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A Thesis

entitled

Metal Chelates as Flame Retardants
and
Photostabilisers for some Vinyl Polymers

submitted by

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Dedication

I would like to dedicate this work
to my family: my mother, father and
sister, who have sustained me with
their love and support and above all
to my beloved maternal grandmother,
to whom I am indebted for all her
kindness and affection.

Acknowledgments

In producing this work I am indebted to many people and I would like to thank them all as follows. First and foremost I wish to express my heartfelt thanks to Professor C.F. Cullis, who is my supervisor in London, for his guidance, encouragement and meticulous care in ensuring that my thesis is accurate in every detail and well presented.

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I would like to thank Mrs. [redacted] for her patience in typing this thesis and for her help in many other ways.

Not forgetting my colleagues in the Combustion Research Group who have helped and assisted me I would like to thank them too especially: [redacted] [redacted] and [redacted] [redacted]

Finally, I would like to thank The British Council for their valuable financial support, without which this work could not have been undertaken, and particularly their representative in London Miss [redacted].

Abstract

The main purpose of the present work was to discover and investigate the action of additives which, when incorporated into simple polyolefins (principally polypropylene), have both flame-retardant and photostabilising properties; and in this connection, particular attention has been paid to metal chelates, especially those containing transition metals.

The Introduction first reviews the combustion of organic polymers and its prevention. Accounts are included of factors affecting polymer flammability, of general principles of flame-retardance and of effects of metal compounds on polymer combustion. Finally, previous work on the photodegradation and photo-oxidation of simple polyolefins is described. A review is given too of the principal types of compound used as photostabilisers for organic polymers in general and particular attention is paid to the use of metal compounds as inhibitors of polymer photo-oxidation.

In the Experimental Section, the techniques used to incorporate the various additives into the polymers are first outlined. There follows a description of the limiting oxygen index method used to measure and compare the flammability of polymer samples and of the apparatus and procedure used to determine their smoke-producing tendency. An account is given of the computer method used to fit polynomial functions to the flammability data and to plot these in the form of triangular diagrams. The sophisticated experimental set-up for making thermoanalytical measurements on the polymer samples is then described. Finally an account is given of the procedures used to investigate the effects of the various additives on the photo-oxidation of polypropylene. Polymer films containing metal chelates were irradiated with u.v. light in air and the rate of oxidation was followed by means of their infra-red spectra. Ultra-violet absorption, fluorescence spectra and chemical tests were also used to elucidate the mechanism.

The Results Section first outlines some work involving polystyrene. However few of the additive systems investigated had useful flame-retardant effects on this polymer. More detailed studies were then carried out with polypropylene, where some four metal chelates viz: zinc(II) acetyl acetonate, tin(IV) bis acetyl acetonate dichloride, bis hydroxohexa benzoato tris iron(III) benzoate and ferrocene, when used in conjunction with an organic chlorine compound (Cereclor 70), raised the limiting oxygen index to about 30. Measurement of the rate of photo-oxidation of polypropylene films containing also the various metal chelates showed that certain compounds, viz. N,N'-bis salicylidene ethylenediamine zinc(II), zinc(II) acetyl acetonate and tin(IV) bis acetyl acetonate dichloride, had a sizeable photostabilising effect. The results are also presented of detailed studies of the thermoanalytical behaviour of polypropylene samples containing the more promising metal chelates, with and without Cereclor.

In the Discussion, attempts are made to account for the flame - retardant and photostabilising properties of certain of the metal chelates. Useful information regarding their flame retardant action is provided by the thermoanalytical results which show that they all function mainly in the condensed phase. Studies of the effect of benzophenone on the photochemical behaviour of polypropylene show that the polymer does not undergo oxidation by a triplet mechanism so that the metal chelates cannot act as triplet quenchers. Finally some likely alternative modes of photostabilising action of the chelates are discussed.

1 - Introduction

1. Introduction

1.1 The purpose of the work

Polymeric materials are by no means always inert and unreactive compounds and they thus generally need various kinds of protection against unwanted chemical reactions. During processing, in particular, polymers may be subjected to quite high temperatures and it is necessary to ensure that they do not, in these circumstances, undergo appreciable thermal or thermooxidative degration. Finished polymeric products need to be protected too against the long-term effects of light as well as against fire, for organic polymers are, for the most part, both photosensitive and flammable materials.

In general, the additives which protect polymers from various kinds of thermal and photochemical decomposition at relatively low temperatures do not appear to give these materials any significant resistance to combustion. In the same way, the common flame retardant compounds do not provide any appreciable protection against oxidation at ambient temperatures. Many metal complexes act as photostablisisers for polymers and these will generally be converted, on exposure to the high temperatures characteristic of combustion, to much simpler metal compounds, such as oxides or halides, many of which can exert a significant flame-retardant action. The object of this work was to discover the extent to which selected compounds could give polymers useful protection both against low temperature oxidation and against combustion. There thus follow two sections reviewing firstly, the combustion of organic polymers (Section 1.2) and secondly, their photo-oxidation (Section 1.3). In both cases, special emphasis is placed on the use of metal compounds.

1.2 The combustion of organic polymers and its prevention

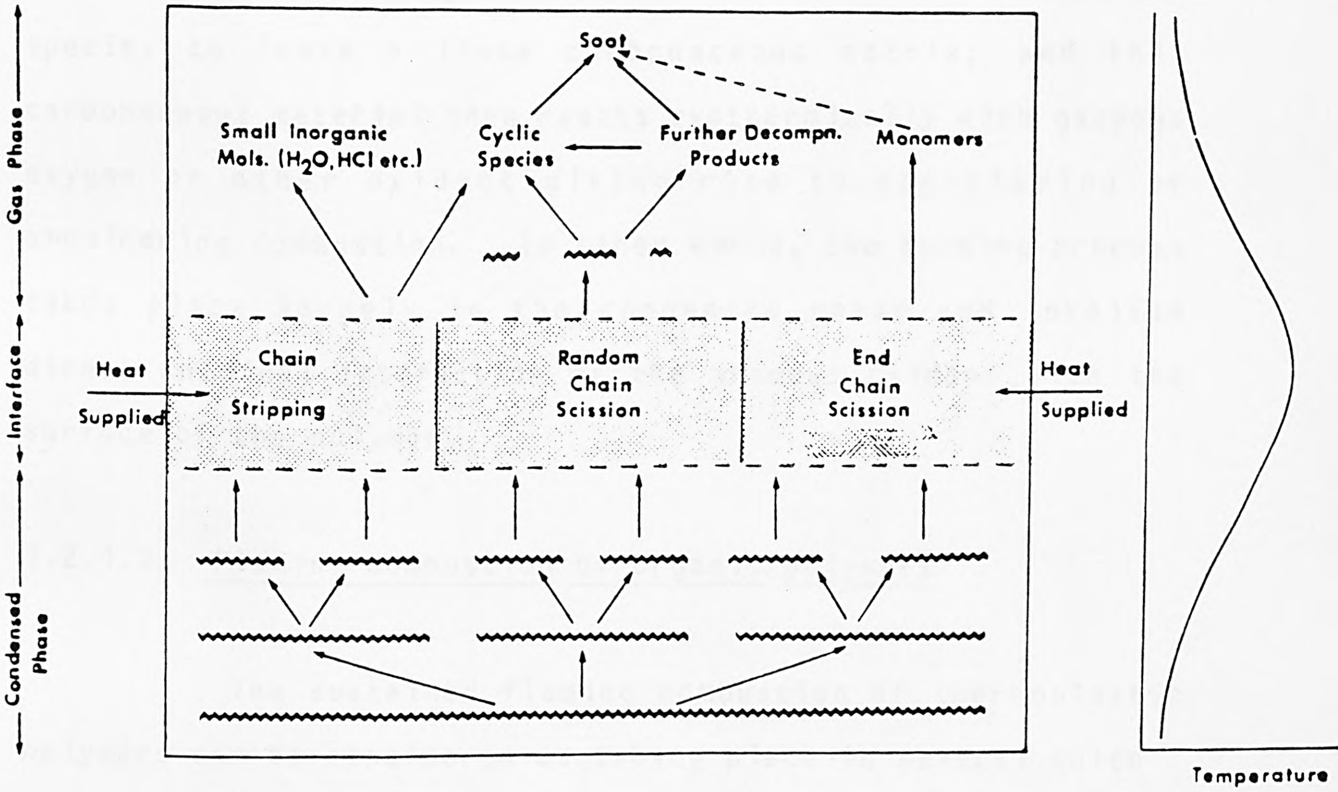
1.2.1 Mechanisms of polymer combustion

1.2.1.1 Introduction

The combustion of organic polymers is invariably a complex process which involves a number of interrelated stages (Cullis and Hirschler, 1981). Chemical reaction takes place in three interdependent regions, namely within the condensed phase of the polymer itself, at the interface between the condensed phase and the gas phase, and in the gas phase. Fig. 1.1 shows diagrammatically the changes which may occur when heat is supplied to the surface of an organic polymer in an inert atmosphere and brings about some thermal decomposition of the polymer (Tkac, 1976). When oxygen or another gaseous oxidant is present, the resulting combustion of the polymer is considerably more complicated.

Basically two types of behaviour may be observed during the combustion of organic polymers. With thermoplastics, such as polyolefins, polystyrene and acrylics, thermal decomposition of the polymer leads to the formation of relatively large amounts of combustible volatile products, which subsequently mix with the

Fig. 1.1 Changes during thermal decomposition of an organic polymer

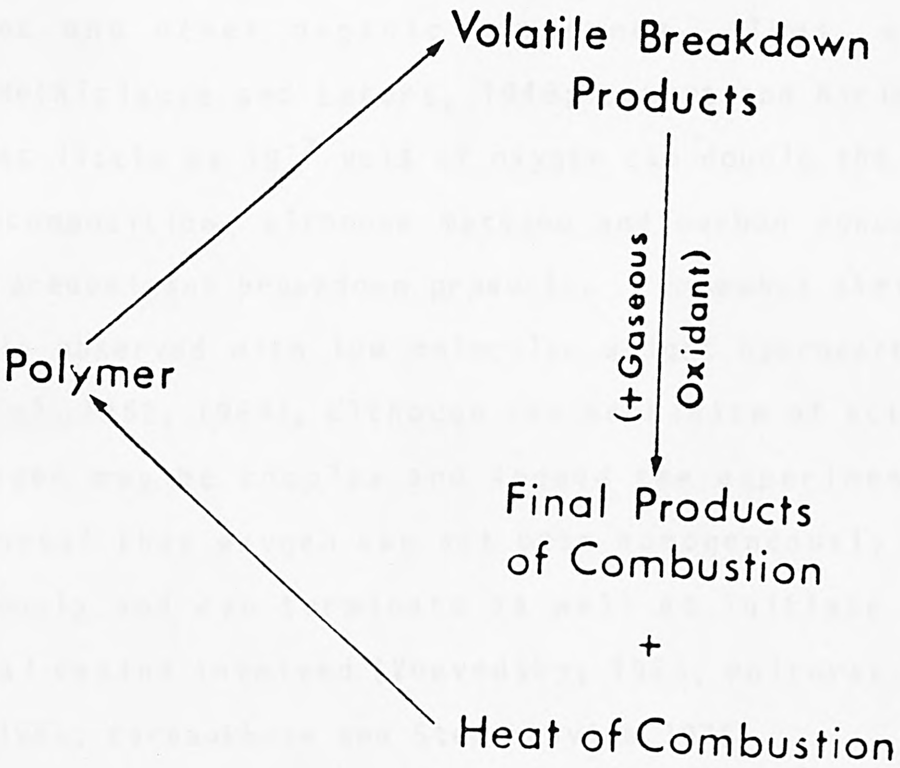


air or other oxidant and then burn in the gas phase above the polymer, giving rise to so-called flaming combustion. On the other hand, with some thermosetting polymers (e.g. phenolic resins and polyethers) and with cellulosic materials, the initial step in the combustion process is generally the splitting off of water or other non-combustible species to leave a loose carbonaceous matrix; and this carbonaceous material then reacts exothermically with gaseous oxygen or other oxidant giving rise to non-flaming or smouldering combustion. In other words, the burning process takes place largely in the condensed phase and involves direct chemical interaction of the gaseous oxidant with the surface of the polymer.

1.2.1.2 Flaming combustion of organic polymers

The sustained flaming combustion of thermoplastic polymers can be considered as taking place in several quite distinct stages (Fig.1.2). The polymer first reacts in the condensed phase to give combustible gaseous products. These products then burn in the flame zone above the polymer, leading to the formation of final combustion products and the liberation of heat. Under steady-state burning conditions, some of this heat is transferred back to the polymer, where it causes further reaction and yields more combustible gaseous products.

Fig. 1.2 Stages involved in flaming combustion of an organic polymer



Although it is generally assumed that it is pure thermal decomposition of the polymer which leads to the volatile breakdown products which actually burn, there is now considerable evidence that, at least under certain combustion conditions and with some organic polymers, the initial breakdown of the polymer is a process which actively involves oxygen. It has long been known that even stoichiometrically insignificant amounts of oxygen can considerably alter the rate and course of decomposition in the gas phase of hydrocarbons and other organic compounds. Thus, with acetaldehyde(Niclause and Letort, 1948; Letort and Niclause, 1949a,b) as little as 10^{-3} vol% of oxygen can double the rate of decomposition, although methane and carbon monoxide remain the predominant breakdown products. Somewhat similar behaviour is observed with low molecular weight hydrocarbons (Martin et al.,1962, 1964), although the mechanism of action of the oxygen may be complex and indeed the experimental results suggest that oxygen can act both homogeneously and heterogeneously and can terminate as well as initiate the free radical chains involved (Voevodsky, 1958; Poltorak and Voevodsky,1961; Karnaukhova and Stepukhovich,1975).

It is not perhaps surprising therefore that the kinetics and products of decomposition of many organic polymers are considerably affected by the presence of (often very small amounts of) oxygen. For example, with polypropylene, oxygen decreases the reaction temperature by some 200^0 and reduces the activation energy by about 150 kJ mol^{-1} (Chien and Kiang, 1978;1980), and similar behaviour is found with poly(vinylidene fluoride), where oxygen, in addition to causing a dramatic lowering of the activation energy and the pre-exponential factor, changes a normally second-order reaction to one of zero order (Hirschler, 1982). Poly(vinyl chloride) is another common organic polymer whose decomposition is generally accelerated by oxygen (Gupta and St. Pierre, 1979). Interesting behaviour is observed with styrene-based polymers, where the effect of oxygen depends on the nature of the substituent groups in the aromatic ring (Still and Whitehead, 1976); with polystyrene itself, oxygen considerably decreases the thermal stability but poly(p-hydroxy styrene) breaks down at virutally the same rate in the absence and presence of oxygen (Still and Whitehead, 1977). Polybutadiene is another polymer whose decomposition is very little affected by oxygen (Cullis and Laver, 1978). However the complexity of the action of oxygen is shown by the fact that the gas tends to retard the decomposition of other polymers, such as polyacrylonitrile (Grassie and McGuchan, 1970, 1971).

Experimental evidence for the involvement of oxygen during the initial breakdown stage of polymer combustion is derived from several different types of measurement. Thus studies have been made of the chemical composition of the gases at various positions in the flame above candles of different organic polymers with both air and oxygen-enriched air as the supporting gas (Burge et al., 1967, 1969). With polyethylene burning in air, it was found that, close to the surface of the molten polymer, at least 70% of the flame gases consist of nitrogen, with less than 2% of oxygen and appreciable quantities of oxides of carbon and water. In other words, nearly all the oxygen originally associated with the nitrogen in the air had undergone chemical reaction and disappeared within a very short distance of the polymer surface. This suggests that the carbon oxides and water are formed by oxidation reactions within the surface of the polymer melt rather than in the gas phase. On the other hand, similar experiments with both poly(methyl methacrylate) and polyoxymethylene showed that there were still substantial amounts of unchanged oxygen in the flame gases immediately adjacent to the polymer. In other words, these polymers appeared to undergo principally thermal decomposition to the corresponding monomers, which then reacted with oxygen within the flame. More detailed analysis of the flame gases only 0.1 mm above the surface of burning polyetheylene and polypropylene (Stuetz et al., 1975) also showed very little residual oxygen and substantial amounts of oxides of carbon and water, strongly suggesting that, with both these polyolefins, significant amounts of oxygen diffuse through the flame to the polymer surface and are then absorbed into a well-defined surface layer in which an appreciable proportion of the polymer undergoes oxidative decomposition.

Perhaps more direct evidence for the presence of oxygen in the surface layer of burning polymers during combustion comes from experiments with both polyethylene and polypropylene (Stuetz et al., 1975). Burning candles of these polymers were extinguished by an excess of nitrogen or argon and then cooled in a stream of inert gas. The oxygen content was then determined by neutron activation analysis of a section sliced lengthwise through the samples. In the case of one polypropylene sample, the oxygen content was about 0.3 wt%, 1.6 mm below the surface, but this rose to 12 wt% at a depth of 0.1 mm and extropolation suggested an oxygen concentration of about 26 wt% at the surface.

More indirect evidence suggesting the intervention of oxygen in the decomposition stage of polymer combustion comes from measurement of the temperatures at and near the surface of polymeric materials when they burn. With polyethylene burning in air, for example, the temperature rose rapidly from about 200°C, 5 mm below the surface.

However the temperature at the surface of the molten polymer was approximately 400^{o}C and separate experiments have shown that, in the absence of oxygen polyethylene suffers scarcely any decrease in weight at this latter temperature. However this polymer starts to break down at temperatures as low as 250^{o}C when oxygen is present; and indeed most high molecular weight hydrocarbons undergo rapid oxidation in the liquid phase under these conditions (Rabek 1975). It is thus reasonable to assume that oxidation of the molten polymer could take place in the surface layer, whereas pure thermal decomposition could not.

In experiments involving the thermal irradiation of polyethylene, it was shown that an increase in the oxygen concentration (from 0 to 40 vol%) in the surrounding atmosphere considerably increased the rate of gasification of the polymer (Kashiwagi and Ohlemiller, 1983). The results of a theoretical study suggest too that, with poly(methyl methacrylate), both oxidative and thermal degradation are responsible for the gasification of the polymer (Kumar and Stickler, 1971). Consideration of the energy fluxes for both polyethylene and polypropylene burning in air (Stuetz et al. 1975) also showed that, on the assumption that a small amount of energy is provided by radiation from the flame envelope, it is possible to calculate the extent to which these polymers simultaneously undergoe oxidative decomposition (which is exothermic (Edgerley, 1980)) and thermal decomposition (which is endothermic).

1.2.1.3 Non-flaming combustion of polymers

Smouldering combustion, which involves the propagation of a 'front' involving the gaseous oxidation of the pyrolysis products of an organic polymer, usually occurs with cellulosic materials or certain thermosetting polymers with high surface-to-weight ratios. Smouldering combustion has been very little studied from a fundamental point of view. A minimum thickness of polymeric material is generally needed for combustion to occur but the flow of air across the surface can reduce the minimum thickness to one-eighth of its value for still air. When the air flow rate is increased sufficiently, the smouldering material is eventually extinguished. Smouldering is generally accompanied by generation of smoke due to pyrolysis at or near the surface. Since this smoke is combustible, a transition to flaming combustion may occur, and the amount of smoke formed per unit of heat released then decreases. Smouldering combustion is responsible for about 75 per cent of all fires (Moussa et al., 1977) and for about 50 per cent of all fire fatalities (McCarter,1977). The victims are usually overcome by smoke which is associated with large amounts of carbon monoxide (Hafer and Yuill,1970). Unfortunately, few detailed studies have been made of the gaseous products of smouldering combustion. However, qualitative observation of the gases as they emerge from the glowing material indicate that the products often include volatile organic compounds, such as aldehydes, which are either toxic or irritant.

1.2.1.4 Factors affecting polymer flammability

A stage in the combustion of organic polymers which might be expected to be of considerable importance in determining the ease with which these materials burn is the initial decomposition of the polymer. Thus, if it were possible to design polymers of infinite thermal stability, no volatile combustible products would be formed from them and combustion would not take place. Over the last 40 years or so, a large number of thermally stable polymers (Cassidy, 1980; Critchley et al.,1983) have been developed for special applications. However, as regards the very wide range of other organic polymers, it is important to recognise that it is not simply the ease of breakdown which affects the flammability but also the mechanism of thermal decomposition, which can vary tremendously from one polymer to another.

With some polymers, the breakdown process involves predominantly the fission of bonds making up the main chain of the polymer with the resulting formation of fragments which are small enough to be volatile; in the extreme case, the polymer simply 'unzips' to reform the original monomer and this invariably leads to complete gasification and loss of physical integrity of the polymer. With other polymers, the breakdown process consists merely in the detachment of the side chains; some volatile products are thus formed but the main chain remains virtually intact and and provides some solid residue. Alternatively, the polymer may suffer a molecular rearrangement, with hardly any weight loss or formation of volatile products, to give a polymer with a different structure. Thus various types of product may be formed when a polymer breaks down, and the nature and amounts of the decomposition products are clearly important factors controlling the readiness or otherwise with which a particular polymer burns. If large volumes of highly combustible gases are evolved, flaming combustion will be facilitated but even the formation of non-combustible gaseous products tends to break up the polymer structure, so that small fragments of decomposing solid material become entrained in the escaping combustion gases, eventually appearing in the flame as particles of soot. Liquid products are not as readily combustible as gaseous products but nevertheless tend to spread heat to adjacent parts of the polymer structure. The least flammable products are solid residues, mainly because they help to preserve structural integrity and thus protect neighbouring sections of the polymer from decomposition.

In practice, the mechanism of polymer decomposition and hence the nature products formed, depends strongly on polymer structure and, in particular, on the nature of the substituent groups attached to the main chain. Thus, with vinyl polymers, the yields of monomer vary from 100% to to considerbly less than 1% but, despite the fact that the monomers are often highly flammable, little or no correlation is found between the amounts of monomer formed and the flammability of the polymer (Table 1.1).

The different mechanisms of the thermal decomposition, and in consequence the different types and amounts of products formed, certainly constitute one of the main reasons why overall thermal stability is not a good criterion of the degree of flame retardance exhibited by a polymer. Flammability may be conveniently expressed in terms of the limiting oxygen index (LOI), which is the minimum percentage of oxygen in the surrounding atmosphere which will just support flaming combustion of a particular substance. Thermal stability is often expressed in terms of the temperature at which the material starts to decompose (T_D but in practice this is not always easy to determine from thermogravimetric curves, so that in many ways a more convenient measure is the temperature at which a given small percentage (e.g. 1%) of the substance has decomposed. This latter quantity $T_{1\%}$ has the further advantage over T_D that it is much less sensitive to changes in sample size and in heating rate (Cullis and Hirschler, 1983). Nevertheless, there is little evidence of any correlation between this criterion of the thermal stability of thermoplastic polymers and their flammability (Table 1.2). Another factor which may at least partly account for this lack of correlation is the varying extent to which oxygen is involved during the thermal

Table 1.1 Monomer-forming tendency and flammability of some thermoplastic polymers

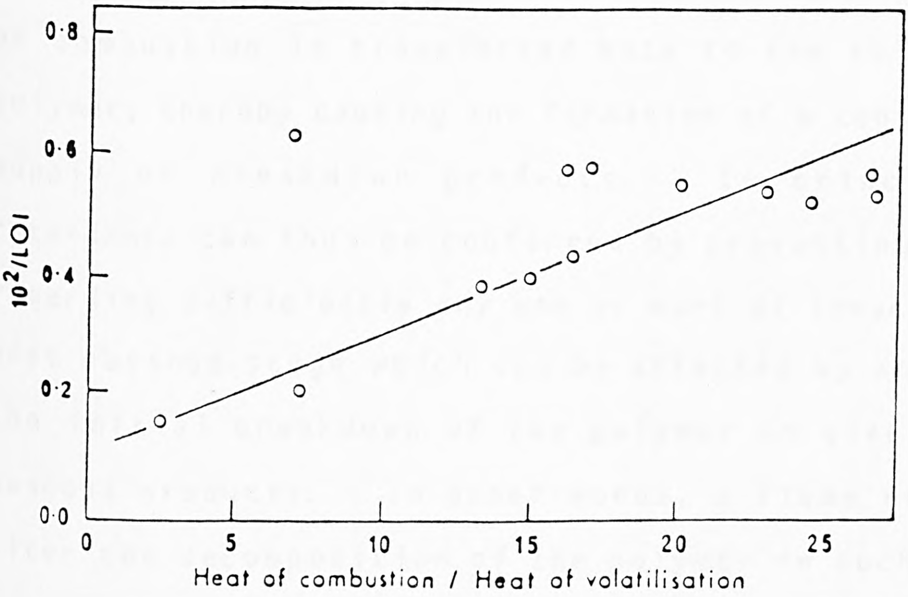
Polymer	% monomer in breakdown products	LOI
Polyformaldehyde	100	15.0
Polytetrafluoroethylene	95	95.0
Poly(methyl methacrylate)	91-98	17.3
Polystyrene	42-45	17.8
Polychlorotrifluoroethylene	28	95.0
Polyisoprene	5	18.5
Poly(4-methylpent-1-ene)	2	18.0
Polybutadiene	1	18.3
Polypropylene	0.17	17.4
Poly(vinyl chloride)	0.07	47.0
Polyethylene	0.03	17.4

Table 1.2 Thermal stability and flammability of of some thermoplastic polymers

Polymer	$T_{1\%}$(K)	LOI
Poly(vinyl alcohol)	379	22.5
Poly(vinyl chloride)	457	47.0
Polybutadiene	507	18.3
Polyisoprene	513	18.5
Polyformaldehyde	548	15.0
Poly(methyl methacrylate)	555	17.3
Polypropylene	588	17.4
Polystyrene	603	17.8
Poly(vinylidene fluoride)	683	43.7
Polytretrafluoroethylene	775	95.0

decomposition of different polymers under combustion conditions. Chemical analysis of the gases at various points in the flames above burning polymers shows that, with certain polymers but not with others, scarcely any oxygen is present in the immediate vicinity of the surface of the polymer (Stuetz et al., 1975). Unless these different extents of oxygen involvement are known, a close correlation between the susceptibility of polymers to purely thermal decomposition and their flammability would not be expected. A further important factor in the operation of the cycle for the flaming combustion of a polymer must be the efficiency of heat transfer back to the original polymer (Fig. 1.2). The rate of temperature rise of a polymer, for a given heat flux, depends on a number of factors, such as its thermal conductivity, its specific heat and its latent heat of volatilisation. In practice, the thermal conductivities of organic polymers are very low compared with those of most other materials and the specific heats tend to lie within a fairly narrow range. Thus, the thermal parameter most likely to vary considerably from one polymer to another is the heat of volatilisation. Since the rate of flow of heat to the polymer depends primarily on the heat of combustion of the gaseous products, a significant quantity controlling the ease with which organic polymers undergo sustained flaming combustion should be the ratio of the heat of combustion (which should be as large as possible) to the heat of volatilisation (which should ideally be as small as possible). However, Fig.1.3 shows that the correlation between the flammability of different polymers and values of this ratio is not very good. Thus, highly flammable polymers might be expected to be those which not only decompose at relatively low temperatures, but also in doing so give large quantities of gaseous products which in turn have a high heat of combustion. In practice, however, satisfactory correlations do not appear to exist between polymer flammability and the parameters government any of the conceptually separate stages of the burning process.

Fig. 1.3 Relation between flammability and ratio of heats of combustion and volatilisation of organic polymers



1.2.2 General principles for the conferment of flame retardance on organic polymers

It has already been seen (Section 1.2.1) that the sustained flaming combustion of polymers may be envisaged as taking place in three fairly distinct stages. The polymer is first converted into combustible gaseous products, these products then burn in the surrounding oxidant-containing atmosphere, and finally at least some of the resulting heat of combustion is transferred back to the solid or molten polymer, thereby causing the formation of a continuous steady supply of breakdown products. In principle, flame retardance can thus be conferred by preventing or at least regarding sufficiently any one or more of these stages. The most obvious stage which can be affected by an additive is the initial breakdown of the polymer to give combustible gaseous products. In other words, a flame retardant may alter the decomposition of the polymer in such a way as to change either the nature or the rate of evolution of the gaseous products. In consequence, when these products mix with the oxidant, the composition of the resulting mixture may no longer lie within the flammable range.

There are, however, several different mechanisms by which the initial breakdown of the solid polymer can be affected. In some cases a flame retardant acts simply by chemical termination in the condensed phase of the free-radical chains by which thermal decomposition of the polymer takes place. A completely different mode of action is that exerted by apparently inert solid fillers incorporated into polymers. Such materials, when they are present in considerable quantities, both act as heat sinks as a result of their heat capacity and conduct heat away by virtue of their thermal conductivity; they may thus prevent the polymer from reaching temperatures at which it breaks down to yield significant quantities of combustible gaseous products. The temperature is of course kept down even more effectively if compounds are used which decompose endothermically. Another quite distinct method of imparting flame retardance is to arrange that the surface of the polymer is covered with a non-flammable protective coating. This will help to insulate the flammable polymer from the source of heat and thus prevent the formation, or at any rate the escape into the gas phase, of the combustible breakdown products. It may also exclude the gaseous oxidant (normally air or oxygen) from the surface of the polymer. Certain compounds which may be initially incorporated into an organic polymer either decompose or react with other materials at high temperatures to give a protective barrier in which the gaseous products of polymer decomposition are trapped as they are formed. An intumescent coating is then said to have been formed on the polymer surface. Alternatively, direct application of a non-flammable layer on the surface of the polymer yields a non-intumescent coating.

The other stage in the burning of an organic polymer which can clearly be inhibited by additives is the combustion of the gaseous products of polymer decomposition. Here again there are several distinct possible modes of action. For example, a flame retardant may cause a reactive gaseous compound to be released into the combustion zone where it enters chemically into the flame reactions, generally replacing highly active free radicals by less reactive ones. In other cases, the additive may cause the evolution during combustion of the polymer of a 'mist' of small particles which catalyse radical recombination and hence chain termination. Another possible mechanism of flame inhibition is for the additive to release, on decomposition, relatively large quantities of an inert gas which changes the composition and the temperature of the gaseous products of polymer decomposition, so that the resulting mixture with the surrounding gaseous oxidant is no longer capable of flame propagation. In some systems, when the polymer burns, the flame-retardant additive appears to be released chemically unchanged and in the form of a heavy vapour which 'smothers' the flame by interfering with the normal interchange of combustible gaseous polymer decomposition products and combustion air or oxygen.

However, it is also sometimes possible to inhibit combustion by interfering with the normal transfer of the heat of combustion back to the polymer. Thus, for example, certain additives may promote depolymerization and hence facilitate melting. As the burning melt drips away from the bulk of the polymer, it carries with it a substantial proportion of the heat which would normally be used to bring about decomposition of the polymer to volatile products and hence feed the flame. Another method of delaying, if not preventing, combustion which is associated with heat transfer effects is to coat or construct the polymer in such a way that, when it burns, incandescent sections disintegrate from the original polymer and remove much of the associated heat with them. This mechanisms of action is known as ablation (Schmidt, 1971; D'Alelio,1971; Milby,1973). A surface char layer is frequently formed which isolates the bulk of the polymeric material from the high temperature environment for at least a short period.

It is not easy in practice to distinguish between the different mechanisms by which the combustion of an organic polymer is being inhibited. Nevertheless, even though the precise modes of action of flame retardants cannot always be identified, information can sometimes be obtained as to whether additives act in the condensed phase or in the gas phase by means of the limiting oxygen index method (Fenimore and Martin, 1966a,b; Fenimore and Jones, 1966). Thus, for example, if an additive acts by interfering with the decomposition of the polymer in the condensed phase, its effect on LOI should be independent of the nature of the gaseous oxidant but would be expected to change with the structure of the organic polymer. If, however, the additive interferes with the flame reactions, its effect would be expected to be different in different oxidizing atmospheres but to be largely independent of the nature of the polymer. Similarly, microanalysis of solid residues remaining after a polymer has undergone combustion can sometimes provide a useful clue. If an element believed to be responsible for flame retardance remains in such residues, that element is likely to have acted in the condensed phase; whereas, if it has all disappeared, it has probably been functioning in the gas phase.

Smouldering combustion, as has been seen, occurs principally with polymeric materials of high surface area which break down during combustion to form a residual carbonaceous char. Here the first stage is thermal or oxidative breakdown of the polymer to form only relatively small proportions of volatile products and a solid char. The second stage consists of the ignition and burning of this char. During smouldering, ignition of the carbonaceous residue may occur at temperatures well below the ignition temperature of the volatile products. Thus the first material to ignite is the char and the volatile products often do not burn, either because there is no local ignition source of sufficient intensity or because their rate of production is so low that a flammable gaseous mixture is never formed. Here again it is possible in principle to inhibit combustion either by retarding or preventing the initial breakdown of the polymer to form a char or by interfering with the further combustion of this char. Flame retardants which affect polymer decomposition must act in the condensed phase. The possible mechanisms are clearly the same as those which apply in the case of flaming combustion. Chemical inhibitors, inert fillers, and protective coatings are all able to slow down or even prevent completely such decomposition. On the other hand, additives which interfere with the combustion of the carbonaceous char can do so by virtue of their effects on reactions taking place either in the solid phase or in the surrounding gas phase. However only relatively few compounds act as inhibitors of the oxidation of carbon. These include borates and phosphates

(Rakszawski and Parker, 1964), which act mainly in the solid phase, and various chlorine compounds (Dahl, 1961; Hippo and Walker, 1975), iodine, and sulphur dioxide (Maahs and Schryer, 1967) which function principally as gas-phase inhibitors.

1.2.3 The effect of metal compounds on polymer combustion

1.2.3.1 Introduction

Compounds containing metals have been used as flame retardants since early times, particularly for decreasing the flammability of textiles (Gay-Lussac, 1821; Perkin, 1913a,b). However, the use of such compounds as inhibitors of the combustion of organic polymers was for a considerable time overtaken by that of compounds containing non-metals (especially boron, phosphorus and the halogens), which even as recently as the 1960's accounted for about 80% of the flame retardants used (Kestler, 1966, 1970). Nevertheless, to-day metal compounds probably constitute about 50% of all flame retardants, due mainly to the dramatic rise in the volume of hydrated alumina but also to the continued use of considerable amounts of antimony oxide for reducing the flammability of certain polymeric materials (Table 1.3).

Metal oxides are the form in which metals are most extensively used as flame retardants. The large majority of metal oxides are reasonably inert compounds which do not, under normal ambient conditions, react chemically with organic polymers. Thus, in general, all metal oxides when introduced into polymeric materials, tend to act to some

Table 1.3 Amounts of metal oxides used as flame retardants for organic polymers (10^3 tonnes)

Year	$Al_2O_3.3H_2O$	Sb_2O_3	Other metal oxides
1974	50(29)	11(6)	a
1976	70(35)	11(6)	a
1978	90(43)	15(7)	a
1980	102(45)	16(7)	9(4)

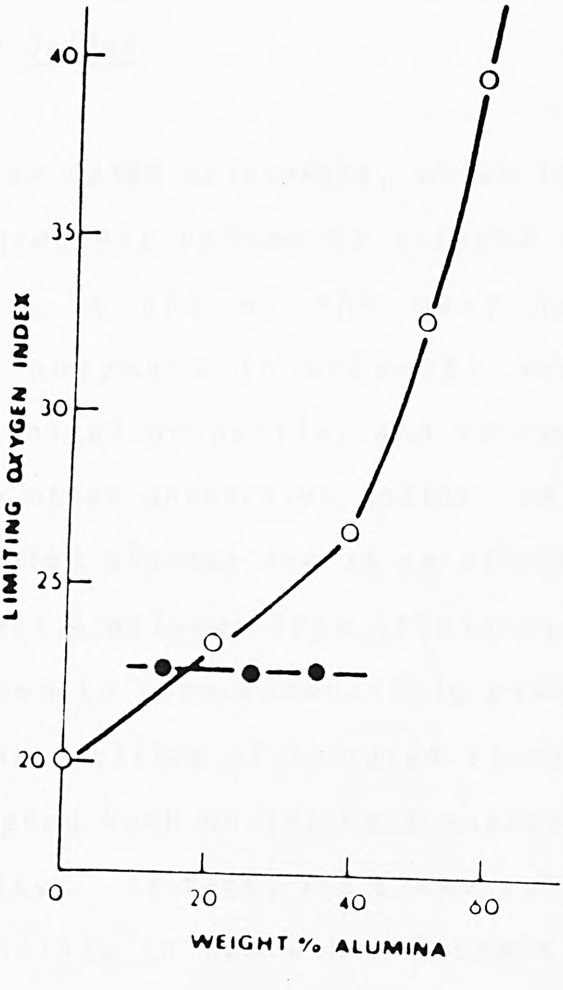
a Data not available

Figures in parentheses represent percentages of all all flame retardants used for the year in question extent as "fillers". However, for such action to be apparent, rather large amounts of oxides usually have to be incorporated into the polymer. In contrast, a wide range of metal oxides, particularly when used in conjunction with an organic halogen compounds, can affect the combustion of polymers when they are present in somewhat lower concentrations; these metal oxides can evidently exert a more specific, presumably chemical, inhibiting effect on the combustion of organic polymers.

The distinction between these two different broad modes of action is not, however, entirely clear-cut. Although hydrated alumina is one of the fillers most extensively used to reduce the flammability of organic polymers, increasing evidence is now available to show that aluminium oxides, when present in polymers in relatively low concentrations, can exhibit synergism with halogen compounds, as a result of some form of chemical interaction. In the same way, metal oxides which can exert a pronounced chemical influence on the reactions involved in polymer combustion must clearly, when incorporated into organic polymers in sufficiently high concentration, have some filler effect. It is not always possible, therefore, to attribute to any given metal oxide a single mode of flame-retardant action. Since the metal oxides most extensively used as flame retardants for polymers are those of aluminium and antimony, accounts are given first of studies of the mechanisms of less flammable (Connolly and Thornton, 1965). The suggested importance of the water in $Al_2O_3.H_2O$ receives support from the fact that anhydrous alumina, when added to epoxy resins, has little effect on the flammability (Fig. 1.4). This of course suggests that the heat capacity of hydrated alumina is not a significant property here, since on any thermal model an increased filler content ought to inhibit combustion by absorbing heat and thus lowering the maximum temperature attained by the polymer. In contrast, aluminium oxide trihydrate exerts considerable flame-retardant action (Fig. 1.4),60 wt% of this compound decreasing the flammability of expoxy resins to a far greater extent than an amount of the anhydrous oxide giving the same ratio of aluminium:polymer. However, although aluminium oxide trihydrate acts in general terms as a filler and is indeed widely believed to have no specific mode of flame retardance, chemical interaction does in certain circumstances take place between it and halogen compounds (Lyons, 1970). Thus, for example, while 20 wt% of $Al_2O_3.3H_2O$ does not by itself decrease the flammability of polyurethane foams (Papa, 1975), a lower concentration has a significant effect if a halogen compound is also present (Green, 1966).

Aluminium oxide, in both hydrated and anhydrous forms, is, however, not only a useful flame retardant but also a good smoke suppressant (Fenimore, 1970). Indeed the ability of $Al_2O_3.3H_2O$ to reduce the amount of smoke produced from

Fig. 1.4 The effect of aluminium oxide on the flammability of an epoxy resin



○, $Al_2O_3.3H_2O$; ●, Al_2O_3.

action of these compounds (1.2.3.2 + 1.2.3.3). The behaviour of other single metal oxides and some metal oxide mixtures are then discussed (1.2.3.4 + 1.2.3.5). Finally the flame-retardant effects of some other metal compounds are described (1.2.3.6-1.2.3.11).

1.2.3.2 Aluminium Oxides

Aluminium oxide trihydrate, which is the compound now used in the greatest volume as a flame retardant for organic polymers, is one of the many inert fillers incorporated into polymers in order to modify certain physical and mechanical properties and to reduce material costs. Like many other unreactive solids, relatively large quantities of hydrated alumina act as an effective heat sink and may thus prevent a polymer from attaining temperatures where it breaks down to form combustible gaseous products. The flame retardant activity of hydrated alumina would thus be expected to depend both on its heat capacity and on its thermal conductivity. In fact, its flame-retardant action is probably due mainly to two other factors. One is its endothermic dehydration to form anhydous alumina, during which it loses nearly 35% of water; the heat of dehydration is 1170 J g^{-1} (Jackson and Jones, 1978). The other factor is the release of large amounts of water vapour into the gaseous products of polymer decomposition which thus become styrene-butadiene rubbers is considerably greater than that of other inorganic fillers (Hecker et al.,1973), suggesting that alumina exerts its smoke-suppressant action by a chemical mechanism. Little fundamental work has been carried out to investigate the nature of the interaction of aluminium oxides and halogen compounds. When anhydrous alumina is heated in the presence of a chlorinated wax, only the organic halogen compound volatilises and there is no indication of the formation of volatile aluminium chloride (Benbow and Cullis, 1974, 1975) (Table 1.4). However, when an organic polymer is also present, aluminium oxides and halogen compounds may act synergistically to improve the flame retardance (Antia, Cullis and Hirschler, 1981). Thus a well-defined effect is found in experiments in which increasing amounts of an organic bromine compound are incorporated into ABS terpolymers. Interaction between the alumina and the halogen compound occurs most readily with the anhydrous oxide, suggesting that water inhibits this reaction. However, the normal release of water vapour from the hydrated oxides probably constitutes a second mode of flame-retardant action. This may explain the observed order of effectiveness of the three aluminium oxides, viz. $Al_2O_3 > Al_2O_3.3H_2O > Al_2O_3.H_2O$ because the monohydrate contains enough water to inhibit its interaction with halogen but not enough to release a significant amount of water vapour. In summary, then, aluminium oxides probably reduce the flammability of organic polymers primarily as a result of a

Table 1.4 Extent of volatilisation of metal oxides when heated with chlorinated wax

Metal oxide	Percentage of metal oxide volatilised	
	600°C	1000°C
Inert oxides		
Al_2O_3	0	0
Cr_2O_3	0	0
NiO	0	0
TiO_2	0	0
ZrO_2	0	0
Catalytic oxides		
CoO	0	0
Fe_2O_3	6	6
Reactive oxide forming involatile chloride		
Ag_2O	0	0
Reactive oxide forming probably volatile chloride		
SnO_2	16	16
Reactive oxides forming easily volatile chlorides		
Sb_2O_3	90	90
Bi_2O_3	100	100
CdO	0	100
CuO	60	94
PbO	3	81
MoO_3	38	79
ZnO	88	88

(Benbow and Cullis, 1975)

filler action and, although they usually have to be incorporated in rather large quantities in order to exert a significant flame-retardant influence, their low cost often gives them economic advantages over other metal oxides. Nevertheless, increasing evidence is now available in support also of a chemical condensed-phase flame-retardant effect of aluminium oxides. (Miller, Petrella and Manca,1976; Antia et al., 1981).

1.2.3.3 Antimony oxides

By far the commonest form in which antimony is available as a flame retardant for organic polymers is as antimony trioxide, the molecular formula of which is Sb_4O_6. Comparative experiments involving the other two antimony oxides, Sb_2O_4 and Sb_2O_5, have shown that the trioxide is easily the best flame retardant for flexible polyurethane foams (Pitts,1973). Antimony trioxide has been used, on its own, as a flame-retardant additive for certain polymers (Mack, 1960), where it has been suggested that it forms a protective inorganic coating on the surface (Pitts, 1973), or somehow encourages the dissipation of heat during the combustion process (Hilado et al., 1970). In general, however, antimony oxide is ineffective by itself (Weil, 1975) and is therefore nearly always used in conjunction with a chlorine or bromine compound. The need for the simultaneous presence of the halogen suggests, of course, that some antimony-halogen species is the active inhibiting entity.

Early work showed that the degree of flame retardance imparted increases with the ease of elimination of hydrogen chloride from the added halogen compound and it wasproposed that the species which inhibited combustion is SbOCl, formed by the interaction of Sb_2O_3 and hydrogen chloride. Since, however, the optimum Sb:Hal ratio for certain polymers is about 1:3 (Pitts, 1972), the active species is more likely to be $SbHal_3$. However, antimony trichloride is hydrolytically too unstable to be incorporated into organic polymers on its own and SbOCl may therefore be a possible precursor for $SbCl_3$, the oyxhalide breaking down by a series of reactions such as:

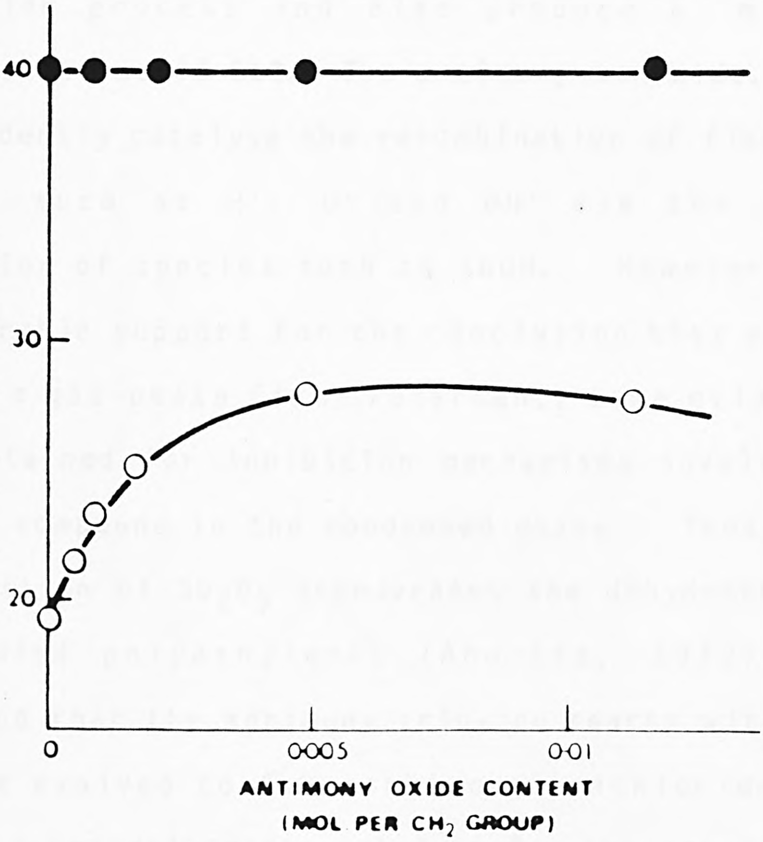
$$5SbOCl \longrightarrow Sb_4O_5Cl_2 + SbCl_3$$

$$4Sb\ O\ Cl \longrightarrow 5Sb_3O_4Cl + SbCl_3$$

$$3Sb\ O\ Cl \longrightarrow 4Sb_2O_3 + SbCl_3$$

and thus leading to the formation of antimony trichloride and antimony trioxide (Pitts et al., 1970). However, mass-spectrometric evidence that no antimony oxychloride is present in the gas phase (Hastie, 1973) casts doubt on the importance of the oxyhalide as an intermediate. The finding that the inhibiting effect on the combustion of polypropylene of an Sb_2O_3-halogen system depends on the nature of the gaseous oxidant (Fenimore and Jones,1966) (Fig. 1.5) suggests that antimony acts in the gas phase. Furthermore, the major part of the antimony (and an even greater proportion of the

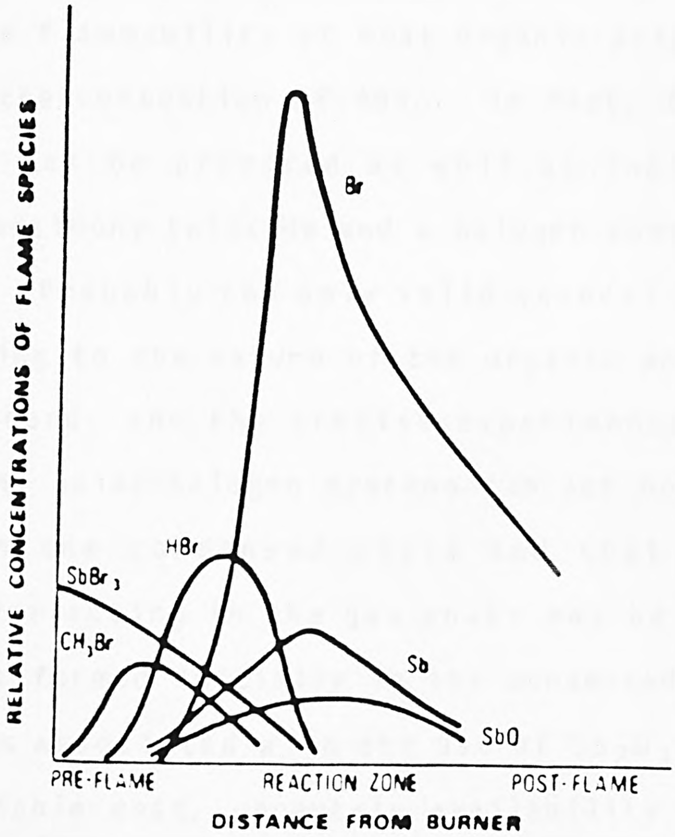
Fig. 1.5 The effect of antimony oxide content on the flammability of a chlorinated polyethylene ($C_2H_{3.94}Cl_{0.06}$).(Fenimore and Jones, 1966)



○, Oxidant O_2; ●, oxidant N_2O

halogen) is lost during the combustion of halogen-containing polymers (Brauman and Brolly, 1976). The direct introduction of $SbCl_3$ and $SbBr_3$ into a premixed methane-oxygen flame leads to the formation of antimony monoxide, SbO, and hydrogen halide in the reaction zone (Hastie and McBee, 1975) (Fig. 1.6). Thus antimony halides may both provide a source of hydrogen halide early on in the combustion process and also produce a 'mist' of fine particles of solid SbO. The antimony monoxide, in this form, can evidently catalyse the recombination of flame-propagating species such as $H^\cdot$, $O^\cdot$ and $OH^\cdot$ via the intermediate production of species such as SbOH. However, despite the considerable support for the conclusion that antimony oxide acts as a gas-phase flame retardant, some evidence has also been obtained for inhibition mechanisms involving reactions of this compound in the condensed phase. Thus, for example, the addition of Sb_2O_3 accelerates the dehydrochlorination of chlorinated polyethylenes (Abu-Isa, 1972), and it is suggested that the antimony trioxide reacts with the hydrogen chloride evolved to form antimony trichloride, which then acts as a Friedel-Crafts catalyst for the dehydrochlorination process. Benzyl chloride, another Friedel-Crafts reagent, has been used in conjunction with Sb_2O_3 in polystyrene and condensed-phase effects have again been found (Brauman, 1979). Other studies also show that the initial reaction between antimony trioxide and halogen compounds takes place in the condensed phase to form the corresponding antimony

Fig. 1.6 The formation of chemical species in a pre-mixed methane-oxygen flame containing antimony tribromide (Hastie, 1973)



trihalides (Brauman, 1976a). It is important to recognise,, however,that the action of antimony trioxide can vary considerably according to the nature of the organic polymer. For example, the introduction of Sb_2O_3-chlorine compound mixtures does not affect the breakdown of polypropylene (Uehara and Suzuki, 1975) but appears to enhance charring in polystyrene and polyesters (Brauman, 1976b). Similarly, the incorporation of antimony trioxide + decabromobiphenyl oxide decreases the flammability of most organic polymers but does not inhibit the combustion of ABS. In fact, the combustion of polymers can be promoted as well as inhibited by the presence of antimony trioxide and a halogen compound (Brauman et al.,1976). Probably the only valid general conclusion is that, according to the nature of the organic polymer and the halogen compound, and the precise experimental conditions used, antimony oxide-halogen systems can act both in the gas phase and in the condensed phase and that the species responsible for acting in the gas phase may be produced via other species formed initially in the condensed phase. The main problems associated with the use of Sb_2O_3 are those of high and variable cost, uncertain availability and toxicity. In addition, fabrics containing the oxide usually have bad after-glow properties (Reeves, 1970) and, when halogen compounds are also present, tend to give during combustion large quantities of greyish-white smoke. Antimony oxide is generally unsuitable for use in transparent plastic articles owing to its strong pigmentation effect; it also makes certain polymers undesirably rigid and brittle (Rhys, 1969). For many years, therefore, attemps have been made to find suitable substitutes for antimony oxide and in this context other metal oxides have been very fully investigated.

1.2.3.4 Other single metal oxides

In the search for possible alternatives for antimony oxide, measurements have been made of the flame-retardant effect on polyethylene (Fenimore and Martin, 1966b, unsaturated polyester resins (Learmonth and Thwaite, 1970) and polyurethane foams (Pitts, 1973) of arsenic and bismuth oxides when used in conjunction with chlorine. Arsenic oxide is more toxic and significantly less effective than antimony oxide, while bismuth oxide appears to be more or less ineffective. On the other hand, Bi_2O_3 has some flame-retardant action on chlorinated polymers (Ballistreri et al. 1979). Stannic acid ($SnO_2.H_2O$) has also been recommended as a replacement for antimony oxide in polyethylene, polypropylene and ABS copolymers (Touval, 1972) but it is less effective (Pitts, 1973). Like Sb_2O_3 it apparently reacts with the halogen compound to form the actual flame-quenching species. Stannic acid is not generally used to reduce the flammability of synthetic polymers, although it is still quite widely employed for conferring flame retardance on cellulosic fibres. Magnesium oxide decreases the smoke-forming tendency of some chlorinated polymers and also lowers the level of smoke formation from polyesters. Molybdenum trioxide is a well-established flame retardant for certain organic polymers and is also an effective smoke-suppressant (Church and Moore, 1975; Skinner, 1976).

In order to compare the likely flame-retardant action of metal oxides with that of antimony oxide, thermogravimetric studies have been made of a whole range of such oxides mixed with a chlorinated wax (Benbow and Cullis, 1974, 1975). Table1.4 shows the extent of their volatilisation as metal chlorides. Inert oxides are not volatilised and do not affect the decomposition of the chlorinated wax. Catalytic oxides appear to change completely the mechanisms of decomposition of the halogen compound. Silver oxide forms a solid residue of involatile silver chloride; SnO_2 is only partially volatilised. Some reactive oxides are more or less completely volatilised but appear to operate by a different mechanism from Sb_2O_3. Oxides of strongly oxidising acids (e.g. CrO_3 and Mn_2O_7) react readily with chlorinated wax to an extent dependent on the efficiency of mixing of the metal oxide with the halogen compound.

1.2.3.5 Mixtures of metal oxides

Work on polymer systems containing two or more metal oxides has been inspired by the desirability either of

Table 1.5. Flammability of polyurethane foams containing 10 wt% antimony trioxide, 5 wt% other metal oxide and 6.3 wt% organic chlorine compound

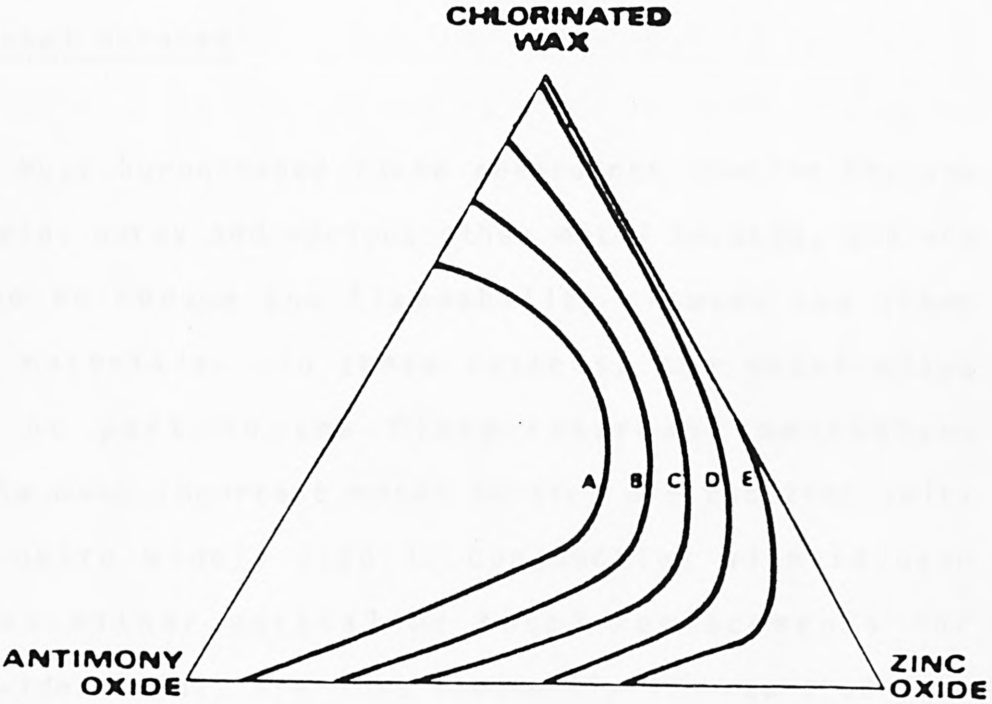
Other metal oxide	Flammability rating	Length of burn (cm)	Burning rate (cm min^{-1})
CaO	Burning	>12	13.7
MgO	Burning	>12	9.4
ZnO	Burning	>12	9.1
MoO_3	Burning	>12	8.9
$Fe_2O_3.H_2O$	Burning	>12	6.3
MnO_2	Self-extinguishing	8.1	8.1
CeO_2	Self-extinguishing	6.3	7.6
Al_2O_3	Self-extinguishing	6.1	7.4
None	Self-extinguishing	5.3	7.4
$Al_2O_3.3H_2O$	Self-extinguishing	5.6	7.4
Bi_2O_3	Self-extinguishing	5.3	7.9
SnO_2	Self-extinguishing	5.3	7.6
SnO^2	Self-extinguishing	5.3	7.6
As_2O_3	Self-extinguishing	5.1	7.4
Fe_2O_3	Self-extinguishing	4.6	7.9
TiO_2	Self-extinguishing	4.6	6.6
CuO^2	Self-extinguishing	4.3	7.6

[a] ASTM D 1692

(Pitts, 1973)

rate, of improving the performance of this compound as a flame retardant. In some cases, quite large amounts of other metal oxides have to be introduced in order to replace a significant proportion of the antimony oxide normally used, whereas in other systems, much smaller quantities of a second oxide may have a useful effect. A considerable number of metal oxides have been investigated as partial replacements for antimony oxide in flexible polyurethane foams containing some chlorine (Pitts, 1973) (Table 1.5). Some of these had a detrimental effect on the flammability of the polymer. Others had virtually no effect on the combustion behaviour, while a few compounds, particularly Fe_2O_3, CuO and TiO_2, improved the flame retardance. Of these last three metal oxides, iron(III) oxide was the most effective inhibitor of polyurethane combustion; the fact that only very small amounts were needed both of this oxide and of CuO suggests that these two compounds exert some sort of catalytic effect. The influence of TiO_2 is less pronounced than that of Fe_2O_3 amd CuO and considerably greater amounts of this oxide are needed to cause a significant improvement in the flame retardant action of antimony oxide. Measurements of the effects of these oxides on the thermal decomposition of antimony oxychloride indicate some interesting and significant results. Thus Fe_2O_3 and CuO, both of which improve the flame-retardant influence of Sb_2O_3, lower the initial decomposition temperature of SbOCl. In contrast, CaO and ZnO, which have an antagonistic effect on the action of antimony oxide, apparently inhibit the breakdown of the oxychloride. This strongly suggests that SbOCl is the first product formed in systems containing Sb_2O_3 and a halogen compound and that this then undergoes thermal decomposition to yield antimony trichloride as the actual species responsible for flame retardance. Molybdenum trioxide has also been used in conjunction with antimony oxide. It acts mainly in the condensed phase since the bulk of the element remains in the ash of the unburnt polymers (Moore, and Tsigdinos, 1977). Studies have also been made of the flame-retardant effects of both anhydrous and hydrated metal oxides as partial substitutes for antimony trioxide in polyethylene (containing a chlorinated wax) and ABS (containing decanbromobiphenyl) (Antia, Cullis and Hirschler, 1982). In ABS, the substitution of SnO_2 for some of the Sb_2O_3 decreased the flame retardance slightly but in polyethylene it caused almost no change in polymer flammability. The flame-retardant effect of $ZnO+Sb_2O_3$ mixtures was generally smaller than that of antimony trioxide alone in both polymers (Fig. 1.7). In contrast, the introduction of Fe_2O_3, especially in low concentrations, enhanced the flame-retardant effect of Sb_2O_3 in polyethylene; this is probably attributable to the fact that Fe_2O_3 lowers the temperature at which the antimony oxide reacts with the chlorinated wax as a result of its catalysis of the decomposition of the halogen compound. However, the main conclusion appears to be that, at least in polyethylene and ABS, when a second metal oxide is used as a

Fig. 1.7 The effect of the composition of ternary mixtures of antimony oxide, zinc oxide and a chlorinated wax on the limiting oxygen index of polyethylene (Antia et al., 1982)



Samples containing 70 wt% of polymer. Limiting oxygen indices: A=2.48; B=24.0; C=23.2; D=22.4; E=21.6

partial replacement for Sb_2O_3, the resulting systems are not generally as effective as those in which antimony oxide is the only metal oxide present. Some experiments were also carried out with the same polymers containing mixtures of SnO+ZnO and $SnO+Al_2O_3 \cdot H_2O$ together with the appropriate halogen compounds (Antia et al., 1982). Although none of these oxides is a very effective flame retardant on its own, they nevertheless show increased activity when mixed.

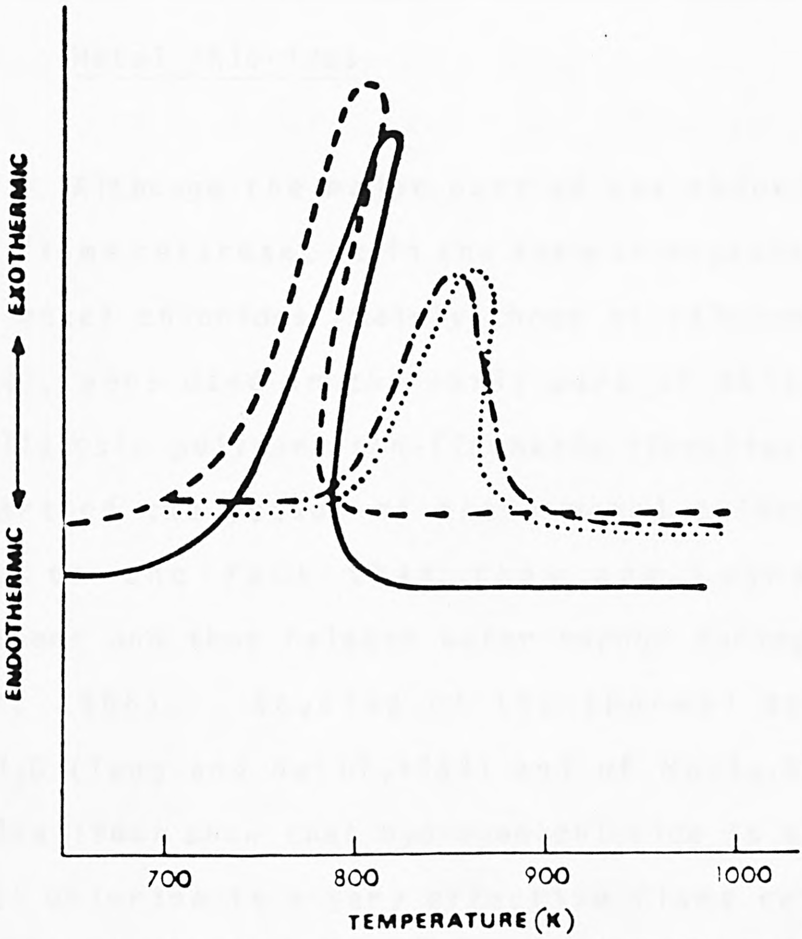
1.2.3.6 Metal borates

Most boron-based flame retardants involve the use of boric acid, borax and various other metal borates, and are widely used to reduce the flammability of wood and other cellulosic materials. In these systems, the metal plays little or no part in the flame-retardant mechanism. Probably the most important metal borates are the zinc salts which are quite widely used in conjunction with halogen compounds as either partial or total replacements for antimony oxide. They are most frequently incorporated into polyesters, polyolefins or halogenated polymers. Zinc halides or oxyhalides appear to be formed and these inhibit the flame reactions (Kestler, 1970). It has been suggested that there is some interaction between the zinc and the boron, because other zinc compounds are not very effective flame retardants on their own. However, comparative studies have been made of the differential thermal analysis curves of poly(vinyl chloride) containing zinc borate alone. Sb_2O_3 alone and a mixture of the two compounds (Woods, 1975) (Fig. 1.8). The thermal behaviour of the polymer containing antimony oxide is almost the same as that of the polymer on its own but samples containing zinc borate react only at temperatures 100° higher. This suggests that the mechanisms of flame-retardant action must be different for the two compounds and that zinc borate probably acts mainly in the condensed phase. Studies have also been made of the flame-retardant effects of barium and calcium borates, which are used to some extent in cotton. However, experiments with polyester resins (Learmonth and Thwaite, 1970; Pitts, 1973) show that these compounds are not very effective flame retardants. Nevertheless, a modified barium metaborate has recently been claimed to be a useful substitute for antimony oxide in certain polymers (Prieto, 1976).

1.2.3.7 Metal phosphates

Both organic and inorganic phosphates are widely used for conferring flame retardance on oxygen-containing polymers such as cellulose. Among inorganic phosphates, the ammonium compounds are the most widely used and have extensive applications in connection with both natural and synthetic organic polymers. For certain purposes, however, some more insoluble metal phosphates have advantages over the

Fig. 1.8 The effect of antimony oxide and zinc borate on the oxidative degradation of poly(vinyl chloride)(Wood, 1975)



—, PVC alone; - -, PVC containing 10 phr Sb_2O_3;
.., PVC containing 10 phr zinc borate; -.-., PVC containing 5 phr Sb_2O_3 + 5 phr zinc borate

ammonium compounds. Thus magnesium ammonium phosphate is widely used in flame-retardant paints since it has a relatively low susceptibility to leaching (Terrisse and Coffignier, 1909). It can also be applied in the form of an aqueous slurry to flexible polyurethane foams where it appears to form an intumescent coating and has little effect on the physical properties of the polymer (Pruitt, 1970).

1.2.3.8 Metal chlorides

Although the major part of the chlorine used today as a flame retardant is in the form of organic compounds, various metal chlorides (mainly those of calcium, magnesium and zinc), were used in the early part of this century to make cellulosic polymers non-flammable (Conklin, 1922). At least part cf the action of these metal chlorides can be ascribed to the fact that they are hygroscopic or deliquescent and thus release water vapour during combustion (Eickner, 1966). Studies of the thermal behaviour of $AlCl_3.6H_2O$ (Tang and Neill, 1964) and of $MgCl_2.6H_2O$ (Langer and Gohlke, 1966) show that hydrogen chloride is also evolved. Iron(III) chloride is a very effective flame retardant for cotton, particularly in the form of blends with polyesters; it causes the formation of only very small amounts of char during combustion (Inagaki et al., 1979). Titanium(IV) chloride is used as a flame retardant for wool (Benisek, 1971). Zirconium compounds are slightly less effective, probably because the smaller titanium ions penetrate the wool more efficiently (Gordon and Stephens 1974; Benisek, 1975) but they do not cause yellowing of the wool as titanium does.

1.2.3.9 Metal sulphates

Metal sulphates, especially those of calcium, aluminium and iron, are among the oldest flame retardants for organic polymers, having been used mainly to reduce the flammability of cellulosic materials. Nowadays the ammonium compounds are the only sulphates used extensively as flame retardants, still having wide application for combating forest fires. However, potassium and ammonium alum are used to a very small extent for flame-proofing paper and polyesters, copper sulphate for treating wood and barium sulphate as a constituent of paints. In none of these compounds is the metal an active flame-retardant constituent and at least with cellulosic polymers, the metal sulphates probably act analogously to ammonium sulphates and sulphamates, by breaking down to yield sulphuric acid. This then forms cellulose sulphate esters, so that there is a change in the route by which the polymer decomposes during the combustion process.

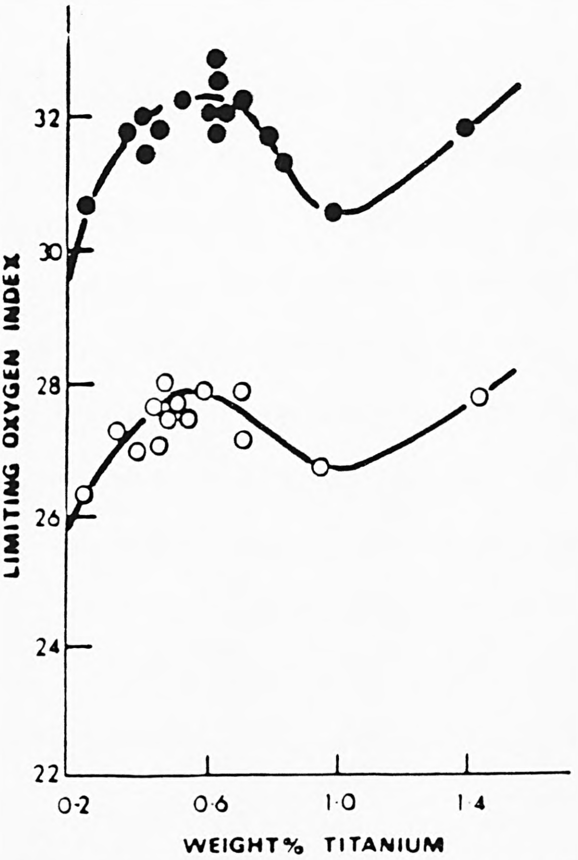
1.2.3.10 Metal carbonates and bicarbonates

Only a few metal carbonates and bicarbonates are used as flame retardants for polymers. One reason for this is that most of these compounds decompose at rather low temperatures, so that they cannot survive normal processing conditions. However, both potassium carbonate (Eickner, 1962) and potassium bicarbonate (Gordon and Stephens, 1974) have been used as flame retardants for wood. They appear to lower the decomposition temperature of α-cellulose and also increase the yield of char (Eickner, 1966). Unfortunately, with metal carbonates which decompose in the correct temperature region (200-400^{o}C), only relatively small amounts of CO_2 are evolved on a weight basis. The more thermally stable carbonates, e.g. Na_2CO_3 and $CaCO_3$, probably act primarily as inert fillers, although they may decompose at higher temperatures. There is no evidence that the metals in carbonates or bicarbonates play an active flame retardant rôle.

1.2.3.11 Metal complexes and organometallic compounds

Many of the metals, which appear to be active constituents of metal-containing flame retardants, can also be used in the form of compounds other than those mentioned earlier. Thus, aluminium-based flame retardants, which function primarily as inert fillers, include a variety of aluminosilicates as well as the oxides. Indeed, various other silicates also act as efficient fillers and recent work has shown that magnesium silicate can have a greater flame-retardant effect than hydrated alumina. Although Sb_2O_3 is by far the most widely used antimony-based flame retardant, other antimony compounds, e.g. Sb_2S_3, Sb_2S_4 and sodium and potassium antimonates, have advantages for certain applications. As regards titanium and zirconium compounds, which are widely used for conferring flame retardance on wool (Benisek, 1974; Gordon et al. 1974, 1977; Beck at al. 1976a,b), it is generally easiest to apply these metals to wool in the form of fluorine-containing complexes (Gordon et al.,1975a,b, 1977; Friedman,1978). The variation of limiting oxygen index with metal content is almost independent of the oxidising atmosphere (Fig.1.9), showing that the metals exert their flame-retardant effect via a condensed phase mechanism. Tin is also used to some extent as hexafluorostannates (Ingham, 1975). Similarly, ammonium and sodium molybdates, molybdenum sulphides and various organomolybdenum compounds are sometimes used in preference to molybdenum trioxide. Finally, ferrocene is an especially useful compound of iron for conferring flame retardance on halogenated polymers, where it increases considerably the formation of aromatic products as well as of char (Lecomte et al., 1977; Bert et al., 1977/1978; Descamps et al., 1980). There is one class of metal-containing flame retardant in which the metal acts primarily as a carrier for the subsequent release of gaseous ammonia. Whereas most ammonium salts contain less than 25 wt% of ammonia, some metal-amine complexes of the type $M(NH_3)_nX$ contain up to

Fig. 1.9 The effect of hexafluorotitanate on the flammability of wool (Gordon et al., 1977)



○ , oxidant O_2; ●, oxidant N_2O

40 wt% of this compound. Thus the complexes, $Ni(NH_3)_6(BF_4)_2$ and $Zn(NH_3)_4(BF_4)_2$ have been claimed to be useful for reducing the flammability of polyethylene (Rapp, 1966) and polypropylene (Wolheim, 1966) and cobalt ammines have been shown to be very good flame retardants for flexible polyurethane foams (Pitts, 1971).

1.3 Photodegradation of Organic Polymers

1.3.1 Introduction

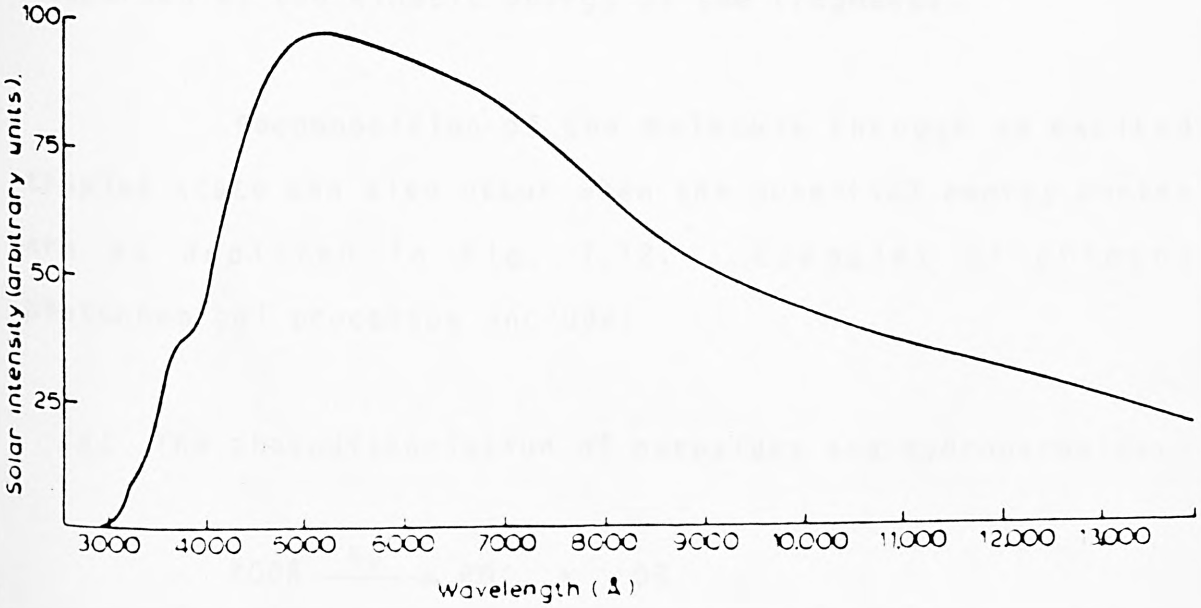
Although polymers vary widely in their resistance to photodegradation, almost every polymer deteriorates on continued exposure to solar radiation during outdoor weathering.

The solar spectrum outside the Earth's atmosphere extends from about 200 to 2500 nm, half of this energy being concentrated in the visible region of the spectrum, 40% in the infrared, and 10% in the ultraviolet. Practically all the radiation below 295 nm is filtered out by the atmosphere so that the solar energy reaching the Earth's surface is distributed according to the spectrum shown in Fig. 1.10. The ultraviolet part of the sunlight that reaches the surface of the Earth (from 400 to 300 nm) is called the solar ultraviolet. It represents only about 6% of the total radiation of the sun, but is the most damaging to polymers.

1.3.2 Photochemical processes

Photochemical processes are chemical reactions in which excited states resulting from absorption of light are involved. A primary photochemical process arises when decomposition or dissociation of the molecule occurs as a

Fig. 1.10 Solar energy distribution at noon in midsummer in Washington, D.C. (Koller, 1965)



direct consequence of the absorption of radiation. In this case the potential energy curves are usually as shown in Fig. 1.11. Fig. 1.11(a) shows electronic excitation resulting from the formation of a dissociative excited state such that the atoms repel each other at any separation distance, r Fig. 1.11(b) shows that a stable excited state is reached but dissociation of the molecule occurs because absorption of energy raises the molecule to a point above the dissociation limit of the upper state. In this case energy may be dispersed as the kinetic energy of the fragments.

Decomposition of the molecule through an excited triplet state can also occur when the potential energy curves are as depicted in Fig. 1.12. Examples of primary photochemical processes include:

(a) The photodissociation of peroxides and hydroperoxides:

$$ROOR \xrightarrow{h\nu} RO^{\cdot} + {}^{\cdot}OR$$

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

These reactions are likely to play an important rôle in the photo-oxidation of polymers.

(b) The photodecomposition of alkyl halides:

$$RCl \xrightarrow{h\nu} R^{\cdot} + Cl^{\cdot}$$

Fig. 1.11 Photodissociation of a molecule (a) by excitation above the dissociative limit of an upper state; (b) through a dissociative excited state

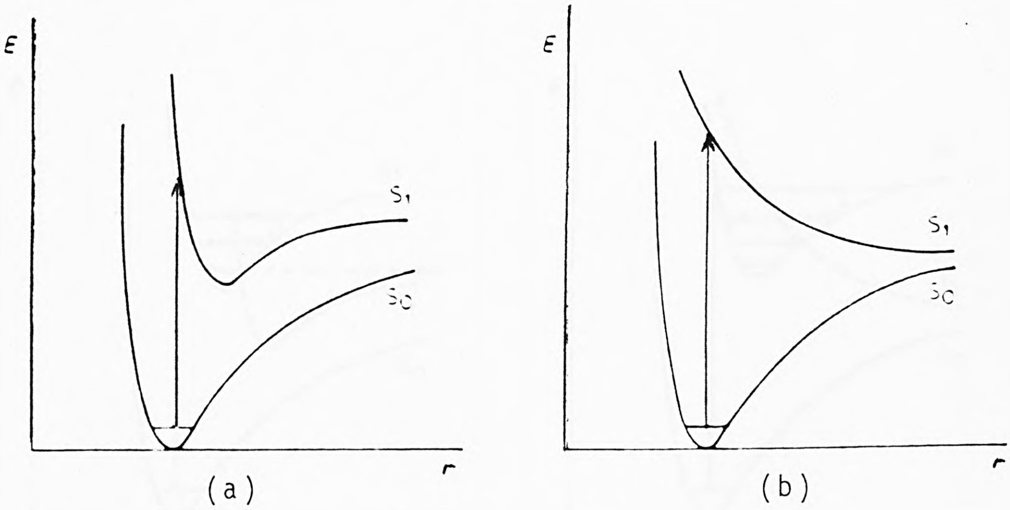
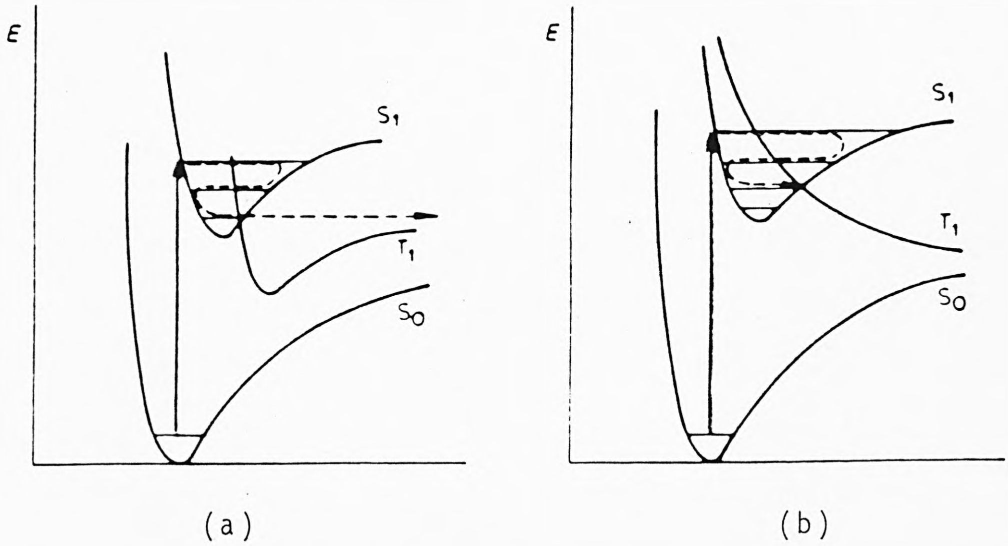


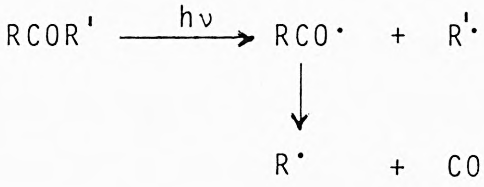
Fig. 1.12 Photodissociation of a molecule through a triplet state



(a) (b)

This type of reaction could be responsible for the initiation of the photodegradation of poly(vinyl chloride).

(c) The Norrish type I process in the photolysis of ketones:



$$\begin{tikzcd} RCOR' \arrow[r, "h\nu"] & RCO^{\cdot} \arrow[d] & + & R'^{\cdot} \\ & R^{\cdot} & + & CO \end{tikzcd}$$

Such a reaction is involved in the photodegradation of many partly oxidized polymers.

The first two processes probably occur through a dissociative excited state (Fig. 1.11(a)). The photolysis of ketones is more complex and it is suggested that the Norrish type I split occurs partly through excitation above the dissociation limit of an upper state. Various types of photochemical reaction, such as addition, substitution, atom abstraction and rearrangement, can arise from either singlet or triplet excited states of molecules. They can be described as secondary photochemical processes. If a secondary photochemical process is to arise from the excited singlet state of a molecule, it must be sufficiently fast to compete with the other deactivation processes. Since excited triplet states have much longer lifetimes, more secondary photochemical processes are likely to occur from levels of that multiplicity.

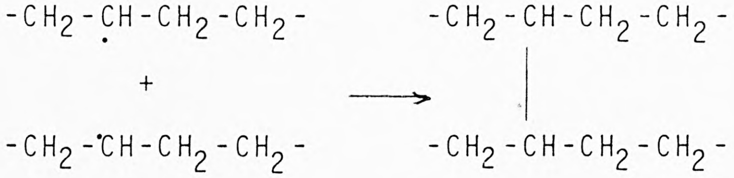
1.3.3 Photodegradation of hydrocarbon polymers

1.3.3.1 Polyethylene

In the absence of oxygen, pure polyethylene is a relatively stable material under u.v.-radiation. After long exposure to u.v. light of short wavelength (253.7 nm) in vacuum or in a nitrogen atmosphere, chain sission (I) and hydrogen abstraction (II) occur. Crosslinking (III) and evolution of hydrogen (IV) are also observed.

$$-CH_2-CH_2-CH_2-CH_2 \xrightarrow{+h\nu} -CH_2-\dot{C}H_2 + \dot{C}H_2-CH_2- \qquad (I)$$

$$-CH_2-CH_2-CH_2-CH_2 \xrightarrow{+h\nu} -CH_2-\underset{\bullet}{C}H-CH_2-CH_2- + \dot{H} \qquad (II)$$



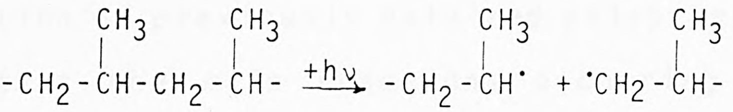
$$-CH_2-\underset{\bullet}{C}H-CH_2-CH_2- + -CH_2-\dot{C}H-CH_2-CH_2- \longrightarrow \begin{array}{c} -CH_2-CH-CH_2-CH_2- \\ | \\ -CH_2-CH-CH_2-CH_2- \end{array} \qquad (III)$$

$$H^{\bullet} + H^{\bullet} \longrightarrow H_2 \qquad (IV)$$

ESR spectroscopy shows that the mechanism of the degradation of polyethylene by u.v. light is more complicated than was at first assumed i.e. reactions (I)-(IV). At present the mechanism of degradation has not been satisfactorily established. The physical properties influence the photoprocesses. It has been shown that the crosslinking of polyethylene chains is increased when the film thickness and crystallinity decrease. Most commercially available samples of polyethylene exhibit in their ultraviolet spectrum a shoulder in the neighbourhood of 280 nm (Oster et al., 1959). This must be attributed to trace amounts of aliphatic carbonyl groups as shown by the small infrared absorption peak at 1720 cm^{-1} (Cross et al., 1950). Since it is known that the wavelength of maximum sensitivity of polyethylene is around 300 nm (Trozzolo, 1972), carbonyl groups present in commercially available samples are most probably responsible for the photodegradation of polyethylene in sunlight.

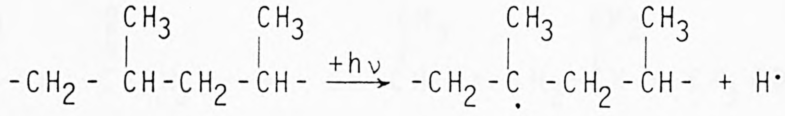
1.3.3.2 Polypropylene

Polypropylene usually exhibits an ultraviolet absorption extending beyond 290 nm, although the pure polymer would not be expected to show an absorption beyond 200 nm. Photodegradation of polypropylene is thus likely to be initiated by impurities such as hydroperoxides or ketonic oxidation products formed during the processing of the sample. The primary events following irradiation of polypropylene with u.v.-light 253.7 nm in vacuum are bond scission (I) and crosslinking (IV):



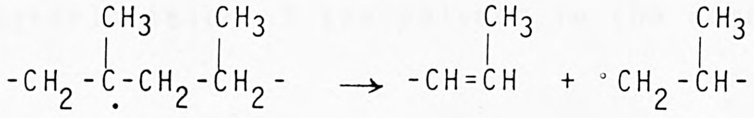
$$-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-\overset{CH_3}{\overset{|}{C}}H- \xrightarrow{+h\nu} -CH_2-\overset{CH_3}{\overset{|}{C}}H^{\cdot} + {}^{\cdot}CH_2-\overset{CH_3}{\overset{|}{C}}H- \qquad (I)$$

Another probable reaction is the dissociation of carbon-hydrogen bonds at the tertiary carbon atom (Ershov and Gak, 1967):



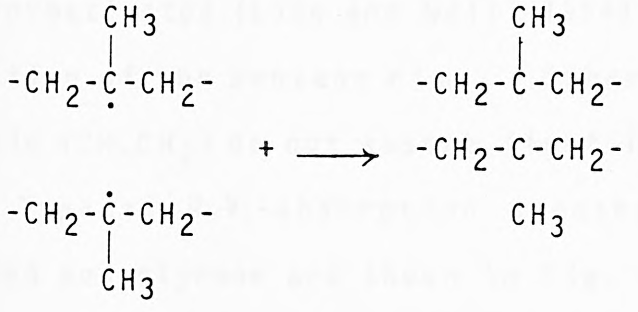
$$-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-\overset{CH_3}{\overset{|}{C}}H- \xrightarrow{+h\nu} -CH_2-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\overset{CH_3}{\overset{|}{C}}H- + H^{\cdot} \qquad (II)$$

which may lead to chain scission by a disproportionation reaction:



$$-CH_2-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\overset{CH_3}{\overset{|}{C}}H_2- \longrightarrow -CH=\overset{CH_3}{\overset{|}{C}}H + {}^{\circ}CH_2-\overset{CH_3}{\overset{|}{C}}H- \qquad (III)$$

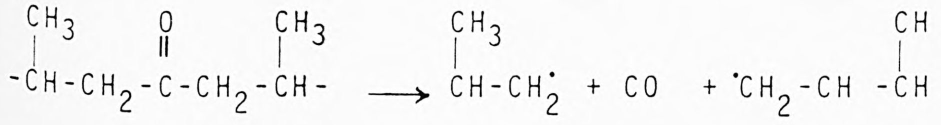
When two polypropylene radicals combine, a crosslink is formed:



$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-CH_2-\dot{C}-CH_2-}} \qquad -CH_2-\dot{C}-CH_2- \;+\; \longrightarrow \; \begin{matrix} CH_3 \\ | \\ -CH_2-C-CH_2- \\ -CH_2-C-CH_2- \\ CH_3 \end{matrix}$$

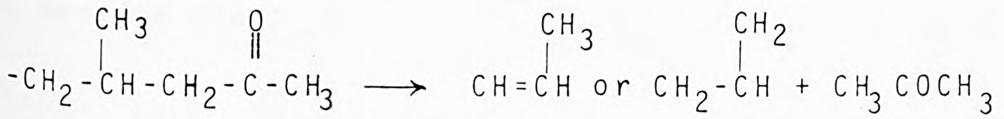
(IV)

Carlsson and Wiles (1969) studied the changes in the infrared spectrum and the composition of the volatile products evolved on irradiation of previously oxidized polypropylene. They concluded that the main reactions occurring during the photolysis are:



$$-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{C}H- \longrightarrow \overset{\overset{CH_3}{|}}{C}H-\dot{C}H_2 + CO + \dot{C}H_2-CH-\overset{\overset{CH}{|}}{C}H$$

(Norrish type I)



$$-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH=\overset{\overset{CH_3}{|}}{C}H \text{ or } CH_2-\overset{\overset{CH_2}{|}}{C}H + CH_3COCH_3$$

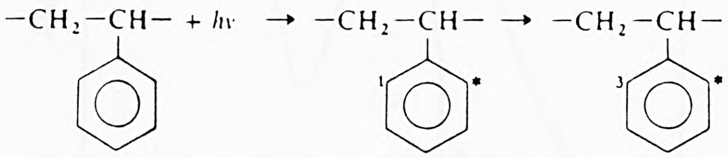
(Norrish type II not involving free radicals)

The photolysis of the polymeric ketones is believed to be the main cause of deterioration of the polymer in the absence of air.

1.3.3.3 Polystyrene

The u.v.-absorption spectrum of polystyrene has been investigated (Loux and Weill 1954) and is due to $^1S \leftarrow S$ transition of the benzene ring. Other parts of the polymer molecule (CH,CH_2) do not absorb light in the region above 200 nm. Typical u.v.-absorption spectra for undegraded and degraded polystyrene are shown in Fig. 1.13.

Absorption of a light quantum by the benzene ring is the first step producing excitation of the ring at excited singlet states which are transformed by intersystem crossing to the triplet state:



The secondary step is the reaction of the triplet state of the benzene ring:

(i) Triplet energy of the excited benzene ring may be used for the dissociation of the C_6H_5-C bond:

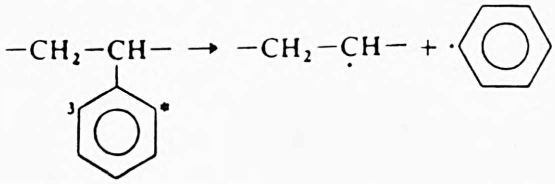
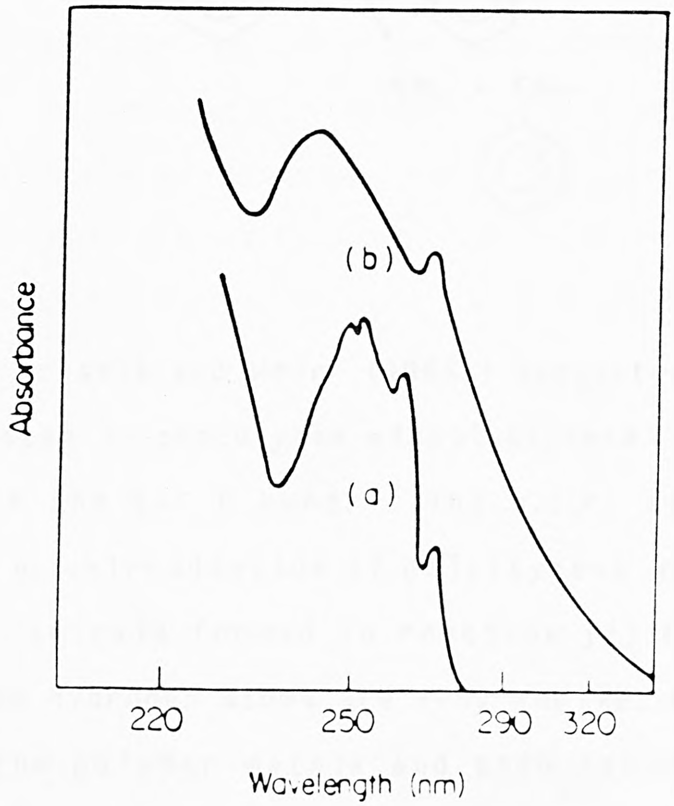
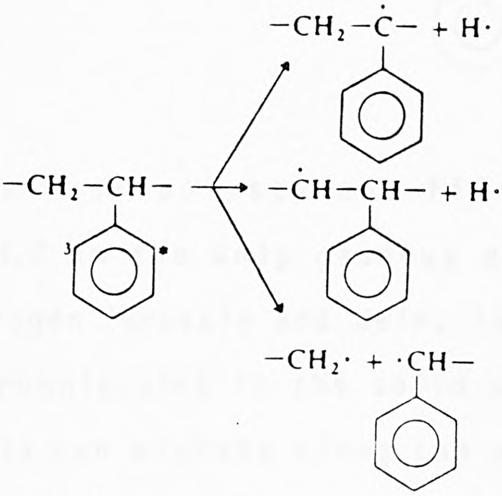


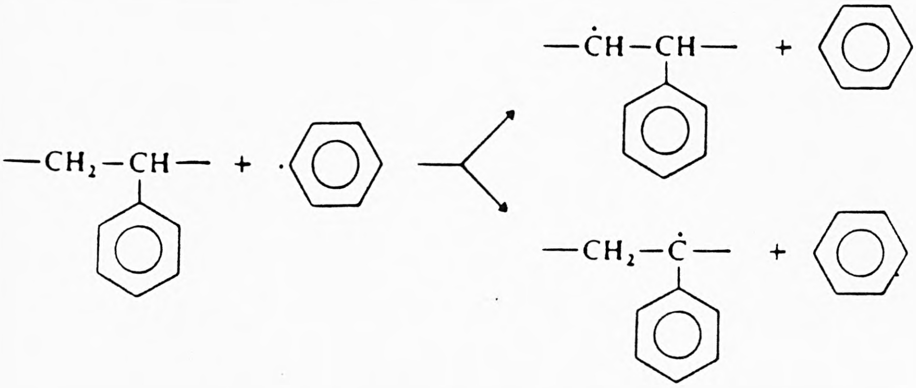
Fig. 1.13 Ultraviolet absorption spectra of: (a) undergraded and (b) degraded polystyrene (Beachell and Smiley, 1967)



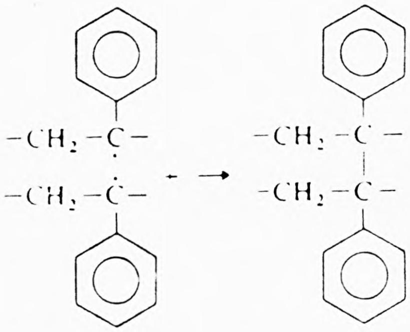
(ii) Triplet energy excitation can be transferred by intramolecular energy transfer to the C-H or C-C bonds:



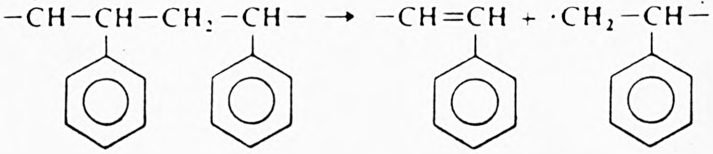
Grassie and Weir (1965a) suggested that the most important step in photolysis of polystyrene in vacuum is the scission of the α-C-H bond. The e.s.r. spectra obtained during the u.v.-irradiation of polystyrene were interpreted as due to radicals formed in reaction (I) (Cozzens et al., 1968). The hydrogen atoms are very mobile; they can diffuse out from the polymer matrix and then recombine with each other to give molecular hydrogen. Phenyl radicals cannot diffuse out, because of their limited mobility, and they are expected to react only in the immediate environment. The most probable reaction is the abstraction of hydrogen atoms from polymer molecules by phenyl radicals:



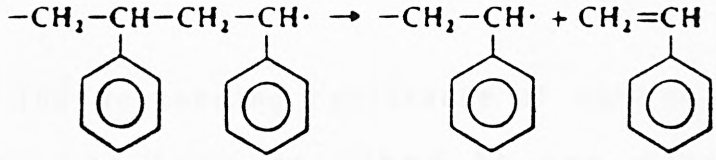
During photolysis of polystyrene films in vacuum with radiation of 253.7 nm the only gaseous product evolved was found to be hydrogen (Grassie and Weir, 1965a). The movement of polymer macromolecules in the solid state is restricted, but free radicals can migrate along the polymer chain until they are trapped by other free radicals or by impurities. When two macroradicals are near to each other, crosslinking may occur:



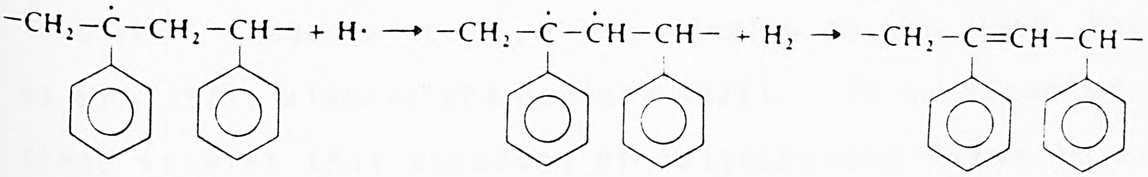
On the other hand macroradicals may disproportionate, involving a scission process:



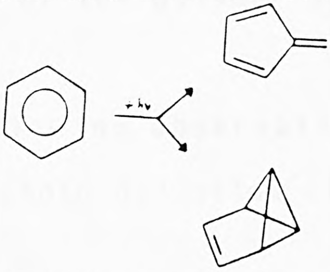
When an end group radical is produced, unzipping may occur with the formation of the monomer:



During u.v.-irradiation polystyrene samples show increased optical density and slight yellowing. This discoloration of polystyrene has been attributed by Grassie and Weir (1965c) to the build-up of conjugated bond sequences in the polymer backbone:



Rabek and Ranby (1974) have attributed the yellow coloration in vacuum to the photoisomerization of benzene molecules present in the photodegraded polymer, or of benzene rings in polystyrene, to fulvene(a) and benzalvene(b).



The yellow colour of fulvene is due to its conjugated double bond system

1.3.4 Photo-oxidation of hydrocarbon polymers

1.3.4.1 Polyethylene

The weathering resistance of commercial grades of polyethylene has been ascribed to the photo-oxidation reactions which occur preferentially close to the surface of the sample (Winslow et al., 1968) and are due to the presence of impurities or extraneous carbonyl groups. A number of investigators have measured changes in the ultraviolet and infrared absorption spectra of samples irradiated in the presence of oxygen as criteria of the photo-oxidation involved (Heacock et al., 1968; Winslow et al., 1969; Hogea et al., 1971; Wiechec and Janicka 1972). It is reported in these studies that exposure of polyethylene films to u.v. light in air leads to the uptake of oxygen, formation of carbonyl, hydroxyl and vinyl groups, evolution of acetone, acetaldehyde, water, carbon monoxide and carbon dioxide, increase in brittleness, formation of crosslinks, and mechanical failure of the polymer samples.

The following observations were made during the initial stages of photo-oxidation of polyethylene:

(i) The initial irradiation of polyethylene with u.v. light of 253.7 nm in either oxygen or nitrogen atmospheres results in an increased absorption peak was assigned to conjugated unsaturation (Charlesby et al., 1962) assumed to arise as a result of the following reaction sequence:

$$-CH_2-\underset{\bullet}{C}H-CH_2-CH_2-CH_2-CH_2- \xrightarrow{+h\nu} -CH_2-\underset{\bullet}{C}H-CH_2-CH_2-\underset{\bullet}{C}H-CH_2- + H^{\cdot} \qquad (I)$$

$$-CH_2-\underset{\bullet}{C}H-CH_2-\underset{\bullet}{C}H-CH_2-CH_2- \xrightarrow[\text{migration}]{\text{radical}} -CH_2-\underset{\bullet}{C}H-\underset{\bullet}{C}H-CH_2-CH_2-CH_2- \qquad (II)$$

$$-CH_2-\underset{\bullet}{C}H-\underset{\bullet}{C}H-CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH=CH-CH_2-CH_2-CH_2- \qquad (III)$$

$$-CH_2-CH=CH-CH_2-CH_2-CH_2- \xrightarrow{+h\nu} --- \rightarrow --- \rightarrow -CH_2-(CH=CH)_3- \qquad (IV)$$

(ii) The multiple conjugated unsaturation disappears in a thermal reaction with a low enthalpy of activation of 23.4 kJ mol^{-1} (Fig. 1.14).

(iii) The hydroxyl (Fig. 1.15) carboxyl and carbonyl (Fig. 1.16) and vinyl (Fig. 1.17) groups are formed at measurable rates only after the disappearance of the multiplet or its precursors.

An auto acceleration of the photo-oxidation process was found and assumed to be caused by an increase in the ultraviolet absorption of polyethylene, which is partly due to the increase in the carbonyl group concentration. Hydroperoxide groups in polyethylene, free or hydrogen bonded, are reported to absorb at 3400 cm^{-1} (Burnett et al., 1955; Mitchell and Perkins, 1967).

Fig. 1.14 Destruction of triene on irradiation at 70, 80 and 90°C (Heacock et al., 1968)

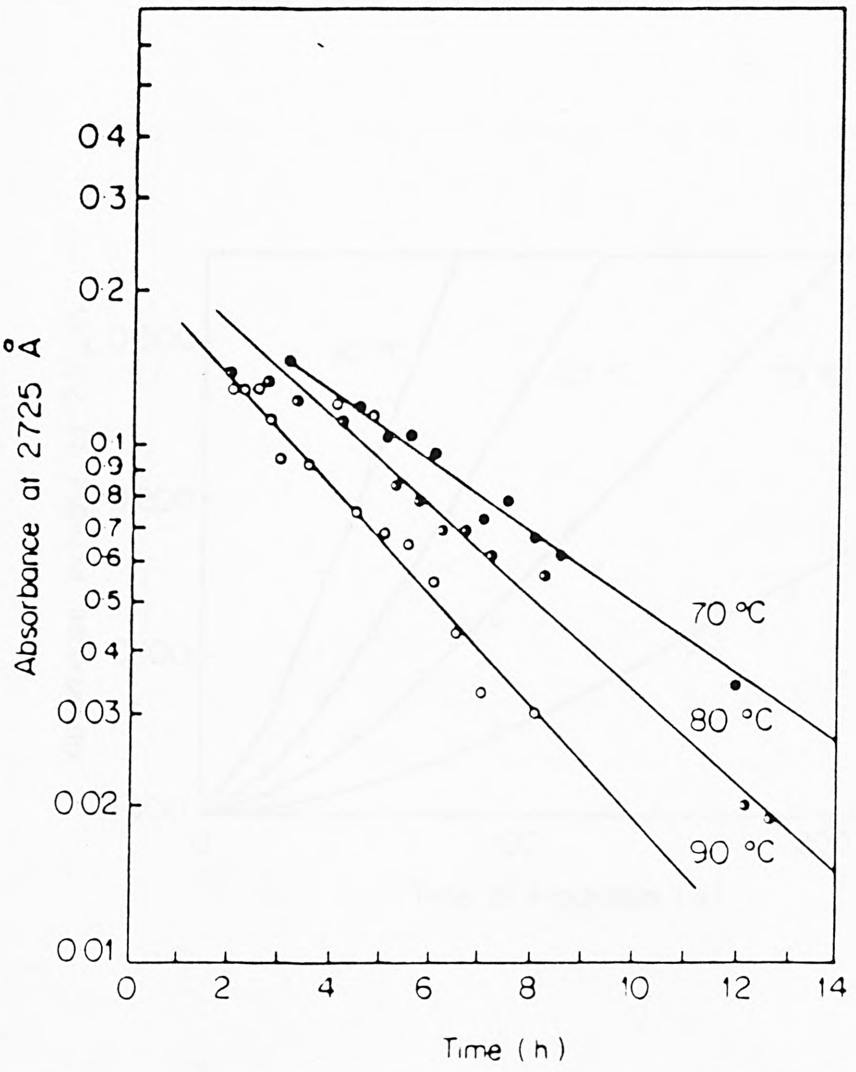


Fig. 1.15 Hydroxyl content of photodegradad
polyethylene film
(Heacock et al.,1968)

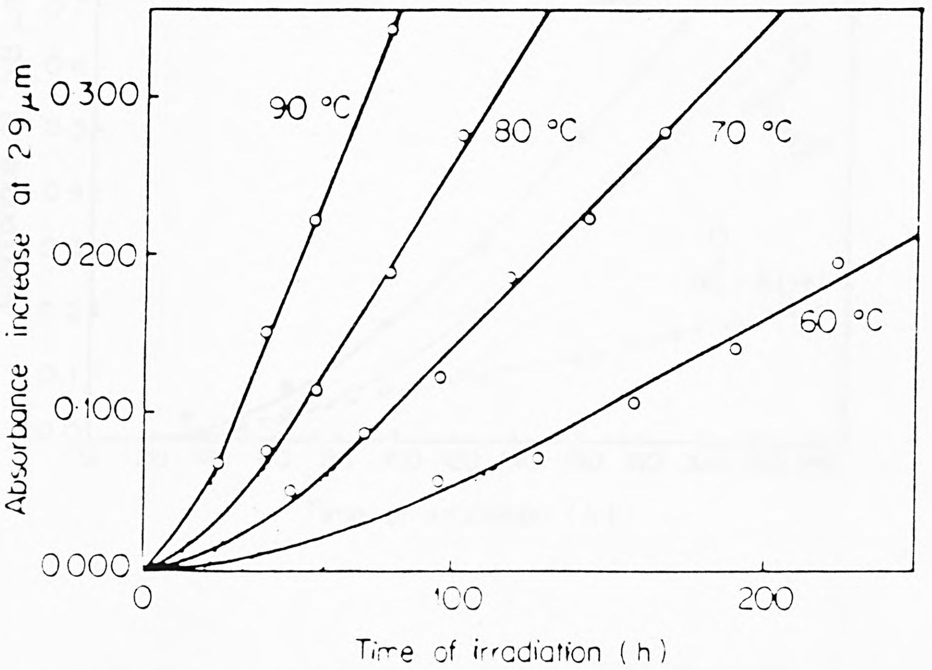


Fig. 1.16 Formation of carbonyl and carboxyl groups in polyethylene film at 60^{o}C (Heacock et al., 1968)

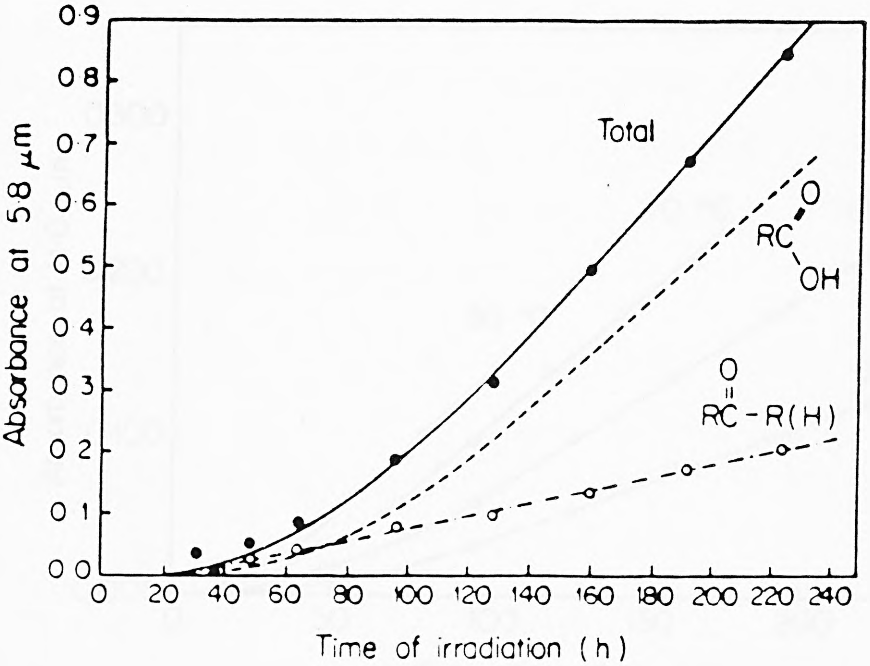
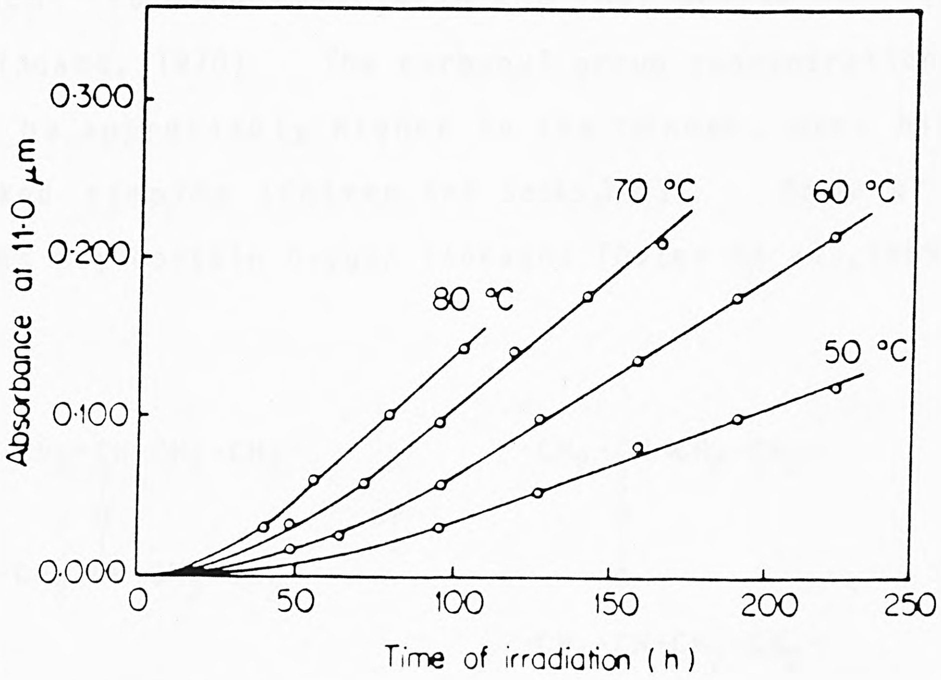
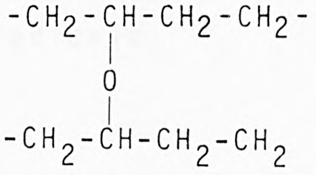


Fig. 1.17 Vinyl content of photodegraded polyethylene film (Heacock et al., 1968)

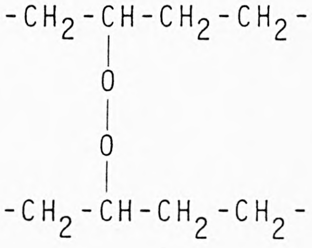


These groups are known to decompose on heating. The fact that this absorption band in photo-oxidised polyethylene does not decrease after heat treatment at 200^{o}C indicates that there is no major contribution by free hydroperoxides to the photo-oxidation process (Burnett et al., 1955). The absorption at 1725 cm^{-1} has been assigned to carbonyl groups, the absorption at 1645 cm^{-1} to vinyl alkene, the absorption at 1717 cm^{-1} to carboxylic acid and that at 1710 cm^{-1} to γ-lactones(Adams, 1970). The carbonyl group concentration was found to be appreciably higher in the thinner, more highly crosslinked samples (Cotten and Sacks,1963). Some of the crosslinks may contain oxygen linkages (Oster et al.,1959):



$$\begin{array}{l}-CH_2-CH-CH_2-CH_2-\\ \qquad\quad |\\ \qquad\quad O\\ \qquad\quad |\\ -CH_2-CH-CH_2-CH_2\end{array}$$

or



$$\begin{array}{l}-CH_2-CH-CH_2-CH_2-\\ \qquad\quad |\\ \qquad\quad O\\ \qquad\quad |\\ \qquad\quad O\\ \qquad\quad |\\ -CH_2-CH-CH_2-CH_2-\end{array}$$

A wide absorption band at 1250-1170 cm^{-1} in u.v.-irradiated polyethylene further indicates the presence of ether-type linkages (Beachell and Nemphos,1956). The ratio of scission to crosslinking during u.v.-irradiation depends upon the oxygen concentration (Cotten and Sacks,1963). The rate of diffusion of oxygen into amorphous regions is greater than that into crystalline polymer, and chain segments in amorphous parts of the polymer are more likely to crosslink. The long wavelength u.v. absorption in polyethylene samples (up to 400 nm) is considered to be due to the formation of charge transfer complexes between the polymer and molecular oxygen (Heacock et al., 1968; Tsuji and Seiki, 1971a,b; Wood and Kollman, 1972). The increased formation of radicals observed during the photolysis of polyethylene in oxygen can be attributed to additional absorption of light energy by charge-transfer complexes. Possible mechanisms for the participation of charge-transfer complexes in radical formation are as follows (Tsuji and Seiki, 1971a):

(i) The complex absorbs light energy which is transferred to other parts of the polymer molecule to produce free radicals

or

(ii) the complexes themselves form free radicals from excited states due to ultraviolet radiation.

1.3.4.2 Polypropylene

The exposure of polypropylene to ultraviolet radiation in air produces rapid photo-oxidation (Carlsson and Wiles, 1969, 1970, 1971, 1972) with marked effects on the mechanical and other physical properties of the polymer (Carlsson and Wiles, 1970, 1971).

The photo-oxidation of polypropylene can be initiated as a consequence of hydroperoxide formation either by reaction of the free radicals with oxygen:

$$R^{\bullet} + O_2 \longrightarrow R\dot{O}_2 \xrightarrow{RH} ROOH$$

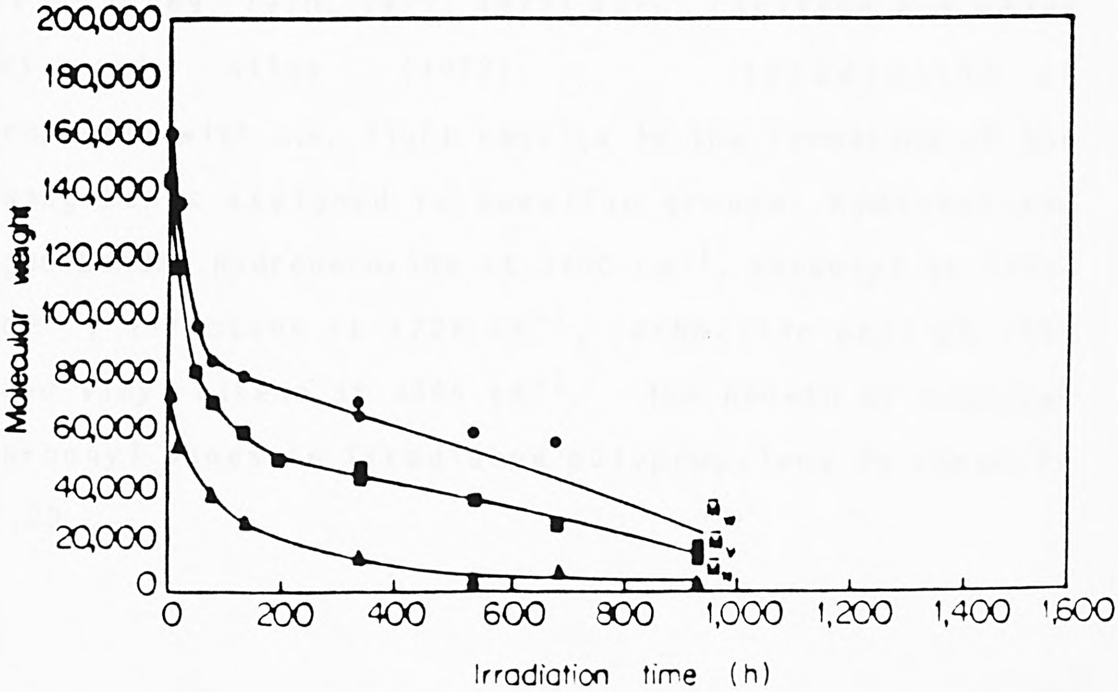
or by the reaction of singlet oxygen with unsaturated chain ends:

$$-CH_2-CH=CH_2 + {}^{1}\Delta_g O_2 \longrightarrow CH=CH-CH_2OOH$$

Hydroperoxide photolysis by sunlight in the presence of air is considered to be the main source of free radicals and backbone scission during the photo-oxidation of polypropylene.

The molecular weight of polypropylene decreases rapidly with time of u.v. irradiation (Fig. 1.18).

Fig. 1.18 Molecular weight of photodegraded polypropylene (20μm sheet) (Adams, 1972)



The rate of chain scission, initially a linear function of irradiation time, increases at longer exposures, indicating an autocatalytic mechanism for the photo-oxidation (Fig. 1.19). After longer exposures a sheet of polypropylene develops tiny cracks and becomes brittle. Infrared spectra of polypropylene samples during photodegradation and photo-oxidation have been investigated by Adams (1970), Carlsson and Wiles (1969, 1970, 1971, 1972), Kato, Carlsson and Wiles (1969) and Wiles (1972). Irradiation of polypropylene with u.v. light results in the formation of the following bands assigned to specific groups: hydroxyl and hydrogen-bonded hydroperoxide at 3400 cm^{-1}, carbonyl at 1715-1720 cm^{-1}, γ-lactone at 1728 cm^{-1}, carboxylic acid at 1715 cm^{-1} and vinyl alkene at 1645 cm^{-1}. The growth of hydroxyl and carbonyl bands in irradiated polypropylene is shown in Fig. 1.20 .

Fig. 1.19 Rate of chain scission per polypropylene molecular chain as a function of radiation time (Adams, 1972)

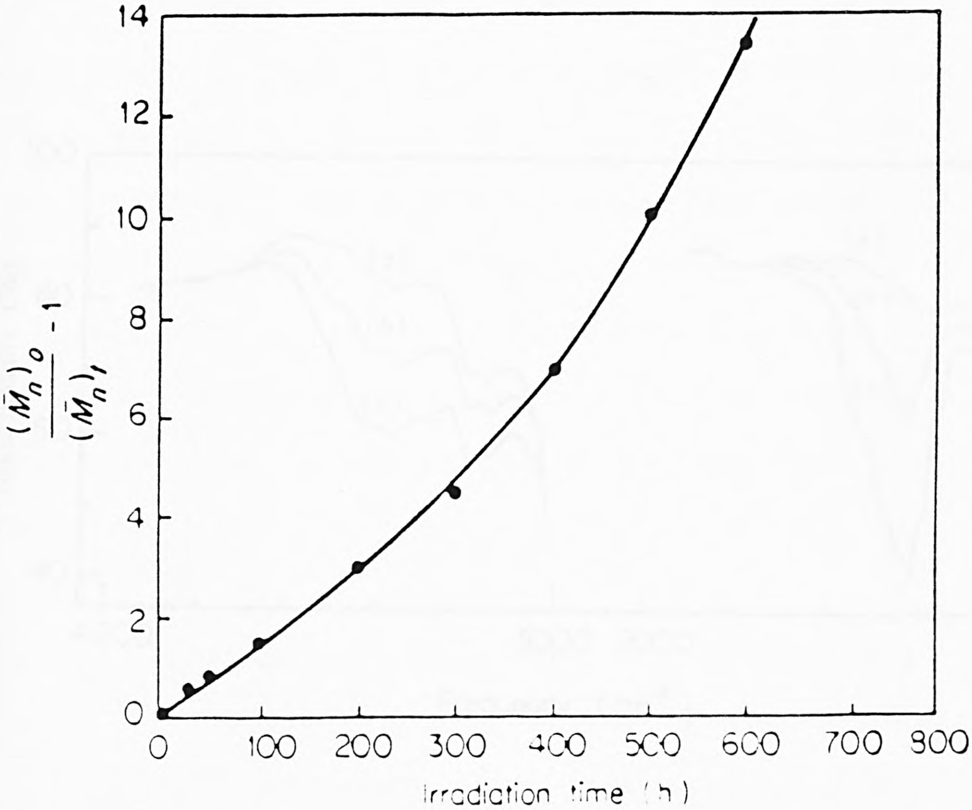
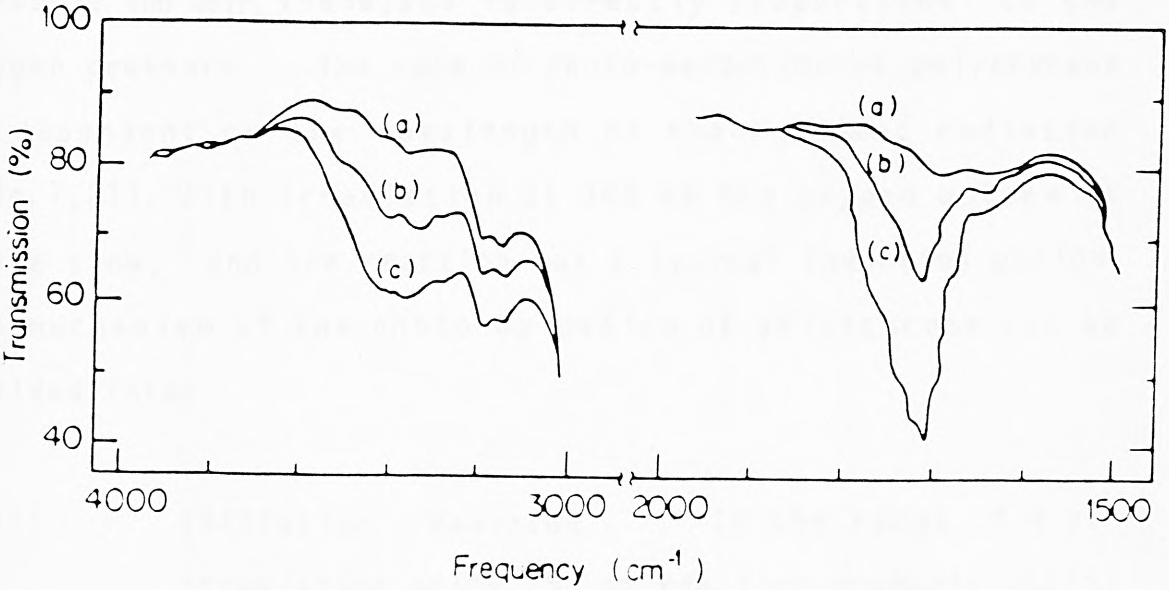


Fig. 1.20 Photo-oxidation of polypropylene film, -OH and C=O build up in air: (a) 0 h, (b) 65h, and (c) 110h (Kato et al., 1969)

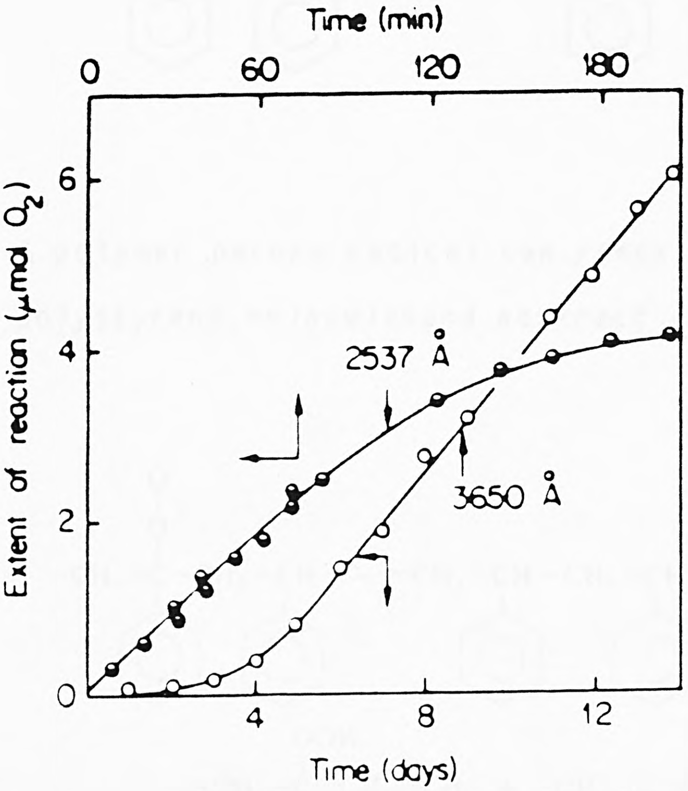


1.3.4.3 Polystyrene

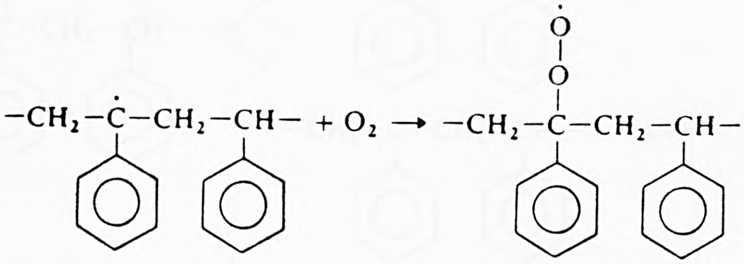
During u.v. irradiation of polystyrene film in air (or oxygen) a rapid change of mechanical properties is observed. The film becomes brittle and strongly yellow coloured. The main reactions are scission, crosslinking and oxidative degradation (Kaminska, 1970, 1972a,b). The rate of photo-oxidation is independent of molecular weight (Grassie and Weir, 1965b)and is directly proportional to the oxygen pressure. The rate of photo-oxidation of polystyrene is dependent on the wavelength of the incident radiation (Fig. 1.21). With irradiation at 365 nm the oxygen uptake is quite slow, and the reaction has a typical induction period. The mechanism of the photo-oxidation of polystyrene can be divided into:

(i) Initiation reaction. In the range of u.v.-irradiation below 280 nm reaction probably starts with the formation of macroradicals formed by dissociation of C-H or C-C bonds. Rabek and Ranby (1974) have proposed a new mechanism for the initial stage of the photo-oxidation in which singlet oxygen reacts with the polystyrene molecule. The mechanism of initiation by u.v. irradiation above 280 nm is not however yet fully understood.

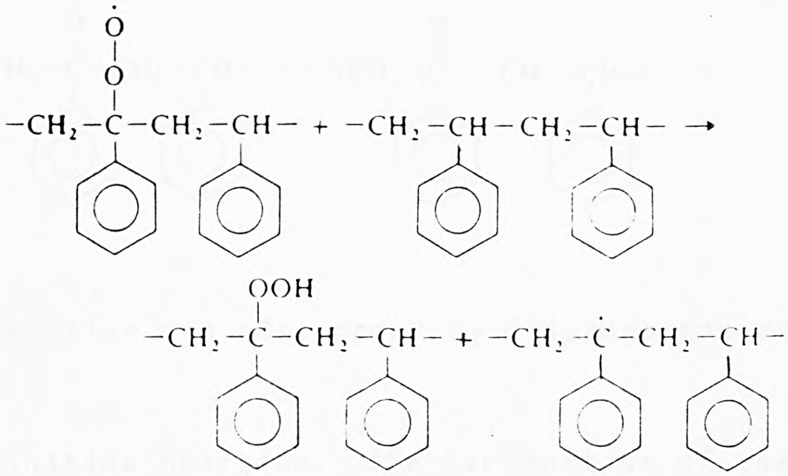
Fig. 1.21 Course of oxidation of polystyrene under 253.7nm and 365nm radiation (Grassie and Weir, 1965b)



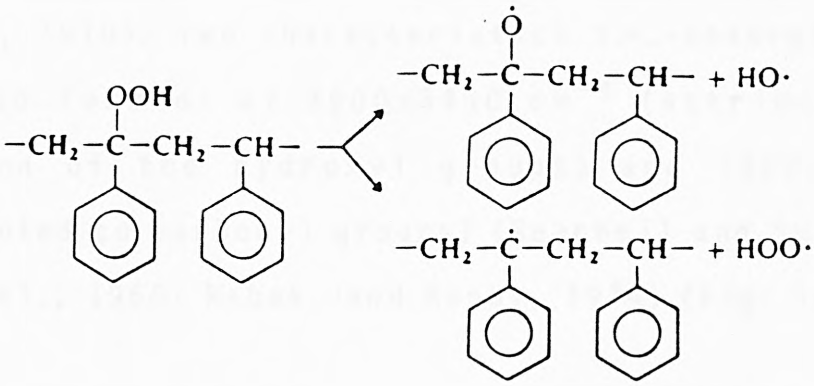
(ii) Propagation reaction. Macroradicals formed during the initiation reaction can react with oxygen molecules producing polymer peroxy radicals:



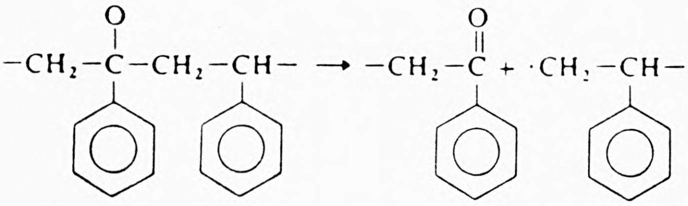
A polymer peroxy radical can react with the surrounding polystyrene molecules and abstract a hydrogen atom:



On exposure to light the polymer hydroperoxides can decompose according to the following reactions:



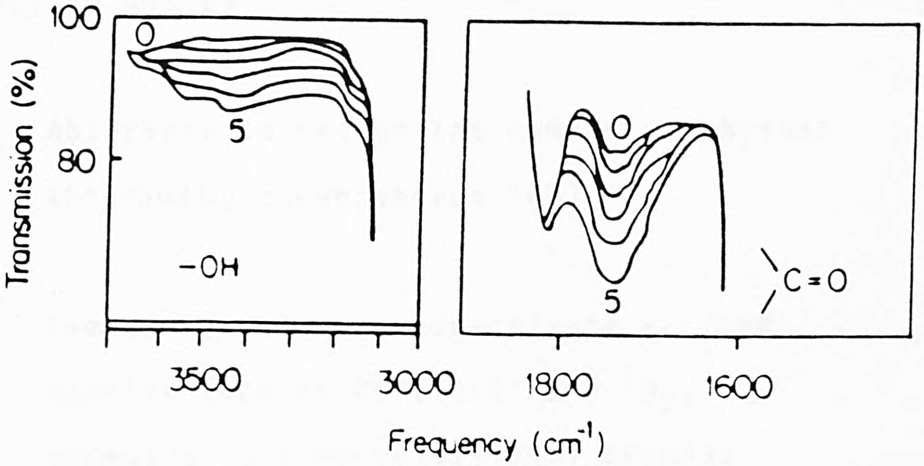
Alkoxy polymer radicals produced during the photolysis of hydroperoxide groups may decompose by -scission:



The scission reaction can also occur by disproportionation.

(iii) Termination reaction. The termination of the radical chain is due to the reaction of free radicals with each other in which inactive products are formed. During the photo-oxidation of polystyrene, hydrogen, carbon monoxide, carbon dioxide, water, methane, benzene, styrene, benzene alcohol and benzophenone are the volatile products liberated from the polymer (Grassie and Weir, 1965a,b; Jellinek and Lipovac, 1970). Two characteristics i.r.-absorption bands are also formed: at 3600-3400 cm^{-1} (attributed to the formation of the hydroxyl groups) and 1800-1700 cm^{-1} (attributed to carbonyl groups) (Beachell and Smiley, 1967; Fox et al., 1968; Rabek and Ranby, 1974) (Fig. 1.22).

Fig. 1.22 Change of i.r. spectra during 0-5h duration of u.v. irradiation of polystyrene sample (Ranby and Rabek, 1974)



1.3.5 Polymer photostabilisation

1.3.5.1 Introduction

The photostabilisation of polymers involves the retardation or elimination of photochemical processes in these materials. 'Ultraviolet stabilisers' are added to plastics and other polymeric materials in order to prevent the photodegradation or photocrosslinking caused by ultraviolet light, present in sunlight and various kinds of artificial light sources. U.v. stablisers may be categorised according to their ability to act as:

(i) Absorbers to reduce the number of photons absorbed by chromophores (Ch).

(ii) Compounds which can deactivate excited species such as Ch$^\cdot$, C=O$^\cdot$ and $^1O_2$, normally in some collisional process.

(iii) Compounds which can catalyse the decomposition of hydroperoxides before these groups absorb photons.

(iv) Compounds which can react with free radicals and thus interrupt degradative chain processes.

1.3.5.2 Stabilizers for commercial polymers

A. Pigments and dyes

Organic pigments

Many different kinds of pigment can be used for the protection of polymers against light. Pigments which are opaque to ultraviolet light act as screens by reflecting the ultraviolet light and thereby limiting its penetration into the polymer. Not all polymers are protected to the same degree by a given pigment because of differences in the absorption spectra of pigments and polymers. Other imoportant factors are the dispersion of pigments and their effect on physical properties, such as electrical properties. The chemical nature of a pigment is also very important. Many organic pigments such as azo, anthraquinone and thioindigo compounds, quinoacridones, isoindolinones, perylenes, dioxazines and phthalocyanines have wide applications in the plastics industry. Some, e.g. phthalocyanine blues and greens, exhibit good ultraviolet absorption properties and are good photostabilizers (Kwei, 1968; Ershov and Ankundinova, 1969).

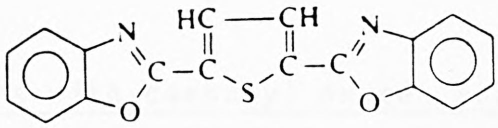
Carbon black

The various carbon blacks are traditionally classified according to their method of manufacture (Burges et al., 1965). Their high efficiency as light stabilisers for polymers is due mainly to their ability to act as inner filters for ultraviolet radiation, thus reducing the propagation of the initial photochemical attack (Szwarc, 1956). However, some carbon blacks also act as free radical scavengers, because they contain stable free radicals, and others function by quenching singlet and triplet states of polymers.

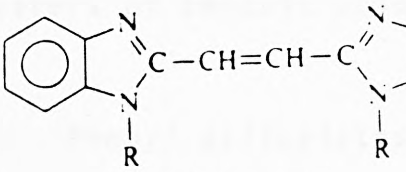
The effectiveness of carbon black is dependent upon the type used, the particle size and the degree of dispersion in the polymer phase (Williams et al., 1965; Howard and Gilroy, 1969). Golemba and Guillet (1969) found that the best carbon black for polyethylene was dispersed at a concentration of 1-2 wt% and had particles of 25 nm in diameter. The stabilizing effect on polyethylene increases with increasing concentration of carbon black. A loss of mechanical properties such as elongation and impact strength was observed when the content of carbon black exceeded 3-5 wt%. In general, carbon black is an excellent photostabilizer and its wide application is only limited by its black colour.

Fluorescent compounds

In fluorescent photostabilizers the ultraviolet light is absorbed and re-emitted at longer wavelengths in the form of fluorescent light. Numerous optical brightening agents absorb ultraviolet radiation and re-emit the energy in the blue region of the visible spectrum. Such compounds are commonly used to compensate for yellowing during the processing of polymers and to increase the brilliance and whiteness. The chemical structure of a few types of optical brightening compounds are presented below:

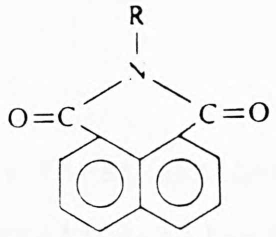


Benzoxazolyl



Benzimidazolyl

(10.4)



Naphthylimide

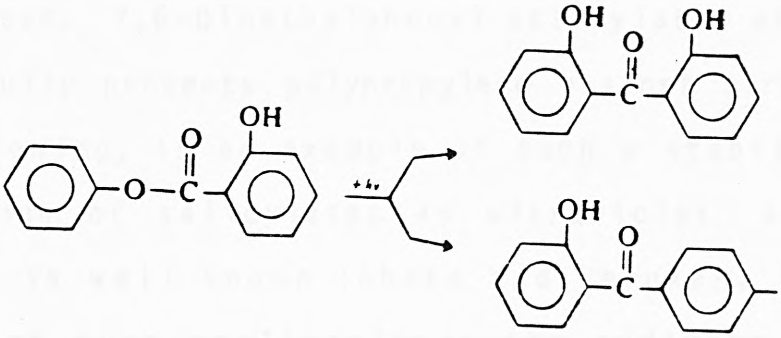
Fluorescent compounds are very effective photostabilisers, but unfortunately the poor light stability and thermal stability of the majority of these compounds results in a gradual decrease in their efficiency. Only one light-stable fluorescent compound, 6,13-dichloro-3,10-diphenyltriphenodioxazine, was found to be an excellent ultraviolet stabiliser for cellulose ester plastics (Chaudet et al., 1961); this stabilizer is apparently in the same class of efficiency as carbon black. Fluorescent compounds may sometimes sensitize photodegradation as a result of the absorption of the luminescence by the polymer (Gardner and Epstein,1961).

B. Absorbers with carbonyl oxygen acceptors

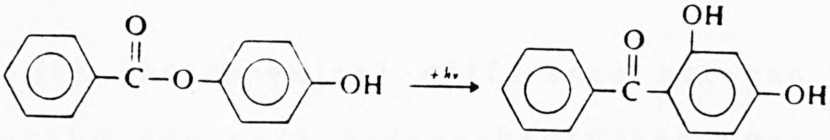
Phenyl esters of benzoic acid

Phenyl salicylates were the first photostabilizers to be used technically and they are still available because of their low price. Unfortunately most of them turn yellow on exposure to ultraviolet light, and this limits their use as ultraviolet absorbers for colourless and transparent plastics. At the present time it is well known that the yellowing of these compounds is due to a photochemical rearrangement of the Fries type, giving derivatives of dihydroxybenzophenone (Newland and Tamblyn, 1964; Bellus and Hrdlovic 1967):

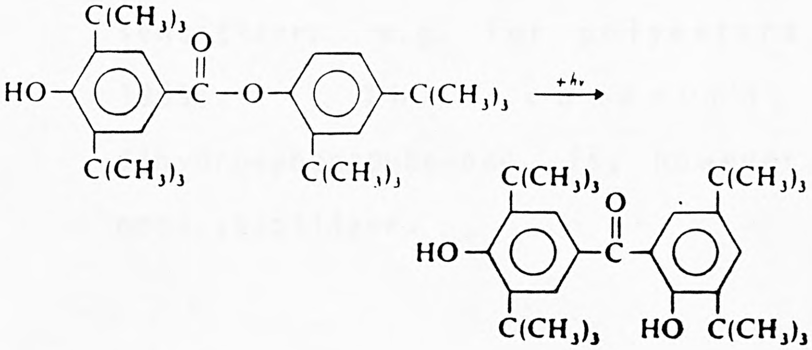
(i) Rearrangement of phenyl salicylate (Salol) to 2,2'-dihydroxybenzophenone and 2,4'-dihydroxybenzophenone (Newland and Tamblin, 1964):



(ii) Rearrangement of resorcinol monobenzoate to 2,4-dihydroxybenzophenone (Stenberg, 1967):



(iii) Rearrangement of the esters of 4-hydroxy-3,5-di-tert-butyl benzoic acid to 2-hydroxybenzophenone (Heller and Blatttman, 1972):



These esters are effective light stabilizers for polyolefins. However, photo rearrangement which results in yellowing is not a prerequisite for the stabilising efficiency of aromatic salicylates. 2,6-Dimethylphenyl salicylate, which fairly successfully protects polypropylene against stress cracking and yellowing, is an example of such a stabilizer. The application of salicylates as ultraviolet absorbers in polymers is well known (Ghate and Vernkar, 1971). An example of such applicationis the addition of p-tert-octylphenylsalicylate to polyethylene which results in a good improvement in weatherability.

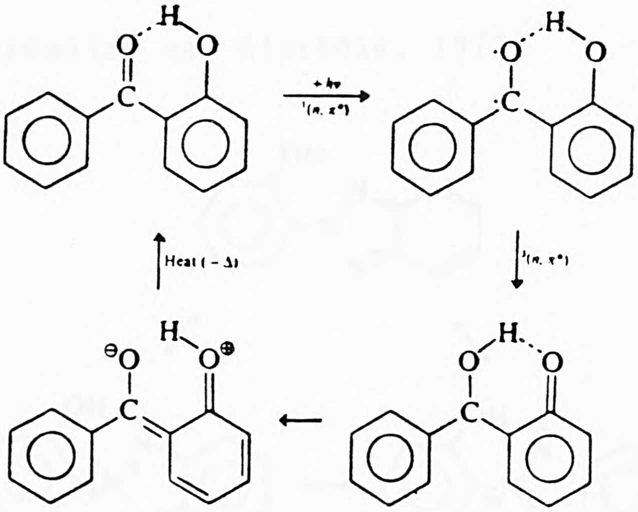
Hydroxybenzophenones

The photochemical difference between the two isomers, ortho and para-hydroxybenzophenones, is very distinct:

(i) The o-hydroxybenzophenones are good photostabilisers, while the p-hydroxybenzophenones act as photodegradation sensitizers, e.g. for polyesters (Heller, 1969). The compound, 2,4-dihydroxybenzophenone, is, however, a very good stabilizer.

(ii) The o-hydroxybenzophenones form internal hydrogen bonds (Lamola and Sharp, 1966). In polar solvents and particularly in hydrogen-bonding solvents such as alcohols, the internal hydrogen bonds are broken and phosphorescence is observed. The quantum yield of fluorescence of the ortho isomers is also lower than that of the non-hydrogen-bonding meta and para isomers.

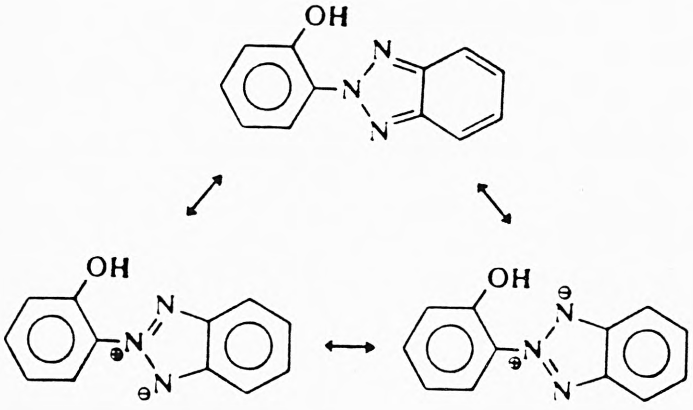
(iii) In comparison with most benzophenones which have a lifetime of around 10^{-5} sec, the o-hydroxybenzenophenones in solution have triplet states of very brief lifetimes (10^{-8} sec). This can be explained as being an effect of fast interconversion of hydrogen bonding to solvent and to internally hydrogen-bonded species. The photostabilisation mechanism of o-hydroxybenzophenones is believed to be a rapid tautomerism in the excited states (O'Connell, 1968; Lappin, 1971):



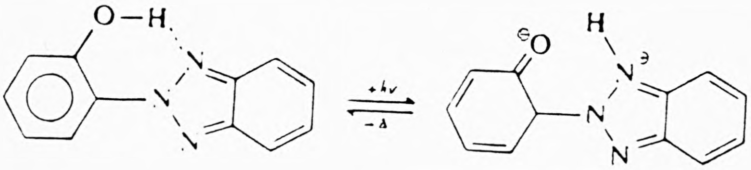
The o-hydroxybenzophenones are widely used commercially as photostabilisers for thermoplastics, including polyolefins (Coleman, 1968; Rothstein, 1968). However, other mechanisms have been suggested. Chakraborty and Scott (1979a) and Vink and Van Veen (1978) have found that o-hydroxybenzophenones operate as radical scavengers and/or hydroperoxide decomposers. Ivanov and Anisimov (1980) believe that o-hydroxbenzophenones exert this stabilising effect by quenching photoactive excited species in polymers.

C. Absorbers with nitrogen acceptors (Benzotriazoles)

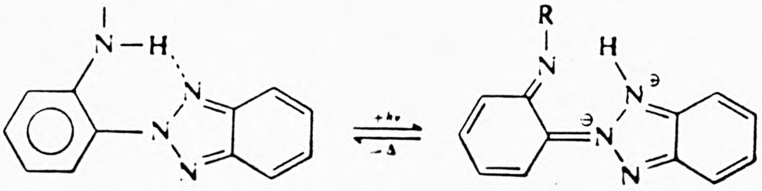
The resonance structures of the hydroxyphenylbenzotriazoles can be represented as in the structures shown below in which the quinoid form has the lowest energy (Heller and Blattman, 1972)



The o-hydroxyphenylbenzotriazoles may form internal hydrogen bonds. Their photostabilising action is also considered to be due to a rapid tautomerism of the excited states (Heller, 1969; Lappin, 1971):



Merril and Bennett (1965) found that o-amidophenylbenzotriazole may form an intramolecular hydrogen bond:



Mikheev et al. (1971) found that o-hydroxyphenylbenzotriazole may also act as a stabiliser by transfer of energy. Hydroxyphenylbenzotriazoles are practically colourless and are highly effective photostabilisers for various commercial polymers (Miyoshi and Konei, 1972; Rady and Heller, 1972; Sedlar et al., 1972). Chakraborty and Scott (1979b) believe that o-hydroxy phenyl benzotriazoles operate as radical scavengers and/or hydroperoxide decomposers.

D. Quenchers of excited states of polymers

Considerable attention has been paid to the photostabilisation of polymers by means of additives which accept electronic excitation energy by a transfer (or quenching) mechanism before bond scission can occur (Wiles, 1978). The sequence:

$$\begin{tikzcd}
\text{Chromophore} \arrow[r, "h\nu"] & Ch^* \arrow[dl] \arrow[dr] \arrow[rr] & & Ch + Q^* \arrow[d] \\
Ch & & \text{Reaction} & Q
\end{tikzcd}$$

illustrates the principle, and it has been shown that energy transfer to additive molecules from initiating chromophores, from carbonyl groups and from singlet oxygen, could in principle be photoprotective. Wiles (1978) found that there is evidence that this does occur in a few specific instances.

Hrdlovic et al. (1972) published comparisons between different photostabilisers acting as quenchers of the excited states of poly(vinyl ketone) and found that the quenching effects of the typical commercial u.v. absorbers are different, e.g.p-tert-butyl phenyl salicylate does not exhibit any quenching activity, while the quenching constants for 2-hydroxy-4-methoxy-benzophenone and 2-(2'-hydroxy-5'-methyl phenyl)-benzotriazole are 28 and 111 litre mol^{-1}, respectively. These experiments illustrate a very important fact, namely that the photostabilisation of polymers by energy transfer depends on the relative energy levels of the triplet state of the polymers and the photostabiliser. Beavan andPhillips (1974) suggested that α,β-unsaturated carbonyl groups are important chromophores in the photo-oxidation of oxidation of polybutadiene. These same authors (1975) have also concluded that stabilising additives such as benzotriazoles owe their effectiveness to quenching of the unsaturated carbonyls. Subsequently Allen and McKellar (1978) suggested that α, β-unsaturated carbonyl groups are important chromophores in a host of polymers and that quenchers for these groups are effective stabilisers. Also Singlet quencher and electron-transfer quencher are also good stabilisers.

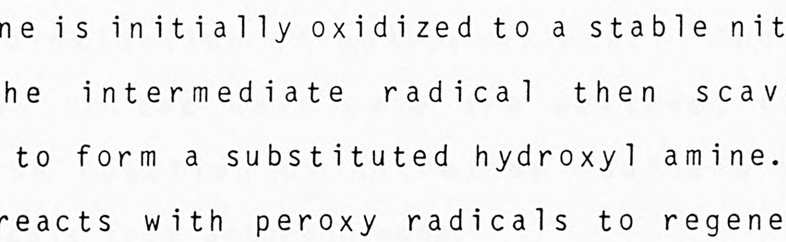
E. Peroxide decomposers

There is good evidence that hydroperoxides, formed in polymers as a result of inadvertent thermal oxidation during processing etc., are significant chromophores in the photo-oxidation and photodegradation of polyolefins (Carlsson and Wiles, 1976a), poly(vinyl chloride) (Carlsson and Wiles, 1975) and polystyrene (Geuskens and David, 1975). In fact these are additives which can catalyse the decomposition of hydroperoxides and thus reduce the rate of photoinitiation of the polymers. In the case of polypropylene, for example, hydroperoxide-decomposing additives, such as transition metal dialkyl-dithiocarbamates and dialkyl-dithiophosphates, can migrate through the solid polymer and destroy -OOH in the relatively long interval (a few days) between -OOH formation and photocleavage during outdoor exposure (Carlsson and Wiles, 1974b). Scott (1976a) has concluded that this phenomenon applies in general to the u.v. stabilisation of polyolefins. The peroxide-decomposing additives and their active products must of course have adequate light stability, and be non-sensitising.

F. Radical scavengers

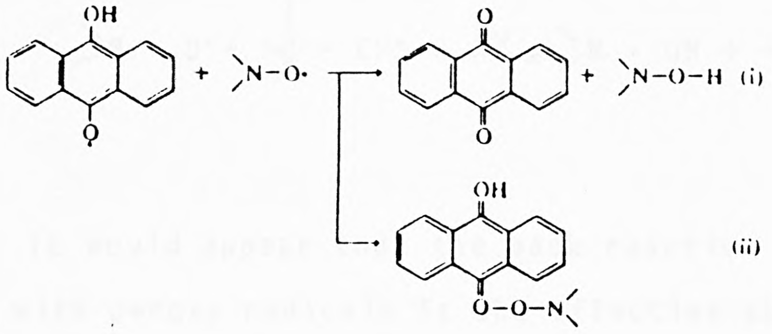
A common feature of the processes by which the useful properties of polymers are lost during outdoor exposure is the homolytic cleavage of covalent bonds. Thus, regardless of the photoinitiators, or of the precise nature of the subsequent photoprocesses, the degrading system will contain radicals such as alkyl(and/or aryl), alkoxy, peroxy, hydroxy, and one or more of these reactive species will be involved in the perpetuation of photodegration. Stabilisation of some polymers (particularly the polyolefins) can therefore be obtained by reducing the number and activity of radicals (Carlsson and Wiles 1976b; Garton et al.,1979).

Of all the commercial photostabilizers on the market, those based on the hindered piperidine structure continue to attract by far the most interest. In fact, these systems dominate many applications where long-term photoprotection is important. Their mode of action involves the processes shown below:



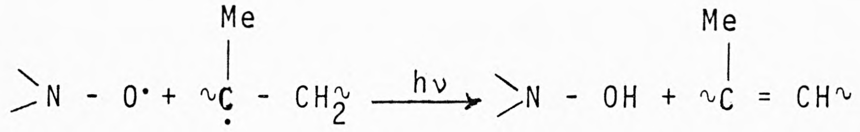
where the amine is initially oxidized to a stable nitroxide radical. The intermediate radical then scavenges macroradicals to form a substituted hydroxyl amine. The latter then reacts with peroxy radicals to regenerate a nitroxide radical. This whole process can then be repeated several times and is the reason why such systems are effective photostabilizers. However, the relative rates of the various steps appear to be important in determining photostabilising efficiency. Oxidation of the amine to the nitroxide radical is believed to occur through reaction with hydroperoxides and Allen (1981) has produced some outstanding evidence to confirm this. Here a correlation was obtained between hydroperoxide concentrations in oxidized polypropylene films and subsequent nitroxide radical concentrations after incorporating a hindered-amine stabiliser.

Carlsson et al. (1982) have confirmed that in the solid state this oxidation process is enhanced through the strong amine-hydroperoxide association. The macroradical trapping efficiency of nitroxide radicals has been criticized and many workers believe this process to be inefficient. Much of the evidence suggests that the hydroxylamine is the important stabilizing intermediate. Allen at al. (1981) have shown that hindered amines and their nitroxide radicals are effective inhibitors of the aromatic ketone and quinone-sensitized photo-oxidation of polypropylene. The two mechanisms shown on the next page are believed to be important for the reaction of nitroxide radicals with semiquinone radicals from anthraquinone:



The semiquinone radical is produced initially by hydrogen-atom abstraction by the photo-excited triplet state of the anthraquinone. The first reaction involves regeneration of the quinone and the hydroxylamine, whereas the second involves the production of an adduct. Both mechanisms appear likely from the work of Felder et al. (1981).

According to Carlsson et al. (1981), the major species present during photostabilisation by hindered piperidine compounds is the grafted bis-hydroxyl amine; and in fact, work by Bagh et al. (1982) has shown that the hydroxylamines are the most effective species in polypropylene. These workers also present a new mechanism for the reaction of nitroxide radicals with tertiary macroradicals to give the hydroxylamine and unsaturation. Nitroxide radicals are actually more stable in air than hydroxylamines.



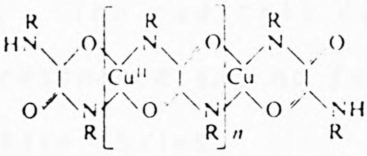
$$>N - O^{\bullet} + \sim\overset{\displaystyle Me}{\underset{\bullet}{C}} - CH_2\sim \xrightarrow{h\nu} >N - OH + \sim\overset{\displaystyle Me}{C} = CH\sim$$

Thus, it would appear that the back reaction of the hydroxylamine with peroxy radicals is the effective stabilizing stage in the overall mechanism.

1.3.6 The use of metal compounds for the inhibition of the photooxidation of polymers

1.3.6.1 Metal deactivators

Hansen et al. (1964) in their study of the stabilization of polypropylene demonstrated both a metal salt catalysis (presumably homogeneous), resulting from dispersion of copper stearate in the polymer matrix, and a bulk metal (interfacial) catalysis that occurred when the polymer was in contact with a copper surface. It was further shown that oxamide and several of its derivatives stabilized polypropylene against both homogeneous and heterogeneous copper catalysis. This class of stabilizer, appropriately termed "copper deactivators", function by chelating active metal species, thus reducing their catalytic effect. However, the most effective copper deactivators fail to retard completely the copper-catalyzed oxidation (Hansen et al. 1965), even in a metal salt-polymer system in which the amount of stabilizer used is in excess of that required to chelate all of the soluble metal salt present in the polymer. An obvious explanation for the failure of metal deactivators to act as complete inhibitors could be that the chelate formed, though less effective than the metal or its oxides, still retains some catalytic activity. Support for this concept was developed by Allara and Chan (unpublished results), who synthesized several complexes of copper with various oxamide derivatives. These complexes were isolated and their structures were examined. Allara and Chan concluded that the complexes are best represented by the polymeric structure below in which n is estimated to vary from 20 to several hundred for a variety of ligands:



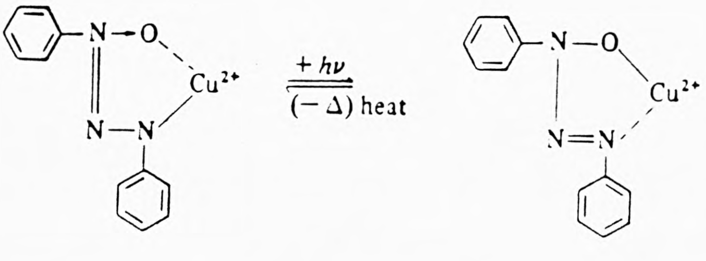
Though each of the ligands used in the formation of these chelates functions as a copper deactivator, nevertheless each corresponding complex showed some residual catalytic effect.

1.3.6.2 Copper chelates

Photo-oxidative degradation of isotactic poly(1-butene) in the presence and absence of copper(II) bis(1,3-

diphenyl triazine-N-oxide) chelate (CPTO) has been studied by Singh and Syamal (1981).

The stabilization of poly(1-butene) by CPTO is effected in several ways. The chelate stabilization process operates by interfering with the photo-initiation process through the absorption of light. By minimizing the amount of ultraviolet energy absorbed by the polymer the primary photochemical processes are prevented. The chelate is able to dissipate the radiation harmlessly, thus acting as a light shielding agent, absorber and quencher. The chelate is also effective at the chain-branching stage and decomposes the hydroperoxide into inert products. CPTO also acts as a free radical scavenger. The radicals derived from the chelate are stabilized by resonance and no further reaction occurs to initiate new oxidative chains.



1.3.6.3 Nickel chelates

It has been proposed by several workers that nickel chelates are of importance in the photo-stabilization of polyolefins (Adamczyk and Wilkinson, 1974; Carlsson et al., 1973, 1974, 1978; Scott., 1976b), polystyrene (George, 1974; Harper and McKellar, 1974) and polydienes (Breck et al.,1974; Zweig and Henderson, 1975). The effectiveness of metal chelates in deactivating singlet oxygen has been studied by Carlsson and Wiles (1972, 1974a), and Furue and Russell (1978). The very high quenching constants of the excited singlet and triplet states of some transition metal chelates may be associated with their low-energy excited states (Adamczyk and Wilkinson, 1974; Carlsson and Wiles, 1972, 1974a). Since it was not possible to obtain direct information on these energies for several nickel chelates, it has been suggested that these compounds operate by processes involving energy transfer (Adamczyk and Wilkinson, 1972; Harper et al., 1974; Allen et al., 1975), and for antioxidant mechanisms (Amin and Scott, 1974; Ranaweera and Scott, 1974, 1976).

Ni(III) stilbene dithiolate (SDT) was reported to be an outstanding thermal inhibitor and also an excellent photostabilizer for polyolefins (Uri, 1975; Ness, 1977). In addition to functioning as a radical trap and hydroperoxide decomposer, this compound is an effective ultraviolet screen. These properties of Ni SDT were confirmed by Lala and Rabek (1981) and also extended to Ni(IV) chelates which are much more effective than Ni(III) chelates as photostabilizers. Ni(V) chelate has been investigated by Briggs and McKellar, (1968), Guillory and Cook, (1973), Flood et al., (1973) and Carlsson et al., (1973, 1974) and was found to be an excellent photostabilizer for polyolefins. It was established that Ni(V) is also a very effective photostabilizer for the oxidative degradation of cis-1,4-polybutadiene. Its stabilizing effect involves various mechanisms such as ultraviolet screening, catalytic destruction of hydroperoxides, radical trapping and singlet oxygen deactivation. The practical use of nickel SDT chelates may be limited because of their intense colour.

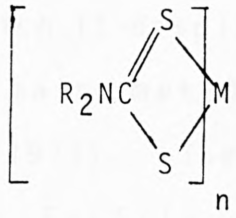
It has been shown (Ranaweera and Scott, 1975, 1976; Scott 1976b; Chakraborty and Scott, 1977, 1979) that the effectiveness of the nickel dialkyl dithiocarbomates as u.v. stabilizers for polyolefins is primarily due to their ability to generate an ionic catalyst for the destruction of hydroperoxides. Chakraborty and Scott (1977) have also observed synergism and antagonism between certain u.v. stabilizers and antioxidants in polyethylene. For example, the nickel dialkyl dithiocarbamates were found to form synergistic combinations with a 2-hydroxybenzophenone stabilizer. In this case the dithiocarbamate is believed to protect the 2-hydroxybenzophenone by decomposing the hydroperoxides formed during processing and/or photooxidation.

On the other hand, nickel dithiocarbamates were found to be antagonistic in the presence of a phenolic antioxidant which apparently photosensitizes the decomposition of the dithiocarbamates. These results could be explained by electron transfer since phenolic antioxidants work by conversion to unreactive phenoxy radicals which could easily be produced by oxidation of the phenol by nickel. Yamagata et al.(1979a,b) found a good correlation between the singlet oxygen-quenching efficiency of transition-metal dithiocarbamates and their ability to inhibit the photoyellowing of polyurethanes.

According to Briggs and McKellar (1968), the photostabilization of polypropylene by nickel oxime chelates proceeds by a triplet transfer mechanism from carbonyl-containing oxidation sites in the polymer to the chelate. Al-Malaika and Scott (1980) found that nickel dialkyl dithiophosphate and nickel xanthates stabilize low-density polyethylene against both thermal and photo-oxidation and their photostabilizing activity is related primarily to the photostability of the metal complexes themselves, which act as light stable reservoirs for the active species in the polymer.

The photostabilizing effect of two nickel chlorides viz. bis(tributyl phosphine) nickel(II) chloride and cyclo pentadienyl(triphenyl phosphine nickel(II) chloride, and three nickel chelates viz. bis(dithiobenzil) nickel, bis(4-dimethylamino dithiobenzil) nickel and 2,2'-thio bis(4-tert-octylphenolato)n-butyl amine nickel, on the oxidative photodegradation of cis-1,4-polybutadiene has been investigated by Lala and Rabek (1981). Their stabilizing effect includes possible mechanisms such as ultraviolet screening, catalytic decomposition of hydroperoxides, radical trapping and singlet oxygen deactivation.

The transition metal complexes of the dithiocarbamic acids (I):



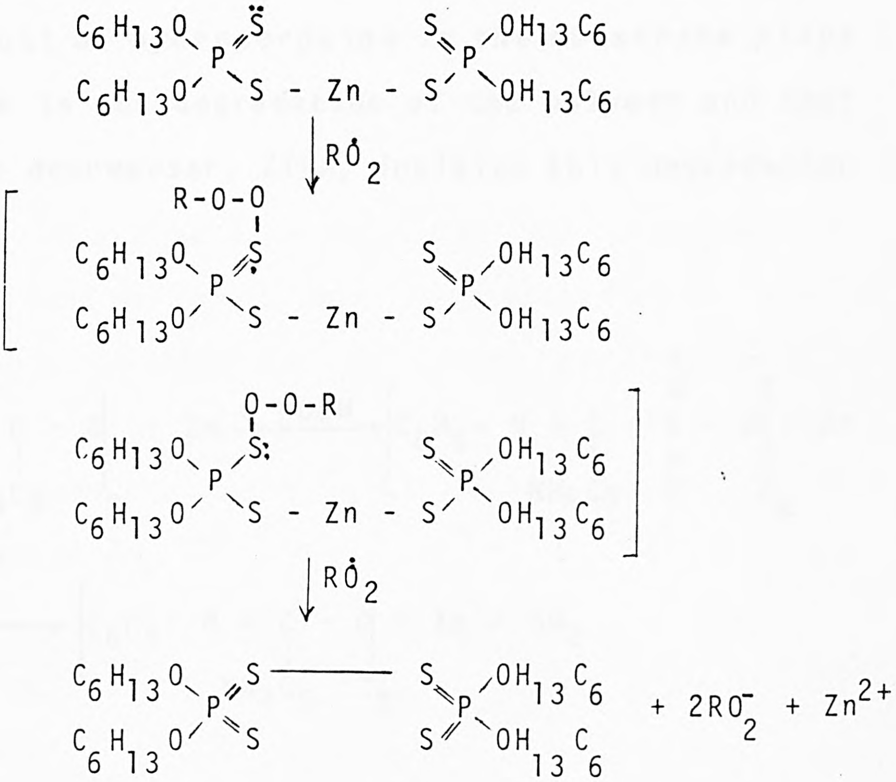
(I)

show two different kinds of behaviour with polymers undergoing photo-oxidative degradation (Scott, 1973). The Ni(II), Co(II) and Cu(II) complexes are effective photo-oxidative stabilizers (Scott, 1973); whereas the Fe(III) and to a lesser extent the Mn(III) complexes are photo-activators after an induction period.

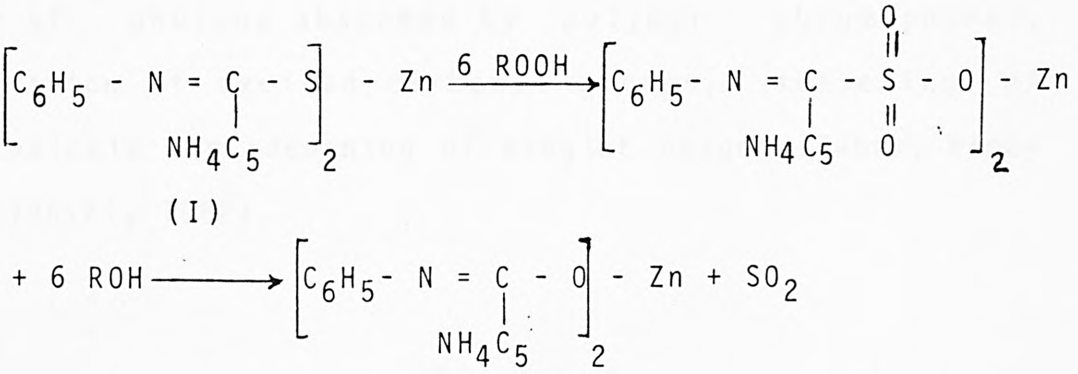
A detailed study of Ni(II)dibutyldithiocarbamate (I, R=Bu, M=Ni, n=2) has shown that it a stabilizer for both thermal and photochemical oxidation due to its ability to destroy hydroperoxides in a catalytic non-radical reaction (Ranaweera and Scott 1975, 1976). The nickel complex itself reacts during this process and the evidence suggests that it is destroyed by hydroperoxides when it acts as a photo-stabilizer rather than by direct photolysis or by quenching of excited states of carbonyl or oxygen (Carlsson et al., 1972,1973;Guillory and Becker, 1974). The iron(III) complex on the other hand is much less stable to light and leads to effective sensitizationof polymers and to photo-oxidation after a much shorter induction period (Amin and Scott, 1974) during which it displays the common ability of all the dithiocarbamate metal complexes to destroy hydroperoxides (Scott, 1973). The reason for the much lower photostability of the Fe(III) complex has not been established, but it may be significant that both Fe(III) and Mn(III) are oxidising species.

1.3.6.4 Zinc chelates

The mechanisms of photostabilization of poly(phenylene oxide) by zinc di-n-hexyl dithiophosphate involve decomposition of the corresponding peroxides as well as reaction with peroxy radicals (Singh and Chandra,1982). In the latter case the mechanism shown below is believed to be important:



The thermal and photostabilizing activity of zinc thiopicoline anilide (ZTPA)(I), incorporated in the matrix of isotactic poly-1-butene, has been studied by Chandra (1981). It was shown that, under the effect of 253.7 nm light, ZTPA is converted into a strongly absorbing product which acts as an inner filter for u.v. light. From the luminescence spectral data, it is clear that energy is transferred from the excited state of the polymer molecules to ZTPA, which has an unsaturated chromophore. It is clear that a minor amount of hydroperoxide in the substrate plays an important role in the degradation of the polymer and that the hydroperoxide decomposer, ZTPA, inhibits this degradation (Chandra, 1981):



$$\left[C_6H_5 - N = \underset{NH_4C_5}{\underset{|}{C}} - S\right]_2 - Zn \xrightarrow{6\ ROOH} \left[C_6H_5 - N = \underset{NH_4C_5}{\underset{|}{C}} - \overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}} - O\right]_2 - Zn$$

(I)

$$+ 6\ ROH \longrightarrow \left[C_6H_5 - N = \underset{NH_4C_5}{\underset{|}{C}} - O\right]_2 - Zn + SO_2$$

Gaseous sulphur dioxide can act as an acid catalyst for the ionic decomposition of hydroperoxide groups to alcohols and ketones (Holdworth et al., 1964; Scott, 1969). Thus the functions of ZTPA may include that of hydroperoxide decomposer, conventional u.v absorber, and the transfer of energy from excited polymer species.

1.3.6.5 Other metal chelates and salts

Dioctyltin bis(iso-octyl thioglycolate) has been found to be an effective stabilizer for PVC (Braunand Kull, 1980). The transition metal acetylacetonates, which are effective quenchers of triplet carbonyl (Chakraborty and Scott, unpublished work) are among the most powerful photoinitiators known for the photo-oxidation of polyethylene Metal salts (Co^{2+}, Mn^{2+}, Ni^{2+}) of 2 [(1-hydroxy-2-naphthalenyl) carbonyl]-benzoic acid can be considered as a new class of stabilizer effective against free radical photo-oxidation and singlet oxygen oxidation of cis-1,4-polybutadiene. These metal salts are active as a result of the combination of several important effects such as reduction in the number of photons absorbed by polymer chromophores, deactivation of excited carbonyl groups, scavening of free radicals and quenching of singlet oxygen (Rabek, Ranby and Golubski, 1982).

2 - Experimental

2. Experimental

2.1 Materials

2.1.1 Polymers

Two polymers were used in this work. Polystyrene (Carinex), in pelleted form, was kindly supplied by Shell Chemicals U.K. Ltd. and polypropylene (Profax 6301), in powdered form, was kindly provided by Hercules Inc.

2.1.2 Additives

2.1.2.1 Organic halogen compound

Cereclor 70 (a wax-grade chlorinated mixture of normal alkanes between C_{20} and C_{28} containing 70 wt% chlorine) was kindly provided by Imperial Chemical Industries Limited.

2.1.2.2 Metal chelates

A. Acetylacetonates

Bis(2,4-pentanedionato)diaquocobalt(II) [(Co II)AcAc] and bis(2,4-pentanedionato) diaquo nickel(II)

[Ni(II) ACAC] were prepared from 2,4-pentanedione and the appropriate metal chloride (Jolly, 1968). Bis(2,4-pentanedionato) zinc(II)[Zn(II) AcAc] was prepared from 2,4-pentanedione and zinc sulphate (Muetterties, 1967). Tris(2,4-pentanedione) aluminium [Al(III) AcAc] was prepared from 2,4-pentanedione and aluminium sulphate (McReynolds, 1946). Tin(IV) dichloride bis acetylacetone [Sn(IV) $AcAcCl_2$] was prepared from 2,4-pentanedione and tin(IV) chloride (Morgan et al., 1924).

B. Salicylaldimino derivatives

Bis(N-phenyl salicylaldimino) cobalt(II) [PheSalAl Co(II)], bis(N-butyl salicyaldimino) copper(II) [BuSalAl Cu(II)], bis(N-3-carboxy phenyl salicyladimino) copper(II) [3-CarbPheSalAl Cu(II)], bis(n-4-carboxy phenyl salicylaldimino) copper(II) [4-CarbPheSalAl Cu(II)], bis(N-3-hydroxyphenyl salicylaldimino) copper(II) [3-HydPheSalAl Cu(II)], bis(N-t-butyl salicyladimino) copper(II) [t-BuSAlAl Cu(II)], bis(N-phenyl salicylaldimino) nickel(II) [PheSalAl Ni(II) and (N-2-hydroxyphenyl salicyladimino) iron(III) [2-HydPheSalAl Fe(III)] were all prepared via a Schiff base. The preparation involved dissolving the chosen amino compound and salicyladehyde in the minimum amount of methanol; the recrystallised Schiff base was then redissolved in methanol and the appropriate metal acetate (metal chloride in the case of the iron) was added slowly as a methanolic solution, whereupon the required complex precipitated out. (N-2-hydroxyphenyl salicylaldimino)dimethyl tin(IV) [2-HydPheSalAl-di-Me.Sn(IV)] was prepared from dimethyl tin(IV) dichloride, salicylaldehyde and 2-aminophenol by the method of Tanaka et al.,(1964).

C. N,N'-Disalicylidene ethylene diamines

N,N'-disalicylidene ethylene diamine zinc(II) monohydrate [Zn(II) Salen] was prepared from salicylaldehyde, ethylene diamine and zinc acetate by the method of Hall and Moore (1966). Chloro-(N,N'-bis salicylidene ethylene diamine) iron(III) [Fe(III) Salen] Cl was prepared from the Schiff's base and anhydrous ferric chloride (Gerloch and Mabbs, 1967). N,N'-disalicylidene ethylene diamine, tin(IV) chloride [$SnCl_4$, Salen H_2] was prepared by mixing ethanolic solutions of tin(IV) chloride and the Schiff base (Bergen et al. 1970).

D. Stilbene derivatives

Bis(stilbene dithiolato) nickel(II) [SDT Ni(II)] and bis(S,S-dimethyl stilbene dithiolato) nickell(II) [S,S-di-Me SDT Ni(II)] were prepared from benzoin and phosphorus pentasulphide by the method of Schrauzer and Mayweg (1965).

E. Other metal chelates

Bis(4-aminopent-3-en-2-onato) nickel(II) was prepared from acetyl acetone, ammonia and nickel chloride by the method of Jameson and Peacock (1969). Bis hydroxo hexa benzoato tris iron(III) benzoate [BHB tris Fe(III)] and tris hydroxo pentabenzoato tris iron(III) benzoate monohydrate were prepared from ferric chloride and sodium benzoate by the method of Earnshaw et al. (1966). Dichloroquinolin-8-olato iron(III) was prepared from quinoline-8-ol and iron(III) chloride (Frazer, Qureshi and Taylor, 1971). Ferrocene was a high-purity commercial sample.

2.1.3 Lubricant

Stearic acid (B.D.H.) was used as a lubricant for polystyrene and polypropylene

2.1.4 Gases

Oxygen, oxygen-free nitrogen and air were obtained from the British Oxygen Company and used without further purification for flammability measurements and thermoanalytical studies.

2.1.5 Preparation of polymer-additive samples

2.1.5.1 Milling procedure

The machine used was a Ruth Schwabenthan two-roll mill in which each of the stainless steel rollers was heated independently by means of an immersion heater embedded in a silicone oil bath enclosed within each roller. For experiments involving polystyrene, Cereclor 70, the metal chelates and 2 phr stearic acid (lubrican) were weighed out prior to incorporation into the polymer. The temperatures of the front and rear rollers were set at 443 K and 438 K respectively. Thereafter pre-weighed quantities of polystyrene (normally 100g), additives and lubricant were physically blended and added to the mill. The mixtures were fused and fluxed until a sheet had been formed on the roller. During the milling, the sheet was frequently cut and folded towards the centre of the roll until a homogeneous crepe was formed. This was achieved in 5-7 min.

Polypropylene crepes were made by milling four batches of 25g of polymer, each containing the appropriate additives and again 2 phr of stearic acid as a lubricant, for 45 sec. The temperature of the front roller was set at 448 K, while that of the back roller was set at 443 K.

2.1.5.2 Compression moulding

This involves the use of a hot and a cold press. The hot press is an electrically-operated and electrically-heated hydraulic press, capable of attaining temperatures up to 500 K at a pressure of 5.5×10^3 kPa The cold press is a water-cooled hand-operated "fly press".

The resulting homogeneous crepe was then moulded in an electric hydraulic press, in which the dimensions of the moulds were 3 x 152 x 152 mm. The polymeric material was sandwiched between two "Melinex" sheets, and the sheets were then placed on top of the mould, which in turn was sandwiched between two steel plates.

Polystyrene crepe was heated to 443 K for 180 sec at atmospheric pressure in a preheated hydraulic press and then pressed at 5.5×10^3 kPa for 120 sec. The combined polypropylene crepe was heated to 443 K for 150 sec in the press and 5.5×10^3 kPa pressure was then applied for 90 sec. The "mould" was removed from the hot press and introduced into a hand-operated water-cooled press.

Films of known thickness were prepared from the polymer samples which were used previously for LOI measurements. Small strips of these polymer samples, length 50 mm, width 6 ± 0.5mm, thickness 3±0.25mm, were heated between two Melinex sheets to 473 K for 150 sec at atmospheric pressure in a preheated hydraulic press and then pressed at 5.5 x 10^3 kPa for 30 sec. After that they were removed from the hot press and introduced into the hand-operated water-cooled press.

2.2 Apparatus and procedure

2.2.1 Measurement of flammability

2.2.1.1 The limiting oxygen index apparatus

The flammability of polymeric samples was determined by measurement of the limiting oxygen index defined as 100 times the ratio of the limiting amount of oxygen corresponding to sustained burning after ignition to the total amount of gas in the corresponding atmosphere. The layout of the equipment is shown schematically in Fig. 2.1 and in detail in Fig. 2.2. The equipment consisted of two sections: a gas-metering system and a test column. In the metering system the flow of each gas was measured before the streams are mixed and fed into the base of the column. The instrument was connected to cylinders containing oxygen and nitrogen via a two-stage regulator, and supply pressures of 170 kPa were employed in order to achieve the required flow rates during the test. Two gas inlets at the rear of the equipment lead to two filters fitted with numerical controls, which enabled the needle valve to be set very accurately. An on-off lever was situated adjacent to each control needle valve in each gas line. From the mixing chamber the homogeneous gas mixture passed directly

Fig. 2.1 Schematic layout of the limiting oxygen index apparatus

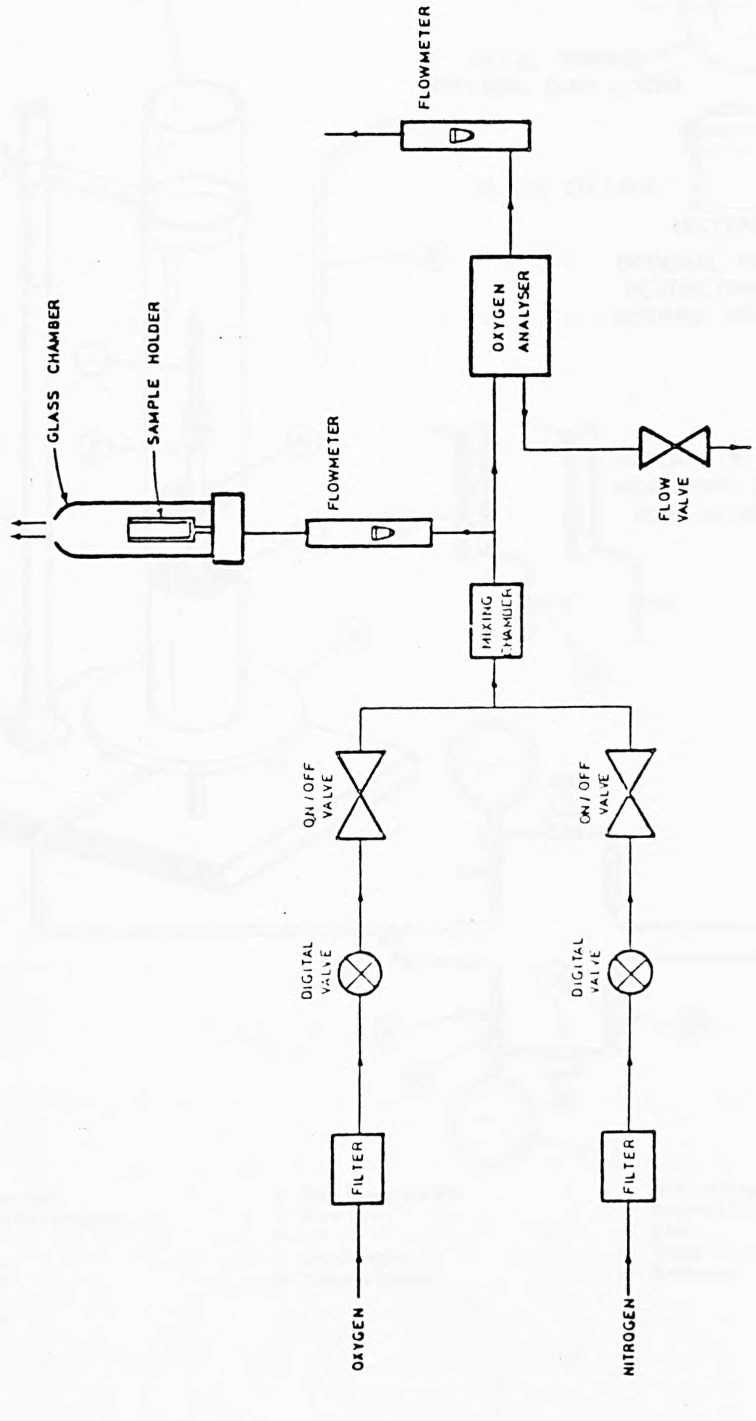
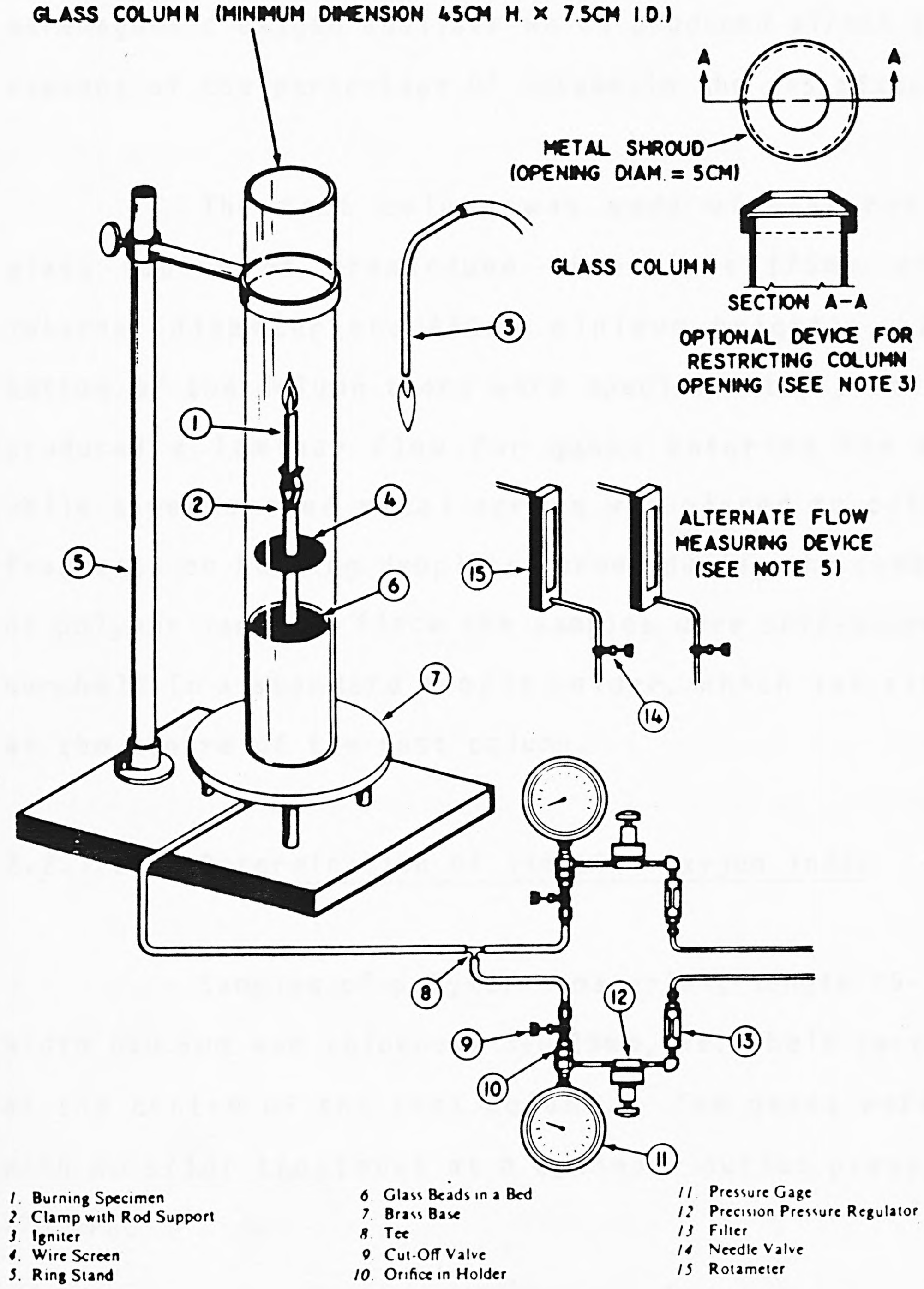


Fig. 2.2 Limiting Oxygen Index Apparatus



through a flowmeter which was calibrated to read from 0-25 $dm^3 min^{-1}$. A small by-pass flow went directly to paramagnetic oxygen analyser which produced direct digital readout of the percentage of oxygen in the gas mixture.

The test column was made of heat-resistant glass tubing of prescribed dimensions (75mm minimum internal diameter and 450mm minimum height). At the bottom of the column there were special entry ports which produced a laminar flow for gases entering the column while a perforated metal screen was placed to catch any fragments or burning droplets formed during the combustion of polymer samples. Since the samples were self-supporting, they wereheld in a standard sample holder, which was situated at the centre of the test column.

2.2.1.2 Determination of limiting oxygen index

Samples of polymeric material, length 75-150mm, width 6±0.5mm and thickness 3±0.25mm, were held vertically at the centre of the test column. The gases were used with no prior treatment at a cylinder outlet pressure of 170 kPa.

The tip of the specimen was ignited for 20s (or until a stable flame was attained) with a standard ignition source (a tube with an orifice of diam. 1-3mm, from which a 6-25mm long gas flame issued). The atmosphere contained a known concentration of oxygen and the total gas flow rate was maintained for at least 30s prior to ignition. The oxygen concentration was measured with a paramagnetic oxygen analyser producing an electrical signal which allowed direct digital read-out of the limiting oxygen index. After ignition, if the polymeric material burned for more than 3 min, the oxygen concentration was gradually reduced and, if the specimen was extinguished in less than 3 min, the oxygen concentration was increased. This procedure was repeated until an oxygen concentration was reached at which extinction occurred 3 min after ignition. The oxygen concentration in which a candle of polymer burned for a period of 3 min was recorded as the limiting oxygen index (LOI).

2.2.1.3 Computer measurements

The City University computer system (Honeywell) was used to analyse the values of the limiting oxygen index as a function of composition. The programme (see Appendix) was set to read an introductory set of statements followed by the observed values of the oxygen index as a function of composition. The composition variables are scaled to a triangular grid, with selected compositions forming the vertices, so as to include most points within the triangle.

The programme then calculates the necessary coefficients for linear, quadratic, reduced cubic, full cubic and quartic equations by the least-squares procedure, conducts a statistical analysis of the observed values by comparing each with the values calculated from the coefficients at that composition and then displays the calculated response surface as a contour plot which may reveal details not immediately apparent from the data itself, such as the optimum proportion of additives. The programme also calculates average coefficients for the additive and the interaction between additives, using the "integral effectiveness" techniques of Baldry (1985).

Polynomials of order 1-4 were tried and the coefficients were defined as follows. Y_i represents the calculated LOI for polynomial of order i and X_1, X_2 and X_3 are the composition coordinates of any point expressed on the triangular coordinate system derived from the selected vertices. (They are thus transformations of the original composition coordinates).

First order polynomial:

$$Y_1 = \sum_{J=1}^{3} a_J X_J$$

Second order:

$$Y_2 = Y_1 + a_4X_1X_2 + a_5X_1X_3 + a_6X_2X_3$$

Third order (reduced):

$$Y_{3r} = Y_2 + a_7X_1X_2X_3$$

Third order (full):

$$Y_3 = Y_{3r} + a_8X_1X_2(X_1-X_2) + a_9X_2X_3(X_2-X_3) + a_{10}X_1X_3(X_1-X_3)$$

Fourth order:

$$Y_4 = Y_3 + a_{11}X_1X_2(X_1^2 + X_2^2 - 3X_1X_2) + a_{12}X_2X_3(X_2^2 + X_3^2 - 3X_2X_3)$$

$$+ a_{13}X_1X_3(X_1^2 + X_2^2 - 3X_1X_3) + a_{14}X_1X_2^2 + a_{15}X_1X_2X_3^2$$

The quality of the fit was assessed from the value of the root mean square difference between calculated and observed LOI values by the multiple regression correlation coefficient (RCC), by the examination of the individual difference between calculated and observed LOI values, and by a sequential F-test to assess the significance of the most recently introduced items (See Appendix).

Data input

1 Name of composition variables

2 " " " "

3 " " " "

4 Title of calculation

5 Control variable

Min LOI, step size, input selector, output selector

$$\text{where step size} = \frac{\text{Max LOI - Min LOI}}{10}$$

Input selector = 1

Output selector = 3

6 - 6th line cavc, h, c sub.

cavc = index for average coefficient calculation

= 0 (no calculation)

= 1 (calculate for 2 additives)

b = additive loading for coefficient calculation

C sub + if cavc = 2, this is the substrate response (LOI)

if cavc = 3, this is the change in additive loading over which incremental calculation is carried out

7 LOI	comparison variable 1	comparison variable 2	comparison variable 3
n ← -1	0.0	0.0	0.0
n+1 ←	composition coordinates of vertices		
n+2 ←	"	" "	"
n+3 ←	"	" "	"

To run

```
←——— CONV* = Frogdata:S

←——— JRN RUNFROG

←——— SNUMB xxxxt

←——— JSTS  xxxxt

←——— JOUT  xxxxt

FUNCTION: ←— ACTIVITY O2

FUNCTION: ←——DIRECT ONLINE
```

Triangular diagrams were plotted using the computer for:

(1) Polypropylene - Ferrocene - Cereclor 70

x(1) - 100% PP

0% Ferrocene

0% Cereclor 70

x(2) - 95% PP

5% Ferrocene

0% Cereclor 70

x(3) - 75% PP

0% Ferrocene

25% Cereclor 70

(2) Polypropylene - zinc acetylacetonate - Cereclor 70

x(1) - 100% PP

0% Zn(II) AcAc

0% Cereclor 70

x(2) - 95% PP

5% Zn(II) AcAc

0% Cereclor 70

x(3) - 75% PP

0% Zn(II) AcAc

25% Cereclor 70

(3) Polypropylene - Stannic bis acetylacetone dichloride - Cereclor 70

x(1) - 100% PP

0% Sn(IV) AcAc Cl_2

0% Cereclor 70

x(2) - 95% PP

5% Sn(IV) AcAc Cl_2

0% Cereclor 70

x(3) - 75% PP

0% Sn(IV) AcAc Cl_2

25% Cereclor 70

(4) Polypropylene - Bis hydroxo hexabenzoatotris iron (III) benzoate - Cereclor 70

x(1) - 100% PP

0% BHB tris Fe(III)

0% Cereclor 70

x(2) - 95% PP

5% BHB tris Fe(III)

0% Cereclor 70

x(3) - 75% PP

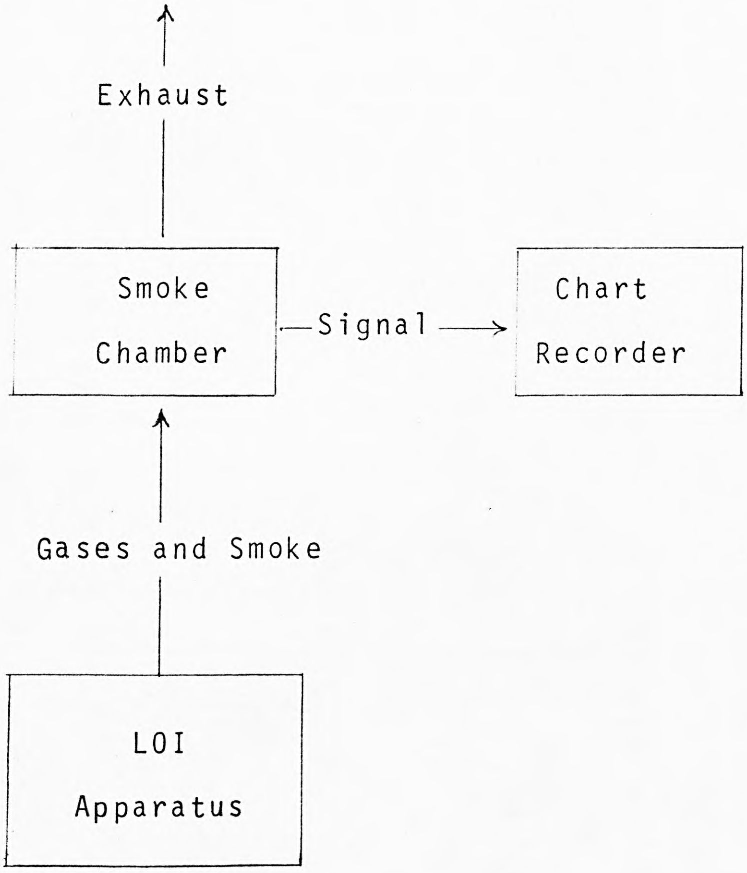
0% BHB tris Fe(III)

25% Cereclor 70

2.2.2 Measurement of smoke

2.2.2.1 The smoke chamber

The amount of smoke generated was determined from measurements, based on light obscuration, in a dynamic smoke chamber. The system consisted essentially of an oxygen index apparatus and a smoke chamber coupled to a chart recorder. The smoke chamber was located above the LOI apparatus from which the gases and smoke flowed into it. The diagrammatic representation of the system is shown below:



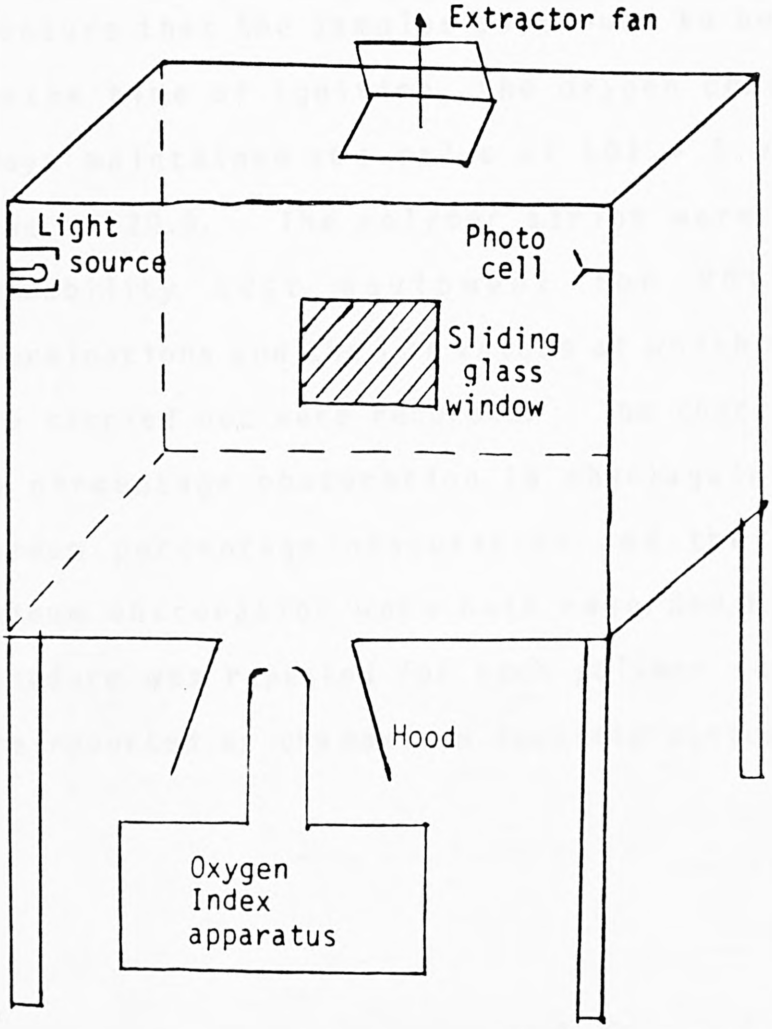
The smoke chamber, which is shown in outline in Fig. 2.3, consisted of a metal cabinet (dimensions 62 cm high, 61 cm deep and 123 cm wide) with a sliding glass window. At the top of the chamber was an extraction flue, operated by an electric fan which discharged the smoke and product gases out into the exhaust tube.

The photometric system consisted of a high-intensity light source on the left of the chamber which shone on to a photo-cell on the right of the chamber. When the smoke chamber was in operation, the intensity of light reaching the photocell was plotted by a chart recorder as percentage obscuration. Thus the instrument measured values of minimum transmittance (or maximum obscuration). The obscuration measurements (% obsc) were converted to specific optical density, D_S, by means of the following equation:

$$D_S = \frac{V}{LA} \log \frac{100}{100 - \%\text{obsc}}$$

where V is the volume of the smoke chamber, L is the length of the light path and A is the area of the exposed polymer sample. The instrument constant $\frac{V}{LA}$ had a value of 1891 for the particular smoke chamber concerned.

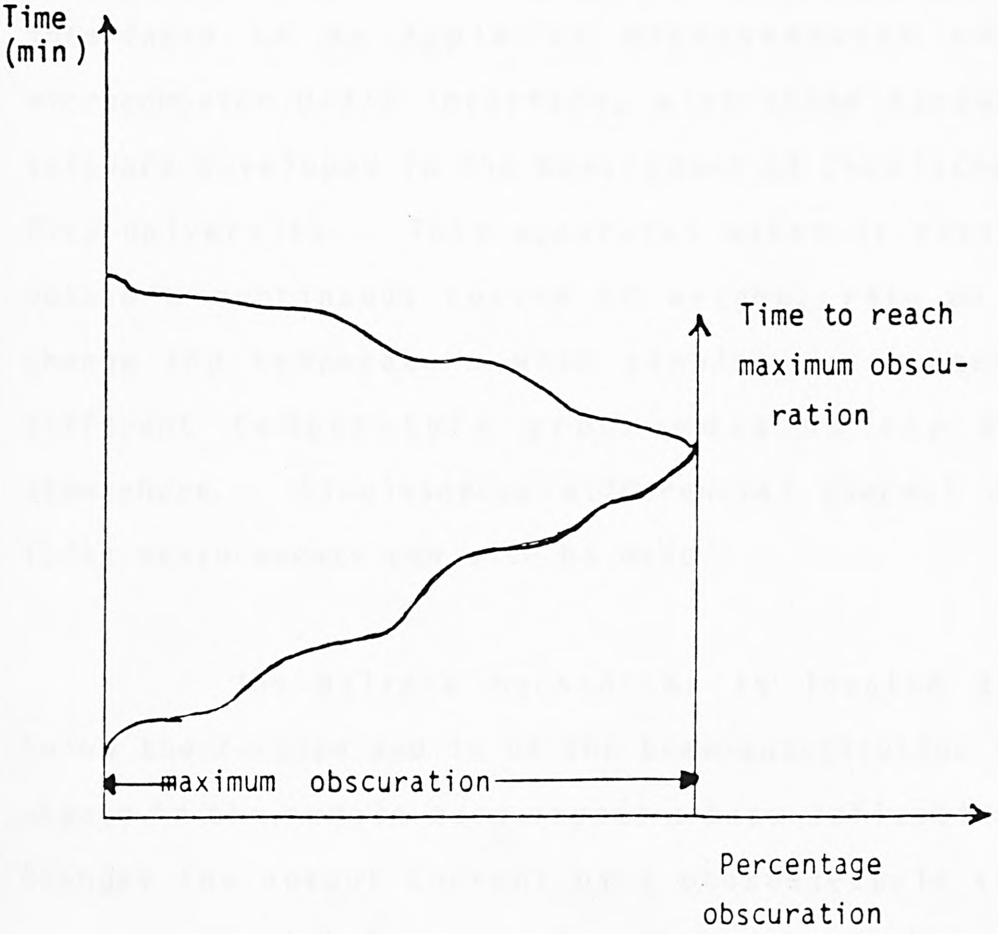
Fig. 2.3 Smoke Chamber



2.2.2.2 Measurement of extent of smoke formation

Prior to carrying out a test, the light source was switched on and the chart recorder was calibrated to read 100 and 0% obscuration when the light was "off" and "on" respectively. Samples of polymeric material, length 100±25mm, width 6±0.5mm, thickness 3±0.25mm, were held vertically in the oxygen index apparatus. In order to ensure that the samples continued to burn after 3 min from the time of ignition, the oxygen concentration was always maintained at a value of LOI + 1 with a minimum value of 20.9. The polymer strips were ignited in the flammability test equipment for 20s as for LOI determinations and the LOI values at which the smoke tests were carried out were recorded. The chart recorder plots the percentage obscuration (% obsc) against time. The maximum percentage obscuration and the time to reach maximum obscuration were both recorded (Fig. 2.4). This procedure was repeated for each polymer sample. Results were reported as the maximum specific optical density (D_s).

Fig. 2.4 Plot of % obscuration against time



2.2.3 Thermoanalytical measurements

2.2.3.1 The thermobalance

Thernoanalytical studies of the degradation and oxidation of polypropylene and of the extent of interaction between various metal chelates and Cereclor 70 were made using a Mettler "Thermoanalyser 2" thermobalance interfaced to an Apple II microcomputer via a U-microcomputer U-A/D interface, with other hardware and software developed in the Department of Chemistry at the City University. This apparatus makes it possible to obtain a continuous record of weight, rate of weight change and temperature when samples are heated under different temperature programmes in any desired atmosphere. Simultaneous differential thermal analysis (DTA) measurements can also be made.

The balance mechanisms is located directly below the furnace and is of the beam-substitution type. A change in the sample mass causes a beam deflection which changes the output current of a photoelectric scanning system. The imbalance in photodiode current is amplified and passed through a coil attached to the balance beam which produces the restoring force. The current in the coil is used to measure the sample mass. The balance allows taring of samples of up to 15.99g and has three sensitivity ranges: 0-1000 mg, 0-100 mg and 0-10 mg respectively. A weight expansion unit provides greater accuracy by electronic amplification of the weight signal by a factor of ten. An accuracy of 0.2% of the range can be attained for all three ranges of sample mass.

The expanded weight signal is electronically differentiated to provide the first derivative of sample weight. The most sensitive range available on the thermogravimetric (TG) unit is 0.5 mg min^{-1} for full-scale deflection. The accuracy of the instrument is 0.4% in the differential thermogravimetry (DTG) range. Temperature measurements are carried out by means of a Pt/10%Rh thermocouple. The hot junction is located underneath and in contact with the crucible. Temperatures can be measured with an accuracy of $\pm 2.5^{o}$ at 100^{o}C and $\pm 2.0^{o}$ at 500^{o}C.

The DTA unit has six ranges: 20, 50, 100, 200, 500 and 1000 V. An accuracy of ±0.2% over the range can be attained for all six ranges. The analog/digital conversion uses an instrumentation amplifier with a linearity error of 0.2% and a 12-bit A/D converter with maximum non-linearity 1 bit (0.024% full scale). The furnace tube is of quartz and is surrounded by a reflecting shield. The heating element consists of a non-inductively wound Kanthal wire filament inside a bifilar quartz spiral (Fig. 2.5). The furnace may be heated from 25 to 1025^{o}C under computer control at a heating rate of up to a maximum of ca. 500^{o}/min (linear up to 100^{o}/min).

Sample holder geometry and composition are of great importance in thermal analysis. Two matched flat-bottomed Pt/10%Rh crucibles were used; these were 8mm in diameter and had a short straight wall rising vertically from the bottom of the crucible. The crucibles were supported on a sintered four-hole capillary tube which had a crosspiece 270mm from the end, bearing two short alumina pegs, 11mm apart. Special metal bands, which have no influence on the accuracy of weighing, were used to connect the thermocouple leads from the crucible holder to the fixed balance housing (Fig. 2.6).

The flow of gas through the furnace is controlled by a pressure-regulating valve and the flow rate is metered by a rotameter. The passage of gas between the balance housing and the reaction area is shielded by a metal baffle which rests in a socket on top of the balance housing when the crucible holder is in position. This prevents any substance which may fall

Fig. 2.5 Bifilar quartz spiral furnace

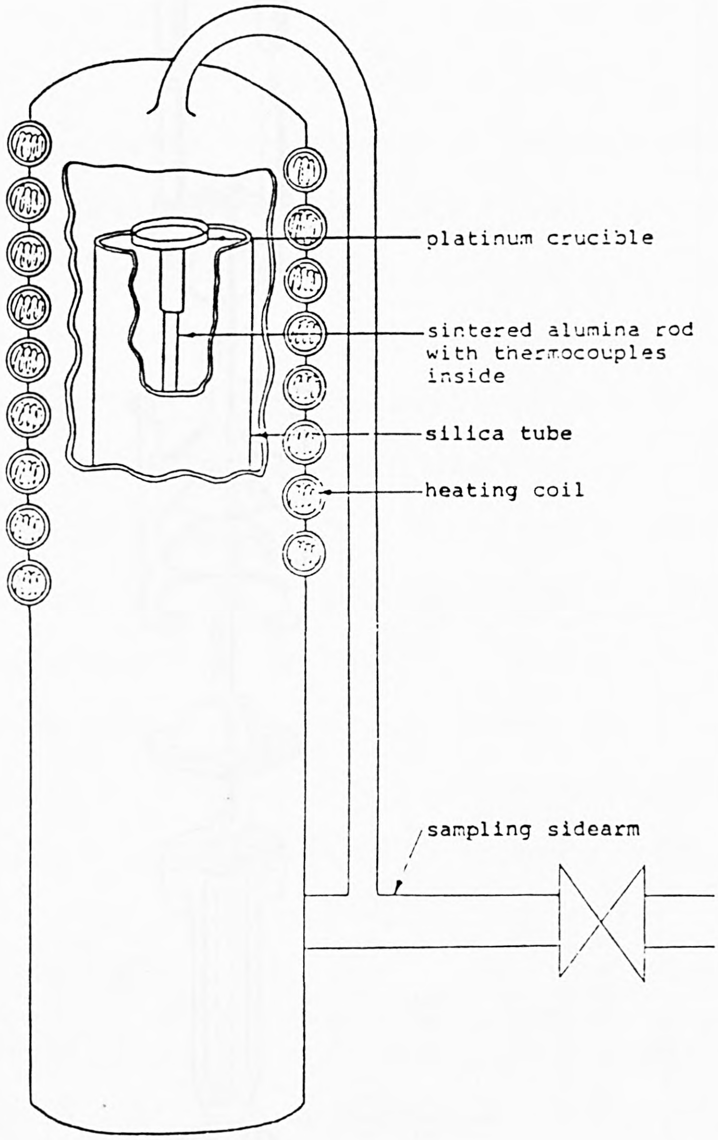
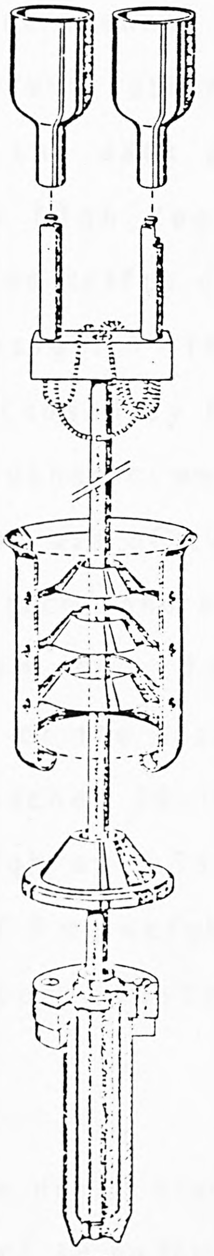


Fig. 2.6 Crucible holder for DTA



from the crucible from entering and contaminating the balance housing. The gases leaving the furnace can be passed through a gas analyser. The limits of error stated in this section for the various channels, other than the temperature channel, are lower than those which can be obtained on most other commercial thermobalances. However, although the data points can be read off the record chart to a high degree of accuracy, this is impaired by base-line drifts caused by defects inherent in the instrument design. The base-line drift in the weight channel is caused by buoyancy effects due to the heating. In some other commercial thermobalances this has been overcome by use of two matched furnaces, one for each arm of the balance, and by symmetrical design of the balance. In the Mettler "Thermoanalyser 2" thermobalance, most of the base-line drift finishes by the time the sample reaches 75-100°C. The extent of this drift can be as high as 0.15 mg, which corresponds to 1.66% in a sample of 9 mg weight. From 100 to 1000°C the base-line rises approximately linearly at ca. 0.03 mg/100°.

Base-line drift also occurs on the DTA channel, which leads to errors in calculation of the peak areas of thermal changes. Because the sample is supported on a long rod inside the furnace, it is impossible to align the crucible with the axis of the furnace. As a result there is a difference in temperature between the sample and reference crucibles, which causes the base-line drift. High heating rates increase the effect significantly. Base-line drift in DTA would be reduced if a furnace with a more even temperature distribution were used.

A 12-channel, 6-point dot recorder simultaneously traces in different coloured inks, the temperature curve, the two weight traces (natural and expanded), the differential of the weight trace and the DTA trace. The dot intervals of the tracings were chosen, so that each curve, according to its gradient, had the optimum point density. When these points are later joined up, a series of curves and lines are obtained. Block schematic diagrams of the balance mechanism and of the recording and electric systems are shown in Figs. 2.7 and 2.8 respectively.

2.2.3.2 Mettler computer interface system

Interface hardware: Fig. 2.9 shows a schematic diagram of the Mettler computer interface system, viz. an Apple II microcomputer with twin disc drives, interfaced through a U-Microcomputer U-A/D interface, consisting of a digital board, plugged into one

Fig. 2.7 Block schematic diagram of the balance mechanism

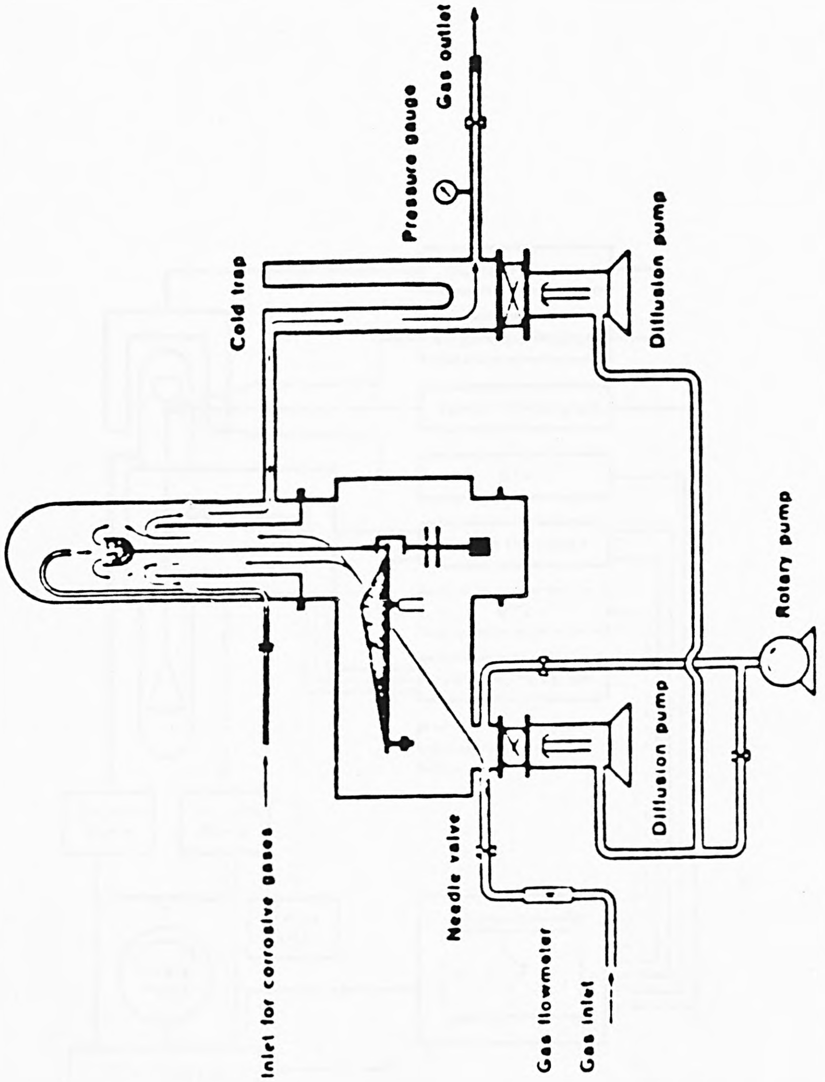


Fig. 2.8 Block schematic diagram of the balance mechanism and the recording and electric systems

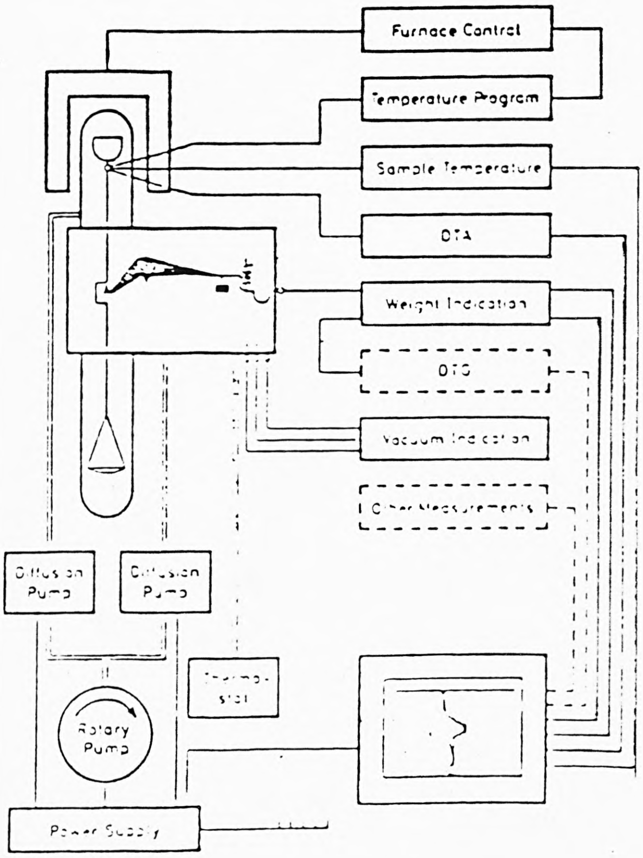
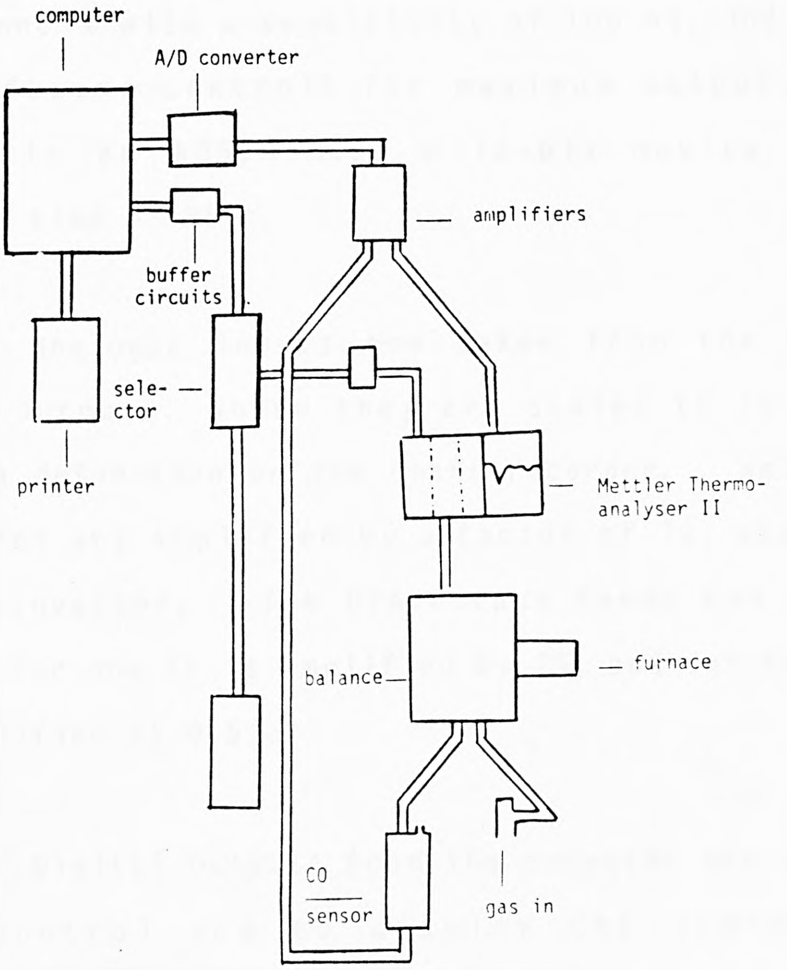


Fig. 2.9 Schematic diagram of Mettler Computer interface system



of the Apple expansion slots and connected to an A/D converter unit. The digital board has two 6522 VIA; one is used for timing and the other for digital output. The A/D computer board has been modified by adding filtering and by changing the input resistors to give a symmetrical input configuration. The A/D converter unit has eight input channels with a sensitivity of 100 mV, 10V or 1V (under software control) for maximum output. The converter is an AD574 i.e. a 12-bit device with a conversion time of 25μs.

Analogue inputs are taken from the Mettler amplifier outputs, where they are scaled to 10 mV for full-scale deflection on the chart recorder. Weight and temperatures are amplified by a factor of 10, and fed to the A/D converter. The DTA output feeds two digital channels; for one it is amplified by 25, and for the other is it amplified by 0.5.

Digital outputs from the computer are used for furnace control and to display the approximate temperature. The computer sends alternatively control codes and data: control codes determine whether the furnace is switched on or off, whether the display is showing figures or is blank, and whether the data which follow are for furnace control or for display. The selector circuit interprets the codes, and routes appropriate data and control signals to the D/A converter or the display. The D/A converter provides a voltage, suitably scaled, which is fed into the furnace control circuits of the Mettler, and a voltage which switches on or off the furnace power. Relays added to the Mettler control unit disconnect the Mettler's timing and temperature programme circuits and connect the D/A converter when power is applied to the converter. The temperature display contains a liquid crystal display and drive circuits which convert the 9-bit binary output from the computer to binary-coded decimal scale from 0 to 1275^{o}C in increments of 5^{o}.

Interface Software

General scheme: Machine-code routines are used to provide control signals to the A/D converter and the control and data signals for furnace control and temperature display, and further routines handle data collection, preliminary signal conditioning and storage. These are used in three programmes: (i) real-time graphical display of input data, for initial setting up, (ii) reading and averaging data provided by standard input conditions for calibration purposes, and (iii) control and data collection during normal running of the Mettler. Program (ii) produces a file of calibration data which are used by program (iii) to convert digital input to numerical data. Program (iii) samples data continuously and writes data (selected by criteria chosen by the user) to one or more data discs.

Further programs deal with the data stored on discs: (i) a plotting program will produce suitably scaled plots of any pair of data items; (ii) a printing program produces a complete listing of the data stored in a particular disc file, and (iii) a tape-punching program produces a paper tape containing selected data from the run; this may be read and stored on a mainframe computer for detailed kinetic analysis and plotting.

2.2.3.3 Procedure for thermal analysis

After the recorder had been switched on, the air flow rate was set at 60 cm^3 min^{-1} for a sample weight of 8-10 mg. Small strips of polymer samples, cut from the centre of a standard plate were spread evenly over the crucible surface. The range shift on the DTG panel was set on manual and a sensitivity of 5 mg min^{-1} per full scale deflection was used throughout. The range used for differential thermal analysis was 200 V, while for temperature readings it was 10 mV; the heating rate used throughout was 5^{o} min^{-1}.

The results of thermogravimetric and differential thermal analysis runs were printed on a 25 cm wide chart of a six-channel chart recorder.

2.2.4 Measurement of photostability

2.2.4.1 Photo-irradiation set-up

Film samples, of length 70mm, width 15mm, thickness 0.2mm, were mounted on the inside of a glass vertical drum and exposed to air and at the ambient temperature to the filtered radiation from a mercury lamp (400 W) and only wavelengths greater than 320 nm were selected by the use of a Corning CS.1-64 filter. The lamp-sample distance was 90mm and the lamp was cooled by water circulation through the water jacket.

The characteristics of the spectrum of a medium-pressure mercury lamp are shown in Table 2.1. The application of monochromators or filter combinations permits the use of a medium pressure lamp for a few narrow, monochromatic bands in the visible and ultraviolet range. The intensity of the lamp used in this work was $3500 \mu V\ cm^{-2}$.

2.2.4.2 Measurement of extent of polymer degradation

Absorption measurements were carried out with Perkin Elmer 457 IR spectrophotometer. Prior to carrying out a run, the spectrophotometer was switched on and calibrated to give 100% and 0% transmittance when the sample beam was 'on' and 'off' respectively for quantitative measurements. Ultraviolet absorption spectrum measurements were made with a Unicam double-beam-type spectrophotometer. Fluorescence measurements were carried out with Perkin Elmer MPF-4 spectrophotometer.

Table. 2.1 Energy distribution in medium-pressure mercury arc[a] (from Calvert and Pitts, Photochemistry, Wiley, New York, 1966, Table 7.2)

Wavelength (nm)	Relative energy
1367.3	15.3
1128.7	12.6
1014	40.6
577-579	76.5
546.1	93.0
435.8	77.5
404.5-407.8	42.2
365-366.3	160.0
334.1	9.3
312.6-313.2	49.9
302.2-302.8	23.9
296.7	16.6
289.4	6.0
280.4	9.3
275.3	2.7
270	4.0
265.2-265.5	15.3
257.1	6.0
257.7	16.6[b]
248.2	8.6
240	7.3
238	8.6
236	6.0
232	8.0
222.4	14.0

[a] Hanovia type A, 673A, 550-W lamp

[b] Reversed radiation

3 - Results

3. Results

3.1 Studies of polymer flammability

3.1.1 Measurements on polystyrene

The effects, on the flammability and smoke-forming tendency of polystyrene and of some metal chelates, both in the absence and presence of Cereclor, are shown in Tables 3.1 and 3.2.

Polystyrene was easy to ignite and burnt with a sooty flame and considerable melting and dripping. None of the additive systems investigated increased the LOI of the base polymer by more than 5 units; but many of the metal chelates were very effective in decreasing the amount of smoke formed and this was particularly true of BuSalAl Cu(II).

Tables 3.1 and 3.2 also show that, with the acetonates and ferrocene, both the flammability of, and the amount of smoke formed from, polystyrene are decreased when the organometallic compounds are used in conjunction with Cereclor. On the other hand, with most salicyaldimino and stilbene dithiolato complexes, the presence of the halogen compound decreases flammability but increases smoke

Table 3.1 The effects of metal chelates, in the absence and presence of Cereclor, on the flammability of polystyrene

Metal chelate	LOI values for polystyrene containing	
	1 phr metal chelate	1 phr metal chelate +20 phr Cereclor 70
Nil	16.0	19.7
Co(II) AcAc	17.8	20.5
Fe(II) AcAc	18.1	20.2
Ni(II) AcAc	18.6	20.6
Zn(II) AcAc	17.8	19.6
PheSalAl Co(II)	18.4	20.0
BuSalAl Cu(II)	18.2	20.0
3-CarbPheSalAl Cu(II)	17.6	19.9
4-CarbPheSalAl Cu(II)	17.4	19.7
3-HydPheSalAl Cu(II)	17.3	20.1
t-BuSalAl Cu(II)	18.0	20.2
PheSalAl Ni(II)	18.3	19.9
SDT Ni(II)	18.8	19.7
S,S-di-MeSDT Ni(II)	17.6	20.5
Ferrocene	18.4	20.9

Table 3.2 The effects of metal chelates, in the absence and presence of Cereclor, on the smoke-producing tendency of polystyrene

Metal chelate	D_s values for polystyrene containing	
	1 phr metal chelate	1 phr metal chelate +20 phr Cereclor
Nil	959	1120
Co(II) AcAc	1277	930
Fe(II) AcAc	1277	644
Ni(II) AcAc	1235	799
Zn(II) AcAc	1419	1235
PheSalAl Co(II)	930	1726
BuSalAl Cu(II)	499	1277
3-CarbPheSalAl Cu(II)	666	1235
4-CarbPhesALAl Cu(II)	799	516
3-HydPheSalAl Cu(II)	849	1277
t-BuSalAl Cu(II)	1195	1138
PheSalAl Ni(II)	959	1592
SDT Ni(II)	800	1020
S,S-di-MeSDT Ni(II)	1036	1891
Ferrocene	708	606

production, the one notable exception being found with 4-CarbPheSalAl Cu(II).

3.1.2 Measurements on polypropylene

3.1.2.1 Polypropylene on its own

Limiting oxygen index (LOI) values for a number of commercial samples of polypropylene have been quoted on numerous occasions in the literature. The results vary from 17.4 to 18.6 (Fenimore and Martin, 1972; Benisek, 1974). The value for the polypropylene used in this work (Profax 6301) was found to be 18.4. This result is consistent with that of Cullis and Hirschler (1984).

Polypropylene burnt readily in air with some melting and dripping but produced very little smoke on its own so that no measurements were made of the effectiveness of additives on the amount of smoke formed from this polymer.

3.1.2.2 Polypropylene/Cereclor

The addition of Cereclor to polypropylene did not increase the limiting oxygen index by more than 6 units (Table 3.3). A sharp increase in the LOI was observed for samples containing up to 10 phr of Cereclor and also for samples containing between 20 and 30 phr (Fig. 3.1). A gradual increase in the LOI was noticed for samples containing between 10 and 20 phr.

Polypropylene, metal chelates and Cereclor

The effects of some metal chelates, both in the absence and presence of Cereclor, on the flammability of polypropylene are shown in Table 3.4. The results show that the nature of the metal was not by itself an important factory controlling the flame-retardant action. None of the metal chelates on their own increased the LOI of the base polymer by more than 2 units, butmany of these additives were very effective in decreasing the flammability of the polymer in the presence of Cereclor. All the nickel chelates were ineffective flame-retardants for polypropylene, even in the presence of Cereclor, except nickel acetyl acetonate which, in conjunction with the chlorine compound. increased the LOI by 6 units. The salicylaldiminoand N,N'-bis salicylidene ethylene diamine complexes, in the presence of Cereclor increased the LOI by 5 to 7 units.

Fig. 3.1 The effect of Cereclor on the flammability of polypropylene

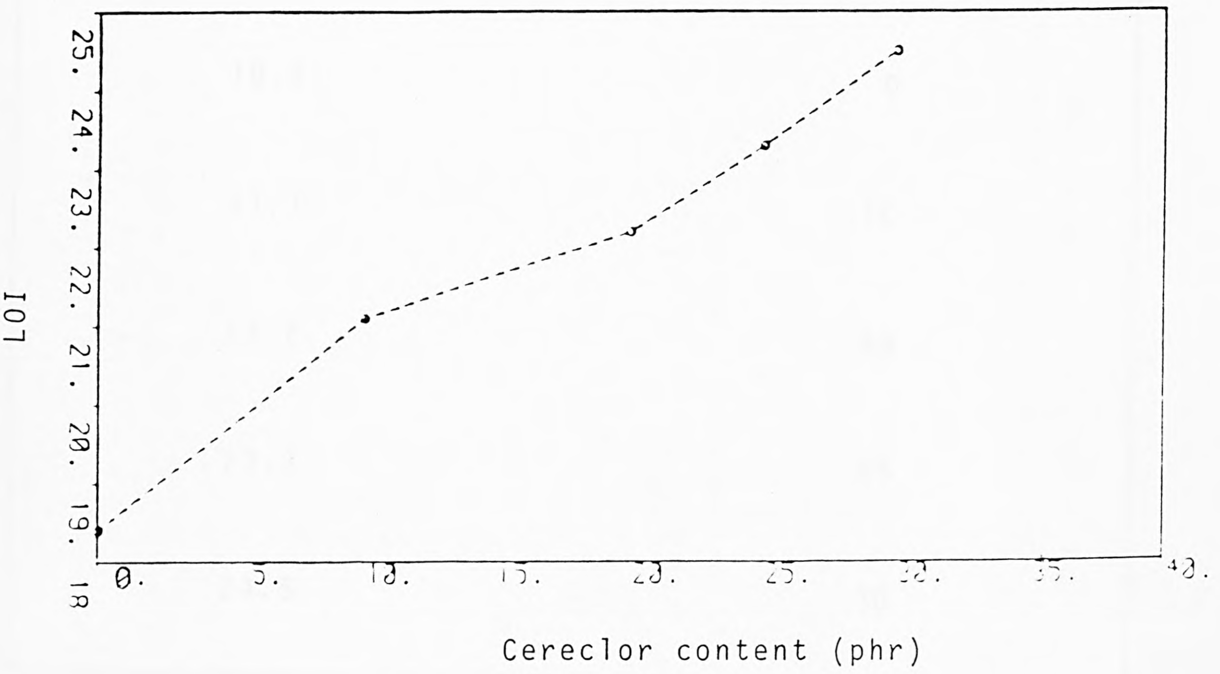


Table 3.3 The effects of Cereclor 70 on the flammability of polypropylene

LOI	Cereclor 70 (Phr)
18.4	0
21.1	10
22.2	20
23.3	25
24.5	30

Table 3.4 The effects of metal chelates, in the absence and presence of Cereclor, on the flammability of polypropylene

Metal chelate	LOI values for propylene containing	
	1 phr metal chelate	1 phr metal chelate +20 phr Cereclor 70
Nil	18.4	22.2
Ni(II) AcAc	19.0	24.5
Ni(II) SDT	18.9	19.9
Ni(II)S,S-di-Me SDT	18.6	19.6
Bis(4-aminopent-3-en-2-onato)Ni(II)	19.6	21.8
Al(III) AcAc	19.8	21.9
3-CarbPheSalAl Cu(II)	19.1	23.2
3-HydPheSalAl Cu(II)	18.9	24.0
t-BuSalAl Cu(II)	19.6	25.2
Bis ethylene diamino Cu(II). CuSO$_4$.6H$_2$O	19.2	23.3
Fe(III) SalenCl	18.9	24.0
SnCl$_4$,(SalenH$_2$)	19.2	24.8
2-HydPheSalAl Fe(III)	20.2	23.9
2-HydPheSalAl-di-Me-Sn(IV)	20.5	25.1
Dichloroquinolin-8-olato iron(III)	19.7	24.9
THBtris Fe(III)	20.1	27.1

3.1.2.4 Polypropylene/Most effective metal chelates/ Cereclor

General

The following systems were studied:

PP + Ferrocene + Cereclor

PP+ Bishydroxohexabenzoato tris iron(III) benzoate + Cereclor

PP + Zinc acetylacetonate + Cereclor

PP + Tin acetylacetonate dichloride + Cereclor

The limiting oxygen index values determined for these systems were plotted in the form of triangular diagrams. Although any three different compositions can be used as vertices of a triangular diagram, only non-equilateral triangles have been used here.

In order to determine the most reliable plots of LOI versus composition and to assess the accuracy of the fit over the range of interest, 28 to 31 compositions were generally used for each of the five systems. These were spread over the composition ranges bounded by the points: (A) 100 wt% PP; (B) 95 wt% PP + 5 wt% metal chelate; (C) 75 wt% PP + 25 wt% Cereclor.

Polypropylene/Ferrocene/Cereclor

More details studies were made of the effect on the combustion of polypropylene of ferrocene, which has been shown to be a good smoke suppressant for poly(vinyl chloride) (Descamps et al. 1980) and for acrylonitrile-butadiene-styrene terpolymer (Deets and Lee, 1979). Consistent with this, excellent flame retardance can be achieved by the introduction of a relatively small amount of ferrocene together with Cereclor (Table 3.5).

When 1 phr of ferrocene was incorporated into polypropylene together with increasing amounts of Cerecor, there was a sharp increase, up to 20 phr Cereclor, in the LOI of 8.2 units, followed by a decrease of 1.5 units between 20 and 29 phr Cereclor.

A similar pattern was observed with 1.5 phr of ferrocene and different concentrations of Cereclor. A sharp increase of 7.4 LOI units was observed with up to 20 phr and followed by a decrease of 2.4 units between 20 and 27 phr Cereclor. It is therefore useless to add more

Table 3.5 The combined effects of Ferrocene and Cereclor on the flammability of polypropylene

Ferrocene (phr)	Cereclor (phr)	LOI
1	0	19.0
2	0	19.9
4	0	19.1
5	0	19.1
10	0	19.4
0.5	0.5	21.2
0.5	5	24.2
0.5	10	26.5
0.5	15	27.6
0.5	20	27.9
0.7	7	25.1
0.7	18	24.7
1	1	21.3
1	5	23.0
1	10	27.0
1	15	27.6
1	20	29.5
1	29	28.0
1.5	5	22.4
1.5	10	24.8
1.5	20	29.8
1.5	27	27.4
1.5	28.5	28.0
2	2	20.0
2	20	30.3
3	7	19.5
5	20	27.7

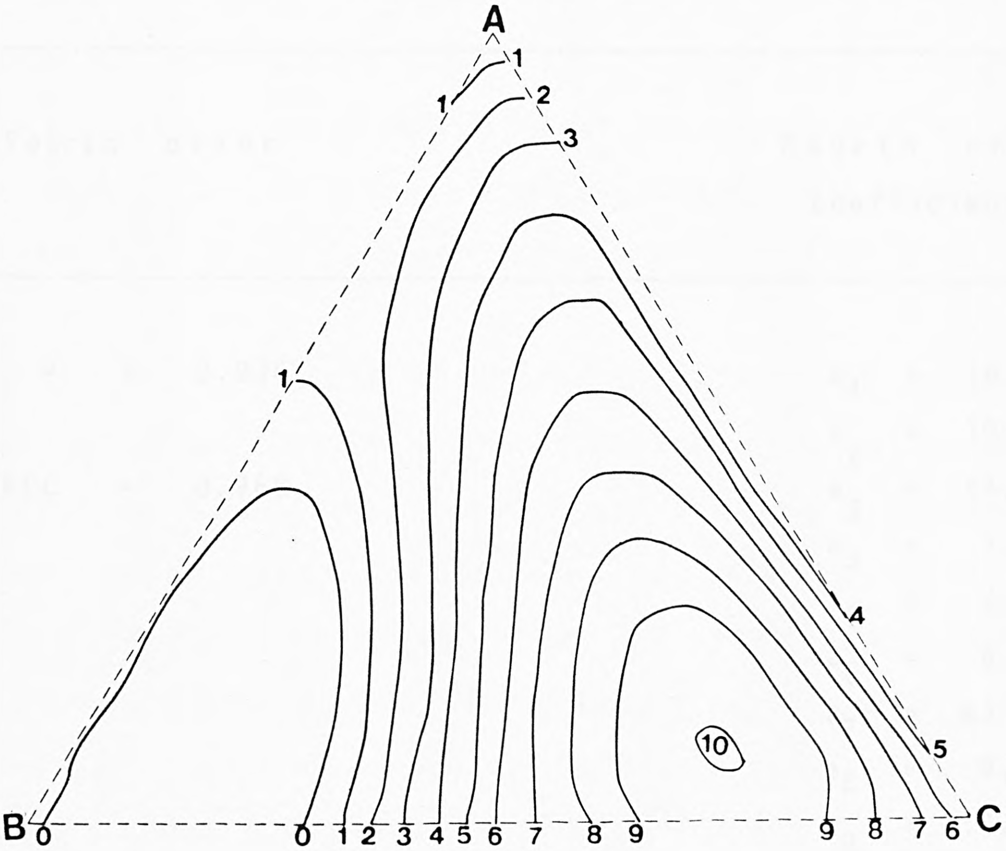
than 20 phr Cereclor to polypropylene-ferrocene systems.

When the weight of Cereclor was kept constant at 20 phr, the limiting oxygen index of the system increased steadily with the concentration of ferrocene between 0.5 phr and 2 phr, followed by a decrease in the oxygen index of 2.6 units between 2 and 5 phr of ferrocene . Thus it is not of value to add more than 2 phr of ferrocene to polypropylene-Cereclor systems.

Fig. 3.2 is a map of the LOI in terms of composition for 10 LOI values calculated from the best-fit polynomial and plotted as contour lines of constant LOI. Table 3.6 contains the root mean square errors and correlation coefficients as well as the coefficients for the fourth order polynomial corresponding to Fig. 3.2.

The triangular diagram shown in Fig. 3.2 indicates that ferrocene has a considerable effect on the flammability of polypropylene-Cereclor systems and the data in Table 3.6 show that the contours plotted in Fig. 3.2 represent accurately the results obtained since the regression correlation coefficient (RCC) has the ideal value of unity and has a value of 0.91. The synergistic interaction between the two additives is maximised at very low levels of ferrocene.

Fig. 3.2 Triangular diagram showing variation of LOI with composition for polypropylene-ferrocene-Cereclor systems



LOI values: 0=18.40, 1=19.59; 2=20.78; 3=21.97, 4=23.15; 5=24.35; 6=25.54; 7=26.73; 8=27.92; 9=29.11; 10=30.30.

Table 3.6 Root mean square error (σ), correlation coefficient (RCC) and coefficients of the best-fit fourth order polynomial shown for polypropylene/ferrocene/Cereclor systems

Fourth order	Fourth order coefficients
σ = 0.916	a_1 = 18.6
	a_2 = 19.5
RCC = 0.968	a_3 = 24.8
	a_4 = 1.8
	a_5 = 4.3
	a_6 = 8.5
	a_7 = 63.8
	a_8 = 9.0
	a_9 = -15.3
	a_{10} = -52.6
	a_{11} = 2.6
	a_{12} = 1.2
	a_{13} = -17.1
	a_{14} = -282.1
	a_{15} = 252.5

Polypropylene/[BHB tris Fe(III)]/Cereclor

Iron compounds are known to enhance the flame-retardant action of other metal-halogen systems (Antia, Cullis and Hirschler, 1982; Cullis 1984). Consistent with this, an effective flame-retardant system can be achieved by adding to the polymer a small amount of BHB tris Fe(III) together with Cereclor (Table 3.7). All the meaningful values were obtained with relatively low levels ($\leqslant$ 2 phr) of BHB tris Fe(III).

When 1 phr of BHB tris Fe(III) was incorporated into polypropylene together with increasing amounts of Cereclor (varying from 1 to 29 phr), there was a sharp increase in the limiting oxygen index for samples containing up to 10 phr Cereclor. A small increase in the LOI of 0.6 unit was noticed for samples containing between 10 and 15 phr Cereclor; this was followed by a steady decrease in the limiting oxygen index from 28.5 to 25.6 for samples containing between 15 and 29 phr Cereclor.

A similar pattern was observed when the weight of BHB tris Fe(III) was kept constant at 0.5 phr. The limiting oxygen index increased sharply with the concentration of Cereclor up to 10 phr, followed by a sudden decrease from 27.7 to 24 for samples containing between 10 and 20 phr Cereclor.

<u>Table 3.7</u> The combined effects of BHB tris Fe(III) and Cereclor on the flammability of polypropylene

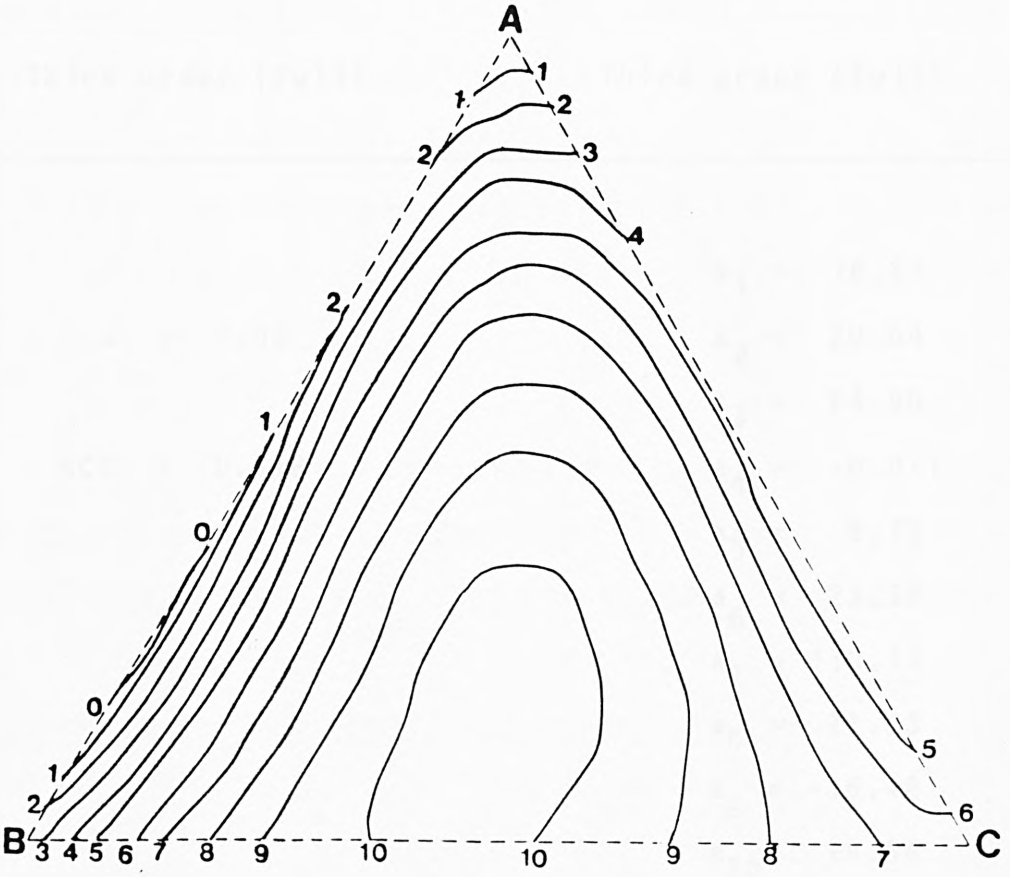
BHB tris Fe(III) (phr)	Cereclor (phr)	LOI
1	0	19.9
2	0	20.4
3.5	0	19.3
5	0	19.6
0.5	0.5	21.4
0.5	10	27.7
0.5	15	25.2
0.5	20	24.0
0.7	7	27.3
0.7	18	25.6
1	1	21.5
1	5	25.8
1	10	27.9
1	15	28.5
1	20	27.2
1	29	25.6
1.5	5	26.6
1.5	10	27.6
1.5	20	27.3
1.5	27	26.8
1.5	28.5	25.4
2	2	22.3
2	20	28.2
3	7	26.6
5	20	25.6

An increase in the amount of Cereclor from 5 to 28.5 phr with a fixed loading (1.5 phr) of BHB tris Fe(III) showed an increase in LOI from 26.6 to 27.7 for samples containing between 5 and 10 phr Cereclor. This was followed by a decrease of 2.2 units betwee 10 and 28.5 phr Cereclor (Fig. 3.4).

With polypropylene-BHB tris Fe(III) systems the best result was therefore obtained with between 10 and 15 phr of Cereclor. This means that the addition of more than 15 phr of Cereclor to polypropylene-BhB tris Fe(III) systems is of no value. When the weight of Cereclor was kept constant at 20 phr, the limiting oxygen index of the system increased sharply as the concentration of BHB tris Fe(III) was increased from 0.5h to 1 phr; this was followed by a small increase from 27.2 to 28.2 between 1 and 2 phr of BHB tris Fe(III). A decrease in the LOI of 2.6 units was observed between 2 and 5 phr BHB tris Fe(III). Thus there is no point in adding more than 2 phr of BHB tris Fe(III) to polypropylene-Cereclor systems.

Fig. 3.3 is a map of the LOI in terms of composition for 10 values calculated from the best-fit polynomial and plotted as contour lines of constant LOI. Table 3.8 contains the root mean square error and correlation coefficient as well as the coefficients for the third order (full) polynomial corresponding to Fig. 3.3. This

Fig. 3.3 Triangular diagram showing variation of LOI with composition for polypropylene-BHB tris Fe(III)-Cereclor systems



LOI values: 0=18.40; 1=19.41; 2=20.42; 3=21.43; 4=22.44; 5=23.45; 6=24.46; 7=25.47; 8=26.48; 9=27.49; 10=28.50.

Table 3.8 Root mean square error, correlation coefficient and coefficients of the best-fit third order (full) polynomial for polypropylene/BHB tris Fe(III)/Cereclor

Third order (full)	Third order (full)
	$a_1 = 18.23$
$\sigma = 1.05$	$a_2 = 20.64$
	$a_3 = 24.90$
RCC = 0.918	$a_4 = -0.071$
	$a_5 = 5.72$
	$a_6 = 23.30$
	$a_7 = 110.11$
	$a_8 = 21.23$
	$a_9 = -16.48$
	$a_{10} = 14.54$

triangular diagram shows an increase in the LOI with increasing concentration of Cereclor along the polypropylene-Cereclor base line. The limiting oxygen index also increased on the addition of a relatively small amount of BHB tris Fe(III) to Cereclor. Along the polypropylene-BHB tris Fe(III) base line, the BHB tris Fe(III) on its own had no noticeable effect on the LOI which increased rapidly with the incorporation of Cereclor. The area of highest flame-retardancy was observed with concentrations of Cereclor between 10 and 15 wt% and of BHB tris Fe(III) between 2 and 3 wt%.

The least squares calculation is in good agreement with the experimental data giving a RMS difference (σ) value of 1.05 and an RCC value of 0.918.

Polypropylene/zinc acetyl acetonate/Cereclor

Zn(II) AcAC on its own did not increase the limiting oxygen index of the base polymer by more than 1.5 units even with concentrations up to 5 phr (Table 3.9). A rapid increase in the LOI was observed on addition of Cereclor to polypropylene-Zn(II) AcAc systems. When the concentration of Zn(II) AcAc was kept constant at 1 phr and the loading of Cereclor was increased, a sharp increase in LOI was noticed for samples containing between 1 and 3 phr of Cereclor and a slower increase from 25.6 to

Table 3.9 The combined effects of Zn(II) AcAc and Cereclor on the flammability of polypropylene

Zn(II) AcAc (phr)	Cereclor (phr)	LOI
1	0	19.4
2	0	19.45
5	0	19.5
0.5	0.5	20.8
0.5	5	25.9
0.5	10	27.5
0.5	15	27.2
0.5	20	28.5
0.7	7	26.4
0.7	18	28.0
1	1	21.2
1	3	25.6
1	5	27.1
1	10	28.0
1	15	28.2
1	20	28.9
1	29	28.6
1.5	5	25.5
1.5	10	28.4
1.5	20	29.0
1.5	27	28.4
1.5	28.5	28.7
2	2	24.1
2	5	25.6
2	20	29.1
3	7	26.8

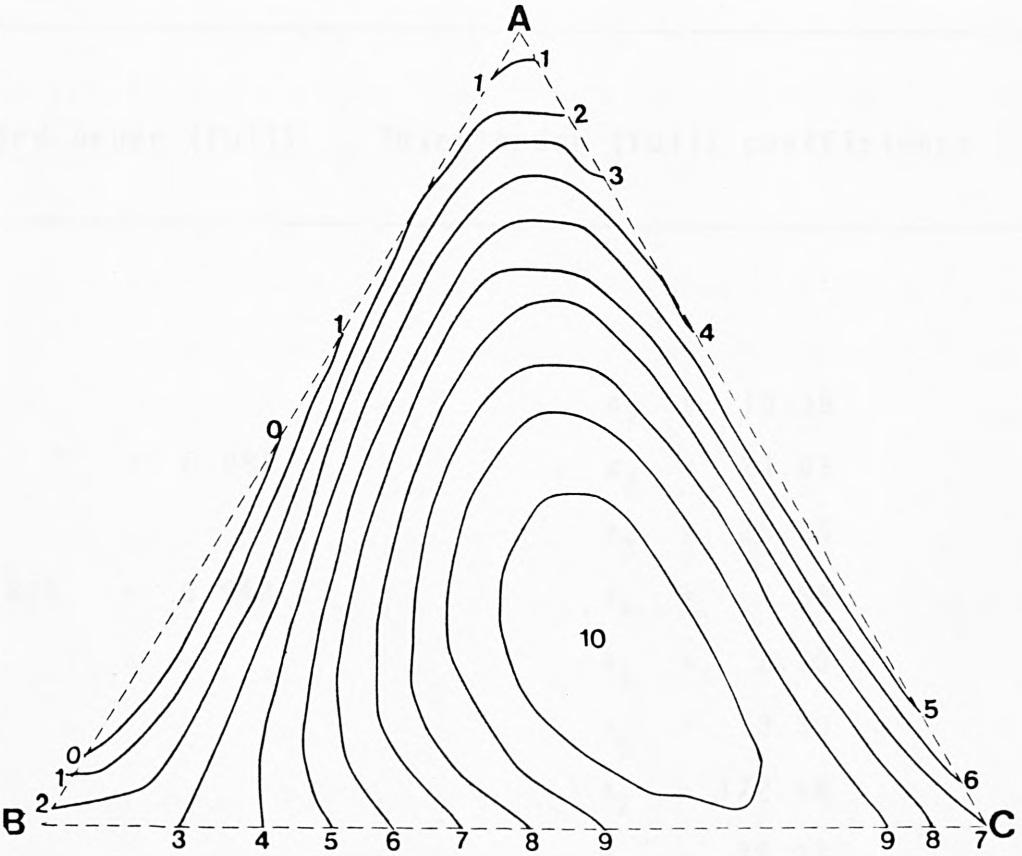
28.9 for samples containing up to 20 phr of Cereclor. There was a small decrease when the Cereclor loading was raised from 20 to 29 phr of Cereclor.

A similar pattern was noticed when the weight of Zn(II) AcAc was kept constant at 1.5 phr. The LOI increased rapidly with the concentration of Cereclor up to 5 phr, then increased more slowly (from 25.5 to 29) for samples containing between 5 and 20 phr of Cereclor. A decrease in the LOI was noticed when the concentration of Cereclor was increased up to 27 phr (Table 3.9). This means that it is of no value to add more than 20 phr of Cereclor to polypropylene-Zn(II) AcAc systems.

The maximum LOI value was achieved with concentrations of 2 phr of Zn(II) AcAc and 2 phr of Cereclor. A small amount of Zn(II) AcAc ($\geqslant$ 2phr) showed an excellent flame-retardant effect on polypropylene-Cereclor systems. Fig. 3.4 is a map of the LOI in terms of composition calculated from the best-fit polynomial and plotted as contour lines of constant LOI.

Table 3.10 contains the root mean square error, correlation coefficient and the coefficients for the third order (full) polynomial corresponding to Fig. 3.4. This triangular diagram shows that Zn(II) AcAc, on its own, has very little effect on the flame-retardancy of

Fig. 3.4 Triangular diagram showing variation of LOI composition for polypropylene-Zn(II) AcAc-Cereclor systems



LOI values: 0=18.40; 1=19.47; 2=20.54; 3=21.61; 4=22.68; 5=23.75; 6=24.82; 7⅜25.89; 8=26.96; 9=28.03; 10=29.10.

Table 3.10 Root mean square error, correlation coefficient and coefficients of the best-fit third order (full) polynomial for polypropylene/Zn(II) AcAC Cereclor systems

Third order (full)	Third order (full) coefficients
	a_1 = 18.38
σ = 0.984	a_2 = 21.03
	a_3 = 25.85
RCC = 0.942	a_4 = 5.88
	a_5 = 2.50
	a_6 = 13.30
	a_7 = 172.46
	a_8 = 25.03
	a_9 = -15.47
	a_{10} = 19.34

polypropylene. An increase in the LOI, when the concentration of Cereclor is raised to 25 wt%, is observed along the Cereclor/polypropylene base line. There is an increase in the LOI on addition of a small amount of Zn(II) AcAc to polypropylene-Cereclor systems and a rapid increase in the LOI is noticed with the addition of Cereclor to polypropylene-Zn(II) AcAc systems. The triangular diagram shows that there is good synergism between Cereclor and Zn(II) AcAc and the optimum area of flame-retardancy is achieved with samples containing between 12 and 19 wt% Cereclor and 1.2 and 2.6 wt% Zn(II) AcAc. In other words, a high loading of Cereclor is needed to achieve a good level of flame-retardancy.

The least squares calculation is in good agreement with the experimental data giving a RMS difference (σ) value of 0.98 and RCC value of 0.94.

Polypropylene/tin(IV) bis acetyl acetonate dichloride/Cereclor

Table 3.11 shows the combined effects of Sn(IV) AcAc Cl_2 and Cereclor on the flammability of polypropylene. Sn(IV) AcAc Cl_2 on its own increased the LOI of polyprylene by 2.3 units for samples containing up to 5 phr. When 1 phr of Sn(IV) AcAc Cl_2 was incorporated into polypropylene together with increasing amounts of

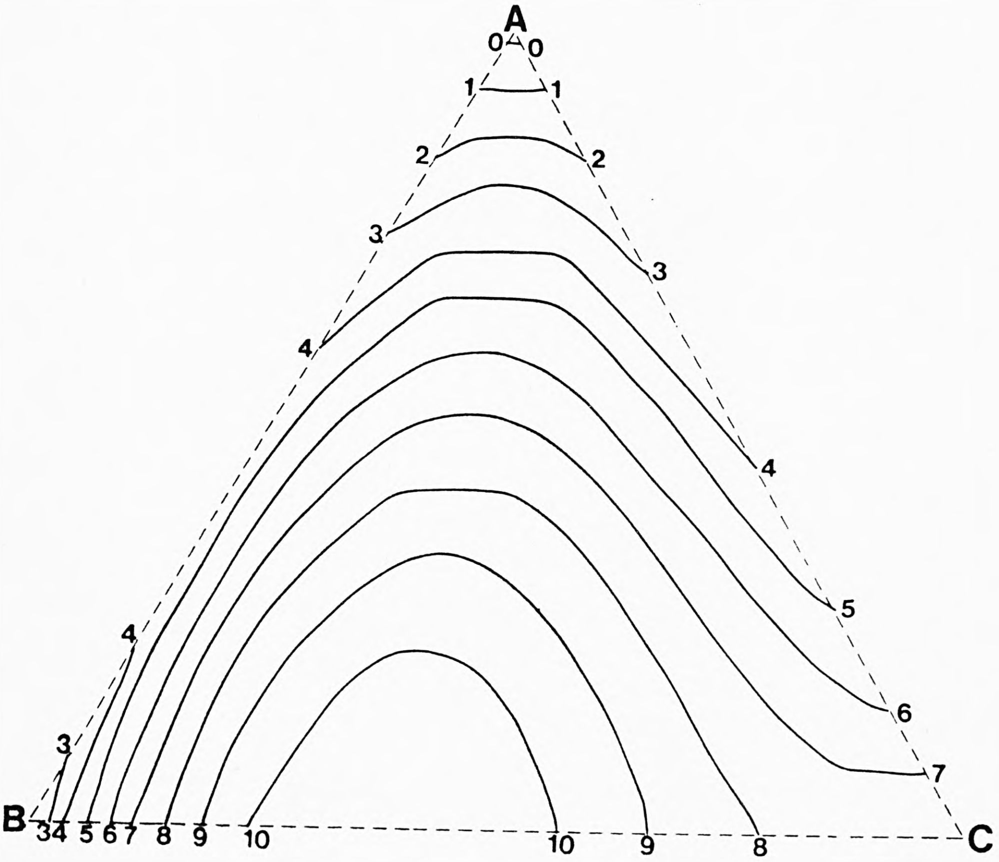
Table 3.11 The combined effects of Sn(IV) AcAc Cl_2 and Cereclor on the flammability of polypropylene

Sn(IV) AcAc Cl_2(phr)	Cereclor (phr)	LOI
1	0	20
5	0	20.7
0.5	5	20.9
0.5	10	23.2
0.5	15	24.2
0.5	20	24.3
0.7	7	23.3
0.7	18	24.4
1	1	21.3
1	5	24
1	10	23.4
1	15	23.8
1	20	25.3
1	29	25.1
1.5	5	25.7
1.5	10	25.1
1.5	20	25.2
1.5	27	25.5
1.5	28.5	26.0
2	2	23.2
2	5	25.8
2	20	26.2
3	7	27.2
5	20	25.5

Cereclor, there was a sharp increase in the LOI of 5.6 units up to 5 phr Cereclor, followed by a small decrease in the LOI between 5 and 15 phr of Cereclor. Again there was an increase in the LOI from 23.8 to 25.3 for samples containing between15 and 20 phr Cereclor,followed by a decrease in the LOI with up to 29 phr of Cereclor. When the weight of Sn(IV) AcAc Cl_2 was kept constant at 1.5 phr, there was a sharp increase in the limiting oxygen index of 7.3 units with concentrations of Cereclor up to 5 phr, followed by a gradual decrease in the LOI for samples containing between 5 and 10 phr of Cereclor. Again there was an increase in the LOI only from 25.1 to 26.0 when the concentration of Cereclor was raised from 10 to 28.5 phr.

Fig. 3.5 is a map of the LOI in terms of composition calculated from the best-fit polynomial (third order (full)) and plotted as contour lines of constant LOI. Table 3.12 contains the root mean square error, the correlation coefficient and the coefficients for the third order (full) polynomial corresponding to Fig. 3.5. The resulting triangular diagram shows that Sn(IV) AcAc Cl_2 on its own has little effect on the limiting oxygen index of polypropylene, and along the polypropylene/SN(IV) AcAc Cl_2 base line, there is an initial increase in LOI followed by a small decrease, with increasing concentration of Sn(IV) AcAc Cl_2. There is also an increase in LOI along polypropylene-Cereclor base line, with increasing concentration of

Fig. 3.5. Triangular diagram showing variation of LOI with composition for polypropylene-Sn(IV) AcAc Cl_2-Cereclor systems



LOI values: 0=18.40; 1=19.28; 2=20.16; 3=21.04; 4=21.92; 5=22.80; 6=23.68; 7=24.56; 8=25.44; 9=26.32; 10=27.20.

Table 3.12 Root mean square error, correlation coefficient and coefficients of the best-fit third order (full) polynomial for polypropylene/Sn(IV) AcAc Cl_2/Cereclor

Third order (full)	Third order (full) coefficients
	a_1 = 18.12
σ = 0.664	a_2 = 20.23
	a_3 = 25.74
RCC = 0.933	a_4 = 12.25
	a_5 = -0.576
	a_6 = 18.44
	a_7 = 39.1
	a_8 = -0.36
	a_9 = 8.35
	a_{10} = 23.59

Cereclor.

The area of highest flame-retardancy is achieved with concentrations of Cereclor between 6 and 14 wt% and concentrations of Sn(IV) AcAc Cl_2 between 2.2 and 3.8 wt%. Thus, the concentration of Cereclor needed to achieve a high degree of flame-retardancy is not large compared with the other systems mentioned.

The observed and calculated RMS difference values agree well ($\sigma =$ 0.66) and the RCC has a value of 0.93.

3.2 Studies of thermal behaviour of polypropylene

3.2.1 General

Metal chelates are known to be particularly effective in altering the oxygen uptake by polyolefins (Laver, 1979). These compounds may act as pro-oxidants in which case they increase the amount of oxygen absorbed by the polymer in the initial stages of degradation. On the other hand, certain metal chelates are anti-oxidants, i.e. they retard or inhibit oxidation of the associated polymeric substrate.

It has been proposed (Ranaweera and Scott, 1974; Benbow, Cullis and Laver, 1979) that metal chelates function initially as anti-oxidants by converting alkyl peroxy radicals to more stable radical ions. Once the chelate has reacted however the metal catalyses the decomposition of the hydroperoxides formed by the subsequent interaction of these radical ions with hydrogen ions.

3.2.2 Degradation of polypropylene on its own

Table 3.13 shows the results of thermoanalytical studies of the degradation of polypropylene. An oxygen uptake stage of 0.35 wt% is observed initially. On being heated further, polypropylene undergoes two weight-loss stages. The

Table 3.13 Thermoanalytical results for polypropylene in the presence of Cereclor

	No additives			10 phr Cereclor
Initial weight (mg)	7.943			9.702
Total weight lost (mg/%)	96.95			92.78
T_D (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)	0.35			0.27
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/[illegible])	152-174			145-167
First Loss				
Wt loss (mg/%)	91.45			74.61
DTG_{max} (mg min^{-1}/% min^{-1})	0.50			0.35
T (DTG_{max}) (°C/[illegible])	290			270
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/[illegible])	174-452			167-395
Second Loss				
Wt loss (mg/%)				9.62
DTG_{max} (mg min^{-1}/% min^{-1})				0.20
T (DTG_{max}) (°C/K)				420
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/[illegible])				395-451
Third Loss	CBO			CBO
Wt loss (mg/%)	5.15			8.30
DTG_{max} (mg min^{-1}/% min^{-1})				0.10
T (DTG_{max}) (°C/K)				497
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/[illegible])	452-510			451-533
Fourth Loss				
Wt loss (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
LOI				
D_s				

main breakdown stage occurs between 174 and 452°C. The second weight loss reaction occurs between 452 and 510°C and the proportion volatilised in this stage (corresponding to a carbon burn-off stage) is 5.15 wt%. Only 3.05 wt% of the original sample remains on further heating. Fig. 3.6 shows the TGA and DTG curves for polypropylene.

3.2.3 Degradation of polypropylene in the presence of Cereclor

Cereclor 70, a chlorinated wax with a chlorine content of 70% w/w, decomposes quantitatively, liberating hydrogen chloride in the main breakdown stage (236-389°C). A carbonaceous residue is left which is burnt off on further heating(Fig.3.7 and Table 3.14). The course of the thermal decomposition of polypropylene in the presence of 10 phr Cereclor is shown in Fig.3.8. Two stages are observed corresponding to the breakdown of the polymer. The total loss during these two stages is 84.21 wt%. The carbon burn-off reaction does not occur until a temperature of 534°C is attained and the amount of char formed is then 8.3 wt% (Table 3.13)

Fig. 3.6 Thermogravimetric analysis curves for polypropylene on its own

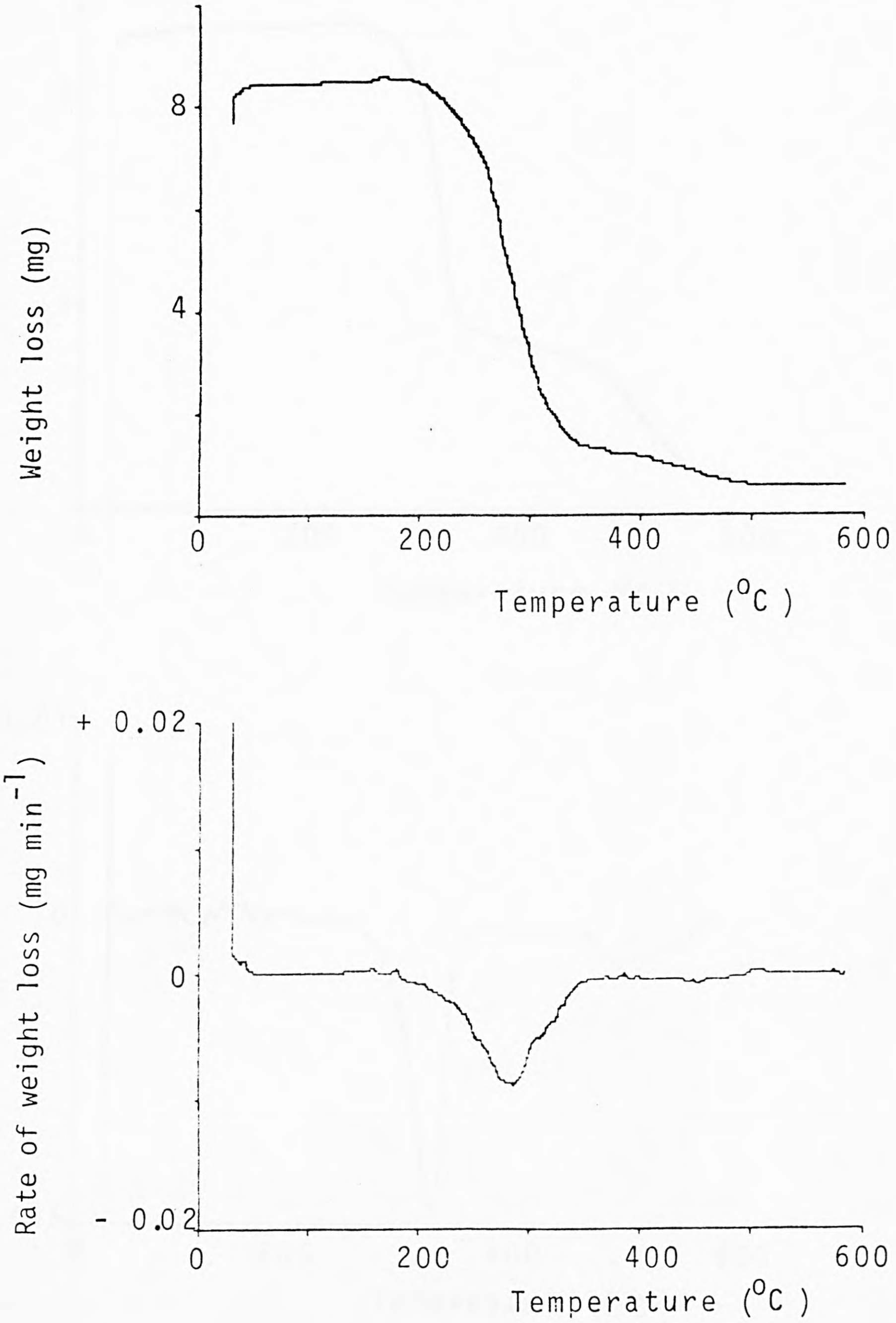


Fig.3.7 Thermogravimetric analysis curves for Cereclor

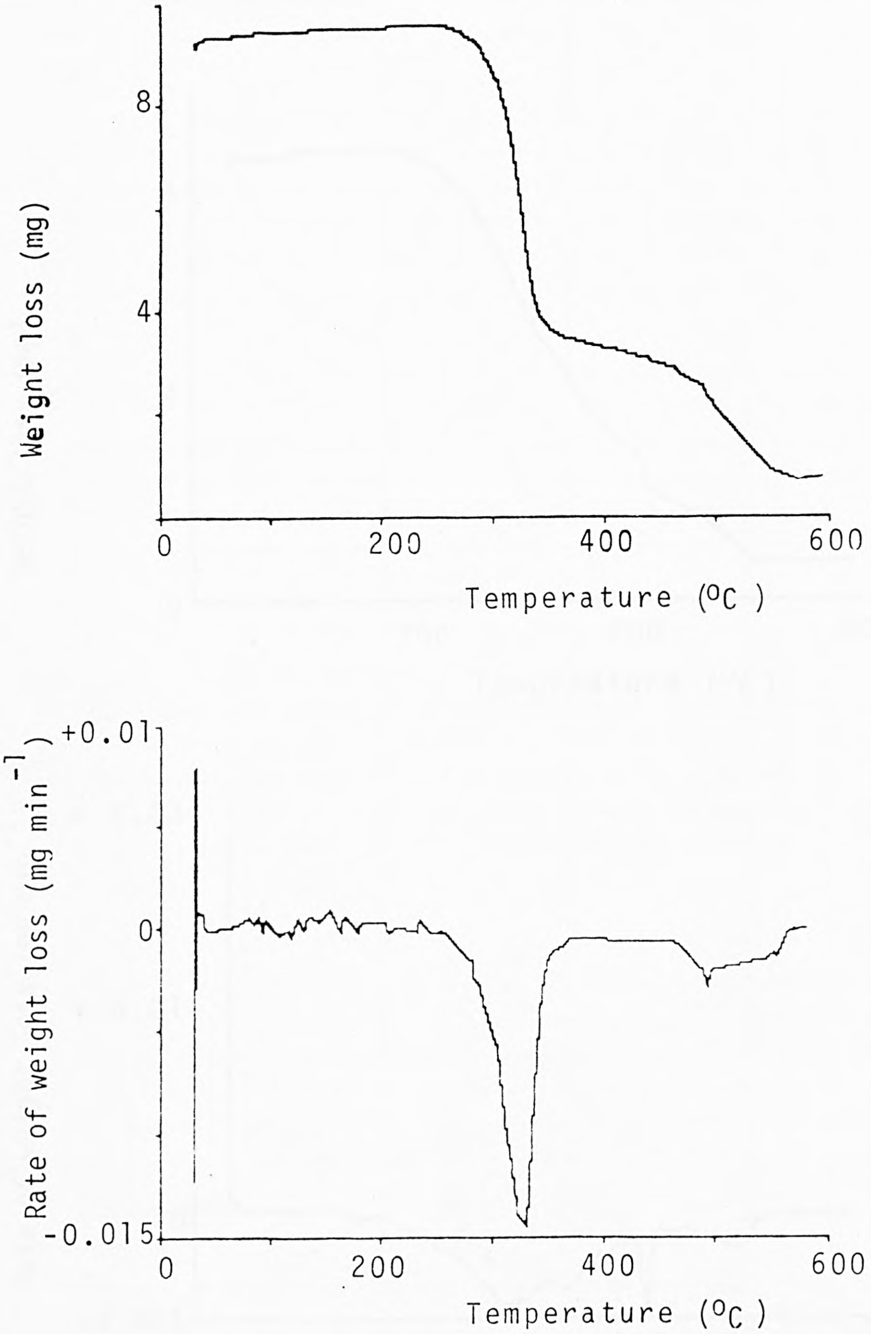


Fig. 3.8 Thermogravimentric analysis curves for polypropylene containing 10 phr Cereclor

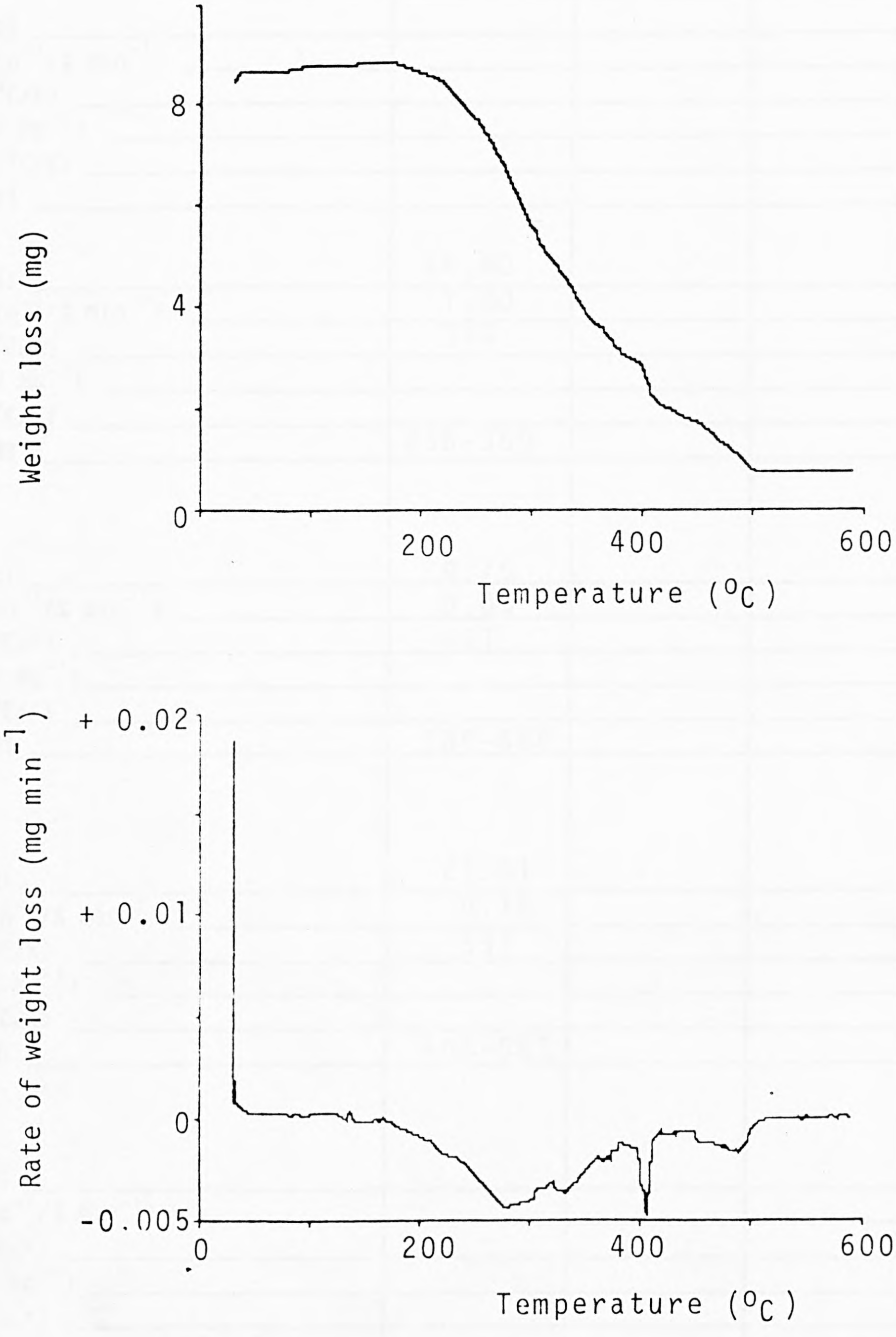


Table 3.14 Thermonanalytical results for Cereclor

Initial weight (mg)	9.630				
Total weight lost (mg/%)	92.56				
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	64.80				
DTG_{max} (mg min^{-1}/% min^{-1})	1.00				
T (DTG_{max}) (°C/[redacted])	334				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[redacted])	236-389				
Second Loss					
Wt loss (mg/%)	4.75				
DTG_{max} (mg min^{-1}/% min^{-1})	0.05				
T (DTG_{max}) (°C/K)	451				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[redacted])	389-468				
Third Loss					
Wt loss (mg/%)	23.01				
DTG_{max} (mg min^{-1}/% min^{-1})	0.18				
T (DTG_{max}) (°C/K)	531				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[redacted])	468-582				
Fourth Loss					
Wt loss (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
LOI					
D_s					

3.2.4 Degradation of polypropylene in the presence ferrocene and Cereclor

When ferrocene is heated in air on its own, it volatilises at 73-167°C and 94.96 wt% is lost (Table 3.15 and Fig. 3.9). The thermal decomposition behaviour of a 3:7 mixture of ferrocene and Cereclor is shown in Fig. 3.10. The first weight loss is observed at 65-182°C and 33.69 wt% is lost during this stage. This stage is attributable to volatilisation of the ferrocene. The second stage occurs at 182-300° when 34.74 wt% is lost due to the liberation of hydrogen chloride as well as some interaction between hydrogen chloride and ferrocene. The amount of char formed in the third weight-loss stage is nearly the same as that formed when Cereclor was heated on its own. This stage is observed at a lower temperature than with Cereclor on its own.

An oxygen uptake stage of 0.54 wt% is observed initially for a polymer sample containing 10 phr ferrocene. Two stages are found during the main breakdown. The temperature range for the first stage is 167-393°C and for the second stage 393-428°C. The carbon burn-off reaction occurs between 428° and 429°C and 9.98 wt% is lost during this stage. Addition of 10 phr ferrocene to polypropylene thus increases the amount of char by 4.83 wt%. Fig. 3.11 shows the TGA and DTG

Fig. 3.9 Thermogravimetric analysis curves for ferrocene

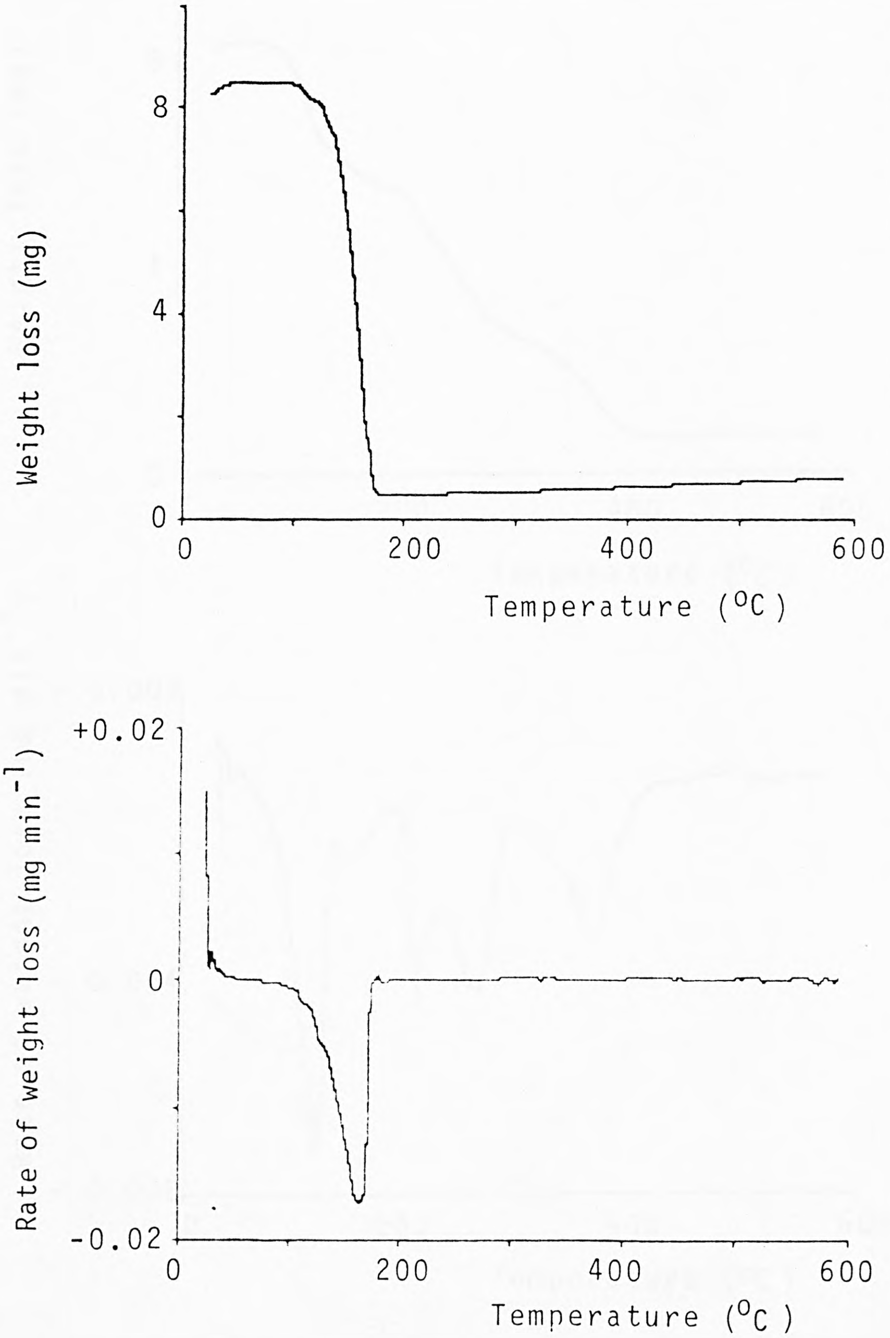


Fig. 3.10 Thermogravimetric analysis curves for a 3:7 mixture of ferrocene and Cereclor

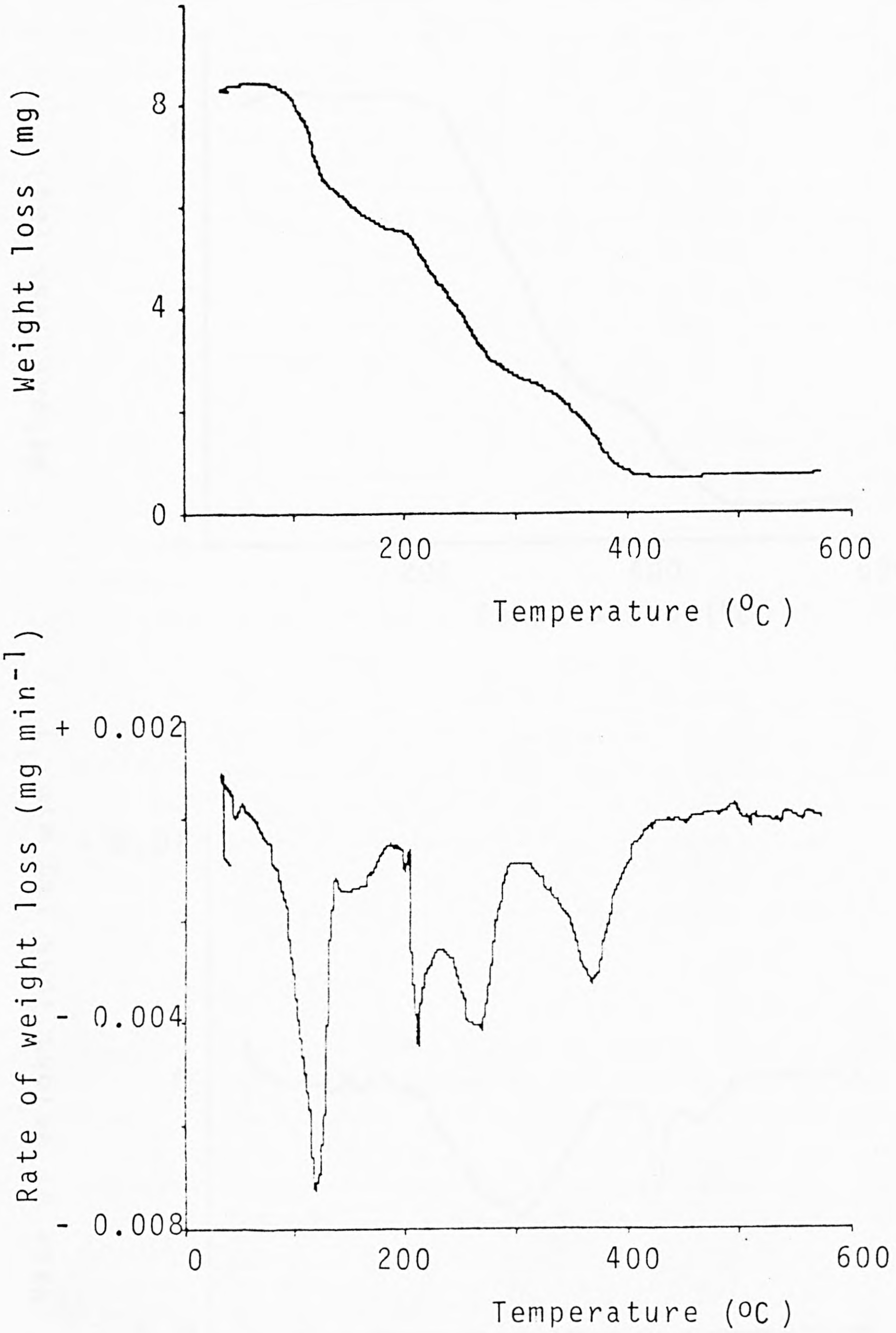


Fig. 3.11 Thermogravimetric analysis curves for polypropylene containing 10 phr ferrocene

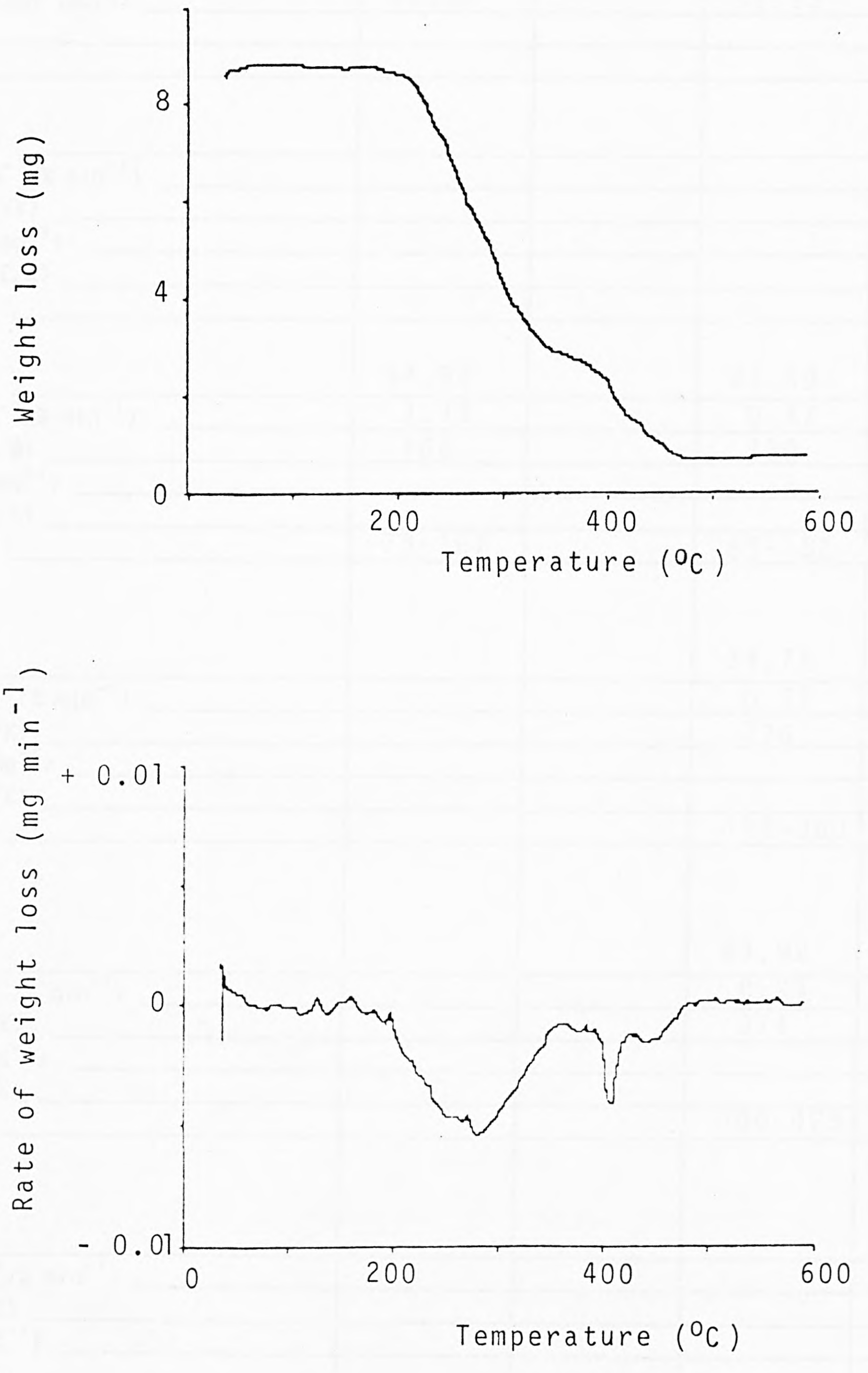


Table 3.15 Thermoanalytical results for a mixture of ferrocene and Cereclor

	Ferrocene		3 Ferrocene: 7 Cereclor		
Initial weight (mg)	8.54		8.52		
Total weight lost (mg/%)	94.96		92.35		
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	94.96		33.69		
DTG_{max} (mg min^{-1}/% min^{-1})	1.12		0.47		
T (DTG_{max}) (°C/[illegible])	166		120		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])	73-167		65-182		
Second Loss					
Wt loss (mg/%)			34.74		
DTG_{max} (mg min^{-1}/% min^{-1})			0.21		
T (DTG_{max}) (°C/K)			270		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])			182-300		
Third Loss					
Wt loss (mg/%)			23.92		
DTG_{max} (mg min^{-1}/% min^{-1})			0.21		
T (DTG_{max}) (°C/K)			374		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])			300-428		
Fourth Loss					
Wt loss (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
LOI					
D_s					

results for polypropylene containing ferrocene.

The thermoanalytical traces obtained for polypropylene samples containing varying amounts of ferrocene and Cereclor are shown in Figs. 3.12 and 3.13 and the numerical results are given in Table 3.16. For a sample containing 3 phr ferrocene and 7 phr Cereclor an oxygen uptake of 0.23 wt% is found and the temperature range is 142-162°C. On being heated the sample exhibits different weight-loss stages. The first is observed at 162-303°C and 10.78 wt% is lost during this stage. The second and third weight-loss stages are observed at 303-401°C and 401-444°C. 10.87 wt% is lost during the carbon burn-off stage which occurs in the temperature range 444-492°C.

For a sample containing 2 phr ferrocene and 20 phr Cereclor, the uptake of oxygen at 139-161°C manifests itself as a weight gain. Three stages are observed corresponding to the main breakdown of the polymer. The first, second and third weight-loss stages are observed at: 161-316°C, 316-392°C and 392-451°C respectively. The final weight loss occurs between 451 and 517°C and the proportion of material volatilised during this stage, which corresponds to the carbon burn-off stage, is 15.08 wt%.

Fig.3.12 Thermogravimetric analysis curves for polypropylene containing 3 phr ferrocene + 7 phr Cereclor

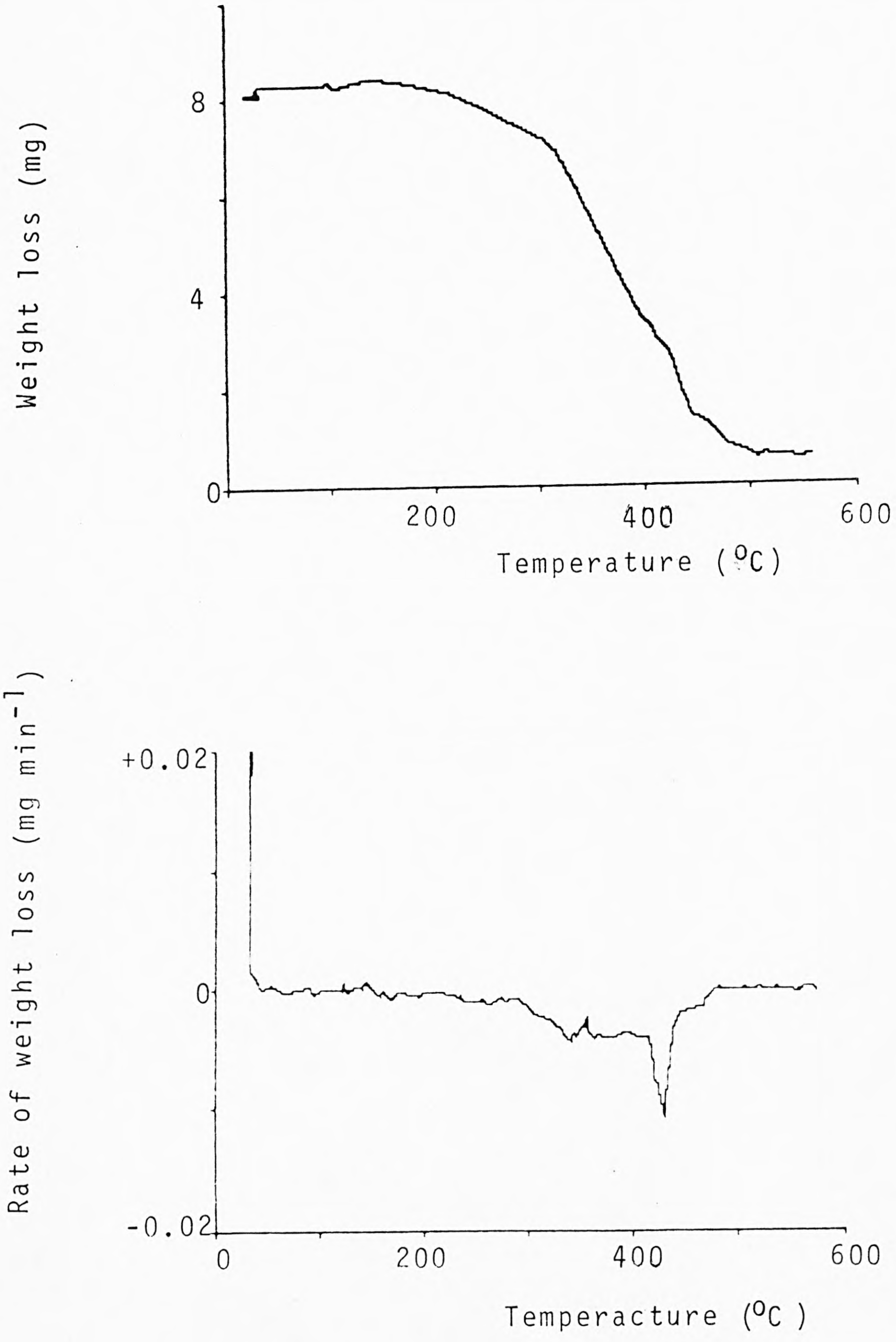


Fig. 3.13 Thermogravimetric analysis curves for polypropylene containing 2 phr ferrocene + 20 phr Cereclor

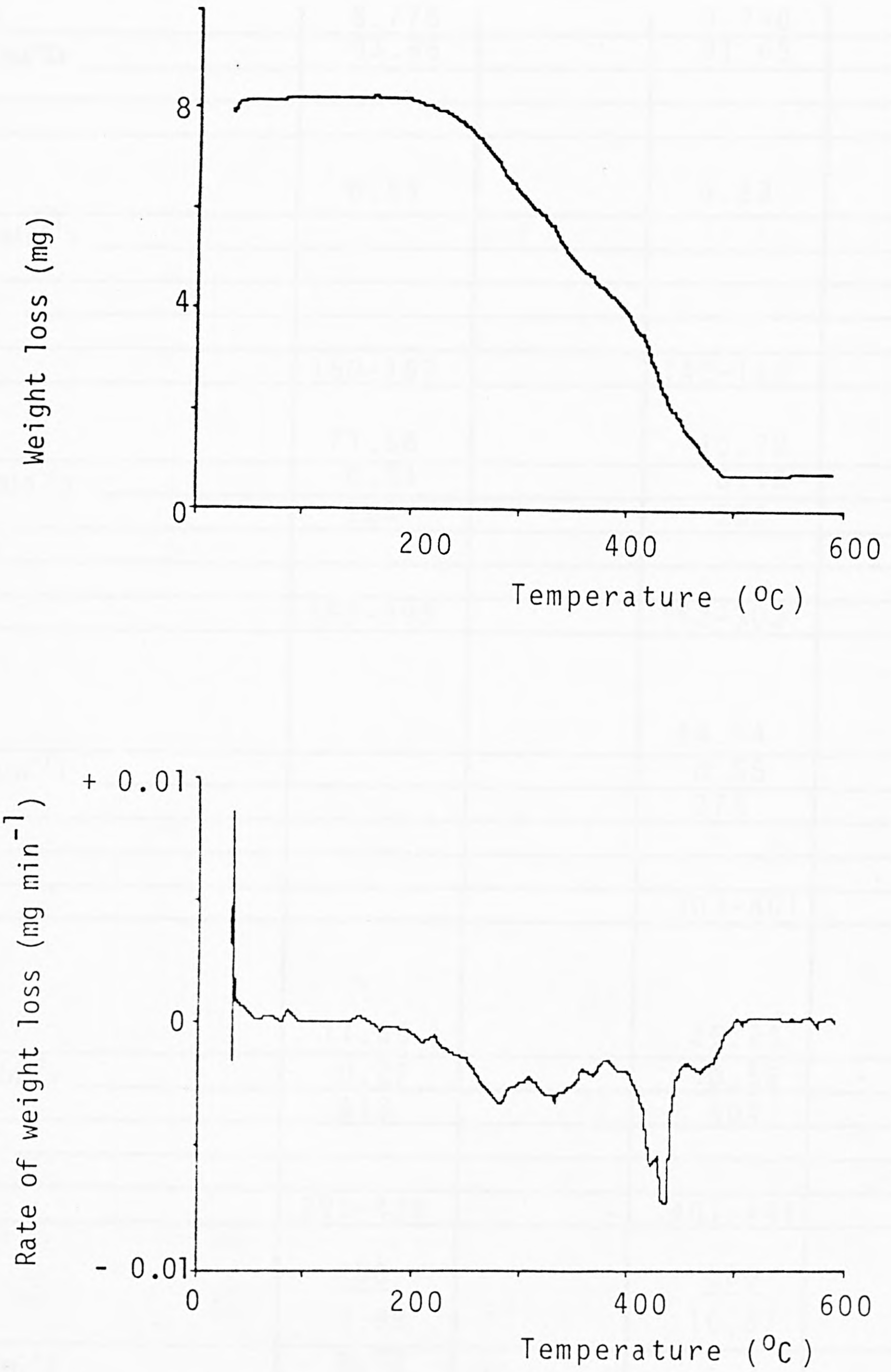


Table 3.16 Thermoanalytical results for polypropylene in the presence of ferrocene and Cereclor

	10 phr ferrocene	3 phr ferrocene + 7 phr Cereclor	2 phr ferrocene + 20 phr Cereclor
Initial weight (mg)	8.776	8.740	8.296
Total weight lost (mg/%)	93.65	91.65	92.45
T_D (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)	0.54	0.23	0.52
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	150-167	142-162	139-161
First Loss			
Wt loss (mg/%)	71.58	10.78	27.71
DTG_{max} (mg min^{-1}/% min^{-1})	0.34	0.10	0.21
T (DTG_{max}) (°C/[redacted])	284	283	281
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	167-393	162-303	161-316
Second Loss			
Wt loss (mg/%)		44.54	22.18
DTG_{max} (mg min^{-1}/% min^{-1})		0.55	0.20
T (DTG_{max}) (°C/[redacted])		375	336
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])		303-401	316-392
Third Loss			
Wt loss (mg/%)	11.55	25.23	26.96
DTG_{max} (mg min^{-1}/% min^{-1})	0.27	0.55	0.51
T (DTG_{max}) (°C/[redacted])	418	404	441
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	393-428	401-444	392-451
Fourth Loss	CBO	CBO	CBO
Wt loss (mg/%)	9.98	10.87	15.08
DTG_{max} (mg min^{-1}/% min^{-1})	0.12		0.15
T (DTG_{max}) (°C/[redacted])	451		476
DTA_{max} (V/ V mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	428-492	444-492	451-517
LOI			
D_s			

The thermal degradation behaviour of polypropylene samples containing ferrocene and Cereclor are different from that of samples containing Cereclor and ferrocene on their own. For example, in the former, three weight-loss stages are observed corresponding to the main breakdown and the weight losses during these stages are smaller. Furthermore more char is formed. There is thus an interaction between ferrocene and the hydrogen chloride evolved from the Cereclor, forming a new species which can act in the condensed phase and affect the thermal stability of the polymer. Table 3.17 shows the correlation between the limiting oxygen index and the amount of char formed during the thermal decomposition. It is observed (Table 3.17) that as the LOI increased, the weight loss during the main breakdown decreases and the amount of char increases.

3.2.5 Degradation of polypropylene in the presence of of Bis hydroxo hexabenzoato tris iron(III) benzoate and Cereclor

The thermal decomposition of BHB tris Fe(III) in air is shown in Fig. 3.14 and Table 3.18. The decomposition of BHB tris Fe(III) involves four weight-loss stages. The first loss is observed at 51-133^{o}C and this may be attributable to loss of the two hydroxy groups.

Fig. 3.14 Thermogravimetric analysis curves for BHB tris Fe(III)

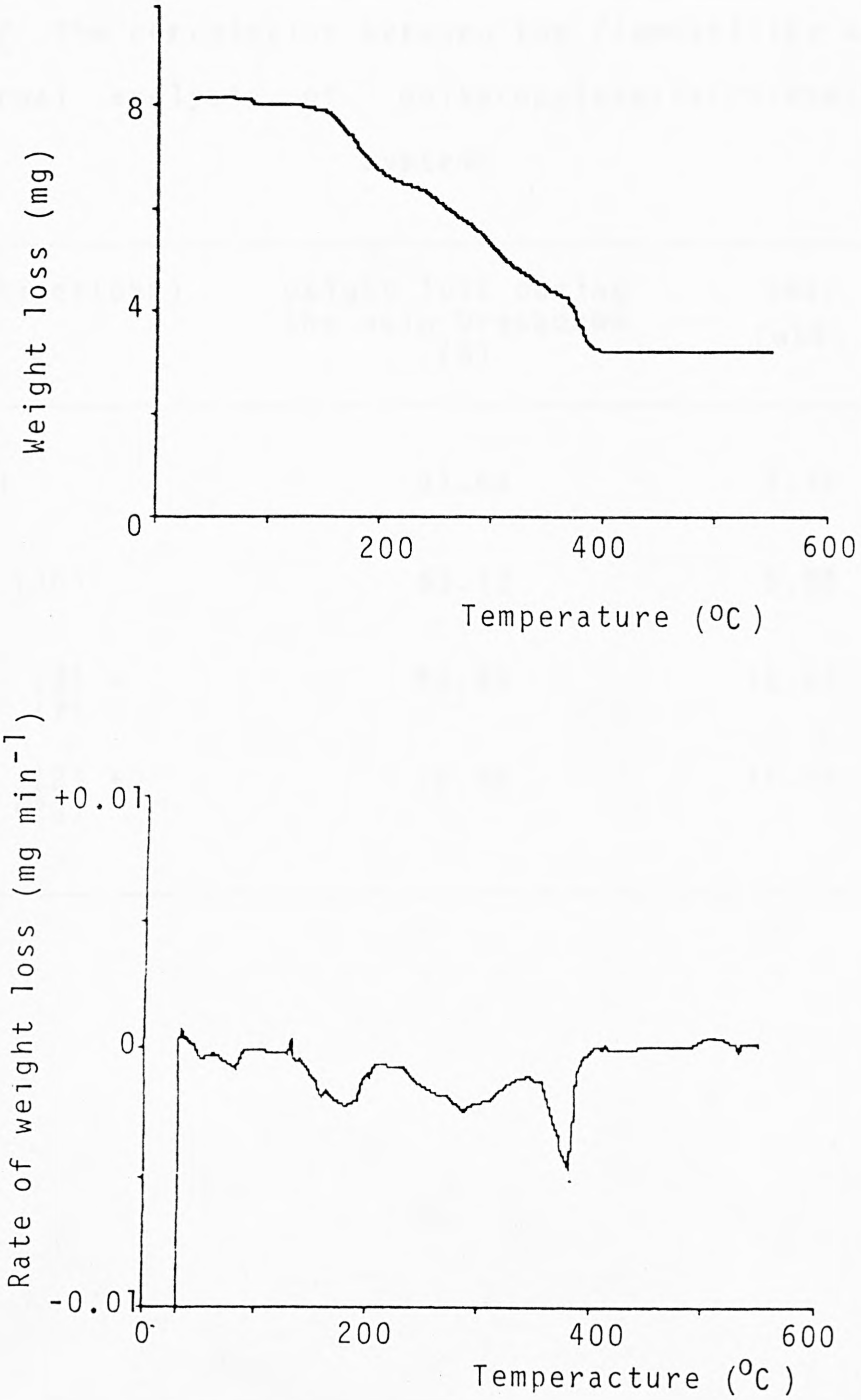


Table 3.17 The correlation between the flammability and the thermal analysis of polypropylene/ferrocene/Cereclor systems

PP + additives(phr)	weight loss during the main breakdown (%)	char (wt%)	LOI
Nil	91.45	5.15	18.4
Ferrocene (10)	83.13	9.98	19.4
Ferrocene (3) + Cereclor (7)	80.55	10.87	19.5
Ferrocene (2) + Cereclor (20)	76.85	15.08	30.3

Table 3.18 Thermoanalytical results for bis hydroxo-hexabenzoate tris iron(III) benzoate

Initial weight (mg)	8.192				
Total weight lost (mg/%)	60.88				
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG$_{max}$ (mg min^{-1}/% min^{-1})					
T (DTG$_{max}$) (°C/K)					
DTA$_{max}$ (μV/μV mg^{-1})					
T (DTA$_{max}$) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	2.95				
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.07				
T (DTG$_{max}$) (°C/[redacted])	81				
DTA$_{max}$ (μV/μV mg^{-1})					
T (DTA$_{max}$) (°C/K)					
T range (°C/[redacted])	51-133				
Second Loss					
Wt loss (mg/%)	18.04				
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.18				
T (DTG$_{max}$) (°C/[redacted])	184				
DTA$_{max}$ (μV/μV mg^{-1})					
T (DTA$_{max}$) (°C/K)					
T range (°C/[redacted])	133-223				
Third Loss					
Wt loss (mg/%)	26.44				
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.15				
T (DTG$_{max}$) (°C/[redacted])	303				
DTA$_{max}$ (μV/μV mg^{-1})					
T (DTA$_{max}$) (°C/K)					
T range (°C/[redacted])	223-362				
Fourth Loss					
Wt loss (mg/%)	13.45				
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.31				
T (DTG$_{max}$) (°C/[redacted])	386				
DTA$_{max}$ (V/ V mg^{-1})					
T (DTA$_{max}$) (°C/K)					
T range (°C/[redacted])	362-410				
LOI					
D_s					

$$[Fe_3(OH)_2(C_6H_5CO_2)_6](C_6H_5CO_2) \rightarrow [Fe_3(C_6H_5CO_2)_6](C_6H_5CO_2)$$

The second stage occurs at 133-223°C and 18.04 wt% is lost during this stage presumably due to the reaction:

$$[Fe_3(C_6H_5CO_2)_6](C_6H_5CO_2) \longrightarrow [Fe_2(C_6H_5CO_2)_5](C_6H_5CO_2)$$

A third weight loss is observed at 223-362°C and the weight loss here corresponds to loss of Fe $(C_6H_5CO_2)$.

$$[Fe_2(C_6H_5CO_2)_5](C_6H_5CO_2) \longrightarrow [Fe(C_6H_5CO_2)_3](C_6H_5CO_2)$$

The final weight loss of 13.45 wt% which is observed at 362-410°C is attributable to the loss of a further $C_6H_5CO_2$ group:

$$[Fe(C_6H_5CO_2)_3](C_6H_5CO_2) \longrightarrow Fe(C_6H_5CO_2)_3$$

Table 3.19 and Fig.3.15 show the results of thermoanalytical studies of polypropylene degradation in the presence of 5 phr BHB tris Fe(III). An oxygen uptake of 0.22 wt% is observed initially and this manifests itself as a weightgain. Three weight-loss stages are noticed during the main breakdown of the polymer and the temperature ranges are 157-325°C, 325-367°C and 367-419°C respectively. 11.99 wt% is lost during the carbon burn-off stage which occurs in the temperature range 419-459°C.

Fig. 3.15 Thermogravimetric analysis curves for polypropylene containing 5 phr BHB tris Fe(III)

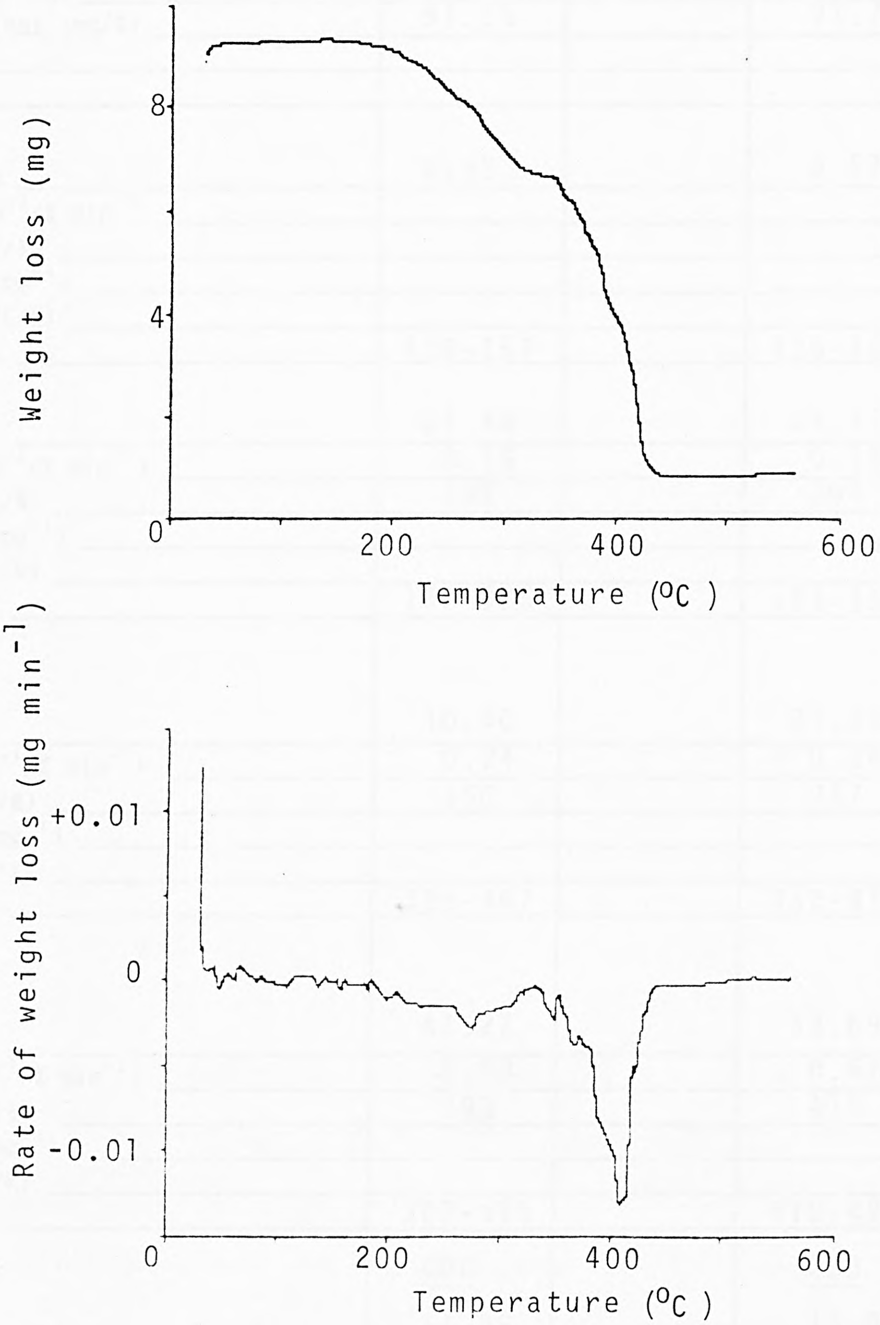


Table 3.19 Thermoanalytical results for polypropylene in the presence of bis hydroxohexabenzoato tris iron(III) benzoate and Cereclor

	5 phr BHBtrisFe(III)	1 phr BHBtris Fe(III)+1 phr Cereclor	1 phr BHBtris Fe(III) + 15 phr Cereclor
Initial weight (mg)	9.180	8.814	9.420
Total weight lost (mg/%)	91.28	93.70	93.13
T_D (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)	0.22	0.57	0.47
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (µV/µV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/■)	138-157	136-153	133-162
First Loss			
Wt loss (mg/%)	27.40	25.17	12.47
DTG_{max} (mg min^{-1}/% min^{-1})	0.19	0.15	0.12
T (DTG_{max}) (°C/■)	292	304	264
DTA_{max} (µV/µV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/■)	157-325	153-352	162-293
Second Loss			
Wt loss (mg/%)	10.40	21.26	14.01
DTG_{max} (mg min^{-1}/% min^{-1})	0.24	0.34	0.15
T (DTG_{max}) (°C/■)	350	357	324
DTA_{max} (µV/µV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/■)	325-367	352-410	293-378
Third Loss			
Wt loss (mg/%)	41.27	33.69	50.85
DTG_{max} (mg min^{-1}/% min^{-1})	0.58	0.67	0.83
T (DTG_{max}) (°C/■)	399	415	427
DTA_{max} (µV/µV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/■)	367-419	410-422	387-437
	CBO	CBO	CBO
Fourth Loss			
Wt loss (mg/%)	11.99	13.01	15.33
DTG_{max} (mg min^{-1}/% min^{-1})	0.42	0.35	
T (DTG_{max}) (°C/■)	428	246	
DTA_{max} (V/ V mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/■)	419-459	422-467	437-482
LOI			
D_s			

The thermoanalytical traces obtained for polypropylene samples containing varying amounts of Cereclor and BHB tris Fe(III) are shown in Figs. 3.16 and 3.17 and the numerical results are given in Table 3.19. For a sample containing 1 phr of BHB tris Fe(III) and 1 phr of Cereclor, the oxygen uptake is 0.57 wt% and the temperature range is 136-153^{o}C. On being heated further the sample exhibits three weight-loss stages. The first stage is observed at 153-352^{o}C and 25.17 wt% is lost during this stage. The second and third weight-loss stages are observed at 352-410^{o}C and 410-422^{o}C. 13.01 wt% is lost during the carbon burn-off stage which occurs in the temperature range 422-467^{o}C.

For a sample containing 1 phr BHB tris Fe(III) and 15 phr Cereclor, there is again a small uptake of oxygen (0.47 wt%) which manifests itself as a weight gain and occurs at 133-162^{o}C. Three stages are observed correponding to the main breakdown of the polymer. The first, second and third weight-loss stages are observed at 162-293^{o}C, 293-378^{o}C and 378-437^{o}C respectively. The final weight loss reaction occurs between 437 and 482^{o}C and the proportion of material volatilised during this stage, which corresponds to the carbon burn-off stage, is 15.33 wt%. The addition of BHB tris Fe(III) to polypropylene decreased the temperature of the main breakdown of the base polymer by 21^{o} and

Fig. 3.16 Thermogravimetric analysis curves for polypropylene containing 1 phr BHB tris Fe(III) + 1 phr Cereclor

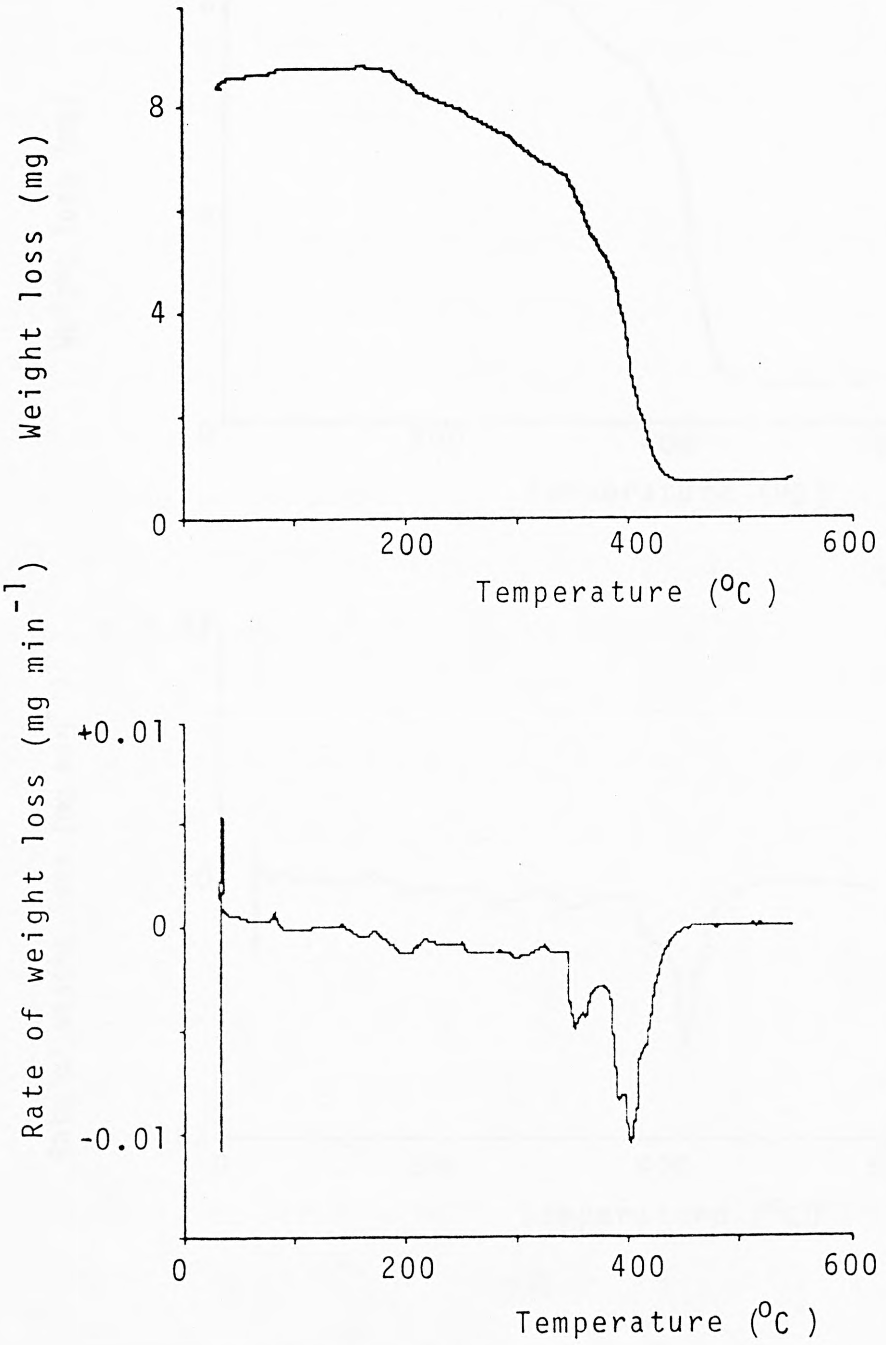
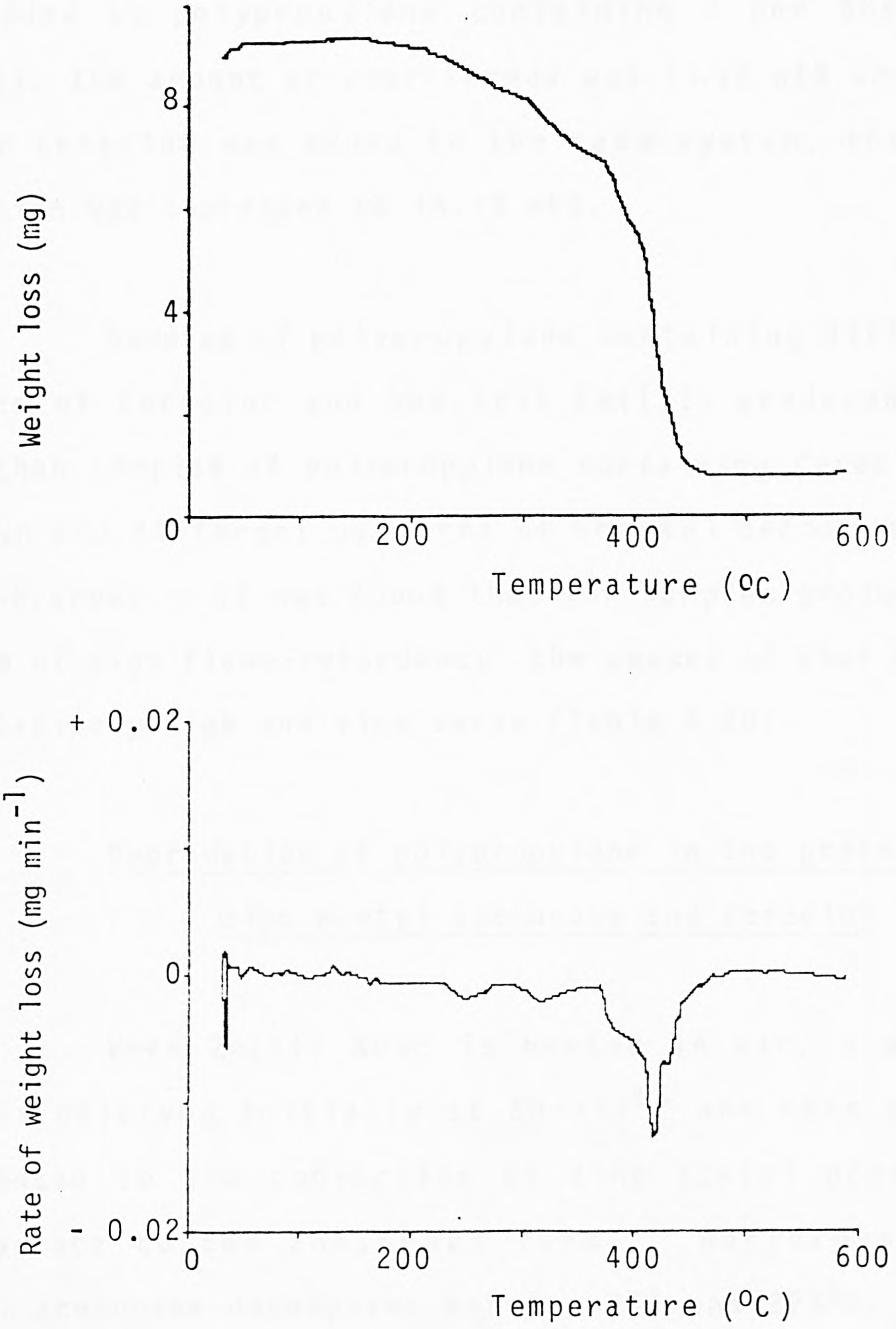


Fig. 3.17 Thermogravimetric analysis curves for polypropylene containing 1 phr BHB tris Fe(III) + 15 phr Cereclor



increased the amount of char by 7.86 wt%. The addition of Cereclor to polypropylene-BHB tris Fe(III) systems increased the amount of char. Thus, when 1 phr Cereclor was added to polypropylene containing 1 phr BHB tris Fe(III), the amount of char formed was 11.99 wt% and when 15 phr Cereclor was added to the same system, the char formation was increased to 15.13 wt%.

Samples of polypropylene containing different amounts of Cereclor and BHB tris Fe(III) produced more char than samples of polypropylene containing Cereclor on its own and different patterns of thermal decomposition were observed. It was found that for samples producing a system of high flame-retardancy the amount of char formed is relatively high and vice versa (Table 3.20).

3.2.6 Degradation of polypropylene in the presence of zinc acetyl acetonate and Cereclor

When Zn(II) AcAc is heated in air, a weight loss is observed initially at 60-117^{o}C and this may be attributed to the conversion of zinc acetyl acetonate monohydrate to the anhydrous form. Anhydrous zinc acetyl acetonate decomposes between 117 and 228^{o}C. Fig. 3.18 shows the TGA and DTG curves for zinc acetyl acetonate monohydrate.

Fig. 3.18 Thermogravimetric analysis curves for Zn(II) AcAc

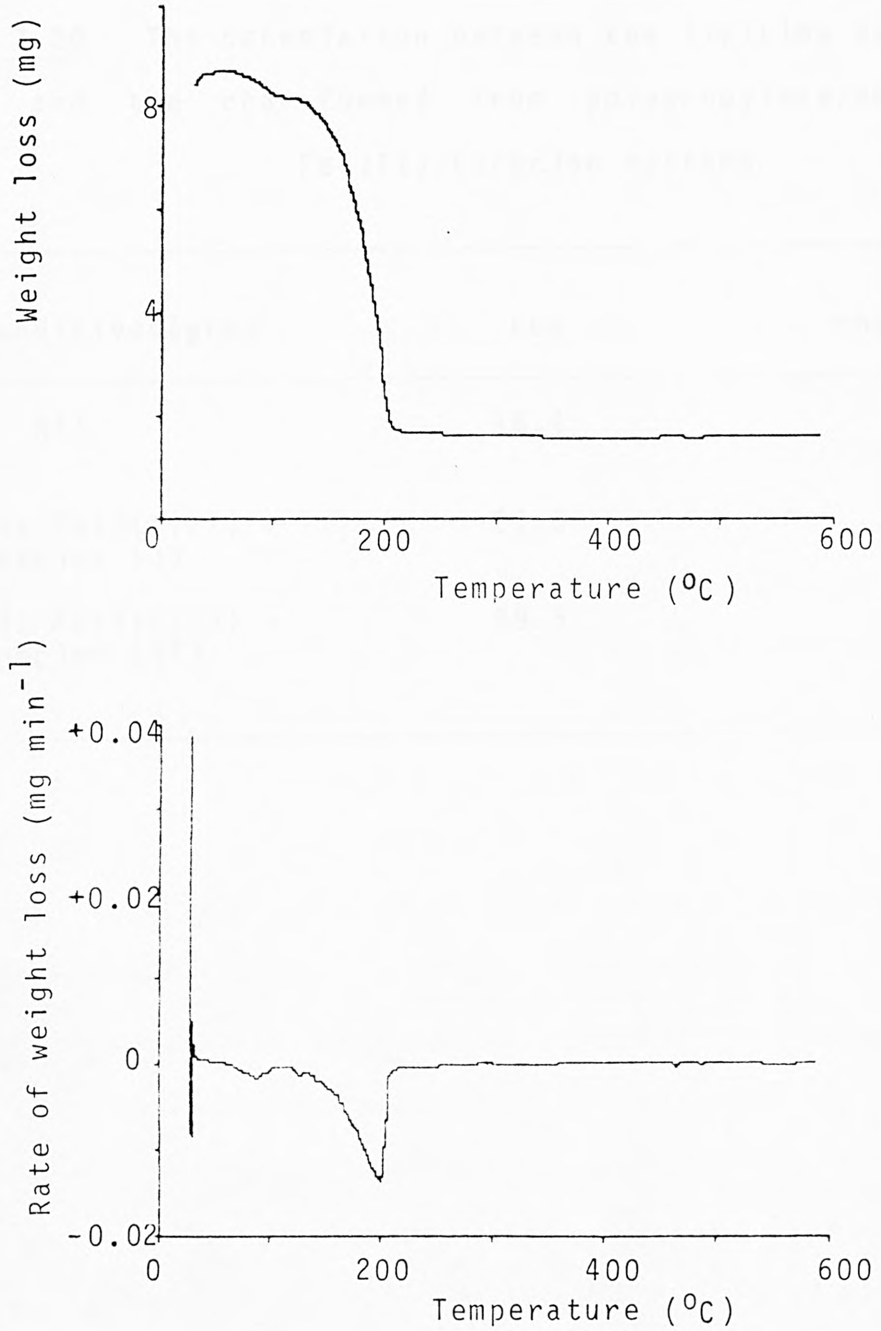


Table 3.20 The correlation between the limiting oxygen index and the char formed from polypropylene/BHB tris Fe(III)/Cereclor systems

PP + additives(phr)	LOI	char (wt%)
Nil	18.4	5.15
BHB tris Fe(III)(1) + Cereclor (1)	21.5	13.01
BHB tris Fe(III)(1) + Cereclor (15)	28.5	15.33

When a 2:5 mixture of Zn(II) AcAc and Cereclor is heated in air, the decomposition behaviour is different from that found with the two components on their own and may be attributed to the direct interaction between them. An increase in the carbonaceous residue formed from Cereclor is observed on addition of Zn(II) AcAc (Table 3.21 and Fig. 3.19)

Table 3.22 shows results for polypropylene containing 5 phr of Zn(II) AcAc. The TGA and DTG traces are shown in Fig. 3.20. There is oxygen uptake (at 148-169°C) which manifests itself as a weight gain. The main breakdown occurs between 169 and 423°C. The carbon burn-off stage is observed at 423-504°C and about 10.19 wt% of the polymer is lost during this stage. The thermoanalytical traces obtained for polypropylene samples containing varying amounts of Zn(II) AcAc and Cereclor are shown in Fig. 3.21 and the numerical results are given in Table 3.22. For a sample containing 2 phr of Zn(II) AcAc and 5 phr of Cereclor, an oxygen uptake of 0.48 wt% is recorded and the temperature range is 140-167°C. On being heated the sample exhibits three weight-loss stages. Two stages are observed corresponding to the main breakdown of the polymer. The total loss during the main breakdown stage is 84.71 wt%. The carbon burn-off reaction is extended to 520°C and the weight loss during this stage is 11.67 wt%.

Fig. 3.19 Thermogravimetric analysis curves for a 2:5 mixture of Zn(II) AcAc and Cereclor

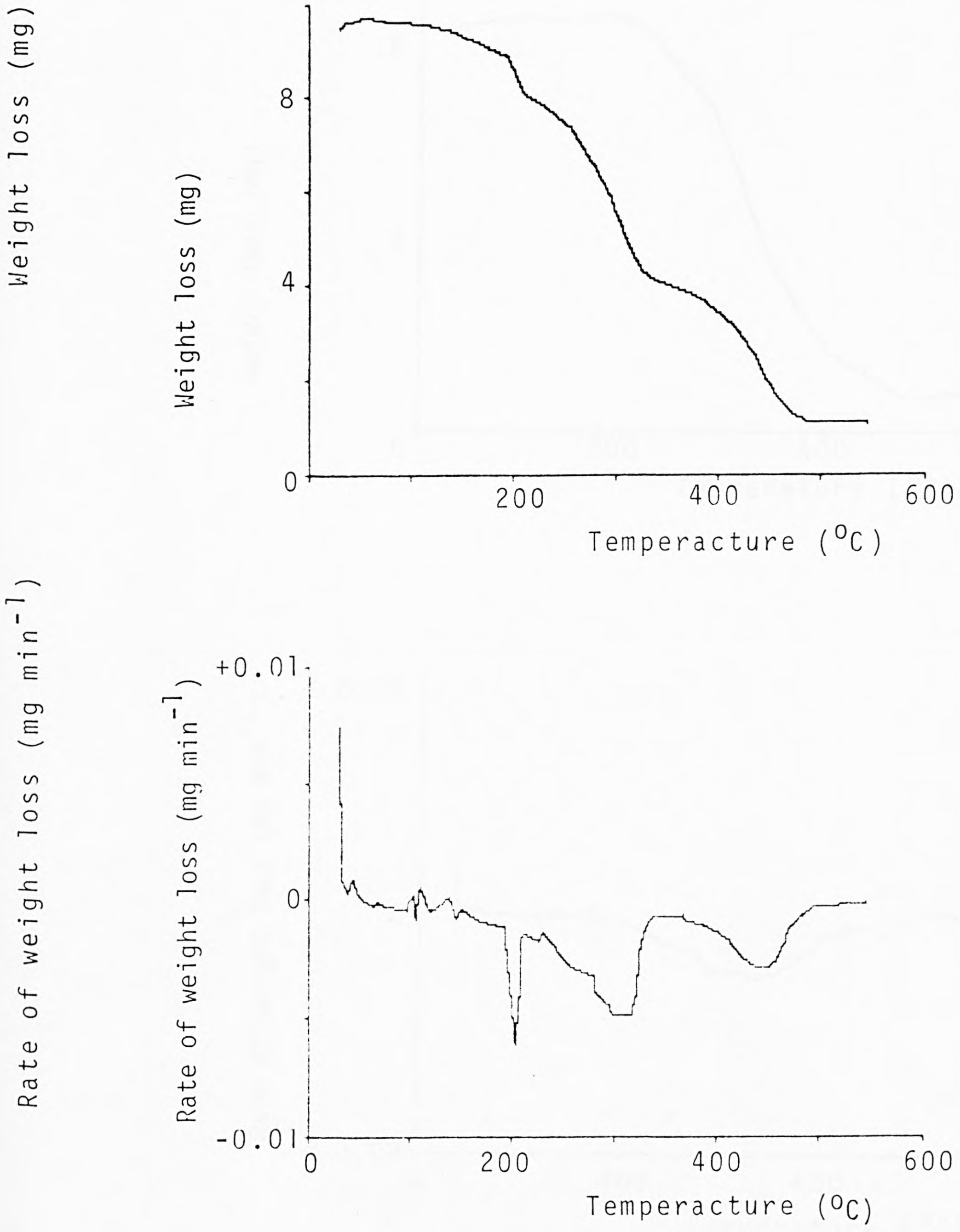


Fig.3.20 Thermogravimetric analysis curves for polypropylene containing 5 phr Zn(II) AcAc

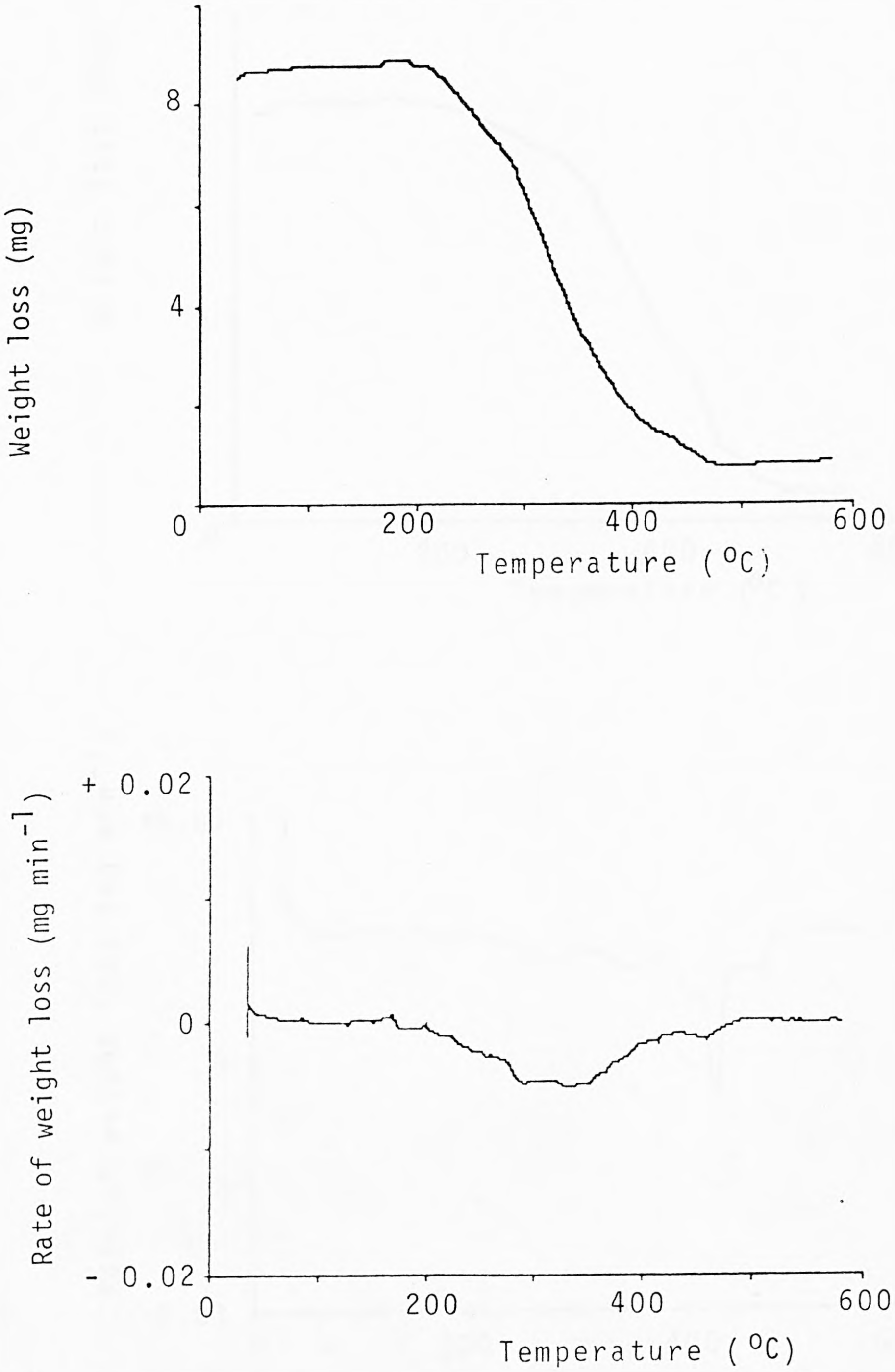
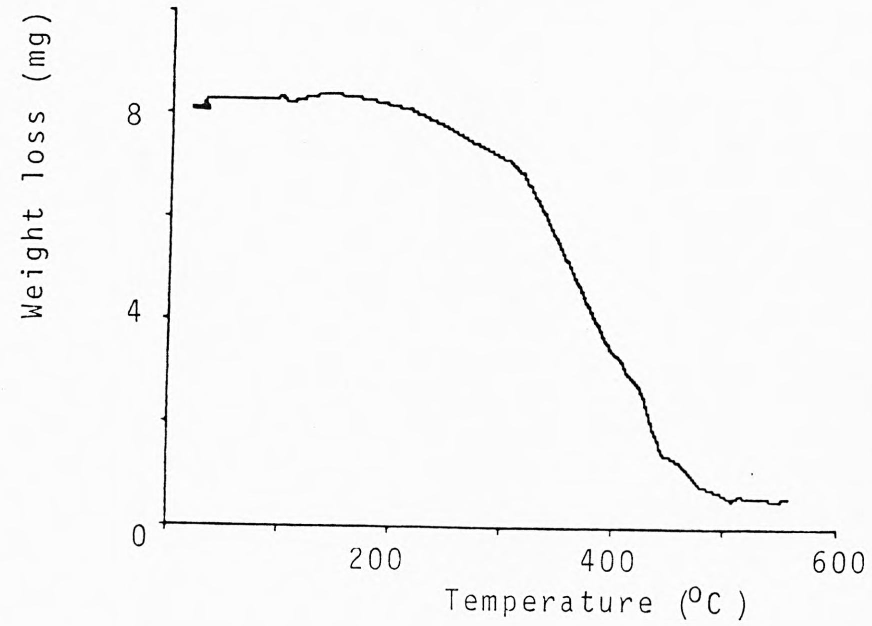


Fig. 3.21 Thermogravimetric analysis curves for polypropylene containing 2 phr Zn(II) AcAc + 5 phr Cereclor



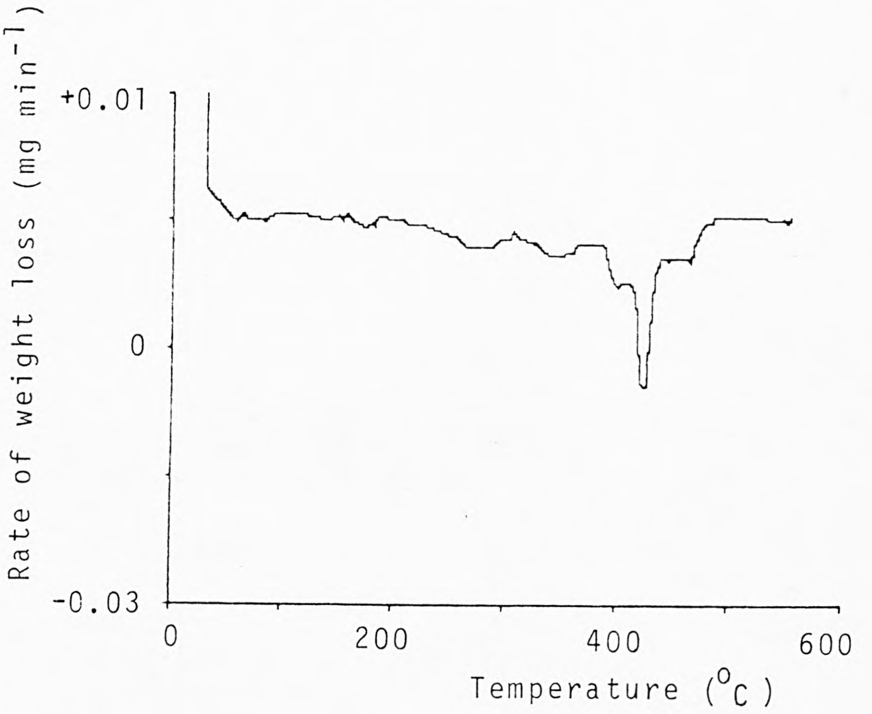


Table 3.21 Thermoanalytical results for Zn acetyl acetonate and Cereclor

	Zn(II) AcAc		2Zn AcAc :5 Cereclor		
Initial weight (mg)	8.733		9.748		
Total weight lost (mg/%)	81.06		89.43		
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	6.29		6.86		
DTG_{max} (mg min^{-1}/% min^{-1})	0.117		0.060		
T (DTG_{max}) (°C/■)	85		172		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/■)	60-117		57-187		
Second Loss					
Wt loss (mg/%)	74.77		16.28		
DTG_{max} (mg min^{-1}/% min^{-1})	0.901		0.420		
T (DTG_{max}) (°C/■)	206		211		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/■)	117-228		187-253		
Third Loss					
Wt loss (mg/%)			33.96		
DTG_{max} (mg min^{-1}/% min^{-1})			0.351		
T (DTG_{max}) (°C/■)			314		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/■)			253-336		
Fourth Loss					
Wt loss (mg/%)			5.25		
DTG_{max} (mg min^{-1}/% min^{-1})			0.072		
T (DTG_{max}) (°C/■)			360		
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/■)			336-420		
Fifth Loss					
Wt loss(mg%)			27.08		
DTG_{max} (oC/■)			0.202		
T(DTG_{max})			451		
T range			420-521		

Table 3.22 Thermoanalytical results for polypropylene in the presence of zinc acetyl acetonate and Cereclor

	5(phr) Zn AcAc	2(phr)Zn AcAc + 5(phr) Cereclor	2(phr) Z AcAc + 20(phr Cereclor
Initial weight (mg)	8.632	8.131	8.690
Total weight lost (mg/%)	98.15	96.86	98.92
T_D (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)	0.44	0.48	0.35
DTG$_{max}$ (mg min^{-1}/% min^{-1})			
T (DTG$_{max}$) (°C/K)			
DTA$_{max}$ (μV/μV mg^{-1})			
T (DTA$_{max}$) (°C/K)			
T range (°C/K)	148-169	140-167	145-167
First Loss			
Wt loss (mg/%)	87.52	67.44	55.90
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.294	0.272	0.201
T (DTG$_{max}$) (°C/K)	382	391	367
DTA$_{max}$ (μV/μV mg^{-1})			
T (DTA$_{max}$) (°C/K)			
T range (°C/K)	169-423	167-423	167-413
Second Loss			
Wt loss (mg/%)		17.27	25.09
DTG$_{max}$ (mg min^{-1}/% min^{-1})		0.631	0.77
T (DTG$_{max}$) (°C/K)		440	441
DTA$_{max}$ (μV/μV mg^{-1})			
T (DTA$_{max}$) (°C/K)			
T range (°C/K)		423-452	413-448
Third Loss			
Wt loss (mg/%)	CBO 10.19	CBO 11.67	CBO 17.58
DTG$_{max}$ (mg min^{-1}/% min^{-1})	0.112	0.141	0.183
T (DTG$_{max}$) (°C/K)	464	483	499
DTA$_{max}$ (μV/μV mg^{-1})			
T (DTA$_{max}$) (°C/K)			
T range (°C/K)	423-504	452-520	448-522
Fourth Loss			
Wt loss (mg/%)			
DTG$_{max}$ (mg min^{-1}/% min^{-1})			
T (DTG$_{max}$) (°C/K)			
DTA$_{max}$ (V/ V mg^{-1})			
T (DTA$_{max}$) (°C/K)			
T range (°C/K)			
LOI			
D_s			

For a sample containing 2 phr Zn(II) AcAc and 20 phr Cereclor, the uptake of oxygen at 145^{o}C manifests itself as a weight gain. Two stages are observed corresponding to the main breakdown of the polymer. The first and second weight-loss stages are observed at 167-413^{o}C and 413-448^{o}C respectively. The last weight loss reaction occurs between 448 and 522^{o}C and the proportion of material volatilised during this stage, which corresponds to the carbon burn-off stage, is 17.58 wt%. Thus, addition of 5 phr Zn(II) AcAc to polypropylene increases the amount of char formed by 5.04 wt%. The addition of Cereclor to polypropylene-Zn(II) AcAc systems affected the pattern of decomposition of the polymer and increased the amount of char formed. In the case of polypropylene containing 2 phr Zn(II) AcAc and 5 phr Cereclor, the amount of char formed was 11.67 wt% and for a sample containing 2 phr Zn(II) AcAc and 20 phr Cereclor, it was 17.58 wt%.

Table 3.23 shows the correlation between the flammability and thermal decomposition of polypropylene-Zn(II) AcAc-Cereclor systems. There is a good correlation between the LOI and the amount of char formed and this is very obvious in the case of a sample containing 2 phr Zn(II) AcAc and 20 phr Cereclor. The LOI was increased by 10.7 units over that of the base polymer and the amount of char increased by 12.43 wt% compared with that formed from polypropylene on its own.

Table 3.23 The correlation between the flammability and thermal decomposition of polypropylene/zinc acetylacetonate/Cereclor systems

PP + additives(phr)	LOI	Char (wt%)
Nil	18.4	5.15
Zn(II) AcAc (5)	19.5	10.19
Zn(II) AcAc (2) + Cereclor (5)	25.6	11.67
Zn(II) AcAc (2) + Cereclor (20)	29.1	17.58

3.2.7 Degradation of polypropylene in the presence of tin(IV) bis acetyl acetonate dichloride and Cereclor

When Sn(IV) AcAc Cl_2 is heated in air, 64.25 wt% is lost in the temperature range 93-346°C. This weight loss may be attributed to the thermal decomposition of Sn(IV) AcAc Cl_2 to SnO_2:

$$SnC_{10}H_{14}O_4Cl_2 \longrightarrow SnO_2$$

Table 3.24 shows the results of the thermal decomposition of a 3:7 mixture of Sn(IV) AcAc Cl_2 and Cereclor. Three weight-loss stages are observed in the temperature ranges 118-231°C, 231-358°C and 358-451°C respectively, which may be attributed to the thermal decomposition of Sn(IV) AcAc Cl_2 to SnO_2 and the liberation of hydrogen chloride from the decomposition of Cereclor. Furthermore SnO_2 and HCl interact to yield volatile $SnCl_4$ and water vapour:

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

The amount of char formed is smaller than that derived from Cereclor on its own (Table 3.24).

The thermal behaviour of a polypropylene sample

Table 3.24 Thermoanalytical results for tin(IV)bis acetyl acetonate dichloride and Cereclor

	$Sn(IV)AcAc\ Cl_2$		$3Sn(IV)AcAc\ Cl_2$: 7 Cereclor		
Initial weight (mg)	9.119		8.340		
Total weight lost (mg/%)	64.25		96.36		
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	64.25		37.29		
DTG_{max} (mg min^{-1}/% min^{-1})	1.30		0.51		
T (DTG_{max}) (°C/[illegible])	287		212		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])	93-346		118-231		
Second Loss					
Wt loss (mg/%)			36.81		
DTG_{max} (mg min^{-1}/% min^{-1})			0.36		
T (DTG_{max}) (°C/[illegible])			346		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])			231-358		
Third Loss					
Wt loss (mg/%)			7.31		
DTG_{max} (mg min^{-1}/% min^{-1})			0.07		
T (DTG_{max}) (°C/[illegible])			387		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])			358-451		
Fourth Loss					
Wt loss (mg/%)			14.95		
DTG_{max} (mg min^{-1}/% min^{-1})			0.14		
T (DTG_{max}) (°C/[illegible])			497		
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/[illegible])			451-553		
LOI					
D_s					

containing 5 phr of Sn(IV) AcAc Cl_2 is shown in Fig. 3.22. Two weight-loss stages are observed at 127-441°C and 441-521°C. The first stage, the main breakdown of the polymer, is observed at a lower temperature than the temperature of degradation of polypropylene on its own. The weight loss during this stage is 89.10 wt%. The second weight loss is the carbon burn-off stage and its temperature is extended to 521°C when the additive is present. 8.43 wt% is lost during this stage (Table 3.25), so that virtually no residue is left.

The thermal degradation behaviour of polypropylene samples containing different concentrations of Sn(IV) AcAc Cl_2 and Cereclor is shown in Figs. 3.23 and 3.24 and the numerical results are given in Table 3.25. For polypropylene containing 0.5 phr Sn(IV) Cl_2 AcAc and 20 phr Cereclor, two stages are observed corresponding to the breakdown of the polymer. The first stage is observed at 185-399°C and the accompanying weight loss is 59.43 wt%. The second weight loss is noticed at 399-464°C and 22.69 wt% is lost during this stage. The temperature of degradation of polypropylene is raised by 11°. The carbon burn-off stage is observed at 465-542°C and 10.9 wt% is volatilised.

With polypropylene containing 3 phr Sn(IV) AcAc Cl_2 and 7 phr Cereclor, the temperature of breakdown of

Fig. 3.22 Thermogravimetric analysis curves for polypropylene containing 5 phr Sn(IV) AcAc Cl_2.

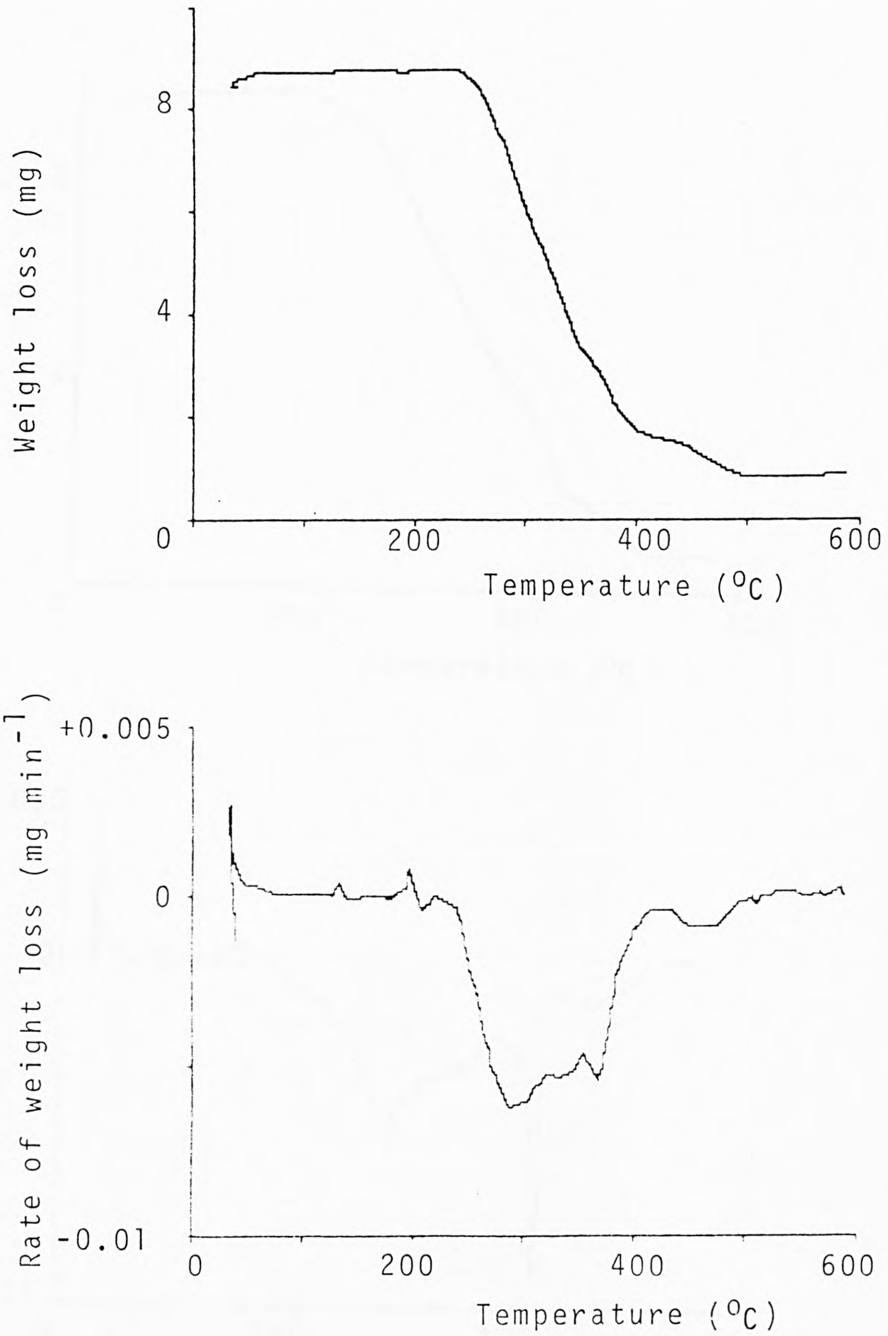
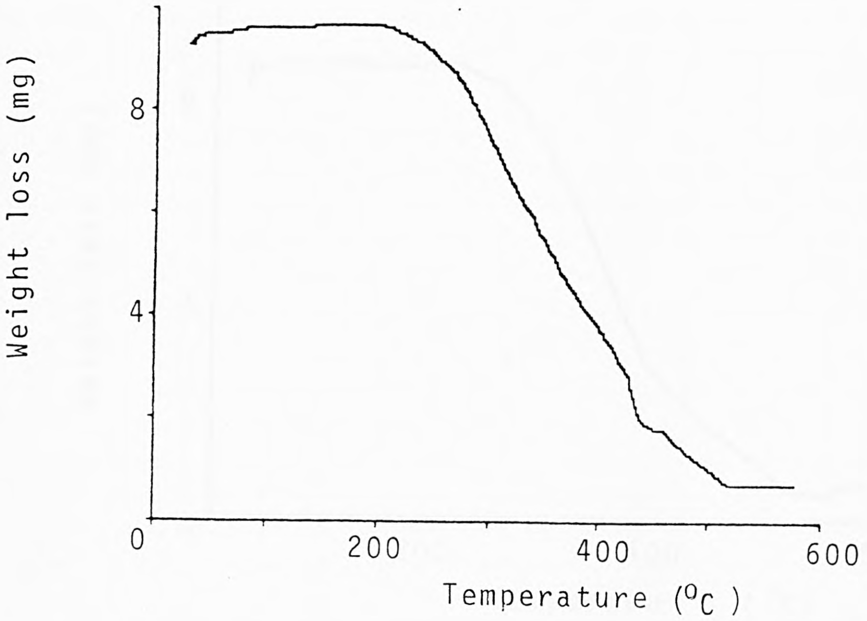


Fig. 3.23 Thermogravimetric analysis curves for polypropylene containing 0.5 phr Sn(IV) AcAc Cl_2 + 20 phr Cereclor



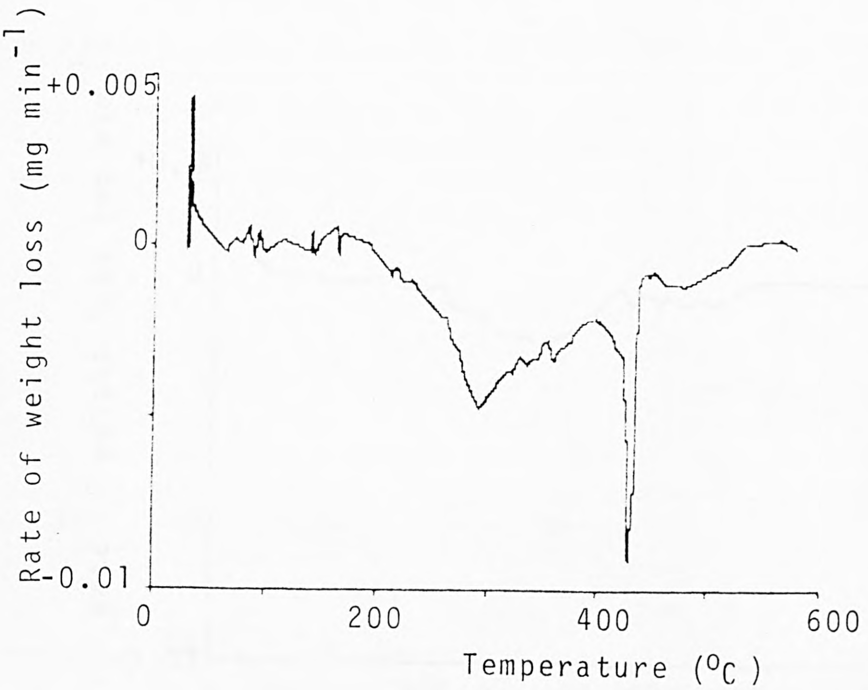


Fig. 3.24. Thermogravimetric analysis curves for polypropylene containing 3 phr Sn(IV) AcAc Cl_2 + 7 phr Cereclor

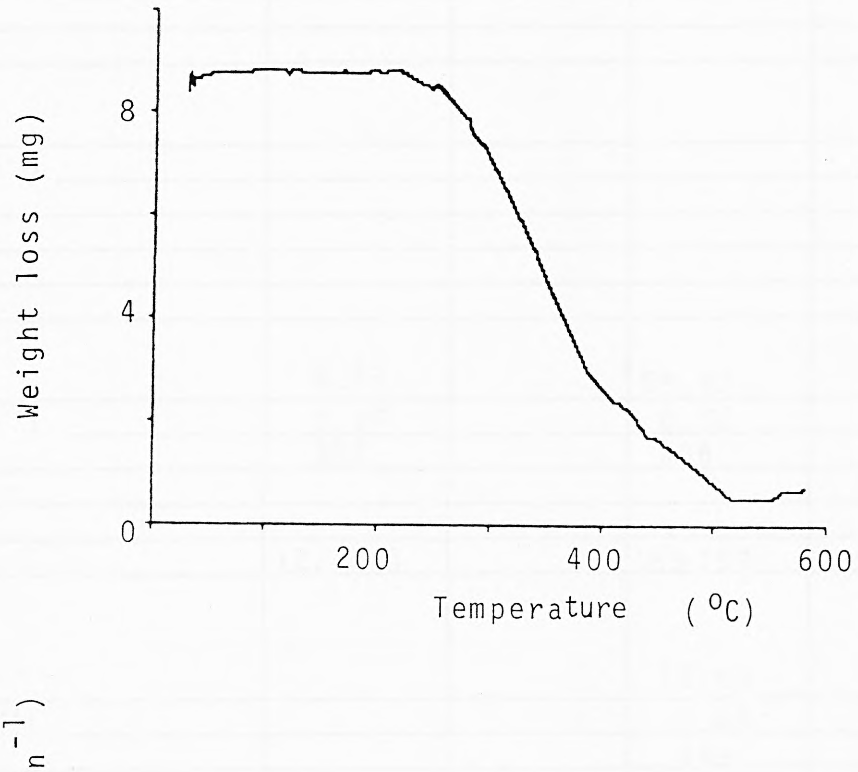


Table 3.25 The thermoanalytical results for polypropylene in the presence of tin(IV) bis acetyl acetonate dichloride and Cereclor

	5 phr $Sn(IV)AcAcCl_2$	0.5 phr $Sn(IV)AcAcCl_2$+20 phr Cereclor	3 phr $Sn(IV)AcAcCl_2$ + 7 phr Cereclor
Initial weight (mg)	8.900	9.737	8.560
Total weight lost (mg/%)	97.53		95.68
T_D (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)			
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)			
First Loss			
Wt loss (mg/%)	8.91	59.43	73.11
DTG_{max} (mg min^{-1}/% min^{-1})	0.37	0.32	0.31
T (DTG_{max}) (°C/[redacted])	302	306	346
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	127-441	185-399	211-411
Second Loss			
Wt loss (mg/%)		22.69	11.47
DTG_{max} (mg min^{-1}/% min^{-1})		0.65	0.25
T (DTG_{max}) (°C/[redacted])		438	441
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])		399-465	411-467
Third Loss	CBO	CBO	CBO
Wt loss (mg/%)	8.43	10.9	11.10
DTG_{max} (mg min^{-1}/% min^{-1})	0.12	0.11	0.12
T (DTG_{max}) (°C/[redacted])	475	510	509
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/[redacted])	441-521	465-542	467-54
Fourth Loss			
Wt loss (mg/%)			
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (V/ V mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)			
LOI			
D_s			

the polymer is raised to 211^{o}C and there is a 84.58% weight loss. The carbon burn-off stage is observed in the same temperature range as for polypropylene containing 0.5 phr Sn(IV) AcAc Cl_2 and 20 phr Cereclor and the amount of char formed is nearly the same. Table 3.26 shows the correlation between the limiting oxygen index and the amount of char formed. The addition of 5 phr Sn(IV) AcAc Cl_2 to polypropylene increased the LOI by 2.3 units and the amount of char by 3.28 wt%. Although the LOI increased from 24.3 to 27.2, the amount of char was nearly the same. No oxygen uptake was observed for polypropylene samples containing the tin chelate.

Table 3.26 The correlation between the limiting oxygen index and the char formed from polypropylene/tin(IV) bis acetyl acetonate dichloride/Cereclor systems

PP + additives (phr)	LOI	char (wt%)
Nil	18.4	5.15
Sn(IV) AcAcCl_2(5)	20.7	8.43
Sn(IV)AcAcCl_2(0.5) + Cereclor(20)	24.3	10.9
Sn(IV)AcAcCl_2 (3) + Cereclor (7)	27.2	11.1

3.3 Studies of photochemical behaviour of polypropylene

3.3.1 General

Several experimental techniques have previously been used to study the rates and course of the photodegradation and photo-oxidation of organic polymers. In the case of polypropylene the extent of degradation of thin films of the polymer has been measured by monitoring the build-up of non-volatile oxidation products; the concentration of these products can then be followed by the increase in the intensity of the hydroxyl and carbonyl bands in the infrared (ir) spectrum. (Carlsson and Wiles 1972). Measurements have also been made of the amounts of volatile products released during polymer photodegradation (Grassie and Weir 1965a,b; Jellinck et al. 1970). The molecular weight of polymers also decreases rapidly with time of u.v.-irradiation and gel-permeation chromatography (GPC) can be used to determine the molecular weight (Adams 1972). Scanning or transmission electron microscopy has been used to detect the changes occurring on a polymer surface during u.v. irradiation (Blais et al. 1972). E.s.r. studies of polypropylene, which had been irradiated with u.v.light in vacuum at-196^{o}C have yielded direct evidence for the formation of methyl methylene and chain-end radicals (Ranby and Yoshida 1966). Spectrophosphorimetry has been used to establish the presence, and to examine the nature, of photoreactive carbonyl groups known to be present in commercial polypropylene (Briggs and McKellar, 1968). The technique of flash photolysis has also been used to examine the effect of additives on a photoexcited species (Briggs and McKellar, 1968).

In this work, it was decided to use a spectroscopic method to determine the rate of photo-oxidation of polypropylene, on account of the practical convenience and accuracy of such methods.

3.3.2 Infrared measurements

Infrared (i.r.) transmission spectroscopy provides a rapid non-destructive technique for the study of the extent and nature of the reactions involved in the photo-oxidative deterioration of polymer films. The main changes reported during the photolysis of polypropylene in air are the build-up of polymeric carbonyl (absorbing at 1715 cm^{-1}) and hydroperoxide (3400 cm^{-1}) derivatives (Blais et al.,1972; Carlsson et al.,1972). In this work, the build-up of carbonyl absorption at 1750 cm^{-1} and hydroperoxide at 3500 cm^{-1} have been used as measures of the extent of photo-oxidation of polypropylene. Blais et al.(1972) showed that the brittleness of polypropylene samples increases dramatically after irradiation with ultraviolet light for about 24h and that this increase is apparently associated with the rapid accumulation of oxidation products on the surface. Consistent with this, the polypropylene films used in this work became brittle after 50h ultraviolet irradiation and the samples containing those metal chelates which sensitized polypropylene oxidation (as shown by i.r.measurements) were very brittle compared with the others, whereas the films containing chelates which behaved as photostabilizers were less brittle.

Table 3.27 and Fig. 3.25 show the variation of absorbance of the carbonyl group with irradiation time for a polypropylene sample, on its own, and in the presence of 0.5 phr benzophenone. Similar results for hydroperoxide absorption are given in Table 3.28. It can be seen that after 150h u.v. irradiation benzophenone does not have any measurable effect on polypropylene. When the time of irradiation was further increased, benzophenone behaved as a photostabiliser for for polypropylene. Tables 3.29 and 3.30 and Figs. 3.27-3.34 show the effects of different metal chelates (lphr) on the photostabilisation of polypropylene. It was observed that both BHB tris Fe(III) and THB tris Fe(III) were excellent sensitizers for polypropylene oxidation. After nearly 50 h irradiation, there was a high increase in the absorbance of carbonyl and hydroperoxide groups in comparison with polypropylene on its own. The other iron chelates were also found to be good sensitizers, causing polypropylene to deteriorate after 110h u.v. irradiation. Thus, all of the iron chelates used in this work were good sensitizers for for polypropylene.

Two copper(II) chelates were used in this work. Neither of them significantly stabilized polypropylene against u.v. irradiation. However t-BuSalAl Cu(II) was slightly more effective than 3-CarbPheSalAl Cu(II). $SnCl_4$,(Salen H_2) and 2-HydPheSalAl-di-Me-Sn(IV) had nearly the same effect on the photo-oxidation of polypropylene.

Fig.3.25 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing 0.5 phr benzophenone

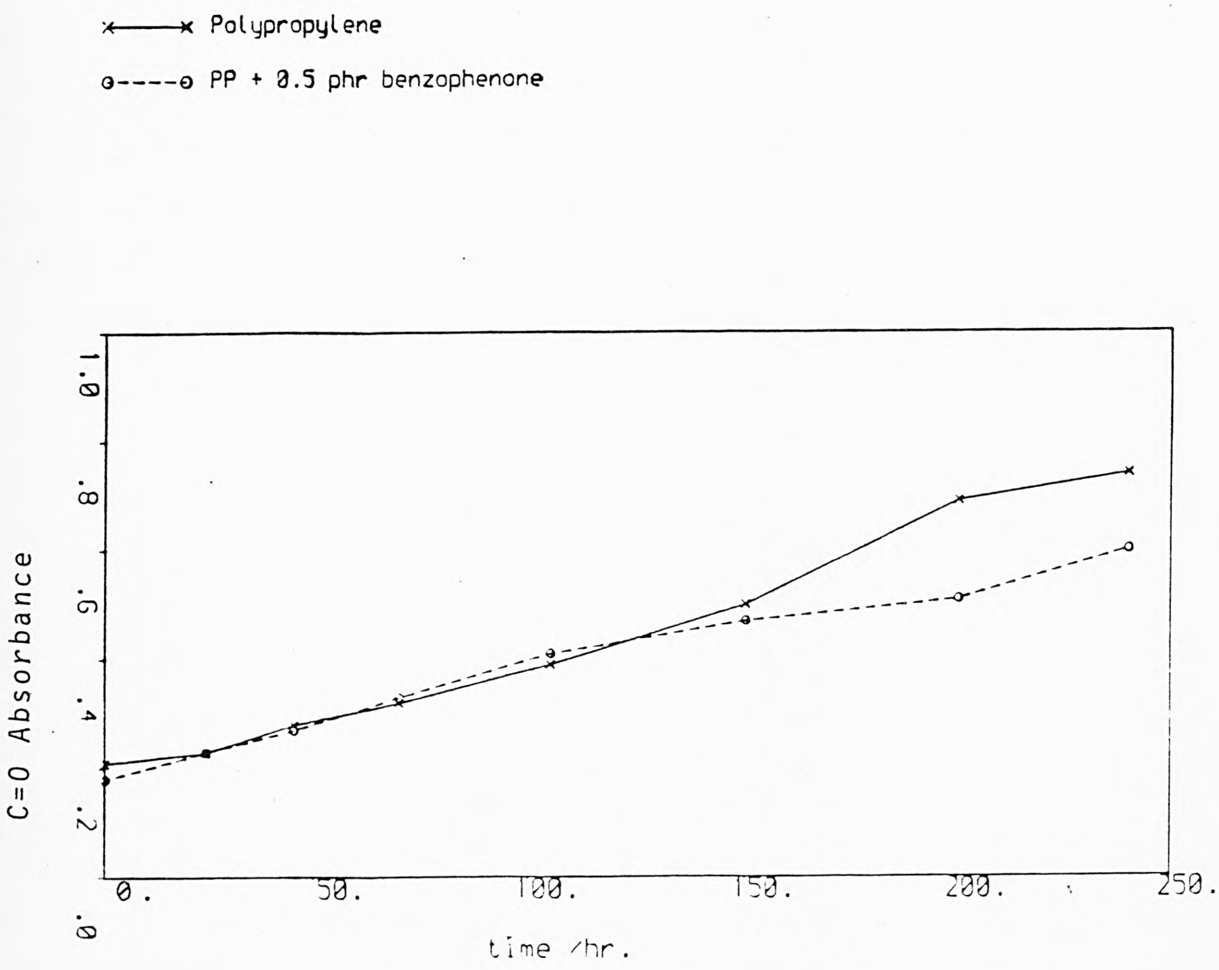


Fig. 3.26 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 0.5 phr benzophenone

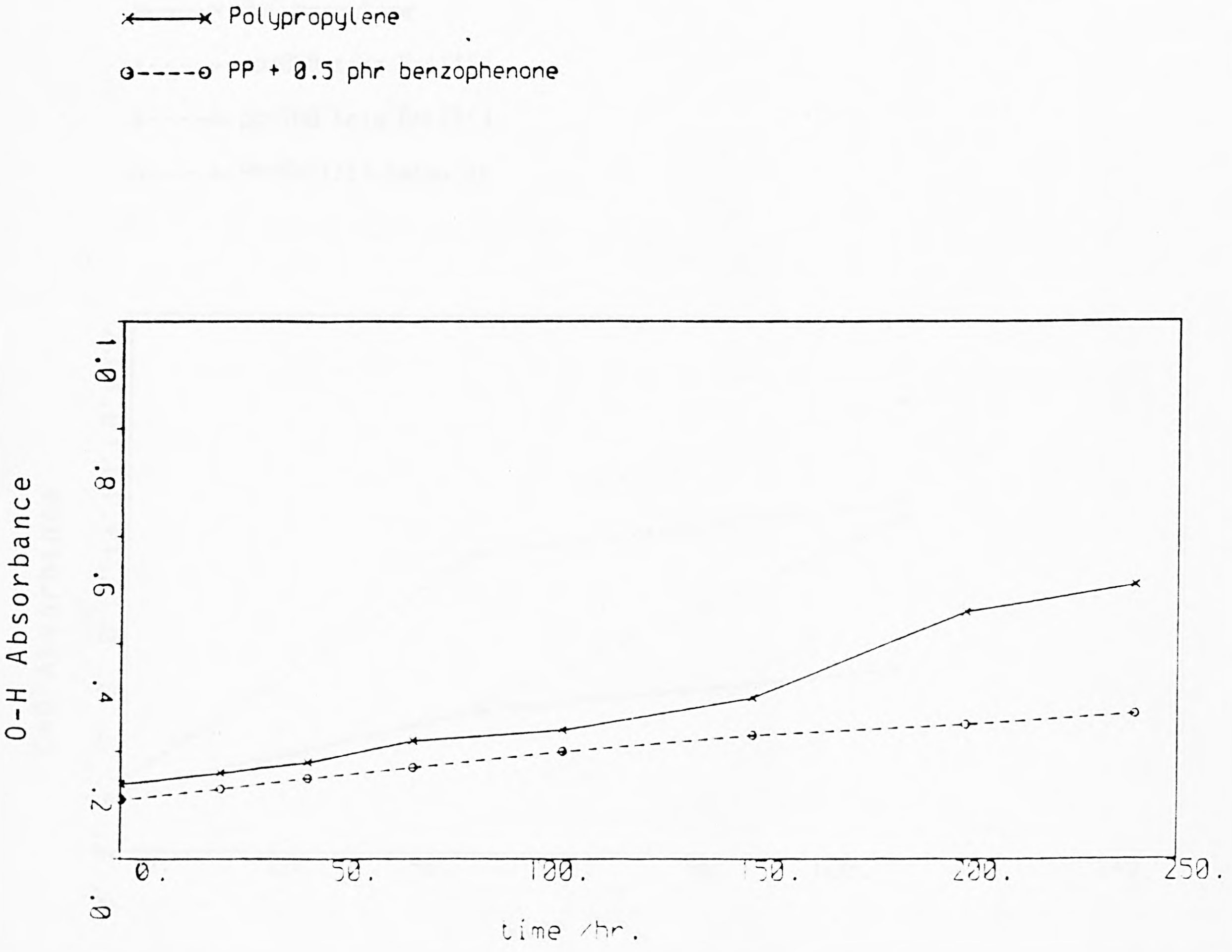


Fig. 3.27 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

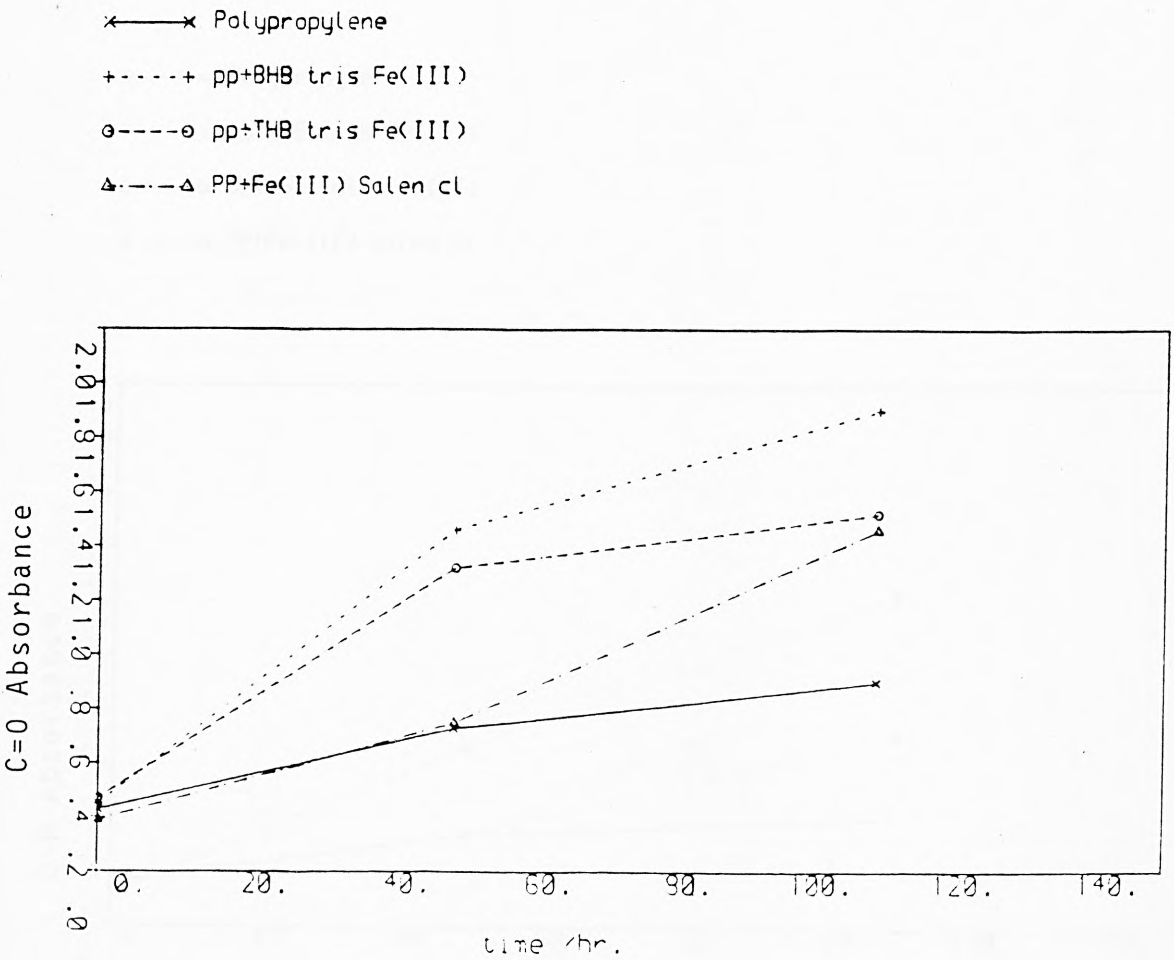


Fig. 3.28 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

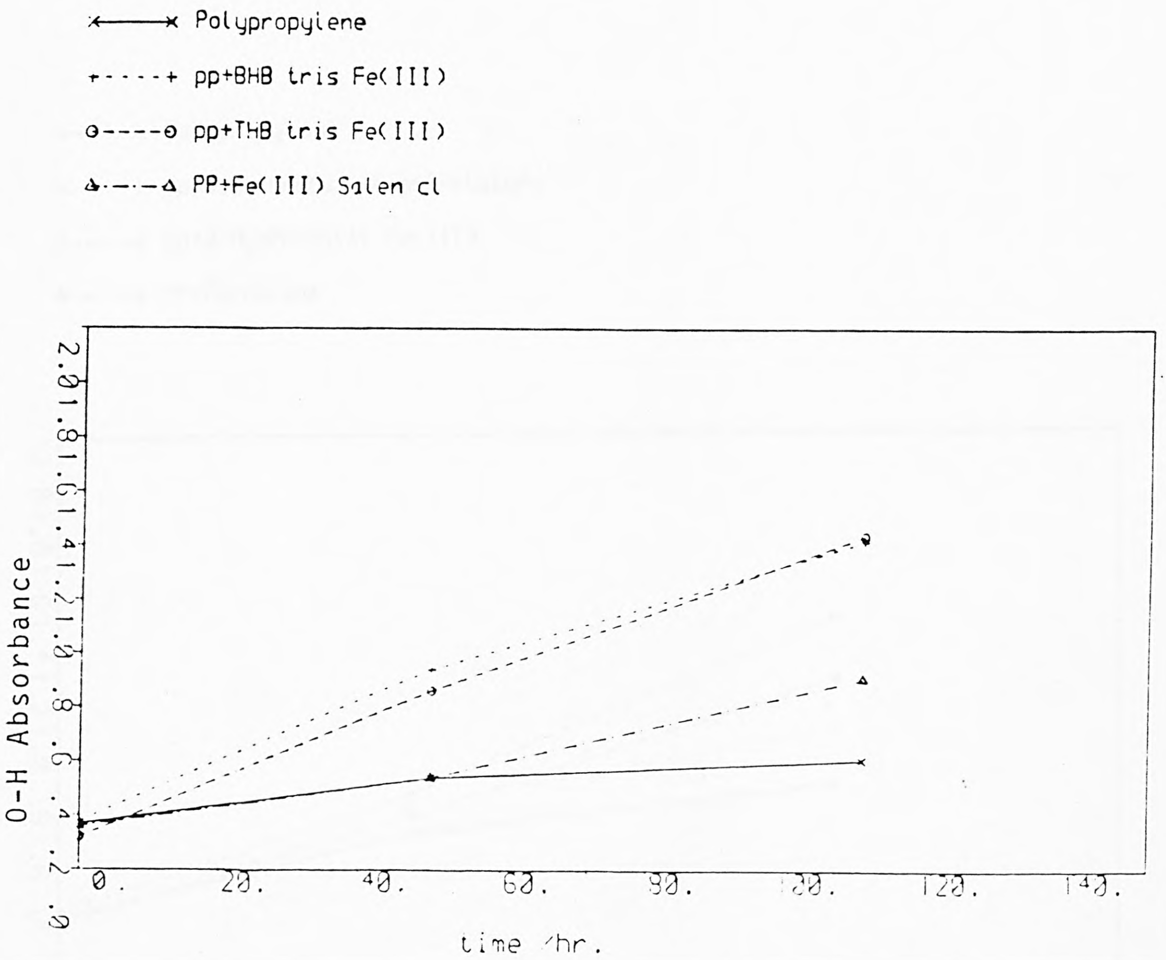


Fig. 3.29 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

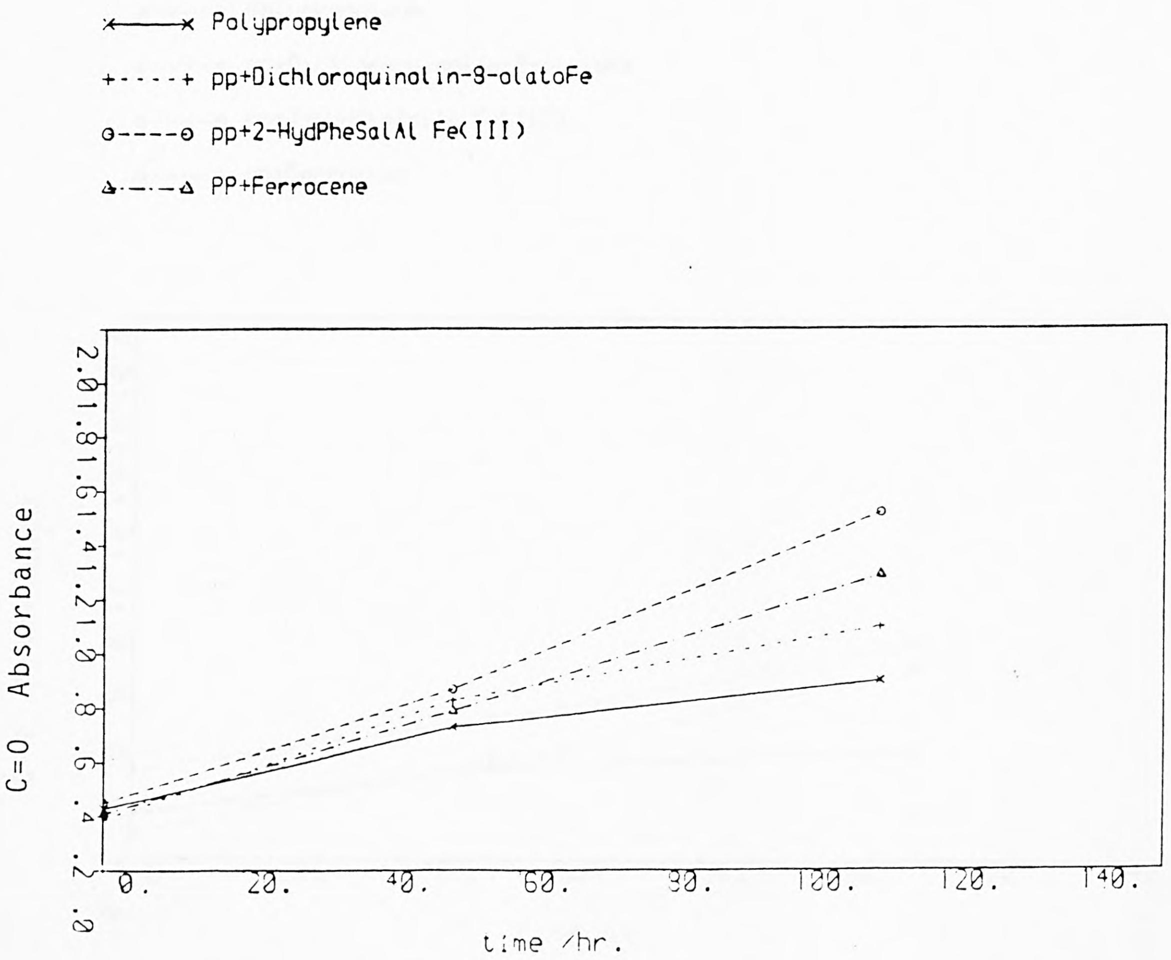


Fig. 3.30 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

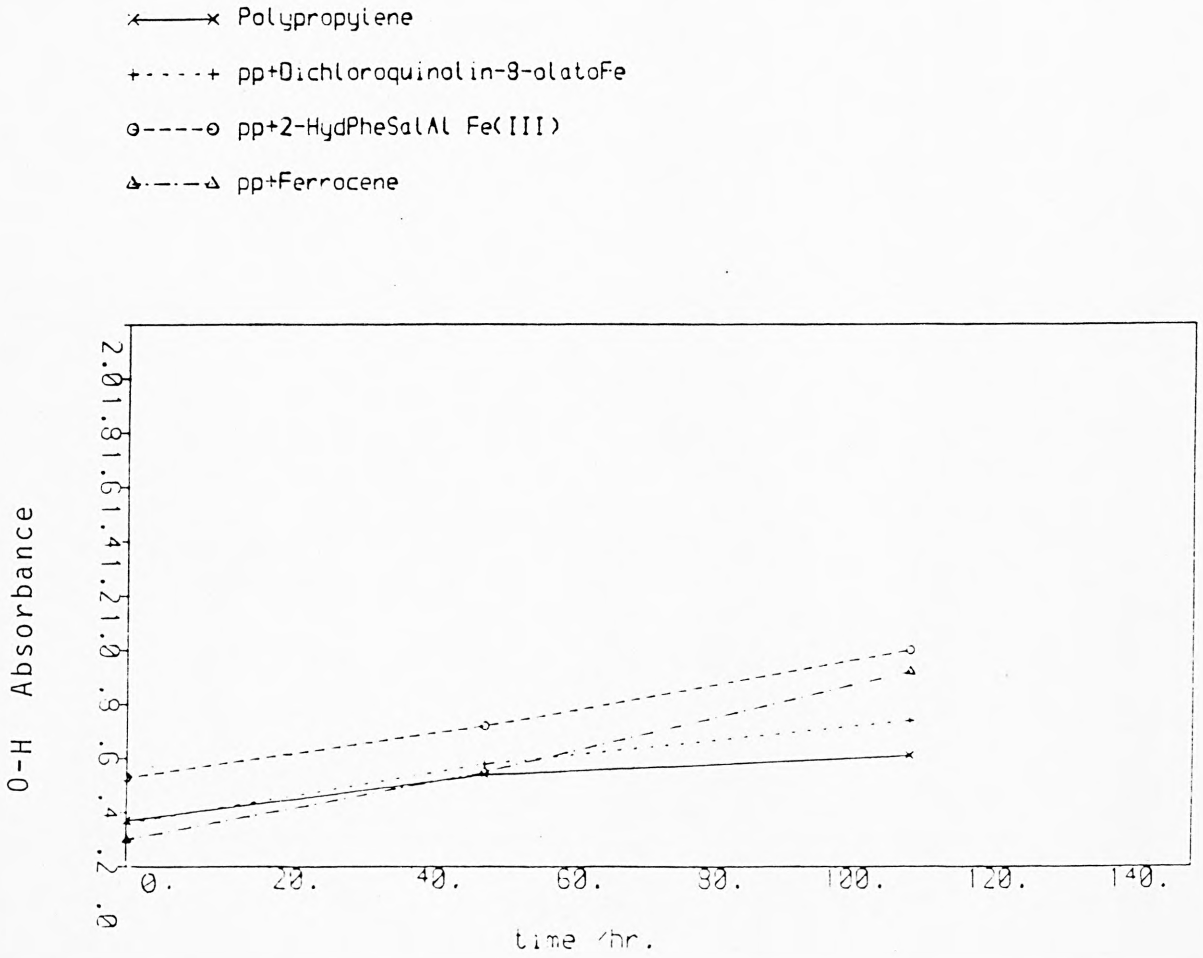


Fig. 3.31 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

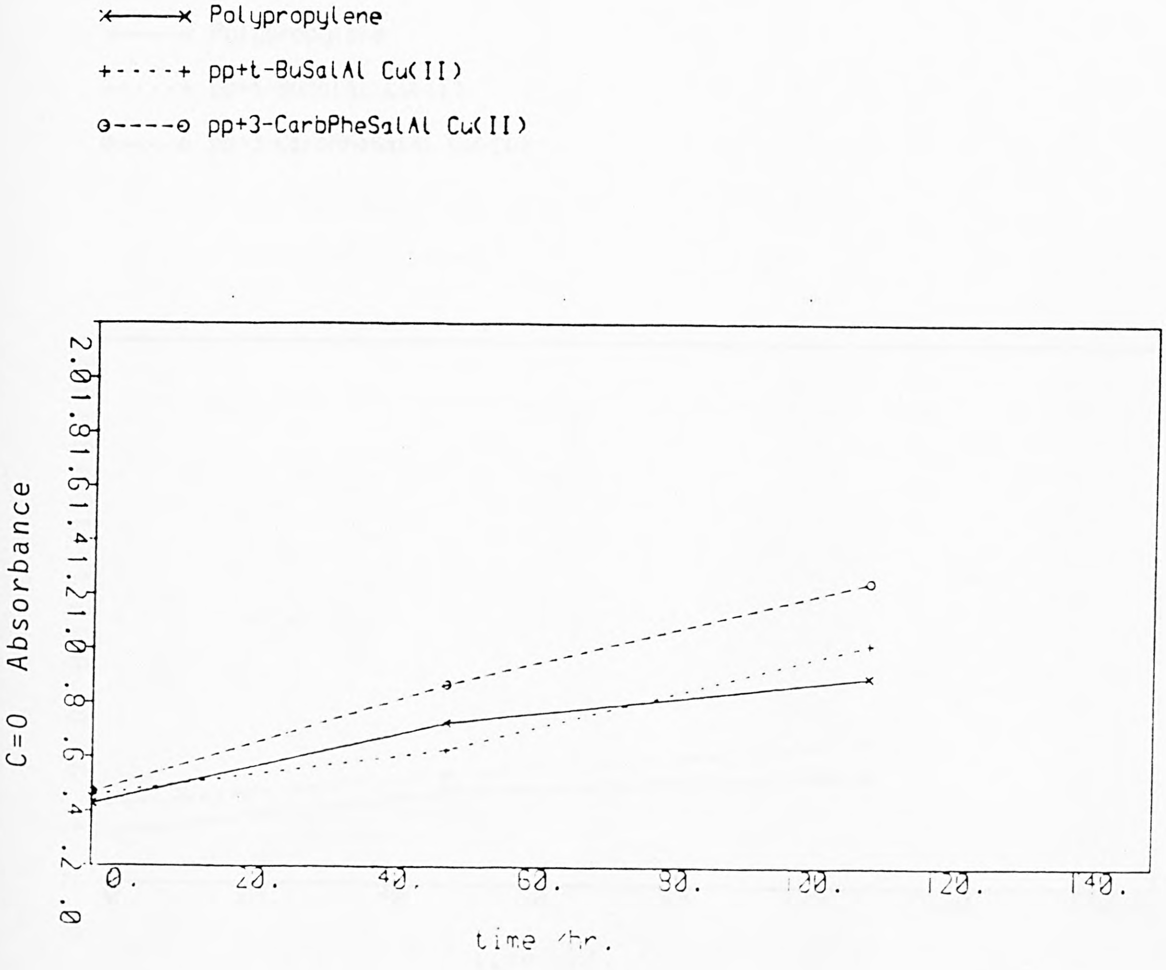


Fig. 3.32 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

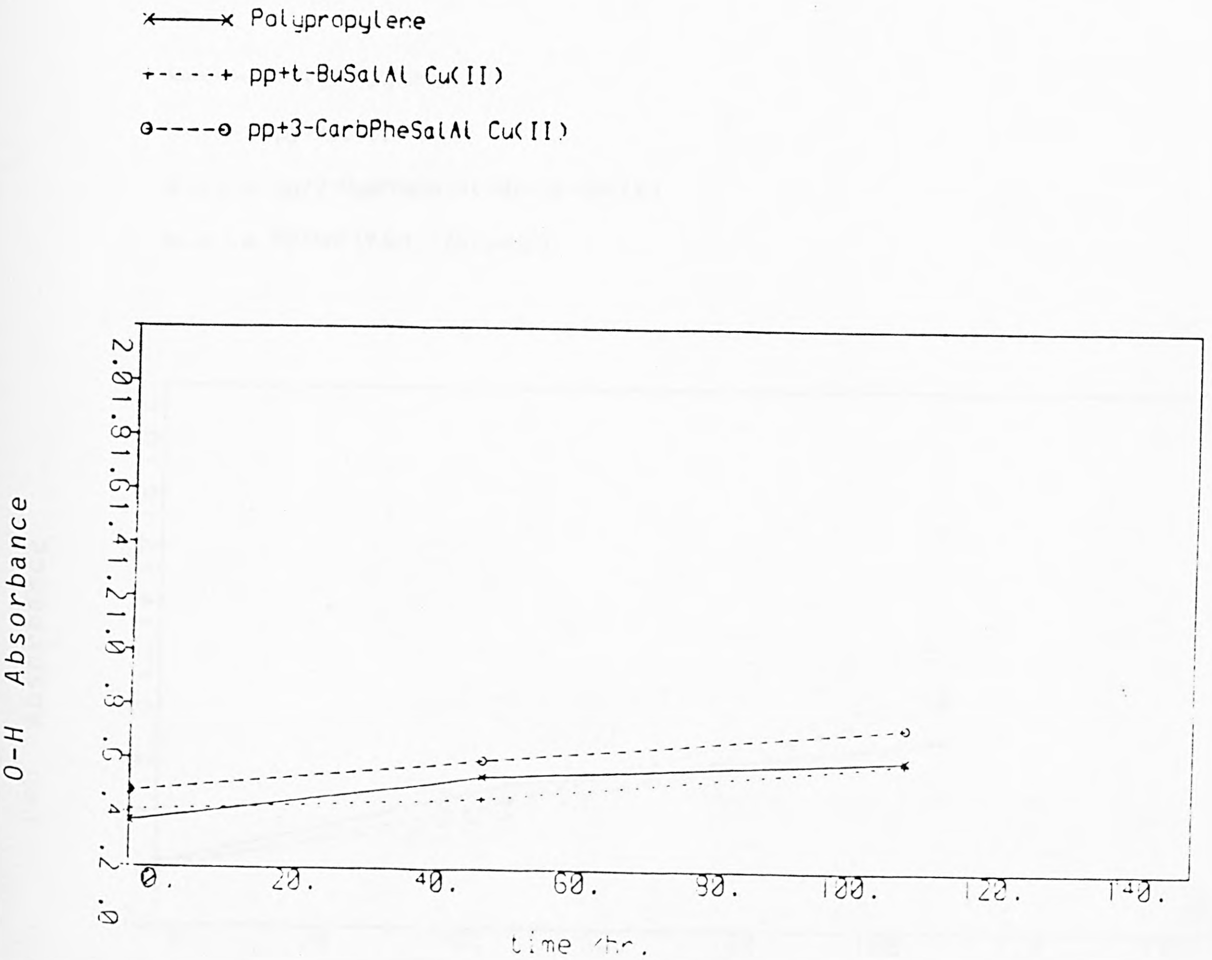


Fig. 3.33 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

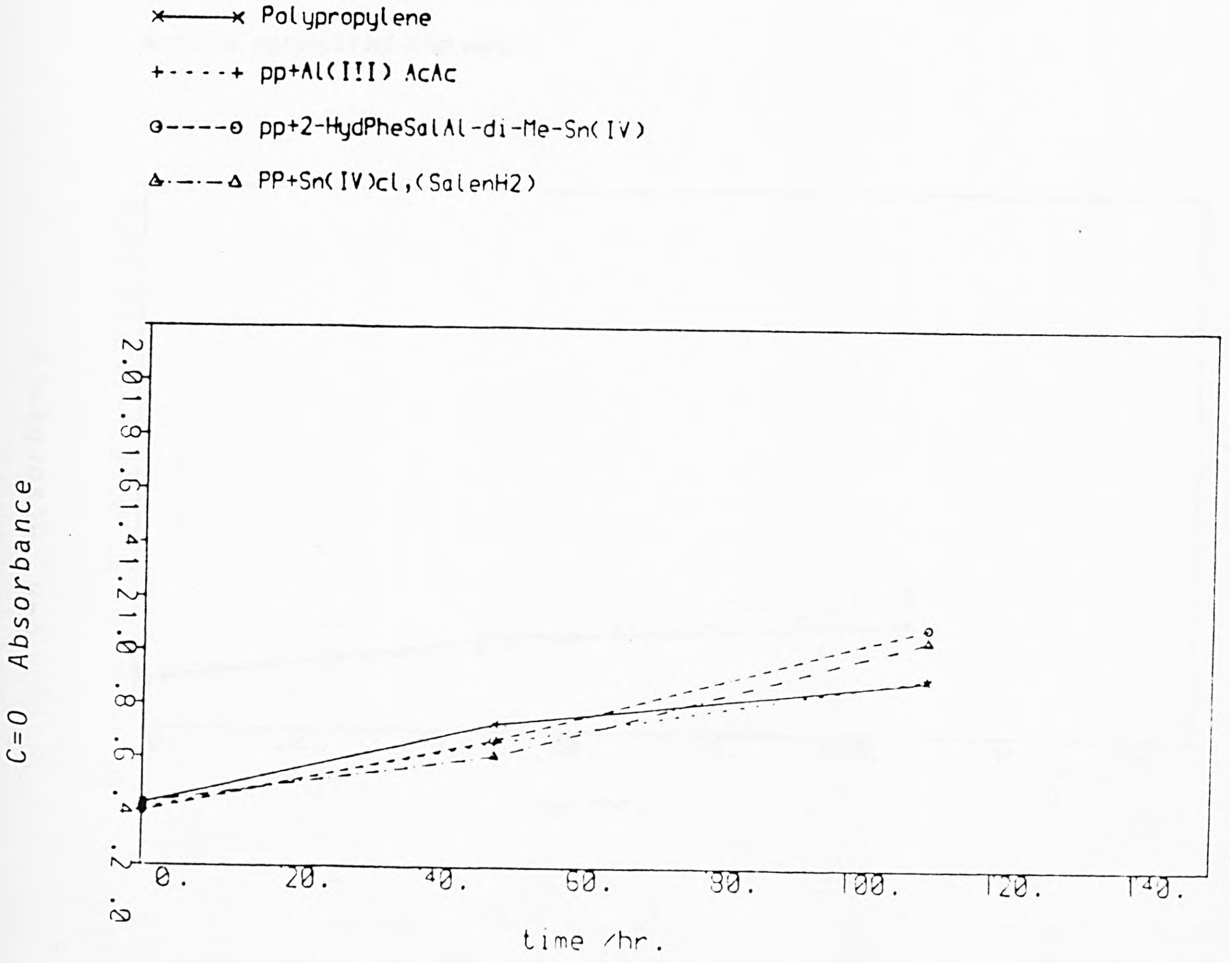


Fig. 3.34 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing 1 phr of different metal chelates

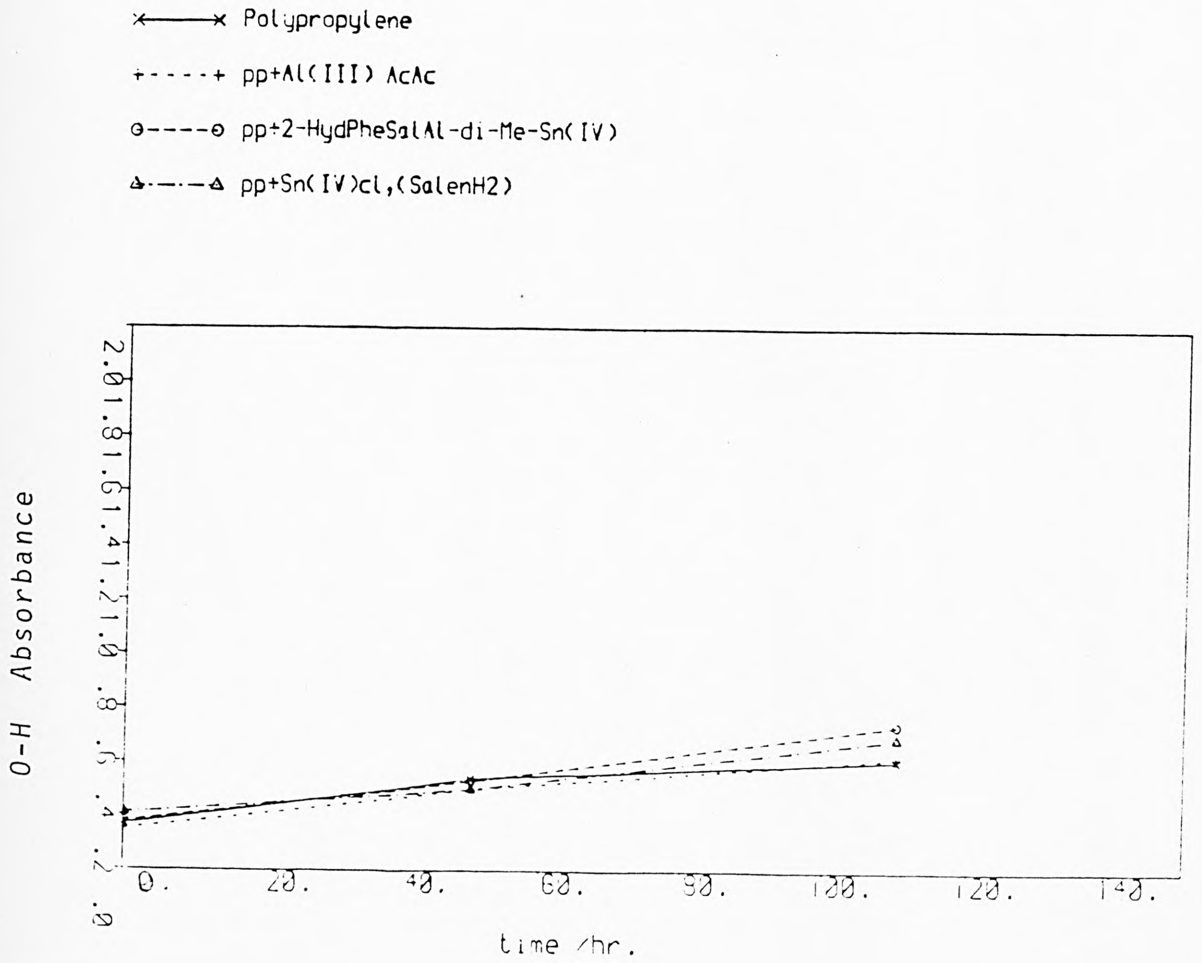


Table 3.27 The effect of u.v. irradiation on carbonyl absorption of polypropylene on its own, and in the presence of benzophenone

Time(h)	Absorbance at 1750 cm^{-1} ($>C=O$)			
	Polypropylene		Polypropylene + 0.5 phr benzophenome	
	A	δA	A	δA
0	0.21		0.18	
24	0.23	0.02	0.23	0.05
45	0.28	0.07	0.27	0.09
70	0.32	0.11	0.33	0.15
105	0.39	0.18	0.41	0.23
150	0.50	0.29	0.47	0.29
200	0.69	0.48	0.51	0.33
240	0.74	0.53	0.60	0.42

Table 3.28 The effect of u.v. irradiation on hydroperoxide absorption of polypropylene on its own and in the presence of benzophenone

Time(h)	Absorbance at 3500 cm^{-1} (-O-H)			
	Polypropylene		Polypropylene + 0.5 phr benzophenome	
	A	δA	A	δA
0	0.		0.11	
24	0.16	0.02	0.13	0.02
45	0.18	0.04	0.15	0.04
70	0.22	0.08	0.17	0.06
105	0.24	0.1	0.20	0.09
150	0.30	0.16	0.23	0.12
200	0.46	0.32	0.25	0.14
240	0.51	0.37	0.27	0.16

Table 3.29 The effects of different metal chelates on carbonyl absorption of polypropylene*

Metal chelates (1 phr)	Absorbance at 1750 cm^{-1} (>C=O)						
	0h	50h		110h		170h	
		A	δA	A	δA	A	δA
Nil	0.23	0.53	0.30	0.70	0.47	1.07	0.84
BHB tris Fe(III)	0.25	1.26	1.01	1.70	1.45		
THB tris Fe(III)	0.27	1.12	0.85	1.32	1.05		
Dichloroquinolin-8-olato iron(III)	0.19	0.63	0.44	0.90	0.71		
2-HydPheSalAl Fe(III)	0.25	0.67	0.42	1.32	1.07	1.52	1.27
Ferrocene	0.21	0.59	0.38	1.09	0.88	1.46	1.25
Fe(III) Salen Cl	0.19	0.55	0.36	1.26	1.07		
$SnCl_4$,($SalenH_2$)	0.23	0.41	0.18	0.85	0.62		
2-HydPheSalAl-di-Me-Sn(IV)	0.20	0.47	0.27	0.90	0.70		
t-BuSalAl Cu(II)	0.26	0.43	0.17	0.82	0.56	1.22	0.96
3-CarbPheSalAl Cu(II)	0.27	0.67	0.40	1.05	0.78	1.41	1.14
Al(III) AcAc	0.21	0.46	0.25	0.71	0.50		

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[*] These experiments were made with intermittent exposure to u.v. radiation.

Table 3.30 The effects of different metal chelates on hydroperoxide absorption of polypropylene*

Metal chelates (1 phr)	Absorbance at 3500 cm^{-1} (-O-H)						
	0h	50h		110h		170h	
		A	δA	A	δA	A	δA
Nil	0.17	0.34	0.17	0.41	0.24	0.65	0.48
BHB tris Fe(III)	0.18	0.74	0.56	1.22	1.04		
THB tris Fe(III)	0.12	0.66	0.54	1.24	1.12		
Dichloroquinolin-8-olato iron(III)	0.16	0.38	0.22	0.54	0.38		
2-HydPheSalAl Fe(III)	0.33	0.52	0.19	0.80	0.47	1.05	0.72
Ferrocene	0.10	0.35	0.25	0.72	0.62	0.92	0.82
Fe(III) Salen Cl	0.16	0.34	0.18	0.71	0.55		
$SnCl_4$,(SalenH$_2$)	0.21	0.30	0.09	0.49	0.28		
2-HydPheSalAl-di-Me-Sn(IV)	0.18	0.33	0.15	0.54	0.36		
t-BuSalAl Cu(II)	0.21	0.26	0.05	0.40	0.19	0.57	0.36
3-CarbPheSalAl Cu(II)	0.28	0.40	0.12	0.53	0.25	0.63	0.34
Al(III) AcAc	0.15	0.30	0.15	0.42	0.27		

* These experiments were made with intermittent exposure to u.v. radiation.

Al(III) AcAc exhibited slightly better results than the Sn(IV) chelates mentioned previously but it is still not effective as a photostabilizer to any useful extent.

More detailed studies were then made on three other metal chelates, Zn(II) Salen, Zn(II) AcAc, and Sn(IV) AcAc Cl_2, which were found to be good stabilizers for polpypropylene. Tables 3.31 and 3.32 and Figs. 3.35 and 3.36 show the effect of u.v. irradiation on the absorbance of carbonyl and hydroperoxide groups in polypropylene in the presence of Zn(II) Salen. Zn(II) Salen was found to be an excellent photostabiliser for polypropylene. It was observed that polypropylene samples containing 0.5 and 1 phr Zn(II) Salen gave a similar degree of protection against u.v. irradiation. Excellent stability against u.v. irradiation was also achieved for a polypropylene sample containing 2 phr Zn(II) Salen.

Tables 3.33 and 3.34 and Figs. 3.37 and 3.38 show the effect of u.v. irradiation on the photostability of polypropylene samples containing different loadings of Zn(II) AcAc. The results indicate that polypropylene samples containing 0.5 phr and 1 phr Zn(II) AcAc exhibit the same behaviour as polypropylene on its own. Excellent photostability was achieved on addition of 2 phr Zn(II) AcAc to polypropylene. Thus, although 1 phr or less of Zn(II)

Fig. 3.35 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing different concentrations of Zn(II) Salen

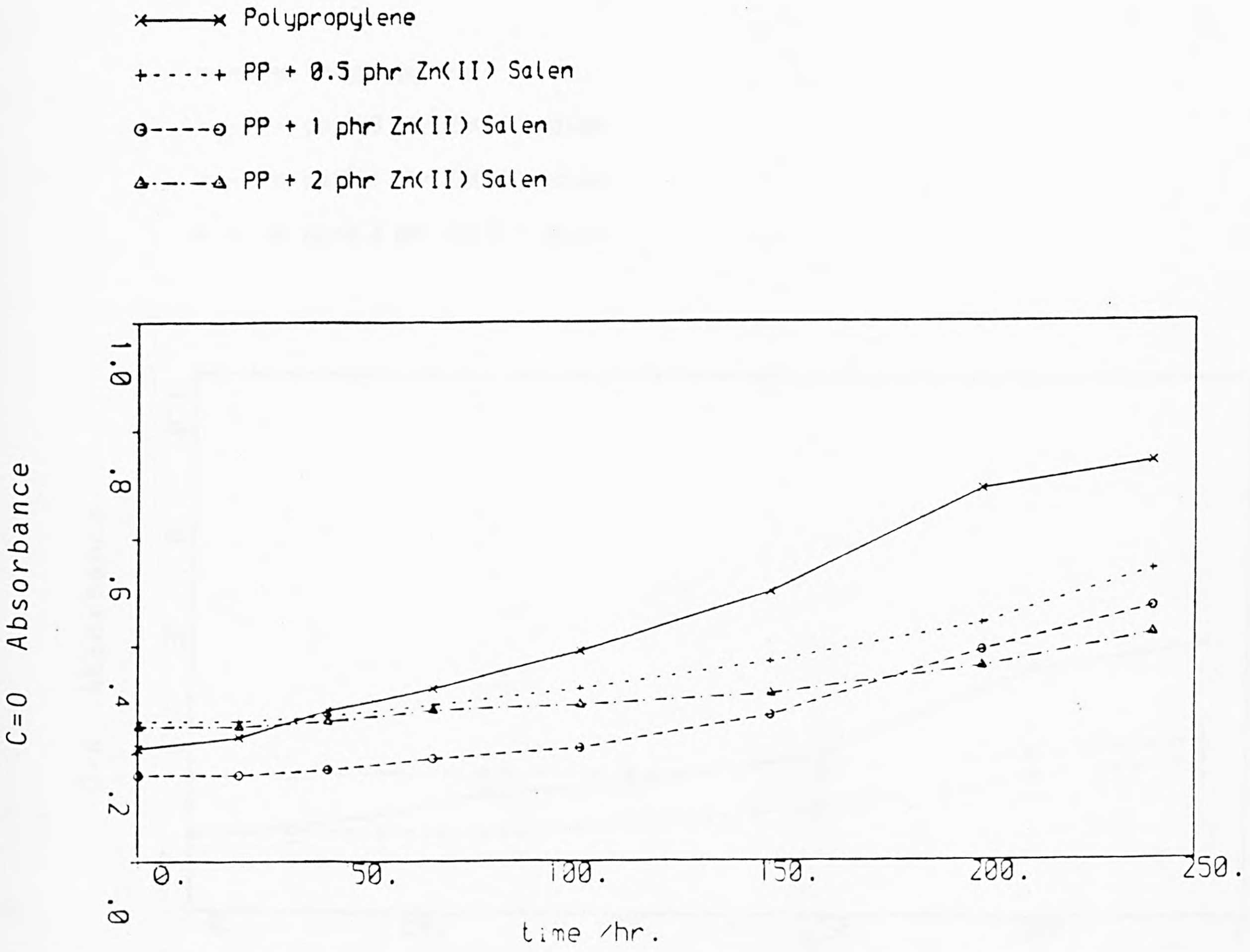


Fig. 3.36 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing different concentrations of Zn(II) Salen

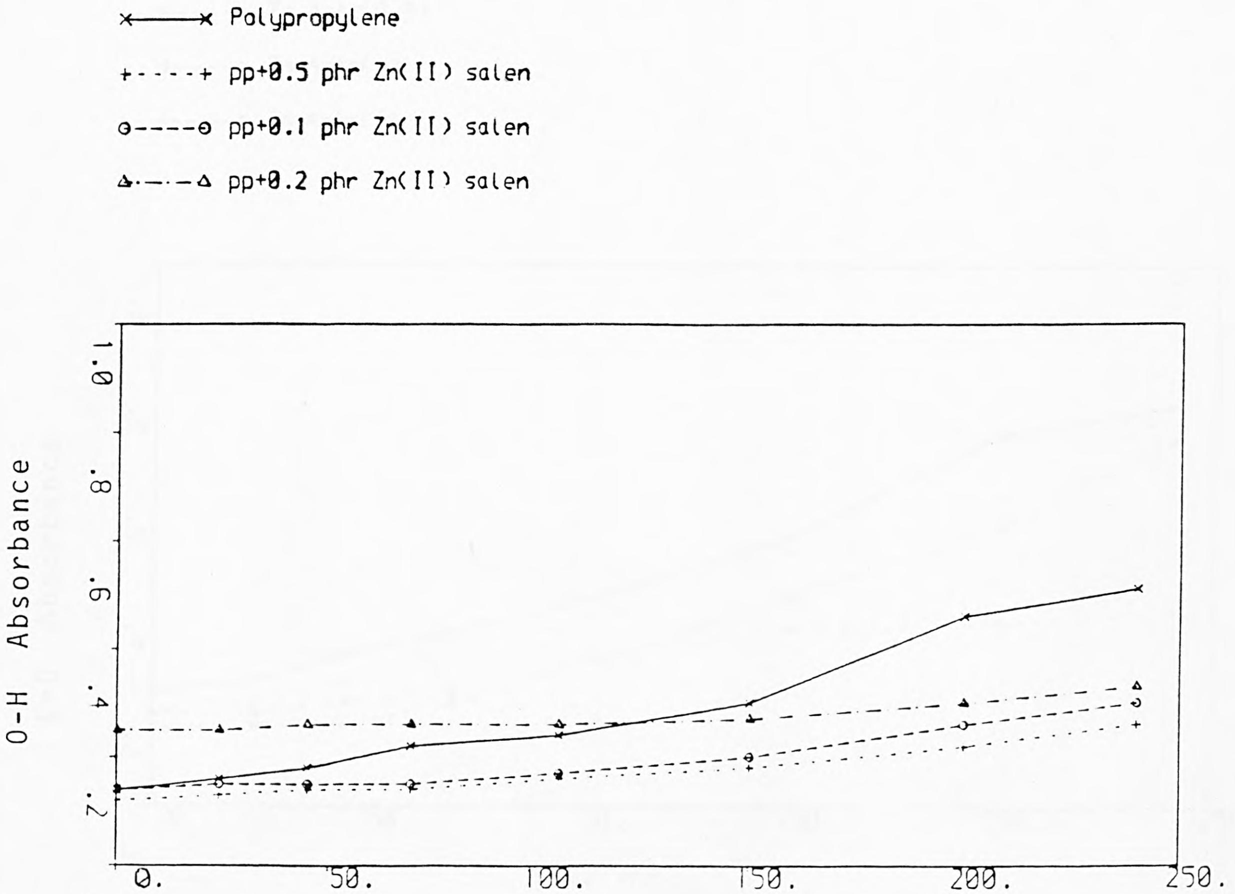


Fig. 3.37 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing different concentrations of Zn(II) AcAc

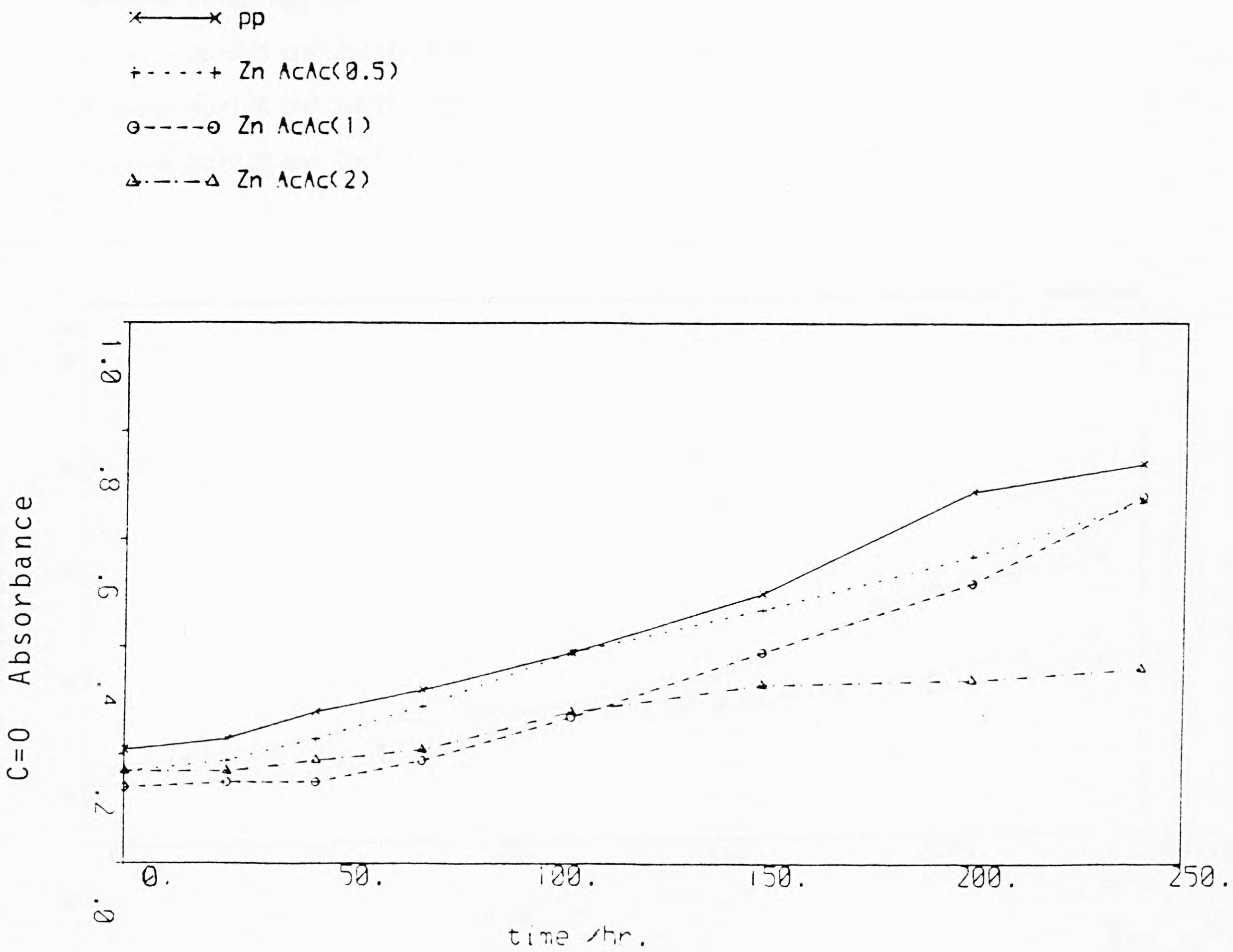


Fig. 3.38 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing differen concentrations of Zn(II) AcAc

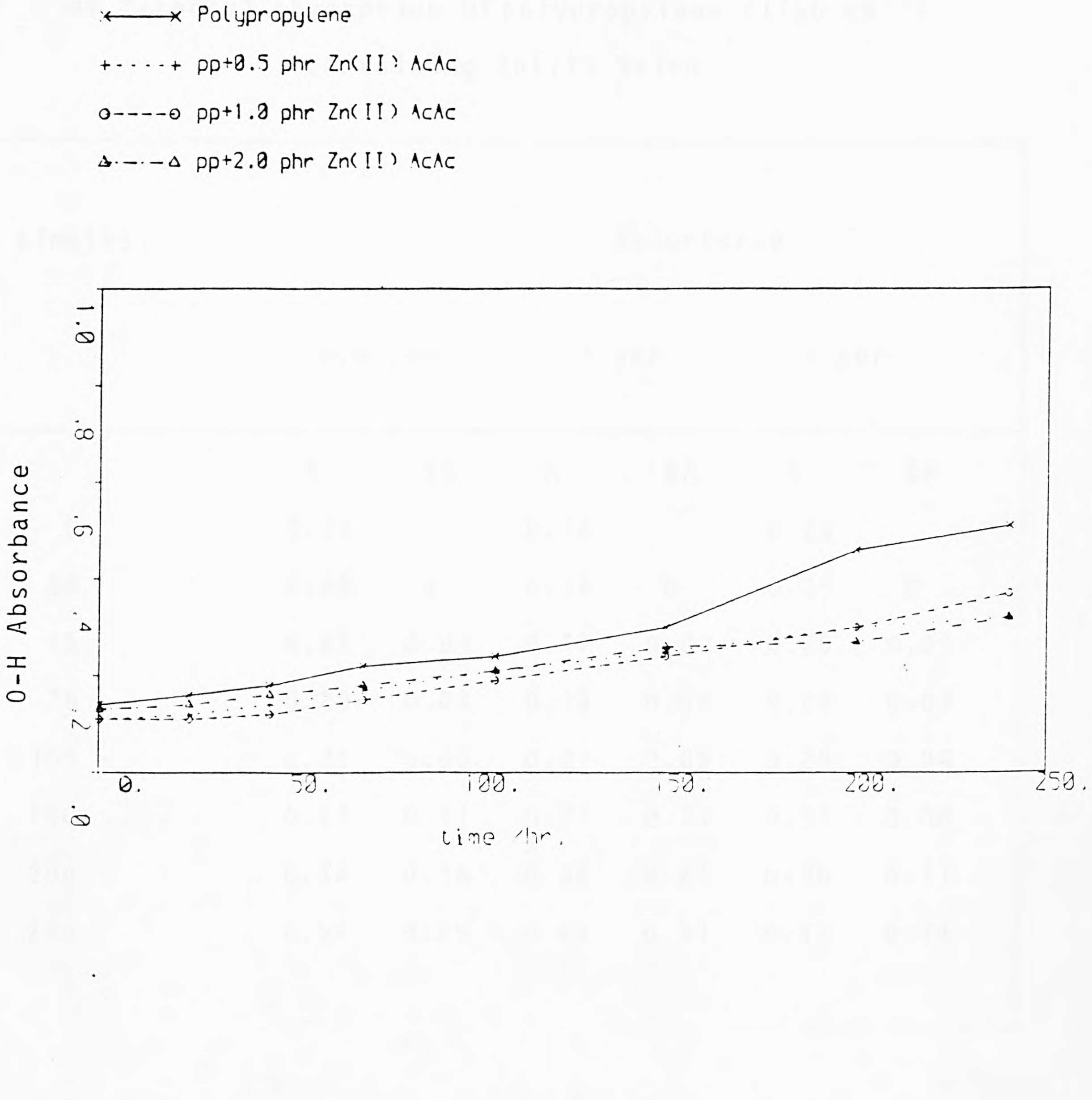


Table 3.31 The variation with u.v. irradation time of carbonyl absorption of polypropylene (1750 cm^{-1}) containing Zn(II) Salen

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.26		0.16		0.25	
24	0.26	0	0.16	0	0.25	0
45	0.27	0.01	0.17	0.01	0.26	0.01
70	0.29	0.03	0.19	0.03	0.28	0.03
105	0.32	0.06	0.21	0.05	0.29	0.04
150	0.37	0.11	0.27	0.11	0.31	0.06
200	0.44	0.18	0.39	0.23	0.36	0.11
240	0.54	0.28	0.47	0.31	0.42	0.17

Table 3.32 The variation with u.v. irradation time of hydroperoxide absorption of polypropylene (3500 cm^{-1}) containing Zn(II) Salen

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.12		0.14		0.25	
24	0.13	0.01	0.15	0.01	0.25	0
45	0.14	0.02	0.15	0.01	0.26	0.01
70	0.14	0.02	0.15	0.01	0.26	0.01
105	0.16	0.04	0.17	0.03	0.26	0.01
150	0.18	0.06	0.20	0.06	0.27	0.02
200	0.22	0.01	0.26	0.12	0.30	0.05
240	0.26	0.14	0.30	0.16	0.33	0.08

<u>Table 3.33</u> The variation with u.v. irradation time of carbonyl absorption of polypropylene (1750 cm^{-1}) containing Zn(II) AcAc

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.17		0.14		0.17	
24	0.19	0.02	0.15	0.01	0.17	0
45	0.23	0.06	0.15	0.01	0.19	0.02
70	0.29	0.12	0.19	0.05	0.21	0.05
105	0.39	0.22	0.27	0.13	0.28	0.11
150	0.47	0.03	0.39	0.25	0.33	0.16
200	0.57	0.04	0.52	0.38	0.34	0.17
240	0.67	0.05	0.68	0.54	0.36	0.19

Table 3.34 The variation with u.v. irradation time of hydroperoxide absorption of polypropylene (3500 cm^{-1}) containing Zn(II) AcAc

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.11		0.11		0.13	
24	0.12	0.01	0.11	0	0.14	0.01
45	0.14	0.03	0.12	0.01	0.16	0.03
70	0.17	0.06	0.15	0.04	0.18	0.05
105	0.21	0.01	0.19	0.08	0.21	0.08
150	0.25	0.14	0.24	0.13	0.26	0.13
200	0.30	0.19	0.30	0.19	0.27	0.14
240	0.32	0.21	0.37	0.26	0.32	0.19

AcAc had little effect this chelate is an effective stabilizer at and above the2 phr level.

The effects of Sn(IV) AcAc Cl_2 on the photostability of polypropylene are given in Tables 3.35 and 3.36 and in Figs. 3.39 and 3.40. The addition of 0.5 phr Sn(IV) AcAc Cl_2 to polypropylene showed a reasonably large effect on the photostability of the polymer. As the concentration of Sn(IV) AcAc Cl_2 was increased, it was observed that Sn(IV) AcAc Cl_2 accelerated the degradation of polypropylene. Thus, for effective stabilisation, the concentration of Sn(IV) AcAc Cl_2 should not be more than 0.5 phr.

3.3.3 Ultraviolet measurements

Polypropylene on its own showed an absorption in the u.v. region at 300 nm which decreased with increasing u.v. irradation time and disappeared after 56h u.v. irradiation (Fig. 3.4.1).

Apolypropylene sample containing 0.5 phr Zn(II) Salen (Fig.3.42) showed a high absorption at 325 nm, which is different from the absorption of polypropylene containing 1 and 2 phr Zn(II) Salen and from the absorption of Zn(II) Salen on its own. This absorption diminished with u.v. irradiation and completely disappeared after 32h u.v. irradiation. Figs. 3.43 and 3.44 show the u.v. spectra

Fig. 3.39 The effect of irradiation time on carbonyl absorbance for polypropylene, on its own, and containing different concentrations of Sn(IV) AcAc Cl_2

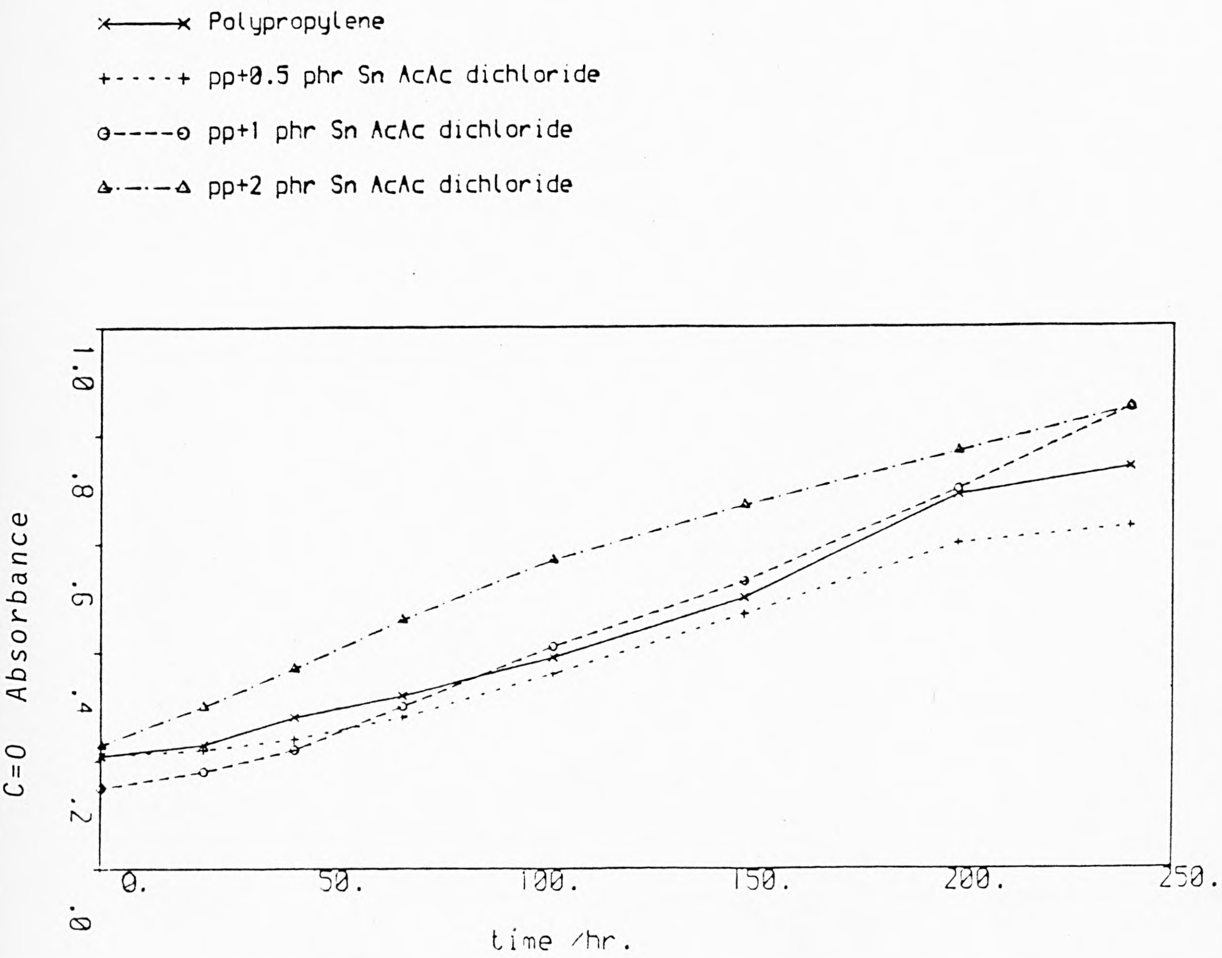


Fig. 3.40 The effect of irradiation time on hydroperoxide absorbance for polypropylene, on its own, and containing different concentrations of Sn(IV) AcAc Cl_2

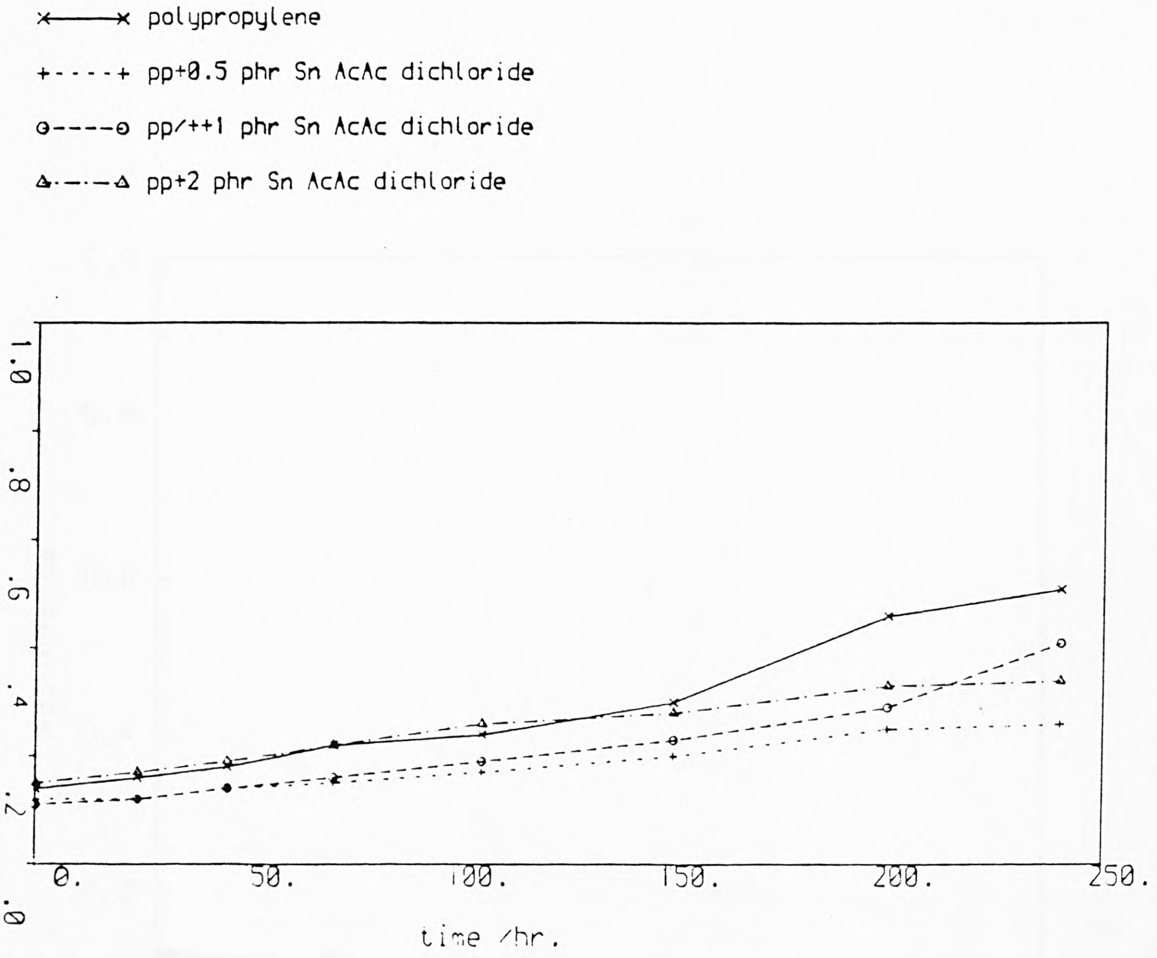


Fig. 3.41 U.v. spectrum for polypropylene on its own

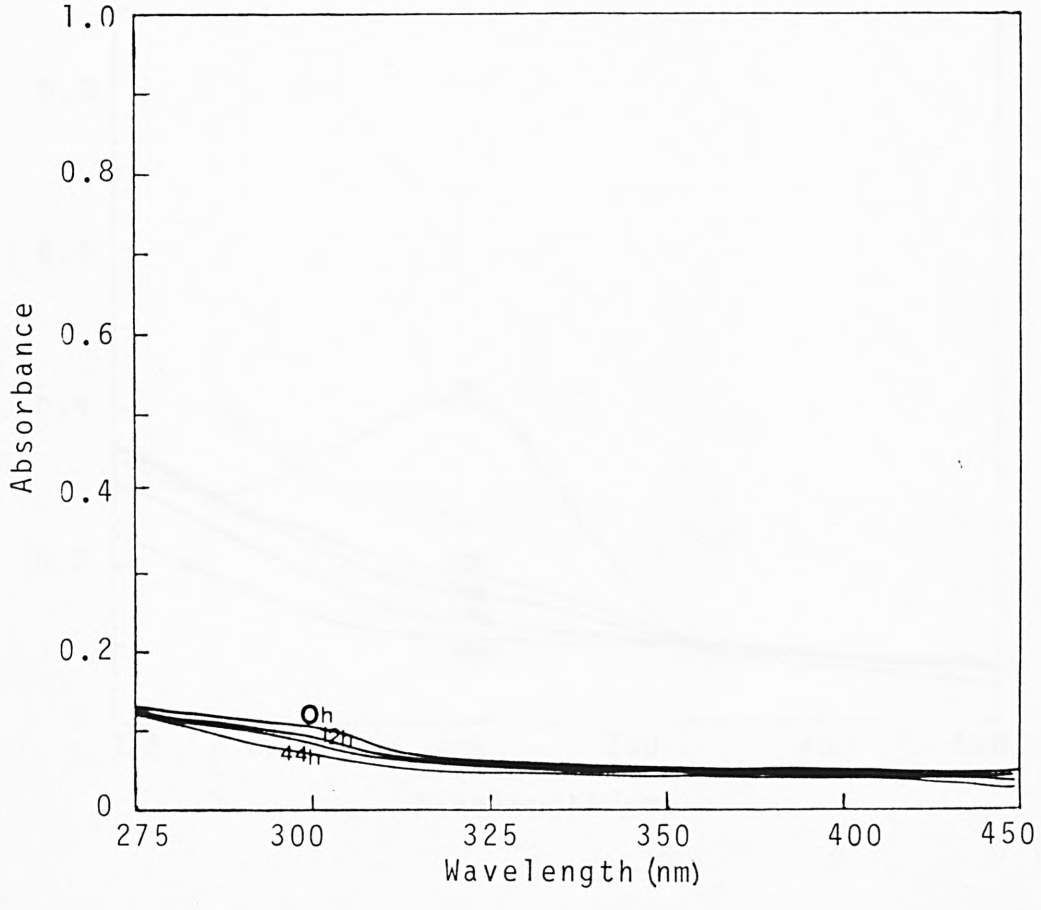


Fig. 3.42 U.v. spectrum for polypropylene containing 0.5 phr Zn(II) Salen

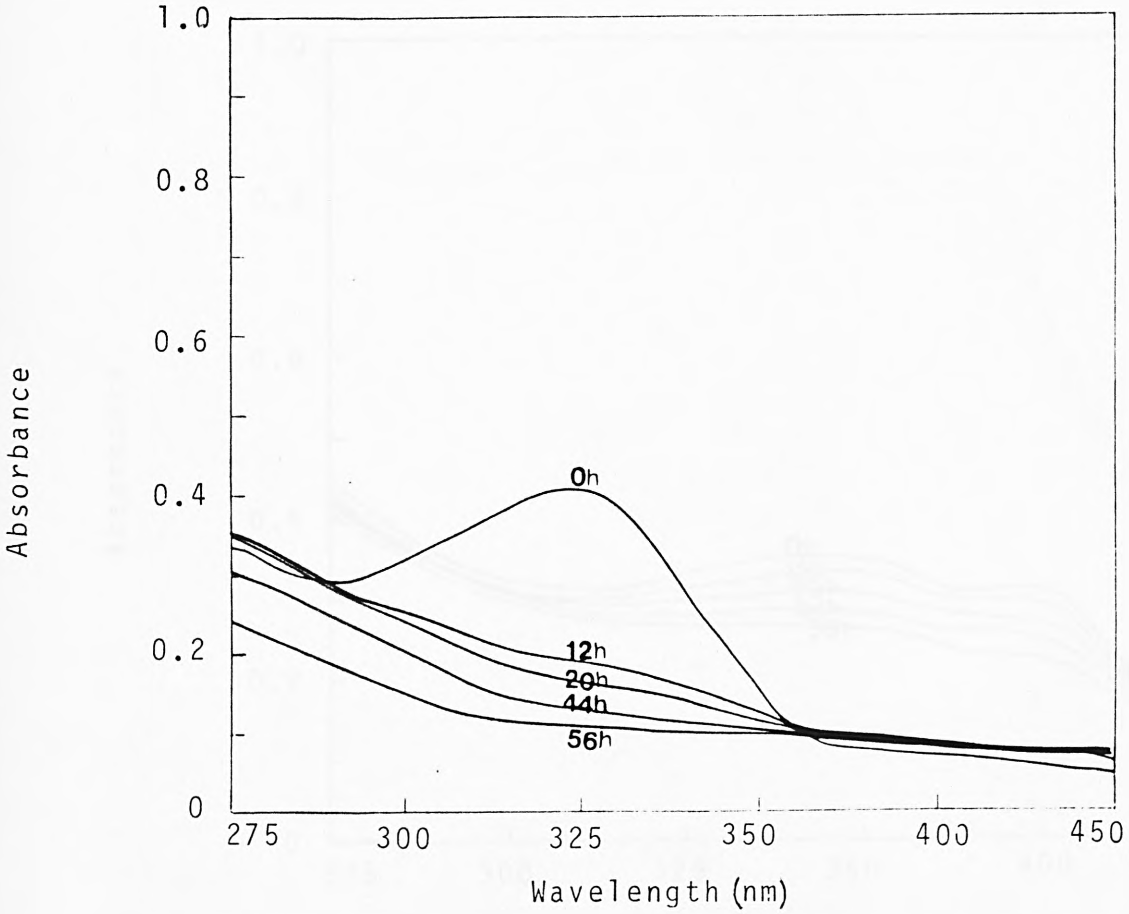


Fig. 3.43 U.v. spectrum for polypropylene containing 1 phr Zn(II) Salen

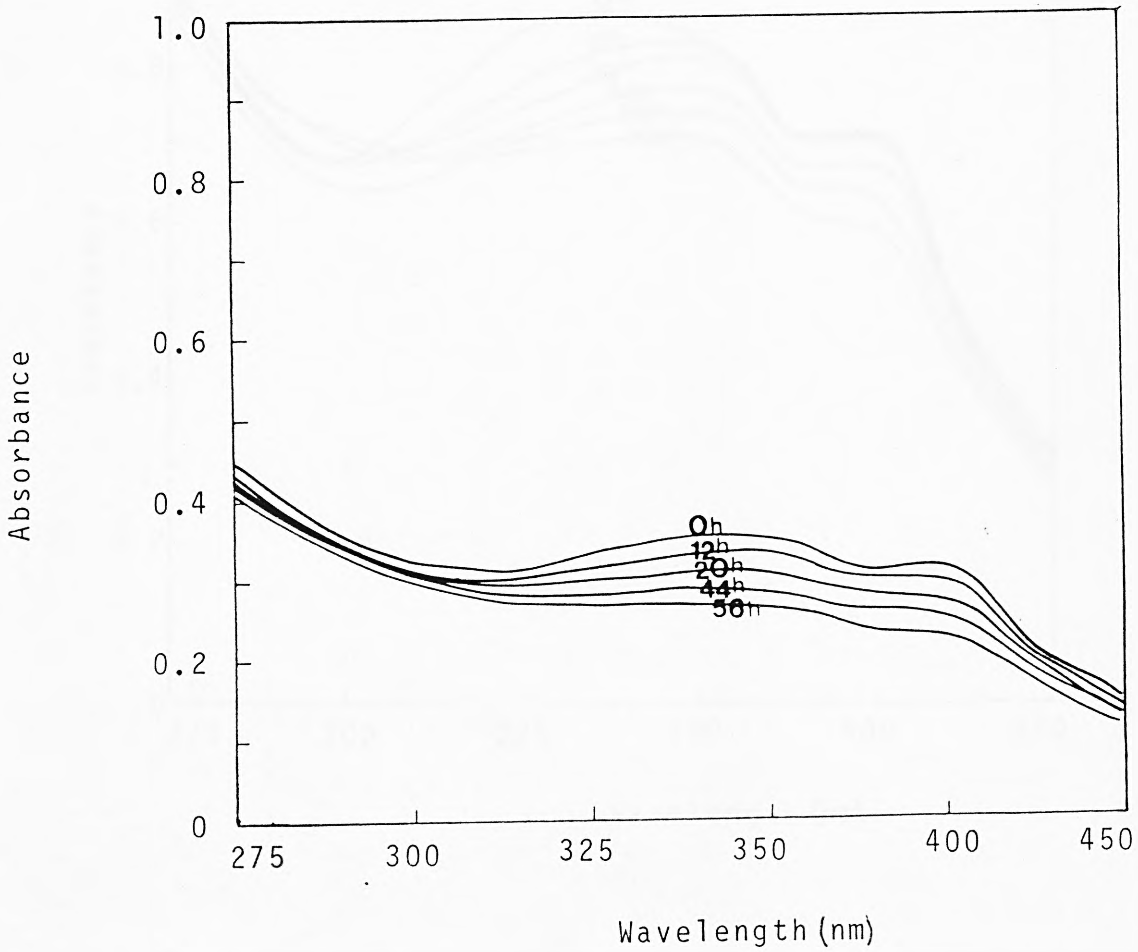


Fig. 3.44 U.v. spectrum for polypropylene containing 2 phr Zn(II) Salen

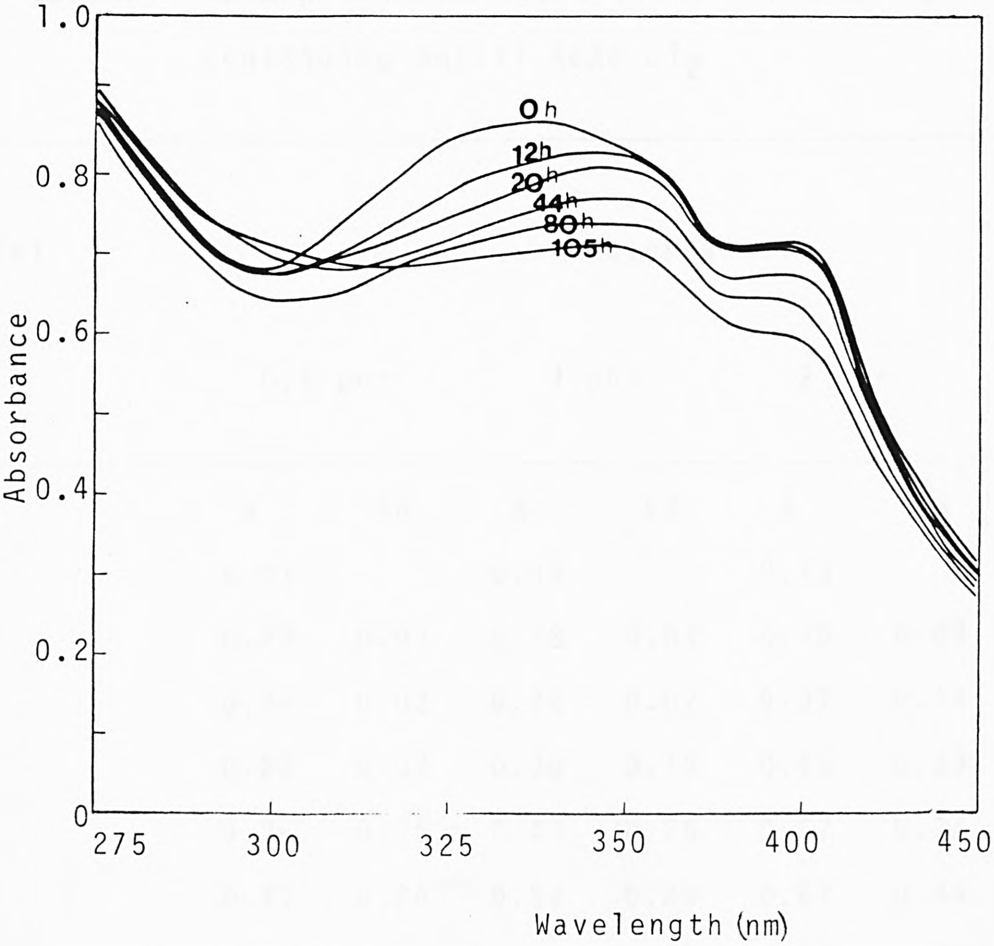


Table 3.35 The variation with u.v. irradation time of carbonyl absorption of polypropylene (1750 cm^{-1}) containing Sn(IV) AcAc Cl_2

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.21		0.15		0.23	
24	0.22	0.01	0.18	0.03	0.30	0.07
45	0.24	0.03	0.22	0.07	0.37	0.14
70	0.28	0.07	0.30	0.15	0.46	0.23
105	0.36	0.15	0.41	0.26	0.57	0.34
150	0.47	0.26	0.53	0.38	0.67	0.44
200	0.60	0.39	0.70	0.55	0.77	0.54
240	0.63	0.42	0.85	0.70	0.85	0.62

Table 3.36 The variation with u.v. irradation time of hydroperoxide absorption of polypropylene (3500 cm^{-1}) containing Sn(IV) AcAc Cl_2

time(h)	Absorbance					
	0.5 phr		1 phr		2 phr	
	A	δA	A	δA	A	δA
0	0.12		0.11		0.15	
24	0.12	0	0.12	0.01	0.17	0.02
45	0.14	0.02	0.14	0.03	0.19	0.04
70	0.15	0.03	0.16	0.05	0.22	0.07
105	0.17	0.05	0.19	0.08	0.26	0.11
150	0.20	0.08	0.23	0.12	0.28	0.13
200	0.25	0.13	0.29	0.18	0.33	0.16
240	0.26	0.14	0.41	0.30	0.44	0.29

for polypropylene samples containing 1 phr and 2 phr Zn(II) Salen respectively. Two absorption peaks at 400 nm and 350 nm, which are attributed to Zn(II) Salen, decreased slowly in size on u.v. irradiation.

Polypropylene containing 0.5 phr and 1 phr Zn(II) AcAc showed a weak absorption at 350 nm which disappeared with u.v. irradiation (Figs. 3.45 and 3.46). Fig. 3.47 shows the u.v. absorption for polypropylene containing 2 phr Zn(II) AcAc. It is observed that the absorption at 350 nm increased with u.v.irradiation. Figs. 3.48-3.50 show the u.v. absorption of polypropylene containing different concentrations of Sn(IV) AcAc Cl_2. There is a high absorption at 300 nm which completely disappeared after 44h u.v. irradiation.

3.3.4 Fluorescence measurements

Polypropylene on its own showed fluorescence emission at 332 nm. This fluorescence has been attributed to the presence of macroaldehydes (Charlesby et al.,1965). Fluorescence measurements were also made on polypropylene samples containing different metal chelates (1 phr) (Table 3.37). The results show a lack of correlation between the effect of these metal chelates on the photo-oxidation of polypropylene and as a fluorescence quencher.

Fig. 3.45 U.v. spectrum for polypropylene containing 0.5 phr Zn(II) AcAc

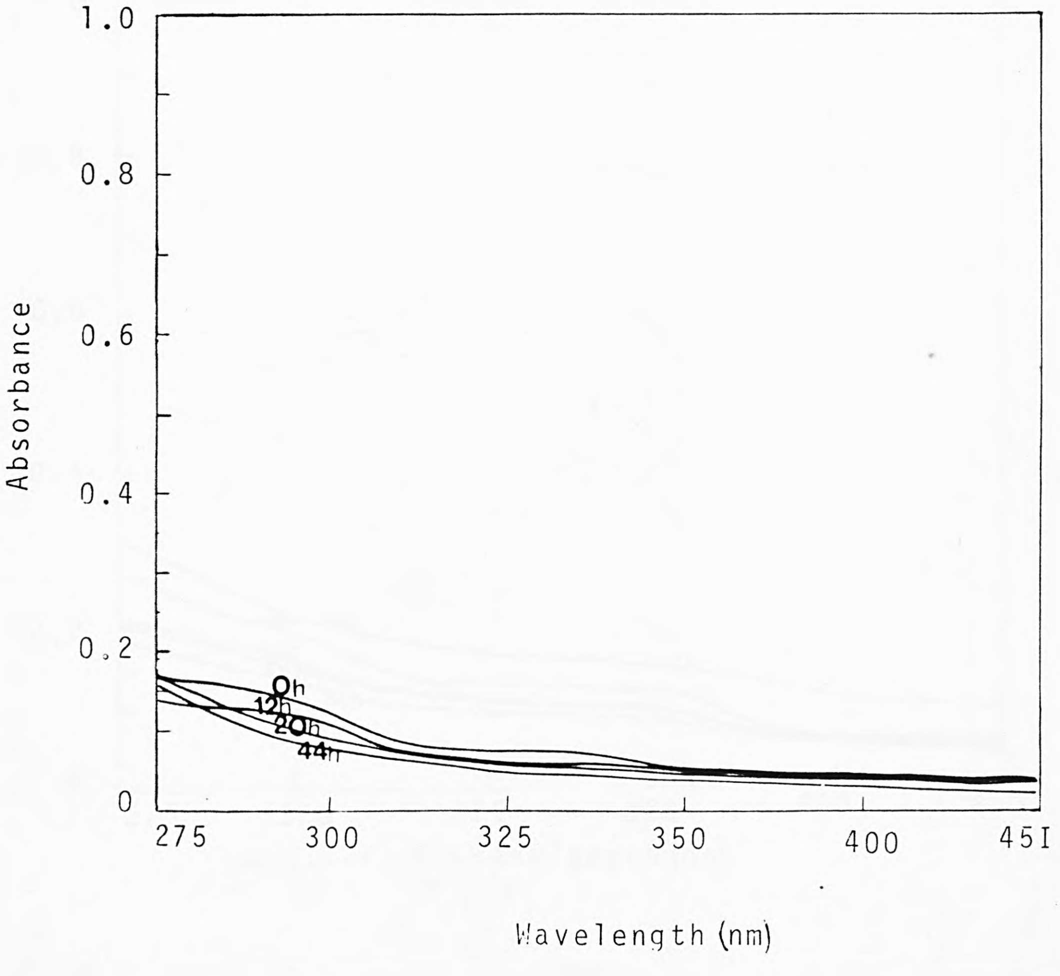


Fig. 3.46 U.v. spectrum for polypropylene containing 1 phr Zn(II) AcAc

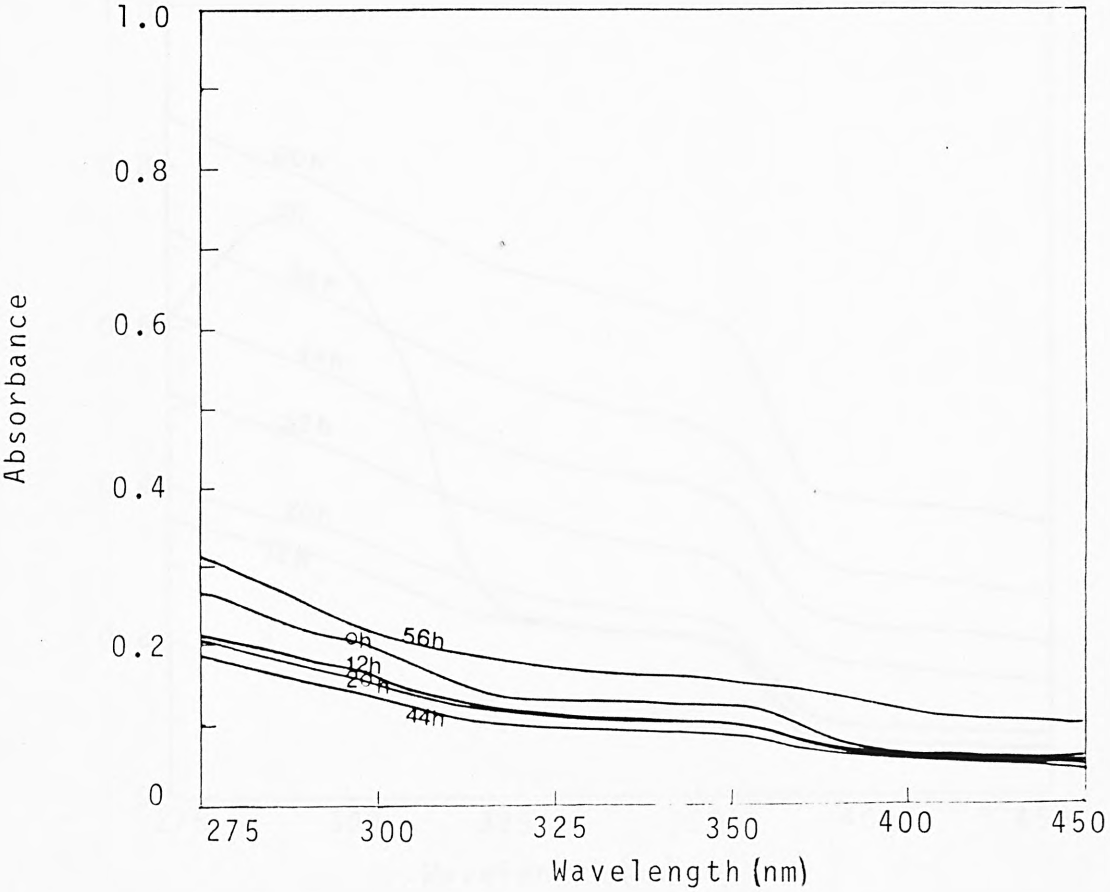


Fig. 3.47 U.v. spectrum for polypropylene containing 2 phr Zn(II) AcAc

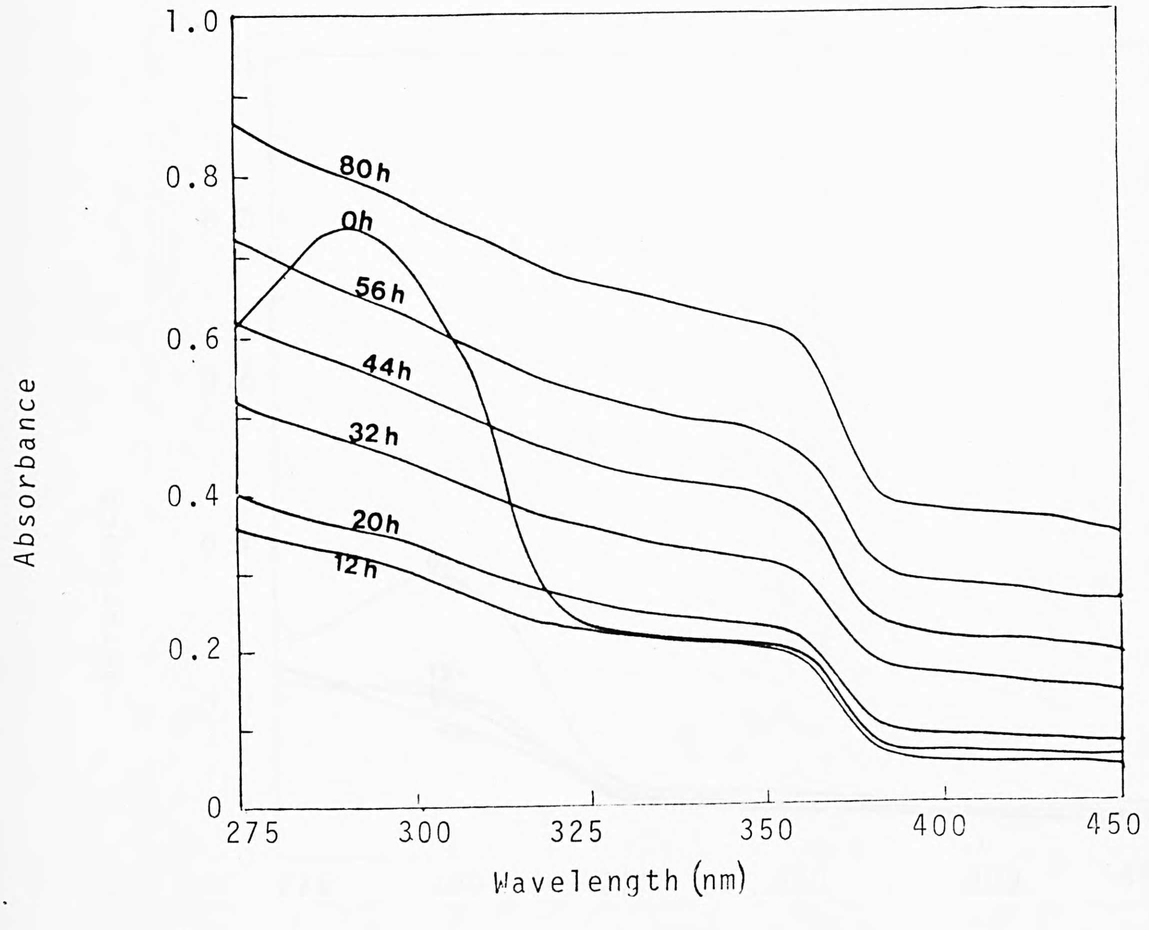


Fig. 3.48 U.v. spectrum for polypropylene containing 0.5 phr Sn(IV) AcAc Cl_2

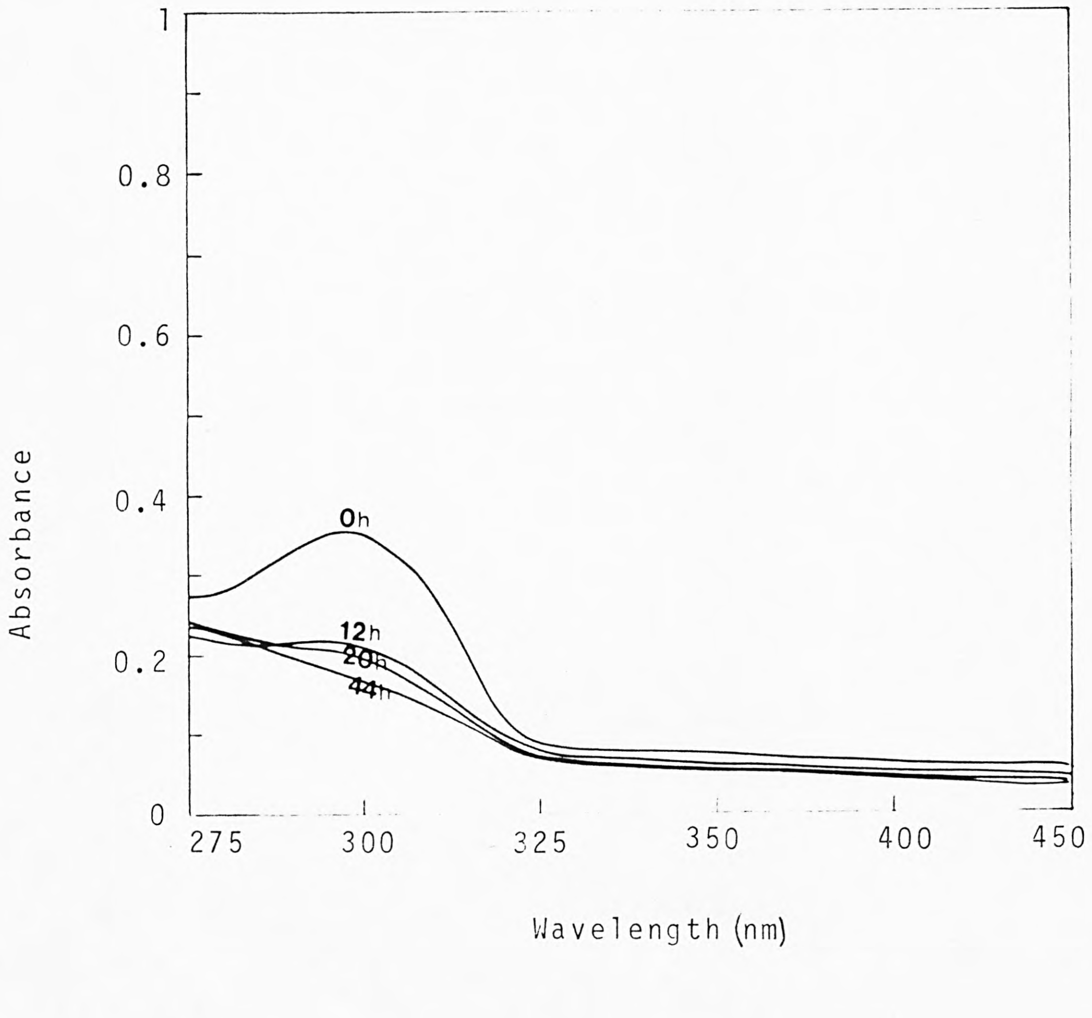


Fig. 3.49 U.v. spectrum for polypropylene contain- 1 phr Sn(IV) AcAc Cl_2

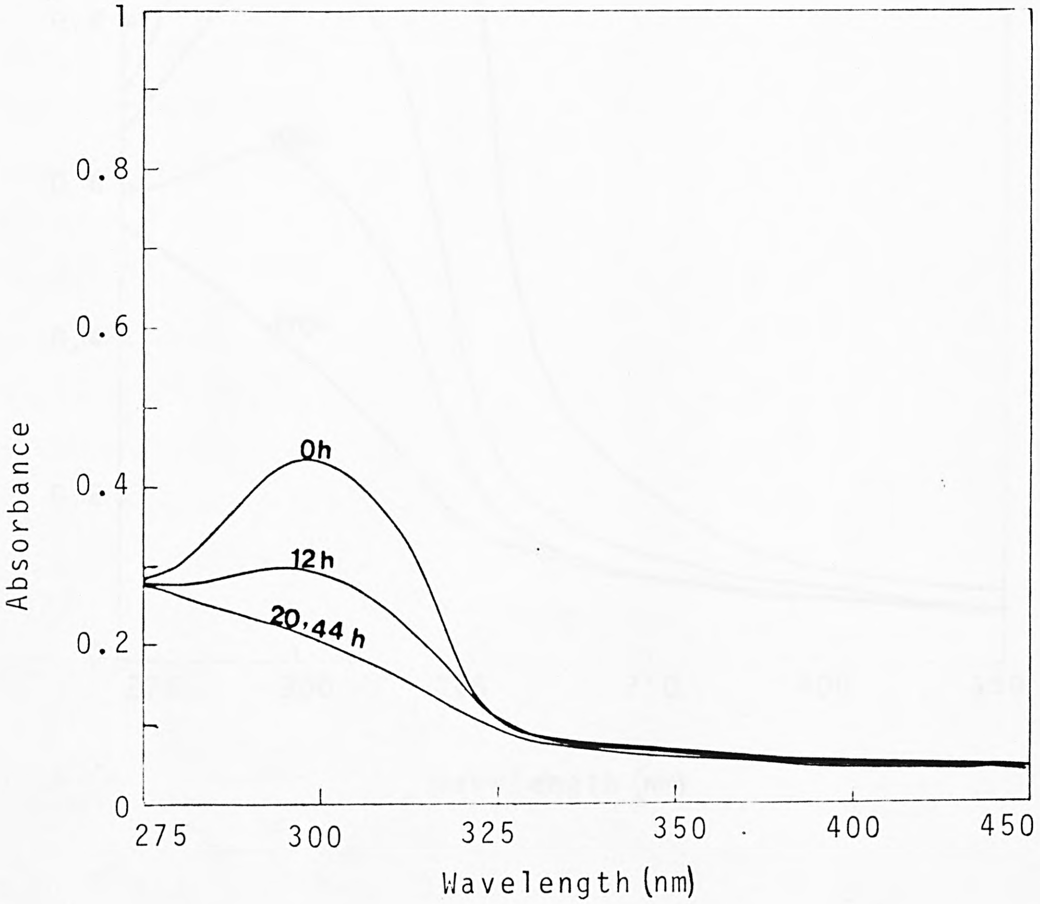


Fig. 3.50 U.v. spectrum for polypropylene containing 2 phr Sn(IV) AcAc Cl_2

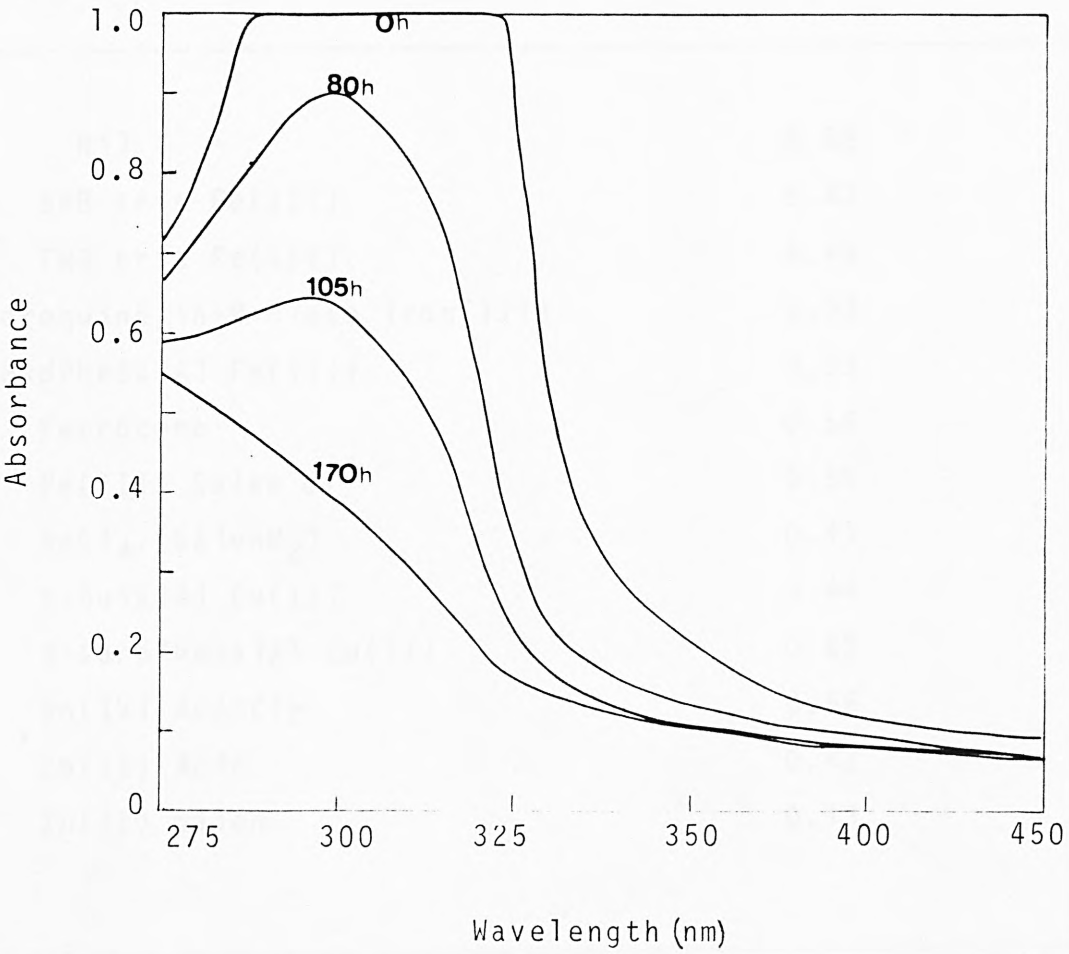


Table 3.37 The effects of different metal chelates on the fluorescence emission of polypropylene

Metal chelates	Emission at 332 nm
Nil	0.68
BHB tris Fe(III)	0.43
THB tris Fe(III)	0.49
Dichloroquinolin-8-olato iron(III)	0.32
2-HydPheSalAl Fe(III)	0.33
Ferrocene	0.58
Fe(III) Salen Cl	0.66
$SnCl_4.(SalenH_2)$	0.41
t-BuSalAl Cu(II)	0.44
3-CarbPheSalAl Cu(II)	0.62
Sn(IV) $AcAcCl_2$	0.56
Zn(II) AcAc	0.42
Zn(II) Salen	0.13

3.3.6 Chemical tests

A sample of polypropylene on its own was boiled in dimethyl sulphoxide solution in the presence of potassium iodide. Hydroperoxides were then tested by means of starch. There was no evidence for the presence of hydroperoxide inpurities in unirradiated polypropylene.

4 - Discussion

4. Discussion

4.1 Studies of polymer flammability

4.1.1 Introduction

Metal compounds are widely used both as flame retardants and as smoke suppressants for organic polymers (Cullis, 1981; Cullis and Hirschler, 1981) and their effectiveness in reducing polymer flammability is often synergistically enhanced by halogen compounds (Donaldson et al. 1983).

Thermoanalytical measurements can, in suitable circumstances, serve as useful indicators of the ease with which polymers burn and of the likely mode of action of flame-retardant additives. (Cullis and Hirschler, 1983). Although such measurements cannot accurately reflect the very complex reactions involved in the combustion of organic polymers, they can nevertheless be helfpul in the elucidation of some of the constituent processes. Mackay (1970) found that polymers with low char yields have oxygen indices close to or lower than the normal oxygen concentration in air while polymers with high char yields have high LOI values. Van Krevelen (1975, 1977) found a linear correlation between the LOI and the char residue weight (CR) at 850^{o}C:

$$LOI = 17.5 + 0.4\ CR.$$

Certain metal chelates are known to affect the initial stages of polymer degradation (Holcik et al., 1978). In some cases, too, they increase the amount of char formed from the polymer and this in turn can produced a significant decrease in polymer flammability (Cullis and Hirschler, 1984).

4.1.2 Polystyrene/metal chelates/Cereclor

Initial studies of the effects of several metal chelates on the flammability and smoke-producing tendency of polystyrene showed that none of the metal chelates used in this work, either in the absence or the presence of Cereclor, increased the LOI of the base polymer to any useful extent. However, many of the metal chelates were very effective in decreasing the amount of smoke formed. The mode of action of the additives studied is related to the mechanisms of formation of carbon from the polymers. Carbon can be formed in essentially two ways from an organic polymer: (a) by the stripping off in the condensed phase, of most or all of the non-carbonaceous material from the polymer backbone leaving a residual char, or (b) by chain-scission reactions in the condensed phase, leading to the formation of volatile low molecular weight compounds which can then undergo dehydrogenation reactions via polyacetylenes or polynuclear aromatic hydrocarbons in the gas phase to produce soot. Mechanism (b) would clearly lead to increased smoke formation compared with mechanism (a). The enhancement by metal chelates of char formation from polystyrene may also be associated with a decrease in smoke production; in other words, such metal chelates produce carbon by promoting chain stripping. Thus, the introduction of Cereclor increases the smoke produced from a polymeric system containing a metal chelate because its action is to enhance chain-scission reactions at the expense of chain-stripping reactions. Indeed this is the normal mechanism by which halogen compounds act when incorporated into polymers on their own. Such action, which results in decreased thermal stability of the polymer, can lead, in the case of some metal chelates, to increased amounts of volatile products and hence greater flammability of the polymeric system. When, on the other hand, the introduction of Cereclor reduces smoke production from a polymeric system containing a metal chelate, it appears that the combination of chelate and halogen compound does not promote chain-scission. In this case, the two additives must exert combined flame-retardant effectiveness, attributable to the larger amounts of carbonaceous residue formed when the polymer undergoes combustion.

4.1.3 Polypropylene/ferrocene/Cereclor

Flammability measurements have shown that the limiting oxygen index of polypropylene does not increase with increasing concentration of ferrocene. However, on addition of a small amount of Cereclor to polypropylene-ferrocene systems, the LOI increases rapidly. There thus appears to be some synergism between ferrocene and Cereclor. The optimum flame retardance was achieved with a high concentration of Cereclor (e.g. 20 phr) and a small concentration of ferrocene (e.g. 2 phr). This indicates that the interaction between additives cannot be related to the formation of the metal halide, as commonly occurs in combinations of metal oxides and halogen compounds. It appears therefore that ferrocene acts as a catalyst to enhance char formation. The thermoanalytical results show that, when ferrocene is heated on its own in air, it volatilises at very low temperatures(73-167^{o}C), and when a 3:7 mixture of ferrocene and Cereclor is heated, most of the ferrocene volatilises at these temperatures. However, it was also observed that the decomposition pattern of Cereclor is changed. This means that a small amount of ferrocene can catalyse the breakdown of Cereclor. It is thus obvious that there is little interaction between ferrocene and Cereclor and no formation of the metal halide. Ferrocene thus seems to act mainly as a catalyst for the breakdown of Cereclor.

When ferrocene is incorporated into polypropylene, a different pattern of thermal decomposition is observed and the ferrocene does not volatilise as expected. It is thus clear that some interaction occurs between ferrocene and polypropylene. (Two stages were observed for the breakdown of polypropylene and the amount of charwas increased). The temperature of maximum rate of breakdown of the polymer is nearly the same in the absence and presence of ferrocene, but with ferrocene present, the maximum rate decreases as does the weight lost during this stage. It is suggested therefore that ferrocene acts in the condensed phase by catalysing mainly the cleavage of bonds between the main polymer chain and the side chains; the former then cross-link so that the remaining structure contains a higher proportion of char. In support of this Ballistreri et al.(1982) have found that the addition of 1 and 5 phr finely-ground ferrocene to PVC suppressed smoke formation and increased the char yield compared with that from pure PVC over the temperature range 200-800^{o}C. Ferrocone, which is otherwise volatile, was retained by the polymer and apparently acted as a crosslinking catalyst during PVC combustion. Reactions (I) and (II) may explain the non-volatility of ferrocene (when incorporated into polypropylene) as well as its action as a pro-oxidant:

$$Fe^{+2} + RO_2H \rightleftharpoons [Fe\text{-}RO_2H]^{2+} \rightarrow Fe^{+3} + RO^{\cdot} + HO^{-} \qquad (I)$$

$$Fe^{+3} + RO_2H \rightleftharpoons [Fe\text{-}RO_2H]^{3+} \rightarrow Fe^{+2} + RO_2^{\cdot} + H^{+} \qquad (II)$$

It is known (Cullis and Hirschler 1984) that Cereclor can affect the thermal behaviour of polypropylene by dehydrogenating larger proportions of the side chain, i.e. the methyl groups attached to the tertiary carbon atoms in polypropylene, which subsequently undergo oxidation. These oxidised side chains then appear to crosslink to leave a carbon skeleton and this increases the extent of char formation.

The addition of Cereclor to polypropylene-ferrocene systems changes the pattern of thermal decomposition of polypropylene. The maximum rate of breakdown of polypropylene decreases compared with that for polypropylene samples containing either ferrocene or Cereclor on their own and the amount of char formed is increased. Thus, ferrocene enhances the action of Cereclor in decreasing volatile product formation from polypropylene and increases production of carbon, which preserves the structural integrity of the polymer (Table 3.17).

4.1.4 Polypropylene/Bis hydroxo hexabenzoate tris iron(III) benzoate/Cereclor

Flammability measurements show that BHB tris Fe(III), on its own, does not increase the LOI of polypropylene by more than 2 units. The addition of small amounts of Cereclor to a prolypropylene-BHB tris Fe(III) system increases the LOI by over 10 units. Optimum flame retardance is achieved with concentrationsof Cereclor between 10 and 15 wt% and of BHB tris Fe(III) between 2 and 3 wt%. It appears therefore that BHB tris Fe(III) acts as a catalyst to enhance char formation.

The thermoanalytical results show that BHB tris Fe(III), on its own, is not a stable compound. It starts to decompose at a very low temperature (51°C), and it decomposes in four stages. Incorporation of BHB tris Fe(III) into polypropylene completely changes the pattern of thermal behaviour of polypropylene. Three stages are observed corresponding to the breakdown of polypropylene and the amount of char increases by 6.84 wt%. The weight loss during the breakdown of polypropylene, in the presence of BHB tris Fe(III), is 79.07 wt% and the temperature of the maximum rate of polypropylene breakdown (290°C) is the same in the presence and absence of the iron compound. However, the maximum rate of polymer breakdown decreases considerably in the presence of BHB tris Fe(III). It appears therefore that

BHB tris Fe(III) acts in the condensed phase mainly by cleavage of the bonds between the side chain and the polymer main chain, and by formation of a large amount of char as a result of crosslinking. The addition of Cereclor to a polypropylene-BHB tris Fe(III) mixture decreases the maximum rate and the temperature of maximum rate of polypropylene breakdown and also increases the amount of char. BHB tris Fe(III) thus seems to enhance the action of Cereclor in decreasing the amount of volatile material and increasing the extent of char formation. (Table 3.20).

4.1.5 Polypropylene/zinc acetyl acetonate/Cereclor

Flammability measurements show that Zn(II) AcAc on its own has no flame-retardant action on polypropylene, but on addition of relatively small amounts of Cereclor (which also by itself has little flame-retardant effect) the LOI increases rapidly. Optimum flame-retardance is achieved with concentrations of Cereclor (e.g. 20 phr) which are high in relation to those of Zn(II) AcAc (e.g. 2 phr). This suggests that the synergism between Zn(II) AcAc and Cereclor is not related to the formation of $ZnCl_2$ as commonly only occurs with systems containing ZnO and Cereclor. On the other hand, Zn(II) AcAc probably acts in the condensed phase by changing the pattern of thermal decomposition of polypropylene.

Thermoanalytical results show that, when a 2:5 mixture of Zn(II) AcAc and Cereclor is heated in air, Zn(II) AcAc affects, to a great extent, the thermal decomposition of Cereclor. Zn(II) AcAc catalyses the decomposition of Cereclor and enhances the formation of char (Table 3.21).

Incorporation of Zn(II) AcAc into polypropylene promotes char formation and decreases the maximum rate of polypropylene breakdown. It seems then that Zn(II) AcAc acts in the condensed phase by promoting cleavage of the bonds between the side chain and the polymer main chain. Thus char formation is increased as a result of the crosslinking which eventually occurs. This result is consistent with that of Cullis and Hirschler (1984). When the concentration of Cereclor is increased, char formation from polypropylene-Zn(II) AcAc systems increases considerably. This suggests that when Zn(II) AcAc reacts with Cereclor a protective charry layer is found on the surface of the polypropylene (Table 3.23).

4.1.6 Polypropylene/tin(IV) bis acetyl acetonate dichloride/Cereclor

Flammability measurements show that Sn(IV) AcAc Cl_2, on its own, has little effect on the flame retardance of polypropylene. On addition of relatively small amounts of Cereclor, the LOI of polypropylene increases. The optimum flame-retardance is achieved with relatively small concentrations of Cereclor (6-14 wt%) and also small concentrations of Sn(IV) AcAc Cl_2 (2.2-3.8 wt%). This suggests that the interaction between the additives involves the formation of the corresponding metal halide as commonly occurs with combinations of metal oxides and halogen compounds.

Thermoanalytical results show that, when Sn(IV) AcAc Cl_2 is heated in air, 64.25 wt% is lost. This weight loss is attributed to the thermal decomposition of $Sn(C_5H_7O_2)Cl_2$ to SnO rather than SnO_2 (Table 3.24); but when a 3:7 mixture of Sn(IV) AcAc Cl_2 and Cereclor is heated in air, 96.36 wt% is volatilised which suggests that $SnCl_4$ is formed rather than $SnCl_2$. It is therefore suggested that the reactions occurring are:

$$Sn((C_5H_7O_2)\ Cl_2 \longrightarrow SnO_2$$

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

Sn(IV) AcAc Cl_2 may also act in the gas phase by interfering with the flame reactions. When Sn(IV) AcAc Cl_2 is incorporated into polypropylene, two stages are observed corresponding to the breakdown of the polymer. The tin chelate destabilises polypropylene which thus undergoes thermal reactions at lower temperatures and yields more char. It is therefore suggested that Sn(IV) AcAc Cl_2 acts mainly in the condensed phase and probably causes increased main chain scission at positions very distant from one another so that volatilisation is decreased and char formation is increased as a consequence of the crosslinking which eventually occurs.

In the case of a polypropylene sample containing 3 phr Sn(IV) AcAc Cl_2 and 7 phr Cereclor, the polymer is stabilised and the temperature of breakdown of the polymer and the temperature of maximum rate of breakdown are both raised. The amount of char formed is also increased. Since chlorinated additives can act both in the condensed phase and in the gas phase, Sn(IV) AcAc Cl_2 is likely to exhibit its effect via two different mechanisms. Firstly Sn(IV) AcAc Cl_2 decomposes to SnO_2 which reacts with Cereclor in the condensed phase and together they produce a protective charry layer on the surface of polypropylene. Secondly tin (IV) chloride volatilises and may exert its inhibiting action in the gas phase. However the present results suggest that Sn(IV) AcAc Cl_2 acts mainly in the condensed phase.

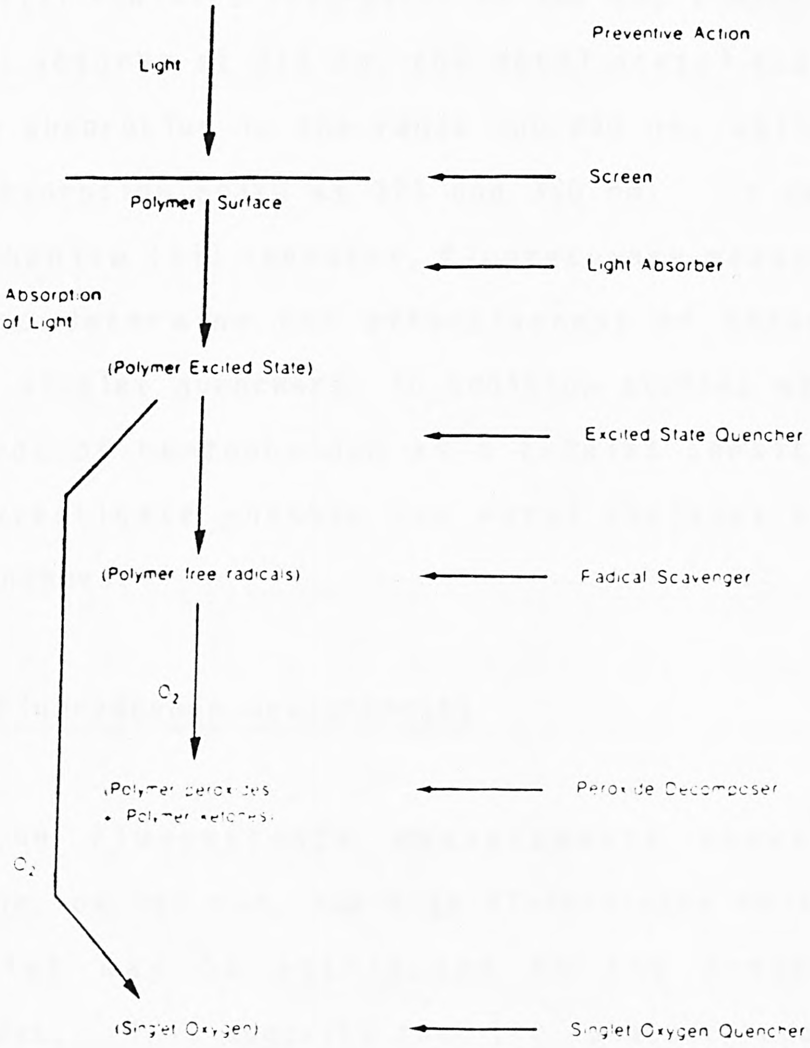
4.2 Studies of the photostability of polypropylene

4.2.1 General

There are already many commercially available additives which are reputed to improve the photostability of organic polymers. A u.v. stabilising additive can inhibit the photo-oxidative deterioration of the solid polymer by preventing either the initiation of the degradation process or the propagation of radical chains. Photo initiation can be prevented or reduced as follows: (i) Screening, as a results of the additive absorbing in the region of the spectrum which causes damage to the polymer. (ii) Deactivation of the excited chromophores in the polymer by the additive; this may involve singlet or triplet states of these chromophores and the excitation energy can be lost by re-emission at longer wavelengths from the excited additive or by vibrational deactivation. (iii) Reaction with radicals or other species generated in the photo initiation step (Fig. 4.1).

The wavelengths of the ultra-violet part of the sunlight that reaches the surface of the earth are 400-300 nm and the mercury lamp, which is used in this work, emits ultra-violet radiation at wavelengths longer than 290 nm. In the present work, polypropylene, on its own, shows a u.v. absorption at 300 nm. Thus, for mechanism (i), the important region of the spectrum is 400-290 nm.

Fig. 4.1 Scheme showing the points at which photodegradation may be interrupted



Some metal chelates used in this work showed strong absorption in the u.v. spectrum in this region (400-290 nm) so that they would be expected to act as a screen for ultraviolet radiation. For example, dichloroquinolin-8-olato iron(III) exhibits absorption at 350 nm, 2-HydPheSalAl-di-Me-SN(IV) absorbs at 315 nm, the metal acetyl acetonates show strong absorption in the range 300-290 nm, while Zn(II) salen has absorption peaks at 375 and 350 nm. To determine whether mechanism (ii) operates, fluorescence measurements were made to determine the effectiveness of these metal chelates as singlet quenchers; in addition studies were made of the effect of benzophenone as a triplet sensitizer in order to investigate whether the metal chelates acted as triplet quenchers.

4.2.2 Fluorescence measurements

The fluorescence measurements showed that polypropylene, on its own, exhibits fluorescence emission at 332 nm which may be attributed to the presence of macroaldehydes. This suggests that the photodegradation of polypropylene occurs according to the mechanism suggested by Neiman (1965):

$$R\text{-}CH_2\text{-}CH_2\text{-}CHO + h\nu \begin{array}{l} \nearrow R'\text{-}CH = CH_2 + CH_3CHO \\ \searrow R\text{-}CH_2\text{-}CH_2^{\bullet} \quad + {}^{\circ}CHO \end{array}$$

and that the oxidative degradation of the polymer then proceeds by the well-known Bolland-Gee mechanisms:

$$R\text{-}CH_2\text{-}C\dot{H}_2 + O_2 \longrightarrow R\text{-}CH_2\text{-}CH_2OO^{\bullet}$$

$$R\text{-}CH_2\text{-}CH_2OO^{\bullet} + R''H \longrightarrow R\text{-}CH_2\text{-}CH_2OOH + R''$$

Further degradation can be initiated by photodecomposition of the hydroperoxides formed:

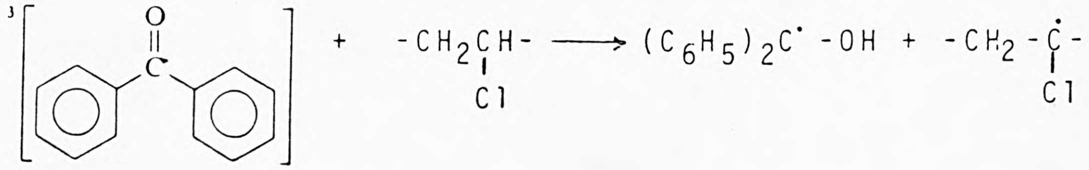
$$R\text{-}CH_2\text{-}CH_2OOH + h\nu \longrightarrow R\text{-}CH_2CH_2O^{\bullet} + {}^{\bullet}OH$$

Fluorescence spectra of polypropylene containing different metal chelates were measured and it was expected that those metal chelates which acted as sensitizers for polypropylene oxidation would not behave as singlet quenchers whereas those which behaved as photostabilisers would function in this way. However, the results showed that Zn(II) Salen, which is an excellent photostabiliser for polypropylene, is a good singlet quencher (i.e. a quencher of the fluorescence emission of polypropylene) while the other metal chelates, both sensitizers and stabilisers, did significantly quench the fluorescence emission. It therefore seems that, if triplet states are not involved, Zn(II) AcAc and Sn(IV) AcAc Cl_2 cannot associate with the chromophore (aldehydic group). This means that these two compounds do not interfere with a single photo-initiation step while Zn(II) Salen may act as a singlet quencher.

4.2.3 Experiments involving benzophenone

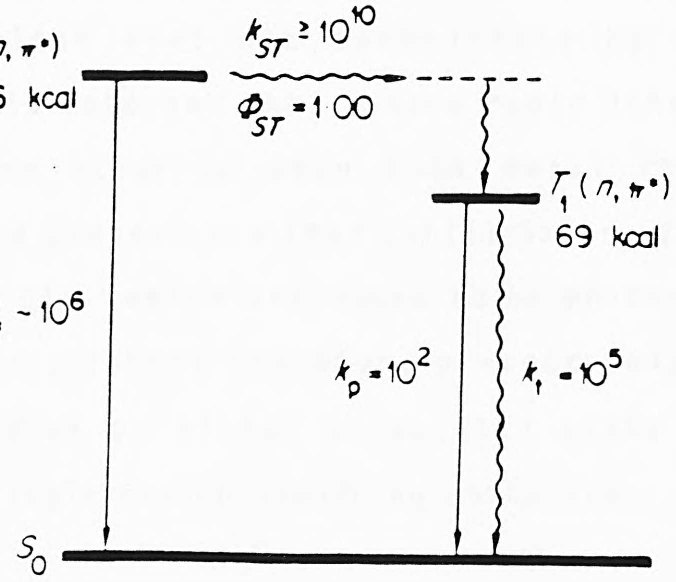
Tables 3.27 and 3.28 and Figs. 3.25 and 3.26 show the build-up of alkyl carbonyl absorption (1750 cm^{-1}) with irradiation time for a polypropylene sample, on its own, and in the presence of 0.5 phr benzophenone. This has been shown by Carlsson and Wiles (1970) to correlate with other measurements of polypropylene degradation.

Benzophenone is a good triplet sensitizer. Its photochemically reactive state is the first triplet excited state (T_1) (Buettner et al., 1971; Schuster et al., 1972). Fig. 4.2 shows the energy state diagram for benzophenone. Owen and Bailey (1972) reported the benzophenone photosensitized degradation of poly(vinyl chloride) under vacuum and in the presence of oxygen. An initial rapid increase in absorption in the 340 nm region strongly implies the formation of ketyl radicals in the initiation process, as a result of the abstraction of hydrogen from poly(vinyl chloride) by excited benzophenone in the triplet state:

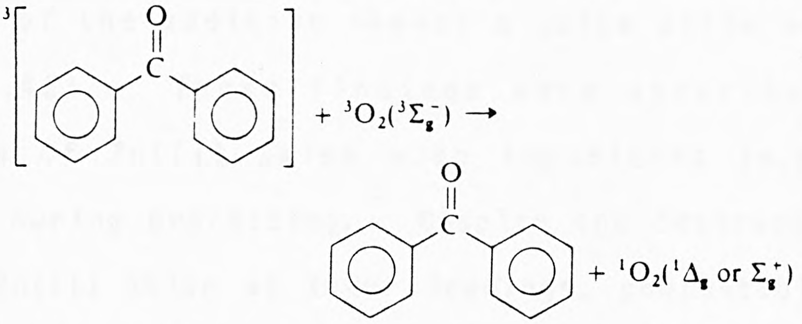


$$+ \quad -CH_2\underset{Cl}{CH}- \longrightarrow (C_6H_5)_2C^{\cdot}-OH + -CH_2-\underset{Cl}{\dot{C}}-$$

Fig. 4.2 Energy state diagram for benzophenone in benzene solution at 25°



Another reaction was proposed in which singlet oxygen can be formed in a reaction between the excited triplet state of benzophenone and molecular oxygen (Trozzolo, 1968):



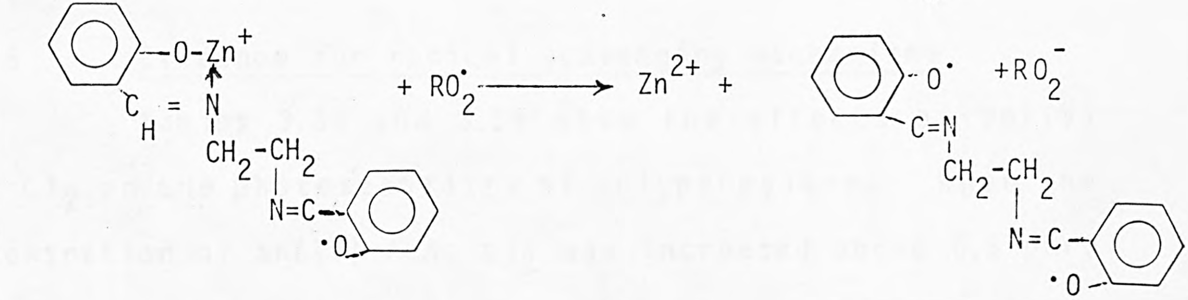
The results obtained in this work are not consistent with this suggestion. Benzophenone, in this work, is acting as a photostabiliser for polypropylene. This strongly suggests that polypropylene does not deteriorate by a triplet mechanism. It is observed that a more rapid deterioration of polypropylene occurred when both metal chelate and benzophenone were present and that Zn(II) Salen, Zn(II) AcAc and Sn(IV) AcAc Cl_2, which are found to be photostabilisers for polypropylene, cannot therefore protect polypropylene against degradation by either an excited state quenching mechanism or a single oxygen quenching mechanism.

4.2.4 Ultraviolet absorption measurements

The results of ultraviolet absorption of polypropylene containing different concentrations of Zn(II) Salen showed.a slow decrease in the absorption of Zn(II) Salen with increasing u.v. irradiation time. This suggests that Zn(II) Salen is not a good u.v. absorber.

The intensity of the absorption spectrum of a polypropylene sample containing 1 phr Zn(II) Salen was relatively low (Fig. 3.43). Moreover the film containing 0.5 phr of the additive showed a quite different spectrum (Fig. 3.42). These findings were attrributed to the reaction of Zn(II) Salen with impurities (e.g. aldehyde groups) during processing. Despite the destruction of some of the Zn(II) Salen at lower loadings, photostabilisation is still observed suggesting that this reaction with impurities either removes photoactive centres or forms photostabilising species. This is also consistent with the longer induction periods observed for polypropylene containing Zn(II) Salen.

The above results confirm that Zn(II)Salen may act as a singlet quencher. It is proposed that Zn(II) Salen can also act as a photostabiliser for polypropylene by a radical scavenging mechanism and the following is suggested:



The radicals formed from the ligand of the chelate would be strongly resonance-stabilised and therefore unlikely to propagate radical chains. Tables 3.33 and 3.34 show the effects of Zn(II) AcAc on the photostabilisation of the polymer. For samples containing 0.5 and 1 phr Zn(II) AcAc, the metal chelates did not significantly protect polypropylene while for polymer samples containing 2 phr Zn(II) AcAc, excellent protection against u.v. irradation is achieved. The u.v. absorption results for polypropylene containing Zn(II) AcAc are consistent with the i.r. results. For polypropylene samples containing 0.5 phr and 1 phr Zn(II) AcAc there was a decrease in the u.v. absorption of Zn(II) AcAc with irradiation time, followed by decomposition of the chelate after 56h irradiation. For samples containing 2 phr Zn(II) AcAc, there was an increase in u.v. absorption at 350 nm with increasing time of irradiation and the polypropylene film became milky white. In other words, some light scattering occurs. This suggests that Zn(II) AcAc may act as a u.v. screen after initial photochemical conversion to another species which is insoluble in polypropylene at higher concentrations resulting in inhomogenities which can scatter light.

4.2.5 Evidence for radical scavenging mechanisms

Tables 3.35 and 3.36 show the effects of Sn(IV) AcAc Cl_2 on the photostability of polypropylene. When the concentration of Sn(IV) AcAc Cl_2 was increased above 0.5 phr, the additive acted as a photosensitizer for polypropylene.

This is the opposite effect to that known as "Catalyst-inhibition conversion" which has been observed with certain metal chelates in thermal oxidation processes (Betts and Uri, 1966, 1698; Uri, 1967; Copping and Uri, 1968)).

The results of u.v. absorption show a decrease in the absorption of Sn(IV) AcAc Cl_2 within 12h irradiation, leading to its complete disappearance after 44h. It therefore seems that Sn(IV) AcAc Cl_2 cannot act as a u.v. absorber. The tin compound may thus act as a photostabiliser by a radical scavenging mechanism. This mechanism is consistent with the results of thermoanalytical measurements on polypropylene samples containing Sn(IV) AcAc Cl_2. There was no absorption of oxygen by polypropylene in the presence of the tin chelate which suggests that it reacts with the radicals responsible for the oxygen uptake. Alternatively, oxygen uptake may result from unsaturation, so that the chelate could react with olefins.

Burchill et al.(1976) proposed that many products resulting from radical scavenging processes may be photosensitizers. Thus Sn(IV) AcAc Cl_2, which acts as a radical scavenger, may produce compounds which are photosensitizers for polypropylene, although this behaviour was observed only at high concentrations of the metal chelate. Alternatively, other mechanisms are possible which could also lead to the observed change in stabilising activity as the concentration of the tin complex is increased. Thus, three mechanisms may be considered, and are shown schematically below (P = polymer, C = tin complex, R = radicals or other reactive species derived from the polymer, S = species derived from C):

(a) $$C + R \longrightarrow P + S$$

$$S + P \xrightarrow{h\nu} R + S \quad \text{or} \quad R + \text{other products}$$

$$R \longrightarrow \text{oxidised products}$$

(b) $$C + P \xrightarrow{h\nu} R + S$$

$$R + S \longrightarrow P + \text{other products}$$

$$R \longrightarrow \text{oxidised products}$$

(c) $$C + R \longrightarrow P + \text{other products}$$

$$C + C \xrightarrow{h\nu} S$$

$$S + P \xrightarrow{h\nu} R + S \quad \text{or} \quad R + \text{other products}$$

$$R \longrightarrow \text{oxidised products}$$

Here, (a) is the mechanism already outlined. In mechanism (b), the complex acts as a sensitiser, but produces a stabiliser during reaction, whereas in mechanism (c) the photosensitiser is generated by a bimolecular process. These mechanisms may be compared in terms of the rate of disappearance of complex C and the rate of formation of oxidised products, both considered as functions of the concentration of complex.

In mechanism (a), disappearance of C would initially be first order with respect to C, but would increase as more S is formed so that the rate of formation of R increases. On the other hand, in (b), the order of reaction will be less than one, since it will depend on the rate of light absorption by the complex, and this will only vary significantly with concentration for absorbance less than ca. 0.5. In mechanism (c), the order will be one, or slightly greater, depending on the relative importance of the first two reactions. (The second will have an order between one and two, depending on the overall absorbance level).

The variation of oxidised product formation with time and concentration of C will also differ: in mechanism (a), all concentrations should show a slow increase in product formation at short times, becoming much more rapid as C is consumed and S is produced. The induction period should be similar at each concentration (assuming pseudo first order loss of C), but high loadings of C should show better stabilisation initially, and greater acceleration after the induction period. Mechanism (b), on the other hand, would lead to initial formation of oxidised products at a greater rate than later in the reaction, and the rate would slow down first at the lowest concentration of C. Mechanisms (c) is similar to mechanism (a) in that initial stabilisation is expected. However, the second step, involving two molecules of C, would lead to rather more rapid formation of S at higher concentrations than in mechanims (a), so that the induction periods should decrease as the initial concentration of C is increased.

Comparison of these predictions with the u.v. spectra (Figs. 3.48-3.50) and the graphs of product formation with time (Figs. 3.39-3.40) shows that the predictions of mechanism (c) are closest to the observed results. Thus the rate of disappearance of C increases as the concentration of C increases. It is difficult to establish a precise order since the absorbance of the 2 phr sample was too high to measure accurately, and the induction period decreases from ca. 40 hr at 0.5 phr to ca. 30 hr at 1 phr to less than 20 hr at 2 phr.

4.3 Conclusions

Of the 20 or so metal chelates investigated, at least four have been shown to have useful flame-retardant properties but usually only when they are used in conjunction with rather large amounts of Cereclor. The thermoanalytical results show clearly that the four most promising compounds all function as flame retardants mainly in the condensed phase and that their predominant mode of action is to enhance the production of a solid charry residue and thus decrease the extent of formation of volatile products.

The situation with regard to the photostabilising action of the metal chelates is more complex. In general the transition metal chelates in which there is the possibility of one-electron redox action, are not effective photostabilisers. Indeed some of these compounds tend to act as photosensitisers. Of the 15 or so chelates investigated, three appear to be possible useful photostabilisers. However these three compounds seem to act by quite different mechanisms. Zn(II) Salen acts partly as a singlet quencher and partly as a radical scavenger. Zn(II) AcAc seems to function entirely by a light-scattering mechanism and Sn(IV) AcAc Cl_2, which can display both photostabilising and photosensitising properties according to its concentration in the polymer, acts primarily as a radical scavenger.

Referring back to the original purpose of this work, however, both Zn(II AcAc and to a lesser extent Sn(IV) AcAc Cl_2 can, under appropriate conditions, exhibit useful properties both as flame-retardants and as photostabilisers. A valuable feature of both these compounds is that they can exert useful effects at relatively low loadings.

5 - Appendix

```
10 common x(100,15),xt(15,100),xtx(15,15),y(100),xty(15),beta(15),
15 & cc(3,3),yc(100),ec(100)
20 dimension vbl(2,15),ap(100,10),xc(10,7),xv(3,3),
25 & vtitle(9),AK(7,16)
30 INTEGER VTL(15),VTM(15)
35 character*30 title,vtitle,vbl*60
40 data xc/1.,2*0.,2*.5,0.,.333333,.666667,
50      & 2*0.166665,0.000000,1.000000,0.000000,0.500000,0.000000,0.500000,
60      & 0.333333,0.166666,0.666666,0.166666,2*0.000000,1.000000,0.000000,
70      & 2*0.500000,0.333333,2*0.166666,0.666666,3*0.000000,0.250000,
80      & 2*0.000000,3*0.111111,0.027778,4*0.000000,0.250000,0.000000,
90      & 2*0.111111,0.027778,0.111111,5*0.000000,0.250000,0.111111,
100      & 0.027778,2*0.111111,6*0.000000,0.037037,3*0.018518/
105 &,vbl/'xo1 = ',' ','xo2 = ',' ','xo3 = ',' ','xo4 = ','xo1 * xo2','xo5 = ',
106 &'xo1 * xo3','xo6 = ','xo2 * xo3','xo7 = ','xo1 * xo2 * xo3',
107 &'xo8 = ','X01*X02(X01-X02)','X09=','X03*X01(X03-X01)','X010=
108 &','X02*X03(X02-X03)','X011 =','X01*X02(X01**X02**2-3*X01*X02)'
109 &,'X012=','X01*X03(X01**2+X03**2-3*X01*X03)','X013=','X02*X03
110 & (X02**2+X03**2-3*X02*X03)','X014=','X01*(X02**2)*X03',
111 &'X015=','X01*X02*(X03**2)'/
119 41 FORMAT(/30X,/'MATRICE X'/30X,9('-')///13X,'X01',9X,'X02',9X,'X03',
120      & 9X,'X04',9X,'X05',9X,'X06'//(10X,6(F3.6,4X)))
130     72 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,3(E12.6,1X)//)
140     61 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15X,'X01',10X,'X02',10X,
150      & 'X03',10X,'X04',10X,'X05',10X,'X05'//(10X,6(E12.6,1X)))
160     71 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,6(E12.6,1X)//)
170     81 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
180      & 10X,'X03',10X,'X04',10X,'X05',10X,'X06'//(10X,6(E12.6,1X)))
190     91 FORMAT(1X,29X,'MODEL POLYNOMIAL OF DEGREE 2'///31X,'MIXTURE OF 3
200      & CONSTITUENTS'/31X,'SPECIFICATION OF VARIABLES :'/)
210 42 FORMAT(/30X,'Input Data'/10X,'No.',7X,'LOI',10X,
215      &'xo1',11x,'xo2',11x,'xo3')
220 43 FORMAT(/30X,'Original Input Data'/10X,'No.',7X,'LOI',10X,
221      &'xo1',11x,'xo2',11x,'xo3')
223 433 FORMAT(/30X,'Original Input Data'/10X,'No.',7X,'Os',10X,
224      &'xo1',11x,'xo2',11x,'xo3')
227 443 FORMAT(I12,F11.3,3F14.6)
230     62 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15X,'X01',10X,'X02',10X,
240      & 'X03'//(10X,3(E12.6,1X)))
250     32 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
260      & 10X,'X03'//(10X,3(E12.6,1X)))
270    221 FORMAT(1X,29X,'MODEL POLYNOMIAL OF DEGREE 1'///31X,'MIXTURE OF 3
280      & CONSTITUENTS'/31X,'SPECIFICATION OF VARIABLES :'/)
290 10 Format(V)
300     11 FORMAT('1',30X,'LINEAR REGRESSION OF MULTIPLE-MIXTURES'/30X,39('-'
310      & )//30X,A30))
320 12 format(A80)
330 20 format(A60)
340 21 format(30x,'Composition Variables:',3(/35x,A60))
350 30 format(7(30x,A5,A60/))
355 31 format(3(30x,A5,A30/2(35x,A80/)),4(30x,A5,A60/))
360     40 FORMAT(/30X,'MATRICE X'/30X,9('-')///13X,'X01',9X,'X02',9X,'X03',
370      & 9X,'X04',9X,'X05',9X,'X06',9X,'X07'//(10X,7(F3.6,4X)))
380     50 FORMAT('1',/30X,'VECTOR Y' /30X,9('-')//10X,10(F5.2,3X)//)
390     60 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15X,'X01',10X,'X02',10X,
400      & 'X03',10X,'X04',10X,'X05',10X,'X06',10X,'X07'//(10X,7(E12.6,1X)))
410     70 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,7(E12.6,1X)//)
420     30 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
430      & 10X,'X03',10X,'X04',10X,'X05',10X,'X06',10X,
440      & 'X07'//(10X,7(E12.6,1X)))
450    90 FORMAT(1X,29X,'REDUCED CUBIC MODEL'///31X,'MIXTURE OF 3 CONSTITUEN
460      & TS'/31X,'SPECIFICATION OF VARIABLES :'/)
```

```
  994 FORMAT(12x,'xC7',8x,E12.6,5x,E12.6)
   94 FORMAT(10X,'COEFFICIENTS'/10X,12('-')/10X,'VARIABLE',6X,'COEFFICIE
     & NT',5X,'SIGMA-SQUARE'/(12X,'X0',I2,8X,E12.6,5X,E12.6))
 96 format('1',9X,'Calculated LOI Values:'/10X,21('-')/10X,'Number',6X,
 & 'Observed LOI',4X,'Calculated LOI',4X,'Difference'/(11X,I3,5X,F12.6,
 & 5X,F12.6,5X,F12.6))
   51 FORMAT(20A4)
 52 format('     Plot of: ',A80)
   53 FORMAT(5X,'LINEAR MODEL',3X,10(F5.2,3X))
   54 FORMAT(5X,'QUADRATIC MODEL',3X,10(F5.2,3X))
   55 FORMAT(5X,'CUBIC MODEL',3X,10(F5.2,3X))
   97 FORMAT('1')
 120 read(5,20,end=1000) (vbl(2,i),i=1,3)
 read(5,12,end=1000) title
 do 699 i=1,3
 do 699 j=1,3
 699 xv(i,j)=xc(i,j)
 write(6,11) title
 write(6,21) (vbl(2,i),i=1,3)
 read(5,10) ymin,pas,nin,nout
 READ (5,10) IAVC,c,csub
 NINM=NIN-1; NINP=NIN+1
 ninm = nin - 2
 if(nin) ,,701
 read(5,10)(y(i),i=1,10)
 do 700 i=1,10
 if(nin.eq.-2) y(i)=1591.*(1.95424-alog10(y(i)))
 do 700 j=1,3
 700 x(i,j)=xc(i,j)
 iin=10;    Det=1.
 go to 710
 701 if(ninm)7011,7011,7012
 7011 write(6,43)
 go to 7013
 7012 write(6,433)
 7013 do 703 iin=1,100
 read(5,10) y(iin),(x(iin,j),j=1,3)
 write(6,443) iin,y(iin),(x(iin,j),j=1,3)
 if(y(iin).lt.0.) go to 704
 xtot=x(iin,1)+x(iin,2)+x(iin,3)
 do 702 i=1,3
 702 x(iin,i)=x(iin,i)/xtot
 if(nin.eq.3) y(iin)=1591.*(1.95424-alog10(y(iin)))
 703 continue
 704 read(5,10)((xv(i,j),j=1,3),i=1,3)
 iin=iin-1
 do 705 i=1,3
 xtot=xv(i,1)+xv(i,2)+xv(i,3)
 do 705 j=1,3
 705 xv(i,j)=xv(i,j)/xtot
 call coord(xv,Det)
 if(Det.ne.0.) go to 707
 write(6,706)
 706 format(' Incorrectly chosen vertices - coordinate conversion not ',
 &'possible.'/' Vertices placed at 100% of each component')
 go to 710
 707 call conv(iin)
 write(1,708)((100.*xv(i,j),vbl(2,j),j=1,3),i=1,3)
 708 format(3(F9.4,'% ',A60/2(' + ',F9.4,'% ',A60/)))
 rewind 1
 read(1,12)(vtitle(i),i=1,9)
 rewind 1
```

```
662 write(6,709) (vtitle(i),i=1,9)
664 709 format(' Composition Limits:'/' x(1) = ',A80/2(6X,A80/),' x(2) = ',A80,
666 &/2(6X,A80/),' x(3) = ',A80/2(6X,A80/))
668 710 write(6,991)
673 if (nin.le.0.or.Det.eq.0.) write(6,30)((vbl(i,j),i=1,2),j=1,3)
674 if(nin.gt.0.and.Det.ne.0.) write(6,31)(vbl(1,j),(vtitle(i),i=3*j-2,
675 &3*j),j=1,3)
680 if(nin.lt.0.or.nin.gt.1) write(6,44)
684 44 FORMAT(/30X,'Input Data'/10X,'No.',7X,'Ds',10X,
685     &'xo1',11X,'xo2',11X,'xo3')
686 610 if(ninp.ne.0.and.ninmm.ne.0) write(6,42)
710   write(6,442)(i,y(i),(x(i,j),j=1,3),i=1,iin)
720 442 FORMAT(I12,F11.2,3F14.6)
722 A=0
724 IF (XV(2,2).EQ.XV(3,3).AND.XV(2,3).EQ.0.AND.XV(3,2).EQ.0) A=XV(2,2)
726 IF (A.EQ.0.OR.B.EQ.0) IAVC=0
728 if(iavc.eq.1) call setk(a,b,ak)
729 6101 if(iavc.eq.2.and.b.ne.0) call setk2(b,ak)
740 620 call gmtra(iin,3,nin)
780 630 call gmprod(1,iin,3)
790 635 if(nout.eq.1) write(6,62)((xtx(i,j),j=1,3),i=1,3)
810 call minv(3,determ,vtl,vtm)
850 640 call gmprod(2,iin,3)
855 if(nout.ne.1) go to 645
860 write(6,72)(xty(i),i=1,3)
870 write(6,32)((xtx(i,j),j=1,3),i=1,3)
910 645 call gmprod(3,iin,3)
920 ssl=0.;lastn=0
930 call calcul(3,iin,vr,ssl,lastn)
940 if(iavc.eq.1) call avcoeff(iavc,b,3,ak,vr)
945 if(iavc.eq.2) call ternco(b,csub,3,ak,vr)
947 if(iavc.eq.3) call avincco(a,b,csub,3,ak,vr)
950 630 write(6,94)(i,beta(i),sqrt(vr*xtx(i,i)),i=1,3)
951 690 if(nin) 693,692,691
952 691 if(ninm) ,692,693
953 692 if(nout.ne.0) write(6,96)(i,y(i),yc(i),ec(i),i=1,iin)
954 go to 694
955 693 if(nout.ne.0) write(6,996)(i,y(i),yc(i),ec(i),i=1,iin)
956 996 FORMAT('1',9X,'Calculated Ds values:'/10X,21('-')/10X,'Number',5X,
957      & 'Observed Ds ',4X,'Calculated Ds ',4X,'Difference'/(11X,I3,5X,F12.6,
958      & 5X,F12.6,5X,F12.6))
1000 694 if(nout.ne.0) write(6,97)
1030 if(nout.ne.0) write(6,52) title
1040 call scale(ymin,pas,iin,ym,yinc)
1042 if(nout.eq.3) call plot(ym,yinc,iin,nout,1,xv,nin)
1044 if(nout.eq.3) write(6,97)
1046 if(nout.eq.3) write(6,52) title
1050 call plot(ym,yinc,iin,nout,3,xv,nin)
1055 iv=6
1057 110 if(iin.le.iv) go to 220
1060 write(6,11) title
1062 if(iv.eq.6)write(6,91)
1063 if(iv.eq.7)write(6,90)
1064 if(iv.eq.10)write(6,111)
1065 if(iv.eq.15)write(6,112)
1068 111 format(30X,' FULL CUBIC MODEL'///31X,' Mixture of
1070 & 3 constituents'/31X,' Specification of variables')
1072 112 format(30X,' QUARTIC MODEL'///31X,' Mixture of
1074 & 3 constituents'/31X,' Specification of variables')
1080 if(nin.eq.0.or.Det.eq.0.)write(6,30)((vbl(i,j),i=1,2),j=1,iv)
1081 if(ninm.eq.0.or.Det.eq.0.) write(6,30) ((vbl(i,j),i=1,2),j=1,iv)
1082 if(nin.ne.0.and.ninp.ne.0.and.Det.ne.0.) write(6,31)(vbl(1,j),(vtitle(i),
```

```
1083 &i=3*j-2,3*j),j=1,3),((vbl(i,j),i=1,2),j=4,iv)
1088 if(nout.ne.1) go to 520
1090 510 if(iv.eq.6)write(6,41)((x(i,j),j=1,6),i=1,iin)
1095 if(iv.eq.7)write(6,40)((x(i,j),j=1,7),i=1,iin)
1100 515 write(6,50)(y(i),i=1,iin)
1130 520 call gmtra(iin,iv,nin)
1170 call gmprod(1,iin,iv)
1180 530 if(nout.eq.1.and.iv.eq.6)write(6,61)((xtx(i,j),j=1,6),i=1,6)
1190 if(nout.eq.1.and.iv.eq.7)write(6,60)((xtx(i,j),j=1,7),i=1,7)
1200 540 call minv(iv,determ,vtl,vtm)
1240 550 call gmprod(2,iin,iv)
1245 if(nout.ne.1) go to 570
1250 560 if(iv.eq.6) write(6,71)(xty(i),i=1,6)
1255 if(iv.eq.7) write(6,70)(xty(i),i=1,7)
1260 if(iv.eq.6) write(6,81)((xtx(i,j),j=1,6),i=1,6)
1265 if(iv.eq.7) write(6,80)((xtx(i,j),j=1,7),i=1,7)
1300 570 call gmprod(3,iin,iv)
1320 call calcul(iv,iin,vr,ssl,lastn)
1330 if(iavc.eq.1) call avcoeff(iavc,b,iv,ak,vr)
1340 if(iavc.eq.2) call ternco(b,csub,iv,ak,vr)
1345 if(iavc.eq.3) call avincco(a,t,csub,iv,ak,vr)
1350 580 write(6,94)(i,beta(i),sqrt(vr*xtx(i,i)),i=1,iv)
1351 590 if(nin) 593,592,591
1352 591 if(ninn) ,592,593
1353 592 if(nout.ne.0) write(6,96)(i,y(i),yc(i),ec(i),i=1,iin)
1354 go to 594
1355 593 if(nout.ne.0) write(6,996)(i,y(i),yc(i),ec(i),i=1,iin)
1400 594 if(nout.ne.0) write(6,97)
1430 if(nout.ne.0) write(6,52) title
1440 call scale(ymin,pas,iin,ym,yinc)
1450 call plot(ym,yinc,iin,nout,iv,xv,nin)
1460 if(iv.eq.15) go to 220
1470 if(iv.eq.10) iv=15
1480 if(iv.eq.7) iv=10
1490 if(iv.eq.6) iv=7
1500 go to 110
1880 220 do 250 i=1,15
1890       BETA(I)=0.0
1900  250 CONTINUE
1910       GO TO 120
1920 1000 call lpconv
1925 stop
1930       END
1940 subroutine scale(ymin,pas,iin,ym,yinc)
1950 common x(100,15),dummy(1725),y(100),dummy2(39),yc(100)
1960 ym=ymin;  yinc=pas
1970 if(ymin.ge.0..and.pas.gt.0.) return
1980 ym=100.;  yx=0.
1990 do 101 i=1,iin
1995 if(x(i,1).lt.0..or.x(i,2).lt.0..or.x(i,3).lt.0.) go to 101
2000 if(y(i).gt.yx) yx=y(i)
2010 if(yc(i).gt.yx) yx=yc(i)
2020 if(y(i).lt.ym) ym=y(i)
2030 if(yc(i).lt.ym) ym=yc(i)
2040 101 continue
2050 if(ymin.gt.ym.and.ymin.lt.yx) ym=ymin
2060 ydiff=(yx-ym)/10.
2070 do 102 i=1,4
2080 ysc=aint(ydiff)+1.
2090 if(ydiff.ge.5.) ysc=10.
2100 if(ydiff.ge.1.) go to 103
2110 102 ydiff=ydiff*10.
```

```
2120 103 if(pas.le.0.) yinc=ysc/10.**(i-1)
2130 if(ymin.lt.0.) ym=yinc*aint(ym/yinc)
2140 return
2150 end
2540 subroutine gmtra(n,m,nin)
2550 common a(100,15),r(15,100),dummy(15,15),y(100)
2560 do 10 i=1,n
2570 do 10 j=1,m
2580 10 r(j,i)=a(i,j)
2582 if(nin.eq.0.or.nin.eq.1) return
2584 do 11 i=1,n
2586 do 11 j=1,m
2588 11 if(y(i).ne.0) r(j,i)=1E6*r(j,i)/y(i)/y(i)
2590 return
2600 end
2650 subroutine gmprod(ncalc,n,m)
2660 common x(100,15),xt(15,100),xtx(15,15),y(100),xty(15),beta(15)
2665 if(ncalc.ne.1) go to 12
2670 do 11 i=1,m
2675 do 11 j=1,m
2680 xtx(i,j)=0.
2690 do 11 k=1,n
2700 11 xtx(i,j)=xtx(i,j)+xt(i,k)*x(k,j)
2710 return
2720 12 if(ncalc.ne.2) go to 14
2730 do 13 i=1,m
2740 xty(i)=0.
2750 do 13 k=1,n
2760 13 xty(i)=xty(i)+xt(i,k)*y(k)
2770 return
2780 14 do 15 i=1,m
2790 beta(i)=0.
2795 do 15 k=1,m
2798 15 beta(i)=beta(i)+xtx(i,k)*xty(k)
2800       RETURN
2810       END
2820 subroutine minv(n,d,l,m)
2825 common dummy(3000),xtx(15,15)
2830 dimension a(225),l(15),m(15)
2831 ia=0
2832 do 5 i=1,n
2834 do 5 j=1,n
2836 ia=ia+1
2838 5 A(ia)=xtx(j,i)
2840CC        SEARCH FOR LARGEST ELEMENT
2850       D=1.0
2860       NK=-N
2870       DO80 K=1,N
2880       NK=NK+N
2890       L(K)=K
2900       M(K)=K
2910       KK=NK+K
2920       BIGA=A(KK)
2930       DO 20 J=K,N
2940       IZ=N*(J-1)
2950       DO 20 I=K,N
2960       IJ=IZ+I
2970    10 IF( ABS(BIGA)-ABS(A(IJ))) 15,20,20
2980    15 BIGA=A(IJ)
2990       L(K)=I
3000       M(K)=J
3010    20 CONTINUE
```

```
3020CCC
3030CCC       INTERCHANGE ROWS
3040CCC
3050       J=L(K)
3060       IF(J-K)35,35,25
3070    25 KI=K-N
3080       DO 30 I=1,N
3090       KI=KI+N
3100       HOLD=-A(KI)
3110       JI=KI-K+J
3120       A(KI)=A(JI)
3130    30 A(JI)=HOLD
3140CCC       INTERCHANGE COLUMNS
3150CCC
3160CCC
3170    35 I=M(K)
3180       IF(I-K) 45,45,38
3190    38 JP=N*(I-1)
3200       DO 40 J=1,N
3210       JK=NK+J
3220       JI=JP+J
3230       HOLD=-A(JK)
3240       A(JK)=A(JI)
3250    40 A(JI)=HOLD
3260CCC
3270CCC       DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT
3280CCC       IS CONTAINED IN  BIGA)
3290CCC
3300    45 IF(BIGA) 48,46,48
3310    46 D=0.0
3320       RETURN
3330    48 DO 55 I=1,N
3340       IF(I-K) 50,55,50
3350    50 IK=NK+I
3360       A(IK)=A(IK)/(-BIGA)
3370    55 CONTINUE
3380CCC
3390CCC       REDUCE MATRIX
3400CCC
3410       DO 65 I=1,N
3420       IK=NK+I
3430       HOLD=A(IK)
3440       IJ=I-N
3450       DO 65 J=1,N
3460       IJ=IJ+N
3470       IF(I-K)60,65,60
3480    60 IF(J-K)62,65,62
3490    62 KJ=IJ-I+K
3500       A(IJ)=HOLD*A(KJ)+A(IJ)
3510    65 CONTINUE
3520CC  C
3530CCC       DIVIDE  ROW  BY  PIVOT
3540CCC
3550       KJ=K-N
3560       DO 75 J=1,N
3570       KJ=KJ+N
3580       IF(J-K)70,75,70
3590    70 A(KJ)=A(KJ)/BIGA
3600    75 CONTINUE
3610CCC
3620CCC       PRODUCT OF PIVOTS
3630CCC
```

```
3640        D=D*BIGA
3650CC
3660CC         REPLACE PIVOT BY RECIPROCAL
3670CC
3680        A(KK)=1.0/BIGA
3690    80 CONTINUE
3700CC
3710CC         FINAL ROW AND COLUMN INTERCHANGE
3720CC
3730        K=N
3740   100 K=(K-1)
3750        IF(K) 150,150,105
3760   105 I=L(K)
3770        IF(I-K) 120,120,108
3780   108 JQ=N*(K-1)
3790        JR=N*(I-1)
3800        DO 110 J=1,N
3810        JK=JQ+J
3820        HOLD=A(JK)
3830        JI=JR+J
3840        A(JK)=-A(JI)
3850   110 A(JI)=HOLD
3860   120 J=M(K)
3870        IF(J-K)100,100,125
3880   125 KI= K-N
3890        DO 130 I=1,N
3900        KI=KI+N
3910        HOLD=A(KI)
3920        JI=KI-K+J
3930        A(KI)=-A(JI)
3940   130 A(JI)=HOLD
3950        GO TO 100
3955 150 ia=0
3960 do 161 i=1,n
3962 do 161 j=1,n
3964 ia=ia+1
3966 161 xtx(j,i)=A(ia)
3968 return
3970        END
3980 subroutine calcul(n,iin,vr,ssl,lastn)
3990 common a(100,15),xt(15,100),dum1(225),c(100),dum2(15),b(15),dum3(9),d(100),
3995 &e(100)
4000     92 FORMAT('1',9x,'STATISTICS'/10x,11('-')/10x,'RESIDUAL VARIANCE',
4010 & 6x,E12.6/10x,'R.m.s. difference',6x,F12.6/10x,            'DEGREES OF FREE
4020      & DOM',12x,I2/10x,'REGR.CORR.COEFFICIENT',2x,E12.6//)
4030     93 FORMAT(10x,'ANALYSIS OF VARIANCE'/10x,20('-')/10x,'SOURCE',5x,
4040      & 'DOF       DIFF-OF-SUM         MEAN SQUARE',6x,'F-TEST RATIO'/10x,
4050      & 'ERROR',6x,I2,5x,E12.6,6x,E12.6/10x,'REGRESSION',1x,I2,5x,E12.6,
4060      & 6x,E12.6,6x,E12.6//)
4070        sumy=0.0
4075 sumw=0.
4080        sumy2=0.0
4085 sumy0=0.
4090        sumy02=0.0
4095 sce=0.;swe=0.
4100 do 190 i=1,iin
4102 w=0.
4104 do 191 j=1,3
4106 191 w=w+xt(j,i)
4110        D(I)=0.0
4120        DO 192 J=1,N
4130        D(I)=D(I)+B(J)*A(I,J)
```

```
4140  192 CONTINUE
4150        E(I)=C(I)-D(I)
4155 sumw=sumw+w
4160        sumy2=sumy2+C(I)*C(I)*w
4170        sumy=sumy+C(I)*w
4175 sumy0=sumy0+D(i)*w
4180        sumy02=sumy02+D(I)*D(I)*w
4185 sce=sce+e(i)*e(i) ;swe=swe+e(i)*e(i)*w
4190  190 CONTINUE
4210 scr=sumy02-sumy0*sumy0/sumw
4215 nl=iin-n
4220 vr=sce/nl; wvr=swe/nl
4230        SCM=SCR/(FLOAT(N))
4240 ratio=scm/wvr
4250 wvr=wvr*iin/sumw
4260 ecvr=sqrt(wvr)
4270 R2=scr/(sumy2-sumy*sumy/sumw)
4280  200 write(6,92)wvr,ecvr,nl,r2
4285 write(6,94) vr,sqrt(vr)
4286  94 format(10x,'(unweighted values: variance ',E12.6,' r.m.s. difference '
4287 &,F12.6,')')
4290  210 WRITE(6,93)NL,SWE,wvr,N,SCR,SCM,RATIO
4292 sse=scr-ssl;ne=n-lastn;ssem=sse/ne;Fseq=ssem/wvr/sumw*iin
4294 write(6,95) ne,sse,ssem,Fseq
4295 vr=wvr
4296 lastn=n;ssl=scr
4298 95 format(//10x,"Sequential F-test for extra variables added in this step"
4299 &/10x,"Extra degrees of freedom ",I2,"  extra sum of squares ",E12.6,
4300 &" mean ",E12.6/10x,"F-test ratio ",F14.5)
4305 RETURN
4310       END
4320 subroutine plot(ym,yinc,iin,nout,ncoeff,xv,nin)
4330 common x(100,15),dummy(1725),y(100),dummy2(15),beta(15)
4340 dimension ppos(51,101),pc(11),yval(11),ycal(2,101),xa(15)
4345 &,xv(3,3)
4350 character*1 ppos,pc
4360 data pc/'0','1','2','3','4','5','6','7','8','9','x'/
4362 ninp = nin + 1
4363 ninmm = nin - 2
4365 if(nout.eq.0) return
4370 if(ncoeff.eq.3) write(6,300)
4380 300 format(' Linear Model')
4390 if(ncoeff.eq.6) write(6,301)
4400 301 format(' Quadratic Model')
4410 if(ncoeff.eq.7) write(6,302)
4420 302 format(' Reduced Cubic Model')
4422 if(ncoeff.eq.10) write(6,330)
4424 330 format(' Full Cubic Model')
4426 if(ncoeff.eq.15) write(6,331)
4428 331 format(' Quartic Model')
4430 if(ninp.eq.0) write(6,3031) ym,yinc,(xv(1,i),i=1,3)
4432 3031 FORMAT(' Min. Ds = ',F8.3,', Increment = ',F7.3,3x,'x(1) = 1.00, (',
4433       &3F8.4,')')
4435 if(ninmm.eq.0) write(6,3031) ym,yinc,(xv(1,i),i=1,3)
4436 if(ninp.ne.0.and.ninmm.ne.0) write(6,303) ym,yinc,(xv(1,i),i=1,3)
4440 303 format(' Min. LOI = ',F8.3,', Increment = ',F7.3,3x,'x(1) = 1.00 , (',
4445 &3F8.4,' )')
4450 if(nout.eq.2.and.ncoeff.eq.3) write(6,304)
 460 304 format(' * = position of data point')
4470 yval(1)=ym
4480 do 305 i=2,11
4490 305 yval(i)=yval(i-1)+yinc
```

```
4500 do 307 i=1,51
4510 do 306 j=1,101
4520 306 ppos(i,j)=' '
4530 ppos(i,i)='.';   ppos(i,102-i)='.'
4540 307 ppos(1,2*i+1)='.'
4550 do 308 i=1,51,5
4560 ppos(i,i)='+';   ppos(i,102-i)='+'
4570 308 ppos(1,2*i-1)='+'
4580 nfirst=0.;  ny=1
4585 if(ncoeff.eq.1) go to 323
4590 do 315 line =1,51
4600 do 310 ip=line,102-line
4610 xa(1)=(line-1)/50.; xa(3)=(ip-line)/100.; xa(2)=1.-xa(1)-xa(3)
4620 xa(4)=xa(1)*xa(2); xa(5)=xa(1)*xa(3); xa(6)=xa(2)*xa(3)
4625 xa(7)=xa(1)*xa(2)*xa(3); xa(8)=xa(4)*(xa(1)-xa(2))
4628 xa(9)=xa(5)*(xa(3)-xa(1)); xa(10)=xa(6)*(xa(2)-xa(3))
4630 xa(11)=xa(4)*(xa(1)*xa(1)+xa(2)*xa(2)-3.*xa(4))
4632 xa(12)=xa(5)*(xa(1)*xa(1)+xa(3)*xa(3)-3.*xa(5))
4634 xa(13)=xa(6)*(xa(2)*xa(2)+xa(3)*xa(3)-3.*xa(6))
4636 xa(14)=xa(2)*xa(7);  xa(15)=xa(3)*xa(7)
4640 ycal(ny,ip)=0.
4650 do 309 j=1,ncoeff
4660 309 ycal(ny,ip)=ycal(ny,ip)+xa(j)*beta(j)
4670 do 310 j=1,11
4680 if(abs(ycal(ny,ip)-yval(j)).lt.yinc/50.) ppos(line,ip)=pc(j)
4690 310 continue
4700 do 314 j=1,11
4710 if(line.eq.51) go to 312
4720 do 311 ip=1+line,102-line
4730 y1=ycal(ny,ip)-yval(j) ;  a1=abs(y1)
4740 y2=ycal(ny,ip-1)-yval(j); a2=abs(y2)
4745 if(a1.eq.0..or.a2.eq.0.) go to 311
4750 if(y1/a1.eq.y2/a2) go to 311
4760 if(a1.lt.a2) ppos(line,ip)=pc(j)
4770 if(a1.gt.a2) ppos(line,ip-1)=pc(j)
4780 311 continue
4790 312 if(nfirst.eq.0) go to 314
4800 do 313 ip=line,102-line
4810 y1=ycal(ny,ip)-yval(j);   a1=abs(y1)
4820 y2=ycal(3-ny,ip)-yval(j); a2=abs(y2)
4825 if(a1.eq.0..or.a2.eq.0.) go to 313
4830 if(y1/a1.eq.y2/a2) go to 313
4840 if(a1.lt.a2) ppos(line,ip)=pc(j)
4850 if(a1.gt.a2) ppos(line-1,ip)=pc(j)
4860 313 continue
4870 314 continue
4880 nfirst=1;   ny=3-ny
4890 315 continue
4900 323 if((nout.ne.2.or.ncoeff.ne.3).and.ncoeff.ne.1) go to 317
4910 do 316 i=1,iin
4920 ix=int(50.*x(i,1)+100.*x(i,3)+1.5)
4930 iy=int(50.*x(i,1)+1.5)
4935 if(nout.eq.2.and.iy.ge.1.and.iy.le.51.and.ix.ge.iy.and.ix.le.(102-iy))
4936 &ppos(iy,ix)='*'
4940 ival=int(y(i)/yinc-ym/yinc+1.5)
4941 if(nout.eq.3.and.iy.ge.1.and.iy.le.51.and.ix.ge.iy.and.ix.le.(102-iy))
4942 &ppos(iy,ix)=pc(ival)
4945 316 continue
4950 317 do 318 i=1,51
4960 ip=52-i
4970 318 write(6,319)(ppos(ip,j),j=1,101)
4980 319 format(10X,101A1)
```

```
4990 write(6,320)(0.1*i,i=1,10)
5000 320 format(9x,'0.0',10(7x,F3.1)/5x,'x(2) = 1.00',90x,'x(3) = 1.00')
5005 write(6,322) ((xv(i,j),j=1,3),i=2,3)
5008 322 format(2x,'(',3F8.4,')',70x,'(',3F8.4,')')
5010 if(ninp.eq.0) write(6,3211) (pc(i),yval(i),i=1,11)
5012 3211 FORMAT(' Ds Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,';
5013      &  ',A1,' = ',F8.2)
5016 if(ninp.ne.0.and.ninmm.ne.0) write(6,321) (pc(i),yval(i),i=1,11)
5020 321 format(' LOI Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,'; ',
5030 &A1,' = ',F8.2)
5040 return
5050 end
5220 subroutine coord(A,Det)
5230 common dummy(3355),c(3,3)
5240 dimension a(3,3),d(4)
5250 amult=-1.
5260 do 601 i=1,3
5270 do 601 j=1,3
5280 amult=-amult
5290 n=0
5300 do 600 id=1,3
5310 do 600 jd=1,3
5320 if(id.eq.i.or.jd.eq.j) go to 600
5330 n=n+1
5340 d(n)=a(id,jd)
5350 600 continue
5360 601 c(j,i)=amult*(d(1)*d(4)-d(2)*d(3))
5370 det = a(1,1)*c(1,1)+a(1,2)*c(2,1)+a(1,3)*c(3,1)
5380 if(det.eq.0.) return
5390 do 602 i=1,3
5400 do 602 j=1,3
5410 602 c(i,j)=c(i,j)/det
5420 return
5430 end
5440 subroutine conv(iin)
5450 common x(100,15),dummy(1655),c(3,3)
5460 dimension xt(3)
5470 do 605 ir=1,iin
5480 do 603 i=1,3
5490 603 xt(i)=x(ir,i)
5500 do 604 i=1,3
5510 x(ir,i)=0.
5520 do 604 j=1,3
5530 604 x(ir,i)=x(ir,i)+c(j,i)*xt(j)
5540 x(ir,4)=x(ir,1)*x(ir,2); x(ir,5)=x(ir,1)*x(ir,3); x(ir,6)=x(ir,2)*x(ir,3)
5545 x(ir,7)= x(ir,1)*x(ir,2)*x(ir,3); x(ir,8)= x(ir,4)*(X(IR,1)
5546 & -X(IR,2))
5548 X(IR,9)=X(IR,5)*(X(IR,3)-X(IR,1))
5549 X(IR,10)=X(IR,6)*(X(IR,2)-X(IR,3))
5550 X(IR,11)=X(IR,4)*(X(IR,1)*X(IR,1)+X(IR,2)*X(IR,2)-3*X(IR,4))
5560 X(IR,12)=X(IR,5)*(X(IR,1)*X(IR,1)+X(IR,3)*X(IR,3)-3*X(IR,5))
5565 X(IR,13)=X(IR,6)*(X(IR,2)*X(IR,2)+X(IR,3)*X(IR,3)-3*X(IR,6))
5570 X(IR,14)=X(IR,2)*X(IR,7)
5580 605 X(IR,15)=X(IR,3)*X(IR,7)
5590 return
5600 end
5610 SUBROUTINE SETK(A,B,AK)
5620 DIMENSION AK(7,16)
5630 DO 1 I=1,3
5640 DO 1 J=1,15
5650 1 AK(I,J)=0
5660 IF (A.EQ.B) GOTO 2
```

```
5670 Q=B/A; R=1./a; S=A/B/B
5680 AK(1,1)=-R; AK(2,1)=-R; AK(1,2)=R; AK(2,3)=R
5690 AK(1,4)=R-R*2*Q/3; AK(2,5)=AK(1,4)
5700 AK(1,8)=R*(1.-2*Q+Q*Q); AK(2,9)=-AK(1,8)
5710 AK(1,11)=R*(1.-4*Q+5*Q*Q-2*Q*Q*Q); AK(2,12)=AK(1,11)
5720 AK(3,6)=S*S*Q**4; AK(3,7)=AK(3,6)-4*AK(3,6)*Q/5
5730 AK(3,14)=2*AK(3,6)*Q/5-AK(3,6)*Q*Q/3;AK(3,15)=AK(3,14)
5740 RETURN
5750 2 AK(1,1)=-1/B; AK(2,1)=-1/B; AK(1,2)=1/B; AK(2,3)=1/B
5760 AK(1,4)=1./3./B; AK(2,5)=AK(1,4)
5770 AK(3,6)=1/B/B; AK(3,7)=0.2/B/B
5780 AK(3,14)=AK(3,6)/15; AK(3,15)=AK(3,14)
5790 RETURN
5800 END
5810 SUBROUTINE AVCOEFF(IAVC,b,ncoeff,ak,vr)
5820 COMMON DUM(3000), XTX(15,15), DUM2(115), BETA(15)
5830 DIMENSION AK(7,16), CAVG(3),TEMP(15,3),CVNEW(3,3)
5840 IF (IAVC.EQ.0) RETURN
5846 IF (IAVC.EQ.2) CALL SETK2(B,AK)
5850 DO 2 I=1,3
5860 CAVG(I)=0
5870 DO 2 J=1,NCOEFF
5880 CAVG(I)=CAVG(I)+AK(I,J)*BETA(J)
5890 TEMP(J,I)=0
5900 DO 1 K=1,NCOEFF
5910 1 TEMP(J,I)=TEMP(J,I)+XTX(J,K)*AK(I,K)
5920 2 CONTINUE
5930 DO 4 I=1,3
5940 DO 4 J=1,3
5950 CVNEW(I,J)=0
5960 DO 3 K=1, NCOEFF
5970 3 CVNEW (I,J)=CVNEW(I,J)+AK(I,K)*TEMP(K,J)
5980 4 CONTINUE
5990 WRITE (6,5) B,(CAVG(I),SQRT(CVNEW(I,I)*VR), I=1,3)
6000 5 FORMAT (10X,'AVERAGE COEFFICIENTS OVER RANGE OF',
6010 \0268 'X2 OR X3 = 0 TO ', F8.5//15X, 'COMPONENT 2',
6020 & F12.5,'S.D.', F12.5/15X, 'COMPONENT 3', F12.5,'S.D.',
6030 & F12.5/15X,'* SYNERGISM *', F15.5,'S.D.',F15.5)
6040 RETURN
6050 END
6099 SUBROUTINE SETK2 (B,AK)
6100 DIMENSION AK(7,16)
6110 BR=1/B; BR2=BR*BR
6120 DO 1 J=1,3
6130 AK(J,1)=-BR; AK(J,J+1)=BR
6140 1 ak(j+3,j+4)=br2
6150 AK(7,8)=BR2*BR; AK(7,15)=2*AK(7,8)/7
6160 AK(7,16)=AK(7,15)
6170 RETURN
6180 END
6200 SUBROUTINE TERNCO(B,CSUB,N,AK,Var)
6210 COMMON DUMMY(3000), OLDX(15,15),DUMMY2(115),OLDBETA(15)
6220 DIMENSION AK(7,16),CAVG(7),TEMP(16,7),CVNEW(7,7),BETA(16),
6230 &XTX(16,16)
6240 BETA(1)=CSUB; XTX(1,1)=0; NCOEFF=N+1
6250 DO 10 I=1,15
6260 BETA(I+1)=OLDBETA(I); XTX(I+1,1)=0; XTX(1,I+1)=0
6270 DO 10 J=1,15
6280 XTX(I+1,J+1)=OLDX(I,J)
6290 10 CONTINUE
6310 DO 1 I=1,7
6320 1 cavG(I)=0
```

```
6330 DO 3 I=1,7
6340 DO 3 J=1,NCOEFF
6350 CAVG(I)=CAVG(I)+AK(I,J)*BETA(J)
6360 TEMP (J,I)=0
6370 DO 2 K=1,NCOEFF
6380 2 TEMP (J,I)=TEMP(J,I)+XTX(J,K)*AK(I,K)
6390 3 CONTINUE
6400 DO 5 I=1,7
6410 DO 5 J=1,7
6420 CVNEW(I,J)=0
6430 DO 4 K=1,NCOEFF
6440 4 CVNEW(I,J)=CVNEW(I,J)+AK(I,K)*TEMP(K,J)
6450 5 CONTINUE
6460 WRITE(6,6)B, (CAVG(I), SQRT(CVNEW(I,I)*VAR),I=1,7)
6470 6 FORMAT(/10X, 'AVERAGE COEFFICIENTS OVER RANGE OF
6480 & X2, X3, X4=0 TO ',F8.5/15X,' TYPE VARIABLE VALUE S.D.'/
6490 & 15X,'LINEAR  2', 2F12.5/ 24X,' 3 ', 2F12.5/
6500 &24X, '4', 2F12.5/15X, ' BINARY 2-3 ', 2F12.5/22X, ' 2-4',
6510 &2F12.5/22X, ' 3-4 ',2F12.5/15X, ' TERNARY   ',2F12.5)
6520 RETURN
6530 END
6540 subroutine avincco(a,bmax,binc,ncoeff,ak,vr)
6550 dimension ak(7,16),ak2(7,16)
6560 b=0.
6570 do 1 i=1,7
6580 do 1 j=1,16
6590 1 ak2(i,j)=0.
6600 2 bbef=b; bbsq=b*b
6610 b=b+binc
6620 if(b.gt.bmax) return
6630 bsq=b*b
6640 do 3 i=1,7
6650 do 3 j=1,16
6660 3 ak(i,j)=ak2(i,j)
6670 call setk(a,b,ak2)
6680 do 4 i=1,2
6690 do 4 j=1,16
6700 4 ak(i,j)=(bsq*ak2(i,j)-bbsq*ak(i,j))/(bsq-bbsq)
6710 do 5 j=1,16
6720 5 ak(3,j)=(bsq*bsq*ak2(3,j)-bbsq*bbsq*ak(3,j))/(bsq*bsq-bbsq*bbsq)
6730 write (6,6) b
6740 6 format(//10x,'Overall coefficients at b = ',F8.5)
6750 call avcoeff(1,b,ncoeff,ak2,vr)
6760 write(6,7) bbef,b
6770 7 format(//10x,'Incremental coefficients over range b =',F8.5,' to',
6780 & F8.5)
6790 call avcoeff(1,b,ncoeff,ak,vr)
6800 goto 2
6810 end
```

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