THE EFFECTS OF GAMMA-IRRADIATION ON ADDITIVES IN FOOD-CONTACT POLYMERS

by

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ABSTRACT

A range of antioxidants (BHT, Irganox 1010, 1076, 1330 and Irgafos 168) were incorporated into polymers (polyethylene, polypropylene, polystyrene and polyvinyl chloride) and subjected to increasing doses of gamma-irradiation (1,5,10,20,25,35 and 50 kGy) from a cobalt-60 source.

The amount of extractable antioxidant from the stabilised polymers was determined chromatographically and a gradual diminution in the total extractable levels of each antioxidant was observed as irradiation progressed, the extent depending on the nature of both the antioxidant and the polymer.

2,6-Di-t-butyl-1,4-benzoquinone was shown to be an extractable degradation product, arising from the effects of gamma-irradiation on the phenolic antioxidants. The extractable degradation product arising from the phosphite antioxidant, Irgafos 168, was identified as tris(2,4-di-t-butylphenyl)phosphate.

It was demonstrated using ^{14}C-labelled Irganox 1076 that degradation products formed during gamma-irradiation are becoming covalently bound to the polymer, as a result of radical coupling processes. There is a pronounced increase in the extent of covalent binding from 0.4% before irradiation to a minimum of 12.4% after an exposure to 50 kGy. Evidence has also been presented of covalent binding of the degradation product of Irgafos 168 to the polypropylene matrix, via polymeric radicals formed during irradiation.

Finally, the effects of gamma-irradiation on the extent of migration of antioxidants from polyolefins into food simulants was studied. It was found that irradiation leads to a decrease in the extent to which hindered phenolic antioxidants migrate from polyolefins into fatty media, consistent with the reduction in extractable antioxidant levels and the increase in the extent of antioxidant-polymer binding.

CONTENTS

CHAPTER 1

INTRODUCTION

1. INTRODUCTION TO GAMMA-IRRADIATION

Gamma-irradiation is likely to be a future method of food preservation and it offers two advantages over other methods, in that it requires no added chemicals and leaves no residue. It is a treatment involving the application of very large doses of ionising radiation to produce some desired changes in food. The resulting changes are beneficial to the health and well-being of mankind, because:-

i) certain food-borne pathogens are destroyed, thus making the food supply safer, and

ii) the treatment prolongs the shelflife by killing micro-organisms and delaying the deterioration process, thus increasing the food supply.

In certain types of food, radiation processing is superior to other processes of food preservation; for example, it will kill micro-organisms in food that are in hermetically-sealed packages or in the frozen state. Moreover, the treatment can be carried out at room temperature without raising the temperature of the product[1].

1.1 History of Food Irradiation

The use of ionising radiation as a process for food preservation has been under study for over twenty five years. In the United Kingdom, Food (Control of Irradiation) Regulations 1967 prohibited the irradiation of food for sale for human consumption. Scientific evidence on the safety of irradiated food was accumulated between 1970 and 1981, through the International Project on Food Irradiation, centred at Karlsruhe, Germany. A Joint Expert Committee of the International Atomic Energy Authority (IAEA), the World Health Organisation (WHO) and the Food and Agriculture Organisation (FAO) of the United Nations was set up in 1971, whose function was to review and guide research into food irradiation. This committee produced reports in 1977[2] and 1981[3] on 'The Wholesomeness of Irradiated Foods'. The UK Government set up its Advisory Committee on Irradiated and Novel Foods in May 1982, which reported in April 1986[4]. Like the previous committee, it recommended that there were no special safety reasons why food should not be irradiated up to a dose of 10 kGy (1.0 Mrad). The UK Government is currently considering the findings of this report and the comments from all interested parties before Government Policy is determined in this field.

1.2 Sources of Gamma-Irradiation

The physical principle on which food irradiation is based is essentially the absorption of energy quanta of electromagnetic radiation by the treated food. The radiation employed is either continuous, emitted by the isotopes ^{60}cobalt and ^{137}caesium during their radioactive decay, or discontinuous, emitted by linear electron

accelerators or X-ray sources[5].

The radiation plants operated by Isotron PLC (Swindon) involve the use of megacurie quantities of the isotope ^{60}cobalt. This isotope is produced in large quantities in certain nuclear reactors by neutron bombardment of inactive cobalt[6]. Since it has a halflife of 5.3 years, its radioactivity diminishes by about one percent each month and therefore needs replacing at suitable intervals. At every disintegration, ^{60}cobalt emits two gamma photons of 1.17 and 1.33 MeV (totalling 2.5 MeV per disintegration)[6]. The energy level of the gamma rays emitted from ^{60}cobalt is far below the critical 'threshold' value required to induce radioactivity in any of the elements present in products being irradiated.

^{137}Caesium is a rival to ^{60}cobalt (having a halflife of around 30 years), but the single gamma photon of 0.66 MeV in 86% of disintegrations puts it at a disadvantage compared with cobalt. In addition, the radiation from ^{60}cobalt is more penetrating than from ^{137}caesium, and gives a more uniform dose distribution throughout the irradiated samples[7]. ^{137}Caesium is present in the very large quantities of fission product liquor, but the cost of separation is very high, thus making it an unattractive source of gamma-irradiation compared with cobalt.

Linear electron accelerators have the advantage of a very high dose rate of several tens of kGy per second, which is much faster than gamma-irradiators, (typically 12 kGy per hour). Consequently, the duration time of irradiation is shortened sufficiently to permit the

installation of an accelerator as part of a continuous production line. However, the disadvantages of linear accelerators include a rise in temperature in the irradiated product, and a limited penetrating power of only a few centimetres[5,8].

X-ray accelerator sources are a very recent development and no commercial installation is as yet available in the United Kingdom.

X-rays are produced when electrons, supplied by electron accelerators, are stopped in a metal converter plate. The process of stopping electrons converts their energy to X-rays and heat. X-rays are more penetrating than gamma rays from ^{60}cobalt or ^{137}caesium. The disadvantage of this source is that X-rays are inefficient to produce[5,7].

1.3 Radiation Doses

Doses of radiation are defined in terms of the energy absorbed by the substance irradiated. The unit for radiation dose is the gray (Gy) which is defined as the dose corresponding to the absorption of one joule of energy per kilogramme of the matter through which the radiation passes. The gray is now used in place of the rad[4].

1 Gray = 1J/kg material ≡ 100 rad

1.4 Methods for Detection of Irradiated Foods

There is currently no easy way of detecting whether most foods have been irradiated, and if so, how many times and with what doses.

Methods do exist which show differences between irradiated and unirradiated foods but their reliability has not been demonstrated in practice and quantitative estimates cannot be made of the radiation dose received by individual foods[5].

These include detection of levels of ortho-tyrosine in meats as biomarkers of irradiation. Since more than 50% of the weight of raw meat is water, upon irradiation, the water is split into hydroxyl radicals and hydrated electrons.

$$H_2O \longrightarrow \cdot OH + e^-_{aq} + H^+$$

The hydroxyl groups interact with the aromatic rings of amino acids forming hydroxylated products, which are unique to irradiation and can therefore act as internal dosimeters[9].

Other methods involve identification of residual free radicals in bone and hard tissue after irradiation by electron spin resonance (ESR). The rapid decay of radicals at ambient temperature and in contact with water opposes the use of this technique for routine food control[5]. Other approaches involved the use of the chemiluminescence effect of irradiation treatment on spices as measured against a control sample. However, the chemiluminescence intensities have a rather broad band and can only be identified for about 2-3 weeks[10], and the pattern of changes in chemiluminescence response were inconsistent[11].

1.5 Introduction to Food-Contact Plastics and the Implications for Migration of Additives from such Materials

Plastic food-contact packagings are advantageous over 'traditional' packagings, such as paper or cardboard, in that they are capable of providing hygienic protection. This is achieved by preventing or retarding detrimental changes in the product due to external changes in atmospheric oxygen, light and micro-organisms. The plastic wrapping ensures that pasteurised or treated food remains in good quality, without affecting degradation for an extended period[12].

It is well known that these plastic materials contain low molecular weight additives[13], e.g. heat and light stabilisers, antioxidants, lubricants and plasticizers, all of which are necessary for the processing and stability of the plastic. However, such low molecular weight compounds frequently possess a high mobility in plastic materials, and are capable of migrating from the plastic into the food, thereby presenting a source of contamination to the food and a potential health risk to the consumer. Thus, strict regulations are necessary to control the use of such additives in food-packaging[13,14].

It is generally considered that the migration of polymer additives into foodstuffs is a diffusion problem, and depends on many variables[12]. As the determination of migrated polymer additives in heterogeneous foodstuffs is a difficult and time-consuming task, it has become common practice to study the migration of polymer additives into a series of homogeneous liquid, food simulant media under standard conditions, e.g.

a polymer surface area of 2 dm^2 exposed to 100 ml simulant over a period of 10 days at 40°C. A range of oily, alcoholic and aqueous simulants specified by the EEC Directive[15] has been widely used in such studies.

Many additives are known to undergo changes during processing or whilst performing their intended function in the plastic, and compounds often found to migrate into the food are not those originally added to the plastic. The finished plastic may also be subjected to various treatments, which may significantly influence the nature and quantity of the migrating substances.

With the growing interest in the possibility of using gamma-irradiation as a means of extending the shelflife of prepackaged foods, an investigation into the consequences of irradiation on migration was initiated. Little is known about the effects of gamma-irradiation on the many additives present in plastics used for food-packaging[16], although it has been established that changes do occur in the migration behaviour of such additives[17].

Changes are also observed to occur in the polymers, in that during the course of gamma-irradiation, oxygen diffuses into the amorphous regions of the polymer and interacts with the polymeric radicals generated, thus resulting in degradation of the polymer. Since electron beam irradiation is delivered at a much faster rate than gamma-irradiation, polymeric radicals are therefore produced at a much faster rate. Some of these polymeric radicals may disappear by reactions with atmospheric oxygen, but the majority of radicals recombine to form crosslinks

within the polymer, resulting in changes in the physical properties of the polymer.

1.6 Aims of the Investigation

Whereas the nutritional properties of many types of irradiated food have been studied in depth, comparatively little is known of the chemical effects of gamma-irradiation on the many additives (both intentional and non-intentional) that are present in polymeric materials, which may be in contact with a foodstuff. It is possible that toxic substances might be formed, which could subsequently migrate into the foodstuff and present a hazard.

The aims of this investigation were:-

i) to monitor changes in the levels of specific additives in given polymer compositions as the irradiation dose is progressively increased, with particular attention being paid to doses up to 10 kGy,

ii) to detect, separate and identify the degradation products arising from the above additives on irradiation,

iii) to study the effects of gamma-irradiation on the rate of migration of polymer additives present in packaging materials into food simulants,

iv) to determine the effect of variations in the nature of the base polymer on the rate of degradation of the antioxidant, and

v) to indicate whether antioxidant-polymer binding occurs during gamma-irradiation.

Polymers and antioxidants used throughout this investigation were:-

Polymers

low density polyethylene (LDPE)

high density polyethylene (HDPE)

polyvinyl chloride (PVC)

polypropylene (PP) homopolymer (only containing propene monomer)

polypropylene (PP) copolymer (containing approximately 10% ethene monomer with propene monomer, incorporated as block copolymer).

Antioxidants

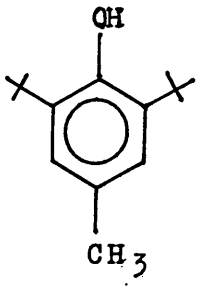
BHT [2,6-di-t-butyl-4-methylphenol, butylated hydroxytoluene] (I)

Irganox 1076 [octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] (II)

Irganox 1010 [tetrakis (methylene 3-(3,5-di-t-butyl-4-hydroxy-phenyl) propionate) methane] (III)

Irganox 1330 [1,3,5-trimethyl-2,4,6-tris(-3',5'-di-t-butyl-4-hydroxybenzyl) benzene] (IV)

Irgafos 168 [tris(2,4-di-t-butylphenyl) phosphite] (V)



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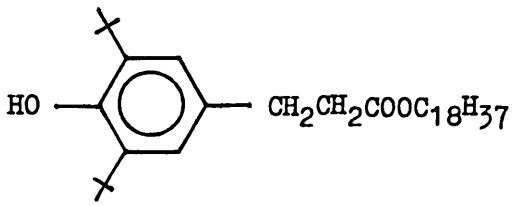

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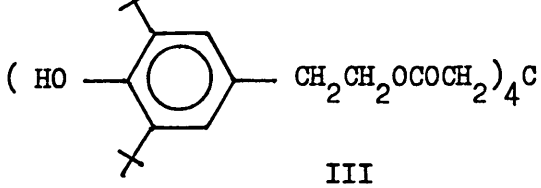

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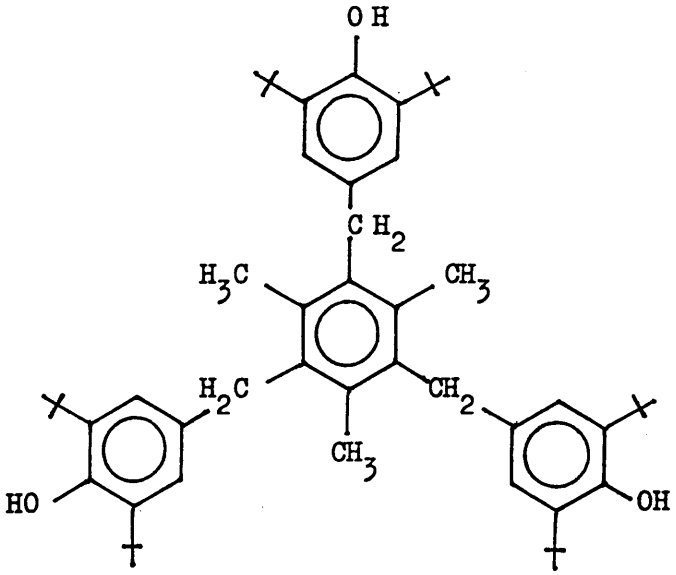

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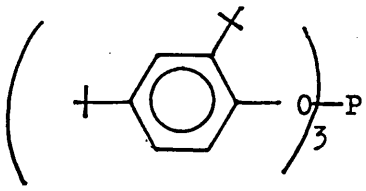


V

Notation used throughout this investigation:-

PP/1010/0.25/50

where PP represents the polymeric matrix,

1010 represents the antioxidant incorporated into the polymeric matrix,

0.25 represents the amount of antioxidant added (%), and

50 represents the gamma-irradiation dose received (kGy).

2. EFFECTS OF IRRADIATION ON POLYMERS

Gamma-irradiation induces the following chemical changes in polymers:-

i) crosslinking

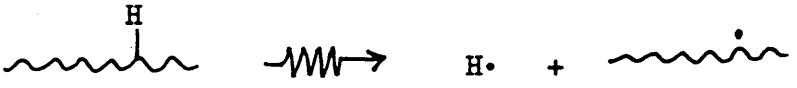
ii) degradation

iii) unsaturation

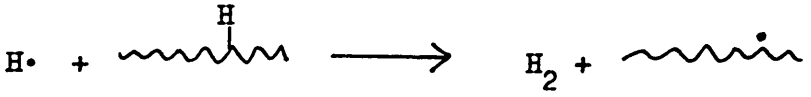
iv) formation of volatile products

The effect of each of these chemical changes on the polymer is discussed below:-

i) Crosslinking - this involves the combination of polymeric radicals to form crosslinks, thereby making the polymer progressively insoluble. Irradiation induces the formation of a polymeric radical.

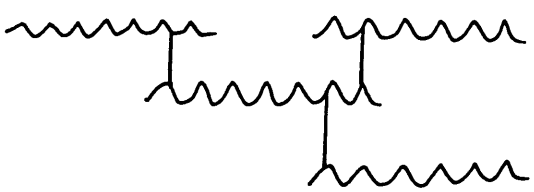


The hydrogen radical abstracts another hydrogen from a neighbouring polymer molecule, resulting in a polymeric radical.

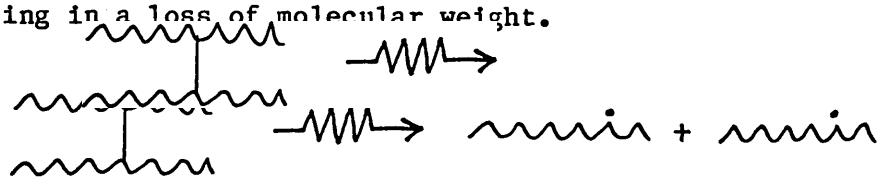


These polymeric radicals recombine

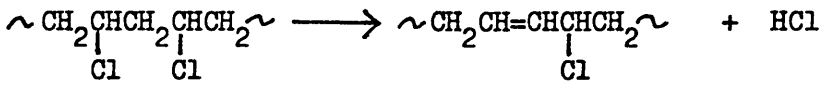
leading to the formation of a three-dimensional crosslinked network.



ii) Degradation - this may result from chain scission, by random rupturing of bonds forming two polymeric radicals, thereby resulting in a loss of molecular weight.



iii) Unsaturation - this is induced by elimination of two substituent atoms on adjacent carbon atoms resulting in the formation of a double bond.



iv) Formation of volatile products - a majority of polymers yield hydrogen and low molecular weight hydrocarbons, which are the products of degradation reactions involving terminal alkyl groups.

In addition to the above reactions, when irradiation proceeds in the presence of air, radiation-induced oxidative degradation takes place (the reactions are outlined in Table 1.1) which are similar to the oxidative degradation processes occurring during thermal processing of the polymer in air. These result ultimately in the formation of volatile compounds such as carboxylic acids and aldehydes which are

Radiation Induced Polymer Radical Reactions[18]

Initiation $RH \xrightarrow{\sim} R\cdot + H\cdot$

Polymer Radical Oxidation Reactions

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$$

$$ROOH \longrightarrow RO\cdot + HO\cdot$$

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

$$HO\cdot + RH \longrightarrow R\cdot + H_2O$$

Radical Reactions During Irradiation

$$RO_2\cdot \xrightarrow{\sim} R\cdot + O_2$$

$$R'RO_2\cdot \xrightarrow{\sim} R\text{-}CHO + R'O\cdot$$

$$R'ROOH \xrightarrow{\sim} R'RO\cdot + HO\cdot \rightarrow RC{=}O + R^{!}\cdot + HO\cdot$$

$$R'ROOR \xrightarrow{\sim} R'RO\cdot + RO\cdot \rightarrow RC{=}O + R^{!}\cdot + RO\cdot$$

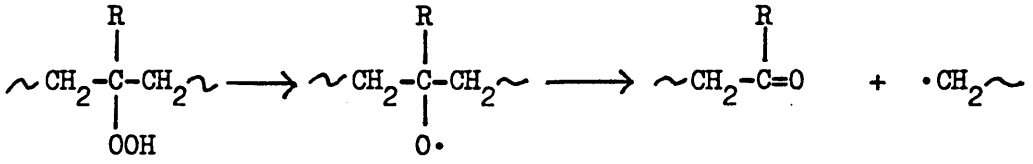
Termination Reactions

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

$$2RO_2\cdot \longrightarrow ROOR + O_2$$

responsible for the unpleasant odour (taint) in irradiated polyolefins.

At thermal processing temperatures, polymeric radicals are formed, but to a far smaller extent than on gamma-irradiation. These polymeric radicals react with atmospheric oxygen to form peroxyl radicals, which abstract hydrogen atoms from polymer molecules forming hydroperoxides and alkyl radicals, the latter then continuing the reaction with atmospheric oxygen[19]. At processing temperatures, polymeric alkyl hydroperoxides are decomposed to alkoxyl and hydroxyl radicals. Both of these radicals may abstract hydrogen from the polymer, with further generation of alkyl radicals. However, a proportion of radicals decompose by β-scission to produce a carbonyl compound and a terminal alkyl radical[19].



During gamma-irradiation in air, peroxyl radicals are easily formed, due to the high reactivity of oxygen towards alkyl radicals, and lead to the formation of peroxides, by the same reactions described during thermal processing[18]. These peroxides undergo scission, resulting in the formation of carbonyl compounds and the regeneration of alkyl radicals. Alkyl radicals may recombine in the termination stage of the reaction, forming an alkane. Peroxyl radicals also recombine, forming peroxides, with the evolution of oxygen.

2.1 Reactions in Polyethylene

Two types of polyethylene have been used in this investigation, namely high and low density polyethylene. High density polyethylene is essentially a high molecular weight linear alkane, which is 90% crystalline. The polymer contains long segments of a regular structure which can readily fit into a crystal lattice. Low density polyethylene contains a large number of both long and short branches in the amorphous region of the polymer. The polymer is 55% crystalline and crystallisation occurs in the segments of chain between the branches.

Irradiation of polyethylene in air results in crosslinking[20-22], and the reactions attributable to this effect within the polymer have been previously described. Identical reactions also take place during photo-degradation of polyethylene. It is known that unsaturation in the polymer may also promote crosslinking[23].

Reactions of oxygen with the radicals formed in polyethylene ultimately result in the formation of carbonyl or hydroxyl groups on the polymer chain[24].

Low density polyethylene is more susceptible to oxidation than high density polyethylene, which is due to the lower degree of crystallinity of low density polyethylene[25] and the greater number of tertiary carbons at the branched sites. The amorphous polymer structure allows diffusion of oxygen and presents less steric hindrance to attack than the crystalline structure[26].

Products of carbon-hydrogen bond scission predominate over those of carbon-carbon bond scission. This may be due to the fact that hydrogen atoms can diffuse relatively freely from the polymer side chain, while main chain carbon-carbon bond scission would result in relatively immobile radicals, which would not easily diffuse apart, so that recombination would be highly probable.

2.2 Reactions in Polypropylene

Two types of polypropylene have been used in this investigation, namely a homopolymer and a copolymer. Polypropylene is a two phase system of amorphous and crystalline regions, including a discontinuity at the amorphous-crystalline boundary. During irradiation, energy is transferred uniformly and radicals are formed throughout the two regions. However, different chemistry results, since oxygen and stabilisers are excluded from the crystalline region[18], and therefore oxidation occurs exclusively in the amorphous region[27-30]. A high proportion of radicals remain in the crystalline regions of polypropylene and slowly migrate to the crystal surfaces, where oxidation takes place, causing further degradation of the polymer[31].

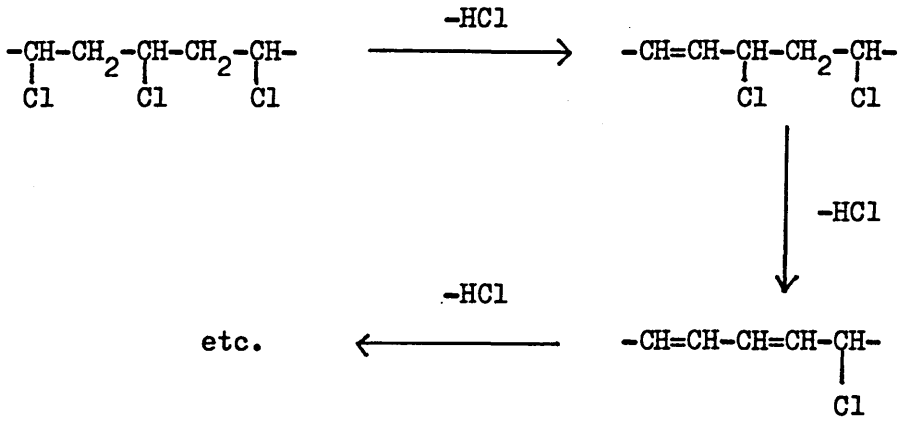
Polypropylene is even more susceptible to oxidation than polyethylene, which is attributable to the higher proportion of relatively easily abstracted tertiary hydrogen atoms on the polymer chain[27].

If irradiation proceeds in air, then degradation of polypropylene results, whereas in the absence of air, crosslinking predominates[20,22].

During irradiation, the dominant species in both amorphous and crystalline regions is the alkyl radical[18]. However, in the amorphous regions, this radical is rapidly oxidised,[32-34] and the products formed are degraded,[19,34-37] which results in a reduction in the molecular weight of the polymer.

2.3 Reactions in Polyvinyl Chloride

PVC readily undergoes decomposition either during gamma-irradiation, or at temperatures over 100°C or under the influence of light. The indication of decomposition is the development of discolouration. In air, the colour develops through yellow→orange→brown→black. This is due to the production of conjugated polyene sequences, $-[CH=CH]_n-$, with the evolution of hydrogen chloride, due to dehydrochlorination reactions.



Structures of this type contain highly delocalised systems of π-electrons and begin to exhibit colour when there are about 5-7 double bonds in conjugation[24,38].

3. COMPOSITION OF POLYMERS

Polymers usually contain several non-polymeric components in amounts from less than 1 part per million (ppm) to several percent. These are present either unavoidably (as a result of the manufacture process) or by deliberate additions to the polymer (in order to improve some aspect of manufacture or final polymer properties)[39]. Without these components, most hydrocarbon polymers would fail at their processing temperatures of 170-280°C, due to thermal and thermo-oxidative degradation[40].

The non-polymeric components may be divided into three groups:-

i) Polymerisation residues - these are substances whose presence is to a large extent unavoidable, such as low molecular weight oligomers, catalysts, polymerisation solvents and impurities picked up from the plant materials.

ii) Processing aids - these include substances such as thermal antioxidants and heat stabilisers added to prevent decomposition of the polymer during moulding, and slip additives to facilitate moulding. Typical antioxidants are notably hindered phenols, aromatic amines and organic sulphides.

iii) End-product additives - these are deliberately added to the polymer to improve the properties of the final polymer, such as light stabilisers.

Antioxidants are an important component of the polymer, both during thermal processing (preventing degradation at the high temperatures by reaction with atmospheric oxygen) and throughout its service life (where polymers are exposed to oxygen at temperatures substantially lower than during processing)[29].

There is considerable variation in the degree of degradation incurred by the polymer throughout its service life. It is this extent of degradation which determines the level of antioxidant to be added, in order to protect the polymer. The requirements for the protection of the polymer during processing and storage differ from those for long-term applications. Throughout the long-term applications, antioxidants prevent oxidation and embrittlement of the polymer, which occurs as a result of atmospheric aging and prevent damage to the polymer caused by solar radiation during weathering.

Additional antioxidants are often incorporated into the polymer, to help resist accelerated aging. This is particularly important where relatively high temperatures are involved, as in contact with hot food or in tropical areas where substantial exposure to ultraviolet radiation is likely to be encountered[39].

4. CLASSES OF OXIDATION STABILISERS AND MECHANISMS

The first main class of stabiliser is the hydroperoxide (ROOH) decomposer, which act by transforming hydroperoxides into non-radical compounds. Chain-breaking antioxidants comprise the second main class of oxidation stabilisers. They are more widely used than hydroperoxide

decomposers and function stoichiometrically in relation to the amount of free radicals to be scavenged in the propagation and chain-transfer steps[41].

The essential features of chain autoxidation are transfer (1),(2), branching (3a,b,c) and termination (4)[42]. In the following scheme, RH is the hydrocarbon polymer; R• , RO• , ROO• and ROOH are derived radicals and hydroperoxide, respectively.

$$R\bullet + O_2 \longrightarrow RO_2\bullet \qquad (1)$$

$$RO_2\bullet + RH \longrightarrow ROOH + R\bullet \qquad (2)$$

$$ROOH \longrightarrow RO\bullet + \bullet OH \qquad (3a)$$

$$2ROOH \longrightarrow RO\bullet + ROO\bullet + H_2O \qquad (3b)$$

$$ROOH + RH \longrightarrow RO\bullet + R\bullet + H_2O \qquad (3c)$$

$$2ROO\bullet \longrightarrow \text{non-radical products} \qquad (4)$$

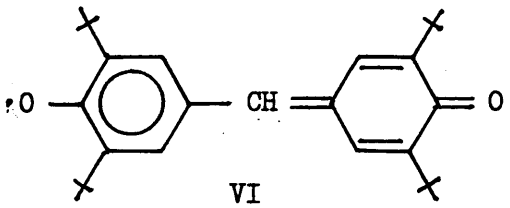
Chain-breaking antioxidants (InH) interfere with reaction (2). They may be radical species or conjugated molecules which scavenge peroxyl radicals. In most cases, however, they are inhibitors of the InH type, able to deactivate the propagating peroxyl (ROO•) radical, while giving rise to another, more stable radical In• which does not take part in chain-transfer and reacts by a different sequence of reactions:[42,43]

$$InH + ROO\bullet \longrightarrow In\bullet + ROOH$$

There are two types of chain-breaking antioxidants, namely chain-breaking acceptors and chain-breaking donors.

4.1 Chain-breaking acceptors

Antioxidants which act by oxidising or trapping alkyl radicals are generally inhibitors of polymerisation in the absence of oxygen. They include benzoquinone and aromatic nitro compounds, but the most important are the 'stable' free radicals, of which galvinoxyl (VI) and nitroxyl (VII) are the most effective[42,44].



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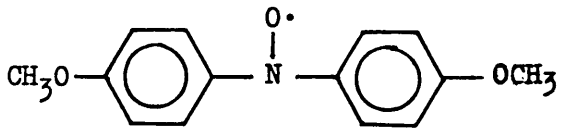

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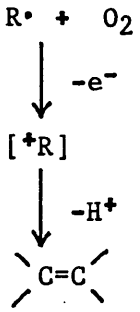
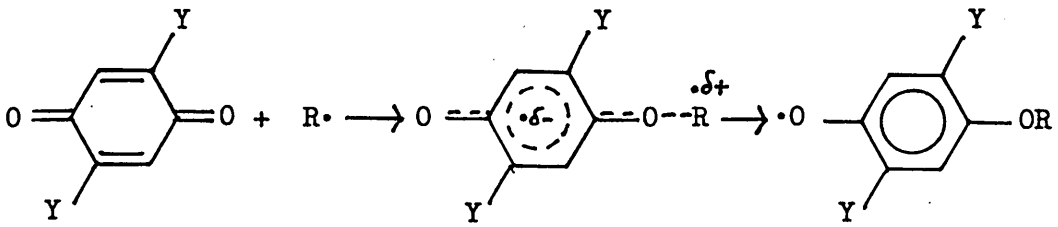
In the presence of an oxidising agent, the alkyl radical can be removed to give a carbonium ion and subsequent inert reaction products, such as olefins by elimination of a proton[44-46].



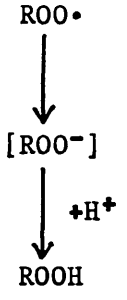
Macroalkyl radicals, unlike alkylperoxyl radicals, are not powerful oxidising agents, but they are themselves readily oxidised by electron acceptors[47].



Electron withdrawing and delocalising groups (Y) both increase the alkyl affinity and hence antioxidant affinity of quinones[45].

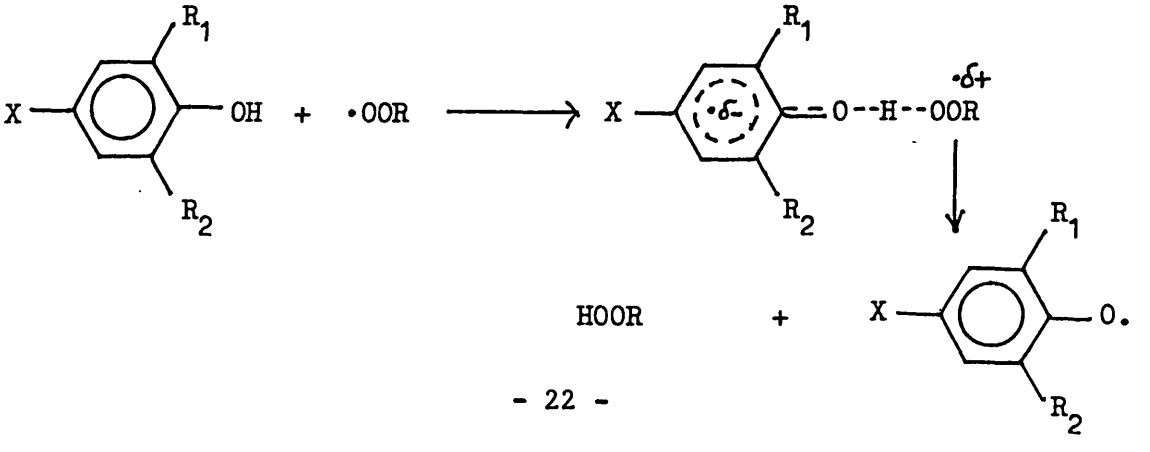
4.2 Chain-breaking donors

The two best known classes of commercial antioxidants are the hindered phenols and the aromatic amines. Both are able to donate a hydrogen to an alkylperoxyl radical, to give a hydroperoxide[45,46].



The chain-breaking donor mechanism is normally observed in hydrocarbons under ambient oxygen pressures, because the alkylperoxyl radical is the species present in the highest concentration in the polymer[45,46]. As the oxygen concentration is reduced, alkyl radical termination by the chain-breaking acceptor mechanism plays an important part.

The effect of substituent groups in the aromatic ring is to reduce the energy of the transition state, which involves electron transfer to the peroxyl radical and electron delocalisation in the aromatic ring[45,46].



The activities of phenolic antioxidants are strongly dependent on their structures. In the general case, the transition state involves both electron delocalisation and charge separation. Consequently, groups in the 2,4 and 6 positions, which extend the delocalisation of the unpaired electrons (e.g. phenyl or methyl), increase activity. Electron-releasing groups (R_2N, RNH, RO, R, etc) decrease the energy of the transition state and consequently increase the antioxidant activity, whereas electron-attracting groups (Cl, CN, COOH, NO_2, etc) decrease activity. The presence of at least one tertiary alkyl group in the ortho position is necessary for high antioxidant activity. Many of the most effective antioxidants are substituted in both ortho positions by tertiary alkyl groups. This steric enhancement of antioxidant activity is due to the increased stability of the derived phenoxyl radical which reduces the rate of the chain transfer reaction[44]:

$$A\bullet + RH \longrightarrow AH + R\bullet$$

5. TRANSFORMATION PRODUCTS OF ANTIOXIDANTS ARISING FROM THERMAL/OXIDATIVE PROCESSES

Phenolic antioxidants, used in long term stabilisation of polymers, are effective processing stabilisers for polyolefins and may be used without any other additive for that purpose. Originally, butylated hydroxytoluene (BHT) was the first choice of antioxidant to provide or to improve processing stability of polyolefins. Combinations of BHT with higher molecular weight phenolic antioxidants have been used quite extensively. Recently, BHT has been almost completely replaced by combinations of higher molecular weight phenolic antioxidants with

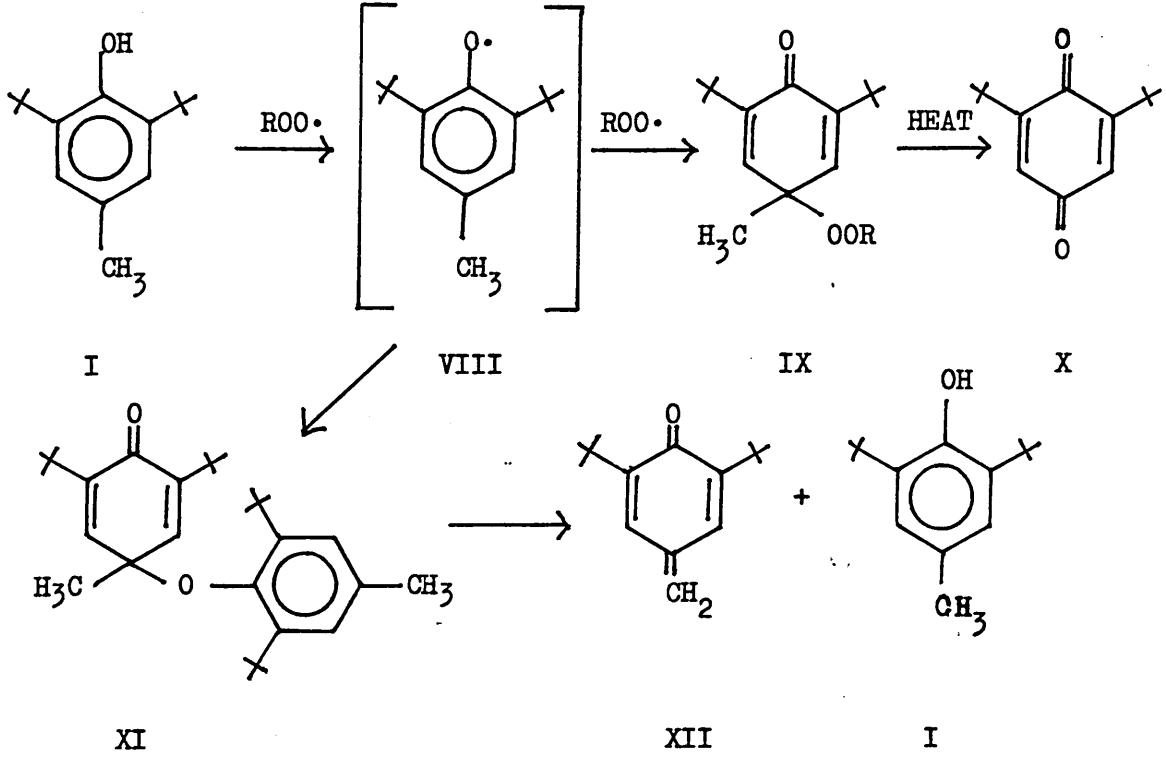
is that they are considerably less prone to discolouration[48].

The problem in stabilisation of polymers is the loss of additive either during processing due to thermal volatility or during ultraviolet exposure following migration to the surface of the polymer[49]. Since antioxidants are known to reduce oxidative degradation of polymers, either by reacting with oxygen in the melt, with polymeric radicals (alkyl, alkoxyl or alkylperoxyl)[50] or with peroxides, they would also be expected to reduce the production of volatile irritants (e.g. formaldehyde, acetaldehyde, formic and acetic acids) during processing. The addition of effective antioxidants strongly reduces the absolute amounts of degradation products during the induction period, but does not change their relative quantities[51].

Published information about the degradation of antioxidants of interest are reviewed below.

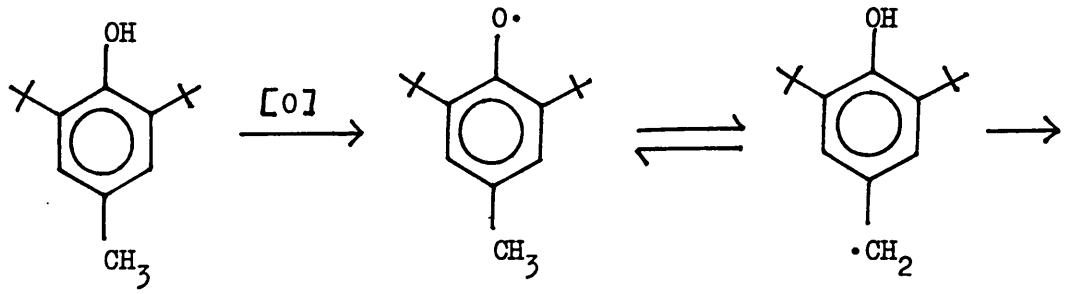
BHT (2,6-di-t-butyl-4-methylphenol) is a relatively volatile antioxidant and is therefore not used in polymers at high temperatures, due to its rapid physical loss.

BHT (I) initially reacts by hydrogen transfer with an alkylperoxyl radical, to give the aryloxyl radical (VIII). The addition of a second radical could give a peroxycyclohexadienone (IX), which under extrusion conditions will break down to 2,6-di-t-butyl-benzoquinone (X)[52-54]. Dimerisation of the aryloxyl radical results in a quinol ether (XI) being formed, which disproportionates to BHT and the quinone methide (XII)[33,55,56].

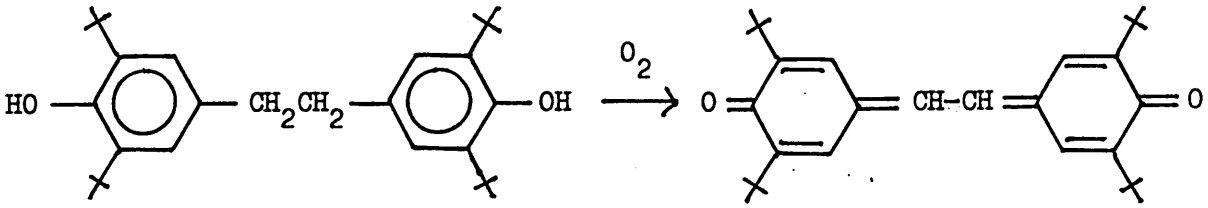


The quinone methide (XII) is highly reactive and readily undergoes further transformations[57-59].

Oxidation of BHT has been shown to yield 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl) ethane (XIII), which is able to react by the hydrogen transfer process (ie. ROO• + InH ⟶ ROOH + In•) to form 3,5,3',5'-tetra-t-butylstilbene-4-4'-quinone (XIV)[57,60-65]. It has been suggested that the dimerisation occurs via the corresponding benzyl radical, and that this radical is formed directly from oxidation of BHT[66,67].

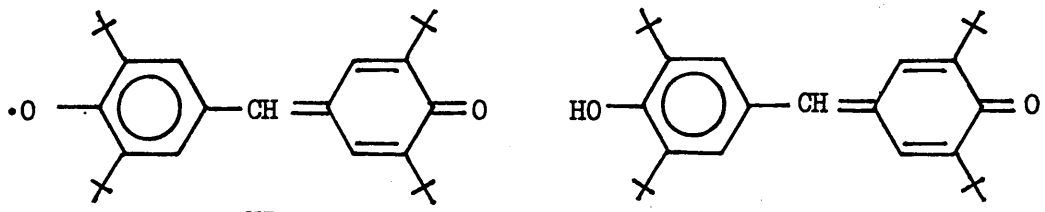


I



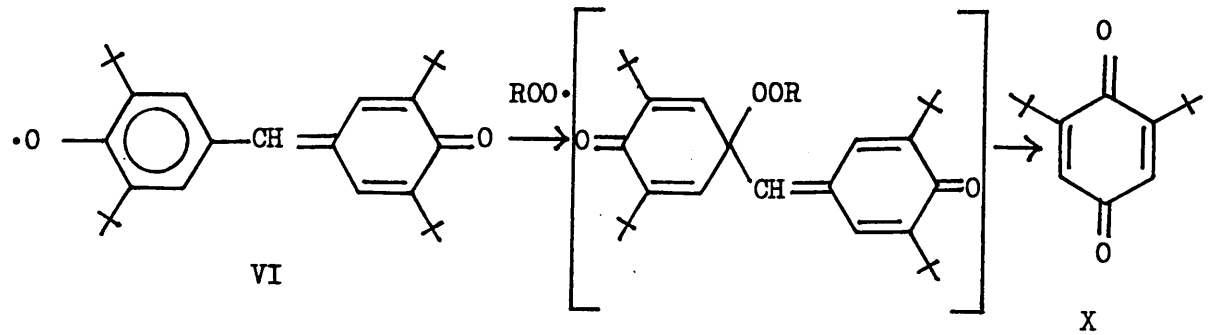
XIII XIV

The oxidation process also leads to the formation of the stable phenoxyl radical, galvinoxyl (VI).



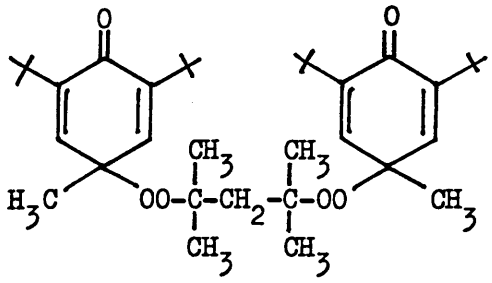
VI XV

When used at one tenth of the concentration of BHT, galvinoxyl is a more effective stabiliser than BHT[68]. Galvinoxyl is rapidly converted to the corresponding phenol, hydrogalvinoxyl (XV), in polypropylene during processing[69]. Galvinoxyl is a very much less efficient antioxidant than hydrogalvinoxyl in the presence of excess oxygen[70]. Gas chromatographic examination of extracts of processed polypropylene film showed the presence of 2,6-di-t-butyl-benzoquinone (X). It appears that galvinoxyl is irreversibly oxidised to X via a quinone intermediate, similar to that thought to be involved in the antioxidant action of a variety of hindered phenols[70].

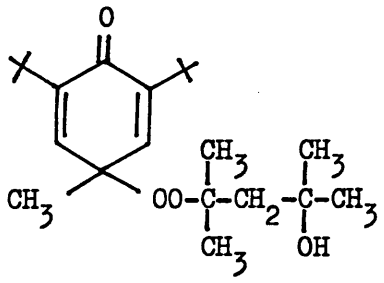


VI X

In the reaction of BHT with a bishydroperoxide (simulating polypropylene oxidised at the two closest tertiary carbon atoms), a more complicated process takes place, giving rise to the biscyclohexadienone derivative (XVI) and to 2,4-dimethyl-2-(1-methyl)-3,5-di-t-butyl-cyclohexa-2,5-diene-4-onylperoxy)-4-pentanol (XVII)[66].

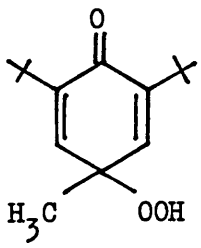


XVI

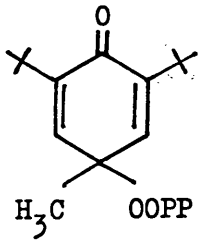


XVII

In a similar reaction, photo-oxidation of BHT gave rise to 2,6-di-t-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadienone (XVIII)[53,54].



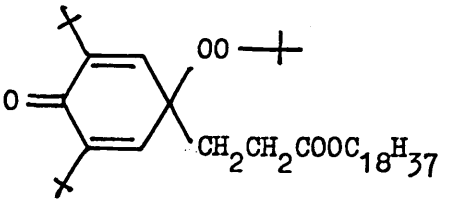
XVIII



XIX

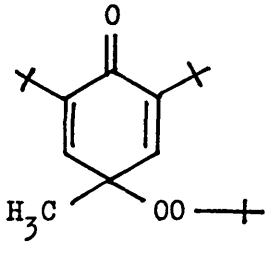
Oxidation of atactic polypropylene (PPH) was used in the preparation and characterisation of the hydroperoxide (PPOOH), from which radicals PPOO• were generated. Their interaction with BHT demonstrated transformations of the antioxidant, leading on the one hand, to peroxycyclohexadienone (PPOO-CHD, XIX) in which the aroxyl radical of BHT is bound to PPOO•, and on the other, to compounds resulting from the oxidative coupling of BHT; of these ethylene bisphenol (XIII) and stilbene-quinone (XIV) were identified[67].

The antioxidant-radical interaction proceeding in the stabilisation process involving Irganox 1076 was simulated by the reaction of Irganox 1076 (octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) (II) with t-butyl peroxyl radicals, modelling the oxidised skeleton of polypropylene. The reaction resulted in a 4-alkylperoxycyclohexadienone (XX) being formed[71-73].

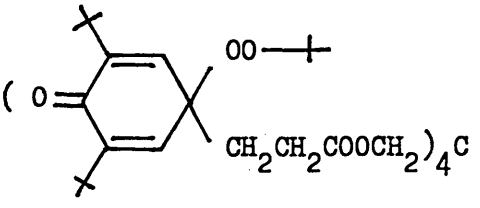


XX

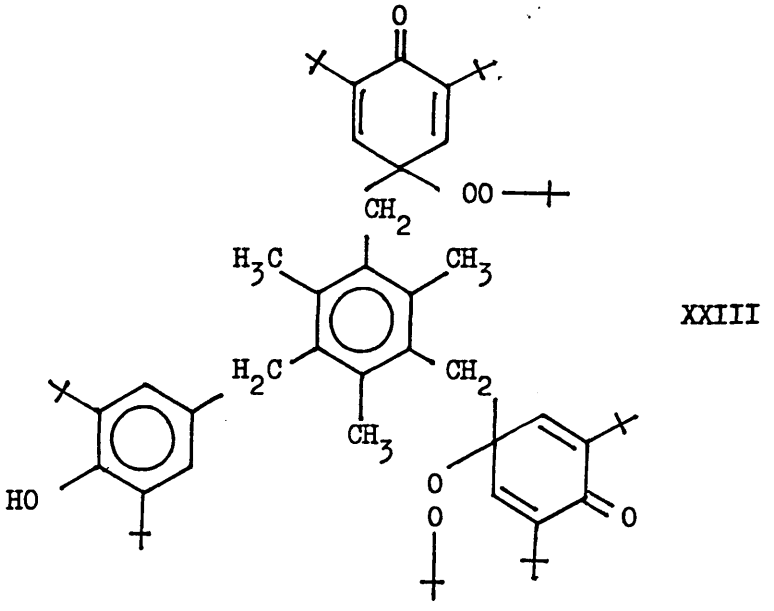
Compounds of this type were also found as oxidation products of the technically important antioxidants, BHT (as XXI)[64], Irganox 1010 (as XXII)[74] and Irganox 1330 (as XXIII) with partial oxidation and (as XXIV)[75-78].



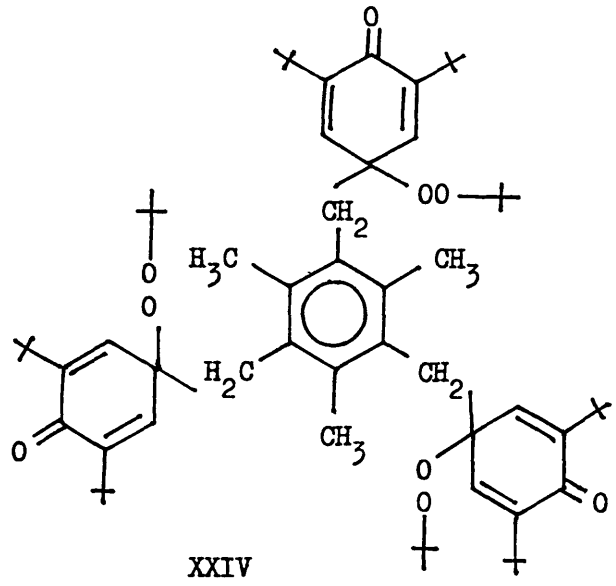
XXI



XXII



XXIII

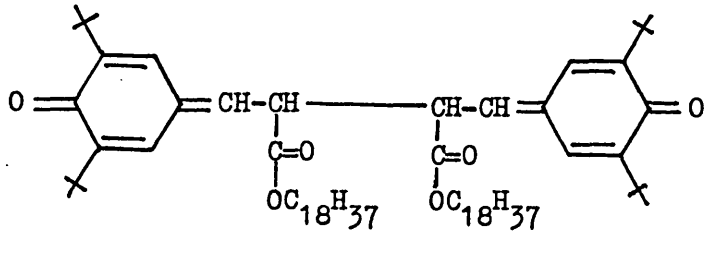


XXIV

The product, a 4-alkylperoxycyclohexadienone, is general for both simple and high molecular weight phenolic antioxidants, substituted in the positions 2 and 6 with t-butyl groups and in position 4 with the methyl group or a substituted methyl group[73].

The esters of octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionic acid are among the most frequently used antioxidants for polymers, because of their efficiency and non-staining properties. In contrast to BHT, other studies on oxidation products of Irganox 1076, 1010 and 1330 are sparse.

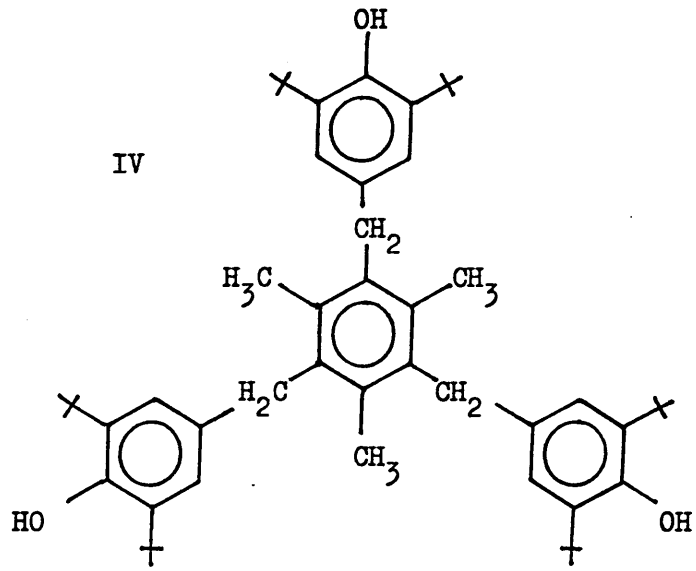
Oxidation of Irganox 1076 with potassium ferricyanide yields the dimeric oxidation product (XXV)[79,80].

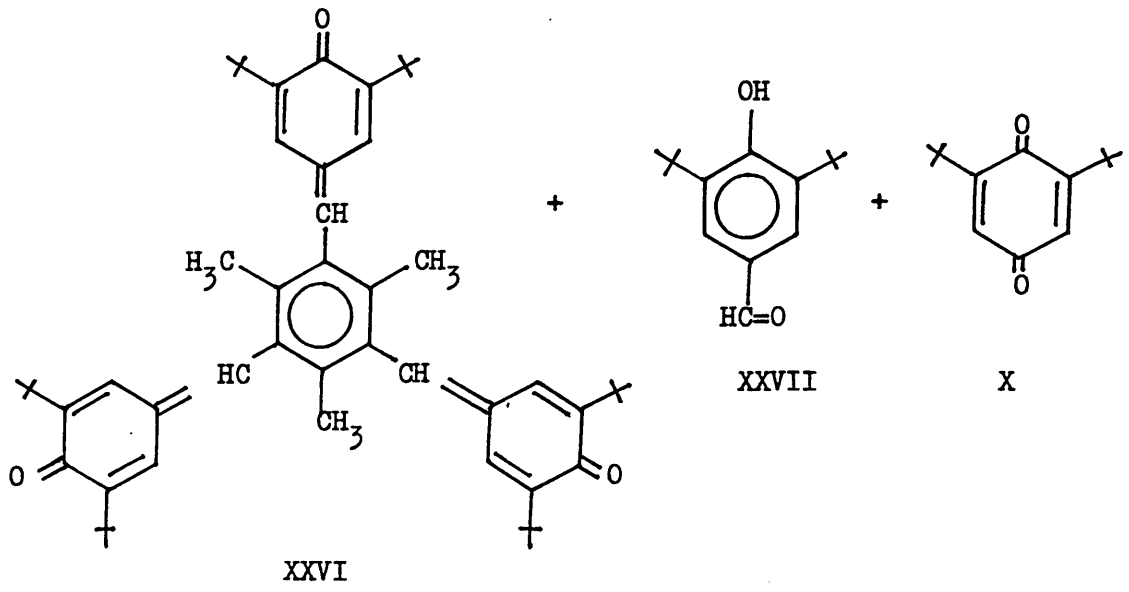


XXV

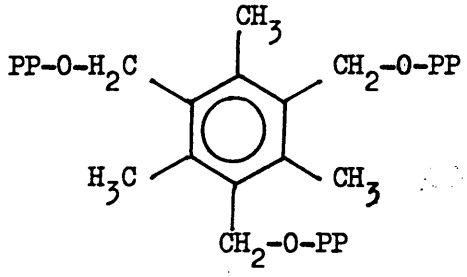
Thermal oxidation of Irganox 1010 revealed that at least two different decomposition products could be detected by thin layer chromatography, one absorbing at 280 nm (UV-re-emission maximum) (possibly aromatic) and one at 320 nm (possibly with quinoid character). However, the decomposition products have not yet been identified and therefore, not yet determined quantitatively[34].

Thermal oxidation of Irganox 1330 (IV) leads to the formation of quinone methide (XXVI), as well as 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXVII) and 2,6-di-t-butyl-benzoquinone (X)[75].

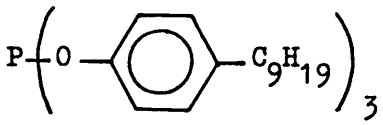




Thirteen products of oxidative degradation of Irganox 1330 have been identified in autoxidised polypropylene by mass spectrometry[76]. The possibility of chemical binding of antioxidant fragments to the polypropylene chain must be anticipated, as it had been demonstrated that part of the oxidised molecule of the antioxidant becomes bonded to the polypropylene molecule[77]. The antioxidant fragment could possibly be bound to polypropylene as follows[57]:



Organo-phosphorus antioxidants of the tri(nonylphenyl) phosphite (TNPP) type (XXVIII) have been used for many years as antioxidants.



XXVIII

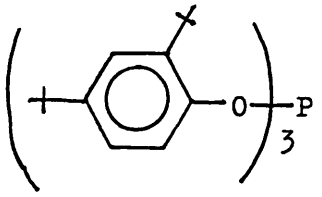
Their mode of action is to reduce hydroperoxides to alcohols by an ionic mechanism[81]:

$$ROOH + P(OR')_3 \longrightarrow RO^- + HO\text{-}P^+(OR')_3 \longrightarrow ROH + O{=}P(OR')_3$$

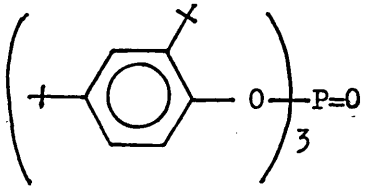
However, certain arylphosphites, in addition to their role in reducing hydroperoxides, are capable of acting as radical chain-terminating antioxidants, by reaction with peroxyl radicals to give aroxyl radicals[82-85].

$$RO\bullet + P(OAr)_3 \longrightarrow ROP(OAr)_2 + \bullet OAr$$

In the case of Irgafos 168 (V), the thermal degradation product arising from this antioxidant was tris(2,4-di-t-butylphenyl)phosphate (XXIX)[86].



V



XXIX

The mechanisms of organo-phosphorus antioxidant action and relationships between structure and efficiency are known far less than those of phenols[82-84].

This review has illustrated the reactions of antioxidants occurring during thermal processing, and the simulated reactions expected to occur by interaction of antioxidants with polymeric radicals during the service life of polymers. It may therefore be assumed that similar transformation products will be formed, by the effect of gamma-irradiation on the antioxidants present in the polymers.

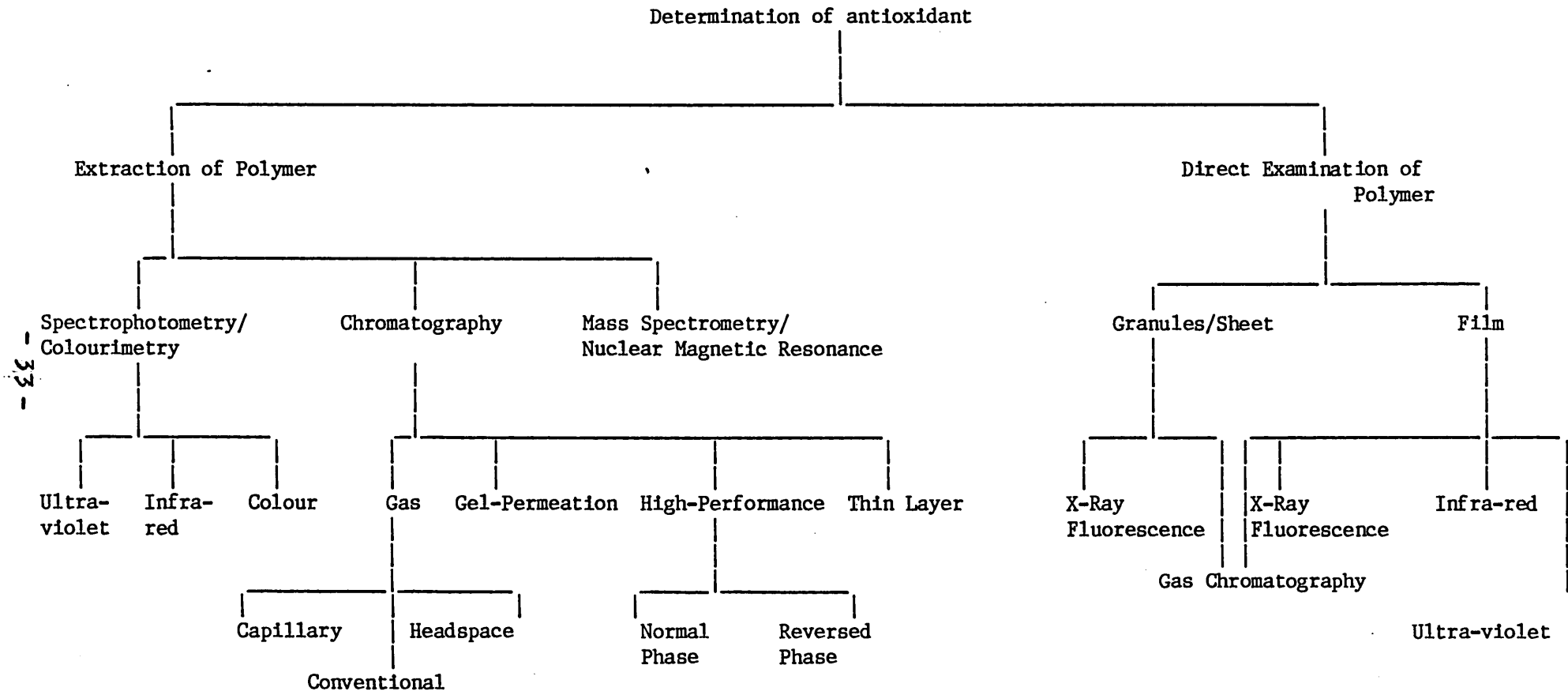
6. REVIEW OF METHODS FOR THE DETERMINATION OF ANTIOXIDANTS

Methods for the determination of antioxidants in polymers may be classified as shown in Table 1.2.

Few methods are available to determine the amount of antioxidant present in solid polymers without previous separation, therefore the

Table 1.2

Classification of Methods for the Determination of Antioxidants in Polymers



antioxidant must either be extracted from the polymer (e.g. by Soxhlet extraction) or the antioxidant and polymer completely dissolved in a solvent.

The preparation of samples for analysis by Soxhlet extraction is time-consuming[87] and there is the possibility of degradation of the antioxidant, however, this may be retarded by lowering the temperature during extraction[88]. Many methods do use Soxhlet extraction, but it does not allow protection of the antioxidant in the polymer with another synergic antioxidant in solution.

Complete dissolution of polymer samples for the determination of antioxidants is unique to gas and high performance liquid chromatography, where only small amounts of sample are required, thereby reducing the amount of polymer injected on the analytical column.

Difficulties in identifying and determining polymer additives arise from three factors:

i) the high reactivity and low stability of the antioxidants,

ii) the low concentrations (0.1 - 1.0%) at which they are present, and

iii) the relatively insoluble polymer matrix.

i) and ii) require careful handling of the extracts for quantitative work[89]. The involvement of many steps in extraction procedures leads

to a reduction in the amount of antioxidant, the extent of which is difficult to control reproducibly. Use of a suitable internal standard in chromatographic determinations helps to improve the precision of the analysis, in relation to extraction as well as to injection technique[90].

A typical extraction procedure for polyvinyl chloride would be to dissolve the sample, then precipitate out the polymer, evaporate the filtrate to dryness and reconstitute before injecting into a chromatographic system[91]. When applied to polypropylene, hot decalin has been used to dissolve the polymer, which on cooling precipitates out. This method is not very efficient at removing polymeric material, as the filter becomes partially clogged with low molecular weight oligomers and has to be regenerated[92].

6.1 Spectrometric and Colourmetric Methods of Analysis

Spectrometric methods assume that the identity of the antioxidant is known and that it is the only one present in the polyolefin under test[93,94]. Measurement of UV absorption provides an excellent means for quantifying the phenolic antioxidants, which give rise to the characteristic π-π^* transitions.

Ultraviolet (UV) and infrared (IR) spectroscopic methods are routinely used for quality control of thin film samples, but both antioxidants and UV stabilisers or two antioxidants with overlapping absorption bands in the UV and IR spectra may be present in the polymer[95-97]. More recently, derivative spectroscopy has been shown to reduce the interference due to light scattering and matrix effects in the

determination of BHT in polypropylene[98]. Use of IR spectroscopy allows determination of additives directly in the polymer by examining thick films, solid or melt[99]. Direct film analysis is used when there are additives with strong spectral characteristics, e.g. BHT. The advantage of these methods is that they do not require a separation stage[100].

Colourimetric methods depend on the phenolic and reducing properties of the antioxidant, and are applicable to both raw and cured polymers. Such methods cannot differentiate between mixtures of antioxidants - only the total antioxidant present is estimated.

One such method involves the use of the least specific oxidising agent, ferric chloride, and in this study it was found that the sensitivity of each antioxidant to ferric chloride differs[101]. Obviously, any other compound capable of reducing ferric iron will interfere. Another procedure involves coupling diazotized p-nitroaniline with the antioxidant extract. The solution is then made alkaline and the visible absorption spectrum is determined. However, the method is not applicable to highly oxidised samples or to phenolic antioxidant mixtures, because oxidised antioxidants couple differently or not at all - depending upon the extent of oxidation[102]. Yet another method involves extraction of the antioxidant from the polymer before adding nickel peroxide. The higher sensitivity of the UV procedure enables identification to be made with much smaller samples than would be required for IR. The method also employs thin layer chromatography to separate the residues before adding nickel peroxide[103].

6.2 Voltammetric and Coulometric Methods of Analysis

Cyclic voltammetry and controlled-potential coulometry have been used in attempts to determine oxidation potentials. In addition to the mechanistic and analytical information derived from this investigation, the oxidation potentials give some indication of the relative ease of oxidation of the members of the Irganox series. Previous studies have reported attempts to correlate oxidation potentials with the effectiveness of phenols as antioxidants[104]. Cyclic voltammetry is unlikely to be useful analytically.

6.3 Thin Layer Chromatographic Methods of Analysis

Thin layer chromatography (TLC) has been used in the separation and determination of antioxidants more extensively than any other technique. The reason for this includes its simplicity and low cost. However, it does not have the ability to identify degradation products - tentative confirmation of the identity is made by development of a further aliquot of the sample solution together with an authentic specimen of the suspected compound.

Problems with variations in the R_f value may be due to extreme conditions of relative humidity of the atmosphere; excessively high or low concentrations of the antioxidant; and/or the presence of significant amounts of low molecular weight polymer[105]. It must be noted that the number of chromatographic spots is dependent on purity of a compound and may vary from batch to batch. TLC is a rapid method of analysis (results within three hours instead of one day or longer)[106].

sufficiently high state of purity to enable identification by spectroscopic methods[107,108]. It has been used for identification of an oxidation product of BHT[109]. TLC, however, is usually now carried out when only some preliminary separation of non-volatile materials is required for mass spectrometric examination, or to provide confirmatory or supplementary analytical evidence. Spots to be submitted for the mass spectrometric examination can usefully use methanolic iodine as the colour-developing reagent, as it does not over-complicate the mass spectrometry[100].

6.4 Gas Chromatographic Methods of Analysis

The attraction of gas chromatography (GC) lies in its ability to separate and determine nanogram amounts of complex mixtures simultaneously. One of the most important factors in the GC-analysis of phenols is the choice of suitable solid supports. As the phenolic antioxidants are relatively non-volatile, low stationary phase loadings are necessary to reduce the retention time to a sensible value. Adsorptive properties and catalytic activity of the support not only limits the use of some liquid phases, but also decreases the accuracy of quantitative analysis.

Gas chromatography with a flame ionisation detector (FID) is readily used in the determination of some antioxidants - both without[90,110] and with extraction from the polymer[87,90,110-113]. A method for phenolic antioxidants which does not involve an extraction step uses a modified

polymer. The evaporated antioxidant is then concentrated on a cold part of the column, and the residual polymer sample is removed[110].

In GC analysis, modern stationary phases operated at high temperatures permit the elution of relatively high molecular weight additives. Nevertheless, the high molecular weight and polarity of many antioxidants and UV stabilisers often precludes the use of GC. Therefore, derivatisation and/or degradation to produce more volatile species has been used. For example, acid-catalysed transesterification using methanol with antioxidants has been applied to the relatively large antioxidant molecule, Irganox 1076, enabling determination by GC[114].

GC, when coupled to a mass spectrometer, appears to be one of the few techniques able to allow both separation and characterisation of additives,[97,115] and is now widely used for this purpose.

Capillary GC may also be used for the determination of additives. If on-column injection is combined with the high resolution of capillary columns, semi-quantitative analysis can be completed in a very short period of time. Nevertheless, there are problems in accurate quantitative analysis due to injection splitting problems, using conventional capillary GC. Capillary GC is used when very complex mixtures need to be analysed. However, this is not usually the case for antioxidants, as only two or three additives are commonly present in the same polymer.

6.5 High Performance Liquid Chromatographic Methods of Analysis

High performance liquid chromatography (HPLC) is a simple, sensitive and rapid method of analysis; offering all the advantages of GC, and in addition, the increased flexibility of a liquid mobile phase. With a suitable detection system, it allows accurate determination of the components of a mixture of degradation products of the additives and the presence of other extractable constituents can also be detected[116].

Partition chromatography involves two types of phases, normal and reversed-phase. Normal phase employs mobile phases consisting of hydrocarbons and a small amount of a more polar solvent with a polar stationary phase, whereas reversed-phase employs aqueous mobile phases with varying concentrations of water-miscible organic solvents with a non-polar stationary phase. Methanol is the most commonly used organic solvent in reversed-phase, since it is relatively cheap. Mobile phases of low refractive index are only required for refractive index (RI) detectors[117].

The use of a reversed-phase guard column before the analytical column, when analysing polymer extracts, takes advantage of the strong interaction between the stationary phase and the polymeric material and thus polymeric material is effectively removed by the guard column[118]. There is a problem of precipitation of the polymer from the extracts in the injection ports, but this can be easily avoided by the use of a slightly different mobile phase[117].

Analysis of complex mixtures of additives from polymer pellets has been reported to be more reliable by HPLC than by conventional spectroscopic techniques. However, HPLC methods are more lengthy and require solvents with a higher purity than those employed in spectroscopic methods[96]. Identification is based on a comparison of peak retention times or capacity factors with those of known standards. Errors may arise when not all the suspected compounds are available for comparison, and also due to chemical similarity of many compounds and the relatively poor separating ability of HPLC (compared with capillary GC)[119]. One method involves the use of a gradient-elution mobile phase, in which thermal and photochemical transformation products of certain antioxidants are eluted and detected - but only two products have been identified[120]. Conventional LC detectors are not very specific in the information that is obtained for eluted peaks. However, when used in conjunction with mass spectrometry, the identity of the eluted compound can be obtained.

No HPLC methods for antioxidants using diode array detectors to aid identification have been found to date.

Gel permeation chromatography (GPC) (size exclusion chromatography SEC) is an extension of HPLC and offers good routine monitoring techniques, but separation on older columns takes approximately three hours, although much shorter separation times can be achieved with more modern columns. GPC is limited severely in the number of components which can be resolved, since many additives are of similar molecular size. It employs a single mobile phase and retention times are reproducible. However, resolution is poor and sensitivity using conventional RI detection is low due to both broad peaks and the high refractive index

of the mobile phase. Nowadays, other detectors such as ultraviolet or fluorescence may be used to overcome these problems.

GPC is used for analysis of relatively high molecular weight additives and their decomposition products. There is a limitation on sensitivity, which has been established to be due to sample size, because of peak broadening due to viscosity effects[121]. Difficulties arise in GPC when complex mixtures are analysed and the elution peaks of some components overlap. If analysis is carried out on a mixture of compounds obtained by extraction from an aged polymer, oxidation and decomposition products of additives makes quantitative determination impossible[122].

6.6 Mass Spectrometric Methods of Analysis

Mass spectrometry (MS) may be used for the identification of additives in polymers. It has a number of features and advantages:

i) the amount of sample needed is small,

ii) relative molecular weights can usually be obtained directly from the spectra, and

iii) mixtures can be analysed (when MS is coupled to GC or LC)[123,124].

It does have the ability to distinguish between closely related compounds of differing relative molecular mass (rmm). However, the presence of large amounts of low rmm oligomers from polymers such as

polyethylene and polypropylene can cause interference by producing a high hydrocarbon background extending to several hundred relative atomic mass units. In this case, TLC can be used as a clean-up procedure.

The use of GC-MS is to separate and identify complex mixtures of components that are extracted, and pyrolysis GC-MS is of particular value when minor components need to be identified[100]. Recent advances have involved the use of a mass spectrometer as a detector for HPLC. This technique may be used in series with a UV detector, so as to measure absorbance amd mass spectrometric detection on eluted chromatographic peaks.

Computerised data manipulations such as background subtractions, spectrum averaging and construction of mass chromatograms provide new capabilities for detecting and identifying partially resolved and minor components by LC-MS[123]. Computerised MS is able to compile data for pattern recognition applications and a retrieval library search on the spectrum of interest[124].

Use of chemical ionisation (CI) MS has been reported for the determination of additives in polypropylene without prior separation. The additives are vaporised from the polypropylene sample in a heatable glass probe (heated from 30°C to 350°C at 20-30°C/min) and ionised under CI conditions using a low-energy proton transfer reagent (ammonia). The heatable glass probe is placed into the source of the MS, modified for CI operation. The additive begins to vaporise rapidly from the sample when the probe temperature reaches 175-180°C, approximately the melting point of the sample of polypropylene.

However, care must be taken to ensure that the bulk of the decomposition products of polypropylene do not contaminate the metal surfaces in the accelerator region of the mass spectrometer. This application of ammonia CIMS follows extensive use in the characterisation of many types of organic compounds. Because of its high proton affinity, ammonia frequently gives very simple CI spectra consisting of $(M+H)^+$ and/or $(M+NH_4)^+$ ions with very little fragmentation[126], but unfortunately less structural information may be deduced as a consequence.

The flexibility and widespread availability of reversed-phase columns and variable wavelength UV detection makes HPLC an obvious choice in the determination of both low and high molecular weight antioxidants.

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CHAPTER 2

DEVELOPMENT OF EXPERIMENTAL METHODS

1. EQUIPMENT, REAGENTS AND SAMPLES

The equipment used in this investigation is described below.
Gas chromatographic analyses were carried out using a Perkin-Elmer instrument (model 8310B) with graphics printer (Perkin-Elmer, model GP-100). The column used was a 6' x 1/8" i.d. stainless steel column packed with 10% OV-275 on Chromosorb WHP 80/100 mesh (Chrompack, Batch No. 1617-4). An injection volume of 0.2 µl was used for all standards and samples. Quantification was carried out by measuring peak-height or peak-area ratios.

The high performance liquid chromatographic system (HPLC) consisted of a pump (model 302, Gilson), a manometric module (model 802, Gilson), a sample injector (model 7125, Rheodyne) and an ultraviolet-visible detector (model HM/HPLC, Gilson Holochrome), set at a sensitivity of 0.1 AUFS and a 10 millivolt range single pen recorder (Omniscribe, Houston Instruments). Injection volumes of 5-10 µl were used for the extracts of standards and samples. Quantification was carried out by measuring peak-height ratios. Sample extracts were filtered through nylon-66 filters (0.45 µm), which fitted into the 13 mm sample filtration unit, supplied by Anachem Ltd. The column was a reversed-phase analytical column (25 cm x 4.6 mm i.d.) slurry-packed with Spherisorb ODS (10 µm), supplied by Jones Chromatography. The

analytical column was protected by a small guard column (5 cm x 4.6 mm i.d.) dry-packed with Lichroprep RP-18 (25-40 μm), supplied by Anachem Ltd. Throughout the migration studies, two additional columns were used, namely an analytical column (10 cm x 4.6 mm i.d.) slurry-packed with Spherisorb S5 ODS1 (5 μm), which was sometimes protected by a small guard column (2 cm x 4.6 mm i.d.) dry-packed with Spherisorb S10 ODS1 (10 μm). Both columns were supplied by Phase Separations.

The liquid scintillation counter was an LKB-Wallac RackBeta (model 1212), operating in mode 2 for ^{14}C. The count time was set at 60 seconds and the counts were recorded in counts per minute (cpm). The counter used for the solid polymers was a Mini-Monitor G-M tube, series 900 model EL (soft betas). The window of the tube was encased in a lead oven of set geometry, 1 cm away from the samples. The counts per second were recorded every five seconds for two minutes. Counts were made on at least four samples, and the mean values were calculated.

Infra-red spectra were recorded using a Perkin-Elmer model 783, scanning from 4000 cm^{-1} to 200 cm^{-1} in six minutes. Ultraviolet spectra were recorded using a Unicam model SP800A. Electron impact mass spectra were recorded using a VG Micromass model 30F. ^{1}H and ^{31}P n.m.r. spectra were recorded using Bruker WP 80SY and AM 250 spectrometers. Samples were dissolved in deuteriochloroform. ^{1}H chemical shifts were recorded on the δ scale, using tetramethylsilane as internal standard (δ=0 ppm). ^{31}P chemical shifts were similarly recorded with respect to 85% orthophosphoric acid as external standard. Shifts to high field are negative in sign.

Sheets of polystyrene containing various additives were prepared using a Churchill-Rapra Torque Rheometer (model TR-1), with a mixing temperature of 130°C, a mixing time of 7 minutes, a mixing pressure of 5 bar and a rotor speed of 35 rpm.

The bench top centrifuge was an MSE Centaur 2 obtained from Fisons. Preparative layer chromatography was carried out using plates supplied by Merck, (TLC plates, silica gel 60 F_{254} precoated for preparative layer chromatography. 20 x 20 cm, with a layer thickness of 2 mm).

Equipment used by the NATEC Institute (für naturwissenschlaftlich-technische Dienste GmbH), Hamburg, for the preparation of polypropylene and high-density polyethylene sheets: Plasticorder, model GNF 106/2 with extruder fitting, type 20D, Brabender OHG, Duisberg, (FRG). Stranggranulator (strand granulator), type SG5; Condux-Werke, Wolfgang b. Hanau (FRG). Film moulding press: Johs. Krausse, Maschinenfabrik Hamburg (FRG), subsequently modified. Liquid scintillation spectrometer (Betaszint BF5000, Laboratorium Prof. Dr. Berthold, Wildbad (FRG).

The reagents and samples used throughout this investigation are itemised below.

The following were supplied from Aldrich Chemical Company Ltd: acetonitrile (99%), benzene (99+%, thiophene free), 2,6-di-t-butyl-1,4-benzoquinone (98%), 3,5-di-t-butyl-4-hydroxybenzaldehyde (99%), ethanol (HPLC grade), ferric chloride hexahydrate (laboratory grade),

galvinoxyl free radical [2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)p-tolyloxy, free radical], iso-octane [2,2,4-trimethylpentane] (HPLC grade), magnesium sulphate anhydrous (technical grade) and tetralin [1,2,3,4-tetrahydronapthalene] (99%).

The following were supplied from BDH Chemicals Limited: acetone (reagent grade), butylated hydroxytoluene (BHT) [2,6-di-t-butyl-4-methylphenol], chloroform (laboratory grade), ether (laboratory grade), low density polyethylene (LPDE) powder, high density polyethylene (HDPE) pellets, potassium ferricyanide (99%, GPR), Scintran Cocktail 0 (toluene based scintillation cocktail) and Scintran Cocktail T (aqueous based scintillation cocktail).

Nitrogen (oxygen free) and ammonia gas were supplied by BOC. Hexane (spectrograde) was supplied by Fisons PLC. Ethyl acetate and methanol (both of HPLC grade) were supplied by Koch-Light Ltd. Manganese dioxide (commercial grade) was supplied by Hopkin and Williams Ltd. Tertiary-butylhydroperoxide (70% aqueous), cyanuric chloride [2,4,6-trichloro-1,3,5-triazine] (98%), octanethiol (98%) and potassium t-butoxide were supplied by Lancaster Synthesis Ltd. Glacial acetic acid (99.6% min., laboratory grade) and sodium sulphite (95% min., laboratory grade) were supplied by May and Baker Ltd. Biphenyl (GPR) was supplied by J. Preston Ltd. The synthetic test fat HB 307 and polypropylene (HF 22) were supplied by ICI, Chemicals and Polymers Group. Polystyrene and polyvinyl chloride (Breon S110/10) were supplied by Diamond Shamrock UK Ltd. Tetrahydrofuran (THF) was collected from a glass still following drying over potassium. Water was freshly double distilled from a Fi-stream unit.

Irgafos 168 [tris- [2,4-di-t-butylphenyl) phosphite], Irganox 565 [2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-t-butylphenylamino)-1,3,5-triazine], Irganox 1010 [tetrakis (methylene 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane], Irganox 1076 [octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] and Irganox 1330 [1,3,5-trimethyl-2,4,6-tris(3',5'-di-t-butyl-4-hydroxybenzyl) benzene] were supplied by Ciba-Geigy Industrial Chemicals.

All of the above were used as supplied.

2. A GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF BHT IN POLYVINYL CHLORIDE AND POLYSTYRENE

Although many gas chromatographic methods were available in the literature [1-9] for the determination of BHT, none of them involved the use of an internal standard, for the quantitative analysis of whole polymers. In order to eliminate any errors incurred as a consequence of irreproducible injection techniques, a method was developed in which an internal standard was used. Furthermore, the whole polymer could be completely dissolved, thus correcting for inefficient extractions. However, this dissolution procedure was only applicable to the more readily soluble polymers, such as polyvinyl chloride and polystyrene.

2.1 Chromatography

The GC unit and column were as described in Section 1. The column was maintained at 170°C, the injector and detector temperatures were maintained at 200°C. The carrier gas was nitrogen, at a flow rate of 25 ml min^{-1}.

2.2. Procedure

Samples of polyvinyl chloride or polystyrene (100.0 mg) were placed in glass volumetric flasks (10 ml) with ground glass stoppers. The samples were dissolved in THF (ca.9 ml) and the internal standard (biphenyl) was added (1.0 mg in 10 µl THF). The samples were left overnight to dissolve at room temperature, in the dark and under nitrogen. The solutions were made up to volume with THF, before being chromatographed.

2.3 Calibration

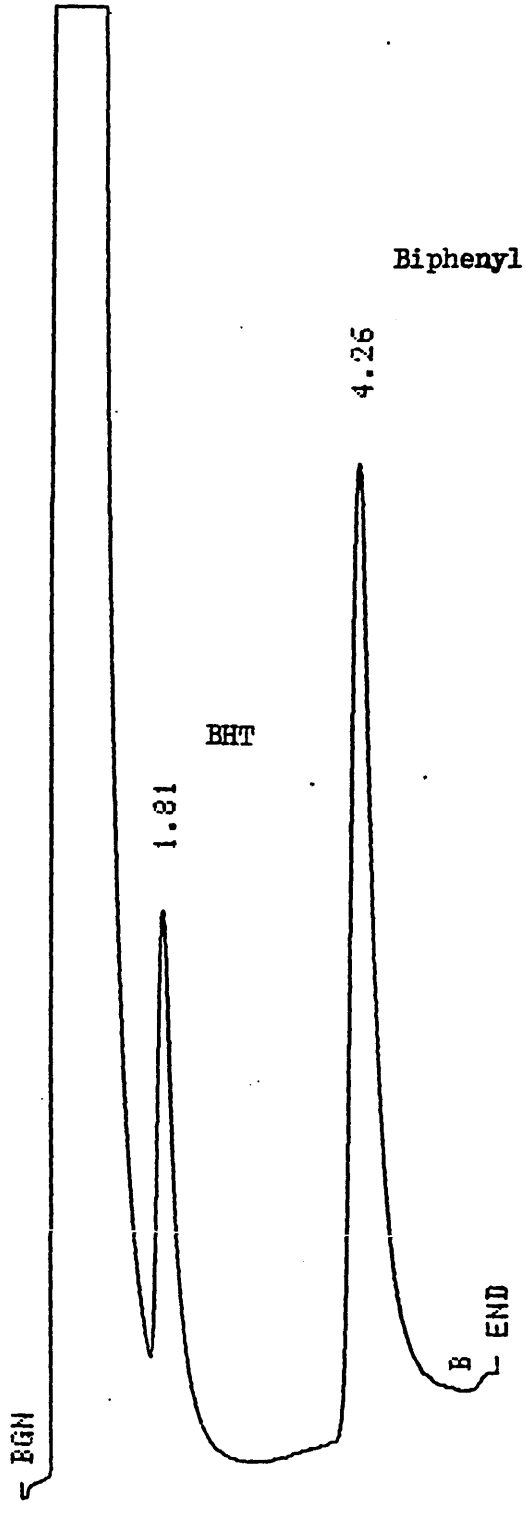
Blank polyvinyl chloride and polystyrene were spiked with known amounts of BHT (0-500 µl of a 10 mg ml^{-1} solution in THF) and the above procedure was followed. The blank polymers provided clean chromatographic traces in the regions of interest (retention times of BHT and internal standard were 1.8 and 4.3 minutes, respectively), (Figure 2.1). The calibration graphs were linear, with high values for the regression coefficients. Using 100 mg of polymer, the detection limit for BHT was about 5 µg ml^{-1} in the injected solution (0.05% in the original polymer).

2.4 Reproducibility

The reproducibility of the method was investigated by analysing ten replicate samples of unirradiated polyvinyl chloride nominally containing 1% of BHT, and blank polyvinyl chloride spiked at 1% BHT. The resulting within-batch relative standard deviations of peak-height ratios of BHT to the internal standard were 6.6% and 1.3% for the

Figure 2.1 A typical GC trace of polyvinyl chloride containing

BHT at 1%, before irradiation



milled and spiked samples, respectively. The higher value for the milled samples indicated the heterogeneous distribution of BHT within the polyvinyl chloride matrix.

3. A HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF IRGANOX 1010,1076,1330, AND IRGAFOS 168 IN POLYMERS.

A reversed-phase HPLC method has been developed for the higher molecular weight antioxidants, allowing the determination of any of the antioxidants using another as the internal standard. Where possible, the use of an internal standard was preferred in the procedure, in order to correct for any losses incurred during extraction and during the concentration stage, since the reduced final volumes were subject to variation and unknown quantities would be injected.

This HPLC method appeared to offer advantages over available methods [5, 10-25] in that it was applied at ambient temperature; it involved the use of an internal standard and the system was eluted isocratically.

3.1 Chromatography

The HPLC instrument and columns were as described in Section 1. The columns were maintained at ambient temperature and were eluted with a mixture of ethyl acetate: methanol: water (50:40:8 v/v) that had been purged with helium. With a flow rate of 2 ml min^{-1}, the pressure was approximately 4000 p.s.i. The detecting wavelength was set at 275 nm.

3.2 Calibration

Blank polyethylene pellets were spiked with known amounts of the antioxidant to be determined (0-100 µl of a 50 mg ml^{-1} solution in chloroform) and the proposed procedures were followed in Section 6, (Figure 2.2). The blank polymers provided clean chromatographic traces in the regions of interest, (see below). All calibration graphs were linear, with high values for the regression coefficients. Other blank polymers were spiked with a known amount of the antioxidant, to determine the effect on recoveries of different polymeric matrices. Acceptable recoveries of 105% and 111% for polypropylene and polyvinyl chloride were found.

Antioxidant	Capacity ratio k'	Limit of detection (% in polymer)
1010	0.50	0.005
1330	0.69	0.005
565	1.05	
1076	1.51	0.10
168	1.99	0.005

Where $k' = \frac{t_R'}{t_m}$

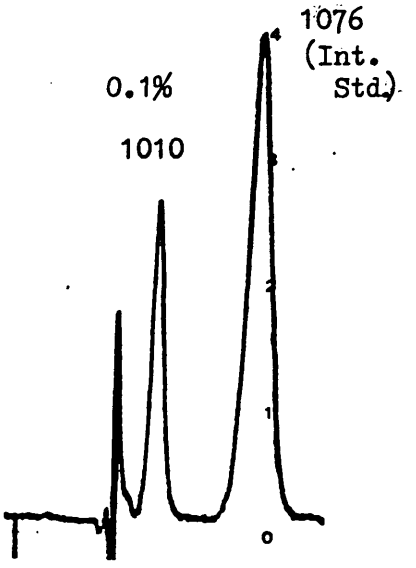
t_R' = the adjusted retention time (min) = $t_R - t_m$

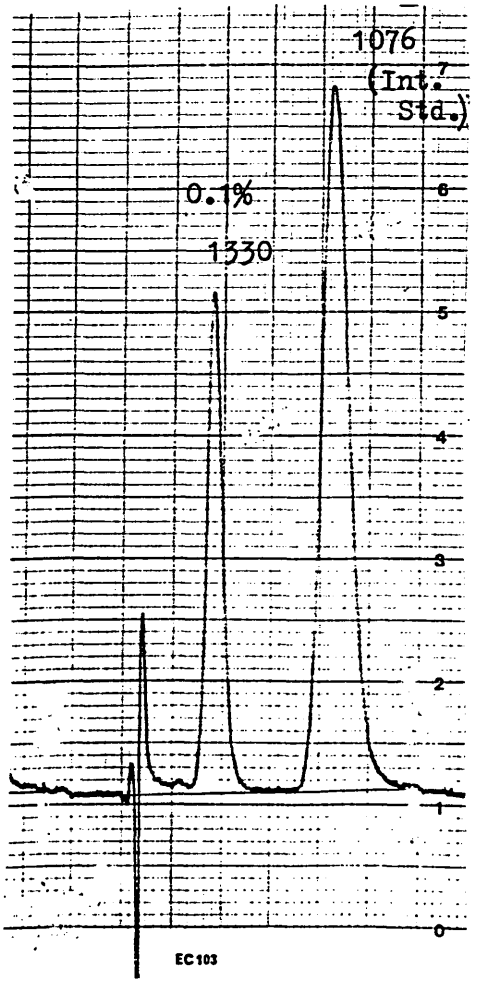
t_m = time for solvent front to appear (min)

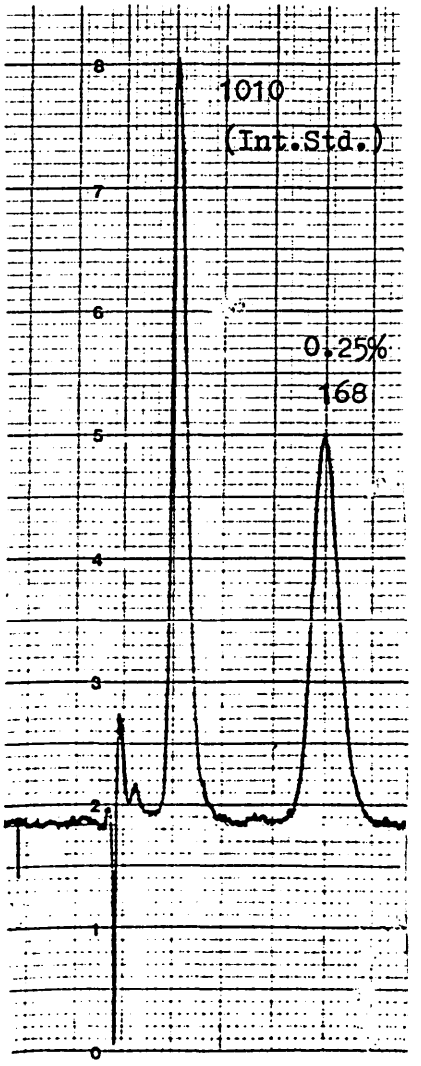
t_R = retention time (min)

The lowest calibration standards gave peak-heights of several times the baseline noise.

Figure 2.2 Typical HPLC traces for polypropylene spiked with antioxidants and their relevant internal standards







3.3 Reproducibility

The reproducibility of the method was investigated by analysing ten replicate samples of blank polyethylene pellets spiked at 0.5% Irganox 1076, and blank polypropylene pellets spiked at 0.1% Irganox 1010, 0.1% Irgafos 168 and 0.1% Irganox 1330. In addition, ten replicate samples of unirradiated polymers were analysed.

	% RSD		% RSD
Spiked Irganox 1330	1.33%	PP/1330/0.1/0	2.35%
Spiked Irgafos 168	1.85%	PP/168/0.1/0	2.03%
Spiked Irganox 1010	3.45%	PP/1010/0.1/0	5.70%
Spiked Irganox 1076	1.06%	PE/1076/0.5/0	3.82%

The resulting within-batch relative standard deviations (RSD) of peak-height ratios of the antioxidants of interest to the internal standard were acceptably low.

3.4 Determination of a synergistic mixture of Irganox 1010 and Irgafos 168 in polypropylene

In the search for an internal standard in the determination of both Irganox 1010 and Irgafos 168, Irganox 565 seemed ideally suited, eluting between 1010 and 168. Calibration of 1010 and 168 was performed on unirradiated blank polypropylene pellets and the results were acceptable (i.e. the graph was linear and a high value for the regression coefficient was obtained). However, the method did not

permit the use of this internal standard in the analysis of irradiated polymers, as Irganox 565 was itself destroyed under these conditions and the degradation products formed were likely to interfere with the determination of both Irganox 1010 and Irgafos 168. Therefore, calibration of 1010 and 168 in polypropylene was performed by the external standard method and relied upon reproducible extraction, concentration and injection techniques.

Further investigations of the interation of Irganox 565 with irradiated polymers, and the degradation products thereof, will be described in Section 7.

4. PREPARATION OF POLYMER SAMPLES PRIOR TO GAMMA-IRRADIATION

Numerous types of polymers have been used throughout this investigation. The polymer compositions, however, have been kept as simple as possible, whilst reflecting commercial reality in terms of the level of antioxidant present. The polymer samples have been grouped according to the supplier and their mode of preparation is described below.

Lankro Chemicals Ltd

Polyethylene and polypropylene sheets each containing either Irganox 1076, 1010 or 1330, at an initial level of 0.5%, were prepared by hot-milling. Two samples of polyvinyl chloride were prepared containing 1% and 5% BHT, and two additional samples each containing Irganox 1076 or

1010 at an initial concentration of 0.5% were also prepared by hot-milling. The sheets were cut up into small pieces prior to irradiation.

ICI

Unstabilised polypropylene (homopolymer) powder, polypropylene stabilised with either Irganox 1010, 1330 or Irgafos 168 at an initial level of 0.1% and a synergistic mixture of both Irganox 1010 and Irgafos 168, each at an initial concentration of 0.1%, were supplied as raw powder mixes and milled samples (which were prepared by conventional hot-milling or sintering to produce small pellets). In addition, homopolymer and copolymer types of polypropylene containing 0.5% Irganox 1076 were prepared by sintering to produce small pellets. Thin sheets of both homopolymer and copolymer types of polypropylene containing either Irganox 1076 or 1010 at an initial concentration of 0.25% were prepared by hot-milling, followed by compression moulding techniques.

BP Chemicals Ltd

Low and high density polyethylene containing Irganox 1076 at concentrations of 0.2% and 0.035% respectively, were prepared by sintering to produce small pellets.

Sheffield City Polytechnic

Polystyrene sheets containing BHT at 1.5% were prepared using the Churchill-Rapra Torque Rheometer. The unstabilised polystyrene beads were mixed at 130°C before adding the antioxidant and mixing for a further seven minutes. The stabilised polystyrene was compression moulded at 130°C under 10,000 kilogrammes (in a 16 x 16 cm mould) for ten minutes. The sheets were cut into manageable sized pieces before being placed into labelled glass vials.

NATEC Institute

Homopolymer polypropylene and high density polyethylene containing ^{14}C-labelled Irganox 1076, at concentrations of 0.20% and 0.19% respectively, were prepared by extrusion and granulation, prior to compression moulding into sheets. The outer 2 cm of the sheets were removed and were then cut into pieces of the size 1.8 x 0.9 cm, and placed into labelled glass vials, wrapped in aluminium foil. Details of preparation and characterisation of these polypropylene and high density polyethylene sheets are described in Appendix 1.

5. GAMMA-IRRADIATION FACILITIES

The polymer samples were subjected to progressive doses of gamma-irradiation from a cobalt-60 source, by Isotron PLC (Swindon). The actual doses received were 1, 5, 10, 20, 25, 35 and 50 kGy; the dose rate was 12.5 kGy per hour. The samples were subjected to the R&D process,

in which the cobalt-60 tubes are mounted in a circular array at the bottom of a 20 foot deep water pond. Samples are loaded into water-tight containers, which are lowered into the centre of the source array and the exposure accurately timed.

Immediately prior to irradiation, each carton received a radiation indicator label, a plant reference number and date. The indicator label changed from yellow to bright red during irradiation, the colour change being specific for the treatment. This label is based on polyvinyl chloride impregnated with acid-sensitive dyes, and helps to ensure against confusion between irradiated and unirradiated products. The labels are by no means quantitative in their response; they simply fulfil a 'go' or 'no go' function. In addition, film systems, usually clear or red polymethyl methacrylate were used to monitor the radiation dose in routine plant operation. Duplicate dosimeters were present in every batch of the process. The dosimeters were read and recorded before irradiated products could be released.

After receipt, the irradiated samples were stored in the dark.

6. EXTRACTION PROCEDURES FOR ANTIOXIDANTS PRIOR TO ANALYSIS BY HPLC

In this Section, extraction procedures for the determination of antioxidants present in a range of polymers, are described.

6.1 Extraction of antioxidants versus time

The purpose of this work was to indicate the length of time required for extraction, to obtain a reproducible result for the amount of antioxidant extracted.

Extractions were performed on unirradiated polypropylene containing Irganox 1330 at an initial concentration of 0.1%.

Six replicates of the polymer of known weight (500.0 mg) were each added to chloroform (10 ml) and the internal standard (Irganox 1076, 3.0 mg in 100 µl chloroform) was added. The resulting mixtures were heated under reflux for up to a maximum of six hours, one sample being removed after each hour. The chloroform extracts were filtered, evaporated to ca. 0.5 ml under nitrogen, before being chromatographed. The results were as follows:-

Time of extraction/hour	% Irganox 1330 found (+/- 0.005%) *
1	0.005
2	0.076
3	0.087
4	0.091
5	0.095
6	0.094

* calculated 95% confidence limit

$x \pm \frac{ts}{N}$ where x = mean value

t = statistical factor dependent on number of degrees of freedom and confidence level

s = standard deviation

N = number of readings

Extraction times of 1- and 2- hours gave results which were obviously unacceptable. The 3-hour extraction result was within the 95% confidence limits of the result for 5- and 6- hours. These latter extraction times were ideal, but unfortunately, not practical because of the large number of samples to be analysed. Consequently, subsequent extractions were carried out using a reflux time of either 3- or 4- hours, as indicated in each experiment. In this study, it was not necessary to obtain the absolute values, because as long as each sample has been treated and extracted in the same way, a comparison of the level of antioxidants may be made.

Additional work was performed on samples of low density polyethylene, as it had been suggested that an extraction time of 10 hours minimum was necessary. It was of interest, therefore, to make a comparison of the results of antioxidant extracted after an overnight (17½ hours) and a 3 hour extraction. Using an internal standard of Irganox 1010 (1.0 mg in 100 µl chloroform), the results were as follows:-

Irradiation dose	% Irganox 1076 found (+/- 0.03%)	
/kGy	overnight	3 hours
0	0.26	0.22
1	0.26	0.22
5	0.23	0.20
10	0.21	0.17
20	0.17	0.13
25	0.15	0.12
35	0.11	0.08
50	0.09	0.07

Both sets of results were noted to have followed the same decreasing trend, with the results of a 3 hour extraction being only slightly lower. Results obtained after a 3 hour extraction were within or just slightly out of the 95% confidence limits of the overnight extraction results.

6.2 Extraction procedure for antioxidants in polypropylene and polyethylene

A known weight of polymer (500.0 mg) was placed in a round bottomed flask (25 ml) and chloroform (10 ml) was added, together with the appropriate internal standard (either Irganox 1010, 1.0 mg in 100 µl chloroform or Irganox 1076, 3.0 mg in 100 µl chloroform). The mixture was then heated under reflux for three or four hours, before being filtered. The extracts were evaporated to ca. 0.5 ml under nitrogen and then chromatographed.

6.3 Extraction procedure for antioxidants in polyvinyl chloride and polystyrene

These polymers required a different extraction procedure, owing to their partial solubility in chloroform.

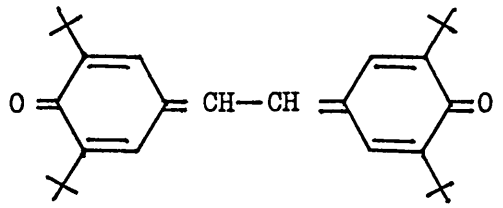
A known weight of polymer (500.0 mg) was placed in a glass vial and THF (10 ml) was added, together with the appropriate internal standard (either Irganox 1010, 1.0 mg in 100 µl chloroform or Irganox 1076, 3.0 mg in 100 µl chloroform). The polymer was left to dissolve overnight, in the dark and under nitrogen. Methanol (20 ml) was added, with vigorous stirring, in order to precipitate the polymer. The samples were filtered and left overnight. During this time, further polymer had settled out. The supernatant liquid was decanted and evaporated to ca. 0.5 ml under nitrogen, before being chromatographed.

7. METHODS OF SYNTHESIS OF DEGRADATION PRODUCTS ARISING FROM ANTIOXIDANTS

Some degradation products, arising from certain antioxidants present in polyolefins after gamma-irradiation, have been identified by comparison with the authentic material, prepared by various synthetic routes.

7.1 Synthesis of 3,5,3',5'-tetra-t-butylstilbene-4,4'-quinone

This product (I) was prepared by the oxidation of BHT with alkaline ferricyanide [26].



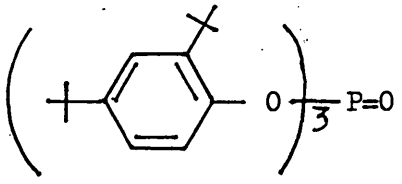
I

BHT (10 g, 0.045 mol) in benzene (100 ml) was oxidised with a solution of potassium ferricyanide (90 g, 0.275 mol) and potassium hydroxide (16 g) in water (150 ml). After stirring for twenty four hours at 60°C, the layers were separated and the volume of benzene was reduced. The red stilbene-quinone crystallised first, and was then recrystallised from benzene and ethanol, to yield 1.4 g (0.0037 mol). The melting point of the product was 314-315°C (literature [26] melting point was 315-316°C).

The purity of the stilbene-quinone was checked by TLC on silica plates using hexane: toluene (80:20 v/v) and visualised in iodine vapour. The stilbene-quinone (Rf=0.28) contained no visible trace of BHT (Rf=0.52).

7.2 Synthesis of tris-(2,4-di-t-butylphenyl) phosphate

This product (II) was prepared by oxidation of Irgafos 168 with a peroxide.



II

Irgafos 168 (1.94 g, 3 mmol) and t-butylhydroperoxide (1.16 g, 9 mmol) were dissolved in acetone (10 ml) and heated under reflux for 1½ hours. The colourless solution turned pale yellow. This was added to an excess of water (150 ml) containing sodium sulphite (0.93 g, 9 mmol). The emulsion was then solvent extracted with four aliquots of chloroform (50 ml). The collected aliquots of chloroform were dried over anhydrous magnesium sulphate and evaporated under nitrogen. The impure product (yellow oil) was recrystallised from acetonitrile. The resulting pure white crystals were filtered and dried in air. The melting point of the product was 98-101°C.

Microanalysis

	Found	Theoretical	Difference
% C	76.09	75.88	- 0.21
% H	9.57	9.68	0.11
% N	0.00	0.00	0.00

The ^{1}H n.m.r. spectrum (Figure 2.3) was consistent with the structure, showing two signals to be present, one at a shift value of 1.3δ indicative of t-butyl hydrogens, and the second at a shift value of 7.4δ indicative of aromatic hydrogens. The ^{31}P n.m.r. spectrum (Figure 2.4) showed one signal to be present at a shift value of -20 ppm, which was consistent with the phosphate, and was the only phosphorus resonance present. The mass spectrum (Figure 2.5) of this compound exhibited a molecular ion at $^{m}/_{z}$ 662, and other fragments, which were consistent with the structure.

Figure 2.3 ^{1}H nmr spectrum of tris-(2,4-di-t-butylphenyl)phosphate

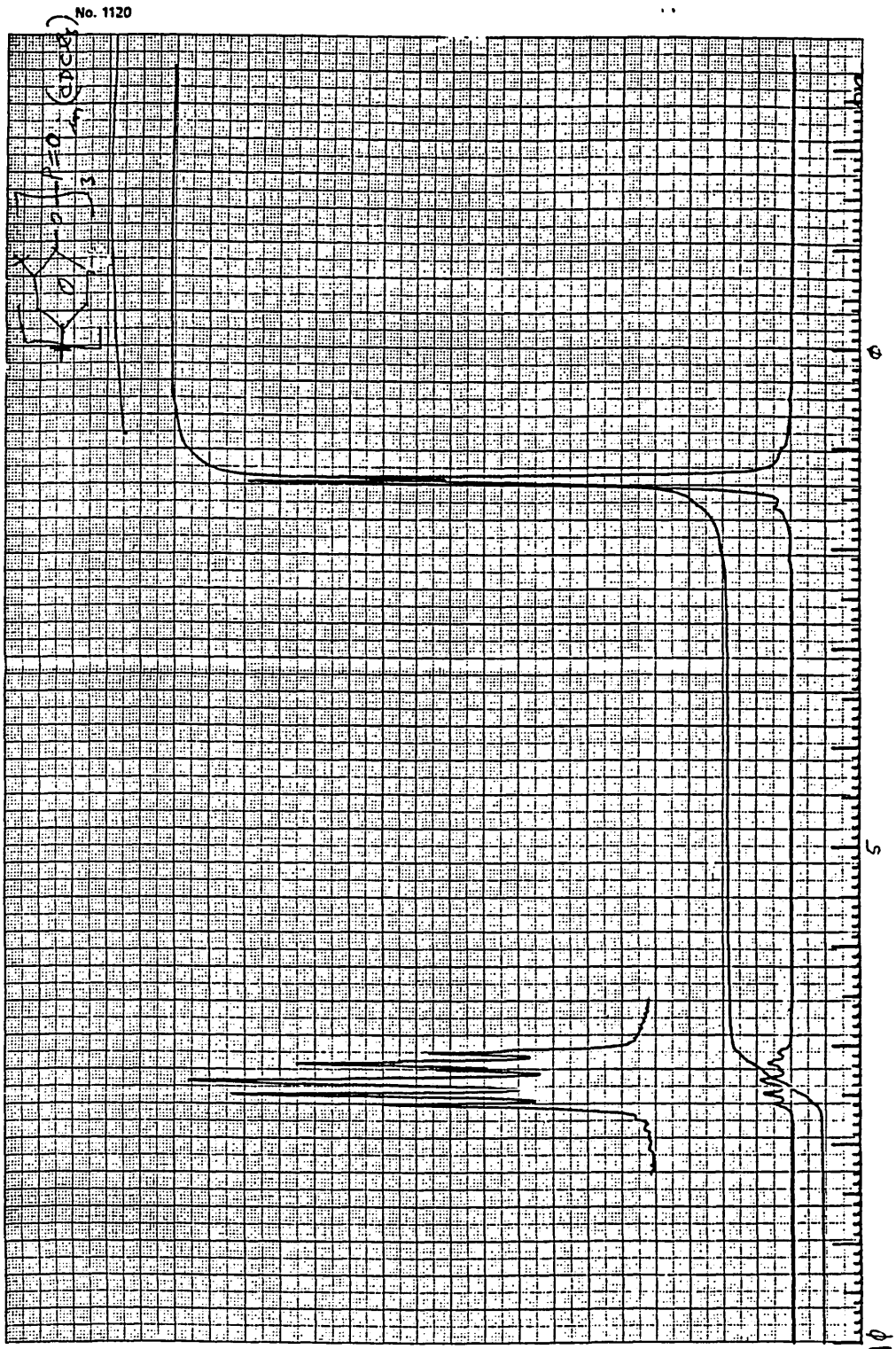


Figure 2.4 ^{31}P nmr spectrum of tris-(2,4-di-t-butylphenyl)phosphate

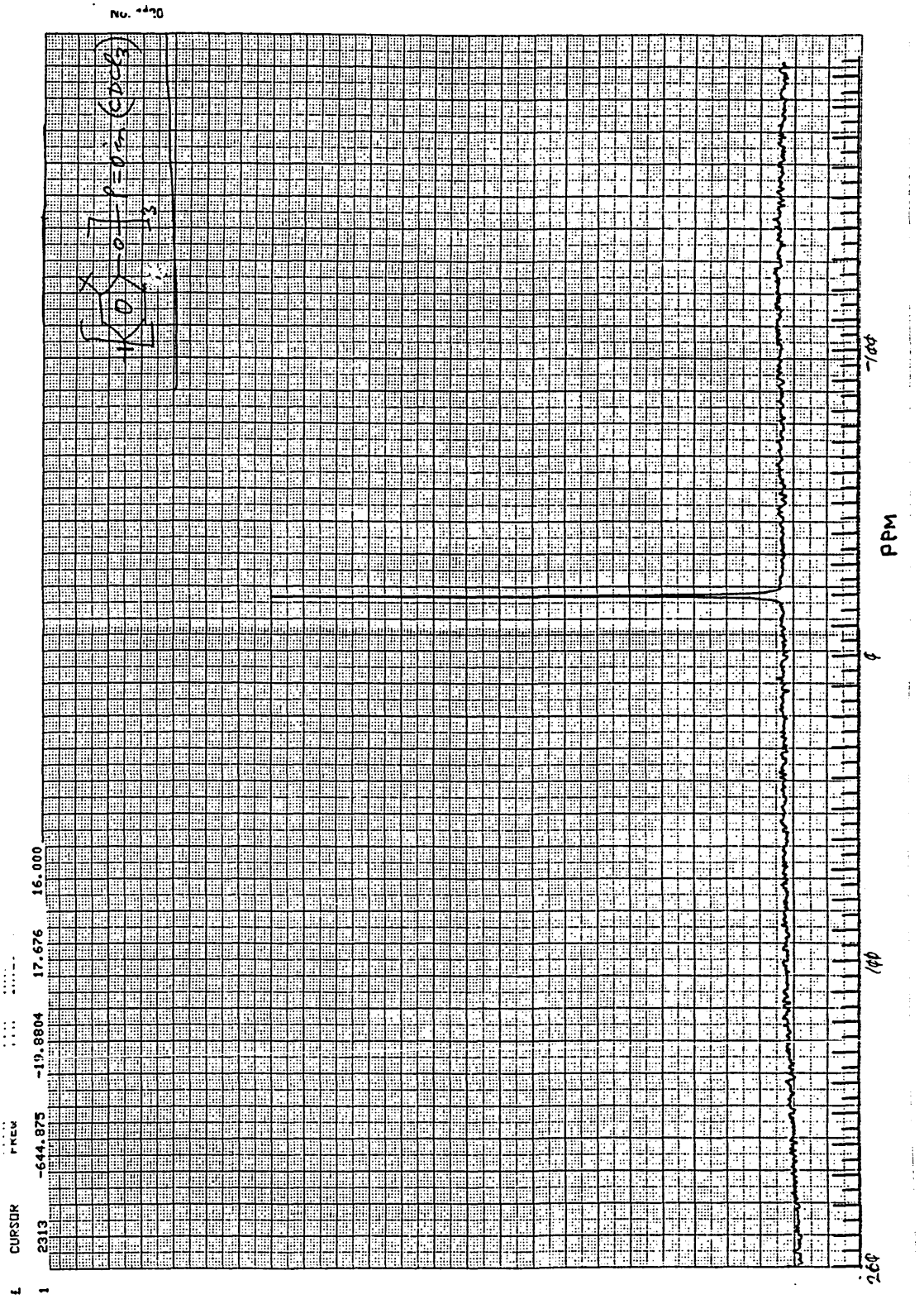
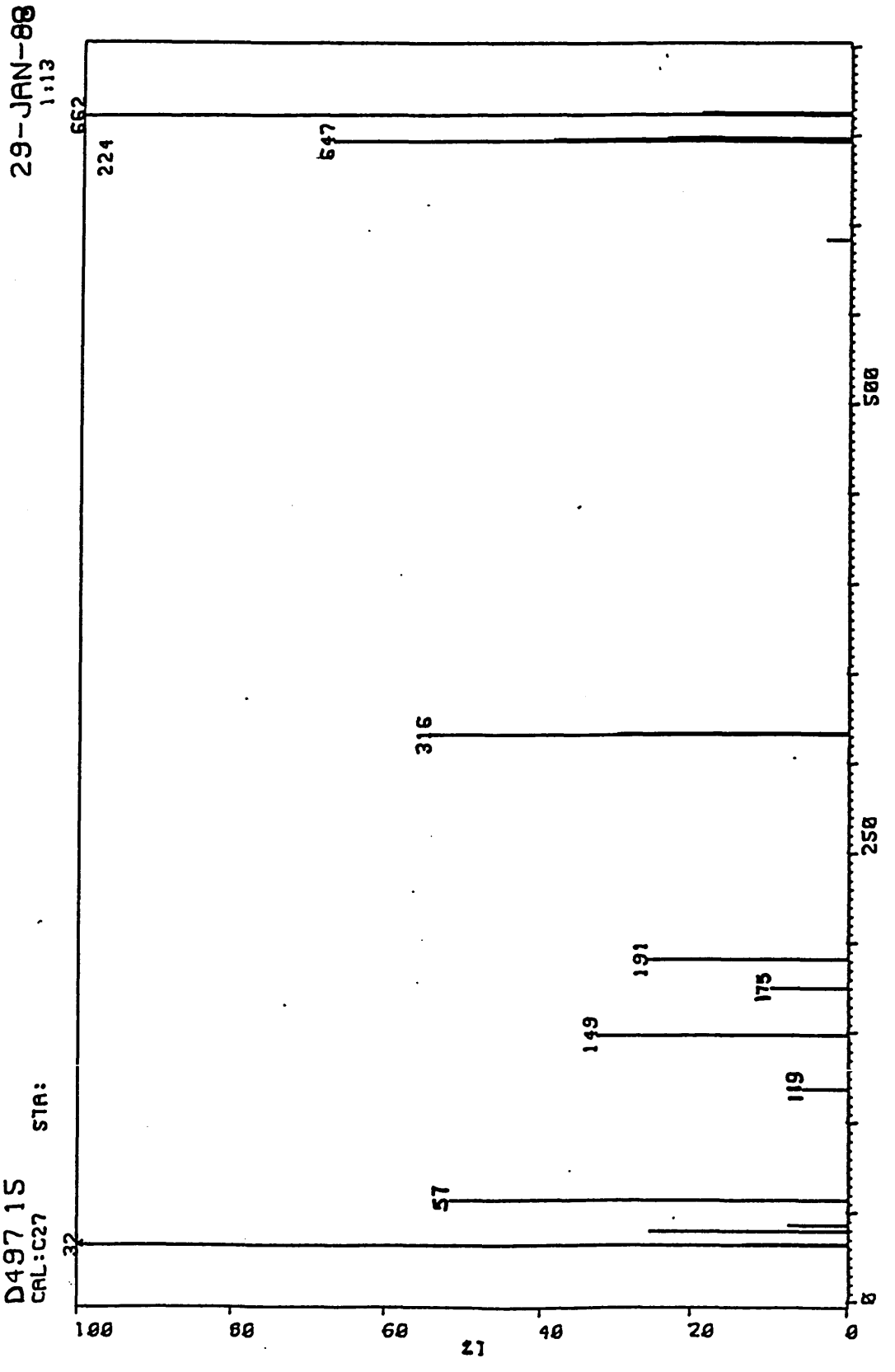


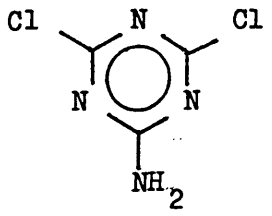
Figure 2.5 Mass spectrum of tris-(2,4-di-t-butylphenyl)phosphate



7.3 Synthesis of 1-amino-3,5-di(octylthio) triazine

7.3.1 Preparation of 1-amino-3,5-dichlorotriazine

1-amino-3,5-dichlorotriazine (III) was prepared as described by Diels[27].



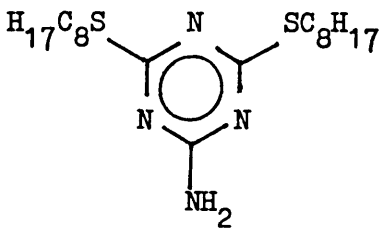
III

Cyanuric chloride (5 g) was dissolved in dry ether (100 ml), cooled to 0°C and treated with dry ammonia gas until the solution was saturated. The resulting white solid (NH_4Cl) was filtered off, washed with ether, and the combined filtrate and washings evaporated. The crude solid was then redissolved in dry ether, the solution filtered to remove residual inorganic material, and the clear filtrate evaporated to give the product, 3.0 g. The melting point was 240°C, with earlier partial sublimation. The mass spectrum exhibited a molecular ion at $^{m}/_{z}$ 164 (M^{+} ^{35}Cl=164) with characteristic splitting patterns of 9:6:1 for two ^{35}Cl and ^{37}Cl atoms.

7.3.2 Conversion to 1-amino-3,5-di(octylthio) triazine

1-amino-3,5-dichlorotriazine (0.83 g) was added to a solution of octanethiol (1.5 g, 2 mol) in ethanol (10 ml) containing potassium t-butoxide (1.12 g, 2 mol). The addition was accompanied by the evolution

of considerable heat. The resulting mixture was then poured into water (30 ml), with stirring. The solid product was filtered, washed with aqueous ethanol and dried, to yield 2.05 g. Recrystallisation from ethanol gave the pure material (IV), with a melting point of 68°C.



IV

7.4 Isolation of degradation products from Irganox 565 reactions

7.4.1 Isolation of 1-amino-3,5-di(octylthio)triazine

a) Irganox 565 (0.1 g) and ferric chloride (0.5 g) were dissolved in aqueous ethanol (5 ml) and heated to reflux for one hour. The mixture was solvent extracted with four aliquots of chloroform (5 ml) and the combined extract was reduced to ca. 0.5 ml. The extract was applied to a preparative TLC plate and developed four times using chloroform: hexane (1:1 v/v).

The lower band (Rf=0.14-0.26) was removed, chloroform extracted and evaporated to dryness. The impure product was recrystallised from methanol. The melting point of the product (IV) was 67-68°C.

	Found	Theoretical	Difference
% C	59.46	59.33	0.13
% H	9.37	9.43	-0.06
% N	14.52	14.56	-0.04

The infrared spectrum (Figure 2.6) of this compound contained characteristic peaks (1650 cm^{-1} for N-H bend, 3400 and 3300 cm^{-1} for N-H str) for the compound 1-amino-3,5-di(octylthio)triazine.

The upper band (Rf=0.66-0.79) was removed, chloroform extracted and evaporated to dryness. The infrared spectrum (Figure 2.7) of this compound was identical with that of 2,6-di-t-butyl-1,4-benzoquinone (Figure 2.8). The ^{1}H n.m.r. spectrum (Figure 2.9) was consistent with the structure of the benzoquinone, showing two signals to be present, one at a shift value of 1.3δ indicative of t-butyl hydrogens and the second at a shift value of 6.5δ indicative of aromatic hydrogens.

b) Irganox 565 (0.1 g) and ferric chloride (0.5 g) were dissolved in aqueous ethanol (5 ml) and left in the cold for 6 hours. On standing overnight, fine needles of the product had formed. The mass spectrum (Figure 2.10) of this compound exhibited a molecular ion at $^{m}/_{z}$ 384 and other fragments, which were consistent with the structure of 1-amino-3,5-di(octylthio)triazine.

Figure 2.6 Infrared spectrum of 1-amino-3,5-di(octylthio)triazine

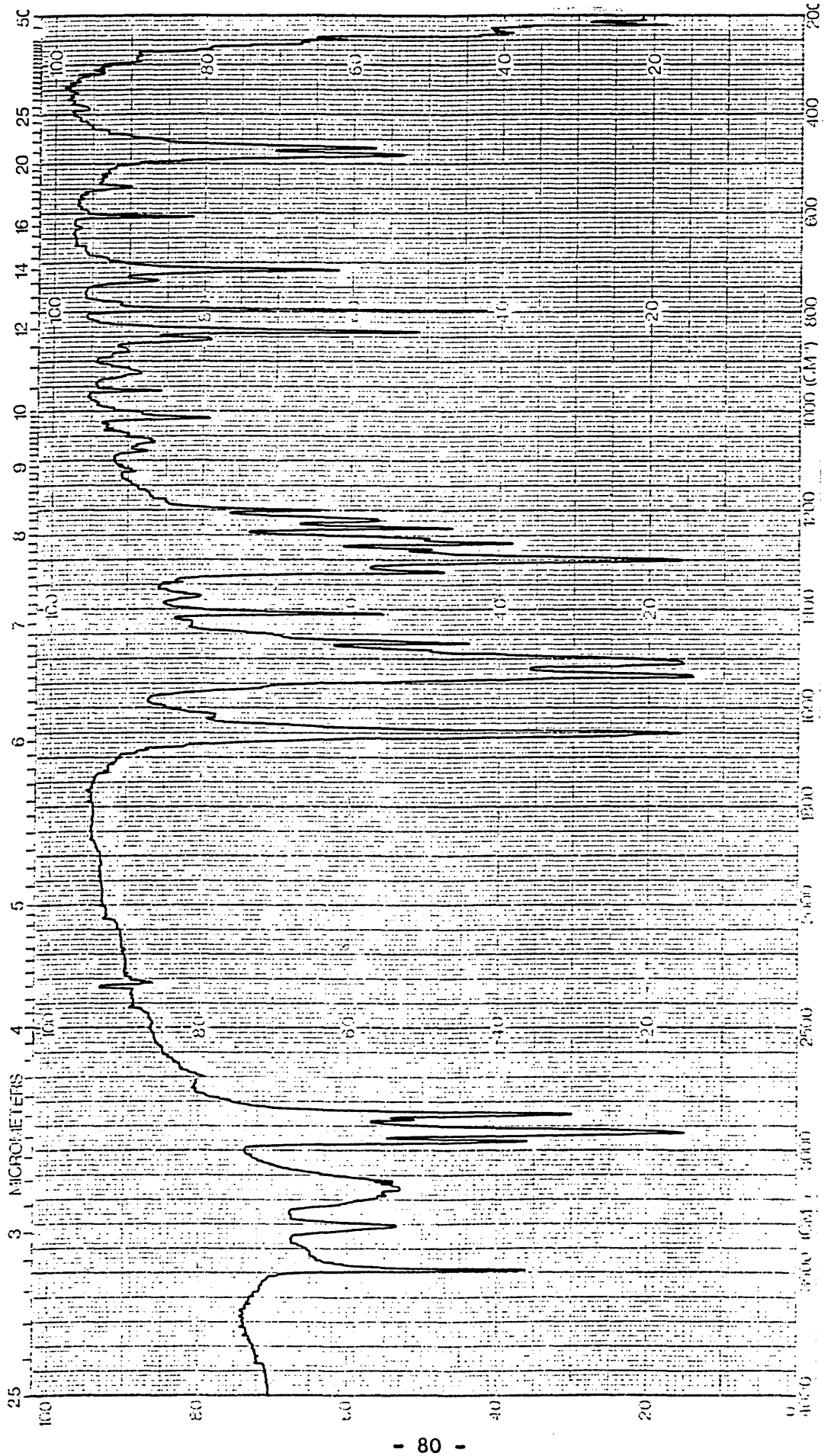


Figure 2.7 Infrared spectrum of TLC upper band from Irganox 565 and ferric chloride reaction

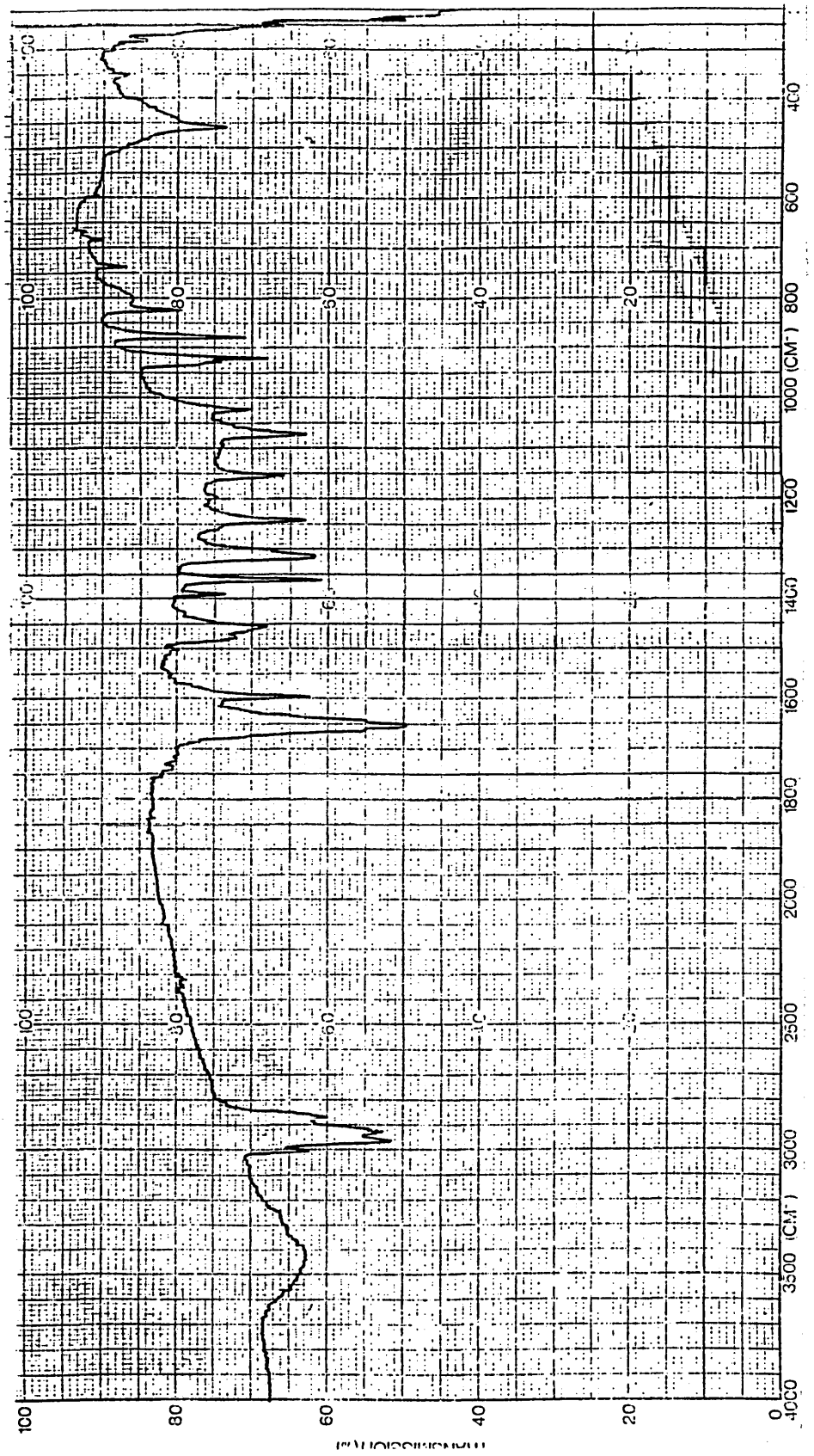


Figure 2.8 Infrared spectrum of 2,6-di-t-butyl-1,4-benzoquinone

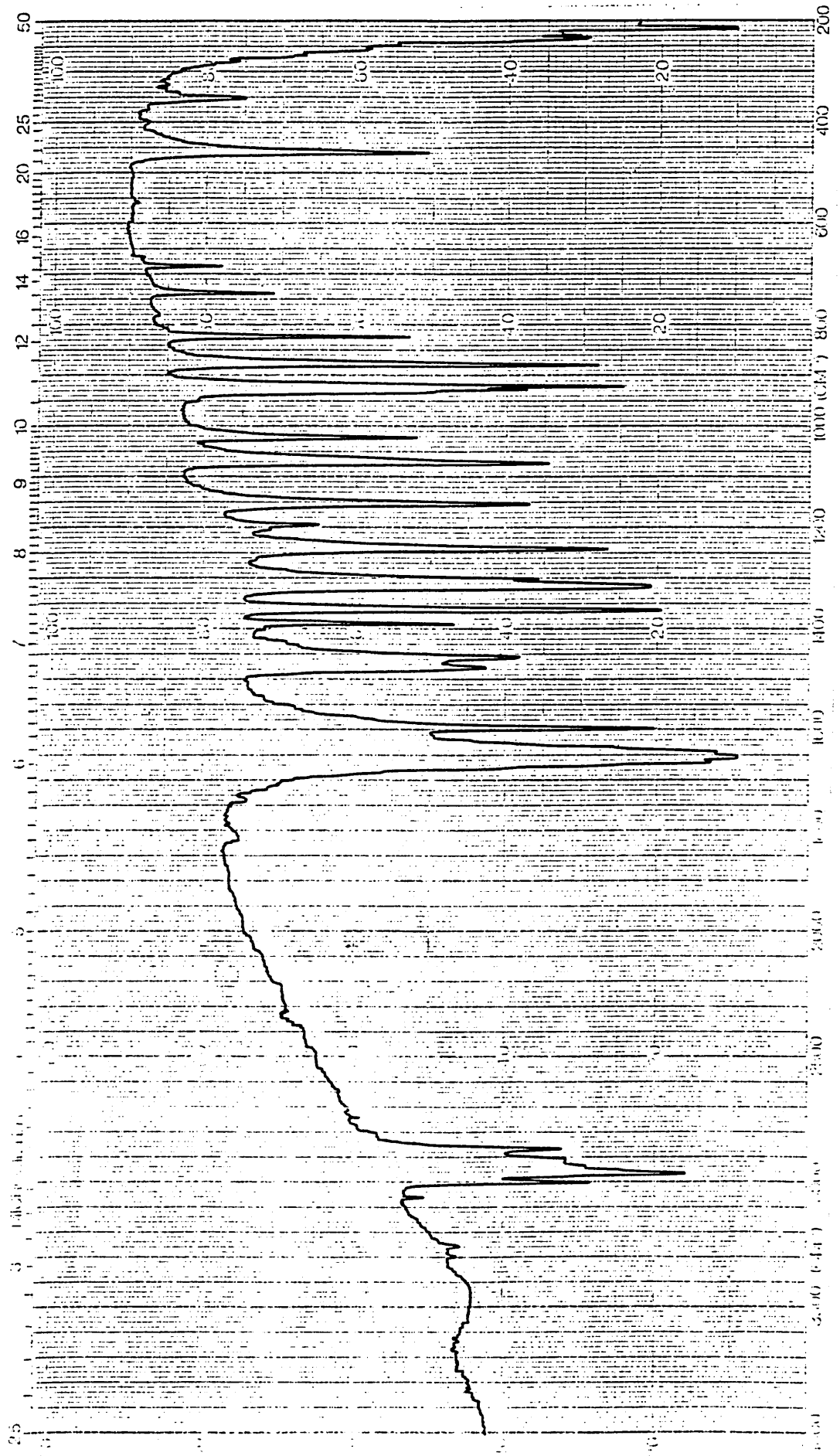


Figure 2.9 ^{1}H nmr spectrum of TLC upper band from Irganox 565 and ferric chloride reaction

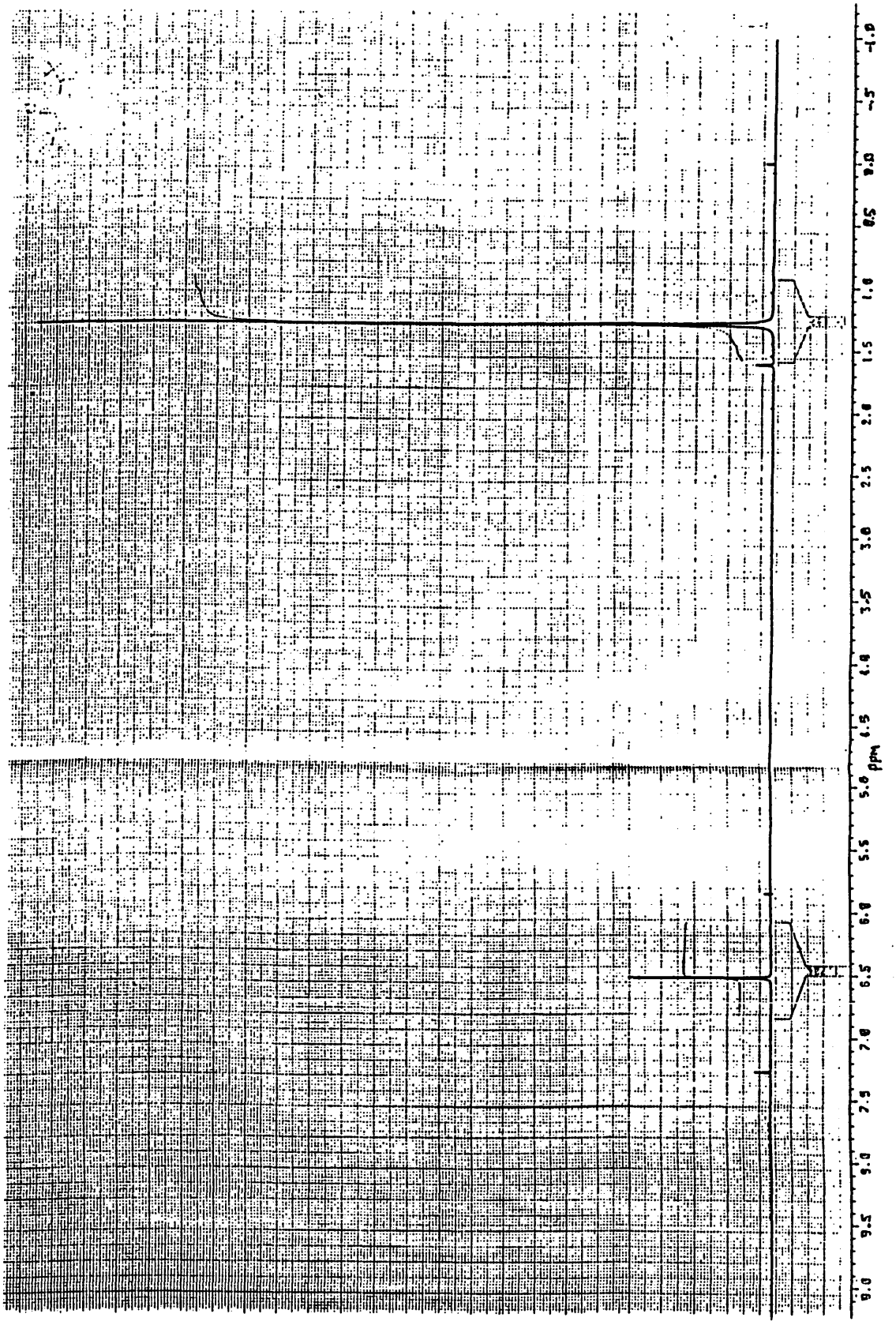
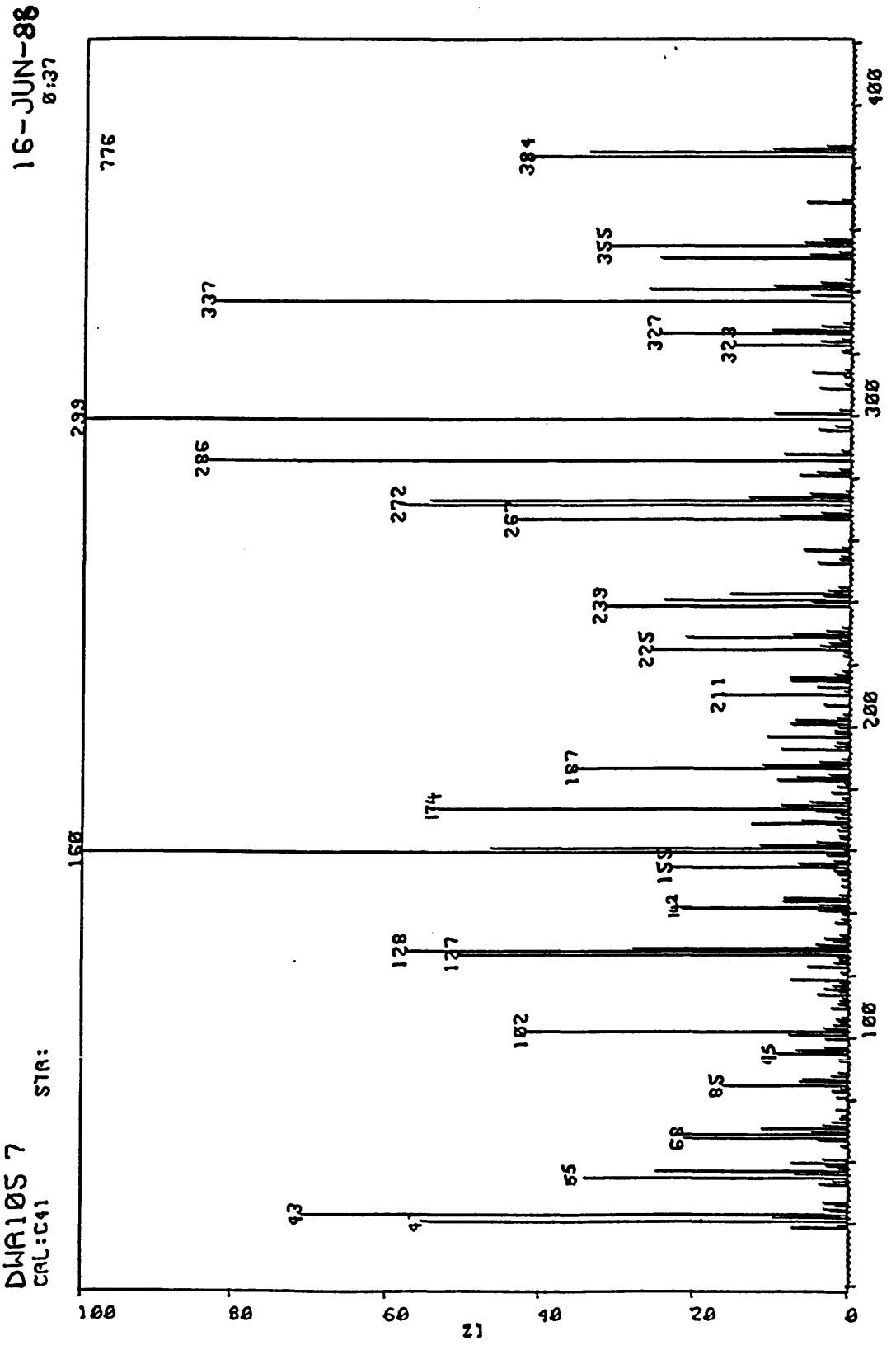


Figure 2.10 Mass spectrum of 1-amino-3,5-di(octylthio)triazine



7.4.2 Isolation of N-[4,6-di(octylthio)-1,3,5-triazin-2-yl]-2,6-di-t-butylbenzoquinone monoimine

Irganox 565 (0.2 g) and manganese dioxide (2.0 g) were added to chloroform (8 ml), with stirring, for three hours. The mixture was filtered and evaporated to leave a yellow oil.

Microanalysis

	Found	Theoretical	Difference
% C	67.64	67.53	0.11
% H	9.47	9.27	0.20
% N	9.48	9.54	-0.06

The mass spectrum (Figure 2.11) was consistent with the structure (V) having a molecular ion at $^{m}/_{z}$ 586 and other fragments, which were consistent with the structure. The infrared spectrum (Figure 2.12) of this compound revealed differences in the spectrum of Irganox 565 (Figure 2.13) with the absence of the O-H stretch band at 3620 cm^{-1} and the presence of the C=O stretch band at 1650 cm^{-1}. The ^{1}H n.m.r. spectrum (Figure 2.14) revealed four major signals to be present, the first at a shift value of 0.9δ indicative of the methyl hydrogens at the end of the octyl group, the second at δ=1.3 indicative of t-butyl hydrogens, the third at a shift value of 3.1δ indicative of hydrogens on the carbon adjacent to the sulphur group and the fourth at 6.5δ indicative of the aromatic hydrogens.

Figure 2.11 Mass Spectrum of N-(4,6-[illegible]-

triazin-2-yl)-2,6-di-t-butylbenzoquinone monoimine

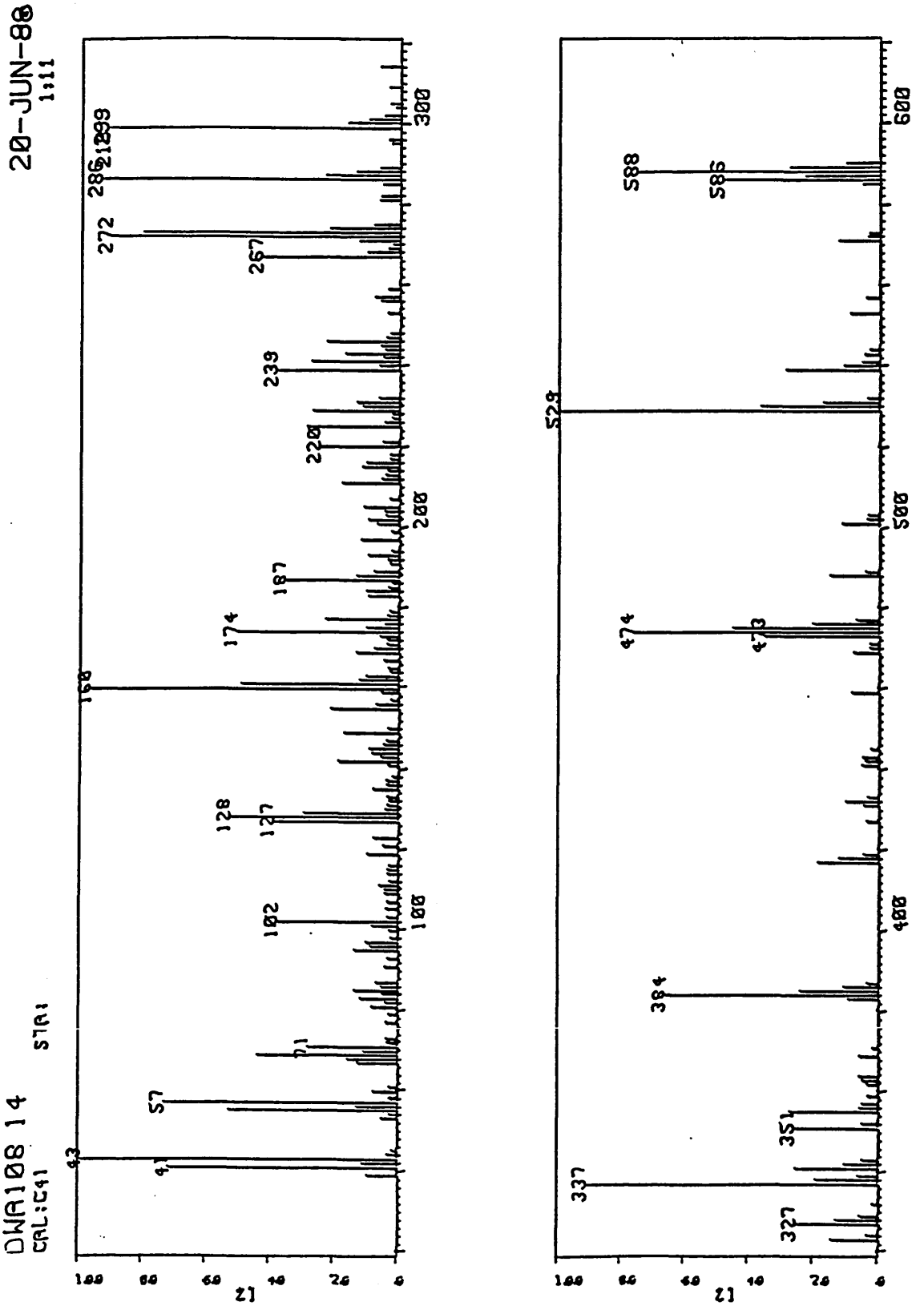


Figure 2.12 Infrared spectrum of N-(4,6-di(octylthio)-1,3,5-triazin-2-yl)-2,6-di-t-butylbenzoquinone monoimine

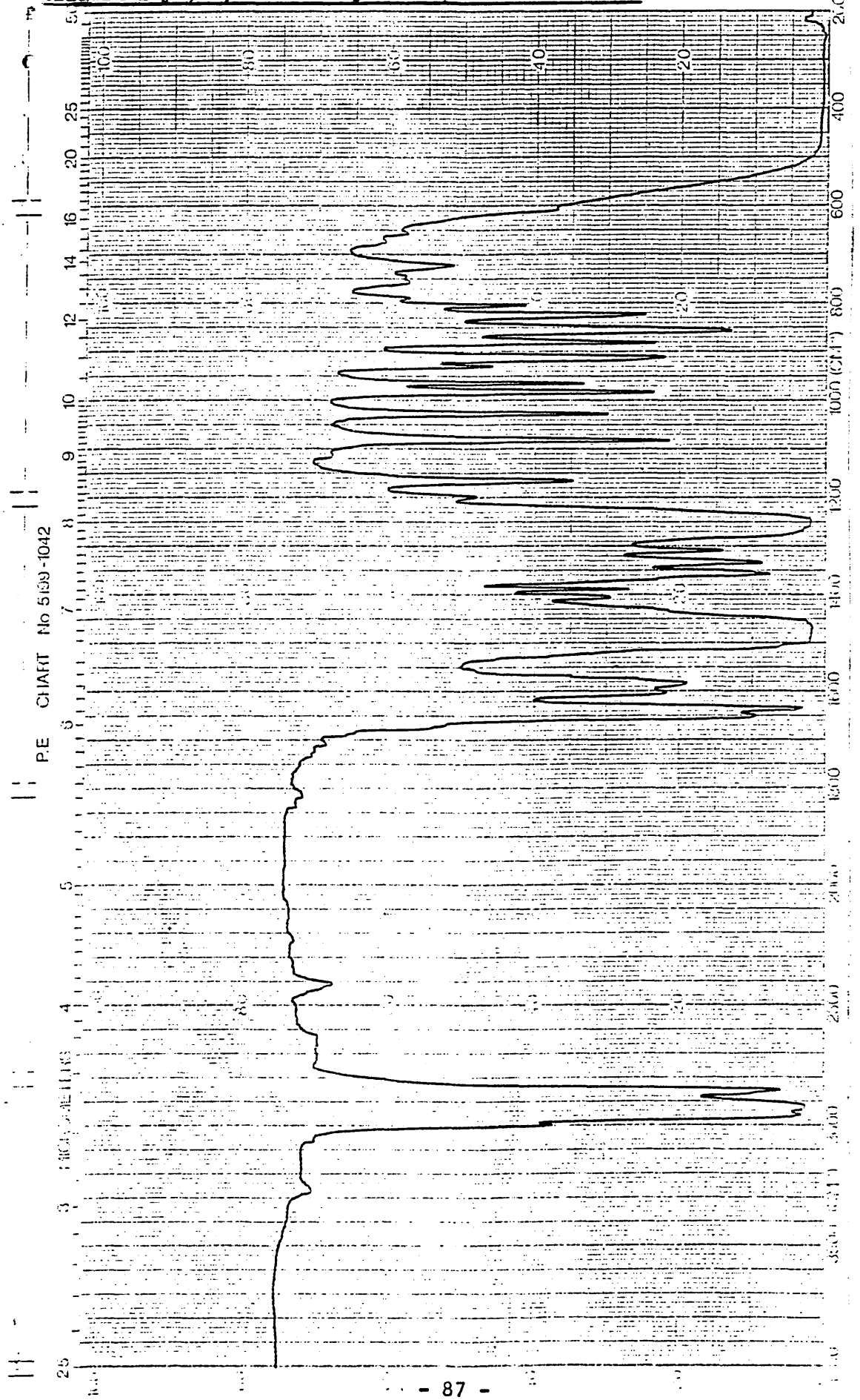


Figure 2.13 Infrared spectrum of Irganox 565

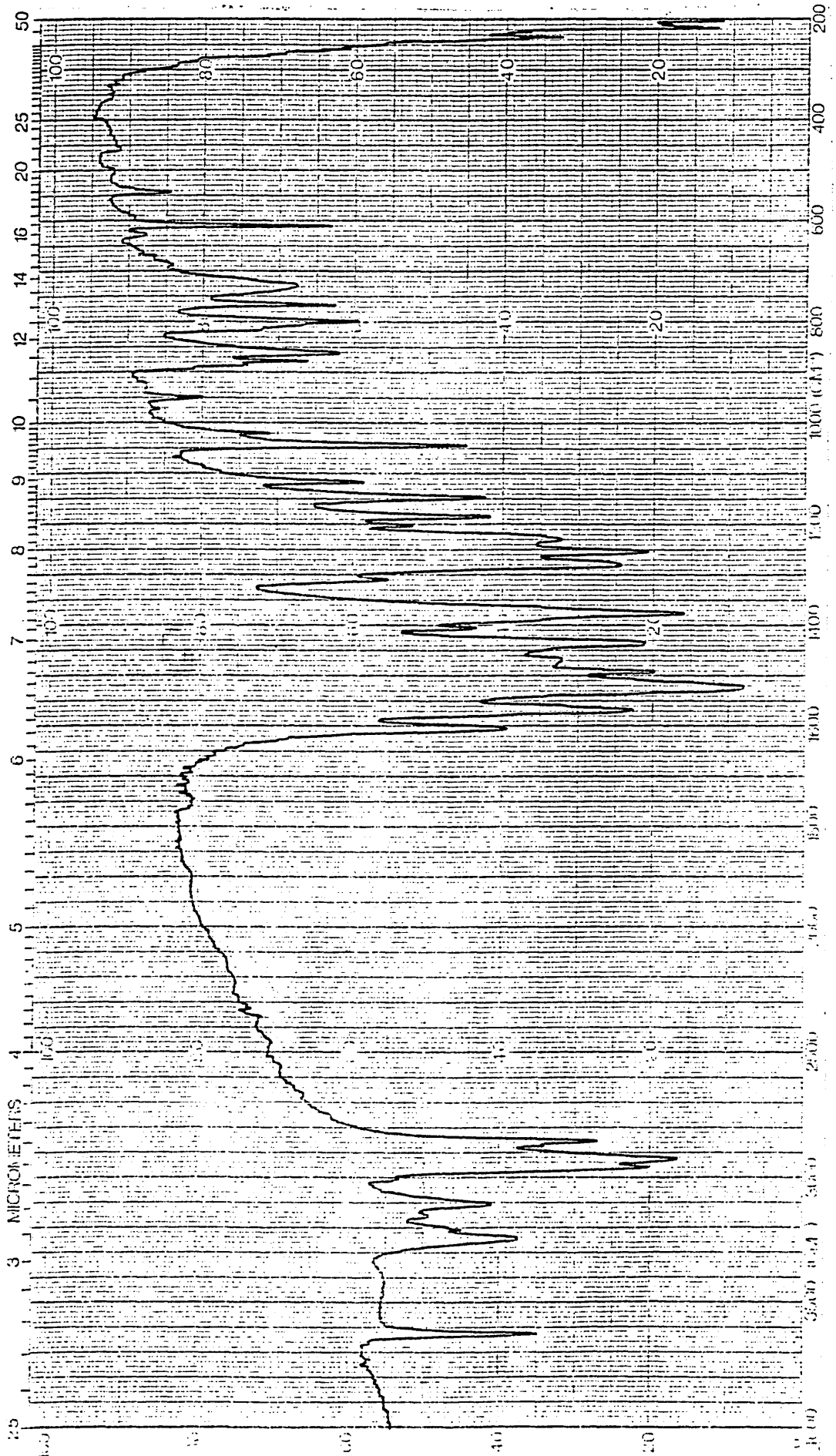
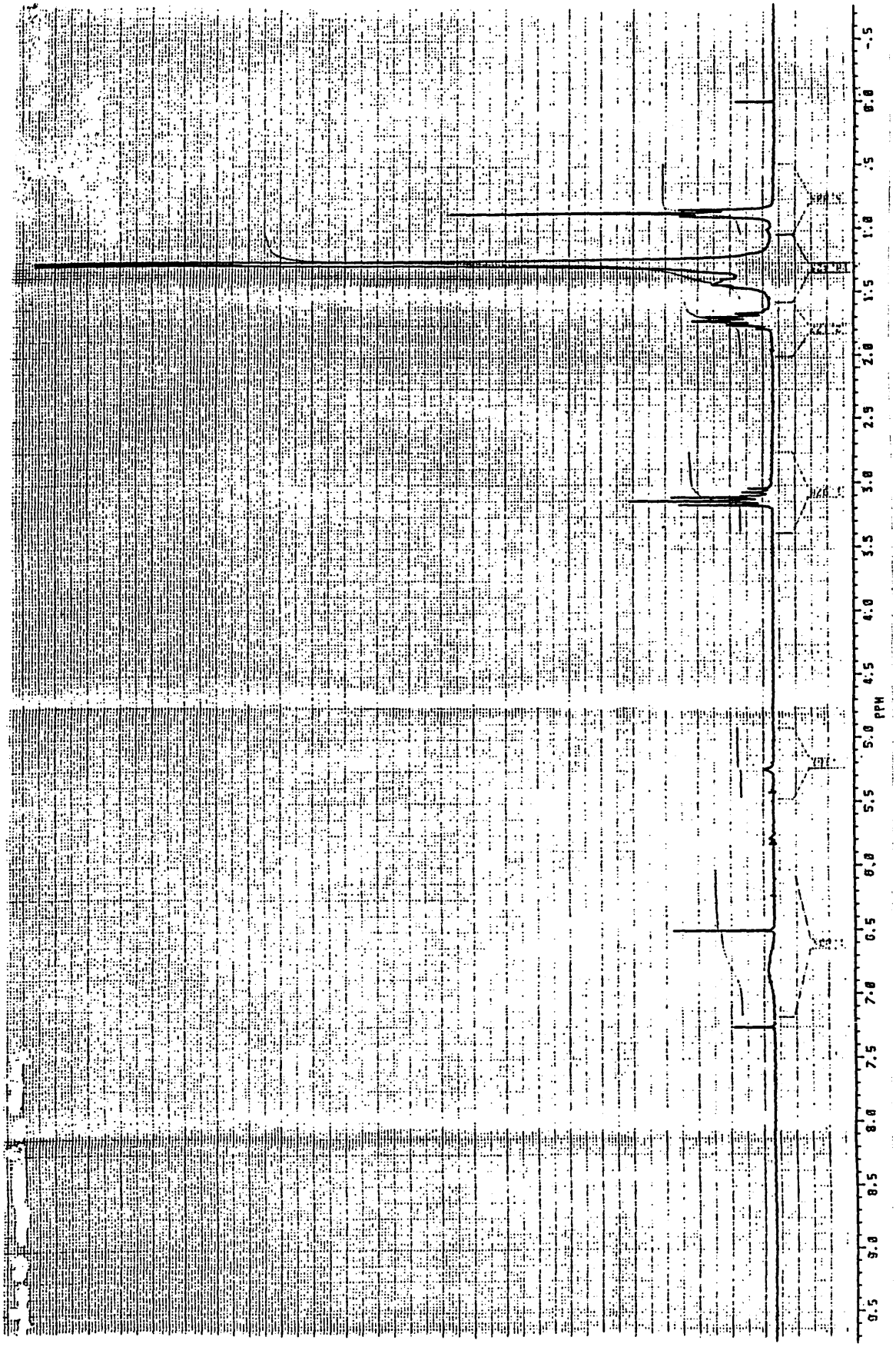
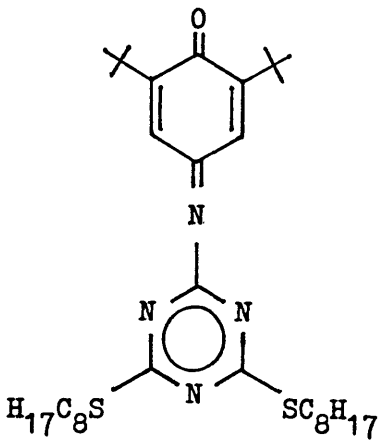


Figure 2.14 ^{1}H nmr spectrum of N-(4,6-di(octylthio)-1,3,5-triazin-2-yl)-2,6-di-t-butylbenzoquinone monoimine





V

8. MIGRATION OF ANTIOXIDANTS FROM IRRADIATED POLYMERS

Migration studies were carried out with unirradiated and irradiated samples, in order to determine the extent to which antioxidants or their degradation products migrate out of the polymer into various food simulants.

The range of oily, alcoholic and aqueous simulants used in this study were:-

distilled water

3% acetic acid

15% ethanol

HB 307

iso-octane

It should be noted that the test fat HB 307 was used instead of edible oils (eg. olive oil), since the latter present great analytical difficulties because of their natural varied composition which in turn, results in extremely complex chromatographic traces.

The test fat HB 307 consists of a synthetic triglyceride mixture (glyceride distribution C_{22}-C_{50}), which possesses a similar fatty acid composition (fatty acid distribution C_6-C_{18}) as an edible fat and which covers, in its extraction efficiency, all other edible fats. It possesses the following advantages: it has a constant chemical composition and therefore always yields comparable extraction and migration values; it is free from interfering impurities; it possesses a much better optical transmission; and it can be stored for extended periods of time without quality losses.

The results of investigations by Figge have led to the conclusion that the synthetic test fat HB 307 can be used universally for the analytical control of the migration of low-molecular components from packaging materials into pure edible oils or fat-releasing components[28]. In addition to the use of HB 307, iso-octane has been proposed [29,30] as a fatty food simulant which provides a convenient alternative to fats such as HB 307 and olive oil, in that the determination of migration into iso-octane is significantly easier, thereby providing a fast, cheap and simple predictive method for migration into fatty media. However, criticisms have been made of the use of iso-octane for this purpose [31,32]. Nevertheless, studies were conducted using both iso-octane and HB 307, so that a comparison could be made, of the extent of migration from the polymers used in this study.

For the simulants distilled water, 3% acetic acid, 15% ethanol and HB 307, the test conditions were 10 days at 40°C. The iso-octane simulant was subjected to test conditions of 2 days at 20°C, in accordance with the recommendations[29]. However, in all cases, the ratio of surface area of polymer sample to volume of simulant was 2 dm^2 exposed to 100 ml, respectively. Throughout these studies, the surface area of the sample was reduced to 4.32 cm^2 in 2 ml of simulant. The correct ratio of surface area to simulant volume was still maintained, but a small contribution from the edges was taken into account, and the size of the polymer samples was adjusted accordingly to 1.8 x 0.9 cm.

The polymer samples used were as follows:-

polypropylene (homopolymer) containing nominally 0.25% Irganox 1076
polypropylene (copolymer) containing nominally 0.25% Irganox 1076
polypropylene (homopolymer) containing nominally 0.25% Irganox 1010
polypropylene (copolymer) containing nominally 0.25% Irganox 1010

The above had been gamma-irradiated over the dose range 0,10,25 and 50 kGy.

8.1 Procedure

Each of the samples were studied in duplicate in each of the named simulants under their test conditions. In addition, blank simulants were studied to determine whether any substances would migrate from the polypropylene caps and interfere with the analysis. After the contact

time had elapsed, the polymer pieces were removed and the amounts of migrated antioxidant were determined, using the external standard method, with the exception of HB 307 samples.

Chromatographic conditions were as mentioned previously in Section 3, with the exception of the analytical column. The new analytical column was a (10 cm) S5 ODS1, used without a guard column. The limits of detection for Irganox 1076 and 1010 were 3 $\mu g\ ml^{-1}$ (of twice signal to baseline noise) in the extract, corresponding to 0.006% in the polymer.

8.2 Determination of antioxidants in HB 307 after migration

The samples of HB 307 could not be analysed by direct injection into the HPLC (as for other migration simulants), since at room temperature, HB 307 solidifies.

However, two methods [33,34] were available which described the extraction of antioxidants from HB 307 by dissolution of the fat into hexane and solvent extraction with acetonitrile, before chromatography. Chromatographic conditions were as above, with the addition of a guard column (S10 ODS1) to prolong the life of the analytical column.

Numerous problems were encountered when attempts were made to employ this solvent extraction method. The extraction of Irganox 1010 from hexane into acetonitrile did not appear to be totally efficient. Upon doubling the concentration of the antioxidant from 50 $\mu g\ ml^{-1}$ to 100 $\mu g\ ml^{-1}$, the peak heights did not increase accordingly, thereby casting

doubt on the quantitative extractibility of this antioxidant from hexane. In addition, Irganox 1076 was not extracted from the hexane layer into acetonitrile. This is presumably due to the effect of the long hydrocarbon chain ($C_{18}H_{37}$ moeity) of the molecule, which prefers to remain in the non-polar hydrocarbon solvent. Injection of the hexane fraction showed Irganox 1076 to be present, but the traces were complex due to the additional peaks arising from HB 307. Consequently, this method could not be used successfully in the determination of either antioxidant in HB 307.

An additional method, involving UV spectrometry, had previously been shown [28] to determine Irganox 1076 in HB 307, to a limit of detection of 15 $\mu g\ ml^{-1}$, corresponding to 0.26% of antioxidant in the polymer, by dissolving the sample in chloroform and measuring the absorbance at 277 nm. Unfortunately, this method could not be used as the limit of detection for Irganox 1076 was not sensitive enough for the samples after gamma-irradiation.

9. INVESTIGATION OF COVALENT BINDING OF ANTIOXIDANTS AND THEIR DEGRADATION PRODUCTS TO THE POLYMERS AFTER GAMMA-IRRADIATION.

It is a distinct possibility that degradation products derived from the antioxidants could become covalently bound to the polymer as a result of radical coupling processes during irradiation. Since it is known that polyolefins on irradiation give rise to macroalkyl radicals[35-38], such radical coupling processes could readily occur in the irradiated polymer, and if this is so, concerns over potential migration of

degradation products may be much reduced. Hence, a ^{14}C-labelled antioxidant, Irganox 1076, has been incorporated into polyolefins and the extent to which the radiolabelled additive becomes permanently bound to the polymers following irradiation has been studied.

9.1 Extraction procedure

Four pieces of the sample were placed in a clean glass round-bottomed flask and chloroform (4 ml) was added. The contents were heated under reflux for four hours. The extract and washings (1 ml) were pipetted into a glass vial. A further aliquot of chloroform (4 ml) was added and the procedure was repeated. The extracts and washings were added and mixed thoroughly. An aliquot of the extracts (3 ml) was removed into a scintillation vial, before being evaporated to ca. 1 ml. Scintran Cocktail 0 (2 ml) was added, the mixture was mixed thoroughly, and then counted immediately on a liquid scintillation counter. Residual radioactivity, retained by the extracted polymer pieces, was counted by a Geiger-Muller tube, in a fixed geometry mode.

9.2 Reproducibility

The reproducibility of the procedure was investigated by analysing four replicate samples of unirradiated polymer materials. The resulting within-batch relative standard deviations were 5.8% and 13.3% for polypropylene and high density polyethylene, respectively. These values were half of those obtained (12.8 and 22.0%, respectively) when experiments were performed on six replicate samples of one polymer piece each. Details of this work can be found in Appendix 2.

The high relative standard deviation value of 13.3% for high density polyethylene was attributed to the inhomogeneity of the distribution of the ^{14}C-labelled Irganox 1076 within the polymer. The high crystallinity of this polymer (typically $\sim$75%) indicates that only a small region of the structure ($\sim$25%) is available for the additive, which may therefore have a tendency to aggregate in the amorphous regions between the crystallites [39,40]. Hence the distribution of Irganox 1076 within the polymer would be heterogeneous. On this basis, however, in polypropylene, the distribution of the antioxidant would be expected to be more even, in agreement with the observed improved precision.

9.3 Studies on the extent of migration from the radiolabelled polymers after gamma-irradiation.

The advantage of conducting migration studies on these radiolabelled samples was that much lower levels of determination for migration could be recorded (far below the sensitivity of the HPLC method).

Migration studies were performed in HB 307, 15% ethanol and iso-octane, under test conditions previously mentioned in Section 8. After the corresponding time period, the polymer sheet was removed and 1 ml of the simulant was pipetted into a scintillation vial. 2 ml of the appropriate scintillation cocktail was added and the contents of the vial were mixed thoroughly, before being counted immediately on a liquid scintillation counter.

In order to convert the corrected cpm per ml of HB 307 into an actual amount of migrated antioxidant, a standard of known concentration was required. Consequently, unirradiated pieces of polypropylene and high density polyethylene were exhaustively extracted with chloroform and the extracts were made up to a known volume. An aliquot was pipetted into a scintillation vial and was evaporated to dryness under nitrogen. The standards were matrix-matched by reconstituting in HB 307 and the contents were mixed thoroughly both before and after the scintillation cocktail was added. The standards were then counted immediately.

9.4 Studies on the extent of polymer binding by the antioxidant

An investigation was initiated to establish the extent to which the antioxidant binds to the polymer as a result of exposure to gamma-irradiation.

A piece of polypropylene sheet containing ^{14}C-labelled Irganox 1076 was dissolved in tetralin (15 ml) at 150°C. Upon cooling, the dissolved polypropylene formed a gel. In order to precipitate out all of the polymer fraction from the dissolved material, hexane (20 ml) was added with vigorous stirring. The samples were centrifuged at 3000 rpm for ten minutes. The upper tetralin and hexane layer was removed and the hexane fraction was evaporated, leaving only the tetralin behind. The lower fine precipitate was washed with a further six aliquots of hexane (20 ml), the washings were retained separately and each was evaporated to dryness under nitrogen and reconstituted in tetralin (2 ml). The washed gel was redissolved in tetralin (10 ml) at 150°C for one hour, then cooled. 1 ml of the gel and samples were placed into glass-lined

scintillation tubes, together with Cocktail O (2 ml). The contents of the vials were mixed thoroughly and counted immediately on a liquid scintillation counter.

These experiments were performed on unirradiated polypropylene and also after an exposure of 50 kGy of gamma-irradiation. However, this study could not be repeated using high density polyethylene because as soon as the polymer had been exposed to any dose of gamma-irradiation, it was found to become impossible to dissolve, presumably due to crosslinking.

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CHAPTER 3

THE FATE OF ANTIOXIDANTS WITH RESPECT TO IRRADIATION

1. EFFECTS OF IRRADIATION ON THE COLOUR OF STABILISED POLYMERS

On irradiation, the majority of the thermally processed polymers were observed to undergo a colour change, the extent of which varied with dose received. The colours are recorded in Tables 3.1-3.5.

In summary, all stabilised polymer pellets and sheets were white or transparent after thermal processing, with the exception of polyvinyl chloride sheets containing either Irganox 1076 or Irganox 1010 at a concentration of 0.5%, which were pale orange in colour. In all cases, following progressive doses of gamma-irradiation, a colour change was observed, the intensity of which increased with increasing irradiation.

The appearance of colour in the stabilised polymers is largely attributable to the presence of degradation products, arising from the effect of gamma-irradiation on the antioxidants. Reactions of these antioxidants with radicals generated by irradiation result in the formation of conjugated compounds such as benzoquinone, quinone methide and stilbene-quinone, [1,2] which are discussed in detail in Chapter 1. These compounds are highly coloured and when present in the polymer, cause discolouration. It may be deduced that as the irradiation dose increases, more radicals are generated, which interact to a greater

Table 3.1

Effect of irradiation on the colour of stabilised, thermally processed polymers.

Irradiation dose/kGy	PVC/BHT/1	PVC/BHT/5	PVC/1076/0.5
0	Clear	Clear	Pale Orange
1	Clear	Clear	Pale Orange
5	Yellow/Green	Turquoise	Brown
10	Darker Green	Turquoise	Dark Brown
20	Darker Green	Darker Turquoise	Very Dark Brown
25	Yellow/Brown	Light Green	Very Dark Brown
35	Darker Brown	Light Green	Brown/Black
50	Darker Brown	Light Green	Brown/Black

	PVC/1010/0.5	PS/BHT/1.5	Blank PS
0	Pale Orange	Clear	Clear
1	Pale Orange/Brown	Clear	Clear
5	Orange/Brown	Clear	Clear
10	Darker Brown	Clear	Clear
20	Dark Brown	Pale Turquoise	Clear
25	Dark Brown	Pale Turquoise	Clear
35	Dark Brown	Pale Turquoise	Clear
50	Brown/Black	Turquoise	Clear

Table 3.2

Contd.

Irradiation dose/kGy	PE/1076/0.5	PE/1010/0.5	PE/1330/0.5
0	White	White	White
1	White	White	White
5	White	Off White	Off White
10	White	Pale Yellow	Off White
20	Slightly Yellow	Pale Yellow	Slightly Yellow
25	Pale Yellow	Pale Yellow	Pale Yellow
35	Pale Yellow	Pale Yellow	Pale Yellow
50	Pale Yellow	Yellow	Yellow

	LDPE/1076/0.25	HDPE/1076/0.03	HDPE/*1076/0.19
0	White	White	White
1	White	White	
5	White	Off White	
10	Off White	Off White	Off White
20	Off White	Off White	
25	Slightly Yellow	Off White	Pale Yellow
35	Slightly Yellow	Off White	
50	Slightly Yellow	Slightly Yellow	Yellow

Table 3.3

Contd.

Irradiation dose/kGy	Blank PP (raw mix)	Blank PP (pellets)	PP/1076/0.5
0	White	White	White
1	White	White	White
5	White	White	White
10	White	White	White
20	White	White	Slightly Yellow
25	White	White	Pale Yellow
35	White	White	Pale Yellow
50	White	White	Yellow

	PP/1010/0.1 (raw mix)	PP/1010/0.1 (pellets)	PP/1010/0.5
0	White	White	White
1	White	White	White
5	White	White	Off White
10	White	Off White	Pale Yellow
20	White	Slightly Yellow	Pale Yellow
25	White	Slightly Yellow	Yellow
35	White	Pale Yellow	Yellow
50	White	Pale Yellow	Yellow

Table 3.4

Contd.

Irradiation dose/kGy	PP/1330/0.1	PP/1330/0.5	PP/168/0.1
0	White	White	White
1	White	White	White
5	Off White	Off White	Off White
10	Off White	Off White	Off White
20	Pale Yellow	Pale Yellow	Off White
25	Pale Yellow	Pale Yellow	Off White
35	Pale Yellow	Pale Yellow	Pale Yellow
50	Pale Yellow	Yellow	Pale Yellow

	PP/1076/0.5 Homopolymer	PP/1076/0.5 Copolymer	PP/1010,168/0.1
0	Clear	White	White
1	Clear	White	White
5	Clear	White	Off White
10	Off White	Off White	Off White
20	Off White	Off White	Slightly Yellow
25	Slightly Yellow	Slightly Yellow	Slightly Yellow
35	Pale Yellow	Slightly Yellow	Pale Yellow
50	Yellow	Pale Yellow	Yellow

Table 3.9

Contd.

Irradiation dose/kGy	PP/1076/0.25 Homopolymer	PP/1076/0.25 Copolymer	PP/*1076/0.2
0	Clear	White	White
10	Off White	Off White	Off White
25	Pale Yellow	Slightly Yellow	Pale Yellow
50	Pale Yellow	Pale Yellow	Pale Yellow

	PP/1010/0.25 Homopolymer	PP/1010/0.25 Copolymer
0	Clear	White
10	Off White	Off White
25	Slightly Yellow	Slightly Yellow
50	Pale Yellow	Pale Yellow

these coloured degradation products. Hence, the intensity of the colour increases with irradiation dose.

The appearance of colour may also be attributable to degradation of the polymers themselves. In the case of polyvinyl chloride, the colour that develops is due to the production of conjugated polyene sequences, by the loss of hydrogen chloride. These reactions occur at temperatures above 100°C (during processing) or under the influence of light and are not only induced by the effects of gamma-irradiation. The degradation of polymers by gamma-irradiation is discussed in detail in Chapter 1.

2. EFFECTS OF IRRADIATION ON THE ANTIOXIDANT PRESENT

2.1 Changes in the levels of extractable antioxidants following irradiation.

The emphasis here has been to monitor the changes in the levels of specific additives in a given polymer composition as the irradiation dose is progressively increased. Particular attention has been paid to doses up to 10 kGy (1 Mrad), but the effects of larger doses have also been studied.

The results are presented in Tables 3.6 and 3.7. It is important to note that in every stabilised polymer, a small (occasionally large) fraction of the added antioxidant has been lost prior to irradiation.

Table 3.6

Effects of Irradiation on Phenolic Antioxidants present in Polyvinyl Chloride, Polystyrene and Polyethylene

	Polyvinyl Chloride				Polystyrene		Polyethylene			
Irradiation dose/kGy	% BHT +/- 0.07	% BHT +/- 0.07	% 1076 +/- 0.03	% 1010 +/- 0.01	% BHT +/- 0.07	% 1076 +/- 0.03	% 1010 +/- 0.01	% 1330 +/- 0.005	LDPE % 1076 +/- 0.03	HDPE % 1076 +/- 0.03
0	0.49	3.04 (3.37)	0.44	0.62	1.07 (1.04)	0.36	0.16	0.25	0.26	0.031
1	0.42 (0.38)	3.05	0.29 (0.40)	0.46 (0.39)	1.01	0.28 (0.43)	0.12 (0.12)	0.22	0.26	0.032
5	0.44	3.05	0.27	0.46	0.97	0.23	0.11	0.22	0.23	0.021
10	0.41 (0.39)	2.98 (3.24)	0.12 (0.37)	0.43 (0.38)	0.98 (0.97)	0.22 (0.34)	0.10 (0.09)	0.22	0.21	0.021
20	0.38	2.32	0.17	0.37	0.94	0.20	0.07	0.15	0.17	0.020
25	0.38 (0.30)	2.53 (2.69)	0.18	0.31 (0.24)	0.93 (0.97)	0.14 (0.28)	0.07 (0.07)	0.15	0.15	0.013
35	0.37	2.73	0.19	0.30	0.86	0.14	0.05	0.16	0.11	0.009
50	0.36 (0.29)	2.75 (3.01)	0.15 (0.31)	0.24 (0.24)	0.78 (0.84)	0.11 (0.18)	0.04 (0.04)	0.13	0.09	0.009
Extraction time/hrs			3	3		3	3	3	17.5	17.5

ND = not detected

() = results for sample six months after irradiation

Table 3.7

Effects of Irradiation on Phenolic Antioxidants present in Polypropylene

	Polypropylene													
							Homopolymer	Copolymer			Homopolymer	Copolymer	Homopolymer	Copolymer
Irradiation dose/kGy	% 1076 +/- 0.03	% 1010 +/- 0.01	% 1010 +/- 0.01	% 1330 +/- 0.005	% 1330 +/- 0.005	% 168 +/- 0.003	% 1076 +/- 0.03	% 1076 +/- 0.03	% 1010 +/- 0.01	% 168 +/- 0.003	% 1076 +/- 0.03	% 1076 +/- 0.03	% 1010 +/- 0.01	% 1010 +/- 0.01
0	0.34	0.08	0.48	0.08	0.38	0.067	0.47	0.53	0.08	0.069	0.235	0.186	0.143	0.134
1	0.37	0.07	0.48	0.07	0.37	0.035	0.53	0.48	0.05	0.010				
	(0.41)	(0.07)	(0.44)											
5	0.38	0.05	0.44	0.06	0.36	0.009	0.45	0.51	0.04	ND				
10	0.38	0.04	0.41	0.06	0.30	0.004	0.42	0.51	0.03	ND	0.173	0.160	0.069	0.071
	(0.38)	(0.04)	(0.31)											
20	0.36	0.02	0.33	0.05	0.27	ND	0.35	0.50	0.02	ND				
25	0.35	0.02	0.33	0.04	0.25	ND	0.34	0.39	0.01	ND	0.142	0.117	0.042	0.038
	(0.34)	(0.02)	(0.23)											
35	0.30	0.01	0.28	0.04	0.22	ND	0.28	0.40	0.01	ND				
50	0.30	0.01	0.18	0.03	0.23	ND	0.31	0.38	0.01	ND	0.134	0.103	0.016	0.015
	(0.28)	(0.01)	(0.16)											
Extraction time/hrs	3	3	3	3	3	3	3	3	3		3	3	3	3

ND = not detected

() = results for sample six months after irradiation

stabilisation of the polymer during thermal processing. It is seen that there is a gradual diminution in the total extractable levels of each antioxidant as irradiation progresses, the extent depending on the nature of both the antioxidant and the polymer, and the processing history of the sample.

For the antioxidant BHT in polystyrene and polyvinyl chloride, only a slight loss of 8-16% is incurred after a dose of 10 kGy. In a second sample of polyvinyl chloride containing a much higher concentration of BHT, after 10 kGy there is no detectable change in the level of the antioxidant.

For antioxidants Irganox 1076 and 1010 in polyvinyl chloride and polyethylene, approximately 30-40% has been destroyed after a dose of 10 kGy. Surprisingly, the extent of the degradation of these two antioxidants in polypropylene is significantly lower than in the other polymers, there being no detectable change in the level of 1076 and only a 14% decrease in the concentration of 1010 (from an original concentration of 0.48%) after a dose of 10 kGy. Similarly, after a dose of 25 kGy, the level of 1076 is unchanged, while that of 1010 has decreased by 31%. However, in a second sample of polypropylene, originally containing a much lower concentration of 1010, a marked reduction in the level of antioxidant is observed, approximately 50% having been consumed after a dose of 10 kGy. It is of interest to compare these results with a brief earlier report of the effects of a 25 kGy exposure of Irganox 1010 present in polypropylene (at an

original concentration of 0.47%), which resulted in a 65% decrease in the level of the antioxidant[3].

The antioxidant Irganox 1330 in polyethylene suffered only a 12% loss after 10 kGy. However, in both samples of polypropylene containing different concentrations of the antioxidant, more significant losses of 20-25% are observed after 10 kGy, even at the much lower initial concentration of 0.08%.

Irgafos 168 in polypropylene was almost totally consumed after 10 kGy, above which little antioxidant remained. It is clear that the hindered phosphite antioxidant is destroyed far more rapidly than hindered phenolic antioxidants. The rate of destruction would seem to be even greater in the presence of the hindered phenolic antioxidant, Irganox 1010, with complete destruction of Irgafos 168 after a dose of 5 kGy. However, in this system, Irganox 1010 suffers degradation at a very similar rate to that observed previously[4]. This finding is comparable with the work performed by Horng and Klemchuk[3], in that an original concentration of 0.34% Irgafos 168 in polypropylene was found to decrease by 80% after a dose of 25 kGy, and after six months following irradiation, Irgafos 168 was not detected, indicating that virtually all of the antioxidant had been consumed.

In order to determine whether variations in the type of base polymer have a bearing on the rate of destruction of the antioxidant after irradiation, several types of base polymer have been studied. The results for the homopolymer and copolymer pellets of polypropylene, containing 0.5% Irganox 1076, indicate that the homopolymer has a

tendency to lose 11% of the antioxidant after a dose of 10 kGy, and 28% after 25 kGy. In contrast, the copolymer appears to remain unaltered up to 25 kGy with no detectable change in the level of Irganox 1076, but above 25 kGy, the sample has lost a similar amount of 26%. The extent of degradation of the antioxidant after 50 kGy was 28-34% for both samples. Results obtained for homopolymer and copolymer sheets of polypropylene containing a lower concentration (0.25%) of Irganox 1076 (as was used in the migration studies), were in agreement with the previous findings. The homopolymer had lost 26% of the antioxidant after 10 kGy and 40% after 25 kGy, whereas the copolymer had only lost 14% after 10 kGy and after a dose of 25 kGy, 37% of the antioxidant had been consumed. Thus, variation in the base type of polypropylene does appear to have a bearing on the rate of destruction of Irganox 1076 after irradiation. However, a comparison of the behaviour of Irganox 1010 in homopolymer and copolymer polypropylene sheets indicated that there was no difference in the rate of destruction of this antioxidant in both polymer base types, since after an exposure of 10 kGy, between 47 and 52% of Irganox 1010 was destroyed immediately. Furthermore, both base types revealed a 70% loss after 25 kGy and after 50 kGy, 89% loss of antioxidant was evident from both samples.

Studies were also conducted on two base types of polyethylene stabilised with Irganox 1076. Low density polyethylene containing 0.2% of the antioxidant had lost 19% after 10 kGy. The level of Irganox 1076 continued to decrease with increasing irradiation dose, until after 50 kGy, 65% had been lost. In high density polyethylene, stabilised however, with a much lower concentration of Irganox 1076

(0.035%), there is a much more obvious decrease in the level of the antioxidant. After an exposure of 10 kGy, 32% had been lost. Nevertheless, it must be noted that these latter results are at the 95% confidence limit of the analytical method, and although a decreasing trend is observed for the level of the antioxidant, there is some doubt as to the accuracy of these results. Hence a comparison cannot be made for polyethylene because of the differing concentrations of the antioxidant within the polymer.

It is well known that a problem arising from the irradiation of polymers is the post-gamma-irradiation effect [1,2,5-7]. The chemical transformation of polyolefins initiated by gamma-irradiation results in the formation of macroalkyl radicals which in turn, leads ultimately to the loss of impact strength of the polymer, because of the reactivity of the radicals with molecular oxygen. This process takes place during the irradiation of the polymer and continues steadily during the storage of irradiated materials in the air atmosphere.

Radicals survive for a long time in solid polymeric hydrocarbons. The post-irradiation effect is generated during the contact of irradiated polymers with air. The residual radicals are quickly transformed into peroxyl radicals. Phenolic antioxidants are scavengers of these radicals and interaction of the two results in transformation of the antioxidant, leading to the formation of antioxidant-derived degradation products. Therefore, there may be the possibility of slow consumption of the antioxidant during subsequent storage at room temperature. Hence, six months after irradiation, a selection of polymer samples containing BHT, Irganox 1076 and Irganox 1010 were re-

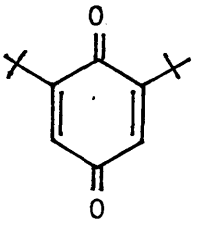
analysed. The results indicate that there are no significant long-term post-irradiation degradation losses of the antioxidant, the results being (within the 95% confidence limits of the methods) identical with those obtained immediately following irradiation (with the exception of the Lankro samples, polyvinyl chloride containing nominally 5.0% BHT, both polyvinyl chloride and polyethylene containing nominally 0.5% Irganox 1076 and polypropylene containing nominally 0.5% Irganox 1010, in which the antioxidant would appear not to be homogeneously distributed throughout the polymer).

Therefore, it may be deduced that as a consequence of increasing the irradiation dose, there is an increase in the number of radicals generated, which interact with the antioxidant to an increasing extent, resulting in degradation of the antioxidant. It is known from Section 1 that the irradiated stabilised polymers are coloured, thereby indicating some degree of degradation of the antioxidant. As the amount of antioxidant diminishes, this is reflected in the decrease observed in extractable antioxidant levels. The extent of this degradation, however, is dependent upon the nature of both the antioxidant and the polymer.

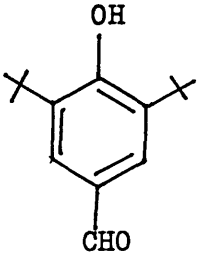
2.2 Detection of degradation products

The course of degradation of BHT on thermal oxidation is well-known (as demonstrated in Chapter 1) and a number of simple oxidation products have been characterised. Some of these degradation products are also formed in oxidative degradation of the more complex "BHT-like"

antioxidants. It is considered important that such simple degradation products be recognised, since these are likely to be among those compounds most likely to migrate from a polymer film. However, under the conditions employed for the determination of BHT, the degradation products 2,6-di-t-butyl-1,4-benzoquinone (I), 3,5-di-t-butyl-4-hydroxybenzaldehyde (II), galvinoxyl (III) and 3,5,3',5'-tetra-t-butylstilbene-4,4'-quinone (IV) were not detected.



I



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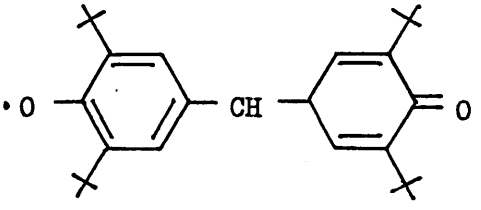

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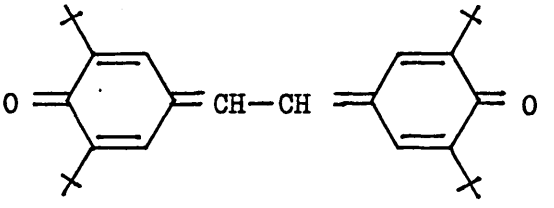


IV

In the case of the hindered phenolic antioxidants (Irganox 1076, 1010 and 1330), the presence of any extractable degradation products derived from the antioxidants have not yet been detected under the chromatographic conditions employed. However, it has been observed that the chloroform extracts of the irradiated polyolefins containing these antioxidants become increasingly yellow as the irradiation dose increases, suggesting the formation of some extractable degradation

products. Studies with known oxidative degradation products derived from BHT have shown that such compounds can be detected at wavelengths significantly different from those used in the HPLC analytical procedures for the determination of the above antioxidants, in which the degradation products do not interfere. Chromatographic studies of the most intense yellow polymer extracts, arising from polymers stabilised with Irganox 1330 after an irradiation dose of 50 kGy, at higher wavelengths indicated the presence of stilbene-quinone (IV). Further chromatographic evidence showed the presence of benzoquinone (I) in the irradiated samples, after 50 kGy. Although benzoquinone may be detected at the operating wavelength of 275 nm, the compound is not retained by the column and elutes in the solvent front, making reliable determination impossible under these chromatographic conditions.

There is the possibility that other degradation products are becoming covalently bonded to the polymer as a result of radical coupling reactions occurring during irradiation. It has recently been shown that gamma-irradiation of hindered phenols in benzene solution gives rise to phenylated derivatives resulting from coupling of radicals derived from the antioxidants with phenyl radicals derived from the solvent[8]. Gamma-irradiation of polyolefins is well known to give rise to macroalkyl radicals [1,7-9] and the trapping of antioxidant degradation products is therefore probable. Evidence to support this hypothesis has now been adduced from studies using ^{14}C-labelled Irganox 1076 present in both polypropylene and polyethylene. This will be discussed in Chapter 4.

In the case of the hindered phosphorus antioxidant, Irgafos 168, upon irradiation, an extractable degradation product was detected. This work will be discussed in Chapter 5.

2.3 Effects of irradiation on migration of antioxidants into food simulants

The effects of gamma-irradiation on the extent of migration of Irganox 1076 and Irganox 1010 from polyolefins into the synthetic triglyceride fatty food simulant HB 307 and, for comparison, into iso-octane, have been investigated.

The results of these migration experiments are presented in Table 3.8, as specific migration values (mg antioxidant per dm^2 contact area). Samples of polypropylene containing Irganox 1076 and Irganox 1010 were used in the studies in iso-octane, detection being by HPLC and the polymers containing the ^{14}C-labelled Irganox 1076 were used in studies into HB 307, the extent of migration from the latter samples being assayed by conventional liquid scintillation techniques. The attraction of experiments on the latter samples is that much lower levels of migration can be recorded (far below the sensitivity of the HPLC method). In separate experiments, it was demonstrated by TLC techniques that the ^{14}C-activity migrating into the simulant was due predominantly to unchanged ^{14}C-labelled Irganox 1076, although smaller amounts of another, as yet unidentified, substance could also be detected. It is justifiable, therefore, to assume that the ^{14}C-activity of the simulant reflects the degree of migration of the antioxidant.

Table 3.8

Effects of Irradiation on Migration of Antioxidants into Fatty Food Simulants

	ISO-OCTANE		HB 307	
Irradiation dose /kGy	Irganox 1076 (0.25%) mg/dm^2	Irganox 1010 (0.25%) mg/dm^2	^{14}C-Irganox 1076 (0.2%) mg/dm^2	(0.19%) mg/dm^2
	Polypropylene a	Polypropylene a	Polypropylene a	HDPE
0	2.6	0.8	1.0	1.3
10	2.1	0.3	0.7	1.0
25	1.3	<0.2	0.5	0.7
50	0.4	<0.2	0.2	0.3

	ISO-OCTANE	
Irradiation dose /kGy	Irganox 1076(0.25%) mg/dm^2	Irganox 1010(0.25%) mg/dm^2
	Polypropylene b	Polypropylene b
0	5.1	2.8
10	4.3	1.4
25	2.7	0.5
50	1.3	0.3

a as homopolymer

b as copolymer

In the studies with iso-octane and HB 307, it is clear that the extent of migration into both simulants decreases steadily as irradiation progresses, consistent with the reduction in the amounts of extractable antioxidant revealed in the earlier study[14].

In the migration experiments involving unirradiated polypropylene, 13% of the added radiolabelled antioxidant was shown to migrate into HB 307. This value decreased to 9.6% and then to 2.4% after exposure of 10 and 50 kGy, respectively. Identical studies with unirradiated high density polyethylene showed that 17% of the added antioxidant had migrated, decreasing to 13.6% and 3.6% after exposures of 10 and 50 kGy, respectively. Results obtained by Figge and Freytag[10] revealed that 45.4% of Irganox 1076 in high density polyethylene had migrated into HB 307, prior to irradiation. However, it must be noted that the samples used in the present study were twice the thickness and contained twice the concentration of Irganox 1076 as those used in Figge's work.

It is of interest that the extent of migration of Irganox 1076 into iso-octane is significantly greater than that of Irganox 1010, which can be related to the comparable levels of free additive remaining in the polymer after a given irradiation dose and the greater lipophilicity of Irganox 1076 compared with Irganox 1010. Furthermore, while the extent of migration of Irganox 1076 into iso-octane is greater than into HB 307 under the stated conditions, the results are nevertheless comparable in magnitude, thus providing some justification for the use of iso-octane as a convenient indicator simulant for migration into fatty foods. Studies carried out by De Kruijf et al[11]

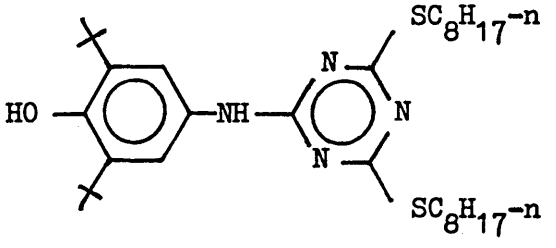
revealed that the use of iso-octane as a migration simulant appeared to be a suitable substitute for determinations in olive oil, taking into account the poor reproducibilities and accuracy associated with tests in the latter. Iso-octane is suitable in the determination of migration from the majority of food contact plastics[12]. However, the migration results from certain plastics (namely polyvinyl chloride and polyurethane) indicate that iso-octane is not a suitable replacement simulant for olive oil[12,13].

Studies of the migration of the antioxidants from the polymer samples into distilled water, 15% ethanol and 3% acetic acid have revealed that gamma-irradiation does not lead to any increase in migration into aqueous based simulants which can be detected by HPLC techniques. Using scintillation techniques, however, the extent of migration into 15% ethanol increased marginally as irradiation progressed and was in good agreement with migration results obtained in distilled water for polypropylene sheets containing Irganox 1076 after an exposure of 25 kGy[10]. Quantification of these results, performed by matrix-matching the extracted standards with the samples, revealed that with unirradiated polypropylene, 0.025% of the added radiolabelled antioxidant had migrated into 15% ethanol. This value increased marginally to 0.129% and 0.349% after 10 and 50 kGy, respectively. Identical studies, involving unirradiated high density polyethylene, revealed that 0.192% of the added antioxidant had migrated, increasing to 0.631% and 0.472% after exposures of 10 and 50 kGy respectively. The extent of migration of antioxidants into aqueous based simulants is therefore negligible in comparison with that into the fatty food simulants.

The key conclusion from this study, however, is that gamma-irradiation leads to a decrease in the extent to which hindered phenolic antioxidants migrate from polyolefins into fatty media.

2.4 Degradation of Irganox 565 in the determination of antioxidants in gamma-irradiated polyolefins by HPLC

In the determination of a synergistic mixture of Irganox 1010 and Irgafos 168 in polymers, Irganox 565 (V) was selected as the internal standard because of its favourable retention behaviour relative to the two analytes under the conditions employed, (as described in Chapter 2, Section 3.4).



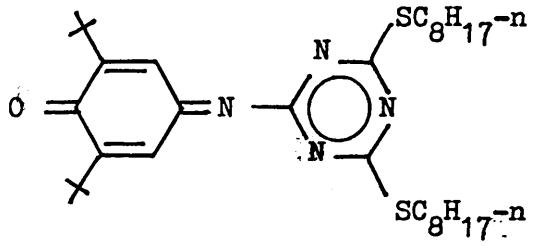
V

Samples of polymer were spiked with Irganox 565 as the internal standard and then extracted under reflux in chloroform. Irganox 565 was observed to function as an acceptable internal standard in the analysis of unirradiated polypropylene. However, when samples of irradiated polypropylene, stabilised with both Irganox 1010 and Irgafos 168, were analysed, the internal standard was found to be progressively destroyed during the reflux period.

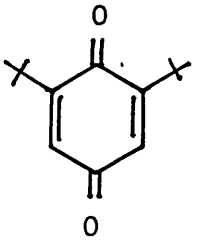
Further studies of the behaviour of Irganox 565 with irradiated polymers were carried out on unstabilised polypropylene, and both high and low density polyethylene, after irradiation doses of 1,10, 25 and 50 kGy, respectively. In the case of polypropylene, Irganox 565 was completely destroyed after an irradiation dose of 1 kGy. With irradiated low density polyethylene, destruction of Irganox 565 was slower than with polypropylene, but was significantly dose-related, with complete destruction of the internal standard being observed after a dose of 50 kGy. In contrast to polypropylene and low density polyethylene, only a very small degree of degradation of Irganox 565 was observed in the presence of high density polyethylene after progressive doses of irradiation. Further investigations of the behaviour of Irganox 565 in the presence of gamma-irradiated unstabilised polypropylene or low density polyethylene, revealed that it is converted to N-[4,6-di(octylthio)-1,3,5-triazin-2-yl]-2,6-di-t-butylbenzoquinone monoimine (VI), identified by comparison with the authentic compound (whose method of synthesis is described in Chapter 2, Section 7.4.2, prepared by oxidation of Irganox 565 with manganese dioxide in chloroform).

It is probable that VI is formed from the reaction of Irganox 565 (V) with polymeric peroxyl groups, which are generated at tertiary carbon sites during irradiation of the polymers in air. The significantly smaller number of sites available to be oxidised in irradiated high density polyethylene would appear to explain why Irganox 565 is not completely destroyed, even after high irradiation doses. Model studies of the reaction of Irganox 565 with t-butyl hydroperoxide in chloroform revealed that VI was readily formed, together with 2,6-di-t-butyl-1,4-

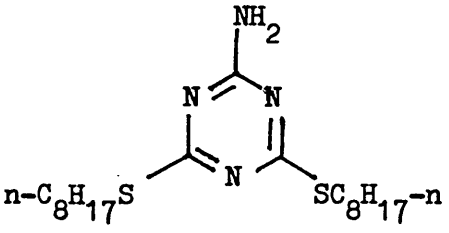
arising from the hydrolysis of VI by traces of water in the peroxide reagent.



VI



VII



VIII

Recently, much interest has been generated into developing simple, reliable tests, which will reveal whether food has been irradiated or not. The above study may have the potential as the basis of a novel method of detection of irradiated food-contact plastics.

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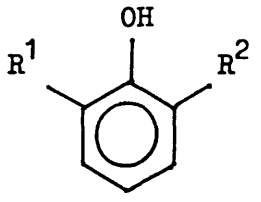
DETERMINATION OF THE EXTENT OF ANTIOXIDANT - POLYMER BINDING AFTER GAMMA-IRRADIATION

In this Chapter, two investigations are described which reveal the extent to which a radiolabelled antioxidant becomes bound to the polymers (polypropylene and high density polyethylene) following increasing doses of gamma-irradiation.

It is a distinct possibility that the degradation products derived from the antioxidants could become covalently bound to the polymer as a result of radical coupling processes during irradiation. It has recently been shown that gamma-irradiation of hindered phenols (Ia-c)



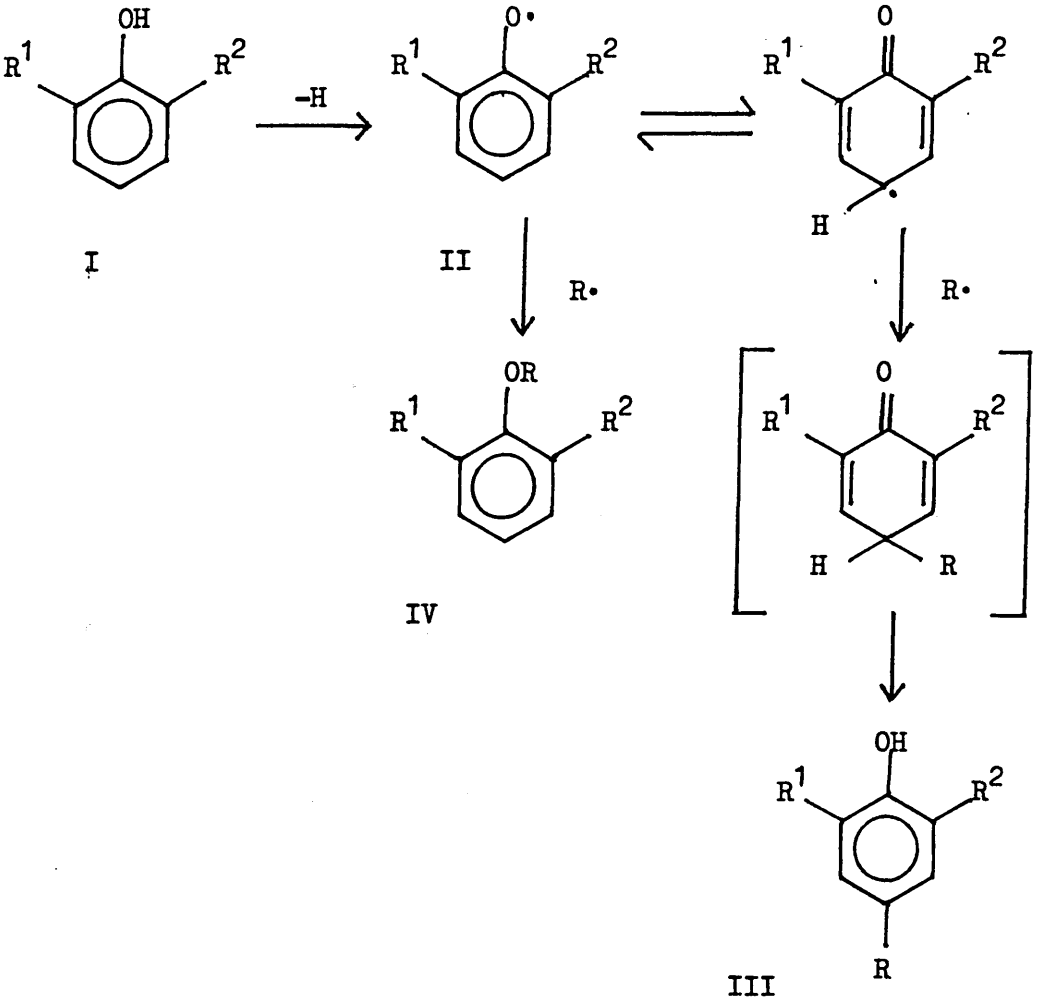
I

a : $R^1=R^2=Me$

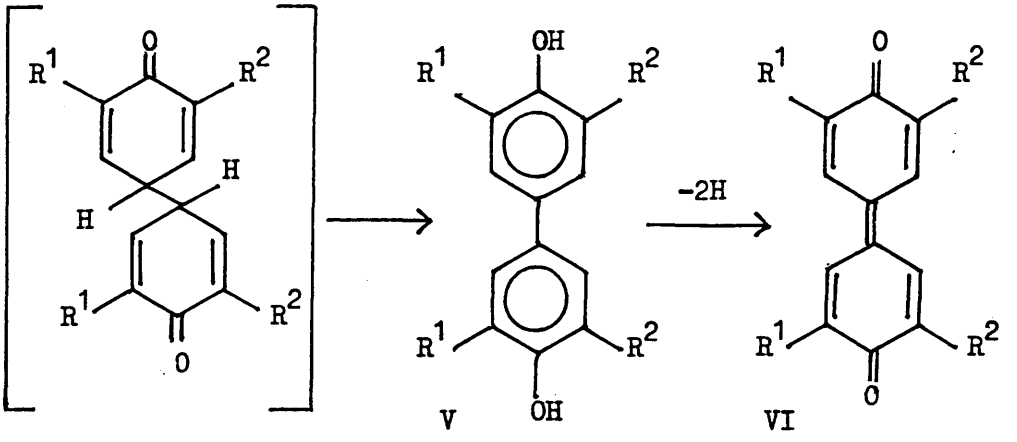
b : $R^1=Me, R^2={}^tBu$

c : $R^1=R^2={}^tBu$

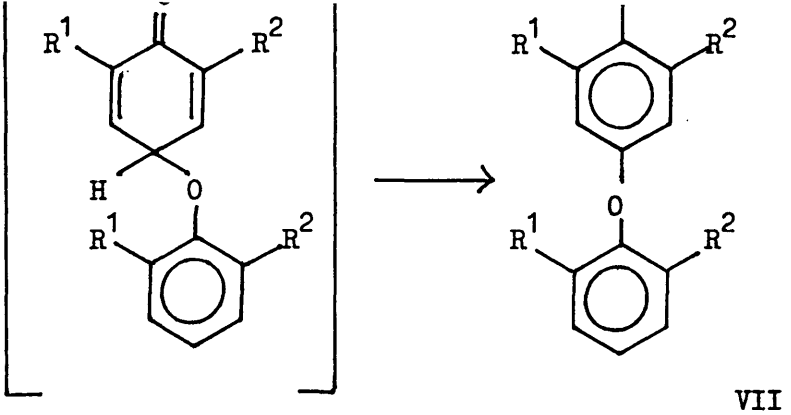
in benzene solution results in the formation of phenylated derivatives (III,IV) which arise as a result of coupling of phenyl radicals (R·) (from the solvent) with antioxidant-derived products[1].



There will, of course, be C-C coupling reactions between the carbon-centred cyclohexadienonyl radical of II resulting in the formation of V, which is oxidised to VI.



In addition, C-O coupling of both mesomeric forms of II results in the formation of VII[1].



VII

It is known that polyolefins on irradiation give rise to macroalkyl radicals[1-4], and therefore such radical coupling processes could readily occur in the irradiated polymer, leading to covalent binding of antioxidant transformation products. If this is so, concerns about potential migration of degradation products may therefore be much reduced.

1. Results of the investigations

The first investigation involved subjecting the unirradiated and irradiated polymers to extractions of eight hours in chloroform, after which the residual radioactivity of the samples was counted. (Separate experiments, described in Appendix 2, showed that in the case of unirradiated polypropylene, extraction for twelve hours did not result in any increased radioactivity in the extract, and that for high density polyethylene, the eight hour extraction was 98% complete). The chloroform extracts were pooled and counted to reveal the extractable radioactivity of the samples. The duplicate results are presented in Table 4.1. Despite some scatter in the results, the residual radioactivity of the extracted polymers clearly increases to a marked

Table 4.1

Effects of Irradiation on ^{14}C-labelled Irganox 1076 present in Polypropylene and High Density Polyethylene.

Irradiation dose/kGy	Residual radioactivity corrected cpm/sample Polypropylene		High Density Polyethylene	
0	17.6	≡ 0.4%	80.2	≡ 1.7%
10	182.5	≡ 3.7%	292.1	≡ 6.3%
25	384.7	≡ 7.8%	522.1	≡ 11.3%
50	1185.9	≡ 24.1%	1007.8	≡ 21.8%
0 - unextracted	4918.6		4619.9	

Irradiation dose/kGy	Chloroform extractable radioactivity corrected cpm/0.1g polymer Polypropylene		High Density Polyethylene	
0	150899	≡ 100%	162972	≡ 100%
	147605		196572	
10	128167	≡ 92%	125735	≡ 77%
	146826		152677	
25	111823	≡ 83%	92021	≡ 63%
	134535		134480	
50	90822	≡ 58%	49285	≡ 28%
	81625		51851	

extent as irradiation dose increases (Figures 4.1 and 4.2). Conversely, the total extractable radioactivity decreases as the dose increases (Figures 4.3 and 4.4).

The results for the residual radioactivity of the extracted polymer were expressed as a percentage of those arising from the unirradiated, unextracted polymer. After extraction, unirradiated polypropylene contained only 0.4% of the radioactivity due to the added antioxidant. After a gamma-irradiation dose of 10 kGy, 3.7% of the radioactivity remained in the polymer. This value was observed to increase to 7.8% and 24.1% after exposures of 25 and 50 kGy. The same trend was also observed in samples of high density polyethylene. The unirradiated polymer contained only 1.7% of the radioactivity due to the added antioxidant after extraction, (consistent with the 98% extraction efficiency noted above). After an exposure of 10 kGy, there was a very marked increase with 6.3% of the added radioactivity remaining in the polymer. As the irradiation dose increased to 25 and 50 kGy, the residual radioactivity increased accordingly to 11.3% and 21.8% respectively. Thus for both polypropylene and high density polyethylene, very significant increases in 'bound' radioactivity were found as a result of irradiation.

The results for the total extractable radioactivity of polypropylene indicate that 92% of the antioxidant is extractable after 10 kGy, decreasing to 83% and 58% after 25 and 50 kGy, respectively. In the case of high density polyethylene, after an irradiation dose of 10 kGy, only 77% of the antioxidant could be extracted, and subsequent doses of

Figure 4.1 Residual radioactivity in milled polypropylene samples containing 0.2% ^{14}C-Irganox 1076 after chloroform extraction on gamma-irradiation

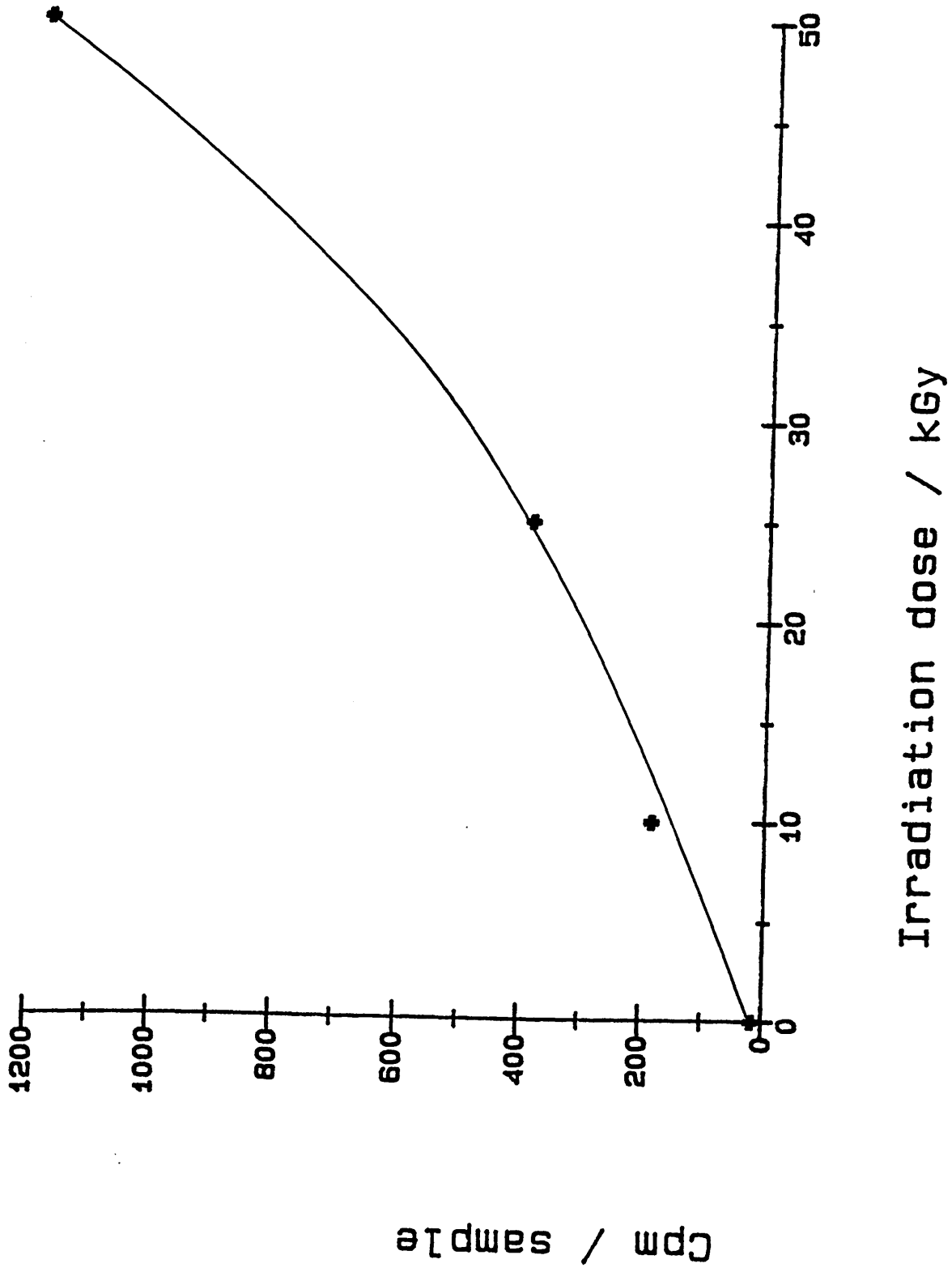


Figure 4.2 Residual radioactivity in milled high density polyethylene samples containing 0.19% ^{14}C-Irganox 1076 after chloroform extraction on gamma-irradiation

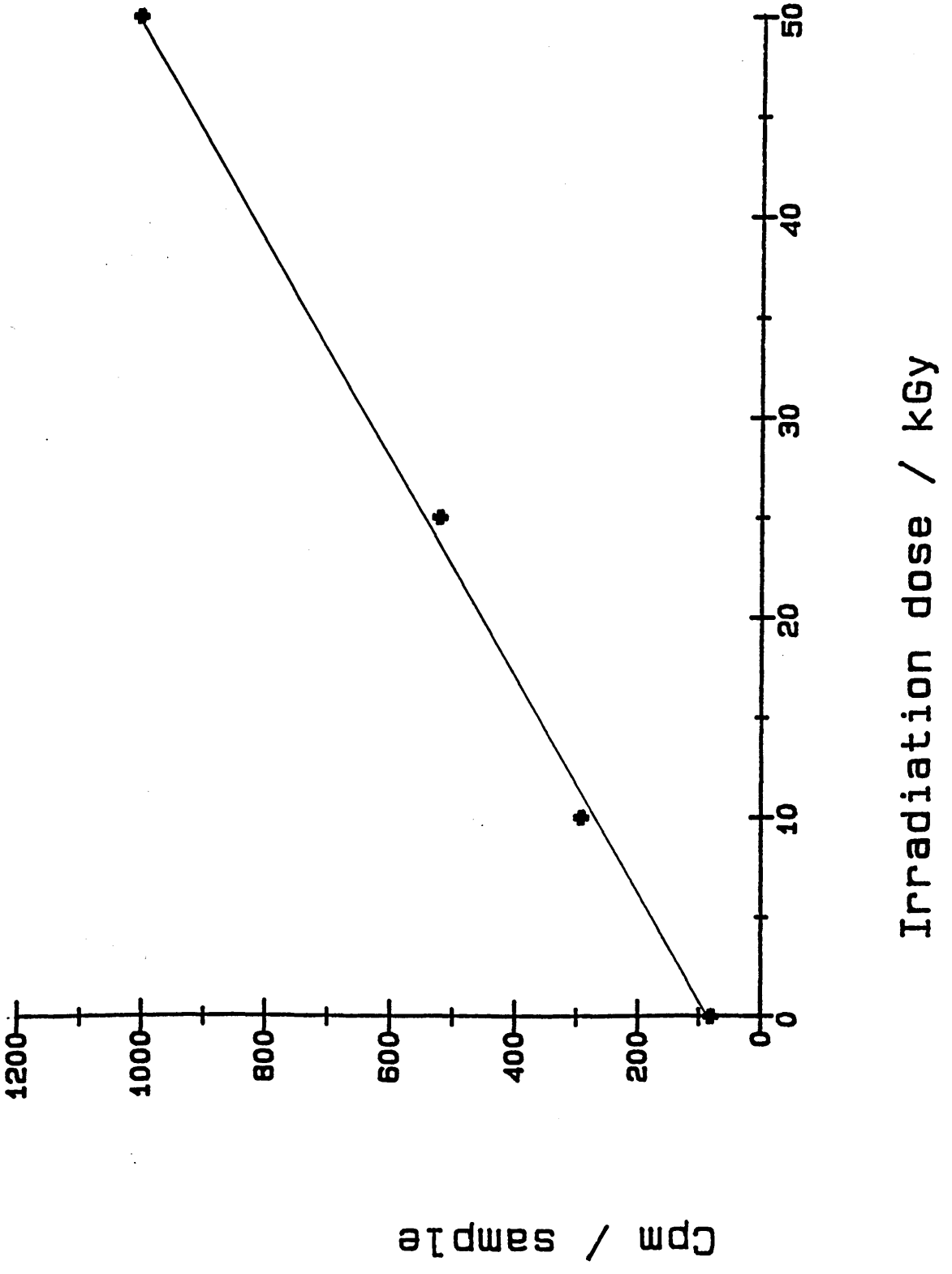


Figure 4.3 Effects of gamma-irradiation on the chloroform extractable radioactivity in polypropylene containing 0.2 % ^{14}C-Irganox 1076

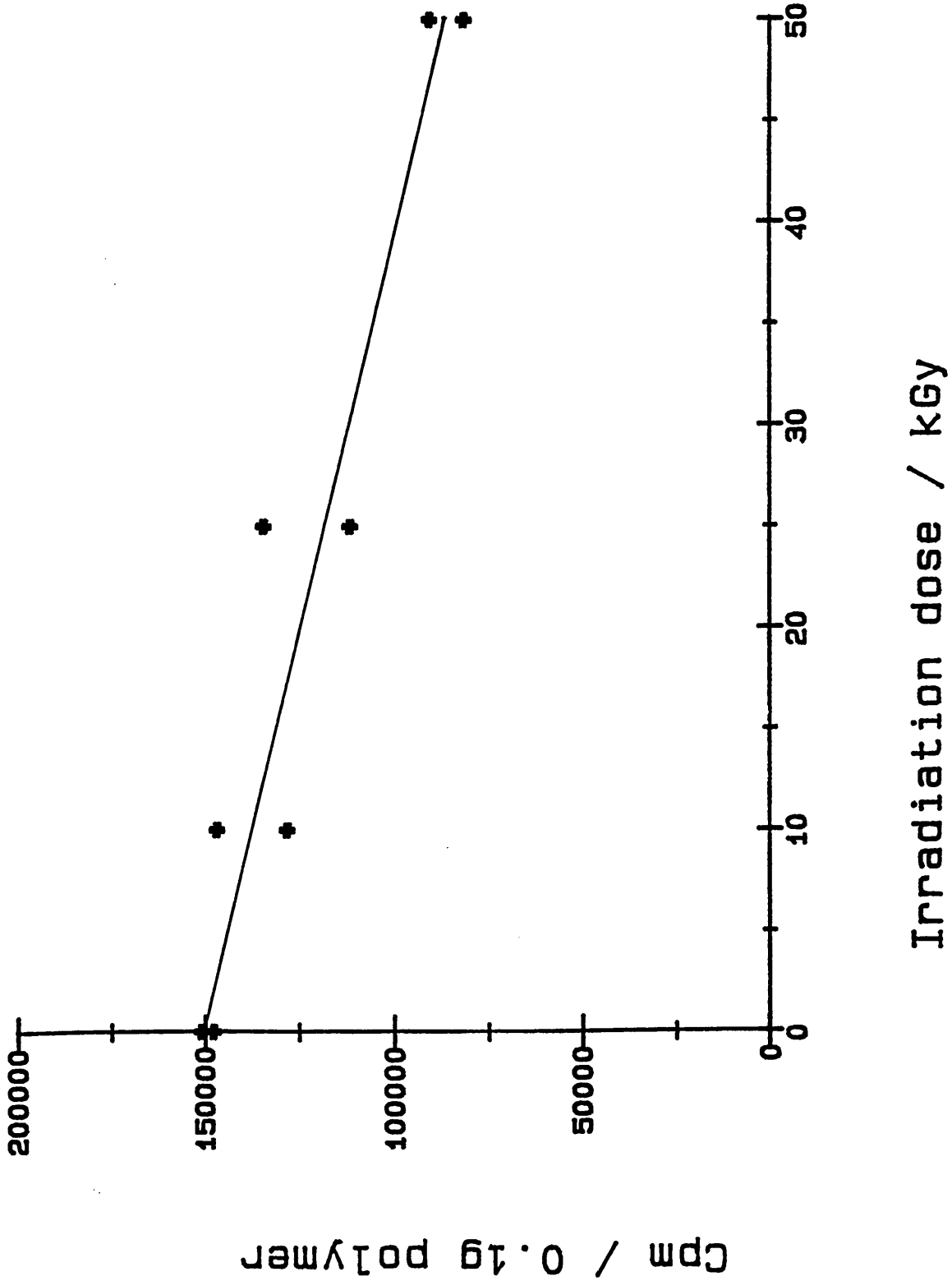
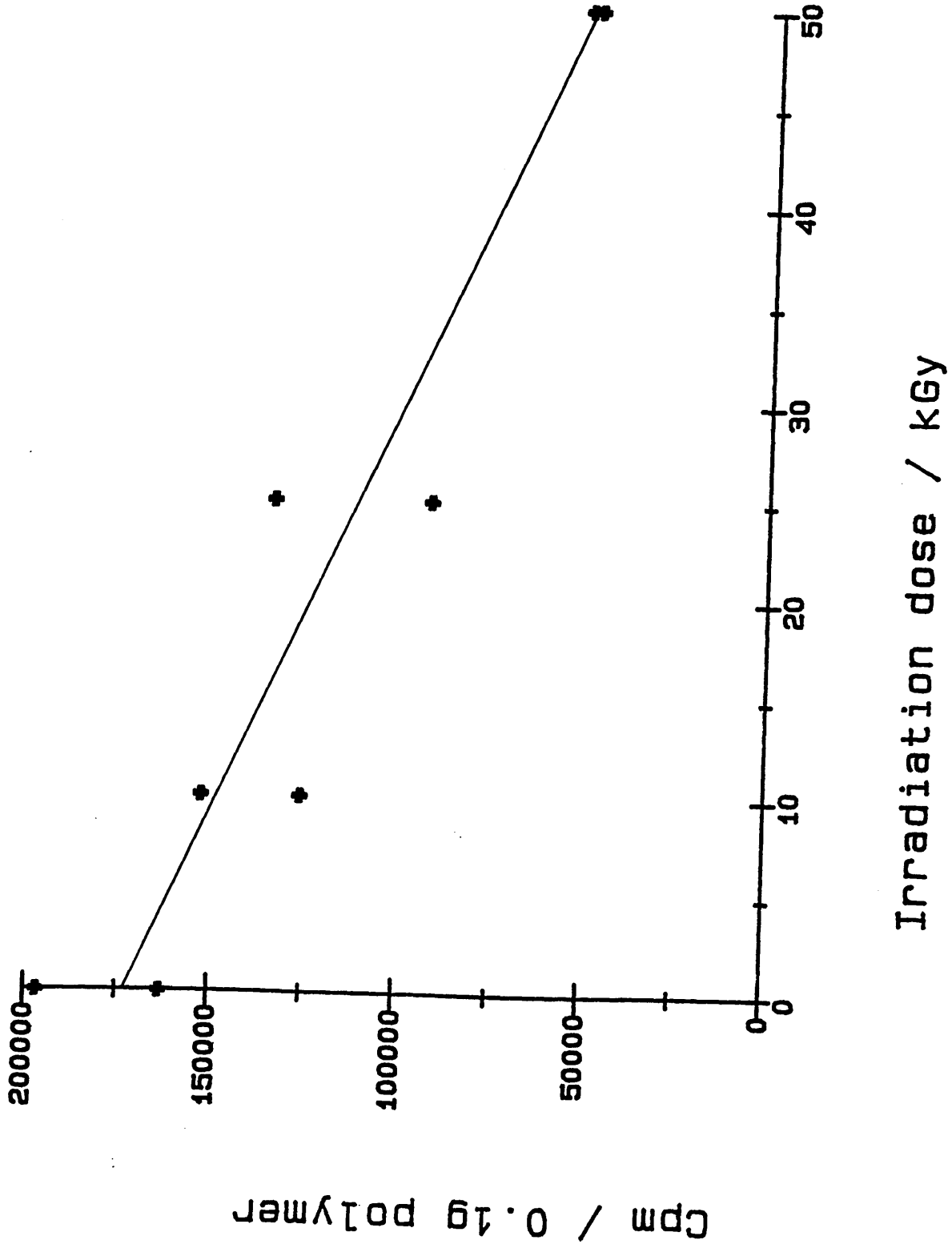


Figure 4.4 Effects of gamma-irradiation on the chloroform extractable radioactivity in high density polyethylene containing 0.19 % ^{14}C-Irganox 1076



25 and 50 kGy revealed that the level of extractable antioxidant diminished markedly to 63% and 28%, respectively.

A problem with the above investigation was that it could not distinguish between antioxidant which was polymer-bound and antioxidant retained by physical entrapment within the crosslinked or degraded polymeric matrix, as a result of the effects of gamma-irradiation. Hence, a second investigation was initiated to determine the extent to which the antioxidant becomes covalently bound to the polymer following gamma-irradiation. It involved complete dissolution of the polypropylene sample in tetralin, followed by precipitation of the polymer by the addition of hexane. It was considered that any unbound antioxidant would be removed in the tetralin fraction and the bound fraction would be precipitated with the polymer. The polymeric precipitate was repeatedly washed with hexane to remove any residual unbound activity. The gel was counted after a total of six washings with hexane. The amount of gel arising from the 50 kGy irradiated sample was approximately half that of the unirradiated sample. This is probably due to the effects of irradiation causing degradation of the polypropylene by chain scission, resulting in the formation of tetralin-soluble lower molecular weight oligomers.

The results are presented in Table 4.2. The unirradiated sample of polypropylene contains 0.35% of the added radioactivity in the tetralin-insoluble, hexane washed gel fraction. After an irradiation dose of 50 kGy, the amount of radioactivity bound to the polymeric gel increased to 12.4%.

Table 4.2

Effect of Irradiation on the Extent of Antioxidant Binding to Polypropylene

Fraction to be counted	Unirradiated		After 50 kGy	
	Corrected radioactivity (cpm)	% of total radioactivity	Corrected radioactivity (cpm)	% of total radioactivity
Tetralin	1080060	90.388	658500	83.588
1st wash	90924	7.609	28990	3.680
2nd wash	17046	1.427	2118	0.269
3rd wash	2228	0.186	178	0.023
4th wash	310	0.026	118	0.015
5th wash	66	0.005	68	0.008
6th wash	42	0.004	76	0.009
Gel (after 6 washes)	4230	0.354	97740	12.407

The investigation could not be repeated using high density polyethylene because as soon as the polymer had been exposed to any dose of gamma-irradiation, it was found to become impossible to dissolve, presumably due to crosslinking.

This marked increase in radioactivity of the gel can be attributed to the formation of radiolabelled degradation products, derived from the antioxidant, which have become covalently bound to the polymer as a result of the gamma-irradiation process.

2. Discussion

There is a pronounced increase in the amount of covalent binding of ^{14}C-labelled degradation products, arising from gamma-irradiation of the antioxidant.

Investigations on unirradiated polypropylene revealed that a small percentage of the ^{14}C-labelled radioactivity (0.4%) is retained by the polymer, after extraction or dissolution (Table 4.1 and 4.2). It is known that during both thermal processing and gamma-irradiation, alkyl and peroxyl radicals derived from the polymer are formed[2]. Irganox 1076 inhibits the oxidation of these radicals and, when a radiolabelled sample of Irganox 1076 is used, this results in ^{14}C-labelled degradation products becoming covalently bound to the polymer. This process occurs to a small extent in unirradiated polymers after thermal processing.

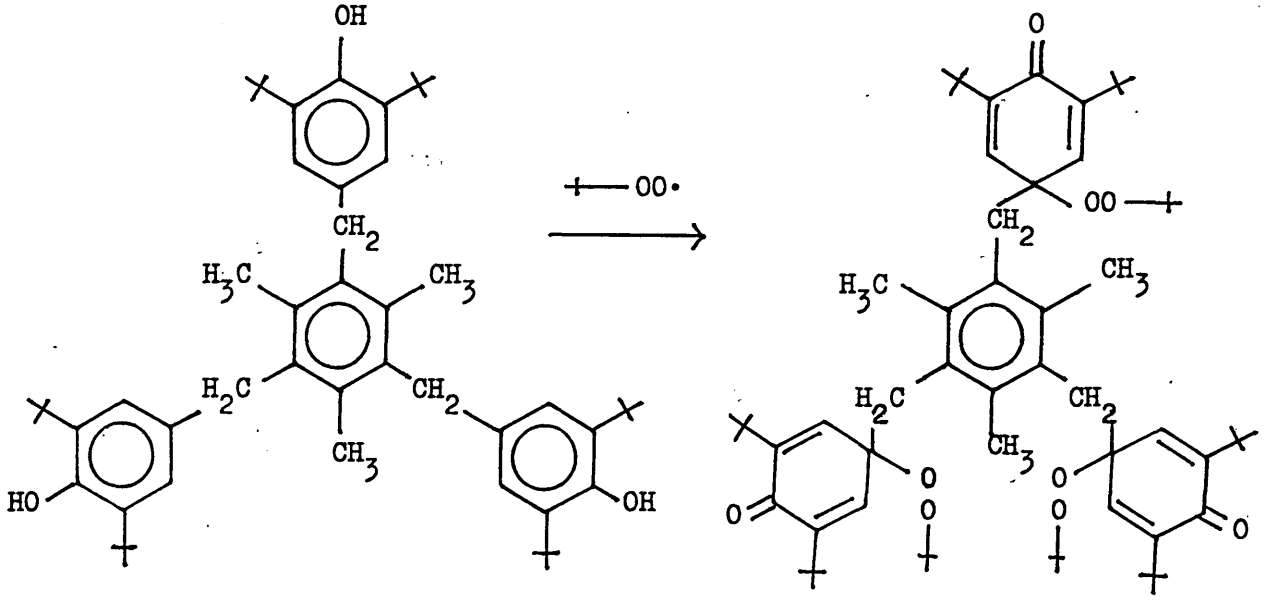
increase in ^{14}C-labelled degradation products bound to the polymer, but the actual results were subject to variation. The value of 42% for antioxidant-polymer binding (Table 4.1, i.e. the difference from the extracted radioactivity (58%) after 50 kGy) may be an overestimate, because a proportion of the radiolabelled antioxidant could be physically trapped within the degraded polymeric matrix. In the case of high density polyethylene, gamma-irradiation has been shown to cause crosslinking of the polymer (Chapter 1), and therefore the polymer-bound antioxidant value of 72% (Table 4.1, i.e. the difference from the extracted radioactivity (28%) after 50 kGy) is certainly an overestimate, since a significant proportion of this antioxidant will be physically trapped in the crosslinked matrix. Thus, the actual percentage of antioxidant-polymer binding in the irradiated samples cannot be determined with any degree of accuracy by the above approaches.

The determination of residual radioactivity of the solid pieces is subject to systematic errors. These include a contribution of counts which are undetected owing to self-absorption of the beta particles by the polymer itself and beta particles which are ejected away from the window of the detector. Although these results confirm that there is a marked increase in polymer binding, arising from irradiation, the absolute values remain in doubt. Obviously these contributions will vary to different extents for the unextracted and extracted polymers, in terms of the number of counts arising from the samples.

The value of 12.4% for ^{14}C-labelled degradation products bound to the polymer, obtained by the tetralin/hexane study, appears low in comparison to the results obtained from the solvent extraction experiments, after an exposure of 50 kGy (Table 4.1). It is possible that low molecular weight oligomers containing the covalently bound-radiolabelled fraction of the antioxidant were not precipitated with the polymer by hexane. Hence the soluble oligomers were possibly counted along with unbound fraction, giving an erroneously low result, which can be expressed as the 'minimum percentage' of polymer binding.

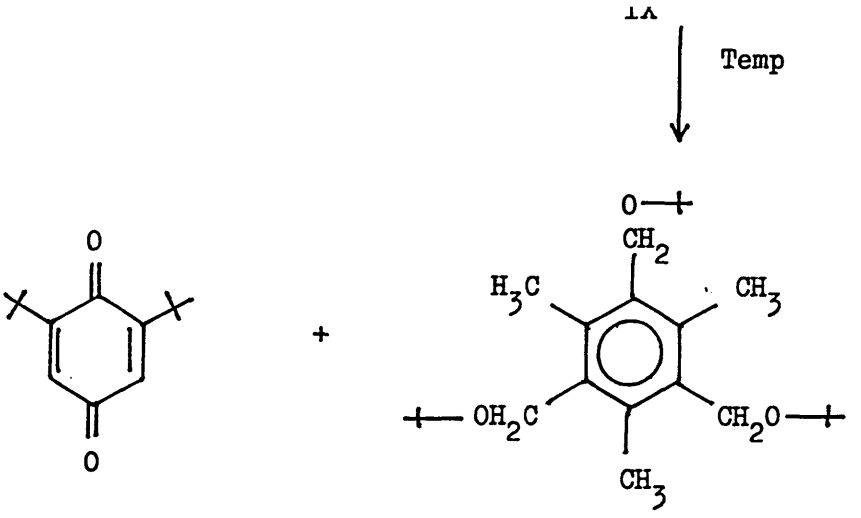
A possible explanation for the interaction of the antioxidant with the polymer leading to covalent binding is described below.

The reaction between Irganox 1330 (VIII) and t-butyl hydroperoxide was demonstrated by Koch[5,6], the latter modelling the oxidised skeleton of polypropylene. The t-butyl peroxyl radical was shown to bind to the antioxidant forming the intermediate IX which decomposed to form X and benzoquinone (XI).



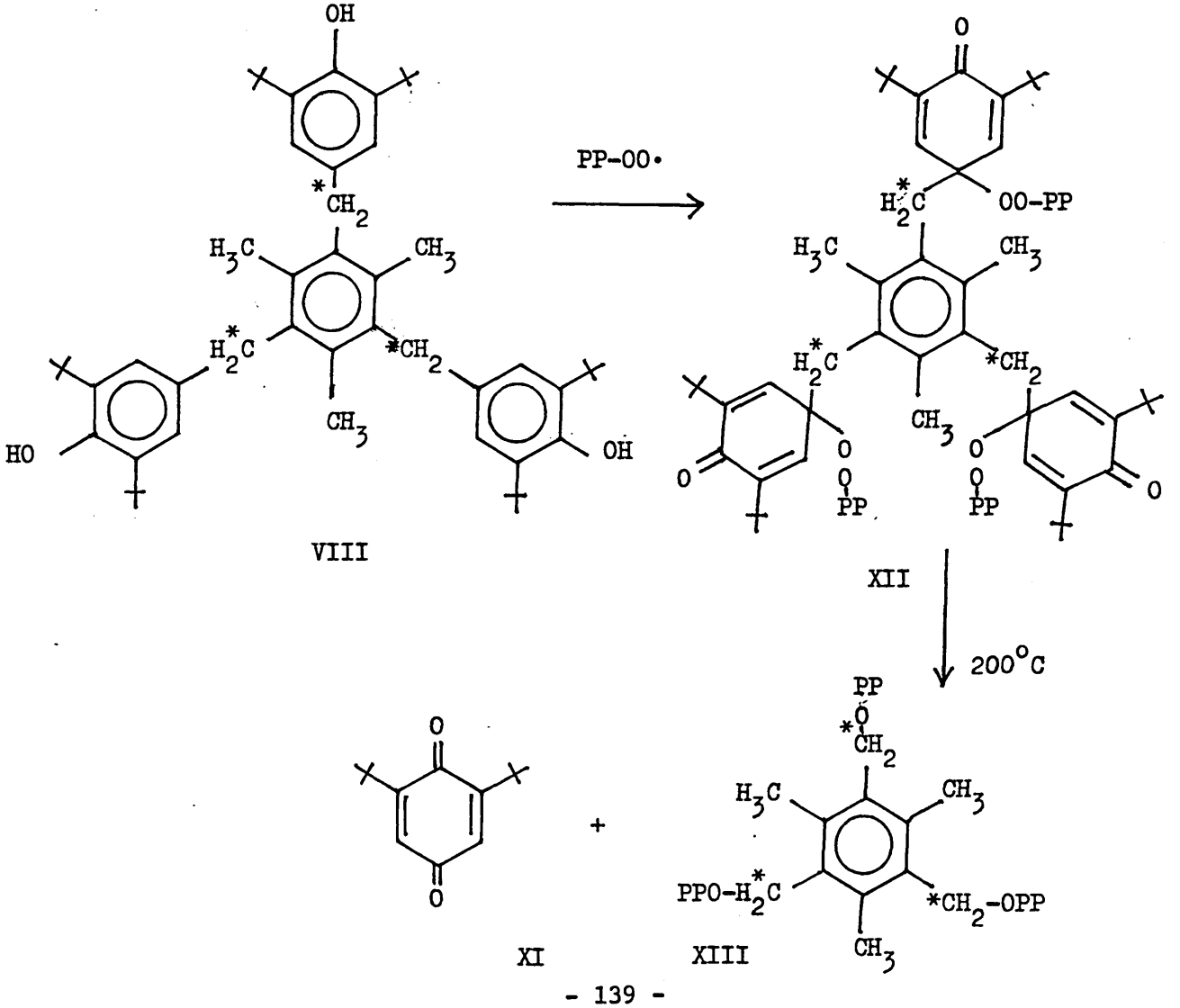
VIII

IX



XI X

In a similar study, Koch and Figge[7] revealed that the same reaction occurred when polypropylene containing ^{14}C-labelled Irganox 1330 (VIII) was kneaded in the presence of air at 200°C.

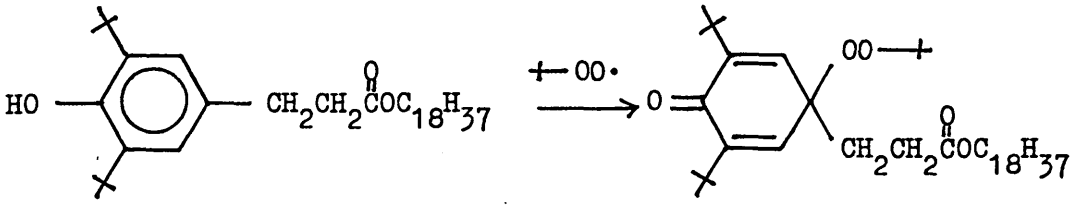


VIII XI XIII

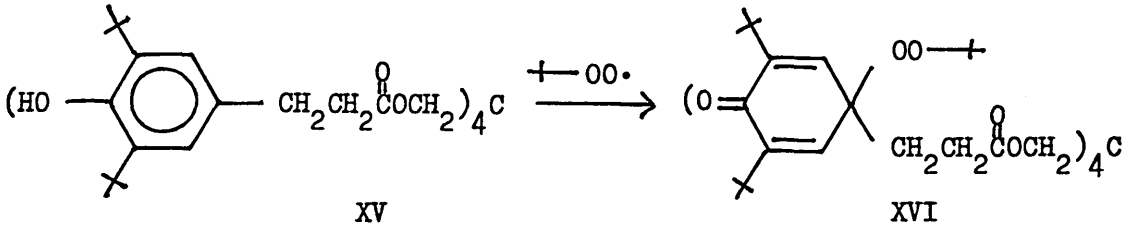
The macroalkyl peroxyl radicals (PP-OO•) were generated by the effect of thermal processing on the polymer. Again, the radicals were shown to bind to the antioxidant forming XII, which decomposes at 200°C to form XIII and the benzoquinone (XI). The above polymer after thermal processing was exhaustively extracted with chloroform and a residual radioactivity of 39% was found in the polymer[7]. This is convincing evidence for the chemical incorporation of the central body of the antioxidant molecule into the autoxidised polypropylene.

In the case of ^{14}C-labelled Irganox 1076 in both polypropylene and high density polyethylene, a similar type of reaction is believed to take place.

It is known that reactions of t-butyl hydroperoxide with Irganox 1076 (XIV) and Irganox 1010 (XV) produce compounds of type (XVI) (4-alkylperoxycyclohexadienones)[8,9].

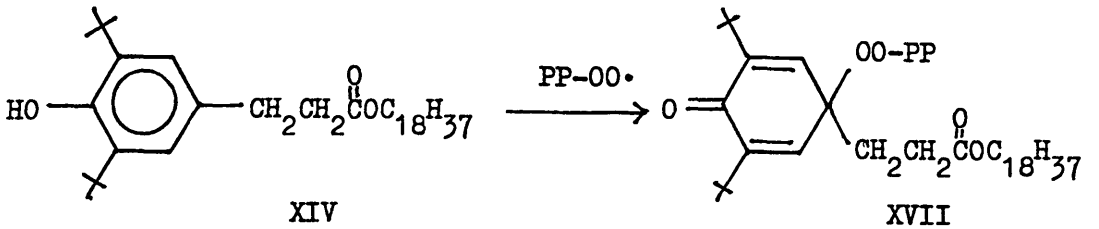


XIV XVI

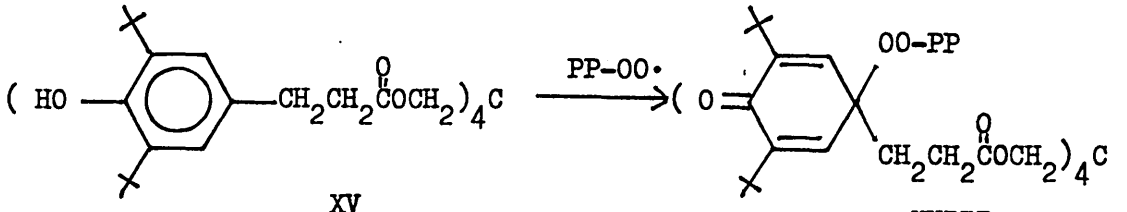


XV XVI

It is probable, therefore, that the same type of reaction will also occur in polypropylene containing Irganox 1076 or 1010:

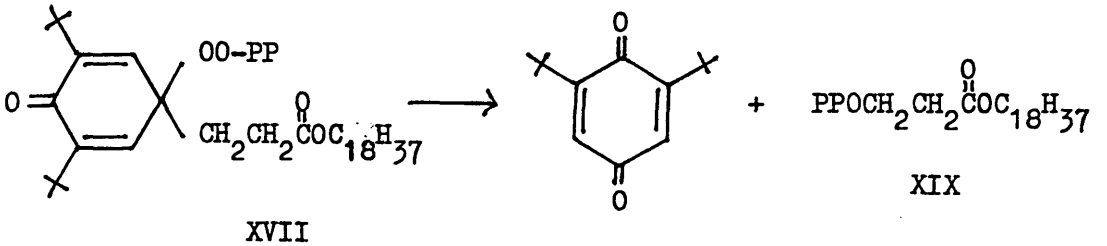


XIV XVII



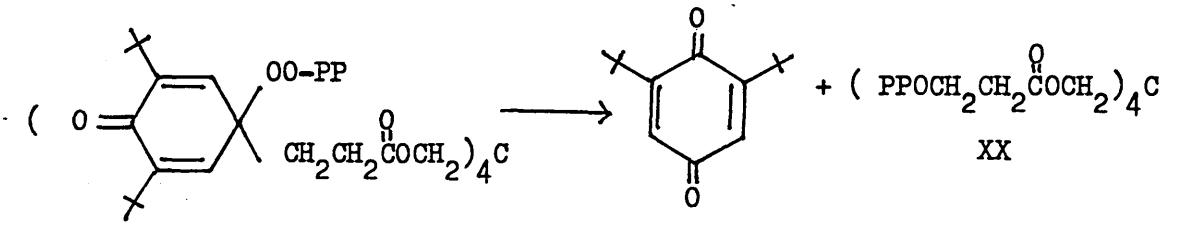
XV XVIII

There is the possibility that these products XVII and XVIII may then undergo degradation in some way (as in the Irganox 1330 reactions) to produce benzoquinone (XI) and XIX or XX.



XVII XI XIX

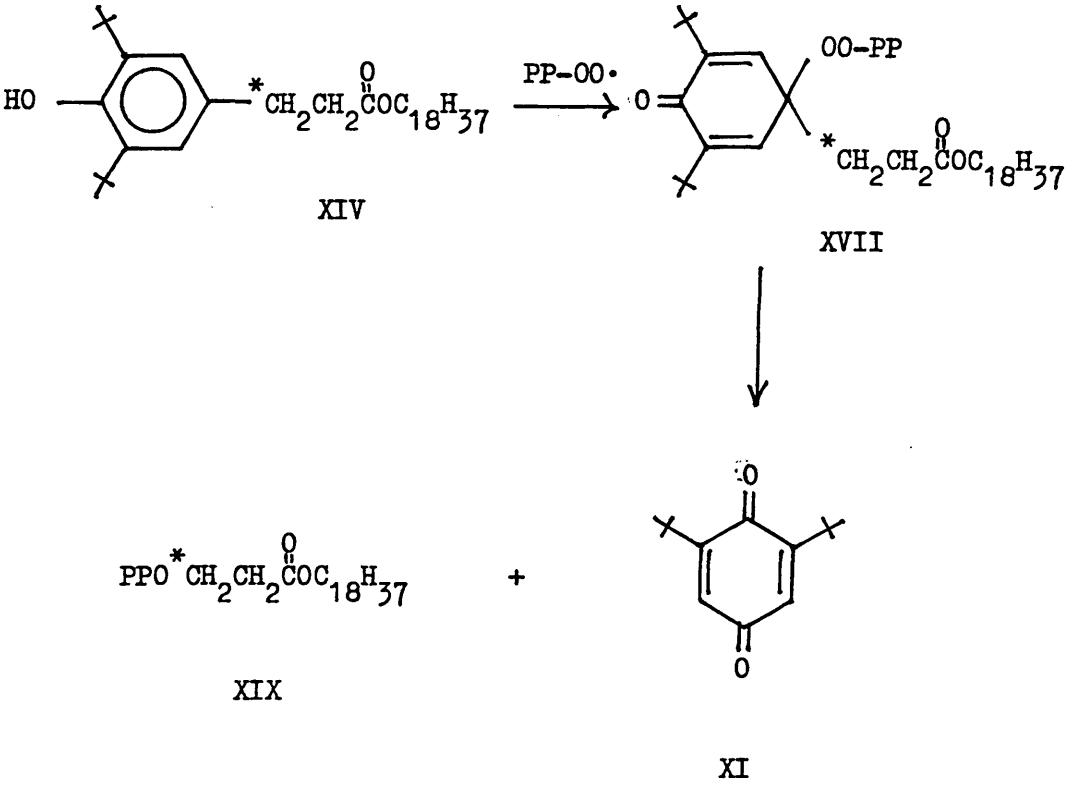
Similarly with Irganox 1010:



XVIII XI XX

This projected reaction would appear to occur during gamma-irradiation since benzoquinone (XI) was detected in the present study in extracts of irradiated polymers stabilised with Irganox 1076, 1010 and 1330.

Thus, in the case of ^{14}C-labelled Irganox 1076 in polypropylene and polyethylene:



XIV

XVII

XIX

XI

Since the formation of macroalkyl peroxyl radicals readily occurs during gamma-irradiation, the reaction would be expected to proceed to a greater extent than observed during thermal processing. The findings from these investigations are in agreement with this, in that whereas only 0.4% of the radiolabelled degradation products were covalently

had become bound after an exposure of 50 kGy.

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CHAPTER 5

IDENTIFICATION OF THE DEGRADATION PRODUCT IN IRRADIATED POLYPROPYLENE CONTAINING IRGAFOS 168

Arylphosphites are widely used as stabilisers in polyolefins, protecting polymers against colour changes during processing and retarding discolouration in end-use applications[1,2]. Their practical importance is comparable with that of sterically hindered phenols. Nevertheless, the mechanisms of their antioxidant action and the relationships between structure and efficiency are known in far less detail than those of phenols[3-5].

Generally, phosphites are hydroperoxide decomposing antioxidants, undergoing conversion to their related phosphates [5-10] but certain arylphosphites may be capable of acting as radical chain-terminating antioxidants by trapping peroxyl radicals to give aroxyl radicals[6].

In reactions with hydroperoxides, all organic phosphites function as secondary antioxidants, decomposing hydroperoxides in a non-radical way to form phosphates and alcohols:

$$ROOH + P(OR')_3 \longrightarrow RO^- + HO\text{-}P^+(OR')_3 \longrightarrow ROH + O{=}P(OR')_3$$

and so suppressing the chain-branching step:

$$ROOH \longrightarrow RO\cdot + \cdot OH$$

Phosphites are known to exhibit a significant synergistic effect in mixtures with phenols, which is attributed to their different, and complementary, modes of action[2,11-13].

$$ROO\bullet + AH \longrightarrow ROOH + A\bullet$$

$$ROOH + P \longrightarrow \text{non-radical products}$$

where AH is the phenolic antioxidant and P is the phosphite.

The radicals and hydroperoxides formed, as a result of either thermal processing or gamma-irradiation, are all polymeric in nature.

In reactions with phosphites as chain-breaking antioxidants, arylphosphites (I) are oxidised by alkylperoxyl radicals to give phosphates (II) and alkoxyl radicals.

$$ROO\bullet + P(OAr)_3 \longrightarrow ROO\dot{P}(OAr)_3 \longrightarrow RO\bullet + O{=}P(OAr)_3$$

I II

Arylphosphites react further with alkoxyl radicals by substitution to give the related alkoxydiaroxyphosphite (III) and a chain-terminating aroxyl radical,

$$RO\bullet + P(OAr)_3 \longrightarrow RO\dot{P}(OAr)_3 \longrightarrow ROP(OAr)_2 + \bullet OAr$$

III

which is capable of terminating the autoxidation reaction:

$$ROO\bullet + \bullet OAr \longrightarrow \text{inactive products}$$

In a similar manner, alkylphosphites (IV) react with alkylperoxyl radicals by oxidation to form the corresponding phosphate and alkoxyl radicals, which then react further with alkylphosphite to form another mole of phosphate, together with chain-propagating alkyl radicals,

$$ROO\bullet + P(OR')_3 \longrightarrow ROO\dot{P}(OR')_3 \longrightarrow RO\bullet + O{=}P(OR')_3$$

IV

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

which are oxidised to alkylperoxyl radicals, to continue the above reaction.

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

The different products arising from aliphatic and aromatic phosphites in the reaction with peroxyl radicals are predominantly due to the different behaviour of the intermediate alkoxyphosphoranyl radicals (V) and (VI) formed in the reaction of alkoxyl radicals with the phosphites.

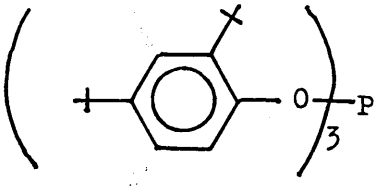
$ROP(OR')_3$ V

$ROP(OAr)_3$ VI

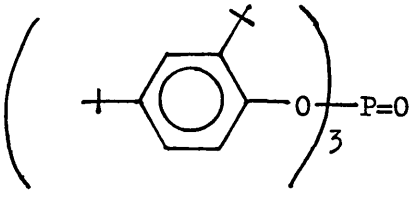
The intermediate phosphoranyl radical V undergoes β-scission to give a phosphate and an alkyl radical, whereas VI forms a phosphite and an aroxyl radical by α-scission[4-6].

It has been shown in Chapter 3 that drastic reductions in the level of Irgafos 168 occur during gamma-irradiation, to such an extent that little remains after a dose of 10 kGy. The rate of destruction of Irgafos 168 was even faster when in combination with the hindered phenolic antioxidant, Irganox 1010.

Studies of the extracts of polypropylene, stabilised with Irgafos 168 (VII) at a nominal concentration of 0.1% after an irradiation dose of 25 kGy, revealed the presence of traces of an apparent degradation product. The ^{31}P n.m.r. spectrum (Figure 5.1) showed a single resonance peak at a shift value of δ=-20 ppm, which was due to tris-(2,4-di-t-butylphenyl) phosphate (VIII) and was identical with the ^{31}P n.m.r. spectrum of the authentic compound (Figure 5.2). Consistent with HPLC data, no signal due to unchanged Irgafos 168 (δ=130 ppm, Figure 5.3) was observed.



VII



VIII

Figure 5.1 ^{31}P nmr spectrum of a chloroform extract of milled polypropylene containing 0.1% Irgafos 168 after 25 kGy of gamma-irradiation

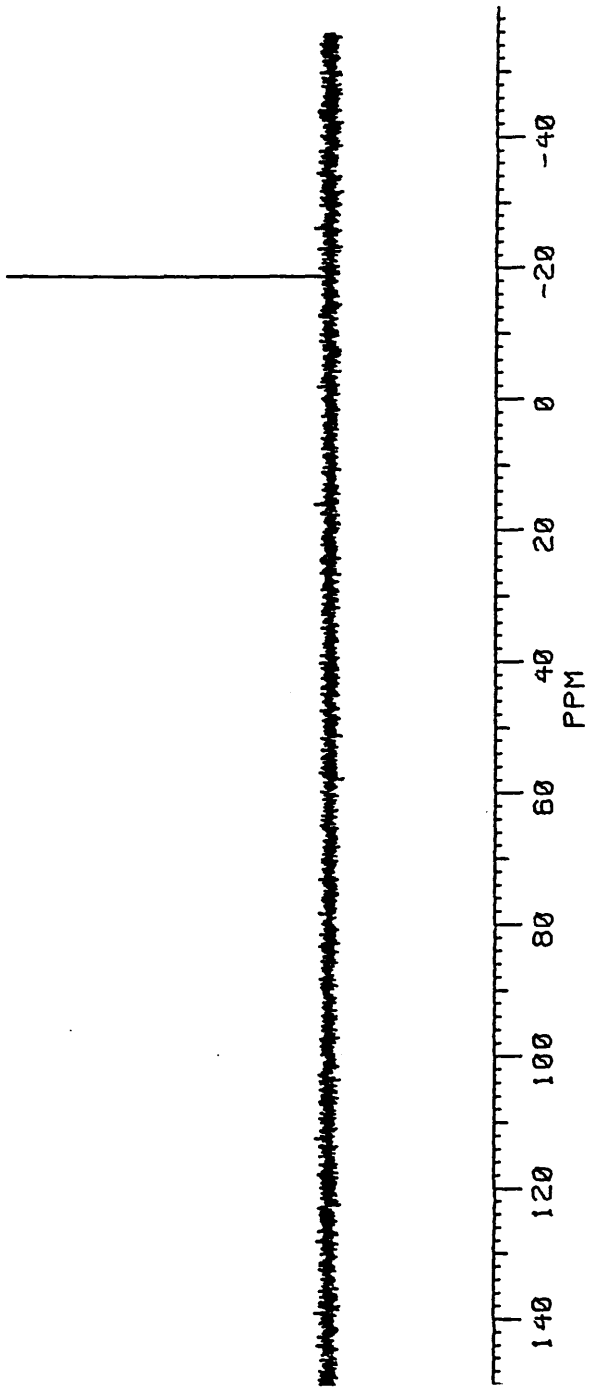


Figure 5.2 ^{31}P nmr spectrum of tris-(2,4-di-t-butylphenyl)phosphate

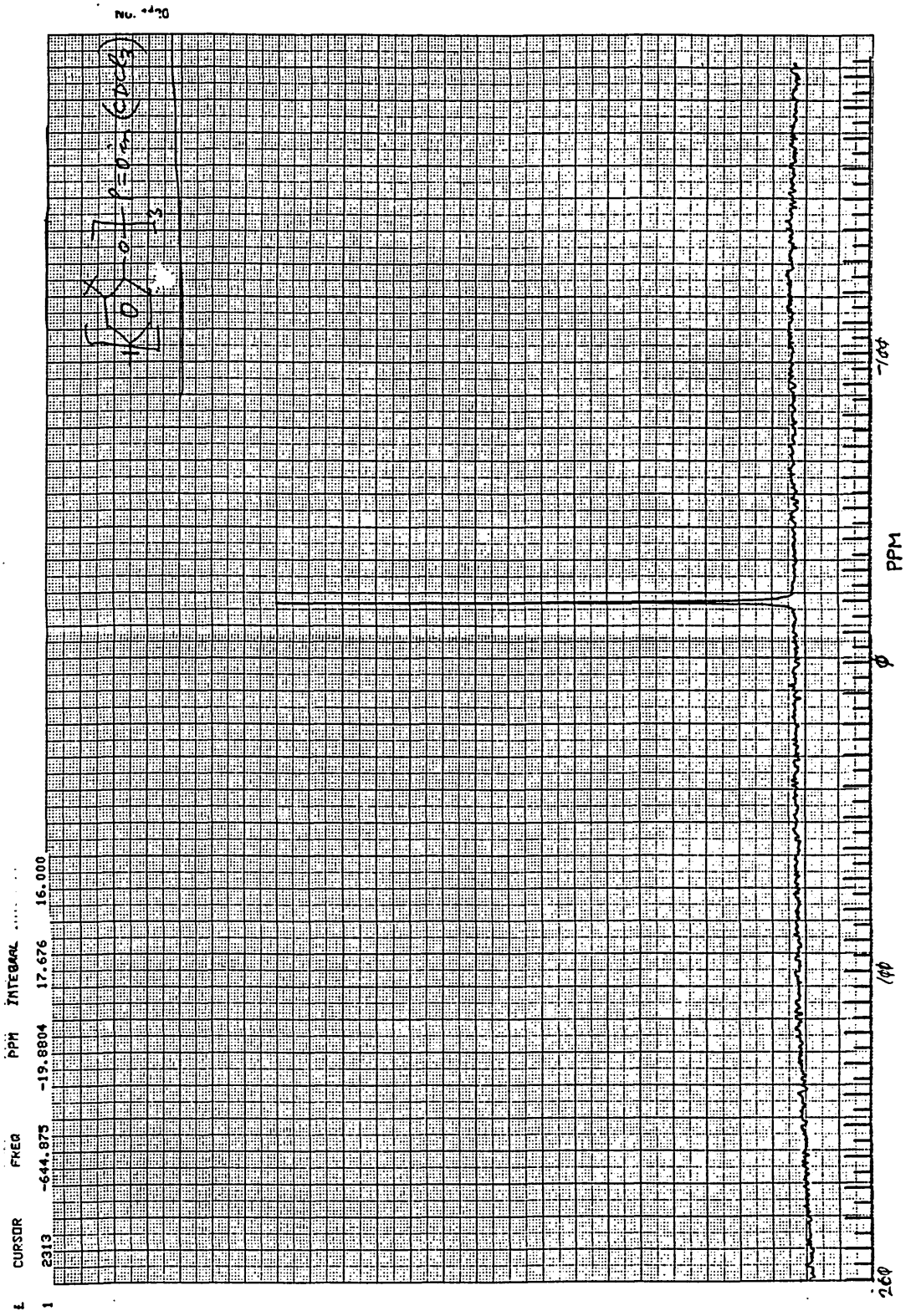
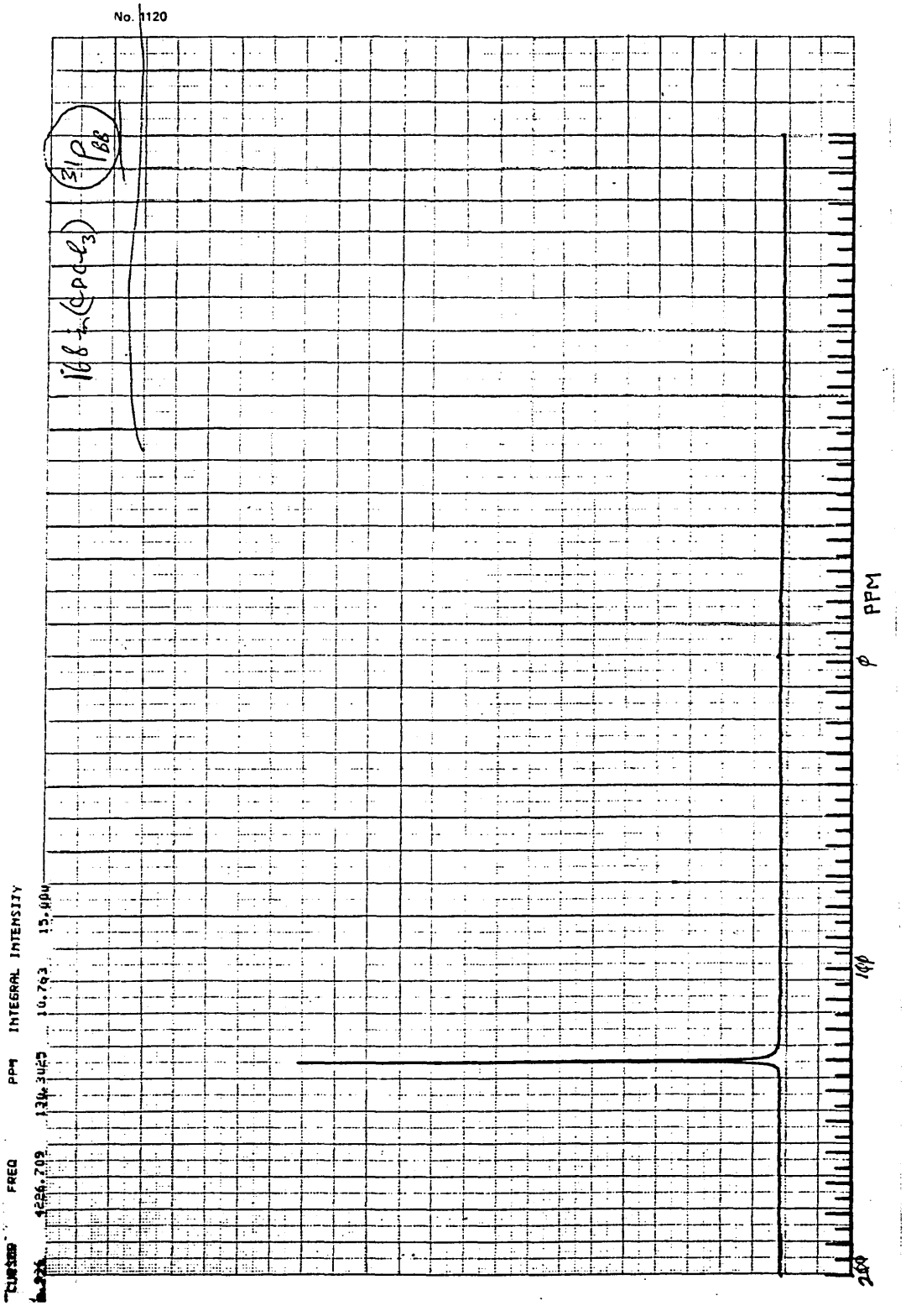


Figure 5.3 ^{31}P nmr spectrum of Irgafos 168

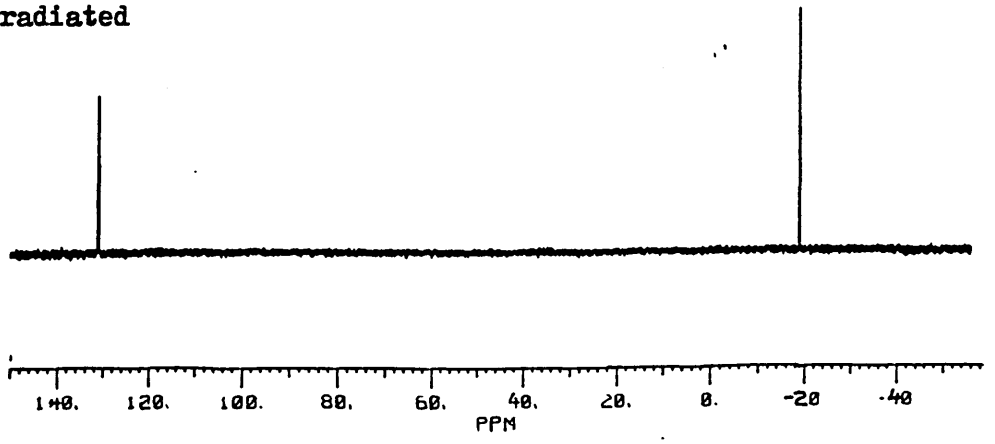


In order to demonstrate the degradation of Irgafos 168 and the formation of the phosphate with increasing doses of gamma-irradiation, samples of polypropylene containing Irgafos 168 at 0.1% before irradiation and after 1, 10 and 50 kGy, in addition to a sample of raw powder mix of this blend after 50 kGy, were extracted with chloroform, the extracts were evaporated and investigated by ^{31}P n.m.r. and HPLC analysis.

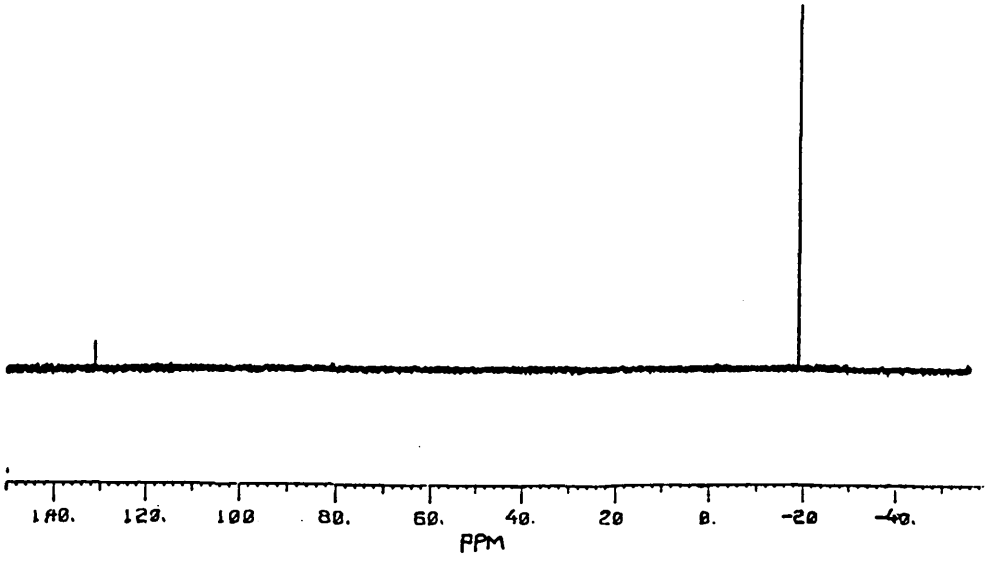
The ^{31}P n.m.r. spectrum of the unirradiated sample (Figure 5.4a) shows two signals, one at a shift value of 130 ppm, which is due to Irgafos 168, and a second larger signal at a shift value of -20 ppm, which is due to the phosphate. It is important to note that the baseline noise in all spectra is comparable in magnitude, and therefore the intensities of the signals may also be compared for each dose. No other phosphorus resonances were observed in the spectrum of the extract. After the samples had been exposed to a dose of 1.0 kGy (Figure 5.4b), the height of the signal due to Irgafos 168 (δ=130 ppm) was very much reduced and there was an increase in the height of the signal due to the phosphate (δ=-20 ppm). An irradiation dose of 10 kGy (Figure 5.4c) resulted in the complete destruction of Irgafos 168 (no signal at δ=130 ppm) and a notable increase in the intensity of the phosphate signal. However, after a dose of 50 kGy (Figure 5.5a), the intensity of the phosphate signal was significantly reduced, indicating that the phosphate had either been destroyed or become polymer-bound and was no longer extractable into chloroform. It is of interest to compare these spectra with one obtained for the raw powder mix of this

Figure 5.4 ^{31}P nmr spectra of chloroform extracts of milled polypropylene containing 0.1% Irgafos 168 after gamma-irradiation

a) unirradiated



b) after 1 kGy



c) after 10 kGy

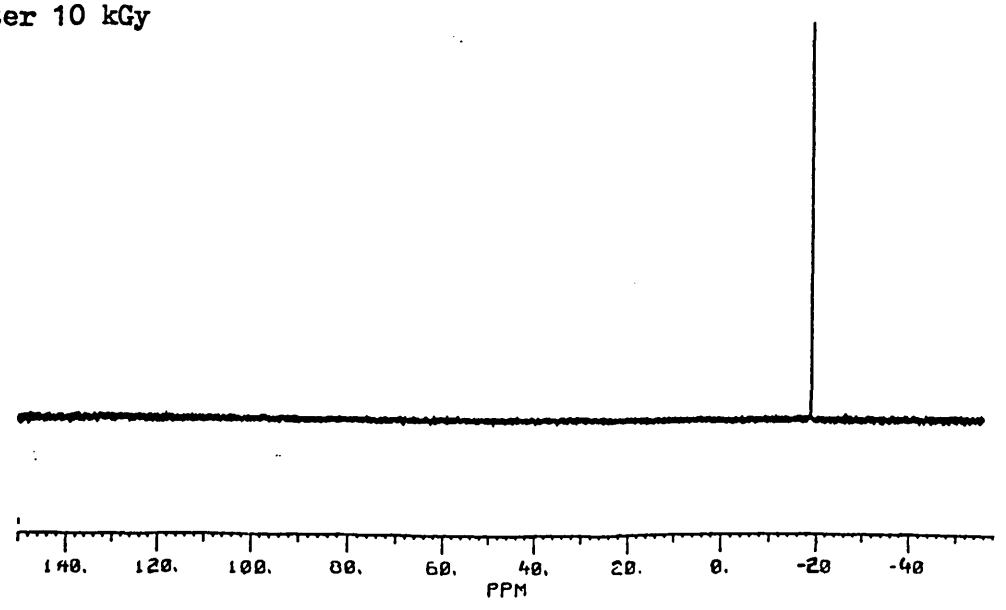
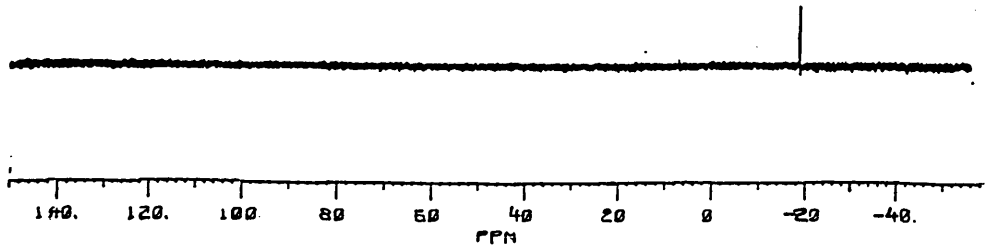
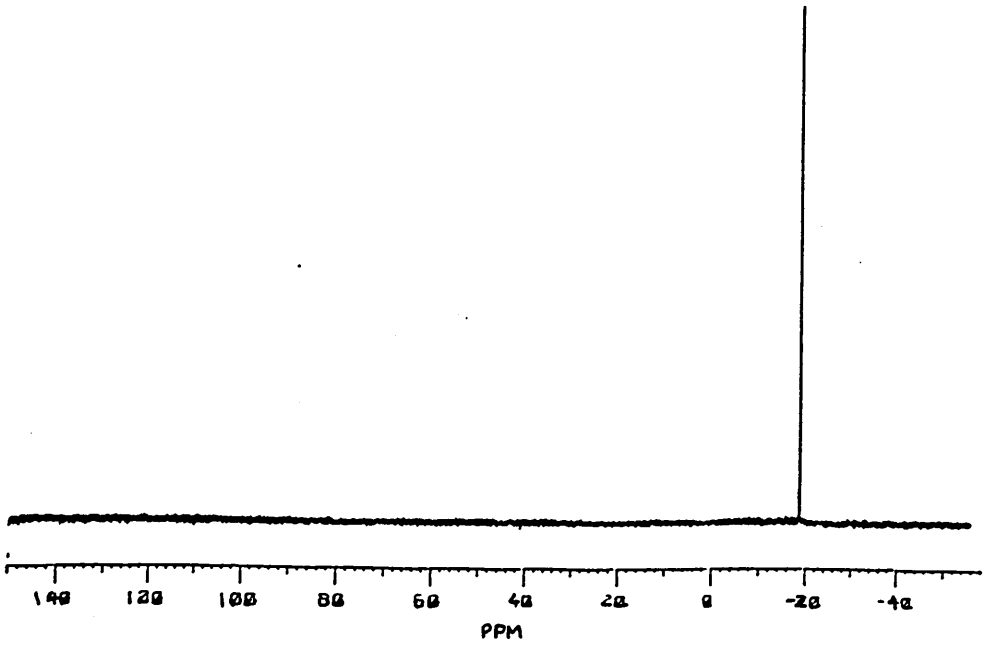


Figure 5.5 ^{31}P nmr spectra of chloroform extracts of milled polypropylene containing 0.1 % Irgafos 168 after gamma-irradiation

a) after 50 kGy



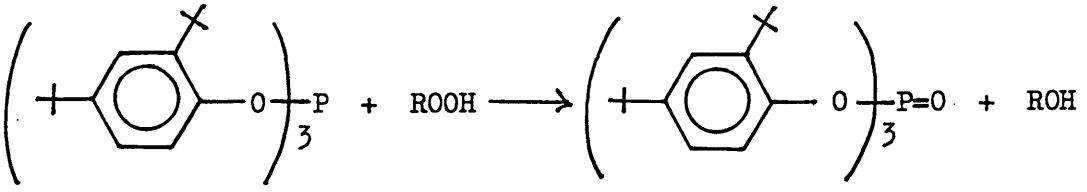
b) raw mix after 50 kGy



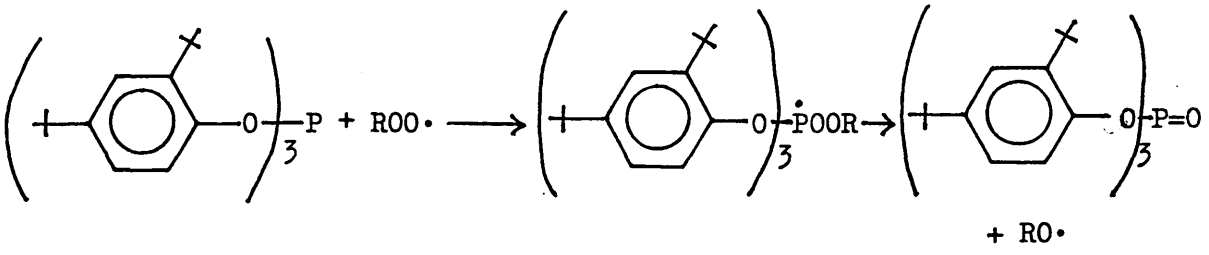
blend after 50 kGy (Figure 5.5b). Again no signal for Irgafos 168 was observed, but the intensity of the signal for the phosphate was greater than that in the milled samples.

The results from the above ^{31}P n.m.r. spectra are in good agreement with those obtained by HPLC. The ^{31}P n.m.r. spectra (Figures 5.4 and 5.5) revealed that after a gamma-irradiation dose of 10 kGy and above, Irgafos 168 was completely transformed to the related phosphate, which may have occurred by two distinct reactions:

i) with hydroperoxides

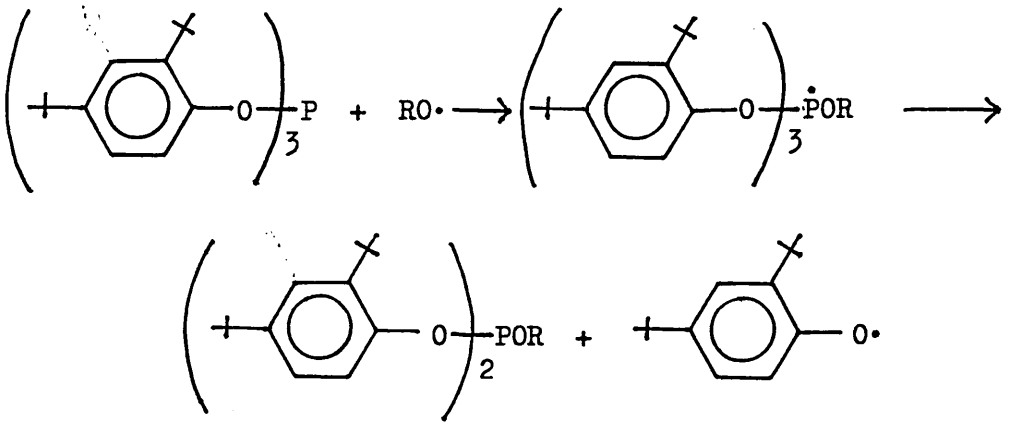


ii) with peroxyl radicals



It is thought that both reactions proceed during gamma-irradiation. The hydroperoxide reaction results in the formation of the corresponding alcohol. The reaction with peroxyl radicals generates

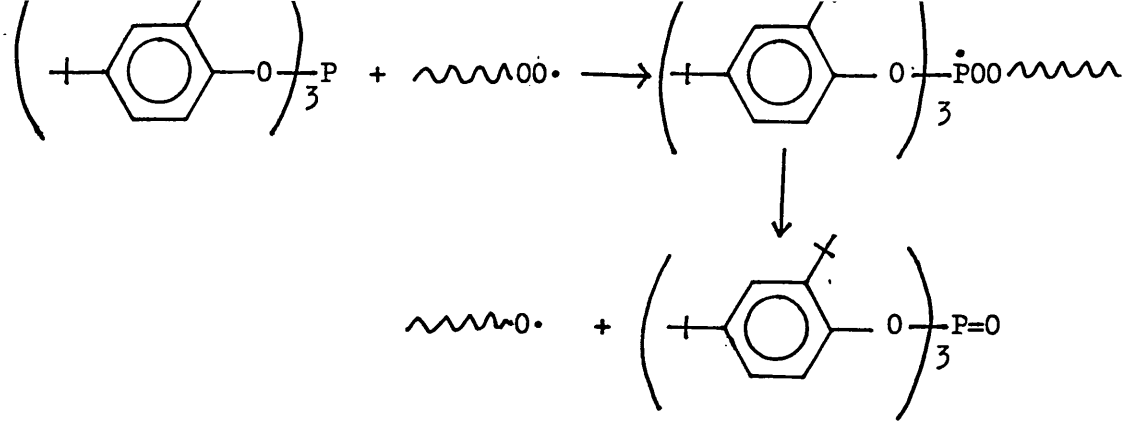
Irgafos 168 resulting in the formation of alkoxydi(2,4-di-t-butyl-phenyl) phosphite (IX) and aroxyl radicals[4,14].

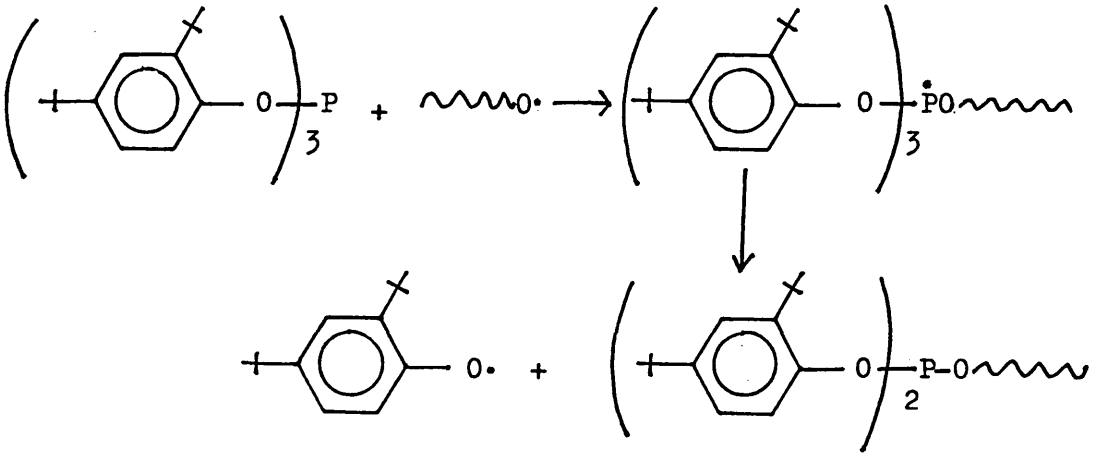


IX

Presumably, the alkoxy-substituted phosphite (IX) would have a ^{31}P chemical shift value similar to that of Irgafos 168 (δ=130 ppm). However, at higher irradiation doses, the only phosphorus resonance observed in the extracts of the polymers was that corresponding to the phosphate of Irgafos 168. Therefore, in the absence of a signal corresponding to the substituted phosphite (IX), it may be deduced that either the proposed reaction does not proceed or the phosphite has become covalently bound to the polymer, and is therefore unextractable.

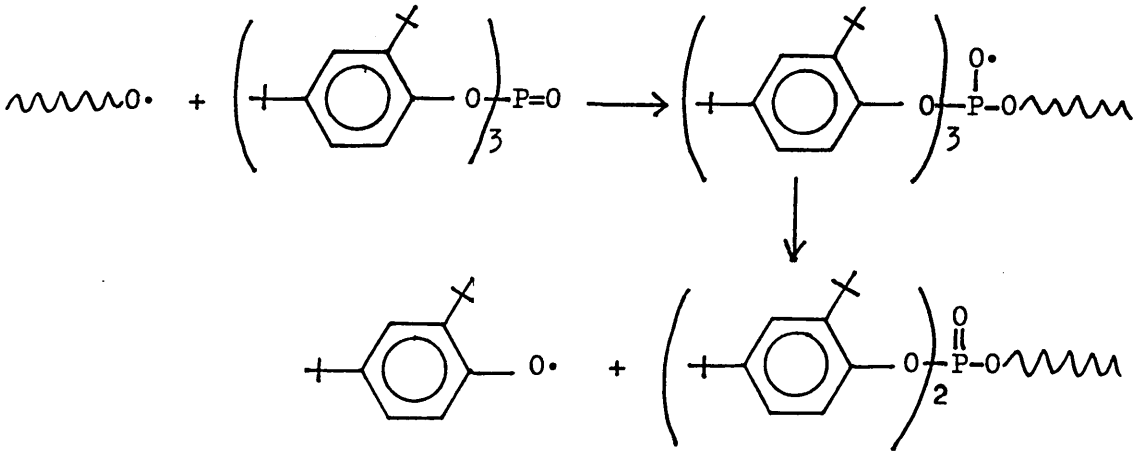
A possible explanation for this involves the interaction of Irgafos 168 with polymeric radicals, resulting in the formation of polymer-bound degradation products.





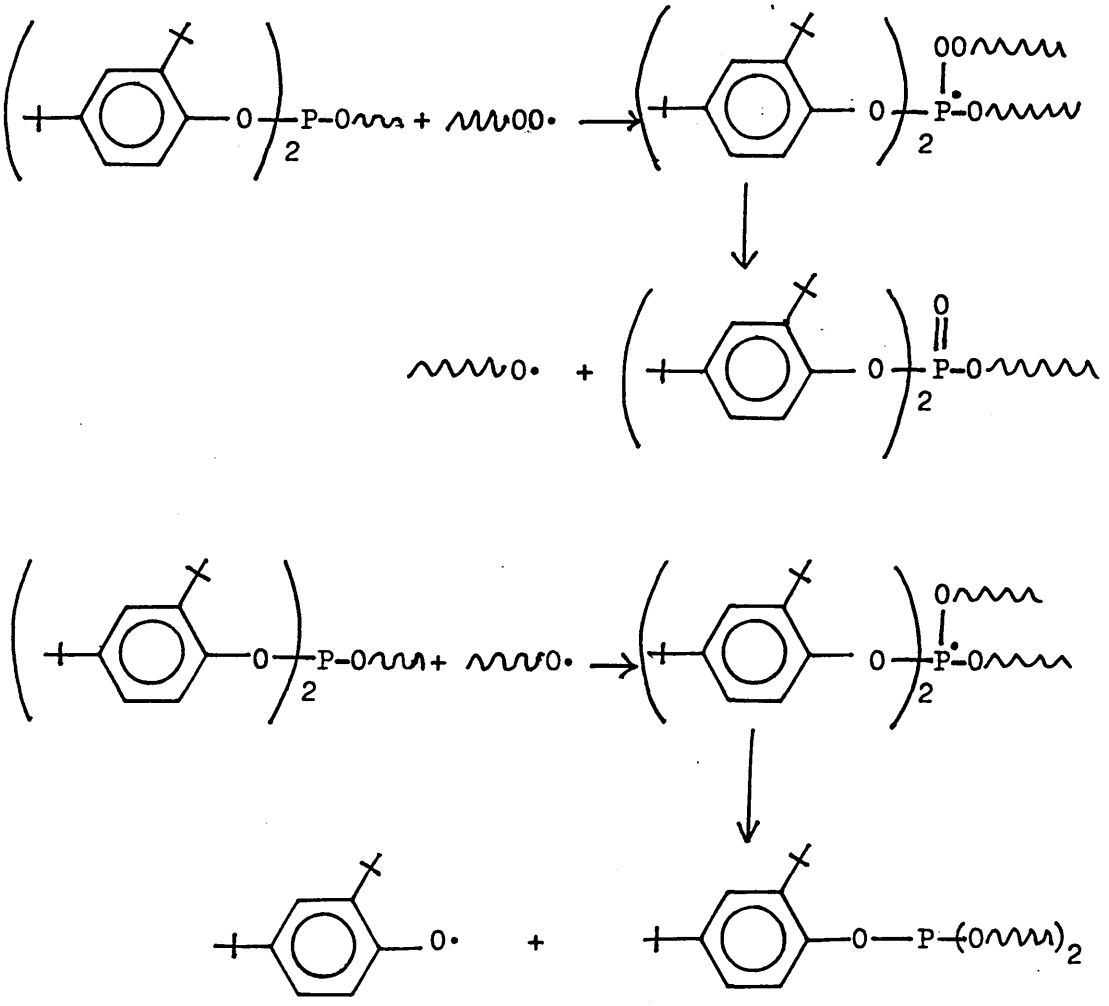
IX

It has been shown (Figures 5.4c and 5.5a) that with increasing irradiation dose, there is a pronounced reduction in the height of the signal corresponding to the phosphate of Irgafos 168. This may be explained by attack of the phosphate by an alkoxyl radical, resulting in covalent binding of the phosphate to the polymer (X).



X

Also, it is feasible that in the absence of Irgafos 168 (after its complete destruction) and with increasing gamma-irradiation, the alkoxy-substituted phosphite (IX) may follow the same course of degradation as the antioxidant, Irgafos 168:



These reactions indicate how both the phosphite and phosphate may become covalently bound to the polymer. Thus, this explanation would appear to account for the observed reduction in height of signal of the Irgafos 168-derived phosphate in irradiated milled samples. However, in the ^{31}P n.m.r. spectrum of the raw mix of polypropylene granules and antioxidant after an exposure to 50 kGy of gamma-irradiation (Figure 5.5b), it was revealed that all of the Irgafos 168

had been completely oxidised to the related phosphate. Since the antioxidant was not dissolved in the polymer (as in the milled samples), polymeric radicals, arising as a consequence of gamma-irradiation, would be unable to combine with the antioxidant owing to their physical separation. Consequently the resulting unbound oxidised phosphate was extractable into chloroform, hence giving rise to the large signal observed in Figure 5.5b.

Upon increasing the irradiation dose, the stabilised polymer was observed to undergo a colour change from white (unirradiated) to pale yellow (after 50 kGy) (Chapter 3), thus indicating the formation of coloured degradation products. It is known that unstabilised polypropylene pellets remain white after irradiation[15] and that the crystals of tris-(2,4-di-t-butylphenyl) phosphate are also white, and therefore some other degradation products are responsible for the colour. It has been suggested[15] that the phenoxyl radicals, generated from the degradation of Irgafos 168, can dimerise, disproportionate or continue to react with other polymer radicals. Reactions with polymer peroxyl radicals result in the formation of peroxycyclohexadienones and quinoid compounds, which absorb in the visible region of the spectrum and hence discolour the polymer[15].

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CHAPTER 6

CONCLUSIONS

The aims of this investigation have been achieved. The main conclusions are as follows:

The majority of the thermally-processed stabilised polymers were observed to undergo a colour change following exposure to doses of gamma-irradiation. It was noted that as the dose was increased, the intensity of the colour was also observed to increase. The appearance of colour in the stabilised polymers was largely attributable to the formation of degradation products arising from the effects of gamma-irradiation on the antioxidants.

As a consequence of increasing the irradiation dose, there is an increase in the number of polymeric radicals generated, which interact with the antioxidant to an increasing extent, resulting in degradation of the antioxidant. It is observed that there is a gradual diminution in the total extractable levels of each antioxidant from the polymers, as irradiation progresses. The extent of this degradation, however, is dependent upon the nature of both the antioxidant and the polymer.

The effects of the tendency of antioxidants to migrate from polyolefins into food simulants after irradiation were studied. The extent of migration of antioxidants into aqueous-based simulants was shown to be negligible in comparison with that into fatty food simulants. However, gamma-irradiation leads to a decrease in the extent to which hindered

phenolic antioxidants migrate from polyolefins into fatty media, consistent with the reduction in the amounts of extractable antioxidant revealed earlier, with increasing irradiation doses.

It has been observed that the chloroform extracts of the polyolefins stabilised with antioxidants, after exposure to large doses of gamma-irradiation, became increasingly yellow in colour, thereby suggesting the formation of some extractable degradation products. An extractable degradation product, giving rise to the intense yellow colouration of the extracts, was shown to be 2,6-di-t-butyl-1,4-benzoquinone. Traces of the intensely coloured compound, 3,5,3',5'-tetra-t-butylstilbene-4,4'-quinone were also detected in the chloroform extracts of polymers stabilised with Irganox 1330 after large doses of irradiation.

Since no other degradation products have been detected, it is possible that the transformation products derived from phenolic antioxidants may become covalently bound to the polymer, as a result of radical coupling processes, during irradiation. It has been shown, using a radiolabelled antioxidant incorporated into polyolefins, that the extent of binding of antioxidant degradation products to the polymer increased with increasing irradiation dose. A small fraction of 0.4% of the antioxidant was shown to bind with the small number of polymeric radicals formed during thermal processing, however, after an exposure of 50 kGy of gamma-irradiation, a minimum of 12.4% of radiolabelled degradation products of the antioxidant had become bound to the polymer.

In the case of the hindered phosphorus antioxidant, Irgafos 168 undergoes conversion to the related phosphate during both thermal

processing and gamma-irradiation and consequently becomes covalently bound to the polymer by a series of reactions involving polymeric radicals. It has also been postulated that an alkoxy-substituted phosphite is formed from Irgafos 168, and this, too, is covalently bound to the polymer.

As degradation products derived from antioxidants during gamma-irradiation are becoming covalently bound to the polymer, it is justifiable that concerns about potential migration of degradation products may therefore be much reduced.

Further work is required into the investigation of the gamma-irradiation induced degradation of Irganox 565, as a possible test for irradiation of food-contact plastics. It is necessary to quantify the degradation of Irganox 565 with increasing irradiation dose, and determine whether the proposed test is workable after prolonged storage of the irradiated polymers, with respect to their post-irradiation degradation.

It would also be of considerable interest to determine the migration of the chloroform extractable degradation product, 2,6-di-t-butyl-1,4-benzoquinone, from irradiated stabilised polyolefins into food simulants.

APPENDIX 1

PREPARATION AND CHARACTERISATION OF POLYPROPYLENE AND HIGH DENSITY POLYETHYLENE SHEETS CONTAINING ^{14}C-LABELLED IRGANOX 1076 AS REPORTED BY THE NATEC INSTITUTE

1.1 Preparation of the high density polyethylene (HDPE) and polypropylene (PP) test sheets

Commercially available polymers were used to prepare test sheets. Whereas the HDPE was supplied as grit and was therefore used as such, the PP material was ground before mixing with the additive.

1.2 Preparation of the labelled antioxidant

The synthesis of [^{14}C] Irganox 1076 (n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-[3-^{14}C] propionate) was done following the procedure of Ciba-Geigy Ltd., Basle, Switzerland. The radiochemical purity was checked via radio-TLC on silica using two different solvent systems:

- n-hexane : acetone = 8 : 2 (v/v)
- toluene : ethyl acetate = 9 : 1 (v/v)

(Figures 1.1 and 1.2)

Figure 1.1 Scanner diagram of ^{14}C-Irganox 1076 on silica using n-hexane : acetone (8 : 2 v/v)

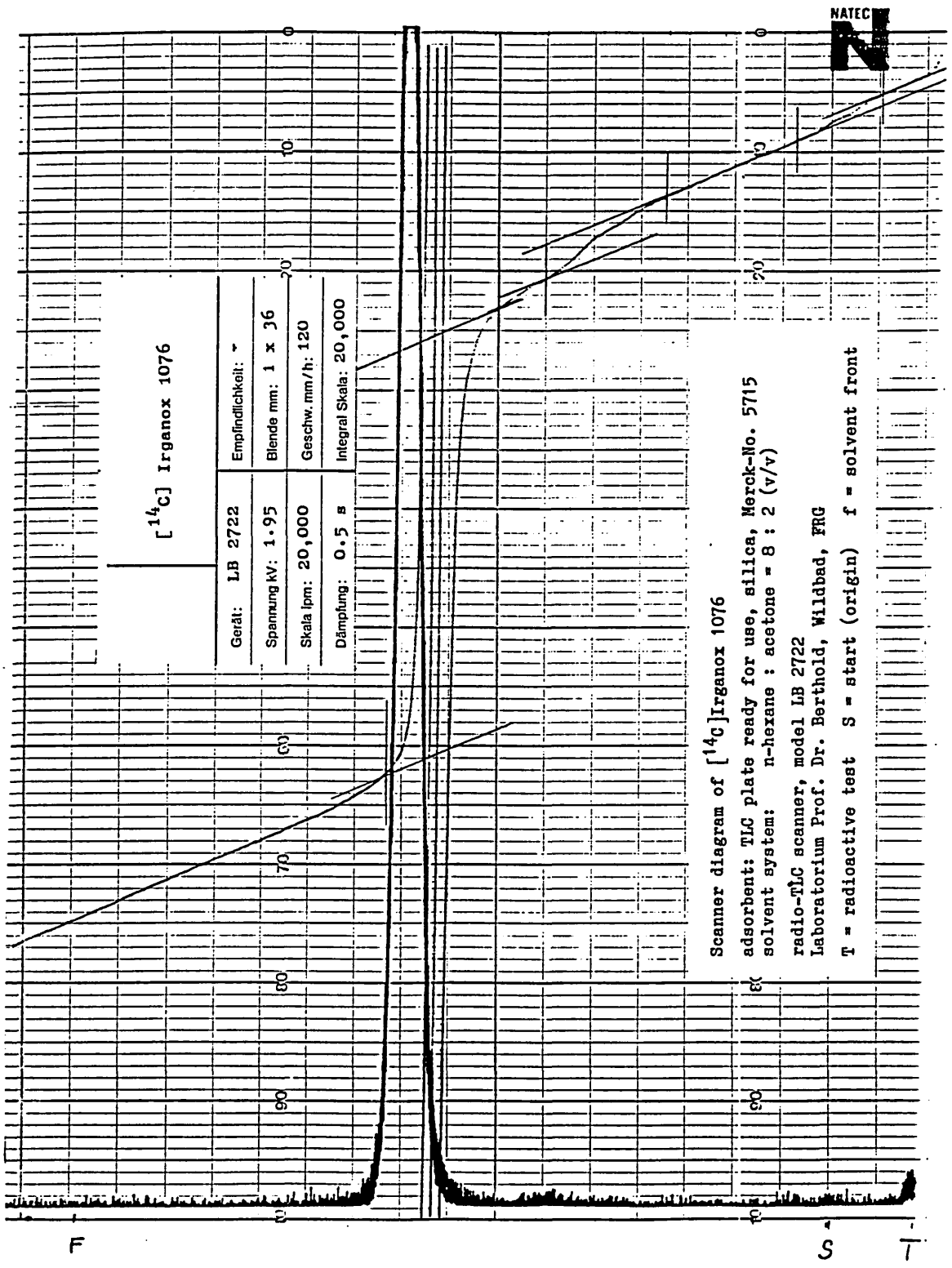
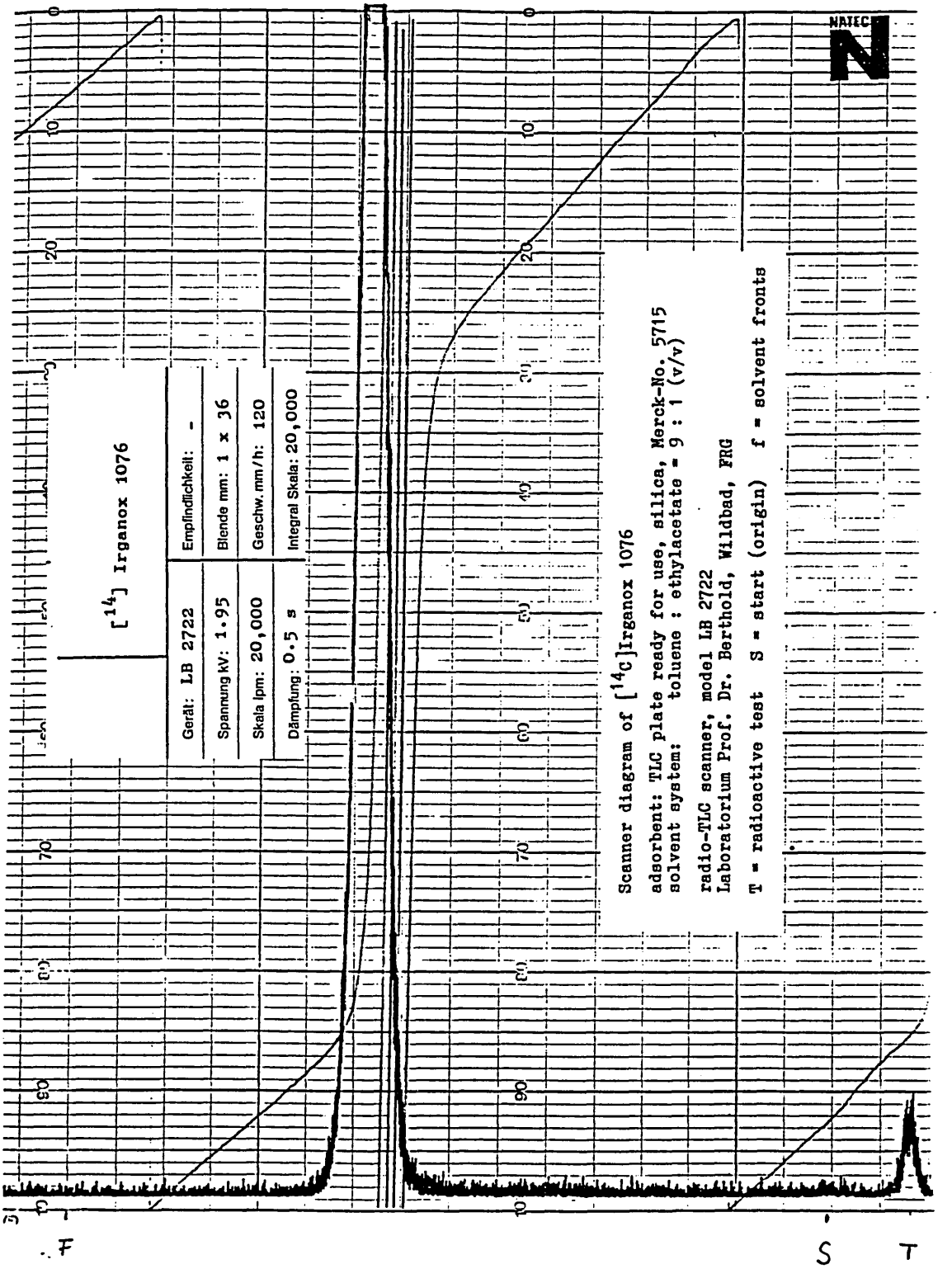


Figure 1.2 Scanner diagram of ^{14}C-Irganox 1076 on silica using toluene : ethyl acetate (9 : 1 v/v)



The product is characterised by the following data:

total radioactivity	:	371 MBq (10 mCi)
spec. radioactivity	:	626.2 kBq/mg (332 MBq/mMol)
radiochem. purity	:	98.9% (on April 8, 1987)

The ^{14}C-labelled antioxidant was used to prepare test sheets of HDPE and PP, containing 0.2% by weight of the antioxidant.

1.3 Preparation of the polymer mixtures

The ^{14}C-labelled antioxidant was diluted with unlabelled Irganox 1076 (ex. Ciba-Geigy) resulting in a specific radioactivity of 65.15 kBq/mg. 2.0 g (130 MBq) of this antioxidant were mixed with 1.0 kg polymer grit in a drum with tumbling for 30 minutes at room temperature.

1.4 Extrusion/Granulation

The mixtures were extruded and granulated as follows:-

	HDPE	PP
Temperature extruder zone 1	200	145°C
extruder zone 2	210	170°C
mould	230	190°C
Screw speed	60	70 rpm
Diameter of the extruder nozzle	3	3 mm

1.5 Compression moulding

The polyolefin granulates were compression moulded to test sheets under the following conditions:-

moulding temperature	200°C
pressure	225 bar
pressing frame	thickness 800 µm
	size 23 x 23 cm

To begin with, the granulate was preheated under slight initial pressure for 5 minutes. Full pressure was then applied with the press jaws for 3 minutes at maximum temperature and a further 3 minutes under cooling of the press jaws with tap water.

1.6 Determination of the radioactivity of ^{14}C-labelled Irganox 1076 in the polyolefin samples

In order to determine the specific radioactivities of the test sheets, ten random samples of approximately 50 mg each were taken from a separate sheet, using a punching knife.

To begin with, the random samples from the granulates and test sheets were weighed into scintillation vials and dissolved in 20 ml of a tetralin-based scintillation cocktail each, at 150°C with occasional shaking in the absence of moisture. Subsequently, the solution was cooled slowly to room temperature and the gel-type precipitations were distributed evenly in the scintillation cocktail by agitation.

The samples prepared in this way were measured in a liquid scintillation spectrometer, which computes the impulses counted per unit time to the actual disintegrations (dpm) based on a stored quench curve. From the corrected measured values, the specific radioactivities (kBq or Bq per g) or the total radioactivities (kBq or Bq) of the polyolefin materials were calculated.

The test sheets are characterised by the data contained in Table 1.1.

Table 1.1 Characteristics of polyolefin test sheets

Polymer type	HDPE Lupolen 5261Z	PP Propathene LYM 42
supplier	BASF	ICI
density[a] [g • cm^{-3}]	0.949 - 0.953	0.905
melt index[a] [g/10 min]	1.7 - 2.3[d]	9.0[e]
amount[b] [% by wt.]	99.8	99.8
[^{14}C]Irganox 1076		
amount[b] [% by wt.]	0.2	0.2
Test sheet		
spec. radioactivity [kBq/g]	123 ± 7[f]	133 ± 7
thickness [mm]	0.78	0.80
contents of [^{14}C]Irganox 1076[c] [% by wt.]	0.19	0.20

a) data according to the supplier
b) used for preparation of the mixture
c) calculated from the specific radioactivities of the antioxidant and of the test sheets
d) 190°C/21.6 kp
e) 230°C/ 2.16 kp
f) standard deviation according to $s = \sqrt{\frac{\Sigma (x_i - m)^2}{n - 1}}$

x_i = individual result
m = mean value
n = number of parallel measurements
here: n = 10

A STUDY TO ESTABLISH THE CAUSE OF THE HIGH RELATIVE STANDARD DEVIATION IN THE REPRODUCIBILITY OF EXTRACTIONS OF ^{14}C-LABELLED IRGANOX 1076 FROM HIGH DENSITY POLYETHYLENE

A study was initiated in order to establish the source of the high relative standard deviation in the reproducibility of extractions of ^{14}C-labelled Irganox 1076 from high density polyethylene. As previously mentioned in Chapter 2, Section 9.2, the relative standard deviations were 12.8% and 22.0% for polypropylene and high density polyethylene, respectively, for six single replicates of the polymer.

This high value may be due to four possible errors arising from:-

i) sample handling

ii) sample counting

iii) incomplete extraction

iv) heterogeneity of the antioxidant within the sheet.

Each of the above sources of error has been investigated and is discussed below.

2.1 Effect of sample handling

In order to demonstrate that no contamination of the samples occurred, a blank extraction was performed. The procedure was followed in Section 9.1, but no polymer pieces were added. The

blank gave an average count of 173 cpm. This value consisted of contributions from the counter itself, the scintillation cocktail and the vial. It also demonstrates the negligible extent to which contamination arises from the flask, condenser and pipettes.

2.2 Effects of sample counting

The chloroform extracts from the polymer samples were mixed with scintillation cocktail and were counted on three separate occasions during the day. The relative standard deviation arising from these results is less than 1% and therefore does not account for the large variation of 22%.

2.3 Effects of incomplete extraction

Duplicate samples of one piece of polymer were extracted for four hours, the extract collected, evaporated and counted. A second and third extraction was performed and counted. The results are shown below and have been corrected for any background counts.

	HDPE	PP
No. of extractions	corrected cpm	
1	71623	84640
2	16104	1518
3	1300	-30

The results for polypropylene indicate that after the first extraction, 98% of the radiolabelled Irganox 1076 had been extracted. A further 1-2% was removed after the second extraction. The third extraction revealed that the amount of radiolabelled additive found was less than the background correction, (hence giving a negative value).

However, results for high density polyethylene revealed that after the first extraction, 80% of the radiolabelled antioxidant had been extracted. A further 18% was removed after the second extraction. The third extraction indicated an additional 1-2% which could still be extracted.

Since the studies were carried out using a total of eight hours extraction time, this would indicate that all of the antioxidant from polypropylene and 98% of the antioxidant from high density polyethylene has been extracted, and therefore the high value cannot be explained in terms of incomplete extraction.

From the above experiments, it was deduced that a possible explanation for the high relative standard deviation value was the random distribution of Irganox 1076 in only the amorphous regions of the polymer. Therefore, in subsequent experiments, by extracting four pieces of polymer, instead of only one, the relative standard deviation was halved.

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Thanks are also due to Mr. R. Ashby of ICI Chemicals and Polymers Group, for both useful discussions and the supply of materials.

I would like to thank my husband, Martyn, for his patience and support during the writing of this thesis, and Jill Leah for her assistance in producing this thesis.

COURSES AND CONFERENCES ATTENDED

Selected lectures and self-learning units of particular relevance from the MSc course in Instrumental Chemical Analysis were:-

i) Separation Methods,

ii) Nuclear Magnetic Resonance,

iii) Optical Molecular Spectroscopy, and

iv) Mass Spectrometry.

Conferences attended:-

The Fifth International ICI/Unilever Symposium on Migration, 10/11 September 1987, London.

The Third International Conference on Radiation Processing for Plastics and Rubber, 2-4 November 1987, Warwick.

communications to the Editor

Effects of gamma-irradiation on hindered phenol antioxidants in poly(vinyl chloride) and polyolefins

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There is considerable current interest in the possible use of ionising radiation as a means of food preservation. Irradiation can be used to kill or reduce the numbers of pathogenic or spoilage organisms in food and to control infestation in stored products. In its recent report, the Advisory Committee on Irradiated and Novel Foods[1] has advised that the irradiation of food up to an overall average dose of 10 kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government is currently considering this report and comments from the public that have been made on it.

Whereas many types of irradiated foods have been studied in depth, there is much less information on the effects of irradiation on the many additives present in plastics used for food packaging, although it has been established that changes do occur in the migration behaviour of such additives.[2] Recently, studies of the effects of gamma-irradiation on the fate of organotin additives in poly(vinyl chloride) (PVC)[3,4] have been reported and now a study has commenced of its effects on various hindered phenol antioxidants present in a range of polymers, notably PVC, polyethylene and polypropylene. Such antioxidants are present not only to stabilise the polymer during initial processing and fabrication, but also during subsequent service, their main role being the removal of alkoxy and alkylperoxo radicals which would otherwise lead to degradation of the polymer. These compounds would be expected to have an important role to play in the suppression of the ambient-temperature oxidation of polyolefins following gamma-irradiation.[5-8]

Table **Effects of irradiation on antioxidants present in poly(vinyl chloride), polyethylene and polypropylene**

	PVC		Polyethylene		Polypropylene		
	Percentage		Percentage		Percentage		
Irradiation Dose/kGy	Irganox 1076[a]	Irganox 1010[b]	Irganox 1076[a]	Irganox 1010[b]	Irganox 1076[a]	Irganox 1010[b]	Irganox 1010[b]
0	0.44	0.62	0.36	0.16	0.34	0.48	0.08
1	0.29	0.46	0.28	0.12	0.37	0.47	0.07
5	0.27	0.46	0.23	0.10	0.38	0.44	0.05
10	0.12	0.43	0.22	0.09	0.38	0.41	0.04
20	0.17	0.37	0.20	0.07	0.36	0.33	0.02
25	0.18	0.31	0.14	0.07	0.35	0.33	0.02
35	0.19	0.30	0.14	0.05	0.30	0.28	0.01
50	0.15	0.24	0.11	0.04	0.30	0.18	0.01

[a] ± 0.03 per cent; [b] ± 0.01 per cent

In this Communication, a preliminary report is presented of studies which have revealed the progressive destruction of such additives on irradiation, and, in particular, draw attention to the diminution in antioxidant levels which occurs after an irradiation dose of 10kGy.

Two commercially important hindered phenol antioxidants, octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate (Irganox 1076®), and pentaerythritoltetrakis-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate (Irganox 1010®), respectively, have been incorporated into various polymers at appropriate levels by hot-milling or sintering to produce small pellets. The resulting polymers were then subjected to progressive doses of gamma-irradiation from a cobalt-60 source. Following irradiation, the levels of antioxidants were determined by h.p.l.c. techniques, using appropriate internal standards, after extraction and separation from the irradiated polymers. The results are presented in the Table.

It is seen that there is a gradual diminution in the levels of each antioxidant as irradiation progresses, the extent depending on the nature of both the antioxidant and the polymer. For both antioxidants in PVC and polyethylene, approximately 30-40 per cent has been destroyed after a dose of 10kGy. Surprisingly, the extent of the degradation of these antioxidants in polypropylene is significantly lower than in the other polymers, there being no detectable change in the level of Irganox 1076 and only a 14 per cent decrease in the concentration of Irganox 1010 (from an original level of 0.48 per cent) after a dose of 10 kGy. Similarly, after a dose of 25 kGy, the level of Irganox 1076 is unchanged, while that of Irganox 1010 has decreased by 30 per cent. However, in a second sample of polypropylene, originally containing a much lower concentration of Irganox 1010, a marked reduction in the level of the antioxidant is observed, approximately 50 per cent having been consumed after a dose of 10 kGy. It is of interest to compare these results with another brief report of the effects of a 25kGy exposure of Irganox 1010 present in polypropylene (at an original concentration of 0.47 per cent) which resulted in a 65 per cent decrease in the level of

the antioxidant.[5] Clearly, much will depend on the nature of the base polymer, the level of the antioxidant, and the processing history of the sample.

So far, the chromatographic techniques used by the authors have not revealed the presence of detectable amounts of low molecular weight degradation products derived from the antioxidants, and it is possible that such products have become covalently bonded to the polymer as a result of radical coupling processes. It has recently been shown that gamma-irradiation of hindered phenols in benzene solution gives rise to phenylated derivatives resulting from coupling of radicals derived from the antioxidants with phenyl radicals derived from the solvent.[8] Gamma-irradiation of polyolefins is known to give rise to macroalkyl radicals and the trapping of antioxidant degradation products is therefore probable. Thus, the migration of products derived from these antioxidants may not prove to be a major problem in gamma-irradiated prepackaged food.

The authors are indebted to the following for the supply of information and materials: Dr R. Ashby and Mr K. Hayes, ICI Petrochemicals and Plastics Division; Mr D. Shorten, BP Chemicals (Suisse) SA; Mr R. Bland, Ciba-Geigy, Industrial Chemicals, Manchester; Drs M.T.J. Mellor and J.W. Burley, Lankro Chemicals Ltd.

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Contributions should have novelty and must be brief. Manuscripts must be submitted in accordance with the instructions to authors, which are published in the 5 October 1987 issue (p696). Authors are requested to note that manuscripts which do not accord with these instructions are currently being returned without consideration; in the case of overseas contributions return is by *seamail*. In order to expedite publication of accepted manuscripts, proofs are not circulated to authors outside the UK.

Gamma-irradiation of food contact plastics: the rapid destruction of an arylphosphite antioxidant in polypropylene

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In a recent Communication[1], preliminary details were reported of a study of the effects of progressive doses of gamma-irradiation on the extractable levels of various hindered phenol antioxidants (Irganox 1076® and Irganox 1010®) present in a range of food contact polymers. It was shown that there is a gradual diminution in the extractable levels of each antioxidant in the polymer as irradiation progresses, the extent depending on the nature of the antioxidant and the base polymer. However, in all cases an appreciable proportion of the original antioxidant (>50 per cent) was shown to remain unchanged after an irradiation dose of 10 kGy (1Mrad), the maximum irradiation level likely to be permitted should gamma-irradiation of prepackaged food be approved in the UK. (In its recent report, the Advisory Committee on Irradiated and Novel Foods[2] has advised that irradiation of food up to an overall average dose of 10 kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government is currently considering this report, and the comments from the public that have been made on it.)

Now, a preliminary report is presented of a similar study of the effects of gamma-irradiation on polypropylene containing an arylphosphite antioxidant, Irgafos 168®, (tris-(2,4-di-*t*-butylphenyl)phosphite) either as the sole antioxidant present or as a component of synergistic mixture with the hindered phenolic antioxidant Irganox 1010® (pentaerythritoltetrakis-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate). Such arylphosphites are widely used as stabilisers of polyolefins, and are known to exhibit a significant synergistic effect in mixtures with phenols. Although relatively inert to molecular oxygen, their main role is to trap hydroperoxy and alkylperoxy radicals, undergoing conversion into the related phosphate under thermal processing conditions.[3-6]

Table Effects of irradiation on Irgafos 168 present in polypropylene

Irradiation dose/kGy	Irgafos 168 as sole antioxidant (per cent) Irgafos 168[a]	Combination of Irgafos 168 + Irganox 1010 (per cent) Irgafos 168[a]	(per cent) Irganox 1010[b]
0	0.067	0.069	0.08
1	0.035	0.010	0.05
5	0.009	–	0.04
10	0.004	–	0.03
20	–	–	0.02
25	–	–	0.01

[a] ±0.003; [b] ±0.01

Samples of polypropylene stabilised as above were prepared by sintering to produce small pellets which were then subjected to progressive doses of gamma-irradiation from a cobalt-60 source. Following irradiation, the levels of antioxidants present were determined by h.p.l.c. techniques using appropriate internal standards, after chloroform extraction and separation from the irradiated polymers. The results are presented in the Table. It is clear that Irgafos 168 is destroyed far more rapidly than hindered phenol antioxidants on irradiation, little remaining after a 10 kGy exposure. The rate of destruction would seem to be even greater in the presence of the hindered phenol antioxidant Irganox 1010. However, the latter suffers degradation at a very similar rate to that observed previously.[1]

The authors have also detected the triarylphosphate ester oxidation product of Irgafos 168 in the extracts of the irradiated polymer by h.p.l.c., ^{31}P n.m.r. spectroscopy and mass spectrometry. The ^{31}P n.m.r. spectrum of a chloroform extract of a sample of polypropylene originally containing Irgafos 168 at *ca* 0.07 per cent by weight and subjected to an irradiation dose of 25 kGy showed a single resonance at $\delta = -20$ ppm (relative to 85 per cent H_3PO_4, $\delta = 0$ ppm), due to tris(2,4-di-*t*-butylphenyl)phosphate. Consistent with the h.p.l.c. data, no signal due to unchanged Irgafos 168 ($\delta = 130$ ppm) was observed. The formation of the phosphate ester reflects the role of Irgafos 168 in destroying the various peroxo radicals generated during gamma-irradiation, which is clearly much more damaging in the case of polypropylene than is thermal processing. These findings are consistent with an earlier brief report on the almost complete destruction of Irgafos 168, originally present in polypropylene at 0.34 per cent by weight, after a gamma-irradiation dose of 25 kGy.[7]

The authors are indebted to R. Ashby and K. Hayes, ICI Chemicals and Polymers Group for the supply of information and materials. Also, Dr B.F. Taylor, Department of Chemistry, University of Sheffield is thanked for the ^{31}P n.m.r. spectrum of the irradiated polymer extract.

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The effects of gamma irradiation of food contact plastics on the extent of migration of hindered phenol antioxidants into fatty food simulants

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Plastic food-contact packaging materials offer many advantages over traditional materials such as paper or cardboard in providing protection against external contamination and improved storage conditions, and preventing dehydration and loss of flavour. However, it is well known that such plastics contain low molecular weight additives, e.g. heat and light stabilisers, antioxidants, lubricants and plasticisers, all of which are necessary for the processing and stability of the polymer. Such additives are capable of migrating from the plastic into the foodstuff, thereby presenting a source of contamination and a potential health risk to the consumer. Thus, strict regulations are necessary to control the use of such additives in food-packaging.[1,2]

It is generally considered that the migration of polymer additives into foodstuffs is a diffusion problem, and depends on many variables.[3] As the determination of migrated polymer additives in heterogeneous foodstuffs is a difficult and time-consuming task, it has become common practice to study the migration of polymer additives into a series of homogeneous liquid, food simulant media under standard conditions, e.g. a polymer surface area of 2 dm^2 exposed to 100 cm^3 simulant over a period of 10 days at 40°C. A range of oily, alcoholic and aqueous simulants specified by an EEC Directive,[4] has been widely used in such studies.

In view of current interest in the possible use of gamma-irradiation of pre-packaged food in the UK, the authors have been investigating the effects of varying exposure to gamma radiation from a ^{60}Co source on a range of additives present in food-contact packaging polymers.[5-7] In a recent[6] report, it has been shown that progressive exposure to gamma irradiation causes a gradual diminution in the total extractable levels of phenolic antioxidants (Irganox 1076 (octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate) and Irganox 1010 (pentaerythritoltetrakis-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate) present in PVC and polyolefins, the extent depending on the nature of the antioxidant and the base polymer. However, in all cases an appreciable proportion of the original antioxidant (>50 per cent) was shown to remain unchanged after an irradiation dose of 10 kGy (1Mrad), the maximum irradiation level likely to be permitted should gamma-irradiation of pre-packed food be approved in the UK. (The Advisory Committee on Irradiated and Novel Foods[8] has advised that irradiation of food up to an overall average dose of 10kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government is currently considering this report and the comments from the public that have been made on it.)

Now, a preliminary report is made of the effects of gamma-irradiation on the migration of Irganox 1076 and Irganox 1010 present in polyolefins into the synthetic triglyceride fatty food simulant HB307 (10 days at 40°C) and, for comparison, into iso-octane (2 days at 20°C). The latter has been proposed[9] as a fatty food simulant which provides a convenient alternative to fats such as HB307 and olive oil in that the determination of migration into iso-octane is significantly easier, thereby providing a fast, cheap and simple predictive method for migration into fatty media. However, criticisms have been made of the use of iso-octane for this purpose.[10,11]

Samples of polypropylene in sheet form, containing Irganox 1076 and 1010, respectively at *ca* 0.2 per cent by weight, were prepared by conventional hot-milling and compression moulding techniques. These were used in studies of the extent of migration into iso-octane at 20°C over 2 days, the antioxidants being determined by h.p.l.c. techniques. For studies of migration into the synthetic fat HB307 at 40°C over a period of 10 days, a ^{14}C-labelled Irganox 1076 antioxidant was similarly incorporated into both polypropylene and high density polyethylene (HDPE). The extent of migration was assayed by conventional liquid scintillation techniques. In separate experiments, it was demonstrated by t.l.c. techniques that the ^{14}C-activity migrating into the simulant was due predominantly to unchanged ^{14}C-labelled Irganox 1076, although small amounts of another, as yet unidentified, substance could also be detected. The authors feel justified, therefore, in assuming that the ^{14}C-activity of the simulant reflects the degree of migration of the antioxidant. Prior to the

Table **Effects of irradiation on migration of antioxidants into fatty food simulants**

	Iso-octane		HB307	
	Irganox 1076	Irganox 1010	^{14}C-Irganox 1076	
Irradiation dose/kGy	mg dm^{-2} polypropylene	mg dm^{-2} polypropylene	mg dm^{-2} polypropylene	mg dm^{-2} HDPE
0	2.6	0.8	1.0	1.3
10	2.1	0.3	0.7	1.0
25	1.3	<0.2	0.5	0.7
50	0.4	<0.2	0.2	0.3

migration experiment, the polymer samples were subjected to varying doses of gamma-irradiation from a cobalt-60 source. The results of the migration experiments are presented in the Table as specific migration values (mg antioxidant migrated per dm^2 contact area).

It is clear that the extent of migration into both iso-octane and HB307 decreases steadily as irradiation progresses, consistent with the reduction in the amount of extractable antioxidant revealed in the earlier study.[6] These results are also consistent with an earlier report[12] of the effects of a 25 kGy gamma dose on the migration of Irganox 1076 into HB307. It is of interest that the extent of migration of Irganox 1076 into iso-octane is significantly greater than that of Irganox 1010 reflecting the greater lipophilicity of the former. Furthermore, while the extent of migration of Irganox 1076 into iso-octane is greater than into HB307 under the stated conditions, the results are nevertheless comparable in magnitude, thus providing some justification for the use of iso-octane as a convenient indicator simulant for migration into fatty foods. The key conclusion from this study, however, is that gamma irradiation leads to a decrease in the degree to which hindered phenol antioxidants migrate from polyolefins into fatty media.

The authors are indebted to ICI (Chemicals and Polymers Group) plc, and Ciba Geigy plc, for the supply of information and materials, and also for financial assistance in the preparation of ^{14}C-labelled materials. This work was supported by funds provided by the UK Ministry of Agriculture, Fisheries and Food, to whom thanks are also due. The results of this work are the property of MAFF and are Crown Copyright.

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Modified Corey reaction for aromatic ester synthesis

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Corey's method[1] for selective conversion of α,β-unsaturated aldehydes into methyl esters is an ingenious combination of three different consecutive processes. The author was more interested in a direct synthesis of benzils from aromatic aldehydes by a modified procedure in which acetic acid is excluded. It was considered that a normal benzoin condensation of the aldehydes might occur on their exposure to cyanide ion and the products would then be oxidised by activated manganese dioxide.[2]

When the reaction was conducted in alcoholic solvents, esters were formed readily. Apparently, the benzoin condensation is slow in comparison with interception of the cyanohydrin anion intermediates by MnO_2 in the relatively anhydrous conditions. It is interesting to note a recent report[3] on the preparation of methyl esters from aldehydes using pyridinium dichromate/dimethylformamide in the presence of methanol. However, the latter reaction is unsuitable for aromatic aldehydes.

Table

Ester	Percentage yield
$PhCO_2Me$	70
$PhCO_2Et$	77
$PhCO_2Pr^i$	25
$(p)MeC_6H_4CO_2Me$	82
$2\text{-}FurCO_2Me$	80
$2\text{-}FurCO_2Et$	74

Generally, methyl and ethyl esters are obtained in good yields, by heating for 20h a mixture of the aldehyde (1.5g) under reflux with sodium cyanide (0.1g) and activated MnO_2 (15g) in an alcohol ($20cm^3$) with magnetic stirring (see Table).

In the absence of cyanide ion the yields of product were very poor. By taking advantage of the oxidisability of benzylic alcohols by MnO_2 the synthetically more appealing transformation of benzylic alcohols to the esters has been accomplished.

$$ArCH_2OH + ROH \xrightarrow[(CN^-)]{MnO_2} ArCO_2R$$

Thus, methyl benzoate and methyl *p*-toluate were isolated in 65 and 66 per cent yield, respectively.

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THE EFFECTS OF GAMMA IRRADIATION ON ADDITIVES PRESENT IN FOOD CONTACT PACKAGING MATERIALS

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The effects of varying doses of gamma irradiation on organotin stabilisers present in PVC, and on a range of hindered phenol and arylphosphite antioxidants present in PVC, polyethylene and polypropylene, have been studied. Organotin stabilisers suffer dealkylation to form monoalkyltin trichloride and tin(IV) chloride. Phenolic antioxidants are progressively destroyed, the rate of loss depending on the antioxidant and the base polymer. Arylphosphite antioxidants are rapidly destroyed on gamma irradiation to form the related phosphate.

INTRODUCTION

There is growing interest in the possibility of using gamma-irradiation as a means of extending the shelf-life of pre-packaged foods. In its recent report, the Advisory Committee on Irradiated and Novel Foods (1) has advised that the irradiation of food up to an overall average dose of 10 kGy (1 Mrad) presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government is currently considering this report and the comments from the public that have been made on it. Whereas the nutritional properties of many types of irradiated food have been studied in depth, comparatively little is known of the chemical effects of gamma-irradiation on the many additives (both intentional and non-intentional) that are present in polymeric materials which may be in contact with a foodstuff. It is possible that toxic substances might be formed, which could subsequently migrate into the foodstuff and present a hazard.

RESULTS AND DISCUSSION

In recent work, we have shown that organotin stabilisers of the type Bu_2SnX_2 (X = $SCH_2CO_2C_8H_{17}$ or $O_2CCH{=}CHCO_2C_8H_{17}$) present in poly(vinyl chloride) (PVC) and subjected to varying doses of gamma irradiation in the range 1-200 kGy (0.1-20 Mrad) suffer degradation with dealkylation to form monobutyltin trichloride and tin(IV) chloride (Tables I and II), which have been characterised by a subsequent alkylation procedure followed by gas

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chromatographic analysis. The extent of degradation of the stabilisers on prolonged gamma irradiation is much more severe than during thermal degradation leading to comparable blackening of the polymer (Allen et al, (2-5)).

TABLE I

Analysis of irradiated PVC samples containing dibutyltin bis-(iso-octylthioglycollate) (1.2% w/w) [$Bu_2Sn(IOTG)_2$]

Exposure (kGy)	Relative proportion of degradation products[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
0	92	6	2
5	87	10	3
10	88	7	5
15	75	15	10
20	72	17	11
25	70	16	14
50	52	14	34
100	35	18	47
200	15	17	68

[a] X = $SCH_2CO_2C_8H_{17}$ or Cl

TABLE II

Analysis of irradiated PVC samples (milled) containing dibutyltin bis(iso-octylmaleate) (2% w/w) [$Bu_2Sn(IOM)_2$]

Exposure (kGy)	Relative proportion of degradation products[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
0	97	3	1
5	91	5	4
10	90	7	3
15	92	4	4
20	92	4	4
25	89	6	5
50	68	16	16
100	59	22	19
200	41	17	42

[a] X = $O_2CCH{=}CHCO_2C_8H_{17}$ or Cl

We are currently investigating the fate of hindered phenol and arylphosphite antioxidants (e.g. Irganox 1076, 1010, and 1330, and Irgafos 168) present in a range of polymers, including PVC, polyethylene and polypropylene. Our hplc analytical results have revealed the progressive destruction of the antioxidants on irradiation, the rate of loss depending on the nature of both antioxidant and base polymers (Allen et al, (6)) (Tables III and IV). In most cases, a significant (but not drastic) loss of antioxidant (ca. 30%) occurs on exposure to a gamma irradiation dose of 10 kGy (1 Mrad), the maximum dose likely to be permitted should food irradiation gain general approval in the UK. Reanalysis of the polymers after a six-month interval has revealed little subsequent post-irradiation degradation of the antioxidants.

In the case of the hindered phenol antioxidants, we have not yet detected degradation products which can be extracted from the irradiated polymer, and it is suspected that such products are becoming covalently bound to the polymer as a result of radical coupling processes. It has recently been shown that gamma irradiation of hindered phenols in benzene solution gives rise to phenylated derivatives resulting from coupling of radicals derived from the antioxidants with phenyl radicals derived from the solvent (Brodlihova et al, (7)). Gamma-irradiation of polyolefins is known to give rise to macroalkyl radicals, and hence the trapping of antioxidant degradation products is therefore probable. If this is so, then concerns over the migration of potentially toxic degradation products are much reduced. Experiments involving a ^{14}C-labelled antioxidant in polyolefins are currently in hand in order to explore this aspect further.

However, in the case of the arylphosphite stabiliser, Irgafos 168, we have shown that drastic reductions in the level of the antioxidant occur during gamma irradiation, to such an extent that little remains after a dose of 10 kGy (Table IV). In addition, we have detected the triarylphosphate oxidation product of Irgafos 168 in the extracts of the irradiated polymers by both hplc and ^{31}P nmr techniques.

TABLE III

Effects of irradiation on phenolic antioxidants present in poly(vinyl chloride), polyethylene and polypropylene

	PVC		Polyethylene			Polypropylene			
Irradiation Dose/kGy	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1330[c]	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1010[b]	% Irganox 1330[c]
0	0.44	0.62	0.36	0.16	0.25	0.34	0.48	0.08	0.38
1	0.29	0.46	0.28	0.12	0.22	0.37	0.47	0.07	0.37
5	0.27	0.46	0.23	0.10	0.22	0.38	0.44	0.05	0.36
10	0.12	0.43	0.22	0.09	0.22	0.38	0.41	0.04	0.30
20	0.17	0.37	0.20	0.07	0.15	0.36	0.33	0.02	0.27
25	0.18	0.31	0.14	0.07	0.15	0.35	0.33	0.02	0.25
35	0.19	0.30	0.14	0.05	0.16	0.30	0.28	0.01	0.22
50	0.15	0.24	0.11	0.04	0.13	0.30	0.18	0.01	0.23

[a] ±0.03%

[b] ±0.01%

[c] ±0.05%

TABLE IV

Effects of irradiation on Irgafos 168 present in polypropylene

Irradiation Dose/kGy	Irgafos 168 as sole antioxidant % Irgafos 168[a]	Combination of Irgafos 168 + Irganox 1010 % Irgafos 168[a]	% Irganox 1010[b]
0	0.067	0.069	0.08
1	0.035	0.010	0.05
5	0.009	-	0.04
10	0.004	-	0.03
20	-	-	0.02
25	-	-	0.01

[a] ±0.003

[b] ±0.01

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FOOD ADDITIVES AND CONTAMINANTS, 1988, VOL. 5, SUPPLEMENT NO. 1, 433–435

The effects of gamma irradiation on the fate of polymer additives and the implications for migration from plastic food contact materials

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There is growing interest in the possibility of using gamma-irradiation as a means of extending the shelf-life of pre-packaged foods. In its recent report, the Advisory Committee on Irradiated and Novel Foods (1986) has advised that the irradiation of food up to an overall average dose of 10 kGy (1 Mrad) presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK government is currently considering this report and the comments from the public that have been made on it. Whereas the nutritional properties of many types of irradiated food have been studied in depth, comparatively little is known of the chemical effects of gamma irradiation on the many additives (both intentional and non-intentional) that are present in polymeric materials which may be in contact with a foodstuff. It is possible that toxic substances might be formed, which could subsequently migrate into the foodstuff and present a hazard.

Following initial studies of the effects of gamma-irradiation on organotin compounds present in PVC, (Allen *et al.* 1985a, b, 1987a, b) we are currently investigating the fate of hindered phenol and arylphosphite antioxidants (e.g. Irganox 1076, 1010, and 1330, and Irgafos 168) present in a range of polymers, including PVC, polyethylene and polypropylene. Our results have revealed the progressive destruction of the antioxidants on irradiation, the rate of loss depending on the nature of both antioxidant and base polymers (Allen *et al.* 1987c,d)(tables 1 and 2). In most cases a significant (but not drastic) loss of antioxidant (*ca* 30%) occurs on exposure to a gamma irradiation dose of 10 kGy (1 Mrad), the maximum dose likely to be permitted should food irradiation gain general approval in the U.K.

In the case of the hindered phenol antioxidants we have not yet detected degradation products which can be extracted from the irradiated polymer, and it is suspected that such products are becoming covalently bound to the polymer as a result of radical coupling processes. It has recently been shown that gamma irradiation of hindered phenols in benzene solution gives rise to phenylated derivatives resulting from coupling of radicals derived from the antioxidants with phenyl radicals derived from the solvent (Brodlihova *et al.* 1986). Gamma irradiation of polyolefins is known to give rise to macroalkyl radicals, and hence the trapping of antioxidant degradation products is therefore probable. If this is so,

Table 1. Effects of irradiation on phenolic antioxidants present in poly(vinyl chloride), polyethylene and polypropylene

	PVC		Polyethylene			Polypropylene			
Irradiation dose(kGy)	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1330[c]	% Irganox 1076[a]	% Irganox 1010[b]	% Irganox 1010[b]	% Irganox 1330[c]
0	0·44	0·62	0·36	0·16	0·25	0·34	0·48	0·08	0·38
1	0·29	0·46	0·28	0·12	0·22	0·37	0·47	0·07	0·37
5	0·27	0·46	0·23	0·10	0·22	0·38	0·44	0·05	0·36
10	0·12	0·43	0·22	0·09	0·22	0·38	0·41	0·04	0·30
20	0·17	0·37	0·20	0·07	0·15	0·36	0·33	0·02	0·27
25	0·18	0·31	0·14	0·07	0·15	0·35	0·33	0·02	0·25
35	0·19	0·30	0·14	0·05	0·16	0·30	0·28	0·01	0·22
50	0·15	0·24	0·11	0·04	0·13	0·30	0·18	0·01	0·23

[a] ± 0·03.
[b] ± 0·01.
[c] ± 0·005.

Table 2. Effects of irradiation on Irgafos 168 present in polypropylene

		Combination of Irgafos 168 + Irganox 1010	
Irradiation dose (kGy)	Irgafos 168 as sole antioxidant (Percentage Irgafos 168[a])	Percentage Irgafos 168[a]	Percentage Irganox 1010[b]
0	0·067	0·069	0·08
1	0·035	0·010	0·05
5	0·009	—	0·04
10	0·004	—	0·03
20	—	—	0·02
25	—	—	0·01

[a] ± 0·003.
[b] ± 0·01.

then concerns over the migration of potentially toxic degradation products are much reduced. Experiments involving a ^{14}C-labelled antioxidant in polyolefins are currently in hand in order to explore this aspect further, and preliminary results from this work lend support to the above suggestion. Samples of polyethylene and polypropylene containing ^{14}C-labelled Irganox 1076 at 0.2% by weight have been subjected to doses of gamma irradiation in the range 10–50 kGy. Following irradiation, the samples have been exhaustively extracted with chloroform under reflux, so as to remove all remaining free additive and degradation products. The residual radioactivity of the extracted polymers has been found to increase steadily as the irradiation dose increases. Conversely, the total extractable radioactivity decreases as the dose increases. Future studies will include detailed HPLC and TLC analyses of the extracts using a ^{14}C-detector, in order that any extractable labelled degradation products may be detected and subsequently characterized.

In the case of the arylphosphite stabilizer, Irgafos 168, we have shown that drastic reductions in the level of the antioxidant occur during gamma irradiation, to such an extent that little remains after a dose of 10 kGy. (table 2). In addition, we

have detected the triarylphosphate oxidation product of Irgafos 168 in the extracts of the irradiated polymers.

We have also begun an investigation of the effects of irradiation on the migration of Irganox 1076 and 1010 from polyolefins. Preliminary studies have revealed that gamma irradiation does not lead to any increases in migration into aqueous-based simulants which can be detected by HPLC techniques. In addition, we have shown that migration of these antioxidants from polypropylene into iso-octane (a fatty food simulant) decreases with increasing irradiation dose. It is of interest that, in this study, the migration of Irganox 1076 is greater than that of Irganox 1010 for a given irradiation exposure, which can be related to the comparative levels of free additive remaining in the polymer. These results are consistent with an earlier report (Figge and Freytag 1977) of the effect of a 25 kGy exposure on the migration of Irganox 1076 from polyolefins into the synthetic fat HB 307.

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Contributions should have novelty and must be brief. Manuscripts must be submitted in accordance with the instructions to authors, which are published in this issue (p40). Authors are requested to note that manuscripts which do not accord with these instructions are currently being returned without consideration; in the case of overseas contributions return is by *seamail*. In order to expedite publication of accepted manuscripts, proofs are not circulated to authors outside the UK.

The unexpected degradation of an internal standard in the h.p.l.c. determination of anti-oxidants in gamma-irradiated food contact polyolefins: a possible basis for a chemical test for an irradiated plastic

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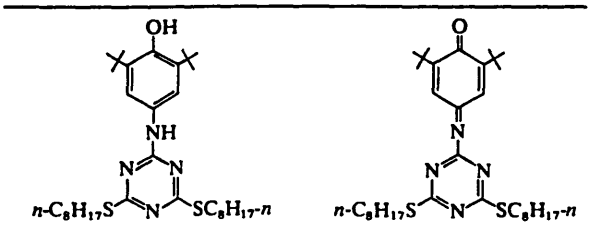
In the course of studies of the fate of antioxidants present in food contact polymers subjected to varying doses of gamma irradiation,[1-3] the authors have developed h.p.l.c. procedures for the determination of a range of hindered phenolic antioxidants (e.g. Irganox 1076, 1010) and the related hindered phosphite, Irgafos 168. These methods have involved the use of one of the related antioxidants as an internal standard in the determination of one of the other substances.

However, for the determination of Irgafos 168 in the presence of Irganox 1010 in synergistically-stabilised systems, it was necessary to seek an alternative internal standard, and the triazine, Irganox 565, 2,4-bis(*n*-octylthio)-6-(4-hydroxy-3,5-di- *t* -butylphenylamino)-1,3,5-triazine (I) was selected because of its favourable retention behaviour relative to the two analytes under the conditions employed. In the analytical procedure, samples of polymer were extracted under reflux in chloroform, which had been spiked with Irganox 565 as internal standard. In the analysis of unirradiated, thermally processed polypropylene, Irganox 565 functioned as a perfectly acceptable internal standard. However, when applied to samples of irradiated polypropylene and low density polyethylene (LDPE), it was found that the internal standard was progressively destroyed during the reflux period.

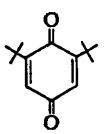
In the case of polypropylene which had received a dose of 1 kGy, the Irganox 565 was completely destroyed. With irradiated LDPE, the rate of destruction was slower but significantly dose-related, complete destruction only being observed after a dose of 50 kGy. In contrast, little degradation was observed in the presence of irradiated high density polyethylene (HDPE). Investigation of the behaviour of Irganox 565 in the presence of gamma-irradiated-polypropylene or -LDPE, containing no other antioxidants, revealed that it is converted into the iminoquinone (II), identified by comparison with the authentic material prepared by oxidation of the triazine (I) with manganese dioxide in chloroform at room temperature.

It is likely that the iminoquinone (II) is formed from the reactions of Irganox 565 with hydroperoxo groups formed at tertiary carbon sites in the irradiated polymers.

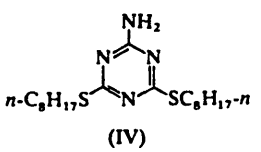


(I)

(II)



(III)



(IV)

Although hydroperoxides are formed during the thermal processing of polymers, it is clear that a much greater number of such groups are formed during gamma-irradiation in air. As pointed out above, no degradation of Irganox 565 occurs in the presence of an unirradiated (but thermally processed) polyolefin. The significantly smaller number of easily peroxidisable sites in irradiated HDPE doubtless accounts for the much reduced rate of destruction of the triazine (I). The authors have carried out model studies of the reaction of compound (I) with *t*-butyl hydroperoxide in chloroform solution, showing that the iminoquinone (II) is readily formed, together with the quinone (III) and the aminotriazine (IV), arising from the hydrolysis of the iminoquinone (II) by traces of water in the peroxide reagent.

There is, at present, much interest in the development of simple tests for the detection of irradiated food. This, unexpected, chemistry may indicate an alternative approach in that it may be possible to devise reagents which would reveal whether a food contact plastic has been irradiated.

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