THE BEHAVIOUR OF ANTIOXIDANTS IN POLYOLEFINS

UNDER CONDITIONS OF U.V. EXPOSURE

by

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A Thesis submitted for the Degree

of

Doctor of Philosophy

of

The University of Aston in Birmingham

AUGUST 1977

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SUMMARY

The effects of antioxidants and stabilizers on the oxidative degradation of polyolefins (low density polyethylene [LDPE] and polypropylene [PP] have been studied after subjecting to prior high temperature processing treatments.   The changes in the both chemical and physical properties of unstabilized polymers occurring during processing were found to be strongly dependent on the amount of oxygen present in the mixer. Subsequent thermal and photo-oxidation showed very similar characteristics and the chromophore primarily responsible for both thermo and photo-oxidative degradation of unstabilized polymers was found to be hydroperoxide formed during processing. Removal of hydroperoxide by heat treatment in an inert atmosphere although increasing ketonic carbonyl concentration, markedly decreased the rate of photo-oxidation, introducing an induction period similar to that of an unprocessed sample.   It was concluded that hydroperoxides are the most important initiators in normally processed polymers during the early stages of photo-oxidation.

Antioxidants such as metal dithiocarbamates which act by destroying peroxides into non-radical products were found to be efficient melt stabilizers for polyolefins and effective UV stabilizers during the initial photo-oxidation stage, whilst a phenolic antioxidant, n-octadecyl-3-(3',5'-di-tertbutyl 4'hydroxyphenyl) propionate (Irganox 1076) retarded photo-oxidation rate in the later stages.   A typical 'UV absorber' 2-hydroxy-4-octyloxy-benzophenone (HOBP) has a minor thermal antioxidant action but retarded photo-oxidation at all stages.   A substituated piperidine derivative, Bis [2.2.6.6-tetramethylpiperidinyl-4] sebacate (Tinuvin 770) behaved as an pro-oxidant during thermal oxidation of polyolefins but was an effective stabilizer against UV light.

The UV absorber, HOBP synergised effectively with both peroxide decomposing antioxidants (metal dithiocarbamates) and a chain-breaking antioxidant (Irganox 1076) during photo-oxidation of the polymers studied whereas the combined effect was additive during thermal oxidation.   By contrast, the peroxide decomposers and chain-breaking antioxidant (Irganox 1076) which were effective synergists during thermal oxidation of LDPE were antagonistic during photo-oxidation.   The mechanisms of these processes are discussed.

POLYOLEFINS,   OXIDATIVE DEGRADATION,   ANTIOXIDANTS,.   UV STABILIZERS, SYNERGISM.

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

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

K. B. Chakraborty

August 1977.

ACKNOWLEDGEMENTS

I wish to express my gratitude to my supervisor Professor Gerald Scott for his most invaluable guidance throughout the course of this study. I thank him sincerely for his continuous encouragement and advice during this period.

I also acknowledge with thanks the co-operation of technical and Library staff of the University of Aston in Birmingham.

I am very grateful to the Association of Commonwealth Universities for awarding me an academic staff scholarship. I am also grateful to the University of Chittagong, Bangladesh for granting me study leave.

I am also indebted to the members of Professor Scott's research group especially to B.B.Cooray for suggestions and encouragement.

Finally, I wish to express my gratitude to my wife, Rekha, for her patience and encouragement during this period.

CONTENTS

SUPPORTING PUBLICATIONS

K.B.Chakraborty and G.Scott, polymer., 18, 98 (1977)

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LIST OF ABBREVIATIONS USED IN THE PRESENT WORK

LDPE   -   Low density polyethylene

PP   -   Polypropylene

CHP   -   Cumene hydroperoxide

BP   -   Benzophenone

MNE   -   Methylnonylethylene

ZnDEC   -   Zn(11)bis(diethyldithiocarbamate)

ZnDBC   -   Zn(11)bis(dibutyldithiocarbamate)

NiDEC   -   Ni(11)bis(diethyldithiocarbamate)

NiDBC   -   Ni(11)bis(dibutyldithiocarbamate)

HOBP   -   2-hydroxy-4-octyloxybenzophenone

Irganox 1076   -   n-octadecyl-3-(3'-5'-ditertbutyl-4'hydroxyphenyl)-propionate

Tinuvin 770   -   Bis(2.2.6.6-tetramethyl-piperidinyl-4)sebacate.

CHAPTER 1

1.1 Introduction

Polyolefin polymers like all other organic materials are susceptible to oxidative degradation by elemental oxygen on exposure to environmental condition. As a result of these chemical changes undesirable changes occur in physical, mechanical and electrical properties. Scott[1] points out that the most important accelerating environmental influences apart from oxygen which are deleterious to polymer stability are heat, light, contamination by metal ions, ozone and mechanical deformation. The nature of degradation varies in rate and extent depending on the polymer chemical structure and composition, presence of impurities and external environment to which they are exposed.

Oxidative deterioration of polymers take place during two stages[2]. The first occurs as the polymer is fabricated into the form in which it is to be used. Conditions encountered during fabrication or processing can be extreme, both in temperature and in mechanical stress during which unavoidable contact with oxygen in the atmosphere may occur to a greater or lesser degree[3]. Although this treatment is only for a comparatively short time, sensitizing groups are often introduced into a small fraction of the total number of molecules and these trace impurities can accelerate deterioration of the polymer during its service life. Trace impurities may also be introduced during the polymerization process.

The second stage of oxidative deterioration occurs during the service life of the fabricated articles. During this period the polymer is exposed to conditions of actual use where it comes direct in contact with sunlight. This phase also includes storage. Although temperature and mechanical stress are usually lower during the second stage than during fabrication or processing, the time of exposure is much longer. Oxidative processes during both the stages bring about an adverse effect on the polymer's useful properties such as mechanical strength, electrical properties, aesthetic appeal etc. The end result of the oxidative degradation of polyolefins is normally embrittlement due to decay of the above properties on outdoor exposure in sunlight. This deterioration is thought to be due to photo-catalysed oxidation. The deleterious effect of sunlight on polymeric materials has been ascribed to a complex set of reactions in which both the absorption of ultraviolet light and the presence of oxygen are participating agents. As a result, the process has been termed oxidative photodegradation.

Although the energy distribution in the solar spectrum in space extends to wave length below 200 nm[4,5], almost all the radiation of wavelength less than 290 nm is absorbed in the earth's atmosphere; therefore very little of the shorter wave length radiation reaches the earth's surface[5,6]. Most of the absorption at the shorter wave length is caused by a layer of ozone which exists at higher altitudes. Therefore only light having a wave length exceeding 290 nm reaches the earth surface. The energy distribution of solar radiation as a function of wave length (Λ) is shown in Fig. (1.1a)[6,7]. Curve A represents the energy which would reach an object on the surface of the earth if there

were no atmosphere to absorb part of the radiation. Curves B and C
represent the energy distribution reaching the earth after passing through
the atmosphere at high noon when the angle of the sun is $30°$ and $60°$ to the
horizontal respectively. It is readily apparent that no radiation with
a wave length shorter than $2900A°$ is transmitted by the atmosphere.
Fig. (1.1b) shows the proportion of the sun's total energy greater than
hC/Λ is plotted as a function of E_Λ. Values of the strength of several
chemical bonds are included for reference. It is evident from the
figure that although over half of the sun's radiation has sufficient
energy to break weak bonds such as the O-O in a peroxide or N-N bond,
very little of the total radiation is sufficiently energetic to break
strong bonds such as the C-C bond and none is expected to break strong
bonds such as C-H, O-H, C=C and C=O which have energies greater than
100 kcal/mole. Therefore pure polyolefins containing only C-C and C-H
bonds are not expected to show any u.v absorption[8,9]. Consequently
they should not be affected by sunlight when exposed to the atmosphere.
The fact that free radicals are formed and photodegradation reactions
occur after irradiation of polyolefins with u.v light in the wave length
range 290-350 nm which constitutes about 5% of the total solar radiation
reaching the earth's surface indicates that some kind of chromophores
must be present in these polymers. Presumably these are introduced
during polymerization and processing resulting in light absorption by
the polymer which may initiate photochemical reactions.

The most important chromophoric groups and impurities which can
initiate photochemical reactions are believed to be hydroperoxide and

The energy distribution of solar radiation as a function of wavelength(λ)

Figure 1.1(a)

The proportion of the sun's total energy greater than hC/Λ as a function of E_Λ
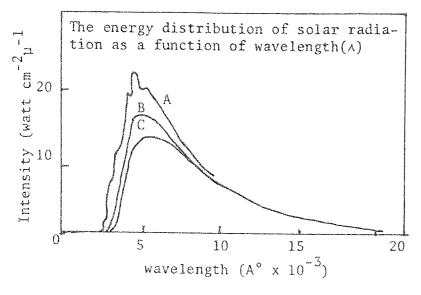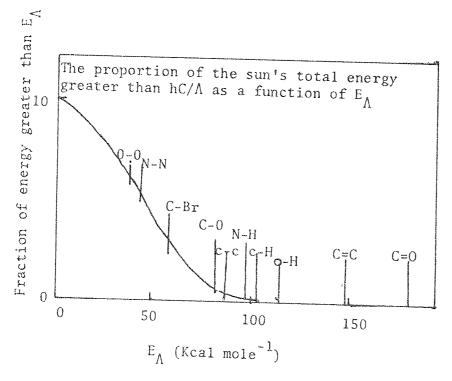
Figure 1.1(b)

carbonyl groups formed during processing. Other agents which may photo-sensitize polymers include aromatic compounds absorbed from the urban atmosphere, metallic impurities during polymerization and processing and oxygen polymer charge transfer complexes with the polymer.

1.1.1 Photoinitiation

i) By hydroperoxide and carbonyl groups:- Alkyl hydroperoxides have continuous absorption spectra that extend from the far ultraviolet to about 330nm in the near ultraviolet. They are, therefore, capable of absorbing sunlight of wave length photochemically harmful to poly-olefins[10,11]. The photochemical reaction brought about by this absorption involves cleavage of the O-O bond[12].

$$ROOH \xrightarrow{h\nu} R\overset{.}{O} + \overset{.}{O}H$$

The quantum efficiency for this reaction is found to be near unity[12,13].

Carlsson and Wiles[14a] studied the photolysis of polypropylene hydro-peroxide generated by prior thermal oxidation of the polymer. These workers found a quantum efficiency of about four for hydroperoxide photolysis in polypropylene. They postulated that photolysis of tertiary hydroperoxides present in the polymer is a key step in the photodegradation mechanism. Their postulation of hydroperoxide initiated photodegradation of polypropylene was later supported by evidence from E.S.R. studies[14b].

According to Scott and coworkers[15-19] the hydroperoxides formed during processing are the main photo initiators in the early stages of

photo-oxidation of commercial polyolefins.   The initial photo-oxidation rate of polyolefins is found to be directly proportional to the hydroperoxide concentration in the polymer formed during processing.   Scott also concludes that the hydroperoxides formed during thermal processing of the polyolefins are the precursors to carbonyl formation.   When carbonyl compounds are formed by thermolysis or photolysis of hydroperoxides, they take part in the later stages of photo oxidation.

It is well known that carbonyl groups are good absorbers of ultraviolet light and absorbs in the near u.v. with a peak around 280 nm and tails extending beyond 300 nm up to about 330 nm.   They can act in a number of ways upon light absorption.   They can cause activation in the chain in the vicinity of carbonyl groups undergo photodissociation or abstract hydrogen from the polymer substrate[20].   In all the cases either excited singlet or triplet intermediate states are involved. For chemical purposes the excited triplet state (formed by intersystem crossing from singlet) is more important than the singlet, since the former has a longer life time.

$$(>C=0) \xrightarrow{h\nu} {}^{1}(>C=0)^{*} \rightarrow 3(>C=0)^{*}$$

The small energy difference between the two states (S_1 and T_1) makes intersystem crossing easier.

The known photochemistry of aliphatic ketones suggest that the principal reactions involving ketone are Norrish type I and Norrish type II reactions[21,22].

Norrish type I reaction: In this process the bond between the carbonyl group and adjacent α-carbon is homolytically cleaved producing two radicals.

$$RCOR' \xrightarrow{h\nu} \begin{cases} R\dot{C}O + \dot{R}' \longrightarrow \dot{R} + CO + \dot{R}' \\ \dot{R} + R'\dot{C}O \longrightarrow \dot{R} + \dot{R}' + CO \end{cases}$$

Norrish type II reactions: A non-radical, intramolecular process which occurs with the formation of a six-membered cyclic intermediates. Abstraction of hydrogen from the γ-carbon atom results in its subsequent decomposition into olefins and ketones.

$$RCH_2 - CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - R' \xrightarrow{h\nu}$$

$$\longrightarrow R\overset{\cdot}{C}H - CH_2 - CH_2 - \overset{\overset{\displaystyle OH}{|}}{C} - R' \longrightarrow RCH = CH_2$$

$$+CH_2 = \overset{\overset{\displaystyle OH}{|}}{C} - R' \text{ (enol form)}$$

$$\downarrow$$

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - R'$$

ketoform

In addition to type I and II reactions of ketones a third process has been observed that leads to cyclobutanol derivatives[23].

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - CH_2 - CH_2 - R' \xrightarrow{h\nu} R - \overset{\overset{\displaystyle OH}{|}}{\underset{\displaystyle CH_2}{\overset{\cdot}{C}}} \quad \overset{\displaystyle \dot{C}H - R'}{\underset{\displaystyle CH_2}{|}}$$

$$\longrightarrow R - \overset{\overset{\displaystyle OH}{|}}{\underset{\displaystyle CH_2}{C}} - \overset{\displaystyle CH}{\underset{\displaystyle CH_2}{|}} - R'$$

But this reaction is not considered to occur to any significant extent in polymeric system compared with type I and II processes.

Norrish reactions I and II are very important in the photodegradation mechanism of polymers as scission of bonds in the main polymer chain occur. The quantum yield of these reactions have been measured for a variety of aliphatic ketones and where both processes are possible, the type I cleavage appears to occur less readily than the type II process[24].

A further possible primary process involving photoreaction of triplet carbonyl groups in the polymer is that of intermolecular hydrogen abstraction from adjacent polymer chains. As in the Norrish type I process, this would result in the formation of macro radical centre in the chain[20,20a,   ]

$$\frac{R_1}{R_2} > C = 0 \quad \xrightarrow{h\nu} \quad \frac{R_1}{R_2} > \dot{C} - \dot{O} \quad \xrightarrow{RH} \quad \frac{R_1}{R_2} > \dot{C}OH + \dot{R}$$

From the fluorescence and phosphorescence study of polyolefins Charlesby and Partridge[25,26] concluded that the species responsible for the phosphorescence and fluorescence bands from polyolefins are carbonyl groups located mainly at the end of the molecular chain. Allen et al.[27,28] examined the role of these phosphorescent species in the thermal and photochemical degradation of the commercial polyolefins. Ketonic/aldehydic type carbonyl impurities were concluded to be potential photoinitiators of commercial polyolefins. It was also suggested by Rå nby et al. and Tsuji[29,30] that the chemical effects of

u.v irradiation of polyolefins are due to carbonyl groups located along the polymer molecule.   Other works have indicated, however, that conjugated carbonyl compounds formed as a result of thermal oxidation could be involved in the initiation step during the early stages of photo oxidation[31].

However, if carbonyl groups act as sensitizers for the photo-oxidation of polyolefins, one would expect that the reaction rate would rise with increased carbonyl concentration.   But in one study[32] it has been shown that this rate is apparently independent of bulk carbonyl concentration in the polymer as well as in model systems containing known concentration of long chain aliphatic ketones.

(ii) Other initiators

Several workers[33,34] suggested the possibility of the formation of peroxide by the attack of singlet oxygen on saturated carbon atom or vinyl groups.   The photoexcited triplet carbonyl groups are quenched by triplet ground state oxygen and the resultant singlet oxygen then reacts with the vinyl groups produced by Norrish type II process.

$$\text{Ketone} \xrightarrow{h\nu} 3(>C=O)^* \xrightarrow{3O_2} >C=O + 1O_2$$

$$RCH_2CH = CH_2 + 1O_2 \longrightarrow RCH = CHCH_2OOH \rightarrow \text{further reaction.}$$

Carlsson and Wiles[35] have shown that napthalene is present in poly-propylene (probably absorbed from the urban atmosphere) and suggested that on photolysis of the polymer any polynuclear aromatic impurity could efficiently generate singlet oxygen by the quenching of its photo-

excited triplet state by ground state oxygen. The excited singlet oxygen thus produced would then be able to attack any nearby double bond forming potentially photo reactive peroxides.

Mill et al.[36], however, could not detect any hydroperoxide formation in the dye sensitized photo oxidation of atactic polypropylene in solution. The dye used (Rose Bengal dye) was known to generate singlet oxygen on photolysis. Breck et al.[37] also observed no hydroperoxide formation when commercial polyolefins are exposed to a gas stream containing singlet oxygen.

It is believed that certain metallic impurities particularly Ti and Fe can efficiently sensitize the photo oxidation of polyolefins[38,39]. These metallic impurities can absorb near ultraviolet radiation causing them to react with the polymer and producing free radicals. Kujirai et-al.[39] found that the oxidative photodegradation of polypropylene in ultraviolet light is dependent on the concentration of oxygen and of catalyst residues (which come from the polymerization process with a Zeigler-Natta catalyst).

The long wave length of u.v absorption in a polyolefin samples(up to 400 nm) is considered to be due to the formation of charge-transfer complexes between the polymer and molecular oxygen[40-42]. The increased formation of radicals observed during the photolysis of polyethylene in oxygen atmosphere can be attributed to the additional absorption of light energy by charge transfer complexes. Several authors[41,43] have suggested that the excited charge-transfer states could initiate photo-oxidation.

$$RH + O_2 \quad \xrightarrow{h\nu} \quad [\overset{+}{RH} - \overset{-}{O_2}] \rightarrow \text{reactive intermediates}$$

At present however, there is no clear evidence for the role of charge-transfer complexes in the photodegradation mechanism of polyolefins.

Recently Carlsson et al.[44] have shown on the basis of theoretical calculations that the low hydroperoxide level detectable in a commercial unstabilized polypropylene sample is alone adequate to account for the photoinitiation kinetics. Initiation by O_2 - polymer charge-transfer complexes, carbonyl impurities or by polynuclear aromatic compounds are probably insignificant.

1.1.2 Mechanism of oxidative degradation of polyolefins

It is now generally accepted that photodegradation of polymers involves the same free radical chain mechanism as thermal oxidative degradation[2,15,] which is largely similar to simple hydrocarbon oxidation[45-47]. Hydroperoxides are key initiators for the process of oxidative degradation of polymers both during thermal oxidative degradation and u.v. initiated degradation. The basic reaction scheme consists of three steps: initiation, propagation and termination.

Initiation:

$$2ROOH \quad \xrightarrow{Ri} \quad RO\overset{\bullet}{O} + R\overset{\bullet}{O} + H_2O \quad \text{Thermal} \quad [1(a)]$$

$$\text{or} \quad ROOH \quad \xrightarrow{h\nu} \quad R\overset{\bullet}{O} + \overset{\bullet}{O}H \quad \text{Photo . . .} \quad [1(b)]$$

$$RO\overset{\bullet}{O} \qquad\qquad ROOH$$

$$R\overset{\bullet}{O} + RH \longrightarrow ROH + \overset{\bullet}{R}$$

$$\overset{\bullet}{O}H \qquad\qquad H_2O$$

Propagation:

$$\overset{\bullet}{R} + O_2 \xrightarrow{k_2} RO\overset{\bullet}{O} \qquad [1(c)]$$

$$RO\overset{\bullet}{O} + RH \xrightarrow{k_3} ROOH + \overset{\bullet}{R} \qquad [1(d)]$$

Termination:

$$2RO\overset{\bullet}{O} \xrightarrow{k_4} \qquad (1e)$$

$$2\overset{\bullet}{R} \xrightarrow{k_5} \text{inactive products } (1f)$$

$$RO\overset{\bullet}{O} + R \xrightarrow{k_6} \qquad (1g)$$

The main difference between thermo-oxidation and photo-oxidation lies in the rate of initiation step. From the results of O Cicchetti[10] it is observed that the rate of u.v. initiated oxidation (both in polymers and in model compounds) is very much faster than that of thermo-oxidation. The high rate of oxidation in u.v. light is believed to be due to rapid homolytic cleavage of initially formed hydroperoxide by light, forming radicals [Reaction 1b].

Hydroperoxide decomposition into radicals is accelerated by various catalysts, notably the transition metals[15,48].

$$ROOH + M^{n+} \xrightarrow[\text{light}]{\text{heat or}} R\overset{\bullet}{O} + M^{n+1} + \overset{-}{OH}$$

$$ROOH + M^{n+1} \xrightarrow[\text{light}]{\text{heat or}} RO\overset{\bullet}{O} + M^{n+} + H^{+}$$

1(h)

The overall reaction is equivalent to bimolecular decomposition of hydroperoxides.

At partial pressures of oxygen equivalent to air or higher concentration, the rate of combination of $\overset{\bullet}{R}$ with O_2 (reaction 1c) is so fast that

$[\dot{R}]<<[R\dot{O}_2]$ and the only termination reaction of consequence will be the bimolecular combination of two $R\dot{O}_2$ radicals [Reaction 1e].

Since the rate of U.V. initiated oxidation is higher, the rate of termination is also higher and the kinetic chain is shorter.

Under steady state conditions and under normal atmospheric pressure, a general expression for the rate of oxidation of the above reaction scheme was derived[2] and is given as

$$\text{Rate of oxidation } [R_{ox}] = \sqrt{Ri} \ \frac{k_3}{k_4} \ [RH] \qquad\qquad 1(i)$$

Under these circumstances the reaction rate depends on the chemistry of the hydrocarbon RH.   The easier it is for hydrogen to be abstracted from RH, the higher will be the value of k_3 and faster will be the rate of oxidation.   The ease of abstraction of hydrogen from different types of carbon atom has been shown by Bolland[49] to increase in the following order

Primary C-H<secondary C-H<tertiary C-H<allylic H

<H in a position to aromatic ring.

Therefore it might be expected that small amounts of chain branching or unsaturation in the polymer might be responsible for initiating degradation by slowly peroxidizing or by providing easily oxidiable sites.

1.1.3 Stabilization

Since oxidative degradation of polymers takes place during fabrication, storage and use, stabilization against oxidative degradation of polymers is thus essential for its useful life time. This may be achieved by the retardation of or inhibition of primary oxidative processes (as discussed in the reaction scheme above) by the incorporation of chemical reagents termed anti-oxidants. There are in principle, four general ways in which these might act on the basis of the preceding discussion.

(i) By removing the reactive radicals formed in the propagating step mainly alkyl and alkyl peroxy radicals known as chain breaking anti-oxidants.

(ii) Prevention of the initiation reaction by deactivating the metal ions and decomposing the hydroperoxides to non-radical products by preventive type anti-oxidants.

(iii) Absorbing u.v light by additives and releasing the photo-absorbed energy in a harmless form such as heat.

(iv) By quenching the photo excited states of polymer molecules or other agents e.g. singlet oxygen which can cause photo degradation by the so called reactive stabilizers or quenchers and dissipating the energy in a harmless manner.

(i) Anti-oxidant acting as chain terminator:
This operates by a radical chain breaking mechanism by removing from the medium the two important species normally involved in the chain propagating step, the alkyl peroxy or alkyl radicals. The anti-oxidant may

react with the propagating radials commonly by hydrogen transfer and by addition or coupling. The most important examples of this class of anti-oxidants are the hindered phenols and secondary amines. Phenols and amines function by virtue of their ability to donate hydrogen in competition with reaction (1d), thus competing with polymer molecules for reaction with propagating radicals .

$$ROO\overset{\bullet}{} + AH \quad\rightarrow\quad ROOH + \overset{\bullet}{A}$$

where 'AH' is the anti-oxidant.

In this reaction, the labile hydrogen donor or chain terminator (AH) reacts with the peroxy radical to form a molecule of hydroperoxide and as a by-product the radical $\overset{\bullet}{A}$. For effective stabilization the anti-oxidant radical $\overset{\bullet}{A}$ must be sufficiently inert that it does not continue to propagate the oxidative reaction. Such radicals are often stabilized by virtue of their multiple resonance structure. They may also undergo a sequence of secondary reactions such as shown below:

(peroxydienone)

There is adequate chemical evidence to show that a single molecule
of phenolic chain terminator can react with more than one propagating
radical. The correlation between anti-oxidant efficiency and chemical
structure of this type of anti-oxidants has been extensively reviewed by
Scott[15(c)]. Phenolic anti-oxidants show some practical limitations.
Once the peroxy dienones are formed, they are rapidly decomposed to give
new initiating radicals at temperature above 140°C which makes phenolic
anti-oxidants relatively inefficient at high temperature.

Since the rate of initiation in the case of u.v initiated oxidation
is higher, the rate of termination is also higher and the kinetic chain
length is shorter. Consequently phenolic anti-oxidants are not very
effective in u.v. initiated oxidation. Moreover, on photolysis phenols
give peroxy dienones and stilbene quinones which may photosensitize the
photo destruction of polymers[15(c)].

Recently, work at Ciba-Geigy A-G (Switzerland) and Sankyo Company
(Japan) has shown that substituted 2,2,6,6-tetramethylpiperidines act
as very good stabilizers in polyolefins. Ciba-Geigy claim that they
act primarily by radical scavenging and to some extent by hydroperoxide
decomposition. Temchin et al. [50] have reported that the 2,2,6,6-
tetramethylpiperidines are better stabilizers than commercially used

nickel dialkyldithiocarbamates or 2-hydroxybenzophenones. The piper-
idines are readily oxidized to the corresponding nitroxides by photo-
lysis of peroxide[51] and nitroxides then scavenge alkyl radicals very
effectively by addition at the oxygen.

(ii) The second class of anti-oxidants act in some way to inhibit or
retard initiation of the free radical mechanism of oxidative degradation
of polymers. Initiation results from peroxide decomposition into radi-
cals which is accelerated by heat, light and metal catalysis. Any agent
that functions by removing sources of free radicals are known as
preventative anti-oxidants. This class includes mainly metal ion deacti-
vators, peroxide-decomposers, u.v. absorbers and quenchers.

Metal ion deactivator functions by deactivating the transitional
metal ions[15(d)] which act as oxidation reduction catalyst in the de-
composition of hydroperoxides [Reactions 1h]. The deactivation process
may be achieved in three ways:

a) Complexing the metal ion to its maximum co-ordination
   numbers by various ligands.

b) Stabilizing one valency state at the expense of the other.

c) Forming an insoluble product, e.g. FeS.

Peroxide decomposers transform hydroperoxides into stable non-
radical products. This anti-oxidant mechanism was recognized many years
ago by Denison and his co-workers[53] and this type of activity has been

found with a variety of sulphur containing compounds of which the most important are dialkylmono and disulphides, metal dialkyldithiophosphates and the metal dithiocarbamates. Bateman and co-workers[54] suggested that the sulphides themselves are not the effective anti-oxidants but rather the sulphoxides and thiosulphinates formed by stoichiometric reactions of sulphides and disulphides respectively with hydroperoxides. But this mechanism cannot explain why many chemically dissimilar sulphide compounds are effective in decomposing hydroperoxides. An even more important def'iciency is that the proposed mechanism did not take into consideration that the process is often catalytic. To take into account the catalytic aspect Hawkins and Sautter[55] proposed that oxidation of sulphur compounds generate sulphur dioxide which subsequently acts as an acid catalyst for the decomposition of ROOH to alcohols and ketones.

Several papers have been published by Scott and co-workers[1,17,18,56-61] on the mechanism of sulphur containing anti-oxidants. In the case of metal dialkyldithiocarbamates and mercaptobenzthiazole, it is now unequivocally recognized that they destroy hydroperoxides by the ionic process generally Lewis acid catalyzed reaction. The Lewis acid in this case is possibly sulphur dioxide or sulphur trioxide which have been formed by the oxidation of the dithiocarbamate complexes with hydroperoxide.

$$(R_2N - \overset{\overset{\textstyle S}{\|}}{C} - S)_2M \xrightarrow{\text{ROOH}} [R_2N - \overset{\overset{\textstyle S}{\|}}{C} - \underset{\underset{\textstyle O}{\|}}{\overset{\overset{\textstyle O}{\|}}{S}} - O]_2M$$

$$\longrightarrow R_2N - \overset{\overset{\textstyle S}{\|}}{C} - OH + SO_2$$

$$\downarrow$$

RN = C = S + ROH
isothiocyanate

The products formed from cumene hydroperoxide with metal dithiocarbamates (on thermal and u.v. oxidation) are phenol and acetone which are diagnostic of a Lewis acid catalyzed process.

$$C_6H_5 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OOH \underset{\text{Acid catalyzed}}{\overset{\text{homolytic}}{\rightleftharpoons}} C_6H_5 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\circ}{O} \xrightarrow{RH} C_6H_5 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH + \overset{\circ}{R}$$

$$C_6H_5OH + (CH_3)_2 C = O$$

The catalytic effect of SO_2 on the decomposition of hydroperoxides can be accounted for on the basis of following regenerative scheme.

$$CH_3 - \underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}} - OOH \xrightarrow{SO_2} CH_3 - \underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{+}{O} S\bar{O_3} H \longrightarrow$$

OH
(phenol)

$$+CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$$

$$+SO_2$$

The mechanism of another class of compounds cyclic phosphite esters[62] is found to be similar in many ways to the behaviour of dithiocarbamates. Catechol phosphite esters are found to be powerful stabilizers for polymers and they also destroy hydroperoxides in a Lewis acid catalyzed reaction. The effective catalyst the corresponding cyclic phosphate is formed from the starting ester by a reaction with hydroperoxide. Products shown to be formed in the reaction between 4-methyl-2-6-di-t-butylphenyl-o-phenylenephosphite (1) and cumene hydroperoxide are the corresponding phosphate (11) and its transformation products (111) and (1V) are powerful antioxidants in auto-oxidations catalyzed by hydroperoxides and are effective catalysts for the decomposition of cumene

hydroperoxide in which they function primarily as Lewis acids. The products formed from cumene hydroperoxide and with (1) are mainly phenol and acetone which are known to be typical products of a Lewis acid catalyzed process.

The mechanism of the catalytic activity of (111) with cumeme hydroperoxide is given below.

(111) + PhCMe$_2$OOH $\longrightarrow$

Other cyclic phosphite esters (V) ethyleneisopropylene phosphite and propylene isopropylene phosphite (VI) were also shown to behave similarly to O-catechol phosphite.

V

VI

U.V absorbers are a class of stabilizers which have intense absorption up to 350 - 370 nm, but are transparent in the visible. They are believed to function by absorbing most of the u.v. light and dissipate the absorbed energy in a harmless manner in the form of heat. The best example in this category are the orthohydroxybenzophenones, orthohydroxybenzotriazoles and salicylates. All these compounds have a common structural feature, the intramolecular hydrogen bond.

orthohydroxybenzophenone   orthohydroxyphenylbenzotriazole

salicylate

It is not known with certainty why orthohydroxybenzophenones and similar types should be capable of effectively degrading the electromagnetic energy, but it does seem likely that the capacity is associated with the presence of hydrogen bonded orthohydroxy group which permits energy transfer and probably hydrogen transfer with subsequent isomerization of the enolic quinone[63].

Recent investigations suggest that the protective efficiency of ortho-hydroxybenzophenones and benzotriazoles in polyolefins is greater than the u.v. absorbing efficiency by these compounds[60,64,65]. This suggests that o-hydroxybenzophenone functions also by other mechanisms in addition to u.v. screening. 2-Hydroxybenzophenone in which the phenolic-OH is involved in intimate intramolecular hydrogen bonding with >C=O apparently do not scavenge peroxy radicals even in the liquid phase. However, under conditions which lead to the uncoupling of the intramolecular hydrogen bonding, these phenols are reported to become free radical scavengers[66]. Hutson and Scott[18] also observed that 2-hydroxy-4-octyloxybenzophenone has mild thermal anti-oxidant property during processing of HDPE and suggested that the anti-oxidant activity results from free radical scavenging.

It has been suggested by many workers that compounds that do not act as u.v. absorbers can stabilize polymers by abstracting the excited state energy from the polymer molecule followed by harmless dissipation. This process is known as energy transfer or quenching. Energy transfer may occur by two important processes: Long range (or Forster) transfer and Collisional (or exchange) transfer. For either process to occur the quencher should reach within quenching distance (about 50°A for long range transfer and 10-15Å for Collisional transfer) of the excited sensitizer within its life time and should possess a high diffusion constant in the substrate. But this process is rather unlikely in the polymer. Heller and Bateman[67] showed that at the concentration of stabilizers used in practice the quenching rate of light stabilizers is

so low that quenching cannot compete successfully with other deactiva-
tion processes of triplet states.   Moreover, for effective quenching
of excited singlet states of primary sensitizer, the additive must
possess an extinction coefficient of more than 5000.

In general this type of stabilization is ascribed to the complex
chelates of the transition metal; usually nickel.   Much of the liter-
ature evidence concerned with this mechanism is contradictory.   It
has been proposed by several workers that reactions of triplet state
carbonyl are of importance in the photodegradation of polyolefins and
that the mechanism of stabilization by reactive stabilizers or quenchers
involve quenching of excited state of carbonyl compounds[68 - 71].   Some
suggest that singlet state oxygen ($1O_2$) is produced by quenching excited
carbonyl impurities which then react with polymer causing photo-
degradation.   Stabilizers quench singlet state oxygen thereby protecting
the polymer[64, 72 - 74].

Most of the conclusions regarding quenching were based more or
less on inference rather than direct experimental evidence.   Moreover
the true importance of excited carbonyl or singlet oxygen involvement
in polyolefin degradation is uncertain in comparison with other photo-
initiation process (as discussed earlier).

1.1.4 Anti-oxidant Synergism

When two or more different types of anti-oxidants are used during polymer auto-oxidations, the resistance of the substrate to oxidation may often be enhanced to an extent which is greater than would be expected based on strict additivity. The anti-oxidants are then said to be synergistic toward one another. The opposite of synergism is termed antagonism. The phenomenon of synergism was first recognized by Olcott and Mattill[75]. The discovery was made in studies of vegetable and animal fats to added anti-oxidants. Greater than the additive effect of a combination of anti-oxidants was observed.

Scott[15] distinguishes two mechanically distinct types of synergism:-

i) Homosynergism, involving two compounds of unequal activity but operating by the same mechanism.

ii) Heterosynergism, arising from the co-operative effect of two or more anti-oxidants acting by different mechanisms.

Both qualitative and quantitative aspects of synergism of such combinations are reviewed by Scott[15] and Reich and Stivala[76].

The mechanism which may be operative in cases of homosynergism (between two chain breaking anti-oxidants of unequal activity) involves the transfer of a hydrogen atom from one inhibitor to another after the latter had lost its active hydrogen to a peroxy radical. In this manner, an efficient anti-oxidant may be regenerated from its oxidation products by a hydrogen donar which is itself a weak anti-oxidant.

Heterosynergism is observed with a wide variety of combinations of preventive anti-oxidants with chain breaking anti-oxidants. The chain breaking anti-oxidants (like arylamine or hindered phenol) retard the formation of peroxides by terminating the kinetic chain promptly, thus effectively eliminating long kinetic chains. However, at least one mole^{cule} of hydroperoxide will be formed in the transfer of hydrogen to a peroxy radical. If the small amount of hydroperoxide formed reacts with a peroxide decomposer to form non radical products, there will be a further reduction in the rate of oxidation. Conversely the preventive anti-oxidant reduces peroxide initiation to a negligible role as a source of free radicals so that the chain breaking anti-oxidant will have fewer kinetic chain to stop and thus can more effectively inhibit the reaction over much longer period of time. It is thus evident that the two anti-oxidants can act in a co-operative manner to give a synergistic effect. A widely used combination of stabilizers for polyolefins is dilaurylthiodipropionate (DLTDP) with 2.6,di-t-butyl-4-methylphenol. Many examples of synergism involving combination of stabilizers including 2-hydroxy-benzophenones as ultraviolet absorbers with either chain breaking anti-oxidants or peroxide decomposers in polyethylene have been reported[15]. The pro-oxidant effect of ultraviolet light which reflects its ability to decompose peroxide to form chain initiating free radicals, can be nullified by a u.v. absorber and thus can reduce the number of kinetic chains to be stopped by the conventional anti-oxidant. Recently Patel and Troth[77] reported that ZnO synergises with various zinc dialkyldithiocarbamate in polyolefins photo-oxidation.

Another important aspect of synergism, known as autosynergism

occurs when two kinds of antioxidant activities are associated in the

same molecule[15].   This explains, for instance, the greater effective-

ness of amine anti-oxidants than the phenolics due to their additional

ability to complex metal ions i.e. the amines not only act as a chain

breaking anti-oxidants but also as a metal ion de-activators.   Carbon

black is also an example of a multi functional inhibitor showing evidence

of reactivity as a free radical trap and hydrogen donar in addition to

its function as a light screen in the stabilization of polymers and its

interaction with iron and other metal ions[78].

Synergistic combinations of additives are of great practical

importance in polymers.   The synergistic combinations cited above are

largely based on an empirical approach rather than from an understanding

of the mechanisms involved.   A better understanding of the function of

synergistic combinations to inhibit or retard oxidative reactions in

polymers (both thermal and photo) requires a more systematic approach

to the problem than has been so far in evidence.   The present investi-

gation represents an attempt to rationalise some of the previously

reported work in this field.

1.2 Scope and object of the present work

Almost all commercial polymers undergo oxidative degradation by

heat and sunlight in the presence of oxygen which is the major cause of

their discoloration, impairment of mechanical properties and subsequent

failure.   Anti-oxidants and stabilizers are normally added to the

polymers to extend their useful temperature ranges and service lives and to permit their use out of doors. Considerable progress has already been made in improving both processing and environmental stability of polymeric materials and the largest contributing factors has been the empirical development of new stabilizing additives and synergistic stabilizing mixtures. The continued development of improved anti-oxidants and synergistic combinations of stabilizers of different types will depend increasingly upon a better understanding of the mechanisms by which these materials function to inhibit or retard the oxidative reactions.

Since the chemical processes occurring during photo-oxidation of polyolefins are basically similar to those occurring during thermal processing operations, the prior thermal history of these polymers will to a major extent determine their behaviour during photo-oxidation. This is again influenced strongly by the presence of anti-oxidants and their effect on subsequent u.v life depends on their function during processing. Studies in these laboratories have shown that hydro-peroxides are the most important initiators for the process of oxidative degradation of polyolefins both during thermal oxidative degradation and u.v initiated degradation[16,17,18]. The main difference between the two processes lies in the rate of initiation step. Therefore, the extent to which hydroperoxides are formed during thermal processing operations will determine the rate of photo-oxidation during the initial stages of light exposure of the polyolefins.

Low density polyethylene (LDPE) and polypropylene (PP) were chosen for the present investigation because of their versatile commercial use in various spheres. One of the purposes of this study is to relate u.v. degradation of the above polymers to the thermal oxidative treatment which is always involved in their manufacture. This has important implications for the mechanism of thermal and u.v. stabilization. In particular the extent to which anti-oxidants and stabilizers have the ability to destroy hydroperoxides will be reflected in their u.v. stabilizing effectiveness.

Metal dialkyldithiocarbamates (particularly Zn and Ni) which are effective melt stabilizers of polyolefins also show remarkable initial effectiveness on photo-oxidation[58, 60]. The effectiveness of the above complexes as u.v. stabilizer is due to their ability to destroy hydroperoxides in a catalytic process. It is therefore, of both theoretical and practical interest to compare the behaviour of this type of u.v. stabilizer with other types of u.v. stabilizers and anti-oxidants both alone and in combination with one another.

Recent studies[60] suggest that 2-hydroxy-4-octyloxybenzophenone (code name u.v. 531), a typical u.v. absorber, also functions by other mechanisms in addition to u.v. screening. Based on this knowledge, the effect of this compound in LDPE and PP as well as in model systems was selected for study in detail under the condition of u.v. exposure in order to explain the mechanism of its functions.

Although in general terms it is known that synergism results from the operation of two or more complementary stabilization mechanisms, relatively little systematic work has so far been done to determine the individual contribution of synergists in u.v. stabilization as opposed to thermal stabilization of polyolefins. Synergism between anti-oxidants and "u.v. absorber" was therefore investigated in low density polyethylene and polypropylene and the results were co-related in model compound studies in an attempt to explain the mechanism of synergistic action.

The anti-oxidant action of a substituted piperidine (Trade name Tinuvin 770, produced by Ciba-Geigy) both in thermal and photo-oxidation of LDPE and PP either alone or in combination with other anti-oxidants and stabilizers were also studied and the results were compared with other stabilizer systems.

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF METAL CHELATES

USED AS ADDITIVES AND GENERAL EXPERIMENTAL TECHNIQUES

2.1 Preparation and characterization of metal chelates used as additives

2.1.1 Preparation of nickel and zinc diethyldithiocarbamates.

$$[(C_2H_5)_2NCS_2]_2M \quad M = Ni \text{ or } Zn$$

Preparative reaction:

$$M(SO_4) + [(C_2H_5)_2N\text{-}CS_2Na]$$
$$\rightarrow [(C_2H_5)_2N\text{-}CS_2]_2M + Na_2SO_4$$

The diethyldithiocarbamates of zinc and nickel were prepared by double decomposition of a 10% solution of the corresponding sodium salt (ex Robinson Brothers) with a saturated solution of the transition metal sulphates.

2.1.2 The following amine complexes were prepared from zinc diethyldithiocarbamates (ZnDEC):

i) n-Butylamine $nC_4H_9NH_2$

ii) Sec-Butylamine $CH_3CH(NH_2)CH_2CH_3$

iii) tert-Butylamine $(CH_3)_3CNH_2$

iv) Di-n-Butylamine $(C_4H_9)_2NH$

v) Di-(2ethylhexyl)amine $(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}CH_2)_2NH$
$$\qquad\qquad\qquad\qquad\qquad C_2H_5$$

vi) Di-nonylamine $(C_9H_{19})_2NH$.

In the case of nickel diethyldithiocarbamate, complexes with sec-butylamine and tert-butylamine were prepared.

Preparation of amine complexes[79]:

To a solution of the amine (0.03 mole) in benzene (20-40 ml) at 50°C was added in portions, the powdered metal diethyldithiocarbamate (0.02 mole). After cooling the resulting solution, 100 ± 20 ml of light petroleum (b.p. 40-60°C) was added. The products crystallised, and were collected, washed with light petroleum and dried in air.

Characterization:

The composition of the Zn(II) and Ni(II) complexes were found to be 1:1. Details of C, H, N and S analysis are shown in Table 2.1. The structure of the amine complexes were confirmed by I.R. spectroscopies studies. The complexes either as solid or in solution are characterized by bands in the N-H stretching region. These are considerably more intense than bands in the corresponding amines and in general absorption occurs at lower frequency than the corresponding amines[79]. Complexed primary amines show N-H stretching absorption bands at 3300 cm^{-1} and 3240 cm^{-1} respectively, indicating a shift of about 160 and 140 cm^{-1} respectively on complex formation. The N-H deformation band of the complexed amines occur at 1580 cm^{-1} which also shows a shift of about 30 cm^{-1} towards lower frequency.

Secondary amine complexes show N-H stretching absorption at 3240 cm^{-1} again indicating a shift on complex formation. The position of many bands in the spectra of metal diethyldithiocarbamate are shifted in the presence of amines.

TABLE 2.1

Compound	Molecular formulae	Mol. wt.	M.P.	Theoretical %C, %H, %N, %S				Experimental %C, %H, %N, %S			
Zinc diethyldithiocarbamate	$C_{10}H_{20}N_2S_4Zn$	363	176°C	33.05,	5.5,	7.7,	36.36	33	6.0,	7.2,	35.8
n-Butylamine-ZnDEC	$C_{14}H_{31}N_3S_4Zn$	436	75°C	35.53,	8.53,	9.63,	30.27	37.85,	8.21,	8.92,	29.98
Sec-Butylamine-ZnDEC	$C_{14}H_{31}N_3S_4Zn$	436	95–96°C	38.53,	8.53,	9.63,	30.27	37.91,	7.85,	8.83,	29.83
tert-Butylamine-ZnDEC	$C_{14}H_{31}N_3S_4Zn$	436	162–163°C	38.53,	8.53,	9.63,	30.27	38.13,	7.99,	9.03,	29.45
Di-n-Butylamine-ZnDEC	$C_{18}H_{39}N_3S_4Zn$	492	52°C	43.90,	7.92,	8.53,	26.82	44.11,	6.97,	8.41,	25.73
Di-[2-ethylhexylamine]ZnDEC	$C_{26}H_{55}N_3S_4Zn$	604	59–60°C	51.65,	9.10,	6.95,	21.85	51.02,	8.67,	6.56,	20.90
Di-nonylamine-ZnDEC	$C_{28}H_{59}N_3S_4Zn$	632	64°C	53.16,	9.33,	6.64,	20.88	53.82,	8.88,	6.26,	19.38
Nickel diethyldithiocarbamate	$C_{10}H_{20}N_2S_4Ni$	359	225°C	33.42,	5.57,	7.94,	36.76	33.28,	5.03,	7.62,	37.04
Sec-Butylamine-NiDEC	$C_{14}H_{31}N_3S_4Ni$	432	155°C	38.88,	7.17,	9.72,	30.55	37.93,	7.46,	8.91,	29.99
tert-Butylamine-NiDEC	$C_{14}H_{31}N_3S_4Ni$	432	202°C	38.88,	7.17,	9.72,	30.55	37.69,	7.56,	9.02,	28.83

2.1.3 In addition to the above metal dialkyldithiocarbamates and dithiocarbamate-amine complexes, the following complexes were also used as additives in LDPE and polypropylene (supplied by Robinson Brothers).

	Observed melting point
a) Zn[N-lauryl]dithiocarbamate	48 - 50°C
b) Zn[Di-hydrogenated Tallow]dithiocarbamate	41 - 42°C
c) Zn[N-oleyaminopropyl]dithiocarbamate	68°C
d) Zn[N-cocylaminopropyl]dithiocarbamate	63 - 65°C

2.1.4 The following commercially available additives were used as stabilizers in low density polyethylene and polypropylene.

a) 2-hydroxy-4-octyloxybenzophenone (trade code UV531), supplied by American cyanamid).

b) A phenolic anti-oxidant, n-octadecyl-3-(3',5'-di-tertbutyl-4'hydroxy-phenyl) propionate [Trade code Irganox 1076, supplied by Ciba-Geigy].

c) A substituted piperidine compound, Bis[2.2.6.6-tetramethyl piperidinyl-4) sebacate, [Trade name Tinuvim 770, Produced by Ciba-Geiby and supplied by Hercules Incorporated].

2.2 Purification of Solvents and reagents

2.2.1 Cumene

Technical grade cumene was washed with concentrated sulphuric acid, sodium bicarbonate and finally with water and was then dried, before fractionally distilling under nitrogen. The fraction boiling at 152°C was collected and stored at 5°C in a well-stoppered flask. (b.p.152°C/760 mm)[80].

2.2.2 Cumene hydroperoxide

Cumene hydroperoxide stabilized with 6% of 15% w/w slurry of aqueous Na_2CO_3 was purified by a modification of Kharasch's method[81]. 50gm(1.25 mole) of caustic soda in 100 ml of water was added to 152gm (1.0 mole) of hydroperoxide in ligorin at 0°C. The sodium salt was filtered, washed with 25% caustic soda solution, then with petroleum ether, and suspended in 500 ml of water. A stream of carbondioxide was bubbled through the suspension and when all the hydroperoxide has been reliberated the solution became opaque, and separated into two layers. The lower aqueous layer was extracted three times with pet-ether and the combined ethereal fraction was washed with dilute sodium carbonate solution and dried over anhydrous sodium carbonate. After removal of solvent the product was distilled at 52-55°C/0.01 mm. Hg, as a colourless liquid; purity by iodometric titration was better than 99%.

2.2.3 Other solvents and reagents:-

Chlorobenzene was fractionated from phosphorous pentoxide and the fraction boiling at 132°C collected.

Benzene (A.R.) was distilled over P_2O_5.

Carbontetrachloride, cyclohexane and hexane were all of spectroscopic grade and used without further purification.

Benzophenone:- recrystallised from 1:1 mixture of benzene and ligorin (m.p. 47°C).

2.3 General Experimental Techniques

In this Chapter materials and general experimental methods are described which were used throughout the course of this work. Other specific experimental methods used are described in the relevant chapters.

2.3.1 Materials

The polymers used were:

i) Low density polyethylene (LDPE) in granular (bead) form containing no anti-oxidant and identified as 'Alkathene' Polyethylene WJG 47 supplied by Imperial Chemical Industries Limited. The polymer was of 0.918 gm/cm^3 density and of melt flow index 2.0 originally. It possessed the characteristic properties of good toughness and flexibility and is used commercially.

ii) Unstabilized polypropylene (PP) in powder form identified as 'Propathene' HF 20C, CV 170 supplied by Imperial Chemical Industries Limited.

All the polymers were stored in the dark at 0°C.

2.3.2 Processing of the polymers in the RAPRA Torque-rheometer

Polymers (both low density polyethylene and polypropylene) were processed using the prototype RAPRA Torque-rheometer[82], which is

essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds. Two rotor speeds are available ('high' and 'low' speed). Most of the processings were done using high speed which corresponded to 60 rev/min. It has a good temperature control and a continuous readout is provided of both melt temperature and the torque required for mixing. The chambers may be operated either open to the atmosphere or sealed by a pneumatic ram. A full charge was calculated out for each polymer according to its density, and when this charge was used the chamber was sealed. When it was desired to process in the presence of air, a charge of about 20 gm was employed, and the chamber was left open to the atmosphere.

The additives were mixed with the polymers at room temperature by tumble mixing for one hour before processing in the Torque-rheometer. Generally the processing temperatures were 150°C and 180°C respectively for low density polyethylene and polypropylene. On completion of mixing, the polymer sample was rapidly removed and quenched in cold water to avoid further uncontrolled thermal oxidation.
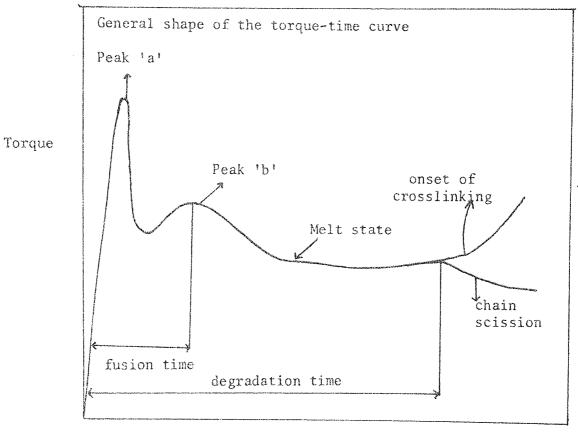
2.3.3 Preparation of films from processed samples:

Polymer films for spectroscopy examination were prepared by compression moulding. The appropriate weight of processed polymer was compression moulded using a special grade of cellophane as a mould releasing agent between two stainless steel glazing plates. Control of film thickness was achieved by using a definite amount of material; about 6 - 7 gm of material was found to produce film of approximately 2.03×10^{-2} cm (.008 inch) thickness. The weighed amount of polymer

material was placed between the glazing plates in two cellophane sheets
and inserted into the press. The temperature of the platen was main-
tained at 150°C and 180°C respectively for low density polyethylene and
polypropylene. The platen was closed and 1 - 2 minutes was allowed
for the material to heat up and soften during which time the pressure
on the 6 inches ram was increased from 0 - 10 tons. The pressure was
then slowly raised to the maximum (28 tons/6" ram) over a period of
one minute and left at full pressure for a further two minutes. The
platen was then cooled to about 50°C by running cold water while main-
taining full pressure. The plates were then removed from the press
and the films were stored in the dark at 0°C. The thickness of each
film over its entire area was measured with a micrometer in order to
select portions of uniform thickness.

2.3.4 Evaluation of torque versus time curve.

Idealized torque vs processing time curve[83] is illustrated
in Fig. 2.1. When the polymer is introduced into the torque rheometer
the torque rises sharply. The polymer is heated and when it reaches
its glass transition temperature (Tg) it becomes rubbery. The torque
then decreases and reaches a minimum which gives rise to a peak "a"
(Fig. 2.1). This stage is followed by the gelation of the material.
The polymer starts to melt causing the torque to increase. When the
melting (or gelation) is completed the torque decreases again giving
rise to a peak 'b'. The time to reach the peak 'b' is called fusion or
flux time. The fusion time for a particular polymer depends mainly on
mechanical stress, temperature and the presence of additives. Cross -
linking or chain scission of polymer is also reflected from torque vs
processing time curve.

General shape of the torque-time curve

Peak 'a'

Torque

Peak 'b'

onset of
crosslinking

Melt state

chain
scission

fusion time

degradation time

t(time) of processing

Figure 2.1

2.3.5 Determination of gel content in the processed polyethylene samples:-

Gel content in the processed low density polyethylene samples were determined in p-xylene at 90°C. 0.5 gm of polymer films (in small pieces) was placed in the Erlenmeyer flask and 50 ml of p-xylene was added. After heating for 30 minutes at 90°C, the solution was filtered hot. Gel was collected and vacuum dried to constant weight.

2.3.6 Measurement of MELT FLOW INDEX (MFI)

Melt flow index was determined on low density polyethylene samples which have been processed with or without additives. The apparatus used was the Davenport polythene grader .

The melt flow index (MFI) is defined as the amount of polymer in grammes extruded through a standard die in a given time (e.g. 10 minutes). It is an inverse measure of melt viscosity of the polymer which is again related to the molecular weight. The melt flow index decreases as the molecular weight of the polymer increases. The appropriate relation-ship of MFI with molecular weight ($\bar{M}n$) and melt viscosity ($\eta*$) are given by the following two equations respectively (in case of LDPE)[84].

$$\bar{M}n = 188 - 30 \log MFI$$

$$\eta*(poise) = 7.5 \times 10^4 \frac{1}{MFI}$$

Since thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such reactions as chain-scission, cross linking

etc. such changes are expected to be reflected in the melt flow index values. Hence melt flow index measurement provides a mean of detecting any oxidation which may occur during heat treatment of the polymer.

The apparatus was brought to a steady extrusion temperature of 190° ± 0.5°C before beginning an experiment. The barrel was then charged with 4.5 gm of polymer, tamping down with the charging tool to exclude air. The time taken to charge the barrel should not exceed one minute. The barrel was closed airtight and nitrogen gas was passed from the cylinder to the barrel. The pressure of nitrogen gas was maintained at 160 lb/in^2 and the polymer was allowed to extrude through 0.2095 cm diameter die. The extrudate was cut with a suitable sharp-edged instrument. The time interval for the first extrudate was 60 seconds and was discarded; then five successive cut-offs were taken each at the end of 30 seconds; any cut-off that contained air bubbles was rejected; each cut-off was weighed separately and their average weight was determined.

2.3.7 Gel permeation chromatography:-

Molecular weight changes during thermal degradation of low density polyethylene have usually been explained by chain scission or cross linking[85]. The study of competitive cross linking and chain scission reactions is facilitated by the use of G.P.C.

A chain scission process shifts the molecular weight distribution (MWD) to lower molecular weight. A molecular enlargement will be observed as an increase of the high molecular weight tail. Molecular

weight and molecular weight distribution (MWD) for the processed low density polyethylene samples were obtained using G.P.C. and were kindly carried out by the Polymer Supply and Characterization Centre of RAPRA. Experimental conditions used were as follows:-

Solvent - o-dichlorobenzene plus 0.1% Ionox 330 as anti-oxidant

temperature:- 138 - 140°C, Columns:-One each of 4ft x 3/8 inch connected in series 1000A° styragel, 3×10^4A°, 5×10^4A°, 10^6A°. Flow rate - 1 ml/min. Polystyrene standards supplied by Waters associates was used for calibration and Mark-Houwink constants($[n]=KM^a$) used for conversion of calibration. Polystyrene K = 1.38×10^{-4}, a=0.70

LDPE, K = 5.06×10^{-4}, a = 0.70.

Molecular weight distribution curves were obtained by the plot of dw/dlogM versus logM.

2.3.8 Estimation of hydroperoxide in model systems:-

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

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

Dialkyl peroxides too can oxidize the iodide to iodine, but slowly. The conditions used are important and many modifications of this procedure have been published. The method used in this work is the modified procedure adopted by Mair and Graupnor[86] of the method by Wagner, Smith and Peters[87].

The medium of the reaction is isopropanol containing glacial acetic acid, and sodium iodide is used as the source of iodide instead of potassium iodide.

This method has the following advantages:-

1. The use of sodium iodide in place of the potassium salt, due to its greater solubility will keep the equilibrium

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

far to the right with the result that

a) the loss of liberated iodine due to purging or boiling

is prevented as the tri-iodide ion is involatile.

b) the tri-iodide ion will not add to the double bonds so

that errors due to unsaturation are eliminated.

2. The use of isopropanol as solvent and the absence of strong acids eliminates atmospheric oxidation of the iodide,

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

Reagents:-

10% (V/V) acetic acid: isopropanol (A.R grade) containing less than 0.1% water

20% (W/V) sodium iodide in isopropanol

Sodium thiosulphate (0.01N).

Sodium thiosulphate was prepared with boiled filtered water, stabilized with a few drops of chloroform and stored in flasks covered with aluminium foil. The exact strength of thiosulphate was determined using a standard solution of potassium iodate.

Method:- To 25 ml of 10% acetic acid in isopropanol was added 0.5 ml of the solution under test. This was refluxed for five minutes, allowed to cool. Then five to ten millilitres of water was added and the liberated iodine was titrated against 0.01N sodium thiosulphate.

2.3.9 Estimation of peroxide in low density polyethylene and polypropylene:

a) Chemical Method:- Iodometric method based on the oxidation of sodium iodide was used. Liberated molecular iodine was determined by titration with standard 0.01N sodium thiosulphate. The method used by Manasek-et al.[88] and Geddes[89] was modified as follows:- 0.5 - 1 gm of polymer film (in small pieces) was introduced into 21.7 ml (approx) of chloroform and purged with nitrogen for half an hour. This was then allowed to swell for 18 hours (this time was determined to give a maximum hydroperoxide concentration), 3.3 ml of glacial acetic acid was then added and the solution was purged with nitrogen for five minutes before and after addition of 2 ml of a freshly prepared deaerated 5% solution of sodium iodide in methanol. In addition to deaeration during carrying out hydroperoxide determination, all solvents were also deaerated in bulk prior to use with nitrogen gas and the procedure using rubber seals was employed. After storage for four hours (low density polyethylene) and two hours (for polypropylene) in the dark for complete reaction, the liberated iodine was titrated using standard 0.01N sodium thiosulphate.

b) I.R. Method:- Thermally oxidized low density polyethylene gives a sharp band in the I.R. spectra at 3555 cm^{-1} which is due to O-H stretching of free hydroperoxide[90-92]. This band was measured as index (defined as A_{3555}/A_{1895}). No such sharp band was found in polypropylene. A very good co-relation was found between hydroperoxide measured chemically and hydroperoxide measured by the I.R. method in the case of low density polyethylene (Fig. 2.2).
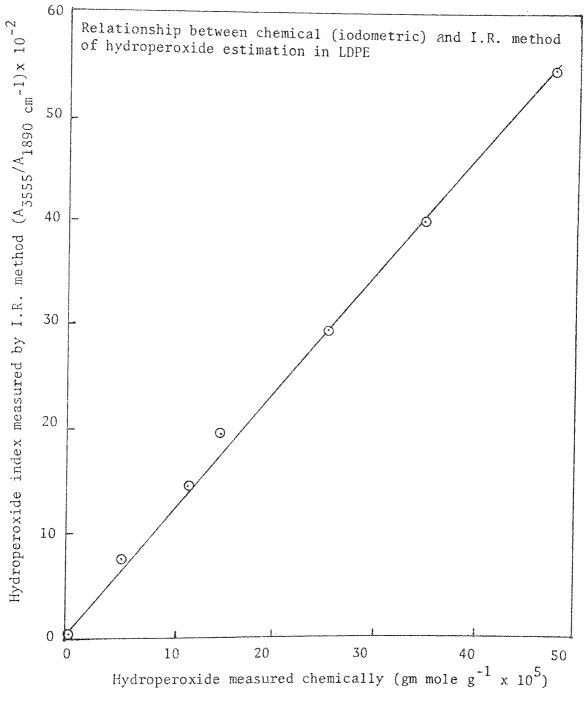
Figure 2.2

2.3.10 Ultraviolet cabinet:

U.V. irradiation of the samples were carried out in the
ultraviolet cabinet. Ultraviolet cabinet comprised of a metal cylinder
of about 110 cm in outer diameter and having a concentric circular
rotating sample drum whose circumference was 15 cm from the periphery of
the metal cylinder (Photograph No.1). 32 fluorescent tube lamps were
mounted on the inside face of the cylinder. The rotating arrangement
of the samples allows an identical amount of total radiation to fall on
every sample. The cylindrical cabinet was opened to the atmosphere on
both, the lower and upper sides, and the circulation of the air in the
cabinet was ensured by the driven ventilator situated under the rotating
frame.
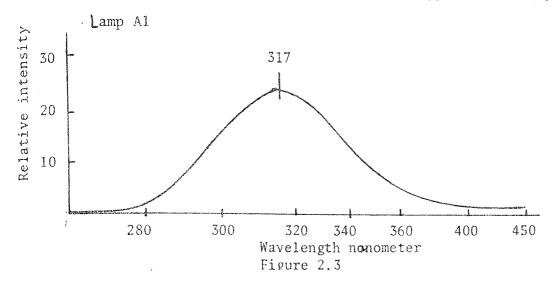
The samples were attached to a separately made hard brown paper-
board with aluminium foil backing which was mounted vertically on the
circumference of the rotating wheel fixed inside the cabinet. In this
position the light beam fell perpendicularly on the surface of the film.
The temperature recorded inside the cabinet with the lamp on was 29±1°C.

The radiation source consisted of the cylindrical array of 20W fluor-
escent tube lamps, positioned on the inner side of the cabinet. 24
lamps type C (Philips actinic blue 05) and 8 lamps type A1 (Westinghouse
sunlamps FS20) were used and these were symmetrically distributed so
that the combination was one lamp type A1 for every three lamps of type
C. The spectral distribution of both types of lamps used is shown in
Figs. 2.3 and 2.4 for the lamp A1 and lamp C respectively. The maximum
in the relative intensity of the lamp A1 is at 317 nm and of the lamp C

PHOTOGRAPH NO. I

Spectral distribution of fluorescent lamp type A1 (Westinghouse Sunlamp FS20)

Wavelength nonometer
Figure 2.3

Spectral distribution of flourescent lamp type C (Philips Actinic Blue 05)

Wavelength nonometer
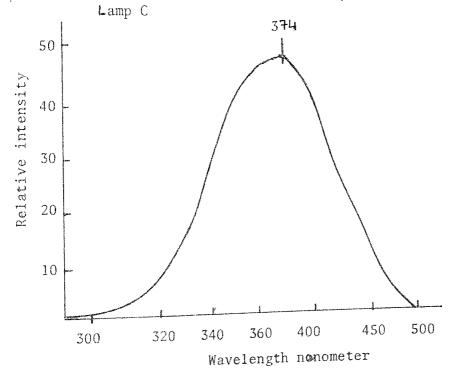
Figure 2.4

at 374 nm.   The available wavelength with the above combination of lamps was between 280 nm - 500 nm and the radiation intensity I_o at the sample surface was I_o = 44.3W/m^2.

To minimise the problem of decline in lamp output, the tubes were replaced sequentially every 2000 hours of exposure.

2.3.11 The accelerated thermal oxidations of processed polymers were carried out in a Wallace oven at 110°C.   This has separate seven cells and has very good temperature control.   There is an arrangement for controlling air flow through the cells.   Each sample film was contained in a separate cell. Air flow rate was maintained at 4 C.F.H

2.3.12.   Measurement of brittle fracture time of polymer samples:

This is a destructive test method.   Films of identical size and of uniform thickness containing different additives along with a control were irradiated and were periodically checked and their times to embrittlement were determined by folding the film back on itself 180° manually.

2.3.13 Infra-red Spectroscopy:

All the infra-red spectra were recorded using a Perkin Elmer grating infra-red spectrophotometer Model 457.   The spectra from 4000 cm^{-1} to 250 cm^{-1} were recorded at medium scan speed.

Infra-red spectroscopy has been widely used to determine the nature of oxidation products,and rate of formation of these products during

thermal and photo-oxidation of polyolefins.   It is a non destructive
test and particularly useful for quantitative purposes since the same
test sample can be used repeatedly.

Since thermal and photo-oxidation of polymers result in the build
up of different oxidation products for example, hydroxyl, carbonyl,
carboxyl, vinyl etc. the kinetics of the growth of these functional
groups, as the irradiation proceeds have been followed by observing the
changes in the characteristic absorption peaks at different wave length,
and these were assigned by a comparison with the values for long chain
ketones, aldehydes, acids, esters etc.[90].

Procedure:-

In all quantitative analysis the following combined form of Beer-
Lambert equation was used[93].

$$A = \log_{10} I_0/I = ECl$$

where

A = Absorbance or optical density

I_0 = Intensity of radiation effectively

entering the sample

I = Intensity of radiation emerging

from the sample

E = Extinction coefficient expressed in

litres $mole^{-1}$ cm^{-1}

C = Concentration of absorbing group

present in the sample mole/litre.

l = Path length of radiation within the

sample in cm.

The samples were exposed for regular intervals of time and the spectra were run on the same chart paper for comparison purposes.

To minimise errors due to variation in film thickness as well as errors due to the instrument, an internal standard, a characteristic absorption peak at 1895 cm^{-1} for low density polyethylene and 905 cm^{-1} for polypropylene were used. Those peaks remained constant during irradiation. The growth or decay of observed absorption peaks (for functional groups) were expressed as indices which were defined as the ratio of the absorbance of functional group peaks to that of the reference peak.

$$\frac{\text{Absorbance of the functional group}}{\text{Absorbance of a standard peak}}$$

Calculation of absorbance:-

The base line technique[94] was used to calculate the optical density or absorbance due to various functional groups. This was done as shown in (Fig. 2.5) by drawing a straight line (base line) tangential to adjacent absorption maxima or shoulders, then erecting a perpendicular through the analytical wave length until it intersects the base line. At 'A' the concentration of the functional group to be determined is zero and at 'B' there appears an absorption peak whose height serves to calculate the concentration. Before putting the sample in, the spectrophotometer was adjusted to read 100% transmission and this was known as background line.

However, with an absorption such as shown in (Fig. 2.6), the proper location of base line is less obvious, but in the present work to determine
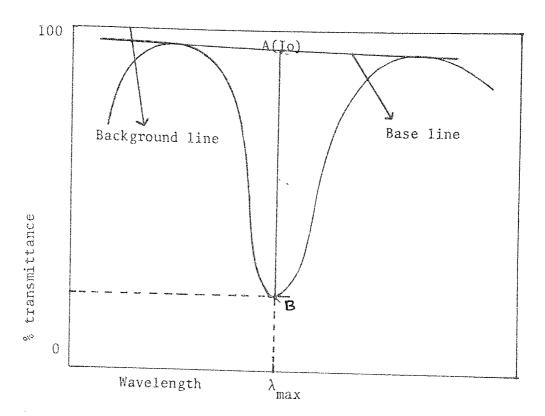
Figure 2.5
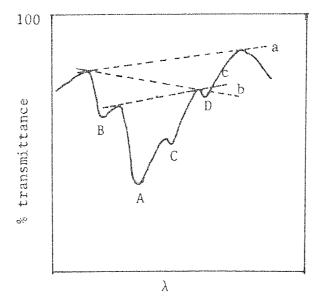
Figure 2.6

the absorbance of peak 'A', the base line is taken to be either a, b or c depending on the width of the shoulders B, C and D.   If all three shoulders B, C and D are narrow, 'a' is used as the base line and so on. And in this situation which frequently occurs, one particular way to draw the line is adopted in all the samples for the same functional group.

2.3.14 U.V.Spectroscopy:

Ultraviolet spectra of polymer films with additives and all solution spectra were recorded using Perkin Elmer 137 Ultraviolet visible spectrophotometer.   For obtaining compensated spectra of films containing additives, a film of unprocessed polymer of identical thickness without additive was used in the reference beam.   U.V. absorption maxima of the additives in the film was always compared with the absorption maxima of the additives in solution (e.g. carbontetrachloride, cyclohexane, hexane etc.) and it was found that they corresponded closely with one another (Figs. 2.7 - 2.9).   In case of solution, the spectra were recorded using quartz cells of 10 mm and/or 1mm path length with the pure solvent in the reference beam.

2.3.15 Actinometry.

A chemical actinometer was used to measure the intensity of ultra-violet light.   An actinometer contains a photo-sensitive chemical substance which undergoes chemical change on exposure to light, the magnitude of this change or the extent of decomposition depending on the intensity of the light absorbed.

Until recent years the most widely used actinometer was Uranyl

Ultra-violet spectra of HOBP in cyclohexane and in LDPE film

HOBP in LDPE film

HOBP in cyclohexane solvent

Absorbance

200   250 Wavelength(Millimicrons)   300   350

Figure 2.7

- 55 -

Ultra-violet spectra of NiDEC in cyclohexane solvent and in LDPE film

NiDEC in LDPE film

NiDEC in cyclohexane solvent

Wavelength(Millimicrons)

Figure 2.8

Ultra-violet spectrum of ZnDEC in cyclohexane solvent and in LDPE film.

ZnDEC in LDPE (film)

ZnDEC in cyclohexane solvent

Absorbance

Wavelength (millimicrons)

Figure 2.9

oxalate[95]. But today this has been superceded by potassium ferri-oxalate system developed by Parker and Hatchard[96-98]. It can be used over a wide range of wave lengths and is one thousand times more sensitive than Uranyl oxalate.

The photolyte consists of a solution of potassium ferri-oxalate, $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ in 0.1N H_2SO_4. In acid solution the trioxalato-ferric ions are largely dissociated into monoxalate and dioxalate complexes. On exposure to light the following reactions occur:

$$[Fe(C_2O_4)]^+ \xrightarrow{h\nu} Fe^{2+} + (C_2O_4)^- \qquad (1)$$

$$(C_2O_4)^- + Fe(C_2O_4)^+ \longrightarrow 2CO_2 + Fe^{2+} + (C_2O_4)^{2-} \qquad (2)$$

The product Ferrous ion (Fe^{2+}) so produced is converted to its 1,10-phenenthroline complex and the latter determined absorptiometrically. It is a stable complex and has a strong absorption peak at 510 nm.

Procedure:- The preparation of potassium ferri-oxalate was carried out by mixing three volumes of 1.5 molar A.R. potassium oxalate with one volume of 1.5 molar A.R. Ferric-chloride with vigorous stirring. The precipitated potassium ferri-oxalate was recrystallised thrice from warm water, and dried at 50°C. The green crystals were stored in the dark. The 0.006M actinometer solution was prepared by dissolving 2.957 gm of the crystals in 800 ml of water, to this 100 ml of 0.1N sulphuric acid was added, and the solution was diluted 1 litre and mixed. This solution was kept in an amber bottle in a dark room.

To determine the incident light intensity of the u.v. light source, a known volume V_1 of 6×10^{-3} molar acidified solution of potassium ferri-oxalate was irradiated in a 4 cm path length cell for t seconds. The solution was stirred during exposure with a current of nitrogen to prevent air oxidation of ferrous ions. After irradiation, a known volume V_2 was pippetted from the irradiated solution into a small volumetric flask V_3, to which was added in succession about 2 ml of 0.1% 1, 10-phenathroline solution, 5 ml buffer solution (made from 600 ml 1.0N Na-acetate and 360 ml of 1N-sulphuric acid) and diluted with water up to the neck. The solution was mixed well and was allowed to stand for 1 hour in the dark. An identical solution for use as blank in the reference beam was prepared using unirradiated solution and was allowed to stand as before. The optical density of the solution was measured at 510 nm using 1 cm cell with a spectrophotometer (P.E. 137), with the blank solution in the reference beam.

The number of ferrous ion (nFe^{2+}) formed during photolysis was then determined from the following relation

$$nFe^{2+} = \frac{\log_{10} \frac{I_0}{I} \times V_1 \times V_3 \times N}{V_2 \times \ell \times E_\Lambda}$$

where

V_1 = volume of actinometer solution irradiated (ml)

V_2 = volume of aliquot used for analysis (ml)

V_3 = final volume to which aliquot volume was diluted (ml)

N = Avogadro's number i.e. 6.023×10^{23}

E_Λ = The experimental value of the molar extinction coefficient of Fe^{2+} complex as determined from the slope of the calibration plot.

The extinction coefficient E_Λ was determined by using a very dilute solution of $FeSO_4$ (i.e. 0.4×10^{-3} M/L) in 0.1N H_2SO_4 and its value was found to be 1.1×10^4 litre $mole^{-1}$ cm^{-1}.

Thus knowing nFe^{2+} from the above equation, the value of quantum yield for Fe^{2+} ion formation (QFe^{2+}) was selected from the table of Parker[97] ($QFe^{2+} = 1.22$).

The intensity of incident light I_0 was calculated using the equation

$$I_0 = \frac{nFe^{2+}}{QFe^{2+} \times t \times (1-10^{-a\ell})}$$

where a = concentration of ferri-oxalate solution.

Thus knowing nFe^{2+} and QFe^{2+}, I_0 can be calculated.

CHAPTER 3

THE EFFECTS OF THERMAL PROCESSING ON THE THERMAL

OXIDATIVE AND PHOTO-OXIDATIVE STABILITY OF POLY-

OLEFINS

3A.   Low density polyethylene (LDPE)

The simplest structure for unbranched and linear polyethylene is represented by the formula

$$CH_3 - (CH_2 - CH_2)_n - CH_3$$

This structure is not closely maintained by polyethylene prepared by the usual commercial process.   It contains not only methylene groups but also several methyl groups per molecule, the latter (CH_3 group) being associated with branching in the molecule.   Investigation of low density polyethylene prepared by high pressure processes using infra-red spectroscopy[99] indicates the presence of about 20 to 30 methyl groups per 1000 carbon atoms.   The quantitative determination of methyl content based on the measurement of the intensity of absorption band at 1378 cm^{-1} (7.26) was reported by Cross, Richard and Willis[100].   From their results it was shown that a typical LDPE of molecular weight 32000 and MFI 1.8 contained 23 methyl groups per 1000 carbon atoms and 52 methyl groups per molecule.   This indicated about 50 branch points in the chain. Although the presence of branches in LDPE has been established, the length of such branches is still under debate.   It is generally assumed that both short and long branches are present in polyethylene.   According to

Fox and Martin[101] branching was assumed to be methyl. Elliot et al[102] suggested that the branches were longer than the methyl groups. Later work by a number of workers[103,104] on careful quantitative analysis of I.R. spectra of low density polyethylene indicated the presence of ethyl and butyl branches in the polymer. There is no doubt that branching in polyethylene, whatever their nature, greatly effects the physical and chemical properties of the polymers. The short chain branches are known to give a low degree of crystallinity in the polymer[105], since branches prevent the close approach of molecules in the unit cell. Other properties like density, melting point, modulus, yield stress, elongation at break, permeability to gas and vapours etc. are also dependent on short branching. The long chain branching mainly affects the rheological properties (viscosity, MFI, etc.) and leads to broad molecular weight distribution.

In addition to branching, low density polyethylene also contains unsaturation. Three different olefinic double bonds namely terminal or vinyl group ($RCH=CH_2$ absorbs at 909 and 1640 cm^{-1} in the infra-red spectrum), internal or chain double bond ($RCH=CHR'$, absorbs at 964 cm^{-1}) and vinylidene or side chain methylene groups ($R_1R_2C=CH_2$ absorbs at 888 cm^{-1}) are found to be present in LDPE. The distribution of different types of unsaturation in a polyethylene sample was determined by Rugg et al.[103]. The results were 1.4% (C=C by weight) as $R_1R_2C=CH_2$, 0.5% as $RCH=CHR'$ and 0.5% as $RHC=CH_2$ out of total 2.4% unsaturation.

Oxygen containing groups viz peroxide and carbonyl are also found to be present in LDPE which are inadvertently formed by thermal oxidation during polymerization or during subsequent processing.

Thus it appears that the main structural features in low density polyethylene which largely determines its reactivity towards light, heat, oxygen as well as other physical and chemical behaviour are vinylidene unsaturation, chain branching and oxygen containing functional groups.

3.A.1. Evaluation of physical and chemical changes occurring in LDPE under processing conditions

3.A.1.1 Experimental

Processing:-

Low density polyethylene was processed at three different temperatures (viz. 150°C, 165°C and 175°C) in the RAPRA-torque rheometer for various length of time under three different conditions, (a) half full chamber (20 gms of polymer) with the chambers open to the atmosphere, (b) full chamber (35 gms of polymer) with the chamber closed after purging with argon (i.e. in an oxygen deficient atmosphere) and (c) the polymer was heated without processing but at the processing temperature in an argon atmosphere. The polymers were then compression moulded at 150°C for two minutes into sheets of thickness 0.008 inch as described in the experimental Chapter (Section 2.3.3).

Melt flow index, gel content, molecular weight distribution, hydroperoxide content and carbonyl formation of processed low density polyethylene samples were determined as described in the experimental section (Chapter 2).
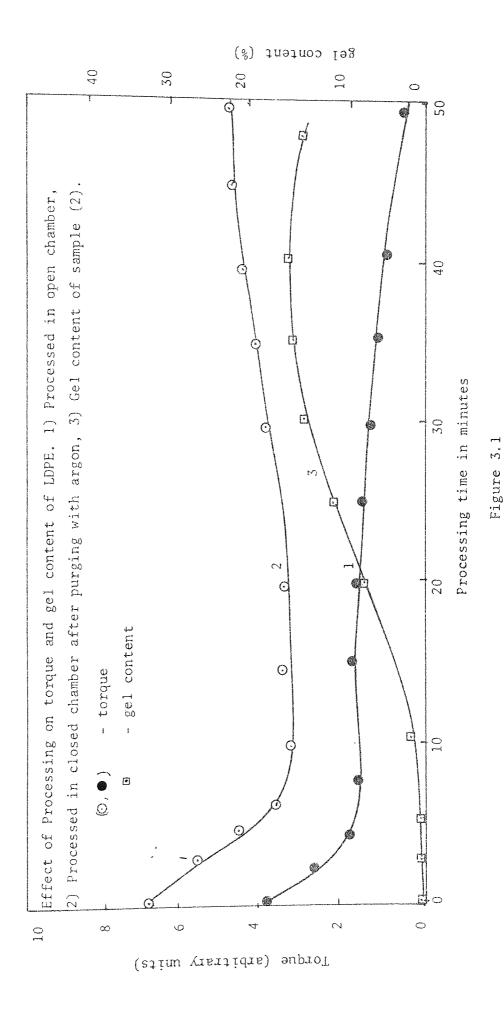
3.A.1.2. Results
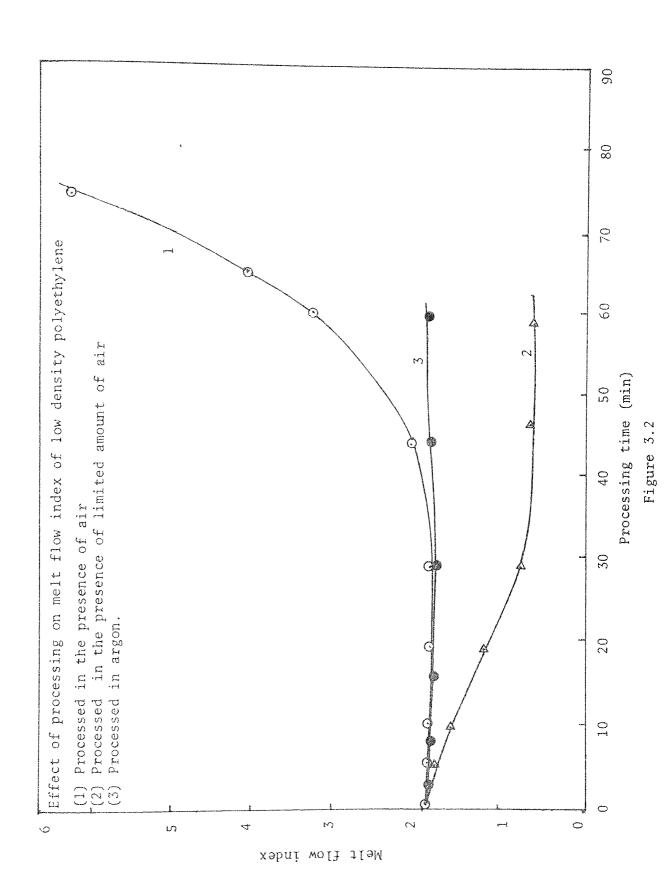
The change in applied torque with time during the processing of low density polyethylene in the RAPRA torque-rheometer at 150°C is shown in the figure 3.1. Curves 1 and 2 represent the change in torque of LDPE processed in the open chamber and closed chamber respectively. Solvent insoluble gel (in P-xylene at 90°C) was determined in poly- ethylene samples processed in the closed chamber i.e. in presence of less air. No gel was found in the LDPE samples processed in the open chamber i.e. in presence of excess air. Figure 3.1 (curve 3) also relates the formation of solvent insoluble gel in the polymer to the applied torque in the mixer. Two distinctly different processes are observed, in the open chamber torque decreases after an induction period and no gel was detected in this sample, whereas torque increases with time and gel was found when the polymer was processed in the closed chamber.
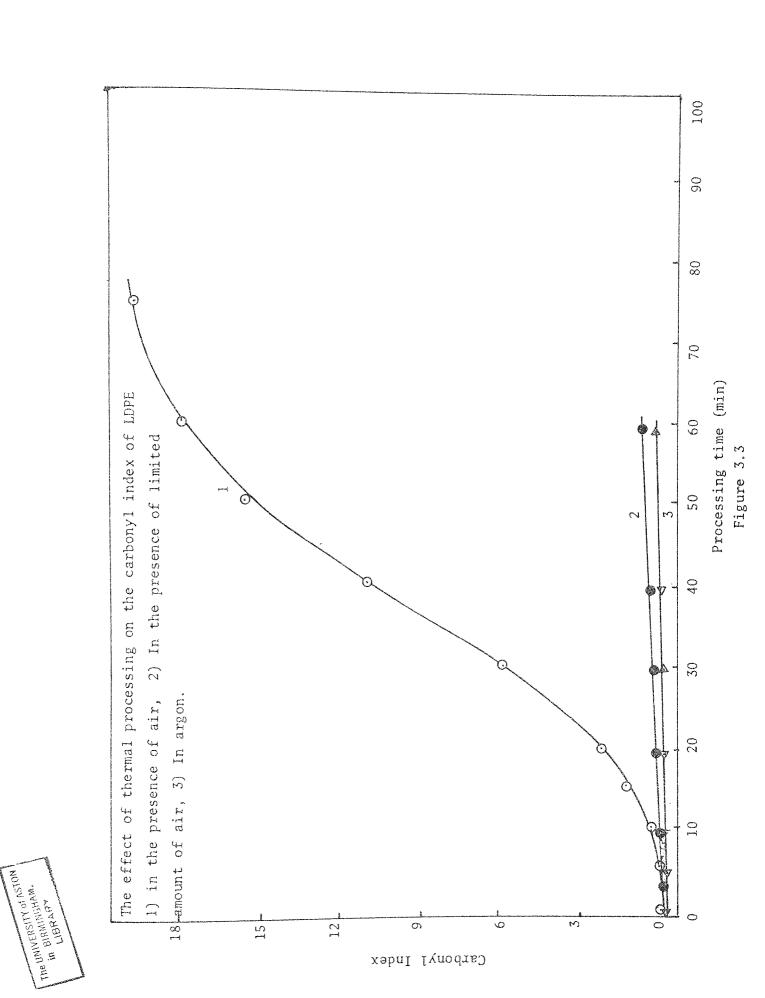
Figure 3.2 shows that the changes in melt flow index (MFI) occurring during above thermal processing conditions at 150°C also depend very markedly on the oxygen availability in the mixer. When air is accessible to the molten polymer (Fig. 3.2, curve 1, open mixer), there is an induction period of about 30 minutes before a significant change in MFI can be detected. Figure 3.3, curve 1, which relates the carbonyl formation to processing time under the same conditions shows that chemical changes occur even after 5 minutes of processing which are not reflected in changes in melt rheology.

Processing in the presence of less air (closed mixer) has a quite different effect. Under these conditions (Fig. 3.2, curve 2), the melt flow index (MFI) decreases in an auto-accelerating mode from the beginning of processing suggesting a rapid cross-linking reaction. There is only minor evidence of chemical change as reflected in carbonyl formation under these conditions (Fig. 3.3, curve 2). As might be anticipated when oxygen was excluded completely by continuous purging with argon, both rheological (Fig. 3.2, curve 3) and chemical changes (Fig. 3.3, curve 3) were eliminated completely. Fig. 3.4 which relates molecular weight distribution to processing time for LDPE processed in air, shows that there is no change in M_w up to 30 minutes processing. At longer times, a decrease in M_w occurs which corresponds to the increase in the MFI in fig. 3.2. No significant broadening of the molecular weight distribution is observed, indicating that little cross linking occurs under these conditions. In a closed mixer however there is an increase in average molecular weight (Fig. 3.5) which is very evident even at 20 minutes of processing. Again there is little evidence of molecular weight broadening, indicating little chain scisson under these conditions.

The formation of peroxides (measured chemically) in thermally processed LDPE at temperatures between 150°C and 175°C is shown in fig. 3.6. In each temperature (processed in the open chamber),peroxide content increases rapidly to a very sharp maximum and then declines. As the processing temperature is increased the formation of peroxide starts earlier and time taken to reach maximum and the maximum concentration are both reduced. Less peroxides are formed in the closed mixer which has limited excess of air (Fig. 3.6, curve 150 C). However, the

Effect of Processing on torque and gel content of LDPE. 1) Processed in open chamber, 2) Processed in closed chamber after purging with argon, 3) Gel content of sample (2).

Figure 3.1

Effect of processing on melt flow index of low density polyethylene

(1) Processed in the presence of air
(2) Processed in the presence of limited amount of air
(3) Processed in argon.

Figure 3.2

Melt Flow index

Processing time (min)

The effect of thermal processing on the carbonyl index of LDPE
1) in the presence of air, 2) In the presence of limited
amount of air, 3) In argon.

Figure 3.3

The effect of thermal processing at 150°C in air on the molecular weight distribution of LDPE. (Numbers on curves are processing time in minutes)

Figure 3.4

The effect of thermal processing at 150°C in a limited amount of air on the molecular weight distribution of LDPE.(Numbers on the curves are processing time in minutes)

Figure 3.5

The effect of processing temperature and time on peroxide concentration in processed LDPE. (Numbers on curves are processing temperatures, C indicates a closed mixer).

Figure 3.6

Formation of peroxide in LDPE during processing at various temperatures measured by IR method(Numbers on curves are processing temperature).

Processing time (minutes)

Figure 3.7

Hydroperoxide index $(A_{3555cm^{-1}}/A_{1895cm^{-1}} \times 10^{-2})$

150

165

175

initial rate (up to 10 minutes processing) is substantially faster than in the later stages and is comparable with that in an open mixer. No hydroperoxide was detected in polymer sample heated at the processing temperature in the presence of argon. Hydroperoxide measured by infrared method (band at 3555 cm^{-1})[90,91] expressed as index (A_{3555}/A_{1895}cm^{-1}) is also shown in the fig. 3.7 for comparison purposes.

It is observed from the IR spectra of the samples processed in the presence of air (spectra shown in the next section) that initially the main carbonyl peak is at 1720 cm^{-1} (ketonic carbonyl) and in the later stages of processing the main carbonyl band shifts towards 1710 cm^{-1} (Acid) having the following shoulders:- 1785 cm^{-1} (Peracid), 1765 cm^{-1} (Perester), 1745 cm^{-1} (ester), 1730 cm^{-1} (aldehyde) and at 1685 cm^{-1} conjugated carbonyl)[91]. The vinylidene (band at 888 cm^{-1}) which is initially present in the polymer remains almost constant up to 30 minutes of processing and then starts to decrease. No appreciable amount of vinyl content (band at 910cm^{-1}) or vinylene content (band at 964 cm^{-1}) is observed.

3.A.1.3 Discussion

The above results show that marked changes in torque (figure 3.1, curve 2), melt flow index (fig. 3.2, curve 2) and molecular weight (fig. 3.5) occur in LDPE subjected to a relatively mild thermal pro-oxidant condition, under conditions where no corresponding chemical changes occur (fig. 3.3, curve 2). By contrast conditions of more severe oxidations which lead to rapid chemical changes (fig. 3.3, curve 1) in the polymer appear not to give rise to commensurate change in molecular weight (fig.

3.4) and MFI (fig. 3.2, curve 1) of the polymer. This indicates a
very delicate balance of cross-linking and chain scission reactions
during the early stages of thermal oxidation of LDPE which has previously
been observed in rubber modified polymers[106,107] and in PVC[108,109],
both of which contain significant amount of unsaturation. The increase
in molecular weight and the formation of solvent insoluble gel under
conditions of limited oxygen access is clearly related to the similar
cross-linking reactions observed in the photo-oxidation of LDPE at
ambient temperatures[110]. It was previously suggested that the cross-
linking process was associated with the disappearance of the vinylidene
unsaturation and possible addition reactions of alkoxy radicals to the
double bonds were proposed to account for both cross-linking and double
bond disappearance. In the thermal processes being considered in the
present studies, however, no change in vinylidene concentration occurred
during the period of molecular weight increase. Moreover, no ether
linkage is detected in the spectrum of gel which suggests that cross-
linking occurs through a dimerisation of allylic radicals (scheme 3.1(a)).
This reaction will predominate in an oxygen deficient system whereas
further hydroperoxide (and ultimately carbonyl formation) will occur
(scheme 3(1b), 3(1c) in the presence of excess oxygen. Both processes
are readily inhibited by anti-oxidants (described in the Chapter 4)
confirming the free radical nature of the intermediates.

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - CH_2 \cdot \quad \longrightarrow \quad - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{OOH}{|}}{CH}$$

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{OH}{|}}{CH} \qquad \overset{-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2\cdot}{\underset{\longleftarrow}{}} \qquad - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\overset{\cdot}{O}}{|}}{CH}-$$

$$+$$

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

(b) / \ (a)

(c)

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{OOH}{|}}{CH}- \qquad \text{Dimers} \atop \text{(crosslink)}$$

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{O}{\|}}{C}$$

$$+ - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{OH}{|}}{CH}-$$

Disproportionation

SCHEME 3

A comparison of figures 3.3 (curve 1) and 3.6 shows that hydro-peroxide is formed rapidly prior to the formation of carbonyl in the presence of excess oxygen. Similar conclusions have been reached in the case of other polymers containing unsaturation [106,107]. It is observed from figure 3.6 that hydroperoxide concentration-time curve passes through a maximum for LDPE processed in the open chamber. As the processing temperature is increased formation of hydroperoxide starts earlier and the time taken to reach maximum concentration is shorter. The formation and decomposition of peroxides are temperature dependent. In the first stage of the oxidation process, the rate of formation of ROOH predominates over the rate of its decomposition. After the maxima, the rate of decomposition of ROOH is faster than the rate of formation. Rate of decomposition of ROOH may be enhanced by increase in temperature and also by the oxidation products formed from decomposition of hydroperoxides; mainly by acid[111]. On decomposition of hydroperoxide groups, various carbonyl groups are produced, which give rise to bands in the region of 1800 - 1675 cm^{-1} in the infra-red spectrum. From the known extinction coefficient values[100, 118] of various carbonyl groups and intensity of bands of maximum absorption it is observed that the main carbonyl oxidation product involved is ketonic carbonyl (1720 cm^{-1}) with lesser amounts of acid (1710 cm^{-1}), ester (1745 cm^{-1}) and aldehyde (1730 cm^{-1}) in order of decreasing concentration. Other carbonyl bands appeared at 1765 cm^{-1} and 1785 cm^{-1}. These bands have been attributed to peresters and peracids respectively[91].

Hydroperoxide formation precedes carbonyl formation when LDPE is processed in presence of air. Chain-scission takes place in the later

stages of processing as is shown by the decrease in torque, increase in MFI values and shifting of molecular weight distribution towards lower molecular weight. This is further supported from the analysis of I.R. spectra (shown in the next section) which shows the formation of peracid, perester, acid and ester in the later stages of processing.

Cross-linking reaction, forming insoluble gel occurs when LDPE is processed in presence of less air which is shown by the increase in torque, decrease in MFI values, almost constant carbonyl indices values and shifting of molecular weight distribution toward higher molecular weight.

Neither of the above processes occur when LDPE is heated at process- ing temperature in absence of air (in argon).

3.A.2. <u>Effect of processing on thermal oxidative stability of low density polyethylene</u>

The accelerated thermal oxidations of processed low density-polyethylene samples were carried out in a Wallace oven at 110° in the presence of air. Chemical changes occurred during accelerated thermal oxidations were determined by infra-red spectroscopy. Rate of oxidation was monitored by following changes in different functional groups viz carbonyl, vinylidene and hydroperoxide expressed as index.

3.A.2.1. <u>Results</u>
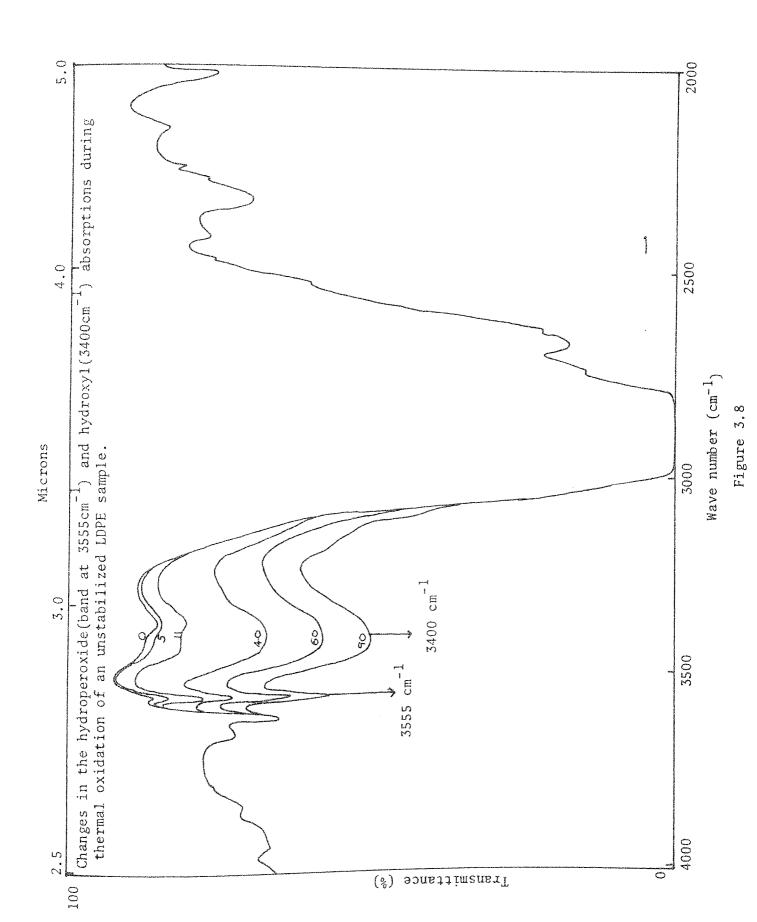
Figures 3.8 and 3.9 show infra-red spectra of processed LDPE samples which were thermally oxidized for various lengths of time at 110°C in air. The three regions in the spectrum viz 3600 - 3000 cm^{-1} (fig. 3.8) 1850 - 1600 cm^{-1} and 1200 - 850 cm^{-1} (fig. 3.9) where the changes are found to be most pronounced, have been related broadly to the absorption frequencies associated with O-H stretching modes[90, 112, 113] in various hydroxy containing compounds, $C = O$ stretching vibration in carbonyl oxidative products[90, 114] and C - H bending or deformation modes in olefinic double bond compounds respectively.
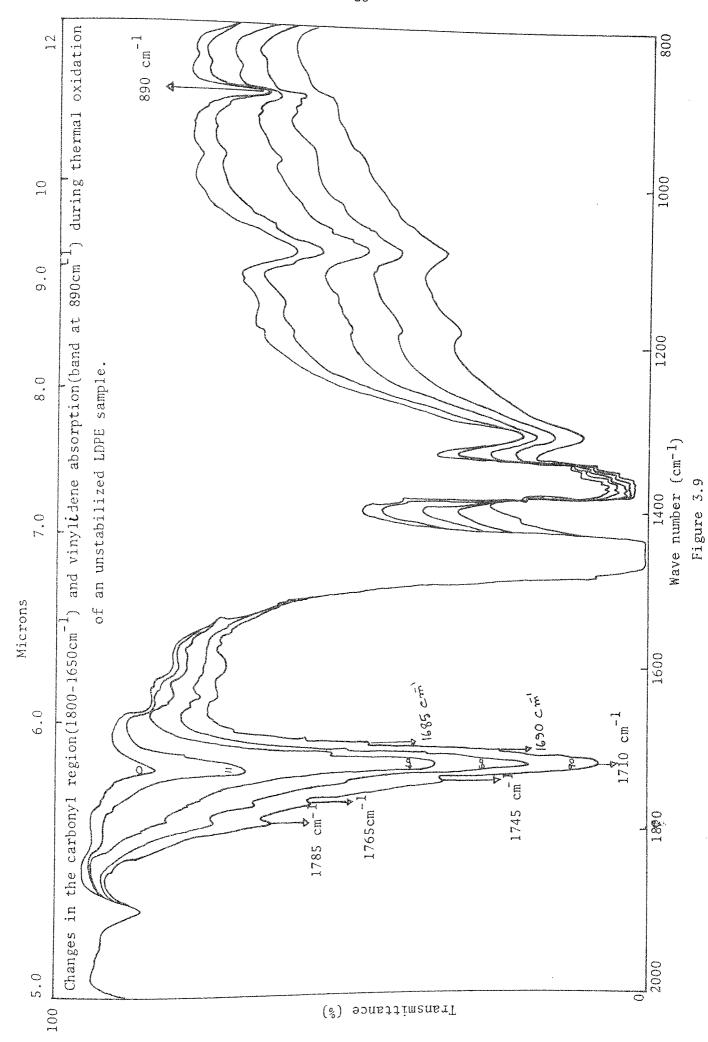
Rugg and co-workers[90] observed that during the oxidation of low density polyethylene at 140°C in air the infra-red absorption band at 2.81 μ (3555 cm^{-1}) became more intense as the oxidation proceeded. This absorption was attributed to hydroperoxide groups. The wave length of this band was shown to be identical to the wave length of the band due to O - H stretching vibration in t-Butyl hydroperoxide, cumene hydroperoxide and cyclohexene hydroperoxide[115]. It was indicated that the 2.81 μ band denotes the presence of a free hydroperoxide group, whereas 2.9 μ band denotes an associated hydroperoxide group.

Baum[116] also observed the formation of hydroperoxide (2.81 μ)
during thermal oxidation of polyethylene (DYNH) at 140°C in air. Luongo[91]
observed the formation of hydroperoxide in 3555 cm^{-1} region in the early
stages of heat oxidation of low density polyethylene. Hydroperoxide
starts to grow after 2 hours heating at 120°C in air and then attains
maximum at almost 8 hours and then starts to decrease. He[91] suggested
that the α-carbon atom is quite susceptible to oxygen attack after auto-
catalytic oxidation had begun. The present study also shows the sharp
band at 3555 cm^{-1} (2.81 μ) which grows when LDPE is heated at 110°C in
an oven (fig. 3.8).

The band at 3380 cm^{-1} (fig. 3.8) which is typical of hydrogen
bonded alcohol and hydroperoxide groups was initially present in the
polymer but of weak intensity and as the reaction progressed, the intensity
of absorption around 3400 cm^{-1} frequency increased gradually and finally
became much more broad indicating formation of more hydroxy compound as
a result of thermal oxidation.

In the carbonyl region (1800 - 1600 cm^{-1}), (fig. 3.9), thermally
oxidized polyethylene showed a complex absorption with a large number of
bands, the intensity of which increased with heating time. Each of
these bands was due to a different type of carbonyl compound formed during
thermal oxidation in air. The initial carbonyl absorption in the un-
processed film with very weak intensity was observed at 1725 cm^{-1} (due
to methyl ketone (fig. 3.9). The growing carbonyl band shifted towards
1710 cm^{-1} (acid) with increased heating time. Other carbonyl products
were also observed as shoulders in the later stages of oxidation. The

Figure 3.8

Changes in the hydroperoxide(band at 3555cm^{-1}) and hydroxyl(3400cm^{-1}) absorptions during thermal oxidation of an unstabilized LDPE sample.

Figure 3.9

Changes in the carbonyl region(1800-1650cm^{-1}) and vinylidene absorption(band at 890cm^{-1}) during thermal oxidation of an unstabilized LDPE sample.

shoulders on the main carbonyl band were identified as peracid (1785 cm^{-1}), perester (1763 cm^{-1}), ester (1745 cm^{-1}), aldehyde (1730 cm^{-1}) and conjugated carbonyl (1685 cm^{-1}). Luongo[91] suggested that all oxygen containing groups formed are the result of hydroperoxide decomposition. H.C.Beachell et al[117] have shown the existence of aldehyde and ketone in the first oxidation step after hydroperoxide formation in branched polyethylene. They suggested that aldehydes are the products of chain scission reaction. J.H.Adams[118] observed free hydroperoxide at 3550 cm^{-1} for polyethylene. The main carbonyl products in oxidized polyethylene are acid and ketone. He suggested that ketone in polyethylene would be internal rather than methyl ketone. Acid can only be due to chain scission.

Another effect of thermal oxidation of LDPE in the presence of air was observed in the region 1200 - 800 cm^{-1} (fig. 3.9) which corresponds to the absorption due to various types of olefinic unsaturation. It was found that the band at 888 cm^{-1} (due to vinylidene unsaturation) which is already present in the polymer, started to decrease after an induction period (fig. 3.9). Other types of unsaturation viz vinyl (band at 910 cm^{-1}) and vinylene (band at 964 cm^{-1}) which are present in very minute quantities in the polymer showed almost no changes during thermal oxidation (fig. 3.9).

Functional groups present in low density polyethylene during process-ing and accelerated thermal oxidation are shown typically in Table 3.1.

Table 3.1

Functional Groups	ν (cm^{-1})	Reference
- OOH (free)	3555 cm^{-1}	90, 91, 116
Polymeric associated		
- OH	3380 cm^{-1}	113
Methyl ketone	1725 cm^{-1}	14(a)

Internal ketone	1720±1 cm^{-1}	90, 91

Aldehyde		
	1730 cm^{-1}	90, 91

Carboxylic acid		
	1710-1715 cm^{-1}	91, 14(a)

ester - C - OR	1745 cm^{-1}	90, 91

cont'd

Functional groups	ν (cm^{-1})	Reference
Perester		
$-C\begin{smallmatrix} \diagup O \\ \diagdown OOR \end{smallmatrix}$	1765 cm^{-1}	91
Per acid		91
$-C\begin{smallmatrix} \diagup O \\ \diagdown OOH \end{smallmatrix}$	1785 cm^{-1}	
α-β unsaturated ketone		
$-CH = CH - \overset{\overset{\displaystyle O}{\|}}{C} -$	1685 cm^{-1}	90, 114
C - O in carboxylic acid	1185 cm^{-1}	100
vinylidene group		
$\begin{smallmatrix} R_1 \diagdown \\ \diagup \\ R_2 \end{smallmatrix} C = CH_2$	887±1 cm^{-1}	90
vinyl group		
$R_1\ CH = CH_2$	909	"
vinylene group	964	"
$R_1\ CH = CH - R_2$		
-CH$_3$ group content in PE	1378 cm^{-1}	119
(C - C) in long chain in the amorphous phase	1080 cm^{-1}	"

Figure 3.11 shows the effect of thermal oxidation at 110°C on poly-ethylene films which have been processed for various lengths of time at 150°C in an open chamber. The initial low rate observed during the auto-accelerating period for the unprocessed (0) and mildly processed (10 minutes) LDPE, is no longer observable for the 30 minutes processed sample. Initial auto-acceleration again becomes evident at longer processing time. Figure 3.12 shows the hydroperoxide formation during thermal oxidation at 110°C of the above processed LDPE samples. In each case hydroperoxide concen-tration rises to a maximum and then decays with heating time. The maximum concentration of hydroperoxide is greater in a mildly processed sample (10 minutes) than in a heavily processed sample . The 30 minutes processed sample containing appreciable amount of hydroperoxide (fig. 3.6) when heated in argon at 110°C, hydroperoxide concentration decayed to zero in less than 20 hours (fig. 3.12, curve 30 A). The maximum rate of initial carbonyl formation observed in fig. 3.11 is associated with higher initial hydroperoxide concentration (fig. 3.6) and higher rate of hydroperoxide formation during subsequent thermal oxidation (fig. 3.12)

Fig. 3.13 presents curves showing the change in vinylidene concen-tration with heating time at 110°C of the above LDPE samples. In un-processed LDPE, vinylidene decay shows an induction period. With the increasing time of processing in air at 150°C, vinylidene decreases slightly up to 60 minutes processing time and the auto-accelerating period to rapid vinylidene decay at 110°C decreases up to 30 minutes processing time (which contains maximum hydroperoxide (fig. 3.6) and then shows little change with longer processing time. The rate of vinylidene decay at the end of induction period varies little with length of processing.

Figure 3.14 shows the formation of carbonyl in LDPE films which have been processed for various lengths of time and subsequently heated in argon at 110°C. The heavily processed sample (60 minutes processing) and very mildly processed sample (5 minutes) containing undetectable level of hydroperoxide show almost no change in carbonyl concentration. But 30 minutes processed sample which contains an appreciable hydroperoxide concentration (fig. 3.6) gives a significant increase in carbonyl concentration on heating in argon. Vinylidene content in each case remains constant.

3.A.2.2 Discussion

In thermal oxidation, the sample which contains the maximum hydroperoxide concentration (30 minutes processed sample, fig. 3.6) achieved at 150°C during processing in air gives the maximum rate of oxidation (fig. 3.11) followed by auto-retardation. Auto-retardation occurs as a result of reduction in the concentration of hydroperoxide by thermolysis to give carbonyl. Auto-acceleration is always preceded by hydroperoxide formation (figs. 3.11 and 3.12). An unprocessed or mildly processed (10 minutes) sample which contains initially undetectable level of hydroperoxide shows an induction period before the growth of carbonyl. Peroxide formation appears to occur long before the end of carbonyl induction period (fig. 3.12). This period appears to be the time required for the build up of sufficient peroxides and their free radical decomposition products in causing a rapid autocatalytic oxidation. Although initial rate of carbonyl formation in 30 minutes processed sample is higher than 60 minutes processed sample, the rate of oxidation at 20 - 30 hours is higher in the 60 minutes processed sample than in the 30 minutes. This

Effect of thermal oxidation on carbonyl index of low density polyethylene. (Numbers on curves are processing time in minutes)

Figure 3.11

Change of hydroperoxide concentration with time of LDPE films heated in air at 110°C. (Numbers on curves are processing times at 150°C in air; A indicates heated in argon.

Figure 3.12

Change in vinylidene index with time of heating of LDPE films (Numbers on curves are processing time in minutes)

Figure 3.13

Vinylidene Index ($A890cm^{-1}/A1895cm^{-1}$)

Time of heating at $110°C(h)$

Unprocessed

0

10

30

60

- 68 -

Change of carbonyl index with time of LDPE films heated in argon at 110°C. (Numbers on curves are processing times in minutes, and, in paranthesis, peroxide concentrations (g.g^{-1} x 10^{-5})

Figure 3.14

may be due to catalyzed reaction of oxidation products (mainly acid and ketonic carbonyl)with hydroperoxide producing more carbonyl[15,111]. 60 minutes processed LDPE contains a reasonable amount of carboxylic acid and ketone carbonyl.

Fig. 3.14 shows that only the sample containing hydroperoxide (30 minutes processed at 150°C in air) gives an increase in carbonyl on thermolysis in argon at 110°C. Hydroperoxide of this sample decays to zero within 20 hours of heating in argon (fig. 3.12, curve 30 A). By comparison of figures 3.11 and 3.14 it is clear that over twice as much carbonyl is formed in the presence of oxygen as in its absence for the same sample, confirming that hydroperoxide is involved as an initiator in the oxidative process.

On the basis of the above results and discussion it may be said that same reaction path is followed during both processing and extended thermal oxidation in LDPE. Hydroperoxide is key initiator for both processes results from attack on the allylic position and its decomposition gives alkoxy, alkyl peroxy and hydroxyl radicals. Alkoxy radicals may be stabilized either by hydrogen abstraction forming alcohol (as observed by an increase in absorption at 3400 cm^{-1} in the infra-red spectrum, fig. 3.8) and producing new polymeric alkyl radical (Ṙ) which can continue the chain reaction or by forming ketone. Initially the above two reactions probably compete with each other and finally the formation of carbonyl predominates, whereas the OH peak at 3400 cm^{-1} levels off after some time. Alkylperoxy radicals may be converted to alkyl hydroperoxide by hydrogen abstraction in a chain reaction. Hydroxyl radicals may also be stabilized by hydrogen abstraction forming water and simultaneously producingnew

alkyl radical which can propagate the chain reaction. In the later stages of thermal oxidation chain scission takes place which is shown by the formation of peracid, perester, ester, aldehydes and acid. Chain scission is also confirmed by G.P.C. analysis. The molecular weight distribution shifts towards lower molecular weight on heating (figures 3.15 and 3.16). Narrowing of molecular weight distribution curve (figs. 3.15 and 3.16) toward lower molecular weight shows that more molecules of this average molecular weight distribution are formed due to chain scission.
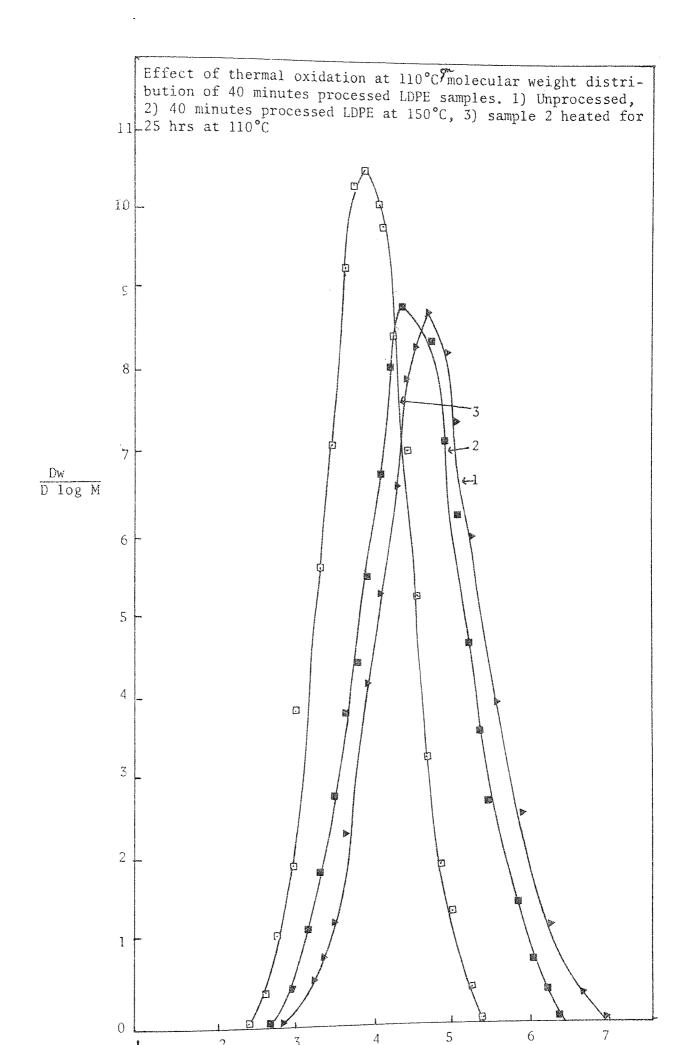
The suggested reaction scheme for thermal oxidation of LDPE is as follows:

$$
-CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{OOH}{|}}{CH}- \longrightarrow -CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{\dot{O}}{|}}{CH}- + \dot{O}H
$$

(1)

or

$$
2-CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{OOH}{|}}{CH}- \longrightarrow CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{\dot{O}}{|}}{CH}- +CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{\dot{O}O}{|}}{CH}
$$

$$+ H_2O$$

$$
-CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{\dot{O}O}{|}}{CH} +RH \longrightarrow CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{OOH}{|}}{CH} +\dot{R}
$$

(2)

$$\dot{R} + O_2 \longrightarrow R\dot{O}O$$

and repeats the reaction (1)

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

(3)

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \text{ and continues chain propagation}$$

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle\cdot O}{\|}}{CH-} \longrightarrow - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - \quad + -CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle OH}{|}}{CH} \quad (4)$$

(disproportionation)

β- scission

$$-CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{\overset{}{C\cdot}} \qquad + \ \dot{C}H_2 - CH_2 - \qquad (5)$$

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{\overset{}{C\cdot}} \xrightarrow{\ RH\ } - CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - H \quad + \dot{R} \quad (6)$$

aldehyde

further oxidized

acid

O_2

$$- CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O\dot{O} \qquad (7)$$

$\dot{R}$ or $\dot{H}$

$$-CH_2 - \underset{\underset{CH_2}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - OOR \text{ or } H \text{ (peracid or}$$
perester)

(8)

ester or acid

Effect of thermal oxidation at 110°C/molecular weight distribution of 40 minutes processed LDPE samples. 1) Unprocessed, 2) 40 minutes processed LDPE at 150°C, 3) sample 2 heated for 25 hrs at 110°C

Figure 3.16

3.A.3. Effect of processing on the photo-oxidation of LDPE

3.A.3.1 Experimental

Low density polyethylene was processed in the RAPRA-torque-rheometer for various lengths of time at 150°C both in the open chamber and closed chamber. The polymers were then compression moulded at 150°C for two minutes into sheets of thickness 0.008 inch.

The polymer films were exposed to ultraviolet radiation in the u.v. cabinet; detailed procedure is given in section (2.3.10).

In another set of experiments the processed polymer films were heated in argon at 110°C for 20 hours prior to u.v. exposure.

Infra-red analysis of the photo-oxidized films were carried out using PE457 spectrophotometer. The spectra of each sample were taken at regular intervals of irradiation time and were recorded on the same chart paper for comparison purposes. The rate of oxidation was followed by the appearance and development of carbonyl band and unsaturation band expressed as index;

$$[\text{viz. carbonyl index} = \frac{A_{1715 - 1710 \text{ cm}^{-1}}}{A_{1895 \text{ cm}^{-1}}} \qquad \text{vinyl index} = \frac{A_{910 \text{ cm}^{-1}}}{A_{1895 \text{ cm}^{-1}}}$$

$$\text{and vinylidene index} = \frac{A_{888 \text{ cm}^{-1}}}{A_{1895 \text{ cm}^{-1}}} \quad]$$

3.A.3.2 Results

Figures 3.17 and 3.18 show the changes with u.v. irradiation in the different regions in the infra-red spectrum of low density polyethylene
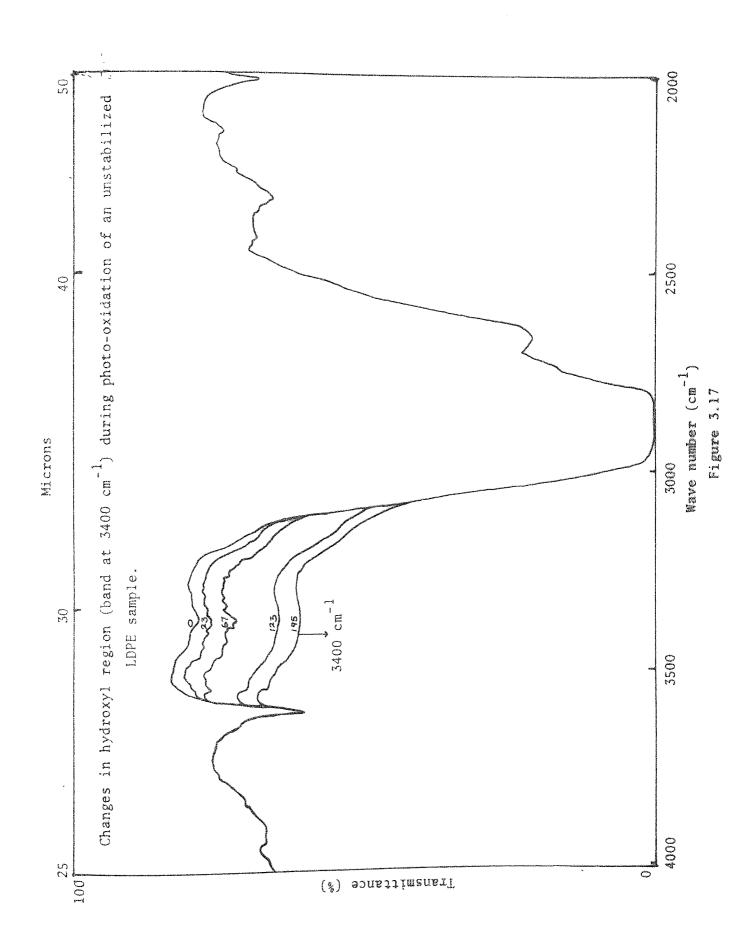
film.   The following differences were observed between the spectra of thermally oxidized (figs. 3,8 and 3.9) and photo-oxidized (figs.3.17 and 3.18) polyethylene films.

No free hydroperoxide groups (band at 3555 cm^{-1}) were detected by I.R. methods in the photo-oxidation of LDPE, although such groups were detected in thermo-oxidized film (fig. 4.8).   This may be, as has been suggested by Winslow[120], because hydroperoxides decompose as soon as they are formed and their rate of decomposition is much higher than their rate of formation in photo-oxidation.   But it does not mean that all peroxides are removed from the system, there must be an equilibrium concentration somewhere otherwise the oxidation would cease.   The equilibrium peroxide concentration may be so low that it is not detectable by I.R. method.   But like thermally oxidized film, the intensity of absorption around 3400 cm^{-1} frequency (due to hydrogen bonded alcohol, figure 3.17) increased gradually and finally became much more broad indicating the formation of more hydroxy compounds as a result of photo-oxidation.   It is generally believed that tertiary alcoholic groups may be formed (in addition to some secondary alcohol) through hydrogen abstraction by alkoxy radical during prolonged exposure.   These are hydrogen-bonded and are responsible for broader band around 3400 cm^{-1}.

In the carbonyl region (1800-1650cm^{-1},figure 3.18) photo-oxidized polyethylene like thermally oxidized polyethylene (fig. 3.9) showed a complex absorption with a large number of bands, the intensity of which increased with exposure time.   But the distribution of carbonyl groups differs.   During prolonged irradiation the absorption peaks were dominated by doublets at 1710 and 1730 cm^{-1} (due to acid and aldehyde

respectively).   The formation of acid in highly photo-oxidized film was further substantiated by the occurrence of another band at 1185 cm^{-1} (fig. 3.18) which was accounted for single bonded C-O vibration within the carbonyl group.   In the later stages of photo-oxidation the absorption due to the carboxylic group predominated, indicating the formation of this species as one of the major oxidation products in the u.v. degradation of LDPE.   The contribution of carboxylic acid groups to the carbonyl region absorption was   investigated[58] by converting the acid group into carboxylate ion by treatment with alcoholic sodium hydroxide.   After 3 days of treatment, the band around 1710 cm^{-1} was found to decrease and a new band appeared at 1575 cm^{-1} due to carboxylate ion,   .   .   Other carbonyl products like peracid (1785 cm^{-1}), perester (1763 cm^{-1}) and conjugated carbonyl (1690 cm^{-1}) were also found as shoulders in the main peak (fig. 3.18).

Another major difference was found between thermo-oxidized and photo-oxidized LDPE film in the unsaturated region (1650-800 cm^{-1}, figure 3.18).   In processed LDPE, vinylidene groups (band at 888 cm^{-1}) initially present decayed rapidly on u.v. irradiation.   The increase in concentration of vinyl (910 cm^{-1}) which was present to a much smaller extent in the processed polymer was observed during u.v. irradiation which almost paralleled carbonyl formation (figure 3.18).   Some increase in internal double bond (band at 964 cm^{-1}) was also observed during u.v. irradiation. Cross et al.[100] also have shown marked differences produced in the carbon-carbon unsaturation in polyethylene during photo-oxidation compared with that during heat oxidation.

Changes in hydroxyl region (band at 3400 cm^{-1}) during photo-oxidation of an unstabilized
LDPE sample.

Figure 3.17

Changes in carbonyl (1800-1650 cm^{-1}), vinyl (910 cm^{-1}) and vinylidene (890 cm^{-1}) absorptions during photo-oxidation of an unstabilized LDPE sample.
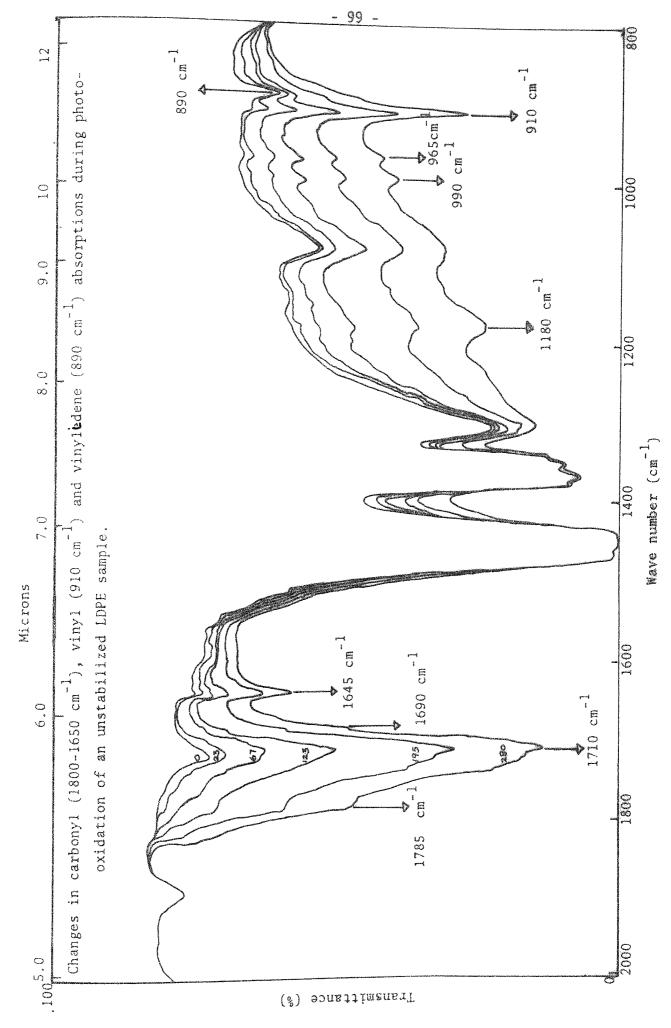
Figure 3.18

Changes in concentration of carbonyl, carboxyl, vinylidene and vinyl groups during u.v. irradiation of processed LDPE (processed in an open chamber at 150°C) are represented respectively by the figures 3.20, 3.20(a), 3.21 and 3.22. Figure 3.20 shows that the general shapes of the oxidation curves for unprocessed (0) and severely processed (30) polymers are very similar to those of the polymer samples processed for the same time but thermally oxidized at 110°C (fig. 3.11). In the case of samples containing hydroperoxide and vinylidene (30) there was a sharp increase in carbonyl formation due to the above photo-oxidation which destroys both vinylidene and hydroperoxide. More heavily processed samples (60 minutes processing, fig.3.20,curve 60) have a lower peroxide and vinylidene content but a higher initial concentration of carbonyl. On u.v. irradiation of this sample an initial decrease in carbonyl concentration occurred before the recommencement of carbonyl growth. It has been suggested that this is due to photolysis of ketone groups[110]. This is confirmed by the irradiation of the same sample in argon (heated in argon at 110°C for 20 hours to remove peroxide completely prior to u.v. irradiation in argon) which leads to a similar reduction in carbonyl concentration fig.3.23,curve 60 (HA,IA). [HA = heated in argon prior to irradiation, IA = irradiated in argon].

Although the initial concentration of carbonyl is considerably lower in the 30 minutes processed film than in the 60 minutes processed film (fig.3.20, curves 30 & 60), its rate of photo-oxidation is very similar in the second stage of oxidation to that of 60 minutes processed sample suggesting that the same group (carbonyl) is involved as photo-initiator in the latter stages of oxidation.

Figure 3.20(a) presents curves showing the formation of carboxyl groups in the above LDPE samples during photo-oxidation. It is seen from this figure that the carboxyl groups in the later stages of LDPE photo-oxidation is one of the main carbonyl products.

Figure 3.21 shows that the effect of prior heat treatment on vinyl-edene decay during u.v. irradiation is very similar to its effect on thermal decay of vinyledene (fig. 3.13). In particular, the auto-accelerating period decreases with prior heat-treatment and is of similar duration at 110°C (fig. 3.13) in the absence of light as it is at 30°C on u.v. irradiation. The decay of vinyledene in photo-oxidation of LDPE cannot be followed accurately at low concentrations due to the growth of vinyl by the Norrish II photolysis of ketone. Decay of vinyl-edene on u.v. irradiation precedes the formation of significant amounts of carbonyl (fig. 3.20). This suggests that vinyledene decay must be in some way associated with the photo-initiation step.
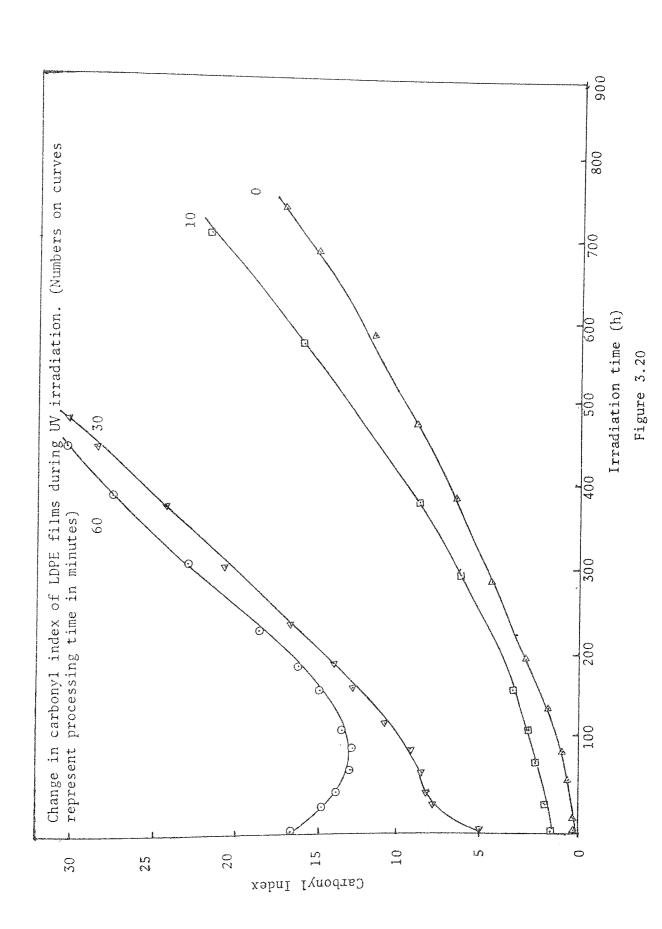
The formation of vinyl (910 cm^{-1}, fig. 3.22) which is present to a much smaller extent in the processed polymer also parallels carbonyl formation and appears to be consequent upon it. This is the expected sequence of events if vinyl is formed by Norrish II breakdown of carbonyl.
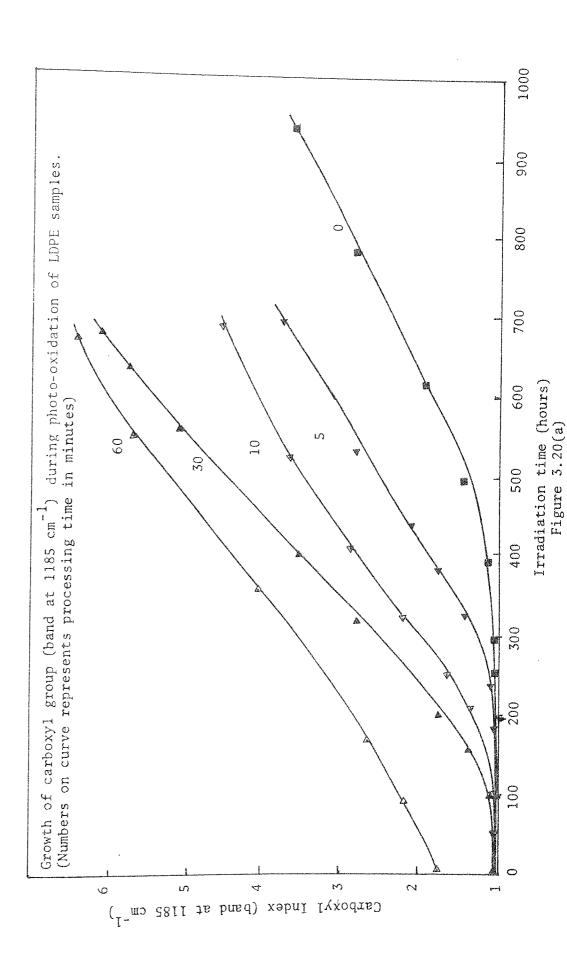
Figure 3.24 shows the effect of initial hydroperoxide concentration and carbonyl concentration in the photo-oxidation of LDPE. Curve (a) shows the effect of a substantial concentration of hydroperoxide (containing 48.0 gm mole gm^{-1} x 10^5) and carbonyl introduced by a severe processing operation (processed for 30 minutes at 150°C), on the sub-sequent photo-oxidative behaviour of polyethylene. Curve (b) is a similar sample which in addition has been subjected to a high temperature annealing process in argon (at 110°C for 20 hours) to remove hydroperoxide by thermolysis. It can be seen that the latter, although it contains a higher concentration of ketone (1720 cm^{-1}) than (a), photo-oxidizes at a
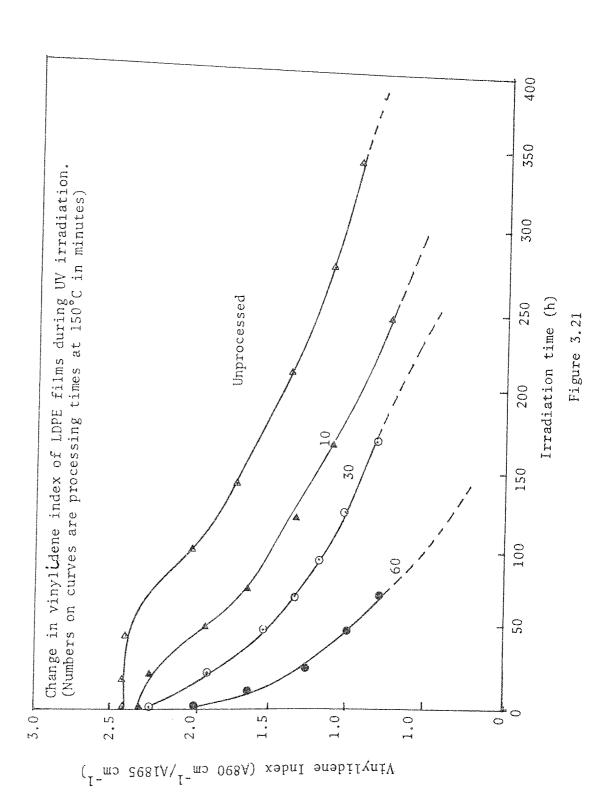
slower rate.   Furthermore, the rate of photo-oxidation of (b) is very similar to that of a control sample (c) which has had no thermal oxidative processing treatment and which contains only a fraction of the carbonyl concentration of (b) and it actually photo-oxidizes slower than (d) which was processed in small amounts of oxygen.   This experiment clearly shows the dominating importance of peroxide as a photo-initiator over carbonyl. The time to embrittlement for the argon heated sample (1200 hours) was longer than that of the untreated sample (900 hours) but was less than that of control (1800 hours).
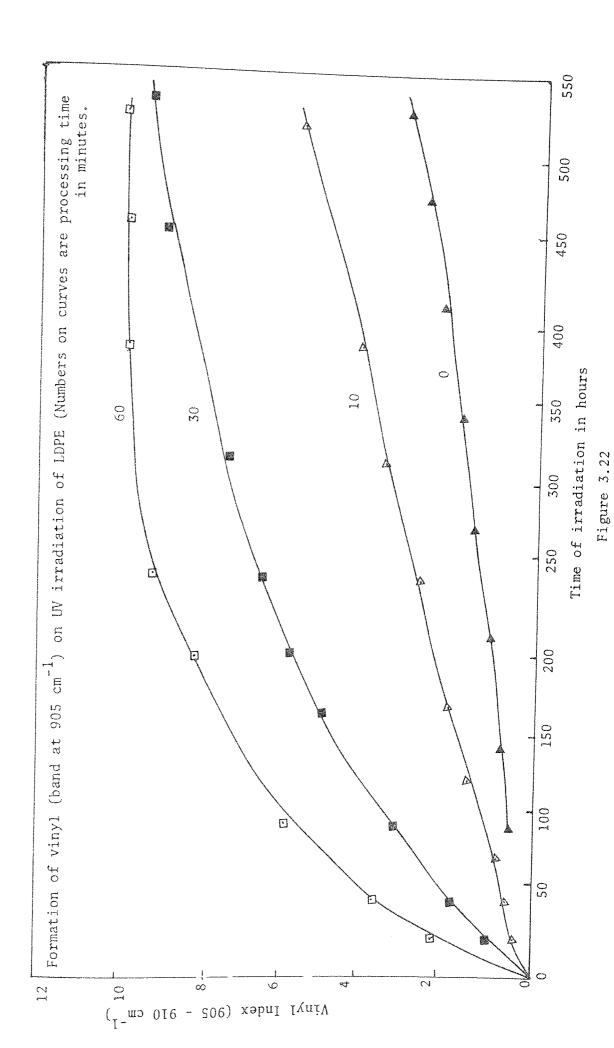
3.A.3.3. Discussion

The above results show that photo-oxidation rate and photo-stability of low density polyethylene clearly depend on the prior thermal oxidative treatment.   In particular, the extent to which hydroperoxides are formed during thermal processing operations determines the rate of photo-oxidation during initial stages of light exposure of LDPE.   The modes and rates of carbonyl formation under thermal oxidative conditions at 110°C (fig. 3.11) and under photo-oxidative conditions (fig. 3.20) are similar.   The similarity in shape of the carbonyl formation for the 30 minutes processed film is particularly striking and indicates a similar initiating function of peroxides under the two sets of conditions. In both thermal and photo-oxidations, this sample, which contains the maximum hydroperoxide concentration achieved at 150°C gives the maximum rate of oxidation followed by autoretardation.   Autoretardation occurs as a result of reduction in the concentration of hydroperoxide either by thermolysis or photolysis to give carbonyl[110].   A plot of initial photo-oxidation rate against initial hydroperoxide concentration showed

Change in carbonyl index of LDPE films during UV irradiation. (Numbers on curves represent processing time in minutes)

Figure 3.20

Growth of carboxyl group (band at 1185 cm^{-1}) during photo-oxidation of LDPE samples. (Numbers on curve represents processing time in minutes)

Figure 3.20(a)

Change in vinylidene index of LDPE films during UV irradiation.
(Numbers on curves are processing times at 150°C in minutes)

Figure 3.21

Formation of vinyl (band at 905 cm^{-1}) on UV irradiation of LDPE (Numbers on curves are processing time in minutes.

Figure 3.22

Figure 3.23

Effect of processing and subsequent heat treatment in argon on the photoxidation of LDPE (30 minutes processed LDPE Sample)

HA, heated in argon
IA, irradiated in argon
C, closed mixer

Figure 3.24

Figure 3.25

a linear relationship (fig. 3.25). No correlation was found between photo-oxidation rate and initial carbonyl concentration. Also convincing evidence that hydroperoxide rather than carbonyl is primarily responsible for photo-initiation is obtained by removing hydroperoxide from the 30 minutes processed film which initially photo-oxidizes very rapidly (fig. 3.24, curve a). After thermolysis of the hydroperoxide in argon which was shown to reduce its concentration to an undetectably low concentration, the carbonyl concentration increased by 100%, but the initial rate of photo-oxidation was reduced to a similar value (fig. 3.24, curve b) to that of LDPE film which had been prepared by compression moulding, and which again gave a negative test for peroxide, (fig. 3.24, curve c).

There is no evidence that increased concentration of carbonyl in LDPE (fig. 3.24) leads to a higher rate of initiation of photo-oxidation either direct hydrogen abstraction or by the triplet state or by the formation of singlet oxygen and its subsequent reaction with vinyl[33].

$$
\begin{array}{c}
\overset{\displaystyle O}{\underset{\displaystyle \parallel}{}} \\
RC\,CH_2 - CH_2\,R'
\end{array}
\xrightarrow{\;h\nu\;}
\begin{array}{c}
\overset{\displaystyle \cdot O}{\underset{\displaystyle |}{}} \\
R - C - CH_2 - CH_2 - R' \\
\text{triplet}
\end{array}
\xrightarrow{\;RH\;}
$$

$$
\begin{array}{c}
OH \\
| \\
R - C - CH_2\,CH_2 - R' \\
\overset{\cdot}{} \\
+ \overset{\cdot}{R}
\end{array}
$$

$$
\overset{\displaystyle O}{\underset{\displaystyle \parallel}{}} \; R - C\,CH_2\,CH_2\,R' + {}^1O_2
$$

$$
R''\,CH_2\,CH = CH_2 \; + {}^1O_2 \longrightarrow RCH = CH\,CH_2\,OOH
$$

The initial reduction in carbonyl concentration (fig. 3.24, curve b) and simultaneous vinyl formation is associated with carbonyl photolysis and clearly indicates that triplet carbonyl was formed. The presence of an allylic methylene group in LDPE is a particularly favourable situation for hydrogen abstraction by the triplet state since it has been shown that the reaction of triplet carbonyl with olefins is two orders of magnitude faster than with saturated hydrocarbon[121].

Russel and his co-workers[37] found that singlet oxygen did not react with polyethylene foams exposed to singlet oxygen over a six hour period. Similar studies in these laboratories on polyethylene films have confirmed these conclusions[122]. The absence of hydroperoxide formation through singlet oxygen attack on the olefin groups suggests that this species if it is formed under the conditions of experiment must be quenched by other molecules present.

Studies of model compounds in these laboratories have confirmed that both unsaturation and peroxides are important in the photo-initiation process rather than carbonyl[123]. The model compound diamyl ethylene

$$CH_3(CH_2)_4 \overset{\overset{\displaystyle CH_2}{\|}}{C} (CH_2)_4 CH_3$$

auto-oxidizes in the presence of u.v. light in the classical auto-accelerating mode. The introduction of a hydroperoxide (TBH) removes the induction period completely, whilst the addition of diamyl ketone

$$CH_3(CH_2)_4 \overset{\overset{\displaystyle O}{\|}}{C} (CH_2)_4 CH_3$$

although it undergoes photolysis as evidenced by the initial reduction in carbonyl concentration has a negligible effect on the induction period or on the rate of photo-oxidation. Similar conclusions have been reached in the case of HIPS[107,124].

Nevertheless, the carbonyl groups present undergo photolysis since there is a rapid formation of vinyl, formed by the Norrish II process

$$R\ CO\ CH_2\ CH_2\ R' \longrightarrow R\ CO\ CH_3 + CH_2 = CH\ R'$$

This process is known to be favoured over the alternative Norrish I photolysis in the initial stages of photolysis of solid polymers[24,125].

$$R\ CO\ CH_2\ CH_2\ R' \longrightarrow R\ \overset{\circ}{C}O + \overset{\bullet}{C}H_2\ CH_2\ R'$$

But in the later stages of photo-oxidation formation of aldehydes ($1730\ cm^{-1}$) and carboxylic acid ($1710\ cm^{-1}$) are almost certainly a consequence of Norrish I photolysis of carbonyl. Both types of above processes are very important in polymer degradation as polymer chains break to give lower molecular weight compound. These results support the conclusion arrived at earlier[16, 18,126], that once significant amounts of carbonyl are present in the polymer either as a result of thermal oxidation or by u.v. catalyzed oxidation then they are involved in the photo-degradation process. However, the rapid disappearance of vinylidene suggests that other photo-oxidation reactions occur involving this group and that this process precedes carbonyl formation.

The discussion of the above results suggests that neither triplet carbonyl nor derived singlet oxygen are of practical importance as photo-

initiators in LDPE polymers but the most important photo initiator in LDPE during initial stages of photo-oxidation are hydroperoxides and that the mode and rate of photo-oxidation of this polymer is critically dependent upon its thermo-oxidative history.

The carbonyl index produced in a photo-oxidized sample by hydroperoxide photolysis is somewhat less than that formed by thermolysis in argon (fig. 3.24) and substantially less than that formed by thermolysis in air (fig. 3.11). This indicates that polymer free radicals formed by photo-decomposition of hydroperoxide can undergo both cross-linking and chain scission reactions, although chain scission predominates in the presence of oxygen. Cotten and Sacks[127] have reported oxidative cross-linking of PE by u.v. light. They suggested the occurrence of cross-linking through an oxygen linkage.

It seems now probable that alkoxy radicals formed by photo decomposition of polymer hydroperoxide can add to vinylidene double bond giving cross-linked products (ether linkage absorption band at 1087 cm^{-1}), peroxy-linkages are less important because of their very unstable nature in u.v. light. The initial cross-linking in LDPE during u.v. exposure (as determined by gel content and solubility test) has also been reported by Gan and Scott[128].

The oxidative cross-linked products are however, less stable than those composed of C-C bond in u.v. and it is quite likely that these weakly cross-linked compounds can rapidly dissociate under the influence of u.v. light as the irradiation proceeds. This was evident from the

observed decrease in 1087 cm^{-1} absorption band (due to ether linkage) at the later stages of photo-oxidation. This was also supported by an initial increase followed by a decrease in elongation at break, a decrease followed by an increase in MFI[129] and a decrease followed by an increase of dynamic modulous[58].

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

further oxidation to
acids, aldehydes etc.

cross linking

$$R'O^{\cdot} + -CH_2 - \underset{\underset{R}{|}}{C} = CH_2 \longrightarrow CH_2 - \underset{\underset{R}{|}}{\overset{\cdot}{C}} - CH_2 \; OR'$$

cross linked

3.B. Polypropylene

The chemical structure of polypropylene, being a hydro-carbon containing tertiary hydrogen groupings makes it particularly susceptible to oxidation. Isotactic polypropylene has the structure

$$-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$$

But commercially produced polypropylene is said to consist of both an isotactic phase and an atactic phase. The isotactic phase has been shown to be mostly crystalline whereas the atactic phase is considered to be mostly amorphous. Among the bands in the infra-red spectrum, several have been assigned to each of the two phases present. The infra-red spectra of isotactic polypropylene were thoroughly studied by a number of workers[130-135]. Many bands in the infra-red spectra viz 1450, 1370, 1171, 975 and 890 cm^{-1} were found to be nearly independent of temperatures. Bands whose intensity decreased at higher temperatures were found at 1330, 1305, 1220, 1105, 1045, 995, 846 and 810 cm^{-1}. In view of the sharp drop of these intensities in the melting region of polymer, and from a comparison of spectra of crystalline and fully amorphous polypropylene, it was concluded that the temperature sensitive bands are connected with a degree of crystallinity[132,135]. Luongo[135] used the ratio of 974 cm^{-1} band to the 846 cm^{-1} band as a means of measuring crystallinity. All the above bands were assigned due to bending or wagging vibrations of $-CH_3$, $-CH_2$ or $-CH$ groups in polypropylene.

Besides the presence of tertiary carbon atoms in polypropylene Luongo[135] also demonstrated that it contains unsaturation. Pendant or vinylidene type ($R_1R_2C=CH_2$, band at 888 cm^{-1}) unsaturation was shown to be present in polypropylene.

Polypropylene is much more susceptible to oxidation than polyethylene because its most labile hydrogen atom is more easily lost than one from polyethylene in the rate determining step of the auto-oxidation chain reaction. The transition state involves both radical and cationic character on the reacting carbon atom and since a methyl group both increases electron density on the carbon atom being oxidized and de-localizes the electron by hyper-conjugation, polypropylene oxidizes many times faster than polyethylene[129].

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
-C-H\text{--------}\overset{.}{O}OR \longleftrightarrow & \overset{\delta^+}{C}\text{------}\overset{.}{H}\text{-----}\overset{\delta^-}{O}OR & \overset{.}{C}\text{----}\overset{\delta^+}{H}\text{----}\overset{\delta^-}{O}OR \\
| & | & | \\
CH_2 & CH_2 & CH_2 \\
|
\end{array}
$$

3.B.1 Effect of processing on photo-oxidative stability of polypropylene

3.B.1.1 Experimental

Polypropylene was processed at 180°C in the RAPRA torque-rheometer for various lengths of time in both open chamber and closed chamber. The polymers were then compression moulded at 180°C for two minutes into sheets of thickness 0.008 inch.

Infra-red analysis of the processed and subsequent photo-oxidized films were carried out using PE 457 spectrophotometer. The rate of photo-oxidation was measured by following carbonyl index[17]
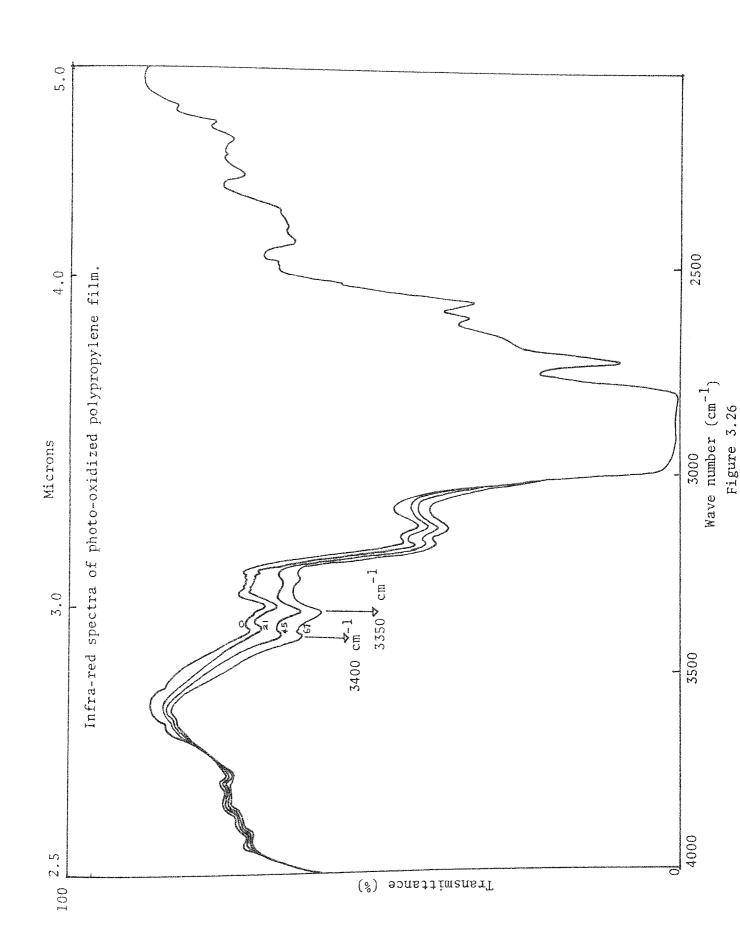
(expressed as $\dfrac{A_{1715\ cm^{-1}}}{A_{905\ cm^{-1}}}$)

Hydroperoxide content of the processed and u.v. irradiated samples were measured chemically (section 2.3.9.).

3.B.1.2 Results

Figures 3.26 and 3.27 show the spectra of photo-oxidized polypropylene film. The first region of interest is the 4000 - 3000 cm^{-1}, OH stretching region. A broad band from 3500 - 3300 cm^{-1} with two peak heights at 3400 cm^{-1} and 3350 cm^{-1} respectively was observed (fig. 3.26). Both the peak heights continued to increase steadily with oxidation. No band at 3555 cm^{-1} (due to non-hydrogen bonded hydroperoxide group) was observed either in photo-oxidized or thermally oxidized polypropylene film as was observed in thermally oxidized low density polyethylene film. The absence of this peak from the polypropylene film spectra may be due to the presence of neighbouring hydroperoxide which causes them to remain in intramolecular H- bonded form. Chien[136] has shown from the infra-red spectra of ethylene propylene copolymer that about 70% of hydroperoxides are intramolecular hydrogen bonded. The broad band in the hydroxyl region is probably due to hydrogen bonded alcohols and hydroperoxides.

The carbonyl region, from 1850 to 1650 cm^{-1} is shown in the figure 3.27. The conjugated carbonyl (band at 1685 cm^{-1}) which was found to be present initially in the unprocessed polymer, disappeared either on processing polypropylene in the open chamber for higher times or on u.v. irradiation. But the carbonyl peak at 1720-1710 cm^{-1} began to grow rapidly. Like low density polyethylene, the main carbonyl peak contained

Infra-red spectra of photo-oxidized polypropylene film.

Figure 3.26

Infra-red spectra of photo-oxidized polypropylene film.
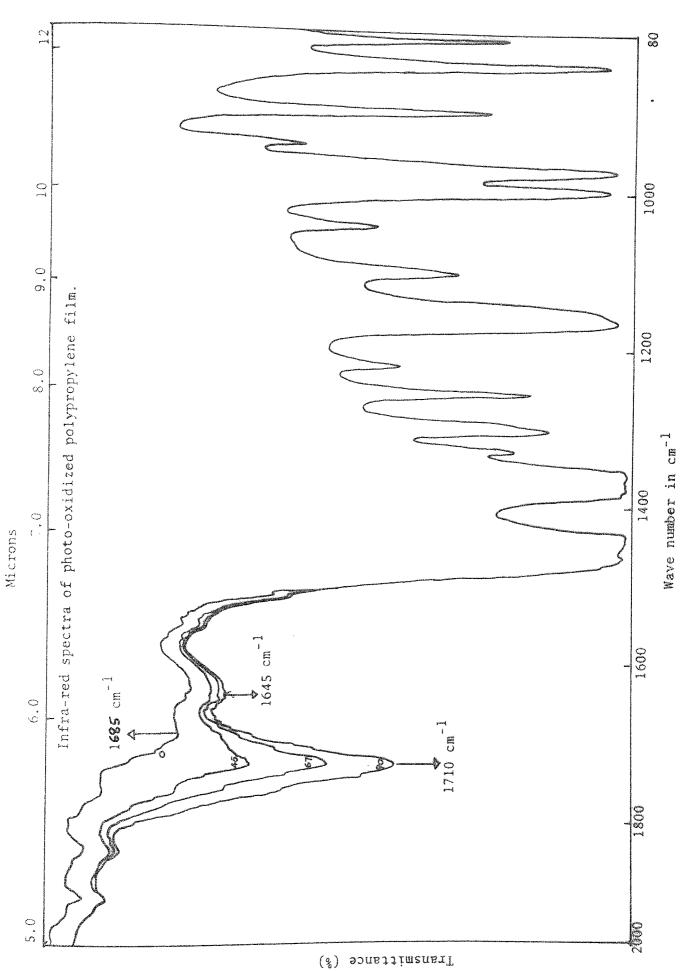
Figure 3.27

many shoulders indicating the presence of various carbonyl species. Although the typical -C=O bands due to aldehyde, esters and ketones were merged into a single broad, ill defined band between 1715-1750 cm^{-1}, the band for acid near 1710 cm^{-1} was quite distinct. This peak due to carboxylic acid began to form almost from the beginning and remained the strongest during and after oxidation, showing the acid groups to be one of the major oxidation products of polypropylenes. J.H.Adams[137] also found various carbonyl products in photo-oxidized polypropylene and he also calculated the concentration of various carbonyl products by infra-red spectroscopy and chemical reactions.

No particular bands for olefinic unsaturation (e.g. 964 cm^{-1} for ethylinic unsaturation , 910 cm^{-1} for vinyl and 888 cm^{-1} for pendant type unsaturation) were observed either in unoxidized or oxidized polypropylene. This is due to the presence of various bending or wagging bands of polypropylene itself in those regions. But a broad band at 1645 cm^{-1} fig. (3.27) indicated the presence of olefinic unsaturation in polypropylene. Moreover, the presence of conjugated carbonyl in unprocessed polypropylene also confirms the presence of unsaturation, although the nature of the unsaturation is not known.

Fig. 3.28 (curve 1) shows the hydroperoxide concentration (measured by chemical method) grows rapidly in unstabilized polypropylene subjected to a severe processing operation (processed at 180°C in the open chamber) in a simulated commercial mixing procedure (RAPRA-torque rheometer). Fig. 3.28 curve 2 also shows the growth of hydroperoxide concentration in polypropylene subjected to a mild processing operation (processed at

180°C in the closed chamber). Under the latter conditions there is an induction period before hydroperoxide can be detected and it then grows rapidly up to 10 minutes and continues to increase slightly up to 30 minutes of processing. Conjugated carbonyl (band at 1685 cm^{-1}) which is initially present in the polymer shows a longer induction period to further growth (fig. 3.28 curves 3 & 4 respectively) under both sets of conditions and under severe conditions it is destroyed after 20 minutes of processing. The polypropylene samples from these experiments were compression moulded to films and exposed to the u.v. cabinet for photo-oxidations. The rate of photo-oxidation was measured by following carbonyl index (carbonyl band at 1715 cm^{-1})(fig. 3.29). The sample containing maximum initial hydroperoxide concentration (20 minutes processed sample in the open chamber) is found to oxidize more rapidly. A plot of initial photo-oxidation rate against initial hydroperoxide concentration showed a linear relationship (fig. 3.30). No correlation was found between photo-oxidation rate and initial conjugated carbonyl concentration.

Figure 3.31 presents the curves (curve 1 & 2) relating the formation of hydroperoxide and carbonyl respectively during u.v. irradiation of a polypropylene sample (the former was determined chemically). Figure 3.31 curve 3 also shows the plot of $[ROOH]^{1/2}$ with time of irradiation. The initial linearity of this plot implies that the hydroperoxide initially formed in the film can account for the photo-initiation.
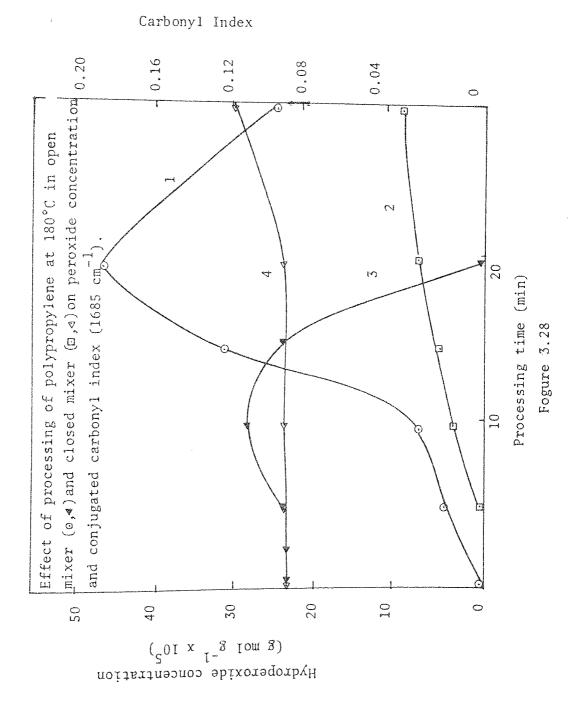
Figure 3.32 compares the rate of photo-oxidation of two identical (both 15 minutes processed at 180°C in the open chamber) polypropylene

films but one containing hydroperoxide (about 33.0 mole g^{-1} x 10^5) and
in another, hydroperoxide was completely removed by heating in argon at
110°C for 50 hours before u.v. exposure (curves 1 & 2 respectively).
In spite of the very high concentration of ketonic carbonyl in the latter
(curve 2) the initial photo-oxidation rate was reduced to zero.   Further-
more the argon treated sample showed an induction period of about 30 hours
before photo-oxidation recommenced, compared with about 10 hours for a
compression moulded control (curve 3) with a negligible initial carbonyl
concentration.

Figure 3.33 shows the relationship between both initial hydroperoxide
concentration and carbonyl concentration of the processed polypropylene
samples and time to embrittlement on u.v. irradiation of the above samples.
It was found that results obtained by processing in the presence of excess
air fell on the same straight line as those obtained in the presence of
less air.   Embrittlement time also decreased as a function of initial
ketonic carbonyl (1720 cm^{-1}) concentration but in this case two different
curves were obtained for the two sets of processing conditions (fig.3.33,
curves 2 & 3) and the samples with the same carbonyl concentration were
found to degrade at very different rates.

3.B.1.3 Discussion

Polypropylene shows a very similar behaviour on photo-oxidation
to low density polyethylene (section 3.A.3.3).   Both the rate of photo-
oxidation and photo-oxidative stability are markedly dependent on
previous thermal treatment.   It has also previously been shown[17]
that polypropylene is markedly sensitized to photo-oxidation by the thermal
processing sequence involved in its conversion to fabricated products.

Effect of processing of polypropylene at 180°C in open mixer (⊙,▼) and closed mixer (⊡,◄) on peroxide concentration and conjugated carbonyl index (1685 cm⁻¹).

Fogure 3.28

Effect processing on the rate of carbonyl formation during the photo-oxidation of polypropylene.
(Numbers on curves are processing time in minutes)

Carbonyl Index

Irradiation time (h)

Figure 3.29

Figure 3.30

Growth of peroxide and carbonyl on UV irradiation of polypropylene

Figure 3.31

Effect of peroxide and carbonyl on photoxidation of polypropylene.

HA, heated in argon for 50 hours at 110°C prior to UV exposure.

15, fifteen minutes processed sample.

Figure 3.32

Initial Carbonyl Index

UV lifetimes of processed polypropylene as a function of initial peroxide concentrations and carbonyl (1720 cm⁻¹) indices (—○— peroxide concentration in samples mixed in an open chamber, —△— peroxide concentrations in samples mixed in a closed chamber, —▽— carbonyl (1720 cm⁻¹) concentration in samples mixed in an open chamber, —□— carbonyl (1720 cm⁻¹) concentration in samples mixed in a closed chamber.

Time to embrittlement

Figure 3.33

Initial peroxide concentration (g mol g⁻¹ x 10⁵)

Both hydroperoxides[17,18,138] and ketonic carbonyl[33,14,139] or conjugated carbonyl [31] have been proposed as photo-initiators during the early stages of photo-oxidation of polypropylene. All these impurities are formed as a result of thermal oxidation during fabrication or processing of polypropylene. But the present studies clearly demonstrate that hydroperoxide rather than saturated carbonyl or conjugated carbonyl is the main photo-initiator during the early stages of photo-oxidation of polypropylene. It is seen from fig. 3.28 that the rate of growth of conjugated carbonyl shows an induction period and is slower both in excess air and in deficiency of air than is the growth of hydroperoxide. Furthermore, although the rate of photo-oxidation as measured by carbonyl formation can be directly related to the concentration of peroxide (fig. 3.30) it bears no relation to the concentration of conjugated carbonyl.

The linearity of $[ROOH]^{1/2}$ with time of initial u.v. irradiation (fig. 3.31, curve 3) also implies that hydroperoxide initially formed is alone responsible for the photo-initiation kinetics. More recently Carlsson et al.[44] showed a similar type of half order hydroperoxide concentration dependence on initial irradiation time and concluded that the low hydroperoxide level detectable in a commercial unstabilized polypropylene sample is alone adequate to account for the photo-initiation kinetics and additional initiation by carbonyl impurities is insignificant. Emanuel[140] also demonstrated the formation of hydroperoxide on u.v. irradiation of polypropylene which precedes the formation of carbonyl.

The importance of peroxide as a photo-initiator is also confirmed by heating in argon a film of polypropylene which contained a substantial

amount of hydroperoxide and which before this treatment photo-oxidized rapidly (fig. 3.32). This treatment destroyed hydroperoxide completely, with the corresponding increase in the ketonic carbonyl concentration. Although the argon treated sample contained/ higher a concentration of carbonyl than the untreated sample, the initial photo-oxidation rate of the former (fig. 3.32, curve 2) was reduced to zero and/even oxidized more slowly than the unprocessed control film (fig. 3.32, curve 3). This experiment also demonstrates that carbonyl or singlet oxygen (produced by quenching triplet carbonyl[33]) does not take part in the photo-initiation process.

Again it can be seen from fig. 3.33 that although embrittlement time is a direct function of peroxide concentration in samples thermally processed both in excess and in deficiency of oxygen, the embrittlement time carbonyl concentration relationship is quite different for the two modes of thermal treatment indicating that carbonyl concentration, although related to peroxide concentration since it is formed from it, is not directly involved in the photo-initiation process during the early stages of photo-oxidation.

However, the time to embrittlement for the argon treated sample [in fig. 3.32] (53 hours) was longer than that of the untreated sample (40 hours) but was less than that of control (113 hours). This is consistant with the observation that ketonic carbonyl plays some part as a secondary photo-initiation during the later stages of photo-degradation by Norrish I and II photolysis[141].

3.C. Conclusions

It was shown earlier[16, 18, 110, 141] that since the chemical processes occurring during photo-oxidation of the polyolefins are basically similar to those occurring during thermal processing operations, the prior thermal history of these polymers will to a major extent determine their behaviour during photo-oxidation. The results of this present study also show that photo-oxidation rate and photo-oxidative stability of both low density polyethylene and polypropylene are markedly dependent on the previous thermal history which appears to depend primarily on the amount of hydroperoxide formed during processing. Removal of hydroperoxide by heat treatment in an inert atmosphere, although it increased ketonic carbonyl concentration, markedly decreased the rate of photo-oxidation, introducing an induction period similar to that of an unprocessed sample. It is concluded that hydroperoxides are the most important initiators during the early stages of photo-oxidation of normally processed LDPE and polypropylene. When substantial quantities of carbonyl compounds are present in the polymers either by thermolysis or photolysis of hydroperoxide, they are intimately involved as initiators in the later stages of photo-oxidation. Ultimate photo-oxidation products of LDPE and polypropylene are carboxylic acid which are formed by the photolysis of in chain ketone by Norrish I and II reactions. The presence of carbonyl actually causes photolysis rather than photo-initiation during the early stages of photo-oxidation.

Neither triplet carbonyl nor singlet oxygen (produced by quenching triplet carbonyl by ground state oxygen) are of practical importance as photo-initiators in LDPE or in polypropylene.

On this basis, for stabilization of LDPE and polypropylene, peroxide decomposers and u.v. absorbers will have a complementary function, the former being more important initially during photo-oxidation and the latter in the later stages. Synergistic effects are, therefore, to be expected and this will be discussed in the subsequent chapters.

CHAPTER 4

EFFECTS OF ANTI-OXIDANTS AND STABILIZERS ON PROCESSING
AND SUBSEQUENT THERMAL AND PHOTO-OXIDATION OF POLYOLEFINS

4.A. Effect of anti-oxidants and stabilizers on processing and subsequent thermal and photo-oxidation of LDPE

4.A.1.1 Experimental

The additives were tumble-mixed with either 20 gms or 35 gms of unstabilized LDPE ('Alkathene' WJG 47, supplied by I.C.I.Ltd.). The compounded polymer was processed at 150°C for various lengths of time using the prototype RAPRA Torque Rheometer (described in the experimental sections, Chapter 2) either with the chamber left open to the atmosphere (when 20 gm charge was used) or in the closed chamber (when 35 gm charge was used). On completion of processing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation. This was compression moulded to films of thickness 8×10^{-3} inches at 150°C.

The above samples were heated in separate cells of the Wallace forced air ageing block (H.W.Wallace Co.Ltd., Croydon) set at 110°C for accelerated thermal oxidation and were exposed in a u.v. cabinet for photo-oxidation; detailed procedure is given in Section 2.3.10.

Screening experiments were carried out as follows: the samples under investigation were mounted on quartz slides behind a polyethylene film (containing the additives) of identical thickness and size which was interposed on the lamp-ward side of the quartz slide.   The samples to be investigated received light which had been screened through the stabilizer-containing film.

The rate of thermal and photo-oxidation was monitored by measuring carbonyl index and vinyl index as described in the previous chapter.

The rate of disappearance of additives in the polymer film was measured using a P.E. 137 ultraviolet spectrophotometer.

The anti-oxidants and stabilizers are listed below with the code name used in this and subsequent chapters.

Additives		Code Name
	M = Ni, n = 2	NiDEC
	M = Zn, n = 2	ZnDEC
	M = Ni, n = 2	NiDBC
	M = Zn, n = 2	ZnDBC

Additives   Code Name

$$[Et_2N - \overset{\overset{\displaystyle S}{\|}}{C} - S -]_2 \overset{\overset{\displaystyle NH_2R}{\downarrow}}{M} \quad RNH_2 = \text{n-Primary Butylamine}$$

M = Zn or Ni   M(n-Butylamine)DEC

RNH_2 = Sec-Butylamine   M(sec-Butylamine)DEC

RNH_2 = tert-Butylamine   M(tert-Butylamine)DEC

$$[Et_2N - \overset{\overset{\displaystyle S}{\|}}{C} - S-]_2 \overset{\overset{\displaystyle NHR_2}{\downarrow}}{Zn} \quad R_2NH = \text{Di-n-Butylamine} \quad \text{Zn[Di-n-Butylamine]DEC}$$

R_2NH = Di-2ethylhexylamine

Zn[Di-2ethylhexylamine]DEC

R_2NH = Di-nonylamine   Zn[Di-nonylamine]DEC

Zn-[N-lauryl]dithiocarbamate

Zn-[Di-hydrogenated Tallow]dithiocarbamate

Zn-[N-oleylaminopropyl]dithiocarbamate

Additives

Zn-[N-cocylaminopropyl]dithiocarbamate

Zn-[N-oleylaminopropyl]dithiocarbamate

HOBP

Irganox 1076

Tinuvin 770

The concentration of the additives used were

1×10^{-4}, 3×10^{-4}, 6×10^{-4} and 10×10^{-4} mol/100 g of polymer.

4.A.1.2 Results
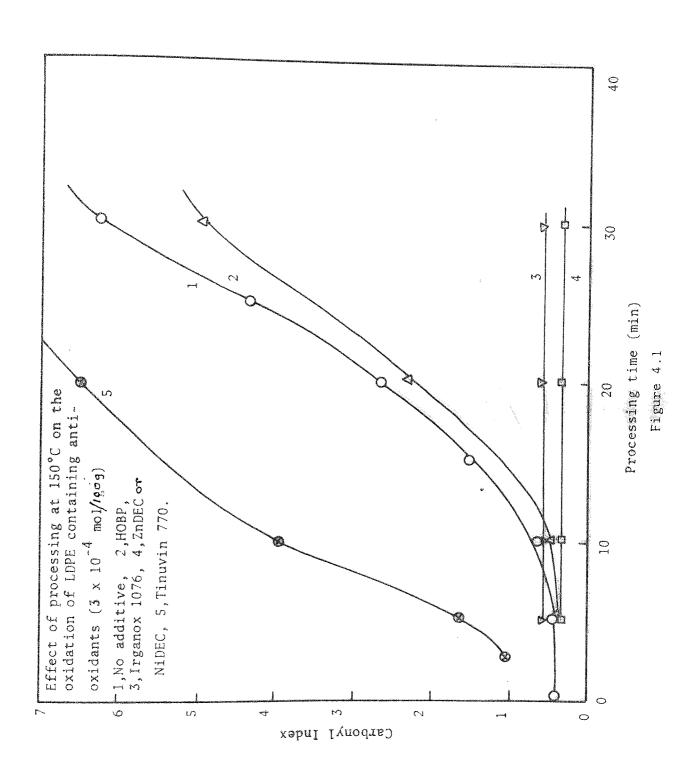
The effect of a typical 'u.v. absorber' HOBP and substituated piperidine compound Tinuvin 770 (Produced by Ciba-Geigy), on the oxidative stability of LDPE during processing are compared with that of peroxide decomposing anti-oxidants zinc-diethyldithiocarbamate (ZnDEC), nickeldiethyldithiocarbamate (NiDEC) and an effective commercial chain breaking anti-oxidant (Irganox 1076) at the same molar concentrations in fig. 4.1. It is clear that the 'u.v. absorber' has only a minor effect on the oxidative stability of the polymer compared with hydroperoxide decomposer and chain breaking anti-oxidant (curves 2, 3 & 4). The dithiocarbamate containing films (curve 4) have shown almost no oxidation during processing. They are therefore, all powerful melt stabilizers for the polymer at the concentration used and this was confirmed by measuring the change in melt flow index (MFI) of LDPE during the processing operation. It was found to be almost constant (1.98) after 30 minutes of processing. No hydroperoxide formation was detected (chemically or spectroscopically) in LDPE containing dithiocarbamates, although it is present in substantial amount in a control film without additive under the same conditions (fig. 4.1(a)). Hydroperoxide formation is not inhibited by the presence of HOBP during thermal processing operation (fig. 4.1(a)).

All the amine complexes of Zn or Ni-diethyldithiocarbamates showed almost similar behaviour in LDPE as parent dithiocarbamates during processing.

The methyl substituated piperidine (Tinuvin 770) shows increased oxidation over control (fig.4.1,curve 5) during processing under the same conditions. It did not inhibit hydroperoxide formation as an appreciable amount of hydroperoxide was measured both chemically and spectroscopically (fig. 4.1(a), curve 2).

The stabilizing effect of the anti-oxidants (Zn or Ni dithiocarbamate and Irganox 1076) was still in evidence when samples processed for 10 minutes were heated in an air oven at 110°C in the form of compression moulded films (fig. 4.2). An induction period of about 110 hours was found for both Irganox and Zn or NiDEC respectively compared with only 10 hours for the control and u.v. absorber (HOBP). The substituated piperidine (Tinuvin 770) again shows an accelerating effect over the control on thermal oxidation of LDPE (fig. 4.2, curve 5).

It has already been shown in the preceding chapter (Chapter 3) that the effect of processing on unstabilized LDPE is to markedly reduce u.v. stability. This is associated with the thermal oxidative formation of hydroperoxides which are the primary photo-initiators. Removal of peroxides by heating in the absence of oxygen leads to the effective photo-stabilization of the polymer, comparable to that of LDPE which has not been subjected to a processing operation. This implies that the extent to which anti-oxidants and u.v.stabilizers have the ability to destroy hydroperoxides will be reflected in their u.v.stabilizing effectiveness. The effect of chain-breaking anti-oxidant (Irganox 1076), hydroperoxide decomposers (ZnDEC and NiDEC) and u.v.absorber (HOBP) in 10 and 30 minutes processed LDPE (Processed in the open chamber at 150°C) on

Effect of processing at 150°C on the oxidation of LDPE containing anti-oxidants (3×10^{-4} mol/100g)

1,No additive, 2,HOBP, 3,Irganox 1076, 4,ZnDEC or NiDEC, 5,Tinuvin 770.

Figure 4.1

Effect of processing on peroxide formation of LDPE with additives. (Processed at 150°C in an open chamber). 1,Control, 2,Tinuvin (770), 3,HOBP, 4,Irganox 1076. (Concentration of additive 3 x 10⁻⁴ mol/100g of polymers)

Figure 4.1(a)

Effect of thermal oxidation (oven aging) at 110°C on LDPE films containing anti-oxidants (3 × 10⁻⁴ mol/øg).
All samples processed at 150°C/1o mins in open mixer. 1,No additive, 2,HOBP, 3,Irganox 1076, 4,ZnDEC, 5, Tinuvin 770.
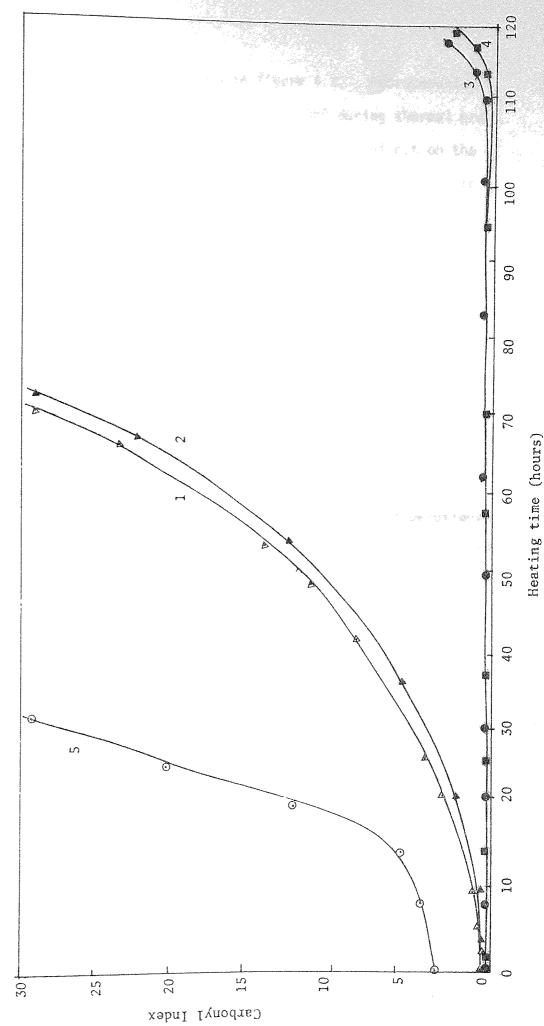
Figure 4.2

subsequent photo-oxidations are shown in figure 4.3.   Hydroperoxide formation is not inhibited by the presence of HOBP during thermal processing and the 'u.v. absorber' has a relatively minor effect on the peroxide induced photo-initiation reaction (fig. 4.3, curve 8).   In spite of this, however, the rate of carbonyl formation is lower at all stages due to the screening effect of the u.v. stabilizer in the polymer. It effectively retards photo-oxidation in a mildly processed sample (fig. 4.3, curve 7).   Under the same conditions, no hydroperoxide could be detected in LDPE in the presence of either ZnDEC or NiDEC.   Not only was the build up of carbonyl inhibited during processing (fig. 4.1) but the initial rate of carbonyl formation during u.v. irradiation was also much lower (fig. 4.3, curves 3 & 4 respectively).   Thermal processing considerably reduces the effectiveness of HOBP (fig. 4.3, curve 8) presumably due to its inability to inhibit the formation of peroxides and derived carbonyl compounds (fig. 4.1).   By contrast ZnDEC and NiDEC are equally as effective as u.v. stabilizers following a severe processing operation as they are in mildly processed samples.The higher efficiency of NiDEC compared with ZnDEC at the same molar concentration particularly during the early stages of photo-oxidation appears to be associated with the higher u.v. stability of the former.   This is shown in figure 4.4. in which the first order decay of the u.v. absorbance maxima at 330 nm for NiDEC and 285 nm for ZnDEC respectively are plotted (curves 1 & 2). The nickel complex has a higher initial molar extinction coefficient than the Zn complex (about twice) and its half life is about 3.75 times that of the Zn complex under the same conditions.   U.V. absorption intensity of additives in polyethylene film after processing is shown in Table 4.1.

HOBP is considerably more stable, although its molar extinction coefficient is only about 0.7 that of NiDEC, its half life is about 4.67 times that of NiDEC and 17.5 times that of ZnDEC (fig. 4.4, curve 3).

The equal effectiveness exhibited by NiDEC and ZnDEC as u.v. stabilizers in both severe and mild processing operation indicates that their peroxide decomposing activity is carried through to the u.v. exposure stage and this persists until the complexes are destroyed by u.v. light. The similarity of the induction period to carbonyl formation ($\simeq$ 250 hours) for NiDEC (figure 4.3, curve 4) and the time to complete destruction of the metal complex (fig. 4.4, curve 2) is consistent with this view. The zinc complex shows a similar correlation at a shorter time (figs. 4.3, curve 3 and 4.4, curve 1).

Irganox 1076, a typical phenolic anti-oxidant has a similar activity to ZnDEC as a thermal anti-oxidant, giving an almost identical induction period at the same molar concentration at 110°C (fig. 4.2, curve 3 & 4). In photo-oxidation, it differs from ZnDEC which exhibits most of its activity in the initial stages of photo-oxidation, Irganox 1976 is a more effective retarder during the later stages of photo-oxidation (fig. 4.3, curves 5 & 6). Although Irganox 1076 is less effective than HOBP as a u.v. stabilizer under mild processing conditions, under severe processing conditions it is more effective particularly during the early stages of photo-oxidation due to its greater ability to limit the development of hydroperoxide under these conditions (fig. 4.3, curve 6 and fig. 4.1(a), curve 4).

The UV stabilization effectiveness of HOBP is also found to be
markedly dependent on prior processing conditions. When LDPE is proces-
sed in less air (closed chamber) with HOBP, a better stabilization effect
is obtained on photo-oxidation than the sample processed in the presence
of air (fig. 4.5, curves 5 & 6). But Zn and NiDEC show very little
difference in stabilizing effectiveness when subjected to the same pro-
cessing conditions.

On increasing chain length in the alkyl group of metal dithiocarbamate,
the UV stabilizing effect of nickel complex is found to increase in LDPE,
but the zinc complex does not show any increased effectiveness on increasing
chain length. Figure 4.6 compares the effect of ethyl and butyl dithio-
carbamates of zinc and nickel on photoxidation of LDPE at the same molar
concentration (3 x 10^{-4} mol/100g of polymer) under identical conditions.
It is found that the induction period (250 hours) observed with nickel
diethyldithiocarbamate (NiDEC) is increased to about 400 hours with
nickel dibutyldithiocarbamate (NiDBC)(fig. 4.6, curves 1 & 2 respectively).

Complexes of zinc and nickel diethyldithiocarbamate with primary and
secondary aliphatic amines and particularly the primary amine complexes
are found to give much improved u.v. stabilization effectiveness in LDPE
over the parent dithiocarbamates. Figures 4.7 and 4.8 present the
curves comparing the u.v. stabilizing effect of amine complexes of Zn and
Ni-diethyldithiocarbamate with the parent complexes at the same molar
concentration (3 x 10^{-4} mol/100g of polymer) under identical conditions.
Stabilizing effect with Zn[sec-Butylamine]DEC and Ni[sec-Butylamine]DEC

are remarkably improved over ZnDEC and NiDEC respectively and which are almost similar in effect to HOBP(fig. 4.7, curves 5, 7 & 8 respectively). But the n-Butylamine complex does not show much improved stabilization effectiveness because it is largely destroyed during processing (Table 4.1). Secondary amine complexes do not show any better stabilization effect over the parent metal dirhiocarbamates (fig. 4.8). This is again due to destruction of the complexes during processing probably by volatalization (Table 4.1) of the amine.
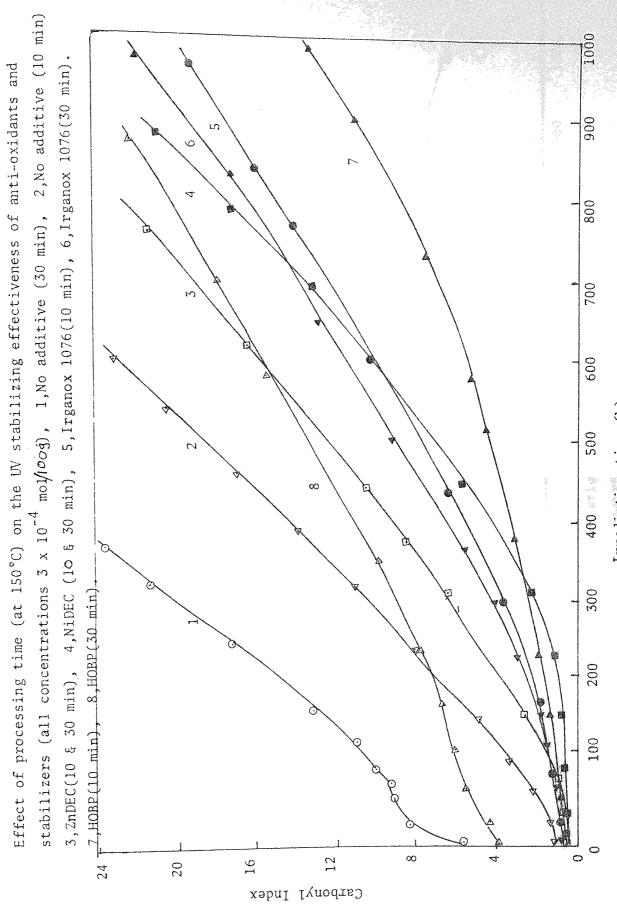
Although a pro-oxidant effect was observed with Tinuvin 770 during processing and subsequent thermal oxidation of LDPE at 110°C (fig. 4.1, curve 5 and fig. 4.2, curve 5 respectively), it exhibits a very good u.v. stabilization effect in LDPE on photo-oxidation (fig. 4.9, curves 1 & 2). As more carbonyl is produced during processing with this additive than the control sample, initial drop in carbonyl is observed on u.v. irradiation presumably due to photolysis of carbonyl by Norrish I and II reactions. Photolysis of carbonyl is also observed by the parallel vinyl formation (figure 4.9(a), band at 910 cm^{-1}). After the decrease in carbonyl subsequent carbonyl formation shows a very long induction period.

Embrittlement times of LDPE with the anti-oxidants and stabilizers used as an additive are shown in Table 4.2.

Figure 4.10 compares the effectiveness of anti-oxidants and stabilizers as additives and as screens when present in a separate film, (at the same molar concentration as when used as additives) in the photo-

oxidation of LDPE. In the screening experiment 30 minutes processed unstabilized LDPE films are exposed behind a film which is identical except that it contains additives. The unstabilized film can only receive light which has passed through the stabilizer containing film. It is clear from the figure 4.10 that the contribution of screening to the stabilizing effect is minimal compared with the effect when the anti-oxidants and stabilizers are incorporated into the polymer. The initial rapid oxidation stage (due to photolysis of hydroperoxide) followed by auto-retardation which is observed in the unprotected film is also evident in all screened films. After the initial rise of carbonyl, the rate of photooxidation in the later part is reduced by both NiDEC and HOBP used as screening agent (curves 3 & 4 respectively) compared to that of the control. HOBP acts as better u.v. screener than NiDEC. The protective effect of u.v. absorber (HOBP) on the photo-oxidation of LDPE is partly due to screening of u.v. light but as is implied in figure 4.10,(curves 4 & 5), this is not the complete explanation. Since, like the dithiocarbamates HOBP is much more effective when present as an additive than when it is in a separate screening film. ZnDEC and Tinuvin 770 do not seem to screen u.v. light at all, because the rate of photo-oxidation of the samples screened by these additives are almost the same as that of the control. All the compounds are more effective as additives than as screening agents.

All the amine complexes of zinc and nickel diethyldithiocarbamate show exactly the same screening activity as the dithiocarbamates themselves at the same molar concentration.

Effect of processing time (at 150°C) on the UV stabilizing effectiveness of anti-oxidants and stabilizers (all concentrations 3 x 10^{-4} mol/100g), 1,No additive (30 min), 2,No additive (10 min) 3,ZnDEC(10 & 30 min), 4,NiDEC (10 & 30 min), 5,Irganox 1076(10 min), 6,Irganox 1076(30 min). 7,HOBP(10 min), 8,HOBP(30 min).

Carbonyl Index

Irradiation time (h)

Figure 4.3

Change in the UV absorption spectrum of additives during the photo-oxidation of LDPE (Processed at 150°C for 10 mins, concentration of additives 3×10^{-4} mol/100g). 1, ZnDEC(λ_{max} at 285 nm), 2, NiDEC (λ_{max} at 330 nm),, 3, HOBP (λ_{max} at 330 nm).

Figure 4.4

Effect of processing on the photo-oxidation of LDPE containing additives (Processed at 150°C for 10 mins. Concentration of additives 3×15^{-4} mol/l00g)

1,ZnDEC(open chamber), 2,ZnDEC(closed chamber), 3,NiDEC(open chamber), 4,NiDEC(closed chamber), 5,HOBP(open chamber), 6,HOBP(closed chamber).

Figure 4.5

Effect of ethyl and butyl groups in Zn & Ni dithiocarbamates on photo-oxidation of LDPE(processed at 150°C in the open chamber for 10 mins.(Concentration of additives 3 x 10^{-4} mol/100g). 1, NiDEC, 2,NiDBC, 3,ZnDEC, 4,ZnDBC.

Figure 4.6

Effect of primary amine complexes on photoxidation of LDPE (Processed at 150°C for 10 minutes in the open chamber. Concentration of additives 3×10^{-4} mol/(δoj)

1, ZnDEC   2, Zn[n-Butylamine]DEC,   3, Zn[sec-Butylamine]DEC,
4, Zn[tert-Butylamine]DEC,   5, NiDEC,   6, Ni[tert-Butylamine]DEC,
7, Ni[sec-Butylamine]DEC,   8, HOBP

Figure 4.7

Effect of secondary amine complexes on photoxidation of LDPE (Processed at 150°C/10 min. in the open chamber). Concentration of additives 3 x 10⁻⁴ mol/(l00g). 1, ZnDEC, 2, Zn[Di-2-ethylhexylamine]DEC, 3, Zn[Di-nonylamine]DEC, 4, Zn[Di-n-Butylamine]DEC, 5, Zn[sec-Butylamine]DEC.

Figure 4.8

Effect of Tinuvin 770 on photoxidation of LDPE (Processed at 150°C in the open chamber concentration of additive = 3×10^{-4} mol/100g of polymer.

1,Tinuvin 770(10 mins), 2,Tinuvin 770(30 min), 3,HOBP(10 min), 4,HOBP(30 min)
5, Control (10 min), 6,Control (30 min).

Figure 4.9

Effect of Tinuvin 770 on vinyl formation during photoxidation of LDPE. Numbers on the curve represent processing time in minutes.

Figure 4.9(a)

Time of irradiation in hours

Vinyl index

Comparison of behaviour of stabilizers as screen and as additives in LDPE (Processed at 150°C/30 min. in the open chamber). 1,No additive, 2,ZnDEC or Tinuvin 770 (screen), 3,NiDEC (screen), 4,HOBP (screen), 5,HOBP(additive), 6,ZnDEC (additive), 7,NiDEC (additive), 8,Tinuvin 770 (additive)

Figure 4.10

TABLE 4.1

U.V. absorption intensity of additives in polyethylene film after processing (all processed at 150°C in an open chamber, concentration of additives 3×10^{-4} mol/100g of polymer each).

Additive	λ max (nm)	Absorbance 10 min	30 min
NiDEC	330	0.940	0.920
	395-400	0.200	0.200
ZnDEC	285	0.50	0.50
HOBP	330	0.650	0.480
Ni[Sec-Butylamine]DEC	330	1.12	
	400	0.32	
Zn[Sec-Butylamine]DEC	285	0.71	
Zn[tert-Butylamine]DEC	285	0.730	
Zn[n-Butylamine]DEC	285	0.360	
Zn[Di-n-Butylamine]DEC	285	0.320	
Zn[Di-nonylamine]DEC	285	0.320	

TABLE 4.2

Effect of processing times on the u.v. life time of low density polyethy-lene films containing additives (concentration 3×10^{-4} mol/(100g).

Additive	Time to embrittlement (hours)	
	10 min	30 min
Control	1200	900
ZnDEC	1400	1400
ZnDBC	1400	1400
NiDEC	1800	1800
NiDBC	2200	2200
HOBP	2200	1600
Irganox 1076	1800	1750
Tinuvin 770	2250	2400
Zn-[n-Butylamine]DEC	1500	
Zn-[Sec-Butylamine]DEC	1900	
Zn-[tert-Butylamine]DEC	1650	
Zn-[Di-n-Butylamine]DEC	1500	
Zn-[Di-2ethylhexylamine]DEC	1450	
Zn-[Di-nonylamine]DEC	1500	
Ni-[tert-Butylamine]DEC	2100	
Ni-[sec-Butylamine]DEC	2250	

4.A.1.3 Discussion

In the previous chapter (Chapter 3) experimental evidence has been sought with the aim of elucidating the possible oxidative degradation mechanism occurring during the thermal and photo-oxidation of LDPE. The significance of hydroperoxide acting as a key initiator during the both types of oxidative processes of LDPE has been clearly established. In view of this evidence an understanding of the behaviour of different types of anti-oxidants and u.v. stabilizers on thermal and photo-oxidation of LDPE should be possible.

The u.v. stabilizing mechanism of many commercial additives has not been fully established and many reports in the literature[1,142] differ on basic u.v. mechanisms. This is especially true for metal complexes (chelates), typified in the present study by the dithiocarbamates. Several workers have suggested that the u.v. stabilizing action of nickel-dibutyldithiocarbamate is due to the quenching of photo-excited chromophores present in the polymer as oxidation products[64, 143, 144]. While others suggest that quenching of excited singlet oxygen by NiDBC is more important than quenching of chromophores[74]. Both of these reported mechanisms for the u.v. stabilization of polymers by addition of nickel-chelates are an extension of the original proposal for the photo-initiation of polymers involving carbonyl triplet states and subsequent quenching by ground state oxygen forming singlet state oxygen[33]. The experimental evidence in the preceding chapter (Chapter 3) clearly shows that excited triplet carbonyl and hence singlet oxygen play an insignificant role in the photo-initiation of polyolefins. However,

the evidence does suggest that hydroperoxides are the potential initiators
in thermal and photo-oxidation of LDPE. Consequently the u.v. stabilizing
activity of metal-dithiocarbamates and other additives will be discussed
with reference to hydroperoxidation.

It is clear from figs. 4.1 and 4.2 that a typical chain-breaking
anti-oxidant (Irganox 1076) and ZnDEC or NiDEC which is typical of
peroxide decomposing class[15(d)] are equally effective as thermal stabi-
lizers for LDPE whereas a u.v. absorber (HOBP) has only minor thermal
anti-oxidant property. Clearly, the peroxide decomposing anti-oxidant
behaviour of ZnDEC or NiDEC begins in the polymer during heat treatment
and is carried through to the u.v. exposure stage (fig. 4.3). A
characteristic feature of the activity of these anti-oxidants is a very
sharp end to the induction period, when free metal ions are liberated by
oxidative destruction of the complex. Both ZnDEC and NiDEC showed an
induction period on u.v. irradiation which lasted just as long as the
spectrum of the metal complex could be observed in the polymer by u.v.
spectrophotometry (fig. 4.4, curves 1 & 2). This is in agreement with
previously published results on the anti-oxidant action of the dithio-
carbamates[56, 145], in which it was shown that the metal dithiocarbamate
complex is not itself an anti-oxidant but that a Lewis acid formed from
it is responsible for a rapid catalytic destruction of hydroperoxide.
It was shown that sulphur dioxide or sulphur trioxide formed by reaction
between hydroperoxide and dithiocarbamate and which catalytically de-
composes hydroperoxides by an ionic process (discussed in section 1.1.3)
are probably responsible for their activity. Metal dithiocarbamate
complexes vary in u.v. stability. The nickel complex (NiDEC) is

relatively stable to u.v. light compared with ZnDEC (fig. 4.4) and acts
as a powerful u.v. stabilizer, because as well as decomposing hydroperoxide,
it can also act as a u.v. screening agent (fig. 4.10), which has also
previously been shown by Ranweera and Scott[60].

Primary amine complexes (particularly sec-butylamine) with zinc and
nickel dithiocarbamate showed a remarkable increase in u.v. stabilization
effectiveness in LDPE compared with the parent dithiocarbamate (figure
4.7 and Table 4.2). Amine complexes act by decomposing hydroperoxide
into non radical products like dithiocarbamates themselves. No hydro-
peroxide could be detected during processing and subsequent early stages
of photo-oxidation. The complexes are destroyed at the sharp end of
the induction period. Amine complexes are also equally effective in
both mildly processed and severely processed LDPE samples. Hydroperoxides
decomposition efficiency is found to increase by the amine complexes over
the parent dithiocarbamates (this will be discussed in Chapter 5).
This may be due to an increase in electron density at the metal atom by
the amine which enhances the formation of the effective Lewis acid cata-
lyst for hydroperoxide decomposition (Chapter 5).

Secondary amine complexes and the n-Butylamine complex of zinc and
nickel diethyldithiocarbamate did not show much improved u.v. stabilization
effectiveness. This may be due to destruction of complexes during

processing possibly by volatalization *of the amine.* After *the* processing operation very small amount of complex remains in the polymer as determined by the u.v. spectrophotometry (Table 4.1).

The following factors might contribute to the overall u.v. stabilization effectiveness of amine complexes in LDPE: 1) increased peroxide decomposition capacity, 2) increased solubility of complexes in polymer, 3) higher u.v. stability and 4) improved u.v. screening efficiency. All the factors will be considered in more details in the next chapter on the basis of model compound study.

A typical 'u.v. absorber' HOBP acts as mild thermal anti-oxidant (figures 4.1, 4.1(a) and 4.2) in LDPE as has also been observed previously in HDPE[18]. It was suggested that this anti-oxidant activity associated with HOBP occurs by a free-radical chain stopping reaction rather than by peroxide decomposition. When HOBP is used as additive or screening agent for LDPE the same inflexion in the carbonyl indices as in the unstabilized sample is observed indicating that stabilizing activity of HOBP is not by removing hydroperoxides (fig. 4.10). It is also clear from figure 4.10 that the u.v. protective action of HOBP when incorporated into the polymer is much more greater than when it is present in a separate screening film. This indicates clearly that HOBP protects the polymer partly due to its known u.v. screening behaviour but that this is not the sole protective action. The same phenomenon has also been observed by other workers[60, 65, 146].
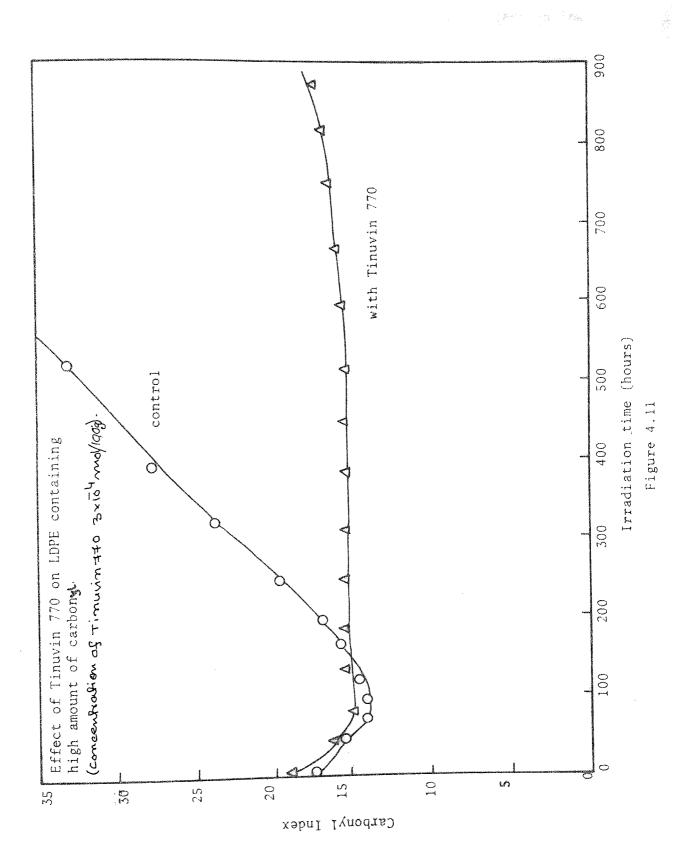
Figure 4.3 shows that the retardation of the photo-oxidation rate in a severely processed sample (30 minutes) by HOBP is not as great as it is in a mildly processed sample (10 minutes). This result suggests that some interaction may occur between the u.v. absorber and radicals produced by hydroperoxide decomposition which reduces the activity of HOBP in a severely processed sample. A similar conclusion may also be reached from figure 4.5 (curves 1 & 2). It is found that LDPE processed with HOBP in a closed chamber (which produces only minor amounts of hydro-peroxide) on exposure to u.v. light is more u.v. stable than a sample which is processed in the open chamber (producing more hydroperoxide). The time to embrittlement of LDPE also differs under these conditions which are respectively 2400 and 2200 hours. The same interaction of radicals with HOBP might contribute to the u.v. stabilization mechanism of HOBP in addition to u.v. screening. Carlsson and Wiles[147] have recently presented preliminary evidence which indicates that 2-hydroxy-benzophenone can scavange some of the polypropylene hydroperoxide photo-lysis products. Evidence for macroalkyl radical scavanging by 2-hydroxybenzophenone has also been presented by Chaudet and Tamblyn[148]. Radicals were produced by x-radiation or photolysis of polypropylene. For a series of 2-hydroxybenzophenones, stabilizer effectiveness was found to correlate with radical scavanging ability. Radical scavanging behaviour of 2-hydroxybenzophenone was also reported in a recent review by Carlsson and Wiles[149]. The function and mechanism of action of HOBP will be further discussed in Chapter 6.

The substituted piperidene, Tinuvin 770 acts as pro-oxidant during processing and subsequent thermal oxidation of LDPE at 110°C (figure 4.1,

4.1(a) and 4.2). By contrast, it effectively stabilizes LDPE during photo-oxidation (fig. 4.9 and Table 4.2). It is also observed from figure 4.9 that a severely processed sample (30 minutes) shows a better u.v. stabilization effect than the mildly processed sample (10 minutes) which indicates that the pro-oxidant activity of Tinuvin 770 during processing is associated with its stabilizing effectiveness. The above results suggest that Tinuvin 770 operates by one mechanism during thermal oxidation of polymer and by a completely different mechanism during photo-oxidation. Neither the formation nor the decomposition of peroxides are affected by this compound during thermal oxidation of LDPE. However, the rate of thermal oxidation is accelerated as compared to the control. This pro-oxidant activity may be explained as the oxidation of the amine to the corresponding nitroxide by peroxide[51]. Under the conditions of high temperature oxidation, nitroxide radicals may probably abstract hydrogen from the polymers substrate producing new polymer radicals which can propagate the auto-oxidation chain reaction.

$$\dot{R} + O_2 \longrightarrow RO_2 \text{ etc.}$$

The UV stabilizing activity of Tinuvin 770 does not appear to be associated with either *catalytic* peroxide decomposition (shown in the next chapter) or screening of u.v. light (fig. 4.10). It does not absorb light in the region of 280 - 350 nm, moreover it has no effect on the photolysis

of carbonyl.   An LDPE sample containing Tinuvin 770 (at concentration of 3 x 10^{-4} mol/100g of polymer) which also contained a higher initial amount of carbonyl and no hydroperoxide showed a similar initial reduction of carbonyl to the control, figure 4.11.   This demonstrates that Tinuvin 770 does not function by quenching the triplet state of carbonyl.   Heller and Blatman [67] have also reported that the Tinuvin 770 and other similar substitu.ted piperidene compounds have no quenching ability for triplet carbonyl or singlet oxygen.   It seems likely then that u.v. stabilizing property of Tinuvin770 is associated with free radical scavanging activity by the compound itself or by nitroxide radicals derived therefrom.   Nitroxide radicals are well known trapping agents for propagating free radicals (Particularly $\dot{R}$) in photo-oxidation of polymers to give stable molecular products [52, 150 - 153].   More fundamental studies are needed to confirm the mechanism of its action.

Effect of Tinuvin 770 on LDPE containing
high amount of carbonyl.
(concentration of Tinuvin 770 3×10^{-4} mol/100g).

control

with Tinuvin 770

Carbonyl Index

Irradiation time (hours)

Figure 4.11

4.A.2. <u>Synergistic action of anti-oxidants and stabilizers in low density polyethylene</u>

<u>Results and Discussion</u>

It was shown in the previous section that peroxide-decomposing anti-oxidant, zinc diethyldithiocarbamate (ZnDEC) and a commercially effective chain-breaking anti-oxidant (Irganox 1076) are equally effective as thermal stabilizers for low density polyethylene whereas u.v. absorber (HOBP) has only a minor effect on the thermo-oxidative stability of LDPE compared with both anti-oxidants (fig. 4.2).

The effects of ZnDEC and Irganox 1076 alone and in combination with one another at the same molar concentration (3×10^{-4} mol g^{-2}) on the thermo-oxidative stability of LDPE are compared in figure 4.12 and Table 4.3.   It can be seen from Table 4.3 that ZnDEC or Irganox 1076 alone produced an induction period of about 110 hours in the accelerated thermal oxidation of LDPE (heated at 110 °C in a Wallace oven).   However, there was a remarkable improvement in the oxidative resistance when ZnDEC was combined with Irganox 1076.   This combination shows an induction period of 330 hours which is far in excess of the additive effect of the same two anti-oxidants used separately (220 hours).   This remarkable improvement in thermo-oxidative stability of LDPE is attributed to the synergism between ZnDEC and Irganox 1076 whereas the combined effects of u.v. absorber (HOBP) and the peroxide decomposer (ZnDEC) under the identical conditions were found to be just additive (fig. 4.12 and Table 4.3).

The synergistic effect between ZnDEC and Irganox 1076 can probably be explained by viewing each of the components - ZnDEC and Irganox 1076 as protecting the polymer by different and complementary mechanisms. The anti-oxidant action of dithiocarbamates[56,145], like other sulphur anti-oxidants[59], involves an initial radical generating step before the formation of a Lewis acid (probably SO_2 or SO_3) anti-oxidant which destroys hydroperoxide by an ionic process. An important function of chain-breaking anti-oxidant (Irganox 1076) in this situation is to inhibit radical generation[1, 15, 57, 76]. Subsequently the Lewis acid anti-oxidant reduces peroxide content by converting it into non-radical products so that fewer $R\dot{O}_2$ or $R\dot{O}$ radicals are produced to be removed by Irganox 1076. On the other hand Irganox 1076 removes chain propagating $R\dot{O}_2$ radicals to lower the chain length of the oxidative process and effectively decreases the amount of peroxide which ZnDEC must eliminate, thus extending the useful life of the peroxide de-composer. It is thus evident that the two anti-oxidants can act in a co-operative manner to give a synergistic effect.

Although an equimolar mixture of hydroperoxide decomposer (Zn or NiDEC) and 'u.v. absorber' HOBP (3 x 10^{-4} mol/100g) showed only an additive effect during thermal oxidation of LDPE (fig. 4.12 & Table 4.3), the same combination shows a very powerful synergistic stabilizing effect during photo-oxidation of LDPE. This is shown in figures 4.13 and 4.14. The effect of processing conditions on the u.v. life time of polyethylene films containing synergistic u.v. stabilizers is also shown in Table 4.4. Both ZnDEC and NiDEC alone gave rise to induction periods relative to the control but had a minor effect in the subsequent rate of photo-oxidation (fig. 4.13, curve 3 and fig.4.14 curve 4). HOBP alone on the other hand

showed slower photo-oxidation at all stages and is found to be more effect-
ive in mildly processed sample than in the severely processed sample. How-
ever, the combination of both ZnDEC and NiDEC with HOBP is more effective
than that of HOBP alone even under the mildest conditions (fig.4.13, curve 7
and fig.4.14,curve 6). The most notable feature in both cases is that the
deleterious effect of the processing operation on HOBP is completely elimi-
nated. These results suggest that peroxide decomposers protect the u.v.
absorber during processing and initially during photo-oxidation and that
the u.v.absorber in turn has a protective effect on the metal complexes
during u.v.irradiation, thereby extending the period of their action.
Figure 4.15,curves 5 and 6, shows a first order plot of the decay of the
combined absorptions at 330 nm of ZnDEC and HOBP and of NiDEC and HOBP
which are both additive. For the first half of the decay, the rate is
the same order as that of HOBP alone (curve 4) and very much lower than
that of the dithiocarbamate alone (curves 1 & 2). The visible colour
of the nickel diethyldithiocarbamate decayed much more slowly in the
presence of HOBP than in its absence. The absorption at 390-5 nm was
followed kinetically and after an induction period it again decayed in
a first order reaction. The time of complete disappearance (fig. 4.15,
curve 3) corresponded almost exactly to the end of induction period to
photo-oxidation (fig. 4.14, curve 6). However, the rate of photo-
oxidation at the end of the induction period was much lower than that of
NiDEC alone (fig. 4.14, curve 4) and it appears from figure 4.15, curves
5 and 6 that the product formed from the dithiocarbamate in turn exerts
a protective effect upon HOBP. This can also be seen from the rate of

decay of HOBP in the later stages of oxidation in presence of metal complexes; the rate of decay of HOBP in presence of NiDEC or ZnDEC is considerably lower than that of HOBP alone.

Another interesting feature of this synergistic combination is that although ZnDEC alone is very much less effective than NiDEC, the synergistic combination of ZnDEC and NiDEC with HOBP gave a similar stabilization effect in LDPE on photo-oxidation. This finding has considerable practical significance since this combination does not impart any colour in the polymer after the processing operation whereas the nickel dithiocarbamate system imparts a green colour to the polymer.

The synergistic stabilizing effect observed in the polymer (figures 4.13 and 4.14) is not due to the cumulative screening effects of the two additives. This is clearly demonstrated by figure 4.16 which compares the u.v. stabilizing effectiveness of the individual additives and the combination of additives when used as screens in separate polymer films and as additives. The contribution of screening is found to be minimal compared with the effect of the mixture when incorporated into the polymer. A noticable feature of the synergistic combination is the complete absence of the initial rapid oxidation stage followed by auto-retardation which is always observed in the unprotected control during the first 100 hours and which is also evident in the screened films (fig. 4.16). This confirms the view that a primary function of the metal dithiocarbamates is to destroy peroxides during processing and subsequent photo-oxidation.

Figure 4.17 compares the protective effect of HOBP on ZnDEC as screen and as additive in LDPE processed at 150°C for 10 minutes (all concentrations 3×10^{-4} mole g^{-2}). Curve 3 represents photo-oxidation rate of LDPE containing ZnDEC as additive screened by control film containing no additive, whereas curve 4 shows the rate of photo-oxidation of LDPE containing ZnDEC as additive but screened by an identical film containing HOBP. Curve 5 shows the effect of ZnDEC and HOBP both as additives but screened by control. It is clear that HOBP can protect ZnDEC partly due to screening of u.v. light (curves 3 & 4) but it is also seen that additive effect of ZnDEC with HOBP is much greater than the screening effect on ZnDEC by HOBP (curves 4 & 5).

It was shown in the preceding section as well as by other workers[60] that NiDEC also acts as u.v. screener in addition to hydroperoxide de-composition. Fig. 4.18 shows the contribution of screening of u.v. light by NiDEC on HOBP and vice versa to the total u.v. stabilization effectiveness by HOBP and NiDEC as additive. It is clearly found that contribution due to screening of u.v. light by NiDEC or HOBP on one another cannot account for the total stabilization effect when used as additive together.

The above results suggest that both u.v. screening and some other chemical stabilization processes are involved in the effective photo-stabilization of dithiocarbamate complexes by HOBP. It has previously been suggested[64, 65, 148] that the hydroxybenzophenone u.v. stabilizers can accept energy from triplet carbonyl although it has been shown that this stabilization mechanism can only be important in polymers which

contain a substantial amount of carbonyl[60]. In principle the hydroxy benzophenone may quench photo-excited states of the dithiocarbamates but this is not the only possibility. Removal of free-radicals might also be involved. Again after the disappearance of the NiDEC spectrum (fig. 4.15, curve 3) the first order rate constant for the decay of the mixture fell below that of HOBP alone. It seems therefore that in addition to the above process, a product formed from the dithiocarbamate must be responsible for the protection of the u.v. absorber. It is known[56] that the anti-oxidant function of the dithiocarbamates is not due to the metal complex itself but to a Lewis acid (or acids) formed from it. It seems probable therefore that the protection of HOBP is due to the removal of hydroperoxides by the derived products.

Primary amine complex (particularly sec-Butylamine complex of ZnDEC) shows a much greater synergistic effect with HOBP in LDPE than does ZnDEC itself under the same conditions. The synergistic effect of sec-Butylamine-ZnDEC and HOBP in LDPE processed at 150°C for 10 minutes (3×10^{-4} mol/100 gm each) is shown in fig. 4.19 and Table 4.4. The improved synergistic effect obtained with this combination may be due to the fact that sec-Butylamine-ZnDEC acts as more powerful hydroperoxide decomposer than ZnDEC and is more stable towards u.v. light (see the next chapter).

Irganox 1076 although reasonably effective as a u.v. stabilizer alone under both prior mild and severe processing conditions in LDPE (figure 4.3) is found to be antagonistic towards the peroxide decomposer in spite of the good thermal stabilization achieved with this combination

(fig. 4.12).   Figure 4.20(a) compares the effectiveness of equimolar
$(3 \times 10^{-4}$ mol/100 gm each) mixture of both hydroperoxide decomposer
(ZnDEC) and Irganox 1076 with either component of the mixture alone.
It is found that an equimolar mixture of ZnDEC and Irganox 1076 is less
effective than either component of the mixture alone and the same
behaviour is observed with NiDEC and Irganox 1076 (fig. 4.20(b)).
Antagonism between anti-oxidants suggests that the two substances inter-
fere with each others action.   The first order rate constant for the
decay of the dithiocarbamate is increased by the presence of phenolic
anti-oxidant (figure 4.21).   This clearly shows the phenol photo-
sentizes the decomposition of the dithiocarbamate leading to a decrease
in their effectiveness (fig. 4.20 and Table 4.4).   This is almost
certainly due to the presence of quinonoid products (stilbene quinones
and peroxy dienones) which are major products of the normal function of
phenols as anti-oxidants[15, 154].

Although Irganox 1076 and the peroxide decomposer in combination
show antagonistic affect on photo-oxidation of LDPE, an equimolar
mixture of Irganox 1076 and 'u.v. absorber' HOBP $(3 \times 10^{-4}$ mol/100g of
polymer each) synergises effectively in u.v. initiated oxidation of LDPE
subjected to both mild and severe processing conditions, figure 4.22 and
Table 4.4.   The synergistic action between Irganox 1076 and HOBP may be
explained on the basis of the fact that the phenolic anti-oxidant has
the ability to protect the hydroxybenzophenone from peroxides formed
during processing and during u.v. exposure (due to removal of chain
propagating radicals) and HOBP as well as behaving as a screen can
stabilize the quinonoid photo-sensitizers formed from the phenol.

Tinuvin 770 acts as proxidant in thermal oxidation but exerts very good stabilization effectiveness in photo-oxidation of LDPE. It is of practical interest to find whether Tinuvin 770 can synergise with other type of anti-oxidant. The effect of Tinuvin 770 and peroxide decomposer NiDEC (at equimolar concentration 3×10^{-4} mol/100g of polymer each) on photo-oxidation of LDPE processed at 150°C for 10 minutes in the open chamber is shown in figure 4.23. It is found that the combined effect of Tinuvin 770 and NiDEC is less than either component of the mixture alone which clearly shows the antagonism between the two additives. At present the reasons for this antagonism is not clear and requires further study.

It is clearly established that peroxide decomposers (ZnDEC, NiDEC or Zn[sec-Butylamine]DEC synergise effectively with 'u.v. absorber' HOBP at equimolar concentration (3×10^{-4} mol/100 gm of polymer each) during photo-oxidation of LDPE subjected to both mild and severe processing conditions and the evidences suggest that peroxide decomposers protect HOBP during processing and subsequent initial photo-oxidation of polymer by decomposing peroxide into non radical products and in turn HOBP protects metal complex partly by screening of u.v. light and also by other chemical processes. Therefore, there must exist an optimum concentration ratio of the additives in the synergistic mixture where all the processes are the most efficient. The importance of optimum concentration ratio of additives in the synergistic combination has also been pointed out by many workers[1, 76, 92, 155]. In order to establish the synergistic optimum, the effect of varying the concentration of

additives in the photo-stabilization of LDPE was studied maintaining the total molar concentration of ZnDEC and HOBP constant. The following concentration ratios were used:

Concentration = $mol/100g$ of polymer

ZnDEC	HOBP
0	6×10^{-4}
1×10^{-4}	5×10^{-4}
2×10^{-4}	4×10^{-4}
3×10^{-4}	3×10^{-4}
4×10^{-4}	2×10^{-4}
5×10^{-4}	1×10^{-4}
6×10^{-4}	0
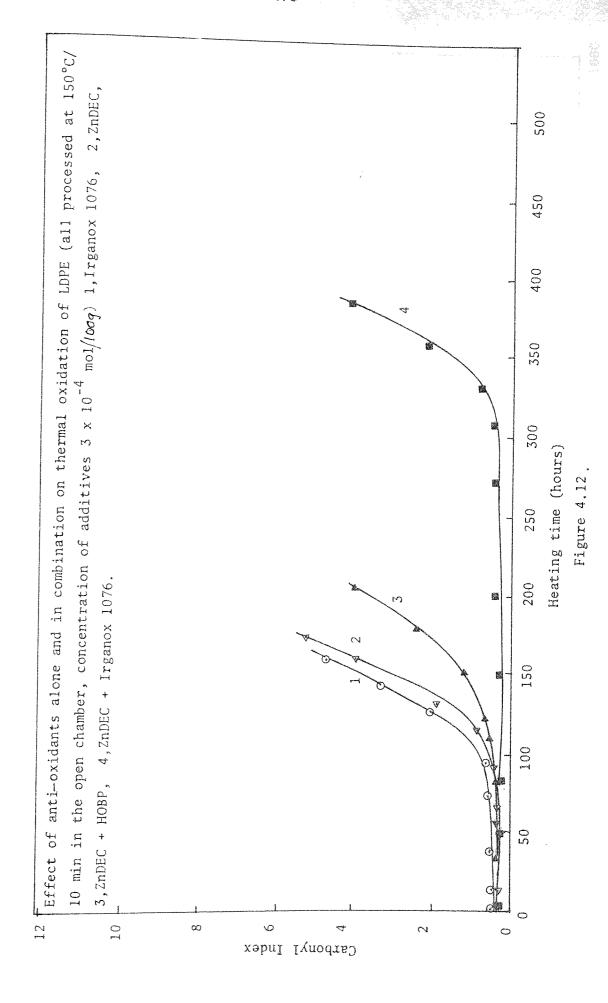
Similar experiments were also carried out with Zn[sec-Butylamine] DEC and HOBP. The induction periods given by each concentration ratio on photo-oxidation of LDPE is plotted against mole fraction of peroxide decomposer with respect to HOBP in figure 4.24. It is found that both ZnDEC and its sec-Butylamine complex in combination with HOBP show a maximum length of induction period at concentration ratio of 2×10^{-4}: 4×10^{-4}, i.e. 1:2 of peroxide decomposer to HOBP.

Continuous films of even thickness of LDPE containing synergistic mixtures of ZnDEC, Zn[sec-Butylamine]DEC and NiDEC with HOBP at total molar concentrations of 6×10^{-4} $mol/100g$ and 12×10^{-4} $mol/100g$ were extruded using an 18mm Betol, (Betol Machinery Ltd., Luton, Bedford-shire). Fixed temperature settings were used throughout all operations.
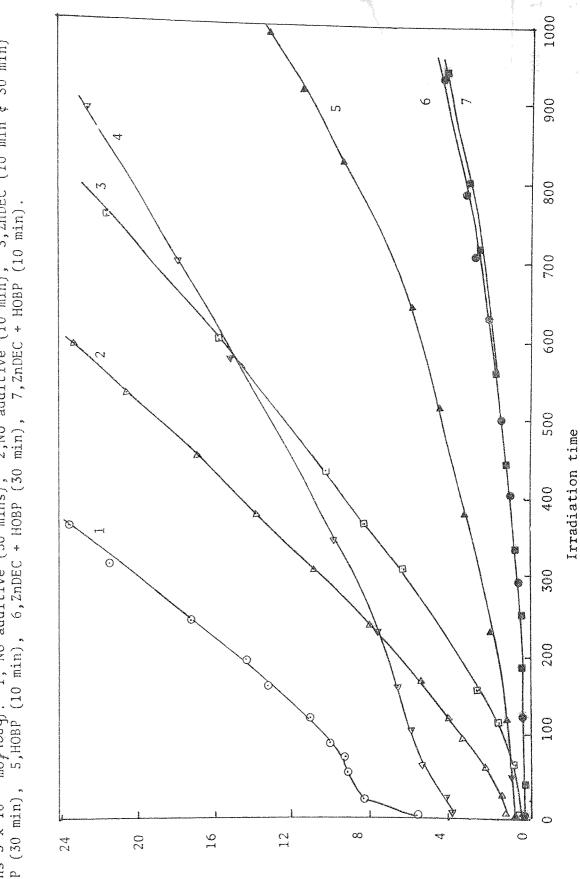
These were as follows: barrel zone 3 at 160°C, barrel zone 2 at 150°C, barrel zone 1 at 140°C, die zone 1 and 2 at 160°C. The top take-off was set at 60°C and the bottom at 40°C. Take-off speed was fixed at 10 ft/min and screw speed at 40 rev/min.

Continuous film of even thickness of LDPE with the above synergistic mixtures at total molar concentrations of 6×10^{-4} mol/100g of polymer was also prepared using the Barand film blower coupled with Humbold extruder. Melt temperature at screw tip was fixed at 160°C.
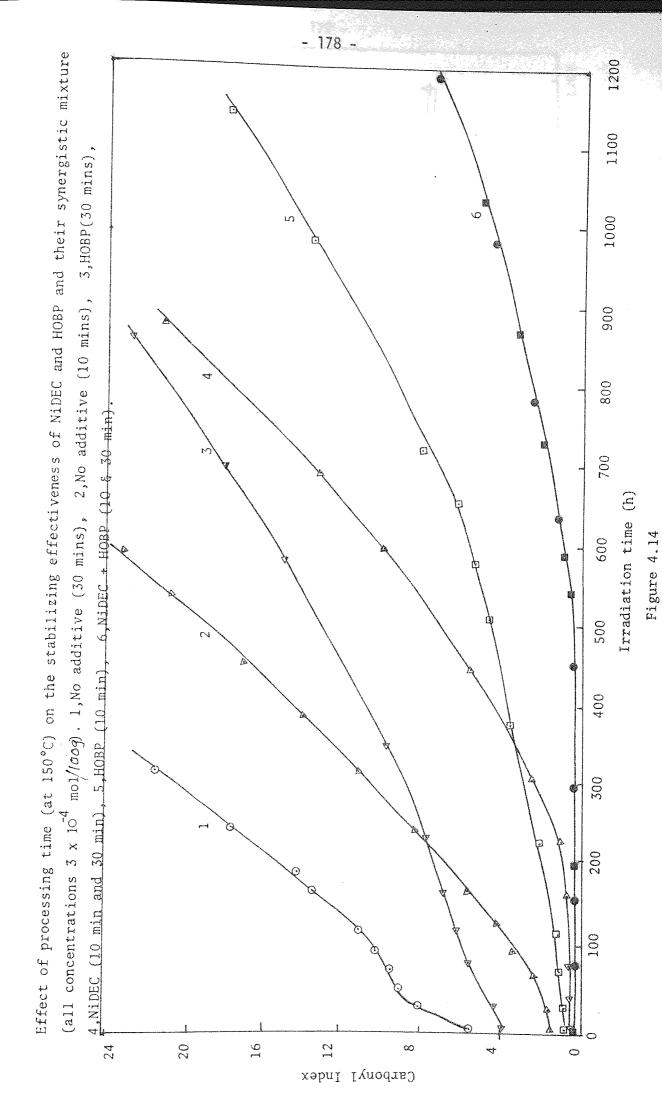
The extruded and blown films of the above formulations are being exposed under the conditions of natural weathering as well as in the u.v. cabinet for artificial weathering. Results from these experiments are not yet available and will be verbally reported.

Effect of anti-oxidants alone and in combination on thermal oxidation of LDPE (all processed at 150°C/10 min in the open chamber, concentration of additives 3×10^{-4} mol/100g) 1,Irganox 1076, 2,ZnDEC, 3,ZnDEC + HOBP, 4,ZnDEC + Irganox 1076.

Figure 4.12.

Effect of processing time on the^effectiveness of ZnDEC and HOBP and their synergistic mixture (all concen-
trations 3×10^{-4} mol/100g). 1, No additive (30 mins), 2,No additive (10 mins), 3,ZnDEC (10 min ¢ 30 min)
4, HOBP (30 min), 5,HOBP (10 min), 6,ZnDEC + HOBP (30 min), 7,ZnDEC + HOBP (10 min).

Stabilizing

Carbonyl Index

Irradiation time

Figure 4.17

Effect of processing time (at 150°C) on the stabilizing effectiveness of NiDEC and HOBP and their synergistic mixture (all concentrations 3 x 10⁻⁴ mol/100g). 1,No additive (30 mins), 2,No additive (10 mins), 3,HOBP(30 mins), 4.NiDEC (10 min and 30 min), 5,HOBP (10 min), 6,NiDEC + HOBP (10 & 30 min).

Figure 4.14

Change in the UV and visible absorption spectrum of additives during the photo-oxidation of LDPE (processed 10 min. at 150°C, concentration of additives, 3 x 10⁻⁴ mol/(log). 1, ZnDEC (285 nm), 2, NiDEC (330 nm), 3, NiDEC + HOBP (390-5 nm), 4, HOBP (330 nm), 5, ZnDEC + HOBP (330 nm), 6, NiDEC + HOBP (330 nm).

Figure 4.15

Comparison of behaviour of stabilizers as screens and as additive in LDPE (Processed at 150°C/30 min)
1, No additive; 2, NiDEC(screen); 3, HOBP(screen); 4, NiDEC+HOBP(screen); 5, HOBP(additive)
6, NiDEC(additive); 7, HOBP+NiDEC(additive).

Figure 4.16

Comparison of protective effect of HOBP on ZnDEC as screen and as additive in LDPE processed at 150°C/10 min. (All concentrations 3 x 10⁻⁴ mol/(00g). 1, No additive; 2, ZnDEC(additive); 3, ZnDEC(additive screened by film with no additive) 4,ZnDEC(additive screened by HOBP); 5,ZnDEC+HOBP (screened by film with no additive).

Figure 4.17

Comparison of protective effect of HOBP on NiDEC and NiDEC on HOBP as screens and as additive in LDPE processed at 150°C/10 min. (All concentrations 3 x 10⁻⁴ mol/100 g). 1, NiDEC(additive screened by film with no additive); 2, HOBP(additive screened by film with no additive); 3, NiDEC(additive screened by HOBP); 4, HOBP(additive screened by NiDEC; 5, NiDEC+HOBP(additive screened by film with no additive).

Figure 4.18

Effect of 2n-[sec-Butylamine]DEC and HOBP and their synergistic mixture (all concentrations 3 x 10^{-4} mol/100g) on photoxidation of LDPE (Processed at 150°C/10 min).

1, No additive (10 min);
2, Zn-[sec-Butylamine]DEC;
3, HOBP;
4, HOBP+Zn-[sec-Butylamine]DEC.

Figure 4.19

Effect of processing time at 150°C on the stabilizing effectiveness of Irganox 1076 and its synergistic mixture with ZnDEC in LDPE (all concentrations 3 x 10^{-4} mol/00g). 1, No additive (30 min);2, No additive (10 mins); 3, ZnDEC+1076 (10 mins); 4, ZnDEC+1076 (30 min); 5, ZnDEC(10&30 min); 6,1076(30 min); 7,1076(10 min).

Figure 4.20(a)

Effect of processing time at 150°C on the stabilizing effectiveness of Irganox 1076 and its synergistic mixtures with NiDEC in LDPE (All concentrations 3×10^{-4} mol/$100g$). 1,No additive (30 min); 2, No additive (10 min); 3, NiDEC+Ir.1076(10 min); 4, NiDEC+Ir.1076(30 min); 5,NiDEC (10&30 min); 6,Irganox 1076(30 min); 7, Irganox 1076(10 min).

Figure 4.20(b)

Change in the UV absorption intensity of ZnDEC and NiDEC in the presence of Irganox 1076 during photoxidation of LDPE (all concentrations 3 x 10^{-4} mol/100g). 1,ZnDEC+Irganox 1076; 2,ZnDEC; 3, NiDEC + Irganox 1076; 4,NiDEC.

Figure 4.21

Effect of processing time (at 150°C) on the stabilizing effectiveness of Irganox 1076 and its synergistic mixture with HOBP in LDPE. (Concentration of additives 3×10^{-4} mol/100g each).

1, No additive (30 min); 2, HOBP (30 min); 3, 1076 (30 min); 4, 1076 (10 min); 5, HOBP (10 min); 6, 1076+HOBP (30 min); 7, 1076+HOBP (10 min).

Figure 4.22

Effect of Tinuvin 770 and NiDEC alone and in combination on photoxidation of LDPE(processed at 150°C/10 min in open chamber, concentration of additive 3 x 10⁻⁴ mol/100g of polymer each). 1,NiDEC; 2,NiDEC+Tinuvin 770; 3,Tinuvin 770.

Figure 4.23

Synergism between peroxide decomposers (ZnDEC and its amine salt) and HOBP at constant total concentration

Zn[sec-Butylamine]DEC + HOBP

ZnDEC + HOBP

Peroxide decomposer (mole per cent)

Induction period

Figure 4.24

TABLE 4.3

Induction periods to onset of carbonyl formation in the thermal oxidation of LDPE films (110°C). All concentrations 3×10^{-4} mol/100g.

Formulation	Induction period (hours)	Calculation on additive basis
No additive	10	—
HOBP	10	—
Irganox 1076	110	—
ZnDEC	110	—
NiDEC	105	—
Irganox 1076 + ZnDEC	330	220
Irganox 1076 + NiDEC	320	215
HOBP + ZnDEC	130	120

TABLE 4.4

Effect of processing conditions on the u.v. life time of polyethylene films containing synergistic u.v. stabilizers (concentration 3×10^{-4} mol/100g of polymer).

Stabilizer	Time to embrittlement (hours)	
	10 mins	30 mins
Control	1200	900
ZnDEC	1400	1400
HOBP	2200	1600
Irganox 1076	1800	1750
NiDEC	1800	1800
ZnDEC + HOBP	>4000	>4000
ZnDEC + Irganox 1076	1250	1250
NiDEC + HOBP	>4000	>4000
NiDEC + Irganox 1076	1580	1580
Irganox 1076 + HOBP	>3500	>3500
Zn-[sec-Butylamine]DEC	1900	
Zn-[sec-Butylamine]DEC + HOBP	4600*	
Tinuvin 770	2250	2400
Tinuvin 770 + NiDEC	1850	

* Polymer started to embrittle at 4500 hours and embrittled completely at 4800 hours.

4.B. Effect of anti-oxidants and stabilizers on processing and subsequent u.v. exposure of polypropylene
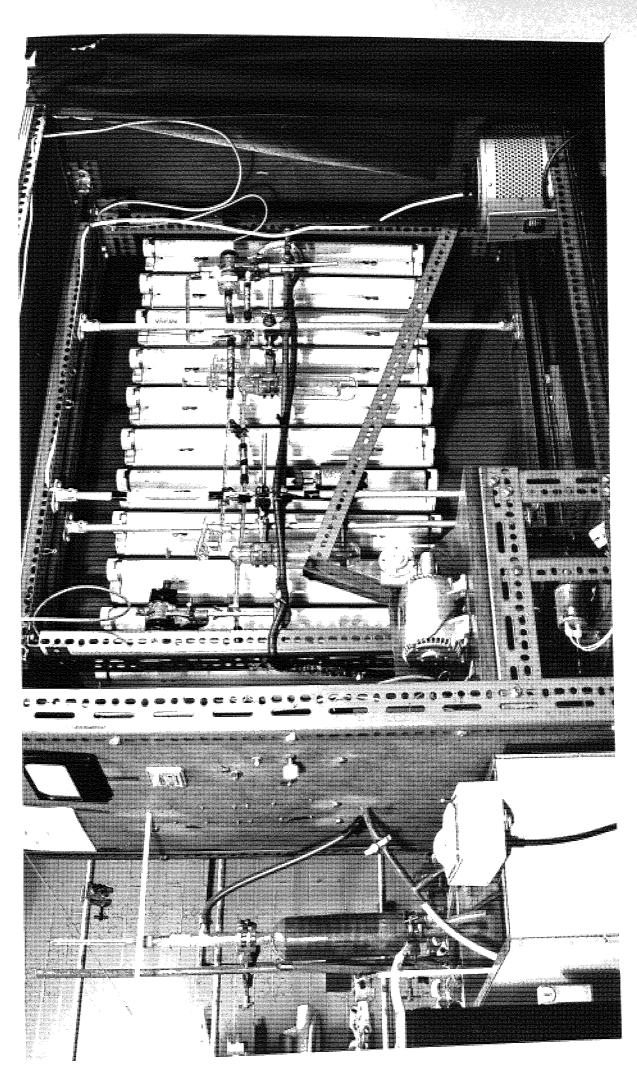
4.B.1 Experimental

Processing of polypropylene with the additives was carried out as follows: The additives were initially tumble-mixed with polypropylene powder for at least one hour. The compounded polymer was then processed at 180°C in the RAPRA Torque-Rheometer for various times. The processed samples were then compression moulded to films of thickness 8×10^{-3} inches at 180°C.

The polymer films with additives were exposed in the u.v. cabinet for photo-oxidation (shown in photograph I).

Irradiation of polypropylene films containing additives was also carried out at different temperatures viz 30°C, 40°C and 50°C. This was done in a u.v. cabinet shown in photograph 2. Here two identical sets of tubes were arranged on the reciprocating rack (10 cm) in front of light source. Samples (up to 30 cm^2) were fixed onto the face of inner (pyrex) tube. This was enclosed in a larger (fused quartz) tube. The film was maintained at constant temperature by pumping thermostatically controlled water through the inner tube and cooling the returning water by means of a water condenser. This arrangement enabled the reaction temperature to be varied from 15°C to 70°C.

The rate of photo-oxidation of polypropylene with the additives was followed by measuring carbonyl index expressed as $A_{1715cm^{-1}}/A_{905cm^{-1}}$.

PHOTOGRAPH NO. 2

4.B.1.1 Results and Discussion

The behaviour of anti-oxidants and stabilizers in polypropylene under the conditions of processing and subsequent u.v. exposure are found to be in most cases similar to that of LDPE. When polypropylene was processed with hydroperoxide decomposer (ZnDEC, NiDEC or their amine complexes) or chain-breaking anti-oxidant Irganox 1076 at 180°C either in open or in closed chambers, a constant value of carbonyl index is found up to 30 minutes of processing and the value is very much lower compared to control (fig. 4.25). No hydroperoxide was detected in the samples containing metal dithiocarbamate complexes which suggest that they are all good melt stabilizers for polypropylene. On the other hand HOBP does not act as melt stabilizer in polypropylene as peroxide was formed when polypropylene was processed in an open chamber with HOBP. However, the rate of formation of carbonyl is lower than for the control, figure 4.25.

The effect of the above classes of additives on photo-oxidation of polypropylene in the form of compression moulded film (all processed at 180°C for 10 minutes in a closed chamber, concentration of additives 3×10^{-4} mol/$100g$ each) is shown in figure 4.26. On u.v. irradiation, the carbonyl indices of the polymers stabilized with ZnDEC and NiDEC, which were initially low, remained constant for 100 hours and 325 hours respectively. At the end of this time, the rate of carbonyl formation became similar to that for the control. This clearly suggests that peroxide decomposing activity begins in the processing operation which is carried through to the initial u.v. exposure stage. ZnDEC is less effective as a photo-stabilizer compared

to NiDEC as the former is less stable towards u.v. light than the latter. This is shown in figure 4.27 & 4.27(a) where the disappearance of u.v. absorption maxima for both complexes in the polymer are plotted against time of irradiation.

Although HOBP showed a better stabilization effect in LDPE in comparison to peroxide decomposers and chain-breaking anti-oxidants, its activity is not even as good as NiDEC or Irganox 1076 in polypropylene at the same molar concentration fig. 4.26. This may be due to the fact that polypropylene is a more oxidizable substrate than LDPE. Consequently more peroxide is formed in polypropylene within shorter exposure time also during thermal oxidation which causes destruction of HOBP. It was suggested in the preceding section that HOBP might also act as radical scavanger in addition to screening u.v. light. The same phenomenon may also be observed from figure 4.28 where it is shown that the photo-oxidative stability of polypropylene is very much reduced when it is processed in an open chamber with HOBP compared to the sample processed in the closed chamber at the same molar concentration (3×10^{-4} mol/100g of polymer). But ZnDEC and NiDEC do not show much difference in stabilizing activity under the both processing conditions.

The principal mode of operation of hindered phenolic anti-oxidant Irganox 1076 on photo-oxidation of polypropylene is to undergo a chain-transfer reaction with a propagating alkyl peroxy radical by donating a hydrogen forming hydroperoxide plus a relatively stable phenoxy radical[15].

$$AH + R\overset{.}{O}\overset{.}{O} \longrightarrow ROOH + \overset{.}{A}$$

Termination of the phenoxy radical by reaction with another alkyl peroxy radical producing a peroxy dienone[34] or by dimerisation will reduce the kinetic chain length (shown in Chapter 1, section 1.1.3). The consequences of this are seen clearly during photo-oxidation of polypropylene (fig. 4.26) as a retardation of the oxidation curve in the later stages. However, the absence of a sharp induction period is believed to be due to photolytic breakdown of the peroxy dienone producing initiating alkoxy radicals.

Figure 4.29 shows the concentration effect of ZnDEC, NiDEC, HOBP and Irganox 1076 on u.v. life time of polypropylene. Increasing the concentration of NiDEC and HOBP in polypropylene from 1×10^{-4} mol/100g to 10×10^{-4} mol/100g progressively increases the u.v. life time of polypropylene. However, the increased stability observed by addition of NiDEC to polypropylene is accompanied by a green colouration which is typical of this transition metal complex and is comparatively dark at higher concentrations. Although the colour fades during photo-oxidation of polypropylene film, embrittlement occurs before a significant loss of colour. Increasing concentration of ZnDEC in polypropylene resulted in only slightly improved photo-stability. The chain-breaking antioxidant, Irganox 1076, also does not show a significant concentration effect on the u.v. life time of polypropylene (fig. 4.29).
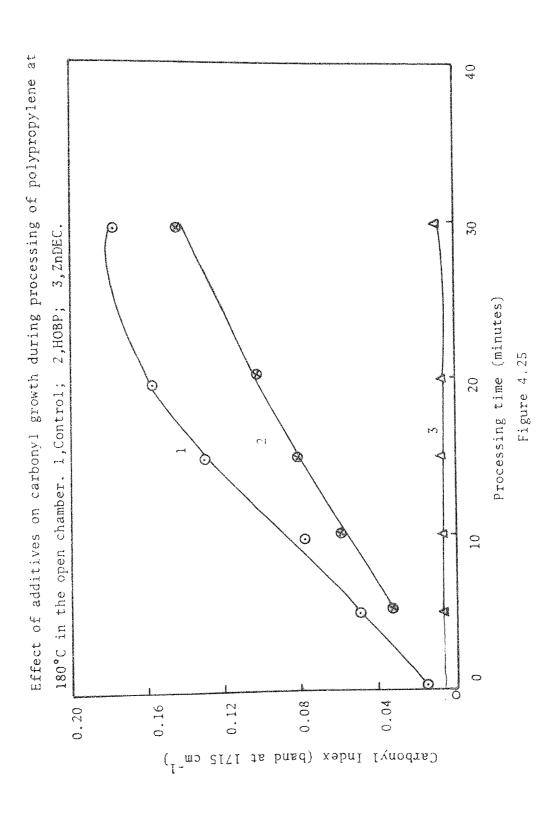
Figures 4.30 and 4.31 compare the stabilizing activity of various amine complexes of Zn and nickel diethyldithiocarbamates on the photo-oxidation of polypropylene, each at a concentration of 3×10^{-4} mol/100g of polymer. Polypropylene was processed with the amine complexes at
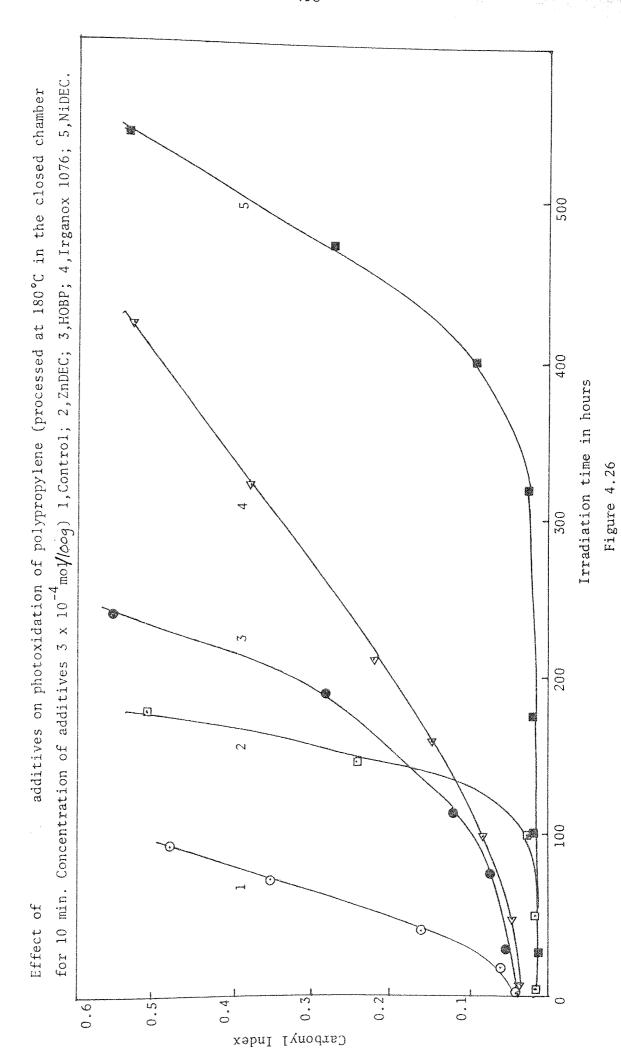
180°C for 10 minutes in a closed chamber. It is again evident from figures 4.30 & 4.31 that the sec-butylamine complexes of both Zn and Ni-diethyldithiocarbamate showed better stabilization effectiveness in polypropylene compared to other amine complexes. This effect is even greater than the dithiocarbamates themselves. UV stability of sec-butylamine complexes are compared with metal dithiocarbamates in figures 4.32 and 4.32(a) which show the stability of the metal dithio-carbamates are improved by amine complexing.
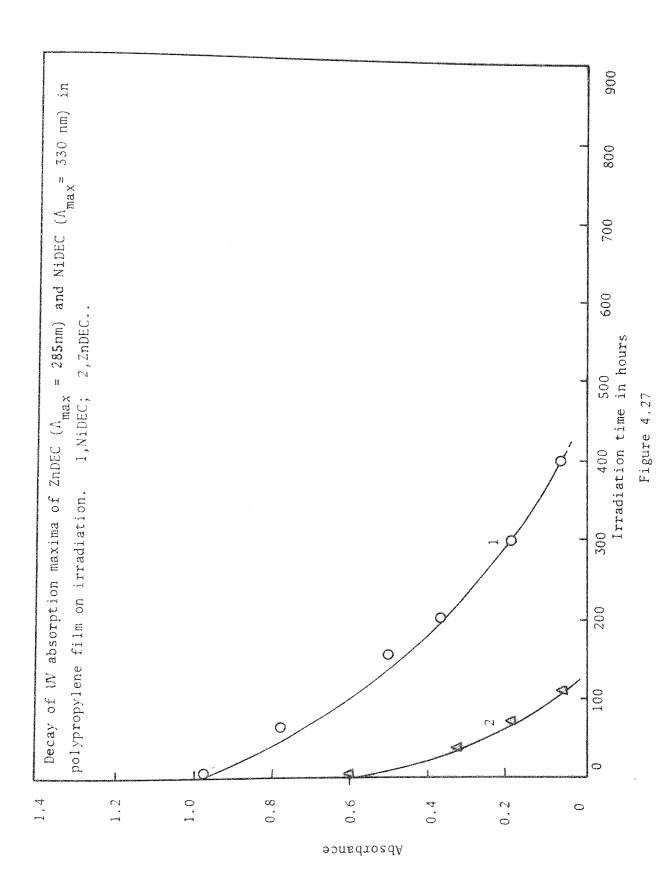
Other zinc dithiocarbamates viz Zn-[N-Lauryl]dithiocarbamate, Zn-[Di-hydrogenetedtallow]dithiocarbamate, Zn-[N-cocylaminopropyl]di-thiocarbamate and Zn-[N-oleylaminopropyl]dithiocarbamate showed only marginally improved activity with respect to the control figure 4.33. The effect is very much less than ZnDEC under identical conditions.
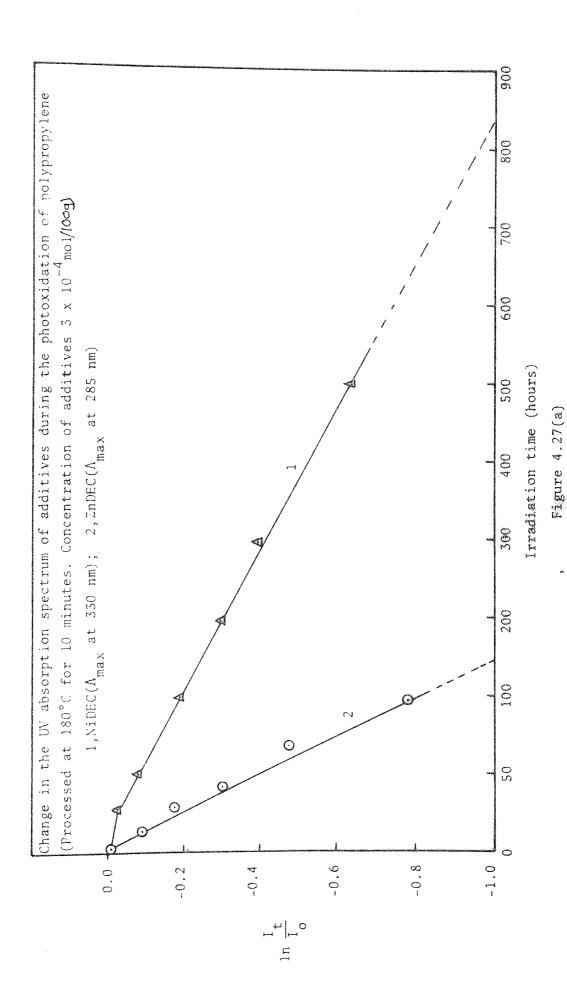
Embrittlement times of polypropylene with additives are shown in Table 4.5.
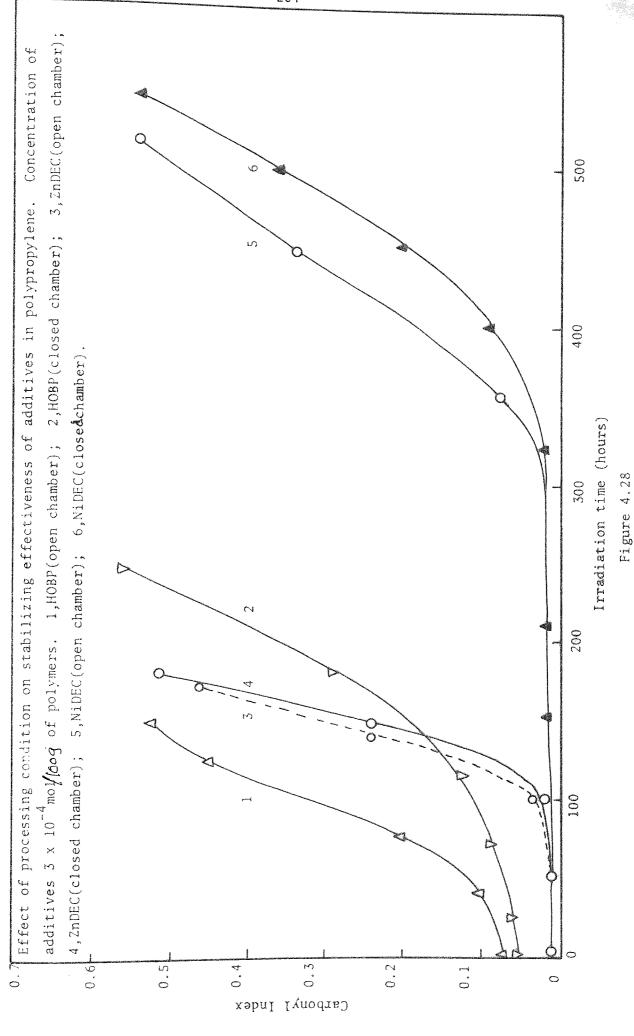
Table 4.5 also compares the u.v. life time of polypropylene with substituated piperidene compound, Tinuvin 770 with other anti-oxidants and stabilizers under identical conditons. The stabilizing activity of Tinuvin 770 is found to be better compared to other anti-oxidants and stabilizers. The carbonyl index of polypropylene containing Tinuvin 770 remained almost constant during photo-oxidation until embrittlement.

Effect of additives on carbonyl growth during processing of polypropylene at 180°C in the open chamber. 1,Control; 2,HOBP; 3,ZnDEC.

Figure 4.25

Effect of additives on photoxidation of polypropylene (processed at 180°C in the closed chamber for 10 min. Concentration of additives 3×10^{-4} mol/(oog) 1,Control; 2,ZnDEC; 3,HOBP; 4,Irganox 1076; 5,NiDEC.

Irradiation time in hours

Figure 4.26

Decay of UV absorption maxima of ZnDEC (Λ_{max} = 285nm) and NiDEC (Λ_{max} = 330 nm) in polypropylene film on irradiation. 1,NiDEC; 2,ZnDEC..

Figure 4.27

Change in the UV absorption spectrum of additives during the photoxidation of polypropylene (Processed at 180°C for 10 minutes. Concentration of additives 3×10^{-4} mol/100g)
1,NiDEC(A_{max} at 350 nm); 2,ZnDEC(A_{max} at 285 nm)

Figure 4.27(a)

Effect of processing condition on stabilizing effectiveness of additives in polypropylene. Concentration of additives 3 x 10⁻⁴ mol/(l00g of polymers. 1,HOBP(open chamber); 2,HOBP(closed chamber); 3,ZnDEC(open chamber); 4,ZnDEC(closed chamber); 5,NiDEC(open chamber); 6,NiDEC(closedchamber).

Figure 4.28

Effect of concentrations of additives on UV life time of polypropylene. (All are processed at 180°C in closed chambers).

Concentration of additives x 10 mol/100g of polymer

Figure 4.29

Comparison of stabilizing effectiveness of amine complexes of ZnDEC on photoxidation of poly-propylene (Processed at 180°C/10 min in closed chamber) Concentration of complexes = 5 x 10^{-4} mol/100 gm each case. 1,Control; 2,Zn-[n-Butylamine]DEC; 3,ZnDEC; 4,Zn[tert-Butylamine]DEC; 5,Zn[Di-n-Butylamine]DEC; Zn[Di-nonylamine]DEC; 6,Zn[sec-Butylamine]DEC.

Figure 4.30

Stabilizing activity of NiDEC and its sec-Butylamine complex on photoxidation of polypropylene (Processed at 180°C/10 min). 1,NiDEC(3 x 10^{-4}mol/100g); 2,Ni[sec-Butylamine]DEC (3x10^{-4}mol/100g); 3,NiDEC(10 x 10^{-4}mol/100g); 4,Ni-[sec-Butylamine]DEC(10 x 10^{-4}mol/100g)

Figure 4.31

Disappearance of absorption spectra of amine complexes in polypropylene film on irradiation (all concentrations 3×10^{-4} mol/100g). 1,ZnDEC(Λ_{max} 285nm); 2,Zn[sec-Butylamine]DEC(Λ_{max} 285nm); 3,NiDEC(330nm); 4,Ni[sec-Butylamine]DEC(330 nm).

Figure 4.32

Comparison of first order plot of : sec-Butylamine complex of metal diethyldithiocarbamate with the parent metal diethyldithiocarbamate. 1,Ni[sec-Butylamine]DEC; 2,NiDEC; 3,Zn[sec-Butylamine]DEC 4, ZnDEC.

Figure 4.32(a)

Effect of various Zn-dithiocarbamate complexes at same molar concentration $(3 \times 10^{-4}$ mol/(Øog) on photoxidation of polypropylene (processed for 10min/180°C in closed chamber). 1,Control; 2,Zn-[N-Lauryl]dithiocarbamate; 3,Zn-[N-oleylaminepropyl]dithio-carbamate; 4,Zn-[Di-hydrogeneted Tallow]dithiocarbamate; 5,ZnDEC.

Figure 4.33

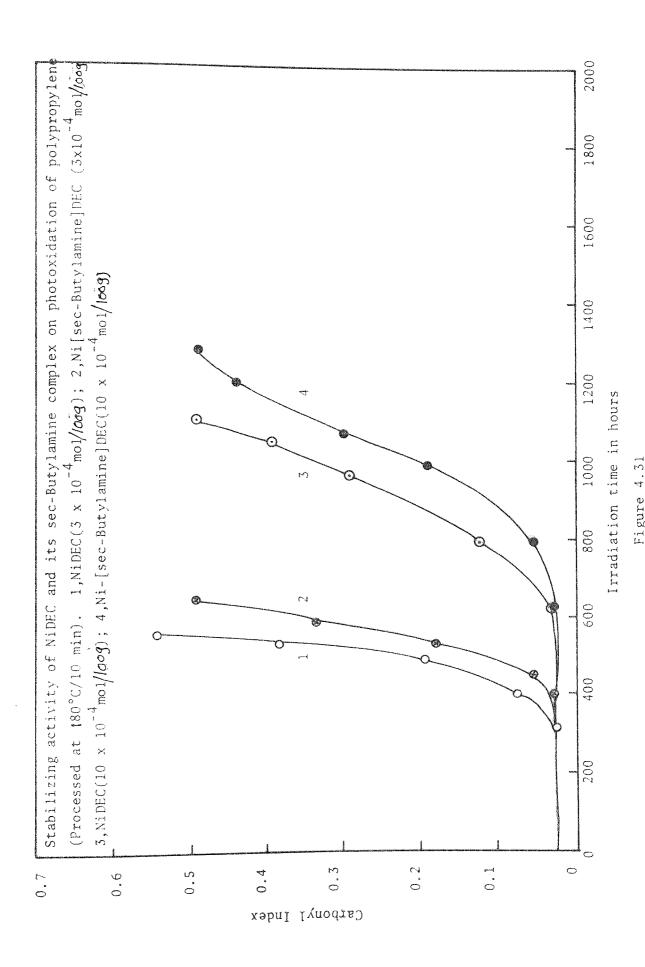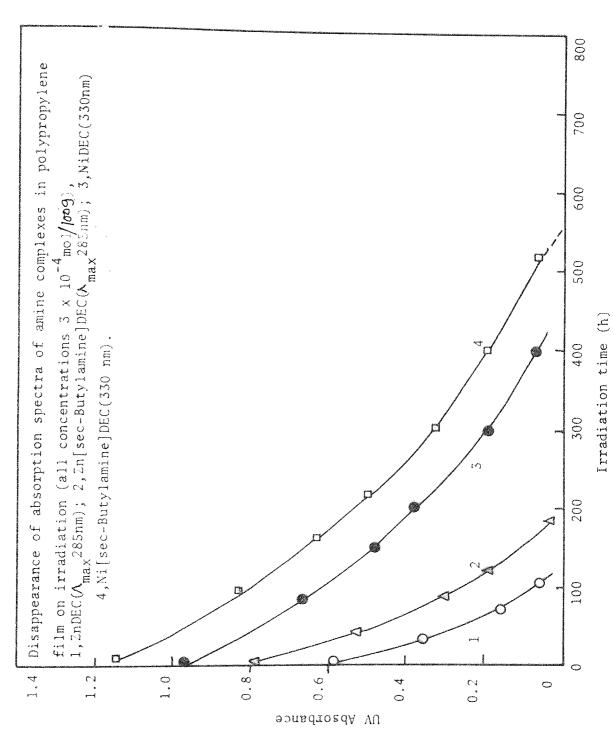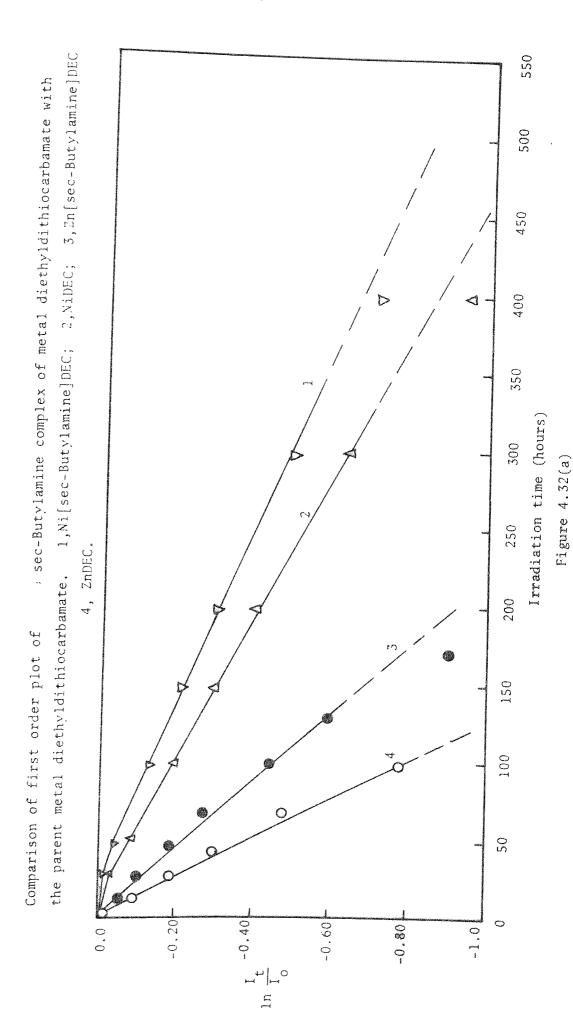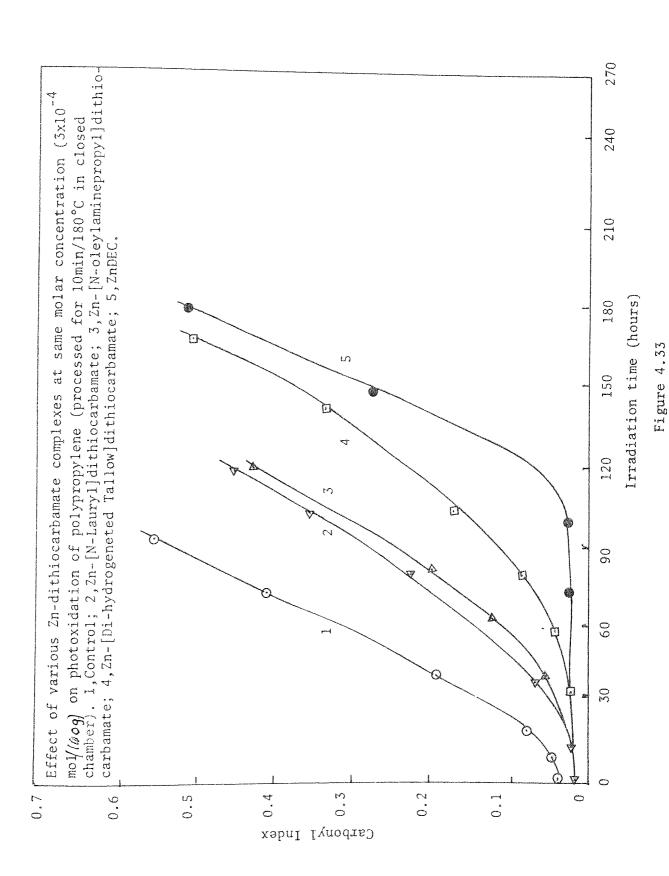TABLE 4.5

Comparison of u.v. life time of polypropylene with various anti-oxidants and stabilizers. (All processed at 180°C for 10 minutes in the closed chamber, concentration of additives 3×10^{-4} mol/100g of polymer).

Additive	Embrittlement times (hours)
Control	90
ZnDEC	175
NiDEC	500
Irganox 1076	325
HOBP	245
Tinuvin 770	700
Zn-[n-Butylamine]DEC	150
Zn-[sec-Butylamine]DEC	230
Zn-[tert-Butylamine]DEC	180
Zn-[Di-n-Butylamine]DEC	190
Zn-[Di-2ethylhexylamine]DEC	185
Zn-[Di-nonylamine]DEC	185
Zn-[N-Lauryl]dithiocarbamate	110
Zn-[Di-hydrogenetedTallow]dithiocarbamate	160
Zn-[N-cocylaminopropyl]dithiocarbamate	118
Zn-[N-oleylaminopropyl]dithiocarbamate	118
Ni-[sec-Butylamine]DEC	600

4.B.1.2 <u>Synergistic action between anti-oxidants and stabilizers</u>

<u>in polypropylene</u>

Although ZnDEC alone is not a good stabilizer in polypropylene photo-oxidation (Table 4.5), the same compound is found to be effective stabilizer, when used in combination with 'u.v. absorber' HOBP in polypropylene. Figure 4.34 shows the combined effect of ZnDEC and HOBP at the same molar concentration (3×10^{-4} mol/100g of polymer each) on photo-oxidation of polypropylene. The stabilizing effect in terms of the induction period or embrittlement times is found to be very much greater than the additive values when the components of the mixture are used separately (Table 4.6). Therefore ZnDEC and HOBP synergise effectively in polypropylene as was found in LDPE. Moreover, synergistic combinations of ZnDEC and HOBP show similar activity to NiDEC and HOBP (figure 4.35 and Table 4.6) at same molar concentration.

The synergistic combination of the sec-Butylamine complex of ZnDEC and HOBP shows an even better stabilizing effect in polypropylene than ZnDEC and HOBP (fig. 4.36 and Table 4.6).

Empirical evaluation of the synergistic action of peroxide decomposer and u.v. absorber in polypropylene shows that the optimum efficiency of this combination is found at 1:2 concentration ratio of peroxide decomposer to u.v. absorbers. This is demonstrated in figure 4.37 where the embrittlement time of polypropylene is plotted against varying concentrations of additives in the mixture at a total molar concentration 6×10^{-4} mol/100g of polymer. It seems likely that the

amount of peroxide decomposing anti-oxidant required to give optimum synergism is a reflection of its efficiency in removing peroxides produced during processing and subsequent initial photo-oxidation stages.
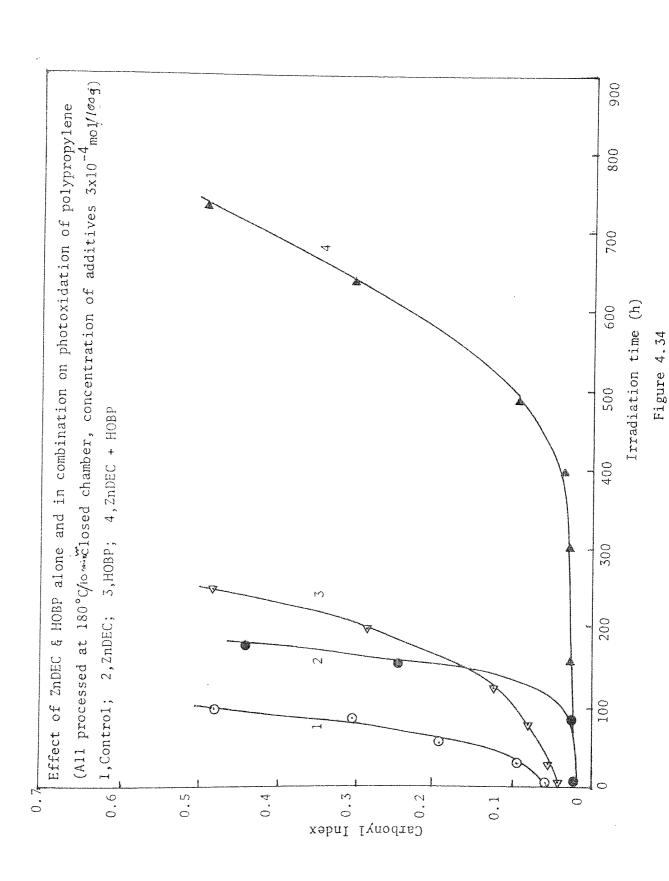
The chain-breaking anti-oxidant, Irganox 1076 also synergises with HOBP in polypropylene during photo-oxidation, although the effect is not as great as with the peroxide decomposer and HOBP (figure 4.38 and Table 4.6).
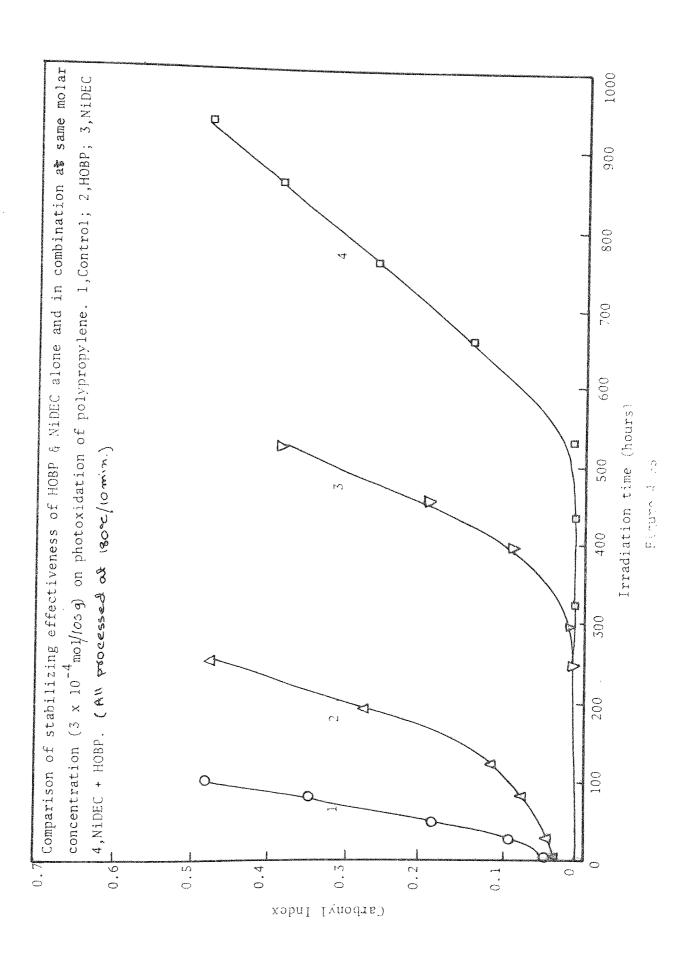
When the total molar concentration of synergistic mixture of peroxide decomposer and 'u.v. absorber' is increased from 6×10^{-4} mol/$100g$ to 12×10^{-4} mol/$100g$ and 20×10^{-4} mol/$100g$, the u.v. life time of polypropylene is found to increase proportionately Table 4.7.

The effect of ZnDEC and HOBP alone and in combination (3×10^{-4} mol/$100g$ of polymer each) on the photo-oxidation of polypropylene at temperatures 30, 40 and 50°C are shown respectively in the figures 4.39, 4.40 and 4.41. The embrittlement times of polypropylene under the above experimental conditions are shown in Table 4.8. The effectivity of HOBP is found to be considerably decreased on increasing temperature (fig. 4.40, Table 4.8) during u.v. irradiation whereas temperature variation has got little effect on photo-stabilizing activity of ZnDEC (figure 4.39 and Table 4.8). This is also evident from the figure 4.42 where u.v. life time of polypropylene containing above additives are plotted against $\frac{1}{T}$ (K) in the form of an Arrhenius type plot. By comparing lines 2 and 3 (fig. 4.42) it is clearly seen that variation of embrittlement time with temperature in case of HOBP is higher than

that of ZnDEC under the above experimental conditions.   This shows HOBP
is more temperature sensitive than ZnDEC.   This may be due to rapid
peroxide formation at higher temperature which causes destruction of HOBP.

It is seen from figure 4.41 that temperature effect on HOBP is
partly nullified when it is used in combination with ZnDEC.   This is
entirely consistant with the above results that ZnDEC can protect HOBP
from rapid peroxide formation in polypropylene at higher temperature
under u.v. irradiation.   Though a synergistic effect is observed with
HOBP and ZnDEC in combination at all temperatures used (fig. 4.41 and
Table 4.8) the temperature dependence of the embrittlement times with the
above combination is found to be even greater than that for HOBP alone
figure 4.42, curves 3 and 4.   It has been suggested in section 4.A.2.
that Lewis acid or acids produced from a series of reaction between
ZnDEC and peroxide protects HOBP from peroxide in the later stages of
oxidation.   But the experimental conditions involved higher temperature
and relatively longer time and under these conditions it is possible
that Lewis acid or acids formed from ZnDEC is lost by diffusion and
volatalization.   This would lead to HOBP being less protected from
peroxide formation and hence render it more sensitive to temperature.

Effect of ZnDEC & HOBP alone and in combination on photoxidation of polypropylene (All processed at 180°C/10min.Closed chamber, concentration of additives 3x10^{-4}mol/100g)
1,Control; 2,ZnDEC; 3,HOBP; 4,ZnDEC + HOBP

Figure 4.34

Comparison of stabilizing effectiveness of HOBP & NiDEC alone and in combination at same molar concentration (3×10^{-4} mol/0.5 g) on photoxidation of polypropylene. 1,Control; 2,HOBP; 3,NiDEC 4,NiDEC + HOBP. (All processed at 180°C/10min.)

Figure 1.23

Irradiation time (hours)

(Carbonyl Index)

Synergism between Zn(sec-Butylamine)DEC and HOBP at same molar concentration (3×10^{-4} mol/100g) in polypropylene.   1,HOBP; 2,Zn(sec-Butylamine)DEC; 3, 1 + 2.

Figure 4.36

Synergism between Ni[sec-Butylamine]DEC & HOBP at same molar concentration (3×10^{-4} mol/100g) in polypropylene.   1,HOBP;   2,Ni[sec-Butylamine]DEC;   3,HOBP + Ni-[sec-Butylamine]NiDEC. (All processed at 180°C/10 mins in closed Chambers).

Figure 4.36(a)

Synergism between HOBP and peroxide decomposers at constant total concentration.

Figure 4.37

Synergism between Irganox 1076 & HOBP (3 x 10^{-4} mol/100g each) in polypropylene. 1,HOBP; 2,Irganox 1076; 3,Irganox 1076 + HOBP.

Figure 4.38

Effect of temperature on stabilizing activity of ZnDEC in polypropylene during UV irradiation.
Concentration of ZnDEC = 3 x 10⁻⁴ mol/100g.   1,Control(50°C);   2,Control(40°C);   3,Control(30°C);
4,ZnDEC(50°C);   5,ZnDEC(40°C);   6,ZnDEC(30°C). (All processed at 180°C/10mins in Closed Chamber).

Figure 4.39

Effect of temperature on stabilizing activity of HOBP in polypropylene during UV irradiation concentration of HOBP = 3 x 10^{-4} mol/100g of polymers. 1,50°C; 2,40°C; 3,30°C.

Figure 4.40

Temperature effect on synergistic action between ZnDEC & HOBP at same molar concentration (3×10^{-4} mol/100g of polymers each) in polypropylene during UV irradiation. $1,50°C;$ $2,40°C;$ $3,30°C.$

Figure 4.41

Irradiation time (hours)

Carbonyl Index

Variation of embrittlement time of PP containing ZnDEC and HOBP alone and in combination with temperature
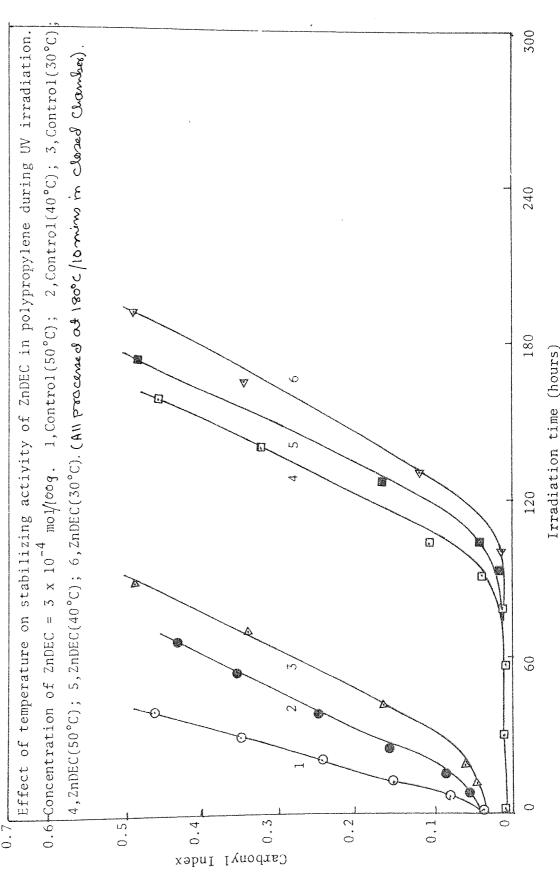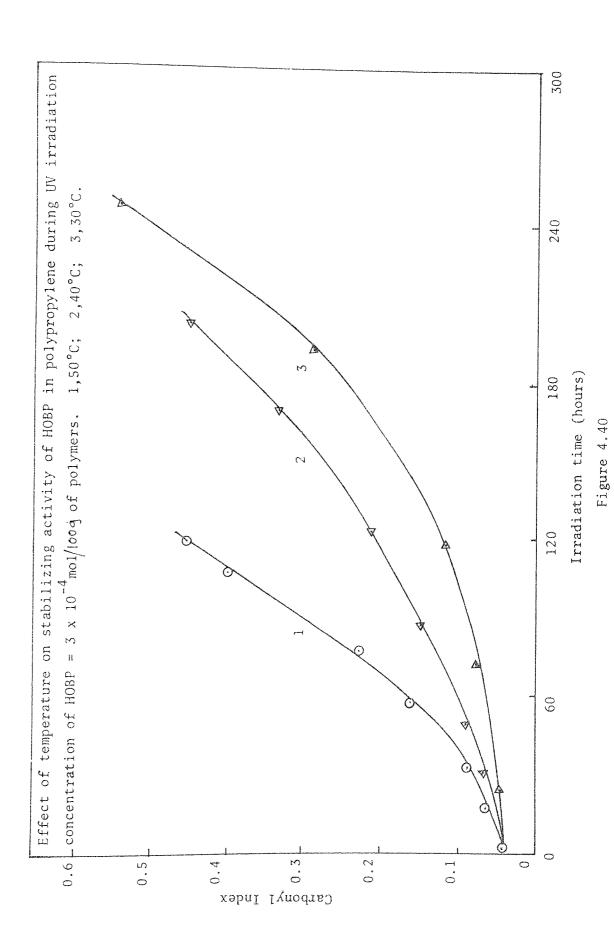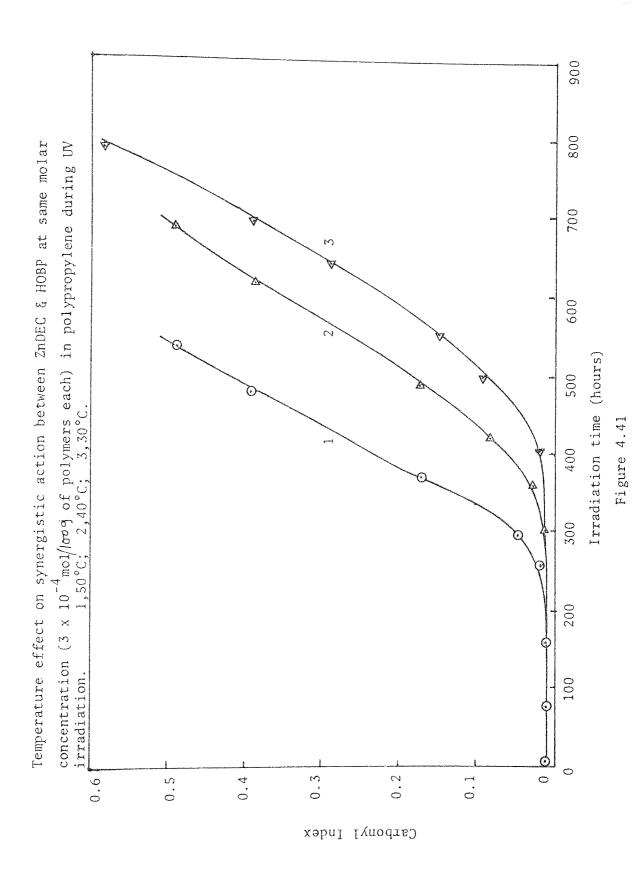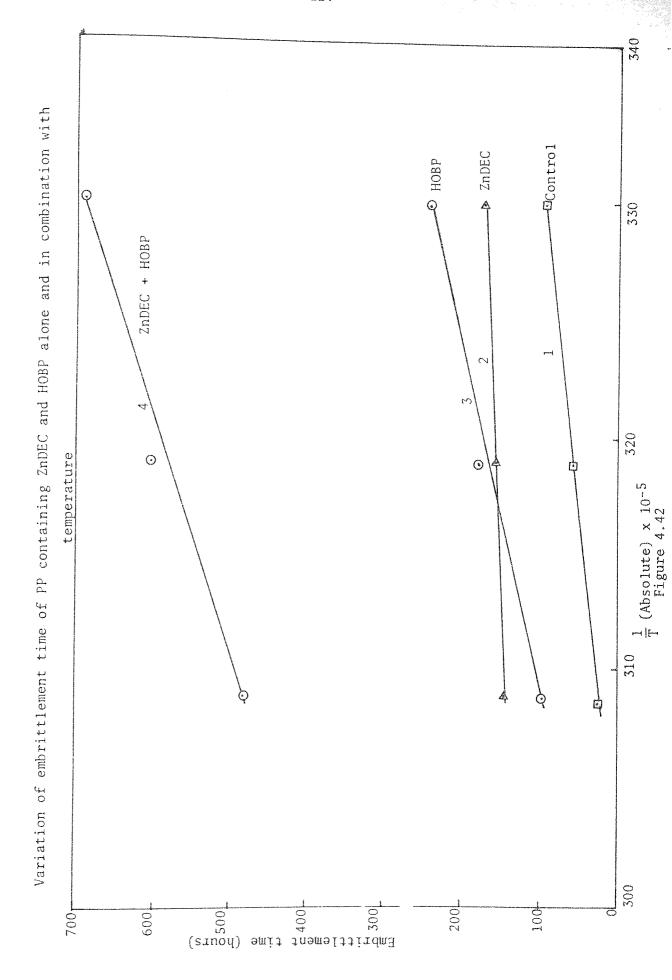

Figure 4.42

TABLE 4.6

Synergistic action between anti-oxidants and stabilizers in polypropylene in a concentration ratio 1:1 at a total molar concentration of 6×10^{-4} mol/100g.

Synergistic mixture	Observed embrittlement times	Calculated on additive basis
Control (no additive)	90	
ZnDEC + HOBP	700	175+245 = 420
NiDEC + HOBP	850	500+245 = 745
Irganox 1076 + HOBP	650	325+245 = 570
Zn-[sec-Butylamine]DEC + HOBP	800	230+245 = 475
Ni-[sec-Butylamine]DEC + HOBP	1200	600+245 = 845

TABLE 4.7

Synergistic action shown by peroxide decomposers and/u.v. absorber HOBP on polypropylene photo-oxidation at different total molar concentration. (All processed at 180°C for 10 minutes in a closed chamber)

Stabilizer	Concentration ratio of peroxide decomposer to HOBP	Total molar concentration	Observed E.T.	Calculated on additive basis
ZnDEC + HOBP	1:2	6×10^{-4} mol/100g of polymer	750	145+300 = 475
ZnDEC + HOBP	1:2	12×10^{-4} mol ″ of polymer	1450	180+550 = 730
ZnDEC + HOBP	1:1	20×10^{-4} mol ″ of polymer	1800	200+600 = 800
Zn[sec-Butylamine]DEC+HOBP	1:2	6×10^{-4} mol ″ of polymer	830	210+300 = 510
″	1:2	12×10^{-4} mol ″ of polymer	1575	270+550 = 820
″	1:1	20×10^{-4} mol ″ of polymer	1950	300+600 = 900
NiDEC + HOBP	1:2	6×10^{-4} mol ″ of polymer	900	400+300 = 700
″	1:2	12×10^{-4} mol ″ of polymer	1450	560+550 = 1110
Ni[sec-Butylamine]DEC + HOBP	1:2	6×10^{-4} mol ″ of polymer	1300	500+300 = 800
″	1:2	12×10^{-4} mol ″ of polymer	1800	670+550 = 1220

TABLE 4.8

U.V. life time of polypropylene with ZnDEC and HOBP alone and in combination at same molar concentration $(3 \times 10^{-4}$ mol/$100g)$ under the condition of u.v. irradiation at different temperatures.

Time to embrittlement (hours)

Stabilizer	30°C	40°C	50°C
Control	90	60	25
ZnDEC	175	165	150
HOBP	245	190	98
ZnDEC + HOBP	700	630	480

4.C. Conclusions

It was shown in the chapter 3 that thermal oxidation and photo-oxidation of LDPE and polypropylene were auto-catalytic, implying the build up of an initiating species during thermal and u.v. exposure. It was concluded that hydroperoxides and not carbonyl are associated with auto-oxidation and are responsible for the oxidative degradation of the polymers studied. It was also shown that polyolefins (LDPE and polypropylene) are stabilized against u.v. light by the removal of peroxides produced during processing. Therefore, those additives which can remove peroxides during processing and on u.v. exposure will be efficient anti-oxidants and stabilizers. In accordance with this view, peroxide decomposers ZnDEC and NiDEC are found to be very good melt stabilizers of LDPE and polypropylene and also effective u.v. stabilizer in the initial photo-oxidation stage. These complexes are known to destroy hydroperoxides by a catalytic (ionic) mechanism involving a Lewis acid (notably sulphur trioxide) generated in a series of initial stoichiometric reactions with hydroperoxides. The major limitation to their effectiveness as u.v. stabilizer is that they are not u.v. stable. ZnDEC is found to be less stable toward u.v. light compared to NiDEC in both polymers. Formation of amine complexes (particularly primary amine especially sec-Butylamine) with Zn and Ni-di ethyldithiocarbamates improves the u.v. stability to some extent of metal dithiocarbamates and this is reflected in their stabilization effectiveness in LDPE and polypropylene. Other factors might contribute to the improved stabilization activity with amine complexes in polyolefins viz increased peroxide decomposition capacity, screening effect and solubility. It is clearly found that

the screening effect of metal dithiocarbamate is not increased on complex formation with amines. The other factors will be examined in the next chapter.

Chain-breaking anti-oxidant Irganox 1076 which acts by removing chain propagating radicals by hydrogen transfer and trapping of radicals is found to be a good melt stabilizer· in both LDPE and polypropylene during processing and exhibits moderate stabilization effect on photo-oxidation of both polymers.

A typical 'u.v. absorber' HOBP (2 hydroxy-4-octyloxybenzophenone) acts as mild thermal antioxidant in both LDPE and polypropylene but as u.v. stabilizer it is not as effective in polypropylene as it is in LDPE. The stabilizing activity of HOBP in polypropylene is even less than NiDEC or Irganox 1076. Moreover, the stabilizing activity of HOBP is found to be markedly dependent on prior processing conditions Experimental evidence on the mechanism of its function suggests that HOBP might also act as radical scavanger in addition to screening of u.v. light.

The substitu ted piperidine derivative (Tinuvin 770) shows strong pro-oxidant effect during thermal processing of polyolefins but stabili-zes them effectively against photo-oxidation.

The u.v. absorber HOBP synergises with both peroxide-decomposing anti-oxidants (metal dithiocarbamates) and chain-breaking anti-oxidants (hindered phenol, Irganox 1076) during photo-oxidation of both LDPE and

polypropylene.   Optimum synergistic action between peroxide decomposer and HOBP is observed (in both LDPE and polypropylene) at a concentration ratio of 1:2 of peroxide decomposer to HOBP.   The most important property of the synergistic mixture is that they are equally effective as photo-stabilizers when subjected to both mild and severe processing operations.   The u.v. life time of polypropylene is found to increase proportionately when total molar concentration of the synergistic mixture in the polymer is increased.   Evidence on synergistic action between peroxide decomposer and HOBP suggests that they mutually protect each other during thermal processing and subsequent u.v. exposure.

By contrast the peroxide decomposers and chain-breaking anti-oxidant (Irganox 1076) which are effective synergists during thermal oxidation of LDPE are antagonistic during photo-oxidation and it is suggested that this may be due to sensitization of the photolytic destruction of the dithiocarbamates by oxidation products of the phenol.

Tinuvin 770, which is alone effective u.v. stabilizer for both LDPE and polypropylene, does not show any synergistic action with peroxide decomposers.

CHAPTER 5

DETERMINATION OF HYDROPEROXIDE DECOMPOSITION RATE,
SOLUBILITY, UV STABILITY AND ANTI-OXIDANT LOSS BY
VOLATILITY OF AMINE COMPLEXES OF
METALDIETHYLDITHIOCARBAMATES

In the preceding chapter (Chapter 4) the effects of peroxide-
decomposers ZnDEC, NiDEC and their amine complexes on processing and sub-
sequent photo-oxidation of polyolefins (LDPE and polypropylene) were
studied.   The results showed that all the metal complexes act as very
good melt stabilizers during processing and effective photo-stabilizer
in the early part of photo-oxidation.   The UV stabilizing activity of Zn
and Ni-diethyldithiocarbamates are found to be generally improved by
complexing with primary aliphatic amines particularly sec-Butyl amine.
But secondary aliphatic amine complexes showed almost the same UV stabilizing
activity in polyolefins as the parent dithiocarbamates.   In order to
explain the stabilizing activity associated with the amine complexes the
following factors which might contribute to the above effect are examined:
1) peroxide decomposition efficiency, 2) anti-oxidant loss due to volatal-
ization, 3) solubility and 4) UV stability.

5.1.1 Experimental

Hydroperoxide decomposition efficiency of metal complexes were determined by reacting pure cumene hydroperoxide (CHP, 10^{-2} M) in chlorobenzene with 10^{-4} M of complexes under u.v. radiation. The kinetics of the reaction was followed by measuring the amount of unreacted hydroperoxide at regular intervals of time, for this the iodometric method described in Chapter 2 was used.

The solubilities of the metal complexes in a hydro-carbon solvent were determined in the following manner. A saturated solution of the solute was made by taking a known weight of solute and dissolving in a known volume of cyclohexane solvent at the appropriate temperature placed in a test tube equipped with a stopper holding a thermometer and stirrer. The solution was filtered, the residue weighed. The filtrate was also evaporated to dryness in a vacuum dessicator and weighed.

The stability of the complexes towards UV light were determined in different hydrocarbon solvents viz hexane, cyclohexane and cumene. Quartz tubes containing the solution of complexes were placed in the UV cabinet described in section (2.3.10) and were exposed for known intervals of time. Rate of decay of complexes were measured by following their absorption maxima (λ_{max}) using P.E. 137 UV Spectrophotometer. This covers the range 190 to 390 nm in the ultraviolet region and 350 to 750 nm in the visible region. Most of the spectra were obtained on fast scan which covers one range of wave lengths in two minutes. Identical absorption bands were obtained for particular complex in the solvents used.

Measurement of the loss of anti-oxidants at high temperature provides data on the behaviour of anti-oxidants during processing where some loss does occur. Loss of anti-oxidants by volatalization was measured at 150°C under nitrogen.

5.1.2 Results

Figures 5.1 and 5.2 compare the efficiency of zinc diethyl-dithiocarbamate and its amine complexes in decomposing cumene hydro-peroxide (CHP) in chlorobenzene on UV irradiation under identical conditions. Figure 5.1, curve 2 shows that the reaction between ZnDEC and CHP does not obey first order decomposition kinetics within the first few minutes (about 60 minutes) but is apparently first order for the rest of the time. The decomposition rate of CHP by the primary amine complexes of ZnDEC follow first order kinetics within shorter time than ZnDEC and in case of tert-Butylamine complex the plot is first order almost from the beginning (fig. 5.1, curves 3, 4 and 5). First order peroxide decomposition rate constants for amine complexes are shown in Table 5.1. This table shows that the first order decomposition rate of CHP is increased by the addition of primary amine complexes compared to ZnDEC. The efficiency of peroxide decomposition by the primary amine complexes increases in the following order.

n-Butylamine < sec-Butylamine < tert-Butylamine

Secondary amine complexes viz Zn[Di-n-Butylamine]DEC and Zn[Di-nonylamine]DEC were found to decompose CHP almost at a similar rate as Zn[n-Butylamine]DEC (fig. 5.2, curves 2 & 3 and fig. 5.1, curve 3, Table 5.1).

Solubilities of Zn and Ni-diethylthiocarbamates and their amine complexes in cyclohexane solvent at 30°C are shown in Table 5.2. It is seen from this table that amine complexes are in general, more soluble in cyclohexane than the parent metal dithiocarbamates. The solubility increases in the case of primary amine complexes in the following order

tert-Butylamine < sec-Butylamine < n-Butylamine

Straight chain secondary amine complexes viz Zn[Di-n-Butylamine)DEC is even more soluble than branched chain primary amine complexes (Table 5.2).

All the amine complexes of ZnDEC are lost by volatalization of the amine. However, the rate of loss differs from complex to complex. When metal amine complexes were heated at 150°C under nitrogen, the percentage of complex remaining in the system with heating time is shown in figure 5.3. The most noticable feature of all the amine complexes is that they all show an initial loss by volatalization at different rates and tend to a maximum loss corresponding to the weight of the amine in the complexes. This, therefore, clearly shows that only the amine part of ZnDEC complex is lost by volatalization. Primary aliphatic amine complexes show a slower rate of loss compared to secondary aliphatic amine complexes. Among the primary aliphatic amine complexes the rate of initial loss increases in the following order

tert-Butylamine < sec-Butylamine < n-Butylamine

The stability of the metal complexes to ultra-violet radiation was

examined by scanning ultraviolet spectra of 1×10^{-4} ML^{-1} of the

complexes in hexane, cyclohexane and cumene, after exposing to UV

radiation for known lengths of time.   All these complexes showed changes

in their absorption maxima (λ_{max}) region on UV irradiation.   Figure

5.3(a) shows the absorption spectra of ZnDEC and NiDEC respectively in

hexane before and after UV irradiation.   Figures 5.4 and 5.5 compare

the stability of ZnDEC and NiDEC in hexane at the same molar concentration

(1×10^{-4} ML^{-1}).   In figure 5.4 the disappearance of absorption maxima

of the above complexes (285 and 330 nm respectively for ZnDEC and NiDEC)

are plotted against time of irradiation and figure 5.5 is drawn as first

order plot.   NiDEC shows an initial induction period before its UV

absorption (330 nm) maxima started to disappear whereas ZnDEC does not

show any induction period in the disappearance of its UV absorption

spectra.   Moreover NiDEC possesses higher initial molar absorption and

it decays at a slower rate than ZnDEC (figures 5.4 and 5.5).   All the

above factors account for the higher UV stability of NiDEC compared to

ZnDEC.

Figures 5.6 and 5.7 compare the UV stability of ZnDEC and its amine

complexes in hexane at the same molar concentration (1×10^{-4} Ml^{-1}).

Figure 5.6 shows that the initial molar UV absorption of ZnDEC is

increased by complexing with amines and all the amine complexes decay

at a slower rate than ZnDEC (fig. 5.7).   Similar results are obtained

with nickel diethyldithiocarbamates-primary amine complexes (fig.5.8).

The stability of the metal dithiocarbamates are found to markedly

depend on nature of the solvent.   This is shown in figure 5.9 where the

(First order plot for the decomposition of CnP by ZnDEC and its primary amine complexes under UV. [Concentration of complex = 1 x 10⁻⁴ ML⁻¹ & CHP = 1 x 10⁻²M]. 1,Control (no additive), 2,ZnDEC. 3,Zn[n-Butylamine]DEC. 4,Zn[sec-Butylamine]DEC. 5,Zn[tert-Butylamine]DEC.

Figure 5.1

First order plot for the decomposition of CHP by ZnDEC and its secondary amine complexes. [Concentration of additive 1×10^{-4} ML^{-1} , CHP $= 1 \times 10^{-2}$M]

1,control (no additive). 2,ZnDEC. 3,Zn[Di-n-Butylamine]DEC.

Figure 5.2

Loss of ZnDEC-amine complexes on heating at 150°C in nitrogen. 1,ZnDEC. 2,Zn[tert-Butylamin]DEC. 3,Zn[sec-Butylamine]DEC. 4,Zn[n-Butylamine]DEC. 5,Zn[Di-nonylamine]DEC

Heating time at 150°C (minutes)

Figure 5.3

Figure 5.3(a)

Ultra-violet spectra of NiDEC and ZnDEC in hexane before and after UV exposure. concentration of additives 1×10^{-4} ML^{-1}

(Wavelength (millimicrons))

Disappearance of UV absorbance of NiDEC (λ_{max} at 330 nm) and ZnDEC(λ_{max} at 285 nm) in hexane during UV radiation. Concentration of complex $1 \times 10^{-4} ML^{-1}$.

1,NiDEC. 2,ZnDEC

Figure 5.4

First order decay of UV absorbance of NiDEC and ZnDEC in hexane under UV. 1,NiDEC. 2,ZnDEC
(Concentration of additives 1×10⁻⁴ M⁻¹).

Figure 5.5

Disappearance of UV absorbance maxima (λ_{max} = 285 nm) of ZnDEC and its amine complexes at same molar concentration (1 x 10^{-4} ML^{-1}) in hexane under UV. 1,ZnDEC. 2,Zn[Di-n-butylamine]DEC,;Zn[Di-nonylamine]DEC, 3, Zn(n-butylamine]DEC, Zn[Sec-butyl amine]DEC or Zn[tert-butylamine]DEC.

Figure 5.6

First order decay plot of ZnDEC and its amine complexes in hexane (λ_{max} = 285 nm) under UV. 1, ZnDEC. 2, Zn[n-butyl amine]DEC, Zn[sec-butyl amine]DEC, Zn[Di-n-butyl amine]DEC.

Irradiation time (hours)

Figure 5.7

Disappearance of UV absorbance maxima of NiDEC and its primary amine complexes
(λ_{max} = 330 nm) at same concentration (1×10^{-4} ML^{-1}) in hexane under UV.
1,NiDEC.   2,Ni[sec-Butylamine]DEC.   3,Ni[tert-Butylamine]DEC.

Figure 5.8

Irradiation time (hours)

Absorbance at 330 nm

Disappearance of UV absorption maxima of NiDEC (λ_{max} at 330 nm) in different hydrocarbon solvents under UV at same concentration ($1 \times 10^{-4} ML^{-1}$) 1, Hexane. 2,Cyclohexane. 3,Cumene

Irradiation time (hours)

Figure 5.9

Absorbance at 330 nm

First order decay of UV absorbance of NiDEC (λ_{max} = 330 nm) in different solvents under UV.

1,hexane.   2,Cyclohexane.   3,Cumene

(Concentration of NiDEC 1x10^{-4} ML^{-1}).

Figure 5.10

TABLE 5.1

First order peroxide decomposition rate constants for ZnDEC and its amine complexes.

Complex	rate constant $(k)\sec^{-1}$
ZnDEC	6.0×10^{-5}
Zn[n-Butylamine]DEC	6.66×10^{-5}
Zn[sec-Butylamine]DEC	7.3×10^{-5}
Zn[tert-Butylamine]DEC	8.1×10^{-5}
Zn[Di-n-Butylamine]DEC	6.2×10^{-5}

TABLE 5.2

Solubilities of metal diethyldithiocarbamates and their amine complexes at 30°C in cyclohexane solvent (g/100 gm of solvent).

Metal complex	Solubility
ZnDEC	0.112
Zn[n-Butylamine]DEC	0.290
Zn[sec-Butylamine]DEC	0.263
Zn[tert-Butylamine]DEC	0.202
Zn[Di-n-Butylamine]DEC	0.285
Zn[Di-nonylamine]DEC	0.290
NiDEC	0.220
Ni[sec-Butylamine]DEC	0.340
Ni[tert-Butylamine]DEC	0.296

disappearance of the UV absorption maxima of NiDEC at λ_{max} 330 nm at the same molar concentration (1×10^{-4} Ml^{-1}) in hexane, cyclohexane and cumene solvents respectively are plotted against time of irradiation. The first order decay of UV absorption (fig. 5.10) of NiDEC in the above solvents shows that the decay rate is faster in more auto-oxidizable solvents (cumene) compared to less auto-oxidizable solvent (hexane).

5.1.3 Discussion

It is clearly shown in the Chapter 4 as well as by other workers[54, 58, 60, 92] that zinc and nickel diethyldithiocarbamates exert their anti-oxidant and UV stabilization action in polymers by catalytically decomposing peroxide into non-radical products. It is also shown in Chapter 4 that the primary and secondary aliphatic amine complexes of the above peroxide decomposers particularly primary amine complexes are better stabilizers for polyolefins than the parent dithiocarbamates. The catalytic decomposition of peroxide is not due to the metal dithiocarbamates themselves, but the effective catalyst for peroxide decomposition (sulphur dioxide or sulphur trioxide) is produced by initial stoichiometric reactions between metal dithiocarbamates and hydroperoxides. Figure 5.1 and 5.2 clearly show that this initial stoichiometric reaction rate of ZnDEC with peroxide is increased on complex formation with amines. This may be explained as follows: the increase in electron density at the metal atom in the dithiocarbamate complex by the amine might enhance the rate of formation of the effective Lewis acid catalyst for hydroperoxide decomposition.

$$R_2N \longrightarrow C \underset{S}{\overset{S}{=}} \quad Zn \quad \underset{S}{\overset{S}{=}} C-NR_2$$

with NH_2R coordinating to Zn.

The effect of co-ordinating an amine with the dithiocarbamate is to render the zinc-sulphur bonds more ionic so that the sulphur atoms of the amine complexes carry higher negative charge densities than do those of the parent dialkyldithiocarbamates. One might therefore expect corresponding differences in the rate of chemical reactions specifically involving the 3P electron of the sulphur groups. The increased nucleophilicity of the sulphur atoms attached to the metal atom may be responsible for the increased rate of initial stoichiometric reaction of the amine complex - ZnDEC with hydroperoxide. The above activity associated with the amine complexes seems to depend on the nature of the alkyl chain attached to the amine group (fig. 5.1). Among the primary aliphatic amine complexes the above reaction rate is found to increase with the number of methyl branching to the carbon atom nearest to - NH_2 group (n-Butyl < sec-Butyl < tert-Butyl). It seems probable that only inductive effect plays a major role in this respect. Higher inductive effect in tert-Butylamine complex compared to sec-Butylamine and n-Butylamine complexes makes the lone pair of electrons on the nitrogen atom of amine more available for metal atom in ZnDEC whereby sulphur atoms attached to zinc becomes relatively more ionic in nature. Consequently Lewis acid formation is facilitated. As the inductive effect decreases from tert-Butyl group to n-Butyl group, ease of Lewis acid formation from the complex is retarded which is reflected in the initial stoichiometric reaction rate (fig. 5.1).

The lower inductive effect associated with Di-n-Butylamine and Di-nonylamine complex of ZnDEC makes them also relatively less effective in the production of Lewis acid in the initial stoichiometric reaction stage fig. 5.2.

Figure 5.1 and Table 5.1 show that the rate of the catalytic process is also affected by ZnDEC on complex formation with amines and the rate is increased in the order

<div align="center">n-Butylamine < sec-Butylamine < tert-Butylamine</div>

The reason for this is not yet clear.   Further studies are needed in this respect.   Relative basicity of the amines as well as other factors such as steric hindrance might contribute in this effect.   It appears from the literature [156, 157] that the basicity values of the above amines in aqueous solution are of similar order of magnitude.   The major factors that contribute to the basicity in aqueous medium are inductive effect and steric hindrance.   Inductive effect tends to increase the basicity while steric hindrance tends to decrease it by reducing solvation.   In the series of primary amines under consideration both the inductive effect and steric hindrance increase in the following order

<div align="center">n-Butylamine < sec-Butylamine < tert-Butylamine</div>

Similarity of basicity values of the above amines in aqueous medium could be due to balancing of these two opposing factors.   However, in the polymer system although the contribution from solvation could be minimal but steric hindrance could influence the subsequent reactions with Lewis acid produced in the initial stage.

The influence of inductive effect might contribute to the stability of M-N bond in the complex. Figure 5.3 shows that tert-Butylamine complex of ZnDEC is relatively more stable to heat (at 150°C) and the rate of loss of amine is slower compared to other amine complexes studied.

Although inductive effect in Di-n-Butylamine complex is slightly higher than n-Butylamine complex, the rate of loss of amine from the former is similar to that of the latter. This is certainly due to higher steric hindrance involved in the former which reduces the inductive effect and makes the M-N bond weaker.

Although the peroxide decomposition efficiency increases and the rate of loss of amine decreases from the n-Butylamine complex to the tert-Butylamine complex of ZnDEC, the solubility of complexes in a hydro-carbon solvent appears to show the reverse behaviour Table 5.2. The n-Butylamine complex has the highest solubility and solubility decreases from the n-Butylamine to the tert-Butylamine complex. The higher solubility of the n-Butylamine complex seems to be associated with a relatively higher straight aliphatic chain in the amine. The same explanation accounts for the relatively higher solubility of Di-nonyl-amine and Di-n-Butylamine complexes in cyclohexane compared to other branched chain amine complexes (Table 5.2).

Figures 5.6 to 5.8 show that the UV stability of metal dithio-carbamates are improved by complexing with amines. Most of the amine complexes show a similar stability to UV light in hexane solvent.

- 250 -

On the basis of the above results and discussion it may be said that the overall increased stabilization effectiveness in LDPE and polypropylene shown by the amine-metal dialkyldithiocarbamates over the parent metal dithiocarbamates (Chapter 4) could be due to the mainly peroxide decomposition efficiency and UV stability where both the factors of ZnDEC are improved on complex formation with amines. Solubility or compatibility might also play some role in this respect.

All the secondary amine complexes and n-Butylamine complex of ZnDEC have not shown much improved stabilizing action in LDPE and polypropylene compared to ZnDEC itself (Chapter 4), because they are lost during processing. It has been shown in Chapter 4, Table 4.2 that UV absorption of the above complexes in LDPE film after processing operation is lower compared to ZnDEC although they have higher molar extinction coefficient than ZnDEC in solution (fig. 5.6). This is also confirmed by figure 5.3 where it is seen that the above complexes are lost very quickly by volatalization when they are heated at 150°C under nitrogen.

Although the tert-Butylamine complex possesses a higher peroxide decomposition efficiency and lower volatility compared to sec-Butylamine complex of ZnDEC, the overall stabilization effectiveness in polyolefins of the latter is found to be higher than that of the former. This may be due to the relatively higher solubility or compatibility of sec-Butyl complex in the polymer than the tert-Butylamine complex (Table 5.2).

It has been shown in Chapter 4 that NiDEC shows greater UV stabilization effectiveness in polyolefins compared to ZnDEC under identical

conditions. This is certainly due to the higher UV stability associated with the former than the latter (figures 5.4 and 5.5). Moreover, NiDEC also functions by screening of UV light in addition to peroxide decomposition (shown in the Chapter 4, figure 4.10, as well as by other workers[62]). The UV screening behaviour of NiDEC may also be observed from figure 5.4. NiDEC shows an induction period before it is destroyed by UV light in hexane whereas ZnDEC started to decay from the very beginning under the identical conditions. The UV stability of NiDEC is found to be greatly affected by the nature of the solvent (fig. 5.10). It is destroyed faster in a more auto-oxidizable solvent like cumene (figures 5.9 and 5.10). Pure cumene photo-oxidizes auto-catalytically[43, 60]. However, it has been shown previously[60] that photo-oxidation rate of cumene is auto-retarded by nickel dibutyldithiocarbamate (NiDBC) and the auto-retardation is explained by the fact that NiDBC destroys peroxide formed in the photo-oxidation of cumene into non radical products. Therefore, the instability of NiDEC in such a photo-oxidizing system (cumene) is certainly due to its destruction by the hydroperoxide formed to give a catalyst for hydroperoxide decomposition in addition to destruction caused by u.v. light.

CHAPTER 6

FUNCTION AND MECHANISM OF ACTION OF 2-HYDROXY-4-
OCTYLOXYBENZOPHENONE (HOBP) AND SUBSTITU.TED
PIPERIDINE (TINUVIN 770) IN THE STABILIZATION OF
POLYOLEFINS

6.1.1 Introduction

In the photoprotection of LDPE and polypropylene by the
2-hydroxy-4-octyloxybenzophenone (HOBP), the measured protective effi-
ciency was found to be greater than the screening efficiency for UV
light (Chapter 4). The same effect with this type of compound has also
been observed by other workers[60,146,158-160]. The increased efficiency
has been attributed by many workers[146, 159, 160] to radiationless energy
transfer from photo-excited centres, such as carbonyl groups, in the
polymer to the UV absorber molecules. However, the only direct physical
evidence for this process in a polymer-stabilizer system has been from
the quenching of luminescence chromophores that are of no significance
in the initiation of polymer photo-degredation [159, 68]. Photo-chemical
studies of polypropylene and ketone model systems[64, 65, 161] have con-
tradicted these photophysical results and, in the polyolefins at least,
it appears that hydroperoxide decomposition and free-radical scavanging
may be more important than electronic energy transfer. In order to find
the possible mechanisms of action of 2-hydroxy-4-octyloxybenzophenone
(HOBP) the behaviour of this compound in some model systems has been
studied.

The behaviour of methyl substituated piperidine (Tinuvin 770) is also studied in a model system.

6.1.2 Results and discussion

When HOBP (1×10^{-4} ML^{-1}) reacts with cumenehydroperoxide (CHP, 1×10^{-2} ML^{-1}) in chlorobenzene at 60°C, the peroxide decomposition rate with this compound is found to be similar to a control containing no additive, figure 6.1. This shows that HOBP cannot decompose peroxide thermally. When methylnonylethylene (MNE), a model compound of LDPE (concentration 3×10^{-2} M) is thermally oxidized with HOBP (2×10^{-4} ML^{-1}) in chlorobenzene at 80°C, peroxide formation from MNE is not inhibited by HOBP, figure 6.2, although peroxide formation is slightly slower than the control. Similar results with this compound have been obtained during processing of LDPE at 150°C (Chapter 4). Therefore, the contribution of peroxide decomposition to this overall stabilization action shown by this compound in polyolefins is probably insignificant. However, it has been shown in Chapter 4 that HOBP is less effective as a photo-stabilizer in a LDPE sample containing an initial higher amount of peroxide compared to a sample containing minor amount of peroxide. More-over it is destroyed faster in the former sample during UV irradiation than the latter. This can also be seen from figures 6.3 and 6.4. The rates of decay of HOBP in different solvents at the same molar concen-trations (1×10^{-4} ML^{-1}) were measured under UV irradiation by following its UV absorption maxima at 330 nm. Figure 6.3 shows that stability of HOBP is markedly dependent on the nature of the solvent. It is relatively more stable in the less auto-oxidizable solvent hexane and

the stability decreases as the solvent is changed from less auto-oxidizable to more auto-oxidizable in the order hexane - cyclohexane - cumene. Moreover, the reaction order of the decay reaction also differs depending on the solvent. In hexane it decays at almost zero order rate and the decay rate tends to be first order in more auto-oxidizable solvents e.g. in cumene (figure 6.4). The UV stability of the UV stabilizer may be explained on the basis of its mode of action. The primary mode of action for such compounds is believed to be the absorption of the UV light and dissipate the photo-absorbed energy in a harmless manner. This means that dissipation of excitation energy should proceed at a faster rate than side reactions. The dissipative mechanisms of excited 2-hydroxybenzophenones are still in dispute. There is some evidence that the rapid keto-enol tautomerization in the excited state is involved[162]. The enol form of the carbonyl group

keto   enol

is assumed to be more stable in the excited state, whereas the ground state is the keto form. Alternatively, H^+ transfer to the $>C=O$ group may occur[163]. Heller and Blattman[67] have reasoned that the existence of the enol form on excitation of 2-hydroxybenzophenone is doubtful from an energetic point of view. They favoured the "loose bolt" effect in which the rotation of the hydroxy phenyl group about the

phenyl-carbonyl bond results in a high Frank-Condon factor between the excited (S_1^*) and ground state (S_0) singlet levels. This leads to a relatively high rate of $S_1^* - S_0$ internal conversion.

Although HOBP possesses a high inherent UV stability, its concentration falls steadily during UV irradiation even in an inert solvent like hexane. This implies that most of the excited HOBP dissipates the absorbed energy by returning to its ground state, but a constant proportion of it is degraded by light. In a more auto-oxidizable solvent like cumene (figures 6.3 and 6.4) HOBP is destroyed faster and the rate of decay is increased to first order. This shows that HOBP is also destroyed in cumene by other agents in addition to UV light. This seems to suggest that HOBP is excited by a photon and then enters into some chemical reaction in this medium which causes additional destruction. It is possible that as cumene is a more oxidizable solvent, rapid peroxide formation occurs on UV irradiation and the radicals produced from UV induced peroxide decomposition might abstract phenolic hydrogen from HOBP causing this additional destruction.

destroyed

The effect of a model compound methylnonyl ethylene (MNE) on the photo-stability of HOBP in hexane was also studied. On UV irradiation of MNE in hexane rapid vinylidene decay is observed with the simultaneous

$$CH_2 = C \overset{\displaystyle CH_3}{\underset{\displaystyle (CH_2)_8 \; CH_3}{}}$$

Methylnonylethylene (MNE)

formation of carbonyl, figure 6.5.   HOBP is found to be destroyed at a faster rate in hexane in presence of MNE (2×10^{-2} M) under UV, figures 6.6 and 6.7.   This faster rate of destruction of HOBP in this situation could be caused by the combined effect of UV light and peroxide formed from MNE under UV.

Benzophenone (BP) itself is also found to affect the UV stability of HOBP in hexane solvent.   HOBP is destroyed faster and follows a first order decay rate in presence of BP, figures 6.8 and 6.9.   Benzo-phenone (BP) is also found to be destroyed in this system and was observed from the disappearance of the peak at 1665 cm^{-1} in the infra-red spectrum.   This might be due to the fact that benzophenone is known to form the triplet state on UV excitation[164] and its triplet state may abstract phenolic hydrogen from HOBP causing its faster rate of destruction.
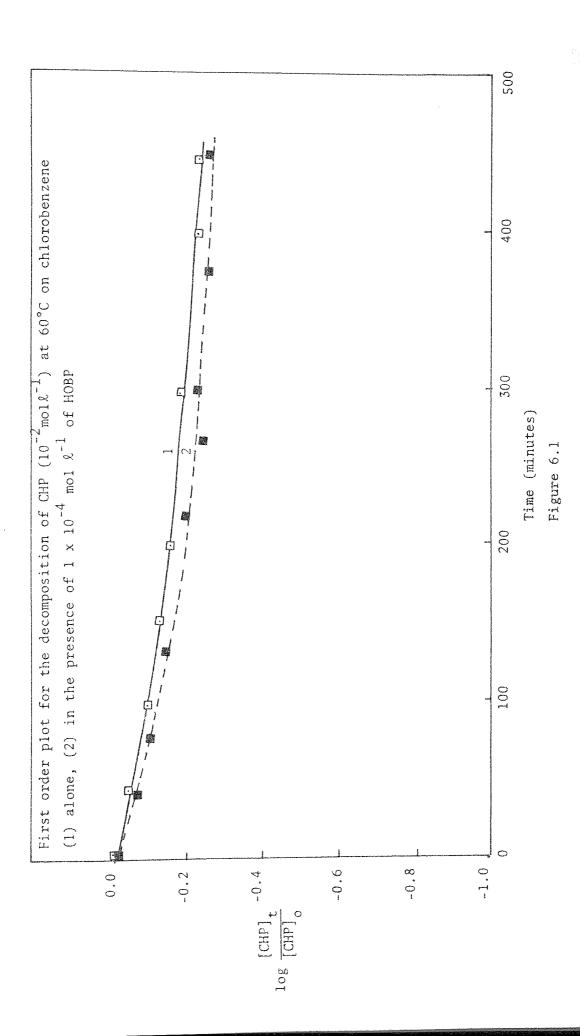
The above model studies seem to suggest that free radicals present in a system are capable of abstracting the phenolic hydrogen from HOBP. Such reactions would amount to a chain terminating process. This implies that HOBP could also function by transferring its phenolic hydrogen to the chain-propagating radicals like conventional phenolic anti-oxidants. Such radical scavanging reactions by HOBP might contribute to the overall UV stabilization effectiveness in polyolefins (Chapter 4) in addition to its known UV screening effect.
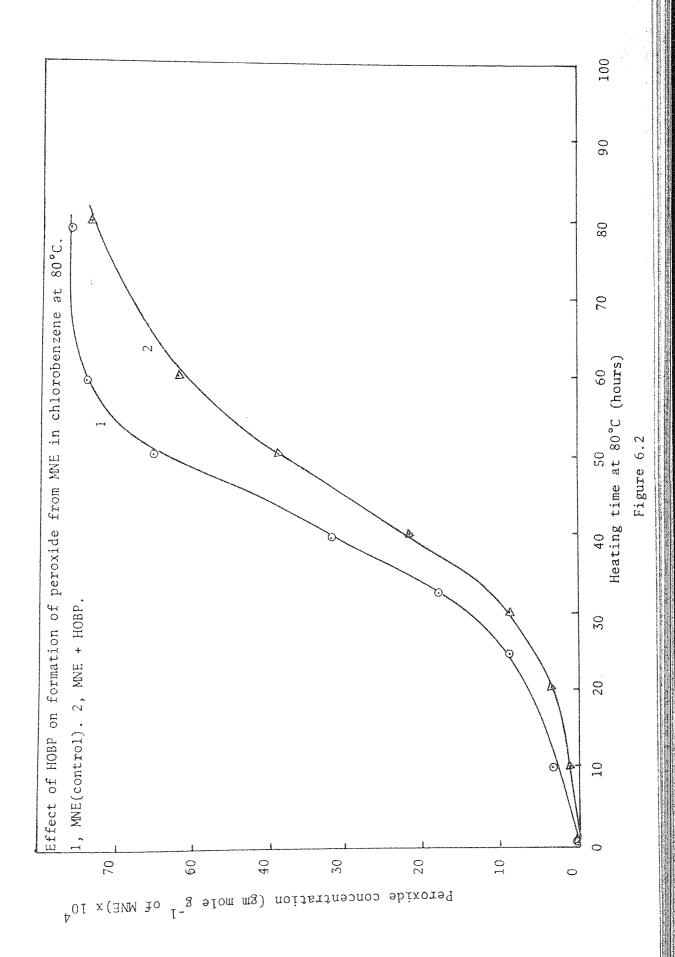
As has been seen in the Chapter 3 that although carbonyl groups do not take any part in the photo-initiation of polyolefins, they undergo photolysis in the later stages of photo-oxidation, when a higher initial amount of carbonyl is present. It is found (figure 6.10) that carbonyl photolysis is substantially inhibited by HOBP. Figure 6.10 demonstrates the effect of HOBP as an additive and as a screening agent on UV irradiation of an LDPE sample containing substantial amounts of carbonyl but no peroxide. This sample was prepared by processing LDPE for 60 minutes in the RAPRA Torque-rheometer at 150°C in an open chamber and was heated in argon for 20 hours at 110°C prior to UV irradiation. On UV irradiation of the control sample screened by a mildly processed LDPE film showed an initial rapid reduction of carbonyl (fig. 6.10, curve 1) with the simultaneous formation of vinyl (fig. 6.11, curve 1). This has been attributed to the photolysis of carbonyl by Norrish I & II processes. On UV irradiation of the same sample screened by a mildly processed LDPE film containing HOBP (3×10^{-4} mol g^{-2}), the rate of the initial drop in carbonyl was
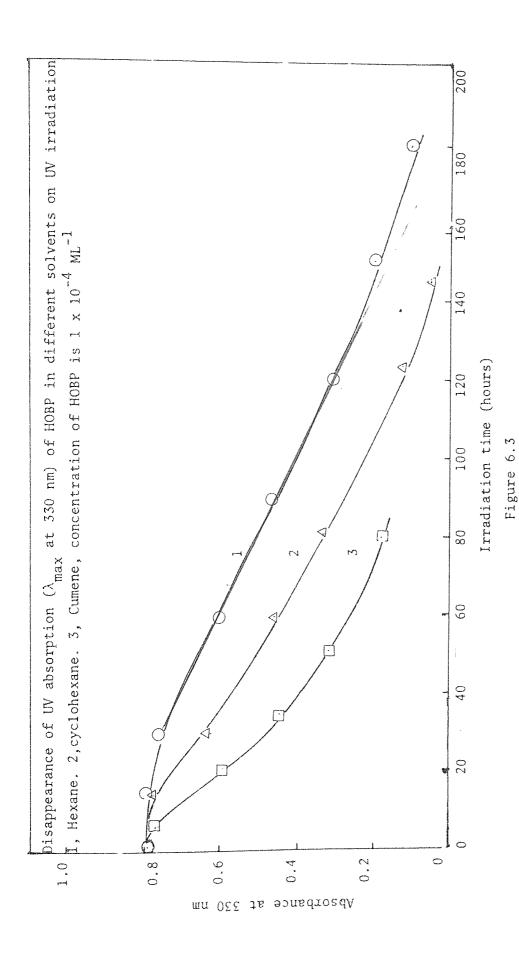
reduced to some extent which is certainly due to the screening of UV light by HOBP present in the top film, figure 6.10, curve 2. Vinyl formation was also found to be slower compared to the control (fig. 6.11, curve 2). However, when HOBP was used as an additive in the same sample (3×10^{-4} mol g^{-2}) screened by a mildly processed LDPE film, the initial reduction in carbonyl on UV irradiation was almost eliminated (fig. 6.10, curve 3) and moreover further growth of carbonyl shows a longer induction period. Vinyl formation also occurred after an induction period. HOBP was also found to be destroyed at a faster rate in this system than in the sample which is very mildly processed, fig. 6.12. This behaviour of HOBP during the photolysis of carbonyl suggests that it may inhibit the carbonyl photolysis partly by screening of UV light and partly by some other mechanism. This might be, as has been previously suggested by other workers, quenching of triplet carbonyl by HOBP[64,65,146,159,160]. However, this mechanism of action of HOBP is not yet clear and further studies are needed before drawing any definite conclusion regarding it.
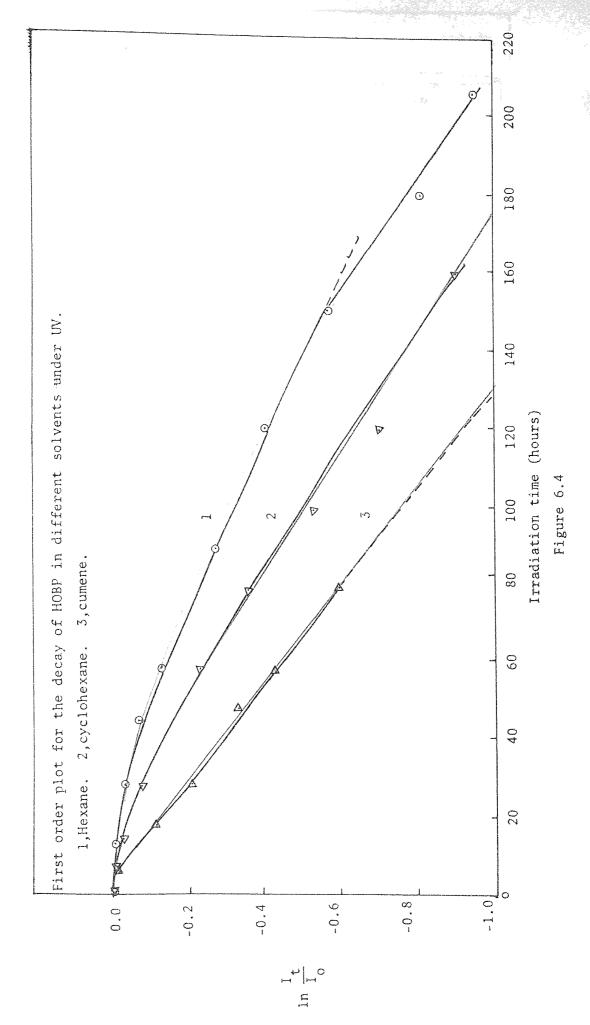
The substituated piperidine derivative (Tinuvin 770) stabilized LDPE and polypropylene effectively against UV initiated degradation but accelerated the degradation of the above polymers during thermal oxidation (Chapter 4). It has also been shown that Tinuvin 770 cannot decompose peroxides and inhibit the peroxide formation during thermal processing and subsequent accelerated thermal oxidation of LDPE. Figure 6.13 and 6.14 respectively show the decomposition rate of cumene - hydroperoxide (1×10^{-2} ML^{-1}) in chlorobenzene in the presence of Tinuvin 770 (1×10^{-4} ML^{-1}) at 60°C thermally and under UV. The first

order decomposition rate of CHP was found to be the same under the both

conditions in the presence of this compound as that of the control.

This result confirms the suggestion made earlier that Tinuvin 770 does

not function by peroxide decomposition.   Preliminary evidence (Chapter

4) also shows that this compound does not act as either by UV screening

or by triplet carbonyl quenching.   Attempts were made to detect any

radicals produced from Tinuvin 770 during thermal and UV oxidation in

the both polymer and model system using E.S.R. technique.   Unfortu-

nately no positive result was observed.   The very limited results

obtained with this compound in polymer and model system seem to suggest

that Tinuvin 770 may function by free radical scavanging mechanism

in the photo-stabilization of polyolefins.

First order plot for the decomposition of CHP (10^{-2} molℓ^{-1}) at 60°C on chlorobenzene (1) alone, (2) in the presence of 1×10^{-4} mol ℓ^{-1} of HOBP

Figure 6.1

Effect of HOBP on formation of peroxide from MNE in chlorobenzene at 80°C.

1, MNE(control). 2, MNE + HOBP.

Figure 6.2

Heating time at 80°C (hours)

Peroxide concentration (gm mole g^{-1} of MNE) x 10^4

Disappearance of UV absorption (λ_{max} at 330 nm) of HOBP in different solvents on UV irradiation 1, Hexane. 2,cyclohexane. 3, Cumene, concentration of HOBP is 1×10^{-4} ML^{-1}

Figure 6.3

First order plot for the decay of HOBP in different solvents under UV.
1,Hexane. 2,cyclohexane. 3,cumene.

Figure 6.4

Figure 6.5

Growth of carbonyl (band at 1710-1715 cm^{-1}) and disappearance of vinylidene unsaturation (band at 890 cm^{-1}) during Photo-oxidation of methyl nonylethylene (MNE) in hexane.

Effect of MNE on the photostability of HOBP in hexane.

1, HOBP alone. 2,HOBP in presence of MNE

Figure 6.6

First order decay of HOBP in hexane in presence of MNE under UV.

1, HOBP alone.   2, HOBP + MNE

Figure 6.7

Effect of benzophenone on UV stability of HOBP in hexane. 1, HOBP alone. 2, HOBP + BP.

Concentrations of HOBP and BP are 1×10^{-4} and 1×10^{-3} m.l^{-1}.

Figure 6.8

First order decay of HOBP in presence of BP in hexane under UV. 1,HOBP alone. 2,HOBP + BP

Irradiation time (hours)

Figure 6.9

$\ln \dfrac{I_t}{I_o}$

Effect of HOBP as an additive and as a screen on
photolysis of carbonyl. 1,Control
2,HOBP as a screen, 3,HOBP as an additive
Concentration of HOBP = 3×10^{-4} moles/100g.

Figure 6.10

Effect of HOBP as an additive and as a screen on the vinyl formation in a LDPE sample containing initial higher amount of carbonyl.

1,Control. 2,HOBP as screen. 3,HOBP as an additive.

Figure 6.11

1, represents the rate of disappearance of HOBP in a LDPE film which is mildly processed

2,   "   "   "   "   "   "   "   " containing initial higher amount of carbonyl.

Concentration of HOBP = 3×10^{-4} mol g^{-2}

Figure 6.12

First order plot for the thermal decomposition of CHP (10^{-2} mol ℓ^{-1}) at 60°C in chlorobenzene. 1, CHP (alone). 2, in the presence of Tinuvin 770 (1×10^{-4} ML^{-1})

Figure 6.13

First order plot for the decomposition of CHP (10^{-2} mol ℓ^{-1}) in chlorobenzene under UV. 1, CHP (alone). 2,in the presence of Tinuvin 770 (1×10^{-4} mol ℓ^{-1})

Figure 6.14

CHAPTER 7

MECHANISM OF ANTI-OXIDANT ACTION: SYNERGISM

BETWEEN ANTI-OXIDANTS AND UV STABILIZER

7.1.1 Introduction

In the preceding chapters the effects of anti-oxidants and
stabilizers on thermal and photo-oxidations of polyolefins (LDPE and poly-
propylene) have been studied and possible mechanisms of action are also
discussed on the basis of the experimental evidence. The metal dithio-
carbamates (ZnDEC and NiDEC) mainly act by decomposing peroxides cata-
lytically into non-radical products whereas a typical 'UV absorber' HOBP
exerts its stabilization action by screening of UV light and also by
some other mechanism, possibly radical scavanging (Chapters 4 and 6). The
differences in mechanism of action of the stabilizers permit them to act
independently but co-operatively (when used in combination) to provide
greater protection than would be predicted by the sum of their
individual but separate effects. As can be seen from Chapter 4, ZnDEC
alone was not very effective in inhibiting the photodegradation of LDPE
and polypropylene. The photodegradative resistance of the above polymers
was considerably improved in presence of HOBP. However, there was a
remarkable improvement in the photo-oxidative resistance when ZnDEC was
combined with HOBP and the combined effect was greater than the sum of the

individual effects taken independently. This shows that the combinations of ZnDEC and HOBP are synergistic. Similar synergistic effect was also obtained when NiDEC was combined with HOBP. It has been suggested that this synergistic action between ZnDEC or NiDEC and HOBP could be due to the mutual protection of the additives by each other, thus extending the life time of their action.

It was also seen in Chapter 4 that peroxide decomposers (ZnDEC and NiDEC) and a chain-breaking anti-oxidant (Irganox 1076) in combination showed a very good synergistic effect during thermal oxidation of LDPE (due to the independent but co-operative action of the anti-oxidants). However, the combined effect of the above combination on the photo-oxidation of LDPE was found to be even less than the effect shown by either of the components of the mixture alone. The decreased effective-ness of the peroxide decomposers in the presence of Irganox 1076, together with the loss of the anti-oxidant action of Irganox 1076 in the presence of metal dithiocarbamates, clearly indicates an antagonistic effect. The reason for this antagonism has been suggested as due to the interference of one during the action of another (Chapter 4).

With a view to finding possible mechanism of synergistic action between peroxide decomposer and 'UV absorber' HOBP, the behaviour of this combination was studied in model systems. A similar model system study was also carried out with peroxide decomposer and chain-breaking anti-oxidant Irganox 1076.

The rate of decay of additives were measured by following their absorption maxima (λmax) using P.E.137 UV spectrophotometer as described in Chapters 2 and 5.

7.1.2 Results and discussion

The UV life time of both NiDEC and HOBP have been found to be increased in a polymer system when they are used together (Chapter 4, figure 4.15). This shows that they protect each other under these conditions. The effect of HOBP as an additive and as screens on the photostability of NiDEC in hexane was also determined following the decay of UV absorption maxima of NiDEC at 395 nm where HOBP does not absorb. The UV irradiation of NiDEC in hexane was carried out in a quartz tube surrounded by an outer jacket made of quartz containing hexane solvent. In order to study the UV screening effect of HOBP on photostability of NiDEC, a solution of HOBP (1×10^{-4} ML^{-1}) in hexane was used in the outer jacket. The disappearance of absorption maxima (λmax at 395 nm) with time of UV irradiation and the first order plot decay of the decay of NiDEC alone, in presence of HOBP and screened by HOBP are compared respectively in the figures 7.1 and 7.2. Figure 7.1, curves 1 & 3 demonstrates that the UV stability of NiDEC is increased in presence of HOBP. Moreover the rate of decay of the NiDEC spectrum is slower in presence of HOBP compared to NiDEC alone, figure 7.2, curves 1 & 3. This result shows that HOBP protects NiDEC against photolytic destruction. The contribution of the screening effect of HOBP to the overall stabilization effectiveness may be estimated from a comparison of curves 2 and 3 in figures 7.1 and 7.2 respectively. This shows that both UV screening

and some other chemical stabilization processes are involved. Evidence of radical scavanging by HOBP (Chapter 4 and 6) suggests that HOBP may function by removing reactive species formed from the dithiocarbamates during irradiation and thus protect them from photolysis. The evidence of the inhibition of carbonyl photolysis by HOBP (Chapter 6) together with suggestions made previously by other workers [60, 64, 65], suggests that HOBP may at least in principle also function by quenching photo-excited states of the dithiocarbamates.

In a further experiment the rate of decay of the combined absorptions of NiDEC and HOBP (λ_{max} at 330 nm, concentration of each 1×10^{-4} ML^{-1}) in hexane containing a vinylidene model compound methyl nonyl ethylene (MNE, concentration 1×10^{-2} ML^{-1}) was measured figure 7.3. This figure shows that the rate of decay of combined absorption due to NiDEC and HOBP (figure 7.3 curve 2) is initially much slower than NiDEC alone (curve 3) and higher than HOBP alone (curve 1). During this initial period it is clear that NiDEC is completely destroyed (fig. 7.2). After the destruction of NiDEC, the absorption at 330 nm of the mixture is expected to be due to HOBP only. At this stage the rate of decay falls below the rate due to HOBP when used alone (figure 7.3, curves 1 & 2). This result seems to suggest that a product formed from the dithiocarbamate must be responsible for the protection of HOBP. Exactly similar results have also been obtained in the polymer system (Chapter 4, figure 4.15). This is certainly due to the removal of peroxide from the system which would otherwise cause additional destruction of HOBP (figure 7.3, curve 1).

It is known [56] that the anti-oxidant function of the dithiocarba-
mates is not due to the metal complex itself but to a Lewis acid (or acids)
formed from it which decompose peroxides catalytically into non radical
products.

On the basis of these results together with the results obtained in
the Chapter 4, the synergistic action shown by the metal dithiocarbamates
and HOBP in polyolefins stabilization may be explained as due to
(a) independent and co-operative action of additives and (b) mutual
protection of additives; thus lengthening the period of their anti-
oxidant and stabilization activity.

It has been suggested earlier that the antagonism between metal
dithiocarbamates and Irganox 1076 is due to the interaction of one into
the action of another.   It has previously been seen in the polymer
system that both the UV stability and decomposition rate of dithiocarba-
mates are markedly affected in presence of Irganox 1076 (fig. 4.21).   The
UV stability of both NiDEC and ZnDEC in presence of Irganox 1076 (concen-
tration of the additives used is 1×10^{-4} ML^{-1} each) were also determined
in hexane following the absorption maxima of the metal complexes viz.
330 nm and 285 nm respectively for NiDEC and ZnDEC.   The results are
shown in figures 7.4 and 7.5.   These results are entirely consistant
with those obtained in the polymer system (figure 4.21).   The UV stability
of the metal dithiocarbamates is decreased and decomposition rate is
increased in presence of Irganox 1076 (fig. 7.4 and 7.5, curves 1 & 2).
This may be due to sensitisation of the photolytic destruction of the

dithiocarbamates by oxidation products of the phenol which have been shown to be peroxydienones and stilbenequinones [15, 154, 165]. Exact nature of the stilbenequinone produced from the UV oxidation of Irganox 1076 could not be identified by T.L.C. but the infra-red spectra of irradiated Irganox 1076 both in the polymer film and in solution showed a quinone carbonyl peak at 1675 cm^{-1}. In order to find the effect of a typical stilbenequinone on the photostability of metal dithiocarbamates, 3,5,3',5'-tetratert-Butyl stilbene 4,4' Quinone was prepared according to the method of Cosgrave and Waters [166]. The effect of this compound $(1 \times 10^{-4} ML^{-1})$ on the photostability of NiDEC and ZnDEC is also shown in the figures 7.4 and 7.5 respectively, curve 3. The rate of photolytic destruction of dithiocarbamates is even more increased in presence of above stilbenequinone than in the presence of Irganox 1076. This difference could be due to two possible factors, (a) the time factor involved in the formation of stilbenequinone from Irganox 1076 in the system and (b) the formation of a different stilbenequinone. However, whatever is the nature of stilbenequinone, it photosensitizes the destruction of dithiocarbamates under UV leading to a decrease in their effectiveness. The photostabilizing activity of metal dithiocarbamates and Irganox 1076 in the photo-oxidation of polyolefins (Chapter 4, figures 4.20(a) and (b) shows that the anti-oxidant activity of Irganox 1076 is reduced in the mixture. The reason for this is not yet clear but it may be due to the scavanging of radicals derived from the dithiocarbamates under condition of UV irradiation. If this reaction occurs the anti-oxidant would be removed faster from the system with consequent reduction in its normal anti-oxidant function.
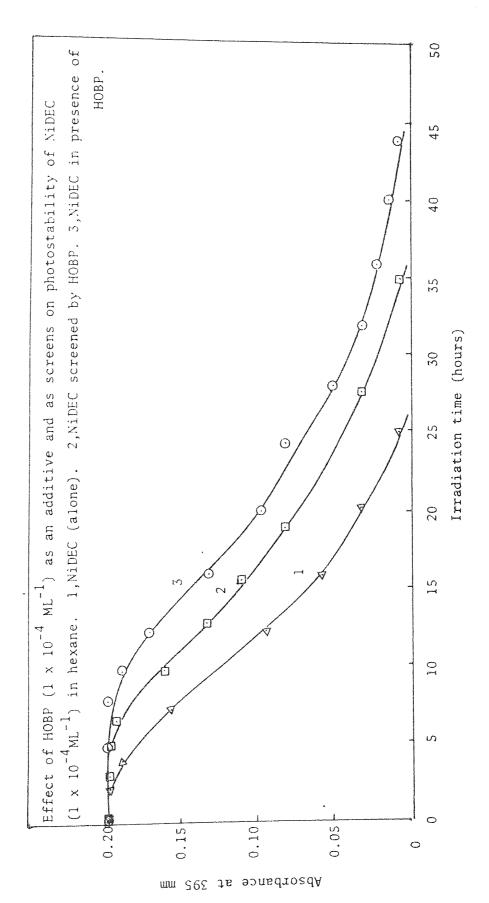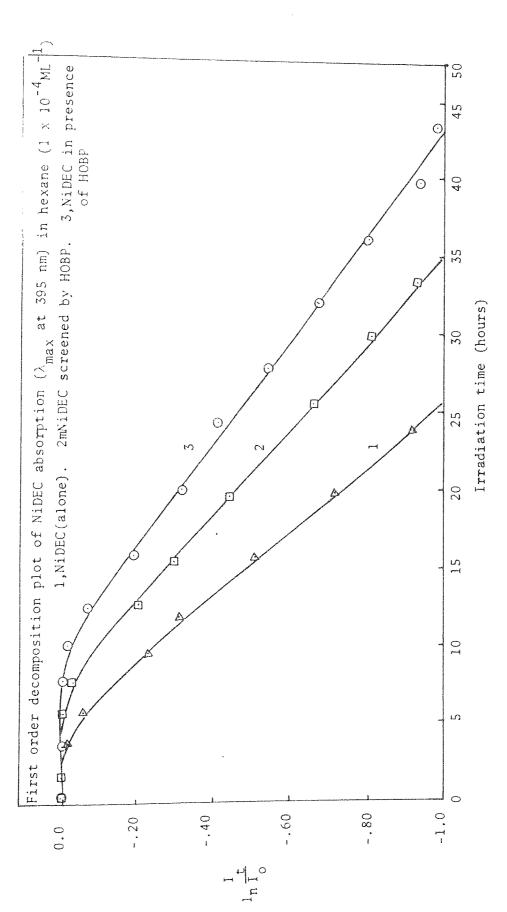
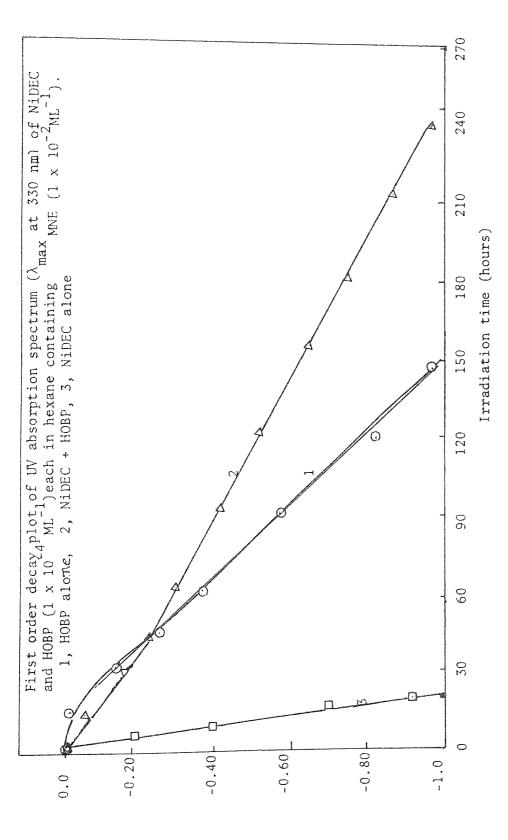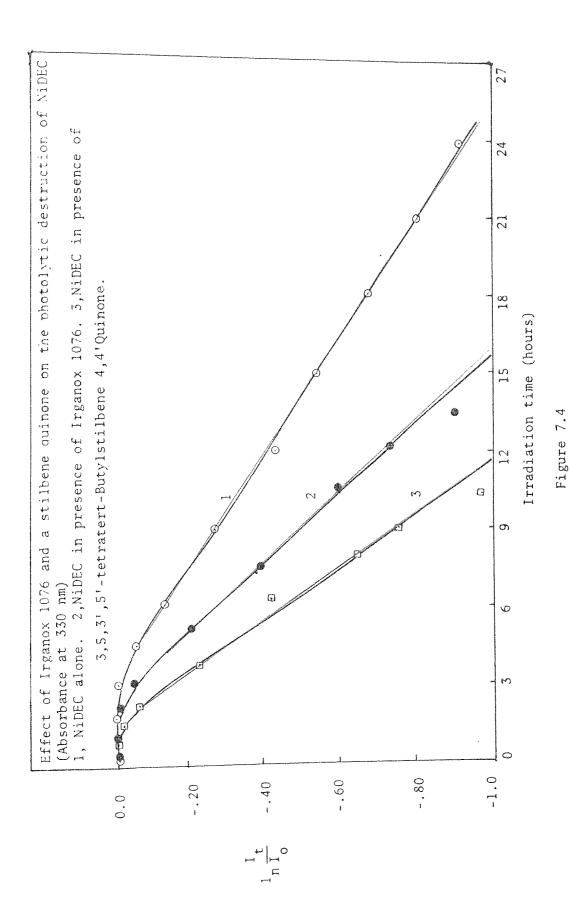Effect of HOBP (1×10^{-4} ML^{-1}) as an additive and as screens on photostability of NiDEC (1×10^{-4} ML^{-1}) in hexane. 1,NiDEC (alone). 2,NiDEC screened by HOBP. 3,NiDEC in presence of HOBP.

Figure 7.1

First order decomposition plot of NiDEC absorption (λ_{max} at 395 nm) in hexane ($1 \times 10^{-4} ML^{-1}$) 1,NiDEC(alone). 2mNiDEC screened by HOBP. 3,NiDEC in presence of HOBP

Irradiation time (hours)

$\ln \frac{I_t}{I_o}$

Figure 7.2

First order decay plot of UV absorption spectrum (λ_{max} at 330 nm) of NiDEC and HOBP (1×10^{-4} ML^{-1})each in hexane containing MNE ($1 \times 10^{-2}ML^{-1}$).
1, HOBP alone, 2, NiDEC + HOBP, 3, NiDEC alone

Figure 7.3

Effect of Irganox 1076 and a stilbene quinone on the photolytic destruction of NiDEC (Absorbance at 330 nm)
1, NiDEC alone.   2, NiDEC in presence of Irganox 1076. 3, NiDEC in presence of 3,5,3',5'-tetratert-Butylstilbene 4,4'Quinone.

Irradiation time (hours)

$\ln \frac{I_t}{I_o}$

Figure 7.4

First order decomposition plot of ZnDEC in hexane under UV (λ_{max} at 285 nm) 1, ZnDEC alone. 2, ZnDEC + Irganox 1076. 3, ZnDEC in presence of 3,5,3',5'-tetratert-Butylstilbene 4,4'Quinone

Time in hours

Figure 7.5

CHAPTER 8

GENERAL CONCLUSIONS

The effect of thermal processing on the chemical and physical properties of polyolefins (LDPE and polypropylene) was found to be strongly dependent on the amount of oxygen present in the mixer.   On processing of the polymers in presence of excess air, hydroperoxide concentration starts at very low level, increases auto-catalytically, and reaches a maximum as the reaction passes into the steady state rate. Chain scission associated with the reduction of molecular weight pre-dominates in the later stages of processing.   Although less peroxides were formed when LDPE was processed in a limited excess of air, the initial rate (up to 10 minutes processing) was substantially faster than in the later stages and was comparable with that in an open mixer. The marked reduction in melt flow index and increase in molecular weight with a simultaneous formation of insoluble gel indicated that a cross-linking reaction predominated under this processing condition.   When oxygen was excluded completely by continuous purging with argon, both rheological and chemical changes were eliminated completely.

Subsequent thermal and photo-oxidations of polyolefins were found to be markedly dependent on the previous thermal history which appears to depend primarily on the amount of hydroperoxide formed during

processing.   The progressive build up of peroxide during processing
photo-activated LDPE and polypropylene towards rapid photo-oxidation
with a corresponding reduction of the auto-acceleration stage.   The
fastest oxidation rate (both thermal and photo) was associated with
the maximum concentration of hydroperoxide.   A plot of initial photo-
oxidation rate against initial hydroperoxide concentration (in both
LDPE and polypropylene) showed a linear relationship.   No correlation
was found between photo-oxidation rate and initial conjugated carbonyl
or unconjugated carbonyl.   These two chromophores have been proposed
as photo-initiators for polyolefins by many workers[28, 31, 33, 139].
The dominating importance of peroxide as a photo-initiator was
confirmed by heating a film of both LDPE and polypropylene containing
a substantial amount of hydroperoxide in argon which before this
treatment photo-oxidized rapidly.   This treatment destroyed peroxide
completely, with the corresponding increase in the ketonic carbonyl
concentration.   In spite of the very high concentration of ketonic
carbonyl the initial photo-oxidation rate of the resulting film was
reduced to zero, introducing an induction period similar to that of
an unprocessed control with a negligible initial carbonyl concentration.
This experiment also clearly demonstrates that neither triplet carbonyl
nor singlet oxygen (produced by quenching triplet carbonyl) are of any
practical significance as photo-initiators in LDPE or polypropylene.
It is concluded that hydroperoxides are the most important initiators
during the early stages of photo-oxidation of normally processed
LDPE and polypropylene and the mode and rate of photo-oxidation of
the polymers studied are critically dependent upon its thermoxidative
history.

The formation of peroxide in LDPE is found to be associated with the disappearance of vinylidene unsaturation initially present in the polymer both during thermal and photo-oxidation and this process preceeds carbonyl formation. This shows that this group is certainly involved in the oxidative degradation of LDPE as a consequence of allylic hydroperoxide formation.

However, when substantial quantities of carbonyl compounds are present in the polymers either by thermolysis or photolysis of hydroperoxide, they are intimately involved as initiators in the later stages of photo-oxidation. The kinetics of the photo-oxidation of LDPE in the later stages is consistent with the view that carbonyl groups are the main photo-initiators at an advanced stage of photo-oxidation[167]. Formation of vinyl and carboxylic acid is certainly due to the photolysis of ketone by Norrish I and II reactions. The presence of carbonyl primarily causes photolysis rather than photo-initiation during the photo-oxidation of polyolefins.

Since hydroperoxides are the potential photo-initiators and responsible for the initial photo-oxidative degradation of polyolefins, it is possible to stabilize the polymers against UV light by removing peroxide from the system. It has been shown that LDPE and polypropylene are stabilized to some extent against UV light by heating the samples in argon prior to UV irradiation which removed peroxide formed during processing. A similar effect has also been obtained by removing peroxides during processing by means of peroxide decomposing

anti-oxidants (ZnDEC and NiDEC). This peroxide decomposition activity persists in the initial UV exposition stage. Both the compounds are found to be very good melt stabilizers of LDPE and polypropylene and are effective UV stabilizers in the initial photo-oxidation stage. They are equally effective as photo-stabilizers in both mildly and severely processed samples. These complexes are known to destroy hydroperoxides by a catalytic (ionic) mechanism involving Lewis acids (notably sulphur dioxide or sulphur trioxide) generated in a series of initial stoichiometric reactions with hydroperoxides. The major limitations to their effectiveness as UV stabilizers is that they are not UV stable. The higher UV stabilization activity shown by NiDEC in polyolefins compared to ZnDEC is found to be due to the secreening of incident UV light associated with NiDEC in addition to its peroxide decomposition activity. Moreover, NiDEC is more stable toward UV light than ZnDEC.

The primary aliphatic amine complexes (particularly sec-Butylamine and tert-Butylamine) of Zn and nickel diethyldithiocarbamates have shown higher stabilization effectiveness in polyolefins compared to the parent dithiocarbamates. The increased stabilization effectiveness of the dithiocarbamate-amine complexes have been found to be mainly due to improved peroxide decomposition efficiency and UV stability of dithiocarbamates on complex formation. Secondary aliphatic amine complexes did not show any improved stabilization activity because they are destroyed during processing by volatalization of the amine.

A typical high molecular weight phenolic anti-oxidant (Irganox 1076) which acts by removing chain propagating radicals by hydrogen transfer and trapping of radicals was found to be effective as thermal stabilizer in polyolefins. It behaved as a weak photo-activator during the auto-accelerating stage and as a retarder of the maximum rate of photo-oxidation.

A typical 'UV absorber', 2-hydroxy-4-octyloxybenzophenone (HOBP) behaved quite differently in thermal and UV stabilization of LDPE. It has only very slight activity as a thermal anti-oxidant. Hydro-peroxides and carbonyl groups are formed in the polymer after an induction period which differs little from the control without anti-oxidant. In spite of this however, the photo-oxidation rate is lower at all stages due to the screening effect of the UV stabilizer in the polymer. The UV stabilizing activity of HOBP is not as great in the severely processed sample as it is in a mildly processed sample. Experimental evidence on the mechanism of its function suggests that HOBP also functions by radical scavanging mechanism in addition to screening of UV light. Moreover, inhibition of carbonyl photolysis by HOBP also suggests that quenching of excited triplet carbonyl might be another possible contributor to the overall stabilization mechanism.

The methyl substituated piperidine derivative (Tinuvin 770) behaved as a strong pro-oxidant during thermal oxidation of polyolefins but stabilized them effectively against photo-oxidation . The evidence suggests that the stabilizing activity of Tinuvin 770 is not associated

with peroxide decomposition, UV screening effect or quenching of triplet carbonyl state. The UV stabilizing property of Tinuvin 770 appears to be associated with free-radical scavanging activity by the compound itself or by nitroxide radicals derived therefrom.

Combinations of peroxide decomposers (ZnDEC or NiDEC) and Irganox 1076 showed synergistic effects in thermal oxidations of LDPE, whereas the combined effects of HOBP and the peroxide decomposers were additive. By contrast the above combinations behaved quite differently in photo-oxidation. HOBP synergised effectively with peroxide decomposing anti-oxidants (metal dithiocarbamates) whereas Irganox 1076 interacted antagonistically with metal dithiocarbamates. However, Irganox 1076 synergised with HOBP in polyolefins during photo-oxidation, although the effect is not as pronounced as with the peroxide decomposer and HOBP. Optimum synergistic action between peroxide decomposer and HOBP has been observed at a concentration ratio of 1:2 of the peroxide decomposer to HOBP. The most noticable feature of the synergistic mixture is that they are equally effective as photo-stabilizers when subjected to both mild and severe processing operations. Another interesting aspect of the synergistic combination is that although ZnDEC alone is less effective as photo-stabilizer compared to NiDEC, synergistic mixture of ZnDEC and HOBP showed similar stabilizing effect to the NiDEC/HOBP mixture. The studies on the mechanism of synergistic action showed that the additives protect each other during thermal processing and subsequent UV exposure stage and hence lengthen the period of their independent and co-operative action. HOBP is

found to be destroyed by peroxide formed during processing and during
subsequent UV exposure stage.   Metal dithiocarbamates protect HOBP
from peroxide and in turn HOBP protects metal complexes from photolytic
destruction both by screening of UV light and other chemical processes.
The chemical processes involved are probably the removal and de-activation
of photo-excited reactive species formed from the dithiocarbamates
during irradiation.

The antagonism between Irganox 1076 and metal dithiocarbamates
has been found to be due to sensitization of the photolytic destruction
of the dithiocarbamates by oxidation products of the phenol (particularly
stilbenequinone) leading to a decrease in their effectiveness.

Substituated piperidine compound, Tinuvin 770 alone is an
effective photo-stabilizer in polyolefins, did not synergise with
metal dithiocarbamates, instead tends to interact antagonistically
with dithiocarbamates.   The reasons for this are not yet clear and
require further study.

Suggestions for further work

The protective effect of HOBP on photo-stabilization of metal dithiocarbamates is not due entirely to UV screening, the nature of this additional protection has been suggested as could be due to the removal and de-activation of reactive species formed from the dithio-carbamates under irradiation. In order to establish clearly the mechanism of the chemical stabilization processes involved in HOBP it is suggested that the quenching of the fluorescence of photo-excited species (carbonyl and dithiocarbamate) by HOBP should be studied in detail. Moreover it is necessary to identify the products formed from HOBP and from the photo-sensitiser in the system by T.L.C.or G.L.C. Similarly the antagonistic effect of phenols on the dithio-carbamates during UV exposure may also be chemically examined by identi-fying products in model systems.

The nature of the stabilization action of substituated piperidine compound (Tinuvin 770) has not been clearly established. An attempt should be made to identify by ESR of the various radicals produced in situ during photolysis and thermolysis of this compound both in polymer and in model systems.

In order to understand more clearly the stabilization action of metal dithiocarbamate-amine complexes, it is necessary to study a wide variety of amines in these complexes both in polymer and model system in order to establish the contribution of complex stability, peroxide decomposition activity, UV screening activity and compatability effects.

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