To my Parents and Brothers

METAL COMPLEX PHOTO-ACTIVATORS FOR THE TIME-CONTROLLED, PHOTO-OXIDATION OF POLYOLEFINS

by

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DECLARATION

The work described herein was carried out at the University of Aston in Birmingham between January 1979 and April 1982. It has been done independently and submitted for no other degree.

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SUMMARY

The University of Aston in Birmingham

Metal Complex Photo-Activators For The Time-controlled, Photo-oxidation Of Polyolefins

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The use of antioxidant photo-activator (APA) which is based on a combination of a photo-activator (ideal e.g., iron dialkyldithiocarbamate (FDMC) and conventional e.g., iron acetylacetonate (FAcAc)) and U.V. stabilizer has been examined in both low density polyethylene (LDPE) and polypropylene (PP). The U.V. stabilizers used were zinc and nickel diethyldithiocarbamates (ZDEC and NDEC), tetraethylthiuram disulphide (TETD) and 2-hydroxy-4-octyloxybenzophenone (HOBP). The two-component APA system (e.g., FDMC + NDEC) gives a more controllable lifetime and at much lower activator concentration than does the ideal photo-activator (e.g. FDMC) alone. During U.V.-irradiation both the induction period and the rate of photo-oxidation can be varied independently. It seems that the stabilizer concentration primarily determines the length of the induction period while the activator concentration controls the slope of the photo-oxidation curve and hence the embrittlement time.

Reactions of ZDEC, NDEC, FDMC and the corresponding disulphides in the presence and absence of free radical and peroxide initiators, free radical inhibitors and different bases, in inert and oxidisable substrates are investigated by oxygen absorption techniques, peroxide decomposition studies and by product analysis.

It is shown that the mechanism of action of these metal complexes involves both free radical scavenging and peroxide decomposition but that the contribution of each to the overall mechanism is influenced by the nature of the metal centre and by its presence. The nature of intermediates involved in reactions of ZDMC and CHP were examined by spectrophotometric methods. Zinc thiocarbomyl sulphenate and sulphinate were found to be amongst the first transformation products formed from the above reactions. There is also evidence of the formation of disulphide from nickel and iron complexes, but not from the zinc dithiocarbamate during reaction with hydroperoxide. Details of the mechanism of action are presented.

KEY WORDS

PLASTICS FOR AGRICULTURAL USES
U.V. STABILIZERS
ANTIOXIDANT PHOTO-ACTIVATORS
MECHANISMS OF METAL DITHIOCARBAMATES
HYDROPEROXIDE DECOMPOSERS

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LIST OF ABBREVIATIONS

PE	Polyethylene
PP	Polypropylene
PVC	Poly vinyl chloride
LDPE	Low density polyethylene
HDPE	High density polyethylene
APA	Antioxidant photo-activator
PD	Peroxide decomposers
PD-S	Stoichiometric peroxide decomposers
PD-C	Catalytic peroxide decomposers
CHP	Cumene hydroperoxide
TBH	Tertiary butyl hydroperoxide
FDMC	Ferric dimethyldithiocarbamate
NDEC	Nickel diethyldithiocarbamate
ZDEC	Zinc diethyldithiocarbamate
TETD	Tetraethylthiuram disulphide
TMTD	Tetramethylthiuram disulphide
TRTD	Tetraalkylthiuram disulphide
MDRC	Metal dialkyldithiocarbamate
NaDMC	Sodium dimethyldithiocarbamate
NaDMCSO	Sodium dimethylthiocarbomylsulphenate
$NaDMCSO_2$	Sodium dimethylthiocarbomylsulphinate
ZDMC	Zinc dimethyldithiocarbamate
ZDMCSO	Zinc dimethylthiocarbomylsulphenate
$ZDMCSO_2$	Zinc dimethylthiocarbomylsulphinate
FAcAc	Iron III acetylacetonate

HOBP	2-Hydroxy-4-octyloxybenzophenone
CM	Closed mixer
OM	Open mixer
10,CM	10 minutes processing in a closed mixer
30,OM	30 minutes processing in an open mixer
PIP	Photo-oxidative induction period
I.R.	Infra-red
U.V.	Ultra-violet
TLC	Thin layer chromatography
GLC	Gas liquid chromatography
MFI	Melt flow index
Conc	Concentration

CHAPTER ONE

INTRODUCTION

The tremendous expansion in the use of plastics as packaging materials in the late sixties and the fast growing utilization of plastic films in agriculture and horticultural fields brought with it problems of waste disposal and litter. 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 plastics wastes(1,2). This contrasts with the objectives of modern stabilization technology which aims at extending the useful service life of polymers.

Less than a decade later, it appeared that there would be a shortage of raw materials for the synthesis of plastics and consequently increases in the prices of polymeric materials(3). This change was expected to decrease the use of plastic packaging materials and therefore attention was directed towards recovering or recycling of waste plastics in order to conserve the material resources rather than the degradation and subsequent disintegration of plastics materials.

Although recycling of clean factory process waste is already practised extensively(4,5), the position is very different with consumer waste. Not only does this require a tedious collection and transportation operation, but it has to a greater or lesser extent been contaminated with other compounds which are normally found in the collected waste such as paper, metal, glass etc. Separation of plastics from such a mixture and effectively cleansing it from deleterious contaminants are extremely difficult tasks and even if these operations are feasible, the cost would be prohibitive in many cases (6).

In addition to the above limitations, waste plastics which have been exposed to the environment suffer from extensive changes in their chemical composition and these chemical changes greatly affect their behaviour on reprocessing. Furthermore, reprocessing of such mixed plastics gives rise to fabricated products which are much inferior in mechanical performance e.g., tear strength, impact resistance, to the original components used separately (4,7). This is due to the mutual incompatibility of some of the common polymers e.g., PVC, PE and PS.

It seems very clear that the use of plastics waste from consumer sources presents considerable economical and technical problems, therefore, recycling of waste plastic does not at present make a significant contribution to the problems of waste disposal and conservation of material resources (8).

Table 1.1 lists the annual production of the most important plastics in U.K. since 1976 (9) and Figure 1.1 the oil prices for the same period (10). It is evident that the use of plastics has not decreased as oil-based products became more expensive. Their advantages over traditional materials will continue to allow them to compete with paper, metal and glass on the basis of both cost and energy(11). Moreover, for certain uses, plastics with predetermined lifetimes would have important advantages. Such uses include short-term crop protection films (mulching films), baler twines, protective netting for fruit crops and disposable packaging.

1.1 Plastics in Agriculture

Plastics have provided some of the most notable innovations in agricultural technology during the past thirty years. The versatility and availability of many widths, thicknesses, colours, formulations and cost make them suitable for many applications. These applications include greenhouse coverings, mulches, row covers, solar collectors, growing containers, netting, packaging and grain and silage storage as well as many others. In a recent report(12) the total utilization of polymers in agricultural production in U.K. is estimated at 85,000 Tonnes per year.

Plastics mulches are used to increase crop yields, improve quality, save labour, lower costs, permit out-of-season crop and improve cultural practices. In arid and semi-arid regions, it is the plastics films which make the growing of certain crops possible. Although mulch applications constitute about 10% of the total amount of plastics used in agriculture, it is by far the backbone of other plastic applications in this field. It controls the conditions of the soil which constitutes the root bed of the growing plants.

Type of plastics	Consumption x1000 tonnes						
	1976	1977	1978	1979	1980	1981	1982
LDPE	417	425	455	502	415	428	455
HDPE	120	135	150	176	160	169	170
PP	185	196	230	246	205	228	229
PVC	422	400	418	448	351	378	400
Total	2041	2094	2192	2372	1955	2039	2101

Table 1.1 Consumption of plastics in the U.K.(9)

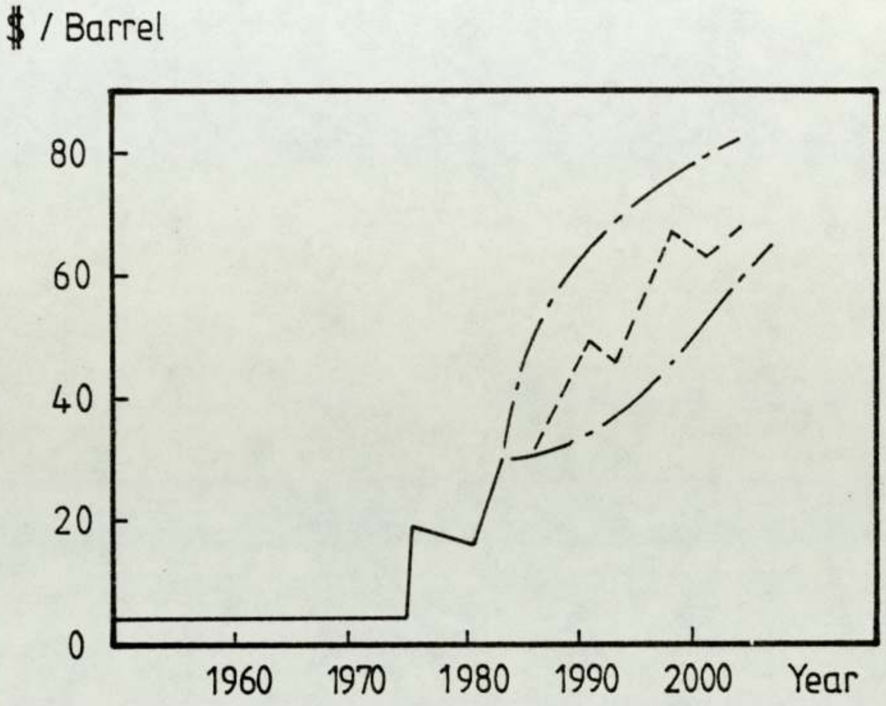


Figure 1.1 The (——) present and (----) future oil prices(10) (—·—) represents the maximum and minimum predicted prices

The level of moisture content of the soil under plastics films is generally higher than that in bare ground, except after rain or watering. This is because the dew formed on the underside of the mulch during the night condenses back into the soil in a closed circuit keeping the humidity level the same all the time. This regulating effect of the plastic film minimises therefore the risk of the moisture content falling to the wilting point for crops which are not watered and thus saves substantial amounts of water in irrigation. It is reported(13) that a reduction of 80% in the water requirement is achieved by using mulch together with drip-irrigation. This is a very important factor in arid or semi-arid farming. The advantage of evenly distributed moisture in soil as a result of using mulch is connected to the fact that in uncovered land there is a gradient of moisture from complete dryness of the top strata to the relatively moist sub-layers. The roots following this gradient leave the richly aerated and microbiologically active layer to follow the moisture into relatively inert and infertile regions of the soil with consequent decrease in yield. In mulched soil the moisture is much more evenly distributed and roots remain nearer to the surface.

Transparent plastic film spread over the soil, produces a greenhouse effect. The sun's energy is absorbed by the soil and partly converted into heat. The plastic mulch insulates the soil from the atmosphere, thereby causing an increase in the soil temperature as well as at the plant level. This leads to an increase in yields of summer crops like tomatoes(3,15).

Plastic mulching films lead to an intensification of photosynthesis. This is because it is practically impermeable to gases, hence it diverts the escaping flow of carbon dioxide to the holes through which the plants are growing, that is, around the leaves. It is thought(14) that the increased yields obtained in practice are partly due to this phenomena and this has been confirmed experimentally by Dogny and Veso(14). Scheldrake(14) recorded that in the cultivation of melons the amount of carbon dioxide at soil level was 325 ppm with no mulch and 1300 ppm under a film of black polyethylene.

In regions where the soil is alkaline or the irrigation water has a high mineral content, cultivation is extremely difficult. By the combined use of drip-irrigation and plastic mulch, either at soil or slightly buried, these lands can be and have been brought under cultivation(15). The downward movement of water (as a result of the mulch) leads to the leaching out of the salts with a consequence that hydrogen and sodium ions exchange calcium ions in the soil gels, with the result that salt deserts can and do bring forth rich crops, even using water of high salt content.

Another advantage of the use of plastics mulch is that the structure resulting from the preparative working of the soil is retained because the film acts as a protective screen with regard to bad weather, heavy rain and drying winds. The absence of soil compaction allows free circulation of water and oxygen and thereby ensures adequate access of these essential elements to the roots.

Oriented polyolefins, particularly polypropylene, has been increasingly used as a replacement for sisal based twines(12). 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 tonnes of polypropylene was used(12). 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 photo-degradation. Commercial products are normally photostabilized by the use of ferric oxide(15). 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. Unstabilized fibre-forming polymer is unsuitable to be used for this application unless an especially designed stabilizer system is used. U.V. stabilised polymer which is currently in use lasted too long(14) and eventually created a litter problem. It is therefore necessary to use a controlled life time polymer to overcome the above problems and thus a new antioxidant system needs to be devised (see Chapter Four).

In spite of the advantages offered by mulching films as discussed above, these films have also some limitations. They cause immediate increase in pollution due to the waste plastics at the end of the process(12). Not only does the plastic residue represent an ecological nuisance, but it is a formidable agrotechnical obstacle. Unless removed, it will impede subsequent cultivation operations, obstruct machinery and hamper the growth of the following crop. It is therefore essential to remove the plastic film from the fields.

The usual way of removing the plastic residues is by laborious collection and then burning. However, this still leaves many residual pieces on the field. 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 minimize litter problems but also reduce labour requirement. Manual removal of plastic mulch film takes from 30-60 man hours per hectare(14).

1.2 Essential Requirements for Ideal Degradable Mulching Film

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. Clearly 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 since it cannot be used in conjunction with mechanised harvesting. For an ideal degradable mulching film therefore, two requirements must be adequately controlled. These are; first the presence of an induction period; and second a rapid decay in physical and mechanical properties at the end of the induction period. A polyethylene film for example which is designed to remain intact for six weeks or for twelve months must degrade at this specified time with an accuracy of ± 5 days(15).

1.3 Attempts to Prepare Plastics of Controlled Lifetime for Agricultural Uses

1.3.1 Biodegradable Plastics

Biodegradable plastics are plastics which, because of their chemical composition or formulation, are susceptible to assimilation by the action of micro-organisms. Heat, oxygen and moisture are essential factors for this process.

Many naturally occurring polymers e.g., cellulose, are susceptible to fungal and bacterial attack. Synthetic polymers, on the other hand, are less susceptible to microbiological attack. This, in terms of controlled-life polymers, however, appears to be an effect of marginal utility since it is highly dependent on the microbial environment of the plastic.

High resistance of PE, PP and PVC to biodegradation has led workers to develop different techniques to modify the chemical composition or formulation of the polymer system. This controls the lifetime of plastic films for agricultural uses. Some of these techniques are described below.

1.3.2 Photosensitive Plastic

1.3.2.1 Unstabilized Polymers

It is known that oxygen containing groups and other impurities are normally introduced into the polymer backbone during the processing and fabrication stage(16-20). These impurities have a powerful photosensitising effect on the polymer during subsequent environmental exposure to normal weathering conditions. In theory, therefore, omission of conventional antioxidants and melt stabilizers 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(21) has prepared a photodegradable plastic based on 1,2 polybutadiene resin. The resin is inherently degradable by U.V. light without addition of, or copolymerization with light sensitizers by virtue of the tertiary allylic groups in the chain. Depending on the degree of crystallinity, products will disintegrate under direct sunlight in periods ranging from one week to more than one year.

Princeton chemical research(22,23) has also prepared inherently unstable polymer based on polybutene-1 suitable for agricultural mulches. Since polybutene-1 is so susceptible to U.V. degradation, it is possible that U.V. catalytic additives may not always be necessary. However, the main limitation of development of photolytically unstable mulching films based on these polymers appears to be the high cost of butene-1 and 1,2 butadiene monomers. Also stabilization of both polymers present particularly difficult problems and it has been reported(2) that for technologically useful products, these polymers have to be stabilized with conventional stabilizers.

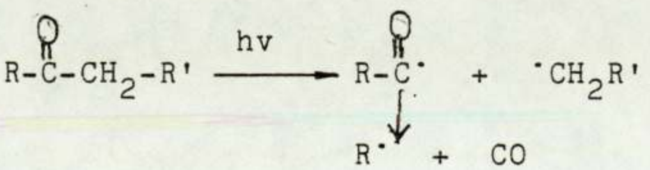
1.3.2.2 Carbonyl-modified Polymers

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 (radiation in the region 290-330 nm). On absorption of light quanta, carbonyl groups are activatad to their excited singlet state (S_1) which is capable of undergoing intersystem crossing to triplet state (T_1)(24) (Equation 1.1).

$$>C{=}O \xrightarrow{hv} [>C{=}O]^1 \longrightarrow [>C{=}O]^3 \qquad (1.1)$$

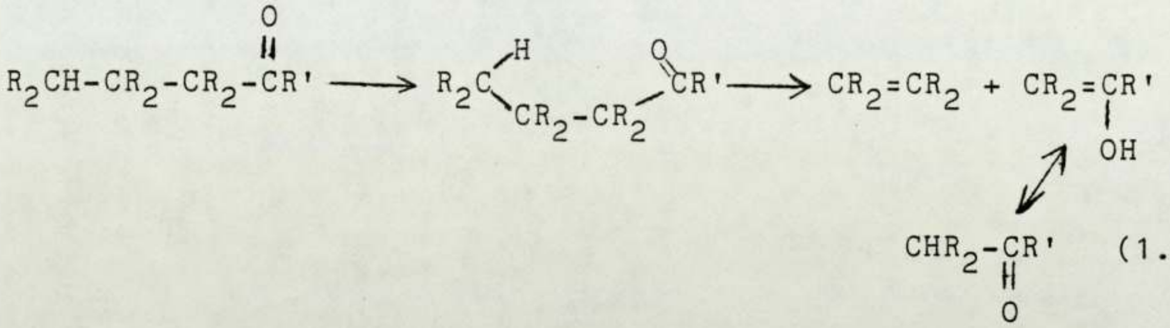
Both these excited states are capable of undergoing a variety of reactions. They can activate the polymer chain in the vicinity of the carbonyl group(25) (intramolecular energy transfer), undergo photodecomposition(26) or abstract a hydrogen atom from the polymer substrate.

The main photo-dissociative reactions of aliphatic ketones are Norrish reactions type I and II(26). In Norrish type I reactions, the bond between the carbonyl group and the adjacent α-carbon atom is homolytically cleaved (Equation 1.2).



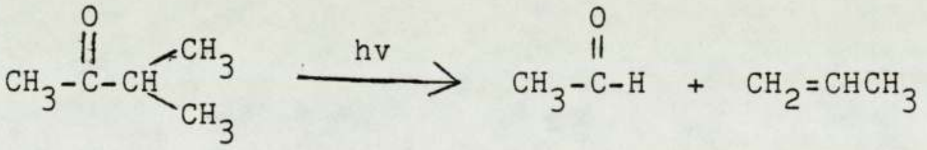
$$R-\overset{O}{\overset{\|}{C}}-CH_2-R' \xrightarrow{hv} R-\overset{O}{\overset{\|}{C}}^{\cdot} + {}^{\cdot}CH_2R' \qquad \text{(1.2)}$$
$$R-\overset{O}{\overset{\|}{C}}^{\cdot} \longrightarrow R^{\cdot} + CO$$

While in Norrish type II reactions, a non-radical intramolecular process occurs with the formation of a six-membered cyclic intermediate. Abstraction of a hydrogen for γ-carbon results in its subsequent decomposition to olefin and alcohol or carbonyl compound (Equation 1.3).



(1.3)

A similar reaction to Norrish II is also observed(27a). This is a non-radical intramolecular process, but it involves transfer of a β-hydrogen e.g., in methylisopropylketone. It results in the formation of an aldehyde and olefin through scission of the C-C bond adjacent to the carbonyl group (Eq.1.4)



(1.4)

Intermolecular hydrogen atom abstraction from an adjacent polymer chain(28,29) is another possible process which involves photo-reaction of carbonyl groups in polymers. As in Norrish type I reactions this could result in the formation of macroradical centres in the chain (Equation 1.5).

$$>C{=}O \xrightarrow{h\nu} >C^{\cdot}{-}O^{\cdot} \xrightarrow{PH} >C^{\cdot}{-}OH + P^{\cdot} \qquad (1.5)$$

By taking advantage of these fundamental studies and by conceptually inverting the objectives of them, Guillet and his coworkers were able to develop carbonyl-containing polymers with enhanced sensitivity to U.V. irradiation(30-32). They achieved the purpose by normal copolymerization of vinyl monomer with vinyl ketone or carbon monoxide.

Polymers of this type do not require oxygen to initiate photodegradation since this occurs rapidly on absorption of a photon by the molecule as mentioned above. Because of the small amount of the keto group in the polymer, the quantum yield for chain scission is low. However, few backbone scissions are enough to cause catastrophic breakdown of the polymer by Norrish reaction types I and II. Guillet copolymers therefore, may degrade very rapidly and by varying the concentration of the photosensitive groups in the polymer, time control can be easily achieved.

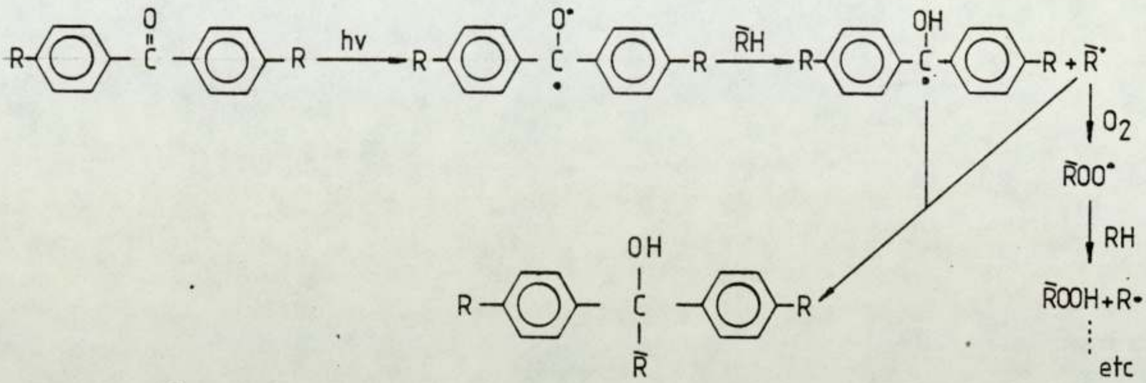
The most important feature in Guillet's photodegradable plastic is that the photosensitive groups are chemically attached to the polymer, hence, cannot be extracted or removed by leaching. Such polymers are, therefore, suitable for disposable cups, plates and other similar items. The same polymers could be very useful as agricultural mulches, but so far there are no reports on the use of these materials in the agricultural field. The reason is probably the cost of producing such materials on the rather limited scale at present envisaged.

1.3.3 Photoactive Additives

1.3.3.1 Aromatic Ketones

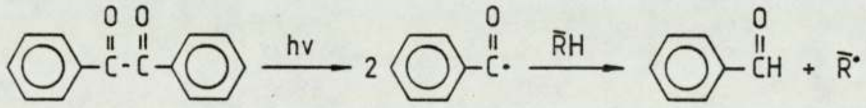
Most aromatic ketones absorb strongly above 300 nm(33,34). Unlike their aliphatic analogues, aromatic ketones cannot undergo Norrish photodecomposition reactions, the excited triplet states are the highly active species and can abstract a hydrogen from the polymer substrate thereby initiating the oxidative chain processes.

Owen and Bailey reported(35) that benzophenone photosensitises degradation of PVC under vacuum and in the presence of oxygen. They have observed an initial rapid increase in absorption in the 340 nm region which suggests the formation of ketyl radicals in the initiation process. This involves abstraction of a hydrogen atom from the polymer by the excited benzophenone (in its triplet state). A similar reaction was observed by Trudelled and Noel(36) in the case of oxidative degradation of polyvinylalcohol in the presence of benzophenone. Other workers(37-42) also reported that benzophenone is an effective photo-pro-oxidant for the more oxidisable polymers such as polypropylene(37-40), polystyrene(42) and polyisoprene(41), but is much less effective in oxidatively stable polymers such as polyethylene(43,44). In the latter case, the photodegradation was retarded and this became particularly noticeable at higher concentrations of benzophenone. The retardation process has been ascribed by Scott and Amin(44) to be due to 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)



Reaction Scheme 1

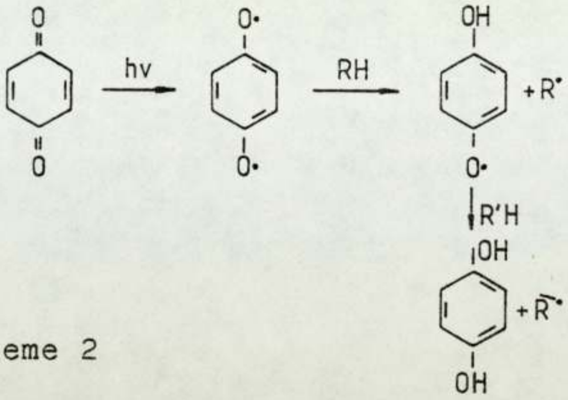
Aromatic diketones are also very effective photosensitisers for plastics materials(47). Benzil is one of the most extensively studied aromatic diketones. When photolyzed, benzil gives benzoyl radicals which are highly reactive and can abstract hydrogen atoms from the polymer substrate (Equation 1.6).



(1.6)

Quinones form another class of carbonyl compounds. These are used as accelerators for photodegradation of polymers. Reactions of quinones in the presence of U.V. light involve their carbonyl groups and the ring double bonds. The excited states of quinones show typical biradical properties(48).

They are, therefore, capable of abstracting hydrogen from the polymer substrate or any other hydrogen donor compound (Scheme 2).



Reaction Scheme 2

Rabek(27b) has reported that exposure of cis 1,4 polyisoprene in benzene solution to light in the presence of different p-quinones leads to rapid degradation. Similar results were obtained for polystyrene(49) both in solution and in films. It has also been reported(50) that quinones can enhance the photodegradation of polypropylene. On the other hand, quinones increase formation of gel during irradiation of polyethylene(51).

Although there has been considerable patent activity in this field, no commercial products have become established. Moreover, it is unlikely that useful photosensitisers for agricultural purposes could be achieved by this kind of photosensitisation process alone since, in the long term, these additives are autoretarder antioxidants(43,44) whereas what is required is an auto-accelerating pro-oxidant(15).

1.3.3.2 Transition Metal Carboxylate and Related Metal Complexes

In the early thirties many workers showed that atoms and free radicals could be produced on irradiation of metal ions or ion pair complexes in solution$^{(52)}$ and these atoms or radicals could initiate polymerization of vinyl monomers$^{(53)}$. The process by which these radicals were formed has been interpreted in terms of an electron transfer mechanism$^{(54)}$. An electron which is associated with one ion (or molecule) transfers to another ion (or molecule) as a result of U.V. irradiation. The intermediate so formed then undergoes dissociation to give the atom or free radical. For example, the photo-oxidation of ferrous salts (Equation 1.7).

$$Fe^{2+} + H_2O \xrightarrow{hv} [FeHOH]^+ \longrightarrow Fe^{3+} + OH^- + H^\cdot \qquad (1.7)$$

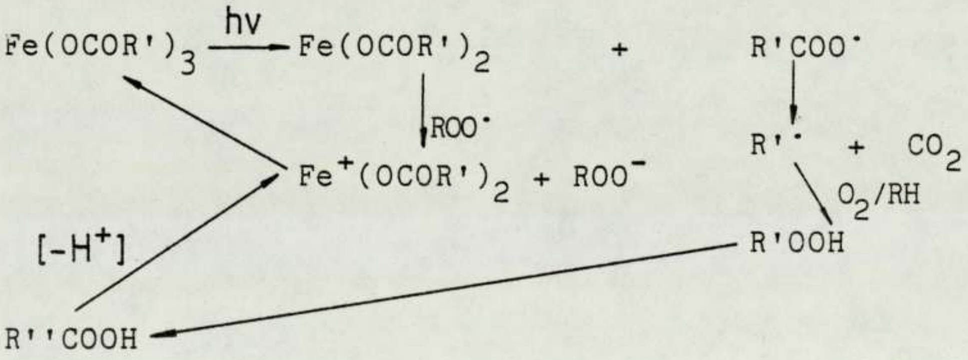
Other ferric complexes such as thiocyanate, oxalate, citrate, chloride etc., have also been used as sensitisers in photopolymerization of vinyl monomers$^{(27c)}$. The absorption spectra of these ion pairs shifted towards the visible region as the electron affinity of the anions decreased$^{(55)}$.

In the case of coordination complexes in which the transition metal ions are bonded to one or more ligands, two distinct absorption bands are observed$^{(56)}$. One band occurs mainly in the visible region associated with a d-d transition and causes repulsion between the ligand and the metal ion. The other band which is in the ultra-violet region, has a much greater extinction coefficient and is due to transition of one electron from the ligand to the metal ion(56), which facilitates a homolytic fission of the metal-ligand bond. It might be expected that absorption in the region of the charge transfer spectrum leads to a redox reaction while absorption by d-d transitions leads to ionic splitting and hence to substitution reactions. The extent of these two processes depends on the wavelength of absorbed radiation and the oxidizability of the ligand. With easily oxidizable ligands and low electron affinity, photochemical redox reactions predominate over substitution reactions(57).

From the above discussion of the ultra-violet absorption spectra of different transition metal complexes and their photo-oxidation-reduction behaviour, it seems clear that some complexes may be useful as U.V. activators in initiating polymer photo-oxidation.

Thus many workers(1,2,43-45,58,59,61,62) reported that transition metal carboxylates or halides cause acceleration in the oxidative degradation of polymers. Other metal complexes such as those of acetyl acetonates (43,44,61,62) have the most damaging effect on polymers during photo-oxidation and the stearates of these metals were among the earliest transition metal photosensitisers to be examined as possible basis of photodegradable polyethylene for agricultural mulch(60).

The mechanism which is thought to be involved when transition metal complexes (e.g., ferric acetyl acetonate) are used is based on photo-reduction of these salts with the formation of an initiating free radical which starts a normal auto-oxidation chain. However, the fast acceleration effect shown by these complexes cannot be attributed to the effect of this radical alone. Scott et al(15) proposed that after the initial stages of photo-oxidation of the polymer containing ferric complexes (e.g., ferric acetyl acetonate) macro carboxylic acid is formed. This, in the presence of peroxy radicals can convert the divalent ion formed in the photo-reduction reaction back to the ferric carboxylate which repeats the reaction again (Scheme 3)



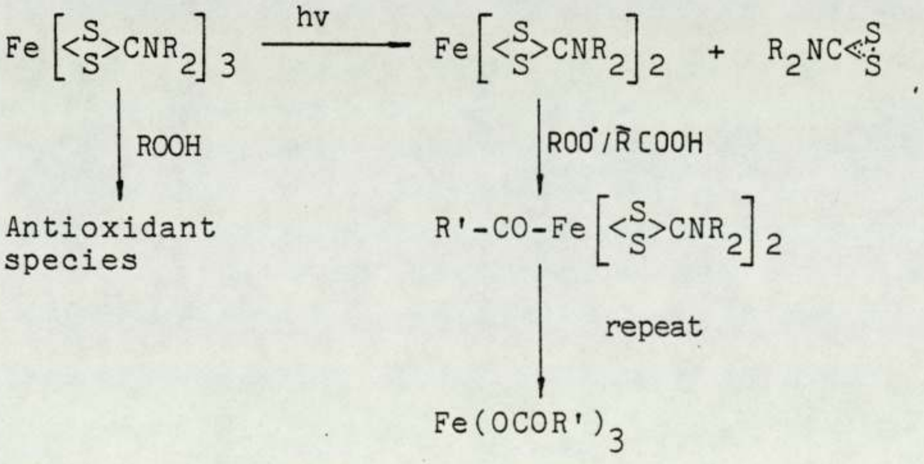
Reaction Scheme 3(15)

Thus transition metal carboxylates and related compounds can accelerate the photo-oxidation of polymers. They are, however, unstable at the processing temperatures of polyolefins(15,43). The polymer requires, therefore, an additional melt stabilizer during processing. Transition metal complexes thus satisfy only one requirement of the ideal photosensitiser, that is the rapid and auto-accelerating mode of photo-oxidation, hence they are of little technological value when used alone. Commerical developement of polymers of variable but controlled lifetimes based on transition metal complexes alone has not so far been reported.

1.3.3.3 Antioxidant-based Photoactivators

Antioxidant photoactivators (APA) are additives which act as antioxidants during processing and have stabilizing activity, although for a limited period, on subsequent U.V. irradiation before becoming extremely powerful activators. Scott and Amin(1,15,44) found that iron dialkyldithiocarbamates behave quite differently from other dialkyldithiocarbamates during photo-oxidation. Ferric dialkyldithiocarbamates behave in a way similar to that of the corresponding ferric stearates and acetylacetones. They are photolyzed rapidly giving rise to similar photo-prooxidant species. Unlike the latter, however, they are effective melt stabilisers during processing(44) (see mechanisms of antioxidant action, Section 1.4). Similar behaviour was also exhibited by the ferric complex of 2-hydroxyacetophenoneoxime(44).

Although both antioxidant photoactivators and conventional photoactivators have similar photoactivation action in the later stages of polyolefins photo-oxidation, they have however, different actions at the early stages of photo-oxidation. The photo-oxidation of the polymer containing APA does not commence until the APA complex has been completely destroyed by U.V. light. In this respect, the antioxidant activity of APA is similar to other metal dithiocarbamates. 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. Zinc and nickel salts formed as end products from zinc and nickel dithiocarbamates have no pronounced photo-pro-oxidant effect$^{(44)}$ but ionic iron behaves very differently. Iron ion reacts with the macrocarboxylic acid formed from the polymer oxidation and is converted to the corresponding carboxylate$^{(15)}$. This, as in the case of ferric stearates, causes the rapid oxidation at the end of the induction period (see Reaction Scheme 4).



Reaction Scheme 4$^{(15)}$

By varying the concentration of the iron-based antioxidant in the polymer, both the induction period and the rate of photo-oxidation at the end of the induction period can be easily controlled.

Commercial development of polymers of variable but controlled lifetime based on this antioxidant photoactivator system is now in use as mulch film in the Middle East(15). The main advantages of this system are the low cost of producing such materials and simplicity of the techniques used. However, the main limitation of this photodegradable mulch film is that it does not give the control necessary for long cropping periods under the severe exposure conditions found in the Middle East(15). In addition, it is too stable for crops grown in cold conditions such as those prevailing in Britain.

1.4 Mechanisms of Antioxidant Action

Modern theories of the mechanism of oxidative degradation of polymers are substantially based on studies by Bolland, Bateman and Gee during the 1940's(68). The free radical chain mechanism (Scheme 5), which they postulated for the auto-oxidation of model alkenes related to natural rubber, has been found to apply almost to most hydrocarbon polymers.

$$\left.\begin{array}{l} ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH \\ ROOH \longrightarrow ROO^{\cdot} + H_2O + {}^{\cdot}OR \end{array}\right) \text{ initiation}$$

$$\begin{aligned} RO^{\cdot} + RH &\longrightarrow ROH + R^{\cdot} \\ HO^{\cdot} + RH &\longrightarrow H_2O + R^{\cdot} \\ ROO^{\cdot} + RH &\longrightarrow ROOH + R^{\cdot} \end{aligned}$$

$$\left.\begin{aligned} R^{\cdot} + O_2 &\longrightarrow ROO^{\cdot} \\ ROO^{\cdot} + RH &\longrightarrow ROOH + R^{\cdot} \end{aligned}\right) \text{ chain reaction}$$

$$\left.\begin{aligned} 2R^{\cdot} &\longrightarrow R\text{-}R \\ R^{\cdot} + ROO^{\cdot} &\longrightarrow ROOR \\ 2RO^{\cdot} &\longrightarrow \text{non radical products} \\ &\qquad + O_2 \end{aligned}\right) \text{ termination}$$

Reaction Scheme 5

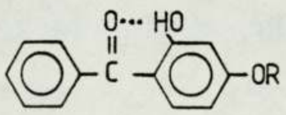
In principle, there are therefore two ways in which stabilisers can retard the above oxidation process. They can destroy hydroperoxides and thus reduce the rate of peroxide initiation (preventive antioxidants), or they may intercept the chain-propagating free radicals and terminate the chain mechanism (chain-breaking antioxidants).

1.4.1 Preventive Antioxidants

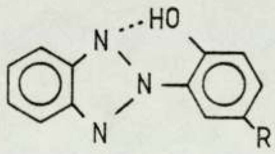
These antioxidants interfere with the production of free radicals in the initiation step of an auto-oxidising system. Their function is therefore to suppress the degradation rate by physical processes (absorbing, screening, quenching), or by chemical reactions (decomposing hydroperoxides).

Light screens function either by absorbing damaging radiation before it reaches the polymer surface or by limiting its penetration into the polymer bulk. Light screens include coating as paints and pigments. A typical example of the former is the coating of polyethylene with aluminium powder(69), and the latter is carbon black which is the most effective pigment, but because it is black its use is limited.

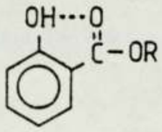
Ultra-violet absorbers function by absorbing and dissipating ultra-violet radiation harmlessly which otherwise initiates degradation of the polymer. A good ultra-violet absorber should have a high absorptivity in the wavelength range of 290-400 nm which is the most harmful region of the sunlight to polymers. Examples of stabilisers of this type are o-hydroxybenzophenones I, o-hydroxyphenylbenzotriazoles II and salicylates III.



I

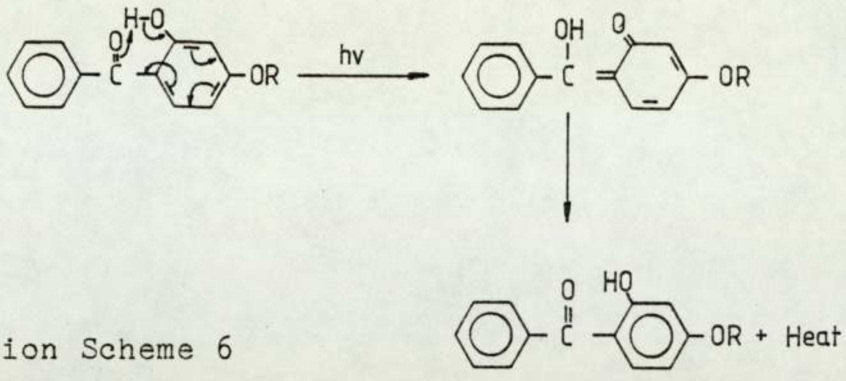


II



III

The effect of these antioxidants in the protection of polymers from photodegradation is due to the fact that the hydroxy group being very close to the carbonyl group or nitrogen atom, makes intarmolecular hydrogen bonding easier and permits energy transfer with subsequent isomerization of enolic quinone(70) (see Reaction Scheme 6).



Reaction Scheme 6

The evidence supporting this mechanism is that the ability of benzophenone in protecting the polymer from ultra-violet degradation is lost if the hydroxyl group in the ortho position of benzophenone is replaced by methoxy group$^{(71^{a})}$.

Recently many workers$^{(72-74)}$ have examined the efficiency of orthohydroxybenzophenones and benzotriazoles in polyolefins and found that it is greater than just the ultraviolet absorbing efficiency of these compounds. These workers concluded that these U.V. stabilisers must act by other mechanisms in addition to their U.V. screening ability. One of these mechanisms is expected to be free radical scavenging by the phenolic hydroxy group$^{(75-77)}$.

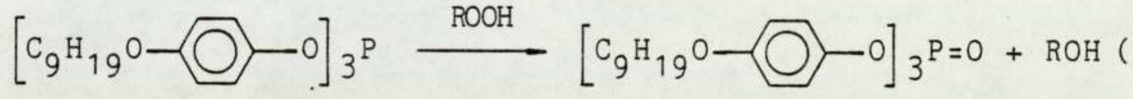
The use of quenching agents (Q) in protecting polymers against photo-oxidation involves abstraction of the excited state energy (S*) from the polymer molecule followed by harmless dissipation$^{(78)}$. Efficient energy transfer, however, can only occur if the triplet energy (E_T) of the quencher lies slightly below that of the polymer chromophore$^{(77)}$. In principle, therefore, the commercial

U.V. stabiliser, U.V. 1084 (NiII n-butylamino 2,2' thiobis-tertiary octyl phenolate) (E_T = 27000 cm^{-1}) is expected to quench triplet states of α-β unsaturated carbonyls (E_T = 29500 cm^{-1}) more efficiently than 2-hydroxy-4-octoxybenzophene (HOBP) with E_T = 25000 cm^{-1} on account of better energy matching. Quenching of excited states of hydroperoxides is, in principle, an attractive alternative to carbonyl quenching. The dissociative nature of these states, however, makes it difficult to achieve(78).

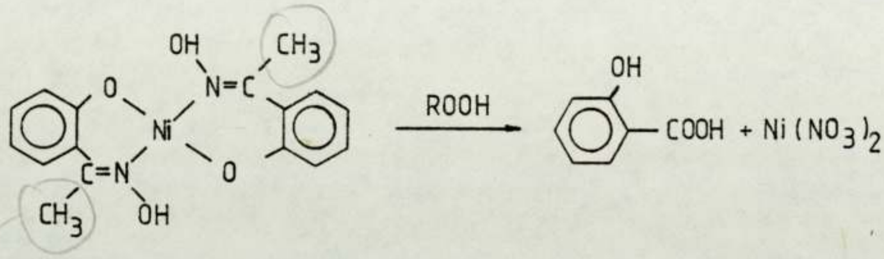
Long range energy transfer (S*→Q) may take place when emission spectrum of S* and the absorption spectrum of Q overlap significantly. This can be an efficient route for the transfer of energy at low quencher concentration(78). Energy transfer by the collisional mechanism can only become important at high quencher concentration.

Decomposition of hydroperoxides in non-radical generating processes or their protection against decomposition represent a preventive form of oxidation inhibition(77). In both cases, the hydroperoxide radical initiation mechanism(77) under both thermal and photo-oxidative conditions are interrupted.

Scott has classified the function of peroxide decomposers (PD) into two main mechanistic classes(64): the stoichiometric peroxide decomposers (PD-S) and catalytic peroxide decomposers (PD-C). The main requirement of compounds falling into the (PD-S) class is that they should substantially reduce hydroperoxides to alcohols without the substantial formation of free radicals. The most widely used (PD-S) antioxidants are the phosphite esters(64) and the Ni complex of acetophenone oxime(80) (Equations 1.8 and 1.9).



(1.8)



(1.9)

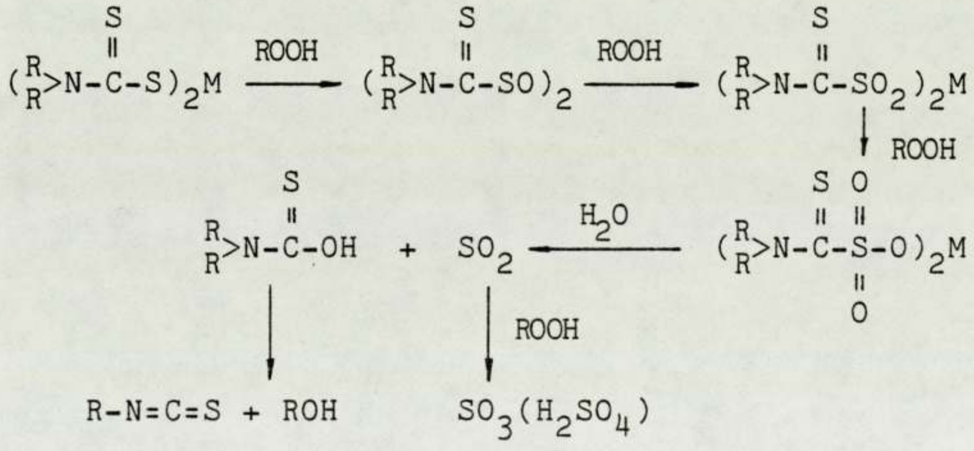
where does this go

perhaps goes CO_2

Catalytic peroxide decomposers (PD-C) are organic compounds, containing sulphur, nitrogen, phosphorous, selenium or sulphur and phosphorous simultaneously(80). Examples include disulphides, monosulphides, xanthates, dithiocarbamates, dithiophosphates, mercaptobenzthiazol. All these compounds have one thing in common which is the ability to destroy hydroperoxides through the formation of acidic products in a non-radical process. 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 compound(64). Thus, 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. In the case of monosulphides and disulphides, considerable initial pro-oxidant effects are normally observed(64).

Scott and co-workers have published several papers(15,16,43-46) on the mechanism of sulphur containing antioxidants. They found(87) that sulphur dioxide and isothiocyanate are among the breakdown products of metal dialkyl dithiocarbamates. On subsequent work, it was found that sulphur dioxide(65,66), during its reaction with hydroperoxides, is converted into sulphur trioxide and the latter is the Lewis acid species which is primarily responsible for catalytic hydroperoxide decomposition.

In the light of this evidence, Scott and his co-workers proposed the following mechanism (Reaction Scheme 7) to account for the antioxidant action of metal dithiocarbamates.



where M = Ni, Zn, etc.

R = CH_3, C_2H_5, etc.

Reaction Scheme 7

However, there was no further evidence such as the isolation of dithiocarbamate oxides to support fully the above mechanism. This study attempted to isolate the intermediate reaction products described in the above reaction scheme and this will be discussed in Chapter Five (Chapter 5, Section 5.2.8.2).

Subsequent studies by Howard and co-workers(82,83) on the antioxidant action of dithiocarbamates have cast doubt on the importance of heterolytic decomposition of hydroperoxides as the primary mechanism involved. These workers followed only the early stages of the reactions between metal dithiocarbamates and hydroperoxides using a stopped-flow technique over the temperature range 30-50°. They concluded that the homolytic decomposition of hydroperoxide was responsible for the antioxidant function of the transition metal dithiocarbamates. Analogous investigations into the mechanism of the dithiophosphates(82,83) has led to similar conclusions.

1.4.2 Chain Breaking Antioxidants

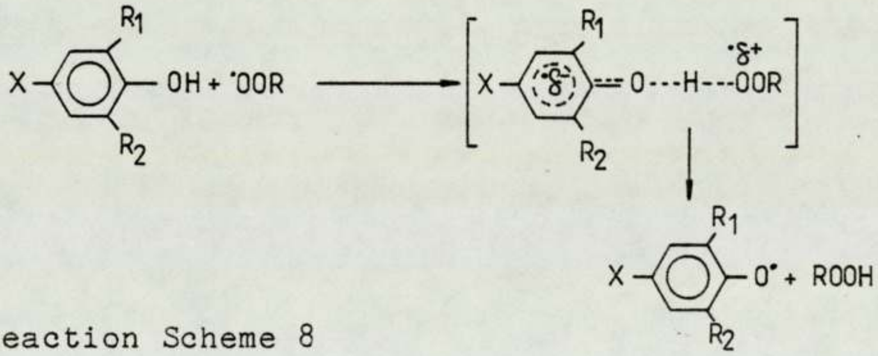
The removal of alkyl and alkyl peroxy radicals are potential chain breaking processes(63^b). The former involves an electron acceptor (oxidising agent) and the latter an electron donor(84) (reducing agent) (see Equation 1.10).

$$\begin{tikzcd}
R^\cdot + O_2 \arrow[r] \arrow[d, "(-e)"] & ROO^\cdot \arrow[d, "(+e)"] \\
R^+ & ROO^-
\end{tikzcd} \tag{1.10}$$

chain breaking acceptor mechanism (CB-A)

chain breaking donor mechanism (CB-D)

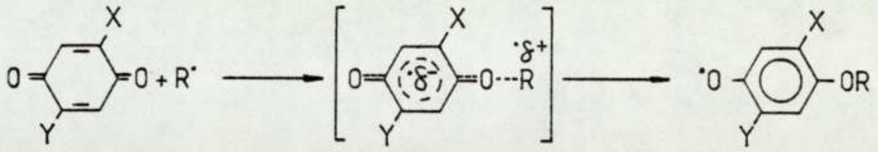
Hindered phenols and secondary amines are widely used as chain breaking donor antioxidants in polymers and other hydrocarbon compounds$^{(84)}$. The antioxidant activity of phenols and amines is associated with their ability to donate electrons (hydrogen atom) to alkyl peroxy radicals resulting in consumption of the inhibitor (see Reaction Scheme 8).



Reaction Scheme 8

The phenoxy radicals may recombine or react with other peroxy radicals, consequently the stoichiometric coefficient (f) of the inhibitor is normally 1 or 2.

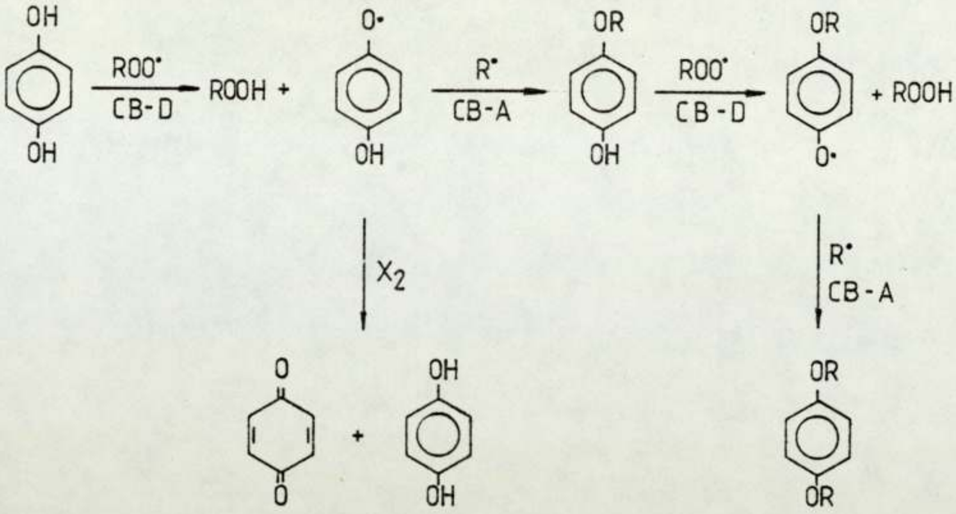
Macro-alkyl radicals, unlike macro-alkyl peroxy radicals, are not powerful oxidising agents, they are themselves readily oxidised by electron acceptors. A variety of oxidising agents are capable of removing alkyl radicals from an auto-oxidising system. These include quinones, nitrocompounds and stable free radicals of which nitroxyls and phenoxyls have been most studied.



(Reaction Scheme 9)

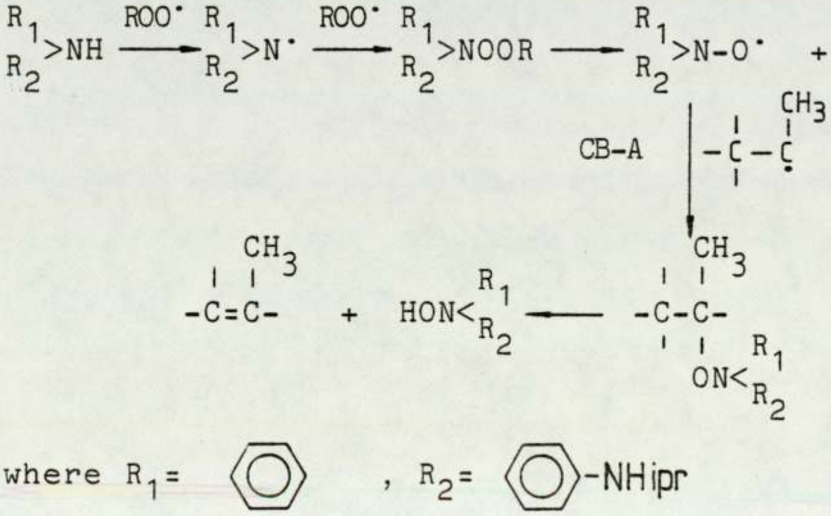
From the above discussion, it is clear that CB-D antioxidants function most effectively when the alkyl peroxy radicals are present in a high concentration in the system (excess oxygen). The CB-A mechanism, on the other hand, operates best in oxygen deficiency conditions or at high initiation rates. Antioxidants which exhibit both kinds of activity clearly have an advantage over those operating by a single mechanism since in most oxidation processes both alkyl and alkyl peroxy radicals are present to some extent. A typical example of antioxidants operating by both mechanisms is hydroquinone which is converted to benzoquinone by the CB-D mechanism, Reaction Scheme 10. However, benzoquinone is itself a very effective alkyl radical trap and many radicals may be removed from the system before antioxidant inactive products are finally obtained.

Some chain breaking antioxidants have the ability to alternate between the oxidised and reduced state and hence they exhibit regenerative behaviour under conditions where both



Reaction Scheme 10

alkyl and alkyl peroxy radicals are present(85,86). An example of this type of antioxidants is diarylamines(87). Their antioxidant activity is shown to be due to their conversion to the corresponding nitroxyl radicals (see Reaction Scheme 11) and the latter species are capable of undergoing a continuous regenerative mechanism involving the hydroxylamine(85).



Reaction Scheme 11

1.5 Scope and Object of the Present Work

Photodegradable plastics have contributed much to agriculture and horticulture technology. In agriculture, their main use is that of mulching film in the temperate zones where a lifetime between 1-4 months is required. Ferric dialkyldithiocarbamates have proved very effective in providing accurate time control over this span. In more northerly climates, the sunshine availability is only one third of that in the temperate zones and here the time scale required is from $\frac{1}{2}$-3 months. The lower end of this time scale cannot be achieved with the iron dithiocarbamates only, but there is evidence(15) that a combination of ferric dialkyldithiocarbamate and nickel, zinc dithiocarbamates, tetraethylthiuram disulphide or 2-hydroxybenzophenone at certain concentrations gives a much sharper change over from a photostabiliser to photoactivator than does ferric dialkyldithiocarbamate alone. One of the objects of this project is to find this particular concentration and to show how the two component systems function as very effective U.V. stabilisers for a limited period of time before becoming extremely powerful photoactivators.

It has been shown that ferric acetylacetonate acts as an effective activator for polyolefins but it suffers from the disadvantage that it is unstable during processing(44). Attempts have been made in this work to modify the polymer system in the presence of ferric acetylacetonate to achieve rapid oxidation rate after a limited length of induction period. The effect of such a system is compared with the dithiocarbamate two component systems.

In horticulture, the main use of degradable film is in degradable protective netting for which lifetimes between 1-3 months are required. The main film forming polymers are high density polyethylene and polypropylene. Both are photo-oxidised much more readily than low density polyethylene and are not therefore useful alone for this purpose. Polymers which are stabilised by commercial U.V. stabilisers cannot be used in conjunction with mechanised harvesting. It is therefore necessary to devise a new antioxidant system which provides adequate time control over this span. In the present work, an antioxidant photoactivator based on mixed metal chelates has been investigated as a possible solution to this specific technological problem.

Although the chemistry of the antioxidant action of metal dithiocarbamate complexes has been the subject of intensive investigation over the past twenty years(16-18,43-46,63d,72,82,83), the detailed mechanism of its oxidative breakdown still remains an open question. One of the aims of the present study is to re-examine the peroxide decomposing activity of these complexes and their oxidation products by a systematic comparative study in model compounds at elevated temperatures and under U.V. exposure conditions, and to establish the mechanism of their antioxidant actions.

CHAPTER TWO

EXPERIMENTAL

2. Experimental

In this chapter synthesis of the additive compounds and general experimental methods which were used throughout the course of this work are described.

2.1 Materials

Polypropylene (PP): Unstabilized polypropylene in a powder form identified as "propathane" HF20/CV170 was supplied by Imperial Chemical Industries (ICI).

Low density polyethylene (LDPE): LDPE in a granular (bead) form containing no antioxidant and identified as "Alkathene WJG47" supplied by ICI. The polymer was of 0.918 g/cm^3 density and melt flow index 1.98 originally.

2.2 Stabilizers

Sodium salts of dialkyldithiocarbamate NDRC (R=Me, Et) were purified and used for the preparation of transition metal dithiocarbamates. 2-hydroxy-4-octyloxybenzophenone (cyanamide cyasorb UV 531) was used as received. Apart from the above additives, all other additives were prepared by the methods discussed later in this chapter (see Section 2.5).

2.3 Solvents

Technical grade solvents were used for all the preparations, and were distilled when required for crystallization. Analar and spectroscopic grades were used for all operations involving spectral studies of solutions. Puriss grade chlorobenzene was used as received in peroxide decomposition studies.

2.4 Purification of Hydroperoxides

Cumene and tertiary butyl hydroperoxide technical grades were purified by a modified version of Kharasch method(88), as described below.

Cumene Hydroperoxide (CHP) - a solution of 200 g cumene hydroperoxide (Koch-Light) and 200 ml low-boiling petroleum ether in a 1000ml beaker was cooled to 0°C, and 160 ml 25% aqueous NaOH was added with stirring. The beaker was placed in an ice-salt bath for 30 minutes. The sodium salt which precipitated was collected by vacuum filtration and washed several times with cold 25% NaOH solution. The salt was then suspended in petroleum ether, and the free hydroperoxide was liberated by dropwise addition of glacial acetic acid. When all the hydroperoxide has been reliberated the solution separated into two layers. The ligrion layer was washed three times with water and dried over Na_2SO_4. The solvent was removed on a rotary evaporator and the remaining CHP was distilled under vacuum at 52-55° (0.01 torr). The resulting colourless CHP was better than 98% pure (by iodometric titration).

Tertiary Butyl Hydroperoxide (TBH) - the 70% tertiary-butyl hydroperoxide (Koch-Light) was stored over molecular sieves for 48 hours, dried with Na_2SO_4 and fractionally distilled under vacuum. The fraction boiling at 60°/12 torr was collected and checked iodometrically to be 98% pure.

2.5 Chemical Synthesis and Characterisation of Additives

2.5.1 Preparation of Transition Metal Dithiocarbamates

The following compounds were used:

I Iron III tris dimethyldithiocarbamate (FDMC)
II Nickel II bis diethyldithiocarbamate (NDEC)
III Zinc II bis diethyldithiocarbamate (ZDEC)

These metal complexes of carbamic acid were prepared by the following procedure(43):

wrong ref!

To 0.04 mol (0.06 mol in the case of FDMC) of sodium dialkyldithiocarbamate dissolved in 100 ml of warm water, 0.02 mol (slight excess) of the corresponding metal chloride dissolved in 75 ml of warm water was added slowly with continuous stirring. The precipitate obtained was washed several times with water, dried in a vacuum oven at room temperature and recrystallised from benzene. These metal complexes were identified by their colours, melting points, elemental analysis (Table 2.1), I.R. spectra and U.V. spectra (Table 2.2 and Figures 2.1-2.6).

2.5.2 Preparation of Tetraethyl thiuram disulphide(TETD)(98)

To 0.02 mol of sodium diethyldithiocarbamate dissolved in 100 ml of distilled water, 0.02 mol of iodine solution in methanol was added drop by drop with continuous stirring. A pale yellow solid was precipitated during the addition of iodine solution. The addition of iodine was stopped when the iodine colour started to appear. A few drops of sodium diethyldithiocarbamate solution was then added just to neutralise the excess iodine. The solution was filtered off and the precipitate was washed several times with water and finally dried in a vacuum oven at room temperature. TETD was recrystallised from hexane and the melting point was 70°(lit. 70°)(98) (for detailed analysis, see Tables 2.1 and 2.2 and Figures 2.7 and 2.8).

2.5.3 Attempt to Synthesise Sodium dibenzophenonedithiocarbamate

The following two stage process was proposed for preparation of sodium dibenzophenonedithiocarbamate. If this compound could be prepared, then it was planned to convert it to

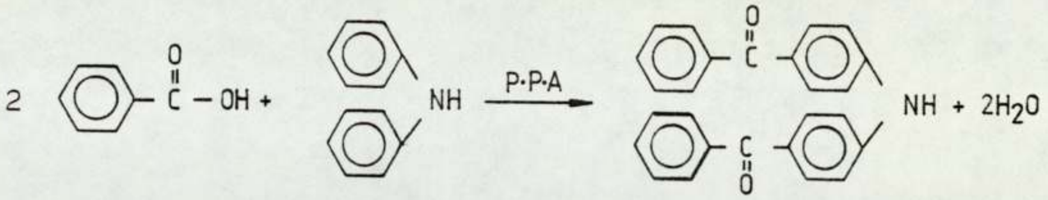
Compound	Colour	Melting Point(^{o}C)	C%	H%	N%	S%	
TETD	Pale Yellow	70	40.70	7.00	9.20	43.40	Found
			40.54	7.79	9.46	43.24	Calc.
ZDEC	White	170	33.20	5.70	8.30	36.10	Found
			33.09	5.55	7.90	35.34	Calc.
NDEC	Green	225	34.00	5.50	7.64	36.40	Found
			33.80	5.67	7.88	36.10	Calc.
FDMC	Black	>300dec	25.60	4.40	10.10	45.00	Found
			25.90	4.35	10.04	46.00	Calc.

Table 2.1 Elemental analysis,colour and melting points for some derivates of dithiocarbamic acid

Compound	Heptane		Ethanol		Ref	I.R. data (cm^{-1})	Ref
	$\lambda_{max}^{m\mu}$	log ε	$\lambda_{max}^{m\mu}$	log ε			
Tetra Methyl Thiuram Disulphide (TMTD)	223 250(s) 278(s)	4.17 - 3.93	222 250(s) 275(s)	4.15 - 3.96	89	1497 ν C-N	94
Tetra Ethyl Thiuram Disulphide	225 250 278	4.20 4.16 4.03	220 252 276	4.10 3.91 3.87	89	1495 ν C-N	94
Zinc diethyl dithiocarbamate(ZDEC)	262*	4.23*	260.5	4.23	90,91	1505 ν C-N 300-400 ν Zn-S	95,96
Nickel diethyl dithiocarbamate(NDEC)	328 388	4.50 3.78	328 388	4.54 3.80	92	1512 ν C-N 375 ν Ni-S	96
Ferric dimethyl dithiocarbamate(FDMC)			389 346 282(s) 267	3.92 4.02 4.48 4.52	92,93	360 νFe-S	97

(s=shoulder) *This measurement was carried out in ether

Table 2.2 Peak wavelengths and molar extinction coefficients and I.R. data for some derivatives of dithiocarbamic acid the corresponding disulphide and other metal salts e.g., Ni, Zn, Fe.



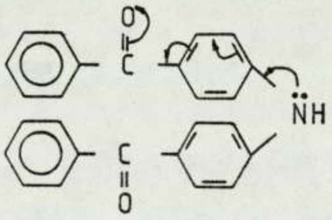
Step 1: Preparation of 4,4' dibenzoyldiphenylamine(99)
Diphenyl amine (13 g) and benzoic acid (19 g) in polyphosphoric acid (100 g) were stirred together at 140°C for 30 minutes. During the heating, some benzoic acid sublimed from solution and the colour of the solution turned green. At the end of 30 minutes, the mixture was cooled down to room temperature and 100 ml of 2N hydrochloric acid was added. A dark green crude 4,4'-dibenzoyldiphenylamine precipitated out. This was removed and recrystallised from glacial acetic acid (+ charcoal). Burnished glistening green plates (5 g) with melting point 242-243° (lit. 243-244°)(99) were obtained. The elemental analysis of 4,4'-dibenzoyldiphenylamine is shown in Table 2.3 and its I.R. spectrum in Figure 2.9.

Step 2: Preparation of sodium dibenzophenone dithiocarbamate
A general procedure for the preparation of sodium salt of dithiocarbamic acid was followed. 0.01 mol of carbon disulphide was added to 0.02 mol of 4,4'-dibenzoyldiphenylamine followed after 10 minutes by 0.02 mol of NaOH in 20 ml of distilled water. The solution was refluxed for

Elemental analysis		I.R. data (cm^{-1})		
N% found	N% calc	N-H	C=O	aromaticity
3.66	3.71	3300 single (sharp)	1640- 1650 doublet	1600

Table 2.3 Elemental analysis and I.R. data for 4,4'-dibenzoyldiphenylamine

60 minutes and at the end of refluxing the starting materials were recovered, which indicated that the reaction did not take place. This is probably due to the weak basicity of the amine. The presence of two powerful electron-withdrawing groups at the para positions of the benzene rings shifts the unpaired electron on the nitrogen atom towards the oxygen atom of the carbonyl group via the delocalised orbital of the nucleus and thereby weakens enormously the basicity of the amine.



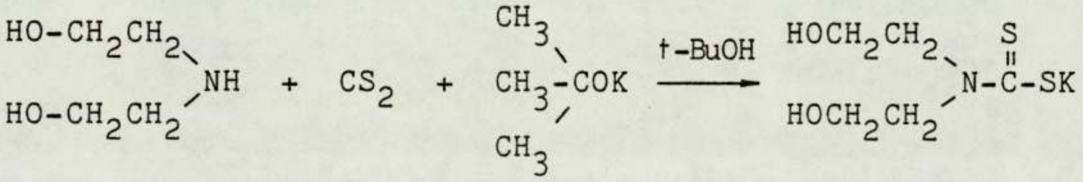
Thus, in order to prepare a dithiocarbamate salt containing benzophenone as the R group, the two benzophenone groups must be separated from the nitrogen atom by at least a CH_2

group to break the mesomeric effect and thereby to provide the right basicity. The following section will explain the procedure for achieving this purpose.

2.5.4 Attempt to Synthesise Transition Metal Complexes of Bis(4-benzoyl-3-hydroxy phenyl-oxy ethyl)dithiocarbamate and the Corresponding Disulphide

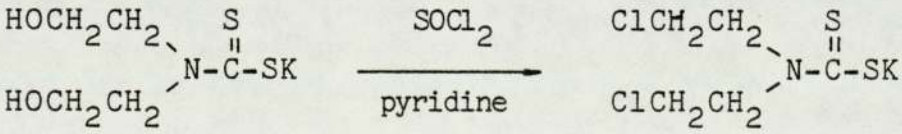
In order to prepare multifunctional stabilisers based on a dithiocarbamate and a U.V. absorber within the same molecule, the following scheme was followed (see Reaction Scheme 1).

Step 1



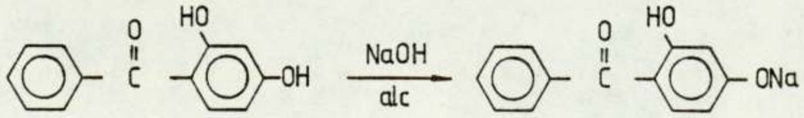
$$\begin{matrix}HO\text{-}CH_2CH_2\diagdown\\ \qquad NH\\ HO\text{-}CH_2CH_2\diagup\end{matrix} + CS_2 + \begin{matrix}CH_3\diagdown\\ CH_3\text{-}COK\\ CH_3\diagup\end{matrix} \xrightarrow{t\text{-}BuOH} \begin{matrix}HOCH_2CH_2\diagdown\\ \qquad N\text{-}\overset{\overset{S}{\|}}{C}\text{-}SK\\ HOCH_2CH_2\diagup\end{matrix}$$

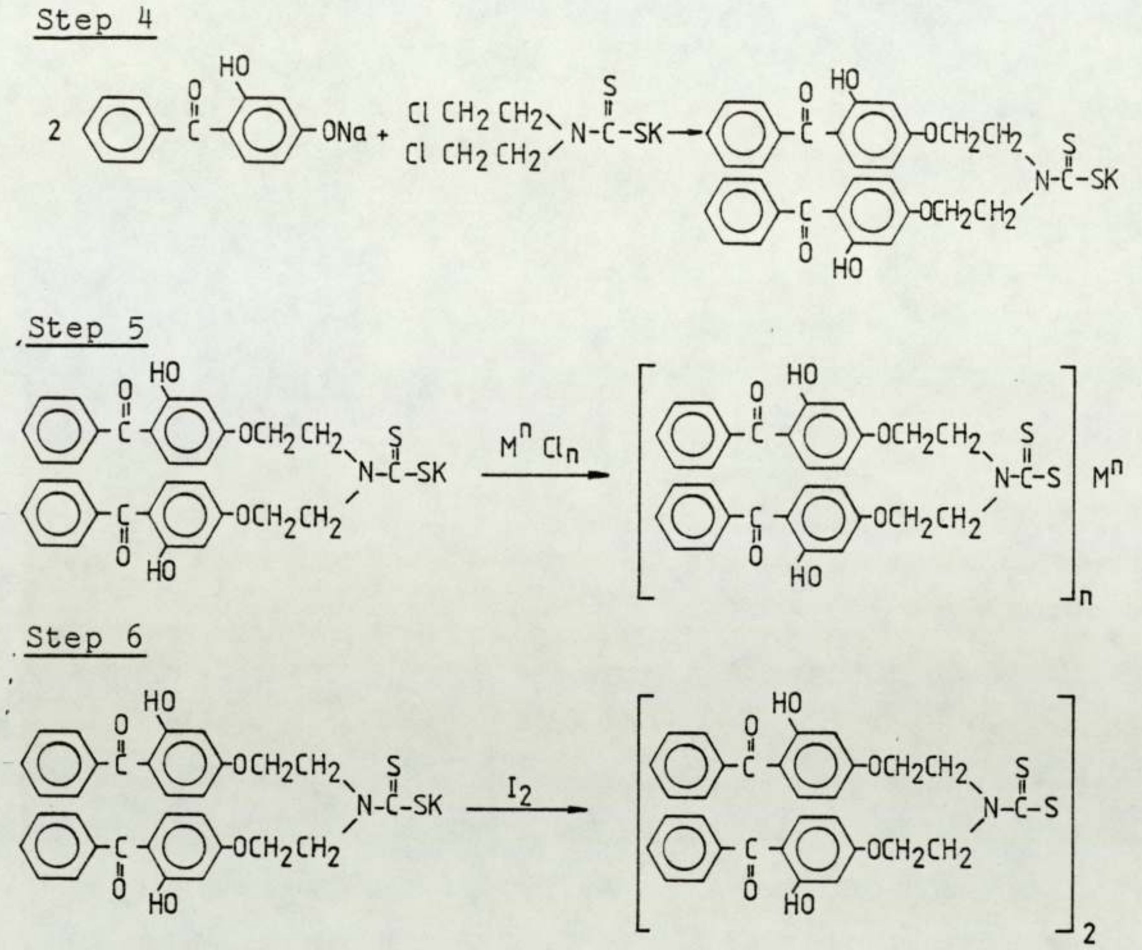
Step 2



$$\begin{matrix}HOCH_2CH_2\diagdown\\ \qquad N\text{-}\overset{\overset{S}{\|}}{C}\text{-}SK\\ HOCH_2CH_2\diagup\end{matrix} \xrightarrow[\text{pyridine}]{SOCl_2} \begin{matrix}ClCH_2CH_2\diagdown\\ \qquad N\text{-}\overset{\overset{S}{\|}}{C}\text{-}SK\\ ClCH_2CH_2\diagup\end{matrix}$$

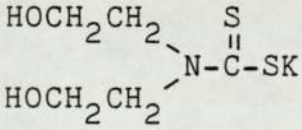
Step 3





Reaction Scheme 1

Step 1 Preparation of potassium diethanoldithiocarbamate(100)



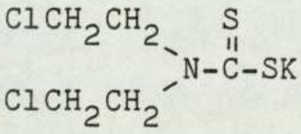
9.2 g (0.4 mol) sodium metal in 400 ml tertiary butanol was placed in a dried Erlenmeyer flask equipped with a reflux condenser. The mixture was stirred at 60° to complete the reaction before it was cooled to room temperature. Then 45.6 g (0.6 mol) of CS_2 was added with continuous stirring.

While still maintaining continuous stirring, 42 g (0.4 mol) of diethanol amine was added dropwise over a period of 60 minutes and the stirring continued for 2 days at room temperature. The solvent was then removed under vacuum giving a pale yellow solid. The product was then washed with tetra hydrofuran followed by ethyl ether, dried under vacuum and obtained quantitatively. See Table 2.4 for elemental analysis and Figure 2.10 for I.R. spectrum.

C%	H%	N%	S%	
27.1	4.7	6.54	29.03	found
27.27	4.50	6.36	29.09	calculated

Table 2.4 Elemental analysis data for potassium diethanol dithiocarbamate

Step 2 Preparation of potassium di(β-chloroethyl)dithiocarbamate

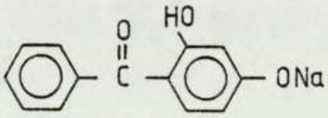


$$(ClCH_2CH_2)_2N-\overset{S}{\overset{\|}{C}}-SK$$

In a 500 ml three-neck round-bottomed flask fitted with a dropping funnel and double surface condenser, 87.6 g (0.4 mol) of potassium di(β-hydroxyethyl)dithiocarbamate and 100 ml of pure pyridine were placed. 73 ml (0.8 mol) of redistilled thoinyl chloride was added from the dropping funnel with continuous stirring. The reaction was exothermic and an ice-bath was used to maintain the temperature. During the addition of thionyl chloride which lasted 3 hours, a white solid was formed and this was partially dissolved as the reaction proceeded. After the complete addition of thionyl chloride, the mixture was refluxed for 45 minutes and the white solid pyridinium salt dissolved completely. The mixture was cooled to room temperature, filtered to remove the pyridinium salt and then distilled under reduced pressure to give a highly red viscous product. This was thoroughly washed with ethyl ether and dried over phosphorous pentoxide. On complete drying the product became a yellow solid but was rapidly converted to a red viscous substance once it was exposed to the atmosphere which indicated that it was highly hydroscopic.

I.R. data - C-Cl stretching vibrations 680 cm^{-1} (see Figure 2.11 for further detail).

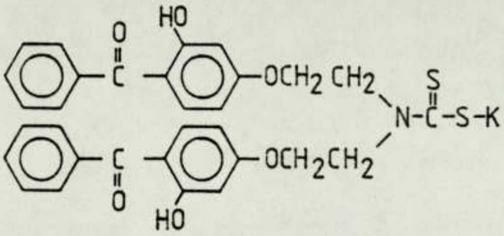
Step 3 Preparation of sodium(4-benzoyl-3-hydroxy)phenoxide



42.0 g (0.2 mol) of 2,4-dihydroxybenzophenone and 0.8 g (0.2 mol) of sodium hydroxide were dissolved in 150 ml of methanol. After stirring for half an hour, the solvent was removed by rotatory evaporation and the brown solid was dried in a desiccator containing anhydrous calcium chloride. The infra-red spectrum of this compound is shown in Figure 2.12.

Analytical data -	C%	H%	
	66.4	3.8	found
	66.1	3.8	calculated

Step 4 Preparation of potassium bis(4-benzoyl-3 hydroxy phenyl-oxy ethyl)dithiocarbamate

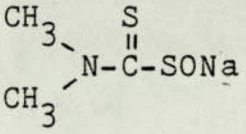


0.2 mol of sodium(4-benzoyl-3-hydroxy)phenoxide solution was added dropwise with continuous stirring to the aqueous solution of potassium di(β-chloroethyl)dithiocarbamate (0.1 mol). Upon the addition, the deep brown-red colour of the solution was gradually changed to orange and then a light yellow semi-solid product eventually separated out. The solution was then distilled under reduced pressure and a pale yellow solid was obtained. Chemical analysis of this pale yellow product (I.R. and melting point) indicated that it is 2,4-dihydroxybenzophenone. It seems likely here that the potassium bis(4-benzoyl-3 hydroxy phenyl-oxy ethyl)-

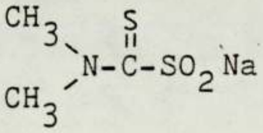
dithiocarbamate did form initially since the colour of the reactants was changed from brown-red to orange, but because it is highly unstable, it underwent decomposition to 2,4-dihydroxybenzophenone.

2.5.5 Preparation of Oxidation Products of Sodium Dimethyldithiocarbamate(101)

Sodium dimethylsulphinylthiocarbamate (I) and sodium dimethylsulphonylthiocarbamate (II) were prepared according to the following procedure.



(I)



(II)

0.02 M of sodium dimethyldithiocarbamate was dissolved in 50 ml of distilled water and to this solution an equimolar solution of 30% H_2O_2 was added dropwise with continuous stirring. The reaction was exothermic and therefore the temperature was maintained at $0^{\circ}C$ by the use of an ice bath. During the addition of H_2O_2, a pale yellow solid was formed which, after identification, was found to be tetra methylthiuram disulphide. On complete addition of H_2O_2, the disulphide was removed by filtration and the sodium dimethyl sulphinylthiocarbamate (I) was obtained from the solution by vacuum distillation.

A similar procedure but double the concentration of H_2O_2 was used for preparation of sodium dimethylsulphonylthiocarbamate. The two compounds were identified by I.R. (see Figure 2.13) and elemental analysis (see Table 2.5).

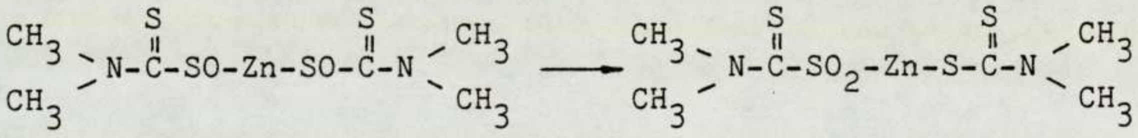
Compound	C%	H%	N%	S%	
I	16.80	5.80	6.60	31.1	found
	16.90	5.63	6.57	30.04	calculated
II	16.20	5.30	6.00	26.90	found
	15.72	5.25	6.11	27.94	calculated

Table 2.5 Elemental analysis data for sodium dimethylsulphinyl thiocarbamate I and sodium dimethylsulphonyl thiocarbamate II.

2.5.6 Preparation of Oxidation Products of Zinc Dimethyldithiocarbamate(101)

Since the alkali metal salts of both dimethyldithiopercarbamate and dimethyl thiocarbomyl sulphinate appear to possess some degree of stability, it was of interest at this point to explore the possibility of preparing other heavy metal salts. Initial efforts were directed towards preparing the zinc dimethylpercarbamate by the usual method of double decomposition. A stable white crystalline compound (m.p. 229°C dec) was obtained in high yield (90%). Infra-red studies showed that this compound still contained a dithiocarbamate moiety, yet analytical data (see Table 2.6) confirmed the presence of two oxygen atoms. Using thin layer chromatography, no zinc dimethyldithiocarbamate could be detected, thus eliminating the possibility that this reaction product is a mixture of the zinc salt of dimethyldithiopercarbamate and zinc dimethyldithiocarbamate. The presence of a dithiocarbamate linkage was also shown by reaction with methyl iodide to produce the methyl ester of dimethyldithiocarbamic acid.

These findings led to the assignment(101) of unsymmetrical structure (II) to this material which involves an intramolecular rearrangement of an oxygen atom.



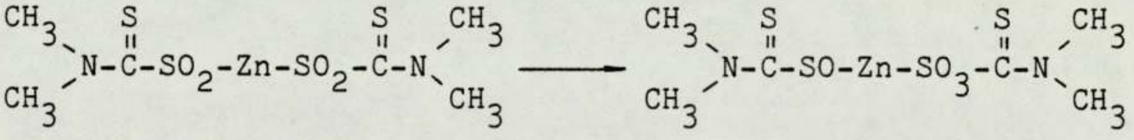
I

II

The infra-red spectrum of this compound is shown in Figure 2.14. It is believed(101) that the 1095 cm^{-1} band can be ascribed to S-O bond or possibly to SO_2 group.

Using the same procedure, the nickel complex could not be prepared. This complex underwent deep-seated decomposition when allowed to stand, even at room temperature.

The same general preparative methods were used for zinc dimethylthiocarbomyl sulphinate. A stable white crystalline compound (m.p. 197°C dec) in 85% yields was obtained. Elemental analysis of this compound (Table 2.6) showed the presence of between 4-5 atoms of oxygen. The presence of a fifth atom of oxygen can be explained$^{(101)}$ if it is assumed that this compound exists as a monohydrate. This may not be the case, but the analytical data tends to fit the monohydrate formula closely. Its infra-red spectrum, shown in Figure 2.15, does not show the 1095 cm^{-1} band previously considered due to the presence of an SO_2 group. Brooks$^{(101)}$ suggests that the compound could be in the form of unsymmetric IV.



III IV

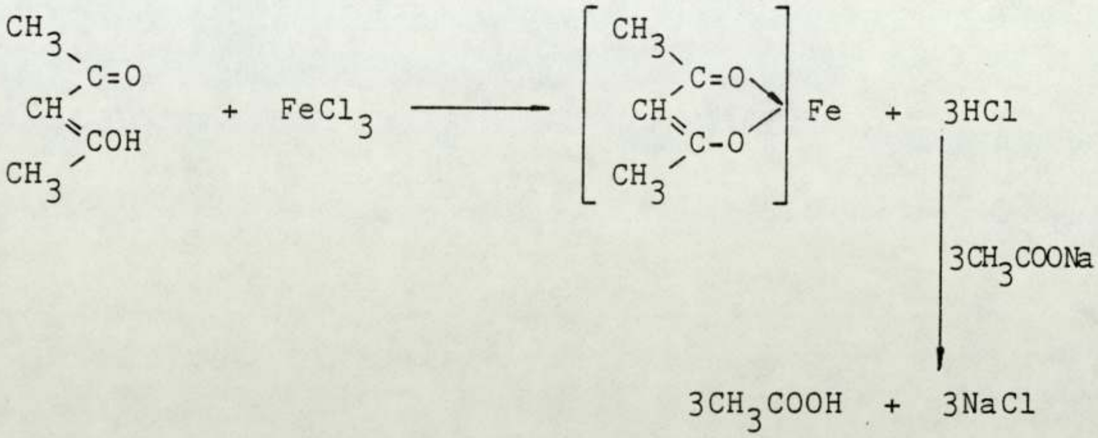
Nickel complex was completely unstable and could not be prepared.

Compound	C%	H%	N%	S%	
I	20.10	3.6	7.80	35.1	found
	20.28	3.94	7.88	36.05	calculated
III	19.30	3.7	7.20	32.1	found
	18.60	3.61	7.23	33.07	calculated

Table 2.6 Elemental analysis data for zinc dimethylthiocarbomyl sulphenate and sulphinate

2.5.7 Preparation of Ferric Acetylacetonate

Iron III acetylacetonate was prepared by the following method(102):



30 g (0.3 mol) of acetyl acetone in 100 ml methanol was added to a solution of 27 g (0.1 mol) ferric chloride hexahydrate in 150 ml of water with constant stirring. This was followed by addition of a solution of sodium acetate (0.3 mol) in 100 ml of water while stirring was still maintained. The sodium acetate was used as a buffer solution which acts by increasing the pH of the reaction mixture and thereby caused the final product to precipitate out easily.

The evolution of HCl, as the reaction proceeded according to the above equation, decreased the pH of the solution which made the separation of the final product difficult. After the addition of sodium acetate, the mixture was heated on a hot plate, cooled to room temperature and placed in a refrigerator for several hours. The red precipitate was filtered off, washed with water and dried in a vacuum desiccator. The complex was recrystallised from methanol-water and the melting point was 183°C (lit. 183°C). (For detailed analysis, see Table 2.7 and Figure 2.16).

	Elemental analysis		I.R. cm^{-1}			Visible & U.V.
	C%	H%	C=C	C-O	Fe-O	λmax nm
found	50.8	6.1	1572	1525	663	434
calc	51.01	5.99	-	-	434	352
			-	-	411	273

Table 2.7 Elemental analysis, I.R., visible and U.V.data for ferric acetyl acetonate

2.6 Samples Preparation

2.6.1 Processing of the Polymer

The polymer sample was processed using a proto-type RAPRA torque-Rheometer(103) which is essentially a small mixing chamber containing mixing screws contra rotating at different speeds. Two rotor speeds are available (high,60 R/m and low, 40R/m). All of the processing was done using high speed (60 R/m). The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. The charge was 35 g of polymer and when this charge was used, the chamber was sealed with ram down (C,M) and processed for varying periods. When it was desired to process in the presence of oxygen (O,M) a charge of 20 g was employed and the chamber was left open to the atmosphere. All processes were carried out at 160°C in the case of polyethylene, and at 180°C in the case of polypropylene.

On completion of processing, the polymer samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. The polymer samples in the form of crepe were then stored in the dark at 0°C.

2.6.2 Preparation of Polymer Films

Films were compression moulded using stainless steel glazing plates. The plates were thoroughly washed and cleaned before use to ensure smooth surfaces and a special grade of cellophane paper was used to prevent the film from sticking to the plate. Control of film thickness was achieved by using a standard quantity of polymer, about 8 g was found to produce a film of approximately 2 x 10^{-2} cm thickness. The weighed amount of polymer additive mixture in the form of crepe was placed between the glazing plates and inserted into the press whose platens were maintained at 160± 2°C and 180± 2°C for polyethylene and polypropylene respectively. The platen was closed and two minutes was allowed for the material to heat up and soften. The pressure was then slowly raised to a maximum of 28 ton/6" ram and left at full pressure for 1 minute. The platen was then cooled to about $40^{\circ}C$ by running cold water while maintaining full pressure. The plates were then removed from the press and the films were stored in the dark at $0^{\circ}C$. The required thickness was then measured with a micrometer for further examinations.

2.7 Accelerated Testing Devices

2.7.1 Ultra-violet Cabinet

Ultra-violet irradiation of the polymer samples was carried out in an ultra-violet cabinet (Figure 2.17). The ultra-violet cabinet consists of a metal cylinder of about 110 cm in outer diameter having a concentric circular rotating sample drum whose circumference is 15 cm from the periphery of the metal cylinder. Twenty eight fluorescent tube lamps are mounted on the inside of the cylinder. The rotating arrangement of the samples allows an identical amount of total radiation to fall on every sample. The cylinder cabinet is open to the atmosphere on both the lower and upper sides and the circulation of the air in the cabinet is ensured by the driven ventilator situated under the rotating frame. The sample films 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 falls perpendicularly onto the surface of the film. The temperature recorded inside the cabinet with the lamp on was 30 ± 1°C.

The radiation source consisted of a cylindrical array of 20 W fluorescent tube lamps, positioned on the inner side of the cabinet. Twenty one lamps, type C (Actinic blue) and 7 lamps, type A1 (Westinghouse sunlamps FS20) were used, which were symmetrically distributed so that the combination was one lamp type A1 for every 3 lamps of type C. The spectral distribution of both types of lamps is shown in Figure 2.18. Figure 2.19 compares the spectral distribution of lamp A1 and lamp C with sunlight(104). The maximum in the relative intensity of lamp A1 is at 317 nm and of lamp C, 374 nm. The available wavelength with the above combination of lamps was between 285 and 500 nm and the radiation intensity I_o at the sample surface was 44.3 W/m^2.

To minimise the problem of decline in lamp output, the tubes were replaced sequentially every 200 hours of exposure. Exposure times are indicated on a counter clock to the nearest 3 seconds.

2.7.2 Heat-ageing Oven

A Wallace oven (conforms to the British standards for thermal testing of polymer films) was used for heat ageing tests. The oven consists of six separate identical compartments, fitted with temperature control (± 2) and an air flow of 3 cu ft/h was maintained throughout the tests. Each test film was suspended in one of the compartments to prevent the cross-contamination of the additives by volatilisation and was subjected to the right temperature (LDPE 110°, pp 140°C).

2.7.3 Oxygen Absorption

The apparatus used to measure the rate of absorption of oxygen by auto-oxidising substrates consists (see Figure 2.20) of a 50 ml three-necked round-bottomed flask fitted with a tap having a luer needle adaptor. This enables a syringe to be connected to the apparatus for calibration purposes. The second neck is connected to a pressure transducer (Pye Ether type Up1) by a glass capillary tube. The third neck contains a sample addition device which is in the form of a V tube adaptor. The other end of the transducer is connected to a ballast vessel which is a mirror-image of the sample vessel except that the sample adding device is replaced by a glass stopper. The two vessels were immersed in a thermostatted oil bath at 110 ± 0.1°C. Stirring of the reaction mixture was achieved by addition of a small glass-sheathed bar magnet which was rotating by a powerful external horseshoe magnet.

In use, the vessel was charged with 5 ml of a mixture of the oxidisable substrate (cumene), antioxidant (in cumene) and the initiator (in cumene), and then purged with oxygen before being connected to the pressure transducer. After a short period of stabilisation, the vessels were isolated from the atmosphere and the transducer was activated by the application of a suitable voltage.

Two systems were employed both using cumene as the oxidisable substrate. The first used 0.1M cumene hydroperoxide as an initiator and the second 0.01M azobisisobutyronitrile (AZBN) as a free radical precursor. The two systems could establish the relative importance of an additives peroxide decomposing function or free radical chain breaking function$^{(105)}$. Furthermore, information on the type of reaction involved could be gleaned from the shape of the oxygen absorption graph.

To determine absolutely the amount of gas that was absorbed or evolved during the course of the reaction, a luer syringe was fitted to the reaction vessel and a known volume of oxygen was drawn from the flask. The resulting deflection of the chart recorder was used to quantify the oxygen absorption results obtained later in the experiment.

2.8 Monitoring of Oxidation Degradation and Additives in Films and Solutions

2.8.1 Melt Flow Index (MFI)

Melt flow index of LDPE and PP samples which were processed with or without additive was determined. The apparatus used was a Davenport Melt Indexer (Serial No 985). The melt flow index is defined as the amount of polymer (in gramms) extruded through a standard die in a given time (e.g., 10 minutes). It is a measure of melt viscosity of the polymer which is inversely related to the molecular weight.

The approximate relationship of MFI with molecular weight ($\overline{Mn}$) and melt viscosity (η) for LDPE$^{(106)}$ are given by the following two equations:

$$\sqrt{\overline{Mn}} = 188 - 30 \log \text{MFI}$$

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

Since thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such reactions as chain scission, cross-linking etc., such changes are expected to be reflected in the melt flow index values. Hence, melt flow index measurement provides a 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 ± 1°C for LDPE and 230 ± 1°C for PP before beginning any experiment. The barrel (cylinder) was then charged with the correct amount of the polymer (4 g) in the form of crepe. The time taken to charge the barrel (damping down with the charging tool to exclude air) 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 0.2095 cm and 0.1162 cm diameter respectively for LDPE and PP. The time interval for the first extrudate or cut-off was 60 seconds and was 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 weight 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:

$$\text{MFI} = \frac{600 \text{ x average wt of cut-off in gramme}}{\text{interval time in second}}$$

2.8.2 Determination of Torque-vs-time Curve

An idealised torque-vs-processing time curve$^{(107)}$ is depicted in Figure 2.21. Initially there is a sharp rise in the torque when the polymer is introduced into the processing chamber of the RAPRA torque rheometer (point a). As the polymer gradually melts, the torque decreases and reaches a minimum (point b). This is then followed by a slight increase in torque due to the transition from the rubbery to the melt phases (point c). The fusion time of a particular polymer shows a strong dependence on mechanical stress, temperature and the presence of additives. Irreversible changes due to thermal oxidative degradation (e.g. chain scission or cross-linking) during further processing of the polymer may be reflected by the subsequent increase or decrease of torque.

2.8.3 Measurement of Embrittlement Time

This is a destructive test method. Films of identical size and of uniform thickness containing different additives along with a control sample were irradiated and were periodically checked for embrittlement time by folding the film back on itself through 180° manually. The method was found to be inconsistent in some cases and reproducibility was not very good. This was perhaps due to slight variation in thickness along the different parts of the sample and also due to unequal application of force at the time of testing which was done by hand. However, to get acceptable reproducibility, each polymer sample was carried out in triplicate. Variation from the mean value was of the order of ±5%.

2.8.4 Infra-red Spectroscopy

All infra-red spectra were recorded using a Perkin-Elmer infra-red spectrophotometer model 599. I.R. spectra (4000-200 cm^{-1}) were recorded at medium scan speed which took 6 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 polymers. It is a non-destructive test and particularly useful for semi-quantitative purposes since the sample test can be used repeatedly. Since thermal and photo-oxidation of polymers result in the build-up of different oxidation products e.g., carbonyl, hydroxyl, carboxyl, vinyl, the kinetics of the growth of these functional groups, as the irradiation proceeds, have been followed by observing the change in the characteristic absorption peaks at different wavelengths and these were assigned by a comparison with the values for the long chain ketones, aldehydes, acids, esters, etc.

2.8.4.1 Procedure

In all analysis, the following combined form of Beer Lambert's equation was used$^{(108)}$:

$$A = \log_{10} I_o/I = ECL$$

where A = Optical density or absorbance

I_o = Intensity of radiation effectively entering the sample

I = Intensity of radiation emerging from the sample

E = Extinction coefficient expressed in litres $mol^{-1} cm^{-1}$

C = Concentration of absorbing group present in the sample in mol/litre

L = Path length of radiation in the sample in cm.

The evaluation of the thermal or photo-oxidation by I.R. method was done by exposing the samples to U.V. 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. Peaks at 1895 cm^{-1} and 2715 cm^{-1} characteristics of LDPE and PP respectively were used as reference peaks or internal standards to minimize errors due to variation in sample thickness as well as those due to the instrument, as these bands whose intensity was directly proportional to film thickness were found to remain unchanged during irradiation. The growth and decay of observed absorption peaks were expressed as indices which were defined as the ratio of the absorbance of functional group peaks to that of the reference peak.

2.8.4.2 Calculation of Absorbance

The base line technique(109) was used to calculate the optical density or absorbance due to various functional groups. This was done as shown in Figure 2.22 by drawing a straight line (base line) tangential to adjacent absorption maxima or shoulders, then erecting a perpendicular line through the required wavelength until it intersects the base line. The height (AB) is a measure of the concentration.

Before the commencement of any spectral

measurement, the spectrophotometer was adjusted to 100% transmittance and this was known as the background line.

2.8.5 Ultra-violet Spectroscopy

U.V. and visible absorption spectra of stabilisers in solution or in polymer films were recorded on a Unicam SP800 spectrophotometer. The disappearance of different stabilisers under photo-oxidative and thermo-oxidative (in film) conditions was followed by monitoring the U.V. characteristic absorption bands of the stabiliser. Similarly, reactions between hydroperoxides (TBH) with different metal complexes and also the disulphide (TETD) were monitored by spectrophotometry both at fixed wavelengths and continuous scanning over the wavelength range required.

2.9 Decomposition of Cumene Hydroperoxides (CHP)

2.9.1 Reaction Cell and Experimental Procedure

A specially designed cell (Figure 2.23) was used in the study of the thermal decomposition reaction of CHP. A slow steady stream of nitrogen was normally allowed to purge the solvent and reactants before and during the course of the reaction. One ml samples were normally withdrawn at 5 minute intervals.

In a typical experiment, the reaction cell was placed in a thermostated oil bath (110 ± 0.5°) for an initial period of 5 minutes. The exact amount of the solvents was introduced and allowed a further 5 minutes to attain the bath temperature. A calculated amount of CHP stock solution (prepared in the same solvent) was added, which was then followed (after 5 minutes) by the addition of the required amount of the additive stock (prepared in the same solvent) solution. A further 5 minutes was allowed to ensure better mixing before the commencement of the kinetic run.

2.9.2 Hydroperoxide Determination

Iodometric titration was used for the determination of hydroperoxides during both thermal and photodecomposition in the absence and presence of additives.

The iodometric method(110,111) involved quantitative conversion of iodide ion to iodine by hydroperoxide in the presence of an acid medium

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

The iodine liberated was titrated against sodium thiosulphate. The method was found to be inconsistent especially in cases where the concentration of sulphur containing additive to peroxide was high e.g., 1:1 molar ratios. However, in most cases the results were satisfactory.

The following reagents were used in the present work:

20% w/v sodium iodide in isopropanol
10% w/v glacial acetic acid in isopropanol, and
0.01 N sodium thiosulphate (AR grade)

The thiosulphate solution was prepared in boiled distilled water and stabilised with a few drops of chloroform, and stored in the dark. The following procedure was used throughout the study.

To 25 ml of 10% acetic acid in isopropanol and 10 ml of 20% sodium iodide in isopropanol was added 1 ml of the solution under test. This was refluxed for 5 minutes to ensure complete reaction of NaI and peroxide and then cooled down to room temperature. The liberated iodine was titrated against 0.01N sodium thiosulphate.

2.9.3 Kinetics of Disappearance of Additive

Rates of disappearance of additives, during their reaction with TBH, were followed by U.V. spectrophotometry at different temperatures. A 1 cm quartz cell was allowed to attain the required temperature (using thermostated cell block accessory on Unicam SP800) prior to the introduction of the appropriate amount of TBH/solvent stock solution. A calculated amount of an additive stock solution (prepared in the same spectral grade solvent) was then injected and thoroughly mixed. Changes in the additive spectrum were monitored at different time intervals.

In addition to this, repetitive scans over the spectral range 450-200 nm were also recorded. In other experiments a Beckman DU-8 U.V. spectrophotometer was used to follow kinetics of TBH reactions with metal complexes of dithiocarbamic acid.

2.10 Product Analysis

Products of both thermal and photodecomposition of CHP, in the presence and absence of additives, were analysed by gas-liquid chromatography. The instrument used was Pye Unicam which had a high accuracy temperature programmer and flame ionisation detection facilities. The column used for this analysis was 2 meters glass packed with 10% polyethylene glycol adipate on chromosorb W. Good separation of CHP products was achieved using an initial temperature of $85^{\circ}C$ which was held for a minute after which the temperature was programmed at $8^{\circ}C$ per minute until a temperature of $150^{\circ}C$ was attained. The flame ionisation detector was used with nitrogen carrier gas at a flow rate of 30 ml/min. A typical chromatogram obtained for this analysis is given in Figure 2.24.

For the calibration of individual components, a series of solutions was made up in chlorobenzene containing varying amounts of the substance and a fixed amount of an internal standard; iodobenzene, such that the ratio of the weight of the substance to the weight of the internal standard varied from zero to approximately 1.2. The solutions were then analysed under the conditions described above. The ratio of the peak area of the substance to the peak area of the internal standard was obtained from the chromatogram. A graph was then plotted of the peak area ratios against the weight ratios (see Figures 2.25-2.30).

In cases where decomposition of hydroperoxides was not complete (kinetic), the undecomposed hydroperoxide was reduced to α-cumyl alcohol by the addition of excess triphenyl phosphine(112) to the sample before G.L.C. analysis. Using a separate analytical technique for hydroperoxide determination (iodometry) and a second calibration curve relating the weight ratios with the peak area for α-cumyl alcohol, the quantity of cumyl alcohol derived from the phosphine reduction of hydroperoxide could be estimated and thus an accurate assessment of the amount of cumyl alcohol present before the addition was obtained.

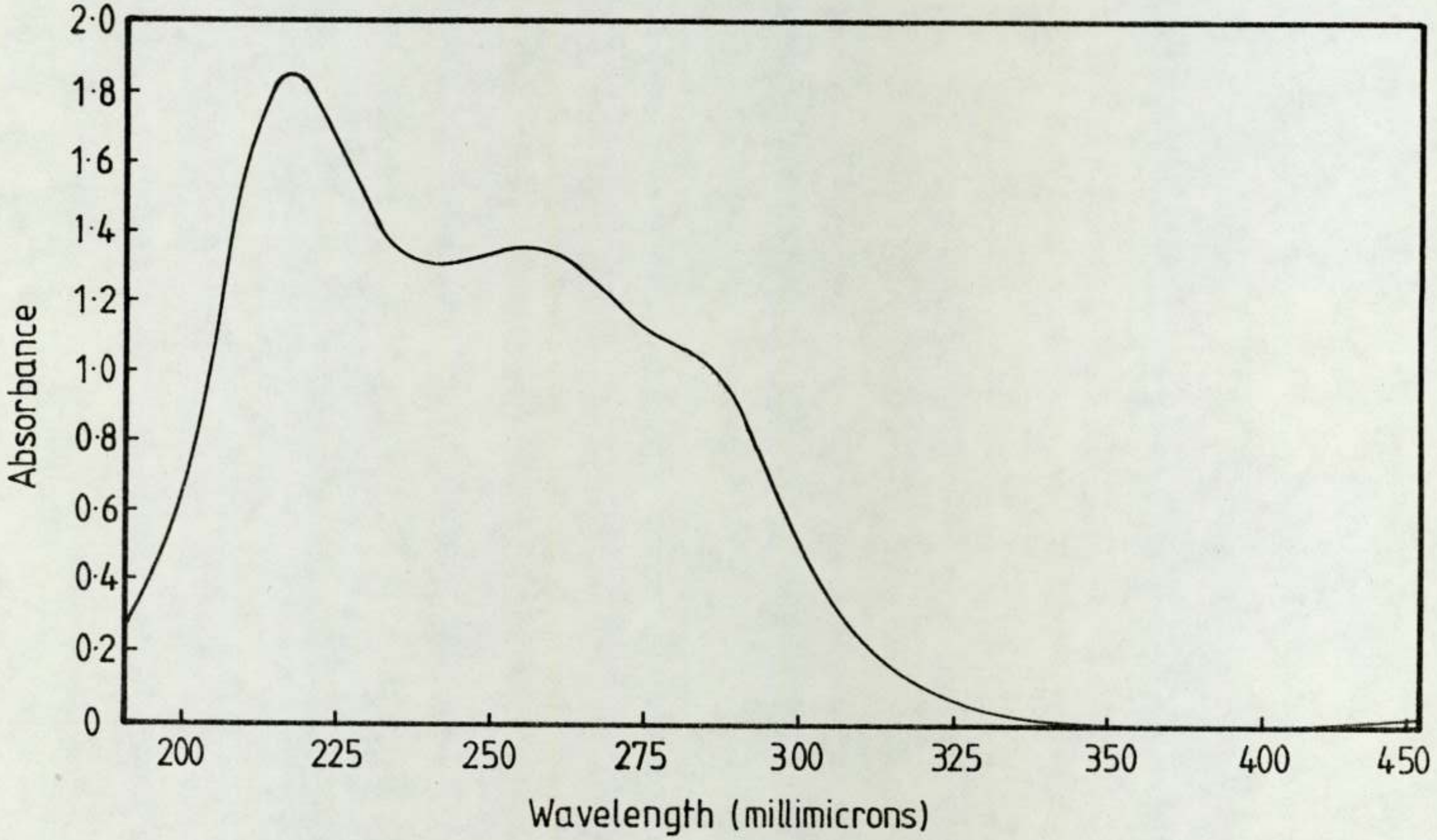


Figure 2:1 UV-spectrum of Iron III trisdimethyldithiocarbamate (1×10^{-4} M/l) in ethanol

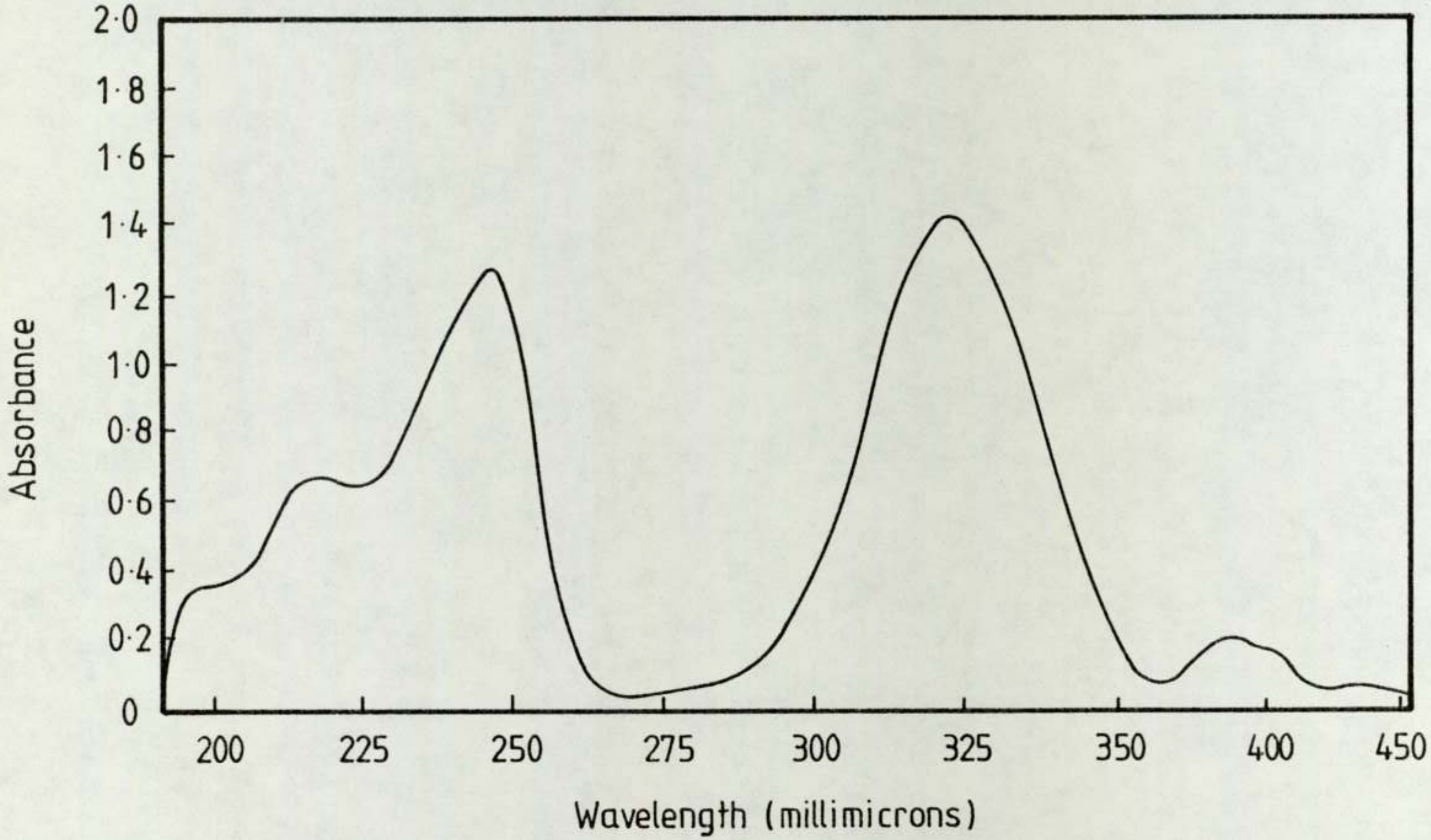


Figure 2:2 UV-spectrum of nickeldiethyldithiocarbamate (5×10^{-5} M/l) in ethanol

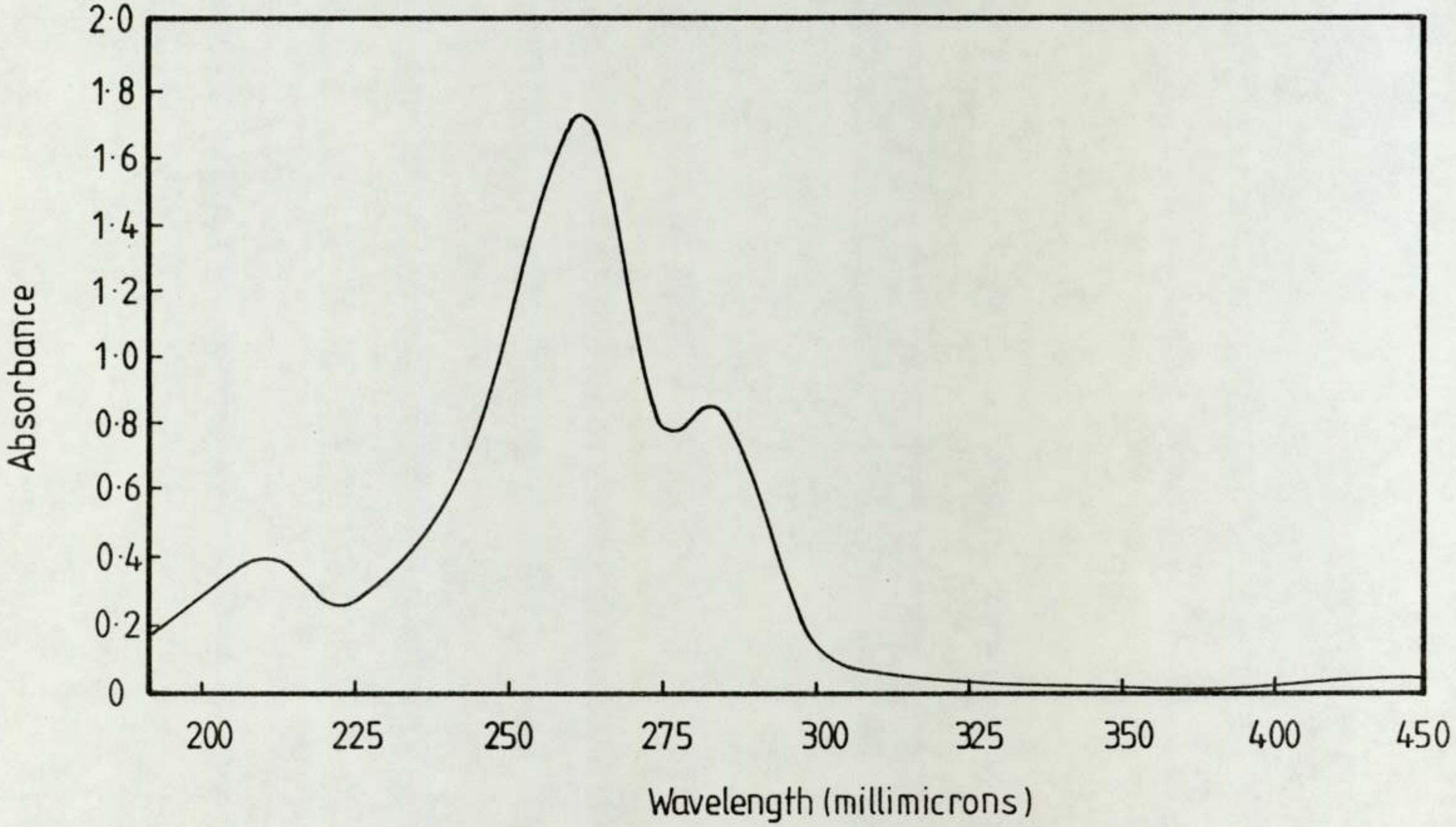


Figure 2:3 UV-spectrum of zinc diethyl dithiocarbamate (5×10^{-5} M/l) in ethanol

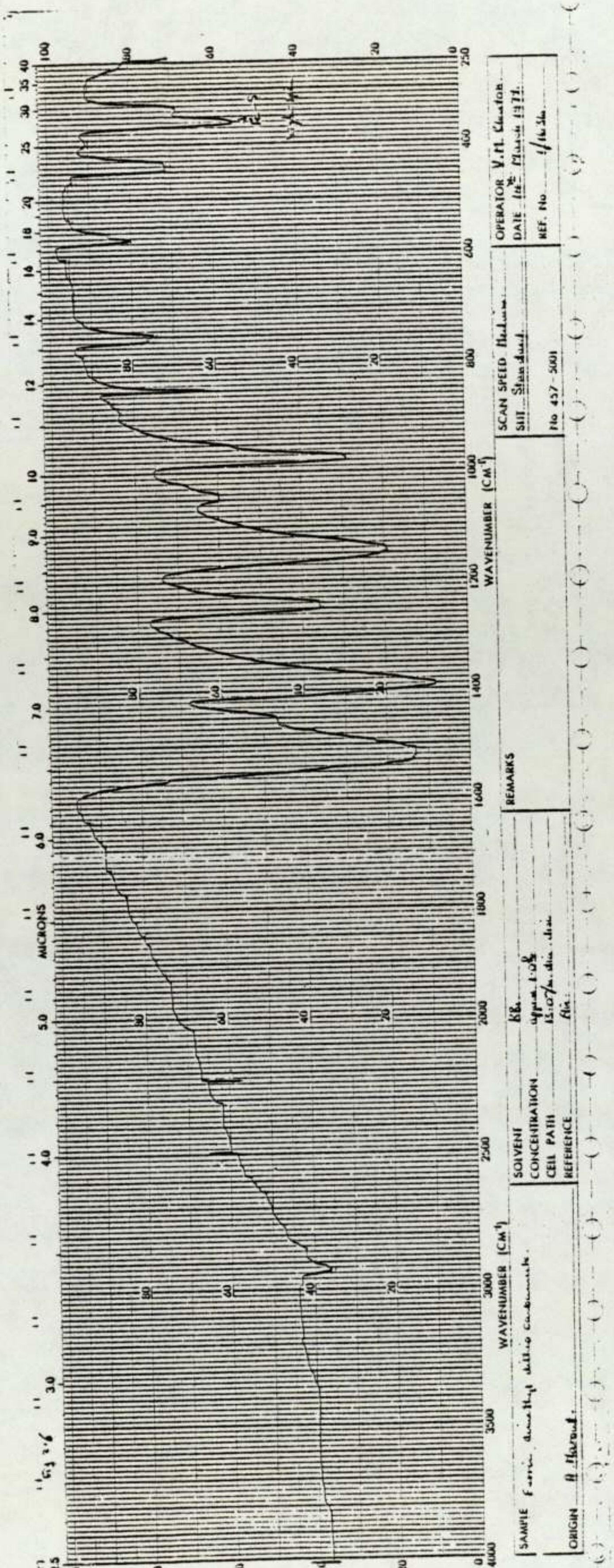
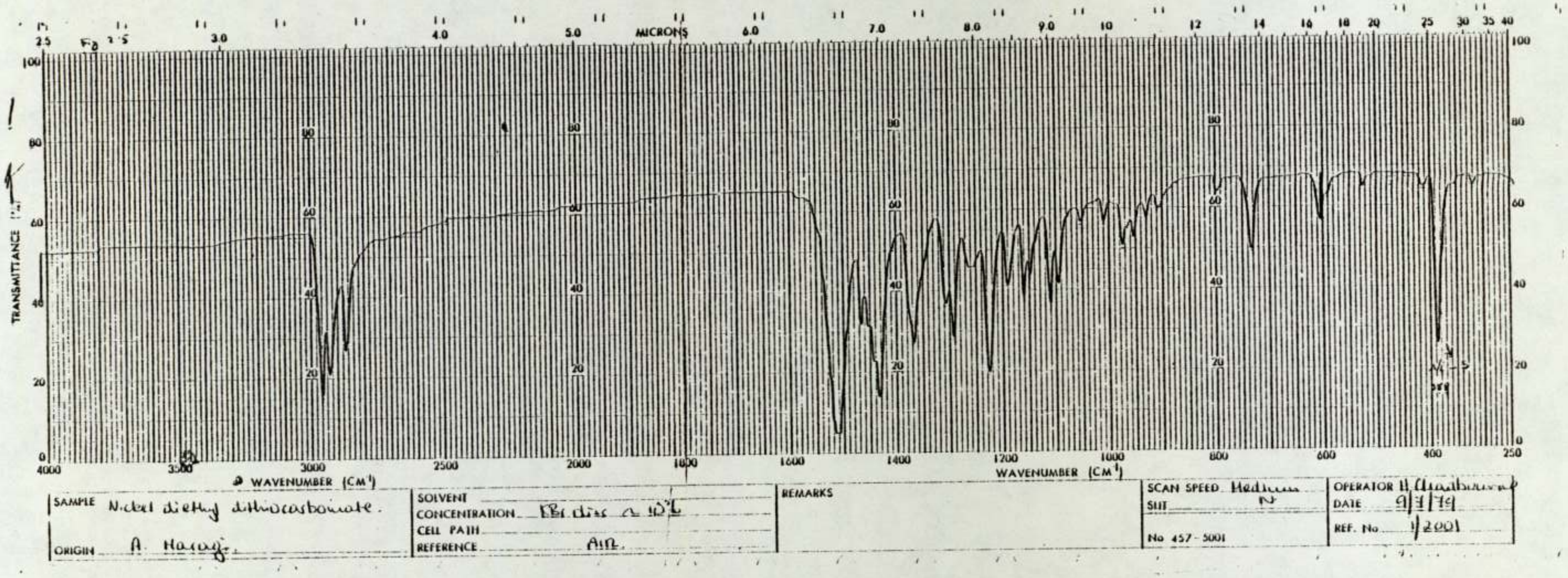
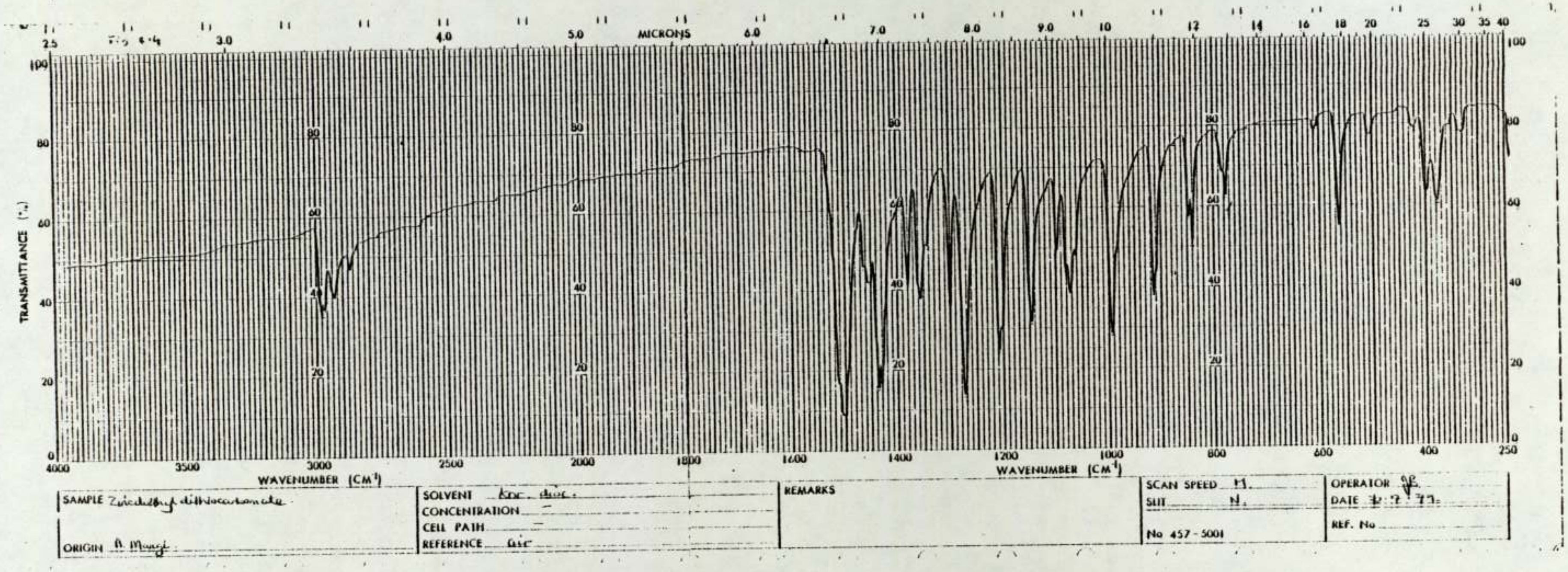


Figure 2.4 Infra-red spectrum of Iron III trisdimethyldithiocarbamate



SAMPLE Nickel diethy dithiocarbamate.
ORIGIN A. Harazi.
SOLVENT
CONCENTRATION KBr disc c 10%
CELL PATH
REFERENCE AIR.
REMARKS
SCAN SPEED Medium
SLIT N
No 457-5001
OPERATOR H Chadbourne
DATE 9/7/79
REF. No 1/2001

Figure 2.5 Infra-red spectrum of Nickel II bisdiethyldithiocarbamate



SAMPLE Zincdiethyl dithiocarbamate.

ORIGIN A. Mungi.

SOLVENT Kbr. disc.

CONCENTRATION –

CELL PATH –

REFERENCE air

SCAN SPEED M.

SLIT N.

OPERATOR AB.

DATE 12:7:77.

REF. No

Figure 2.6 Infra-red spectrum of Zinc II bisdiethyldithiocarbamate

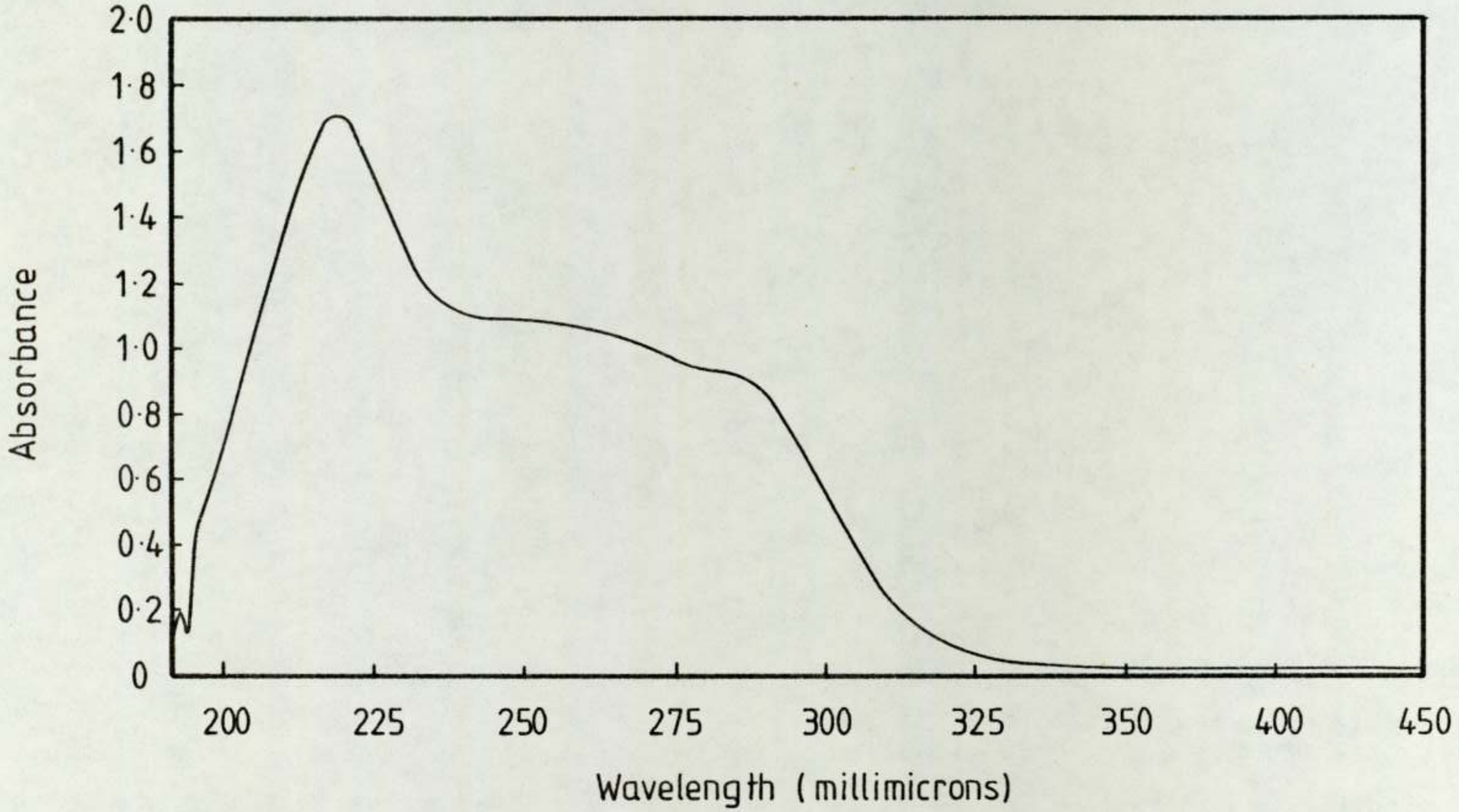


Figure 2:7 UV-spectrum of tetraethylthiuram disulphide (5×10^{-5} M/l) in ethanol

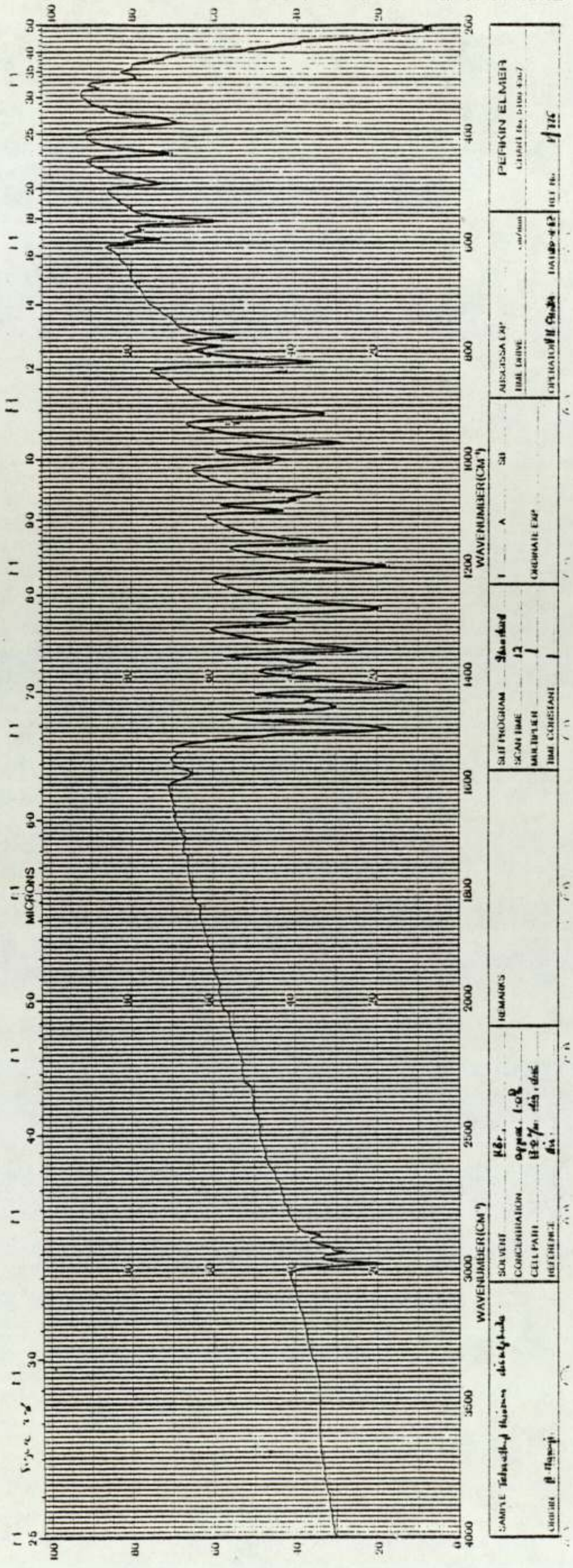


Figure 2.8 Infra-red spectrum of Tetraethylthiuramdisulphide

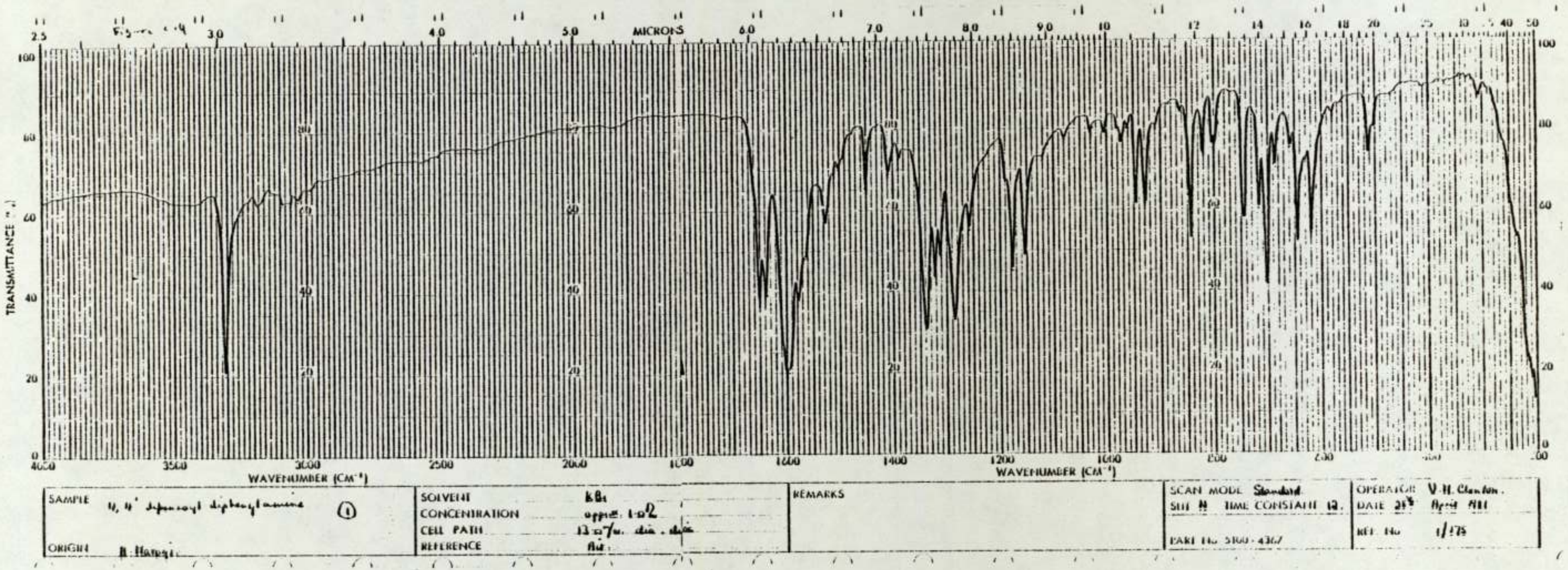


Figure 2.9 Infra-red spectrum of 4,4′-dibenzoyldiphenylamine

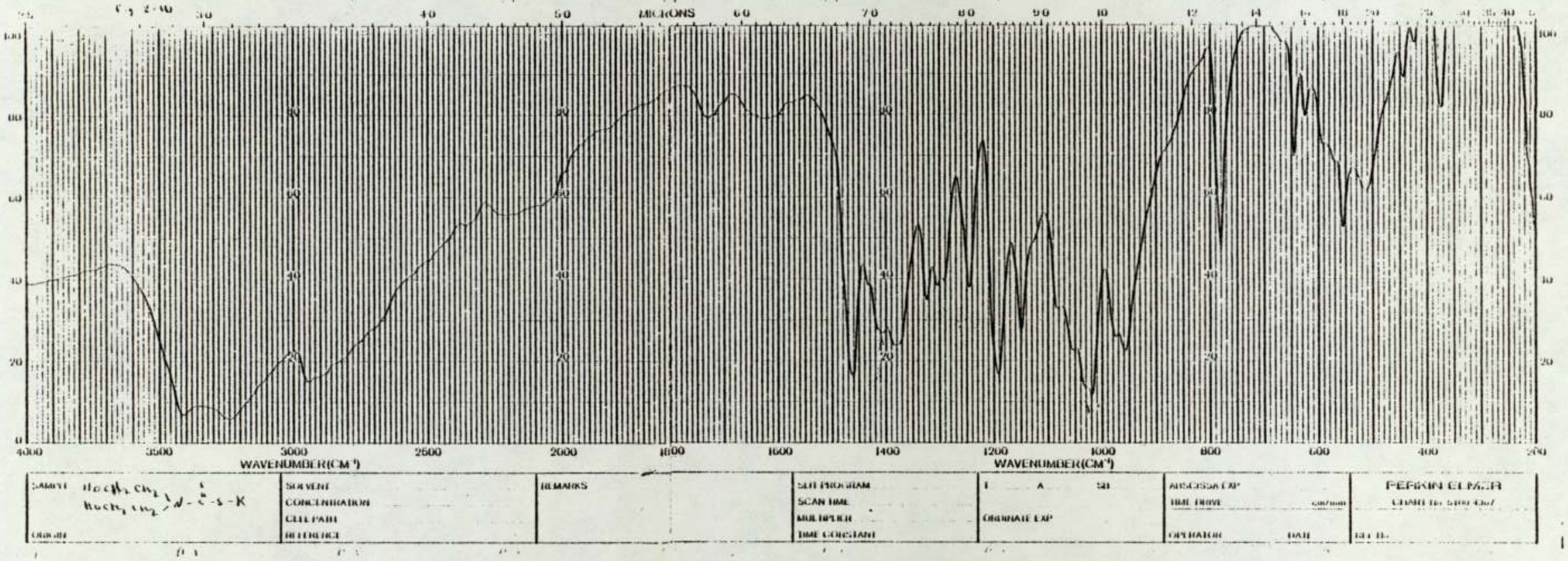


Figure 2.10 Infra-red spectrum of potassium diethanol dithiocarbamate

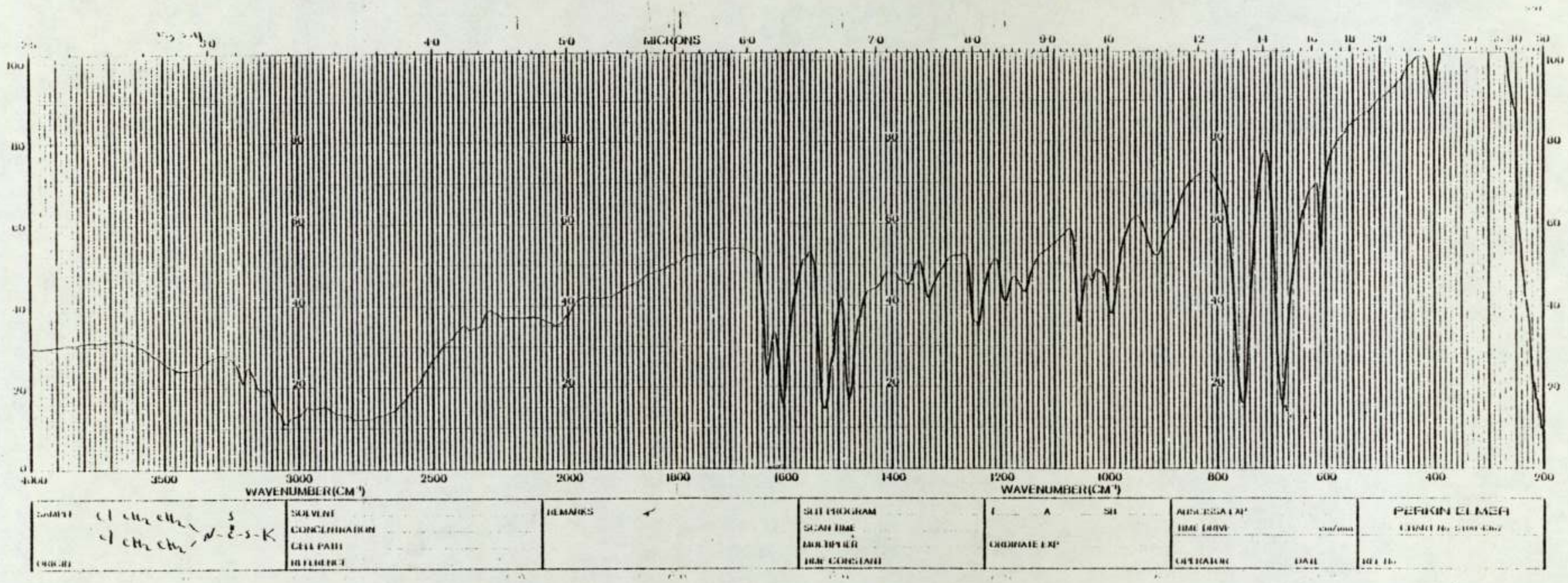


Figure 2.11 Infra-red spectrum of potassium di(β-chloroethyl) dithiocarbamate

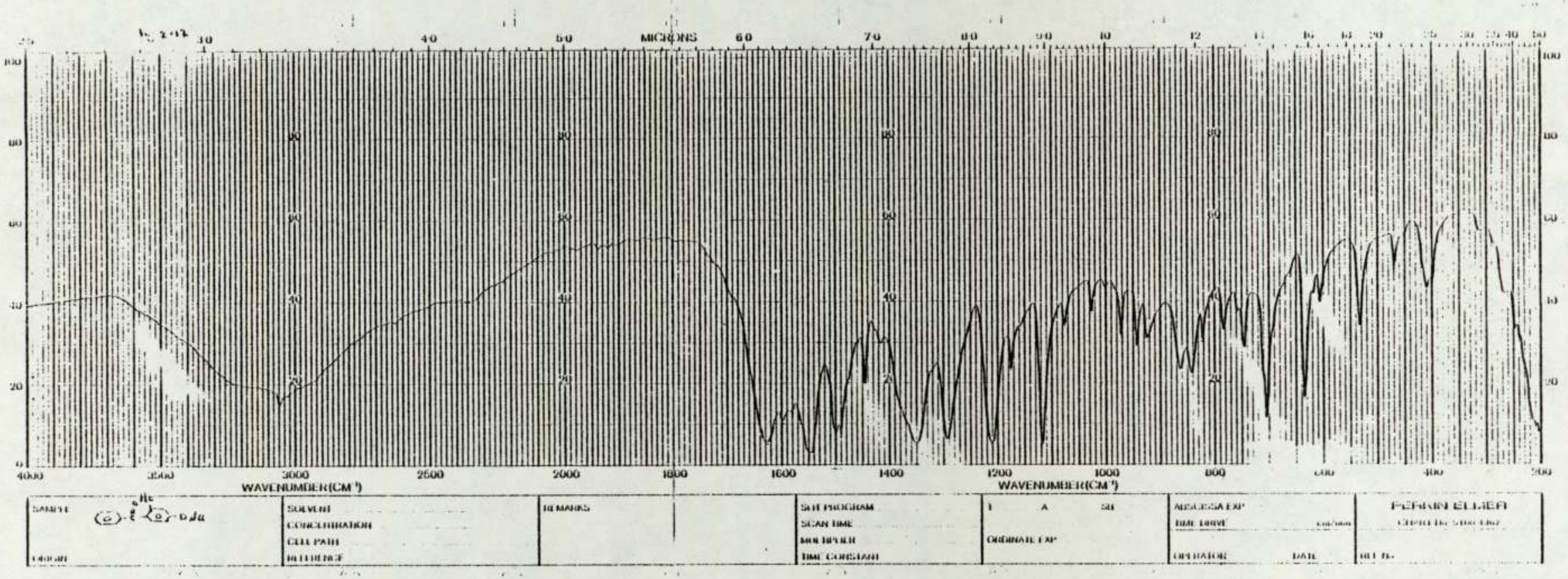


Figure 2.12 Infra-red spectrum of sodium (4-benzoyl-3hydroxy)phenoxide

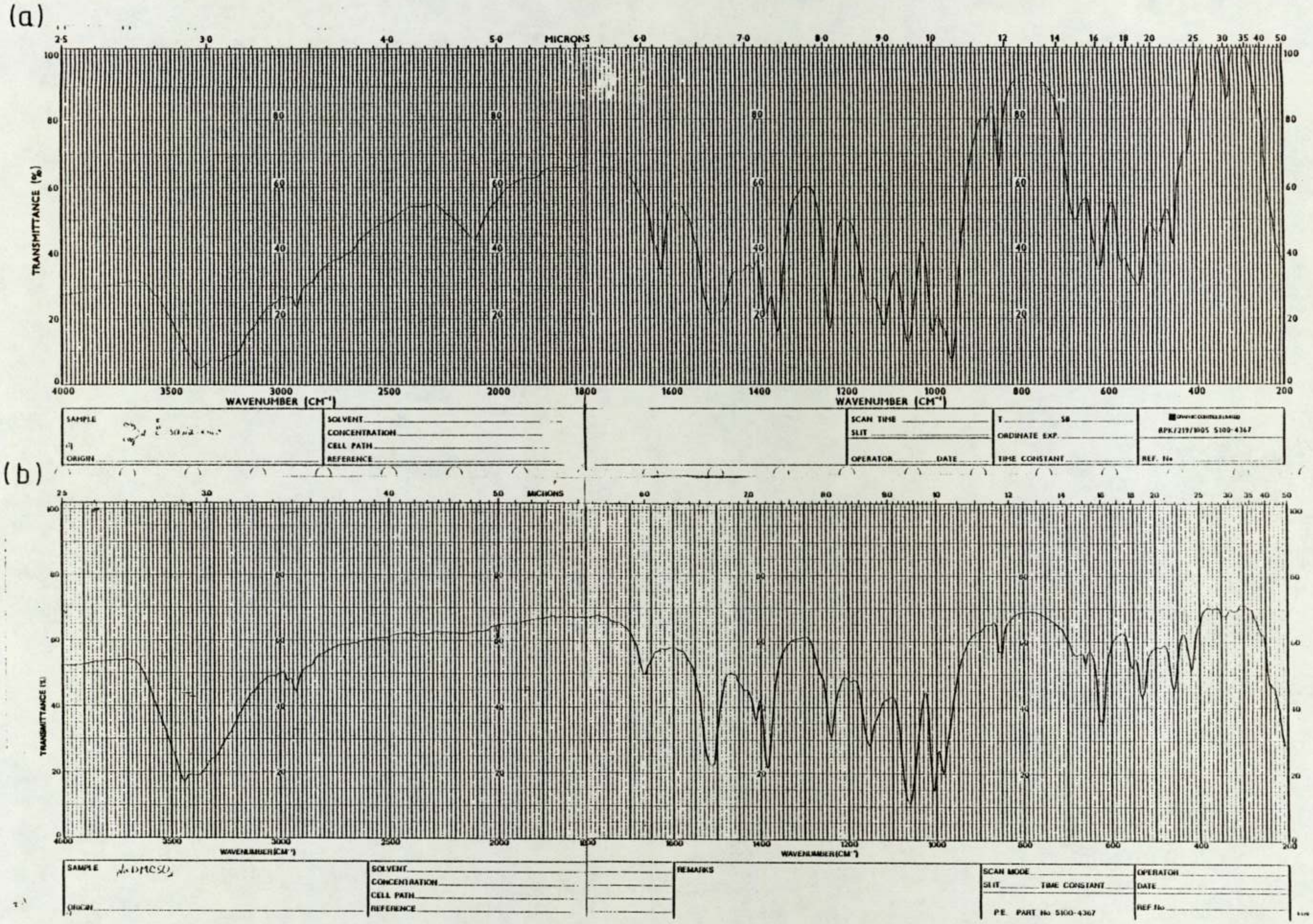


Figure 2:13 Infra-red spectrum of (a) sodiumdimethyl thiocarbomyl sulphenate (b) sodium dimethylthiocarbomylsulphinate

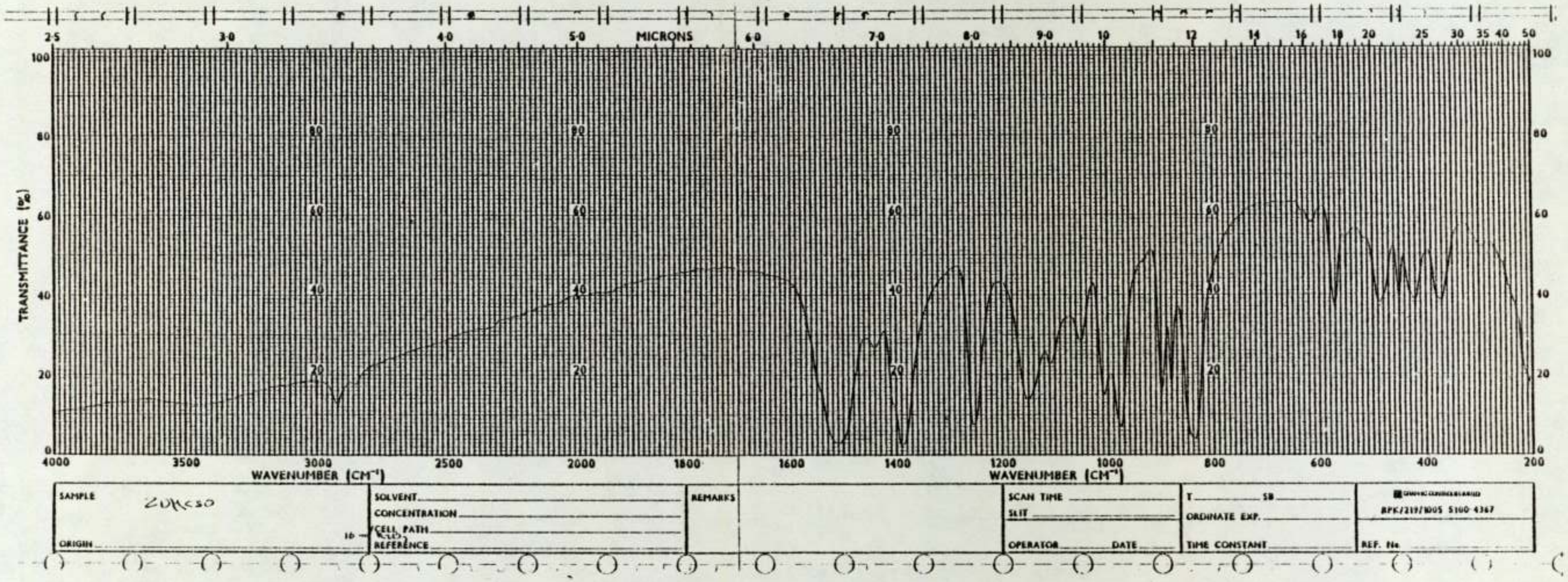


Figure 2.14 Infra-red spectrum of zincdimethyldithiopercarbamate

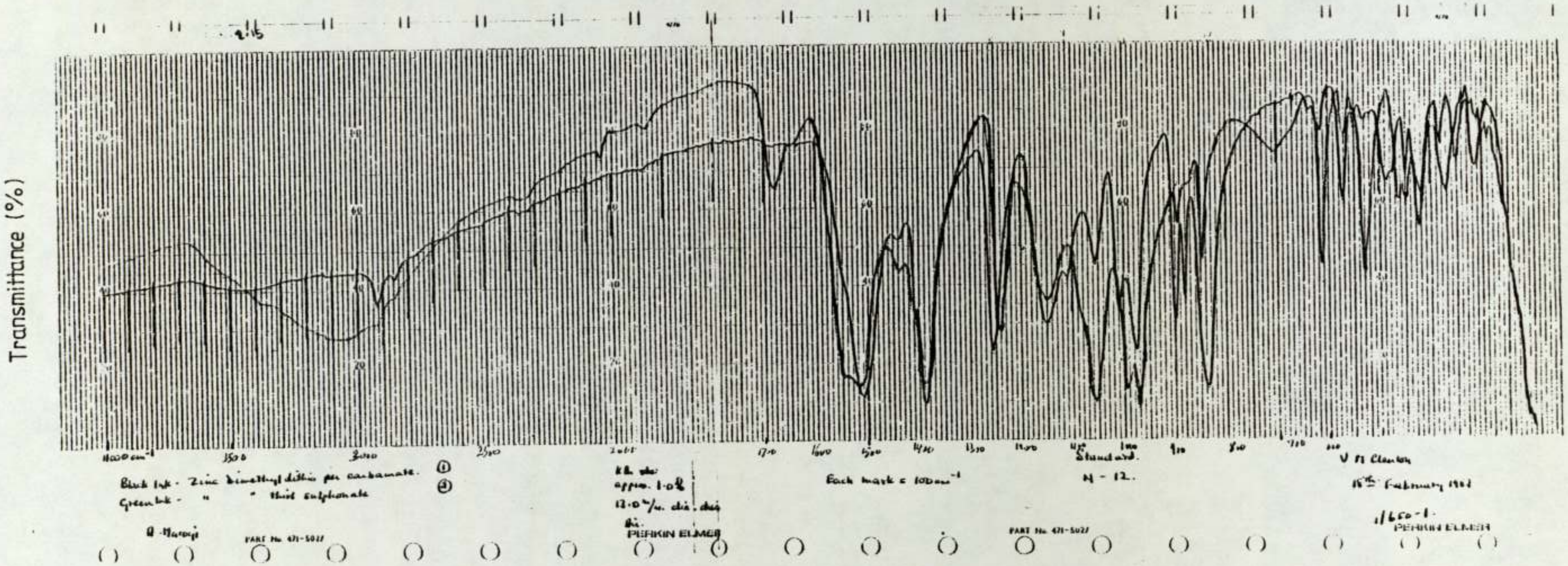


Figure 2.15 Infra-red spectrum comparison of zincdimethylthiocarbomylsulphenate (ZDMCSO) and zincdimethylthiocarbomylsulphinate ($ZDMCSO_2$)

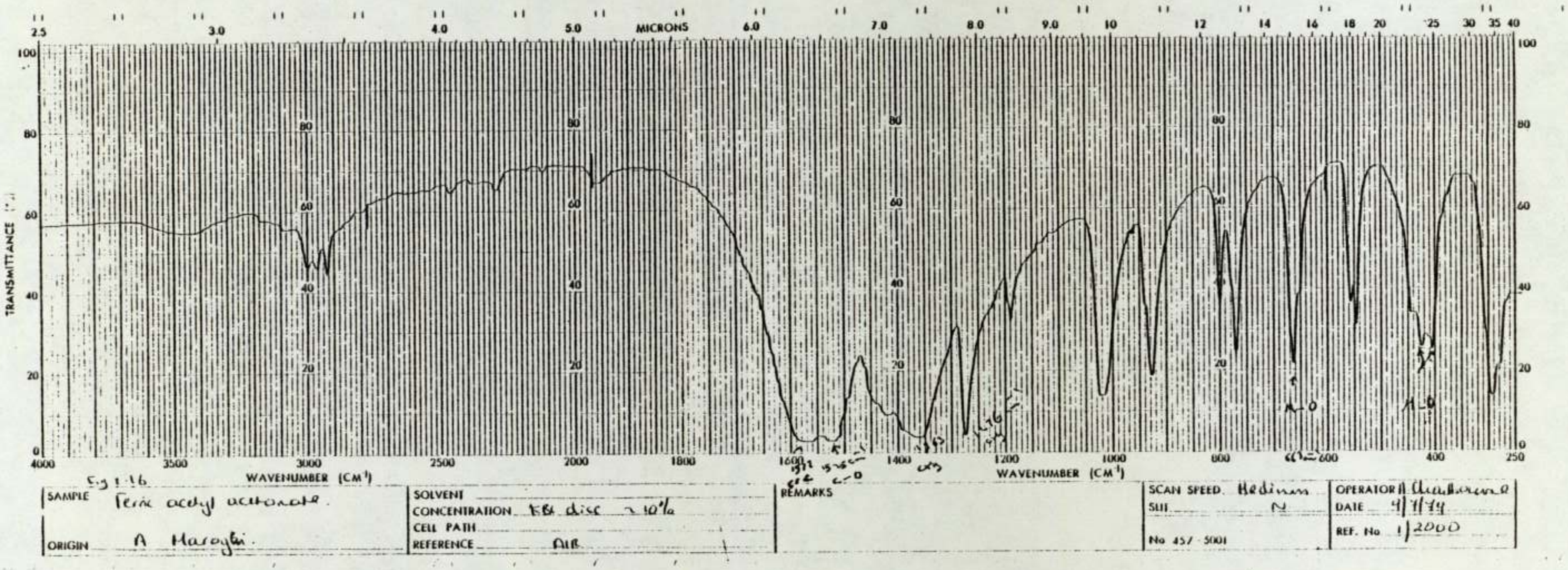


Figure 2.16 Infra-red spectrum of Iron III acetylacetonate

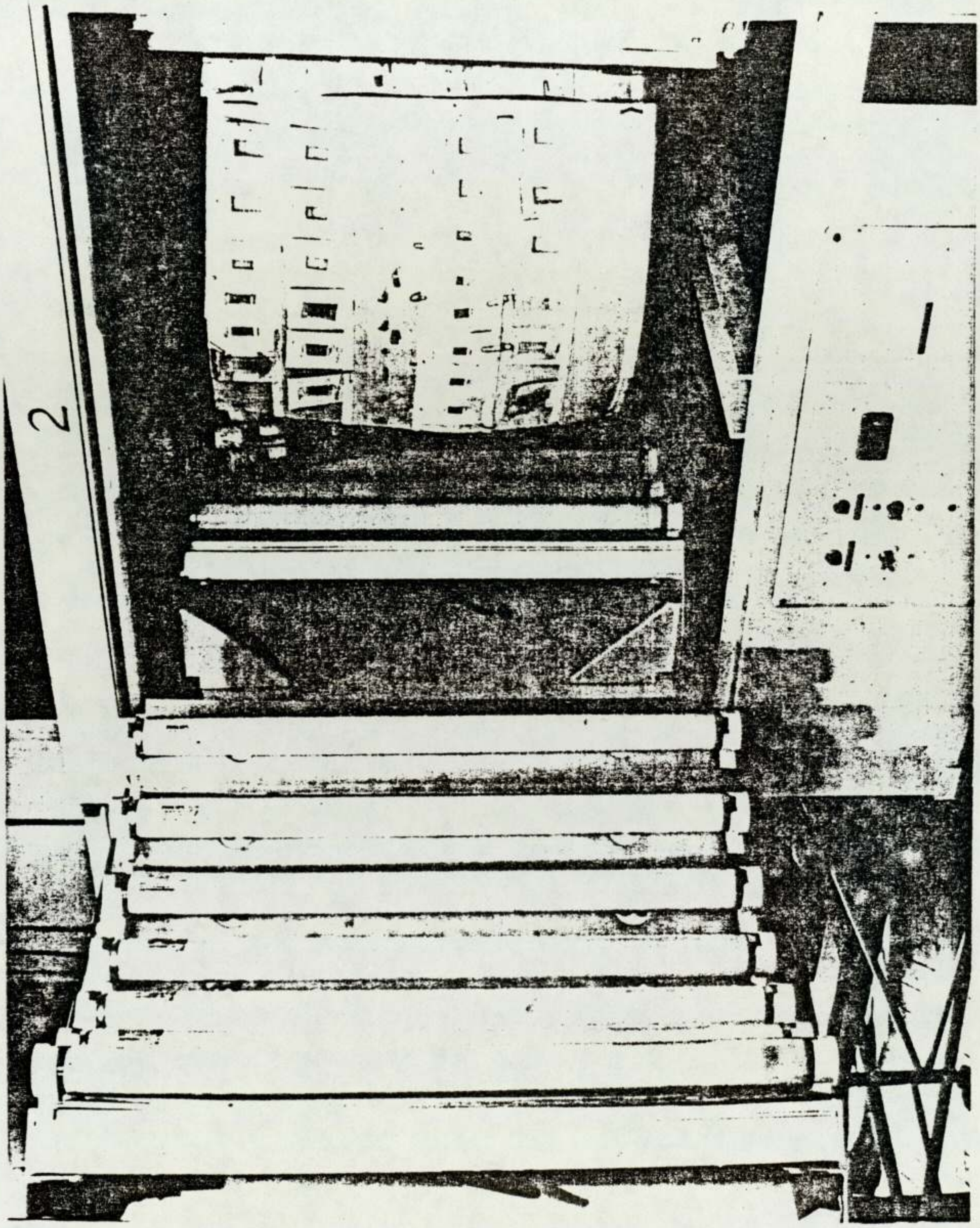


Fig. 2:17 UV-exposure cabinet

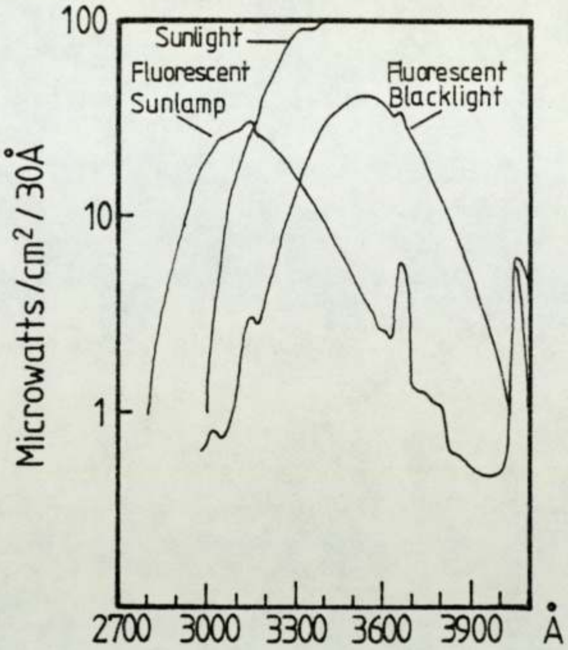


Figure 2:18 Ultra violet spectral distributions of the fluorescent sunlamp and fluorescent black light (Ref.104)

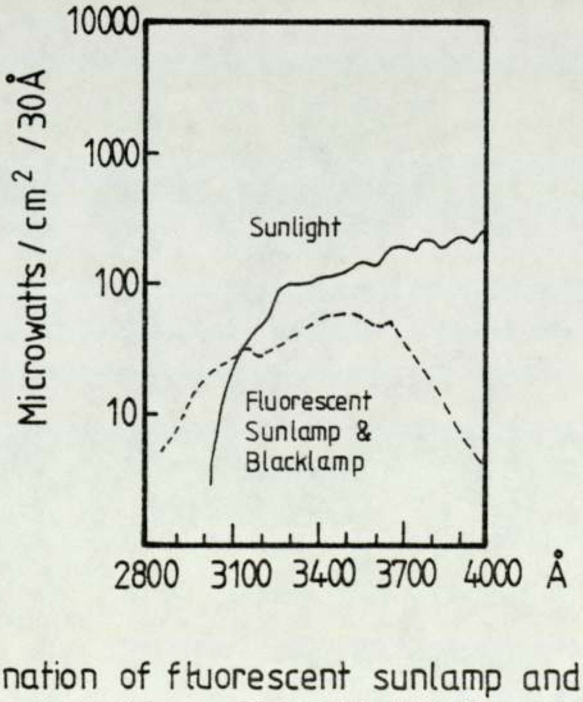


Figure 2:19 Combination of fluorescent sunlamp and blacklamp compared with sunlight (Ref.104)

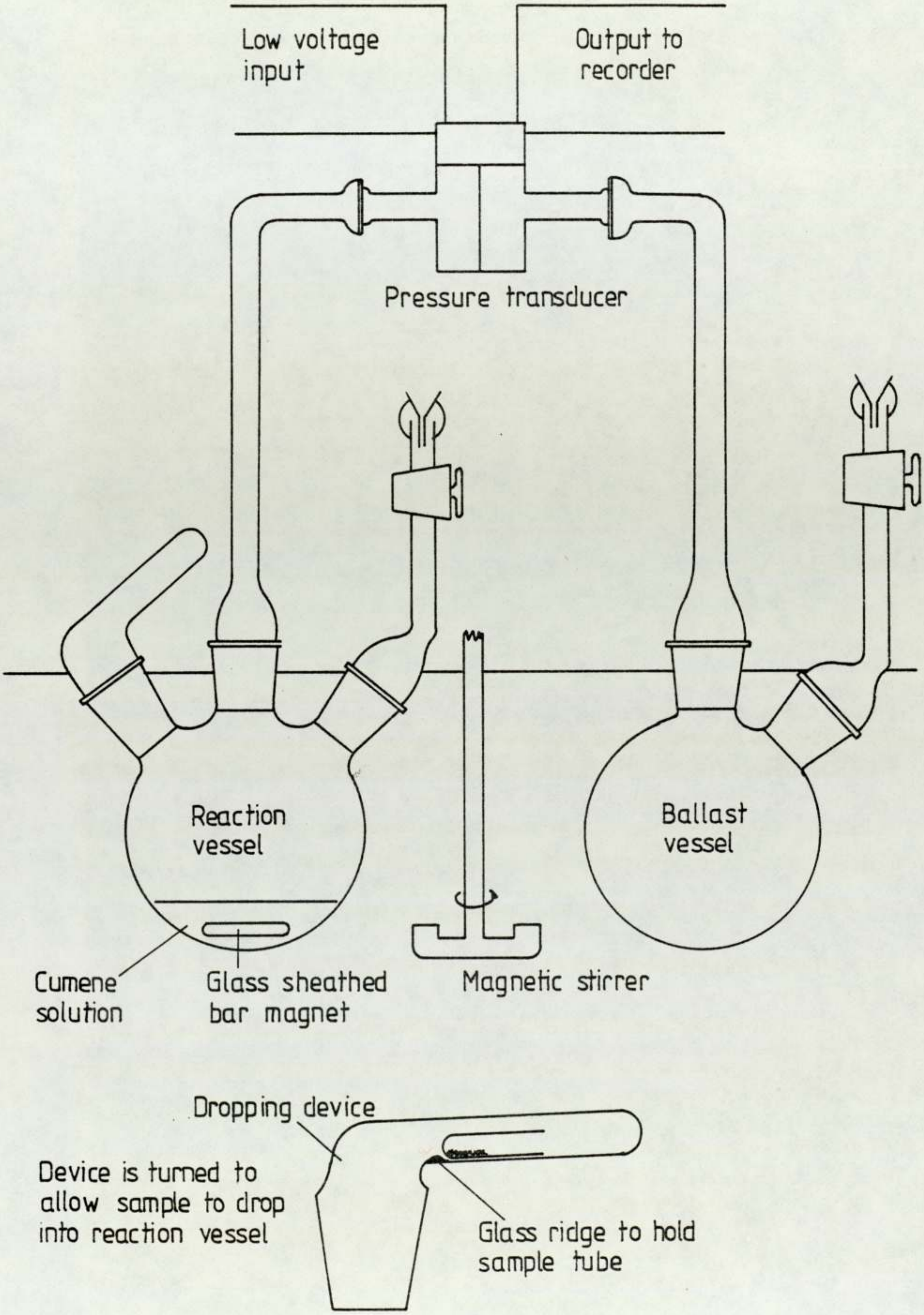


Figure 2:20 Oxygen absorption apparatus

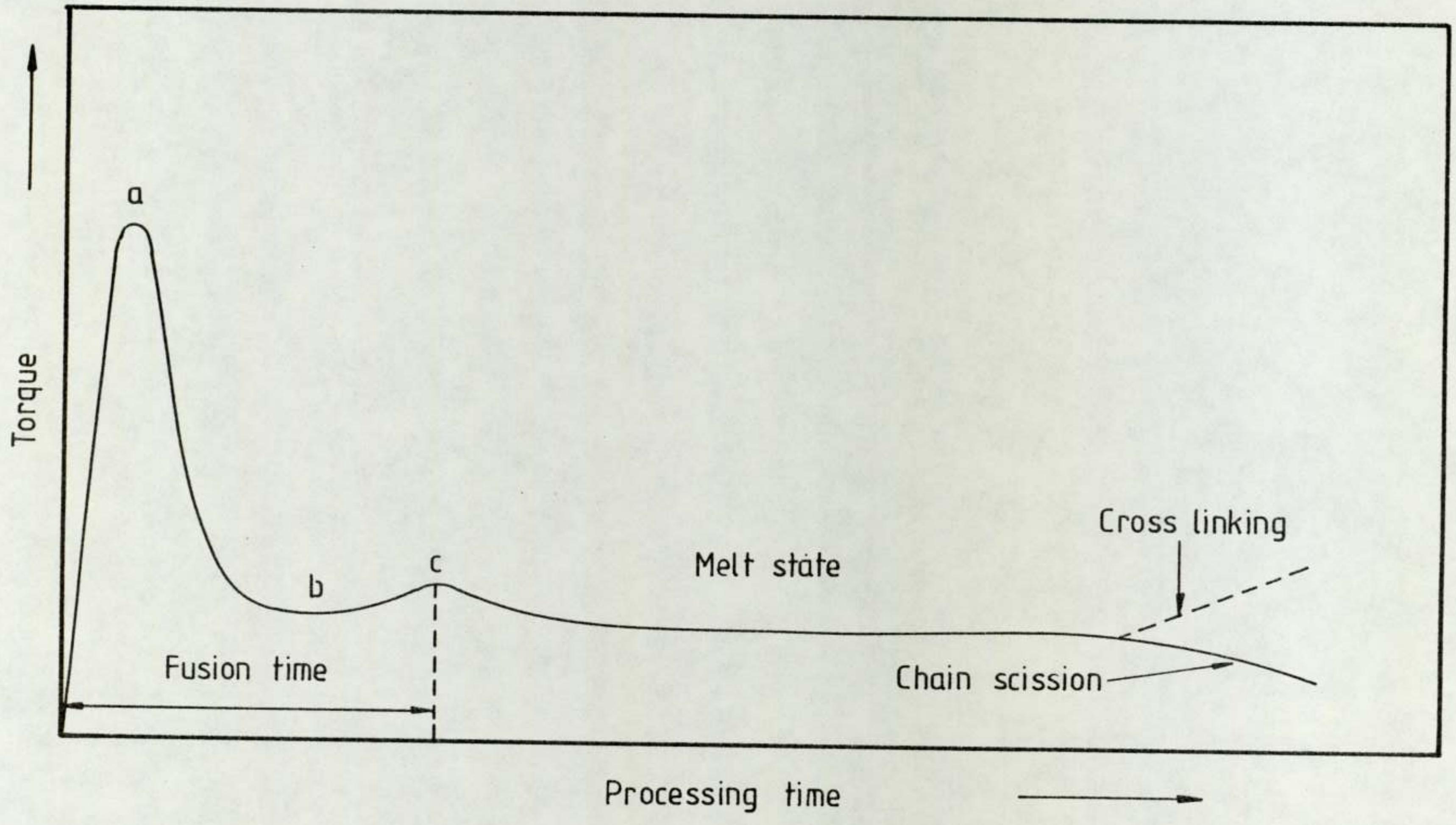


Figure 2:21 Changes in torque with time during processing of polyolefins (a typical curve)

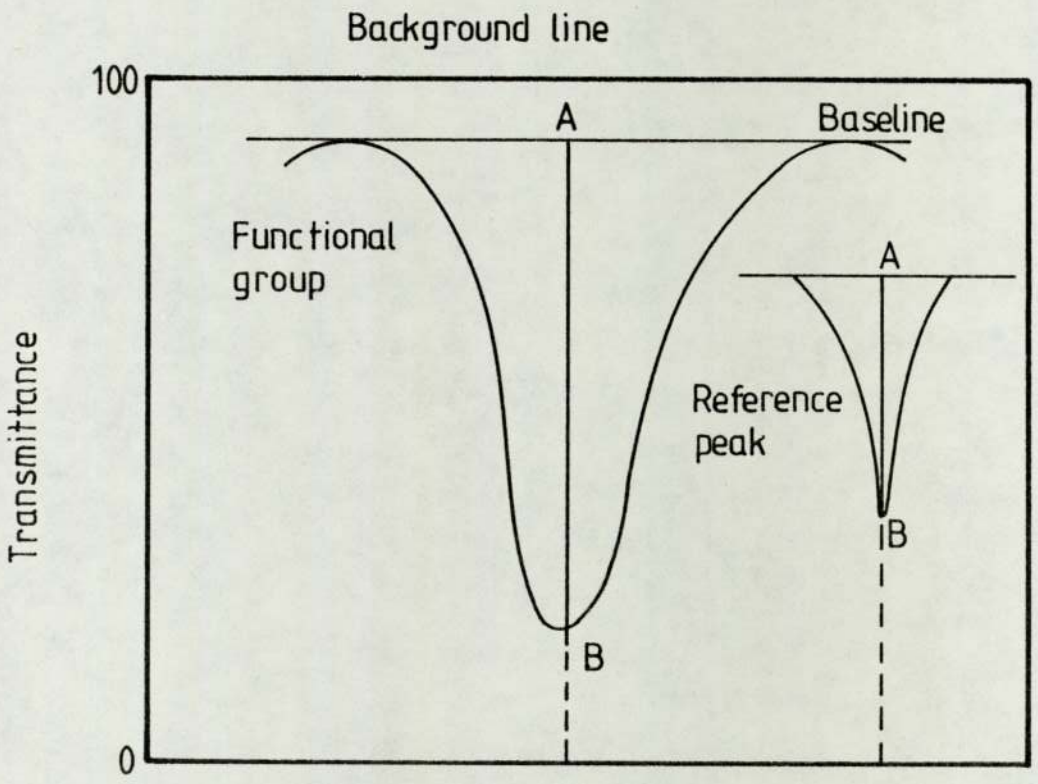


Figure 2:22 Functiönal group index measurement (by baseline technique)

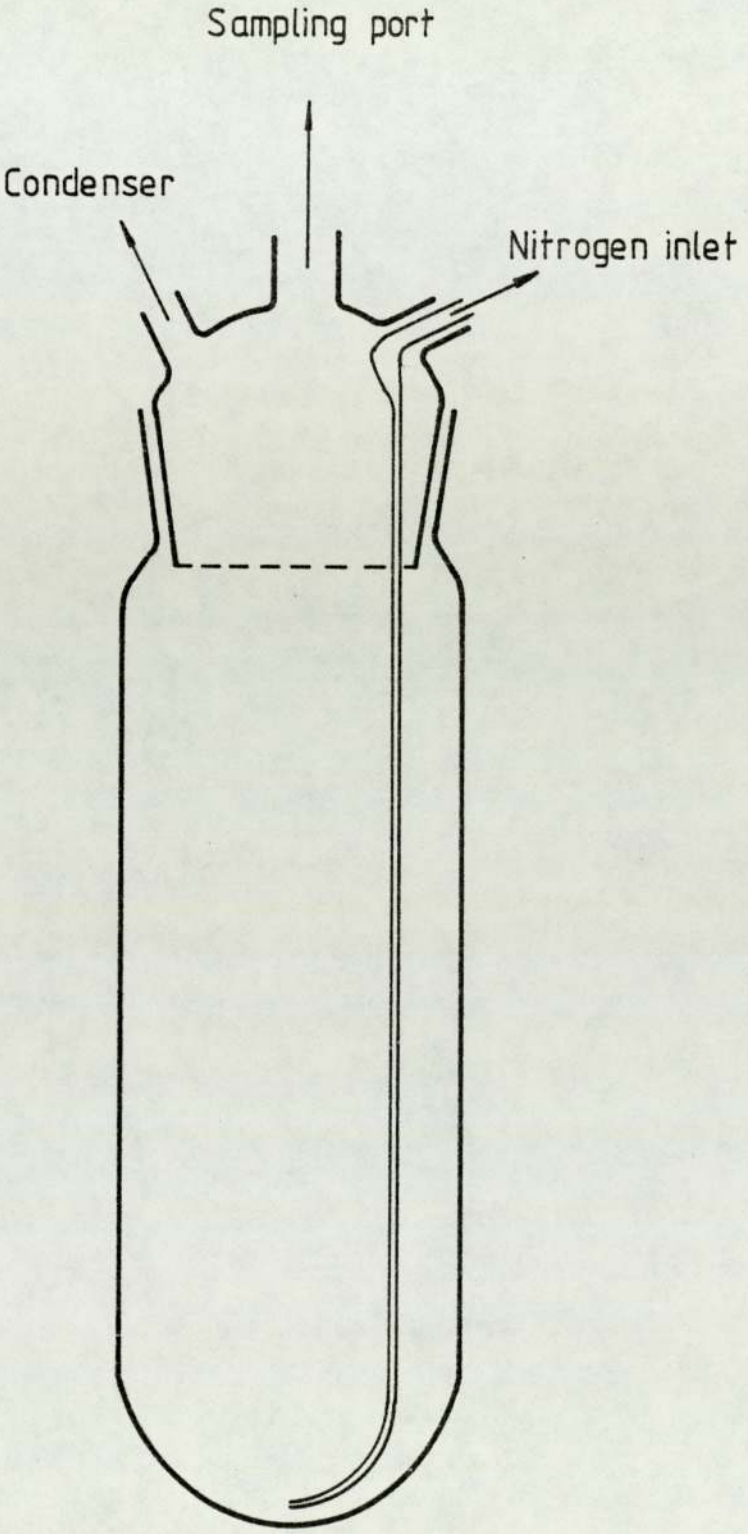


Figure 2:23 Apparatus for decomposition studies of CHP

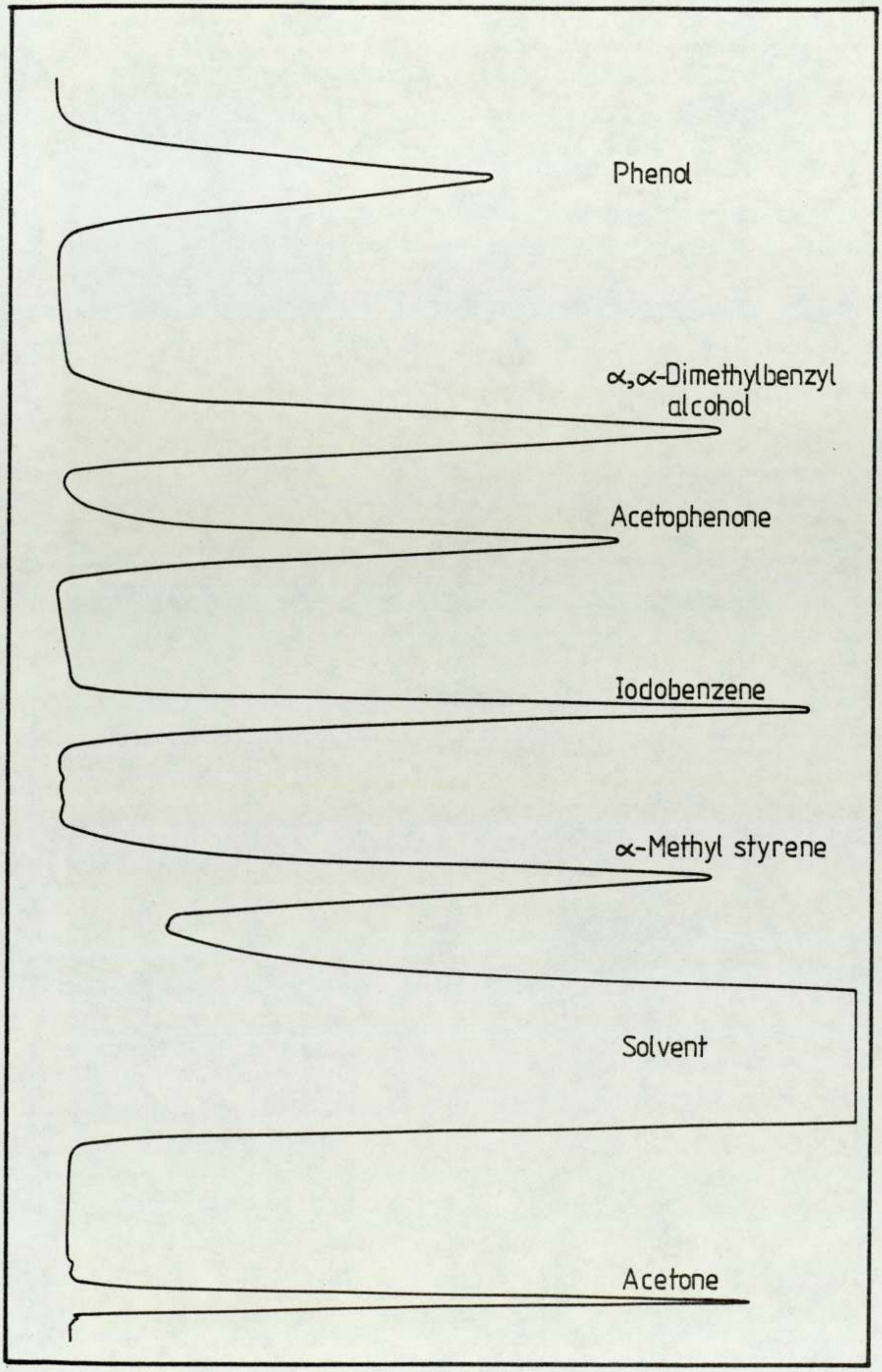


Figure 2:24 Analysis of the decomposition products of Cumene hydroperoxide.

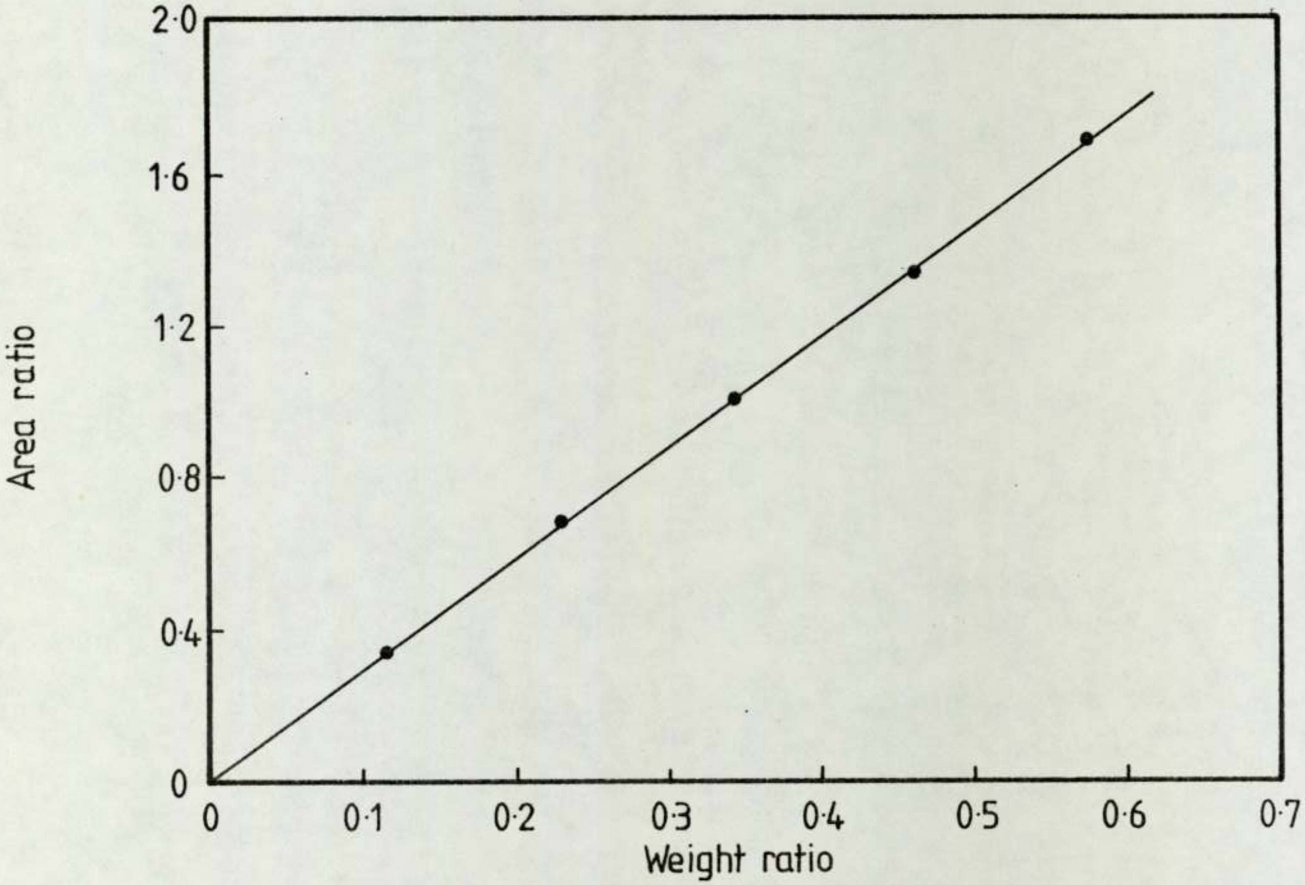


Figure 2:25 Calibration graph for α-methyl styrene

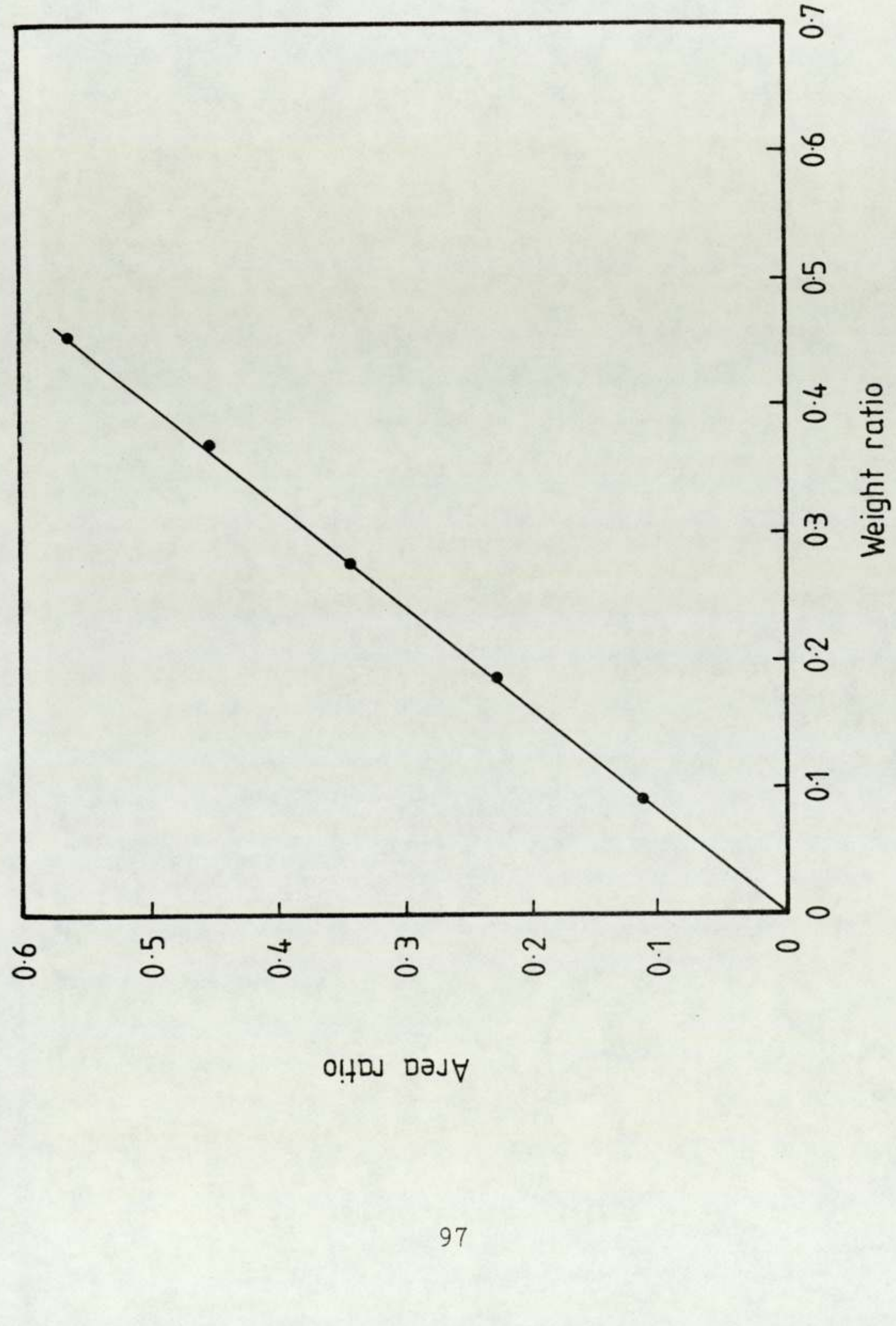


Figure 2:26 Calibration graph for phenol

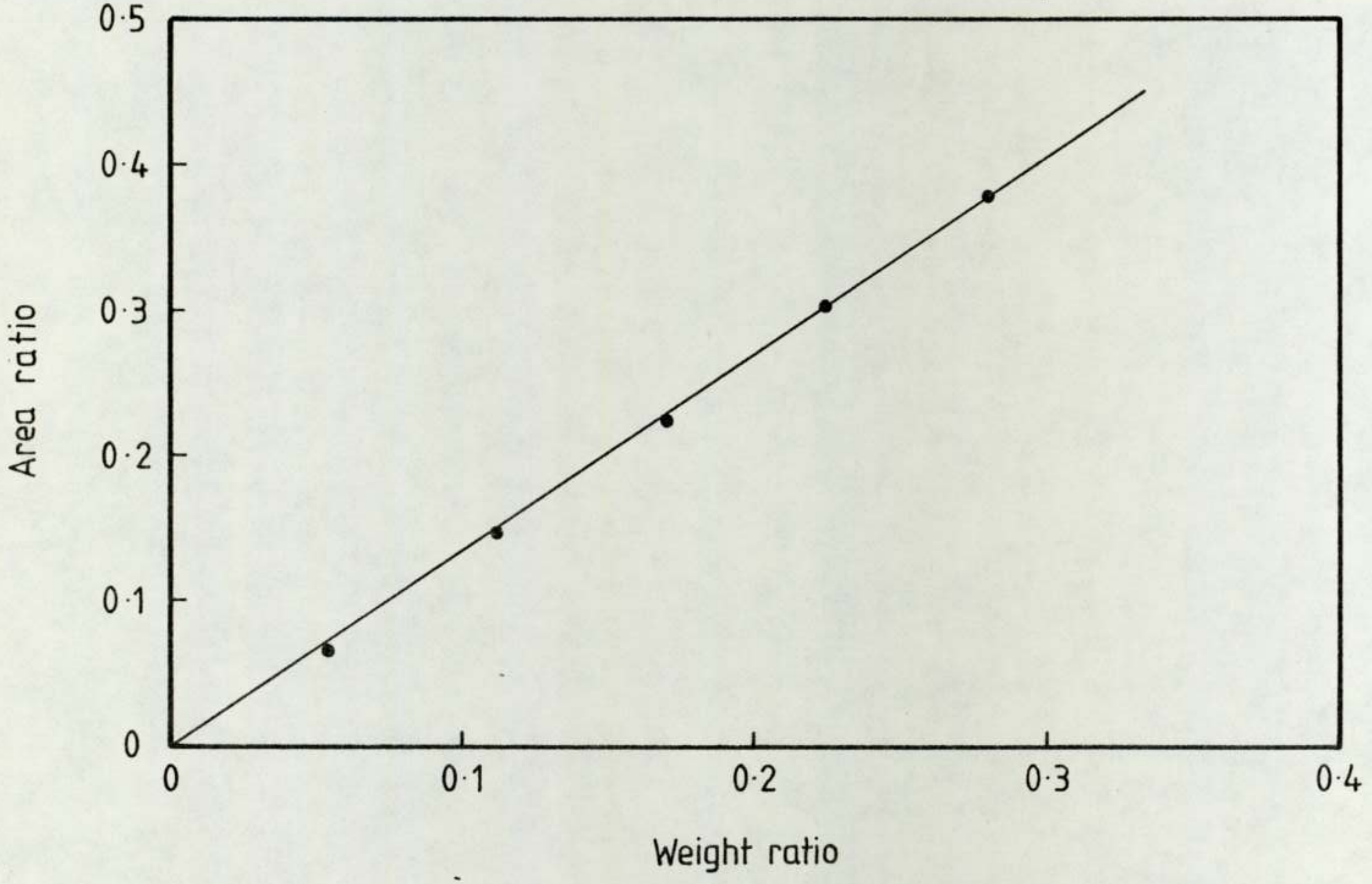


Figure 2:27 Calibration graph for acetone

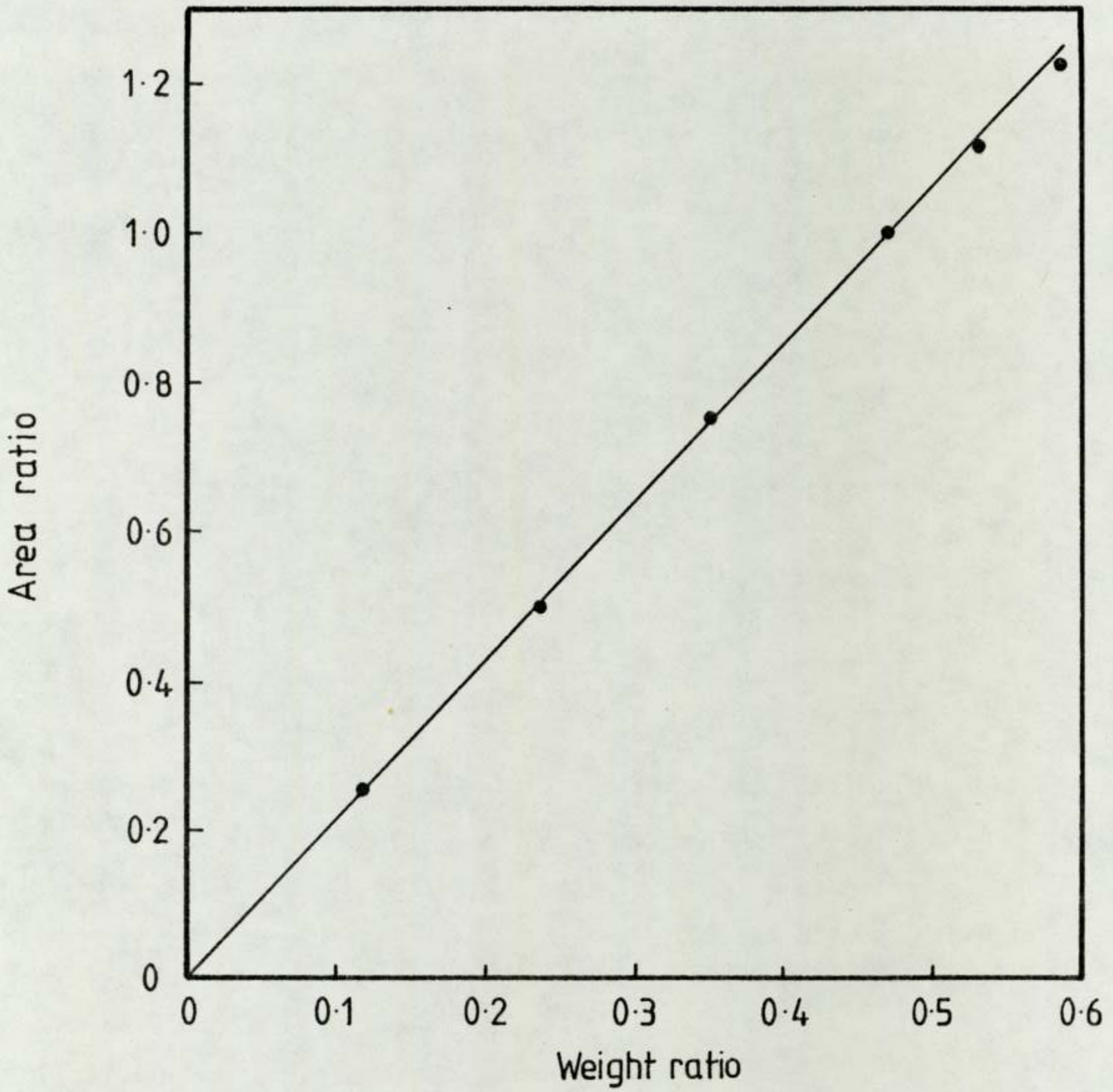


Figure 2:28 Calibration graph for aceto phenone

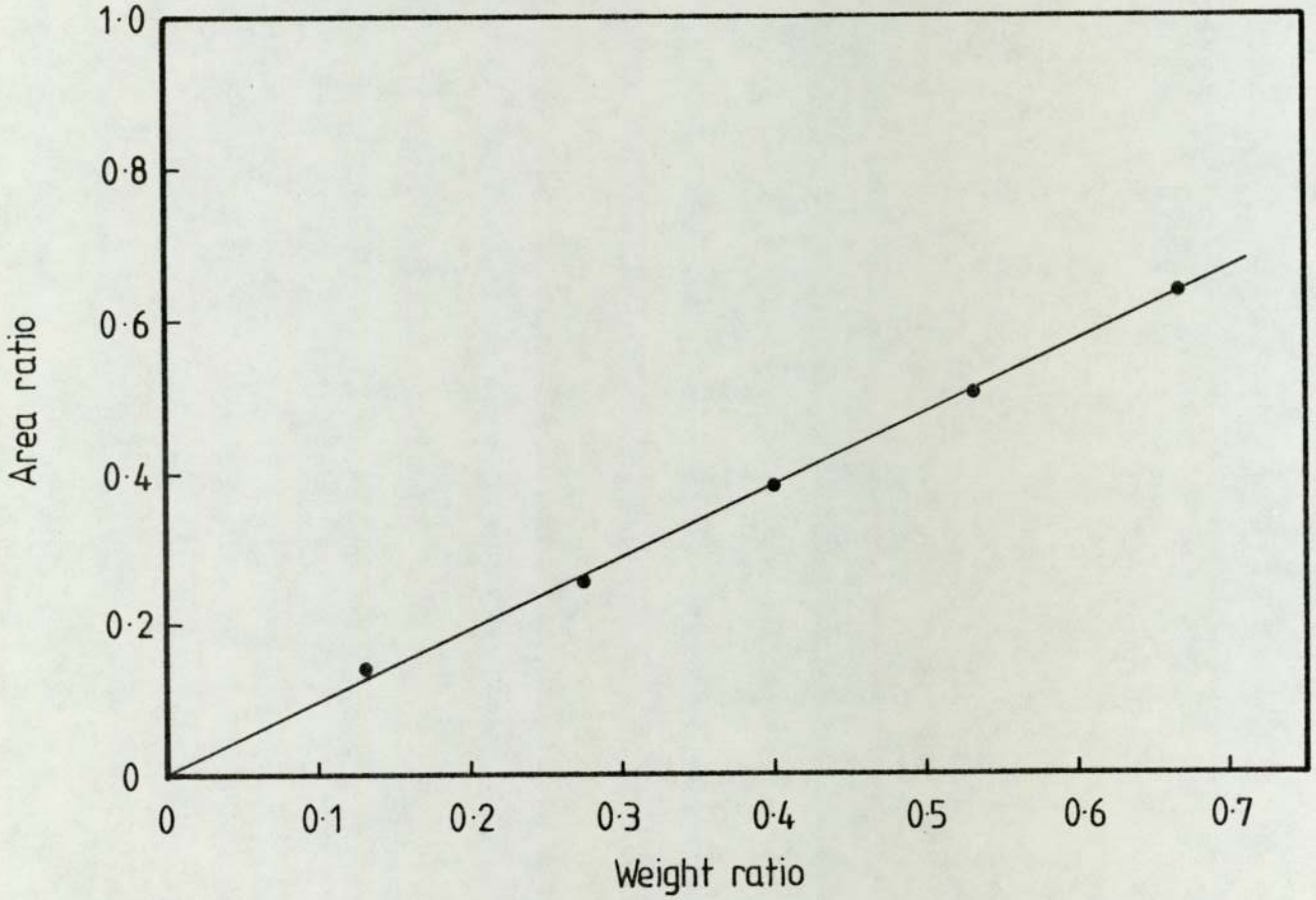


Figure 2:29 Calibration graph for α-cumyl alcohol

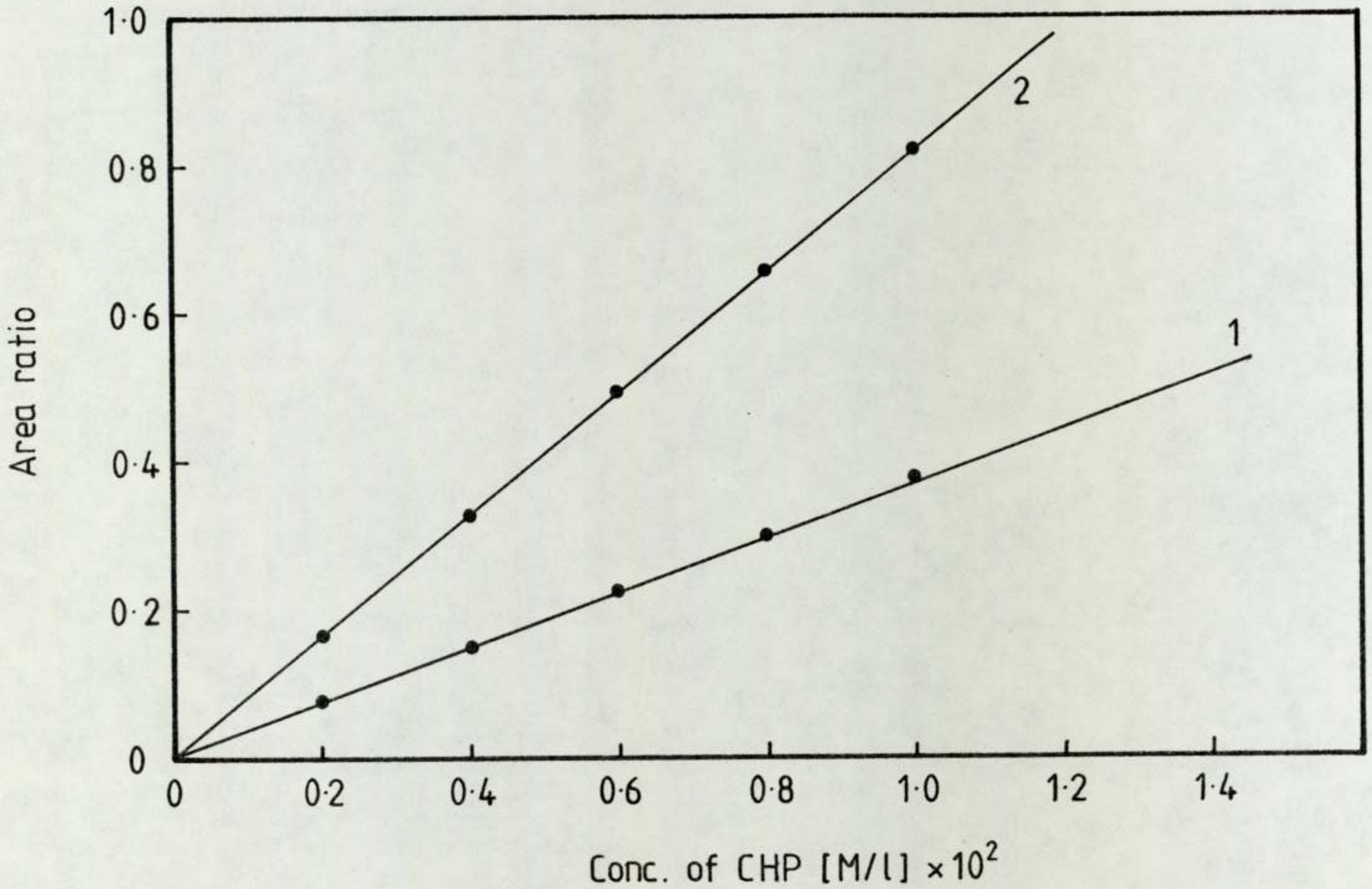


Figure 2:30 Calibration graph for the yield of ∝ -cumyl alcohol (1) during decomposition of CHP on GLC column (2) affected by ph_3 p prior to GLC analysis.

CHAPTER THREE

THE INFLUENCE OF IDEAL AND CONVENTIONAL PHOTOACTIVATORS ALONE AND WITH ANTIOXIDANTS ON THE PHOTO-OXIDATIVE STABILITY OF LDPE

3.1 Object

In this chapter the photo-oxidative stability of LDPE is examined in the presence and absence of ideal (ferric dimethyldithiocarbamate FDMC) and conventional (ferric acetylacetonate FAcAc) photoactivators. The effect of combinations of each of these activators with a peroxide decomposer (zinc diethyldithiocarbamate ZDEC, nickel diethyldithiocarbamate NDEC and tetraethylthiuramdisulphide TETD) or a U.V. absorber (2-hydroxy 4-octoxybenzophenone HOBP) on photo-oxidative stability of LDPE is also evaluated.

Typically the additive is mixed with unstabilised LDPE and processed for various lengths of time in a closed (CM) and open (OM) mixer of the torque-rheometer at 160°C. Test films were then prepared from the crepe PE samples by compression moulding. Sections of comparable thickness (2×10^{-2} cm) were cut from these films and were exposed in the U.V. cabinet and subsequently tested. Spectral changes occurring during the course of the U.V. exposure are followed by infra-red and ultra-violet spectrophotometry. Lifetimes of these tested films are also determined under these photo-oxidative conditions.

3.2 Results

3.2.1 The Effect of Different Additives on Melt Stability of LDPE

The effect of a delay-action photoactivator (FDMC) on the oxidative stability of LDPE during processing is compared with that of a conventional photoactivator (FAcAc) at the same molar concentration in Figure 3.1. Typical U.V. absorber (HOBP) and peroxide decomposing antioxidants (ZDEC, NDEC and TETD) are included for comparison. It is clear that the delay-action photoactivator has a powerful melt stabilising effect on LDPE at the concentration used. Over a period of 40 minutes processing at 160°C in an open mixer, the initial carbonyl index of the polymer remained sensibly constant at a value of 0.29. Other transition metal dithiocarbamates and the disulphide (TETD) were similarly effective melt stabilisers. The conventional photoactivator (FAcAc), on the other hand, showed a steady increase in the initial carbonyl index with processing time indicating considerable oxidation during processing. The effect of U.V. absorber (HOBP) on the oxidative stability of LDPE during processing is only minor when compared with metal dithiocarbamate complexes or the corresponding disulphide.

Changes in torque of LDPE containing different additives during processing are shown in Figure 3.2. It is clear that in the presence of FDMC, the torque remains almost constant,after an initial decrease,for the rest of the processing time. For the polymer containing FAcAc, a remarkable decrease in torque is observed in the later stages of processing. This observation agrees with the previous observation of the initial carbonyl index (Figure 3.1) and suggests that FAcAc causes considerable oxidation to the polymer during processing while FDMC acts as a good melt stabilizer in a way similar to the related peroxide decomposers zinc and nickel dithiocarbamates.

3.2.2 Photo-oxidative Stability of Unstabilized LDPE

Infra-red absorption spectra of unstabilized PE film, before and after photo-oxidative ageing (Figure 3.3) shows changes in the absorption regions of 3600-3000 cm^{-1}, 1850-1650 cm^{-1} and 1650-850 cm^{-1}. These changes have been found to correlate directly with the degree of polymer oxidation(18,113).

The band at 3380 cm^{-1}, typical of hydrogen bonded alcohol and hydroperoxide groups, is initially present in the polymer but is of weak intensity. As irradiation proceeds, the band around 3400 cm^{-1} gradually becomes broader indicating formation of more hydroxy compounds as a result of photo-oxidation. No free hydroperoxide groups (3558 cm^{-1}) could be detected by the I.R. during photo-oxidation although such groups can be detected in thermally oxidised films(18).

Photo-oxidised PE film shows a complex absorption in the carbonyl region (1850-1650 cm^{-1}) with a large number of bands, the intensity of which increased with exposure time. Bands in this region are due to different types of carbonyl groups formed during photo-oxidation (see Table 3.1). The initial weak carbonyl absorption around 1725 cm^{-1} in the unoxidised film has been shown to be due to methyl ketone(71c,114). During prolonged irradiation, the contribution of acidic (1715 cm^{-1}) and aldehydic (1735 cm^{-1}) species increases(114,115). The formation of acid in highly photo-oxidised films is further substantiated by the occurrence of another band at 1185 cm^{-1} due to single bonded C-O vibration of the carbonyl group(116).

Changes in the region of unsaturation (1650-850 cm^{-1}) are mainly due to vinylidene (889 cm^{-1}) and vinyl (909 cm^{-1}) groups. During photo-oxidation, vinylidene absorption decays gradually with a concomitant increase in the vinyl absorption. The internal double bond (vinylene at 1645 cm^{-1}), which is initially weak, also increases during U.V. irradiation.

3.2.3 Effect of Processing Conditions on Photo-oxidative Stability of LDPE With and Without Additives

Figure 3.4 shows the effect of processing conditions on photo-oxidative stability of unstabilized PE. It is clear that increasing processing time reduces markedly the U.V. stability of the polymer. Processing in the presence of oxygen excess, causes a dramatic reduction in the lifetime of the polymer on subsequent U.V. irradiation. Table 3.2 shows the lifetime of PE processed under different conditions.

The effect of processing severity on photo-oxidation of LDPE film containing ideal and conventional photoactivators is shown in Figure 3.5. It is clear that more severe processing (30 min open mixer) drastically reduces the lifetime of PE containing FAcAc. The high initial carbonyl index value for the 30 minute processed sample in the open mixer clearly indicates that FAcAC could not resist the processing conditions and considerable oxidation takes place during processing as a result of its thermal decomposition. Carbonyl groups start to build up rapidly during the early stages of U.V. exposure in an auto-accelerating mode. The ideal photoactivator (FDMC), like other metal dithiocarbamate complexes, affords a clear stabilization even under severe (30 min OM) processing conditions (under milder processing conditions (10 min CM) the photo-induction period, PIP = 320 h). After the initial photo-induction period, PE film containing FDMC shows autocatalytic behaviour similar to that offered by FAcAc.

Stabilization afforded by the disulphide TETD (Figure 3.6) indicates that TETD becomes a better photostabilizer when processed in the presence of an excess supply of oxygen. Figure 3.6 shows that the effect of processing in the presence of excess air is almost similar to that of doubling the concentration. (curves 3 and 7 Fig 3.6)

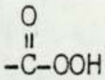
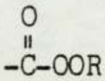
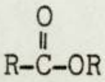
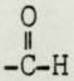
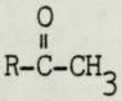
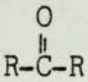
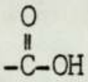
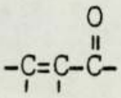
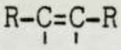
Functional Group	Structure	cm^{-1}	Ref
-OOH free	-OOH	3558	113,115
Polymeric associated -OH	-OH	3380	18
Per acid	 $-\overset{\overset{O}{\|}}{C}-OOH$	1785	113
Per ester	 $-\overset{\overset{O}{\|}}{C}-OOR$	1765	113
Ester	 $R-\overset{\overset{O}{\|}}{C}-OR$	1745	113,115
Aldehyde	 $-\overset{\overset{O}{\|}}{C}-H$	1730	113,115
Terminal or methyl ketone	 $R-\overset{\overset{O}{\|}}{C}-CH_3$	1725	114
Internal ketone	 $R-\overset{\overset{O}{\|}}{C}-R$	1720	113,115
Carboxylic acid	 $-\overset{\overset{O}{\|}}{C}-OH$	1710-1715	113,115
α-β unsaturated ketone	 $-\underset{\mid}{C}=\underset{\mid}{C}-\overset{\overset{O}{\|}}{C}-$	1685	115,119
Internal double bond	 $R-\underset{\mid}{C}=\underset{\mid}{C}-R$	1645	115
C-O in carboxylic acid	C-O	1185	116
C-C in amorphouse region	C-C	1080	120
Vinyl group or terminal double bond	$RCH=CH_2$	909	115
Vinylidene group	$RRC=CH_2$	889	115

Table 3.1 Functional groups which occur in PE before and after UV irradiation

Condition	Embrittlement Time (in hours)
Unprocessed	2200
5 min OM	2010
10 min OM	1930
20 min OM	1840
30 min OM	1805
40 min OM	1720

Table 3.2 UV lifetime of PE film processed under different conditions

Severe processing conditions (30 min OM) reduces considerably the effectiveness of HOBP on subsequent U.V. irradiation (Figure 3.7 curves 3 and 4); HOBP effectively retards photo-oxidation in a mildly processed sample. ZDEC is equally as effective as it is in mildly processed sample (Figure 3.7 curve 5).

3.2.4 Effect of Varying the Concentration of Additives on U.V. Stability of LDPE

The effect of varying the concentration of FAcAc on photo-oxidative stability of LDPE is shown in Figure 3.8. At all concentrations examined, FAcAc showed a powerful pro-oxidant effect. The rate of carbonyl formation is auto-accelerating and a maximum rate of photo-oxidation is observed at the optimum concentration of 2.5×10^{-4} mol/100g. The iron complex based on sulphur chelates (FDMC), on the other hand, showed quite interesting features (Figure 3.9). At relatively high concentrations of FDMC, photosensitisation can be achieved after a substantial induction peroid (Figure 3.9 curves 7.5 and 10). This is an important objective of an ideal activator system. At low concentrations of FDMC, however, a pro-oxidant effect predominates (Figure 3.9 curves 0.5-2.5). The optimum concentration range of FDMC which gives the maximum rate of photo-oxidation (minimum embrittlement time) lies in the range 1.25×10^{-4} mol/100g (see Figure 3.9).

Other metal dithiocarbamates (ZDEC and NDEC) show increasing stabilization effect with concentration (Figures 3.10 and 3.11). However, at low concentrations they appear to have almost no effect (curves 1.25 and 0.25 of Figures 3.10 and 3.11 respectively). Similarly, the disulphide (TETD) is found ineffective at concentrations of 2.5×10^{-4} and below (curves 0.25-2.5 in Fig. 3.12). At high concentrations, however, very effective stabilizing is observed (curves 5 and 10 in Figure 3.12).

3.2.5 Screening Effect of Additives on Photo-oxidation of LDPE

Figure 3.13 compares the effectiveness of antioxidants and activators as additives and as screens (at the same molar concentration) during the photo-oxidation of LDPE. In the screening experiment 30 minute processed (OM) unstabilised films were exposed behind an identically processed film but in the presence of the additive in question. The unstabilized film can only receive light which has passed through the stabilizer containing film. It is clear from Figure 3.13 that the contribution of screening to the stabilizing effect is minimal compared to the effect when the antioxidants and activators are incorporated into the polymer as additives. The rate of photo-oxidation at the later stages (after the initial rise of carbonyl) is reduced by NDEC and HOBP when used as screening agents (curves 3 and 4 in Figure 3.13 respectively) compared to that of the control. HOBP is a better U.V. screen than NDEC while FDMC has virtually no screening effect in LDPE. The protective effect of these additives on the photo-oxidation of LDPE is therefore only in part due to screening of U.V. light. FAcAc and ZDEC like FDMC do not seem to screen U.V. light to any appreciable extent (Figure 3.13 curve 2).

3.2.6 Mode of Decay of Additives in Polymer During U.V. Exposure

The antioxidant photo-activator system (FDMC) differs from conventional photoactivator (FAcAc) in one particularly important aspect. That is the photo-activation does not commence until the antioxidant metal complex inhibitor (FDMC) has been photolytically destroyed. In this respect FDMC is similar to other metal dithiocarbamate complexes e.g., NDEC and ZDEC, which show auto-accelerating decay of their U.V. absorption bands (Figure 3.14) on U.V. irradiation. The decay of these bands are completed almost at the end of the photo-oxidative induction period(77,121). Spectral characteristics of the iron complex could not be detected in the polymer after processing. However, its colour was still observable in the processed film and visual comparison of the above film with pressed PE containing FDMC at various concentrations indicated that about 0.07% of the complex was still present after processing. The colour faded within a few hours of U.V. exposure (dotted line in Figure 3.14) and the induction period was correspondingly short. In a separate experiment in which a much higher concentration of the iron complex was used, an induction period similar to those found for Ni and Zn complexes was observed(43).

The antioxidant efficiency of NDEC is found to be much greater than ZDEC or FDMC at the same molar concentration and under the same conditions. Concentration of additives in PE film after processing is shown in Table 3.3.

3.2.7 The Effect of Two Component Systems on Photo-oxidation of LDPE

Figure 3.15 shows the effect of FDMC concentration on the photo-oxidation of LDPE in the absence and presence of 2.5 x 10^{-5} mol/100g NDEC. Addition of a very small amount of NDEC causes a dramatic change in the polymer. The sharpening of the rate of photo-oxidation observed by FDMC alone becomes, after the addition of NDEC, very pronounced and the length of the induction period can be varied within a wide range. This effect is quite significant when the polymer is used in agricultural mulching film. A similar effect, but to a lesser extent, was also observed on reducing the concentration of NDEC in the combination (Figure 3.16). The variation of embrittlement times of LDPE with FDMC concentration in the absence and presence of different concentrations of NDEC is shown in Figure 3.17. It is clear that identical

Antioxidant	Amount of antioxidant remaining in film	
	Concentration (M/100g)	Percentage
ZDEC	1.42×10^{-4}	56.80
NDEC	1.73×10^{-4}	69.29
TETD	0.79×10^{-4}	31.60
HOBP	0.84×10^{-4}	33.36
FDMC	Very low	-
FAcAc	-	-

Table 3.3 Persistance of additives in LDPE film processing (10,CM) at 160°C and compression moulding.Initial concentration of additive is 2.5×10^{-4}M/100g

embrittlement times can be achieved by using two different combinations of the stabilizing and activating components. The optimum concentration for the lowest embrittlement time is found at 2.5×10^{-4} FDMC/0.25×10^{-5} NDEC and 5×10^{-4} FDMC/ 0.125×10^{-4} NDEC (concentration in mol/100g). These results could be very useful in designing photodegradable mulching film of controlled lifetime for the northerly climate where the sunshine availability is very low.

The addition of ZDEC to LDPE containing FDMC also effects the stability of the polymer. Figures 3.18-3.20 show that the length of the induction period increases with the increasing concentration of ZDEC in the combination. However, the rate of photo-oxidation at the end of the induction period is in general lower compared with that containing a single component system (FDMC). As a result, embrittlement times are longer than that obtained when using FDMC alone (Figure 3.21). This achievement could be very important in the design of a polymer of controlled lifetime under severe exposure conditions e.g., in the Middle East.

Figures 3.22-3.26 relate the carbonyl formation in LDPE containing different concentrations of FDMC/TETD with time of U.V. irradiation. These figures show that the induction period, ranging from 50 hours up to 500 hours, can be achieved using this two component system. As in the case of NDEC/ FDMC combinations (Figures 3.15 and 3.16), very sharp rates of oxidation are observed at the end of the induction period.

The effect of increasing the TETD concentration in the combination is to increase the stability of the polymer as revealed from the lengthening of the induction period (see Figure 3.27). The higher the concentration of FDMC in the combination, the faster the rate of photo-oxidation at the end of the induction period (see Figures 3.22-3.26). Thus it seems that the stabilizer (TETD) concentration primarily determines the induction period while the activator concentration determines the rate of the slope of the photo-oxidation curve and hence the embrittlement time. The variation of the embrittlement time of LDPE containing TETD with concentration of FDMC is shown in Figure 3.28.

The same behaviour is found for the HOBP/FDMC combination. Figures 3.29-3.31 show the variation of carbonyl index of PE in the presence of different molar ratios of FDMC/HOBP with time of U.V. irradiation. Induction periods ranging from 150-350 hours are achieved using this system. The rate of photo-oxidation is sharp at high concentrations of FDMC in the combination. As a result of the action of these additives (FDMC/HOBP), embrittlement times ranging from 450 up to 1750 hours for LDPE are obtained (see Figure 3.32).

It was shown in Figure 3.7 that FAcAc causes auto-acceleration of the rate of photo-oxidation and correspondingly reduces the embrittlement of the polymer. It was also shown in Figures 3.1 and 3.2 that considerable oxidation occurs during processing in the presence of FAcAc. The oxygen metal complex (FAcAc), therefore, satisfies one of the two requirements (see Chapter One, Section 1.2)of the ideal photosensitiser; rapid and autoaccelerating mode of photo-oxidation. Thus it has little technological value when used alone due to its thermal pro-oxidant behaviour. However, this disadvantage can be suppressed in theory by the use of appropriate stabilizers which act as restrainers for thermal oxidation during processing. Figures 3.33-3.35 show the effect of adding a hydroperoxide decomposer to FAcAc on photo-oxidation of LDPE. At the three different concentrations of ZDEC used, an induction period is observed during U.V. irradiation. This again is proportioned to the concentration of ZDEC in the polymer. The most interesting fea ture observed here is when the concentration of ZDEC in the combination is 5 x 10^{-4} mol/100g (Figure 3.34). At this particular concentration, the requirements of an ideal photodegradable plastic for agricultural mulching film can be achieved; a substantial controlled induction period and a rapid rate of photo-oxidation after the induction period. The higher the concentrations of FAcAc in this combination, the faster is the rate of photo-oxidation. Figure 3.36 shows the effect of this combination (different molar ratios) on the lifetime of LDPE. It is clear that the minimum time to embrittlement occurs at much shorter times of U.V. irradiation compared with the other two component systems studied here. These results could be very useful in developing mulching films for the short life crops.

3.3 Discussion

3.3.1 The Effect of Different Additives on Melt Stability of LDPE

The significance of hydroperoxdies as the key initiators during both thermal and photo-oxidative processes of LDPE has been well established(18,43,44). In view of this evidence, it follows then that any additive which can remove peroxides (or their decomposition radicals) during processing will be efficient melt stabilizers. Metal dithiocarbamates and the corresponding disulphides (TRTD) are known to destroy the hydroperoxides by catalytic (ionic) mechanism involving Lewis acid generated in a series of initial stoichiometric reactions with hydroperoxides(65,81,123,124). They are, therefore, expected to be powerful melt stabilizers in LDPE. This has been confirmed here as shown in Figure 3.1. The formation of hydroperoxides in LDPE is completely inhibited during processing in the presence of FDMC, NDEC, ZDEC and TETD (Figure 3.1). No change in the value of the initial carbonyl index is observed over 40 minutes processing. By contrast, a conventional photoactivator (FAcAc) accelerates peroxide formation and typical U.V. absorber (HOBP) is virtually without effect under the same conditions.

Changes in torque of LDPE containing different additives during thermal processing offer an alternative means of measuring the melt stabilizing activity of those additives.

Figure 3.2 shows that no oxidation can be detected in LDPE containing FDMC. During 40 minutes of processing in open mixer at 160°C, the torque remains almost constant (after an initial decrease). However, LDPE containing FAcAc shows considerable oxidation as it is clear from the later stages of processing (curve 2 in Fig. 3.2). The thermal decomposition of FAcAc during processing was further confirmed by U.V. studies on pressed LDPE film containing this complex. Whereas NDEC, FDMC, ZDEC and TETD survived the thermal treatment (survival of their characteristic U.V. absorption bands, Table 3.3), FAcAc did not show any sign of the characteristic U.V. absorption after processing. Moreover the carbonyl region absorption in the I.R. was found to be exceedingly large, which is a clear indication of thermal oxidation of the polymer. This is associated with the thermal decomposition of FAcAc during processing. The metal ion generated from the thermal decomposition of FAcAc starts the oxdiation of the polymer by the well known redox reactions with hydroperoxides$^{(125)}$.

$$\begin{array}{llr}
\mathrm{ROOH} + \mathrm{M}^{n} \longrightarrow [\mathrm{RO}\overset{\mathrm{H}}{\mathrm{O}}\ldots\mathrm{M}^{n}] \longrightarrow \mathrm{RO}^{\cdot} + {}^{-}\mathrm{OH} + \mathrm{M}^{n+1} & & (3.1) \\
\mathrm{ROOH} + \mathrm{M}^{n+1} \longrightarrow [\mathrm{RO}\underset{\mathrm{H}}{\mathrm{O}}\ldots\mathrm{M}^{n+1}] \longrightarrow \mathrm{ROO}^{\cdot} + {}^{+}\mathrm{H} + \mathrm{M}^{n} & & (3.2) \\
\hline
2\mathrm{ROOH} \longrightarrow \mathrm{RO}^{\cdot} + \mathrm{ROO}^{\cdot} + \mathrm{H_2O} & & (3.3)
\end{array}$$

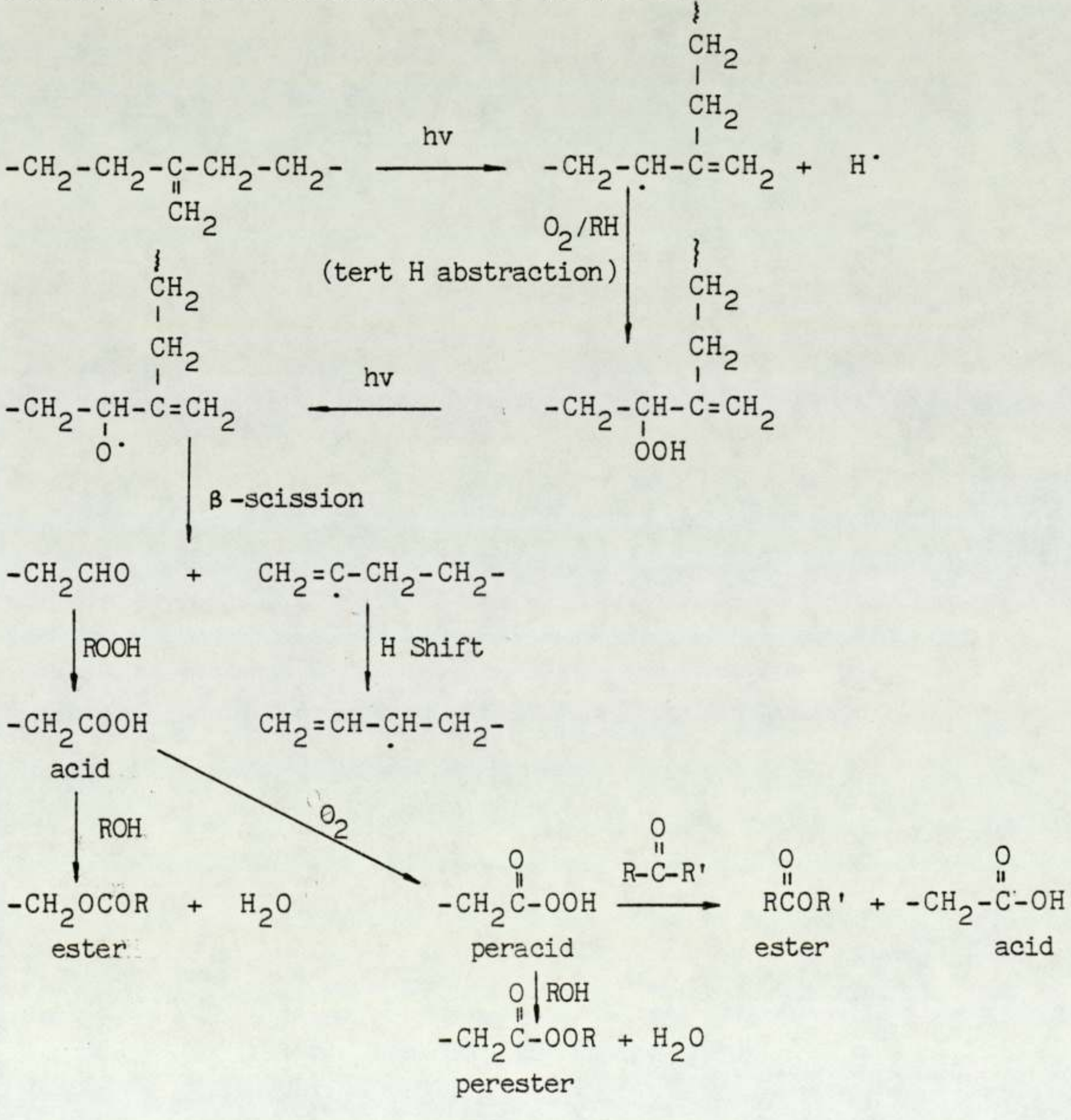
It is concluded from the above discussion then, that FAcAc unlike FDMC fails to satisfy the first requirement for the ideal photo-sensitiser that is functioning as antioxidant during processing.

3.3.2 Photo-Oxidative Stability of Unstabilized PE

One of the changes in the I.R. spectra of LDPE observed during U.V. irradiation is in the region of 3600-3000 cm^{-1} which corresponds to the absorption of different hydroxyl vibrations. Determination of the nature of the hydroxyl group is very difficult due to overlapping of various hydroxyl bands. It is generally believed(71b) that tertiary alcoholic groups (which may be formed in addition to some secondary alcohol through abstraction by alkoxyl radical during prolonged exposure) become associated and are responsible for the broader band around 3400 cm^{-1} (see Figure 3.3). The rate of hydroxyl group production is, however, much slower when compared to that of carbonyl formation (Figure 3.3). This is due to the competition of abstraction of a hydrogen by alkoxyl radicals to form an alcohol with photodecomposition of alkoxyl radicals to give ketonic products and the latter reaction is possibly dominated in LDPE photo-oxidation.

As U.V. irradiation proceeds, the absorption maxima in the carbonyl region shifts from 1725 cm^{-1} to 1721 cm^{-1}. The latter is the characteristic absorption band for compounds with internal ketonic groups and the former is due to terminal ketones (see Table 3.4). Such ketones can only form if the splitting of branched alkoxyl radical has occurred in β-scission(71e). The formation of additional carbonyl oxidative products e.g., aldehyde, acid, peracid, ester and perester are presumably through the decomposition of hydroperoxide by light. In highly oxidised film, the contribution due to acidic carbonyl group absorption (1710 cm^{-1}) is very much pronounced. This is due to the more oxidising nature of the intermediate products such as aldehyde, hydroperoxide etc., which are finally converted to relatively stable acids.

The decay of vinylidene group and formation of vinyl group and other oxidative products during U.V. irradiation of LDPE film have been explained by many workers(17,44,77) and the following chain mechanism was proposed:



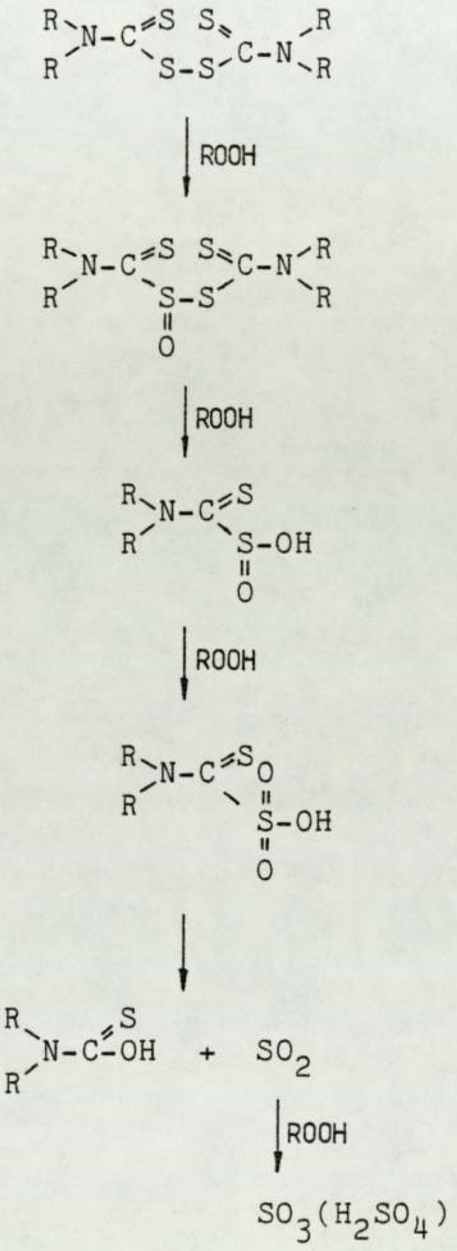
3.3.3 Effect of Processing on Photo-oxidation of PE in the Presence and Absence of Additives

It is shown in Figure 3.4 that processing considerably reduces the U.V. stability of the unstabilised polymer. The higher rate of photo-oxidation observed with prolonged processed sample is a result of the higher amount of hydroperoxide which is formed with increased processing time(18,128) Chackraborty and Scott reported(17,128,129) that there is a linear relationship between initial photo-oxidation rate and initial hydroperoxide concentration during photo-oxidation of polyolefins. This implies that hydroperoxides formed during processing can account for the photo-initiation. Further evidence supporting this was provided(128) by an experiment during which hydroperoxides were removed from processed sample (by heating in an inert gas). It was found that in spite of the high concentration of ketonic carbonyl, the initial photo-oxidation is reduced to a low level. Table 3.2 shows the lifetime of LDPE processed under different conditions. It is clear from these results that shorter but different U.V. lifetimes compared with unprocessed sample can be achieved by varying the severity of the processing. It was proposed(15) that this approach could be one way of achieving a photodegradable polymer of limited lifetime. However, this is not true since unless melt stabilizers were used, irreversible and uncontrollable changes may occur in the melt viscosity of the polymer during processing(4,15) (see Figures 3.1 and 3.2) which results in irreproducibility of the performance during outdoor use.

Processing of unstabilised PE in the presence of 2.5 x 10^{-4} mol/100 g of FDMC did not give rise to much difference in the rate of carbonyl formation on subsequent U.V. exposure with increasing processing severity (Figure 3.5). This compound must, therefore, be acting to remove hydroperoxides formed during processing as well as during the early stages of U.V. exposure. Similarly, the effectiveness exhibited by NDEC, ZDEC as U.V. stabilisers under both severe and mild processing operations indicates that their peroxide decomposing activity is carried through to the U.V. exposure stage and this persists until the complexes are destroyed by U.V. light.

Photo-oxidation of LDPE containing FAcAc is greatly effected by processing conditions. The pro-oxidisability revealed by the mildly processed sample becomes more drastic in the severely processed (30 min O.M) sample. In this respect FAcAc resembles metal stearates which have reportedly been shown to possess similar thermal and U.V. activating properties.

The importance of oxidation products of simple alkyl disulphides (or monosulphides) and disulphide of dithioic acid as auto-oxidation inhibitors in polymers and model compounds, rather than the disulphides themselves, has been suggested.(130,131,141) This is corroborated here from the photo-oxidative stability of TETD-stabilised PE. Figure 3.6 shows that stabilisation of PE in the presence of TETD is far better in the condition of an ample supply of air than in a limited oxygen system. This implies that generation of sulphur acids from TETD is much easier when excess oxygen is available (see Scheme 1).



Scheme 1

A typical U.V. absorber HOBP is particularly sensitive to the severity of the processing operation. Figure 3.7 shows that the retardation of the photo-oxidation rate in a severely processed sample (30 min O,M) by HOBP is not as great as it is in a mildly processed one (10 min C,M). This result suggests that HOBP decomposes more in a severely processed sample than in a mildly processed one. This destruction of HOBP, during processing, is reported(77,132-135) to be due to its interaction with radicals produced by hydroperoxide decomposition. Radical scavenging behaviour of 2-hydroxybenzophenone during thermal processing was reported by many workers(132-135) and recently by Scott(77).

3.3.4 Effect of Varying the Concentration of Additives on U.V. Stability of LDPE

In general all metal dithiocarbamate complexes and their corresponding disulphides are effective antioxidants during both processing and subsequent U.V. irradiation. Their stabilising effect is found to be due to their ability to decompose hydroperoxide (see Chapter 5, Sec. 5.2.2) which is the main initiating species in both thermal and photo-oxidation. However, it is found that there is a critical concentration below which they are ineffective. This finding is illustrated in Figures 3.9-3.12 for FDMC. ZDEC, NDEC and TETD respectively. The ineffectiveness of similar sulphur compounds was also reported previously(44,71d). The initial carbonyl index value of PE containing these complexes at and below the critical concentration was as low as that of the unprocessed PE film. This implies that they are still protecting the polymer during the thermal processing operation. The ineffectiveness of these additives observed in the subsequent U.V. exposure, might then be due to the fact that these complexes have been consumed almost completely during the thermal processing treatment. When higher concentrations than the critical one from these complexes were used, the stabilizing effect was accordingly increased (see Figures 3.9-3.12). This finding was also observed by other workers(133).

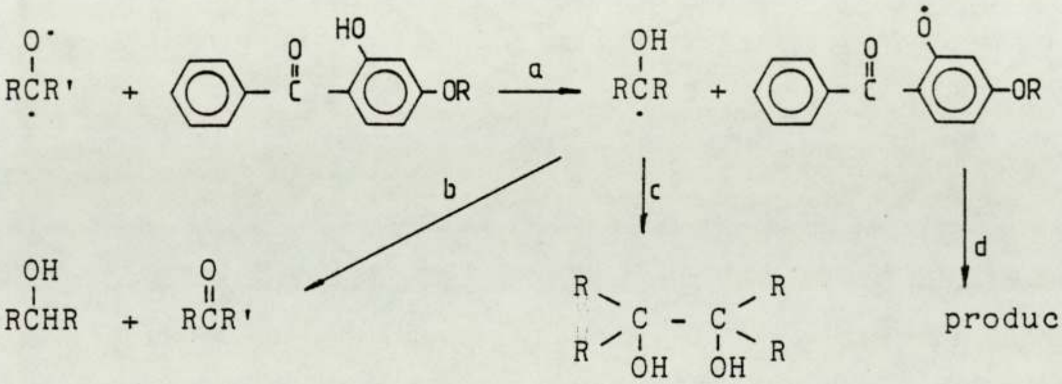
Metal acetyl acetonates like other metal carboxylates were found(44) to behave as pro-oxidants during both thermal processing and U.V. irradiation stages. Their pro-oxidant effect was found to increase with concentration (Figure 3.8). Amin and Scott attributed this effect to the decomposition of these complexes during both thermal and U.V. irradiation stages (Figures 3.1, 3.2 and 3.5). The higher the concentration of FAcAc in the polymer, the higher is the concentration of sensitiser species generated during FAcAc decomposition and hence the faster is the rate of oxidation.

3.3.5 Effect of Additives Screening on Photo-oxidation of LDPE

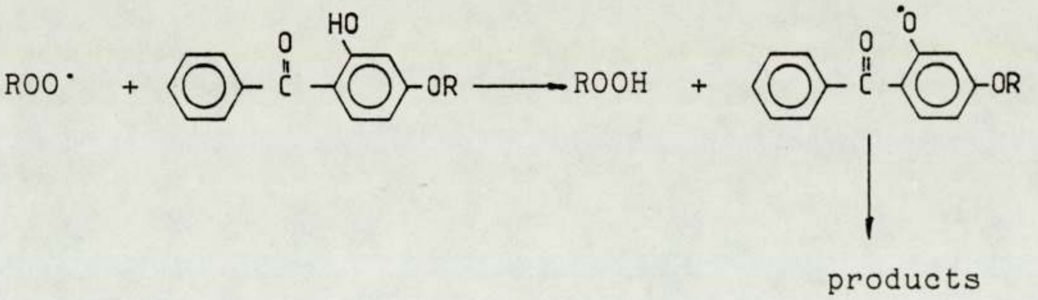
It has been reported(72,136) that some transition metal dithiocarbamates act in part as U.V. screens. Figure 3.13

shows the contribution of the screening of U.V. light by these metal complexes. It is clear (Figure 3.13) that the screening role of NDEC cannot account for the total stabilization effect when this is used as an additive. The results suggest that both screening and some other chemical stabilization processes are involved in the effective photostabilization of these compounds and that screening makes a relatively minor contribution to the overall stabilization function(72, 73,136). ZDEC, FDMC and TETD do not seem to screen U.V. light at 290 nm at all because the rate of photo-oxidation of the samples screened by samples containing the above additives are almost the same as that of the control. The primary function of these complexes in photo-oxidation of polyolefins is reported to be destruction of hydroperoxide in an ionic process and this has been confirmed in the present work in polymer as well as in model compounds (see Figures 3.9-3.12 and also Chapter 5).

The contribution of screening to the overall stabilizing effect of HOBP is more when compared to its contribution with NDEC. However, this does not account for the total stabilizing effect offered by HOBP. It has previously been suggested(135) that hydroxy benzophenone U.V. stabilizers can accept energy from triplet carbonyl. Chakraborty and Scott(135) showed in a separate experiment which involved detailed study of this effect in heavily oxidised PE from which hydroperoxide was removed by thermolysis in an inert atmosphere, that the 2-hydroxybenzophenone appears to play two distinct roles. The first is physical screening of U.V. light, which is a relatively minor effect. The second is a sacrificial interaction with the excited carbonyl chromophore (Eq. 3.4). Thus these workers concluded that HOBP can quench the photo-excited carbonyl chromophore but this is not the only possibility. Removal of free radicals might also be involved(30-34) (Eq. 3.5).



(3.4)



(3.5)

3.3.6 Mode of Additives Decay in Polymer During U.V. Exposure

It is clear from Figure 3.4 that all the three metal dithiocarbamates exert antioxidant effects in the polymer. The induction period observed was consistent with the time of decay of these additives. So long as the metal complex is present in the system it functions as a reservoir for the acidic peroxide decomposer(141). When the complex is destroyed however, the polymer photo-oxidises at a rate which is determined by the pro-oxidant activity and concentration of the free metal in the system. The zinc and nickel salts formed as end products during ZDEC and NDEC photolysis have very little photo-pro-oxidant effect(44) but ionic iron behaves very differently. Acceleration of photo-oxidation is similar to that observed in the polymer in the presence of FAcAc and this was proposed previously(15) to be due to the formation of FeIII carboxylate from the macromolecular carboxylic acids which are the main oxidative product of LDPE (see Chapter 1 Scheme 4).

The difference in behaviour of ZDEC, NDEC and FDMC during the early stages of photo-oxidation (c.f. induction periods curves 1, 2 and 3 in Fig. 3.14) is associated with the difference in their U.V. stability. The half-life of NDEC is about four times that of Zn complex and the latter is far more than the Fe complex under the same conditions.

3.3.7 The Effect of Two Component Systems on Photo-Oxidation of LDPE

Metal dialkyldithiocarbamates (NDEC. ZDEC and FDMC) were shown to be good U.V. stabilizers (Figures 3.9-3.11) at a certain concentration below which they were ineffective (curves 0.25-1.25 in Figs 3.9-3.11). This behaviour is also observed in the two component systems. Figure 3.15 shows that addition of 2.5×10^{-5} mol/100 g NDEC to LDPE containing FDMC decreases the stability of the polymer as is clear by comparing the induction period with the polymer containing FDMC alone. The slope of the rate of photo-oxidation at the end of the induction period becomes sharper. These results suggest that below (Figure 3.16) and at this concentration (2.5×10^{-5} mol/100 g) NDEC photosensitises FDMC giving rise to a shorter induction period and sharper slope of the rate of photo-oxidation. The NDEC has probably undergone photo-decomposition while it is exerting its function as stabilizer at the early stages of U.V. irradiation and as a result photosensitiser species are formed which reduces the effect of FDMC in the polymer. However. it was shown(139) that when the concentration of NDEC in the combination is high (higher than the critical 1.25×10^{-4} mol/100 g) the stability of the polymer is improved compared with the stability of the polymer containing FDMC alone. Similar results are also observed in PP at high concentration of NDEC (Chapter 4, Section 4.2.7). The higher the concentration of the NDEC in the combination, the longer the induction period observed.

Similar behaviour was also observed by using ZDEC instead of NDEC. Figures 3.18-3.20 show that increasing the concentration of ZDEC in the combination increases the length of the induction period accordingly. It seems probable here that ZDEC is capable of protecting FDMC for a longer time and this protection effect is a function of ZDEC concentration in the combination. At the end of the induction period the photolyzing products of both FDMC and ZDEC start accelerating the photo-oxidation in a catalytic mode as is clear from the slope of the rate of photo-oxidation. However, it was observed that when the concentration of ZDEC in the combination was 1.25 x 10^{-4} mol/100 g, the rate of photo-oxidation was much faster than the one containing FDMC alone. This effect was similar to that observed in the FDMC/NDEC combinations when the concentration of NDEC was below the critical level. At this particular concentration (1.25 x 10^{-4} mol/100 g), ZDEC has an adverse effect on the stability of the polymer. Therefore. the sensitising effect observed could be due to the ZDEC photodecomposition products which reduce the effect of FDMC (see Figure 3.18).

In the TETD/FDMC combination, it is observed that FDMC reduces the stabilizing activity of TETD considerably. The higher the concentration of FDMC in the combination, the faster the rate of photo-oxidation at the end of the induction period, Figures 3.22-3.26. The effect of TETD on FDMC on the other hand, is shown in Figure 3.27. It is clear that the higher the concentration of TETD in the combination, the longer the induction period. In this behaviour, TETD is similar to metal dithiocarbamate complexes (NDEC and ZDEC at high concentration) in that photolytically it is more stable than FDMC and can last longer under the effect of U.V. light. This gives rise to a longer induction period compared with the sample containing FDMC alone. Once the disulphide is completely photolytically destroyed then both

why

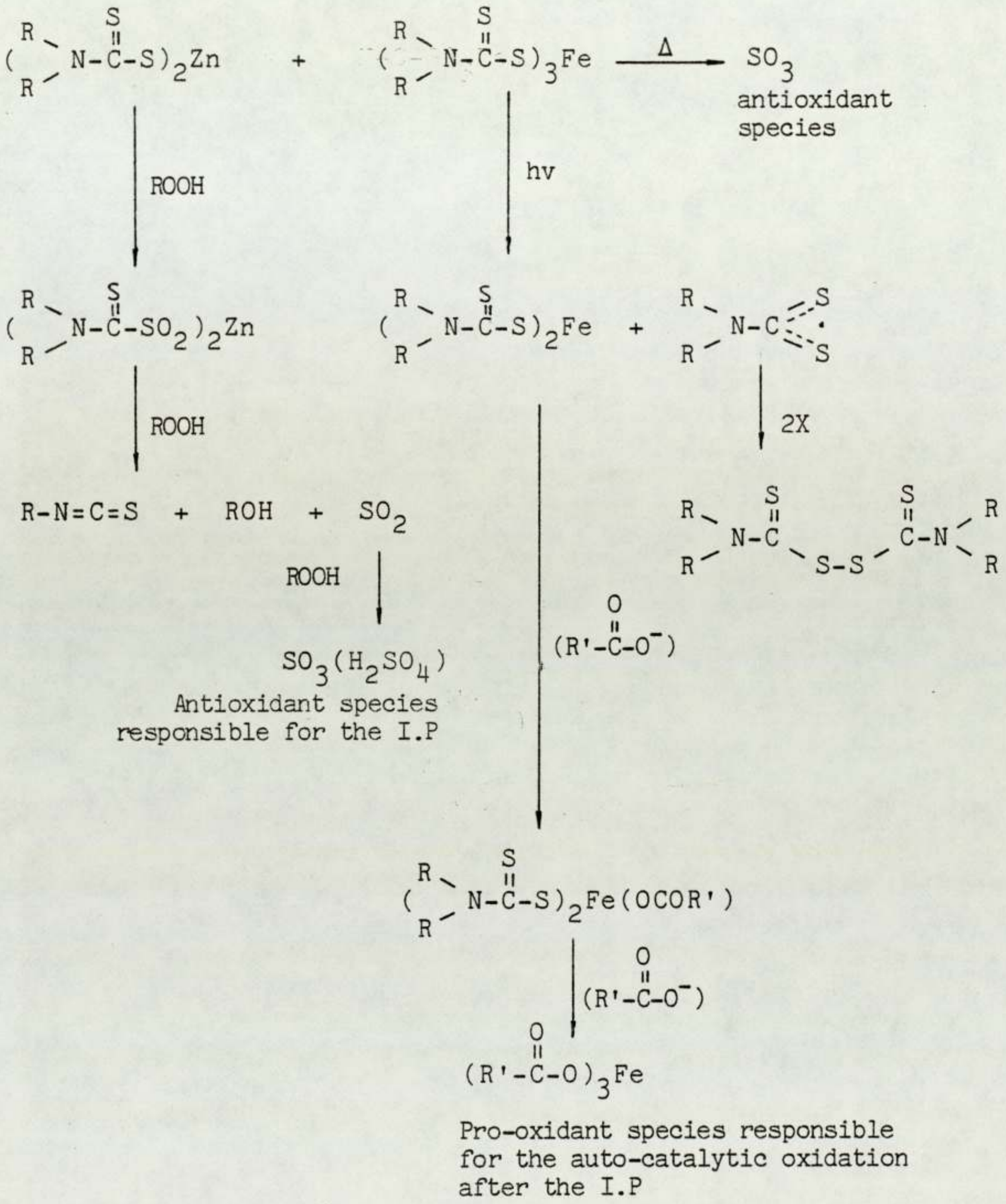
Fe ion and other sensitising species arising from sulphur ligand start accelerating the oxidation in the manner observed in Figures 3.22-3.26.

HOBP is particularly sensitive to the processing operation (see Sections 4.2.3. and 4.3.3) and this reduces its effectiveness on the subsequent U.V. irradiation. FDMC on the other hand, is very unstable under U.V. exposure conditions but it is however a good melt stabilizer (see Sec. 4.2.1 and 4.3.1). Combination of these two additives should, therefore, be performed in a way similar to ZDEC, NDEC and TETD/FDMC combinations. Figures 3.29-3.31 show the effect of this combination (HOBP/FDMC) at different molar ratios on photo-oxidation of LDPE. As it is clear that the HOBP is responsible for the photo-induction period observed since its complete decay is consistent with the end of the induction period. The photo-oxidation rate seems to be controlled by the concentration of ionic iron in the combination. The higher the concentration of FDMC in the combination, the faster is the rate of photo-oxidation (Figures 3.29-3.31).

It has been shown that FAcAc autoaccelerates photo-oxidation in the same manner as FDMC does, but it is incapable of protecting the polymer from oxidation during thermal processing treatment (see Sec. 4.2.1 and 4.3.1). To avoid this disadvantage of thermal pro-oxidant effect, addition of a melt stabilizer is essential. Figures 3.33-3.35 show that addition of ZDEC completely inhibited the thermal oxidation during processing and also gives rise to an induction period before photo-oxidation is started. ZDEC must therefore be acting as a hydroperoxide decomposer during processing and also in the early stages of U.V. irradiation, thereby protecting FAcAc from destruction by hydroperoxides. FAcAc on the other hand, exerts its function normally after the induction period. The acceleration of photo-oxidation is evidenced in all combinations studied. Figure 3.34 shows interesting features, these being the substantial controlled induction period and the fast rate of photo-oxidation at the end of the induction period. These features are the essential requirements of an ideal photoactivator for agricultural mulching film.

In conclusion, it must be emphasised that NDEC, ZDEC and TETD are controlling the length of the induction period when they are used at concentrations higher than a critical level. FDMC on the other hand, is responsible for the rate of photo-oxidation following the induction period (see Scheme 2). When the concentration of the hydroperoxide decomposers (NDEC, ZDEC and TETD) in the combination is at or below the critical level, photosensitisation is due to these additives as well as to the FDMC. Combinations of FAcAc and hydroperoxide decomposer, and also of HOBP/FDMC showed similar behaviour to those of FDMC/hydroperoxide decomposers.

what are the
sensitizing prods'
from Zn or Ni or [illegible]
(at low conc. only?!)


Δ
SO3
antioxidant species
ROOH
hν
ROOH
2X
R-N=C=S + ROH + SO2
ROOH
SO3(H2SO4)
Antioxidant species responsible for the I.P
(R'-C-O⁻)
(R'-C-O)3Fe
Pro-oxidant species responsible for the auto-catalytic oxidation after the I.P

Scheme 2

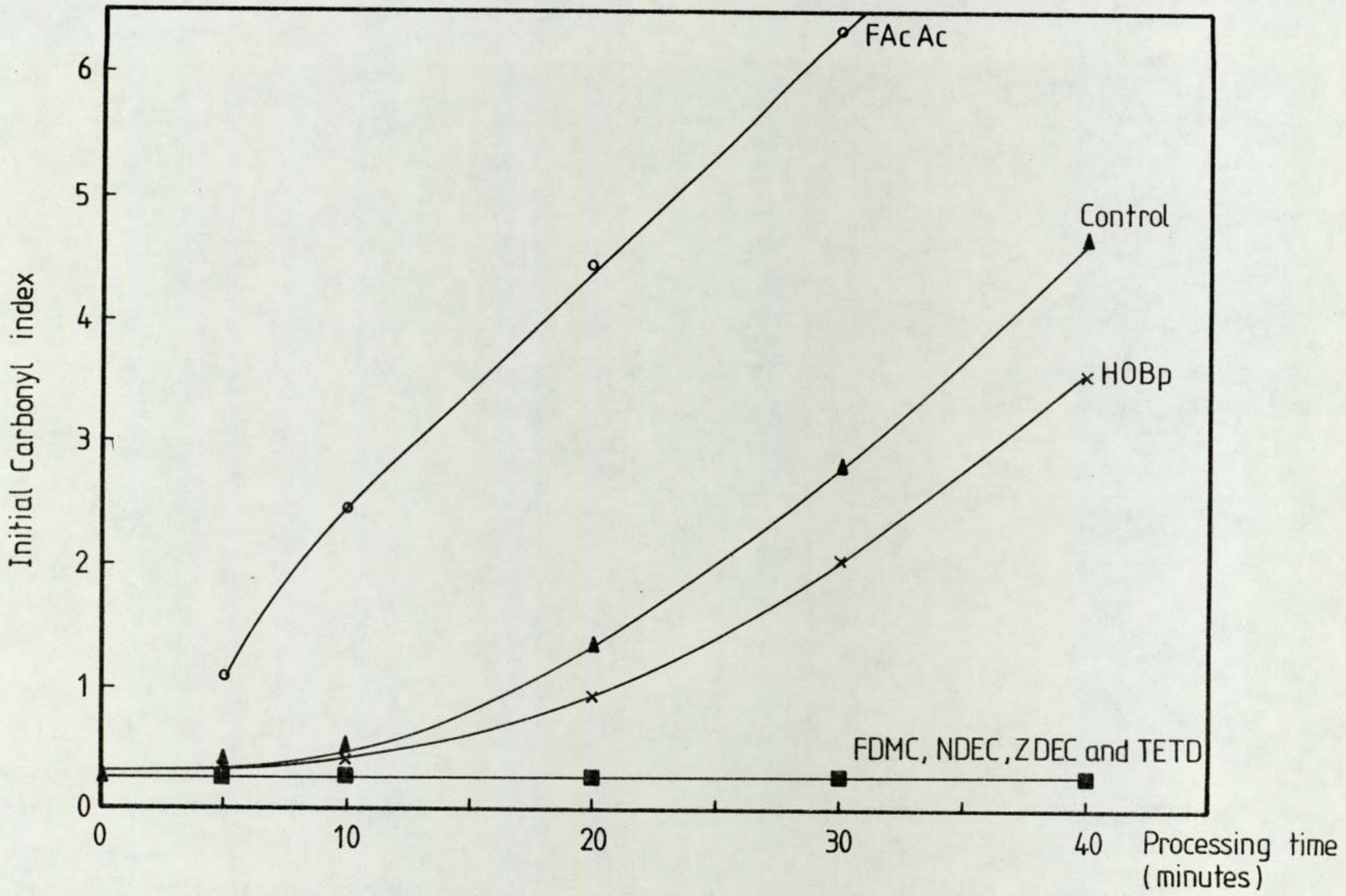


Figure 3:1 The effect of different additives on the oxidative stability of LDPE during processing in O,M (Conc of additives is $2{\cdot}5 \times 10^{-4}$ mol/100g) 160°

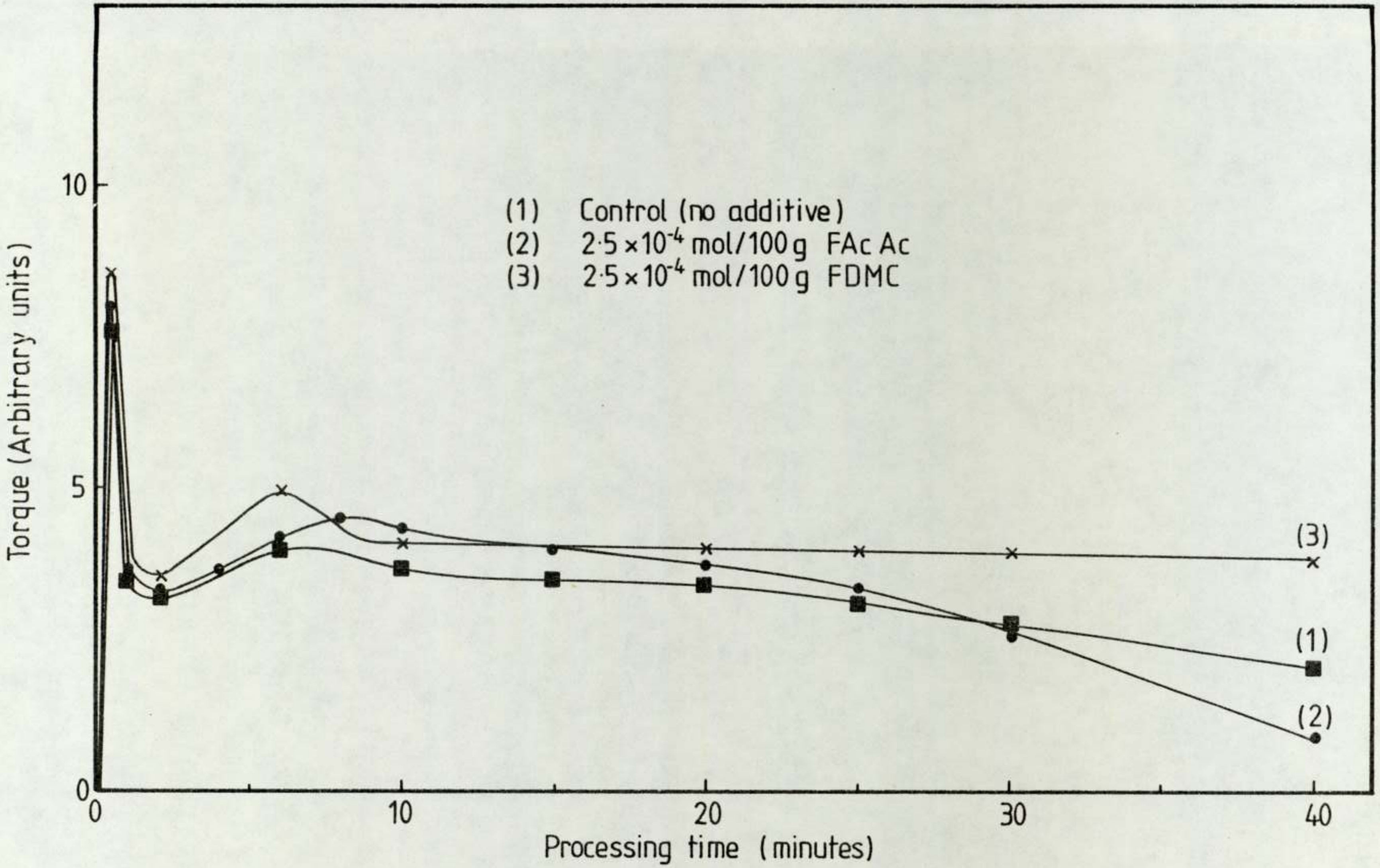


Figure 3:2 Dependance of torque of LDPE on processing time at 160°C in the presence of different additives

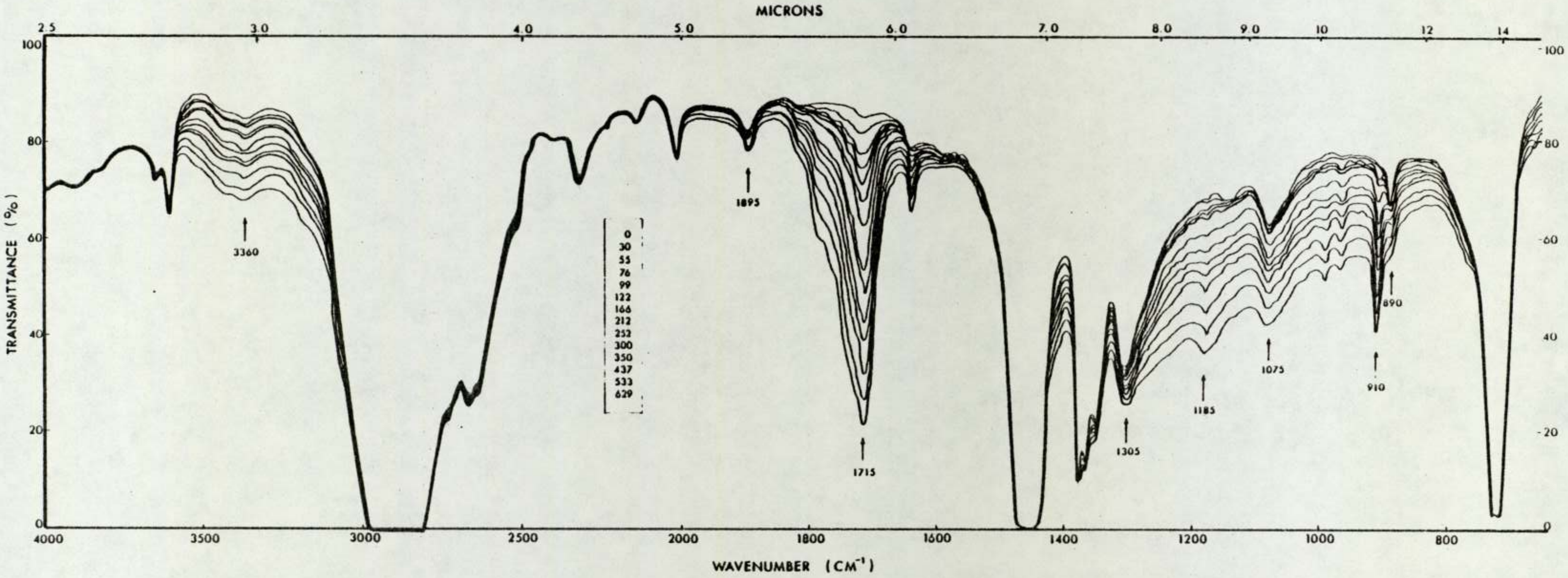


Figure 3:3 Changes in the infra-red spectra of unstabilised LDPE (10 minutes in closed mixer) during photo-oxidation Irradiation times are shown in the rectangle.

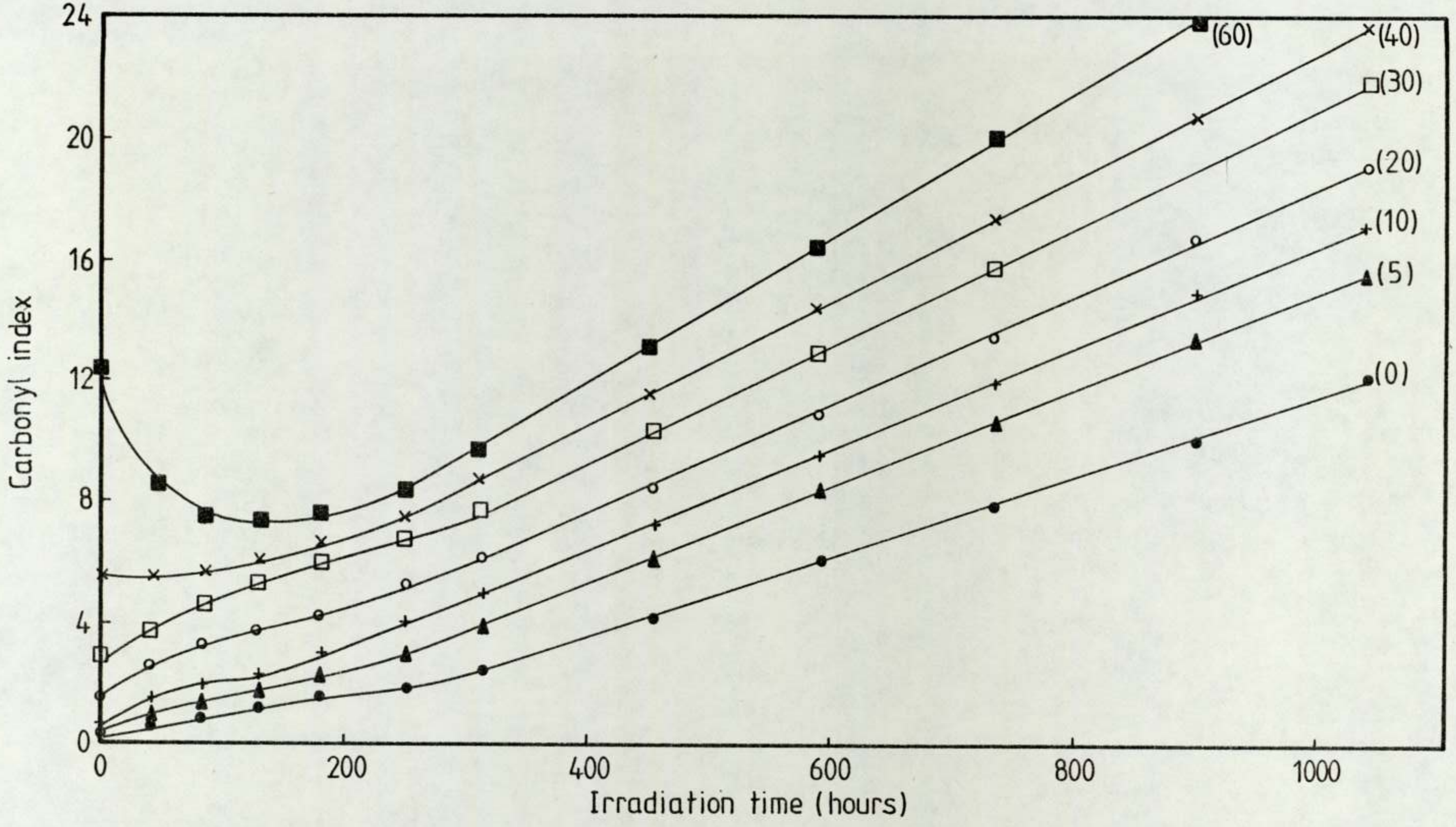


Figure 3:4 Variation of carbonyl index with irradiation time for LDPE processed in open mixer for varying times (Figures in parentheses are times of processing in minutes) 160°

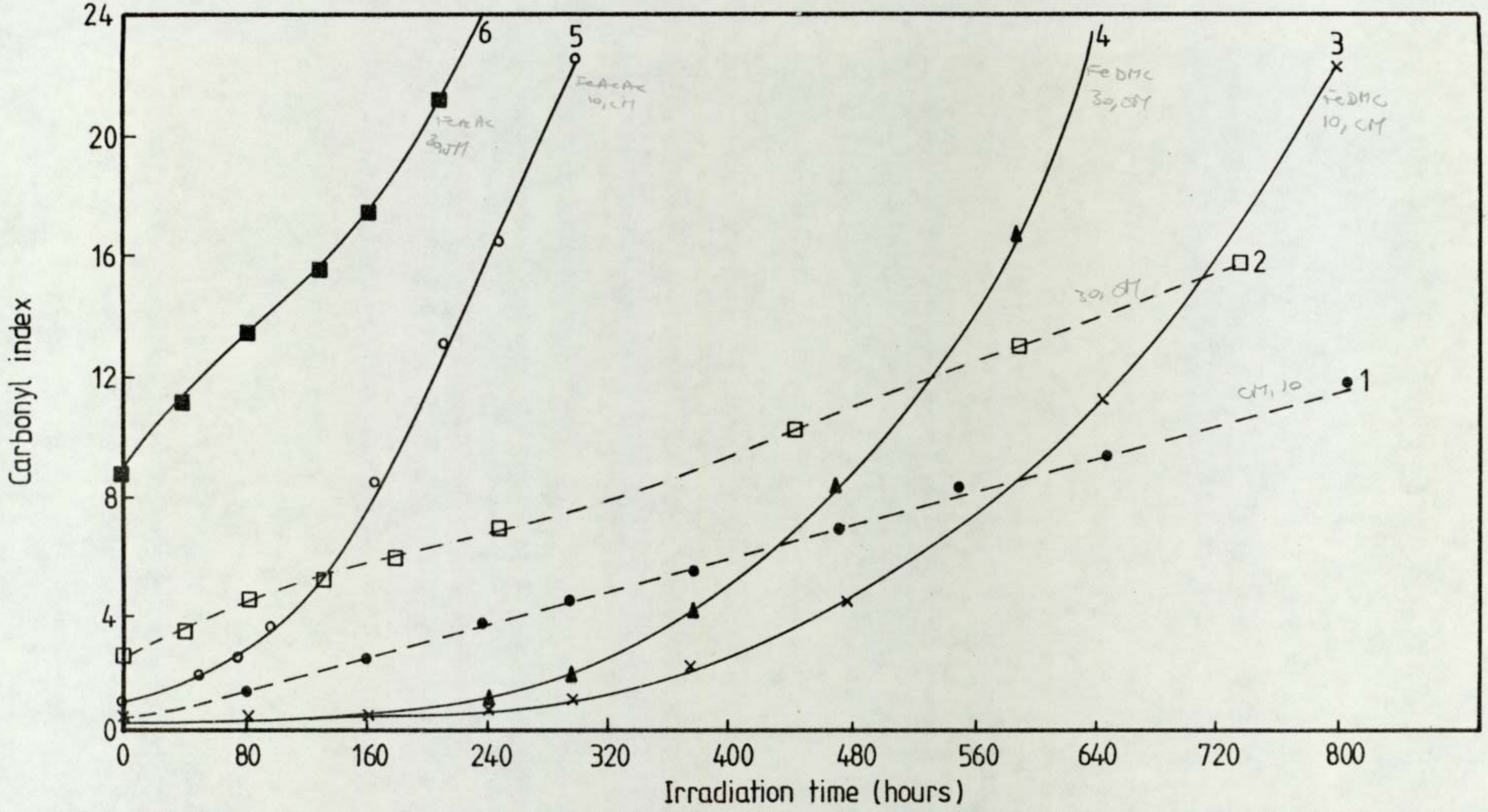


Figure 3:5 Effect of processing time on U.V. stability of LDPE containing ideal (FDMC) and conventional (FAcAc) photoactivators (Conc of additives 1×10^{-3} mol/100g)
1. No additive 10, CM 2. No additive 30, OM 3. FDMC 10, CM 4. FDMC 30, OM
5. FAcAc 10, CM 6. FAcAc 30, OM

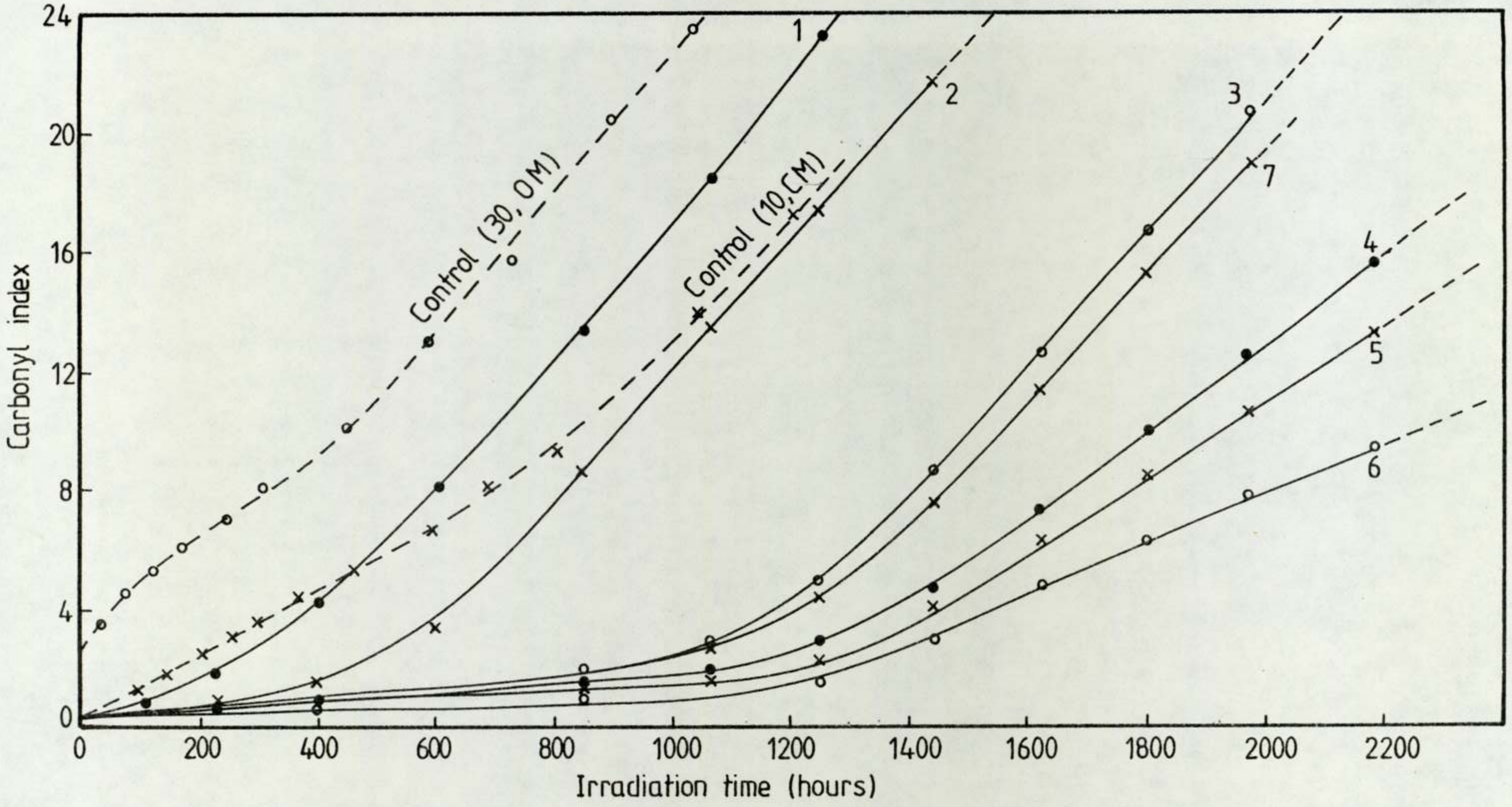


Figure 3:6 The effect of processing conditions on photo - oxidation of LDPE containing TETD

1. $2{\cdot}5 \times 10^{-4}$ mol/100g TETD 10 min Closed mixer
2. $2{\cdot}5 \times 10^{-4}$ mol/100g TETD 10min Open mixer
3. $2{\cdot}5 \times 10^{-4}$ mol/100g TETD 30min OM
4. 10×10^{-4} mol/100g TETD 10min CM
5. 10×10^{-4} mol/100g TETD 10min OM
6. 10×10^{-4} mol/100g TETD 30min OM
7. 5×10^{-4} mol/100g TETD 10min CM

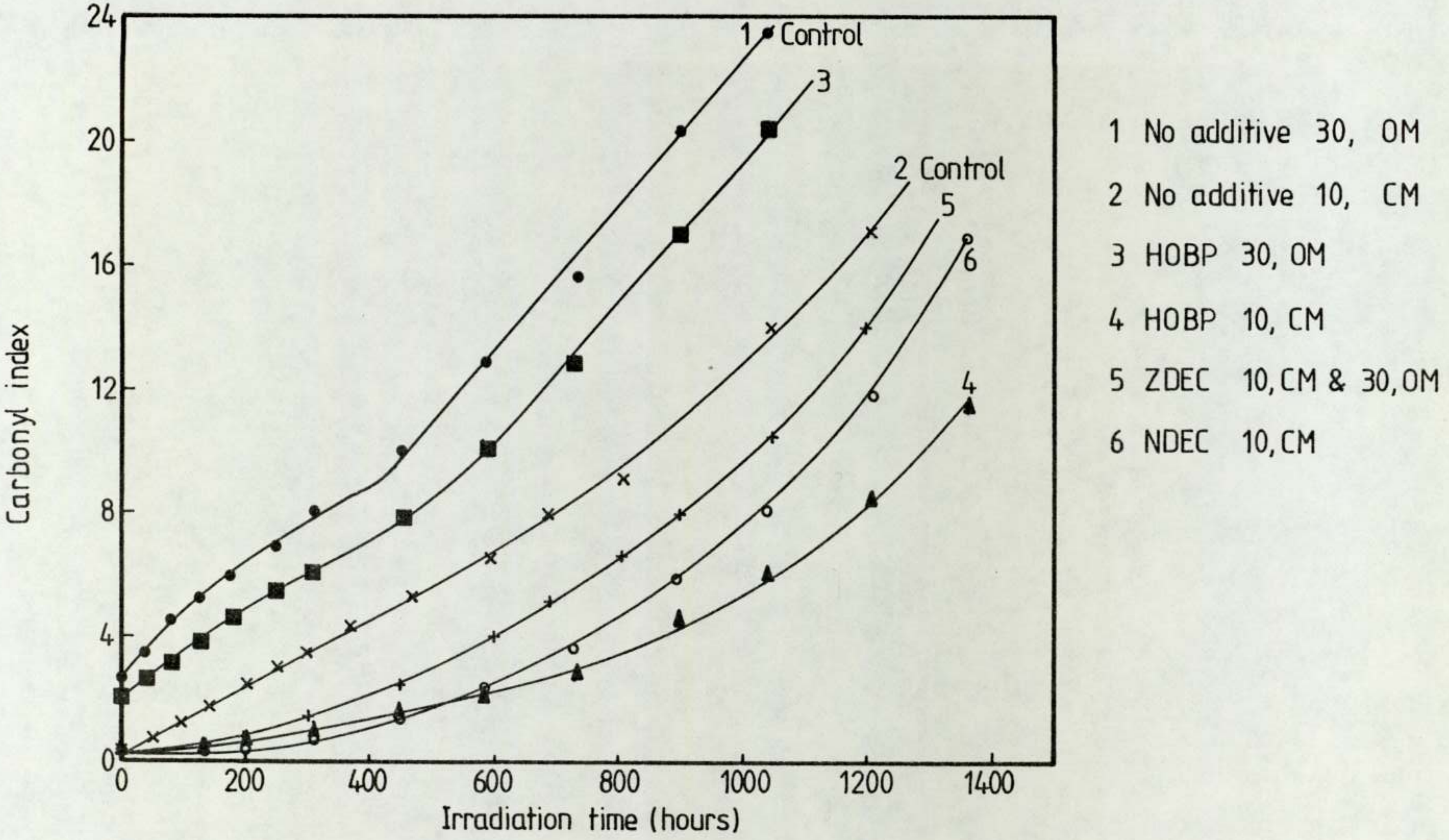


Figure 3:7 Effect of processing time at 160°C on U.V. stabilizing effectiveness of antioxidants and stabilizers (Conc. of additive $2{\cdot}5 \times 10^{-4}$ mol/100g)

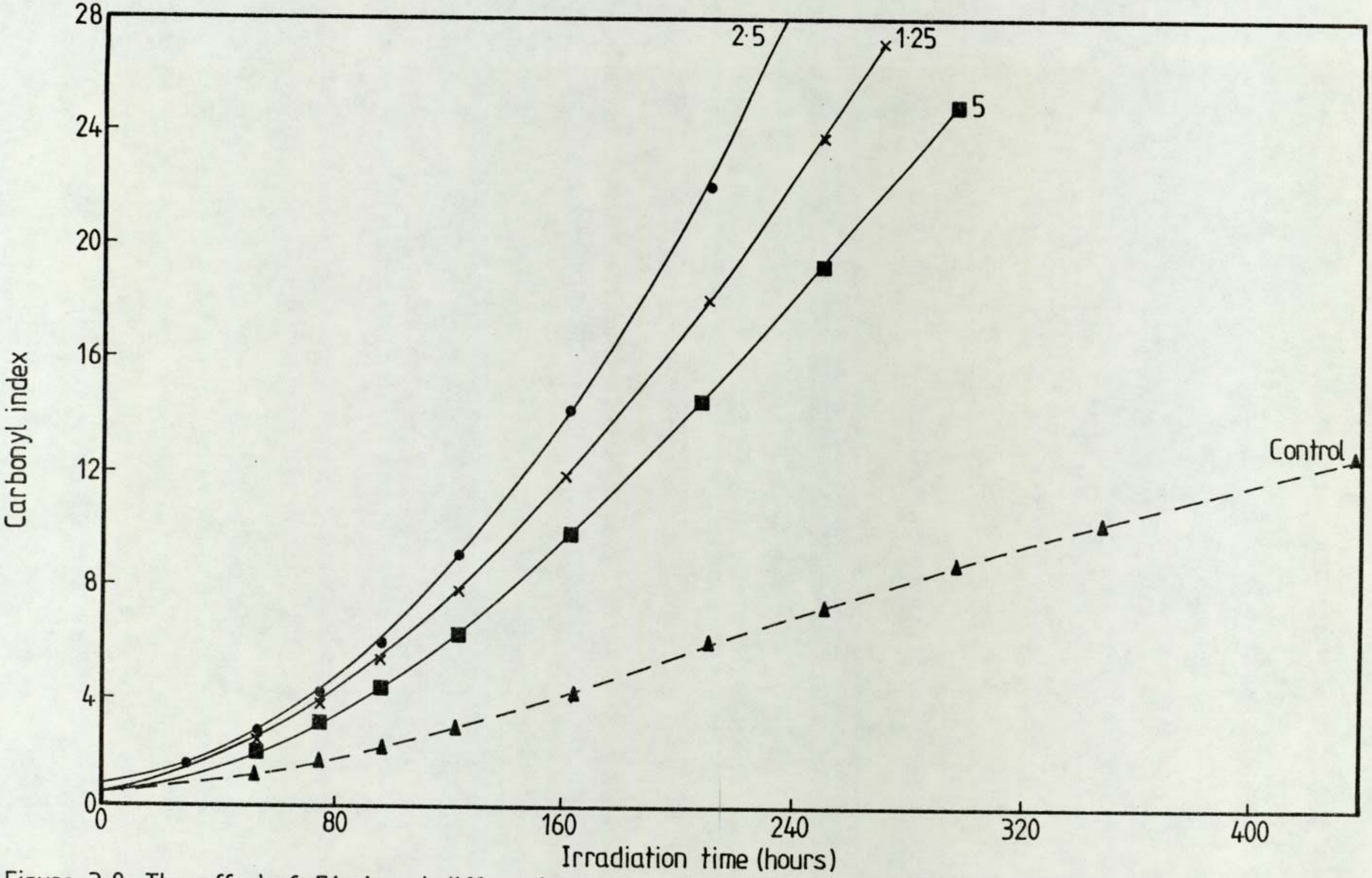


Figure 3:8 The effect of FAcAc at different conc. on photo-oxidation of LDPE. Samples processed at 160°C in open mixer for 10 minutes. (Number on curves are conc. of FAcAc $\times 10^{-4}$ mol/100g)

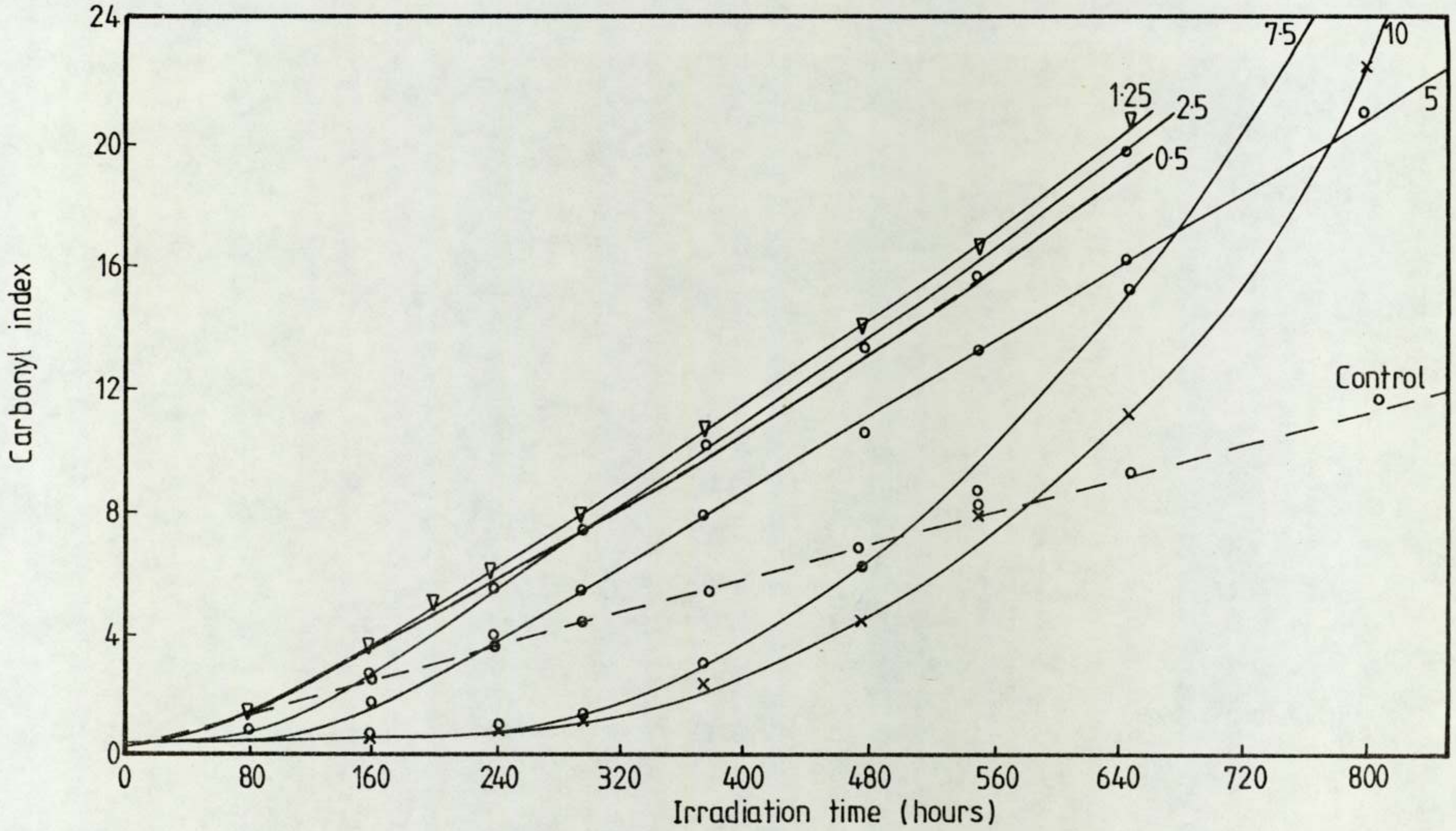


Figure 3:9 The effect of FDMC at different conc. on photo-oxidation of LDPE. Number on curves are conc. of additives ($\times 10^{-4}$ mol/100 g) CH, 10

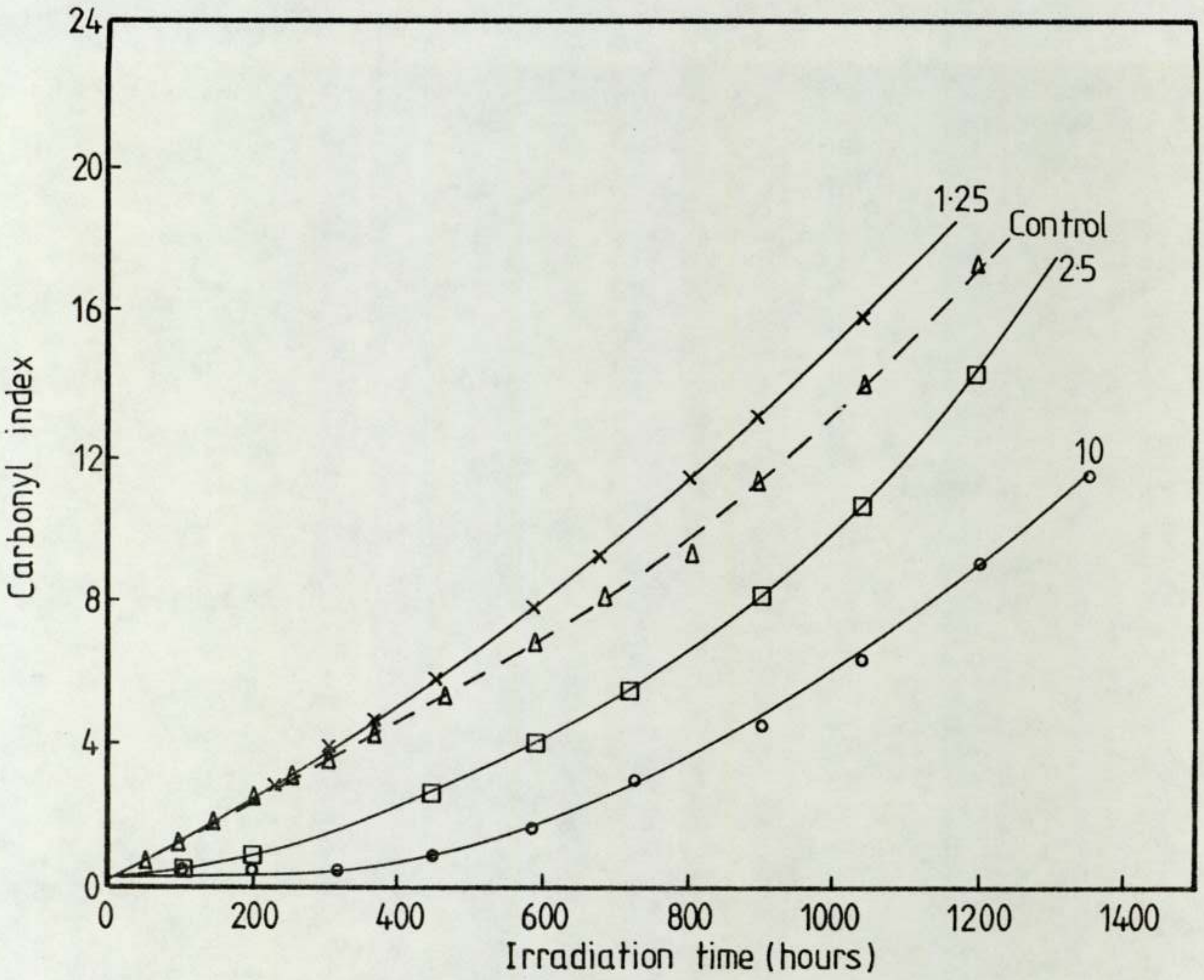


Figure 3:10 Effect of varying the conc. of ZDEC on photo-oxidation of LDPE (processed at 160°C for 10 min. in CM) Number on curves are conc. of additive (× 10^{-4} mol/100g)

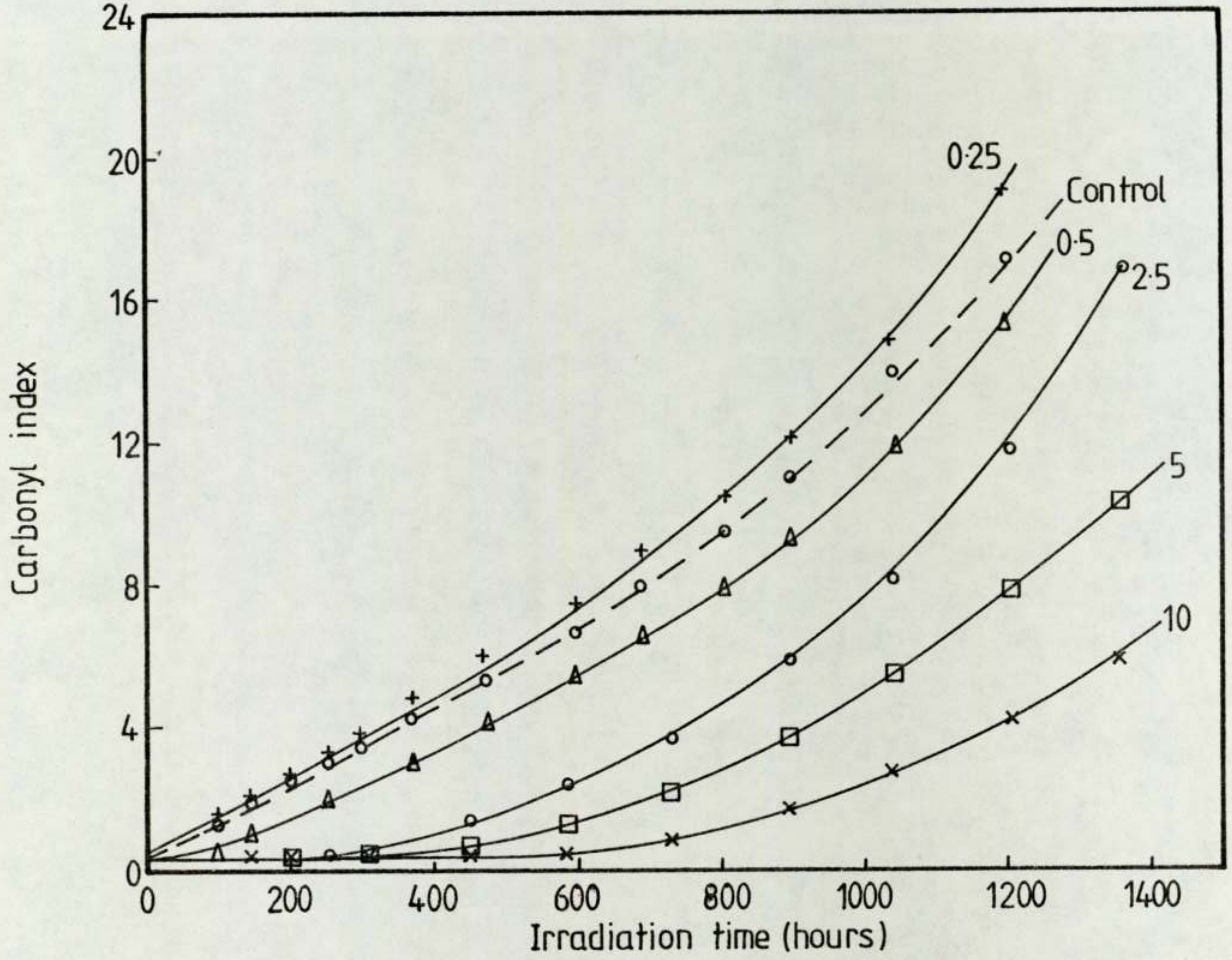


Figure 3:11 Effect of varying the conc. of NDEC on photo-oxidation of LDPE (processed at 160°C for 10 min. in CM) Numbers on curves are conc. of NDEC (× 10^{-4} mol/100g)

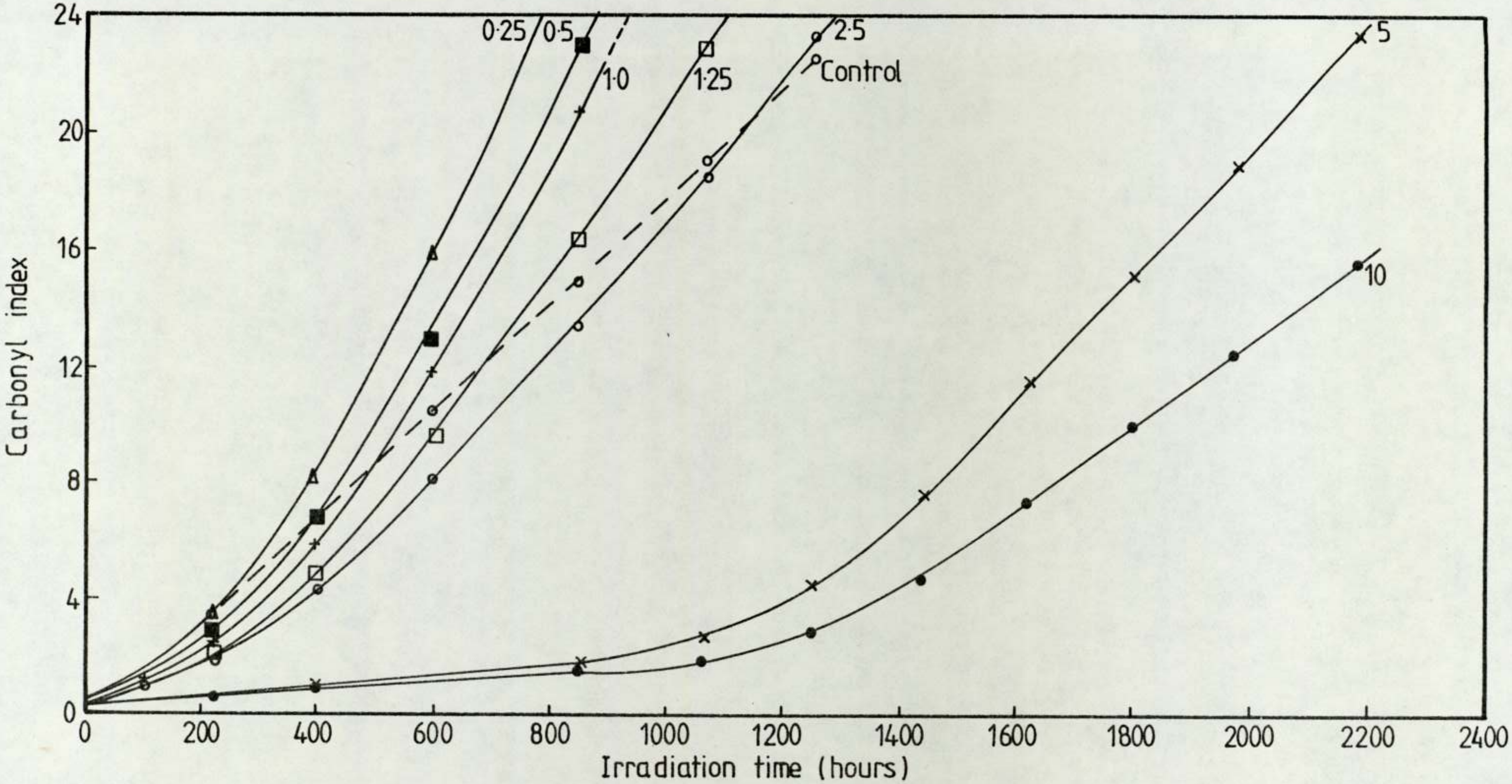


Figure 3:12 The effect of TETD at different concentrations on photo-oxidation of LDPE processed in a closed mixer for 10 minutes at 160°C (Numbers on curves are conc. × 10^{-4} mol/100g)

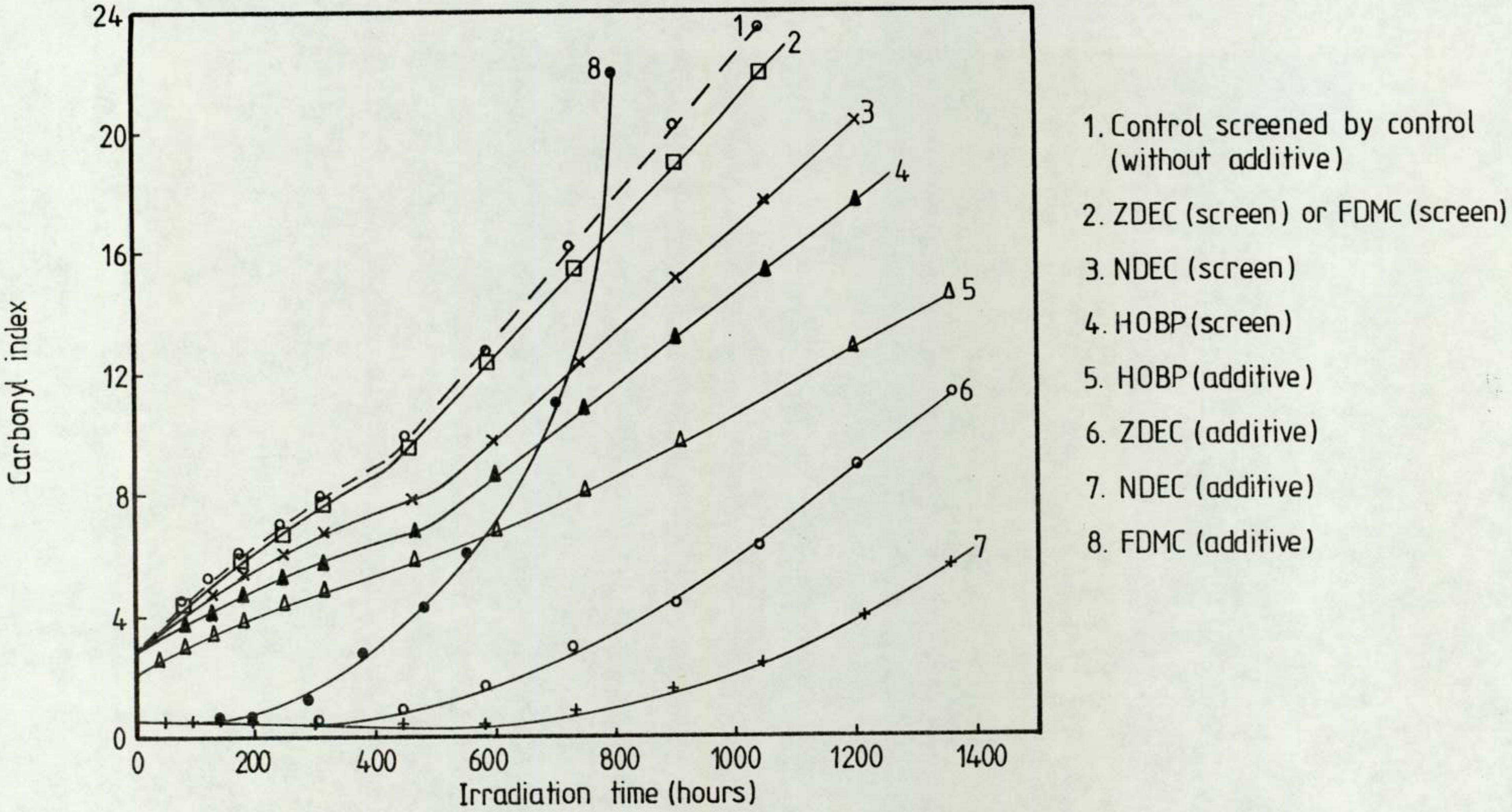


Figure 3:13 Comparison of behaviour of stabilizers as screen and as additives in LDPE (processed at 160°C / 30 min. Open mixer. Conc of stabilizers 1×10^{-3} mol/100 g)

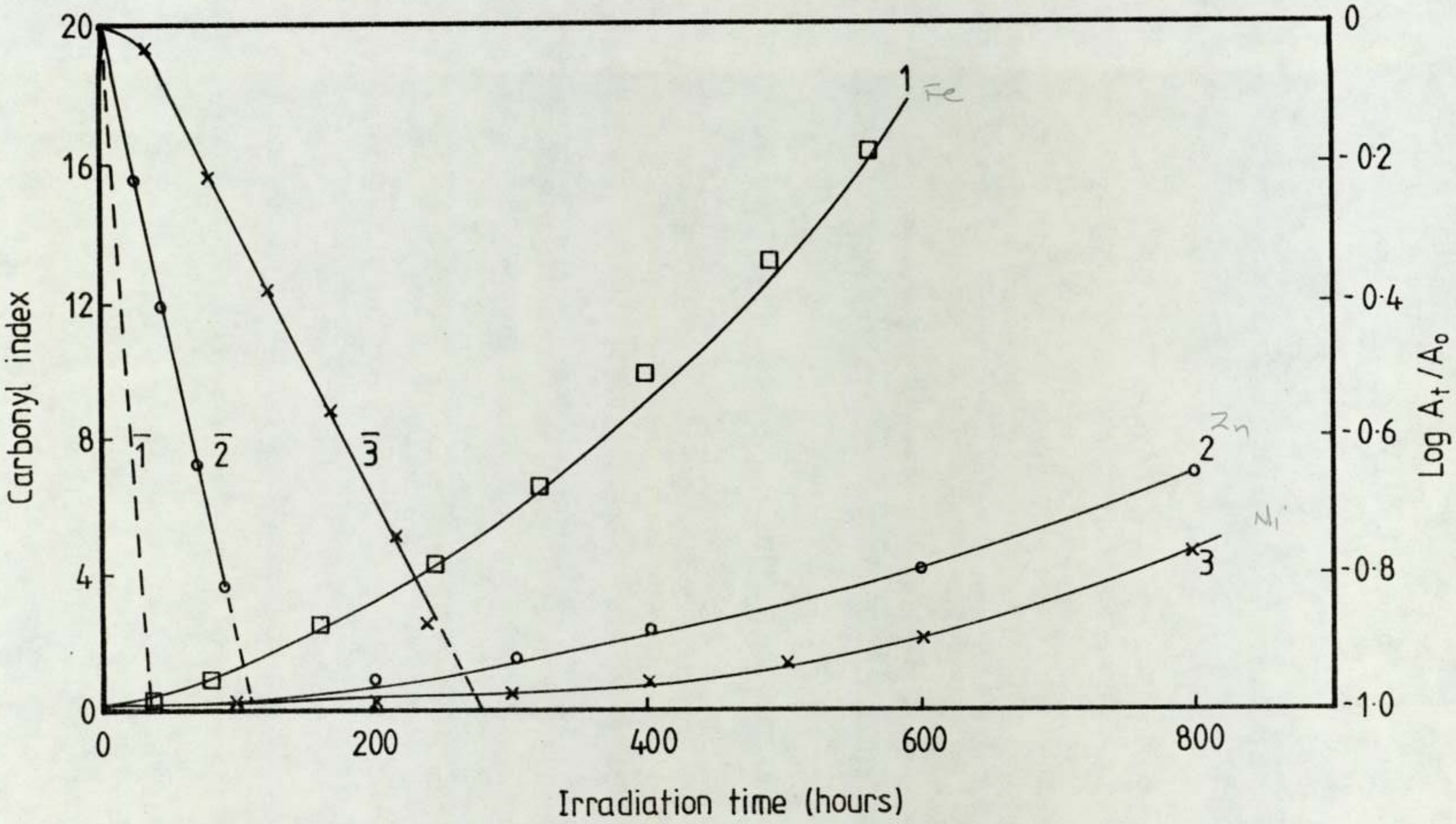


Figure 3:14 Correlation of the decay of U.V. absorbance of metal dithiocarbamates in LDPE with photo-oxidation induction period (Conc. of additive $2\cdot5 \times 10^{-4}$ mol/100g)

1. FDMC — $\overline{1}$. Colour decay of Fe complex
2. ZDEC — $\overline{2}$. UV decay of ZDEC
3. NDEC — $\overline{3}$. UV decay of NDEC

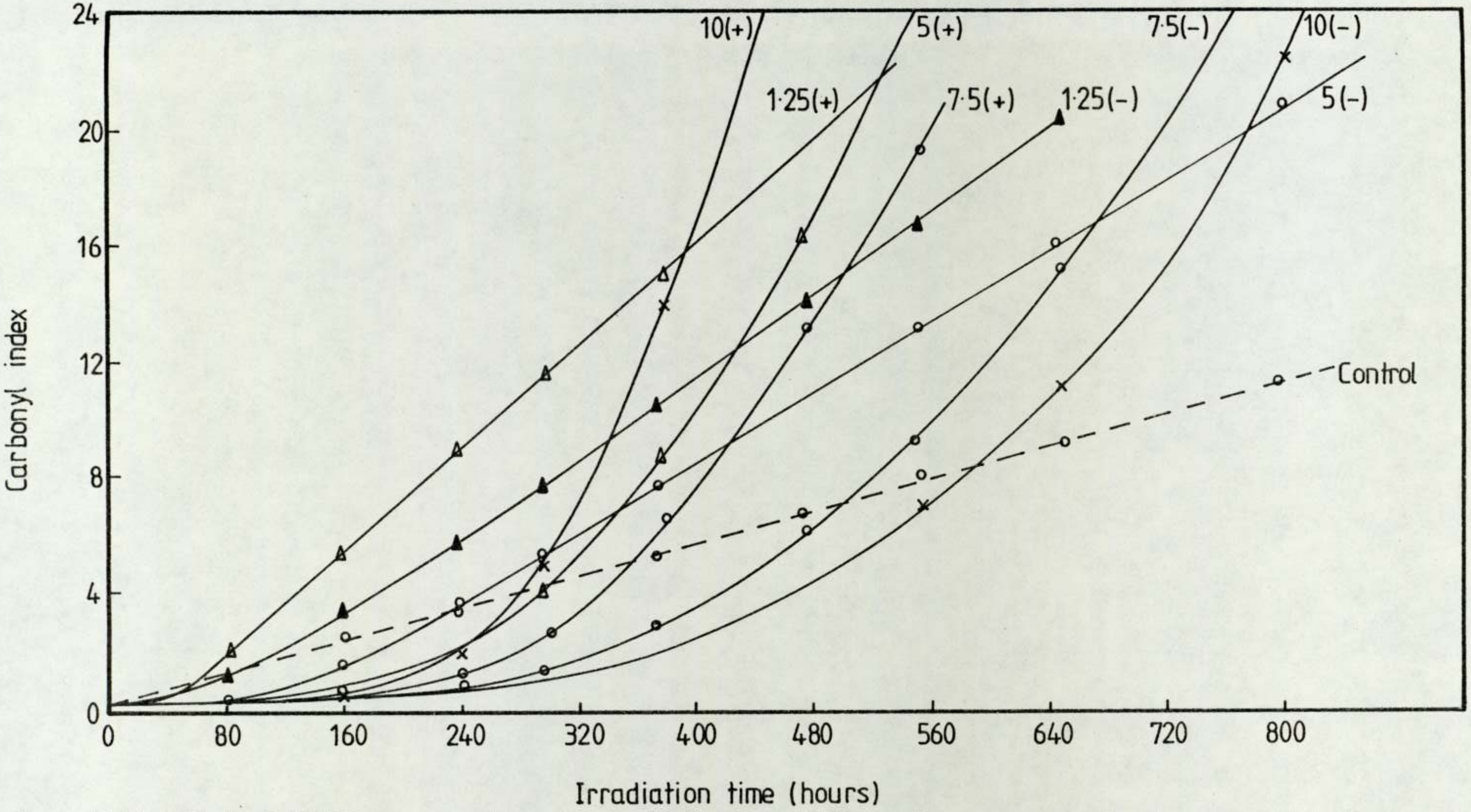


Figure 3:15 Effect of FDMC conc. on the photo-oxidation of LDPE in the presence (+) and absence (-) of $2 \cdot 5 \times 10^{-5}$ mol/100g NDEC (Numbers on curves are FDMC conc. in mol/100g $\times 10^4$)

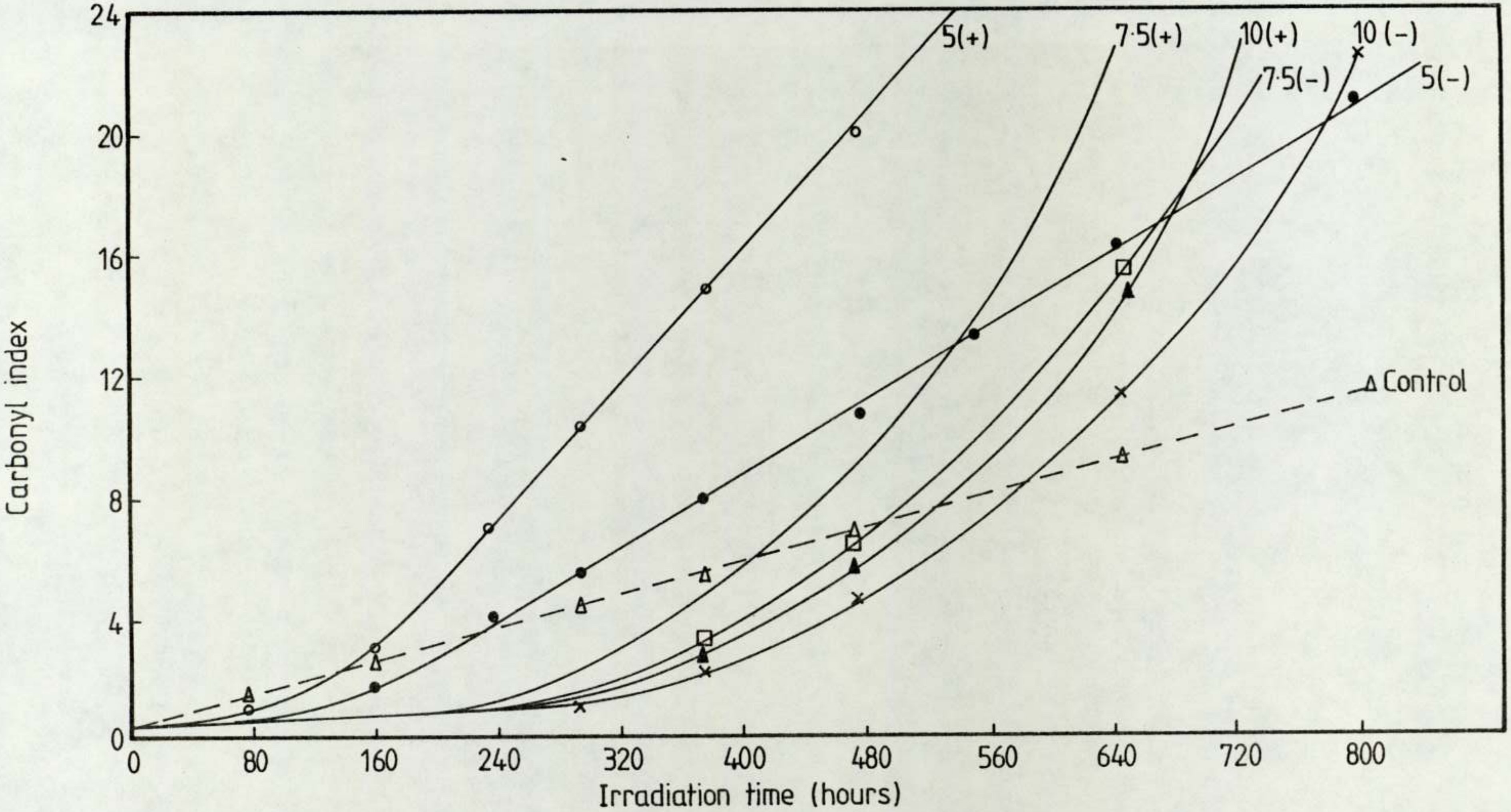


Figure 3:16 Effect of FDMC conc. on the photo-oxidation of LDPE in the presence (+) absence (−) of $0{\cdot}25 \times 10^{-5}$ mol/100g NDEC (Numbers on curves are FDMC conc. in mol/100g $\times 10^4$)

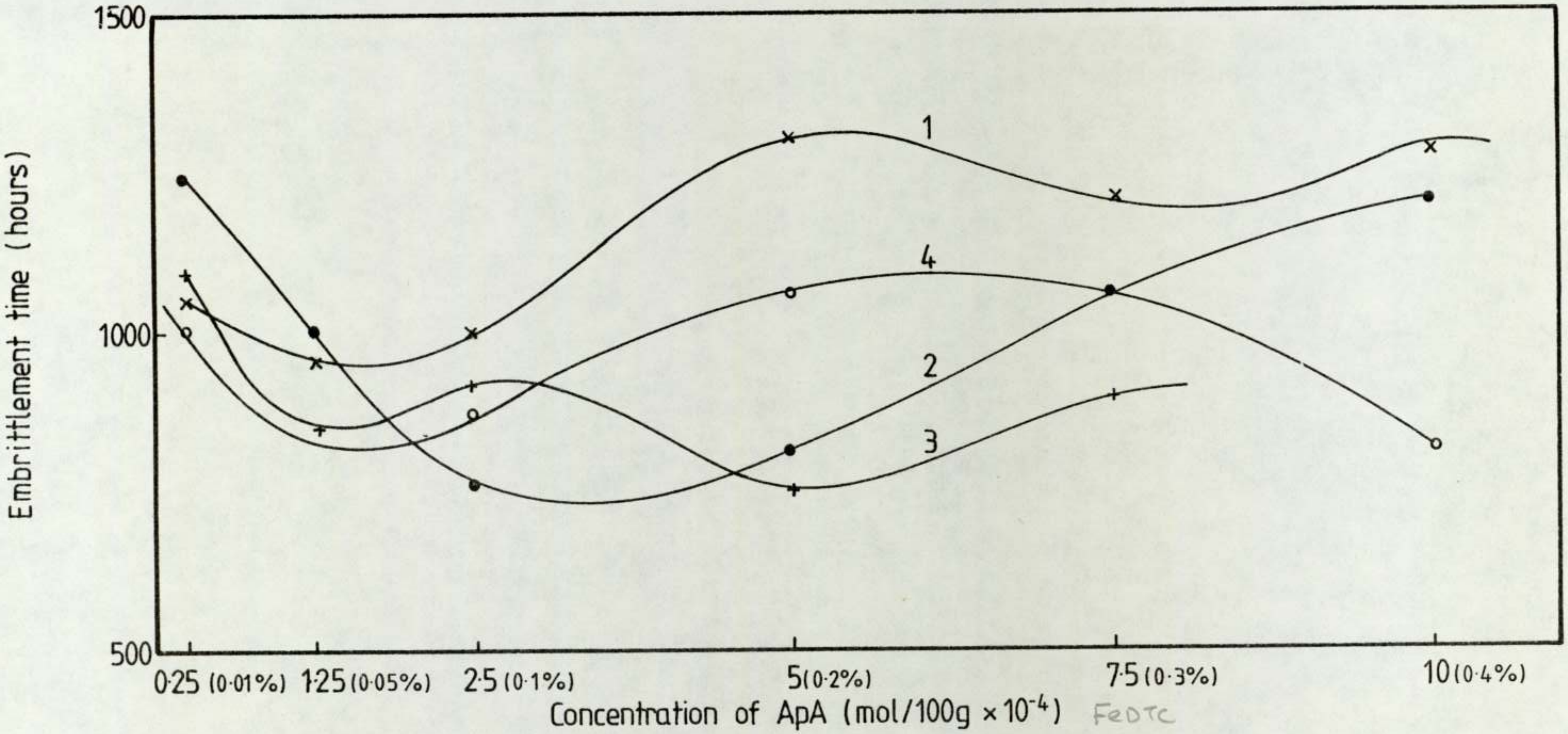


Figure 3:17 The effect of a peroxide decomposing antioxidant on a delay-action photo-activator (ApA) system

1. FDMC alone
2. FDMC + 0·025 × 10^{-4} NDEC
3. FDMC + 0·125 × 10^{-4} NDEC
4. FDMC + 0·25 × 10^{-4} NDEC

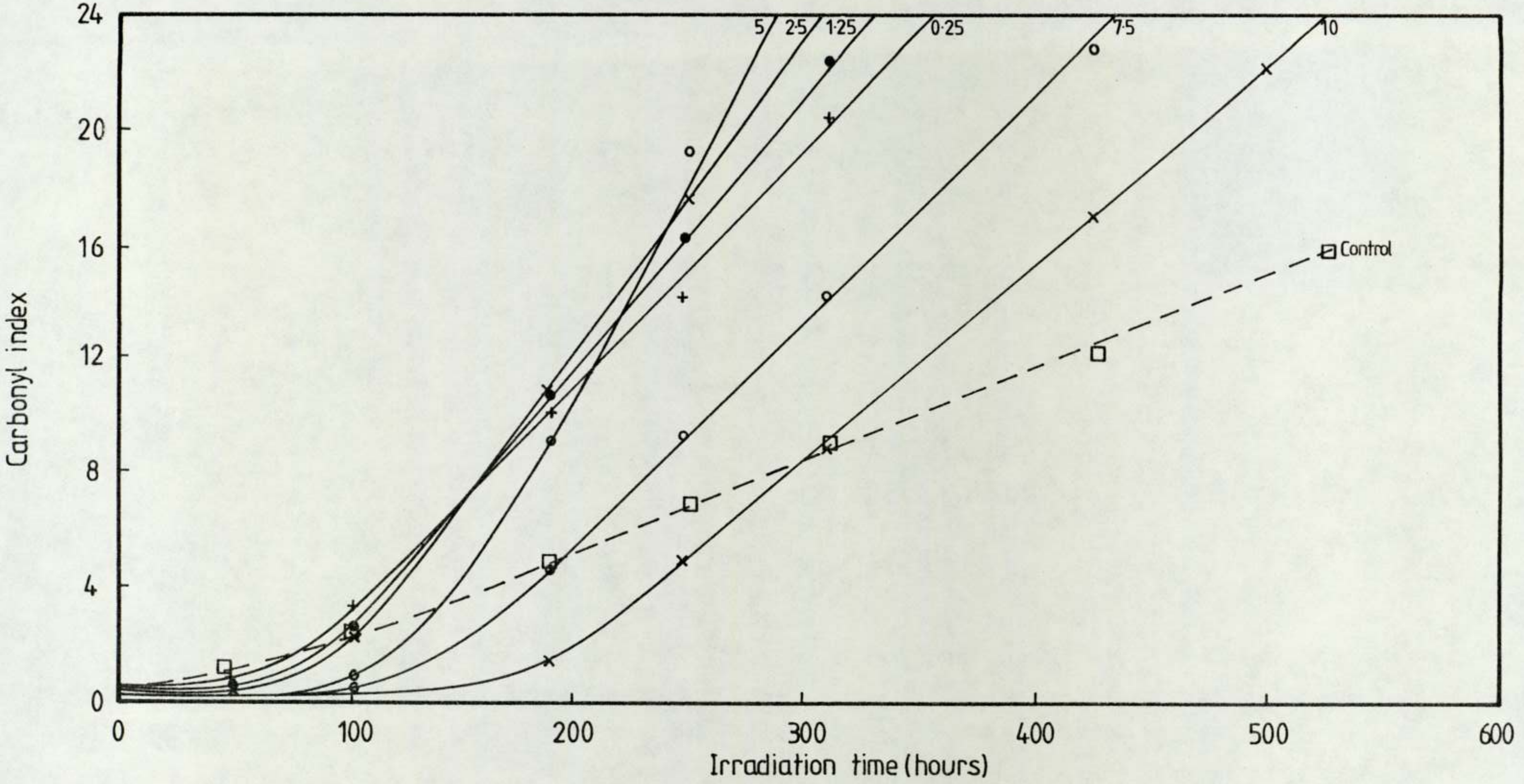


Figure 3:18 The effect of ZDEC ($1{\cdot}25 \times 10^{-4}$ mol/100g) in combination with FDMC at different conc. on photo-oxidation of LDPE processed for 10 mins. in a closed mixer at 160 °C (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

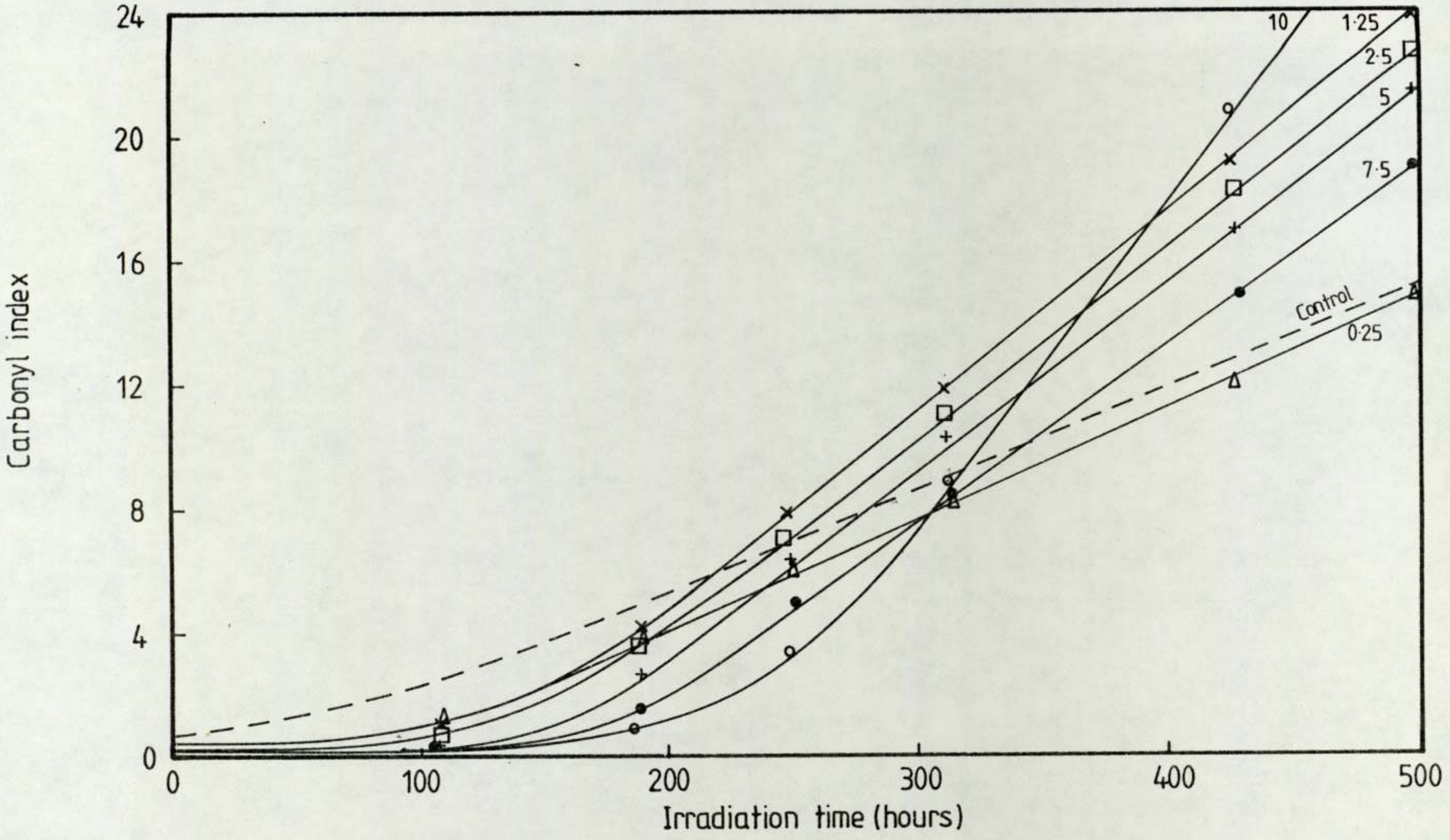


Figure 3:19 The effect of $2{\cdot}5 \times 10^{-4}$ mol/100 g ZDEC in combination with FDMC at different conc. on photo-oxidation of LDPE processed for 10 mins. in a closed mixer at 160°C (Numbers on curves are conc. of FDMC in mol/100 g $\times 10^{-4}$)

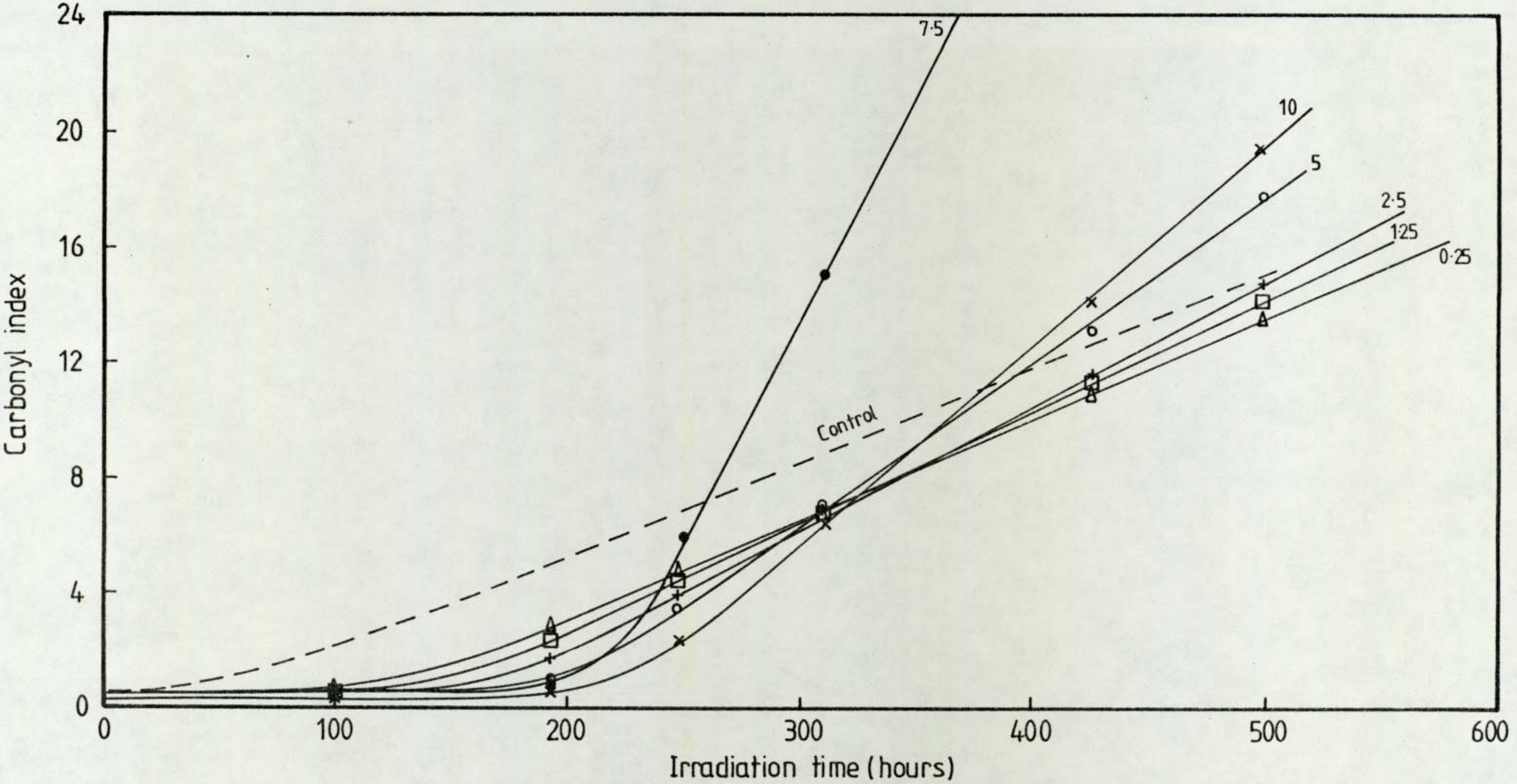


Figure 3:20 The effect of 10×10^{-4} mol / 100g ZDEC in combination with FDMC at different conc. on photo-oxidation of LDPE processed for 10 min. in a closed mixer at 160°C (Numbers on curves are conc. of FDMC in mol / 100g $\times 10^{-4}$)

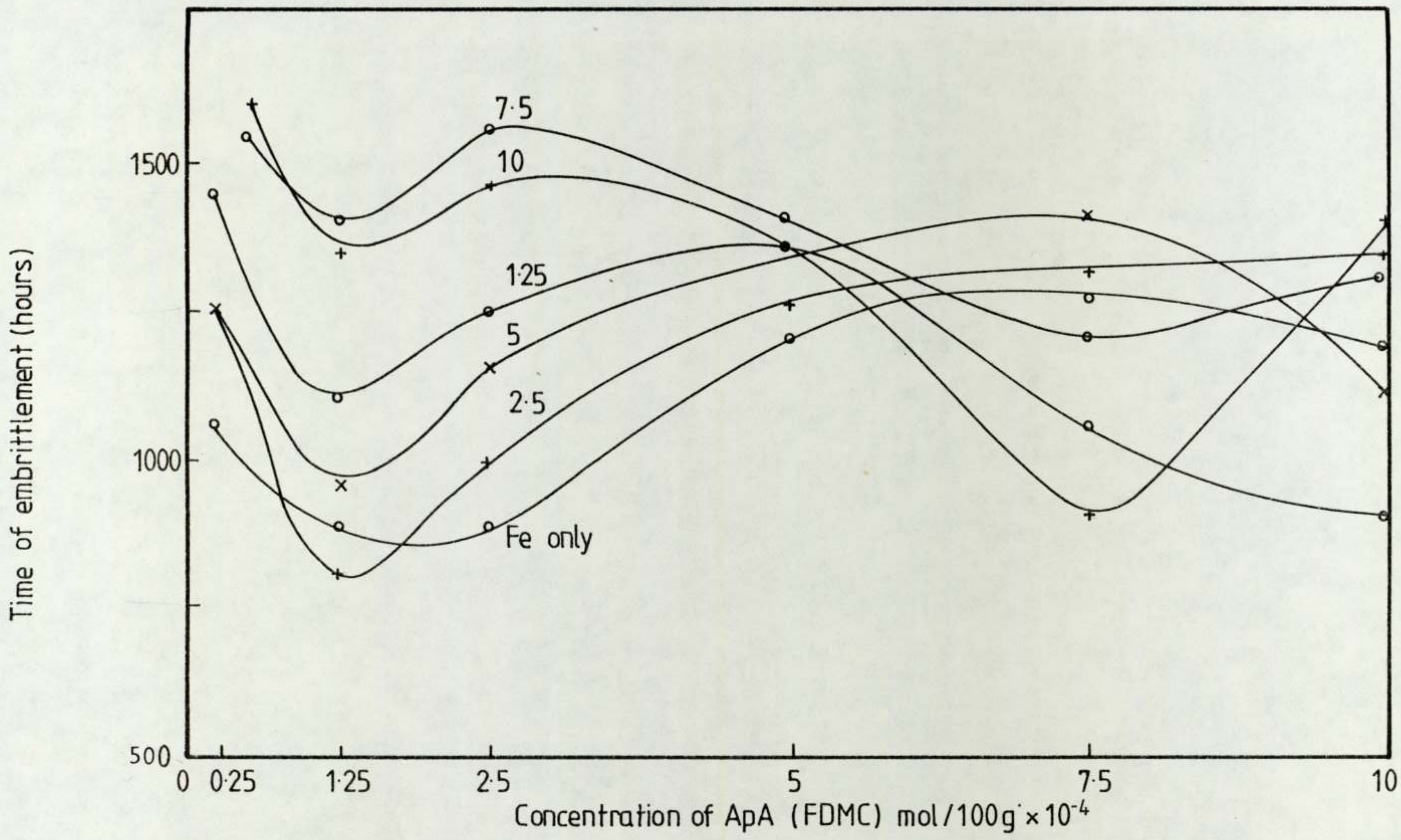


Figure 3:21 The effect of a peroxide decomposing antioxidant on a delay-action photo-activator(ApA) system. Numbers on curves are concentrations of ZDEC in mol/100 g × 10^{-4}

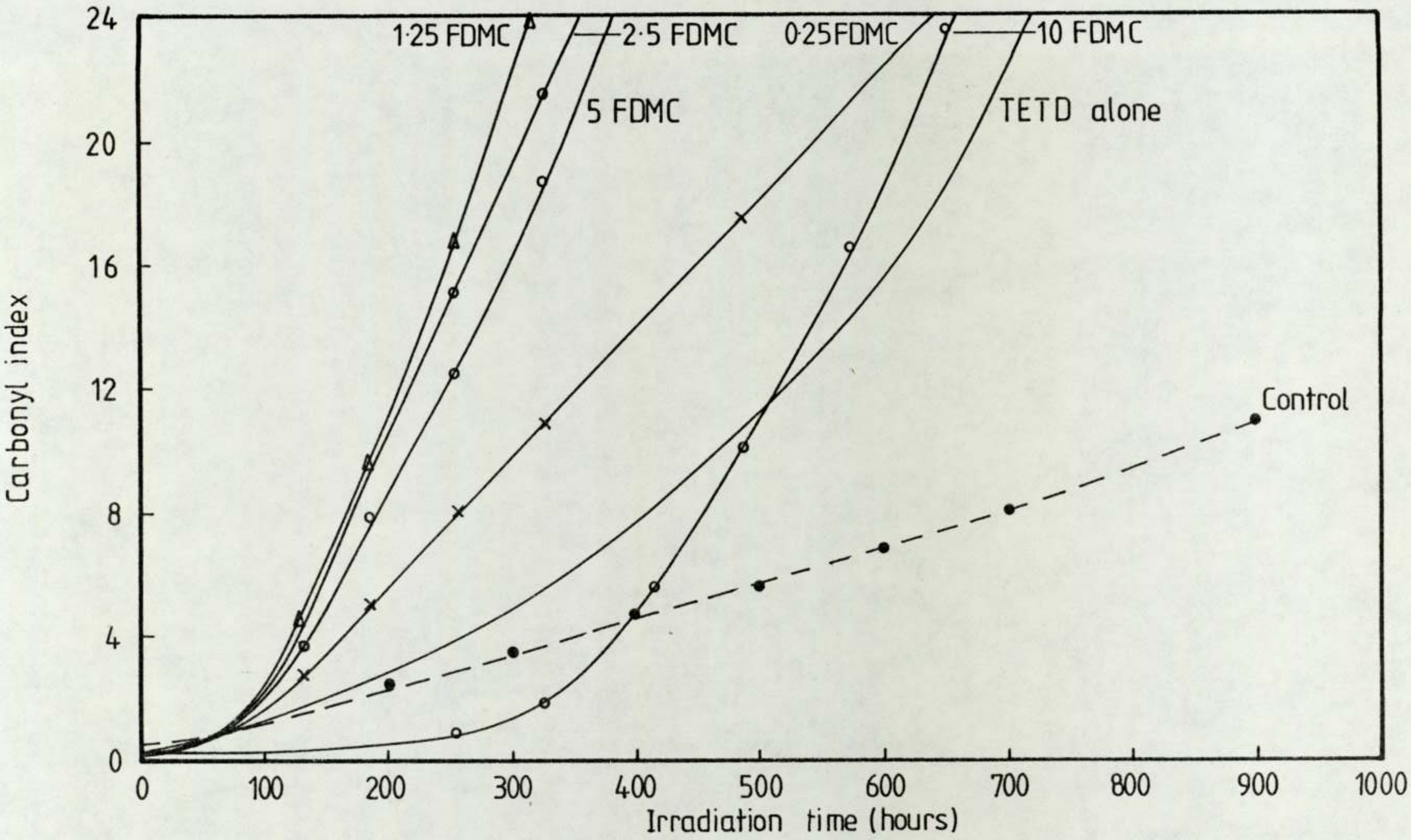


Figure 3:22 The effect of $0{\cdot}25 \times 10^{-4}$ mol/100g TETD on photo-oxidation of LDPE containing different conc. of FDMC (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

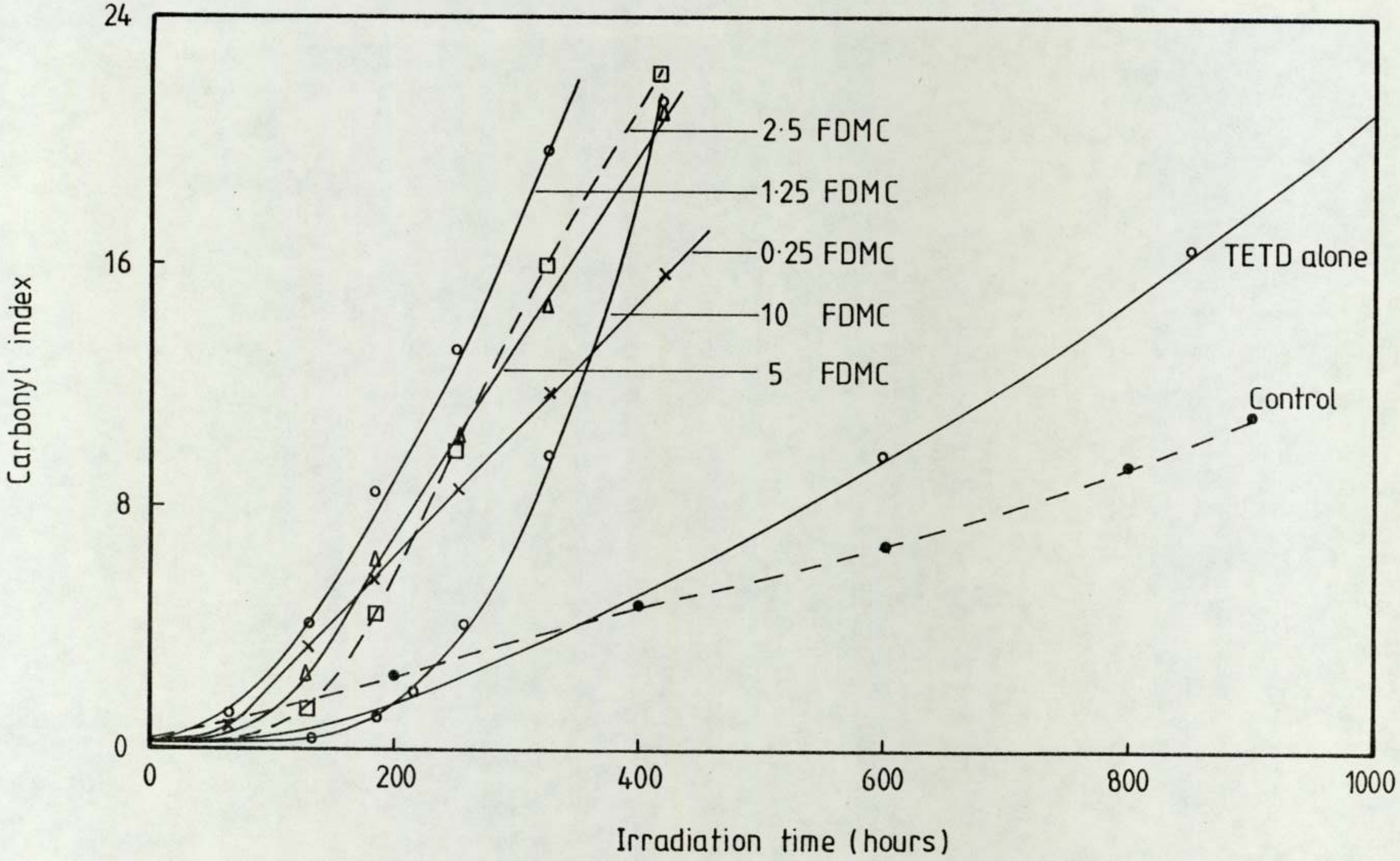


Figure 3:23 The effect of $1{\cdot}25 \times 10^{-4}$ mol/100g TETD on photo-oxidation of LDPE containing different conc. of FDMC (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

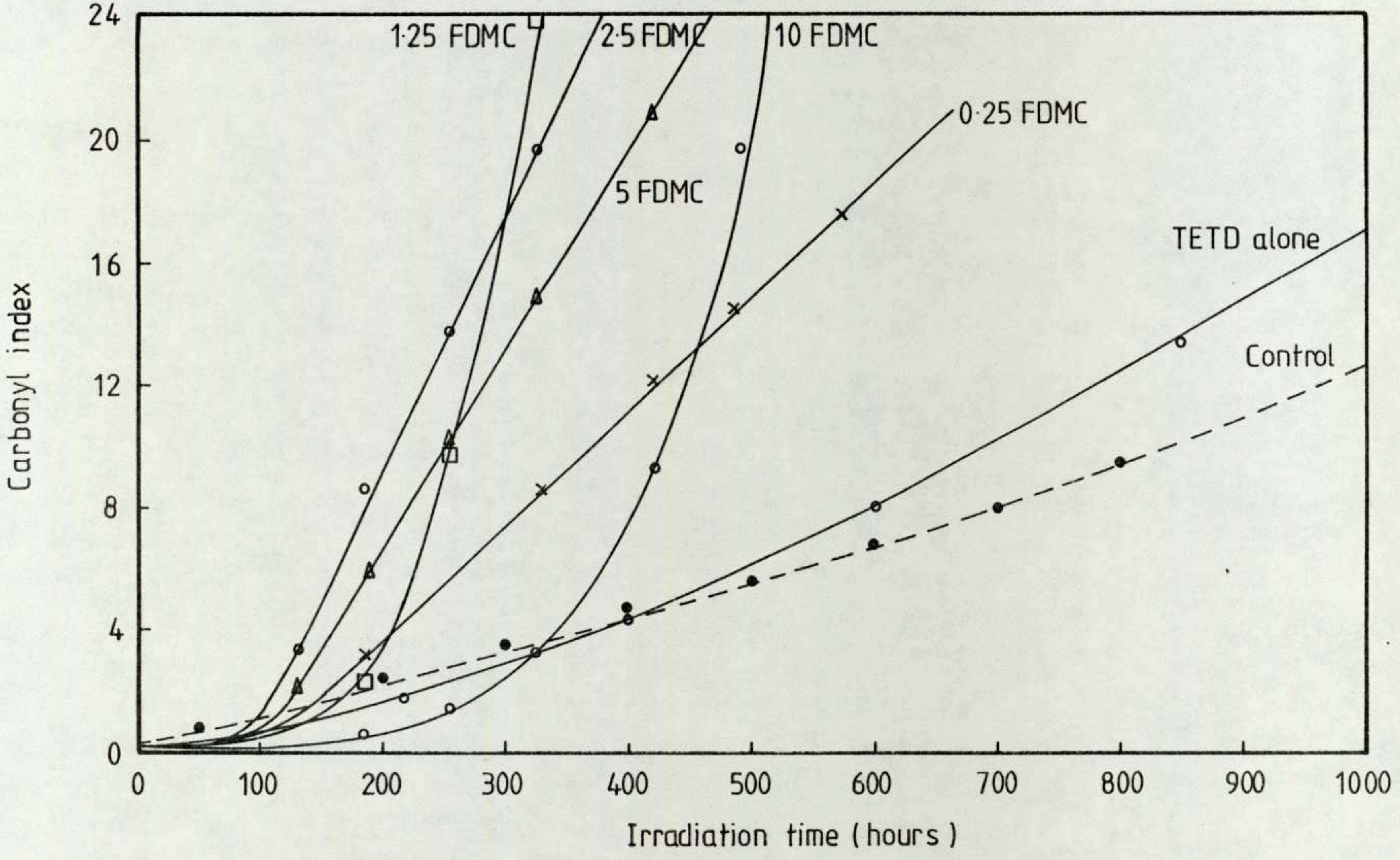


Figure 3:24 The effect of $2{\cdot}5 \times 10^{-4}$ mol / 100g TETD on photo-oxidation of LDPE containing different conc. of FDMC (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

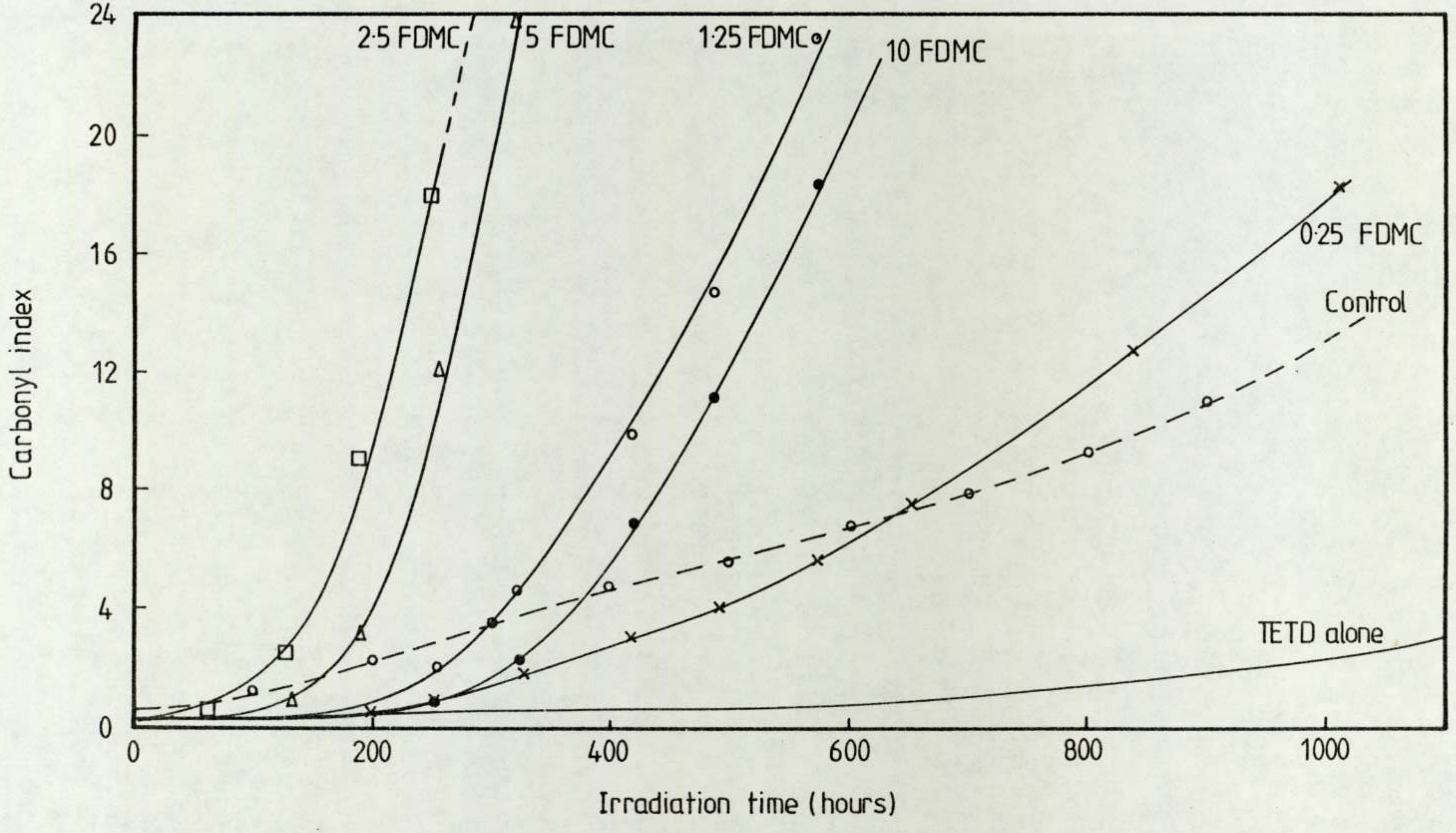


Figure 3:25 The effect of 5×10^{-4} mol/100g TETD on photo-oxidation of LDPE containing FDMC (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

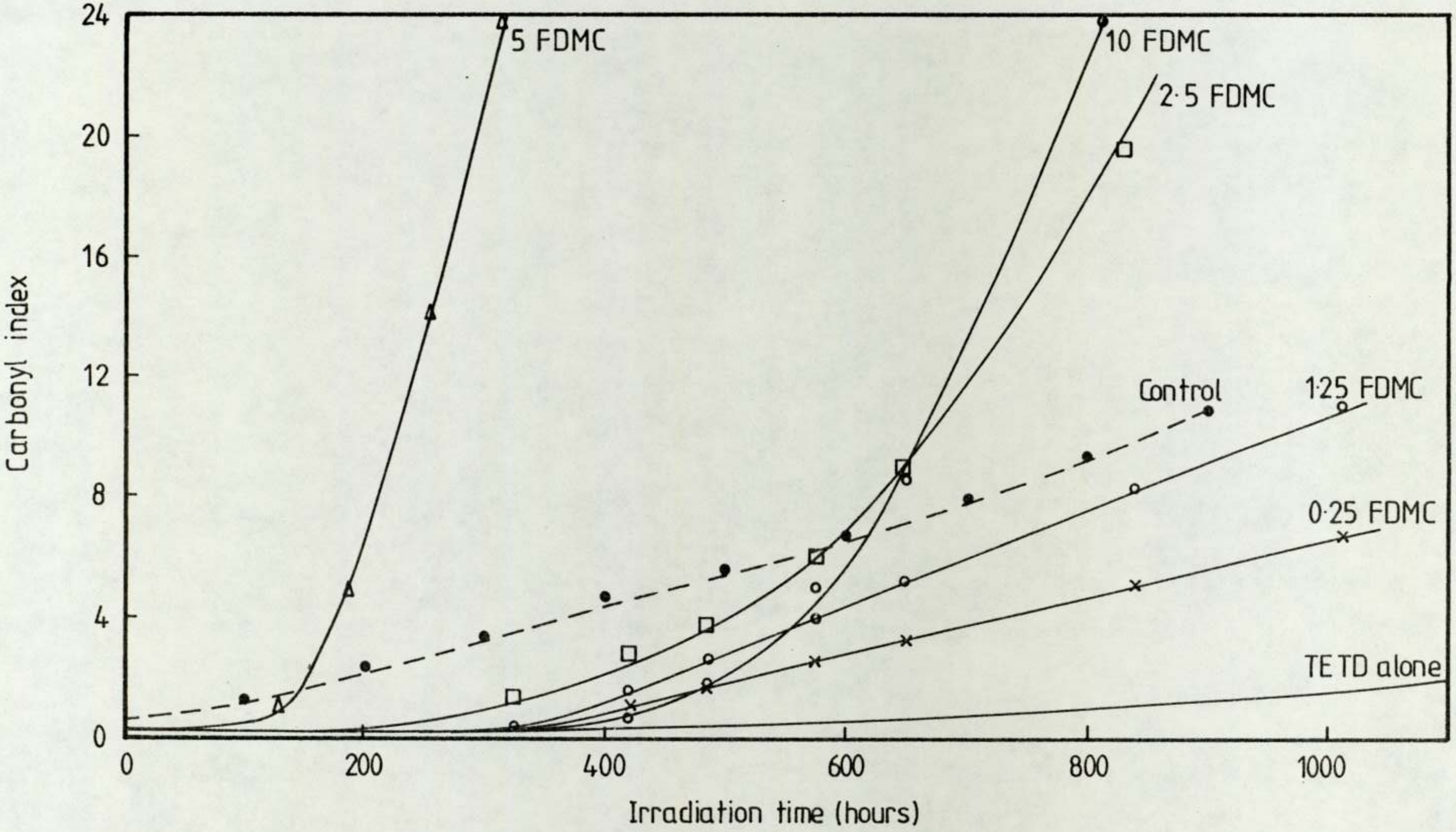


Figure 3:26 The effect of 10×10^{-4} mol/100g TETD on photo-oxidation of LDPE containing different conc. of FDMC (Numbers on curves are conc. of FDMC in mol × 100g × 10^{-4})

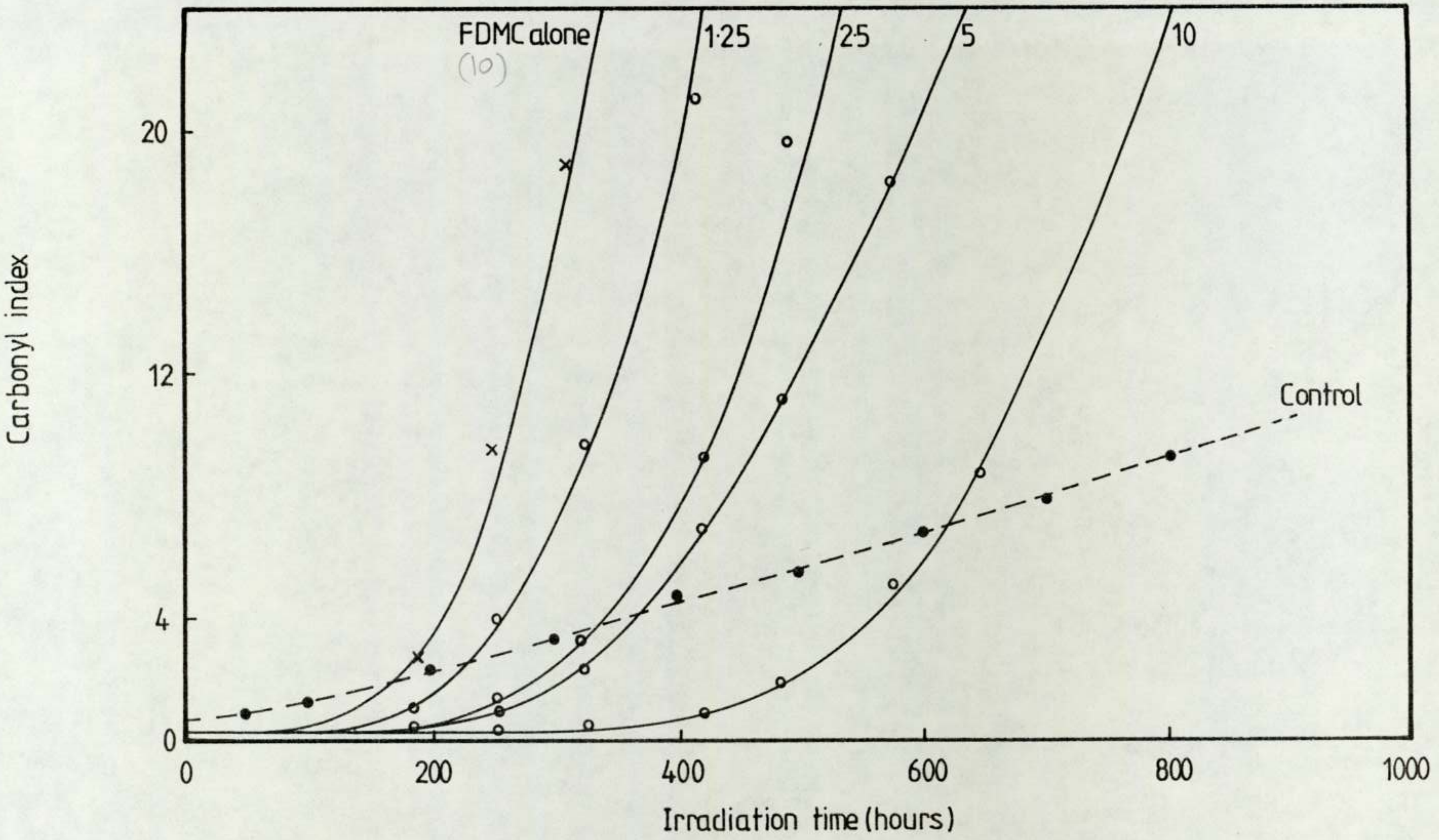


Figure 3:27 The effect of increasing TETD conc. on the photostability of LDPE, processed for 10 min. in a closed mixer at 160°C, containing 10×10^{-4} mol/100g FDMC (Numbers on curves are conc. of TETD $\times10^{4}$ mol/100g)

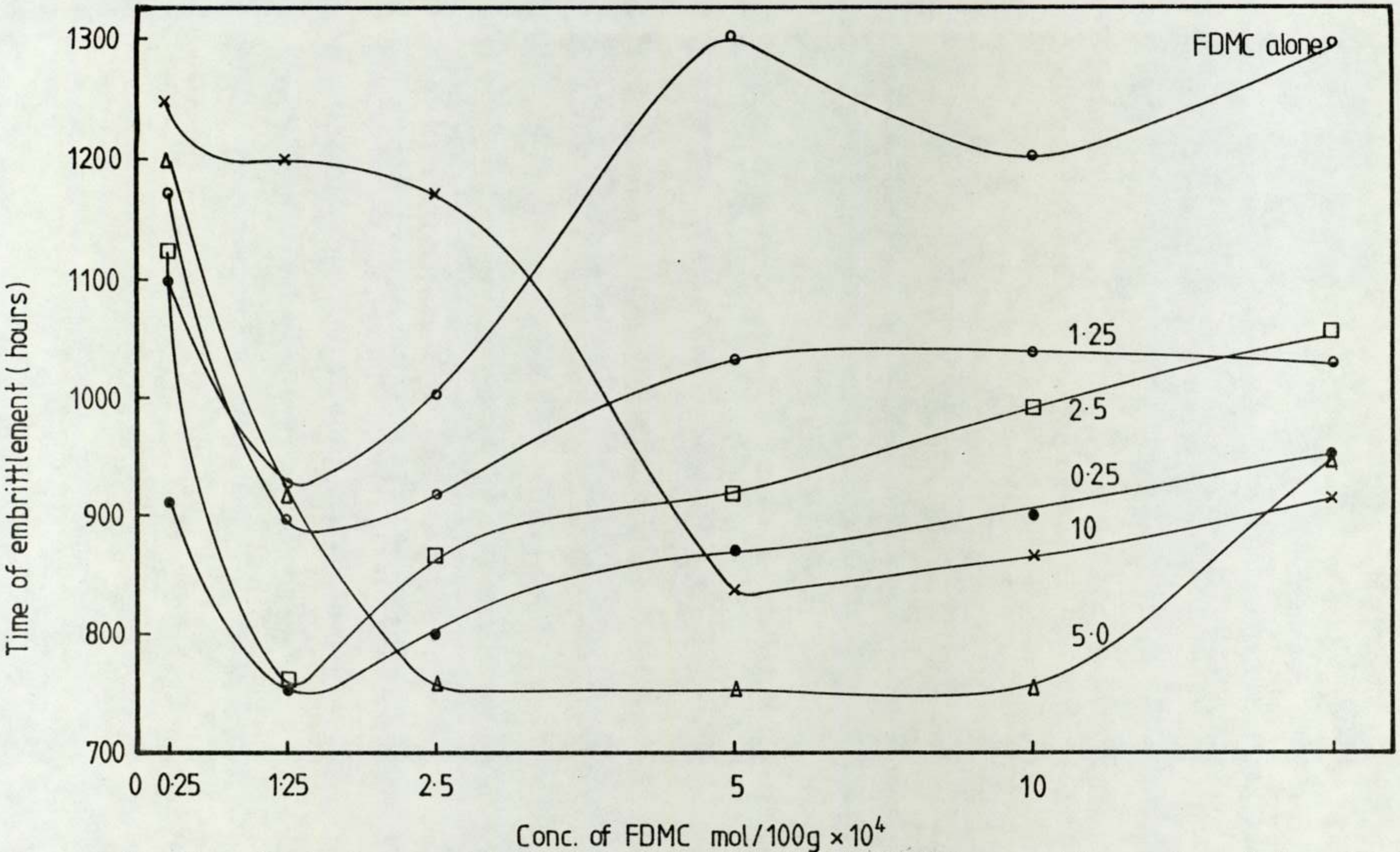


Figure 3:28 The effect of a peroxide decomposing antioxidant (TETD) on a delay-action photo-activator (FDMC) system. Numbers on curves are concentrations of TETD in mol/100g × 10^{-4}

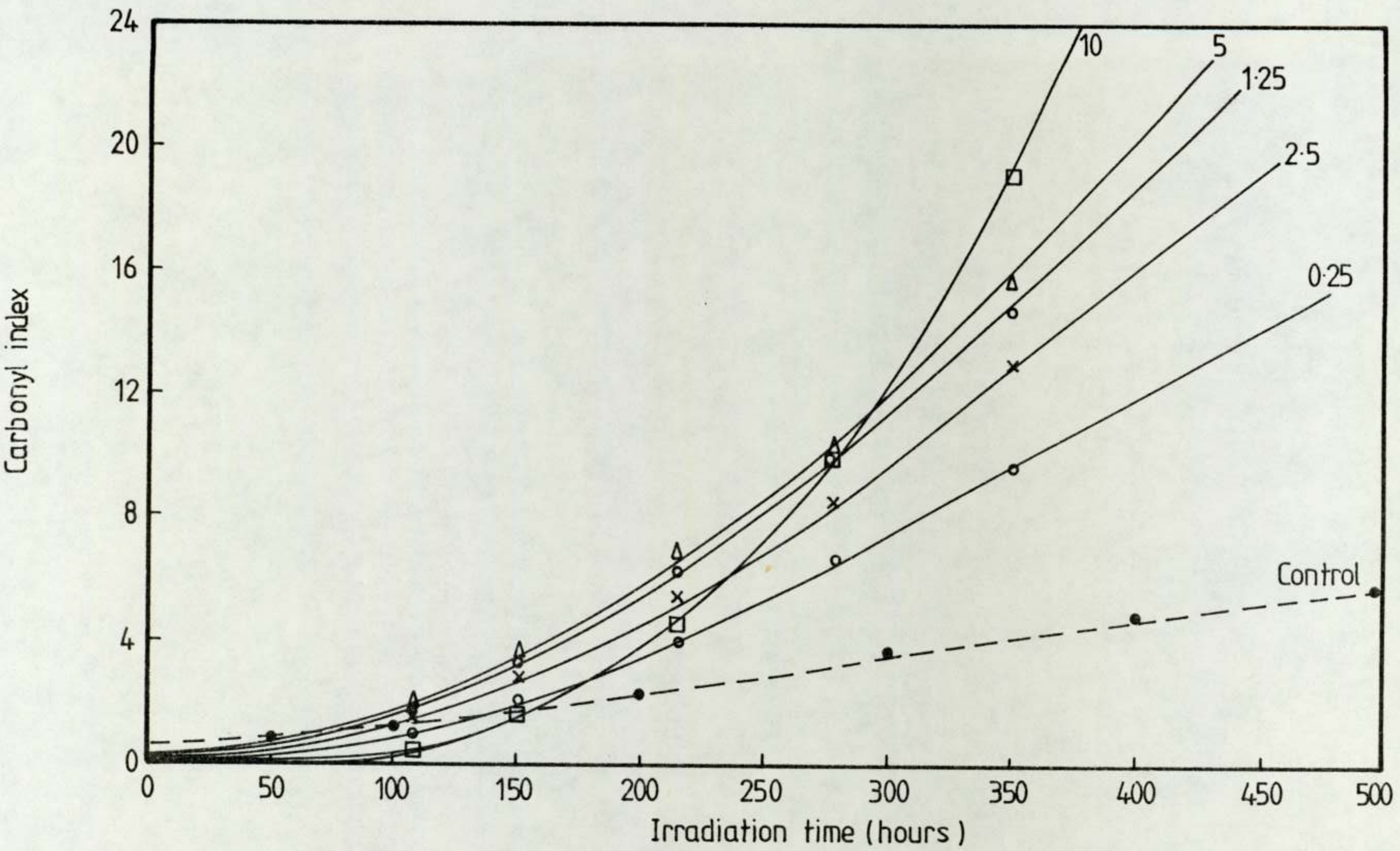


Figure 3:29 The effect of $2{\cdot}5 \times 10^{-4}$ mol/100g HOBP in combination with FDMC at different conc. on photo-oxidation of LDPE processed for 10 min. in a closed mixer at 160°C (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

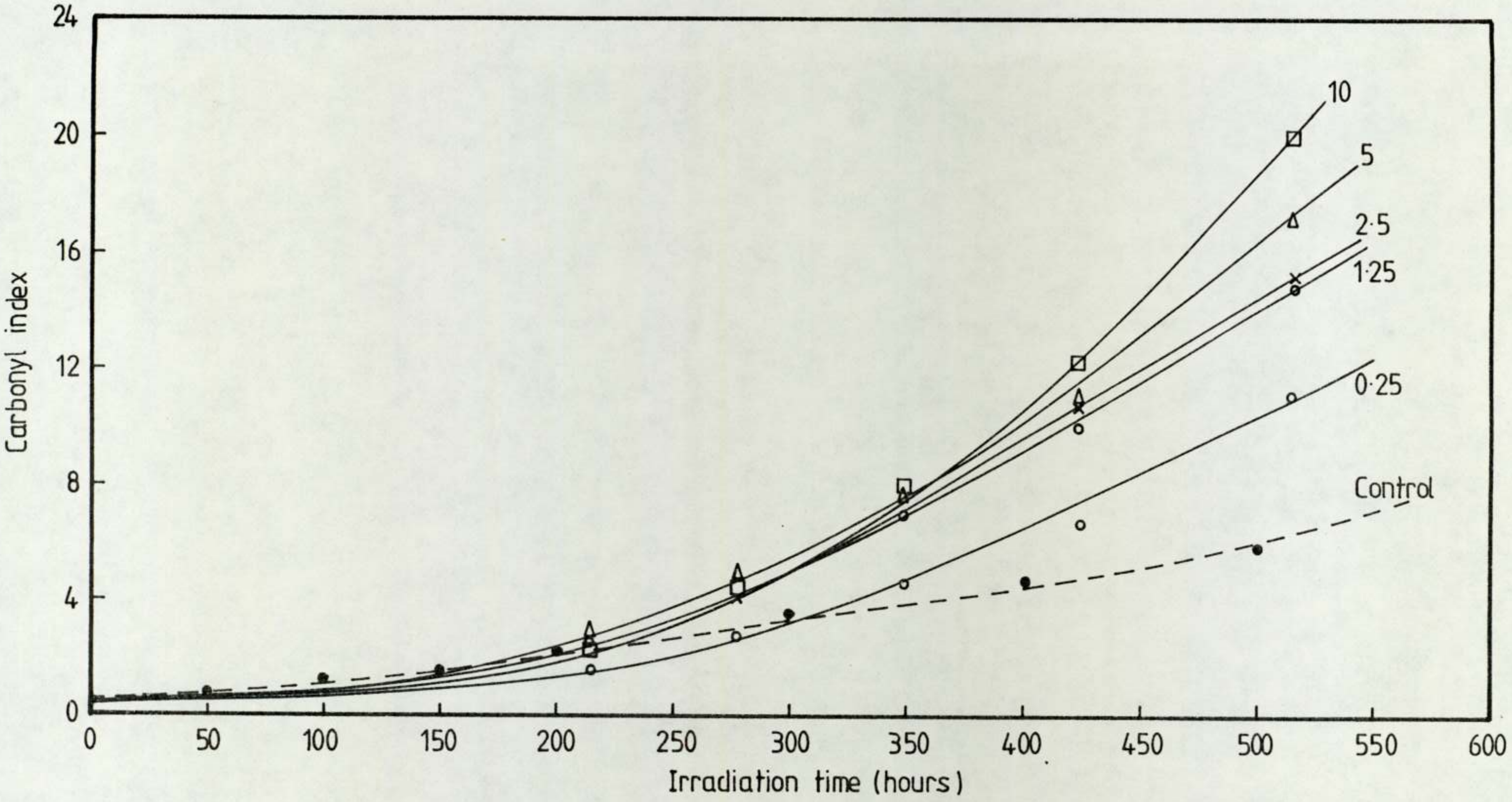


Figure 3:30 The effect of 5×10^{-4}mol/100g HOBP in combination with FDMC at different conc. on photo-oxidation of LDPE processed for 10 min. in closed mixer at 160°C (Numbers on curves are conc. of FDMC in mol/100g $\times 10^{-4}$)

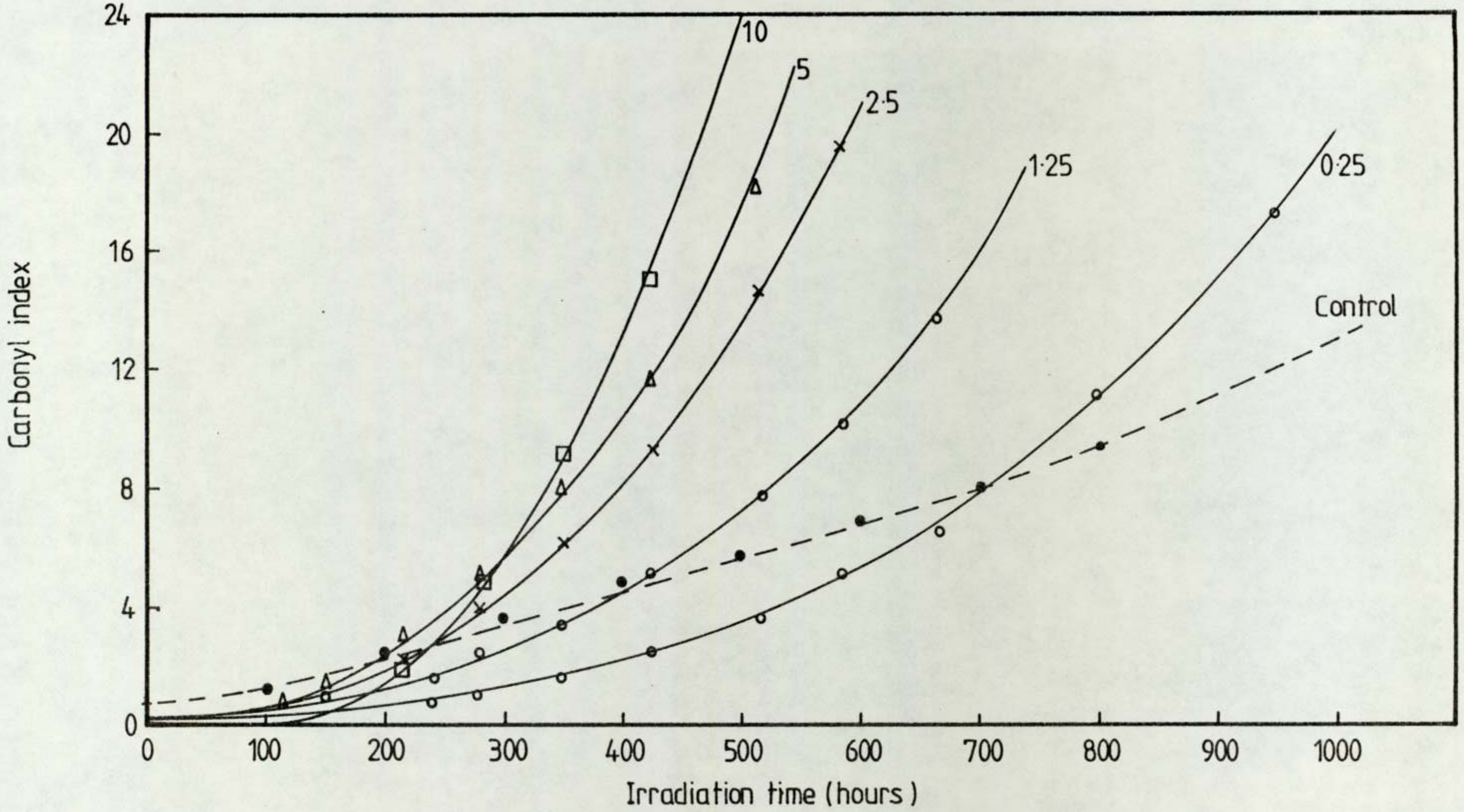


Figure 3:31 The effect of 10×10^{-4}mol/100g HOBP in combination with FDMC at different conc. on photo-oxidation of-LDPE processed for 10 min. in closed mixer at 160°C (Numbers on curves are conc. of FDMC in mol/100g$\times10^{-4}$)

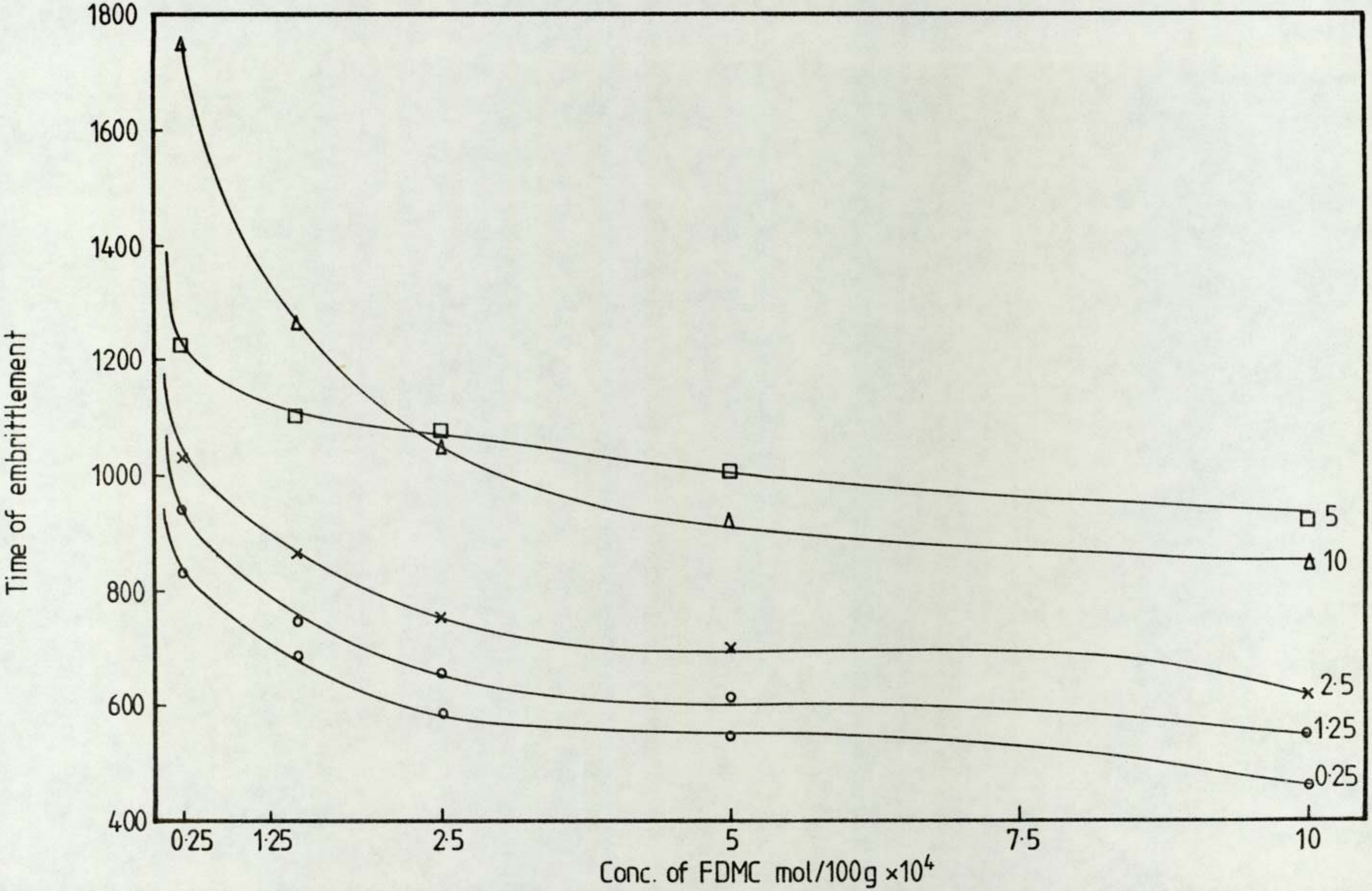


Figure 3:32 Effect of FDMC conc. on U.V. embrittlement time of LDPE in the presence of HOBP (Numbers on curves are conc. of HOBP in mol/100g × 10^{-4})

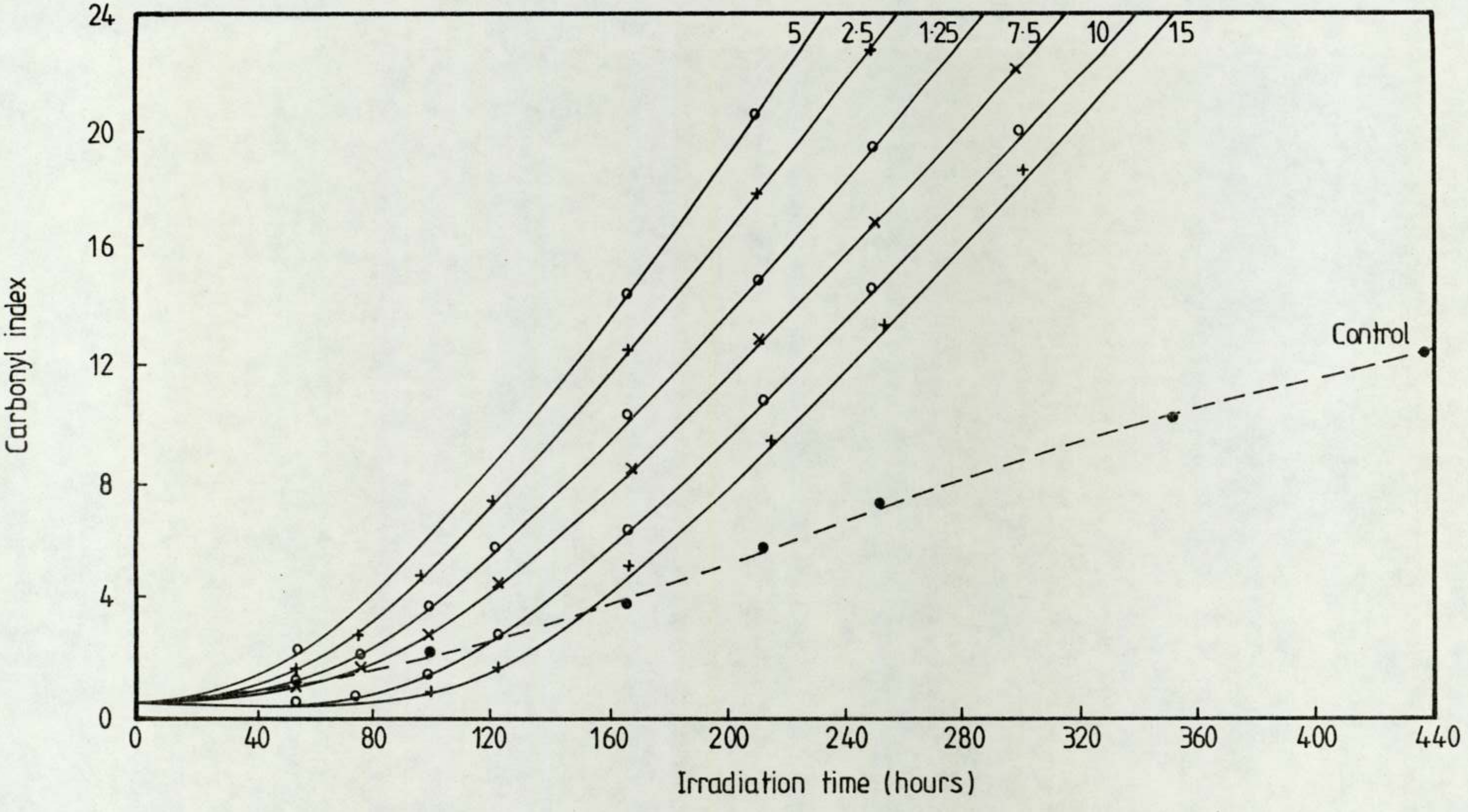


Figure 3:33 The effect of 1·25 × 10^{-4} mol/100g ZDEC in combination with FAcAc at different conc. on photo-oxidation of LDPE processed for 10 mins. in closed mixer at 160°C (Numbers on curves are conc of FAcAc in mol/100g × 10^{-4})

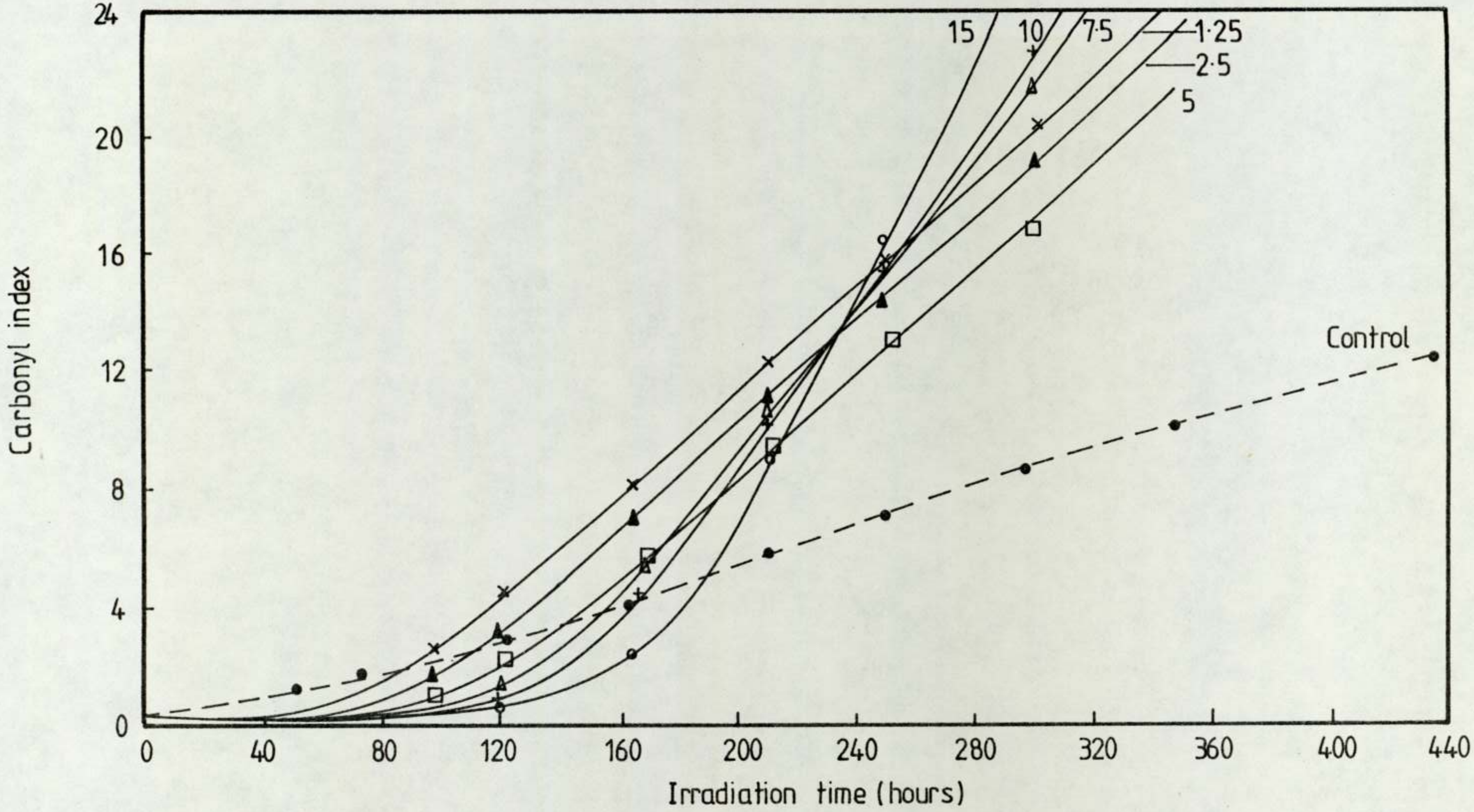


Figure 3:34 The effect of 5×10^{-4} mol/100g ZDEC in combination with FAcAc at different conc. on photo-oxidation of LDPE processed for 10 min. in closed mixer at 160°C (Numbers on curves are conc. of FAcAc in mol/100g $\times 10^{-4}$)

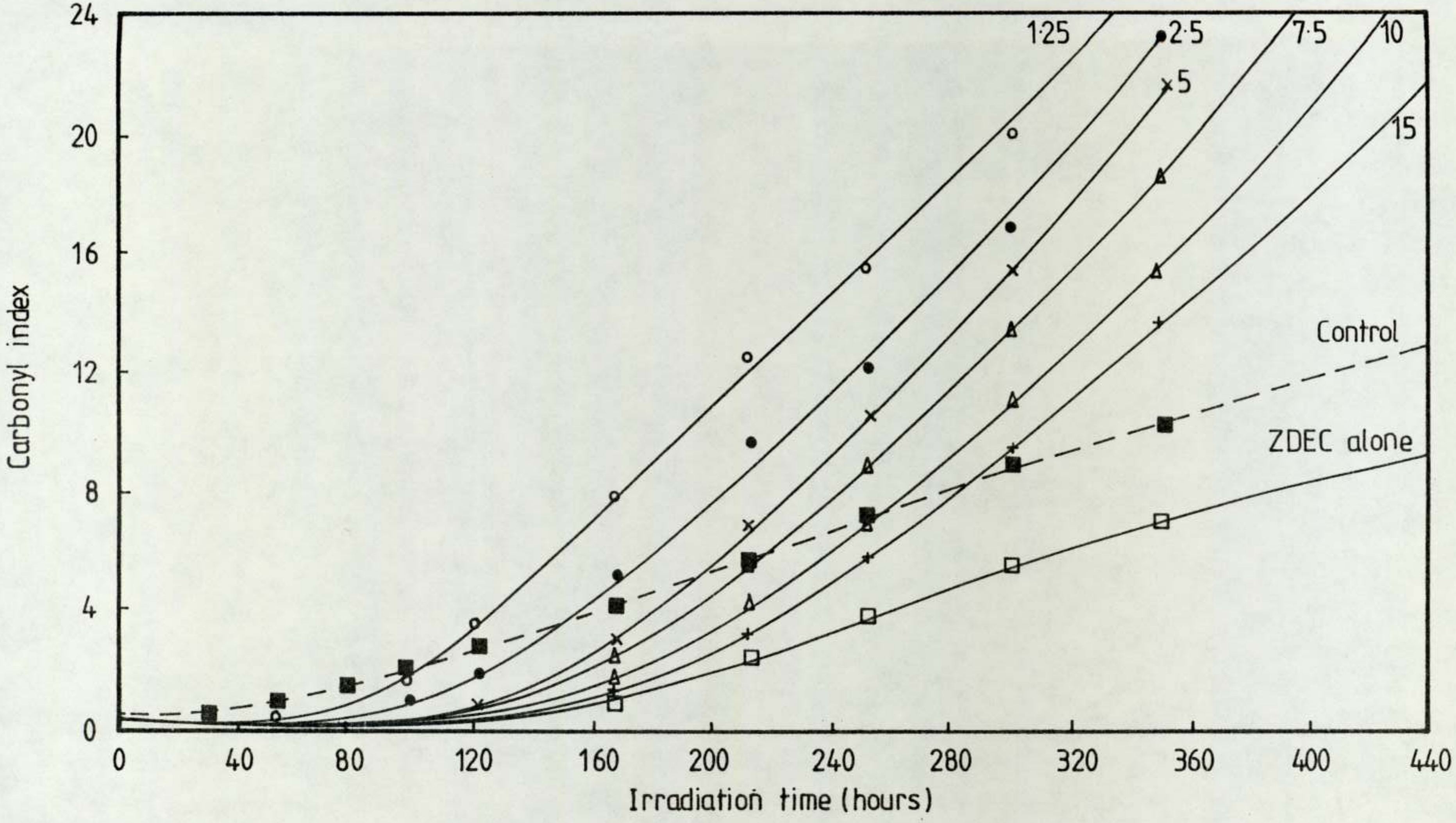


Figure 3:35 The effect of 10×10^{-4}mol/100g ZDEC alone and in combination with FAcAc at different conc. on photo-oxidation of LDPE processed for 10 min. in closed mixer at 160°C (Numbers on curves are conc. of FAcAc in mol/100g $\times 10^{-4}$)

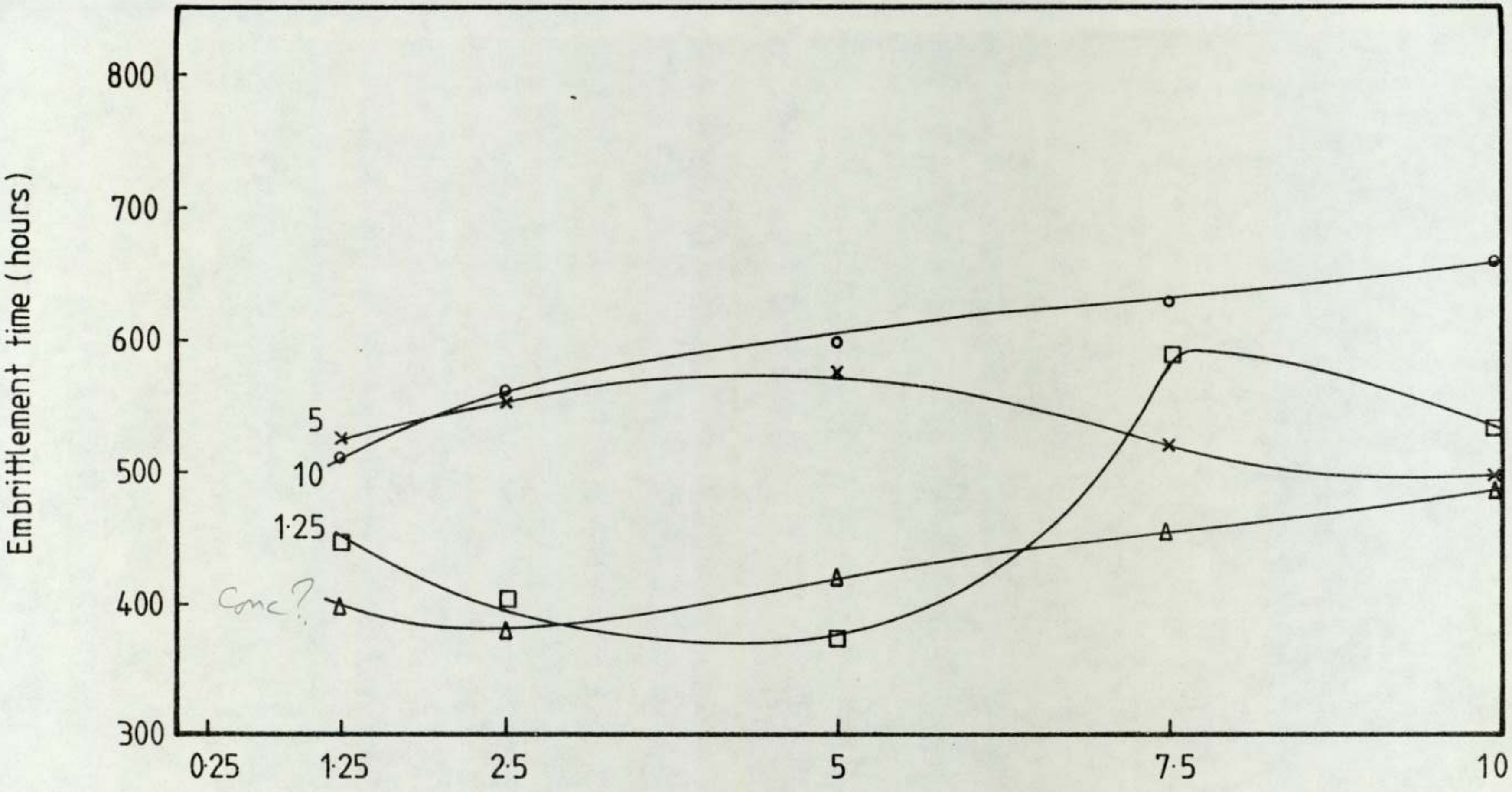


Figure 3:36 Effect of FAcAc conc. on U.V. embrittlement time of LDPE in the presence of ZDEC
(Numbers on curves are conc. of ZDEC in mol/100g × 10)

CHAPTER FOUR

TIME CONTROLLED STABILIZATION OF POLYPROPYLENE

4.1 Object

In this chapter the photo-oxidative stability of polypropylene is examined in the presence and absence of different photoactivators and antioxidants. Antioxidant photoactivators (APA) based on mixed metal chelates have also been examined in an attempt to find an adequate time-control system for the mechanised harvesting of important agricultural crops. The mixed chelates are based on a mixture of FDMC or FAcAc and a U.V. absorber (HOBP) or hydroperoxide decomposing antioxidants (NDEC, ZDEC and TETD).

The photoactivator and antioxidant were tumble-mixed with 35 gm of unstabilized polyporpylene. The compounded polymer was processed in a closed mixer of the torque rheometer (see Chapter 2, Sec. 2.6.1) for 10 minutes at 180°C. On completion of processing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation. This was compression moulded to films of thickness 2 x 10^{-2} cm at 180°C.

The above samples were exposed in a U.V. cabinet for different intervals and changes in the U.V. and I.R. spectra of these films were followed. The rate of photo-oxidation was monitored by measuring carbonyl index and embrittlement time.

4.2 Results

4.2.1 Photo-oxidation of Polypropylene

The infra-red spectrum of polypropylene before U.V. irradiation showed two absorption bands with peak maxima at 3340 cm^{-1} and 3400 cm^{-1} (Figure 4.1). These bands have been found to increase in intensity during the course of U.V. irradiation. The band at 3340 cm^{-1} was ascribed to hydrogen-bonded hydroperoxides which are produced by the oxidation of the tertiary C-H bonds(142,143). As in the case of LDPE, no free hydroperoxide was found by the I.R. technique (at 3555 cm^{-1}) on U.V. exposure of polypropylene film. This is due to immediate dissociation occurring at the weak O-O link (40 Kcal/mol)(162) after the absorption of a highly energetic photon (95 Kcal/einstein at 300 nm).

In the carbonyl region, an absorption band centred at 1685 cm^{-1} (see Figure 4.1) was found before U.V. irradiation. This absorption band, which is due to conjugated carbonyls(27d), disappeared during U.V. exposure and a broad absorption band extending from 1650-1850 cm^{-1} was formed. The latter band is an overlapping of five peaks; ester 1740 cm^{-1}, γ-lactone 1728 cm^{-1}, ketone 1725 cm^{-1}, aldehyde 1720 cm^{-1} and acid 1715 cm^{-1}. As in the case of LDPE, the main carbonyl products in photodegraded polypropylene are the carbo~~n~~xylic acids.

In the unsaturation region, the only carbonyl band observed in the I.R. spectrum of polypropylene film is at 1645 cm^{-1}. This band, which is ascribed to vinyl ketone(27d), showed little increase in intensity on U.V. exposure (Figure 4.1). No vinyl (909 cm^{-1}) or vinylidiene (887 cm^{-1}) absorption bands are observed before or after irradiation. This is probably because of the large number of wagging and bending vibrations exhibited by polypropylene in this region.

4.2.2 The Effect of Photoactivators and Antioxidants on Thermo-oxidative Stability of Polypropylene During Processing

The effect of photoactivators (FAcAc and FDMC) and antioxidants (ZDEC, NDEC, TETD and HOBP) on the melt stability of PP, as measured by changes in melt flow index, is shown in Figure 4.2. It is very clear that thermal oxidation of PP is completely inhibited during processing in the presence of transition metal dithiocarbamate complexes (NDEC, ZDEC and FDMC) and the corresponding disulphide (TETD). A typical U.V. stabilizer HOBP slows down but does not inhibit thermal oxidation and the typical photoactivator (FAcAc) has an accelerating effect on thermal oxidation of polypropylene, particularly during the early stages.

The effect of the same additives on the thermal oxidation of PP during processing as measured by the carbonyl index follows the same pattern as the MFI (see Figure 4.3). In the case of metal dithiocarbamate complexes (ZDEC and NDEC) and the corresponding disulphide (TETD), no change in carbonyl index value (after processing and before U.V. irradiation) occurs over 40 minutes processing whereas the conventional photoactivator (FAcAc) shows a steady increase with processing time. HOBP has virtually no melt stabilizing effect on PP. Similar results have been found in LDPE containing the same additives (see Chapter 3, Sec. 3.2.1).

4.2.3 Effect of Processing Severity on Photo-oxidative Stability of PP Containing Photoactivators and Antioxidants

Figure 4.4 shows the effect of processing severity on photo-oxidative stability of PP in the presence of photoactivators (FDMC and FAcAc) and antioxidants (NDEC, ZDEC, TETD and HOBP). It is clear that severe processing conditions adversly effect the photostability of metal dithiocarbamates and HOBP-stabilized PP when compared with mildly processed (CM,10) analogues (see also Table 4.1 for the embrittlement times). In contrast to this, severely processed (OM,30) PP in the presence of TETD exhibits greater photo-oxidative stability when compared to a mildly processed (CM,10) analogue (Figure 4.4 and Table 4.1).

A comparison of Figures 4.4 and 3.6 (Sec. 3.2.3) reveals the greater photo-stabilizing effectiveness of TETD in PP

Additive	Embrittlement Time (hours)	
	CM,10	OM,30
Control	80	38
FAcAc	65	6
FDMC	155	138
ZDEC	175	160
NDEC	740	512
TETD	470	690
HOBP	275	88
ZDMCSO	190	170
$ZDMCSO_2$	148	125

Table 4.1 Effect of processing severity on the UV lifetime of PP films containing additives (concentration of additive 2.5×10^{-4} mol/100g)

compared with its performance in LDPE (see Figure 4.4 inset). Compared to the control, mildly processed (CM,10) TETD-stabilized PP exhibits appreciable photo-oxidative stability (∿300 h induction period) whereas TETD-stabilized PE, at the same molar concentration (Figure 4.4 inset) shows almost no antioxidant effect.

The typical photoactivator (FAcAc) is extremely sensitive to the processing severity. Mildly processed (CM,10) PP in the presence of FAcAc reduces the lifetime of the polymer to nearly half that of the control (see Table 4.1 and Figure 4.4) and severe processing (OM,30) results in a sticky unprocessable material. A similar effect has also been observed in LDPE (Sec. 3.2.3).

4.2.4 Effect of Concentration of Additives on Photo-Oxidation of PP

Figure 4.5 shows the effect of concentration of antioxidant photoactivator (FDMC) on the photo-oxidation of PP. At all concentrations used, FDMC shows a stabilizing activity and this is found to increase with FDMC concentration. The above results show that FDMC, which is a very powerful melt stabilizer for PP (see Section 4.2.2), also stabilizes PP against photo-oxidation. However, an increase in FDMC concentration does not lead to a significant increase in the lifetime of the polymer; a doubling of concentration from 5 to 10 x 10^{-4} mol/100g (0.21 to 0.42 g/100 g) extends the embrittlement time by only 100 hours (~30%). This disadvantage limits the use of this antioxidant photo-activator in agriculture for long cropping periods especially under severe exposure conditions.

A comparison between Figure 4.5 and Figure 3.9 (Sec. 3.2.4) reveals that at low concentrations, FDMC behaves differently in PP compared with LDPE. At these low concentrations, FDMC shows a pro-oxidant activity in LDPE whereas in PP, at the same molar concentrations, FDMC shows stabilizing behaviour. At higher concentrations, however, FDMC shows a similar stabilizing activity in both LDPE and PP.

The effect of concentration of conventional photo-activator (FAcAc) on photo-oxidation of PP is shown in Figure 4.6. It is very clear that FAcAc exerts a powerful photo-pro-oxidant activity and this is found to increase with concentration. The rate of carbonyl build-up is autoaccelerating and embrittlement times are correspondingly shorter than the control. However, considerable oxidation is found to occur during processing as shown by the intercept on the carbonyl index (Figure 4.6) leading to a commensurate change in melt flow index (see Figure 4.2 and Sec. 4.2.2). Similar results were also found with LDPE (Chapter 3,Secs. 3.2.3 and 3.2.4).

Other metal dialkyldithiocarbamates (NDEC and ZDEC) and the corresponding disulphide (TETD) are found to behave in a similar manner to that of FDMC in PP (Figures 4.7, 4.8 and 4.9).

Increasing the concentration of these additives causes a parallel increase in the length of the induction period. However, the efficiency of stabilization afforded by these additives is found to differ. Whereas NDEC is found to be the most effective antioxidant, ZDEC is the least effective and the disulphide functions as a moderate antioxidant. Figure 4.10 shows that the stabilizers fall into two classes. The effective stabilizers (NDEC, TETD and HOBP) are strongly concentration dependent whereas the ineffective stabilizers (FDMC and ZDEC) are not.

Figure 4.11 shows the effect of the concentration of commercial U.V. absorber (HOBP) on the photo-oxidative stability of PP. From this it is clear that autoretardation of photo-oxidation characterises the behaviour of HOBP-stabilized PP. No definite induction period, as in the case of metal dithiocarbamates-stabilized PP, is observed. However, the retardation activity is found to increase with concentration (see Figure 4.11).

4.2.5 Effect of Oxidation Products of Metal Dithiocarbamates on Photo-stability of Polypropylene

It has been suggested by many workers(4,66,72,81,124,137,138,145) that products formed by oxidation of metal dithiolates are effective antioxidants for polyolefins rather than the metal complexes themselves. It is, therefore, of interest to compare the effect of some oxygenated intermediates of metal dithiocarbamates with the parent complexes. Zinc dimethylthiocarbomylsulphenate (ZDMCSO) and sulphinate ($ZDMCSO_2$) were chosen for this study and their effect on photo-oxidation of PP at two different concentrations are compared with the parent zinc dimethyldithiocarbamate (ZDMC) in Figure 4.12. It is clear that $ZDMCSO_2$ decreases the photostability of PP compared to the parent complex (ZDMC), whereas the sulphenate (ZDMCSO) improves it. However, in both cases the extent of change is not great, ranging from 20-40 hours only. On increasing the concentration of these oxygenated sulphur intermediates, a parallel increase in the photo-stability of PP is observed (see Figure 4.12). However this improvement is not again significant. The oxygenated sulphur intermediates, like the parent complex (ZDMC), are therefore not strongly concentration dependent and hence are weak stabilizers.

The effect of processing severity on the efficiency of ZDMCSO and $ZDMCSO_2$ as antioxidants in PP is shown in Table 4.1. It is clear that variation in the processing severity does not effect the efficiency of these oxygenated sulphur intermediates as antioxidants in the photo-oxidation of PP to any great extent. Similar results are also observed in the case of the parent dithiocarbamate complex (ZDEC) (see Figure 4.4 and Table 4.1).

4.2.6 Screening Effects of Additives on Photo-stability of Polypropylene

The effect of antioxidant photoactivator and stabilizers both as screens and additives in the photo-oxidation of polypropylene are compared in Figure 4.13. In the screening experiment, an unstabilized film (processed at 180° for 10 minutes in a closed mixer) is exposed behind a film which is identical with the former except that it contains antioxidants (concentration of additive = 5×10^{-4} mol/100 g). The unstabilized film under these conditions can only receive light which has passed through the stabilizer containing film. The photostability of unstabilized film is determined and is compared with the photostability of a film containing antioxidants as additives. It is clear from Figure 4.13 that the screening effect of ZDEC does not contribute to the overall mechanism to any extent, because the rate of photo-oxidation of the sample screened by this additive is almost the same as that of the control screened by control (Figure 4.13). The protective effect of FDMC, TETD, NDEC and HOBP on the photo-oxidation of PP is partly due to screening of U.V. light (Figure 4.13). The order of screening effectiveness of these additives is as follows NDEC>HOBP>FDMC=TETD. However, as Figure 4.13 implies, the screening effect exhibited by these stabilizers cannot explain their overall stabilizing effect when present in the film as additives. The poor correlation between U.V. absorption ability and polypropylene stabilization for these stabilizers has also been pointed out for PE in Chapter 3, Sections 3.2.5 and 3.3.5. It seems, therefore, that other stabilisation mechanisms are operating in addition to U.V. screening in the stabilization of polypropylene by these additives (NDEC, HOBP, FDMC and TETD).

4.2.7 Photo-stabilization of Polypropylene by Two Component Systems

It has been reported(15) that a mulching film based on a single component system (FDMC), which although it gives adequate time-control for short cropping periods, does not give the control necessary for longer cropping periods especially under severe exposure conditions. This is due to the system becoming relatively insensitive to concentration as the polymer becomes more stable. Thus, doubling the concentration of FDMC from 2.5×10^{-4} to 5×10^{-4} mol/100 g increases the lifetime of PP only by 60 hours (≃25%) (see Figures 4.14 and 4.15). However, addition of NDEC to the system makes the sensitiser system (FDMC) much more concentration-dependent at low concentration. Thus, in the presence of only 2.5×10^{-4} mol/100 g NDEC (≃0.1 g/100 g) a decrease of FDMC concentration from 1.25×10^{-4} to 0.25×10^{-4} mol/100g (0.05 to 0.01 g/100 g) increases the lifetime of polypropylene from 450 to 700 hours (see Figure 4.14). Similar curves, but displaced to the right on the time axis, are also observed at higher NDEC concentrations (Figure 4.15). It is therefore very clear from Figures 4.14 and 4.15 that APA based on a combination of the stabilizer complex (NDEC) and activator complex (FDMC) gives a more precise controllable activation at much lower activator concentration. The photostability of polypropylene can be varied by a factor of almost 25 within the concentration range used. Figures 4.14 and 4.15 also show that identical embrittlement times can be achieved by using two different combinations of stabilizing and activating components. The two component APA system is, therefore, expected to be entirely successful and gives the very sharp termination to film life that is required for automated harvesting of tomatoes and other soft fruits even under severe exposure conditions.

Further examination of Figures 4.14 and 4.15 reveals that the FDMC has a vital effect on the time-controlled photostability of PP. The higher the concentration of FDMC in the combination, the shorter is the length of the induction period and in general, the higher is the rate of photo-oxidation at the end of the induction period. It seems possible that the antioxidant (NDEC) concentration primarily determines the induction period and the activator (FDMC) concentration - the slope of the photo-oxidation curve and hence the embrittlement time.

The above observations have been further confirmed by fixing the concentration of NDEC in the polymer samples at 2.5×10^{-4} mol/100 g while the concentration of FDMC in the combination was varied over a range as shown in Figure 4.16 and the decay of the characteristic charge transfer band of NDEC at 325 nm was followed during U.V. irradiation of the polymer samples. It is quite clear from Figure 4.16 that the higher the concentration of FDMC, the faster is the rate of decay of the NDEC band. The time for the complete decay of the NDEC band correlates with the length of the induction period (compare Figure 4.14 with 4.16). It is therefore,possible to conclude that NDEC is presumably responsible for the substantial induction period observed while FDMC controls its variation and also controls the rate of photo-oxidation following the induction period and hence the embrittlement time.

The effect of another hydroperoxide decomposer (ZDEC) in combination with FDMC has been found to be different from the effect shown by NDEC/FDMC system. Figures 4.17-4.19 show that varying the concentration of FDMC in the presence of a fixed concentration of ZDEC gives an almost additive stabilizing effect. Moreover, increasing concentration of ZDEC from 2.5×10^{-4} to 10×10^{-4} mol/100 g did not show any remarkable increase in the photo-stability of PP at any particular ratio of ZDEC/FDMC. However, much better time-controlled photo-stability of PP is achieved using ZDEC/FDMC system compared with that achieved by a single APA system (FDMC). The embrittlement times of PP containing the ZDEC/FDMC system are shown in Table 4.3. It is clear that identical embrittlement times can be achieved by using two or more different ratios of the stabilizing and activating components.

Figures 4.20 and 4.21 show the decay of ZDEC in the absence and presence of FDMC in PP film during U.V. irradiation. It may be mentioned here that in the combination, both ZDEC and FDMC absorb in almost the same place at 265 nm (see Figures 2.1 and 2.3). However, the absorption due to FDMC is very small compared to ZDEC. FDMC (10 x 10^{-4} mol/ 100 g) was found to decay almost completely in 100 hours. In another experiment, it has been found that ZDEC decays almost completely at about 60 hours (Figure 4.20). Moreover, the combined absorption has been found to decay at about 250 hours, clearly showing that the two components protect each other during photo-oxidation.

Comparison of the ZDEC/FDMC and NDEC/FDMC systems (Figures 4.14, 4.15, 4.17-4.19) reveals that the addition of NDEC is much more effective than ZDEC in stabilization of PP. Thus a combination of 2.5 x 10^{-4} mol/100 g NDEC/2.5 x 10^{-4} mol/ 100 g FDMC gives 410 hours embrittlement time in PP while combination of ZDEC/FDMC at the same concentrations gives only 275 hours (see Tables 4.2 and 4.3 for further comparison). This difference in effectiveness between ZDEC and NDEC in combination with FDMC suggests that NDEC is operating by additional mechanisms other than hydroperoxide decomposition. Similar observations have previously been seen on using these additives (ZDEC and NDEC) alone in both PE and PP polymers (see Sections 4.2.4 and 3.2.4).

NDEC concentration (mol/100g)x10^{-4}	Embrittlement Time (hours)						
	Concentration of FDMC (mol/100g)x10^{-4}						
	0	0.25	1.25	2.5	5.0	7.5	10.0
0.00	80	85	135	150	210	280	336
0.25	140	140	140	140	160	185	210
2.50	740	680	490	425	380	380	340
10.00	1840	1475	1110	980	860	800	760

Table 4.2 Effect of varying the concentration of stabilizer (NDEC) and photoactivator (FDMC) in unstabilized polypropylene

ZDEC concentration (mol/100g)x10^{-4}	Embrittlement Time (hours)						
	Concentration of FDMC (mol/100g)x10^{-4}						
	0	0.25	1.25	2.5	5.0	7.5	10.0
0.00	80	85	135	150	210	280	336
2.50	175	180	200	275	360	410	460
5.00	200	208	250	295	362	436	525
10.00	250	285	365	400	437	500	550

Table 4.3 Effect of varying the concentration of stabilizer (ZDEC) and photoactivator (FDMC) in unstabilized polypropylene

Figures 4.22-4.24 compare the effect of FDMC concentration in the presence and absence of TETD. It is very clear from these figures that the disulphide has a similar effect on FDMC to other hydroperoxide decomposers (NDEC and ZDEC). The lifetime of the FDMC-stabilized PP increases on addition of TETD. Thus embrittlement times ranging from 160-1070 hours can be achieved using this two component system (see Table 4.4). The rate of photo-oxidation at the end of the induction period is in general not affected by the presence of TETD and it is the same as that observed in the single APA system (FDMC).

The effect of FDMC on PP containing TETD is found to depend on the FDMC concentration. At low concentrations, FDMC antagonises TETD while at high concentrations, FDMC is either synergistic or additive (see Table 4.4).

Figure 4.25 shows the effect of FDMC alone and in combination with a typical U.V. absorber (HOBP). It can be seen that although the addition of HOBP to polypropylene containing FDMC increases the lifetime of the polymer substantially, the rate of photo-oxidation at the end of the induction period is much lower than that observed in a single component system (FDMC). This retardation of photo-oxidation becomes even greater at higher FDMC concentrations in the combination. Similar results, but displaced to the right of the time-axis are observed at higher HOBP concentrations (see Figures 4.26 and 4.27). The effect of FDMC on the efficiency of HOBP in

TETD concentration (mol/100g)x10^{-4}	Embrittlement Time (hours)					
	Concentration of FDMC (mol/100g)x10^{-4}					
	0	0.25	1.25	2.5	5.0	10.0
0.00	80	85	135	150	210	336
0.25	210	160	255	430	640	-
0.50	275	200	315	475	655	-
1.00	365	230	400	510	700	-
1.25	420	250	475	545	765	-
2.50	475	325	550	725	815	-
5.00	730	430	740	875	970	-
10.00	1070	475	800	925	1070	-

Table 4.4 Effect of varying the concentration of TETD and photoactivator (FDMC) on unstabilized polypropylene

PP is again variable. At low concentration, FDMC decreases the stabilization action of HOBP (compare Figure 4.11 with Figures 4.25-4.27), while at higher FDMC concentrations, an efficient synergistic behaviour is observed. On increasing the HOBP concentration in the combination, the retardation of photo-oxidation of PP after the induction peroid becomes very clear (see Figure 4.26). Retardation of photo-oxidation is typical behaviour of HOBP even when it is present alone in PP (see Figure 4.11). Table 4.5 shows the effect of independently varying the concentrations of photo-stabilizer (HOBP) and photo-activator (FDMC) on unstabilized PP. It can be seen that the photo-stability of PP using this system can also be varied by a factor of almost 25 within the concentration range shown. Table 4.5 also shows that at a relatively high concentration of APA (HOBP/FDMC), photo-sensitisation can be achieved after a substantial induction period. This is an important object of the ideal photo-activator system and is particularly important for the more photo-unstable polymers such as polypropylene. However, the disadvantage in this system is that the rate of photo-oxidation following the induction period is relatively slow.

Figure 4.28 shows the decay of HOBP band at 330 nm in PP during U.V. irradiation in the presence and absence of different concentrations of FDMC. It can be seen clearly that the decay of 330 nm band is faster at low FDMC concentrations compared with the decay of the analogue band in the sample containing no FDMC. However, at high concentrations of

HOBP concentration (mol/100g)x10^{-4}	Embrittlement Time (hours)						
	Concentration of FDMC (mol/100g)x10^{-4}						
	0	0.25	1.25	2.5	5.0	7.5	10.0
0.00	80	85	135	150	210	280	336
2.50	275	225	300	785	880	1020	1159
5.00	425	325	510	800	1400	1710	2005
10.00	1250	710	1530	1830	2195		

Table 4.5 Effect of varying the concentration of photo-stabilizer (HOBP) and photoactivator (FDMC) on unstabilized polypropylene

FDMC, the decay of the HOBP band is slower. In both cases the time of the complete decay of HOBP band is not equal to the length of the induction period observed in Figure 4.25.

Figure 4.29 shows the effect of conventional photo-activator (FAcAc) concentration in the presence and absence of 2.5 x 10^{-4} mol/100 g NDEC on photo-oxidation of PP. It is very clear that in the absence of NDEC, FAcAc accelerates the rate of photo-oxidation of PP and the higher the concentration of FAcAc in the polymer, the higher is the rate of photo-oxidation. In addition, the photo-oxidation commenced as soon as the polymer sample was exposed to U.V. light. No induction period is observed which is typical behaviour of conventional photo-activators. The absence of the photo-induction period in FAcAc system limits, therefore, the use of this activator in agricultural applications (see Chapter 1, Sec. 1.3.3.2). Figure 4.29 also shows the effect of addition of NDEC to PP containing FAcAc. An induction period of about 50 hours is observed and the rate of photo-oxidation following the induction period is higher at higher FAcAc concentration. This system is, therefore, similar to the NDEC/FDMC system except that the length of the induction period is shorter. At higher NDEC concentrations in the combination (Figures 4.30 and 4.31) the length of the induction period becomes longer although it is not significant and the rate of photo-oxidation becomes lower. The NDEC is, therefore, suppressing the activation action of FAcAc during both processing (see Table 4.6 for MFI) and the initial

FAcAc conc x 10^{-4}M/100g	MFI		
	Conc of NDEC x 10^{-4}M/100g		
	2.5	5.0	10
1.25	0.64	0.62	0.60
2.5	0.66	0.64	0.64
5.0	0.65	0.66	0.65
7.5	0.66	0.65	0.64
10.0	0.64	0.64	0.63
15.0	0.65	0.65	0.66

Table 4.6 Effect of FAcAc/NDEC combinations on thermal stability of PP during processing (CM,10)

stages of U.V. irradiation giving rise to an induction period. Figure 4.32 shows that the time to complete decay of NDEC band (325 nm) during U.V. irradiation of PP containing FAcAc is not equal to the length of the induction period to the carbonyl growth. Furthermore, on increasing the FAcAc concentration and keeping the NDEC concentration constant, the rate of NDEC band decay and the length of the photo-induction period to carbonyl growth are not changed significantly (see Figure 4.32). However, the rate of photo-oxidation following the induction period is found to increase.

Table 4.7 compares the embrittlement times of PP films containing both NDEC and FAcAc alone and when they are in combination at different molar ratios. It is clear that addition of NDEC to PP containing FAcAc considerably increases its lifetime. Thus the embrittlement time of PP containing 1.25 x 10^{-4} mol/100 g FAcAc is 70 hours and it becomes 400 hours on addition of a small concentration of NDEC (2.5 x 10^{-4} mol/100 g). Table 4.7 also shows that FAcAc decreases the stabilizing action of NDEC in the same manner as FDMC does to NDEC (see Figures 4.14-4.16).

4.3 Discussion

4.3.1 Photo-oxidation of Polypropylene

It has been shown$^{(146)}$ that polypropylene is markedly sensitised to U.V. light by the thermal-oxidative conditions of

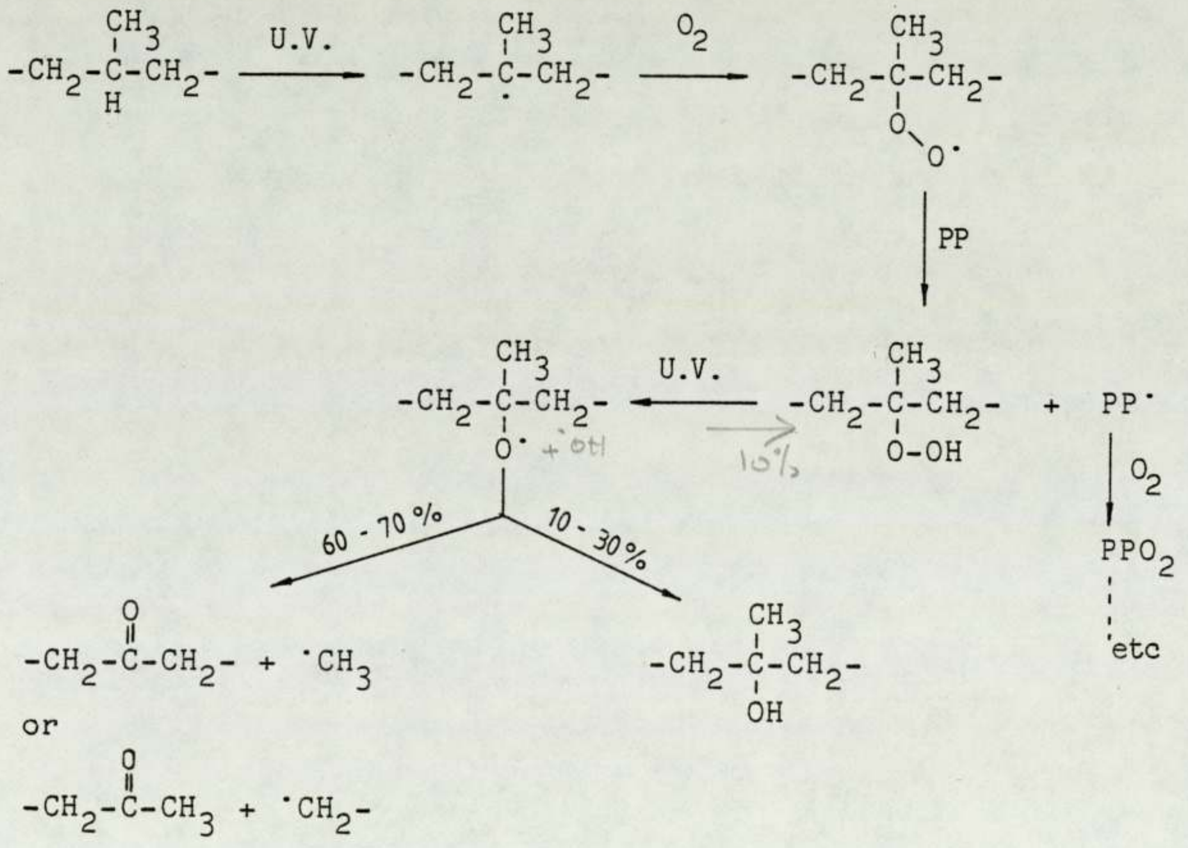
NDEC concentration (mol/100g)x10^4	Embrittlement Time (hours)					
	Concentration of FAcAc (mol/100g)x10^4					
	0	1.25	2.5	5.0	7.5	10.0
0.00	80	70	60	50	40	35
2.50	740	400	370	340	300	275
5.00	1200	558	480	470	430	400
10.00	1890	1055	1025	1025	905	815

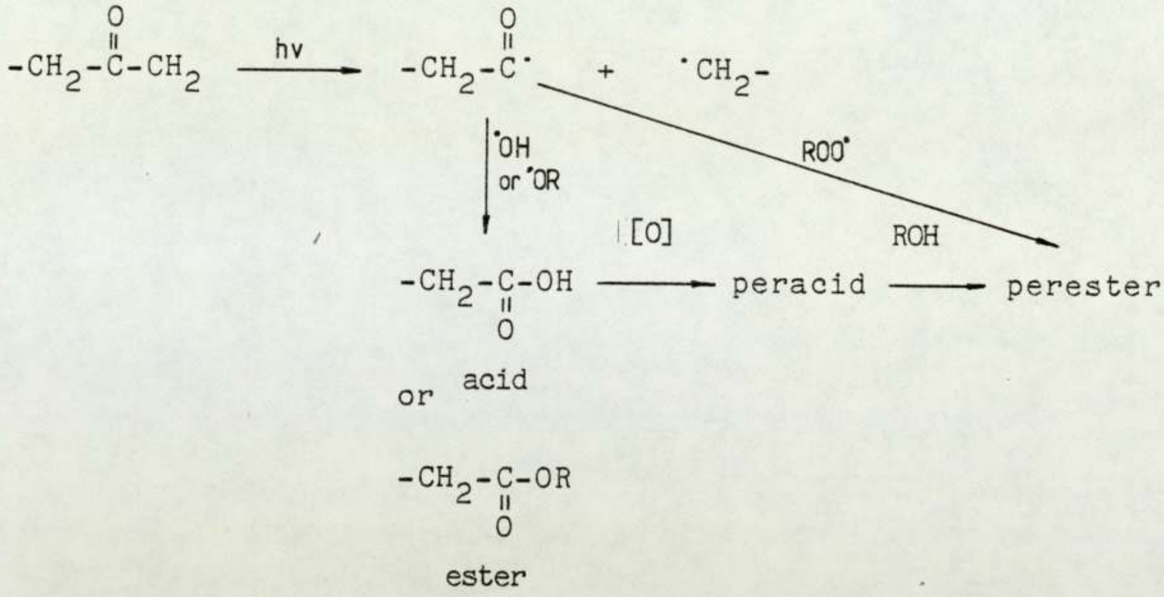
Table 4.7 Effect of varying the concentration of stabilizer (NDEC) and photoactivator (FAcAc) in unstabilized polypropylene

the processing operation. As in the case of LDPE (see Sec. 3.2.2), hydroperoxides rather than carbonyl has been shown(17) to be the main photo-initiator during the early stages of photo-oxidation of polypropylene.

Exposure of PP films to terrestrial radiation (>290 nm) results in the rapid oxidation of the films which eventually become embrittled. The reason for this easy oxidation is the labile hydrogens in the PP structure which are readily removed during the auto-oxidation. The process is further facilitated by the fact that the methyl group inductively enhances electron density on the carbon atom being oxidised and delocalises the electron by hyperconjugation(146). The radicals so formed are readily attacked by oxygen to give the macroperoxy radicals and the latter will be either terminated in the cage or escape to abstract a hydrogen from another polymer chain to form hydroperoxides. Thus the hydroperoxides are readily detectable during U.V. irradiation as shown in Figure 4.1. The 3400 cm^{-1} absorption predominantly results from hydroperoxide groups which are hydrogen bonded. The absence of free hydroperoxides as indicated by I.R. has been explained(27d) in terms of hydrogen bonding to each other and to carbonyl or other secondary products.

The photo cleavage of tert-macrohydroperoxides leads to tert-macroalkoxy radicals which will be followed by either the β-scission or by the hydrogen abstraction processes. Carlsson and Wiles(147) conclude from the product distribution resulting from the U.V. photolysis of polypropylene hydroperoxide groups in PP that only 10% of the macroalkoxy radicals abstract hydrogen to give alcohol, 10% give peroxides and the bulk of the remainder undergo β-scission to give carbonyl products. These results not only explain that β-scission is favoured to hydrogen abstraction in PP but also explain why the rate of hydroxyl formulation is much lower than the rate of carbonyl formulation during U.V. irradiation of PP. The following mechanistic equations have been suggested to account for the photo-oxidation of PP(147).





4.3.2 The Effect of Photo-activators and Antioxidants on the Thermo-oxidative Stability of PP During Processing

An understanding of the behaviour of different types of antioxidants and activators on thermal processing of polymers will only be possible if the oxidative degradation mechanism of polymers during the processing is elucidated. Our understanding of general inhibition chemistry has generally improved in recent years, but the processing area has not been fully investigated. It has been generally assumed that the rapid rate of initiation of polymer breakdown during processing necessitates the use of low molecular weight mobile antioxidants. Scott(17) has shown that the key initiator during both thermal and photo-oxidative processes of polyolefins is the same and it is the hydroperoxide. In view of this evidence, it follows that the key to an effective melt stabilizer should be a material that can preferably deactivate the hydroperoxides in a harmless manner before they undergo decomposition into free radicals. Also any material which accelerates the decomposition of peroxides into radicals will be an efficient activator. Thus processing of unstabilized polypropylene in the presence of 2.5 x 10^{-4} mol/100 g of NDEC, ZDEC, FDMC and the corresponding disulphide (TETD) did not give rise to increased levels of either MFI (Figure 4.2) or carbonyl index (Figure 4.3) with increasing processing severity. These compounds must, therefore, be acting to remove hydroperoxides formed during processing. Furthermore, the effectiveness of these additives in decomposing hydroperoxides was shown in the present work (see Chapter 5 Secs. 5.2.4 and 5.3.2) to be chiefly due to the formation of an ionic catalyst which can destroy the hydroperoxides. Similarly, the effectiveness of the same additives as melt stabilizers for PE was verified (Chapter 3, Secs. 3.2.1 and 3.3.1). Relative to the control (PP without additive), the increased levels of both MFI (Figure 4.2) and carbonyl index (Figure 4.3) in PP containing FAcAc with increasing processing severity indicates that FAcAc has an activation effect on PP oxidation during thermal processing. The activation effect of FAcAc probably like other transition metal stearates and halides arises from its ability to decompose peroxides into free radicals in redox reactions(15,128) (see Equations 3.1, 3.2 and 3.3).

A typical U.V. absorber HOBP acts as a weak melt stabilizer (Figures 4.2 and 4.3) in PP as has also been observed previously in LDPE (see Chapter 3, Sections 3.2.1 and 3.3.1) and HDPE(72, 135). It was suggested (123,135,149,150) that this antioxidant activity associated with HOBP occurs by a free-radical chain stopping reaction rather than by peroxide decomposition. A similar conclusion may also be reached from Figure 4.4.

4.3.3 Effect of Processing Severity on Photo-oxidation of PP Containing Additives

It has been shown (128) that PP which has been subjected to severe processing conditions produces a higher level of hydroperoxides than when it is processed under mild conditions. It is also shown (178) that hydroperoxides lead to the rapid destruction of metal dithiocarbamates under conditions of U.V. irradiation. It is therefore to be expected that metal dithiocarbamates will be less effective as U.V. stabilizers when they are subjected in the polymer to severe processing conditions than mild conditions (see Figure 4.4). In contrast to this poor performance by metal dithiocarbamates, the corresponding disulphide e.g., TETD, exhibits much better photostabilization activity under the same severe processing conditions (see Figure 4.4, curves TETD (CM,10) and (OM,30) and also Table 4.1).

By analogy with simple disulphides e.g., alkyl, aryl and thiophosphoryl disulphide, which themselves have been found (145,148) to be poor hydroperoxide decomposers (compared to their oxidation products), the actual process of decomposition of hydroperoxides in the case of the tetraethylthiuram disulphide (TETD) is, therefore, due to its oxidation products.

The importance of oxygen (or hydroperoxide indirectly) in enhancing the antioxidant performance of TETD was clearly demonstrated (see Table 4.1). This also explains why the disulphide has a better performance in PP than in PE since oxidation of PP produces a much higher level of hydroperoxide than PE does (see Figures 4.4 and 3.6 and also Scheme 2 in Chapter 3).

It is known that FAcAc decomposes hydroperoxides into radicals through a redox reaction (see Equations 3.1, 3.2 and 3.3). The more hydroperoxides in the system, the more radicals are formed. It is, therefore, expected that severe processing conditions (OM,30) which produces a maximum level of hydroperoxide in PP(131) will drastically reduce the lifetime of PP film containing FAcAc. Thus severely processed (OM,30) PP in the presence of FAcAc results in a sticky unprocessable material (see Figure 4.4 curve FAcAc OM,30 and also Table 4.1).

A typical U.V. absorber, HOBP, was shown in PE (Chapter 3, Sections 3.2.4 and 3.3.4) to be particularly sensitive to the severity of the processing operation. Similar behaviour has also been observed in PP (see Figure 4.4 curves HOBP(CM,10) and (OM,30). It can be seen from Figures 4.2 and 4.3 that HOBP, unlike the disulphide, does not prevent the formation of hydroperoxides during processing, thus giving rise to its rapid destruction during photo-oxidation(123,135,149,150).

4.3.4 Effect of Concentration of Additives on Photo-oxidation of PP

All metal complexes of dithiocarbamic acid (NDEC,ZDEC and FDMC) and the corresponding disulphide (TETD) are shown to be good stabilizers during the U.V. irradiation of PP (see Figures 4.5, 4.7-4.9). Their antioxidant action was shown by Scott and his coworkers(4, 66, 72, 81) and also in the present work (Chapter 5,Sec. 5.2.4) to be due to acidic catalysts formed through their reactions with hydroperoxides which is the main cause of oxidation of hydrocarbons(17). The acidic catalyst is found to be sulphur trioxide(66) which catalyses the decomposition of hydroperoxides in a non-radical process. Thus the higher the concentration of these additives in the polymer, the higher the concentration of the acidic catalyst formed and then the longer is the U.V. stabilization of the polymer.

Further examination of Figures 4.5 and 4.7-4.9 reveals that these metal complexes are quite different in their U.V. stabilization efficiency. Whereas NDEC and TETD showed effective stabilizing action as evidenced by the lifetime of PP containing these additives (see Figure 4.10), iron III and zinc II dithiocarbamates act as weak U.V. stabilizers.

This different behaviour can only be explained on the basis that they either differ in their hydroperoxide decomposing activity or differ in their stability towards U.V. light, or it could be due to additional U.V. stabilization mechanisms other than hydroperoxide decomposition.

The difference in behaviour of metal dithiocarbamates in photo-oxidation is not a reflection of a difference in hydroperoxide decomposing activity since it has been shown (77,147) that under thermal-oxidative conditions metal dithiocarbamates and related dithiolates have very similar antioxidant activity. Other workers(134,151) and also the present work (see Sections 4.2.5, 4.3.5, 5.2.1 and 5.3.1) showed that mechanisms other than hydroperoxide decomposition are also involved in the action of these additives. The U.V. screening ability of NDEC and FDMC is found to account partly for their U.V. stabilization of PP. A free radical scavenging mechanism(152) is also found to be operating with all these additives (see Chapter 5, Sec. 5.2.1). Both U.V. screen and free radical scavenging mechanisms presumably, therefore, contribute to different extents to the overall polymer U.V. stabilization process.

It has been suggested previously(123,149) that stability of the additives under U.V. irradiation conditions is one of the basic requirements for it to act as a U.V. stabilizer. On the basis of this requirement, NDEC has been found to possess a good photolytic stability in solution (see Figure 4.34) , whereas ZDEC and FDMC were found to photolyse very quickly. It is, therefore, possible to conclude that the different U.V. stabilization efficiency exhibited by metal dithiocarbamates and the corresponding disulphide is due to their different stabilities towards U.V. light and also because they are operating to a different extent by additional U.V. stabilization mechanisms other than hydroperoxide decomposition.

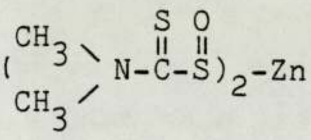
The different behaviour exhibited by FDMC at low concentrations (up to 5×10^{-4} mol/100 g) in LDPE and PP is not really a reflection of different mechanisms of FDMC in both polymers but is rather due to the difference in the photostability of the polymers themselves. The delayed action photoactivation is the type of behaviour exhibited by FDMC in both polymers and this gives (within the concentrations mentioned above) an induction period of 40-80 hours in both polymers before photo-oxidation commenced. Thus the action of FDMC in PP appears as stabilization since the control film without additive embrittles within the time of the induction period (≃80 hours). In LDPE, the rate of photo-oxidation following this induction period is tremendously increased due to the pro-oxidant species (ionic iron, thiyl radical etc.,) generated from FDMC photolysis. Thus relative to the control PE film which embrittles over 2000 hours, the action of FDMC appears as a pro-oxidant.

The effect of a typical photo-activator (FAcAc) concentration on photo-oxidation of PP is found to correlate well with its action in LDPE (see Figure 4.6 and Sections 3.2.4 and 3.3.4). The photo-oxidation rate is found to increase with FAcAc concentration. This observation suggests that FAcAc probably follows an oxidative mechanism both during thermal treatment and during subsequent U.V. exposure, which is entirely different from that followed by ideal photo-activator (FDMC) under similar conditions. That is, FAcAc behaves not only as thermal pro-oxidant (see Figures 4.2 and 4.3) but it also decomposes very quickly under the influence of light (see Figure 4.6 inset) giving metal carboxylates as well as radicals from the ligand(15). The proposed photo-decomposition of FAcAc is consistent with the U.V. absorbance data (Figure 4.6 inset) where it shows the near U.V. absorption band 275 nm disappears completely within 15 hours of U.V. irradiation.

The anti-oxidant action of HOBP lies in its effective screening activity (see Section 4.2.6 and 4.3.6) during the early stages of photo-oxidation when hydroperoxides are the primary photoinitiators. The retardation of photo-oxidation observed in HOBP-stabilized PP is, therefore, due to the inability of HOBP to inhibit the formation of hydroperoxides completely. The screening of U.V. light by an additive is concentration dependent. Thus the higher the concentration of HOBP in the polymer, the greater is the retardation of the photo-oxidation (see Figure 4.11). In addition to the U.V. screen, HOBP also acts by other stabilization mechanisms at the later stages of photo-oxidation of the polymer. This will be discussed in more detail in Section 4.3.6.

4.3.5 Effect of Oxidation Products of Metal Dithiocarbamates on Photostability of PP

It has been reported previously(154,155) that sulphoxides and thiolsulphinates are more effective while thiolsulphonates are less effective as antioxidants than their parent sulphides and disulphides in both model compounds and polymers. In the present work similar observations have been found with sulphenate I and sulphinate II complexes of ZDMC. The former is found to be more effective than ZDMC whereas the latter is less effective in PP photo-oxidation (see Figure 4.12). Brooks(101) also found similar behaviour by these oxygenated intermediates in natural rubber.



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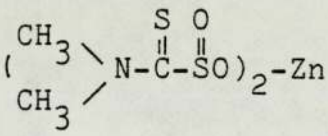


II

The fact that sulphoxides and thiolsulphinates are more effective and thiolsulphonates are less effective as antioxidants from their original sulphides and disulphides is explained by many workers(154,155) to be associated with their thermal stability. Scott and his coworkers(154) found that the dimethyl sulphinyl and thiolsulphinyl dipropionate are more effective as antioxidants because they are much less thermally stable than the parent dimethylthio and dithio dipropionates. On the other hand, thiolsulphonate is found to be a less effective anti-oxidant relative to the parent disulphide because it is thermally stable. Similar conclusions were reached by Shelton(155) on using dimethylsulphide and disulphide and their oxygenated intermediates. Thus by analogy with these model sulphur compounds, it may be said that ZDMCSO (I) is a more effective anti-oxidant than ZDMC because it is probably less thermally stable, whilst $ZDMCSO_2$ (II) is less effective than ZDMC because of its thermal stability.

The equal effectiveness exhibited by ZDMCSO, $ZDMCSO_2$ and ZDMC as U.V. stabilizers in both severe and mild processing operations (Table 4.1) indicates that their peroxide decomposing activity is carried from thermal processing through to the U.V. exposure stage and this persists until the complexes are destroyed by U.V. light. Table 4.1 also shows that ZDMCSO and $ZDMCSO_2$ like the parent ZDMC are not themselves anti-oxidants rather than products formed from their oxidation.

4.3.6 Screening Effect of Additives on Photostability of PP

It has been recognised for many years that some metal dithiocarbamates are effective U.V. stabilizers(63c). Since they have a high molar extinction coefficient in the region of 300-330 nm, effective screening of the incident light was considered to be a primary function. The U.V. screening effect of NDEC, FDMC, TETD and ZDEC is compared in Figure 4.13

with their stabilizing activity when they are present in PP as additives. It is very clear from Figure 4.13 that NDEC has a greater U.V. screening ability than the rest of the dithiocarbamates. FDMC and TETD show a weak U.V. screening ability and ZDEC does not screen at all. These observations are found to correlate well with their U.V. absorbance data. Whereas NDEC absorbs strongly at 325 nm, FDMC has a weak U.V. absorbance at 318 nm and ZDEC does not absorb in this region at all. The weak screening activity exhibited by TETD is probably due to the tail of its U.V. absorbance band at 285 nm which extends till 325 nm. However, the U.V. screening effect of these compounds is not in itself sufficient to account for their very high activity (see Figure 4.13) and photophysical investigation has led to the suggestion(156,157) that these compounds may also deactivate photo-excited species formed in polymers under the influence of light.

Although there is little doubt that these metal complexes can deactivate excited states of potential chromophores(156,158) in polymers or singlet oxygen formed by their quenching with ground state oxygen, the importance of this kind of process in the stabilization of polymers under practical conditions is still very much in question(159). The function of these metal complexes has been previously(72,160,161) and also in the present work (Chapter 5, Sections 5.2.1 and 5.2.2) explained on the basis of kinetic chain-breaking and hydroperoxide decomposing mechanisms.

A typical U.V. absorber (HOBP) behaves essentially as a U.V. screen during the early stages of photo-oxidation when hydroperoxides are the primary photo-initiators (see Figure 4.13 curve HOBP (screen)) while it acts by other mechanisms at later stages of photolysis (see Figure 4.13 curves HOBP (screen) and HOBP (additive)).

The initial photolysis of carbonyl in polyolefins, by Norrish II process is known(135) to be followed by a Norrish I process upon further oxidation. The former does not give rise to photo-initiating species and will, therefore, play little or no part in the oxidation. However, once the Norrish I process becomes dominant, then HOBP becomes involved in the deactivation of the triplet state(128) of the in-chain carbonyl compounds giving rise to some auto-retardation at later stages of photo-oxidation (see Figure 4.13, curves HOBP (screen) and HOBP (additive)). In addition to this triplet carbonyl deactivation, HOBP also acts as a sacrificial antioxidant in removing chain initiating radicals formed from hydroperoxides and derived carbonyl compounds(128,149).

4.3.7 Photostabilization of PP by Two Component Systems

Although melt stabilizing activity of FDMC was remarkable (see Figures 4.2 and 4.3), it was not effective under U.V. exposure conditions. This limits its use as agricultural mulching film especially under severe exposure conditions. The relatively poor U.V. stabilizing behaviour of FDMC was attributed to the photo-reduction reaction of the FDMC excited complex. Thus in order to prolong the persistance of FDMC during U.V. irradiation, it must, therefore be protected by an efficient excited states quencher or by a good U.V. absorber.

It has been shown earlier in this chapter (Sections 3, 4 and 6) that the NDEC is an effective U.V. stabilizer. Screening of the U.V. light is considered to be one of its functions in addition to its PD-C activity. This complex was also proposed(156,157) to have the ability to quench and deactivate the photo-excited species formed from other compounds. It is, therefore, expected that a combination of NDEC and FDMC will lead to more effective time controlled stabilization than that exhibited by FDMC alone. Indeed, the components of this combination showed much better stabilization activity in PP than that showed by FDMC alone (see Figures 4.14 and 4.15) but was, however, less effective than NDEC alone.

The improvement in the photostability of PP by NDEC/FDMC combination compared to the stabilization afforded by FDMC alone is probably due to the ability of NDEC to protect FDMC from photolytic destruction. Figure 4.33 shows the contribution of screening of U.V. light by NDEC on FDMC to the total U.V. stabilization effectiveness by NDEC and FDMC as additives. It is clearly found that the contribution due to screening of U.V. light by NDEC on FDMC cannot account for the total stabilization effect when used as additives together.

The above results suggest that both U.V. screening and some other chemical stabilization processes are involved in the effective photostabilization of FDMC by NDEC. It has previously been suggested(156 - 158) that NDEC can accept energy from triplet carbonyl although it has been shown that this stabilization mechanism can only be important in polymers which contain a substantial amount of carbonyl(72). In principle the NDEC may quench photo-excited states of the FDMC (or its photodecomposition products) and this could contribute to the stabilization exhibited by the combination FDMC/NDEC in the polymer.

The antagonistic effect exerted by FDMC on NDEC suggests that the FDMC interferes with the action of NDEC. The first order rate constant for the decay of the NDEC is increased by the presence of FDMC complex (see Figure 4.16). This clearly shows the FDMC photosensitises the decomposition of the NDEC leading to a decrease in its effectiveness (see Figures 4.14 and 4.15). The decrease in the effectiveness of NDEC is a function of the FDMC concentration. The higher the concentration of FDMC in the combination, the less is the stabilization effectiveness of NDEC (see Figures 4.14 and 4.15). Thus the antagonistic action of FDMC on NDEC seems to be due to the presence of ferric carboxylates and thiyl radicals which are major products of the normal function of FDMC as an antioxidant(15). This has been confirmed indirectly from Figures 4.29-4.31. The presence of FAcAc which has a similar action to ferric stearate decreases the stabilization effectiveness of NDEC (see Scheme 2 in Chapter 3).

It was established many years ago(4,66,72,81) that all metal dithiocarbamate complexes had a common stabilizing action which was shown to be the catalytic ionic decomposition of hydroperoxides by a product or products formed from them. However, the exact mechanisms by which these complexes are forming the active catalyst for the ionic hydroperoxide decomposition, are still unclear. Scott and his coworkers(146) showed that these metal complexes are first oxidised to the corresponding disulphides with the elimination of the metal and then the latter is further oxidised to the sulphur acid (SO_3) which is the main catalyst for the ionic decomposition of hydroperoxides. Russian workers(153) have found that the disulphide is the first oxidation product formed from NDEC but they could not detect it from ZDEC oxidation. These workers, accordingly, proposed that the mechanisms of stabilizing action of NDEC and ZDEC must differ. No further mechanistic detail for the oxidation of these metal complexes was given. In the present work (see Chapter 5, SEc. 5.2.2), ZDEC was found to decompose hydroperoxides in a mode which is quite different from NDEC. Furthermore, it was possible to isolate zinc sulphenate and sulphinate from the reaction of ZDEC with hydroperoxides but it was not possible to isolate similar intermediates from NDEC (see Chapter 5, Sec 5.2.8.2).

On the basis of the above evidence, it is therefore possible to suggest that ZDEC has quite different mechanisms of stabilizing action than NDEC. It follows then, that different results should be expected when these stabilizers are added to FDMC-stabilized PP. The additive effect shown by the combination of ZDEC and FDMC clearly suggests that the two components protect each other during photo-oxidation of PP. The screening of U.V. light by ZDEC on FDMC does not contribute to any extent to the total stabilization. On the other hand, the contribution of the screening of U.V. light by FDMC on ZDEC is very small and cannot account for the total stabilization effect when these stabilizers are used as additives together (see Figure 4.13). It might be then, the two components cooperate in decomposing the same amount of the hydroperoxides present in the system thereby showing the additive effect. The evidence supporting this explanation is that the combined decay of ZDEC and FDMC in PP is almost consistent to the length of the induction period observed before the photo-oxidation is commenced (see Figures 4.18 and 4.21).

It has been mentioned at the beginning of this section that FDMC is a powerful melt stabilizer (Figures 4.2 and 4.3) in PP and effective U.V. stabilizer in the initial photo-oxidation stage (see Figures 4.4 and 4.5). The major limitation to its effectiveness as a U.V. stabilizer is that it is light unstable and will photolyse rapidly under conditions of U.V. exposure. The typical U.V.

absorber (HOBP) on the other hand, is unable to inhibit the formation of hydroperoxide(123,135,149,150) in PP during processing (see Sections 4.2.2 and 4.3.2) and does not destroy it during photo-oxidation, although it is rapidly destroyed by hydroperoxide under these conditions(123,135,149,150). HOBP is, therefore, an indifferent antioxidant during processing and appears to behave essentially as a screen during early stages of photo-oxidation (see Figure 4.13) when hydroperoxides are the primary photo-initiator(123,135,149,150). It behaves less effectively the more severe the processing operation (see Figure 4.4).

A combination of FDMC (PD-C) and HOBP (U.V. absorber) should, therefore, lead to extensive stabilization. Indeed, the components of this combination behaved as effective synergists when the molar concentrations ratio of FDMC:HOBP is equal to unity or higher (see Figures 4.25-4.27). However, when the molar ratio of FDMC:HOBP in the combination is less than unity, antagonistic behaviour is observed. These observations are also verified by the comparison of the embrittlement times of the combination with the additive effect of the two components of the FDMC/HOBP system (see Table 4.4).

The synergistic effect observed for the combination (FDMC/HOBP) at molar ratio of unity or higher can be explained on the basis of the cooperative action of each stabilizer. The deleterious effect of processing on HOBP is prevented via the powerful hydroperoxide decomposing activity of FDMC.

On the other hand, HOBP protects the metal complex from photolytic destruction both by screening of U.V. light and by removing (sacrificially quenching) photo-excited reactive species formed from the dithiocarbamate during irradiation. The synergistic system of FDMC/HOBP combines, therefore, the desirable features of both stabilizers. The long induction period afforded by the protected U.V. stabilizer and the good melt stability by the peroxide decomposer (FDMC). Similar synergistic effects between NDEC and ZDEC and U.V. absorber HOBP have also been observed in both PP and PE polymer(123,149).

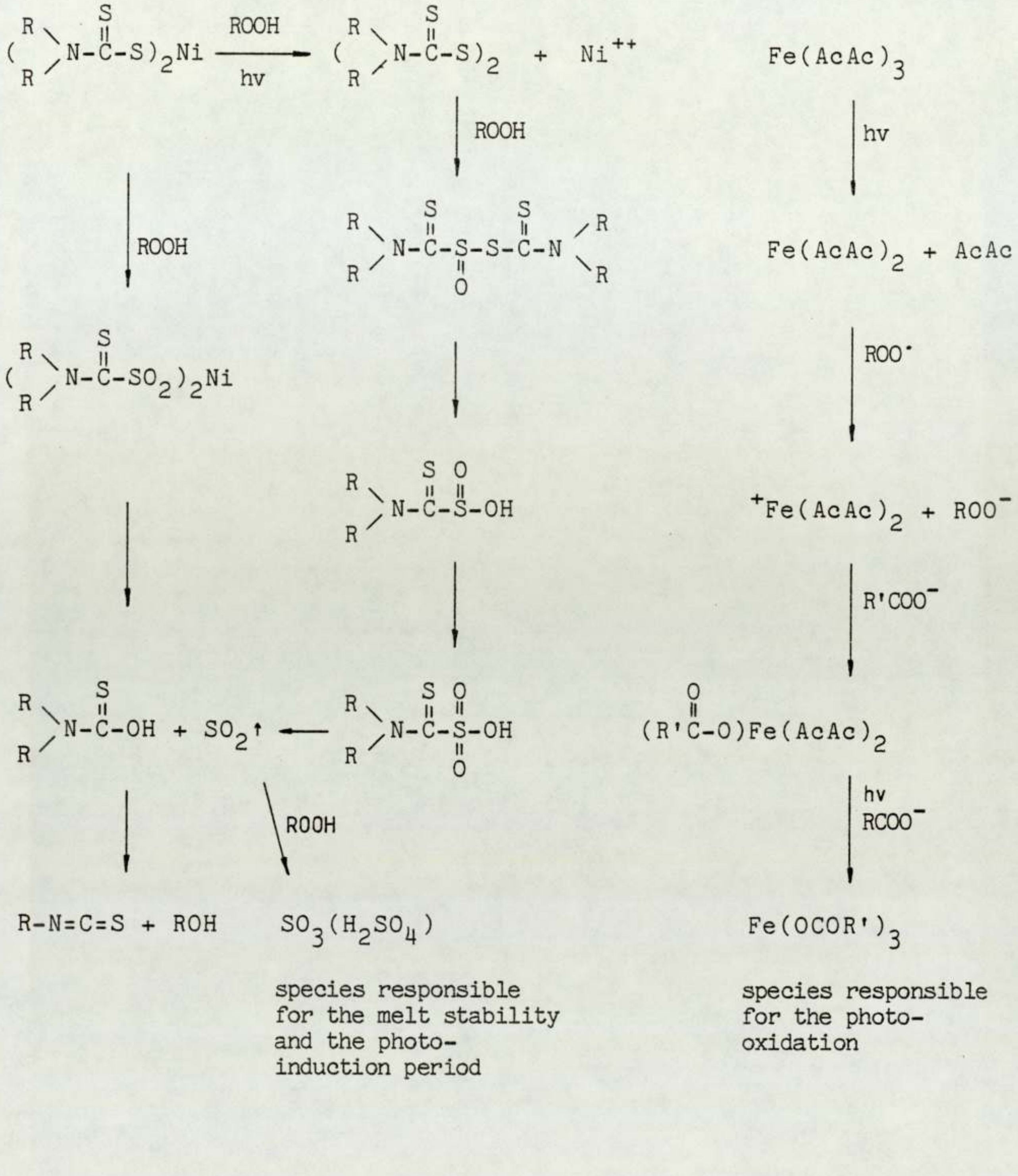
FAcAc is a well known activator during both thermal processing operation (see Figure 4.2 and 4.3) and subsequent U.V. irradiation (see Figure 4.6). Its function during thermal processing is to catalyse the hydroperoxides decomposition through a redox reaction leading to the formation of an initiating free radical which starts a normal auto-oxidation chain. During U.V. irradiation, FAcAc has been found to behave exactly as FDMC except there was no safety induction period for the polymer before photo-oxidation. The oxygen ligand metal complex (FAcAc) thus satisfies one of the requirements of the ideal photosensitiser: a rapid and auto-accelerating mode of photo-oxidation. To be of any technological value in the field of the time-controlled photodegradable plastics, FAcAc has to be protected during thermal processing by a very good melt stabilizer. NDEC and ZDEC were shown to be good melt stabilizers (Figures 4.2 and 4.3) due to their ability to destroy hydroperoxides into non-radical products (see Chapter 5, Secs. 5.2.2 and 5.2.8.1).

A combination of metal dithiocarbamates with FAcAc is, therefore, expected to combine the desirable features of both additives. The well known melt stabilizing activity of the peroxide decomposer and the photo-activation of FAcAc. Indeed, the components of this combination (FAcAc/NDEC) show these expected features in PP (Figures 4.29-4.31). The combination of FAcAc/NDEC not only does stabilize the polymer in the molten state (see Table 4.6) but also during the early stages of U.V. irradiation giving rise to an induction period ranging from 50-200 hours.

The above results suggest that NDEC has suppressed completely the action of FAcAc during the thermal processing operation. The hydroperoxide decomposing action of NDEC was dominant during processing and also extended through to the early stages of U.V. irradiation. In addition to hydroperoxide decomposition, NDEC also protected FAcAc from photolytic destruction by screening the U.V. light (see Figure 4.33).

Figure 4.32 shows that the induction period to the carbonyl growth during photo-oxidation of PP containing FAcAc/NDEC is not consistent with the time for complete decay of NDEC. This observation suggests that NDEC, whose stabilizing action was dominant during the thermal processing operation and the early stages of photo-oxidation can no longer protect

FAcAc from the photolytic destruction. It seems, therefore, highly probable that NDEC and FAcAc are both exerting their actions at the same time during the later stages of photo-oxidation. Thus the antagonistic effect exerted by FAcAc on NDEC can be explained on the basis that both acetyl acetonyl radical and ferric carboxylate, which are the major products of the normal function of FAcAc as activator, are affecting adversely the performance of NDEC leading to a decrease in its antioxidant activity (see Scheme 1).



species responsible
for the melt stability
and the photo-
induction period

species responsible
for the photo-
oxidation

Scheme 1

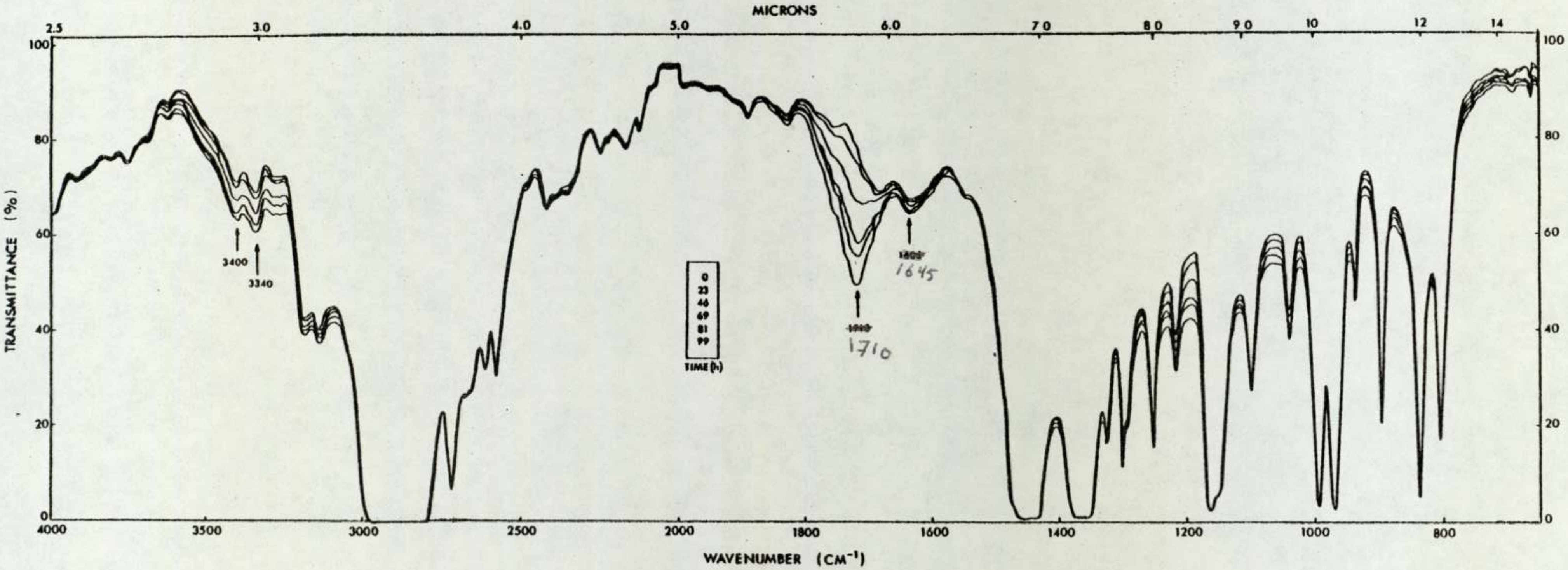


Figure 4.1 Infra-red absorption spectra recorded during photo-oxidation of unstabilised PP. Irradiation times are shown in the rectangle

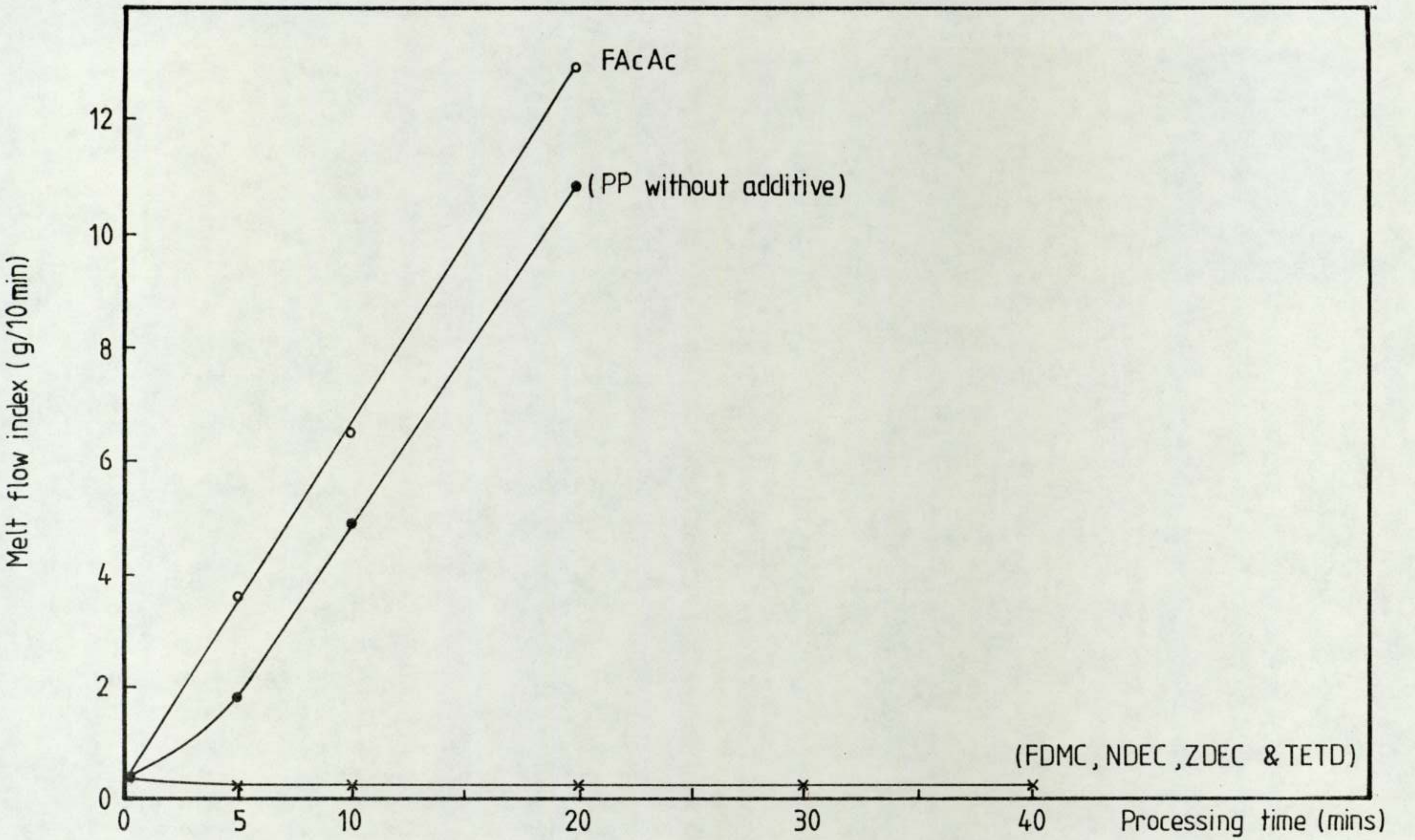


Figure 4: 2 Effect of photoactivators and antioxidants ($2{\cdot}5 \times 10^{-4}$ mol/100g) on the change in melt flow index (MFI) of PP. processed at 180°C in open mixer

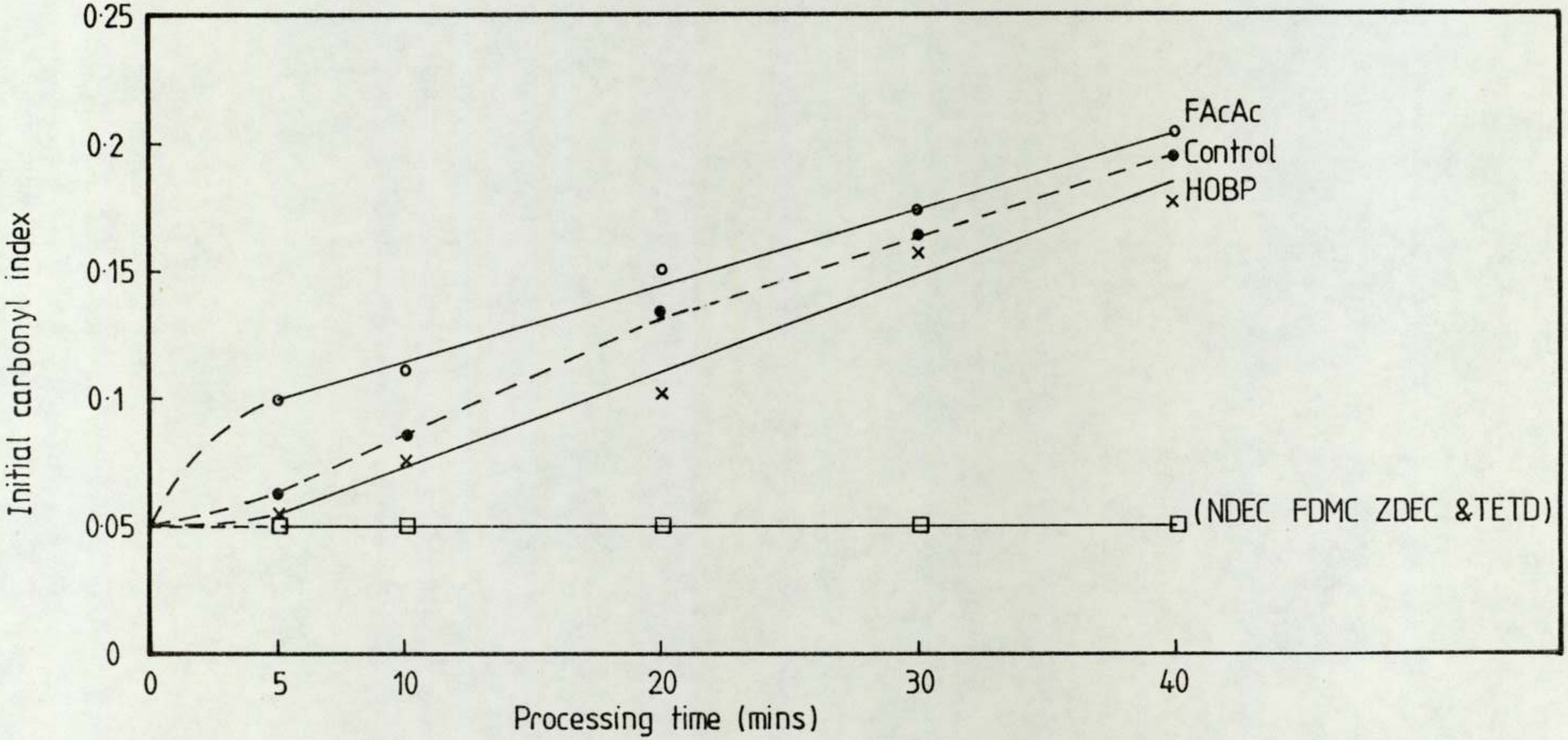


Figure 4:3 Variation of initial carbonyl index with processing time of PP processed at 180°C in open mixer (Conc of additives $2{\cdot}5 \times 10^{-4}$ mol/100 g)

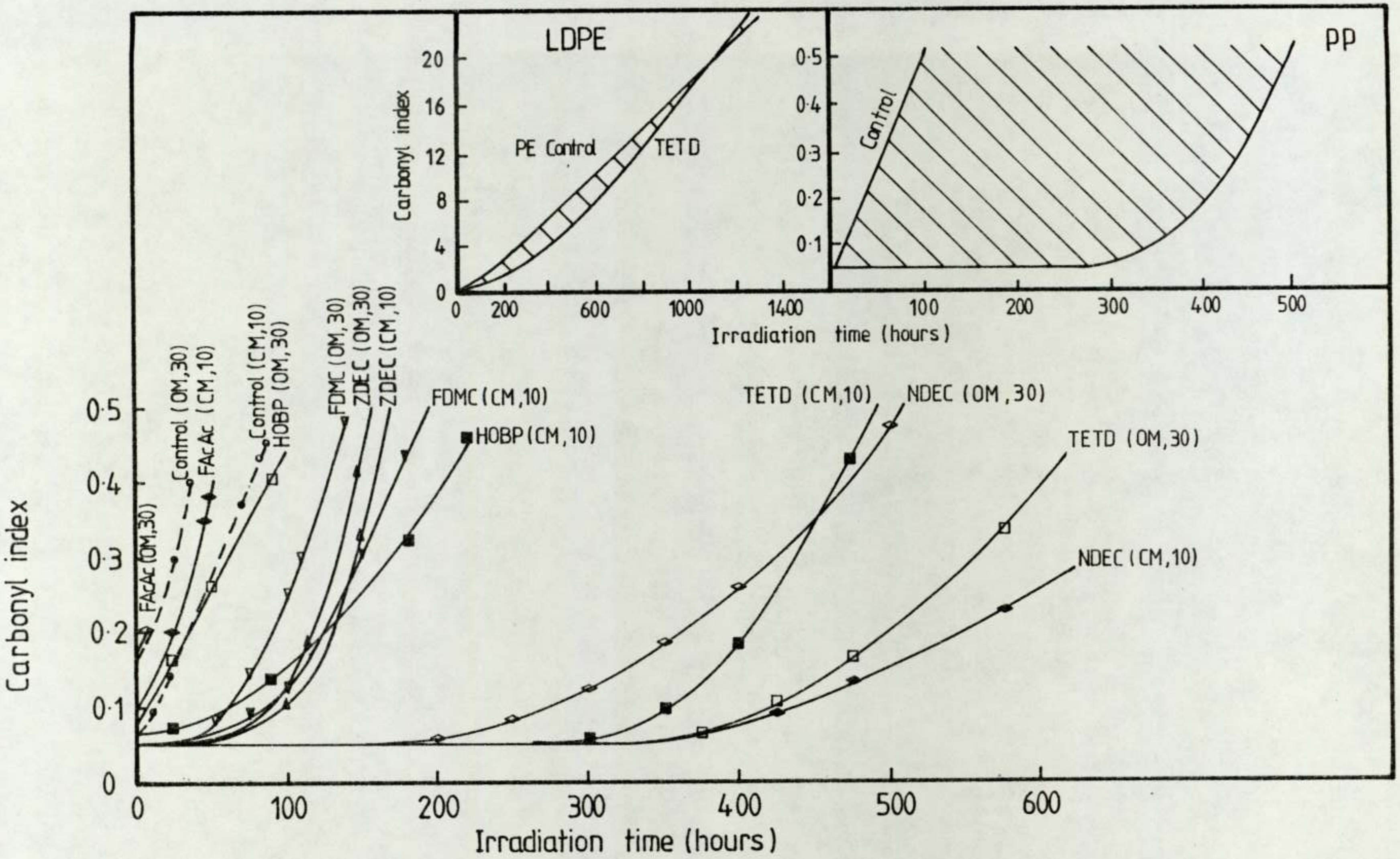


Figure 4:4 Effect of processing severity on photo-oxidation of PP with and without additive (Conc. of additives 2.5×10^{-4} mol/100g) Inset compares photostabilising effectiveness of mildly processed (CM,10) TETD in LDPE and PP

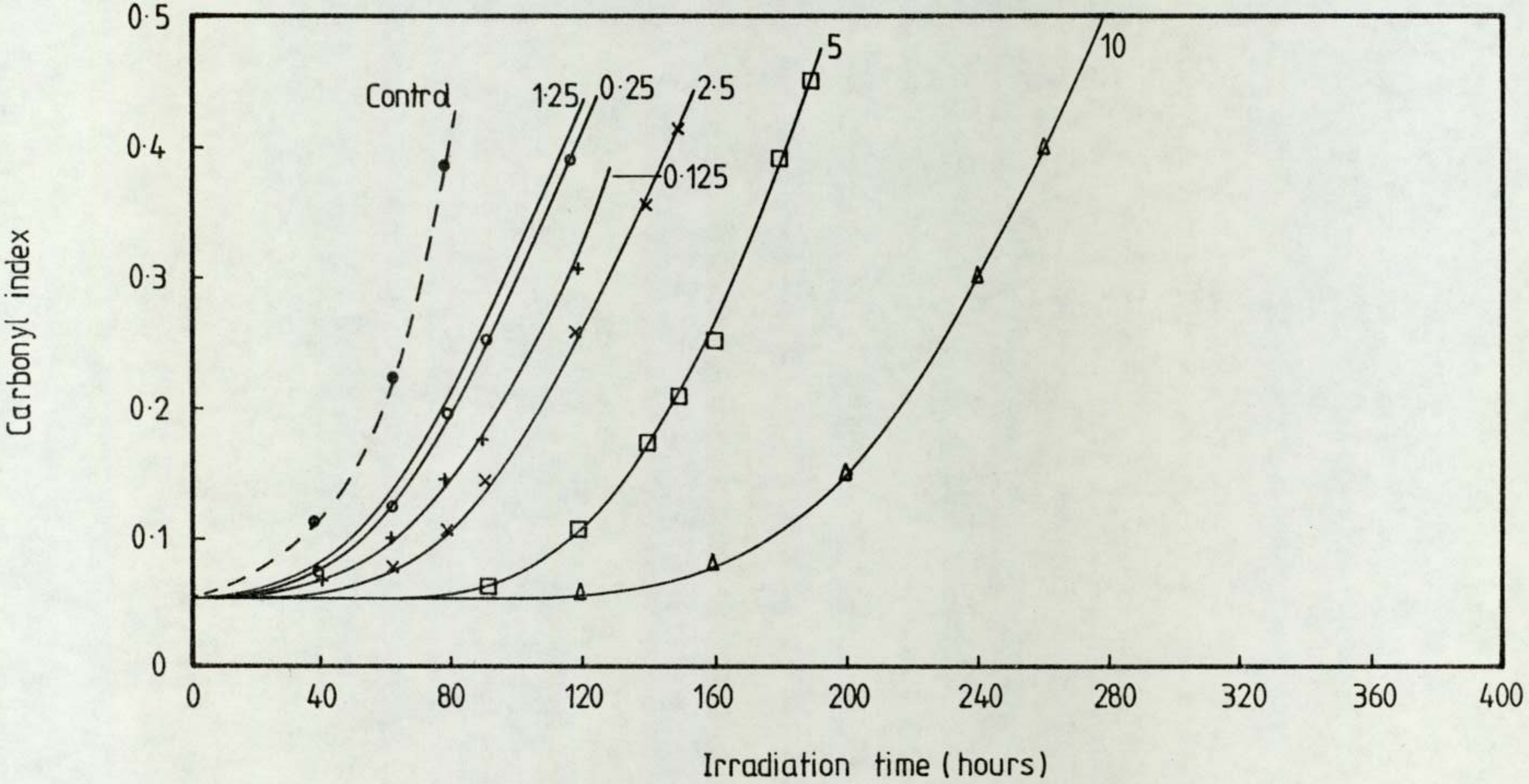


Figure 4:5 The effect of FDMC at different conc. on photo-oxidation of PP processed at 180°C in closed mixer (Numbers of curves are conc. $\times 10^{-4}$ mol/100g)

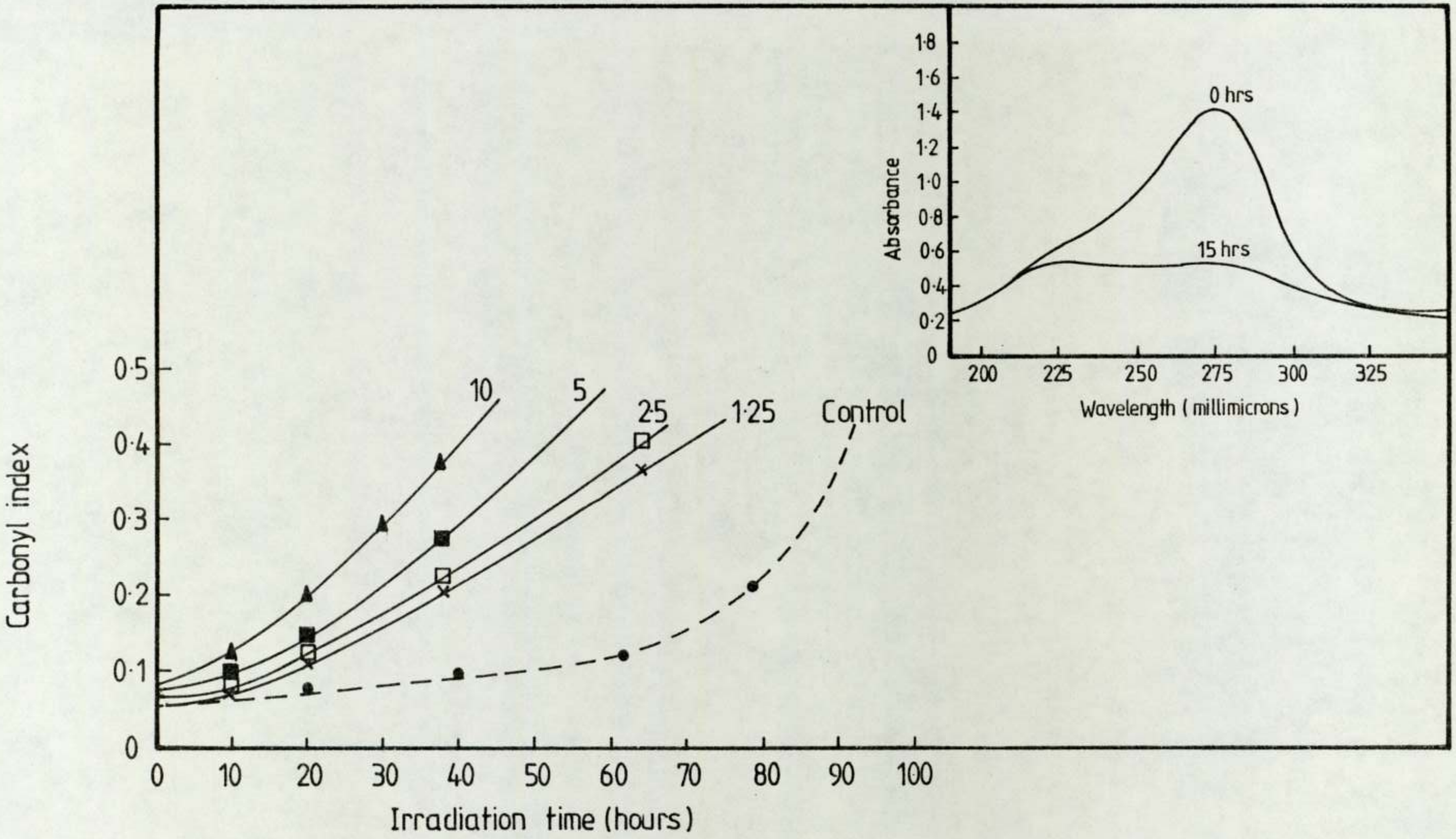


Figure 4:6 The effect of concentration of FAcAc on photo-oxidation of PP processed at 180°C for 10 minutes in a closed mixer (Numbers on curves are concentrations × 10^{-4}mol/100g) Inset: The decay of 5×10^{-4}mol/100g FAcAc in PP during UV irradiation

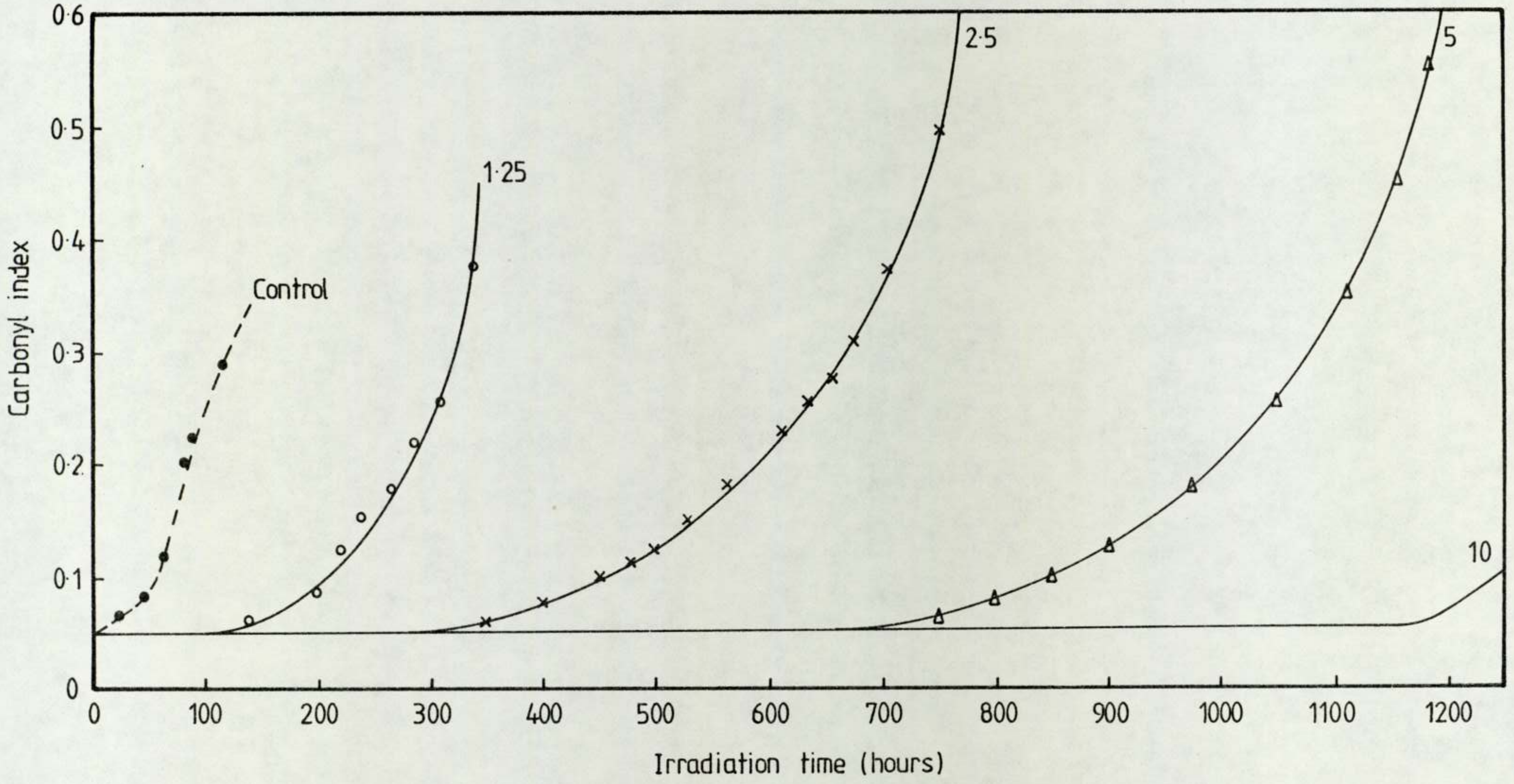


Figure 4:7 Effect of conc. of NDEC on photo-oxidation of PP processed at 180°C for 10min. in closed mixer (Numbers on curves are conc. × 10^{-4} mol/100g)

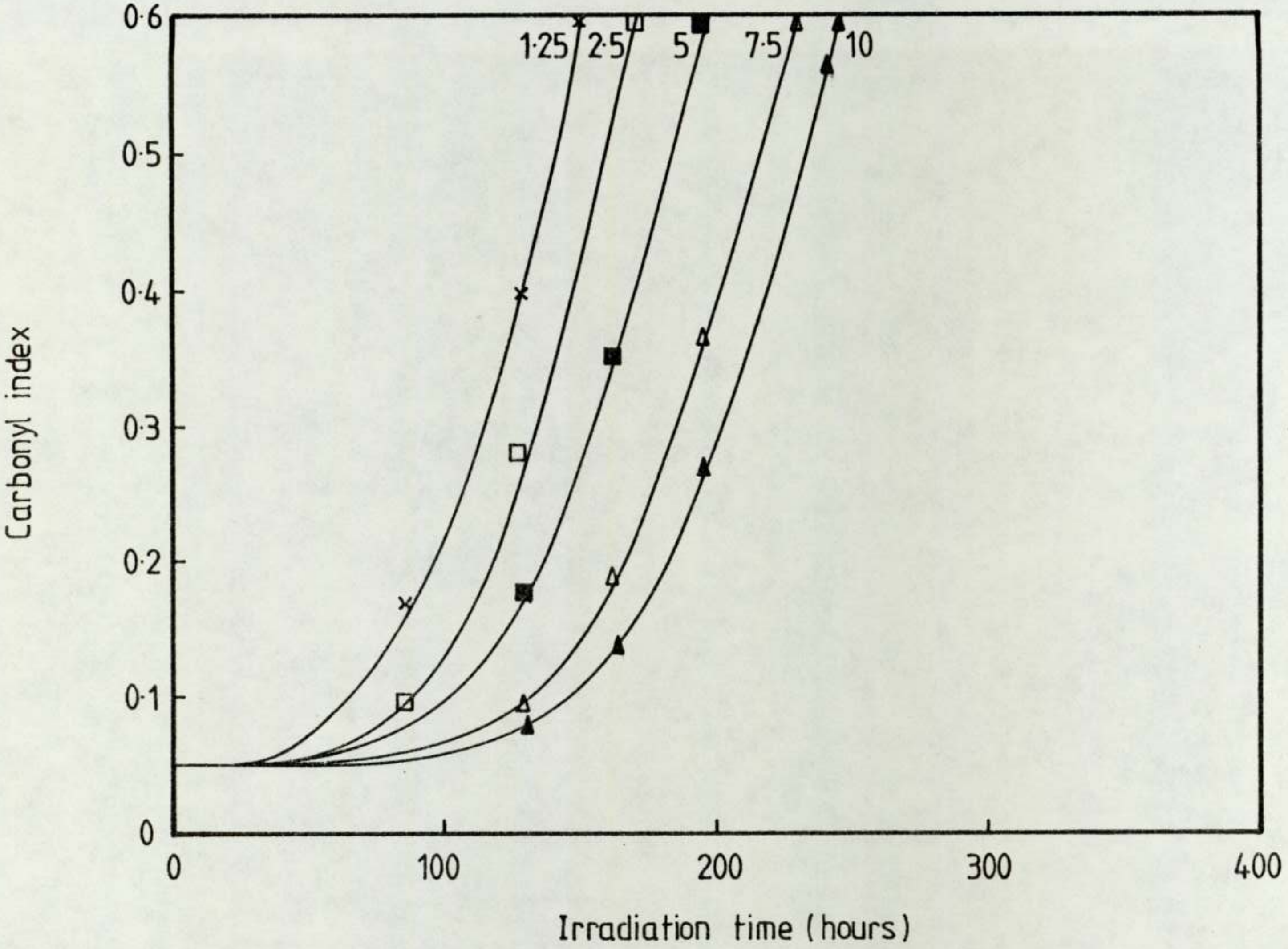


Figure 4:8 The effect of conc. of ZDEC on photo-oxidation of PP processed at 180°C for 10 mins. in closed mixer (Numbers on curves are conc. $\times 10^{-4}$ mol/100g)

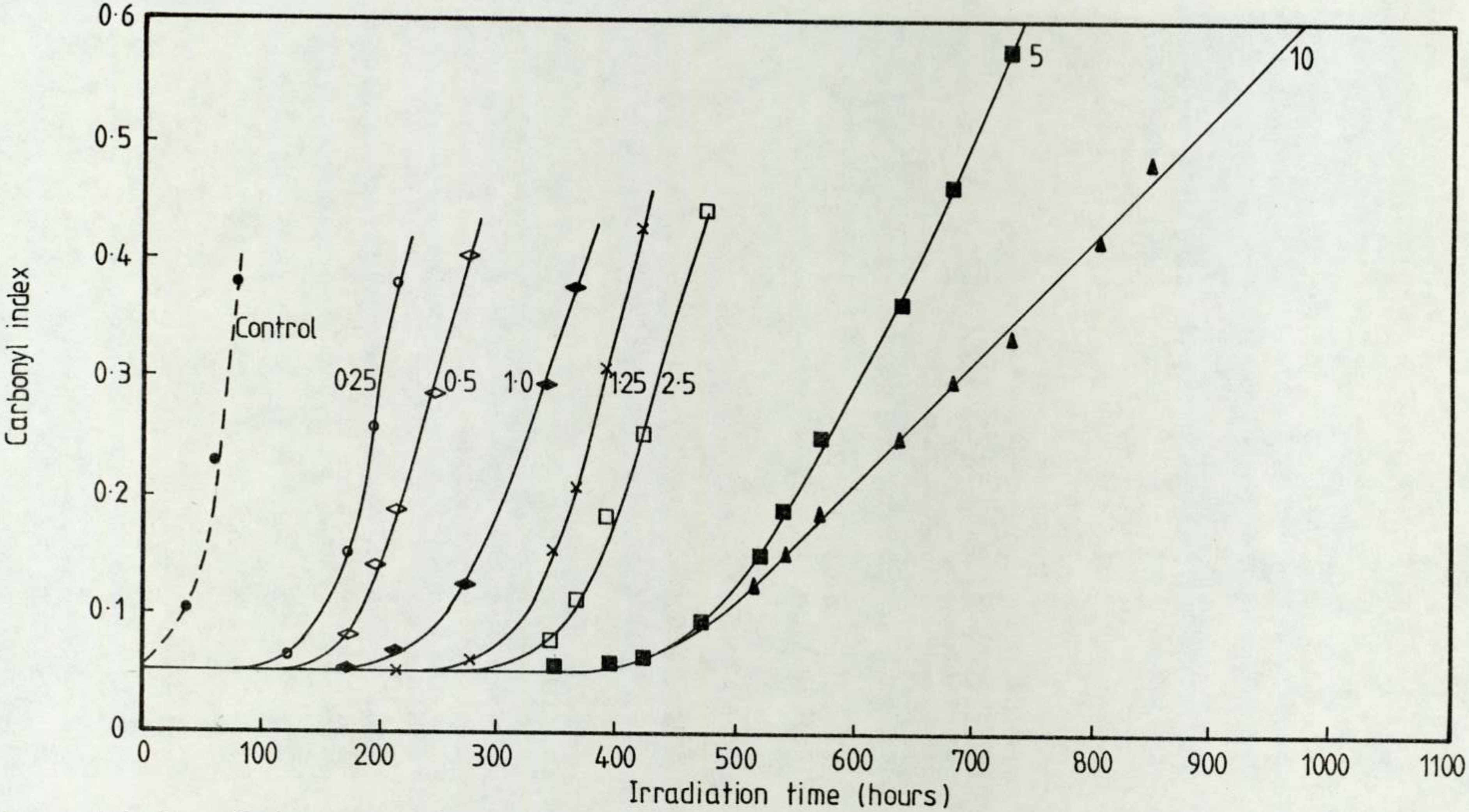


Figure 4:9 The effect of TETD at different conc. on photo-oxidation of PP processed at 180°C for 10 min. in closed mixer. (Numbers on curves are conc. $\times 10^{-4}$ mol/100g)

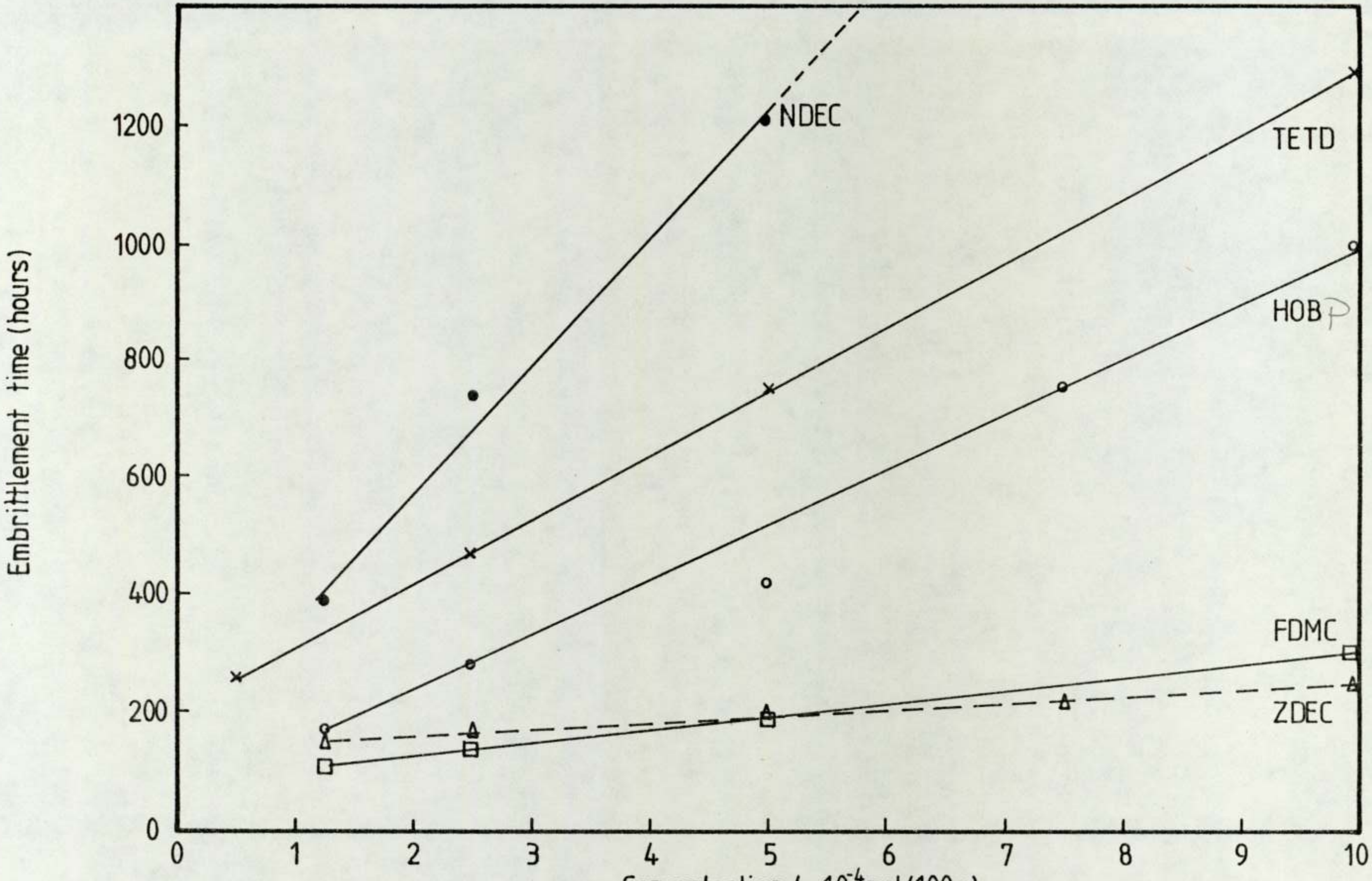


Figure 4:10 Effects of additives conc. on photostability of PP

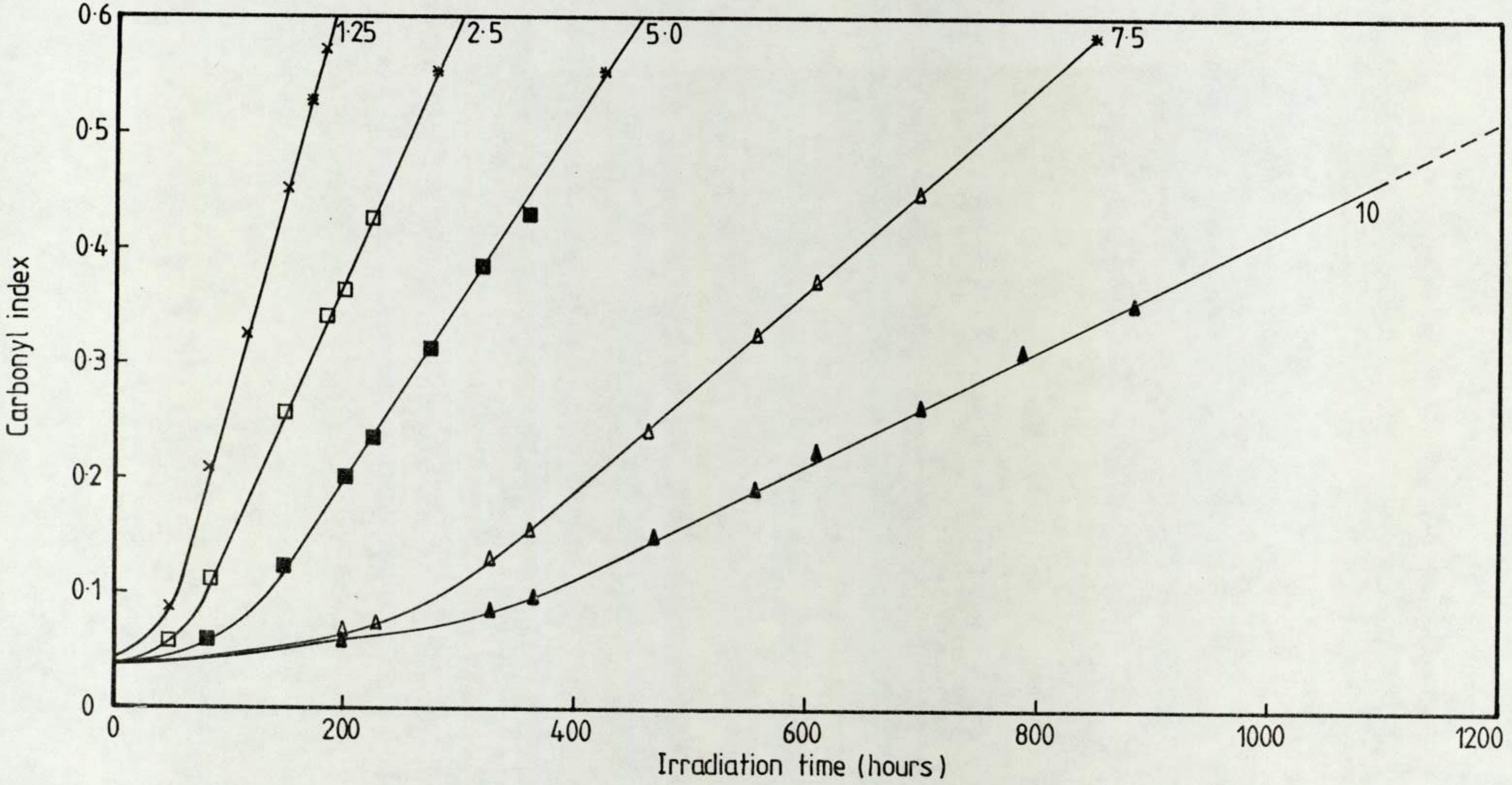


Figure 4:11 The effect of conc. of HOBP on photo-oxidation of PP processed at 180°C for 10 min. in closed mixer (Numbers on curves are conc. of HOBP in mol/100g × 10^4 , ✱ represents embrittlement point)

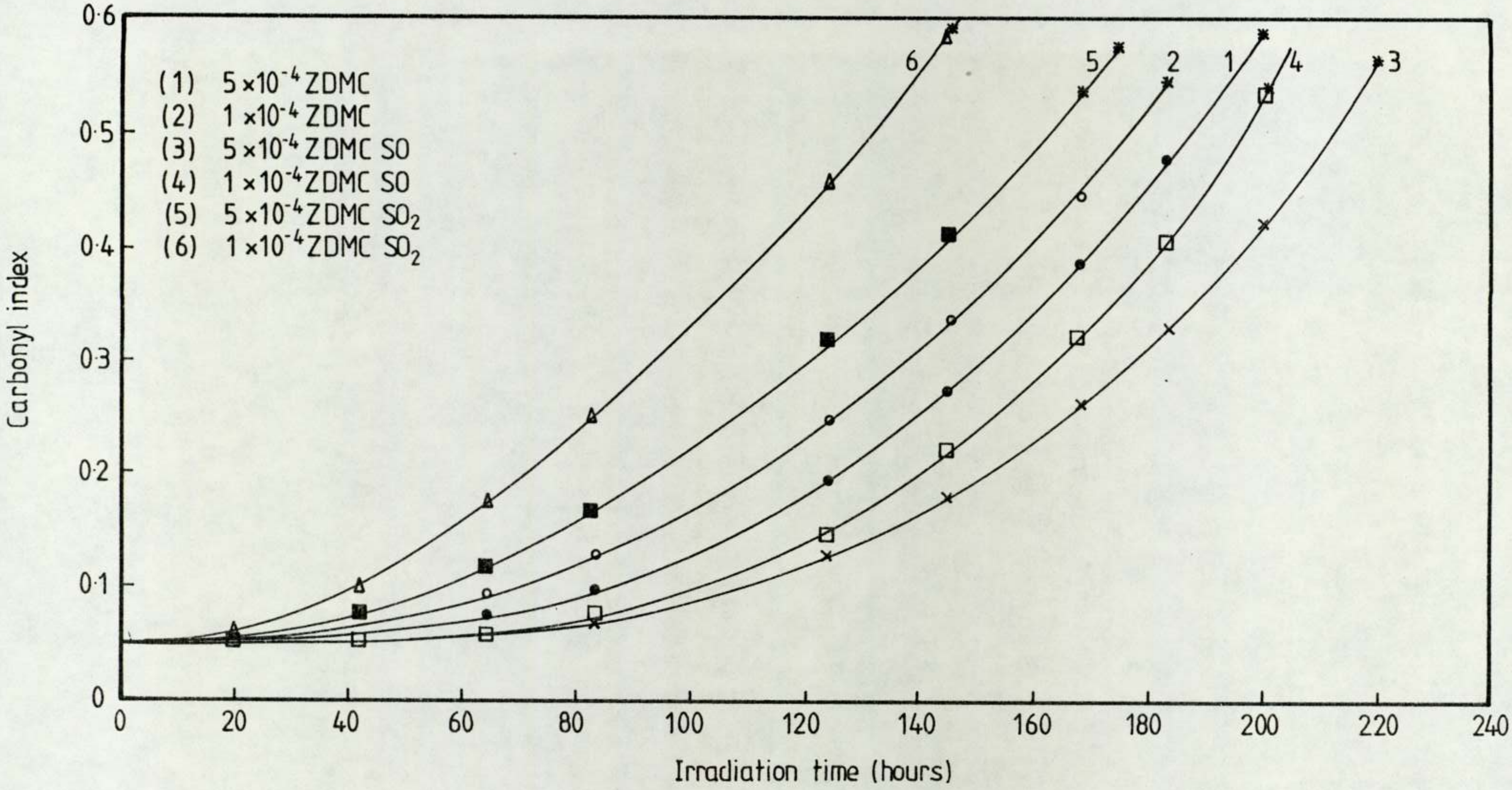


Figure 4:12 The effect of conc. of ZDMC and its oxidation products on photo stability of PP processed at 180°C for 10 min. in closed chamber.

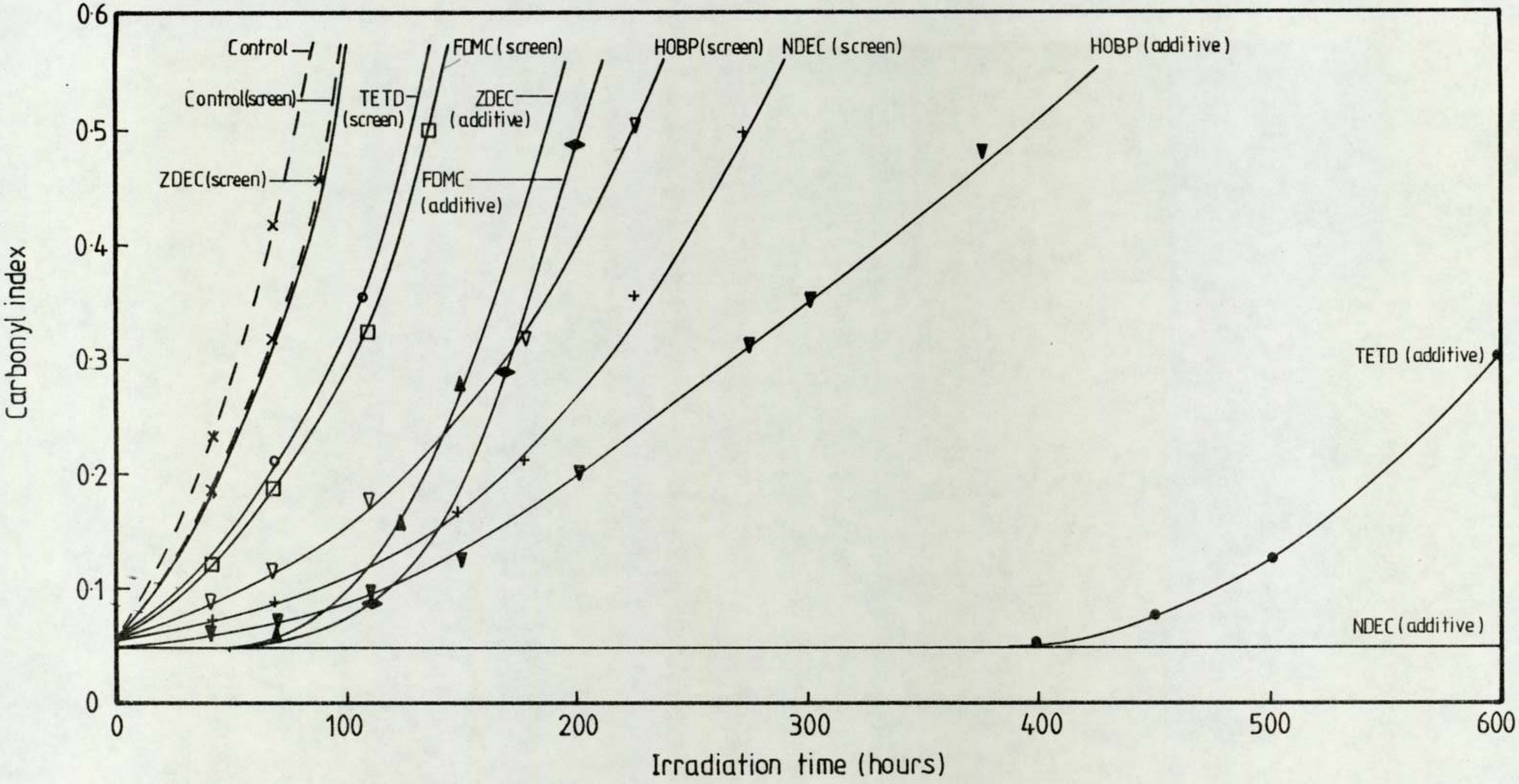


Figure 4:13 Comparison of behaviour of stabilizers as screen and as additive in PP processed at 180°C for 10 minutes in a closed mixer. Concentration of additives is 5×10^{-4} mol/100g

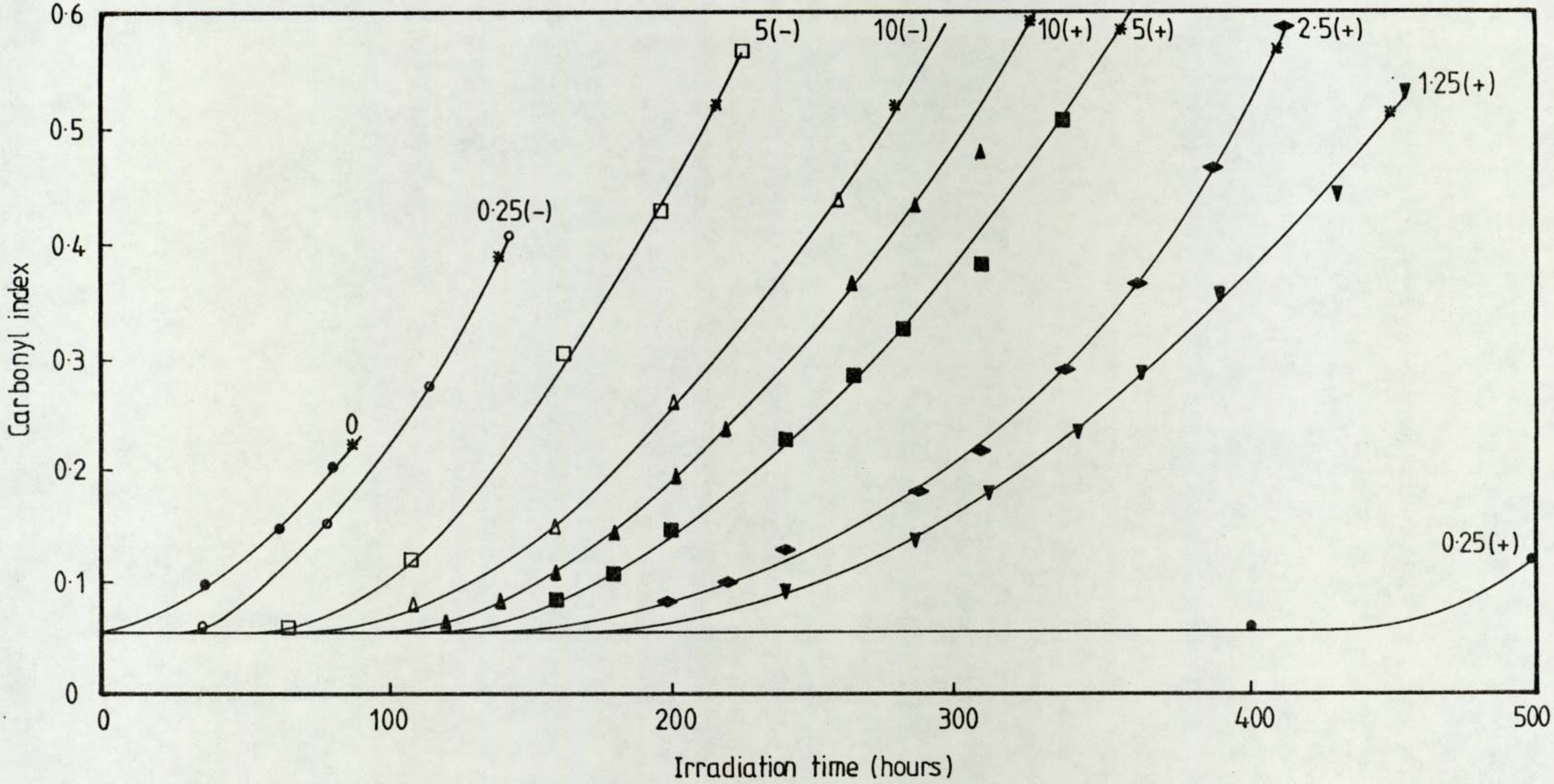


Figure 4:14 The effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (-) of $2{\cdot}5\times10^{-4}$ mol/100g of NDEC (Numbers on curves are FDMC concentrations in mol/100g $\times 10^4$), * indicates embrittlement of sample

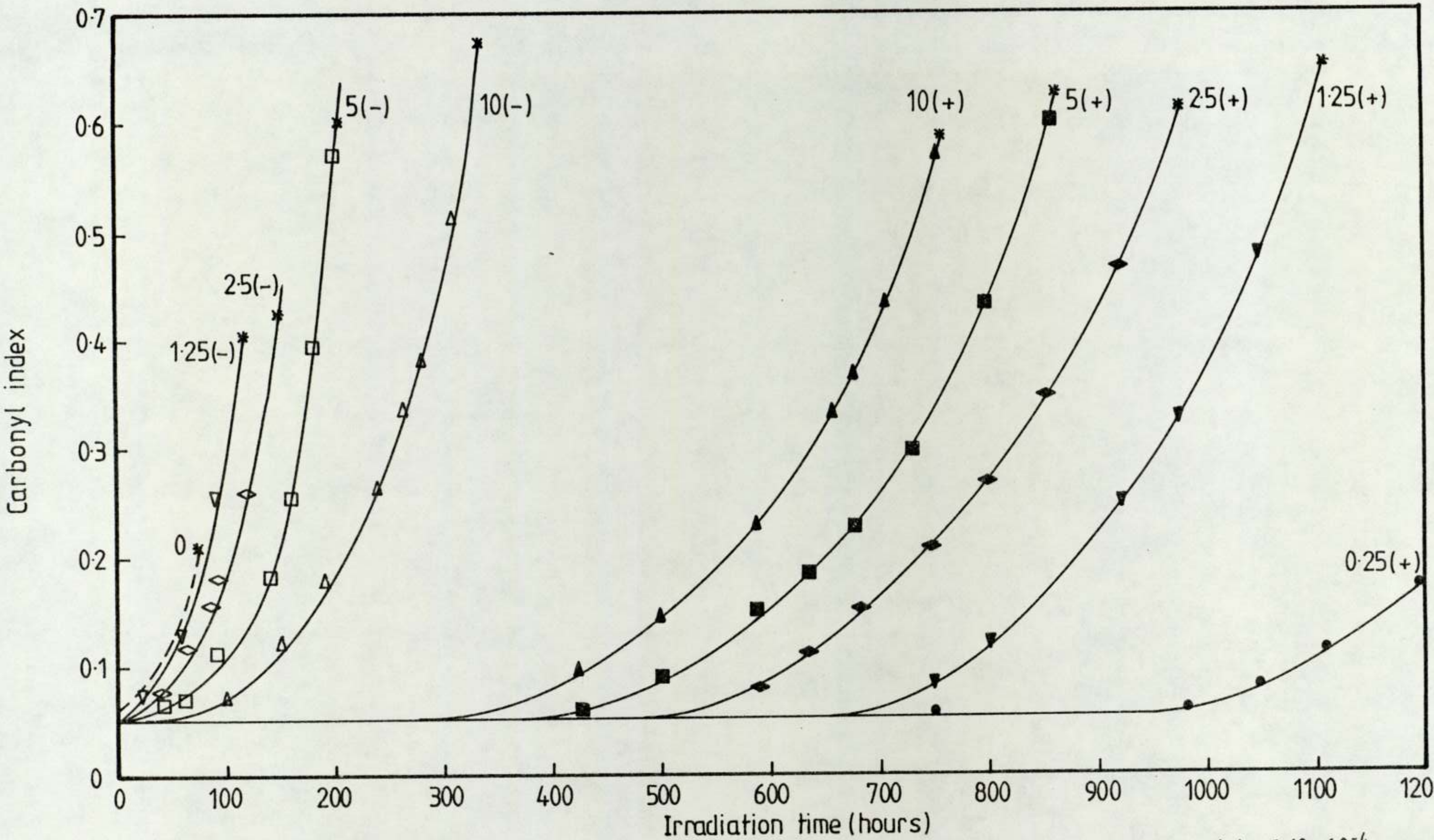


Figure 4:15 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (–) of 10×10^{-4} mol/100 g of NDEC (Numbers on curves are FDMC concentrations in mol/100 g $\times 10^{4}$), $*$ indicates embrittlement of sample.

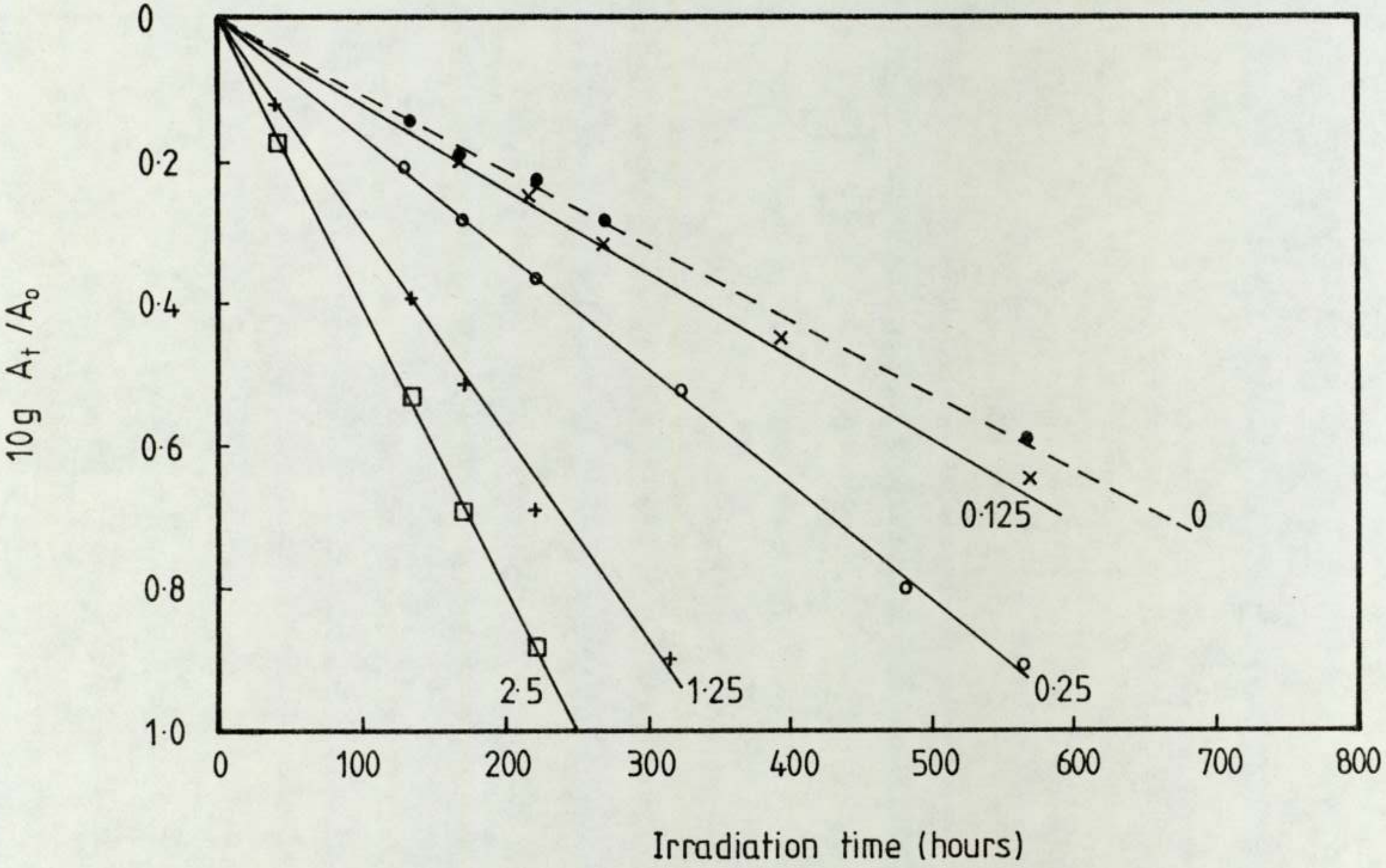


Figure 4:16 Change in the UV absorption intensity of $2{\cdot}5 \times 10^{-4}$ mol/100g NDEC at 325 nm in the presence of FDMC during photo-oxidation of PP (Numbers on curves are concentrations of FDMC in mol/100g $\times 10^{-4}$)

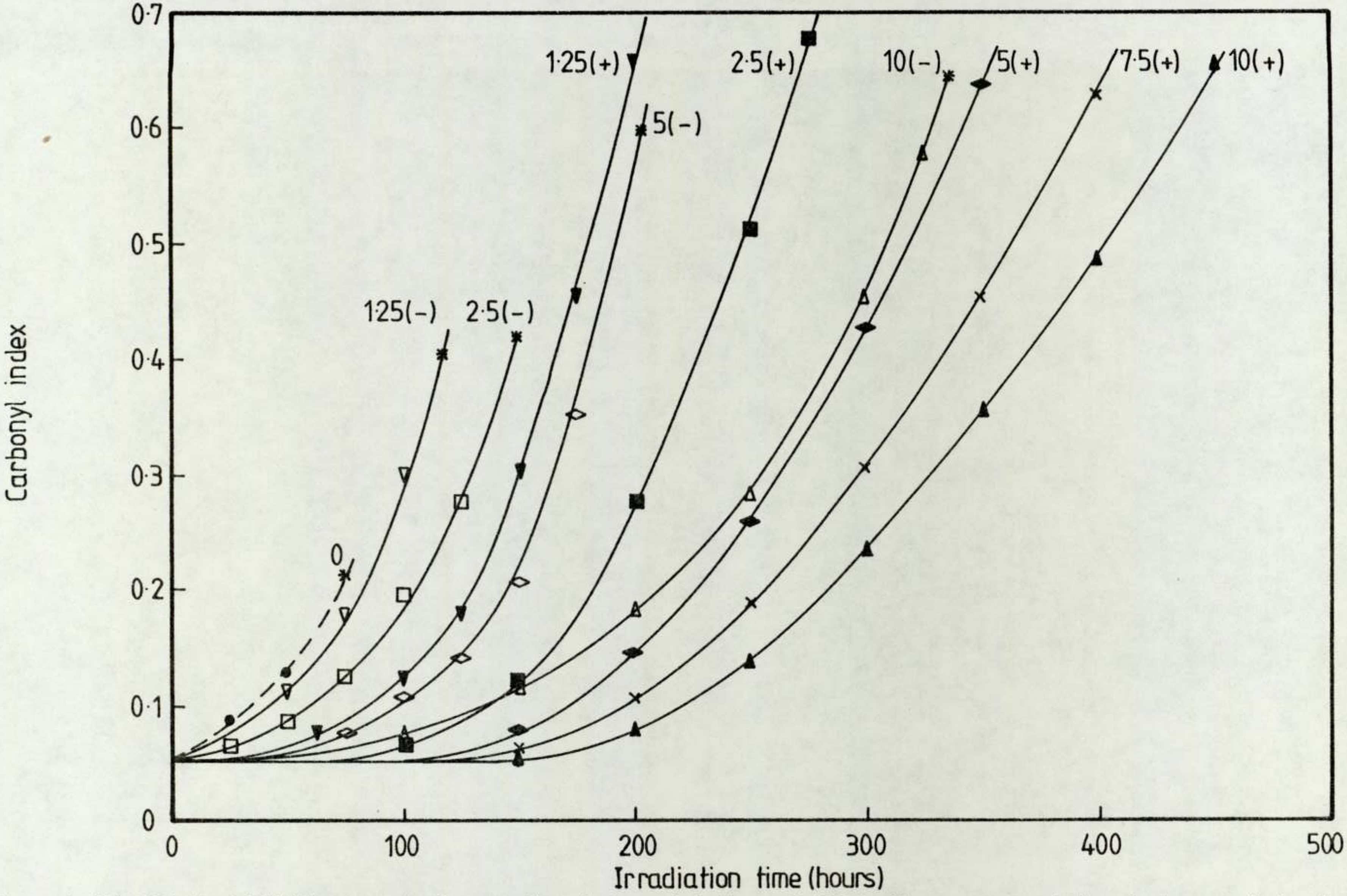


Figure 4:17 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (−) of $2{\cdot}5\times10^{-4}$ mol/100g ZDEC (Numbers on curves are FDMC concentrationsin mol/100 g $\times 10^{-4}$)

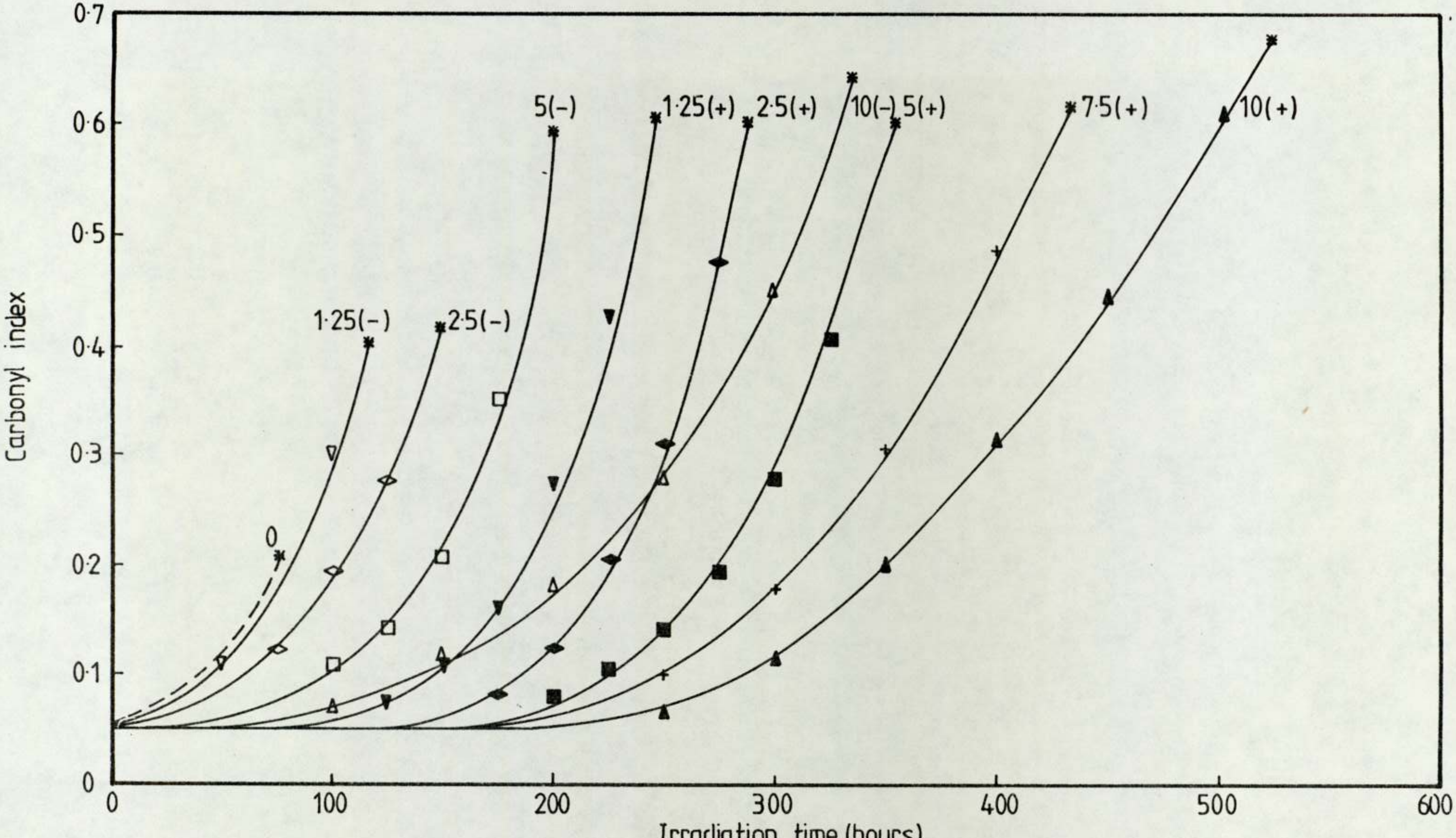


Figure 4:18 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (-) of 5×10^{-4} mol/100g ZDEC (Numbers on curves are FDMC concentrations in mol/100g $\times 10^{4}$), ✱ indicates embrittlement of sample

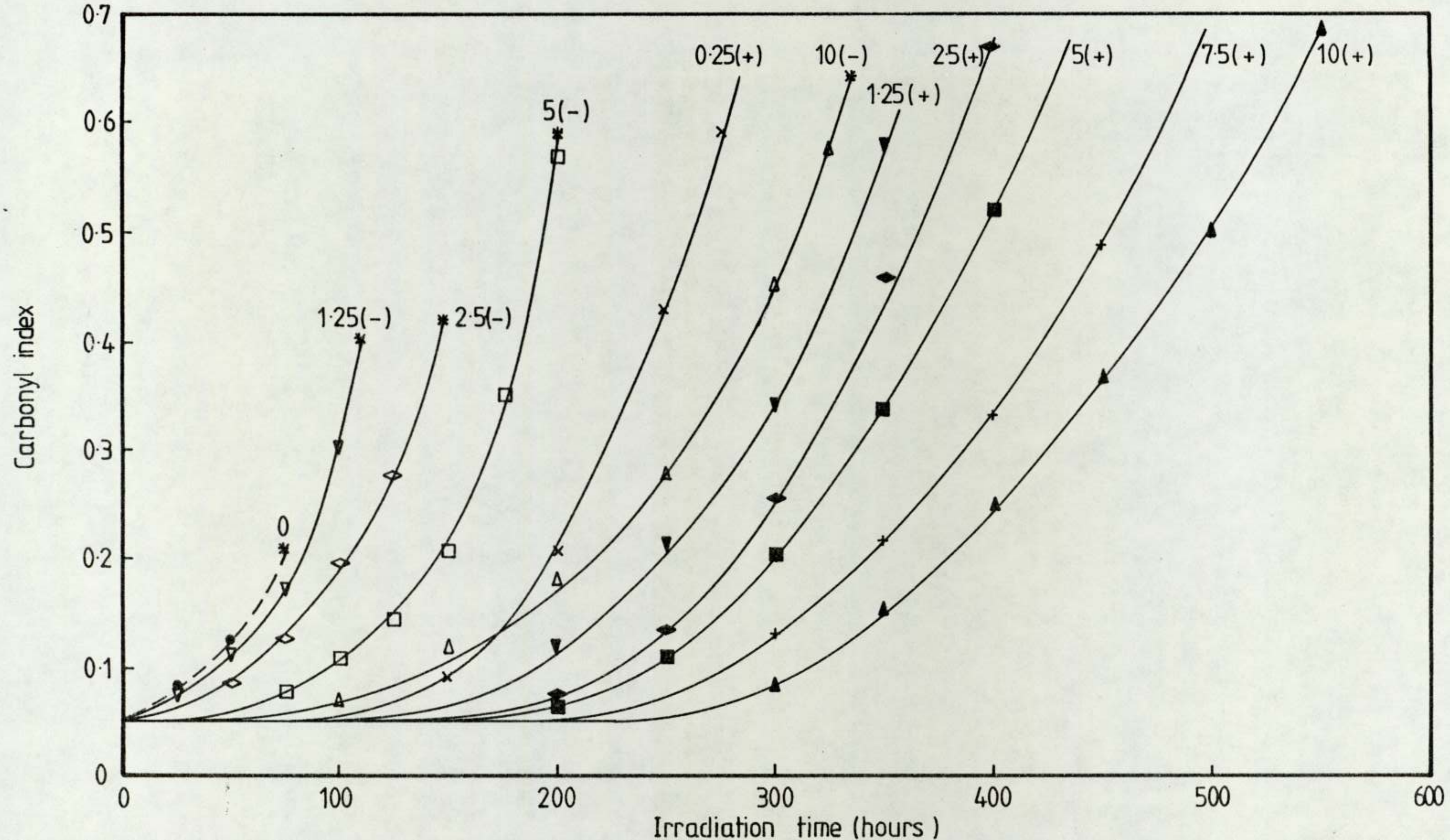


Figure 4:19 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (−) of 10 × 10^{-4} mol/100g ZDEC (Numbers on curves are FDMC concentrations in mol/100g × 10^{-4})

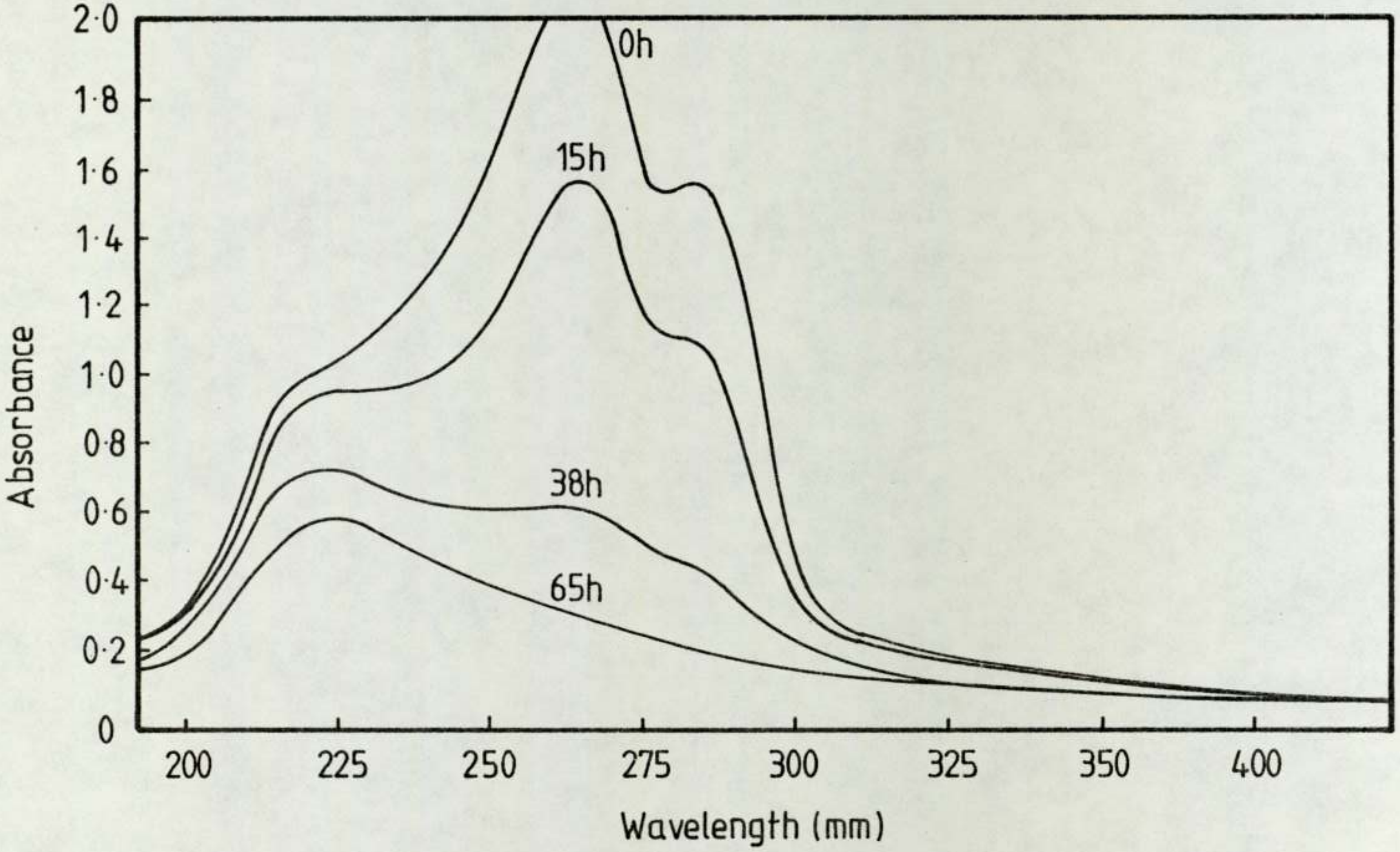


Figure 4:20 Changes in the UV spectra of ZDEC (5×10^{-4} mol/100g) in PP film during UV irradiation
Exposure times are shown on curves

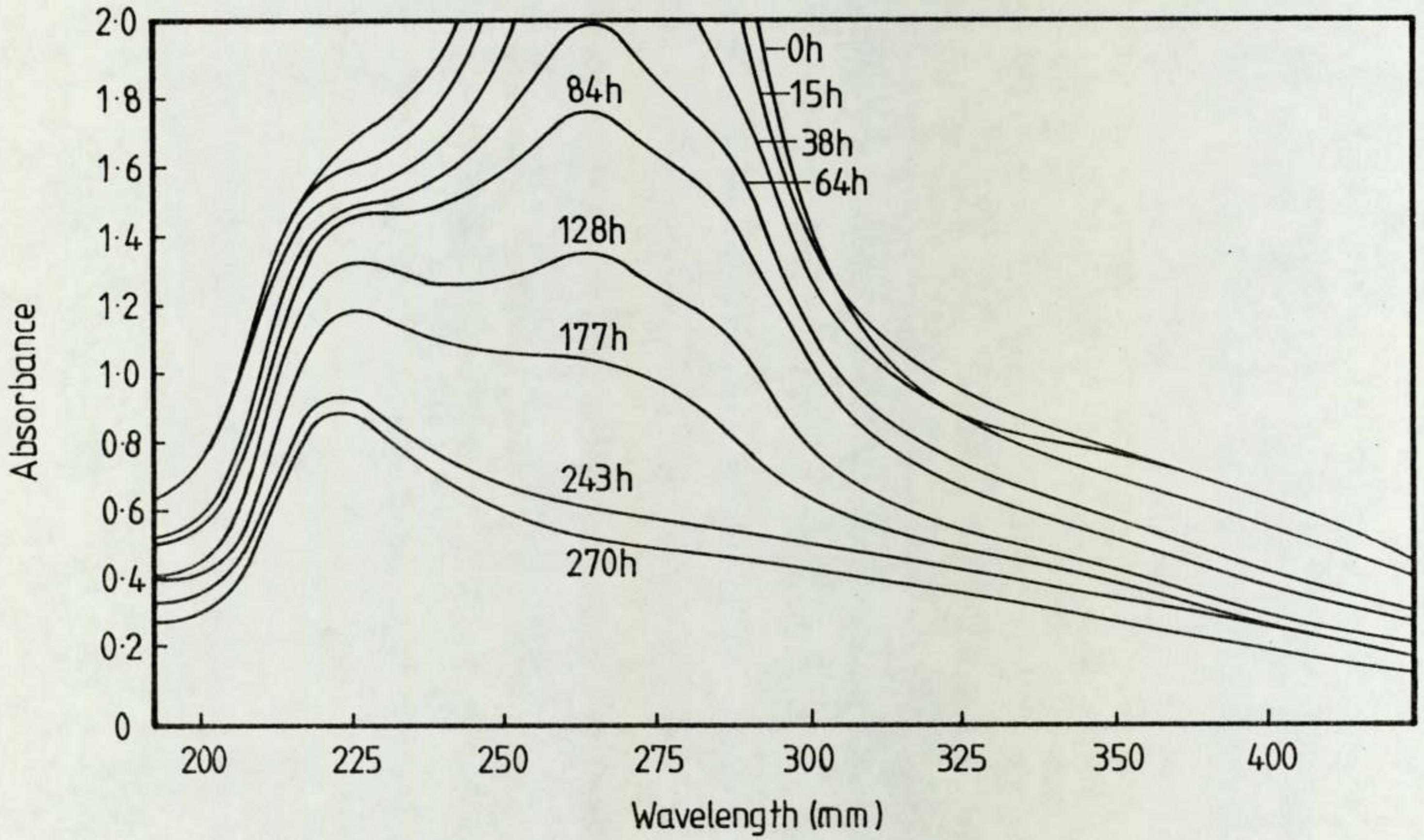


Figure 4:21 Changes in the UV spectra of ZDEC (5×10^{-4}mol/100g) in the presence of FDMC ($2{\cdot}5\times10^{-4}$mol/100g) in PP film during UV irradiation. Exposure times are shown on curves.

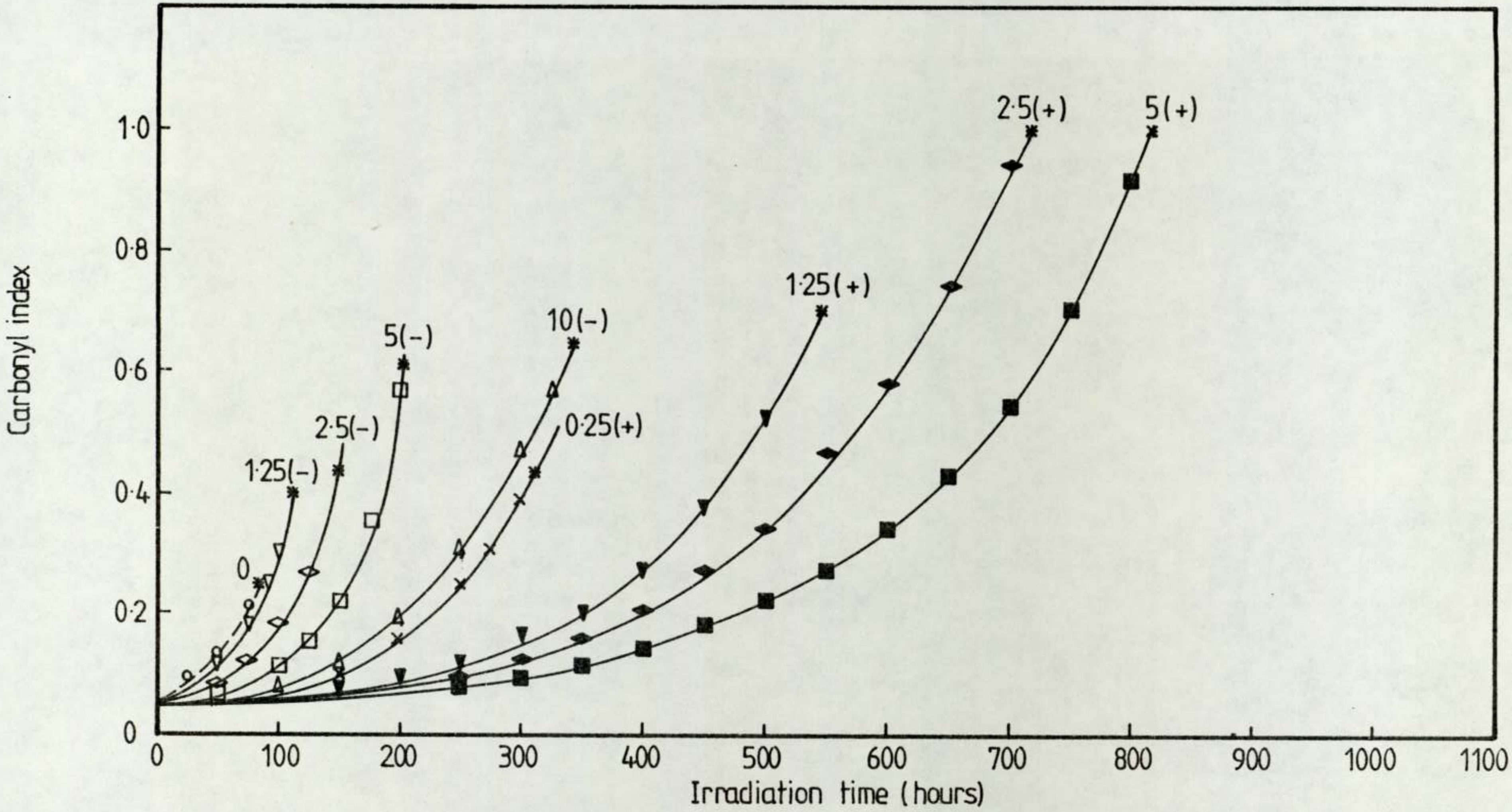


Figure 4:22 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence of $2{\cdot}5\times10^{-4}$ mol/100g TETD (Numbers on curves are FDMC concentrations in mol/100g $\times 10^{-4}$, ✱ indicates embrittlement of sample)

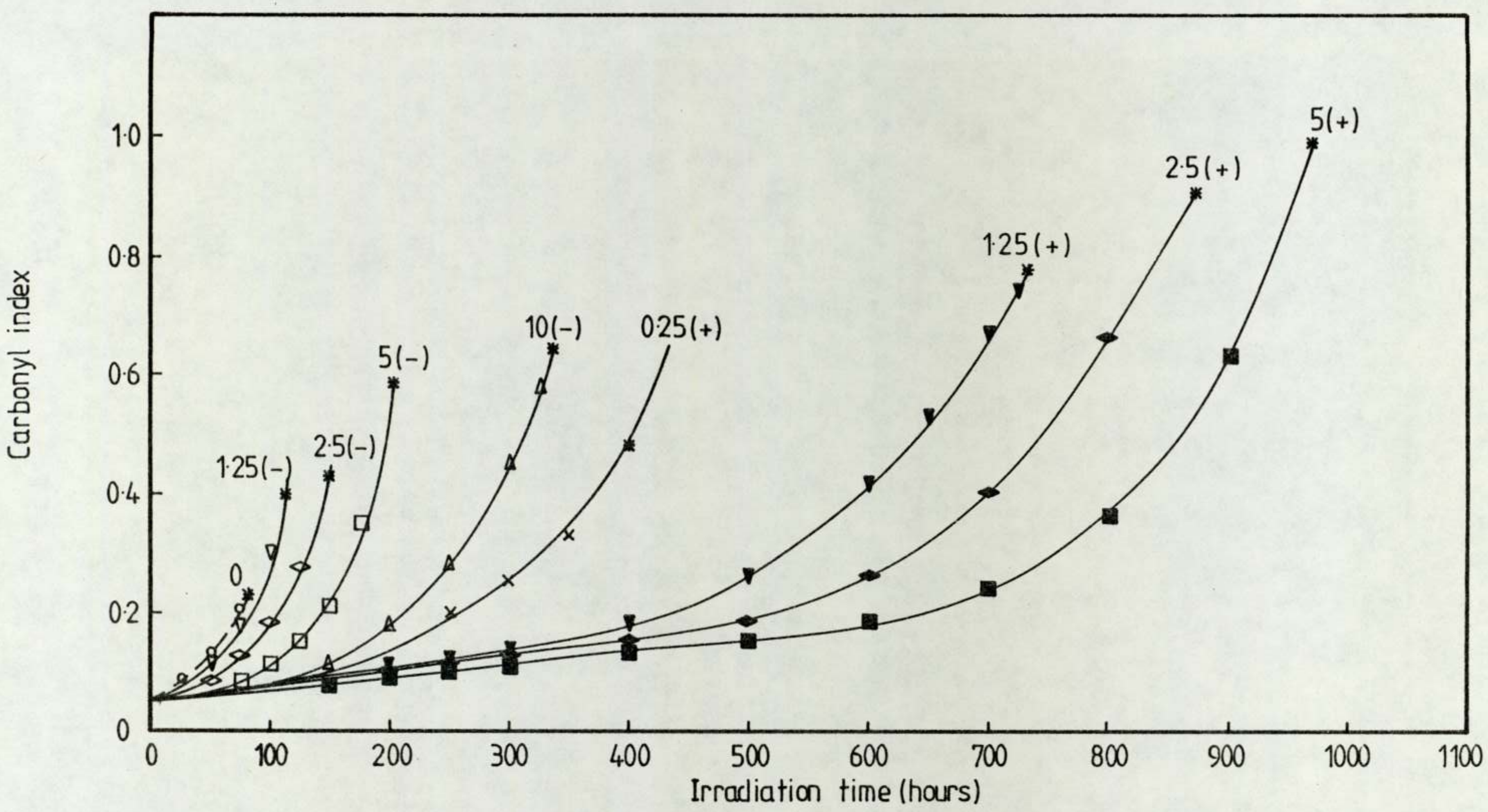


Figure 4:23 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (-) of 5×10^{-4} mol/100g TETD (Numbers on curves are FDMC concentrations in mol/100g $\times 10^{4}$, * indicates embrittlement of samples)

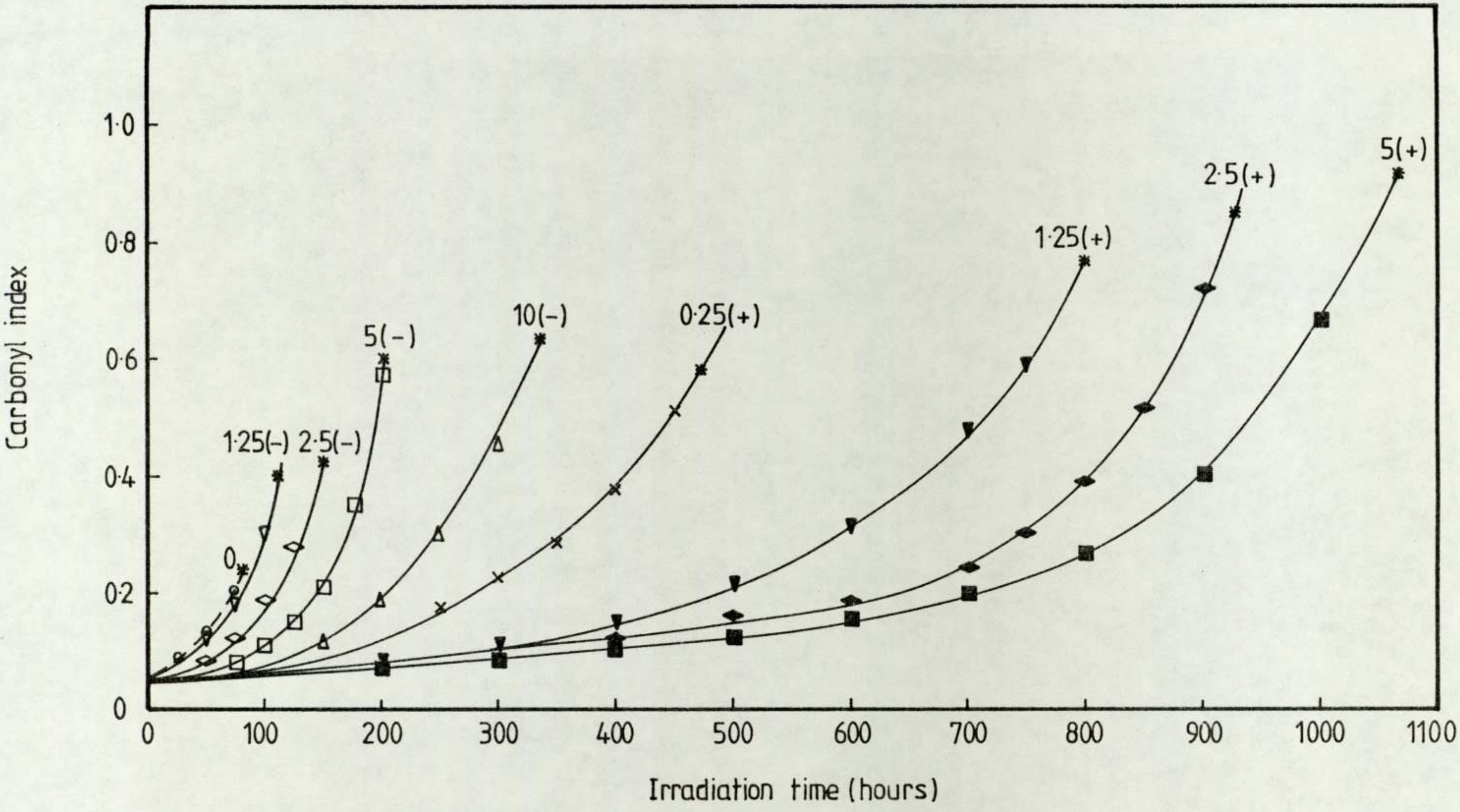


Figure 4:24 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (–) of 10×10^{-4}mol/100g TETD (Numbers on curves are FDMC concentrationsin mol/100g × 10^{-4} , ∗ indicates embrittlement of samples)

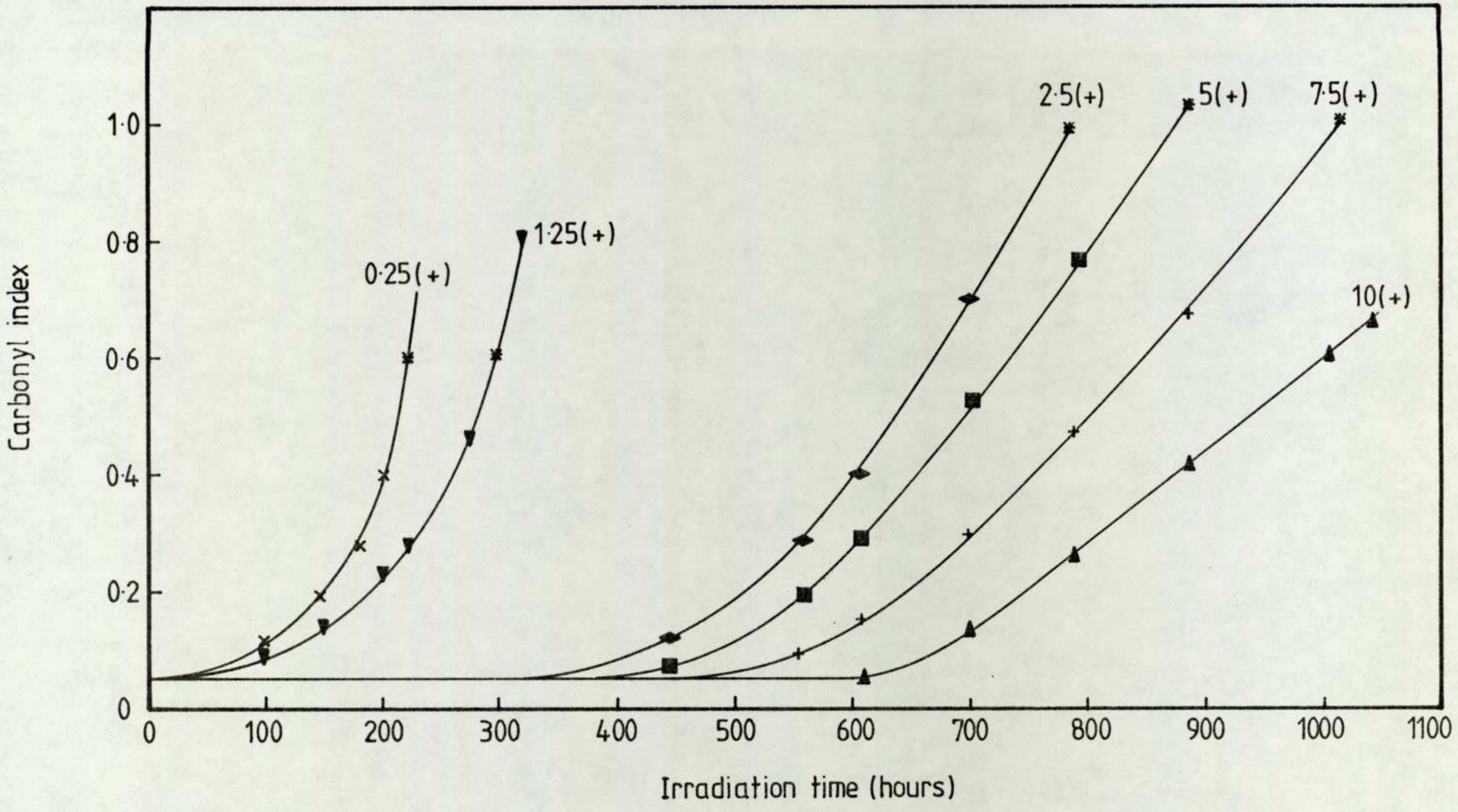


Figure 4:25 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (−) of $2{\cdot}5 \times 10^{-4}$ mol/100g HOBP (Numbers on curves are FDMC concentrations in mol/100g $\times 10^{-4}$)

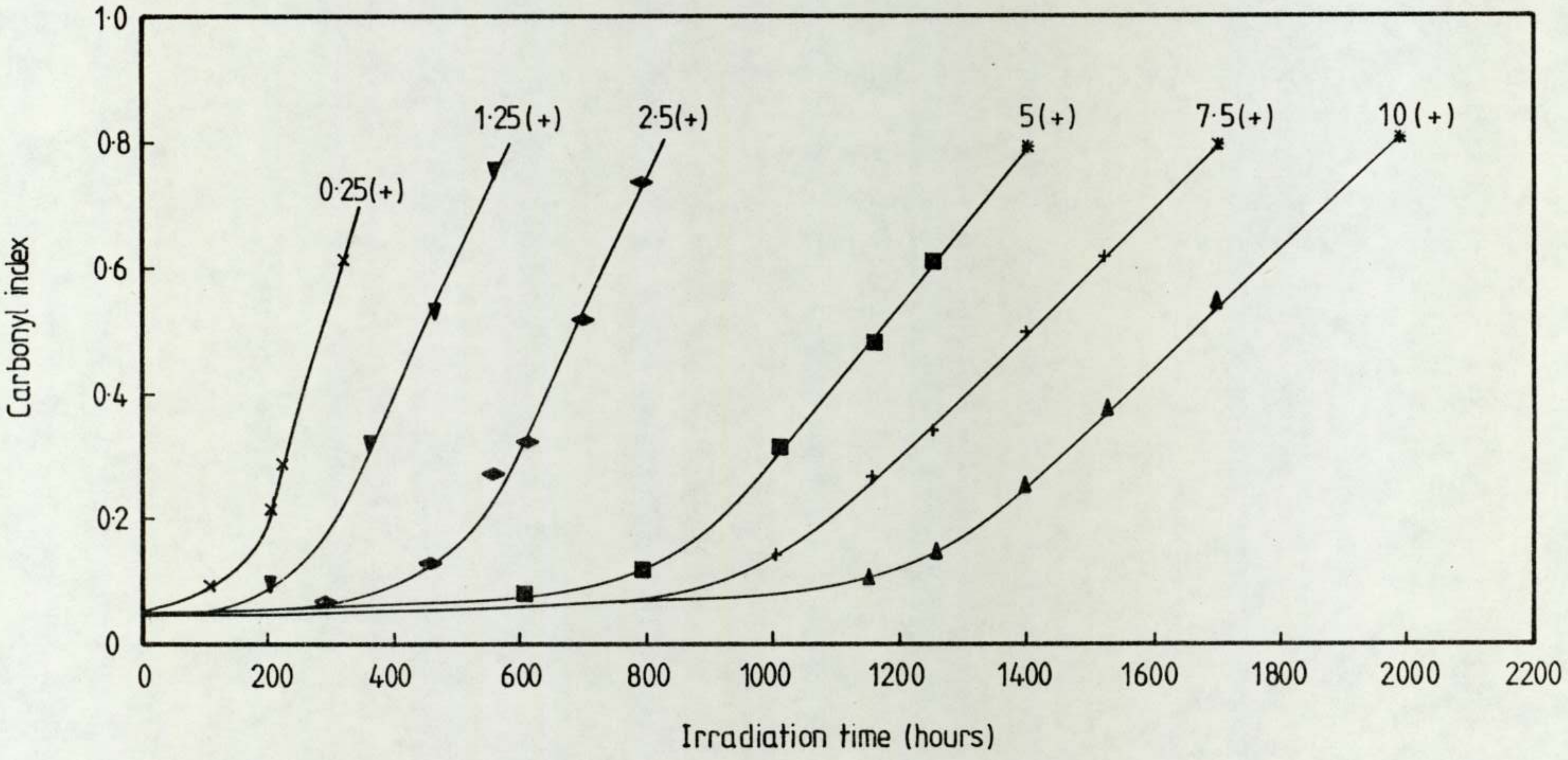


Figure 4 : 26 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (-) of 5×10^{-4} mol/100g HOBP (Numbers on curves are FDMC concentrations in mol/100g $\times 10^{-4}$)

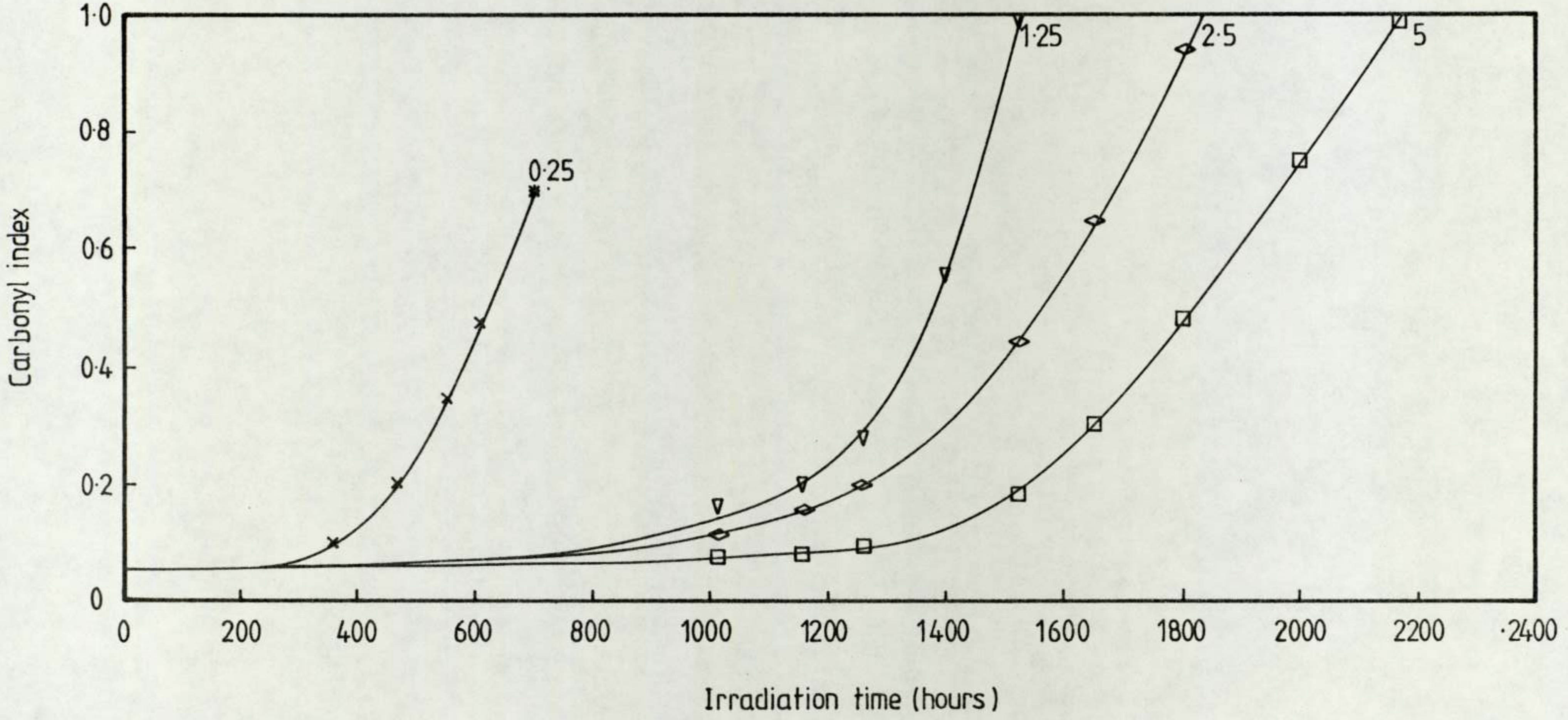


Figure 4:27 Effect of FDMC concentration on the photo-oxidation of PP in the presence (+) and absence (−) of 10×10^{-4} mol/100g HOBP (Numbers on curves are FDMC concentrations in mol/100g)

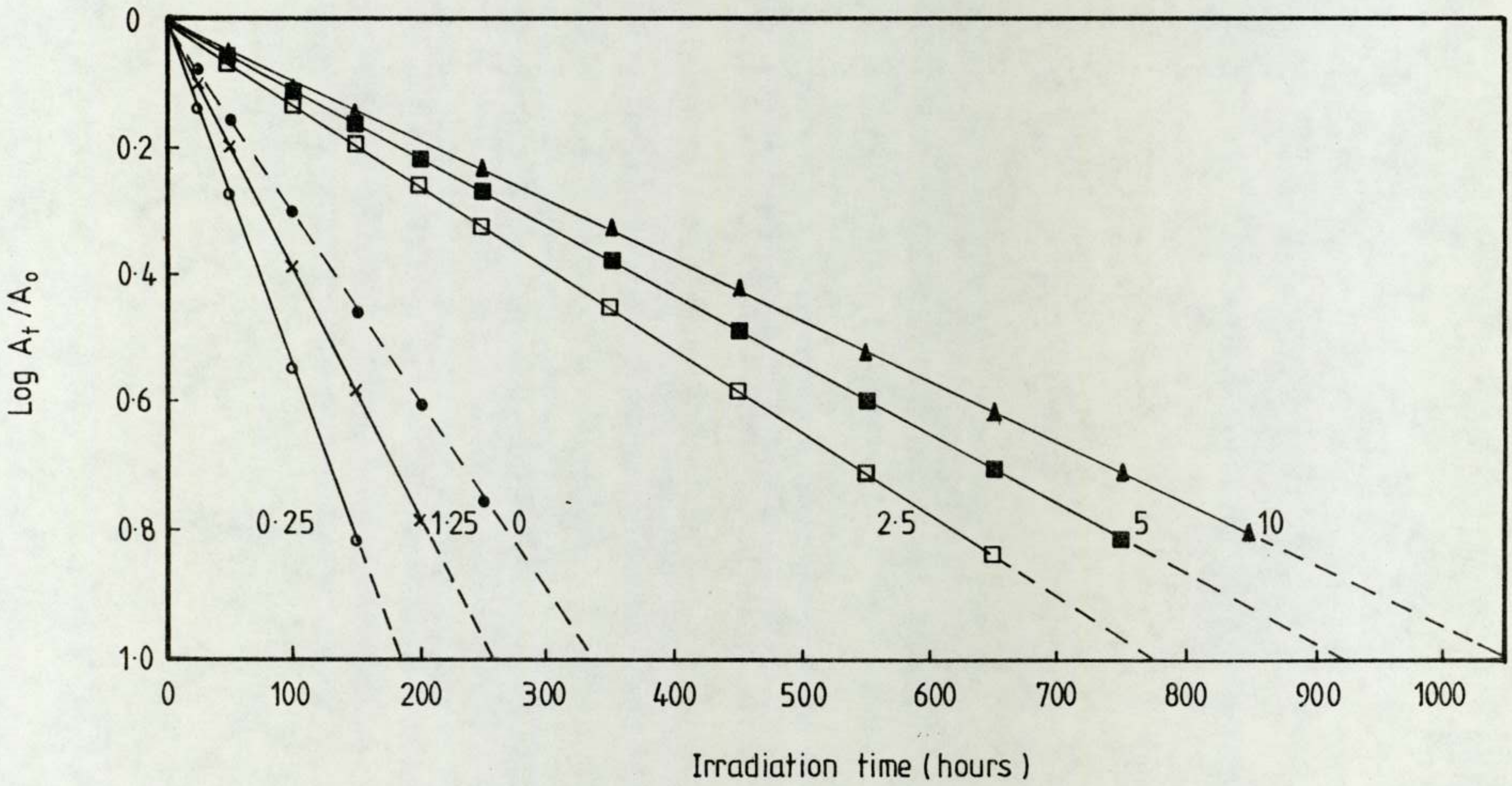


Figure 4:28 Change in the UV absorption intensity of $2{\cdot}5 \times 10^{-4}$ mol/100g HOBP at 330 nm in the presence of FDMC during photo-oxidation of PP processed at 180° C for 10 minutes in a closed mixer. (Numbers on curves are concentrations of FDMC in mol/100g $\times 10^{-4}$)

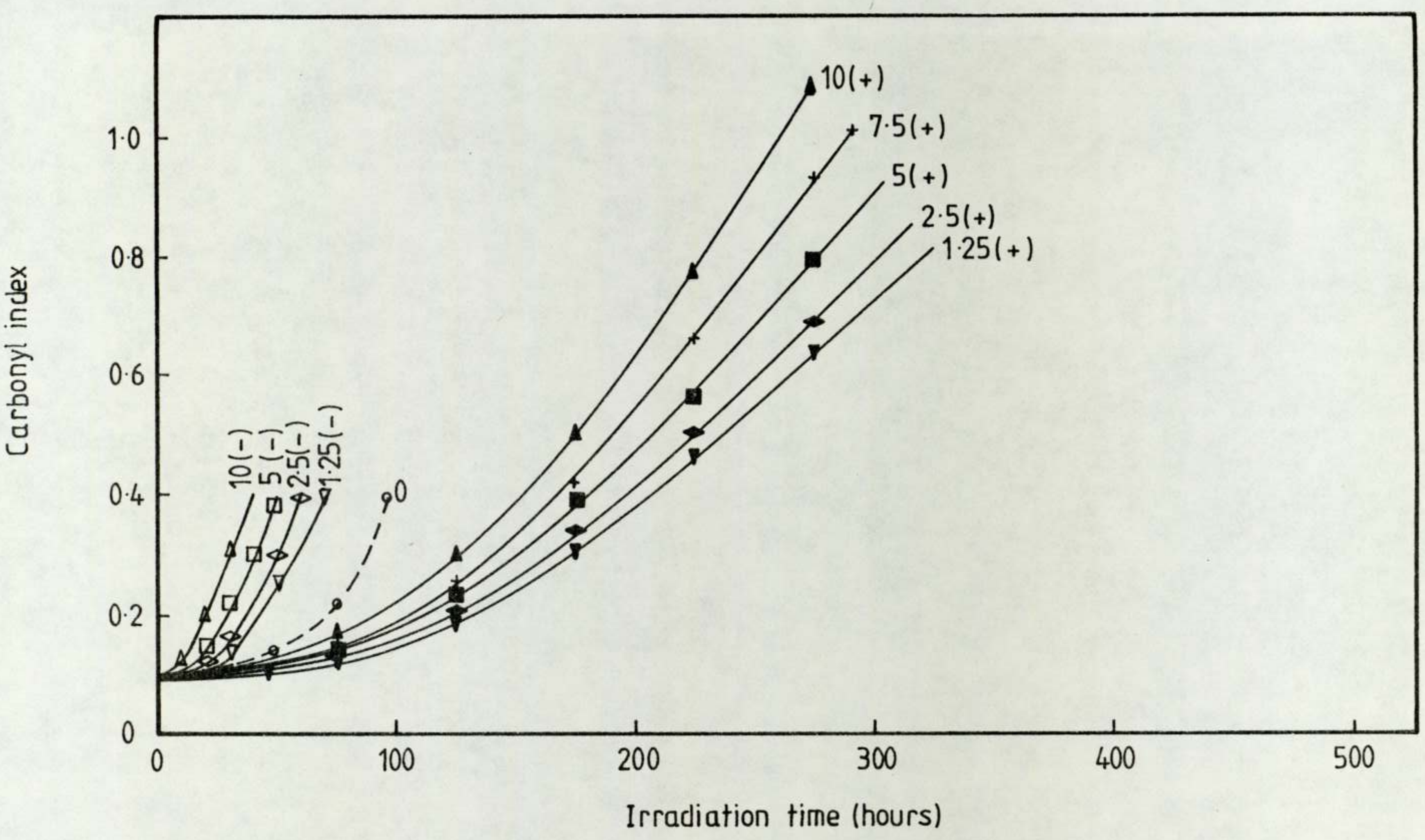


Figure 4 : 29 Effect of FAcAc concentration on the photo-oxidation of PP in the presence (+) and absence (-) of $2{\cdot}5 \times 10^{-4}$ mol/100 g NDEC (Numbers on curves are FAcAc concentrations in mol / 100g $\times 10^{-4}$)

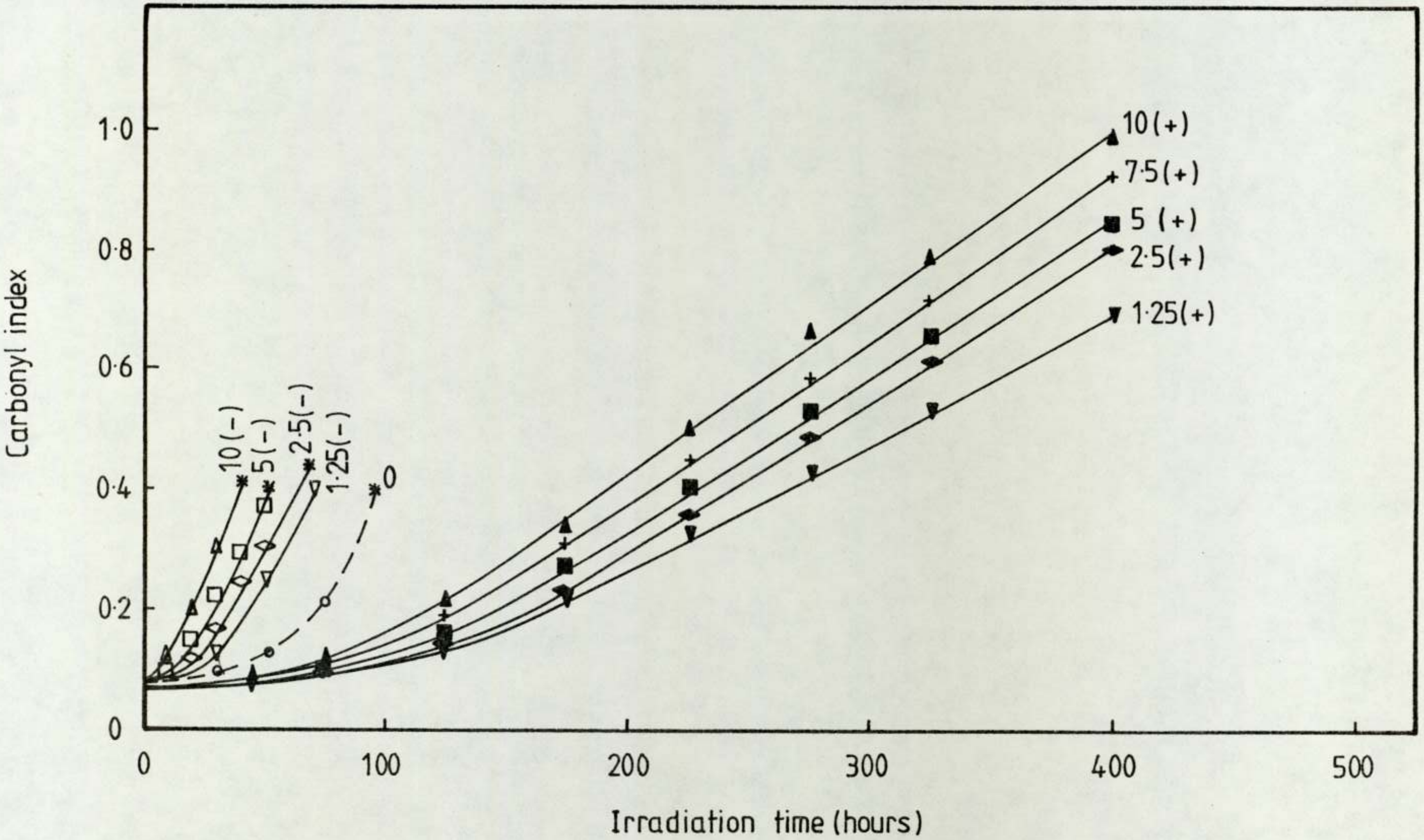


Figure 4:30 Effect of FAcAc concentration on the photo-oxidation of PP in the presence (+) and absence (−) of 5×10^{-4} mol/100g NDEC (Numbers on curves are FAcAc concentrations in mol/100g $\times 10^{-4}$)

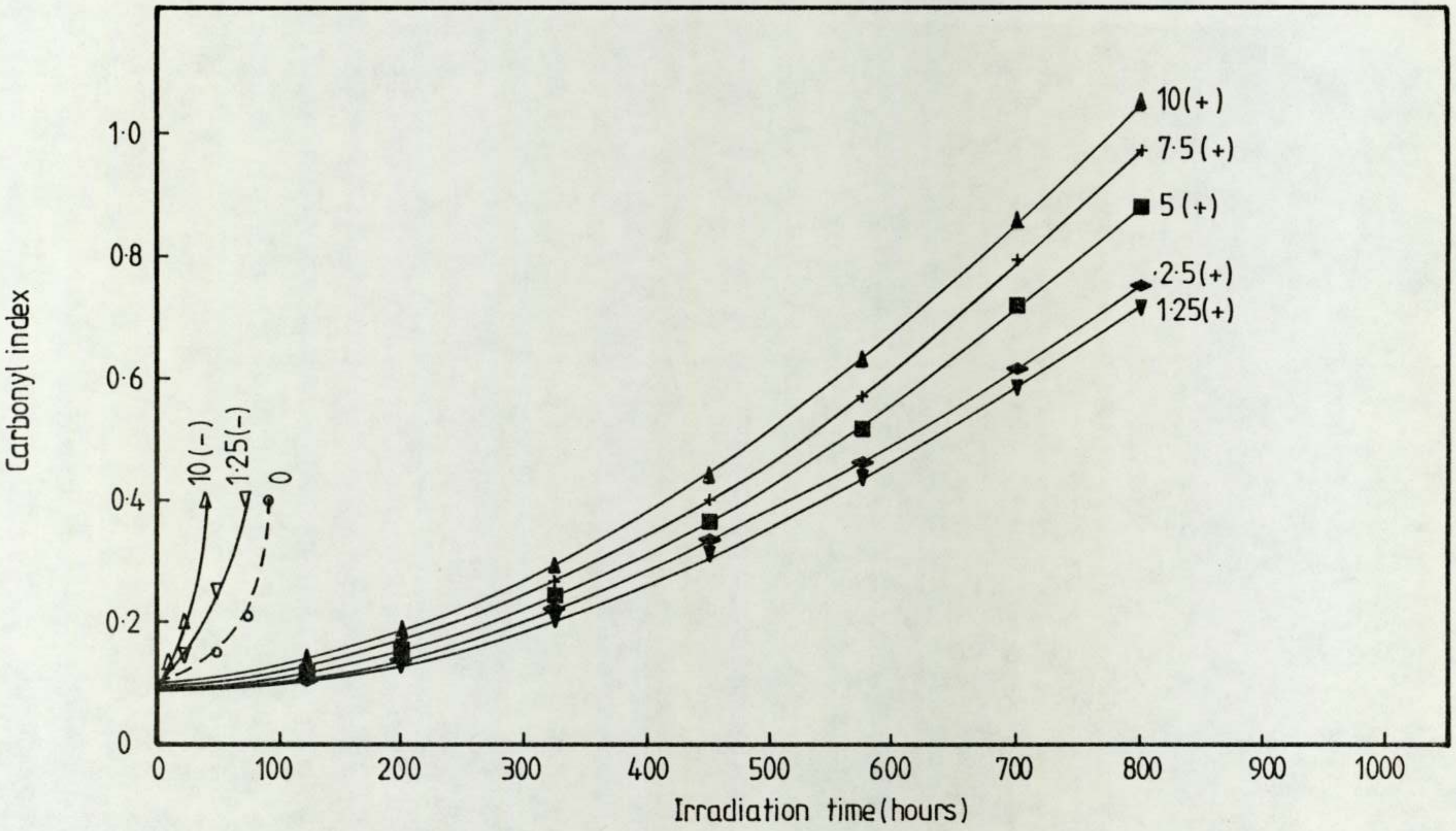


Figure 4:31 Effect of FAcAc concentration on the photo-oxidation of PP in the presence (+) and absence (−) of 10×10^{-4} mol/100g NDEC (Numbers on curves are FAcAc concentrations in mol/100g $\times 10^{-4}$)

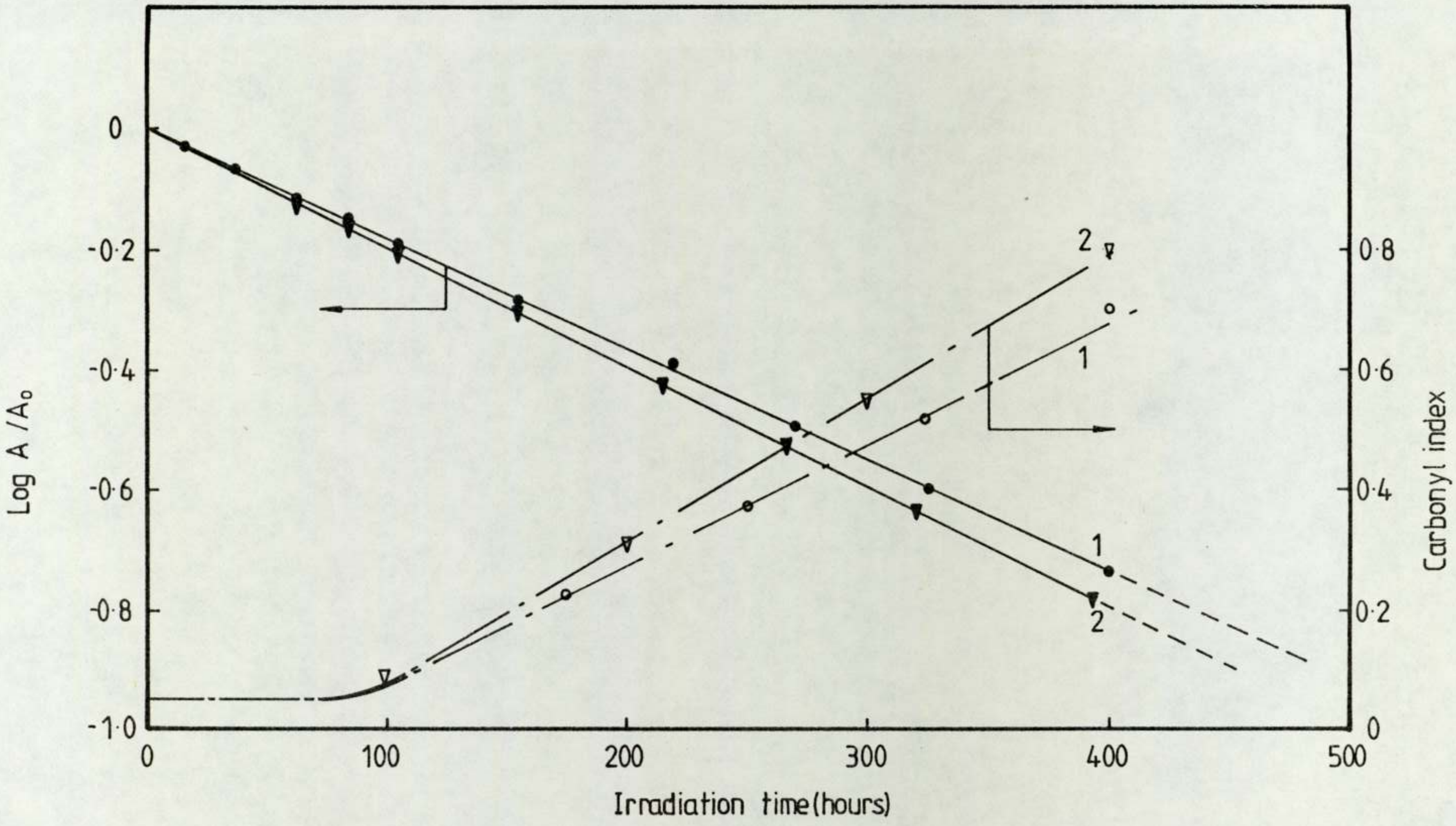


Figure 4:32 Comparison of the length of the photoinduction period to carbonyl formation of FAcAc/NDEC stabilised PP with the decay of NDEC band at 325 of same sample
(1) $1{\cdot}25\times10^{-4}$ FAcAc / 5×10^{-4} NDEC (2) $2{\cdot}5\times10^{-4}$ FAcAc / 5×10^{-4} NDEC

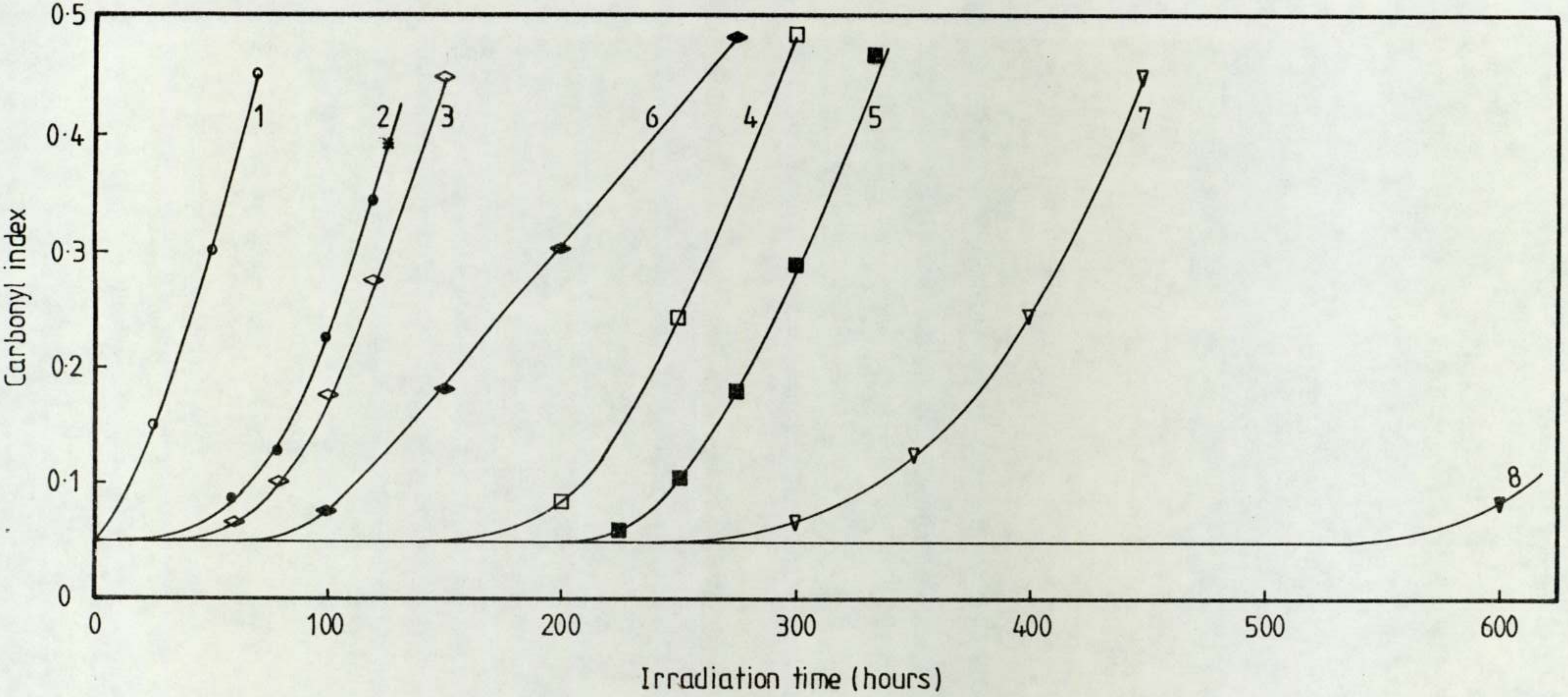


Figure 4:33 Comparison of protective effect of NDEC and HOBP on FDMC or FAcAc as screen and as additive in PP processed at 180°C for 10 minutes (concentration of activator is $2{\cdot}5 \times 10^{-4}$ mol/100g and the stabiliser 5×10^{-4} mol / 100g)
(1) FAcAc (additive) (2) FAcAc (additive screened by film containing NDEC (3) FDMC (additive)
(4) FDMC (additive screened by film with NDEC (5) FDMC (additive screened by film with HOBP
(6) NDEC + FAcAc (additive) (7) NDEC + FDMC (additive) (8) HOBP + FDMC (additive)

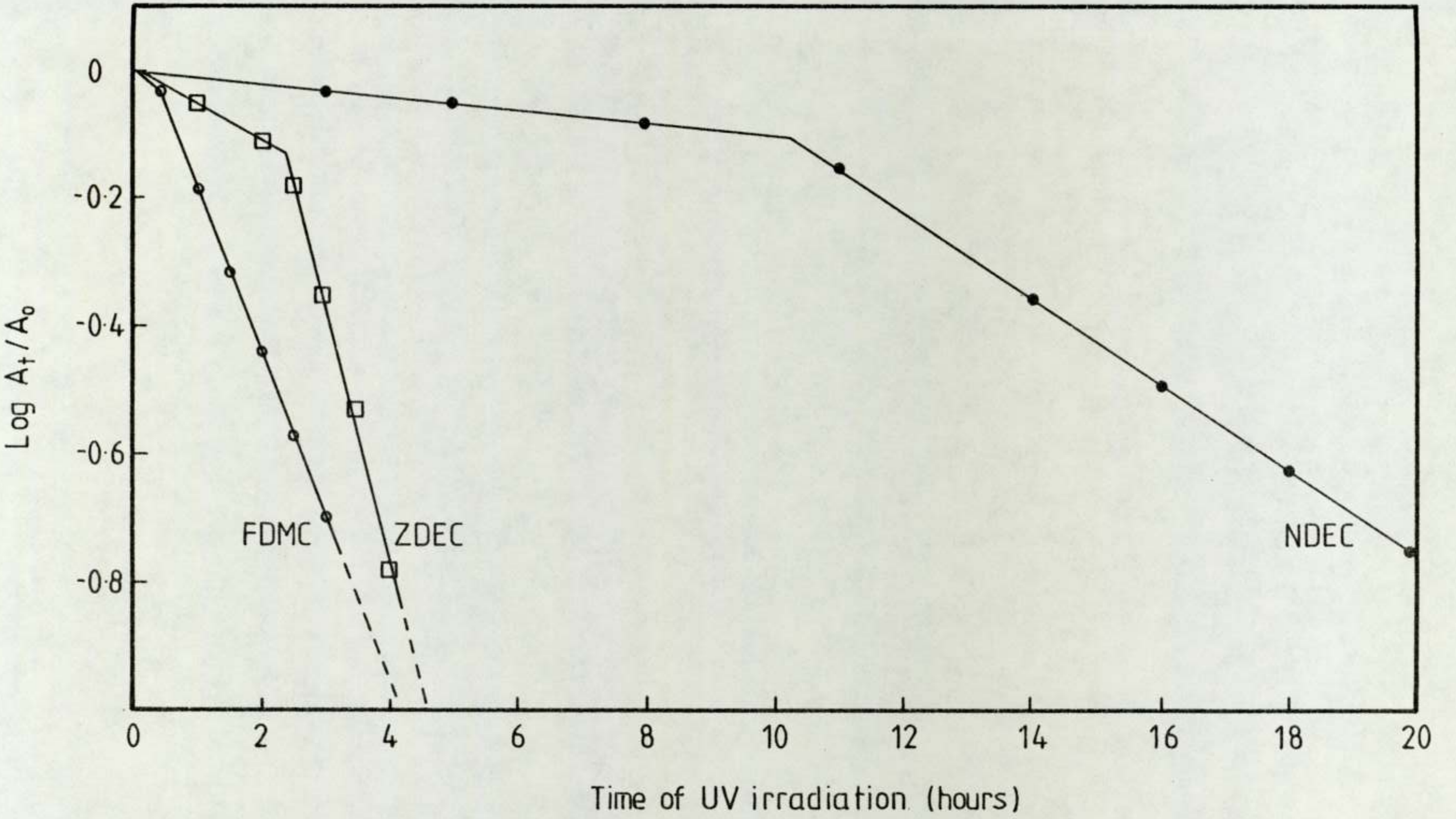


Figure 4:34 1st order decay of NDEC (λ_{max}= 325nm); ZDEC (λ_{max} = 286nm) and FDMC (λ_{max} = 257nm) in hexane. Concentration of additive is 5×10^{-5} M/l

CHAPTER FIVE

MECHANISM OF ACTION OF METAL DITHIOCARBAMATES

5.1 Object

In this chapter, both chain-breaking and peroxide decomposing activities of metal dithiocarbamate complexes (ZDEC, NDEC and FDMC) and the corresponding disulphides are investigated. The reactions of these metal complexes with free-radicals are studied in cumene hydrocarbon initiated by azobisisobutyronitrile(ABIN) at low temperature in an oxygen atmosphere. Products formed from these reactions are also analysed. Peroxide decomposition by these dithiocarbamates is examined in both inert and oxidisable substrates and in the presence of different bases, gaseous trap and free-radical inhibitor. Intermediates and products formed from the peroxide decomposition reactions with metal complexes are examined by GLC, TLC and U.V.-spectrophotometry techniques. Results show that the mechanism of action involves both free-radical scavenging and peroxide decomposition but that the contribution of each to the overall mechanism is influenced by the nature of the metal centre and by its presence. Details of the mechanism of action are presented.

5.2 Results

5.2.1 Reaction of Metal Dialkyldithiocarbamates with Alkyl Peroxy Radicals

The reaction of peroxy radicals with transition metal complexes of dithiocarbamic acid has been studied in thermally initiated oxidation of cumene. In the absence of additives, cumene is found to undergo auto-oxidation (see Figure 5.1). This has been explained in terms of a free radical chain mechanism(68,125,163) in which the predominant chain-carrying species is the peroxy radical. The oxidation of cumene is considerably delayed in the presence of ZDEC, NDEC and FDMC at 110°C (see Figure 5.1). Since the normal oxidation of cumene at 110° leads to the formation of both peroxy radicals and hydroperoxides(63a), the existence of a long induction period in the oxidation of cumene in the presence of the above transition metal complexes indicates that these dithiocarbamates are able simultaneously to break the auto-oxidation chain and to decompose the organic hydroperoxides in the oxidising system.

The reaction of peroxy radicals with metal dialkyl dithiocarbamates was further confirmed using a non-peroxidic initiator such as azobisisobutyronitrile (ABIN). By carrying out the reaction at a low temperature (50°C), to avoid initiation by the hydroperoxide product, the ABIN is the sole source of free radicals. Any antioxidant which lowers the rate of oxidation when added to such a system must, therefore, act by removal of chain-propagating peroxy radicals. The response of ZDEC, NDEC, FDMC and TETD to such a test is illustrated for cumene in Figure 5.2. These results clearly show that metal complexes of dithiocarbamic acid act as chain-breaking inhibitors. The fact that inhibition occurs from the beginning of oxidation, under mild temperature conditions, indicates that the complexes themselves and not their decomposition products remove peroxy radicals. Furthermore, the metal-free dithiocarbamate ligands (TETD) shows no real induction period. The presence of an induction period in metal dithiocarbamates is, therefore, attributed to the metal ions.

Further investigation of Figures 5.1 and 5.2 reveals that the chain-breaking activity exhibited by these metal dithiocarbamates (ZDEC, NDEC and FDMC) cannot alone explain the excellent stability observed for cumene at 110°C (Figure 5.1). This implies that the chain-breaking activity plays only a minor part in the whole stabilization mechanisms involved with the metal dithiocarbamates. The formation of hydroperoxides from cumene in an oxygen atmosphere at 110°C is highly feasible. These metal dithiocarbamates must, therefore, have the ability to destroy peroxides in a non-radical mechanism. Figure 5.3 shows the effect of metal dithiocarbamates (ZDEC, NDEC and FDMC) on the thermal oxidation of cumene at 110°C in the presence of cumene hydroperoxide (CHP;0.1 M) as initiator. These results clearly demonstrate the activity of these inhibitors in decomposing the peroxides and also explain the excellent stability observed for cumene without initiator at 110°C (Figure 5.1). With CHP as initiator, an initial pro-oxidant effect was observed followed by a fast period of gas evolution and then, in each case, the shape of the curve indicated auto-inhibition. This implies that the antioxidant activity of these metal dithiocarbamates (ZDEC, NDEC and FDMC) is due to their oxidation products and that the gas product evolved could play a vital part in the whole stabilization mechanism.

To clarify the mechanisms of the interaction of these metal complexes (ZDEC, NDEC and FDMC) with radicals, product analysis was carried out. A solution of ZDMC (0.01 M) and ABIN (0.025 M) in benzene (sodium dried), through which a slow current of oxygen was bubbled, was boiled under reflux for 5 hours. The reaction mixture which was initially colourless became yellow on refluxing and this was further intensified at a longer reaction time. At the end of the reflux (5 hours), the reaction mixture was filtered off to give a colourless solid and light yellow filtrate. The solid was extracted several times with methanol and the white solid remaining after extraction has a melting point of >300°C. This was identified as zinc cyanide (identical I.R. spectrum to authentic, see Figure 5.4). Removal of the solvent (methanol) from the extract gave a white-yellow solid which had a melting point of 34°C and its I.R. spectrum (see Figure 5.5) indicated the presence of an isothiocyanate group (2090 cm$^{-1)}$ in addition to conjugated carbonyl group (1630 and 1715 cm^{-1}). Evaporation of the benzene from the original filtrate gave a viscous liquid which was extracted with petroleum ether (40-60° b.p.) several times. A brown gum remained undissolved and this was extracted again from methanol to give a compound of m.p. 245°C which was identified as ZDMC (identical I.R. spectrum to authentic, see Figure 5.6).

The petroleum ether solution gave a pale yellow liquid which crystallised on standing to give pale yellow crystals of 121°C m.p.. Recrystallisation of the latter product from heptane gave crystals of m.p. 156°C identified as tetramethylthiuramdisulphide (TMTD) (see Figure 5.7 for I.R. spectrum). The petroleum ether solution which remained after separation of TMTD was found to contain a small amount of the initiator (ABIN) (see Figure 5.8). Similar products were also observed in the reactions of NDMC (or FDMC) and ABIN.

5.2.2 Thermal Decomposition of CHP in the Presence of Metal Dithiocarbamate Complexes and the Corresponding Disulphide

The mode of decomposition of CHP at 1 x 10^{-2} M in chlorobenzene at 110°C in the presence of metal dialkyldithiocarbamate complexes (ZDEC, NDEC and FDMC) is shown in Figure 5.9. In the absence of additives, CHP was found to undergo insignificant decomposition (see control curve in Figure 5.9). Chlorobenzene itself is an inert solvent and is thermally stable at 110°C.

The decomposition curves of CHP in the presence of NDEC and FDMC showed three characteristic features: Rapid initial catalytic stage, secondary induction period and a slower first order catalytic reaction. ZDEC curve showed only the last two stages. The rapid initial catalytic stage was missing.

The effect of varying the concentration of NDEC and FDMC on the kinetics of decomposition of CHP (1×10^{-2} M) in chlorobenzene at 110°C are displayed in Figures 5.10 and 5.11 respectively. These results show that on going from the stoichiometric to catalytic ratios i.e., 1:1 to 50:1, the secondary induction period appears to increase with notable decrease in the contribution of the initial catalytic stage. In the case of ZDEC reaction with CHP (see Figure 5.12), the lower the concentration of ZDEC in the reaction mixture, the shorter the induction period and the faster the second catalytic stage. This behaviour of the zinc complex is exactly opposite to that exhibited by nickel and iron complexes (see Figure 5.13).

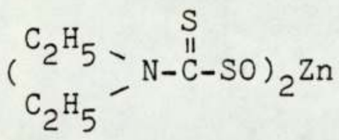
In order to clarify the role of each of the metal ions and the sulphur ligands in the complex, metal free ligand (TETD) was investigated under the same conditions as in metal complexes. Results shown in Figure 5.14 indicate the absence of a secondary induction period which must, therefore, be associated with metal complexes. The reaction of CHP (1×10^{-2} M) with disulphide followed first order kinetics (see Figure 5.14 . b) from the beginning of the reaction, which in turn is faster than the second catalytic stage from a corresponding reaction of CHP with NDEC or FDMC at the same molar concentration (see Figure 5.15).

5.2.3 Thermal Decomposition of CHP in the Presence of Oxidation Products of Metal Dithiocarbamates

A careful examination of Figures 5.9-5.12 reveals that these metal dithiocarbamates (NDEC, FDMC and ZDEC) are not themselves the real catalysts for peroxide decomposition since they give an initial or secondary induction period before the catalytic hydroperoxide decomposition takes place. This observation suggests that an oxidation product or products of these metal dithiocarbamates (NDEC, FDMC and ZDEC) might be the active species for the catalytic peroxide decomposition. The first oxidative products which are expected to be formed from these metal complexes (NDEC, ZDEC and FDMC) are the corresponding sulphenate and sulphinate complexes. Therefore, priority was given to the preparation of such intermediates and exploration of their peroxide decomposing activity. It might be useful to mention here, that preparation of such intermediates was only possible with zinc dialkyldithiocarbamate complexes (for further details see the experimental Chapter, Section 2.5.6). However, controlled oxidation of NDEC and FDMC by peroxides or indirectly by oxidation of the sodium salt and then conversion of the corresponding sodium sulphenate or sulphinate by double decomposition to the corresponding nickel or ferric sulphenate or sulphinate, led to the formation of unstable products coupled with the disulphide (TRTD). Thus it seems likely that ZDRC exerts its antioxidant action through the formation of sulphenate and sulphinate intermediates whereas the nickel and iron complexes form the disulphide as one of their oxidation products.

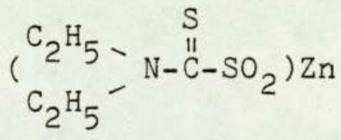
The formation of the disulphide from NDEC and FDMC was further confirmed by the addition of tellurium powder at the early stages of the induced hydroperoxide decomposition reaction by NDEC or FDMC (at molar ratio of CHP:additive of 10:1 to 1:1). At the first 4 minutes of the reaction of NDEC or FDMC with CHP, the normal colour of the solution changed to brick-red on addition of tellurium powder indicating that the disulphide which is formed as an intermediate at this stage of the reaction, is reacting with tellurium powder to form the divalent tellurium dithiocarbamate(101). However, such colour was not developed on addition of tellurium powder to ZDEC-induced hydroperoxide decomposition reaction.

Since the zinc salt of both diethyldithiopercarbamate (see Structure I) and diethylthiocarbomylsulphinate (see Structure II) appeared to possess some degree of stability, it was of interest at this stage to explore their peroxide decomposing activity. Figure 5.16 compares the peroxide decomposing activity of zinc diethyldithiopercarbamate and zinc diethylthiocarbomyl sulphinate with the parent ZDEC complex. It is clear that the rates of hydroperoxide decomposition in the presence of zinc sulphenate and sulphinate are faster than that of the original complex. However, an induction period was still observed, suggesting that the zinc sulphinate must decompose in some way to form the active species for the catalytic hydroperoxide decomposition.



$$\left(\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}{>}N-\overset{\overset{S}{\|}}{C}-SO\right)_2Zn$$

I



$$\left(\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}{>}N-\overset{\overset{S}{\|}}{C}-SO_2\right)_2Zn$$

II

5.2.4 Effect of Base on Decomposition of CHP in the Presence of Metal Dialkyldithiocarbamate Complexes and the Corresponding Disulphide

In order to determine if the observed hydroperoxide decomposition was due to acidic products resulting from the decomposition of zinc dithiocarbamate complex, the reaction of zinc complex with CHP was repeated in the presence of a base. Powdered $CaCO_3$ was selected and suspended by shaking in chlorobenzene solution of the reactants. The effect of $CaCO_3$ base on the activity of zinc dithiocarbamate complex is shown in Figure 5.17. The control with no sulphur additive shows that $CaCO_3$ has no effect on CHP at 110°C in chlorobenzene under nitrogen. Addition of a small amount of $CaCO_3$ base (molar ratio CHP:additive:$CaCO_3$ was 30:1:0.25) slowed down both the initial reaction of metal complexes with CHP and the subsequent catalytic decomposition. When excess of the base was present (molar ratio CHP: additive:$CaCO_3$ was 10:1:0.5) the initial reaction was slowed down even more, but ultimately consumed all the CHP. The decomposition of CHP was almost completely stopped with excess base (molar ratio CHP:additive:$CaCO_3$ 10:1:2) consistent with neutralisation of an acid catalyst presumed to be SO_3(65,66) formed by oxidation of the additive by CHP.

The above results were confirmed further by using oxygen absorption technique. The base (pyridine) was added to the cumene substrate in a 50 ml vessel (see the experimental chapter, Section 2.7.3) and this was followed by addition of the antioxidant. The apparatus was allowed to equilibrate in the thermostated bath at 110°C for 10 minutes before being isolated from the atmosphere. Agitation of the reaction vessel was rapid enough to ensure that solution of oxygen was not rate-controlling. The results of FDMC, NDEC and ZDEC are shown in Figure 5.18. It is clear that the antioxidant function of these additives is completely removed by pyridine,suggesting that the real antioxidant must be a powerful acidic catalyst(101) which is responsible for the decomposition of peroxides.

5.2.5 Effect of Free Radical Inhibitor on the Activity of Metal Dialkyldithiocarbamate Complexes on Decomposing CHP

The catalytic hydroperoxide decomposition which ultimately is observed in the presence of metal complexes of dithiocarbamic acid is clearly an acidic catalysed polar process (Section 5.2.4). However, the detailed chemistry by which this acid catalyst is formed is still unclear. Radicals generated by homolytic cleavage of hydroperoxide may induce decomposition of the metal dithiocarbamate complexes (as proposed by many workers(164)) which could lead eventually to the formation of the active catalyst. In order to clarify the involvement of free radicals in the generation of acidic species during the reaction of dithiocarbamate complexes with CHP, the well known radical inhibitor 2,6 ditert butyl-4-methyl phenol was added to the reaction mixture of CHP and metal dithiocarbamate complexes. Figure 5.19 shows that the hydroperoxide decomposition is totally suppressed in the presence of this inhibitor. However, addition of radical trapping agents after the catalytic decomposition has commenced had no effect at all.

5.2.6 Effect of Gas Trapping Agent on the Inhibition Action of Metal Dithiocarbamate Complexes

It was clearly established in the previous sections (see Sections 5.2.2 and 5.2.3) that the metal dithiocarbamate complexes are not themselves peroxide decomposers,but acidic species formed from their interaction with peroxides are the main antioxidant species. However, the nature of these acidic species is still unknown. Scott and his coworkers suggest(65,66) that the main acidic species is probably SO_3 formed at the later stages of the oxidation of metal dithiocarbamates. If this species is the true antioxidant species, it should then be capable of being trapped by any good gas trapping agent such as a molecular sieve (5A). Figure 5.20 shows the effect of molecular sieve (5A) on the thermal oxidation of cumene hydrocarbon initiated by CHP and in the presence of transition metal complexes (ZDEC, NDEC and FDMC) as inhibitors. It is very clear that the antioxidant function of metal dithiocarbamate complexes is substantially removed by the addition of molecular sieve.

Further examination of Figure 5.20 reveals that the gas acidic species is not the only species inhibiting the normal oxidation of cumene. Since the inhibition action is not completely removed by the addition of molecular sieve. This observation coupled with the fact that pyridine prevents the inhibition action of metal dithiocarbamates completely, suggest that acid catalysts other than SO_3 (or SO_2) gaseous species are involved with the antioxidant action of metal dithiocarbamate complexes.

5.2.7 Photodecomposition of CHP in Chlorobenzene in the Presence and Absence of Metal Dithiocarbamate Complexes

U.V.-induced decomposition of CHP (1×10^{-2} M) in chlorobenzene was studied both in absence and presence of metal dithiocarbamate complexes. Figure 5.21 shows that in the absence of additives, CHP is found to undergo slow but gradual decomposition when a solution of CHP (1×10^{-2} M) in chlorobenzene was exposed to U.V. light. However, photodecomposition of CHP is greatly enhanced when metal dithiocarbamate complexes are present (curves ZDEC, NDEC and FDMC in Figure 5.21). The features displayed by the decomposition curve of CHP in the presence of metal complexes (FDMC, ZDEC and NDEC), in U.V. light, are similar to those obtained during thermal reaction at 110°C (c.f. Figure 5.9 with Figure 5.21). The effect of TETD (Figure 5.21) on the photodecomposition of CHP in chlorobenzene under the same conditions, was similarly found to correlate well with results of thermal decomposition of CHP (c.f. Figure 5.21 with Figure 5.14). However, a slower rate of decomposition of CHP is noted here when compared with analogous curves in thermal decomposition. The high temperature used in the thermal decomposition (110°C) as compared with 30°C used in photodecomposition could be the reason for this.

5.2.8 Product Analysis

5.2.8.1 Gas-Liquid Chromatography

Products obtained from the thermal decomposition of CHP (1×10^{-2} M) at 110°C in chlorobenzene in the presence of metal dithiocarbamate complexes (FDMC, NDEC and ZDEC) were analysed by GLC. Kinetics of formation and disappearance of products were also followed during the course of the reaction. The unreacted CHP was reduced to α-cumyl alcohol (α,α'-dimethyl benzyl alcohol) by the addition of triphenyl phosphine. The product yield of α-cumyl alcohol was corrected with the aid of a calibration graph (see Section 2.10). 10

The variation in the reaction products of CHP(1×10^{-2} M) with FDMC, NDEC and ZDEC at different molar ratios (1-100) are shown in Figures 5.22-5.24. It is clear that α-cumyl alcohol and acetophenone are exclusively formed at, and below, molar ratio of 10. This situation is drastically altered at higher molar ratios when products of the ionic reaction phenol and α-methyl styrene predominate i.e., CHP: additive>10. Under the experimental conditions used for the thermal decomposition studies i.e., at 110°C and continuous purging with N_2 volatile products of the reaction e.g., acetone are not retained in the reaction medium. The product distribution for the reaction of CHP (1×10^{-2} M) with TETD at different molar ratios and under similar conditions to that of the reaction of metal complexes and CHP is shown in Figure 5.25. It is clear that ionic products are the major decomposition products of CHP in this case. Both phenol and α-methyl styrene are found to occur in appreciable amounts even at stoichiometric ratios (≈40% phenol and 40% α-methyl styrene). The free radical products, on the other hand, are found to occur to an extent which is much lower than that obtained from the reaction of CHP with metal complexes ZDEC, NDEC and FDMC (<20%).

Kinetics of formation of products during the decomposition reactions of CHP (1×10^{-2} M) with NDEC, ZDEC and FDMC at 110°C in chlorobenzene are respectively shown in Figures 5.26-5.28 at fixed molar ratios of 10:1 and 30:1 (CHP:additive).

The build-up of ionic products during the progress of the reaction, at the expense of free radical reaction products, is clearly evident. Similar kinetic behaviour is also observed for the reaction of CHP (1×10^{-2} M) with the disulphide (TETD) (see Figure 5.29).

5.2.8.2 U.V.-Spectrophotometry

The formation of intermediates and products from the reaction of TBH (2.5×10^{-2} M) and ZDMC, at molar ratio 250:1, in ethanol at 50°C is followed by U.V.-spectrophotometry. Figure 5.30 shows a continuous scan of this reaction and Figures 5.31 and 5.32 display the spectra of the intermediates and products formed from the above reaction. These figures show that the decay of the ZDMC bands at 257 nm and 275 nm was accompanied by the formation of new absorptions around 315 nm and 252 nm. The similarity of these spectral features with those of zinc dimethyldithiopercarbamate (see Figure 5.33) is striking. Based on these results the new product formed from the reaction of TBH and zinc dithiocarbamate at high molar ratio (250:1) is the zinc dimethyl dithiopercarbamate. Continuing the reaction, these new intermediates bands were found to disappear with the appearance of a new band at 273 nm. The new spectral absorption feature was found to be very similar to those obtained from an authentic sample of zinc dimethylthiocarbomyl sulphinate (see Figure 5.35). Further reaction, led to the disappearance of the absorption band at 273 nm and the emergence of another absorption feature centred around 243 nm. The latter band was found to be unaffected by the undecomposed TBH, see Figure 5.32.

The formation of zinc dimethylthiocarbomyl sulphenate (ZDMCSO) and sulphinate ($ZDMCSO_2$) from the reaction of ZDMC and TBH was further confirmed by carrying out their reactions with TBH under the same conditions used for the ZDMC and TBH reaction. Figure 5.33 shows a continuous scan of the reaction of ZDMCSO (1×10^{-4} M) and TBH (2.5×10^{-2} M), at molar ratio 1:250, in ethanol at 50°C. This reaction appears faster than that of ZDMC and TBH and leads to the formation of the same spectral features (see Figures 5.33 and 5.34) observed in ZDMC and TBH reaction. Thus, the build-up and decay of zinc dimethylthiocarbomyl sulphinate ($ZDMCSO_2$) intermediate during the reaction of the TBH and ZDMCSO is very clear from the appearance and disappearance of the band at 273 nm. The unknown band at 243 nm appears at the end of the reaction and is not affected by the undecomposed hydroperoxide.

The reaction of $ZDMCSO_2$ (1×10^{-4} M) and TBH at molar ratio 1:300, was similarly followed by continuous scan of the U.V.-absorption spectra of the $ZDMCSO_2$ (see Figure 5.35). The decay of the characteristic absorption band (273 nm) of the $ZDMCSO_2$ was accompanied by the formation of a new spectral absorption band at 243 nm. The similarity of this band with those obtained at the end of the reaction of ZDMC (or ZDMCSO) and TBH is striking.

5.2.8.3 Thin-Layer Chromatography

The formation of intermediates and products from the reaction of CHP (1×10^{-1} M) and metal dithiocarbamates (NDEC, FDEC and ZDEC), in chlorobenzene at 110°C and under nitrogen atmosphere, is followed by TLC technique. Pure compounds, prepared in the same solvent (chlorobenzene) were also run at the same time for comparison. The analysis (Figure 5.38) shows that metal dithiocarbamate compelxes (NDEC, FDEC and ZDEC), phenol and α-cumyl alcohol are immobilised by silica gel and accordingly they remain near the starting point. On the other hand, α-methyl styrene and tetraethyl thiuram disulphide are very mobile on silica gel and they appeared slightly behind the solvent front. The position of acetophenone is intermediate between the two extremes.

The analysis of intermediates and products for the reaction between CHP (1×10^{-1} M) and NDEC, FDEC and ZDEC (2×10^{-3}M) in chlorobenzene at 110°C and under an inert atmosphere is shown in Figure 5.39(a and b). At the beginning of the reaction of CHP and NDEC (or FDEC), the formation of the disulphide is indicated by a TLC spot in addition to the acetophenone spot. The spot of the disulphide

(Rf values = 0·94) appeared slightly above that of the α-methyl styrene (Rf value =0·92) and disappeared on longer reaction time. However, the reaction between CHP (1 x 10^{-1} M) and ZDEC did not give such an intermediate (TETD) and this confirms the results described earlier in Section 5.2.3 that the disulphide is the intermediate of the CHP/NDEC (or FDEC) reaction and not from the CHP/ZDEC reaction. At the completion of the reaction of metal dithiocarbamates and CHP, α-methyl styrene and acetophenone were found to co-exist in addition to an unresolved spot presumed to be of phenol, α-cumyl alcohol or metal complex (NDEC, FDEC or ZDEC).

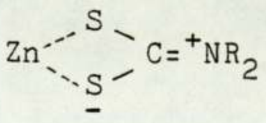
The analysis of products from the reaction between CHP (1 x 10^{-1} M) and the disulphide (TETD; 2 x 10^{-3} M) in chlorobenzene at 110°C and under nitrogen atmosphere is also followed by TLC (Figure 5.39 (c)). Similar to the metal dithiocarbamate reaction (at high molar ratio), α-methyl styrene is the major product as indicated by its intense spot together with a small (faint spot) amount of acetophenone. The spot remaining at the starting point could be of phenol.

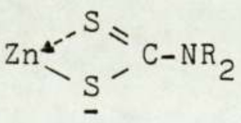
5.3 Discussion

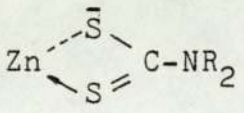
5.3.1 Metal Complexes of Dithiocarbamic Acid as Chain-breaking Antioxidants

It is now generally accepted$^{(68,163)}$ that the liquid phase auto-oxidation of a hydrocarbon involves a free-radical chain mechanism in which the predominant chain-carrying species in solution is the peroxy radical(125) (see Scheme 5 in Chapter 1). Thermal energy or metal ions promote decomposition of the hydroperoxide initially produced resulting in auto-catalysis (see curves FAcAc and cumene in Figure 5.1). As a consequence of this mechanism, two types of antioxidants have been recognised(125) (see Chapter 1, Sec.1.4), chain-breaking antioxidants which suppress propagation by removal of alkyl and alkyl peroxy radicals and peroxide-decomposers which remove hydroperoxides by non-radical decomposition.

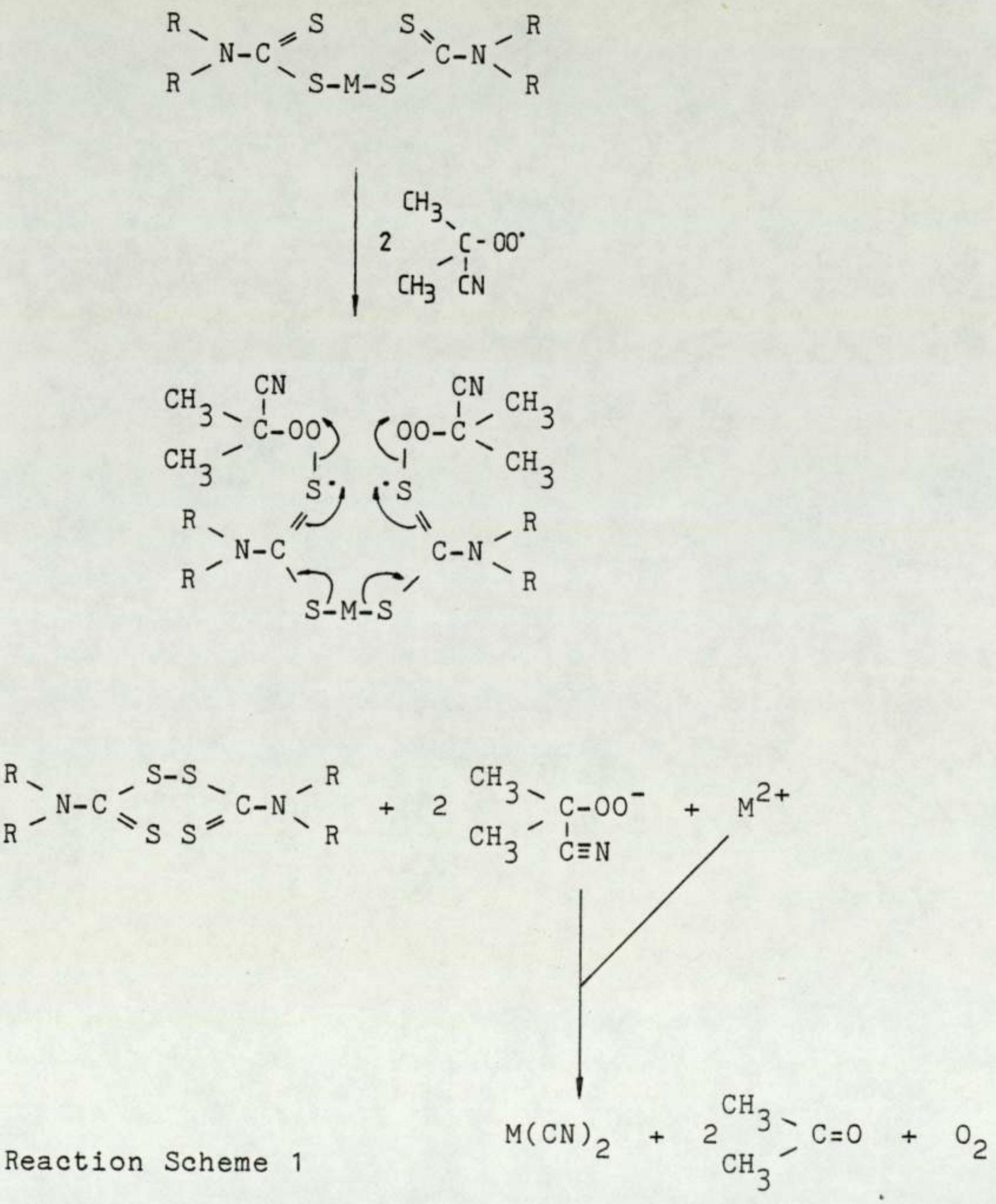
The ability of metal complexes of dithiocarbamic acid (ZDEC, NDEC and FDMC) in breaking-out the free-radical chain oxidation of cumene is clearly demonstrated in Figures 5.1 and 5.2. The action of these metal complexes (ZDEC, NDEC and FDMC) in interrupting the oxidation chain, therefore, resembles the action of hindered phenols and amines antioxidants. The latter perform their chain-breaking antioxidant actions through a hydrogen transfer to the peroxy radicals(63b). With the metal dithiocarbamate complexes (ZDEC, NDEC and FDMC), this hydrogen transfer is unlikely since there is no suitably activated hydrogen atom available. The structure of metal dithiocarbamate e.g., ZDEC, is represented by a hybrid of the following canonical forms(165).







With all these structures, the peroxy-radical can be converted into a peroxy-anion(166-168) by the abstraction of an electron from the electron-rich sulphur atom. Results shown in Figure 5.2 together with the isolation of disulphide and metal cyanide (see Section 5.2.1) from the reaction of these metal complexes (ZDEC, NDEC and FDMC) with ABIN in an oxygen atmosphere, lend strong support to propose a similar mechanism (see Scheme 1) to that previously proposed by Burn(169) in the case of metal dialkyldithiophosphates.



Reaction Scheme 1

The function of the metal in the above reaction scheme is to provide an easy route for heterolysis of the proposed radical intermediate. The absence of this route in the case of the disulphide (TETD) being the reason for its inactivity although it is a dithiolate (see Figure 5.2). Russian workers(170) found that the inhibiting activity of a series of divalent metal complexes of dithiocarbamic acid depends on the nature of the metal. The more easily the complex is oxidized, the more effectively it inhibits the oxidation of the hydrocarbon(170). This probably explains why NDEC is more effective as a free radical trap than ZDEC (see Figure 5.2). However, the same workers(171) found that this correlation is not held for the trivalent metal complexes of dithiocarbamic acid. They attributed this to the steric factors which exist on the addition of the alkyl peroxy radical to the octahedral structure of these trivalent complexes e.g., FDMC.

Unlike the metal-containing complexes (ZDEC, NDEC and FDMC), TETD is a weak inhibitor and causes only a small decrease in the rate of the oxidation of cumene (see Figure 5.2). The inhibitory action of the disulphide (TETD) may be due to the following reactions, which result in chain termination.

$$ROO^{\cdot} + R'S\text{-}SR' \longrightarrow RO_2\text{-}SR' + R'S^{\cdot} \qquad \text{Eq. 5.1}$$

$$R'S^{\cdot} + ROO^{\cdot} \longrightarrow RO_2\text{-}SR' \qquad \text{Eq. 5.2}$$

A similar mechanism for the inhibition by TMTD was proposed(172,173) for the polymerization of styrene and methyl methacrylate at 30-80°C.

5.3.2 Thermal Decomposition of Hydroperoxide in the Presence of Metal Complexes of Dithiocarbamic Acid and Their Oxidation Products

It has been found that the interaction of metal complexes of dithiocarbamic acid with hydroperoxide e.g., CHP, may take place according to two mechanisms (see Section 5.2.8.1). The first, which involves a radical mechanism, assumes a great significance at low molar ratios of peroxide to metal complex. The second mechanism, which favours a high molar ratio of peroxide to metal complex, takes place through an ionic intermediate.

The free radical mechanism by which tetra alkyl thiuram disulphide, acetophenone and α-cumyl alcohol products are formed, accounts for the initial rapid catalytic stage in the decomposition of CHP with FDMC or NDEC in chlorobenzene at 110°C under a nitrogen atmosphere (see Figures 5.9-5.11). The ionic mechanism accounts for the second slower catalytic stage observed in the CHP decomposition curve by these metal complexes NDEC and FDMC (see Figures 5.9-5.11) which leads to phenol and acetone products. The relative contribution of each mechanism not only depends on the molar ratio of CHP to metal complex but also to the total molar concentration(174) of each of the metal complexes and the hydroperoxide, even though they may co-exist in the same relative molar ratio.

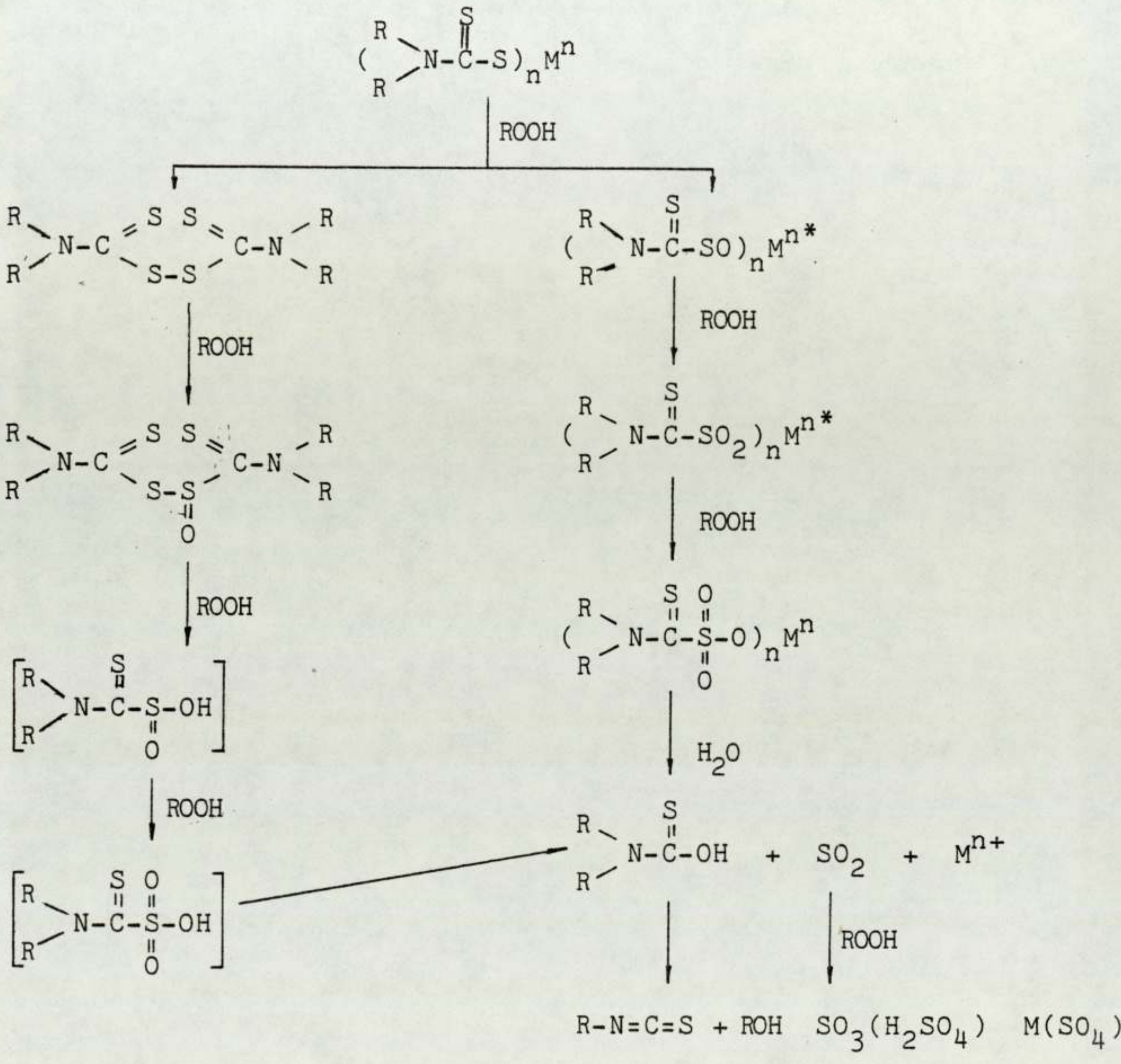
The presence of an induction period in the decomposition curve of CHP with metal complexes (NDEC and FDMC) (see Figures 5.9-5.11), indicates that the ionic catalysts which are responsible for the second catalytic stage start to form and build up as a consequence of the initial rapid catalytic stage. Also, at the end of this induction period it was found that a precipitate was formed which may be attributed to metal sulphate. The formation of the sulphate salt during and after the induction period indicates the formation of sulphur acid in the system.

Different metal dithiocarbamates are found to decompose CHP in different ways. While the NDEC and FDMC behave similarly and decompose hydroperoxide in three distinct stages (see Figures 5.9-5.11), ZDEC is found to decompose CHP in a two-stage process. Moreover, the position and the length of the induction period is found to be different (see Figures 5.9 and 5.13). In the case of ZDEC/CHP system, the induction period appears at the beginning and increases with ZDEC concentration, while in the case of FDMC or NDEC/CHP system, it appears as a secondary induction period and increases with decreasing the metal complex concentration.

The difference in the mode of decomposition of CHP in the presence of metal complexes of dithiocarbamic acid (FDMC, NDEC and ZDEC) seems to be a reflection in difference in their mechanistic actions. The reason may be the metal ion since it has been found(170) that NDEC undergoes oxidation much easier than the ZDEC. This difference in oxidation could be due to the completely filled 3d-electron cloud of the zinc ion and this probably accounts for the failure of detecting the disulphide (TETD) among the reaction products of the ZDEC/CHP system.

It appears from the above discussion that metal dithiocarbamates can react with peroxide either through their conversions to the corresponding disulphides first and then to the sulphur acids, or through their further oxidation products which form the sulphur acids (see Reaction Scheme 2). The ease of the metal complex to follow either of these pathways depends on the oxidizability of the central metal ion. Thus it is most probable that ZDEC exerts its antioxidant action through its conversion to oxidation products (see Figures 5.30-5.37 and Section 5.2.8.1) while both NDEC and FDMC are oxidised first to their disulphides. Evidence supporting the above mechanisms comes from the identification of the disulphide in the case of NDEC and FDMC/CHP system and failure to detect it in the case of ZDEC. Other workers(138) also detected the disulphide intermediate in the reaction of FDBC and TBH. Moreover, in the case of

ZDMC/TBH reaction, the oxygenated oxidation products of ZDMC were identified from the reaction of ZDMC and TBH (see Figures 5.30-5.37 and Section 5.2.8.2).



Reaction Scheme 2

(* isolated products from ZDMC/TBH reaction)

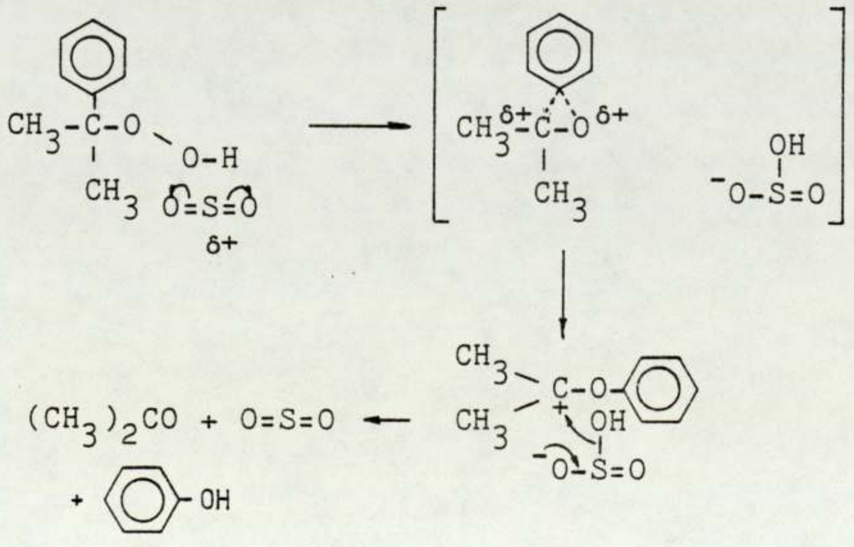
Metal complexes of dithiocarbamic acid are not themselves responsible for the catalytic decomposition of CHP but rather their oxidation products. This statement is clearly justified from the addition of a base ($CaCO_3$) to the reaction mixture of CHP and the metal complex (see Figure 5.17). The addition of $CaCO_3$ slows down the decomposition and when a high concentration of the base is added, the CHP decomposition is almost totally suppressed. Similarly the antioxidant action of these metal complexes (ZDEC, NDEC and FDMC) in cumene initiated by CHP is completely lost on addition of pyridine base (see Figure 5.18).

It appears very clear then that the acidic species are responsible for the antioxidant action of these metal complexes. Addition of the molecular sieve (5A) to the cumene system initiated by CHP and in the presence of dithiocarbamate complexes (NDEC, ZDEC and FDMC) removes substantially the antioxidant action of these complexes (see Figure 5.20) though not completely. This indicates that the gaseous products e.g., SO_2 and SO_3, are not the only species inhibiting the oxidation. Several workers(155) assume that sulphenic and sulphonic acids are also capable of decomposing the hydroperoxides. Such compounds are very likely to be formed from the decomposition of metal dithiocarbamate complexes.

It is well known(63d,65) that the cumene hydroperoxide undergoes decomposition to phenol and acetone in an ionic medium and α-cumyl alcohol and acetophenone in a free radical environment. Products analysis of CHP can, therefore, serve as a guide to distinguish between the two catalytic processes i.e., ionic and free radical mechanisms, which take place during the decomposition of CHP by sulphur-containing antioxidants. The presence of α-methyl styrene among the reaction products indicates the presence of an acidic catalyst and is, therefore, generally associated with the ionic mechanism in the decomposition of CHP(175).

The importance of the two mechanisms in the antioxidant performance of metal dithiocarbamate complexes is concluded from the study of several decomposition ratios of CHP in the presence of metal dithiocarbamate complexes (ZDEC, NDEC and FDMC) (see Figures 5.22-5.29). These observations show that at molar ratios of CHP:additive<10, the products formed from CHP are almost entirely those expected on the basis of radical mechanism viz acetophenone and α-cumyl alcohol with only traces of α-methyl styrene and phenol. At molar ratios of CHP:MDRC>10, the formation of acetophenone and α-cumyl alcohol are considerably reduced and the ionic decomposition products, phenol and α-methyl styrene become major products. The presence of a constant but low proportion of α-cumyl alcohol and acetophenone products at high molar ratios indicates that the radical process makes a contribution at all ratios. A striking similarity is apparent from a comparison between product distribution from CHP decomposition in the presence of metal complexes of dithiocarbamic acid (ZDEC, NDEC and FDMC) (see Figures 5.22-5.29) with that observed in the presence of SO_2(65).

The similarity between the product distribution formed from CHP in the presence of MDRC and in the presence of SO_2(65) at all molar ratios studied argues strongly in favour of the formation of SO_2 as an oxidation product from MDRC. Scott and his coworkers(81) observed liberation of SO_2 gas in the reaction of hydroperoxide and metal dithiocarbamates. The slow liberation of SO_2(81) or its oxidation product SO_3(65,66) will then catalyze the CHP decomposition. If the concentration of SO_2 (or SO_3) formed from MDRC is almost equal to that of the peroxide present in the system, then a free radical mechanism will predominate. If, however, the concentration of SO_2 (or SO_3) relative to the hydroperoxide is very low, then SO_2 (or SO_3) will decompose peroxides according to the ionic mechanism. Scott(65) explains the activity of SO_2 in decomposing CHP ionically by the following reaction scheme.



Reaction Scheme 3

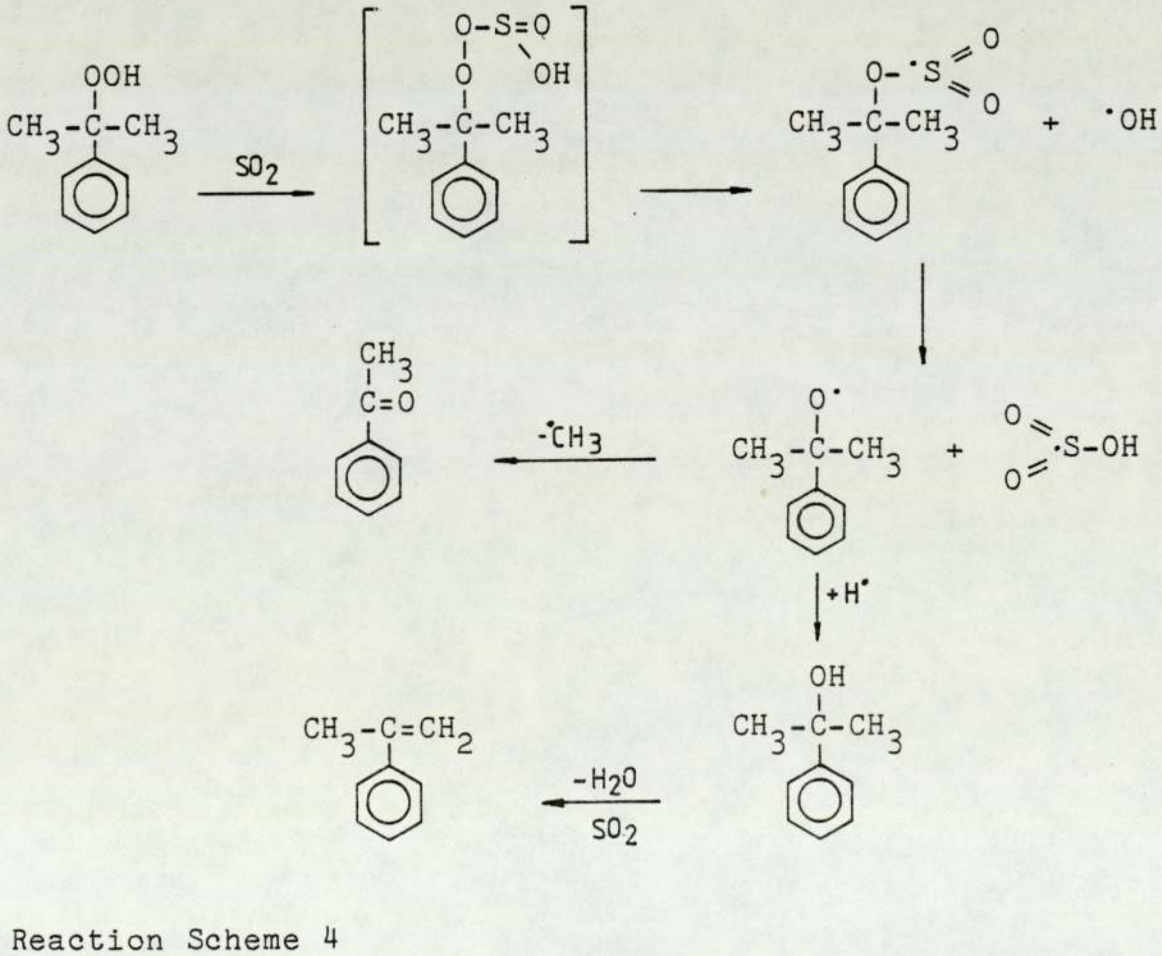
Free radical formation in the reaction of SO_2 and TBH has been demonstrated by the use of electron spin resonance techniques $^{(176)}$ and also free radical acceptors$^{(177)}$. The results were interpreted in terms of the following reactions:

$$RO_2H + SO_2 \longrightarrow RO^{\cdot} + HO\dot{S}O_2 \qquad \text{Eq. 5.3}$$

$$RO_2H + SO_2 \longrightarrow HO^{\cdot} + R\dot{O}SO_2 \qquad \text{Eq. 5.4}$$

$$HO^{\cdot} + SO_2 \longrightarrow HO\dot{S}O_2 \qquad \text{Eq. 5.5}$$

In the decomposition of CHP by SO_2, these free radical reactions would manifest themselves by production of the typical free radical products, acetophenone and α-cumyl alcohol. The following reaction scheme was proposed$^{(65)}$ to account for the radical mechanism:



Reaction Scheme 4

Thus it appears that SO_2 (or SO_3) is responsible for both ionic and free radical mechanisms and this explains the formation of radical products at high molar ratios of CHP: MDRC and also the formation of ionic products at the low molar ratios of CHP:MDRC.

It has been reported recently(137) that the initial stage of the reaction of nickel dibutyldithiophosphate and CHP leads to the formation of the corresponding disulphide which then undergoes further oxidation to sulphur acids which are responsible for the ionic catalytic decomposition of hydroperoxide and the hydration of derived alcohols. The similarity in the mechanism of the antioxidant function of the metal dithiophosphates and metal dithiocarbamates is also reported(63d,81). It is, therefore, highly probable that the disulphide could be an intermediate in the reaction of metal dithiocarbamates and hydroperoxides.

TLC analysis (see Section 5.2.8.3) has indeed shown the presence of such intermediate in the early stage of the reaction of NDEC and FDMC (2×10^{-3} M) with CHP (1×10^{-1} M). The presence of disulphide under this molar ratio could suggest similar product formation during the transformation reactions of NDEC and FDMC complexes in the presence of different molar ratios of CHP. In the reaction of ZDEC and CHP, however, the formation of the disulphide could not be detected.

The formation of the disulphide from the reaction of NDEC and FDMC with hydroperoxides is entirely analogous to the formation of disulphide from the reaction of metal complexes of mercaptobenzthiazole (66) or dithiophosphate (137) and hydroperoxides. The absence of the disulphide in the reaction of ZDEC and hydroperoxide has been explained earlier in this section to be due to the central ion.

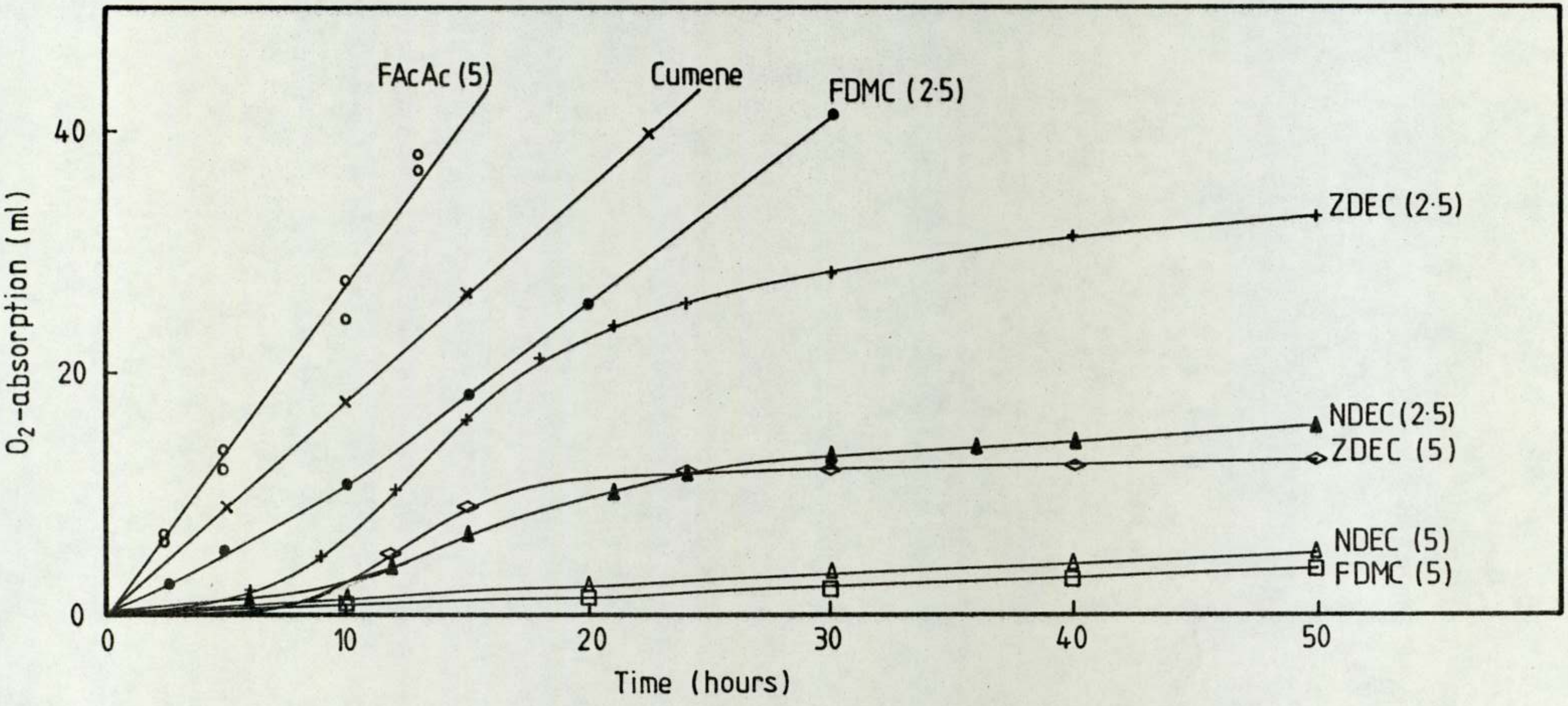


Figure 5:1 Effect of sulphur containing additives on oxidation of cumene at 110°/760 mm Hg
(Numbers on curves are concentrations of additive × 10^{-5} mol/L)

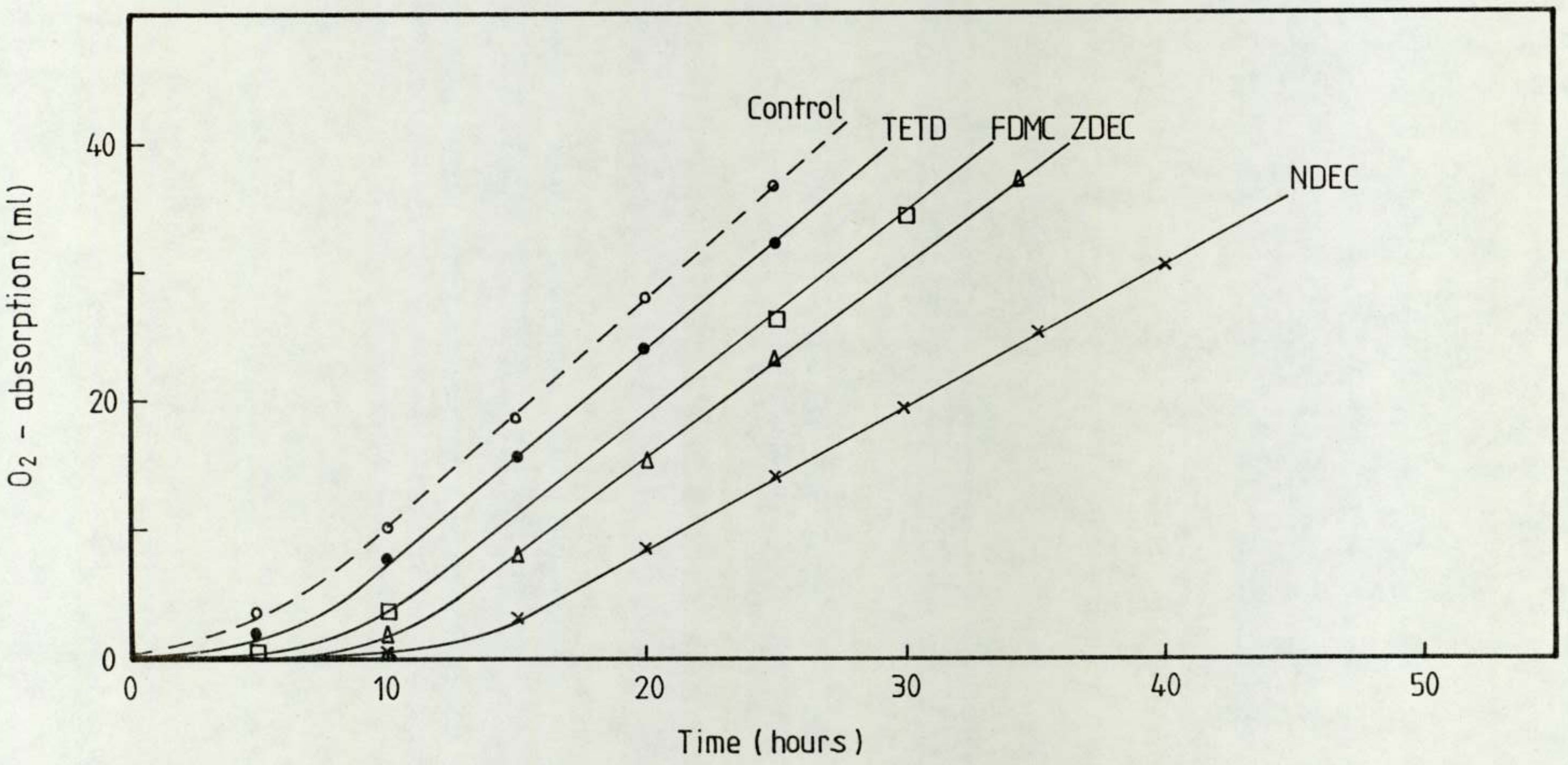


Figure 5:2 Effect of sulphur containing additives of 5×10^{-5} M/L on oxidation of cumene at 50°/760mmHg initiated by ABIN (0·01 M)

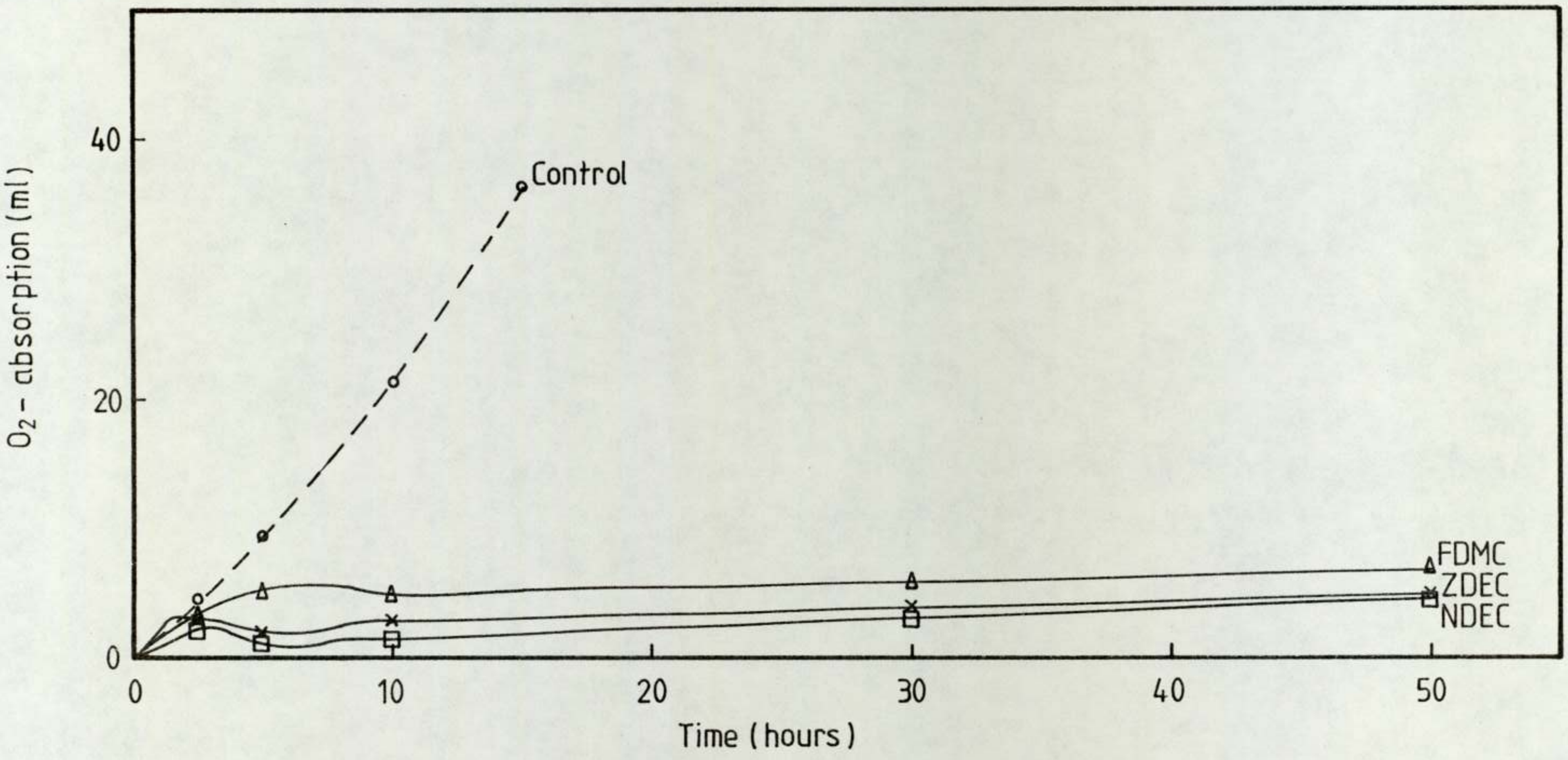


Figure 5:3 Effect of sulphur containing additives (5×10^{-5} M/L) on oxidation of cumene at 110°/760 mmHg in the presence of CHP (0·1 M) as initiator

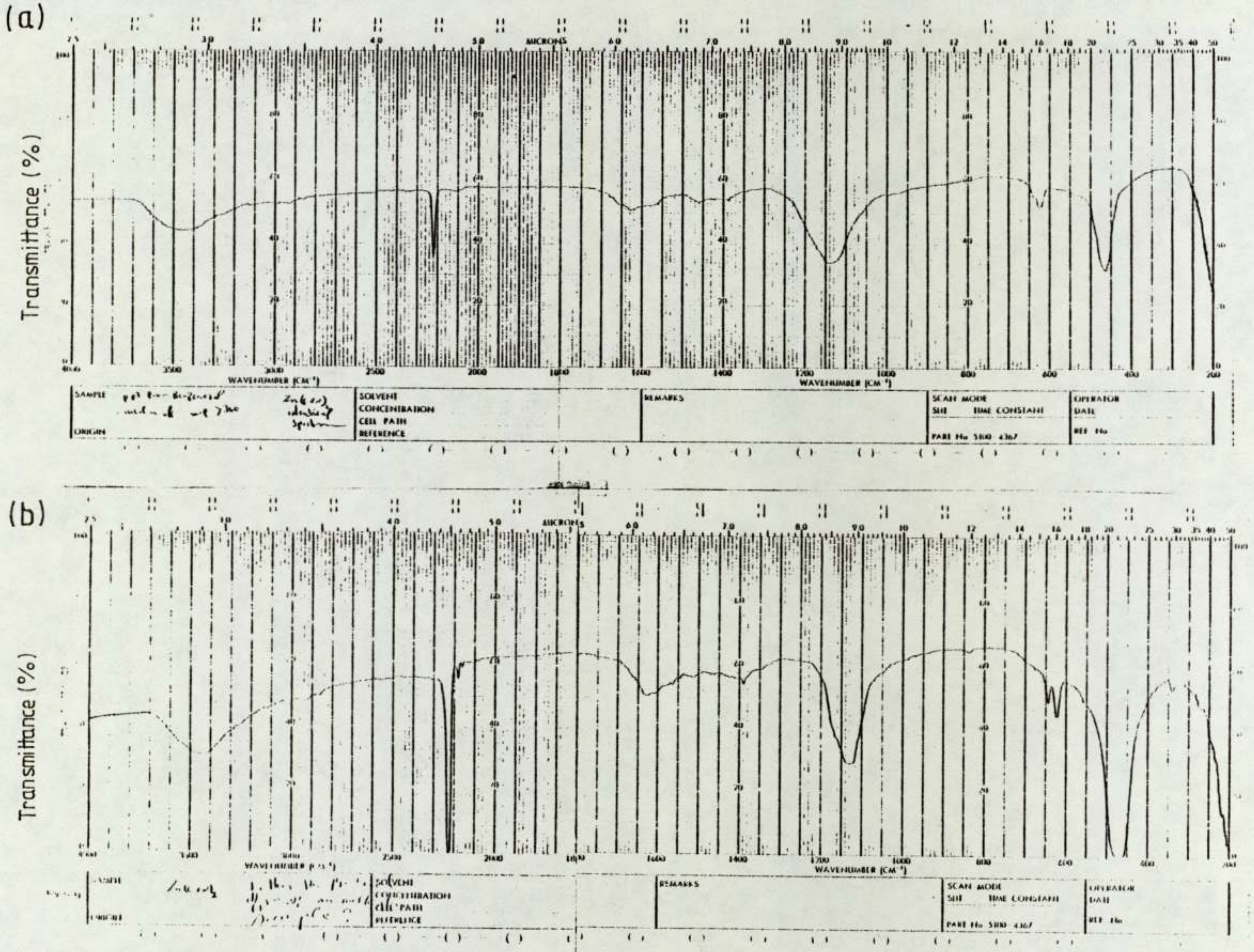


Figure 5.4 Infra-red spectrum of Zinc cyanide (a) isolated from the reaction of Zinc dimethyldithiocarbamate and azobisisobutyronitrile (b) authentic sample

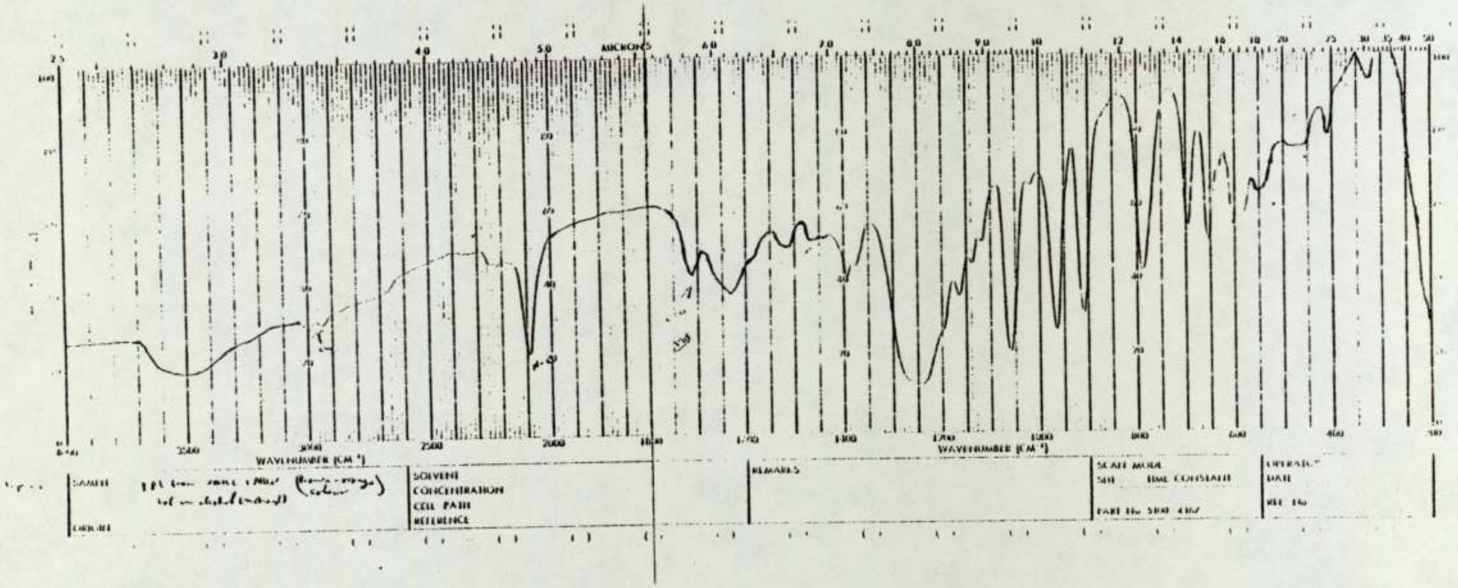


Figure 5.5 Infra-red spectrum of an unknown product isolated from the reaction of ZDMC and ABIN

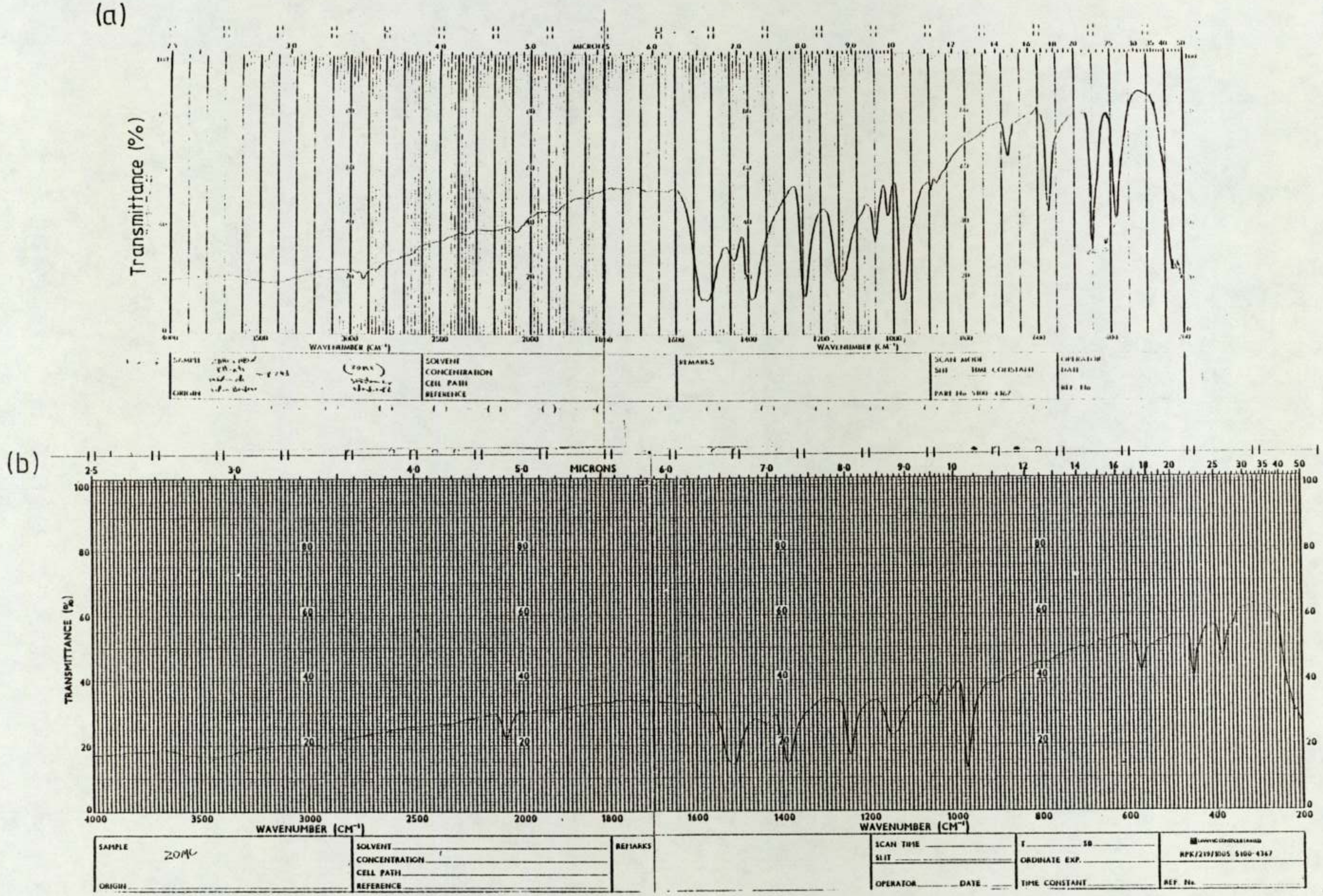


Figure 5.6 Infra-red spectrum of zincdimethyldithiocarbamate (a) isolated from the reaction of ZDMC and ABIN (b) authentic sample

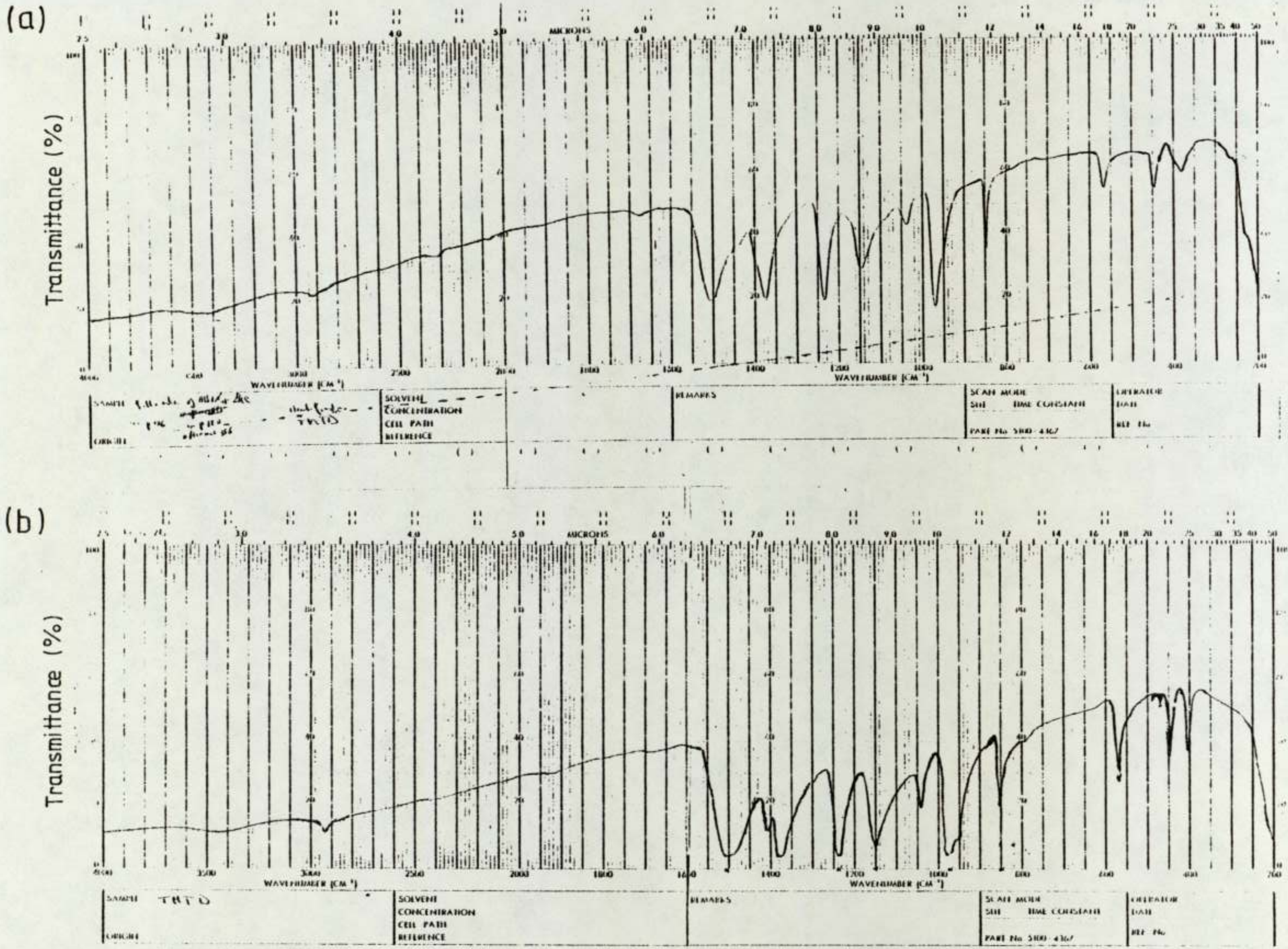


Figure 5.7 Infra-red spectrum of Tetramethylthiuramdisulphide (a) isolated from the reaction of ZDMC andABIN (b) authentic sample

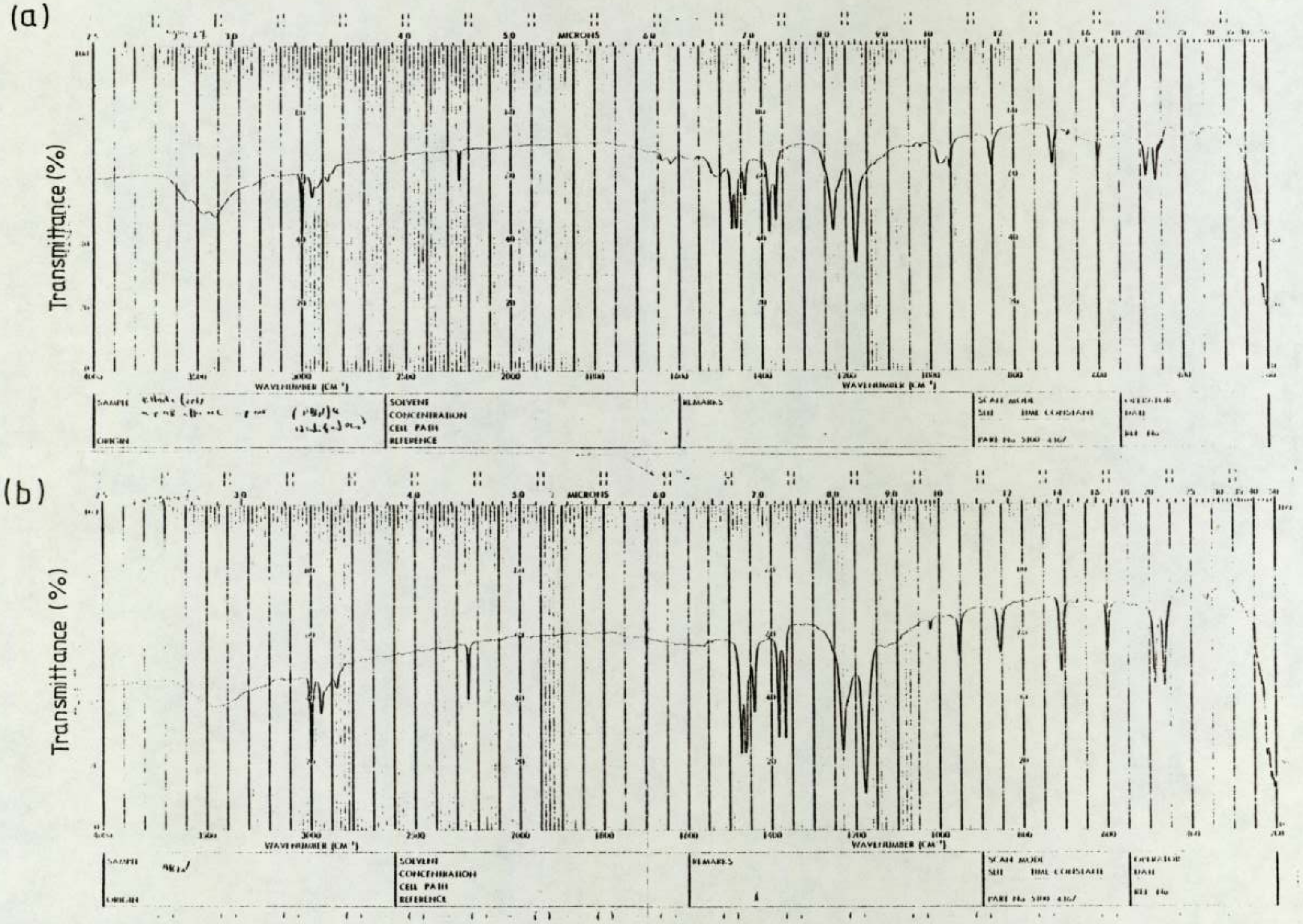


Figure 5.8 Infra-red spectrum of Azobisisobutyronitrile (a) isolated from the reaction of ZDMC and ABIN (b) authentic sample.

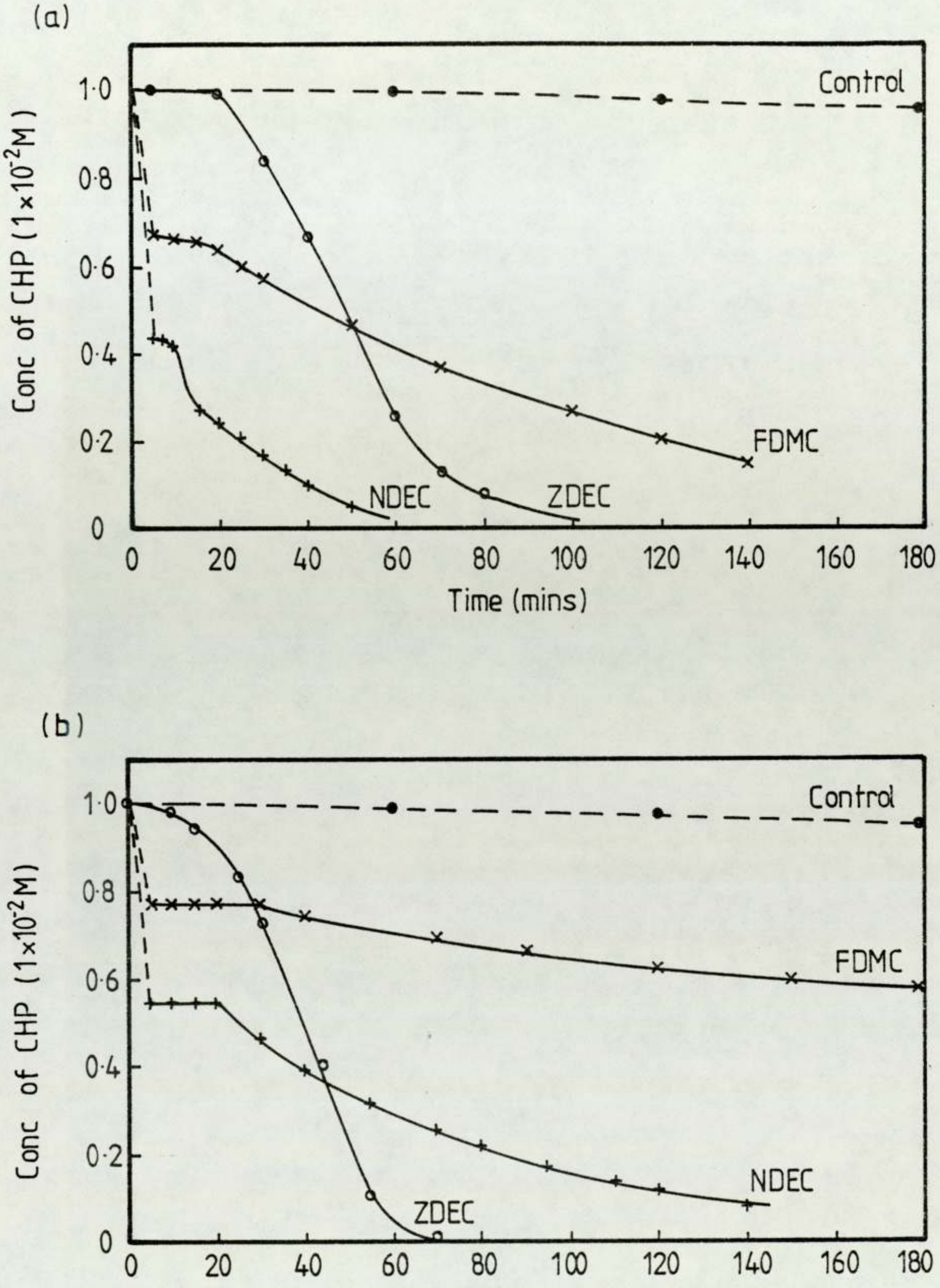


Figure 5:9 Decomposition of CHP (1×10^{-2} M) in chlorobenzene in the presence of Ni, Zn & Fe dithiocarbamates at molar ratios of (a) 30 : 1 (b) 50 : 1

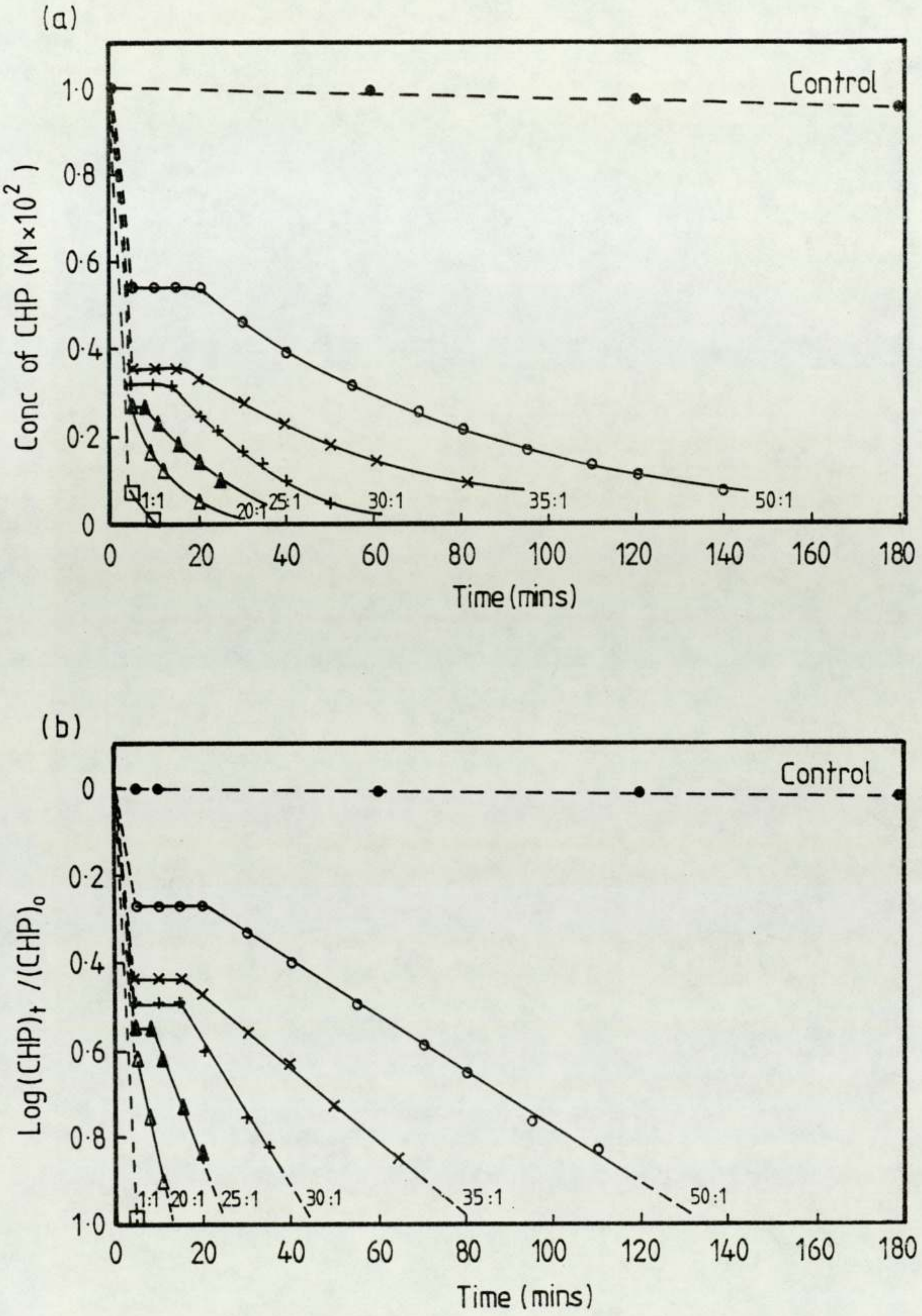


Figure 5:10.a.Decomposition of CHP (1×10^{-2} M) in chlorobenzene in the presence of NDEC at molar ratios shown (at 110° C)
.b.1st order kinetic plots for the third stage of the same reactions.

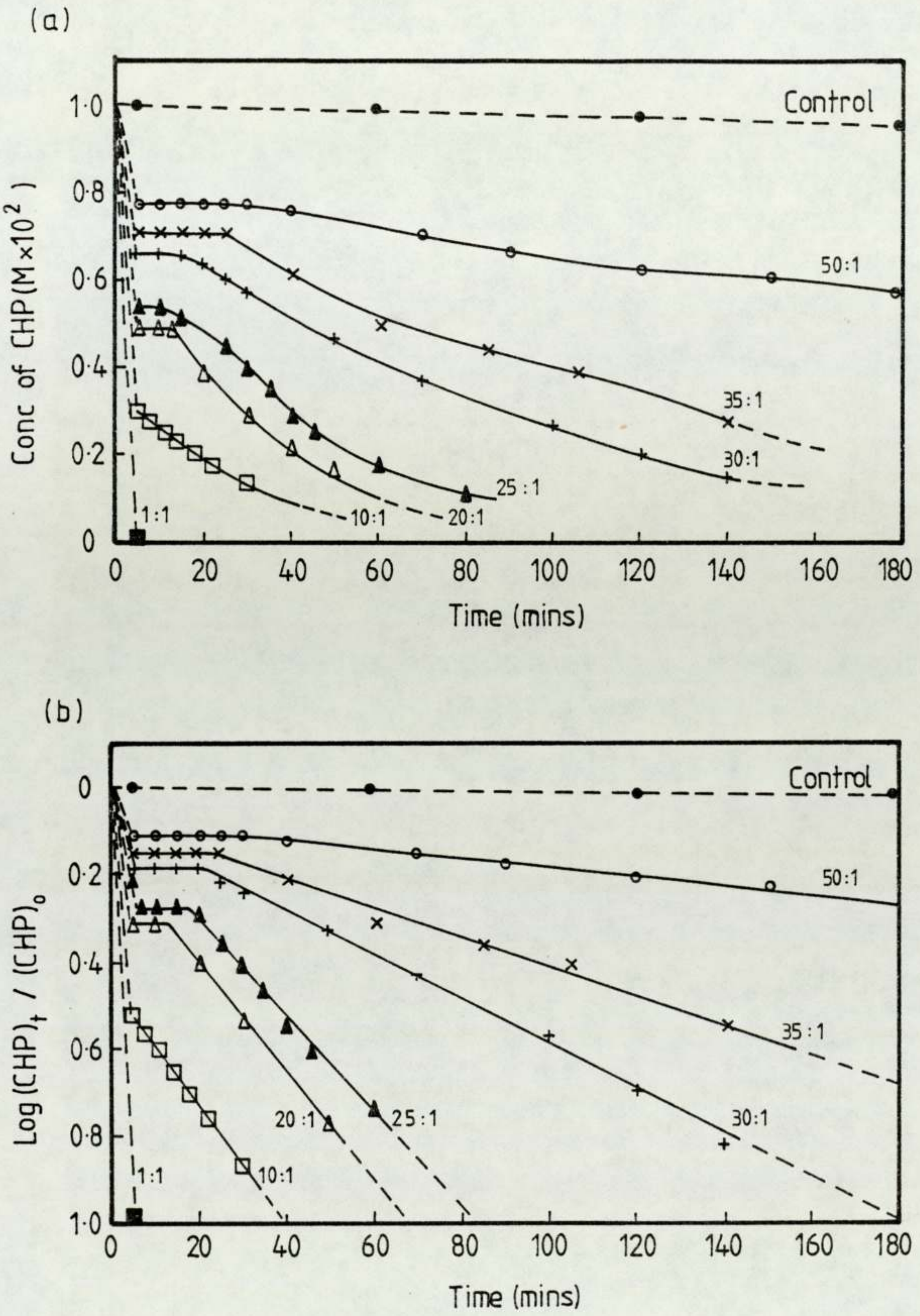


Figure 5:11.a. Decomposition of CHP (1×10^{-2} M) in chlorobenzene at 110°C in the presence of FDMC at molar ratios shown
.b. 1st order kinetic plots for the third stage at the same reactions

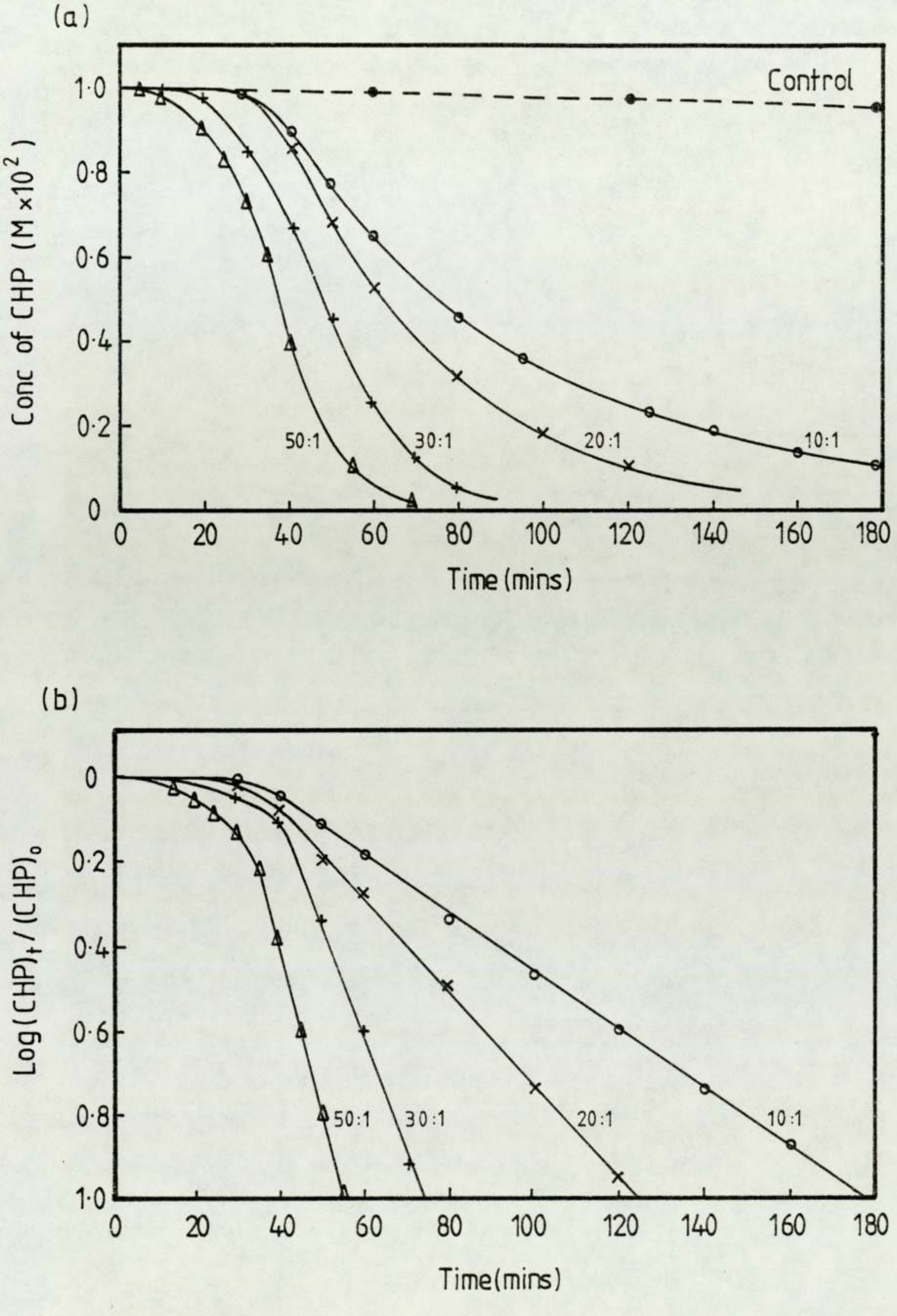


Figure 5:12. a. Decomposition of CHP (1×10^{-2} M) in chlorobenzene at 110° C in the presence of ZDEC at molar ratios shown
b. 1st order kinetic plots for the second stage of the same reactions

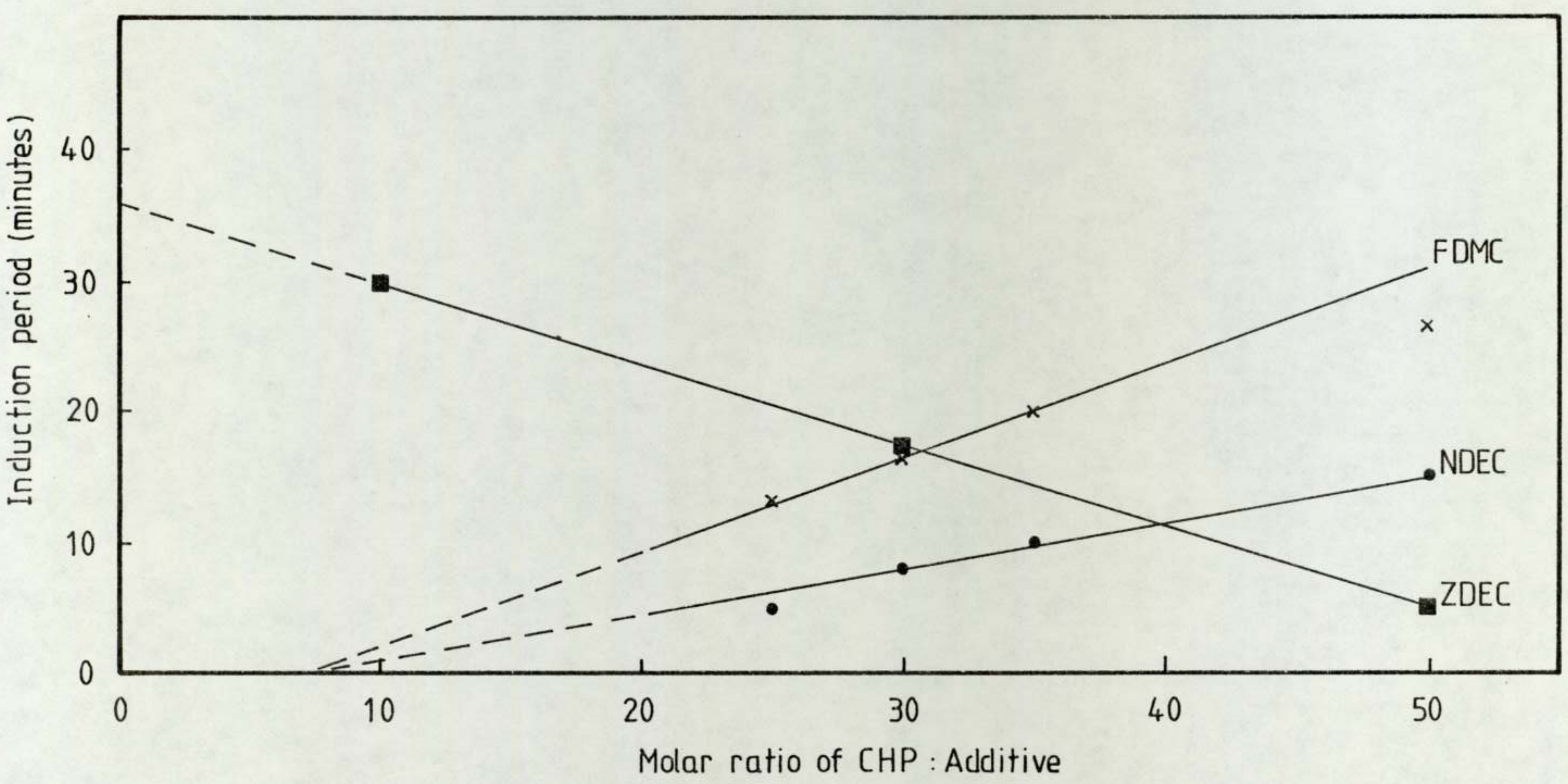


Figure 5:13 The variation of the induction period with the molar ratio of CHP : Additive

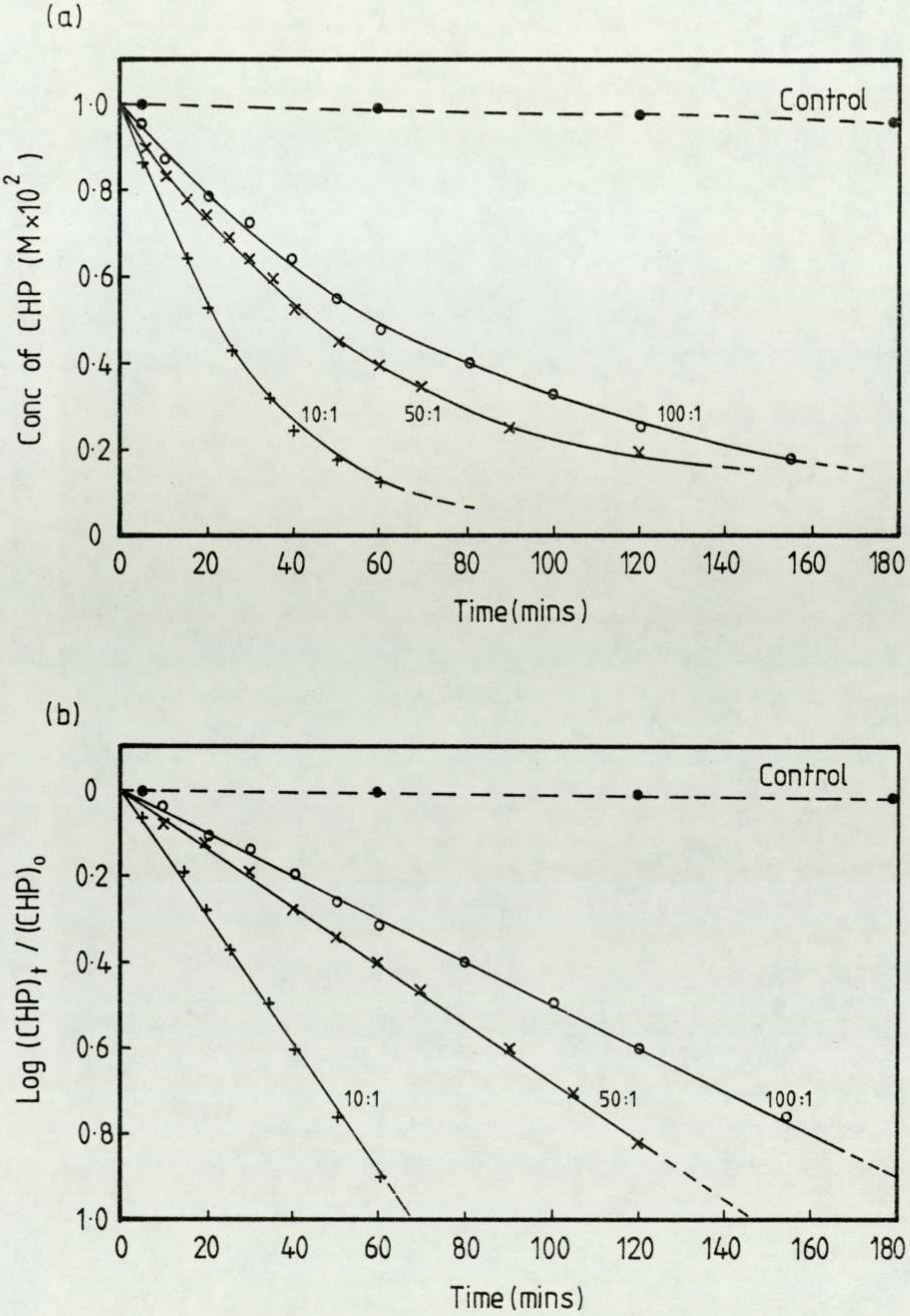


Figure 5:14 .a. Decomposition of CHP ($M \times 10^{-2}$) in chlorobenzene at 110° in the presence of TETD at molar ratios shown
.b. 1st order kinetic plots for the same reactions.

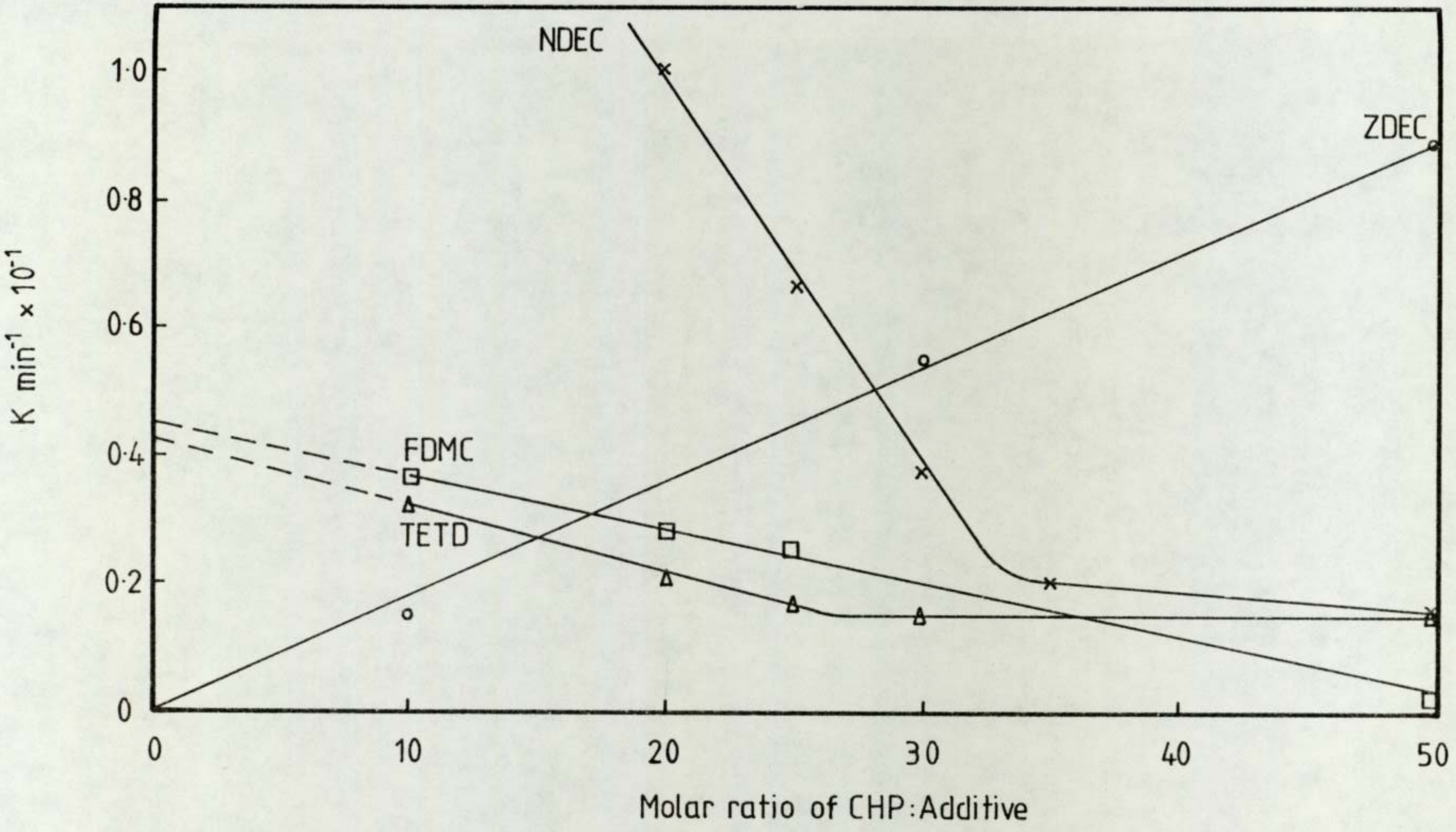


Figure 5:15 The variation of rate constant of the reaction of CHP/additive with molar ratio

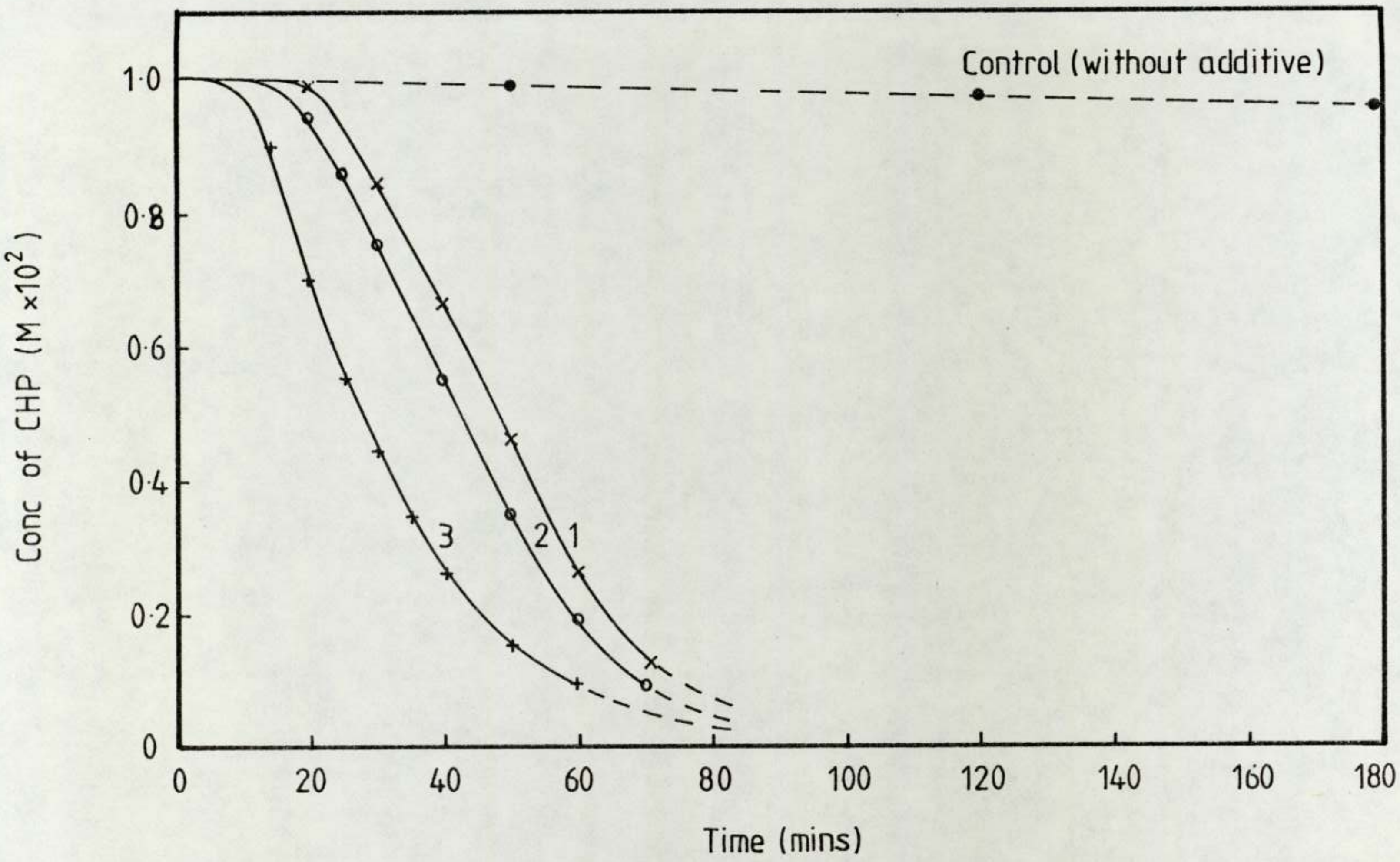


Figure 5:16 Decomposition of CHP (1 × 10^{-2} M) in the presence of additive in chlorobenzene at 110°C at molar ratio CHP:Additive 30:1
(1) ZDMC (2) ZDMCSO (3) $ZDMCSO_2$

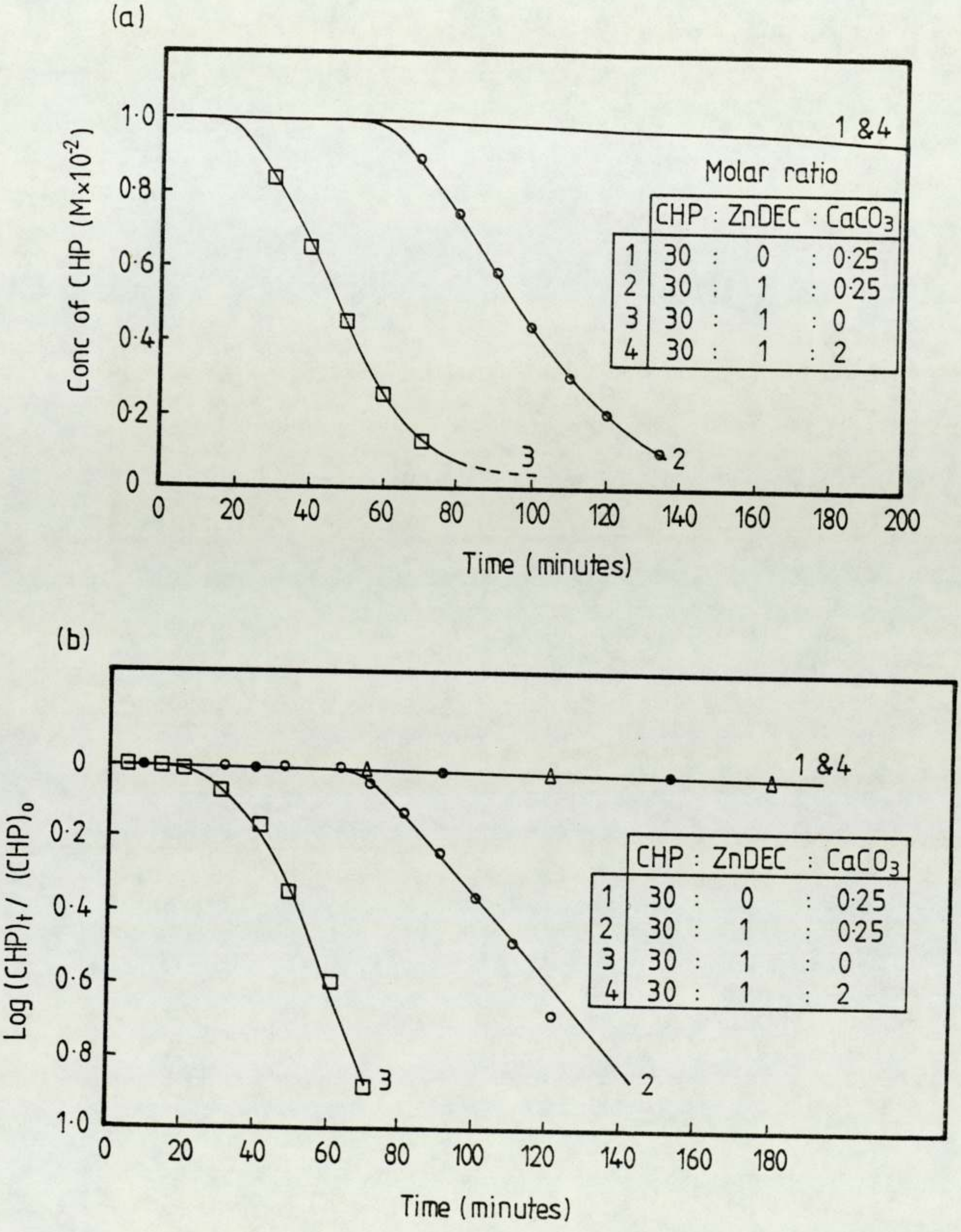


Figure 5:17a Effect of a base ($CaCO_3$) on thermal decomposition of CHP (1×10^{-2}M) at 110°C in chlorobenzene in presence and absence of ZnDEC

b. 1st order kinetic plots for the same reactions

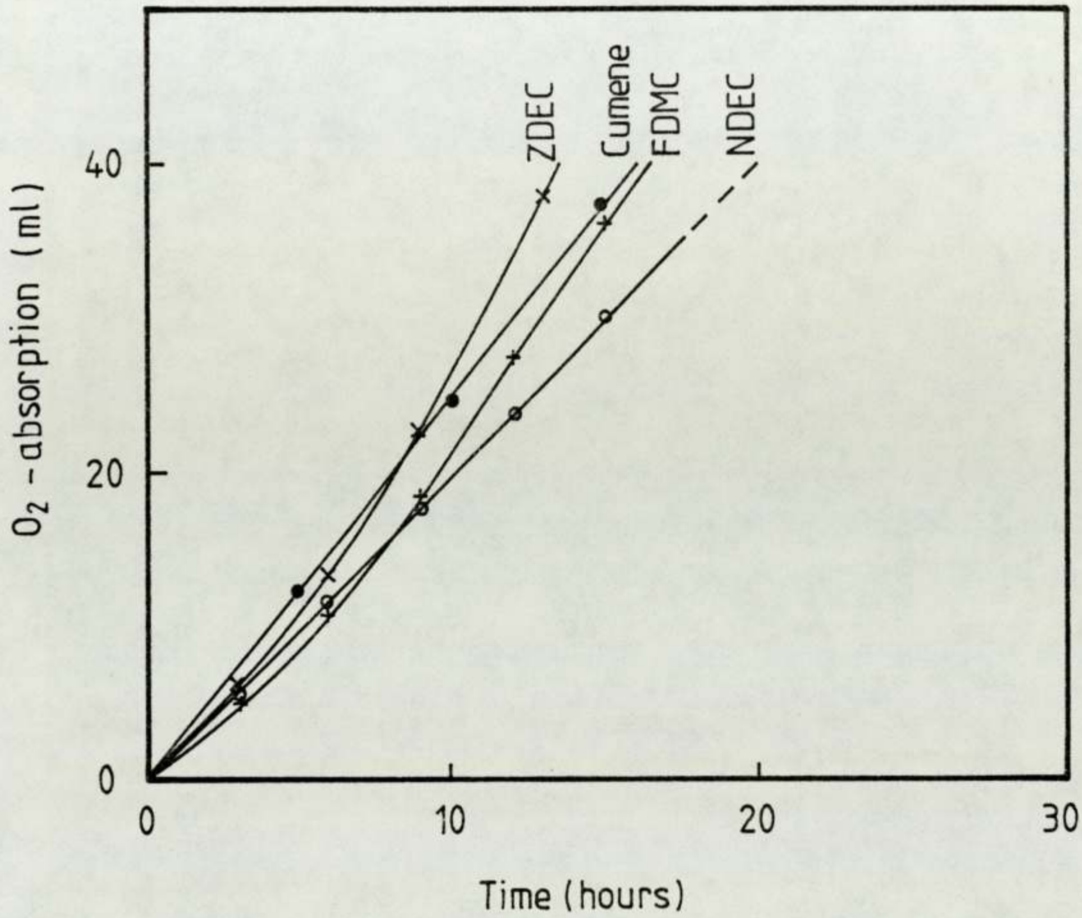


Figure 5 : 18 Effect of pyridine (5×10^{-5}M/L) on the oxidation of cumene at 110° / 760mmHg in the presence of metal dialkyldithiocarbamates (5×10^{-5}M) and CHP (0·1M)

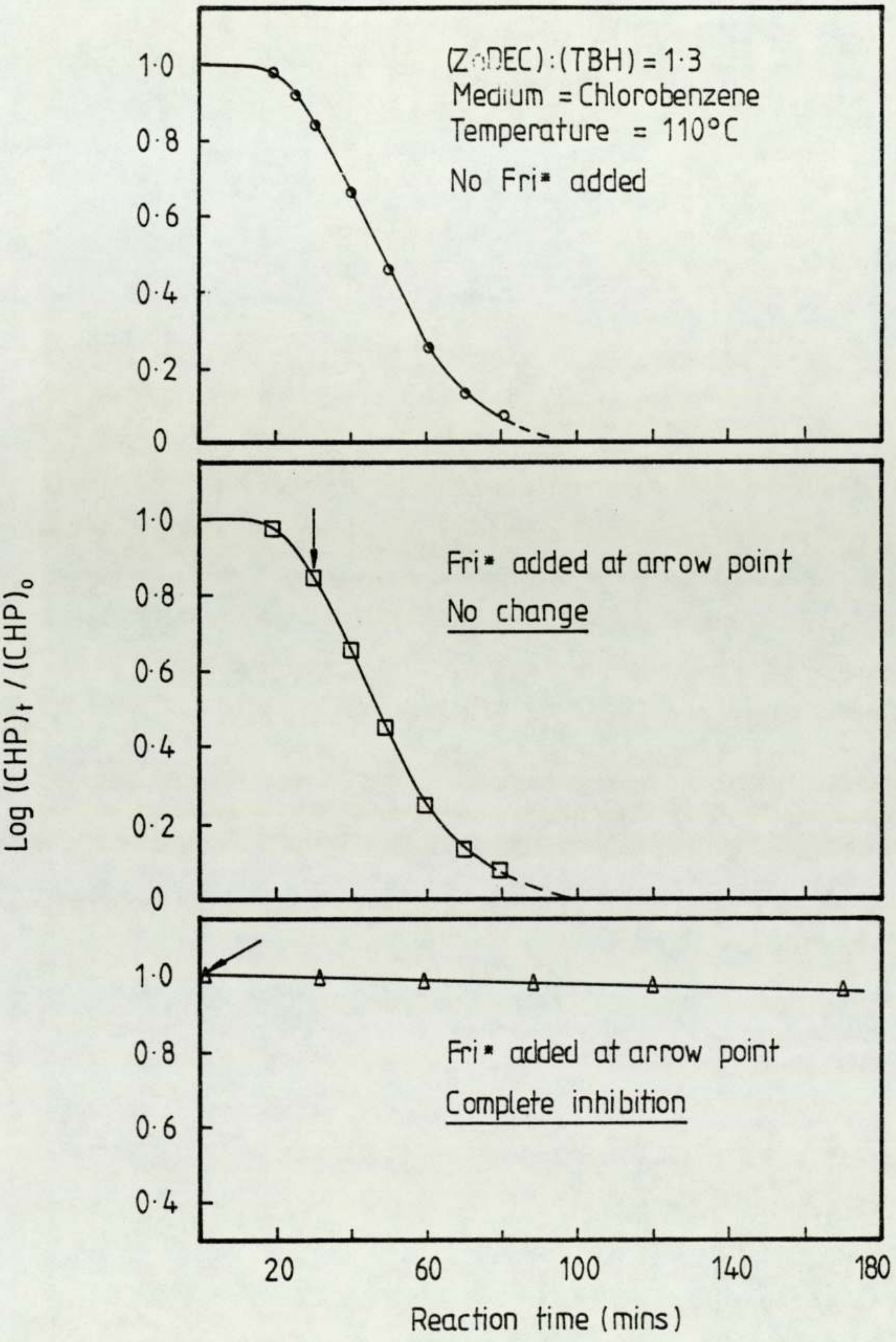


Figure 5:19 Effect of free radical inhibitor, Fri*, (2,6 -d$_i$ tertiary butyl- 4-methylphenol) at different stages during the reaction of TBH with Z DEC.

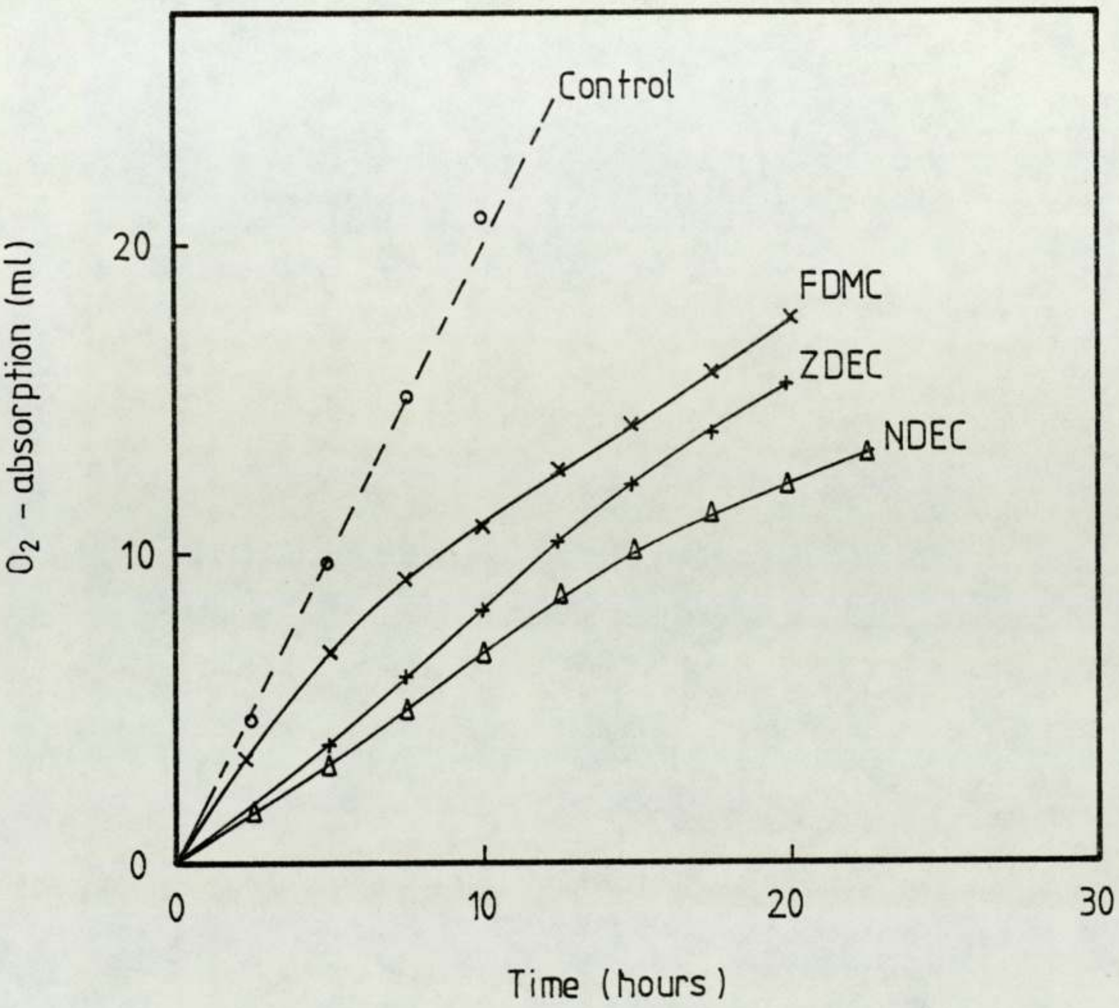


Figure 5:20 Effect of molecular sieve (5A) on the oxidation of cumene at 110°/760 mmHg in the presence of sulphur containing additives (5×10^{-5} M) and CHP (0·1M)

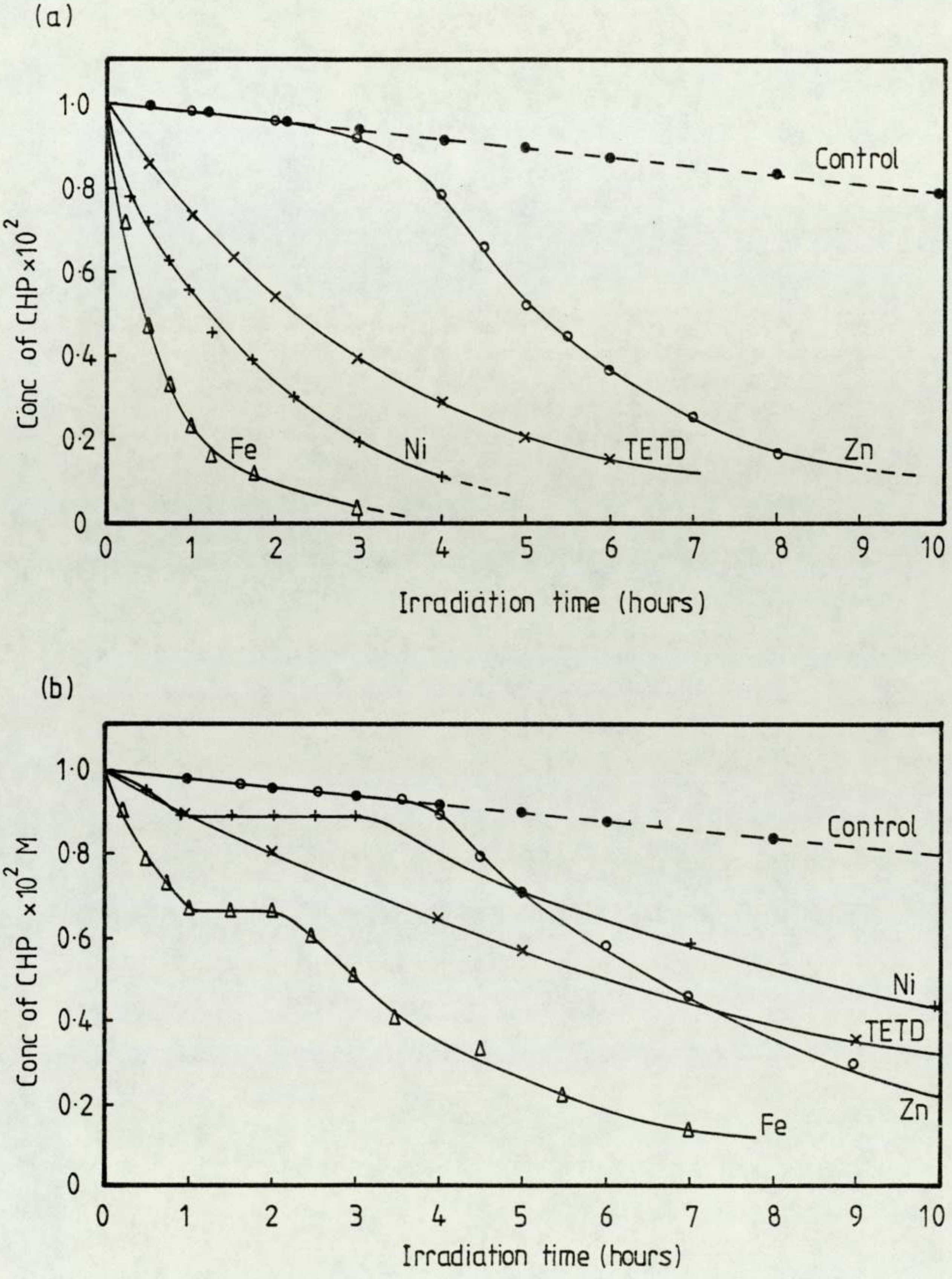


Figure 5:21 Decomposition of CHP (1×10^{-2} M/L) in chlorobenzene at room temperature in the presence of UV light & Fe, Ni, ZDEC & TETD at molar ratios (a) 10 : 1 (b) 30 : 1

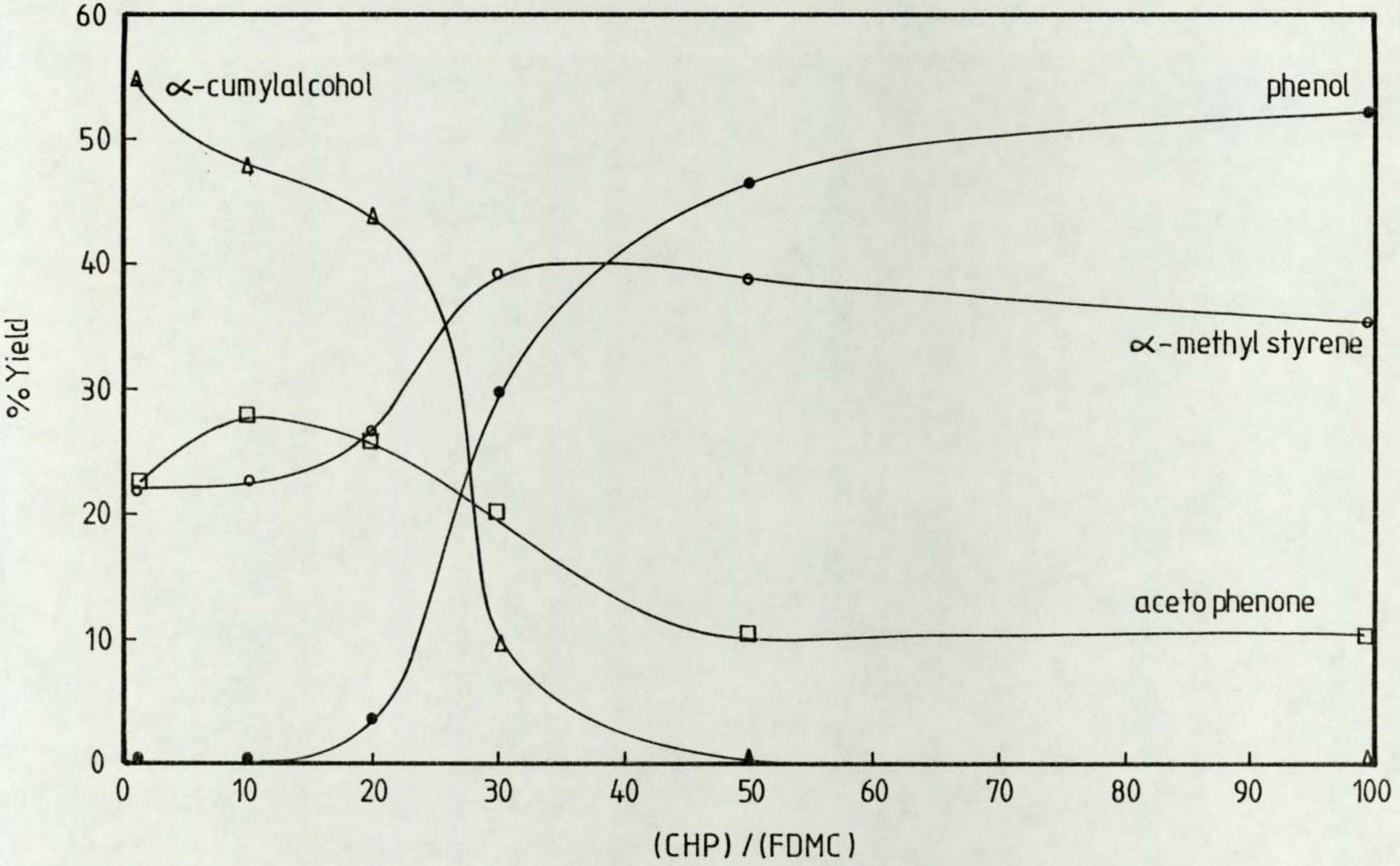


Figure 5:22 Product yields after complete reactions of FDMC with CHP at 110° in chlorobenzene at various molar ratios (CHP)/(FDMC).

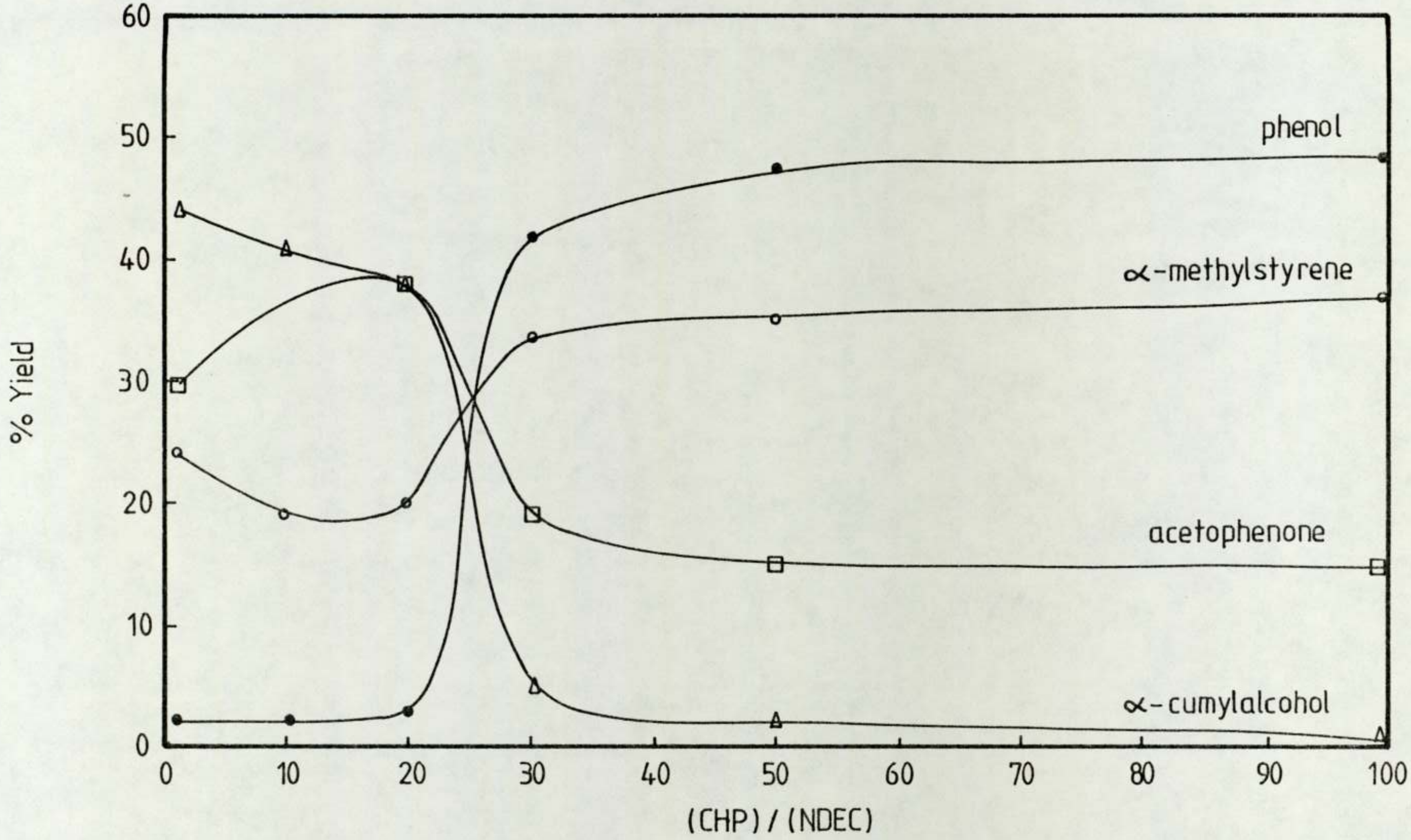


Figure 5:23 Product yields after complete reactions of NDEC with CHP at 110°C in chlorobenzene at various molar ratios (CHP) / (NDEC)

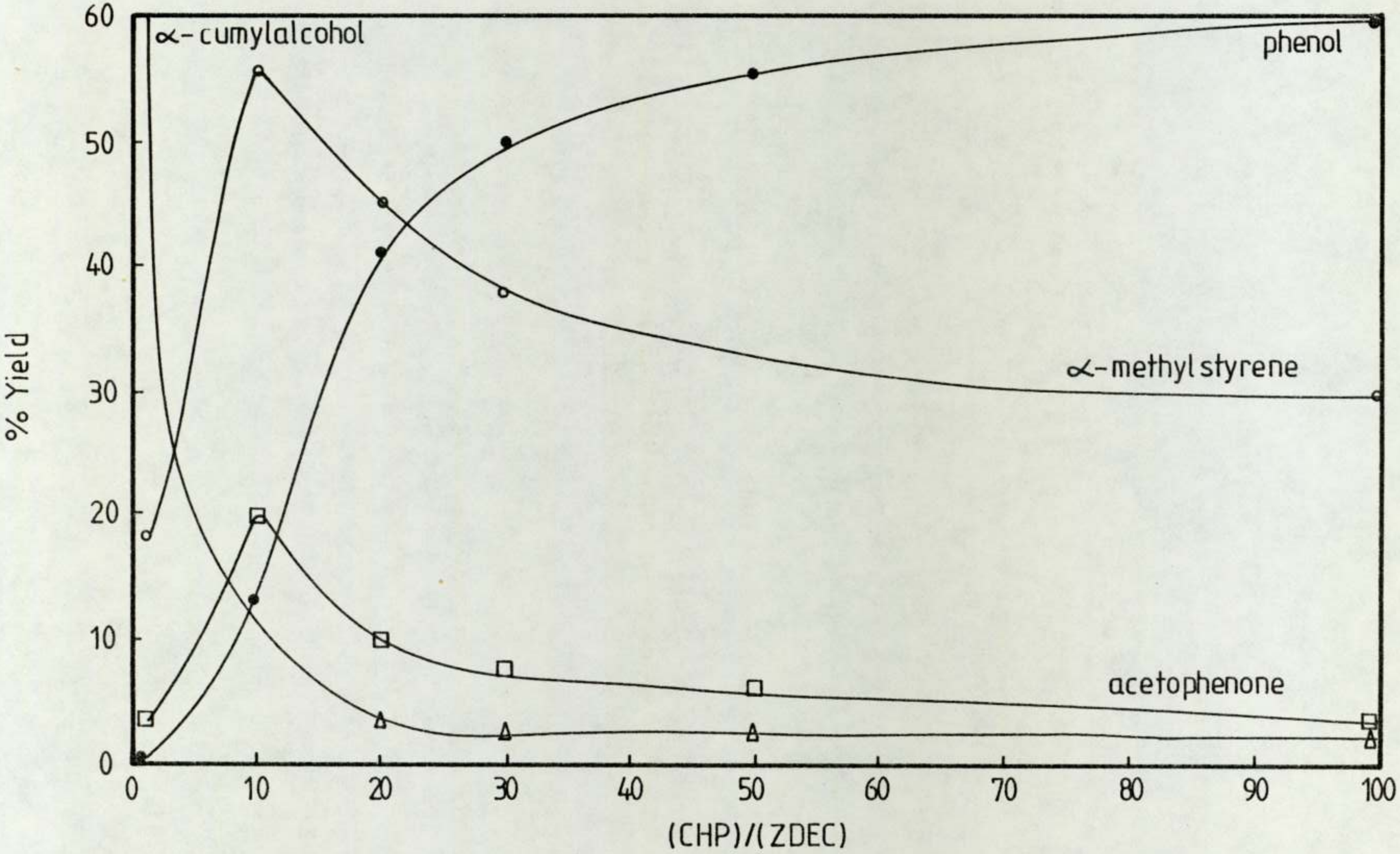


Figure 5:24 Product distribution from reactions of ZDEC and CHP in chlorobenzene at various molar ratios (CHP)/(ZDEC)

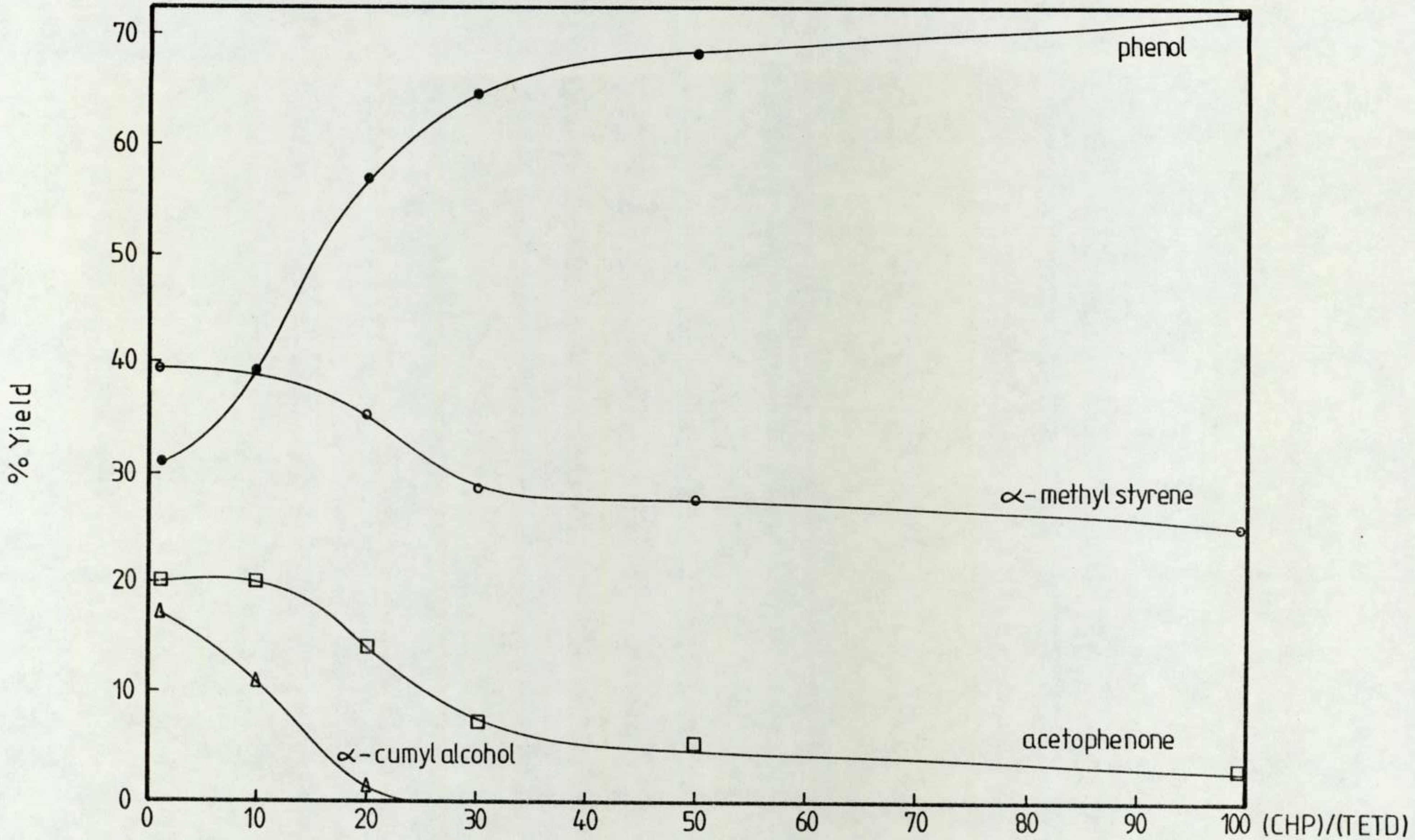


Figure 5:25 Product distribution from reactions of TETD and CHP in chlorobenzene at various molar ratios (CHP)/(TETD)

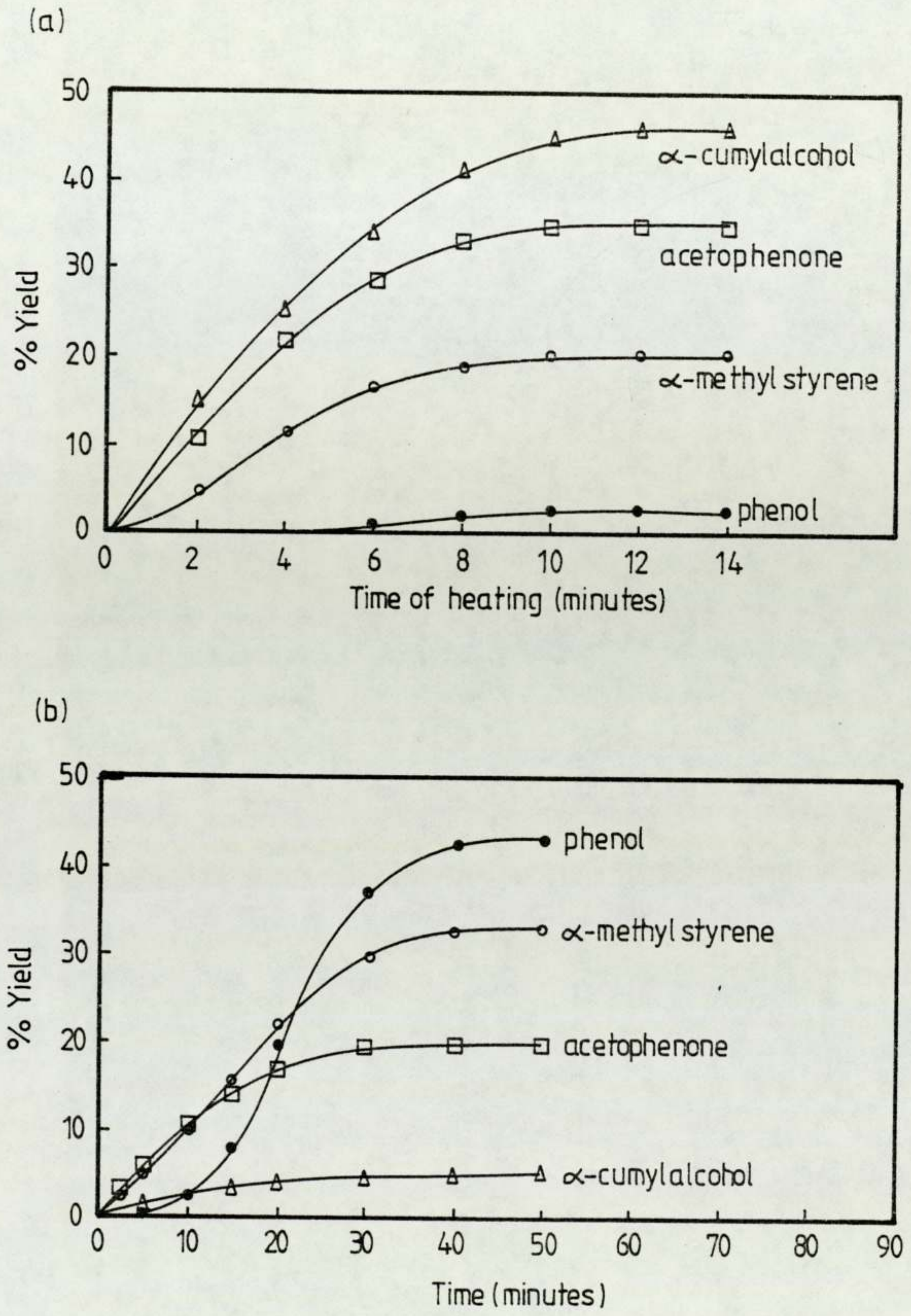


Figure 5:26 Kinetics of the products formed from CHP/NDECD in chlorobenzene at 110°C at molar ratios (a) 10:1 (b) 30:1 (Concentration of CHP 1×10^{-2} M)

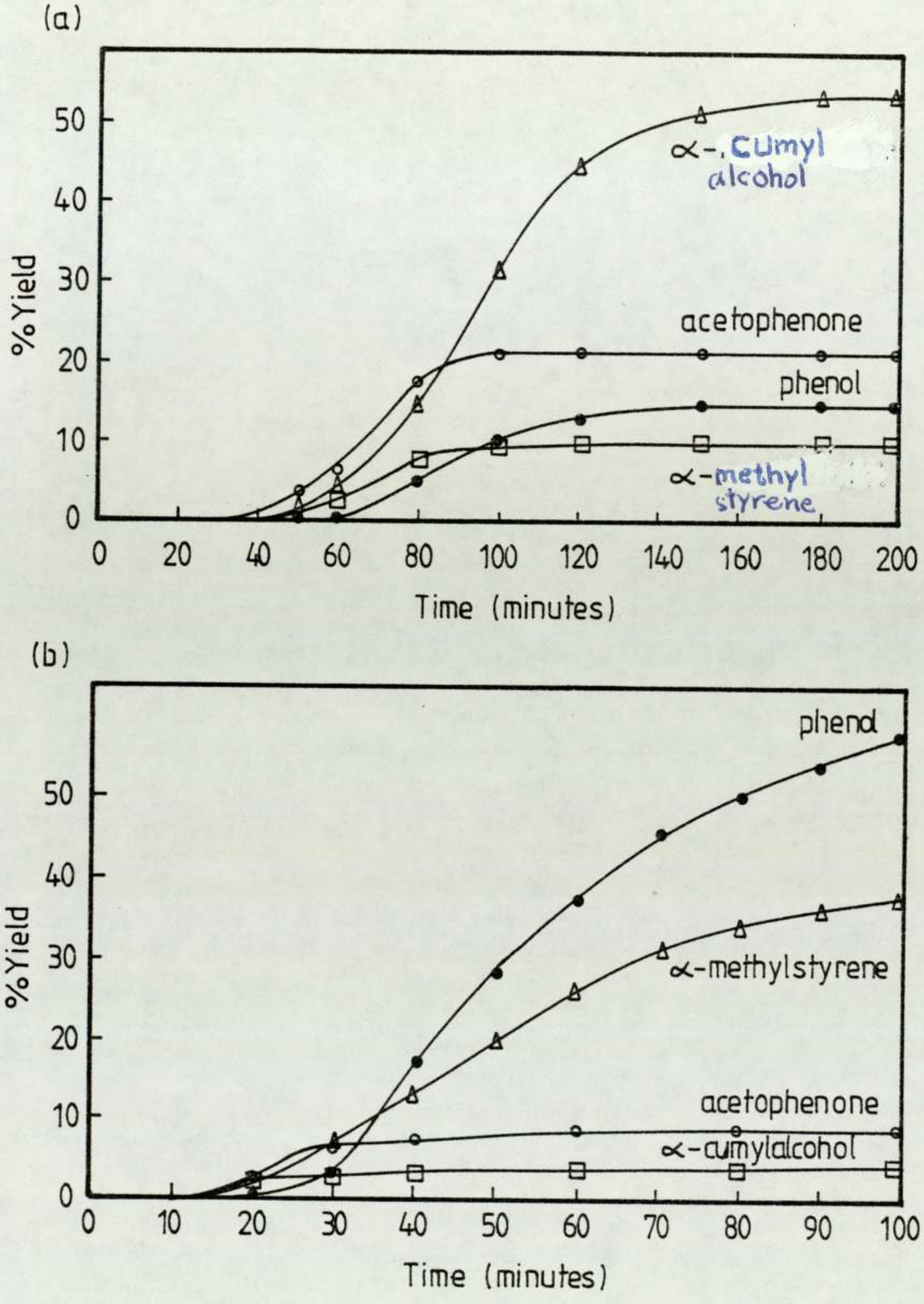


Figure 5.27 Kinetics of the products formed from CHP / ZDEC in chlorobenzene at 110°C at molar ratios (a) 10 : 1 (b) 30 : 1. Concentration of CHP 1×10^{-2} M

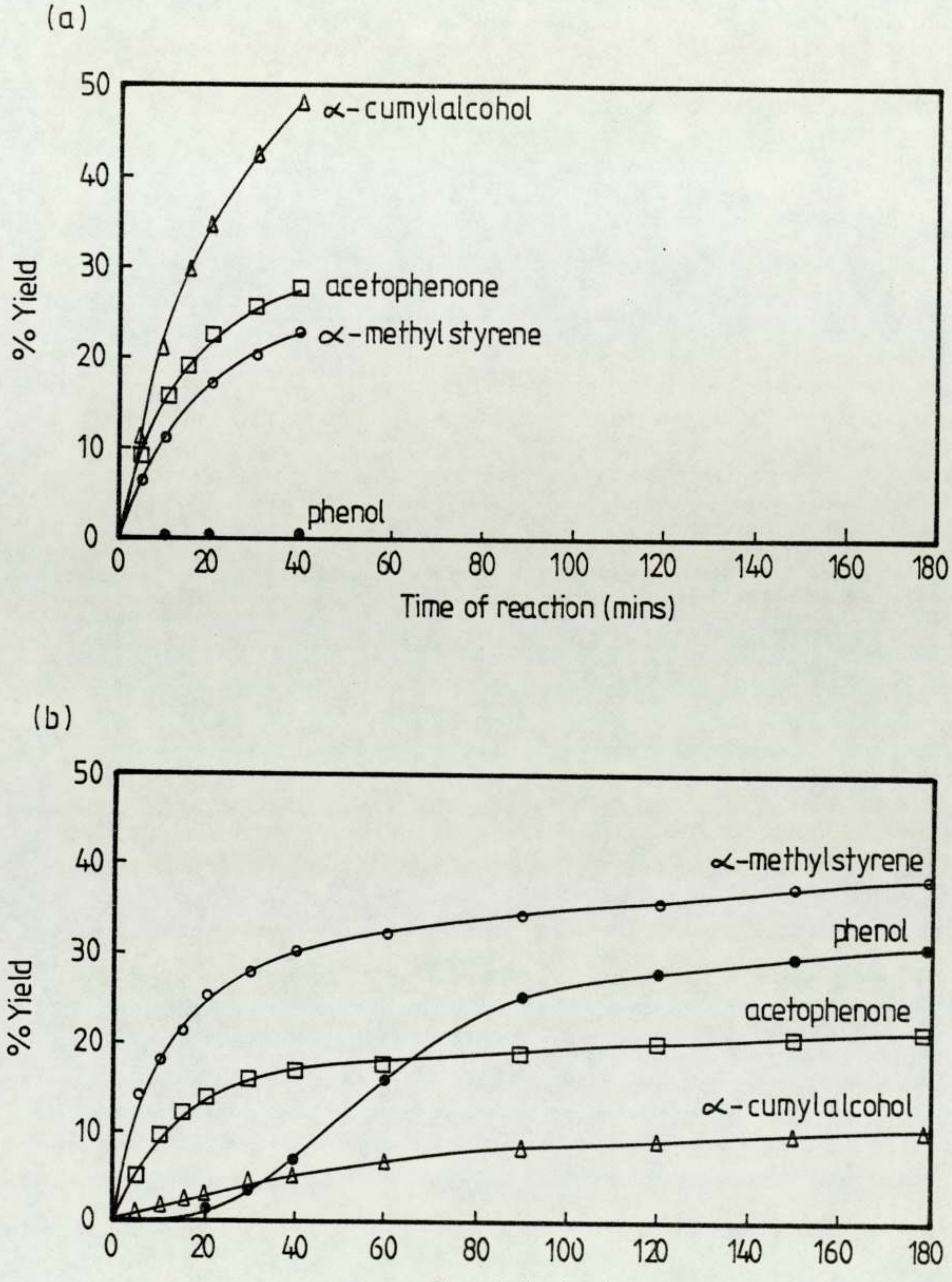


Figure 5:28 Kinetics of the products formed from CHP & FDMC in chlorobenzene at 110°C at molar ratios (a)10 : 1 (b)30 : 1 Concentration of CHP 1×10^{-2} M

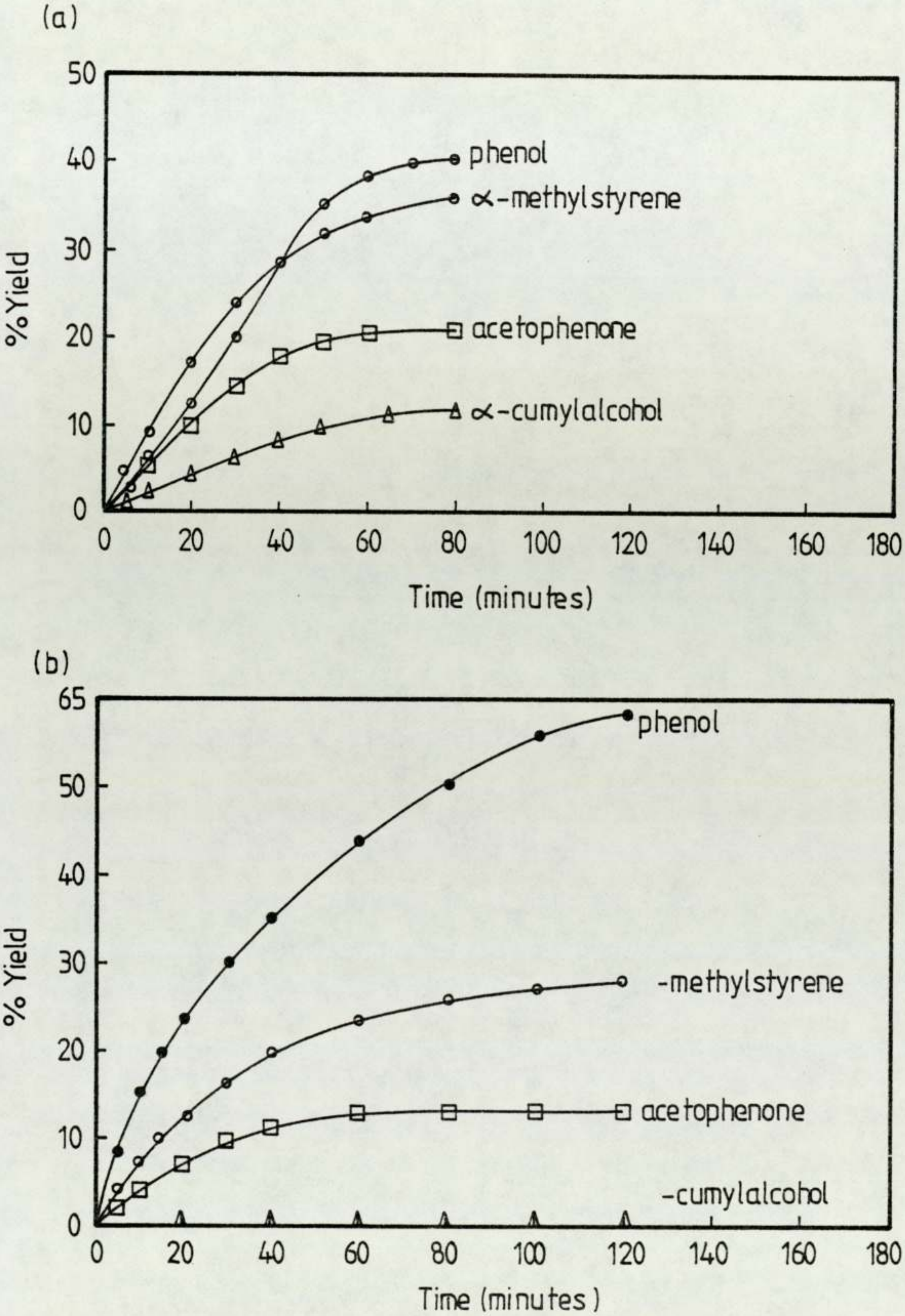


Figure 5:29 Kinetics of the products formed from CHP/TETD in chlorobenzene at 110° C at molar ratios(a) 10 : 1 (b) 30 : 1 Concentration of CHP 1×10^{-2} M

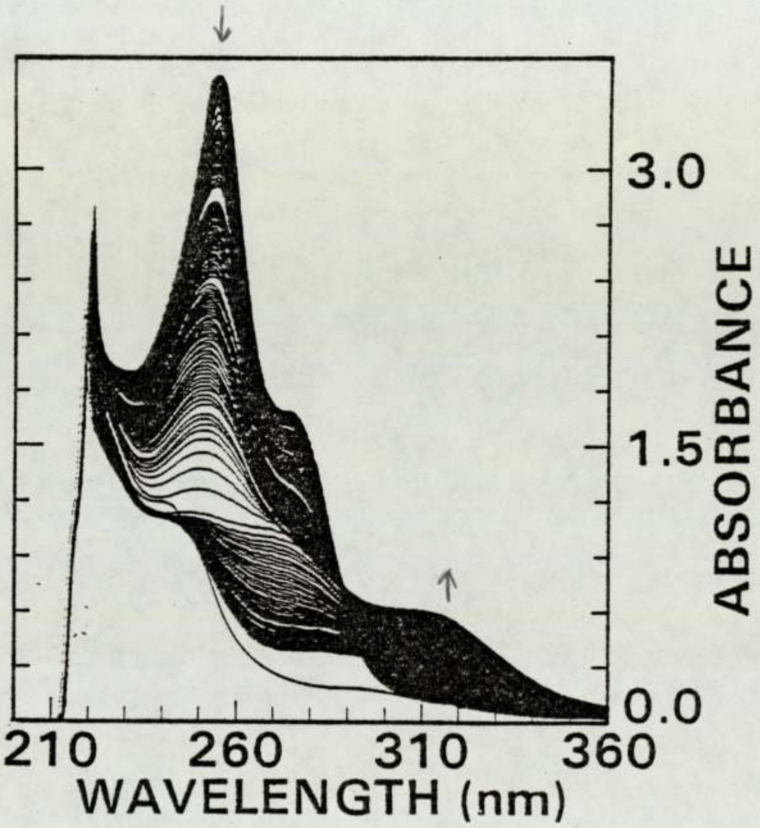


Figure 5.30 Superimposed (continuous run) UV-spectra during the reaction of ZDMC (1×10^{-4}M) with TBH ($2 \cdot 5 \times 10^{-2}$M) at 50°C in ethanol

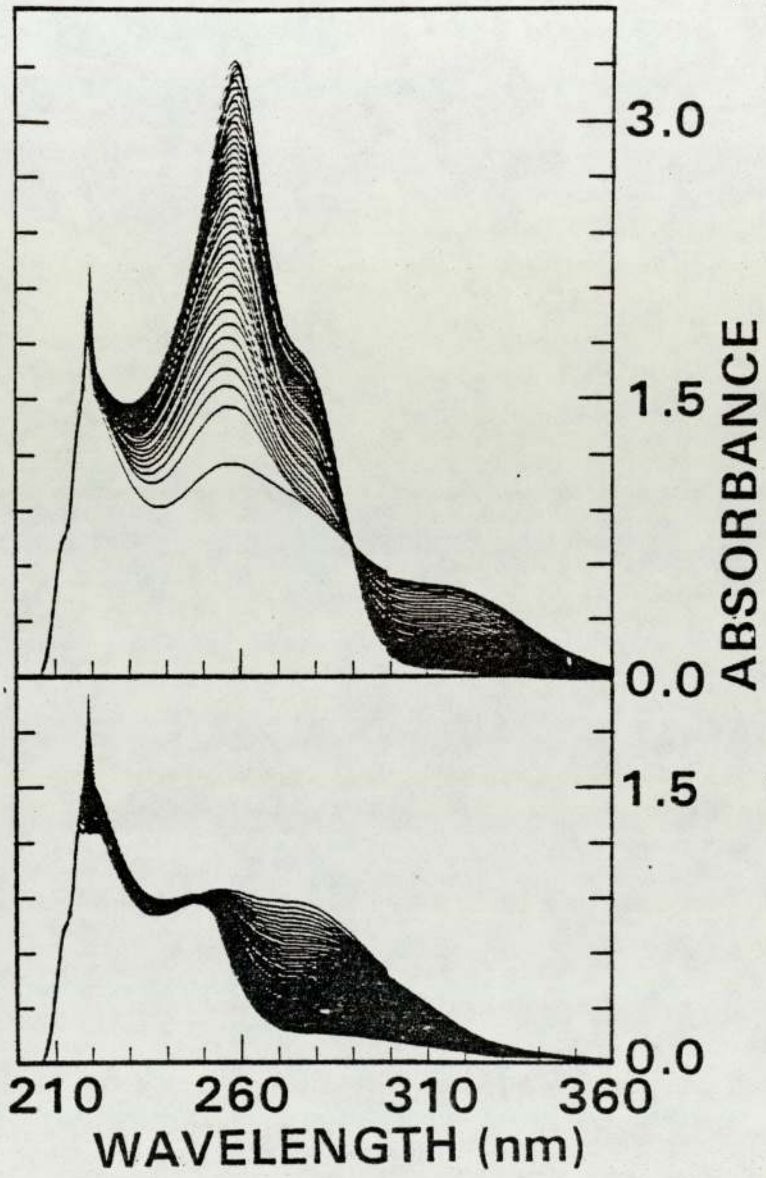


Figure 5.31 Spectral changes during the reaction of ZDMC with TBH in ethanol at molar ratio of 1 : 250 [[TBH] = 2·5 ×10^{-2}M]

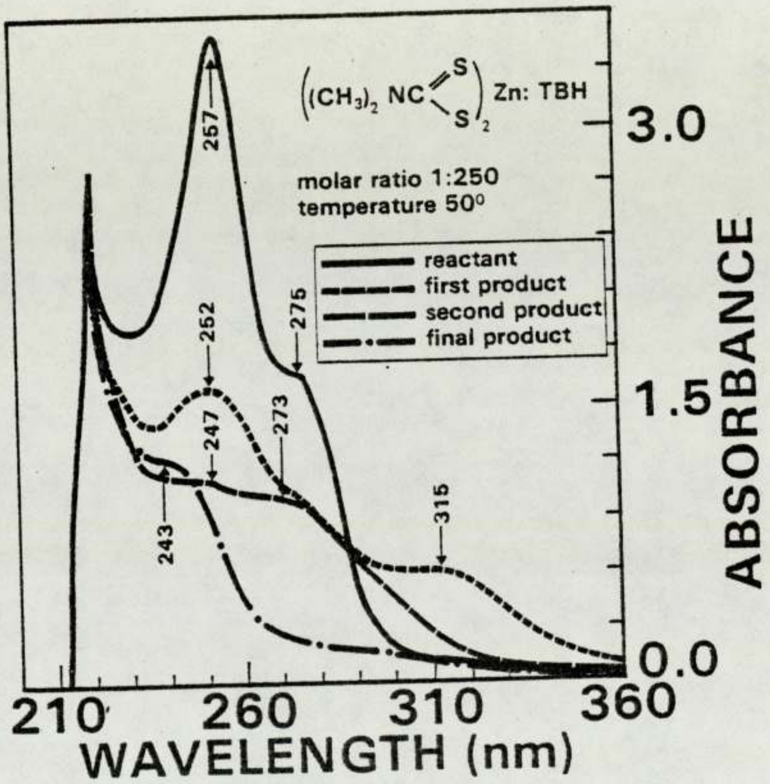


Figure 5.32 UV spectra of ZDMC (1×10^{-4} M) and its intermediates formed during its reaction with TBH ($2 \cdot 5 \times 10^{-2}$M) in ethanol at 50°C

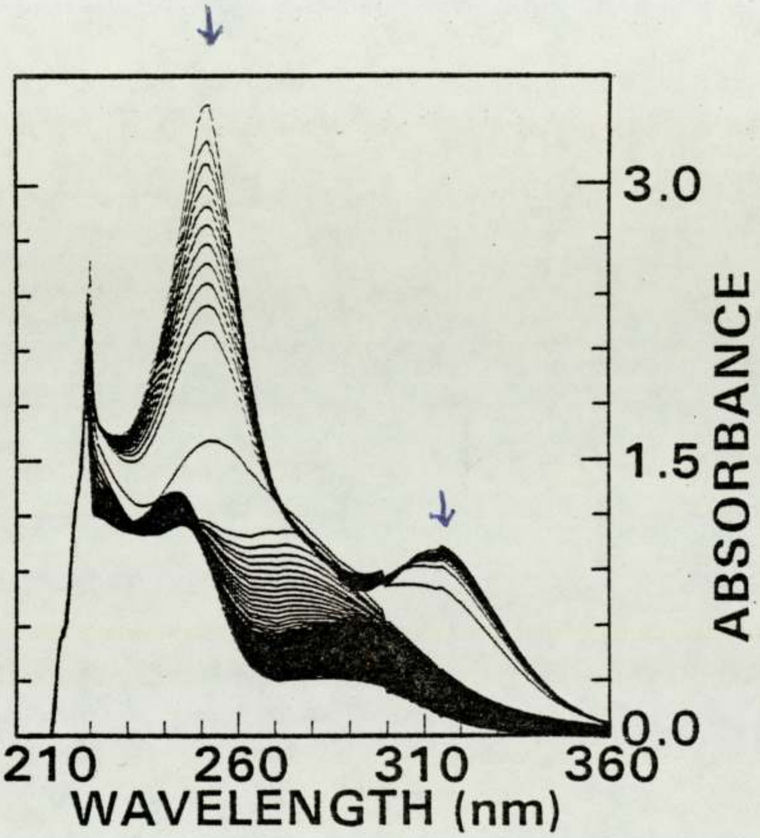


Figure 5.33 Superimposed (continuous run) UV-spectra during the reaction of ZDMCSO (1×10^{-4}M) with TBH ($2{\cdot}5\times10^{-2}$M) in ethanol at 50°C

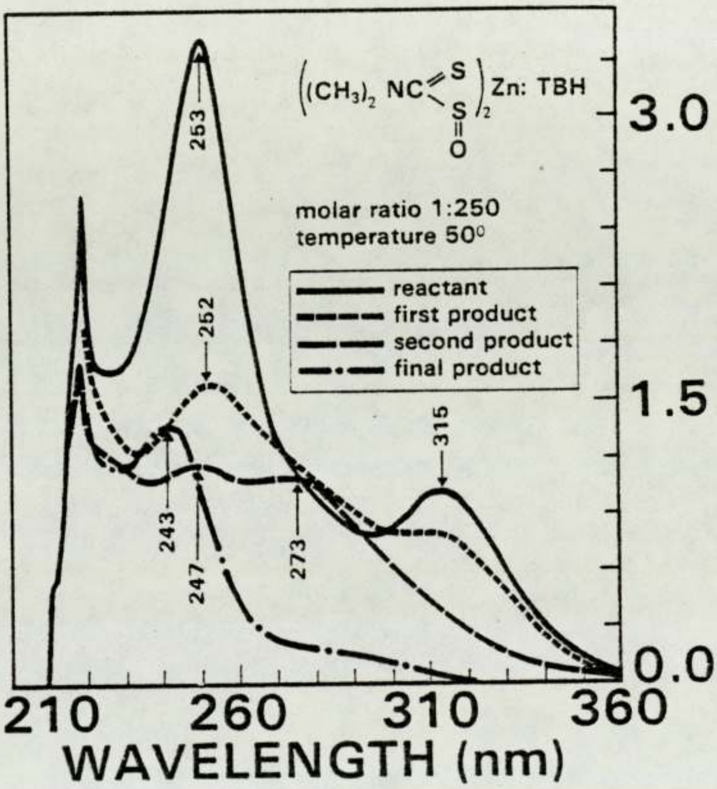


Figure 5.34 UV-spectra of the ZDMCSO (1×10^{-4}M) and its ~~intermediates~~ Products formed during its reaction with TBH ($2{\cdot}5 \times 10^{-2}$M) in ethanol at 50°C

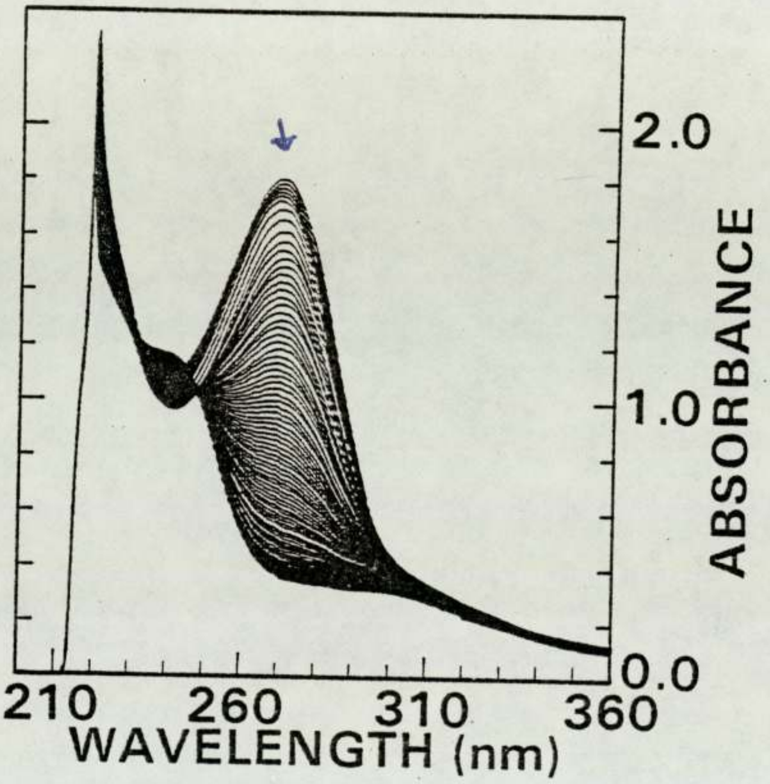


Figure 5.35 Superimposed (continuous run) UV-spectra during the reaction of $ZDMCSO_2$ (1×10^{-4}M) with TBH ($2{\cdot}5 \times 10^{-2}$ M) in ethanol at 50° C

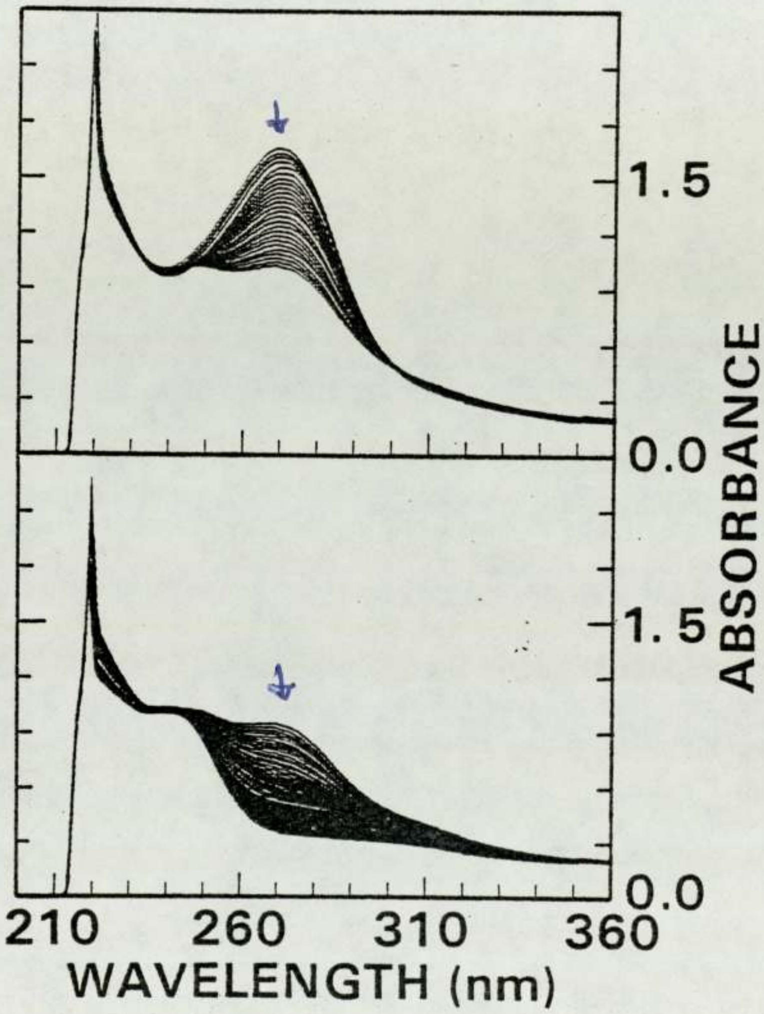


Figure 5.36 Spectral changes during the reaction of $ZDMCSO_2$ with TBH in ethanol at molar ratio of 1:250 [[TBH] = $2{\cdot}5 \times 10^{-2}$ M]

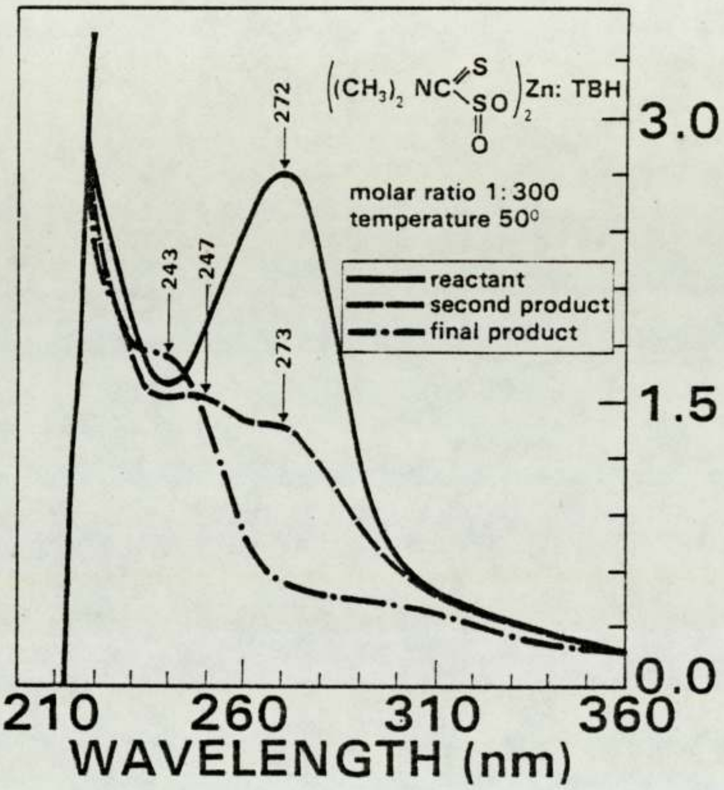


Figure 5.37 UV-spectra of $ZDMCSO_2$ (1×10^{-4}M) and its intermediates and products during its reaction with TBH ($2{\cdot}5 \times 10^{-2}$M) in ethanol at 50° C

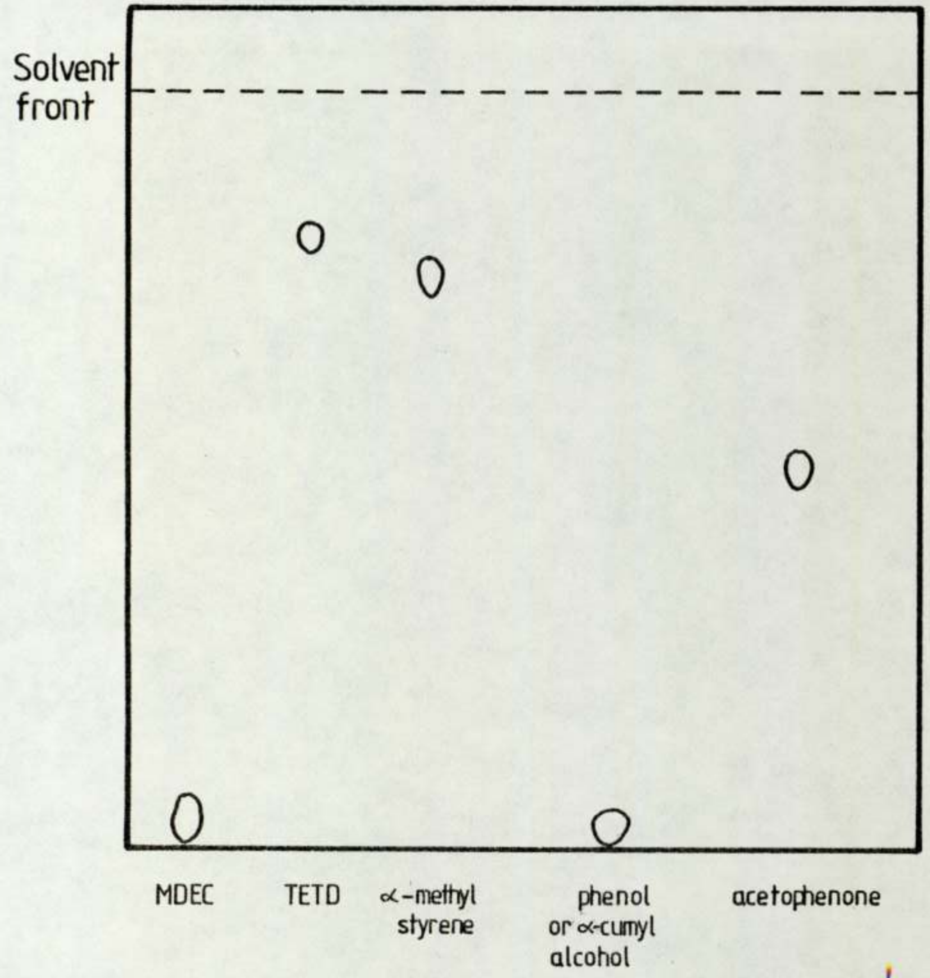


Figure 5:38 TLC run of authentic compounds in chlorobenzene

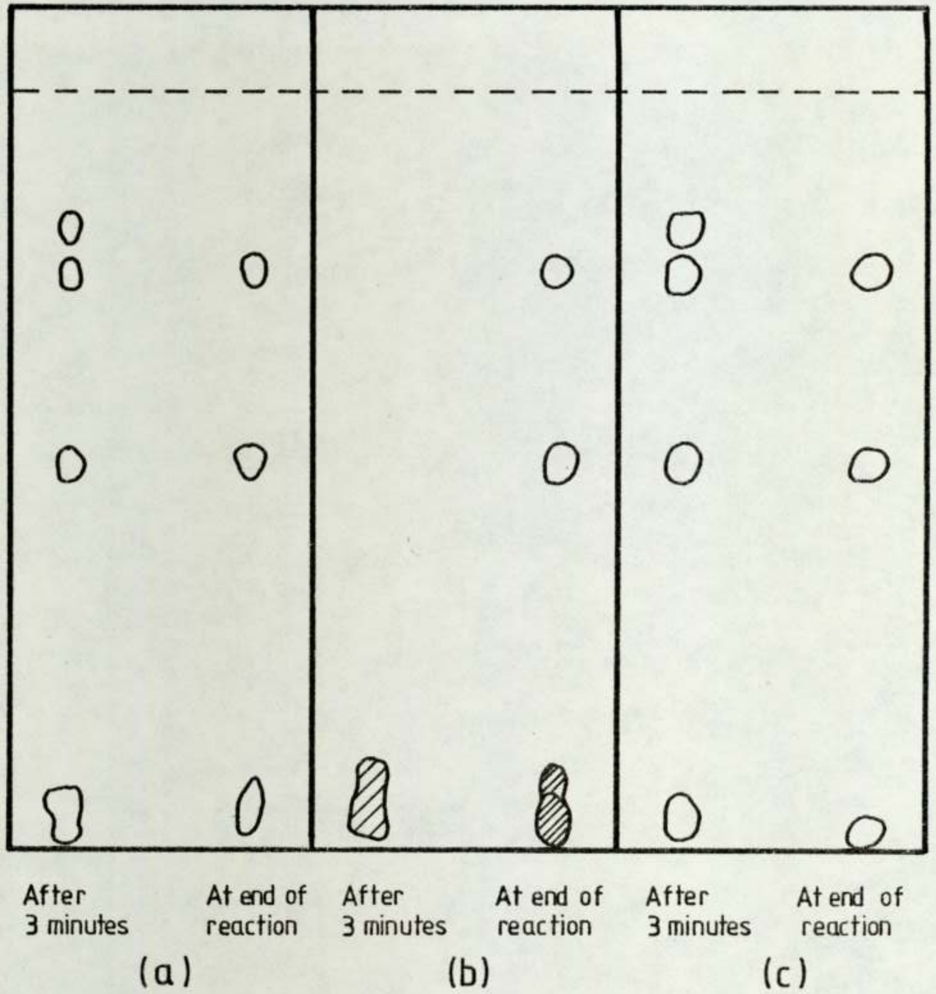


Figure 5:39 Product from the reaction of metal dithiocarbamates and the corresponding disulphide (2×10^{-3}M) with CHP (1×10^{-1}M) (a) NDEC or FDEC (b) ZDEC (c) TETD

CONCLUSIONS

1. A single component antioxidant photo-activator (APA) system based on FDMC was found useful for the shorter crop lifetime. However, it did not give the control necessary for longer cropping periods under severe exposure conditions. The two-component APA system based on a hydroperoxide decomposer (NDEC, ZDEC or TETD) and ideal photo-activator (FDMC) was found to be entirely successful and gave the very sharp termination to lifetime that is required for automated harvesting of tomatoes and other fruits.

2. The two-component APA system was found to perform extremely well in PP. The substantial long but controlled induction period followed by rapid and complete degradation are the requirements needed for the time-controlled baler twines and fertiliser packaging. PP stabilized by the two-component APA system can, therefore, replace successfully the non-biodegradable baler twines and fertiliser packaging where attempts to recycle these have failed to make any impression on the litter problem.

3. The limitations in the usage of plastics mulches in cold climates can now be resolved by the use of the two-component APA system based on a hydroperoxide decomposer (NDEC) and conventional photo-activator (FAcAc). This system was found to give a short controllable induction period followed by rapid and complete decay of the film's physical properties.

4. Although the two-component system based on a U.V.-absorber and ideal photo-activator (FDMC) gave a substantial safety induction period in both LDPE and PP, the rate of photo-oxidation following the safety induction period was relatively slow. This disadvantage could limit the use of this system in the automated agricultural sector. The reason for the slow rate of photo-oxidation was found to be the U.V.-absorber. This stabilizer exerts its chemical inhibiting activity at the later stages of photo-oxidation when carbonyl initiation becomes important.

5. In the two-component APA system based on a hydroperoxide decomposer (NDEC, ZDEC or TETD) and ideal photo-activator (FDMC), the stabilizer concentration was found primarily to determine the length of induction peroid and the activator concentration, the rate of photo-oxidation, and hence the embrittlement time. In the case of HOBP/FDMC and MDRC/FAcAc two-component systems, this correlation was found not to hold. The stabilizer was still not destroyed during the later stages of oxidation of the film.

6. Metal complexes of dithiocarbamic acid and the corresponding disulphide (NDEC, ZDEC, FDMC and TETD) were found to be efficient melt stabilizers for both LDPE and PP. However, they were found to act differently under U.V.

irradiation conditions. Whereas NDEC was found to be the most effective U.V.-stabilizer, ZDEC was the least effective and the disulphide functioned as a moderate U.V.-stabilizer. The photo-stabilizing activity of FDMC in LDPE was found to depend on the concentration. At low concentration, FDMC was photo-activator whilst it acted as a delayed action photo-activator at relatively higher concentration.

7. The photo-stabilizing action of metal complexes of dithiocarbamic acid and the corresponding disulphide in LDPE and PP has been found to be a function of processing conditions. In the case of the disulphide, increasing processing severity was marked by improved photo-stability of the polymer matrix. The opposite effect was found in the case of metal dithiocarbamates.

8. The mechanism of antioxidant action of metal dithiocarbamates was established from studies conducted on model compounds. It was found that these metal complexes are capable of trapping free radicals as well as decomposing hydroperoxides. The free radical scavenging by these metal dithiocarbamate complexes leads to the formation of the disulphide while their interaction with peroxides leads to the formation of sulphenate and sulphinate products. The latter underwent further oxidation into sulphur oxides which then catalysed the hydroperoxide decomposition. The antioxidant action of these

metal dithiocarbamate complexes was completely removed in the presence of base consistent with neutralisation of acid catalyst produced. Addition of a free radical trapping agent was also found to paralise the antioxidant ability of these metal complexes of dithiocarbamic acid.

9. Unlike the complexes of dithiocarbamic acid, tetra alkyl thiuram disulphide was found to be a weak free radical inhibitor. However it was found to decompose hydroperoxides catalytically to non-radical products at almost all hydroperoxide/disulphide molar ratios.

SUGGESTIONS FOR FURTHER WORK

1. The performance of both single and two-component systems was evaluated in polymers under laboratory irradiation conditions. For practical purposes, a systematic study on the performance of these systems under outdoor weatherability conditions should be undertaken. This necessitates subjecting the film specimen repeatedly to a mechanical performance test which should match the mechanised harvesting requirements.

2. On the basis of this study, iron carboxylates are believed to be responsible for the rapid film oxidation in both single and two-component systems. Chemical evidence must, therefore, be needed to support the proposed mechanism. Similarly, the formation of the thiyl radical during irradiation of FDMC must be supported by evidence. This can be done by the use of ESR techniques at liquid nitrogen temperature or indirectly by carrying out photopolymerisation of vinyl monomers e.g., styrene, using the FDMC as a probable initiator.

3. The formation of sulphenate and sulphinate intermediates have been isolated from the reaction of zinc dialkyl dithiocarbamates and hydroperoxide in solution. The formation of such intermediates in film during processing or subsequent irradiation has to be justified. This could be done by extracting the additive by suitable solvent at different intervals during both processing and

subsequent irradiation processes and then subjecting the extract for examination e.g., HPLC and U.V.-spectrophotometry.

4. Disulphides are not themselves antioxidants rather than their oxidation products, synthesis of these oxidation products may provide unequivocal proof for the mechanism of action of those disulphides proposed in the basis of the present study.

5. Since the stabilization effectiveness of the disulphides greatly depends on the amount of the oxygen (or hydroperoxide) presence in the polymer during processing,an investigation of the added hydroperoxide to the polymer during processing is important. The added hydroperoxide is expected to prolong the polymer lifetime and to reduce the need for long processing times. The latter are normally required to generate the active sulphur acid antioxidant from the disulphide.

6. Metal dithiophosphates and their corresponding disulphides have been found to be bound partially into the polymer backbone during processing. Similar behaviour is expected in the case of the metal dithiocarbamate analogues. The study of the extent of binding of these dithiocarbamate complexes and their corresponding disulphides may provide an additional insight into their modes of antioxidant action.

7. Finally, it is worthwhile to study the effect of changing the ligand in both Fe III and U.V.-stabilizers, since it has been shown that the oxime complex of Fe III acts as a delayed action photoactivator and nickel oxime complex as a hydroperoxide decomposer.

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