A STUDY OF THE ROLE OF HYDROPEROXIDES IN THE DEGRADATION AND STABILISATION OF POLYMERS

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The photo-degradation mechanism of polyethylene was studied by means of functional group analysis using infrared spectroscopy. The rates of appearance and disappearance of key functional groups such as hydroperoxide, carbonyl, vinylidene and vinyl formed during the photoxidation of the polymer were studied and compared.

The effect of metal complexes which are supposed to be effective photoactivators for the autoxidation of polyethylene was also studied. The efficiency of these complexes as well as nitrobenzene, and plant pigments as photoactivators in the autoxidation of natural rubber was looked into. The mechanism of action of nitrobenzene in natural rubber was found to be due to the generation of singlet oxygen; the latter causing depolymerisation of the polymer. The technological properties of the soft and viscid products thus obtained were also studied.

Hydroperoxides

Singlet oxygen
Photo-degradation

Photo-activators

Depolymerisation

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1. INTRODUCTION

Polymers in general undergo deterioration during service, losing their useful chemical and physical properties. The rate of such degradation processes depends on the chemical structure, the presence of trace impurities in the polymer and on the environment.

Impurities that promote deterioration can be foreign materials, such as metal ions from polymerisation catalysts, or they can be an integral part of the polymer molecules such as partially degraded molecules, which are a common impurity in polymers and these modified molecules are mainly responsible for the initiation of the deterioration. Traces of these impurities have a pronounced effect on polymer stability. Although pure paraffins are transparent to visible and near UV light penetrating the atmosphere, chromophores are nearly always present in the polyolefins, as impurities introduced during pressing, twisting or sheeting out operations. These include oxidation products (eg. carbonyl compounds and hydroperoxides) or even oxygen substrate complexes. Consequently, the UV light may be absorbed Which Cause its accelerating action on the oxidation rate. Most of the harmful radiations emitted by the sun are absorbed by the atmosphere, and only about 5% of this harmful energy reaches the earth. This includes the UV region of the spectrum, 300 to 400 nm, and it is this fraction that causes polymer degradation, through chromophores present in them.

The stability of polymers is also dependent on the physical structure or morphology[2] of them.

The effect of physical structure is related to the arrangement of molecules, in ordered (crystalline) and disordered (amorphous) regions of the polymer matrix. Many polymers are semicrystalline and thus have both ordered and disordered regions. The density of an individual polymer is directly related to its degree of crystallinity. This is modified in many instances by annealing, crosslinking and deterioration. Factors affecting permeability of polymers have an important effect on deterioration. As deterioration proceeds, diffusion of volatile products out of the polymer mass and progressive changes in morphology can reduce the rate at which the reactants like oxygen and ozone diffuse into the polymer. Thus deterioration or rate of oxidation of a polymer becomes diffusion controlled in later stages of the reaction although it is not so initially. Permeability of reactants, like oxygen into the polymer matrix varies with the degree of crystallinity and compactness of amorphous and crystalline regions. Studies of the deterioration of linear and branched polyethylenes above their melting points (140°C) has[5,6,7,8] shown that they are completely disordered at these temperatures and differences in crystallinity evident in the solid state have no effect.

1.1 Thermal-Oxidative Effects in Polymer Deterioration

The chemical sequence involved in the oxidation of polymers under processing conditions is now well understood[1,2]. Autoxidation of polymers that takes place between room temperature and about 300°C proceeds by a typical free radical chain mechanism. Hydroperoxides are the first products formed during the autoxidation of polymers and the well known auto-accelerating behaviour is due to their increasing concentration[4,33,36]. Hydroperoxides have proved in general are difficult to isolate and in many cases their structure can be inferred only from the nature of their breakdown products[4]. Recognition of the peroxides as the key intermediate in autoxidation leads to a clear understanding of the mechanism of this process. On this basis the following kinetic scheme has been proposed[1,114] to account for the autoxidation of low molecular weight hydrocarbons.

$\text{Initiator} \longrightarrow X^{\cdot}$ Initiation

$X^{\cdot} + RH \longrightarrow R^{\cdot} + XH$

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$

Propagation

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$

$ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}$

$RO^{\cdot} + RH \longrightarrow ROH + H^{\cdot}$ Chain branching

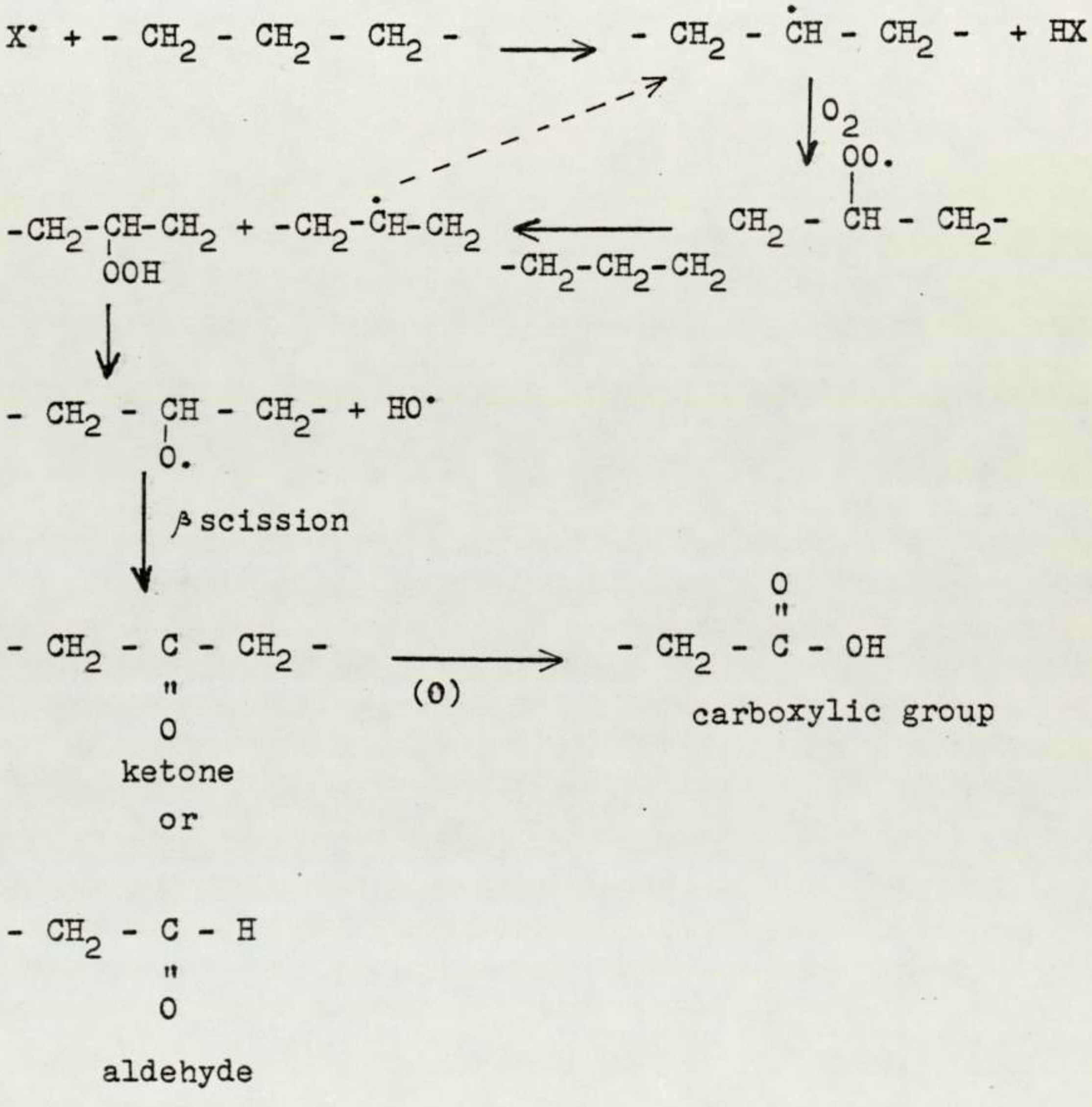
$HO^{\cdot} + RH \longrightarrow HOH + R^{\cdot}$

$2ROO^{\cdot} \longrightarrow \text{Inert Products}$ ____ Termination

$ROO^{\cdot} + HA \longrightarrow ROOH + A^{\cdot}$ ____ Inhibition

This scheme clearly indicates the role of hydroperoxides on auto-acceleration.

When RH stands for the $- CH_2 - CH_2 - CH_2$ molecule, it can be represented as follows:



Hutson and Scott[9,34] in their experiments to relate processing time in the torque rheometer to embrittlement time have reported that in the case of polyethylene the embrittlement time is markedly dependent on the initial carbonyl concentration. Also, they have shown that there is a difference in this behaviour between the two polymers polyethylene and polypropylene. In polypropylene, photodegradation rate does not depend on carbonyl concentration. Wood and Kollman[61], in agreement with Hutson and Scott have shown that the preexisting chromophores formed due to a simulated processing operation, particularly carbonyl, do not play an important role in initiating the photo oxidation of normal non-stabilised polypropylene in accelerated weathering for the following reasons:

1. Oxygen uptake measurements have shown that PP powder, dried and stored in the absence of oxygen and photo-oxidised without any processing, have a similar induction period to a commercial PP powder, which has been exposed to air for several months. This period is slightly greater than that for sheet made by compression moulding the latter polymer at 220°C, with no special precautions to exclude oxygen; because the antioxidants will remove the effects of prior air oxidation.

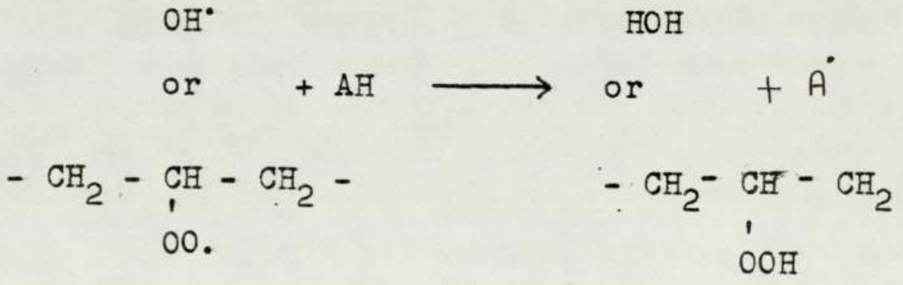
2. Drastic prior ultraviolet irradiation ($\lambda > 300$nm) in hydrogen of PP sheet makes no significant difference to its rate of subsequent photoxidation. Therefore, Wood & Kollman[61] have concluded that an ultraviolet absorbing PP-oxygen charge transfer complex is likely to be the main initiating species and not the chromophores formed during the prethermal treatment.

Scott et al.[9,10] have clearly shown that under processing conditions embrittlement time depends on the way in which the initially formed hydroperoxide, which is probably the primary chromophore in both cases, subsequently breaks down. The ultimate products of thermal oxidation of polyolefins are primarily aldehydes and ketones with lesser amounts of carboxylic acids.

1.1.1. Stabilization against thermal oxidation

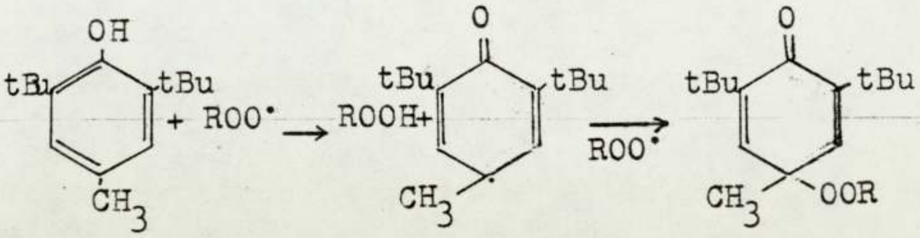
A variety of chemical compounds termed antioxidants are used to inhibit or retard the process of autoxidation and these fall into mechanistically distinct classes.

The first type of antioxidant AH, acts by interrupting the kinetic chain reaction[13], primarily by trapping alkyl peroxy radicals.



$$\begin{array}{c} OH^{\bullet} \\ \text{or} \\ -CH_2-\underset{OO.}{CH}-CH_2- \end{array} + AH \longrightarrow \begin{array}{c} HOH \\ \text{or} \\ -CH_2-\underset{OOH}{CH}-CH_2 \end{array} + A^{\bullet}$$

The structural feature of A• must be such that it will be too stable to initiate further oxidation. amines amines and phenols behave as in the above equation. Quinones and polycyclic hydrocarbons behave in a different way by trapping active free radicals. The active hydrogen in aryl amines and hindered phenols compete with polymer for peroxy radicals and hence they are particularly effective as antioxidants[1,35]. These compounds interrupt the chain propagation due to hydrogen transfer.



This mechanism has been supported by kinetic isotope studies[14] by substitution of deutrium for the labile H atom in these compounds. The second group of stabilizers retard or inhibit the oxidizability by decomposing the hydroperoxides by a nonradical mechanism. This is dealt in detail under photostabilization. Inhibition of chain propagation by a process of electron transfer is known. Under certain conditions metal ions in lower oxidation states eg. Cu^{2+}, Mn^{2+} can inhibit oxidation by destroying radicals.

$$ROO^{\cdot} + M^{2+} \longrightarrow ROO^{-} + M^{3+}$$

Peroxide decomposition is normally accelerated by certain redox systems; transition metal ions introduced during processing can be an important factor. If the metal ion is reducing:

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

and if oxidising:

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

Ligands capable of complexing with such metal ions and thereby acting as anti-oxidants have been reported[15].

1.2 Photoxidation of Polymers

Ultraviolet radiation has an adverse effect on the stability of polyolefins and therefore the problem of photodegradation becomes important when used for outdoor applications. Though the solar spectrum extends below 300 nm, most of the radiation below 350 nm is absorbed in the upper atmosphere. About 5% of the sunlight that reaches the earth's surface falls in the UV range of wave lengths less than 350 nm; having energy ranging up to 397.9 KJ mol^{-1}. This is the fraction that is harmful to polyolefins.

eg.

Bond	Bond energy kJ/mol
C - H	412.9
C - C	347.3
C - Cl	308.1
C - O	351.1

Due to the very low quantum yield of such fragmentations, degradation by direct absorption of UV radiation appears to be of little importance.

Although a number of functional groups in polymeric systems are sensitive to UV light (eg. olefinic units, carbonyl, and hydroperoxide groups), the primary process of photoxidation of polymers initiated by UV light may be caused by the contaminants[1,16,17] introduced during the following stages:-

(a) Impurities introduced during manufacture such as olefins, chain branches and metal ions.

(b) Impurities introduced during processing such as carbonyl and hydroperoxide groups.

(c) Impurities introduced by the environmental contamination such as polycyclic hydrocarbons, soot, metal vapours, ozone and singlet oxygen.

In the next section, the photo-catalysed interaction of oxygen with the hydrocarbon itself, in the absence of impurities, will be considered. Although it is not normally of great significance, under practical conditions, it may possibly be relevant to polymers which have not been subjected to prior oxidation.

1.2.1 Initiation caused by oxygen and oxygen substrate

A possible initiation process is the excitation of oxygen by UV light from the ground state to the excited state of higher inter nuclear distance than in the ground state via the Herzberg forbidden transition[18]. In this higher energy state the life time of the oxygen molecule is very short and hence dissociation occurs, giving active atomic oxygen.

$$O_2\ (^3\Sigma_g^-) + h\nu \longrightarrow O_2(^3\Sigma_u^+) \longrightarrow 2O\ (^3P)$$

However, since the Herzberg band is near 245.2 nm, if there is excitation of oxygen by solar radiation according to this equation, this should be absent in the UV light reaching the earth's surface. An absorption band situated at 759 -765 nm and 687 -692 nm which is very weak and responsible for the Fraunhofer lines in the solar spectrum, could cause oxygen absorption corresponding to the strongly forbidden transition.

$$O_3\ (^3\Sigma_g^-) + h\nu \longrightarrow O_2\ (^1\Sigma_g^+)$$

This fraction is also missing in sunlight, due to absorption in the upper atmosphere. A second possible mode of initiation is the excitation of the oxygen perturbed singlet to the triplet $S \longrightarrow T$ transition, which is known in olefinic and aromatic hydrocarbons. No simple relationship exists between the $S \longrightarrow T$ absorption intensity and oxygen concentration. However, in this regard, little or nothing is known about aliphatic hydrocarbons. Free radicals might also be obtained by photolysis of the charge transfer complexes between oxygen and various sites along the polymer chains and on this basis Chien[22,54] has shown that the rate of peroxide formation is a function of oxygen concentration. In wavelength regions where no permitted transitions exist, UV absorptions for oxygen saturated cyclohexane have been reported. Similar absorptions have also been reported for aromatic[19] and for nitrogen[20] containing compounds. These absorptions have been identified as absorptions due to excited charge transfer states[31,32] ^3CT. A complex of this type in the absence of light has recently been proposed for oxygen tetralin and oxygen indene systems[21].

Chien[22] investigated the photoxidation of alkanes and alkenes under conditions which minimized initiation by photolysis of impurities (hydroperoxides and ketones etc.). at wavelengths 253.7 nm and 313 nm. He found that the hydrocarbons under examination, when saturated with oxygen,exhibit UV absorption bands with tails going beyond 300 nm,where the oxygen-free hydrocarbons are completely transparent. Such tails are more intense for olefins. Absorption intensities are directly proportional to the concentration of oxygen, and of the substrate and increase with decreasing temperature.

On the basis of the experimental conditions adopted,Chien excluded the possibility of assigning these absorptions to the "high pressure" bands of oxygen, discovered by Wulf.[126] On the basis of this and of other considerations, the UV absorptions observed for the alkanes-oxygen systems have been mainly attributed to charge transfer transitions and those observed for alkenes-oxygen systems to the sum of charge transfer excitations and of oxygen perturbed S $\longrightarrow$ T excitations.

The initial rates of oxidation have been determined by the oxygen absorption technique[48]. The overall initiation reaction through hydroperoxide intermediates has been schematized as follows:

$$RH + O_2 + h\nu \longrightarrow 2R^{\cdot} + \text{other products}$$

where the quantum yield was found to be of the order of magnitude of 10^{-2} moles per einstein. on the basis of the absorption intensities of the Herzberg bands, the quantum yield of the free radical formation must exceed 4 to account for the asserted initial rates of photoxidation (order of magnitude 10^{-7}moles/sec). Therefore, processes involving direct excitation of oxygen have been considered scarcely probable.

By analogy with the absorption intensity, the initial rate of oxidation depends on the oxygen and the substrate concentrations. Since UV light absorptions have been entirely by alkenes or partially by alkanes through charge transfer transitions, these have been assumed to contribute to the initiation of photoxidation in all the systems studied, particularly in the photoxidation of methyl cyclohexane. Chien proposed the following reaction:

$$RH + O_2 + h\nu \longrightarrow (RH^{+} + O_2^{-})$$

The separation of ionic species in nonsolvating media has low probability[23]. However since these initial photoxidations are low quantum efficiency processes, reactions of those ionic species which have escaped cage recombination cannot be completely discounted as initiating species. Chien admitted other alternative possibilities. The cage recombination of RH^+ and O_2^- might produce free radicals or the charge transfer absorption might be partially dissociative, giving rise to radicals; these two possibilities cannot be readily differentiated.

Two other suggested reactions are:

$$^3CT \longrightarrow {}^1CT \longrightarrow {}^3RH + {}^3O_2$$

$$^3CT \longrightarrow {}^3RH + {}^1O_2$$

It has so far been impossible to evaluate the relative importance of these reactions in photoxidation. Finally it was assumed that the part of absorption due to the oxygen-perturbed S $\longrightarrow$ T excitation that may be found in an alkene-oxygen system might start photoxidation according to the following two reactions[24].

$$^3A + O_2 \longrightarrow \text{peroxide}$$

$$A + O_2 + h\nu \longrightarrow {}^3A + O_2\ (^1\Delta g)$$

where acceptor A is the olefin. Probably, reaction

$^3A \quad + \quad O_2 \ \text{———}$ peroxides predominates in the processes.

It is of some interest to consider the initiation of photoxidation with respect to olefin groupings. It is well known that polyolefins, when obtained by polymerization, using Ziegler-Natta catalysts[25,26] contain terminal double bonds as well as internal double bonds. If the initiation processes considered so far are important, they will only affect the very early stages of the polymer oxidation; in the subsequent stages the predominant role in initiation of photoxidation should be played by the oxidation products hydroperoxides, ketones etc. Amin[41] has shown that the slow initial linear rate is due to the breakdown of hydroperoxides.

The primary initiation schemes, previously described, also concern the mechanisms proposed by Millinchuk[27] to explain the results obtained when studying the formation of free radicals in the presence of oxygen and light. The tests were carried out at the temperature of liquid nitrogen. The free radicals were studied by means of electron spin resonance (ESR) technique and it was found that, when oxygen was present, UV light of wavelength 300 nm caused the formation of free radicals in different hydrogen containing polymers (polyethylene, polypropylene, natural rubber etc.).

The formation of radical was attributed to oxygen for the following reasons:

(a) Free radicals form only in the presence of oxygen and not under vacuum over the wavelength of light studied.

(b) The rate of formation and the specific concentration of the radicals increase with increasing oxygen content in a cell exposed to light. But very recently Ashley Scott[91] has shown that free radicalsare formed on radiolysis of polybutadiene (λ> 300 nm) even in the absence of oxygen as evidenced by its more rapid subsequent photoxidation. Free radicals have been shown to reach a limiting concentration lower than that in the presence of oxygen; but it looks as though polymers containing unsaturation can be activated without oxygen.

The hyperfine structure of the ESR spectrum shows that the initial radicals produced in the polymer at 77°K was of the alkyl type. Mullinchuk assumed that UV light converts molecular oxygen first to an excited state or into atomic oxygen. Successively the active form of oxygen abstracts a hydrogen atom from the macromolecule according to the reaction:

$$RH + O^{\bullet} \longrightarrow R^{\bullet} + OH^{\bullet}$$

and yields an alkyl and a hydroxyl radical. The latter, being very reactive, abstracts a second hydrogen.

$$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O$$

and again forms an alkyl radical. The sum of these two reactions is equivalent to reaction $RH + O_2 + h\nu \longrightarrow 2R^{\cdot}$ proposed by Chien. According to Millinchuk, the free radicals produced are especially stabilized at the polymer surface.

Recently, Tsuji[65] has found evidence to support the view that radicals of the type $-CH_2-\cdot CH-CH_3$ are formed on irradiation of polyolefins to light of wavelength greater than 280 nm rather than the superposition of two kinds of free radicals $-CH_2-\overset{\bullet}{C}H_2-$ and $-CH_2-\cdot CH-CH_2-$ in his ESR studies. Also the samples irradiated in air or O_2 have given an asymmetric spectrum characteristic of peroxy radicals.

1.2.2 Initiation caused by impurities

A variety of adventitious agents generally can be incorporated into the polymers during the processing and extrusion stages. They are mainly catalytic residues consisting mainly of metal impurities or traces of hydroperoxide[37,38] and carbonyl moities. The polyolefins obtained by polymerization in the presence of Ziegler-Natta catalysts always contain transition residues such as titanium which are left behind in the polymers due to the difficulty in removing them. The concentration of such metal impurities is generally less than 50 ppm and their nature generally depends on the purification process.

It is a well known fact that such transition metal ions act as sensitizers for the photoxidation of polyolefins. Kujirai[101] et al have shown that the oxidative degradation of polypropylene in ultraviolet light is dependent on the concentration of oxygen and of the metal catalyst residues and this led to their conclusion that the oxidative photodegradation is sensitized by the initiator residues,

This cannot of course be true in LDPE which does not involve a metal catalyst. The data available indicate that the transition metal compounds absorb UV light and generates free radicals for the initiation of photoxidation processes. In liquid phase reaction of this kind it has been shown[17] that metal cations such as Hg^{2+} (λ max 180 nm) Cu^{2+} (λmax 200nm) Pb^{2+} (λ max 208.5 nm) Fe^{3+} (λ max 230 nm) undergo photoreduction via electron transfer. They absorb strongly with an E_{max} of 10^4 at λ_{max} in this medium and the electron donor in this case is apparently the water of hydration. These electronic transitions which are caused by electron transfer from one ion to another or to the solvent are responsible for most organic photochemical reactions.

$$M^{+n}H_2O \quad + h\nu \quad \longrightarrow \left[M^{(n-1)+}H_2O^{+}\right] \begin{array}{l} \nearrow M^{(n-1)+} + H_2O + .OH \\ \searrow M^{(n-1)+} + \cdot OH + H^{+} \end{array}$$

Ion pairs formed by complexing these cations with different anions gives rise to absorption spectra, shifted towards the visible region and the magnitude of the shift is almost directly proportional to the decrease in electron affinity of the anion. Thus the λ_{max} for Fe^{3+} Cl^-, $Fe^{3+}Br^-$, and Fe^{3+} SCN- are 320, 380 and 460 nm respectively. The results obtained in different solvents for molar extraction coefficients of 3 compounds of Ti^{4+} at various wavelengths still confirms the inverse proportionality to the electron affinity of the anion. This suggests that in the ion pair, the anion is the electron donor and that the primary act of absorption involves the formation of an intermediate followed by several reactions including dissociation.

$$M^{n+} + X^- + h\nu \xrightarrow{a} M^{(n-1)+} + X^{\bullet}$$

$$M^{(n-1)+} + X^{\bullet} \xrightarrow{b} M^{(n-1)+} + X^{\bullet}$$

Where M is the transition metal ion and X^- is the anion. Photo excited electron transfer of this type has recently been used to explain the action of traces of Fe^{3+} as a photosensitizer in polymers[38b]. To conclude, the transition metal residues of the polymerization catalysts act as sensitizers in the photoxidation of polyolefins and of polymers in general according to a mechanism that should involve light absorption and the production of free radicals through a photo-excited electron transfer from the anion to the cation. After rapidly reaching thermal equilibrium, the free radicals start the oxidation of the substrate following the reaction pathways discussed above. The nature of the anion associated with the metal ion impurity is also very important for the resistance of the polymer to photo-xidation. As the electron affinity of the anion increases the absorption of the metal compound shifts towards shorter wavelengths than those present in sunlight at earth level. This is the reason why $FeCl_3$ absorbs very little radiation from the sun falling only within the range 200 -400 nm whereas ferric acetylacetonate absorbs radiation of longer wavelength reaching the earth's surface.

1.2.3 Initiation due to oxidation products of the polymer

Processing and fabrication operations of polymers generally involve an application of heat during which unavoidable contact with oxygen in the atmosphere causes the formation of hydroperoxide groups. It is now generally accepted that photodegradation of polymers involves the same free radical chain mechanism as in thermal oxidative degradation. Although the alkyl hydroperoxides show the maximum of the 1st absorption band in the 200 nm region, the tail of the band extends to about 350 nm indicating that they can absorb a part of the sunlight that reaches the earth ($\lambda > 300$ nm).

The light absorption by peroxides is due to the transition that probably occurs between the two closer lying levels Px,y $\longrightarrow$ Pz, resulting in absorptions shifted to longer wavelengths[40]. Therefore the sunlight they absorb breaks the O-O bonds and creates two free radicals according to the scheme:

$$ROOH \xrightarrow{h\nu} RO^\cdot + OH^\cdot$$

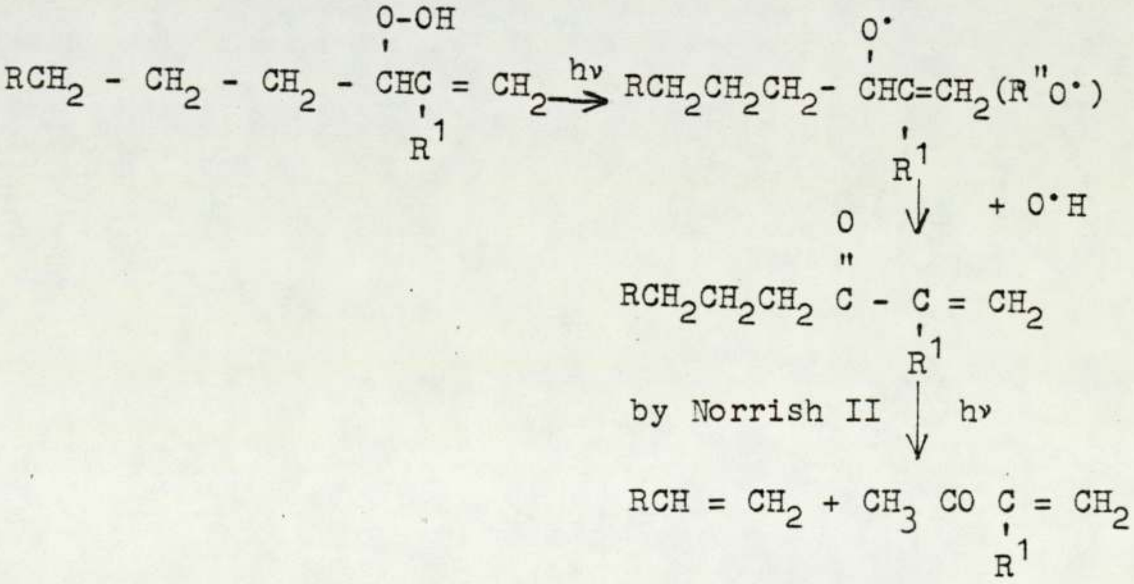
Norrish and Searby[42] have shown that the quantum yield for this reaction is about one. The radical pair thus obtained ($RO^\cdot$ and $OH^\cdot$) starts the free radical chain:

$$RH + \dot{O}H \longrightarrow R^\cdot + H_2O$$

$$ROOH + R^\cdot \longrightarrow RO^\cdot + ROH$$

$$RO^\cdot + RH \longrightarrow R^\cdot + ROH$$

On the basis of their observation of rapid disappearance of vinylidene groupings during the rapid oxidation of polymer and on the observation of the formation of the insoluble crosslinked gel during this period, the following sequence of chemical reactions have been proposed by Kugler and Frank and also by Amin and Scott[39,41] to account for the main features of the degradation process.



$$RCH_2-CH_2-CH_2-\underset{R^1}{\overset{O-OH}{CHC}}=CH_2 \xrightarrow{h\nu} RCH_2CH_2CH_2-\underset{R^1}{\overset{O^\cdot}{CHC}}=CH_2(R''O^\cdot)$$

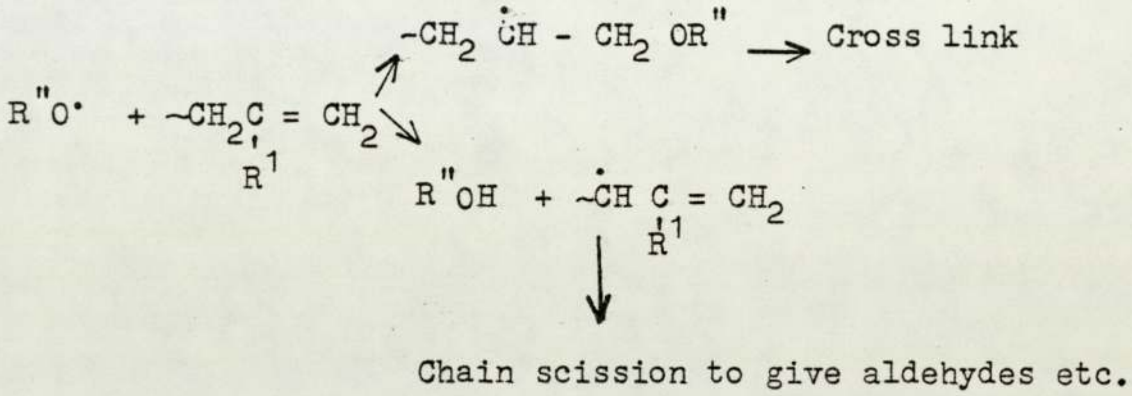
$$\Big\downarrow + O^\cdot H$$

$$RCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-\underset{R^1}{C}=CH_2$$

$$\text{by Norrish II}\ \Big\downarrow\ h\nu$$

$$RCH=CH_2 + CH_3CO\underset{R^1}{C}=CH_2$$

Photo initiation occurs by further reactions of the primary alkoxy and hydroxyl radicals and crosslinking through vinyl addition competes with chain scission through allylic hydroperoxide breakdown to give aldehydes, ketones etc.

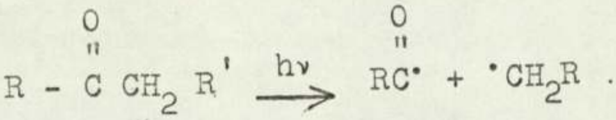


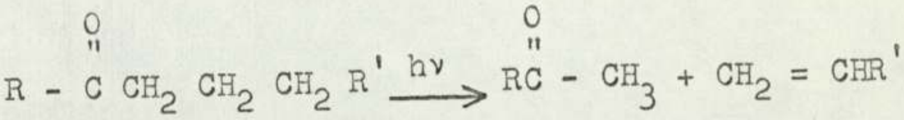
$$R''O^{\bullet} + \sim CH_2\underset{R^1}{C} = CH_2 \nearrow -CH_2\dot{C}H - CH_2OR'' \longrightarrow \text{Cross link}$$

$$R''O^{\bullet} + \sim CH_2\underset{R^1}{C} = CH_2 \searrow R''OH + \sim\dot{C}H\underset{R^1}{C} = CH_2 \downarrow \text{Chain scission to give aldehydes etc.}$$

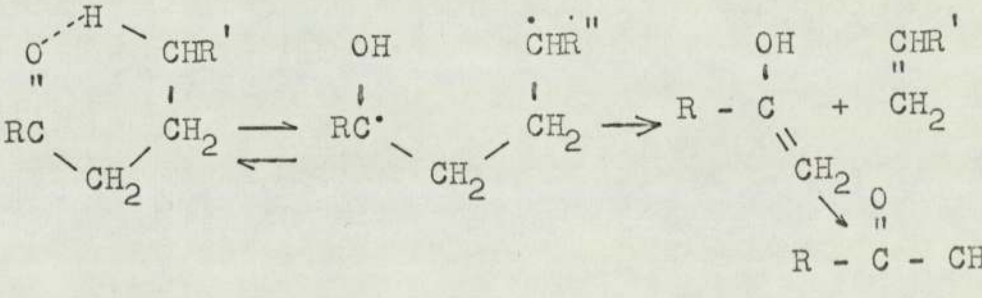
1.2.4 Initiation due to carbonyl groups

As a result of a "forbidden" electronic transition which causes an electron to be promoted from a nonbonding n-orbital localized on the oxygen atom to a delocalized antibonding π^* orbital that is distributed over the entire carbonyl group, aliphatic carbonyl groups particularly aldehydes and ketones show a relatively weak absorption band with a maximum between 270 and 290 nm and extending into the region beyond 300 nm. This excited $^1(n\pi^*)$ singlet state forms the triplet state $^3(n\pi)^*$ by the process[42] called intersystem crossing. Both these excited states are capable of undergoing a variety of cleavage reactions. Principal routes available for chain scission are the Norrish type I reaction and Norrish type II reaction as suggested by the known photochemistry of aliphatic ketones.

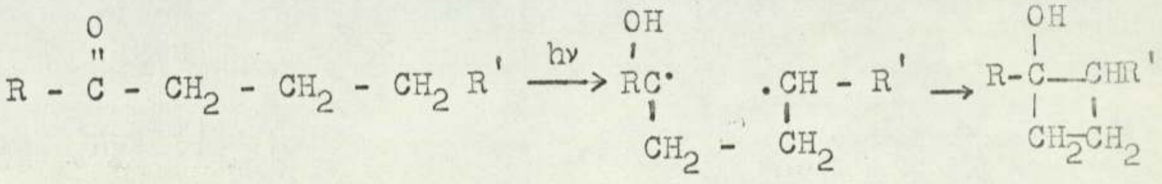
Norrish I process :

$$R-\overset{O}{\overset{\|}{C}}CH_2R' \xrightarrow{h\nu} R\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_2R\ .$$

Norrish II process:

$$R-\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2R' \xrightarrow{h\nu} R\overset{O}{\overset{\|}{C}}-CH_3 + CH_2=CHR'$$

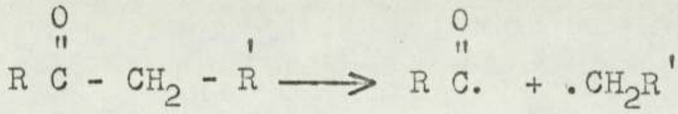
Quantum yield measurements of these reactions for aliphatic ketones has shown that typeI cleavage appears to occur less frequently than the type II process. Yang, Elliot and Kim suggested the existence of a biradical intermediate that quickly fragments[45] or returns to the starting ketone as the mechanism of the type II cleavage of ketones.



Another reaction involving a biradical intermediate similar to that of the type II process which leads to cyclobutanol derivatives[45] has been observed:

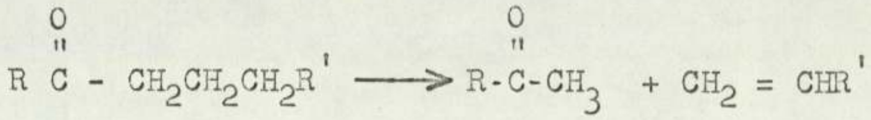


But this is not considered to occur to any significant extent in polymeric systems compared with the type II process. The importance of both type I and type II processes in the photodegradation of polymeric systems containing carbonyl groups, was first pointed out by Guillet and Norrish in the photolytic reactions of polymethyl vinyl ketones. Elegant studies by Hartley and Guillet[46] on ethylene-carbon monoxide copolymers clearly indicated the importance of the type II process as a main source of chain scission in model systems related to polyethylene. Moreover Guillet and coworkers[47] have reinforced Osborn's suggestion that carbonyl photo-cleavage reactions may be the major cause of photodegradation in the wide variety of carbonyl containing polymers as well as in polymers which always contain at least traces of carbonyl functions as a result of oxidation during processing. Further Guillet[63] et al. and Trozzolo and Winslow[64] have shown that although the principal routes available for chain scission are the Norrish type I reaction:



$$R\overset{\overset{O}{\|}}{C} - CH_2 - R' \longrightarrow R\overset{\overset{O}{\|}}{C}. + .CH_2R'$$

and the Norrish type II reaction:



$$R\overset{\overset{O}{\|}}{C} - CH_2CH_2CH_2R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2 = CHR'$$

quantum yields of these reactions indicate that the type I cleavage appears to be much less important than the type II process where the quantum yields are in the range 0.2-0.3.

Additional evidence favouring this view comes from several studies[41,49] of photolysis of polyethylene where infrared studies indicated the presence of vinyl groups in the oxidised polymers.

1.2.5 Protection from photoxidation

Polymers are usually protected against photoxidation by the addition of stabilisers to extend their usefulness. These additives protect the polymer from photodegradation in 4 different ways[49,52,54,64,102,103,104].

(a) By absorbing the UV radiation and undergoing a radiationlesss relaxation process. They are said to be screening agents and they will be effective whether incorporated in the polymer or when present as an external screen.

(b) By extracting energy absorbed by an excited chromophore in a polymer. These are the triplet quenchers.

(c) By acting as hydroperoxide decomposers in a non radical forming reaction.

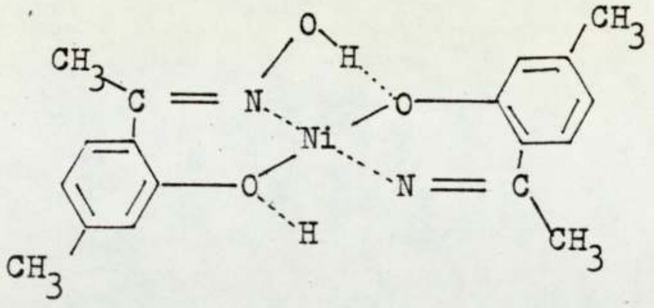
(d) Synergistic combinations involvimg more than one, such as phenols with UV absorbers with which phenols are synergistic.

Some of the mechanistic suggestions that have been proposed to explain the activity of these stabilisers are speculative, and have not been confirmed as due to the quenching mechanism. Also more than one mechanism may be involved with some stabilisers. Another theoretical possibility which has to be confirmed is a UV stable radical trap. One reason phenols may become effective in the presence of a UV absorber is because the latter protects them from photolysis by UV light.

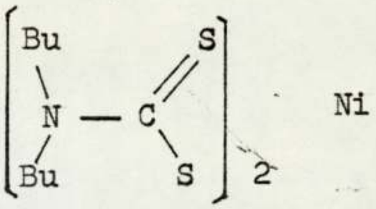
1.2.5 (a) UV Screening

Light screening agents in polymers function either by absorbing damaging radiation before reaching the polymer surface or by limiting its penetration in the bulk of the polymer. Light screens can be exterior coatings on the polymer surface, protective films that are extruded or compression moulded from within the polymer bulk, or additives that are homogenously dispersed throughout the polymer. As far as the chemical reactions of light screens are concerned, additives that are dispersed throughout the polymer are the most important compounds. The active stabilizers which fall into this category are mainly metal chelates such as oximes, and diethyl dithiocarbamates, 2-hydroxybenzophenones and 2-hydroxy benztriazoles.

Many attempts have been made by past workers to explain the mechanism of UV stabilizing effectiveness of nickel chelates.



Ni-o-hydroxy acetophenone oxime



Ni-dibutyl dithiocarbamate

Recently Scott et al.[48] have reported from their results of the experiments with cumene initiated by cumene hydroperoxide and benzophenone, that nickel dibutyldithiocarbamate is at least in part a UV screening agent. They suggest that the mechanism involved in the UV stabilising activity of this nickel complex is not primary quenching of photoexcited states but decomposition of hydroperoxides in polymers[49]. He has shown this clearly by an experiment carried out when it is present as a screen in a separate solution compared with its behaviour as an additive at equivalent screening effectiveness.

He has concluded that catalytic hydroperoxide decomposition is not involved to any extent in the stabilization by nickel oxime; but non-catalytic decomposition of hydroperoxides occur in this process.

Guillory and Cook have also shown that nickel chelates do not entirely behave as light screeners,[50] but also .

at least partly they contribute as UV screening agents, supporting the view of Scott. Further, they have shown that the 2-hydroxybenzophenones function as screeners but also act by a second mechanism[83] which extends the polymer film life time by several orders of magnitude over that resulting from a screening effect alone.

These views indicate that at least partly, screening contributes to the photostabilization of the polymers from UV radiation. Harmful UV radiation absorbed by the stabilisers will then be released in the form of harmless radiation of longer wavelength and thus the polymer is protected.

1.2.5 (b) Excited state quenching

In recent years singlet oxygen ($^{1}\Delta_{g}{}^{1}O_{2}$) has been shown to undergo facile reactions with unsaturation sites on polyolefins. Experiments on photosensitized oxidation of polyisoprene have been carried out by Mayo and Irwin who have shown that, without a sensitizer, oxygen absorption proceeded with a measurable initial rate, but soon stopped. Benzophenone sensitized reactions showed an almost sixfold increase in total oxygen comsumption[74]. In all the photosensitized oxidations, natural pigment sensitizers such as chlorophyll and carotene utilize lower energy portions of visible light and are excited to the first excited singlet state[75].

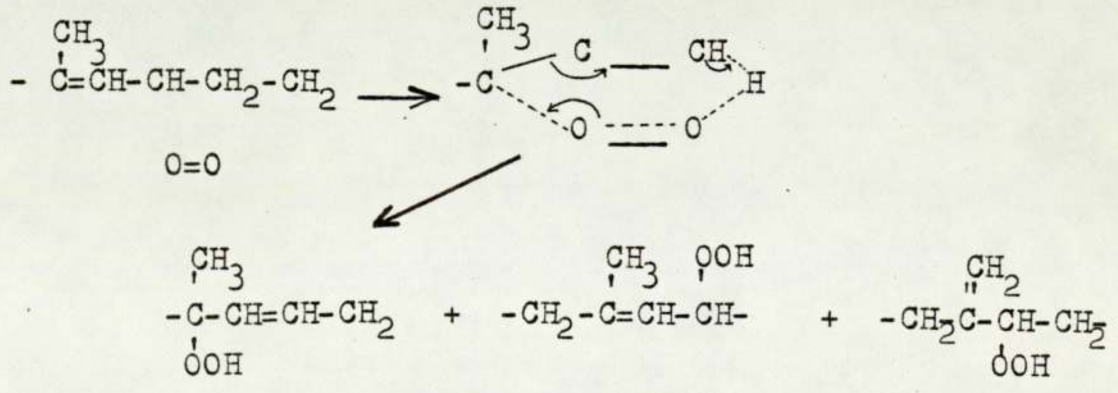
$$\text{Sens}_o + h\nu \longrightarrow {}^1\text{Sens}_o^* \longrightarrow {}^3\text{Sens}^*$$

Initial conversion leads to the first triplet state (${}^3S^*$) which then transfers energy to ground state molecular oxygen ${}^3O_2$; yielding singlet oxygen (${}^1O_2^*$) and a sensitizer molecule in the ground state[76].

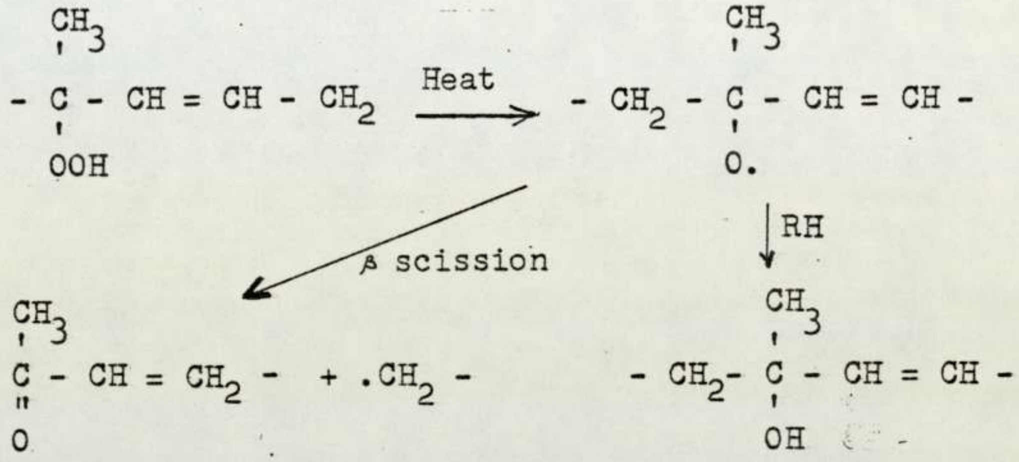
$${}^3\text{Sens}^* + {}^3O_2 \longrightarrow {}^1\text{Sens}_o + {}^1O_2^*$$

According to a suggestion by Trozzolo and Winslow[51], during the photodegradation of polyethlene, UV excited macro-carbonyl impurities in the polymer may be quenched by ground state triplet oxygen to yield singlet oxygen. This singlet oxygen then attacks the polymer back-bone to give the hydroperoxide groups which initiate photodegradation. Singlet oxygen is an extremely reactive relatively long lived intermediate, when formed in certain reactions such as (NaOCl/H_2O_2) is capable of immediate addition to conjugated 1,3 dienes[77], rubber and to anthracenoid hydrocarbons.

In the case of rubber it forms allylic hydroperoxide by the following mechanism:



These hydroperoxides undergo thermal break down to give ketones and hydroxy compounds as given below. Photodegradation of these hydroperoxide groups have already been explained in Page 3.



Much work has been done in the past to quench the excited states of the activating groups hence to prevent the photodegradation of polymers.

Chien and Conner[54] have reported that diethyl ketone sensitized photoxidation of cumene can be effectively retarded by the addition of nickel chelates of 22' thiobis (1,1,3,3, tetramethyl butyl) phenol. According to this conclusion the retardation is attributed to the quenching of excited states of diethyl ketone by Ni (1). They have further concluded that Ni (1) also quenches the phosphorescence of diethyl ketone in ethyl, propyl, alcohol (EPA) glass in the same manner and the resonance excitation energy transfer is probably the principal quenching mechanism. But Carlsson and Wiles[105] in their recent investigation of the effects of some of the photostabilisers for polypropylene under vacuum and in air have shown that nickel chelates inhibit the formation of Norrish type I and II products from the macro ketones. But they suggest that they operate via a collisional quenching process and radical scavenging rather than by long range energy transfer. Further, they have not detected the quenching of the macro-ketone phosphorescence at 77°K with any of the investigated stabilisers.

Carlsson, Suprunchuk and Wiles[106] have also shown that effective photo stabilisers operate by both chromophore quenching radical scavenging and hydroperoxide decomposition. They have been able to show that effective stabilisers of thin films do not depend on UV absorption for their protective action whereas some relatively inefficient additives operate solely as UV screeners. Adequate UV protection have been observed when small amounts (0.01% by wt.) of effective stabilizers were concentrated on the surface of commercial films, and the remaining bulk of the film contained only a very low concentration of uniformly blended additive.

In a recent study of the UV stabilization behaviour of nickeldibutyldithiocarbamate (NiDBC), Guillory and Becker concluded that it did not quench carbonyl triplet. They have further suggested that since it was destroyed more rapidly in the presence of oxygen than in its absence interaction with singlet oxygen might be involved.

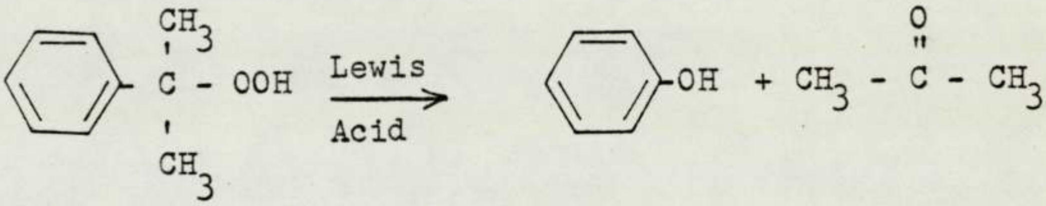
Further on the basis of the rapid destruction of Ni dibutyldithiocarbamate in the presence of hydroperoxides, Scott suggests that only two mechanisms are involved in the UV stabilizing behaviour of Ni DBC, namely screening and peroxide decomposition. He has suggested that the quenching of photoactivated species does not play a significant role in the photoxidation of polymers[49], under practical conditions. It may be involved in polymers which contain a substantial amount of deliberately introduced carbonyl without peroxides.

Regarding the light stabilizing action of nickel oxime chelates in polypropylene, Briggs and McKellar[52] have suggested from the results of their phosphorimetry and flash photolysis experiments that stabilization by the oxime chelates is achieved by a mechanism of efficient energy transfer from photoreactive carbonyl groups to the chelate where the energy is harmlessly dissipated.

The results of the experiments carried out with aromatic photosensitisers indicate that the photostabilization of polymers caused by the metal chelates may at least partly cause the quenching of either the excited chromophores or singlet oxygen in their mode of action. However Ranaweera[49]'s work has shown that this makes a negligible contribution to inhibition of photo-oxidation of cumene.

1.2.5 (c) Hydroperoxide Decomposition

It is now a widely accepted fact that some polymer stabilizers probably operate by hydroperoxide decomposition. Simple cyclic phosphates react with hydroperoxides catalytically in a Lewis acid catalysed manner[55] to form non radical products.

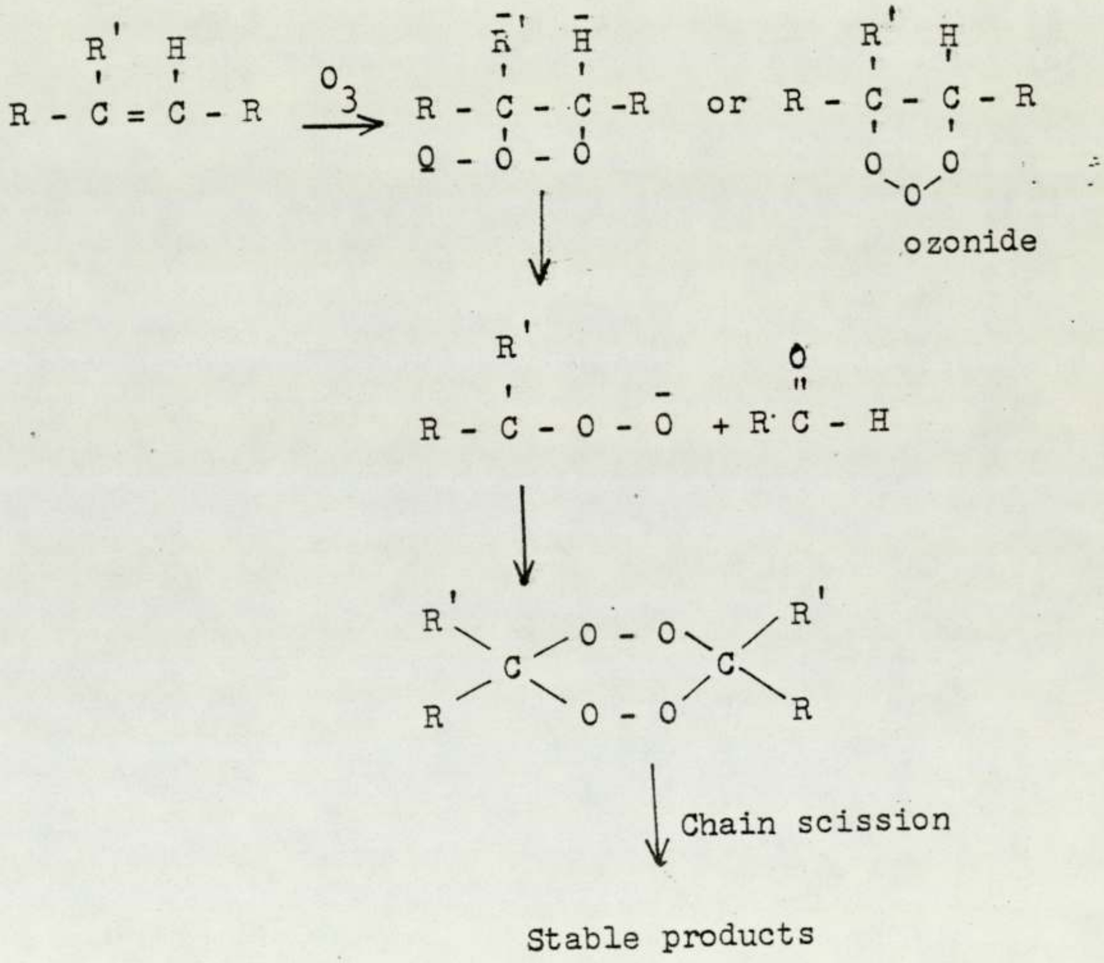


Metal dialkyldithiocarbamates are rapidly destroyed by hydroperoxide in a process which gives rise to an effective catalyst for hydroperoxide destruction and this phenomenon has been adduced to explain the powerful UV stabilising effect of the dithiocarbamates. Also Carlsson and Wiles[95] have shown that the quantum efficiency of radical initiation for polypropylene hydroperoxde is much higher than it is for the derived carbonyl compounds. Bolland from his kinetic studies of polymer oxidation concluded that the well known auto accelerating rate is due to the increase in concentration of hydroperoxides.

PART B

1.3 Degradation of natural rubber

It has been found that the molecular weight of natural rubber (NR) decreases due to oxidation; and that a trace of ozone is capable of destroying the characteristic macromolecular structure of unsaturated polymers like natural rubber[107,108]. Surface cracking and perishing of rubber is a result of this deterioration.



Although the structure of NR has been known for many years, the nature of the chain scission reaction in the process of oxidation has proved to be difficult to characterise. All the possible mechanisms investigated to explain the deterioration of rubber were based on the ultimate products of oxidation.

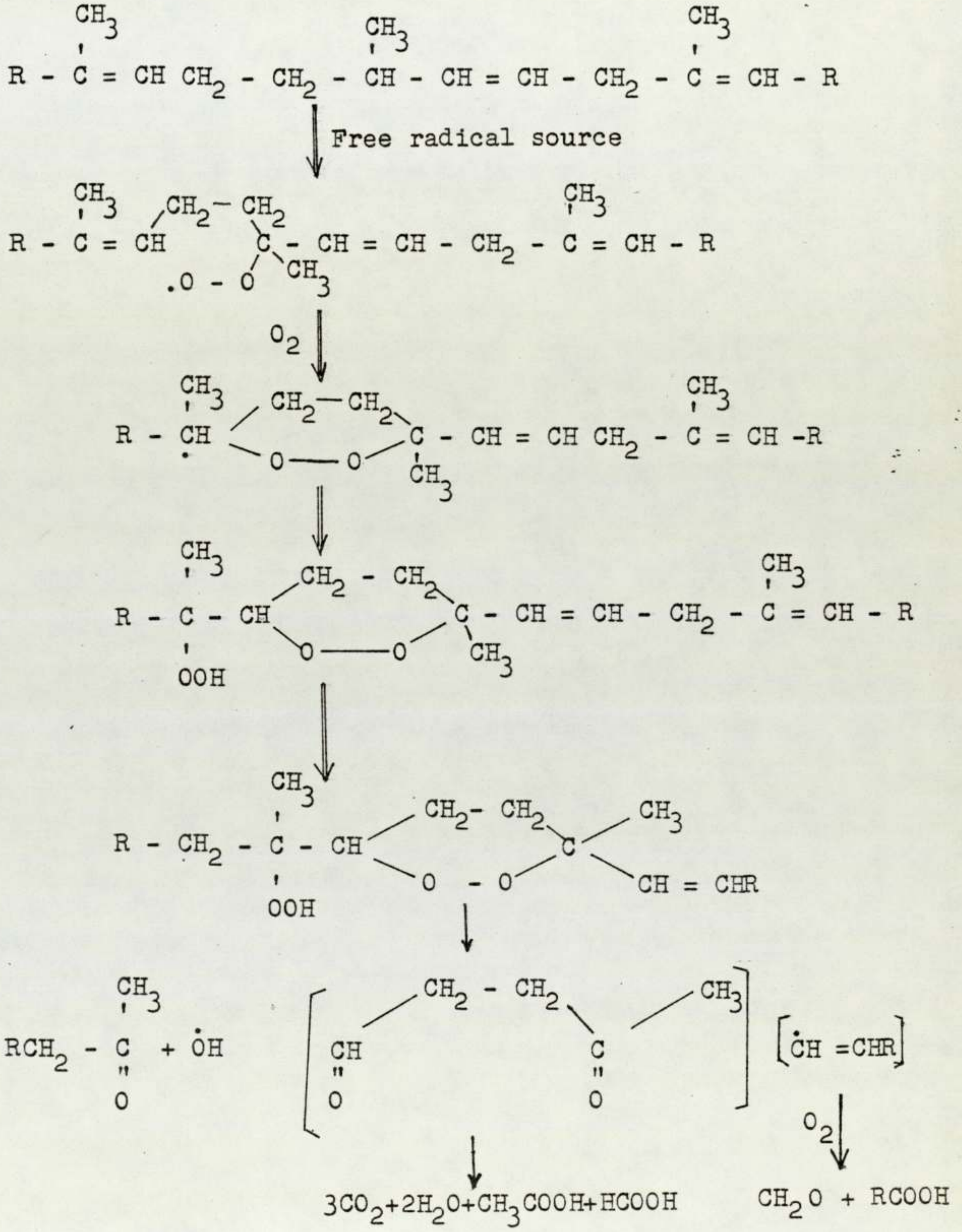
The first detectable product of oxidation on rubber was found to be rubber hydroperoxide[93]. The ultimate products were carbon monoxide, carbon dioxide, and carboxylic acids.

As in the case of polyolefins, initial formation of hydroperoxide involves the attack of the rubber molecules by free radicals. These free radicals are formed in the rubber during the process of compounding, processing and fabrication. These processes involve the application of heat, exposure to direct sunlight, and contamination by metal ions as in the case of polyolefins.

According to Kauzman and Eyring[92], carbon carbon bonds of the polymer backbone break directly into free radicals:

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

These free radicals then follow the scheme given below causing the degradation of the rubber molecule through hydroperoxide intermediates. Hydroperoxide formation reaction is more pronounced in rubber than in polyolefin due to a higher degree of unsaturation of rubber. Bevilaqua[93] has proposed a mechanism for the breakdown of the rubber molecule through the following hydroperoxide group giving products which accords better with the structure of rubber:



1.3b Stabilization of natural rubber

As in the case of synthetic polyolefins, stabilization of natural rubber involves the incorporation of antioxidants into the polymer by one of the following methods:

a) By mixing antioxidants into the rubber dissolved in a suitable solvent and then removing the solvent.

b) By mixing solid rubber with antioxidants on a roll mill or in a Banbury.

c) By mixing antioxidants with the rubber in the latex form and then coagulating by means of a coagulant.

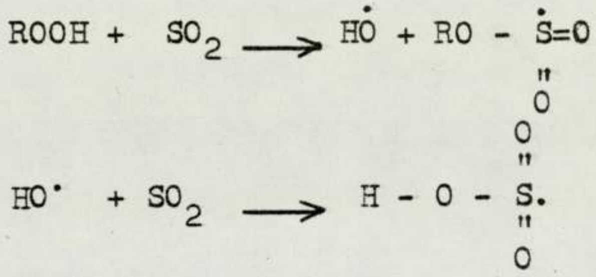
Out of these, the third method generally gives a more uniform mixture. Although there are several methods of incorporating antioxidants into natural rubber, in principle the most successful method should be to graft the antioxidant into the polymer backbone in order to prevent the problem of antioxidant loss by volatility and extractability[60,70,109,110]. This also ensures the presence of antioxidant groups throughout the life time of the article. A successful method developed to graft antioxidant molecules onto the rubber chain, as in the case of polyethylenes is by means of hydroperoxide groups formed on them.

1.3.1 Reactions of hydroperoxides and the use of hydroperoxides in polymers for initiation polymerisation reactions

Hydroperoxides are the first products formed during the autoxidation of polymers including rubber and the well known autoaccelerating behaviour is due to their increasing concentration. Regarding their instability and the very low concentrations present, an accurate method is not available for the measurement of their concentration. Wagner[57] proposed an iodine liberation titrimetric method using isopropyl alcohol as the medium for the measurement of hydroperoxides. But this method is found to be inaccurate for the hydroperoxide groups formed on the oxidised polymer films. Sully[58] has proposed a modification to Wagner's method to avoid the contamination by atmospheric oxygen. The method reported by Bocek is capable of measuring 10^{-6} moles of hydroperoxide formed on polymers by a colorimetric method. All methods available for hydroperoxide estimation are dealt with in detail in the next chapter.

1.3.1.1 Reactions of hydroperoxides

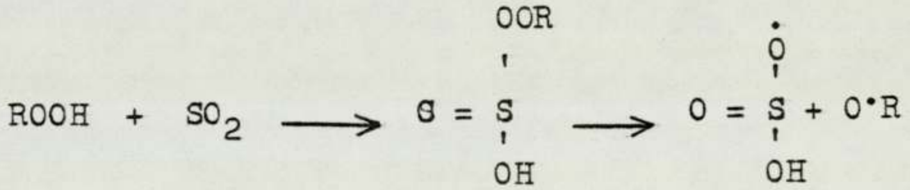
Hydroperoxides are found to undergo reaction with SO_2 gas giving an intermediate[66] which is very unstable and hence rapidly breaks down to give radicals. Hence this system acts as a convenient radical source for initiating copolymerisation of sulphur dioxide with alkenes at low temperatures[111,112]. Recently it has been found possible to initiate the radical polymerisation of vinyl monomers with this catalyst system[113]; and strong nucleophiles such as sodium methoxide can prevent sulphur dioxide from copolymerising with the vinyl monomer. The nature of the radical intermediates has however, remained uncertain. I.vin[112] et al have found that the radical (HO $\dot{S}O_2$) or the radical ion SO_3^- formed by the reactions;



$$ROOH + SO_2 \longrightarrow H\dot{O} + RO - \underset{\overset{\|}{O}}{\dot{S}}{=}O$$

$$HO^{\cdot} + SO_2 \longrightarrow H - O - \underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}.$$

and



$$ROOH + SO_2 \longrightarrow O = \underset{OH}{\overset{OOR}{S}} \longrightarrow O = \underset{OH}{\overset{\dot{O}}{S}} + O^{\cdot}R$$

In 1959 Walling and Rabinowitz[67] found that trialkyl phosphites decomposed hydroperoxides, giving trialkyl phosphates and alcohol according to the reaction:

$$ROOH + (R'O)_3P \longrightarrow ROH + O{=}P(OR')_3$$

In certain studies it is proposed that in the intermediate step an ion pair $[(R'O)_3\overset{+}{P} - OR, \overset{-}{O}H]$ is formed; in other work the formation of a pair with a different structure[68] $(R'O)_3P^+ - OH, OR^-$ which is converted to the product by transfer of a proton is considered more probable.

Later Pobidimskii[69] studied the kinetics of the consumption of TBHP in the interaction with triphenyl phosphite by the method of polarography in the presence and absence of oxygen. The results of this study have shown that the reaction of TBHP with phosphites apparently proceeds according to a radical mechanism as represented below:

$$ROOH + (R'O)_3P \longrightarrow R\bar{O}OH \;......\; {}^+P^{\cdot}(\dot{O}R')_3$$

$$ROH + O{=}P(OR')_3 \longrightarrow R\dot{O}\dot{P}(OH)(OR')_3$$

This could be used as a radical generating process in polymer chemistry.

1.4 Vulcanization of rubber

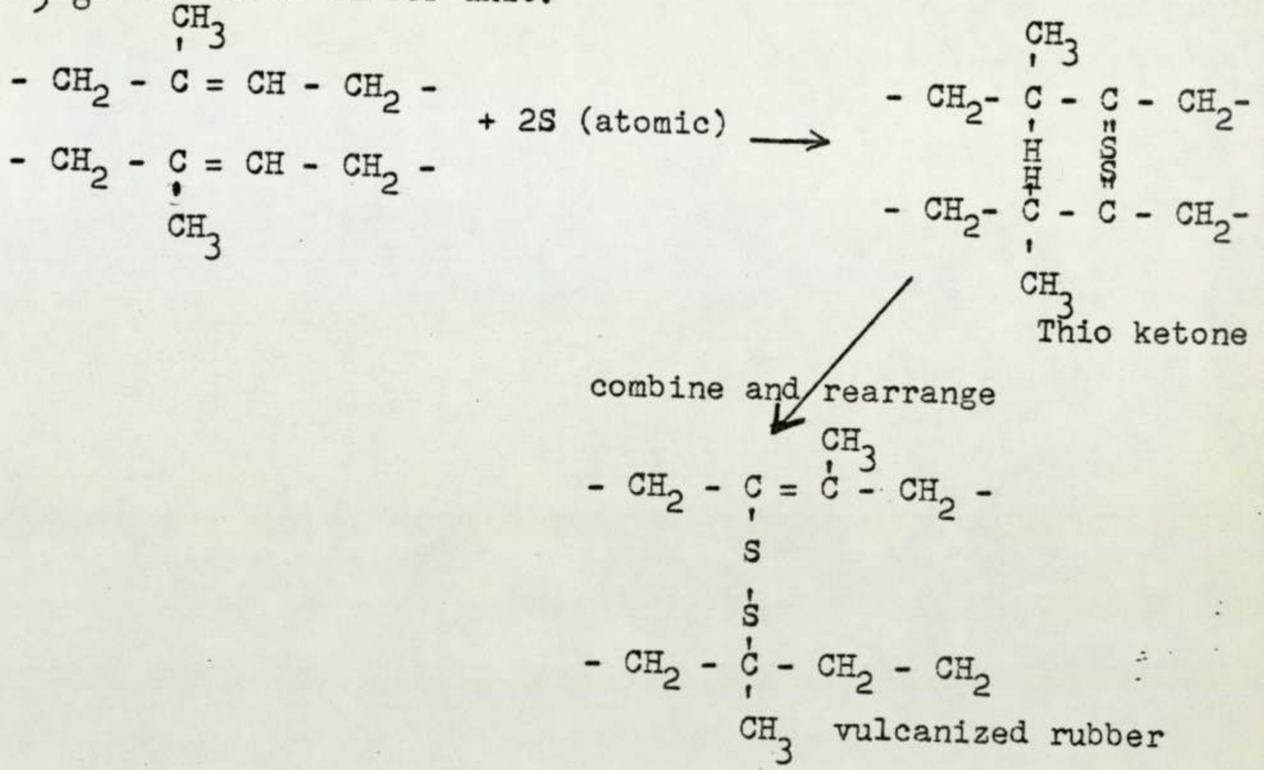
Vulcanization is the process whereby rubber and rubber like elastomers are treated with certain chemicals to increase their strength, durability and fitness for commercial use[136]. Since the discovery of this process in 1839 many refinements and discoveries have followed so that the modern rubber technologist, without undue difficulty can compound and vulcanize an elastomer to obtain a satisfactory product with predetermined specific physical properties. In general any elastomer subjected to the vulcanization process show the following changes:

1. Elimination of tackiness
2. Increase in tensile strength
3. Decrease in solubility in solvents
4. Decrease in cold flow and plasticity
5. Increase in elasticity
6. Decrease in temperature sensitivity

Many theories have been suggested throughout the course of the years dealing with possible explanations on the mechanism of vulcanization. But apparently the mechanism of vulcanization is not a simple chemical phenomenon. Even today, no adequate explanation has been offered for some of the observations made on the combination of rubber with sulphur in the presence of other chemicals such as accelerators under various conditions.

As illustrated below vulcanization is primarily a crosslinking process. This is generally accepted for the more important rubbers such as NR and SBR.

If we consider the vulcanization of rubber to be similar to the reaction of sulphur with unsaturated organic compounds to form sulphur bridges then we can write the following equations involving atomic sulphur and isoprene (C_5H_8) the basic rubber unit.

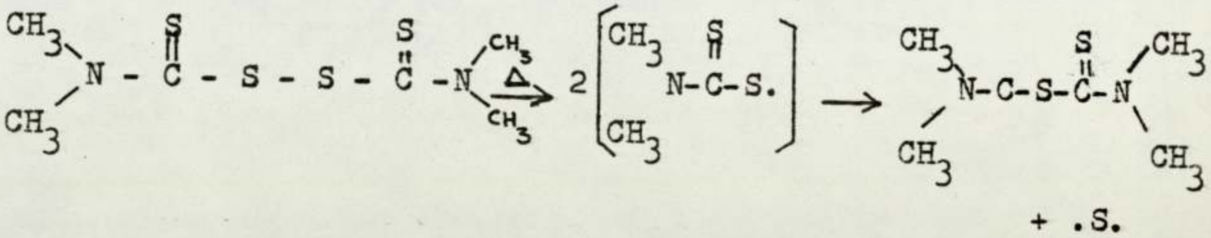


One theory has postulated the formation of the thio ketone which then combines with itself to form a disulfide linkage or thio ether and thus effect "cross linking". Some preference has been shown for structures written differently from the above, where sulphur links the two chains at carbon atoms other than those illustrated. This example illustrates the important point that in this manner two long chain unsaturated hydrocarbon units may thus be bridged to form a three dimensional high molecular weight network to which the term 'vulcanized' has been applied. These sulphur linkages may occur at widely separated points or in clusters on successive repeating units of the above rubber molecule.

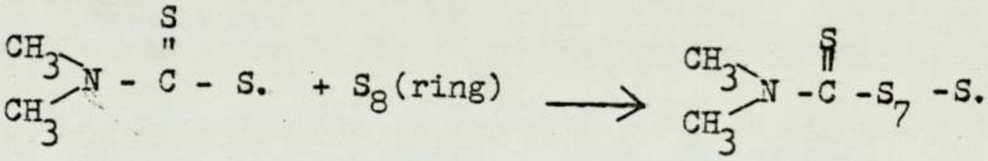
1.4.1Accelerators of vulcanization

The precise function of an accelerator of vulcanization is to catalyse or speed up the formation of sulphur radicals which are the active species in the vulcanization reaction so that vulcanization can be achieved in a matter of minutes or even seconds compared to hours when no accelerator is used.

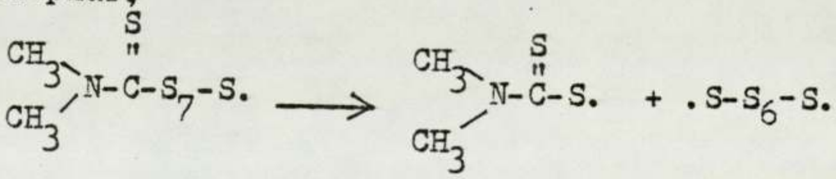
It is well known that under the influence of heat an accelerator of the following type will dissociate through the free radical stage as follows:



A free radical of this type in contact with added inert S_8 sulfur will affect ring opening with formation of a chain radical.



The long chain radical may then be thought of as dissociating back to the accelerator free radical and sulphur chain radical which further dissociates into smaller fragments and eventually atomic sulphur,



$$.S - S_6 - S. \longrightarrow 2.S - S_2 - S. \longrightarrow 2.S - S - S. + 2.S.$$

The atomic sulphur thus formed immediately reacts with the unsaturated portion of the elastomer molecule and it is reasoned that the two fragments combine since two sulphur atoms have been found in the average crosslink in vulcanization of the elastomer. The conversion of a linear polymer into a network results in several fundamental changes in its physical properties as given above.

1.5 Scope and objectives of the work

The exact mechanism of photoxidation of polyethylene and the role played by hydroperoxide groups formed in the oxidation process is not fully established. The main objective of the present work is therefore to study the mechanism of the photo-initiated process in polyethylenes and also to study the possibilities of using hydroperoxide groups for grafting of antioxidant molecules to stabilize the polymer.

Another objective of the present work is to investigate the functional groups formed in these oxidations; to try and relate the processing conditions and nature of the additives, which are mainly destroyers and initiators of hydroperoxides, to the products formed and to understand the role played by these additives in these oxidation and stabilization processes respectively.

The work described in this thesis will provide information on products and functional groups formed and also the embrittlement times of polyolefins under various conditions of oxidation. Behaviour of these polyolefins in the presence of additives which are powerful photo activators such as FeAcAc and CoAcAc, delayed action activators such as FeDBC and also photo stabilisers such as NiDBC and Ni o-hydroxy acetophenone oxime have been studied by means of the rate of appearance and disappearance of certain functional groups on the IR spectrum of these polymers at different stages of exposure to UV light.

This will help to understand the mechanism of photodegradation of polyolefins, and hence to select the suitable type of photostabiliser to be used in various polymers.

Oxidation of NR via singlet oxygen in the presence of various photo activators was carried out to make liquid rubber with good physical properties and hence suitable for practical applications.

2. EXPERIMENTAL METHODS

2.1. Selection of Material for Investigation

Polyethylene is a high molecular weight polymer obtainable in pure form. Like low molecular weight waxes[116], polyethylene exhibits a marked induction period at lower temperatures when no change in physical properties is observed, but during which oxygen is slowly absorbed and hydroperoxide groups are produced. Polyethylenes, in whichever way prepared, are known to be mixtures of crystalline and amorphous materials, and the high density polyethylenes (HDPE) contain a higher proportion of crystalline material which gives rise to the higher melting point, greater stiffness and other advantages associated with them. These polymers are known to contain relatively low tertiary carbon atoms per molecule[117] and are the most stable to oxygen of all the simple polyolefins in the solid state.

Both high density polyethylene, and low density polyethylene are available as stabilized or unstabilized pellets. Unstabilized polypropylene (PP) is available only in the form of an amorphous powder, which can be mixed very easily even when the additive is in the liquid form.

Natural rubber is a very high molecular weight polyisoprene polymer which contains varying amounts of proteins, aminoacids, amines, phenols and many other compounds as non rubber constituents. The amount of these substances present varies from clone to clone and also on the process by which the dry rubber is obtained. Some of the non rubber substances are natural antioxidants and these effect the oxidation process, hence inconsistency of results obtained for different clones. Hence experiments have also been carried out with NR after acetone extraction of the natural antioxidants present to avoid this difficulty.

The high molecular weight and the opacity of this polymer to visible light makes the analysis of the functional groups difficult. Also the fragility of very thin films of unvulcanized raw rubber films makes the quantitative IR analysis of the functional groups very difficult. This effect is well marked in the case of oxidised rubber. Casting the rubber film on a KBr disc for IR analysis was also unsuccessful as all these experiments were carried out in the aqueous phase. Only the experiments with rubber carried out in chlorobenzene were analysed spectroscopically.

Hence the major part of the work described here has been done with polyolefins and mainly with LDPE. When necessary, other compounds also have been used to establish certain specific points in the mechanism of oxidation.

2.2 Spectroscopy

Infrared spectra were recorded using Perkin-Elmer spectrometers 457 and 257. Nuclear magnetic resonance spectra were run on Perkin-Elmer R 14 100 Mc/Sec spectrometer. Tetramethyl silane was used as the internal standard. Mass spectra were obtained using an AEI M59 double focusing spectrometer with 70 ev acceleration.

2.3 Gas Chromatography

Analysis of the products of the reaction between sulphur dioxide and tert-butyl hydroperoxide was carried out on a Pye series 104 chromatograph with flame ionization detector, using polyethylene glycol columns.

2.4 Synthesis of Additives

2.4.1 Cobalt (II) acetyl acetonate dihydrate

This compound was prepared[70] by adding a solution of acetyl acetone (10 g, 0.1 mol) in aqueous sodium hydroxide (4g in 15 ml of water) to a solution of 4.76g (0.05 mol) of cobaltous chloride hexahydrate in 60 ml of water. The orange precipitate formed was filtered, washed with water and recrystallised from a mixture of ethanol and chloroform (3:2 by volume).

$$HC_5H_7O_2 + NaOH \longrightarrow NaC_5H_7O_2 + H_2O$$

$$2NaC_5H_7O_2 + CoCl_26H_2O \longrightarrow Co(C_5H_7O_2)_2(H_2O)_2 + 2NaCl + 4H_2O$$

2.4.2 Cobalt (III) acetylacetonate

This compound was prepared[86] by adding 60 ml of 10% hydrogen peroxide drop wise to a heated solution of 5g of cobalt (II) carbonate (0.042 g mol) in 40 ml of acetyl acetone (0.4 mol) while stirring. At the end of the reaction which took about 45 mins, the mixture was chilled in an ice-salt mixture and filtered. The green solution was recrystallised from a solution of benzene and petroleum ether.

Nickel dibutyldithiocarbamate (NiDBC) and Ni complex of hydroxy acetophenone oxime was obtained from Mr. M.R.N. Fernando of the Department of Chemistry.

Ferric acetylacetonate Fe $(C_5H_7O_2)_3$ and ferric dibutyl dithiocarbamate (Fe DBC) was obtained from Dr. E.A. Boga a research fellow attached to the Chemistry Department.

2.5 Infrared spectroscopic studies of model compounds

Infrared scans were made of diisobutene and oct-1-ene in the presence and absence of the UV stabilizer NiDBC using sodium chloride cells. The solution containing additives were irradiated in the sunlamp and black lamp (SB) cabinet using 25 ml silica tubes and samples were taken from time to time and scanned in the spectrometer. Spacer was selected in such a way that the absorption due to vinyl group was of at least medium size.

2.6 Purification of reagents

Tert-butyl hydroperoxide stabilized with 6% of a 15% w/w slurry of aqueous sodium carbonate, (Koch - light Ltd.) was purified by the following procedure. 50 g (1.25 mole) of caustic soda in 10 ml of water was added to 90 g (1.0 mole) of hydroperoxide in ligroin at 0°C, the sodium salt filtered and this was washed with 25% caustic soda solution; then with petroleum ether, and suspended in 500 ml of water. A stream of carbon dioxide was bubbled through the suspension and dry ice was added instead of carbon dioxide gas, and when all the hydroperoxide had been re-liberated, the solution became opaque and separated into two layers. The lower aqueous layer was extracted three times with petroleum ether, and the combined ethereal fraction washed with dilute sodium bicarbonate solution, and dried over anhydrous sodium carbonate. After removal of the solvent the product was distilled at 52 - 55°C 0.01 torr as a colourless liquid $M_d^{22} = 1.5238$ (53°C $M_d^{20} = 1.5242$). Purity by iodometric titration was better than 98%.

Styrene was washed with aqueous 5% sodium hydroxide to remove inhibitors and then with water, dried with anhydrous magnesium sulphate and distilled under reduced pressure.

Diisobutene and oct-1-ene were purified by passage through a column of alumina of activity grade 1 and were stored under N_2 in the refrigerator. This compound was tested for hydroperoxide groups using IR spectroscopy before use.

3. REACTIONS AND DETERMINATION OF HYDROPEROXIDES

3.1. Iodometric determination of hydroperoxides

Iodometry is one of the most widely used techniques for the estimation of hydroperoxides. In this method the iodide is oxidised quantitatively to iodine by the hydroperoxide in acid medium.

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

Peroxides also oxidise iodide to iodine, but slowly. The conditions used are important and many variations of this technique have been published.

The method used in this work was the modified procedure adopted by Dudley Sully[57 & 58] of the method of Wagner which utilizes chloroform as the solvent and which also acts as the indicator of the titration. Potassium iodide was used instead of sodium iodide in this titration.

The method has the following advantages:

(a) The loss of liberated iodine due to purging or boiling is prevented due to the formation of the triiodide ion which is involatile.

$$I_2 + I^- \rightleftharpoons I_3^-$$

(b) The triiodide ion will not add to the double bonds so that errors due to unsaturation are eliminated.

(c) The use of chloroform as solvent and the absence of strong acids in the system eliminates atmospheric oxidation of iodide.

(d) Heavy and inert chloroform vapour prevents atmospheric oxygen entering the reaction vessel.

(e) The plane glass condenser of length 75 cm which acts as the fractionating column, and the water jacket at the top, prevents the escape of the solvent.

(f) The absence of water in the system avoids low results due to retardation of the iodide-hydroperoxide reaction.

In addition the method is rapid, accurate and needs only simple apparatus.

Reagents

Glacial acetic acid
Analar grade chloroform
Analar potassium iodide crystals

0.01 N sodium thiosulphate solution stabilized with a few drops of chloroform was stored in a bottle covered with aluminium foil. The sodium thiosulphate solution was standardised using a standard solution of potassium iodate.

Method

A 100 ml round bottom flask was fitted with a ground glass joint to a plain reflux tube about 75 cm long and 9 mm internal diameter, the upper 15 cm of the tube was cooled with a water jacket. 10 ml of chloroform and 10 ml of acetic acid were added to the flask and the mixture boiled until the vapour rises to the top of the tube, where it was condensed by the water jacket. The plain portion of the tube acted as a fractionating column to remove traces of dissolved oxygen, and further, by adding potassium iodide solution and the sample through the column it was possible to ensure that they too were de-aerated before a reaction occurs with the reagents in the flask. When the acetic acid-chloroform mixture was refluxing steadily, a solution of 1g of potassium iodide was poured slowly down through the column, for refluxing from the water jacket to continue without interruption. Then added the organic peroxide (which is to be determined) either in the form of a liquid or as oxidised strips of film, down the column. The cooling water was turned off in order to raise the condensation level and thus ensured that the entire sample was washed into the flask. The sample was boiled for a further 3 mins. The contents of the flask were cooled and the liberated iodine was titrated with 0.01 N sodium thiosulphate in the usual way.

$$\text{Percentage of hydroperoxide and dihydroperoxide} = \frac{3.3 \times N \times V}{2 \times W}$$

Where V = Volume of thiosulphate used

N = Normality of thiosulphate solution

W = Weight of the sample

One of the drawbacks of this method is the interference of dihydroperoxides.

3.1.2 Colorimetric determination of hydroperoxides

Very few methods of peroxide analysis are sufficiently sensitive to measure very low concentrations found in processed polymers. The method of Bocek[128] is capable of measuring 10^{-6} moles in polymer samples of convenient size. The method was found to be irreproducible when applied to polyethylene filsm and two contributory reasons were identified which accounted for this:

1. The iron phenanthrolene complex, which is estimated by UV spectrophotometry at 510 nm, is unstable to light of this wave length and repeat measurements on replicate samples are necessary.
2. Due to the slow penetration of the solution into the polymer film, it was found that measurements were reproducible only after the solution was in contact with the film for 2 hours. Then the absorption at 510 nm becomes maximum. A minimum time of 2½ hours was used in practice. The method was calibrated using pure tert-butyl hydroperoxide.

Reagents

(a) 5% solution of o-phenanthrolene in benzene.

(b) The buffer solution - containing 1.5 ml of orthophosphoric acid in 1000 ml of methanol.

(c) 0.025 M ferrous sulphate solution stabilized with concentrated sulphuric acid in benzene and methanol mixture.

Procedure:

The film containing the hydroperoxide and dihydroperoxide groups were cut into thin strips and placed in a small conical flask. Exactly 10 ml of the 0.025M ferrous sulphate solution and 1 ml of the phosphoric buffer solution were added and allowed to stand for half an hour at room temperature. The liquid part was drained into a 25 ml graduated flask, the polyethylene strips were washed, and the washings were collected in the same graduated flask. To this system 1 ml of the o-phenanthrolene solution was added by means of a pipette and kept in the dark for not less than 2½ hours.

This was diluted by mixing 2 ml of this orange coloured solution with 3 ml of methanol and measured the absorption at 510 nm using the PE 137 UV spectrophotometer.

A standard curve was drawn using varying amounts of tert-butyl hydroperoxide.

3.13 Infrared spectroscopic method for the estimation of hydroperoxide content in oxidised polyolefins

Several methods have been presented by previous workers for the estimation of hydroperoxide groups. The methods used could be divided into two types.

(a) Direct method: where the absorption of hydroperoxide group is measured.

(b) Indirect method: where the hydroperoxide group is converted into a derivative[66] and the absorption of the derivative is measured.

One of the major difficulties encountered in using the direct method is that the hydroxyl groups tend to form hydrogen bonds among themselves and with other polar groups. The intensities of the absorption depend on the degree of association in the system. Although most of the previous workers have used the intensity of the hydrogen bonded hydroperoxide groups as the hydroperoxide band intensity, there are many other hydroxyl groups which are commonly present in oxidised polymers appearing at the same region of wave numbers.

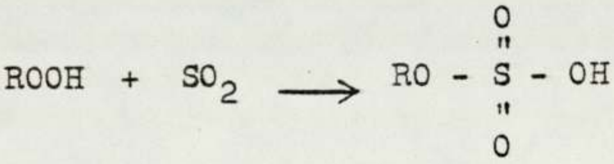
The band due to pure isolated hydroperoxide groups which is very sharp and not very stable at temperatures above 100°C due to thermal decomposition appears at 3550 cm^{-1} which is completely separated from the hydrogen bonded and associated hydroperoxide band. (Fig 4, Page 74)

$$2\ \mathrm{ROOH} \rightleftharpoons \underset{\text{Associated}}{(\mathrm{ROOH})_2}$$

Hence all the hydroperoxide intensity measurements were made corresponding to the total intensity of the pure hydroperoxide band and not by measuring the hydrogen bonded hydroperoxide band.

3.1.4 Indirect measurement of hydroperoxides by IR spectroscopy

Fairly rapid reaction has been observed by Mitchel and Perkins[94] of sulphur dioxide with hydroperoxide groups formed during the early stages of oxidation of polyethylene. Measurements in the infrared spectrum of the resulting strongly absorbing groups which could be a stable fragment of this unstable sulphate forms the basis for this new, specific, sensitive method of analysis.



$$\mathrm{ROOH} + \mathrm{SO_2} \longrightarrow \mathrm{RO}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\mathrm{OH}$$

With slight modification, this method is suitable for rough determination of hydroperoxides in polypropylene and other polyolefins.

Procedure: Samples of polyethylene films (1 mil film) were thermally oxidized by heating in air. After different periods of time, portions were scanned in a double beam infrared spectrophotometer PE 457. The same specimens were then placed in a desiccator, air was evacuated, and gaseous sulphur dioxide introduced to a pressure of 1 atmosphere. After several hours exposure, samples were removed from the desiccator and rescanned. Band intensities at 920 cm^{-1}, 1195 cm^{-1} and 3520 cm^{-1} were measured using base line technique.

Band at 920 cm^{-1} is due to hydroperoxide sulphate
Band at 1195 cm^{-1} is due to hydroperoxide sulphate
Band at 3520 cm^{-1} is due to pure hydroperoxide

3.2 RESULTS AND DISCUSSION

3.2.1 Estimation and reactions of hydroperoxides

The results of the experiments carried out using the iodometric titration indicate that the method is applicable for estimation of hydroperoxide formed in the polymer during the process of heating the sample at temperatures close to 150°C for more than an hour. Use of an indicator is not necessary as the final change in colour is from yellow to colourless. The accuracy of the method depends on the following factors:

(a) Manner in which the samples are arranged in the oven, that is the geometry of the arrangement of the samples in the oven.

(b) Availability of a sufficient supply of oxygen or air.

Misleading results are obtained when the films are piled up in the flask. Oxidation of the films on a petri dish does not give good results as the film becomes brittle and sticks on to the dish on ageing, making the transfer into the titration flask difficult. Hence the results are not accurate and not reproducible under these conditions.

The difficulties can be overcome by evenly spreading the film, cut into small pieces, in single layers, in the open conical flask. Ageing and titrating being carried out in the same flask. Air inlet to the ageing oven is open throughout the ageing period.

In this process of oxidising the film, the temperature was maintained between 145° and 150°C because at temperatures below 145°C the amount of hydroperoxide formed cannot be detected by iodometric titration. Temperatures above 150°C cannot be used as the film of polymer melts and charring occurs above 150°C.

In any case hydroperoxide contents obtained by Wagner's method for different sets of film samples of the same thickness followed no definite pattern.

Table 1 - Results of titrations

Ageing temp. and TIME	Wt. of the polypropylene film	Vol. of 1.025N $Na_2S_2O_3$ used	Hydroperoxide content
1½ hrs at 150°C	0.1446 g	23.0 ml	564×10^{-6}moles
1½ hrs at 150°C	0.1152 g	18.8 ml	459×10^{-6}moles
1½ hrs at 150°C	0.2117 g	28.0 ml	690×10^{-6}moles
1½ hrs at 150°C	0.2874 g	30.6 ml	755×10^{-6}moles
2½ hrs at 150°C	0.2535 g	25.4 ml	625×10^{-6}moles
2½ hrs at 150°C	0.3190 g	25.0 ml	615×10^{-6}moles
2½ hrs at 150°C	0.2562 g	30.0 ml	740×10^{-6}moles

3.2.1.1 Inconsistent Results

Inconsistency in the hydroperoxide concentration obtained by ageing and titrating polyethylene may be due to the preoxidised parts of the unstabilised polymer or due to the method of oxidation of the polymer in the oven. Visual observation and manual removal of the discoloured brittle portions of the material was essential to obtain reproducible results like those Carlsson and Wiles[95] obtained in their colorimetric determination. Also these errors were found to be minimised when Sully's[58] modofication was used indicating that both those factors contribute to the final results.

3.2.2 Spectroscopic methods for hydroperoxides

The sulphate methods for the determination of hydroperoxides formed on the polyethylene film has been found by careful analysis to be a good method[66] although

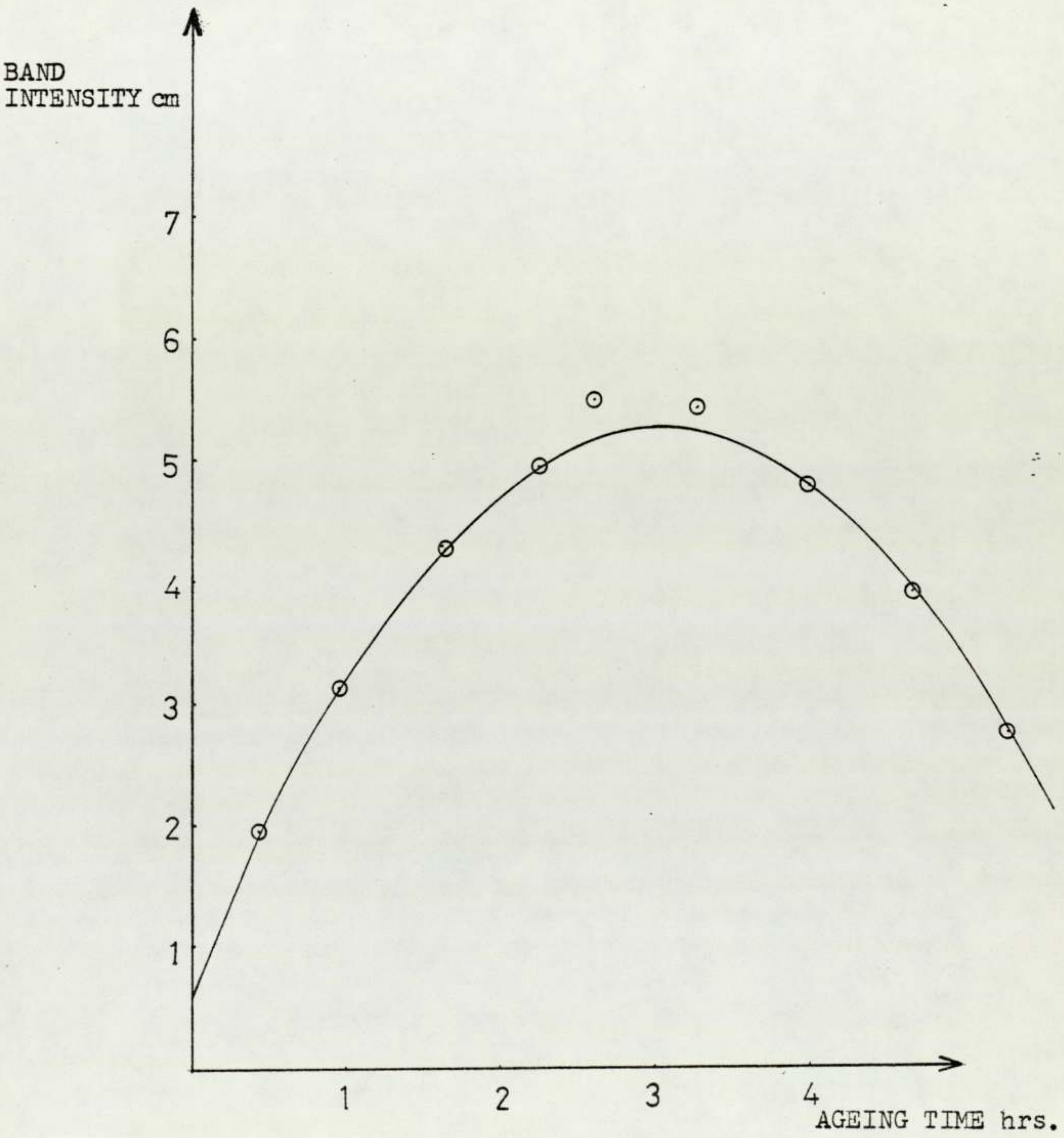


Fig. 1

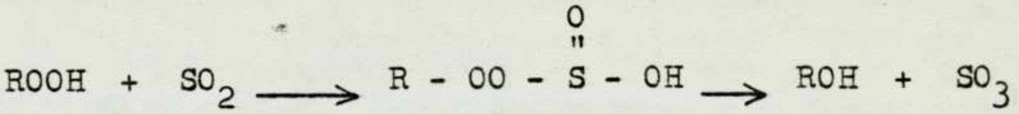
Variation of intensity of the band at 920 cm^{-1}

with ageing time.

criticised by Carlsson and Wiles[37]. There are two important bands in the IR spectrum of the film containing hydroperoxide after sulphur dioxide treatment.

1. Carbonyl band which appears at 1720 cm^{-1} region, which slightly decreases after SO_2 treatment of the film.
2. New band appearing after SO_2 treatment of the oxidised film which appears at 920 cm^{-1}.

Band due to pure hydroperoxide that is formed on the film on oxidation and appearing at 3520 cm^{-1}. This band disappears after the SO_2 treatment.



$$ROOH + SO_2 \longrightarrow R-OO-\overset{\overset{O}{\|}}{S}-OH \longrightarrow ROH + SO_3$$

The intensity of all these bands increased proportionately with the time of ageing reaching a maximum at 4 hrs. Beyond 4 hours they decreased again owing to thermal decomposition. It was also noticed that the intensity of the band due to the sulphate at 920 cm^{-1} as well as the band at 3520 cm^{-1} decreases with time of exposure of the film to air outside the SO_2 chamber. In the case of the band at 920 cm^{-1} this decrease occurs gradually until it reaches an equilibrium point where only the bonded sulphate groups remain on the film. The decrease is supposed to be due to the unbonded surface absorbed sulphur dioxide molecules lost from the surface under atmospheric conditions.

Intensity decrease of the band due to unbonded hydroperoxide at 3520 cm^{-1} is due to the breaking down of the unstable hydroperoxide groups to ketonic groups under atmospheric conditions. This can happen even in the absence of oxygen and light.

In measuring the intensity of the band only the sag due to the band at that particular wavelength is measured. The carbonyl band at 1710 cm^{-1} is found to decrease slightly but proportionately to the amount of oxidation that has been taking place after sulphur dioxide treatment.

The intensity of the band at 920 cm^{-1} for a sulphur dioxide treated oxidised polyethylene film can be used for the quantitative determination of the hydroperoxide concentration on that film by comparison with a standard.

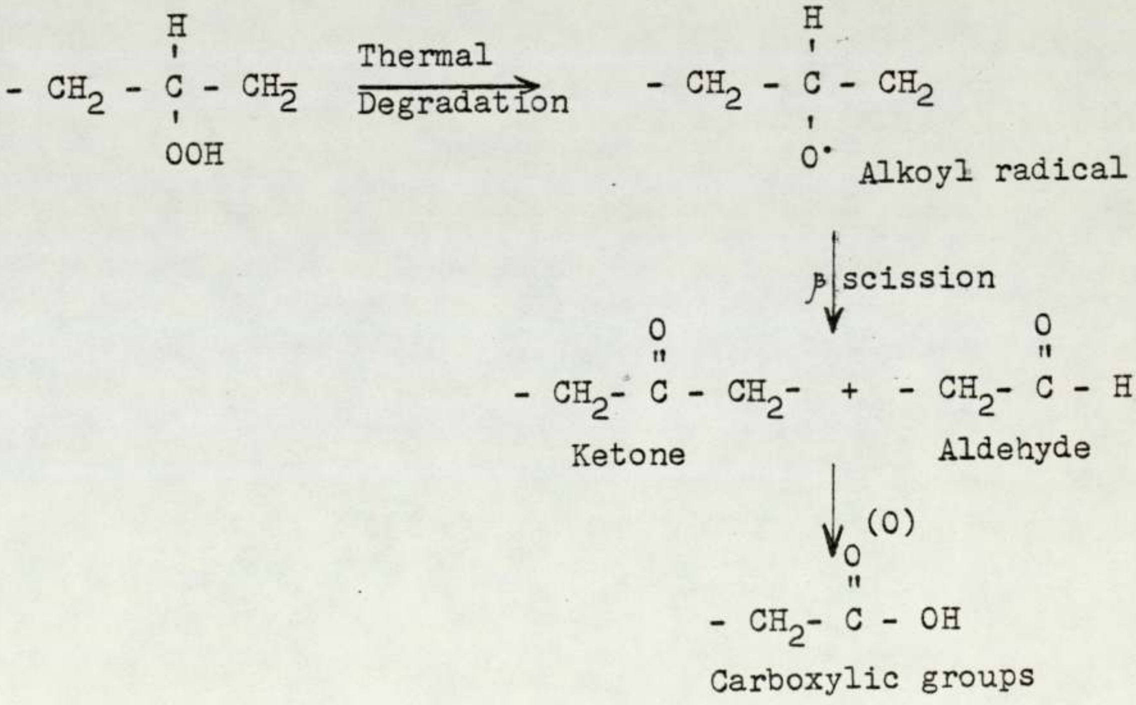
The standard was part of the oxidised polyethylene film whose hydroperoxide content has been determined by iodometric titration prior to the sulphur dioxide treatment. IR analysis of both test samples and standard was then carried out (Fig.1).

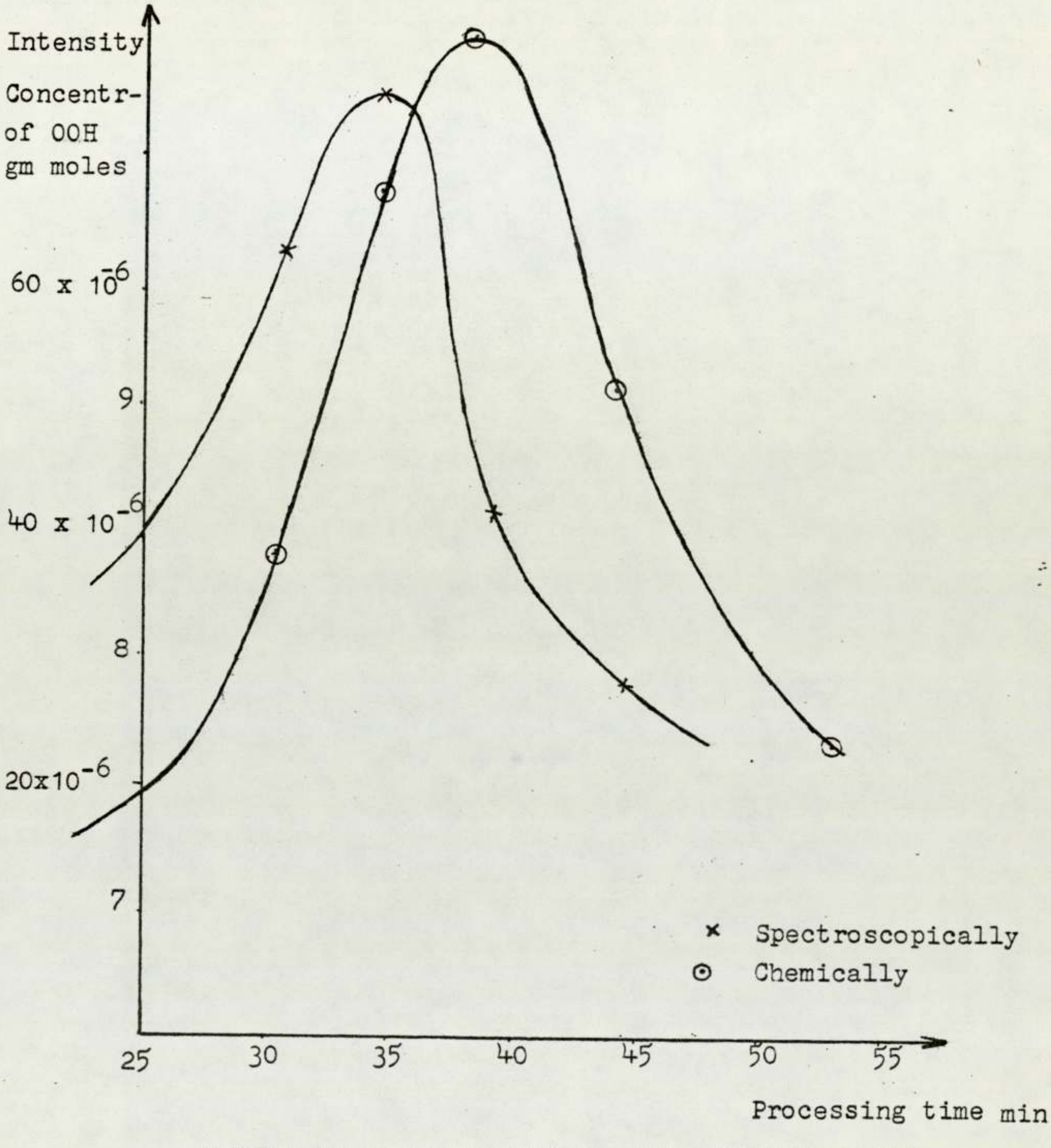
For example if the intensity of the band roughly measured using a ruler at 920 cm^{-1} for a sample containing hydroperoxides up to 5% is 3.5 cm; then the concentration of hydroperoxide on a film which is also aged at the same time, at the same temperature, and SO_2 treated, which gives a band of intensity X cm at the wave number is :-

$$= \frac{5.0}{3.5} \times X \text{ percent}$$

This gives an approximate value for the hydroperoxide concentration formed on the film. The same procedure is applicable to the pure hydroperoxide band also. But in this case a test piece of the standard need not be treated with SO_2.

In the case of hydroperoxide and carbonyl bands, when the ageing time exceeds 4 hours at 150°C, the intensity of the carbonyl band increases slightly, whereas the intensity of the hydroperoxide band drops. This can be explained by the following reaction:





VARIATION OF HYDROPEROXIDE CONCENTRATION WITH IRRADIATION TIME (MEASURED CHEMICALLY AND SPECTROSCOPICALLY MEASURING THE BAND INTENSITY AT 3520 CM^{-1} DIRECTLY)

Fig. 1b.

Some of the hydroperoxides undergo thermal decomposition followed by oxidation to give more and more carboxyl and carbonyl groups. These 3 groups appear at 1710 cm^{-1} - 1720 cm^{-1} region in the IR spectrum. The intensities of the carbonyl and sulphate bands obtained for different ageing times were plotted on the same graph. It is clearly seen that on both curves near the transition point the intensity of the band varies anomalously giving points scattered over that region due to varying concentration of the hydroperoxides at that stage. This is the stage at which the rate of thermal breakdown of hydroperoxides starts to exceed the rate at which they are formed. In the ascending part of the curve the rate at which they are formed is always greater than the rate of decomposition.

$$2\ ROOH \rightleftharpoons RO. + ROO. + H_2O$$

3.2.3 Colorimetric determination of hydroperoxide

Very few methods of peroxide analysis are sufficiently sensitive to measure the very low concentrations found in processed polymers. Bocek[128] has proposed a colorimetric determination of hydroperoxides using a standard ferrous ion solution. This method seems to be sensitive enough to measure 10^{-6} moles in polymer samples of convenient size.

In this method a specimen containing hydroperoxide groups is immersed in a standard solution of ferrous sulphate solution in the presence of phosphoric acid buffer. The hydroperoxide groups in the specimen then reacts with the ferrous ions by oxidising them to ferric ions.

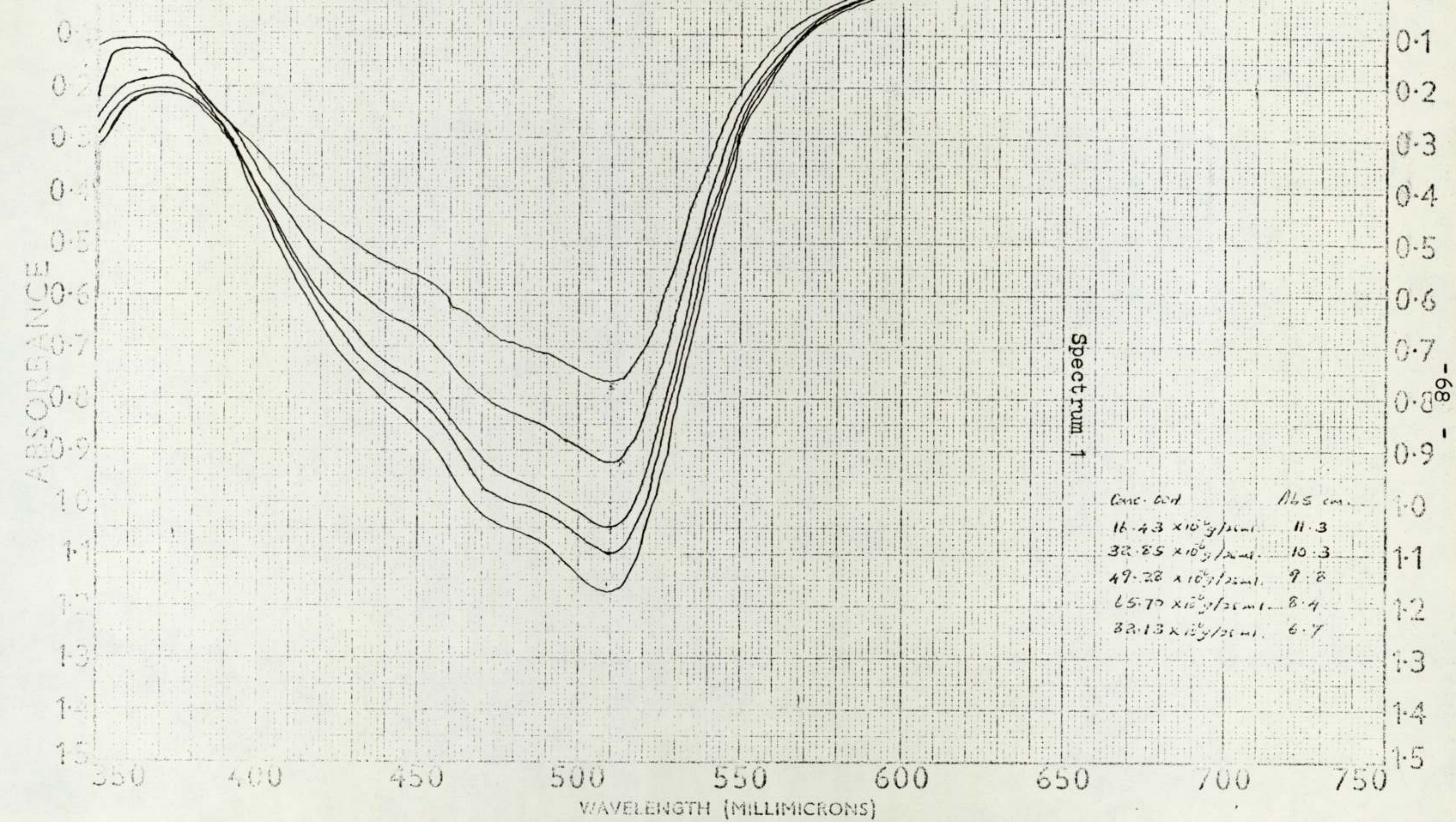
$$ROOH + Fe^{2+} \longrightarrow RO. + OH^{-} + Fe^{3+}$$

After some time this solution is treated with 1,10-phenanthrolene. Only the ferrous ions in excess of those which reacted with ROOH and was converted to ferric ions, reacts with o-phenanthrolene to give an orange coloured solution, the intensity of which is measured later. The following facts have to be taken into account:

1. It was observed that the iron-phenanthrolene complex, which is estimated by UV spectrophotometry at 510 nm, is unstable to light of the wave length and repeat measurement on replicate samples are necessary.

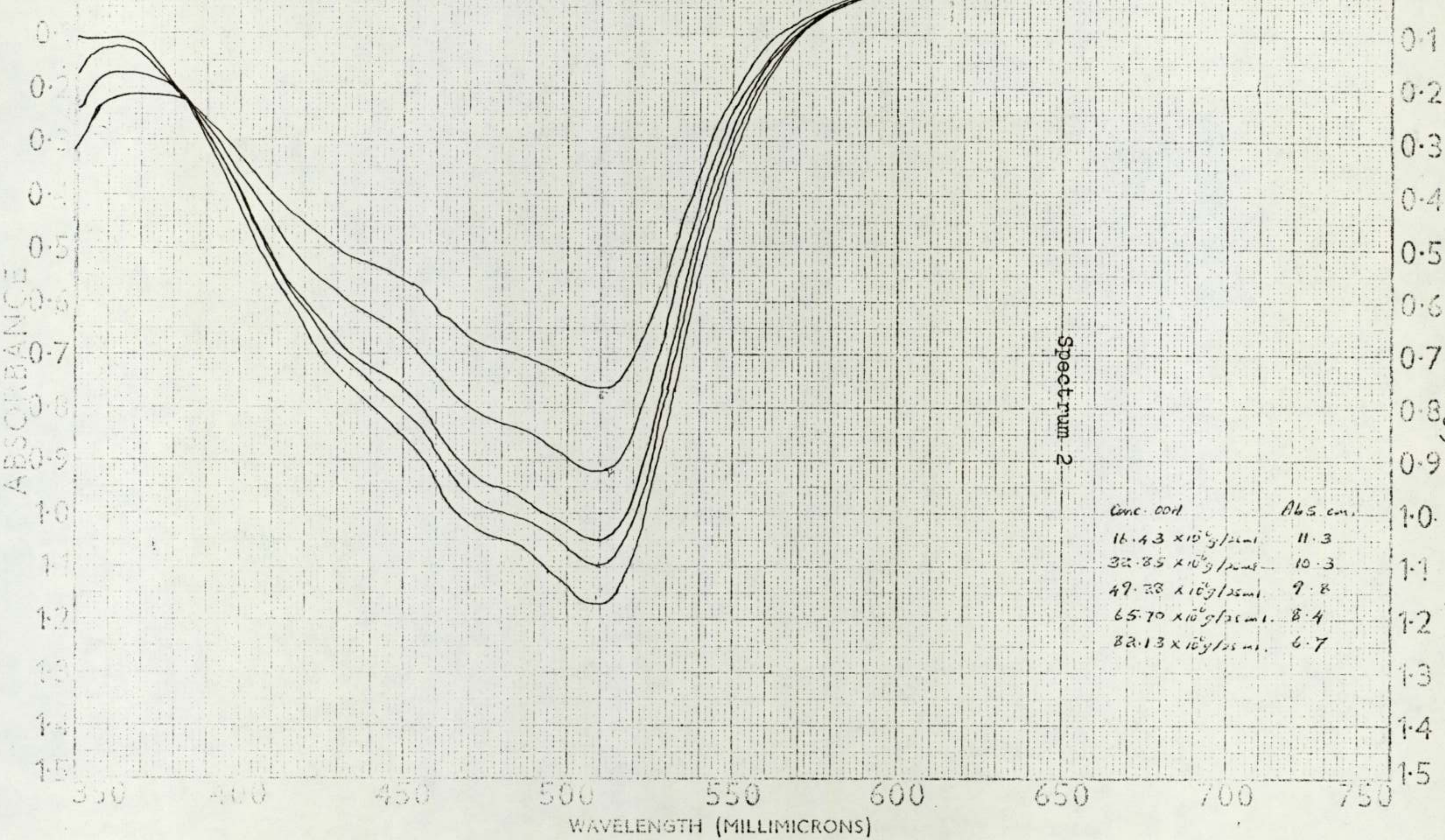
2. Due to the slow penetration of the solution into the polymer film, it was found that measurements were reproducible only after the solution was in contact with the films for 2 hrs. A minimum time of 2½ hrs was used in practice. The method was calibrated using pure tert-butyl hydroperoxide.

This procedure was found to be the best of all the methods given in the literature. Also the procedure is found to be reproducible and capable of measuring concentrations of 10^{-6} mol/l in polymer samples of convenient size, whereas



Absorption at 510 nm for Ferrous o-phenanthrolene complex

(For the unknowns)



Conc. ooH	Abs. cm.
16.43×10^{-6} g/25 ml	11.3
32.85×10^{-6} g/25 ml	10.3
49.28×10^{-6} g/25 ml	9.8
65.70×10^{-6} g/25 ml.	8.4
82.13×10^{-6} g/25 ml.	6.7

ABSORPTION AT 510 nm FOR Ferrous o-phenanthrolene complex

(For the standard curve)

other methods cannot be used where concentrations are low.

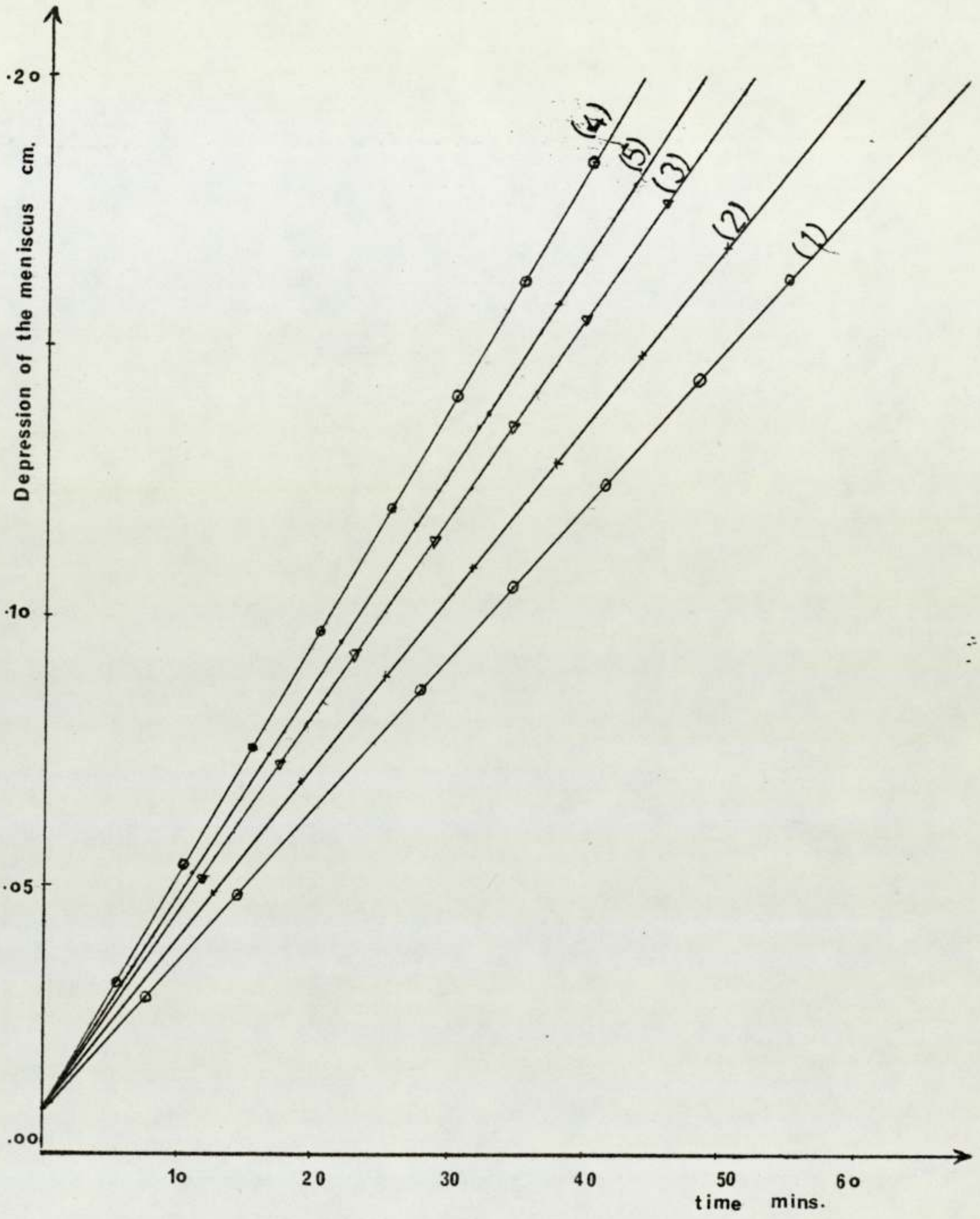
3.3 Reactions of hydroperoxides with sulphur dioxide and triphenyl phosphite

The formation of radicals by the reaction of sulphur dioxide gas and triphenyl phosphite with tert-butyl hydroperoxide was studied by means of styrene polymerisation by dilatometry.

A mixture of freshly distilled styrene with varying concentrations of the initiator system purged with a stream of N_2 gas was used in the polymerization studies using dilatometers. The initiator used was a mixture of tertiary butyl hydroperoxide with a solution of sulphur dioxide gas dissolved in carbon tetra chloride. The same experiment was repeated with triphenyl phosphate dissolved in carbon tetrachloride in place of the hydroperoxide/sulphur dioxide mixture.

The reaction was carried out in a water bath at 80°C and the kinetics of the reaction was followed by measuring the depression of the liquid meniscus in the dilatometer using a cathetometer at different intervals of time. Extremely low concentrations of SO_2 were used as the complex formed between hydroperoxide and sulphur dioxide is very unstable and decomposes violently liberating a large amount of heat. The rate of polymerisation initiated by hydroperoxide in the absence of any other additive was also studied at 80°C.

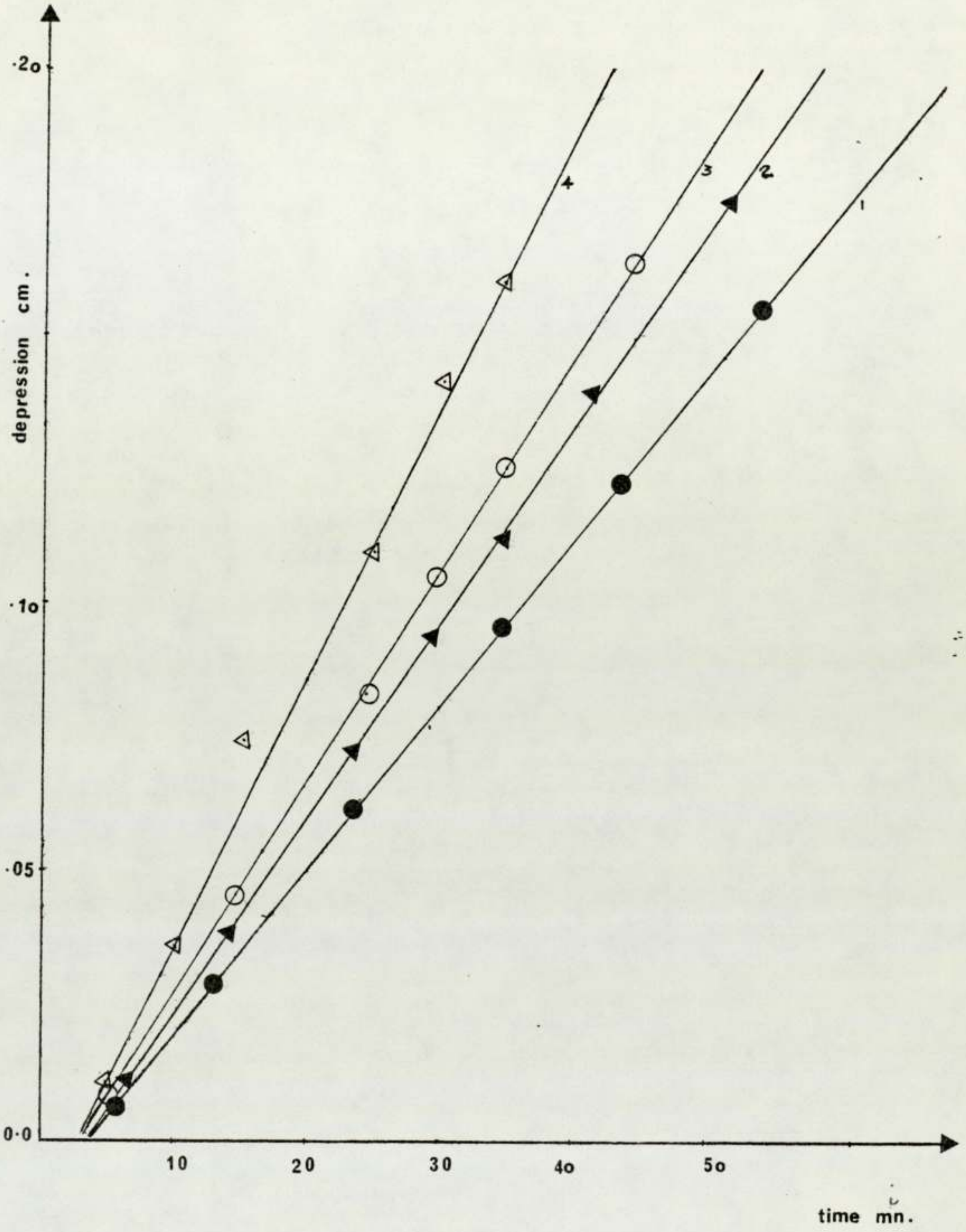
Decomposition of tert-butyl hydroperoxide in the presence of sulphur dioxide was rapid at the beginning and the rate of decomposition retarded gradually and



Effect of triphenyl phosphite content on the rate of polymerisation of styrene initiated by constant amount of TBHP

Fig. 2

1. 0.011g moles of TBHP with 0.0007g moles of TP
2. " " " 0.0008 " "
3. " " " 0001 " "
4. " " " .0012 " "
5. " " " .0013 " "



Effect of concentration of sulphurdioxide on the rate of polymerisation of styrene initiated by a constant amount of TBHP

Fig. 3

1. .011g moles of TBHP with .005 g moles of SO_2
2. " " " .010 " "
3. " " " .02 " "
4. " " " .015 " "

reached a slow almost steady rate of decomposition (fig. 3).

The highest concentration of sulphur dioxide showed the highest activity and the autoretardation commenced at a lower hydroperoxide concentration compared to that observed with lower concentrations of sulphur dioxide.

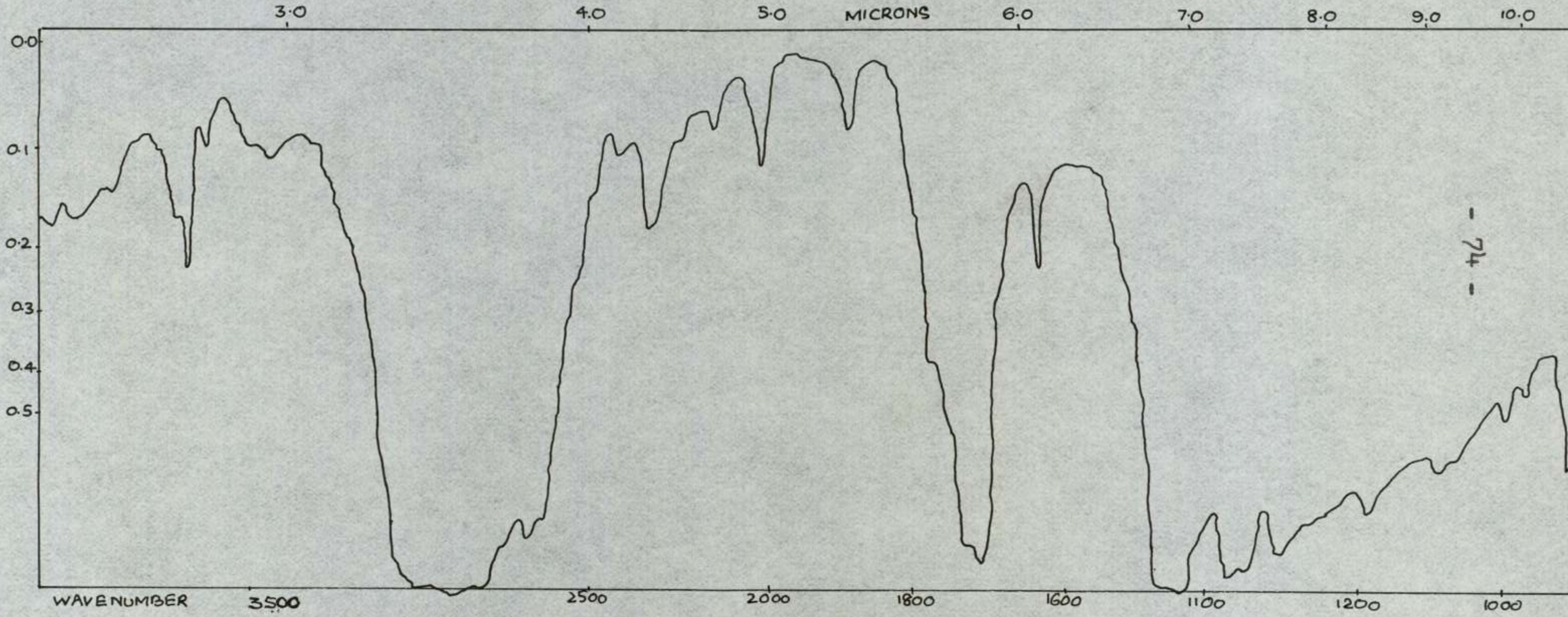


Fig. 4: IR Spectrum of oxidised LDPE (Band at 3520 nm is due to hydroperoxide)

The SO_2 concentration was kept constant at 0.0010 moles. The rate of decomposition of hydroperoxide was found to increase with the concentration of sulphur dioxide used. Therefore this reaction is a pseudo first order reaction of the type.

$$\frac{-d\ (\text{hydroperoxide})}{dt} = K_2\ (\text{Hydroperoxide})\ (SO_2)$$

(Hydroperoxide) = Concentration of hydroperoxide

(SO_2) = Concentration of sulphur dioxide

Sulphur dioxide should either be in excess or should not be consumed in the reaction in order to obtain the observed kinetics.

The rate of decomposition of hydroperoxide in the presence of triphenyl phosphite was not as rapid as it was in the case of sulphur dioxide. The highest rate of polymerisation was shown by a critical concentration of.0012moles of phosphite above which the rate drops again.(Fig.2).

3.4 Gas chromatography

Analysis of the products[80] of the reaction between t-butyl hydroperoxide and sulphur dioxide gas was carried out on a Pye 104 chromatograph with flame ionization detector. Matched glass columns of five feet long and quarter of an inch in diameter packed with 15% polyethylene glycol 20 M on 80-100 mesh universal support were used. Nitrogen was used as the carrier gas at a flow rate of 60 ml/min. The method required that the column be operated according to the following temperature conditions:

Constant temperature of 145°C for 5 minutes.
Detector temperature of 200°C.

for the analysis of the reaction products, reactants were diluted with carbon tetrachloride and the two components mixed just before analysis while the reaction vessel was immersed in ice. 5-10 micro litres of the diluted solutions were used in the chromatograph. Different oxidation products were identified by sending pure t-butyl hydroperoxide and pure sulphur dioxide gas dissolved in carbon tetrachloride and comparing the retention times.

Retention times of the different compounds under the above conditions are given below:

TABLE 3 - RETENTION TIMES AND RELATIVE INTENSITIES OF TBHP AND ISOPROPYL ALCOHOL IN THE GLC

Compound	Retention time (min)	Relative Intensity
Pure TBHP	1.5	Weak
	5	Strong
	7	Medium
Isopropyl alcohol	1.5	Very strong and the only peak

From this it is clear that one of the products of the reaction between tert-butyl hydroperoxide and sulphur dioxide is isopropyl alcohol.

Another very sharp peak was also seen in the chromatogram at a very short retention time indicating that it is due to a gaseous product. Although it was suspected that this could be due either to uncombined SO_2 gas or due to the SO_3 gas produced in this reaction, it was not possible to confirm it.

4. EFFECT OF PROCESSING AND THERMAL-OXIDATION ON UV STABILITY OF POLYETHYLENE

The deterioration of polyolefins on outdoor exposure may be induced by a number of factors. Among those factors UV radiation, oxygen, moisture, ozone and metal vapours are the most important in causing the degradation of polyolefins. The mechanism of such degradation particularly in polyolefins is now generally accepted as an oxidative chain reaction initiated by UV light. In polymer photoxidation those factors or agents which cause this initiation to occur are more important than any other factor, and indeed in free radical mechanism it is the initiation reaction that allows the subsequent reaction steps like propagation to take place.

It is known that the most important chromophoric groups which are the initiators of photoxidation in polyolefins, are hydroperoxides and their breakdown products, notably carbonyl compounds. The purpose of this study is to relate the rate of UV degradation of the polyolefins to the thermal oxidative treatment which is always involved in their manufacture.

Wiles and his co-workers have shown that the quantum efficiency of radical initiation for polypropylene hydroperoxide is much higher than it is for the derived carbonyl compounds[95]. Polyolefins containing varying concentrations of hydroperoxide and carbonyl groups were prepared by processing it in the torque rheometer for varying time periods at different temperatures.

4.1 Experimental

4.1.1 Processing in the Torque Rheometer

Processing conditions were simulated by use of the prototype RAPRA Torque Rheometer[82] which is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds. It has good temperature control, and a continuous read out is provided of both melt temperature and the torque required for mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. Experiments showed that this provided a virtually air-tight seal. A full charge was 35 g of HDPE and when this charge was used the chamber was sealed. When it was desired to process in the presence of oxygen, a charge of 20 g was employed, and the chamber left open to the atmosphere. A minimum mixing time of 5 mins was required to ensure complete gelation of the polymer.

On completion of mixing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation. The material was compression moulded at 160°C for 2 mins into sheets of thickness 0.008 in. using a special grade of cellophane as mould release agent.

4.1.2 Infrared spectroscopic method for the estimation of carbonyl content in oxidised polyethylene

The infrared spectroscopic technique is widely used in the estimation of carbonyl groups and many other functional groups formed in polymers during oxidation. Estimation of carbonyl groups present in irradiated and oxidised polymer films were carried out using the Perkin-Elmer 457 spectrophotometer. A thin film of thickness 7 to 9 mil mounted on bristol-board frames was used for the measurement of carbonyl absorbance while the reference is air. Weak absorptions due to different types of carbonyl groups appeared as shoulders on either side of the main absorption at 1715 cm^{-1}. The total intensity of the carbonyl absorption of the sample at 1715 cm^{-1} and in the neighbourhood of 1715 cm^{-1} was measured as absorbance. The base line technique was used to determine Io. The term absorbance A refers to the quantity:

$$A = \mathrm{Log}_{10} \frac{Io}{I}$$

Where Io is the intensity of the IR irradiation effectively entering the sample.

And I is the intensity of IR irradiation before leaving the sample.

From Beer - Lambert's law

Absorbance $A = Ecl$

Whre E = Extinction coefficient

c = Concentration of the absorbing material

l = Path length of the IR irradiation

Another method to determine the relative amount of carbonyl groups is by the measurement of the carbonyl indices. This is done mainly to compensate for the errors arising due to variation in sample thickness. Carbonyl index is the ratio of the carbonyl absorbance to the absorbance of the group chosen as the standard.

$$\text{Carbonyl Index} = \frac{\text{Absorbance of carbonyl peak}}{\text{Absorbance of the standard peak}}$$

One of the requirements in choosing the standard peak is that it should not vary with any treatment of the material. Reasonably accurate values of carbonyl indices could be obtained only when the standard peak is of medium intensity. The accuracy of this method drops when a very large peak or a very small peak is used as the standard.

The absorption band at 1895 cm^{-1} which is due to an overtone of C-H stretching in the spectrum of polyethylene was of the required size at the thickness range used and was chosen as the standard peak.

4.1.3 Infrared spectroscopic measurement of vinyl and vinylidene groups

Infrared spectroscopy is widely used for the estimation of vinyl group formation on oxidised polyethylene. But (regarding the low intensity and the short lifetime on UV irradiation) there is no published information on estimation of the variation of vinylidene band intensity in polyethylene subjected to UV light.

Important, interesting data were obtained in the laboratory by the careful measurement of vinylidene band intensity using the base line technique[79]. Before the samples are subjected to UV irradiation vinylidene band at 887 cm^{-1} has a fairly measurable intensity. But on irradiation this band started to disappear while the vinyl band at 909 cm^{-1} started to grow gradually. The rate of growth of the vinyl band is so fast that after a very short time of irradiation weak absorption due to the vinylidene band appeared as a shoulder of the vinyl band. At this stage accurate measurement of the intensity of the vinylidene band was very difficult without the use of Du Pont analyser. This machine greatly helped to resolve the two interfering peaks by the principle of Fourier analysis to a fairly good accuracy. Vinylidene and vinyl indices were calculated with respect to the intensity of the band at 1895 cm^{-1}.

4.1.4 Gel content determination

1g samples of pure and additives incorporated LDPE films irradiated for different lengths of time were taken in 25 ml conical flasks containing 15 ml of chlorobenzene and heated to boiling until the undissolved pieces completely disappears. The solution was filtered through No. 3 accurately weighed sintered glass crucibles and dried in the oven at 70°C and the crucible containing the gel part reweighed.

4.1.5 Experiments with singlet oxygen

The experimental[82] set up is shown in Fig. No. 5. The flow tube system is constructed of 13 mm quartz tubing. Air was admitted to the flow system at a few torr pressure (2-10 torr) with an estimated flow rate of 10^{-3} ml/min and passed over mercury at 23°C and then through the discharge region in a micro wave cavity. The discharge was generated by a Raytheon Microtherm generator at 2350 M Hz. The mercury forms a brown coating of mercuric oxide down stream from the discharge, which efficiently removes oxygen atoms and apparently enhances the $^1O_2^*$ concentration. The presence of the slightest trace of singlet or triplet atoms was easily detectable by the existence of a yellow green emission from nitrogen dioxide. Checks were made from time to time to confirm the absence of this emission. The gas emerging from the discharge region was passed into the sample vessel which was also a glass vessel fitted with an outlet tube. Formation of $^1O_2^*$ was checked by having carotene in the sample vessel which discoloured on exposure to $^1O_2$.

Procedure

Film samples both pure and those containing excited state quenchers were placed in the sample vessel and $^1O_2^*$ was allowed to pass through for varying periods from 1 hour to 10 hours. After exposure, they were scanned on the PE 457 IR spectrophotometer to check the appearance of new functional groups.

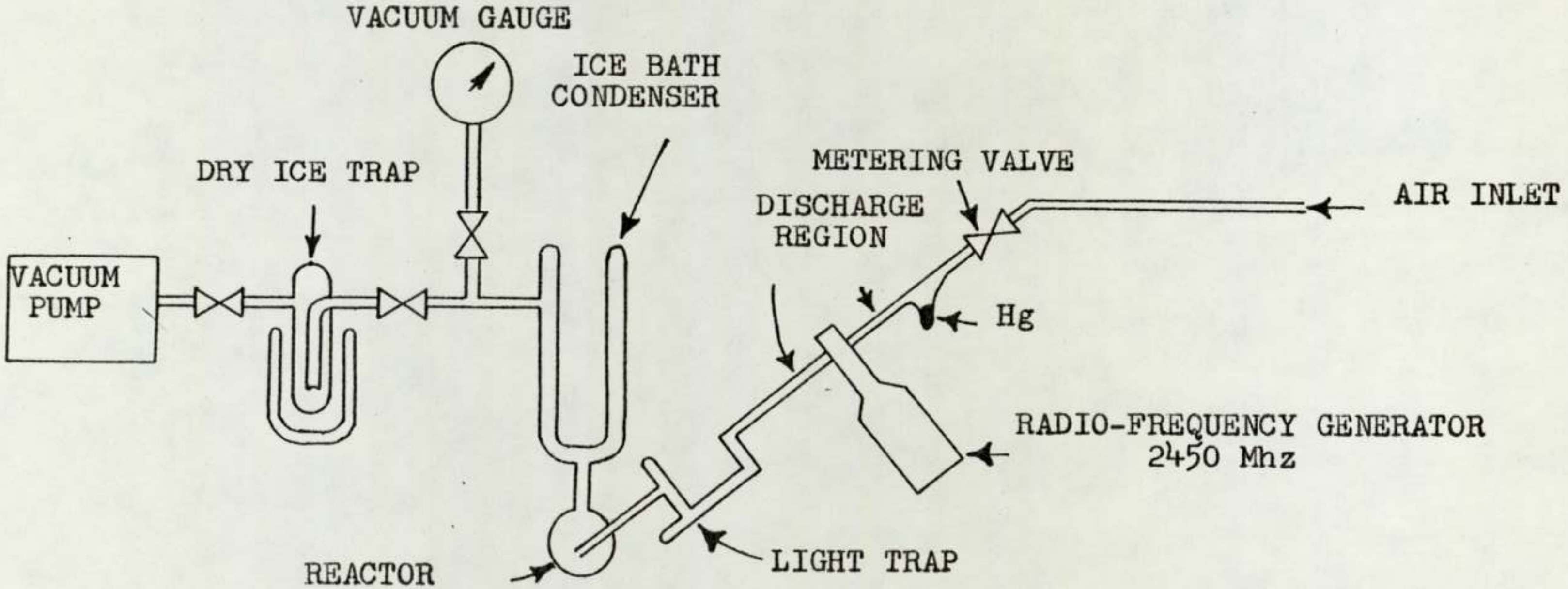


Fig. 5. Diagrammatic representation of flow system used in excited singlet oxygen quenching experiments.

4.1.6 Embrittlement Testing

Embrittlement testing was done by flexing a fresh piece of the sample through 180°, or by means of the impact modulus tester (fig.6) using a falling weight of 5 g. Normally repeat tests gave values for embrittlement time lying within 10% of the mean value. Occasionally, values lying well outside this range were obtained. The reason for this is being investigated but these values were ignored. Normally not more than 3 tests were required; in no case was more than five samples needed.

Impact modulus testing was carried out by placing the sample on the sample platform and covering it with the upper platen. Then a medium weight of mass 5 g held at a height of exactly 30 cm from the sample film by means of the magnetic arrangement is carefully released. After every impact samples were taken out and examined for tiny cracks in the central area. Repeats were done with fresh samples of exactly the same thickness.

4.1.7 Determination of carboxyl groups in the presence of carbonyl groups

Acids, ketones and aldehydes, which are the end products reported from these oxidations, have similar spectra in the 5.5 - 6.0μ region. It is only in this carbonyl stretching region that the products have suitable absorptivity to give quantitative data. The absorption

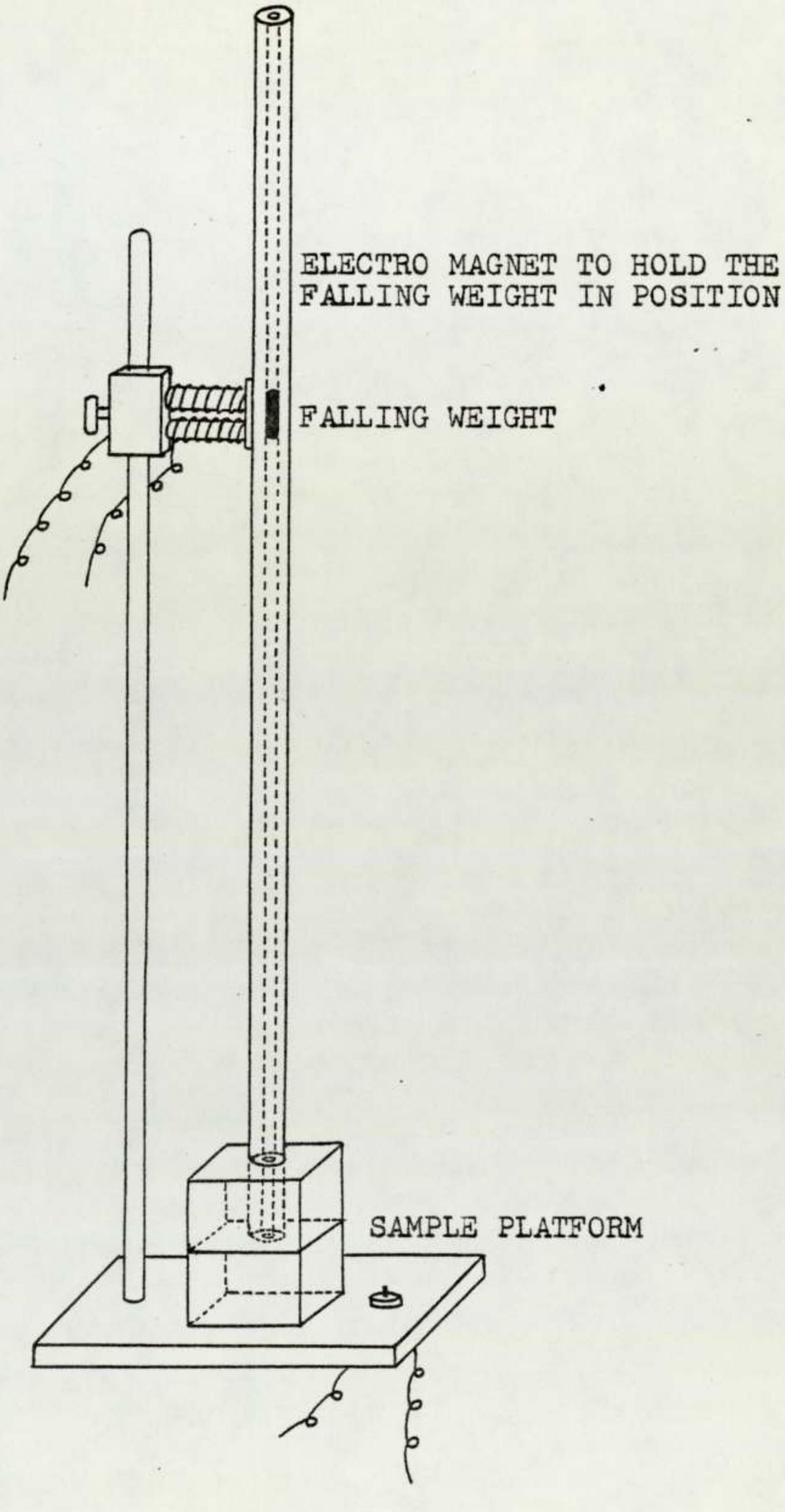


Fig. 6 . Impact modulus tester.

band of the acid (5.84μ), ketone (5.81μ) and aldehyde (5.77) groups present in polyethylene overlap to give only a broad band on laboratory standard spectrometers. Interpretation of these data, based on the increase in total carbonyl rather than on a single chemical moiety could lead to incorrect conclusions because of the large differences in the absorptivity of the various oxidation products. Acid absorptivity has been reported to be 2.4 times greater than that of ketones and 3.1 times greater than that of aldehydes[84,87].

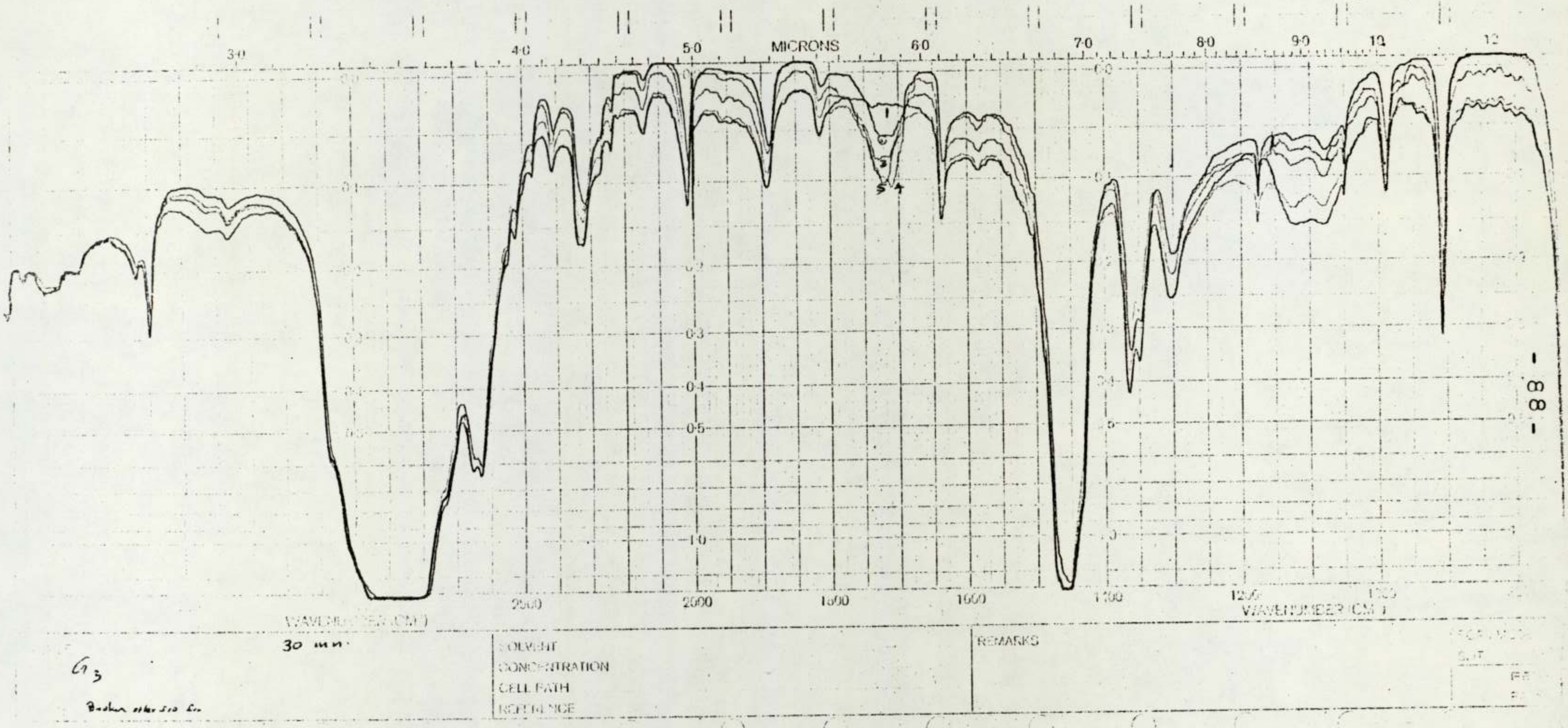
Cooper and Prober[87] have used alcoholic sodium-hydroperoxide to convert the acid groups to sodium carbonate which appears at (6.4μ) to analyse polyethylene oxidised with corona discharge in the presence of O_2 and ozone.

Procedure:

Films containing carbonyl groups after oxidising for different time intervals were placed in a 250 ml conical flask and 25% w/w solution of sodium hydroperoxide in ethyl alcohol was added and allowed to react at room temperature for 4 days; films were taken out washed with water and alcohol and dried in a desiccator for 24 hours. Dry films were scanned in IR spectrophotometer.

4.1.8 UV treatment

Polymerisation and UV ageing tests for the polymer films were carried out in the sun lamp black



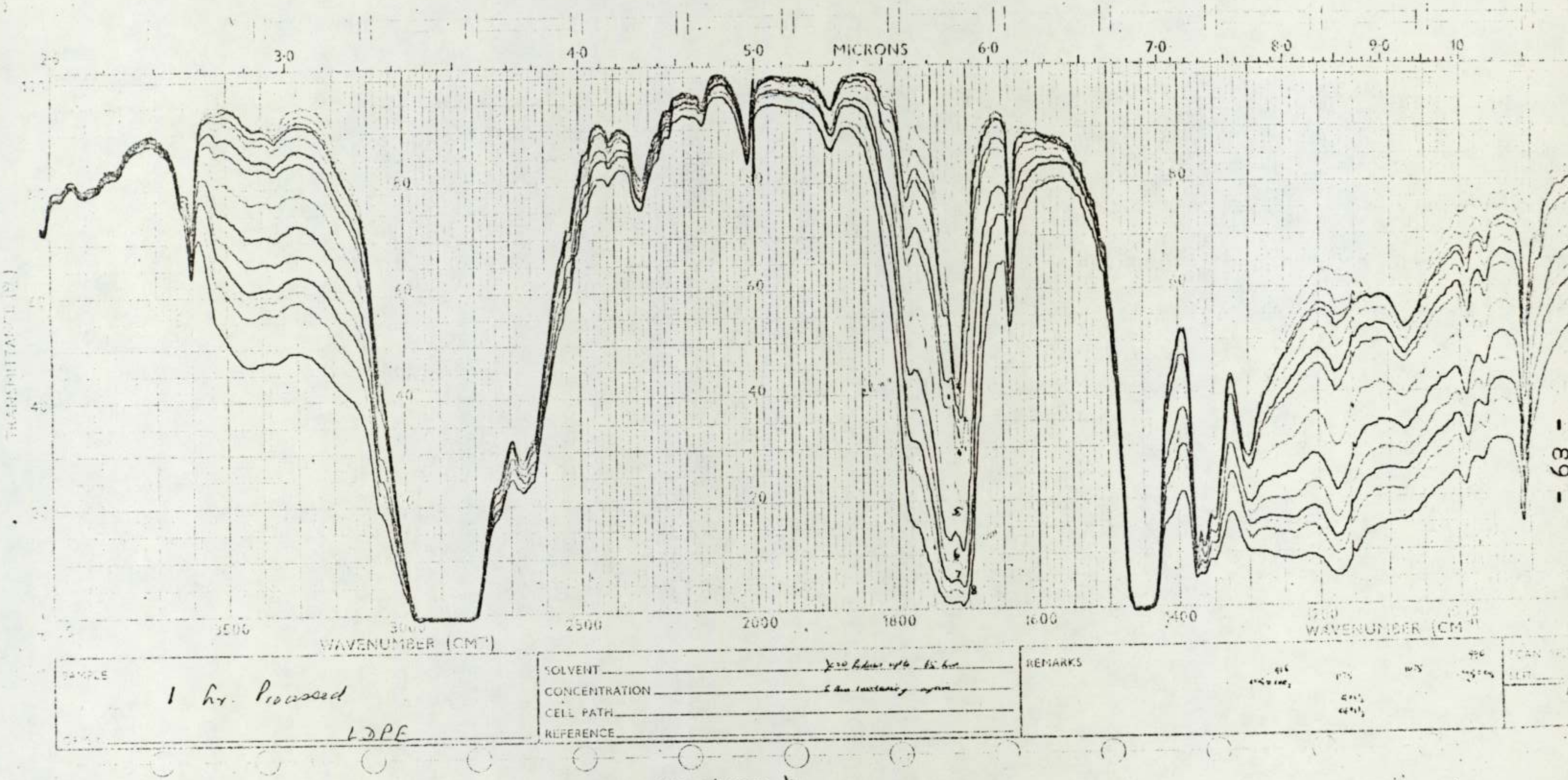
Spectrum 3

CHARACTERISTIC SPECTRUM OF HDPE WHEN EXPOSED

TO UV LIGHT

Processing time 30 min

Exposure times
1. 0 hrs
2. 20
3. 42
4. 65



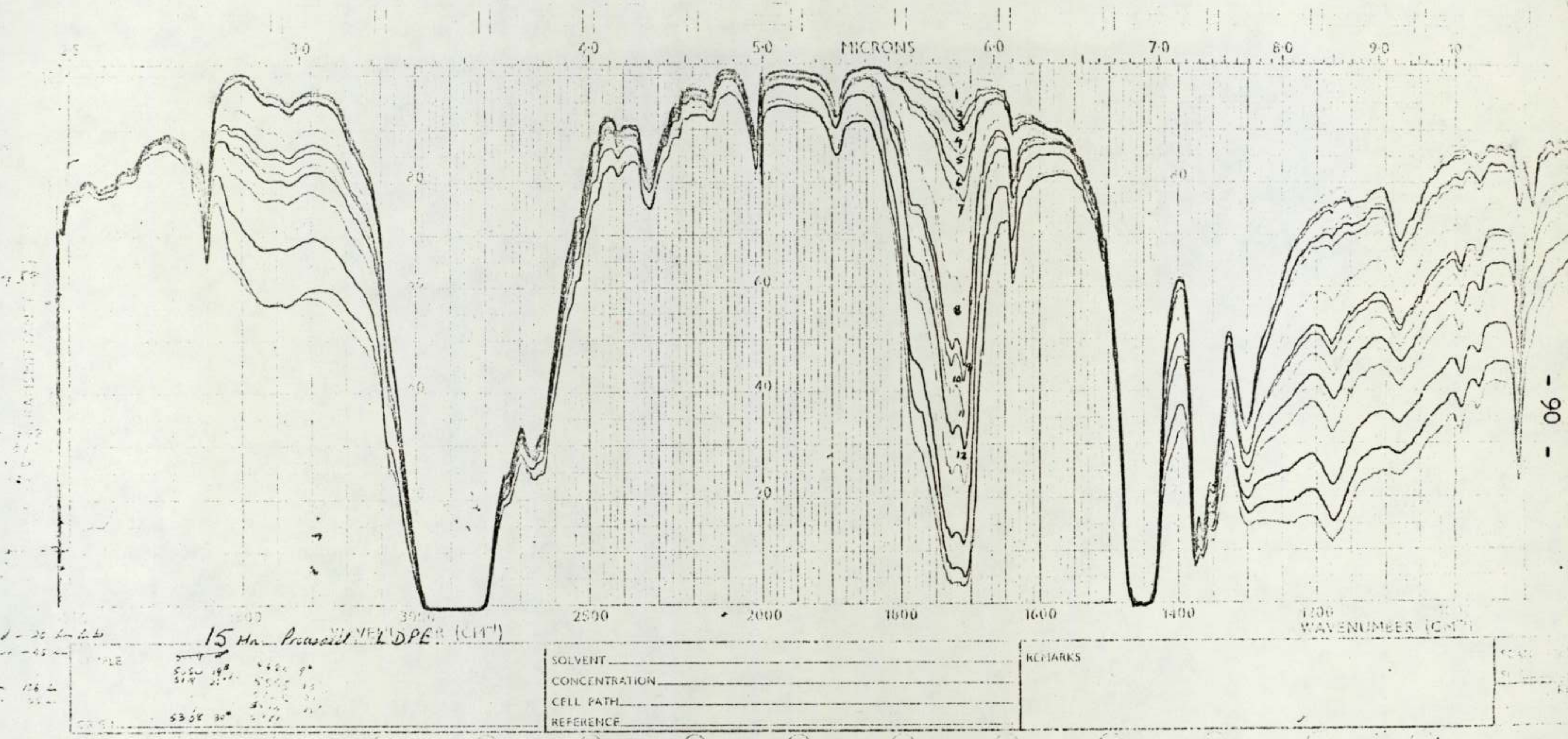
spectrum 4

VARIATION OF FUNCTIONAL GROUP INTENSITIES OF LDPE

EXPOSED TO UV RADIATION (1 hr-processed at 160°C)

Exposure times

1. 0hr
2. 26
3. 50
4. 65
5. 85
6. 110



Spectrum 5

VARIATION OF FUNCTIONAL GROUP INTENSITIES OF LDPE

EXPOSED TO UV RADIATION(15 min processed at 160°C)

Exposure times

1. 0hr
2. 26
3. 50
4. 65
5. 85
6. 110

lamp (SB) cabinets supplied by CIBA - Geigy Ltd . These cabinets[59,96] consisted of cylindrical metal bodies with 30, twenty watts lamps mounted around the periphery. The lamps were alternating equal numbers of fluorescent sun lamps and black lamps, the spectral characteristics approximating to 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 fluorescent sun lamps have intensity less than sunlight at the longer wave lengths and much more intensity below 300 A°. Since the emission extends to shorter wave lengths than sunlight, ageing tests on clear plastics are harsher. Quartz glass facilities the use of the higher energy for polymerisation purposes.

Evans[59] has compared the transmission characteristics of quartz tubes to pyrex and soda glass tubes and reported that quartz transits throughout the scanning range, but the others only begin transmission at wave lengths above 300 nm. Hence quartz tubes were used for the sample solutions and were sealed with rubber stoppers. The sample tubes or the films mounted on cardboard frames were hung on the circumference of a motor driven wheel which is concentric with the cabinet and could be rotated at a constant speed. Temperature inside the open ended cabinet was 33 ± 2°C.

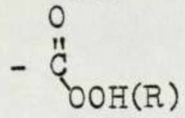
4.2 Results and discussion

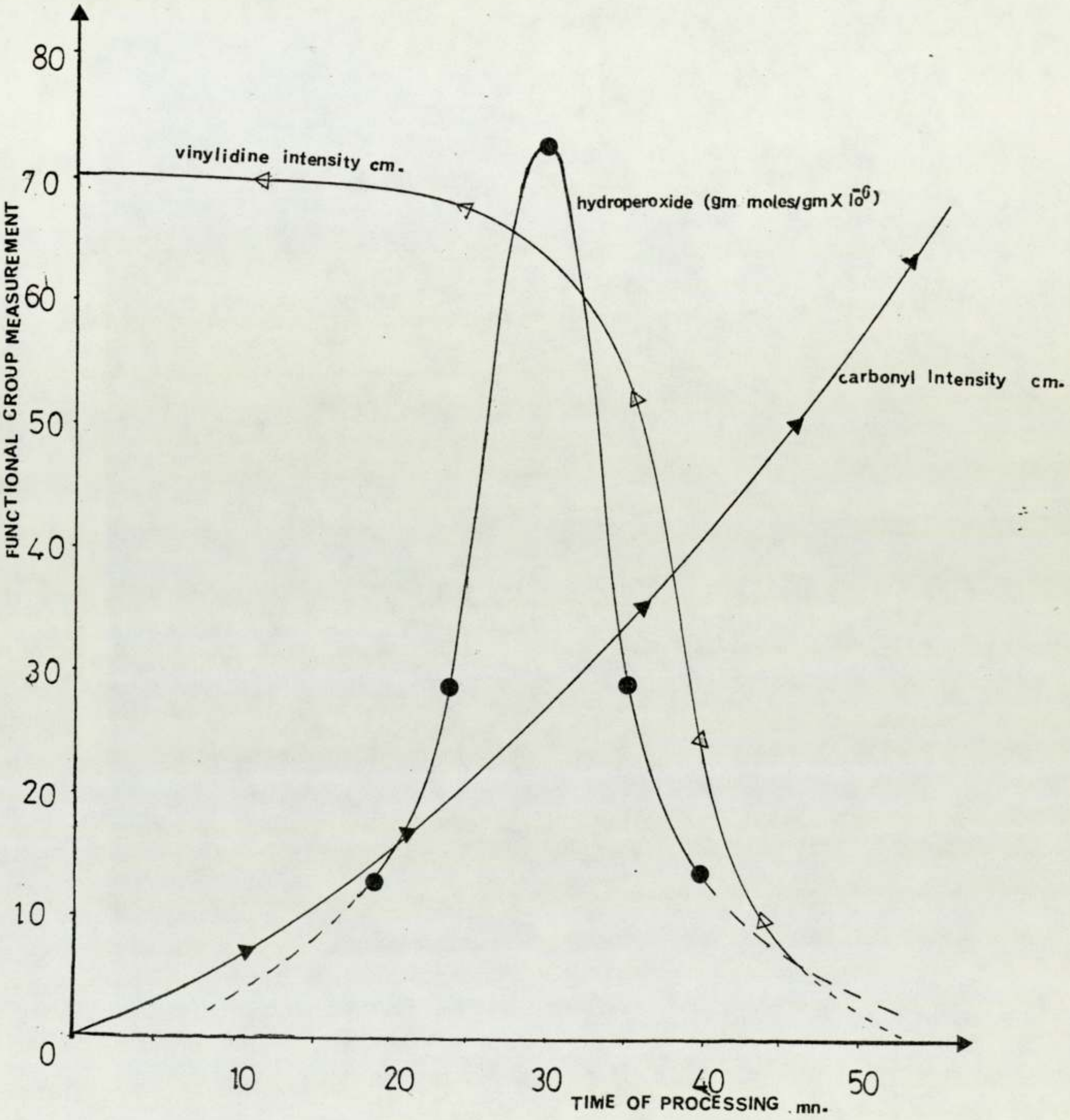
When low density polyethylene is processed in the torque rheometer at 160°C for more than 10 mins marked differences were observed in the IR spectrum (fig 7) specially in the 3500, 1700 and 900 nm regions. Bands at 990 and 909 are due to the presence of unsaturation points of vinyl type ($-CH=CH_2$). Unsaturation of the pendent type ($R_1R_2C= CH_2$) usually known as vinylidene and appearing at 887 cm^{-1} was found to be highly unstable when the polymer was exposed to UV light. Both hydroperoxide (3550 cm^{-1}) and vinylidene band intensities were found to decrease rapidly when the processed polymer was exposed to UV light while the vinyl at 909 cm^{-1} and carbonyl bands at 1700 - 1785 cm^{-1} were growing. The disappearance of vinylidene cannot be followed to completion since in the later stages of degradation, the 887 cm^{-1} absorption is observed only as a shoulder on the 909 cm^{-1} absorption. However the peak height can be measured reproducible until the intensity has been reduced to 25% of the initial value by means of the Du Pont curve analyser.

Amin[41] and Luongo[91] have identified the functional groups present at the end of a mild processing operation and they are as given in table 4 .

Table 4

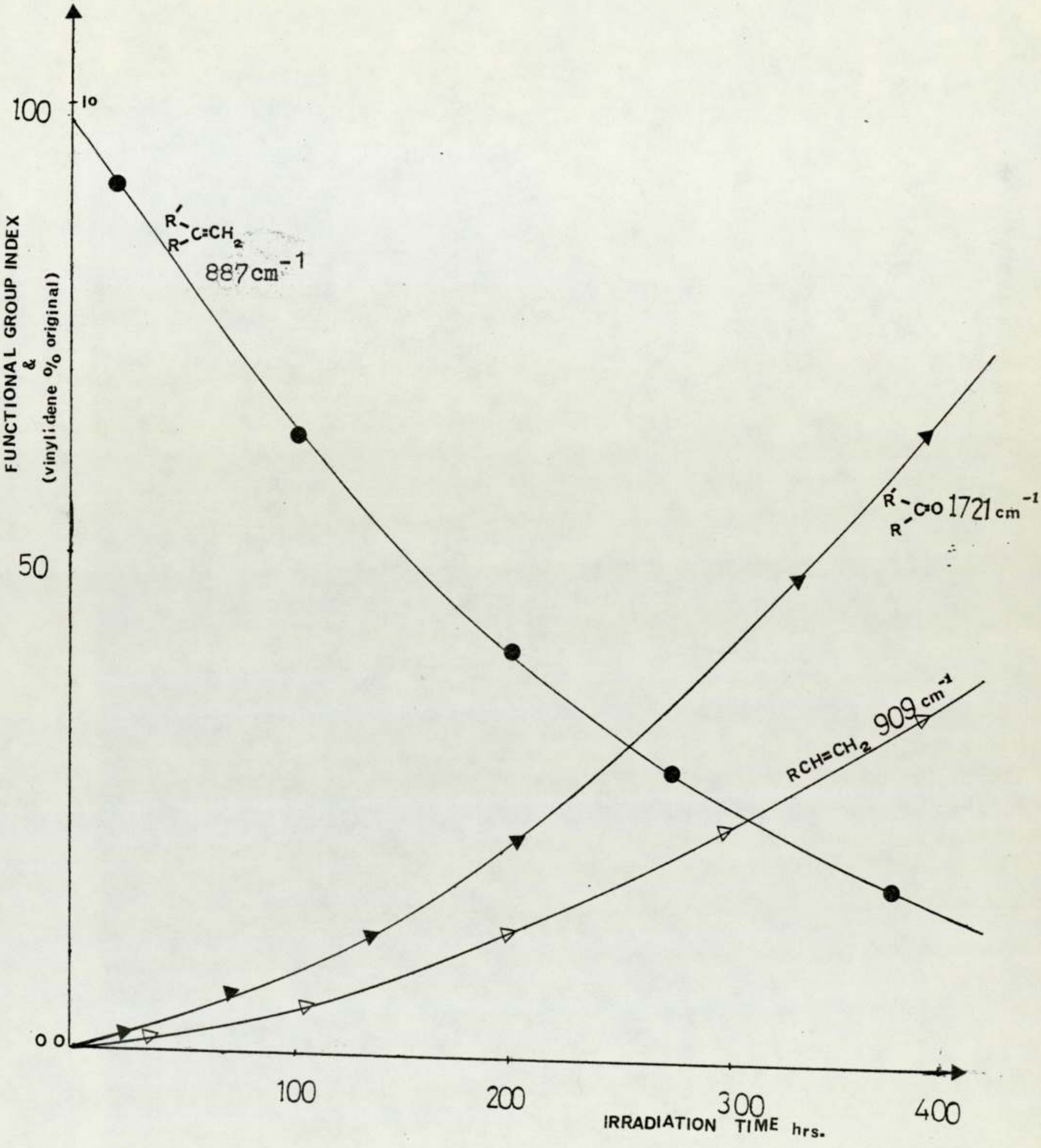
Functional groups identified in typical LDPE film before and after UV irradiation

Functional group	(cm^{-1})	Absorbance	
		Unirradiated	Irradiated (1500h)
$RCOCH_3$	1725 ± 1	0.005	-
$RCOR'$	1720 ± 1	-	0.815
-OH	3400	0.015	0.067
-COOH	1710-13	-	0.929
$\genfrac{}{}{0pt}{}{R}{R'}C = CH_2$	887 ± 1	0.045	-
$R-CH=CH_2$	909	0.006	0.268
$RCH=CHR'$	1645 ± 1	0.013	0.083
- CHO	1735	-	0.929
- COOR	1748	-	0.698
 $-\overset{\overset{O}{\|}}{C}OOH(R)$	1785	-	0.333



Variation of functional group intensities with time of processing in the torque rheometer for LDPE

Fig. 7

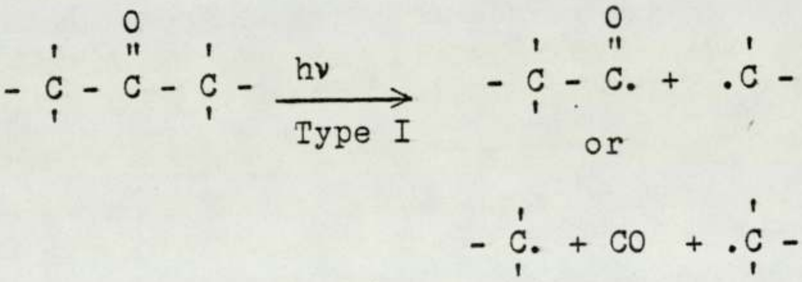


Variation of functional group indeces with irradiation time for LDPE

Fig. 8

Rapid disappearance of vinylidene (887 cm^{-1}) initially present in a mildly processed sample on UV irradiation accompanied by the formation of significant amount of carbonyl (Fig. 8) suggests that vinylidene decay must be in some way associated with the photo initiation step. It was also noticed that the vinyl (909 cm^{-1}) band intensity also increases in parallel with carbonyl intensity during this period. This is the expected sequence of events if vinyl is formed by Norrish II breakdown of carbonyl.

The vinyl intensity curve levels off on prolonged irradiation. This could be associated with the fact that carbonyl concentration decreases as irradiation proceeds, owing to the formation of volatile carbonyls such as formaldehyde and acetone and gaseous products such as carbon monoxide and carbon dioxide.

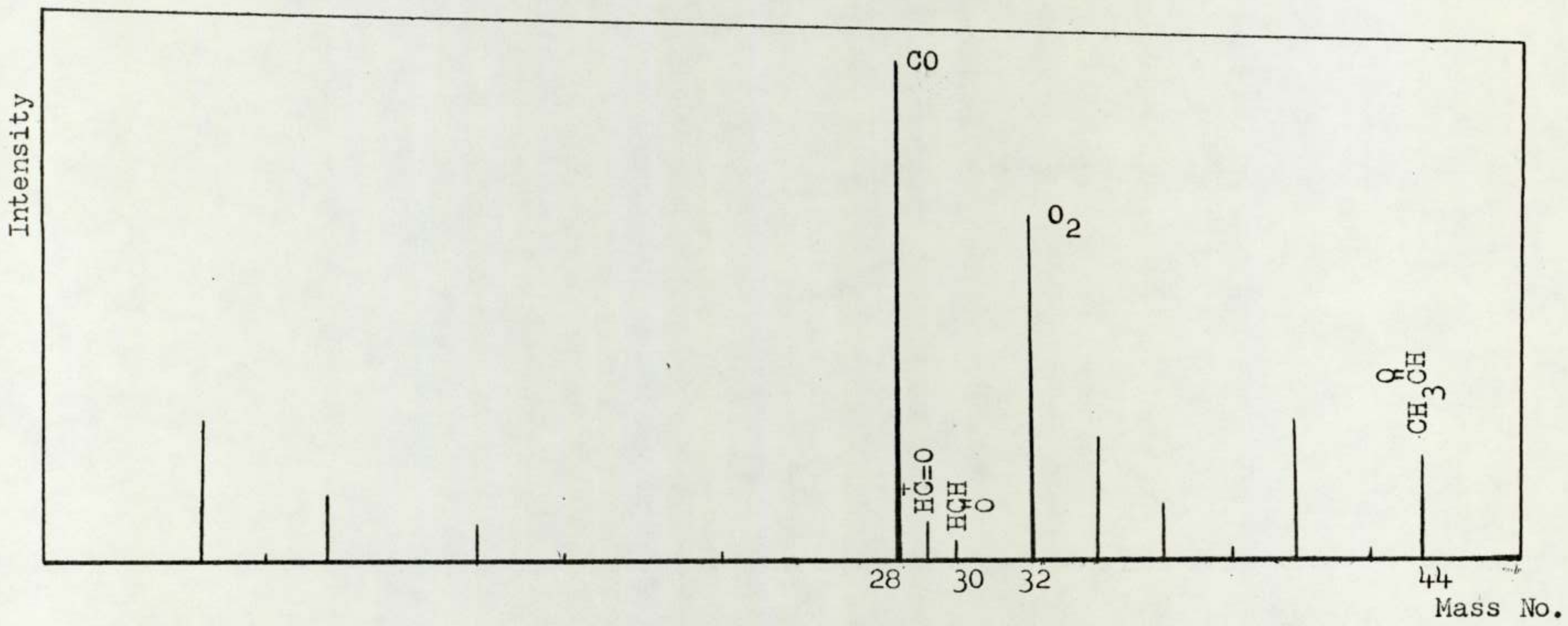


$$-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}- \xrightarrow[\text{Type I}]{h\nu} -\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}\cdot + \cdot\overset{|}{C}-$$

or

$$-\overset{|}{\underset{|}{C}}\cdot + CO + \cdot\overset{|}{\underset{|}{C}}-$$

Irradiation of a sample of LDPE in vaccuo inside a silica tube and analysis of the gaseous products by mass spectrometry shows that formaldehyde, acetaldehyde and carbon monoxide are formed in this reaction. (SPECT. 6)



MASS SPECTRUM OF GASEOUS PRODUCTS WHEN LDPE IS

EXPOSED TO UV LIGHT

Spectrum 6

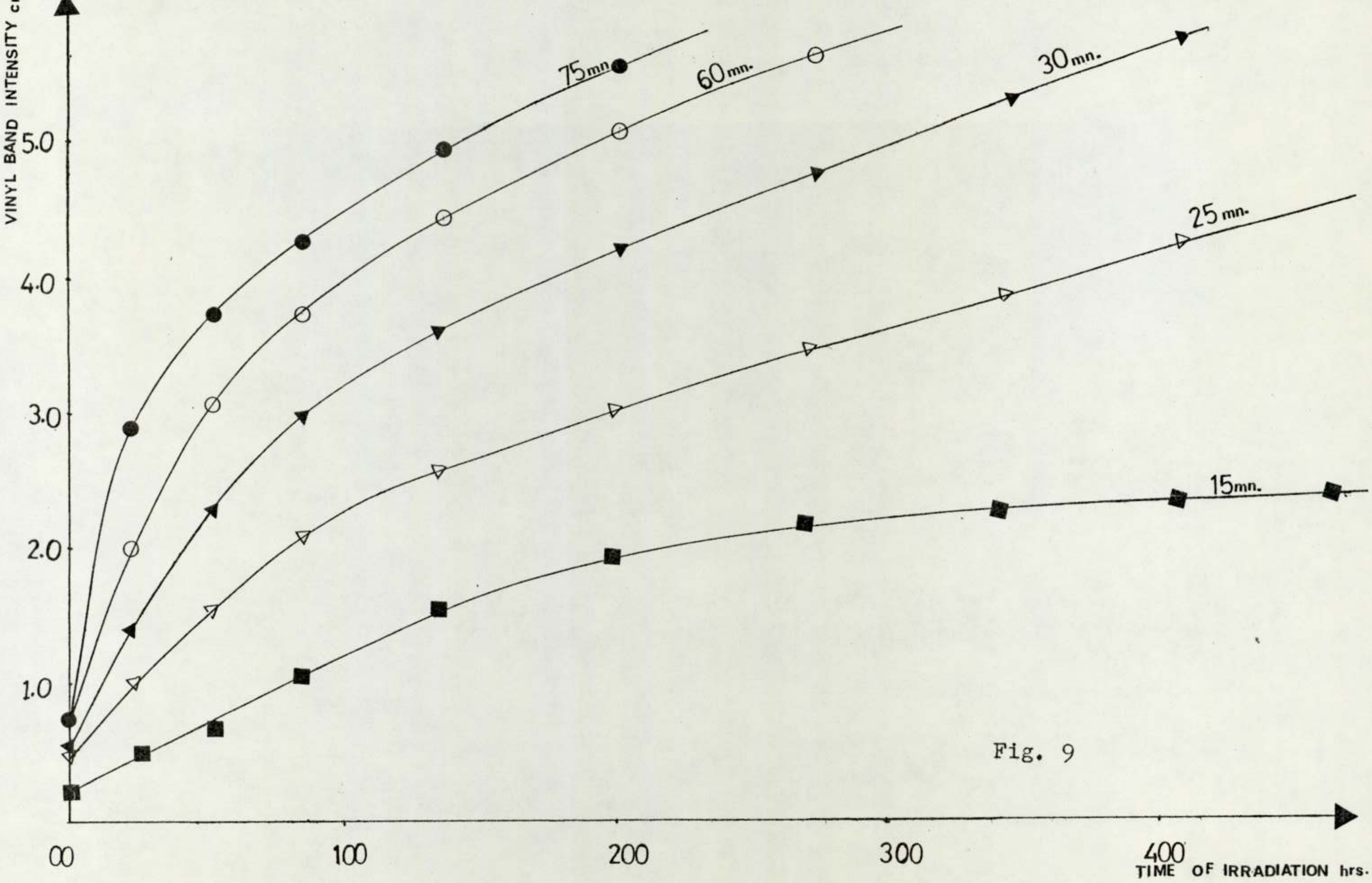


Fig. 9

Variation of vinyl band intensities with irradiation time for LDPE

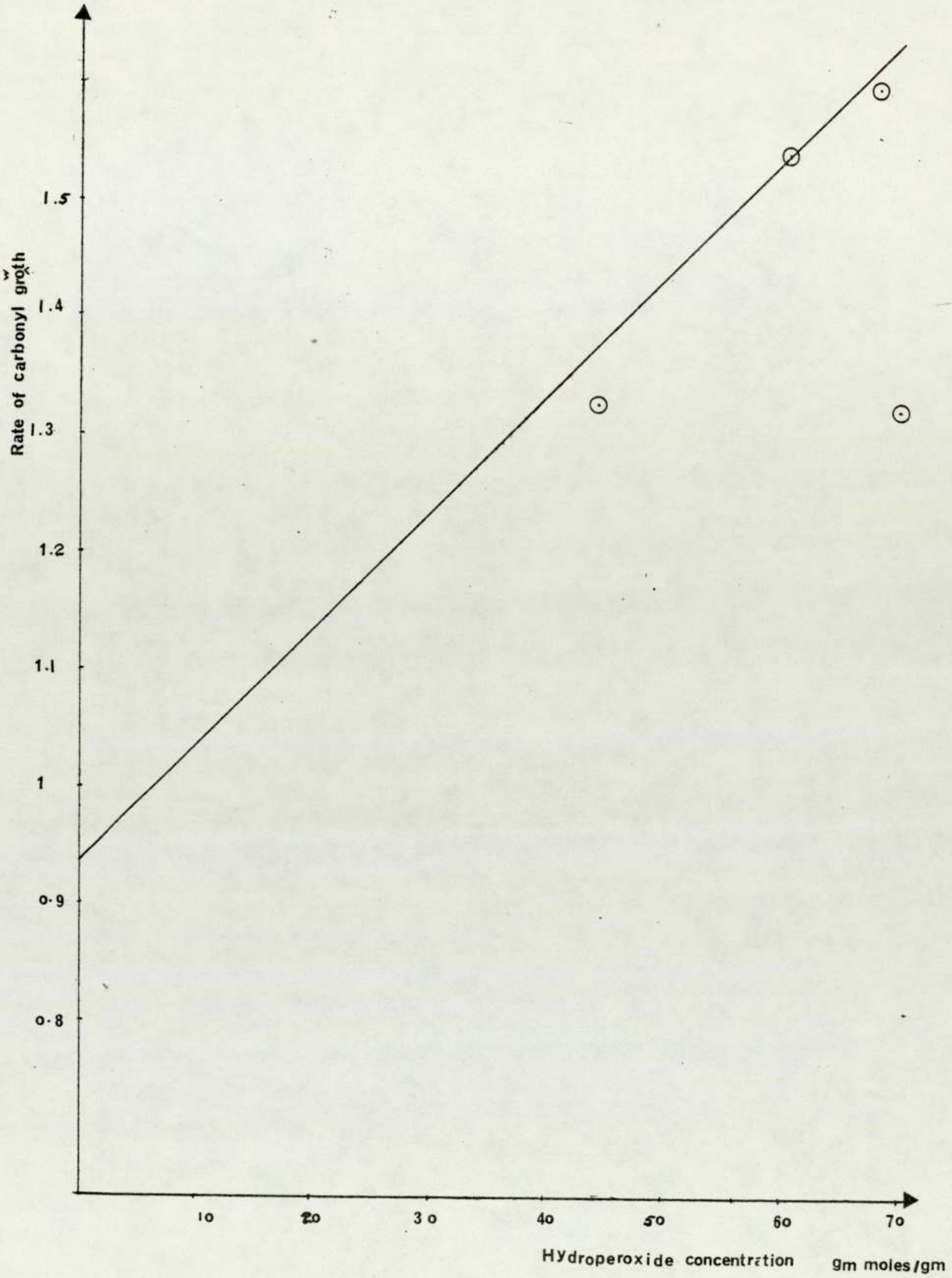
TABLE 5 - MASS SPECTROSCOPIC ANALYSIS OF GASEOUS PRODUCTS FROM IRRADIATED POLYETHYLENE

Peak at Mass No.	Probable compound
28	Carbon monoxide
30	Formaldehyde
44	Acetaldehyde or Carbon dioxide

The formation of aldehydes (1735 cm^{-1}) and carboxylic acid (1185 cm^{-1}) are almost certainly a consequence of Norrish I photolysis of carbonyl. These results support the conclusion arrived at earlier[47] that once significant amounts of carbonyl are present in the polymer either as a result of thermal oxidation or by UV catalysed oxidation then they are involved in the photodegradation process. However the rapid disappearance of vinylidene suggests that other photoxidative reactions occur involving this group and that this process precedes carbonyl formation.

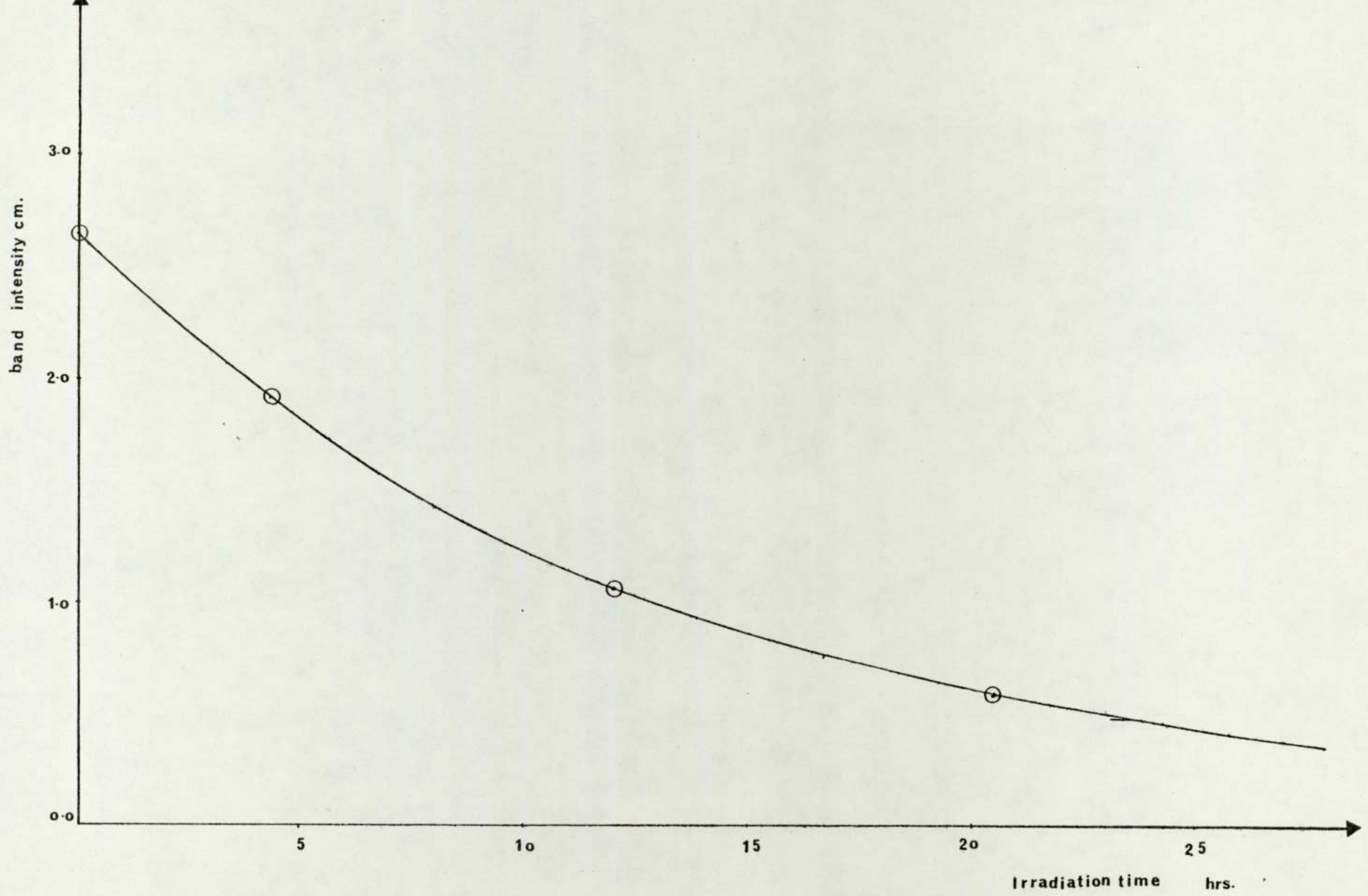
Samples of polyethylene processed in the presence of air were examined for hydroperoxide by the method of Bocek modified as described in the experimental section. (Fig.7) shows the results which were obtained and the associated changes in vinylidene and carbonyl during processing operation.

It was seen that formation of carbonyl was first order with respect to initial hydroperoxide



Variation of rate of carbonyl formation during irradiation with initial hydroperoxide content for LDPE processed in the torque rheometer

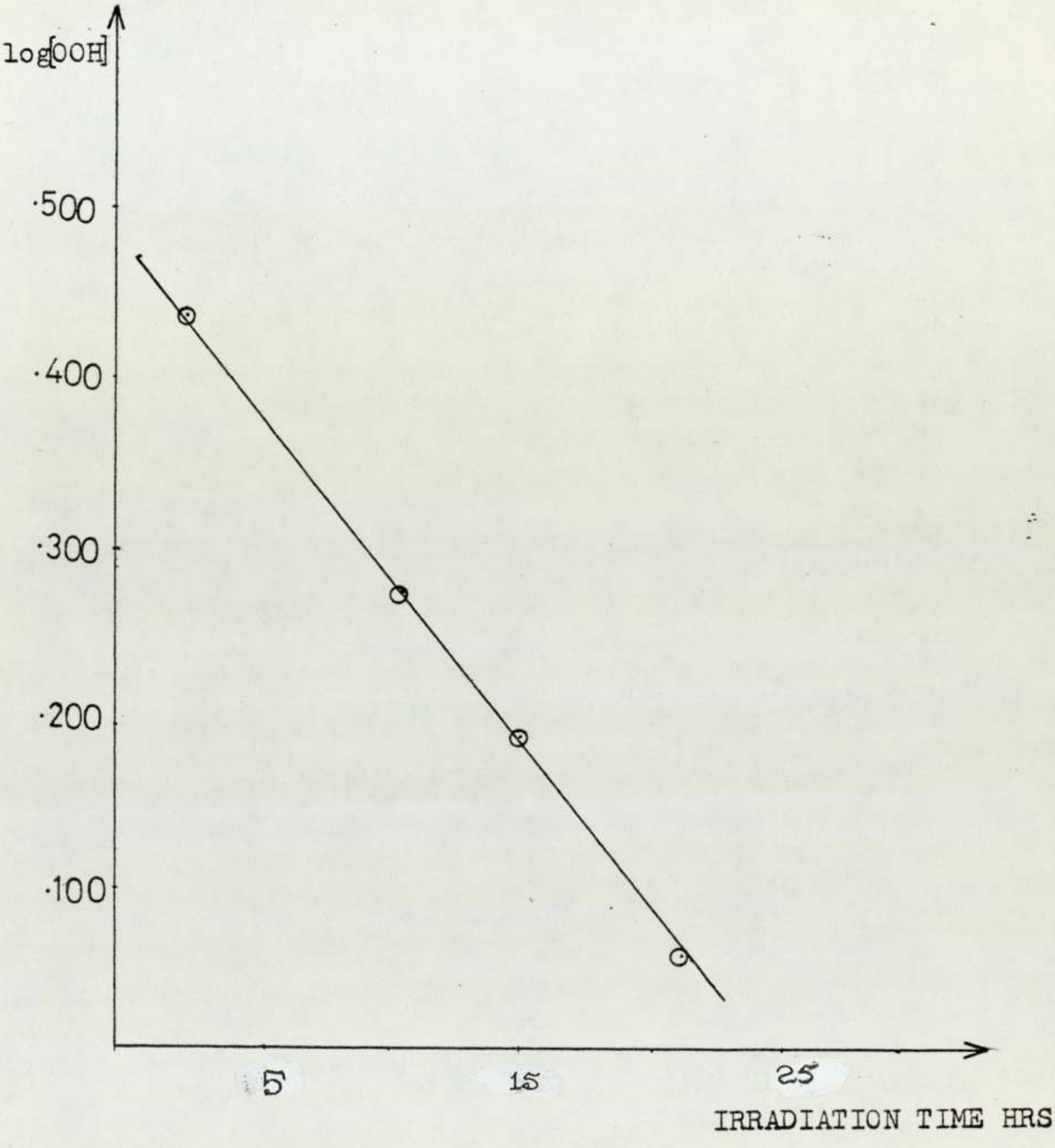
Fig. 10



Rate of disappearence of hydroperoxide group formed on oxidised polyethylene on UV irradiation

Fig. 11

concentration and this is clear from the (Fig. 10) which is a plot of rate of carbonyl formation with the initial hydroperoxide concentration. Hydroperoxide could not be accurately determined by this method before 20 min or after 40 mn processing. It reached a very sharp maximum at about 30 mins and samples stored at room temperature in the dark were found to have the same hydroperoxide concentration after several weeks. It is stated in the literature that the hydroperoxide band formed in processed polyethylene is highly unstable[85] and disappears at room temperature in a few minutes. It is clear that hydroperoxide formation precedes carbonyl formation when the polymer is processed in the presence of air and that under mild processing conditions, where changes in the UV lifetime of the polymer are greatest, hydroperoxide and vinylidene must both be involved in the photoinitiation process. This is in accord with the autoaccelerating nature of the carbonyl formation during the initial stages of both thermal and photoxidation and confirms the essential similarity of the two processes. Fig. 11 clearly indicates the instability of pure hydroperoxide band at 3520 nm in the IR spectrum of the oxidised polyethylene which drops steadily with irradiation time. Further a plot of logarithm of hydroperoxide band intensity Vs irradiation time is a straight line (Fig12) indicating that this breakdown is 1st order with respect to irradiation time.



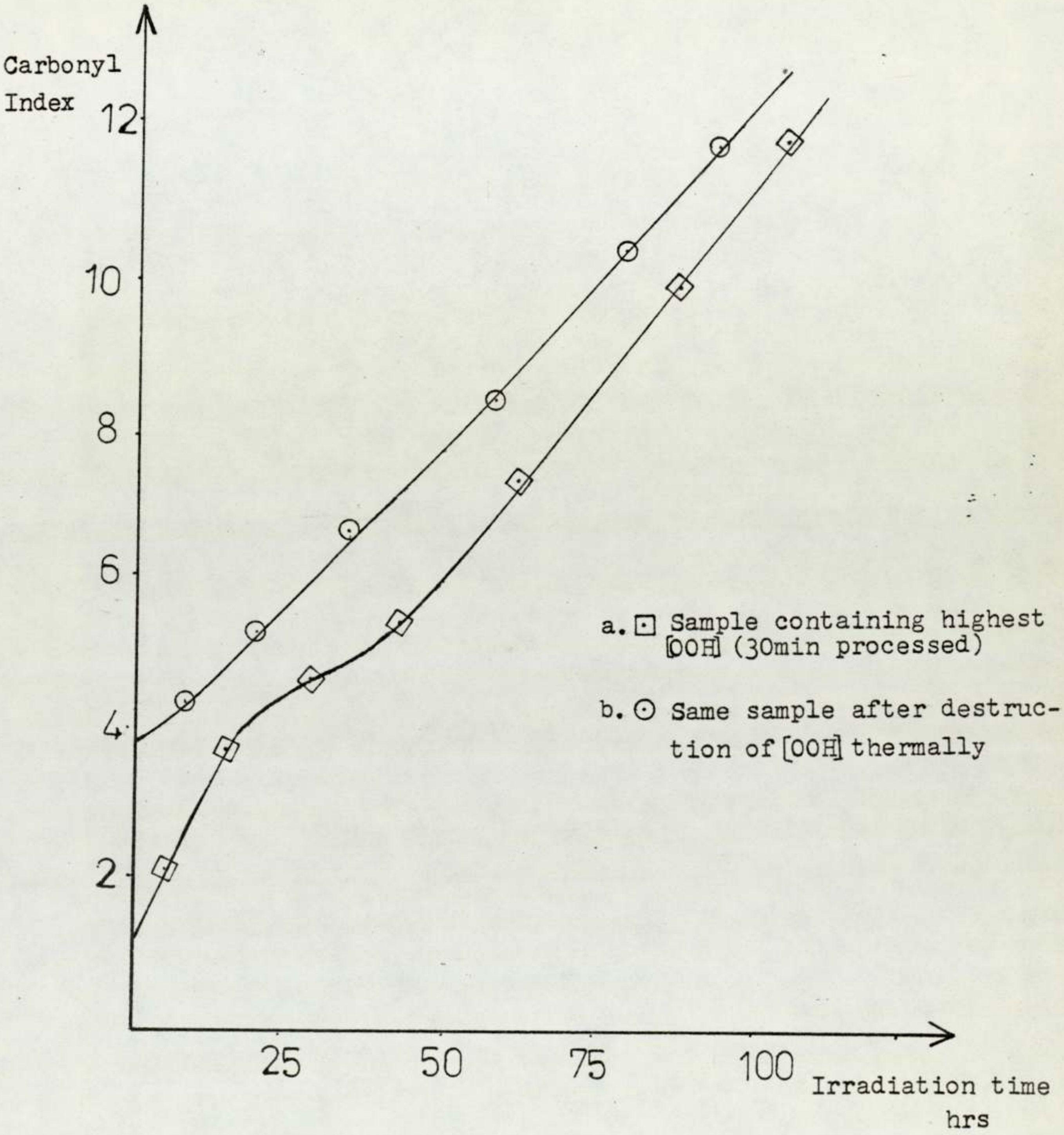
LOG(OOH) BAND INTENSITY vs Irradiation time for LDPE

Fig. 12

From (Fig. 7) it is clear that the disappearance of vinylidene during processing is related to the formation of hydroperoxide and indeed, the hydroperoxide concentration curve appears to be a slightly displaced integral of the vinylidene concentration curve. This is the behaviour expected if the rate of disappearance of vinylidene is directly related to the hydroperoxide concentration.

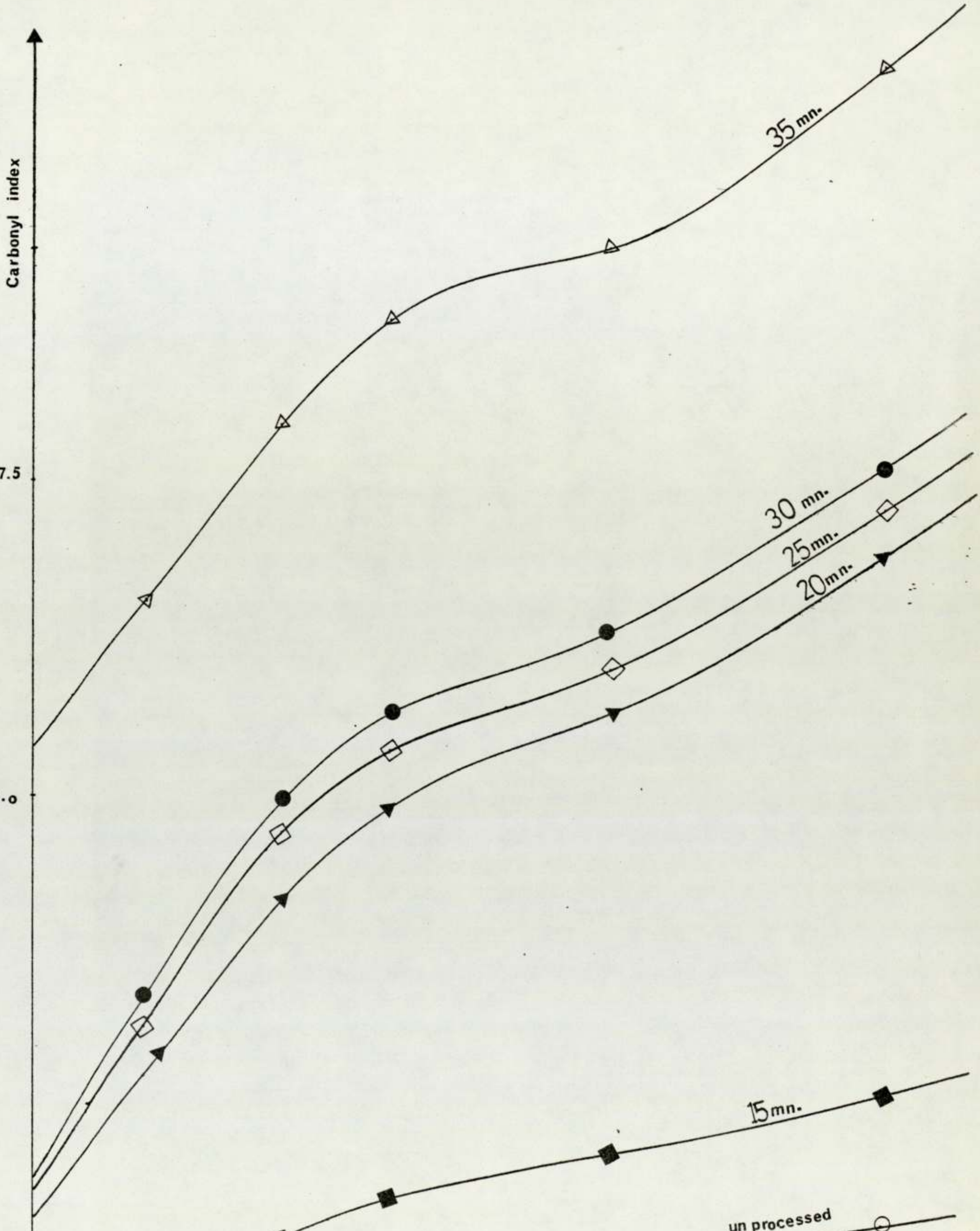
(Fig. 8 and 14) relate the change in vinylidene and carbonyl concentration respectively on UV irradiation to the processing conditions and to carbonyl initially present in the processed polymer. Films prepared from the polymers produced in the series of experiments reported in (Fig.15) were irradiated and the carbonyl indices were measured at intervals. In the case of samples containing hydroperoxide and vinylidene there was a sharp increase in carbonyl formation due to the above photoxidation which destroys both vinylidene and hydroperoxide. This is clear from Fig. (13) where the curve (a) represents the rate of carbonyl growth with irradiation time. In the initial part of this curve the rate is much higher due to the presence of vinylidene and optimum concentration of hydroperoxide, which are undergoing destruction under UV light resulting in carbonyl groups.

When the hydroperoxide concentration of the same sample is reduced to a minimum by heating at 150°C in a vacuum for 10 min, the initial sharp increase in



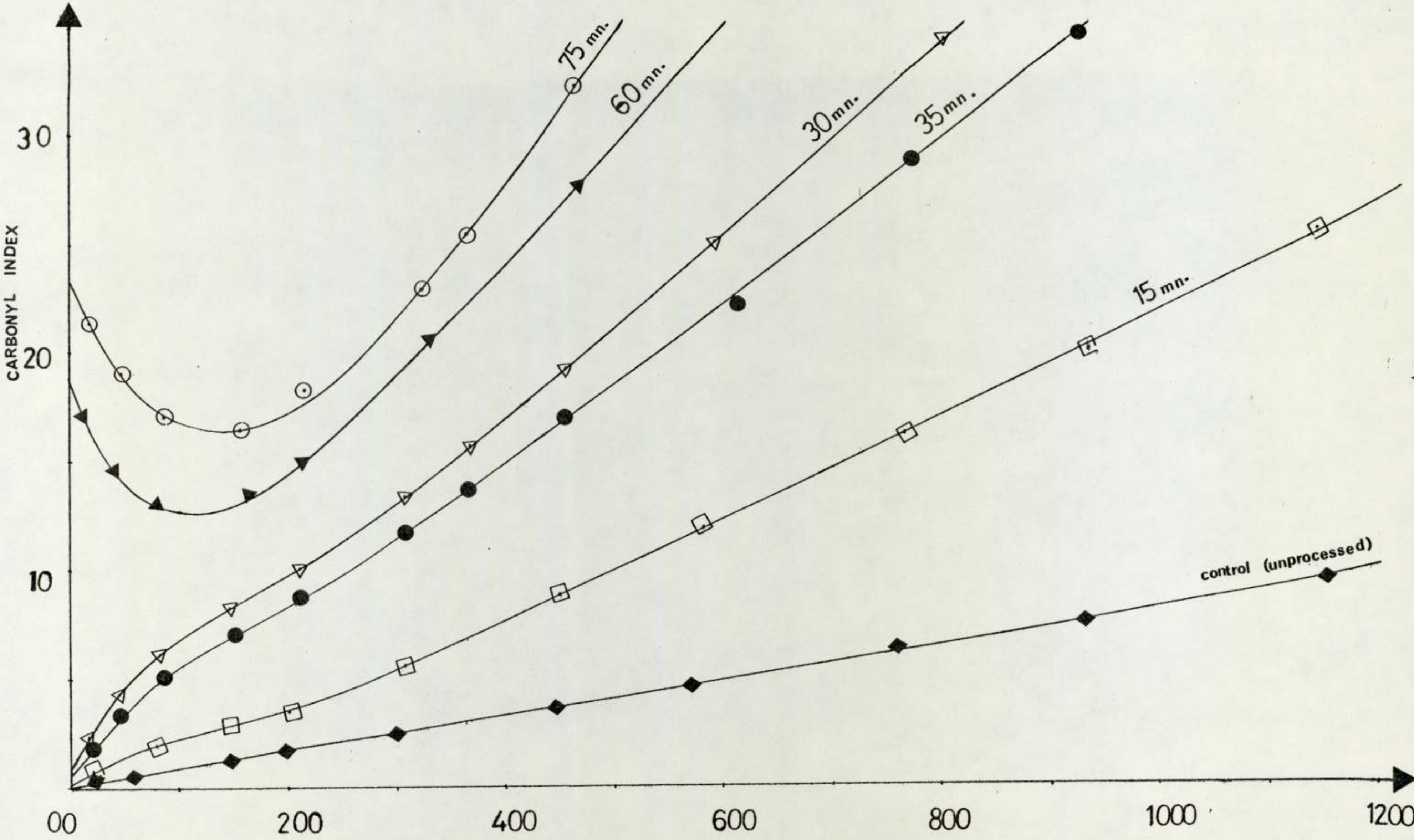
VARIATION OF CARBONYL INDEX WITH INITIAL[OOH] ON EXPOSURE TO UV RADIATION

Fig. 13



Variation of carbonyl index with irradiation time for LDPE

Fig. 14



Variation of carbonyl indeces with irradiation time for LDPE processed in the torque rheometer for varying time peri

Fig.15 .

carbonyl content disappears as indicated by the curve (b). The behaviour of the carbonyl growth curve is then as in the case of extensively oxidised samples; supporting the mechanism suggested below. More extensively oxidised samples have a lower peroxide and vinylidene content but a higher initial concentration of ketonic carbonyls (1721 cm^{-1}). This photolyses rapidly by Norrish type II process and is followed by a slower growth of secondary carbonyl compounds, notably carboxylic acid, peracid and aldehyde. Ketonic carbonyl cannot be detected in the later stages of photoxidation. Also, the photolysis of polyolefins containing higher concentrations of carbonyl groups in vacuum indicated the formation of volatile carbonyls such as formaldehyde and acetaldehyde as shown in spectrum No. 6, which volatilise and escape from the film surface. These also cannot be detected in the IR spectrum of the film. This may be one of the reasons for the slight drop in carbonyl growth rate as the irradiation continues as indicated in (Fig.15).

In the case of the curves for extensively oxidised samples, photolysis of initial concentration of carbonyls resulting in volatile components could be the reason for the initial drop in carbonyl growth curve. But with the slower growth of secondary carbonyl compounds with irradiation the curve starts rising again.

The fact that the more lightly oxidised polymers exhibit a sharp pro-oxidant effect whereas the heavily oxidised polymers undergo photolysis is of great significance and indicates that hydroperoxide initiation of vinylidene oxidation is much more important than activation of carbonyl in commercial plastics. A commercial processing operation would normally be of shorter duration than that involved in the present studies and would involve lower oxygen content than the experiments described, although at the higher temperatures used the induction period to hydroperoxide formation would be shorter. From this it follows that antioxidants which destroy peroxides or in some other way inhibits the oxidative chain reaction are likely to be much more effective in commercial polymers than agents which quench excited states of photoactivated carbonyl although this may be significant at advanced degrees of photoxidation. The significance of these results for the mechanism of UV stabilisation has been discussed in the next chapter.

The results obtained serve to explain the puzzling reversal of the change in mechanical properties of LDPE which is observed during photoxidation. This is exemplified by an initial increase followed by an increase in melt flow index and a decrease followed by an increase of dynamic modulus. A study of dynamic modulus decrease carried out under the conditions described has shown that this occurs during the first 30-50 hours after which reversal occurs due to the supervention of chain scission. This is the same period during which rapid oxidation of the polymer occurs (Fig. 8) and vinylidene disappears rapidly. An insoluble cross-linked gel is also formed during this period.

4.3 Gel content determination

The gel content of irradiated LDPE was determined by dissolving a accurately weighed piece of LDPE in hot chlorobenzene (at 160°C) and then filtering through No. 5 sintered glass crucible. Pure LDPE dissolves completely without leaving a residue whereas cross linked LDPE does not dissolve completely due to the crosslinks. The crucible containing the gel part was then dried completely in the vacuum desiccator for 2 days and weighed accurately. It was seen that the percentage gel content increased with irradiation time and reached a maximum after about 100 hours in the case of pure LDPE. When the above procedure was repeated with LDPE containing a hydroperoxide decomposer such as NiDBC, it was found that the gel formation is very much slower and after 100 hours the percentage gel content was about 20%. This indicates that crosslinking occurs through the radicals formed by hydroperoxide breakdown and in the presence of a hydroperoxide decomposer the cross-linking ability is much lower. Fig 16

The following sequence of chemical reactions is proposed to account for the main features of the photo-degradation process.

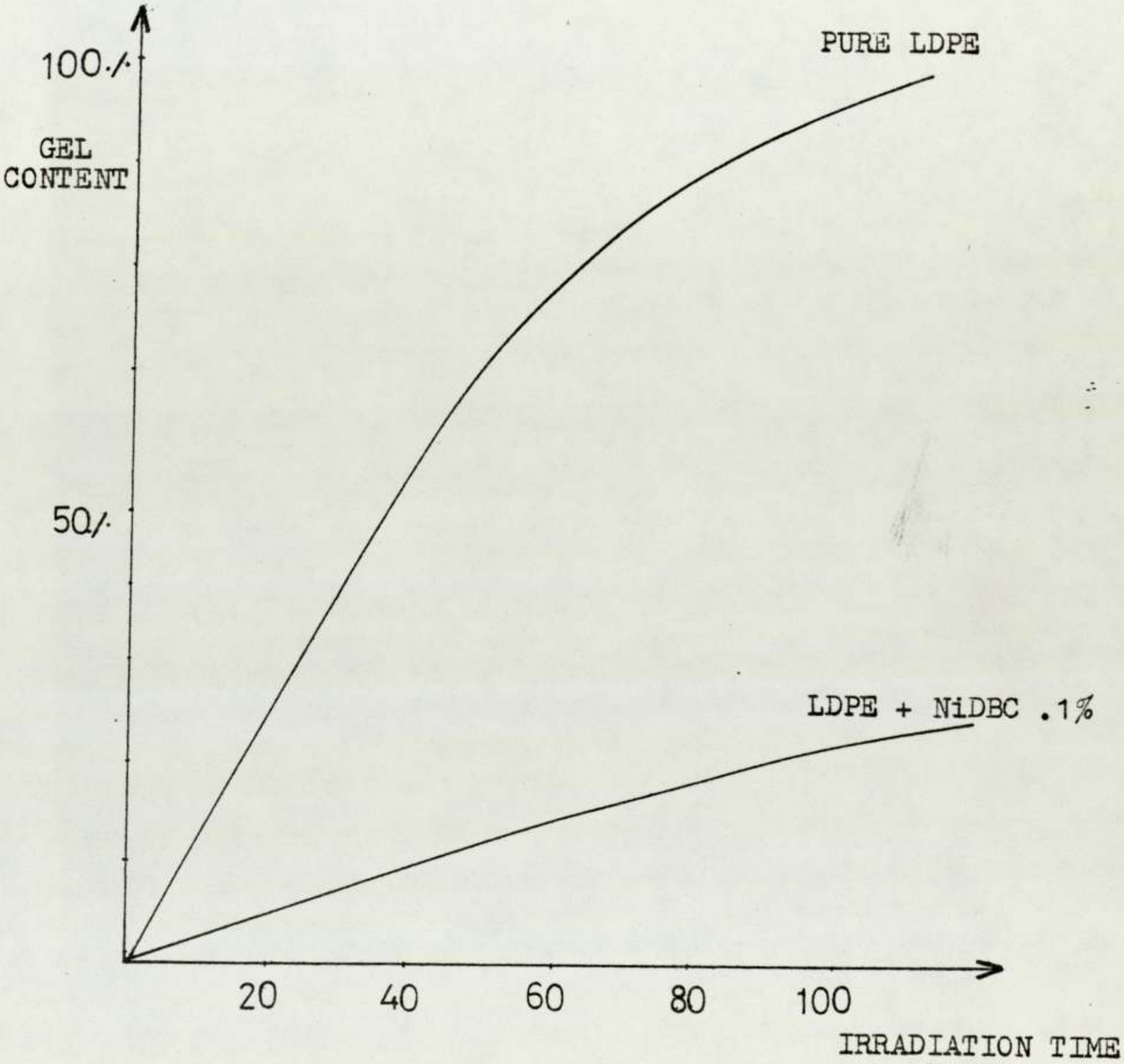
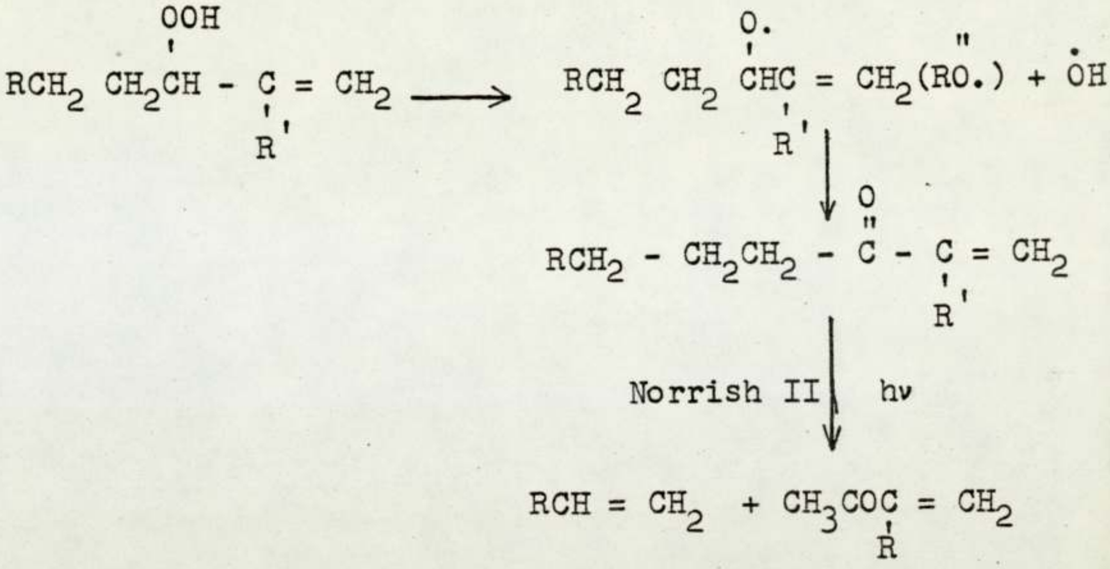
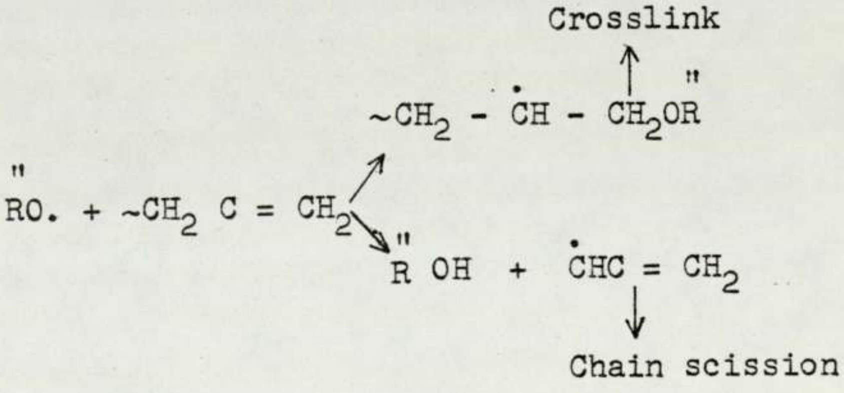


Fig. 16

Variation of gel content with irradiation time.

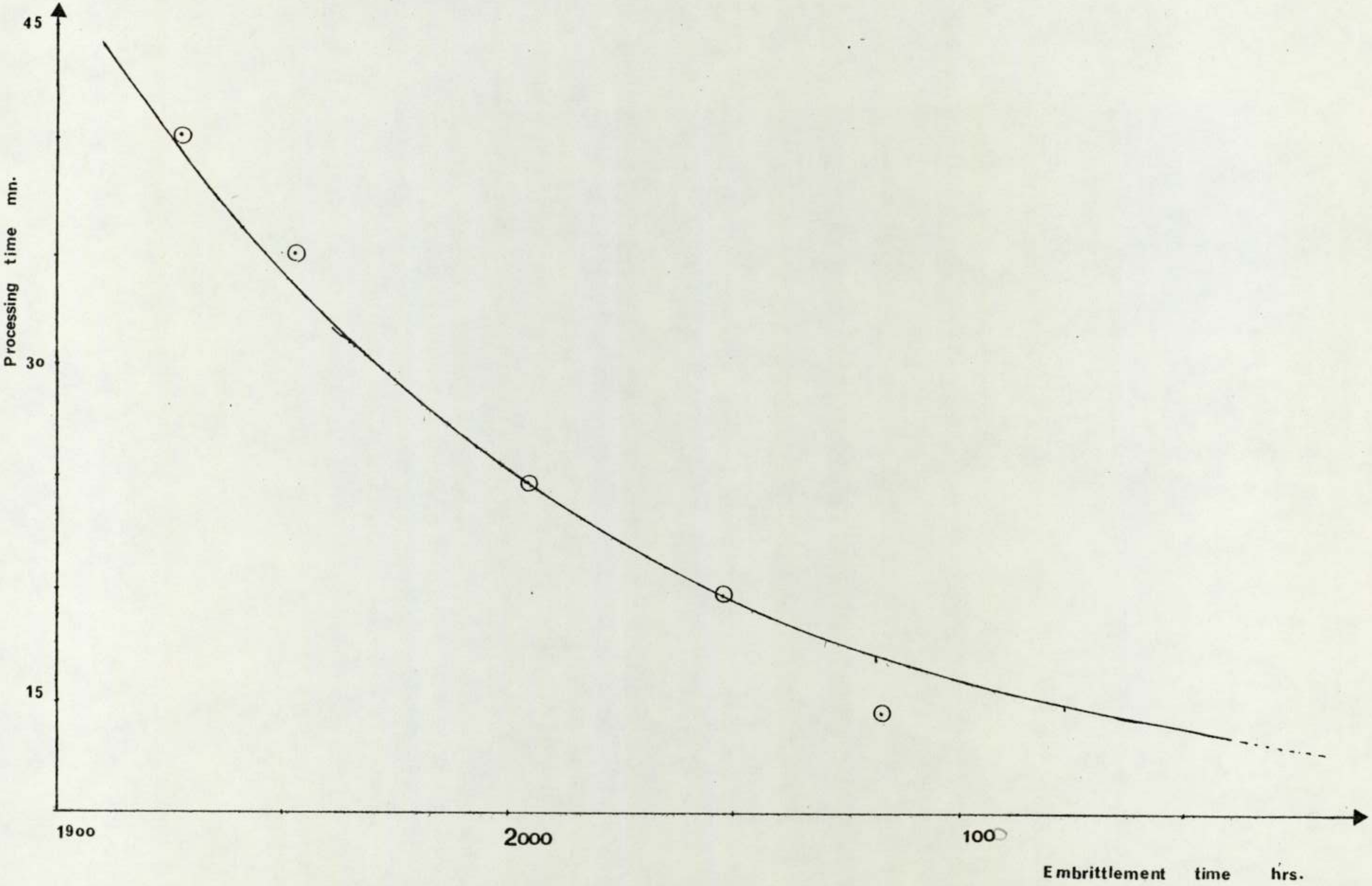


Appearance of a shoulder to the carbonyl band at 1685 cm^{-1} in the spectrum of oxidised LDPE is an evidence for the formation of conjugated ketones. Photo-initiation occurs by further reactions of the primary alkoxy and hydroxyl radicals and cross-linking through vinyl addition competes with chain scission through allylic hydroperoxide breakdown.



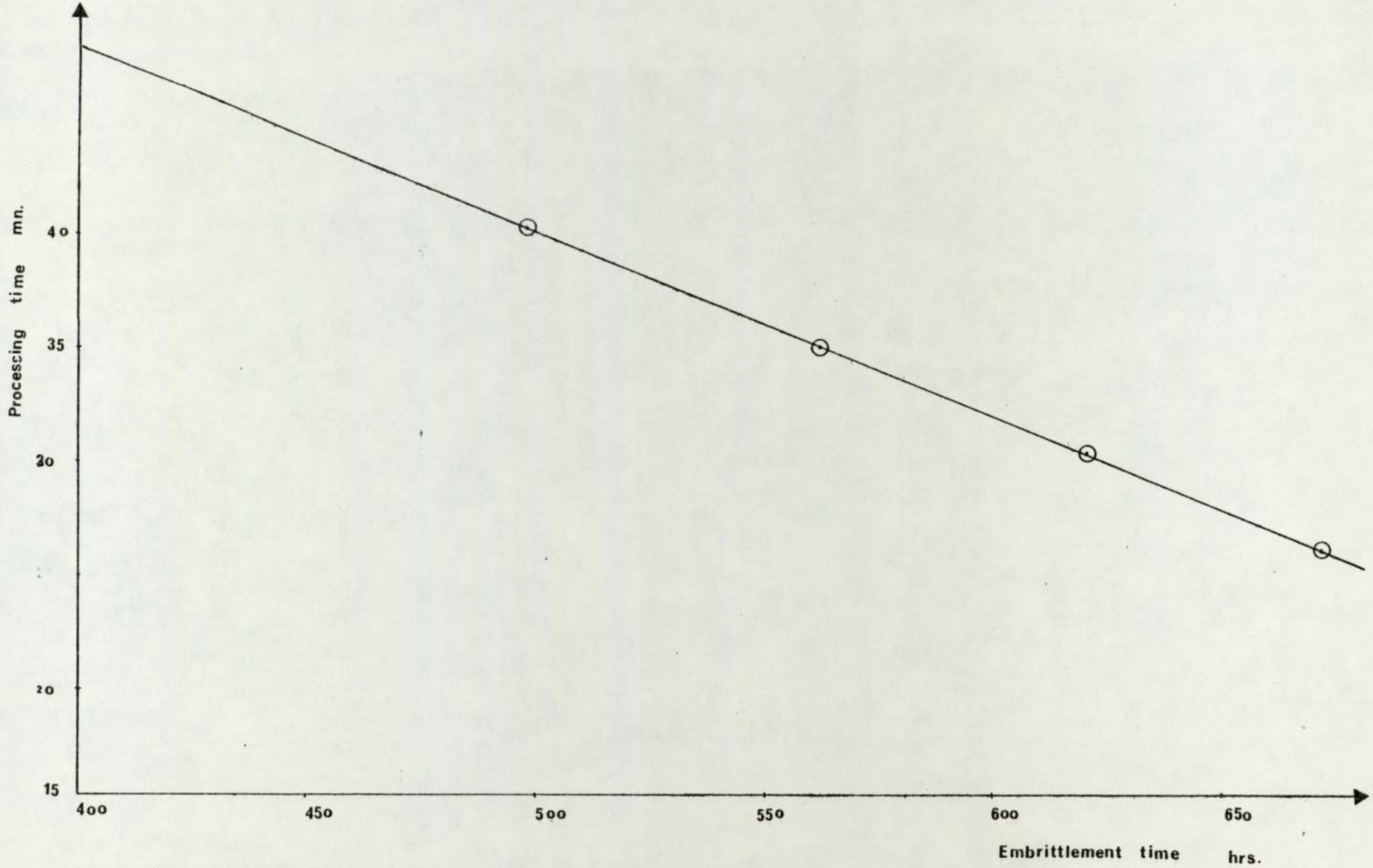
4.4. Dependence of embrittlement time of LDPE on initial thermal treatment

(Fig. 17) indicates that the ultra-violet life time in a fluorescent sun lamp/black lamp cabinet



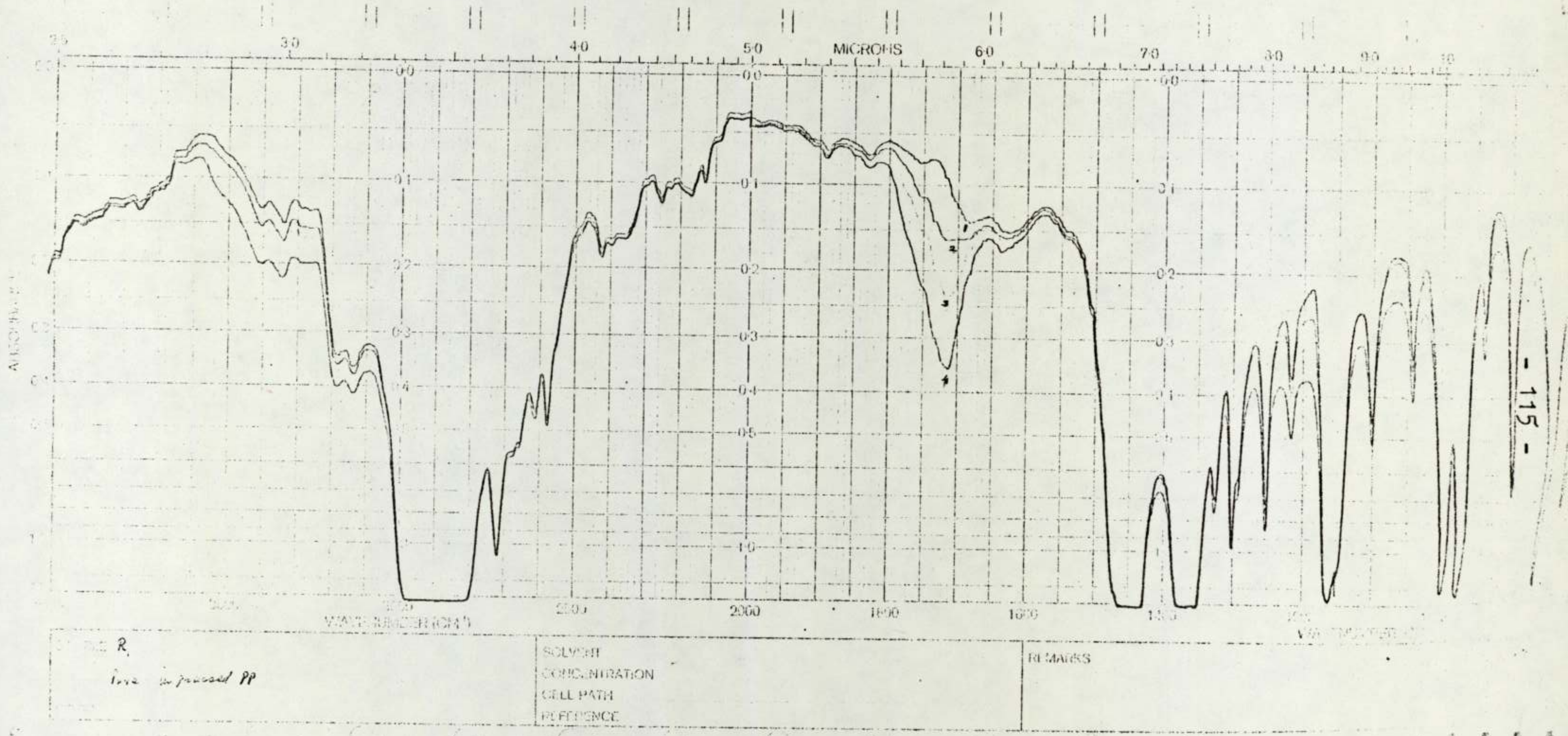
Variation of embrittlement time with processing time in the torque rheometer for LDPE

Fig. 17



Variation of embrittlement time with processing time in the torque rheometer for HDPE

Fig. 18



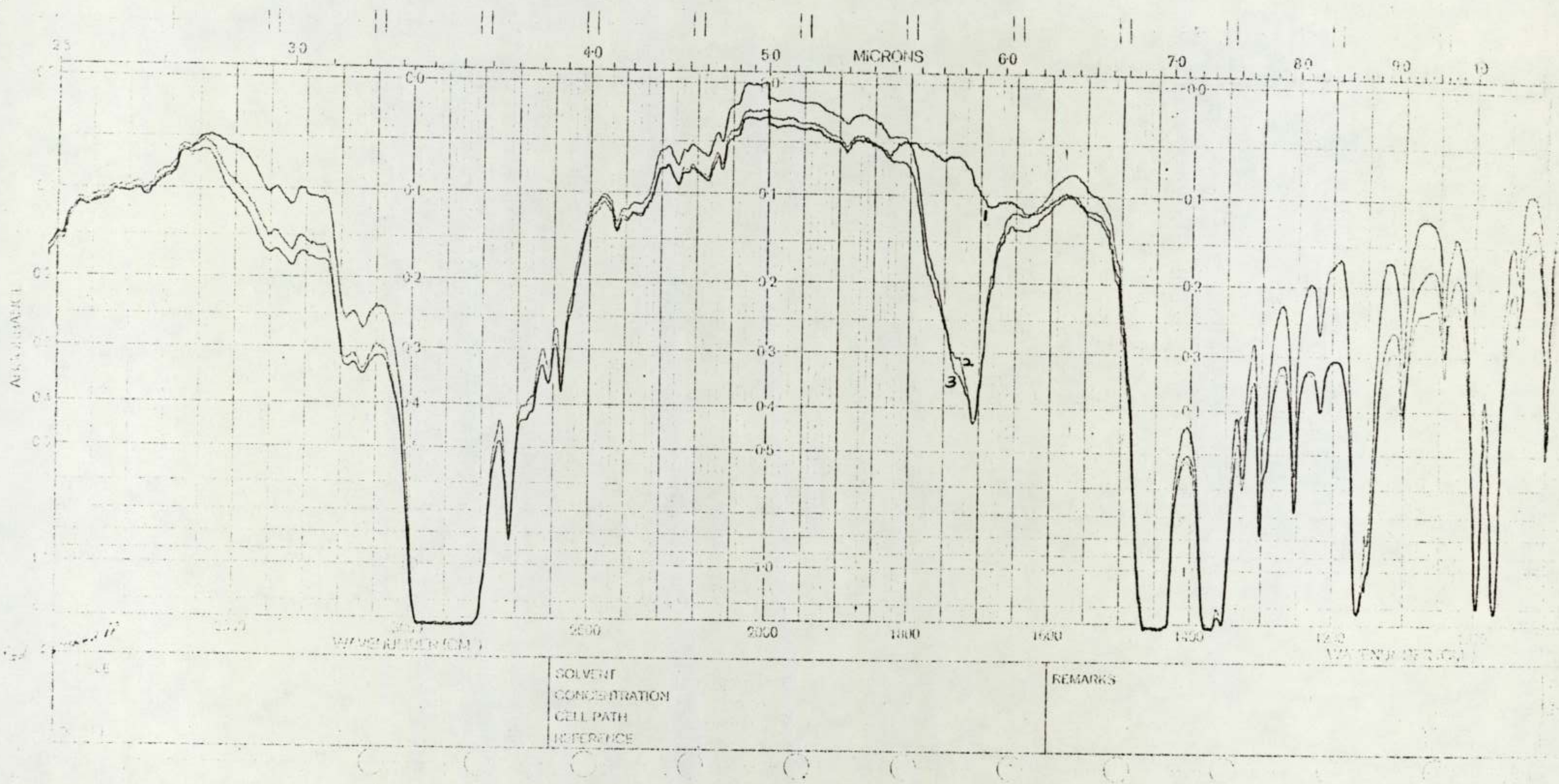
EXPOSURE TIMES

1. 0 hrs
2. 20
3. 46
4. 65

SPECTRUM OF PURE UNPROCESSED POLYPROPYLENE

EXPOSED TO UV LIGHT

Spectrum 7



SPECTRUM OF POLYPROPYLENE BEFORE AND AFTER

OZONE TREATMENT

Spectrum **8**

Time of exposure to ozone
at the rate of 1 ml/min

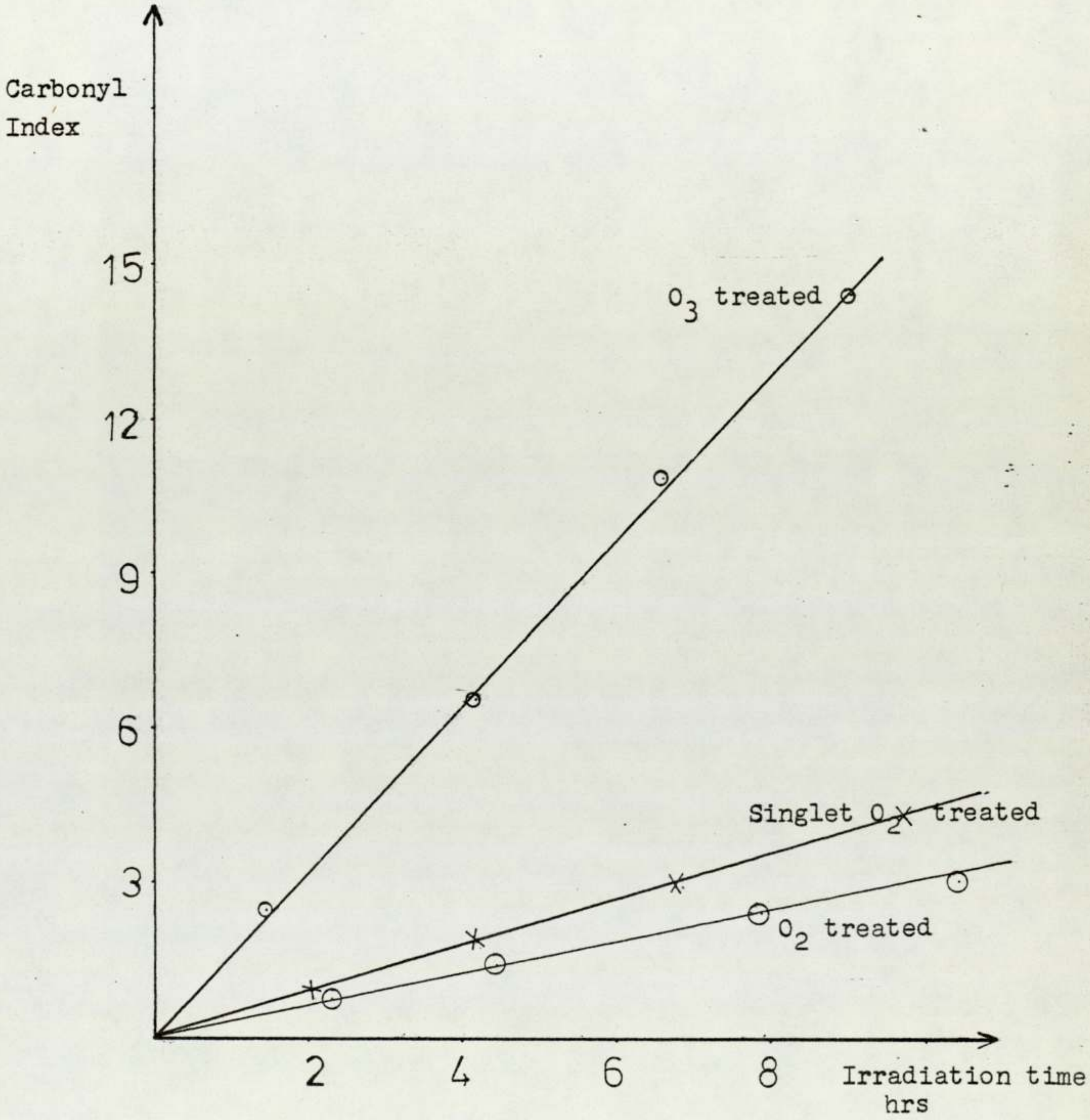
1.0 hrs
2.2
3.4

which is directly proportional to the embrittlement time is critically dependent upon the extent of oxidation. A similar but straight line dependence of embrittlement time on oxidation of high density polyethylene is also obtained as shown in (Fig. 18).

At the initial stages of processing, the carbonyl content which is the most important chromophore in polyethylene degradation is low. But at higher processing times carbonyl content increases and hence the life time of the polymer drops. But there was no linear relationship between the initial carbonyl content and the irradiation time.

4.5 Experiments with singlet oxygen

Experiments carried out with singlet oxygen, by exposing LDPE films directly to singlet oxygen stream indicated that singlet oxygen has no reaction with pure LDPE. Exposure to the gas stream followed by IR analysis of the polymer film indicates no band due to hydroperoxide groups. But as in the case of a stream of pure oxygen carbonyl band intensity varies with irradiation time indicating that there is no change in the rate of carbonyl formation when LDPE is exposed to singlet oxygen (Fig. 19). Films of carotene exposed to the same gas stream undergo a colour change indicating that singlet oxygen has been formed although it does not react with the polyethylene film.



VARIATION OF CARBONYL INDEX WITH IRRADIATION TIME FOR LDPE TREATED WITH O_3, O_2 & SINGLET OXYGEN

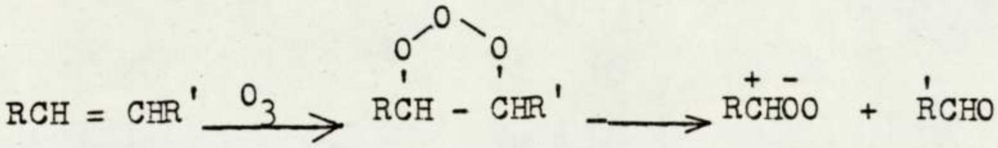
Fig. 19

4.6 Action of ozone on LDPE

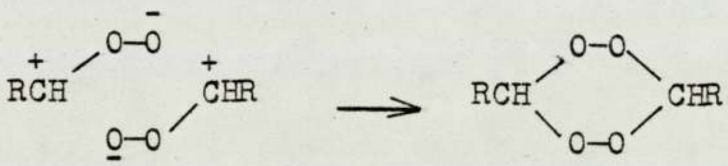
In order to determine the nature of the oxidised groups in the polyethylene exposed to ozone, polyethylene films which had been exposed to ozone for 6 to 18 hours were scanned in the Perkin Elmer 457 spectrophotometer(Spec 8). There was virtually no difference between the IR spectrum of this and of pure unexposed polyethylene spectrum except in the carbonyl region. Even the analytical method failed to show the presence of any hydroperoxide groups. Carbonyl absorbance of the sample exposed to O_3 was slightly higher than that of the film exposed to oxygen (Fig. 19). In addition to the carbonyl band the spectra of both types of oxidised films showed a broadening of the OH bands around 3200 cm^{-1}, prpbably due to the OH of carboxylic acids, and a band of low intensity at 1415 cm^{-1}, which is characteristic of ketones having long paraffin chains attached to the carbonyl groups. The absence of any detectable absorption at 3360 cm^{-1}, indicates that no appreciable amount of alcoholic hydroxyl groups were present. The 3550 cm^{-1} band associated with hydroperoxide groups was also absent. The carbonyl band which had its maximum absorbance at 1717 cm^{-1} had a shoulder at 1745 cm^{-1}, which is consistent with aldehyde groups, but which is believed to be due principally to associated carboxylic acid groups. The position of the main band is consistent with ketones or associated carboxylic groups; esters and anhydrides in polyethylene absorb at considerably higher frequencies. There may be ozonide groups present the film after the ozone treatment. But there is no experimental method available to detect the presence of these groups. Presence of dialkyl hydroperoxide groups is also doubtful as the analytical method for hydroperoxide groups gave negative results. The contribution of carboxylic acid groups to the absorbance at 1717 cm^{-1} was determined[87] by converting the acid to carboxylate ions and measuring the change in the absorbance.

4.7 Conversion of the carboxylic acid group to carboxylate ion

Samples of oxidised film were allowed to stand in 0.2 N solution of sodium hydroperoxide in 95% ethanol at room temperature. The film was removed, rinsed with water and its infrared spectra was measured. The shoulder at 1735 cm^{-1} disappeared, and a new band, characteristic of the carboxylate ion appeared at 1575 cm^{-1}. In the case of a sample exposed to ozone, sample from the discharge area showed a slight decrease in absorbance at 1717 cm^{-1} with a corresponding increase in absorbance at 1575 cm^{-1}. It has been known for many years that the ozonization of a variety of olefins leads to the formation of chemically defined peroxidic bodies, the ozonides, although any absorption due to hydroperoxy groups was not seen. The chemical studies of Criegee and Bailey give strong support to the idea originally proposed by Staudinger that the ozonide is a secondary product of ozonisation and that an initial unstable molozonide must be formed by addition of ozone to the double bond which arranges rapidly with scission of the original double bond.



This indicates the absence of any hydroperoxy groups formed by the reaction and the increase in carbonyl content after exposure to ozone can also be explained from this reaction. Chemical analysis of the polyolefin samples after ozonolysis indicates that there is no hydroperoixde group formation in this process. But there may be dialkyl peroxide group formation according to the mechanism given below. Also the behaviour of the films exposed to ozone towards UV light was exactly the same as films containing initial varying concentration of carbonyl from preoxidation.



5. EFFECT OF METAL COMPLEXES ON UV STABILITY OF POLYETHYLENE

Metal complexes such as cobalt acetylacetonate (CoAcAc), ferrous acetylacetonate (FeAcAc), Nickel n dibutyldithiocarbamate,(NiDBC) Nickel oxime and carotene which are powerful activators and retarders of photodegradation of polymers were used in this study. The following two standard methods were used.

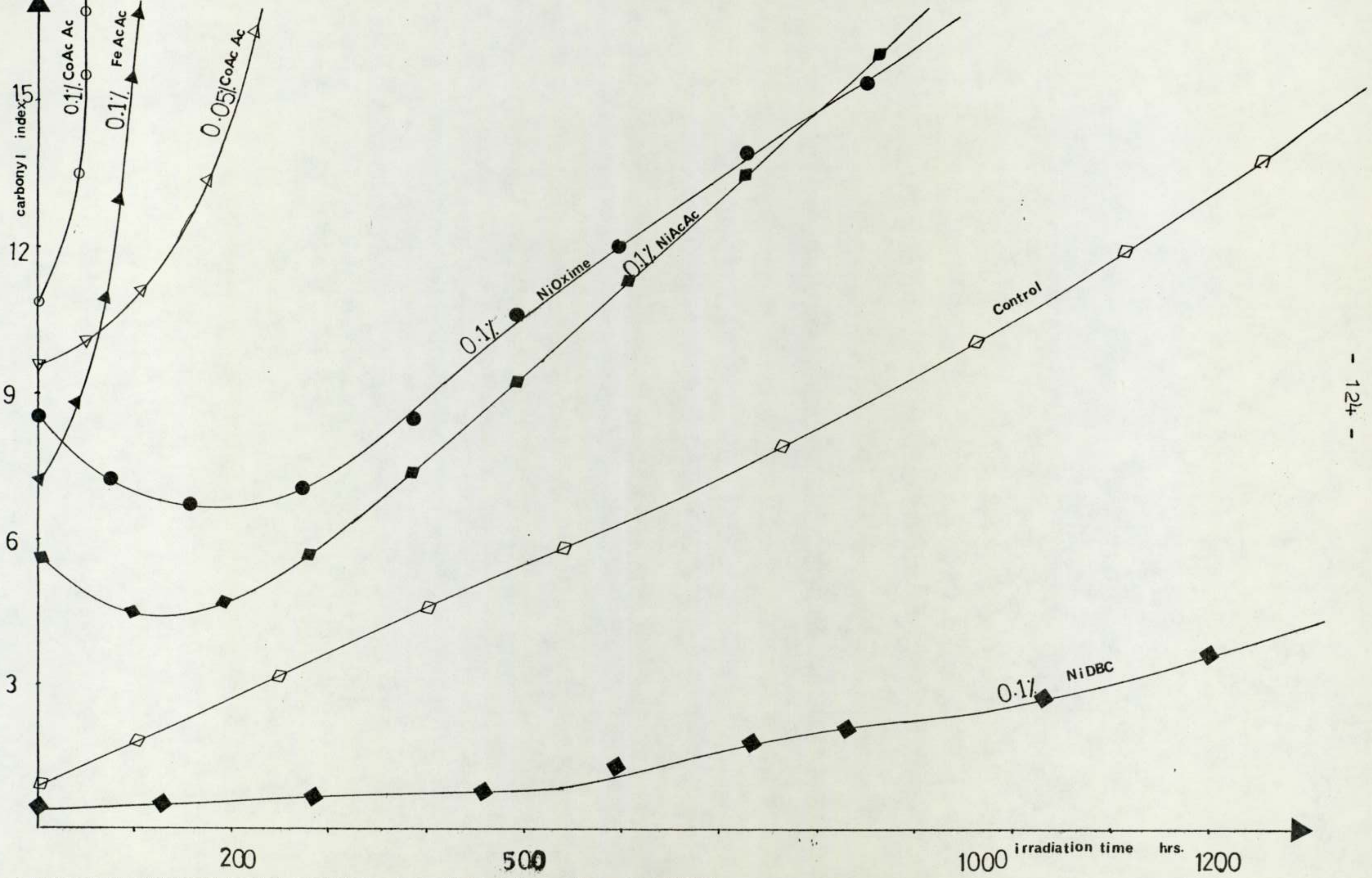
1. Infrared spectroscopic studies of the formation and disappearance of functional groups on polyolefin films incorporated with the above compounds in the torque rheometer.
2. Oxygen absorption of a thin film of the polyolefin in the presence and absence of the above compounds.

In the infrared spectroscopic measurements films containing varying concentrations of the above compounds were scanned in the PE 457 IR spectrometer after exposure to UV light in the SB exposure cabinets for varying lengths of time. All these spectroscopic experiments were carried out at room temperature with attenuator in the reference beam. The four concentrations used were 0.01%, 0.05%,0.1% and 0.25% by weight of the polymer. Mixing was done in the torque rheometer at 160°C for 5 mins. Films of thickness 7-9 mil were used for both oxygen absorption and IR measurements. All IR spectra were run at medium scan and the growth of carbonyl, vinyl and hydroperoxide groups were studied carefully. In the case of processing experiments at 160°C, the disappearance of the vinylidene group was studied carefully.

All the oxygen absorption experiments were carried out in 100% oxygen atmosphere inside silica cells. By comparing the oxygen absorption curves obtained in the presence of different additives with the oxygen absorption curve of uncatalysed pure polyethylene films, the accelerator activity of the two metal complexes CoAcAc and FeAcAc were compared. In all these oxygen absorption experiments, the sample and the reference tubes were inside the SB cabinet at 35°C. Detailed studies of this oxygen absorption experiment could not be carried out as the UV exposure chamber was not free for more than 2-3 weeks. Results of these experiments are given below.

5.1 Results

In these experiments the accelerating activity of the metal complexes was found to be in descending order (Fig. 20 to 25): CoAcAc > FeAcAc > FeDBC > NiDBC > Carotene > Ni oxime. This is the same order as that found by Coomarasamy in similar studies carried out with methyl cyclohexene. Of the complexes studied acetyl acetonates of ferrous and cobalt metals showed powerful oxidation activities (Fig. 24 and 25) while Ni DBC and Fe DBC like compounds retarded the oxidation at the beginning as shown



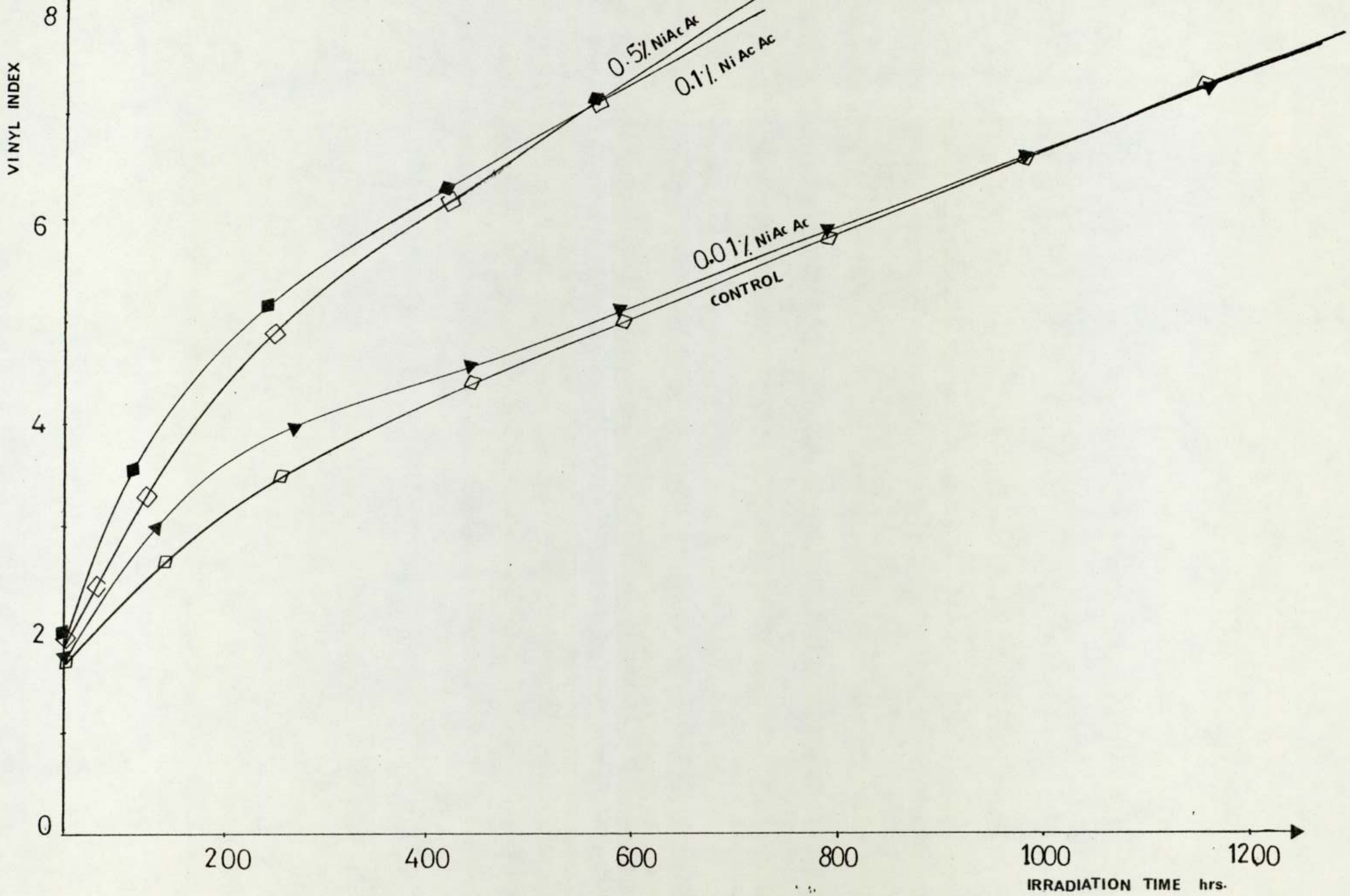
Effect of different metal chelates on carbonyl formation in LDPE

Fig. 20

Table 6 -Variation of carbonyl indices with irradiation times for LDPE incorporated with metal complexes

Additive Irr.Time hrs	CoAcAc 0.1%	FeAcAc .1%	CoAcAc .05%	Ni oxime .1%	NiAcAc .1%	Control	NiDBC.1%
50	15.2	9.6	9.9	7.1	5.0	0.95	0.50
100	27	17.3	10.3	6.6	4.4	1.6	0.50
150	-	19.2	12.1	6.2	4.1	2.2	0.51
200	-	-	14.2	6.1	4.3	2.4	0.51
250	-	-	20.3	6.2	5.5	3.1	0.52
300	-	-	-	9.0	7.5	4.0	0.52
500	-	-	-	11.3	10.0	5.7	0.70
750	-	-	-	14.0	13.7	7.5	2.0
1000	-	-	-	18.2	20.1	10.9	2.8

by a long induction period (Figs 27,30 and 34). After exceeding this induction period, activity was much faster than in the case of the pure LDPE film indicating its delayed action activity. This is clear from the carbonyl growth and vinyl growth curves as shown in Figs. 20,21, and 26.



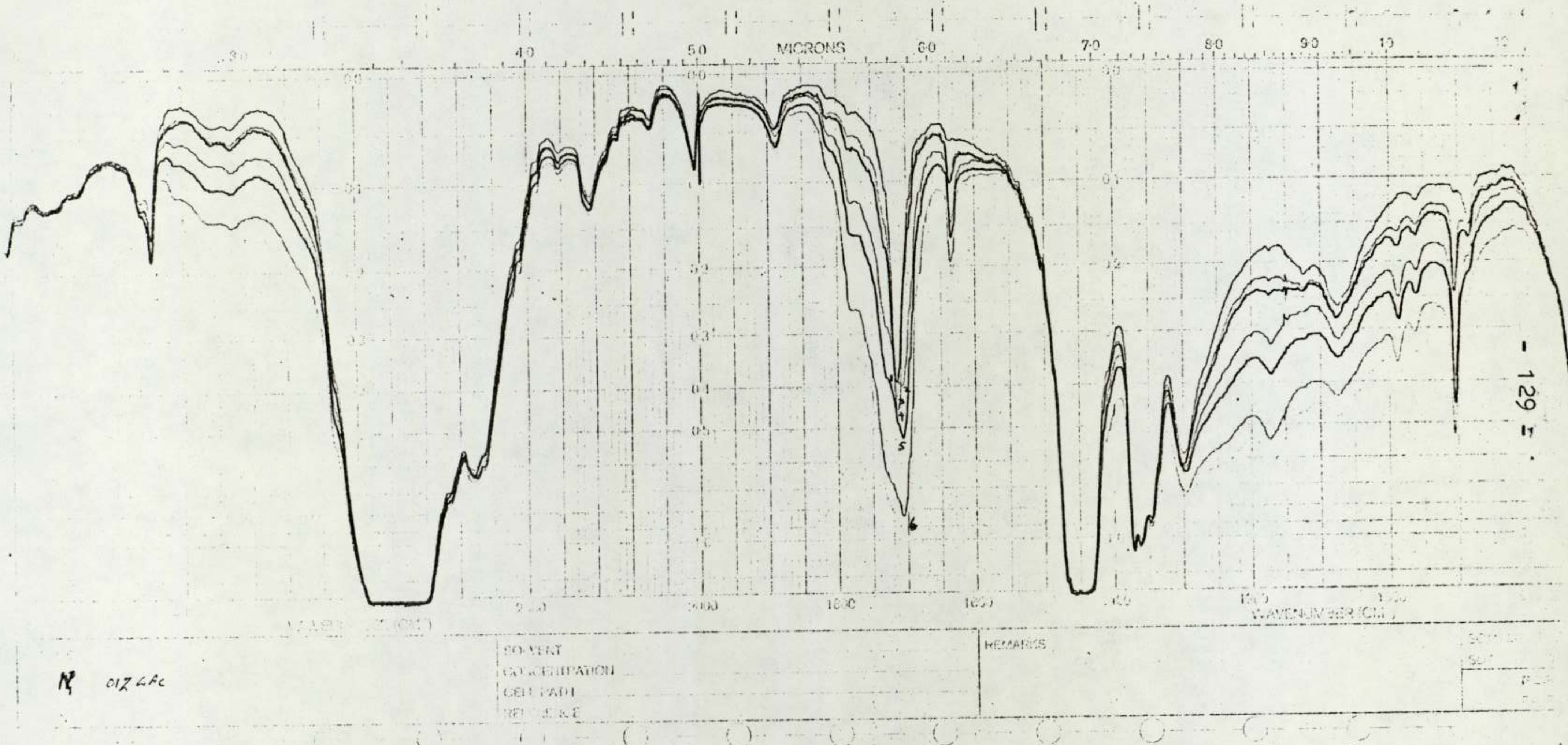
Effect of concentration of NiAcAc on vinyl formation in LDPE during UV irradiation

Fig.21

The rate of oxidation of polyethylene in the presence of FeAcAc is much faster than in the case of polyethylene containing FeDBC. In the case of the polymer containing the latter although the metal ion is the same the initial rate of oxidation (within the induction period) was lower than the steady rate of oxidation in the absence of any additive. This shows that the complexing agents or the ligand also a~~e~~ffects the activity of metal ions. The redox potential of the metallic ion in its environment was considered important to explain this difference in activity. Extent of oxidation in all these cases is shown by the rapid increase in the carbonyl content of vinyl contents of the compound (Graph 21, 22 and 23) as these are the products of photodegradation of polyolefins or by the embrittlement time. In oxygen absorption measurements, this is indicated by the rapid rise in the rate of oxygen consumption of the material. A change in colour of the films exposed to UV light is also noted in these experiments.

According to these results the metal complexes studied seem to fall into 3 main categories which are given below.

1. Metal complexes which are powerful activators for oxidation from the initial stages.
2. Metals which act initially as powerful activators, but lo~~o~~se their activity gradually and in some cases become antioxidants.



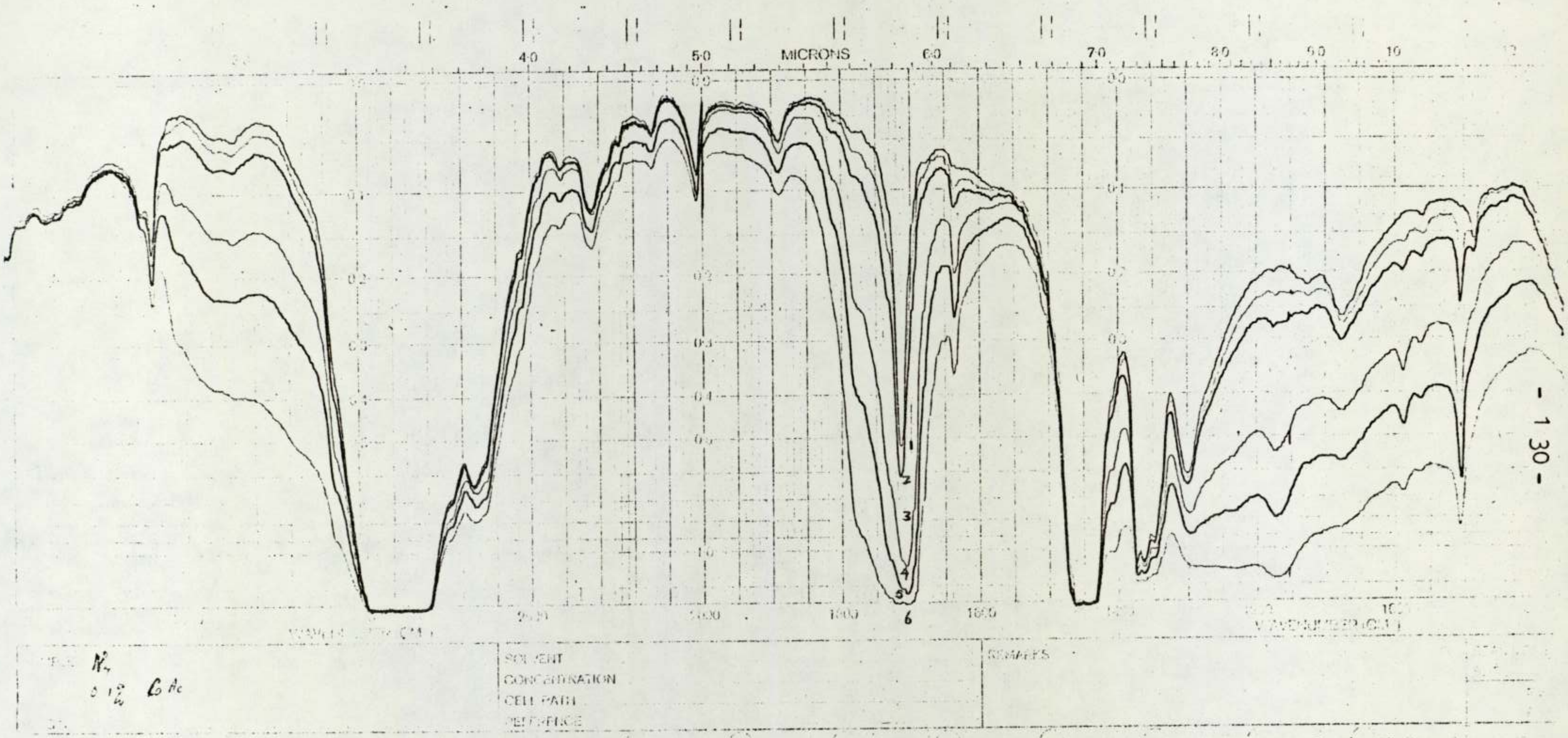
Time of exposure

1. 0 hrs
2. 50
3. 150
4. 200
5. 250

VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.01% CoAcAc

Spectrum 9



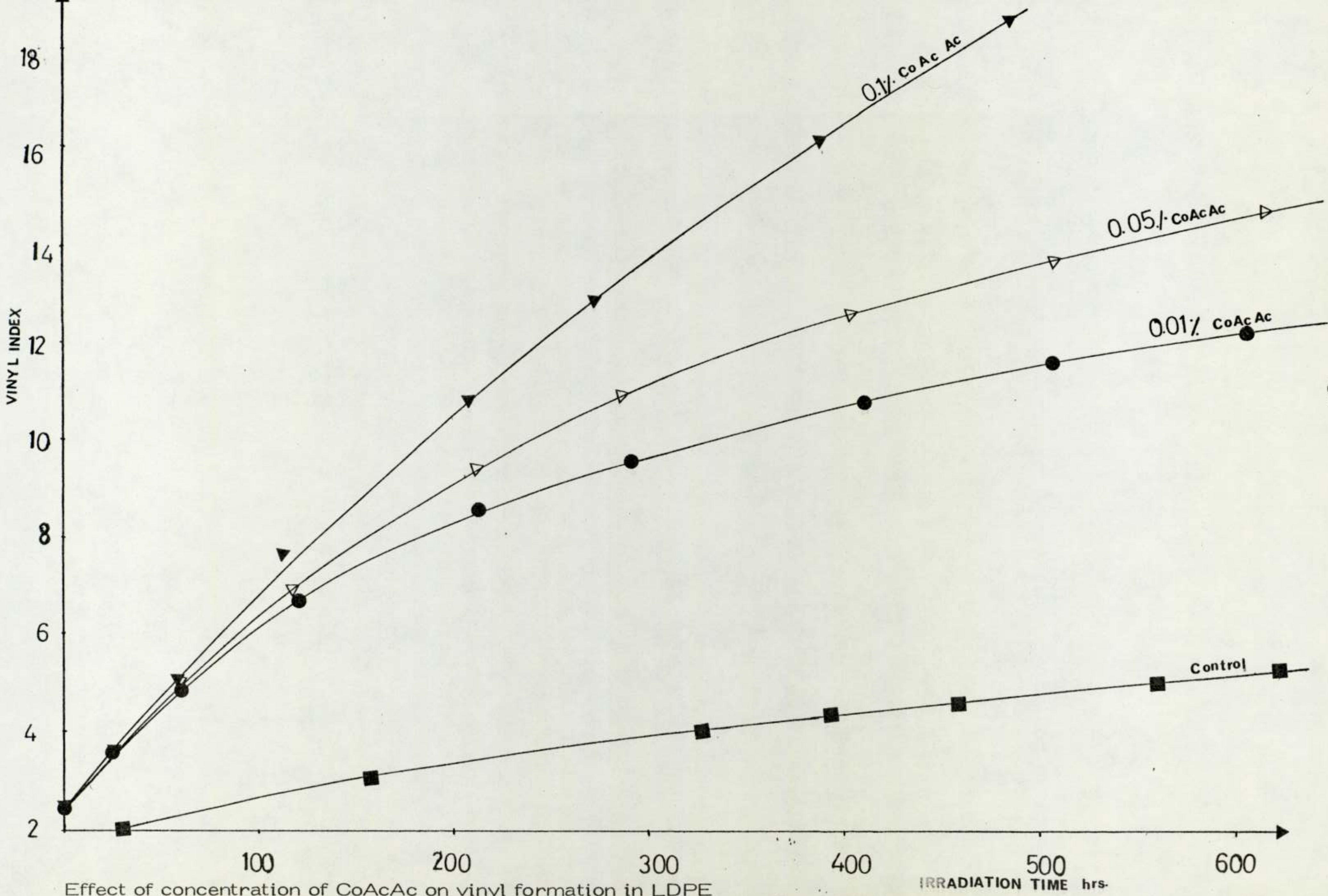
VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.1% CoAcAc

Spectrum 10

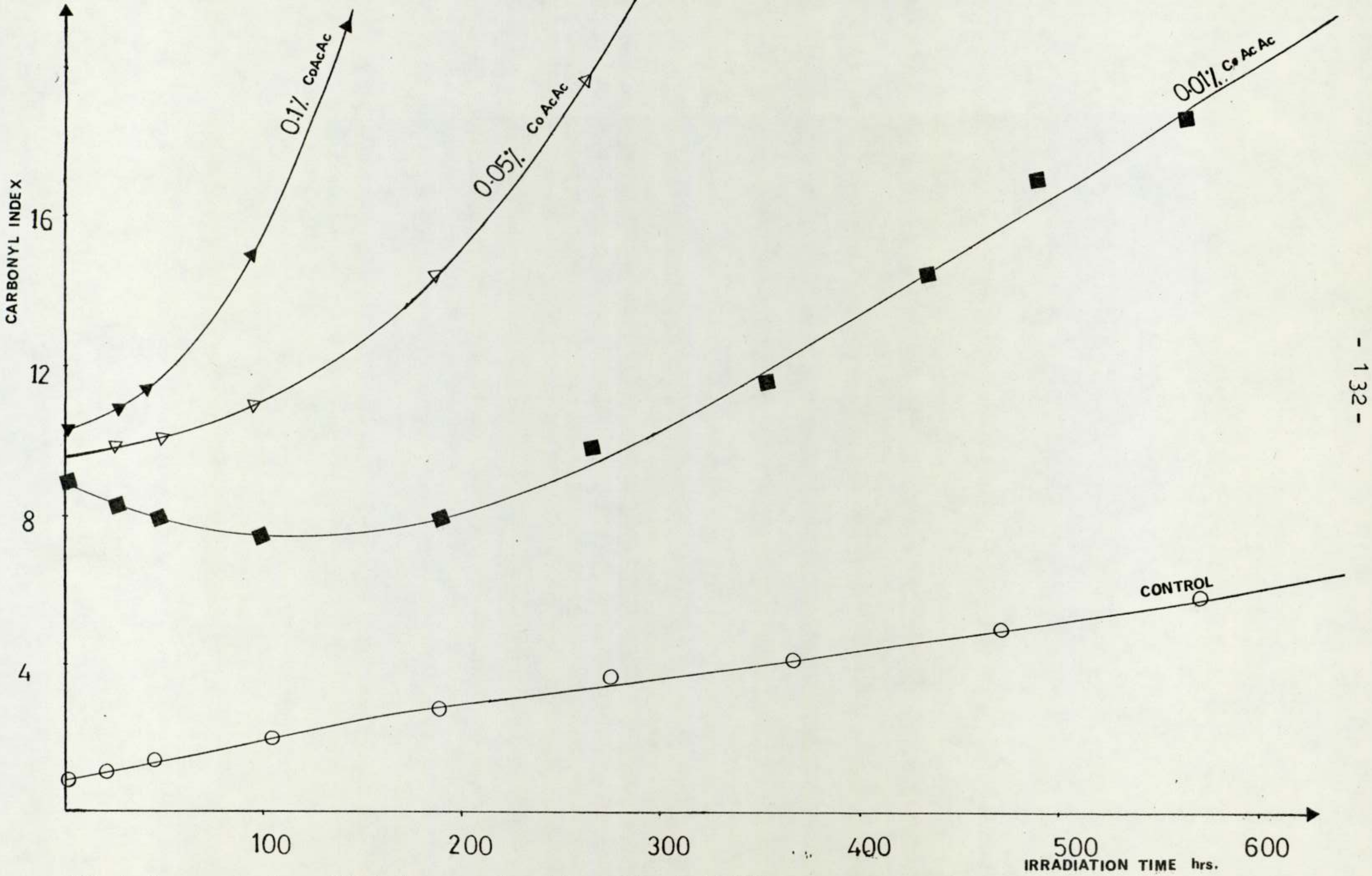
Exposure times

1. 0 hrs
2. 50
3. 100
4. 150
5. 200



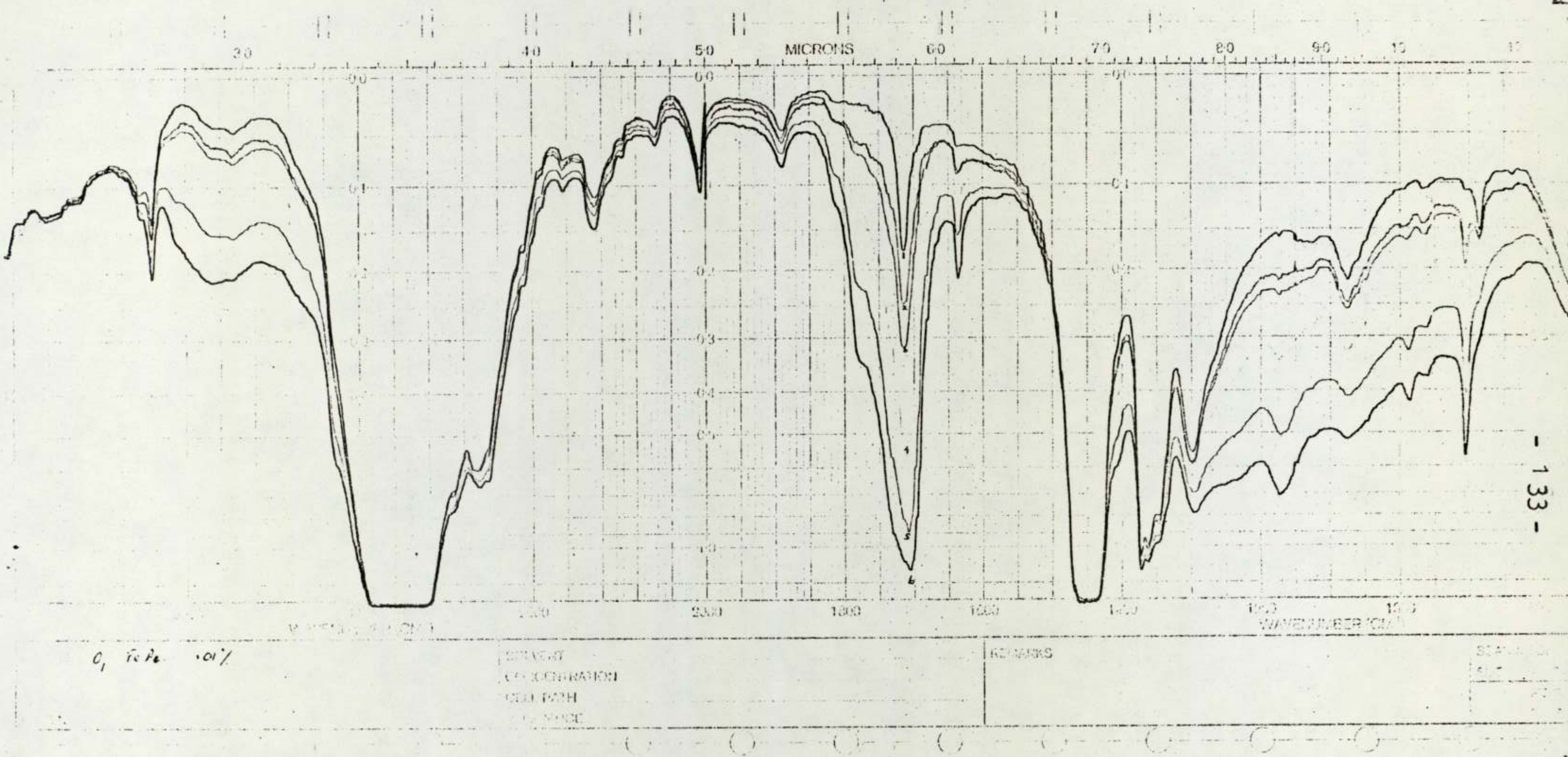
Effect of concentration of CoAcAc on vinyl formation in LDPE

Fig. 22



Effect of concentration of CoAcAc on carbonyl formation in LDPE

Fig.23.



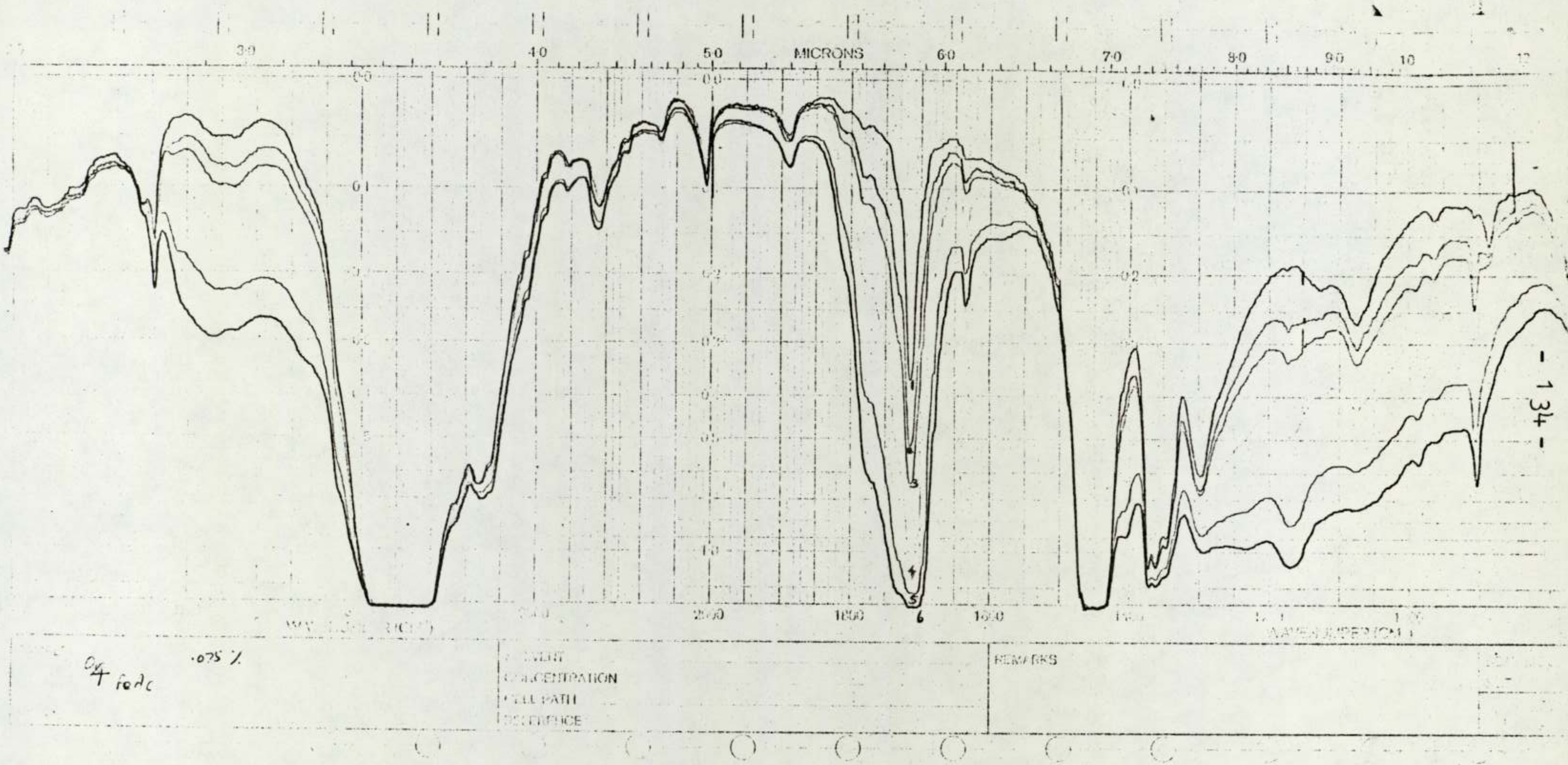
VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.01% FeAcAc

Spectrum 9

Exposure times

1. 0hrs
2. 50
3. 100
4. 150
5. 200



VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.075% FeAcAc

Spectrum10

Exposure times

1. 0 hrs
2. 50
3. 100
4. 150
5. 200

3. Metals which retard the oxidation initially, showing induction periods, but become pro-oxidants at later stages of oxidation; these are the delayed action activators.

5.2 Discussion

The photoxidation of olefins and hydrocarbons in general at moderate temperature and pressure is a free radical chain process which could be schematically represented by the following reaction sequence.

Initiation which is the production of radicals $R^{\bullet}$ and $RO_2^{\bullet}$

$$ROOH \xrightarrow{h\nu} RO^{\bullet} + \dot{O}H$$

$$2ROOH \longrightarrow RO^{\bullet} + RO_2^{\bullet} + H_2O$$

Propagation:

$$R^{\bullet} + O_2 \longrightarrow \dot{RO_2}$$

$$RO_2^{\bullet} + RH \longrightarrow RO_2H + R^{\bullet}$$

$$RO_2^{\bullet} + RH \longrightarrow RO_2M^{\bullet}$$

$$RO_2M + O_2 \longrightarrow RO_2MO_2^{\bullet}$$

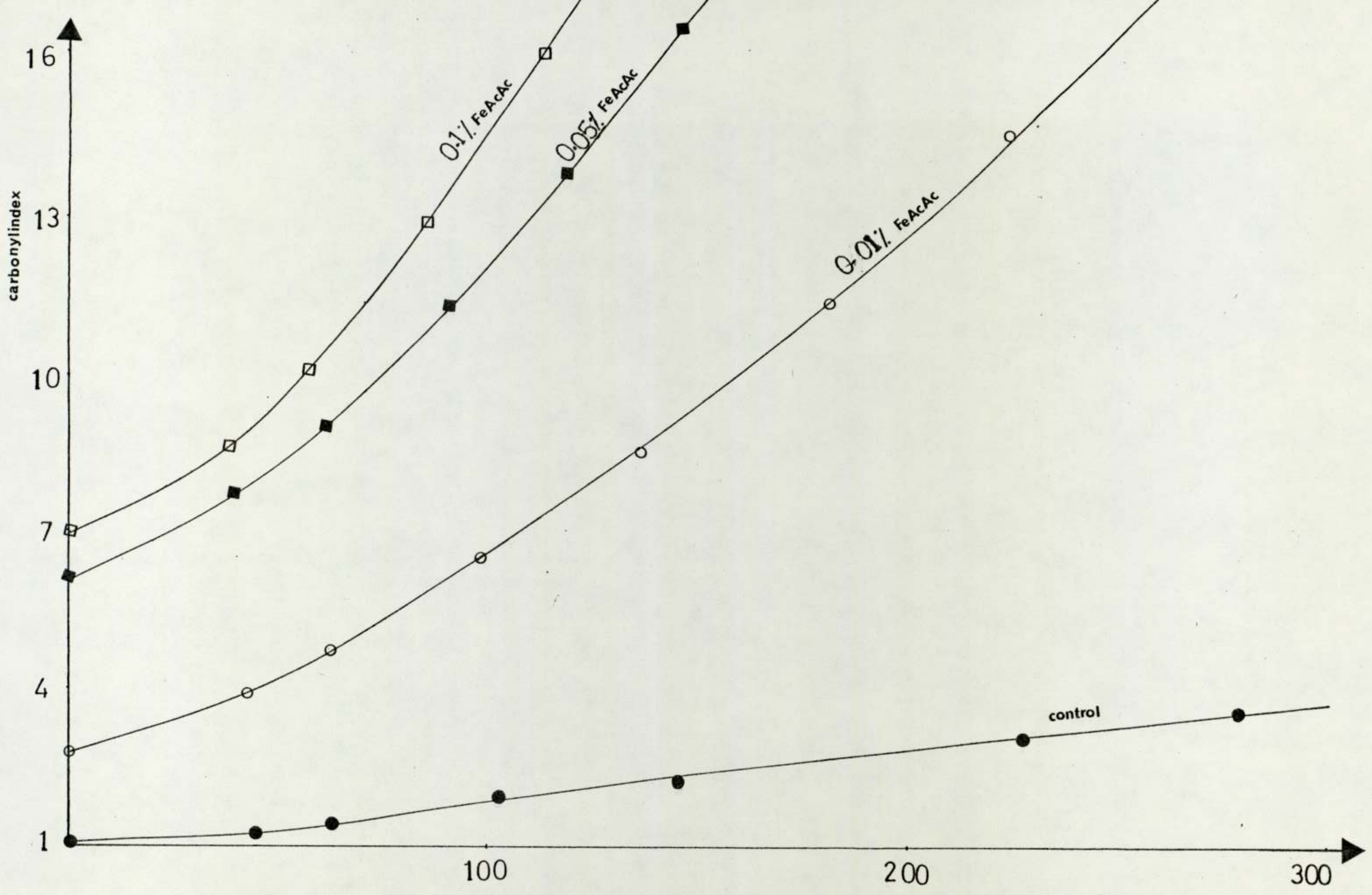
$$RO_2M^{\bullet} \longrightarrow RO^{\bullet} + MO$$

$$RO^{\bullet} + RH \longrightarrow ROH + R$$

$$RO^{\bullet} + RH \longrightarrow ROM$$

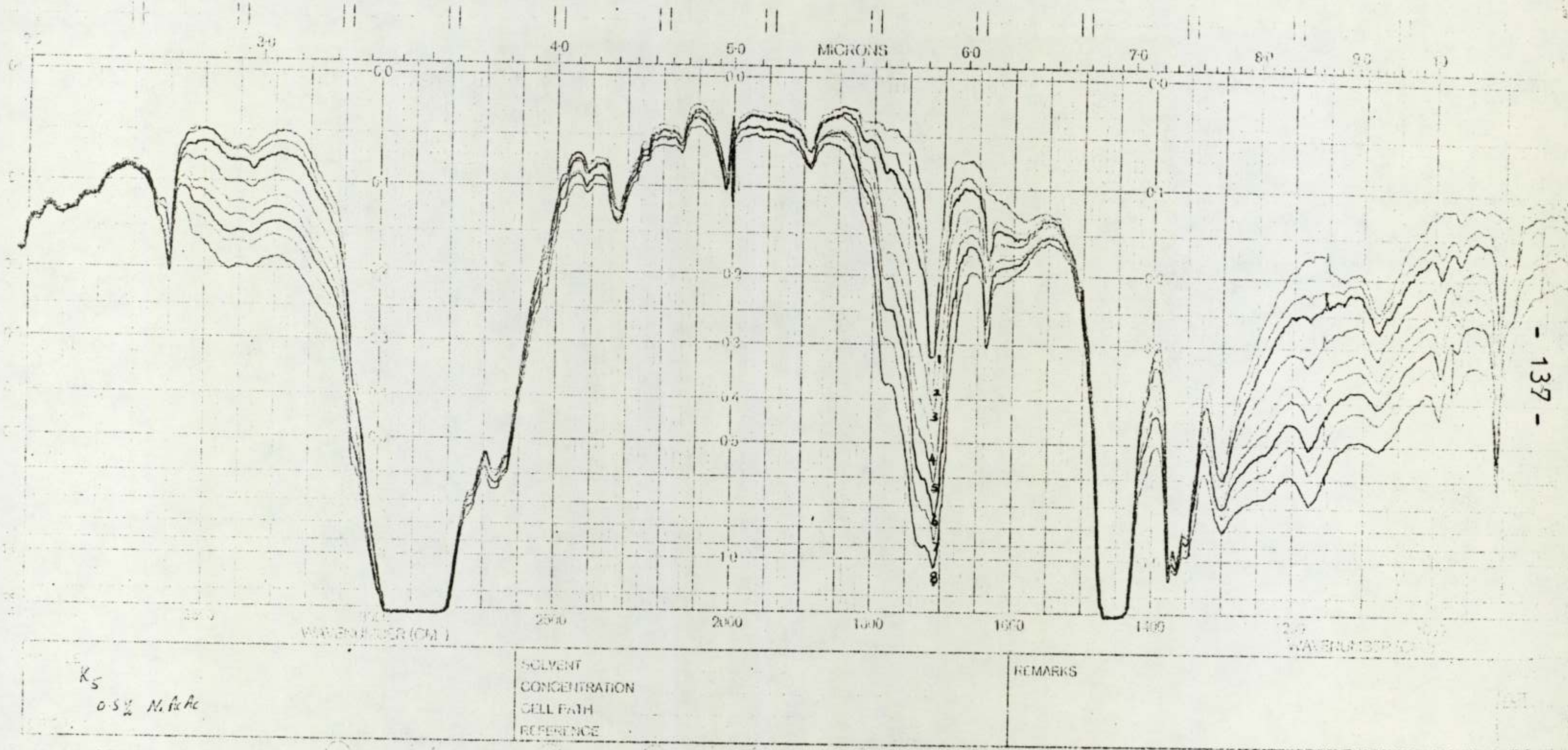
Termination

$$\left.\begin{array}{l} 2R^{\bullet} \\ R^{\bullet} + RO_2^{\bullet} \\ 2RO_2 \end{array}\right\rangle \longrightarrow \text{Non radical products}$$



Effect of concentration of FeAcAc on carbonyl formation in LDPE during irradiation

Fig. 24(b)

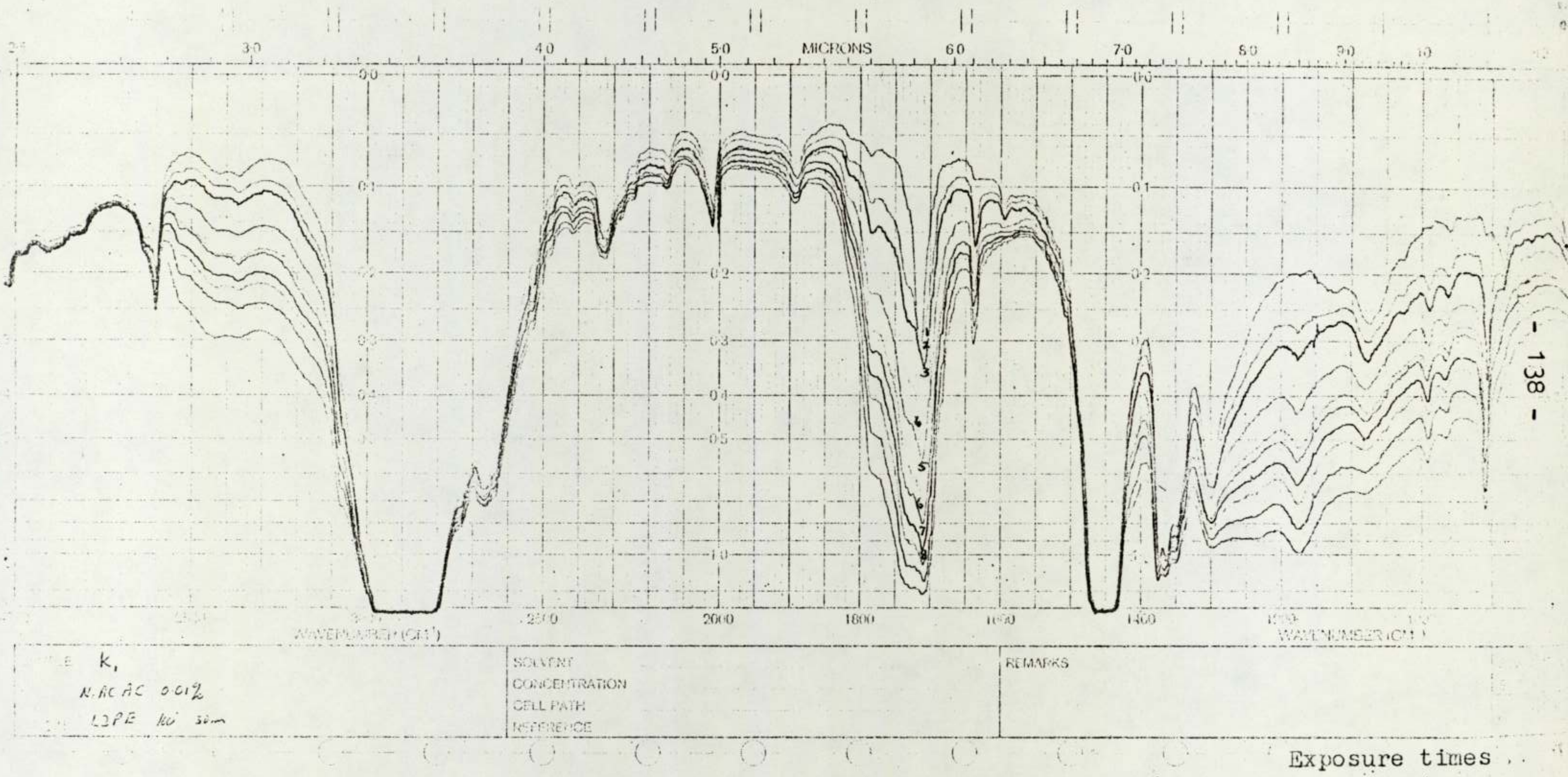


VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.5% NiAcAc

Spectrum 11

Exposure times
1. 0 hrs
2. 50
3. 100
4. 150
5. 200



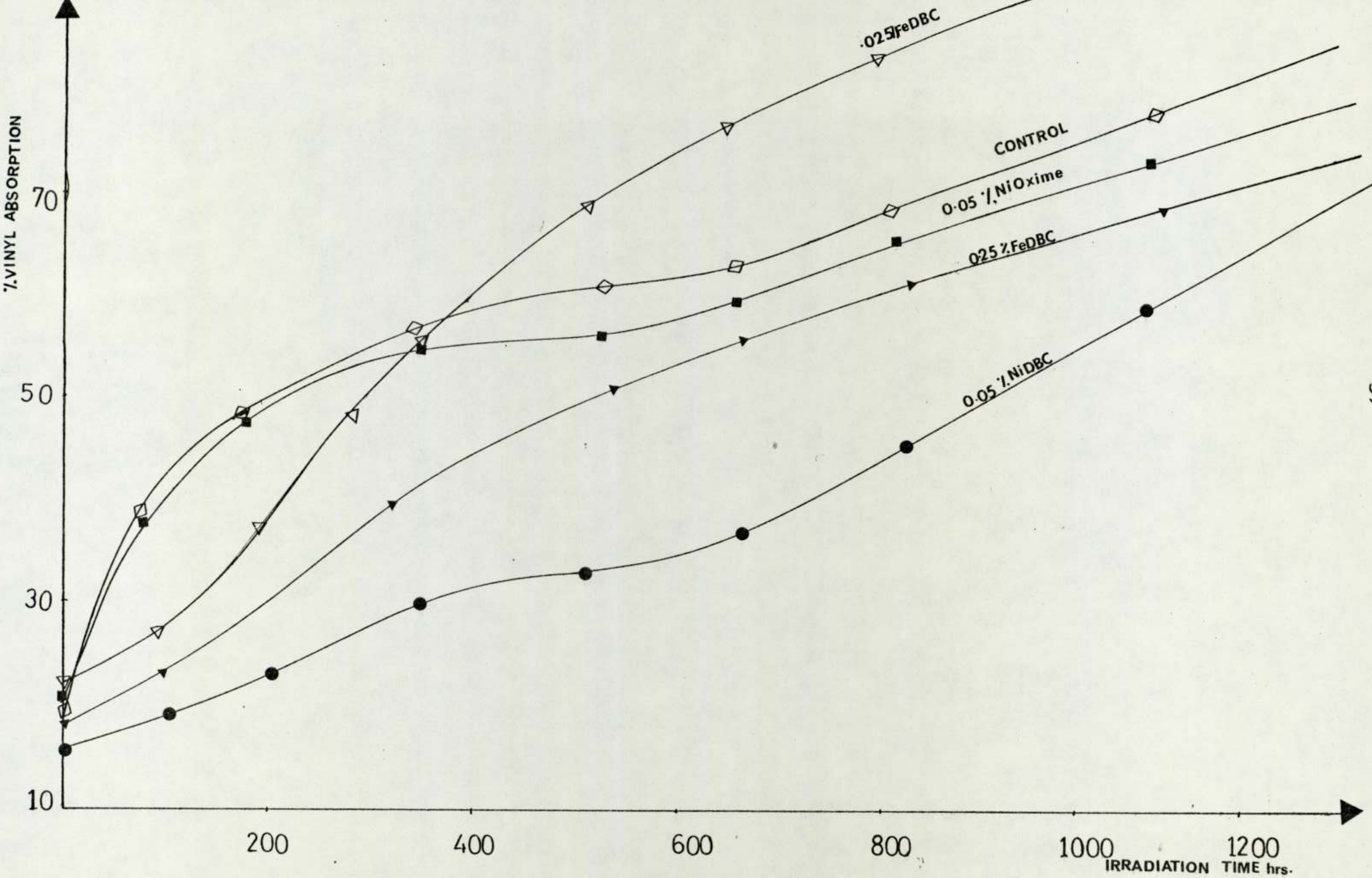
VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.01% NiAcAc

spectrum 12

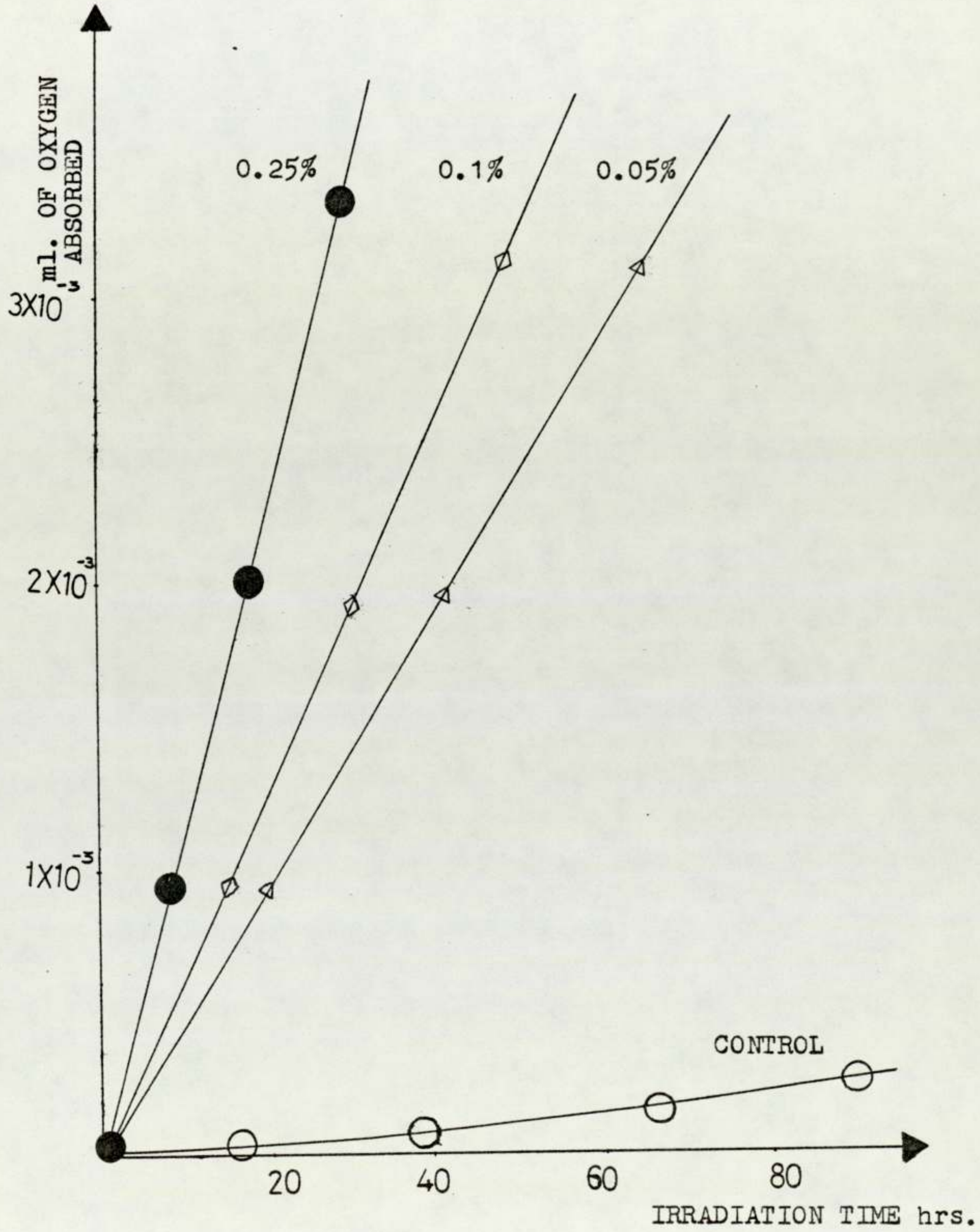
Exposure times

1. 0 hrs
2. 50
3. 100
4. 150
5. 200
6. 250



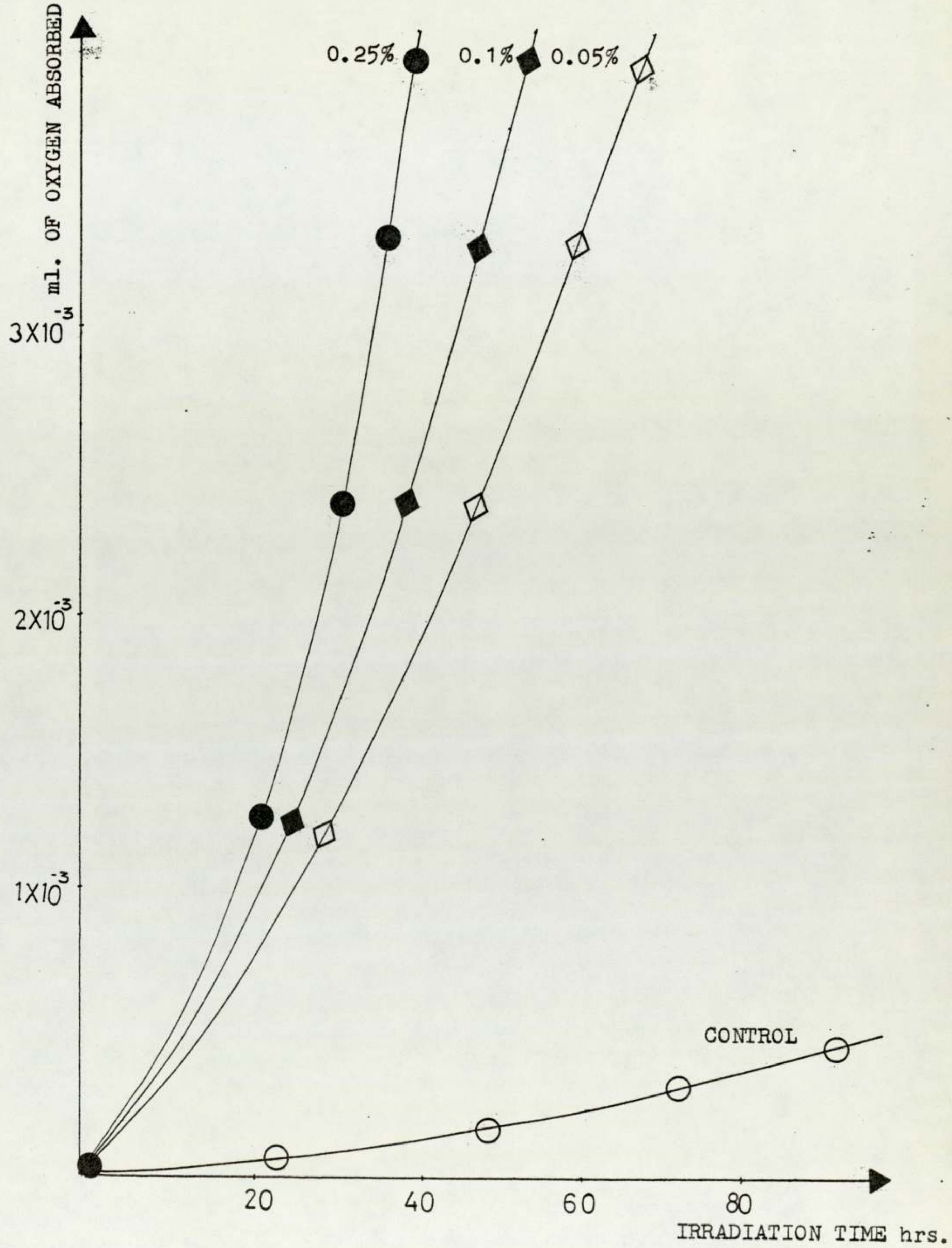
Effect of different metal chelates on vinyl formation in LDPE

Fig. 26



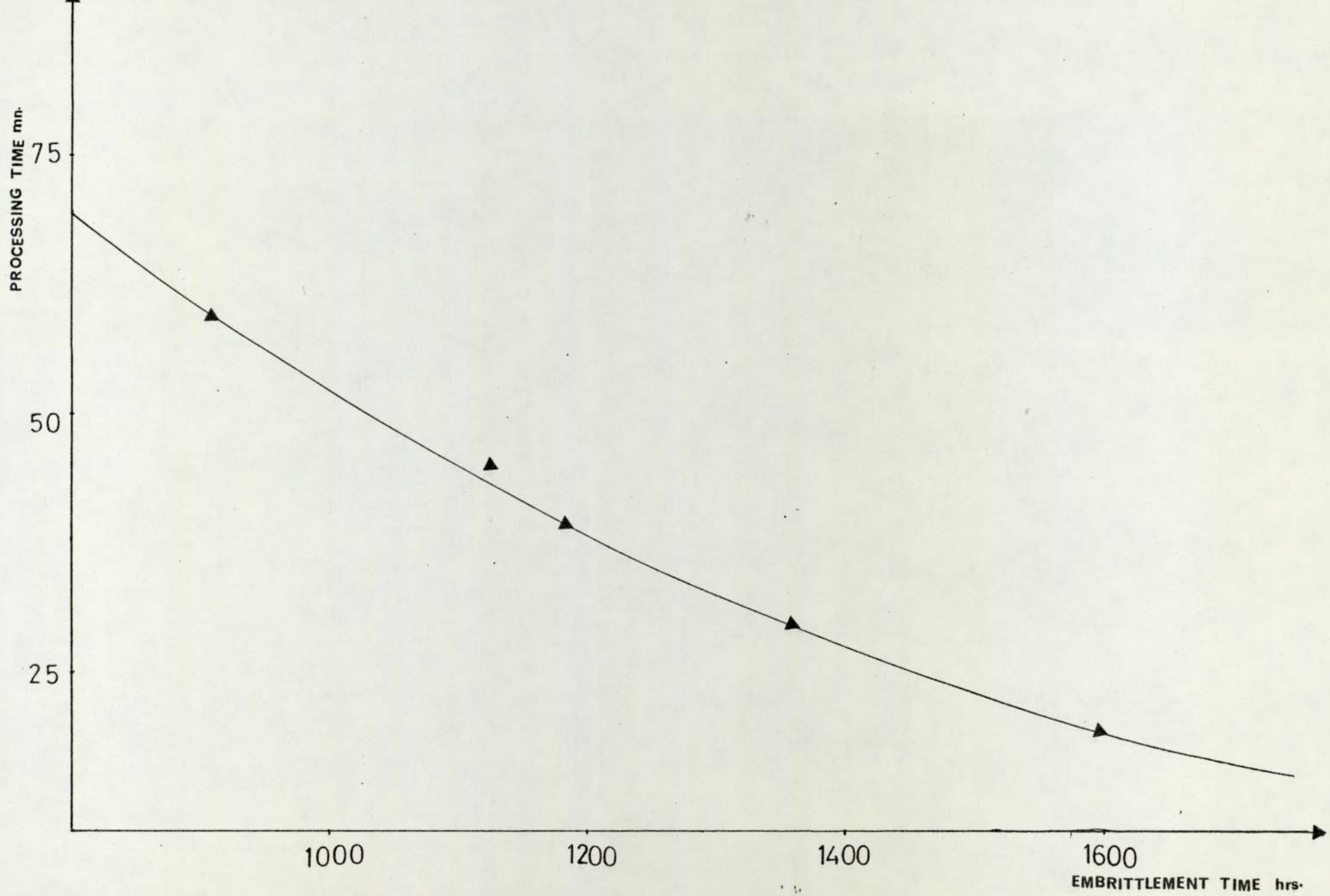
Oxidation of LDPE in the presence of Co (II) AcAc complex.

Fig. 24



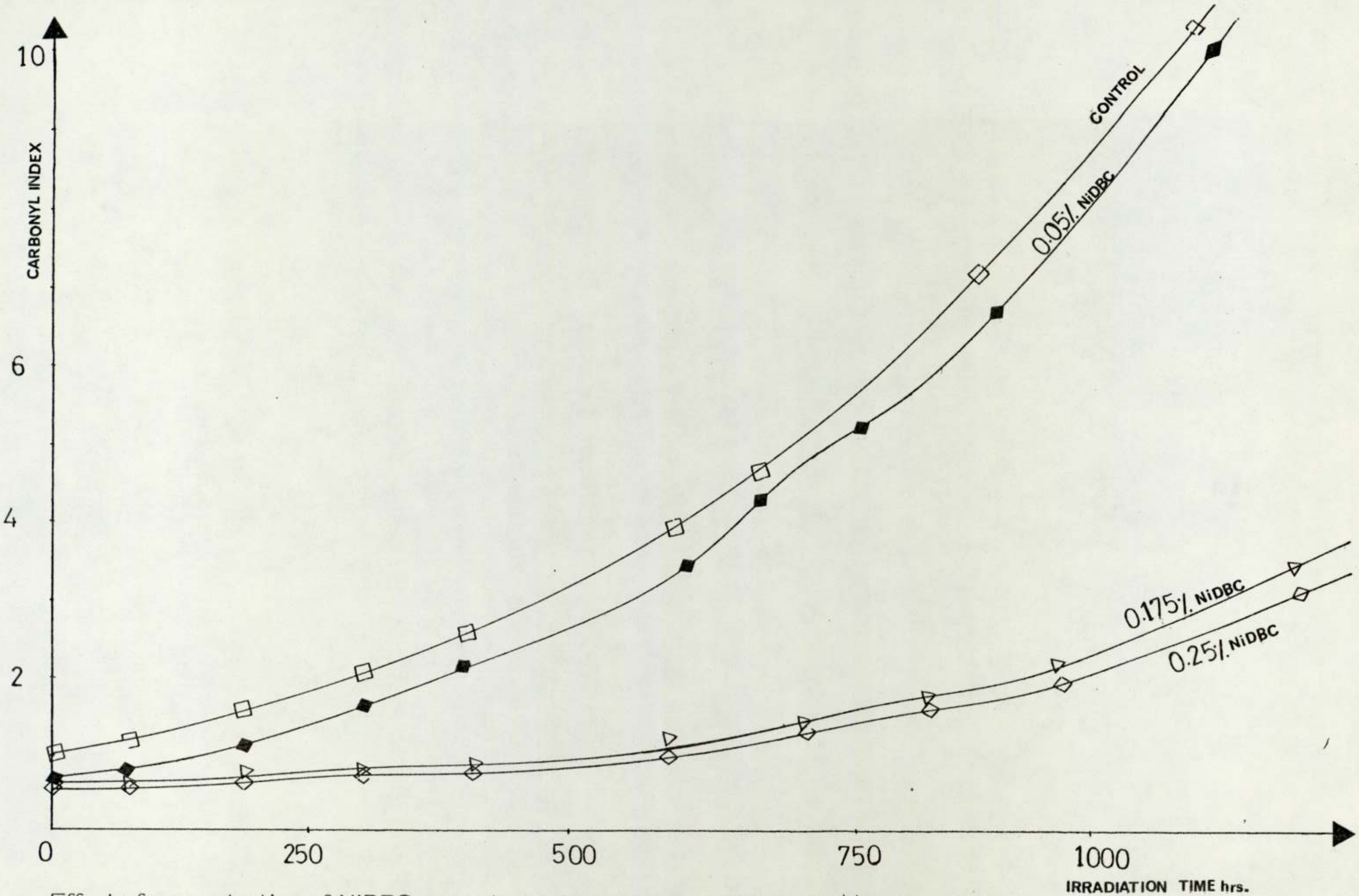
Oxidation of LDPE in the presence of Fe (II) AcAc complex.

Fig.25



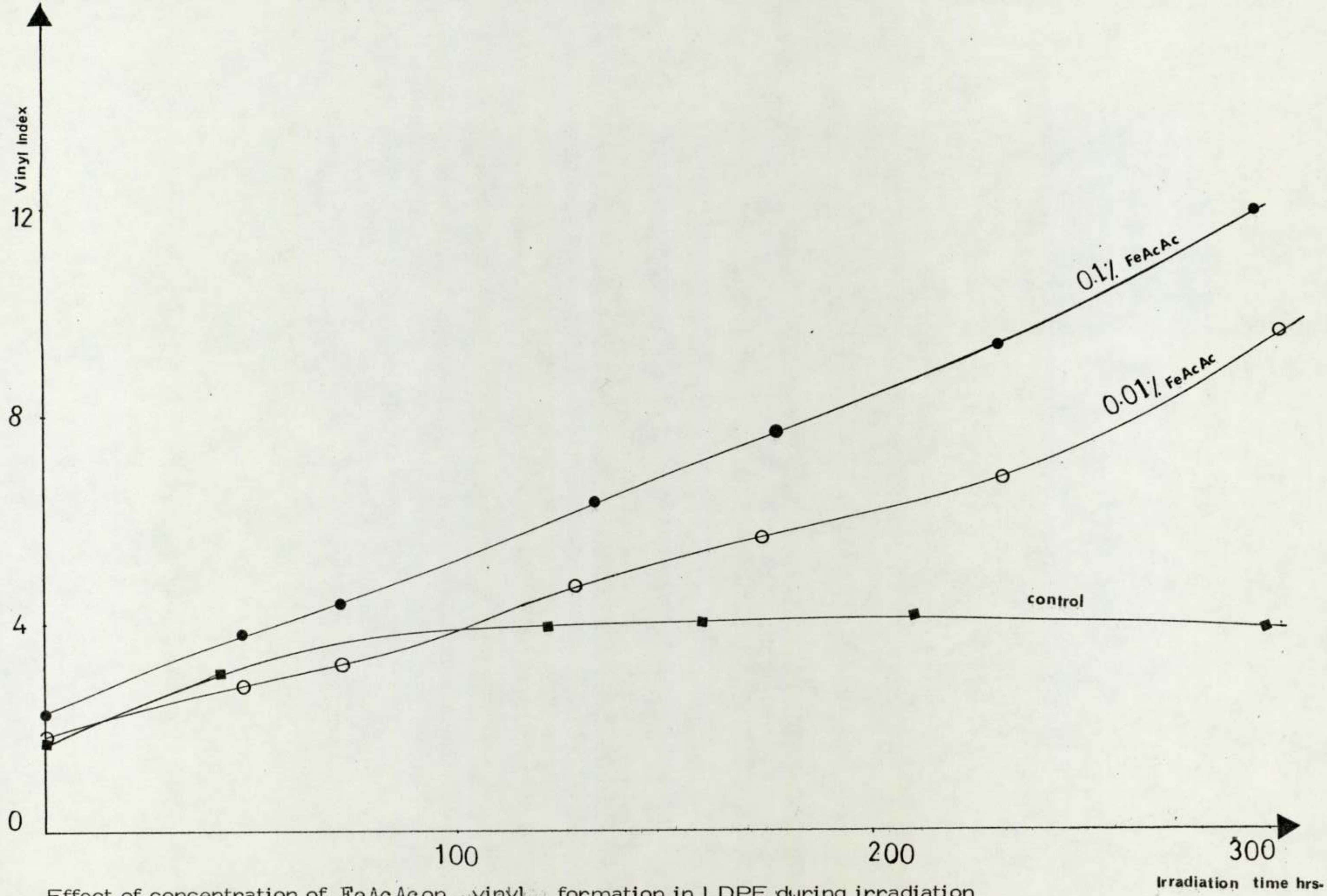
Effect of processing on the embrittlement time in LDPE containing FeDBC

Fig.25b



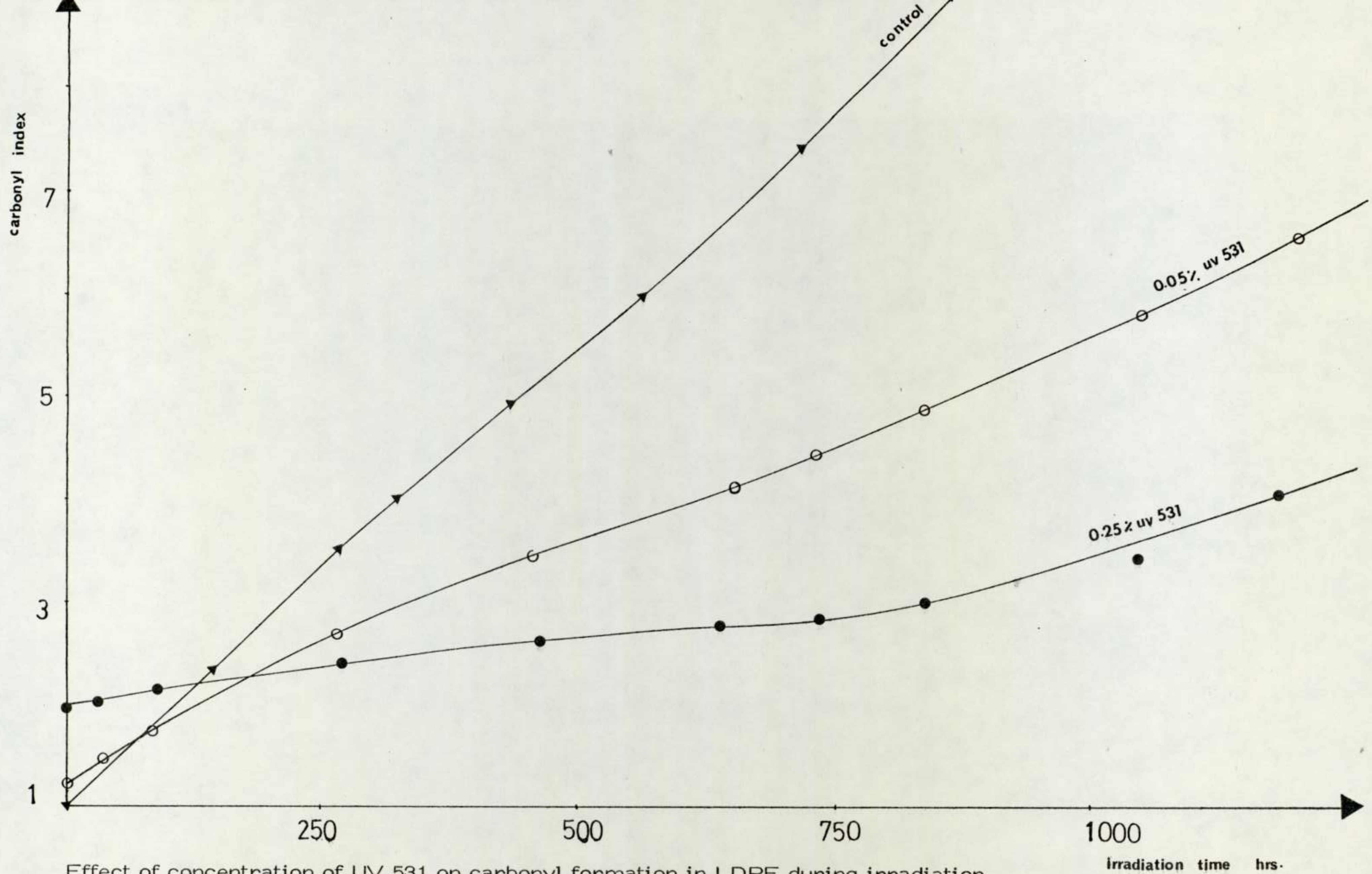
Effect of concentration of NiDBC on carbonyl formation in LDPE during UV irradiation

Fig, 27



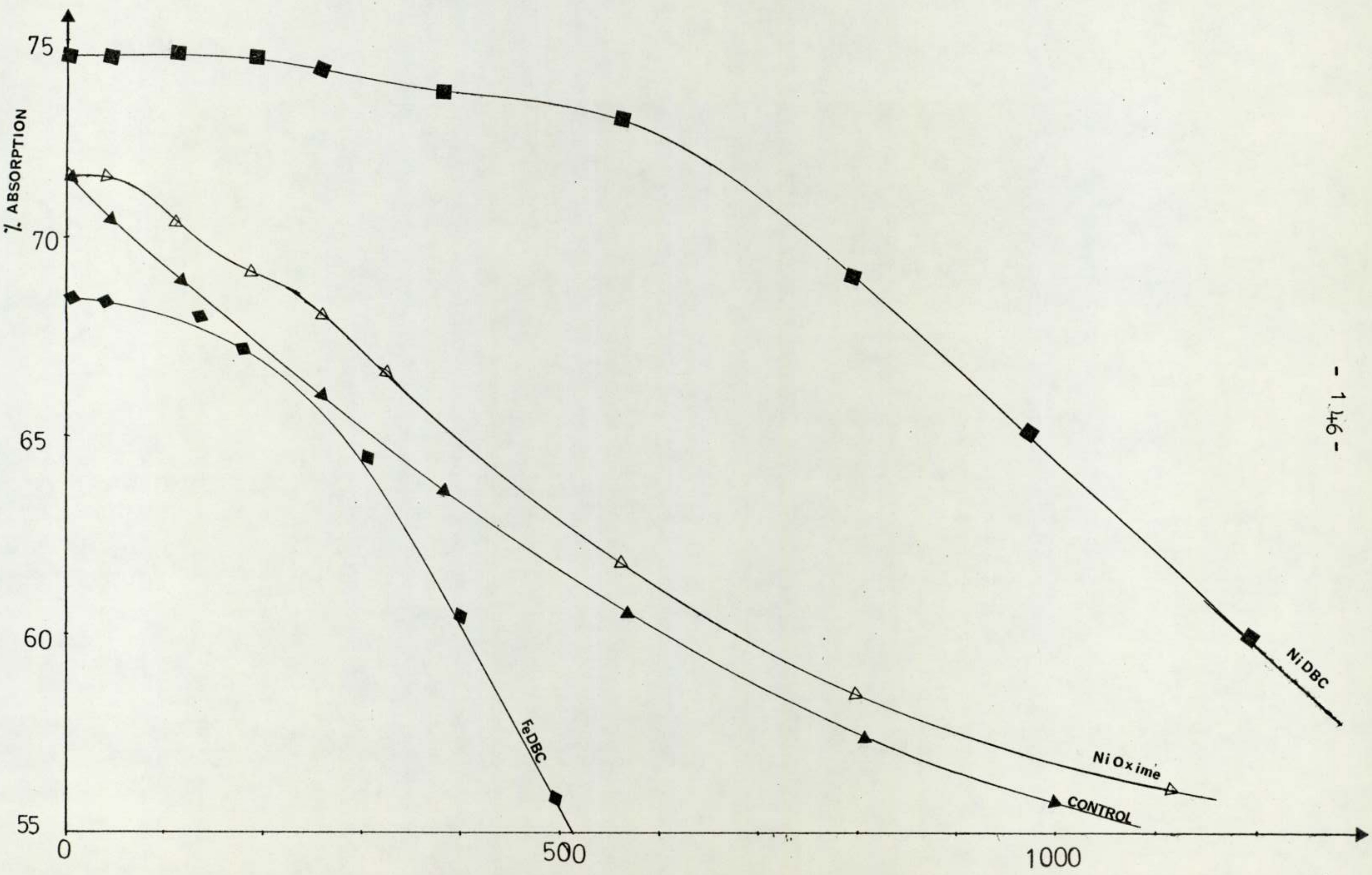
Effect of concentration of FeAcAc on vinyl formation in LDPE during irradiation

Fig. 28



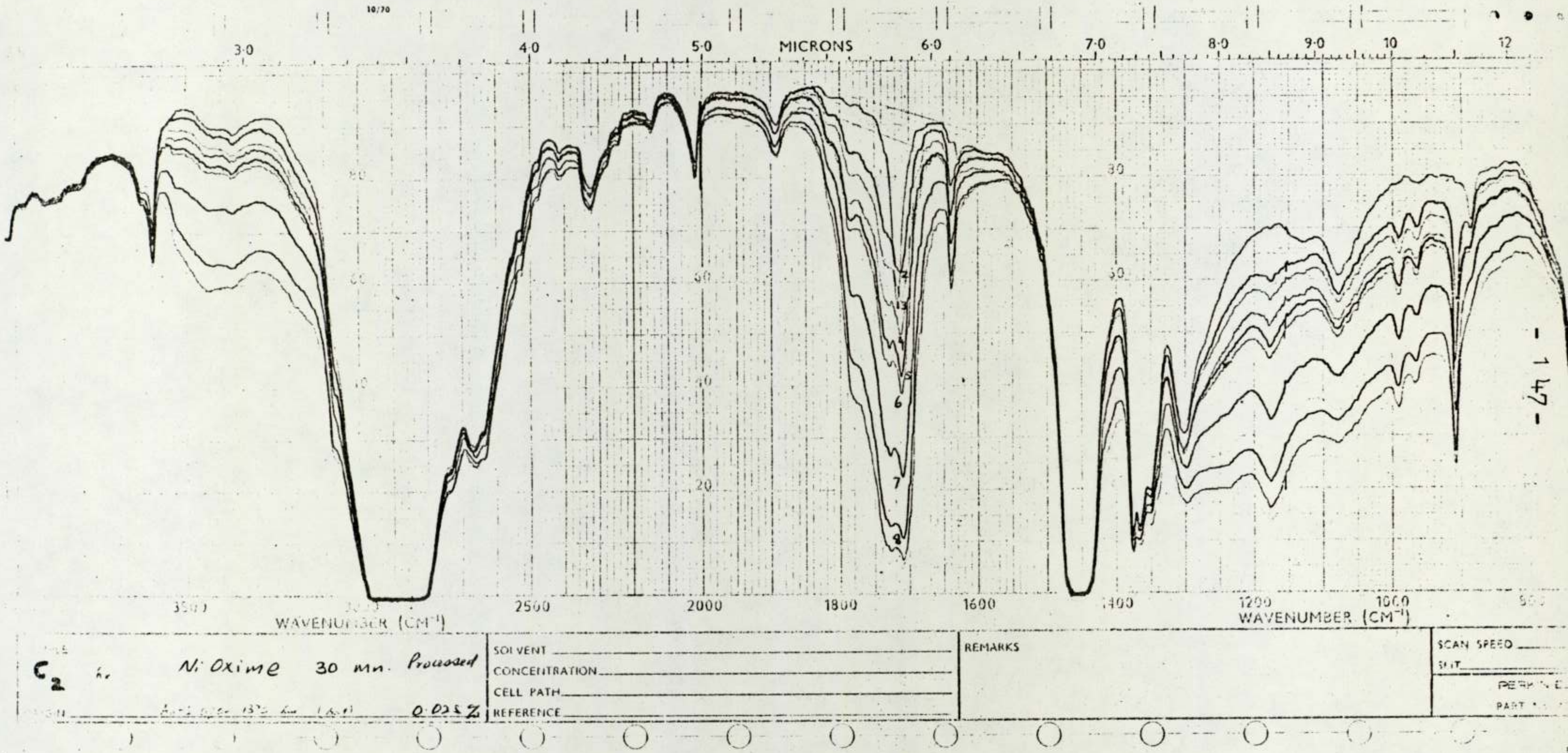
Effect of concentration of UV 531 on carbonyl formation in LDPE during irradiation

Fig. 29.



Effect of various metal chelates on vinylidene band intensity in LDPE during UV irradiation

Fig. 30

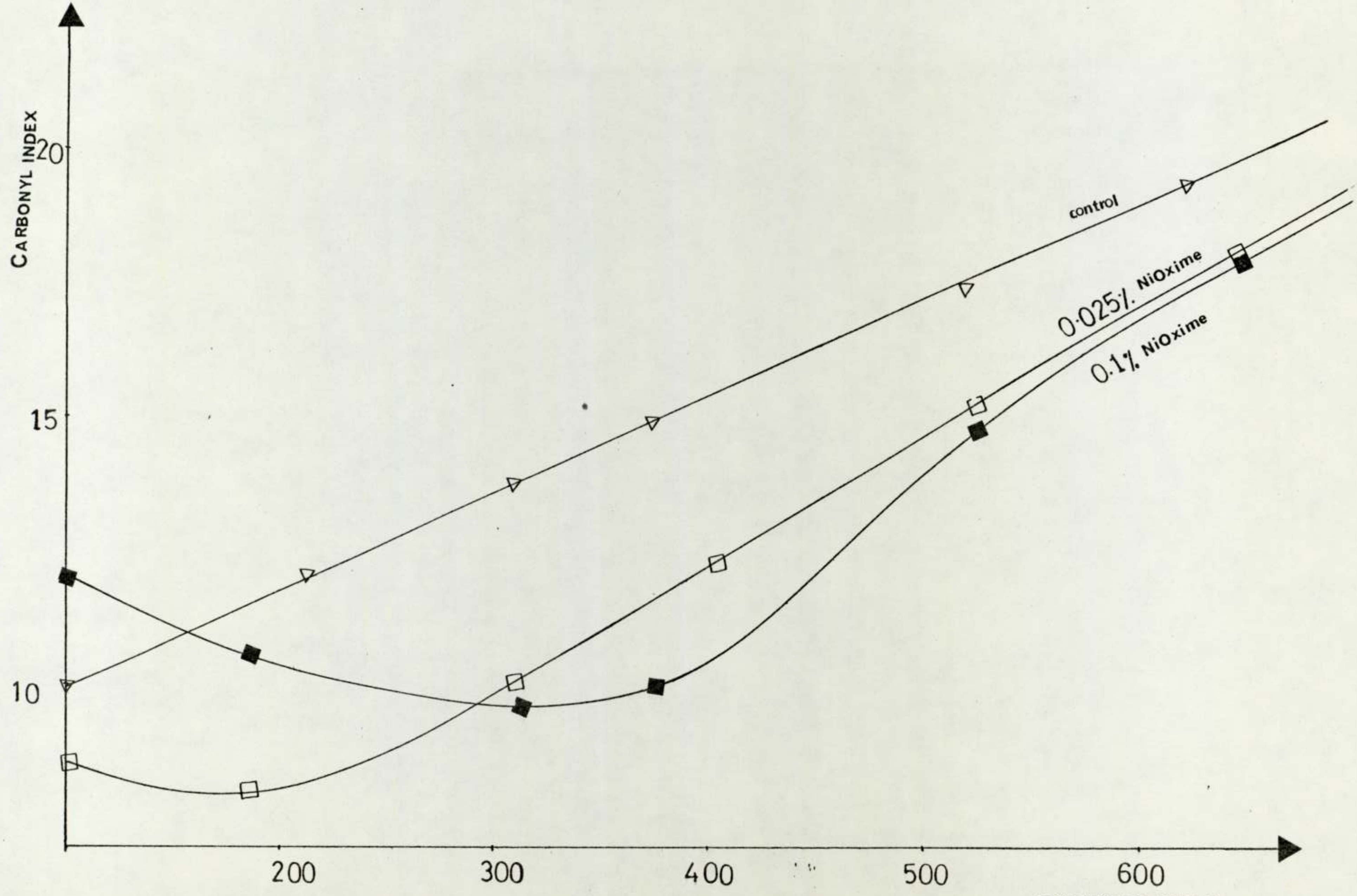


VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.025% NiOxime

Spectrum 11

Exposure times
1. 0 hrs
2. 50
3. 100
4. 150
5. 200
6. 250



Effect of concentration of Nioxime on carbonyl formation in LDPE during UV irradiation

Fig. 31

Where M denotes the unsaturated monomer, RH. Compounds which retard the oxidation of the olefin are known as antioxidants. Compounds which protect the polymers from photoxidation caused by UV radiation are known as UV stabilisers.

Activity of UV stabilisers have been explained by three mechanisms:

1. Screening of UV light
2. Quenching of photochemically excited states
3. Decomposition of hydroperoxides

The first is well established in the case of 2-hydroxybenzophenones and 2-hydroxybenzotriazoles. But most of the arguments for the second and third mechanisms are based on inference rather than direct observation. For example it is known that many nickel complexes are efficient UV stabilisers in polyolefins and are effective in quenching carbonyl triplet states or oxygen singlet states which can be formed from them by energy transfer to oxygen triplet. However, there is a lack of correlation between quenching ability and UV stabilising effectiveness. For example ferric acetylacetonate is an effective quenching agent for triplet carbonyl and yet is a photo-activator for polyolefin photodegradation.

The mechanism of the action of hydroperoxide decomposers can be explained by the following equation.

If A stands for the hydroperoxide decomposer:

$$\text{ROOH} + \text{A} \longrightarrow \text{Inactive products which do not split into radicals}$$

Compounds like triphenyl phosphite, sulphur dioxide and some of the metal complexes like NiDBC behave in this manner. The activity of triphenyl phosphite and sulphur dioxide on hydroperoxides have been studied in detail in chapter 3. This chapter deals with the activity of NiDBC and many other metal complexes on the photodegradation of polyolefins.

The activity of radical deactivators or scavengers in their role of stabilising polyolefins from photodegradation can be explained as follows:

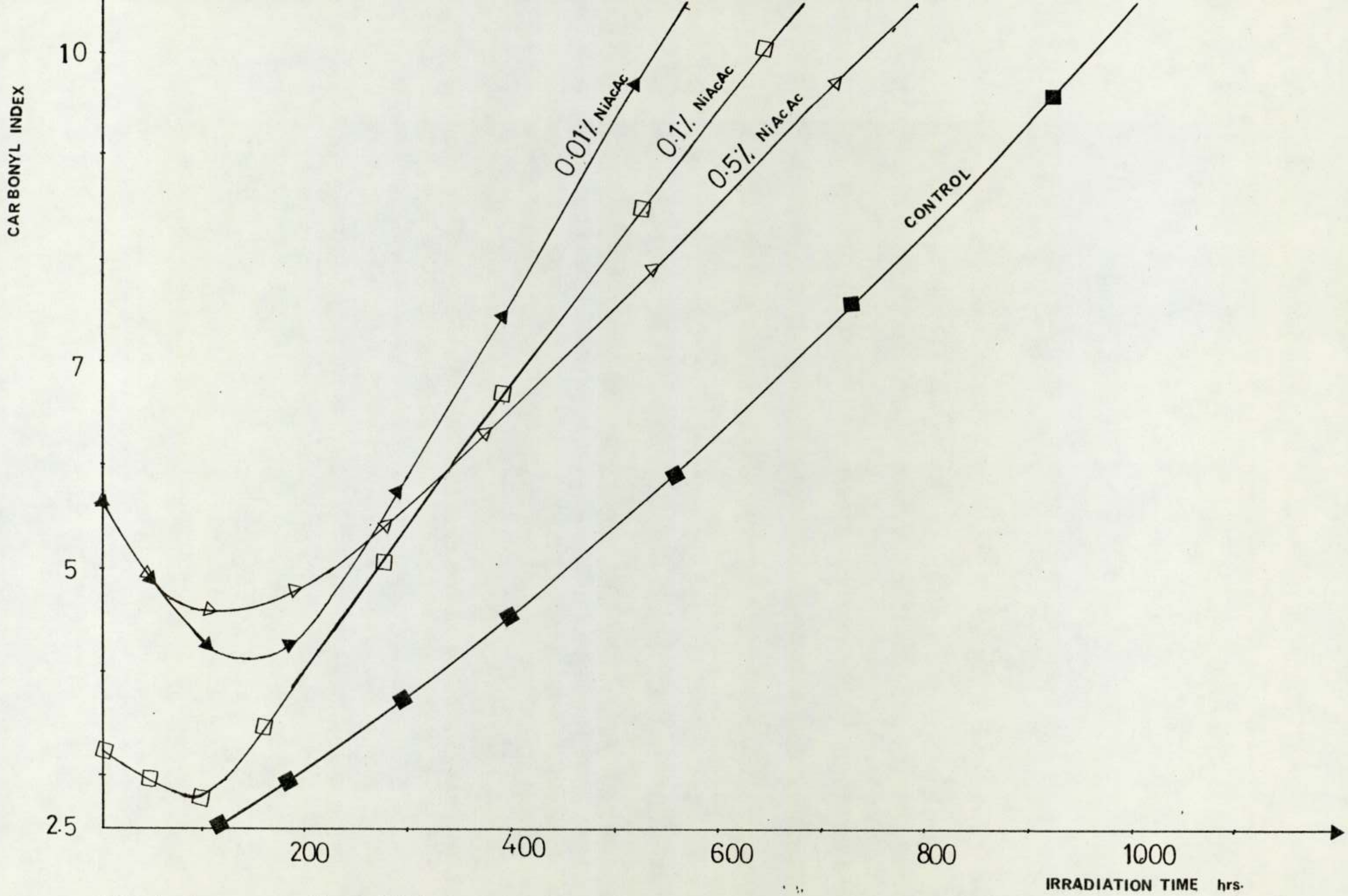
$$\text{RO}_2^{\bullet} + {}^{\bullet}\text{IH} \longrightarrow \text{ROOH} + \text{I}^{\bullet}$$
$$\text{RO}_2^{\bullet} + \text{A} \longrightarrow \text{ROA} \longrightarrow \text{Inactive products}$$

Formation of inactive products or inert radicals prevent the propagation of the chain reaction.

5.2.1 Activity of metal ions on hydroperoxides

In metal catalysed oxidations metal catalysts can react with hydroperoxides during autoxidation.

$$\text{RO}_2\text{H} + \text{Me}^{n+} \longrightarrow \text{RO}^{\bullet} + \text{Me}^{(n+1)+} + \text{OH}^- \quad \text{— (a)}$$
$$\text{RO}_2\text{H} + \text{Me}^{(n+1)+} \longrightarrow \text{RO}_2^{\bullet} + \text{Me}^{n+} + \text{H}^+ \quad \text{— (b)}$$
$$\overline{\text{RO}_2\text{H} + \text{Me}^{n+} \longrightarrow \text{RO}^{\bullet} + \text{RO}_2^{\bullet} + \text{H}_2\text{O} + \text{Me}^{n+}}$$



Effect of concentration of NiAcAc on carbonyl formation in LDPE during UV irradiation

Fig.32

The products formed in the above equations are exactly the same as those obtained in bimolecular decomposition of hydroperoxide and metal acts as a catalyst in promoting this decomposition. The metal reversibly changes to higher and lower oxidation states. This first reaction (a) or the second (b) or both, will preferentially occur depending mainly on the type of metal catalyst used.

Other reactions of metal catalysts during autoxidation include those with oxygen substrate and with oxy radicals.

In the above experiments some metal ions were found to be more active than other metal ions or complexes. Similar observations have been made by earlier workers in oxidation of cis-polyisoprene rubbers and they have shown than even the same metal in two different oxidation states such as cobalt (II) and cobalt (III) show this type of behaviour.[119] This may be due to the difference in rates of reaction (a) and (b) with the two different oxidation states of the metal ions and the overall rate of production of radicals in the presence of one ion may be different from the rate of production of radicals in the presence of the ion of different oxidation state.

In most of these cases the faster rate of oxidation in the presence of the complex with metal ion in the lower oxidation state may be due to the production of radicals by direct attack of the metal ion in its lower oxidation state on the substrate[89,119].

The change in colour of most of the films in the presence of cobaltous and ferrous salts after exposure to UV for some time may be due to the conversion of the metal ion from one oxidation state to the other (mainly from lower to higher oxidation state).

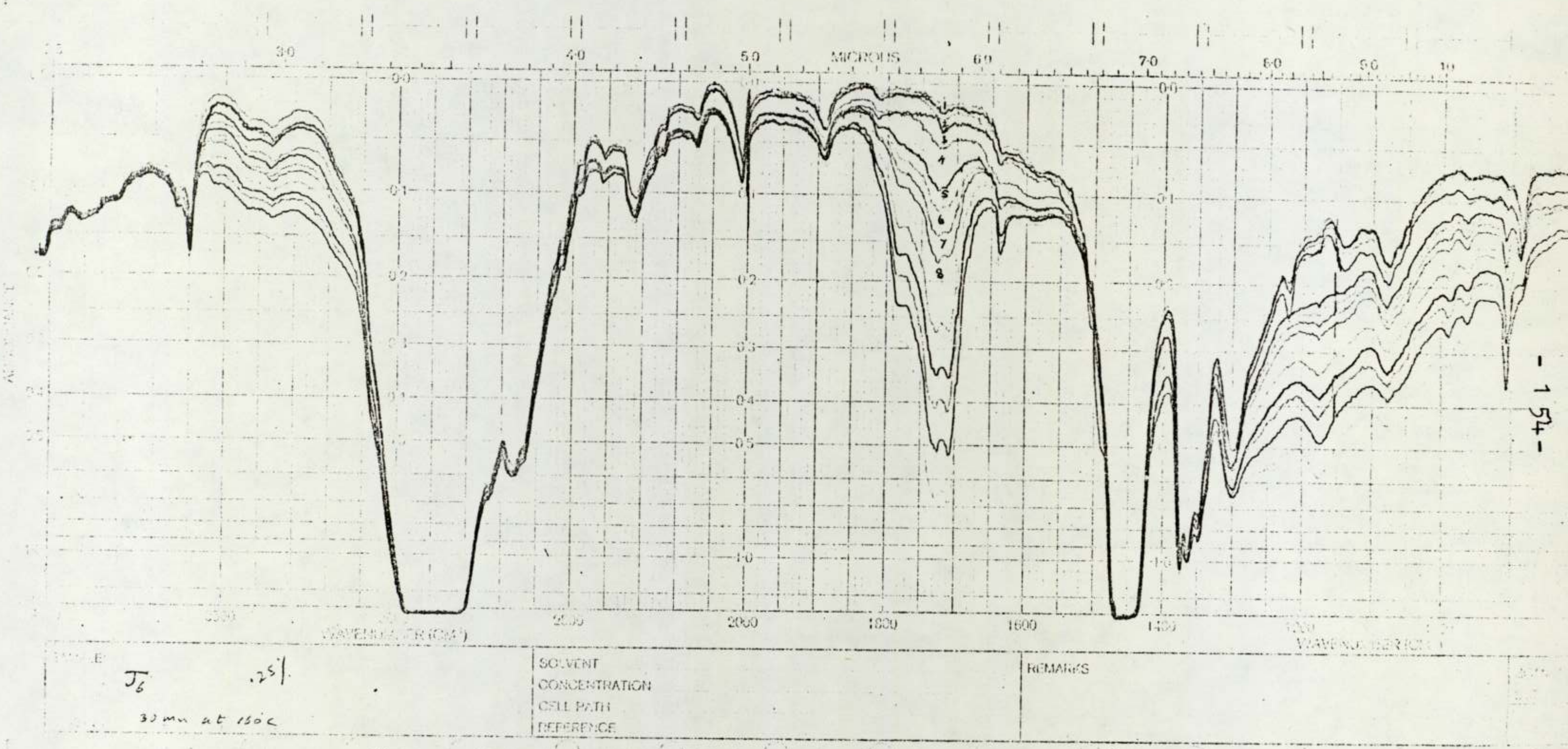
Results obtained in these experiments with some metal complexes when present in varying concentrations show that higher concentrations are in fact less active than lower concentrations. This may be due to the fact that the concentration optimum of the catalysts were low and that the concentrations used in the experiments were higher than the concentration optimum.

Ingold[89] has investigated that the antioxidant activity of cobalt ions above a certain concentration can inhibit the oxidation completely. Reduction of alkyl peroxy radicals to the corresponding anion has been suggested.

$$ROO^{\cdot} + Co^{2+} \longrightarrow ROO^{-} + Co^{3+}$$

Another reaction suggested was that of interaction of alkyl peroxy radical with the metal. Thus some of the metal ions react with peroxy radicals as follows.

$$MA_2 + RO_2^{\cdot} \longrightarrow RO_2 - MA_2$$

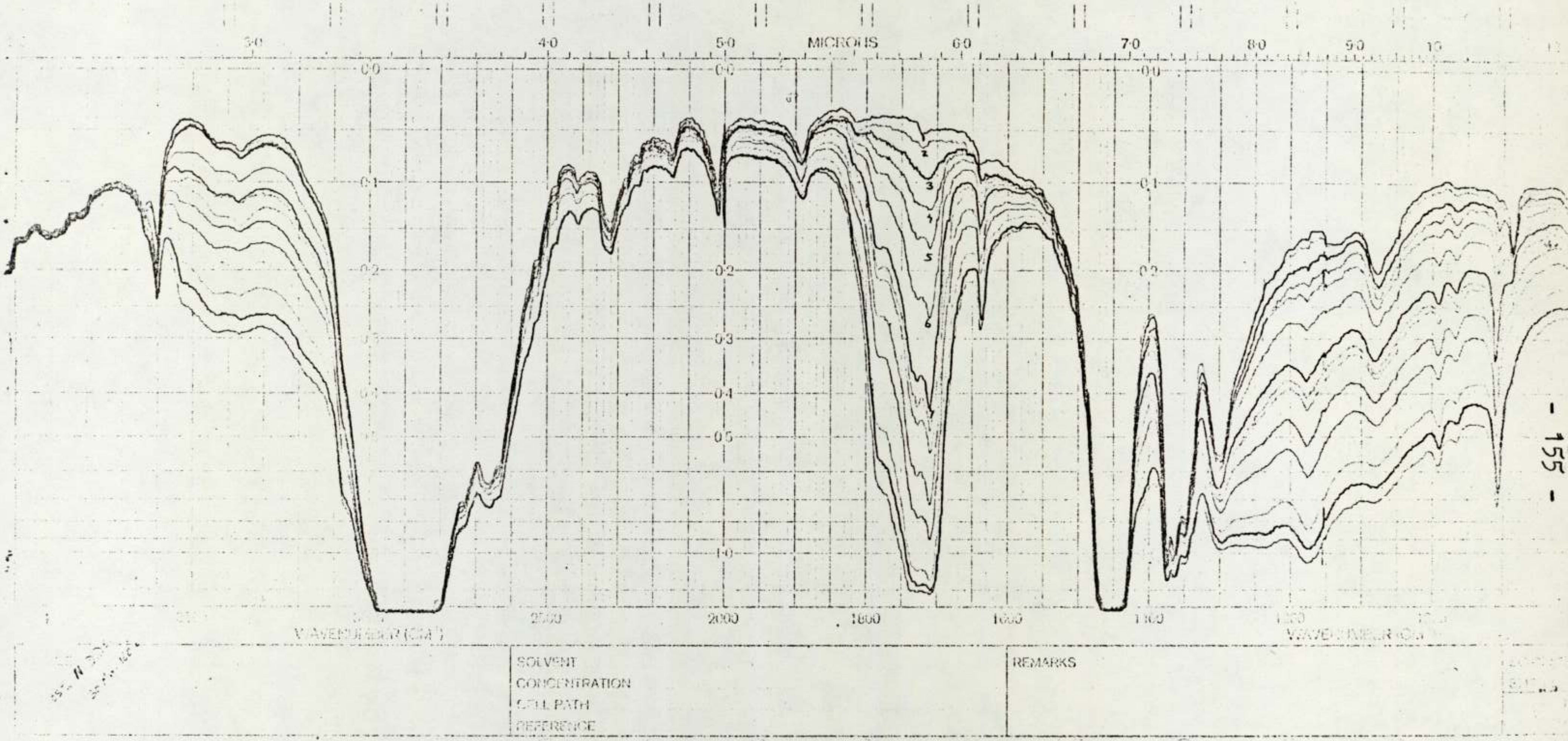


VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.25% NiDBC

Spectrum 12

Exposure times
1. 0 hrs
2. 50
3. 100
4. 150
5. 200
6. 250
7. 300

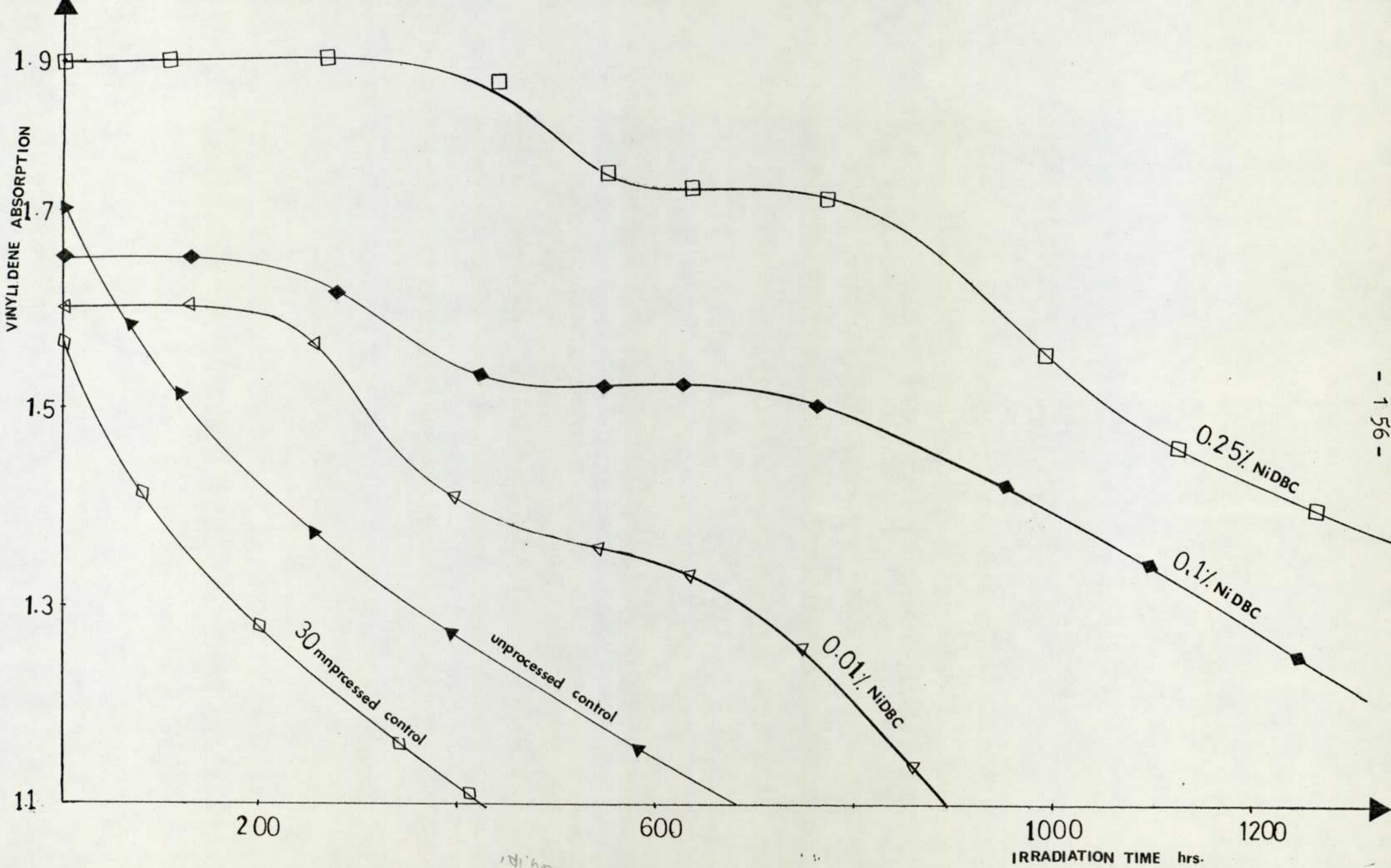


VARIATION OF CARBONYL BAND INTENSITY WITH IRRADIATION TIME

FOR LDPE CONTAINING 0.05% NiDBC

Spectrum 13

Exposure times
1. 0 hrs
2. 50
3. 100
4. 150
5. 200
6. 250



idene

Effect of concentration of NiDBC on vinyl disappearehce in LDPE during UV irradiation

Fig. 33

Such reactions may be responsible for the lower activity of metal catalyst, when higher concentrations were used. This reaction may be responsible for the loss of activity observed as the reaction proceeded. The loss of activity of the metals during the reaction may be due to the less active or insoluble complexes formed with the oxidation products. This type of inactive compounds formation may be the reason for the steps obtained in the vinyl band intensity Vs. irradiation time cure (Fig. 33) for LDPE incorporated with NiDBC complex. This behaviour was not seen in any other complex other than in NiDBC.

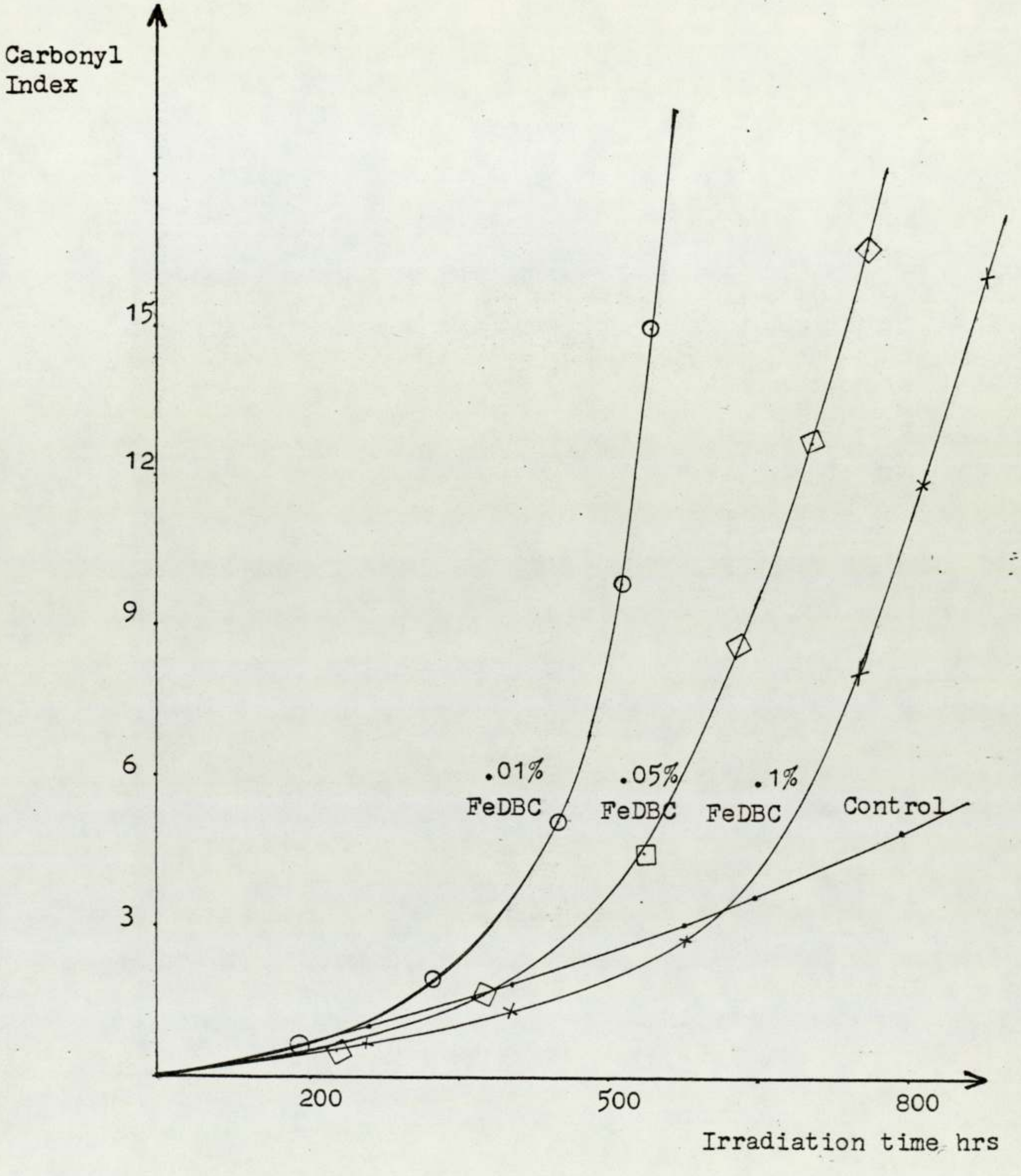
E. Boga[90] has shown that there is precipitate formation in the case of methyl cyclohexane incorporated with $Co(AcAc)_3$ exposed to UV radiation. This precipitated compound is supposed to be inactive when compared to $Co(AcAc)_3$ and he has found a sharp inflexion in the oxygen absorption curve at the point of appearance of the precipitate.

Compared to Co (II) complex the ferric complex was found to be moderately active and the oxygen absorption profile obtained (Figs. 24 and25)suggests that the interaction of metal with the hydroperoxide is the probable mode of action. When LDPE containing NiDBC was exposed to UV light some steps were seen in the vinylidene intensity Vs Irradiation time curve (fig. 33). This was not seen in the presence of any other complex. This can be due to the formation of a compound which is inactive as a photostabiliser by the action of UV light and hydroperoxide formed on the polymer on the metal complex. In this work, when this complex was dissolved in benzene containing 2% tert-butyl hydroperoxide and irradiated, a precipitate was formed and on analysis this was found to be nickel sulphate.

5.2.2 Delayed action photo activators

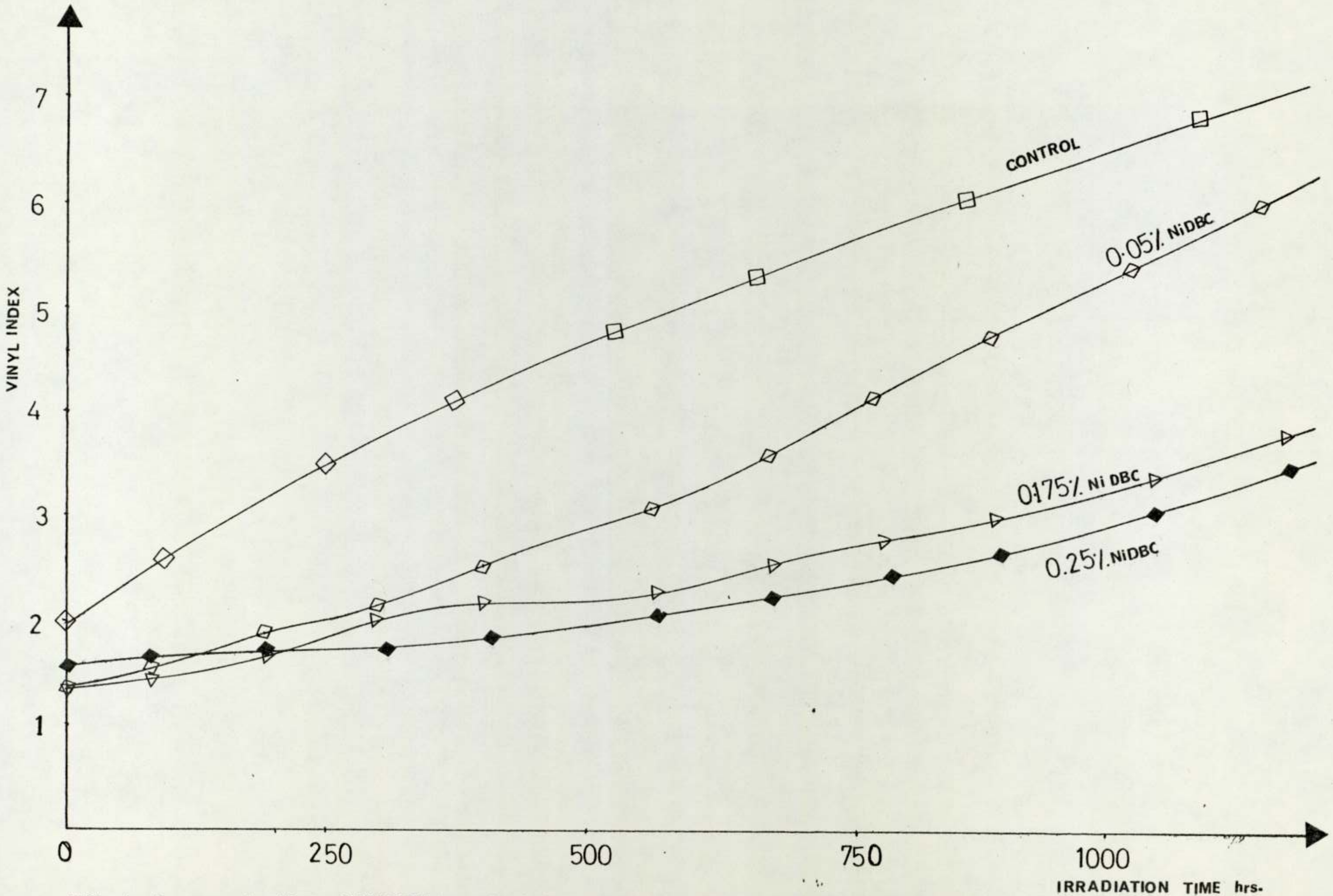
In the above paragraphs the development of antioxidants which act by catalytically destroying hydroperoxides during polymer processing and subsequent exposure to UV light was discussed. They are however, destroyed at the end of the photoxidation induction period and subsequently catalyse the photodegradation process. This type of system has considerable potential as a delayed action photoinitiator for the environmental destruction of polyethylene type plastics.

Fundamental studies of the mechanism of the antioxidant action of metal dithiocarbamates has shown that they act by generating a Lewis acid which acts as a catalyst for the destruction of hydroperoxides. At the same molar concentration, all the metal dithiocarbamates destroy hydroperoxide in a first order reaction at the same rate[62] The length of the induction period to peroxide destruction does vary, however. The products formed from cumene hydroperoxide are phenol and acetone which are diagnostic of a Lewis acid catalyzed process.



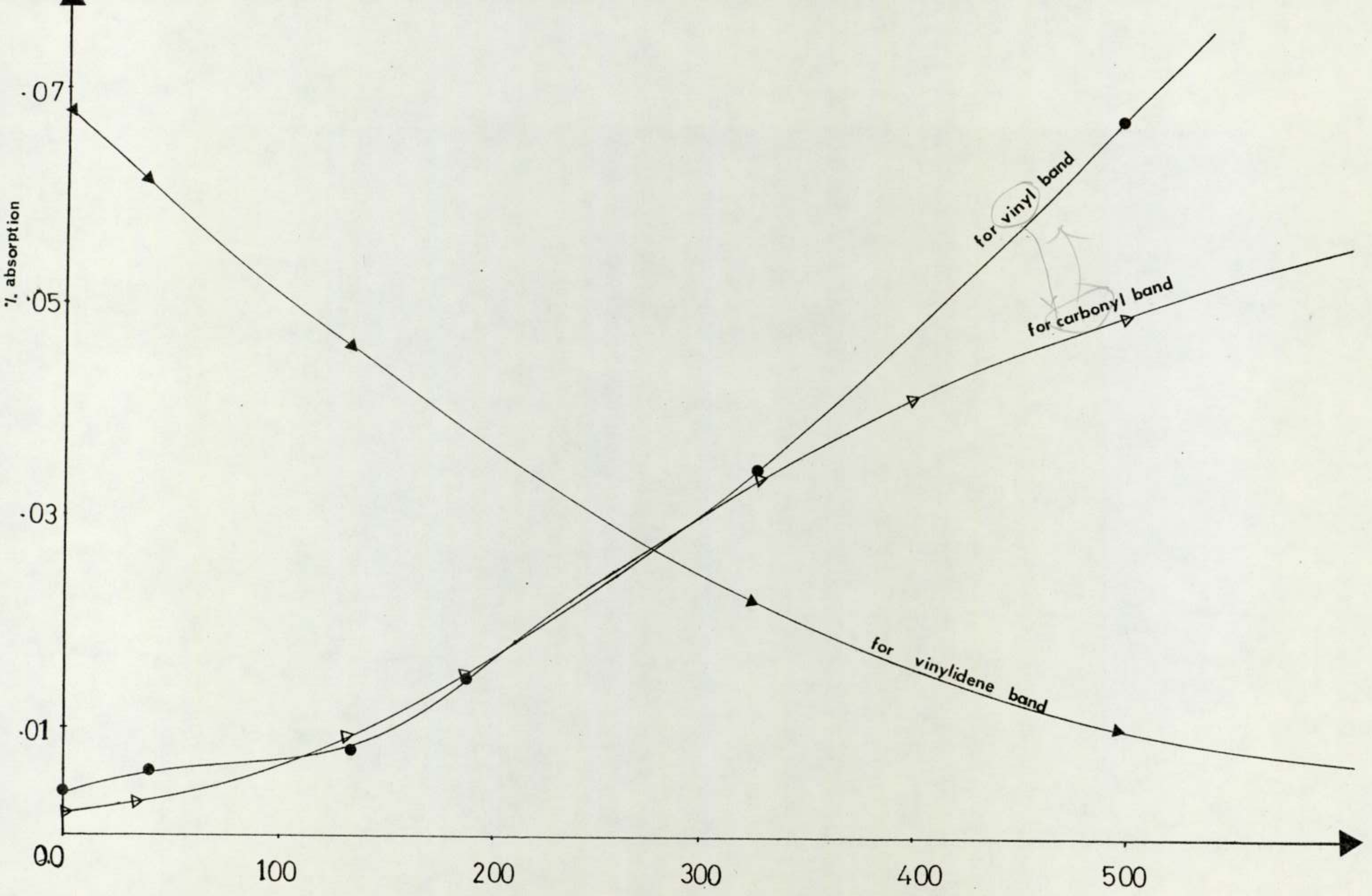
VARIATION OF CARBONYL INDEX WITH IRRADIATION TIME FOR LDPE CONTAINING DIFFERENT CONCENTRATIONS OF FeDBC

Fig. 34



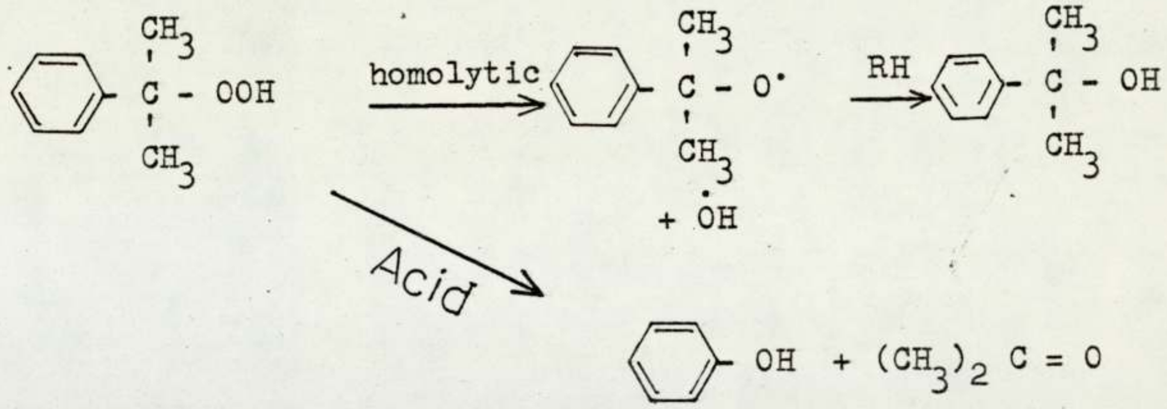
Effect of concentration of NiDBC on vinyl formation in LDPE during UV irradiation

Fig. 35

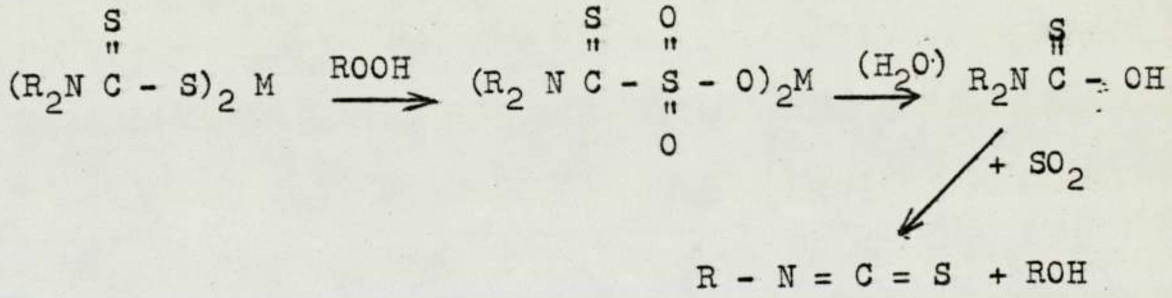


Variation of functional group intensities in LDPE incorporated with FeDBE during UV irradiation

Fig. 36



This Lewis acid in this case is believed to be SO_2 or possible SO_3 which has been shown to be formed by the oxidation of the dithiocarbamate complexes.



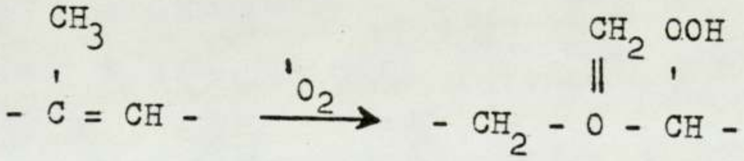
The formation of sulphur dioxide is believed to be the reason for the very powerful antioxidant activity of the dithiocarbamate complexes under processing conditions in the polymer, but unlike some other peroxide decomposing antioxidants, the dithiocarbamate also reacts rapidly with hydroperoxides at ambient temperatures. This is almost certainly the reason for the UV stabilizing activity of this class of antioxidants. But it is found that at higher concentrations ferric diethyl dithiocarbamate is an effective stabilizer. With decreasing concentration, the behaviour of this metal complex changes from that of a UV stabiliser through a delayed action UV activator (in which the rate of UV degradation during the induction period is lower than it is for the control sample), to a powerful UV activator. This unusual behaviour is characteristic of a large class of peroxide decomposing antioxidants based on sulphur and nitrogen ligands and is quite different from the energy transformers of which benzophenone and a variety of substituted benzophenones are typical. The latter are activated to the triplet (diradical) state by UV light and have the ability to hydrogen abstract from the polymer, followed by the expected radical reactions of the polymer radical so produced. In the presence of oxygen, this initiates the normal free radical chain process. As might be expected, the rate of oxidation initiated by the benzophenone triplet will be related to concentration in a different way. In fact, very much higher concentrations are required to achieve a rate of oxidation similar to that found with the metal complex activators. Moreover, instead of being auto-accelerators of oxidation, these materials in the later stages lead to autoretardation and under comparable conditions much longer times are required for embrittlement even at high concentration than are possible with the metal complexes, (Fig 34) shows that at concentration between .05% and .01% induction period is minimal. At concentrations around 0.1% quite substantial induction periods are obtained in polymers processed under industrial processing conditions. This process is proving of considerable commercial significance because as mentioned earlier, the package user requires a minimum useful lifetime in his products and this can be arranged by adjusting the concentration of the photo activator.

The delayed action system shows an initial delay time before changing autocatalytically. Scott has shown that the delayed action UV activator system is not limited to sulphur ligands only, but a ferric complex not containing sulphur acts in a parallel way to the dithiocarbamate complexes.

Delayed action activators consisting of transitional metal ion with a complexing agent to restrain the metal ion during processing are proving to be very useful because of the wide range of delay times and photodegradation rates that can be achieved.

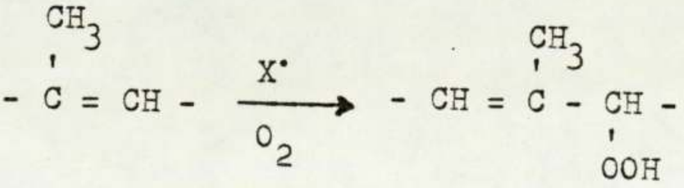
6 A. MANUFACTURE OF LIQUID RUBBER FROM SINGLET OXYGEN OXIDATION OF NR AND COMPARISON OF THE ACTIVITY OF $^1O_2$ WITH METAL COMPLEX AND PLANT PIGMENT CATALYSED OXIDATION

Singlet oxygen was used as it is very active and can attack double bonds in an unsaturated polymer, producing hydroperoxide groups unlike the case of free radical initiated oxidation, where hydroperoxide formation occurs only on the allylic methylene groups of the polymer chain[130]. Also hydroperoxide formation by singlet oxygen does not involve chain scission at the moderate temperatures used, and hence, there is no molecular breakdown, carbonyl group formation or cross linking such as occurs in the case of the free radical initiated process. Further a higher concentration of hydroperoxide may be obtained by singlet oxygen attack. Singlet oxygen oxidation of 1-methyl olefin leads to the formation of vinylidene groups(1); and hence the increase in the intensity of the vinylidene band is evidence of singlet oxygen attack[76].



$$-\overset{\overset{CH_3}{|}}{C}=CH- \xrightarrow{^1O_2} -CH_2-\overset{\overset{CH_2}{\|}}{O}-\overset{\overset{OOH}{|}}{CH}- \qquad (1)$$

This compares with reaction (2) which is a typical radical initiated reaction.



$$-\overset{\overset{CH_3}{|}}{C}=CH- \xrightarrow[O_2]{X^{\cdot}} -CH=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{OOH}{|}}{CH}- \qquad (2)$$

In 1-methyl olefins, the reaction of photochemically formed singlet oxygen should be distinguishable from the more familiar radical oxidation (2), which can be initiated by sensitizers such as benzophenone with hydrogen abstraction.

Isopropyl alcohol is a very reactive acceptor (A) for radical oxidation, according to the following reaction, but it is inert in dye-sensitized photoxidation[130]:

$$R^{\cdot} + AH \longrightarrow RH + A^{\cdot}$$

$$A^{\cdot} + O_2 \longrightarrow AO_2^{\cdot}$$

$$AO_2^{\cdot} + RH \longrightarrow R^{\cdot} + AO_2H$$

Where AO_2H is the peroxide formed, and $R^{\cdot}$ is the radical.

There are two mechanisms given for the explanation of dye sensitized photoxidation of organic compounds. The first mechanism was originally suggested by Schönberg[133] and was generally accepted until recently. In this mechanism the triplet sensitizer reacts with triplet oxygen to give a sensitizer-oxygen complex. This complex then reacts with acceptor (A) to give the product (AO_2) and regenerates the sensitizer:

$$\text{Sens} \longrightarrow {}^{'}\text{Sens}$$

$$^{'}\text{Sens} \longrightarrow {}^{3}\text{Sens}$$

$${}^{3}\text{Sens} + {}^{3}O_2 \longrightarrow \text{Sens} - O_2$$

$$\text{Sens} - O_2 + A \longrightarrow AO_2 + \text{Sens}$$

The second mechanism was originally proposed by Kautsky[124] in 1931. In this mechanism, energy is transferred from triplet sensitizer to oxygen to give excited singlet molecular oxygen. The singlet oxygen then reacts with acceptor to give the peroxide:

$$^3\text{Sens} + {}^3O_2 \longrightarrow \text{Sens} + {}^1O_2$$

$$^1O_2 + A \longrightarrow AO_2$$

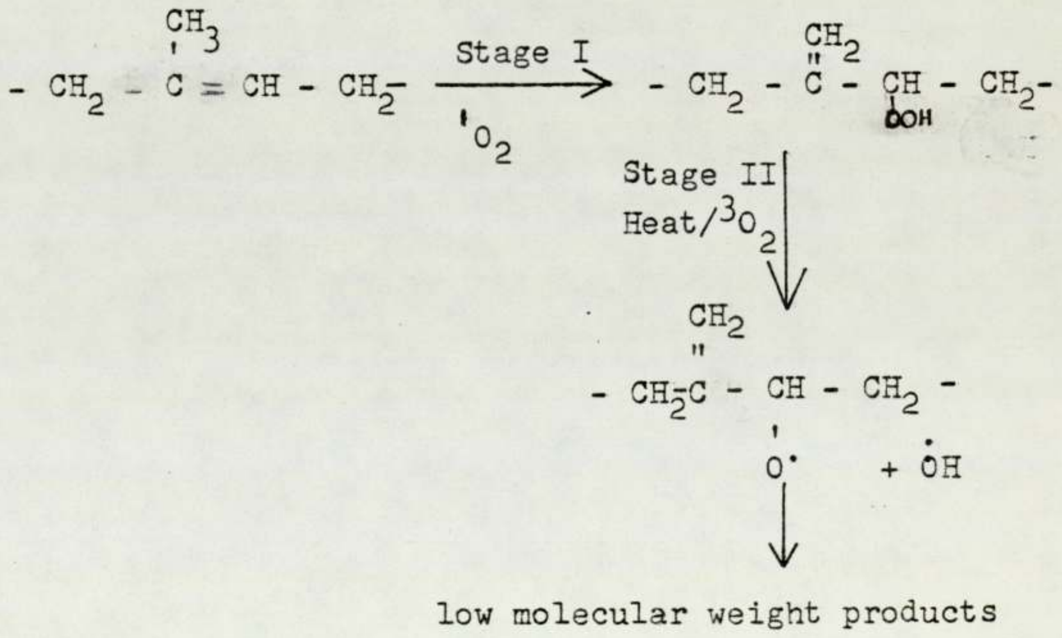
This mechanism was largely ignored although it was occasionally discussed as a possibility.

Energy transfer from triplet sensitizer to triplet oxygen, forming singlet oxygen is a spin allowed process. The lowest energy states of oxygen are shown below with the electron distribution in the highest occupied orbitals which is the degenerate[131] state. The $^1\Delta g$ state has only 22 K cal energy , above the ground state; both electrons are carried in a single orbital, leaving the other vacant. This state resembles ethylene electronically, but is more electrophylic whereas the higher singlet state ($^1\Sigma_g^+$) resembles ground-state oxygen and might be expected to undergo one electron free radical reaction. Both these states have been identified spectroscopically as products of electrode-less discharge and of the chemiluminescent reaction of sodium hypochlorite and hydrogen peroxide. The $^1\Delta g$ has been shown to have a much longer lifetime than the $^1\Sigma_g^+$, and is the major product of the hypochlorite-hydrogen peroxide reaction.

State of the O_2 molecule	Occupation of orbitals	Energy above ground
Second excited state	↑ ↓	37 K Cal.
First excited state	↑↓ —	22 K Cal.
Ground state	↑ ↑	

6A.1 Reactions of NR with singlet oxygen

It has been shown[123] that the degradation of rubber by singlet oxygen, $HOCl/H_2O_2$ occurs in two stages:



$$-CH_2-\overset{CH_3}{C}=CH-CH_2-\xrightarrow[{}^1O_2]{\text{Stage I}}-CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{OOH}{CH}-CH_2-$$

$$\xrightarrow{\text{Stage II Heat}/{}^3O_2}-CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{O^\bullet}{CH}-CH_2-\ +\ \dot{O}H\longrightarrow\text{low molecular weight products}$$

The purpose of this study is to examine the chemistry at the two stages in more detail. The rubbers obtained by singlet oxygen degradation were vulcanised at optimum cure after examination in the Monsanto

Rheometer to study the curing characteristics. Tensile properties were measured in order to determine the technological behaviour of these rubbers and to relate these to molecular weight, and functional group concentrations.

6A.2 Metal complex catalysed oxidation of elastomers

The main feature of metal ion catalysed oxidation is that the reaction is free radical initiated and the hydroperoxide formation is at the allylic position and not at the double bond as in the case of the singlet oxygen initiated process.

In metal catalysed oxidation, metal catalysts can react with hydroperoxides during autoxidation[1,119]; and the process may be schematically represented as follows:

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

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

The products formed in the above equations are exactly the same as those obtained in bimolecular decomposition of hydroperoxide and the metal acts as the catalyst in promoting the decomposition. The metal reversibly changes to higher and lower valency states.

No vinylidene formation is expected in this case, based on studies in model compounds. Chain scission with the formation of compounds are expected as concomitants of hydroperoxide formation.

In this study photo-activating metal complexes such as FeAcAc and CoAcAc were used. These metal complexes in their role as photo-activators are known to be unstable in UV light and hence breakdown[79,49] to give free radicals which initiate the photo-degradation process as explained above.

The solubility of these rubbers oxidised by means of metal complexes were tested in the NR solvent, turpentine, in order to determine the possibility of gel formation in the sequence of these reactions. Reactions of NR in UV radiation in the presence of the singlet oxygen generator, chlorophyll, and singlet oxygen quencher, carotene, were also studied to see whether these plant pigments have any effect in regard to their high absorb-tivity of UV radiation.

6.A.3 Experimental

6A.3.1 Oxidation of NR by singlet oxygen

Singlet oxygen was generated by the reaction of 5% of hypochlorite (NaOCl) containing 10-14 % available chlorine with H_2O_2 The hypochlorite solution was prepared by saturating a solution of 10% NaOH, cooled in ice, with chlorine gas and then diluting the resulting solution with water until the chlorine content was 10-14% when titrated with standard sodium thiosulphate solution. The latex used was pure unstabilised field latex, with 30% dry rubber content (DRC). To prevent coagulation during the reaction, the latex was stabilised by adding a solution of Vulcastab LW in water (3 g of Vulcastab LW in 46 ml of water to 100 ml of field latex).

The mixture of dilute latex and sodium hypochlorite was cooled to 0°C, with ice in a flask and more sodium hypochlorite was added. Hydrogen peroxide solution was added dropwise from a burette below the surface of the latex/sodium hypochlorite mixture, while stirring it vigorously so that the singlet oxygen, as it was formed, was rapidly dissseminated through the solution. The mixture was stirred for five hours at 0°C, after the addition of the hydrogen peroxide, because Foote[120] et al. have shown that singlet oxygen is unstable at 30°C whereas it is stable between -50°C and 0°C. The measurement of hydroperoxide concentration after the reaction at 0°C (Stage I) was extremely difficult, since the solution was turbid, a part of the unconverted H_2O_2 remained trapped in the coagulum during the titration, and the hydroperoxide concentrations present were extremely low. At the end of 5 min the temperature was raised to 80°C and another three 5 ml portions of H_2O_2 were added at intervals of ½ h to allow the reaction to complete (stage II). The mixture was stirred for another 1h and a 100 ml portion of the latex was taken and coagulated with acetone. The coagulum was then washed with water, followed by acetone, and dried in a vacuum desiccator. The amounts of hydrogen peroxide and sodium hypochlorite used were varied for different runs while the temperature and the time were kept constant. Hydroperoxide contents of the final rubber were determined by iodometric titrations.

6A 3.2 Molecular weight determination by viscometry

After coagulation and drying, the samples of rubber treated with singlet oxygen were dissolved in toluene. The concentration of rubber in the solutions was not allowed to exceed 2% by weight. Anhydrous magnesium carbonate was added to absorb moisture from these solutions and then the solutions appeared transparent and clear. Aliquots were taken from each of these solutions and their viscosities determined at three different temperatures, using the Ubbelohde dilution viscometer.

6A 3.3. IR spectroscopic analysis of the rubber samples exposed to UV light and singlet oxygen

Small quantites of the rubber treated with singlet oxygen or exposed to UV light were dissolved in carbon tetrachloride. To remove the cloudiness of the solution, which was due to moisture, a little anhydrous sodium sulphate was added and the solution allowed to settle for some time. The clear solution thus obtained, containing not more than 2% of rubber by weight, was then scanned in the infrared spectrometer, using sodium chloride cells. This experiment was repeated for rubber samples containing varying amounts of hydroperoxides after singlet oxygen treatment and also for samples exposed to UV light for different lengths of time. A similar experiment was carried out for a liquid rubber sample, prepared in the same way, which contained a higher concentration of hydroperoxide and was kept under vacuum for 24 hours.

6A 3.4 Activity of metal activators and plant pigments on the photo degradation of NR

The action of the metal activators FeAcAc, and CoAcAc, the stabiliser NiDBC, and also carotene and chlorophyll contaminated with other Plant Pigments on the photo degradation of NR was studied as follows:

Pale crepe IX rubber, which is the purest and whitest available form of natural rubber, and therefore would offer less resistance to the penetration of sunlight than any other form of NR was used. Samples of this material were impregnated with 0.01%, 0.05% and 0.25% by weight of the above named complexes, by mixing in an open mill for 2 min until a homogeneous colour was obtained and then sheeted out into films 0.5mm thick. These sheets were placed flat on plane glass plates and exposed to sunlight for varying periods of time, ranging from 1h to 8h until the final product was soft and plastic. The compressibility, or the initial plasticity, of these rubber samples was determined by means of a Wallace Rapid Plastimeter, which gives a measure of the molecular weight of the material. As the molecular weight drops following oxidation, the rubber becomes softer and consequently the initial Wallace Plasticity number (P_o) drops.

The Wallace Rapid Plastimeter provides an accurate method of measuring the oxidisability of materials like rubber. The determination of the Plasticity Retention Index (PRI) by means of this instrument consists of two steps:

1. Determination of the initial Wallace Plasticity number (P_o) which shows the compressibility of a sample 1 mm thick before heating, and
2. Determination of the plasticity number (P_{30}) after rapid ageing, which is the compressibility, determined in the same way, for a sample of rubber heated for 30 min. at 140°C, in air.

For uncompounded raw rubber $P_{30} < P_o$. Then the plasticity retention index is given by the ratio

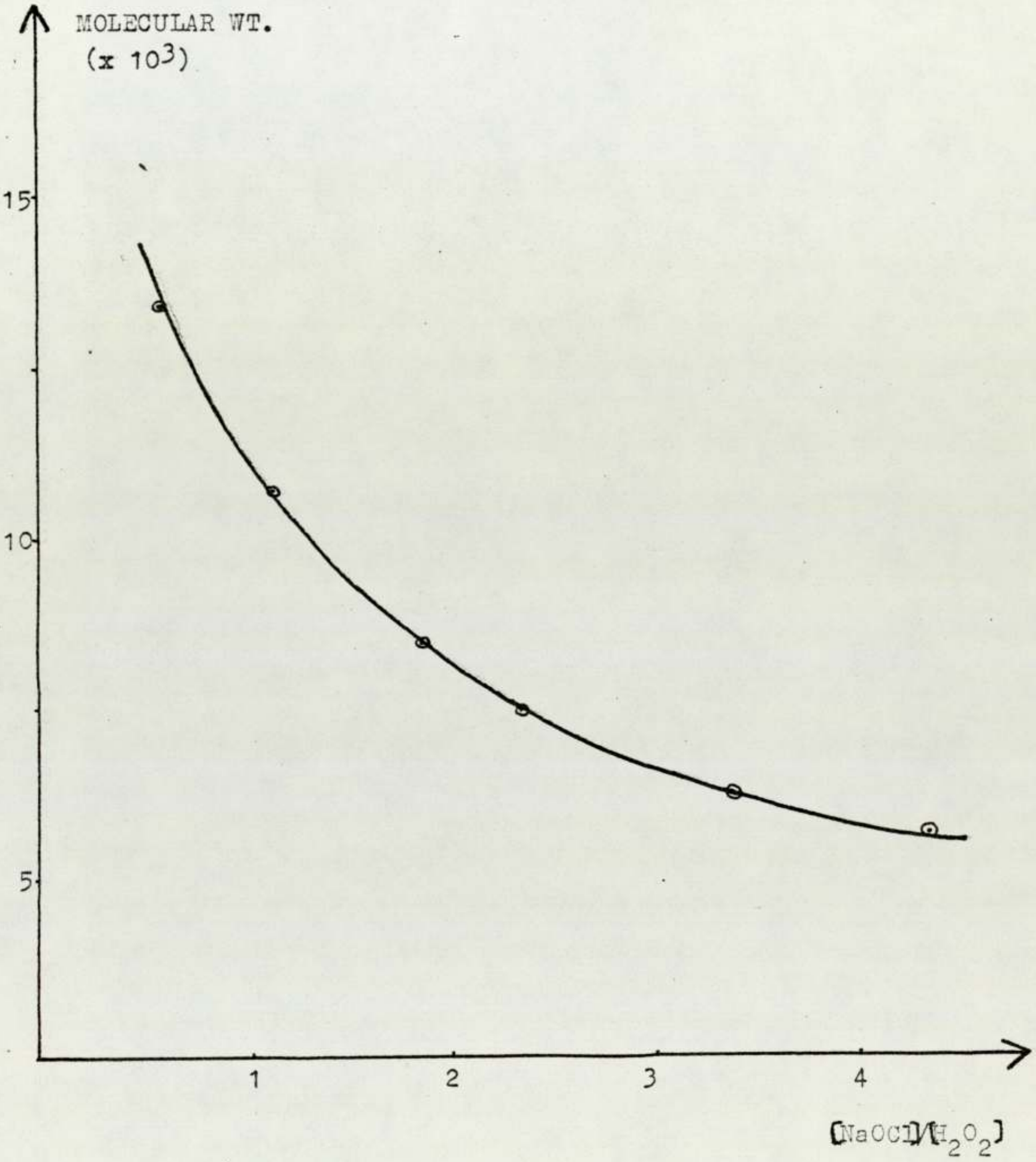
$$\frac{P_{30}}{P_o} \times 100$$

This method of assessing photo degradation was found to be more suitable than any other for crepe rubber subjected to UV treatment. It was not applicable to rubber oxidised by $NaOCl/H_2O_2$ treatment as the rubber took more than 5 days to dry, due to emulsion formation in all cases, and during this period it was impossible to prevent contact with oxygen. The emulsion was formed because this reaction was carried out in an aqueous phase.

6A 4. Results and Discussion

The product obtained by the $NaOCl/H_2O_2$ method was much softer than that obtained by any other method. When the hydrogen peroxide content was kept constant and the volume of NaOCl was increased; for systems where more than 20 ml of NaOCl was used for oxidation, an almost viscid product was produced. At this stage, further PRI determination was impossible as the product was too soft. It was also observed that coagulation and drying of the viscid product is difficult and hence no viscosity measurements could be carried out on these samples. The flow rate of each of the less oxidised samples at the end of stage 2 of the reaction at the same predetermined hydrogen peroxide concentration is a measure of its viscosity (μ). The relationship of μ to the average molecular weight $\overline{M}n$ is given by the equation:

$$\mu = K'' \overline{M}n$$



RATE OF CHANGE OF MOLECULAR WEIGHT OF NR WITH [NaOCl] / [H_2O_2] RATIO

FIGURE 37

The molecular weight drops gradually as the molar ratio: $NaOCl/H_2O_2$ increased as shown in Table 7. $\bar{M}n$ for ordinary NR varies from 50,000 to 100,000.

Table 7

Variation of molecular weight $\bar{M}n$ with the amount of NaOCl used at the end of stage II of the reaction

Temperature	Molar ratio of $[NaOCl]/[H_2O_2]$ keeping $[H_2O_2]$ constant			
	0.25	0.33	0.417	0.50
35°C	5997.6	4699.0	3712.8	3226.7
40°C	5589.6	4528.8	3508.8	3063.3
45°C	5304.0	4324.8	3345.6	2907.1

Fig. 37 gives the relationship between molecular weight and the concentration of NaOCl used. It shows the rapid drop in molecular weight, as the rate of formation of singlet oxygen increases. The rapid increase of carbonyl groups in the sample of rubber treated with the highest concentration of singlet oxygen, when exposed to UV light, is shown in Fig. 38. This cannot be related to the initial hydroperoxide content on the polymer as some of the hydroperoxide was converted to carbonyl under the conditions in which the reaction was carried out. This is clear from Table (7b) where the initial hydroperoxide contents are given against the rate of initial carbonyl increase. As the final products after $^1O_2$ treatment were liquids this study could be carried out only in the solution phase, using carbon tetrachloride as the solvent. Measurement of [OOH] was extremely difficult, using the colorimetric technique, as the solution was turbid after dissolving the rubber. Hence the values obtained are given in table 7 b as approximate values. The titrimetric method for hydroperoxide measurement failed as the final colour change could not be accurately detected owing to the turbidity of the solution.

Table 7 b

Initial [OOH] g moles (approx) per g.	Initial rate of oxidation in rate of increase of carbonyl index/min
0.047	1.33
0.053	1.18
0.021	0.97

The results show that, when the concentration of H_2O_2 was about four times as high as that of NaOCl, the

CARBONYL INDEX VS IRRIDIATION TIME FOR NR
CONTAINING VARYING AMOUNTS OF (OOH)

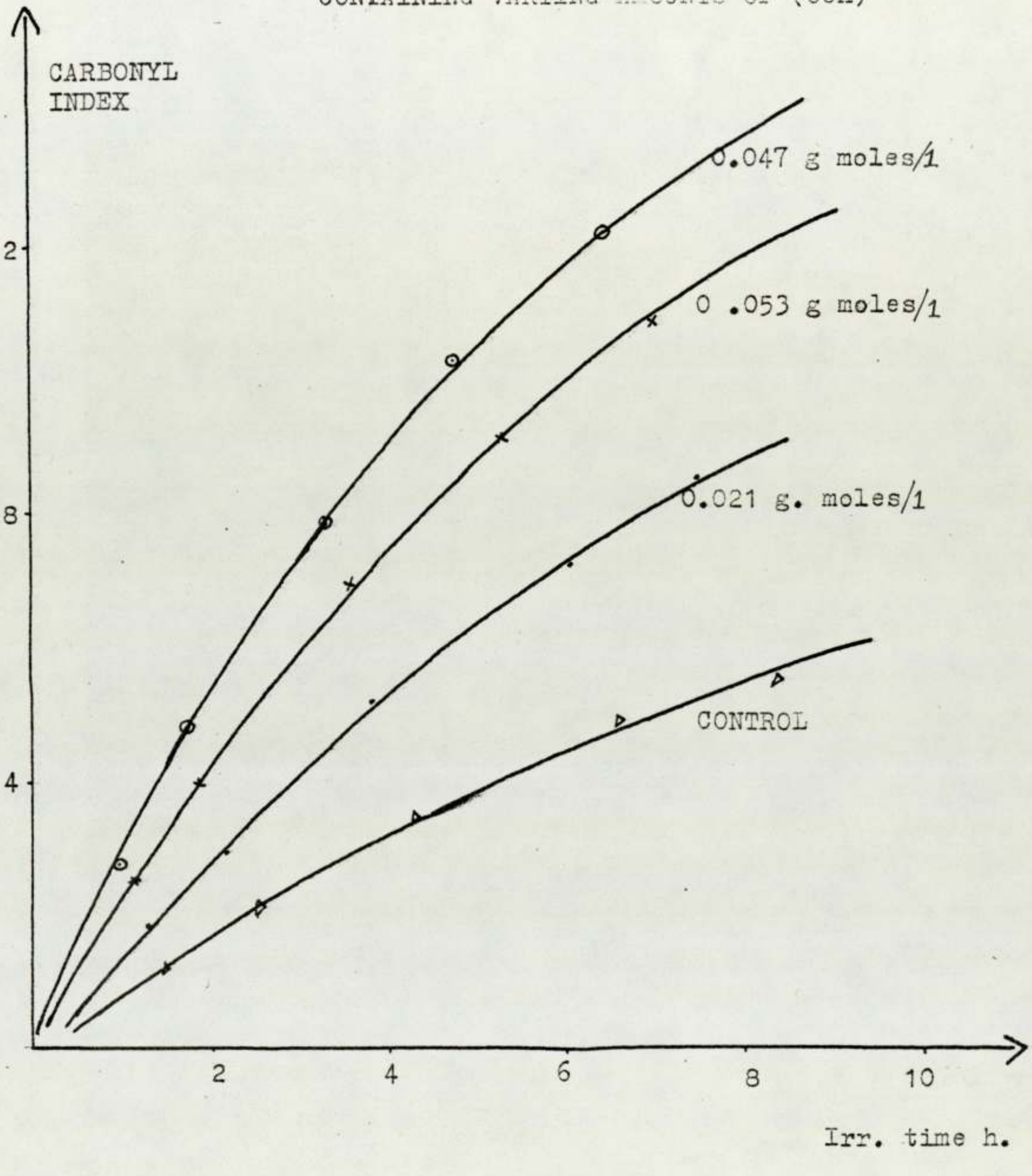
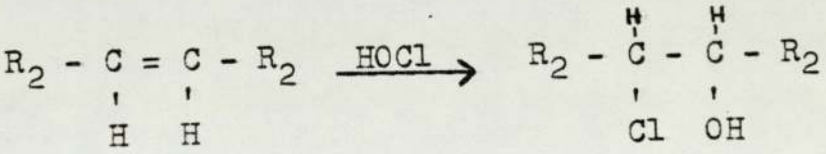


FIGURE 38

approximate rate of singlet oxygen formation was determined by the concentration of NaOCl. There was no indication of any chlorine or HCl being evolved during the reaction, except from the NaOCl solution, before it was added. This was confirmed by the NH_4OH vapour test. There was also no indication of any substituted chlorine groups in the spectra of the films after treatment.

The use of a non-ionic stabilizer prevented the coagulation of latex during the addition of sodium hypochlorite and during deammoniation prior to the reaction. The coagulation was due to the change of pH in the latex by hypochlorous acid and hydrochloric acid.

In the presence of unsaturated compounds, hypochlorous acid may add to a double bond by an ionic addition reaction.



$$R_2 - \underset{H}{C} = \underset{H}{C} - R_2 \xrightarrow{HOCl} R_2 - \overset{H}{\underset{Cl}{C}} - \overset{H}{\underset{OH}{C}} - R_2$$

High temperatures accelerate the decomposition of sodium hypochlorite and hydrogen peroxide and also promote the transition of oxygen from the singlet to the triplet state. Singlet oxygen is comparatively stable below 0°C, but the oxidation of latex could not be carried out below 0°C, as the latex solidifies due to the formation of ice. During the second stage of the experiment, when air was passed through the reaction mixture, chain scission was accelerated. In all sets of experiments the change in molecular weights recorded in Table 7 are all after completing the stage II of the reaction. To obtain a liquid rubber there should be chain scission of the high molecular weight rubber. Chain scission was observed when the sample treated with $NaOCl/H_2O_2$ was heated in the presence of air, because atmospheric oxygen causes oxidation of the polymer chain, as shown by Hernendez and Quim[122].

6A 4.1 Study of the effect of metal activators on rubber by plasticity determination

Samples of pale crepe IX rubber, when mixed with different quantities of metal complexes and exposed to sunlight became soft, forming liquid rubber. The rate of softening was fastest when the concentration of the metal complex was highest. Concentrations ranging from 0.1 to 0.25% by weight of crepe rubber were used in the study of the complexes: ferric acetylacetonate, nickel dibutyldithiocarbamate and cobalt acetylacetonate. The rate of decrease in initial Wallace Plasticity number (P_o) which measures the compressibility of the rubber sample at 100°C indicated the rate at which the breakdown of the rubber molecules took place in the presence of sunlight.

P_o Vs IRRADIATION TIME FOR NR CONTAINING METAL COMPLEXES

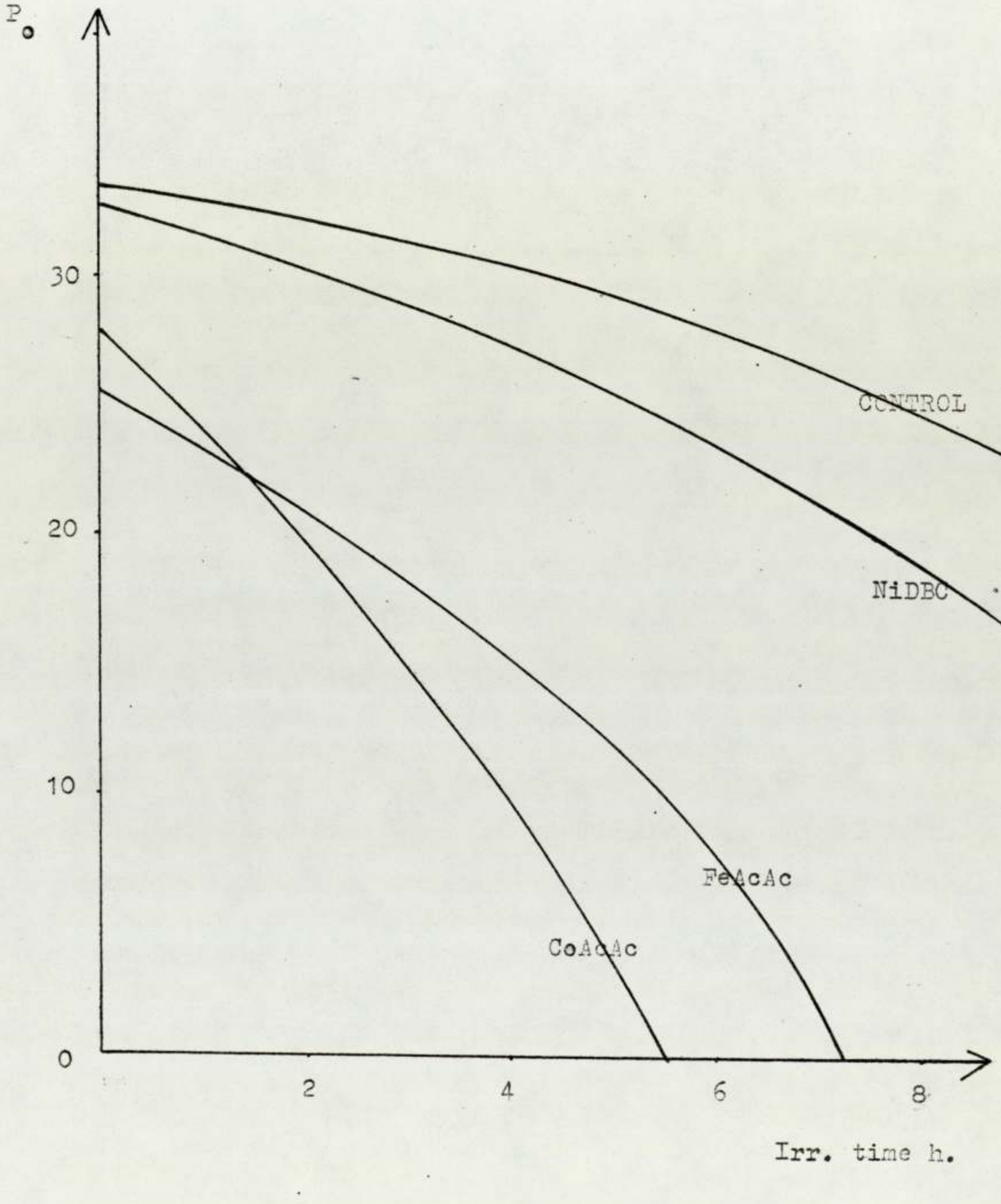


FIGURE 39

Fig. 39, showing the variation of initial plasticity number with irradiation for these systems, indicates that the cobalt complex is most active for rubber too, as had already been observed for LDPE. The order of their activity is again Co > Fe > Ni. As rubber is a long chain hydrocarbon like polyethylene, the mechanism of the activity of the metal complexes is the same as that for polyethylene degradation in the presence of metal chelates, except for NiDBC which has already been discussed in an earlier Chapter. In rubber, NiDBC acts as a photoactivator as shown in Fig. 39, whereas it is a well known photostabiliser for LDPE. When the concentration of the metal chelate is 0.25% the rubber samples became viscid after about 6 hours exposure to sunlight and hence plasticity determinations were impossible beyond this point (Fig. 39). IR spectroscopic studies of these liquid rubber samples in carbon tetrachloride show the increase in the intensity of the carbonyl band with irradiation time, thus confirming the mechanism suggested for the breakdown of LDPE in the presence of these activators. Unlike in the case of LDPE, the nickel dithiocarbamate complex in this experiment did not show any stabilising effect. This may be due to the fact that the Ni complex in rubber is unstable and undergoes fragmentation to give metal ions and the metal ions then react with the hydroperoxides to give free radicals, causing the photolytic degradation as in the case of other metal complexes, by the mechanism given below:

$$RO_2H \quad + \quad M^{n+} \longrightarrow RO^{\bullet} + Me^{(n+1)+} + OH^{-}$$

$$RO_2H \quad + Me^{(n+1)+} \longrightarrow RO_2^{\bullet} + Me^{n+} \quad + H^{+}$$

The hydroperoxide ROOH thus obtained undergoes photolysis causing the degradation of the molecule[49,90] and acts as a pro-oxidant. It is also a well known fact that the dithiocarbamates of Ni are good hydroperoxide decomposers. But if the hydroperoxide decomposing effect in this case is not as powerful as the photolytic effect of light on the complex it leads to a pro-oxidant effect.

The mechanism given above indicates that the metal ion is undergoing reversible redox reaction. These redox reactions of metals are almost always associated with colour changes. This may be the reason for the colour changes that have been observed, when these rubber films, incorporated with metal ions, undergo irradiation in sunlight.

The effect of these metal complexes during thermal oxidation was studied by heating samples of NR containing 0.25 % of each of these complexes and nitrobenzene, in an oven at 100°C. There was no marked difference in the case of any of these metal complex incorporated samples compared to UV irradiation. Only the sample containing FeAcAc became soft faster, than

P_o VS TIME OF AGEING FOR NR CONTAINING ADDITIVES

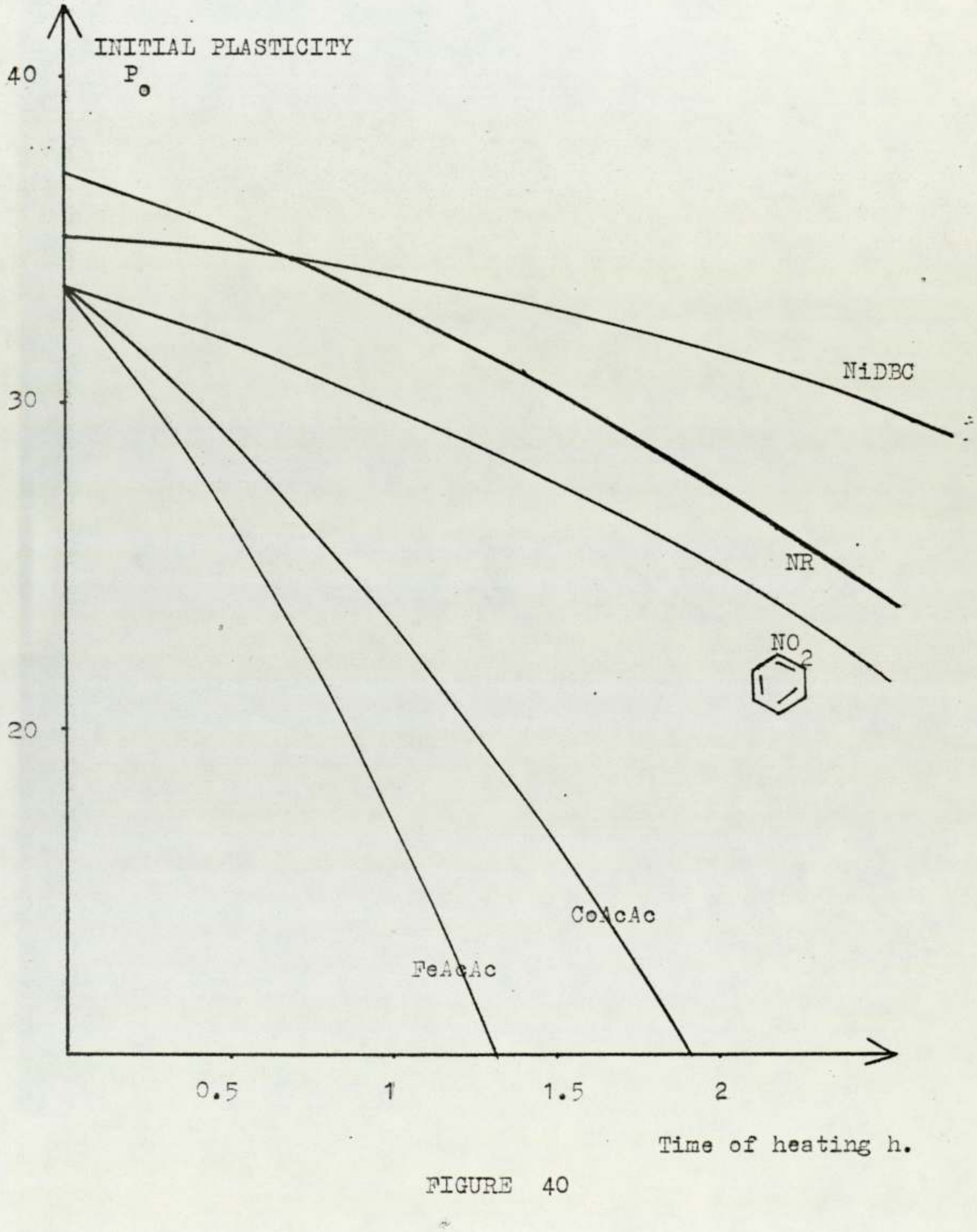


FIGURE 40

the samples containing the other complexes (Fig.40). The sample containing nitrobenzene did not show any effect compared to the control, except for the initial low Plasticity number recorded, due to the incorporation of nitrobenzene in the mill. The sample containing NiDBC showed resistance to heat ageing compared to the other metal complexes. It showed antioxidant properties for thermal ageing.

6A 4.2 Effect of carotene and chlorophyll on photoxidation of NR

NR was extracted with acetone for 48h to get rid of naturally occurring photosensitizers such as chlorophyll, singlet oxygen quenchers such as carotene and the naturally occurring antioxidants in NR, which play an important role in the autoxidation of rubber. Using this as the control, chlorophyll extracted from leaves, and carotene (synthetic product) were in turn incorporated with the extracted rubber in the two roll mill and exposed to sunlight for varying lengths of time. Samples were taken after different intervals of exposure time and dissolved in benzene. IR spectra were run on each of these solutions and the growth and decay of the hydroperoxide band and the growth of the vinylidene band were measured.

In the case of pure rubber free of natural antioxidants, oxidation is much faster than unextracted pale crepe (fig.41) and the hydroperoxide band intensity increases with irradiation time. Reverse results were

OOH BAND INTENSITY VS IRRADIATION TIME FOR

NR CONTAINING PLANT PIGMENTS

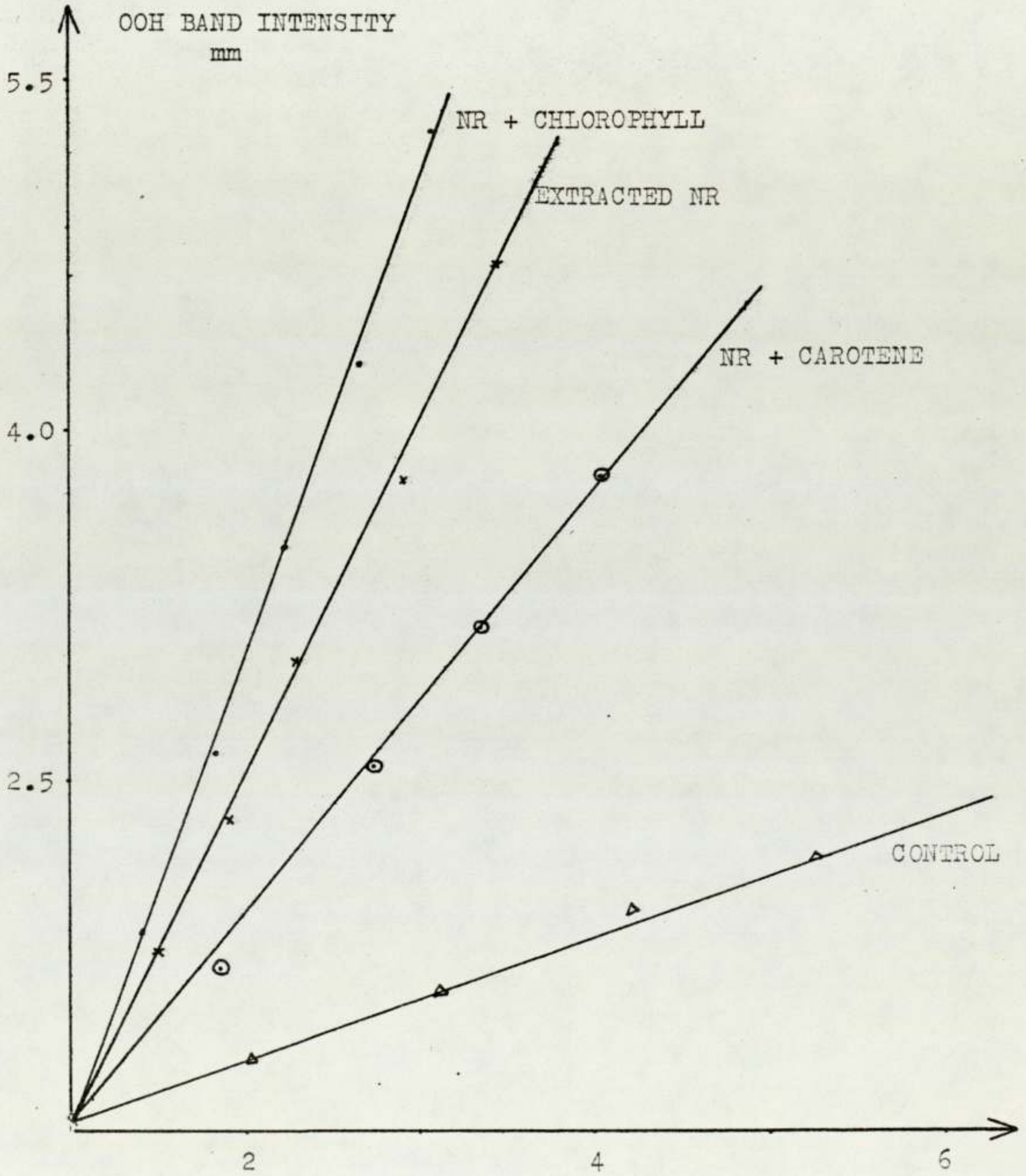


FIGURE 41

VINYLIDENE INTENSITY VS IRRADIATION TIME

FOR NR CONTAINING PLANT PIGMENTS

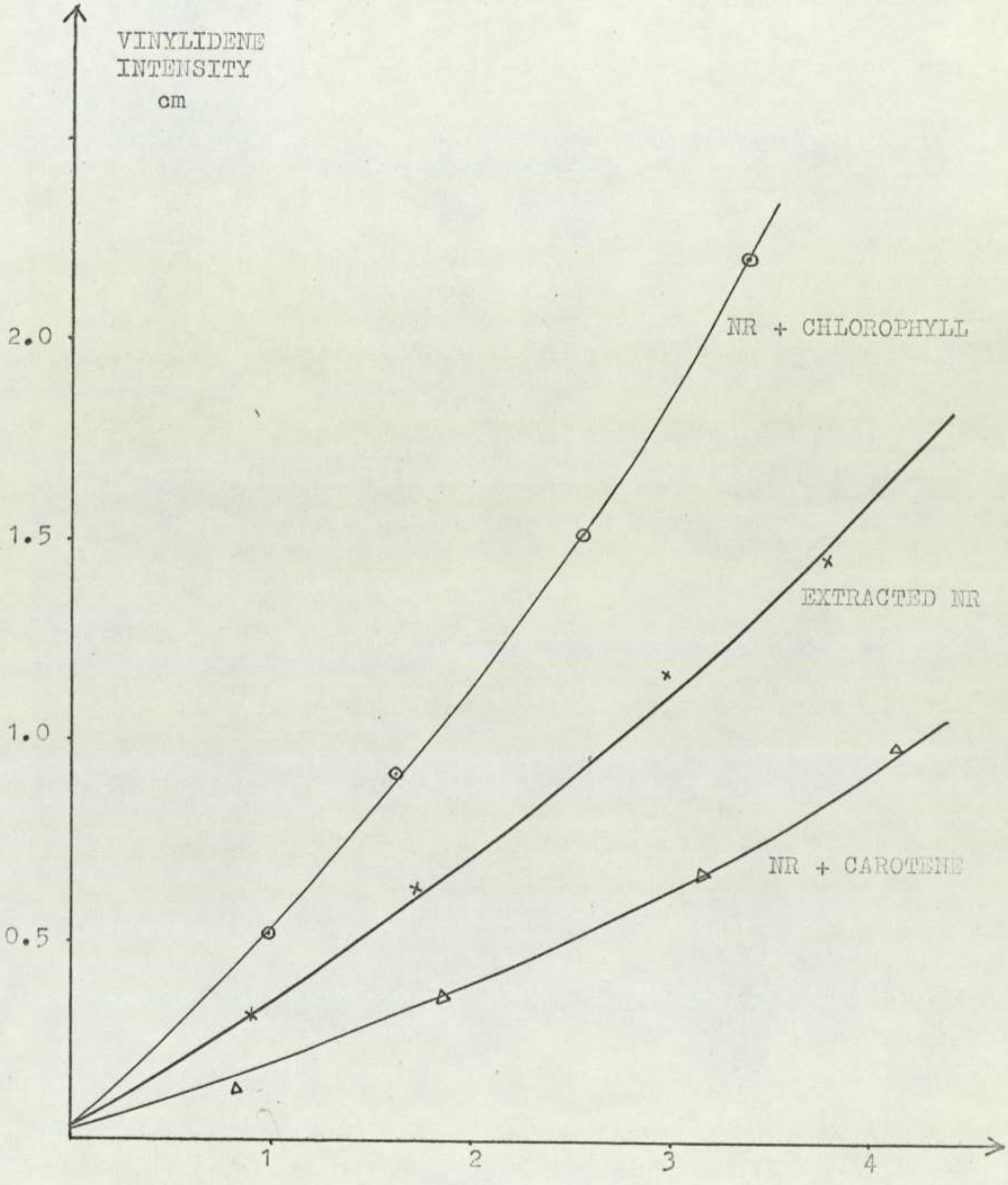


FIGURE 42

obtained in the case of extracted NR samples incorporated with carotene, where it acted as a photostabiliser. This may be because carotene is a well known quencher of singlet oxygen.

The growth of the vinylidene band in the latter case was pronounced, compared to the slow growth of vinylidene in the pure extracted rubber (Fig.42). There were also indications of shifts in the absorption of the ene-chain double bond in all cases wherethe additive was incorporated.

Caroteneis a singlet oxygen quencher. Increase in the vinylidene band intensity in the presence of chlorophyll is an indication of singlet oxygen attack. Hence the explanation that could be given is that chlorophyll acts as a singlet oxygen generator in UV light by the mechanism suggested by Canava[75] and Oster[98]. In their view, natural pigments, which are the sensitisers utilize the lower energy photons of visible light and become excited to the first excited singlet state:

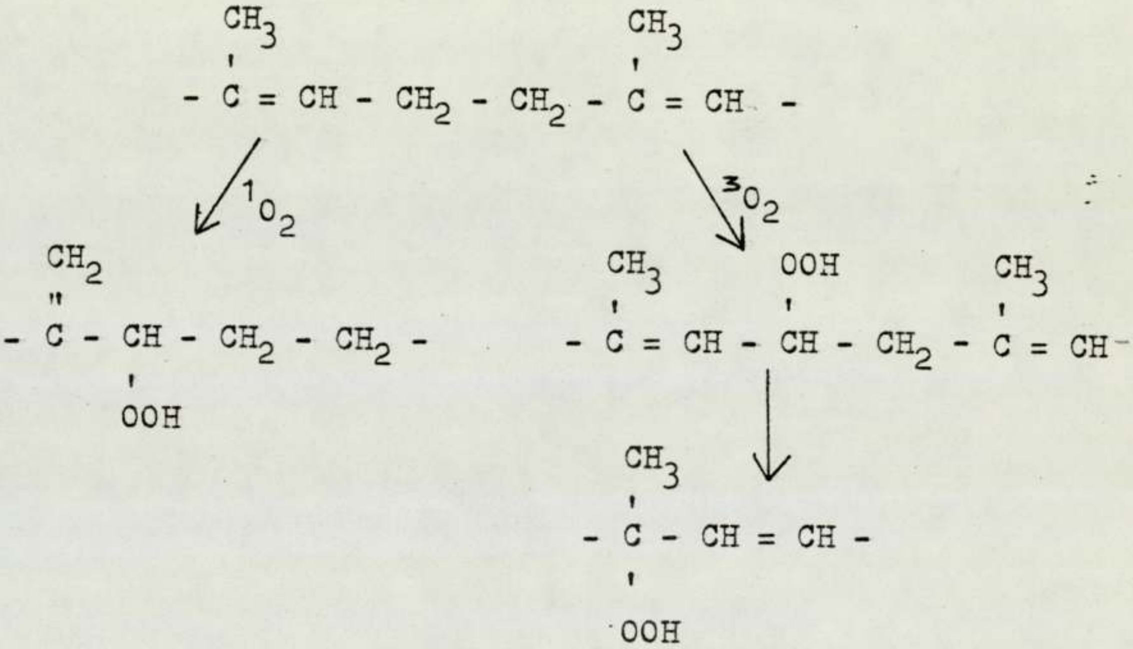
$$\mathrm{Sens}_o + h\nu \longrightarrow {}^1\mathrm{Sens}^* \longrightarrow {}^3\mathrm{Sens}^*$$

The singlet state then undergoes internal conversion to the triplet state $({}^3S)^*$ which then transfers energy to the ground state molecular oxygen ${}^3O_2$, yielding singlet oxygen ${}^1O_2^*$ and a sensitiser molecule in the ground state:

$${}^3\mathrm{Sens}^* + {}^3O_2 \longrightarrow {}^1\mathrm{Sens}_o + {}^1O_2^*$$

This is the species which causes the rapid oxidation in the presence of UV radiation, when singlet oxygen generators, such as chlorophyll, are incorporated.

The normal radical oxidation does not involve the methyl group to a great extent, whereas hydrogen migration from the methyl group is the preferred reaction in the case of singlet oxygen attack resulting in a vinylidene group:



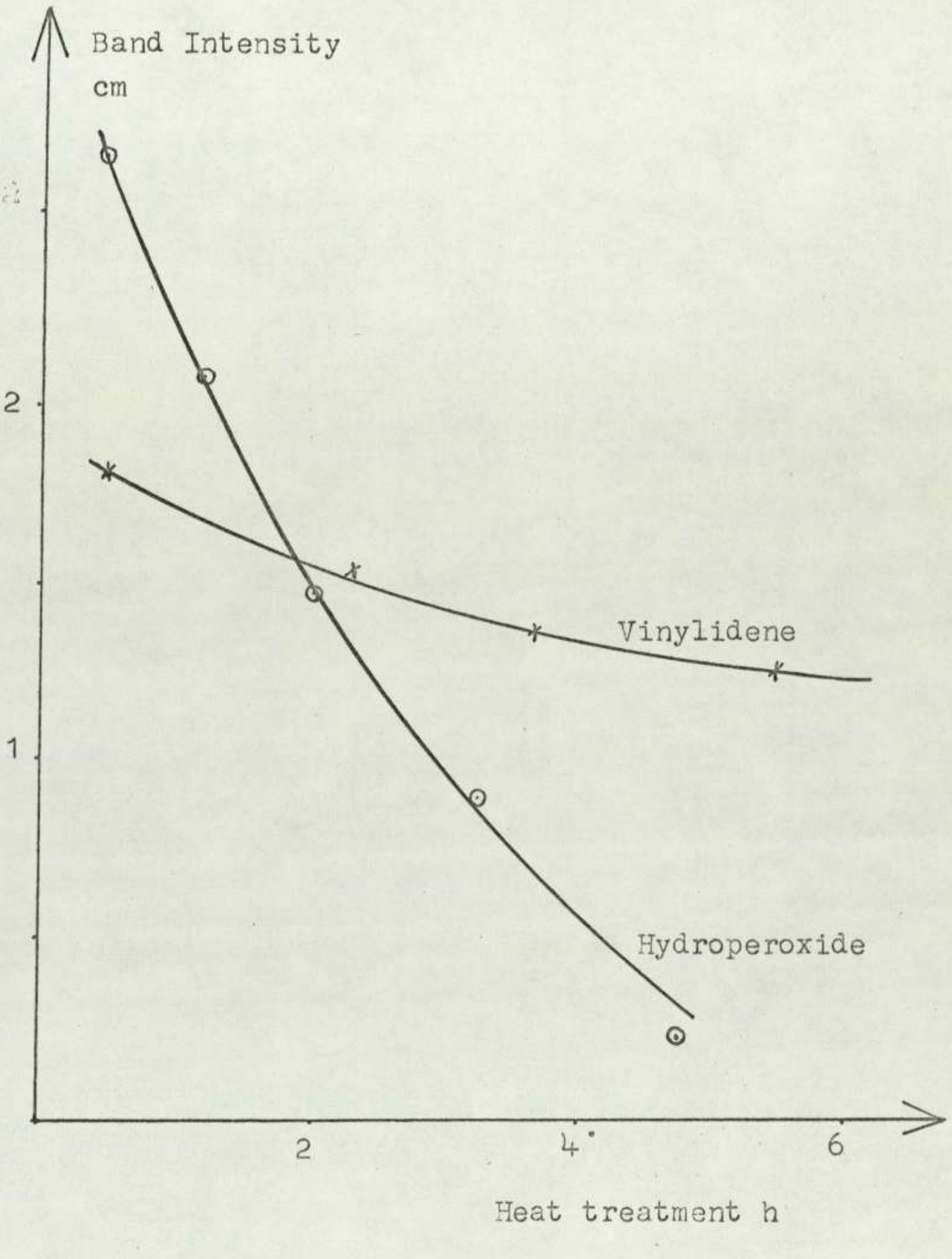
This mechanism explains the growth of the hydroperoxide band and the shift of the ene chain double bond towards the vinylidene region.

6A 4.3 Heat treatment of oxidised rubber

Samples of rubber mildly treated with $^{1}O_2$ by the $NaOCl/H_2O_2$ method were milled and divided into two portions. Samples which were heavily treated could not be subjected to this heat treatment as they were viscid and complete drying for spectroscopic analysis was impossible. The first portion was heated at 100°C for 6h in a vacuum desiccator. The second was heated at 100°C for 6h in air, followed by 6h in a vacuum. The concentrations of hydroperoxide, vinylidene and carbonyl groups were measured spectroscopically at different intervals of time. Colorimetric techniques could not be used for hydroperoxide measurements as the concentrations of hydroperoxide present on these samples treated with low concentrations of $NaOCl/H_2O_2$ mixture were too low for measurement.

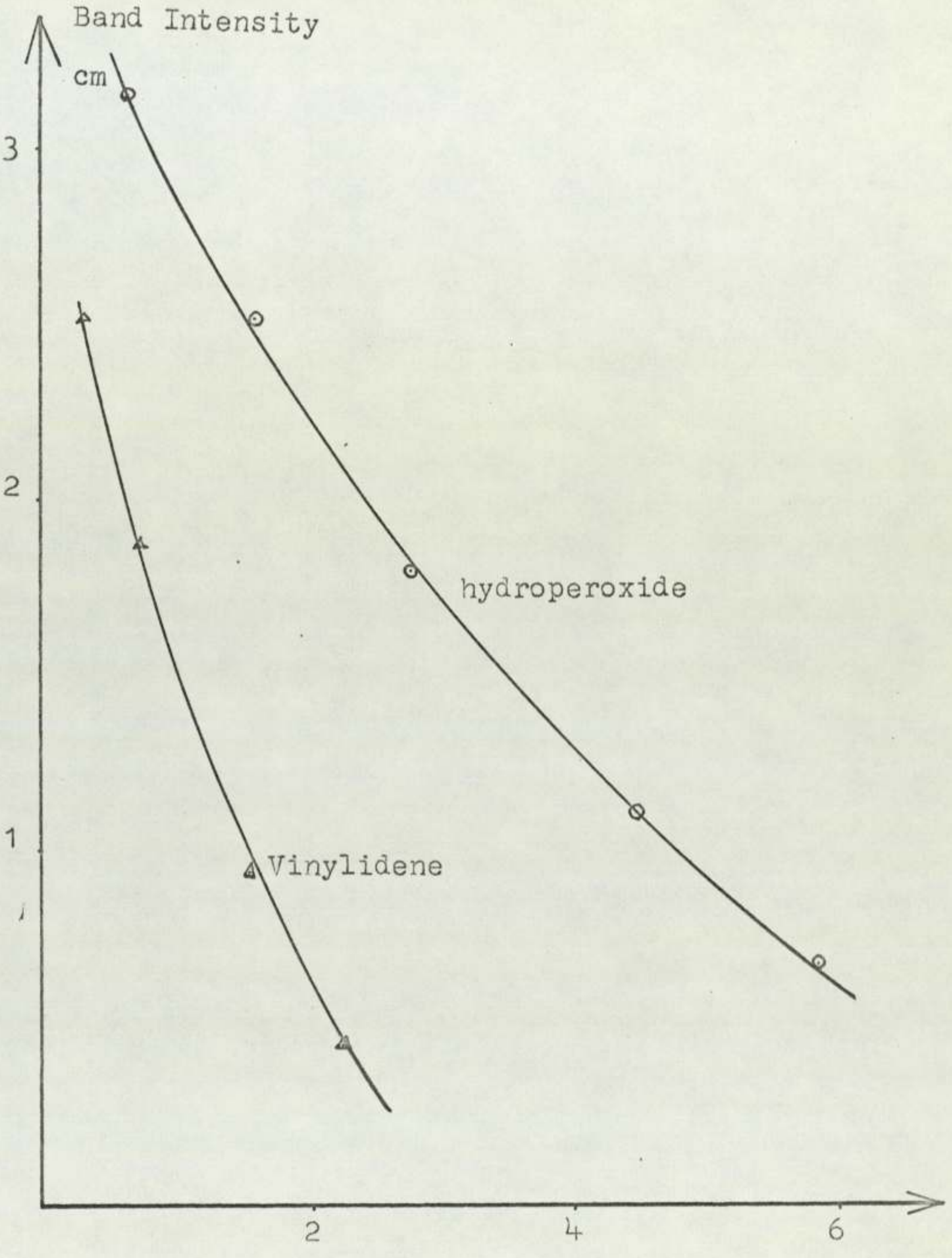
In the first case when the samples were heated in a vacuum there was a gradual drop in hydroperoxide content. But no gel was seen in the samples after this heat treatment in vacuum. Vinylidene band intensity also did not show any appreciable change (Fig.43).

In the second case when the singlet oxygen samples were heated in air, the vinylidene band intensity dropped to a minimum with increasing hydroperoxide concentration (Fig.44). Samples were not completely soluble in benzene due to gel formation as in the case of metal complex initiated oxidation. All these results are in agreement with the free radical type of oxidation, where gel formation is an indication of cross linking. There was a steady increase in carbonyl content (Fig.45) when these samples were subjected to UV radiation.



Fig, 43

VARIATION OF HYDROPEROXIDE AND VINYLIDENE BAND INTENSITIES WITH time of Heat treatment FOR NR IN A VACUUM



Plot of Vinylidene vs hydroperoxide during heat treatment in air

Fig. 44

CARBONYL INDEX VS IRRADIATION TIME PLOT
FOR [NaOCl][H_2O_2] TREATED SYSTEM

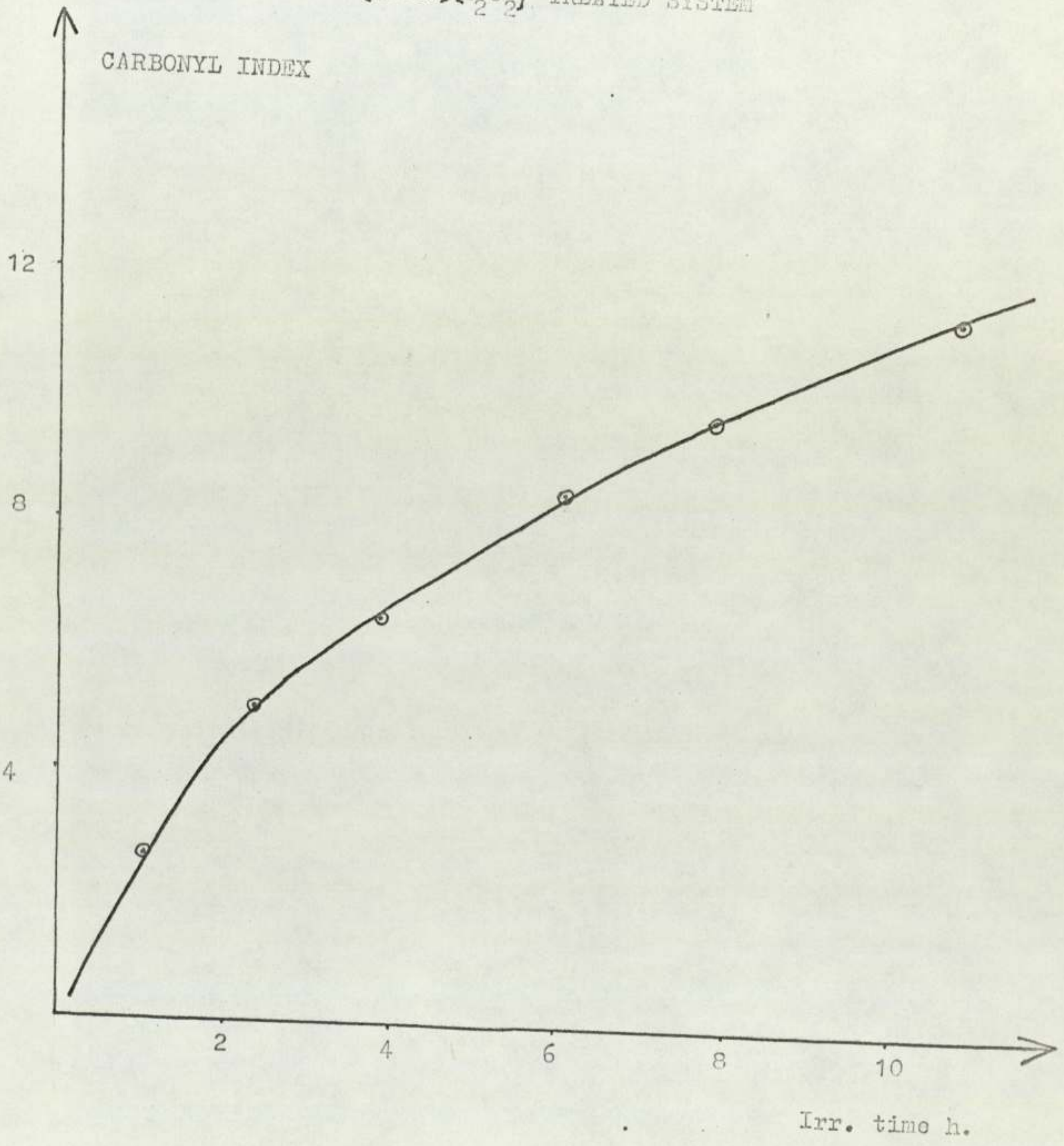
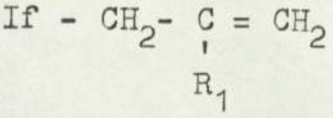
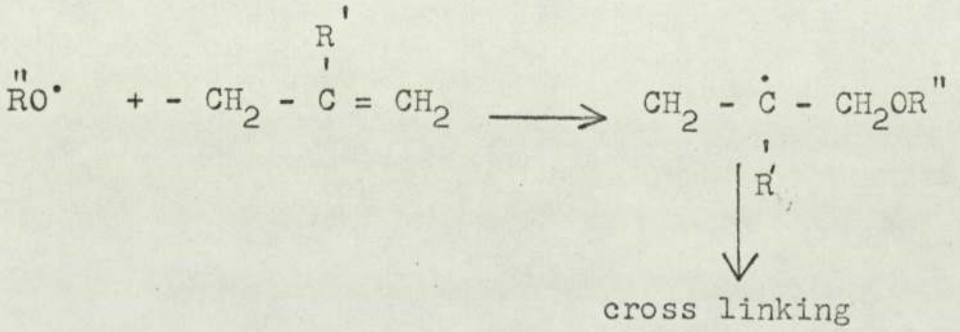


FIGURE 45

Similar behaviour was seen in the case of LDPE when exposed to UV light as explained in a previous chapter. If  $-CH_2-\underset{R_1}{\underset{|}{C}}=CH_2$ stands for the general formula of the polymer, the cross linking caused by the hydroperoxy radical from singlet oxygen attack followed by degradation could be explained as follows:



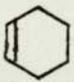
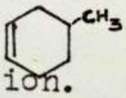
$$R''O^{\bullet} + -CH_2-\overset{R'}{\overset{|}{C}}=CH_2 \longrightarrow CH_2-\underset{R'}{\underset{|}{\dot{C}}}-CH_2OR''$$

cross linking

The amount of gel formation in this case was so small that quantitative estimation was difficult; but this was possible in the case of LDPE where the gel was fairly hard and easy to separate.

6 B. MECHANISM OF NITROBENZENE AS A PHOTOSENSITISER FOR THE DEGRADATION OF RUBBER

It has been shown previously by MRPRA that nitrobenzene causes rapid molecular weight reduction of NR during UV exposure, to give a viscid product which is miscible with non-polar organic solvents. It differs from other photosensitisers such as metal complexes which appear to give a gel. The reason in the process was suspected to be due to the absence or lowering of vinylidene in this case and this was investigated. The oxidation mechanism in this case was also studied.

Nitrobenzene containing rubbers were exposed to sunlight for varying lengths of time and the formation of peroxides, vinylidene and carbonyl group intensities was measured and attempts were made to compare with similar degradation caused by nitrobenzene to unsaturated model compounds such as  and  in order to determine the mechansim of the reaction.

6B 2 Results and Discussion

When the rubber incorporated with nitrobenzene samples, were exposed to direct sunlight, the sample containing 0.5% of nitrobenzene became very soft after 2 h; but was not viscid. The samples with 1.0% and 2% nitrobenzene became viscid in less than 1h exposure to sunlight, as given in Table 9.

Table 9

Results of the nitrobenzene initiated oxidation of NR

% nitrobenzene by weight	Exposure time to sunlight	Appearance of the product
0.5%	1h	Fairly soft. But opaque
0.5%	2h	Not viscid. But very soft and opaque
1.0%	1½h	Viscid, transparent and yellowish in colour like a thick oil
2.0%	1h	Viscid, transparent and yellowish in colour

It was also noted that the pro-degradant activity of nitrobenzene on rubber in UV light is very much faster than that of the metal complexes (Fig.42). Further the final products of nitrobenzene initiated systems ~~is~~ were pale ? yellowish in colour whereas the product obtained in metal complex initiated systems were of dark colour. It is also clear on comparison of Figs. 41 and 42 with Fig. 46 that the vinylidene and hydroperoxide concentration increases with the time of irradiation indicating that the photoactivity of nitrobenzene is through the formation of singlet oxygen and not through free radical formation. This is confirmed by the absence of gel formation in nitrobenzene initiated oxidised products of rubber. If it is a radical reaction the reverse should have been the case.

From the results it could be concluded that nitrobenzene on exposure to UV light gets excited to an excited triplet state and the ground state oxygen absorbs this energy to reach the activated singlet state, which ultimately causes the degradation reaction. If nitrobenzene is denoted by NB, the reaction could be explained by a set of equations as follows:

$$\mathrm{NB} \xrightarrow{h\nu} {}^{1}\mathrm{NB}$$

$${}^{1}\mathrm{NB} \longrightarrow {}^{3}\mathrm{NB}$$

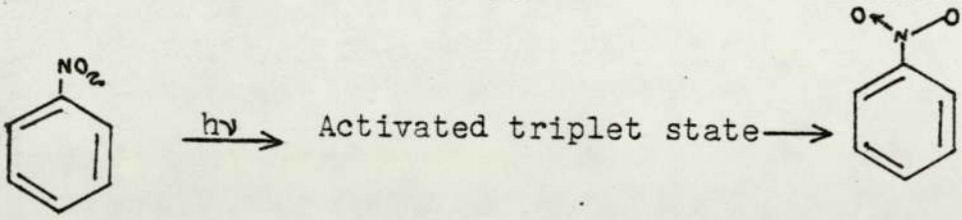
$${}^{3}\mathrm{NB} + {}^{3}\mathrm{O}_2 \longrightarrow \mathrm{NB} + {}^{1}\mathrm{O}_2$$

NB ≡ Nitrobenzene

^{1}NB ≡ Nitrobenzene in singlet state

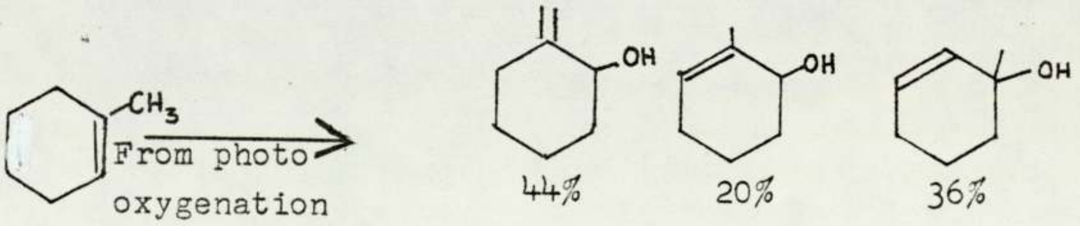
^{3}NB ≡ Nitrobenzene in triplet state

But there is no evidence to show that a radical initiated process of the following type occurs in this reaction:



Abstract hydrogen as
a free radical generator

When methyl cyclohexene was used as the model compound to study the photoactivity of nitrobenzene, identical results were obtained. There was an increase in the vinylidene and hydroperoxide level intensities of the IR spectrum of the treated compound. These were in good agreement with the results obtained by Foote[120] in his photoactivated process for methyl cyclohexene, which is now accepted as due to the action of singlet oxygen. Percentages and nature of products obtained by him in this reaction are given below:



Gas liquid chromatographic studies of these products to determine the percentages of products could not be done due to unavoidable circumstances.

BAND INTENSITY VS IRRADIATION TIME FOR NITROBENZENE INITIATED SYSTEM

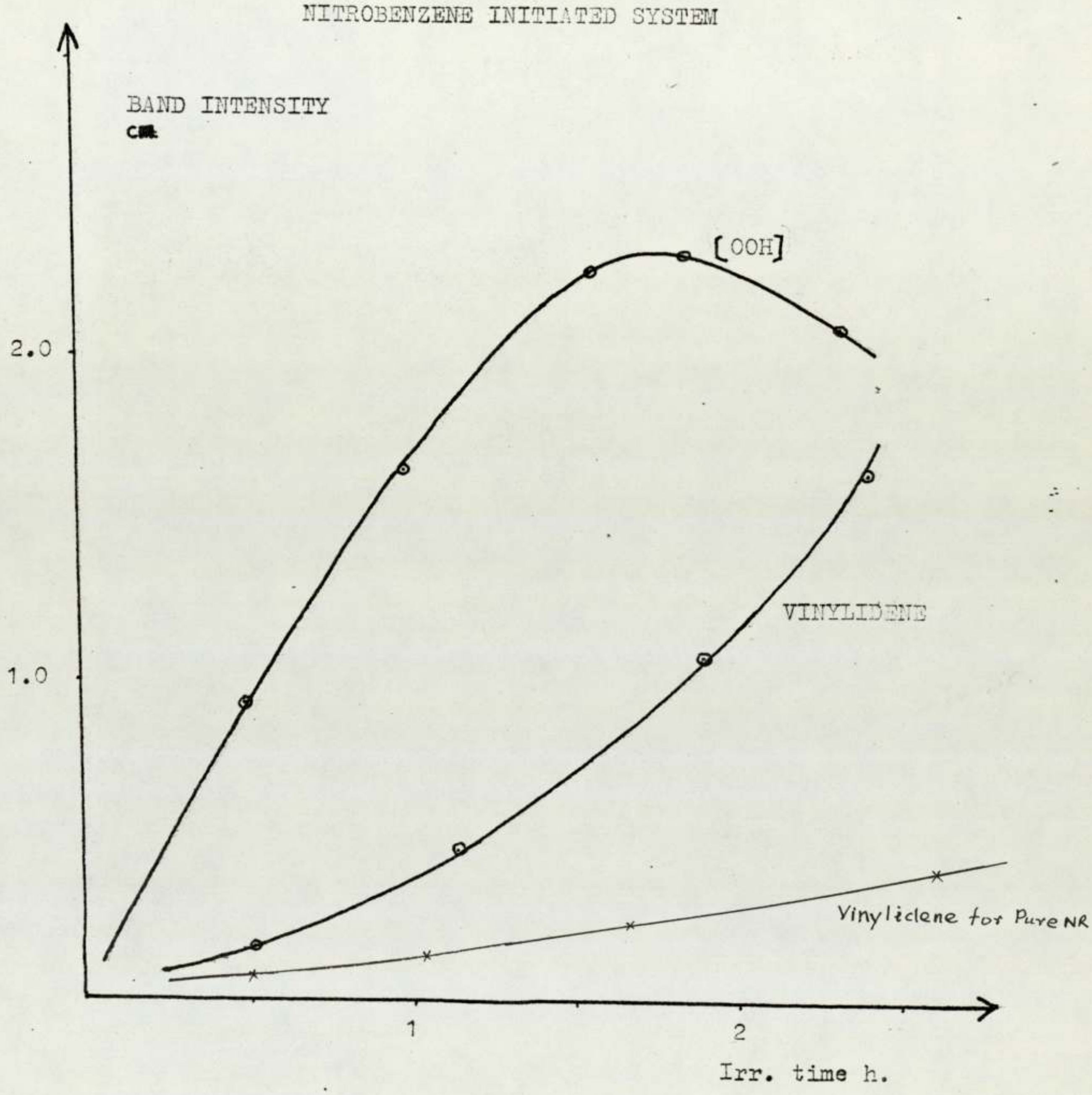


FIGURE 46

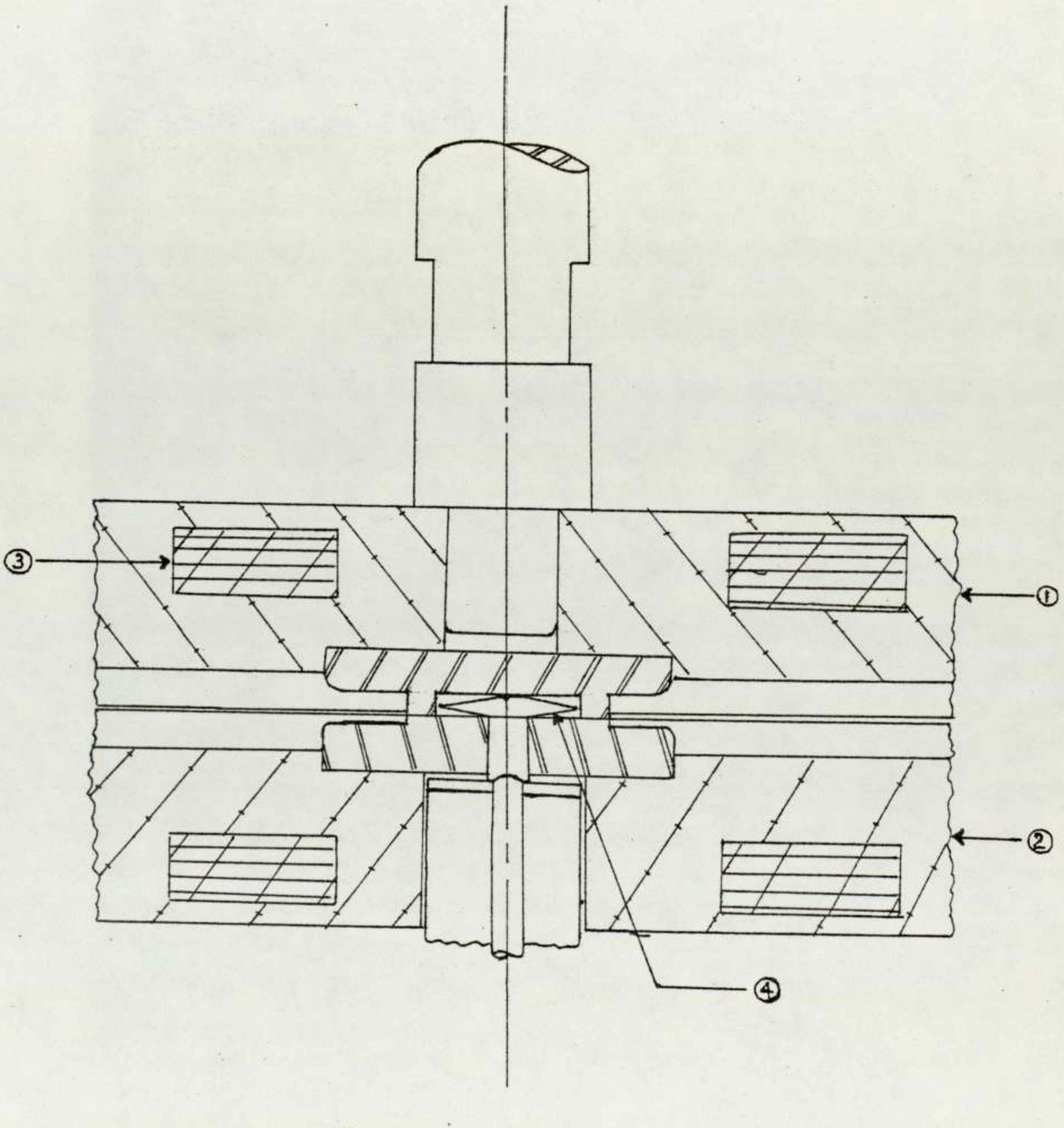
7. VULCANISING CHARACTERISTICS OF LIQUID RUBBER OBTAINED BY SINGLET OXYGEN OXIDATION AND PHOTOXIDATION OF NR

It has been shown in the previous chapter that in addition to the NaOCl/H_2O_2 system, nitrobenzene causes rapid molecular weight reduction of NR during exposure to UV to give liquid rubber which is miscible with non-polar solvents in any proportion. The technological properties of these liquid rubbers obtained by all these methods have been studied by mixing them with vulcanising chemicals in a ball mill, with 10% mineral terpentine as a thinning agent, and curing at 120°C to produce test peices in a mould, for tensile tests. A Monsanto Rheometer was used to assess the curing characteristics of liquid natural rubber, obtained by various processes. The Monsanto Rheometer provides information regarding the curing behaviour of the vulcanizate, hence the theoretical aspects of this method are described briefly:

7.1.1 Monsanto Rheometer studies of a vulcanisate

This instrument provides a continuous smooth curve of variation of the elastic modulus (S) with cure time[134]. This curve is ideally suited for direct comparison of elastomers. A specimen of the compounded polymer is placed in the vulcanisation chamber under the test temperature and pressure and a metal disc is oscillated through a small arc exerting a shear strain on the test specimen (see diagram overleaf). The torque required to oscillate the disc is proportional to the stiffness or the shear modulus of the polymer and this increases when cross links are formed during

CURE METER ASSEMBLY



① UPPER PLATEN

② LOWER PLATEN

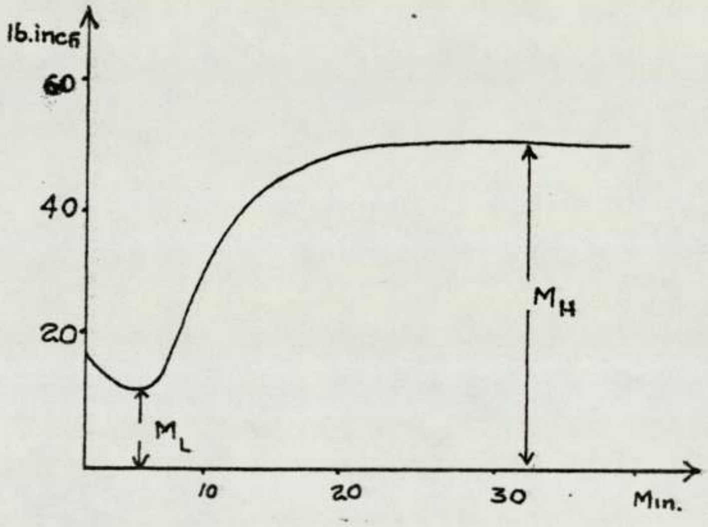
③ HEATER

④ BICONICAL DISC

Fig 47

cure.

A complete cure curve is obtained when the recorder torque value either increases to an equilibrium value or a maximum value. The time required to obtain a cure curve is a function of the test temperature and the vulcanisation characteristics of the polymer specimen. In certain cases this maximum can further increase or decrease after some time, indicating a secondary vulcanisation or a reversion, respectively. Reversion can be caused by the breakdown of cross links.



The following measurements can be read off a rheograph:

(1) Time for incipient cure or the scorch time :tsx

(2) Minimum torque : M_2

(3) Equilibrium torque: M_{HF}(lb inch), or the maximum torque in the case of reverting curve: M_{HR}

(4) Highest torque attend in a cure where no equilibrium or maximum value M_{HR} is attained.

TYPES OF CURE CURVE

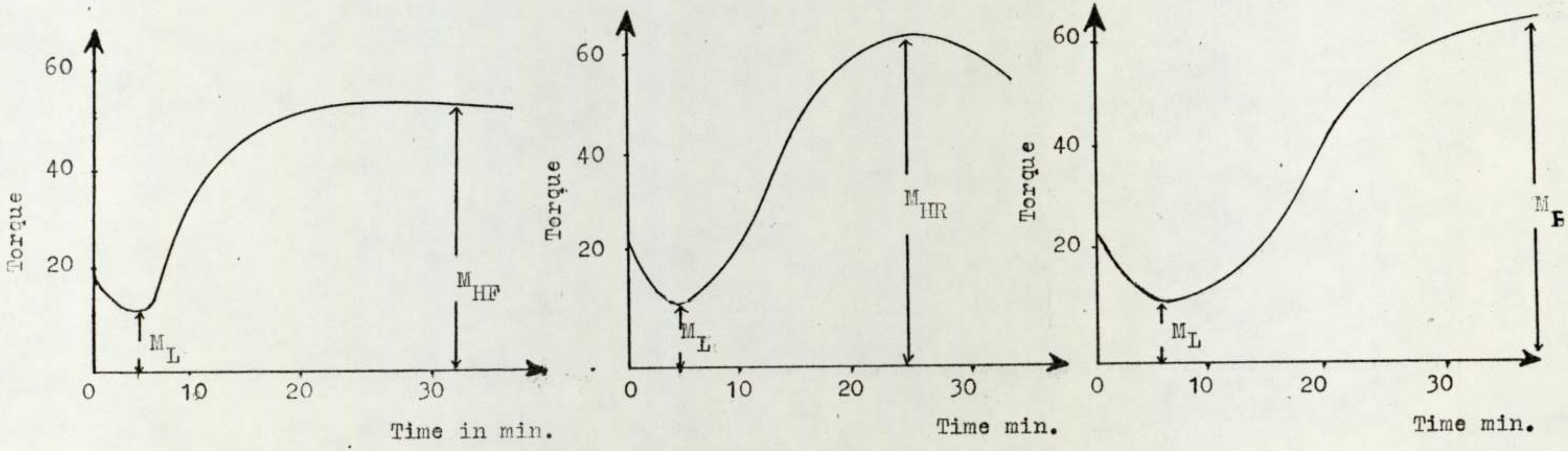


Fig.48

Minimum torque is proportional to the viscosity of the uncured compound. Scorch time is a measure of the process safety: Fully cured torque is a measurement of the shear modulus or stiffness of the compound. It should be noted that the value M_{HR} must be selected on the basis of closeness of fit, since reversion or even secondary cross link formation can occur. This gives a measure of the ultimate cross link density. The method used to assess the ageing characteristics of liquid rubber vulcanisates is by continuous stress relaxation.

7.1.2 Stress relaxation

The dependence of a stretched rubber like elastomer upon time of application, when held at a constant temperature and elongation, provides valuable information about the material. This employs simple apparatus, but measurements of a high degree of accuracy and reproducibility can be obtained. This method of accelerated ageing has been successfully used in the rubber industry to predict various reactions taking place during the thermal oxidation of vulcanised rubber[135].

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

$$f = SkTA_o \frac{l}{l_o} - \left(\frac{l_o}{l}\right)^2$$

Where f is the tension, S is the number of chains per unit volume supporting the stress, k is Boltzmann's constant, T the absolute temperature, $1/1_o$ the ratio of stretched to unstretched length and A_o the unstrained cross sectional area.

Therefore, if a sample of rubber can be maintained in extension at a constant length and temperature the value of the stress f will be proportional to S the number of stress supporting chains.

$$f/f_o = S/S_o$$

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

A Wallace extension stress relaxometer was used in the following experiments where the sample of the vulcanised rubber was held extended between two fixed points and fully submerged in a thermostatically controlled ageing oven with a regular replacement of preheated air. The stress of the extended piece of rubber is balanced by a helical spring. If the tension in the strip falls, a small servo motor reduces the length of the spring to decrease its tension so that this balance is maintained. This is automatically recorded. The stress at any particular instant can be directly read from the record chart.

STRESS RELAXATION APPARATUS

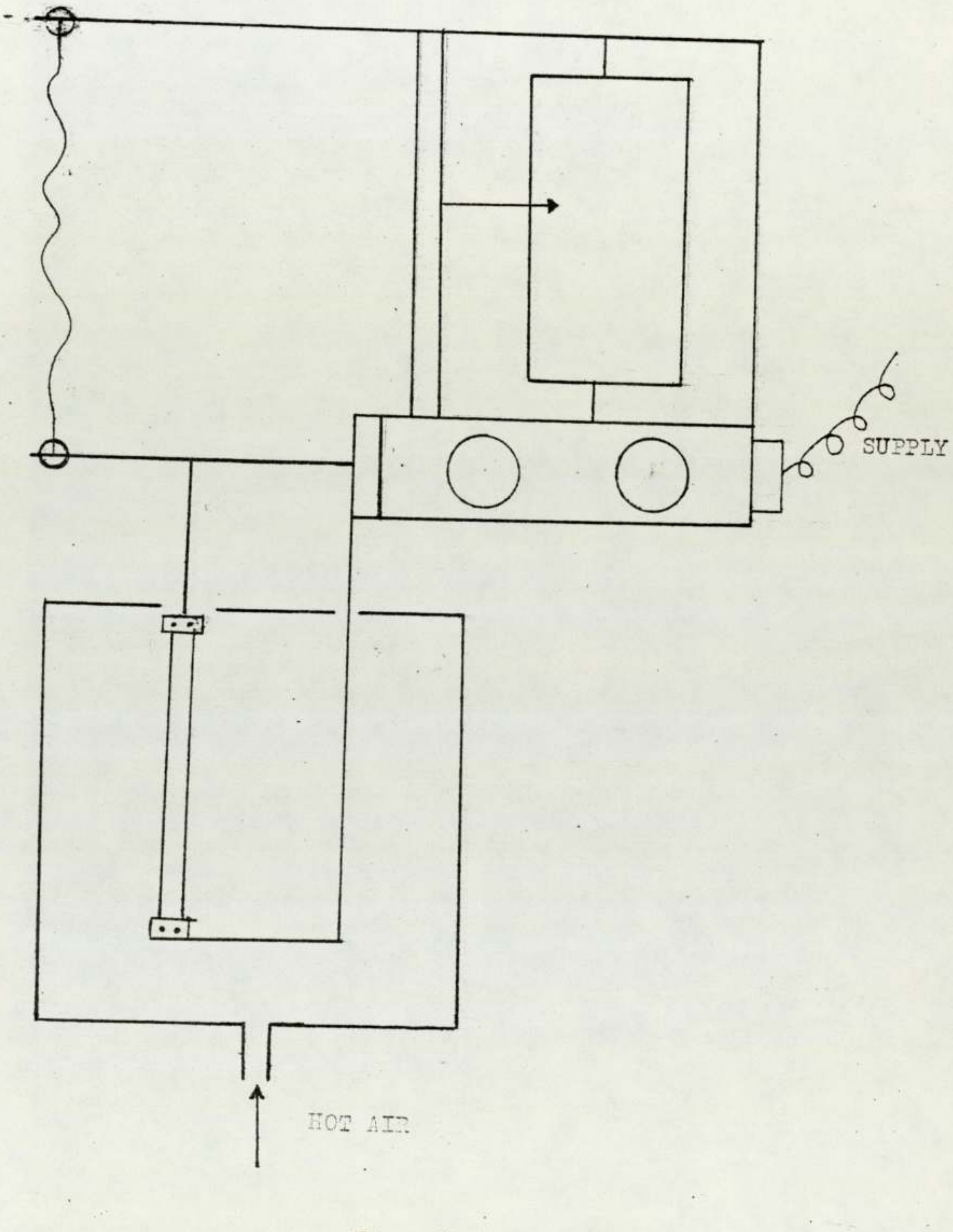


Fig. 51

Adhesion properties of the liquid rubber compounded to the above two recipes were tested by applying the compounds containing turpentine on vulcanised rubber sheets and pasting them on rubber, wood and cotton fabrics, respectively.

7.2 Experimental

About 20g of liquid polymer mixed in a motor, to the recipe No.2 given below, were placed one at a time in the die cavity located in the large electrically heated platens of the Rheometer at 120 ± 0.5°C and the platens were closed.

The disc oscillation motor when started, makes the disc oscillate through a small arc of 3 degrees by means of an eccentric wheel attached to the motor shaft. The force required to oscillate the disc which applies a shearing strain to the polymer specimen is measured electrically by the torque arm transducer and a smooth continuous cure curve of modulus versus cure time is thus obtained.

Vulcanising Recipes

Recipe No. 1

Liquid NR - 100g
ZnO - 5.0g
ZDC - 1.0g
S - 2.0g
ZIX - 1.0g
Curing at room temp. in 48h
or in 10min at 120°C

Recipe No.2

Liquid NR - 100g
ZnO - 3.0g
ZEP - 3.0g
HX - 1.5g
S - 3.0g
MBTS - 0.25g
Curing at room temp. in
15h in 2-3 min at 120°C

7.3 Results and Discussion

Monsanto Rheographs of the liquid and soft rubber compounds made to recipe No. 2 above do not show an initial drop in the viscosity (see Rheographs) of the compounded rubber which is usually seen in raw natural rubber. This is due to the very soft nature of the compound initially, which does not undergo appreciable softening in the Rheometer. Rheometric studies of liquid rubber products obtained by $NaOCl/H_2O_2$ treatment were not possible as the ultimate product emulsified, and the separation of moisture from this emulsion was impossible by drying or centrifuging. But the Rheograph of the mildly treated sample by that method is given below along with the other curves Fig. 47.

Cure time for the nitrobenzene initiated system was found to be between the cure times obtained for Co and Fe complex initiated systems as shown in the diagram. Cure time for a sample of rubber mildly treated with $NaOCl/H_2O_2$-was almost the same as for the nitrobenzene initiated sample.

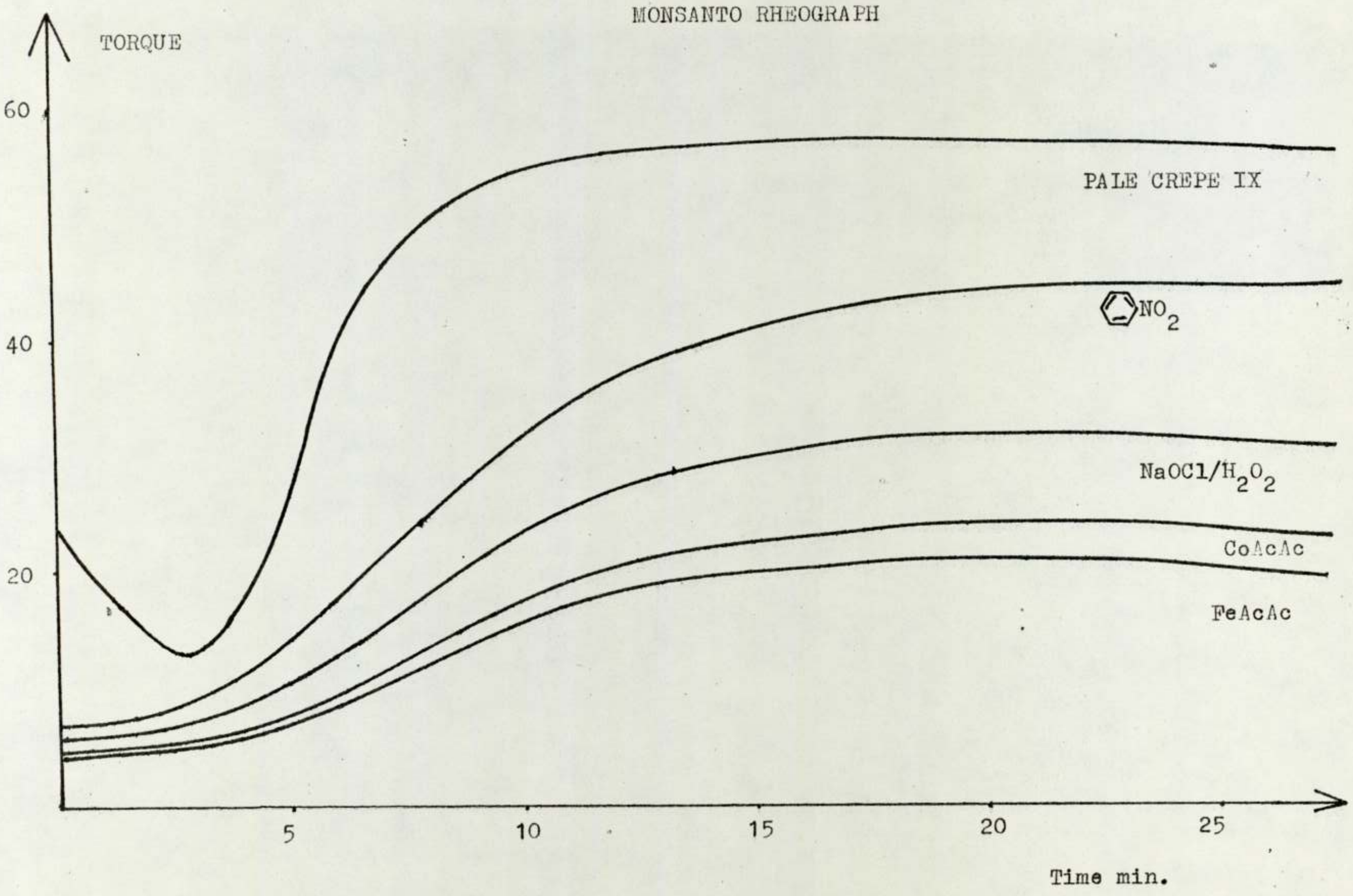

MONSANTO RHEOGRAPH
TORQUE
60
40
20
5
10
15
20
25
Time min.
PALE CREPE IX
NO$_2$
NaOCl/H$_2$O$_2$
CoAcAc
FeAcAc

Fig 50

Table 10

Properties of the vulcanised products

Test	Co complex incorporated	Fe complex incorporated	Nitrobenzene incorporated	NaOCl/ H_2O_2 mildly treated
MOD	4.04	4.42	4.22	3.87
Tensile strength	400 Psi at 700% elongation	344 Psi at 600% elongation	410 Psi at 700% elongation	384 Psi at 700% elongation
Cure time	36mins	18 mins	22 mins	23 min

The tensile strength of untreated NR is about 450 Psi at breaking point. The Co complex initiated system gave a tensile strength of 400 Psi, which is comparable to that of NR; but the Fe initiated sample gave a value of 344 Psi, which is considerably lower than for NR. Compared to the metal complex initiated systems, the nitrobenzene initiated system gave the highest tensile strength, which was closest to that of NR. The value obtained for a sample of rubber mildly treated with NaOCl/H_2O_2 was also low as in the case of the Fe initiated complex.

The Malaysian Rubber Producers Research Association (MRPRA) had studied the use of nitrobenzene for producing liquid rubber[125]; however, they did not pursue these studies, perhaps due to the difficulty of getting a good end product at the lower sunlight intensity at which they worked. Under Sri Lanka conditions, the nitrobenzene initiated viscid rubber, when compounded with fast accelerators, as described, showed excellent room temperature curing adhesive properties. But there was no means of measuring the bond strength of these adhesives at the Rubber Research Institute laboratories.

7.3.1 Ageing Properties - Stress relaxation

Liquid rubber samples, mixed with a mortar and pestle to the recipe No. 2 above, were vulcanised separately into sheets of 5-7μ thickness.

Long thin samples were cut using a die and their continuous relaxation curves were obtained at 100°C while passing air at the rate of 20 ml per minute. The same procedure was repeated with the control samples of pure pale crepe mixed to the same formula as in recipe No.1. From the curves obtained, plots of log f/f_o against the time were made and are shown in the Fig. 48.

As clearly seen from this diagram the stress of the metal complex initiated system decays very much faster than the nitrobenzene initiated systems. This may be due to the combined effect of the cations Fe^{+++} and Co^{+++} which are good initiators of radical oxidation of polymers and the anions acetyl acetonate which is also pro-oxidant active. In this study too, only the samples of rubber mildly treated with $NaOCl/H_2O_2$ were used as the heavily treated samples gave emulsions which could not be separated by easy techniques. Therefore, it can be concluded that, in ageing too nitrobenzene initiated viscid rubber gives better properties compared to liquid rubber obtained by other methods.

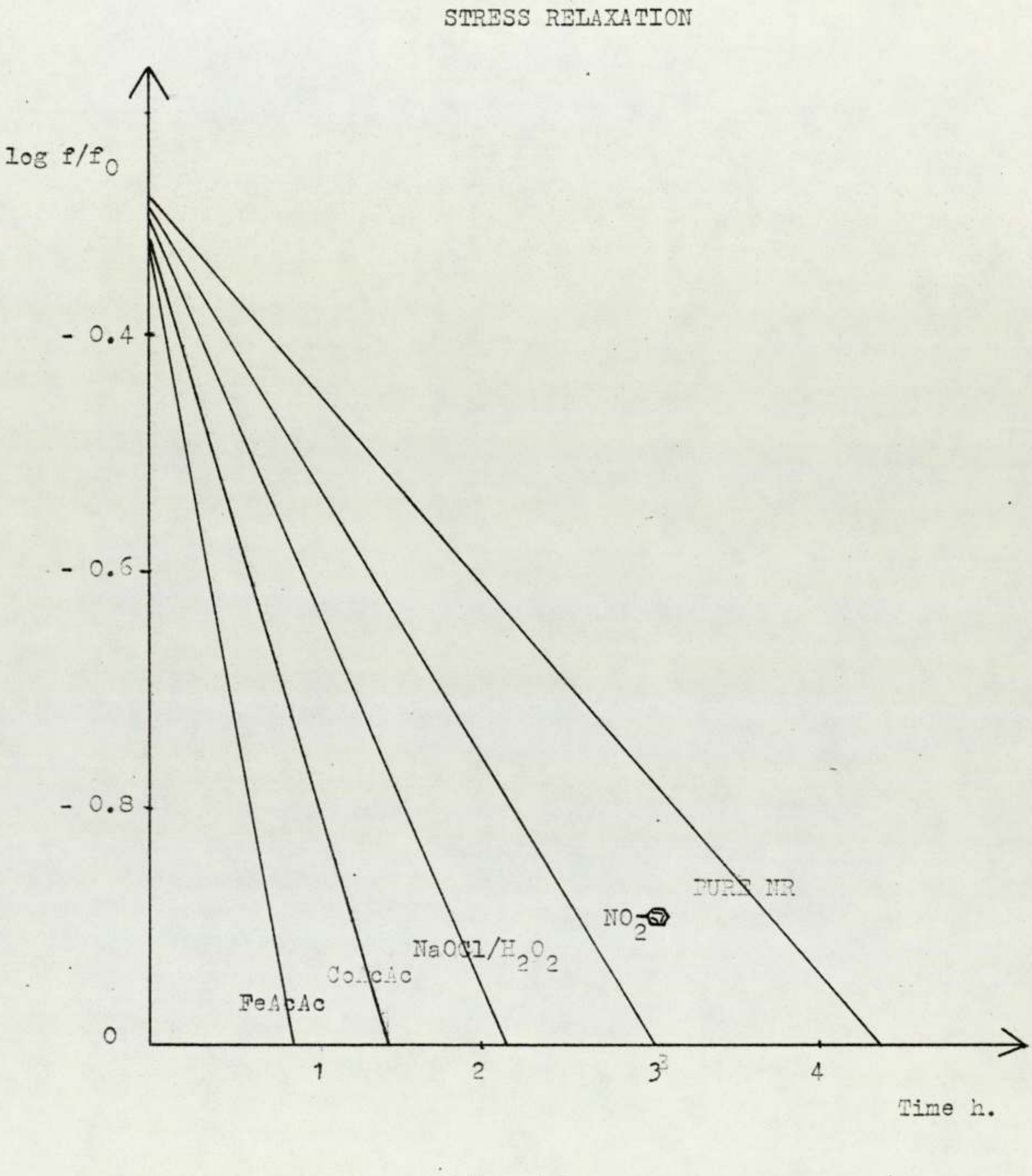

STRESS RELAXATION
log f/f0
- 0.4
- 0.6
- 0.8
0
1
2
3
4
Time h.
FeAcAc
CoAcAc
NaOCl/H2O2
NO2
PURE NR

Fig. 49

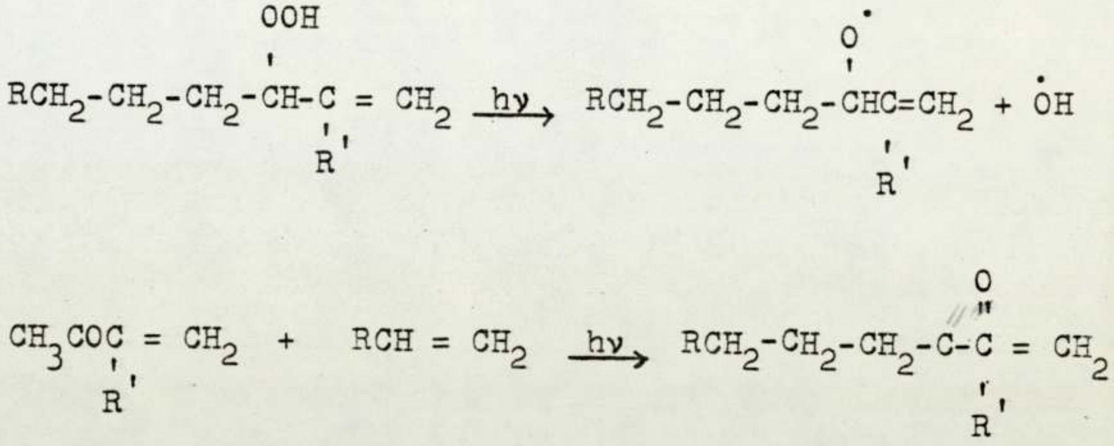
8. CONCLUSIONS

The work described in this thesis show that the ferrous ion o-phenanthrolene technique is capable of measuring 10^{-6} moles of hydroperoxide groups present in oxidised films. However this method would have been irreproducible when applied to polyethylene if the two contributory reasons which have been identified in this work were not taken into account.

In these studies it is shown that, during the processing of low density polyethylene, the hydroperoxide content increases rapidly to a very sharp maximum and then declines. Vinylidene groups initially present in the polymer decreases to zero after an induction period and the rate of destruction is related to hydroperoxide concentration.

Carbonyl concentration increases in an auto-accelerating mode in a process which follows the formation and delay of hydroperoxide, when the carbonyl concentration is low, hydroperoxide and vinylidene are the main sources of the photoinitiation step. In the latter stages of the reaction Norrish II photolysis of carbonyl is the most important process.

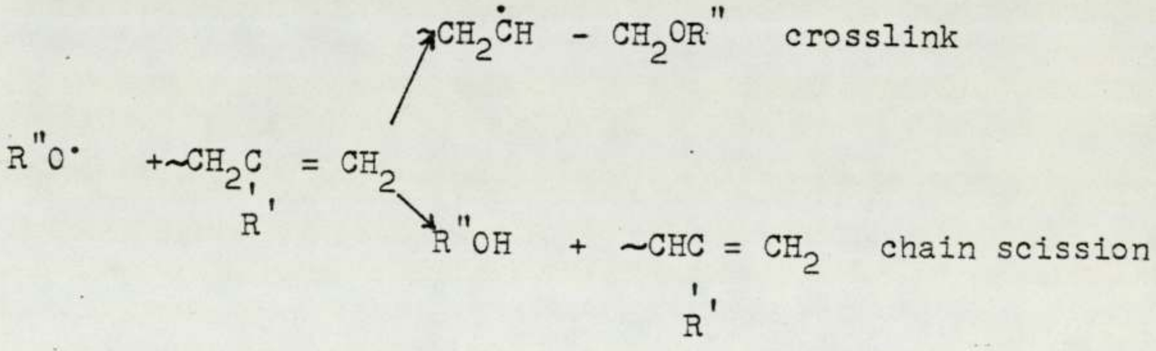
These results serve to explain the puzzling reversal of the change in mechanical properties of LDPE observed during photoxidation; that is the reversal of dynamic modulus that occurs during the first 30-50h exposure to UV radiation which is due to the supervention of chain scission. This is found to be the same period during which rapid oxidation of the polymer occurs and vinylidene disappears rapidly, forming an insoluble gel.



$$RCH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{OOH}{C}H\text{-}\underset{R'}{C} = CH_2 \xrightarrow{h\nu} RCH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{O^{\bullet}}{C}H\underset{R'}{C}{=}CH_2 + \dot{O}H$$

$$CH_3CO\underset{R'}{C} = CH_2 + RCH = CH_2 \xrightarrow{h\nu} RCH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R'}{C} = CH_2$$

Photoinitiation occurs by further reactions of the primary alkoxy and hydroxy radicals, and cross linking through vinyl addition competing with chain scission through allylic hydroperoxide breakdown.



$$R''O^{\bullet} + \sim CH_2\underset{R'}{C} = CH_2 \nearrow CH_2\dot{C}H - CH_2OR'' \quad \text{crosslink}$$

$$\searrow R''OH + \sim CH\underset{R'}{C} = CH_2 \quad \text{chain scission}$$

In the study of the activity of metal complexes on photo degradation of polyolefins, by IR technique and by oxygen absorption studies, three kinds of behaviour were observed. Some metal complexes acted as powerful accelerators for oxidation from the start; others acted initially as retarders but gradually increased their activity and became activators;

while still others acted as antioxidants from the initial stages. When mixed with rubber and exposed to daylight, acetylacetonates of Co (II) and Fe (II) showed much more effective photoactivation than was observed in the case of polyethylene. The rate of carbonyl formation was auto accelerating and the final product became progressively softer on exposure to light. Nitrobenzene is the best out of all the photoactivators tested. After about 2h exposure to direct sunlight, the rubber containing 1% of the nitrobenzene became almost flowable. Mechanism of photodegradation of natural rubber caused by nitrobenzene is shown to be through the formation of singlet oxygen, as a result of which there is vinylidene formation during this photolytic process. Vulcanising properties of the gummy product thus obtained was as good as in ordinary rubber. This is a very good method for making liquid rubber using solar energy and allows the complete elimination of the pre-mastication step, which is normal in the process lines in making rubber articles and is of particular importance in view of the world wide energy shortage.

9. SUGGESTIONS FOR FURTHER WORK

Further investigations of the behaviour of these metal complexes in breaking down the rubber molecules and improving the vulcanisate properties of the product that is formed with carbonyl end groups, using a bifunctional carbonyl reagent, such as bis hydrazide as the vulcanizing agent, might help to produce liquid rubber with superior properties. Inferior technological properties of liquid rubbers obtained by photoxidation when compared to ordinary crepe rubber is supposed to be due to the low molecular weight of the degraded molecules. Another factor which reduces the number of end uses of the liquid product is the carbonyl type end groups of the short molecules which cannot be crosslinked by means of ordinary vulcanising agents. Hence by means of suitable chemical modifications of the molecule, the number of end uses of the liquid rubbers obtained by the above mentioned methods and specially from the nitrobenzene initiated system could be improved. Some of the possible ways of modifying the liquid rubber obtained from nitrobenzene initiated system are:

1. By epoxidation of the low molecular product in order to get the epoxide which could be used as a reinforcing agent for fibres, as a substitute for epichlorohydrin.

2. By chlorination of the liquid rubber. One of the defects of chlorinated rubber made by chlorinating NR latex is the insolubility of the chlorinated product in solvents. But owing to the short molecular nature of the chlorinated product obtained from liquid rubber, this defect could be completely eliminated.

3. By converting the carbonyl end groups of the liquid rubber molecules to hydroxyl or $-NH_2$ groups by suitable chemical reactions, and which could be more easily crosslinked by means of simple chemicals to get better vulcanising properties.

Further attempts will be made by the author to analyse the molecular weight distribution, of the liquid product by means of gel permiation chromatography and also the functional group distribution, in collaboration with various other organisations other than the Rubber Research Institute of Sri Lanka, which will result in a great deal of improvement to the liquid rubber obtained.

10. BIBLIOGRAPHY

1. G. Scott. Atmospheric oxidation and antioxidants, Elsevier, Amsterdam, (1965).
2. W.L. Hawkins. Polymer stabilization, Wiley, New York, (1971).
3. R.H. Hansen, W.H. Martin & T. de Benedicts. Trans. Inst. Rubb. Ind. 39, 6, p.301, (1963).
4. D. Atherton & T.P. Hilditch. J. Chem. Soc. 105 (1944).
5. F.W. Winslow & W.L. Hawkins. Crystalline olefin polymers, Interscience, New York, (1965).
6. W.L. Hawkins, W. Matreyek & F.H. Winslow. J. Polym. Sci., 41, 1, (1959).
7. F.H. Winslow, M. Hellman, W, Matreyek, Polym. Eng. Sci., 6, (3),1, (1966).
8. F.H. Winslow, C.J. Aloisio et al. Chem. Ind. p.533 (1963).
9. G.V. Hutson & G.Scott. Chem. Ind. Sept. 16 p.725 (1972).
10. D.C. Meller, A.B. Moir & G.Scott. Europ. Polym. J. p.219, (1973).
11. F.M. Rugg, J.J. Smith & C. Bacon. J. Polym. Sci. XIII, p.535-547 (1954).
12. J. Burnett, R. Miller & H. Willis, J. Ame. Chem. Soc. 81, p.5960 (1960).
13. H.M.N. Bandara, M.Sc. dissertation, University of Aston, (1974).
14. J.R. Shelton, E.T. McDonel, J. Polym. Sci. 32, p.75, (1958).

15. O. Bailly, J. Gaume. Bull. Soc. Chim. France 5, 3, p.1396, (1936).

16. G. Scott. Photoinitiated degradation of polymers, Helsinki, 2, p.354,(1963).

17. O. Cichetti, Adv. Polym. Sci. 7, p.70-112, (1970).

18. J.C. Calvert & N. Pitts. Photochemistry, Wiley, New York, p.205-245, (1966).

19. D.F. Evans. Mole. association of oxygen and aromatic solvents, J. Chem. Soc. p.345, (1953).

20. H. Tsubomura & R. Mulliken. J. Am. Chem. Soc. 82, p.5966, (1960).

21. D.J. Carlsson & J.C. Robb. Trans. Faraday Soc. 62, p.3403, (1960).

22. J.C.W. Chien. J. Polym. Chem. 69, p.4317, (1965).

23. A.O. Allen & A. Hummel. Discuss. Faraday Soc. 36 p.95, (1964).

24. W.A. Noyes, G.S. Hammond & J. Pitts. Advances in photochemistry, 1, Interscience, New York, p.23, (1963).

25. P. Longi, G. Mazzanti & A. Ruggers. Macro mole. Chem. p.61-63, (1963).

26. K. Ziegler, K. Nagel & Pfohl. Leibigs Ann. Chem. 629.210, (1960).

27. V.K. Millichuk, Vyosokomdekul Soyodin, 7, p.1293, (1965).

28. D.R. Kearns. Chemical Reviews, 71, (4), (1971).

29. G.O. Schenek. Naturwissenschaften, 35, p.28 (1948).

30. I.B. Berlman, G.R. Goldschmidt et al. Chem. Plane lett. 4, p.338, (1960).

31. J.C.W. Chien. J. Phy. Chem. 69, 12 Dec. (1965).

32. H. Tsubomura & R.S. Mulliken. J. Am. Chem. Soc. 82,p.5966, (1960).

33. J.C.W. Chien & C.R. Boss. J. Polym. Sci. P.t A I 5, p.3091, (1967).

34. G.V. Hutson & G. Scott. Europ. Polym. J. 10, p.45-50, (1974).

35. K.J. Humphris & G. Scott. Int. Union of pure & appl. Chem. 36, p.163, (1973).

36. S.S. Stivala & L. Reich. PIA 2nd Ann. Conf. p.68 Nov. (1964).

37. D.J. Carlsson & D.M. Wiles. Macromolecules, 4, p.174, (1971).

38. Y. Katon, D.J. Carlsson & D.M. Wiles. J. Appl. Polym. Sci. 13, p.1447, (1969).

39. F. Kugler & H.P. Frank. Inter. Symp. on stab. and degrad. of polymers, Brussels (1974).

40. J.G. Calvert & J.N. Pitts. Photochemistry, Wiley, New York, p.441, (1966).

41. M.U. Amin. Ph.D. thesis, University of Aston, (1973).

42. R.G.W. Norrish & M.H. Searby. Proc. Roy. Soc. (Lond)., p.A237, 464, (1967).

43. F.O. Rice & E. Teller. J. Chem. Phy. 6, p.489, (1938).

44. T.J. Dongherty. J. Am. Chem. Soc., 87, p.4011, (1965).

45. N.C. Yang & D.D.H. Yang. J. Am. Chem. Soc., 80, p.2913, (1958).

46. G.H. Hartley & J.E. Guillet. Macromolecules p.1,165, 413, (1968).

47. J.E. Guillet, J. Dhanraj et al. Adv. Chem. Ser. 85, Am. Chem. Soc. p.272, (1968).

48. R.P.R. Ranaweera & G. Scott. Chem. Ind. 774, (1974).

Eu. P.J.

49. R.P.R. Ranaweera & G. Scott. J. Polym. Sci. 13, 2, 71, (1975).

50. J.P. Guillory & C.F. Cook. J. Polym. Sci. Pt. A1, 9, (1971).

51. A.M. Trozzolo & F.H. Winslow. Macromolecules, 98, Comm. to the editor, 1, (1), (1968).

52. P.J. Biggs & J.F. Mckellar. Jap. Polym. Sci. 12, p.1825, (1968).

53. D.J. Carlsson, T. Suprunchuk & D.M. Wiles. Polym. letters ed. 11, p.61 (1973).

54. J.C.W. Chien & W.P. Conner. J. Am. Chem. Soc., 90, 4, (1968).

55. K.J. Humphris & G. Scott. Inter. Union Pure and Appl. Chem. 36, (1973).

56. D.G. Pobedimskii & A.L. Buchackenko. Bull. Acad. Sci. USSR. div. chem. sci., p.1125, (1968).

57. Wagner. Anal. Chem. 19, p.976, (1947).

58. D. Sully. Analyst, 79, p.86, (1954).

59. B.W. Evans, Ph.D. thesis, University of Aston, (1972).

60. MU Amin, Evans BW & G. Scott (Unpublished work).

61. G.M. Wood & T.M. Kullman, Chemy. Ind. p.423 (1972).

62. G, Scott. Delayed action photoactivator for the degradation of packaging polymers. Reprint from polymers and ecological problems. Plenum, New York, (1973).

63. J.E. Guillet, J. Dhanraj et al. 153rd meeting of the Am. Chem. Soc. April (1967).

64. A.M. Trozzolo & F.H. Winslow. Macromolecules, Comm. to the editor, 99, 1, (1) Jan.-Feb. (1968).

65. K. Tsuji. Adv. Polym. Sci. 12, 132, (1973).

66. L.M.K. Tillekeratne, M.Sc. dissertation, University of Aston (1973).

67. C. Walling & R. Rabinovitz. J. Am. Chem. Soc. 81, p.1243, (1959).

68. D.B. Denny, W.F. Goodyear & B. Goldstein. J. Am. Chem. Soc. 82, (1960).

69. D.G. Pobedimskii, A.L. Buchchenko. Izvestiga Akademii Nauk USSR, 6, p.1181, June, (1968).

70. B.W. Evans & G. Scott. Europ. Polym. J. 10, (1974).

71. M.G. Evans, M. Santappa & N. Uri. J. Polym. Sci, 7, p.243 (1951).

72. C.G. Menon & M. Santappa. Can. J. Chem. 35, p.267, (1957).

73. C.C. Menon, S.L. Kapoor. J. Appli. Polym. Sci. 1, (3), p.372, (1959).

74. Theodore et al. Rubb. Chem. Technol. 41, p.296, (1968).

75. J.J. Canava. Rubb. J. p.36. (1971).

76. C.S. Foote, S. Waxler & W. Ando. J. Am. Chem. Soc. p.96,976, (1968).

77. R. Higgins, C.S. Foote & H. Cheng. Adv. in Chem. 77, (1968).

78. A. Tkac & V.E. Kello. Rubb. Chem. Technol. 28, p. 383, 968,989, (1955).

79. M.U. Amin. Ph.D. Thesis, University of Aston, (1973).

80. D.W. Grant. Gas liquid chromatography, Van Nostrand, New York, p.179, (1971).

81. P. Bocek, Ustav Vyzkumny. Macromolecules, Chem Abs. p.68, 3198e. 96148 g (1968).

82. K.T. Paul. RAPRA Bull. 2,p.29, (1972).

83. J.P. Guillory & C.F. Cook. J. Polym. Sci. (Polym. Chem. ed.), II , p.1927-37 (1973).

84. J.F. Heacock. J. Appl. Polym. Sci. 7, p.2319-22 (1963).

85. F.M. Rugg, J.J. Smith & R.C. Bacon. J. Polym. Sci. 13, p.535, (1954).

86. J.B. Ellern & R.O. Ragsdale. Inorganic Synthesis, 12, p.82.

87. G.D. Cooper & M. Prober. J. Polym. Sci. XLIV, p.397-409 (1960).

88. D. Barnard, J. Chem. Soc. p.4675, (1975).

89. H. Hock, & S. Lang Ber, 77B,p.257, (1944).

90. E. Boga. University of Aston, Unpublished work (1974).

91. A.G. Gaffar, A. Scott & G. Scott. Europ. Polym. J. 11, p.271-275 (1975).

92. H. Staudinger. Ber, 5,p.278, (1930).

93. E.M. Bevilaqua. Science, p.126,396, (1957).

94. Mitchel & Perkin. App. Polym. Symp. No. 4 p.167-173 (1967).

95. D.J. Carlsson & D.M. Wiles. Macromolecules 2,597 (1969).

96. R.C. Hert & N.Z, Searle. App. Polym. Sym. 4, p.61 (1967).

97. J.P. Luongo. J. Polym. Sci. Vol.XLII, p.139 (1960).

98. G. Oster & O. Shibata. J. Polym. Sci. 26, p.233 (1957).

99. W. Cooper & M. Fielder. J. Polym. Sci. 27, p.442 (1958).

100. M.G. Evans, M. Santappa & N. Uri. J. Polym. Sci. 7, 243, (1951).

101. C. Kujirai, S. Hashiya, et al. J. Polym. Sci. A-1, 6, 589, (1968).

102. M.L. Kaplan & P.G. Kelleher. J. Polym. Sci. B 9, 565, (1971).

103. D.J. Carlsson, T. Suprunchuk and D.M. Wiles. Macromolecules, 5, 659, (1972).

104. J. Flood, K.F. Russel and J.K.S. Wan. J.Polym. Sci. 6,669, (1973).

105. D.J. Carlsson & D.M. Wiles. Macromolecules, 7, 3, 259, (1974).

106. D.J. Carlsson, T. Suprunchuk, & D.M. Wiles. J. Appl. Polym. Sci. 16, 615, (1972).

107. M. Morton, Introduction to rubber technology. Reinhold Pub. Corp. N.Y.

108. J.L. Bolland, & H. Hughes. J. Chem. Soc. 492, (1949).

109. M.U. Amin, B.W. Evans, and G. Scott. Chem. Ind. 206, (1974).

110. E.K. Kleiner (J.R. Geigy Ltd), Fr. Pat. 2,11,412 (1970).

111. B.D. Flockhart et al. Chemical communications (1971).

112. G. Ibing & W. Schacht. Bunsengellschaft Phy. Chem. 542, 77B (1944).

113. C. Mazzolini, L. Patron et al. Ind. & Eng. Chem. (in Press).

114. A.R.S. Kartha, J. Sci. Ind. Res. 17B, 284 (1958).

115. G. Menon & S.L. Kapur. J. Appl. Polym. Sci. 1,372, (1959).

116. F. Francis.J. Chem. Soc. 121, 496, (1922).

117. Jones, R.V. & P.J. Boeke. Ind. Eng. Chem. 48, 1155, (1956).

118. F.R. Mayo & K.C. Irwin. Poly. Eng. Sci. 9, 282 (1969).

119. L. Reich & S.S. Stivala. Autoxidation of hydrocarbons and polyolefins. Marcel Dekker Inc. (1969).

120. C.S. Foote, S. Wexler, & W. Ando. J. Polym. Chem. 90,976, (1968).

121. Mellor's comprehensive treatise on inorganic chemistry supplement II, Part I. p.550.

122. F. Hernandez. Quim. E. Ind. 8, 173-180, (1931).

123. A.M.A. Amarapathy, Ph. D. Thesis, Aston University (1975).

124. H. Kaustsky. Biochemistry, 2,291, 271, (1937).

125. J.I. Cunneen. Rubb. Chem. Tech. 41, 182, (1968).

126. O.R. Wulf. Proc. Natl. Acad. Sci. U.S. 14, 609 (1928).

127. J.P. Guillory, & R.S. Becker. J. Polym. Sci. 12, 993, (1974).

128. P. Bocek. Vyzkumny Ustar Makromol. Chem. Abs. 68, 3193 e, (1968).

129. A. Coomarasamy, Ph.D. Thesis, Aston University (1973).

130. G.O. Schenck, H.D. Becker. Ber. 96, 509, (1963).

131. G. Herzberg. Molecular spectra and molecular structure. Van Nostrand, New York, p. 560, (1950).

132. J.S. Arnold et al. Photochem. photobiol. 4, 963, (1965).

133. A. Schonberg. Ann. 518, p.299, (1935).

134. Operation and Service Manual Rheometer M100, Monsanto Company, Ohio, USA.

135. A.V. Tobolsky, I.B. Prettyman & J.H. Dillon. J. Appl. Phy. 15, p.380, (1944).

136. A.Y. Coran. Rubb. Chem. Tech. 3, 37, p.689, (1964).

137. The Vanderbilt Rubber Handbook. R.T. Vanderbilt Co. New York.

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