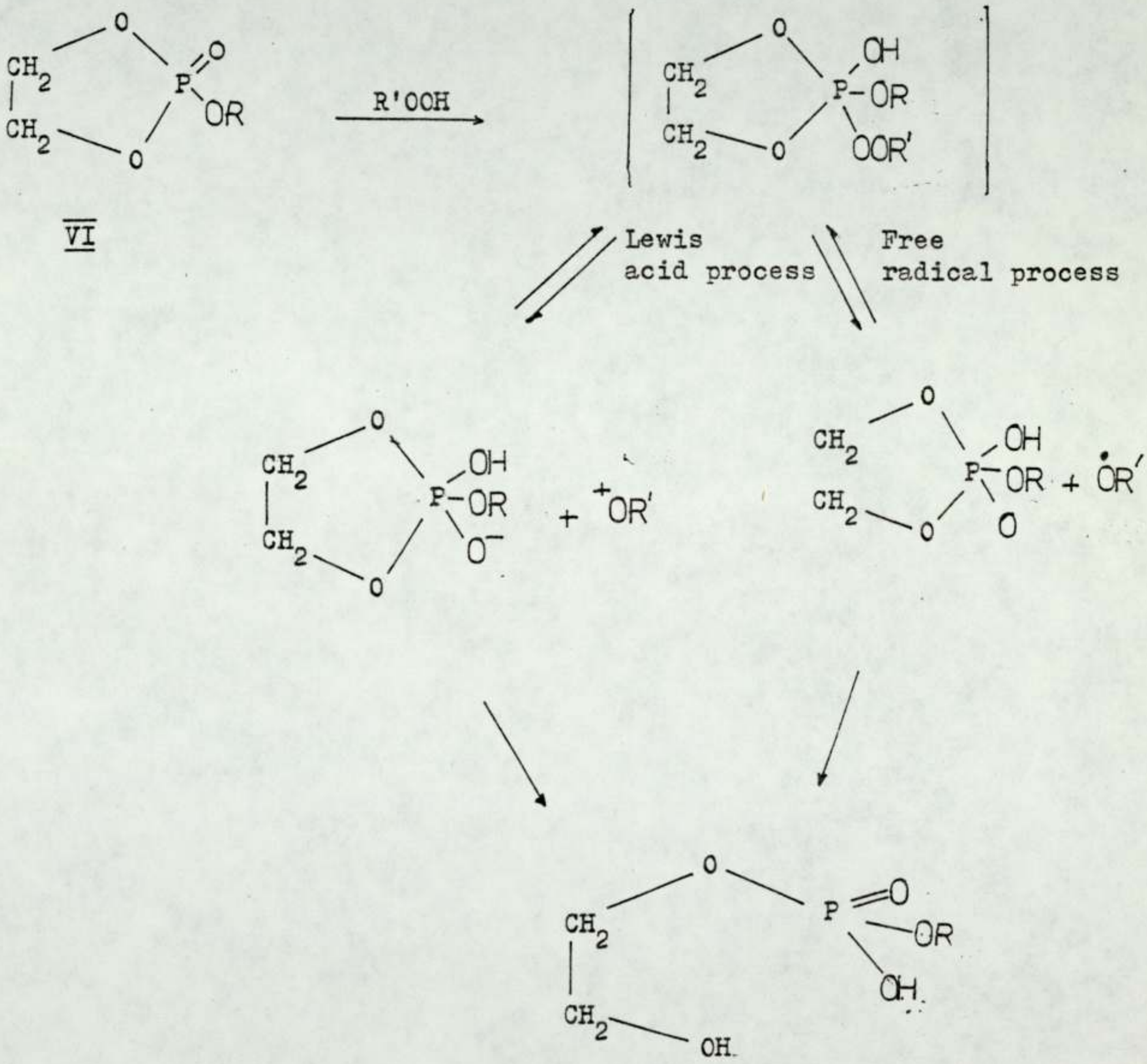


(V)

The phosphate undergoes further reactions with hydro-peroxide to give a catalytic species which appears to have the ability to decompose hydroperoxides contemporaneously in two quite different ways, one



being Lewis acid catalysed process and the other is said to follow a free radical process.[58]

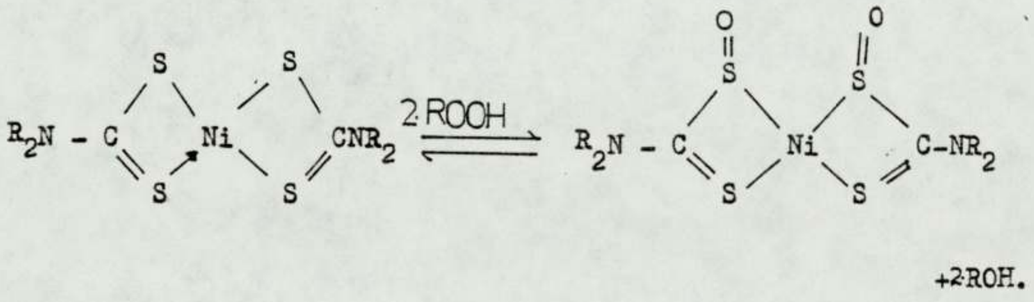


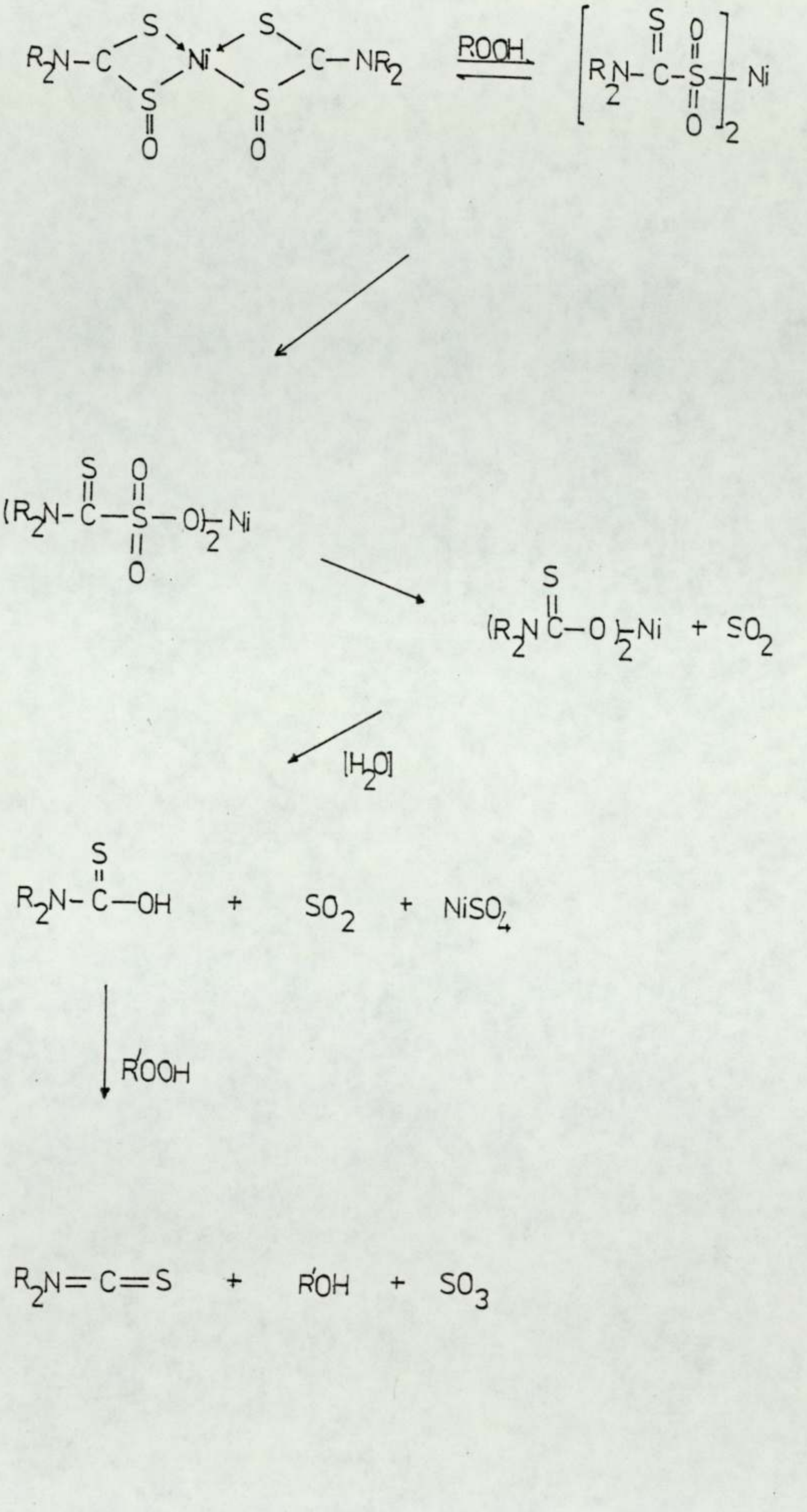
VI

VII

The formation of a compound of the type VI from VII for effective catalytic decomposition is said to depend on the free rotation of $CH_2 - CH_2$ and other bonds in the molecule. If the free rotation of $CH_2 - CH_2$ bond in VII is restricted by substituting a benzene ring as in catechol phosphites the catalytic activity is said to be greatly enhanced.[59]

The thermal antioxidant and UV stabilizing behaviour of many dithiocarbamates complexes is well documented and has been shown to be due to hydroperoxide decomposition in a non-radical process[60, 61, 62]. This use of metal complexes of dithiocarbamic acids as UV stabilizers, depends on their ability to withstand oxidative treatment at high temperatures during processing operations. The zinc and nickel derivatives are known to be thermally stable[60]. The following mechanism for the non-radical decomposition of NIDBTC, involves the initial attack of hydroperoxides with the formation of a sulfoxide. Further oxidation in the presence of hydroperoxides followed by hydrolysis, is said to give an isothiocyanate, SO_2, SO_3 and nickel sulfate as end products[62, 63, 64].




ROOH
[H2O]
R'OOH
+ SO2
+ NiSO4
R2N=C=S + R'OH + SO3

The oxides of sulfur so formed have been shown to decompose hydroperoxides to non-radical products.

$$\text{ROOH} + SO_2,\ SO_3 \longrightarrow \text{Non radical products}$$

It has been observed by Ranaweera and Scott[65], that hydroperoxide decomposition thermally at 60°C proceeded at about the same rate as the light reaction at 29°C in the presence of NiDBTC leading to identical decomposition products. They have arrived at the following conclusions with regard to the UV stabilizing function of NiDBTC.

(1) NiDBTC is an auto-synergistic antioxidant involving more than one complementary stabilizing mechanisms.

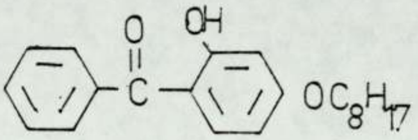
(2) Mechanisms involved in the case of NiDBTC are

- (i) Catalytic destruction of hydroperoxides
- (ii) UV screening
- (iii) Kinetic chain breaking.

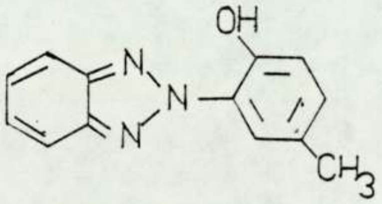
ZnDBTC on the other hand, has been shown by Carlsson and Wiles[66], to have (i) reduced activity towards hydroperoxides (ii) no UV screening ability and (iii) to have lower singlet oxygen quenching ability than NiDBTC. However, recent research into the mechanism of antioxidant activity of ZnDBTC has shown that thermal peroxide decomposition of the two dithiocarbamate derivatives Ni and Zn are equivalent[67]. The main difference between them as UV stabilizers is their UV stability. ZnDBTC has been shown to decompose and disintegrate on irradiation with UV light approximately three-times faster than NiDBTC.[67]

4.1.a.3. ULTRA-VIOLET ABSORBERS AND HINDERED PIPERIDENE DERIVATIVE

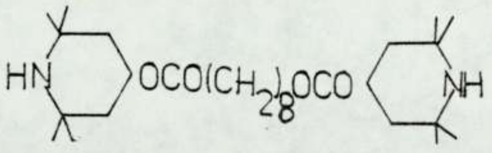
These stabilizers were incorporated into ABS by processing in the torque rheometer at 190°C for three minutes. Films were obtained by compression moulding of processed ABS, between two polished steel plates at 190°C for three minutes.



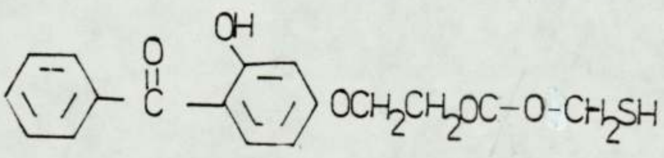
UV 531



Tiniuin P



Tiniuin 770



EBHPT

TABLE 10 - INDUCTION PERIODS AND EMBRITTLEMENT TIMES OF ABS STABILIZED FILMS ON PHOTO-OXIDATION AT CONCENTRATION 3.06×10^{-3} MOLE STABILIZER/100g POLYMER

ADDITIVE	INDUCTION PERIOD (Hours)	EMBRITTLEMENT TIME (Hours)
None	2 - 3	22
UV531	10 - 11	35
Tiniun P	12	40
Tiniun 770	16	37
EBHPT	17	52

No visible colour was detected in the ABS films at the end of induction period or even up to 25 hours after the embrittlement time is reached. The embrittlement time observed for the stabilizers are in the following order of effectiveness,

EBHPT $>$ Tinium P $>$ Tiniun 770 $>$ UV531

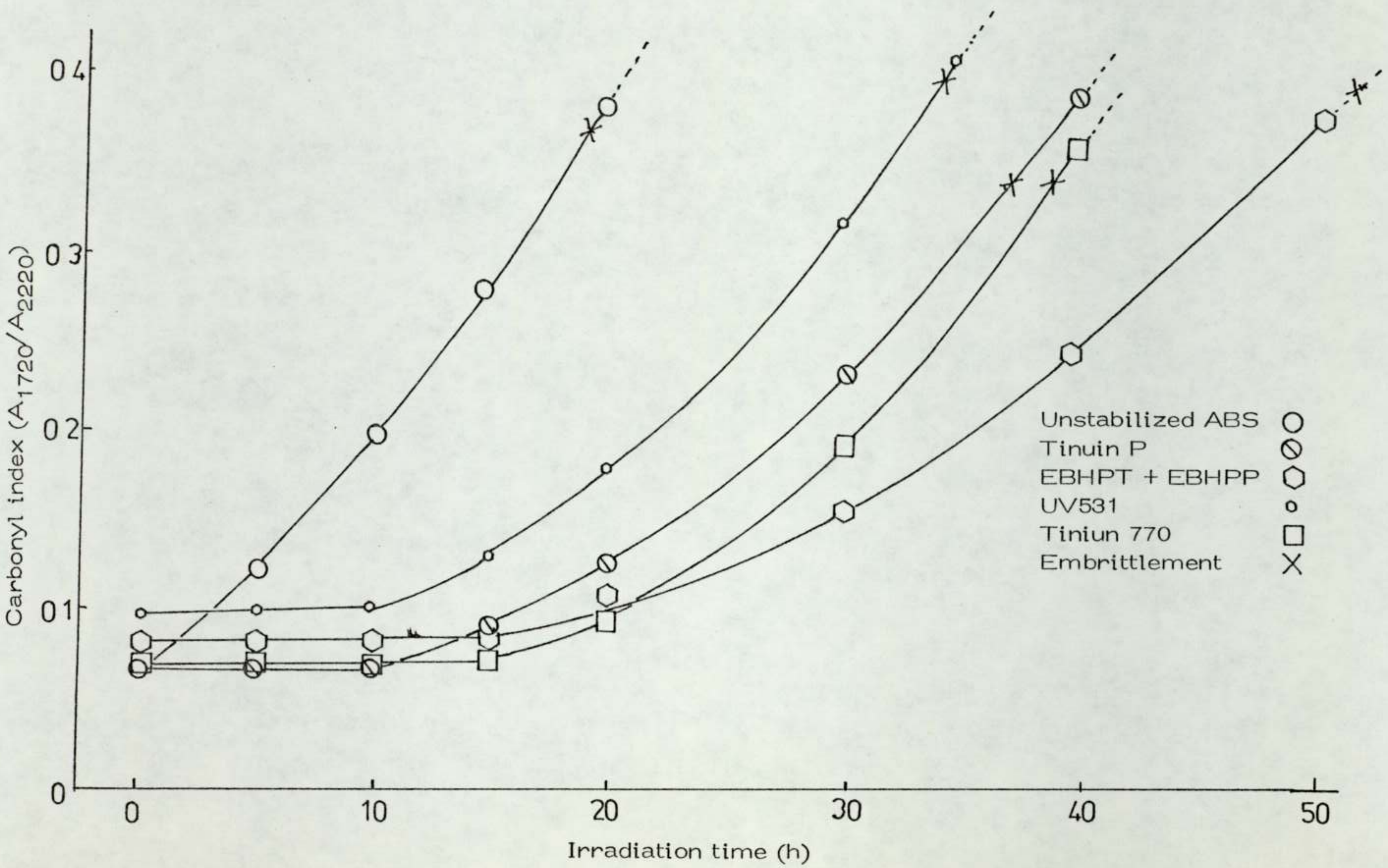
whereas the induction periods are in the order shown below. Figure 25.

EBHPT $>$ Tinium 770 $>$ Tiniun P $>$ UV531

4.1.a.4. DISCUSSION

The essential requirements of an effective UV stabilizer are as follows :

Figure 25 Development of carbonyl functional group on photo-oxidation of ABS films containing UV stabilizers α Tiniun 776 (3.06×10^{-3} mole stabilizer/100g ABS)



1) It should be retained in the polymer during its life time

2) It should be extremely photostable

and 3) It must be capable of harmlessly disposing of the absorbed UV energy.

Durmis et. al.,[68] by measuring the loss of derivatives of 2-hydroxy benzophenone, and 2(2-hydroxy phenyl) benzotriazole from isotatic polypropylene showed a linear dependence of the logrithm of the rate constant upon molecular weight on increasing the size of the linear aliphatic substituent. For example, 2-hydroxy-4-methoxy benzophenone was lost 400 times faster at 60°C than 2-hydroxy-4-octyloxy benzophenone. The 2-hydroxy-benzophenone derivatives selected, ie. UV 531 and EBHPT can probably be assumed to be lost from the polymer more or less at the same rate due to their long chain aliphatic substituents in the 4 position.

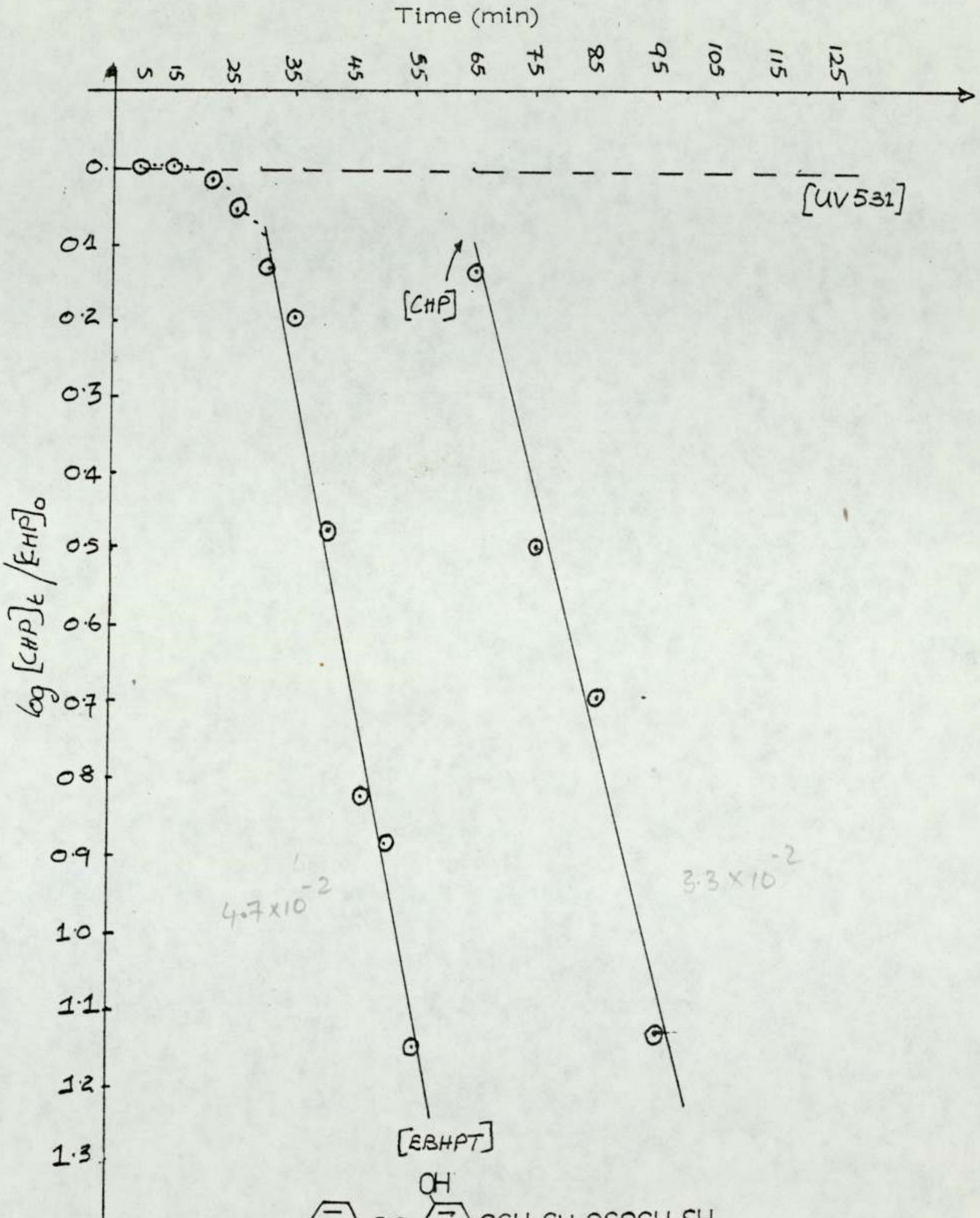
The major mechanism of photostabilization by UV absorbers is said to be by the dissipation of electronic energy into vibrational energy through a radiationless route called internal conversion. This is facilitated by the rapid tautomerism in the excited state of the molecule due to the presence of a strong intramolecular hydrogen bond, in 2-hydroxy benzophenones and benzotriazoles. This concept of light absorption followed by internal conversion cannot alone account for the activity of UV absorbers. It has been observed that incident UV light is reduced by only 50%, after penetrating 50 μm of polymer containing 0.1%W/W of UV absorber . In addition to the UV screening ability of UV absorbers Carlsson and Wiles[66], have shown excited state quenching of carbonyl groups by these derivatives. Hutson and Scott[69], have also shown that 2-hydroxy-4-octyloxy benzophenone (UV 531) acts as weak radical scavenger to retard oxidation under processing conditions.

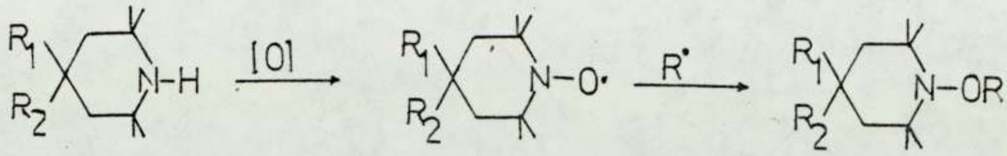
The enhanced activity of the sulfur derivative of 2-hydroxybenzophenone EBHPT over other stabilizers tested could be due to its additional hydroperoxide decomposing ability, Figure 26. The hydroperoxide decomposition of EBHPT and other derivatives will be discussed under section 4.a. of this Chapter.

The piperidene derivative, Tiniuin 770, showed a longer induction period than UV531 or Tiniuin P but the embrittlement was reached much more rapidly than in the case of the U.V. absorbers. When the induction time was subtracted from the embrittlement time for ABS film containing Tiniuin 770, the rate of formation of carbonyl from this point was comparable to that of unstabilized ABS. This probably indicates destruction of the stabilizer by the end of the induction period.

The piperidene derivatives are readily oxidised to the corresponding nitroxides by photolysis in the presence of hydroperoxides[66]. No UV screening ability or quenching properties have been detected for these amines or their nitroxides[70]. The nitroxides have been shown to react readily with alkyl radicals to give stable products[66].

Figure 26. Decamposition of CHP in the presence of 2-hydroxy benzophenone derivative EBHPT at 70°C (EBHPT : CHP I : IO).

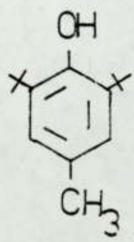




4.2.a. CHAIN BREAKING ANTIOXIDANTS

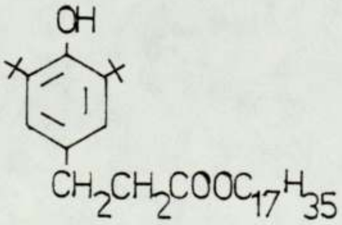
4.2.a.1. HINDERED PHENOLS AS PHOTO-STABILIZERS

Phenolic antioxidants were incorporated into ABS powder by solvent evaporation using ether. The stabilized ABS was processed in the torque rheometer at 190°C for three minutes. The concentration of antioxidants used was 4.87×10^{-3} moles / 100g polymer. Films from processed ABS samples were obtained by compression moulding at 190°C for three minutes. These were UV irradiated and the oxidative degradation was followed by the development of carbonyl absorbtion using infra-red spectroscopy, Figure 27. Induction periods and embrittlement times on photo-oxidation are given in Table 11.

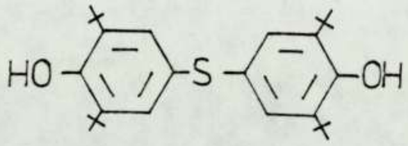


BHT

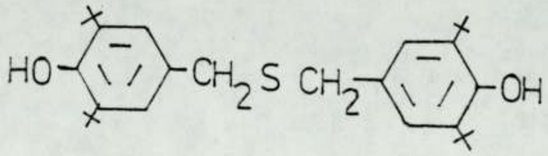
× = tBu



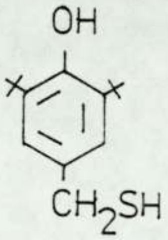
1076



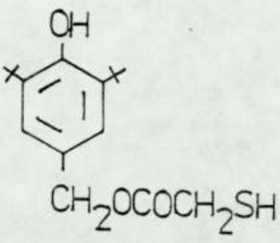
TBPS



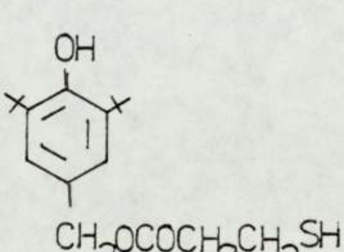
TBMP



BHBM



BHBT



BHBP

Figure 27 Development of carbonyl index functional group on photo-oxidation of ABS films containing hindered phenol derivatives. Concentration: 4.87 × 10^{-3} mole stabilizer/100g ABS

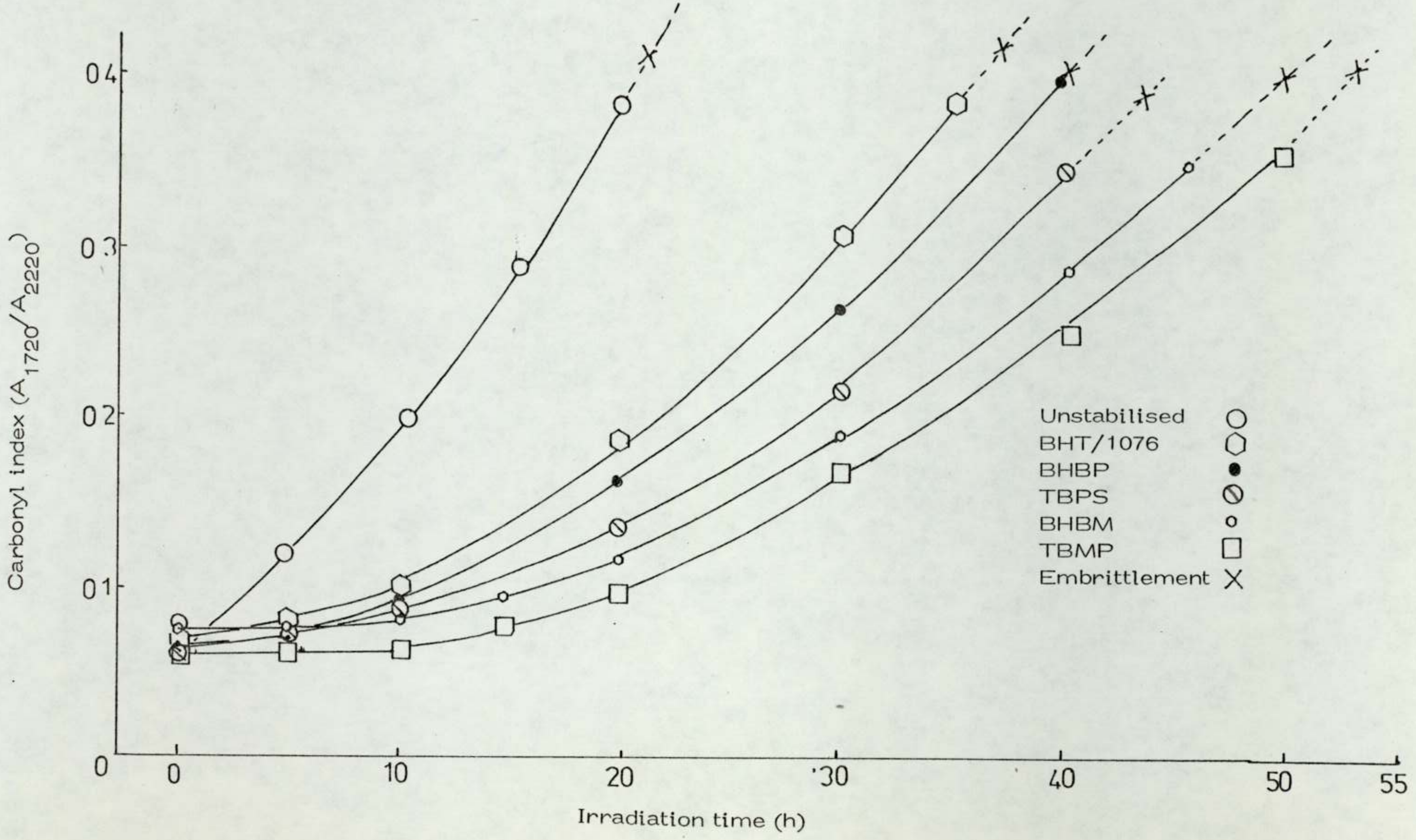


TABLE 11 - INDUCTION PERIODS AND EMBRITTLEMENT TIMES ON PHOTO-OXIDATION OF ABS FILMS CONTAINING PHENOLIC ANTIOXIDANTS AT CONCENTRATION 4.87×10^{-3} MOLE STABILIZER/100g POLYMER

STABILIZER	INDUCTION PERIOD (hours)	EMBRITTLEMENT TIME (hours)
None	2 - 3	22
BHT	9 - 10	34
1076	9 - 10	34
BHBP	6 - 8	40
BHBT	7 - 8	40
TBPS	10	42
BHBM	12	50
TBMP	12	52

All phenolic antioxidants tested imparted a yellow colour to ABS after the induction period. The intensity of the colour was much higher for BHBP and BHBT at a given time, than for the rest of the phenolic antioxidants.

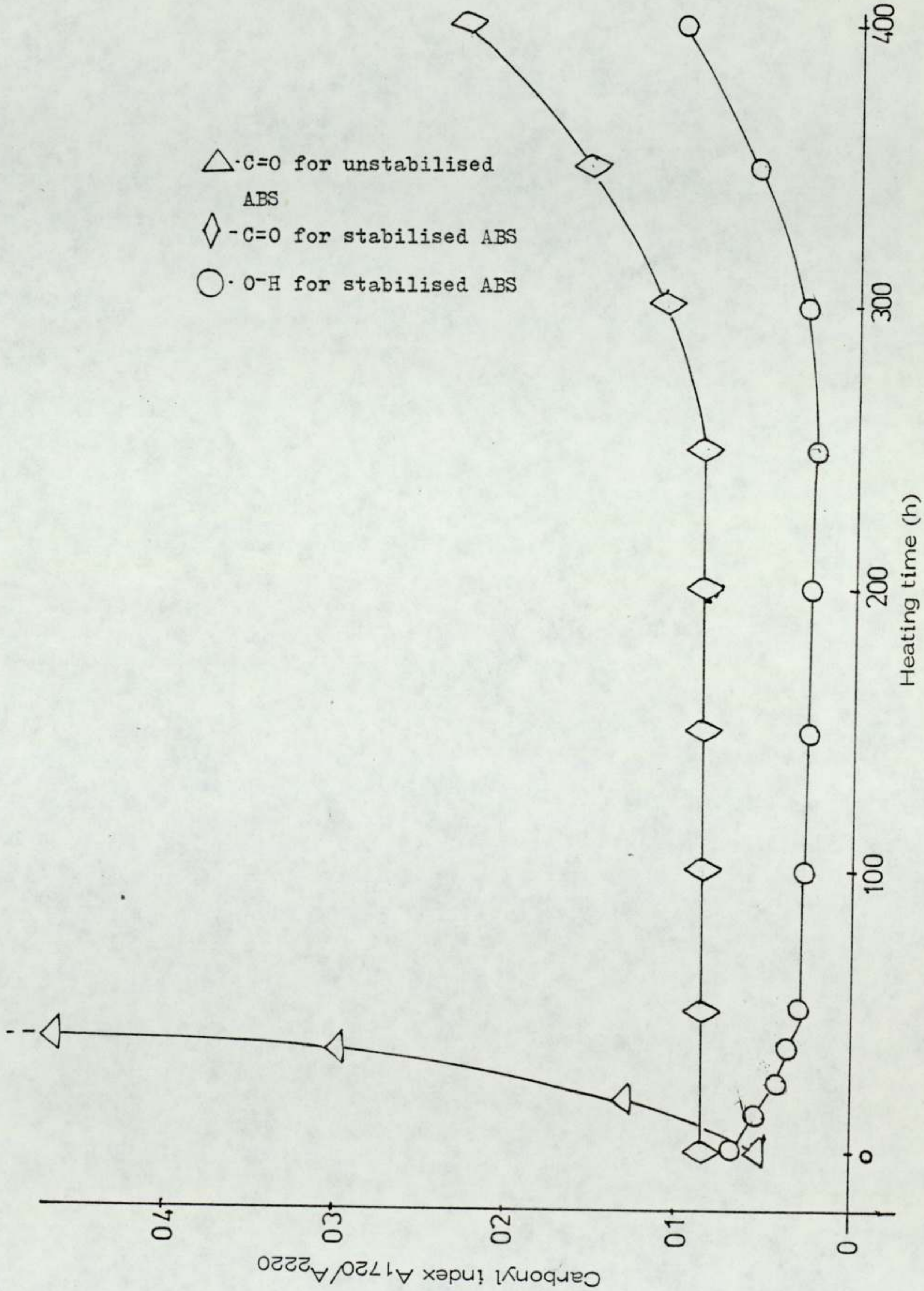
4.2.a.2. HINDERED PHENOL DERIVATIVES AS THERMAL STABILIZERS

The ABS films obtained for these studies were prepared in a similar manner to that described under section 2.a.2. above, using the same additive concentration (4.87×10^{-3} moles / 100g polymer) as was used for UV irradiation studies. Oven ageing of these films were carried out in a Wallace oven at 100°C in air flowing at $\frac{1}{2}$ cu.ft. per hour. The oxidative degradation was followed by the development of the carbonyl and hydroxyl groups using infra-red spectroscopy. A typical curve for stabilized ABS film is given in Figure 28. The initial decrease in the hydroxyl peak of stabilized ABS centred around 3450 cm^{-1}, is always accompanied by a decrease in the absorption in 1200 - 1000 cm^{-1} region. This behaviour was not observed for unstabilized ABS on oven ageing. This is probably due to its faster rate of degradation, as the embrittlement time is reached in 30 hours at this temperature. The increase in the carbonyl region (1730 - 1630 cm^{-1}) after the induction period is accompanied by the hydroxyl and the absorbtion around 1200 - 1000 cm^{-1}. The induction period and embrittlement times observed for various antioxidants are given in Table 12.

TABLE 12 - INDUCTION PERIOD AND EMBRITTLEMENT TIMES OF ABS STABILIZERS FILMS ON OVEN AGEING IN AIR AT 100°C AT CONCENTRATION 4.87×10^{-3} MOLE STABILIZER / 100 g OF POLYMER

STABILIZER	INDUCTION PERIOD IN HOURS	EMBRITTLEMENT TIME IN HOURS
None	3	30
Factory Stabilized	220	300
BHBT	230	300
BHBP	240	310

Figure 28. Typical curves for the development of O-H and C=O absorbtions on oven ageing of a stabilised ABS film in air at 100°C.



STABILIZER	INDUCTION PERIOD IN HOURS	EMBRITTLEMENT TIME IN HOURS
BHT	280	350
1076	370	520
TBPS	400	530
BHBM	420	550
TBMP	675	800

4.2.a.3. DISCUSSION

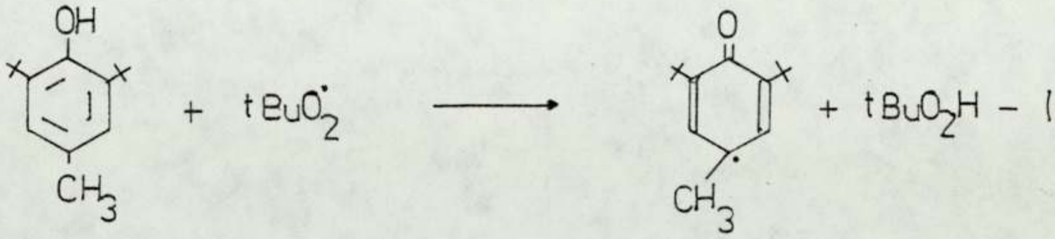
The fate of phenolic antioxidants during autoxidation has been released to the occurrence of the following steps[71] :-

$$RO_2^{\bullet} + AH \longrightarrow RO_2H + A^{\bullet} \qquad - (6)$$

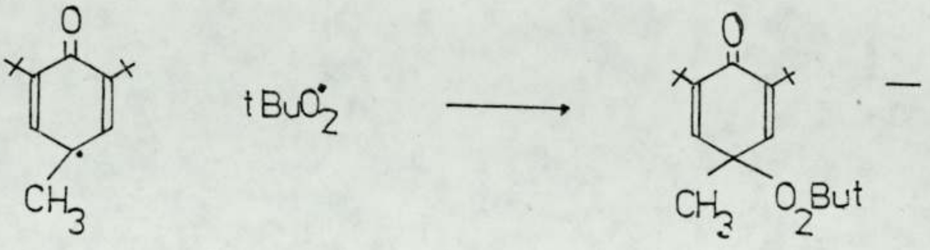
$$A^{\bullet} + RO_2^{\bullet} \longrightarrow RO_2A \qquad - (7)$$

$$2A^{\bullet} \longrightarrow \text{Products} \qquad - (8)$$

Campbell and Coppinger[72], reported the products of condensation between tert butyl hydroperoxide and 2,6-tert-butyl-4-methylphenol (BHT) involved the reaction (6) and (7) as indicated by (9) and (10).



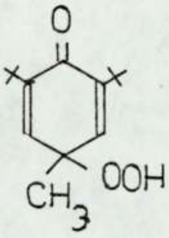
(9)



(10)

VIII

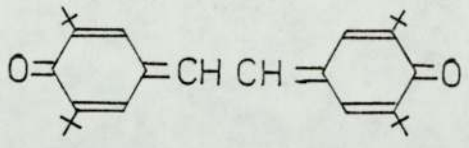
When BHT was photo-oxidized under very mild conditions, Tamir and Pospisil[73], were able to isolate the hydroperoxy analogue of VIII 2,6-ditert-butyl-4-methyl-4-hydroperoxy cycolhexadiene-1-one (IX) in very high yields.



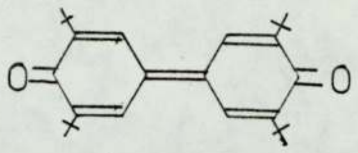
IX

This indicates that the mechanism of stabilization of both thermal and photo-oxidation in the presence of hindered phenol antioxidants is similar at least during the initial stages of oxidation. When photo-sensitized oxidation of BHT was carried further an oily mixture containing ten major oxidation products was obtained. Of these, they found the only compounds visible on TLC plates were 3,5 3'5' tetra-tert-butyl-stilbene-4 4'quinone (X) and3,5 3'5'- tetra-tert-butyl-

-diphenoquinone (XI).

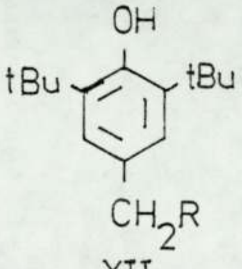


X



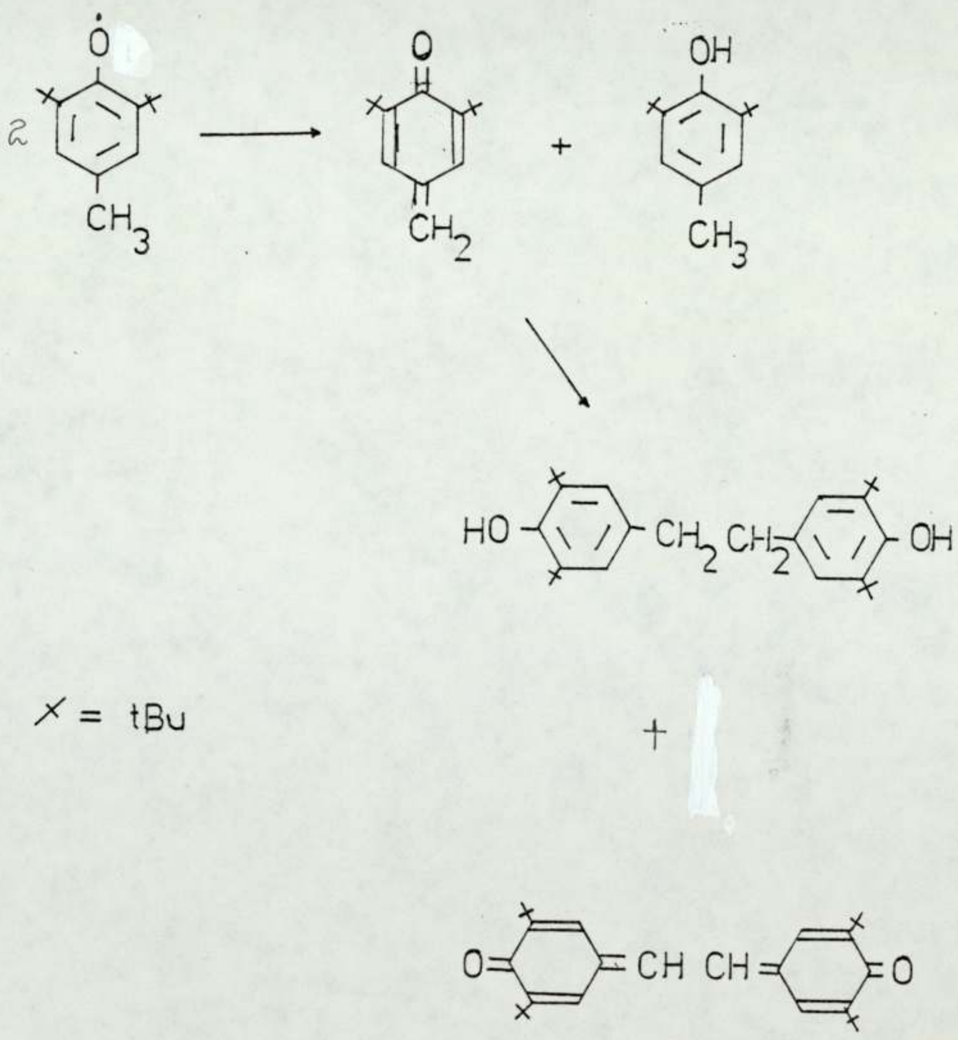
XI

Westfahl[74], observed that for derivatives of compound XII (Where R = H, OH, SH, Salkyl Sbenzyl), the stilbenequinone derivative (X) is formed on one electron oxidation. Furthermore, the stilbenequinone derivative was identified as one of the major products of oxidation of compounds BHBM, BHBP, BHBT and TBMP during the attempted adduct formation reactions in emulsion under redox conditions (Chapters 6 and 7). Therefore, it can be concluded that the visible colour observed during photo-oxidation of ABS films containing hindered phenol derivatives is due mainly, to the formation of stilbene quinone (X) as one of the major products of oxidation. The question arises as to why the intensity and the rate of formation of colour is high with thiol acid esters derivatives of 3,5 di*tert* butyl 4-hydroxy benzylalcohol, than the rest.



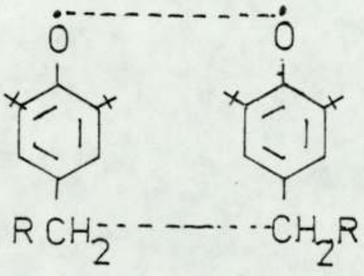
XII

It has been observed that 2,6 di*tert* butyl 4 methyl phenoxy is the only radical which can be detected during the oxidation of the parent phenol, although stilbenequinone (X) is the major end product of the reaction[75]. One suggestion is that, disproportionation of the phenoxyl radical to a p-quinone-methide followed by the dimerisation and reduction of the ethane grouping leading to compound (X)[76].

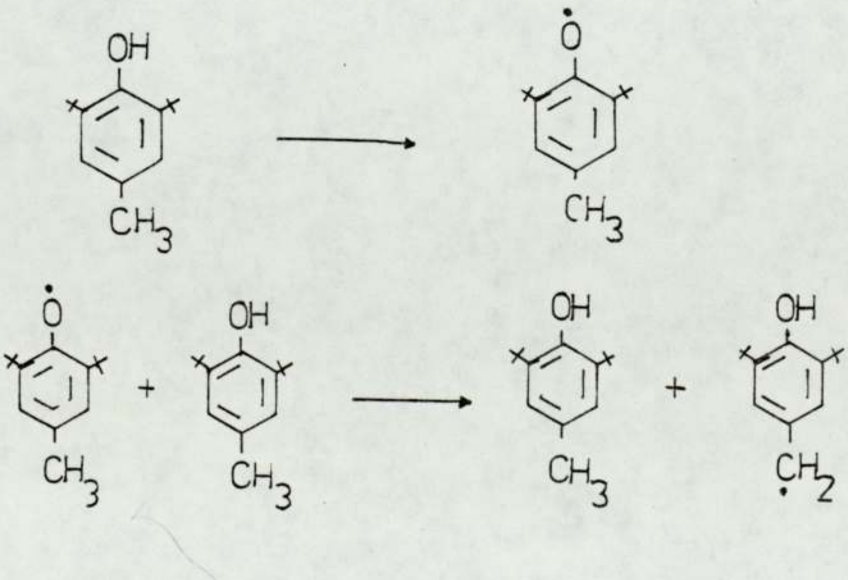


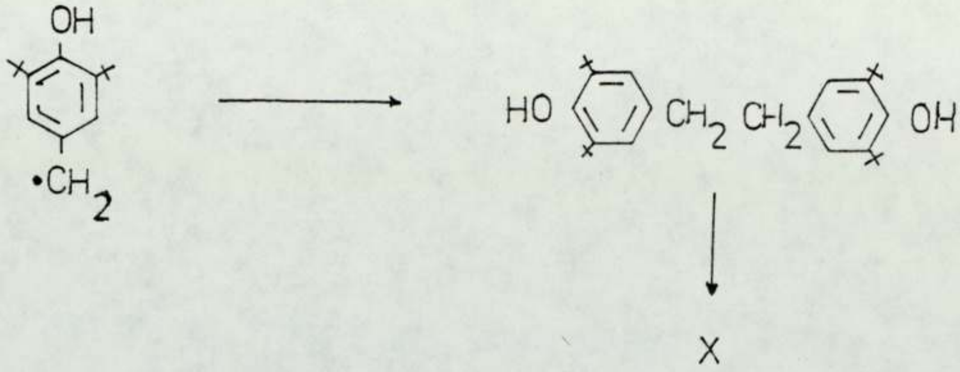
X̄

An alternative suggestion has been made that the ethane derivative is formed directly from a dimeride complex (XIII).[75] This theory is said to give a better account of the effect of ortho substituents than the first but conclusive evidence is lacking[73]. It has been observed that BHT can be grafted to NR in the presence of redox system of initiators[80]. This has been attributed to the possibility of abstraction of hydrogen by primary radicals from the 4 methyl group leading to the formation of 3,5 di<u>tert</u> butyl 4 hydroxy benzyl radical. Stilbenequinone derivative (X) can be obtained from this radical by the dimerisation and reduction of the ethane grouping (6).



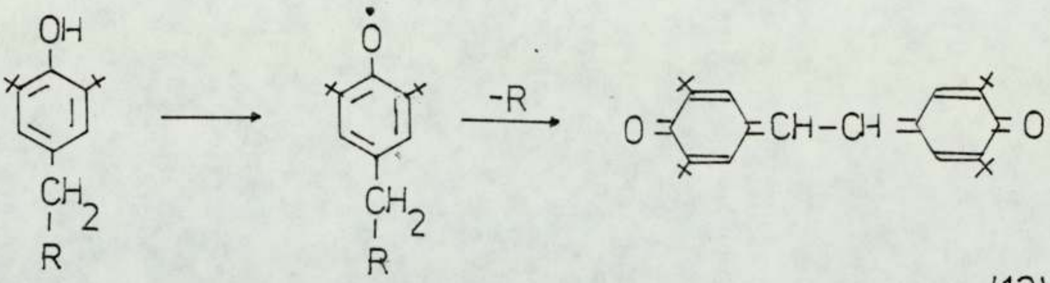
XIII





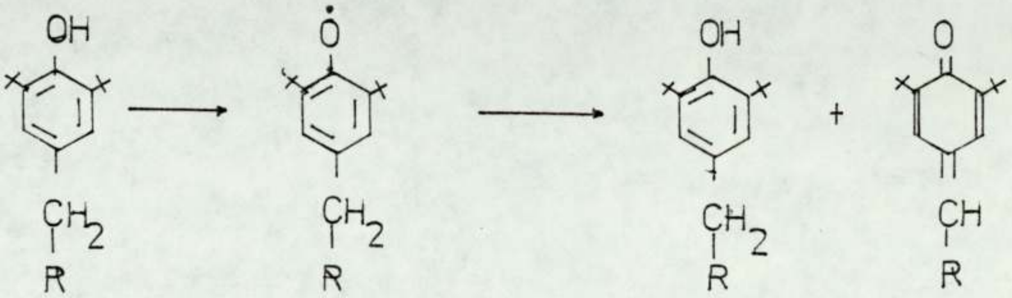
(11)

Based on the evidence from one electron oxidation, Westfahl[74], was able to divide 3,5 di*tert* butyl 4 hydroxy benzyl derivatives (XII) into two general classes. The primary radical formed from one class of derivatives of (XII) undergoes dimerisation and dispropotionation to give the stilbene quinone derivative (12). The primary radical from the second class decomposes by dispropotionation to form one molecule of the parent phenol, and a stable mono substituted 3,5 di*tert* butylquinonemethide (XIV) (13). Derivatives of (XII) where the C-R bond is weak are said to belong to the first general class of antioxidants (12) Of the hindered phenol derivatives tested the C-R bond is weakest in the benzylalcohol derivatives, due to high electronegativity of the oxygen atom and the electron affinity of the phenyl ring. (Further implications of Westfahl's observations will be discussed in Chapter 6). As a result BHBP and BHBT can be expected not only to develop colour faster than the rest of the antioxidants but also to offer less protection to the polymer even though they contain a sulfur atom capable of peroxide decomposition. Table 12. Furthermore, it has been observed by Taimir and Pospisil[73], that the substituent R of the C-R bond of compound XII also governs the nature of the oxidation products



XII X

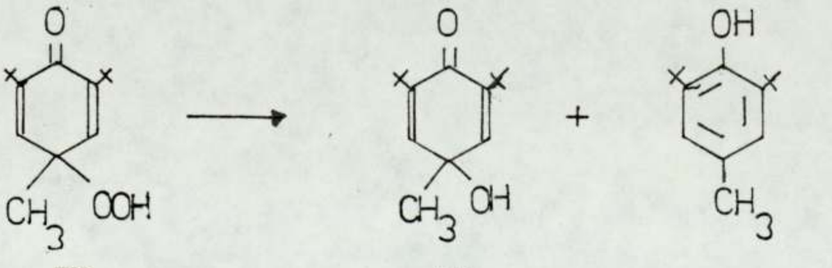
(12)



— (13)

XII XIV

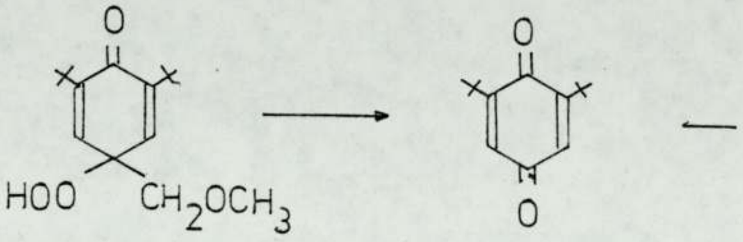
of the peroxydienone. Thus when R is H as in IX, the compound undergoes exothermal decomposition above 130°C with formation of parent phenol and 2,6 di*tert* butyl-4-methyl-4-hydroxy 2,5 cyclohexadiene-1-one (XV) as major products - (14).



— (14)

IX XV

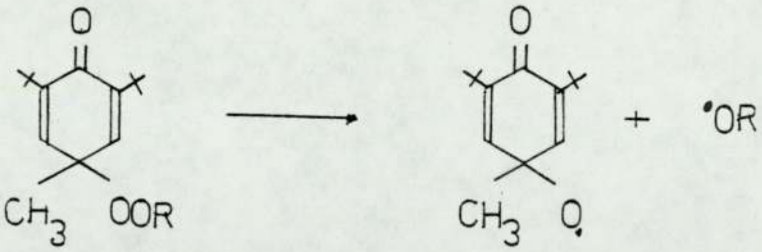
The hydroperoxide XVI (where R is OCH_3) is decomposed at a temperature lower than 20°C leading to the quinone (XVII) as the major product (15). This can explain the reduced activity of thiol derivatives BHBP, BHBT than



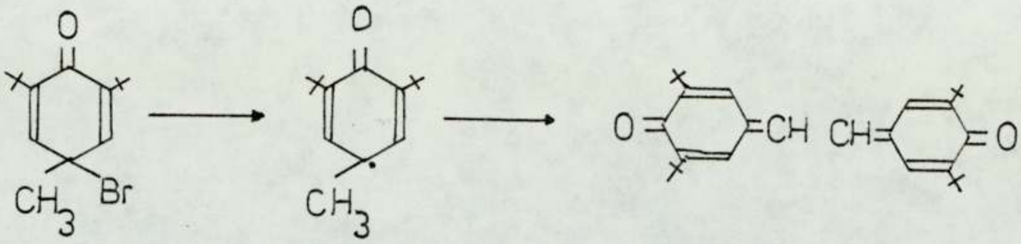
XVI XVII

(15)

BHT or BHBM on thermal oxidation of stabilized ABS films. The formation of free radicals on the decomposition of peroxy dienones has been reported by Scott[81]. The formation of free radicals at a lower temperature, and the absence of regeneration of the parent phenol as in (14) can account



for the lower stability of ABS films containing thiol derivatives BHBT and BHBP. Table 12. The oxidation products such as (XV) too have the ability to form stilbene quinone derivatives thereby increasing the rate of colour formation as well as the intensity of colour in all cases. Thus, Cook et. al.,[82], were able to show the formation of stilbene quinone derivative from the 4 bromo analogue of XV (16)[77].

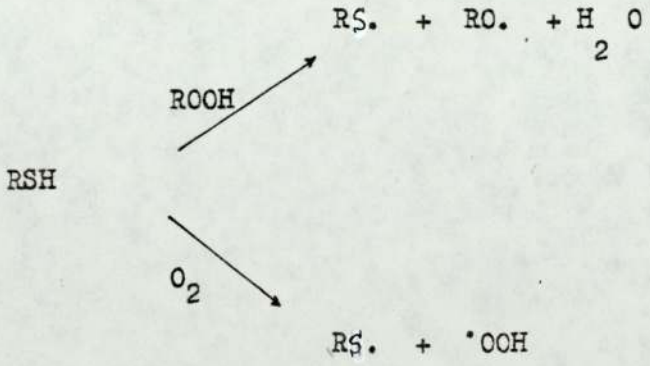


– (16)

The difference in the activities of the rest of the sulfur containing derivatives TBMP, BHBM and TBPS can be attributed to their peroxide decomposing ability. Cumene hydroperoxide decomposition studies at 70°C in the presence of sulfur containing hindered phenols showed that all but TBPS decomposed hydroperoxides rapidly and catalytically after a short induction period. Figures 29 and 30. A non-catalytic very nearly stoichiometric reaction was observed for the decomposition of cumene hydroperoxide by TBPS at 95°C after a long induction period ($\approx$ 90 minutes) Figure 29. The white precipitate obtained from this reaction was identified by spectroscopic analysis as the corresponding sulfoxide. This apparent lack of catalytic activity of TBPS can be related to the absence of methylenic protons in the molecule by comparison with BHBM and TBMP, as similar behaviour observed for diphenyl sulfides[83], rule out any interference by the phenolic group on the decomposition reaction. The influence of these protons on the reaction is further evidenced from the work done by Barnard[84], and Hargrave[85]. In contrast to the high yields of sulfoxides obtained by the reaction of saturated sulfides with hydroperoxides the yield of allylic sulfides varies both with the nature

1740cm^{-1}

of the unsaturated sulfide with the hydroperoxide, and with the solvent.[77] As the rate of decomposition of hydroperoxides by BHBM and TBMP were found to be similar (Figures 29 and 30) it is possible to assume that the difference in the activity of the two on thermal oxidation of ABS films lies in their mechanism of hydroperoxide decomposition. It has been observed that thiols generate free radicals by redox reactions with hydroperoxides[86] as well as with oxygen[78]. The formation of such radicals as alkoxy in the presence of BHBM can not only influence the initiation and propagation of auto-oxidation, but also decrease the concentration of the active antioxidant by the hydrogen abstraction from the hindered phenol group (6). On the otherhand, there is no convincing evidence to suggest that free radicals are involved in the oxidation of sulfides to sulfoxides, sulfones, thiol sulfinates etc.[87]. In the case



of monosulfides the available evidence suggests a normal second order reaction with respect to hydroperoxide and first order with respect to sulfide and that the final products are produced by a synchronous bond rearrangement[88] .

Figure 29. Decomposition of CHP in the presence of TBMP and TBP at 70°C (TBMP/TBPS: CHP I : IO).

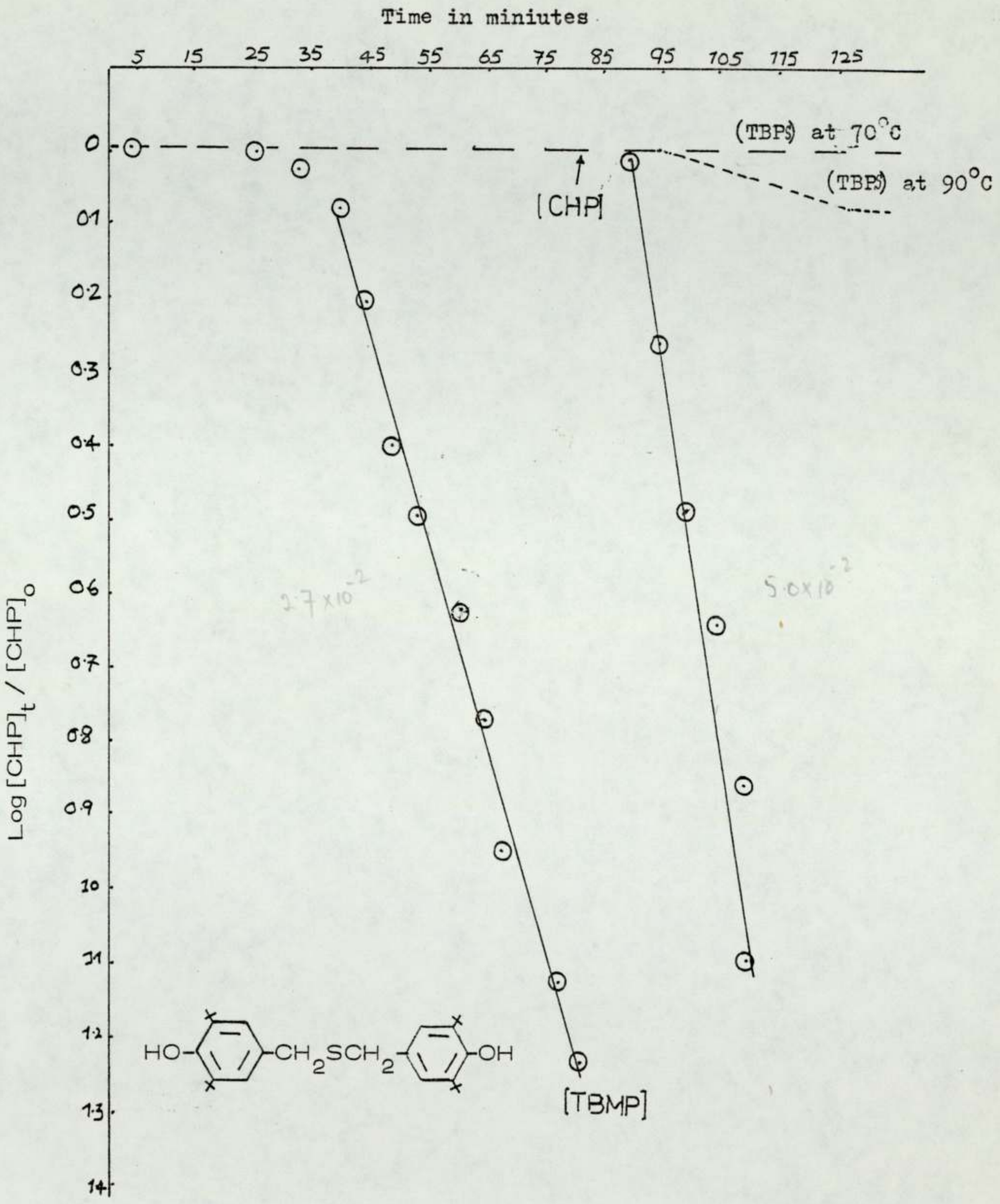


Figure 30 Decomposition of cumene hydroperoxide in the presence of BHBM at 70°C. (BHBM:CHP, 1:10)

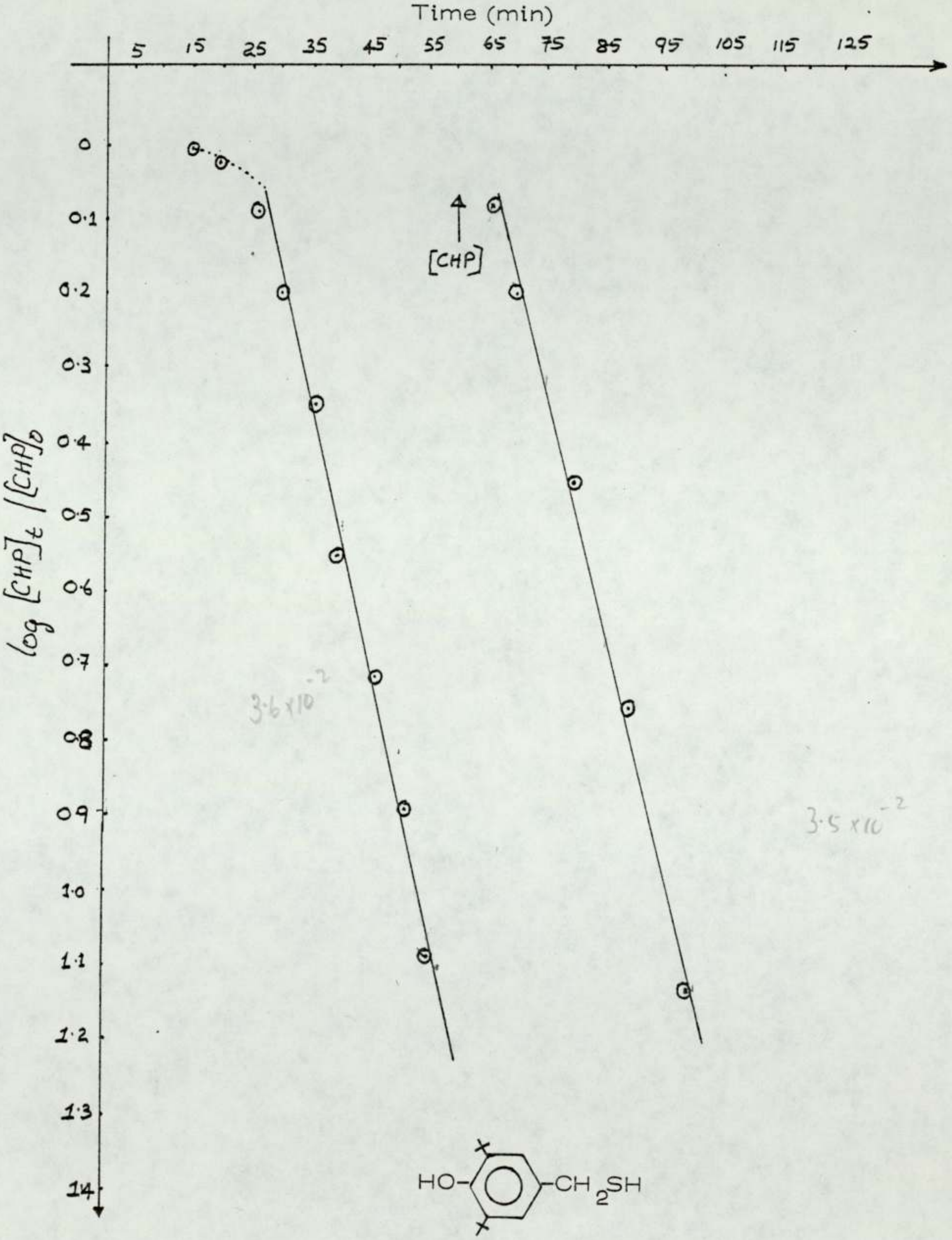
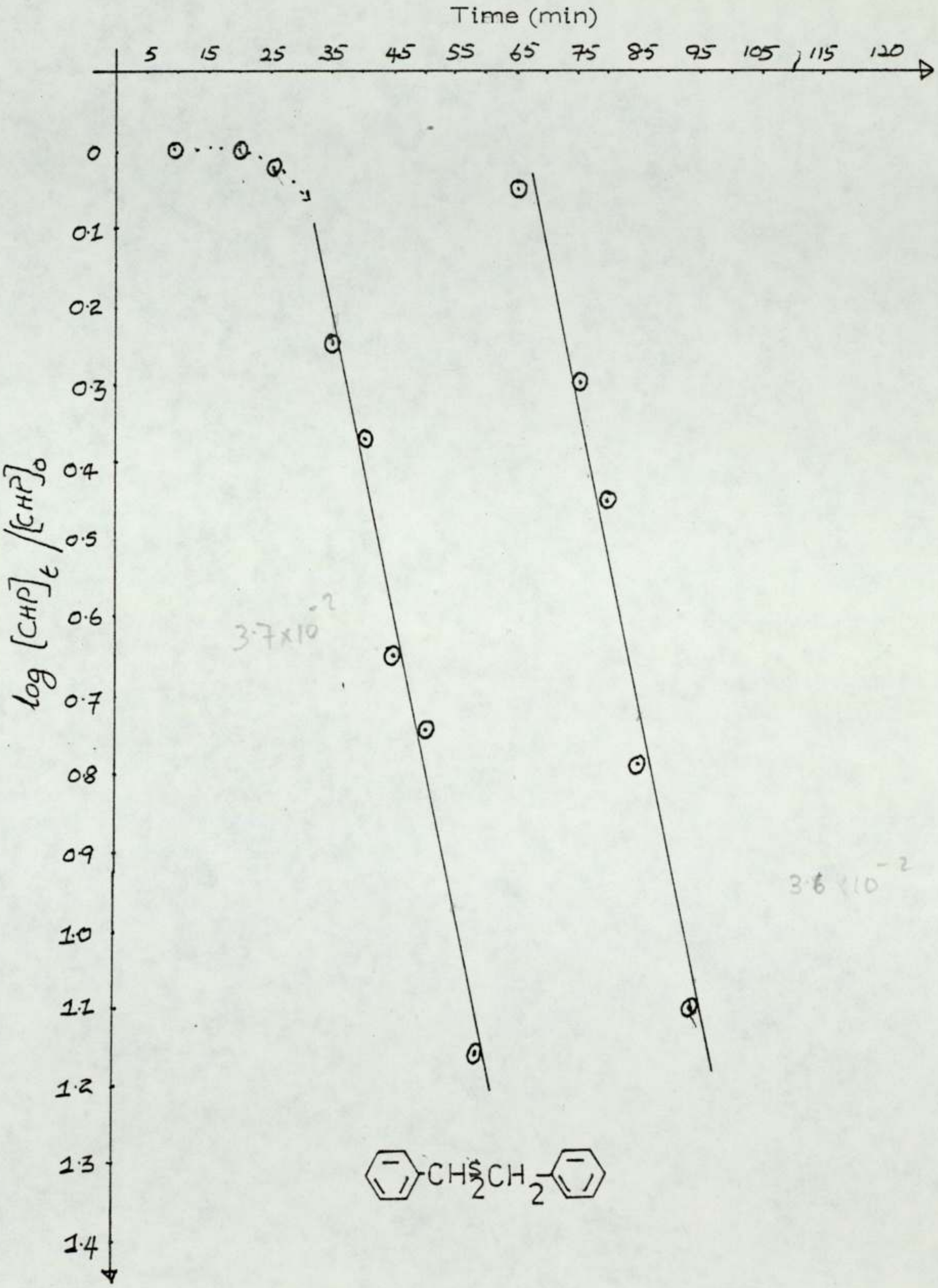
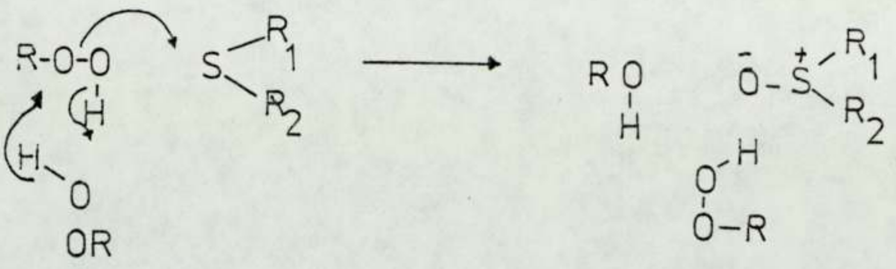
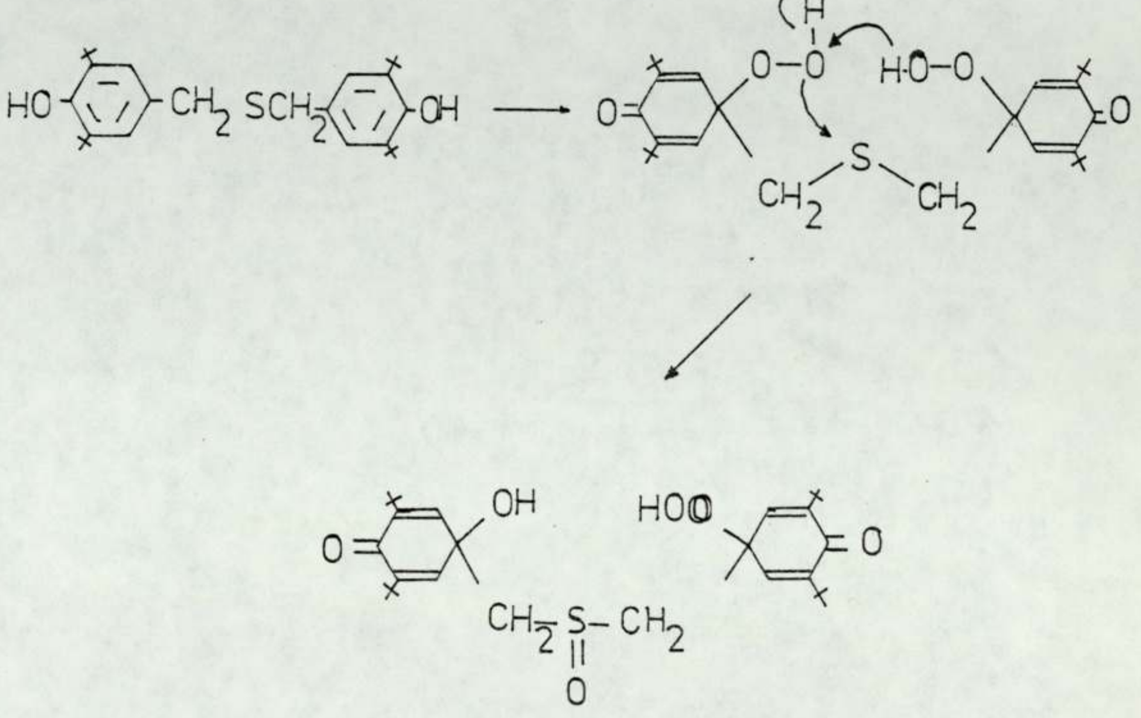


Figure 3I.- Decomposition of CHP in the presence of dibenzyl monsulfide (DBM) at 70°C (DBM : CHP I : IO).



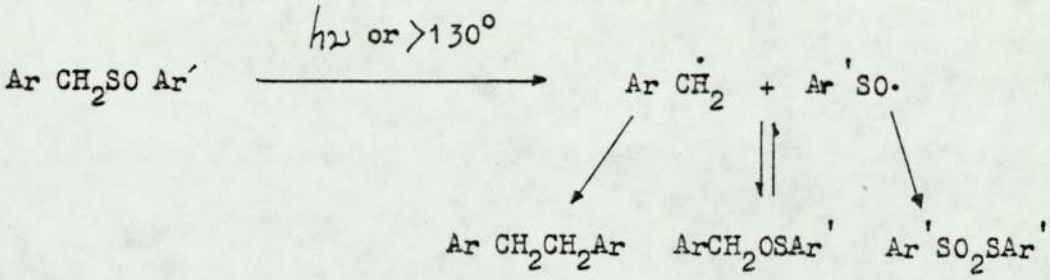




XVIII

A number of workers have studied the thermal decomposition of sulfoxides.[89,90] It has been observed that sulfoxides which decomposes below 100°C usually contain β-hydrogen atoms which facilitate a five-centre first order elimination with the formation of an olefin.

Abbot and Stirling[89], and Mislow and his co-workers[90], have shown that in the case where there is no β-hydrogen atom, a sulfenate ester is formed reversibly above 130°C via radical intermediates. Such decompositions of aryl alkyl, alkyl and alkenyl sulfoxides with formation of free radicals on photolysis have been observed by Shelton and Davies [91]. Since ovenageing tests of ABS films containing the antioxidants were carried out at 100°C such decompositions involving free radicals can be ruled out. Furthermore, hydroperoxide decomposition by TBMP as well as the dibenzyl sulfide (Figures 29 and 31) at 70°C show catalylic behaviour. This not only rules out homolytic decomposition of these sulfoxides but probably indicates a peroxide induced decomposition of it. The homolytic decomposition of the sulfoxide derived from TBMP on ovenaging of ABS films can also be ruled out due to the lack of development of colour on thermal oxidation. Thus, contrasts with the behaviour on photo-oxidation, as the benzyl radical inevitably formed on such a decomposition invariably leads to the brightly coloured stilbenequinone derivative.



The relative antioxidant activity on thermal oxidative degradation of stabilized ABS films obtained with BHT as standard are compared in the following Table 13, with those observed by Jirackova and Pospisil[92, 93] on oxidation of stabilized isotactic polypropylene at 180°C and in the azobis isobutronitrile initiated oxidation of tetralin at 65°C. The oxidation temperature of 180°C has been chosen by these workers on the basis of earlier studies which showed the effect of sulfur in a molecule of thiobisphenol became marked only at elevated temperatures[94]. The temperature at which stabilized ABS films were aged (100°C) was chosen on the basis of studies by Plant and Scott[95], and Durmis et. al.,[96], where it has been observed that the efficiency of the antioxidant depended on polar and steric factors but also factors leading to low volatality at high temperatures. A study of mononuclear phenolic antioxidants have shown that high volatality of these compounds plays a major role at temperatures above 100°C. (The bound antioxidant thiol, BHBM has been studied at both temperatures 100°C and 180°C and the results are given in Chapter 7). It is seen from Table 13, that the results are in general agreement in the order of antioxidant activity. Furthermore, the reduced relative activity when C-R is linked by an oxygen atom, is reflected in all cases including those derivatives with peroxide decomposing activity.

TABLE 13 - RELATIVE ACTIVITIES OF HINDERED PHENOL ANTIOXIDANTS OF THE TYPE XII AT AN ANTIOXIDANT CONCENTRATION OF 0.005 MOLE / 100 g PP, 0.00487 MOLE / 100 g ABS AND 0.0005 MOLE / LITRE OF TETRALIN

R for Compound XII	Relative antiox. activity in PP at 180°C (Reference 92)	Relative antiox. activity in ABS at 100°C	Relative antiox. activity in Tetralin 65°C (Reference 93)
H	1.00	1.00	1.00
OH	0.65	-	0.86
OCH_3	0.75	-	0.61
$OCOCH_2SH$	-	0.82	-

TABLE 13 - Continued....

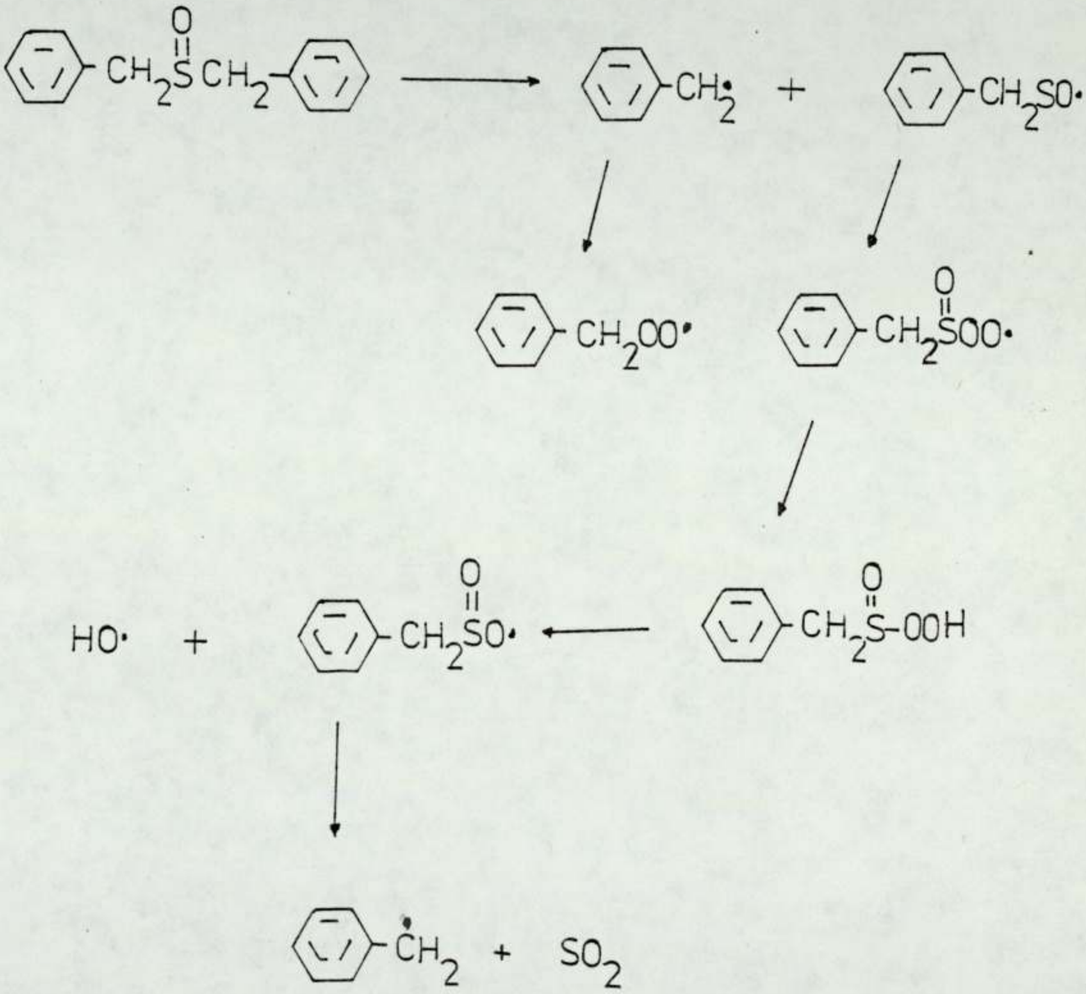
R for Compound	Relative antiox. activity in PP at 180°C [92]	Relative antiox. activity in ABS at 100°C	Relative antiox. activity in tetralin 65°C [93]
$OCOCH_2CH_2SH$	-	0.85	-
SH	1.81	1.50	0.97
SCH_3	1.64	-	1.26
SR'	2.97	2.41	1.90
SSR'	2.88	-	2.67

Standard 2,6 di<u>tert</u> 4 methylphenol (R=H)

R' = 3,5 di<u>tert</u> butyl-4 hydroxybenzyl.

The photo-oxidative stability of ABS in the presence of TBMP in contrast to its thermal oxidative stability with the same adduct shows no improvement over the free thiol BHBM as additive. Table 11. This is probably due to the ability in both cases to form initiating radicals during hydroperoxide decomposition or as a consequence of it. BHBM being a free thiol is capable of undergoing redox reactions with hydroperoxides with the formation of alkoxy type radicals[78]. The formation of free radicals on photolysis of sulfoxides have been demonstrated by Shelton and Davis[91], and was mentioned earlier. The sulfoxides derived from TBMP during the initial stages of oxidations can similarly undergo photolysis during photo-oxidation of ABS with the formation of aralkyl radicals.

The development of colour on irradiation of ABS films containing TBMP as the stabilizer can be explained on the basis of such a decomposition of sulfoxide. This can be illustrated using a similar sequence for the formation of free radicals on pyrolysis of dibenzyl sulfoxide[87].



The benzyl radical so formed in the case of TBMP can act as the precursor to the stilbenequinone derivative which give rise to the colour during photo-oxidation of ABS film.

4.3.a.1. SYNERGISTIC COMBINATIONS

The main objective of the project was to achieve the highest stability of ABS, by chemically bound stabilizers or combination of stabilizers. It is a well established fact that during the processing operations of a polymer various sensitizers capable of initiation of oxidative degradation are introduced into the system. As a consequence, it was decided to carry out the reaction to obtain bound stabilizer in the latex stage. It will be evident from the evidence discussed in Chapters 5 and 6, in the literature survey of bound systems that either olefinically unsaturated, or thiol derivatives of hindered phenols and 2-hydroxybenzophenones are suitable for reactions in the latex stage of an olefinically unsaturated polymer such as ABS. Therefore, the following hindered phenol derivatives and 2-hydroxybenzophenone derivatives were used in combination as additives during processing of unstabilized ABS to assess their combined activity. The ABS polymer with the additives were processed in the torque rheometer at 190°C for three minutes. Films were obtained by compression moulding of processed ABS, between two polished steel plates at 190°C for three minutes. These films were UV irradiated in the UV cabinet (Chapter 2) and the photo-oxidation was followed by the development of carbonyl absorbance using infra-red spectroscopy. Figure 32. The induction periods and embrittlement times for these films are given in Table 14.

Figure 32 Development of carbonyl functional group on photo-oxidation of ABS films containing various combinations of additives. Hindered phenol 4.87 x 10^{-3} mole stabilizer/100g ABS
2-hydroxy BP derivative 3.06 x 10^{-3} mole stabilzer/100 gABS

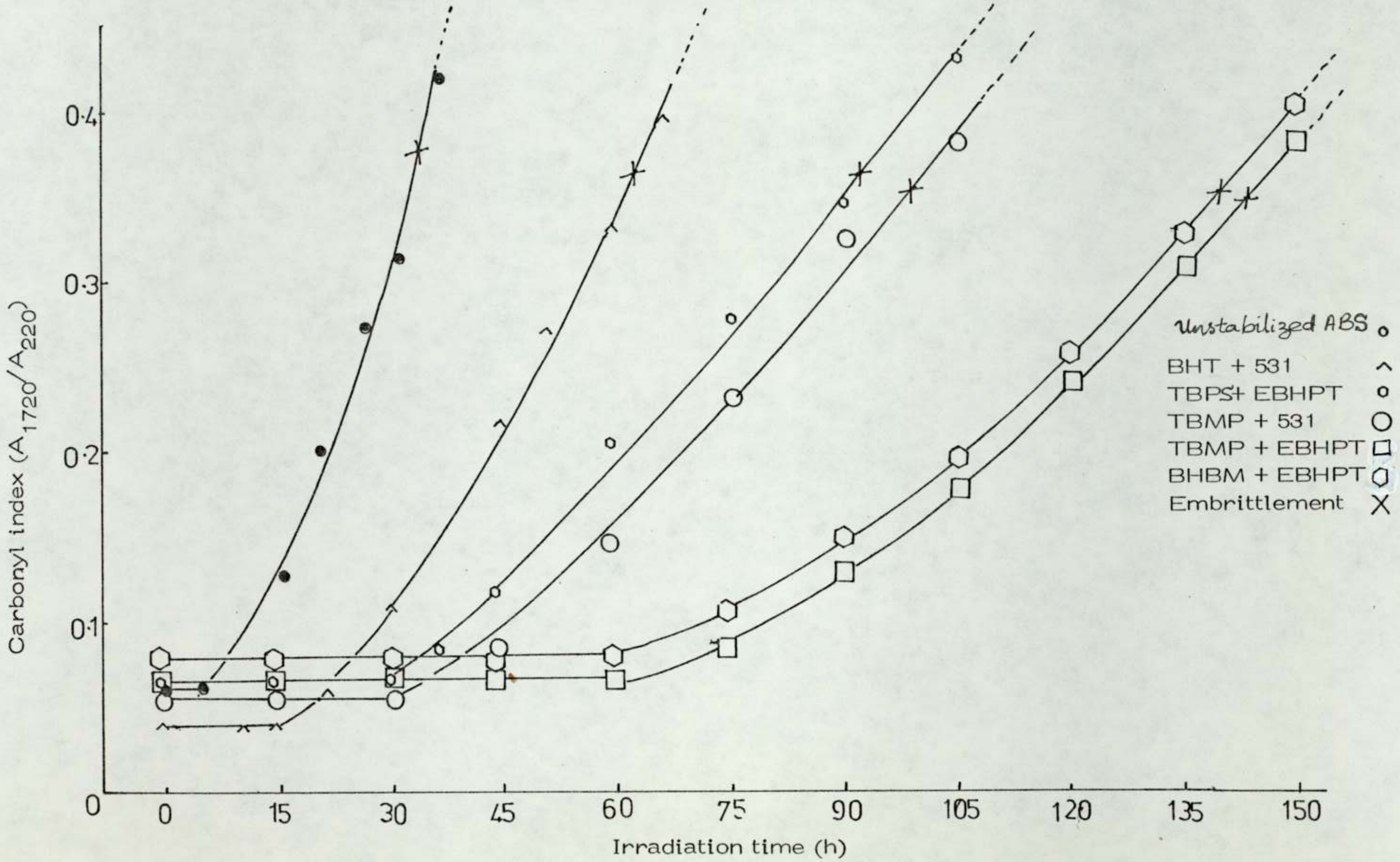


TABLE 14 - INDUCTION PERIODS AND EMBRITTLEMENT TIMES OF ABS STABILIZED FILMS ON PHOTO-OXIDATION

2 hydroxybenzophenone derivatives	3.06×10^{-3} mole stabilizer/100g ABS
DLTP	1.94×10^{-3} mole stabilizer/100g ABS
Hindered phenol derivatives	4.87×10^{-3} mole stabilizer/100g ABS

Stabilizer Combination	Additive effect		Combined effect	
	Induction period	Embrittlement time	Induction period	Embrittlement time
Factory stabilized	-	-	6-7	35
BHT + UV531	20	69	22	65
BHT + UV531 + DLTP	25	94	25	85
TBPS + UV531	20	77	25	87
TBMP + UV531	24	88	40	100
TBPS + EBHPT	27	92	35	95
TBMP + EBHPT	30	103	75	140
BHBM + EBHPT	29	102	75	138

The additive effects shown in Table 14 were obtained by using the results described early in this Chapter (Tables 9, 10, and 11).

4.3.a.2. DISCUSSION

Synergistic effects were observed when the thiol derivative BHBM or the monosulfide TBMP was combined with the thiol derivatives EBHPT respectively.

As expected, the diphenyl sulfide derivative, TBPS showed only a marginal increase in activity in combination with 2-hydroxybenzophenone derivatives. This can be attributed to its lack of auto-catalytic hydroperoxide decomposition activity.

Though the combined effect on the induction period in the presence of DLTP, BHT and UV 531 was similar to the additive effect, the embrittlement time was reached much faster. This is probably due to a formation of the derived sulfoxide from DLTP accelerating the process of oxidation.

Thiol derivatives are known to decompose peroxides under redox conditions leading to free radicals.[78] The probabilities of recombination of thiol radicals to form disulfides are much higher in the presence of another thiol derivative as in the case of BHBM and EBHPT (Table 14).

$$ROOH \xrightarrow{R'SH} R'S. + RO. + H_2O$$

$$R'S. + \overset{''}{R}S. \longrightarrow R'SS\,R''$$

Less systematic work has been done on antioxidant effects of disulfides. In this connection thiols must be considered in the same context, due to their ready conversion to disulfides under oxidative conditions and the

$$2\ \mathrm{RSH} \xrightarrow[\mathrm{ROOH}]{\mathrm{O_2}} 2\ \mathrm{RS^{\cdot}} \rightleftharpoons \mathrm{RSSR}$$

reversibility of this reaction[87]. The oxygenated products of thiols are a also readily inter-convertible with oxygenated disulfides[97], as

$$2\ \mathrm{RSO_2H} \longrightarrow \mathrm{RSO_2SOR} + \mathrm{H_2O}$$

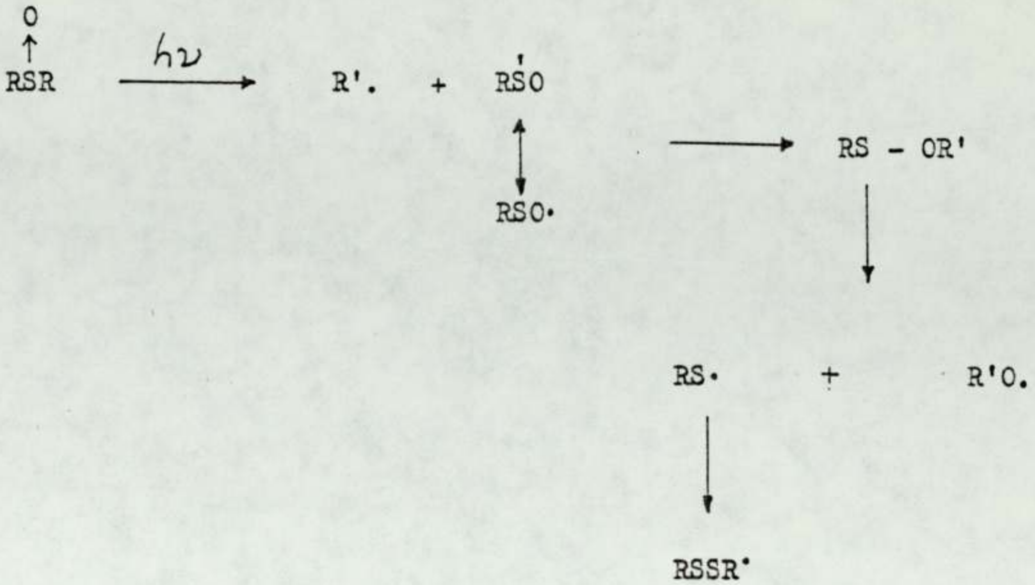
$$\mathrm{RSOSR} + \mathrm{R'SO_2H} \longrightarrow 2\mathrm{RSO_2SR'}$$

are also sulfenic acids formed by breakdown of sulfoxides.

$$\mathrm{R'SOH} \longrightarrow \mathrm{R'SSOR'} + \mathrm{H_2O} \longrightarrow \mathrm{R'SSO_2R'} + \mathrm{R'SSR'}$$

Blundell and Scott[98], have examined 2 2'-dibenzoylaminodiphenyl disulfide both in tretralin and in polypropylene. At peroxide/disulfide ratios in the region of 50:1 an auto accelerating induction period was observed. The same kind of kinetics were observed at 165°C in polypropylene where this compound shows antioxidant properties. The addition of a hydroperoxide to this system reduces the observed induction period.

The possibility of formation of such disulfides in the presence of TBMP and EBHPT can be suggested in the light of work done on photolylic behaviour of sulfoxides of various monosulfides by Shelton and Davis.[91] Products derived from initially formed alkyl and sulfinyl radicals confirmed the expected homolytic cleavage of the C-S bonds of the sulfoxides on photolysis.



The probability of the formation of disulfides is greatly increased on a similar decomposition of sulfoxides of TBMP in the presence of free thiol EBHPT. The formation of disulfides and their oxidation can be put forward as a possible explanation for the observed synergistic effects in the presence of these two hindered phenol derivatives with EBHPT. It follows from the above discussion that free radicals such as alkoxy radicals can be formed in the presence of both BHBM and TBMP. As a consequence of their formation, similar performances might be expected.

4.4.a. HYDROPEROXIDE DECOMPOSITION WITH SULFUR DERIVATIVES

The enhanced ability of sulfur containing derivatives to inhibit ABS oxidation was attributed to their peroxide decomposing ability. The reactivities of these compounds were studied using cumene hydroperoxide (CHP) purified by the method of Kharasch[99].

4.4.a.1. EXPERIMENTAL

Decomposition experiments :- Into a 100 ml 3-necked flask, fitted with a reflux condenser N_2 inlet and a stopper in a constant temperature bath at 70 ± 0.5°C, was placed an accurately weighed sample CHP ($\sim$ 0.01M) in chlorobenzene and the organic sulfur compound ($\sim$ 0.001M) if any were added, in chlorobenzene. The total volume was brought to 50 ml with chlorobenzene. At various times 2 ml aliquot removed and titrated for peroxide content. The reactions were repeated in air. Further sample of accurately weighed CHP ($\sim$0.01M) was placed at the end of the initial decomposition reaction to follow the catalytic effects of the products of decomposition.

Iodometric Titration :- The iodometric method of Wagner, Smith and Peters[29], was used to determine the hydroperoxides in aliquots. A solution of 20 ml freshly distilled isopropanol, 2 ml of glacial acetic acid and the aliquot was heated to reflux, 10 ml of isopropyl alcohol saturated with sodium iodide was added and the solution was refluxed for five minutes. The solution was cooled momentarily and titrated with 0.01N sodium thiosulfate solution. A titration of 2 ml chlorobenzene was used as a blank.

4.4.a.2. RESULTS AND DISCUSSION

The following compounds were studied in the decomposition experiments:-

(1) Bis (3,5 di<u>tert</u>-butyl-4-hydroxyphenyl) monosulfide (TBPS)

(2) Bis (3,5 di<u>tert</u> butyl-4-hydroxybenzyl) monosulfide (TBMP) 2·7 ,5·0

(3) 3,5 di<u>tert</u>-butyl-4-hydroxy benzylmercaptan (BHBM) 3·6 , 3·5

(4) 3,5 di<u>tert</u> butyl-4-hydroxy benzylthiopropionate (BHBP) 3·3 2·5

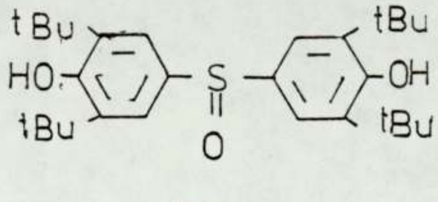
(5) 3,5 di<u>tert</u> butyl-4-hydroxy benzyldecylsulfide.(DBBS) 3·6 , 3·8

(6) 4 Benzoyl-3-hydroxy o-ethylthioglycollate (EBHPT) 4·7x , 3·3

(7) Benzylmonosulfide. 3·7 , 3·6

All but TBPS were active cumenehydroperoxide decomposers at 70°C. The decomposition reaction in all cases assumed first order kinetics after a short induction period and was found to be uneffected by oxygen in air. Furthermore, all active decomposers showed repeated first order kinetics for catalylic decomposition of CHP in chlorobenzene at 70°C - Figures 26, 29, 30, 31, 33 and 34.

TBMP on the otherhand, reacted stioichiometrically with CHP at a higher temperature of 95°C. Spectroscopic analysis of the precipitate formed on cooling the reaction mixture, showed the product was the corresponding sulfoxide (XIX) derivative. The hindered phenol groups remains uneffected after the reaction.



XIX

Figure 33. Decomposition of CHP in the presence of 3,5 ditert-butyl 4 hydroxy benzyldecylsulfide (DBBS:CHP I:IO).

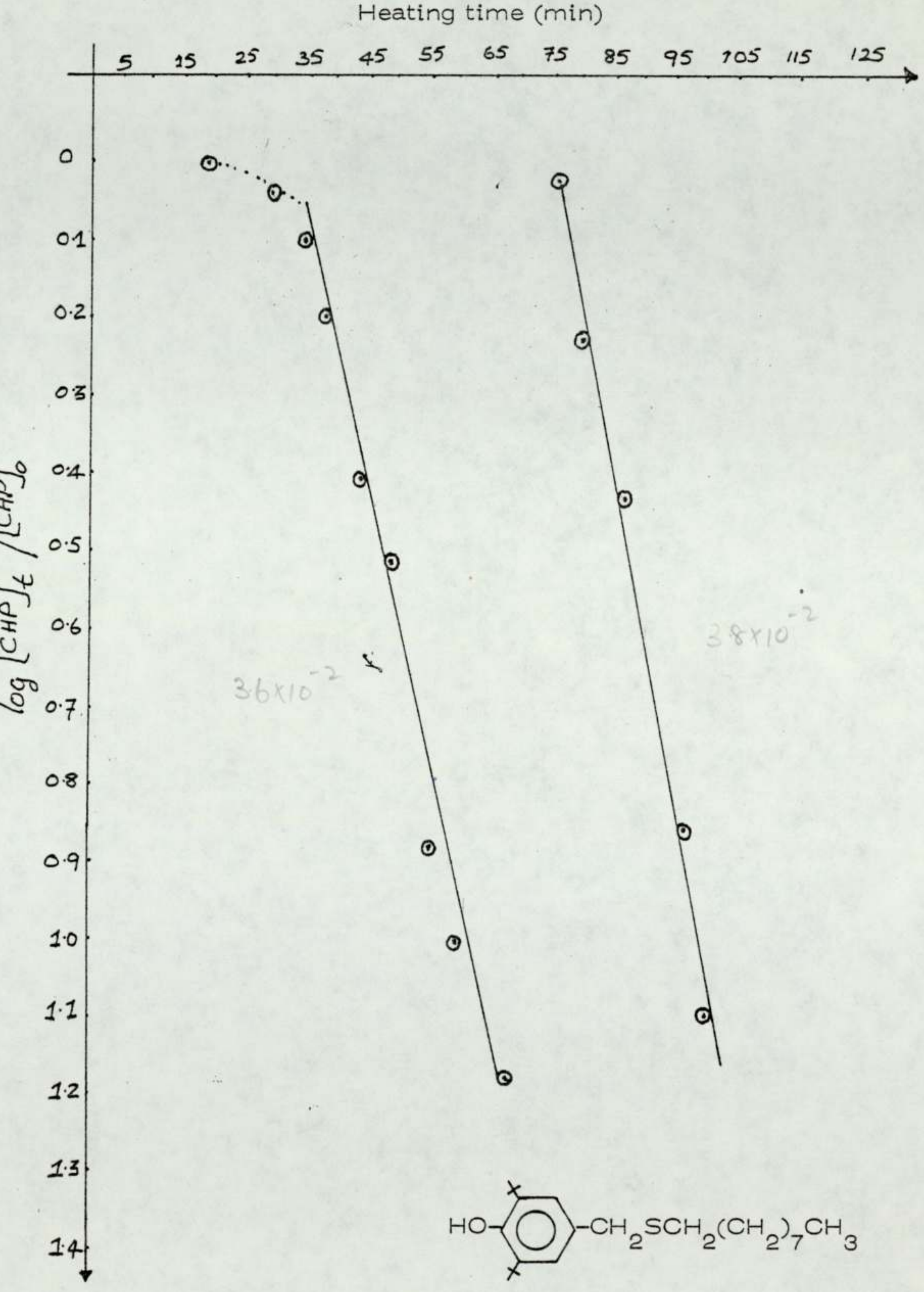
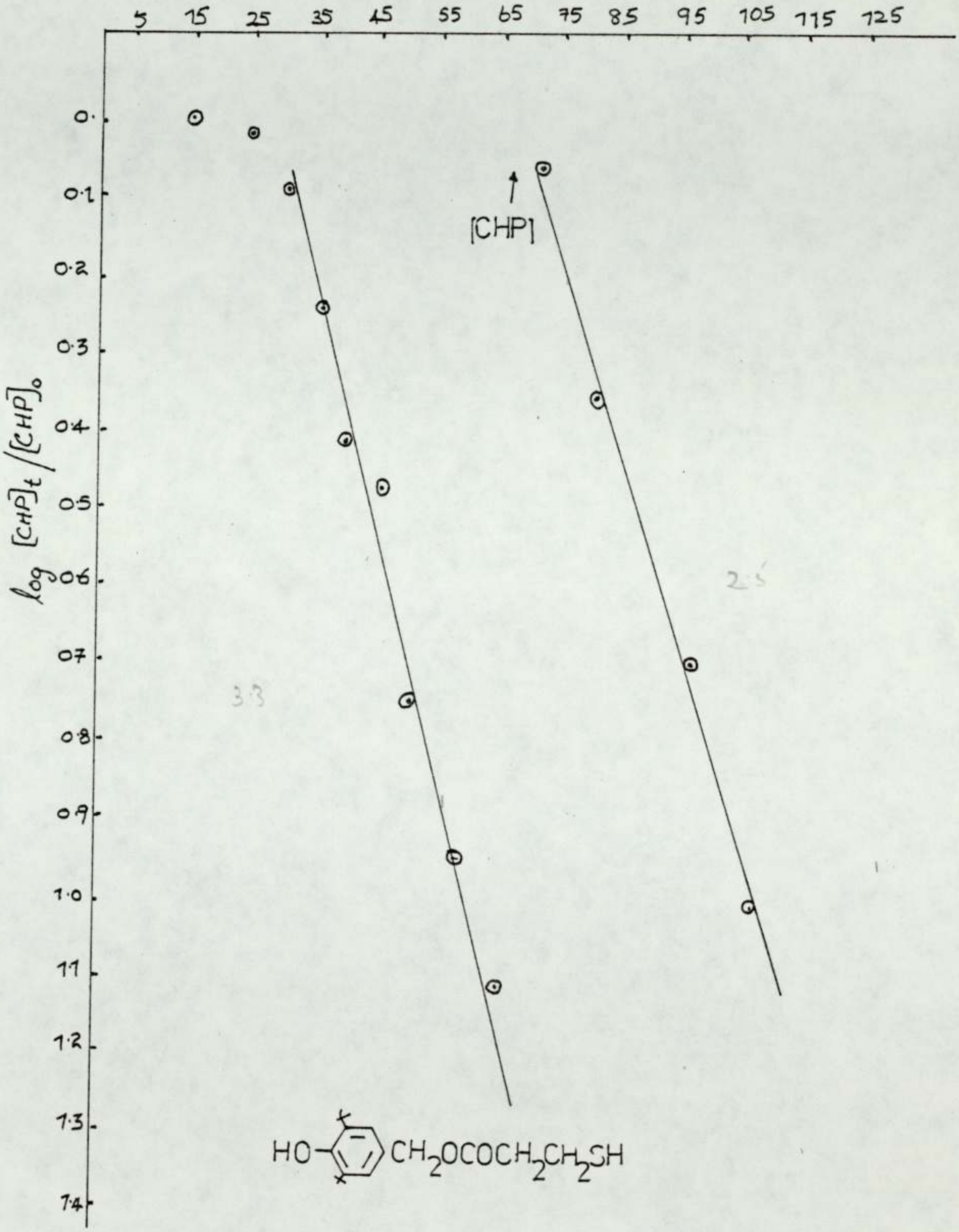


Figure 34. Decomposition of CHP in the presence of 3,5 ditert-butyl-4-hydroxy benzylthiopropionate (BHBP:CHP I:IO).

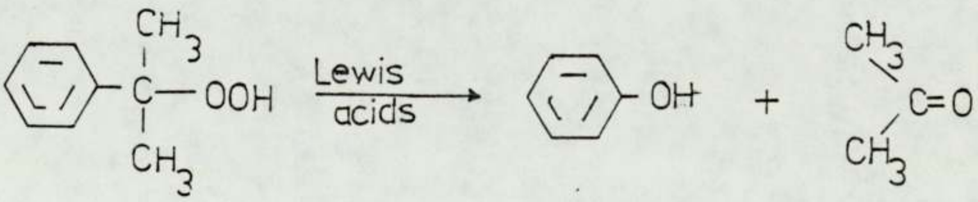


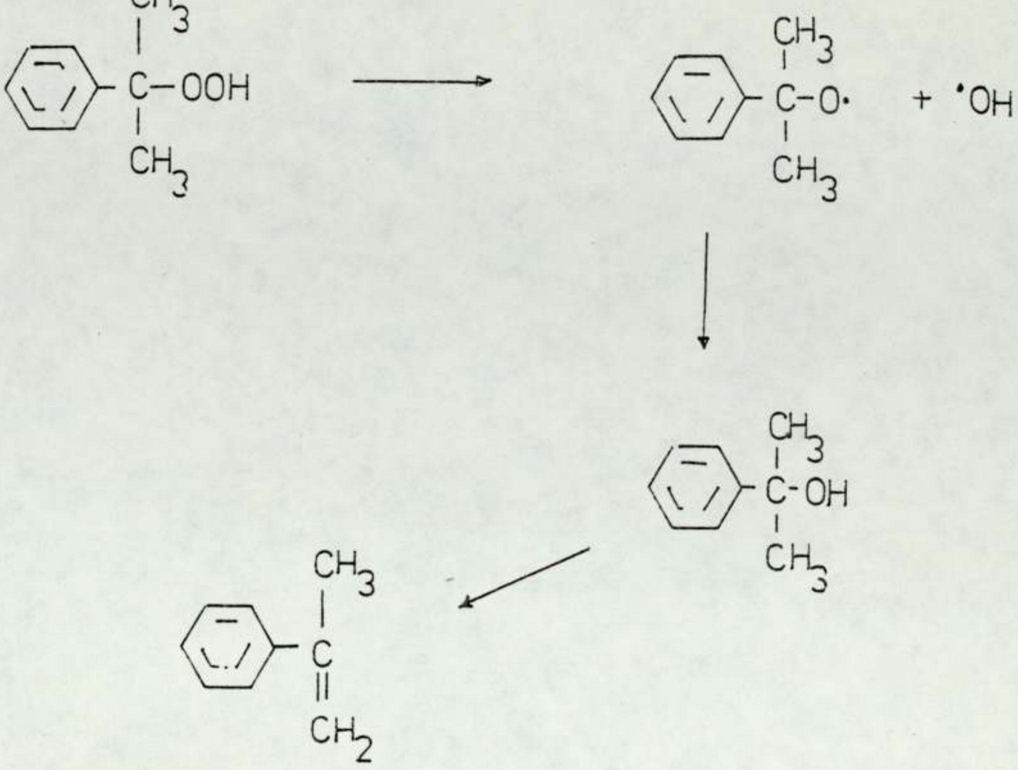
An analogus reaction has been observed for phenyl sulfide[83]. Furthermore, $PhSCHPh_2$, $(PhCH_2)_2S$, and $PhSCH_2Ph$ have been found to inhibit the azobis cyclohexanenitrile catalysed oxidation of cumene to CHP at 110°C. Phenylsulfide has not been found to inhibit this reaction.[100] It can be concluded from these observations, that aryl monosulfides acts as effective stabilizers and peroxide decomposers only in the presence of labile hydrogens.

The CHP decomposition studies also show a shorter induction period at this temperature for free thiols BHBM, EBHPT and BHBP than for monosulfides. This may be a function of reported ability of thiols to undergo redox reactions with hydroperoxides[78]. Though free radicals are involved in this

$$ROOH + R'SH \longrightarrow RO^{\cdot} + RS^{\cdot} + H_2O$$

process GLC decomposition products in the presence of the above thiols show a Lewis acid catalysed process leading to the formation of phenol and acetone. No α-methyl styrene was detected. The monosulfides TBMP and dibenzyl sulfide too showed the same products of decomposition.





The following compounds were identified as major oxidation products of hindered phenol derivatives BHBM, TBMP, and BHBT, on TLC analysis using R_F values, for authentic samples[73].

3,5 di*tert*-butyl-4-hydroxy benzylalcohol

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

2,6 di*tert*-butyl 1.4 dibenzo quinone.

3,5 3'.5' di*tert* butyl stilbene 4 4' quinone was identified as a minor product of oxidation resulting in the development of colour during the decomposition studies. The formation of stilbene quinone derivative from phenoxy radicals was discussed in Chapter 4 under section 2.a.3. The alkoxy radicals derived from thiol / CHP redox reactions or sulfenic acid /CHP redox reactions[17], demonstrated by Armstrong and Scott[56] on decomposition of hydroperoxides by sulfides can give rise to these phenoxy radicals.

$$RSOH + R'OOH \longrightarrow R\dot{S}O + R\dot{O} + H_2O \quad - \quad (17)$$

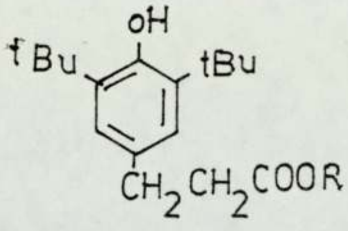
Analysis for antioxidant derivatives after the decomposition reaction show, that major products exist as alcohols, aldehydes and as quinone. These all lack the heteroatom, sulfur of the original compound. The loss of sulfur suggests that SO_2 may be involved in a Lewis acid catalysed decomposition of hydroperoxides by these sulfur derivatives. This has been suggested for similar antioxidant behaviour of thiodipropionates[55].

CHAPTER 5 - POLYMER BOUND STABILIZERS

The choice of stabilizers for a particular polymer and use is governed by such technical considerations as

1. Solubility of the stabilizer in polymer (compatibility).
2. Rate of stabilizer loss from the polymer through exudation, volatisation, leaching or other processes.
3. Initial colour and colour change of stabilized polymer on exposure to light or heat.
4. Toxicity of the stabilizer.
5. Ease of compounding with the polymer.
6. Cost/performance ratio.[IOI]

'Compatibility' of the additive with the polymer is a problem. This term includes such properties as solubility of the additive in polymer, the rate of diffusion of the additive through the polymer. There are several approaches to solving the problem of stabilizer compatibility. Studies by Plant and Scott[IO2], have shown that for the series I, volatility decreased with increase in the molecular weight of the additive, and the activity of the antioxidant also increased for the series. Similarly for ultra violet absorbers a linear dependance of the logrithm of the rate constant (for the loss of stabilizer) was found while increasing the size of the linear aliphatic substituent[96].



I

$R = CH_3$
C_6H_{13}
$C_{12}H_{25}$
$C_{17}H_{35}$

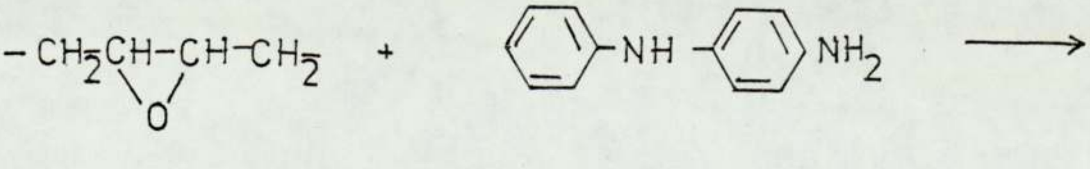
Increase in the molecular weight has been achieved by polymerisation of vinyl stabilizers to give polymeric stabilizers. Alternatively, compatibility can be greatly improved by chemically bonding stabilizers to the polymer chain. It is possible to distinguish two major schools of thoughts, towards achieving these bound systems :-

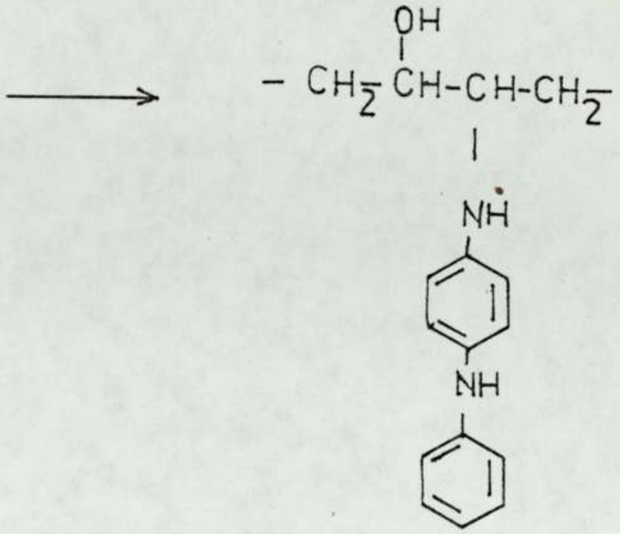
(a) Modification of macromolecules to take up commercially available simple stabilizers.

(b) Introduction of functional groups such as olefinic unsaturation to available stabilizers to be used in normal polymerisation and graft copolymerisations etc.

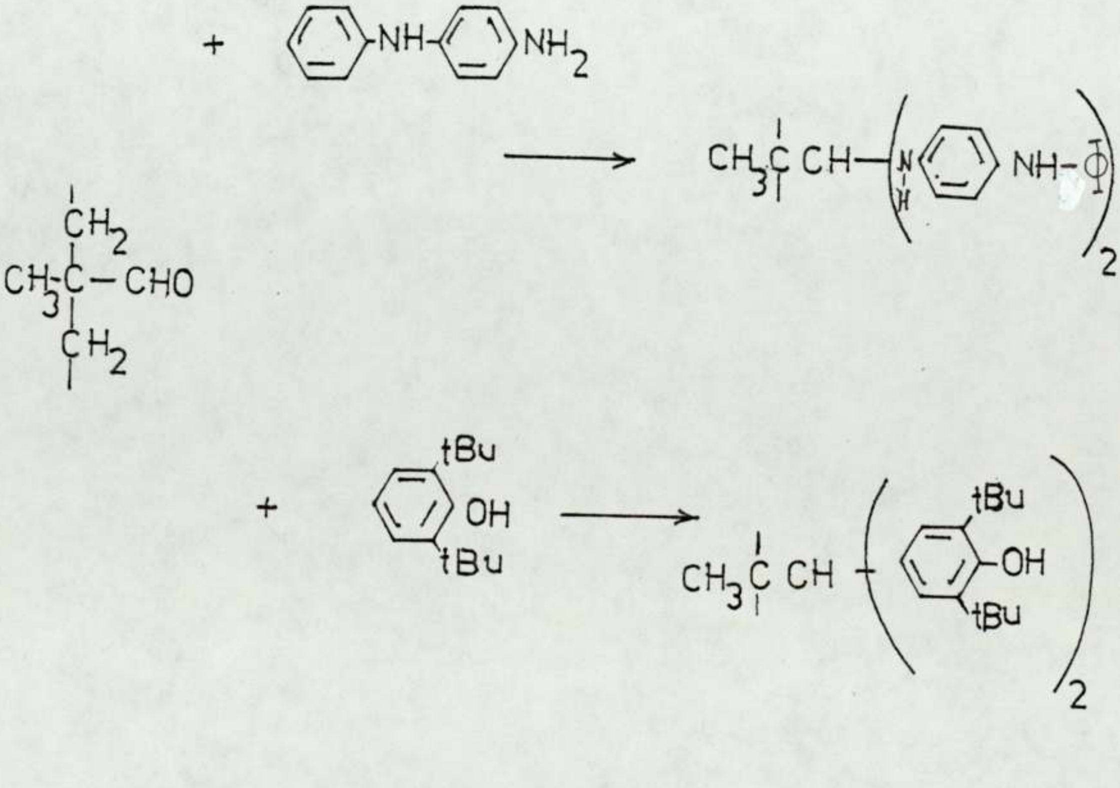
5.1. MODIFICATION OF MACROMOLECULES

(a) Epoxidation of olefinic double bonds - Antioxidants such as p aminodiphenyl amnie[IO3] and 3,5 ditert butyl 4 hydroxy benzylalcohol[IO4] were reacted with epoxidised rubber to form bound systems.

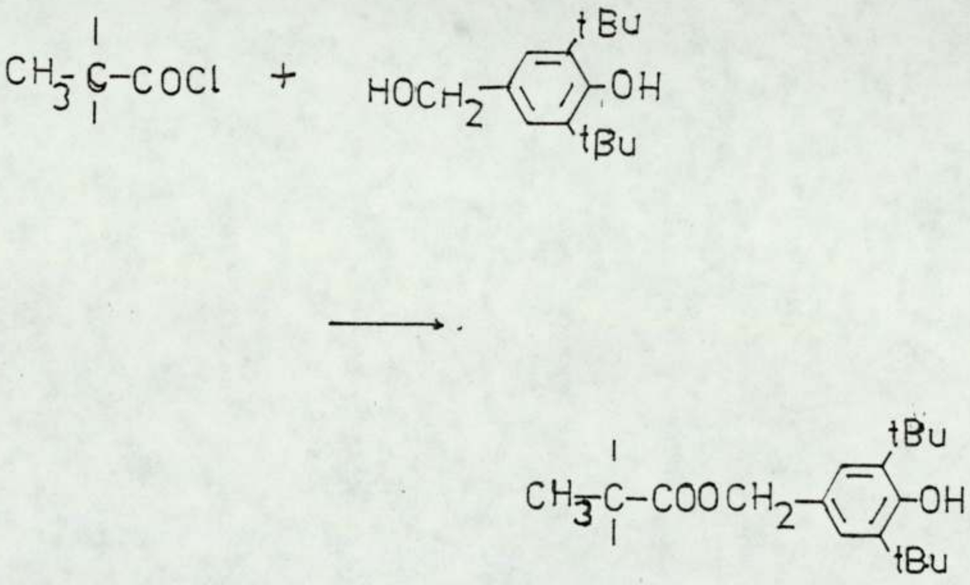




(b) Introduction of aldehydes - Aldehyde groups were introduced by copolymerisation of methacrolein with butadiene,[105].

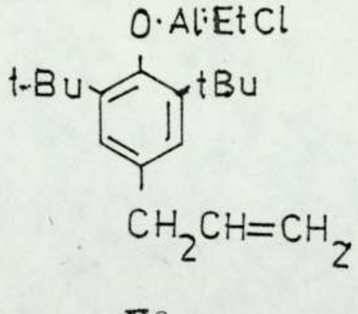


(c) Conversion of carboxylic acids to acid chlorides - Carboxylic acid groups of terpolymers such as acrylonitrile, methacrylic acid butadiene were converted to acid chloride.[I06] The efficiency of such polymer modifications depends particularly on the solubility parmeters of the macromolecules.



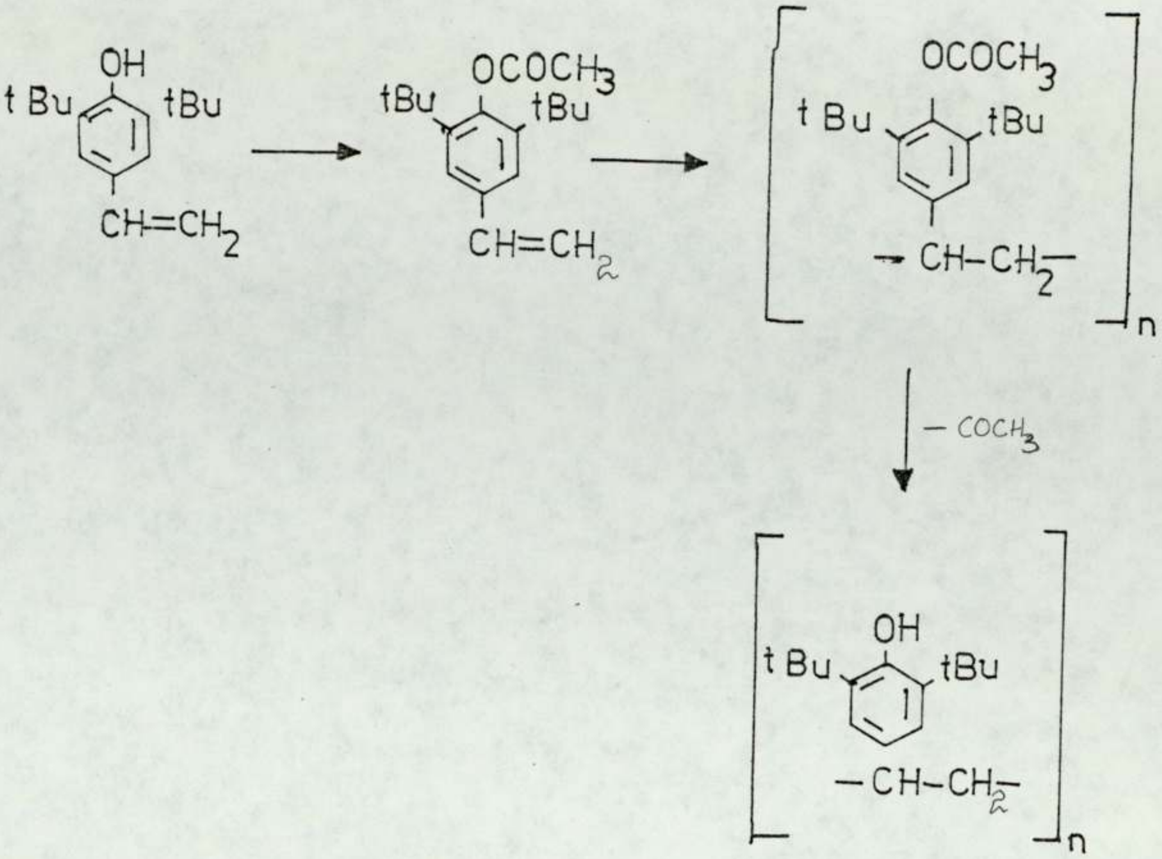
5.2. MODIFICATION OF STABILIZERS

Since the beginning of 1960, the volume of papers and patents, with conflicting claims of efficiencies on copolymerisation of various derivatives of stabilizers, began to grow. The early reports were mainly concerned on the developments in the field of UV absorbers of the type 2-hydroxy benzophenones and 2-hydroxy phenyl benzotriazole, probably due to the lack of inhibitory tendencies of these derivatives towards catalysts used in polymerizations. However, the copolymerisation efficiency of some alkenoxybenzophenones has proved to be wholly inadequate with only 15% actually becoming part of the chain.[107] Adverse effects of polar compounds on Ziegler Natta catalysts have been reported, but Patton and Horeczy[108] claimed copolymerisation of 4(but-3-enyl) 2,6 di*tert*butylphenol with propylene. Even after this discovery Iwata and Sarsaki[109] described a method to eliminate the problem of catalyst deactivation by substituting the phenol (III) with an aluminium compound.

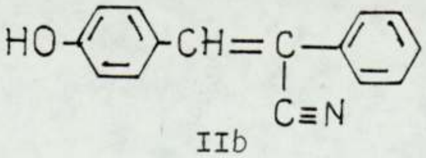


IIa

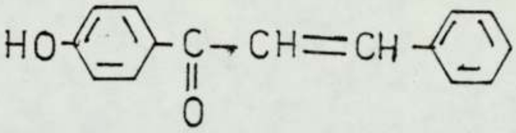
Early attempts to copolymerise hindered phenol derivatives by radical polymerisation were made in the general belief that the hydroxyl group would interfere with the polymerisation process by trapping of radicals. Reported polymerisation of hindered phenolics have involved blocking the hydroxyl group by acylation, followed by polymerisation, and hydrolysis to regain the phenol.[110]



Phenolic monomers of the type IIb and III were incorporated by aqueous copolymerisation, into SBR by Ladd[111] using AZBN as the free radical source. Kleiner[112], reported homopolymerisation and copolymerisation of a series of vinyl derivates of hindered phenols of the ester types (IV) including acrylates methacrylates etc, with styrene, vinyl acetate using high molecular weight peroxides such as lauryl and decanoyl. However, the more common initiators such as hydroperoxides, benzoyl peroxides etc were not able to initiate



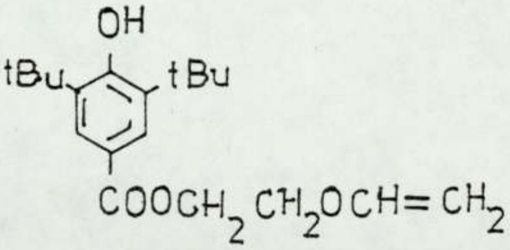
IIb



III

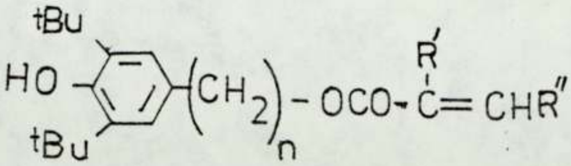
polymerisation because the aryloxy and alkoxy radicals abstracted H-atoms from the antioxidant substituents of the monomers instead of initiating polymerisation.

Kato et. al.,[113,114] also observed that vinyl derivatives of a hindered phenol (IV) can be copolymerised with styrene, maleic anhydride and methyl methacrylate in the presence of AZBN but not with cumene hydroperoxide. Meyer and co-workers,[115] attributed

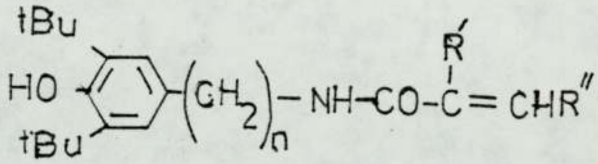


IV

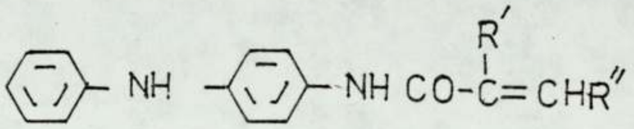
the lack of copolymerisation of hindered phenol derivatives with hydroperoxides and redox initiators, to the presence of impurities in the monomers. They claimed to have copolymerised highly purified monomers of the type VI, VII, VIII , with SBR, and NBR, in high yields, under emulsion polymerisation conditions.



VI



VII



VIII

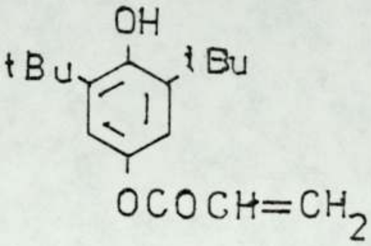
Having achieved these copolymerisations, they arrived at the following conclusions.

(i) Somewhat higher initiator levels and/or increased temperature appears to be required to achieve normal polymerisation rates in the presence of hindered phenol derivatives.

(ii) The only incompatible initiator monomer combinations with amine antioxidants are those of persulfate and benzoyl peroxide.

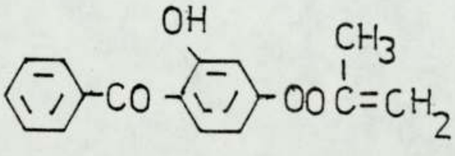
Further proof of copolymerisations of vinyl derivatives of hindered phenols in aqueous emulsions were obtained by Levy[II5] Howarth and co-workers[II6]. They do not mention the purity of antioxidant monomer as a criterion for successful co-polymerisation, in the presence of hydroperoxides and redox systems.

The grafting of polypropylene film with 3,5 ditert butyl 4-hydroxy phenylacrylate IX, has produced a bonded antioxidant system which is non extractable[32]. Graft copolymerisation of these types of monomers in the aqueous phase in natural rubber latex has been attempted with considerable success.[80].

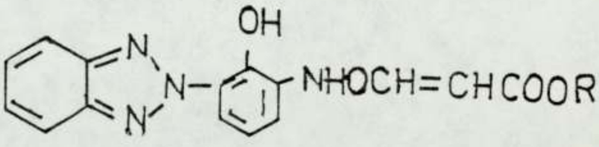


IX

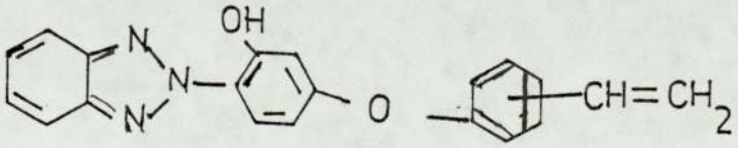
The success of the copolymerisation of substituted 2-hydroxy benzophenones and 2-hydroxy benzotriazoles is well documented. Thus, copolymers of ethylene with [117] X, copolymers of XI, [118] with various monomers, copolymers of XII[119] with styrene etc., are all claimed to be superior to compositions containing conventional UV stabilizers as additives.



X

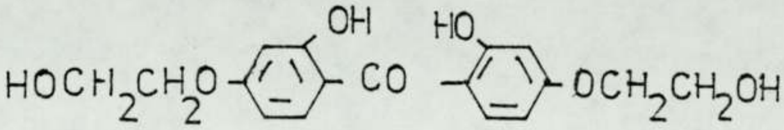


XI



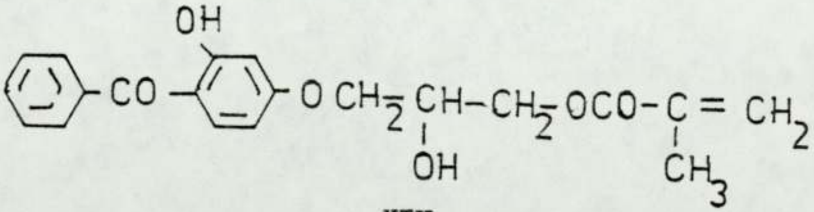
XII

Polyesters or polyurethanes containing xiii as part of the glycol component are also claimed to be unusually resistant to sunlight.[119]



XIII

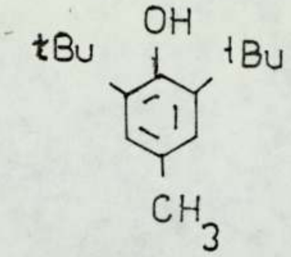
Graft copolymerisations of commercially available polymerisable UV absorber Permasorb MA (xiv) have been carried out successfully on polypropylene films[120]. Acryloxy derivatives of 2-hydroxy benzophenones were successfully graft copolymerised in emulsion graft copolymerisation of ABS using hydroperoxides as initiators[121].

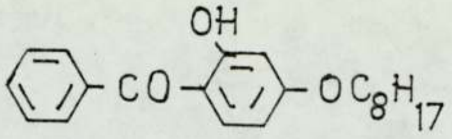


XIV

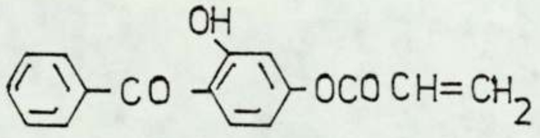
5.3. ATTEMPTED GRAFT COPOLYMERISATION OF ETHYLENICALLY UNSATURATED STABILIZERS WITH ABS

The following stabilizer combination was found to give a considerable induction period as additive on photoxidation of ABS.

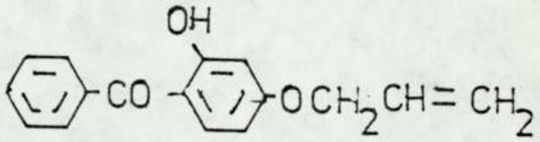




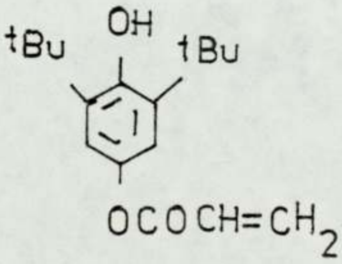
As methods of preparation, and most aspects of copolymerisation behaviour of ethylenically unsaturated stabilizer types illustrated below are known, it was decided to attempt to chemically bind these to ABS macromolecules, in order to obtain desired effect as observed in the above combination as discussed in Chapter 4.



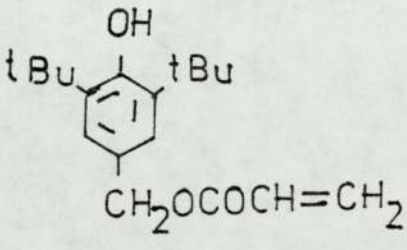
BHBA



BHAA



DBPA



DBBA

5.3.a.1. PROCEDURE

The following formulations were used in the attempted graft polymerisations.

TABLE 14 - FORMULATIONS FOR THE GRAFT COPOLYMERISATION OF ABS IN THE PRESENCE OF VINYL DERIVATIVES OF STABILIZERS

	I	II
Styrene	54.0	54.0
Acrylonitrile	30.0	30.0
Polybutadiene/in latex	15.7	15.7
Dresinate	1.75	-
NaOH	0.036	-
Cerelose	0.7	-
Distilled Water	125.0	125.0
Antioxidant Monomer (DBPA/or DBBA)	1.0	1.0
UV absorber monomer (BHBA/or BHAA)	1.0	1.0
Cumene hydroperoxide	0.8	-
$FESO_4$/TSPP solution	5.0 ml	-
Na Stearate	-	1.75
$K_2S_2O_8$ / 50 ml water	-	0.6
$Na_2S_2O_5$/ 50 ml water	-	0.6
Tert Dodecylmercaptan	0.3	0.5 - 0.6

Polymerisation time - 3 hours

Polymerisation temp. - 58°C

Atmosphere - N_2

Styrene, Acrylonitrile monomers were used without further purification as supplied by the manufacturers.

The stabilizer monomers were dissolved in the flowing phase, which consisted of,

Styrene

Acrylonitrile

Cumene hydroperoxide

for formulation I, and

Styrene

Acrylonitrile

Stabilizer monomer

Dodecylmercaptan

$Na_2S_2O_5$ / 50 ml water

for formulation II.

The latices were coagulated in the usual manner, dried in a vacuum oven and the dried crumb was extracted with hexane to remove unreacted stabilizers. The bound stabilizer contents were estimated by the methods described earlier in Chapter 2.

5.3.a.2. RESULTS

The amounts of bound stabilizer was estimated using calibration curves for each compound (see Chapter 2, section II) and the results are given in Table 15.

TABLE 15 - PERCENTAGE YIELD OF ABS AND BOUND STABILIZER (VINYL) ON GRAFT COPOLYMERISATION

Stabilizer Type	Initial Concentration in phr	Yield of ABS	% Bound CHP/Fe^{+2} System	% Bound S_2O_8/S_2O_5
None	-	95%	-	-
DBPA	1	92%	15	18
DBBA	1	Inhibitory	-	-
BHBA	1	93%	20	20
BHAA	1	82%	Amount small difficult to estimate	

5.3.a.3. ADDUCT FORMATION ON FINAL LATEX - PROCEDURE

ABS latex supplied by Borg Warner Co., containing approximately 33% dry polymer was used in the formulations given over the page.

TABLE 16 - FORMULATION FOR GRAFT COPOLYMERISATION OF VINYL DERIVATIVES OF STABILIZERS

ABS latex 33% / ml	300	300
Stabilizer emulsion /ml (1g/100 ml)	100	100
Cumene hydroperoxide /g	0.5	-
Fe^{+2} / TSPP solution / ml	4	-
$K_2S_2O_8$ / 50 ml water	-	0.3
$Na_2S_2O_5$ / 50 ml water	-	0.05 - 0.1
Cerelose /g	1	-
Atmosphere	N_2	N_2

Graft copolymerisation time - 3 hours

Polymerisation temperatures - (a) 50°C (b) 58°C.

Stabilizer emulsions were prepared by the method described in Chapter 2. The ABS was coagulated in the usual manner dried in a vacuum oven and extracted with hexane, for the evaluation of bound stabilizer.

5.3.a.4. RESULTS

The hexane extracts were analysed for stabilizers by methods described earlier in Chapter 2, and bound stabilizer concentrations were deduced using calibration curves.

TABLE 17 - PERCENTAGE YIELDS OF BOUND VINYL STABILIZERS

Stabilizer Type	Initial Concentration of Stabilizer	% Bound CHP/Fe^{+2} System	% Bound S_2O_8/S_2O_5 System
DBPA	1	17	23
DBBA	1	0.0	0.0
BHBA	1	18	25
BHAA	1	12	20

5.3.a.5. DISCUSSION

The amount of bound stabilizer was too low to give an appreciable protection to the polymer and hence, further tests on ageing behaviour were abandoned. The question arises as to why the previously reported copolymerisation reactions in the presence of antioxidant monomers[II2], and UV absorber monomer derivatives with styrene, [112] butadiene or acrylonitrile and butadiene were successful, whereas the above graft polymerisation reactions with similar monomers gave very poor yields. The basic difference probably lies in the mechanism of copolymerisation and graft copolymerisation reaction.

Thus, a system to be copolymerised, prior to initiation contains ,

(a) aqueous phase(containing very low concentrations of monomer)

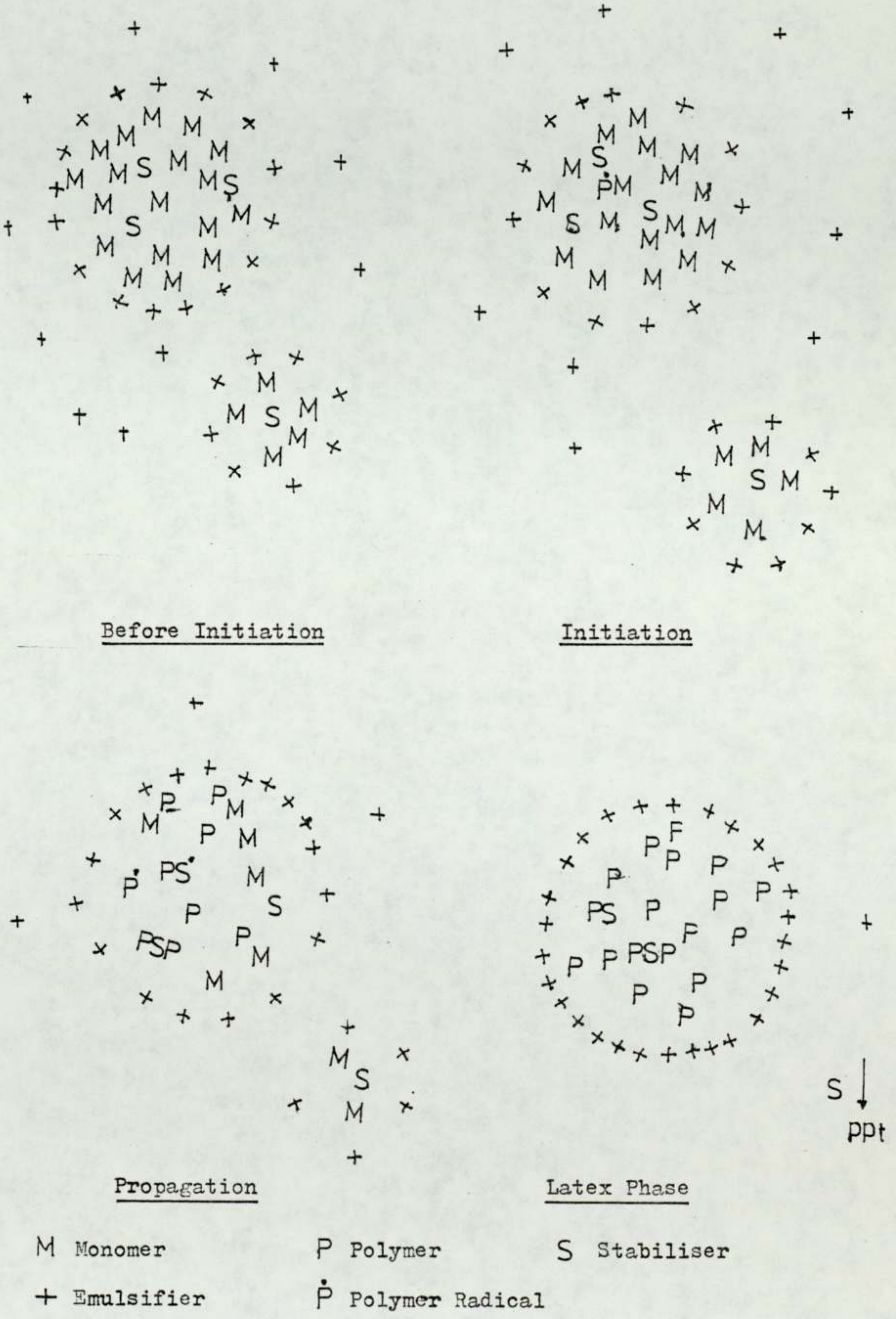
(b) monomer droplets dispersed throughout the aqueous phase

(c) emulsifier micelles containing solubilized monomer.

In an ideal system, the initiation is supposed to take place in the aqueous phase and polymerisation starts when a free radical enters a monomer swollen micelles. The polymerisation proceeds in this micelle and it becomes a latex particle. As the polymer molecule begins to grow, emulsifier is adsorbed (from the aqueous phase) on the surface of this particle and acts as a protective colloid preventing floculation.

Stabilizer monomers are usually charged before initiation of the copolymerisation reaction either as a solution in monomers or dissolved in a polar solvent. Since the monomer-swollen micelles are the largest particles in the reaction mixture ($\sim 1 \mu$), there is every possibility that a major percentage of stabilizer monomer is present in these. Therefore, the chances of stabilizer

Figure 35. Representation of the stages of co-polymerisation in the presence of vinyl derivatives of stabilizsrs.



Before Initiation

Initiation

Propagation

Latex Phase

M Monomer

P Polymer

S Stabiliser

+ Emulsifier

Ṗ Polymer Radical

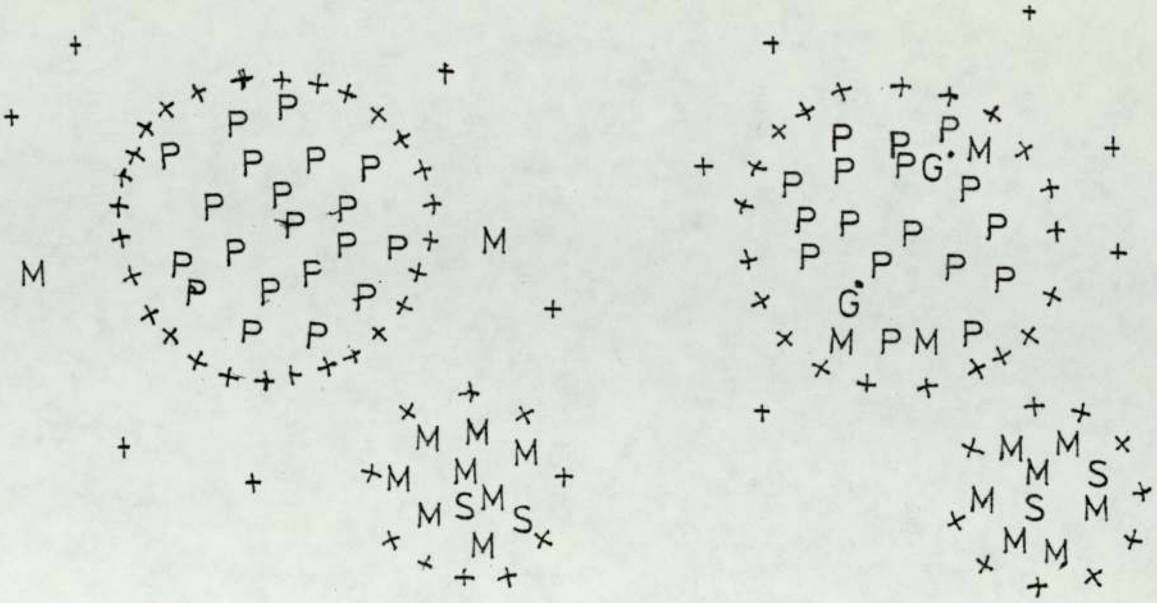
monomer incorporation into the copolymer are high. The chances of stabilizer monomer dissolved in monomer droplets taking part in the copolymerisation reaction, depends on the diffusion through the aqueous phase. These stabilizer derivatives are usually solids at polymerisation temperatures. Therefore, it is possible to assume that the rate of diffusion of stabilizer from the monomer droplets to the reaction centre (the micelles) through the aqueous phase is low. As a result, stabilizer molecules trapped in monomer droplets probably precipitate when the monomer is depleted by its faster rate of diffusion to the reaction centre. Since the percentage of stabilizer in monomer droplets is low under copolymerisation conditions, high yields of bound systems are possible.

A system where graft copolymerisation of vinyl stabilizers are attempted, prior to initiation contains

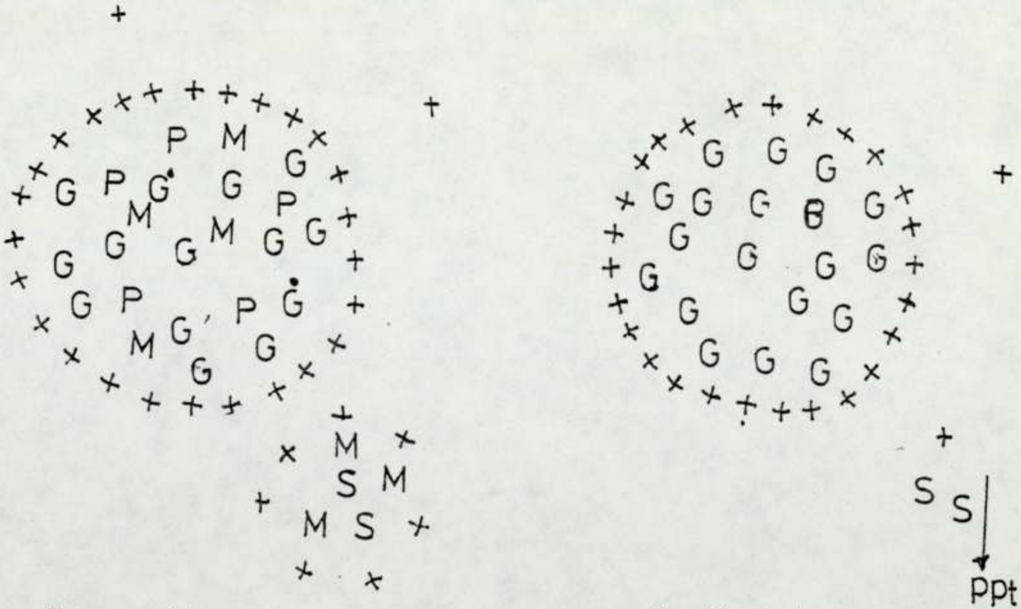
(a) aqueous phase
(b) latex particles protected by emulsifier
(c) unreacted monomers (concentration very low)
(d) emulsifier dispersed in aqueous phase.

The monomers are added dropwise (slowly) during graft copolymerisation reaction. It is possible to assume that in an ideal system initiation takes place in the aqueous phase. The probability

Figure 36. Representation of the stages of graft co-polymerisation of ABS in the presence of vinyl derivatives of stabilizers.



Before Initiation Initiation



Propagation Graft Latex

P Polybutadiene S Stabilizer M Monomer

G Graft Co-polymer + Emulsifier

of radical migration to latex particles from the aqueous phase for the initiation of graft copolymerisation is high due to

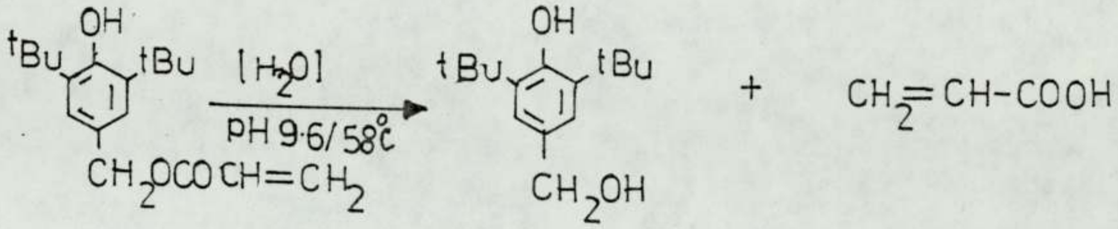
(a) the polarity of latex particles

(b) the amount of latex particles in the system compared to monomer droplets.

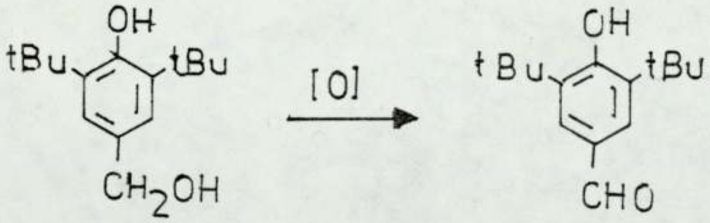
Therefore, the efficiency of graft reaction depends on the rate of diffusion of monomer to latex particles containing the initiating radicals through the aqueous phase.

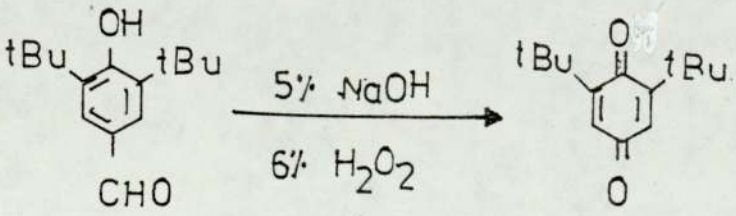
The stabilizer monomers used, were all solids at the polymerisation temperature. Therefore, migration of these molecules through the aqueous phase to the latex particles is probably negligible compared to the more labile monomers styrene and acrylonitrile. acrylonitrile. As a result the stabilizer monomer dissolved in the more labile monomers probably precipitates with the depletion of the latter due to diffusion towards the reaction centre. This relative lack of diffusion of the vinyl stabilizer derivatives through the aqueous is probably the reason for the observed low yield of bound stabilizer during the attempted graft copolymerisation on ABS in latex Table 17.

The inhibition of the graft copolymerisation of ABS in the presence of antioxidant monomer DBBA is probably due to the formation of dibenzoquinone derivate, on hydrolysis followed by oxidation of the monomer.



These reaction conditions are probably adequate for such a hydrolysis of the C - O bonds, weakened by the combined effect of electronegativity of oxygen and the electron affinity of the benzene ring. The benzyl alcohol derivative so formed is probably oxidised to the benzaldehyde first followed by the formation of dibenzoquinone. It was observed,(Chapter 2, section 14), that the benzaldehyde derivative can easily be oxidised to its dibenzoquinone in the presence of hydrogenperoxide in alkali.





The conditions for oxidation are probably present in the reaction mixture, as the latex used has a pH of 9.6 and hydroperoxides are used as initiators.

Thin layer chromatography shows the presence of benzaldehyde, dibenzoquinone as well as stilbene quinone derivatives in the unreacted monomers Table 18. These quinones probably act as the inhibitor in the graft copolymerisation reaction.

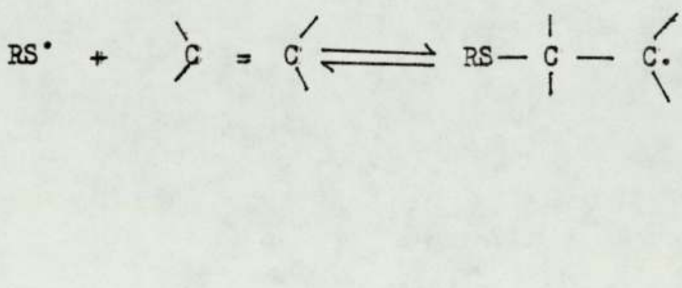
CHAPTER 6 - THE FREE RADICAL ADDITION OF THIOL DERIVATIVES OF STABILIZERS TO ABS

6.1. FREE RADICAL ADDITION OF THIOLS TO UNSATURATED COMPOUNDS

Since the discovery of the anti-Markownckoff addition of thiols to unsaturated compounds in 1905 by Posner,[124] and its much later formulation as a free radical chain reaction[125], this process has been the subject of many reviews[126]. These additions originally had to be initiated either by exposure to UV irradiation or by addition of chemical initiators. Free radical additions nowadays are carried out safely on an industrial scale with ^{60}Co radiation sources[127].

6.1.a.1. MECHANISM OF ADDITION OF THIOLS

The free radical addition of thiols is a typical chain reaction, the initiation product being alkylthiyl or arylthiyl radicals, which subsequently add to unsaturated substrates to form a carbon radical, the second stage being usually reversible

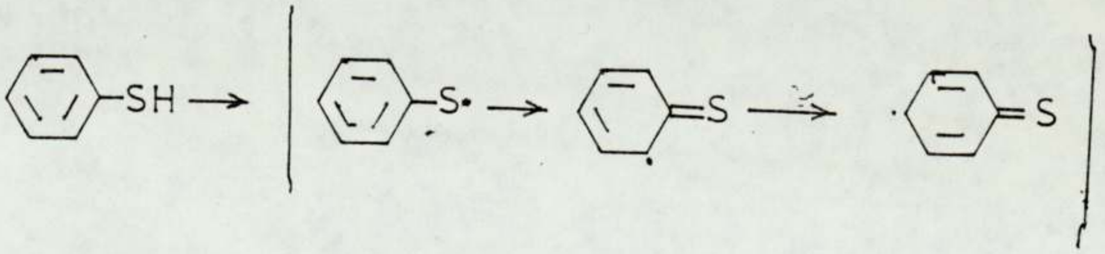


The carbon radical then reacts with a thiol molecule to give the final product and a new thiyl radical, thus propagating the radical chain.

$$RS-C-C\cdot + RSH \longrightarrow RSC-C\text{-}H + RS\cdot$$

Both the addition of the thiyl radicals and the hydrogen transfer are normally exothermic with the result that the overall reaction is fast and has kinetic chain lengths between a few hundred to several thousand[128].

Hydrogen transfer is generally the rate determining step. Since this involves the clevage of a S-H bond, its rate is strongly influenced by the structure of the thiol to be added. Thus, aromatic thiols are better chain transfer agents than aliphatic thiols since in the former case the energy required to break the S-H bond is lowered by resonance stabilization of th thiyl radical formed.[129]



The rate of the hydrogen transfer influences all the variables that depend on the lifetime of the intermediate carbon radical such as

a. the degree of reversibility of the primary reaction (carbon radical formation)

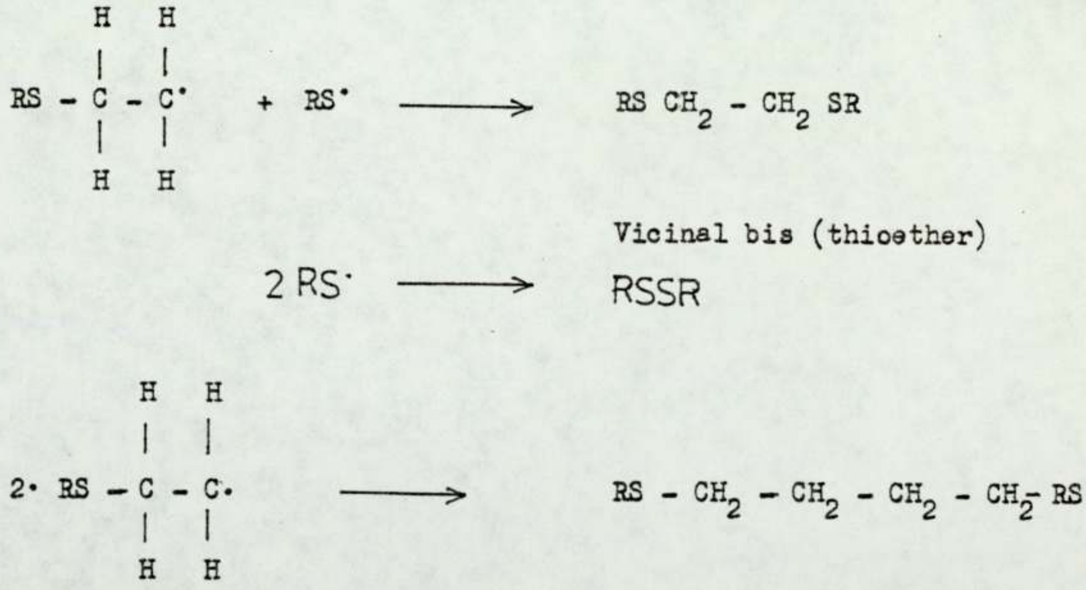
b. the stereochemical course of the overall reaction

c. possible rearrangements of the intermediate carbon radical

d. the extent of telomerization

e. the chain termination reactions.

The termination steps may yield various products.[129]



$$RS-CH_2-CH_2^{\cdot} + RS^{\cdot} \longrightarrow RS\,CH_2-CH_2\,SR$$

Vicinal bis (thioether)

$$2\,RS^{\cdot} \longrightarrow RSSR$$

$$2\cdot RS-CH_2-CH_2\cdot \longrightarrow RS-CH_2-CH_2-CH_2-CH_2-RS$$

Crosslink

Simple thiol adducts with polymers, in general follow the same reaction mechanism. Though various polymers containing olefinic double bonds, undoubtedly react with thiols under appropriate conditions, the present discussion will be limited to diene homopolymers and copolymers including natural rubber (NR), emulsion polymerised polyisoprene PBD, copolymers of butadiene with styrene, and acrylonitrile.

6.1.a.ii. ADDITION OF ALKANE THIOLS TO POLYMERS

The higher alkane thiols have been extensively used as chain transfer agents (modifiers) in emulsion polymerisation with monomers such as butadiene, styrene, acrylonitrile, and chloroprene etc. The transfer reaction represents a competition between the transfer agent and telomerisation of the carbon radical. Telomerisation occurs when on an average the intermediate carbon-radical reacts more rapidly with the unsaturated substrate than by hydrogen abstraction with the chain transferring thiol.

Therefore, it is natural to consider the rate of disappearance of modifier relative to that of free monomer. Some results, for the effect of alkyl chain length upon this disappearance of alkyl mercaptan in butadiene emulsion polymerisation are shown in Figures 37 and 38.[131, 132] For mercaptans having chain lengths up to C_{10} the rate of disappearance is virtually independant of molecular weight but those n.alkyl mercaptans having more than 10 carbon atoms are consumed progressively more slowly as the molecular weight increases. Similar data have been obtained for SBR emulsion polymerisations too.[131] Smith concludes that when the alkyl chain length exceeds 10 carbon atoms, the transfer of mercaptan from monomer droplets through the

Figure 37. Modifier consumption curves for n-alkyl mercaptans of various alkyl chain lengths during persulfate initiated emulsion polymerisation of butadiene at 50°C.[I32]

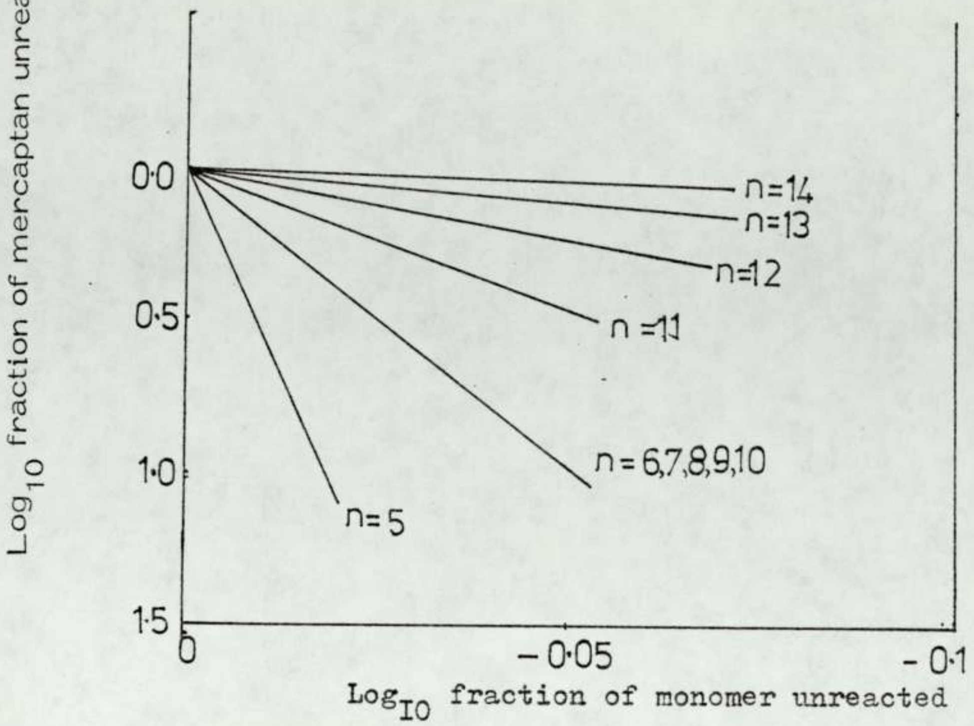
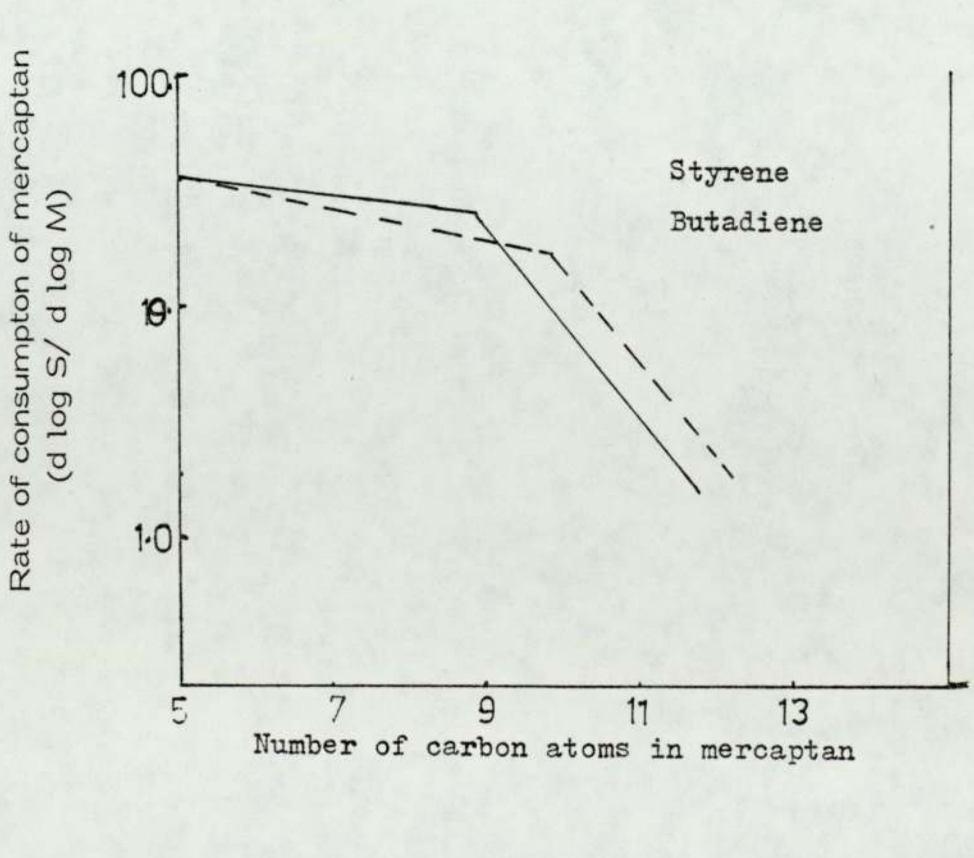


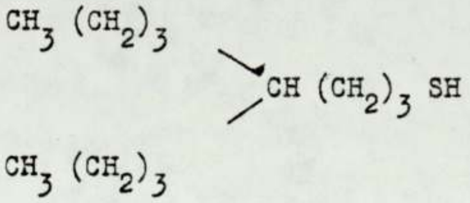
Figure 38. Effect of alkyl chain lengths on rate of consumption of n-alkyl mercaptans relative to rate of polymerisation of monomer[I3I].



aqueous phase to the reaction loci, becomes the rate controlling process. Additional support for this view comes from the observation that the rate of consumption of n-alkyl mercaptans having alkyl groups larger than C_{10} can be increased by raising the pH of the aqueous phase. It appears that in the case of mercaptans of high molecular weight, diffusion of mercaptan through the aqueous phase is supplemented by diffusion of mercaptide ions. These ions by appropriate shift in equilibrium are presumably able to make the corresponding mercaptan available for free radical addition reactions.

$$RS^- + H_2O \rightleftharpoons RSH + OH^-$$

Furthermore, Kolthrof and Harris[133], found that for C_{12} mercaptans where diffusion through the aqueous phase is the rate controlling process, the order of increasing rate of consumption is tertiary $<$ secondary $<$ primary. According to Frank et. al.,[134] the amount of branching in the mercaptan molecule is an important factor in determining diffusion rate, and that the shorter is the longest linear sequence of atoms in the molecule (as in I) the faster the rate of diffusion.



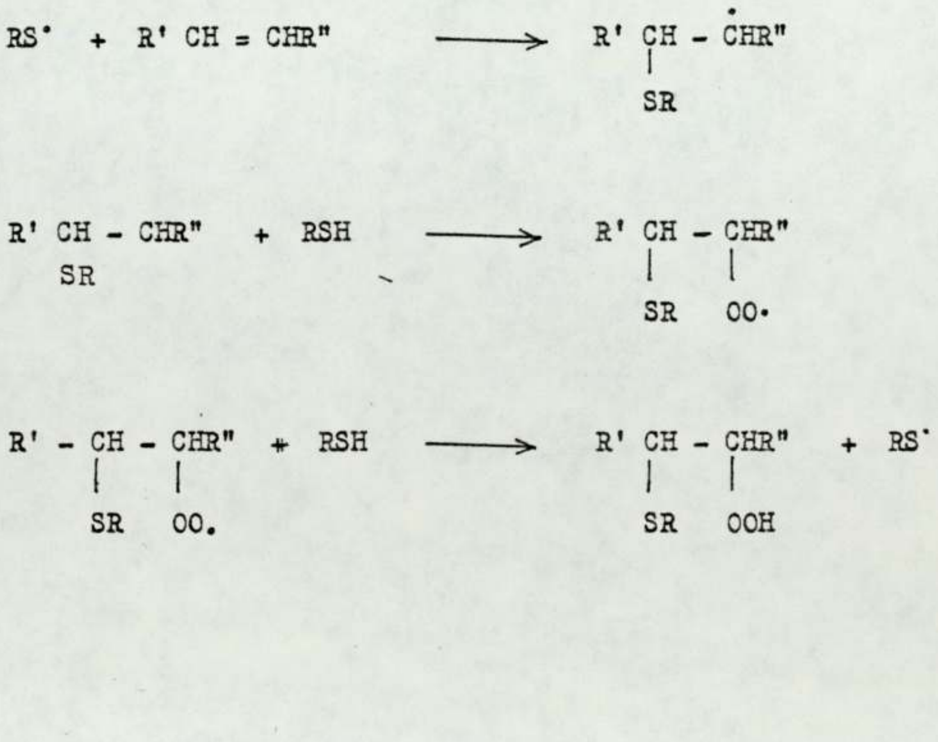
$$(CH_3(CH_2)_3)_2CH(CH_2)_3SH$$

I

$$CH_3(CH_2)_{11}SH$$

II

Adduct formation of alkane thiols with homopolymers and copolymers of butadiene have been carried out both in solution and aqueous emulsion Studies of this kind have included thiols over the range of methyl to octadecyl. Serinuk Banes and Swaney[135], found that the quantity of ethanethiol reacting at 50°C in the absence of oxygen with SBR appear to reach a limiting value of about 25% saturation. Fryling[136], observed that the presence of oxygen during adduct formation of alkane thiols with SBR caused cleavage of polymeric chains resulting in low molecular weight 'syrupy' products. The following mechanism for the formation of these products in the presence of oxygen, has been suggested[130]. The hydroperoxides formed in oxygen are decomposed by reactions similar to that during oxidative degradation of polymers yielding low molecular weight products.



$$RS^{\bullet} + R'\,CH = CHR'' \longrightarrow R'\,\underset{SR}{CH} - \dot{C}HR''$$

$$R'\,\underset{SR}{CH} - CHR'' + RSH \longrightarrow R'\,\underset{SR}{CH} - \underset{OO^{\bullet}}{CHR''}$$

$$R' - \underset{SR}{CH} - \underset{OO.}{CHR''} + RSH \longrightarrow R'\,\underset{SR}{CH} - \underset{OOH}{CHR''} + RS^{\bullet}$$

Subsequent reactions which gives rise to breakdown products have been described in Chapter 4,

It appears that all primary alkane thiols up to dodecyl, react sufficiently to yield highly saturated adducts. Little work has been reported on the evaluation of the many possible adducts and their properties, except for those prepared with methanethiol, the oxygen absorbtion curves for PBD - CH_3SH adduct is given in Figure 8 .[26]

6.1.a.3. INTRODUCTION OF FUNCTIONAL GROUPS AND ISOMERISATION OF DOUBLE BONDS BY THIOLS

Adduct formation by thiols, have been used to introduce functional groups to unsaturated polymers. Thus, Marvel and co workers[137], used thiol adducts to introduce polar groups such as $C \equiv N$, OH, thioesters and COOH to polybutadiene. Both Serniuk [138] and Brown[139], have reported the introduction of COOH groups by the addition of thioglycollic acid and other mercaptoacids to copolymers of butadiene using hydroperoxides as initiators. Similarly, ethyl thioglycollate was found to add to natural rubber to saturate 13.6% of double bonds in seven days at 0°C in the presence of p.menthane hydroperoxide as the initiator.[140]

Thiol derivatives especially those from relatively stable thiyl radicals such as thiophenol, thio benzoic acid, and napthyl analogues have been found to cause isomerisation of double bonds of polymers with low level of adduct formation. Golub[141], converted 14 PBD having high cis content to an equilibrium mixture of cis-trans forms by thionapthol.

For simple unsaturated compounds such as trans and cis piperylene, the isomerisation mechanism is believed to be through an allyl radical by resonance.[142] The mechanism of isomerisation of double bonds in polymers is less understood. It could probably be due to a loss of allylic hydrogen in cis 14 polybutadiene, enabling a three centre distribution of electron by resonance as for piperylene. The low yields of adducts could be adduced as further evidence of transfer of an allylic hydrogen, during the reaction, resulting in the isomerisation of double bonds.

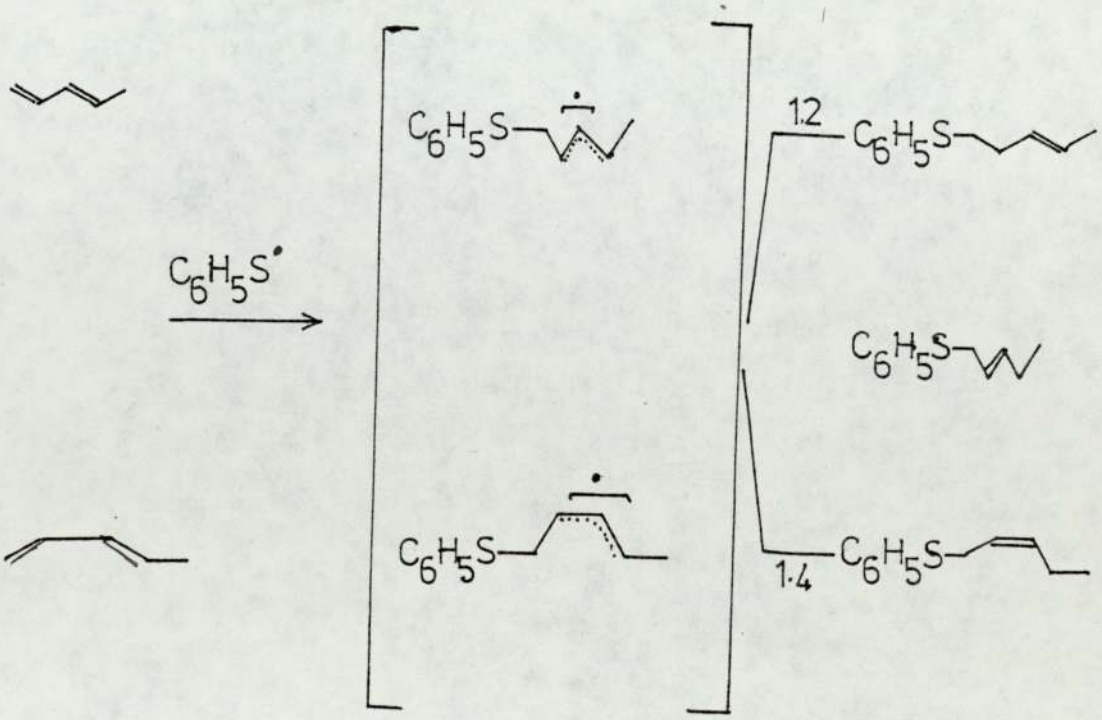
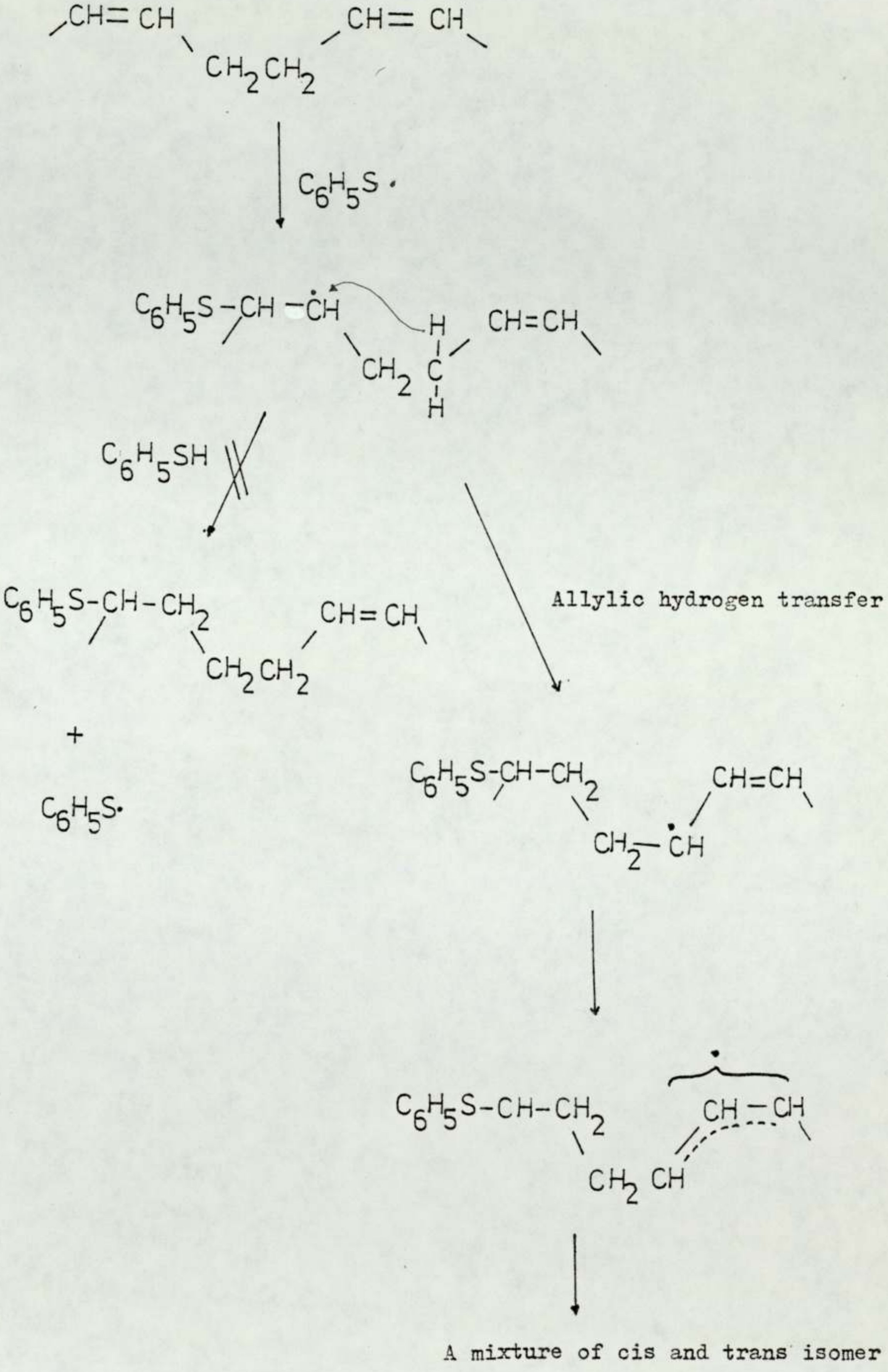
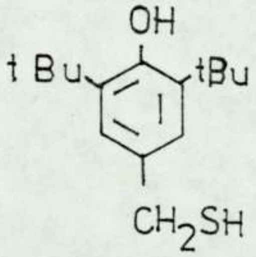


Figure 39. Mechanism of isomerisation of double bonds in PBD by aryl thols.



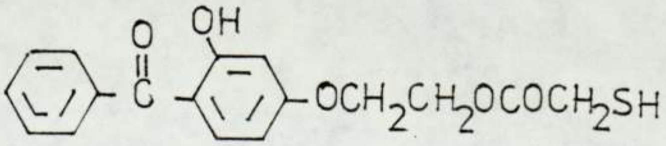
6.1.a.4. INTRODUCTION OF STABILIZERS BY THIOL GROUPS

An entirely novel approach to obtain bound antioxidants was processed successfully by Fernando.[143] 3,5 di*tert* butyl 4 hydroxybenzylmercaptan (III) was added across the double bonds of natural rubber, in solution and in latex using AZBN as initiator. The use of tert.butylhydroperoxide-polyamine redox system has been shown to increase the yields of adduct formation up to 70% and lower the temperature of the reaction considerably.[144] Furthermore, a mercapto derivative of a 2 hydroxy benzophenone (iv) was added across the double bonds of polybutadiene in latex using $K_2S_2O_8$ as the initiator.[145]



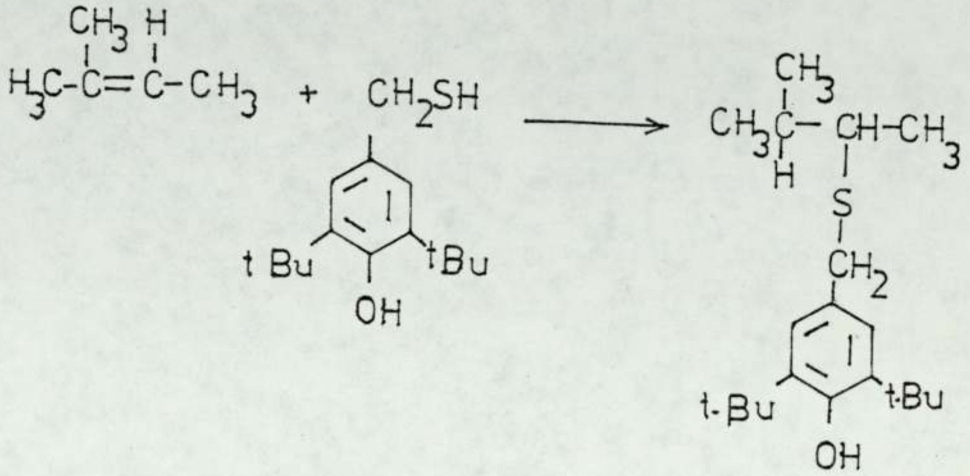
III

Model compound studies show that the thiol stabilizers, like the simple thiols do not follow Markownicoff's rule during adduct formation. Thus, 2 methyl but-2;ene and 3,5 di*tert* butyl 4 hydroxy benzylmercaptan (III) gave a saturated adduct in the presence of AZBN as the initiator[143].



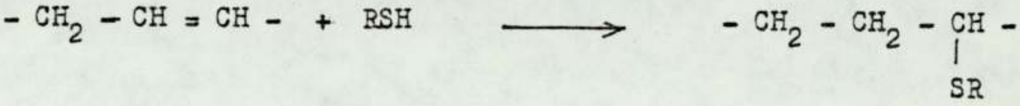
IV

The physical and chemical properties of 'adduct natural rubber' containing 1 phr have been found to be uneffected by the presence of bound stabilizer derivative.[143, 144].

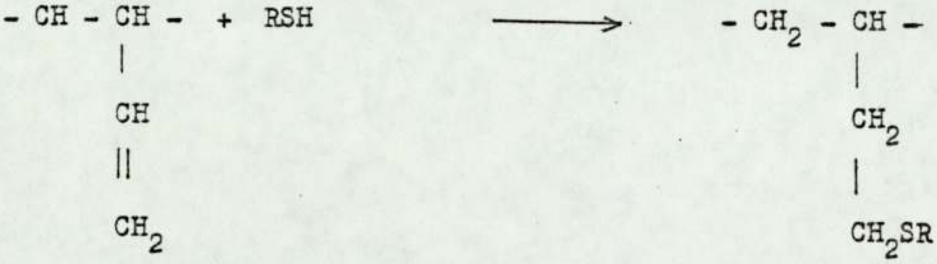


It was established (Chapter 4) that the sulfur containing stabilizer derivatives TBMP and EBHPT offered a better resistance towards oxidative degradation of ABS, than their counterparts. Synergistic effects too were observed when these two stabilizers were combined. Furthermore, attempts to obtain bound system of stabilizers in ABS using vinyl types of derivates of conventional stabilizers failed to introduce acceptable amounts for effective stabilization of the polymer (Chapter 5).

As a consequence of these studies and from the evidence of the above survey of simple thiol adducts of polymers, the use of mercapto derivatives of stabilizers to obtain bound systems in ABS appear to be a better proposition. The aim of the project was to attempt the adduct formation of mercapto derivatives BHBM and EBHPT with the double bonds offered by the polybutadiene component of ABS. These double bonds were found to remain unaffected by the graft copolymerisation reaction, since only the allylic positions are involved in the latter process. Therefore, it is possible to assume that the following reactions, to take place during the adduct formation of thiols with polybutadiene component of ABS.



$$- CH_2 - CH = CH - + RSH \longrightarrow - CH_2 - CH_2 - \underset{\displaystyle SR}{\underset{|}{CH}} - \qquad (1)$$



$$- CH - \begin{array}{c} CH \\ | \\ CH \\ \| \\ CH_2 \end{array} - + RSH \longrightarrow - CH_2 - \begin{array}{c} CH \\ | \\ CH_2 \\ | \\ CH_2SR \end{array} - \qquad (2)$$

This addition reaction can be attempted during the following stages :-

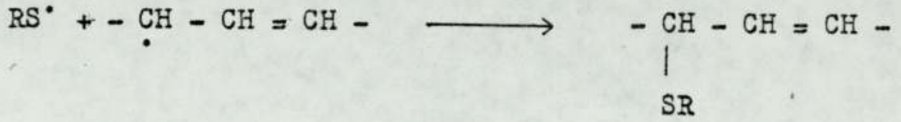
a) Graft copolymerisation of ABS

b) On ABS latex.

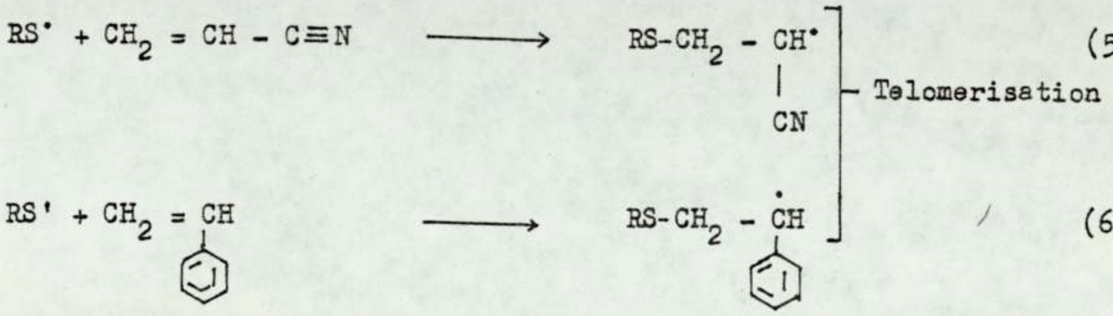
The stabilizer derivatives can be introduced during the graft copolymerisation of ABS as a solution in the monomers. This is an obvious advantage as the introduction of the stabilizers to ABS latex for the reaction (b) necessitates the formation of a dispersion of the stabilizers.

The following side reactions may interfere with the adduct formation of thiols during the graft copolymerisation of ABS.

$$RS^{\bullet} + -CH_2 - CH = CH - \longrightarrow -\underset{\bullet}{CH} - CH = CH - + RSH \qquad (3)$$



$$RS^{\bullet} + -\underset{\bullet}{CH} - CH = CH - \longrightarrow -\underset{\displaystyle SR}{\underset{|}{CH}} - CH = CH - \qquad (4)$$



$$RS^{\bullet} + CH_2 = CH - C\equiv N \longrightarrow RS-CH_2 - \underset{\displaystyle CN}{\underset{|}{CH^{\bullet}}} \qquad (5)$$

$$RS' + CH_2 = CH(C_6H_5) \longrightarrow RS-CH_2 - \dot{C}H(C_6H_5) \qquad (6)$$

The reactions 5 and 6 could well influence the physical properties of the final products by reducing the number of graft points in the system. The extent of such reactions will depend on a number of factors including the rate of addition reaction, reactivity ratios of the monomers, rates of diffusion of the monomers and the thiols through the aqueous phase, nature of the redox system etc.

On the other hand, the addition reactions of thiol stabilizers with ABS in latex should proceed without much interference due to the decrease in the probabilities of side reactions described above, as a result of;

a) the reduction in number of allylic hydrogen sites due to graft formation

b) steric hinderence at the tertiary allylic hydrogen sites for the abstraction of hydrogen by RS' radicals

c) the presence of only residual amounts of unreacted monomers in the system.

6.2. ATTEMPTED ADDUCT FORMATION WITH 3,5 DI TERT BUTYL 4 HYDROXY BENZYLMERCAPTAN (BHBM).

6.2.a. PROCEDURE

Both formulations, the commercial Borg Warner, and laboratory method of preparation as illustrated in Chapters 2 and 3, were used for the attempted graft copolymerisation. The antioxidant (to give a concentration of 1 parts per hundred ABS) was dissolved in the monomer solution styrene and acrylonitrile, for the reaction. The chain transfer agent commonly referred to as the modifier, tert dodecyl mercaptan was excluded from both formulations. Experiments were conducted in an atmosphere of N_2.

6.2.b. RESULTS

The attempted graft copolymerisations were unsuccessful. The unreacted monomer and the polybutadiene latex separated into two layers after the reaction. The following compounds were identified as oxidation products of the antioxidant BHBM, by thin layer chromatographic analysis of the monomer phase of the reaction mixture by comparing with the R_F values of authentic samples. Table 18.

TABLE 18 - R_F VALUES OF OXIDATION PRODUCTS ON A SILICA GEL LAYER

COMPOUND	MOBILE PHASE M_1 Heptane/ Benzene	M_2 Benzene	Detection
2,d di*tert* butyl 4 methylphenol	0.56	-	a
3,5,3'5' tretra *tert*.butyl Stilbene 4,4' quinone	0.32	0.43	a,b
2,6 di *tert* butyl 1,4 benzoquinone	0.17	-	a,c
3,5 di *tert* butyl 4 hydroxybenzylalcohol	-	0.28	a
3,5 di*tert* butyl 4 hydroxybenzaldehyde	-	0.18	a,c

Mobile phases

M_1, heptane / benzene (1:1)

M_2, benzene only.

a) Solution of 8gm of $KMnO_4$ in 500 ml of water + 1.5 ml of conc H_2SO_4, excess of reagent carefully removed with water.

b) Compound visible.

c) 0.4% solution of 2,4 dinitrophenyl hydrazine in 2N HCl.[73]

The compounds identified from the reaction mixture were

a) 2,6 ditert butyl 1,4 benzoquinone.

b) 3,5 ditert butyl 4 hydroxy benzylalcohol.

c) 3,5 ditert butyl 4 hydroxybenzaldehyde.

d) 3,5 3'5' tretra tert.butyl stilbene 4 4'quinone.

Steam distillation of the reaction mixture yielded approximately 85% of the monomers used in the reaction, for both formulations.

6.3. ATTEMPTED ADDUCT FORMATION WITH 4-BENZOYL 3-HYDROXYPHENYL O-ETHYL THIOGLYCOLLATE. (EBHPT)

6.3.a. PROCEDURE

Both formulations for the preparation of ABS were used for the attempted adduct formation. The UV stabilizer was dissolved in the monomers for the reaction at a concentration to give one part per hundred in the resulting ABS. The chain transfer agent, tert dodecylmercaptan was excluded from both formulations.

6.3.b. RESULTS

Steam distillation for unreacted monomers in the resulting latex showed a reduction in the yield of ABS from 95-98% to 82%. The bound stabilizer content measured by the method described in Chapter 2 showed 32 - 35% being retained in the polymer after extraction with hexane.

6.4. ATTEMPTED ADDUCT FORMATION OF 3,5 DITERT BUTYL 4 HYDROXY BENZYLMERCAPTAN WITH ABS IN LATEX

6.4.a. PROCEDURE

Borg-Warner 'ABS' latex and ABS latex made in the laboratory by the method described in Chapter 3, were used in the two experiments conducted. The antioxidant BHBM emulsion was made by the procedure described in Chapter 2. The formulations are illustrated in the following table, Table 19.

The following materials were added in aliquots during the first half of the reaction :-

Antioxidant emulsion

Cumene hydroperoxide

$Na_2S_2O_5$ solution.

The latex was acid coagulated and the dried crumb was soxlet extracted with hexane for the estimation of bound stabilizer content.

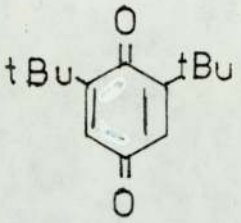
TABLE 19 - FORMULATIONS FOR ATTEMPTED ADDUCT FORMATION OF BHBM WITH ABS IN LATEX

ABS latex (33% dry ABS) (ml)	300.0	300.0
Antioxidant emulsion (1 phr) (ml)	100.0	100.0
Cumene hydroperoxide (g) /25 ml of water	0.5	-
Glucose in 10 ml of water in gm	1	-
Fe^{+2}/ TSPP Solution (ml)	4	-
$K_2S_2O_8$ / in 50 ml of water	-	0.2
$Na_2S_2O_5$ / in 50 ml of water	-	0.2

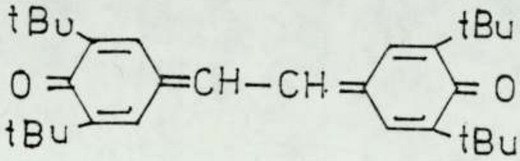
Reaction temperature °C	a) 50	b) 57
Reaction time in hours	a) 4	b) 3

6.4.b. RESULTS

The amount of bound BHBM in ABS was found to be very small (less than 10%). The latices, after the reaction, developed a yellow surface film on standing. Analysis of an ether extract of this film by thin layer chromatography showed the presence of the following compounds (Table 18).



2,6 di<u>tert</u> butylbenzoquinone



3,5 3',5' tetra tert butyl stibenequinone.

Oven ageing of unextracted ABS films offered very little resistance towards thermal oxidative degradation (embrittlement time 65 hours in air at 100°C).

6.5. ADDUCT FORMATION OF 4 BENZOYL 3 HYDROXYPHENYL OETHYL THIO-GLYCOLLATE (EBHPT) WITH ABS IN LATEX

6.5.a. PROCEDURE

The procedure was similar to 6.4.a. except for the following :-

Reaction temperature °C	a)	45	b)	50
Reaction time in hours	a)	6	b)	$3\frac{1}{2}$

UV stabilizer emulsion 1 gm in 100 ml.

The material was extracted with hexane for the estimation of bound UV stabilizer.

6.5.b. RESULTS

The percentage of bound UV stabilizer (EBHPT) obtained under the different reaction conditions are shown in Table 20.

TABLE 20 - ESTIMATED BOUND EBHPT UNDER THE DIFFERENT EXPERIMENTAL CONDITIONS

PERCENTAGE OF BOUND UV STABILIZER	REACTION TEMPERATURE / TIME	REDOX SYSTEM
48	a/a	CHP/Fe^{+2}
54	a/a	S_2O_8/S_2O_5
53	b/b	CHP/Fe^{+2}
58	b/b	S_2O_8/S_2O_5

6.5.c. MODIFICATION OF PROCEDURE 6.5.a. FOR ADDUCT FORMATION OF EBHPT IN ABS LATEX

Changing the reaction conditions and the concentrations of initiator systems of the above procedure did not result in a marked increase in bound UV stabilizer in the system. Therefore, the following modification was tried for reasons that will be discussed later in the Chapter.

6.5.c.1. PROCEDURE

The formulations were as in 6.5.a., but in place of the UV stabilizer emulsion, sodium salt of EBHPT solution (I) was used. This was added to ABS latex and pH of the resulting mixture was adjusted to 9.5 - 9.6 by adding dilute acetic acid, before initiation of the reaction. The latex was acid coagulated, dried in a vacuum oven at 55°C to a constant weight. The material was extracted with hexane for estimation of bound stabilizer content.

6.5.c.2. RESULTS

TABLE 21 - AMOUNT OF BOUND EBHPT WHEN USED AS ITS SODIUM SALT

PERCENTAGE OF BOUND EBHPT	REACTION TEMPERATURE / TIME AS IN 6.5.a.	REDOX SYSTEM AS IN 6.4.a.
55	a/a	CHP/Fe^{+2}
58	a/a	S_2O_8/S_2O_5
63	b/b	CHP/Fe^{+2}
65	b/b	S_2O_8/S_2O_5

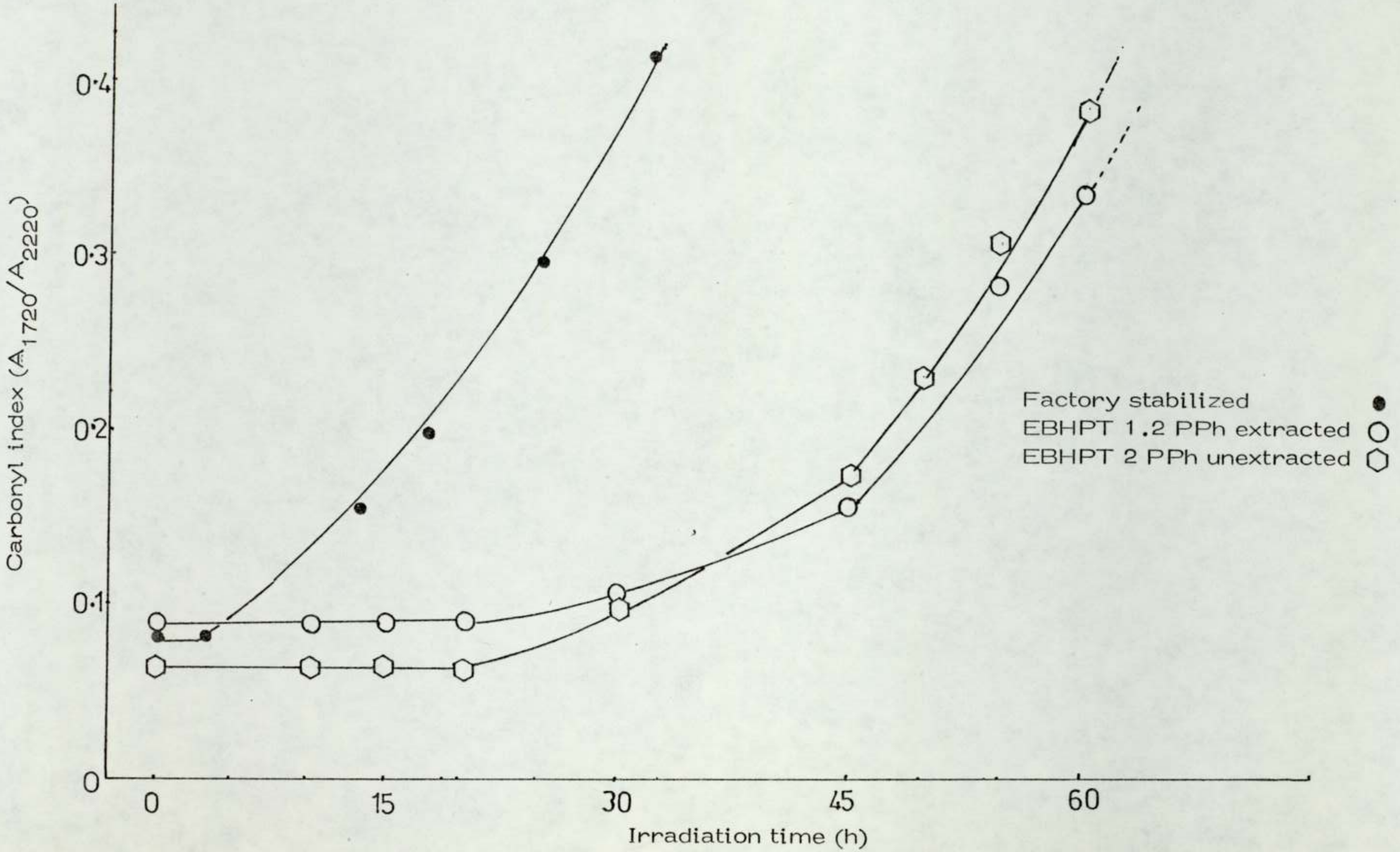
The latices or the dry ABS obtained after the reaction did not show any discolouration on adduct formation with the sodium salt of EBHPT.

Photoxidatation of ABS films containing approximately 60% of the bound UV stabilizer were followed by the development of carbonyl absorbtion using infra-red spectrometry. A typical curve obtained is illustrated in Figure 40. The accompanying Table 22, gives the induction period and embrittlement times at four different concentrations of the UV stabilizer, before and after extraction of ABS.

TABLE 22 - INDUCTION PERIOD AND EMBRITTLEMENT TIMES ON PHOTOXIDATION OF ABS FILMS CONTAINING BOUND EBHPT

Initial Concentration (Before extraction) in gms	Concentration of bound EBHPT (After extraction) in gms	Induction Period in hours		Embrittlement time in hours	
		Before extraction	After extraction	Before extraction	After extraction
Control (unstabilized)	-	2	2	23	23
1	0.6	20	17	52	48
1.25	0.8	23	22	53	51
1.50	0.9	25	23	57	53
2.0	1.20	27	25	62	60
Factory stabilized (Cycolac 211)	-	6	2	30	24

Figure 40 Development of carbonyl absorption on uv exposure of ABS pressed films (refer table 22)



6.6. EFFECT OF 2,6 DITERT.BUTYLPHENOL DERIVATIVES ON THE GRAFT COPOLYMERISATION OF ABS

The possibility of addition of thiol derivatives across the double bonds of PBD component of ABS was discussed at the beginning of this Chapter. The implications of possible telomerisation in the presence of thiols were also discussed. The above experiments show very little hinderance to graft copolymerisation of ABS in the presence of mercapto derivative of 2-hydroxy benzophenone, EBHPT. The phenolic antioxidant derivative (BHBM) on the otherhand, shows complete inhibition of graft copolymerisation of ABS as well as failure to react with the available double bonds of PBD component of ABS in latex. Furthermore, similar behaviour was observed in the attempted graft copolymerisation of 3,5 di*tert* butyl 4 hydroxy benzylacrylate (DBBA), Chapter 5, section 3.

This is probably due to the combined effect of the phenolic hydroxyl group and the electronegative atom linking the benzyl group with the rest of the molecule. In order to investigate the possibility of such an effect, graft copolymerisation of ABS was conducted in the presence of 2,6 di*tert* butylphenol derivatives in the usual manner.

6.6.a. PROCEDURE

Graft copolymerisation of ABS was conducted using the procedure described under section 2,a of this Chapter, to determine the effect of the chemical structure of the hindered phenol derivatives on the grafting reaction.

6.6.b. RESULTS

The reaction mixtures were steam distilled to ascess the extent of graft copolymerisation in the presence of these derivatives. The graft copolymerisation was attempted in the presence of redox systems, a) cumene hydroperoxide/Fe^{+2}, and b) $K_2S_2O_8/Na_2S_2O_5$.

TABLE 23 - EFFECT OF GRAFT COPOLYMERISATION OF ABS IN THE presence VARIOUS ADDITIVES

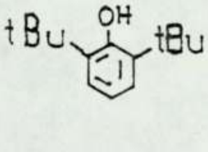
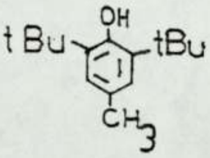
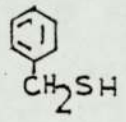
Compound	Structure	Percentage of monomer unreacted (steam distillation	
		CHP/Fe^{+2}	S_2O_8/S_2O_5
1 Control (no additive	-	3	3
2 2,6 di*tert* butyl phenol		4	5
3 2,6 di*tert* butyl 4 methylphenol		5	5
4 Benzylmercaptan		3	3
5 Benzyl mercaptan + 2,6 di*tert* butyl 4 methylphenol		3	3

TABLE 23 - Continued....

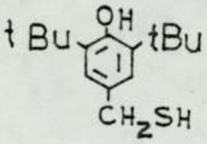
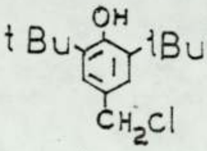
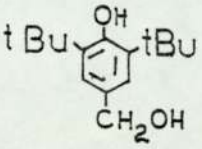
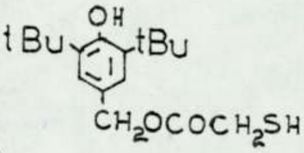
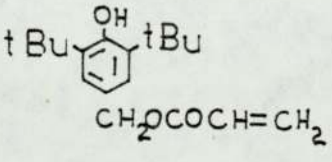
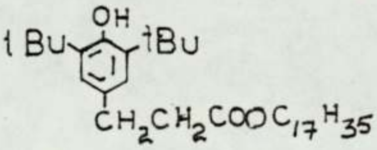
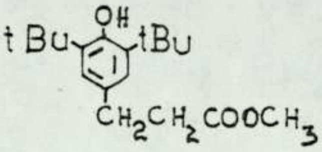
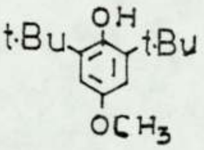
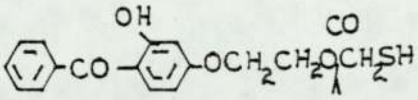
Compound	Structure	Percentage of monomer unreacted (steam distilled	
		CHP/Fe^{+2}	S_2O_8/S_2O_5
6 BHBM		80	80
7 3,5 di*tert* butyl 4 hydroxy benzyl-chloride		80	72
8 3,5 di*tert* butyl 4-hydroxy benzyl-alcohol		80	80
9 3,5 di*tert* butyl 4 hydroxy benzyl-thioglycollate (BHBG)		70	75
10 3,5 di*tert* butyl 4-hydroxy benzyl-acrylate (DBBA)		60	55
11 Irganox 1076		5	5

TABLE 23 - Continued....

Compound	Structure	Percentage of monomer unreacted (steam distillation	
		CHP/Fe^{+2}	S_2O_8/S_2O_5
12 Irganox 1300		5	5
13 Thioglycollic acid (sodium salt)	$HSCH_2COONa$	3	3
14 Toponol 354		15	15
15 EBHPT		12	12

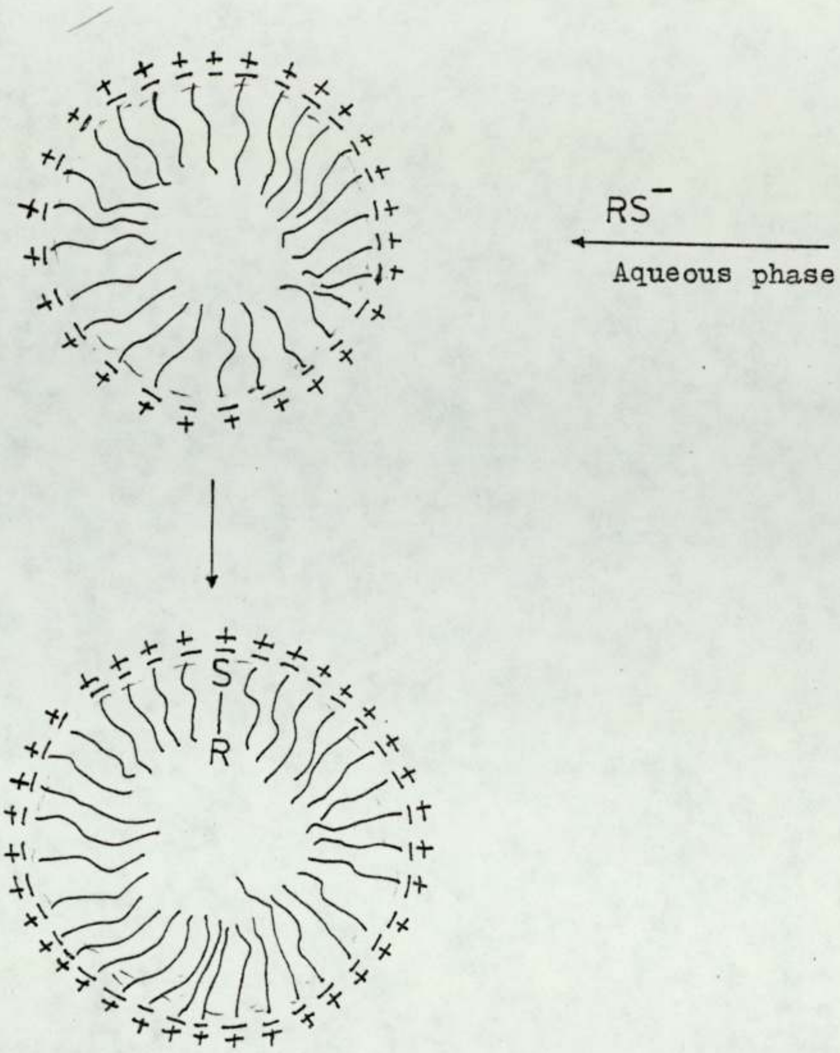
6.7. DISCUSSION

The striking feature of the graft copolymerisation in the presence of the two stabilizer derivatives BHBM and EBHPT is the pronounced inhibitory effect of the hindered phenol derivative in the presence of both redox systems. The loss of 12% of ABS in the presence of EBHPT (Table 23 - 15) is probably due to a combined effect of the phenolic hydroxy and the thiol SH groups on the free radical propagation reactions. When ABS latex was used as the substrate for the adduct reaction the sodium salt of EBHPT gave better yields than its emulsion. These results can be correlated to the work carried out by Smith[131] on the influence of pH upon the rate of disappearance of high molecular weight alkyl mercaptan chain transfer agents in emulsion polymerisation. The acid dissociation constant of thiols are in the range of 10^{-11}.

$$RS^- + H_2O \rightleftharpoons RSH + OH^-$$

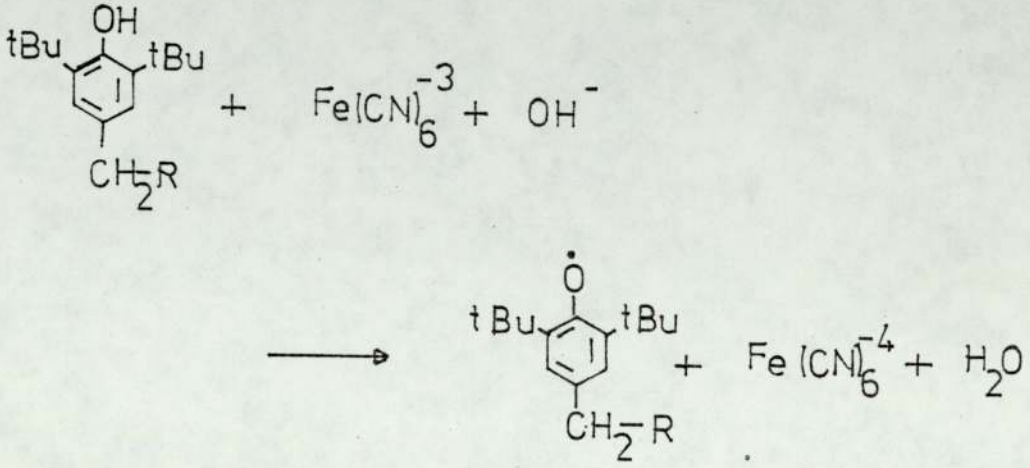
The RS^- anion in equilibrium below a pH of 11 offers very little more resistance to diffusion through the aqueous phase than the thiol itself.. Having diffused through the aqueous phase, the change on the anion could help the radical to penetrate the electrical double layer surrounding the polymer latex particle.

As long as the pH remains below the acid dissociation constant of the thiol the shift in the equilibrium can produce thiol SH necessary for formation of free radicals RS$^\bullet$ for the adduct reactions

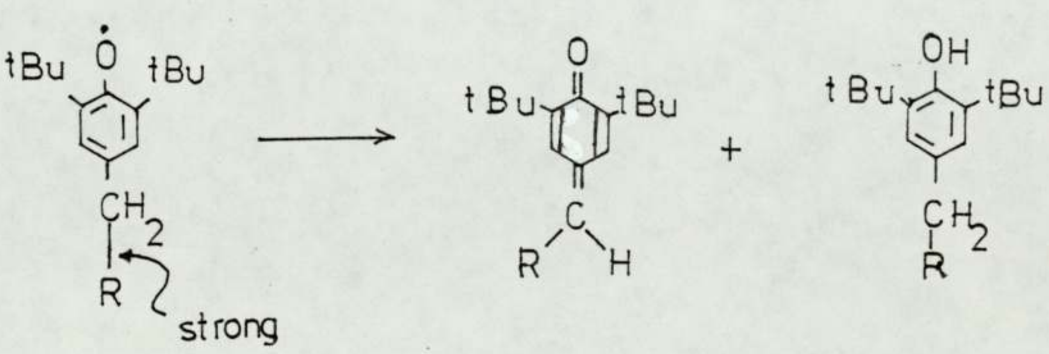


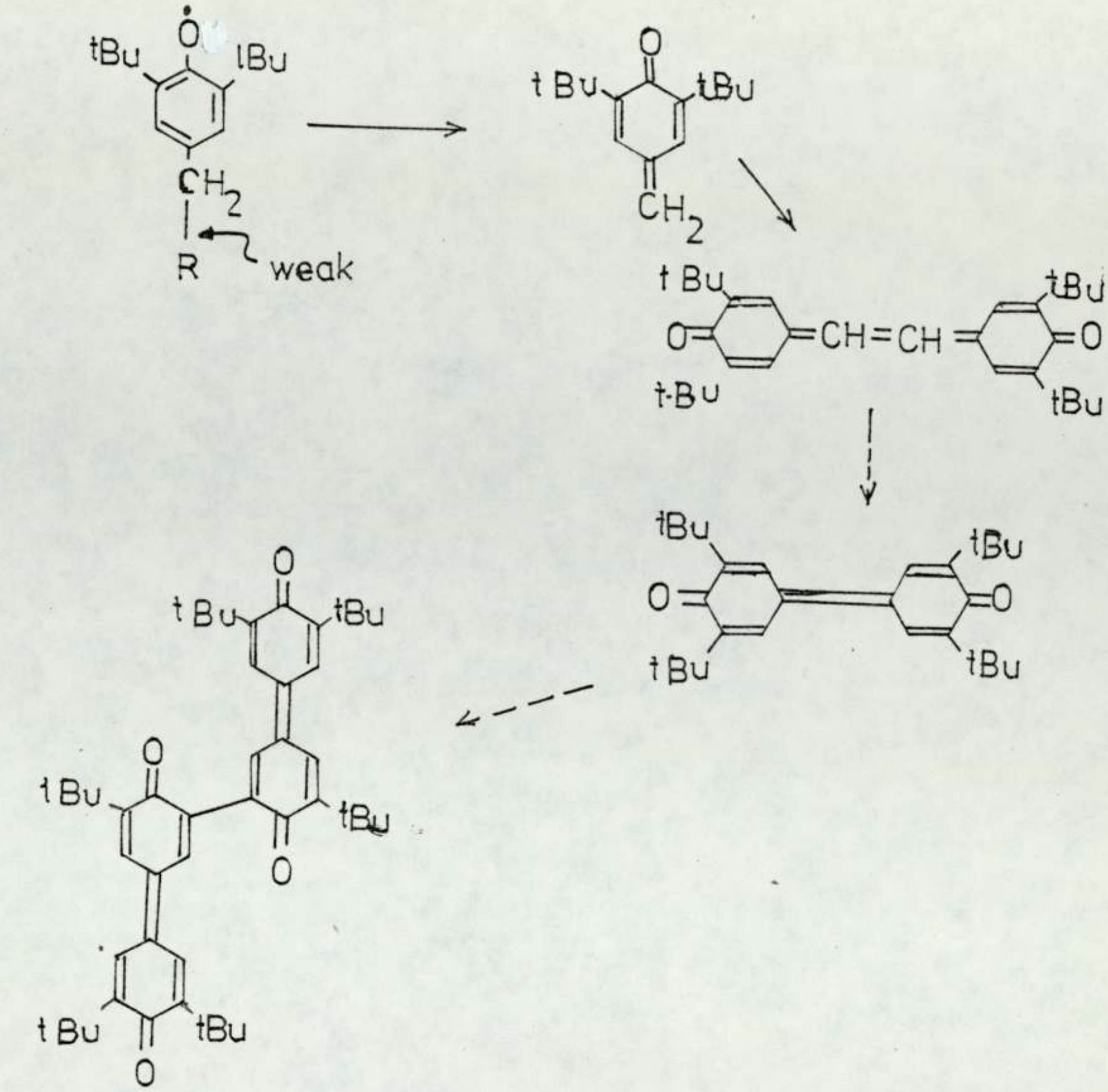
Embedded latex particle.

According to Westfahl[74] studies by esr have indicated 3,5 di*tert* butyl 4 hydroxy benzyl derivatives can be divided into two general classes based on their behaviour towards one electron oxidation, (ferricyanide ion as the oxidising agent). The first stage of the oxidation is the abstraction of hydrogen from the hindered phenol group (7). If the bond between the benzyl group and the rest of the molecule is strong (as R = - CH_2 CH_2 COOH) a phenoxy radical of considerable stability will form (8). No other free radicals have been observed.

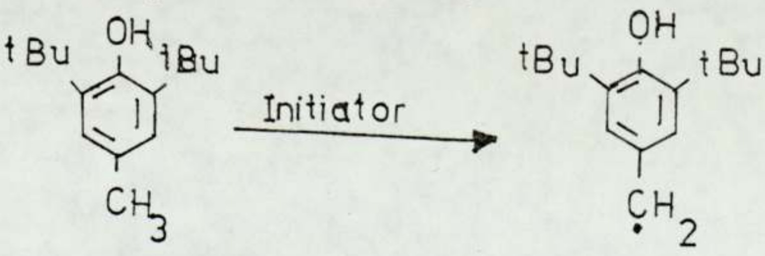


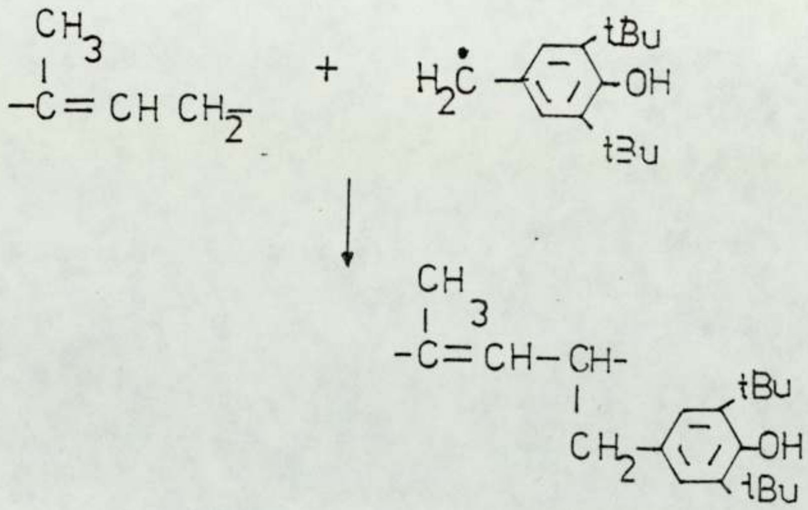
If the bond between R and the benzyl group is weak, a loss of R occurs either by ionic or free radical process to give very unstable 2,6 di<u>tert</u> butylquinone methide. The sequence of reactions which subsequently follow leads to highly conjugated quinone-like structures.



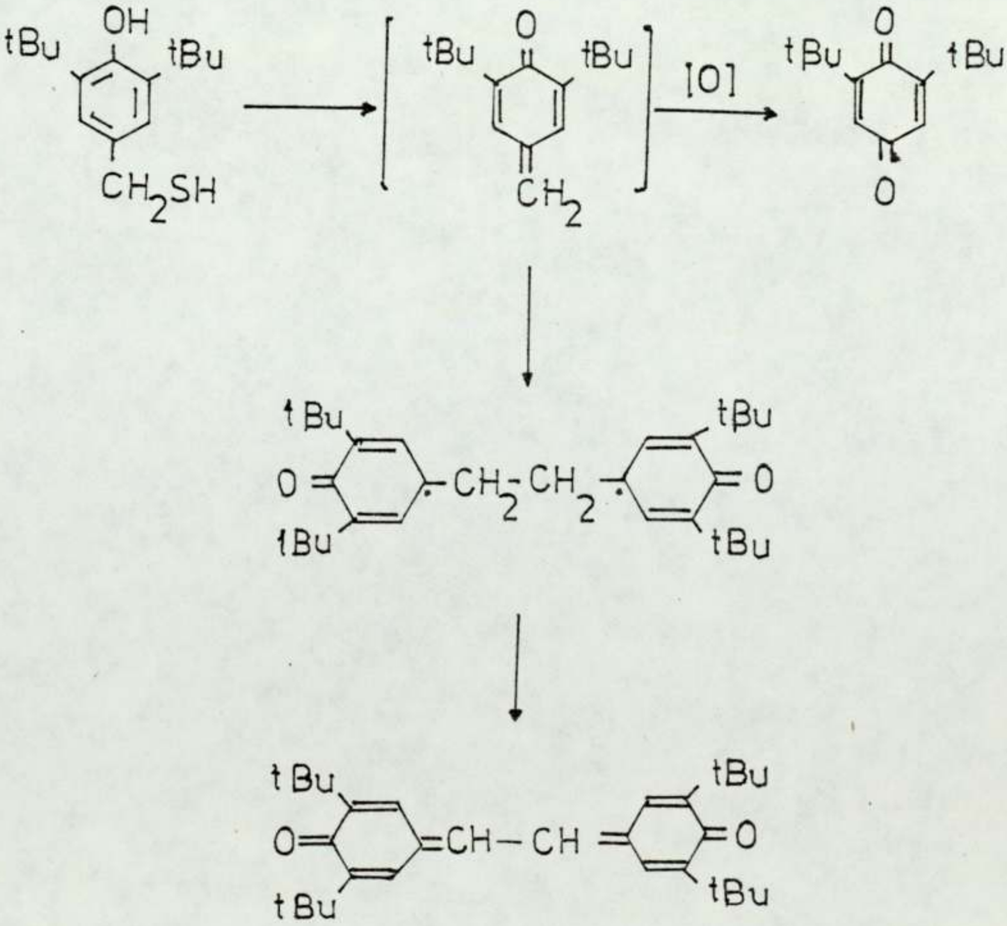


Compounds where R = H, Cl, OH, N , S and phenyl are examples of this class. Though Westfahl[74], observed 2,6 ditert butyl 4 hydroxytoluene (where R = H) to undergo oxidation in the presence of ferricyanide, other workers have found otherwise. The stability and the formation of the benzyl radical from above was confirmed by the graft reaction of the latter with natural rubber[80,144], in the presence of redox system of initiators.





However, it is possible to conclude that the quinonemethide is probably formed as the initial product during the oxidation of BHBM in the presence of redox initiators.



The formation of the quinone methide in this case is probably facilitated by the weakening of the bond between the benzyl and the thiol group due to electronegativity of the sulfur atoms and the electron affinity of the aromatic ring. The formation of such a quinonemethide is followed by a series of reactions in the presence of redox systems, leading to quinones, which are quite well known polymerisation inhibitors. Those compounds which inhibit the graft copolymerisation reaction shown in Table 23, probably behave in a similar manner to the mechanism followed by BHBM.

The effect on the above mechanism by different substituents at the benzylic carbon atom other than electronegative substituents is shown in Table 23 - 11 and 12. As expected when the SH group was replaced by an electron releasing group such as - CH_2 COOR the graft copolymerisation proceeded without inhibition.

The part played in the mechanism by the phenoxy group and the electronegative substituent at the benzyl carbon in the same molecule is shown by the uninhibited graft copolymerisation in the presence of 2,6 di*tert* butyl 4 methylphenol and benzylmercaptan, Table 23 - 3, 4, 5, 6. The promoting effect observed in the presence of benzylmercaptan is probably due to its solubility in the aqueous phase increasing the probability of the formation and the diffusion of the thiyl radicals to the reaction loci.

6.7. PART PLAYED BY MONOMER, INITIATOR IN THE INHIBITION OF GRAFT COPOLYMERISATION OF ABS, BY BHBM

It was difficult to isolate and study the part played by the monomer and/or initiator on the inhibition reaction of BHBM under emulsion polymerisation conditions, due to the presence of other additives described in the formulations. These can be eliminated if the polymerisations are carried out under free radical conditions in organic solution, using UV light or thermal energy for the decomposition of initiators.

6.7.a. PROCEDURE

The polymerisations were carried out, in quartz tubes, in UV light, under an atmosphere of N_2. The tubes were suspended in the UV cabinet described in Chapter 2, section 7. The samples were exposed for varying lengths of time depending on the degree of polymerisation in the presence of different additives. The monomer stabilizer molar ratios were kept constant at 100:1.5. The initiator concentration was restricted to 0.3% W/W of monomer. Qualitative estimation of the extent of polymerisation was determined for selected systems by relative viscosities of benzene solutions of the resulting polymer/monomer solution in an Ubbelohde viscometer. The polymer was precipitated by adding methanol to benzene solutions of the exposed samples.

6.7.b. RESULTS

Evolution of H_2S was detected using lead acetate paper. The formation of sulfurdioxide was established by passing the gas to $BaCl_2$ solution.

TABLE 24 - INFLUENCE OF VARIOUS ADDITIVES ON HOMOPOLYMERISATION OF ACRYLONITRILE AND STYRENE

	Compound	Solvent/ Monomer	Initiator	Irradiation Time (Days)	Observations
1	BHBM	Benzene	-	4	High mol.wt. quinone separate out from yellow solution containing stilbenequinone (TLC) Evolution of H_2S
2	BHBM	Benzene	CHP	4	Stilbene quinone (by TLC) SO_2 was formed
3	-	Styrene	CHP	2	Polymerised to a solid
4	-	Styrene	AZBN	2	Polymerised to a solid

TABLE 24 - Continued...

	Compound	Solvent / Monomer	Initiator	Irradiation Time (days)	Observations
5	-	Acrylonitrile	AZBN	2	Polymerised to a solid
6	-	Acrylonitrile	CHP	2	Polymerised to a solid
7	BHBM	Styrene	AZBN	4	Polymerised to a solid. Polymer contained bound BHBM
8	BHBM	Styrene	-	10	Polymerised to a solid. Polymer contan bound BHBM
9	BHBM	Styrene	CHP	30	Inhibitory No evolution of gases. Traces of stilbene quinone was detected by TLC (see Figure 4I)
10	BHT (Toponol OC)	Styrene	CHP	10	Polymerised to a solid. Bound BHT was detected in the polymer.
11	BHBM	Acrylonitrile	CHP	4	Polymerised to a solid. Polymer contained bound stabilizer

TABLE 24 - Continued.....

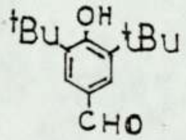
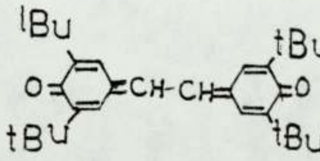
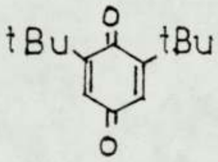
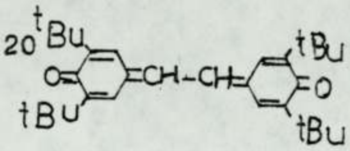
	Compound	Solvent / Monomer	Initiator	Irradiation Time in days	Observations
12	BHBM	Acrylonitrile	AZBN	4	Polymerised to a solid. Polymer contained bound stabilizer
13	BHBM	Styrene	tBH	30	Inhibitory
14	BHBM	Acrylonitrile	tBH	66	Polymerised to a solid.
15	Benzyl-mercaptan	Styrene	CHP	2	Polymerised to a solid. (see Figure 4I)
16	Benzyl-mercaptan + Toponol oC (5/2 W/W)	Styrene	CHP	5	Polymerised to a solid. (see Figure 4I)
17		Styrene	CHP	10	Polymerised to a solid
18		Styrene	CHP	30	Polymerised to a viscous liquid (see figure 4I)
19		Styrene	CHP	15	Polymerised to a viscous liquid solid polymer in 25 days (see Figure 4I)

TABLE 24 - Continued....

Compound	Solvent/ Monomer	Initiator	Irradiation	Observations
20 	Acrylonitrile	CHP	6	Polymerised to a solid
21 -do-	Styrene	-	10	Polymerised to a viscous liquid solid polymer in 25 days (see Figure 4I)

CHP = Cumenehydroperoxide

tBH = tert. butylhydroperoxide

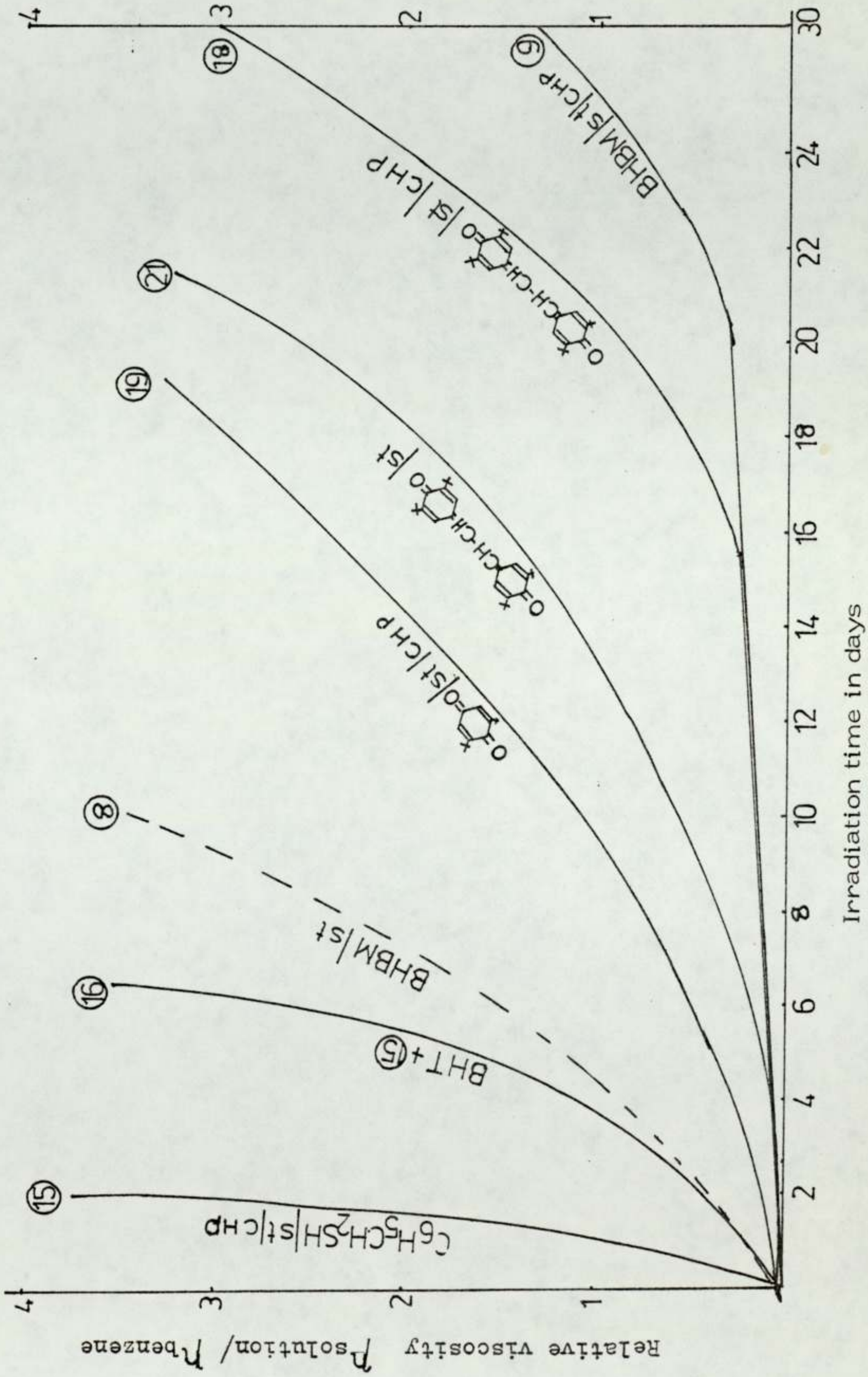
BHT = 2,6 di*tert*.butyl 4 methylphenol (Toponol OC)

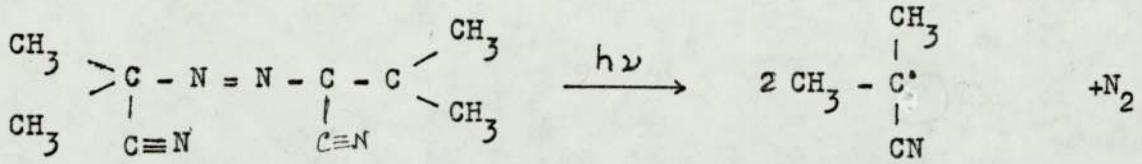
AZBN = Azobis isobutronitrile

6.7.c. DISCUSSION

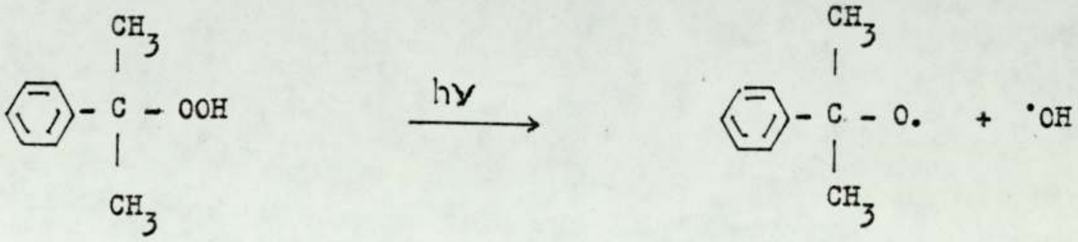
The two free radical initiators used in the above experiment dissociate on irradiation to give the following free radicals.

Figure 4I. Change in relative viscosities of polymer/monomer solutions on irradiation (solvent : benzene, numbers refer to the sequence in the table 24).

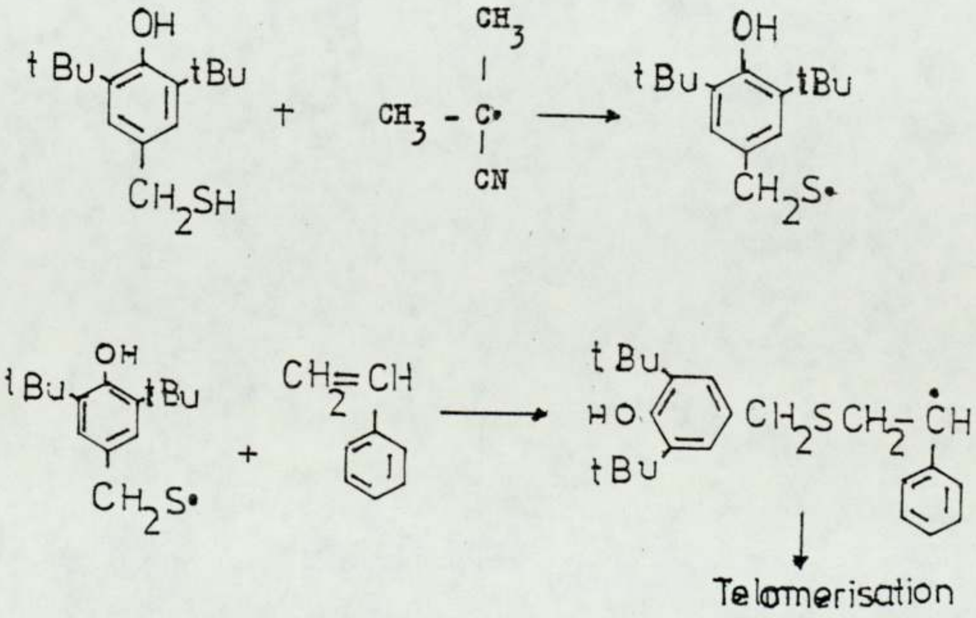




AZBN



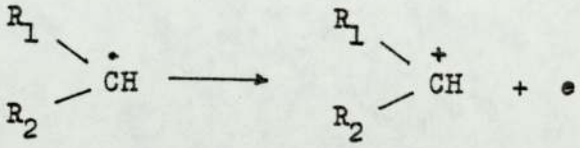
It was observed that in the presence of AZBN, hindered phenol derivative BHBM showed no inhibitory effects towards homopolymerisation of styrene. Analysis of this polymer showed some bound stabilizer in the system. Therefore, it is possible to assume that under these conditions the alkyl radical preferentially attack the thiol group.



This preferred attack of the alkyl radical on the thiol group even in the presence of chain breaking hindered phenol group is probably due to the following reasons :-

a) The steric hinderance for hydrogen abstraction from the phenoxy group due to the interaction of bulky tert.butyl groups of the antioxidant and methyl groups of the initiator radical.

b) The alkyl radicals differ from alkyl peroxy radicals in that they tend to give up, rather than gain an electron. One consequence of their character is their facile reaction with double bonds and this is particularly important for secondary and tertiary alkyl radicals which are unreactivein the competing hydrogen abstraction reaction[77]. Thus, it has been observed alkyl radicals are capable of polymerisation of vinyl monomers quite effectively in the presence of phenolic antioxidants so long as oxygen is excluded.



$$(R_1)(R_2)\dot{C}H \longrightarrow (R_1)(R_2)\overset{+}{C}H + e$$

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

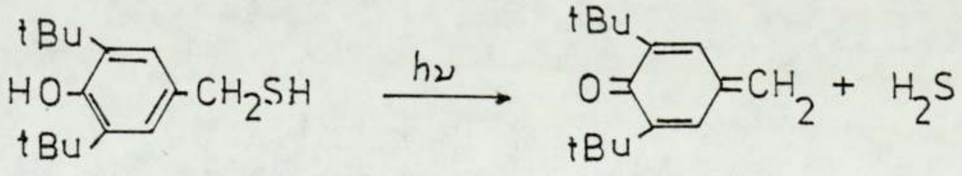
Homopolymerisation of styrene in the presence of BHBM was observed in the absence of any initiator additives. The reaction mixture was found to contain traces of stilbenequinone derivatives, and the polymer was found to contain some bound stabilizer. It was observed that when BHBM was irradiated in benzene solution, H_2S was evolved with the formation of some stilbenequinone derivatives. It has been demonstrated by Morgan et. al.,[I47] that thiols are capable of adduct formation on irradiation in the presence of photosensitizers. Initiation in this case is said to occur by abstraction of a hydrogen atom from the thiol group by the excited $n\pi^*$ triplet of a ketonic photosensitizer. Aromatic carbonyls have been found to be the most effective sensitizers for the reaction.

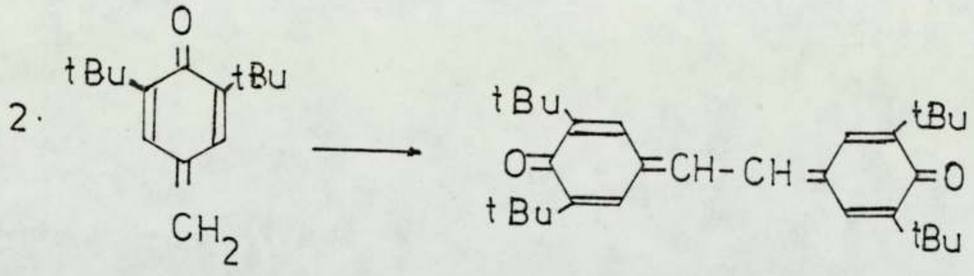
$$R_2C = O \longrightarrow R_2C = O \qquad {}^1(n\pi^*)$$

$$R_2C{=}O^1\ (n\pi^*) \longrightarrow R_2CO\ \ {}^3(n\pi^*)$$

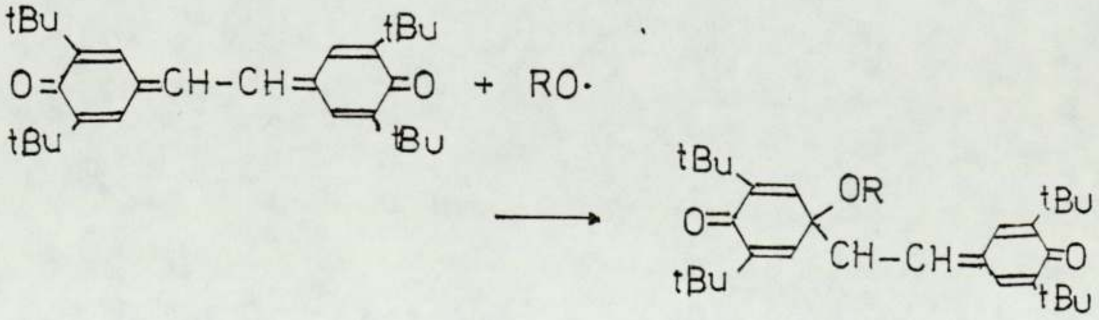
$$R_2C = O\ \ {}^3(n\pi^*) \xrightarrow{R'SH} R_2\,\dot{C}OH \ + \ RS.$$

Thus formation of a small amount of stilbenequinone on irradiation could act as the photosensitizer for the homopolymerisation of Styrene in the presence of BHBM.





The difference between the reactivity of BHBM in the presence of CHP and AZBN is probably due to the nature of radicals formed from the two initiators. The radicals of cumene hydroperoxide offer very little steric hinderance to hydrogen abstraction from the phenolic group of BHBM. Once the phenoxy radical is formed it can undergo further reactions leading to the formation of quinones discussed under section 8 of this Chapter. It has been established that quinones can act as photosensitizers for the addition reaction of thiols on irradiation[I47]. But alkoxy and peroxy radicals on the otherhand, can react with stilbene quinone derivatives to interrupt the congugation, and hence, the photosensitizing ability of the quinone.



It was observed that hydroperoxide delayed the homopolymerisation of styrene on irradiation in the presence of stilbenequinone derivatives Table 24 - 18 and 21 also Figure 41.

The question then is why and how such inhibition takes place in the presence of styrene and not acrylonitrile. The answer lies probably in the polarity of the two monomers. Acrylonitrile being a highly polar solvent, can effectively solvate the hydroperoxides as well as the radicals formed from them. Once the radicals are formed the probability of initiation of polymerisation is greater than the abstraction of hydrogen from the phenoxy group due to effective solvation.

On the other hand, when styrene is used as the monomer, the thiol antioxidant, BHBM, being more polar can effectively solvate hydroperoxides. This brings the phenoxy group within reach of any radicals formed from the hydroperoxides.

From these observations it is possible to conclude that if adduct formation reaction of BHBM with an unsaturated substrate is carried out a) in the absence of a less polar monomer such as styrene and/or b) with an initiator system which does not produce radicals small enough to abstract hydrogen from the phenoxy group, high yields of reaction products can be achieved.

Examples of such initiator systems suitable for emulsion polymerisation conditions are CHP/Fe^{+2}, S_2O_8 / S_2O_5 redox systems, and water soluble azo initiators such as 4,4' azo bis (4 cyanovaleric acid).

CHAPTER 7 - PREPARATION OF THIOL STABILIZER ADDUCTS OF ABS AND THIO ACTIVITY TOWARDS OXIDATIVE DEGRADATION

The two mercapto derivatives discussed so far viz. BHBM and EBHPT differ profoundly in their activity towards adduct formation reactions in the presence of monomers. The evidence gathered so far points to the fact that the failure of BHBM to undergo adduct reaction is probably due to a combined effect of the less polar monomer and the less sterically hindered free radical/radicals of the initiator. Therefore, it follows that if just one of the two unfavourable factors is excluded during the reaction, the adduct formation of BHBM with ABS in latex should proceed unhindered.

The consequences of replacing the initiator system presently being used to manufacture ABS, with a new system are not foreseeable. The unexpected would not only arise from the byproducts of decomposition of the initiator system but also from properties such as molecular weight and its dispersion, cross-linking density etc., of the finished product. Therefore, in order to use the present initiator system, it is necessary to exclude the less polar monomer, styrene, during the adduct formation reaction.

The amount of unreacted monomers (residual monomers) in ABS latex can be as high as 4% W/V. A fully saturated aqueous solution acrylonitrile contains about 7% monomer whereas styrene is only sparingly soluble in water, and therefore, probably exist as monomer droplets in latex. It is possible to visualise ABS latex as a dispersion of latex particles and styrene droplets in an aqueous solution of acrylonitrile and the emulsifier. It styrene is dispersed in latex as monomer droplets, the cohesive forces between the medium should be quite low. This would make it easier to effectively remove residual styrene than acrylonitrile from latex.

7.1. PREPARATION OF STRIPPED LATEX - PROCEDURE

A 2-necked flask fitted with a stirrer was connected to a vacuum pump, via a liquid nitrogen trap, through a tube with a small bore (0.5 mm). The flask was immersed in a water bath and the temperature was raised slowly within an hour to around 60°C. The latex was stirred at around 30 rpm during this period.

It was found that 600 ml of ABS latex (containing approximately 200 gm dry ABS), could be stripped when the temperature was allowed to rise to 60°C in 50 minutes. About 50 ml of distilled water was added to the latex before stripping, to compensate for what is lost during the operation.

7.2. G.L.C. ANALYSIS OF STRIPPED LATEX FOR RESIDUAL STYRENE

Analysis was carried out in a Perkin Elmer model F30 gas chromatograph, using a porapak Q 80 - 100 mesh stainless steel $\frac{1}{8}$" thick column, six feet long.

Injection temperature	150°C
Detection temperature	250°C
Column temperature	230°C
Carrier gas	N_2
Detector	Flame ionization type

Under these conditions styrene is eluted approximately after nine minutes of injection of the sample.

7.2.a. BORG WARNER CHEMICALS AND PLASTICS GROUP TEST METHOD

Essential features of this method are[148],

(i) injection of a small quantity (1 μl) of latex to obtain the chromatogram

(ii) comparison of these peaks with the peaks of solutions containing known amounts of monomer.

Though this method was applicable for determination of acrylonitrile owing to its solubility in the aqueous phase, sparingly soluble styrene gave erroneous results, possibly due to uneven dispersion of the monomer droplets in the aqueous phase, of the latex.

7.2.b. ANALYSIS OF LATEX EXTRACTS

Hexane was found to be the best solvent for the extraction of the residual monomer styrene from ABS latex.

7.2.b.1. PROCEDURE

50 ml of stripped latex, 50 ml of distilled water and 50 ml of hexane were taken in a 250 ml flask and shaken in a mechanical shaker for varying lengths of time. It was found that consistent results were obtained after an hour in the mechanical shaker.

The GLC peaks were compared with a known solution of styrene in hexane (0.5% W/V). The peaks were cut and weighed for comparison.

7.2.b.2. RESULTS

GLC peaks obtained for styrene/hexane solution and hexane extracts were cut from the chart and weighed for the estimation of maximum allowable residual styrene in latex for uninhibited reaction with BHBM.

Average weight for 1 µl of 0.5% solution of styrene in hexane = 0.0323 g

Average weight for 1 µl of hexane extract of stripped latex = 0.0148 g

1 µl of 0.5% solution ≡ 2.18 µl of hexane extract.

∴ Concentration of styrene in stripped latex = 0.230% W/V of ABS latex

7.3. ADDUCT FORMATION OF BHBM WITH STRIPPED ABS LATEX

Stripped latex was prepared by the method described in this Chapter unders section 1.

7.3.a. PROCEDURE

TABLE 25 - FORMULATION USED FOR THE BHBM ADDUCT FORMATION

ABS latex stripped in ml (30% dry ABS)	330
BHBM emulsion in ml (1 g BHBM)	100
Cumene hydroperoxide in gms (CHP)	0.2 – 2.0
Fe^{+2} / TSPP solution in ml	2 – 10
Glucose (gm in 10 ml of water)	1 – 2.5
Time in hours	3
Temperature in °C	57°
Atmosphere	N_2

The amount of initiator CHP/Fe^{+2} and the reducing sugar concentrations were varied to study the effect on the adduct formation reaction. Cumene hydroperoxide and the antioxidant emulsion were added in aliquots within the first half of the reaction.

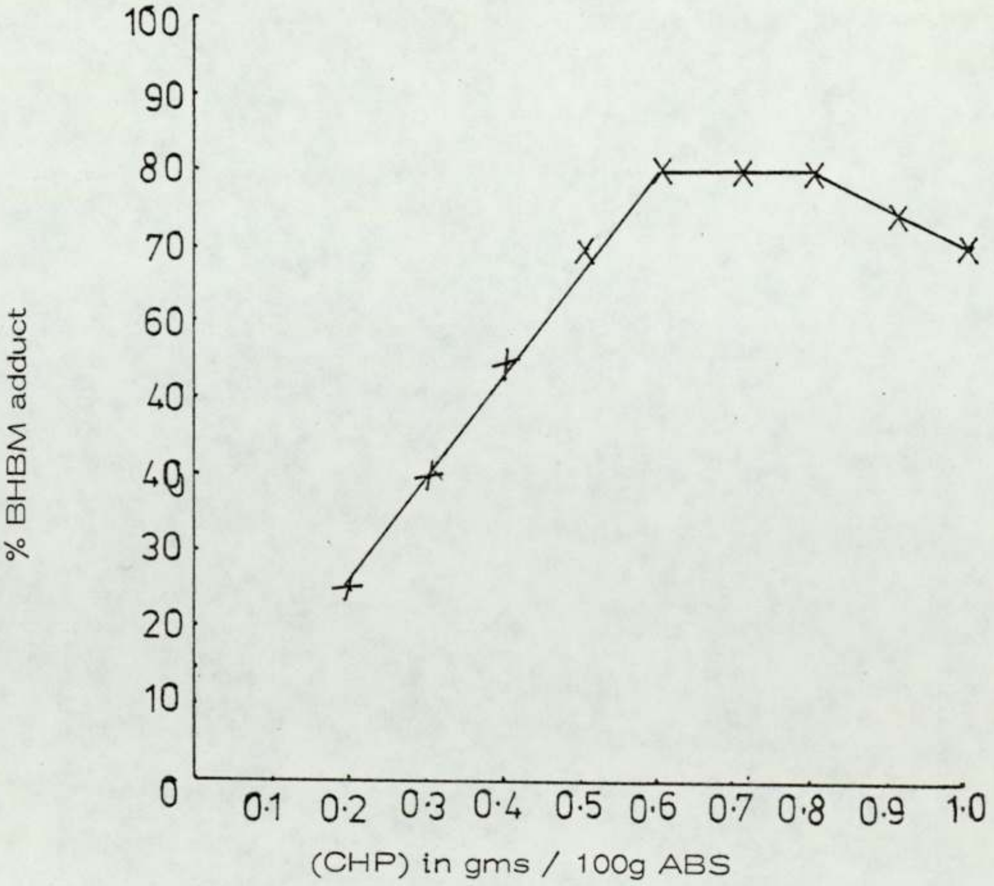
The resulting latex was acid coagulated, washed neutral with distilled water, and dried in a vacuum oven at 55°C to a constant weight.

For the purpose of estimation and evaluation of bound BHBM, part of the dried ABS was extracted with hexane.

7.3.b. RESULTS

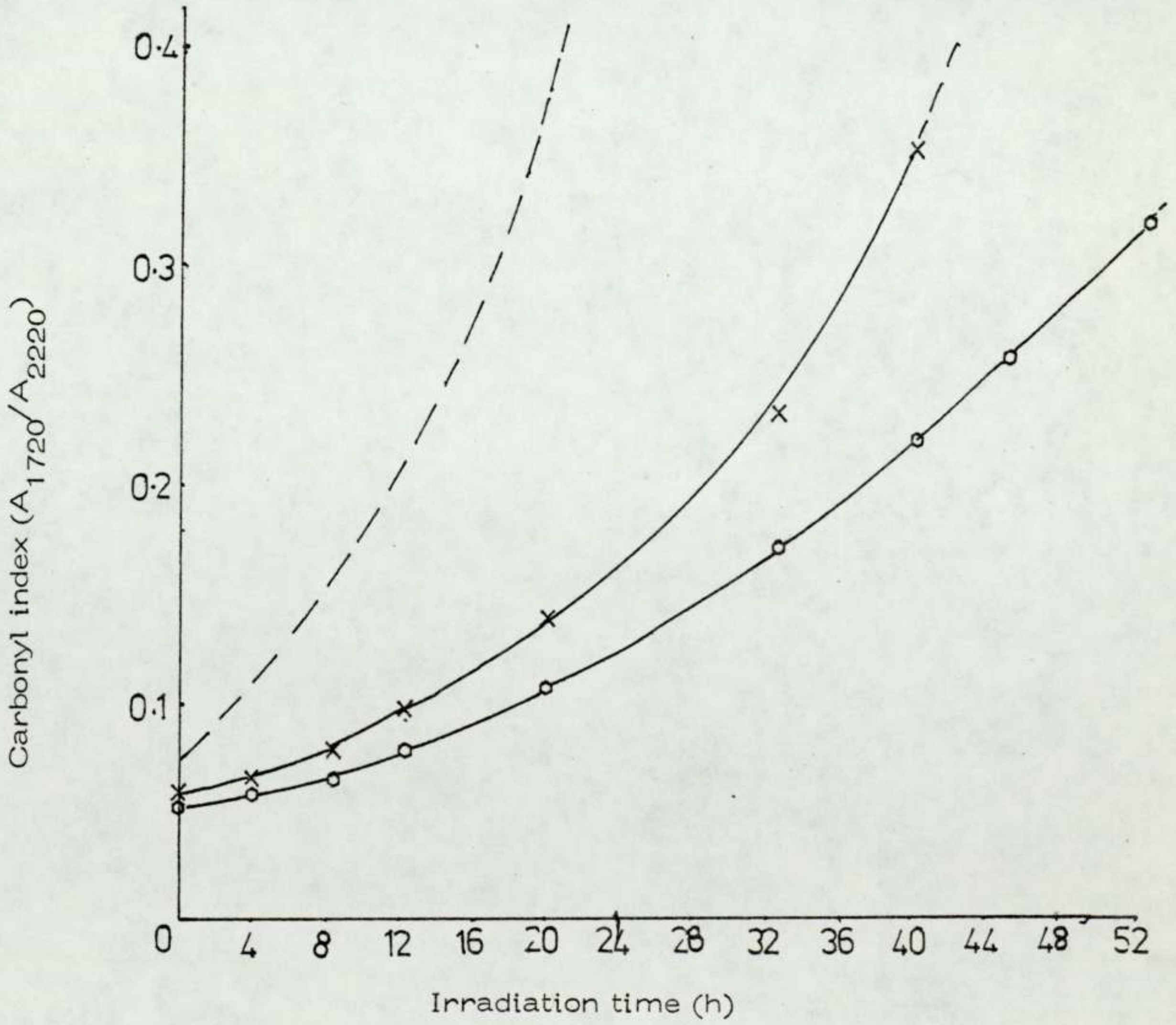
(i) Effect of the concentration of initiator :- The percentage of bound BHBM was found to increase with the concentration of the redox system up to 0.6 parts of cumene hydroperoxide per 100 parts of ABS. Further increase in the concentration of redox initiator system did not increase the extent of adduct formation. Figure 42

Figure 42. Dependance of the concentration of initiator on the adduct reaction (57°C).



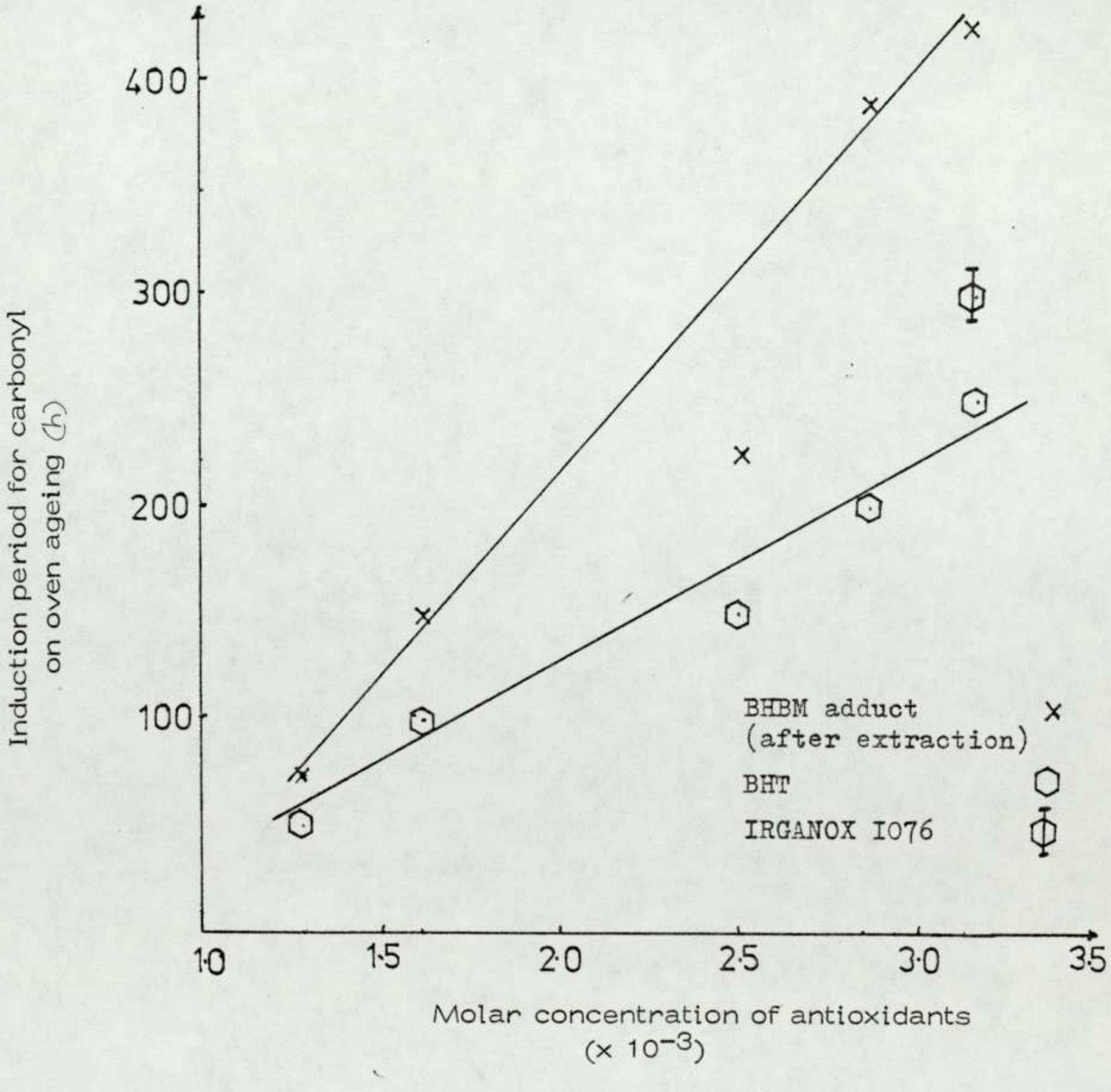
(ii) Effect of bound antioxidant BHBM after extraction on photoxidative degradation of ABS (by the development of carbonyl using IR spectroscopy) at a concentration of 3.187×10^{-3} moles (= 0.8% by weight) are given in figure 43.

Figure 43. Development of carbonyl absorbtion during uv exposure (by infra-red spectrometry) of ABS films containg (a) no stabilizer (b) 3.636×10^{-3} M BHT (c) 3.187×10^{-3} M BHBM adduct after extraction.



(iii) Effect of bound antioxidant BHBM on thermal oxidative degradation of ABS (by the development of carbonyl using infra red spectroscopy) at different concentrations of the adduct are given in Figure 44.

Figure 44. Induction periods on oven ageing of ABS films at 100°C containing (a) BHBM adduct after extraction (b) 3,5 di-tert-butyl 4 hydroxytoluene (BHT) and (c) Irganox I076. (Obtained by monitering the development of C=O by IR spectroscopy).



7·3.c DISCUSSION

As expected the stripping of latex led to the adduct formation reaction with BHBM under redox conditions. The critical concentration of the maximum allowable residual styrene by the analysis of hexane extracts of latex was found to be around 0.230% W/V of latex for 'ABS' latex.

A linear relationship between the concentration of the redox system CHP/Fe^{+2} and the yields of adducts for the reaction of BHBM with ABS in latex was observed up to 0.6 parts of cumenehydroperoxide per hundred parts of the polymer, Figure 42. Further increase in the redox system concentration did not seem to have beneficial effects. In fact, above 0.8 parts of cumenehydroperoxide the amount of bound BHBM began to decrease by about 5% for every increase in 0.1 parts, up to a concentration of 1.0 of CHP/100 parts of ABS. This decrease is probably due to one or more of the following reasons.

(i) Oxidation of BHBM to mono and polysulfides in the excess of the oxidant. One of the general methods of preparation of polysulfides is the oxidation of mercaptans in an alkaline medium. Since ABS latex used in the reaction has a pH of 9.6 - 9.8, the possibility of such an oxidation cannot be completely eliminated in the presence of excess oxidant such as cumenehydroperoxides.

(ii) Decomposition of excess hydroperoxide by the mercaptan, monosulfide and the polysulfides, in the final stages of the reaction. It was found (Chapter 4, section 4.a.) that BHBM and its derivatives decompose hydroperoxides effectively at 70°C with an induction period of about 25 minutes. The adduct formation reaction is usually carried out at 57°C. At this temperature, it was observed that BHBM and its derivatives take approximately 135 minutes to initiate the decomposition of cumenehydroperoxide. This period is well covered by the conditions of adduct formation, where reaction is allowed to continue for 180 minutes at 57°C.

(iii) The redox reaction between cumenehydroperoxide and Fe^{+2} ion in aqueous solution can be illustrated as follows :-

$$ROOH + Fe^{+2} \longrightarrow Fe^{+3} + OH^- + R\dot{O} \qquad (1)$$

$$R\dot{O} + H_2O \longrightarrow ROH + OH^{\bullet} \qquad (2)$$

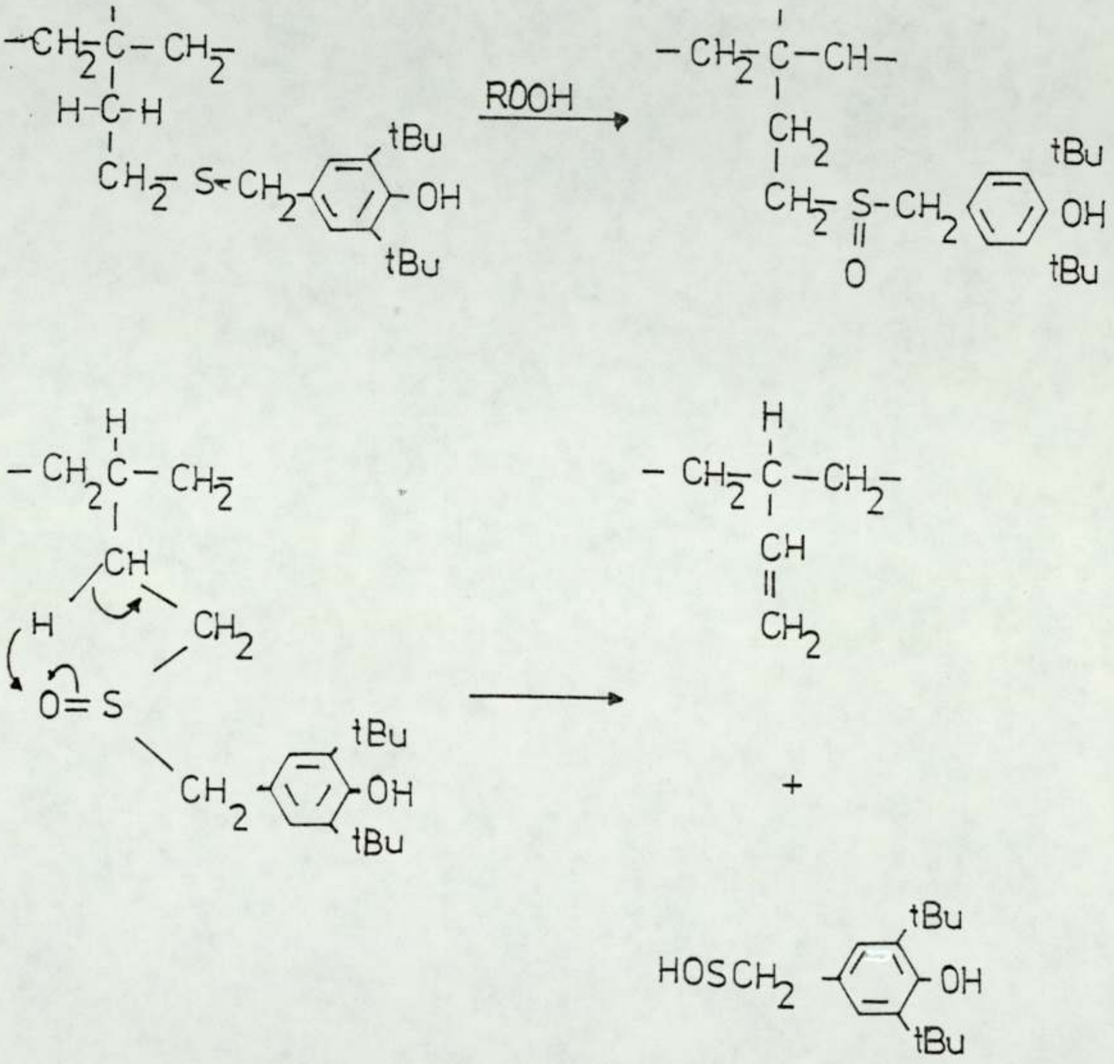
$$OH^{\bullet} + Fe^{+2} \longrightarrow Fe^{+3} + OH^- \qquad (3)$$

If excess of $RO^{\bullet}$ radicals are generated in the system, there is a possibility of accumulation of $^{\bullet}OH$ as explained in reaction (2).

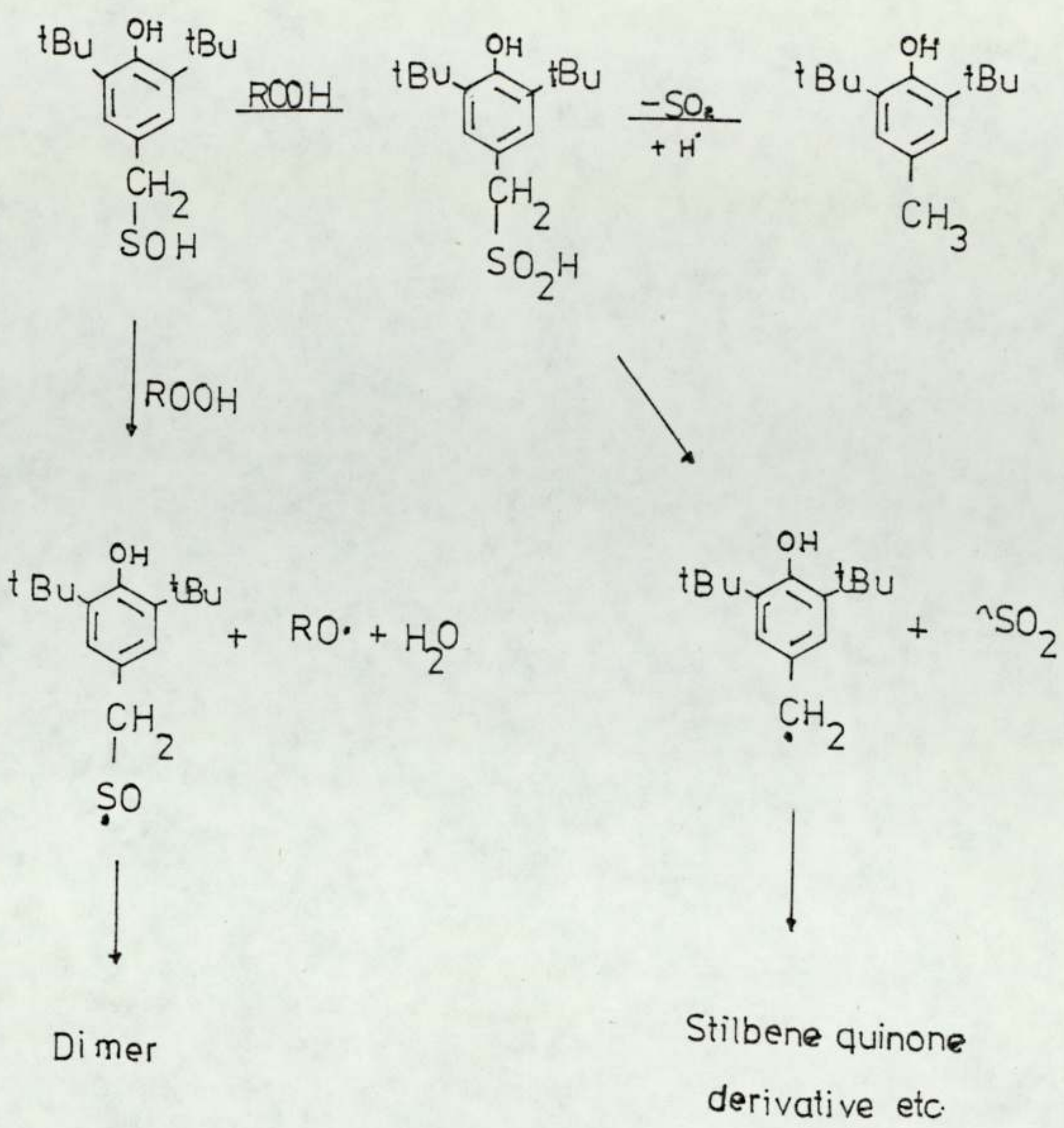
This radical has the highest ability to abstract hydrogen from the hindered phenol group of the antioxidant due to its size. Since the quantitative estimation of phenolic antioxidant depends on the reaction of Fe^{+2} ion with the phenolic hydroxyl group loss of hydrogen in this manner will be registered in the final analysis even if the molecule is bound to the polymer.

Ovenageing of extracted ABS films containing bound BHBM at 100°C show a remarkable improvement in stability over the conventional phenolic antioxidants. Fig 44 Parallel experiments at the same molar concentrations of the extracted BHBM adduct, and BHT as additive show an increase of approximately 225 hours for the induction period of the development of carbonyl absorbtion (by infra red) on oven ageing of ABS films, at a concentration of 3.17×10^{-3} moles /100 gms of ABS. At this concentration another conventional phenolic antioxidant, Irganox 1076 as an additive showed an increase of about 75 hours in the induction period over BHT. Figure 44. This difference is probably due to the recorded low volatality[96] and the higher compatibility of 1076, due to the presence of the stearate substituent, with the polymer.

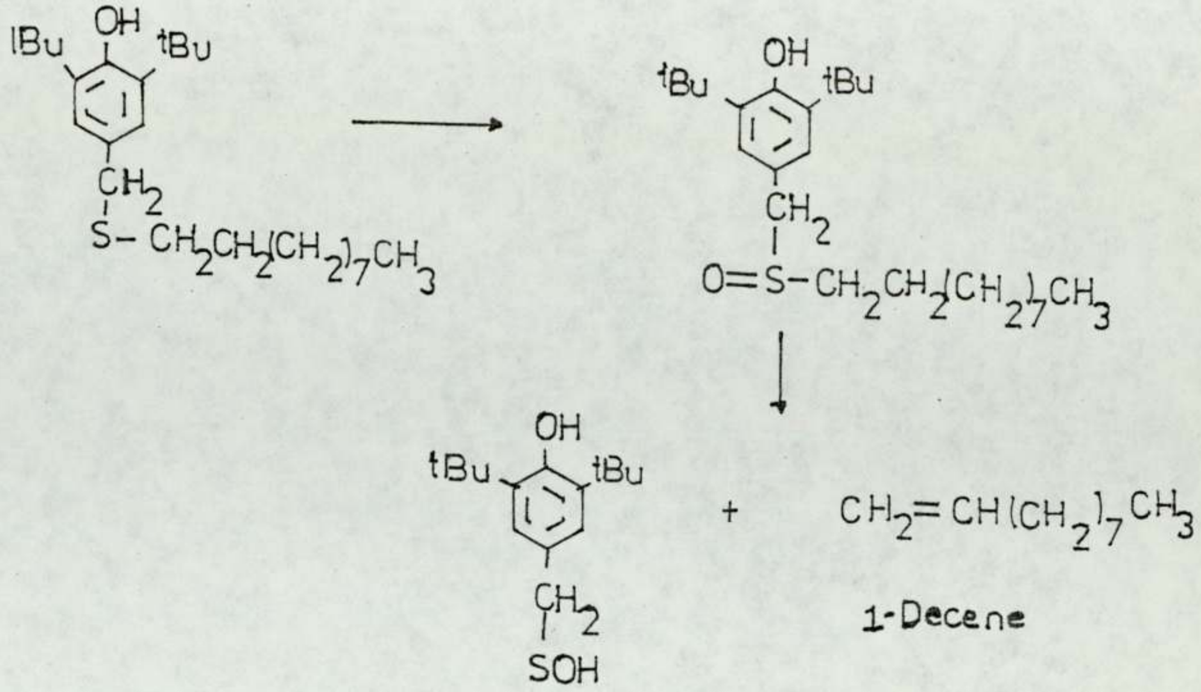
The formation of an adduct saturates a double bond. Such a system can undergo reactions involving β- hydrogen atoms, during the decomposition of hydroperoxides by sulfur compounds, as shown by Scott[150,87], It is possible to arrive at the following mechanism for the decomposition of hydroperoxides by BHBM adducts using the above reference for similar derivatives.

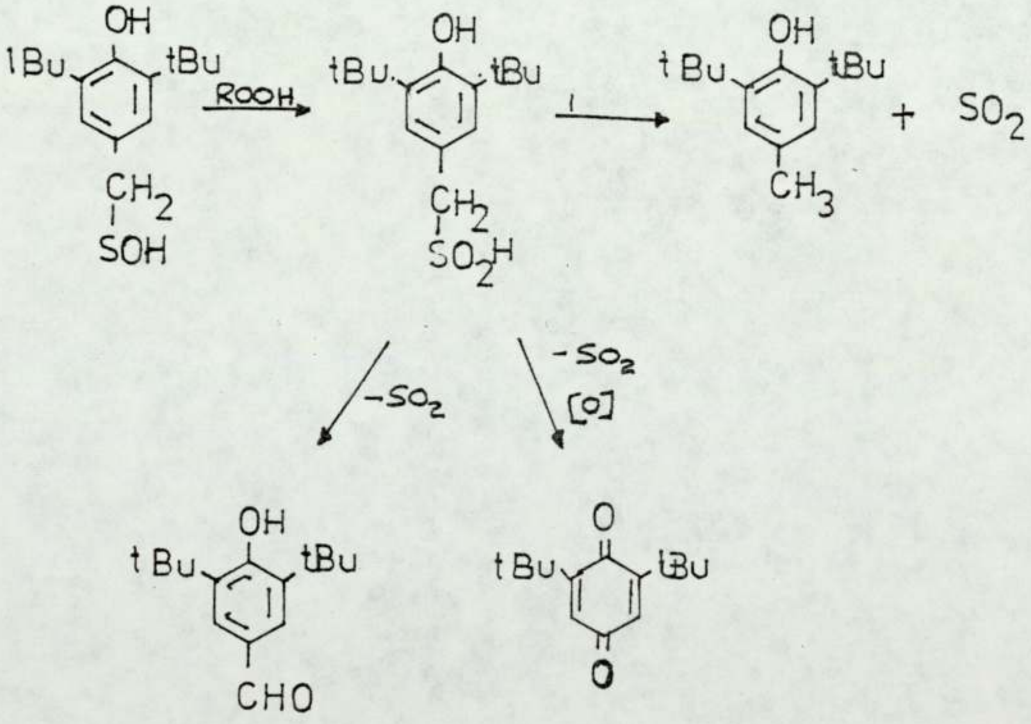


The following mechanism can be suggested for the oxidation of the sulfenic acid derivative of the phenolic antioxidant formed, based on the evidence obtained by the study of the decomposition of cumene-hydroperoxide by 3,5 di<u>tert</u>.butyl 4-hydroxybenzyl decylsulfide.



It was possible to identify, 3,5 ditert butyl 4-hydroxytoluene and 1-decene by TLC analysis of the reaction mixture of cumenehydroperoxide and 3,5 ditert.butyl 4-hydroxy benzyl decyl sulfide soon after the induction period, which at 70°C for this system is 35 minutes. The very faint spot on the TLC plate due to BHT obtained at the beginning of the reaction soon disappeared. The formation of these two products can be explained as follows.





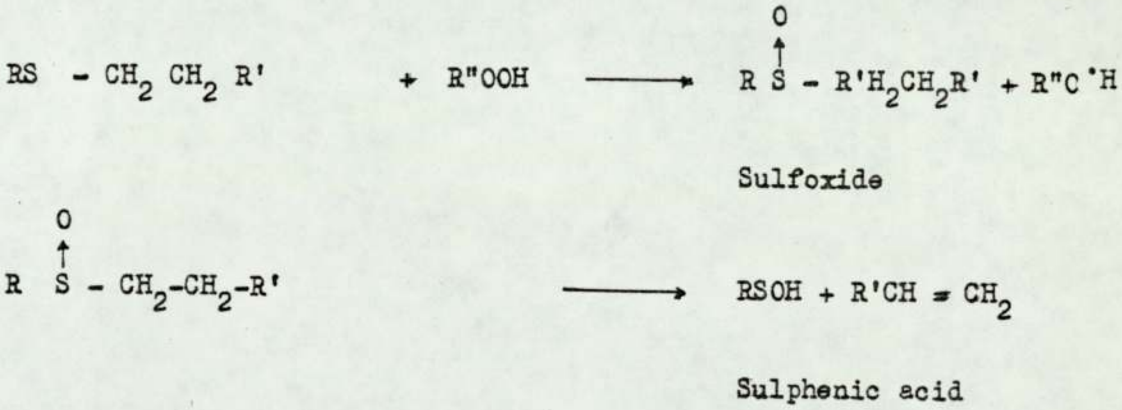
Later stages

The release of antioxidant as the sulfenic acid derivative on oxidation of bound BHBM system re-introduces the lost double bond to the system. This process probably takes place during the induction period, observed in the ovenageing process.

The BHBM adduct shows only a marginal improvement over BHT (as additive), on the photoxidative degradation of ABS, Figure 43. Hydroperoxide decomposition studies of BHBM and its monosulfide TBMP show an induction period of 27 and 35 minutes respectively, at 70°C. After the induction period the process follows first order kinetics with respect to the concentration of hydroperoxide, Figures 29 & 30. It is possible to conclude that both BHBM and TBMP are converted to active peroxide decomposers during the initial stages (induction period) of the decomposition reaction. The discrepancy of the behaviour of the BHBM adduct towards thermal and photoxidation, can probably be explained as follows :-

(i) The decomposition of polymerichydroperoxides on photolysis is almost instantaneous. But it was found that sulfur containing antioxidants reacts with hydroperoxides after a short induction period . As a result, under these conditions sulfur containing phenolic antioxidants are probably incapable of showing the synergistic effects, observed during thermal oxidative degradation of the polymer.

(ii) Sulfenic acid derivatives have been found to be the most effective peroxide decomposers of sulfur compounds[149]. This is formed after an induction period, from sulfides or thiols in the presence of hydroperoxides[150]. It is known that the initial breakdown products of sulfoxides which contain a β -hydrogen atom are sulfenic acids[150]. Shelton and Davis[91], found that when sulfoxides were subjected to both direct and sensitized photolysis, products derived from initially formed alkyl and sulfenyl radicals confirmed the expected homolytic cleavage of the C-S bonds.



$$RS - CH_2\ CH_2\ R' + R''OOH \longrightarrow R\ \overset{O}{\overset{\uparrow}{S}} - R'H_2CH_2R' + R''C^{\cdot}H$$

Sulfoxide

$$R\ \overset{O}{\overset{\uparrow}{S}} - CH_2-CH_2-R' \longrightarrow RSOH + R'CH = CH_2$$

Sulphenic acid

It is possible to assume that such reactions could occur from sulfoxides derived from BHBM adducts during photo oxidation. These photolytic reactions can lead to chain propagating alkoxy and alkylperoxy radicals under oxidative environments. This is probably manifested in the activities of sulfur containing antioxidants under photoxidative conditions.

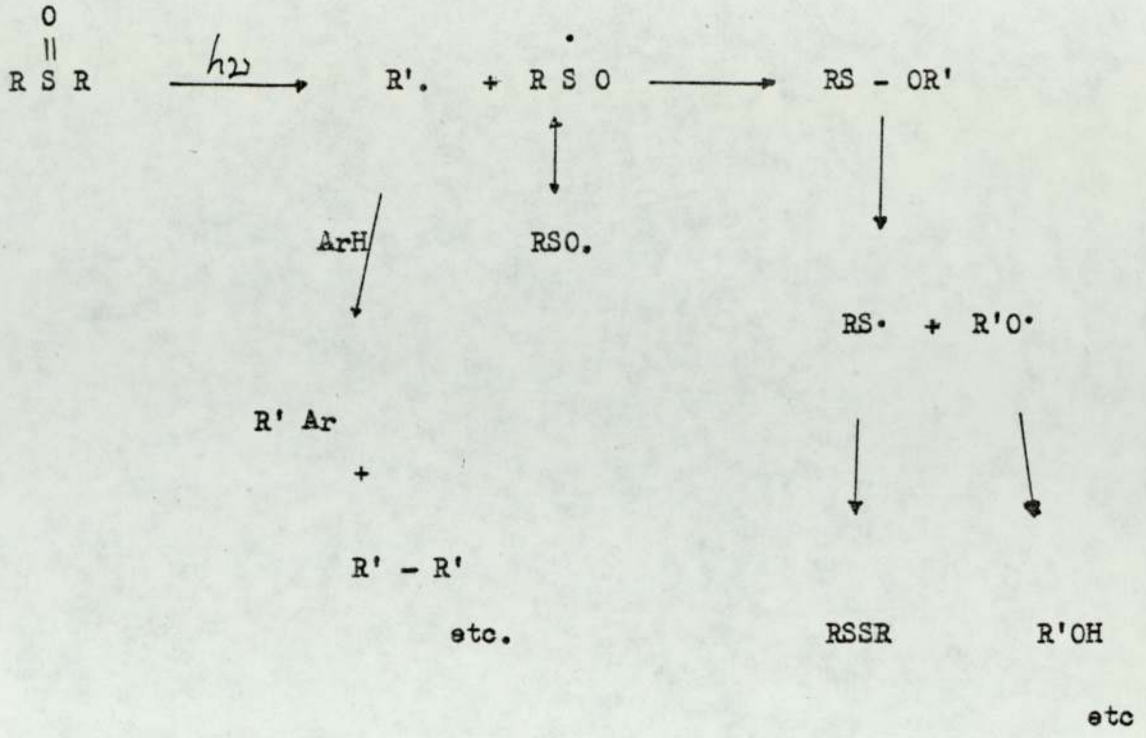


Figure 45. Types of products formed in the photolysis of dialkyl, dialkenyl, alkyl and aryl sulfoxides, 0.1 M in benzene[9I].

It is clear from the above discussion that

a) if the photolysis of polymer hydroperoxides can be delayed to a considerable extent upto or beyond the induction period for the decomposition of hydroperoxides by sulfur containing antioxidants, and

b) the photolysis of sulfoxides of sulfur containing antioxidants are contained to a minimum, considerable improvement in the stability of the polymer against photoxidative degradation could be achieved. Only a screening agent such as a UV absorber has the ability to satisfy both these requirements.

7.4. ATTEMPTED ADDUCT FORMATION WITH THIOL ACID ESTERS OF 3,5 DITERT BUTYL 4 HYDROXY BENZYLALCOHOL (BHBT AND BHBP)

7.4a.1 PROCEDURE

The following formulation was used in the attempted adduct formation :-

ABS latex stripped in ml (30% dry ABS)	330
Antioxidant emulsion in ml (1 gm)	100
Cumene hydroperoxide in gms	0.6
Fe^{+2} / TSPP solution in ml	5
Glucose (gm / 10 ml of water)	1
Time in hours	(a) 3 (b) 4
Temperature in °C	(a) 57 (b) 50
Atmosphere	N_2

The antioxidant emulsion and CHP were added in aliquots during the first half of the reaction. The latices obtained were acid coagulated and the crumb was dried in a vacuum oven at 55°C to a constant weight. For bound antioxidant evaluation, ABS was extracted with hexane.

7.4.a2 RESULTS

The bright white wet coagulum turned pale yellow on drying, in the presence of both antioxidants. The amount of bound antioxidants estimated by the method described in Chapter 2, are given in the following Table 26.

TABLE 26 - CONCENTRATION OF BOUND STABILIZER ON ADDUCT FORMATION OF ANTIOXIDANTS BHBG AND BHBP AND CORRESPONDING INDUCTION PERIODS ON OVEN AGEING

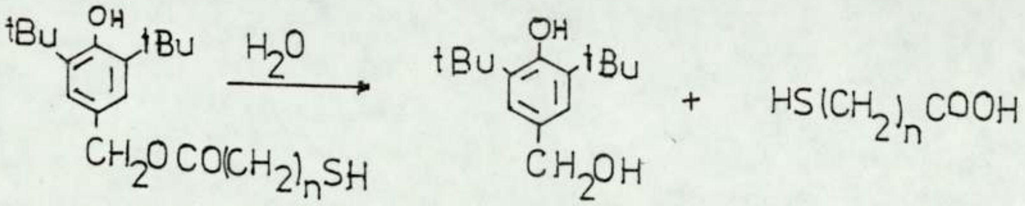
ANTIOXIDANT	TEMPERATURE/TIME	% BOUND ANTIOXIDANT	INDUCTION PERIOD IN OVEN AGEING IN HOURS
BHBT	a/a	22	60
BHBP	a/a	20	60
BHBT	b/b	37	80
BHBP	b/b	33	78

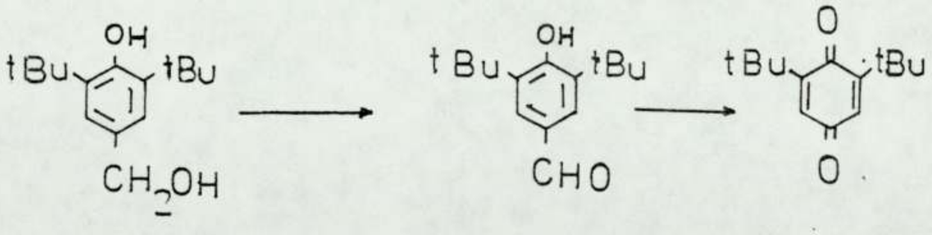
Thin layer chromatography of hexane extract showed three bright spots among others. R_F values (Table 18) of these correspond to the following oxidation products I, II and III.

2,6 di <u>tert</u> butyl 4 hydroxy benzaldehyde	I
2,6 di <u>tert</u> butyl benzo I,4 quinone	II
3,5 3'5' tretra <u>tert</u> butyl stibene I,4 quinone	III

7.4a3 DISCUSSION

The formation of oxidation products described above necessitates the hydrolysis of ester carbon bond of the molecule. Such hydrolysis is probably fascilitated by the weakening of the ester carbon bond due to electronegativity of the ester oxygen atom and the electron affinity of the benzene ring. The loss of antioxidant in this manner is manifested in the performance of the polymer towards oxidative degradation, Table 26.





7.5. EFFICIENCY OF ADDUCT STABILIZERS BHBM AND EBHPT IN COMBINATION

It was observed (Chapter 4) that the individual performance of TBMP and EBHPT as additives in ABS towards thermal oxidative degradation and photoxidation respectively was marginally higher than other stabilizers tested, at approximately the same molar concentrations. The combined effect of these two on the photoxidation of ABS was found to be much higher than that expected on an additive basis. Since the adduct formation reaction with BHBM and EBHPT with ABS in latex was of consierable success; the possibility of latex blending was exploited to obtain a synergistic combination of the two.

7.5.a1 PROCEDURE

Two samples of [redacted] 'ABS' latex (a) stripped (b) unstripped, were reacted with BHBM and EBHPT respectively. The initial concentration of the stabilizers used for this reaction was 2.5 gms for every 100 gms of dry ABS. The resulting latices were combined with the corresponding amounts of unstabilized [redacted] 'ABS' latex to give the following concentrationsin the final product. (Table 27).

The latices were stirred at 220 rpm for 0, 5, 10, 15 and 60 minutes before coagulation. The crumb was dried in a vacuum oven at 55°C, to a constant weight. ABS was extracted with hexane for evaluation of bound stabilizers.

TABLE 27 - FINAL CONCENTRATIONS OF STABILIZERS ON LATEX BLENDING

BHBM gms per 100 gms of ABS	EBHPT gms per 100 gms of ABS	Unstabilized ABS added (in gms of dry ABS)
0.5	1.0	40
0.8	1.0	28
1.0	1.0	20
1.2	1.0	12
1.2	0.8	20
1.5	0.8	8
1.5	1.0	-
1.5	0.6	16

7.3.b. RESULTS

(i) Quantitative estimation of bound stabilizer in the stock latex :-

BHBM	78 - 80%
EBHPT	62 - 65%

(ii) Induction periods and embrittlement times for various combinations on photoxidative degradation of ABS films, by carbonyl absorbance using infra red spectrometry are given in the accompanying

Table 28. A typical curve for the development of carbonyl absorbance in both extracted and unextracted stabilized ABS is given in Figure 46.

TABLE 28 - INDUCTION PERIOD AND EMBRITTLEMENT TIME FOR VARIOUS COMBINATIONS OF BHBM AND EBHPT BEFORE AND AFTER EXTRACTION, ON LATEX BLENDING

Sample No	BHBM/EBHPT Before extraction gms / 100 gms of ABS	BHBM/EBHPT After extraction gms / 100 gms of ABS	Induction period/Emb time in hours Unextracted	Induction period/Emb time in hours Extracted
1	0.5/1.0	0.4/0.62	33 100	32 90
2	0.8/1.0	0.64/0.62	50 120	43 92
3	1.0/1.0	0.8/0.62	70 135	60 130
4	1.2/1.0	0.96/0.62	70 140	65 130
5	1.2/0.8	0.96/0.50	65 135	62 130
6	1.5/0.8	1.2/0.50	80 160	75 140
7	1.5/1.0	1.2/0.62m	80 160	73 140
8	1.5/0.6	1.2/0.37	65 130	55 130
9	Control (Factory stabilized)		6 30	2 24

(iii) Induction periods for the development of carbonyl (by infra red spectrometry) on oven ageing in air at 100°C are given in Table 29. The numbers refer to the sample numbers in the previous Table 28.

Figure 46 Development of carbonyl functional group on UV exposure of ABS pressed films (refer table 28)

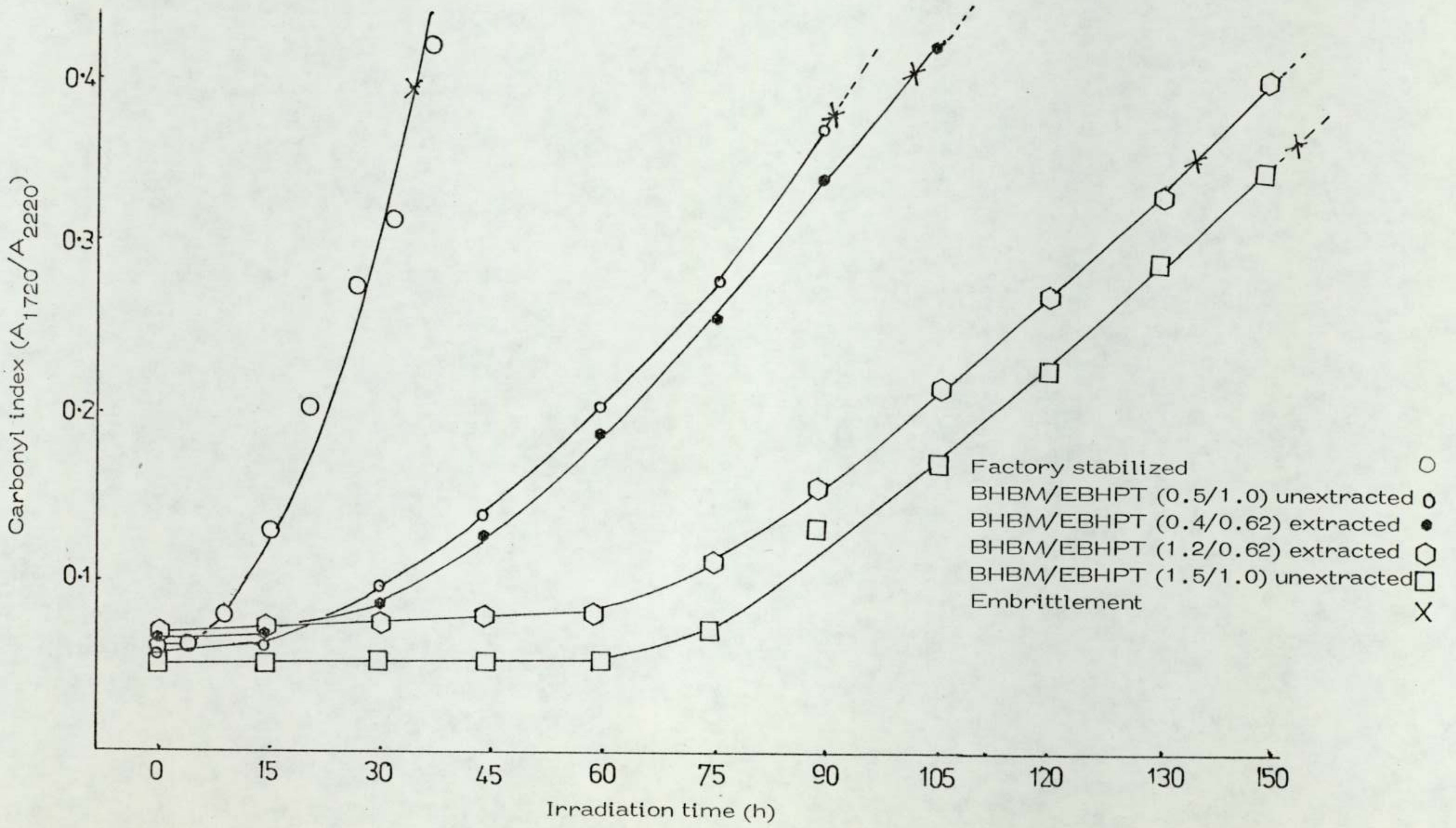


TABLE 29 - INDUCTION PERIODS ON OVEN AGEING IN AIR FOR SAMPLES MADE BY LATEX BLENDING. SAMPLE 1 - 8 REFER TABLE 28

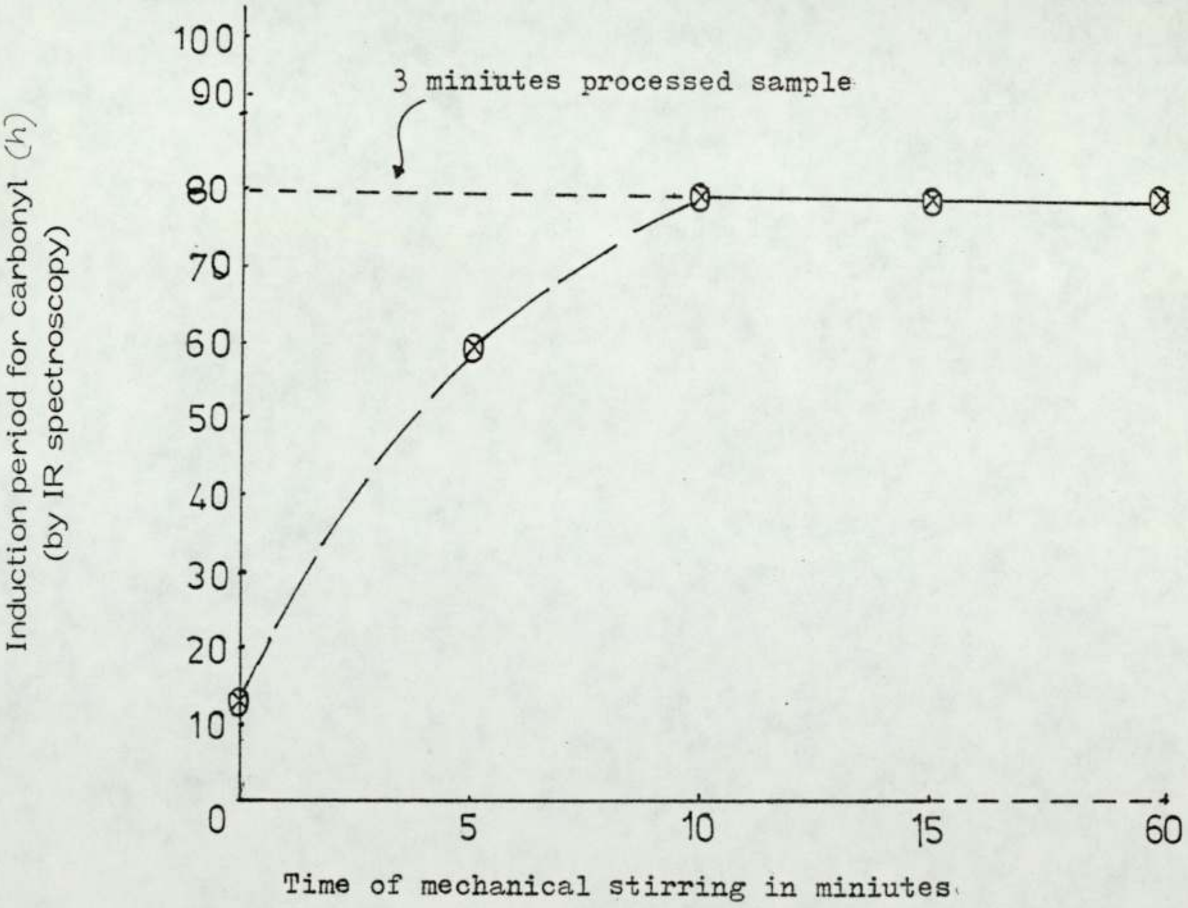
SAMPLE No	INDUCTION PERIOD IN HOURS BEFORE EXTRACTION	INDUCTION PERIOD IN HOURS AFTER EXTRACTION
1	300	225
2	375	300
3	450	400
4	540	490
5	525	475
6	700	600
7	700	600
8	700	600

(iv) No improvement on either thermal oxidative degradation or photoxidative degradation was recorded when EBHPT latex adduct was replaced by the adduct of thio propionic acid derivative of 2-hydroxy 4 β- hydroxy ethoxybenzophenone (EBHPP).

7.5.c. DISCUSSION

The above results were obtained from ABS of latex blends stirred at 220 rpm for a minimum of 10 minutes. The films of ABS powder by directly coagulation of latex blend without any mechanical stirring showed very little stability towards photoxidative degradation. This sample regained its 'expected' stability only on processing in a torque rheometer for 3 minutes at 190°C. Figure 47.

Figure 47. Dependance of photoxidative stability on time of mechanical stirring of latex blend.



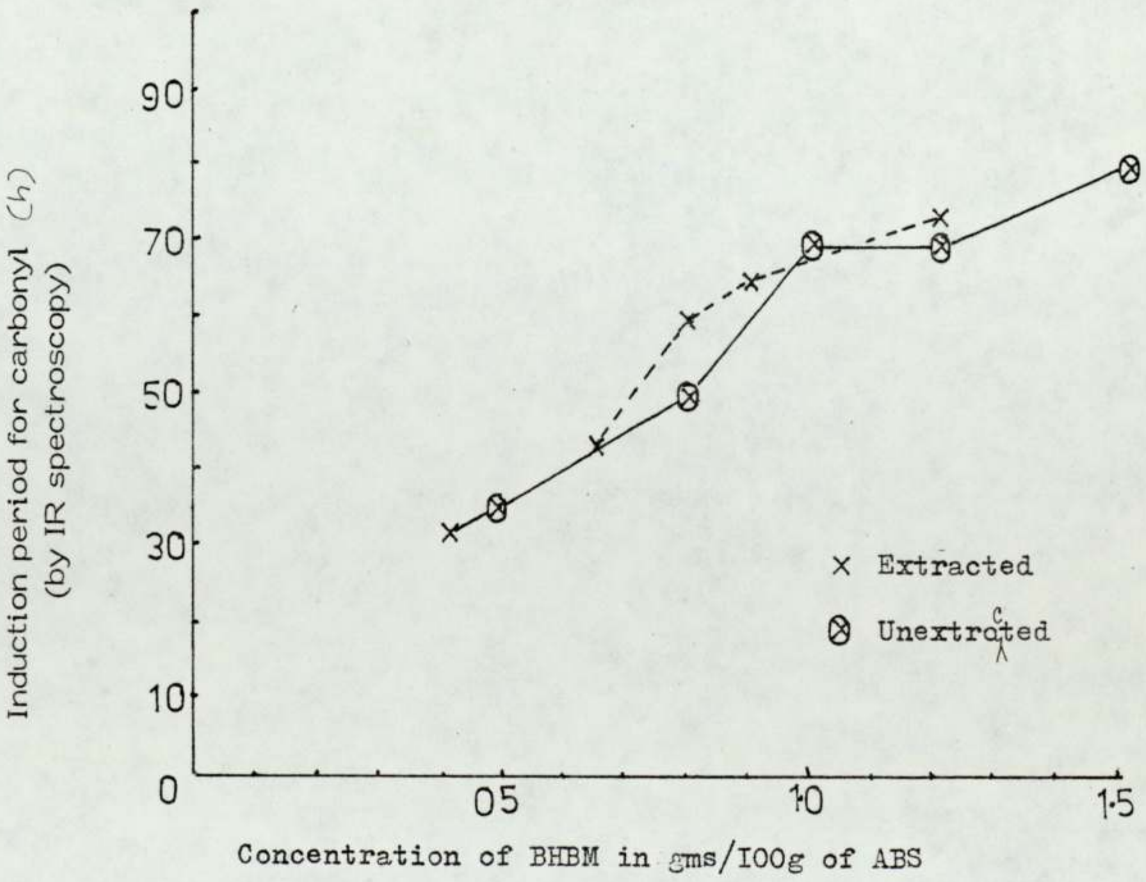
This discrepancy is probably due to the difference in the densities of the adduct ABS. On coagulation, the coagulum usually floats to the surface. If the densities of coagulum in the presence of stabilizers are different, the crumb may take up different positions giving ambiguous results for the final product. Such an ambiguity can be relieved by homogenization of,

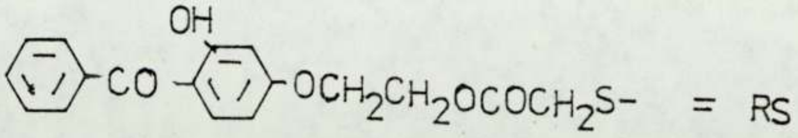
(a) the latex blend on mechanical stirring

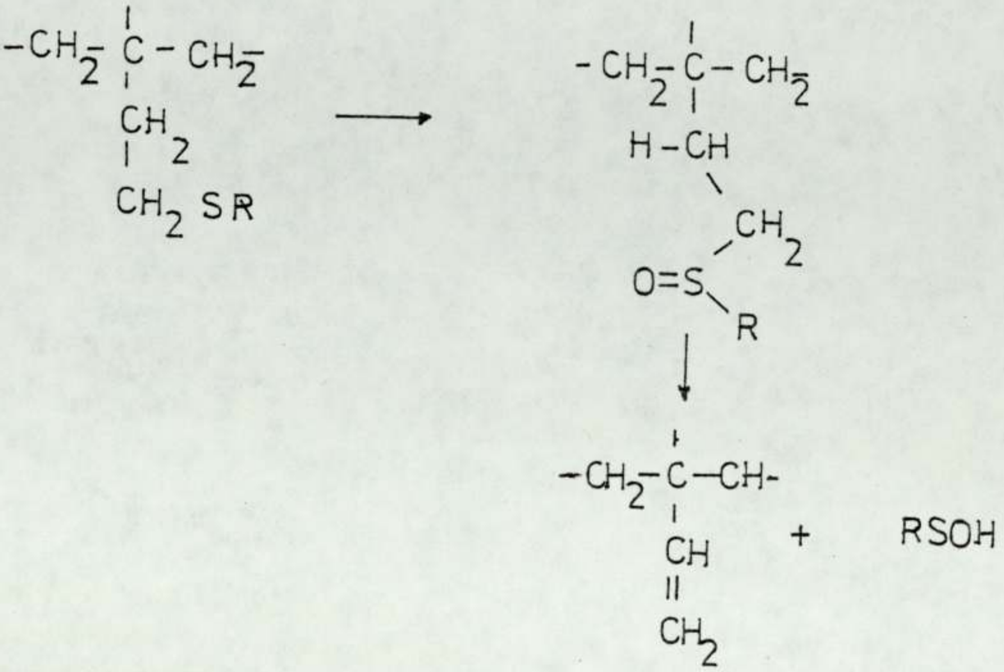
(b) the dry ABS by processing in the melt state

A plot of increase in the concentration of BHBM (bound or unextracted) at constant UV stabilizer concentration, (EBHPT) versus induction period on photoxidation showed almost a linear relationship. Figure 48.

Figure 48. Induction period for the development of carbonyl vs concentration of BHBM (at constant uv stabilser concentration). Refer table 28







$$RSOH + R'OOH \text{ —— } \underset{\substack{\downarrow \\ \text{Initiation}}}{R'\dot{O}} + H_2O + \underset{\substack{\downarrow \\ \text{Inhibition}}}{R\dot{S}O}$$

According to the above mechanism for every two molecules of R'OOH decomposed, an alkoxy radical capable of chain initiation is formed.[87] The chances of neutralization of an alkoxy radical formed, increases in the presence of increased concentration of antioxidant.

7.6. MASTERBATCHING TECHNIQUES

Conventional stabilizers are added either in the latex stage or during the processing of a polymer. An obvious implication of the adduct formation reaction of BHBM and EBHPT with the commercial material is the escalation of the cost of manufacture of the polymer. Therefore, for any future commercial application of this process, such an increase in the cost should be justified by its performance.

The cost of the process can be kept to a minimum if higher than normal amounts of stabilizers can be reacted with a given amount of polymer to form a 'masterbatch', to be diluted in a later stage. Masterbatching of a product is only successful if the performance of the diluted material remains more or less unchanged so as to increase the cost/performance of the overall process, in favour.

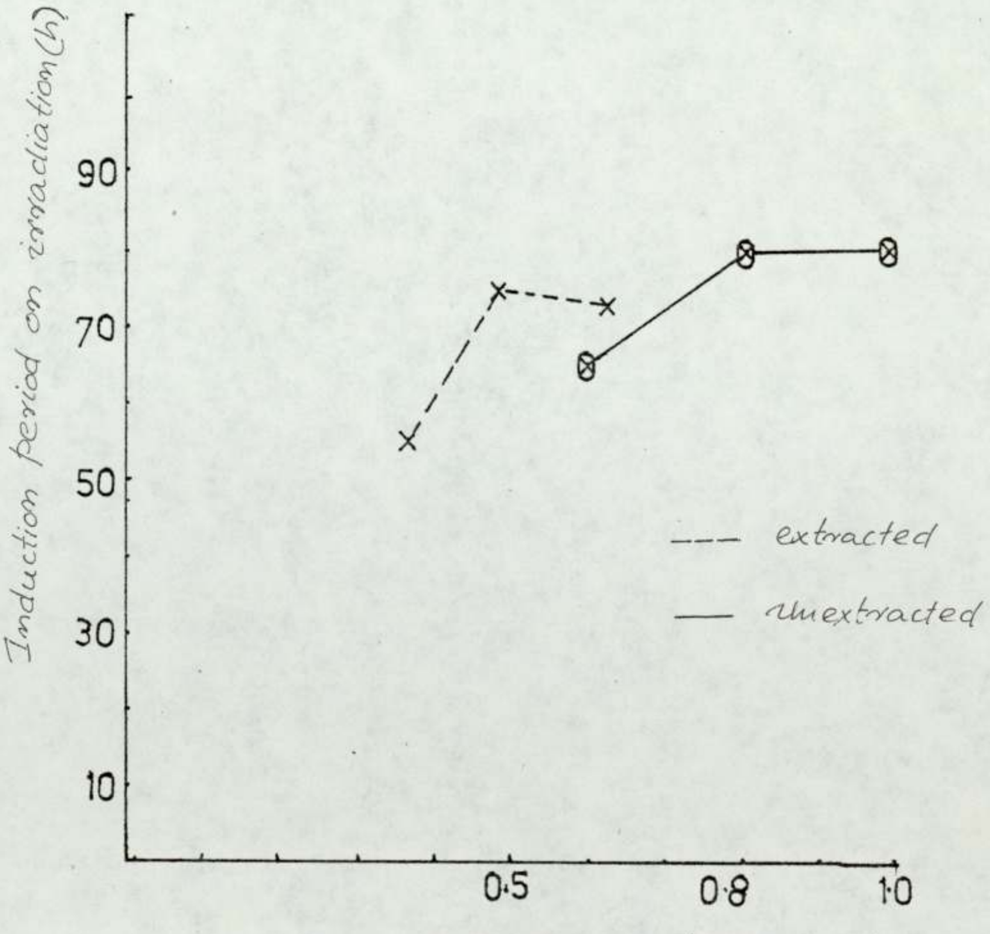
7.6.a. PROCEDURE

The following formulation was used for antioxidant masterbatch formation

ABS latex in ml (stripped 30% dry ABS)	330
Antioxidant BHBM in gms (100 ml solution)	3-10
Distilled water in ml	50
Cumene hydroperoxide in gms	0.8
Fe^{+2} / TSPP solution in ml	8

Similar plots (though only 3 values could be obtained), showed a critical level of EBHPT beyond which no further improvement in the stability of ABS against photoxidative degradation was observed Figure 49. The increase in the efficiency of the system in the presence of antioxidant BHBM, is probably due to the effect of increase in the extent of radical trapping offered by sulfenic acid decomposition products.

Figure 49. Induction period on photo-oxidation of ABS films containing EBHPT as uv stabiliser in the presence of BHBM both as adducts (refer table 28).



Glucose (gm / 10 ml of water)	2
Time in hours	3
Temperature in °C	57
Atmosphere	N_2

The same formulation was used for the UV stabilizer masterbatch formation except that the reaction was conducted at 50°C for 4 hours using unstripped ABS latex. The reaction was carried out at a lower temperature to minimise the possibility of hydrolysis of ester linkage in EBHPT.

The ABS latex and the antioxidant emulsions were purged with nitrogen prior to the reaction. The initiator (oxidant) cumenehydroperoxide and the BHBM emulsion were added in aliquots within the first half of the reaction.

In the case of UV stabilizer EBHPT, the pH of the mixture containing the sodium salt of EBHPT and the latex was adjusted to 9.6 by adding a dilute solution of acetic acid. This mixture was purged with nitrogen before initiation. Cumenehydroperoxide was added in aliquots within the first half of the reaction.

The latices thus obtained were blended with unstabilized latex to give one part of stabilizer per hunded of ABS for the purpose of evaluation of stabilizer performance. The diluted latices were stirred at 220 rpm for 15 minutes before coagulation. The coagulum was dried in a vacuum oven at 55°C to a constant weight. Extraction of ABS wherever necessary was carried out using hexane.

7.6.b. RESULTS

The amounts of bound stabilizer was determined by the methods described in Chapter 2. Before evaluation, the latices were diluted as indicated in the above procedure.

Plots of percentage bound stabilizer versus the initial concentration were made to determine the efficiency of the process (masterbatching) Figure 50 & 5I.

Typical curves for

a) the development of carbonyl

b) the loss of trans 14 unsaturation

c) fall in the impact strength, on UV exposure of ABS films obtained by latex blending and dilution of a masterbatch of 8pph each to 1 pph each are shown in the Figure 52 . On extraction, this sample was found to contain 0.7 pph (377×10^{-3} moles) and 0.60 (1.9×10^{-3} moles) of bound BHBM and EBHPT respectively.

Figure 50. Efficiency of thiol adduct formation at higher than normal concentrations of autioxidaut (BHBM).

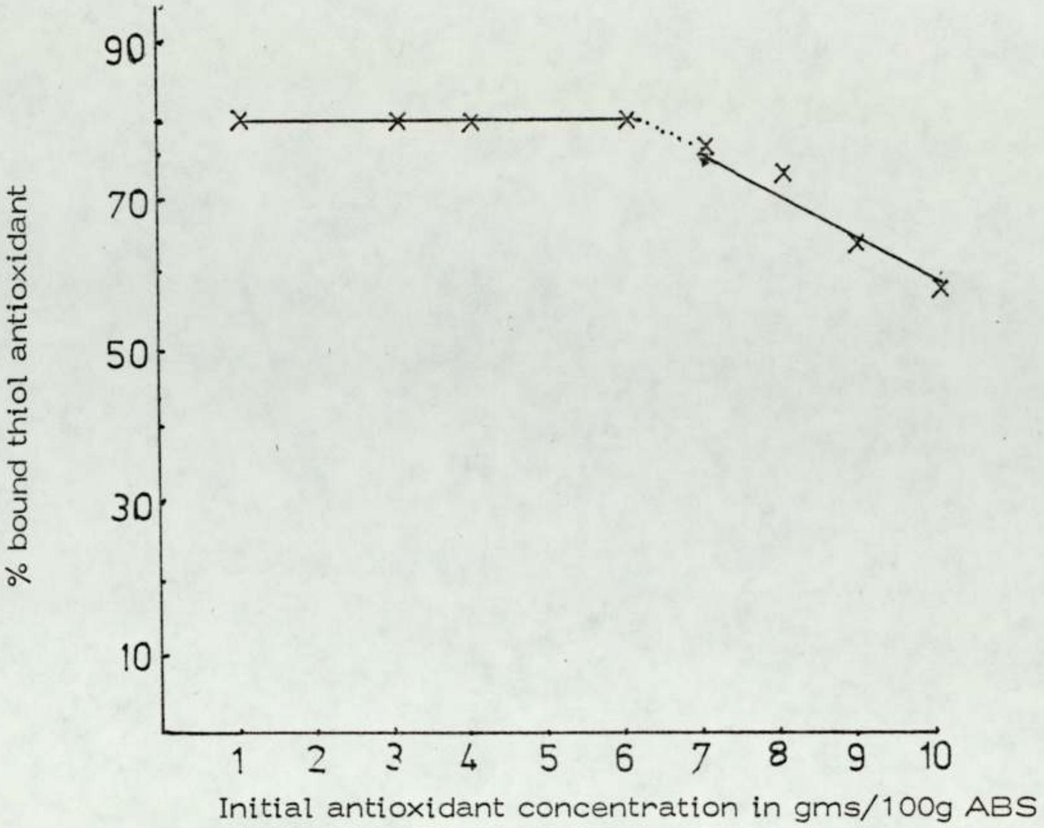


Figure 5I. Efficiency of thiol adduct formation at higher than normal concentration of uv stabilizer.

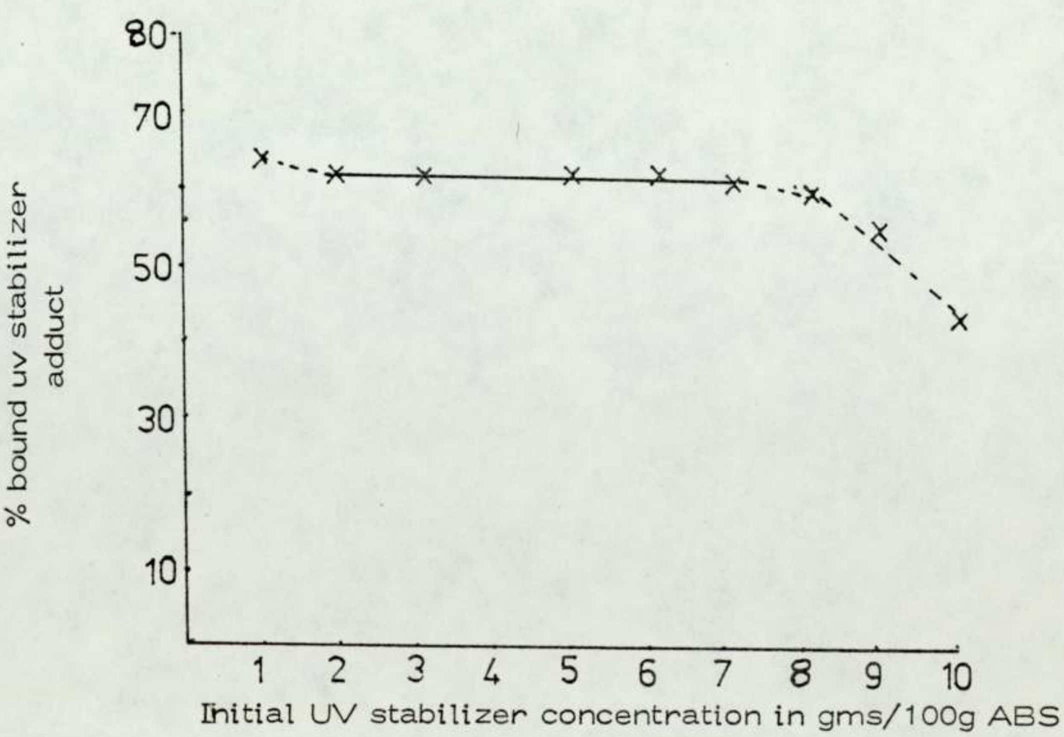
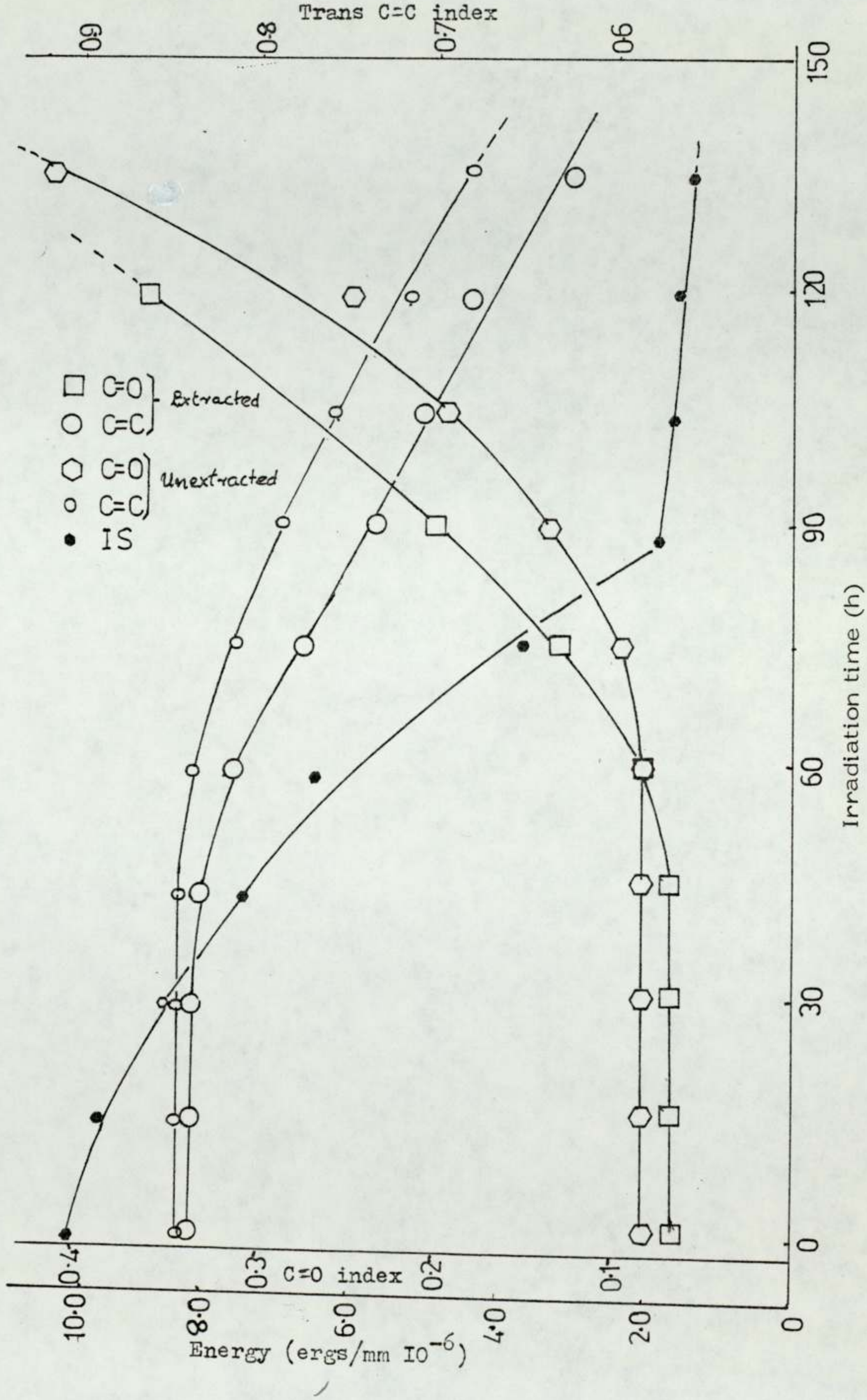


Figure 52. Changes in the functional group indicies (C O & O H by IR spectroscopy) and falling dart impact strength of ABS films obtained by diluting a masterbatch of 8 pph of adduct stabilizers.



Three masterbatches containing 6, 8 and 10 pph of BHBM and EBHPT were diluted with unstabilized latex to give 1 pph of stabilizers respectively. The induction periods and embrittlement times of these samples (unextracted and extracted) are given in Table 30, along with the corresponding values for same concentrations as shown in section 5 of this Chapter.

TABLE 30 - INDUCTION PERIODS AND EMBRITTLEMENT TIMES ON UV EXPOSURE OF ABS PRESSED FILM

SAMPLE No	BEFORE EXTRACTION	AFTER EXTRACTION	IND PERIOD/ EMB TIME IN HOURS UN-EXTRACTED	IND PERIOD/ EMB TIME IN HOURS EXTRACTED
1	1.0 / 1.0 (Table sample 3)	0.8/0.62	70/135	60/130
2	1.0 / 1.0 (Masterbatch 6pph)	0.8/0.62	75/142	62/130
3	1.0 / 1.0 (Masterbatch 8PPh)	0.7/0.60	72/140	58/125
4	1.0 / 1.0 (Masterbatch 10PPh)	0.6/0.43	68/130	53/120

The following samples were sent to Borg-Warner Corporation Laboratories for further evaluation.

Sample A - Masterbatch of 8pph of BHBM adduct diluted to give 1 PPh - (07 pph extracted)

Sample B - Masterbatch of 10 pph of BHBM adduct diluted to give 1 PPh (0.6 pph extracted)

Sample C - Masterbatch of 8 pph each of BHBM and EBHPT adducts diluted to give 1 pph each (0.7 and 0.6 pph of BHBM and EBHPT respectively on extraction).

The following are the results of experiments conducted at the Borg-Warner Laboratories of these samples :-

1. Differential scanning calorimetry.

DSC exotherm	Sample	Start	Peak
	A	233°C	252°C
	B	235°C	253°C
	C	230°C	256°C
	Factory stabilized (Control)	232°C	248°C

DSC isotherm in air at 180°C

Sample A : 80 minutes

B : 60 minutes

C : 79 minutes

Factory stabilized : 20 minutes

2. Oven ageing studies.

Figure 53 shows the development of hydroxyl carbonyl and the loss of 14 unsaturation for cast films of samples A, B and C on thermal ageing in air at 181 °C by infra red spectrometry. Figure 54 illustrates the changes in the functional groups for factory stabilized cycolac resin 211 sample used as the control. The values illustrated in the accompanying Table 31 were obtained with the help of Figures 53 and 54.

TABLE 31 - INDUCTION PERIODS FOR THE DEVELOPMENT OF CARBONYL AND THE LOSS OF 14 UNSATURATION ON THERMAL AGEING OF CAST FILMS OF ABS IN AIR AT 181 °C

SAMPLE	INDUCTION PERIOD IN MINUTES (For the loss of 14 unsaturation 960 cm^{-1})	INDUCTION PERIOD IN MINUTES (Development of carbonyl absorbtion 1720 cm^{-1})
A	190	138
B	130	115
C	180	155
Factory stabilized	19	20

Figure 53 Changes in functional group concentration for films of samples A, B, C, on oven ageing in air at 180°C (by IR spectroscopy)

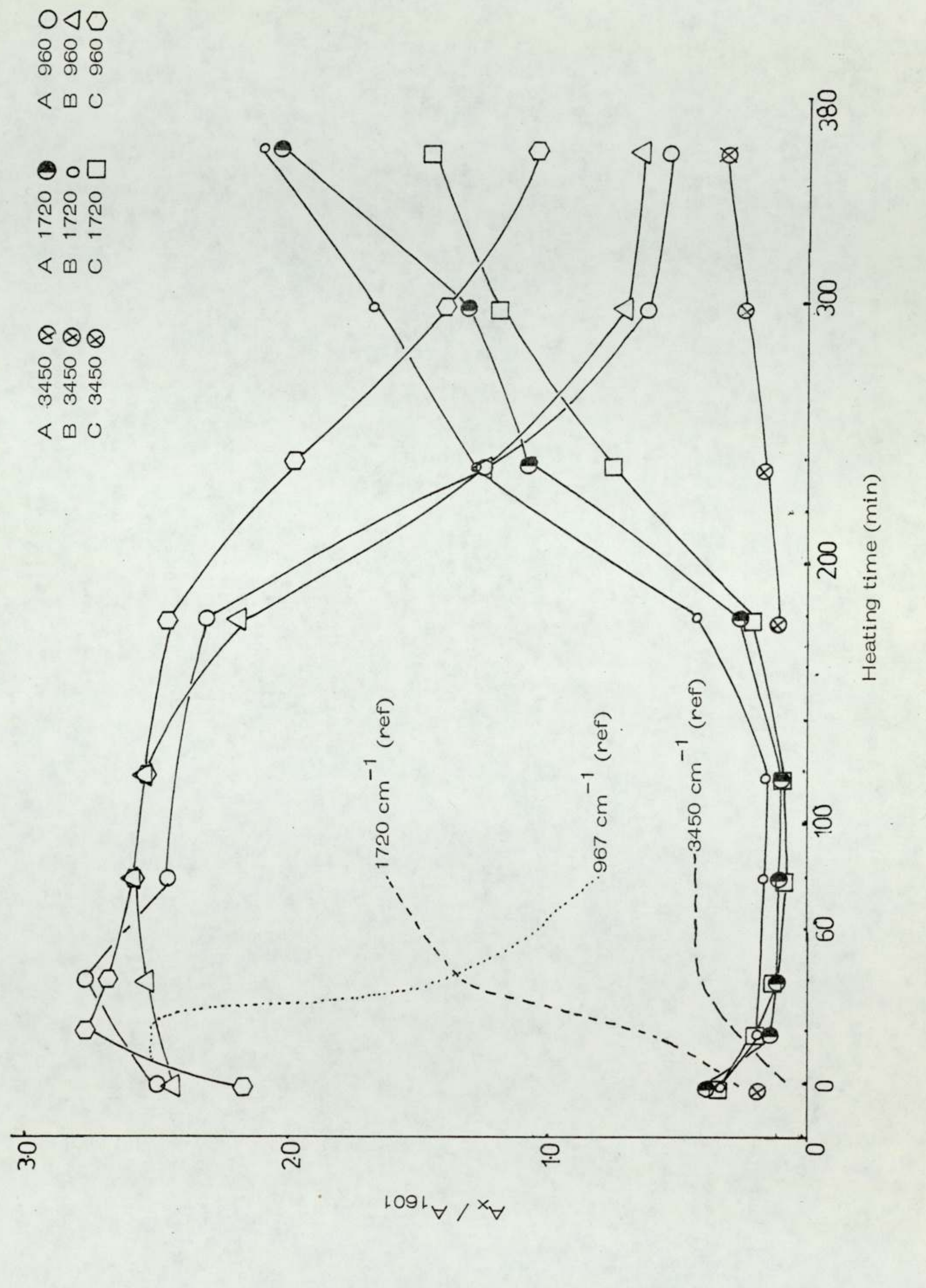
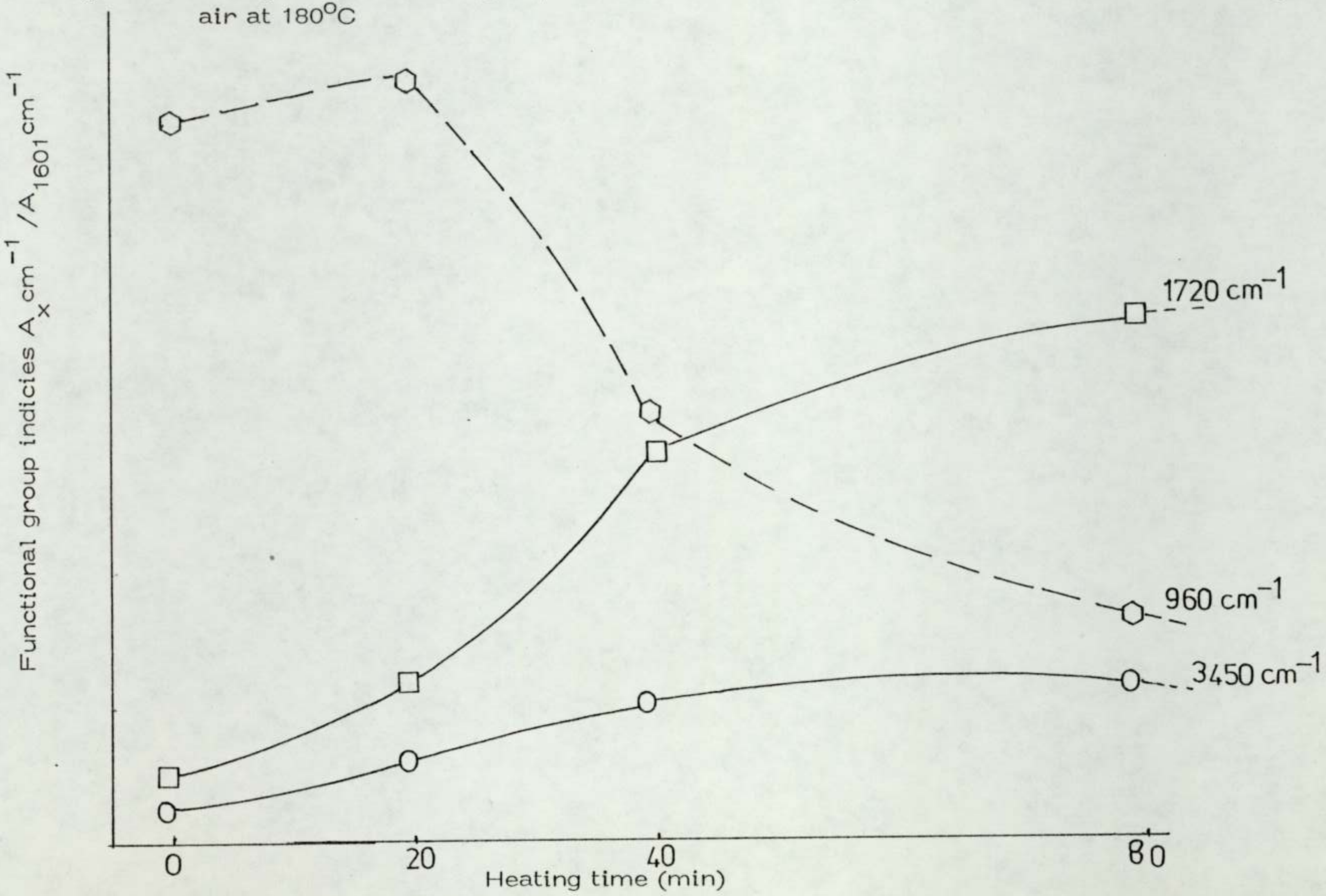


Figure 54 Changes in functional group concentration of factory stabilized ABS films on oven ageing in air at 180°C



3. UV ageing in Xenotest 1200.

(i) The development of visible spectrum on UV ageing of ABS films for samples A, B, and C are given in Figures 55, 56 and 57. These spectra are compared with the reference, factory stabilized cycolac 211 ABS films. The relatively higher degree of absorbtion in the near UV region for sample C is due to the presence of 2-hydroxybenzophenone derivative adduct as the light stabilizer.

(ii) The development of carbonyl, hydroxyl and the loss of 14 trans unsaturation have been studied for samples A, B and C, on UV ageing in Xenotest 1200. The results are given in Figures 58 and 59. The embrittlement times for sample A and B are 150 hours whereas sample C shows much higher stability with an embrittlement time of 330 hours due to the presence of bound UV absorber EBHPT with the antioxidant adduct BHBM.

7.6.c. DISCUSSION

It was observed that the masterbatches of thiol adducts containing up to 8 pph of BHBM and EBHPT, (corresponding to a molar concentration of 3.2×10^{-2} and 2.4×10^{-2} respectively unextracted) can be

Figure 55. Development of visible spectrum on uv ageing of ABS films using Xenotest I200.

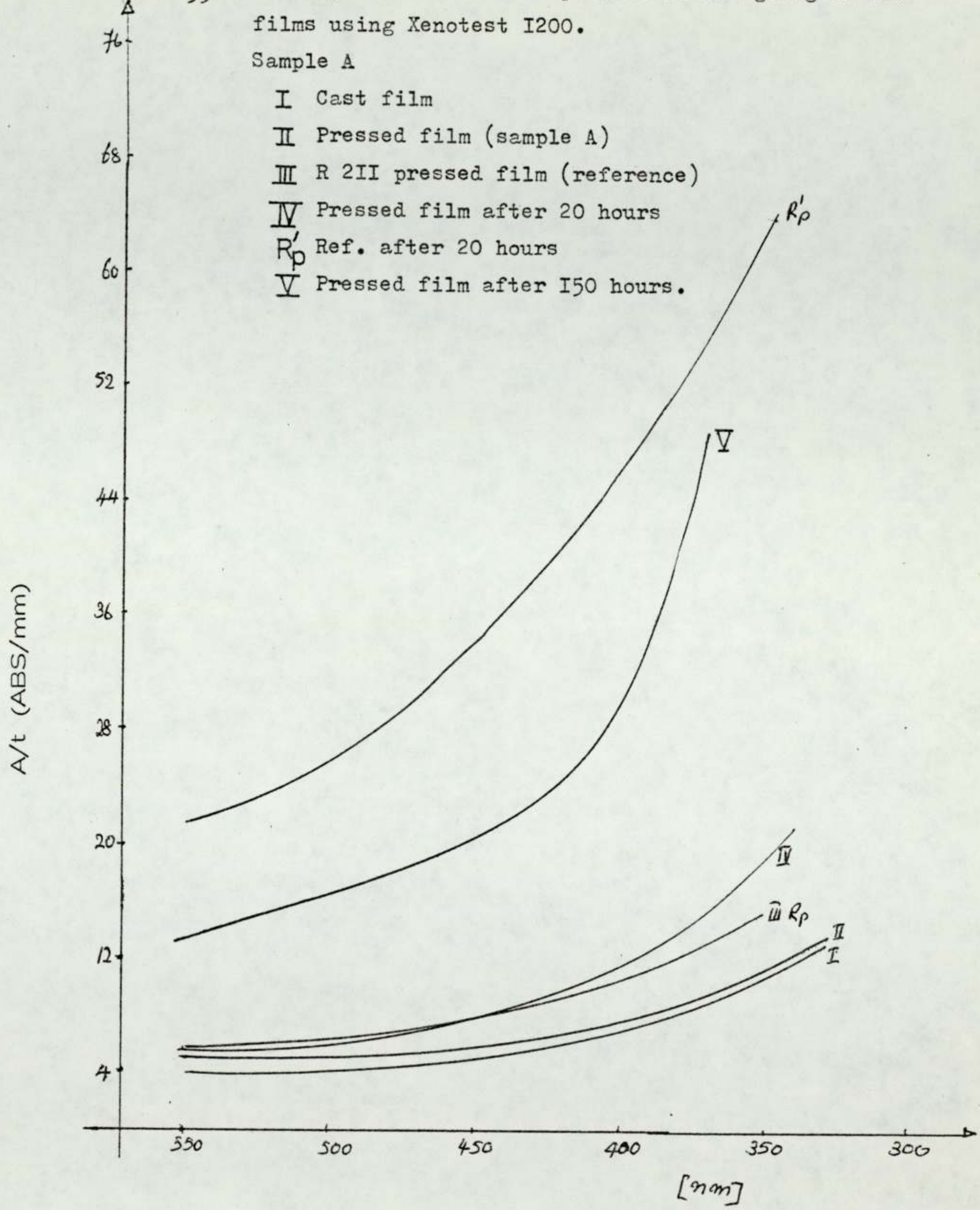


Figure 56. Development of visible spectrum on uv ageing of ABS films using Xenotest I200.

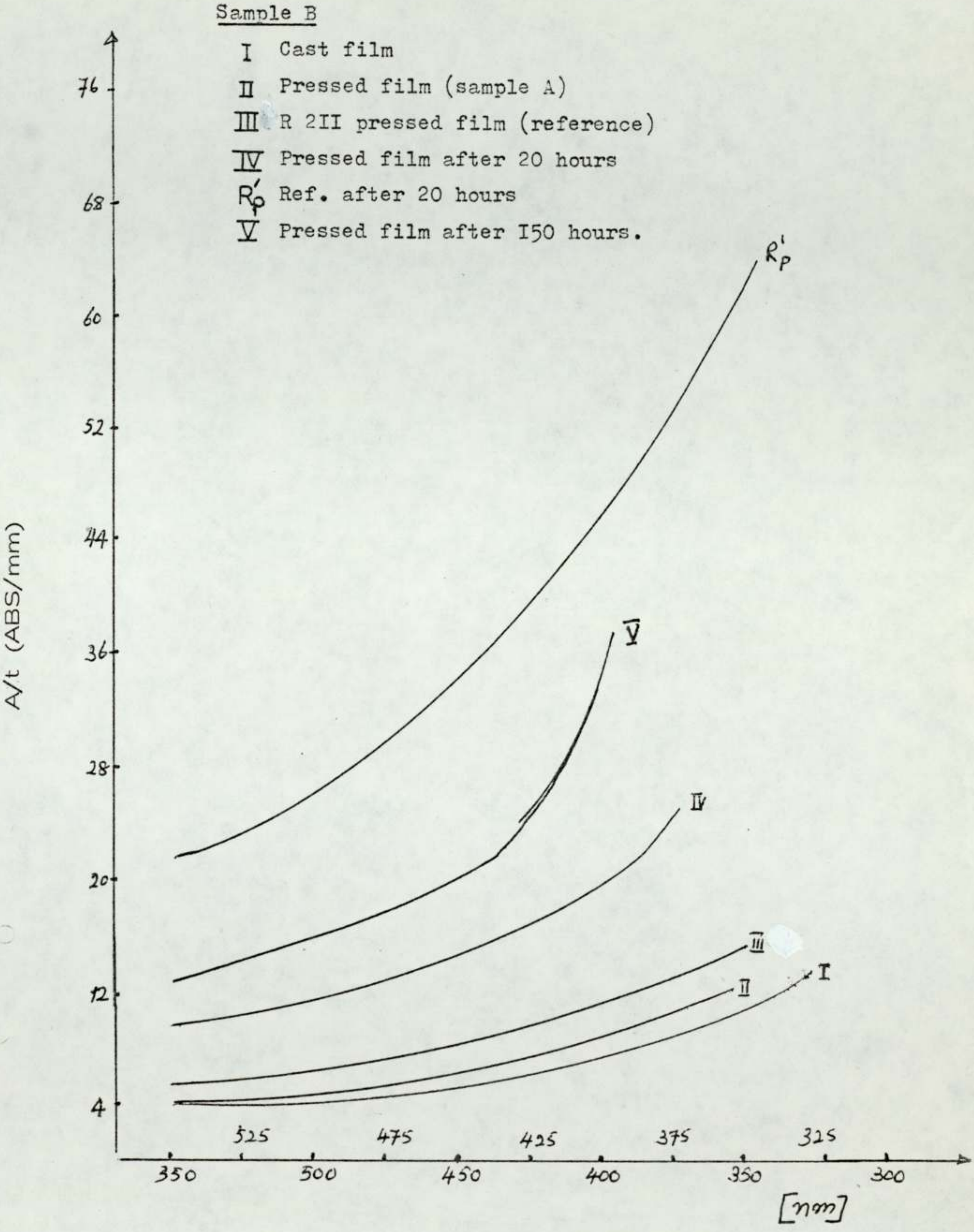


Figure 57. Development of visible spectrum on uv ageing of ABS fims using Xenotest I200.
Sample C

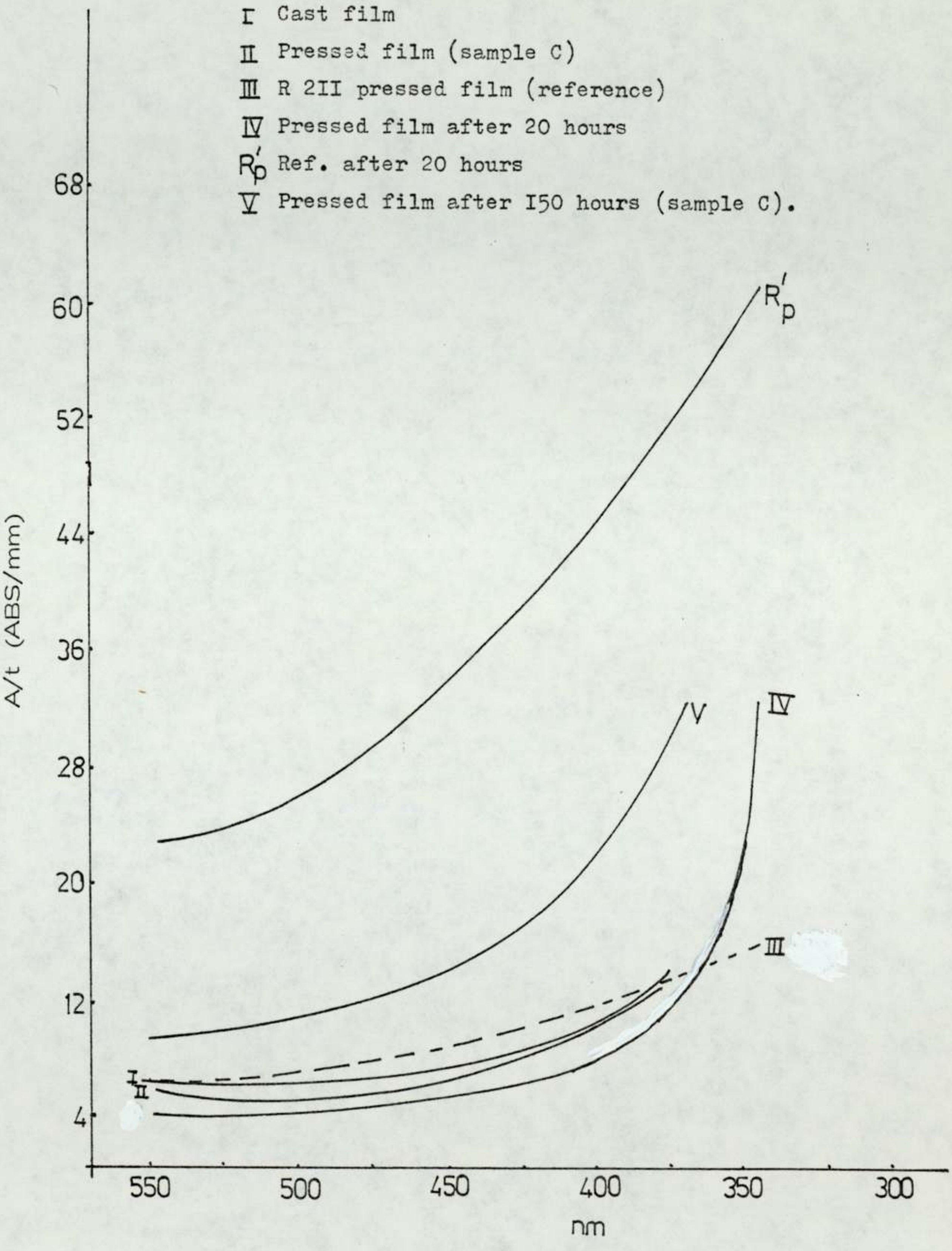
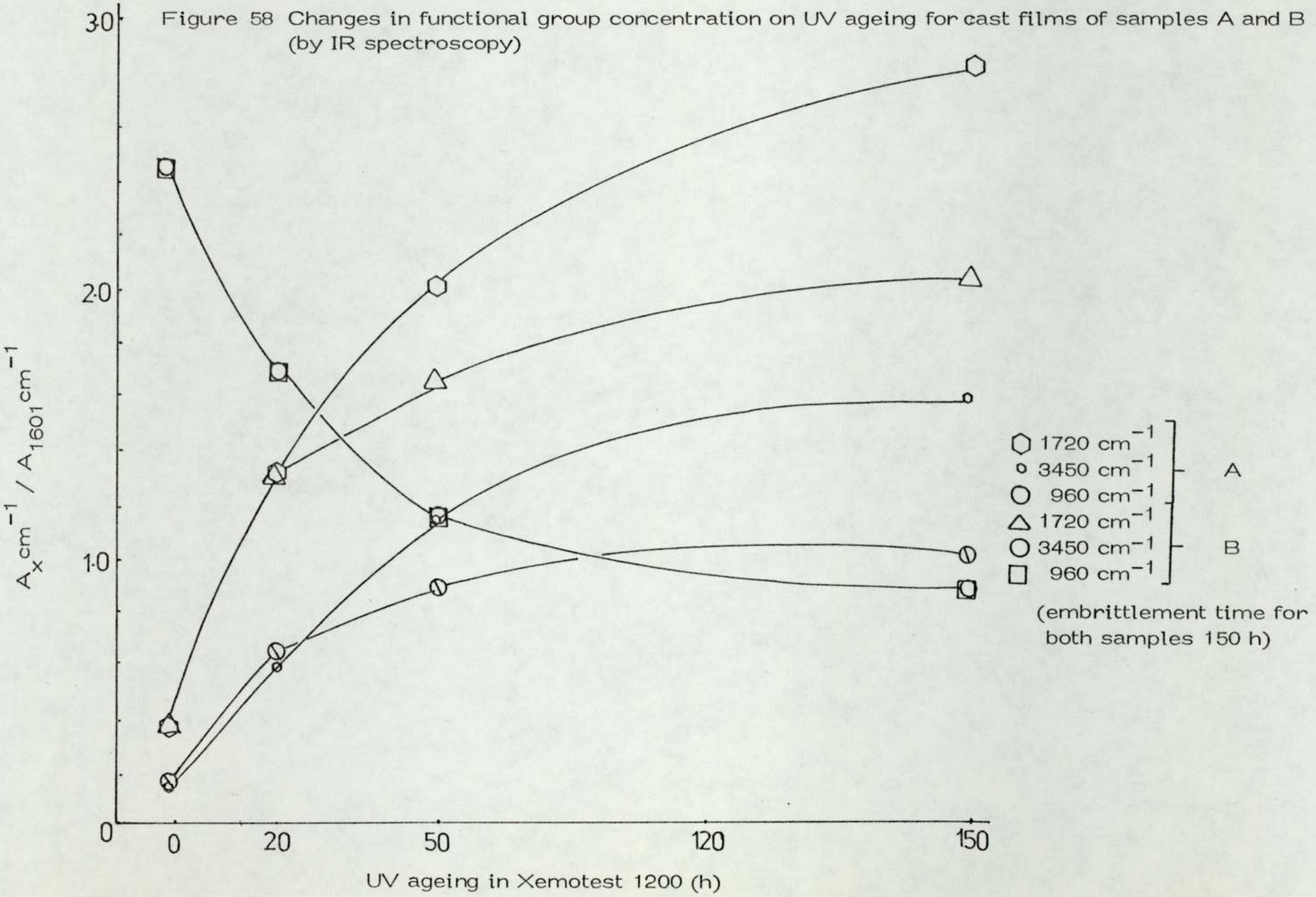


Figure 58 Changes in functional group concentration on UV ageing for cast films of samples A and B (by IR spectroscopy)



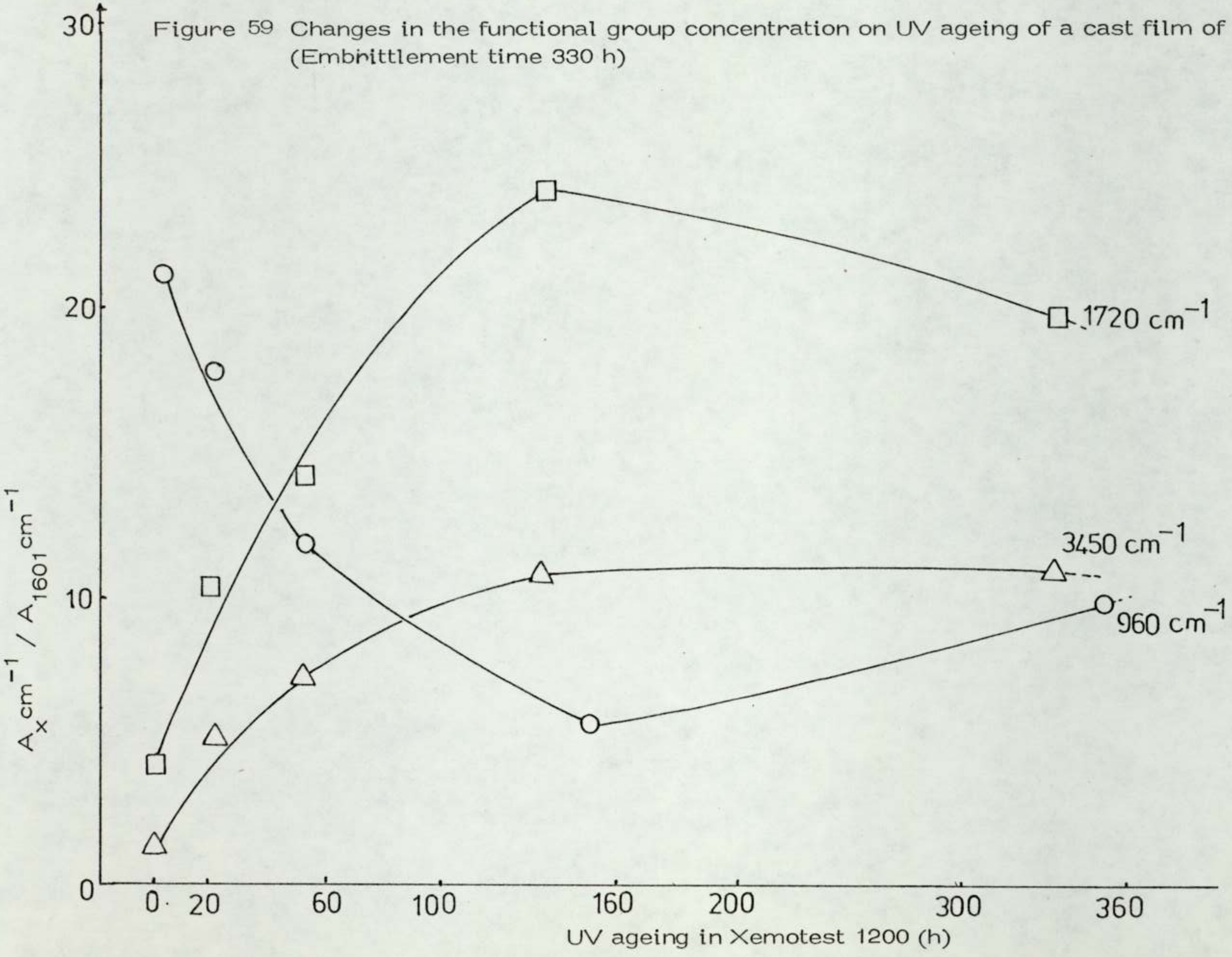
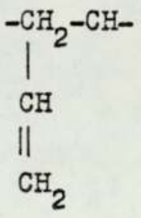


Figure 59 Changes in the functional group concentration on UV ageing of a cast film of sample C
(Embrittlement time 330 h)

reacted with a minimum loss in the yield of bound stabilizer, without either changing the conditions of the reactions or the concentration of other reactants described in Chapter 6, section 5, and section 3 of this Chapter. Furthermore, the performance of these adducts when diluted with unstabilized ABS latex, to obtain stabilizer concentrations for normal applications of the polymer were comparable to those reacted individually at similar concentrations, Table 28 and 30.

The efficiency of the adduct reaction, as well as the stability of the diluted ABS began to fall, for masterbatches containing greater than 8 pph for both stabilizers. The following reasons are suggested for this behaviour by the masterbatch technique.

1. Meyer et al.,[26] in their study of the adduct formation reactions of simple thiols with polybutadiene noted that the oxygen absorbtion of the 'adduct rubber' fell sharply after about 15% saturation of the polymer, Figure 8. This was attributed to the vinyl double bonds of polybutadiene being preferentially saturated at the expense of Cis and trans double bonds of the system probably due to steric reasons. The polybutadiene substrate in ABS contains not less than 10% vinyl double bonds out of the total olefinic unsaturation. This corresponds to a molar concentration of approximately 2.7×10^{-2} moles of



$$-CH_2-\underset{\underset{\displaystyle CH_2}{\|}}{\underset{\displaystyle CH}{|}}{CH}-$$

units per 100 gms of [redacted] 'ABS'. During the masterbatch formation it was observed that 5.6 gms of BHBM corresponding to a molar concentration of 2.24×10^{-2} reacted with ABS. This amounts to almost total saturation of vinyl double bonds in the system, during the adduct formation reaction. Verification of the loss of vinyl double bonds in the system by infra red was not possible due to an overlap of a phenyl group frequency in the spectrum of ABS.

(ii) The yield of adduct formation reaction is also effected due to loss of thiol compounds by side reactions such as peroxide decomposition and oxidation to polysulfides.

The hydroperoxides not only react with free thiols and polysulfides, but also with the bound sulfur derivatives. It was observed (Chapter 4, section 1.a.) that the induction period for the decomposition of hydroperoxides (at the adduct formation reaction temperature) at 57°C was approximately 135 minutes. As the duration of the reaction exceeds the induction period for the decomposition, the loss of free thiol as well as the bound stabilizer in this manner could be considerable.

In addition to the reduction in the yield of adduct formation, the oxidative stabilities of ABS made by diluting masterbatches containing higher than 8 pph of stabilizers, were found to be reduced to a considerable extent. Thus, sample A (from 8 pph masterbatch) showed higher stability towards thermal oxidative ageing than sample B (from 10 pph) as indicated by their DSC and thermal ageing data. Furthermore, sample B after 20 hours exposure to UV showed higher absorbtion in the visible region of the spectrum than sample A, Figures 56 and 57. Similar results were obtained for ABS obtained from masterbatches containing 6, 8 and 10 pph of BHBM and EBHPT, Table 30.

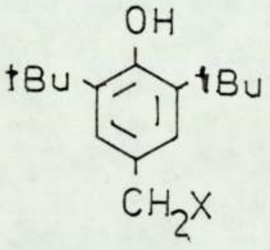
The thermal ageing of samples A, B and C have been carried out at 180°C. At this temperature the loss of stabilizer due to volatilization is considerable. According to Durmis et. al.,[68], the time in hours for 50% loss in the concentration of stabilizer UV 531 (2-hydroxy 4 actyloxy benzophenone) from polypropylene sheet, decreased from 4180 hours at 60°C to 11.5 hours at 120°C. The difference in the stability of the two samples A and B is probably due to the decrease in the amount of bound stabilizer concentration from 75% for sample A to 60% for sample B. Thus, sample B contains 0.15 gms more of unbound antioxidant which could easily evaporate at 180°C, showing a decrease of 60 minutes in the induction period for the loss of 1,4 unsaturation over sample B, Table 31.

The development of absorbtion in the visible region of the spectrum of a polymer is due to either the formation of conjugated carbonyls or conjugated olefinic unsaturation or both. The formation of conjugated carbonyls on oxidative degradation of ABS are explained in Chapter 3.

The lack of the development of visible absorption on UV degration of samples A, B and C compared to the reference, show a considerable improvement in the stability of the polymer towards photoxidative degradation in the presence of sulfur containing stabilizers.

7.7. ADDUCT FORMATION OF BHBM IN THE PRESENCE OF 4 4' AZO BIS (4-CYCANOVALERIC ACID) (AZCV).

The following 3,5 ditert.butyl 4 hydroxybenzyl derivatives were found to inhibit the graft copolymerisation of ABS in the presence of redox initiators.



$X = OH, Cl, SH, OCOCH_2SH,$

$OCOCH{=}CH_2$, SR

Derivatives where x = SH, $OCOCH_2SH$ failed to add across double bonds of polybutadiene component of ABS under redox conditions, till the level of residual styrene was reduced to 0.23% W/V of latex. (Section 2, this Chapter).

The adduct formation of BHBM with ABS in latex also depends on the efficiency of the abstraction H from the thiol group, by peroxy or alkoxy radicals. The formation of thiyl radical should precede the abstraction of hydrogen from the phenol group by peroxy radicals as further reactions of the phenoxy radicals probably inhibit the adduct formation reaction. These reactions of the phenoxy radicals depend on the bond strength of C-X bond and have been discussed in Chapter 6, section 7. It follows from the above discussion that reduction in the level of residual styrene is an effective way of preventing side reactions of phenoxy radicals in the presence of redox initiators.

It was also observed that polymerisation of styrene monomer can be conducted in the presence of 3,5 di*tert* butyl 4 hydroxybenzyl derivatives where X = SH, $OCOCH_2SH$, Cl or OH using AZBN as the initiator. (Chapter 6, section 7). This was attributed to the steric hinderence of the radicals formed from the azo initiator to the abstraction of hydrogen from the phenolic group. Furthermore, when styrene was polymerised with BHBM in the presence of AZBN, the polymer was found to contain the bound stabilizer. This should involve the formation of thiyl radicals from BHBM in the presence of initiator radicals from AZBN.

The use of redox system in the adduct formation reaction with BHBM necessitate a reduction in the residual level of styrene in ABS latex, by mechanical means. If the adduct formation reaction in the presence of BHBM can be carried out using water soluble derivatives of azo bis types of initiators such as 4 4' azo bis (4 cyanovaleric acid) the above step can be bypassed thus, saving considerable time and energy.

7.7.a. PROCEDURE

AZCV was obtained as a 65% active aqueous dispersion from Aldrich Chemicals Limited. The ABS latex Cycolac 211 was used as delivered from Borg Warner Co. without removing the residual monomers (2% W/V of ABS latex).

The following formulation was used for adduct formation reaction.

ABS latex Cycolac 211 (33% dry ABS) in ml.	300
AZCV (65%) in gms.	1
Antioxidant emulsion in ml (1 g BHBM)	100
Time in hours	4
Temperature in °C	63
Atmosphere	N_2

The latex and the antioxidant emulsion was purged with nitrogen before the initiation of the reaction. The initiator was added in aliquots during the first half of the reaction (135 mins) as its sodium salt, made by reacting with a 2% solution of $Na\,H\,CO_3$. The latex obtained was acid coagulated and dried in a vacuum oven at 55°C to a constant weight. For evaluation and estimation of bound BHBM, the reslting polymer was extracted with hexane.

7.7.b. RESULTS

Adducts of up to 70% in yield were obtained by this procedure at an initial concentration of 1 pph of BHBM. The behaviour towards oxidative degradation of the adduct - ABS was quite similar to those obtained with CHP/Fe^{+2} redox initiator system at equal concentrations of the antioxidant. (Section 3, this Chapter). No change in the stability of the synergistic mixtures were observed when this latex was substituted in place of BHBM adduct latex by CHP/Fe^{+2} redox systems for experiments discussed under section 5 of this Chapter, with EBHPT containing latex at similar concentrations.

7.7.c. ANTIOXIDANT MASTERBATCH FORMATION IN THE PRESENCE OF 4 4' AZO BIS (CYANO VALERIC ACID) (AZCV)

7.7.d. PROCEDURE

The formulation described below was used to study the possibility of making masterbatches in the presence of AZCV.

ABS latex (33% dry ABS) in ml	300
Antioxidant (as emulsion in water 100 ml) in gms	2 - 10
AZCV (as sodium salt) in gms	1.2
Time in hours	4
Temp °C	63

For bound stabilizer estimation and evaluation latex masterbatch was diluted with unstabilized latex to give 1 pph concentration of BHBM in ABS. The coagulum was dried and extracted with hexane for estimation purposes.

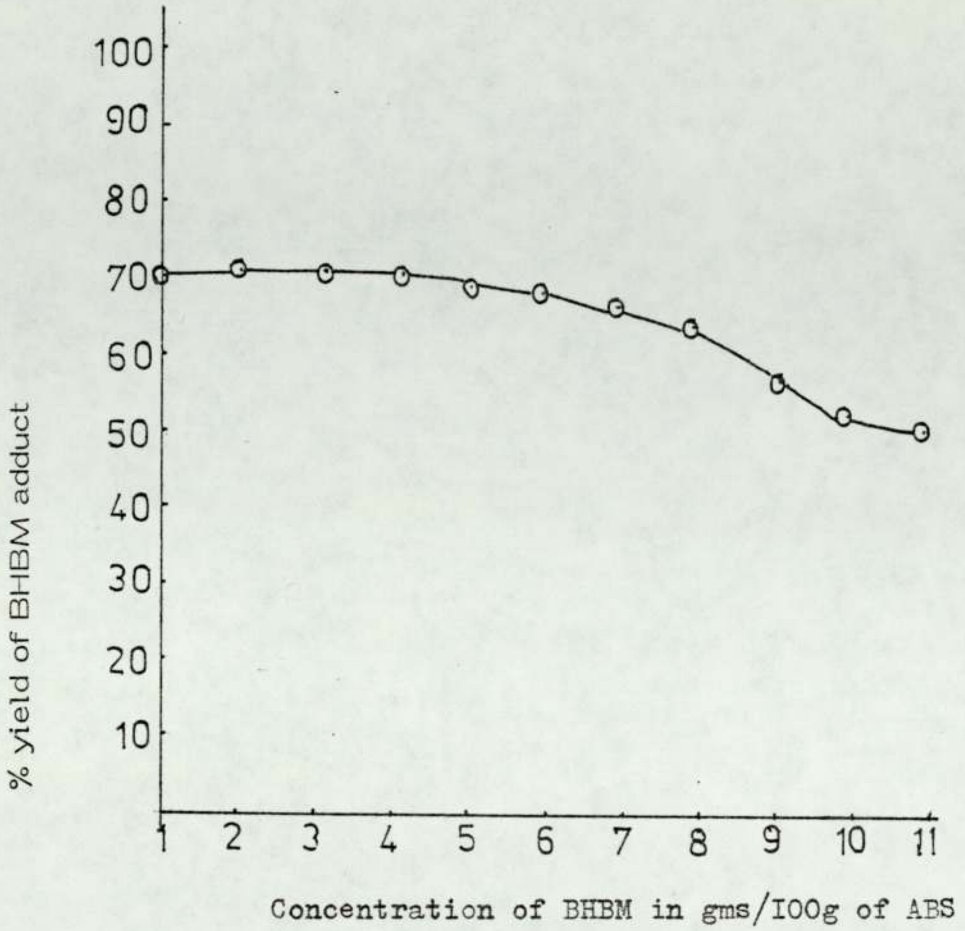
7.7.e. RESULTS

The amount of bound stabilizer was determined by the method described in Chapter 2. Before evaluation, the masterbatch latex was diluted to give 1 pph concentration of BHBM with unstabilized latex and stirred at 220 rpm for 15 minutes prior to coagulation.

Plot of percentage bound stabilizer versus the initial concentration was made to determine the efficiency of the process. Figure 60.

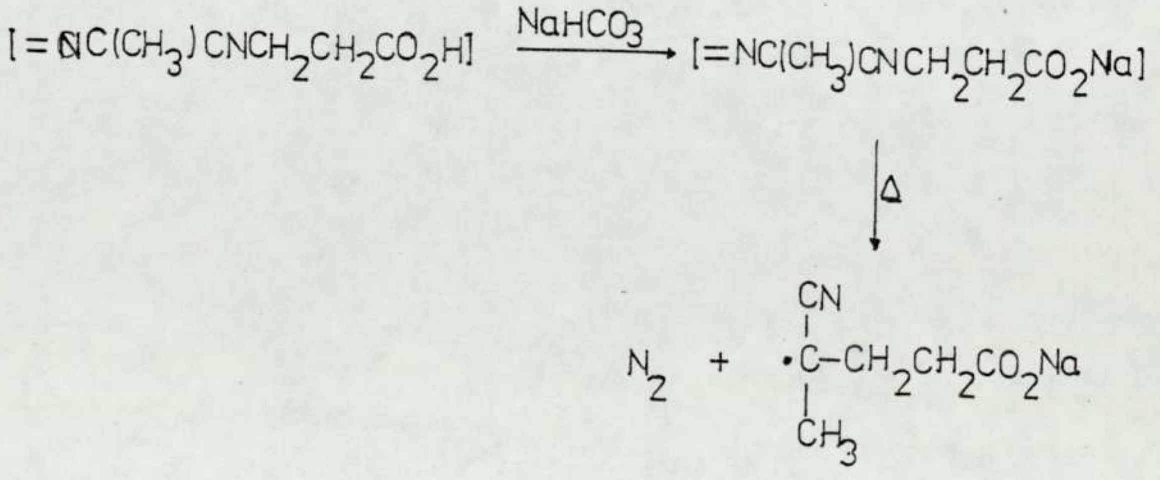
Stability against oxidative degradation was similar to adducts obtained by CHP/Fe^{+2} system at equal concentrations. Synergistic effects similar to those discussed under section 6 were observed when these latices were combined with EBHBT latices.

Figure 60. Efficiency of adduct formation in the presence of AZCV.



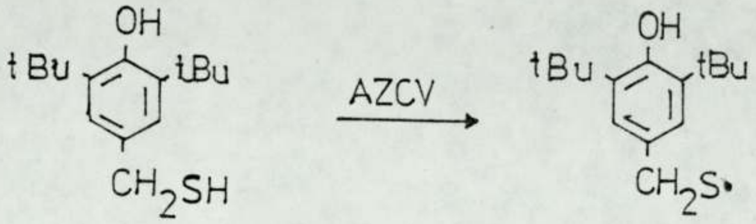
7.7.f. DISCUSSION

The initiator AZCV decomposes to give the two radicals which are very soluble in water.

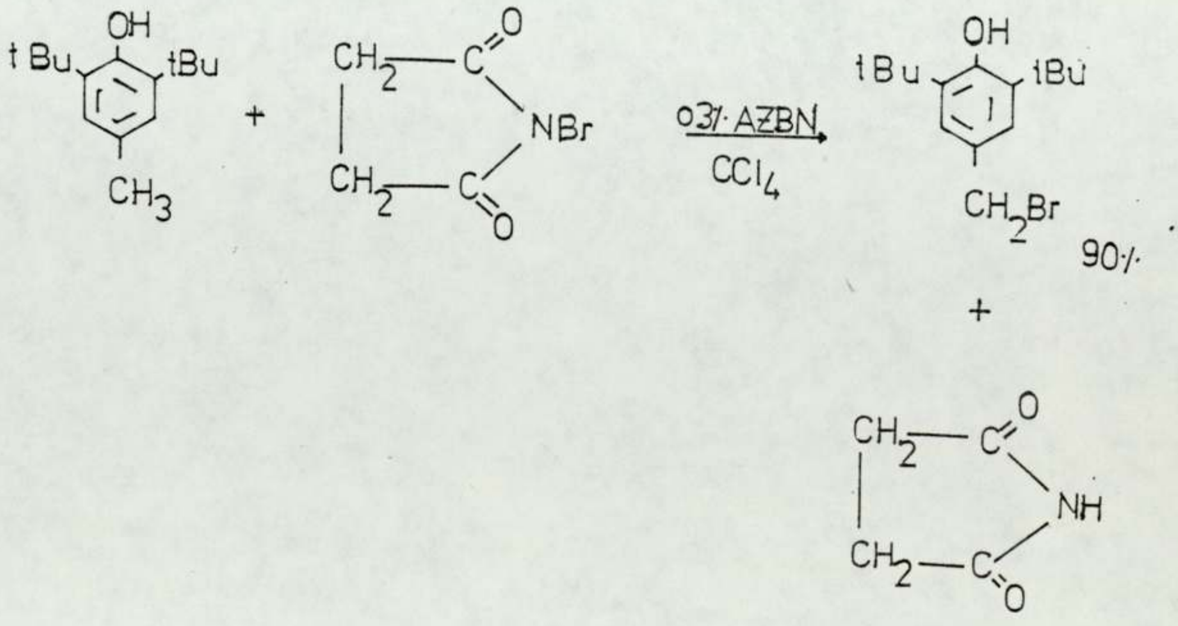


$$[=NC(CH_3)CNCH_2CH_2CO_2H] \xrightarrow{NaHCO_3} [=NC(CH_3)CNCH_2CH_2CO_2Na] \xrightarrow{\Delta} N_2 + \cdot\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2CO_2Na$$

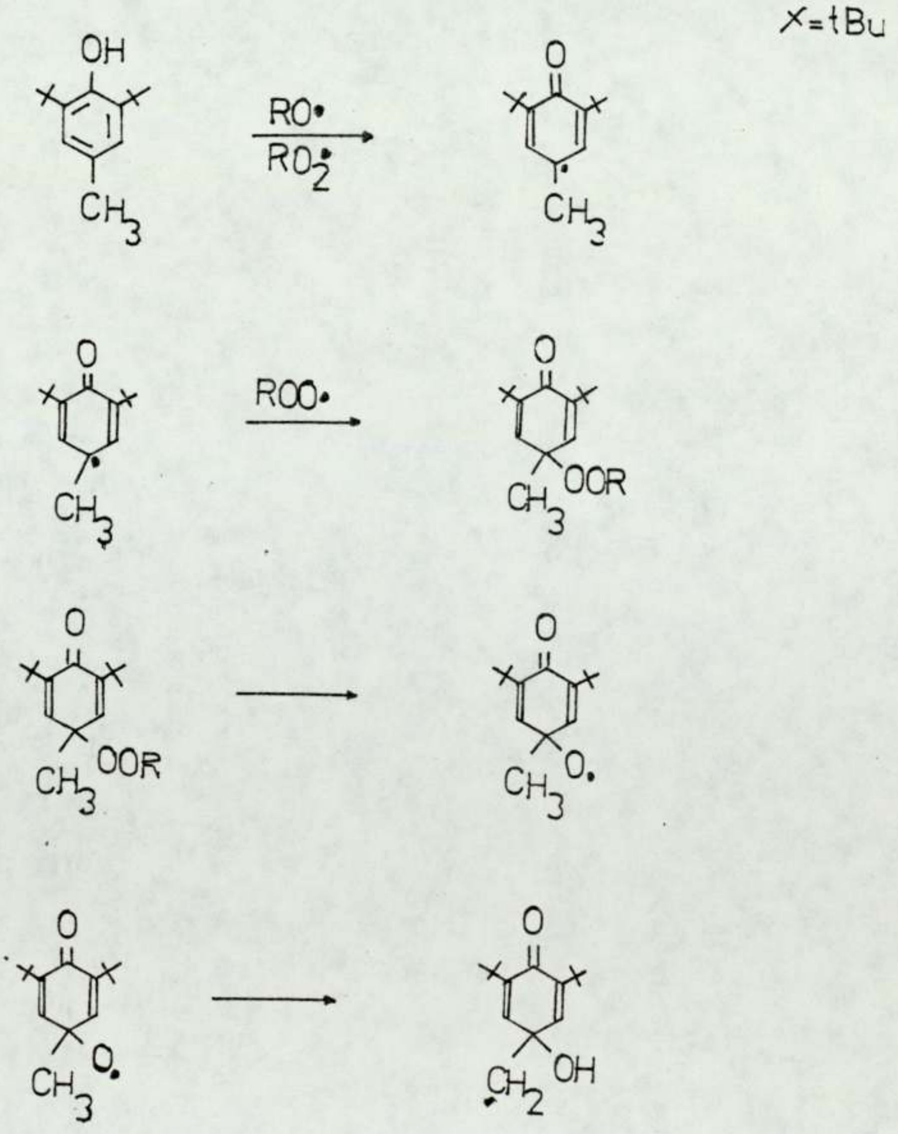
The radicals are probably incapable of hydrogen abstraction from the hindered phenol group due to reasons discussed in Chapter 6, section 9. As a result, the probability of the formation of thiyl radical is much greater, even in the presence of residual monomers.

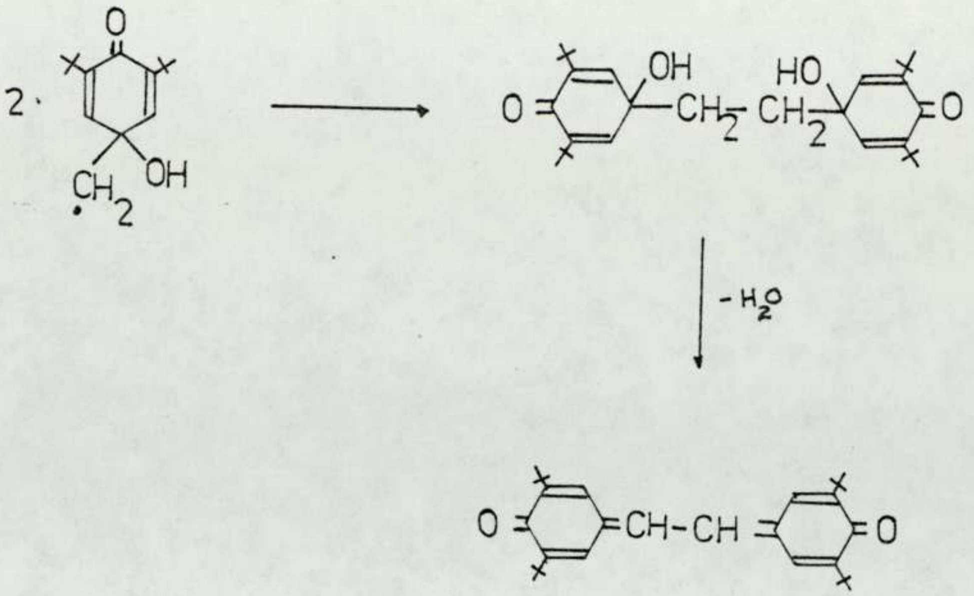


An analogaus reaction was observed during the search for an alternative procedure for the preparation of BHBM. The corresponding benzylbromide was obtained in high yields during the free radical bromination of 2,8 ditert butyl 4 methylphenol using N-Bromosuccinimide when azobisisobutronitrile was the initiator. Chapter 2, section 18a.

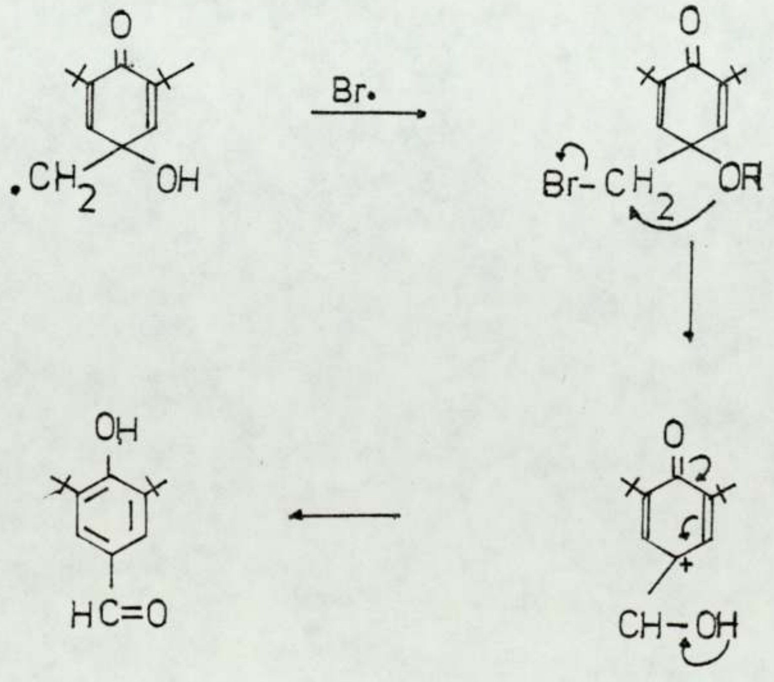


When AZBN was replaced by a peroxide the yield of benzylbromide was quite low (~ 20%). The corresponding benzaldehyde was isolated in 50% yield. The oxidation of 2,6 di*tert*butyl 4 methylpheno in the presence of benzoylperoxide has been used as a general method for the preparation of the corresponding stilbene quinone derivative. Chapter 2, section 17. The following mechanism for the formation of stilbene quinone could help to distinguish the difference in the activities of the two types of initiators.

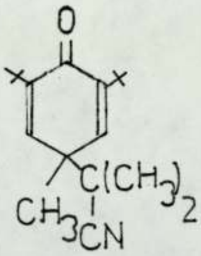




In the presence of Br• radical from N-bromosuccinimide, it is possible to assume the formation of a methylene bromide derivative where bromine being a better leaving group eliminates to form the benzaldehyde.



In the presence of AZBN, even if an intermediate of the type,



is formed, further free radical type reactions similar to those described in the above mechanism are highly unlikely.

CONCLUSIONS

The material characteristics of ABS resin (ie. the tensile strength, elongation impact strength) are closely related to the butadiene content. The deterioration of these properties due to oxidative degradation is caused by the degradation of the polybutadiene moiety of the macromolecules. It is possible to conclude that hydroperoxides are associated with the oxidative degradation of the polybutadiene component of ABS. This component of ABS differs from its copolymers due to

(a) The presence of large numbers of tertiary allylic hydrogen sites introduced during graft copolymerisation.

(b) The presence of C-C linkages (cross-links) between adjacent chains introduced during graft copolymerisation.

(c) The existence of polybutadiene as a continuous chain acting as the basic skeleton.

The introduction of tertiary allylic sites on graft copolymerisation and cross-linking, gives rise to potential allylic tertiary hydroperoxides, decomposition of which to form the carbonyl functional groups, involve the breakage of the basic skeleton viz polybutadiene. This changes the molecular weight and its distribution of the polymer adversely effecting its physical properties.

Therefore, effective stabilization of ABS can only be achieved by protecting the polybutadiene component of the polymer against oxidative degradation. The probable photosensitizers such as transition metal ions and decomposition products of the initiator cumene hydroperoxide, (acetophenone, benzaldehyde etc.) were found to contribute very little towards photoxidation of ABS.

Furthermore, increase in the hydroperoxide levels of unstabilized ABS, determined by iodometry, did not accelerate the degradation of the polymer. It is possible to conclude that the decomposition of these hydroperoxides play a major role in determining the induction period to degradation of the unstabilized polymer.

Additives which act by the decomposition of hydroperoxides such as nickel dibutyl dithiocarbamate (NIDBTC) and phosphites lengthen the induction period to the development of carbonyl functional groups. But these additives failed to slow down the auto-accelerating process of oxidative degradation after the induction period probably due to the destruction of the stabilizers during the initial stages of photo-oxidation. Similar effects were observed for radical traps such as hindered amines and ultra violet absorbers.

Introduction of sulfur containing derivatives of hindered phenols such as bis (3,5 di tert-butyl-4-hydroxybenzyl) mono sulfide (TBMP) capable of hydroperoxide decomposition, in addition to acting as a chain breaking antioxidant, not only lengthen the induction period, but also slowed down the autoaccelerating process of the oxidative degradation. Similar effects were observed from mercapto derivatives of 2-hydroxy benzophenones. Furthermore, synergistic effects were observed on photo-oxidation of stabilized ABS in the presence of TBMP and mercapto derivatives of 2-hydroxy benzophenone.

The attempts to obtain bound stabilizer systems using olefinically unsaturated derivatives of hindered phenol antioxidants and 2-hydroxy benzophenone were unsuccessful. This was attributed to the failure of these derivatives to migrate through the aqueous phase to the reaction loci during the graft co-polymerisation reaction.

The mercapto derivatives, 3,5 di <u>tert</u>-butyl-4-hydroxy-benzyl-mercaptan (BHBM) and thio acid esters of 2-hydroxy- 4(β- hydroxy-ethoxy) benzophenone have been bound to ABS through the thiol group by free radical addition to the double bond. The antioxidant BHBM was found to inhibit adduct formation in the presence of residual monomer (styrene) remaining from the polymer manufacture. This has been overcome by

(a) reducing the residual monomer level (styrene) to 0.23% W/V of ABS latex by mechanical means

(b) by using a water soluble azo-type initiator.

It was observed that azo-bis 4 4' cyanovaleric acid was suitable for this process. Homopolymerisations of styrene and acrylonitrile were studied in the presence of 3,5 ditert butyl-4-hydroxy benzyl derivatives in order to investigate the mechanism of inhibition of adduct formation by BHBM. It was attributed to the reactions of initiator radicals with the oxidation products derived from the antioxidant.

The thio acid ester derivatives of UV absorbers did not inhibit the adduct formation. It was observed that their sodium salts promoted the reaction at a pH below 9.7. This was attributed to the faster rate of diffusion of the reactant under alkaline conditions of the reaction.

These antioxidant and UV stabilizer adducts were effective thermal and photo-oxidative stabilizers for ABS and their effectiveness was not modified by solvent extraction of the polymer. Furthermore, ABS obtained by mixing these latices containing the adducts showed synergistic behaviour towards photo-oxidation.

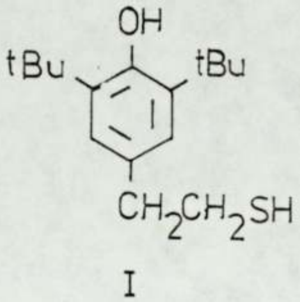
It was found that latex bound antioxidants and UV stabilizers could be produced in concentrated forms and that these, when diluted into normal concentration with unstabilized ABS were as effective as those obtained by reacting with the total latices at lower concentrations. The diluted ABS was not modified by solvent extraction of the polymer. These also showed synergistic behaviour towards photo-oxidation.

The antioxidant masterbatches were prepared by using a) CHP/Fe^{+2} redox system in the presence of stripped ABS latex and b) AZCV initiator in unmodified ABS latex. Both systems were found to be equally effective to adduct formation, and yields of up to 70% were observed for these reactions. The UV stabilizer masterbatches on the other hand, were made by CHP/Fe^{+2} redox system using unmodified Cycolac 211 type of ABS latex.

SUGGESTIONS FOR FURTHER WORK

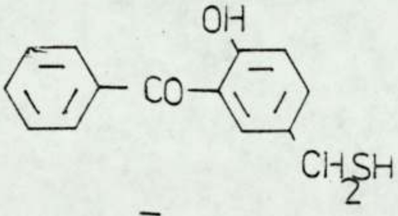
The evidence presented in this thesis for the behaviour of thiol adducts in ABS on oxidation has been based on the measurement of the development and the decay of functional groups (carbonyl, hydroxy and trans 1,4 polybutadiene unsaturation) by infra-red spectrometry. Confirmation of these observations, using other physical measurements such as impact, and tensile strength measurements are necessary for any possible future applications. Furthermore, the performance of the thiol adducts in the presence of various compounding ingredients such as TiO_2 has to be investigated.

It was observed that the antioxidant mercaptan 3,5-di*tert*-butyl-4-hydroxybenzyl-mercaptan tended to inhibit the adduct formation reaction in the presence of residual amounts of styrene under redox conditions. The weakening of the C-S bond in the molecule due to the electron affinity of the benzene ring and the electro-negativity of the sulfur atom was found to promote the side reactions observed during the inhibition. Therefore, it is suggested that attempts should be made to synthesise an antioxidant derivative with the following structure (I) for possible adduct formation without inhibition.

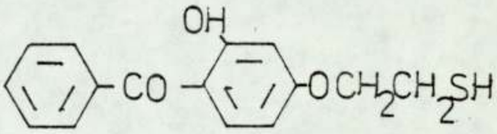


I

The maximum yield obtained on adduct formation of mercapto derivatives of UV stabilizer with ABS in latex was approximately 65% Loss of about 14% in the yield of bound stabilizers has been attributed to the possibility of hydrolysis of the ester linkage of the molecule, under the alkaline conditions of the reaction. Therefore, the systhesis of the following mercapto derivatives of 2-hydroxy benzophenones are suggested, to improve the yield of bound stabilizer by preventing the loss due to hydrolysis.

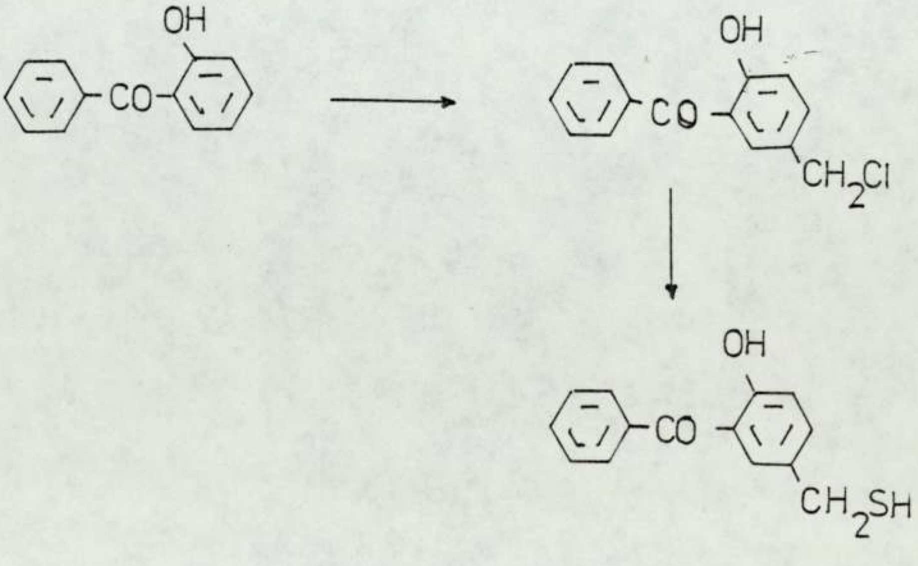


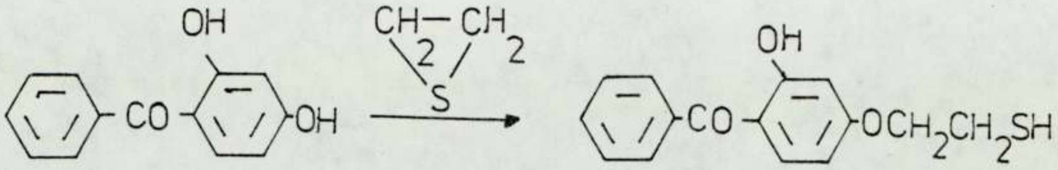
II



III

It may be possible to prepare compounds II and III by the following reactions :-





Chemical analysis for polymer hydroperoxides in unstabilized ABS show a 5 fold increase in concentration, on fluid bed drying of the polymer compared to drying in a vacuum oven. The possibility of the use of these hydroperoxides as initiators for adduct formation of thiol stabilizers in the melt, under processing conditions should be explored. The rate of decomposition of such hydroperoxide would be possible to control to suit the processing conditions by the use of suitable reductants such as polyamines.

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