Time Controlled Photo - oxidation of Polyolefins by Polymer Bound Additives

Shahida Islam B . Sc . (Hons.) , M . Sc . (Dhaka)

A Thesis Submitted for the Degree of
Doctor of Philosophy

Aston University
January 1992

Aston University

Time Controlled Photo-oxidation of Polyolefins by Polymer Bound additives

Shahida Islam

Doctor of Philosophy January,1992

Summary

A variety of iron compounds containing vinyl or thiol functional groups (used as photoactivators) have been synthesised and some of these were successfully bound to both polyethylene and polypropylene backbone during processing in presence of peroxide and interlinking agent . Concentrates (masterbatches) of the photoactivators in PP and PE were prepared and the pro-oxidant effect of the diluted masterbatches in absence and presence of an antioxidant was evaluated . An antioxidant photoactivator (FeDNC) was found to sensitise the photoactivity of pro - oxidants (Metone A / Metone M) whereas an antioxidant (ZnDNC) was found to stabilise the polymer (PP and PE) containing both of these combinations . It was observed that the lower concentration of FeDNC sensitises the stability of the polymer containing very small concentrations of NiDNC whereas higher concentrations of FeDNC stabilises the polymer (LDPE) containing same amount of NiDNC compared to FeDNC alone .

The photostability of unstabilised PP containing FeAc could be varied by varying the concentration of ZnDEC . Both the induction period and the UV - life time of the polymer increased by increasing the concentration of ZnDEC . It is suggested that ligand exchange reaction may take place between FeAc and ZnDNC . A polymer bound UV stabiliser (HAEB) and a thermal stabiliser (DBBA) were used with a non extractable photoactivator (FeAc) in PP . Small concentrations of the stabilisers (HAEB and DBBA) in combination with the photoactivator (FeAc) sensitise the polymer . The antioxidant present in commercial polymer (LDPE and PP) was found to be of a hindered phenol type , which was found to antagonise with ZnDNC when used in combination with the photoactivators .

Key Words : Bound Photoactivators, Time Controlled Stabilisation .

Acknowledgement

I am greatly indebted to Professor Gerald Scott and Dr . S . Al - Malaika for their excellent supervision throughout the execution of this project and continual encouragement and advice during the writing of this thesis .

I am very grateful to Dr . S . Q . Chowdhury and Dr . K . B.Chakraborty for introducing me to Professor Gerald Scott , which has enabled me to get the opportunity to undertake the investigations described in this thesis .

I acknowledge RAPRA Polymer Characterisation Centre for carrying out the MW work described in this work .

I acknowledge the co-operation of all members of the Polymer Processing and Performance research group especially Dr . B . Wirjosentono and Dr . M . R . S . Coker for suggestions and encouragement . Again grateful acknowledgement is also made to Dr. K . B . Chakraborty for his advice , suggestions and ever - willing help .

I also acknowledge with gratitude Dr. Dan Gilead for financial support of this project and the University of Dhaka for granting me leave of absence which has enabled me to carry out the investigations described in this thesis .

I am also indebted to my daughter (Bornali Islam) who suffered a lot during this period . Finally , I wish to convey my sincere appreciation to my husband (Dr . M . Anwarul Islam) for his patience , encouragement and supports provided throughout the course of this work .

This thesis is dedicated to my parents whose constant inspiration always leads to my every success

Contents

Chapter : 1 **Introduction** **Page**

1 . 1 Plastics in agriculture 2
1 . 2 Essential requirements for ideal degradable mulching film 4
1 . 3 Plastics of controlled lifetime for agricultural uses 5
1 . 3 . 1 Biodegradable plastics 5
1 . 3 . 2 Photochemically unstable polymers 5
1 . 3 . 2 . 1 Unstabilised polymers 5
1 . 3 . 2 . 2 Carbonyl modified polymers 6
1 . 3 . 3 Photosensitised polymers 8
1 . 3 . 3 . 1 Aromatic ketones 8
1 . 3 . 3 . 2 Transition metal carboxylates and related metal complexes 11
1 . 3 . 3 . 3 Antioxidant based photoactivators 12
1 . 4 Mechanisms of antioxidant action 14
1 . 4 . 1 Thermal and photo - oxidative degradation of polyolefins 14
1 . 4 . 2 Stabilisation of polyolefins 16
1 . 4 .2 .1 The chain breaking (CB) mechanism 17
1 . 4 . 2 . 1 .1 Chain breaking accepter (CB-A) mechanism 17
1 . 4 . 2 .1 . 2 Chain breaking donor (CB - D) mechanism 18
1 . 4 . 2 . 1 . 3 Complementary mechanisms involving both CB-D and CB-A 19
1 . 4 . 2 . 1 . 4 Regenerative chain breaking antioxidants 20
1 . 4 .2 . 2 . The preventive mechanism 20
1 .4 . 2 . 2 . 1 Peroxydolytic antioxidants 21
1 . 4 . 2 . 2 . 2 UV- absorbers 23
1 . 4 . 2 .2 .3 Metal deactivators 25
1 . 5 Implications and applications of polymer - bound antioxidants 25
1 . 5 . 1 Antioxidant substantivity 25

1 . 5 . 2 Approaches in antioxidant substantivity 27
1 . 6 Previous work at Aston on Bound Antioxidants 28
1 . 7 Object and scope of the present work 29

Chapter : 2 **Synthesis and Characterisation of Additives and General Experimental Techniques**

2 . 1 Materials 32
2 . 2 Chemical synthesis and characterisation of additives 33
2 . 2 . 1 Synthesis of iron (III) salt of thioacetic acid 33
2 . 2 . 2 Synthesis of iron (III) salt of mercaptopropionic acid 34
2 . 2 . 3 Synthesis of iron (III) acrylate 35
2 . 2 . 4 Synthesis of iron (III) maleate 36
2 . 2 . 5 Synthesis of iron (III) crotonate 37
2 . 2 . 6 Synthesis of iron (III) cinnamate 37
2 . 2 . 7 Preparation of 2 - hydroxy - 4 - (acryloyloxy - ethoxy) benzophenone (HAEB) 38
2 . 2 . 7 .a Preparation of 2 - hydroxy - 4 - (hydroxy - ethoxy) benzophenone 39
2 . 2 . 7 . b Preparation of 2 - hydroxy - 4 - (acrylolyloxy - ethoxy) benzophenone (HAEB) 40
2 . 2 . 8 Preparation of 3 , 5 - di - tert . butyl - 4 - hydroxy benzyl acrylate (DBBA) 41
2 . 2 . 8 . a Preparation of 3 , 5 - di - tert - butyl - 4 - hydroxy benzyl alcohol 41
2 . 2. 8 . b Preparation of 3 , 5 - di - tert - butyl - 4 - hydroxy benzyl acrylate (DBBA) 42

Structure and Code Name of the Compounds 44

2 . 3 Processing of polymer samples and additives and preparation of bound concentrates 46
2 . 4 Preparation of films from processed samples 47
2 . 5 Measurement of melt flow index (MFI) 47
2 . 6 Soxhlet extraction of masterbatches in xylene 49
2 . 7 Solvent extraction of polymer films 49
2 . 8 Evaluation of binding 49
2 . 9 Ultraviolet irradiation of polymer films 50
2 . 10 Thermo - oxidative studies using wallance oven 53
2 . 11 Measurement of brittle fracture time of polymer samples 53
2 . 12 Infra - red spectroscopy 54
2 . 13 Ultraviolet spectroscopy 55
2 . 14 Gel permeation chromatography 56
2 . 15 Tensile measurement 57
Figures 59

Chapter :3 **Photo-oxidation of Unstabilised and Commercial LDPE by Photoactivators alone and with Antioxidants and the Thermal stabilisation of Unstabilised LDPE**

3 . 1 Object 81
3 . 2 Results and Discussions 82
3 . 2 . 1 Effect of initiator on the processing history of unstabilised LDPE containing different photoactivators . 82
3 . 2 Assessment of binding of FeAc in unstabilised LDPE 84
3 . 2 . 3 Evaluation of binding of FeTp in unstabilised LDPE 88
3 . 2 . 4 Effect of varying the concentration of different photoactivators on the photo - oxidative degradation of unstabilised LDPE 90
3 . 2 . 5 Effect of initiator on the photo - oxidation of unstabilised

LDPE containing different photoactivators 95
3.2.6 Effect of processing conditions on the photo - oxidative and melt stability of LDPE with and without pro-oxidants 96
3.2.7 Effect of two component systems on the photo - oxidation of unstabilised LDPE : Combination of different pro - oxidants with antioxidant 100
3.2.8 Effect of pro - oxidant alone and in combination with antioxidant on photo - oxidation of commercial LDPE 104 (Riblene CF 2203)
3.2.9 Effect of varying the concentration of different photo - activators on the UV stability of commercial LDPE (BP) 107
3.2.10 Effect of different pro - oxidants on the change of elongation at break of unstabilised LDPE 107
3.2.11 Thermal stabilisation of unstabilised LDPE by different pro - oxidants 108
Conclusions 110
Figures 113

Chapter : 4 **Photo - oxidation of Unstabilised and Commercial Polypropylene by Pro - oxidants alone and in Combination with Antioxidant**

4.1 Object 156
4.2 Results and Discussions 157
4.2.1 Evaluation of binding of FeTp in unstabilised polypropylene 157
4.2.2 Effect of concentration on the photo - oxidation of unstabilised polypropylene 158
4.2.3 Concentration effect of pro - oxidants on the melt stability

changes of polypropylene 163

4 . 2 . 4 Combination of pro - oxidant with an antioxidant on the photo - oxidation of unstabilised polypropylene 164

4 . 2 . 5 Evaluation of binding of HAEB and DBBA and the photostabilising effect of HAEB in unstabilised polypropylene 172

4 . 2 . 5 . 1 Evaluation of binding of HAEB in unstabilised polypropylene 173

4 . 2 . 5 . 2 Photo - oxidative behaviour of HAEB in unstabilised polypropylene 183

4 . 2 . 5 . 3 Evaluation of binding of DBBA in unstabilised polypropylene 185

4 . 2 . 6 Effect of a bound UV stabiliser (HAEB) and thermal antioxidant (DBBA) in combination with FeAc on the photo - oxidation of unstabilised polypropylene 190

4 . 2 . 7 The effect of two component systems on the photo - oxidation of commercial PP 192

Conclusions 196

Figures 198

Chapter : 5 **General Conclusions and Suggestions for Further work**

5 . 1 General Conclusions 224

5 . 2 Suggestions for further work 225

References 227

Chapter One

Introduction

The increasing use of polymer based products in disposable packaging , short term crop protection film , baler twines and protective netting for fruit crops has brought with it the accumulation of the waste products in the countryside and on the sea shore (1, 2) . Although polyolefins have in the past presented the polymer technologist , with one of the most difficult problems in stabilisation technology , in recent years the growing concern and awareness of pollution and other aspects of ecology has led plastic technologists and scientific workers to enquire into the possibilities of accelerated destruction of plastic wastes (3-13) . During the late sixties scientific investigations led to different solutions to this problem (11, 13) . Attempts have been made to modify both the existing polymeric materials and the additives to achieve relatively rapidly degradable polymer.

During the mid seventies, due to the shortage of raw materials (14), attention was directed towards the recovering and recycling of waste plastics (15) . In spite of this the recycling of waste plastics has not made a significant contribution to the problem of waste disposal and conservation of material resources due to the considerable economical and technical problems (16) . In the case of consumer waste it is difficult to obtain homogeneous plastics waste . Plastics waste are always accompanied by paper, metal, glass etc . So, besides the collection and transportation operation , the separation of plastics from non-plastics material and cleaning it from contaminants are very difficult tasks and due to the cost involved in the overall operation , this process is not feasible for most packaging waste . Recycling has been shown to provide a significant contribution where plastic waste could be readily collected and transported to a central collection point as in the case of supermarket waste , but there are still reservations about the recycling , because , the waste plastics which have been exposed to the environment suffers from chemical composition changes . These changes in chemical properties of plastics affect their behaviour on reprocessing . Furthermore, reprocessing of mixed plastics gives rise to fabricated products which are much inferior in mechanical performance e.g., tear strength , impact resistance , to the original component used separately (15). Therefore , recycling of waste plastics does not at present make a significant contribution to the problems of waste disposal and conservation of material resources.

1.1 Plastics in Agriculture

Since the first degradable plastics were discovered in the late 1960's they have been commercially accepted in agricultural technology . The versatility and availability of many width , thickness, colours, formulations and cost make them suitable for many applications . Their applications include agricultural mulches , greenhouse coverings , shelter for young trees , protective netting for fruit crops , packaging and grain storage . Plastic mulches are used to increase crop yields , improve quality, save labour, lower costs, permit out of season cropping and improve cultural practices . In arid and semi-arid regions , it is plastic films which make the growing of certain crops possible . Plastic mulching film controls the conditions of the soil which constitutes the root bed of the growing plants . Conditions of the soil can be controlled in different ways such as by water conservation , by increasing the soil temperature and by controlling the soil born diseases (17,18) .

Oriented polypropylene and HD polyethylene is being increasingly used as a replacement for hessian in binder twines (19) . This is due to severe difficulties in sisal supply and consequently price increases . In 1981 polypropylene based twines made up around 60% of the total market of twines in U.K. and for this around 9000 tones of polypropylene was used (19) . Although polypropylene based twines have the advantage of being rot - proof and not affected by moisture in storage or in the field , they do undergo premature failure in use due to photodegradation . Commercial products are normally photostabilised by the use of ferric oxide (18) . This leads to long-term litter problems . A related but short-term problem is the use of polyolefin netting for the protection of fruit crops against birds . Here the primary requirement is a single season durability followed by rapid and complete degradation . Unstabilised fibre-forming polymer is unsuitable to be used for this application unless an especially designed stabiliser system is used . UV stabilised polymer which is currently in use lasted too long (17) and eventually created a litter problem . It is therefore necessary to use a controlled life time polymer to overcome the above problems.

In spite of the advantages offered by degradable polymers used in agricultural applications , especially as mulching films , their use is associated with a serious problem of pollution and litter due to the waste plastics produced . The usual way of removing the plastic residues is by laborious collection and then burning . Manual collection is a costly and arduous task which still leaves enough residue in the field to cause subsequent problems due to the non-biodegradability of the partially degraded product . It would therefore be of primary importance to the agriculturist as well as to the ecologist if the plastic could be made to disappear once it has served its purpose . This would not only minimise litter problems but also reduce labour requirement . Degradable plastics plays a great role in the plasticulture industry with the development of automated cultivation of soft fruits and vegetables (20).

1.2 Essential requirements for ideal degradable mulching film

In the case of protective netting for fruit crops the primary requirement is a single season durability followed by rapid and complete degradation . In the case of polyolefin-based mulching films and binder twines it is necessary to use a photosensitiser which will provide a controlled life time to the polymer .

It is not enough for plastic films to biodegrade , the ideal degradable film should show no change until shortly before cropping and then it must rapidly lose strength so that it disintegrates easily under the mechanical action of harvesting machines . This is unlike the conventional commercial polymers e.g., polyethylene, which begin to degrade slowly as soon as they are exposed to the outdoor environment and may take many years to become brittle . An agricultural mulching film which has disintegrated well before cropping would be unacceptable, and one which has disintegrated after cropping would be of limited value. Controlled-life mulching film should therefore have two essential properties . They should show no change in physical and mechanical properties until shortly before the end of their useful life (induction period) is reached and then they should undergo a rapid and complete decay of the original properties .

1.3 Plastics of Controlled lifetime for Agricultural uses

Different approaches have been practised to obtain a polymeric material of predetermined lifetime.

1.3.1 Biodegradable Plastics

Many commercially available polymers e.g. cellulose derivatives, polyurethanes, polyamides are susceptible to biodegradation by the action of micro-organisms (21) . Heat , oxygen and moisture are essential factors for this process . However , these biodegradable polymers seem to be marginally effective when considered as a polymer with a controlled life time because these are highly dependent on the microbial environment of plastics (21) .

1.3.2 Photochemically Unstable Polymers

1.3.2.1 Unstabilised Polymers

It is known that oxygen containing groups and other impurities are normally introduced into the polymer backbone during processing and fabrication stage (22 - 26) . This markedly increases their sensitivity to photodegradation during subsequent environmental exposure to normal weathering conditions . In theory , therefore omission of conventional antioxidants and melt stabilisers could lead to fabricated products of reduced lifetime . In practice , this does not provide a satisfactory solution to the problem since this inevitably leads to melt instability of the polymer during processing and irreproducibility of performance during outdoor use .

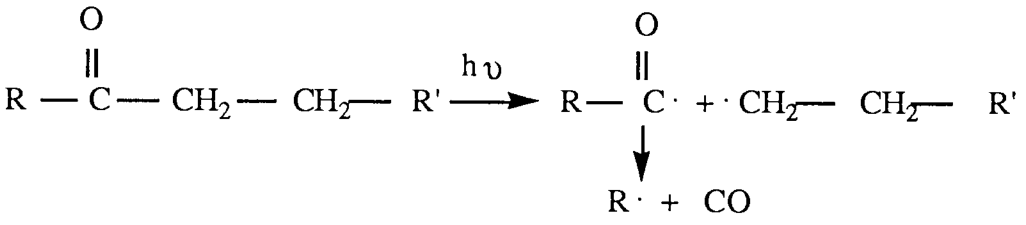
The latter is of practical importance to the mulching film because a predetermined reliable safe-use period is required before any substantial change in mechanical properties occurs . Moreover , for different crops , the required length of the induction period may be different .

In spite of these limitations, Japan Synthetic Rubber Company (27) has prepared a photodegradable plastic based on 1,2- polybutadiene resin . Princeton Chemical research (28, 29) has also prepared inherently unstable polymer based on polybutene-1 suitable for agricultural mulches . However, to be technologically useful both polymers have to be stabilised with conventional uv absorbers . No commercial polymer of controlled lifetime based on this principle has been reported which may be due to the high cost of both monomers.

1.3.2.2 Carbonyl Modified Polymers

Most aliphatic ketones and aldehydes show relatively weak absorption in the ultra violet region with a maximum around 280 nm (tail extends to around 300 nm) . These groups can , therefore , initiate polymer degradation when exposed to outdoor sunlight . On absorption of light , carbonyl groups are activated to their excited singlet state which is capable of undergoing intersystem crossing to the lowest triplet state (30) . Both these excited states are capable of undergoing a variety of reactions. They can activate the polymer chain in the vicinity of the carbonyl group (31) undergo photodecomposition (32) or abstract a hydrogen atom from the polymer substrate .

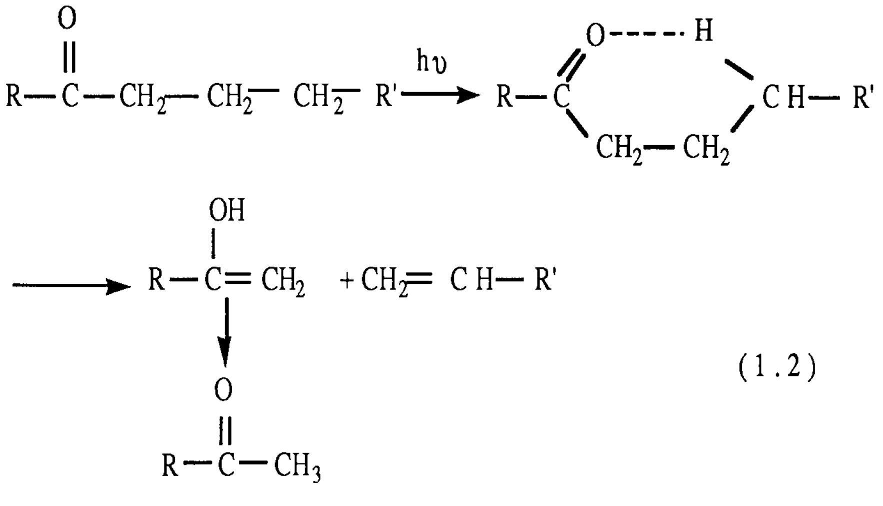
The principal reactions involved in aliphatic ketones are Norrish type I and Norrish type II (32). In the Norrish type I reaction the bond between the carbonyl group and adjacent α–carbon is homolytically cleaved producing two radicals (Reaction 1.1).



$$R-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-R' \xrightarrow{h\upsilon} R-\overset{\overset{O}{\parallel}}{C}\cdot + \cdot CH_2-CH_2-R' \qquad (1.1)$$

$$R-\overset{\overset{O}{\parallel}}{C}\cdot \longrightarrow R\cdot + CO$$

The Norrish type II reaction proceeds as a non-radical, intramolecular process which occurs with the formation of a six membered cyclic intermediate. Subsequent abstraction of a hydrogen atom from the γ – carbon results in decomposition into olefins and ketones (Reaction 1.2).



(1.2)

By taking advantages of these fundamental studies and by conceptually inverting the objectives of them , Guillet and his coworkers (33- 35) were able to develop carbonyl containing polymers with enhanced sensitivity to ultra-violet irradiation . These are based on the copolymerisation of the common monomer with vinyl ketones . Polymers of this type do not require oxygen to initiate photodegradation since this occurs rapidly on absorption of a photon by the molecule.

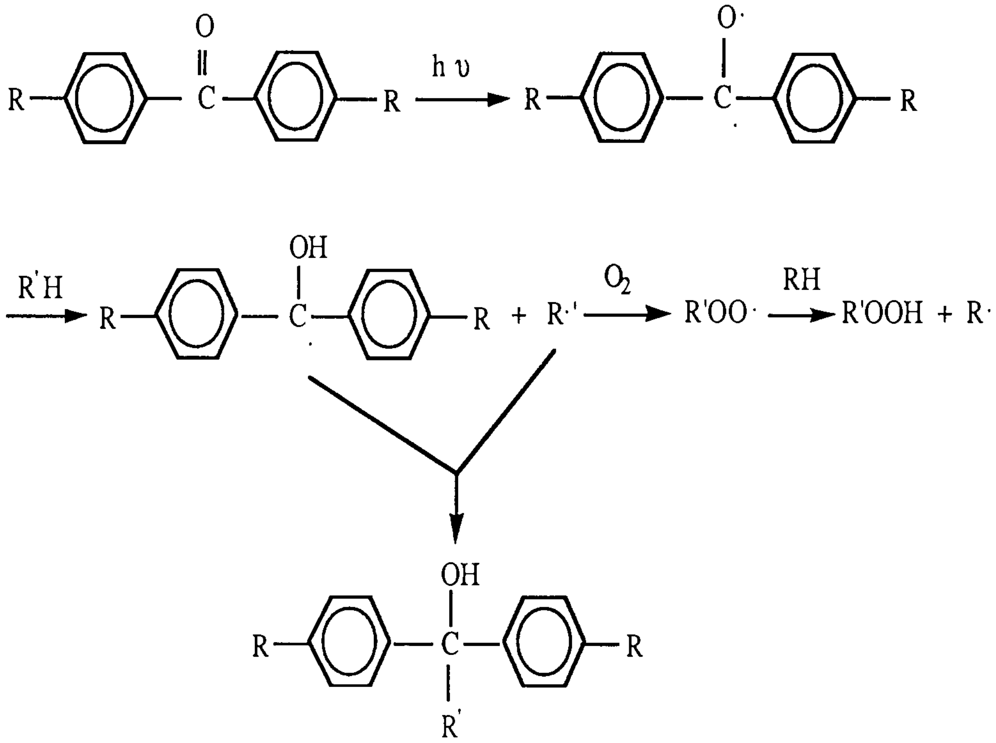
Because of the small amount of the keto group in the polymer , the quantum yield for chain scission is low . However , a few backbone scissions are enough to cause breakdown of the polymer by Norrish reaction types I and II . Photodegradation of vinyl ketone copolymers is therefore a very rapid process and by varying the concentration of the photosensitive group in the polymer, time control can be easily achieved.

The most important feature in Guillet's photodegradable plastic is that the photosensitive group is part of the polymer so it can not be removed by leaching under any circumstances . Such polymers are suitable for disposable cups , plates and other similar items . However , the cost of producing large - scale photolytically unstable mulching films based on copolymerisation is high and there are no reports of the use of these materials in agricultural mulches.

1.3.3 Photosensitised Polymers

1.3.3.1 Aromatic Ketones

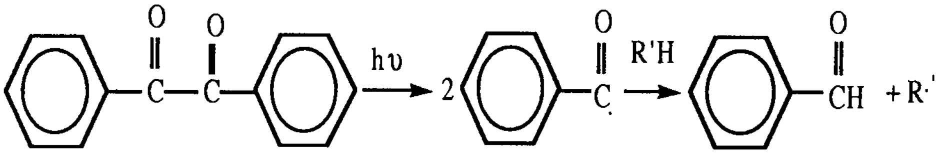
Aromatic ketones e.g. substituted benzophenone are known as effective photopro - oxidants for the more oxidisable polymers such as polypropylene (36), polystyrene (37) and polyisoprene (38). Unlike their aliphatic analogues, aromatic ketones cannot undergo Norrish photodecomposition reactions. The excited triplet are highly active species and can abstract a hydrogen from the polymer substrate thereby initiating the oxidative chain process. Aromatic ketones are less effective for the more oxidatively stable polymers such as polyethylene (39, 40).



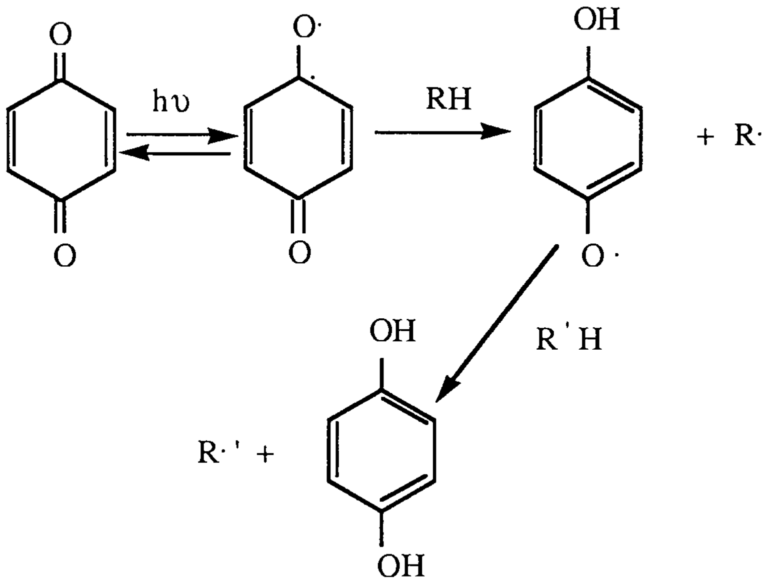
Reaction Scheme 1 . 1

In this case the photodegradation is retarded and this became particularly noticeable at higher concentrations of the ketone. The retardation process has been ascribed by Scott and Amin (39) to be the relative stability of the ketyl radicals formed, which leads to favourable competition between chain initiation and chain termination processes in the mechanism (Reaction scheme 1.1).

Aromatic diketones are also very effective photosensitisers for plastic materials (41) . Benzil (41) is one of the most extensively studied aromatic diketones . On photolysis benzil gives benzoyl radicals which are highly reactive and can abstract hydrogen atom from the polymer substrate (Reaction 1.3) (41) .


(1.3)

Quinones are also used as photosensitisers for the photodegradation of polymers . By absorbing ultra-violet light quinones transform to a biradical excited state (42) . These biradicals can then abstract hydrogen from the polymer substrate thus initiating the degradation process (Reaction scheme 1 . 2) .



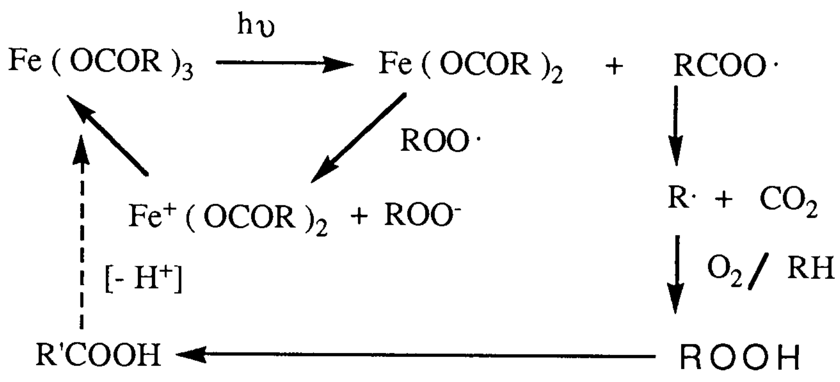
Reaction Scheme 1 . 2

However , because of the autoretarding characteristics typical of this system (39) no commercial products have been established . An auto-accelerating pro-oxidant is required for agricultural purposes (18).

1.3.3.2 Transition metal carboxylates and related metal complexes

It was reported (43) that free radicals and atoms could be produced on irradiation of metal ions or ion pair complexes in solution and these radicals or atoms could initiate polymerisation of vinyl monomers (44) . This has been explained in terms of an electron transfer mechanism (45). As a result of ultra-violet irradiation an electron transfers from one ion to another ion . The intermediate thus formed undergoes dissociation to give an atom or free radical . Iron complexes such as thiocyanate, oxalate , citrate , chloride etc. have been used as sensitisers in photopolymerisation of vinyl monomers (46).

Many workers (11, 13, 40, 47-50) have reported that transition metal caboxylates or halides cause acceleration in the oxidative degradation of polymers . Other metal complexes containing an oxygen ligand e.g. acetyl acetonates are also known as photosensitisers . Among all of the metals iron and cobalt have the most damaging effect on polymers . Stearates of iron and cobalt were among the earliest transition metal photosensitisers examined for agricultural mulches (51) . The mechanism involved in this case is believed (18) to be the photoreduction of iron salt which results in the formation of an initiating free radical which leads to a normal auto-oxidation chain reaction (Reaction Scheme 1 . 3) . Carboxylic acids are the major end products of the photo - oxidation of hydrocarbon polymers (39) . After



Reaction Scheme 1 . 3

the initial stages , the main catalytic products are again the ferric carboxylates formed with the macromolecular carboxylic acids . One major disadvantage with the transition metal carboxylates is their pro - oxidant activity during processing (47) . Hence the polymer needs an additional melt stabiliser during processing . Ferric acetylacetonate behaves similarly to that of transition metal carboxylates.

1.3.3.3 Antioxidant Based Photoactivators

It is obvious that "ideal" delayed action photoactivators should act as an antioxidant during processing and should be transient uv-stabilisers before becoming photosensitisers . Scott and Amin (39) found that iron dialkyl dithiocarbamate behaves in a similar way to that of the ferric stearates and acetylacetonates during uv irradiation . But unlike the latter , they are effective melt stabilisers during processing . Iron dialkyl dithiocarbamate behaves differently from other dialkyl dithiocarbamate e. g. zinc and nickel salts formed as end products from Zn and NiDMC which have no pronounced photo-oxidant effect .

The antioxidant photoactivator differs from conventional photoactivators in the early stage of photo-oxidation . The photo-oxidation of polymers containing antioxidant photoactivator (APA) does not commence until the APA complex has been completely destroyed by uv light . In this respect , the antioxidant activity of APA is similar to other metal dithiocarbamates (52 - 54). Once the metal dithiocarbamate complex is photolytically destroyed , the polymer photo-oxidises at a rate which is determined by the pro-oxidant activity and the concentration of the free metal ion left in the system . The iron based antioxidant chelates permit the accurate control of the induction period and the rate of the photo-oxidation at the end of the induction period. With increasing concentration of the chelate, the antioxidant properties give increasing photostabilisation during uv irradiation by reaction scheme (1 . 6 a) (Section 1 . 4 . 2 . 2 . 1 b) . The concentration of ionic iron increases by photolysis of the dithiocarbamate and at the end of the induction period photosensitising action of the metal carboxylate occurs . The thiocarbomyl radical (I) appears to dimerise (Reaction scheme 1 . 6 c) as long as there is an excess of metal chelate in the system, but there is evidence that the radical (I) may contribute to photosensitisation (55) (Section 1 . 4 . 2 . 2 . 2 . 1 b) .

Commercial polymers of variable but controlled life time based on this antioxidant photoactivator system (FeDMC) are now in use as mulch films in Israel , Europe , the USA and the Far East . A major practical problem with this system is that it becomes relatively insensitive to concentration as the polymer becomes more stable . The other limitation of this single component APA system based on FeDMC is that it does not give the control necessary for long cropping periods under the severe exposure conditions found e . g . in Israel . An APA system based on a combination of the stabiliser complexes (Ni or Co) and an activator complex (Fe) gives a more precisely controllable activation at much lower activator concentration (56 - 59). Two component systems based on the combination of iron and nickel -dithiocarbamates were found to be entirely successful and gave the very sharp termination to film . In this case both the induction period and the rate of photo-induction period of photo-oxidation can be varied independently (56, 57). The stabiliser concentration primarily determining induction period and the activator concentration, the rate of the slope of the photo-oxidation curve and hence the embrittlement time. This system was found to be much more concentration dependent at low concentrations of photoactivator . The desired life of the polymer varies depending on its use from the order of a few weeks to a year or more after it has been exposed to the environment . Thus in the case of packaging it should degrade immediately after discard but no degradation should take place during storage . On the other hand in the case of mulching films for annual crops a lifetime of several months is required whereas in the case of protective shelters for young trees it may be required to stand up to 3 - 4 years before degradation starts .

1.4 Mechanisms of Antioxidant Action

1.4.1 Thermal and Photo-oxidative Degradation of Polyolefins

Thermal degradation occurs at high temperature during the processing operation , or when the solid polymer is exposed to the atmosphere at room temperature or elevated temperature during use . Photodegradation occurs when the polymer is exposed to both oxygen and sunlight , particularly the near ultra-violet component . The basic mechanism of the photo-oxidation of olefinic polymers is the same as that involved in thermal oxidation . Both involve the free radical mechanism (60) , the main difference lies in the much more rapid formation of hydroperoxide in the case of photo-oxidation (61) . Hydroperoxides are considered to play a key role in the initiative steps of the oxidative chain reactions (23, 24, 62 , 63) . In general both the photo-oxidation and thermal oxidation mechanisms of polyolefins can be summarised as follows (64).

Initiation

$$RH + O_2 \longrightarrow ROOH \qquad (1.4)$$

$$ROOH \xrightarrow{h\upsilon\ /\Delta H} RO\cdot + \cdot OH \text{ (at low hydroperoxide concentration)} \qquad (1.5)$$

$$2ROOH \longrightarrow ROO\cdot + RO\cdot + H_2O \text{ (At high hydroperoxide concentration)} \qquad (1.6)$$

Propagation

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (1.7)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (1.8)$$

Termination

$$2ROO\cdot \longrightarrow ROOR + O_2 \qquad (1.9)$$

$$2R\cdot \longrightarrow R - R \qquad (1.10)$$

$$R\cdot + ROO\cdot \longrightarrow ROOR \qquad (1.11)$$

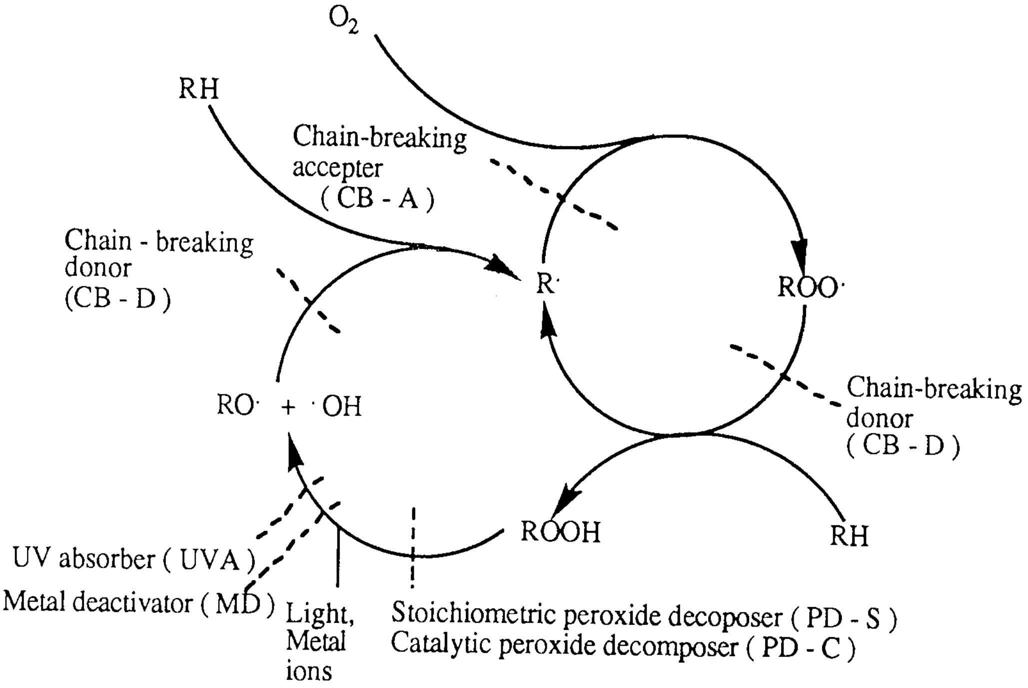
1.4.2 Stabilisation of Polyolefins

Most polymers are subject to oxidative degradation by molecular oxygen during processing and on exposure to environmental conditions . In addition to the deleterious effects of oxygen , the degradation process is accelerated by other environmental influences such as heat , light , contamination by metal ions , ozone and mechanical deformation . Oxidation of hydrocarbons are normally auto - accelerating i.e. the rate is slow or even negligible at first but gradually accelerates , often to a constant value.

Autoxidation is undesirable in the majority of cases because of the deterioration in properties of the polymeric materials . It is therefore necessary to stabilise polymers against the deleterious effects of atmospheric oxidation and this is accomplished by the use of additives known as antioxidants . Antioxidants by definition are materials which are incorporated in polymers to inhibit oxidative degradation either during melt processing (melt stabilisers) or in service (e.g. thermal and photo stabilisers).

The autoxidation chain mechanism involves two inter - related processes (65) (Reaction scheme 1 . 4) . The first process represent the alkyl / alkyl peroxyl chain reaction while the second involves the homolysis of hydroperoxide which feeds the chain reaction with new radicals . The main purpose of adding an antioxidant is , therefore , to prevent the attainment of a constant rate of oxidation by inhibiting or retarding the formation of hydroperoxides as long as possible.

Oxidation of polyolefins can be inhibited by three main processes , (i) by trapping the macroalkyl and macroalkyl peroxyl radicals therefore breaking the chain reaction , (ii) by preventing the hydroperoxide formed in a non-radical process and (iii) by absorbing the UV radiation using a uv screen which disintegrates the absorbed energy harmlessly .



Reaction Scheme 1.4 Autoxidation chain mechanism

1.4.2.1 The Chain Breaking (CB) Mechanism

1.4.2.1.1 Chain Breaking Acceptor (CB-A) Mechanism

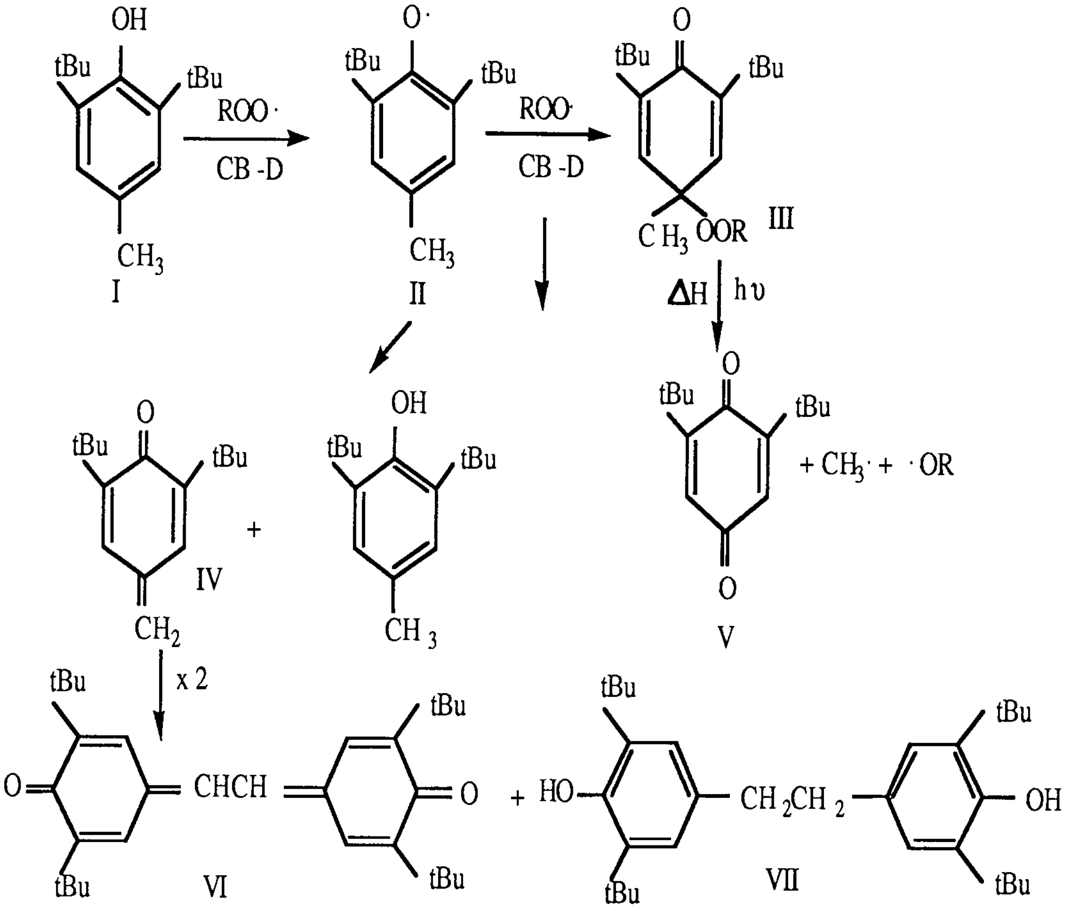
This process will only operate effectively if the oxygen pressure is low or diffusion rate is low . Appreciable concentration of macroalkyl radicals exist when oxygen access is restricted . Nitro-compounds , quinones (66) , nitrones and stable free radicals (67) are the main classes within this group . In the CB-A mechanism , trapping of alkyl radicals by an oxidising agent (i.e. electron acceptor antioxidants) lead to inhibition of oxidation .

1.4.2.1.2 Chain Breaking Donor (CB-D) Mechanism

The chain-breaking donor (CB-D) mechanism generally operates in systems in which substantial oxygen concentrations are present (68,69) . Alkylperoxyl reduction is the most significant process occurring when these radicals are present in excess in the system . Here the antioxidant donates an electron to the macroalkyl peroxide radicals . Hindered phenols and aromatic amines are the best known examples (70) .

The simplest member of the hindered phenol class is 2,6-di-tert-butyl - 4-methyl phenol , normally referred to as butylated hydroxytoluene (BHT) . This is a relatively volatile antioxidant due to its low molecular weight so it cannot be used at high temperatures . Variation of substituents threw some light on this problem .

The oxidation chemistry of a typical hindered phenol is summarised in reaction scheme 1 . 5 (65) . The stilbene quinone (VI) formed from the initially formed aryloxy radical (II) is an effective antioxidant although it functions by a complementary CB- A mechanism . The quinonoid product is less volatile because of high molecular weight than the parent phenol and are therefore superior antioxidants where volatility is important (71). However , the peroxydienone formed by trapping of a second alkylperoxyl radical is unstable due to the labile peroxide bond which leads to the formation of radicals and hence can act as a pro-oxidant .



Reaction Scheme 1.5 Oxidation transformation of BHT

1.4.2.1.3 Complementary Mechanisms involving both CB-D and CB - A

Antioxidants which exhibit both kind of activity (CB-A and CB-D) have an advantage over those which operate by a single mechanism . Since all autoxidative processes involve both alkyl and alkylperoxyl radicals to some extent . Hydroquinone is the best known example of this type of antioxidant (69) .

1.4.2.1.4 Regenerative Chain Breaking Antioxidants

N-isopropyl-N'- phenyl-p -phenylene diamine shows exceptional activity in rubber under conditions of high shear . This is due to the ability of the derived nitroxyl radical to trap alkyl radicals (72,73) . The hydroxylamine so formed is involved in the antioxidant process in a regenerative process . This accounts for the fact that the nitroxyl radical concentration rises to a maximum and then reduces to a low stationary concentration throughout the lifetime of the rubber (72, 73) .

1.4.2.2 The Preventive mechanism

These mechanisms include elimination of all effects which brings about the formation of reactive radicals such as external effects (e.g. heat and radiation), hydroperoxides and excited state species . Since their primary function is to interfere with the generation of free radicals so they are called preventive (70) . Screening of UV light from the polymer by stable chromophores is a preventive mechanism which is specific to UV degradation . Destruction of hydroperoxide in a process which does not give rise to free radicals is also preventive . Complexing agents which have the ability to co - ordinate the vacant orbitals of transition metal ions to their maximum co - ordination number and thus inhibit the co - ordination of hydroperoxides to the metal ions are therefore effective metal deactivators (MD) and hence inhibitors for metal catalysed autoxidation .

1.4.2.2.1 Peroxydolytic Antioxidants

Two mechanistically distinguishable peroxydolytic antioxidants are available (68); (a) stoichiometric peroxide decomposer (PD-S) and (b) catalytic peroxide decomposer.

(a) Stoichiometric Peroxide Decomposer (PD-S)

High molecular weight phosphite esters have been shown to behave as stoichiometric peroxide decomposers (68). Tris-nonyl phenyl phosphite stoichiometrically reduces hydroperoxides to alcohols, without substantial formation of free radicals.

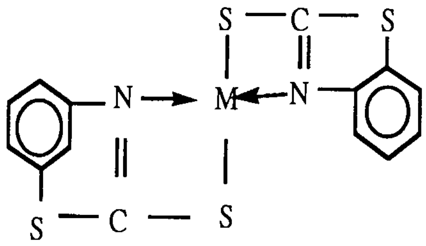
(b) Catalytic Peroxide Decomposer (PD-C)

The majority of agents falling in this class are sulphur compounds. These compounds have the ability to destroy peroxides through the formation of acidic products in a radical generating reaction involving the hydroperoxides. Examples of this class are the thiodipropionate ester (I) (74), the metal complexes of mercaptobenzthiazole (II) (75), the dithiocarbamates (III) (67, 76), the dithiophosphates (IV) (77, 78) and mercaptobenzamidozolates (V) (79).

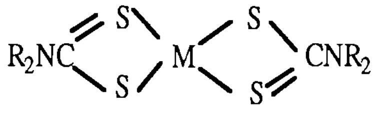
In most cases the antioxidant function is found to proceed by a pro-oxidant stage and the importance of this stage related to the structure of the sulphur

$ROCOCH_2CH_2SCH_2CH_2COOR$

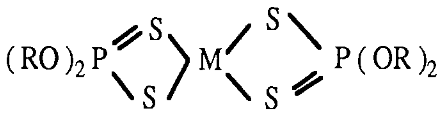
I



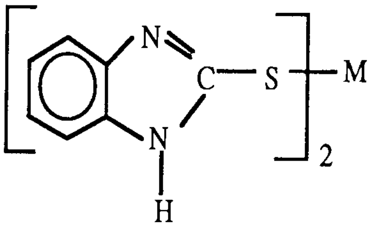
II



III

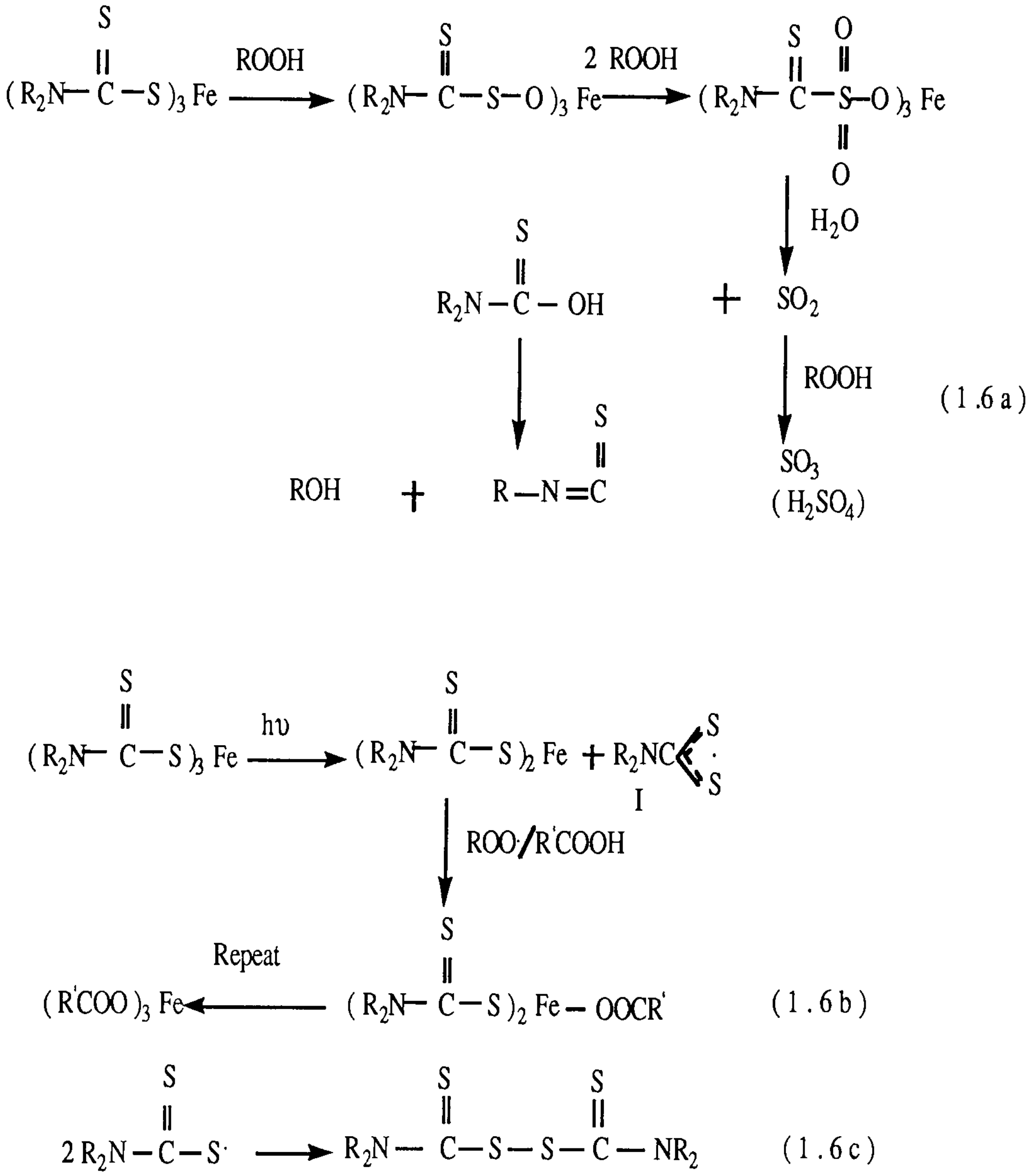


IV



V

compound (68). In the case of dithiocarbamates and dithiophosphates the pro-oxidant effect may be transient and of no great significance to the long term antioxidant function . Scott and co-workers (80) found that sulphur dioxide and isothiocyanate are among the breakdown products of metal dialkyl dithiocarbamates . Sulphur dioxide during its reaction with hydroperoxides is converted to sulphur trioxide which is a Lewis acid responsible for catalytic hydroperoxide decomposition (81) . Latter work(82, 83) in the same laboratory found that two processes were involved in the decomposition of hydroperoxides ; (i) a free radical decomposition of peroxides , which predominate at molar ratio of 10:1 (Cumene hydro peroxide / Zn complex) and (ii) an ionic dissociation predominated at higher ratios, although there is a radical contribution at all ratios . Scott and his co-workers (80 - 81) proposed a mechanism to account for the antioxidant action of metal dithiocarbamates (Reaction scheme 1.6) .



(1.6a)

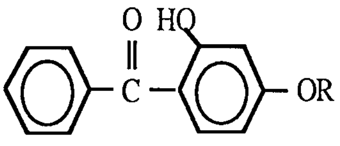
(1.6b)

(1.6c)

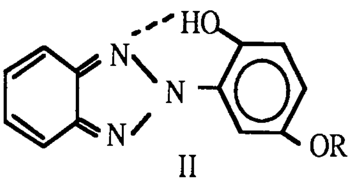
Reaction Scheme 1 . 6

1.4.2.2.2 UV - Absorbers

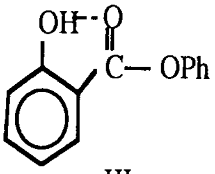
Examples of this class involve o - hydroxy - benzophenone (I), o - hydroxy phenylbenzotriazole (II) and phenyl salicylate (III) (76 , 84) .



I

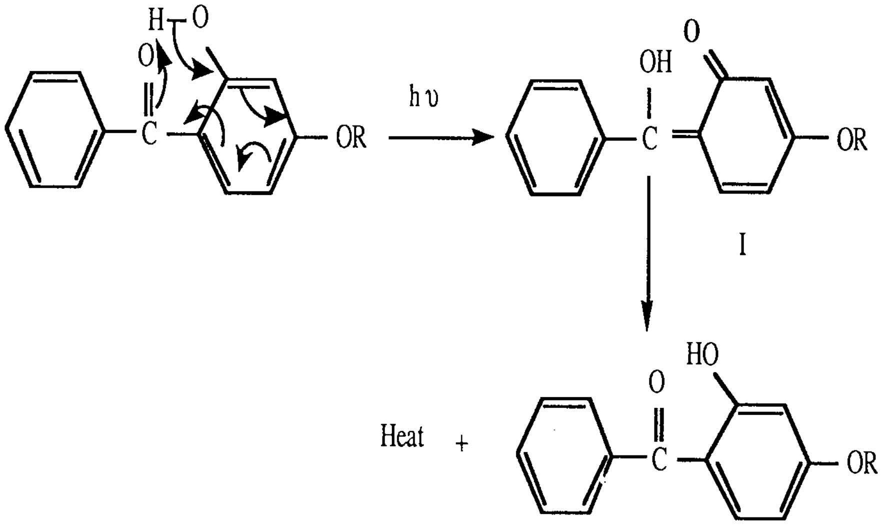


II



III

Strong absorption of these compounds in the region of 330 nm are accounted for the hydrogen bonded interaction between the phenolic hydroxyl group and adjacent double bonded groups (C=O and C=N) . Because it was found that benzophenones without a 2-hydroxy group are effective sensitisers for photo-oxidation . The UV absorbers do not give rise to a triplet state on absorbing UV radiation as do the unsubstituted benzophenones and so they are much more UV stable . It is then assumed that light is absorbed by the ketone group in the usual way that the triplet state is deactivated by the hydrogen transfer as shown below (85) . The quinoid structure (I) undergoes tautomerism to the more stable hydroxy benzophenone . The UV energy initially absorbed is thus emitted as a harmless radiation (Reaction 1 .12) .



(1.12)

1.4.2.2.3 Metal Deactivators

Chelating agents such as salicyldoximes and ketoximes form complexes with transition metal ions and these complexes have the capability to destroy hydroperoxide stoichiometrically in presence of light , so they are effective UV stabilisers . Thus the nickel acetophenone oxime complex is known to quench the excited states of indigenous chromophores in polymer or singlet oxygen (86 - 88).

1.5 Implications and Applications of Polymer-bound Antioxidants

Broadly three factors are responsible for the effectiveness of stabilisers (71, 89). (i) The intrinsic stabiliser behaviour . This is a measure of the efficiency of the antioxidant . (ii) Solubility of the antioxidant in the polymer . The stabiliser should be soluble in the polymer in the concentration used . (iii) The physical permanence or the substantivity of the stabiliser in the polymer . Substantivity is defined as the ability of the antioxidant to remain in the polymer .

1.5.1 Antioxidant Substantivity

Parameters which affect the antioxidant substantivity are (i) distribution, (ii) compatibility , (iii) volatility and (iv) extractability.

(i) ***Distribution of Stabiliser in Polymers***

For an additive to be effective in its stabilisation function, it must be evenly distributed . Even distribution can only be achieved if the additive is compatible with the polymer (90) . But most polyolefins are semi-crystalline substances in which the distribution of stabilisers is not uniform owing to the presence of crystalline and amorphous phases . In such polymers low molecular mass additives are concentrated mainly in the amorphous regions of the polymer (91 - 94) . Such non - uniform distribution of stabilisers in the semi-crystalline polymers appears to be advantageous because the amorphous portion of polyolefins is the most sensitive regions of degradation (91 , 95 - 98) .

(ii) *Compatibility of Stabilisers with Polyolefins*

The interaction between polymers and antioxidants and the total effects can be best described by the term "compatibility". In general the greater the similarity between the polyolefins and the additive the better the compatibility . However , the degree of compatibility can be improved by introducing polar groups into the polar polymers and non-polar groups for non -polar polymers (99).

(iii)*Volatility of Stabilisers*

Many low molecular weight stabilisers are more or less volatile . Evaporation is the major cause of the loss of antioxidants at elevated temperatures . Evaporation of antioxidants from the surface layer produces a concentration gradient . As a result the antioxidants in the bulk start to diffuse into the surface layer , making possible further evaporation of the stabiliser (91) . Consequently the resistance of polyolefins to degradation decreases . The volatility of antioxidants can be reduced by increasing the size of the antioxidant molecule or creating interaction bonds between antioxidants and polymers .

(iv) *Extractability of Stabilisers from Polymers*

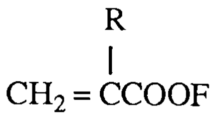
When polymeric materials are applied in contact with a dissolving media such as water , organic solvents , acid , oil detergents , foodstuff etc . extractability of stabilisers may affect the performance of antioxidants . The process is very complex and depends on many factors , e.g. polyolefin type , the chemical structure and molecular weight of the stabiliser , the nature of the extraction liquid and the extraction conditions . Like volatilisation diffusion process also plays an important role in the extractability of antioxidants . Besides the solubility the diffusion of the contact media into the bulk of the polymeric materials also affects the extractability (91) . The performance of stabilisers in polyolefins under aggressive service conditions is therefore much more affected by extraction than by volatilisation.

1.5.2 Approaches in Antioxidant Substantivity

Antioxidant substantivity can be improved either by employing high molecular mass antioxidants or by binding the antioxidant to the polymer backbone . Antioxidants of high molecular mass are in general not very effective due to their limited solubility with commercial polymers (100) . Bound antioxidants and stabilisers are non - migratory and hence resistant to extraction and volatilisation (101 , 102) . In addition polymer-bound antioxidants can be employed to the most oxidatively sensitive regions of the polymers i.e. in the amorphous area or grafted on the surface of the polymeric materials . Scott (103) has reviewed the general methods in preparing polymer - bound antioxidants . Munteanu (102) reviewed the grafting of polymerisable antioxidants into polymers and binding of antioxidant containing reactive groups into grafted polymers .

1.6 Previous Work at Aston on Bound Antioxidants

Recently different attempts have been made in this laboratory to modify polyolefins using acrylate monomers (I) and maleate ester (II) containing antioxidant functional group (F)(104 , 105) .



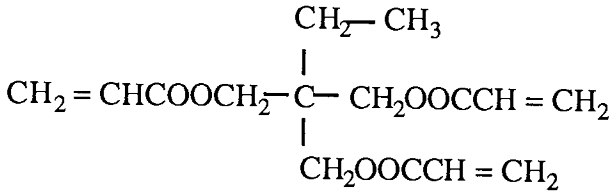
$$CH_2=\overset{\overset{R}{|}}{C}COOF$$

I

$$AOCOCH=CHCOOF$$

II

Most of the studies at Aston have been concerned with antioxidants and UV stabilisers (104) . In general acrylates and methacrylates (I) give low levels of adduct formation due to homopolymerisation and homopolymers are less effective than graft copolymers probably due to phase separation . It was found that maleates can be bound up to 90 % in the case of hindered piperidine (104) . However , there is a need for 100 % bound materials in order to avoid physical loss of additives into the environment which cause pollution . In case of food contact application the leaching of additive from the plastics into the food stuff may cause food toxicity . In addition polymer - bound antioxidants can be employed to the most oxidatively sensitive regions of the polymer i . e . the amorphous area or on the surface of the polymeric materials . From the recent work (105) it was found that di - and tri - acrylate compounds can be 100 % bound to polymers . However , this procedure is not applicable for bulk polymers because in the presence of peroxide multifunctional vinyl monomers there is a change in the melt rheology of the polymer during processing . Consequently attention has been directed to producing masterbatch concentrates of bound additives that can be added to normal polymers in relatively low concentration (105). S . Al - Malaika and G . Scott (105 b) have shown improved binding (approaching 100 %) of monoacrylate derivatives of hindered piperidine into the polypropylene by using trimethylol propane triacrylate (III) as interlinking agent .



$$CH_2=CHCOOCH_2-\overset{\displaystyle CH_2-CH_3}{\underset{\displaystyle CH_2OOCCH=CH_2}{\overset{|}{\underset{|}{C}}}}-CH_2OOCCH=CH_2$$

III

1 . 7 Object and Scope of the Present work

Antioxidants and stabilisers of low molecular weight tend to be lost from the polymer by evaporation during processing , by migration during service life and by extraction in contact with extractable fluids i.e. in food contact application . Loss of additives due to the above factors can be overcome by attaching the stabiliser to the polymer backbone by a chemical bond . Such reactive stabilisers contain a polymerisable group like vinyl or allyl in their side chain . Various workers (101-105) have shown that under certain aggressive conditions the synthetic polymer having chemically bound antioxidants are superior to those containing dispersed antioxidants . So far no attempts have been reported on the polymer bound photoactivators . There is a scope of considerable interest in the search for polymer bound photoactivators . So , the aim of this work is to produce and evaluate polymer bound photoactivators .

Scott (106) invented a polymer composition where different transition metal complexes were used which degrade relatively rapidly on exposure to the environment . It is known that ferric acetylacetonate (56 , 57) acts as an effective activator for polyolefins but it suffers from the disadvantage that it causes oxidative instability during processing . Iron dithiocarbamate has been proved to satisfy the requirement for an ideal photosensitiser for polyolefins . However , it does not give the control necessary for a long cropping periods under the severe exposure conditions found in different countries and it can also be extracted by suitable solvents . Iron stearate behaves similarly .

It is therefore , found that systems like Fe and Ni complexes (acetylacetonate, dithiocarbamate) can be used for packaging and mulching film applications but they can cause atmospheric pollution . Unlike additives for polyolefins used in agriculture , additives used in food contact packaging have to be either non-toxic or incapable of being extracted from the polymer by fats , oils and aqueous foodstuffs . The present work is concerned with designing additives which are nonextractable from polymers in order to avoid the problem of leaching of additives into food stuffs from packaging and in the agricultural fields in the case of agricultural mulches . Bound additives avoid possible characteristics of toxicity and other side effects associated with low molecular mass compounds . With this objective in mind , attempts have been made to synthesise a variety of different iron compounds which should be capable of binding to the polymer . In this investigation sulphur containing iron compounds are used with the aim of achieving high stabilising effects in the polymer melt . Compounds containing polymer reactive groups will also be employed to produce bound photoactivators which are non-extractable from the polymers . Furthermore , it is intended to investigate their behaviour in polyolefins with a view to obtaining rapidly photodegradable polymers of predetermined lifetimes and also to investigate the mechanism involved in the photosensitising action of the complexes in model compounds . Attempts will also be made to achieve time-controlled degradation of these polymer-bound photosensitisers in combination with either non toxic antioxidants e.g. ZnDNC or Irganox 1076 and polymer bound antioxidants and stabiliser. A polymer bound uv stabiliser (HAEB) and a thermal antioxidant (DBBA) will also be investigated in combination with a non-extractable photoactivator .

Chapter Two

Synthesis and Characterisation of additives and General Experimental Techniques

In this chapter synthesis of the additives 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.

2.1 Materials

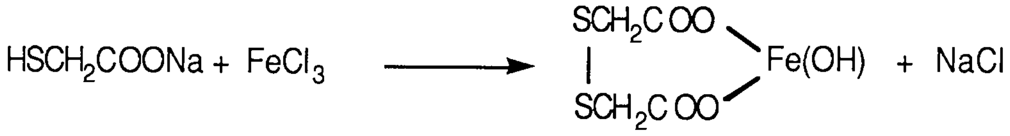
Reagents for the synthesis of the iron compounds were supplied by Aldrich Chemical Co . Sodium thioacetate , 3 - mercaptopropionic acid , acrylic acid , disodium maleate dihydrate , crotonic acid , cinnamic acid and anhydrous ferric chloride were used without further purification . Sodium hydroxide was supplied by BDH Chemical Co . Ltd . Iron dimethyldithiocarbamate (FeDMC) , Iron di - isononyldithiocarbamate (FeDNC) , Zinc diethyldithiocarbamate (ZnDEC), Zinc di - isononyldithiocarbamate (ZnDNC) , 2, 2, methylene dicyclohexanedione (Metone A) and manganese complex of Metone A were supplied by Robinson Brother Ltd .

Unstabilised low density polyethylene in powder form containing no antioxidant and identified as " Alkathene D877" supplied by Imperial Chemical Industries Ltd (ICI) . Unstabilised polypropylene (PP) was supplied in powder form identified as PROPATHENE HF 26 by ICI . Commercial LDPE (Ribelene CF 2203 , Ex Enichem) in granular form was supplied by Robinson Brothers Ltd . BP low density polyethylene (commercial) in granular form identified as DYNTH - 3 natural was supplied by BP . Commercial Himont PP (T 305) was supplied by Robinson Brothers Ltd (Ex Enichem) .

The following chemicals used were supplied by Aldrich Chemical Co. Ltd . 2,4 - Dihydroxybenzophenone , chloroethanol , 2,6 - ditertiarybutyl phenol and paraformaldehyde . All the solvents used for preparation were standard laboratory reagents grade and distilled when required for crystallisation . Spectroscopic grade solvents were used for spectroscopic measurements . Dicumyl peroxide (DCP) supplied by BDH Chemical Co. Ltd. was recrystallised from methanol . Trigonox 101 was supplied by Akzo Chemicals Ltd . Trimethylpropane triacrylate (TMPTA) used as a interlinking agent supplied by Ancomer Ltd.

2.2 Chemical Synthesis and Characterisation of Additives

2.2.1 Synthesis of iron (III) salt of thioacetic acid (FeTa)



$$HSCH_2COONa + FeCl_3 \longrightarrow \begin{matrix} SCH_2COO \\ | \\ SCH_2COO \end{matrix} \!\!> Fe(OH) + NaCl$$

34.23 (0.3 M) of sodium salt of mercaptoacetic acid was dissolved in 700 ml of distilled water to which 48.7 g (0.3 M) of anhydrous ferric chloride in 200 ml of distilled water was added drop by drop with stirring . A brown precipitate was formed . The precipitate was filtered out and washed several times with distilled water . After drying an insoluble brown product was formed . At 270^oC the compound decomposed without melting.

FTIR (KBr disc) data (Fig. 2.1) : -OH, 3441 cm-1 ; CO stretching vibration, 1603 cm-1; Fe-O, 582 and 384 cm-1 .

Elemental analysis data : C = 19.82% (Cal . 18.97%), H = 2.27% (Cal . 1.97%).

2.2.2 Synthesis of iron (III)salt of mercaptopropionic acid (FeTp)

$$3HSCH_2CH_2COOH + FeCl_3 \longrightarrow (HSCH_2CH_2COO)_3Fe + 3HCl$$

To 31.84 g (0.3 M) of 3 - mercaptopropionic acid , 16.22 g (0.1 M) of anhydrous ferric chloride in 500 ml of distilled water was added drop by drop . A pinkish white precipitate was formed . To this precipitate more 500 ml of water was added . The precipitate was allowed to settle for 15 minutes , filtered and washed several times with water . The dried product was dissolved in 200 ml of methanol and filtered . After evaporation of solvent a white product was obtained. The product was recrystallised twice from methanol . The m.p. of the product was 157 - 158^{o}C.

FTIR (KBr - disc) data (Fig.2.2): - SH, 2569 cm^{-1}; CO Stretching vibration, 1698 cm^{-1}; Fe - O , 552 and 371 cm^{-1}.

^{1}H nmr data (DMSO) : (Fig. 2.3) : two >CH_2 proton (triplet) , 2.49 - 2.62 and 2.84 - 2.89 ; -SH proton (singlet) , 5.6 - 5.7 (weak) .

2.2.3 Synthesis of iron (III) acrylate (FeAc)

$$CH_2{=}CHCOOH + NaOH \longrightarrow CH_2{=}CH\,COONa + H_2O$$

$$\xrightarrow{FeCl_3} (\,CH_2 = CHCOO\,)_2\,Fe(\,OH\,)$$

40 g (1M) of sodium hydroxide in 150 ml of distilled water was added with stirring to a solution of 80 ml (1M) of acrylic acid in 100 ml of distilled water. The resultant solution was stirred for an additional 2 hours at 60°C . 54 g (0.33 M) of anhydrous ferric chloride in 150 ml of water was added dropwise to the above solution over a period of 1 hour with stirring at 60°C . A dark red product was formed . The product has a m.p. of 210 - 212°C (dec).

FTIR (KBr - disc) data (Fig. 2.5): - OH group, 3464 cm^{-1} ; CO stretching vibration, 1646 cm^{-1} ; Vinyl unsaturation , 1587 cm^{-1} ; Fe - O 549 and 403 cm^{-1} .

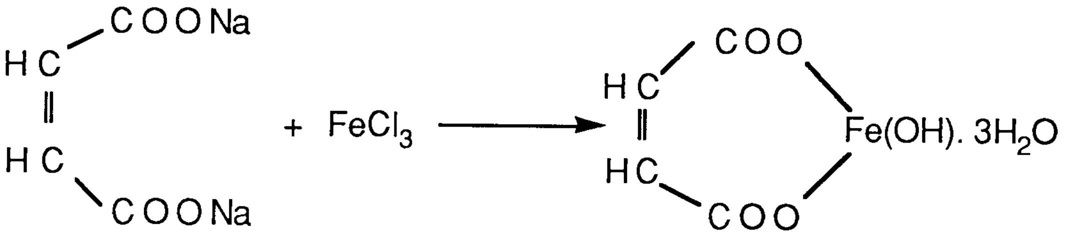
Elemental analysis data : C = 33.72% (Cal. 33.48%) , H = 3.49 % (Cal . 3.25%).

The above product was found to be insoluble in different solvents . A soluble product was synthesised according to the following way . 40 g (1M) of sodium hydroxide in 150 ml of distilled water was added with stirring to a solution of 80 ml (1M) of acrylic acid in 100 ml of distilled water . The resultant solution was stirred for an hour at room temperature . During the reaction the temperature of the solution increased to 35°C . The solution was cooled to room temperature . 54 g (0.33 M) of anhydrous ferric chloride in 150 ml of water was added dropwise to the above solution at room temperature with stirring . A redish brown product was formed . The product was filtered and washed several times with cold distilled water . Dried over a vaccum dessicator and recrystallised from acetone . The product has a m . p . of 204-206 °C .

FTIR (KBr - Disc) data (Fig 2.6) : - OH group , 3426 cm $^{-1}$; CO stretching vibration , 1641cm $^{-1}$; Vinyl unsaturation , 1578 cm $^{-1}$; Fe - O , 401 and 333 cm $^{-1}$.

Elemental analysis data : { For ($CH_2 = CHCOO)_3 Fe \cdot 2 H_2O$ };
C = 35.2% (Cal. 35.4%) , H = 4.1% (Cal. 4.3%) .

2.2.4 Synthesis of iron (III) maleate (FeMa)



32.4 g (0.2 M) of anhydrous ferric chloride in 50 ml of distilled water was added with stirring to a solution of 35.6 g (0.2 M) of disodium maleate in 100 ml of distilled water . A dark red solution was obtained . The solution was heated at 60°C for 2 hours with stirring . The brown precipitate formed was filtered and washed with water to remove water soluble impurities . The product has a m.p. of 290°C (dec).

FTIR (KBr - disc) data (Fig. 2.7) : - OH group , 3415 cm^{-1}; Vinyl unsaturation and carboxylate group , 1562 cm^{-1} ; Fe - O , 542 and 354 cm $^{-1}$.

Elemental analysis data : C = 19.75% (Cal. = 19.91%) ; H = 3.33% (Cal.=3.73%)

2.2.5 Synthesis of iron (III) crotonate (FeCr)

$$CH_3CH=CHCOOH + NaOH \longrightarrow (CH_3CH=CHCOO)Na$$

$$\xrightarrow{FeCl_3} (CH_3CH=CHCOO)_2Fe(OH)$$

20 g (0.5 M) of NaOH in 100 ml of distilled water was added dropwise with stirring to a solution of 43.045 g (0.5 M) of crotonic acid in 200 ml of methanol at 60°C . The addition was done such a rate so that no precipitate came out of solution . The stirring was continued for an additional 2 hours at the same temperature . 27.02g (0.1666 M) of anhydrous ferric chloride in 50 ml of water was added dropwise with stirring over a period of 1 hour to the above solution at 60°C . The dark red product was washed with methanol and distilled water . The compound melts at 198° - 200°C (dec).

FTIR (KBr - disc) data (Fig. 2.8): - OH group, 3425 cm^{-1} ; CO stretching vibration, 1658 cm^{-1} ; Vinyl unsaturation, 1569 cm^{-1} ; Fe - O , 470 and 350 cm^{-1} .
Elemental analysis data: C = 40.15% (Cal. = 39.5%) ; H = 4.80% (Cal. = 4.52%).

2.2.6 Synthesis of iron (III) cinnamate (FeCi)

$$C_6H_5CH=CHCOOH + NaOH \longrightarrow C_6H_5CH=CHCOONa$$

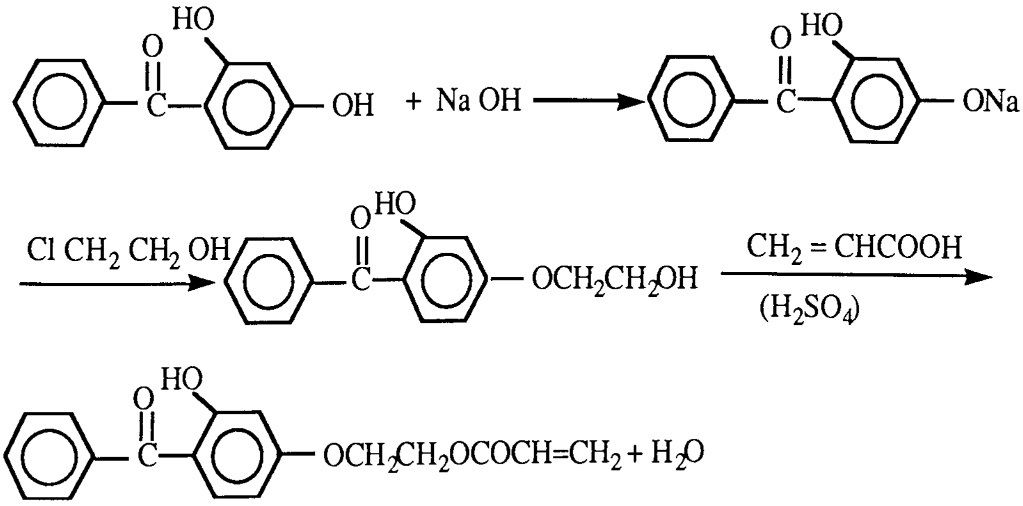
$$\xrightarrow{FeCl_3} (C_6H_5CH=CHCOO)_2Fe(OH)$$

10 g (0.25 M) of sodium hydroxide in 200 ml of distilled water was added drop by drop to a solution of 37.04 g (0.25 M) trans cinnamic acid in 400 ml of methanol . Stirring was continued for an additional 2 hours at 60°C . To the resultant solution 13.51 g (0.0833 M) of anhydrous ferric chloride in 50 ml of water was added over a period of 1 hour with stirring . The temperature of the solution was maintained at 60°C . The dark red product formed was filtered and washed with methanol and water . After drying and grinding an orange product having the m.p. of 260° - 262°C (dec.) was obtained.

FTIR (KBr - disc) data (Fig. 2.9) : OH group, 3414 cm^{-1} ; CO stretching vibration, 1637 cm^{-1}; Vinyl unsaturation, 1578 cm^{-1} ; FeO , 480 and 420 cm^{-1} .
Elemental analysis data : C = 59.8% (Cal. = 58.85%) ; H = 4.19% (Cal. = 4.08%) .

2.2.7 Preparation of 2 - hydroxy - 4 - (acryloyloxy-ethoxy) benzophenone (HAEB)

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



2.2.7.a Preparation of 2 - hydroxy - 4 - (hydroxy-ethoxy) benzophenone(107)

21.4 g (0.1 M) of 2,4 - dihydroxy benzophenone and 4 g (0.1 M) of sodium hydroxide were dissolved in 125 ml of distilled water . 8.1 g (0.1 M) of ethylene chlorohydrin were added all at once to the above solution . The mixture were stirred at 90 - 95°C for 4 hours and then 125 ml of distilled water at 95°C was added to it . The solution was allowed to stand overnight with stirring at room temperature . The next day , the precipitate obtained was washed several times with distilled water and mechanical stirring continued during 24 hours . A white powder was obtained , filtered and dried . The compound was dissolved in a minimum volume of ethanol and equal volume of petroleum ether (b.p. 40 - 60°C) was added to the ethanolic solution and kept for crystallisation . A white crystalline product having the m.p. of 90°C (literature m.p.is 92°C) (107) was obtained.

Elemental analysis data: % of C found = 69.62 ; % of C expected = 69.76 ; % of H found = 5.40 ; % of H expected = 5.42.

FTIR (KBr - disc) data: Phenolic -OH and alcoholic -OH, 3310-3500 cm^{-1}; Benzophenone carbonyl, 1631 cm^{-1}; Aliphatic $-CH_2$, 2924cm^{-1}.

^{1}H nmr data (Fig. 2.10) : Aromatic protons, 7.24 - 7.61 ppm (multiplet); 3 Aromatic protons 6.38 - 6.49 ppm (multiplet) ; Methylenic proton, 3.93 - 3.96 ppm and 4.08 - 4.11 (triplet); Alcholic proton, 2.34 ppm (singlet).

UV data : Benzophenone group absorption at 330 nm .

2.2.7.b Preparation of 2-hydroxy-4-(acrylolyoxy-ethoxy) benzophenone (HAEB)

25.8 g (0.1 M) Of 2-hydroxy-4-(hydroxy-ethoxy) benzophenone and 10 g (0.109 M) of acrylic acid were dissolved in 300 ml of dry toluene . 0.5 ml of concentrated sulphuric acid was added to this solution . The flask was fitted with a Dean and Stark and the solution was refluxed (in an oil bath at 115°C) until the theoretical amount of water was removed (6 hours) . The solution was washed to neutral pH with sodium bicarbonate solution and then distilled water . It was then dried with anhydrous magnesium sulphate . Toluene was removed by rotary evaporation to give a yellow liquid from which a light yellow powdered product was obtained . The compound was recrystallised from ethanol . The m.p. of the product was found to be 72 - 74°C.

Elemental analysis data: % of C found = 69.22, expected = 69.23 ; % of H found = 5.26, expected = 5.12.

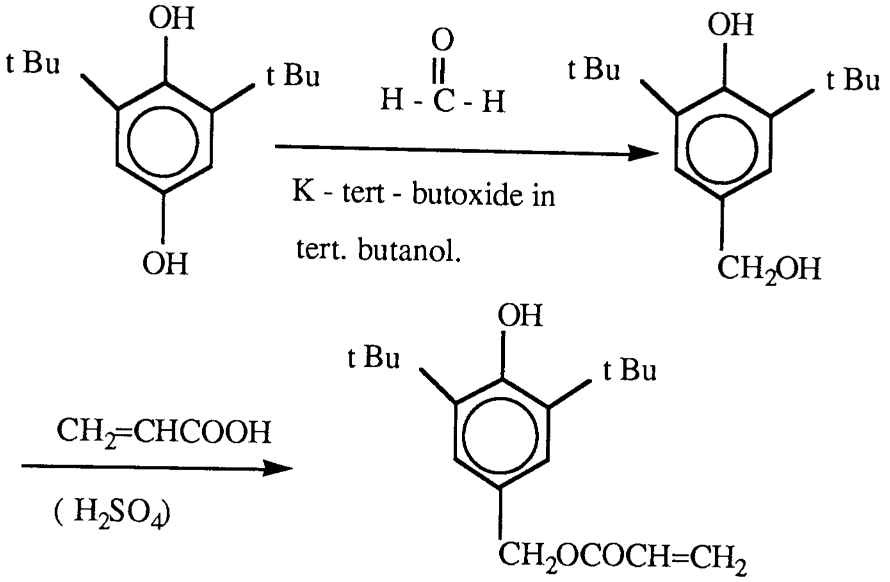
FTIR (KBr - disc) data (Fig. 2.12): Phenolic -OH and alcoholic -OH, 3300-3620 cm^{-1}; Ester carbonyl, 1726 cm^{-1} ; Benzophenone carbonyl and vinyl unsaturation, 1636 cm^{-1} .

^{1}H nmr data: **(Fig. 2.13)** Aromatic protons, 7.24 -7.61ppm ; 3 Aromatic protons 6.38 - 6.49 ppm ; 3 Vinylenic protons, 5.82 - 5.87 and 6.08 - 6.09 ppm ; Methylenic protons, 4.23 - 4.375 ppm and 4.47 - 4.52 ppm .

UV data : Benzophenone group absorption at 330 nm.

2.2.8 Preparation of 3,5-di-tert.butyl-4-hydroxy benzyl acrylate (DBBA)

The compound was prepared according to the following scheme.



2.2.8.a Preparation of 3,5-di-tert-butyl-4-hydroxy benzyl alcohol

This compound was prepared according to the literature (108) as follows: 53.3 ml of a 7.5% solution of formaldehyde (para formaldehyde) in tertiary butyl alcohol (0.140 mole CH_2O), 50 ml of 500 g/l solution of 2,6-di-tertiary butyl phenol in anhydrous tertiary butyl alcohol (0.128 mole 2,6-ditert. butyl phenol) and 14 ml of a 500 g/l solution of potassium tert. butoxide in anhydrous tert - butyl alcohol (0.006 mole) were mixed . All the solutions were ice cooled before mixing . The mixture was then stirred for about 30 minutes under nitrogen . The temperature of the mixture was maintained below 10°C using ice .

The reaction mixture was then poured into equal volumes of ice water and left in the refrigerator overnight. The yellow product formed was filtered, washed with water and then with hexane to give a white powder. The compound was crystallised from chloroform and hexane to give a white product having a m.p. of 137^{o}C (literature m.p. is 137^{o}C) (108).

Elemental analysis data: % of C found = 76.13, % of C expected = 76.27; % of H found = 10.15, % of H expected =10.

FTIR (KBr - disc) data: Phenolic -OH (free), 3588 cm^{-1}; Alcoholic -OH (H-bonded), 3517cm^{-1}.

2.2.8.b Preparation of 3,5-di-tert-butyl -4-hydroxy benzyl acrylate (DBBA) (109)

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

The mixture was allowed to stand at room temperature for six hours and then poured into water. The organic phase was extracted with ether and the excess acrylic acid extracted from the organic phase with aqueous sodium bicarbonate. The ether phase was then dried over anhydrous magnesium sulphate, filtered and the filtrate concentrated on a steam bath. The residue was crystallised twice from petroleum ether to give a white crystalline solid having a m.p. of 68 - 69^{o}C (literature m.p. is 67.5-69^{o}C) (110).

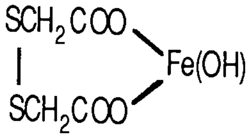
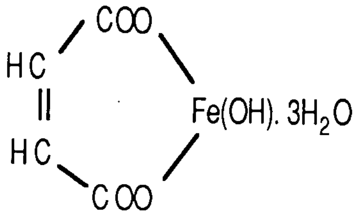
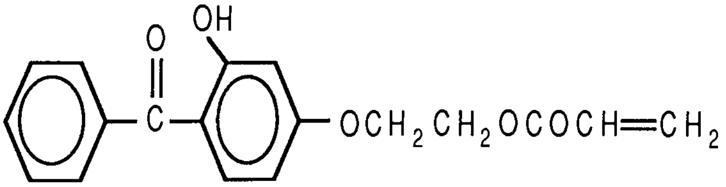
Elemental analysis data: % of C found = 74.34, % of C expected = 74.48; % of H found = 8.92, % of H expected = 8.96.

FTIR (KBr disc) data (Fig. 2.15) : Phenolic -OH (free), 3588 cm^{-1}; Ester carbonyl, 1714 cm^{-1}; Vinyl unsaturation , 1637 cm^{-1}.

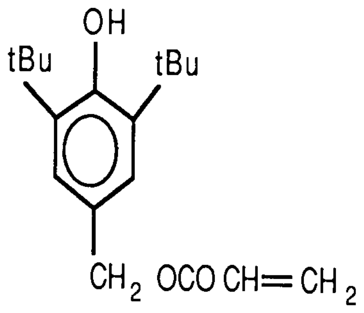
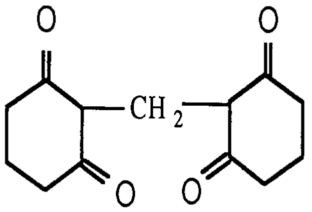
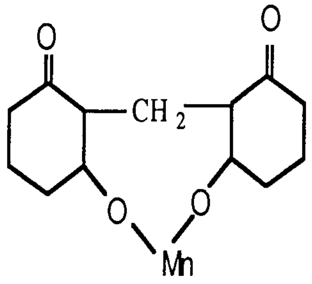
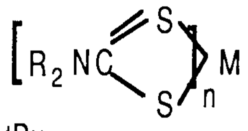
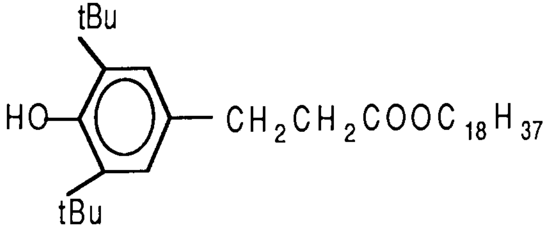
2 , 2$'$ - methylene dicyclohexanedione ((Metone A) and manganese complex of Metone A were supplieed by Robinson Brothers Ltd . The elemental analysis of the samples are as follows :

Metone A : C % = 66 . 50, H % = 6 . 80 (Found) ;
C % = 66 . 10 , H % = 6 .77 (Cal)
Metone M : C % = 52 . 50 , H % = 5 . 05 (Found) ;
C % = 53 . 60 , H % = 5 . 49 (Cal)

Structure and Code name of the Compounds

Structure	Code name
	FeTa
$(HSCH_2CH_2COO)_3Fe$	FeTp
$(CH_2=CHCOO)_2Fe(OH)$	FeAc (insoluble)
$(CH_2=CHCOO)_3Fe.2H_2O$ (Soluble)	FeAc (soluble)
	FeMa
$(CH_3CH=CHCOO)_2Fe(OH)$	FeCr
$(C_6H_5CH=CHCOO)_2Fe(OH)$	FeCi
	HAEB

Continued

Structure	Code name
	DBBA
	Metone A
	Metone M
 M = Fe , Zn , Ni $R=CH_3, C_2H_5, C_9H_{19}$	MDTC
	Irganox 1076

2.3 Processing of Polymer Samples and Additives and Preparation of Bound Concentrates.

The polymer and additives were processed using a RAPRA HAMPPEN torque rheometer head fixed in a Brabender motor . This is essentially a small mixing chamber containing mixing screws contra rotating at different speeds . The speed of the rotation can be changed . All the processing was carried out at a speed of 60 rev/min . The processing chamber may be operated either open to the atmosphere or sealed by a pneumatic ram . A full charge (35 g) of polymer and additive was used for each processing and the chamber was closed (close mixing, CM) . The additive, radical generator and interlinking agent were thoroughly mixed with the polymer by tumble mixing at room temperature before introducing into the torque rheometer chamber . When it was desired to process in the presence of oxygen (open mixing, OM), the chamber was left open to the atmosphere . All the processing were carried out at 160^{o}C in the case of polyethylene and at 180^{o}C in the case of polypropylene .

Concentrates of 5 % , 10% , 15 % and 20 % " masterbatches " were prepared using the polymer and various molar ratios of radical generator and various percentage of interlinking agent and additives . The dilution of the concentrates prepared in the torque rheometer with fresh unstabilised polymer was carried out using the same equipment . On completion of processing, the polymer samples were rapidly removed and quenched in cold water to prevent further thermal oxidation . The polymer samples were then stored in the dark at 0^{o}C.

2.4 Preparation of Films from Processed Samples

Polymer films for uv and thermal ageing and for spectroscopic studies were prepared by compression moulding using an electric press . The polymer samples were placed between two stainless steel glazed plates . The plates were thoroughly cleaned before use to ensure smooth surface and a special grade (heat resistant) cellophane film was used to prevent the film sticking to the plates . Control of film thickness was achieved by using a standard quantity of polymer (7.5 g) for producing a film thickness of 2.0×10^{-2} cm (0.008 inch) . The weighed amount of the polymer was placed between the plates and inserted into an electric press . The temperature of the platen was maintained at $160^{o}C$ and $180^{o}C$ respectively for low density polyethylene and polypropylene . The platen was closed and the polymer was allowed to heated for 1 minute without pressure . The pressure was then slowly raised to 40 $tons/inch^2$ and left for a further 1.5 minutes . The platen was then cooled to about $50^{o}C$ by running cold water while maintaining full pressure . The resultant films were stored in the dark at $0^{o}C$. Sections of uniform thickness were then selected as test films .

2.5 Measurement of Melt Flow Index (MFI)

The melt flow index (MFI), defined as the mass of the molten polymer extruded through a standard die in a given time (usually 10 minutes), is a measure of the melt viscosity of the polymer which in turn is related to the molecular weight . The Davenport Polymer Grader which was employed for this measurement, is designed primarily for determining the melt viscosity of polyethylene although the melt flow properties of other thermoplastics can also be determined by varying the temperature, die size and load . A strict relationship between the melt flow index and the molecular weight only applies to polymers of the same chemical combination and is equally restricted to polymers of the same density since this affects melt viscosity .

The appropriate relationship of MFI with molecular weight ($\bar{M}n$) and melt viscosity (n*) are given by the following two equations respectively (in case of LDPE)(110).

$$\bar{M}n^{1/2} = 188 - 30 \log MFI$$

$$n^* \text{ (poise)} = 7.5 \times 10^4 / MFI$$

Since thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such reactions as chain scission , cross-linking etc., these are expected to be reflected in the melt flow values . Hence , melt flow index measurement provides a means of detecting any oxidation which may occur during heat treatment of the polymer .

The apparatus was brought to a steady extrusion temperature of 190 ± 5°C for LDPE and 230 ± 5°C for PP before begining an experiment . The barrel was then charged with 5 g of polymer in the form of crepe, damping down with the charging tool to exclude air . The time taken to charge the barrel should not exceed one minute . The unloaded piston was then inserted into the barrel and 4 minutes was allowed for the polymer to reach equilibrium temperature . A 2.16 Kg load was then placed on top of the piston and the polymer was allowed to extrude through 0.116 cm diameter . The time interval for the first extrude or cut-off was 60 seconds and discarded ; then 5 successive cut-off's were taken, each at the end of 30 seconds . Any cut-off that contained air bubbles was rejected ; the average of the 5 cut-off's was taken . If the difference between the maximum and minimum values of the individual weighing exceeded 10% of the average , the results were discarded and the test repeated on a fresh portion of the polymer . The melt flow index was calculated from the following relation :

$$\text{MFI} = \frac{600 \text{ x average wt. of cut - off in gm .}}{\text{interval time in sec .}}$$

2.6 Soxhlet Extraction of Masterbatches in Xylene

1 g of the finely cut masterbatch was refluxed in xylene for 48 hours in a Soxlet apparatus to determine the gel content . The extraction thimble was vacuum dried to constant weight .

2.7 Solvent extraction of Polymer Films

Unbound additives and other low molecular mass materials were removed from the film samples by hot Soxhlet extractions using a suitable solvent e.g. methanol , acetone, dichloromethane (depending on the solubility of different compounds) for 48 hours . A steady stream of nitrogen was bubbled throughout the extraction period . After the extraction , the samples were dried under vacuum at a maximum temperature of 40^{o}C for 24 hours .

2.8 Evaluation of Binding

Different masterbatches were cut into small pieces . These films were extracted in suitable solvents e.g. dichloromethane (DCM) , methanol or acetone in a Soxhlet extractor for 48 hours . The extracted films were dried under vacuum for 24 hours . Each experiment was done in triplicate and the average value was used . The carbonyl absorption was used to measure the amount of binding in the form of " carbonyl index ". This is the ratio of carbonyl absorption to the absorption of a polymer (reference peak) . For measurement of binding carbonyl index before and after extraction was calculated.

$$\% \text{ of Binding} = \frac{\text{Carbonyl index after extraction}}{\text{Carbonyl index before extraction}} \times 100$$

2.9 Ultraviolet Irradiation of Polymer Films

All the film samples were irradiated in an ultra - violet light aging cabinet . Ultra - violet cabinet comprised a metal cylinder of about 110 cm outer diameter and having a concentric circular rotating sample drum whose circumference was 15 cm from the periphery of the metal cylinder . Twenty eight fluorescent tube lamps were mounted on the inside of the cylinder . The rotating arrangement of the sample allows an identical amount of total radiation to fall on each sample . The cylindrical cabinet was opened to the atmosphere on both the lower and upper sides and the circulation of air in the cabinet was ensured by the driven ventilation situated under the rotating frame.

The samples were attached to separate sample holders which were 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 (in air)with the lamp on was 30 ± 1^{o}C.

The radiation source consisted of the cylindrical array of 20W fluorescent tube lamps, positioned on the inner side of the cabinet. 21 lamps of type C (Phillips actinic blue 05) and 7 lamps of type A_1 (Westing house sunlamps FS 20) were used and these were systematically distributed so that the combination was one lamp of type A_1 for every three lamps of type C. The spectral distribution of both types of lamps are shown in Fig. 2.20. Figure 2.21 compares the spectral distribution of lamp A_1 and lamp C with sunlight (111). The intensity of UV irradiation at the center of the drum falling on the surface of the films was measured to be 4 . 92 Whm^{-2} as shown below. In order to maintain long term uniform spectral distribution inside the cabinet, the lamps were replaced sequentially every 200 hours of operation in addition to periodical radiation output measurements as described below. Exposure times are indicated on a counter clock while temperature inside the cabinet is usually maintained at about 30°C since the entire lower side (of the cabinet) is open to the atmosphere.

The radiation output in the UV exposure cabinet was monitored sequentially every six months in order to maintain long term uniform spectral distribution inside the cabinet and also to detect positional variations in output.

This measurement is based on the use of polysulphone films as dosimeters. The principle in this method is to relate the degree of deterioration of the films, usually in terms of changes in their spectroscopic properties, to the incident radiation dose (112). The suitability of polysulphone as UV monitors is a direct consequence of their photosensitivity below 320 nm and this in turn is due to the high aromatic content of the material which results in optical density increases on exposure to UV radiation. The increase in UV absorbance at 330 nm of polysulphone film resulting from exposure to a UV source can then be expressed in terms of an equivalant dose of 305 nm monochromatic radiation necessary to produce the same increase in absorbance (112).

The UV monitoring technique was carried out with polysulphone films (granules manufactured by Union Carbide . Polysulphone film (35 - 40 micron thick, usually in triplicate) were mounted in sample holders and the initial UV absorbance at 330 nm (A_{330}) measured with reference to air on a Beckman DU - 7 UV - visible computing spectrophotometer . Films with initial A_{330} in the range 0.15- 0.25 were then irradiated in the UV cabinet . The films were exposed in three different positions of the UV cabinet ; upper , middle and lower positions on the rotating drum . The samples were measured (A_{330}) by UV spectrophotometer at intervals . The exposure period chosen was such that increase in the UV absorbance of the films (A_{330}) is within the range 0.1 - 0.3 (112).

An appropriate conversion table (112) was then used to convert the observed A_{330} of each film to the equivalent dose of 305 nm radiation (d) . The average value of this dose (d) was determined for the set of films , and the corresponding mean intensity (I) in Whm^{-2} calculated using the following equation (113) :

$$I = 60\ d/t$$

where I = radiation output (intensity)

d = equivalent dose of 305 nm radiation for A_{330}

t = exposure time

Figure 2.22 shows the sensitivity of a polysulphone film to wavelengths below 400 nm while Table 1.1 depicts the vertical distribution of radiation

(relative % UV) as is generally obtained in the UV cabinet .

From the result (Table 2.1) it is found that the intensity of light is highest at the middle of the rotating drum and lowest in the lower half of the rotating drum . It has been reported (112) that intensities of the order of 4 Whm^{-2} have been measured outdoors with polysulphone, when the sun is directly overhead and under clear sky conditions . Thus , the mean UV output (4.18 Whm^{-2}) , as determined periodically (subject to seqential replacement of fluorescent tube lamps) is therefore close to the limiting outdoor value .

2.10 Thermo - oxidative Studies using Wallance Oven

The accelerated thermal oxidation of LDPE samples were carried out in a Wallace oven at 110°C (± 2°C) . This has seperate seven cells and has very good temperature control . There is an arrangement for controlling air flow through the cells . Each sample was suspended in a seperate cell to prevent the cross contamination of the additives by volatilisation and was subjected to an air flow of 3.0 cubic feet/hr (85 litres/hr) .

2.11 Measurement of brittle fracture time of polymer samples

This is essentially 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 . Each polymer samples was carried in triplicate (Fig. 2.23) . The reproducibility of the results was found to be acceptable . Variation from the mean value was of the order of ± 5% .

2.12 Infra - red Spectroscopy

All infra - red spectra were recorded using a Perkin Elmer Infra - red Spectrophotometer model 599 . Infra - red spectra (4000 - 200 cm^{-1}) were recorded at a speed of 3 minutes for each run .

Infra - red spectroscopy has been widely used to determine the nature of oxidation products and the 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 samples can be used repeatedly . Since thermal and photo - oxidation of polymers result in the build up of different oxidation products such as hydroxyl , carbonyl , carboxyl , vinyl etc . the formation and 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. (114).

The base line technique (115) was used to calculate the optical density or absorption due to various functional groups . This was done as shown in Fig. 2.24 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, the spectrophotometer was adjusted to read 100% transmission and this was known as background line . The absorbance values were calculated using the combined form of Beer -Lambert equation :

$$A = \log I_o/I = \varepsilon c l$$

where

A = Absorbance or optical density

I_o = Intensity of radiation effectively entering the sample

I = Intensity of radiation emerging from the sample

ε = 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 evaluation of the thermal or photo - oxidation by I.R. method was done by exposing the samples to UV or heat for regular intervals of time and the spectra were run on the same chart for comparison purposes . An increase in the carbonyl absorbance peak at 1710 cm^{-1} during oxidation was followed . 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 LDPE and 2720 cm-1 for PP were used . Those peaks remained constant during irradiation . The growth or decay of observed absorption peaks (for functional groups) were expressed as indices which is defined as the ratio of the absorbance of functional group to that of the reference peak . The carbonyl index in PP can be calculated as

$$\text{Carbonyl Index} = \frac{\log(\text{ carbonyl absorption at } 1710 \text{ cm}^{-1})}{\log(\text{ reference absorption at } 2720 \text{ cm}^{-1})}$$

2 .13 Ultra - violet Spectroscopy

Ultra - violet spectra of polymer films with additives and solution spectra were recorded using the Beckman DU - 7 ultra - violet visible computing spectrophotometer . This instrument was used to monitor the decay of additives during aging by observing the characteristic UV absorption bands of the additives . An unprocessed additive free polymer film of identical thickness was used as reference to compensate for the polymer . In the case of solution studies , spectra were recorded using quartz cells of 1 cm path length with the pure solvent serving as external reference .

2.14 Gel Permeation Chromatography

Molecular weight changes during thermal degradation of low density polyethylene have usually been explained by chain scission or cross - linking(116) . GPC is one of the most important techniques for the determination of molecular weight and molecular weight distribution of polymer samples . A chain scission process shifts the molecular weight distribution (D) to lower molecular weight . A molecular enlargement will be observed as an increase of the high molecular weight tail . The molecular weight and the molecular weight distribution of the masterbatch was carried out at RAPRA polymer characterisation centre using Gel Permeation chromatography (GPC) . The conditions of the measurement :

Columns : P.L.gel 2 x mixed gel, 20 micron packing, 30 cm columns
Solvent : 1,2 - dichlorobenzene, stabilised with 2,6 - ditert. butyl -*p* - cresol
Flow rate : 1.0 ml / minute
Temperature : 140^{o}C
Calibration : Third order polynomial using polystyrene standard
In case of polyethylene samples polyethylene were used as standard .

2.15 Tensile measurement

Tensile force / extension measurements made at room temperature provide a simple, reliable and descriptive method of monitoring the effects of ageing on properties . Tensile properties may be used to follow the progress of chemical or physical changes taking place in the polymer . For example polymers exposed to high heat or ultraviolet light may undergo depolymerisation and oxidation reactions which will be reflected in changes in tensile properties . In a similar manner , when polymers are exposed to an aggressive chemical environment , they may become either more brittle or less brittle and the changes can be conveniently followed through measurement of tensile properties . Boundy and Boyer (117) found that continued processing of polystyrene in extruders and injection moulding machines caused the tensile properties to decrease . Poyne and Scott (118 a) reported that rubber, in common with most organic materials, may change gradually with time due to oxidation . These changes may result in loss of elongation in tensile testing . The tensile properties may be defined as follows (118 b) :

Tensile stress (nominal) is the tensile load / unit area of minimum original cross section within the gage boundaries carried by the test specimen at any given moment . It is expressed in force per unit area .

Tensile strength is the maximum tensile stress supported by the specimen during a tension test .

Elongation is the increase in length produced in the gage length of the test specimen by a tensile load . It is expressed in units of length, commonly as a percentage .

Elongation at break is the elongation at the moment of rupture of the test specimen .

Strain is the ratio of the elongation to the gage length of the test specimen ; that is, the change in length per unit of original length . It is expressed as a dimensionless ratio .

Modulus of elasticity is the ratio of stress to corresponding strain below the proportional limit of a material. It is expressed as force per unit area.

The change in tensile properties caused by UV irradiation were followed using the computing Testometric micro 500. The dimensions of the sample were

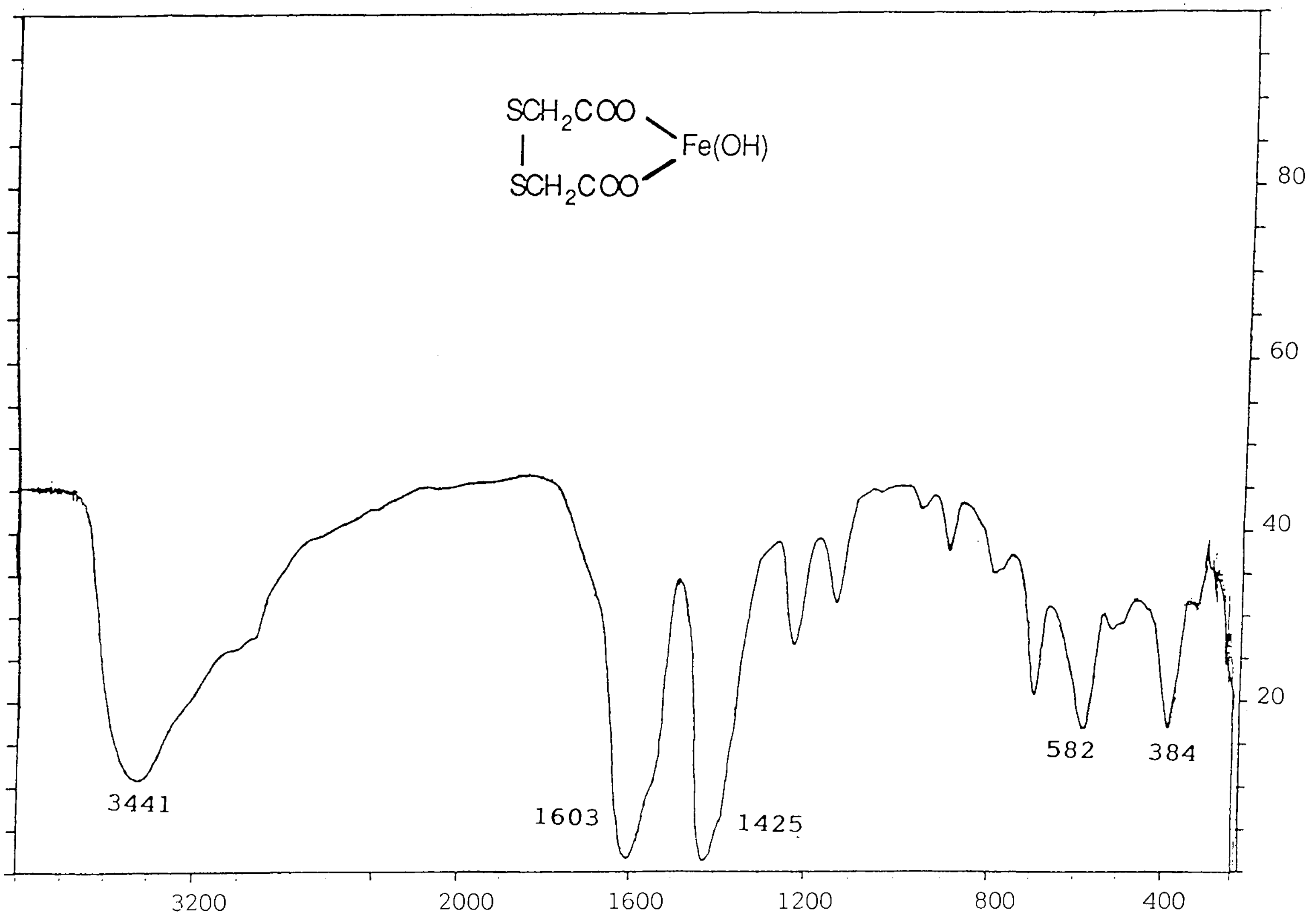
Length = 30 mm

Width = 4 mm

Thickness = 0.1778 mm

Temperature of test = 25^{o}C

100 N load was used and the speed of the test was 499 mm / min. The British standard method 326C (120) was used for the measurement. For each measurement 10 samples were used and the mean value was obtained.

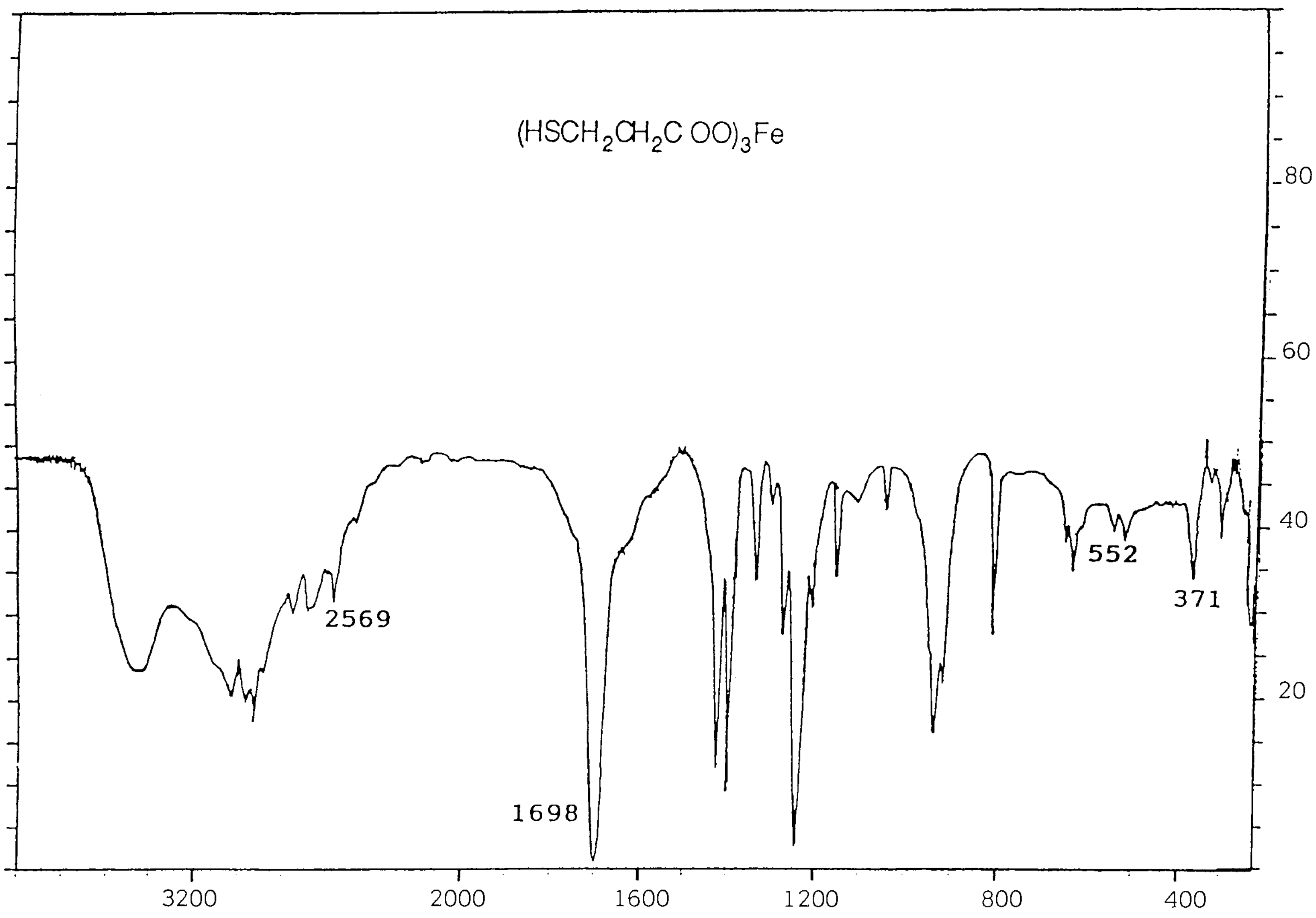


```
PEAK THRESHOLD =  1.00 %T
          CM-1         %T

        3856.0      44.20
        3822.0      44.57
        3753.0      44.64
        3737.0      43.79
        3441.0      10.75

        1603.0       1.57
        1425.0       1.30
        1226.0      26.62
        1137.0      31.57
         955.0      42.55
         839.0      37.80
         793.0      35.08
         694.0      29.77
         582.0      15.73
         521.0      28.43
         384.0      16.81
         294.0      33.58
         278.0      31.72
         273.0      34.32
         254.0      24.20
         245.0      22.47
         233.0       9.92
         229.0       9.92
```

Fig. 2.1 Infra-red spectrum of Fe-thioacetate.



PEAK THRESHOLD = 1.90 %T

CM-1	%T		
1278.0	37.41	3896.0	47
1241.0	1.57	3893.0	48
1210.0	39.45	3875.0	47
1158.0	37.92	3856.0	47
1117.0	42.99	3842.0	47
1051.0	42.15	3822.0	47
939.0	15.91	3802.0	47
921.0	21.78	3787.0	48
815.0	27.35	3772.0	47
658.0	38.38	3753.0	47
642.0	34.79	3745.0	48
552.0	39.78	3738.0	47
528.0	38.53	3714.0	45
452.0	42.40	3692.0	45
424.0	42.21	3678.0	45
371.0	33.92	3651.0	43
338.0	45.15	3451.0	23
332.0	45.21	3029.0	29.4
327.0	45.08	2956.0	19.8
312.0	38.64	2929.0	17.49
300.0	43.99	2917.0	29.97
284.0	45.10	2888.0	23.22
273.0	44.53	2754.0	39.99
251.0	37.97	2685.0	39.42
236.0	23.33	2569.0	31.47
230.0	25.66	2479.0	49.65
224.0	36.25	2347.0	45.67
		2175.0	47.47
		2029.0	47.68
		1698.0	9.75
		1649.0	35.91
		1639.0	36.87
		1562.0	43.95
		1509.0	48.51
		1425.0	11.87
		1409.0	9.91
		1341.0	33.66
		1295.0	42.72

Fig. 2.2 Infra-red spectrum of Fe-thiopropionate.

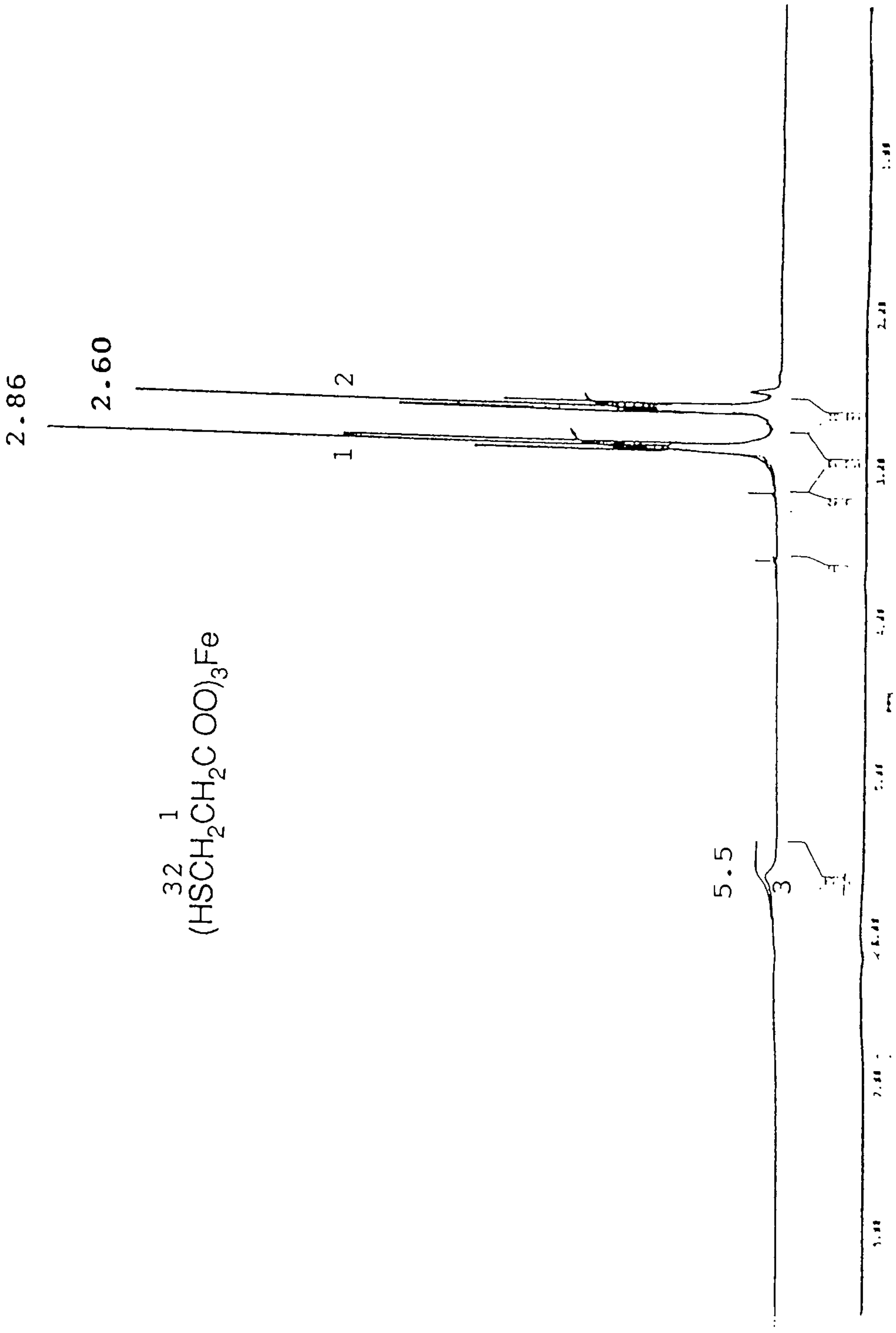


Fig. 2.3 Proton nmr spectrum of Iron thiopropionate

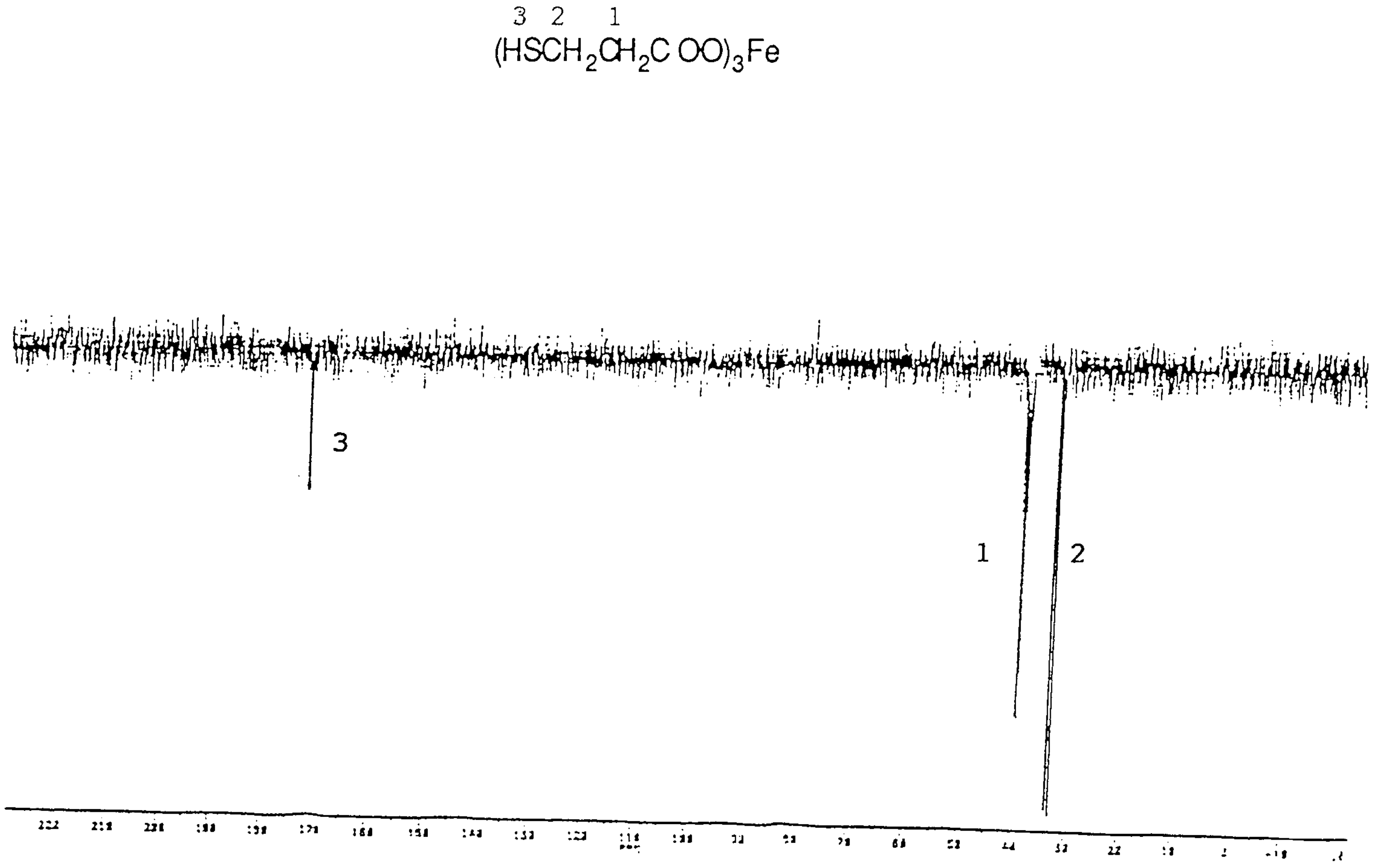


Fig. 2.4 ^{13}C nmr spectrum of Iron thiopropionate

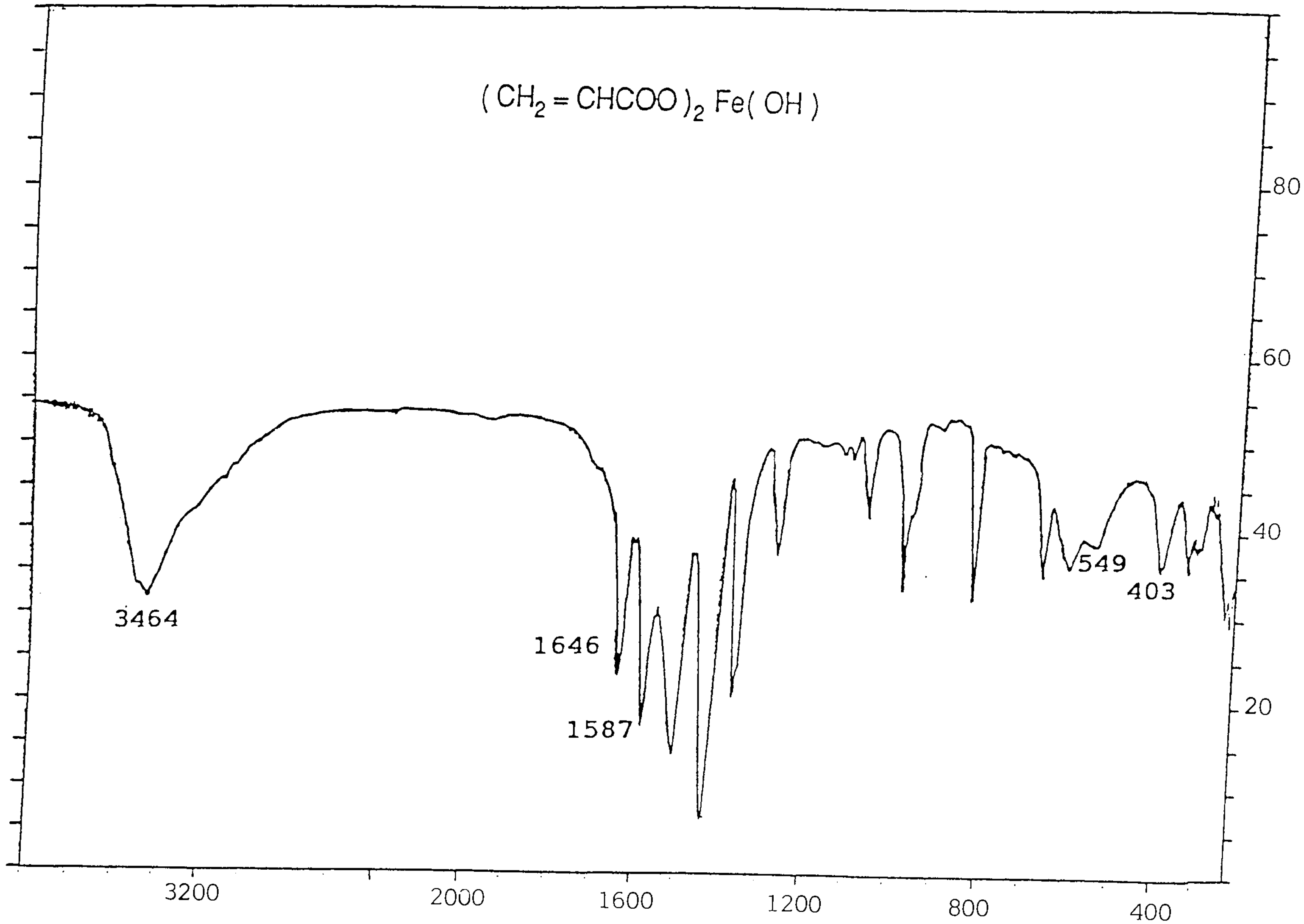
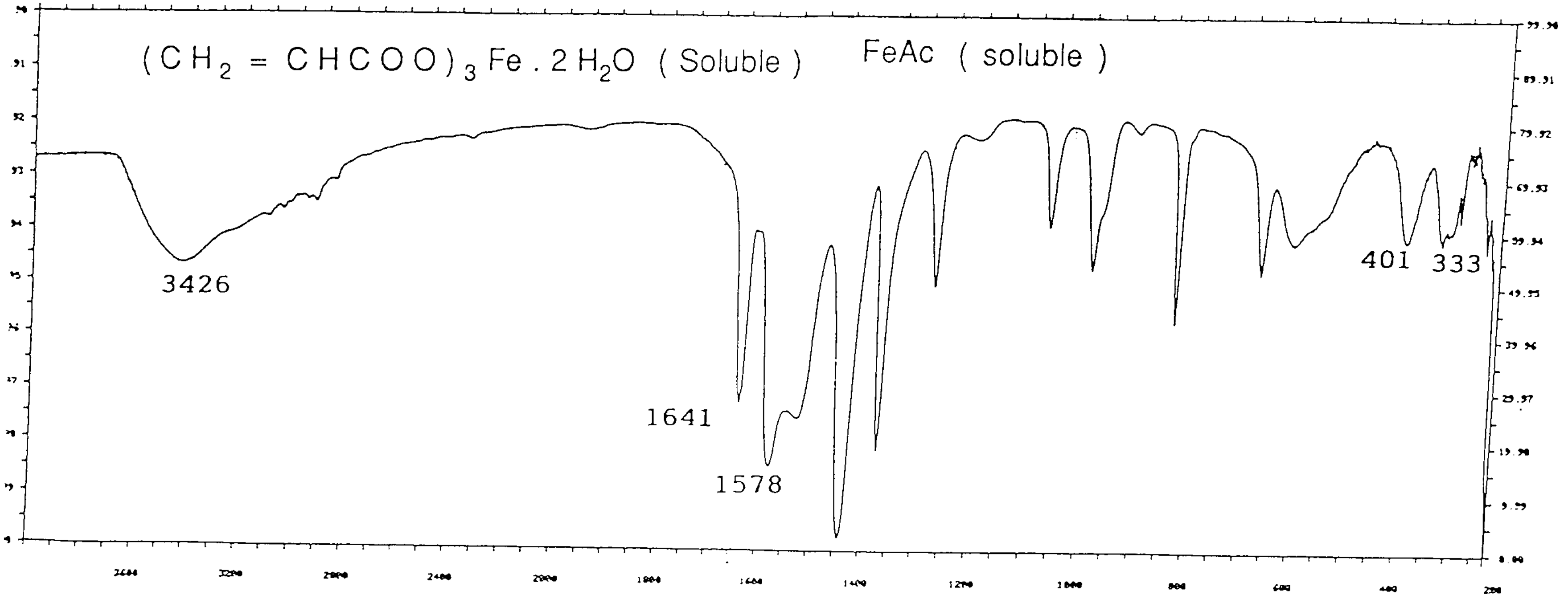


Fig. 2.5 Infra-red spectrum of Fe-acrylate.

PEAK THRESHOLD = 1.0% T

CM-1	%T
3905.9	53.54
3886.9	53.44
3874.9	53.50
3856.9	52.82
3841.9	53.33
3822.9	53.36
3809.9	53.28
3772.9	53.67
3752.9	52.46
3745.9	52.95
[illegible]	52.31
3713.9	51.96
3691.9	51.45
3678.9	50.94
3659.9	49.11
3631.9	46.42
3464.9	31.67
2346.9	52.75
1945.9	52.26
1646.9	23.02
1587.9	17.34
1519.9	14.82
1438.9	5.50
1375.9	20.55
1279.9	37.11
1187.9	45.69
1171.9	49.82
1111.9	48.42
1058.9	41.79
984.9	37.05
912.9	51.77
829.9	31.94
772.9	34.78
611.9	35.29
549.9	38.28
463.9	35.50
338.9	35.47
318.9	37.63



PEAK THRESHOLD = 1.99 %T

CM-1	%T
3426.0	53.01
2926.0	64.98
1641.0	27.83
1578.0	15.72
1528.0	24.76
1439.0	2.72
1373.0	19.15
1275.0	49.87
1204.0	77.37
1069.0	61.40
987.0	53.44
911.0	78.74
838.0	43.17
671.0	52.69
610.0	58.19
401.0	58.84
333.0	58.56
322.0	64.21
301.0	62.94
294.0	73.61
279.0	74.81
246.0	57.16
233.0	54.37
222.0	-1.25

Fig . 2.6 Infra -red Spectrum of Iron acrylate (Soluble)

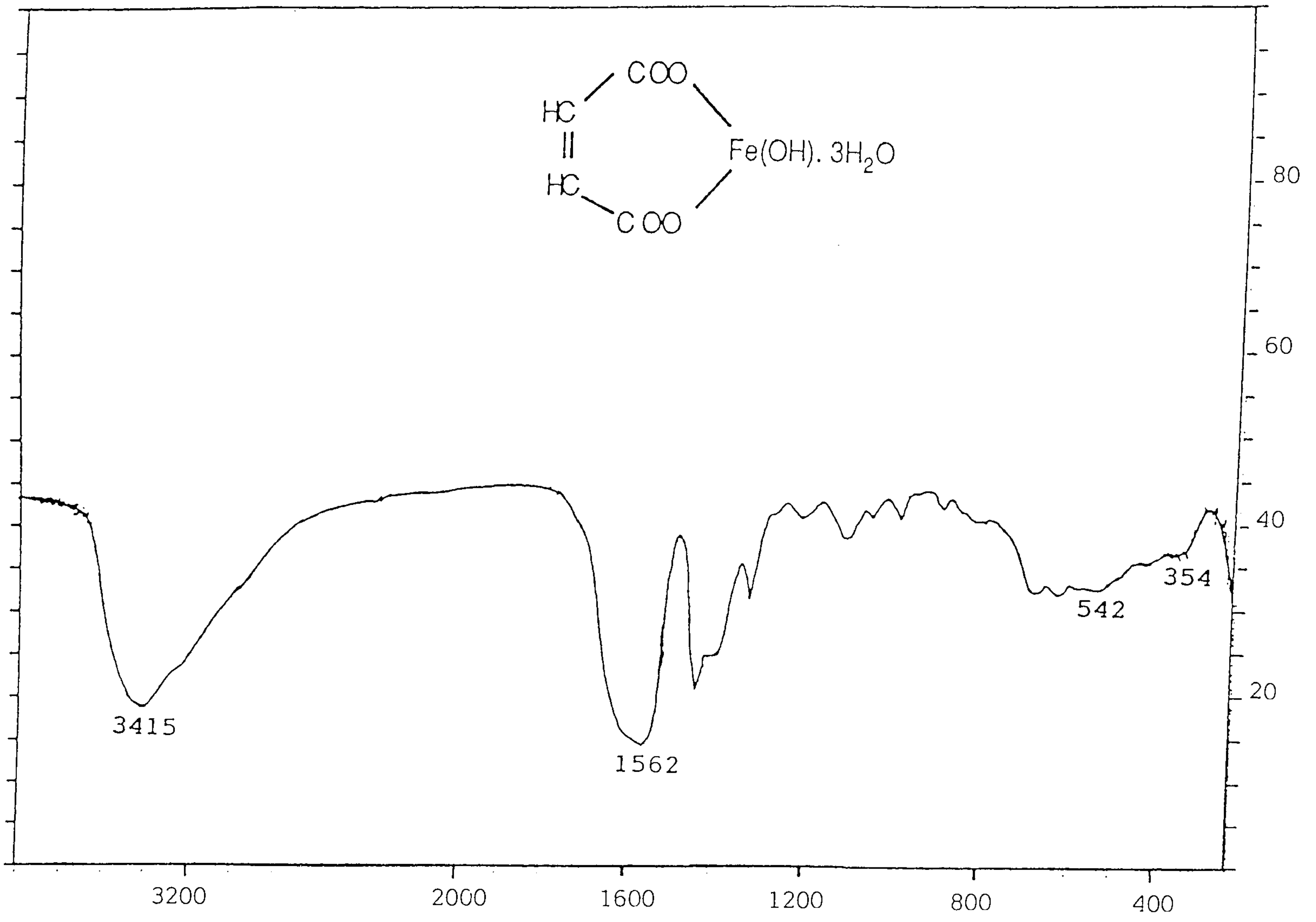
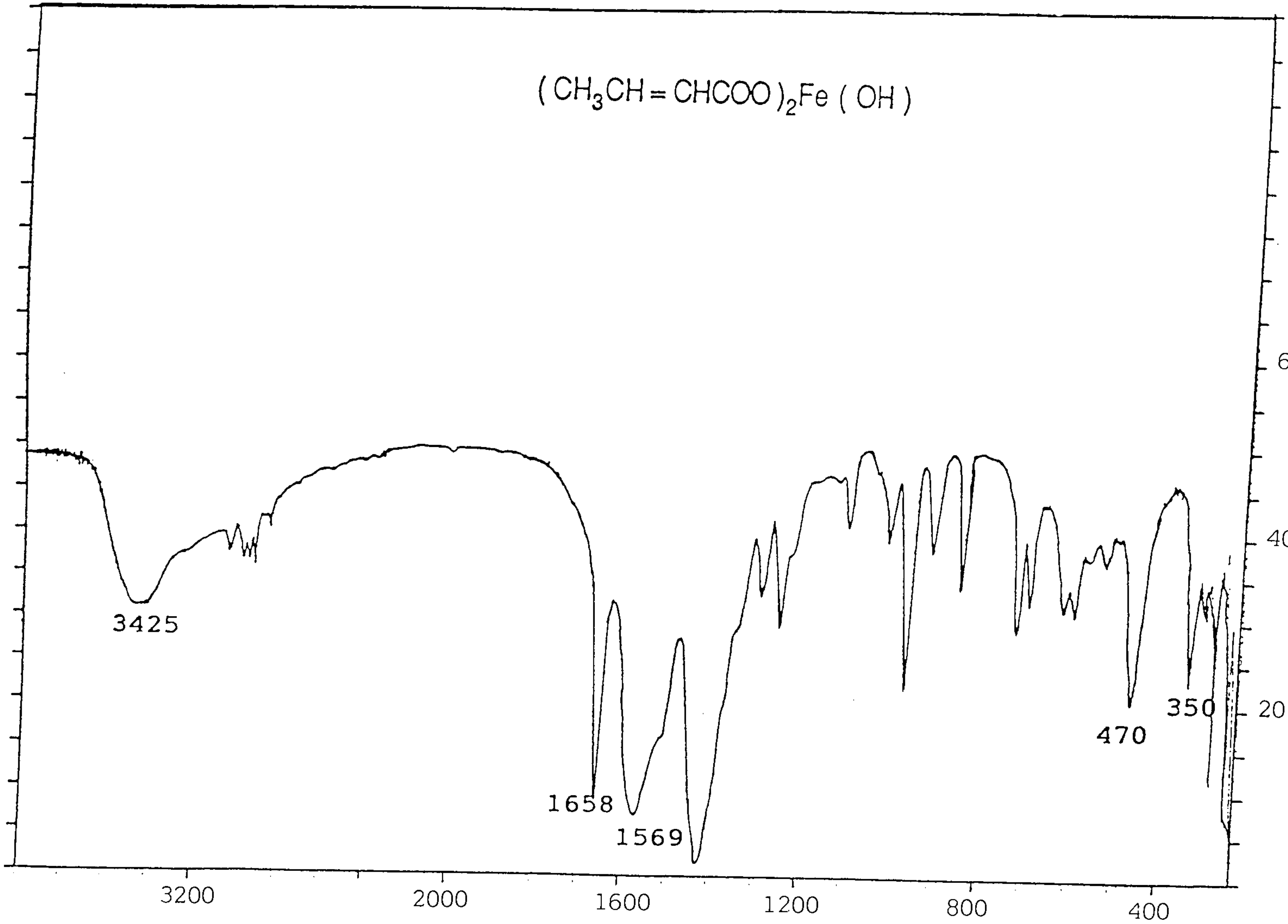


Fig. 2.7 Infra- red spectrum of iron maleate

```
PEAK THRESHOLD =  1.00 %T
      CM-1          %T

     3906.0      42.40
     3894.0      42.52
     3874.0      42.59
     3856.0      41.64
     3841.0      42.27
     3823.0      42.19
     3802.0      42.66
     3772.0      41.63
     [illegible].0     x41.65
     3745.0      41.84
     [illegible]  0      41.93
     [illegible]  0      41 [illegible]
     3714.0      40.73
     3691.0      40.27
     3678.0      32.53
     3651.0      36.84
     3415.0      18.64
     2346.0      42.68
     1562.0      14.72
     1473.0      25.99
     1317.0      31.41
     1199.0      40.52
     1165.0      38.37
     1042.0      40.22
      922.0      40.52
      890.0      41.28
      584.0      32.65
      576.0      31.81
      542.0      32.73
      376.0      36.23
      370.0      35.23
      354.0      35.94
      338.0      36.25
      322.0      33.13
      292.0      41.53
      282.0      42.22
      234.0      41.74
      278.0      40.56
```



```
PEAK THRESHOLD =  1.00  %T
        CM-1          %T

      3966.9      42.15
      3893.9      42.25
      3874.9      42.36
     3856.9      47.53
     3844.9      42.19
     3822.9      42.16
     3799.9      42.93
     3772.9      47.81
     3753.9      47.23
     3748.9      42.99
     [illegible] 9      47.26
     3714.9      47.15
     3691.9      42.78
     3678.9      45.21
     3651.9      44.19
     3621.9      42.28
     3425.9      39.91
     3043.9      37.45
     2979.9      36.65
     2943.9      36.65
     2914.9      35.85
     2851.9      40.25
     2745.9      42.41
     2929.9      42.95
     1658.9       8.93
     1569.9       7.11
     1423.9       1.42
     1298.9      32.99
     1256.9      29.15
     1174.9      45.16
     1197.9      45.97
     1014.9      72.29
      979.9      22.97
      920.9      38.14
      855.9      33.79
      725.9      29.73
      709.9      31.93
      625.9      31.22
```

Fig. 2.8 Infra-red spectrum of Fe-crotonate.

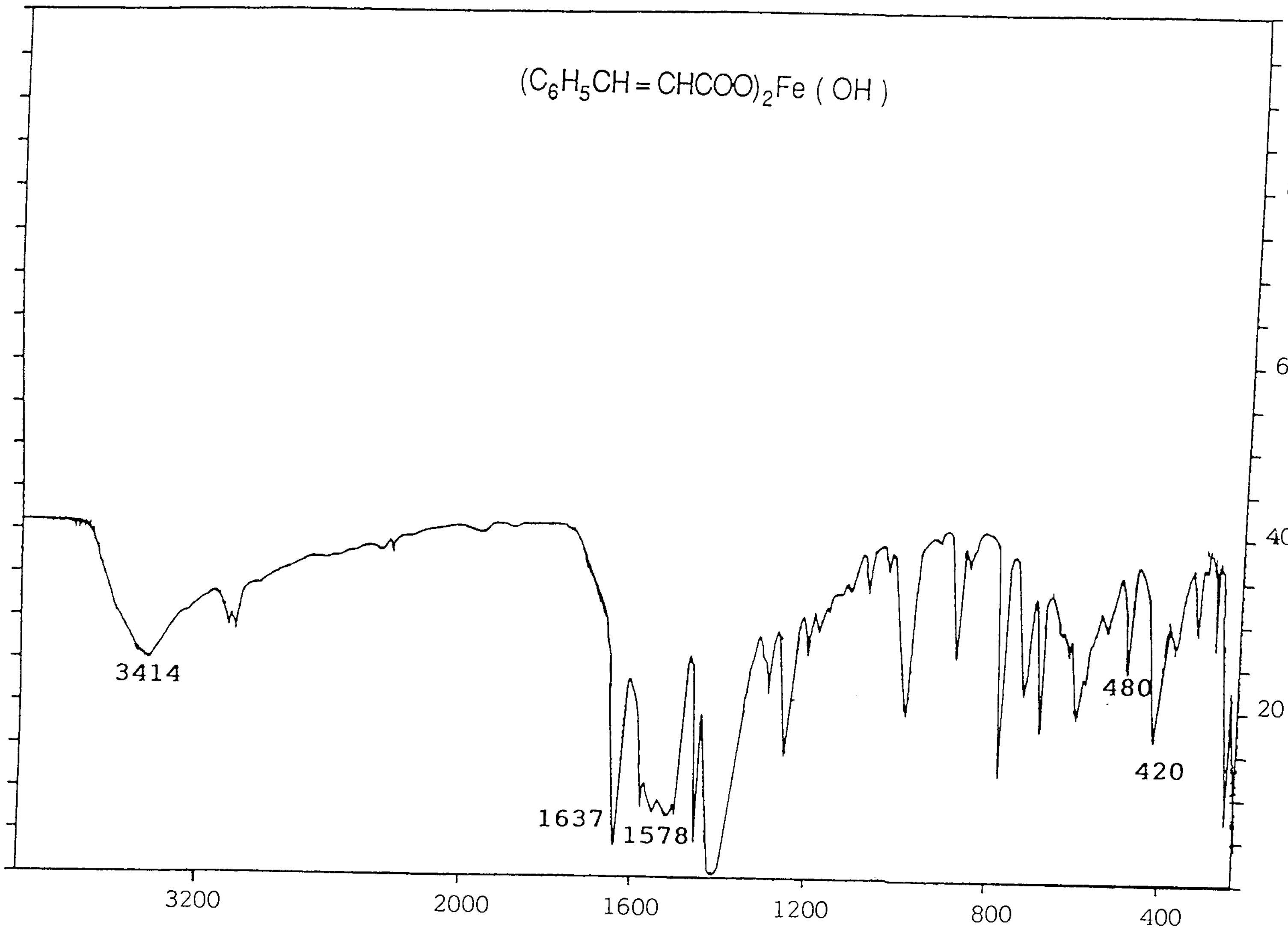


Fig. 2.9 Infra-red spectrum of Fe-cinnamate.

```
PEAK  THRESHOLD =  1 00  %T
         CM-1           %T

        3856 0      40 13
        3822 0      40 63
        3809 0      40 66
        3772 0      40 52
        3761 0      40 45
        3753 0      39 22
        3746 0      40 56
        3737 0      39 90
        3727 0      40 38
        3714 0      39 94
        3703 0      40 31
        3691 0      39 75
        3678 0      39 33
        3670 0      39 37
        3651 0      37 18
        3631 0      35 62
        3549 0      30 51
        3414 0      25 10
        3164 0      32 59
        3062 0      36 57
        3053 0      29 53
        3027 0      29 33
        2934 0      37 72
        2775 0      37 37
        1945 0      39 27
        1884 0      40 45
        1754 0      40 14
        1685 0      31 57
        1637 0       3 44
        1578 0       8 14
        1544 0       7 57
        1512 0       7 49
        1497 0       7 75
        1451 0       7 39
        1442 0       6 74
        1393 0      31 59
        1333 0      14 43
        1264 0      35 12
```

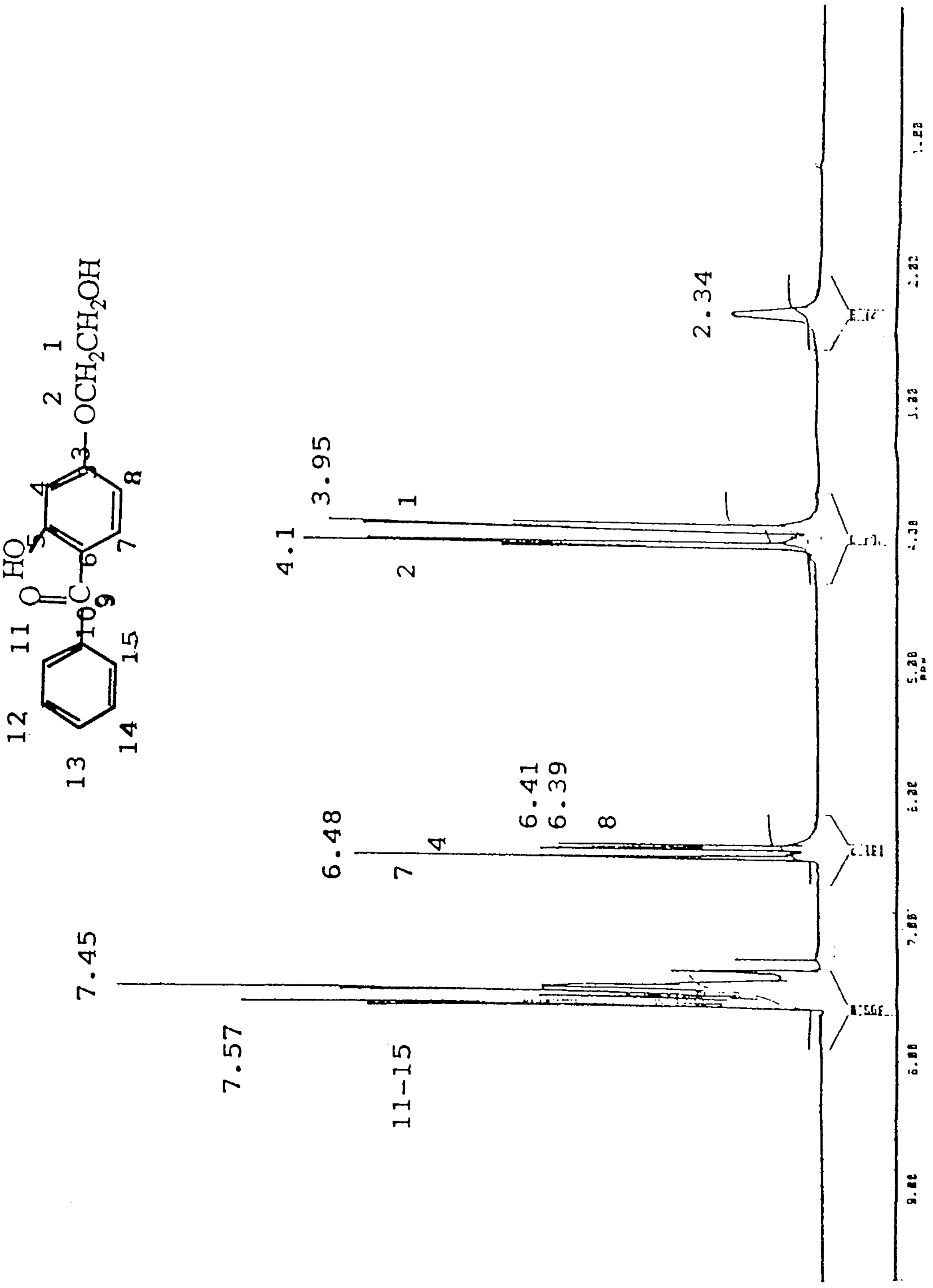


Fig. **2.10** Proton nmr spectrum of 2-hydroxy-4-(hydroxy-ethoxy)benzophenone.

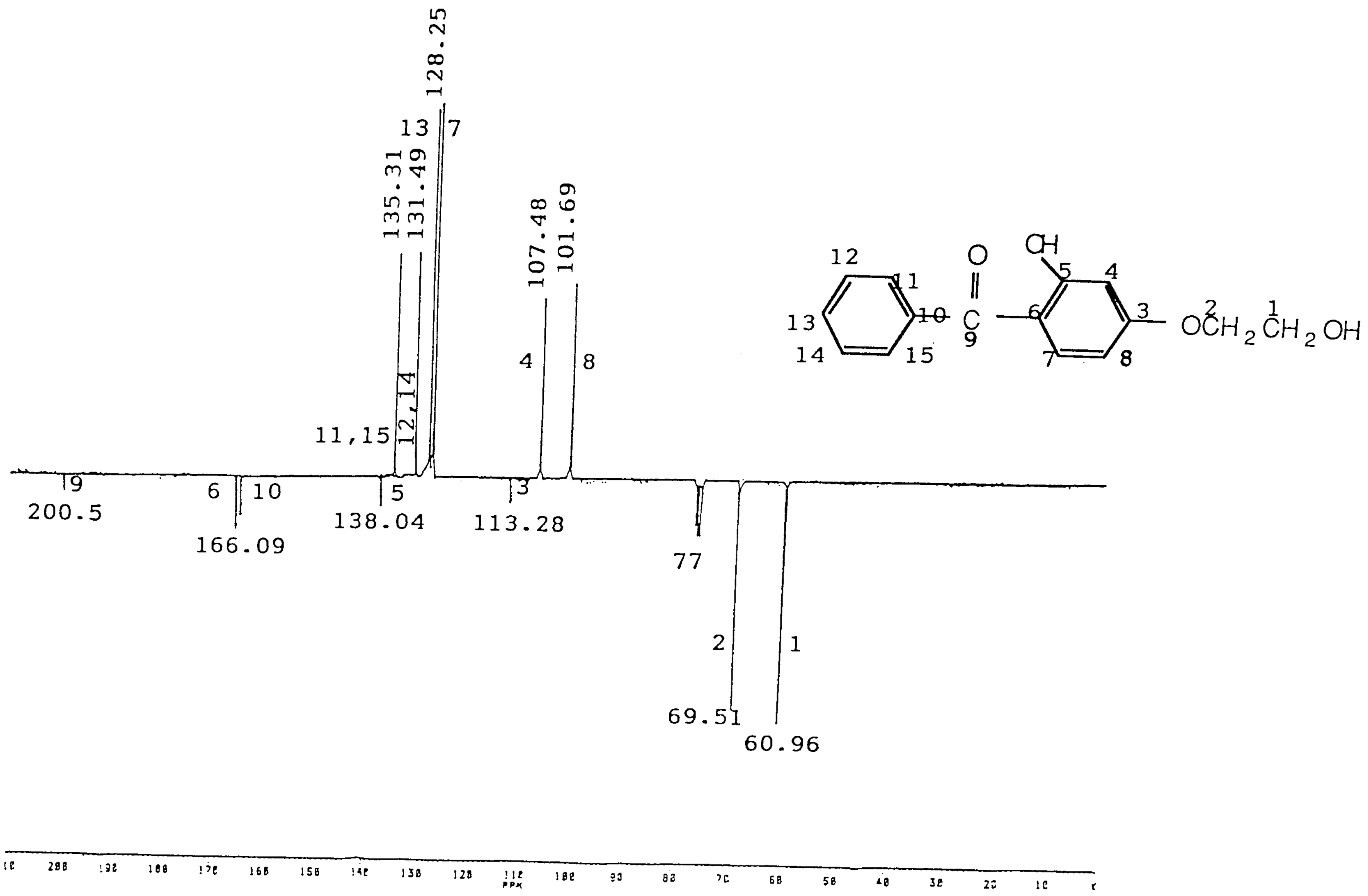


Fig. 2.11 ^{13}C nmr spectrum of 2-hydroxy-4-(hydroxy-ethoxy)benzophenone.

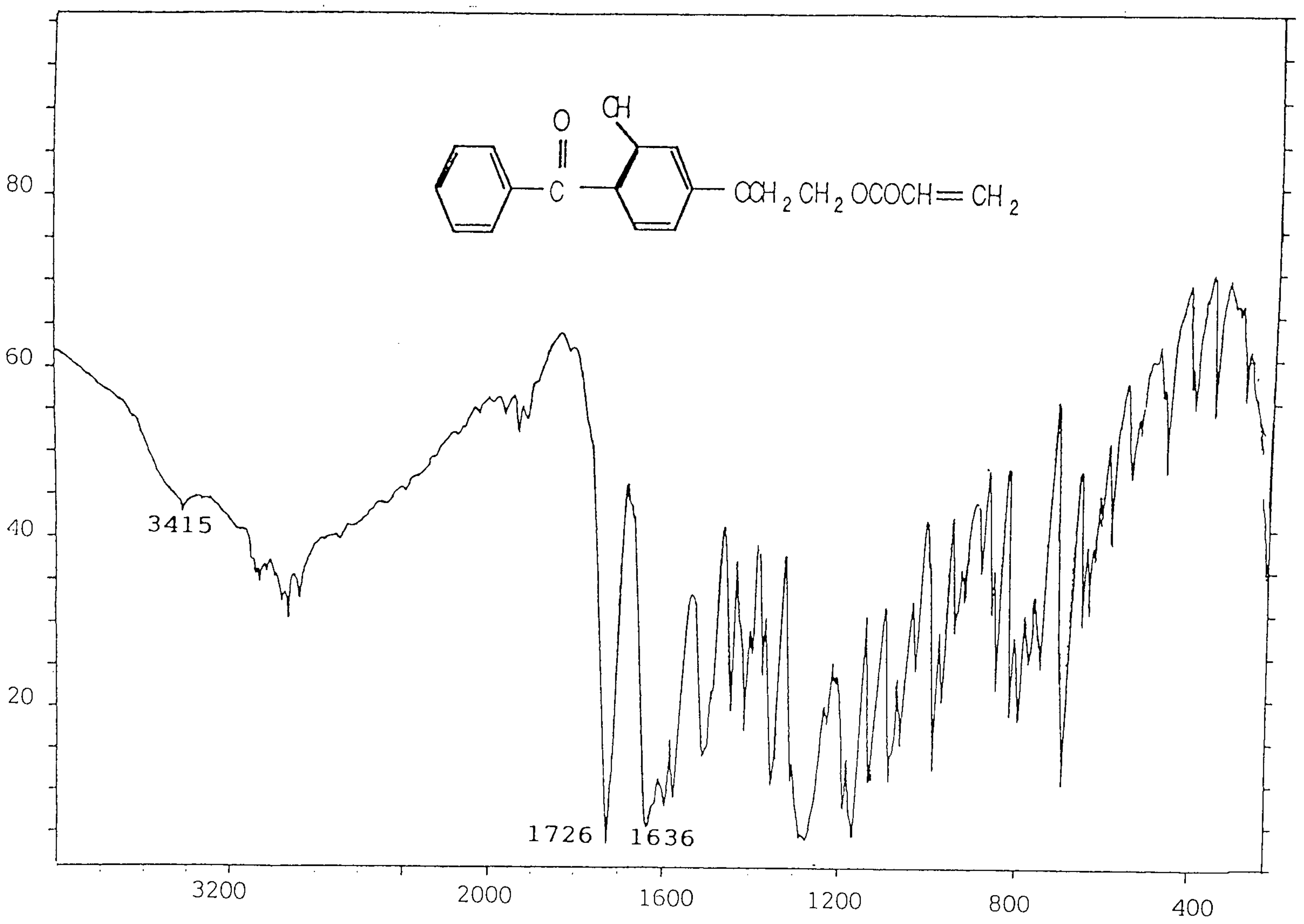
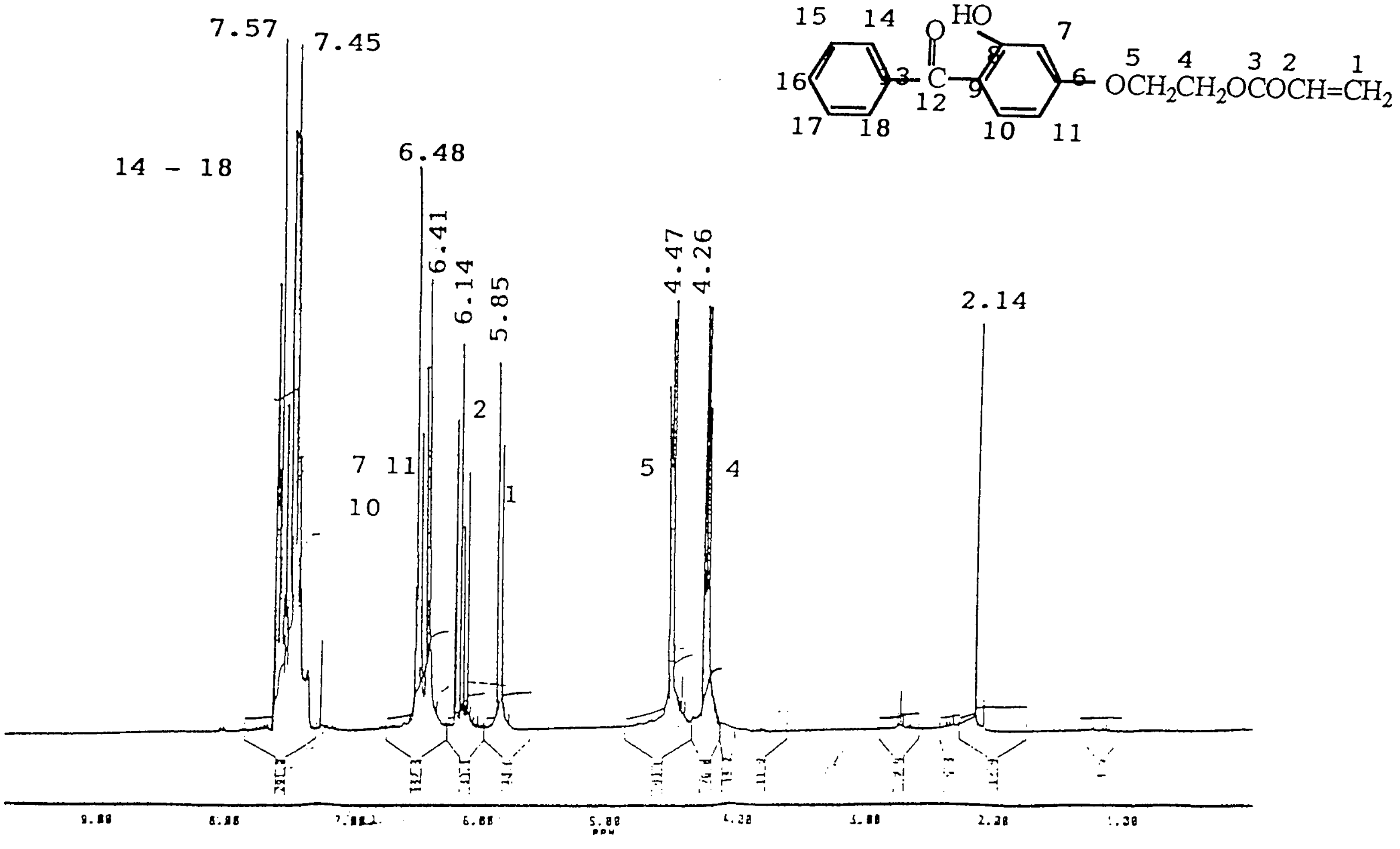


Fig. 2.12 Infra-red spectrum of 2-hydroxy-4-(acryloxy-ethoxy) benzophenone (HAEB)

PEAK THRESHOLD = 1.99 %T

CM-1	%T
3415.0	[illegible]
3060.0	74.73
2959.0	71.32
[illegible]	70.47
2881.0	72.77
[illegible]	54.51
1936.0	52.33
1916.0	53.74
1726.0	3.62
1636.0	5.51
1595.0	8.99
1576.0	6.22
1519.0	14.23
1499.0	20.95
1446.0	19.55
[illegible]	17.31
1399.0	26.43
1374.0	23.92
1352.0	14.79
1305.0	11.25
1273.0	4.29
[illegible]	12.67
[illegible]	[illegible]
1168.0	4.62
1139.0	11.39
1084.0	11.26
1059.0	15.52
1026.0	24.37
[illegible]	12.55
[illegible]	20.68
941.0	23.86
920.0	32.52
[illegible]	75.81
[illegible]	31.66
[illegible]	32.11
817	13.05
[illegible]	18.56
[illegible]	25.22

Fig. 2.13 Proton nmr spectrum of 2-hydroxy-4-(acryloxy-ethoxy)benzophenone (HAEB).



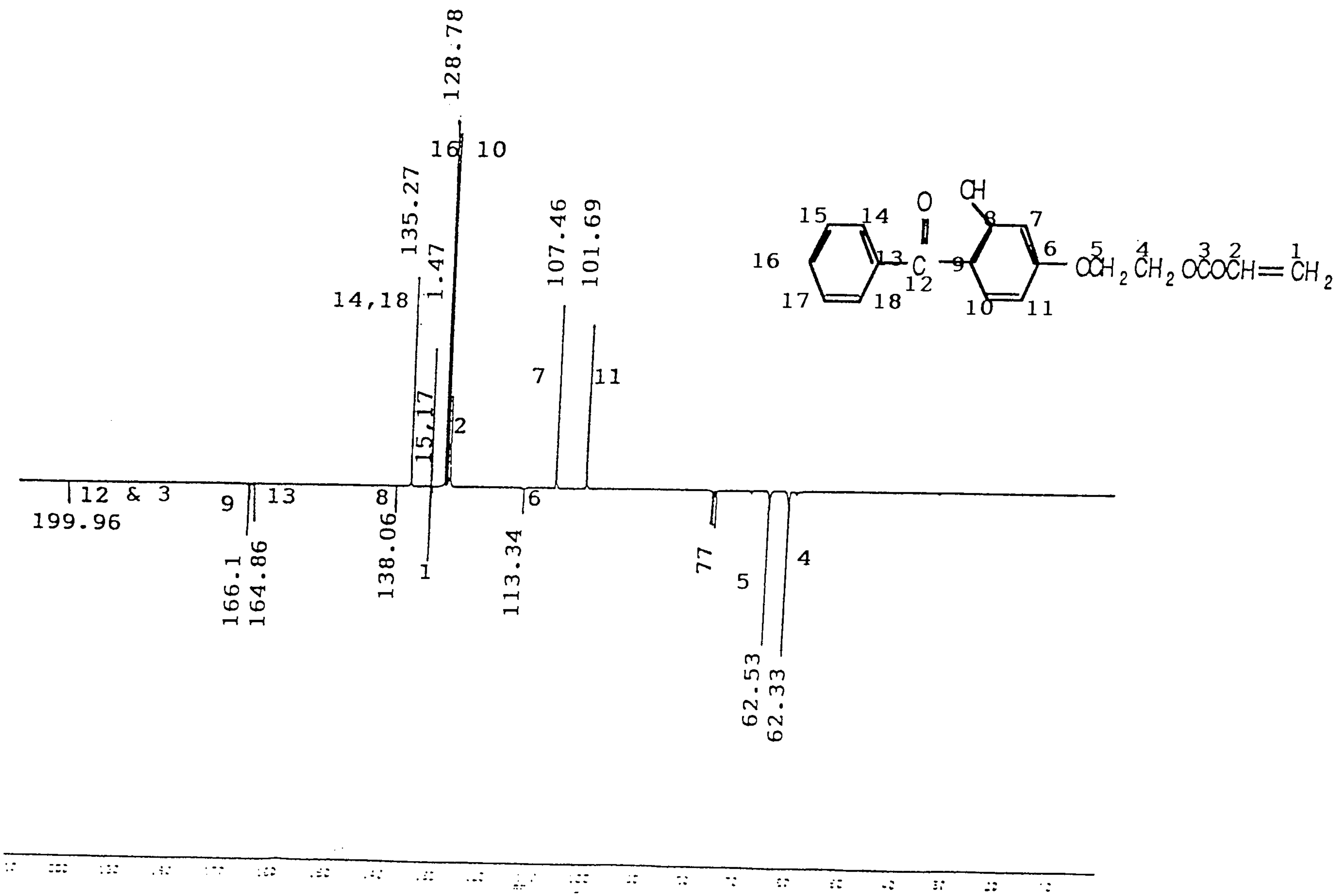
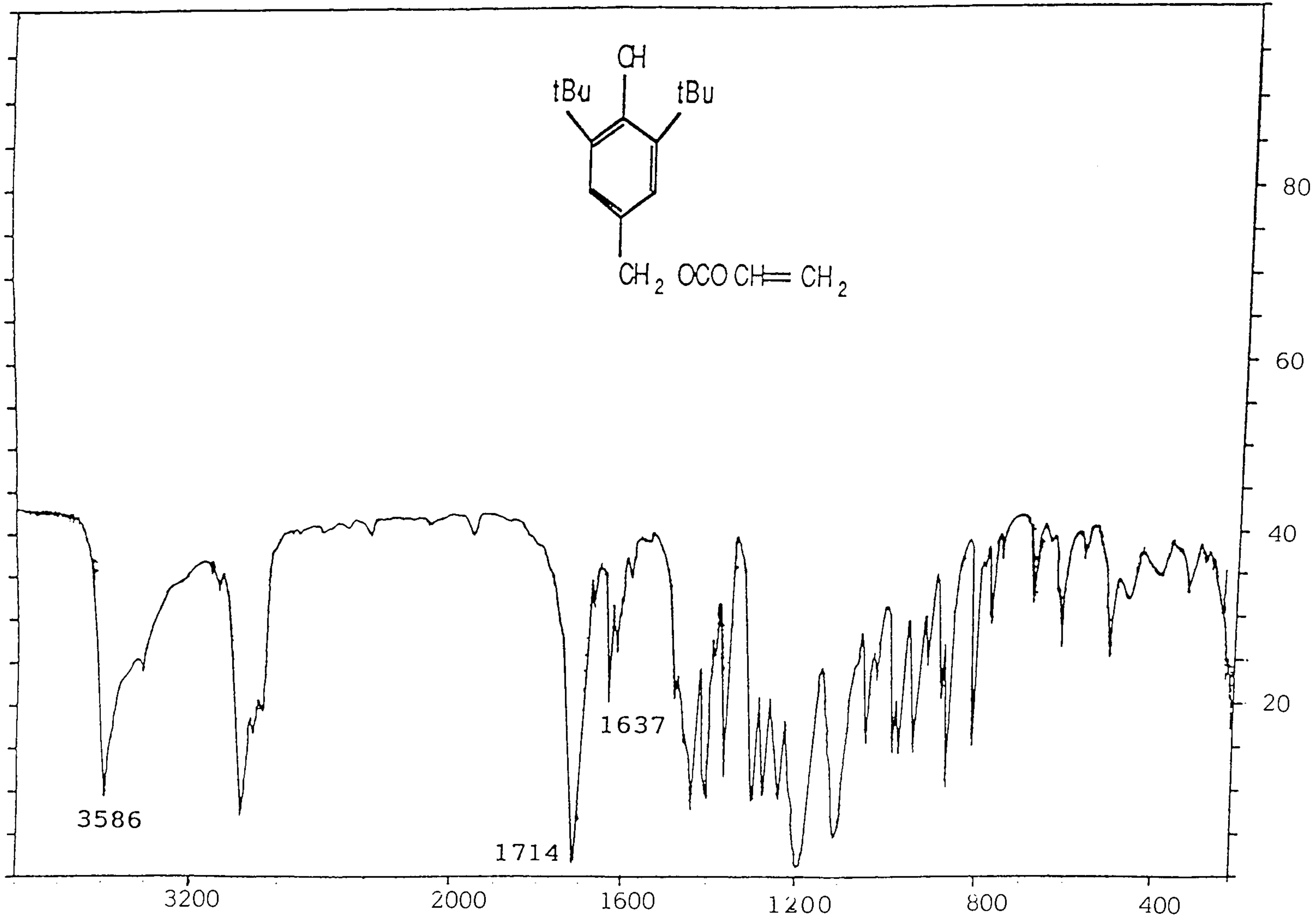


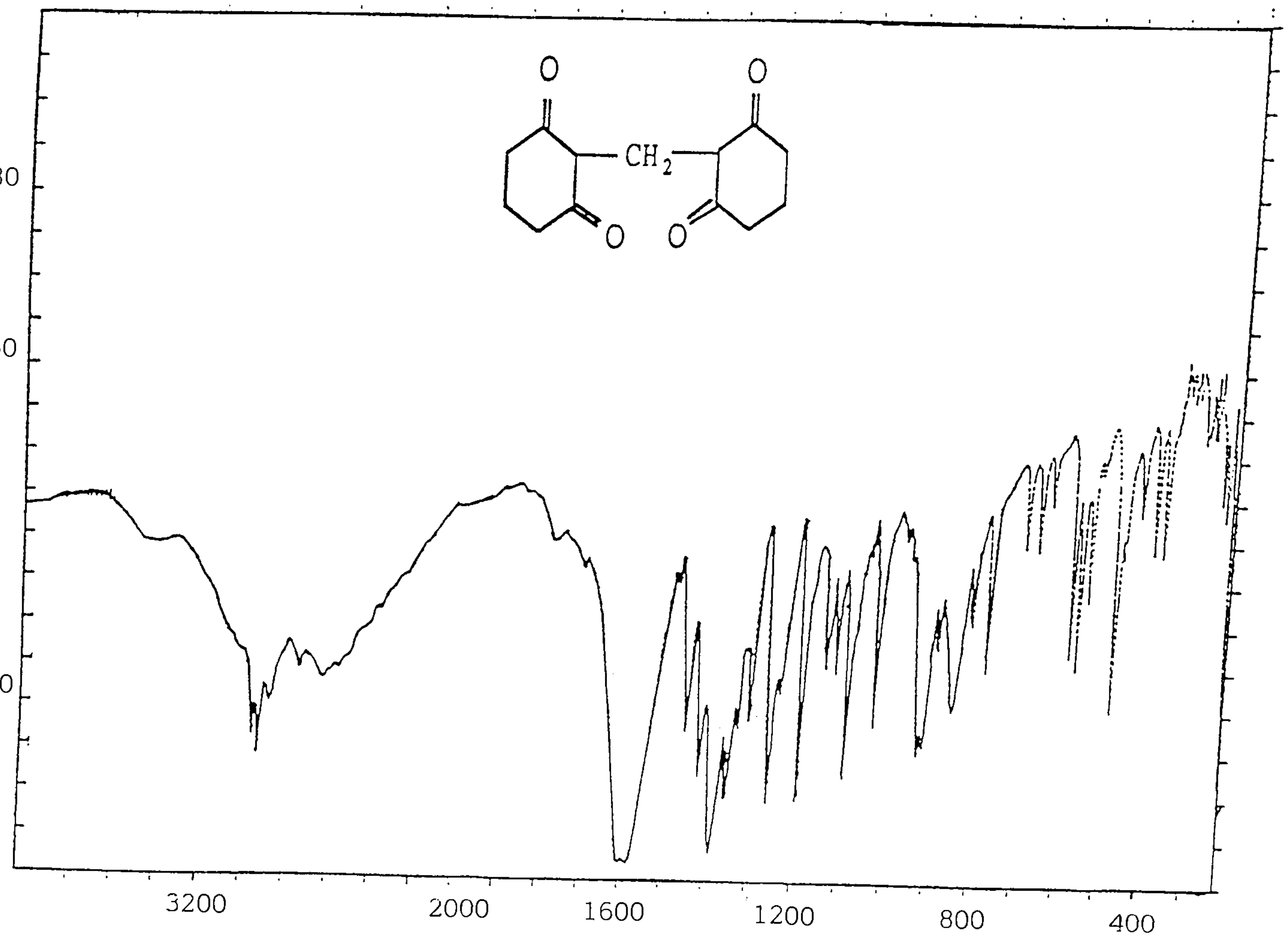
Fig. 2.14 ^{13}C nmr spectrum of 2-hydroxy-4-(acryloxy-ethoxy) benzophenone (HAEB).



PEAK THRESHOLD = 1.00 %T

CM-1	%T	CM-1	%T
		3966.0	42.1
1309.0	8.94	3953.0	42.1
1276.0	9.84	3873.0	42.3
1240.0	9.82	3855.0	41.7
1192.0	1.31	3841.0	42.2
1111.0	4.82	3823.0	42.01
1046.0	15.66	3809.0	42.93
1025.0	23.88	3753.0	41.45
987.0	14.47	3746.0	41.25
974.0	14.37	3737.0	41.23
942.0	14.55	3713.0	41.63
916.0	24.55	3691.0	40.37
885.0	20.53	3678.0	39.43
859.0	10.51	3588.0	9.34
813.0	15.68	3419.0	23.92
775.0	23.15	3197.0	35.24
756.0	35.91	3071.0	33.31
684.0	31.57	2957.0	7.24
649.0	38.84	2915.0	15.88
619.0	35.45	2874.0	19.37
571.0	37.17	2794.0	33.92
510.0	35.40	2592.0	40.61
471.0	32.63	2487.0	40.64
392.0	34.73	2380.0	39.71
330.0	32.92	2187.0	40.92
297.0	34.29	1955.0	39.67
279.0	33.45	1714.0	1.55
254.0	30.79	1673.0	31.27
241.0	33.71	1637.0	20.21
232.0	30.40	1613.0	25.95
227.0	15.82	1588.0	34.77
222.0	10.58	1561.0	38.81
		1483.0	20.84
		1458.0	15.42
		1439.0	7.97
		1409.0	9.52
		1392.0	35.57
		1364.0	11.50

Fig. 2.15 Infra-red spectrum of 3,5-di-tert-butyl-4-hydroxy benzyl acrylate (DBBA).



PEAK THRESHOLD = 3.60 %T

CM-1	%T
2962.6	15.48
2934.6	14.42
2884.6	26.36
2754.6	24.44
2646.6	33.25
1602.6	2.15
1456.6	17.44
1423.6	12.15
1386.6	3.46
1359.6	9.61
1336.6	17.98
1311.6	18.72
1282.6	9.18
1243.6	21.94
1197.6	9.55
1143.6	24.95
1121.6	24.44
1057.6	13.37
1021.6	15.66
924.6	14.57
892.5	27.46
854.6	20.24
817.6	39.48
782.6	24.84
744.6	35.51
673.6	35.25
646.6	44.56
589.6	36.73
572.6	25.46
550.6	33.54
482.6	29.42
468.6	31.45
434.6	47.51
401.6	38.98
389.6	38.69
342.6	57.94
332.6	56.98
321.6	57.54

Fig . 2.16 FTIR Spectrum of 2,2-methylene dicyclohexanedione

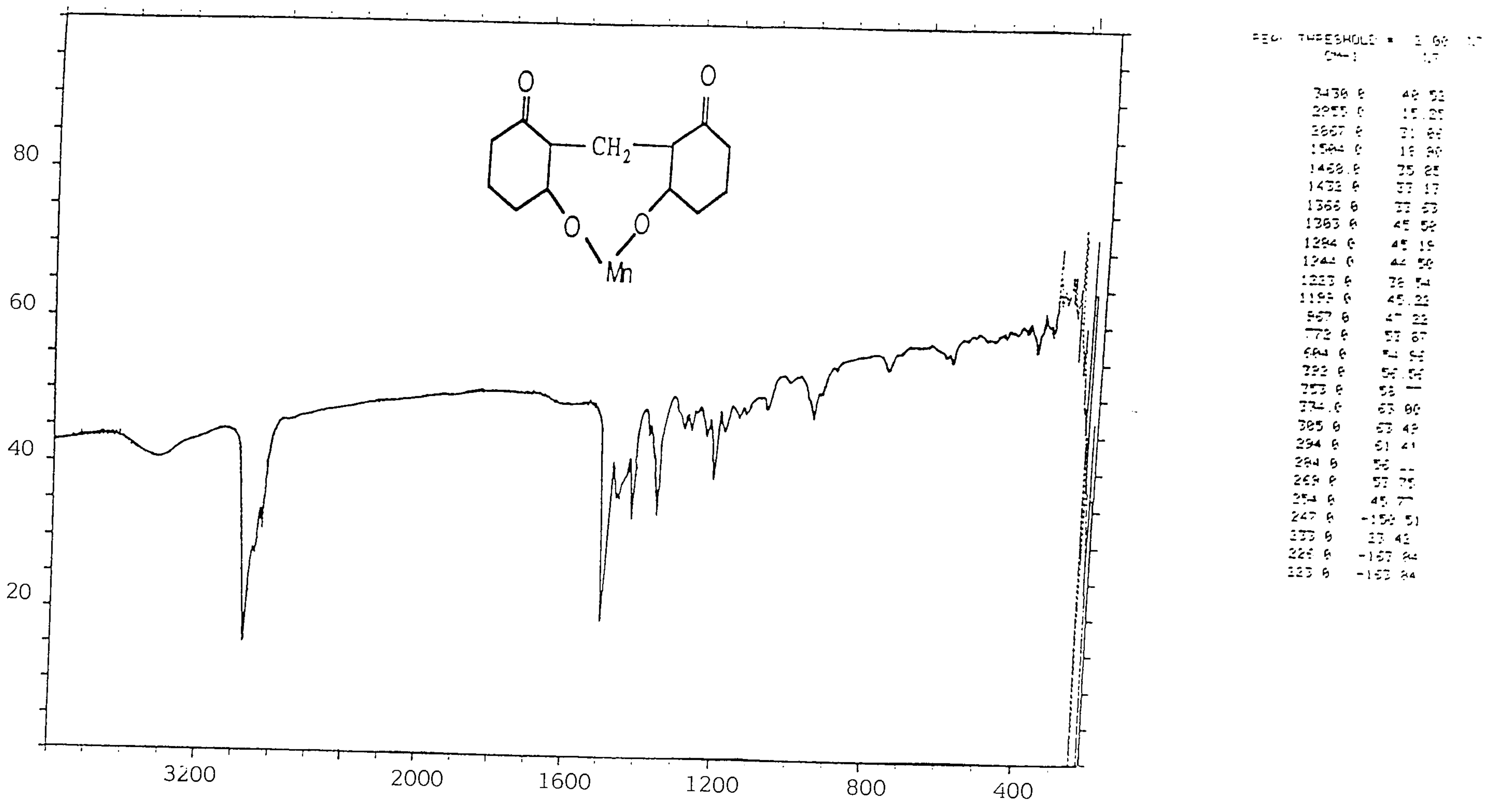


Fig. 2.17 FTIR Spectrum of Manganese (II) 2,2-methylene dicyclohexanedione

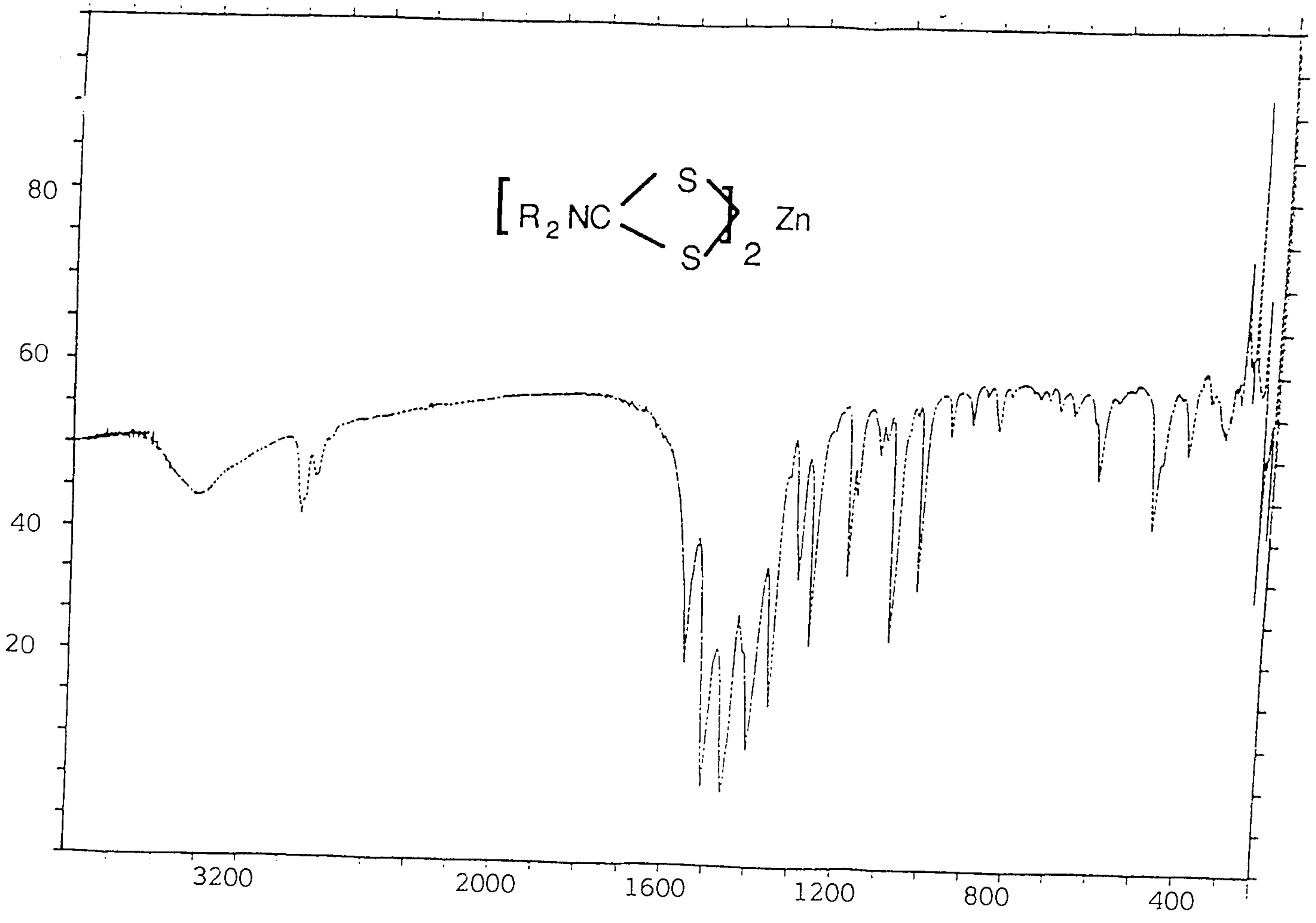
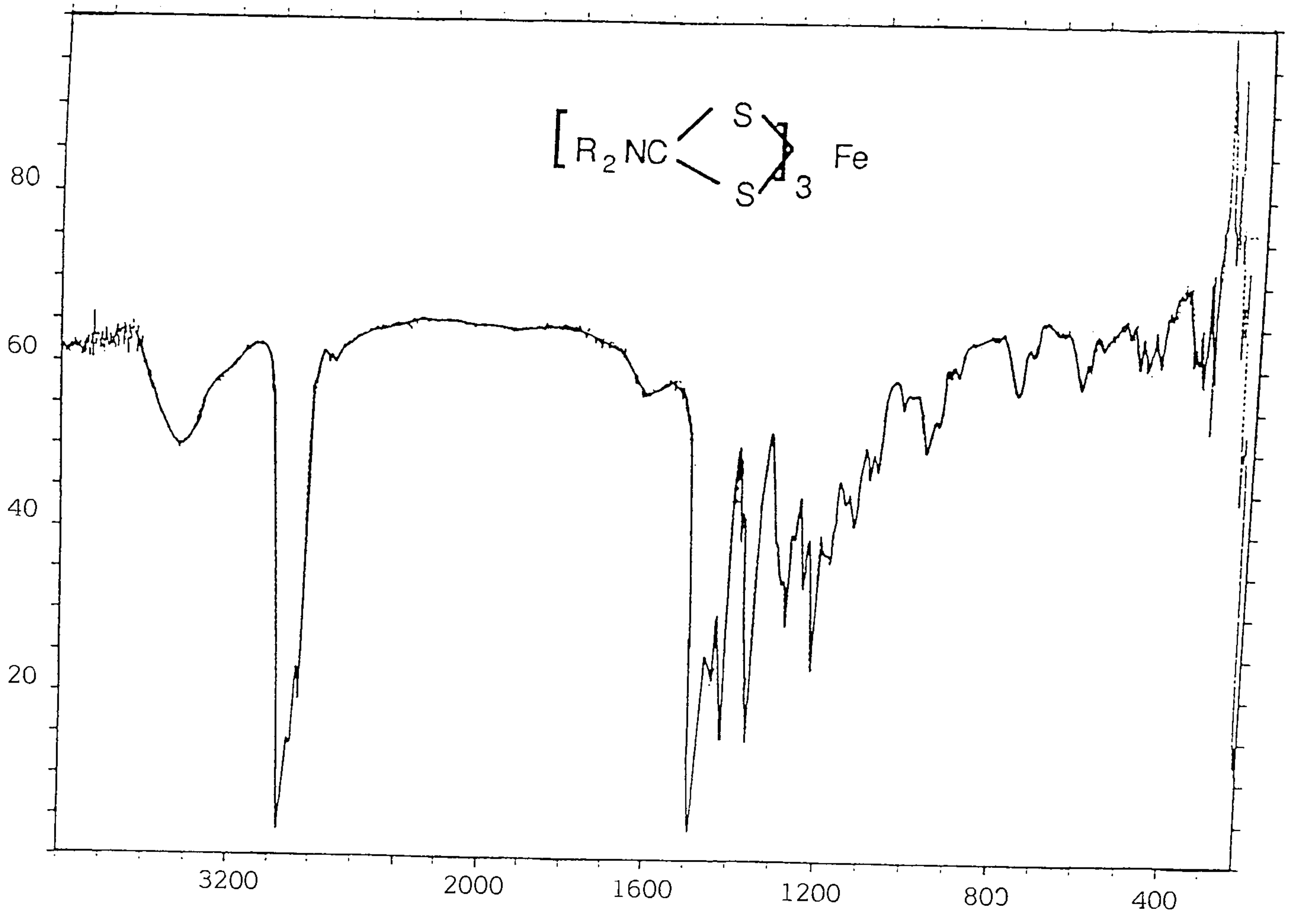


Fig . 2.18 Infra-red Spectrum of Zinc (II) bisdinonyldithiocarbamate

PEAK THRESHOLD = 3.00 %T

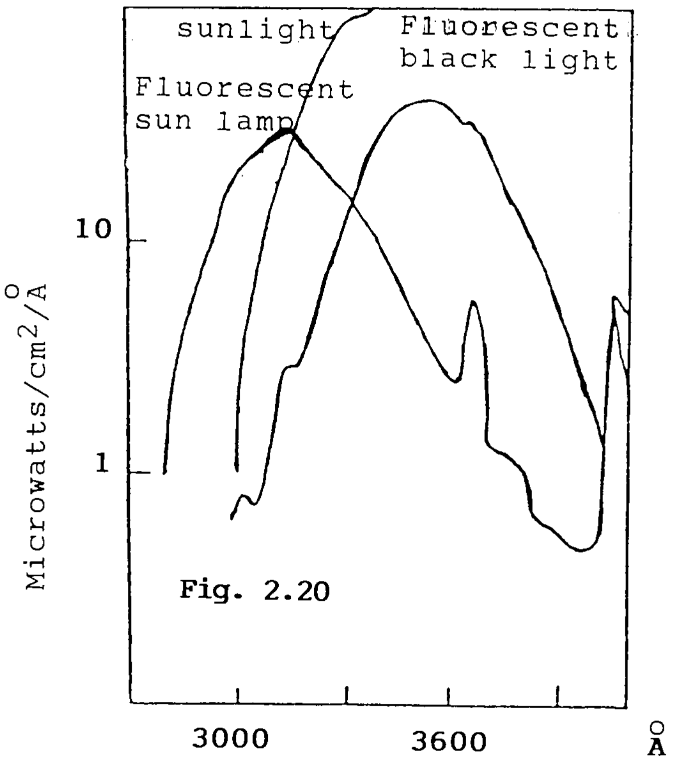
CM-1	%T
3431.6	43.85
2943.6	41.73
2879.6	46.34
1562.6	24.42
1519.6	9.62
1482.6	9.64
1462.6	14.17
1360.6	19.47
1305.6	34.53
1274.6	36.85
1195.6	35.46
1181.6	45.52
1131.6	50.28
1095.6	37.46
1029.6	33.73
969.6	52.73
921.6	54.15
866.6	53.47
718.6	56.66
684.6	55.44
621.6	47.75
496.6	41.77
419.6	50.81
387.6	52.87
369.6	57.69
284.6	57.76
263.6	57.91
247.6	33.35
231.6	41.69
222.6	-154.79



```
PEAK THRESHOLD =  2.00 %T
     CM-1         %T

     3873.6     69.79
     3855.6     60.21
     3822.6     61.23
     3804.6     60.75
     3753.6     61.11
     3737.6     61.39
     3714.6     61.52
     3691.6     60.55
     3678.6     63.16
     3651.6     66.76
     3631.6     66.61
     3447.6     49.26
     2955.6      3.17
     2957.6     13.07
     1530.6     56.31
     1491.6      3.53
     1451.6     22.11
     1428.6     14.82
     1393.6     38.83
     1365.6     14.69
     1344.6     28.66
     1245.6     33.26
     1222.6     23.31
     1187.6     36.32
     1138.6     49.86
     1195.6     45.55
     1988.6     47.41
      986.6     49.92
      776.6     56.[illegible]
      670.6     58.
      592.6     66.44
      482.6     69.16
      449.6     69.59
      371.6     66.88
      361.6     66.95
      348.6     53.23
      327.6     53.95
      304.6     88.47
```

Fig . **2.19** Infra-red Spectrum of Iron (III) tris dinonyldithiocarbamate (FeDNC)



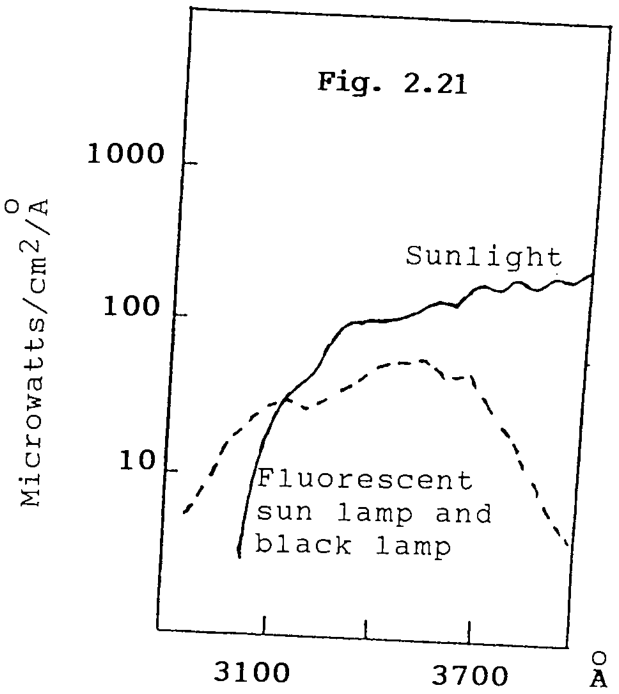


Fig. 2.20 Ultra violet spectral distributions of the fluorescent sun lamp and fluorescent black light (ref.111).

Fig. 2.21 Combination of fluorescent sun lamp and black lamp compared with sunlight (ref.111).

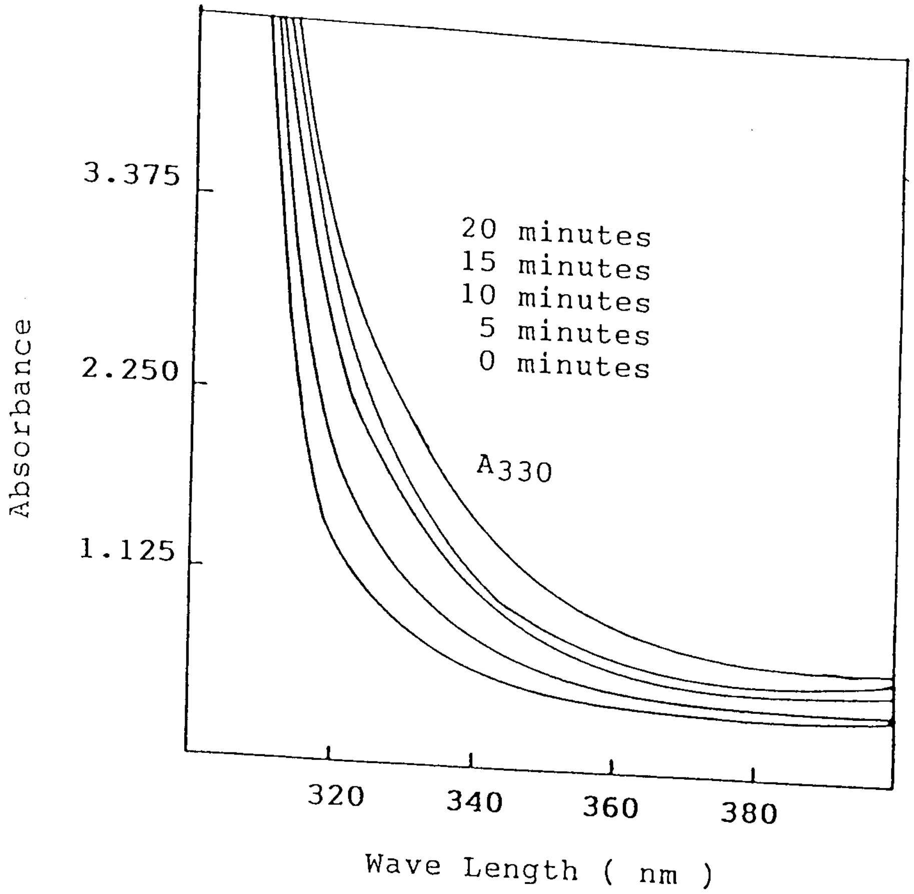


Fig. 2.22 Changes in optical density of polysulphone film during UV irradiation.

Table 1.1 <u>Effect of specimen position on incident UV in UV exposure cabinet (5 minutes exposure).</u>

Specimen position	UV-output (Whm^{-2})	Relative UV (%)
Top	4.14	84.14
Centre	4.92	100
Bottom	3.48	70.7
Mean Value	4.18	

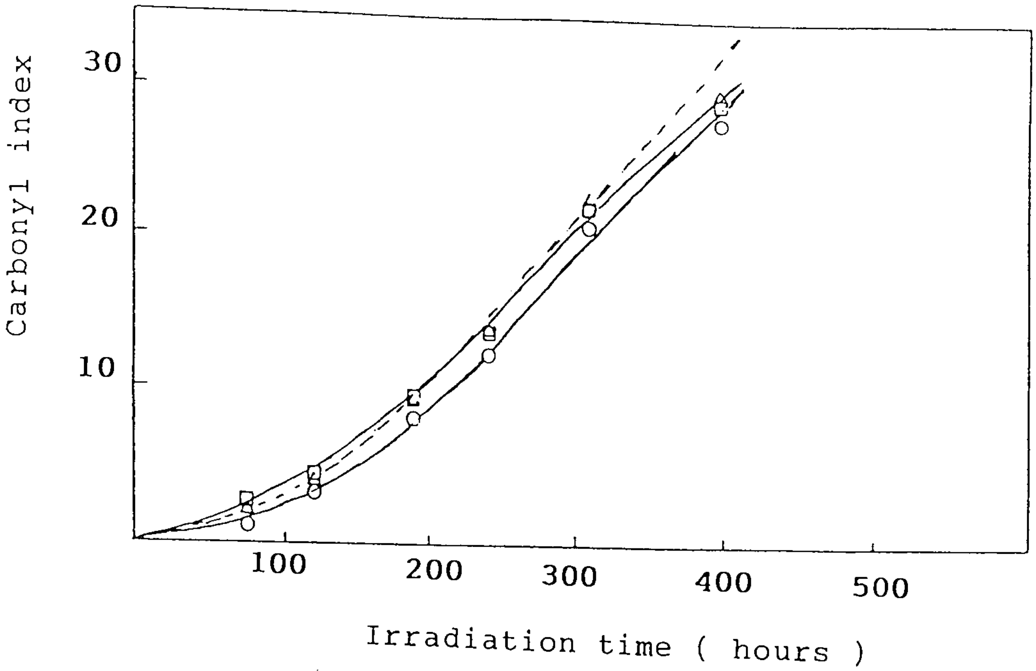


Fig. 2.23 Photo-oxidation of unstabilised LDPE containing 0.05% FeDMC.

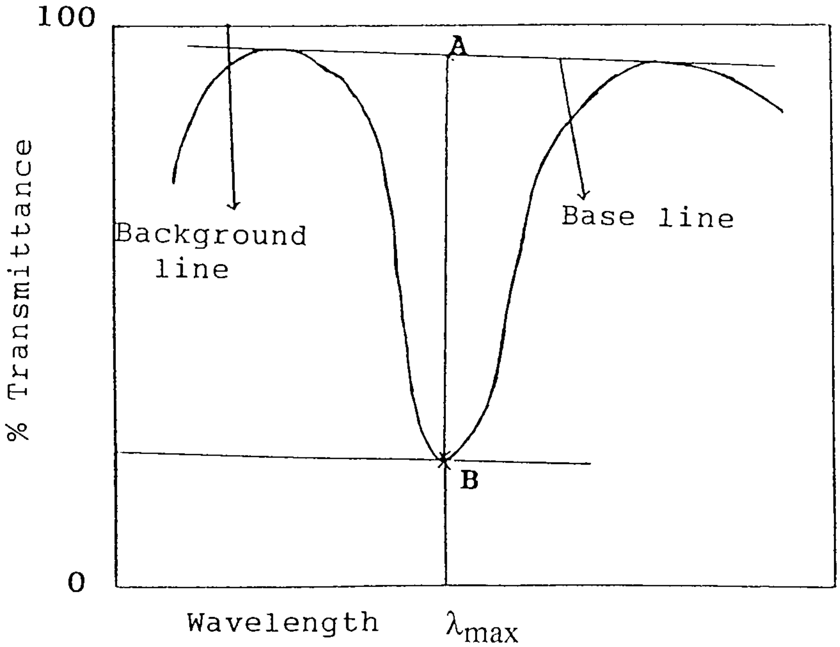


Fig. 2.24 Functional group index measurement by base line technique.

Chapter Three

Photo - oxidation of Unstabilised and Commercial LPDE by Photoactivators alone and with Antioxidants and the Thermal Stabilisation of Unstabilisied LDPE

3.1 Object

The main aim of the work described in this chapter is to obtain LDPE bound photoactivators and a time controlled degradable PE with variable induction periods . The binding efficiency of different photoactivators (FeAc, soluble form ; FeTp) in the absence and presence of peroxide (Trigonox 101) and coagent (TMPTA) in unstabilised LDPE was investigated . The photo - oxidative stability of unstabilised LDPE in the presence of different photoactivators with and without antioxidant was investigated . Various concentrations of antioxidants were used to obtain variable induction periods .

Good pro - oxidants should be good melt and thermal stabilisers, so the melt and thermal stability of photoactivators were measured . The change in mechanical properties of a good photoactivator should be sharp after an induction period . The changes in mechanical properties (e.g . elongation at break) of unstabilised LDPE containing these photoactivators during UV - irradiation were measured . The pro - oxidant effect of different photoactivators in commercial LDPE was also examined . The effect of an iron containing photoactivator (FeDNC) on a non - iron containing photoactivator (Metone A or Metone M) was examined in both unstabilised and commercial LDPE . To show the effect of pro - oxidant on the antioxidant present in commercial polymer , two different grades of commercial LDPE

(Riblene CF 2203 and BP) were used . The effect of ZnDNC on the photostability of commercial LDPE (Riblene CF 2203) containing different photoactivators was also investigated . For different investigations , the insoluble form of FeAc have been used except where mentioned , the soluble form of FeAc was used .

5% masterbatches of different pro - oxidants were made in LDPE with and without peroxide . These were diluted to different concentrations and the photoactivation effect was evaluated . Usually the samples were processed for 10 minutes in a closed chamber of a torque rheometer at 160°C and pressed into thin films (2×10^{-3} cm) at the same temperature . Film samples of comparable thickness were exposed in the UV cabinet and their spectral changes and ultimately embrittlement times were examined .

3.2 RESULTS AND DISCUSSIONS

3.2.1 Effect of initiator on the processing history of unstabilised LDPE containing different photoactivators

5% masterbatches of FeAc (insoluble) and FeCr in LDPE were processed with and without peroxide (160 ° C , 10 minutes) . Three different molar ratios of peroxide (DCP / FeAc) , 0 .032 , 0 .064 and 0 .128 were used . Torque changes during the processing were followed . Fig. 3.1 shows the developement of torque during processing of LDPE containing 5% of FeAc without and with varying concentration of peroxide . It is clear that when FeAc was processed in the absence of initiator (Fig. 3.1, curve 1) no trough or peak was evident in the torque curve and the torque levelled off at the end of processing to a lower value than the PE control (Fig . 3 . 1 , control and curve 1) . While the presence of an initiator (DCP) resulted in the appearance of a trough and a peak under the same processing conditions (see Fig . 3 . 1 , curves 2 and 3) . However , using a higher concentration of peroxide (0.128 molar ratio) lead to the torque value to increase constantly after an initial decrease (Fig. 3.1, curve 4) . FeCr samples (Fig. 3.2) followed the similar pattern to that of FeAc samples except at the higher concentration of peroxide (0.128 molar ratio) the final torque value did reduce although it still remained at a high level (Fig 3 . 2 , curve 4).

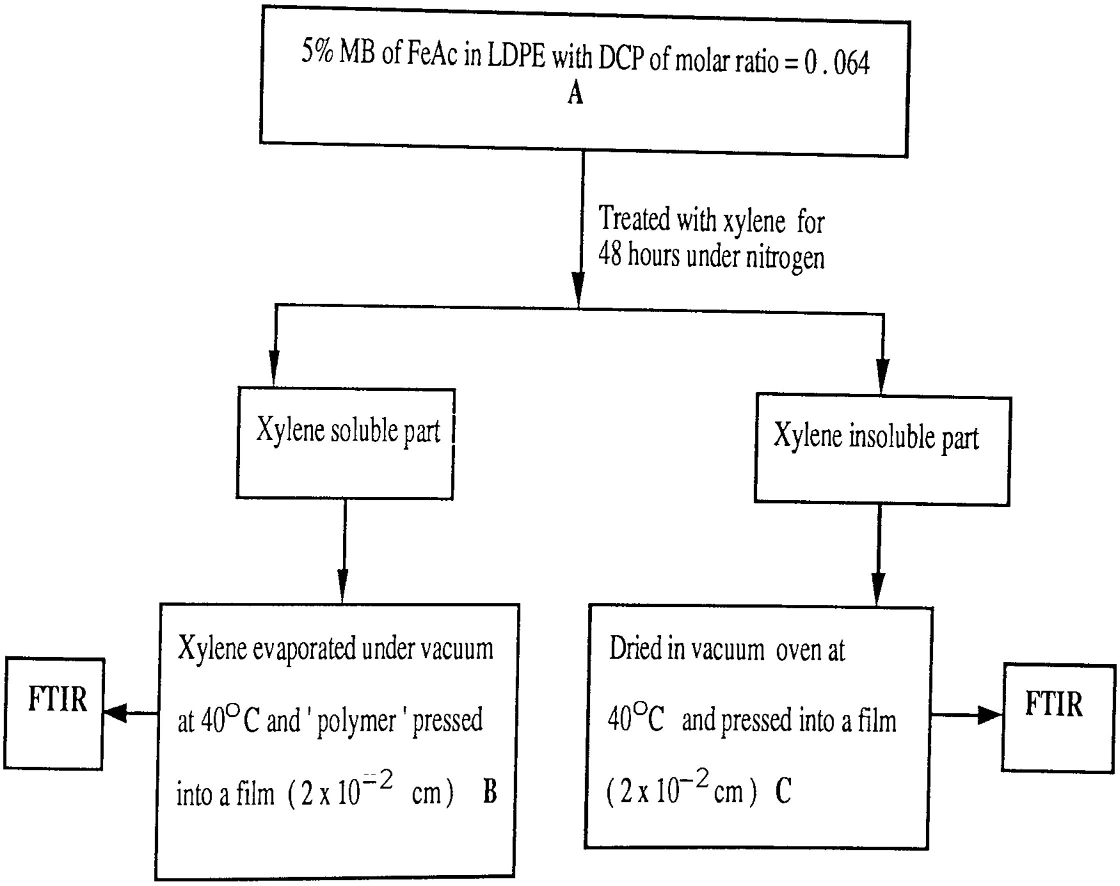
Masterbatches (5 %) containing soluble FeAc were also prepared using initiator (Trigonox 101) and co - agent (TMPTA) and the torque was followed (Fig . 3 . 3) . Again when masterbatches were processed in presence of peroxide and co - agent , the torque showed a trough and a peak (Fig . 3 . 3 , curve 3 and 5) with higher final torque values compared to control and to masterbatch containing no peroxide .

The maxima in the torque curve observed when FeAc is processed in PE in presence of peroxide may be due to some crosslinking of the polymer or the additive and polymer . The higher final torque values at higher peroxide concentrations (e . g . Fig . 3 . 1 , curve 3) suggest that some of the crosslinked material persists in the polymer . The extent of crosslinking must be very high at higher peroxide concentration (e . g . , Fig . 3 . 1 , curve 4) such that the torque curve did not come down .

Similarly in the case of FeAc (soluble) the higher torque values shown when sample was processed with peroxide and co - agent may be due to a similar cross linking reaction which is also reflects in the MFI values (see section 3 . 2.2 , Table 3 . 3) .

3.2.2 Assessment of binding of Fe - acrylate in unstabilised LDPE

Fe - acrylate (FeAc , insoluble form) was found to be insoluble in different solvents and was therefore not possible to measure the percentage of binding by extraction . However , the treatment of 5% masterbatch of FeAc without peroxide in LDPE with xylene for 48 hours left no residue in the extraction thimble but the treatement of 5% masterbatch of FeAc in LDPE with 0.064 and 0.128 molar ratio of DCP left behind 40% and 45% of gel respectively . The colour of the gel was dark red and the xylene extract was almost colourless . To understand the mechanism of binding reaction , xylene soluble and insoluble portion of 5% MB of FeAc in LDPE processed with 0. 064 molar ratio of peroxide were analysed (see flow chart 3. 1).



Flow chart 3 . 1

Fig . 3 . 4 shows the FTIR spectra of FeAc alone (1) (KBr disc) , 5% masterbatch of FeAc in LDPE without peroxide (2) and 5% masterbatch of FeAc with (0 . 064 molar ratio of DCP , 3) . Comparing spectrum (1) of FeAc with processed FeAc in presence of peroxide (3) shows that the unsaturation peak (1587 cm^{-1}) disappeared and a new peak at 1713 cm^{-1} appeared . Treatment of this MB with xylene for 48 hours shows that the appearance of the spectrum of the xylene insoluble portion (C , see flow chart 3 . 1) remains the same (Fig. 3 . 5 , spectrum 3) . However , the spectrum of the xylene soluble portion (B , flow chart 3 . 1 ; Fig. 3 . 5 , spectrum 1) shows a different appearance from that before treatment with xylene or with the xylene insoluble portion . In this case the peak for ester carbonyl (1646 cm^{-1}) has completely disappeared and the vinyl unsaturation peak (1603 cm^{-1}) of the compound was present .

The peak at 1713 cm^{-1} in 5% masterbatch with and without peroxide may be due to some decomposition of the compound to acrylic acid which in the presence of peroxide may be polymerised and hence can not be extracted with xylene . Since in the spectrum there is a peak for ester carbonyl (1646 cm^{-1}) it may be assumed that all the compound did not decompose . The absence of vinyl unsaturation (1587 cm^{-1}) indicates the binding of the compound through a double bond . The xylene soluble portion (Fig . 3 . 5 , curve 1) shows a peak for acid carbonyl (1709 cm^{-1}) and vinyl unsaturation (1603 cm^{-1}) . The absence of ester carbonyl at 1646 cm^{-1} in this spectrum again suggests the formation of acrylic acid .

To find out whether any polymerisation of acrylic acid (decomposition product of FeAc) takes place during processing in the presence of peroxide , 5% MB of acrylic acid in LDPE was also prepared . Fig. 3 . 6 compares segments of IR spectra of 5% MB of polyacrylic acid and 5% MB of acrylic acid (DCP / FeAc) -

molar ratio = 0 . 005 of peroxide . The spectra were found to overlap with each other . So it can be concluded from the above discussion that FeAc does bind to the polymer through double bond and part of the compound may polymerise in the presence of peroxide which then can bind to the polymer backbone and part of the compound can decompose to acrylic acid .

GPC measurements of these samples were made . It was observed that number average molecular weight ($\bar{M}n$) (Fig . 3 . 7) and weight average molecular weight ($\bar{M}w$) (Fig . 3 . 8) reduced in the presence of peroxide compared to masterbatches without peroxide . This may be due to chain scission caused by the peroxide . The xylene insoluble portion (gel) of 5% MB with peroxide shows an increase both in $\bar{M}n$ and $\bar{M}w$ compared to the parent masterbatch containing peroxide . This indicates the formation of crosslinked polymer of high molecular weight . However , the distribution (Fig . 3 .9 and 3 . 10) of this sample (gel) reduced slightly compared to the original masterbatch with peroxide . The xylene soluble portion of the masterbatch with peroxide shows the reduction in all the properties which indicates that this contains the lower molecular weight portion of the masterbatch which is extractable by xylene .

Iron acrylate discussed above was insoluble so direct measurement of binding was not possible . Hence by modifying the procedure for the synthesis of iron acrylate an organosoluble iron acrylate was obtained . The compound was processed with peroxide and interlinking agent . The binding efficiency was measured after extraction with acetone . Table 3 . 1 shows the binding efficiency of FeAc (soluble , based on measurement of absorption at 1641 cm^{-1}) . It was observed that with an increasing amounts of peroxide binding also increased . The combination of peroxide and interlinking agent was also found to be effective for binding . However , with the addition of both peroxide and the interlinking agent the polymer suffers from degradation which was indicated in MFI changes (Table 3 . 1) . With high amounts of peroxide and interlinking agent the MFI could not be measured because the samples did not flow through the die .

Fig 3 . 11 compares the FTIR spectra of FeAc (soluble , KBr disc , curve 1) , 5% MB of FeAc with (curve 3 and 4) and without peroxide (curve 2) . It appears from the figure that 5 % MB of FeAc (curve 2) without peroxide has a new peak at 1724 cm $^{-1}$ compared to FeAc alone (KBr disc , curve 1) . The peak at 1724 cm $^{-1}$ was found to increase in samples processed with peroxide (curve 3 and 4) and remains in the polymer even after extraction with acetone (Fig 3 . 12 , curve 1 and 2).

Table 3 .1 **% of Binding of FeAc (Soluble) in unstabilised LDPE (Total concentration of FeAc + TMPTA = 5%) .**

% of FeAc (Soluble) (W / W)	% of TMPTA (W/ W)	Peroxide concentration (Trigonox 101/ FeAc + TMPTA) - molar ratio	% Binding	MFI g / 10 mins .
Processed LDPE	-	-	-	0 . 550
5	-	-	35	0 . 184
5	-	0 . 01	40	0 . 130
5	-	0 . 05	50	0 . 015
5	-	0 . 1	64	0 . 007
4	1	-	37	0 . 188
4	1	0 . 005	45	0 . 130
4	1	0 . 01	63	0 . 100
4	1	0 . 06	67	*
4	1	0 . 1	69	*

*Samples did not flow through die.

3.2.3 Evaluation of Binding of Fe - thiopropionate in Unstabilised LDPE

Masterbatches (5%) of Fe - thiopropionate (FeTp) in LDPE with and without peroxide were prepared . Binding of these masterbatches was measured (based on measurement of absorption at 1698 cm^{-1}) by extraction with methanol for 48 hours . Results of binding are shown in Table 3.2 . Further increase of peroxide did not increase the level of binding instead it decreased . However , the use of an interlinking agent (TMPTA) increased the level of binding to a considerable extent . To get a high level of binding the amount of interlinking agent required was high .

Table 3.2 % of binding of Fe-thiopropionate (Total concentration of FeTp + TMPTA = 5%) in unstabilised LDPE

% of Fe - thiopropionate	% of TMPTA (W / W)	Peroxide conc. (Trigonox 101/ FeTp + TMPTA) - molar ratio	% Binding
5	-	-	22
5	-	0.03	39
5	-	0.15	55
5	-	0.20	45
3	2	0.15	88

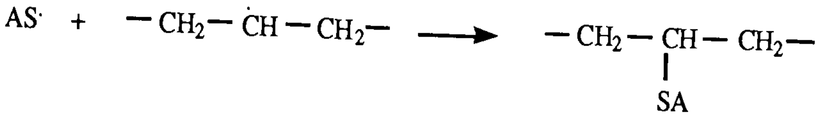
The FTIR spectra of 5% masterbatch of FeTp in LDPE without peroxide before and after extraction with methanol are shown in Fig . 3 . 14 . It is clear that the extraction removed some of the pro - oxidant , because the intensity of the peak due to carbonyl absorption at 1698 cm^{-1} reduced after extraction . Fig . 3 . 15 shows the FTIR spectra of 5% masterbatch of FeTp in LDPE with peroxide of

(Trigonox 101 / FeTp + TMPTA) - molar ratio = 0.15 and with TMPTA of 2% before and after extraction . From the spectra it is evident that in this case high levels of binding takes place . The binding mechanism can be described as follows (Reaction 3 . 1 - 3 . 4) :

$$\mathrm{ROOR} \longrightarrow 2\mathrm{RO}\cdot \qquad (3.1)$$

$$\mathrm{RO}\cdot + -\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}- \longrightarrow -\mathrm{CH_2}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH_2}- \qquad (3.2)$$

$$\mathrm{RO}\cdot + \mathrm{ASH} \longrightarrow \mathrm{AS}\cdot + \mathrm{ROH} \qquad (3.3)$$



$$\mathrm{AS}\cdot + -\mathrm{CH_2}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH_2}- \longrightarrow -\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{SA}}}{\mathrm{CH}}-\mathrm{CH_2}- \qquad (3.4)$$

It is assumed that at the processing temperature the peroxide decomposes to an alkoxyl radical . This radical can abstract a hydrogen atom from the polymer backbone and also from the compound to form a thiyl radical (AS ·) . Hence the binding of FeTp should be through this thiyl radical to the polymer radical . If the spectra 1 and 2 in Fig . 3 . 13 is compared it is found that the absorption due to the -SH group has disappeared , when the compound is processed with LDPE . In the presence of a co - agent (TMPTA) and initiator the binding also takes place through the double bond of the co - agent . In this case there are different possibilities . The compound may be bound through the thiyl group to the double bond of the co - agent which then subsequently becomes bound to the polymer backbone . The co - agent can becomes directly bound to the polymer backbone . The compound alone can also bind to the polymer backbone . So in this case a mixture of products could be formed.

Without peroxide the rate of reaction is slow because in this case the thiyl radical is formed by mechanochemical shear only . In the presence of peroxide the rate of reaction is fast , so the binding level is also increased . However , in the presence of a co- agent and initiator the rate of reaction increases compared to the initiator alone . Hence in this case a high level of binding is obtained .

3.2.4 Effect of Varying the concentration of different photoactivators on the photo - oxidative degradation of unstabilised LDPE

The masterbatches (5% ,w/w) of different pro - oxidants in LDPE were prepared without peroxide at 160 ° C for 10 minutes . These masterbatches were diluted to lower concentrations . The effect of varying the concentration of FeTa on photo - oxidative stability of unstabilised LDPE is shown in Table 3 . 3 and Fig. 3.16 . At relatively high concentrations (0.6%, 0.4%, 0.3%) photosensitisation can be achieved after an induction period (150 hours) . At low concentrations (0.025%, 0.05%, 0.1% and 0.2%), however , a pro - oxidant effect predominates with a shorter induction period (50 hours) . The behaviour of FeTp (Fig. 3.17) is more or less the same as that of FeTa except at higher concentrations of this additive (0.3% - 0.6) , a band at 1710 cm^{-1} appears which is due to carboxylate which increases with increase of concentration . This peak is also present in the spectrum of the compound itself (Chapter 2, Fig.2.2) before introduction into the polymer . This peak reduced in intensity during subsequent irradiation of the film . For example in the case of additive concentration of 0.6% the carbonyl index dropped from 2.03 to 0.63 after 45 hours . Further irradiation increased gradually the carbonyl formation due to oxidation of the polymer film which was lower than the initial carbonyl index up to 140 hours irradiation . After 230 hours it started to increase (2.14 carbonyl index) above the initial carbonyl index . Fig. 3.18 shows the pro - oxidant behaviour of unstabilised LDPE containing FeMa. At all the concentrations used it showed the least pro - oxidant effect . However , the pro - oxidant effect appeared to be almost concentration independent which may be due to the low solubility of the compound in the host polymer . This compound and all the carboxylate compounds except FeTp and FeAC (soluble form) were found to be essentially insoluble in different organic solvents . FeAc (Fig . 3 . 19)

Table 3 . 3 **Effect of varying the concentration of photoactivators in photo-oxidative activity of unstabilised LDPE . (Samples are diluted from 5 % masterbatches containing no peroxide processed at 160°C for 10 minutes) .**

	Photoactivator Concentration (g / 100 g)						
Samples	0 . 025	0 . 05	0 . 1	0 . 2	0 . 3	0 . 4	0 . 6
	Embrittlement time (hrs .)						
LDPE Control	1650						
FeTa	900	900	930	955	980	1000	1050
FeTp	925	1050	925	900	980	1020	1430
FeDMC	900	560	705	730	730	830	3500
FeAc	915	865	780	700	700	600	350
FeMa	1040	985	960	865	960	910	865
FeCi	1340	1300	1220	1010	915	870	725
FeCr	1340	1340	1220	1070	840	840	890

behaved quite differently from the above mentioned pro - oxidants . It showed a pronounced pro - oxidant effect at all concentration used and also it was much more concentration dependent . The pro - oxidant activity of this compound increased as the concentration of the additive increased . However , it was not inert during processing since substantial amounts of carbonyl was present at the end of the processing operation at higher concentrations . The pro - oxidant effect of this compound during processing is demonstrated in the initial carbonyl index in the fabricated film (Table 3 . 4 , Fig. 3 . 19) . FeCr showed the same pattern as FeAc except that it has a lower pro - oxidant effect (Fig . 3 . 20) .

An organosoluble FeAc was also prepared . The compound was bound to the polymer backbone . Masterbatch (5 %) was prepared with peroxide of (T101/FeAc+ TMPTA)-molar ratio = 0.06 and interlinking agent of (1%). Masterbatch without peroxide was also prepared . Both masterbatches were

Table 3.4 Initial carbonyl indices formed during processing in unstabilised LDPE containing different pro - oxidants at various concentrations (samples are diluted from 5 % masterbatches processed at 160^{o}C for 10 minutes).

Samples	Photoactivator Concentrations (g / 100 g)						
	0.025	0.05	0.1	0.2	0.3	0.4	0.6
	Initial Carbonyl Index						
Control	0. 23						
Fe - thioacetate	0. 12	0.12	0.12	0.12	0.12	0.25	0.07
Fe - thiopropionate	0. 10	0.08	0.12	0.25	0.87	0.63	2.03
Fe -DMC	0. 12	0.12	0.12	0.12	0.12	0.12	0.12
Fe - acrylate (Insoluble)	0. 11	0.22	0.22	0.78	0.89	1.00	1.00
Fe -maleate	0. 11	0.11	0.11	0.11	0.11	0.11	0.11
Fe - cinnamate	0. 11	0.11	0.11	0.11	0.11	0.11	0.11
Fe - crotonate	0. 11	0.11	0.11	0.11	0.11	0.11	0.11

diluted and the polymer films were irradiated in the UV - cabinet to examine the photoactivation effect . The results are shown in Table 3 . 5 . The compound showed pro - oxidant effect at the concentration used (0 . 2 %) . The same effect is also observed in extracted sample .

Fig. 3 . 21 shows the effect of concentration of FeCi on the photo - oxidation of unstabilised LDPE . This compound has similar photodegradation behaviour to FeAc . However , it is less concentration dependent compared to FeAc which suggesting a lower solubility of the compound in the polymer . In comparison to FeAc this must be more oxidatively stable because the carbonyl index at all concentrations remained constant .

The iron complex based on sulphur chelate (Fe - DMC , which was used as control) is completely different from the above mentioned

Table 3 . 5 **Effect of FeAC (soluble)on the photo - oxidation of unstabilised LDPE (concentration of the additive= 0.2 %).**

% of FeAc (soluble) (W / W)	% of TMPTA (W / W)	Peroxide concentration (Trigonox 101/) FeAc + TMPTA) -molar ratio	Embrittlement time (hrs .) (0 . 2 %)	
			Unextract.	Extract .
5	-	-	700	600
4	1	0 . 06	650	600

photoactivators (Fig . 3 . 22) . Results from this work are in agreements with previous work (57) . At low concentration of Fe - DMC a pro - oxidant effect predominates (0.025% - 0.2%) . However , at relatively high concentrations of the compound , photosensitisation can be achieved after a substantial induction period (0.3% - 0.4%) . Further increase of concentration resulted in a photostabilisation effect which was evident from the rate of carbonyl formation compared to control . The embrittlement time for the 0.6% concentrated sample is 3500 hours (Table 3.3). The effect of concentration of different pro - oxidants on the UV life time of unstabilised LDPE were compared in Fig . 3 . 23 . Figs . 3 . 24 and 3 . 25 compares the UV life time of unstabilised LDPE containing different pro - oxidants at two different concentrations (0 . 05 % and 0 . 2 % respectively) . At lower concentration (0 . 05 %) a commercial antioxidant photoactivator (FeDMC) shows mostly a pro-oxidative behaviour whereas at higher concentration (0 . 2 %) FeAc (insoluble) found to show comparable photoactivation effect to that of FeDMC . FeAc (soluble) was also gave comparable photoactivation effect to FeDMC at this concentration (0 . 2 %) both in nonextracted and extracted conditions (Table 3.5) .

Mellor , Moir and Scott (47) observed that the photo - activation of iron stearates are due to radical formation by reactions 3 . 5 - 3 . 6 as follows

$$(C_{17}H_{35}COO)_3Fe \xrightarrow{h\upsilon} C_{17}H_{35}COO\cdot + (C_{17}H_{35}COO)_2Fe \qquad (3.5)$$

$$C_{17}H_{35}COO\cdot \longrightarrow C_{17}H_{35} + CO_2 \qquad (3.6)$$

which in the presence of the oxygen generates more hydroperoxide to accelerate the rate of degradation of polymeric material. Japanese workers (120) also found the pro - oxidant effect of iron stearate. Amin and Scott (39) reported the pro -oxidant behaviour of metal acetylacetonate and showed the decomposition of these complexes during both thermal and UV irradiation stages. The higher the concentration of these complexes in the polymer , the higher is the concentration of sensitiser species generated during decomposition of the complexes and hence the faster is the rate of oxidation . FeAc (insoluble form) studied in this investigation behaved quite similarly to metal acetylacetonates and other metal carboxylates at higher concentrations (> 0 . 2%). At lower concentrations (< 0 . 2%) the initial carbonyl index remained the same as the control but at higher concentrations it increased (Table 3 . 4) . The MFI value of 0. 05% concentrated sample was found to be comparable with that of LDPE control hence the possibility of using this compound at the lower concentration level as a photosensitiser. In practice photosensitisers are used in lower concentrations to obtain a photodegradable polymer.

The mechanism of the pro - oxidant effect of the compounds used in this work seems to be the same as other hydroperoxide decomposers by the redox reactions 3 . 7 - 3 .8 .

$$ROOH + M^{+2} \xrightarrow{h\upsilon} RO\cdot + \cdot OH + M^{+3} \qquad (3.7)$$

$$ROOH + M^{+3} \xrightarrow{h\upsilon} ROO\cdot + H^{+} + M^{+2} \qquad (3.8)$$

It is now a well known fact that all transition metal dithiocarbamate complexes are good thermal and UV stabilisers due to their ability to destroy hydroperoxides in a non - radical process (47, 67, 121, 122) . However , iron dithiocarbamates show a pro - oxidant effect at lower concentration whereas at higher concentration they act as a stabiliser similar to other metal dithiocarbamates . The pro - oxidant effect of the iron complex appears to be associated with its much lower photostability than the other complexes . At lower concentrations most of the complexes are utilised to decompose hydroperoxide . It has been suggested that the thiocarbomyl radical as well as the free transition metal ion is involved in the photo - activation process (47, 55) .

3 . 2 . 5 Effect of initiator on the photo - oxidation of unstabilised LDPE containing different photoactivators .

Polyethylene masterbatches (5 %) processed with radical generator were diluted to 0.2 % concentration and the photoactivation behaviour of these diluted samples containing peroxide were compared with a sample processed without initiator . Carbonyl formation was followed during UV irradiation and the embrittlement time of these samples are compared in Table 3 . 6 and Fig . 3 . 28 . From the table it is clear that with higher concentrations of initiators the rate of photo - oxidation of LDPE containing FeTa decreased . FeAc (Fig . 3 . 26) behaved similarly . In case of FeTp samples containing initiator show slightly lower photostability compared to the sample without initiator . FeMa , FeCi and FeCr (Fig . 3 . 27) follow the same pattern as FeTp but the effects are much more pronounced in these cases .

Table 3 .6 Effect of peroxide concentration on the photo - oxidation of LDPE containing different pro - oxidants (concentration of additives = 0 . 2%) .

Additives	Peroxide Concentration		Embrittlement time (hrs .)
	(I / P_o) - molar ratio	g / 35 g	
LDPE Control			1650
FeTa	0.000	0.000	955
	0.032	0.070	955
	0.064	0.140	1050
	0.128	0.280	1100
FeTp	0.000	0.000	900
	0.030	0.040	850
	0.100	0.136	850
	0.150	0.205	820
FeAc (Insoluble)	0.000	0.000	700
	0.032	0.070	960
	0.064	0.140	960
	0.128	0.280	1035
FeMa	0.000	0.000	865
	0.032	0.070	820
	0.064	0.140	820
	0.128	0.280	800
FeCr	0.000	0.000	1070
	0.032	0.070	840
	0.064	0.140	715
	0.128	0.280	700
FeCi	0.000	0.000	1010
	0.032	0.070	955
	0.064	0.140	910
	0.128	0.280	885

I = Initiator , P_o = Pro - oxidant . DCP were used in all masterbatches except FeTp where Trigonox 101 was used .

3 . 2 . 6 Effect of processing conditions on the photo-oxidative and melt stability of LDPE with and without pro - oxidants .

Masterbatches (5%) of different pro - oxidants in unstabilised LDPE without peroxide were diluted to 0.05 % concentration . Both the processing conditions (close mixing , open mixing) and the time of processing (10 min. , 20 min . , 30 min . ,) were varied . Fig . 4 . 29 - 3.33 and Table 3 . 7 show the effect of processing conditions on the photo - oxidation of LDPE with different photo activators . Severe processing conditions reduced the lifetime of LDPE alone and LDPE containing pro - oxidants . However , the embrittlement times for the samples processed in closed chamber for different times (10 min . , 20 min . , 30 min .) did not vary much . In case of FeDMC prolonged processing time (30 min ., CM) in fact increaseed the stability of the polymer . Polymers containing FeDMC (57) and FeTp do not show drastic changes in photo - oxidative stability under severe oxidation conditions . The effect of processing severity on photo - oxidation of LDPE film containing FeTa , FeAc , FeMa etc . was pronounced (30 min . OM , 40 min . OM) . In these cases severe processing caused the oxidation of the polymer during processing as evidenced by the high initial carbonyl index value after processing . Carbonyl formation during the early stages of photo - oxidation was enhanced due to the thermal oxidation during processing .

Table 3 . 7 Effect of processing conditions on the UV lifetime of LDPE containing different pro-oxidant (concentration of additives 1.25 x 10^{-4} mole / 100 g , (0. 05 %)

	Embrittlement time (hrs .)						
Processing conditions	10 minutes CM*	 OM*	20 minutes CM*	 OM*	30 minutes CM*	 OM*	40 minutes OM*
Control	1650	1550	1550	1500	1500	1400	1310
Fe - DMC	560	520	520	520	870	500	500
Fe Ta	900	900	900	855	900	810	720
FeTp	1100	1080	1100	1070	1100	1050	1050
FeMa		985		900		880	800
FeAc(Ins.)		840		700		700	650
FeCi		1300		1130		1100	900
FeCr		1300		1300		1130	1080

CM* = Close mixing ; OM* = Open mixing

The effect of photoactivators on the melt stability of unstabilised LDPE, as measured by change in the melt flow index, is shown in Fig . 3 . 34. It is clear that the thermal oxidation was completely inhibited during processing in the presence of FeDMC and FeTp . FeTa had an accelerating effect on the oxidation of polyethylene . Other photoactivators slowed down but did not inhibit thermal oxidation during severe processing conditions (30 min . , OM ; 40 min . , OM) compared to the control .

The effect of the same additives on the oxidative stability of LDPE during processing as measured by the formation of carbonyl index is shown in Fig . 3 . 35 . It follows more or less the same pattern as the melt flow index change . It is clear that FeDMC and FeTp had a melt stabilising effect on LDPE at the concentration used (0.05 %) . Over a period of 40 minutes processing at 160^{o} C in an open mixer , the initial carbonyl index of the polymer remained sensibly constant . Whereas FeTa caused considerable oxidation to the polymer during same processing time compared to control . The stabilising effect of other photoactivators on the oxidative stability of LDPE during processing was only minor compared to FeDMC and FeTp .

It has been observed that (24, 123) severe processing conditions e . g . processing in presence of excess oxygen and prolonged processing time produces a larger amount of hydroperoxide compared to the samples processed under mild conditions . It is well established that hydroperoxides plays a key role for the thermal and photo - oxidation of LDPE (24, 39, 47) . So any additives which can remove hydroperoxide by an ionic mechanism can act as an effective melt stabiliser during processing . Those which accelerate the decomposition of peroxide into radicals will be effective photoactivators . Metal dithiocarbamate destroy hydroperoxide by an ionic catalytic mechanism (54, 67, 80, 124) . Thus unstabilised LDPE containing

1 . 25 x 10^{-4} mole / 100 g. of FeDMC or FeTp did not show the decrease of MFI value or initial carbonyl index value during severe processing conditions . These compounds therefore act by removing hydroperoxides formed during processing . In case of FeTa increasing processing severity decreased the MFI value and increased the initial carbonyl index value which corresponds to the formation of more hydroperoxides during processing compared to LDPE control . So , this compound had not any ability to destroy hydroperoxide during severe processing conditions . In fact , probably it decomposed peroxide into free radicals which accelerate the destruction of the polymer . This has been observed by other workers in the case of transition metal stearates and halides (18 , 123) . The MFI values and the initial carbonyl index of the other pro - oxidants under the severe processing conditions remained less than that of control indicate that they may destroy hydroperoxide or their decomposition product to certain extent at the concentration used (0 . 05%) .

Scott and Chakraborty (23 , 123) found a linear relationship between initial hydroperoxide concentration and the initial photo - oxidation rate during the photo - oxidation of polyolefins . The hydroperoxide formed during processing can initiate photo - oxidation of the polymer . Polymers containing FeDMC and FeTp did not show much change in photostabilising action on exposure to UV light with increasing processing severity . This is consistent with the observation (54 , 67 , 80 , 124) that these compounds remove hydroperoxide formed during processing and during the early stages of photo - oxidation on UV exposure . Other photoactivators like FeTa , FeAc probably could not destroy hydroperoxide in the severe processing conditions and therefore showed less photostability .

3 . 2 . 7 Effect of two component systems on the photo - oxidation of unstabilised LDPE : Combination of different pro - oxidants with antioxidant .

Masterbatches (5 % w / w) of both the pro - oxidant and antioxidant were prepared in unstabilised LDPE which were then diluted to corresponding concentrations . In the case of FeAc (insoluble) and FeCr samples were diluted from 5% masterbatches containing peroxide of (initiator / pro - oxidant) - molar ratio = 0.128 .

Fig . 3 . 36 shows the variation of ZnDEC concentration on the photo - oxidation of unstabilised LDPE containing 0 . 2% of FeAc . It is found that an increase in ZnDEC concentration in combination with a fixed concentration of FeAc (0. 2%) resulted in the decrease in stability of LDPE . However , lower concentrations of ZnDEC (< 0 . 1%) increased the stability of LDPE . Fig . 3 . 37 shows the variation of FeAc concentration on the photo - oxidation of unstabilised LDPE in the presence (+) and absence (-) of 0 . 025 % ZnDEC . At this lower concentration of ZnDEC a stabilisation effect was observed with all combinations . In these cases no induction period have been obtained due to the use of ZnDEC . The same behaviour was observed in case of FeCr (Fig . 3 . 38 and 3 . 39) . At the lower concentration of ZnDEC (< 0 . 1%) in combination with FeAc or FeCr , no interaction between antioxidant and pro - oxidant taken place but above the critical concentration (> 0 . 05%) of ZnDEC in the combination antagonistic behaviour predominated .

Fig . 3 . 40 and Fig . 3 . 41 show the effect of variation of FeTp concentration in combination with a fixed concentration of Zn DEC (0 . 1 % and 0 . 2 %) respectively . Samples without ZnDEC were also compared . The rate of

Table 3 . 8 Effect of two component systems on the photo -oxidation of unstabilised LDPE .

Samples	Concentrations (% , w / w)	Embrittlement time (hrs.)
LDPE control		1650
Fe - acrylate + ZnDEC	0 . 2 + 0 . 2	885
	0 . 2 + 0 . 2	885
	0 . 2 + 0 . 05	1075
	0 . 2 + 0 . 025	1075
	0 . 2 + 0 . 01	1195
	0 . 4 + 0 . 025	985
	0 . 3 + 0 . 025	1075
	0 . 2 + 0 . 025	1075
	0 . 1 + 0 . 025	1310
	0 . 05 + 0 . 025	1380
	0 . 025 + 0 . 025	1425
Fe - crotonate + ZnDEC	0 . 2 + 0 . 2	650
	0 . 2 + 0 . 1	650
	0 . 2 + 0 . 05	700
	0 . 2 + 0 . 025	785
	0 . 2 + 0 . 01	785
	0 . 4 + 0 . 025	485
	0 . 3 + 0 . 025	532
	0 . 2 + 0 . 025	720
	0 . 1 + 0 . 025	885
	0 . 05 + 0 . 025	885
	0 . 025 + 0 . 025	985
ZnDEC	0 .05	1700
FeDNC	0 . 05	600
FeDNC + Metone M	0 . 05 + 0 . 05	600
FeDNC + Metone A	0 . 05 + 0 . 05	670
ZnDNC	0 . 05	1800
ZnDNC + Metone M	0 . 05 + 0 . 05	1350
	0 . 1 + 0 . 05	1470
ZnDNC + Metone A	0 . 05 + 0 . 05	1470
	0 . 1 + 0 . 05	1470
	0 . 1 + 0 . 025	1470
Metone M	0 . 05	1300
Metone A	0 . 05	1350

carbonyl formation in samples containing ZnDEC were found to be lower than samples without ZnDEC . So the pro - oxidant effect of FeTp is decreased by addition of ZnDEC . Here ZnDEC acts as usual as an antioxidant . But the rate of photo - oxidation in the combination was higher than the ZnDEC alone because of the presence of FeTp which rendered its pro - oxidant behaviour in combination .

Fig . 3.42 shows the variation of ZnDEC concentration in combination with a fixed concentration of FeTa . It is clear that with the increase of ZnDEC concentration the rate of oxidation increased . Figs. 3.43 - 3.45 show the variation of FeTa concentration on the photo-oxidation of polyethylene containing a fixed concentration of ZnDEC . These were compared with samples without ZnDEC. In every case the photo - oxidation of LDPE was higher with ZnDEC compared to samples without ZnDEC .

Table 3.8 also shows the effect of FeDNC and ZnDNC on the photo-oxidation of Metone A and Metone M . Addition of ZnDNC with Metone A or Metone M did not show any pronounced effect on the photoactivity of the polymer . However addition of FeDNC with Metone A or Metone M resulted in photosensitisation of the polymer compared to either Metone A and Metone M alone . To find out which of these additives causes the sensitisation , a mixture of Metone A and FeDNC in hexane was irradiated in a quartz tube and changes in UV absorption were monotored . This was compared to results obtained from similar experiments carried out with Metone A and FeDNC seperately .

Figs. 3 . 46 and 4 . 37 show the ultraviolet spectra of FeDNC (3 . 2 x 10^{-5} mole litre $^{-1}$) and Metone A (5 x 10^{-5} mole litre $^{-1}$) respectively . Fig. 3.48

shows the change in the ultraviolet spectra of 3 . 2 x 10^{-5} mole litre $^{-1}$ of FeDNC in hexane during UV irradiation . The peak at 347 nm completely disappeared after 1 hour irradiation and the peak at 264 nm (ε_{264} = 5 x 10^{4} litres mole^{-1} cm^{-1}) also decreased during UV - irradiation and ultimately disappeared . Fig . 3 . 49 shows the change in the spectra of 5 x 10^{-5} mole litre $^{-1}$ of Metone A in hexane during UV - irradiation . Metone's main absorption at 252 nm (ε_{252} = 2.5 x 10^{4}) increased during UV - irradiation . Fig . 3 . 50 shows the change in the spectra of a mixture of Metone A and FeDNC (2 . 5 x 10^{-5} mole litre $^{-1}$ + 1 . 6 x 10^{-5} mole litre $^{-1}$) in hexane . The absorption maxima of Metone A at 252 nm and of FeDNC at 264 nm appeared as a single absorption peak at 254 nm in the combination . The intensity of this peak gradually decreased during UV - irradiation . After 28 hour of irradiation this peak decreased considerably . Comparing spectra in Figs. 3 . 48 and 3 . 50 show clearly that after 28 hours of irradiation the appearance of both the spectra closely resemble each other . During UV irradiation Metone A alone (Fig . 3 . 49) followed a different pattern . After 28 hours of irradiation the spectrum is completely different from that in combination of Metone A and FeDNC (spectrum 7 in Fig . 3 . 49 and spectrum 5 in Fig . 3 . 50) . Thus, it is FeDNC which is responsible for the photoactivation in the combination of Metone A and FeDNC . So , Metone A has no role in the photoactivation of polymer in the combination of Metone A and FeDNC . It is a mild photoactivator compared to FeDNC .

Fig . 3 . 51 shows the effect of variation of FeDNC concentration on the photo - oxidation of unstabilised LDPE whereas Fig . 3 . 52 shows the same effect in the presence (+) and absence (-) of 0 . 001 % NiDNC . In these combination it is found that with the addition of NiDNC photostabilisation were observed at all concentration of FeDNC except at 0 . 05% compared to FeDNC alone . At higher concentration of FeDNC the addition of NiDNC resulted in the extension of the induction period . The same type of behaviour was observed with other concentrations of NiDNC (0 .005% and 0 .01% , Fig . 3 .53 and 3 .54) . The photosensitising effect observed at the lower concentration of FeDNC with the combination of NiDNC in LDPE was confirmed in solution studies . Fig . 3 .55 shows the UV spectrum of NiDNC (1.6×10^{-5} mole litre $^{-1}$) . The characteristic absorption for NiDNC is at 324 nm ($\varepsilon_{324} = 4.1 \times 10^{4}$) . The UV spectrum for FeDNC is shown in Fig . 3 . 46 . A sample containing 1.6×10^{-5} mole litre^{-1} of NiDNC and 3.2×10^{-5} mole litre $^{-1}$ of FeDNC in hexane was irradiated and the change in the ultraviolet spectra were recorded at intervals . The rate of the disappearance of the absorption maxima at 324 nm (for NiDNC) was followed (Fig . 3 . 56) . The rate of disappearance of this peak was found to be faster in case of the combination of NiDNC and FeDNC compared to NiDNC alone . This result supports the result that was found for the polymer sample .

3 . 2 . 8 Effect of pro-oxidant alone and in combination with antioxidant on photo-oxidation of commercial LDPE (Riblene CF 2203) .

Figs. 3 . 57 and 3 . 58 show the effect of different compounds alone and in combination with antioxidant on the photo - oxidation of commercial LDPE . FeDNC showed a photo - pro - oxidation effect at the particular concentration used (0 .05 %) . Metone M did not show any pro - oxidant effect in commercial LDPE . The combination of ZnDNC with Metone M showed a pro - oxidant behaviour compared to Metone M alone . Combination of Metone M with FeDNC reduced the embrittlement time to greater extent (Table 3 . 9) compared to Metone M alone but it remained the same as FeDNC alone . So it was the photoactivity of FeDNC which reduced the embrittlement time of Metone M . This was confirmed in the combination of FeDNC and Metone A (section 3 . 2 . 7) .

Table 3.9 **Effect of ZnDNC on the photo-oxidation of commercial LDPE containing different pro-oxidants.**

Samples	Concentrations (% , w /w)	Embrittlement time (hrs .)
Commercial LDPE		1700
FeDMC	0 . 05	585
FeDNC	0 . 05	600
FeDNC + Metone M	0 . 05 + 0 . 05	600
FeAc + Zn DNC	0 . 05 + 0 . 05	655
FeAc (Insoluble)	0 . 05	775
Metone M	0 . 05	1700
Metone M + ZnDNC	0 . 05 + 0 . 05	1400
FeTa	0 . 05	825
FeTa + Zn DNC	0 . 05 + 0 . 05	825
FeTp	0 . 05	1255
FeTp + ZnDNC	0 . 05 + 0 . 05	1155

FeAc showed a pro - oxidant behaviour and the combination of ZnDNC increased the rate of photo - oxidation . FeTa and FeTp also showed similar behaviour as FeAc .

The reduction of photostability of LDPE containing different pro - oxidants by the addition of ZnDNC is assumed to be due to the interaction of ZnDNC with the phenolic antioxidant in commercial LDPE . A similar effect was observed in commercial PP (Chapter 4 , Table 4 . 21) . Commercial samples of PP and PE were extracted with hexane and the UV spectra of their extract were compared (Fig . 3 . 59) with that of a phenolic antioxidant (Irganox 1076) . The spectra of the extract are closely related to that of Irganox 1076 suggesting that this was the antioxidant used in the commercial polymer .

With a view to finding whether ZnDNC interacts with the phenolic antioxidant , the UV stability of phenolic antioxidant , Irganox 1076 (0 . 05%) was examined alone and in combination with ZnDNC (0. 05%) in unstabilised LDPE . The UV stability of ZnDNC was found to decrease in presence of Irganox 1076 (Fig . 3 . 60) . The UV stability of ZnDNC (3 . 3 x 10^{-5} mole litre^{-1}) was also followed alone and in combination with Irganox 1076 (9.1×10^{-5} mole litre $^{-1}$) in hexane. Figs. 3 . 61 and 3 . 62 show the UV spectra of Irganox 1076 (4.5×10^{-4} mole litre $^{-1}$) and ZnDNC (3.3×10^{-5} mole litre $^{-1}$) in hexane. The change in the UV spectra of Irganox 1076 (9.1×10^{-5} mole litre $^{-1}$) in hexane is shown in Fig . 3 . 63 . The characteristic peak of Irganox 1076 at 281 nm ($\varepsilon_{281} = 2.2 \times 10^4$) was found to increase in the first 1 hour of irradiation before decaying . After that period the peak gradually decreased and ultimately disappeared . Fig . 3 . 64 shows the change in the UV spectra of ZnDNC (3.3×10^{-5} mole litre $^{-1}$) during UV irradiation . The gradual disappearance of the peak at 263 nm ($\varepsilon_{263} = 5.1 \times 10^4$) with irradiation was recorded . Fig . 3 . 65 shows the change in the UV spectra of Irganox 1076 (9.1×10^{-5} mole litre $^{-1}$) and ZnDNC (3.3×10^{-5} mole litre $^{-1}$) in combination during UV irradiation . The peak at 263 nm was found to decrease with irradiation time and ultimately disappeared . If the Fig . 3 . 64 is compared with Fig . 3 . 65 it is found that the characteristic peak for ZnDNC disappeared faster when used in combination compared to ZnDNC alone .

The disappearance of the absorption band at 263 nm with time of irradiation and the first order plot of decay of absorption maxima in hexane is shown in Fig . 3 . 66 . The result is consistent with that obtained in the polymer system . The UV stability of ZnDNC is decreased and its decomposition rate increased in the presence of Irganox 1076 . Thus it is evident that phenolic antioxidant interact with ZnDNC in the combination system . This may be due to the photolytic destruction of the zinc dithiocarbamate by oxidation products of the phenol leading to a decrease in their effectiveness . The oxidation products of the phenol have been shown to be peroxydienones and stilbenquinones (125) .

3 . 2 . 9 Effect of varying the concentration of different photo - activators on the UV stability of commercial LDPE (BP).

The effect of varying the concentration of FeTp on the photo - oxidative stability of commercial LDPE (BP) is shown in Fig . 3 . 67 and table 3 . 10 . At relatively high concentration of FeTa , photosensitisation can be achieved after a substantial induction period (curve 3 and 5) . This may be the effect of stabiliser in the commercial LDPE . At low concentration however , a pro - oxidant effect predominates (curve 2) . FeTp also shows photosensitising effect at all concentrations used (Fig . 3 . 67) . It seems to be more effective at higher concentration . In this case most photo - sensitising effect was found with the highest concentrated sample (Fig . 3 . 67 , curve 1) .

Table 3 . 10 Effect of varying the concentration of different photo - activators on the UV stability of commercial LDPE (BP).

	Concentration (g / 100 g)		
Samples	0 .05%	0 .10%	0 .20%
	Embrittlement time (hrs .)		
FeTa	960	1150	1200
FeTp	2300	1450	960
Control	2700		

3 . 2 . 10 Effect of different pro-oxidants on the change of elongation at break of unstabilised LDPE .

The loss in the tensile properties of the films under UV irradiation was monitored in accordance with B5 2782 : method 326 C . Masterbatches (5%) of different pro -oxidants were diluted to 0 .2 % and irradiated to observe the change in different physical properties (tensile strength , % of elongation at break) . The results are presented as change in % of elongation at break during UV irradiation . Fig . 3 . 68 illustrates the change in the % of elongation of LDPE containing different pro - oxidants . It is clear that the change in the % of elongation at break in all cases are higher than that of LDPE control . For all samples an induction period (100 hrs) were obtained which is found to be maximum in case of FeDMC . At the end of irradiation the samples were found to disintegrate completely . The rapid loss of physical properties at the end of the induction period is very important in case of time- controlled photodegradable polymer . Because in this case the rapid degradation of the polymer is required after its service period . In this respect FeAc was found to be the most effective among all the samples examined .

3 .2 . 11 Thermal stabilisation of unstabilised LDPE by different pro - oxidants .

Masterbatches (5%) of different pro -oxidants in unstabilised LDPE containing initiator (DCP) of (I / P_O) - molar ratio = 0 .064 were diluted to 0 .2 % concentration . These diluted samples were oven aged in an air oven at 110°C . The carbonyl formation during oven ageing were measured by IR spectroscopy at intervals . The results are shown in Table 3 . 11, Figs. 3 . 69 and 3 . 70. All the pro - oxidants except FeDMC and FeTp had no thermal antioxidant activity compared to LDPE control . However , FeDMC and FeTp show thermal stability to some extent . FeTp was found to have most thermal anti - oxidant activity .

It is clear from Figs . 3 . 69 - 3 . 70 and Table 3 . 11 that a typical peroxide decomposer (126) is an effective thermal stabiliser for LDPE . A characteristic feature of the activity of this antioxidant is a very sharp end to the induction period , when free metal ion is liberated by oxidative destruction of the complex . It showed an induction period of 180 hours compared to 50 hours for

Table 3 .11 Effect of thermal oxidation (oven ageing) at 110^{o}C on LDPE Films containing pro - oxidants (0 .2%) .

Sample	Time to fixed carbonyl value T (>C = O* , 20)
LDPE	235
Metone M	40
FeTa	95
FeCi	120
FeCr	125
FeMa	145
FeAc	165
Metone A	210
FeDMC	290
FeTp	340

* Carbonyl index

All the samples are diluted from 5% masterbatches processed at 160^{o}C for 10 minutes . In case of FeTa , FeCi , FeCr , FeMa and FeAc ; the samples are diluted from 5 % masterbatches containing peroxide of (I / P_{O}) - molar ratio = 0 . 064 (DCP) and in case of FeTp , Trigonox 101 was used as peroxide (0 .15 molar ratio) . I = initiator , P_{O} = Pro - oxidant .

LDPE alone . It was shown (67, 127) that metal dithiocarbamate complexes are not themselves antioxidants but that a Lewis acid formed from them are responsible for a rapid catalytic destruction of hydroperoxide . The thermal antioxidant effect of FeTp is higher than that of FeDMC which suggests that it can destroy hydroperoxide better than that of FeDMC . The induction period was found to increase in the case of FeTp compared to FeDMC . However , other pro - oxidants in this investigation were observed to have less thermal antioxidant activity . Like FeDMC or FeTp they cannot destroy hydroperoxide .

CONCLUSIONS

Two photoactivators FeAc (soluble) and FeTp were successfully bound to unstabilised LDPE using initiator and co - agent . However , a very high concentration of peroxide was needed for binding . The extraction of 5% MB of FeAc (insoluble) containing peroxide of (DCP / FeAc) - molar ratio = 0 .064 , with xylene resulted in an insoluble gel . The colour of the gel was dark red which indicated the presence of the compound (FeAc) . The spectrum of this xylene insoluble gel had close resemblance with the spectrum of 5% MB of FeAc containing peroxide before extraction with xylene . Thus it is clear that the compound is an integral part of the polymer .

The pro - oxidant effect of different compounds at different concentrations were examined . All compounds showed a pro - oxidant effect . FeTa , FeTp and FeDMC showed higher pro - oxidant effects at lower concentrations , whereas FeAc , FeMa and FeCi at higher concentrations . The photo - oxidation of LDPE containing different compound without peroxide were compared with samples containing peroxide . The pro - oxidant activity of LDPE containing FeCr and FrCi were found to increase in the presence of increased peroxide concentration . Whereas FeAc showed low photoactivity effect in the presence of peroxide . FeAc (soluble) was found to give almost the same photoactivity in presence of peroxide compared with sample without peroxide . The photoactivity remained more or less same after extraction .

The effect of different pro - oxidants on the melt stability of LDPE were observed by measuring the initial carbonyl indices of the samples after processing and the MFI values of the samples at different times . FeDMC and FeTp showed most effective melt stabiliser behaviour . FeAc and FeMa are good melt stabilisers at lower processing time (10 minutes) , above that they are not effective melt stabilisers. The processing conditions were also found to affect the UV activity of LDPE containing different pro - oxidants . In the case of FeDMC and FeTp the processing severity did not change the UV stability of LDPE much . Whereas other pro - oxidant showed a decrease in photoactivity in drastic processing conditions . The thermal stability of unstabilised LDPE in presence of different pro - oxidants were examined . Among them only FeTp and FeDMC were found to give good thermal stability behaviour . This coincides with the melt stability of LDPE in the presence of these pro - oxidants . Both of them are good melt stabilisers and so are effective thermal antioxidant . So during processing they act as melt stabilisers and during the storage of film containing these pro - oxidants the properties of the polymer will not change .

The effect of the combination of ZnDEC with different pro - oxidants were followed . It was observed that in the combination of ZnDEC with FeCr and FeAc there was a decrease in the photoactivity of LDPE at the higher concentration of ZnDEC (> 0 .05%) . In contrast , the lower concentrations of ZnDEC (< 0 .1%) in the combination , the photostability of LDPE increased compared to FeAc / FeCr alone. The combination of ZnDEC with FeTa observed to decrease the photostability of the polymer compared to FeTa alone at all concentrations of combination used . The use of ZnDEC with FeTp also increased the stability of the polymer . Both the induction period and the embrittlement time of the polymer extended with the use of ZnDEC .

The combination of FeDNC with Metone A and Metone M showed a photosensitisation effect whereas the combination of ZnDNC showed a photostabilisation effect compared to Metone A or Metone M alone . It was observed that the effect of NiDNC with FeDNC in unstabilised LDPE is the increase of photostability of the polymer compared to FeDNC alone, except at 0 .05% of FeDNC . At this lower concentration of FeDNC in combination with NiDNC a photosensitising effect was observed compared to FeDNC alone .

The photo - oxidation activity of different pro - oxidants in commercial LDPE (Riblene CF 2203) were examined . All the compounds except Metone M showed pro - oxidant effect in commercial LDPE at the concentration used . The effect of an iron containing pro - oxidant (FeDNC) on Metone M was examined in commercial LDPE . The result showed photosensitisation effect in the combination which was due to the pro - oxidant behaviour of FeDNC . The combination of different pro - pxidants with ZnDNC resulted in the reduction of photoactivity of commercial LDPE . This was due to the interaction of phenolic antioxidant in the commercial polymer with ZnDEC .

The photo - oxidation behaviour of commercial LDPE (BP) was examined in presence of FeTa and FeTp . They were found to give pro - oxidant behaviour at all concentration used with considerable induction period . These could be useful as a mulching film for agricultural purposes . Both the induction period and the embrittlement time could be varied by varying the concentration of pro - oxidant .

The change in the percentage of elongation of unstabilised LDPE in the presence of different pro - oxidants were examined . It was observed that in the samples containing pro -oxidant the change of this property were sharp compared to LDPE alone . At the end of irradiation when the values of percentage of elongation were very low the samples were found to disintegrate into pieces . Thus these polymer films can serve the purpose of time - controlled degradable polymer such as in agricultural mulches .

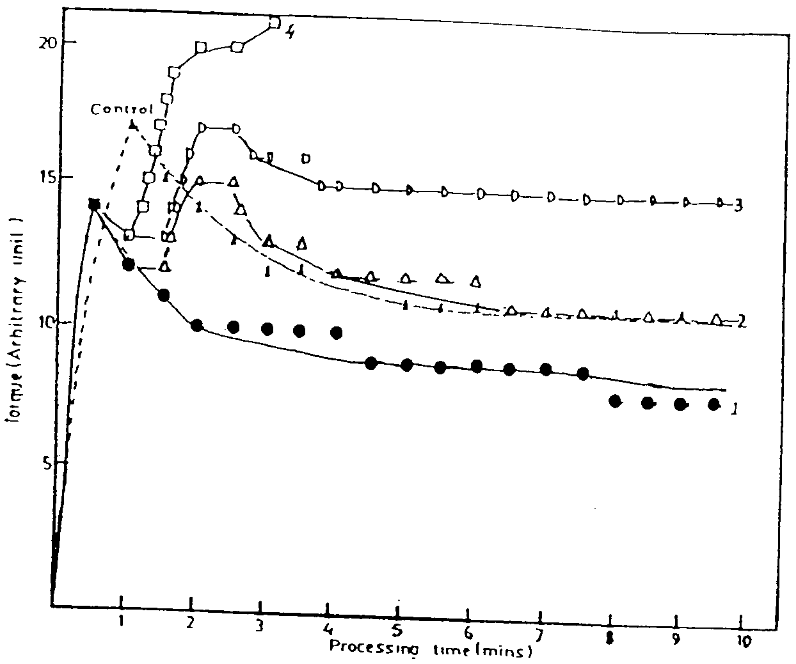


Fig. 3.1 Effect of peroxide concentration (DCP) on torque for 5% iron-acrylate in LDPE at 160°C . 1) without peroxide, 2) with peroxide of 0.032 molar ratio, 3) with peroxide of 0.064 molar ratio and 4) with peroxide of 0.128 molar ratio .

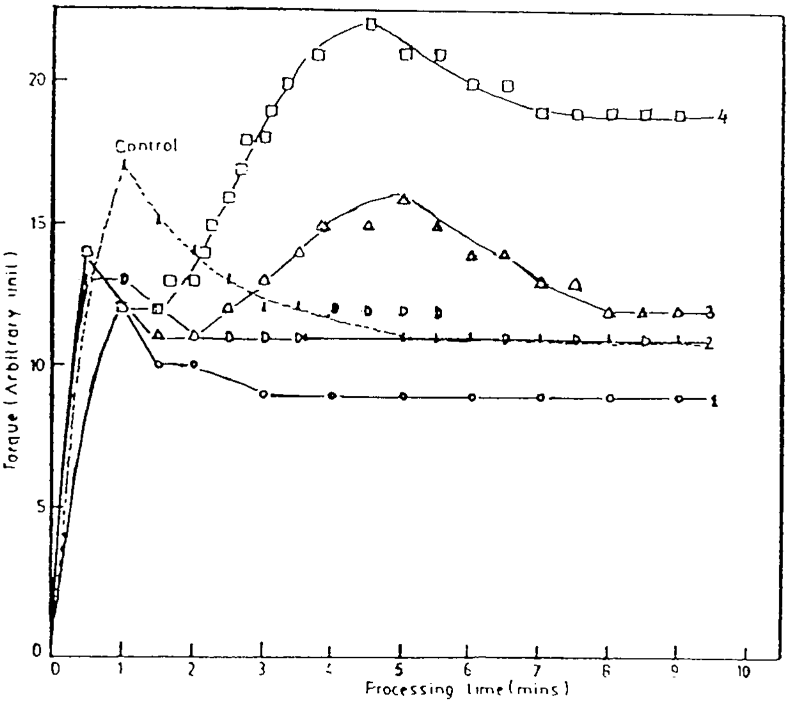


Fig. 3.2 Effect of peroxide concentration (DCP) on torque for 5% iron-cinnamate in LDPE at 160°C . 1) without peroxide, 2) with peroxide of 0.032 molar ratio, 3) with peroxide of 0.064 molar ratio and 4) with peroxide of 0.128 molar ratio .

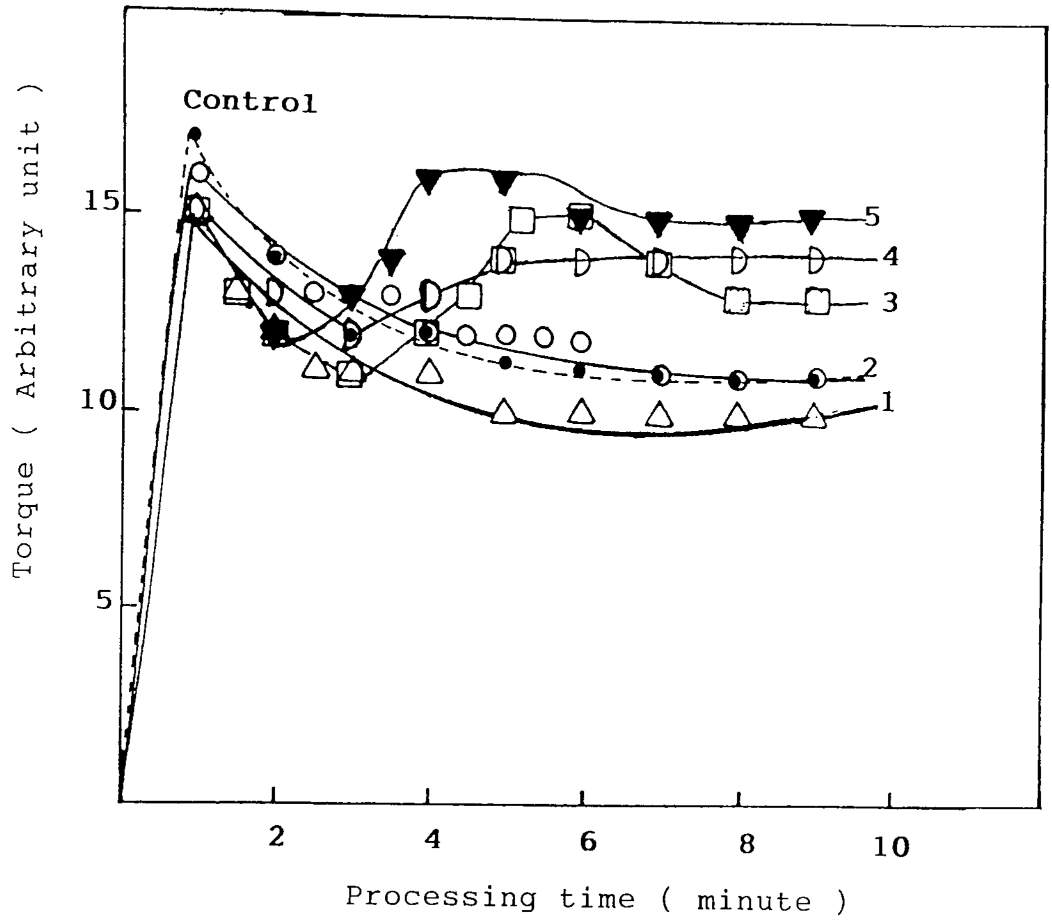


Fig. 3.3 Effect of peroxide (Trigonox 101) and co-agent (TMPTA) concentration on torque for 5% FeAc (soluble) in LDPE at 160^{o}C . 1) With 1% TMPTA (no peroxide), 2) Without peroxide (no TMPTA), 3) With 1% TMPTA and 0.06 molar ratio of Trigonox 101, 4) With 0.1 molar ratio of Trigonox 101 (no TMPTA) and 5) With 1% TMPTA and 0.1 molar ratio of Trigonox 101.

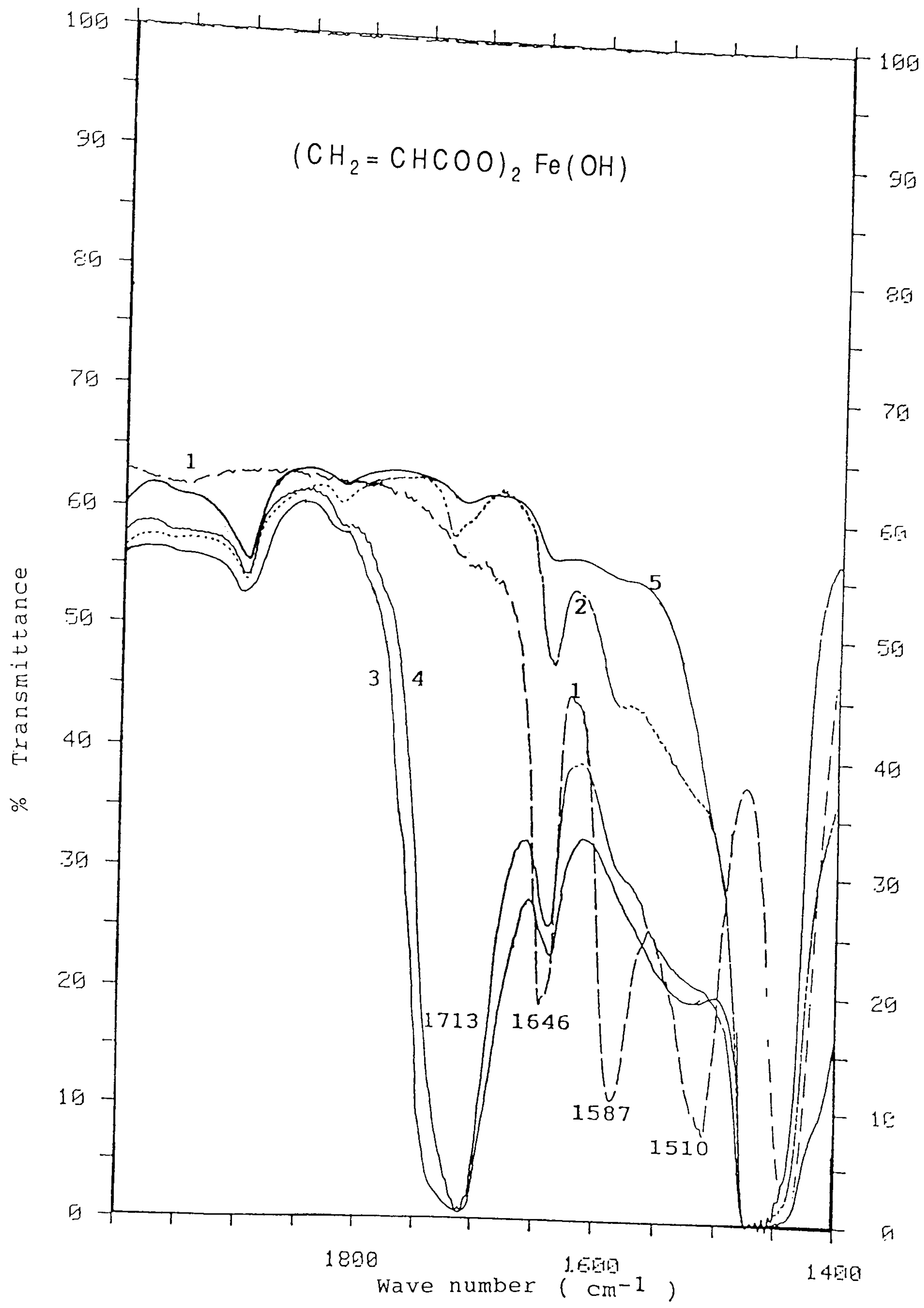


Fig. 3.4 A segment of the FTIR spectra of 1) FeAc (KBr disc), 2) 5% MB of FeAc without peroxide, 3) 5% MB of FeAc with peroxide of (I/P$_o$)-molar ratio = 0.064 (DCP) before extraction , 4) 5% MB of FeAc with peroxide of (I/P$_o$)-molar ratio = 0.064 (DCP) after extraction with xylene and 5) LDPE control (Processed without peroxide).

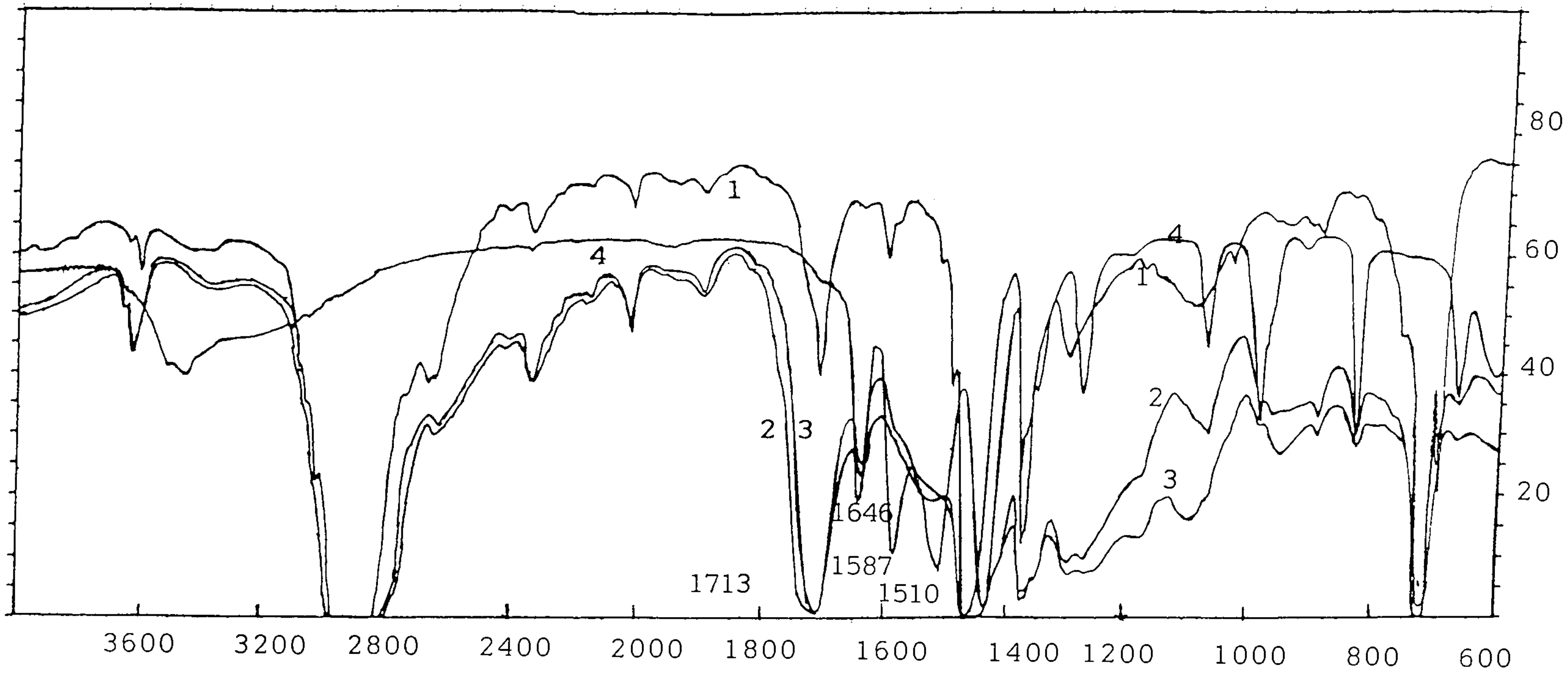


Fig. 3.5 FTIR spectra of Fe-acrylate 1) 5% MB of Fe-acrylate in LDPE with 0.064 molar ratio of DCP (Xylene soluble part), 2) 5% MB of Fe-acrylate in LDPE with 0.064 molar ratio of DCP (before extraction with xylene), 3) 5% MB of Fe-acrylate in LDPE with 0.064 molar ratio of DCP (after extraction with xylene) and 4) Fe-acrylate compound alone (KBr disc).

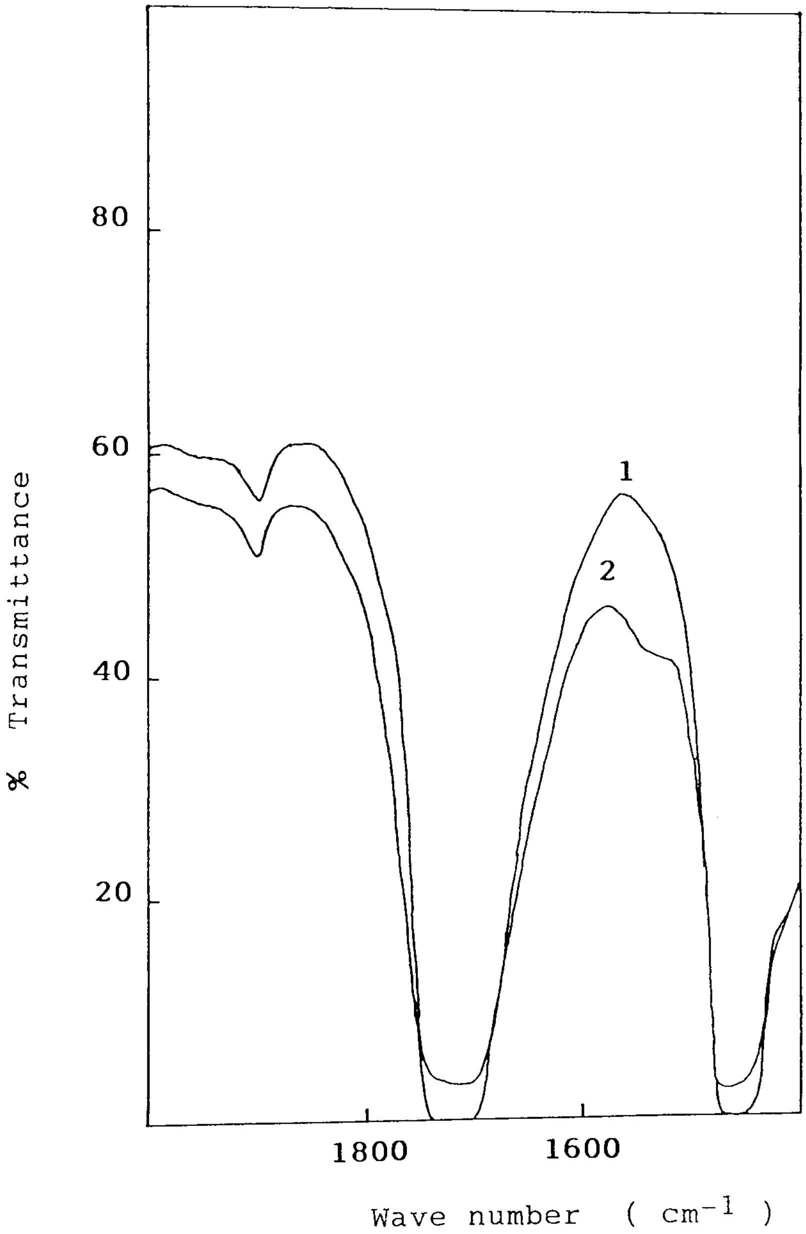


Fig. 3.6 A segment of the FTIR spectra of (1) 5% masterbatch of acrylic acid in unstabilised LDPE with DCP/Iron acrylate = 0.005, (2) 5% masterbatch of polyacrylic acid in unstabilised LDPE (without peroxide) .

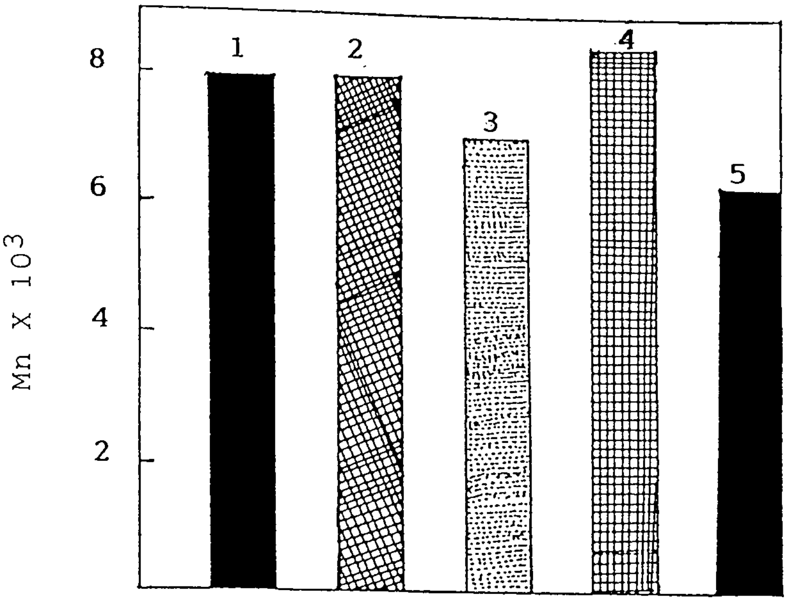


Fig. 3.7 Comparison of no. average molecular weight (Mn) of 1) LDPE (processed), 2) 5% MB of FeAc without peroxide, 3) 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP), 4) Xylene insoluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP) and 5) Xylene soluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP). All samples are processed at 160°C for 10 minutes in closed chamber. I = initiator and P_o = pro-oxidant.

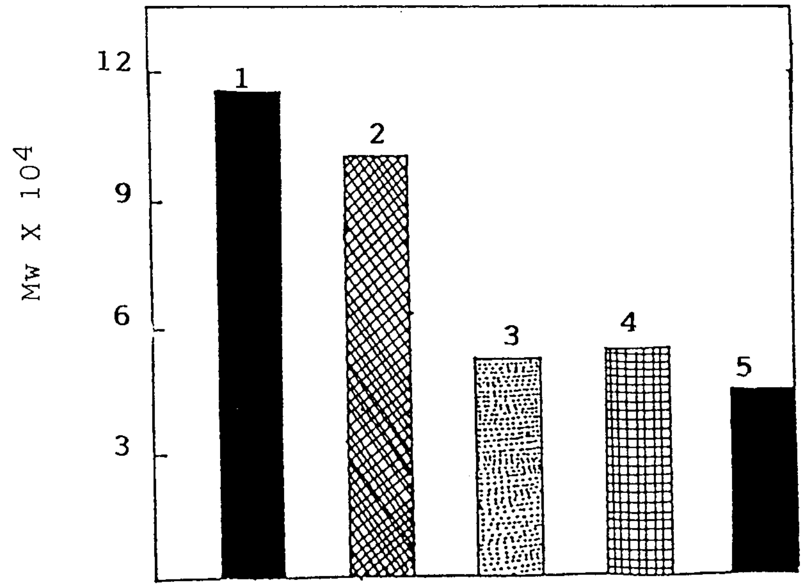


Fig. 3.8 Comparison of weight average molecular weight (Mw) of 1) LDPE (processed), 2) 5% MB of FeAc without peroxide, 3) 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP), 4) Xylene insoluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP) and 5) Xylene soluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP).

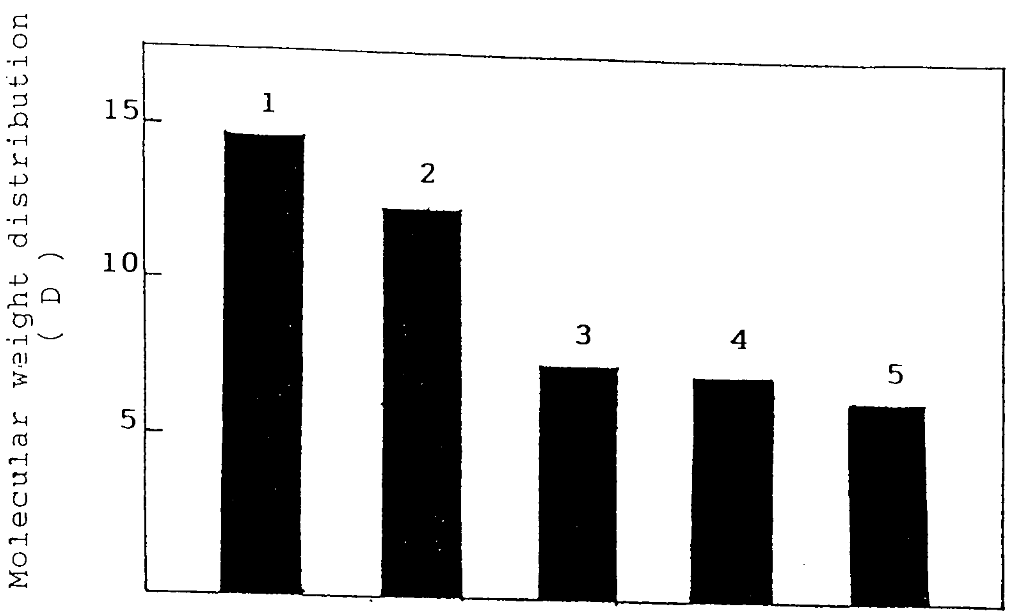


Fig. 3.9 Comparison of molecular weight distribution (D) of 1) LDPE (processed), 2) 5% MB of FeAc without peroxide, 3) 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP), 4) Xylene insoluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP) and 5) Xylene soluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP). All samples are processed at 160°C for 10 minutes in closed chamber. I = initiator and P_o = pro-oxidant.

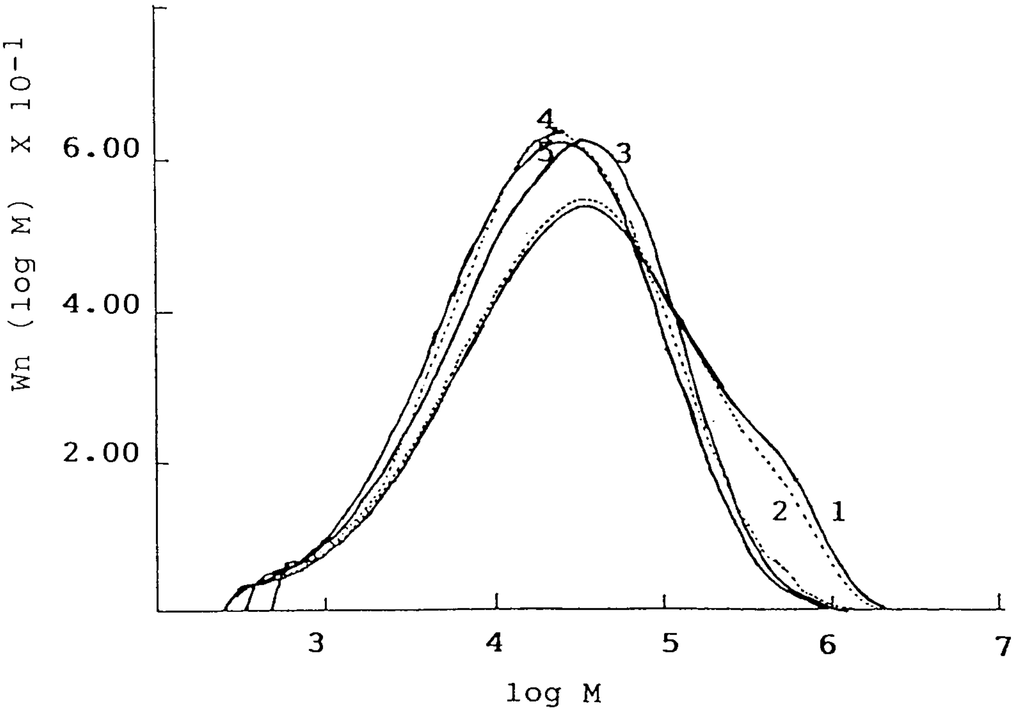


Fig. 3.10 Comparison of molecular weight distribution (D) of 1) LDPE (processed), 2) 5% MB of FeAc without peroxide, 3) 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP), 4) Xylene insoluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP) and 5) Xylene soluble portion of 5% MB of FeAc with peroxide of (I/P_o)-molar ratio = 0.064 (DCP).

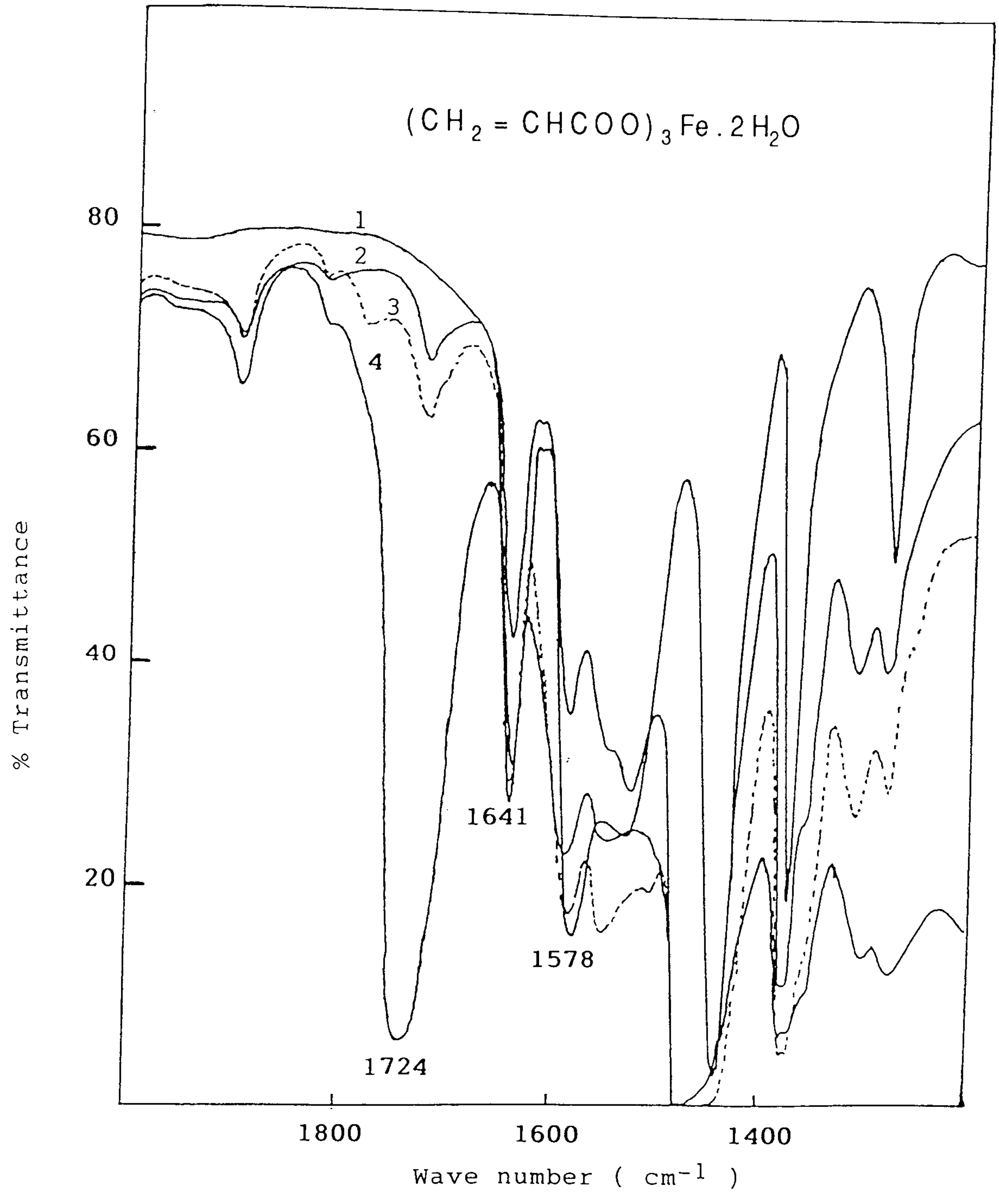


Fig.3.11 A segment of the FTIR spectra of 1) FeAc (soluble, KBr disc), 2) 5% MB of FeAc (soluble) without peroxide, 3) 5% MB of FeAc (soluble) with peroxide of (T101/FeAc)-molar ratio = 0.05 (Trigonox 101) and 4) 5% MB of FeAc (soluble) with peroxide of (T101/FeAc)-molar ratio = 0.1.

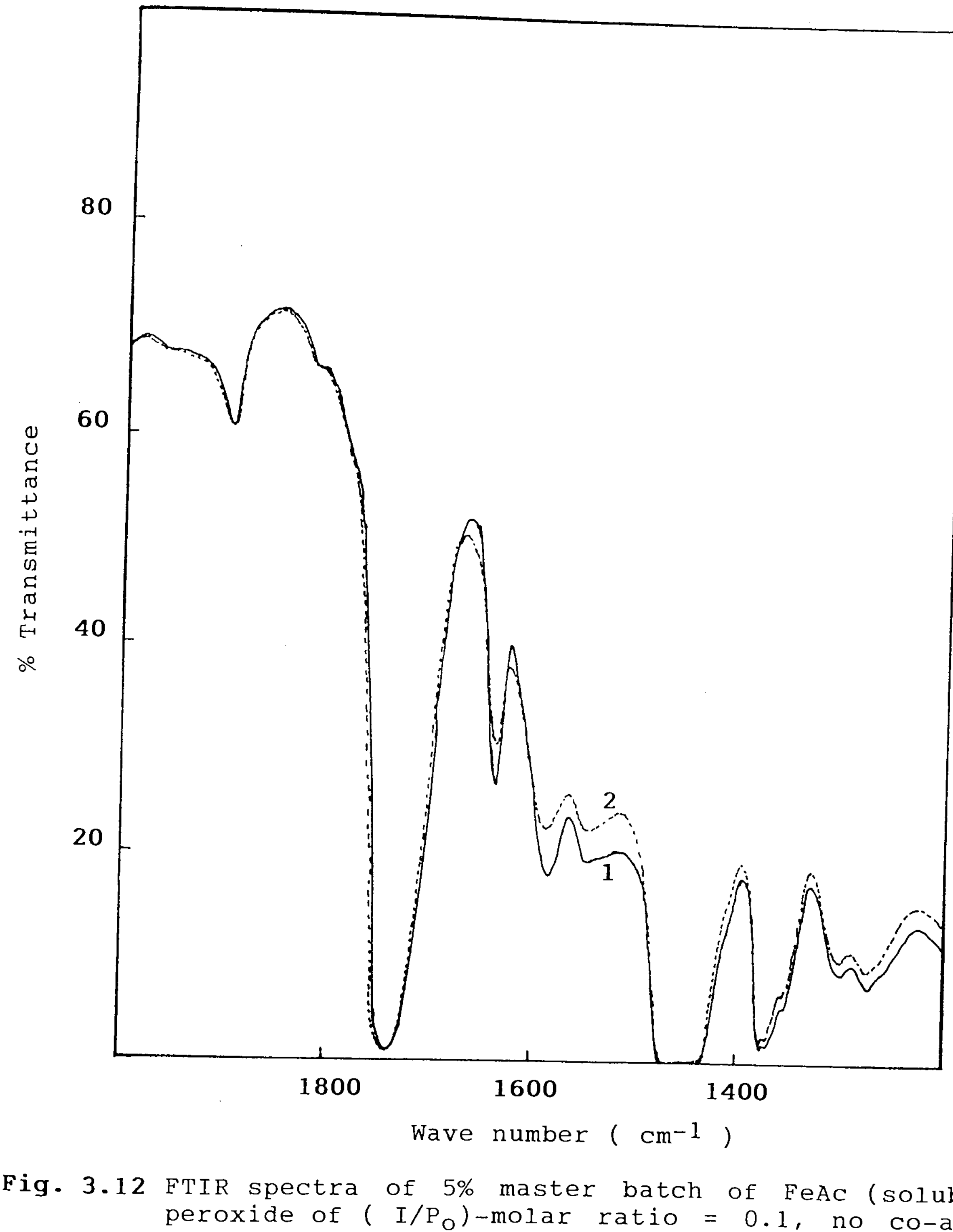


Fig. 3.12 FTIR spectra of 5% master batch of FeAc (soluble) with peroxide of (I/P_O)-molar ratio = 0.1, no co-agent. 1) before extraction and 2) after extraction. I = initiator (Trigonox 101), P_O = pro-oxidant (FeAc).

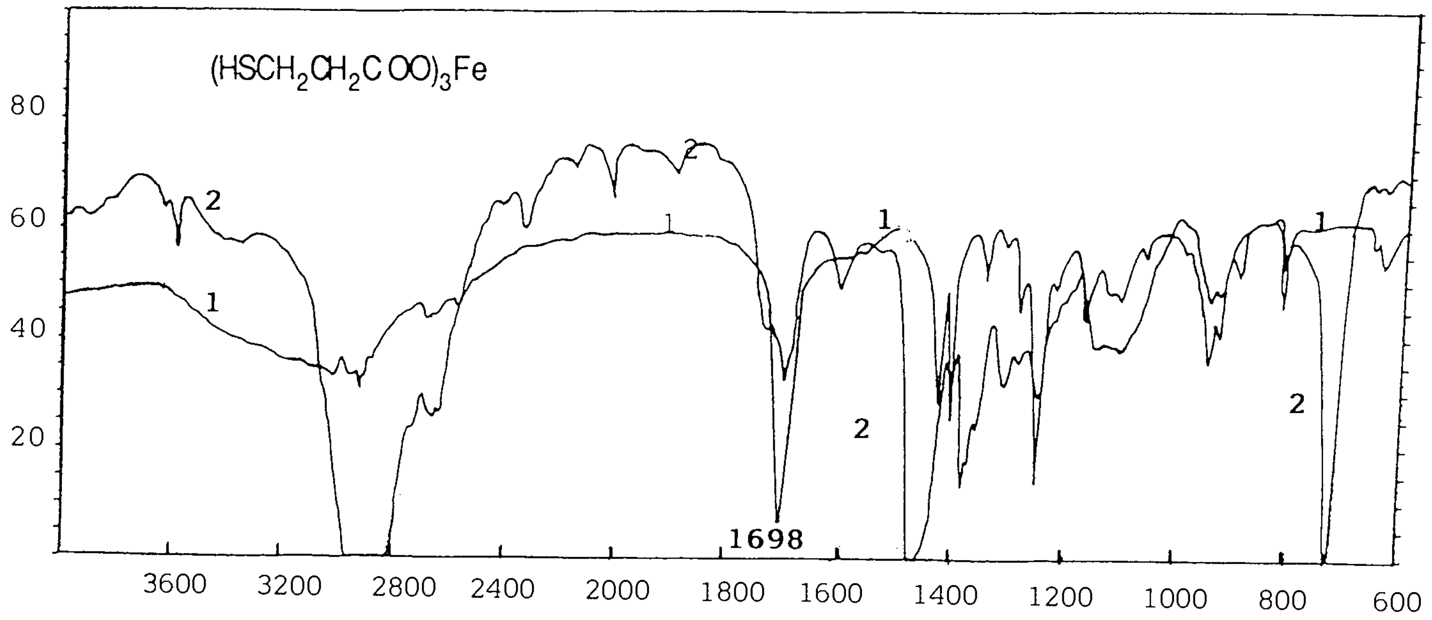


Fig. 3.13 FTIR spectra of Fe-thiopropionate 1) Fe-thiopropionate compoumd alone (KBr disc) and 2) 5% masterbatch of Fe-thiopropionate in LDPE without peroxide.

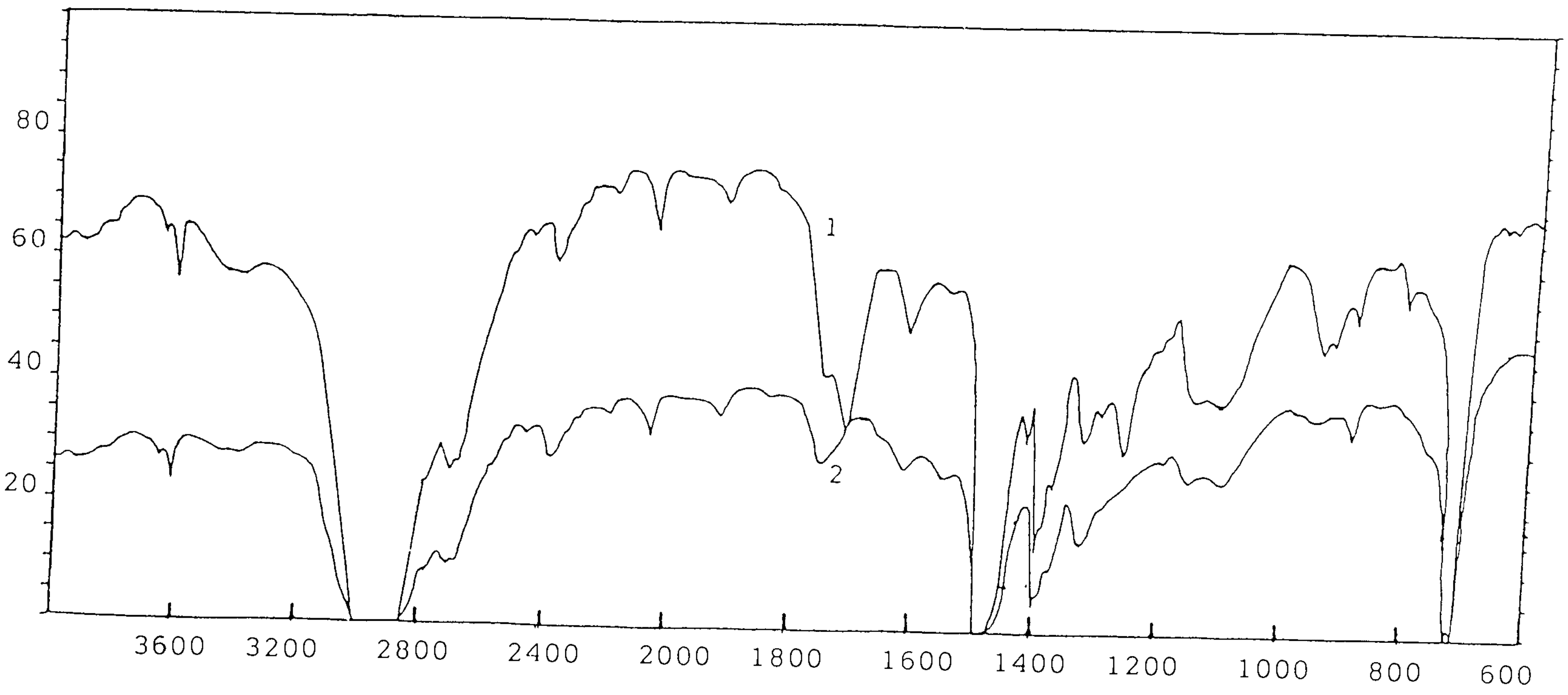


Fig. 3.14 FTIR spectra of 5% masterbatch of Fe - thiopropionate in LDPE without peroxide 1) before extraction 2) after extraction .

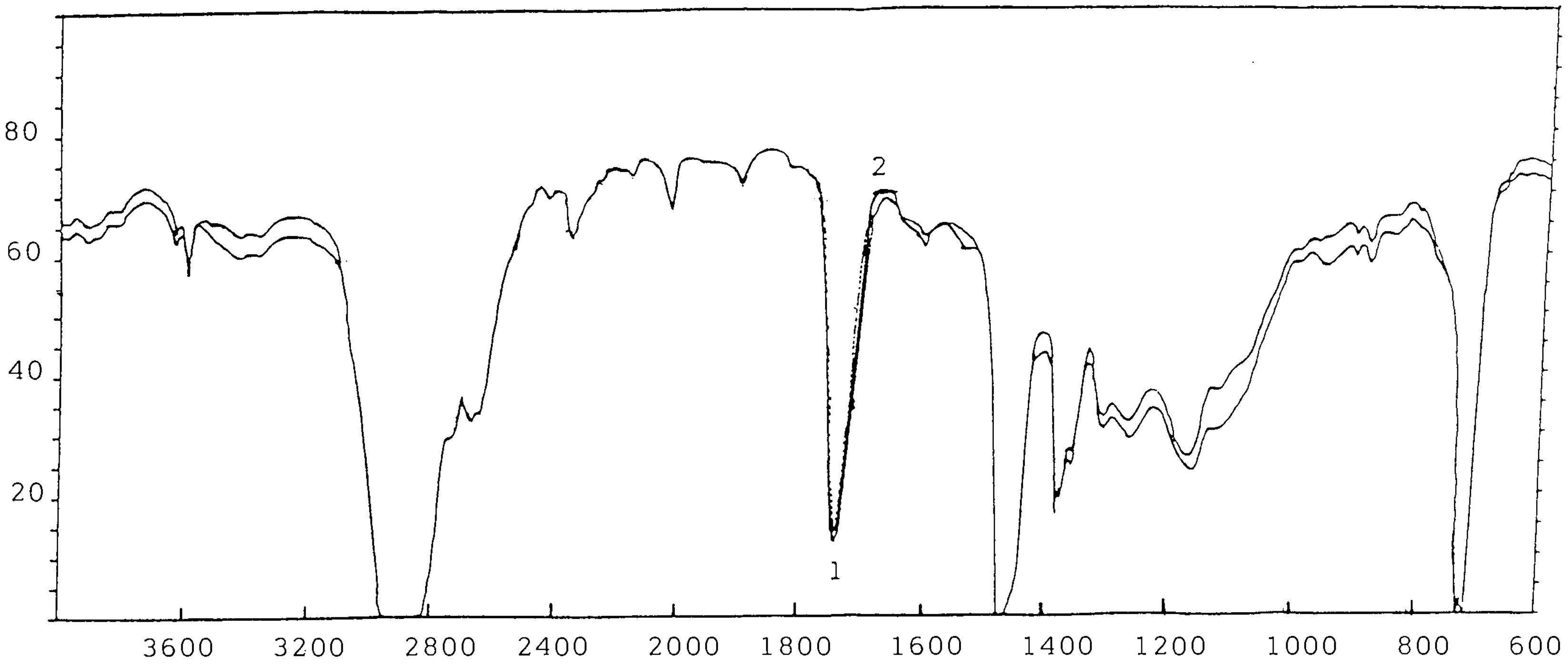


Fig. 3.15 FTIR spectra of 5% masterbatch of Fe-thiopropionate in LDPE with 0.15 molar ratio of Trigonox 101 and 2% TMPTA 1) before extraction and 2) after extraction.

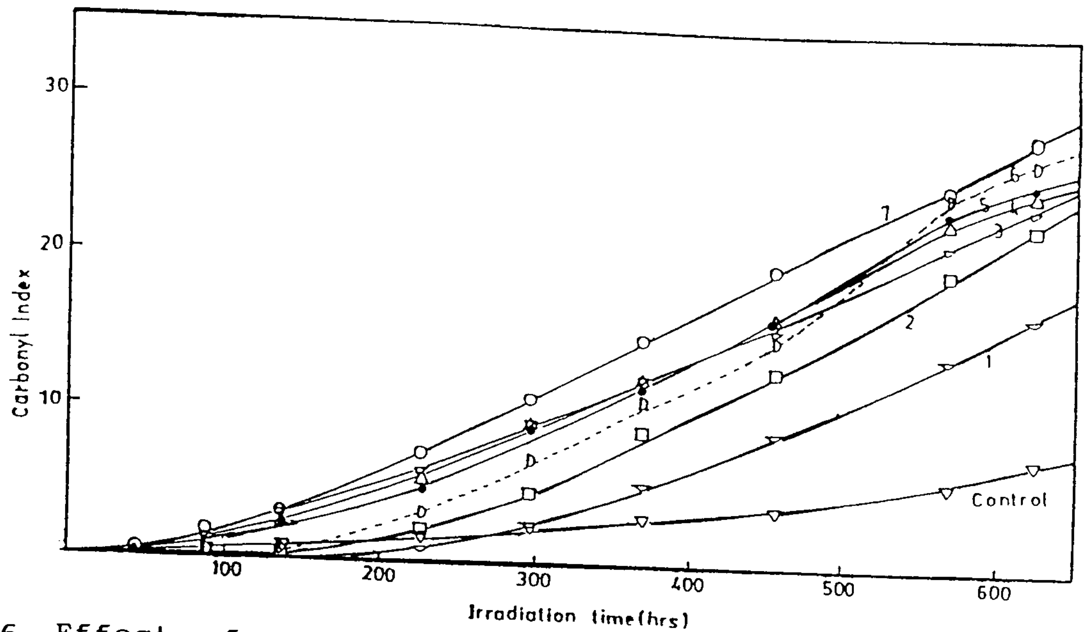


Fig. 3.16 Effect of concentration on the photo-oxidation of unstabilised LDPE(ICI) containing Fe-thioacetate. Samples are diluted from 5% MB processed at 160°C for 10 minutes. (1) 0.6% (2) 0.4% (3) 0.1% (4) 0.2% (5) 0.05% (6) 0.3% (7) 0.025% .

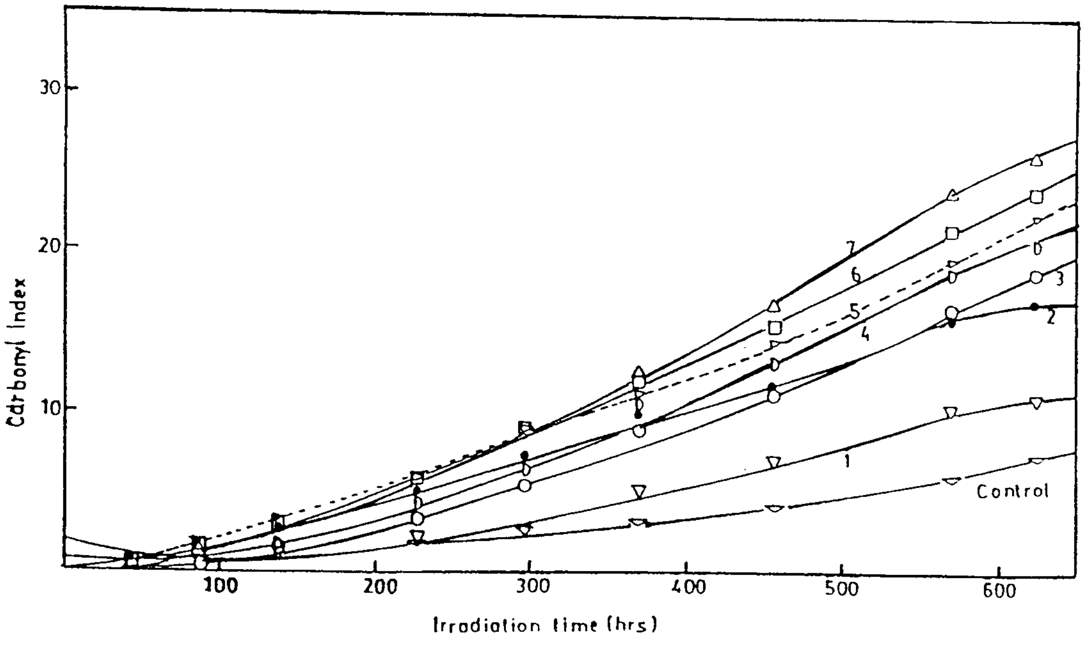


Fig. 3.17 Effect of concentration on the photo-oxidation of unstabilised LDPE(ICI) containing Fe-thiopropionate. Samples are diluted from 5% MB processed at 160°C for 10 minutes. (1) 0.6% (2) 0.05% (3) 0.4% (4) 0.3% (5) 0.1% (6) 0.025% (7) 0.2% .

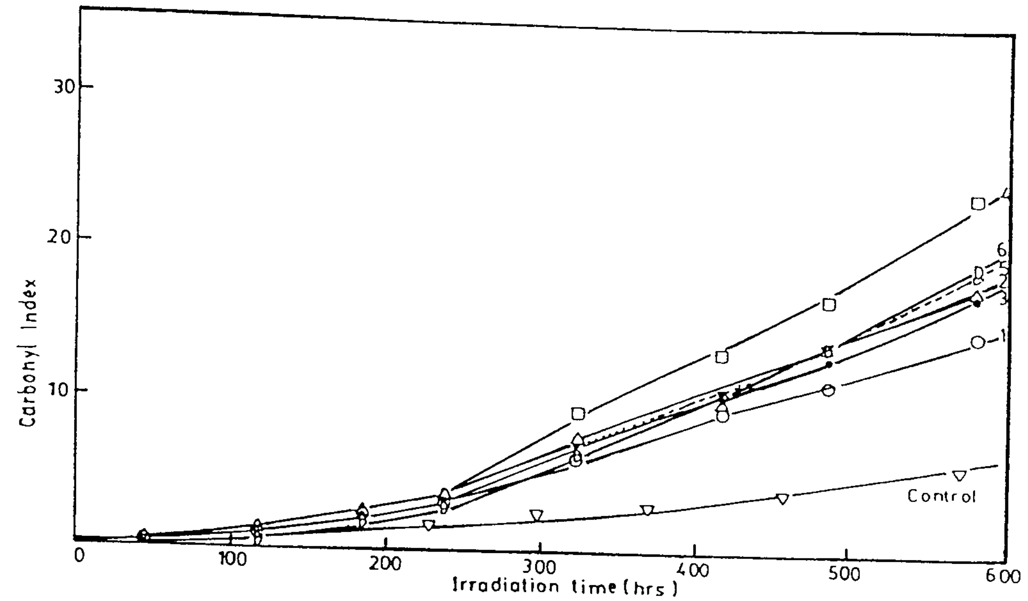


Fig. 3.18 Effect of concentration on the photo-oxidation of unstabilised LDPE (ICI) containing iron maleate. Samples are diluted from 5% MB processed at 160°C for 10 minutes 1) 0.025%, 2) 0.05%, 3) 0.1 and 0.4%, 4) 0.2%, 5) 0.3% and 6) 0.6% .

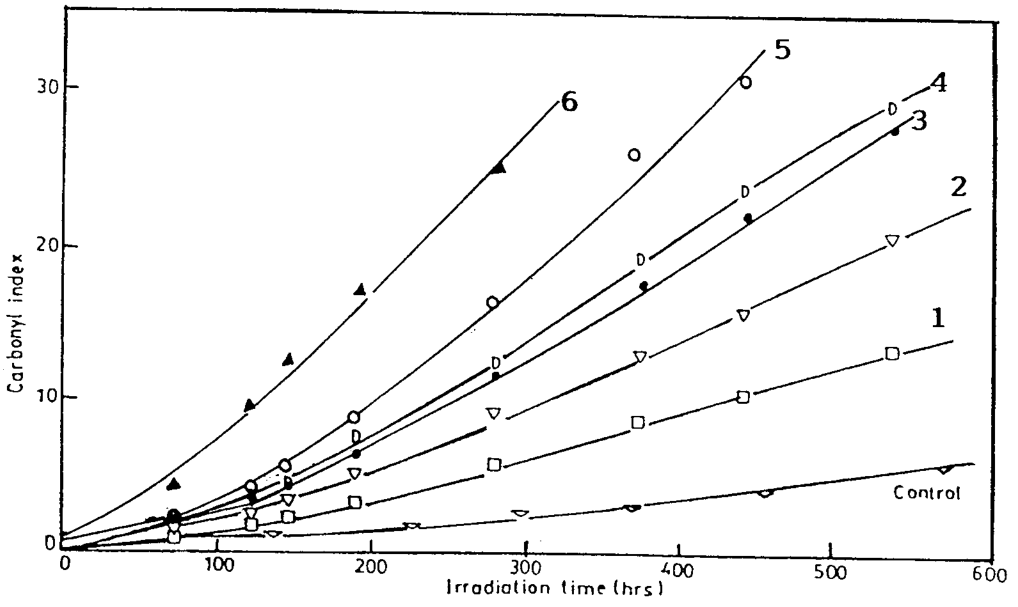


Fig.3.19 Effect of concentration on the photo-oxidation of unstabilised LDPE (ICI) containing iron acrylate. Samples are diluted from 5% MB processed at 160°C for 10 minutes. 1) 0.025%, 2) 0.05%, 3) 0.1%, 4) 0.2 and 0.3%, 5) 0.4% and 6) 0.6% .

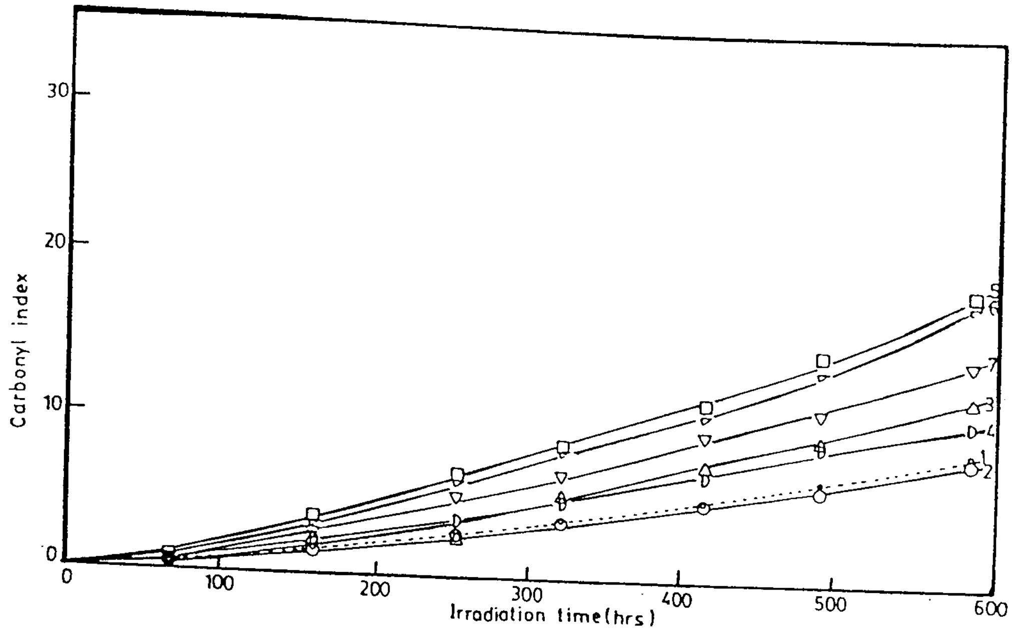


Fig.3.20 Effect of concentration on the photo-oxidation of unstabilised LDPE (ICI) containing iron crotonate . Samples are diluted from 5% MB processed at 160°C for 10 minutes. 1) 0.025%, 2) 0.05%, 3) 0.1%, 4) 0.2%, 5) 0.3%, 6) 0.4% and 7) 0.6% .

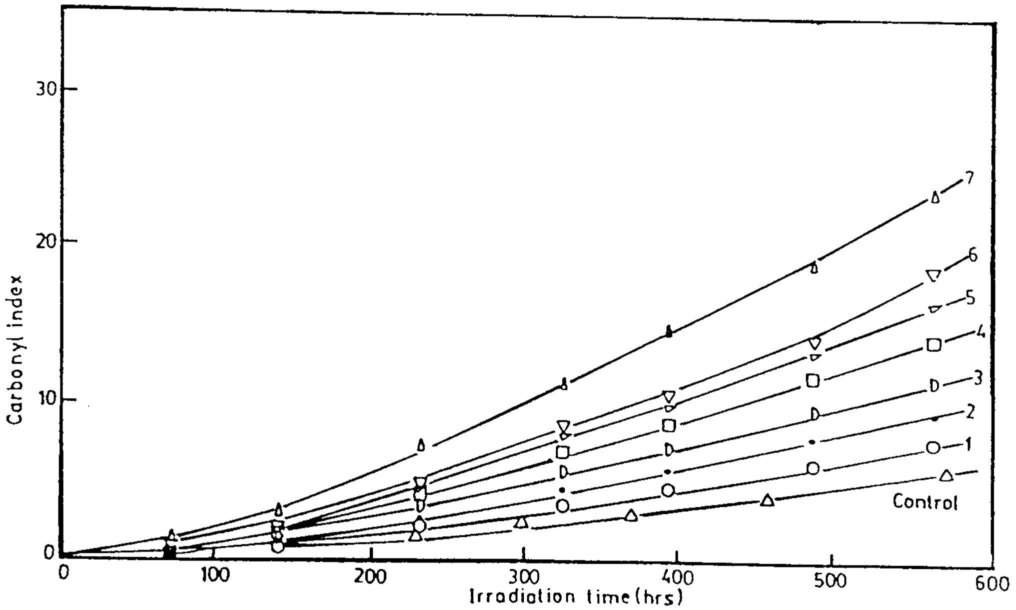


Fig. 3.21 Effect of concentration on the photo-oxidation of unstabilised LDPE (ICI) containing iron cinnamate. Samples are diluted from 5% MB processed at 160°C for 10 minutes. 1) 0.025%, 2) 0.05%, 3) 0.1%, 4) 0.2%, 5) 0.3%, 6) 0.4% and 7) 0.6% .

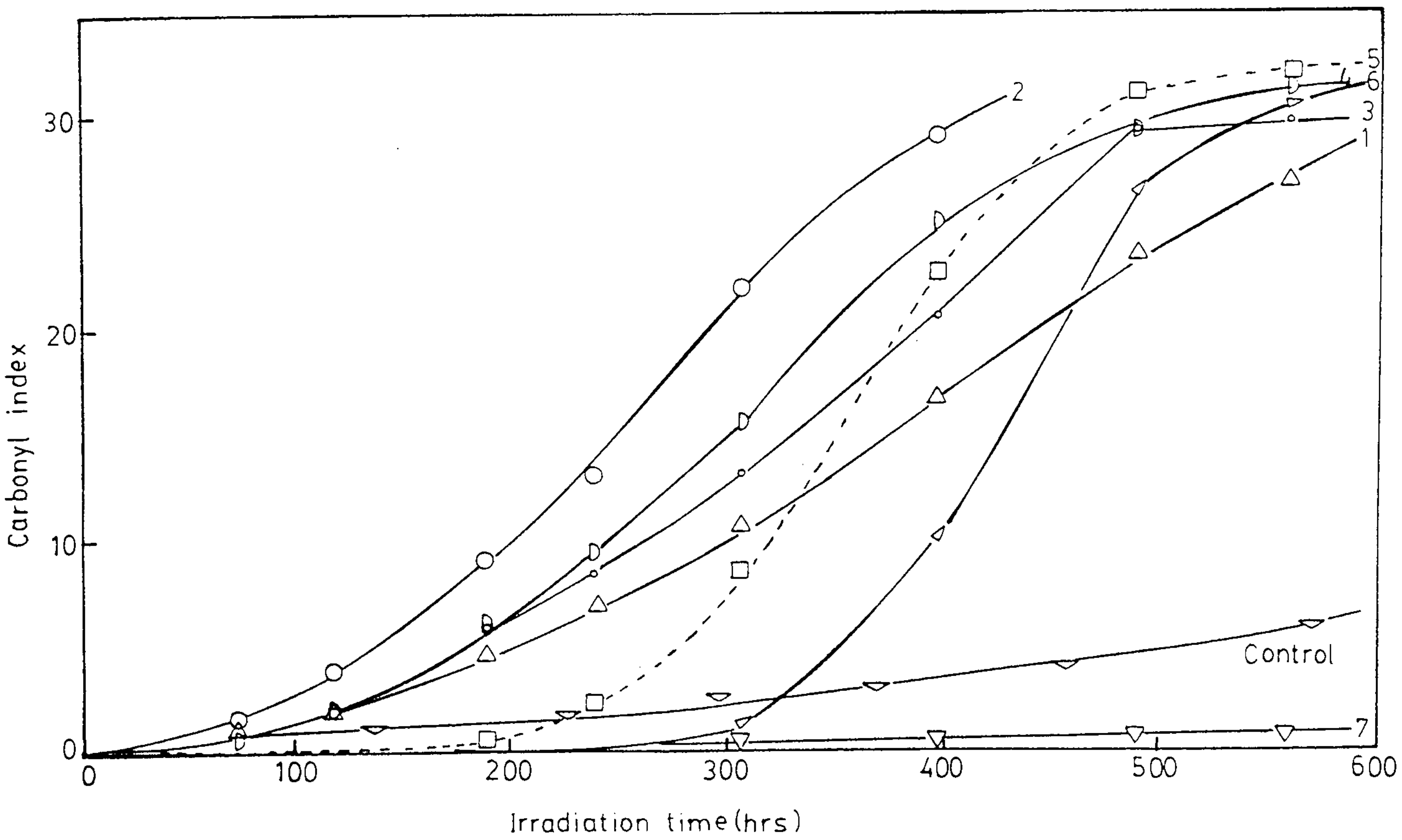


Fig. 3.22 Effect of the concentration on the photo-oxidation of unstabilised LDPE(ICI) containing Fe-DMC . Samples are diluted from 5% MB processed at 160°C for 10 minutes. (1) 0.025% (2) 0.05% (3) 0.1% (4) 0.2% (5) 0.3% (6) 0.4% (7) 0.6% .

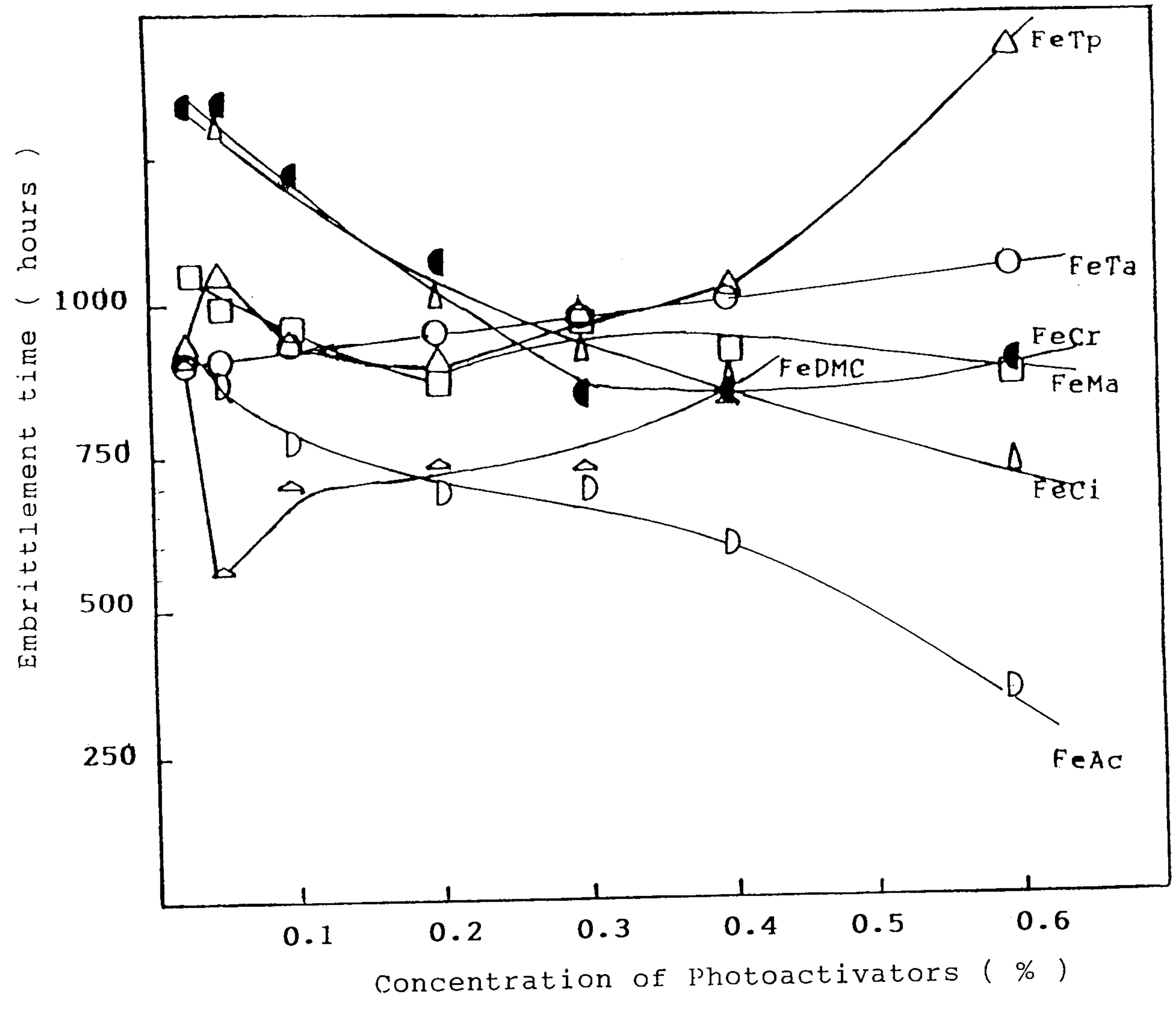


Fig. 3. 23 Effect of concentrations of different pro-oxidants in the UV lifetime of unstabilised LDPE. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in a closed chamber.

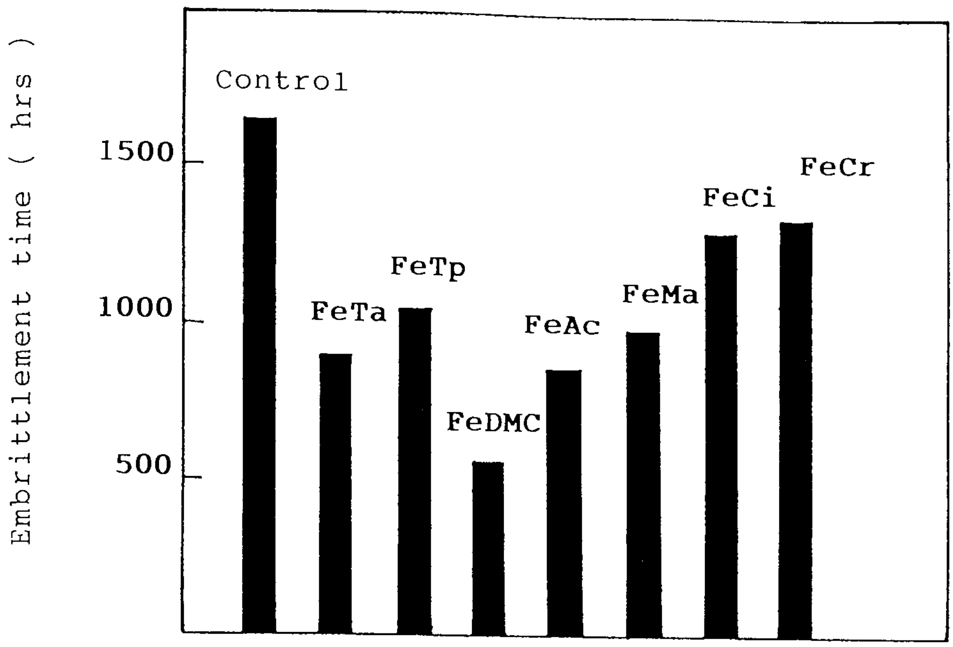


Fig. 3.24 Effect of different photo-activators (0.05%) on the UV life time of unstabilised LDPE. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber.

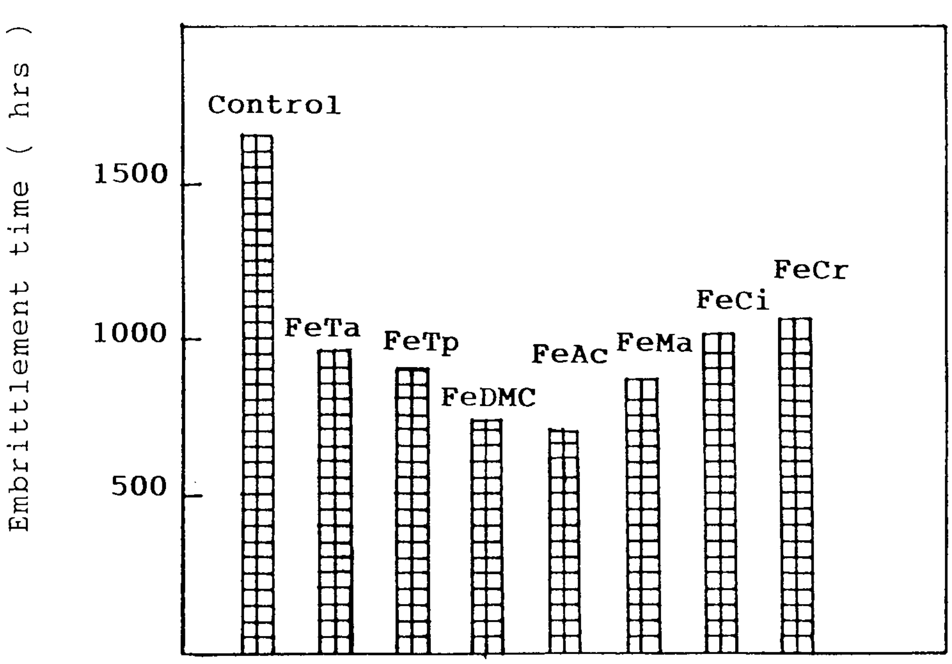


Fig.3.25 Effect of different photo-activators (0.2%) on the UV life time of unstabilised LDPE. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber.

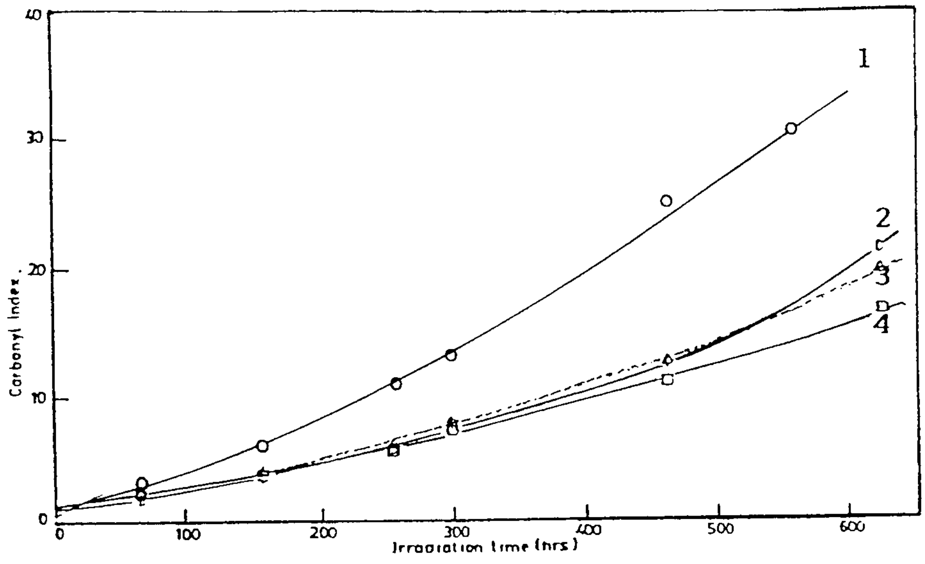


Fig. 3.26 Effect of initiator concentration (DCP) on the photo-degradation of unstabilised LDPE (ICI) containing Fe-acrylate (1) without peroxide (2) 0.07g (3) 0.14g (4) 0.28g.

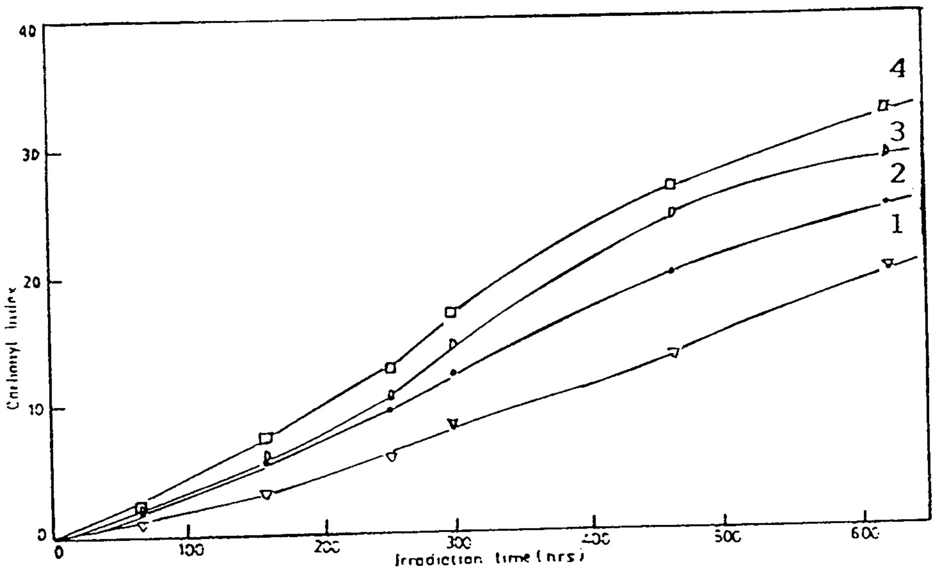


Fig. 3.27 Effect of initiator concentration (DCP) on the photo-degradation of unstabilised LDPE (ICI) containing Fe-crotonate (1) without peroxide (2) 0.07g (3) 0.14g (4) 0.28g.

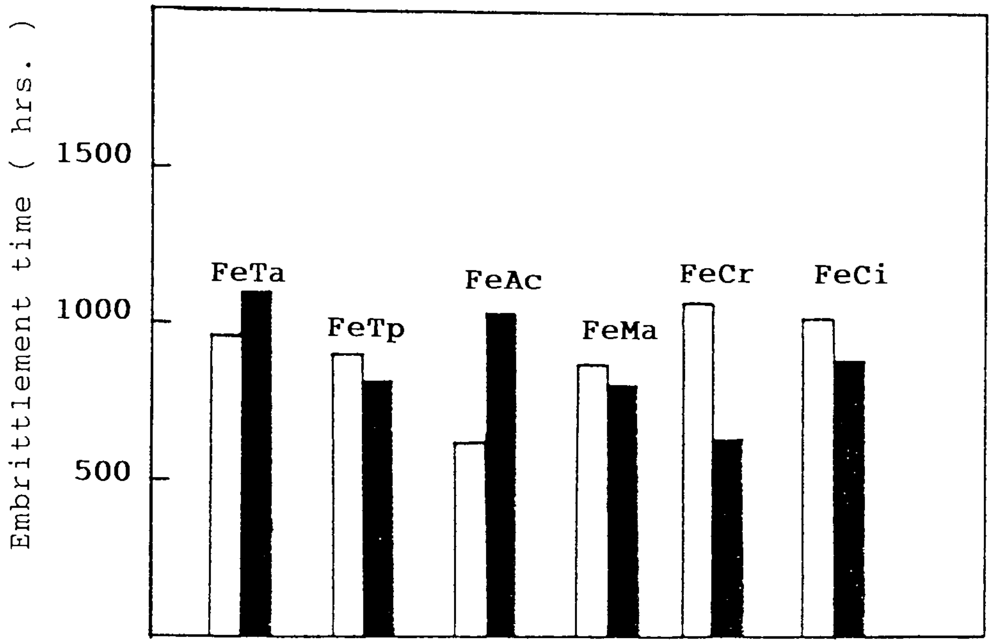


Fig. 3.28 Effect of peroxide on the UV life time of LDPE containing different photo-activators. Concentration of photo-activators is 0.2% . All samples are diluted from 5% masterbatches processed at 160^{o}C for 10 minutes in closed chamber. Solid lines represents the samples diluted from masterbatches containing peroxide of (I/P_o)-molar ratio = 0.128 (DCP). In case of FeTp, Trigonox 101 was used as initiator (0.15 molar ratio).

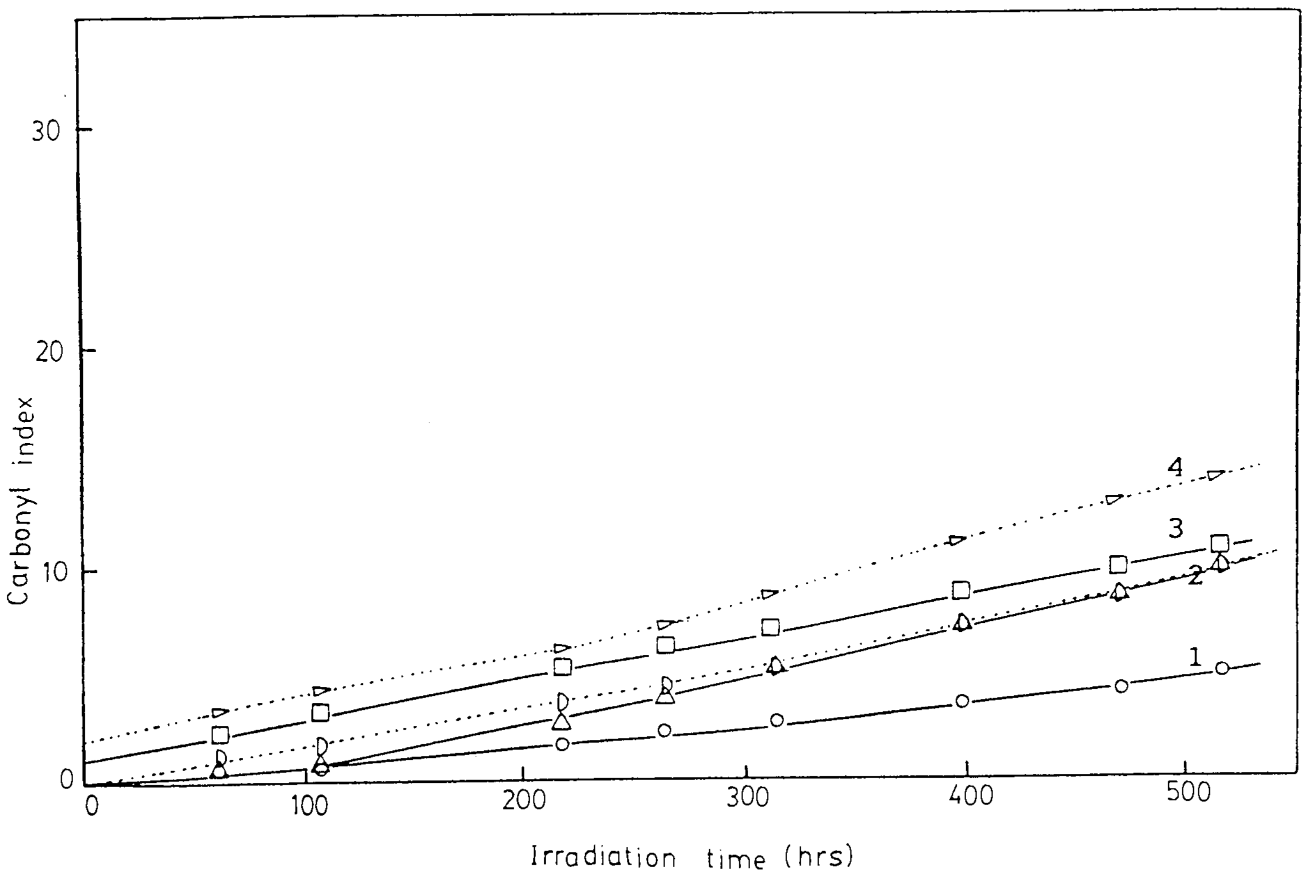


Fig. 3.29 Effect of processing time on the UV stability of LDPE (1) 10 minutes close mixing, (2) 10 and 20 minutes open mixing, (3) 30 minutes open mixing and (4) 40 minutes open mixing.

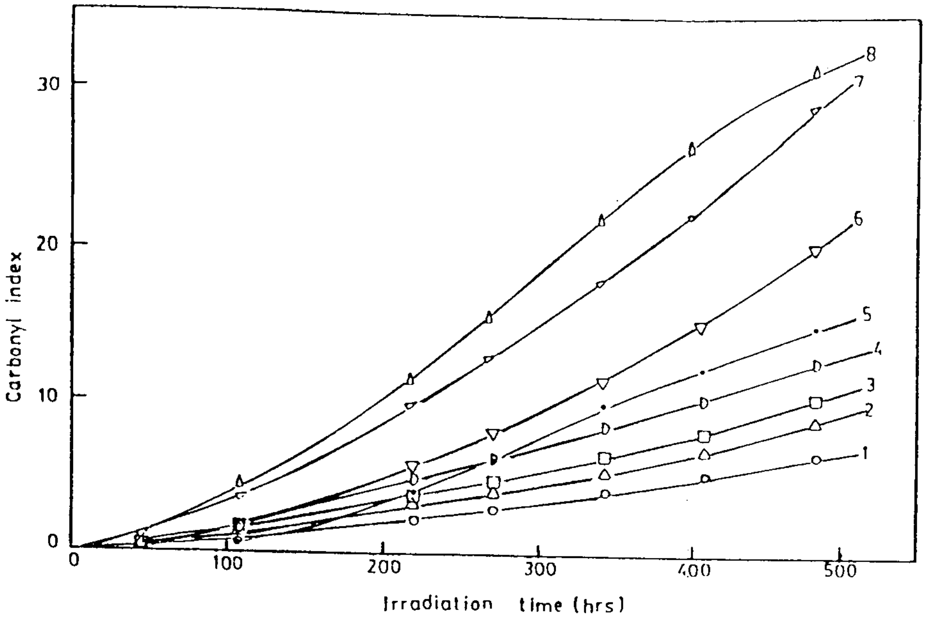


Fig. 3.30 Effect of processing time on the UV stability of LDPE cotaining Fe-DMC and Fe-thiopropionate [conc. of additives 1.25 X 10^{-4} mol/100g (0.05%)] (1) Fe-thiopropionate 10,20 and 30 min CM (2) Fe-thiopropionate 10 min OM (3) Fe-thiopropionate 20 min OM (4) Fe-thiopropionate 30 min OM (5) Fe-DMC 30 min CM (6) Fe-DMC 10 min CM (7) Fe-DMC 10 min OM (8) Fe-DMC 20 min OM .

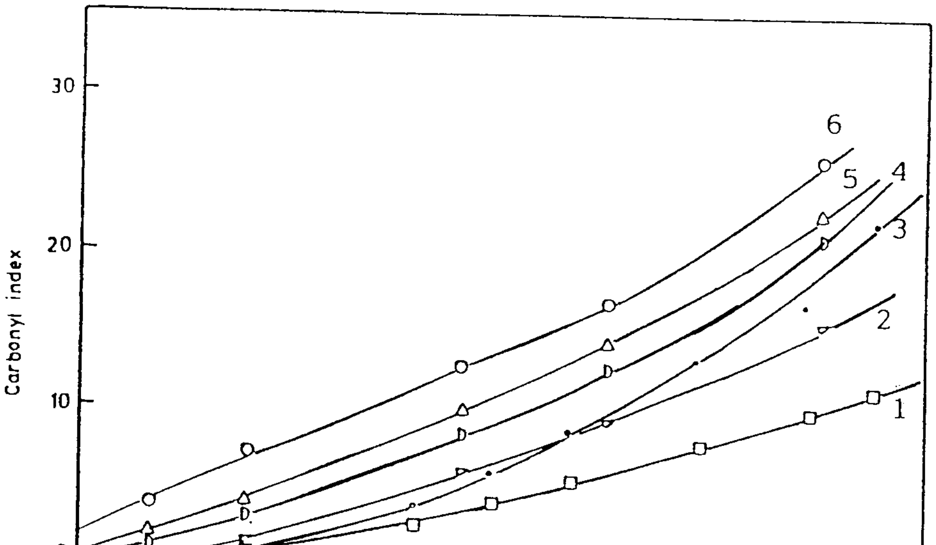


Fig. 3.31 Effect of processing time on the UV stability of LDPE containing Fe-thioacetate [conc. of additives 1.25 X 10^{-4} mol/ 100g (0.05%)] (1) 10 min CM (2) 10 min OM (3) 20 and 30 min CM (4) 20 min OM (5) 30 min OM (6) 40 min OM .

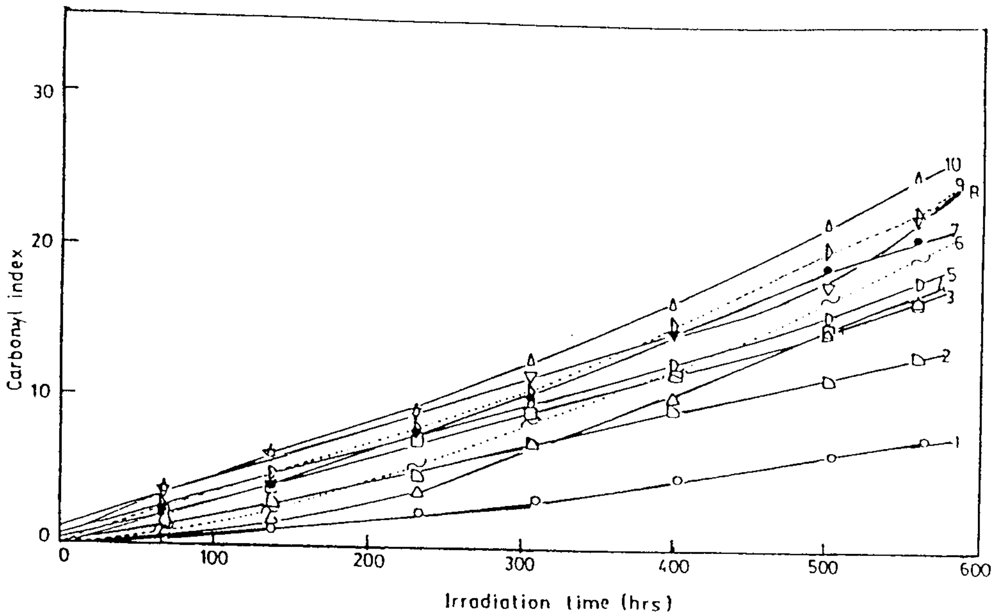


Fig. 3.32 Effect of processing time on the UV stability of LDPE containing Fe-maleate and Fe-crotonate [conc. of additives (0.05%) 1.25 X 10^{-4} mol/100g] (1) Fe-crotonate 10 min CM (2) Fe-crotonate 10 min OM (3) Fe-crtonate 20 min OM (4) Fe-maleate 10 min CM (5) Fe-crtonate 30 min OM (6) Fe-maleate 10 min OM (7) Fe-maleate 20 min OM (8) Fe-maleate 30 min OM (9) Fe-crotonate 40 min OM (10) Fe-maleate 40 min OM .

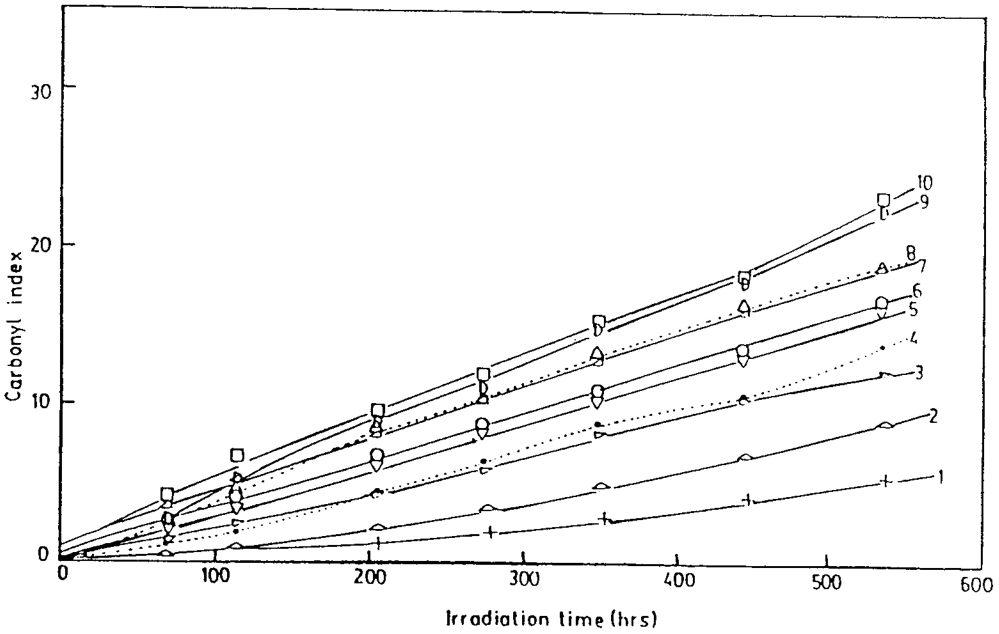


Fig. 3.33 Effect of processing time on the UV stability of LDPE containing Fe-cinnamate and Fe-acrylate [conc. of additives (0.05%) 1.25 X 10^{-4} mol/100g] (1) control 10 min CM (2) Fe-cinnamate 10 min CM (3) Fe-cinnamate 10 min OM (4) Fe-acrylate 10 min OM (5) Fe-cinnamate 20 min OM (6) Fe-cinnamate 30 min OM (7) Fe-cinnamate 40 min OM (8) Fe-acrylate 20 min OM (9) Fe-acrylate 30 min OM (10) Fe-acrylate 40 min OM .

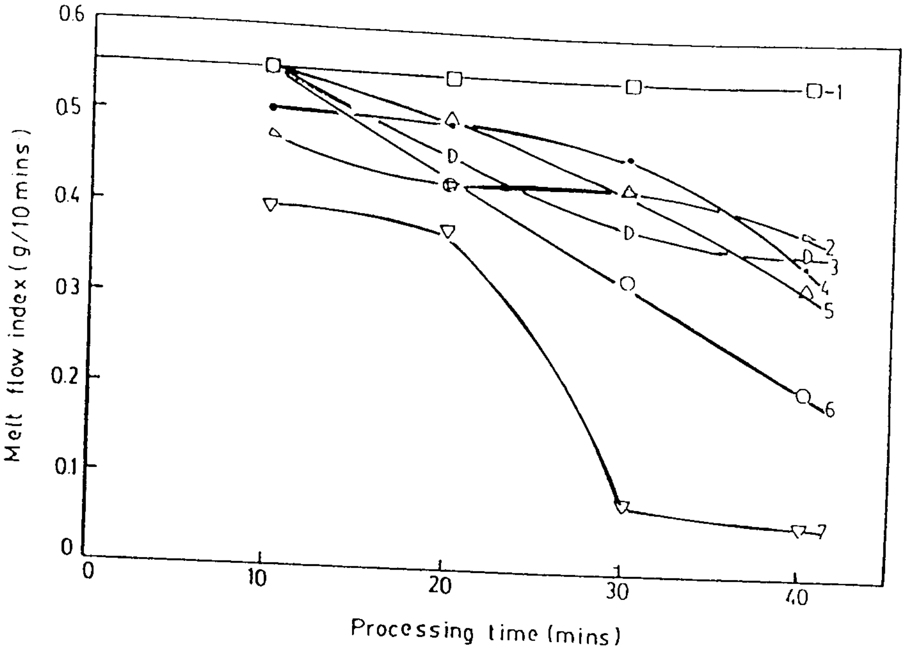


Fig. 3.34 Effect of different additives [conc. of additives 1.25 X 10^{-4} mol/100g (0.05%)] on the change in melt flow index (MFI) of LDPE processed at 160°C in open mixer (1) Fe-DMC and Fe-thiopropionate (2) Fe-cinnamate (3) Fe-acrylate (4) Fe-crotonate (5) Fe-maleate (6) Control (7) Fe-thioacetate .

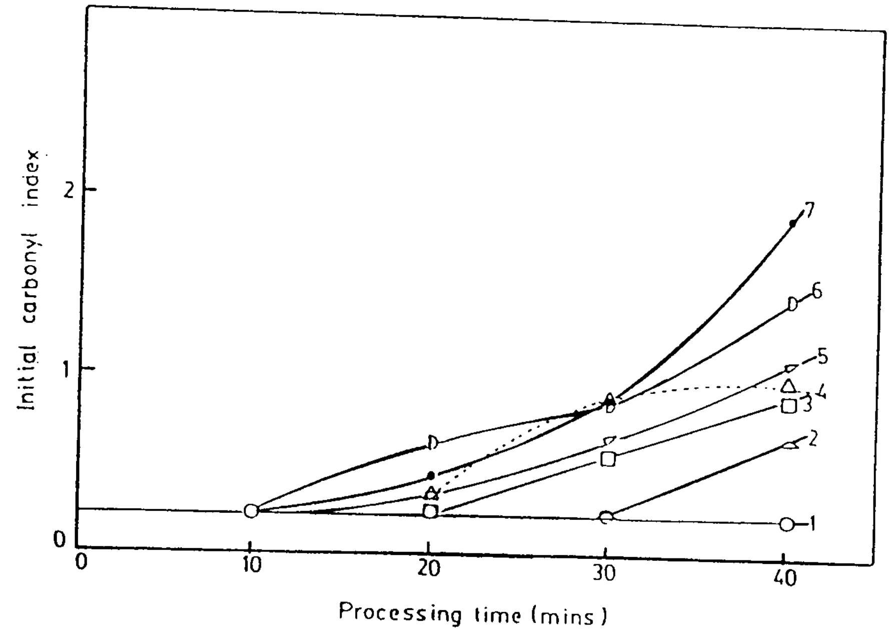


Fig. 3.35 Effect of different additives on the oxidative stability of LDPE during processing in open mixer [conc. of additives 1.25 X 10^{-4} mol/100g (0.05%)] (1) Fe-DMC and Fe-thiopropionate (2) Fe-maleate (3) Fe-acrylate (4) Fe-crotonate (5) Fe-cinnamate (6) control (7) Fe-thioacetate .

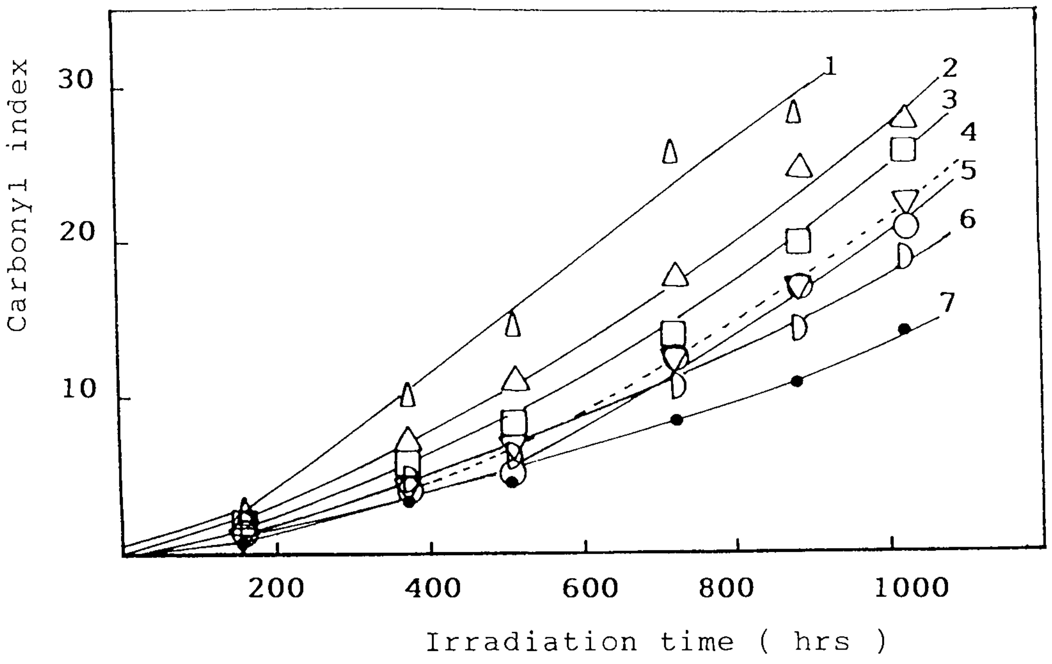


Fig. 3.36 Effect of varying the concentration of ZnDEC on the photo-oxidation of unstabilised LDPE in the presence of 0.2% Fe-acrylate. Fe-acrylate samples are diluted from 5% masterbatch containing 0.28g DCP processed at 160^{o}C for 10 minutes. 1) FeAc + ZnDEC(0.2%+0.2%), 2) FeAc (0.2%), 3) FeAC + ZnDEC(0.2% + 0.025%), 4) FeAc + ZnDEC (0.2% + 0.05%), 5) FeAc + ZnDEC(0.2%+0.01%), 6) LDPE control and 7) ZnDEC(0.2%).

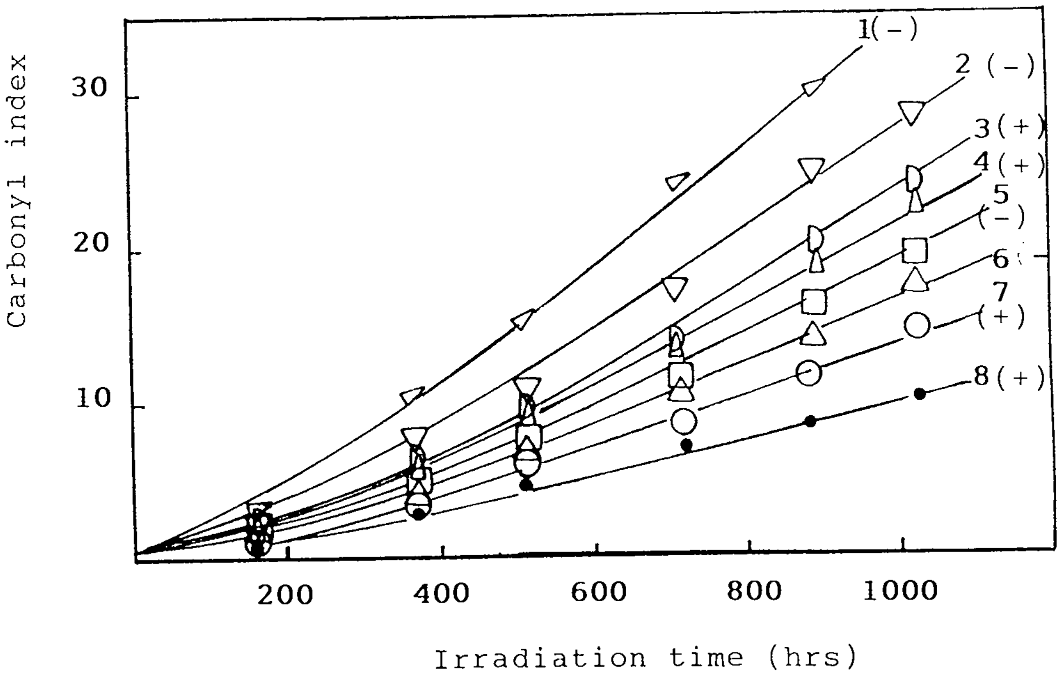


Fig. 3.37 Effect of Fe-acrylate concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.025% ZnDEC. Fe-acrylate samples are diluted from 5% masterbatch containing 0.28g DCP processed at 160^{o}C for 10 minutes. 1) 0.4%(-), 2) 0.2%(-), 3) 0.4%(+), 4) 0.2%(+), 5) 0.1%(-), 6) 0.025% (-), 7) 0.1%(+) & LDPE control and 8) 0.025%(+).

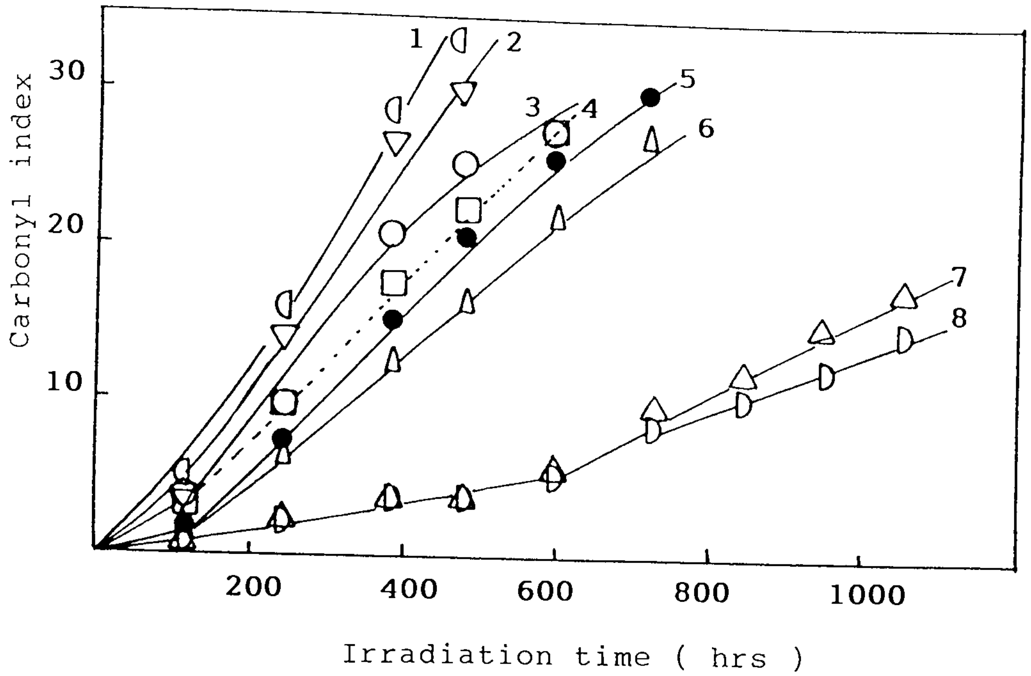


Fig. 3.38 Effect of varying the concentration of ZnDEC on the photo-oxidation of unstabilised LDPE in the presence of 0.2% Fe-crotonate. Fe-crotonate samples are diluted from 5% masterbatch containing 0.28g DCP processed at 160°C for 10 minutes. 1) FeCr + ZnDEC(0.2% + 0.2%), 2) FeCr + ZnDEC(0.2%+0.1%), 3) FeCr(0.2%), 4) FeCr + ZnDEC(0.2%, + 0.05 %), 5) FeCr + ZnDEC(0.2% + 0. 025%),6) FeCr + ZnDEC (0.2% + 0.01%), 7) LDPE control and 8) ZnDEC(0.1% & 0.2%)

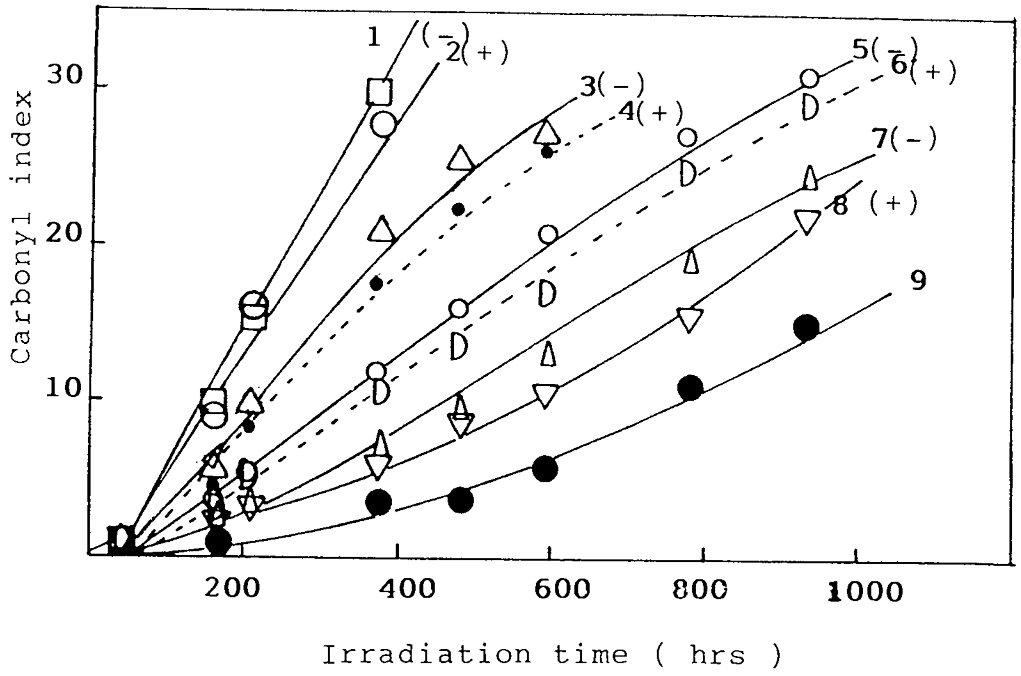


Fig. 3.39 Effect of Fe-crotonate concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.025% ZnDEC. Fe-crotonate samples are diluted from 5% masterbatch containing 0.28g DCP processed at 160°C for 10 minutes. 1) 0.4%(-), 2) 0.4%(+), 3) 0.2%(-), 4) 0.2(+), 5) 0.05(-), 6) 0.05%(+), 7) 0.025%(-), 8) 0.025(+) and 9) LDPE control.

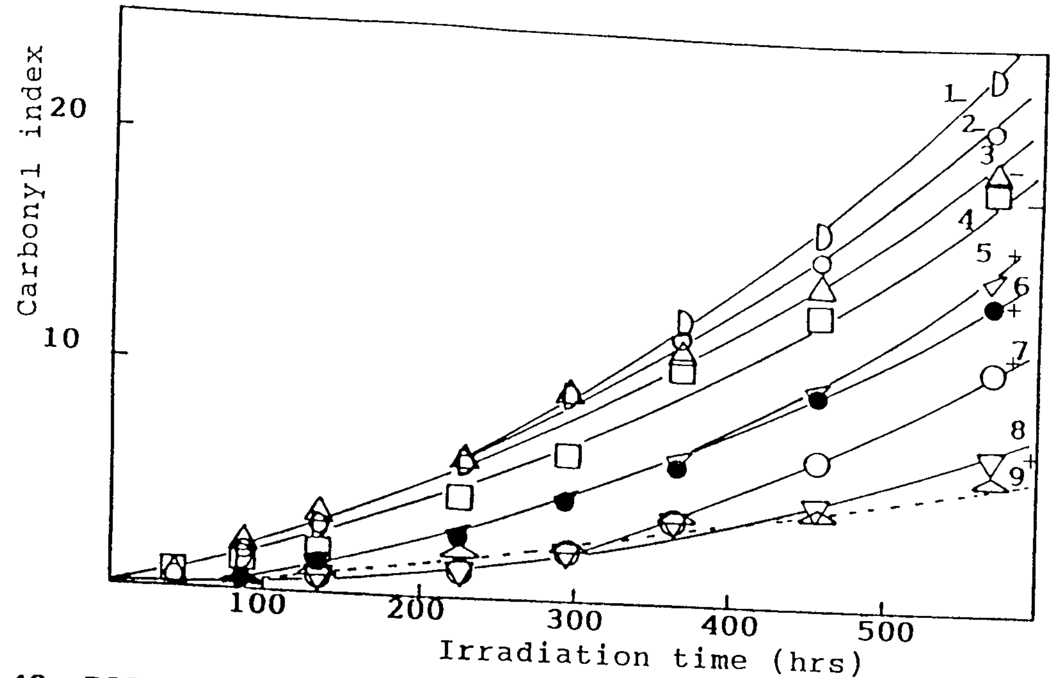


Fig. 3.40 Effect of Fe-thiopropionate conc. on the photo-oxidation of LDPE in the presence(+) and absence(-) of 0.1% ZnDEC 1) 0.2%(-), 2) 0.025%(-), 3) 0.1%(-), 4) 0.3%(-), 5) 0.1%(+), 6) 0.025%(+), 7) 0.2%(+), 8) 0.3%(+) and 9) LDPE control. Samples are diluted from 5% MB with (I/P_o)-molar ratio = 0.15 (Trigonox 101) (no interlinking agent). I = initiator and P_o = pro-oxidant.

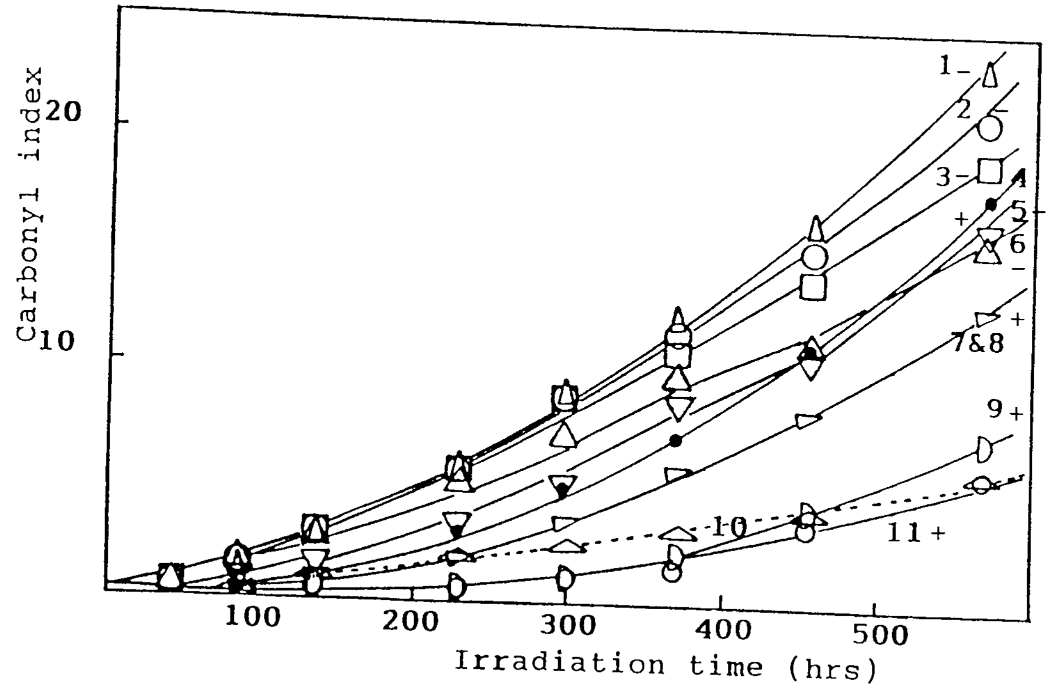


Fig. 3.41 Effect of Fe-thiopropionate conc. on the photo-oxidation of LDPE in the presence(+) and absence(-) of 0.2% ZnDEC 1) 0.2%(-), 2) 0.025%(-), 3) 0.1%(-), 4) 0.025%(+), 5) 0.4%(-), 6) 0.05%(-), 7) 0.05%(+), 8) 0.1%(+), 9) 0.2%(+) 10) LDPE control and 11) 0.4%(+). Samples are diluted from 5% MB with (I/P_o)-molar ratio = 0.15 (Trigonox 101) (no interlinking agent). I = initiator and P_o = pro-oxidant.

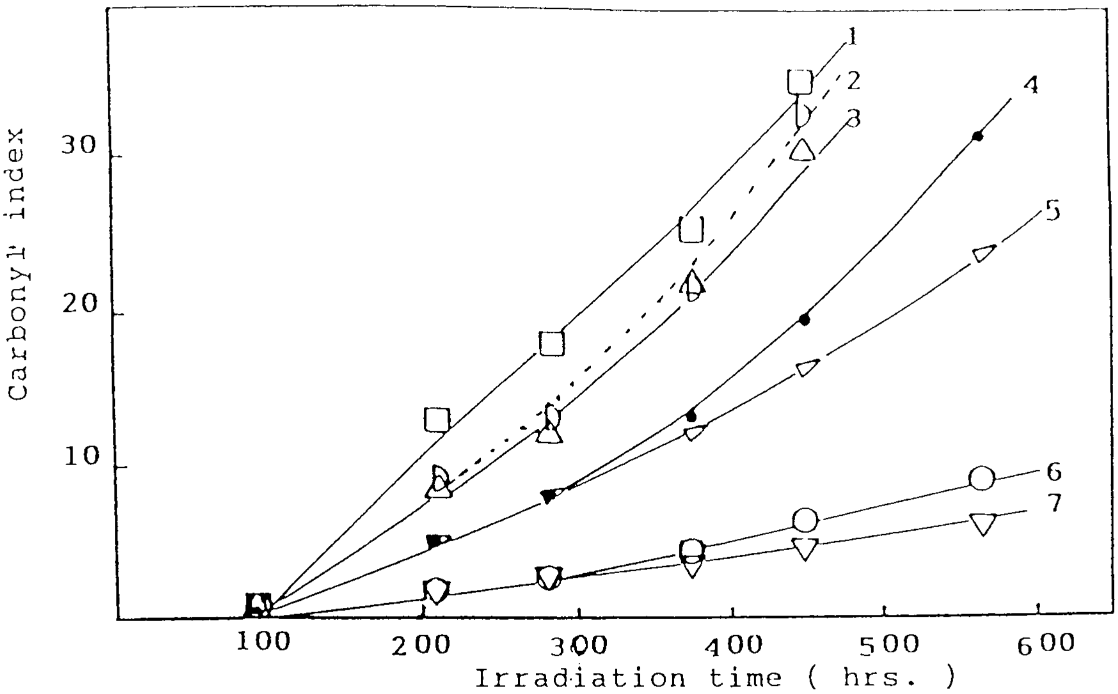


Fig. 3.42 Effect of varying the conc. of ZnDEC on the photo-oxidation of unstabilised LDPE containing 0.05% Fe-thioacetate. 1) 0.4% 2) 0.3% 3) 0.05% 4) 0.025% 5) 0.05% Fe-thioacetate 6) LDPE control 7) ZnDEC (0 . 05%). Samples are diluted from 5% masterbatches containing no peroxide processed at 160°C for 10 minutes .

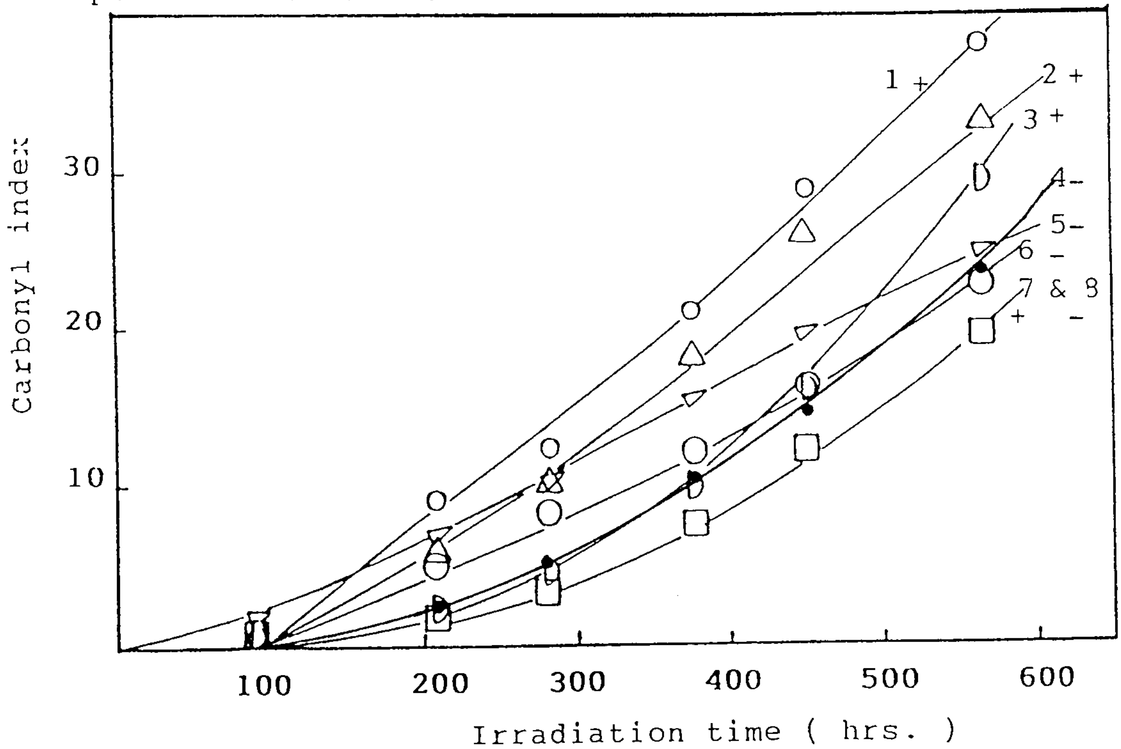


Fig. 3.43 Effect of Fe - thioacetate conc. on the photo - oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.05% ZnDEC 1)0.025%(+) 2)0.2%(+) 3)0.3%(+) 4)0.3%(-) 5)0.025%(-) 6)0.2%(-) 7) and 8) 0.4%(+) and 0.4%(-). Samples are diluted from 5% masterbatches containing no peroxide processed at 160°C for 10 minutes .

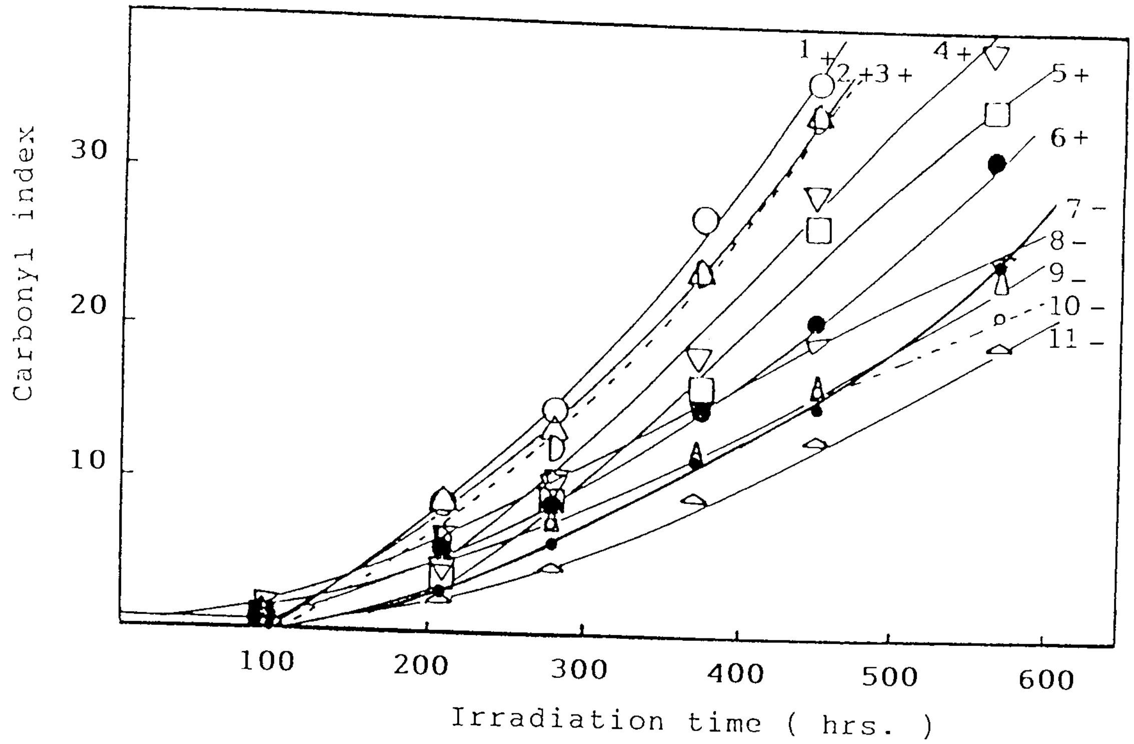


Fig. 3.44 Effect of Fe-thioacetate concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.2% ZnDEC. 1)0.1%(+) 2)0.05%(+) 3)0.2%(+) 4)0.3%(+) 5)0.4%(+) 6)0.025%(+) 7)0.3%(-) 8)0.025%(-) 9)0.05%(-) & 0.2%(-) 10)0.1%(-) and 11)0.4%(-).

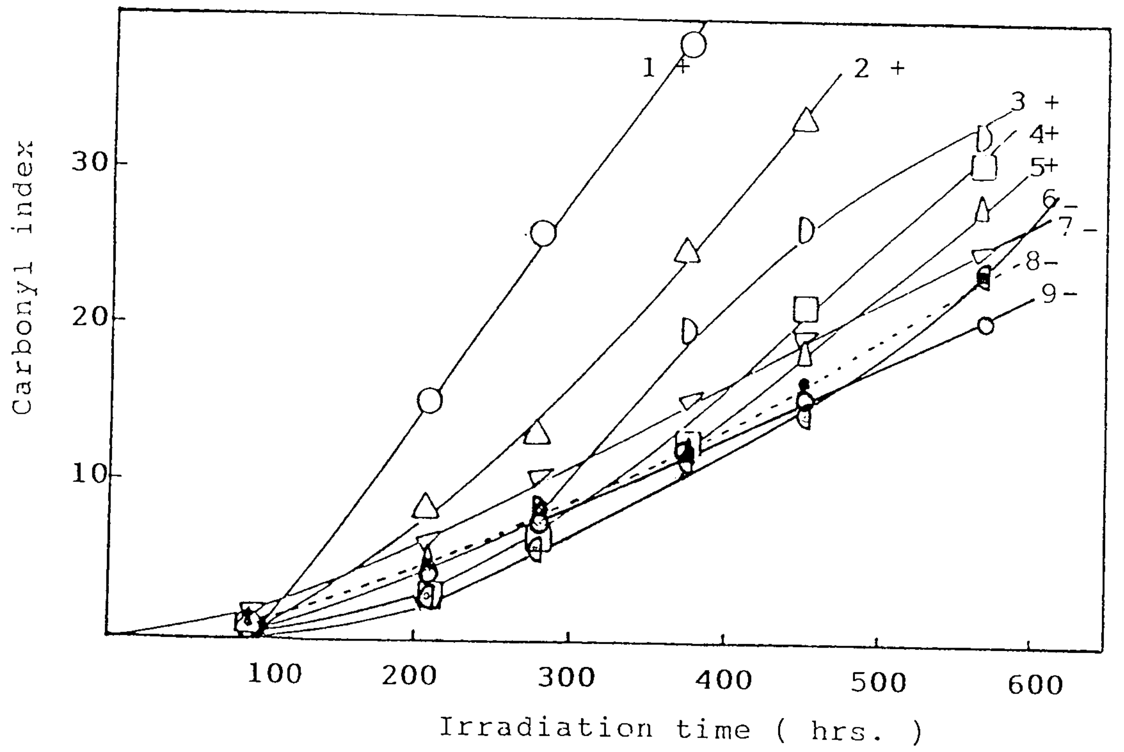
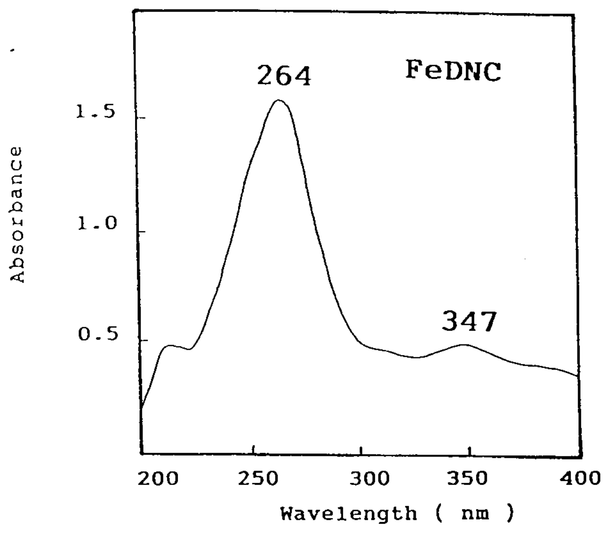


Fig. 3.45 Effect of Fe-thioacetate concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.4% ZnDEC. 1)0.1%(+) 2)0.05%(+) 3)0.2%(+) 4)0.3%(+) 5)0.025%(+) 6)0.3%(-) 7)0.025%(-) 8)0.05%(-) & 0.2%(-) 9) 0.1%(-).



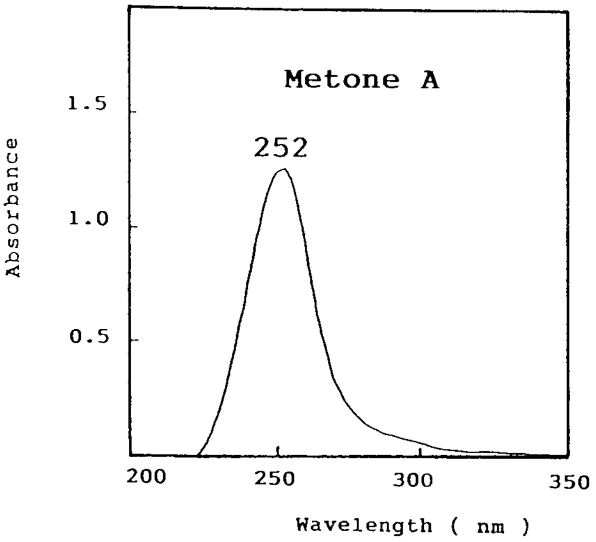


Fig. 3.46 UV-spectrum of iron(III) trisdinonyldithiocarbamate (FeDNC) (3.2 X 10^{-5} mole/litre) in hexane .

Fig. 3.47 UV-spectrum of 2,2'-methylene-bis-1,3-cyclohexanedione (Metone A) (5.0 X 10^{-5} mole/litre) in hexane .

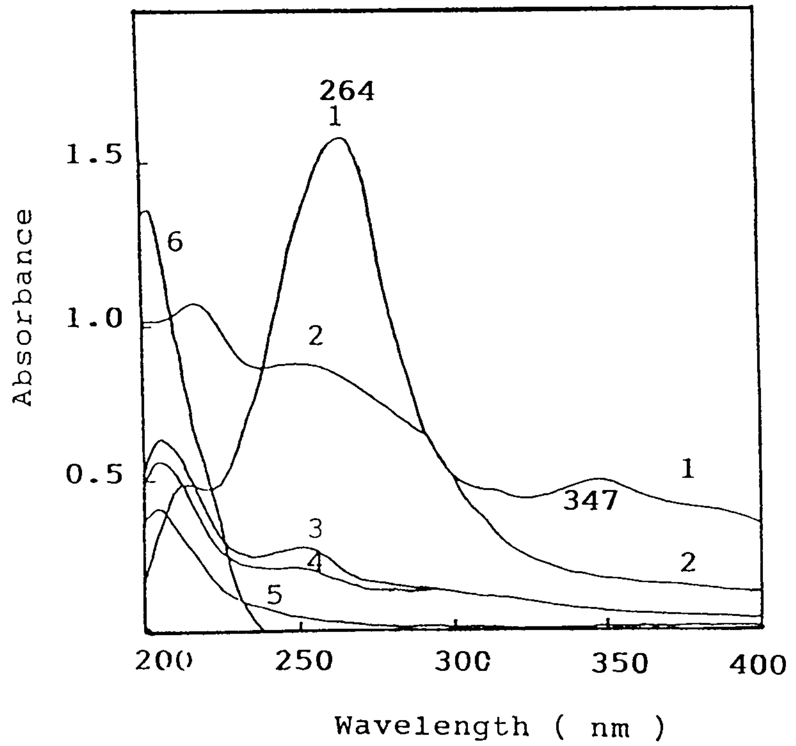


Fig. 3.48 Change in the UV-spectra of FeDNC (3.2 X 10^{-5} mole/litre in hexane during UV-irradiation . 1) 0 hr., 2) 1 hr., 3) 2 hrs., 4) 3.5 hrs., 5) 7 hrs. and 6) 28 hrs. .

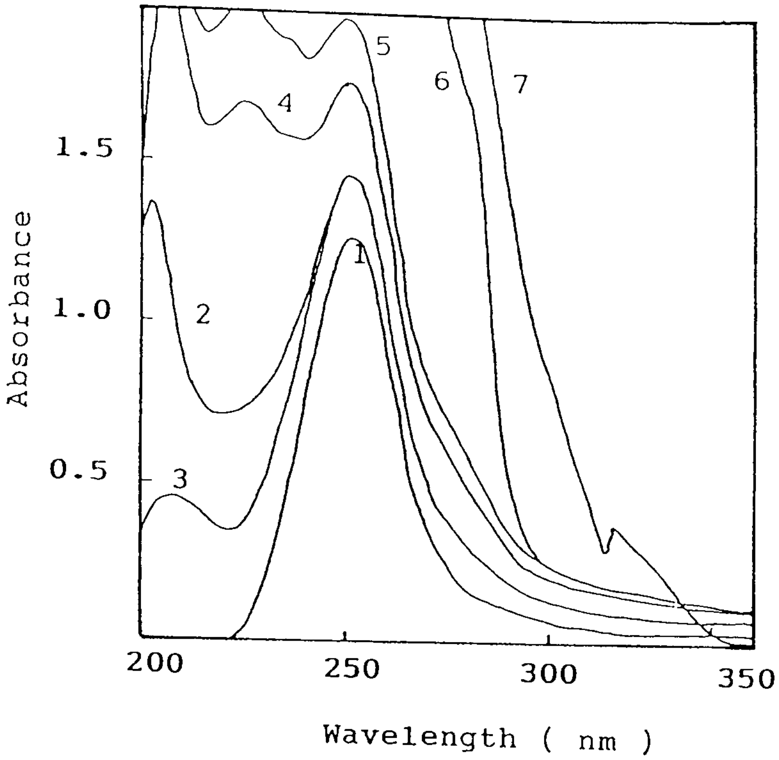


Fig. 3.49 Change in the UV-spectra of Metone A (5 X 10^{-5} mole/ litre) in hexane during UV-irradiation . 1) 0 hr., 2) 1 hr., 3) 2 hrs., 4) 3 hrs., 5) 3.5 hrs., 6) 7 hrs. and 7) 28 hrs. .

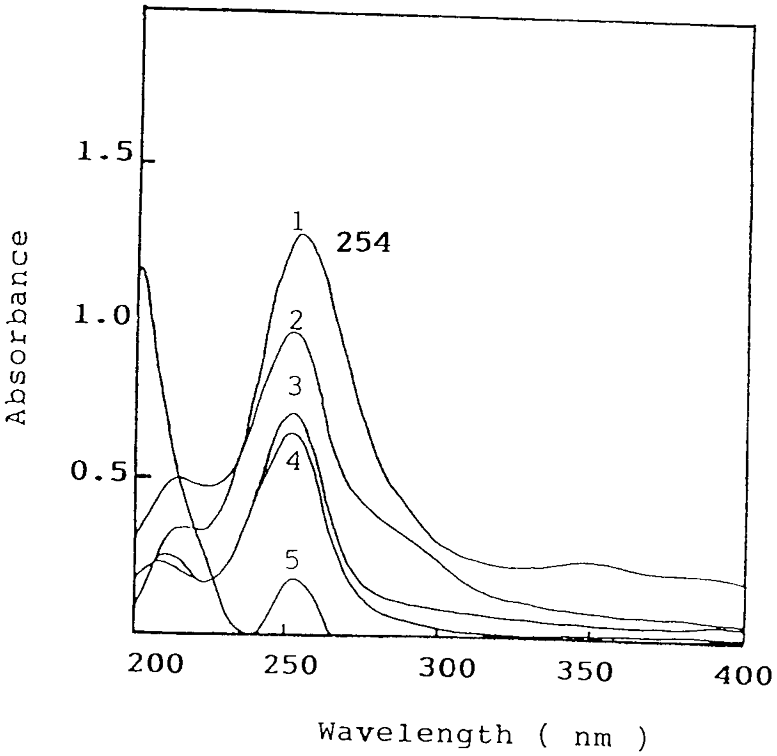


Fig. 3.50 Change in the UV-spectra of FeDNC + Metone A (1.6 X 10^{-5} mole/litre + 2.5 X 10^{-5} mole/litre) in hexane during UV-irradiation . 1) 0 hr., 2) 1 hr., 3) 2 hrs., 4) 7 hrs. and 5) 28 hrs. .

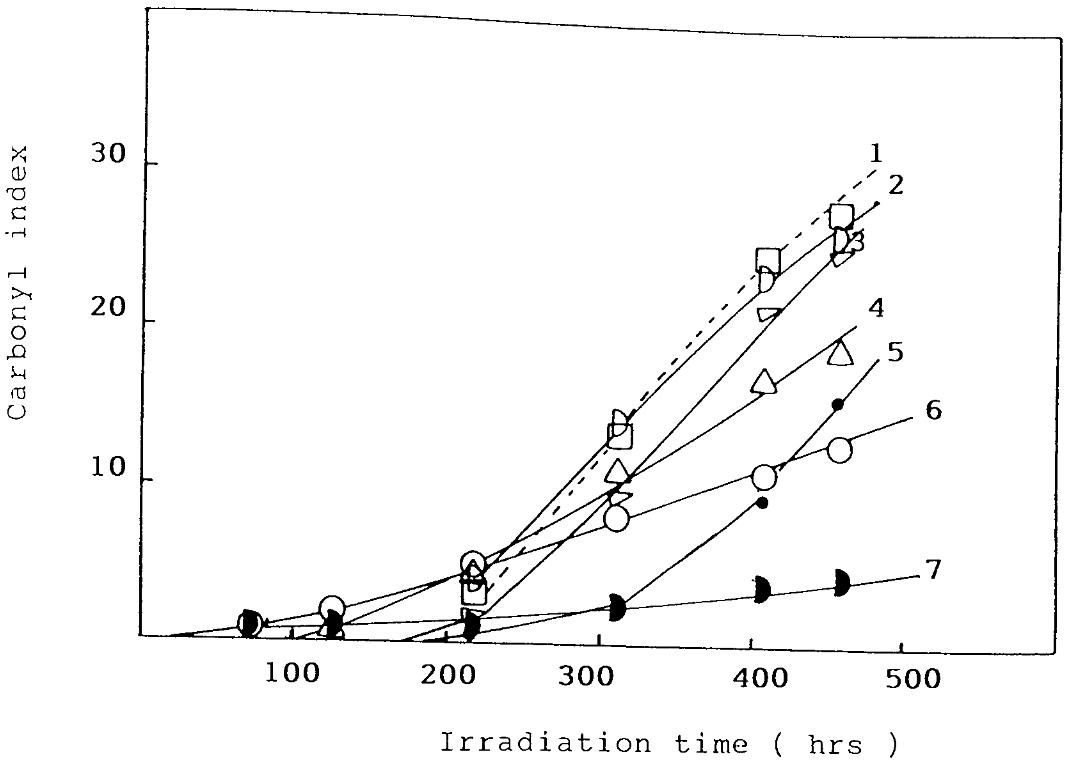


Fig. 3.51 Effect of variation of FeDNC concentration on the photo-oxidation of unstabilised LDPE. Samples are diluted from 5% masterbatch processed at 160°C for 10 minutes. 1) 0.2%, 2) 0.1%, 3) 0.3%, 4) 0.05%, 5) 0.4%, 6) 0.01% and 7) LDPE control.

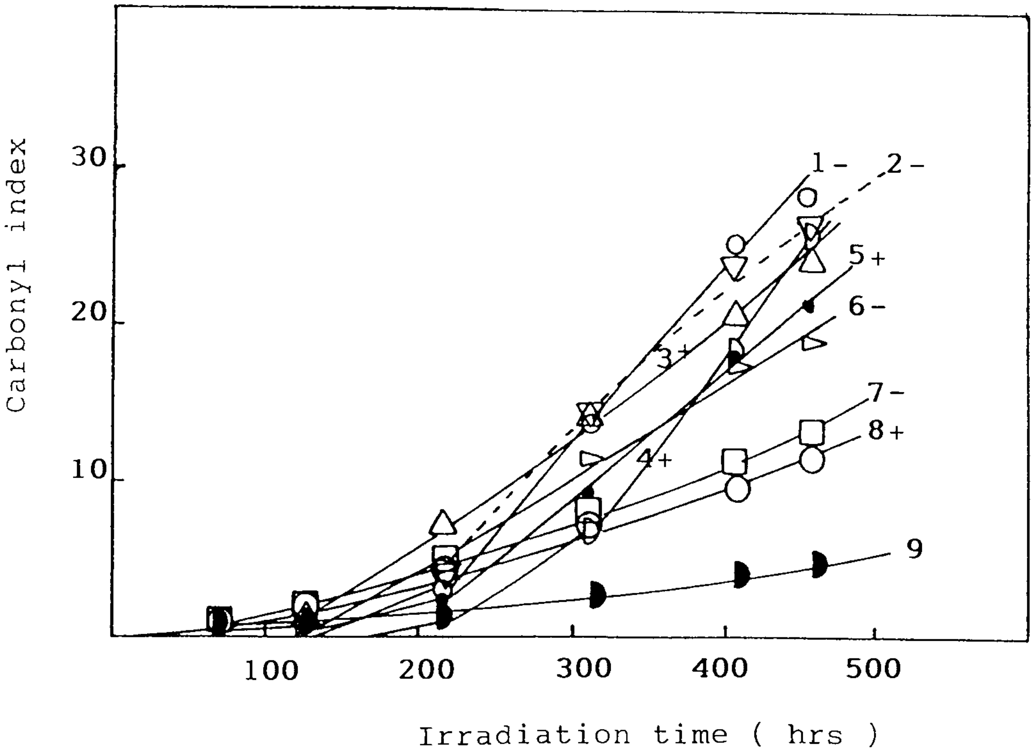


Fig. 3.52 Effect of FeDNC concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.001% NiDNC. Samples are diluted from 5% masterbatch processed at 160°C for 10 minutes. 1) 0.2%(-), 2) 0.1%(-), 3) 0.05%(+), 4) 0.2%(+), 5) 0.1%(+), 6) 0.05%(-), 7) 0.01%(-), 8) 0.01%(+) and 9) LDPE control.

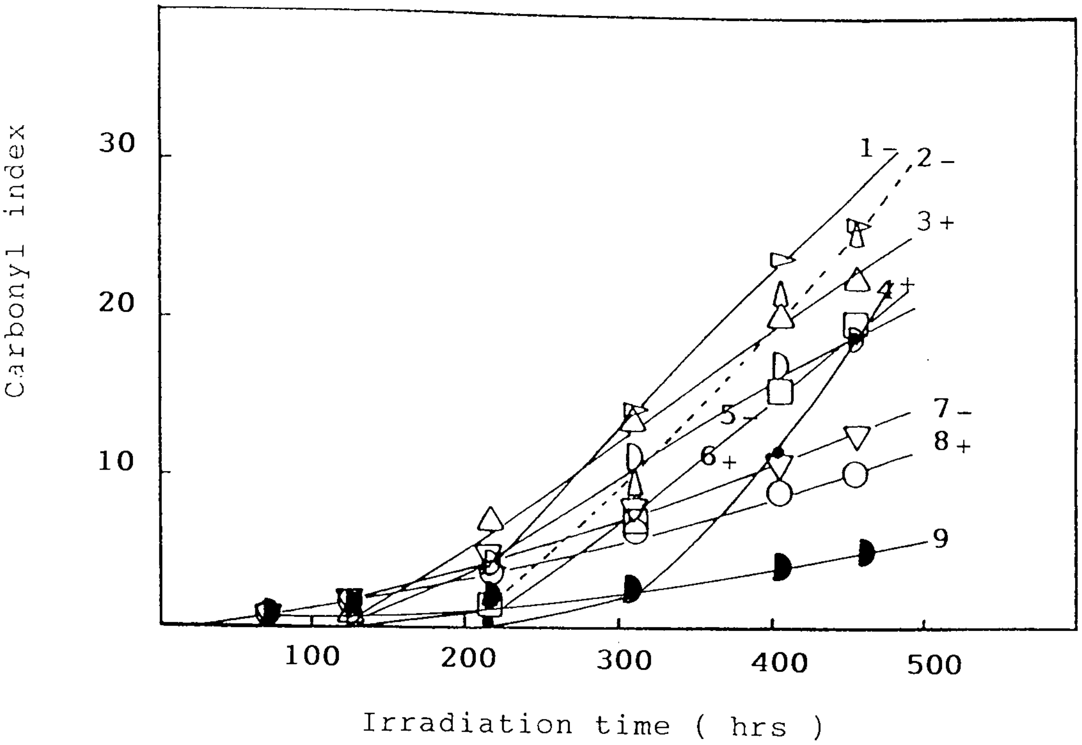


Fig.3.53 Effect of FeDNC concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.005% NiDNC. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes. 1) 0.1%(-), 2) 0.3%(-), 3) 0.05%(+), 4) 0.3%(+), 5) 0.05%(-), 6) 0.1%(+), 7) 0.01% (-), 8) 0.01%(+) and 9) LDPE control.

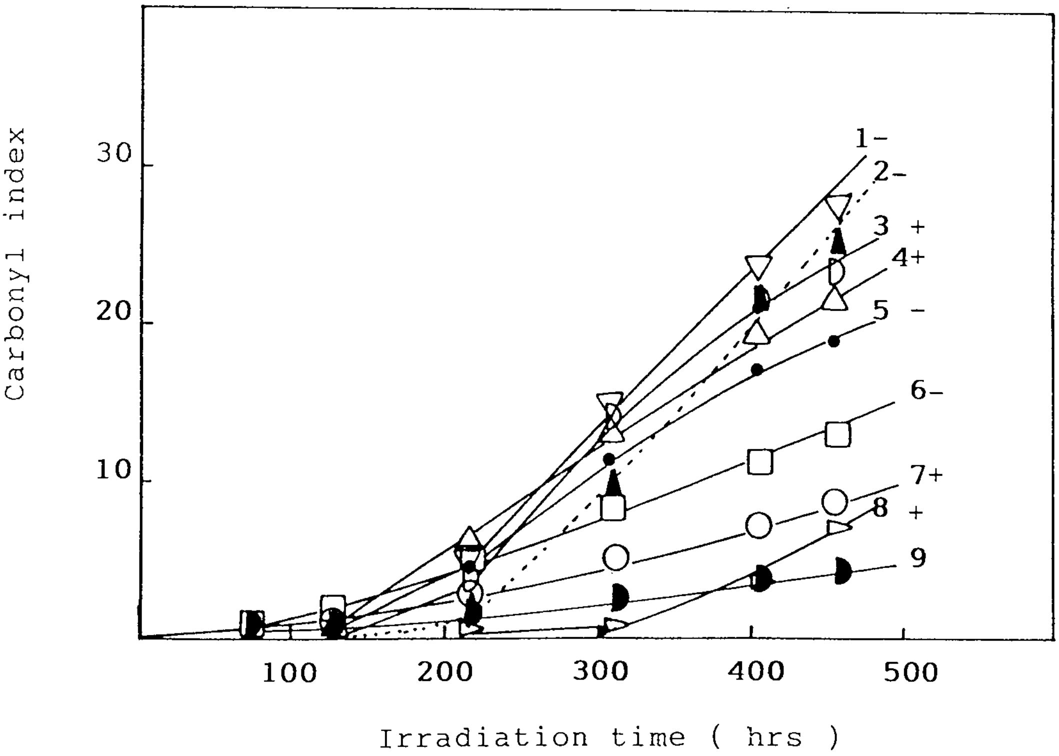


Fig. 3.54 Effect of FeDNC concentration on the photo-oxidation of unstabilised LDPE in the presence(+) and absence(-) of 0.01% NiDNC. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes. 1) 0.1%(-), 2) 0.3%(-), 3) 0.1%(+), 4) 0.05%(+), 5) 0.05%(-), 6) 0.01%(-), 7) 0.01%(+), 8) 0.3%(+) and 9) LDPE control.

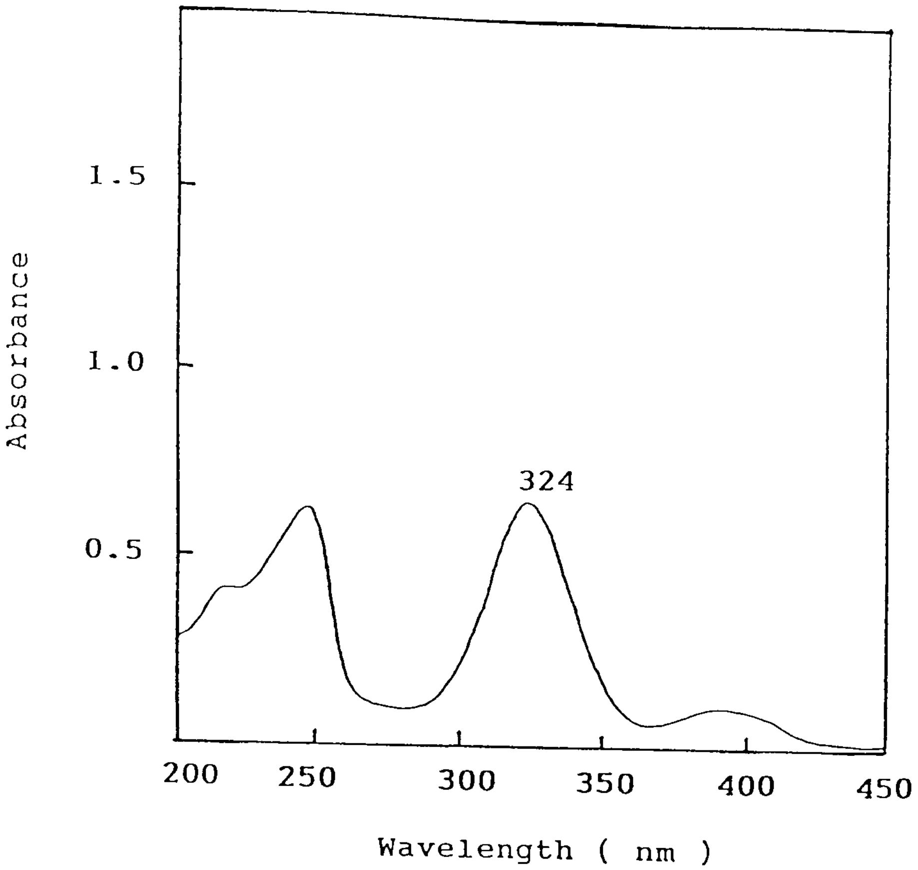


Fig. 3.55 UV-spectrum of NiDNC (1.6 X 10^{-5} mole/litre) in hexane.

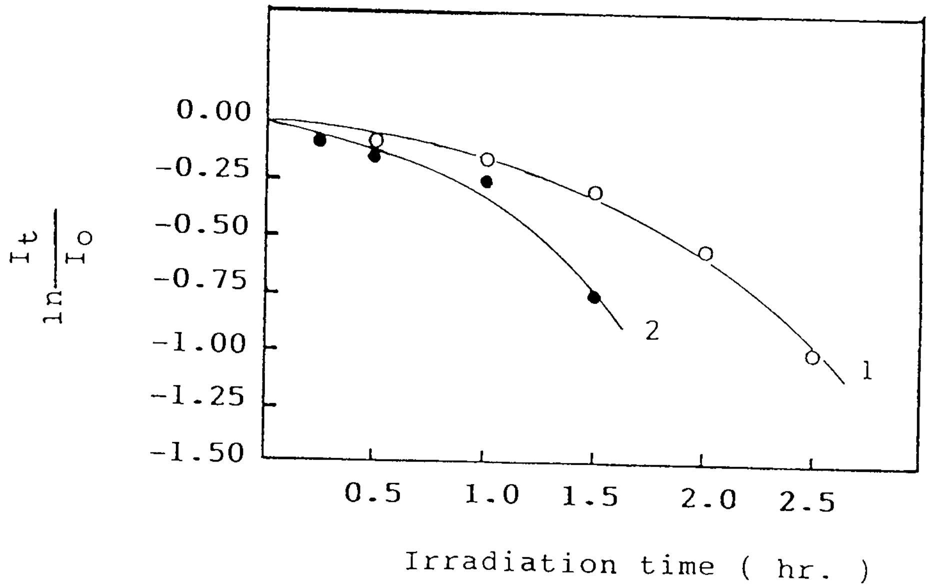


Fig. 3.56 First order decomposition plot of NiDNC (λ_{max} = 324 nm) in hexane during UV-irradiation . 1) NiDNC (1.6 X 10^{-5} mole/litre) and 2) NiDNC + FeDNC (1.6 X 10^{-5}mole/litre + 3.2 X 10^{-5} mole/litre) .

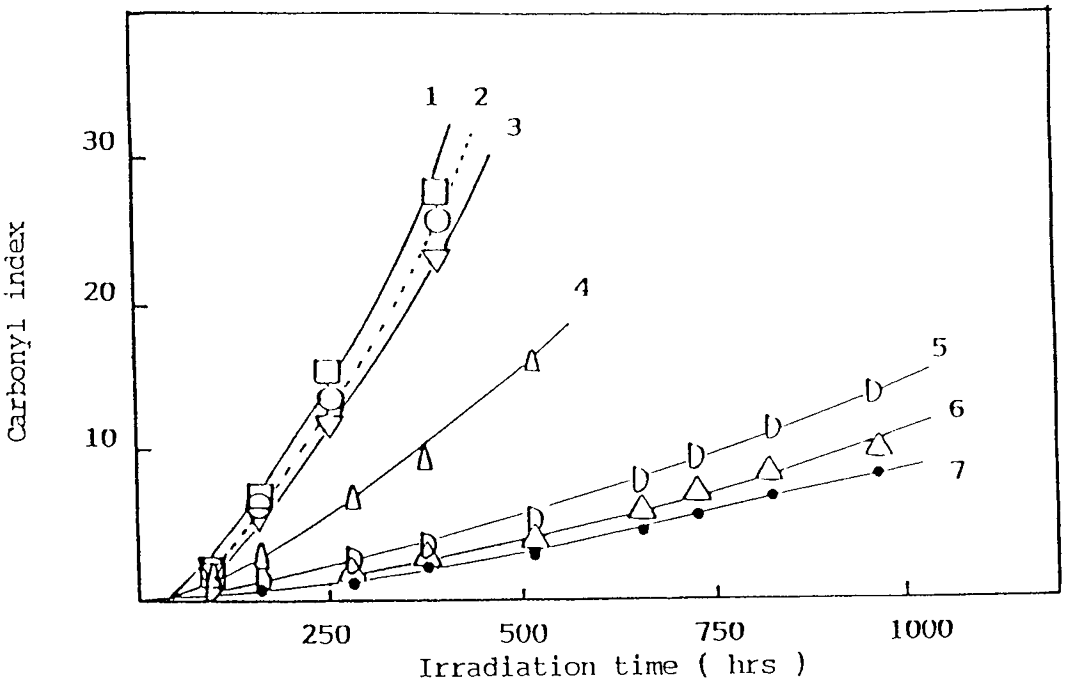


Fig. 3.57 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial LDPE (1) FeDNC(0.05%) (2) FeDNC + Metone M(0.05% + 0.05%) (3) Fe-acrylate + ZnDNC(0.05%+0.05%) (4) Fe-acrylate(0.05%) (5) Metone M + ZnDNC (0.05% + 0.05%) (6) Metone M (0.05%) (7) Control.

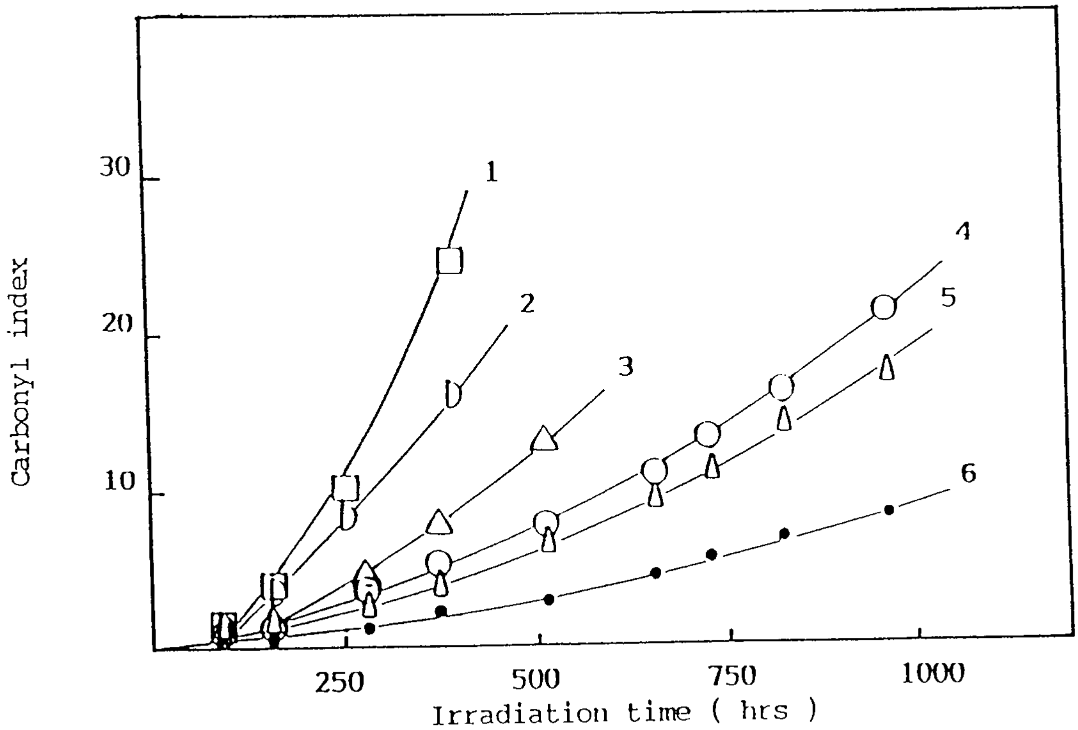


Fig. 3.58 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial LDPE (1) FeDNC(0.05%) (2) Fe-thioacetate + ZnDNC (0.05% + 0.05%) (3) Fe-thioacetate (0.05%) (4) Fe-thiopropionate + ZnDNC(0.05% + 0.05%) (5) Fe-thiopropionate(0.05%) (6) Control.

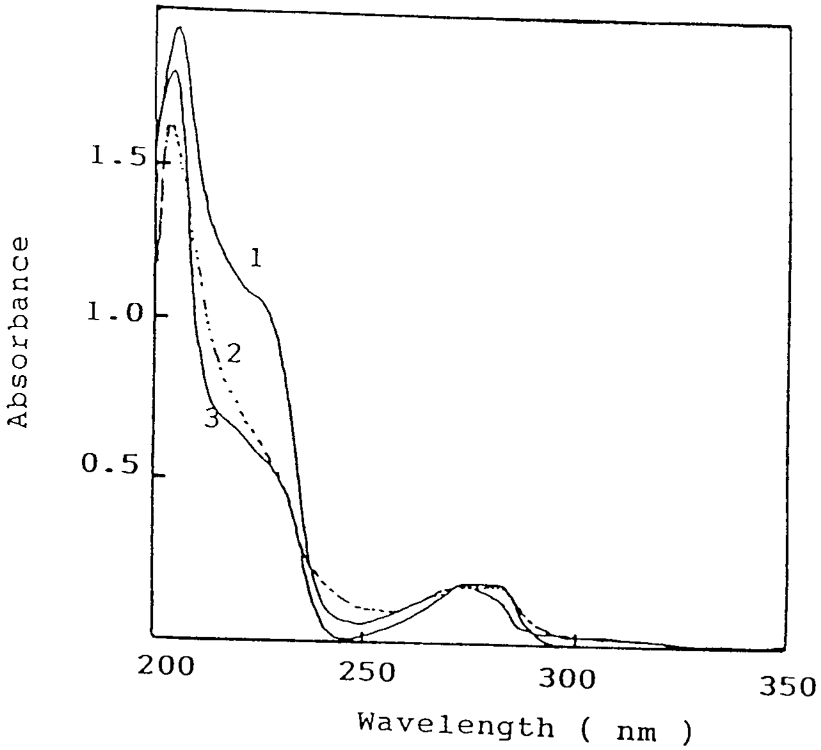


Fig. 3.59 UV-spectra of 1) hexane extract of commercial PP, 2) hexane extract of commercial LDPE and 3) Irganox 1076 in hexane (9.1 X 10^{-5} mole/litre).

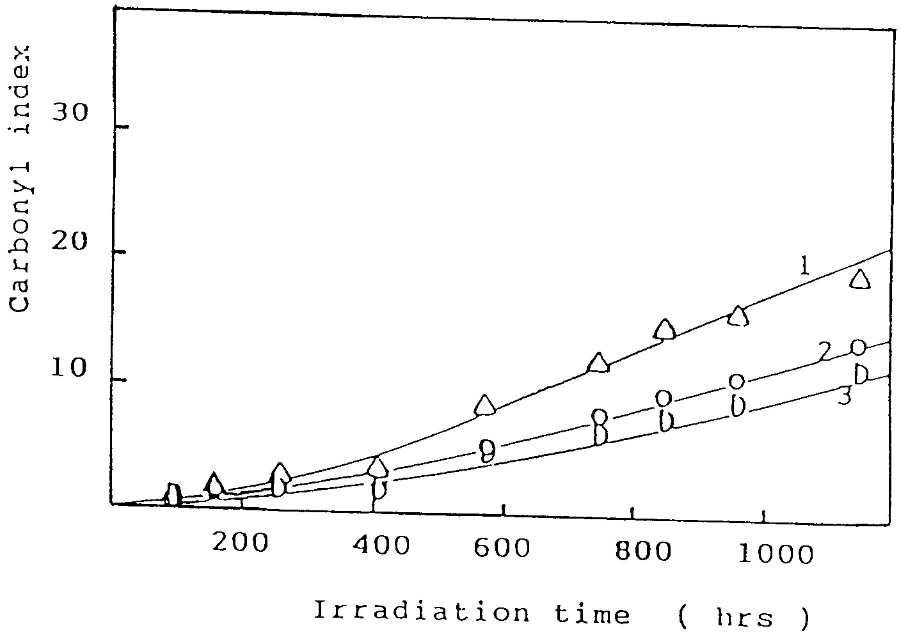


Fig. 3.60 Effect of ZnDNC on the photo-oxidation of unstabilised LDPE containing Irganox 1076 . 1) ZnDNC + Irganox 1076 (0.05% + 0.05%), 2) ZnDNC (0.05%), 3) Irganox1076 (0.05%).

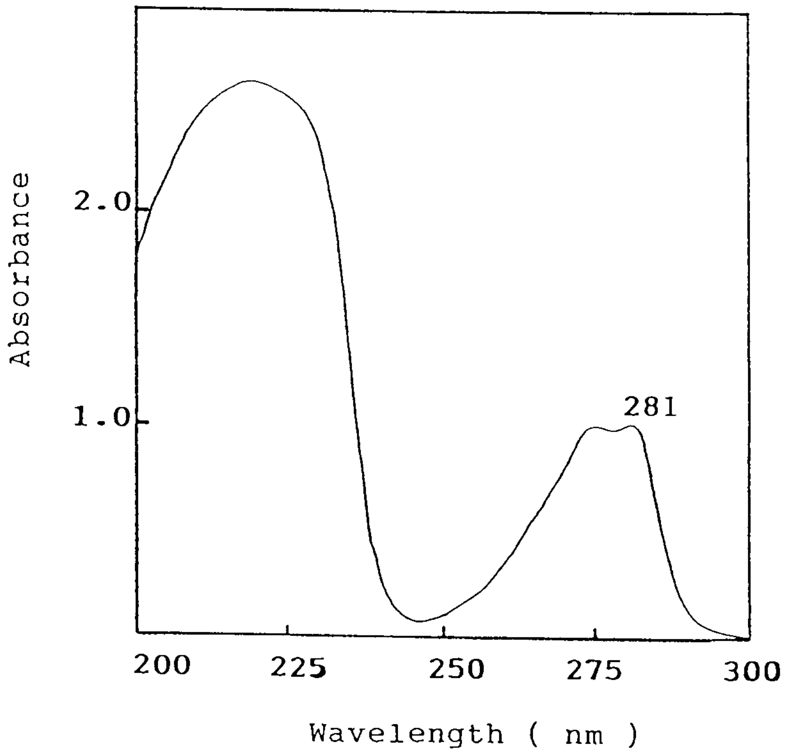


Fig. 3.61 UV-spectrum of Irganox 1076 (4.5 X 10^{-4} mole/litre) in hexane.

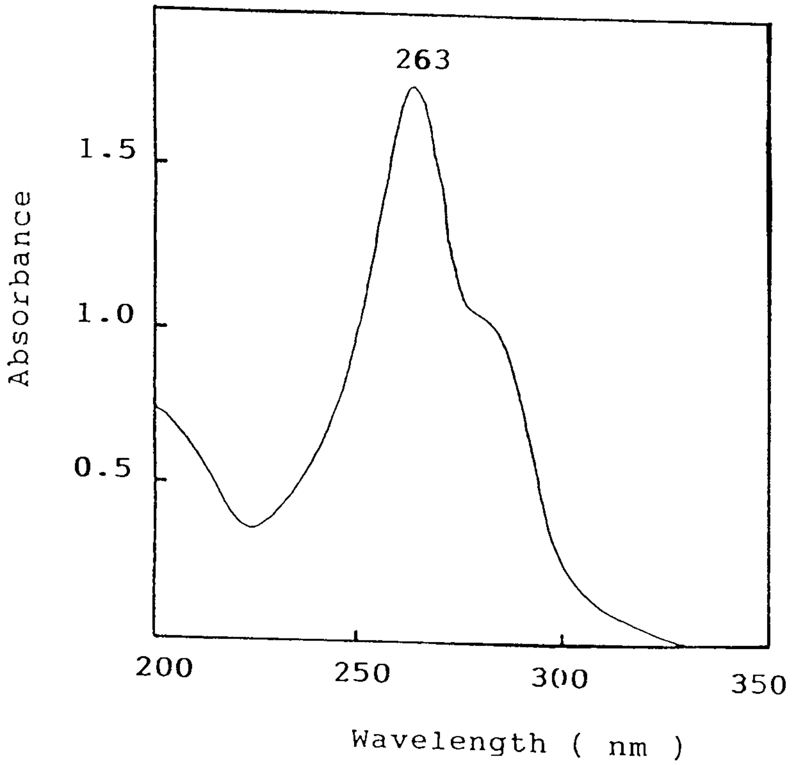


Fig. 3.62 UV-spectrum of ZnDNC (3.3 X 10^{-5} mole/litre) in hexane.

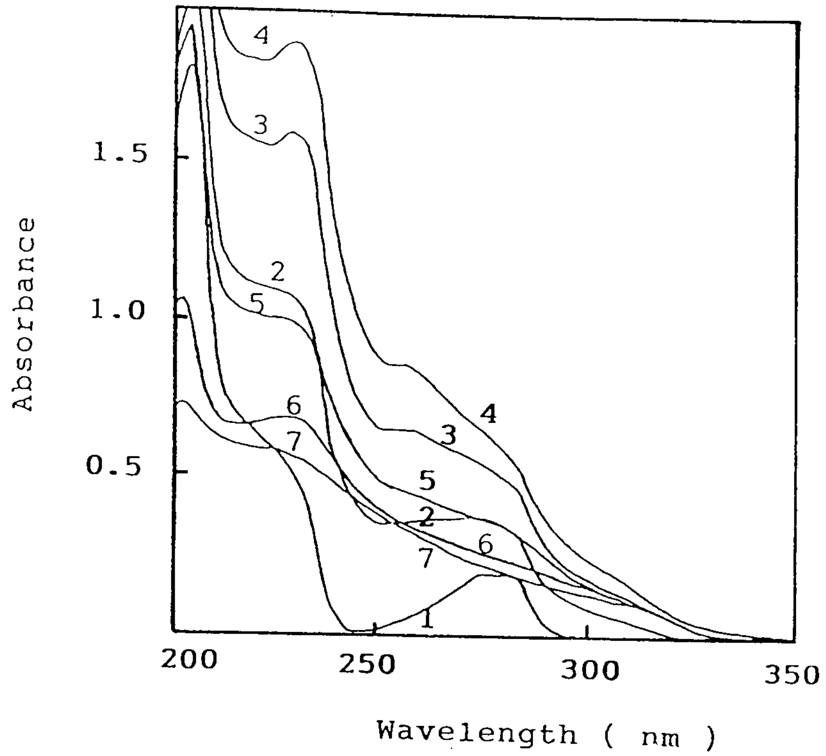


Fig. 3.63 Change in the UV-spectra of Irganox 1076 (9.1 X 10^{-5} mole/litre) in hexane during UV-irradiation . 1) 0 hr. 2) 30 min., 3) 45 min., 4) 1 hr., 5) 2 hrs., 6) 3 hrs. and 7) 5 hrs. .

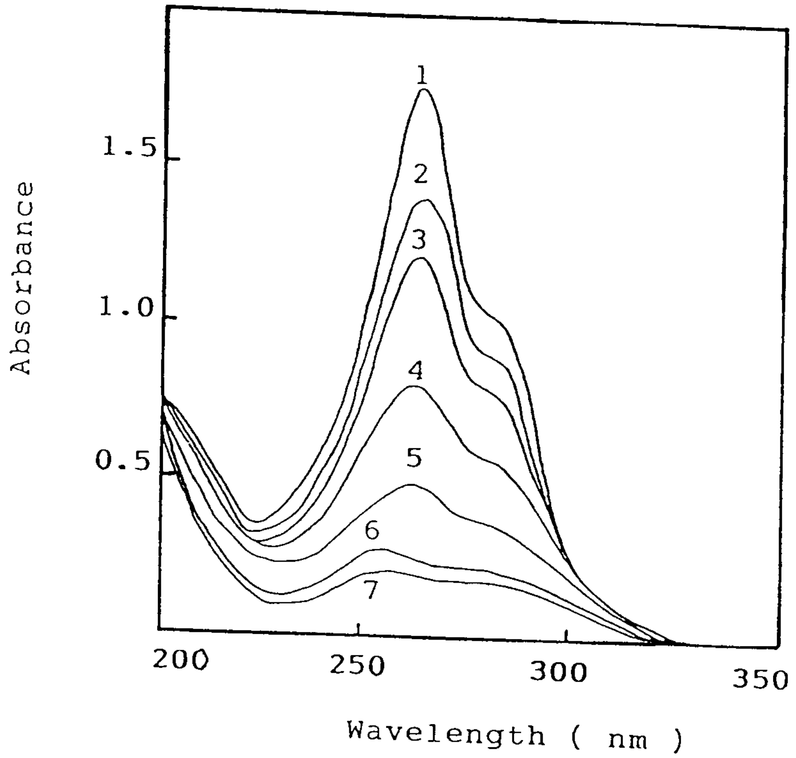


Fig. 3.64 Change in the UV-spectra of ZnDNC (3.3 X 10^{-5} mole/litre) in hexane during UV-irradiation. 1) 0 hr., 2) 15 min., 3) 30 min., 4) 45 min., 5) 1 hr., 6) 1.5 hrs. and 7) 2 hrs.

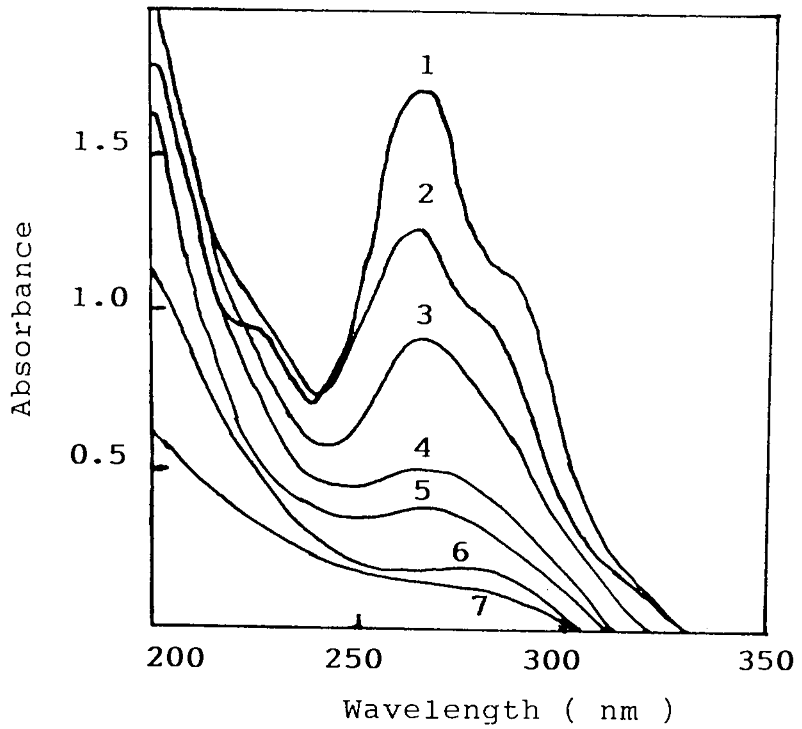


Fig. 3.65 Change in the UV-spectra of Irganox 1076 + ZnDNC (9.1 X 10^{-5} mole/litre + 3.3 X 10^{-5} mole/litre) in hexane during UV-irradiation. 1) 0 hr., 2) 15 min., 3) 30 min., 4) 45 min., 5) 1 hr., 6) 1.5 hrs. and 7) 5 hrs. .

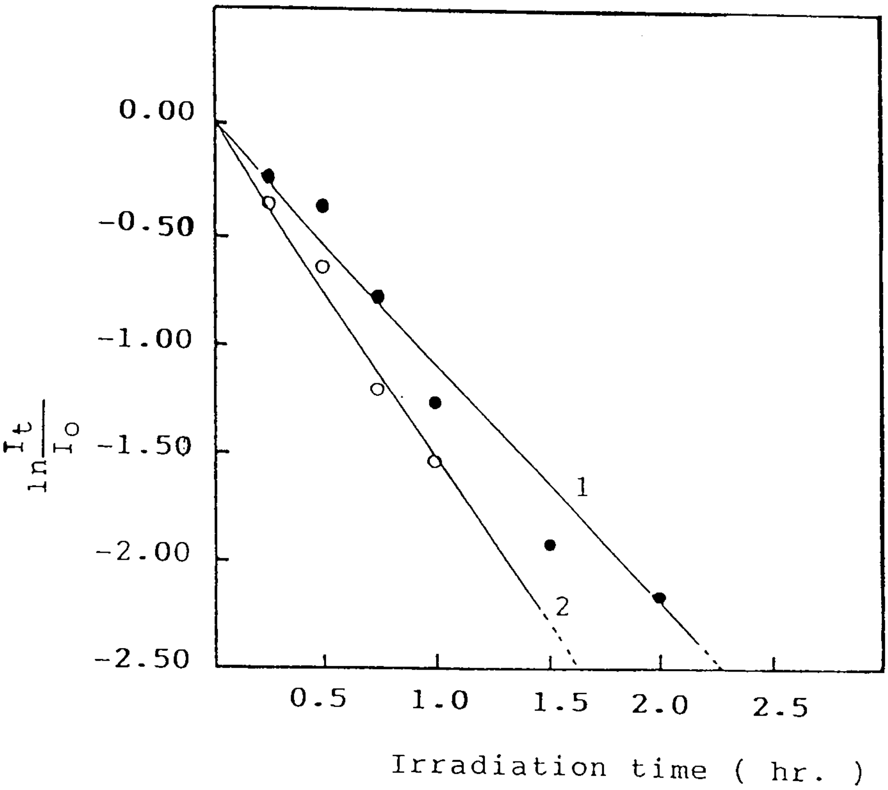


Fig. 3.66 First order decomposition plot of ZnDNC (λ_{max} = 263 nm) in hexane during UV-irradiation. 1) ZnDNC (3.3 X 10^{-5}mole/ litre) and 2) Irganox 1076 + ZnDNC (9.1 X 10^{-5} mole/ litre + 3.3 X 10-5 mole/litre) .

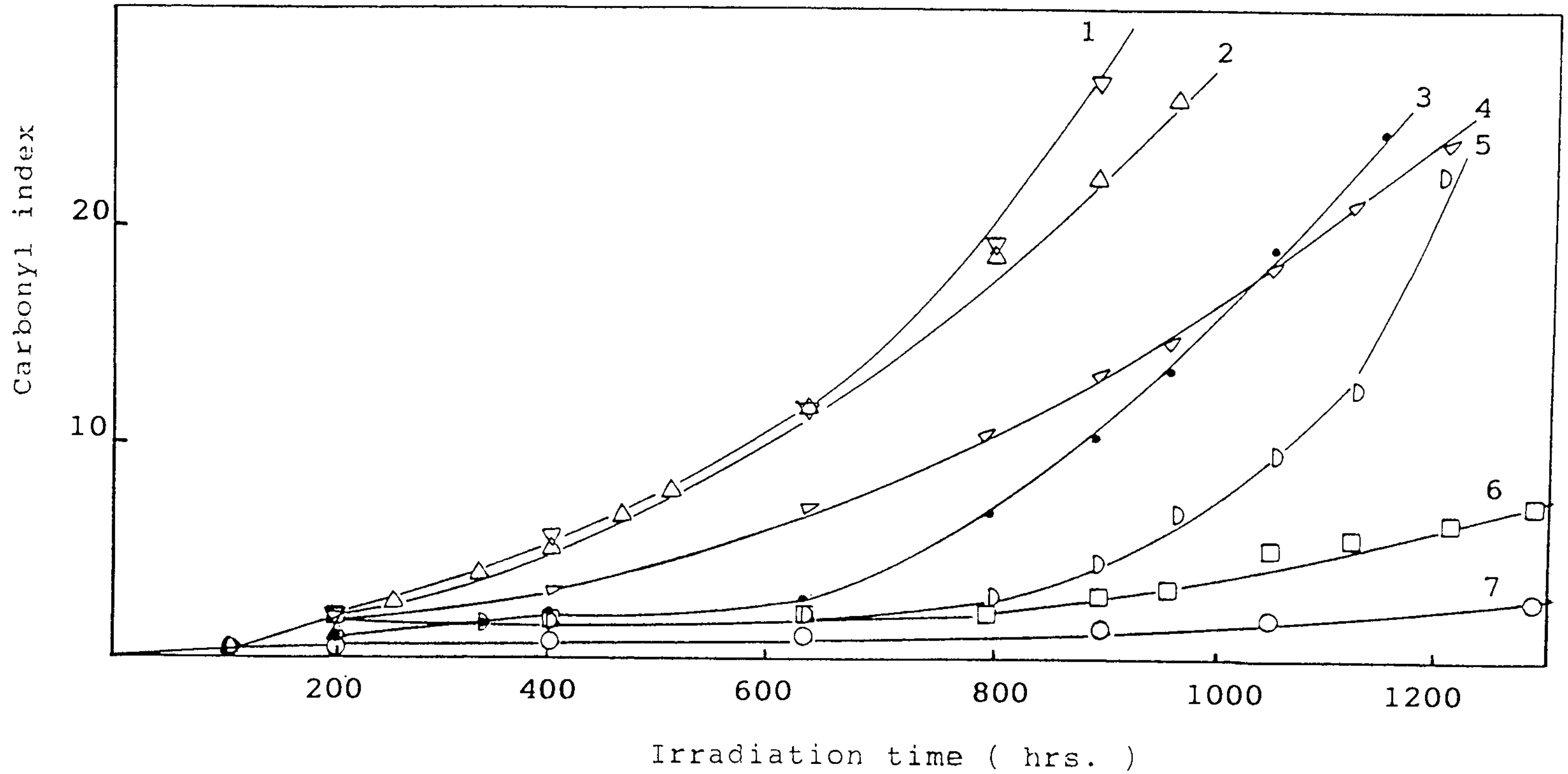


Fig. 3.67 The effect of varying the concentration of Fe-thioacetate and Fe-thiopropionate on the UV stability of LDPE (BP). 1) 0.2% Fe-thiopropionate, 2) 0.05% Fe-thioacetate, 3) 0.1% Fe-thioacetate, 4) 0.1% Fe-thiopropionate, 5) 0.2% Fe-thioacetate, 6) 0.05% Fe-thiopropionate and 7) control .

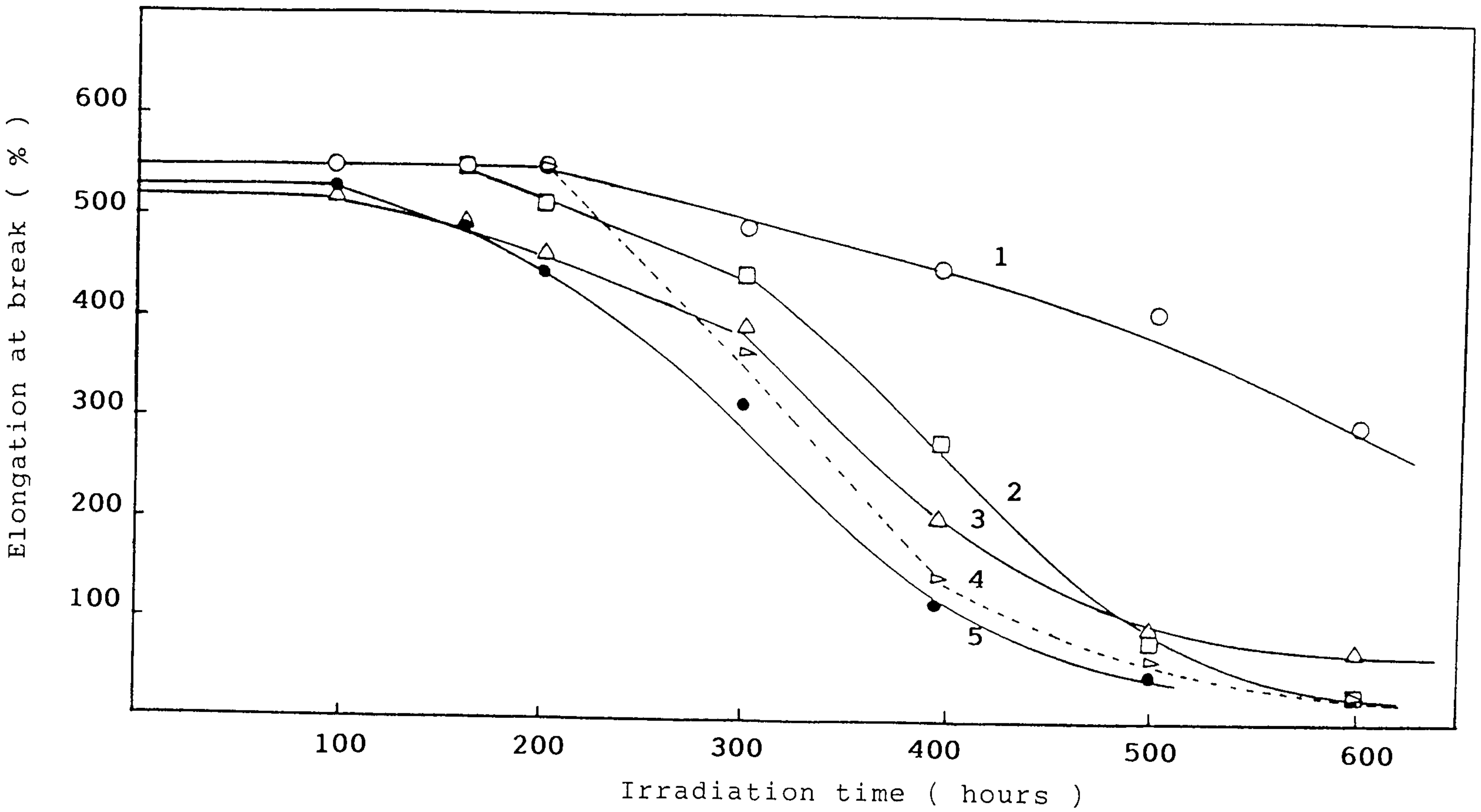


Fig. 3.68 Comparison of the change of percentage of elongation at break as a function of exposure time of unstabilised LDPE containing different pro-oxidants (0.2%). Samples are diluted from 5% masterbatches containing no peroxide. 1) LDPE control, 2) FeTa, 3) FeTp, 4) FeDMC and 5) FeAc .

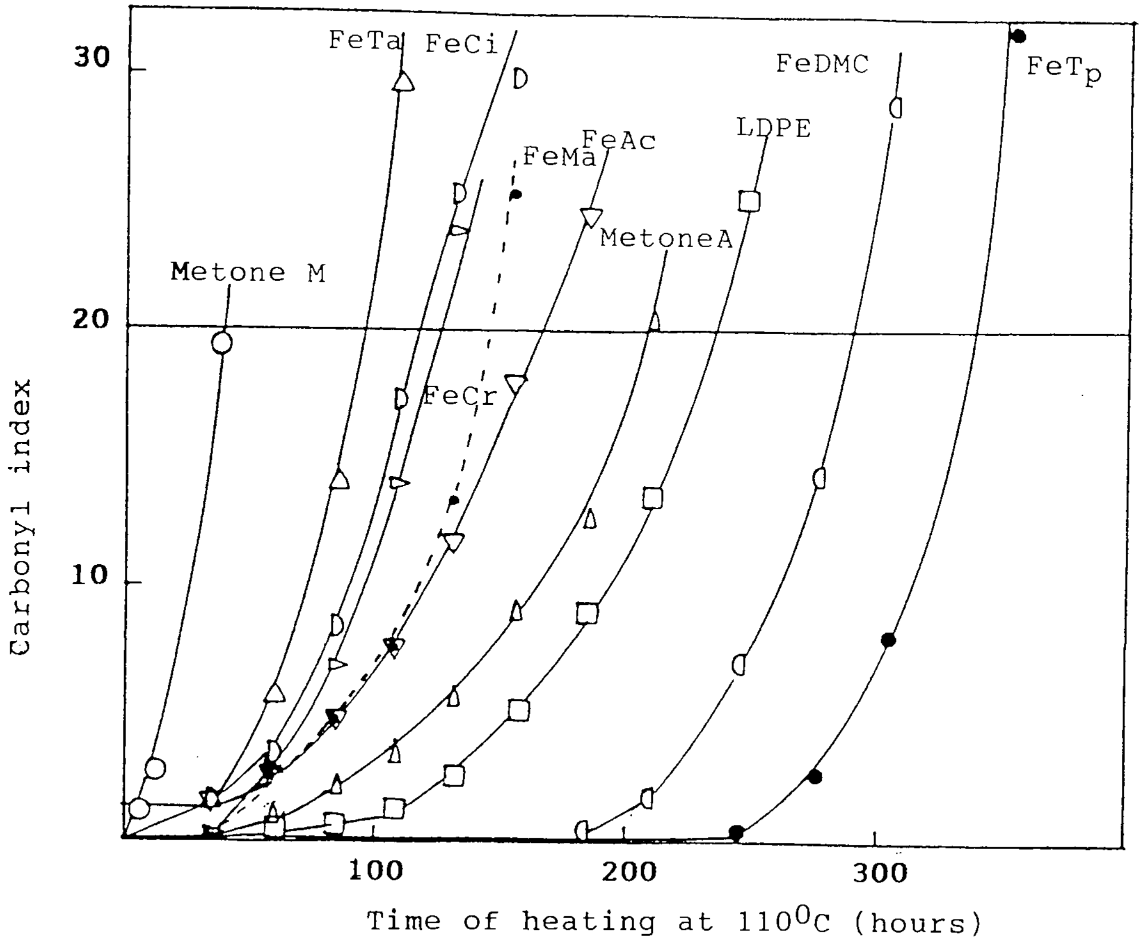


Fig. 3.69 Effect of thermal oxidation (oven ageing at 110° C) on LDPE films containing different pro-oxidants (0.2%). All the samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber. In case of FeTa, FeCi, FeCr, FeMa and FeAc (insoluble), the samples are diluted from masterbatches containing peroxide of (I/P_o)-molar ratio = 0.064(DCP) and in case of FeTp, Trigonox 101 was used as peroxide (0.15 molar ratio). I = initiator, P_o = pro-oxidant.

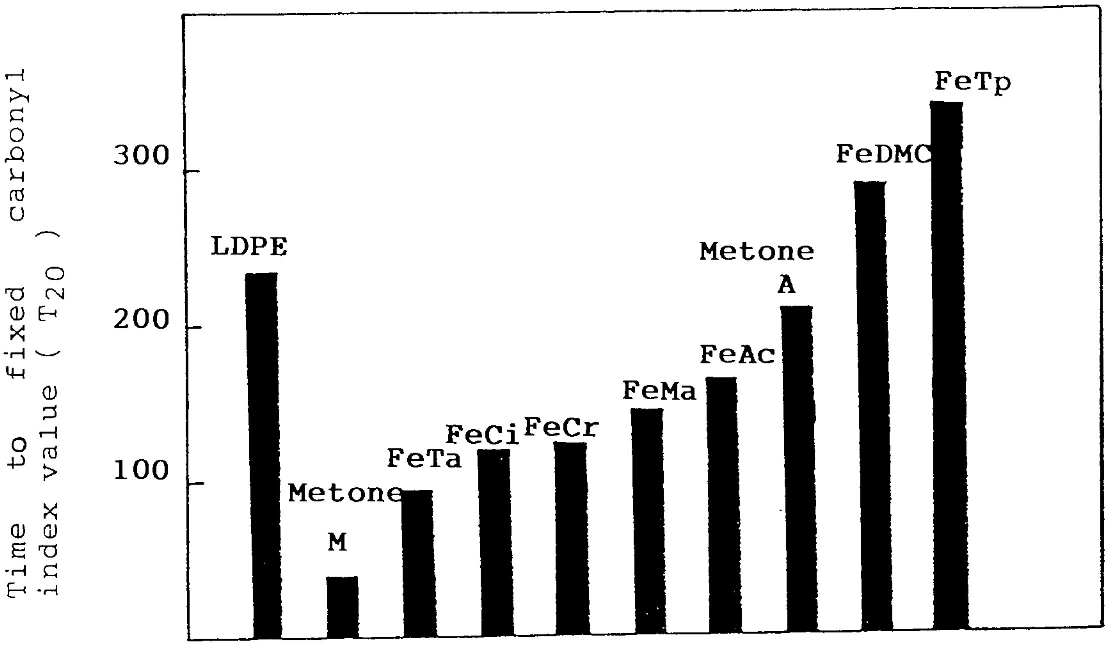


Fig. 3.70 Effect of different photo-activators on the thermal life time of unstabilised LDPE. Concentration of photo-activators is 0.2% . Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber. In case of FeTa, FeCi, FeCr, FeMa and FeAc, the samples are diluted from masterbatches containing peroxide of (I/P_O)-molar ratio = 0.064 (DCP) and in case of FeTp, Trigonox 101 was used as peroxide (0.15 molar ratio). I = initiator and P_O = pro-oxidant.

Chapter Four

Photo - oxidation of Unstabilised and Commercial Polypropylene by Pro - oxidants alone and in Combination with Antioxidants

4 .1 Object

In this chapter photo - oxidative behaviour of different pro - oxidants is examined alone and in combination with antioxidants in unstabilised PP as well as in commercial PP . Masterbatches (5%) of different pro - oxidants and antioxidants were made which were then diluted down to the required concentration . The binding efficiency of one of the pro - oxidants (FeTp) is examined . The photoactivation effect of bound FeTp were compared with nonbound samples both in extracted and non extracted conditions . The insoluble version of FeAc was used throughout the work described in this chapter . HAEB , a polymer bound UV stabiliser and DBBA , a thermal antioxidant were prepared . Bound HAEB or DBBA is used in conjunction with one of the nonextractable pro - oxidants (FeAc) to investigate the effect of these combination on the photo - oxidation of unstabilised PP . The iron compound (FeDNC) which is an antioxidant photoactivator (APA) is used in combination with non - iron containing pro - oxidant (Metone A or Metone M) . Antioxidants like ZnDNC , ZnDEC , NiDNC are used with pro - oxidants to give a time controlled photodegradable polymer of predetermined lifetime .

4 . 2 RESULTS AND DISCUSSIONS

4 . 2 . 1 Evaluation of binding efficiency of Fe - thiopropionate in unstabilised polypropylene .

The binding level of FeTp in unstabilised PP in the presence and absence of a co - agent (based on measurement of 1698 cm^{-1} band in its FTIR)was examined using Trigonox 101 as initiator and TMPTA as a co - agent , see Table 4 . 1 . It is clear that increasing both the concentration of co - agent and the initiator resulted in a corresponding increase in binding efficiency .

Table 4 . 1 **% of binding of Fe-thiopropionate in unstabilised polypropylene using total concentration of FeTp+ TMPTA = 5% . (Methanol was used for extraction) .**

% of FeTp (w / w)	% of TMPTA (w / w)	Peroxide concentration (Trigonox 101) (Peroxide / FeTp + TMPTA) - molar ratio	% Binding
5	-	-	22
5	-	0 . 03	41
5	-	0 . 15	55
4	1	0 . 15	80
3	2	0 . 15	88

It is well known that the effect of shear during processing leads to the formation of free radicals in hydrocarbon polymers(128 -135) . Polymer alkyl radicals react with oxygen giving the alkylperoxyl radical (Chapter 1, reaction 1.4-1.8) ,which abstracts a hydrogen atom from the polymer backbone or from the thiol group of FeTp to generate a thiyl radical . The latter reacts with polymer radicals to form polymer bound FeTp . See Chapter 3, reaction 3.1- 3.4 for the suggested mechanism . Binding of FeTp was shown to take place in the presence and absence of peroxide (Figs. 4.1 and 4.2 , Table 4.1) and increases in the presence of both peroxide (Fig. 4.3) and co - agent (Fig. 4.4) . In the absence of peroxide the thiyl radicals or polymer radicals are supposed to be formed only by mechanochemical shear. Whereas in the presence of the peroxide the mechanochemical shear as well as the decomposing peroxide are responsible for the formation of polymer radicals and thiyl radicals . In the presence of combinations of peroxide and co-agent FeTp may bind through the co-agent or directly to the polymer backbone . Here the rate of reaction is higher because of different possibilities of reaction .

4 . 2 . 2 Effect of pro - oxidant concentration on the photo - oxidation of unstabilised polypropylene .

Masterbatches (MB 5%) of different pro - oxidants without peroxide were made in unstabilised polypropylene using a closed chamber of torque rheometer at 180° C for 10 minutes . The MB's were diluted down to different concentrations . Their photo-oxidative behaviour were determined by UV irradiation .

Table 4 .2 Effect of pro - oxidant concentration on the photo - oxidation of polypropylene .

	Concentration (%)					
Samples	0 .025	0.05	0.1	0.2	0.3	0.4
	Embrittlement time (hrs)					
Control (Processed)	90					
FeTp	75	80	100	155	170	285
FeTa	100	135	210	255	280	280
FeMa	80	80	80	80	80	80
FeAc (Insoluble)	75	70	70	70	60	55
FeCr	65	75	75	70	55	55
FeCi	80	55	55	55	55	55
FeDMC	80	85	140	190	260	310
Metone A	80	70	80	95	125	180
Metone M	95	70	80	100	125	180

Samples are diluted from 5% masterbatches containing no peroxide processed at 180° C for 10 minutes . Data from this table is drawn in Fig . 4 . 21 .

Table 4 . 2 shows the effect of concentration of different pro - oxidants on the photo - oxidation rate of polypropylene . FeTa (Fig . 4 . 5 , Table 4 . 2) shows no pro - oxidation behaviour at all concentrations used, instead photostabilisation of the polymer is evident . In this case, at higher concentrations, photo-oxidation did occur after a considerably long induction period . The photostability increases as the concentration of photoactivator increases . In the case of FeTp (Fig. 4.6) photostabilisation occurs above certain concentrations (> 0 . 05 %) , below which photo - oxidation occurs . With an increase in concentration the induction period also increases . The photoactivation effect of bound FeTp , both in extracted and non - extracted samples were observed (Table 4 . 3). Bound samples show almost a similar behaviour to the non bound system . After extraction the embrittlement time did not change significantly . FeMa (Table 4 . 2) shows some photo - oxidation effect at all concentrations used , however , it appears to have no concentration effect on the photo - oxidation of polypropylene over the concentration range examined . FeAc (Fig . 4 . 7) shows a photo - oxidation effect at all concentrations used . In this case photo - oxidation increases as the concentration of photoactivator increases . FeCr and FeCi (Table 4 . 2) show a

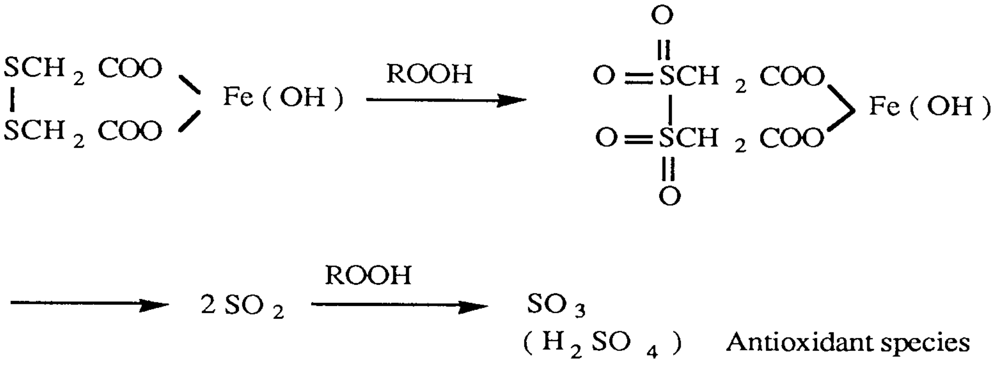
Table 4 . 3 Embrittlement times for different samples diluted from 5 % MB's of FeTp + TMPTA (0 . 05 % and 0 . 2 %), in polypropylene processed at 180^{o}C .

% of FeTp (w / w)	% of TMPTA (w / w)	Peroxide concentration (Trigonox101/ FeTp + TMPTA) - molar ratio	% Binding	Embrittlement time (hrs.) of dilute MB's			
				0 . 05%		0. 2%	
				Unext .	Ext .	Unext .	Ext .
5	-	-	22	80	80	155	145
5	-	0 . 03	41	80	70	155	145
3	2	0 . 15	88	80	80	140	130

photo - oxidation effect at all concentrations used . FeDMC (Fig . 4 . 8) does not show considerable photosensitisation at lower concentrations and at higher concentrations (> 0 . 05%) it exhibits photostabilisation . Metone A (Fig . 4 . 9) and Metone M (Fig . 4 .10) show a photosensitisation effect at lower concentrations . However , at higher concentrations photostabilisation of the polymer occurs . Figs. 4 . 11 and 4 . 12 compares the photoactivity of different compounds at two concentrations . At both lower and higher concentrations (0 . 05 % and 0 .2 %) FeCi show most photoactivation effect . Polymer containing FeTp , FeDMC , Metone A , Metone M and FeTa can be used for wrapping purposes , because at higher concentrations they induce a long induction period , so that at the end of service period when they will be discarded , the disintegration of the film will take place . Whereas FeAC and FeCi can be used in cigarette packet wrapping , they show a good photoactivation effect compared to the PP control .

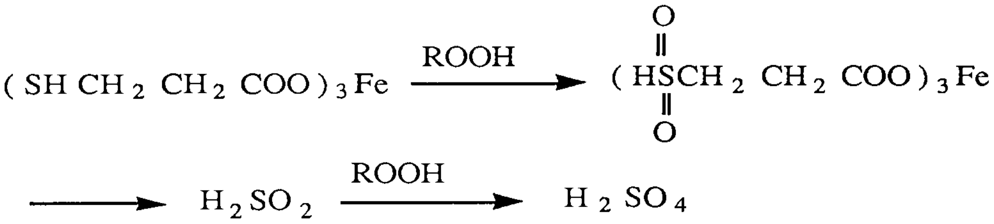
Fe - thioacetate (FeTa) does not show any pro - oxidant effect in unstabilised polypropylene , instead it shows a stabilisation effect which increases with concentration . FeTa may function by decomposing hydroperoxides through the possible formation of sulphur dioxide from its decomposition . The latter oxidise further to sulphur trioxide (a Lewis acid) which is known (81) to be primarily responsible for hydroperoxide decomposition , see reaction scheme 4 . 1 .

Fe - thiopropionate (FeTp) shows a pro - oxidant effect at lower concentrations whereas at higher concentrations (> 0. 05%) it induces photostabilisation . At higher concentrations FeTp may destroy hydroperoxides catalytically , see in reaction scheme 4 . 2 .



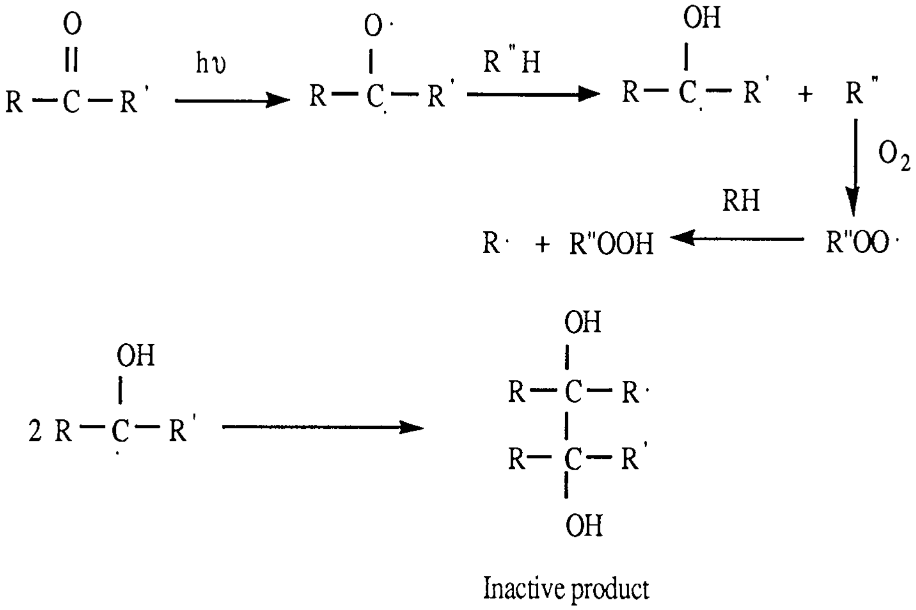
Reaction Scheme 4 . 1

The photoactivity of this compound at lower concentrations may be due to metal - catalysed hydroperoxide decomposition . Other iron compounds examined in this work show a pro-oxidant effect at all concentrations used . The mechanism is believed to be similar to that of iron carboxylate (Chapter 3 , reaction 3 . 7 and 3.8).

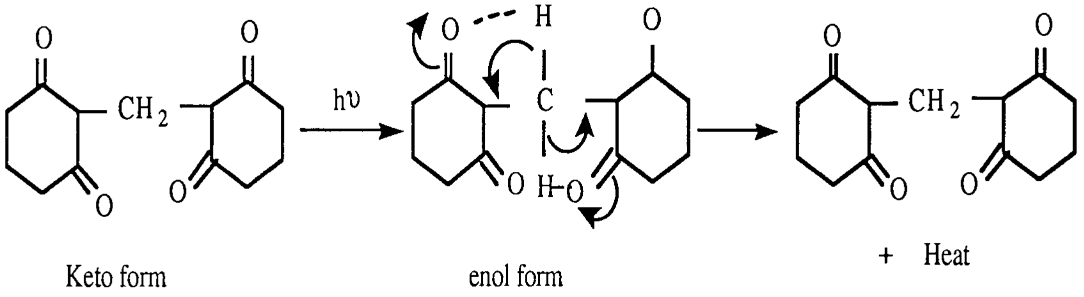


Reaction Scheme 4 . 2

Both Metone A and Metone M show a pro - oxidant effect at lower concentrations , whereas , they show photostabilisation effect at higher concentrations (> 0 . 1) . The pro-oxidant effect of Metone A and Metone M may be due to the formation of an active triplet state by absorbing UV light followed by hydrogen atom abstraction from the polymer, which starts a normal auto-oxidation process (Reaction scheme 4 . 3) . The stabilisation effect shown by Metone A and Metone M at higher concentration may be due to their effect as uv screeners through keto - enol tautomerisation (Reaction scheme 4 . 4) . It is assumed that internal hydrogen transformations may take place in the Matone A molecule by absorbing UV light which is then emitted as radiation thus keeping the polymer molecule intact .



Reaction Scheme 4 . 3



Reaction Scheme 4 . 4

FeDMC acts as a pro-oxidant at lower concentrations (< 0 . 1) whereas at higher concentrations it acts as a stabiliser in unstabilised PP . In LDPE it also acts as a pro - oxidant at lower concentrations but it shows a photostabilisation effect at very high concentrations (> 0 . 4%) . Ionic iron produced by the photolysis of iron -

dithiocarbamate is converted to iron carboxylate which is then responsible for the photosensitisation action of FeDMC at lower concentrations (Chapter 1 , Reaction scheme 1 . 6) (55) .

4 . 2 . 3 Concentration effect of pro -oxidants on the melt stability changes of polypropylene .

Table 4 . 4 shows the MFI changes for different pro - oxidants in polypropylene . It is clear that both FeTa and FeTp show lower MFI values compared to the control at higher concentrations . FeMa shows the same behaviour as FeTa . FeDMC, Metone A and Metone M show lower MFI values at all concentrations used . FeAc shows more or less the same MFI values at lower concentrations , however , at higher concentrations the MFI values increase . FeCi and FeCr behave similar to that of FeAc .

Table 4 . 4 MFI of unstabilised polypropylene containing different pro - oxidants processed at 180^o C for 10 minutes .

Samples	Concentration (%)					
	0 . 025	0 . 05	0 . 1	0 . 2	0 . 3	0 . 4
	MFI (g / 10 min .)					
Control (Processed)	0.58	-	-	-	-	-
FeTa	0 . 67	0 . 81	0 . 47	0 . 71	0 . 44	0 . 34
FeTp	0 . 57	0 . 48	0 .42	0 . 41	0 . 53	0 . 33
FeDMC	0 . 32	0 . 27	0 . 22	0 . 21	0 . 23	0 . 23
FeAc (Insoluble)	0 . 53	0 . 57	0 . 56	0 . 63	0 . 72	0 . 72
FeMa	0 . 68	0 . 62	0 . 82	0 . 49	0 . 35	0 . 36
FeCi	0 . 49	0 . 51	0 . 72	0 . 65	0 . 55	0 . 45
FeCr	0 . 59	0 . 53	0 . 66	0 . 58	0 . 84	0 . 58
Metone A	0 . 37	0 . 41	0 . 35	0 . 36	0 . 29	0 . 35
Metone M	0 . 49	0 . 52	0 . 53	0 . 49	0 . 45	0 . 47

All the samples are diluted from 5% masterbatches without peroxide .

FeDMC is known to destroy hydroperoxides by a catalytic (ionic) mechanism involving Lewis acid generated in a series of initial stoichiometric reactions with hydroperoxides (54 , 67, 80, 124) which lead to stabilisation of the polymer melt (see Chapter 3 , Figs . 3 . 34 and 3 . 35) . FeTp behaves similarly though it is less effective as a melt stabiliser than FeDMC . Like FeDMC and FeTp , FeMa and FeTa can destroy hydroperoxides at higher concentrations (see reaction scheme 4 . 1 and 4 . 2) . However , other iron compounds (FeAc , FeCi and FeCr) do not destroy hydroperoxide , instead the metal ion generated from the thermal decomposition of the iron compounds starts the oxidation of the polymer by the well known redox reactions with hydroperoxides (Chapter 3 , reactions 3 . 7 and 3 . 8) . Metone A and Metone M assumes to destroy hydroperoxide because the MFI values are found to be lower at all concentrations compared to the polypropylene control .

4 . 2 . 4 Combination of pro - oxidants with an antioxidant , on the photo - oxidation of unstabilised polypropylene .

The effect of an antioxidant , zinc diethyldithiocarbamate (ZnDEC) was studied in combination with different pro - oxidants in unstabilised polypropylene . In all cases 5% masterbatches of ZnDEC and an iron compound were prepared seperately which were then diluted to the corresponding concentrations . Fig . 4 . 13 shows the effect of variation of ZnDEC concentration on the photo - oxidation of unstabilised PP containing FeAc (0 . 2%) . In this case the concentration of photoactivator was held constant at a particular concentration whereas the concentration of the anti - oxidant was varied . It is clear that increasing the antioxidant concentration lead to an increase in embrittlement time . With higher concentrations of antioxidant (0 . 3% and 0 . 4 %) considerable induction periods have been obtained . Figs . 4 . 15 and 4 . 16 show the effect of varying concentration of FeAc at constant ZnDEC concentration . From table 4 . 5 it is evident that with the addition of lower concentration of ZnDEC (e . g . 0 . 025% , constant) the photo - oxidation of polypropylene containing FeAc (variable) is similar to that containing FeAc alone . Whereas higher concentrations of ZnDEC (e . g ., 0 . 1% , 0 . 2% and 0 . 4%) causes photostabilisation of the polymer with a considerable induction period . The use of ZnDEC at these particular concentrations in combination with FeAc (variable) , therefore, does not lead to photosensitisation . A similar behaviour to that of FeAc was observed with FeCr , FeTa and Metone M (Figs . 4.14 , 4.17 - 4.20) . Fig . 4 .22 shows the stabilisation effect of different photoactivators in the presence of ZnDEC .

The effect of an iron containing pro -oxidant (FeDNC) with a non - iron containing pro - oxidant (Metone A / Metone M) was examined (Table 4 . 5). The combination of Metone A / Metone M (0 . 05%) with FeDNC (0 . 05%) does not affect the embrittlement time of the polymer containing these pro - oxidants compared to that containing either FeDNC (0 . 05%) or Metone A / Metone M alone . However, the addition of an antioxidant (ZnDNC) with Metone A / Metone M increases the stability of the polymer .

The concentration of FeDNC (variable) with very low concentrations of NiDNC (constant) was studied . As expected and as was shown previously (56 , 57) , it was observed that (Figs . 4 . 24 - 4 . 26) at all concentrations of combination the photostability of the polymer containing NiDNC and FeDNC are higher than the polymer containing FeDNC alone . With higher concentrations of FeDNC in the combination , the induction period was found to be extended compared to FeDNC alone at the same concentrations . At higher concentrations of NiDNC (0 . 005% and 0 . 01%) the induction period extended at all concentrations of

Table 4 . 5 **The effect of two component systems on the photo - oxidation of unstabilised polypropylene .**

Samples	Concentration (% w / w)	Embrittlement time (hrs)
Control (Processed)		90
ZnDEC	0 . 025	120
	0. 050	120
	0 . 1	165
	0 . 2	165
	0 . 3	210
	0 . 4	210
FeAc	0 . 025	75
	0 . 05	70
	0 . 1	70
	0 . 2	70
	0 . 3	60
	0 . 4	55
FeAc + ZnDEC	0 . 2 + 0 . 025	70
	0 . 2 + 0 . 05	100
	0 . 2 + 0 . 1	125
	0 . 2 + 0 . 2	160
	0 . 2 + 0 . 3	170
	0 . 025 + 0 . 025	75
	0 . 05 + 0 . 025	70
	0 . 1 + 0 . 025	70
	0 . 2 + 0 . 025	70
	0 . 3 + 0 . 025	60
	0 . 4 + 0 . 025	55
	0 . 025 + 0 . 1	135
	0 . 1 + 0 . 1	135
	0 . 2 + 0 . 1	125
	0 . 3 + 0 . 1	125
	0 . 025 + 0 . 2	135
	0 . 05 + 0 . 2	180
	0 . 1 + 0 . 2	190
	0 . 2 + 0 . 2	160
	0 . 3 + 0 . 2	145
	0 . 025 + 0 . 4	210
	0 . 1 + 0 . 4	270
	0 . 2 + 0 . 4	235
	0 . 3 + 0 . 4	210

Continued

Samples	Concentration (% w / w)	Embrittlement time (hrs.)
FeCr	0 . 025	65
	0 .05	75
	0 . 1	75
	0 . 2	70
	0 . 3	55
	0 . 4	80
FeCr + ZnDEC	0 . 2 + 0 . 025	70
	0 . 2 + 0 . 05	70
	0 . 2 + 0 . 1	75
	0 . 2 + 0 . 2	160
	0 . 2 + 0 . 3	170
	0 . 025 + 0 . 05	90
	0 . 05 + 0 . 05	80
	0 . 1 + 0 . 05	75
	0 . 2 + 0 . 05	70
	0 . 3 + 0 . 05	85
	0 . 4 + 0 . 05	90
Metone M	0 . 025	95
	0 . 05	70
	0 . 1	80
	0 . 2	100
	0 . 3	125
	0 . 4	180
Metone M + ZnDEC	0 . 1 + 0 . 01	110
	0 . 1 + 0 . 025	110
	0 . 1 + 0 . 05	165
	0 . 1 + 0 . 1	165
	0 . 1 + 0 . 2	170
	0 . 025 + 0 . 025	95
	0 . 05 + 0 . 025	70
	0 . 1 + 0 . 025	100
	0 . 2 + 0 . 025	135
	0 . 4 + 0 . 025	180
Metone A	0 . 025	80
	0 . 05	70
	0 . 1	80
	0 . 2	95
	0 . 3	125
	0 . 4	180

Continued

Samples	Concentrations (% w / w)	Embrittlement time (hrs .)
Metone A + Zn DEC	0.05 + 0.01	75
	0.05 + 0.025	80
	0.05 + 0.05	135
	0.05 + 0.1	135
	0.05 + 0.2	145
FeTa	0.025	100
	0.05	135
	0.1	210
	0.2	255
	0.3	280
	0.4	280
FeTa + ZnDEC	0.025 + 0.05	100
	0.05 + 0.05	145
	0.1 + 0.05	264
	0.2 + 0.05	295
	0.3 + 0.05	295
	0.4 + 0.05	510
	0.025 + 0.2	230
	0.05 + 0.2	245
	0.1 + 0.2	290
	0.025 + 0.4	275
	0.05 + 0.4	285
	0.1 + 0.4	295
	0.2 + 0.4	320
	0.3 + 0.4	490
FeDNC	0.01	70
	0.05	70
	0.1	135
	0.2	150
	0.3	285
	0.4	285
Metone A + FeDNC	0.05 + 0.05	70
Metone A + ZnDNC	0.1 + 0.025	95
	0.1 + 0.05	120
	0.05 + 0.025	95

Continued

Samples	Concentrations (% w / w)	Embrittlement time (hrs .)
Metone M + FeDNC	0.05 + 0.05	70
	0.025 + 0.05	70
Metone M + ZnDNC	0.1 + 0.025	80
	0.1 + 0.05	95
	0.05 + 0.025	70
NiDNC + FeDNC	0.001 + 0.01	70
	0.001 + 0.05	70
	0.001 + 0.1	150
	0.001 + 0.2	220
	0.001 + 0.3	290
	0.001 + 0.4	375
	0.005 + 0.01	95
	0.005 + 0.05	95
	0.005 + 0.1	150
	0.005 + 0.2	220
	0.005 + 0.3	285
	0.005 + 0.4	375
	0.01 + 0.01	120
	0.01 + 0.05	120
	0.01 + 0.1	150
	0.01 + 0.2	220
	0.01 + 0.3	310
	0.01 + 0.4	430

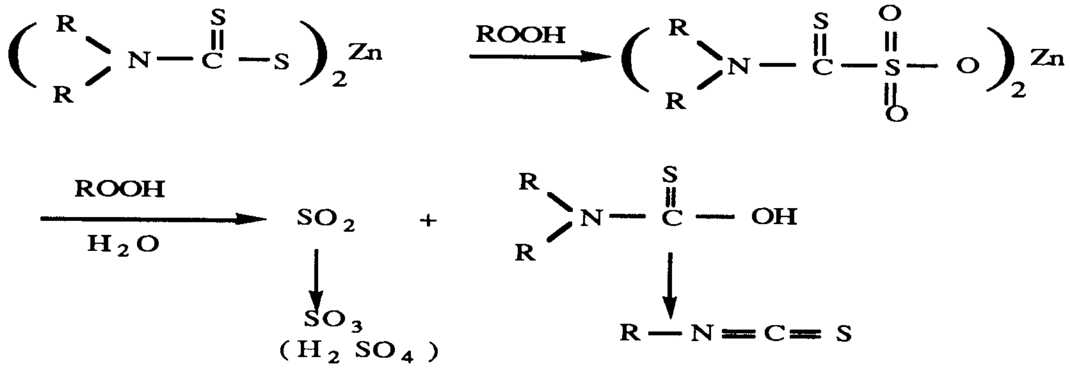
FeDNC in the combination . The rate of photo - oxidation at the end of the induction period was higher for the combinations compared to that of the FeDNC alone (Fig . 4 . 26 curve 10 and 11) .

Metal dithiocarbamates were shown to act as photostabilisers at high concentrations (67 , 76 , 81, 138) . On the otherhand FeAc and FeCr were shown to give a photo - activation effect at all concentrations used (see Table 4 . 5) . The use of small amounts of ZnDEC do not change the embrittlement time but higher concentrations of ZnDEC increase the embrittlement time (Fig . 4 . 22) with the introduction of an induction period . The photostability of polypropylene using an FeAc and ZnDEC combination (compared to photosensitisation afforded by FeAc alone) is probably due to a ligand exchange reaction (reaction 4 . 1) .

$$\text{Fe - acrylate} + \text{ZnDEC} \longrightarrow \text{FeDEC} + \text{Zn - acrylate} \qquad (4.1)$$

FeDEC thus formed may contribute to the stability of polypropylene . The higher the concentrations of ZnDEC in the combination , the higher was the formation of FeDEC leading to higher photostabilisation . A similar mechanism may operate in the case of FeCr . To investigate this the reaction of the FeAc with ZnDEC was carried out in methyl cyclohexane . Here a solution of ZnDEC (0 . 2g) in 200 ml of methyl cyclohexane was made in which 0 . 2 g of FeAc was added . FeAc did not go to solution . The reaction mixture was refluxed for 1 hour . During that period the colour of the reaction mixture turned from trasparent to dark brown and a black precipitate appeared . The solution was diluted to obtain an appropriate spectrum . The UV - Visible spectrum of this solution was compared with the spectra of FeDNC and ZnDEC in methyl cyclohexane (Figs. 4 . 27 and 4 . 28) . The appearance of the spectrum was found to be similar to that of FeDNC . Thus, it can be concluded that during high temperature processing of FeAc and ZnDEC in PP some ligand exchange reaction takes place which will then affect its subsequent UV activity .

Metone A and Metone M show photostability in combination with ZnDEC (see Figs. 4 . 19 and 4 . 20 , Table 4 . 5)) which is most likely due to the antioxidant action of ZnDEC (see reaction scheme 4 . 5) (81 - 83) (effect increases with increasing ZnDEC concentration) .



Reaction Scheme 4 . 5

FeTa does not show any pro - oxidant behaviour in unstabilised polypropylene . Addition of ZnDEC only extend the lifetime of the polymer. In few cases it also extend the induction period . Thus FeTa and ZnDEC does not interfere with each others activity . Both act individually as a photostabiliser in unstabilised polypropylene .

The combination of Metone A or Metone M (0.05%) with FeDNC (0 . 05%) did not change the stability of the polymer compared to Metone A or Metone M and FeDNC alone . This may be due to the fact that at this particular concentration they show their individual activity which will coincide with the activity of each other . However , the addition of ZnDNC instead of FeDNC increases the stability of the polymer which may be assume to be due to the photostability of ZnDNC predominating in the combination .

NiDNC is known to act as an effective U V (76) stabiliser . This complex was also proposed (138 , 139) to have the ability to quench and deactivate the photo - excited species formed from other compounds . A combination of NiDNC and FeDNC is expected to give more effective time controlled stabilisation than that exhibited by FeDNC alone and this was studied previously (58 , 59) . Figs . 4. 24 - 4 . 26 demonstrate this . The improvement in the photostability of PP by NiDNC and FeDNC combination compared to the stabilisation afforded by FeDNC alone is probably due to the ability of NiDNC to protect FeDNC from photolytic destruction . It has previously been suggested (16 , 138 - 140) that NiDEC can accept energy from triplet carbonyl although it has been shown that this stabilisation mechanism can only be important in polymers which contain a substantial amount of carbonyl (76) . In principle the NiDNC may quench photoexcited states of the FeDNC (or its photo - decomposition products) and this could contribute to the stabilisation exhibited by the combination of FeDNC / NiDNC in the polymer .

4 . 2 . 5 Evaluation of binding of HAEB and DBBA and the photostabilising effect of HAEB in unstabilised polypropylene.

Previous work on 4 - benzoyl - 3 - hydroxyphenyl - o - ethyl thioglycolate (EBHPT) shows that it can be 77% mechanochemically bound into ethylene - propylene diene monomer (EPDM) and 20% into polypropylene (141) . Burchill *et al* .(142) have grafted 2 - hydroxy - 4 - (3 - methacryloxy - 2 - hydroxypropoxy)-benzophenone (HMB) to low density polyethylene using a mutual gamma radiation technique in the presence of cupric chloride to inhibit homopolymerisation . Sharma *et al* .(143) have grafted 2 - hydroxy - 4 - (methacryloyloxy) benzophenone and 2 - hydroxy - 4 - (acryloyloxy)benzophenone into the backbone of polypropylene , low density polyethylene and polystyrene by melt processing in the mixer of a Brabender plastocorder . Munteanu *et al* . (144) claimed the stabilisation of LDPE , HDPE and PP by melt grafting of the same uv absorbers using organic peroxides as grafting initiators at a temperature of 130 - 200 °C . They recommend dilauroyl peroxide for low temperature grafting and dicumyl peroxide for grafting at high temperatures. Vogl *et al* .(145) reported the grafting of 2 - (2 - hydroxy - 5 - vinylphenyl) - 2H-benzotrizole into polymers with aliphatic groups .

Evans and Scott (100) have shown that the antioxidant 3 , 4 - di - tertiarybutyl - 4 - hydroxybenzyl acrylate (DBBA) may be grafted to the surface of polymer artifacts . Ibrahim (146) have also shown that the same antioxidant will bind upto 60% in the presence of a peroxide into polypropylene . It was also found (147) that 3 , 5 - di - ter - butyl - 4 - hydroxybenzyl mercaptain (BHBM) became chemically combined to polypropylene to the extent of 68% of the antioxidant present when films containing BHBM were exposed to uv irradiation . Adams and Braun (148) have successfully grafted 2 , 6 - di - tert - butyl - 4 - vinyl phenol to polystyrene .

The binding efficiency of HAEB and DBBA were examined in unstabilised polypropylene using two different types of peroxide , DCP and Trigonox 101 and an interlinking agent (TMPTA) . High levels of binding were obtained in the case of both additives using peroxide alone and in combination with an interlinking agent . Masterbatches (10%) of these bound additives were diluted and used in combination with FeAc to investigate the effect of these combinations . The photostabilisation of HAEB in polypropylene was examined alone for comparison .

4.2.5.1 Evaluation of binding of HAEB in unstabilised polypropylene .

Parameters which could affect the binding efficiency of additives such as the concentration of additive , temperature of processing , processing time and concentration of initiators (149) were all varied to optimise the binding conditions . Fig . 4 . 29 and table 4 . 6 show the effect of varying the temperature of processing at a constant concentration of HAEB (10%) and DCP (0 . 0025 molar ratio) . Maximum binding was obtained at the processing temperature of

Table 4 . 6 **Effect of processing temperature on binding of HAEB (10% MB) , using DCP as initiator at molar ratio of DCP / HAEB =0 . 0025 .**

Processing temperature (^{o}C)	% Binding *
160	24
170	56
180	82
190	87

Table 4 . 7 **Effect of HAEB concentration on binding using DCP as initiator at molar ratio of DCP / HAEB = 0 . 0025 (DCP) in PP at 180^{o} C .**

HAEB concentration (% w / w)	% Binding *
5	81
10	82
15	80
20	80

Table 4 . 8 **Effect of processing time on binding of HAEB (10% MB), using DCP as initiator at molar ratio of DCP / HAEB = 0 . 005 in PP at 180^{o}C .**

Processing time (mins)	% Binding *
5	84
10	86
15	88
20	88

* Binding based on the measurement of 1737 cm^{-1} band in the FTIR .

Dichloromethane (DCM) was used for extraction .

Table 4 . 9 **% of binding of HAEB (HAEB + TMPTA =10%) at various molar ratios of peroxide concentration and various percentage ratios of interlinking agent in PP at 180^{o}C .**

Radical generator used	% of HAEB (w / w)	% of TMPTA (w / w)	Peroxide concentration (I/A_{0} + TMPTA) - molar ratio	% Binding	MFI g / 10 min
Processed PP					0 . 36
	10		0 . 000	3	0 . 36
DCP			0 . 0025	82	2 . 60
			0 . 005	86	3 . 80
			0 . 01	90	4 . 28
			0 . 02	96	9 . 20
	9	1	0 . 003	97	0 . 45
	10		0 . 0025	82	0 . 73
			0 . 0035	82	1 . 90
			0 . 005	85	3 . 12
			0 . 0075	90	5 . 89
			0 . 015	91	11. 45
Trigonox 101	8 . 5	1 . 5	0 . 000	20	0 . 16
			0 . 0025	90	1 . 15
			0 . 0035	95	1 . 15
	9	1	0 . 0025	89	1 . 35
			0 . 0035	96	1 . 35
			0 . 005	100	2 . 11
	9 . 5	0 . 5	0 . 005	88	2 . 15

$190\ ^{o}$ C . It is clear that the temperature of the reaction plays a major role in determining the extent of binding .

Fig . 4 . 30 shows the effect of variation of HAEB concentration on torque . Masterbatch (5%) (Fig . 4 . 30 , curve 3) does not show any trough or peak in the torque versus processing time curve as it passes through the radical initiating , melting and homopolymerisation and binding stages in the polymer . The MB (10%) showed a clear evidence of chain scission which was soon taken over by homopolymerisation and binding of the additive initiated by the polymer radical . After about 4 minutes (at the peak) polymerisation and subsequent binding of the additive results in a modified bound PP . Subsequent processing causes a constant reduction in torque reading which may be the effect of remaining peroxide on the bound polymer . The 15% and 20% curves showed the same pattern except the peak has been shifted to the lower processing time which suggests that a higher rate of reaction and the torque in the peak is higher , giving rise to the formation of cross linked polymer . The levelling off of the curve after the completion of the reaction near the minimum torque suggests that the amount of crosslinking was minimum . However , from the table 4 . 7 it is evident that the concentration of HAEB does not affect the extent of binding in polypropylene . Time of processing was also varied to observe the effect in binding level (Table 4 . 8) but no effect was observed .

Another important parameter which may affect the binding is the concentration of initiator . Different molar ratios of initiator and antioxidant (I / A_0) were used in the preparation of 10% masterbatches . From the results (Table 4 . 9) it is clear that without any radical generator the binding is low and it increased with increasing amount of peroxide . However , the conjugal effect of both the radical generator and interlinking agent has an increased effect on binding . Even with a small amount of radical generator concentration , a 100% binding was observed (Table 4 . 9) .

Figs . 4 . 31 and 4 . 32 show the effect of initiator concentration on torque developed during processing which show that there are no maxima in the torque versus processing time curve without peroxide , whereas in presence of peroxide a maxima is obtained between 3 - 4 . 5 minutes . With the increase of peroxide concentration the intensity of the maxima increased and shifted to the lower processing time . The torque generated during processing is indicative of the resistance of the polymer chains to the shearing action of the rotors . It seems therefore, that the increase in torque generated during processing is due to the homopolymerisation and binding of the additive to the polymer (150) . The increased intensity of the maxima appears to be due to the increased rate of reaction which corresponds to the increased level of binding . Fig . 4 . 31 shows the effect of TMPTA in the presence and absence of peroxide on torque during processing . The use of an interlinking agent (TMPTA) with the initiator does not show any pronounced maxima in the torque versus processing time curve as compared to initiator alone . The appearance of more than one maxima in this case may be due to the different types of reaction . The levelling off of the curve at the end of the processing (Fig . 4 . 33) is found to be higher compared to initiator alone (Figs . 4 . 31 and 4 . 32) .

Although the level of binding increases with increasing peroxide concentration , it has a destructive effect on melt stability of the compound . The MFI value increases with the increase of radical generator concentration (Table 4 . 9 and Fig . 4 . 34) . During the processing operation polypropylene suffers from degradation by chain scission , this melt degradation in presence of radical generator is accelerated even more which leads to an adverse increase in melt flow index causing a decrease in molecular weight . Thus , the increase of binding is in fact at the expence of the melt stability of the polymer which is not desirable . The MFI values of the masterbatch containing interlinking agent is found to be lower than that of the processed control . The effect of interlinking agent can be further shown if the MFI values of masterbatches containing same amount of peroxide is compared with the masterbatches containing peroxide and interlinking agent (Table 4 . 9) . In every case samples containing both peroxide and TMPTA have lower MFI values . Thus , it is evident that the interlinking agent (HAEB : TMPTA = 8 . 5 : 1 . 5) and Trigonox 101 (0 . 0025 molar ratio) is the optimum concentration of interlinking agent and initiator concentration of modifying polypropylene with the stabiliser .

An attempt has been made to optimise the yield of bound antioxidant obtained by varying the concentration of interlinking agent (without any peroxide) . The results given in Table 4 . 10 and Fig . 4 . 35 show that the maximum yield can be obtained at the ratio of (TMPTA : HAEB) = 3 . 7 . However , a further increase of interlinking agent concentration results in a decrease in antioxidant concentration which in turn results in lower binding .

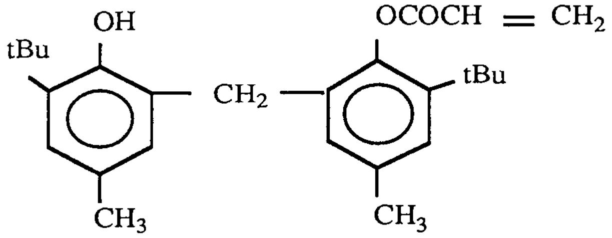
The infrared spectrum of 10% MB of HAEB in PP without a radical generator is shown in Fig . 4 . 36 (1) and is compared with the spectrum of a similar formulation but processed with a radical generator (DCP / HAEB = 0 . 003 molar ratio) and interlinking agent (TMPTA : HAEB = 1 : 9) in Fig . 4 . 36 (2) .

Table 4 . 10 Effect of interlinking agent (TMPTA) concentration without peroxide on binding of HAEB in PP at 180°C (total concentration of HAEB +Interlinking agent = 10%)

Concentration of HAEB (% w / w)	Concentration of TMPTA (% w / w)	% Binding
8 . 5	1 .5	20
7	3	53
5	5	29
3	7	37

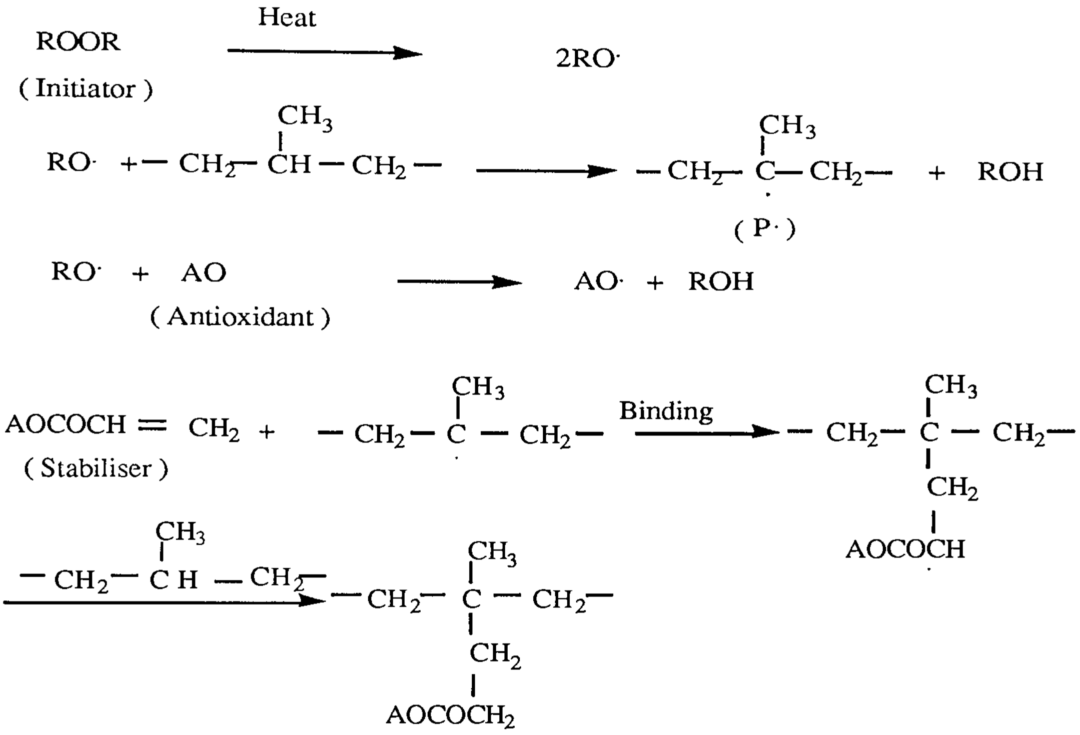
When sample (1) was hot Soxhlet extracted with DCM for 48 hours all absorptions due to HAEB disappeared . Absorptions of particular interest are at 1737 cm $^{-1}$ due to ester carbonyl and 1636 cm $^{-1}$ due to vinyl unsaturation . A similar spectrum to that in Fig . 4 . 36 (2) were obtained with both the radical generator (Trigonox 101 and DCP) and TMPTA . All samples processed with a radical generator and TMPTA were hot soxhlet extracted with DCM for 48 hours but no additive was found to be measurably extracted as the IR spectra were identical to that before extraction . Since in this compound both the benzophenone aromatic groups and the vinyl unsaturation appear to absorb in the same region it is difficult to explain the binding mechanism .

Japanese workers of Sumitomo Chemical Co. Ltd.(151) have demonstrated that a photostabiliser containing an acrylic group (Sumiliser GM) has the ability to trap radicals generated from azoisobutyronitrile (AIBN) .



Sumiliser GM

Based on this evidence it can be suggested that during processing the initial polymer chain scission caused by decomposing peroxide was soon taken over by simultaneous transformation of the additive into bound and polymerised product . The polymer radical P· along with the alkoxyl radicals initiate the polymerisation of the additive . This polymerised product along with the monomers initiated by P · grafted to the polypropylene backbone (see reaction scheme 4 . 5) .



Reaction Scheme 4 . 5

It was observed that when interlinking agent was used alone low levels of binding were obtained which may be due to the fact that in the absence of peroxide the rate of formation of radicals in the polymer chain is low and also there may be several possibilities of reactions which may cause lower levels of binding . In this case the possibility of homopolymerisation of both the additive and interlinking agent is likely to occur . The other reaction route may be the co - polymerisation of additive and interlinking agent . Ultimately there is a competition between the homopolymerised polymer and copolymerised polymer to bind with the polymer fragments. However , in the presence of both peroxide and interlinking agent high levels of binding were obtained which could also be achieved through the use of higher amounts of peroxide . But in the latter case excess peroxide caused degradation of the polymer (high MFI values , see Table 4 . 9 and Fig . 4 . 34) which in turn had a deleterious effect on polymer stability (lower performance) . With the use of peroxide and co - agent this unexpected effect could be removed (lower MFI values than the control) . It is difficult to say whether the rate of hompolymerisation or the copolymerisation is faster or which one is predominent . However , from the above discussion it can be predicted that the predominent reaction route may be the homopolymerisation of the additive followed by subsequent grafting of the homopolymerised additive to the polymer backbone .

It is known that grafting and cross linking of the polymer sample can be evaluated from the changes in molecular weight distribution . The increase in average molecular weight ($\overline{M}w$) and broadening in distribution (D = $\overline{M}w$ / $\overline{M}n$), indicate cross linking (152). Gel permeation chromatogram (GPC) of some of the masterbatches containing additive (HAEB), different initiator concentration and TMPTA were carried out by RAPRA Polymer Characterisation Centre . The results are shown in Table 4 . 11 . In Fig. 4 . 37 chromatograms of 10% MB of HAEB without initiator (2) and (I / A_0) = 0.0025 molar ratio of DCP (3) are compared with that of processed polypropylene . It is clear that both $\overline{M}w$, weight average molecular weight and D , distribution increases in the case of 10% HAEB without radical generator . The chromatogram for this sample also shifted towards the higher molecular weight range . However , although $\overline{M}w$ increases with the sample processed with radical generator (no interlinking agent) the distribution narrowed down compared to the control . The gel content of the 10% masterbatches containing (Trigonox 101 / HAEB) = 0 .0035 and 0 .015 of Trigonox 101 were compared with 10% masterbatch containing 1% interlinking agent and (Trigonox 101 / HAEB + TMPTA) = 0 .005 (Table 4 . 12) . The sample containing TMPTA (100% bound) was found to give more gel content

Table 4 . 11 Molecular weight distribution for polymer samples (masterbatches)

Polymer samples	Initiator concentration (I / A $_0$ + TMPTA) - molar ratio	$\overline{M}w \times 10^5$	$\overline{M}n \times 10^4$	$\overline{D}$ ($\overline{M}w / \overline{M}n$)
Processed PP	0 . 000	1 . 39	1 . 21	11 . 48
10% HAEB	0 . 000	3 . 30	2 . 21	15 . 11
	0 . 0025	2 . 13	3 . 00	7 . 20
	0 . 005	3 . 09	1 . 94	10 . 35
HAEB + TMPTA (8 . 5% + 1 . 5%)	0 . 000	3 . 36	2 . 99	11 . 45
HAEB + TMPTA (9% + 1%)	0 . 005	2 . 50	2 . 15	11 . 70

Table 4 . 12 Xylene insoluble gel content of different masterbatches

Polymer samples	Initiator concentration (I / A $_0$) -molar ratio (Trigonox 101)	% Gel content	% Binding
10% HAEB	0 . 0035	5	82
	0 . 015	5	91
HAEB + TMPTA (9% + 1%)	0 . 005	30	100

(30%) samples , which suggests that in this case a substantial amount of crosslinked structure was formed .

4 . 2 . 5 . 2 Photo-oxidative behaviour of HAEB in unstabilised polypropylene .

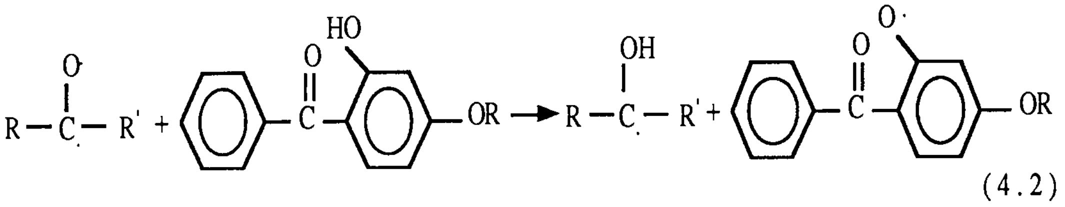
PP masterbatches (10%) of HAEB with and without peroxide and TMPTA were diluted down to two different concentrations (o . 2% and 0 . 4 %) and the photostabilisation effect of these samples (0.2%) are shown in Fig . 4 . 38 and the corresponding embrittlement time of both the extracted and nonextracted samples are shown in Table 4 . 13 . The UV stability of bound additive did not improve much compared to that of the nonbound analogue . In fact samples

Table 4 . 13 Embrittlement times for different samples diluted from 10% MB's of HAEB + TMPTA (0. 2% and 0. 4%), in polypropylene processed at 180°C .

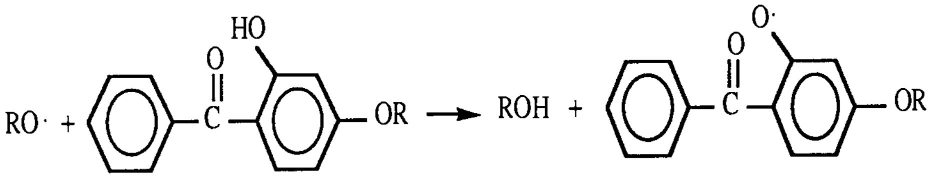
Radical generator	Sample used	Peroxide conc . I / HAEB+ TMPTA (molar ratio)	Embrittlement time (hrs .)				%Binding
			0 . 2% Unextr.	Extr.	0. 4% Unextr.	Extr .	
DCP	10% HAEB	0 . 000	350	160	530	180	3
		0 . 0025	380	280	420	350	82
		0 . 005	370	320	410	330	86
		0 . 01	345	295	380	350	90
		0 . 02	335	300	380	370	96
	HAEB+ TMPTA (9) (1)	0 . 003	380	330	425	400	97
Trigonox 101	10% HAEB	0 . 0025	470	340	610	450	82
		0 . 0035	425	295	575	425	82
		0 . 005	320	225	400	300	85
		0 . 0075	285	210	370	275	90
		0 . 015	250	200	300	230	91
	HAEB+TMPTA (8 . 5) (1 . 5)	0 . 000	400	230	500	280	20
		0 . 0025	375	320	435	385	90
		0 . 0035	375	320	415	380	95
	HAEB+TMPTA (9) (1)	0 . 0025	375	320	415	380	89
		0 . 0035	375	320	415	380	96
		0 . 005	420	370	480	460	88

diluted from masterbatches containing a higher amount of peroxide showed less photostability. Figs. 4 . 39 and 4 . 40 show the percentage of binding and uv embrittlement time as a function of peroxide concentration . The extent of binding increases with an increase in radical generator concentration , however , the uv stability gradually decreases after an initial slight increase . The reduction in the photostability of HAEB is probably due to the formation of a minute amount of photosensitiser impurity during uv irradiation with associated auto - acceleration of the photo - oxidative process . The beneficial effect of binding on uv stability can be observed if the bound extracted sample can be compared with a nonbound one . The extracted bound sample showed a better performance , because extraction removes most of the additives from the non - bound sample . The photostabilising effect of extracted non - bound sample may be due to some polymerisation of the compound which is not soluble in the extracting solvent .

Chakraborty and Scott (153) suggested that the photostabilisation activity of uv absorbers is due to the fact that they interact with the excited carbonyl chromophore (Reaction 4 . 2) . Removal of chain initiating radicals formed from hydroperoxide is another route of uv stabilising activity (Reaction 4 . 3) .



(4.2)



(4.3)

The rate of photo - oxidation of the diluted masterbatches was also monitored by the reduction in the uv absorption band (330 nm) during irradiation . The disappearance of the uv absorption band with time of uv - irradiation and the first order plot of decay of different samples are shown in Fig . 4 . 41 which demonstrates that the uv stability of bound uv absorber is higher than that of the non - bound samples . This may be due to the restriction on the free mobility of the bound antioxidant which in turn reduces the loss of additives through volatilisation .

4 . 2 . 5 . 3 Evaluation of binding of DBBA in unstabilised polypropylene .

Binding of DBBA in PP was studied following the same procedure as in HAEB . High levels of binding were achieved using a higher concentration of radical generator and interlinking agent . Fig . 4 . 42 (a) and Table 4 .14 show the effect of varying the initiator concentration on binding of 10% DBBA concentration (% of binding was based on IR spectroscopic measurements obtained after 48 hours soxhlet extraction in dichloromethane) . It is clear from the figure that in general the higher the initiator concentration, the higher the binding efficiency . However , at high initiator concentration , the polymer showed signs of thermal degradation during processing , which led to an increase in MFI values (Fig . 4 . 43 a) .

Levels of binding of an antioxidant may also be improved by employing an interlinking moiety which can bind effectively to the polymer and to the antioxidant (105) . Fig . 4 . 42 (b) and table 4 . 15 represent the effect of varying the concentration of interlinking agent at a fixed initiator concentration on binding of 10% DBBA concentration . Increase of interlinking agent concentration did not increase the MFI values (Fig . 4 . 43 b) . Table 4 . 16 shows the effect of varying both the concentration of interlinking agent and initiator (DCP and Trigonox 101) . It is clear

Table 4 . 14 Effect of initiator concentration (Trigonox 101) on binding, using 10% DBBA concentration (without interlinking agent) in PP at 180°C .

Initiator concentration (Trigonox 101 / DBBA) - molar ratio	Wt . of initiator in 35 g PP (g)	% Binding *
0 . 025	0 . 0876	32
0 . 05	0 . 1752	36
0 . 1	0 . 3504	48
0 . 15	0 . 5257	59

Table 4 . 15 Effect of interlinking agent concentration on binding at constant initiator concentration (Trigonox 101 /DBBA + TMPTA) = 0 .1 molar ratio , using total concentration of DBBA + interlinking agent = 10% in PP at 180°C .

Interlinking agent concentration (%)	Wt . of interlinking agent in 35 g PP (g)	% Binding *
0	0	48
1	0 . 35	68
2	0 . 7	88
3	1 . 05	89
4	1 . 4	96

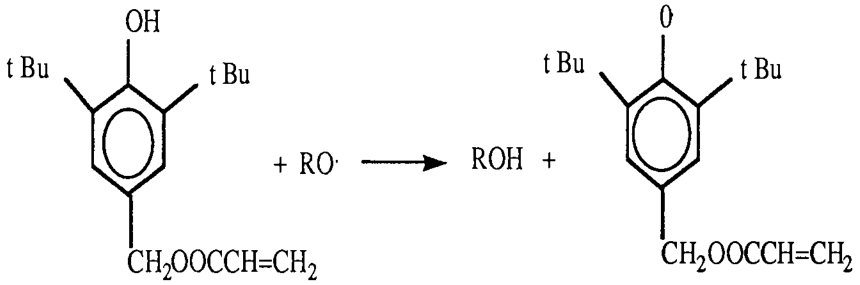
Table 4 . 16 Effect of varying both the interlinking agent concentration and peroxide concentration on binding using total concentration of DBBA + interlinking agent = 10% in PP at 180°C .

Radical generator used	% of interlinking agent used	Initiator concentration (I / A_O + TMPTA) - molar ratio	% Binding *
DCP	1	0 . 025	21
	2	0 . 1	64
	3	0 . 15	94
	4	0 . 295	95
Trigonox 101	1	0 . 02	56
	2	0 . 05	63
	3	0 . 1	89
	4	0 . 15	96

* Binding based on the measurement of 1735 cm^{-1} band of DBBA . Dichloromethane (DMC) was used for extraction .

that with an increase in concentration of interlinking agent the binding also increases (Table 4 . 16) .

The increasing binding of DBBA in PP with high concentration of radical generator and interlinking agent may be due to the tendency of the hindered phenol to trap radicals (67) which reduces the impact of the added peroxide (Reaction 4 . 4) . The results show that the higher the initiator concentration the higher is the level of binding . However , at higher initiator concentrations the MFI values of the masterbatches will increase . It is difficult to evaluate the effect of an initiator when an antioxidant is present . This is mainly due to the possibility of interaction of the initiator with both the polymer and the antioxidant . In comparison with that of polypropylene processed with the same initiator but without antioxidant (PP control) , however , the MFI values of any masterbatches containing antioxidants are much lower (Fig . 4 . 43 a) . This indicates that the initiator (which accelerated thermal degradation) is consumed by the antioxidants which in turn initiates the binding process or homopolymerisation of the antioxidants .



(4.4)

The effect of increasing the concentration of DBBA on the extent of binding was examined . Fig . 4 . 44 and table 4 . 17 show the effect of varying the

Table 4 . 17 Effect of DBBA concentration on binding using constant concentration of peroxide of (Trigonox 101 /DBBA) - molar ratio = 0 . 05 in PP at 180^{o}C (no interlinking agent) .

DBBA concentration (% w / w)	% Binding
2	29
5	35
10	36
15	33
20	19

Table 4 . 18 Effect of processing temperature on binding of DBBA (10% MB) in PP , using initiator of (Trigonox 101/ DBBA) - molar ratio = 0 . 05 (Trigonox 101) (no interlinking agent) .

Processing temperature (^{o}C)	% Binding
160	16
170	36
180	36
190	34

Table 4 . 19 Effect of processing time on binding of DBBA (10% MB)in PP , using constant concentration of peroxide of (Trigonox 101 / DBBA) - molar ratio = 0 . 05 at 180^{o}C (no interlinking agent).

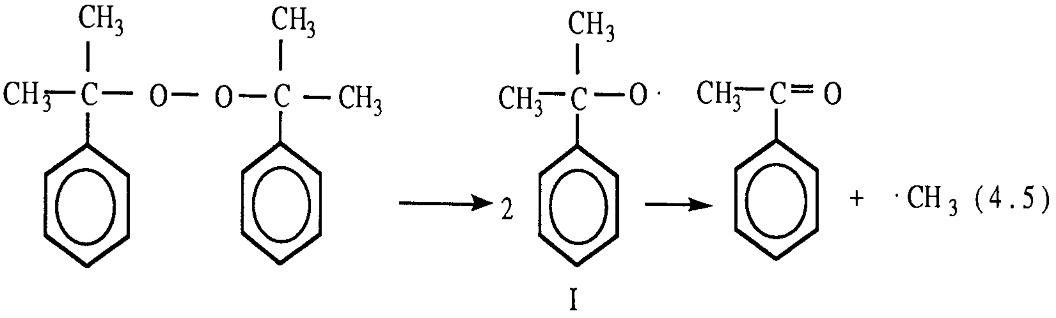
Processing time (mins)	% Binding
5	28
10	36
15	36
20	39

antioxidant concentration in the masterbatch in the presence of (Trigonox 101/ DBBA = 0 . 05 molar ratio of) on the extent of binding . Masterbatch containing 10% DBBA was found to give optimum binding . A further increase in antioxidant concentration leads to a decrease in binding efficiency which appears to be due to the fact that the solubility of the antioxidant at this particular concentration (10 %) is higher which ensures better dispersion and compatibility with the polymer .

The effect of processing temperature (time , 10 minutes) on the binding of 10 % DBBA using 0 . 05 molar ratio of Trigonox 101 was examined . The results are shown in Fig . 4 . 45 and Table 4 . 18 which indicate that the optimum temperature for grafting of DBBA into polypropylene is 170 - 180^{o} C .

Optimum processing time was obtained by a set of experiments keeping the processing temperature constant at 180^{o} C , the concentration of DBBA at 10% and the concentration of initiator (Trigonox 101) at (I / A $_{o}$) - molar ratio = 0 .05 . The results are shown in Fig . 4 . 46 and Table 4 . 19 . It was found that a maximum yield of bound antioxidant could be obtained with higher processing time .

Fig . 4 . 47 (1) shows the IR spectrum of 10% DBBA in PP without radical generator . After extraction of this sample with DCM for 48 hours all of the characteristic bands of DBBA disappears , eg . - OH at 3632 cm^{-1} and vinyl unsaturation at 1632 cm^{-1} . This spectrum is compared with the spectrum of a masterbatch containing peroxide (DCP / DBBA + TMPTA = 0 .2 molar ratio) and coagent (TMPTA : DBBA = 4 : 6) which shows the resultant transformation, Fig . 4 . 47 (2) . After 48 hours Soxhlet extraction the spectrum remain more or less the same except the new band that appeared at 1696 cm $^{-1}$ after processing has ceased. This absorption is presumely due to acetophenone (I , reaction 4 . 5) which was easily extracted along with the unbound additive .



However , when processed with Trigonox 101 no such peak could be observed . From the figure it is also obvious that the absorption due to vinyl unsaturation disappears completely due to the transformation of the compound to the polymer backbone . If we compare the spectra in Fig . 4 . 47 (1) with 4 . 47 (2) it is evident that in bound DBBA the ester carbonyl peak had shifted from 1729 cm^{-1} to 1735 cm^{-1} as would be expected for saturated esters .

4 . 2 . 6 Effect of a bound UV stabiliser (HAEB) and thermal antioxidant (DBBA) in combination with Fe - acrylate on the photo - oxidation of unstabilised polypropylene

The effect of the uv stabiliser (HAEB) and a thermal stabiliser (DBBA) on the photo - oxidation of PP containing FeAc was examined . Masterbatch of DBBA was prepared in PP using 4% interlinking agent (TMPTA) and 6% DBBA using a molar ratio of (Trigonox 101 / DBBA + TMPTA) = 0 . 15 . The percentage of binding was found to be 96% . Similarly , a masterbatch of HAEB in PP was prepared using 9% HAEB and 1% of interlinking agent (TMPTA). Here 0 . 005 (Ttigonox 101 / HAEB + TMPTA) - molar ratio of initiator was used . The percentage of binding was found to be 100% . Masterbatch (5%) of FeAc was prepared in PP without any interlinking agent or initiator . The masterbatches of bound antioxidant , stabiliser and FeAc were diluted to different concentrations which were irradiated to observe the effect of these combinations .

Fig. 4.48 and table 4.20 show the effect of the HAEB on the photo-oxidation of polypropylene containing FeAc. A photosensitisation effect was observed with all concentrations of combination. It is evident that at these lower concentration of combination the photosensitising activity of FeAc predominates over the photostabilising activity of HAEB. However, higher concentration of HAEB in the combination increases the stability of the polymer to some extent compared to FeAc alone. Fig. 4.49 and Table 4.20 show the effect of DBBA on the photo-oxidation of polypropylene containing FeAc. The combination of DBBA and FeAc show a photosensitisation effect compared to that of PP control at the lower concentration of DBBA. At higher concentrations of DBBA in the combination, a photostabilisation effect was observed. It is assumed that in this combination of

Table 4.20 Effect of an uv stabiliser and a thermal stabiliser on the photo-oxidation of PP containing Fe-acrylate.

Samples	Concentrations (%, w / w)	Embrittlement time (hrs)
PP Control		90
FeAc	0.025	75
	0.05	70
	0.1	70
FeAc + HAEB	0.00 + 0.1	130
	0.00 + 0.05	110
	0.075 + 0.025	70
	0.05 + 0.05	70
	0.025 + 0.075	85
	0.0375 + 0.0125	70
	0.025 + 0.025	85
	0.025 + 0.0375	85
FeAc + DBBA	0.00 + 0.1	120
	0.00 + 0.05	120
	0.075 + 0.025	85
	0.05 + 0.05	95
	0.025 + 0.075	105
	0.0375 + 0.0125	75
	0.025 + 0.025	75
	0.0125 + 0.0375	95

antioxidant effect of DBBA predominates over the photosensitising effect of FeAc. The hindered phenol is known to act by a CB- D mechanism involving the donation of hydrogen atom to the alkylperoxyl radical thus forming a hydroperoxide.

4.2.7 The effect of two component systems on the photo - oxidation of commercial PP

The effect of ZnDNC on the photo - oxidation of commercial PP was determined in combination with different pro - oxidants. Fig. 4. 51 and table 4. 21 compare the effect of different iron compounds in combination with ZnDNC in commercial PP. It appears from the figure that ZnDNC has no considerable effect in combination with FeTa on photosensitising commercial PP when compared with FeTa alone. FeTp was found to exhibit a pro - oxidant effect in commercial PP. The addition of ZnDNC in combination with FeTp photosensitises commercial PP compared to FeTp alone. Fig. 4. 52 and table 4. 21 show the effect of an antioxidant (FeDNC) in combination with Metone A on the photo - oxidation of commercial PP. Thus it also show the effect of ZnDNC and Metone A alone on the stability of commercial PP. Both Metone A and ZnDNC alone have a pro - oxidant effect at the concentrations used. It is evident that the introduction of ZnDNC does not change the photo - oxidative behaviour of Metone A to a considerable extent. However, with the addition of FeDNC to the polymer containing Metone A, a photosensitising effect was observed. The higher the concentration (0. 075%) of FeDNC in combination then the higher were the sensitisation effects obtained.

Fig. 4. 53 and Table 4. 21 show the effect of ZnDNC on the photo-oxidation of commercial PP in the presence of FeAc. It seems from the figure and table that with the addition of ZnDNC the embrittlement time is reduced compared to

FeAc alone (0 . 1%) . However , the effect is not pronounced in commercial PP but is much more evident in commercial LDPE (Chapter 3 , Table 3 .9). Figs . 4 . 50 , 4 . 53 and Table 4 . 21 show the effect of ZnDNC and FeDNC on the photo - oxidation of commercial PP containing Metone M . The addition of ZnDNC

Table 4 . 21 Effect of ZnDNC on the photo - oxidation of commercial PP containing different pro - oxidants .

Samples	Concentrations (% w / w)	Embrittlement time (hrs)
Commercial PP		200
FeDNC	0 . 01	125
	0 . 025	115
	0 . 05	95
	0 . 1	100
Metone A + FeDNC	0 . 025 + 0 . 075	90
	0 . 05 + 0 . 05	100
	0 . 075 + 0 . 025	115
	0 . 1 + 0 . 00	175
	0 . 0125 + 0 . 0375	90
	0 . 025 + 0 . 025	105
	0 . 0375 + 0 . 0125	105
	0 . 05 + 0 . 00	165
ZnDNC	0 .05	160
Metone A + ZnDNC	0 . 05 + 0 . 05	180
	0 . 025 + 0 . 075	180
	0 . 075 + 0 . 025	190
	0 . 00 + 0 . 1	160
	0 . 025 + 0 . 025	165
	0 . 0125 + 0 . 0375	165
	0 . 0375 + 0 . 0125	165
	0 . 00 + 0 . 05	160
FeDMC	0 . 1	140
	0 . 05	120
	0 . 025	100
	0 . 01	110

Continued

Sample	Concetration (% w / w)			Embrittlement time (hrs)
Metone M+ FeDNC	0 . 05	+	0 . 05	95
	0 . 025	+	0 . 075	95
	0 . 075	+	0 . 025	145
	0 . 1	+	0 . 00	180
	0 . 025	+	0 . 025	135
	0 . 0125	+	0 . 0375	120
	0 . 0375	+	0 . 0125	120
	0 . 05	+	0 . 00	220
Metone M + ZnDNC	0 . 05	+	0 . 05	160
	0 . 025	+	0 . 075	160
	0 . 075	+	0 . 025	190
	0 . 025	+	0 . 025	170
	0 .0125	+	0 . 0375	170
	0 . 0375	+	0 . 0125	180
FeAc + ZnDNC	0 . 1	+	0 . 00	120
	0 . 075	+	0 . 025	100
	0 . 05	+	0 . 05	100
	0 . 025	+	0 . 075	100
	0 . 05	+	0 . 00	100
FeTp + ZnDNC	0 . 05	+	0 . 00	185
	0 . 05	+	0 . 05	140
FeTa + ZnDNC	0 . 05	+	0 . 00	165
	0 . 05	+	0 . 05	155

in combination with Metone M reduces the embrittlement time compared to Metone M alone . In this case only the highest (0 .075%) or equal (0 . 05%) concentration of ZnDNC with Metone M were found to be effective . An increase of Metone M concentration (0 . 075%) extends the embrittlement time . The use of FeDNC with Metone M had a considerable effect on photosensitising commercial PP . In this case only the highest (0 . 075%) and equal (0 . 05%) concentrations of FeDNC were found to be most effective . An increase of Metone M concentration above 0 . 05%

reduces the photoactivation effect.

The antagonistic behaviour of ZnDNC (Fig . 4 . 48 , curve 5 and Table 4 . 21) in commercial PP assumes to be due to the interaction of ZnDNC with the phenolic antioxidant in commercial PP. The presence of phenolic antioxidant in commercial polymer and the interaction of ZnDNC with phenolic antioxidant is confirmed in solution studies (Chapter 3 , section 3 . 2 . 8) .

The introduction of ZnDNC to Metone A does not change the photoactivity of Metone A . This may be due to the fact that they do not interact with the activity of each system. However, the addition of FeDNC in combination with Metone A does sensitise the polymer which is assumed to be due to the photoactivation of polymer by FeDNC at low concentration. The increase of Metone A in the combination increases the stability of the polymer. Thus, the photoactivity of the polymer containing Metone A in combination with FeDNC is entirely due to the carboxylate formed as an end product of decomposition of FeDNC . The photosensitising activity of FeDNC in the combination of Metone A and FeDNC is confirmed in solution studies (Chapter 3 , Section 3 . 2 . 7) . The introduction of ZnDNC to Metone M reduces the activity of commercial polypropylene. It may be due to the effect of ZnDNC , which interacts with the phenolic antioxidant in the commercial polymer and ultimately the lifetime of the polymer is reduced. Metone M shows a similar behaviour to Metone A in combination with FeDNC. FeAc , FeTp and FeTa show a pro - oxidant behaviour in commercial PP which is due to the formation of iron carboxylate during UV irradiation. The use of ZnDNC reduces the activity of the polymer containing FeAc , FeTp and FeTa .

Conclusions

The binding efficiency of FeTp in unstabilised PP was evaluated . High levels of binding were obtained using both peroxide and an interlinking agent . The effect of pro - oxidants at different concentrations on the photodegradation of unstabilised PP were examined . FeTp , FeDMC , Metone A and Metone M showed a pro - oxidant effect at lower concentrations , whereas at higher concentrations a photostabilisation effect predominates . The higher the concentration the higher the induction period and the embrittlement time . FeTa did not show any pro - oxidant effect at all concentrations used . In the case of FeAc and FeCi the photodegradation of the polymer increased as the concentration increased .

The effect of concentration of different pro - oxidants on the melt flow index change of unstabilised PP were examined . Higher concentrations of FeTa and FeMa were found to have good melt stabiliser behaviour . At higher (> 0.2%) and lower (< 0.1%) concentrations of FeCi the MFI values were lower than that of the PP control . In the case of FeAc and FeCr the MFI values of lower concentrated samples are comparable with the control . However , at higher concentrations they are not good melt stabilisers . Other pro-oxidants such as FeTp, FeDMC and Metone A are good melt stabilisers at all concentrations used . The effect of an antioxidant on the photo-oxidative stability of unstabilised PP containing pro-oxidants was examined. In the case of FeAc the combination with ZnDEC resulted in stabilisation of polymer . As the concentration of ZnDEC increased the induction period also increased . The rate of photo-oxidation at the end of the induction period was sharp. The polymer containing these combinations could be used as a short term mulching film in the case of seasonal crops such as in the production of tomatoes melons etc .

The combination of iron containing photoactivator (FeDNC) with Metone A and Metone M were examined . It was shown that in the presence of FeDNC the polymer containing Metone A and Metone M behaved similar to that of Metone A / Metone M or FeDNC alone . However , the use of ZnDNC in the combination extended the stability of the polymer .

The use of an antioxidant (NiDNC) on the photo - oxidative stability of FeDNC were followed . At all combinations of FeDNC and NiDNC the photostabilisation effect were observed .

A photostabiliser (HAEB) and a thermal antioxidant (DBBA) were successfully bound to the unstabilised PP using a peroxide and interlinking agent . The binding conditions were also optimised . The combined effect of HAEB and DBBA with a pro - oxidant were examined . Higher concentrations of antioxidant in the combination showed a stabilisation effect , whereas the lower concentration induced a sensitisation effect . These systems can be used in disposable plastic cups , plates etc. Because the additives used in these systems are nonextractable, they are also useful for food - stuff contact applications . Another important point is that these are rapidly degradable which is a vital criterion for disposable plastics .

Two component systems containing an antioxidant (ZnDNC) and pro - oxidant were evaluated in commercial PP . The pro-oxidant effect of different compounds in commercial PP were also examined . It was found that in every case the combination of ZnDNC with pro-oxidants resulted in a decrease in photostability of the polymer . The effect of FeDNC on Metone A and Metone M in this polymer was also studied . In all these combinations photosensitisation behaviour was noticed. These systems could be used for short term crop protection films .

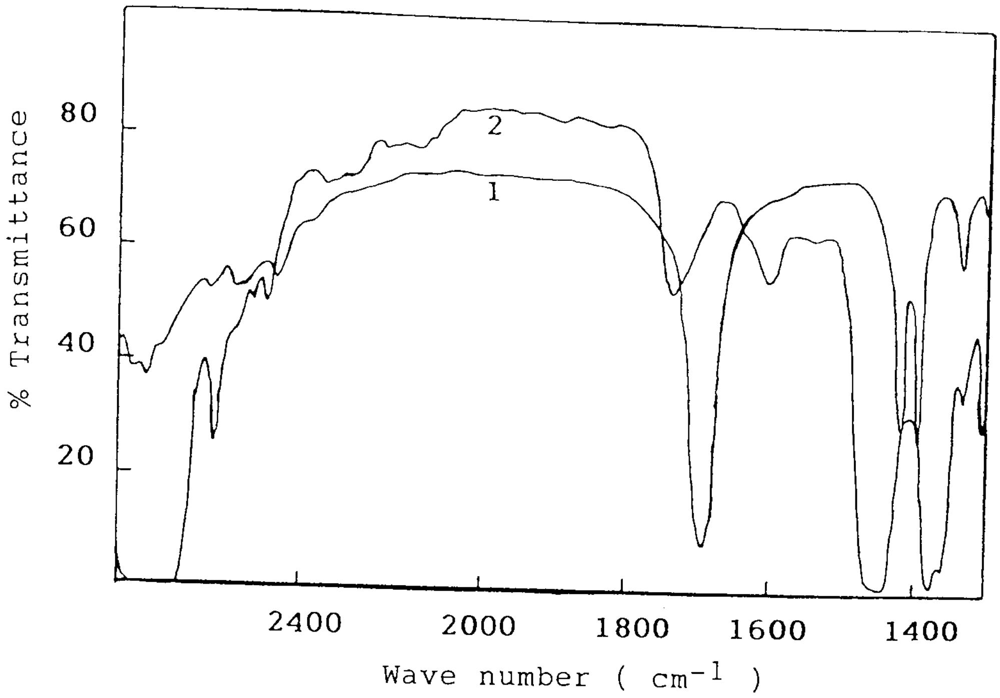


Fig. 4.1 A segment of the IR spectra of iron thiopropionate. 1) FeTp compound alone (KBr disc) and 2) 5% masterbatch of iron thiopropionate in unstabilised PP without peroxide.

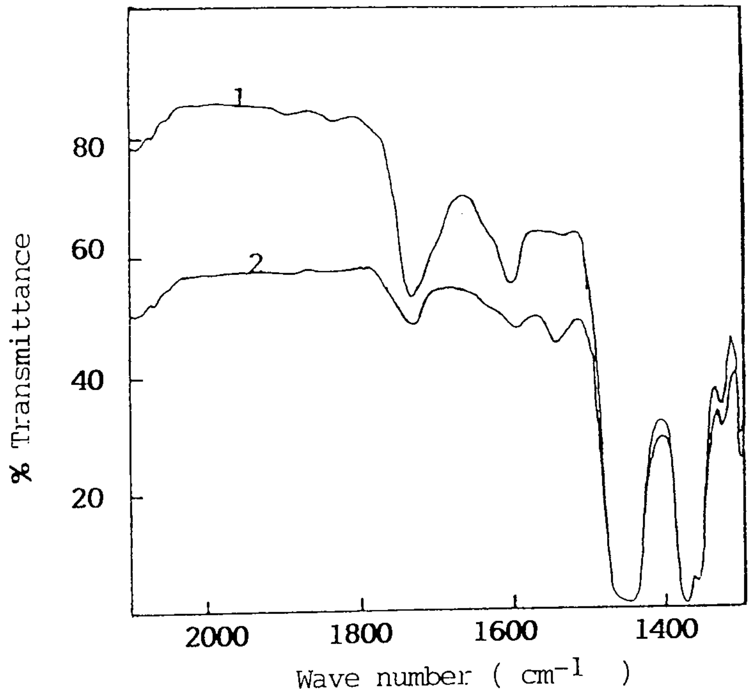


Fig. 4.2 A segment of the IR spectra of 5% masterbatch of iron thiopropionate in unstabilised PP without peroxide . 1) before extraction and 2) after extraction .

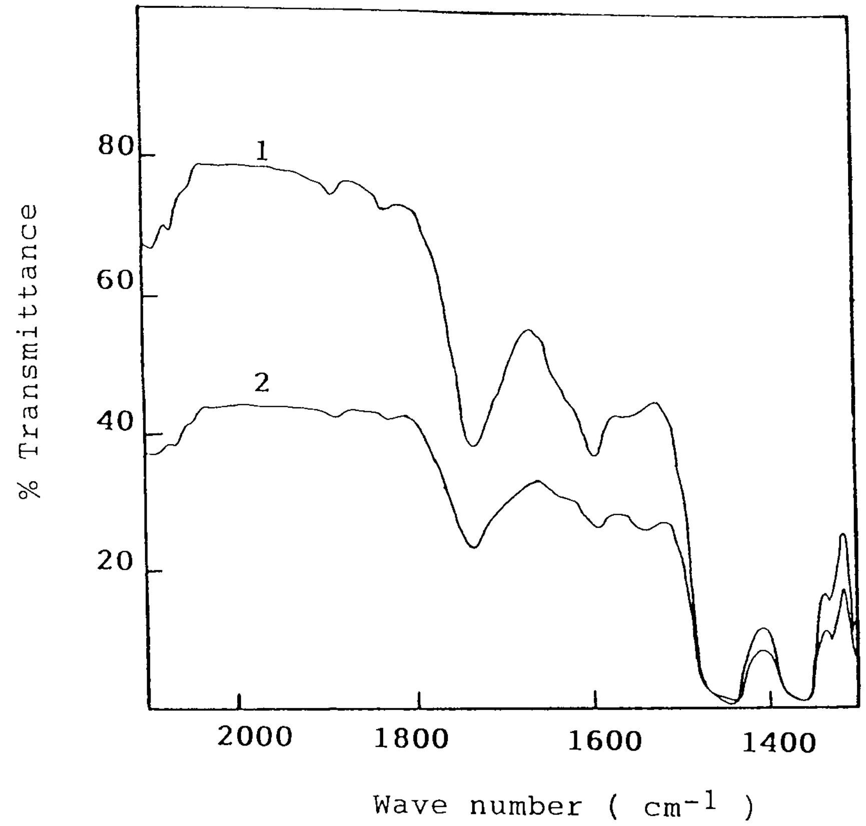


Fig. 4.3 A segment of the IR spectra of 5% masterbatch of iron thiopropionate in unstabilised PP with peroxide of (I/P_O)-molar ratio = 0.15 (Trigonox 101). 1) Before extraction and 2) after extraction. I = initiator, P_O = pro-oxide.

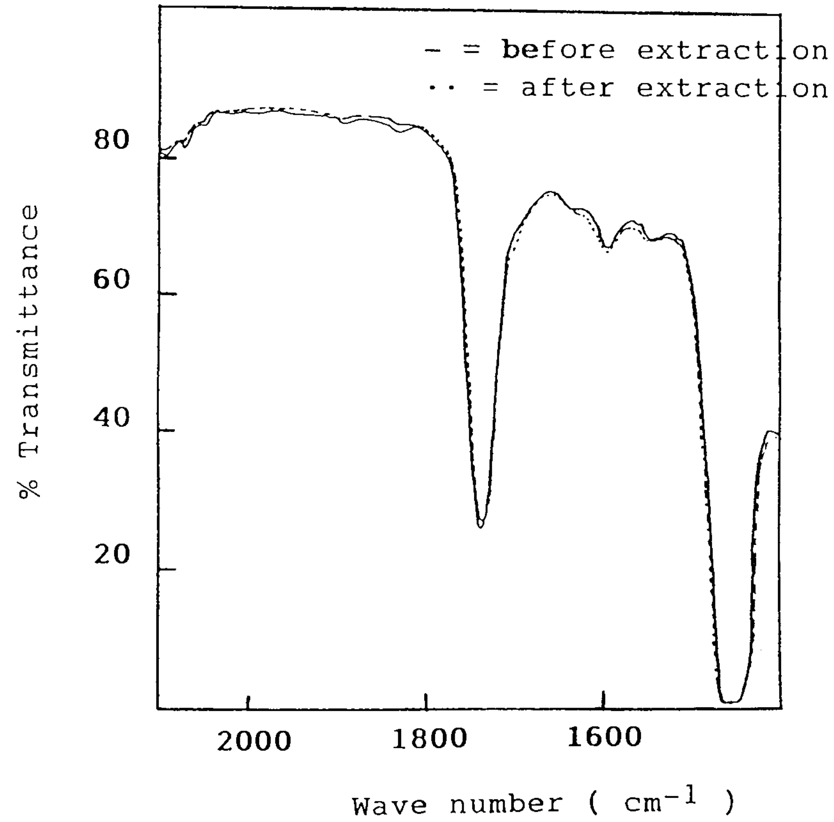


Fig. 4.4 A segment of the IR spectra of 5% masterbatch of iron thiopropionate in unstabilised PP with peroxide of (I/P_O)-molar ratio = 0.15 (Trigonox 101) and 2% TMPTA.

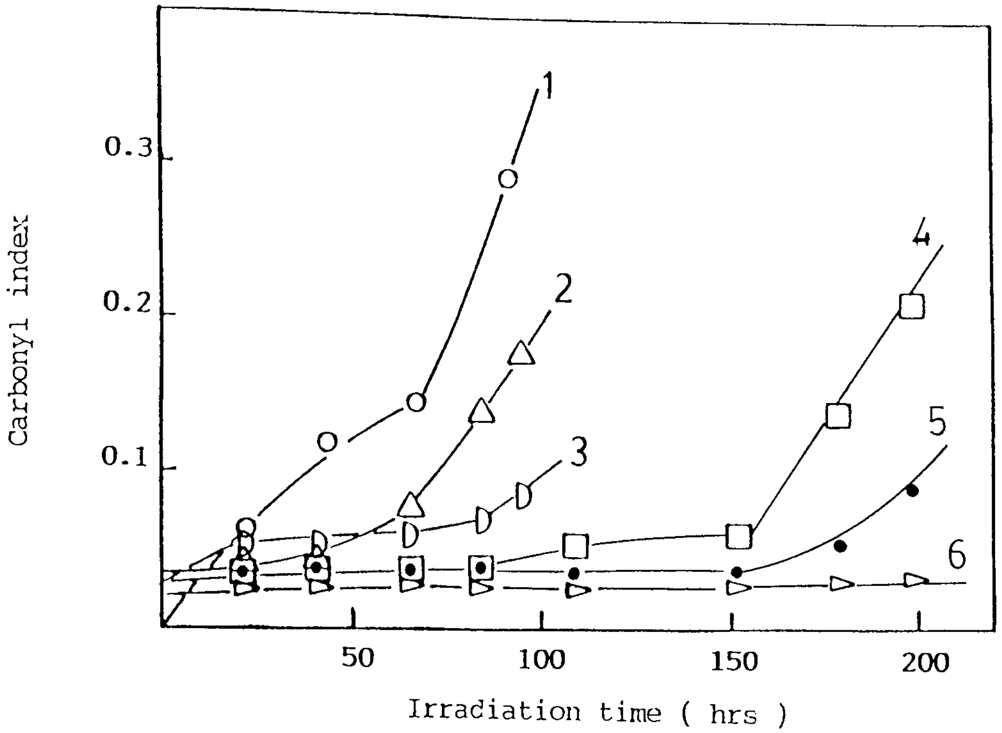


Fig. 4.5 Effect of concentration of Fe-thioacetate on the photo-oxidation of unstabilised polypropylene (1) Control (2)0.025% (3) 0.05% (4) 0.1% (5) 0.2% (6) 0.3% .

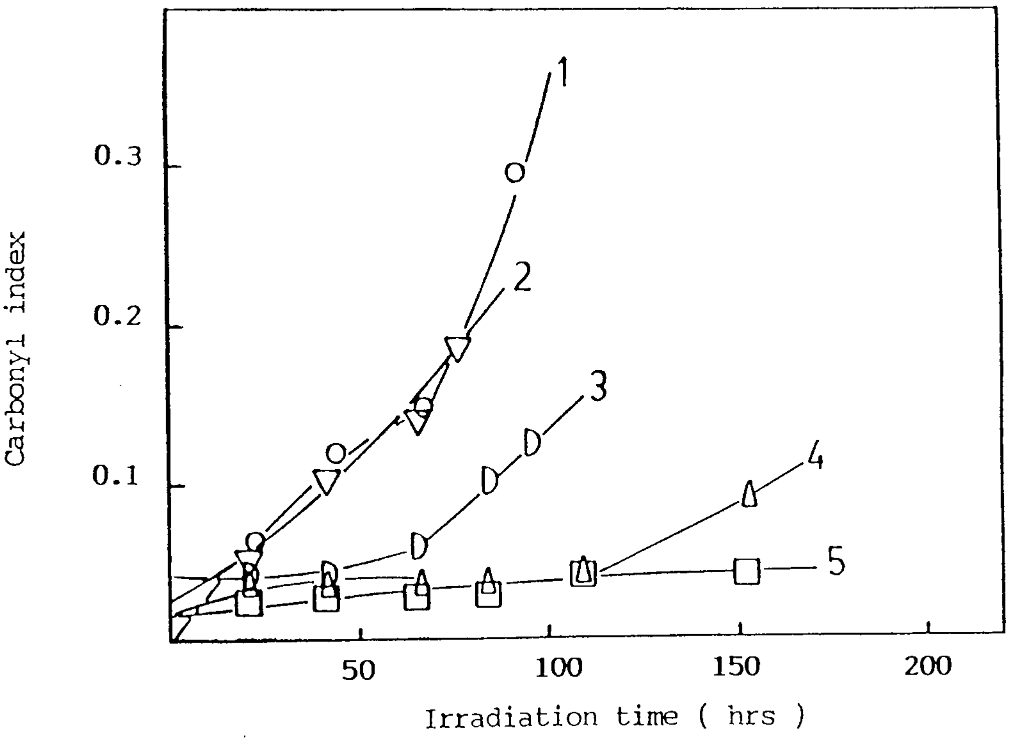


Fig. 4.6 Effect of concentration of Fe-thiopropionate on the photo-oxidation of unstabilised polypropylene (1) Control (2) 0.025% (3) 0.1% (4) 0.2% (5) 0.4% .

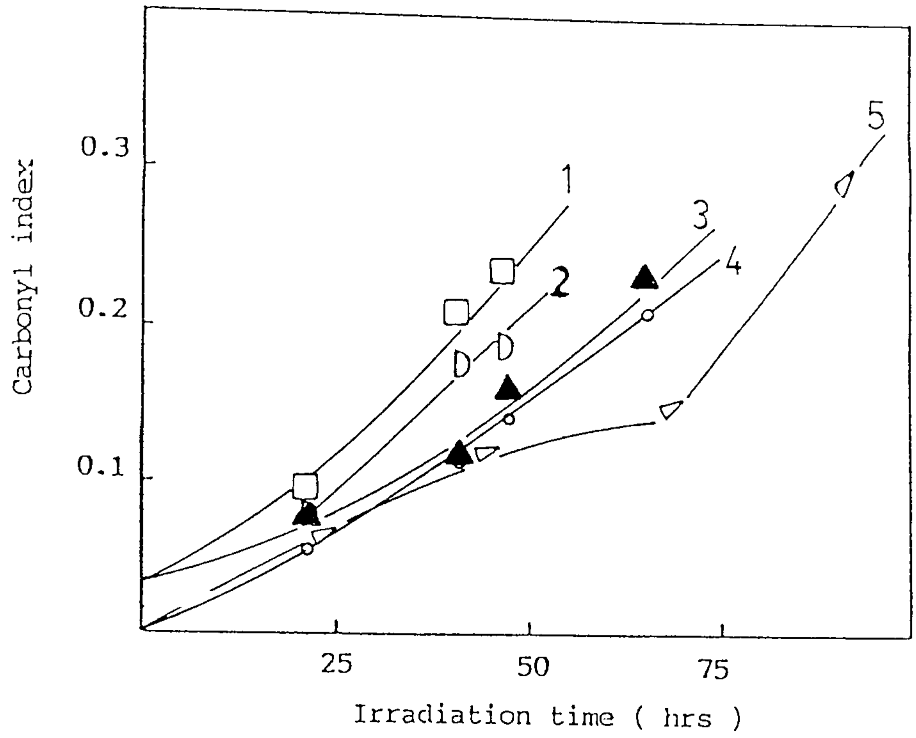


Fig. 4.7 Effect of concentration of Fe-acrylate(FeAc,insoluble) on the photo-oxidation of unstabilised PP. 1)0. 4%, 2)0.2%, 3)0.05%, 4)0.025% and 5) PP control.

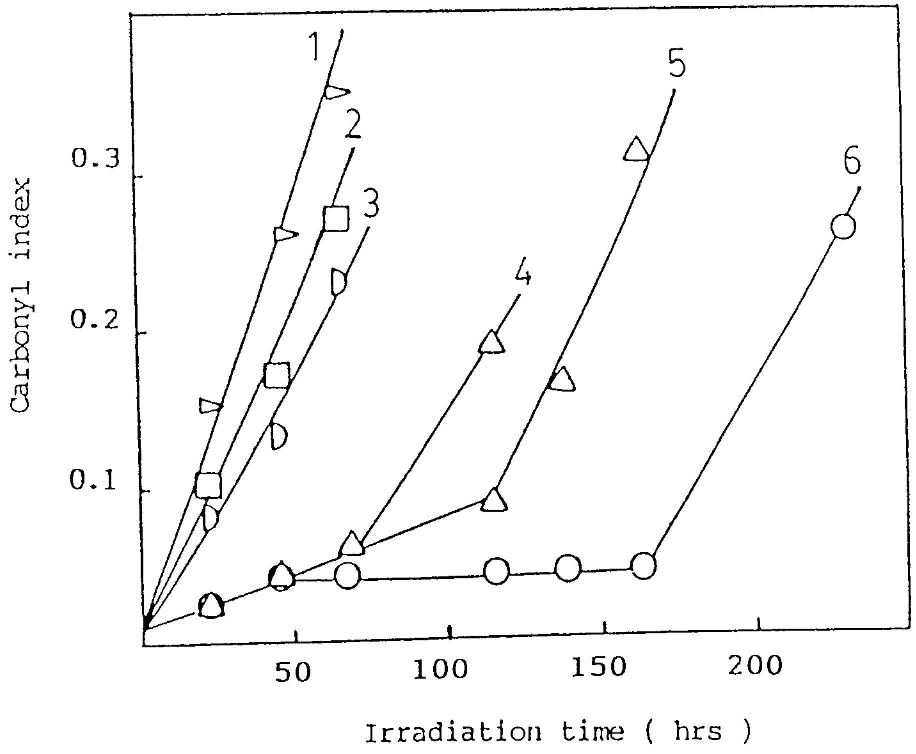


Fig. 4.8 Effect of concentration of FeDMC on the photo-oxidation of unstabilised PP (1) 0.025%, (2) 0.05%, (3) PP control, (4) 0.1%, (5) 0.2% and (6) 0.3% .

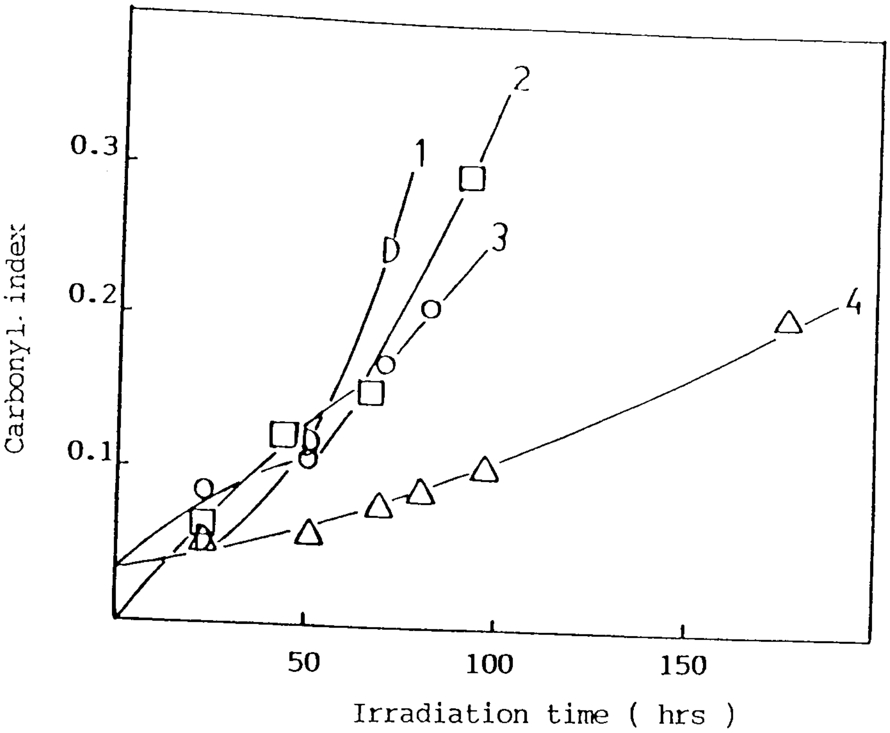


Fig. 4.9 Effect of concentration of Metone A on the photo-oxidation of unstabilised PP (1) 0.05% (2) Control (3) 0.2% (4) 0.4%

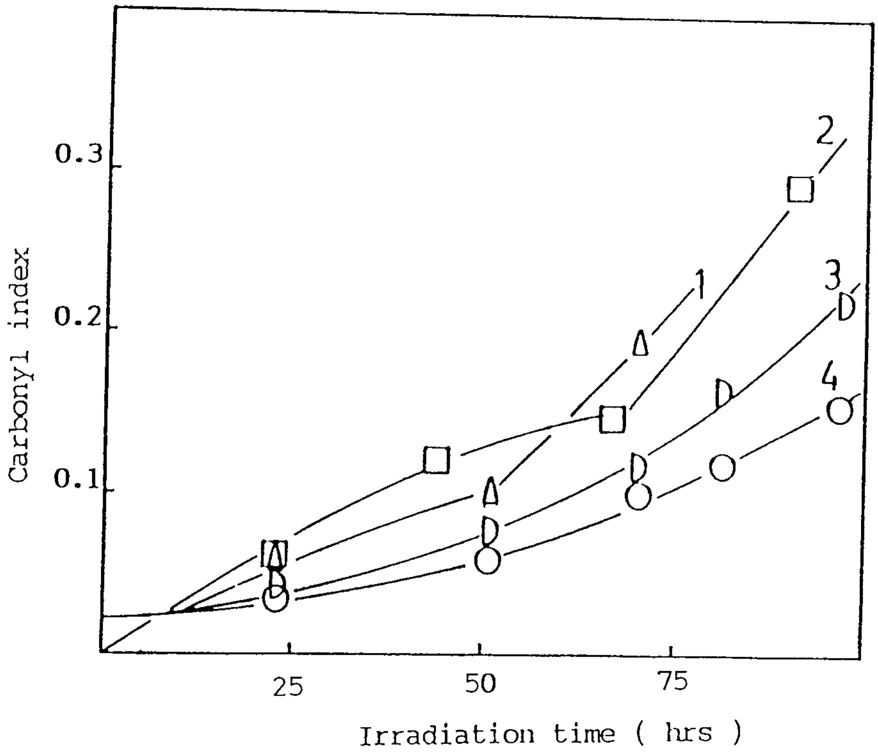


Fig. 4.10 Effect of concentration of Metone M on the photo-oxidation of unstabilised PP (1) 0.05% (2) Control (3) 0.3% (4) 0.4%

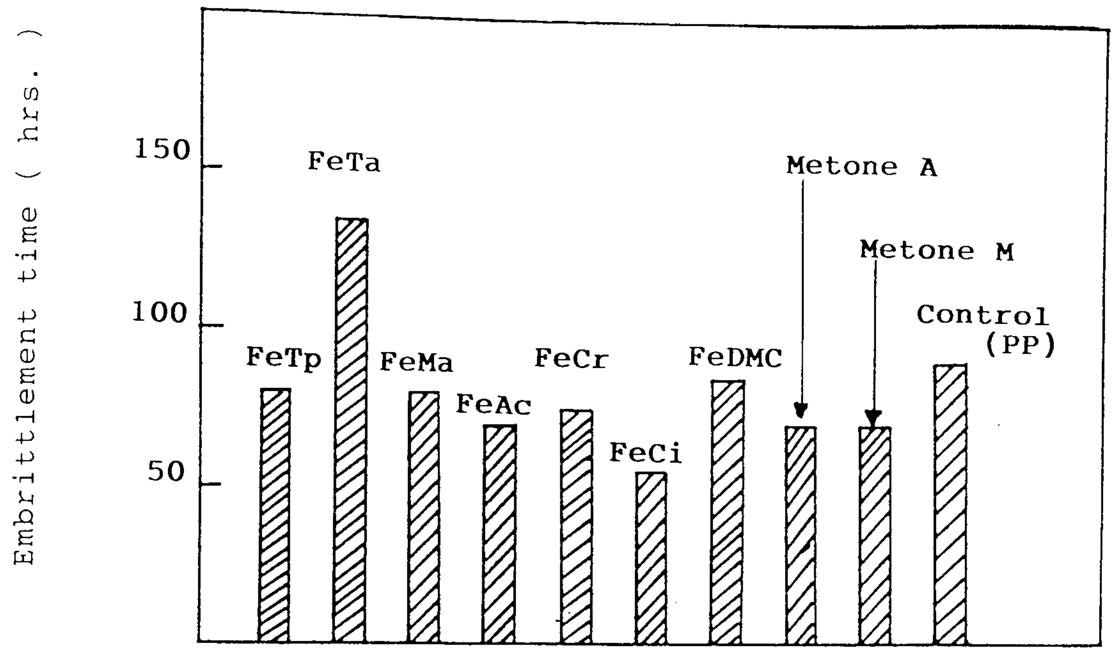


Fig. 4.11 Effect of different photo-activators (0.05%) on the UV life time of unstabilised PP. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber.

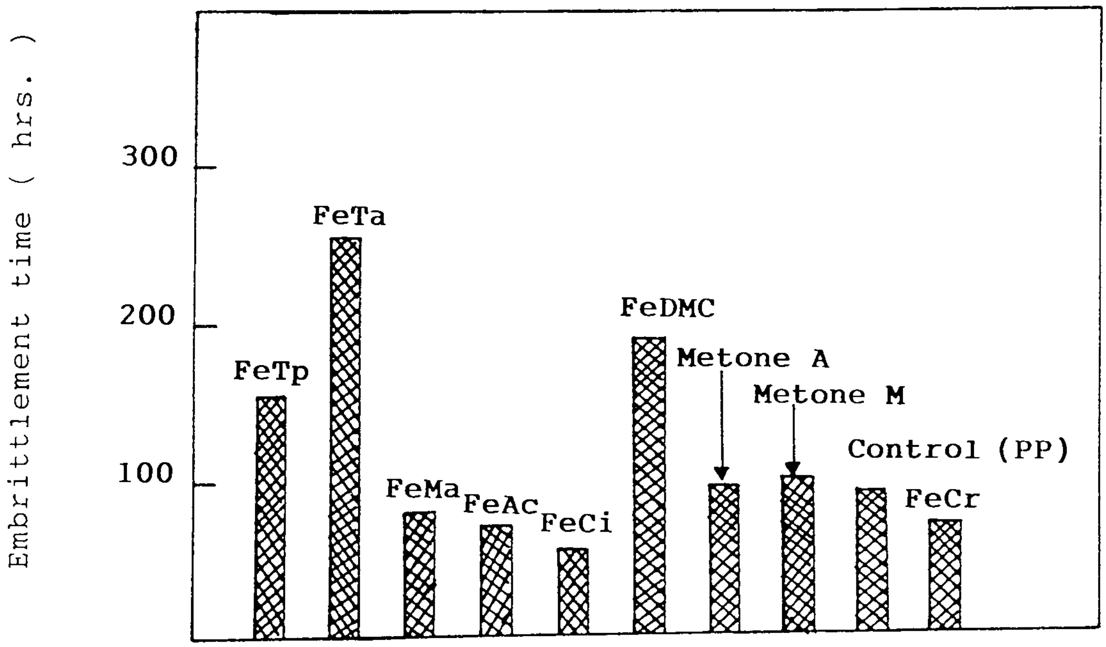


Fig. 4.12 Effect of different photo-activators (0.2%) on the UV life time of unstabilised PP. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes in closed chamber.

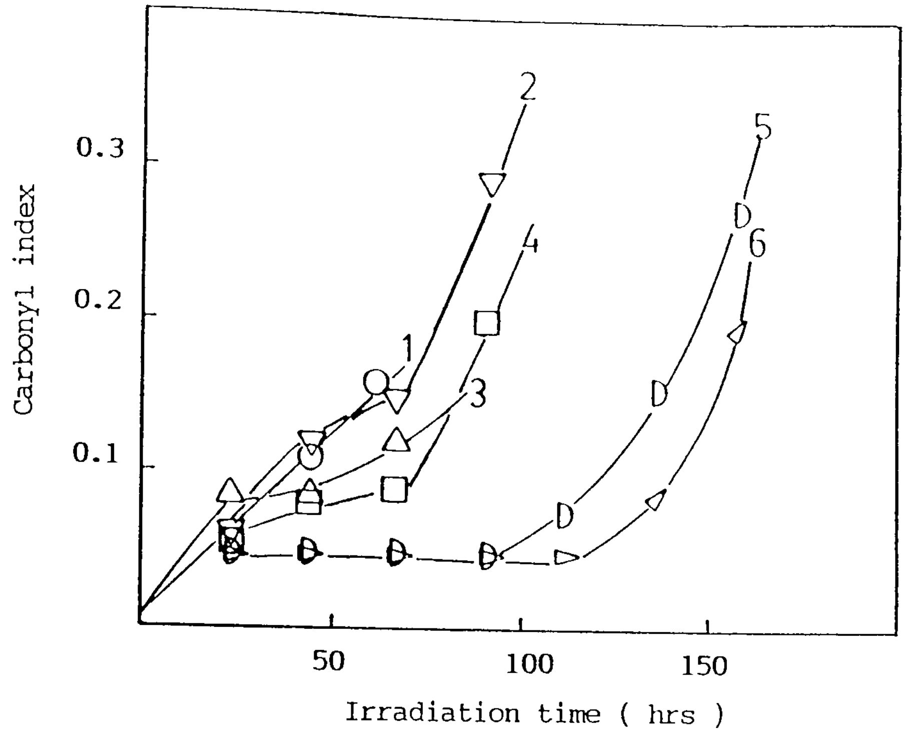


Fig. 4.13 Effect of ZnDEC concentration on the photo-oxidation of PP in the presence of 0.2% Fe-acrylate (1) 0.025% (2) Control (3) 0.05% (4) 0.1% (5) 0.2% (6) 0.3%.

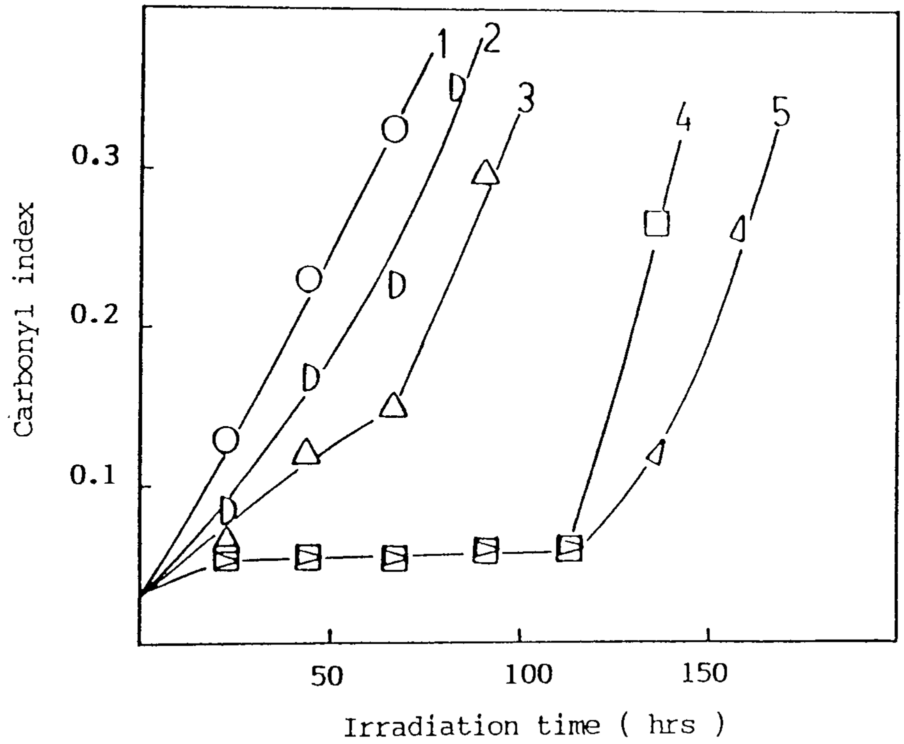


Fig. 4.14 Effect of ZnDEC concentration on the photo-oxidation of PP in the presence of 0.2% Fe-crotonate (1) 0.05% (2) 0.1% (3) Control (4) 0.2% (5) 0.3% .

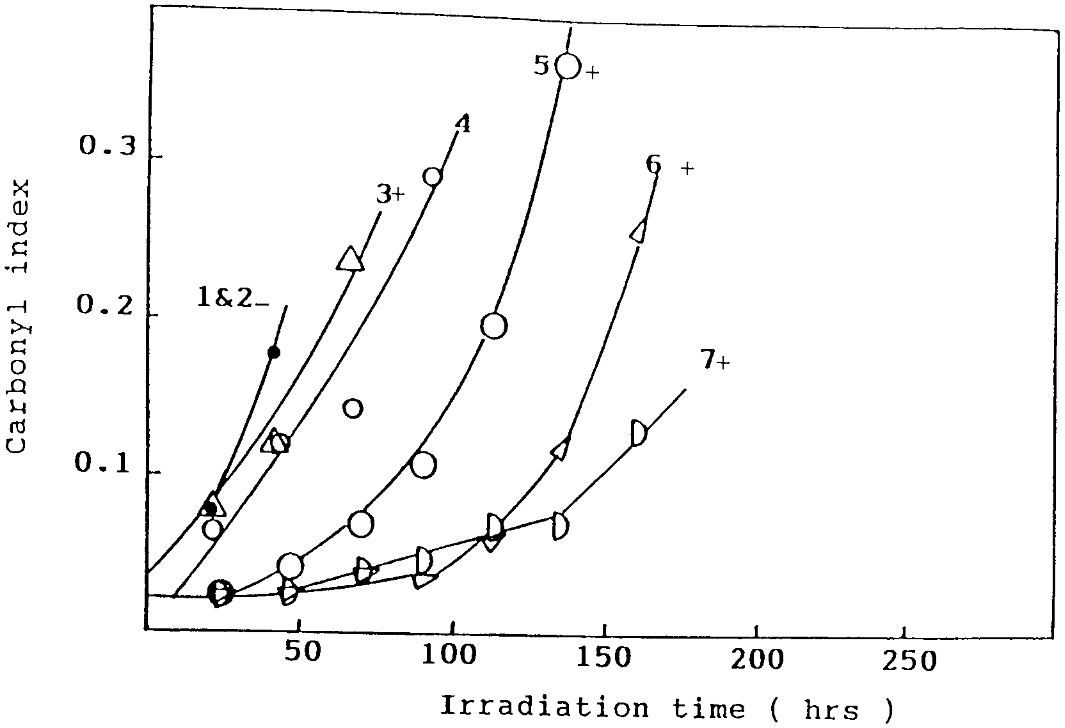


Fig. 4.15 Effect of Fe-acrylate conc. on the photo-oxidation of PP in the presence(+) and absence(–) of 0.2% ZnDEC 1) 0.3%(–) 2) 0.2%(–), 3) 0.05%(–), 4) PP control, 5) 0.3%(+), 6) 0.2%(+) and 7) 0.05%(+).

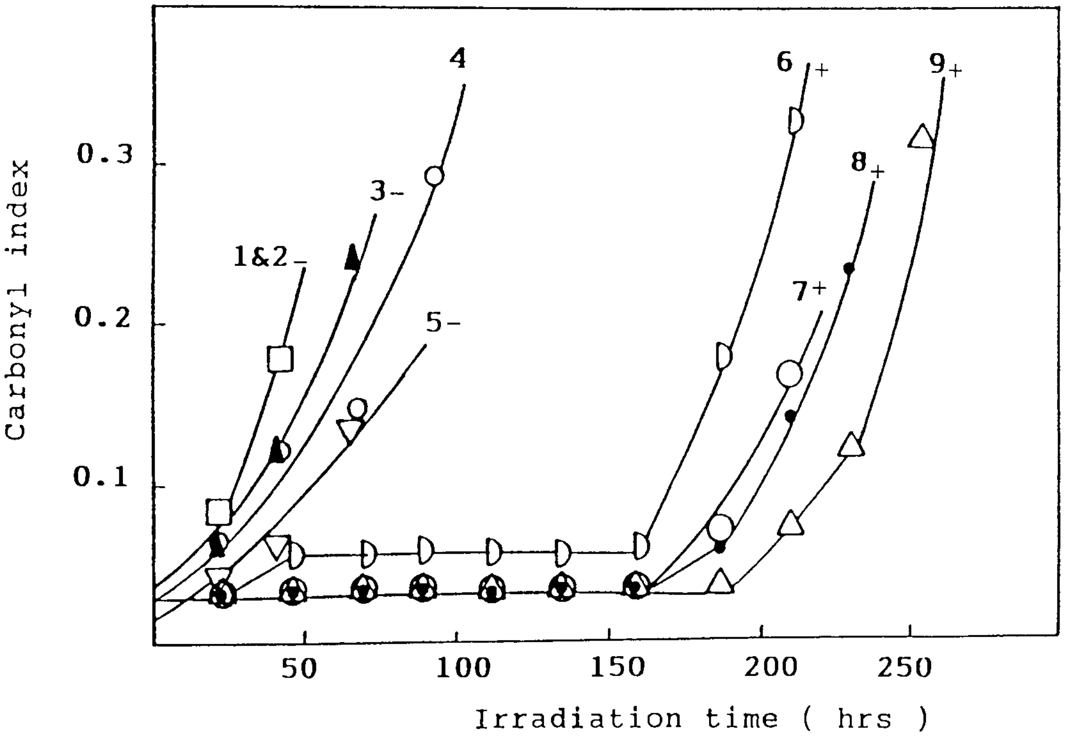


Fig. 4.16 Effect of Fe-acrylate conc. on the photo-oxidation of PP in the presence(+) and absence(–) of 0.4% ZnDEC 1) 0.3%(–), 2) 0.2%(–), 3) 0.1%(–), 4) control, 5) 0.025%(–), 6) 0.3%(+) 7) 0.025%(+), 8) 0.2%(+) and 9) 0.1%(+).

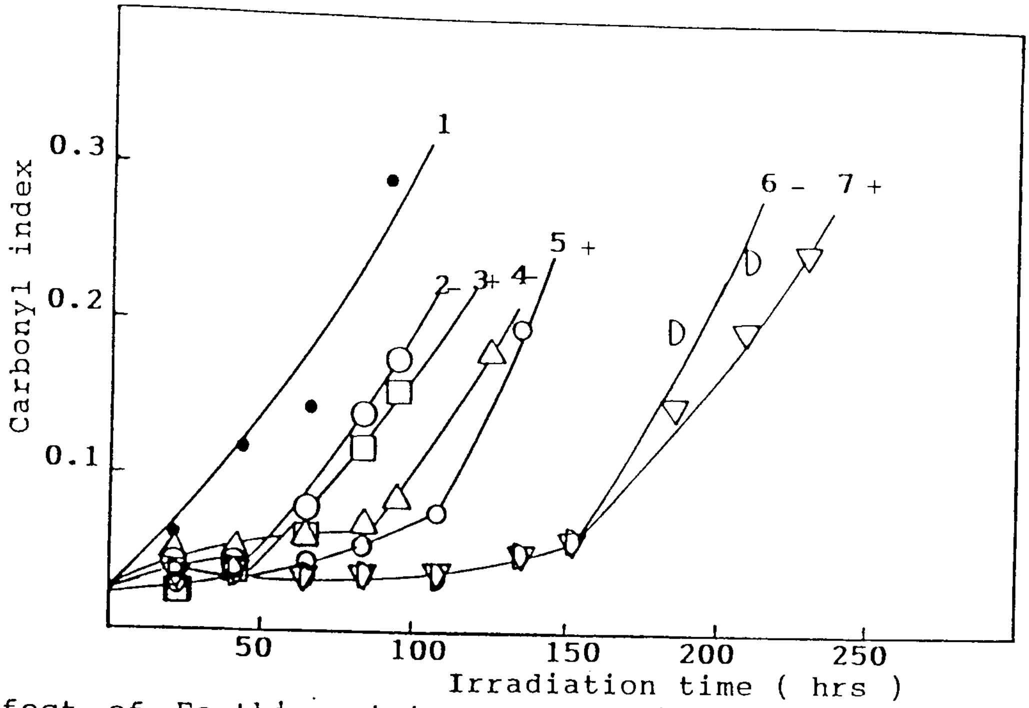


Fig. 4.17 Effect of Fe-thioacetate conc. on the photo-oxidation of PP in the presence(+) and absence(-) of 0.05% ZnDEC 1) PP control, 2) 0.025%(-), 3) 0.025%(+), 4) 0.05%(-), 5) 0.05%(+), 6) 0.1%(-) and 7) 0.1%(+).

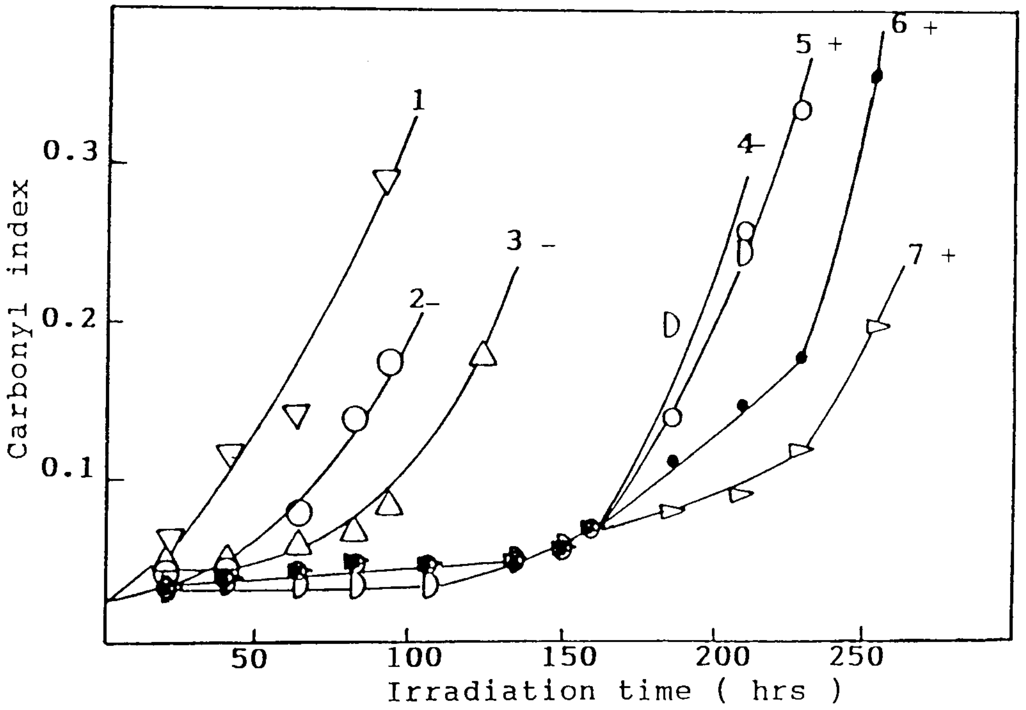


Fig. 4.18 Effect of Fe-thioacetate conc. on the photo-oxidation of PP in the presence(+) and absence(-) of 0.2% ZnDEC 1) PP control, 2) 0.025%(-), 3) 0.05%(-), 4) 0.1%(-), 5) 0.025%(+), 6) 0.05%(+) and 7) 0.1%(+).

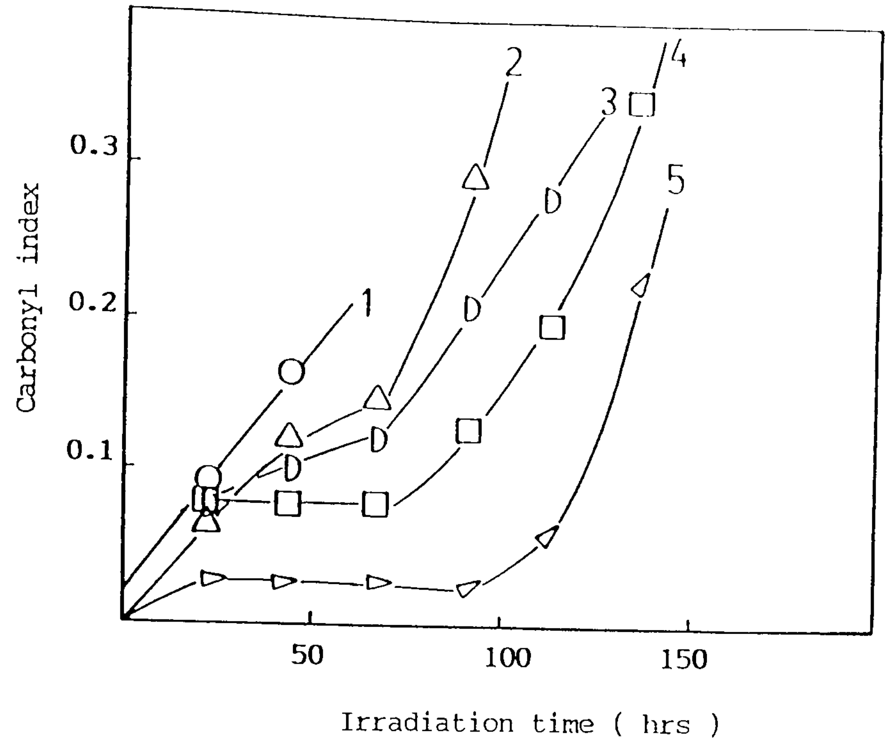


Fig. 4.19 Effect of ZnDEC concentration on the photo-oxidation of unstabilised PP in the presence of 0.05% Metone A (1) 0.01% (2) Control (3) 0.05% (4) 0.1% (5) 0.2% .

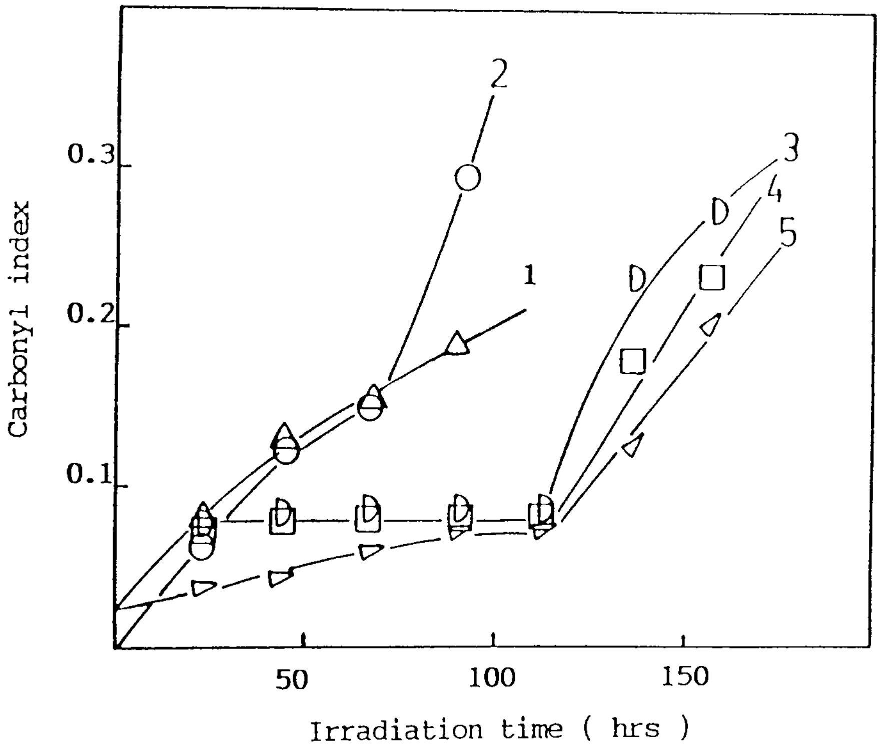


Fig. 4.20 Effect of ZnDEC concentration on the photo-oxidation of unstabilised PP in the presence of 0.1% Metone M (1) 0.025% (2) Control (3) 0.05% (4) 0.1% (5) 0.2% .

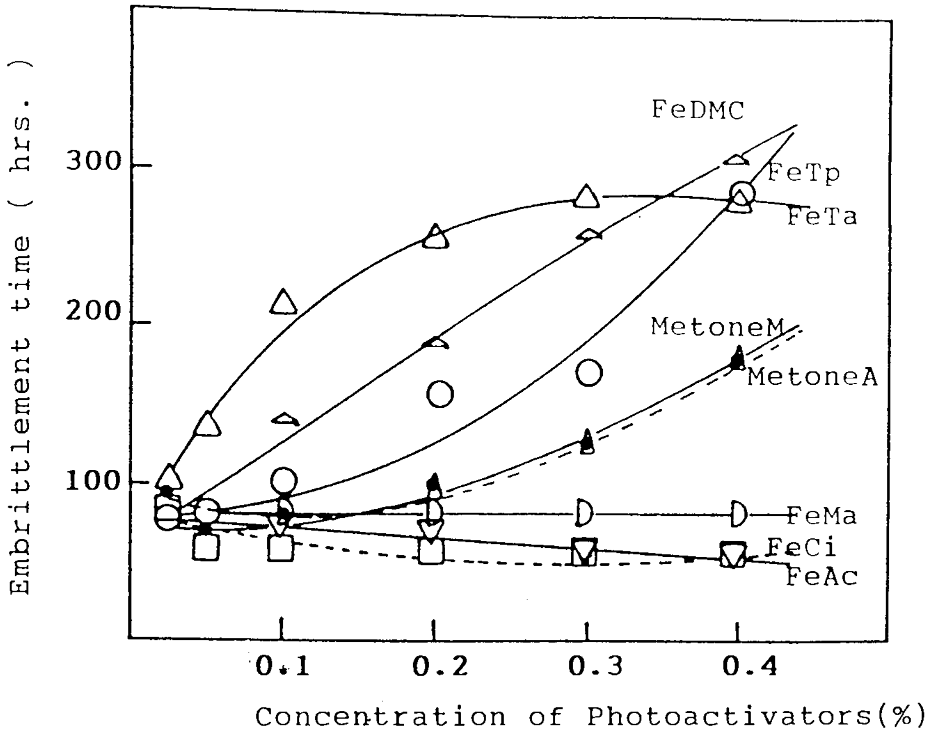


Fig.4.21 Effect of concentrations of different pro-oxidants in the UV life time of unstabilised PP. Samples are diluted from 5% masterbatches prossed at 180^{0}C for 10 minutes in closed chamber.

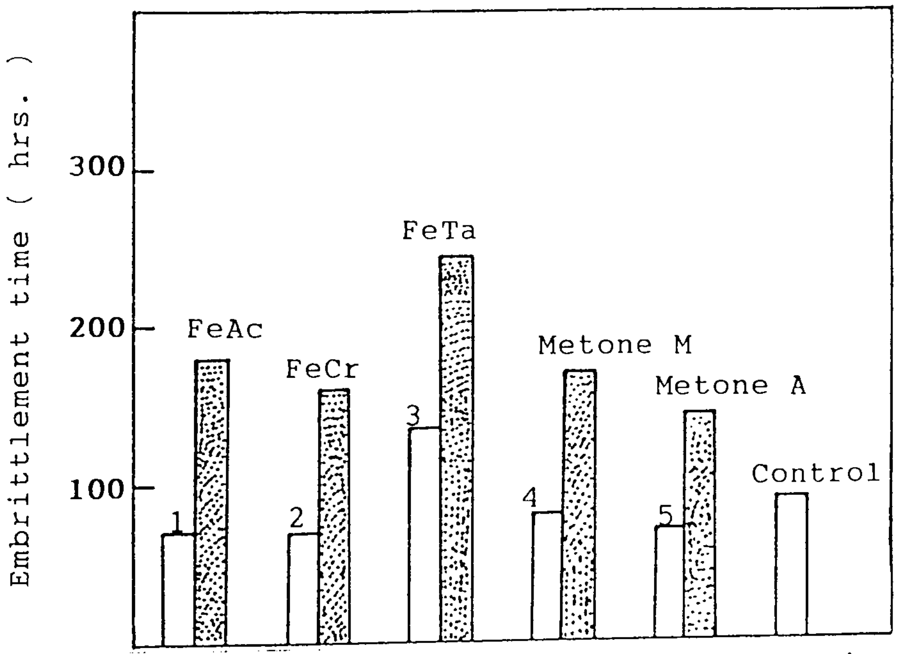


Fig.4.22 Effect of ZnDEC(0.2%) on the UV life time of PP containing different photoactivators. (1) FeAc(0.05%) (2) FeCr(0.2%) (3) FeTa(0.05%) (4) Metone M(0.1%) (5) Metone A(0.05%) and (6) Control. ▨ represents all the samples with 0.2% ZnDEC. All the samples are diluted from 5% masterbatches processed at 180^{0}C for 10 minutes in closed chamber.

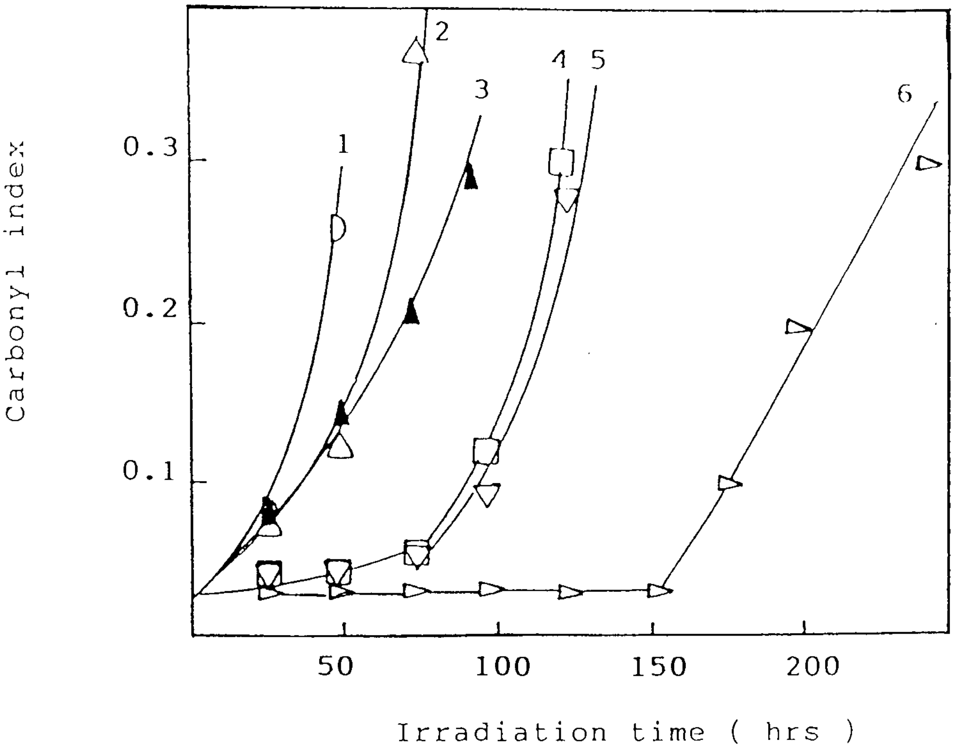


Fig. 4.23 Effect of varying the concentration of FeDNC on the photo-oxidation of unstabilised PP . Samples are diluted from 5% masterbatches processed at 160° C for 10 minutes. 1)0.05%, 2)0.01%, 3)PP control, 4)0.1%, 5)0.2% and 6)0.3%.

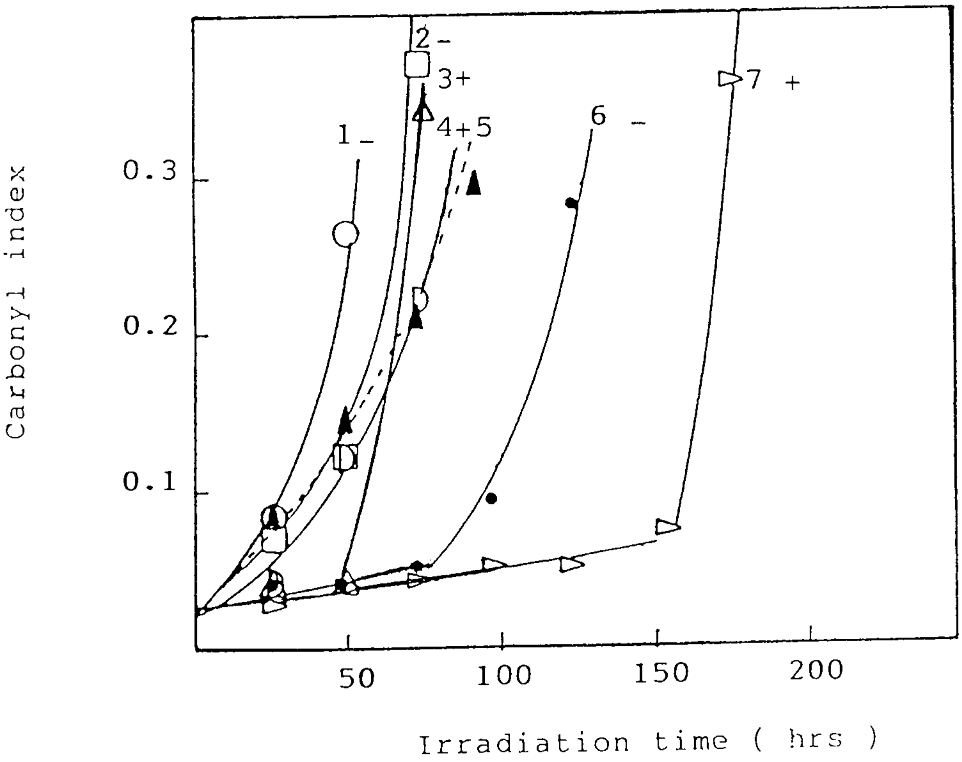


Fig. 4.24 Effect of FeDNC concentration on the photo-oxidation of unstabilised PP in the presence(+) and absence(-) of 0.001% NiDNC . Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes . 1) 0.05%(-), 2) 0.01%(-), 3) 0.05 %(+), 4) **0.01%(+)** 5) Control 6) 0.2%(-) and 7) 0.2%(+) .

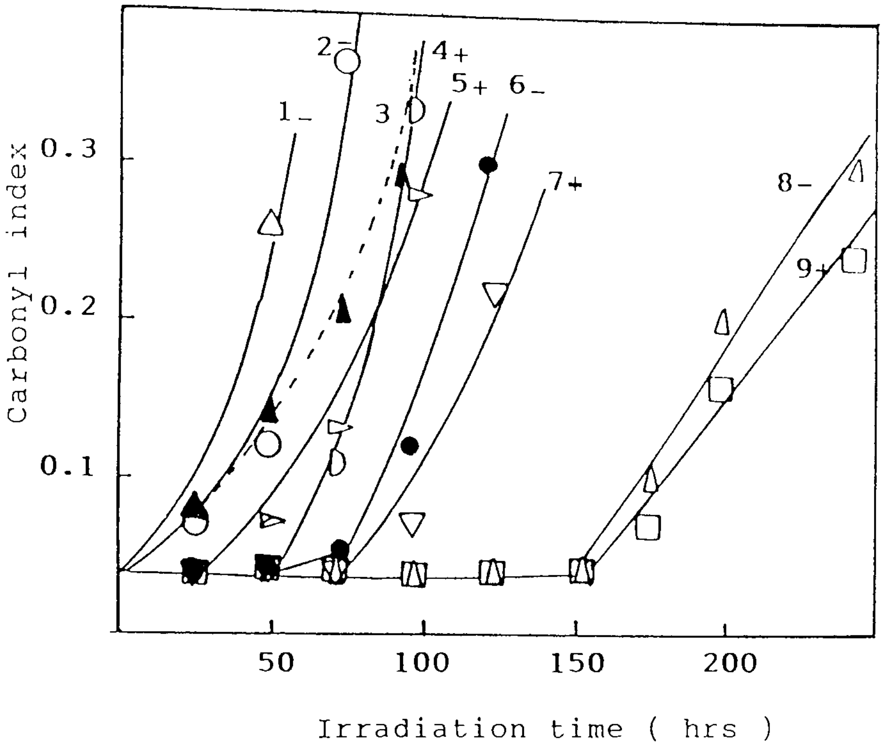


Fig. 4.25 Effect of FeDNC concentration on the photo-oxidation of unstabilised PP in the presence(+) and absence(-) of 0.005% NiDNC. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes. 1) 0.05%(-), 2) 0.01%(-), 3) control, 4) 0.05%(+), 5) 0.01%(+), 6) 0.1%(-), 7) 0.1%(+), 8) 0.3%(-) and 9) 0.3%(+).

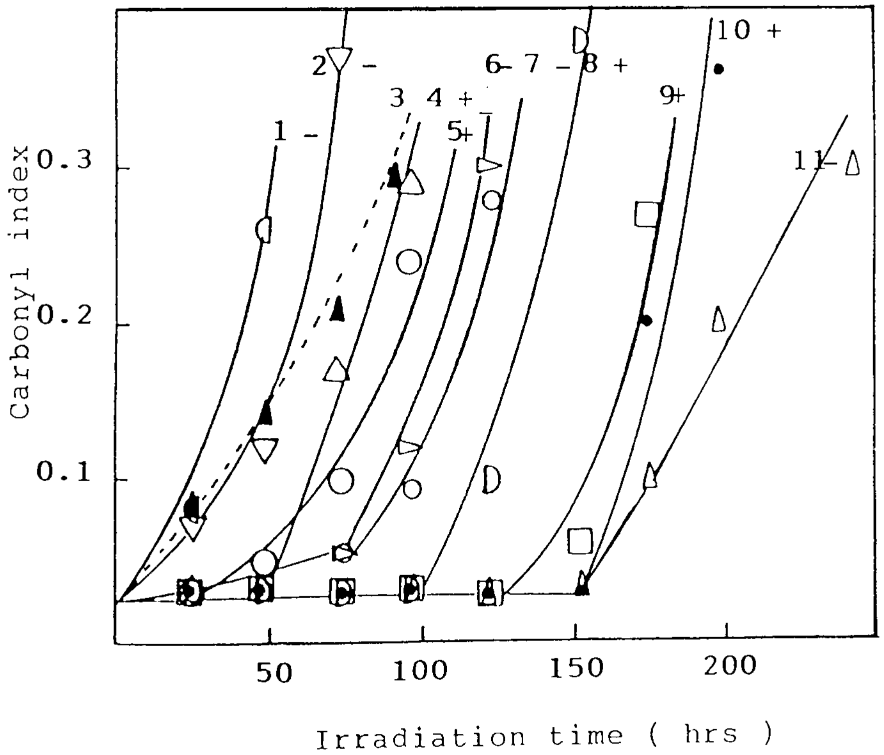


Fig.4.26 Effect of FeDNC concentration on the photo-oxidation of unstabilised PP in the presence(+) and absence(-) of 0.01% NiDNC. Samples are diluted from 5% masterbatches processed at 160°C for 10 minutes. 1) 0.05%(-), 2) 0.01(-), 3) control, 4) 0.05%(+), 5) 0.01%(+), 6) 0.1(-), 7) 0.2(-), 8) 0.1(+), 9) 0.2%(+) 10) 0.3%(+) and 11) 0.3(-).

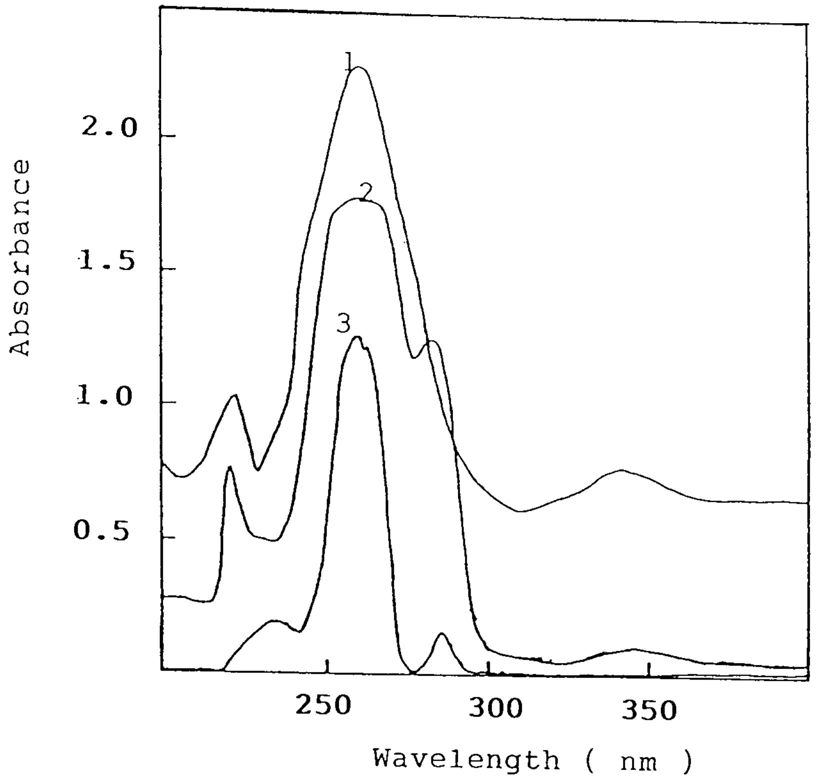


Fig. 4.27 UV-spectra of 1) FeDNC in methyl cyclohexane (4.5 X 10^{-5} mole/litre), 2) FeAc + ZnDEC (0.2% + 0.2%) in methyl cyclohexane after refluxing for 1 hour and 3) ZnDEC in methyl cyclohexane (9.6 X 10^{-5} mole/litre).

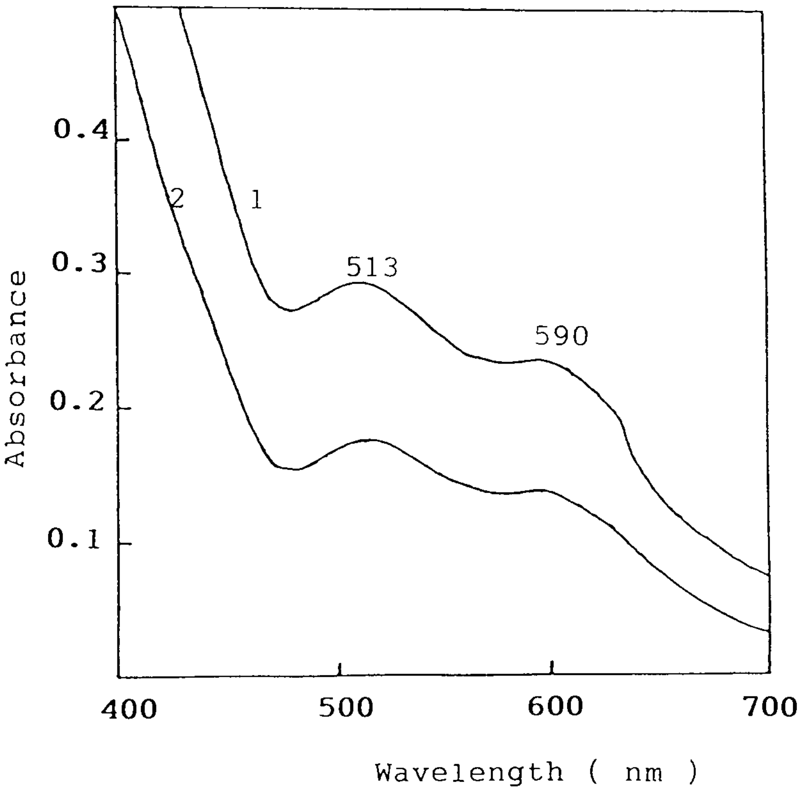


Fig. 4.28 Visible spectra of 1) FeDNC in methyl cyclohexane (4.5 X 10^{-5} mole/litre) and 2) FeAc + ZnDEC (0.2% + 0.2%) in methyl cyclohexane after reaction.

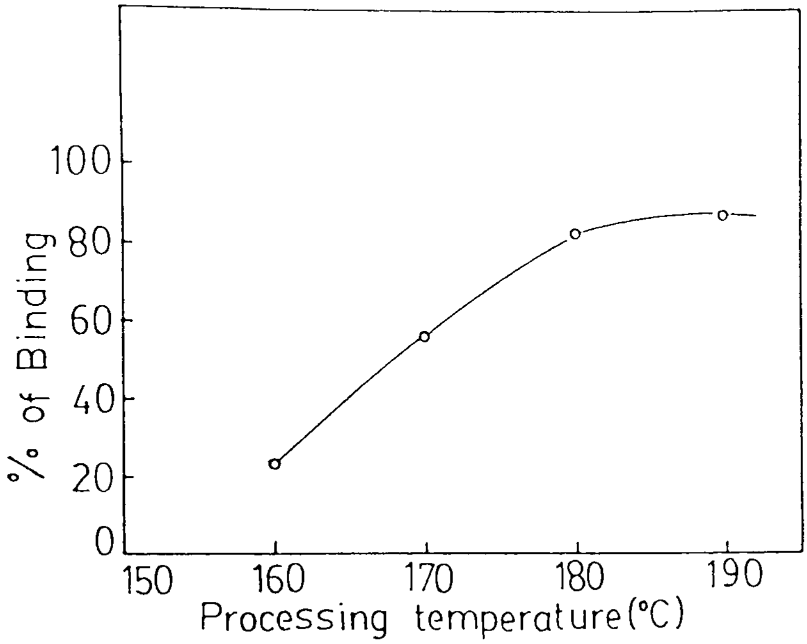


Fig. 4.29 Effect of processing temperature on binding of HAEB (10% MB) in PP, using initiator with (I/A_o)-molar ratio = 0.0025(DCP).

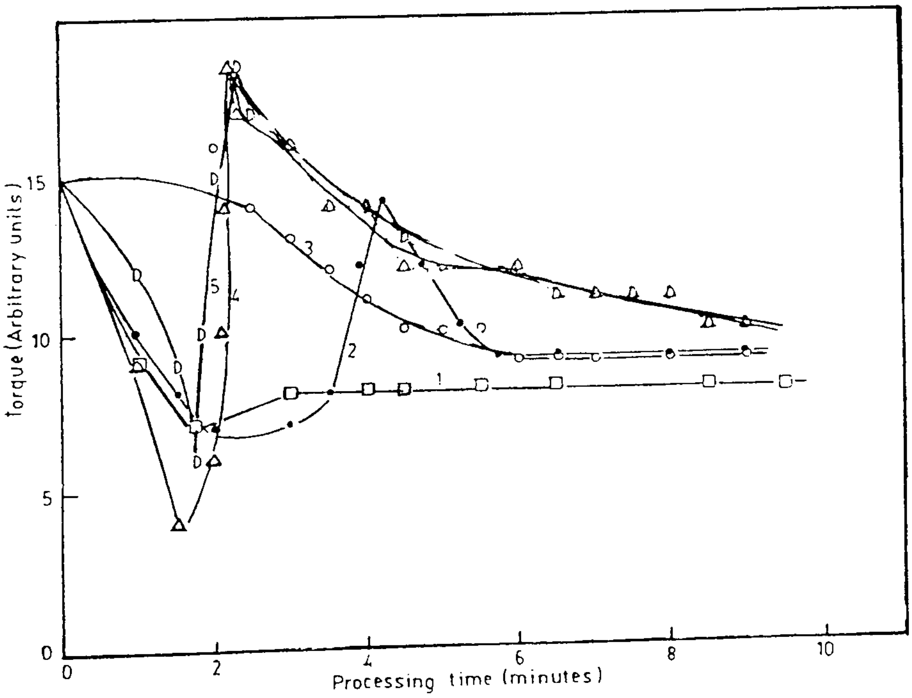


Fig. 4.30 Effect of HAEB concentration in PP on torque during processing at 180°C, using DCP at molar ratio of DCP/HAEB = 0.0025. (1) 10% MB without peroxide, (2) 10% MB with peroxide, (3) 5% MB with peroxide, (4) 20% MB with peroxide and (5) 15% MB with peroxide.

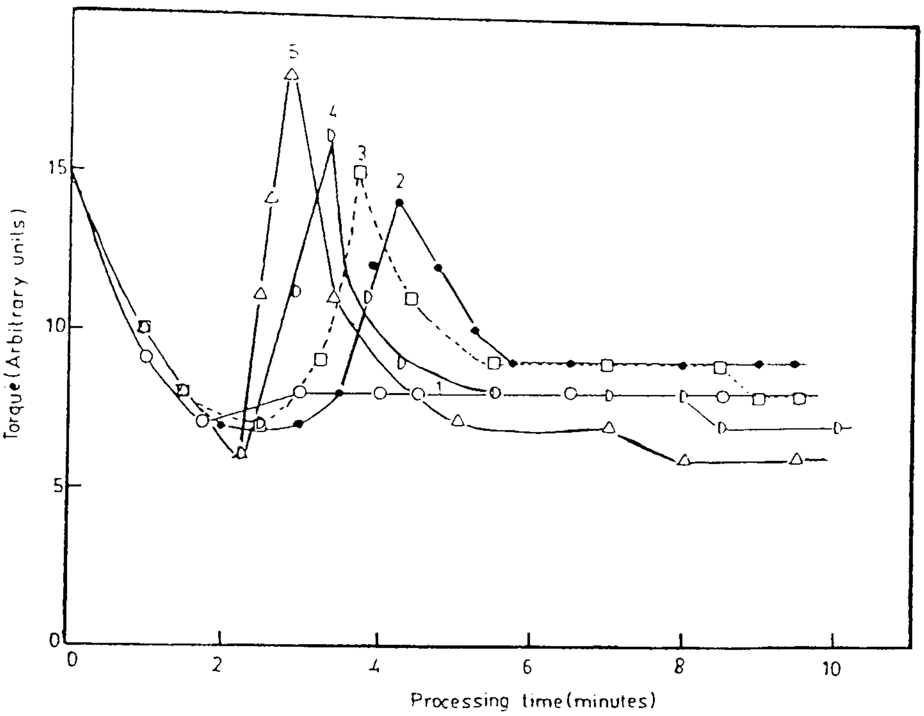


Fig. 4.31 Effect of radical generator concentration (DCP) on torque for 10% HAEB in polypropylene at 180^oC. (1) without peroxide (2) 0.0025 (3) 0.005 (4) 0.01 (5) 0.02. Conc. are at molar ratio of I/A_o, where I = initiator and A_o = anti-oxidant.

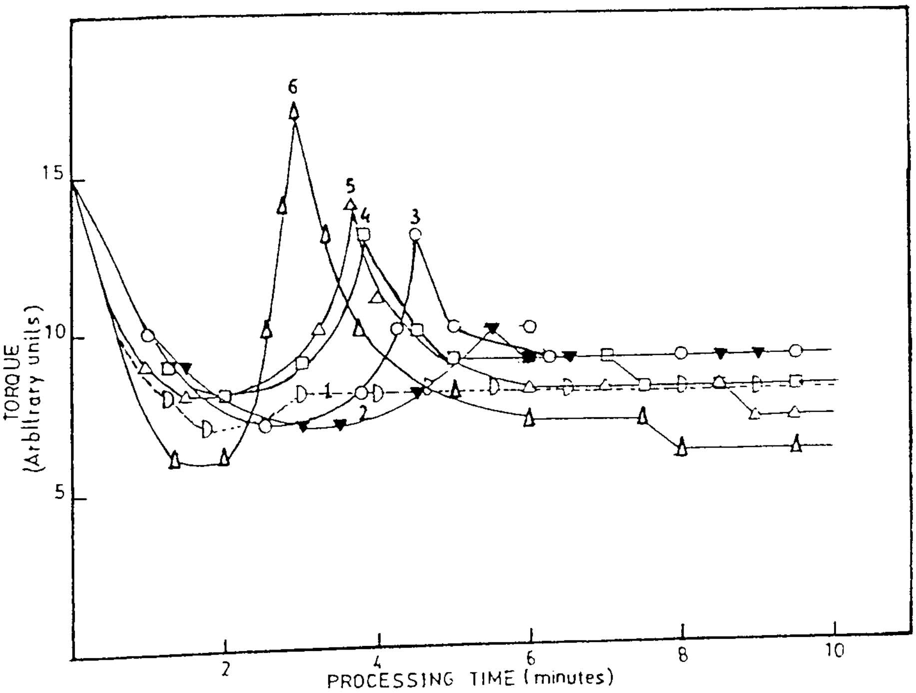


Fig. 4.32 Effect of radical generator concentration (Trigonox 101) on torque for 10% HAEB in polypropylene at 180^oC. (1) without peroxide (2) 0.0025 (3) 0.0035 (4) 0.005 (5) 0.0075 (6) 0.015 . Concentrations are at molar ratio of I/A_o, where I = initiator and A_o= anti-oxidant.

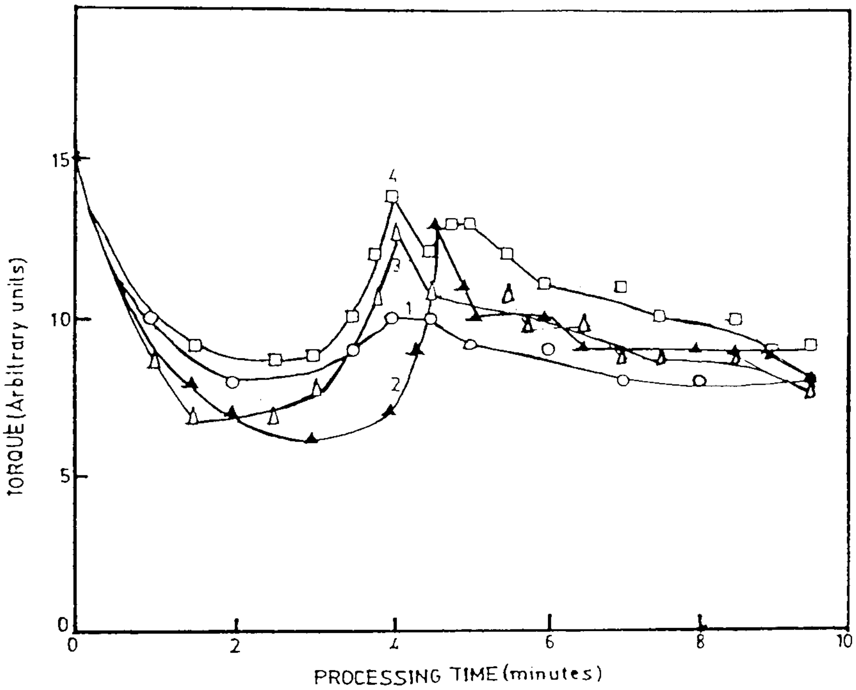


Fig. 4.33 Effect of TMPTA (TMPTA : HAEB = 1.5% : 8.5%) on torque for 10% HAEB in polypropylene at 180°C containing various molar ratios of peroxide (Trigonox 101). (1) TMPTA alone (2) 0.005 (3) 0.0025 (4) 0.0035.

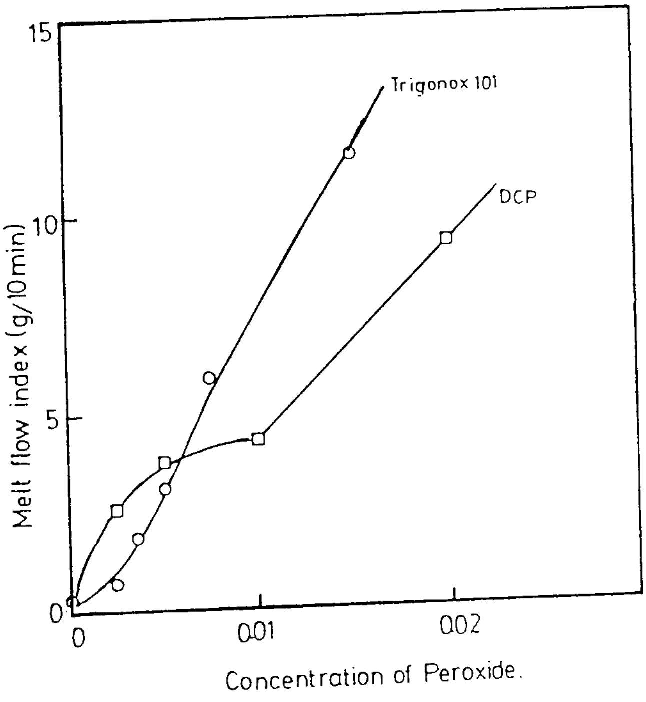


Fig. 4.34 Effect of peroxide concentration (molar ratio) on melt flow index changes of 10% MB's of HAEB in polypropylene (no interlinking agent).

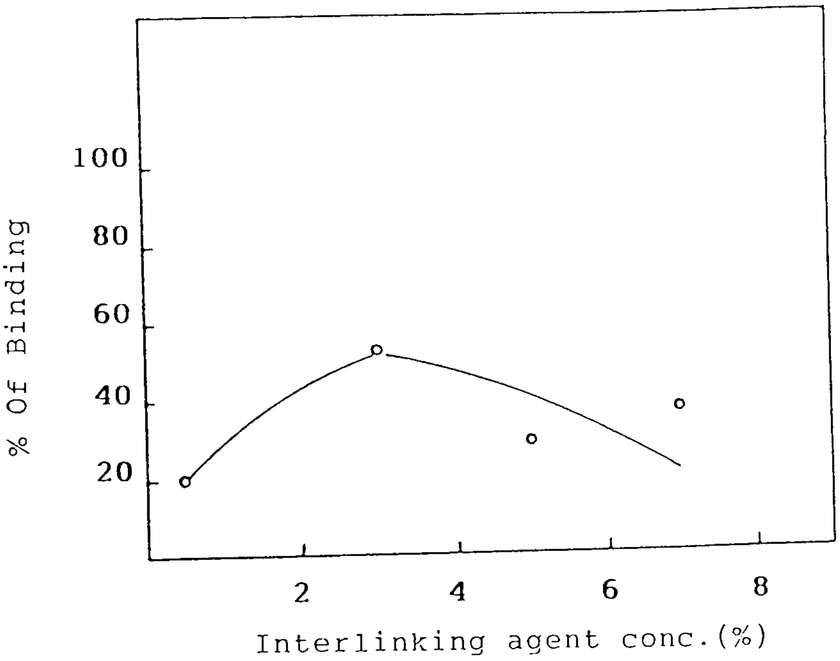


Fig. 4.35 Effect of interlinking agent (TMPTA) concentration (%) on binding of HAEB in polypropylene at 180°C (no peroxide).

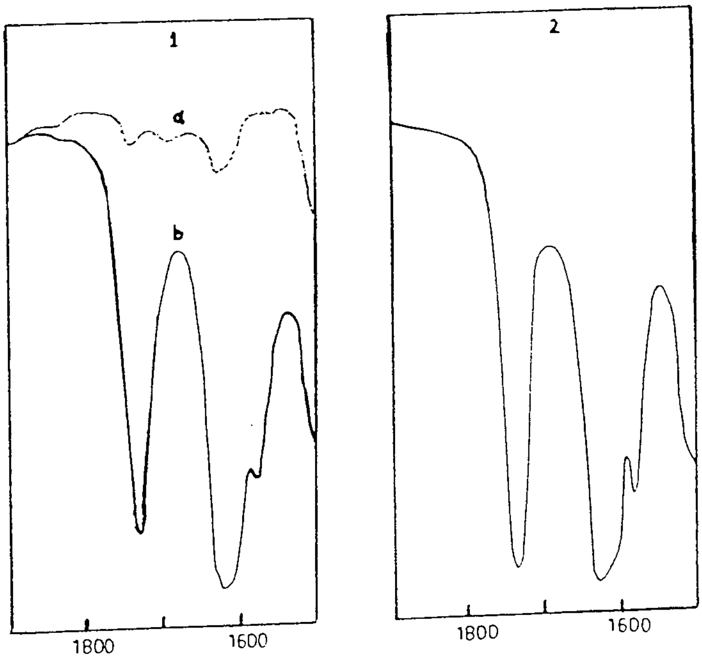


Fig. 4.36 A segment of infra-red spectrum of 10% HAEB in PP. (1) Processed without peroxide (b) before extraction (a) after extraction (2) Processed with peroxide of 0.003 molar ratio (DCP) and 1% interlinking agent at 180°C (before extraction and after extraction).

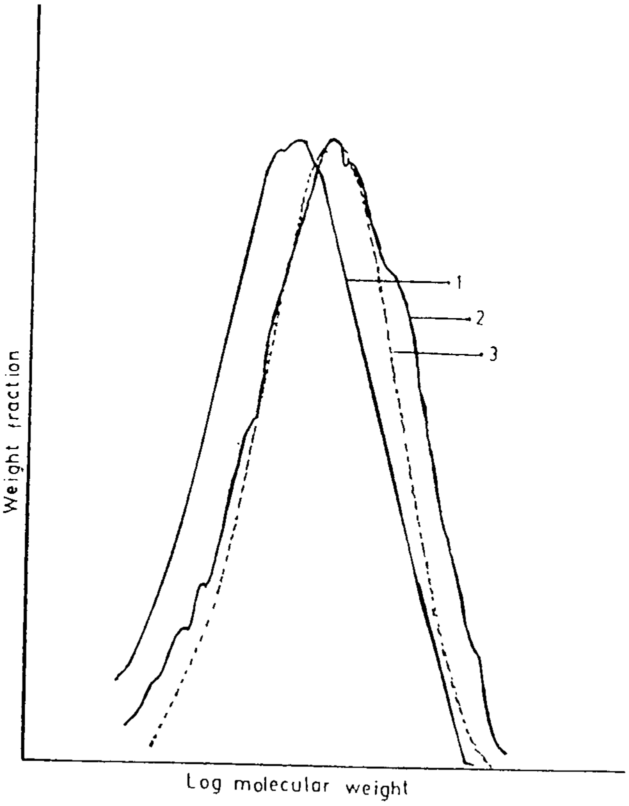


Fig. 4.37 Molecular weight distribution of polypropylene masterbatches containing 10% HAEB with and without peroxide (DCP) processed at 180°C. (1) Polypropylene without peroxide (2) 10% HAEB without peroxide (3) 10% HAEB with (I/A_o)-molar ratio = 0.0025 of DCP.

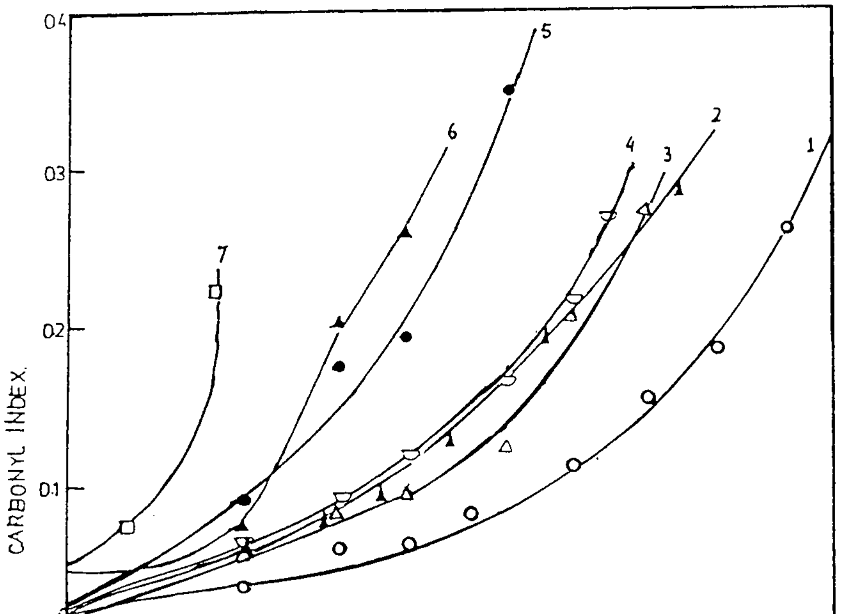


Fig. 4.38 Effect of (0.2%) HAEB on photo-oxidation of polypropylene containing various concentration of peroxide (Trigonox 101) processed at 180°C. (1) 0.0025 (2) TMPTA(1.5%) alone (3) 0.0035 (4) No peroxide (5) 0.005 (6) 0.0075 (7) PP control, samples are diluted from 10% MB's.

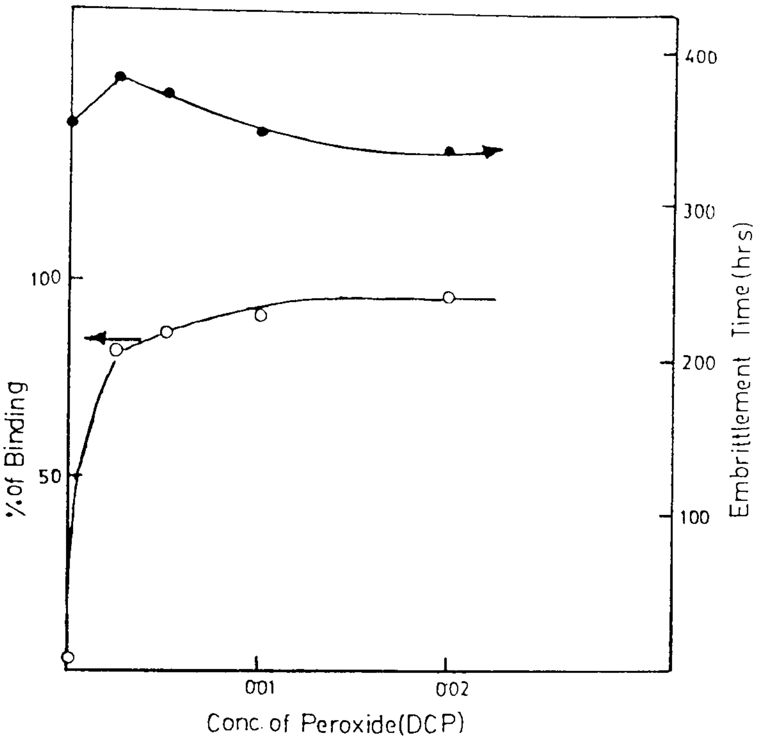


Fig. 4.39 Effect of peroxide concentration (molar ratio) on binding of 10% MB's of HAEB in polypropylene processed at 180°C and on embrittlement time of diluted masterbatches(0.2%).

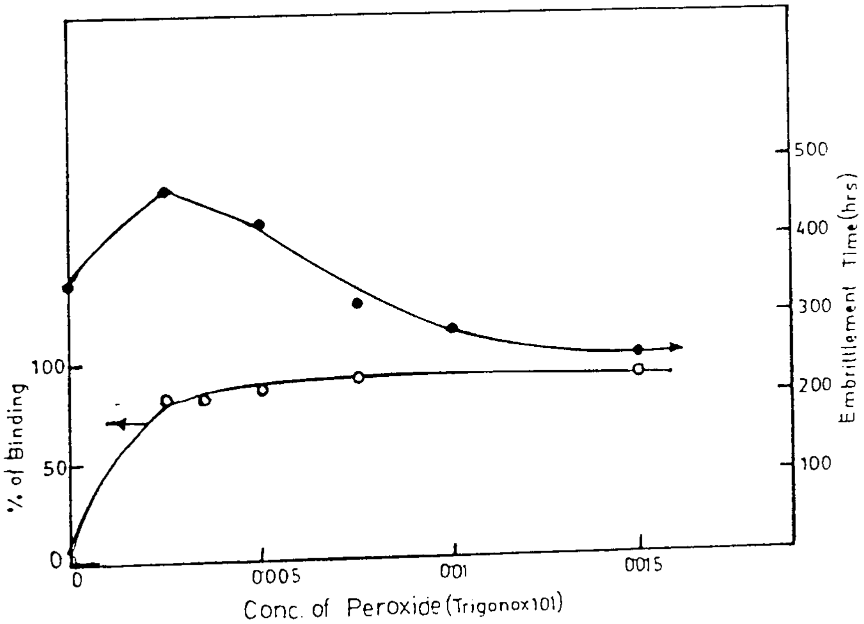


Fig. 4.40 Effect of peroxide concentration on binding of 10% HAEB in polypropylene processed at 180°C and on embrittlement time of diluted masterbatches (0.2%).

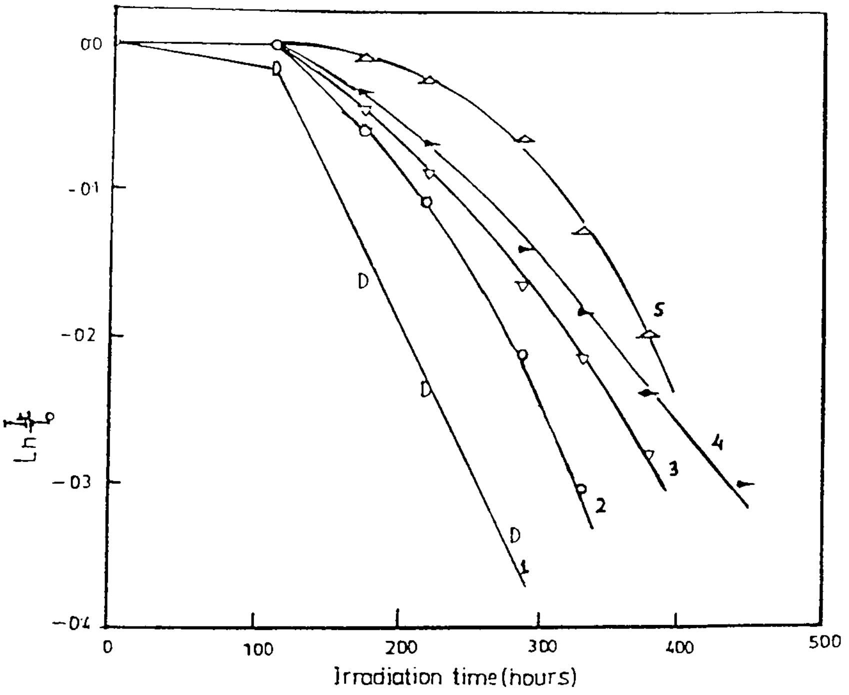


Fig. 4.41 Change in uv absorption spectrum (λ_{max} = 330 nm) of HAEB during the photo-oxidation of PP (conc. of additive = 0.2%). (Trigonox 101 was used as peroxide) (1)Without peroxide (2) 0.0075 (3) 0.005 (4) 0.0035 (5) 0.0025.

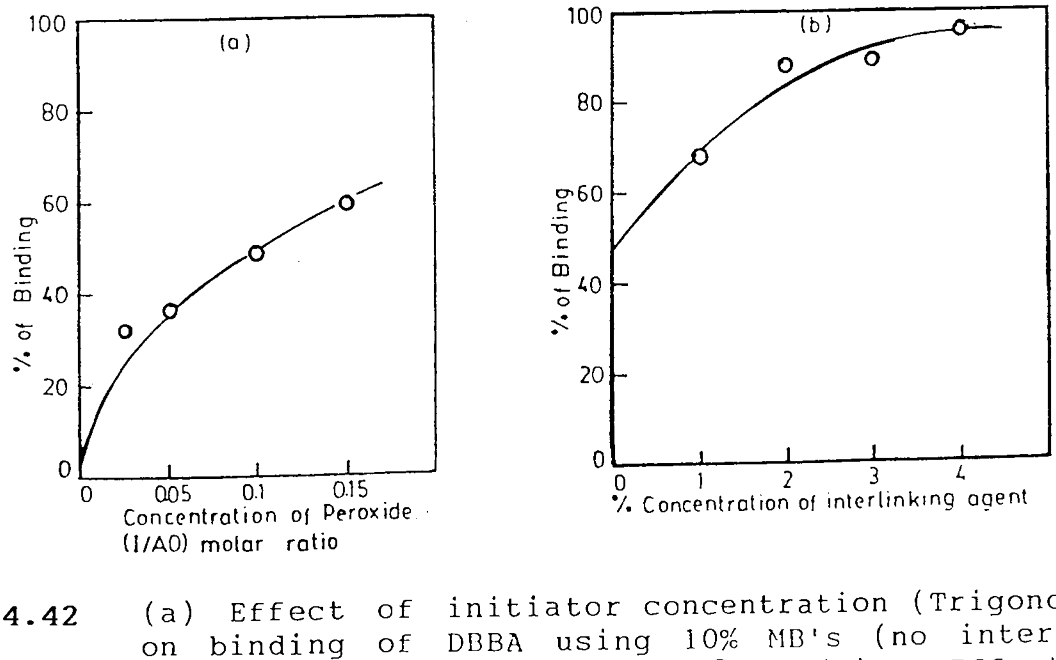


Fig. 4.42 (a) Effect of initiator concentration (Trigonox 101) on binding of DBBA using 10% MB's (no interlinking agent) in PP processed at 180°C. (b) Effect of interlinking agent concentration on binding of DBBA in PP using 0.1 molar ratio of initiator concentration (Trigonox 101) at 10% MB's.

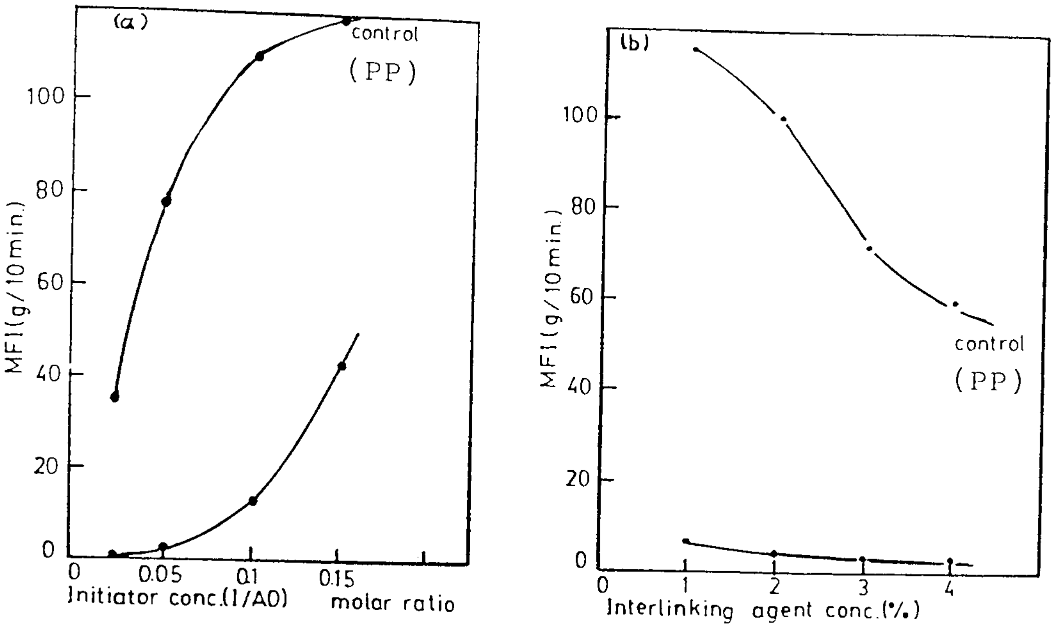


Fig. 4.43 (a)Effect of initiator concentration (Trigonox 101) on melt stability of polypropylene processed at 180°C in absence and presence of DBBA. **(b)** Effect of interlinking agent concentration at constant peroxide concentration (0.1 molar ratio) on melt stability of polypropylene processed at 180°C in absence and presence of DBBA. 10% MB's were used in both cases.

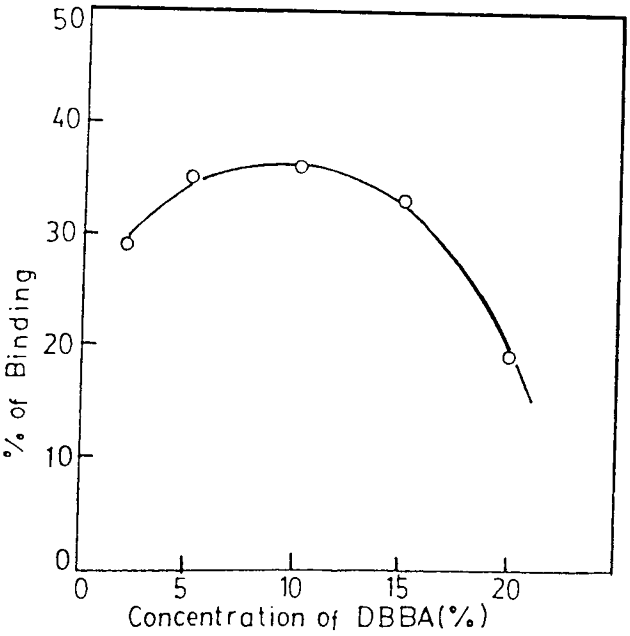


Fig. 4.44 Effect of DBBA concentration on binding using constant concentration of peroxide (Trigonox 101) with (I/A_0)-molar ratio = 0.05 in PP processed at 180°C.

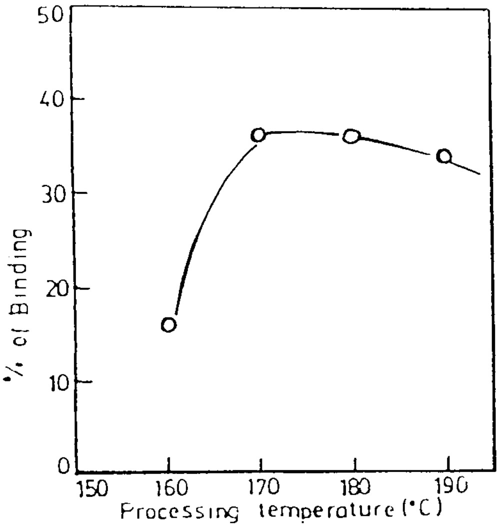


Figure- 4.45

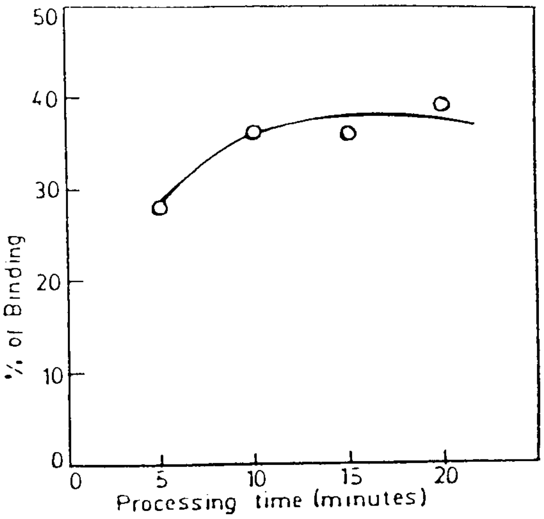


Figure- 4.46

Fig. 4.45 Effect of processing temperature on binding of DBBA (10% MB) in PP using initiator with (I/A_o)-molar ratio = 0.05 (Trigonox 101).

Fig. 4.46 Effect of processing time on binding of DBBA in PP, using constant concentration of peroxide (Trigonox 101) with (I/A_o)-molar ratio = 0.05 processed at 180°C.

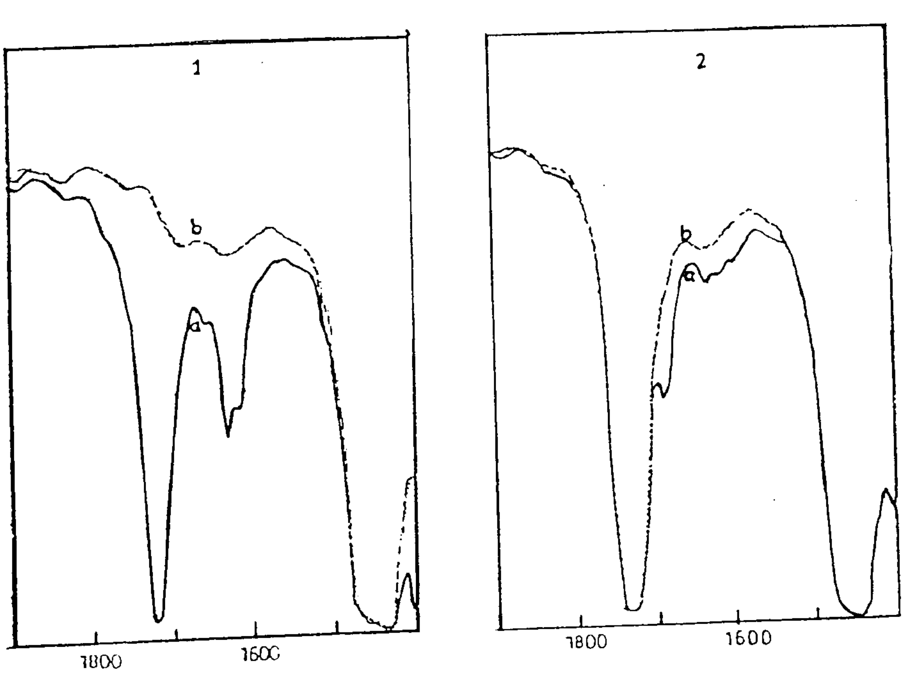


Fig. 4.47 A segment of infra-red spectrum of 10% DBBA in PP (1) processed without peroxide; (a) before extraction (b) after extraction (2) processed with peroxide of molar ratio = 0.2 (DCP) and interlinking agent = 4%; (a) before extraction (b) after extraction.

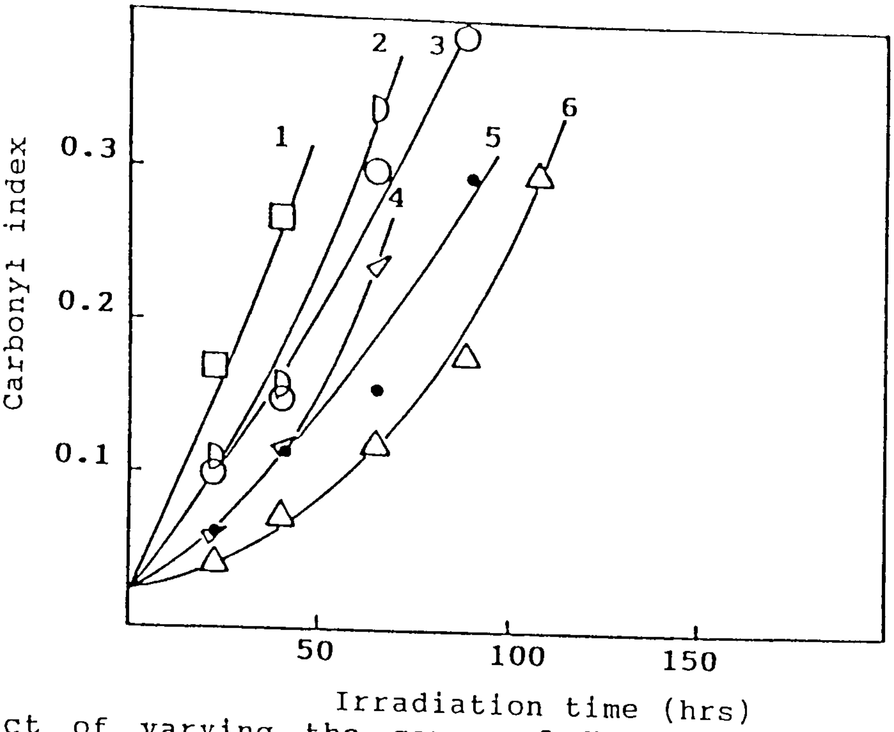


Fig. 4.48 Effect of varying the conc. of HAEB and Fe-acrylate on the photo-oxidation of PP processed at 180°C for 10 mins. in closed chamber. 1) HAEB + Fe-acrylate(0.025% + 0.075%), 2) HAEB + Fe-acrylate(0.05% + 0.05%), 3) HAEB + Fe-acrylate (0.075% + 0.025%), 4) Fe-acrylate (0.1%), 5) PP control and 6) HAEB(0.1%).

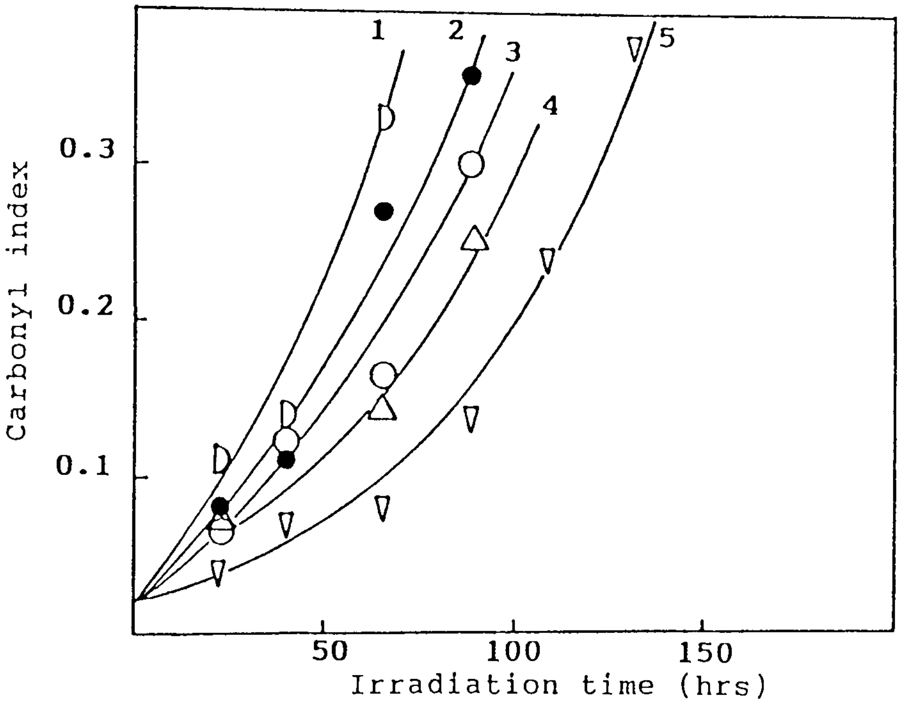


Fig.4.49 Effect of varying the conc. of DBBA and Fe-acrylate on the photo-oxidation of PP processed at 180°C for 10 mins. in closed chamber. 1) DBBA + Fe-acrylate(0.0125% + 0.0375%), 2) DBBA + Fe-acrylate(0.025% + 0.025%), 3) PP control, 4) DBBA + Fe-acrylate(0.0375% + 0.0125%) and 5) DBBA(0.05%).

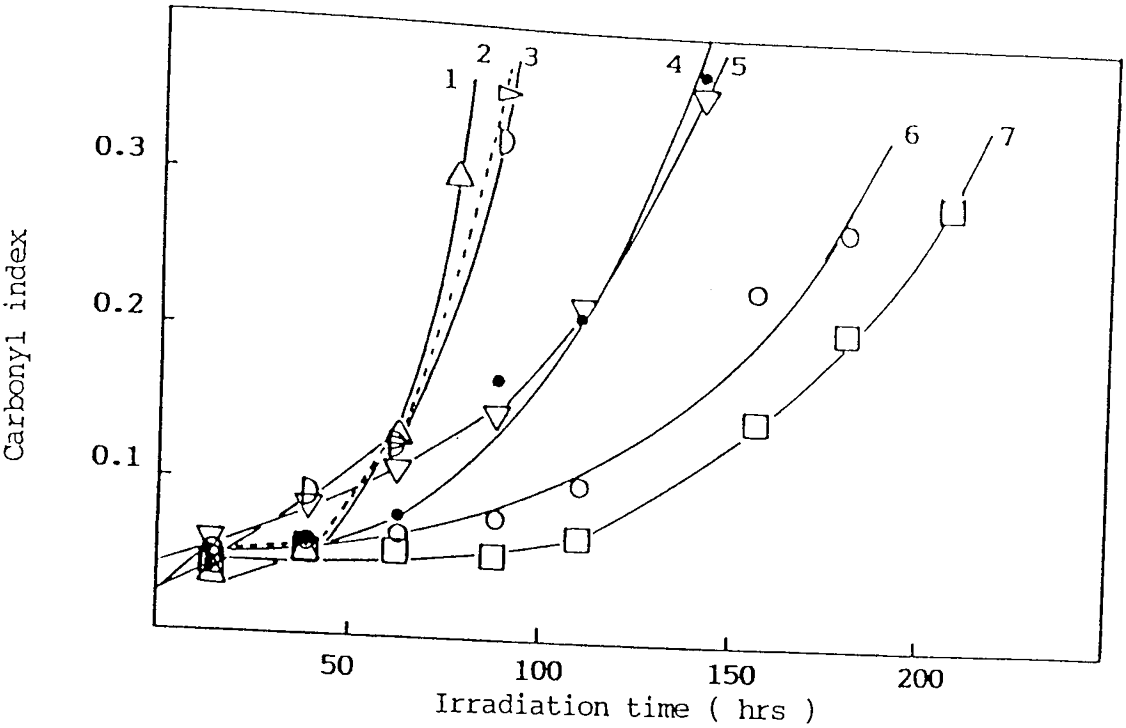


Fig. 4.50 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial PP (1) FeDNC(0.05%) (2) FeDNC + Metone M(0.05% + 0.05%) (3) FeDMC (0.05%) (4) Metone M + ZnDNC (0.05% + 0.05%) (5) ZnDNC (0.05%) (6) Control (7) Metone M (0.05%).

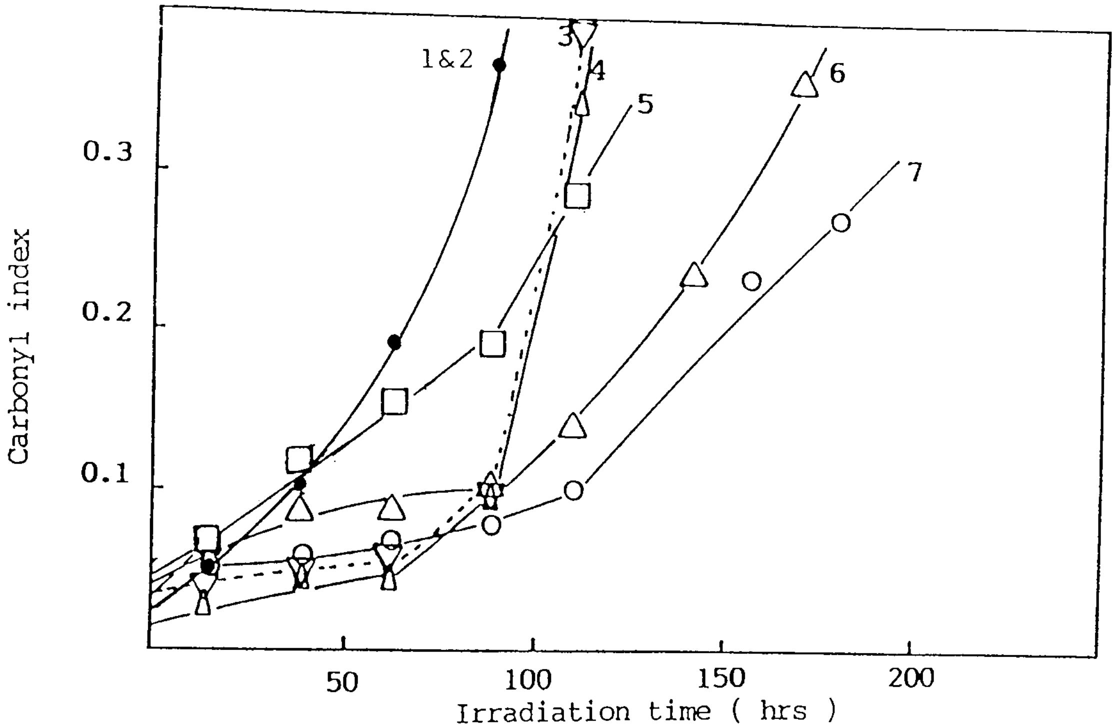


Fig. 4.51 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial PP (1) Fe-acrylate (0.05%) (2) Fe-acrylate + ZnDNC (0.05% + 0.05%) (3) Fe-thioacetate + ZnDNC (0.05% + 0.05%) (4) Fe-thioacetate (0.05%) (5) Fe-thiopropionate + ZnDNC (0.05% + 0.05%) (6) Fe-thiopropionate (0.05%) (7) Control.

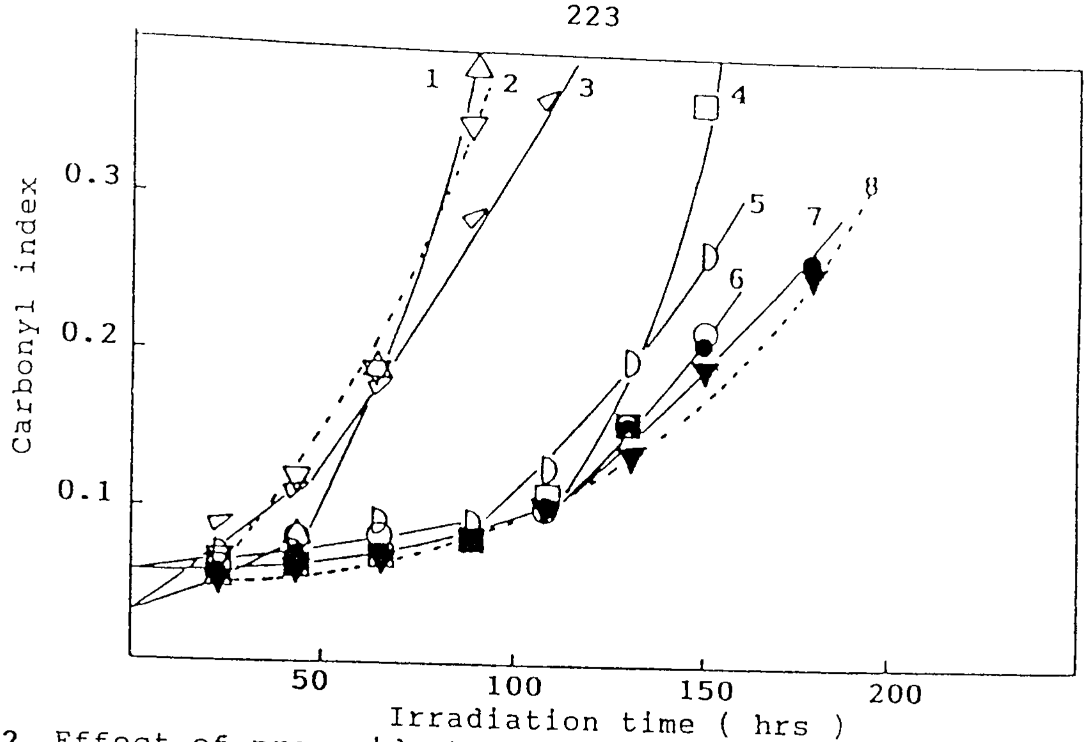


Fig. 4.52 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial PP 1) Metone A + Fe-DNC(0.025% + 0.075%), 2) Metone A + Fe-DNC(0.05% + 0.05%) 3) Metone A + Fe-DNC(0.075% + 0.025%), 4) ZnDNC(0.1%) 5) Metone A(0.05%), 6) Metone A(0.1%), 7) Metone A + ZnDNC(0.05% + 0.05%) and 8) Commercial PP control.

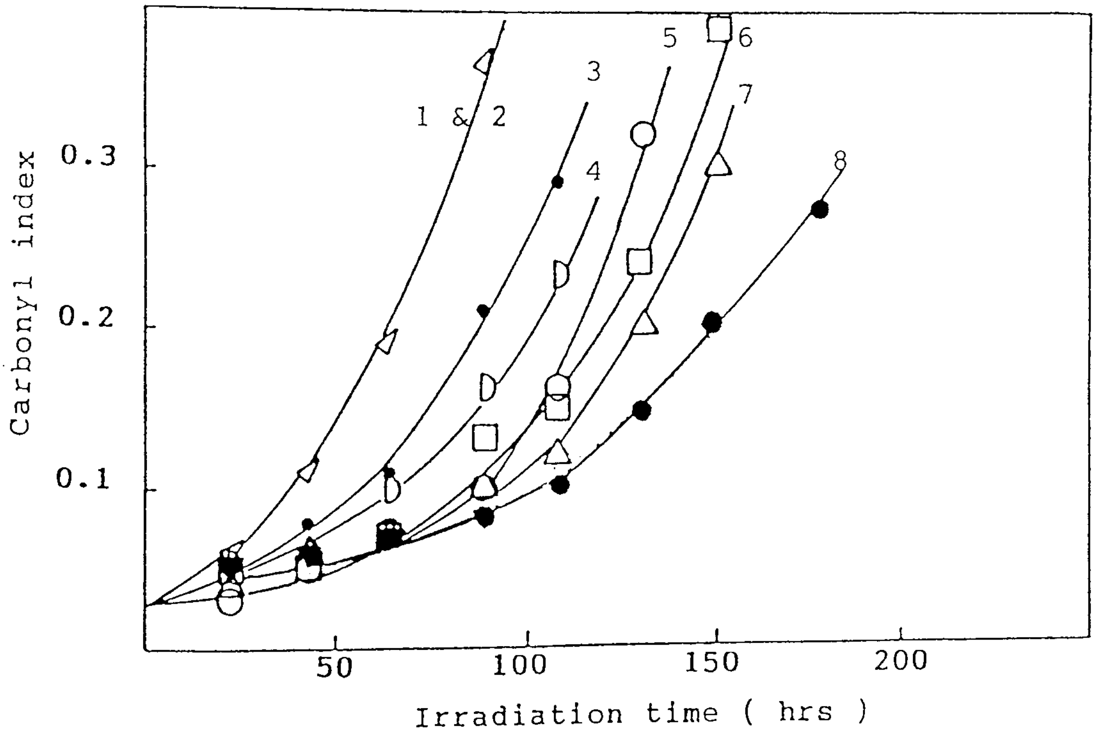


Fig. 4.53 Effect of pro-oxidant alone and in combination with antioxidant on the photo-oxidation of commercial PP 1)Fe-acrylate + ZnDNC(0.05% + 0.05%), 2)Fe-acrylate + ZnDNC(0.025% + 0.0375%), 5)Fe-acrylate(0.1%), 4)Metone M + FeDNC (0.0125% + 0. 075%), 5) Metone M + FeDNC (0.025% + 0.025%), 6)Metone M + ZnDNC(0.025% + 0.025%), 7) Metone M (0.1%) and 8) commercial PP control.

Chapter Five

General Conclusions and Suggestions for Further work

5.1 General Conclusions

1. Different iron compounds containing polymer reactive groups have been synthesised. Sulphur containing iron compounds were used to achieve a maximum stability effect in the polymer melt.
2. Methods of attaching those iron containing compounds to the polymer backbone were established. Two compounds FeTp and FeTa (soluble) were successfully bound to unstabilised LDPE using an initiator and an interlinking agent. Bound pro-oxidant (FeAc and FeTp) showed a photoactivating behaviour which increased further after extraction.
3. The melt stability of the compounds used were compared. FeDMC and FeTp were found to be the most effective melt stabilisers and offer good thermal stability. These behaviours are also reflected in their UV activity of unstabilised LDPE containing these photoactivator when they are severely processed.
4. An antioxidant photoactivator (FeDNC) was found to sensitise a pro-oxidant (Metone A / Metone M) whereas an antioxidant (ZnDNC) was shown to extend the stability of the unstabilised LDPE compared to Metone A or Metone M alone.
5. Lower concentrations of an antioxidant photoactivator (FeDNC) were shown to sensitise an antioxidant photostabiliser (NiDNC) in unstabilised LDPE whereas higher concentrations stabilise, compared to FeDNC alone.
6. An antioxidant (ZnDNC) was shown to antagonise photolytically with the phenolic antioxidant present in the commercial polymer (both in LDPE and PP).

7. The mechanical property changes of these samples were found to occur after an induction period. At the end of their useful lifetime (under uv exposure condition) the samples were found to disintegrate into pieces which is very important in the case of mulching film.

8. Some ligand exchange reaction takes place between the antioxidant (ZnDEC) and the pro - oxidant (FeAc). Both the induction period and the stability of the polymer can be changed by changing the concentration of the antioxidant (in unstabilised PP).

9. The combination of an antioxidant (NiDNC) with an antioxidant photoactivator (FeDNC) was found to stabilise the unstabilised PP.

10. The combination of a bound photostabiliser (HAEB) and a thermal antioxidant (DBBA) with a pro - oxidant (FeAc) were found to sensitise the polymer (unstabilised PP) at the lower concentration of the antioxidant, whereas higher concentrations of antioxidant were shown to induce stability.

5.2 Suggestions for further work

1. FeTa , FeMa , FeCr and FeCi were found to be insoluble in all organic solvents. However , they are found to be soluble in dimethyl sulfoxide on standing overnight. By modifying the original synthetic procedure an organosoluble FeAc was prepared. By following the same procedure more soluble FeCr and FeCi may be possible to be prepared. However , the organosoluble compound of FeMa was found to be unstable during high temperature processing because the absorption due to carboxylate of FeMa was not present in the processed polymer. A modified procedure to synthesise the organosoluble FeMa is therefore required. FeTa was precipitated from a cold solution of sodium thioacetate and ferric chloride

yet it was found to be insoluble in different solvents . A modified procedure to synthesise this compound is also required .

2 . Both FeTp and FeAc were found to be bound to LDPE . However , the binding conditions have to be optimised . Different types of peroxide and interlinking agent could be used to find the suitable condition of binding . Also more work is needed to find the 100% bound compound in the polymer backbone .

3 . In case of FeAc (insoluble) , it was found that with the use of peroxide an additional peak appears which is most likely due to the formation of polyacrylic acid . Similar peak was also observed in case of FeAc (soluble) and this needs to be identified .

4 . The conventional reaction of the compound in model substrates e . g . methyl cyclohexane , dodecane have to be carried out with and without peroxide in case of both FeTp and FeAc (soluble) to clarify the mechanism of binding .

5 . All the compounds were tested under laboratory irradiation conditions . For practical purpuses , a systematic study on the performance of these systems under outdoor conditions should be undertaken .

6 . It is believed that iron carboxylate are responsible for the rapid oxidation of the polymer containing photoactivators . To support this mechanism some chemical evidence is needed .

References

(1) G. Scott , Int . J . Environ . Studies , **3** , 35 (1972) , **7** , 131 (1975) .

(2) J . E . Guillet , Plast . Eng ., **20** , 48 (1974) .

(3) G. Scott , Waste Disposal (B1M) , **5** , 78 (1971) .

(4) G. Scott , Plast . Rubb . Text **1** , 361 (1970) .

(5) G . Scott , Packaging Technology , **18** , 14 (1972) .

(6) G . Scott in Plastics Forming , Ed Beadle , Mc Millan Engineering Evaluations , P 161(1972) .

(7) G. Scott , Design Engineering 77 , Oct (1972) .

(8) G . Scott in Polymers and Ecological Problems , Ed . J . Guillet , Plenum Pub . Corp ., P 27 (1973).

(9) G . Scott , J . Oil . Col . Chem . Assoc. **56** , 521 (1973) .

(10) G . Scott , Australian Plast . and Rubb . , **24** (10) , 53 (1973) .

(11) Plastic Institute Conference on Degradability of Polymers and Plastics , London (1973) .

(12) G , Scott , Royal Soc . of Arts J , **122** , 188 (1974) .

(13) B . Baum and R . D . Deanin , Polym . Plas . Tech . Eng . , **2** , 1(1973)

(14) D . Gilead , Int . J .Polym. Mat . , **6** , 185 (1978) .

(15) G . Scott , J .of Polymer . Sci . Polymer Symposium **57** , 357 (1976) .

(16) G . Scott , Polymer News , **14** , 169 (1989) .

(17) W . M . Stall , H . H . Bryan and P . H . Everett , Proc . Int . Agr . Plast . Congress (1977) .

(18) G . Scott and D . Gilead , " Developments in Polymer Stabilisation - 5 " Chapter - 4 (1982) . Applied Science Publisher Ltd . , London .

(19) Ph.D. Thesis, E . Setoudeh . A Techno-economic study of the recycling of mixed plastics to useful products . Aston University, U. K.1981 .

(20) D. Gilead , Plasticulture , No **43** , 31 (1979) .

(21) H . O . W . Eggins , J . Mills , A Holt and G . Scott , Biodeterioration and Biodegradation of Synthetic Polymers , Chapter in Microbial aspects of Pollution , Ed. Sykes and Skinner P 267 (1972) , Academic Press .

(22) G . Scott , S . Afr . J . chem . **32** , 137 (1979) .

(23) K . B . Chakraborty and G . Scott . Polymer , **18** , 98 (1977) .

(24) M . U . Amin , G . Scott and L . M . K . Tillekeratne , Eur . Polym . J . **11** , 85 (1975) .

(25) C . Sadrmohaghegh and G . Scott , Polym . Deg . and Stab ., **3** , 333 (1981)

(26) Z . Osawa , " Developments in Polymer Photochemistry - 3 " (1982) .

(27) Japanese Synthetic Rubber Co . , Chem . Eng . News , P . 29 , 29th Nov (1971) .

(28) Princeton Chemical Research , Chem . Week , P 44 , 16 th Feb (1972).

(29) Princeton Chemical Research , U.S. Patent 3 , 590 , 528 , July (1971) .

(30) Carvert and Pitts , Photochemistry , John Wiley and Sons , Chapter - 4 , P 350 (1966) .

(31) A . W . Pross and R . M . Black , J . S . C. I. , **69** , 113 (1950) .

(32) C . H . Bamford and R .G.W. Norrish , J .Chem . Soc. , 1504 (1935) .

(33) G . H . Hartley and J . E . Guillet , Macromolecules , **1** , 165 (1968) .

(34) Y . Amerik and J .E . Guillet , Macromolecules , **4** , 375 (1971) .

(35) J .E . Guillet , Naturwissenschaften , **59** , 503 (1972) .

(36) D . J . Harper and J . F . Mckellar , J . Appl . Polym . Sci . **17** , 3503 (1973) .

(37) G. A . George and D.K.C. Hodgeman, Eur . Polym . J., **13** , 63(1977).

(38) T . Mill , K . C. Irwin and F . R . Mayo , Rubb . Chem . Tech . , **41** , 296 (1960) .

(39) M . U . Amin and G . Scott , Eur . Polym . J . , **10** , 1019 (1974) .

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

(41) L . J . Taylor and J . W . Tobias , J . Appl . Poly . Sci . , **21** , 1273 (1977).

(42) J . M . Bruce , Chemical Society ,quart .rev., **21** , 405 (1967) .

(43) F . Haber and J . Weiss , Proc . Roy . Soc . , **A** , **147** , 332 (1934) .

(44) J . H . Baxendale *et al* , Trans . Farad . Soc . , **42** , 155 (1946) .

(45) M . G . Evans , M . Santappa and N . Uri , J . Poly . Sci . , **7** , 243 (1951) .

(46) B . Ranby and J . F. Rabek , " Photodegradation , Photo - oxidation and Photostabilisation of Polymers " Weley , London P. 292 (1975) .

(47) D . C . Mellor , A . B . Moir and G . Scott , Eur . Polym . J . , **9** , 219 (1973) .

(48) G . Scott , Macromolecular Chem . , **8** , 319 (1972) .

(49) E . L . Chew and Z . Osawa , J . Poly . Sci . , **19** , 2947 (1975) .

(50) A . Negishi , Y . Ogiwara and Z . Osawa , J . Appl . Poly . Sci ., **22** , 2953 (1978) .

(51) Eastman Kodak Co . , US Patent **3** , 454 , 510 (1969) .

(52) K .B . Chakraborty and G . Scott , Eur . Poly . J . , **13** , 1007 (1977).

(53) K . B . Chakraborty and G . Scott , Polym . Deg . and Stab . **1** , 37 (1979) .

(54) R . P . R . Ranaweera and G . Scott , Poly. Sci . Polym . Lett . Ed . **13** , 71 (1975)

(55) G . Scott , H . H . Sheena and A . M . Harriman , Eur . Poly . J . , **14** , 1071 (1978) .

(56) S . Al - Malaika , A . M . Marogi and G . Scott , Polymer Deg .and Stab . , **18** , 89 (1987) .

(57) S . Al - Malaika , A . M . Marogi and G . Scott , J . App . Poly . Sci ., **31** , 685 (1986) .

(58) D . Gilead and G .Scott , British Patent 22099 / 78 .

(59) D . Gilead and G . Scott , British Patent Application GB 2 187 193 A (1987) .

(60) G. Scott , " Atmosphearic Oxidation and Antioxidants " , Chapter - 1 , Elsevier Publishing Company , Amsterdam , (1965).

(61) S . Al - Malaika and G , Scott , " Degradation and Stabilisation of Polyolefins,Chapter - 7 , N . S . Allen (Ed .) Applied Science Publishers London , (1983).

(62) D . J . Carlsson and D . M . Wiles , Macromolecules , **2** , 587 (1969) .

(63) P . Vink , " Degradation and Stabilisation of Polyolefins " Chapter - 5 , N . S. Allen (Ed .) , App . Sci . Publisher , London , (1983) .

(64) J . L . Bolland, Quart . Rev . , Chemical Society , **3** , 1 (1949) .

(65) N . Grassie and G . Scott , " Polymer Degradation and Stabilisation " , Chapter - 5 , (1985). Cambridge University Press .

(66) G . Scott , Atmospheric Oxidation and Antioxidants " , P. 216 , (1965) . Elsevier Pub . Co . , Amsterdam .

(67) J . D. Holdsworth , G . Scott and D . Williams , J . Chem . Soc . , 4692 (1964) .

(68) G . Scott , "Development in Polymer Stabilisation - 4 ", Chapter - 1 , (1981) , Ed . by G . Scott . Applied Science Publishers Ltd .London .

(69) G . Scott , " Atmospheric Oxidation and Antioxidants " Chapter - 4 , (1965) . Elsevier , London and New York .

(70) G . Scott , J . of Pure and Appl . Chem . , **52** , 365 (1980).

(71) G . Scott and M. F. Yusoff , Eur . Poly . J . , **16** , 497 (1980) .

(72) E . T . Denisov , " Development in Polymer Stabilisation - 3 " , Ed . by G. Scott , Chapter -1 (1980) .

(73) A . Katbab and G . Scott , Chem .and Ind ., 573 (1980) .

(74) C . Armstrong , M . J . Husbands and G . Scott , Eurp .Polym . J ., **15** , 241 (1979) .

(75) F . A . A . Ingham , G . Scott and J . E . Stuckey , Eurp . Polym . J. **11** , 783 (1975) .

(76) R . P . R . Ranaweera and G . Scott , Chem and Ind . , 774 (1974) ; Eurp . Polym . J . , **12** , 591 , 825 (1976) .

(77) J . G . Pimblott , G . Scott and J . E . Stuckey and , J App .Polym . Sci ., **19** , 865 (1975) .

(78) S . Al - Malaika and G . Scott , Eur . Poly . J . , **16** , 709 (1980) .

(79) H . Dweik , Ph . D . Thesis , University of Aston , (1982) .

(80) M . J . Husbands and G . Scott , Eur . Poly . J ., **15** , 249 (1979) .

(81) M . J . Husbands and G . Scott , Eur Poly J , **15** , 879 (1979) .

(82) S . Al - Malaika , A . Marogi and G . Scott , J . Appl .Polym . Sci ., **30**, 789 (1985) .

(83) S . Al - Malaika , A . Marogi and G . Scott , Polym .Deg. and Stab ., **10** , 237(1985) .

(84) F . Gugumus , in Developments in Polymer Stabilisation - 1 , Ed . G . Scott (1979) , Chapter - 8 , P . 261 . Applied Science Publishers Ltd , London .

(85) A . R . Burgers , " Photodegradation mechanism , N . B . S . Circular **525** , P . 149 .

(86) P . J . Briggs and J . F . Mckellar , J . App . Polym . Sci . , **12** , 1825 (1968) .

(87) A . Adamczyk and F . Wilkinson , J . Chem . Soc . Farad . Trans II ,

68, 2031 (1972) ; J . App . Poly. Sci . , **18** , 1225 (1974) .

(88) D . Bellus in singlet oxygen , Reactions with organic compounds and Polymers (ed . B . Ranby and J . F . Rabek) , Wiley , London , (1978) , P 61 et . seq .

(89) G . Scott , Pure and Appl . Chem . , **30** , 267 (1972) .

(90) J . Fertig , A . I . Goldberg and M . Skoultchi , J . Appl . Polym . Sci ., **10** , 663 (1966) .

(91) N . C. Billingham and P . D . Calvert , Developments in Polymer Stabilisation - 3 , Ed . by G . Scott , A . S . Pupl . (London) , 1980 Chapter - 5 .

(92) N . C . Billingham , P . Prentice and T . J . Walker , J . Polym . Sc . Polym . Symposium No . , **57** , 287 (1976) .

(93) N . C . Billingham , P . D . Calvert , P . Prentice , T . G . Ryan , Polym . Preprints , **18** , 476 (1977) .

(94) N . C . Billingham , T . G . Ryan , P . D . Calvert , Advances in Chemistry Series , Vol . 169 , Stab . and Deg . of Polymers , Ed . by D . L . Alkira and W . L . Hawkins , A . C . S . , P . 261 (1978).

(95) W . L . Hawkins , W . Matreyek , F . H . Winslow , J . Polym . Sc . , **41**, 1 (1959) .

(96) W . L . Hawkins , M . A . Worthington , F . H . Winslow , Rubb . Age , **88** , 279(1960) .

(97) W . L . Hawkins , F . H . Winslow , J . Appl . Polym . Sc . , **C 4** , 29 (1967) .

(98) F . H . Winslow , M . Y . Hellman , W . Matreyek , S . M . Strills , Polym . Eng . Sci . , **6** , 273 (1966) .

(99) J . Luston , Developments in Polymer Stabilisation - 2 , Chapter - 5 , G . Scott (ed .) , App . Sci . , Publ . Ltd ; London , 1980 .

(100) B . W . Evans and G . Scott , Europ . Polym . J . , **10** , 453 (1974) .

(101) G . Scott , " Developments in Polymer Stabilisation - 1 " , Chapter - 9 , G . Scott (Ed .) , App . Sci . Publisher , London, (1979) .

(102) D . Munteanu , " Polyolefins Stabilisation by Grafting " in Developments in Polymer Stabilisation - 8 , Chapter - 4 , G . Scott (Ed .) , App . Sci .Publ . Ltd . , London , (1987) .

(103) G . Scott , A . C . S . Symposium - 280 , Chapter - 14 , P . P . Klemchuk (Ed .) A . C . S . , Washington , (1985) .

(104) S . Al - Malaika , A . Q . Ibrahim and G . Scott , Polymer Degradation and Stabilisation , **22** , 233 (1988) .

(105) (a) S . Al - Malaika , A . Q . Ibrahim and G . Scott , Brit . U . K . Pat . Appl . G . B . **2** , 202 , 226 , March (1987) . (b) S . Al - Malaika and G. Scott , Brit . Pat . Appl . no . 881 8880 (1989) .

(106) G . Scott , British Patent , **1** , 356 , 107 (1974) .

(107) U . S . Patent , 3 , 391 , 110 . July 2(1968) .

(108) U . S . Patent , 893 , 896 (1962) .

(109) U . S . Patent , **3** , 116 , 305 (1963) .

(110) A . Renfrew and P . Morgan , Polyethylene , London (1957) .

(111) R . C . Hirt and N . Z .Searle , Appl . Poly . Symp . , No . **4** , 61 (1967) .

(112) A . Davis and D . Gardiner , Polym . Deg . and Stab ., **4** , 145 (1982) .

(113) A . Davis and D . Gardiner , Polymer Testing **7** , 345 (1987) .

(114) F . M . Rugg , J . J . Smith and R . C . Bacon , J . Poly. Sci ., **13** , 535 (1954) .

(115) Ewing , Instrumental methods of Chemical analysis , McGraw - Hill , P . 137 (1960).

(116) A . Holmstrom and E . M . Sorvik , J . Appl . Poly . Sci ., **18** , 761 (1974), Ibid **18** , 779 (1974) .

(117) R . H . Boundy and R . F . Boyer , Styrene , its Polymers , Copolymers and Derivatives , Reinhold , New York , P . 487 (1952) .

(118) (a) A . R . Payne and J . R . Scott , Engineering Design with Rubber , Interscience , New York , P . 68 (1962) . (b) W. D. Harris , Testing of Polymers , Vol . 4 ; William E. Brown (Ed .) , Interscience Publishers (1969) .

(119) British Standard 2782 : Part 3 : Methods 326 a to 326 c ,(1977) .

(120) Zenjiro Osawa , Kazunage Kobayashi and Etsuji Kayano , Poly . Deg . and Stab . , **11** , 63 (1985) .

(121) G . Scott , Chemical Ind . **7** , 271 (1963) .

(122) G . Scott , Atmospheric oxidation and antioxidants , P . 192 , Elsevier Amsterdam (1965) .

(123) K . B . Chakraborty and G . Scott , Europ . Polym . J . , **13** , 731, (1977) .

(124) G . Scott , Mechanism of action of Sulphur Compounds in autoxidation , Ed . N . Kharasch , Vol . **4** , 99 , (1969) .

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

(126) G . Scott . Atmospheric Oxidation and Anti - oxidants , Elsevier , London and New York (1965) . Chapter - 5 .

(127) J . H . B . Chenier and J . A . Howard , Can . J . Chem . , **54** , 390 (1976) .

(128) N . Grassie and G . Scott , Polymer Degradation and Stabilisation, Camb . Univ . Press , Chapter - 4 , (1985) .

(129) W . L . Hawkins , Degradation and Stabilisation of polymers . Ed . by G . Geuskens , A . S . pubb . (london) , Chapter 4 , (1975) .

(130) W . Kauzmann , H . Eyring , J . American Chem . Soc . , **62** , 3113 (1940) .

(131) M . Pike , W . F . Watson , J . Poly . Sci . , **9** , 229 (1952) .

(132) D . J . Angier , W . F . Watson , Trans IRI , **33** , 22 (1957) .

(133) R . J . Ceresa , W . F . Watson , Trans IRI , **35** , 19 (1959) .

(134) R. J . Ceresa , Trans IRI , 35 , no . **2** , 45 (1960) .

(135) R . J . Ceresa , Plast . Inst . Trans , **28** , 178 (1960) .

(136) G . Scott , M . Tahan , J . Vyvoda , Europ . Polym . J . , **14** , 377 (1978) .

(137) B. B . Cooray , G . Scott , Europ . Polym . J . , **16** , 1145 (1980) .

(138) D . J . Carlsson , T . Suprunchuk and D . M .Wiles , J . Polym . Sci . B Polymer letter Edition , **11** , 61 , (1973) .

(139) J . P . Guillory and R . S . Becker , J . Polym . Sci . , Polymer Chemistry Ed . , **12** , 993 , (1974) .

(140) J . C . W . Chien and W . P . Conner , J . American Chemical Soc . , **90** , 1001 (1968) .

(141) G . Scott and E . Setoudeh , Polymer Degradation and stability , **5** , 81 (1983) .

(142) P . J . Burchill , D . M . Pinkerton , Polymer Degradation and Stabilisation , **2** , 239 (1980) .

(143) Y . N . Sarma , M . K . Naqvi , P . S . Gawande and I . S . Bhardwaj , J . of Appl . Polym . Sci . , **27** , 2605 (1982).

(144) D . Munteanu , V . Aslan , C . Variu , S Turcu , V . Badea , G . Bonecea , R . Necsescu and M . Toader , Romanian Patent 60 611 , (1975) .

(145) W . Pradellok , O . Vogl and A . Gupta , J . Polym . Sci . , Polym. Chem . Ed . , **19** , 3307 (1981) .

(146) Ph . D . Thesis , Abdul Qudir Ibrahim , " Stabilisation of Polypropylene using Polymer - bound Antioxidants " , Aston University , (1986).

(147) G .Scott and M . F . Yusoff . Polym . Deg . and Stab., **3** ,53 (1980-81) .

(148) D. Adams and D . Braun , J . Polym . Sci . , Polym . Lett Ed . , **18**, 629 , (1980) .

(149) G. Scott and E. Setoudeh, Polym. Deg. Stab. **5**, 11 (1983).

(150) S. Al-Malaika, A. Q. Ibrahim, M. J. Rao and G. Scott, Mechanisms of Antioxidant action. Photoantioxidant Activity of Polymer Bound Hindered Amines. Part II. Bis-acrylates, J. Appl. Polym Sci., In Press.

(151) S. Yachigo, Sumitomo Chemical Co. Ltd., PDDG Meeting, The University of Aston in Birmingham, Sept 1987.

(152) J. A. Brydson, Flow Properties of Polymer melt, Chapter - 4, Second Edition, George - Godwin Ltd., London, (1981).

(153) K. B. Chakraborty and G. Scott, Europ. Poly. J. **15**, 35 (1979).