THE EFFECTS OF THE MOLECULAR WEIGHT AND THE ENVIRONMENT OF ANTIOXIDANTS ON THEIR EFFICIENCY

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SUMMARY

Following the commercial exploitation of synthetic high polymers, a considerable amount of effort has been expended in seeking additives for these materials which would suppress their oxidative deterioration. The majority of available information centres upon the search for antioxidants which will provide the optimum chemical efficiency in preventing these oxidation processes.

However, it has become apparent over recent years that other factors, physical rather than chemical in nature, are of primary importance in determining the activity of antioxidants.

The present work has involved an investigation of the effects of these physical phenomena on the efficiency of antioxidants in polypropylene. In particular, it is demonstrated that the loss of antioxidants from polypropylene by volatilisation is of major importance in determining their efficiency. It is shown that although this loss can be curtailed by increasing the molecular weight of phenolic antioxidants, the direct oxidation of the antioxidant itself, to more volatile products, can limit the success of such an approach. Furthermore, it is demonstrated that mechanism of action of sulphur antioxidants markedly reduces the persistence of these stabilisers.

The effects of the compatibility and mobility of antioxidants in polypropylene upon their efficiency are discussed and it is demonstrated that low compatibility and low mobility do not necessarily preclude useful stabilising efficiency. Furthermore, indications are obtained that high compatibility may be detrimental to the efficiency of an antioxidant.

A sensitive technique is introduced for assessing the progress of oxidation reactions in a polymer and the stabilising activity of antioxidants, based upon the measurement of the torsional properties of the polymer.

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1. INTRODUCTION

1.1 The Degradation of Polymers.

During the last decade, the commercial exploitation of synthetic polymers with superior mechanical properties, but with relatively low thermo-oxidative stability, has produced intense activity in the field of polymer stabilisation.

In particular, the introduction of polypropylene emphasised the inadequacies of the more traditional stabiliser systems, and presented new problems during both processing and service life.

Several reviews (1 - 7) have traced the developments in the understanding of the degradation and stabilisation of rubbers and plastics. The contributions made by fundamental studies of low molecular weight analogues of high polymers are discussed by the more recent authors (4, 7).

These exhaustive treatments obviate the necessity for a fundamental appraisal of the mechanisms of polymer degradation and stabilisation in the present investigation, and mention of the chemistry of these processes will only be made selectively during the discussion of experimental procedures and results.

Although the understanding of the chemistry of polymer stabilisation has reached a considerable level of sophistication, it has become apparent over recent years that other factors, physical rather than chemical in nature, must be considered in any attempt to assess the technological efficiency of stabilisers.

Owing to the intractable nature of most high polymer systems, workers have been forced generally to assume that the results of studies in low molecular weight liquid model compounds may be extended with reasonable accuracy to polymer systems, in both the solid and molten state. All too often, however, subsequent investigations have revealed that such assumptions may be made only with the greatest discretion.

Furthermore, wide discrepancies are often found to occur in the different methods of evaluation which are used to examine the efficiency of stabilisers in polymer systems, and also in the performance assessments of stabilisers in polymers under experimental and actual processing or service conditions. Chemical effects certainly play a part in producing these anomalies (8), although it is now apparent that physical phenomena may be of greater importance (9).

The investigation of these physical effects, which is presented later, has centred on one polymer, polypropylene, and two types of stabiliser, phenolic and thioether. Polypropylene still presents problems of stabilisation, and as new stabilisers of improved efficiency continue to be sought for this polymer, it was considered to be one of the more worthwhile materials for examination. Both phenolic and thioether antioxidants are widely used in polyolefin stabilisation and, functioning primarily by the complementary radical scavenging and peroxide decomposing mechanisms, it was hoped that these antioxidants would provide useful comparisons.

However, as information on the present subject is sparse and scattered in nature, discussion of other polymer and stabiliser systems will be necessitated. Thus, although phenolic and thioether antioxidants are used primarily in the prevention of thermo-oxidative degradation, mention will also be made of stabilisers used for the inhibition of photo-induced and metal-catalysed oxidation.

1.2 Physical Effects and the Activity of Stabilisers.

Many indications may be obtained from the literature (10, examples of collected results) that the efficiency of a stabiliser is dependent upon the substrate in which experimental determinations are carried out. Nevertheless, for a given substrate of low or high molecular weight, stabilisers can probably be considered to possess an inherent chemical activity at a given concentration and temperature. However, it is now apparent (9) that other factors may affect the technological efficiencies of stabilisers in polymeric substrates, namely; the compatibility with or solubility in the polymer, the mobility in the polymer, the extractability (leachability) from the polymer, and the volatility from the polymer.

These factors may be inter-related to varying degrees, depending on the chemical and physical nature of the stabiliser and polymer, and on the external environment of the polymer itself. In particular, these factors could be expected to be dependent on the molecular weight of the stabiliser to a considerable degree. The present work has centred on an investigation of these relationships.

1.2.1 Compatibility.

A limited amount of information is available on the compatibility of stabilisers with polymers, but very little has been published on the relationships between the compatibility and the activity of stabilisers.

Difficulties arise in defining the precise meaning of the compatibility of an additive, in low concentrations, with a polymer, particularly when the latter exhibits a crystalline structure.

The direct observation of phase separation in a solid polymer presents considerable difficulties due to the extremely high viscosity of the system. Even when the polymer is softened or melted, the detection of incompatibility by separation into phases is not easy.

Several indirect methods have been developed for the examination of polymer/solvent and polymer/polymer compatibility phenomena, and modifications of some of these techniques have been applied to polymer/stabiliser systems.

The compatibilities of blends and mixtures of polymers have been assessed from studies of the solubility characteristics of each polymeric component in the same solvent, and both theoretical and practical treatments appear in the literature (11 - 15). Although this technique has not been fully developed for the investigation of the compatibility of stabilisers and polymers, commercial technical information on stabilisers usually contains data on their solubility in various solvents, presumably as an indication of the expected compatibility with polymeric substrates. Without similar data on the polymers themselves, and for other reasons mentioned later, information of this type is probably of limited value, particularly where the substrate is a crystalline polymer.

Changes in the mechanical properties of polymer blends with variations in the compatibility of the components have been detected by dynamic determinations (16, 17) and theoretical treatments have been carried out (11, 18, 19). However, Parrini and Corrieri (20) point out that these techniques offer inadequate sensitivity for the examination of stabiliser/ polymer systems at technologically meaningful levels of addition of the stabiliser.

Studies of the first order (21 - 24) and second order (25) transitions of both polymer blends and polymers containing various additives have provided information on the compatibility of these systems. The latter technique has been limited in application by the occurrence of crystallisation effects in the polymer substrates, however, first order transition investigations have been extended to stabilised polymer systems.

Nechitailo and Sanin (26) have used differential thermal analysis to obtain first order transition data on low and high density polyethylene and polypropylene, containing various phenolic and amine stabilisers, and have attempted to relate the depression of the melting point of the polymers to the compatibility of the additives. However, although these workers considered that thermal analysis provided higher sensitivity than dilatometric techniques, they were not able to obtain results with loadings of the stabilisers lower than 10 %.

Nechitailo and Sanin suggested that stabilisers will be disposed between the crystalline and amorphous structural elements of the polymer, depending on the chemical nature and the molecular shape of the additive. They considered that the efficiency of a stabiliser would be dependent on the nature of this distribution but did not amplify this suggestion.

Their discussion of the crystallinity of polymers is rather obscure, however, they conclude that monophenolic stabilisers exhibit a tendency to penetrate the more highly ordered regions of the polymer matrix, whereas the high molecular weight bisphenolic and amine antioxidants which were examined, showed no penetration.

Nechitailo and Sanin used the results of earlier work (27) and Flory's treatment of polymer/diluent systems (28) to discuss the depression of the melting point and concluded that the molecular volume of the additive was the controlling factor in determining the degree to which the stabiliser penetrated the crystalline regions of the polymer.

The inference from this approach, that a similar situation will apply for stabilisers at the considerably lower concentrations used in practice, may not be justified. Additives, at high concentration, may disturb the crystalline structure of the polymer to a considerable degree. Thus, although the monophenolic stabilisers appeared to dissolve in the more highly ordered regions of the polymer and depress the melting point of these regions under the experimental conditions which were used, it is not clear whether a similar situation would have applied if the additives had been incorporated at practical levels of addition.

A similar investigation involving the differential thermal and enthalpic analyses of first order transitions has been carried out by Ambrovic and Mikovic (29). Using polypropylene as a substrate, the work was again carried out with high additions of stabiliser. Monophenolic and bisphenolic antioxidants and UV stabilisers of the alkoxy substituted benzophenone type were examined in compositions containing equal parts of polymer and stabiliser.

These workers concluded, in contrast to the findings of

Nechitailo and Sanin, that bisphenolic antioxidants exhibited greater compatibility with the more ordered regions of polypropylene than the monophenolic stabilisers that were examined. The compatibility of the benzophenone stabilisers was shown to increase as the alkoxy side chain was lengthened.

Ambrovic and Mikovic suggested that stabilisers could be divided into two groups; those which dissolve in the crystalline regions and thereby decrease the melting point of the polymer, and those which dissolve only in the amorphous regions of the polymer, and thus do not decrease the melting point.

However, these conclusions may be confused by other considerations. The conflict between the results of Ambrovic and Mikovic and those of Nechitailo and Sanin may indicate a dependence on the method of measurement of the first order transition. Nechitailo and Sanin determined the endothermic melting point of the substrate polymer during a heating cycle, whereas Ambrovic and Mikovic recorded the exothermic crystallisation from the melt. The reason for the different conclusions drawn from the two techniques is not clear, however, a difference in mobility between the mono- and bisphenolic stabilisers may be an influencing factor. Thus, during a heating cycle, the monophenolic compounds may penetrate the crystalline phase more rapidly than the bulkier bisphenolic species. During crystallisation from the melt, the reverse phenomena could apply, resulting in a greater entrainment of the high molecular weight stabiliser in the more ordered regions of the polymer.

Again, the high concentrations of stabiliser which were used by Ambrovic and Mikovic may have caused confusion due to modifications of the crystal structure of the substrate polymer; as with the work of Nechitailo and Sanin, it is not clear that a similar situation will exist at technologically acceptable levels of addition of the stabilisers.

More generally, there seems no reason to suppose that additives residing in the amorphous region of the polymer will not affect the melting characteristics of the crystalline phase. Thus, conversely, although Ambrovic and Mikovic suggest that stabilisers which have little effect on the melting point of the polymer are probably dissolved solely in the less ordered phase, a similar effect could be produced if the additive had simply a very low compatibility with the amorphous regions of the substrate.

An investigation by Parrini and Corrieri (20), which attempted to overcome some of the difficulties mentioned above, was based on the observation (30 - 32) that a compatible diluent decreases the rate of crystallisation of a crystalline polymer and that the decrease is proportional to the amount of diluent present. Insoluble substances such as pigments can increase the rate of crystallisation by nucleation. (23, 32, 33).

Using a dilatometric technique, it was found possible to separate the effects of compatible and incompatible additives, in various polymers, at concentrations below 1 %. The rate of crystallisation of polypropylene was reduced by decalin, tetralin, and other solvents, was increased by titanium dioxide and silica and remained the same with di - 2 - ethylhexylphthalate.

The Italian workers considered that the latter effect indicated that the phthalate ester was incompatible but, unlike titanium dioxide, did not initiate nucleation. However, it may be postulated that a marginally soluble non-nucleating additive may produce a similar phenomenon **if** the amount of additive in solution is so small that the crystallisation rate of the polymer is not significantly reduced.

The investigation was extended to include polymer blends and it was demonstrated that unless the two polymer components were chemically very similar the rate of crystallisation was not reduced. In agreement with earlier work (11,15, 34 - 36) it was concluded that, except for blends such as ethylene/propylene copolymers in polyethylene, mixed polymer systems were in general incompatible; a conclusion of relevance to the discussions of high molecular weight antioxidants which will be made later.

Ermolina and co-workers (37) demonstrated that phenyl - β - naphthylamine caused nucleation in the crystallisation of polycaproamide. The additive was shown to exhibit normal antioxidant behaviour despite the fact that it would be classed as incompatible by Parrini and Corrieri. In addition to the normal antioxidative effect, Ermolina demonstrated that the formation of a dense spherulitic structure, in the presence of the stabiliser, improved the thermo-oxidative stability of the polymer.

Using the Parrini and Corrieri technique, Cichetti, Dubini, and their co-workers (38) investigated the compatibility of a series of alkoxy substituted benzophenone stabilisers in polypropylene and high density polyethylene.

The work was carried out using a low stabiliser addition (less than 2 %) and in contrast to the findings of Ambrovic and Mikovic (29) the compatibility of the additives with polypropylene remained consistently low as the length of the alkoxy side chain was increased. With high density polyethylene a small increase in compatibility was observed as the length of the side chain was increased to 8 units followed by an abrupt rise to a considerably higher compatibility up to 18 units. Cichetti and Dubini offered no explanation of these differing effects and in the absence of further data, the phenomena remain obscure. However, there is clearly some disagreement between these findings and the conclusions drawn by Mikovic and Ambrovic (29) on a similar series of additives.

Work on the compatibility of an aromatic diamine stabiliser similar to those examined by Nechitailo and Sanin (26) has been extended by Nurmukhametov and his co-workers (39). The fluorescence spectra of di - β - naphthyl - p - phenylenediamine in polypropylene and in liquid solvents were found to be sufficiently similar to indicate that the stabiliser was in solution in the polymer matrix. The investigators made no comment on the precise morphological environment of the stabiliser. However, as Nechitailo and Sanin indicated that β - naphthylamine was 'incompatible' with polypropylene, from their melting point studies, it seems reasonable to assume that the diamine was concentrated primarily in the amorphous regions.

Recently, Frank and Lehner (40) have developed a method for the direct determination of the distribution of stabilisers in polypropylene using ultraviolet microscopy. By recording the absorption of UV radiation by a benzotriazole stabiliser these workers were able, from the absorption patterns, to demonstrate that the stabiliser was rejected from the more highly ordered crystallites of the polymer during a slow crystallisation from the melt. It was concluded that the benzotriazole derivative resided in the non crystalline regions, both between the spherulites and in the areas between the crystalline fibrils of the polymer, within the spherulitic structures. Frank and Lehner considered that the behaviour in this specific example was generally applicable to stabilisers and additives in crystalline polymers. They pointed out, however, that the practical conditions used for the processing of polymers resulted in considerably faster cooling from the melt than they had used experimentally and that the spherulitic growth in such polymers was therefore curtailed significantly. Under rapid crystallisation conditions, these workers found that their technique was not sensitive enough to determine the distribution of the additive between the phases of the polymer.

The above technique, although clearly demonstrating distribution effects, does not indicate whether the additive is actually in solution in the amorphous phase of the polymer at ambient temperatures.

The conclusions of Frank and Lehner are to some extent supported by the work of Alcalay (41), who has demonstrated that solvent sorption in isotactic polypropylene initially occurs in the amorphous phase of the polymer.

Marcincin and his co-workers (42) have determined the compatibility of a series of hydroxybenzophenone light stabilisers in molten isotactic polypropylene by comparing the surface tensions exhibited by the two components. Their approach was based on the work of Hildebrand and Scott (43) who suggested that the compatibility of two liquids will be dependent on the character and intensity of the intermolecular forces between the two components. This concept has been extended (43 - 45) to show that the magnitude of these forces can be expressed quantitatively by the values of the solubility parameter and cohesive energy density and that these values may be related to the surface tensions of the interacting liquids. Though this approach is not generally valid for all liquids, Marcincin had previously shown (46) that the relationship could be applied to the derivatives of benzophenone.

This investigation demonstrated that the longer chain octyloxy- and 2 - ethylhexyloxy-hydroxybenzophenones were compatible with polypropylene in the melt whereas the unsubstituted and methoxy derivatives were incompatible. Marcincin suggested that the efficiency of these stabilisers will be dependent on their compatibility but provided no supporting evidence.

Although the supramolecular environment of the stabiliser in the polymer melt will be markedly different from that in the solid crystalline polymer, the above technique may well provide data of a negative nature. Thus, in all probability, a stabiliser which is incompatible with the molten polymer will not be compatible with the solid crystalline polymer at ambient temperatures. However, the technique may be capable of providing information which is relevant to the conditions arising during the processing of a polymer. Nevertheless, there does appear to be some overall agreement between Marcincin's observations and those of Ambrovic and Mikovic (29) in that the higher homologues in the alkoxy benzophenone series were considered to be more compatible with polypropylene in both investigations.

Newland (47) has attempted to correlate the stabilising efficiencies of a series of alkoxy substituted hydroxybenzophenones in polyethylene and polypropylene with their compatibility. The time which elapsed before a visible exudation of stabiliser to the surface of the polymer occurred was taken as an indication of compatibility, and stabilising efficiency was measured by outdoor exposure.

The exudation time from polyethylene was not found to be simply related to the chain length of the alkoxy substituent; in the series of compounds up to the octadecoxy derivative, the heptoxy and dodecoxy substituted stabilisers were found to exhibit the longest exudation times by two orders of magnitude. Again, Newland's results indicated no direct correlation between exudation time and stabilising activity in the outdoor ageing evaluation. In polypropylene a similarly complex relationship was observed between weathering resistance and the chain length of the alkoxy substituent.

These findings are perhaps not unexpected in that the assessment of compatibility using the criterion of exudation time will be complicated by the rate of diffusion of the stabilisers through the polymer.

It will be seen that the nature of compatibility effects of stabilisers in polymers and, in particular, in crystalline polymers, is not clear. It seems likely that, in general, stabilisers are rejected from the growing crystalline structures of the polymer during the crystallisation process. This has been demonstrated (40) in polypropylene containing a benzotriazole derivative under artificially idealised conditions of crystallisation and although, under the practical conditions of polymer processing, crystallisation occurs extremely rapidly, it does not seem unreasonable to expect a similar, though perhaps less marked, phenomenon to occur.

Thus the compatibility of a stabiliser with a crystalline polymer can probably be considered in terms of the degree of interaction between the additive and the less well ordered regions of the polymer matrix. In polypropylene both the inter-spherulitic amorphous regions and the intra-spherulitic areas of low crystallinity, between the individual crystallites, seem to be capable of retaining the stabilisers.

Fortuitously, the accumulation of stabilisers in the amorphous phase of the polymer matrix appears to be advantageous in preventing degradation; Hawkins and Winslow (48 - 54) have demonstrated that the major initial oxidation reactions in polyolefins occur primarily in the amorphous areas of the polymer; stabilisers tend to reside, therefore, in the regions of greatest oxidative sensitivity. It should be noted, however, that other workers (55, 56) have demonstrated that the photo-oxidative degradation of polypropylene occurs more rapidly as the isotactic content of the polymer increases. Kato (56) suggests that the effect may be due to the presence of a stereodependent step in the sequence of oxidation reactions.

It is clear that conflicting information on compatibility phenomena is obtained from different experimental techniques. Furthermore, it is doubtful whether information obtained from studies of polymers in the melt can be related to the molecular environment of a stabiliser at low concentrations in solid crystalline polymers.

The incompatibility of stabilisers has been a widely evoked and unsupported explanation of low activity, in assessments of stabilisation phenomena. Such conclusions are probably an over-simplification in that, under the conditions of test which are used for assessing the activity of stabilisers, factors such as the volatility and extractability of the additives may be extremely important. Newland (47) pointed out, in his examination of hydroxybenzophenone photostabilisers, that the leaching of these additives, during the outdoor exposure of the stabilised polymer, appeared to make a significant contribution to their activity. Newland also considered that the aliphatic (alkoxy) substituents of the hydroxybenzophenones contributed to the compatibility of these materials with polypropylene. However, the results obtained by Nurmukhametov (39), using fluorescence spectroscopy, have indicated that the presence of alkyl substituents in stabilisers based on aromatic species, may not necessarily be a prerequisite for compatibility with polyolefins at ambient temperatures.

Although intuitively it has generally been considered necessary for a stabiliser to be compatible with a polymer substrate in order to exhibit activity, this has not been demonstrated conclusively in practice. There are indications in the literature that the levels of compatibility at which stabilising activity is exhibited may be lower than has been generally assumed. Hawkins and co-workers (51) have demonstrated that carbon black, which presumably has very low compatibility with polyolefins, as estimated by present techniques, can act as a radical trapping stabiliser in polyethylene. This work was extended to an evaluation in which silica dust was treated with polyhydric phenols to form stable compounds with residual phenolic functionalities on the surfaces of the inorganic particles. Again, these materials, which must have very low compatibility with polyethylene, were found to confer a significant oxidative stability to the polymer.

1.2.2 Volatility.

Although the loss of stabilisers by volatilisation has been recognized as a contributing factor in determining their efficiency for some time, real indications of the full consequences of volatility effects have not been obtained until quite recently.

The effects of cross-contamination by the volatilisation of stabilisers between polymer samples in accelerated aging tests were recognised by early workers on the stabilisation of rubber (57 - 65) and this led to the development of individual cell aging techniques.

In an early examination of the stabilisation requirements of polyethylene hot water pipes, MacLeod (66) measured the efficiency of stabilisers under conditions where volatilisation and leaching could take place. Although it was not possible to separate the two effects, MacLeod concluded qualitatively, that less volatile stabilisers were more efficient in these circumstances. MacLeod's work is one of the few investigations of the effects of volatility in a practical environment, the majority of subsequent studies having concentrated on the assessment and the implications of the volatilisation of stabilisers in accelerated aging tests.

Hawkins and co-workers (67) attempted to separate the effects of the loss of stabilisers by volatilisation and their loss by direct anti-oxidative reaction in polyethylene. Although an accelerated, high temperature, ageing test was used to determine stabilising efficiency, Hawkins attempted to eliminate the effects of volatility in this assessment by using closed oxidation vessels and employing oxygen uptake as an indication of the exhaustion of the stabilisers. Taking these determinations as a guide to the intrinsic efficiency of the additives, stabilised samples of polymer were subjected to a non-oxidative heat treatment under nitrogen and the amount of stabiliser remaining was assessed using the oxygen absorption technique. A range of phenolic, sulphur and amine stabilisers were examined and Hawkins concluded that stabilisers of higher molecular weight were markedly less volatile. In particular, a xylylene disulphide polymeric antioxidant and a sulphur-activated carbon black completely retained their activity after prolonged heat treatment in nitrogen at 105°C. Hawkins extended the examination to the phenol /silica complexes (51) which have been mentioned previously and demonstrated that these materials also had very low volatility.

Angert and his co-workers (68) studied the evaporation of phenyl-β-naphthylamine from various rubbers and concluded that, at a given temperature, the rate of evaporation depended upon the rate of flow of air over the polymer sample, the thickness of the sample and the initial concentration of the stabiliser. The rate of volatilisation was found to be dependent on the polymer substrate and was closely related to the heat of the solution of the stabiliser in the substrate. Furthermore, as the density of the rubber network increased, the rate of volatilisation was found to decrease.

Angert considered that these results indicated a dependence of volatility on both the rate of evaporation of the stabiliser from the surface of the polymer and the rate of diffusion to the surface of the polymer sample. Similar results were obtained by Kapachauskene and Shlyapnikov(69) in studies of phenolic and amine antioxidants in polyethylene and polypropylene. Using a spectrophotometric technique these workers were able to follow the loss of stabiliser from polymer samples during the induction period of stabilisation at elevated temperatures.

Volatility was found to decrease both with increasing molecular weight of the stabilisers and increasing number of polar groups in the stabiliser molecule. In confirmation of Angert's findings, polymer specimens with large mass to volume ratios (low surface area to mass ratios) were found to retain the stabilisers more effectively and have longer induction periods. Again, a parallel to Angert's conclusion on the effect of the density of the substrate was found, in that increased branching of the polymer molecule was found to increase the rate of loss of stabiliser.

It should be noted, however, that results obtained using spectrophotometry may perhaps be confused to some extent by the presence of species formed by stabilisers undergoing antioxidative and direct oxidative reactions.

Investigations of the effects of the polar structure of stabilisers on their volatility have been undertaken by

Temchin and his co-workers (70 - 72). By following the weight losses from samples of pure stabilisers maintained at elevated temperatures, Temchin correlated the volatility and vapour pressures of a series of phenolic and amine stabilisers. It was noted however that volatility did not always mirror the vapour pressure data and inversions of the direct relationship were found. Temchin also found that plots of volatility against temperature for differnet stabilisers could cross, again producing an inversion of the rating of volatility depending on the temperature of measurement.

However, there emerged an overall pattern of decreasing volatility with increasing molecular weight and increasing dipole moment of the stabiliser molecule. In the extreme case, hydrogen bonding through the hydroxyl group of the phenolic antioxidants, hindered to varying degrees, was found to have a noticeable effect on the volatility. The examination (72) of a series of thiobisphenolic antioxidants of constant molecular weight but with varying hindrance of the hydroxyl group demonstrated that the stabilisers capable of intermolecular hydrogen bonding had lower volatility.

Gromova and Piotrovski (73), using a technique similar to that of Temchin, have also produced data on the volatility of a variety of common stabilisers and these workers arrived at similar conclusions.

Spacht and co-workers (74) have attempted to relate the vapour pressures and volatility of pure stabilisers to their loss by volatilisation from vulcanised natural rubber. Vapour pressures were determined by ebulliometry under vacuum and the volatilities were assessed, at a range of temperatures, using two weight loss techniques, from filter papers impregnated with the stabilisers and from open dishes.

Although the vapour pressures were found to obey an Arrhenius relationship for each stabiliser, the weight loss techniques produced curves on plots of reciprocal temperature against the wieght loss, and rather higher volatilities were found than would have been expected from the vapour pressure information. However, the two weight loss techniques were found to rate the stabiliers in the same order of volatility, although they varied in their estimation of the differences between stabiliers.

Increasing the temperature and duration of the determinations, increasing the surface area of the evaporating samples, and increasing the air flow over the samples were all found to produce increases in the losses by volatilisation.

Of the range of amine and phenol stabilisers that was examined, 2,6-di-t-butyl-4-methylphenol was found to be most volatile, by greater than three orders of magnitude, than N,N' - diphenyl - p - phenylenediamine. Spacht selected the former antioxidant and 2 - benzyl - 4 - methyl - 6 - tert - butylphenol for an examination of the effects of volatility in accelerated ageing tests; the former antioxidant had been found to have a vapour pressure over twenty times larger than the benzyl substituted phenol at 100° C.

The volatilisation of these stabilisers from natural rubber at 100° C was monitored by both gravimetry and gas chromatography. At a constant temperature and air flow, losses of the stabilisers were found to be inversely proportional to the thickness of the rubber sample and, contrary to Angert's findings (68), independant of the initial concentration. The difference in the volatilisation rates of the two stabilisers was lower than would have been expected from the vapour pressure and weight loss measurements on the pure materials, but tended towards this relationship as the thickness of the rubber sample was decreased. Again, the solubility and diffusion characteristics of the stabilisers in the rubber would appear to be contributing to the overall volatility properties.

Oxygen absorption, the retention of tensile strength, and the creep behaviour were used to assess the efficiency of the stabilisers and Spacht concluded that the method of assessing degradation had little effect on the determination of stabilising efficiency in comparison with the technique which was used for ageing the samples. In closed tube and restricted atmosphere tests the efficiency of the more volatile stabiliser compared much more favourably with that of the higher molecular weight additive than would have been expected from oven tests using a flowing atmosphere.

Using a series of amine antioxidants similar to those examined in Spacht's earlier work, Lloyd and Payne (75) demonstrated, using a weight loss technique, that increasing the chain length of the alkyl substituent in a series of N - alkyl -

N' - phenyl - p - phenylenediamine antioxidants reduced the evaporative loss from natural rubber.

Blumberg, Boss and Chien (76) carried out an investigation in polypropylene, similar to Spacht's work, using qualitative estimates of the volatility of the bis and trisphenolic stabilisers that they examined. In oxygen absorption and sealed tube tests, the bisphenolic stabilisers were found to exhibit efficiencies comparable with those of the trisphenolic materials. However, oven ageing tests were found to markedly favour the higher molecular weight stabilisers.

The work was extended to include an examination of a series of synergistic mixtures of the phenols with dilaurylthiodipropionate and this investigation revealed that the ratio of the stabilisers that gave the optimum synergism varied with the test method; the relative volatilities of the sulphur and phenol components contributed markedly in determining the optimum initial composition of stabiliser formulation.

Hansen and co-workers (77, 78) have noted similar phenomena with synergistic mixtures of phenol antioxidants and metal de-activators of the oxanilide type, in polypropylene.

Although the volatilisation of stabilisers is now recognized as an important factor, contributing to the efficiency of these additives during both the processing and the environmental life of polymers (79 - 82), very few investigations into the effects of volatility, under practical conditions, have been carried out.

Juskeviciute (83) examined the loss of stabilisers during the compression moulding of polyolefins and noted that the volatilisation which could occur during this process was lower with stabilisers of higher molecular weight.

Newland (47) has recorded the losses of hydroxy-benzophenone light stabilisers from polyethylene films during milling. Although volatilisation generally decreased as the length of the pendant chain of these alkoxy substituted materials was increased, irregularities were noted where compounds of higher molecular weight were lost more rapidly than their neighbouring lower homologues. Newland considered that, in these cases, the compatibilities and mobilities of the stabilisers were contributing to the evaporative effects.

The importance of the low volatility of additives used in thin polymer films has been noted by Mulin and co-workers (84) in an examination of polypropylene coatings but no correlated evidence was presented in this work.

Difficulties arise in practical assessments due to the wide variety of conditions which are encountered during both the processing and life of polymers; thus each processing technique presents different characteristic situations where the volatility of stabilisers may become important. Similarly, during service life, temperatures encountered in different polymer applications may well vary from considerably below ambient temperatures to over 100° C. Alongside these considerations, the dimensions of the fabricated article and the nature and rate of flow of the surrounding atmosphere must also have importance.

1.2.3 Mobility and Extractability.

The practical and theoretical aspects of diffusion phenomena in polymers have been discussed in two extensive reviews (85, 86). In general, investigations have been restricted to two areas of interest; the diffusion of gases and low molecular weight compounds in polymers and the self-diffusion and inter-diffusion of single or blended polymers. Considerably less data is available on the diffusion of materials of intermediate molecular weight in either rubbers or plastics and very little information appears in the literature on the diffusion of bulky polar molecules such as stabilisers, particularly in crystalline plastics.

The phenomena associated with the diffusion of stabilisers can perhaps be divided into two rather different categories, the actual kinetic control of stabilisation reactions by diffusion and general migration and leaching phenomena; the relationships of the latter phenomena to the efficiency of stabilisers have received some attention in empirical investigations, however, very little information is available on the former phenomena.

Jackson and co-workers (87) have pointed out that reactions involving large stabiliser molecules in polymers may well be influenced by the diffusion of one or more of the reactants.

Thus, the efficiency of a stabiliser may depend, in part, upon whether the additive migrates to the site of oxidation or whether the oxidative reaction chain continues until the oxidation site meets the stabiliser (or whether an intermediate situation exists).

Alongside these effects, the phenomena of migration and leaching, which are more obvious experimentally, can be of considerable importance, depending upon the environment of the polymer, in many instances.

The migration of a stabiliser, either to the free surface of a polymer (blooming) where it can be removed,by weathering or abrasion, for example, or to an adjacent polymer,must generally be detrimental to the stabilising efficiency. Furthermore problems of contamination, staining and reduced adhesion at polymer and other interfaces may be introduced.

However, it should be mentioned that, in specific circumstances, migration to the polymer surface may be advantageous, in principle at least. Newland has suggested (47) that blooming can concentrate UV stabilisers at the surface of the polymer where they may be of greatest effect in preventing degradation. Lewis and co-workers (88) and Lake (89) have discussed the beneficial effects of the diffusion of protective waxes and stabilisers to the surface of rubber in the prevention of attack by ozone. However, it would appear that blooming must occur before the polymer is exposed to the oxidising environment, as Braden (90) has demonstrated that the rate of diffusion of p-phenylenediamine antiozonants to the surface of natural rubber is six orders of magnitude slower than the rate of attack by ozone.

The technological effects of the loss of various antioxidants by migration have been noted empirically (78, 88, 91 - 94) and concomitant reductions in the stabilities of the parent polymers have been observed. These examinations were concerned with limited numbers of stabilisers, in different polymers, under different environmental conditions, however, it would appear that,in general,higher molecular weight antioxidants exhibited a lower tendency to be lost by migration.

Although the kinetic control of stabilisation reactions by diffusion phenomena has not been investigated, these phenomena have been postulated as the explanations of various anomalies that have appeared during evaluations of stabilisers (95, 96). Heller (96), for example, suggests that the poor efficiency of high molecular weight phenolic antioxidants in inhibiting the UV catalysed degradation of polypropylene is due to the kinetic control of the stabilising reactions by diffusion.

The great majority of studies of diffusion phenomena in polymers have been based on radiotracer techniques which, although differing in detail, have essentially measured the penetration of radiotagged diffusant into a block or film of the polymer substrate. Gardiner (97), however, has recently described an optical method for monitoring the diffusion of curing agents in rubber.

From the information which is available, various generalised conclusions can probably be extended to the diffusion characteristics of stabilisers.

Several investigators (98 - 108), working primarily with rubbers, have demonstrated that the rate of diffusion and the activation energy of diffusion of an additive or penetrant is related to both the molecular weight and structure of the diffusant. Aitken and Barrer (100) and Prager and Long (101) have shown that the rate of diffusion of low molecular weight hydrocarbons in natural rubber decreases and the activation energy increases as either the molecular weight or the cross-sectional area of the diffusant is increased. The former workers suggested that a longitudinal or needle-like penetration occurred with linear chain diffusants and that diffusion was hindered by branching in the skeleton of the penetrant. Similar results were obtained by Grun (108), in one of the few early investigations of bulky diffusants, where the diffusion of various dyes in natural rubber was examined.

Auerbach and co-workers (104) in an examination of an homologous series of stearate esters noted that the rate of diffusion of these compounds in unvulcanised polybutadiene and polyisobutylene rubbers was inversely related to their molecular weight and these workers were able to calculate the contribution of each methylene unit of the ester chain in this relationship. The rates of diffusion of stearic acid and octadecanol were found to be anomalously low and this discrepancy was attributed to the presence of inter-molecular hydrogen bonding in the diffusants.

Gromov and his co-workers (109 - 110) carried out a very similar investigation of the diffusion of long chain paraffins in polyisobutylene and came to the same conclusions as Auerbach on the relationships between the molecular weights and rates of diffusion of these materials.

In an investigation of the diffusion of a limited range of phenol and amine antioxidants in various rubbers, Lewis and co-workers (88, 91) have demonstrated that the flexibility of the diffusant molecule has an effect upon its rate of diffusion. Antioxidants with bulky and rigid molecular structures were found to exhibit lower rates of diffusion than analogous stabilisers with more flexible backbones.

The diffusion of large molecules through highly crystalline polymers appears to be a rather more complex phenomenon. Several workers (38, 87, 106, 111) have reported that the rate of diffusion of an additive tends to decrease as the crystallinity of the polymer substrate increases. It has been suggested (87, 111) that additives tend to diffuse solely through the less ordered regions of the polymer matrix and that the crystalline structures of the polymer impose an extremely tortuous path upon the diffusant. Michaels and Bixler (111) have also pointed out that the mobility of the polymer chains themselves in the amorphous regions of a crystalline polymer will be limited by the adjacent crystalline structures and that this effect will further constrain the movement of diffusing molecules.

It should however be mentioned that behaviour contrary to that described, has been observed. Yushkevicyute and Shlyapnikov (112) have demonstrated that the rate of diffusion of

2,6 - di - tert - butyl - 4 - methylphenol in low density polyethylene tended to increase when the polymer had been oriented or annealed. Several workers (113 - 115) have observed similar phenomena in studies of the diffusion of gases in polyolefins and Vieth and Wuerth (114) have suggested that this behaviour is due to the formation of defects in the crystalline structure of the polymer.

Apart from the phenomena which are associated with the molecularly ordered structure of crystalline polymers it would appear that diffusion phenomena exhibit similar relationships to those observed in amorphous polymers. Dubini and co-workers (38, 116) have examined various thiodipropionate ester and hydroxybenzophenone antioxidants substituted with alkyl and alkoxy chains of different lengths. The rates of diffusion of these compounds in polyethylene and polypropylene were found to decrease with an increase in the length of the pendant chains. Dubini further demonstrated that the compatibilities of the antioxidants affected the diffusion characteristics. The activation energies for the diffusion of the higher homologues in the hydroxybenzophenone series of antioxidants (C_{12} and C_{18}) were found to be rather lower than expected from calculations based upon the additive effects of methylene groups in the pendant chain. Dubini suggested that compatible diffusants could reduce the overall bulk viscosity of the polymer in the regions of penetration and thereby facilitate the diffusion of the antioxidants. A similar type of behaviour was noted by Gromov and co-workers (109) in their examination of the diffusion of paraffins in an amorphous polymer, polyisobutylene.

The only information relating directly to the control of stabilisation reactions by diffusion has been provided by Chien and Boss (116 - 118). These workers demonstrated that the kinetics of the stabilisation reactions of 2,6 - di - tert - butyl - 4 - methylphenol in squalane and polypropylene were very similar and that the propagation reaction in the autoxidation of polypropylene proceeded by an intramolecular mechanism, its rate being independent of phase changes. Boss and Chien pointed out that the similarity of the stabilisation kinetics in a liquid hydrocarbon and in polypropyleneindicated that the reaction between the stabiliser and the peroxy radical on the polymer was thus not controlled by diffusion phenomena. Attempts to study the ESR spectra of the phenoxy radicals,produced from the antioxidant in autoxidising polypropylene,revealed that these could not be trapped by rapidly cooling the polymer sample. However, the phenoxy radicals formed by a high molecular weight trisphenolic antioxidant were readily trapped and had a half-life of several days at room temperature. By carrying out the spectral examination during the actual autoxidation process Boss and Chien demonstrated that the ESR spectrum of the monophenolic antioxidant radical exhibited a hyperfine splitting which was found to be absent in the spectrum of the trisphenolic radical. It was suggested that the monophenol could therefore undergo rapid molecular tumbling in the polymer whereas this motion was severely restricted with the trisphenol.

Unfortunately Boss and Chien did not demonstrate whether the diffusion of the antioxidant to the oxidative site on the polymer backbone predominated or whether the oxidative kinetic chain continued until an antioxidant molecule was encountered. It was not shown that the immobility of the trisphenolic antioxidant was detrimental to its stabilising efficiency.

Hawkins and co-workers (48,50,51) have provided some evidence that the immobility of an antioxidant need not necessarily preclude stabilising activity. During the evaluations of carbon black and silica/phenol compounds in polyethylene which were described earlier, Hawkins demonstrated that these materials exhibited antioxidant activity and suggested that they would reside primarily in the amorphous phase of the polymer and have very low mobility. The activities of the antioxidants were compared with the efficiencies of conventional low molecular weight mono and bisphenolic stabilisers at temperatures above and below the melting point of the polymer and Arrhenius plots of the induction periods of stabilisation were obtained. The conventional antioxidants exhibited linear Arrhenius relationships through the melting point of the polymer, suggesting that diffusion phenomena were probably not controlling activity in the solid polymer. However, carbon black and the silica antioxidants exhibited a lower activity above the melting point of the polymer than would have been expected from a linear Arrhenius relationship. Diffusion effects in the solid polymer would have resulted in activity being lower than expected below the melting point, and Hawkins suggested that the oxidative sites on the polymer were extending until an antioxidant molecule was encountered. It was postulated that, in contrast to the inorganic antioxidants, the low molecular phenols were residing throughout the amorphous and crystalline regions of the polymer and thus the oxidative sites had further to travel before being quenched. The inorganic antioxidants, being concentrated in the oxidatively sensitive amorphous phase were, therefore, adjacent to the oxidation sites. Hawkins suggested that above the melting point of the polymer no such distinction would exist and the activity of the inorganic antioxidants would be lower than expected.

In the light of earlier comments on the compatibility of antioxidants it is doubtful if the latter part of Hawkin's explanation is completely correct, however, the fact remains that carbon black and the silica/phenol compounds exhibited considerable antioxidant activity in the solid polymer.

The mobility of a stabiliser can probably be considered to have been reduced to its lower limits when the stabiliser functionality is attached to the backbone of the polymer chain. Cain and co-workers (119) have demonstrated that p - phenylenediamine antioxidants, which have been reacted onto the polymer backbone of natural rubber, exhibit similar efficiencies to their equivalent low molecular analogues under test conditions where the loss of antioxidant by volatilisation or migration is not predominant. In test situations where the loss of antioxidant was an important factor, the network bound antioxidants exhibited much higher reactive efficiencies and very little decrease in the stability of the rubber formulations was noted.

However, Cain (120) and other workers (121, 122) demonstrated that various network-bound sulphur antioxidants exhibited very low efficiency and this effect was ascribed (119, 122) to reduced mobility; it will be seen later that this phenomenon may also be associated with the mechanism of action of sulpur antioxidants.

Although good antioxidant efficiency was exhibited by the network-bound amine antioxidants, the antiozonant activity of these materials was poor. Cain (119) points out that these stabilisers cannot migrate to the surface of the rubber, and thus, in accordance with the findings of Lake (89) do not therefore exhibit useful antiozonant efficiency.

The extraction of stabilisers and the concomitant deleterious effects due to the reduction of the concentration of these additives has been mentioned during the discussions of volatility and mobility. The migration of antioxidants between adjacent polymers can be considered as a special example of these more general extraction phenomena. Extraction, however, is usually considered to involve a more aggressive participation from the environment of the stabilised polymer.

Extracting environments vary widely in nature and continue to increase in number as the applications of polymers widen. Two rather different aspects of extraction phenomena have received attention; the contamination of foodstuffs by polymer additives and the more general phenomena associated with the loss of stabilisers from polymers in contact with solvents, water and other media. The former investigations have concentrated primarily on the toxicological aspects of the extraction of stabilisers into foodstuffs and have been concerned with isolated examples of commercial anti-oxidants; little general information on extraction phenomena has been obtained in these investigations.

The deleterious effects of the removal of stabilisers by extractants, in the wider sense, have been recognised for some time, however, the severity of extraction by water has not perhaps been fully appreciated until quite recently. That stabilisers are severely extracted by materials in which they are readily soluble has been pointed out by several workers (67, 78, 123) and extraction has been shown to be further enhanced where the solvent tends to swell the polymer substrate (123).

Although stabilisers in general have very low solubility in water, the contact of stabilised polymers with aqueous media over reasonably short periods of time has been shown to have markedly deleterious effects on stability. Lloyd and Payne (75) and Monsanto Chemicals Ltd. (92) have shown that p - phenylenediamine stabilisers may be lost very rapidly from the rubber of tyre treads in contact with water. These workers noted considerable reductions in the severity of leaching as the length of pendant alkyl chains on the diamines was increased. Grinberg and co-workers (124) have reported similar effects in an examination of p - phenylenediamine stabilisers in various rubbers.

Similar effects of the increasing molecular weight of stabilisers have been reported by Hansen and co-workers (78) in an examination of the extraction of oxanilide metal deactivating agents from polypropylene in contact with mineral oils, plasticised PVC and oil extended rubbers.

Weiner and Connor (125) have examined the dependance of the rates of extraction of various phenolic stabilisers on the thickness of the polymer substrate and the rate of flow of the extractant. The rate of loss of the antioxidants from polypropylene multifilament yarn into water was found to increase as the thickness of the yarn decreased and as the rate of flow of the extractant increased. It will be noticed that these relationships closely parallel those observed in studies of volatility effects. Weiner and Conner also noted a marked reduction in extraction losses as the molecular weight of the antioxidants increased.

Although the molecular weight of a stabiliser and its solubility in the extractant have been shown to be of considerable importance in determining extraction resistance, Latos and Sparks (93) have recently demonstrated the effects of a subtle combination of these phenomena in an examination of the extraction of p - phenylenediamine antioxidants from various rubbers. Although, in two series of N,N' - dialkyl and N - alkyl - N' - aryl derivatives, a general reduction in water extractibility was noticed with increasing molecular weight, the former antioxidants were found to leach faster than the mixed alkyl - aryl derivatives of the same molecular weight; the use of acidified water as the extractant accentuated the differences. It would appear that both the solubility characteristics of the antioxidants, in the aqueous media and the inherently lower mobilities of the antioxidants substituted with the bulkier and less flexible aryl groups may be associated with the differing extractabilities.

1.3 Observations and the Approach to the Present Work.

Over recent years there has been a trend to the use of higher molecular weight antioxidants in polypropylene, based upon the empirical evidence which has been outlined. For example, three industrially important antioxidants for the stabilisation of polypropylene have molecular weights of 542 (Topanol CA; trisphenol; I.C.I. Ltd.), 530 (Irganox 1076; long chain monophenol; Ciba - Geigy Ltd.) and 1176 (Irganox 1010; tetraphenol; Ciba - Geigy Ltd.)

Furthermore, the patent literature indicates that considerable efforts continue to be made to produce still higher molecular weight antioxidants for many polymers. The preparations of polymeric stabilisers are mentioned in this literature together with information on polymers containing bound antioxidant species in their backbones. Little systematic information is available on the activities of these stabiliser systems; however, it is perhaps significant that none appear to have reached industrial importance. A list of patents which discuss polymeric and bound stabilisers is given in the appendix.

The present work has attempted to gain a further insight into the relationships between the molecular weight of antioxidants and their efficiencies in polymers. It was considered desirable to attempt to separate the contributions which the volatility, the compatibility and the mobility of an antioxidant make to its overall performance and to determine whether these physical phenomena make different contributions to the efficiencies of antioxidants which act by the fundamentally different radical scavenging and peroxide decomposing mechanisms.

The investigations involved two series of phenolic antioxidants and a series of thioether antioxidants containing, within each series, the same antioxidant functionality, but differing in molecular weight. The activities of the antioxidants wereinitially determined in a liquid hydrocarbon using a restricted atmospheric environment in an attempt to assess their efficiencies in the absence of any physical constraints. Antioxidant efficiency was then assessed in polypropylene at elevated temperatures under two sets of conditions; evaluations were carried out in a restricted environment in an attempt to suppress volatility effects and in a frequently changing atmosphere where volatilisation would become apparent. In these evaluations it was considered that any compatibility and mobility effects would still exert an influence.

Finally, an attempt was made to separately assess the compatibility of the antioxidants with polypropylene.

It was hoped that comparisons of the results obtained would give some insight into the importance of the constraints which the individual physical phenomena were applying.

2. ANTIOXIDANT ACTIVITY IN DECALIN.

2.1 Experimental approach.

Decalin was chosen as the liquid hydrocarbon substrate; the structure of this material, although not a direct model of polypropylene, does contain the tertiary hydrogen functionality associated with the polymer which was to be used in subsequent work.

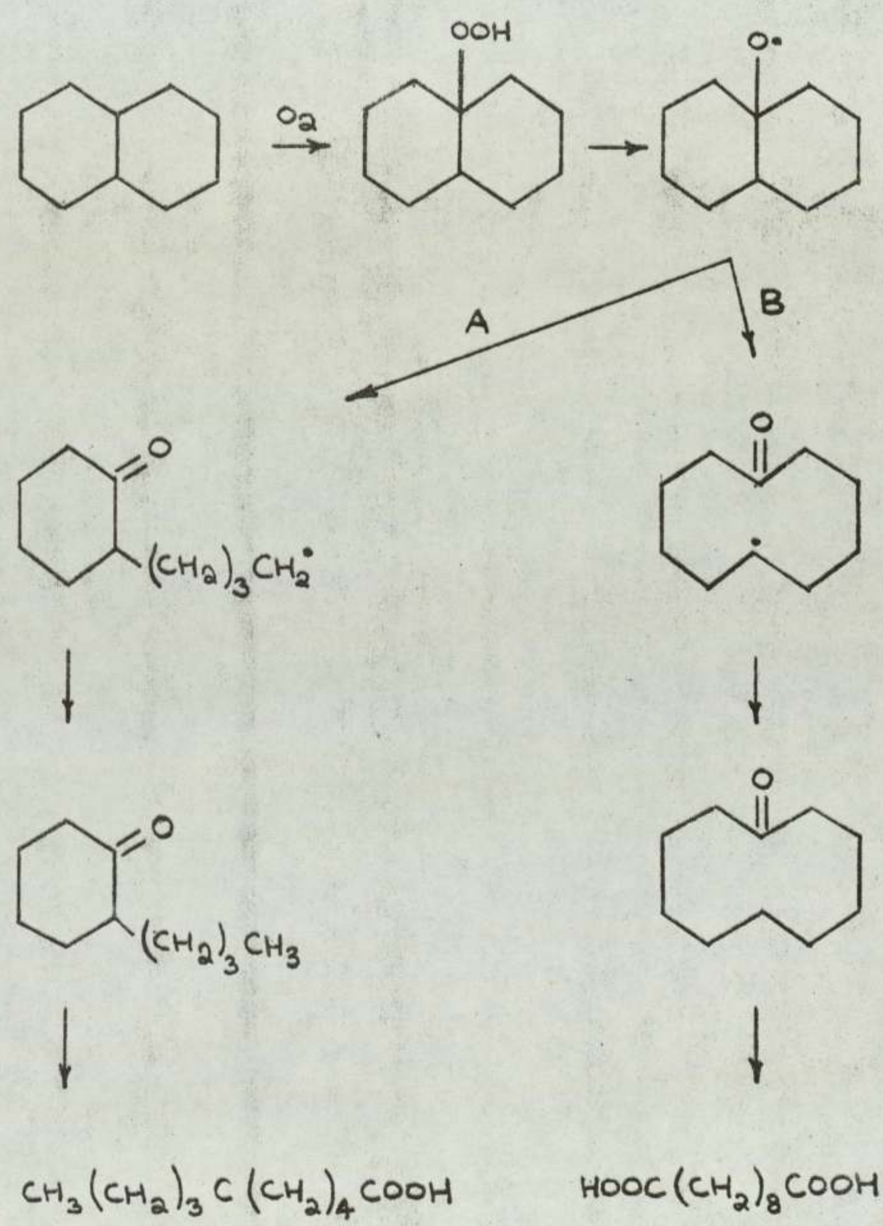
Furthermore, the aliphatic structure of decalin has advantages over other common model compounds, such as cumene or tetralin, in that no phenolic products can form during autoxidation. Thus the confusion caused by adventitious synergism, which may have arisen during studies of sulphur antioxidants, was avoided.

Although the autoxidation of cumene and tetralin has been examined quite extensively in the past, decalin has received rather less attention (126-135). Holmquist and coworkers (136) suggested that at 120°C-130°C the oxidation of decalin could follow the routes shown in Figure 2.1. Route A appeared to be favoured as 2-n-butylcyclohexanone and 6-oxodecanoic acid were found, together with the further oxidation products, adipic and butyric acids.

Decalin exists, of course, in cis and trans isomeric forms and Jaffe and coworkers (137) have demonstrated that the oxidation of decalin is stereodependent, the cis isomer oxidising about four times as fast as the trans isomer. Their work indicates that Holmquist's picture is not complete in that oxidative attack seemed to occur at the 1 and 2 positions as well as at the bridging carbon.

FIG. 2.1.

OXIDATION OF DECALIN (REF. 126)



However, phenolic products can clearly not be formed. Because of the problems that any variation in the cis/trans decalin content would produce in evaluations of antioxidant efficiency, it was considered of major importance that all work should be carried out on one batch of the purified hydrocarbon substrate.

It was envisaged that antioxidant activity should be measured under conditions of accelerated oxidation at elevated temperature (close to Holmquist's temperature range, in fact) using the induction period to the onset of catastrophic autoxidation as an indication of antioxidant efficiency (138). In particular, it was thought desirable to use easily handleable quantities of the hydrocarbon substrate and, at the same time, be able to follow the oxidative reaction well past the time at which the maximum linear rate of oxidation had been reached (138), thus allowing an accurate assessment of the cessation of antioxidant activity (139). As the measurement of induction periods is time consuming it was considered essential that the experimental equipment should be automated.

2.2 Oxygen absorption apparatus.

Schematic diagrams of the equipment are shown in Figures 2.2 and 2.3; after an initial period of experimentation, four identical systems were constructed.

The oxidation vessel consisted of a 50ml three-necked flask; this vessel was immersed in a Gallenkamp constant temperature bath containing silicone fluid. The oxygen absorption bulb

FIG. 2.2.

OXYGEN ABSORPTION APPARATUS.

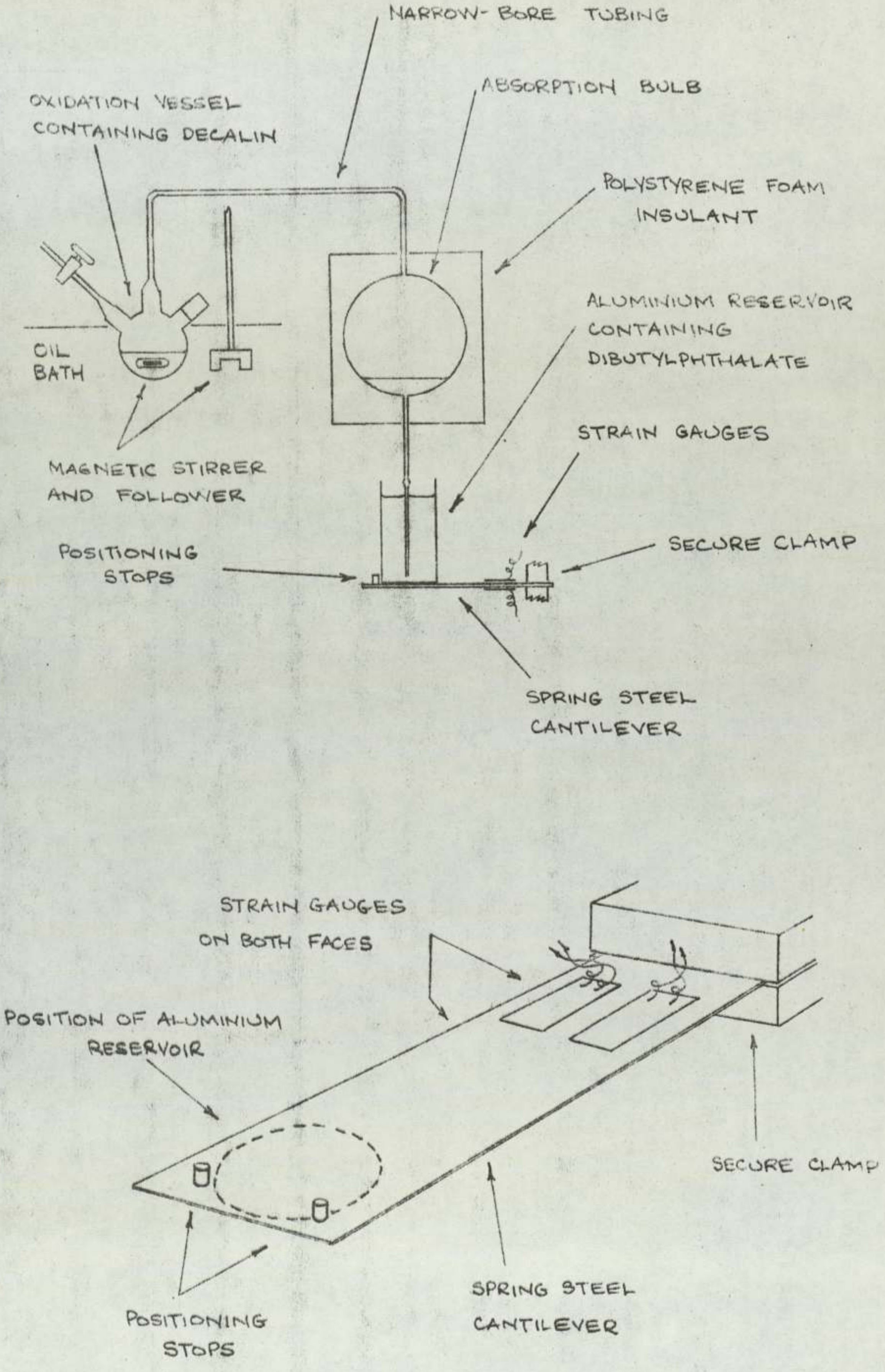
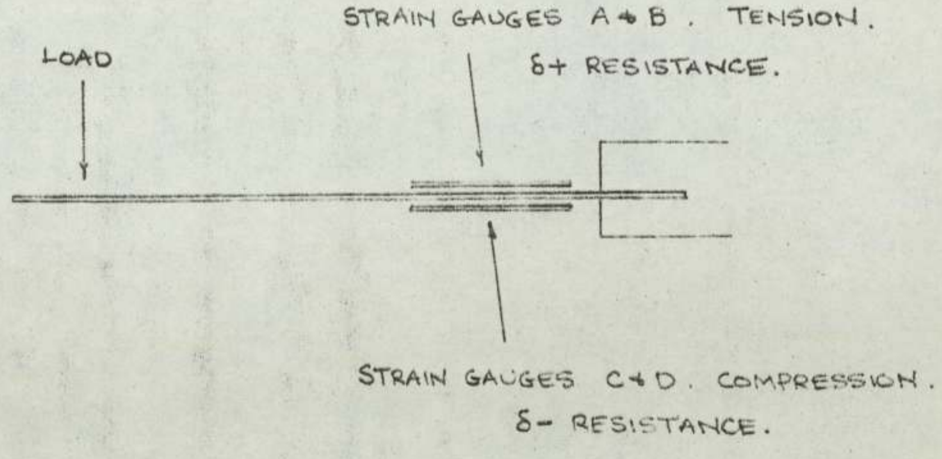
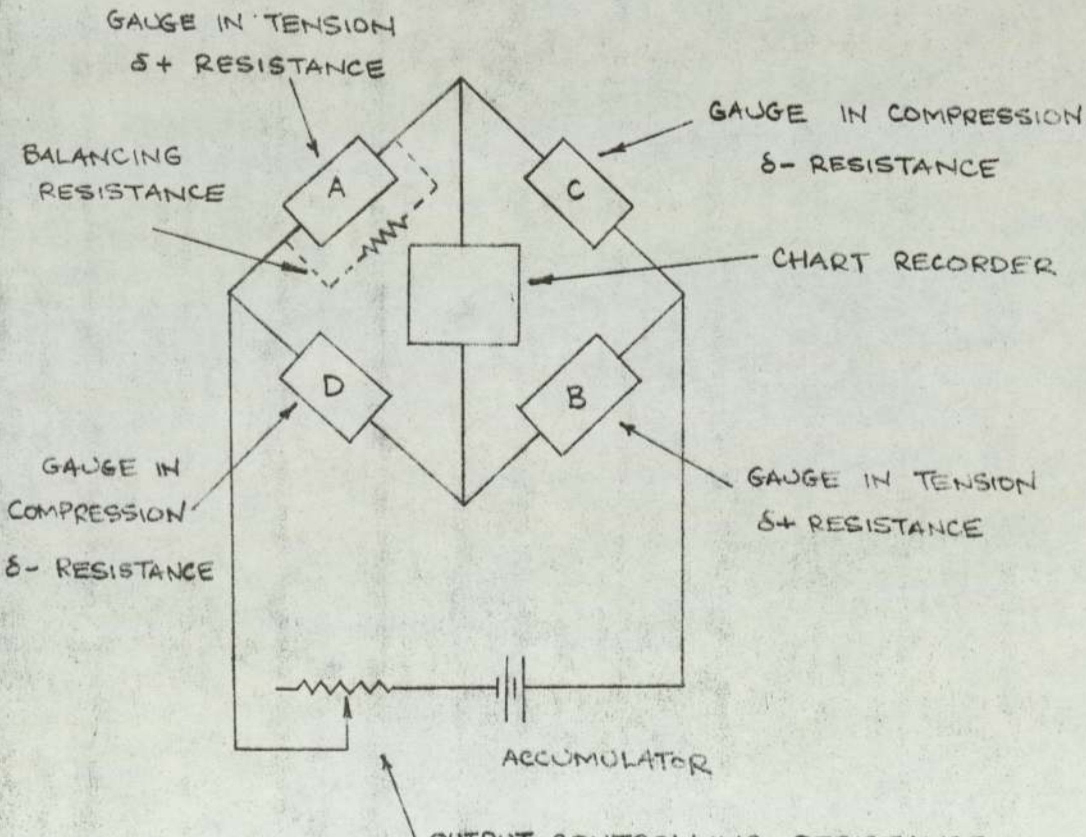


FIG. 2.3.

OXYGEN ABSORPTION APPARATUS





had a volume of 250 ml and was lagged with a bulky layer of polystyrene foam to reduce the effects of gas expansion caused by fluctuations in the room temperature. All tube connections fitted to both the reaction vessel and the absorption bulb were made with glass capillary tubing (internal diameter, 2mm) in order to reduce to a minimum the volume of the apparatus that was not lagged.

Dibutylphthalate, having both low volatility and low oxidative reactivity, was used as the indicator fluid.

The absorption of oxygen by the oxidising decalin caused dibutylphthalate to be withdrawn from the aluminium reservoir into the absorption bulb. This transfer of indicator fluid was followed by an indirect measurement of the weight loss from the reservoir using an electrical strain gauge system on a steel cantilever. An aluminium reservoir was used so that the non-variable static load on the measuring device was kept to a minimum. The reservoir contained 200 ml dibutylphthalate.

The monitoring system consisted of a spring steel plate measuring, 20 cm x 4 cm and 0.7 mm (28 thou") in thickness, fitted with Philips PR9810 strain gauges at approximately 5 cm from one end. Two gauges were spaced equally across each face of the steel plate in directly opposite positions. The gauges were cemented with Araldite epoxy adhesive following the instructions provided by Philips.

Stops were fitted to the other end of the plate to facilitate the reproducible positioning of the aluminium reservoir. The plate was firmly clamped across its full width between sturdy steel bars and these were attached firmly to the bench.

The strain gauges were wired into a bridge system powered by lead/acid accumulators and the output from the bridge was taken to a Leeds and Northrup multichannel recorder. The four oxygen absorption systems were wired into separate channels of this recorder.

2.3 Operating adjustments and calibration.

Various parameters were capable of adjustment in order to obtain the most sensitive, reproducible and convenient detection of weight loss from the reservoir. The parameters, together with the most favourable operating conditions are listed below; the adjustments varied slightly between the four sets of equipment of course:- the free length of the cantilever between the clamp and the centre of the strain gauges (4 cm); the distance between the clamp and the centre of the reservoir (12 cm); the voltage range on the recorder (0-1 millivolts).

Two further adjustments were necessary; in order to obtain a correct electrical balance on the bridge it was always found necessary to wire a high resistance in parallel with one of the strain gauges. The resistance of each gauge was never precisely the same (Philips specify 596 ohms±0.5%) and to obtain zero balance on the recorder a 1 megohm variable resistance was placed across each gauge in turn and adjusted until balance was found. To accommodate any overall minor variations in the output to the recorder from each of the four bridge systems, a small variable resistance was placed in series with the accumulator. All four bridges were powered from the same accumulator. The calibration procedure enabled a direct reading of the weight of indicator fluid remaining in the reservoir (and hence ultimately the volume of oxygen absorbed during an oxidation reaction) to be related to the deflection of the chart recorder. By adjustment of the mechanical and electrical parameters mentioned above together with the polarity of the electrical bridge, it was arranged that when the reservoir contained respectively 200 ml dibutylphthalate (zero oxygen absorption) and no dibutylphthalate (200 ml oxygen absorption), the recorder produced readings of 10 and 90 on a 0 to 100 scale. Thus 80 scale units corresponded directly to a total oxygen absorption of 200 ml. The system was adjusted to produce 'zero' and 'maximum' on scale readings of 10 and 90 rather than 0 and 100 so that any recording drift could be readily detected and corrected.

Intermediate calibrations were made by simply noting the recorder deflection when the reservoir contained quantities of dibutylphthalate between 0 and 200 ml; the indicator fluid was pipetted into the reservoir in 25 ml aliquots.

The apparatus was found to be remarkably sensitive and was capable of detecting changes corresponding to less than 1 ml oxygen absorption (less than 0.5 scale divisions on the recorder).

The linearity of the calibration graph (Figure 2.4) was

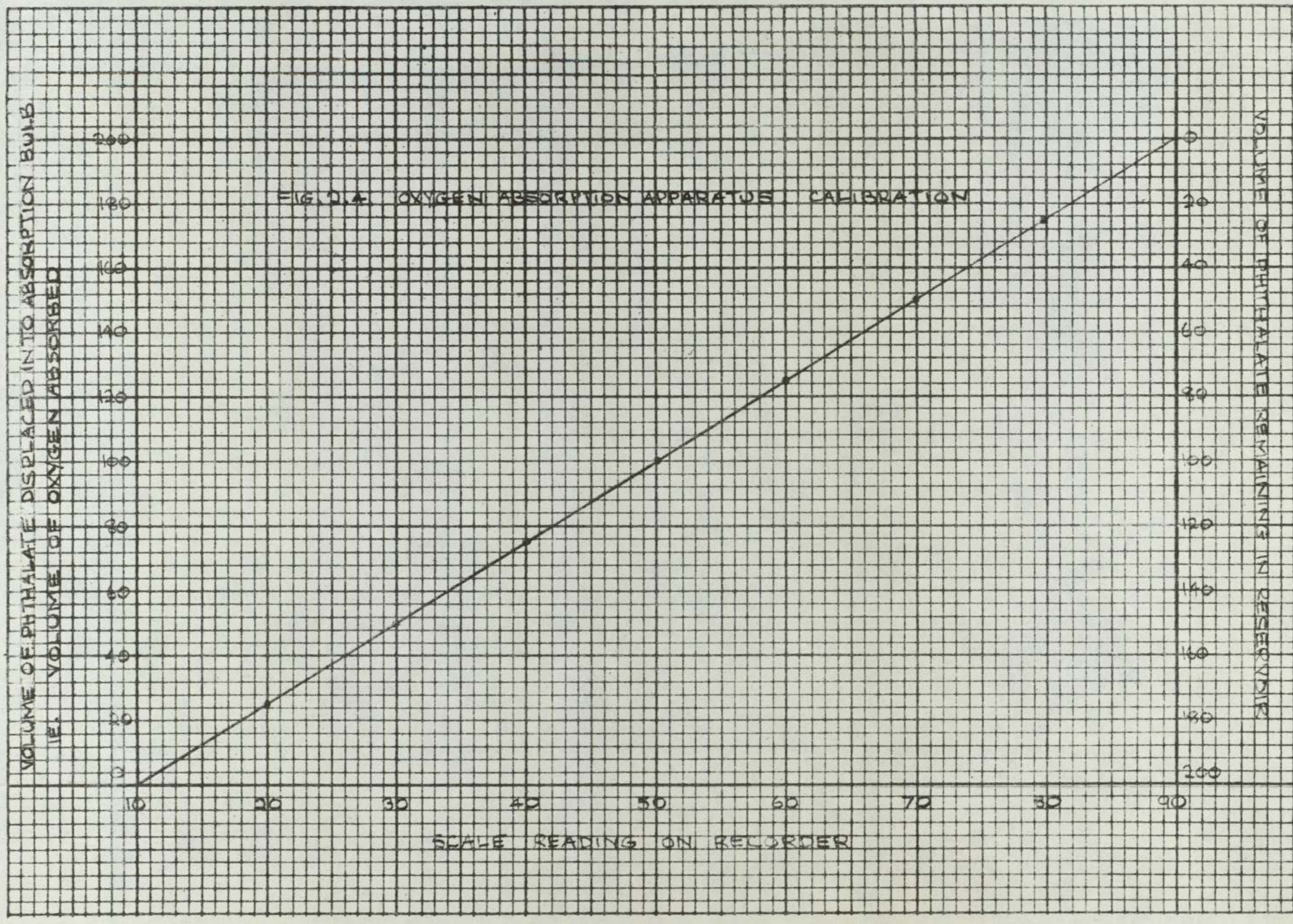


FIG. 2.4 OXYGEN ABSORPTION APPARATUS CALIBRATION

better than this limit of sensitivity; a deviation from linearity outside this limit, at the midpoint of the calibration graph, could not be detected on any of the four rigs.

2.4 Use of the apparatus to monitor the oxidation of decalin.

Before the start of an oxidation run the glass apparatus was dismantled, washed throughout with reagent grade acetone and dried by purging with compressed air. During reassembly the ground glass joints on the oxidation flask and the key of the side-arm tap were lightly lubricated with Apiezon T grease to provide a gas-tight seal. The joints and the tap were clamped with springs. 5 ml decalin was pipetted into the flask through the third neck and a glass magnetic follower was dropped in; the neck was then closed with a greased and clamped stopper. The flask was wrapped in aluminium foil to prevent the ingress of light.

A line from an oxygen cylinder was attached to the side-arm of the flask and oxygen was purged through the system; the decalin was stirred during this operation. The progress of the gas purge was followed by placing a small beaker of dibutylphthalate under the inlet tube to the absorption bulb and, in general, the purge was continued until approximately 4 or 5 complete changes of the atmosphere in the apparatus had occurred (ie in excess of 1500 ml oxygen had been purged). The tap on the side-arm was then closed.

200 ml dibutylphthalate were placed in the absorption reservoir and the correct operation of the bridge system was verified by noting an exact scale reading of 90 on the recorder.

Oxidation experiments were carried out at 120°C and 140°C and the Gallenkamp bath was found to be capable of achieving a temperature control of better than ±0.2°C at these temperatures when MS220 silicone fluid (Midland Silicones Ltd) was used as the heat transfer medium. The oxidation flask was then moved into position in the oil bath and the absorption bulb inlet was placed in the dibutylphthalate reservoir. The start of an experiment was marked on the recorder paper.

It was found that the induction periods of oxidation which were studied could be conveniently measured using a chart speed of 2 inches/hour. The accuracy of the chart speed was checked over a 50 hour period and was found to be a few minutes slow; this constant inaccuracy was neglected, the same recorder was used for all experiments.

Using the apparatus and technique described above it was considered possible to continuously monitor quite large volume absorptions of oxygen with very little variation from atmospheric pressure in the system. The maximum head of indicator fluid was less than 20 cms, lower than the possible daily variation in atmospheric pressure.

2.5 Purification of decalin and preparation of stabilised decalin solutions.

The hydrocarbon was purified using a method similar to that employed by Tipper (140) in his studies of the decomposition of decalin hydroperoxide.

Technical grade decalin (BDH Ltd) was found to be pale yellow as supplied. 2 litres of this material was distilled under vacuum of 40°C (approximately 1 mm Hg) in a nitrogen purged flask and a centre-cut fraction (approximately 90%) was taken.

The decalin was shaken with several 200 ml portions of 10% sulphuric acid until little darkening occurred in either the aqueous or organic phase. The hydrocarbon was then washed several times with 100 ml portions of water, 10% sodium hydroxide and water again and was then dried over calcium sulphate.

The decalin was redistilled under vacuum (40°C, 1 mm Hg) in apparatus which again had been purged with nitrogen; a slow nitrogen purge was continued during distillation. A 90% centre-cut was again taken. This single batch of material was used for all subsequent work.

The hydrocarbon was stored under nitrogen, in a flask wrapped with aluminium foil, at -15°C, in a refrigerator and the flask was always repurged with nitrogen after a decalin sample had been withdrawn.

The antioxidants were added to the decalin on a weight/volume basis. In general, 20 ml or 50ml stabilised hydrocarbon was prepared. Antioxidant was weighed into a 5 ml phial and a small quantity of decalin was added to dissolve the stabiliser. The solution was transferred to a graduated flask; remaining solution was washed into the flask and the the solution was made up to the mark. These solutions were stored under nitrogen in the refrigerator.

Occasionally it was found difficult to prepare satisfactory solutions due to the low solubility of an antioxidant at room temperature. In these circumstances the required amount of antioxidant was added directly to 5 ml decalin in the oxidation flask before the start of the experiment.

A series of evaluations was carried out using sulphur dioxide as the additive. As the volume of sulphur dioxide, that it was required to dispense was small (0.0224ml), the gas was diluted with oxygen before addition to the reaction vessel. A two necked flask of 5550 ml total volume was flushed with oxygen and sealed with serum caps. 24.82 ml sulphur dioxide was then injected with a gas syringe. 5 ml of this gas mixture contained the required quantity of sulphur dioxide and could readily be dispensed using a gas syringe.

The oxidation apparatus, containing unstabilised decalin was purged with oxygen in the normal way and a small quantity of dibutylphthalate was then drawn into the absorbtion bulb, from the reservoir, using a rubber teat attached to the side-arm of the oxidation flask. The tap was closed and the side-arm was further sealed with a serum cap. The tap was then re-opened and 5 ml sulphur dioxide/oxygen mixture was injected through the serum cap and tap,into the flask,without any loss of gas occurring. The oxidation flask was then moved into position in the oil bath and gas expansion returned the majority of the indicator fluid to the reservoir, again without any loss of gas. Finally, when thermal equilibrium had been established, the serum cap was removed and the side-arm tap was rapidly opened and shut to return the marker fluid to its zero position.

2.6 Antioxidants studied.

Figures 2.5 and 2.6 show the antioxidants that were examined.

The antioxidant samples which were supplied by Imperial Chemical Industries Ltd and J R Geigy SA were of research purity and were recrystallised from either petroleum ether or ethanol without change in melting point.

The phenol substituted hexyl and lauryl propionates (HPP and LPP) were prepared by the transesterification of the methyl ester with equimolar quantities of the higher alcohol using sodium methoxide as catalyst. The products were recrystallised several times from ethanol at low temperature.

The methyl and hexyl thiodipropionates (DMTP and DHTP) were prepared by the acid catalysed (sulphuric acid) esterification of thiodipropionic acid (Robinson Brothers Ltd) using an excess of the alcohol. The products were purified by vacuum distillation.

The structures of the materials prpared in the laboratory were verified by IR and NMR spectroscopy and elemental analysis.

The methylene bridged polyphenols were supplied by W W Wright and G J Knight of the Royal Aircraft Establishment, Farnborough. Details of the preparations have been published (141).

FIG. 2.5 PHENOLIC ANTIOXIDANTS STUDIED

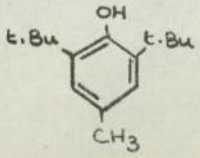
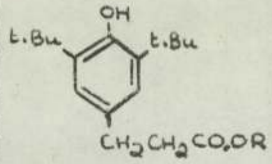
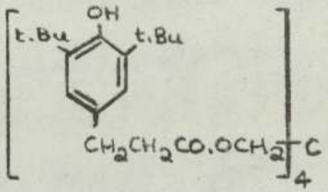
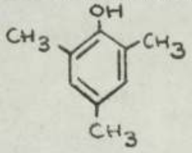
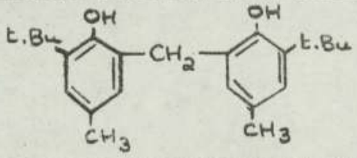
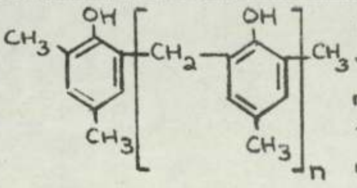
ANTIOXIDANT		ORIGIN	Mp °C	n_D^{20}	MOL. WT	CODE
		ICI	69-70		220	BHT
	R=CH_3	GEIGY	67-68		292	MPP
	R=C_6H_{13}	LAB	≈10	1.4976	362	HPP
	R=$C_{12}H_{25}$	LAB	≈15	1.4917	446	LPP
	R=$C_{18}H_{37}$	GEIGY	51-52		530	SPP
		GEIGY	121-122		1176	4PP
		RAE	71-72		136	MHT
		ICI	119-120		340	2246
	n=1	RAE	144-146		256	MB2P
	n=2	RAE	109-112		376	MB3P
	n=4	RAE	152-154		616	MB5P

FIG. 2.6 SULPHUR ANTIOXIDANTS STUDIED

ANTIOXIDANT		ORIGIN	B.p °C	M.p °C	n_D^{20}	MOL. WT	CODE
$S(CH_2CH_2CO.OR)_2$	$R=CH_3$	LAB	138-140 at 5 mm		1.4753	206	DMTP
	$R=C_6H_{13}$	LAB	184-186 at 0.05mm		1.4644	346	DHTP
	$R=C_{12}H_{25}$	ICI		41-42		514	DLTP
	$R=C_{18}H_{37}$	ICI		57-58		682	DSTP

2.7 Initial studies on unstabilised decalin - Results.

Preliminary experiments showed that reproducible oxidation characteristics could not be obtained with new apparatus, in particular with new oxidation flasks and magnetic followers. Successive oxidations carried out in new flasks tended to exhibit a generally declining rate of oxidation; after several experiments the oxidation behaviour tended to settle down. It was concluded that there was some involvement of active sites,on the glass surface of the oxidation vessels,which tended to initiate or catalyse the oxidative reaction; these sites appeared to be removed or destroyed during early oxidations. Irreproducible behaviour of this type, in studies of liquid phase oxidation, has been noted by several workers (142-144).

In subsequent work all flasks and stirrers were 'aged' by oxidising decalin in them for an extended period (usually 24 hours) and repeating this process twice with the usual interim acetone wash.

Two other factors were suspected of causing irreproducibility, the rate of stirring and the ingress of light. It was found that if the stirring rate was fast enough to produce a deep vortex in the oxidising decalin and thereby break the surface into bubbles, the oxidation characteristics were not controlled by the diffusion of oxygen into the sample of hydrocarbon.

Any possible extraneous catalysis of oxidation by light was eliminated by completely enclosing the oxidation vessels in aluminium foil.

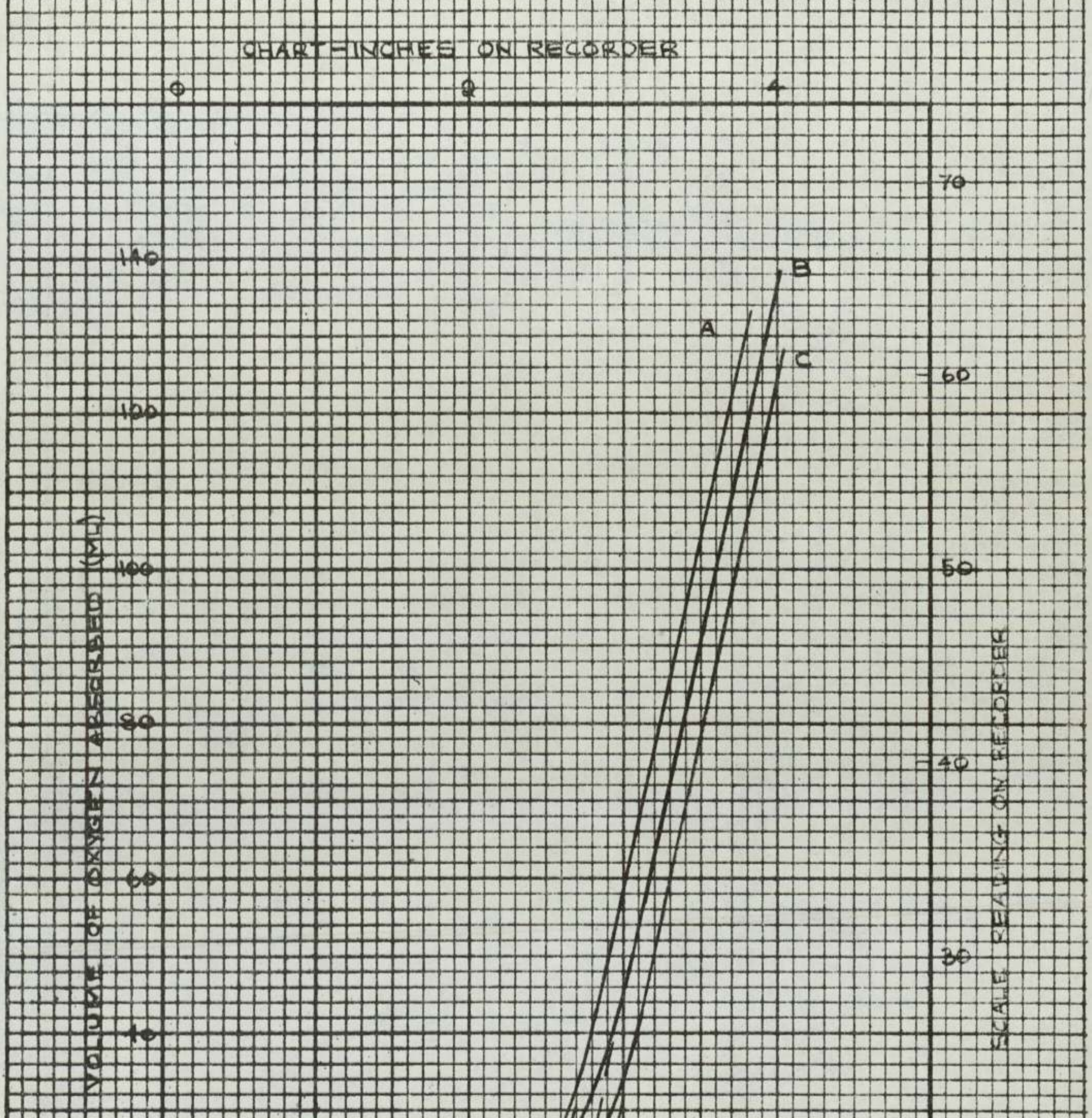
Figure 2.7 shows the results of a series of oxygen absorption experiments at 140°C, in different sets of apparatus, after the oxidation flasks had been fully 'aged'.

It was found that the absorption of oxygen commenced about 20 minutes from the time when the oxidation flask was placed in the oil bath. Part of this initial period was required for the thermal equilibration of the system; this was considered to have occurred when the expansion of oxygen, through the dibutylphthalate reservoir, ceased. As the equilibration time obviously remained the same throughout all the subsequent work, this period was considered to be part of the induction period. The latter was expressed as the intercept of the line of maximum oxidation rate on the time axis (ie at zero oxygen absorption). Curves A, B and C demonstrate the minimum, average and maximum induction periods that were noted during an extended series of trial runs; the induction period for the decalin sample was thus considered to be 1.26±0.08 hours, a reproducibility of ± 6.3%.

The oxidation of 5 ml decalin appeared to reach a maximum linear rate after approximately 40 ml-50 ml of oxygen had been absorbed (0.055 mole-0.070 mole oxygen/mole decalin approximately) and this linear rate was maintained to the limit of the detection system (200 ml, 0.280 mole oxygen/mole decalin).

The linear rate varied between 92.0 ml-95.0 ml/hour for 5 ml decalin (0.129 mole-0.133 mole oxygen/mole decalin/

FIG. 2.7 OXIDATION OF UNSTABILISED DECAL N. 140°C



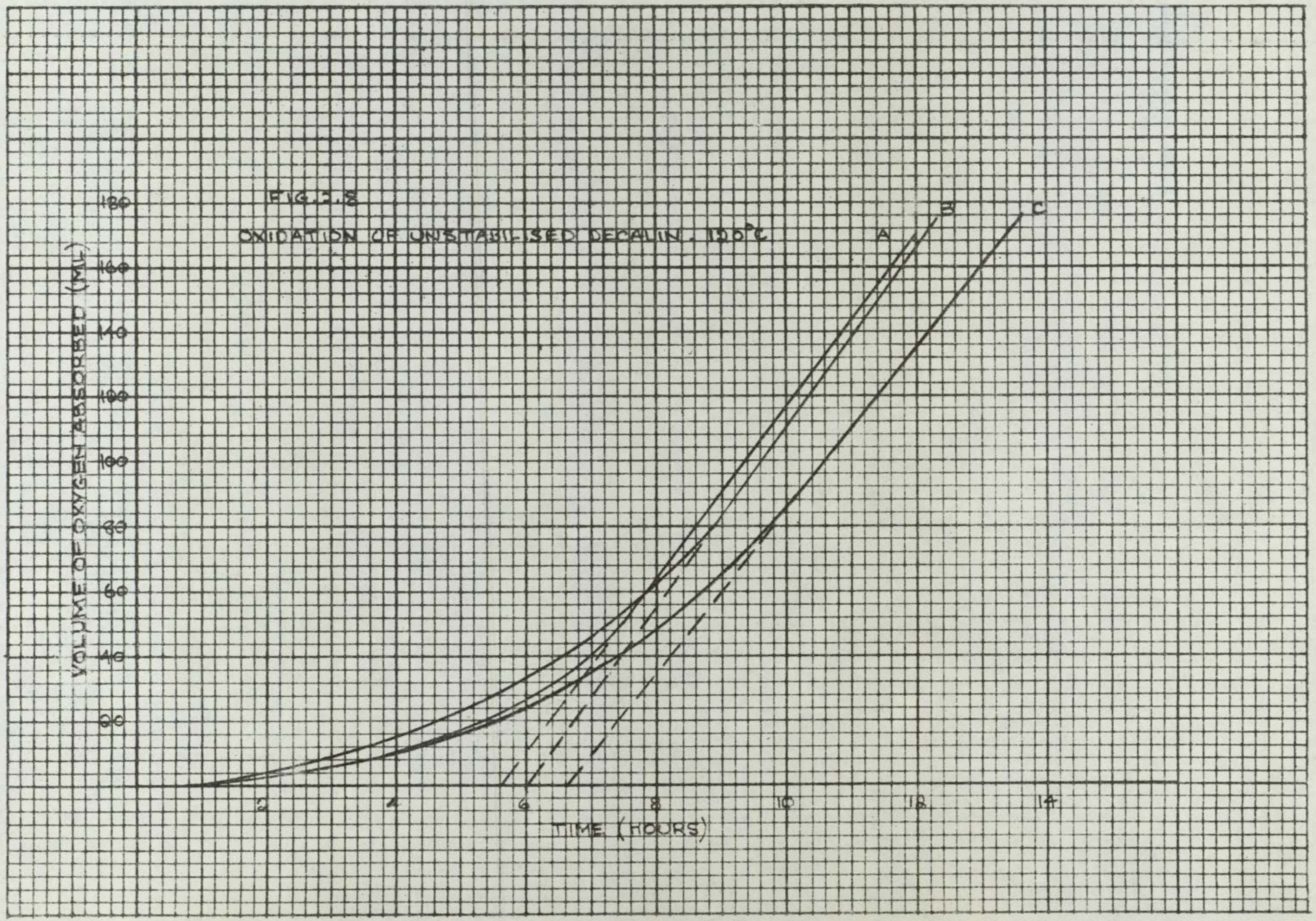


FIG.2.8

OXIDATION OF UNSTABILISED DECALIN, 120°C hour); there appeared to be no simple relationship between the final rates of oxidation and the length of the induction periods. The reproducibility of the oxidation rate determinations was remarkably good, the accuracy with which the recorder chart could be read probably being the most significant of the errors which totalled less than ±1.5%.

The oxidation of decalin was also examined at 120°C (Figure 2.8). Again curves A, B and C demonstrate the minimum, average and maximum induction periods that were noted; the induction period at 120°C was considered to be 6.3 ± 0.5 hours, a limit of accuracy of ±7.9%.

The oxidation appeared to reach a maximum linear rate after approximately 100 ml oxygen had been absorbed (0.14 mole oxygen/mole decalin) and this rate varied between 25.0 ml-28.0 ml/hour (0.035 mole-0.039 mole oxygen/mole decalin/hour), the overall error being ±6.0%.

2.8 Studies of antioxidant activity - Results.

2.8.1 Propionate-substituted phenols and BHT.

Throughout this and all subsequent work the concentrations of the antioxidants which were studied were based upon a molar addition of the active antioxidant functionality.

Figures 2.9, 2.10 and 2.11 show the activity of the series of propionate-substituted phenol (PP) antioxidants at concentrations of 2×10^{-4} mole (ØOH) and 2×10^{-3} mole (ØOH)/100 ml decalin. In comparison with BHT all the

Fig. 2.9 ACTIVITY OF PP SERIES OF ANTIOXIDANTS. DECALIN, 140°C

Antioxidant	Concentration in Decalin		Induction Period (hours)		Linear Oxidation Rate (ml/hour) 5 ml decalin	
	Moles/100 ml	gm/100 ml	Result	Average	Result	Average
BHT	$2x10^{-4}$	0.0440	11.50 11.90 11.50	11.60	105.0 102.5 102.5	103.3
MPP	$2x10^{-4}$	0.0584	7.10 7.70	7.40	107.5 100.0	103.7
HPP	$2x10^{-4}$	0.0724	7.85 7.25 7.55	7.55	105.0 95.0 112.5	104.1
LPP	$2x10^{-4}$	0.0892	6.75 6.25 7.00	6.66	107.5 95.0 100.0	100.8
SPP	$2x10^{-4}$	0.1060	6.90 6.65	6.77	112.5 95.0	103.7
4PP	$5x10^{-5}$	0.0588	8.40 9.55	8.97	102.5 105.0	103.7

Fig. 2.10 ACTIVITY OF PP SERIES OF ANTIOXIDANTS. DECALIN. 140°C.

Antioxidant	Concentration in Decalin		Induction Period (hours)		Linear Oxidation Rate (ml/hour) 5 ml decalin	
	Moles/100 ml	gm/100 ml	Result	Average	Result	Average
BHT	$2x10^{-3}$	0.440	156.35 145.20	150.77	70.0 72.5	71.1
MPP	$2x10^{-3}$	0.584	25.50 28.55 26.30	26.78	87.5 92.5 90.0	90.0
HPP	$2x10^{-3}$	0.724	23.70 25.25 23.00	23.98	87.5 90.0 95.0	90.8
LPP	$2x10^{-3}$	0.892	22.55 22.70 19.90	21.72	87.5 90.0 87.5	88.3
SPP	$2x10^{-3}$	1.060	18.55 17.45	18.00	90.0 92.5	91.1
4PP	$5x10^{-4}$	0.588•	35.45 30.15	32.80	85.0 90.0	87.5

• Not fully soluble cold, but soluble at 140°C. 0.0294 gm added directly to 5 ml decalin in flask.

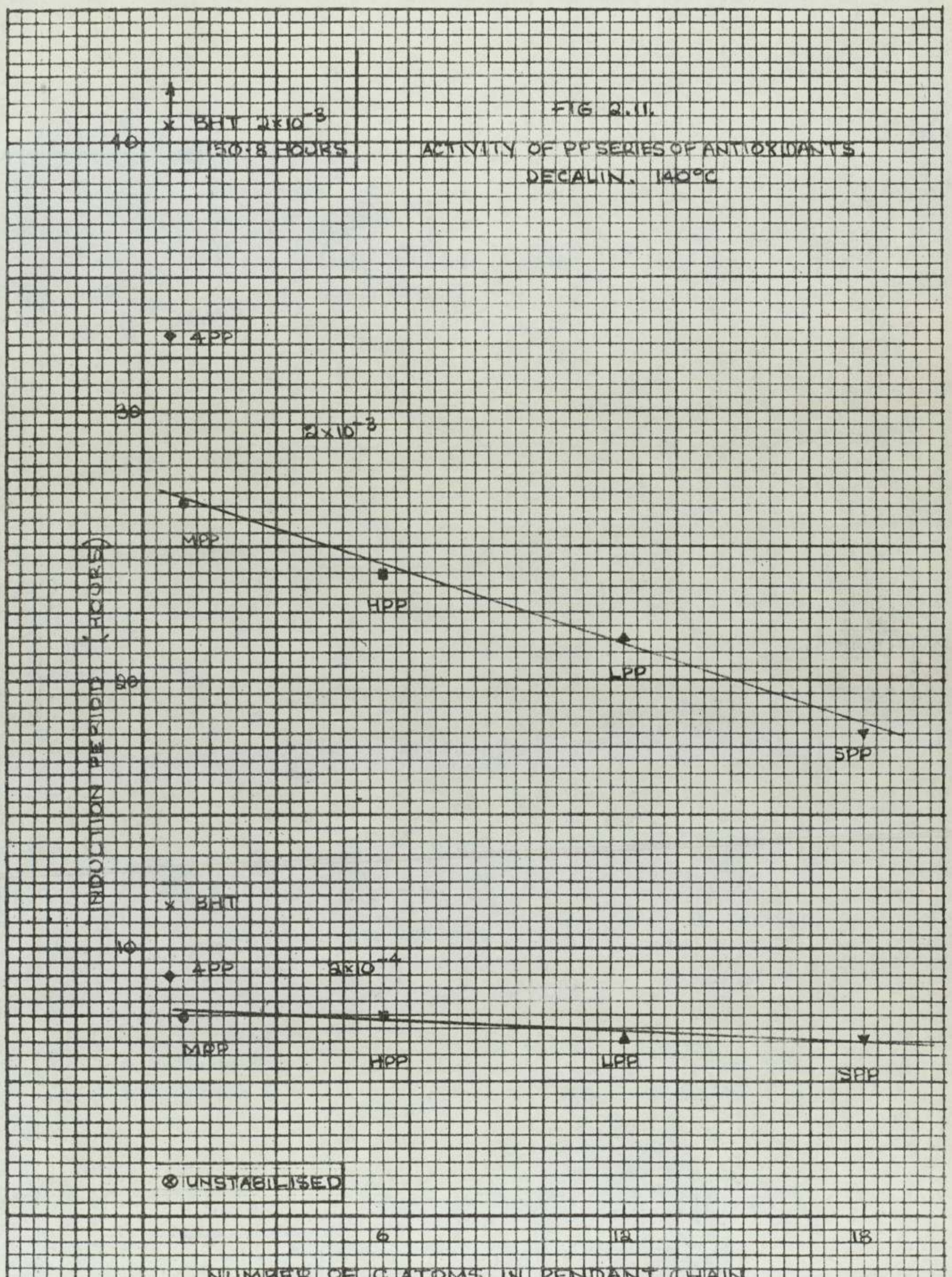


FIG 2.11.

ACTIVITY OF PP SERIES OF ANTIOXIDANTS. DECALIN. 140°C

PP antioxidants exhibit a stabilising efficiency of the same order; there is, however, a marginal decrease in activity as the length of the pendant ester chain increases, this being rather more marked at the higher concentration. The tetra-phenol based upon pentaerythritol (4PP) shows slightly higher efficiencies at both concentrations.

The reason for these variations and for the marked difference in activity between the PP antioxidants and BHT must be involved with the nature of the para-phenolic substituent.

Direct oxidative reactions on the pendant ester chain of the PP antioxidants would not be expected to increase the oxidative susceptibility of the total decalin/stabiliser system as the length of the ester chain increased. The primary and secondary hydrogen structure of the side chains should be considerably more stable to oxidation than the tertiary structure of the decalin substrate.

Furthermore it is difficult to foresee that the electronic interaction of side chains so remote from the phenolic ring could in any way influence the radical-trapping capabilities of the phenolic species (139).

However, it is known that phenolic antioxidants can terminate more than one oxidative kinetic chain by reaction with peroxy radicals at both the phenolic hydroxyl and the 4-position of the phenolic ring, the former reaction involving hydrogen abstraction and the latter an addition of the peroxy radical to the ring (145). An increase in the length of the ester chain in the PP antioxidants may increase the steric hindrance to the peroxy radical reaction at the 4-position, thereby reducing the overall efficiency of the higher homologues. The higher activity of BHT, which is particularly noticeable at the higher concentration, lends some weight to this possibility, although direct comparisons cannot be drawn due to the variation in the electronic affects associated with the different structures (139). However, the activity of the pentaerythritol analogue (4PP) does not coincide with this interpretation. The higher efficiency of antioxidant 4PP is in disagreement with Neiman's suggestion (146) that polyfunctional stabilisers are generally less effective than their corresponding monofunctional analogue at equivalent molar concentrations. The specific structure of the antioxidants under consideration must be of importance and it would appear that general conclusions on this type cannot be drawn.

A comparison of the activities of the PP antioxidants and BHT at the two concentrations is interesting (Figure 2.12). There is clearly a marked difference in behaviour, between the PP antioxidants and BHT, involving reactions which are in some way dependent upon the antioxidant concentration, the indications being that antioxidant/antioxidant reactions are playing a part.

Here again, reactions at the 4-position may be of importance. It is known (145) that, following the initial reaction with peroxy radicals at the phenolic hydroxyl, BHT can undergo dimerisation reactions at the 4-methyl group to produce further active antioxidant species. However, if this type

FIG. 2.12 ACTIVITY OF PP SERIES OF ANTIOXIDANTS. DECALIN. 140°C.

$$\frac{\text{Induction Period at } 2\text{x}10^{-3} \text{ moles } (\phi\text{OH})/100 \text{ ml}}{\text{Induction Period at } 2\text{x}10^{-4} \text{ moles } (\phi\text{OH})/100 \text{ ml}}$$

ANTIOXIDANT	RATIO OF INDUCTION PERIODS (140°C)
MPP	3.62
HPP	3.18
LPP	3.26
SPP	2.66
4PP	3.66
BHT	13.00

of reaction does not proceed so readily in the PP antioxidants, these subsequent antioxidant species may not be formed.

The progress of the dimerisation reactions could be expected to be controlled to some extent by the initial concentration of the antioxidants. Thus the differing behaviour of BHT and the PP antioxidants, at the two concentrations, may well be related to the ease with which further antioxidant species are formed following the initial scavenging reaction.

The behaviour of the 4PP antioxidant, once again, does not fully coincide with this interpretation, however.

The final rates of oxidation do not appear to conform to any significant pattern at either concentration, with the exception of BHT which, at the higher concentration, does show a lower final rate.

At the lower concentration the oxidation rates in individual experiments fall in the range 95.0 ml-112.5 ml oxygen/5 ml decalin/hour (0.133 mole-0.157 mole oxygen/mole decalin/hour), rather higher than those which were noted with pure decalin (0.129 mole-0.133 mole oxygen/mole decalin/hour).

At the higher concentration,the oxidation rates for the PP antioxidants fall in the range 85.0 ml-95.0 ml oxygen/5 ml decalin/hour (0.119 mole-0.133 mole oxygen/mole decalin/hour), somewhat lower than those of pure decalin. BHT, however, exhibits a considerably lower average rate (0.099 mole oxygen/mole decalin/hour).

Thus, at the lower concentration the products from the expended antioxidants appear to slightly accelerate the final rate of decalin oxidation whereas at the higher concentration the reverse effect pertains, particularly in the case of BHT.

Again, this concentration dependence may indicate the involvement of antioxidant/antioxidant reactions during the inhibition period. The lower oxidation rate of the BHT system argues for the presence of residual species with minor antioxidant activity and this behaviour may again be linked with the availability of the 4-methyl group for dimerisation or other reactions.

2.8.2 Thiodipropionates and sulphur dioxide.

Preliminary studies on distearylthiodipropionate demonstrated the considerably higher activity of this antioxidant in comparison with the previous phenolic antioxidants at a 2×10^{-4} mole concentration of the active functionality. The evaluation detailed in Figures 2.13 and 2.14 was carried out to determine the concentration of antioxidant which would give the most conveniently measurable induction periods.

The marked change in antioxidant activity in the concentration range 6×10^{-5} mole-8×10^{-5} mole antioxidant/100 ml decalin must be associated with a fundamental change in the mechanism of the antioxidant reactions. Kennerly and Patterson (147) have noticed a similar effect and have suggested that breakdown products (thiyl radicals) of the sulphur antioxidant cause the catalytic decomposition of hydroperoxides. The

Fig. 2.13 ACTIVITY OF DSTP. DECALIN. 140°C

Antioxidant	Concentration in Decalin		Induction Period (hours)	Linear Oxidation Rate (ml/hour) 5ml decalin
	Moles/100ml	gm/100 ml		
DSTP	$2x10^{-5}$	0.0140	2.90 3.20	97.5 95.0
	$5x10^{-5}$	0.0340	6.75 7.30	85.0 87.5
	$6.5x10^{-5}$	0.0440	41.5 13.4	67.5 62.5
	$8x10^{-5}$	0.0565	95.9 153.8	82.5 75.0
	$1x10^{-4}$	0.0682	>180	-
	$2x10^{-4}$	0.1364	>180	-
BHT	$2x10^{-5}$	0.0044	3.1	110.0

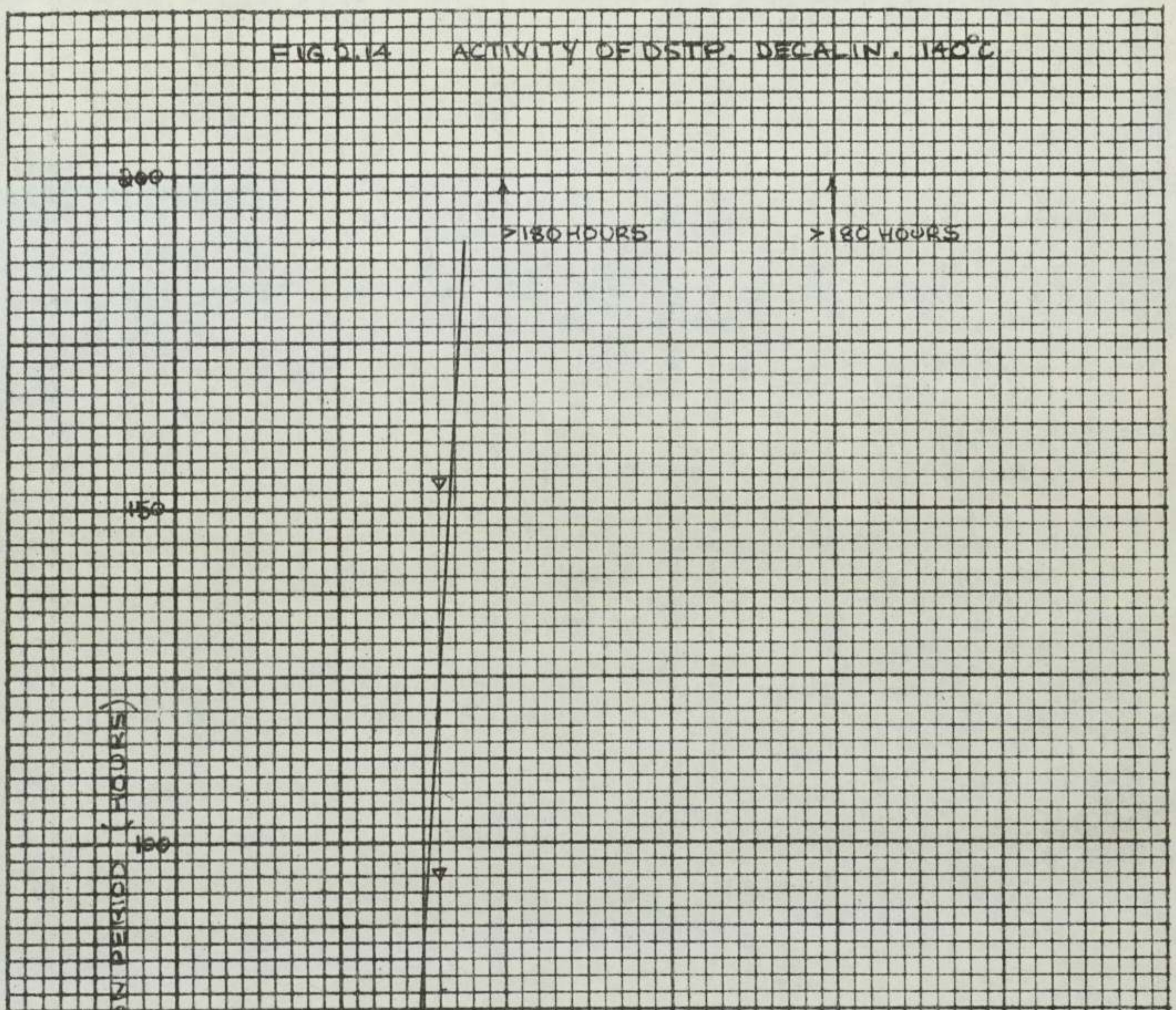


FIG 2.14 ACTIVITY OF DSTP. DECALIN. 140°C

reason for the change in mechanism with increasing concentration was not explained, however.

Recent work by Scott and coworkers (148-152) has demonstrated the major importance of oxidative breakdown products in the mechanisms of sulphur antioxidant reactions. Scott suggests that the active antioxidant species are probably sulphinic and sulphenic acids, sulphur dioxide and other products formed following the initial oxidation of the thiodipropionate.

In the concentration range where the large changes in activity are noted the reproducibility of the induction period measurements was found to be poor. Presumably minor changes in the experimental operating conditions had an inordinately large effect upon the induction period. For example, very small variations in the concentration of the antioxidant would obviously be capable of producing major differences in the measured induction period. At antioxidant concentrations below about $6x10^{-5}$ mole/100 ml decalin it was expected that reproducible results would be obtainable.

The maximum rates of oxidation did not exhibit the irreproducibility which was noticed in the induction period measurements and there was a distinct dependence of the final oxidation rate upon the antioxidant concentration.

At the lowest antioxidant concentration the final rate was similar to that of pure decalin. However at the higher concentrations the final rate was considerably lower than that of decalin alone. It is interesting to note that at an antioxidant concentration of 6.5×10^{-5} moles/100 ml decalin the final rate of oxidation is markedly low. This concentration may well be near the mid-point of the range in which the changes in antioxidant mechanism occur. The participation of antioxidant breakdown products in the final autoxidation stage is again indicated. Unfortunately not enough is known at present about the details of sulphur antioxidant action for an explanation to be formulated.

In order to obtain reproducible and conveniently measureable induction period determinations for the series of thiodipropionates, the oxidation temperature was reduced to 120°C and an antioxidant addition of 2×10^{-5} moles/100 ml decalin was employed. This concentration was lower than the concentrations which were examined subsequently in polymer systems and was below the concentration range at which the mechanistic change was observed. However, it was considered highly probable that the antioxidants in the homologous series that was studied would all exhibit similar changes of mechanism in approximately the same concentration range. The subsequent work in polymer systems was carried out at concentrations well above this range. This assumption was borne out by the results that were obtained in this work.

Figures 2.15 and 2.16 show that the thiodipropionates exhibit activities of the same order although, as with the PP series of phenol antioxidants, there is a slight decrease in efficiency as the length of the pendant side chain

Fig. 2.15 ACTIVITY OF TP SERIES OF ANTIOXIDANTS. DECALIN, 120°C

Antioxidant	Concentration in Decalin		Induction Period (hours)		Linear Oxidation Rate (ml/hour) 5 ml decalin	
	Moles/100 ml	gm/100 ml	Result	Average	Result	Average
DMTP	$2x10^{-5}$	0.0041	27.25 27.90	27.57	20.0 22.5	21.2
DHTP	$2x10^{-5}$	0.0069	27.85 26.4	27.12	20.0 22.5	21.2
DLTP	$2x10^{-5}$	0.0103	26.95 24.00	25.47	20.0 22.5	21.2
DSTP	$2x10^{-5}$	0.0140	25.85 25.05	25.45	22.5 20.0	21.2
Sulphur Dioxide	$2x10^{-5}$	•	27.25 23.55 23.00	24.60	25.5 25.5 27.5	26.6

• 0.0224 ml sulphur dioxide, diluted with oxygen, was added directly to 5 ml decalin in flask (see text).

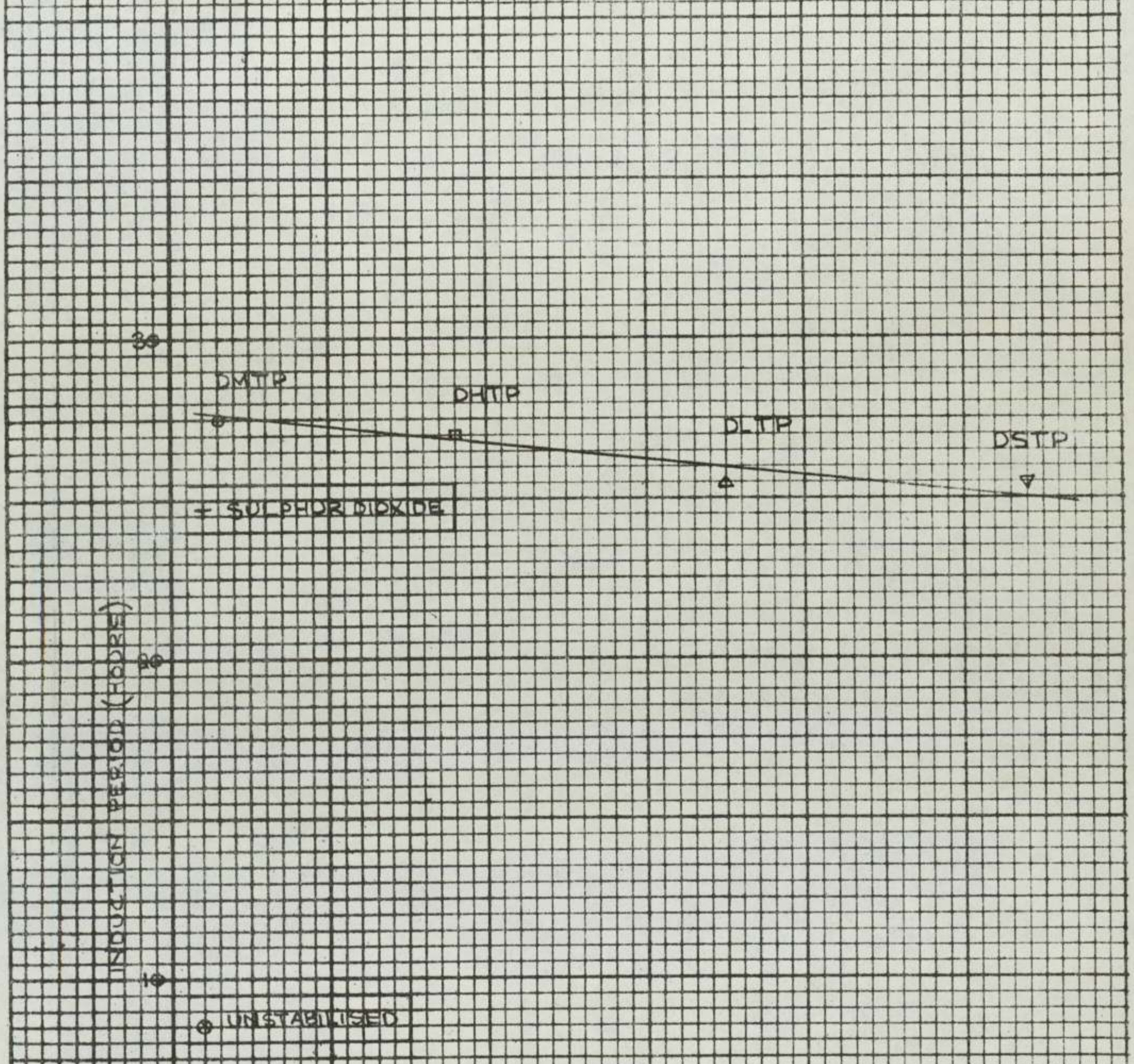


FIG. 2.16.

ACTIVITY OF TP SERIES OF ANTIOXIDANTS. DECALIN. 120°C increases. The magnitude of this variation is only slightly greater than the individual variations in the measurements of the induction periods, however, the effect is considered to be significant. It is interesting that antioxidants acting primarily by radical scavenging and peroxide decomposing mechanisms both exhibit this effect.

In the light of Scott's work on the mechanism of action of sulphur antioxidants (148-152) the efficiency of sulphur dioxide as an antioxidant was considered to be of interest. The addition of this gas, based on an equimolar sulphur concentration produced a stabilising activity only marginally lower than the thiodipropionate antioxidants and this result adds definite weight to the theory that oxidative breakdown products play an important part in the activity of sulphur antioxidants. Further investigation of this phenomena would be valuable, in particular to determine whether the relationship between the concentration and the activity of sulphur dioxide follows a similar pattern to that observed with distearylthiodipropionate.

The final oxidation rates of the thiodipropionate systems fell in the range 20.0 ml-22.5 ml oxygen/5 ml decalin/hour (0.028 mole - 0.031 mole oxygen/mole decalin/hour), slightly lower than that of pure decalin (0.035 mole - 0.039 mole oxygen/mole decalin/hour). The oxidation rate of the sulphur dioxide system appeared to be the same as that for pure decalin. Clearly, the possibilities for the formation of further active species from sulphur dioxide are extremely limited, whereas the thiodipropionates may undergo a much wider range of subsequent oxidative reactions.

2.8.3 Polyphenols.

Figures 2.17 and 2.18 show the activities at 140°C of the polyphenolic antioxidants together with 2,4,6-trimethylphenol (MHT) and antioxidant 2246. At the concentration which was studied ($2x10^{-3}$ mole (ØOH)/100 ml decalin) all these antioxidants exhibited higher activities than the antioxidants in the PP series studied earlier. However, none performed as well as BHT.

Various comparisons of the activities of MHT and BHT appear in the literature; evaluations in petroleum (153, 154) and tetralin (155) have shown MHT to be somewhat more effective than BHT whereas the opposite conclusion has also been drawn in lard (156) and petroleum (157). The considerably higher activity of BHT in comparison with MHT that has been found in decalin has not been noticed in other substrates, however, it is probable that higher activity would be expected in most media (158).

The reason for the alternation of the efficiencies of the MB antioxidants, as the number of phenolic rings in these compounds increases, is not immediately apparent. It might be expected that the bisphenolic antioxidant and its higher homologues would have higher efficiencies than MHT, from considerations of the steric hindrance of the phenolic hydroxyl group. However, although this is found to be the case, the efficiencies of the tri and

Fig. 2.17 ACTIVITY OF MB SERIES OF ANTIOXIDANTS. DECALIN, 140°C

Antioxidant	Concentration in Decalin		Induction Period (hours)		Linear Oxidation Rate (ml/hour) 5 ml decalin	
	Moles/100 ml	gm/100 ml	Result	Average	Result	Average
MHT	2×10^{-3}	0.272	45.00 46.30	45.60	95.0 117.5	106.2
2246	1×10^{-3}	0.340	86.00 82.55	84.27	110.0 95.0	102.5
MB2P	1×10^{-3}	0.256	89.70 87.00	88.30	117.5 100.0	108.8
MB3P	6.6×10^{-4}	0.251	67.20 66.10	66.60	95.0 107.5	101.2
MB5P	4×10^{-4}	0.246	56.85 57.85	57.35	95.0 112.5	103.8

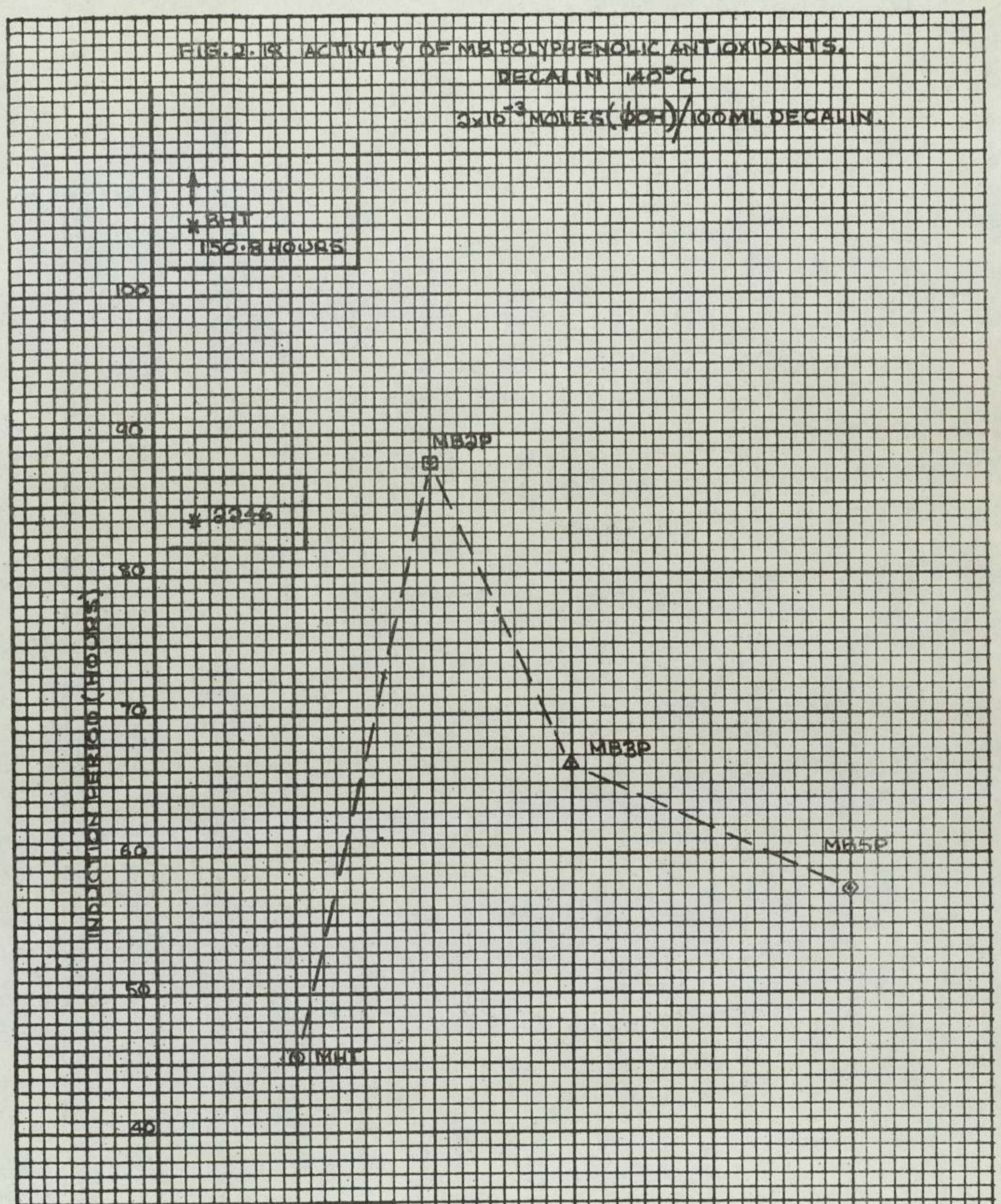


FIG. 2.18 ACTIVITY OF MB POLYPHENOLIC ANTIOXIDANTS.
DECALIN 140°C
2×10^{-3} MOLES (ϕOH)/100ML DECALIN.

pentanuclear antioxidants are seen to be lower than the efficiency of antioxidant MB2P. It is possible that these variations in activity are associated with intramolecular interactions in the polyphenolic antioxidants. From Figure 2.19 it will be seen that the activities of the antioxidants fluctuate in a directly opposite manner to their solubilities in hydrocarbon solvents and in unison with their melting points. Factors such as the intra and intermolecular hydrogen bonding of the compounds may well be influencing their physical characteristics and it would appear that these phenomena are also exerting some influence upon their antioxidant activity. Wright and Knight (141), using IR spectroscopy, have demonstrated that variations in the intensity of intra and intermolecular hydrogen bonding do occur in these compounds. However these workers were not able to obtain an unequivocal interpretation of their results.

The comparison of the activities of the dibutylated antioxidant 2246 and its dimethylated analogue MB2P is surprising. From the relative activities of MHT and BHT and from other work (158) it would be expected that the more hindered antioxidant, 2246, would show higher activity than MB2P; however, in decalin, this appears not to be the case. Again, the reason for this inversion of activity is not fully understood, however, the phenolic hydroxyl of antioxidant 2246 may be so highly hindered that its reaction with a peroxy radical sited on the bridging carbon atom in decalin is sterically retarded.

FIG. 2.19 MB SERIES OF ANTIOXIDANTS.

SOLUBILITY; MELTING POINT; ACTIVITY IN DECALIN; 140°C.

Antioxidant	M.p °C	Solubility* gm/100 ml at 25°C		Induction period (hours)
		Hexane	Toluene	
MHT	71-72	>10		45.60
MB2P	144-146	0.25	4.76	88.30
MB3P	109-112	1.93	7.42	66.60
MB5P	152-154	0.22	2.02	57.35

* Solubilities were determined by preparing saturated solutions at 25°C and weighing these before and after evaporation of the solvent. (See Chaper 5)

In general there appears to be very little correlated information in the literature on the relationships between the activity of antioxidants and the molecular structure of oxidising substrates.

The final rates of oxidation associated with the MB antioxidants do not follow the pattern of variation that was noted with the induction periods, however, with all the antioxidants in this series there is a tendency for the oxidation rates to be higher than those of pure decalin and again there would appear to be some involvement of reaction products in the final rapid autoxidation stage.

2.9 Conclusions.

In decalin, in the absence of the effects of volatility, compatibility and mobility phenomena, the PP phenolic antioxidants and the TP thiodipropionates exhibited very similar efficiencies within each series. The activities of the MB polyphenolic antioxidants showed greater variation but only by a factor of approximately two, in the extreme case. The thiodipropionates were markedly more active than any of the phenolic antioxidants.

3. ANTIOXIDANT ACTIVITY IN POLYPROPYLENE. OXIDATION IN A CLOSED ENVIRONMENT.

3.1 Introduction.

The studies of antioxidant activity in the liquid phase which were described in the previous section were designed to compare the inherent stabilising efficiency of the antioxidants within each series.

The following evaluations were carried out in polypropylene and the determinations of antioxidant efficiency were made in closed apparatus, the intention being that the affects of antioxidant volatility would be eliminated. However, in the highly viscous polymeric medium, other physical factors such as mobility and compatibility were expected to maintain their influence.

3.2 Experimental approach.

The measurement of the induction period to the onset of calamitous oxidation was again used as an indication of antioxidant activity. Unfortunately preliminary experiments revealed that it would not be possible to use the very convenient automatic recording system that was employed for the studies in decalin. It was required to present thin polymer films to the oxygen atmosphere, however, it was found impossible to accomplish this in convenient apparatus with the weight of polymer that was required to produce an easily measurable absorption of oxygen. A series of simple manual absorption systems were constructed which were suitable for the study of small polymer samples.

3.3 Oxygen absorption apparatus.

The apparatus is shown in Figure 3.1. A test tube (10 cm long, 1.5 cm diameter) with a ground glass joint was used as the oxidation vessel; it was wrapped in aluminium foil to prevent light entering.

The absorption tube was over a metre in length and had a nominal internal diameter of 3.5 mm. The tube was calibrated by weighing a measured length of mercury and the variation in internal diameter along the length of the tube was found to be negligible. The volume of the absorption tube was 9.2 ml/100 cm. Six sets of apparatus were constructed and this volume was found to vary by ± 0.02 ml; this small error was neglected.

The cleaning and assembly procedures were similar to those used in the decalin studies and the same oil bath was used.

After placing the polymer in the oxidation tube and purging the system with oxygen, the mercury indicator thread was inserted as follows. The end of the absorption tube was placed in a mercury reservoir to a depth of about 15 cm and the other end of the tube was closed with the oxidation tube. When the absorption tube was removed from the mercury bottle, a thread of the liquid (approximately 2 cm long) broke away and remained in the tube. The thread was then positioned by applying a rubber pipette filler to the bottom of the tube and easing the joint on the oxidation vessel. Before the start of an experiment the mercury thread was placed near the top of the absorption tube so that the thermal

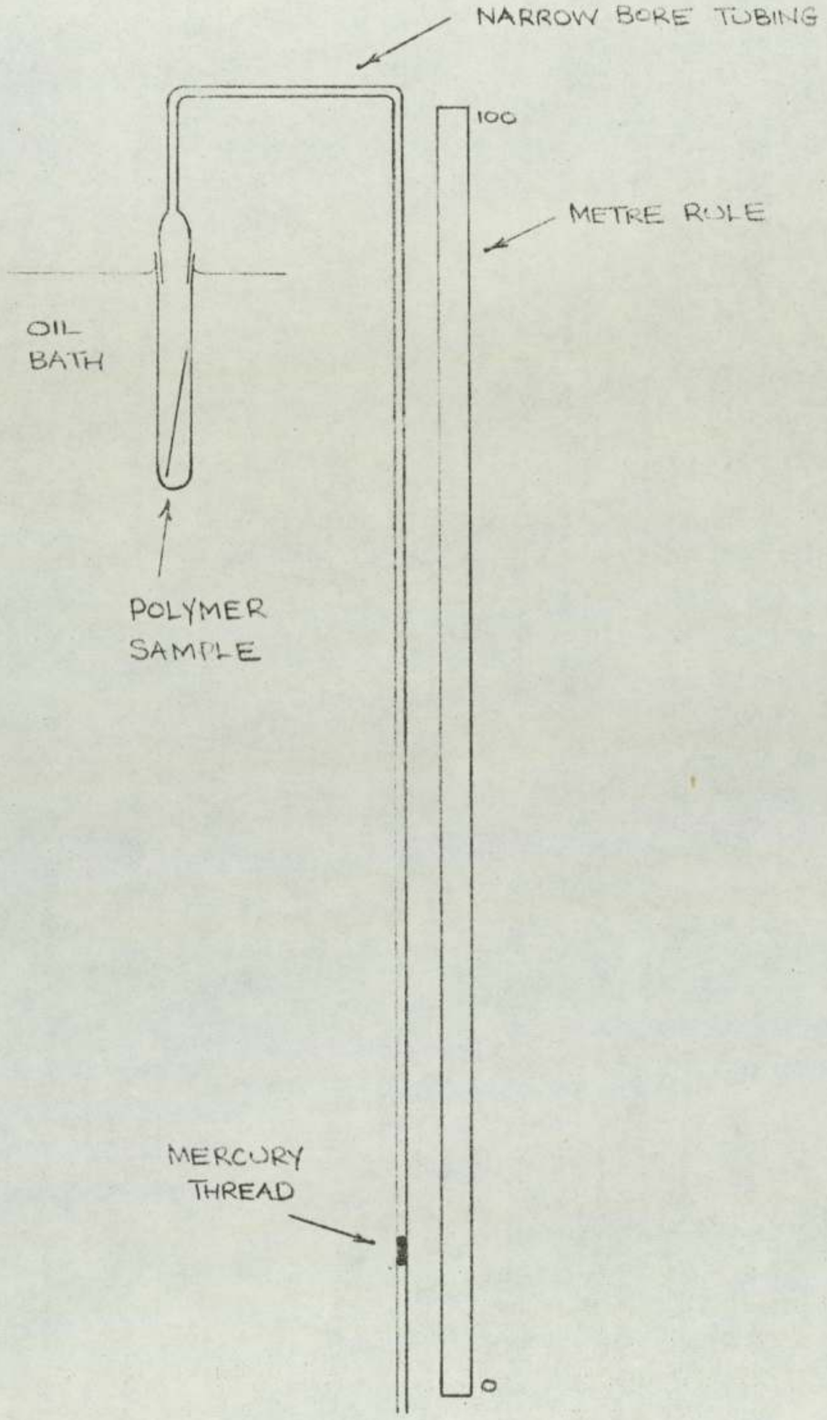


FIG. 3.1 OXYGEN ABSORPTION APPARATUS

expansion of the oxygen atmosphere would bring it to the correct starting position. Thermal equilibration took about 10 minutes, after which time the minimum reading on the metre rule was noted as the starting point.

3.4 Preparation of the samples of polypropylene.

The unstabilised polypropylene was supplied by Imperial Chemical Industries Ltd as an uncompounded powder (HM40C, FN 75689) and was stored in sealed containers in the refrigerator (-15°C).

Sheets ($10 \pm 0.5 \times 10^{-3}$ inches, 0.254 ± 0.012 mm thick) were pressed from the powder between polished steel plates, in a mould constructed from steel shim, at 200°C using a pressing cycle of 2 minutes heat up and 2 minutes under full pressure followed by cooling (3 minutes).

Strips (0.5 cm wide) were cut from this sheet of polymer and their length was trimmed until they weighed 0.10 gm (5 cm approximately).

The samples of stabilised polymer were prepared by shaking the polypropylene powder (50 gm) with a solution of antioxidant in dichloromethane (50 ml-100 ml) for a few minutes and then removing the solvent by rotary evaporation at 25°C-30°C under slightly reduced pressure. Small extra additions of solvent were sometimes made to wash stray polymer back into the bulk. After the solvent had been removed,the polymer powder was left to tumble in the evaporator for about 30 minutes. These samples were again stored in the refrigerator.

3.5 Oxidation of unstabilised polypropylene - Results.

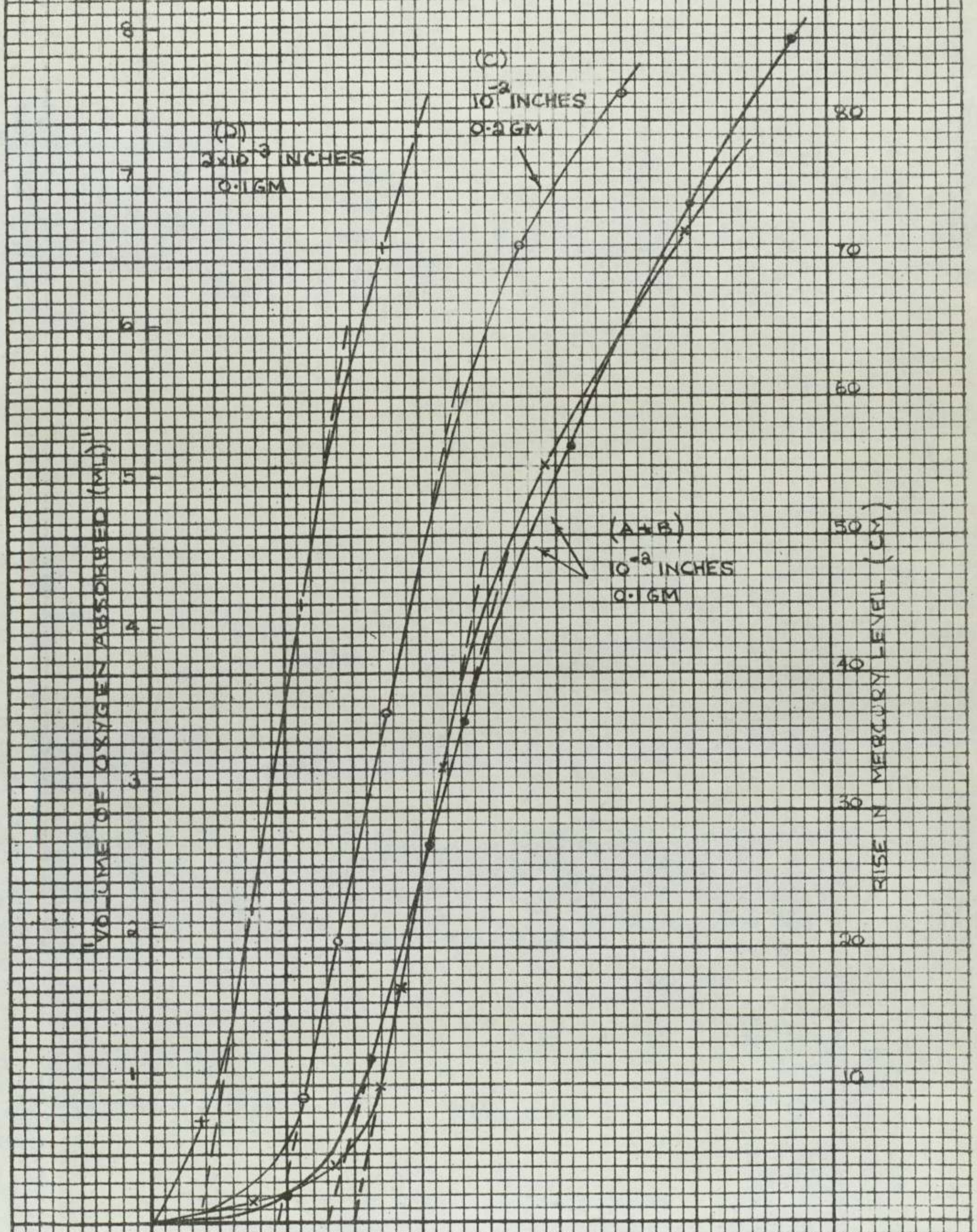
Figure 3.2 shows the oxygen absorption curves that were recorded with unstabilised polypropylene at 140°C.

Curves A and B demonstrate the maximum and minimum induction periods that were noted using the standard sample size and weight (10×10^{-3} inches thick, 0.1 gm). During the early experimentation, absorption runs were carried out on samples taken from sheets which had been pressed separately and the induction period always fell between these limits. The average induction period, taken from 12 determinations, was 56 minutes, the limits of accuracy being estimated as ± 5 minutes.

The absorption of oxygen exhibited the characteristic (159-163) autoaccelerating behaviour in the early stages and reached a maximum rate after approximately 10 ml oxygen/gm polymer had been absorbed. The maximum rate was maintained until about 30 ml oxygen/gm polymer had reacted and then an apparent autoretardation of the oxidation ensued and continued to the limits of the detecting system.

This retardation did not appear to be due to the exhaustion of oxygen in the apparatus and various effects may be involved. The oxidation of polypropylene has been shown (164) to be accompanied by the formation of low molecular weight products. The evolution of volatile oxidation products, in molar excess of the volume of oxygen consumed, would produce an apparent decrease in the rate of oxygen consumption. Various workers (165-167) have included

FIG. 3.2 OXIDATION OF UNSTABILISED POLYPROPYLENE. 140°C



absorbing materials (particularly for water and acidic products) in the oxidation chamber, in an attempt to obtain true final rates of oxygen absorption in studies of both polyethylene and polypropylene. However, the literature is in disagreement as to whether catalysis (76) or retardation (168) of polypropylene oxidation is produced by the accumulation of oxidation products. The conclusions drawn from this type of work would seem to depend upon which part of the oxidation reaction is considered.

Venn (169), during studies on polyethylene, noted that both the induction period and the eventual rate of oxidation decreased as the weight of the sample increased in an apparatus of the same volume and these variations were ascribed to the accumulation of oxidation products.

A similar behaviour was observed in the present work (Curve C). 0.2 gm polypropylene showed an induction period of 37 minutes and the volume of "oxygen absorbed"/unit time, rather than doubling remained approximately the same as that observed with 0.1 gm polymer.

Thus the early part of the oxidation, before the maximum oxidation rate is achieved seems to be accelerated by the presence of oxidation products whereas the later stages of oxidation appear to be (or are actually) retarded.

Reducing the thickness (Curve D) of the polypropylene specimen (0.1 gm) also decreased the induction period and this effect may be due to a reduction of the hindrance of the oxidation by the limited diffusion of oxygen. There are conflicting views in the literature concerning the effects of oxygen diffusion phenomena upon the oxidation of polymers (76, 167, 168, 170-179). In particular these discussions centre upon the effects of the limited diffusion of oxygen upon the measurement of induction periods and maximum rates of oxidation in studies of unstabilised polymers. These investigations have usually been concerned with determining the acceptable thickness of samples below which oxygen diffusion was not controlling oxidation. However, the existence of such criteria is still contested.

In the present work it would be expected that the shorter induction period exhibited by the thin sample would be associated with a higher final rate of oxygen absorption. It seems likely that the interference of oxidation products is again involved.

As the primary objective of the present work was the evaluation of antioxidant activity these topics have not been progressed further, however, these phenomena do indicate the extreme care which must be taken in studies of the kinetics of the oxidation of polymers.

In the present work, all experiments were carried out on 0.1 gm polymer (10^{-3} inches thick), using the same type of apparatus throughout, in an attempt to overcome the interferences mentioned above.

Figure 3.3 Activity of PP phenolic antioxidants. Polypropylene. 140°C. 2×10^{-3} moles (ØOH)/100 gm polymer.

Antioxidant	Number of samples tested	Induction period (hours)
BHT	3	140 ± 10
MPP	4	95 ± 5
HPP	6	315 ± 15
LPP	4	420 ± 20
SPP	3	200 ± 10
4PP	5	620 ± 20

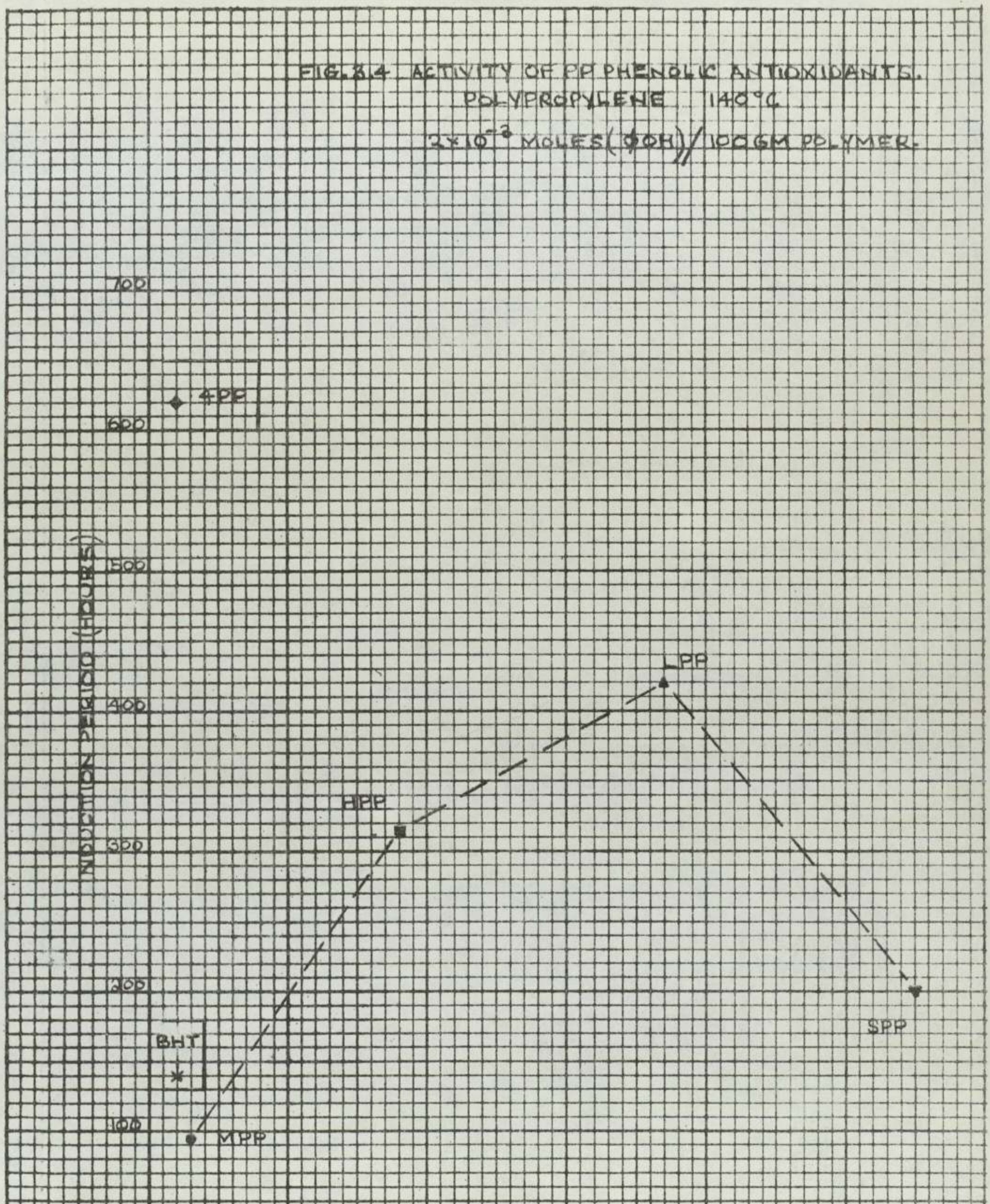


FIG. 3.4 ACTIVITY OF PP PHENOLIC ANTIOXIDANTS.
POLYPROPYLENE 140°C
2×10^{-3} MOLES(ΦOH)/100GM POLYMER.

3.6 Studies of antioxidant activity - Results.

These evaluations were carried out upon the same antioxidants that were examined in decalin. Because the induction periods, before the start of the rapid autoxidation stage, were generally several hundred hours long, it was usually not possible to monitor the progress of the final autoxidation reaction.

The accuracy of the induction period measurements depended to some extent on when the induction period ended; in general three determinations were made, but if the rapid autoxidation stage commenced during a weekend, the experiment was repeated. The accuracy limits that are quoted in the following results combine the errors due to the absence of the observer and those due to variations in samples.

3.6.1 Propionate-substituted phenols and BHT - Results.

Figures 3.3 and 3.4 show the induction periods of polypropylene samples, containing 2×10^{-3} moles (ϕOH) antioxidant/100 gm polymer, when aged at 140°C.

It was found that very little absorption of oxygen occurred before the end of the induction period. Minor rises and falls of the mercury column were noted, covering about 1 cm during the total induction period; these fluctuations could often be related directly to slight changes in the ambient temperature. There are obvious differences in the relative efficiencies of the antioxidants in decalin and in polypropylene, however, any discussion of these variations in antioxidant activity will be delayed until further information has been presented.

3.6.2 Polyphenols - Results.

The activities of the antioxidants at 140°C in polypropylene, at a concentration of 2×10^{-3} moles (ϕOH)/100 gm polymer, are shown in Figures 3.5 and 3.6.

As was observed with the PP series of phenolic antioxidants, no absorption of oxygen could be detected until the end of the induction period had been reached.

Any discussion of the results will again be deferred until later.

3.6.3 Thiodipropionates - Results.

Early in the evaluation of the sulphur antioxidants a distinct difference from the behaviour of the phenolic antioxidants became apparent, the absorption apparatus revealing no induction period in the oxidation of the polypropylene.

Figure 3.7 shows the absorption curves obtained in an examination of distearylthiodipropionate at a range of concentrations at 140°C.

Between four and seven oxidation experiments were carried out at each concentration, samples being taken both from the same and different pressed sheets of stabilised polypropylene. Whilst individual samples produced reasonably smooth absorption curves (apart from the small fluctuations due to changes in the ambient temperature), the variations between samples were considerable. The

Figure 3.5 Activity of MB polyphenolic antioxidants. Polypropylene. 140°C. 2×10^{-3} moles (ØOH)/100 gm polymer.

Antioxidant	Number of samples tested	Induction period (hours)
MB2P	5	230 ± 7
MB3P	4	200 ± 10
MB5P	5	125 ± 8
2246	3	255 ± 10

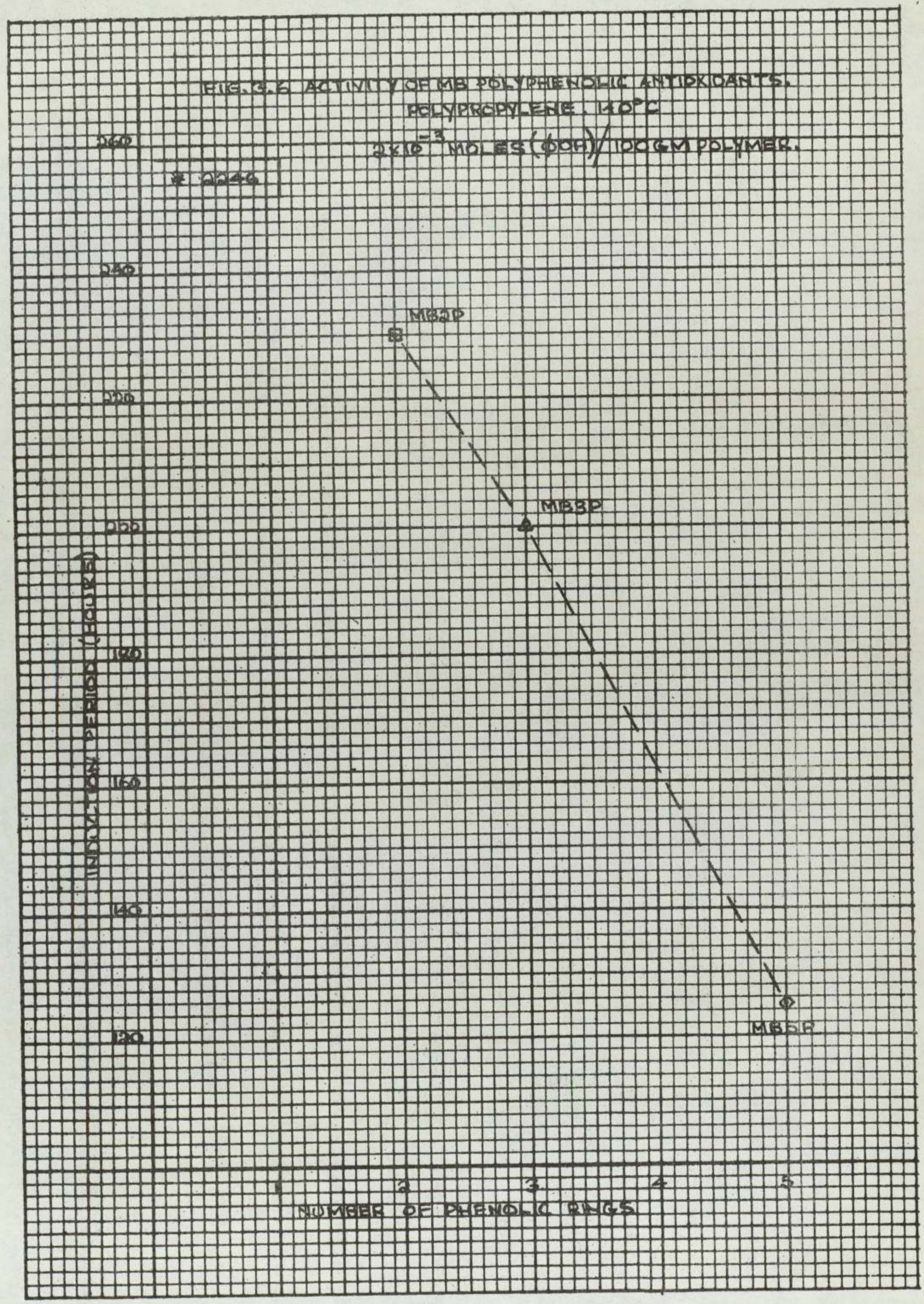


FIG. 3.6 ACTIVITY OF MB POLYPHENOLIC ANTIOXIDANTS.
POLYPROPYLENE. 140°C
2×10^{-3} MOLES (ΦOH)/100 GM POLYMER.

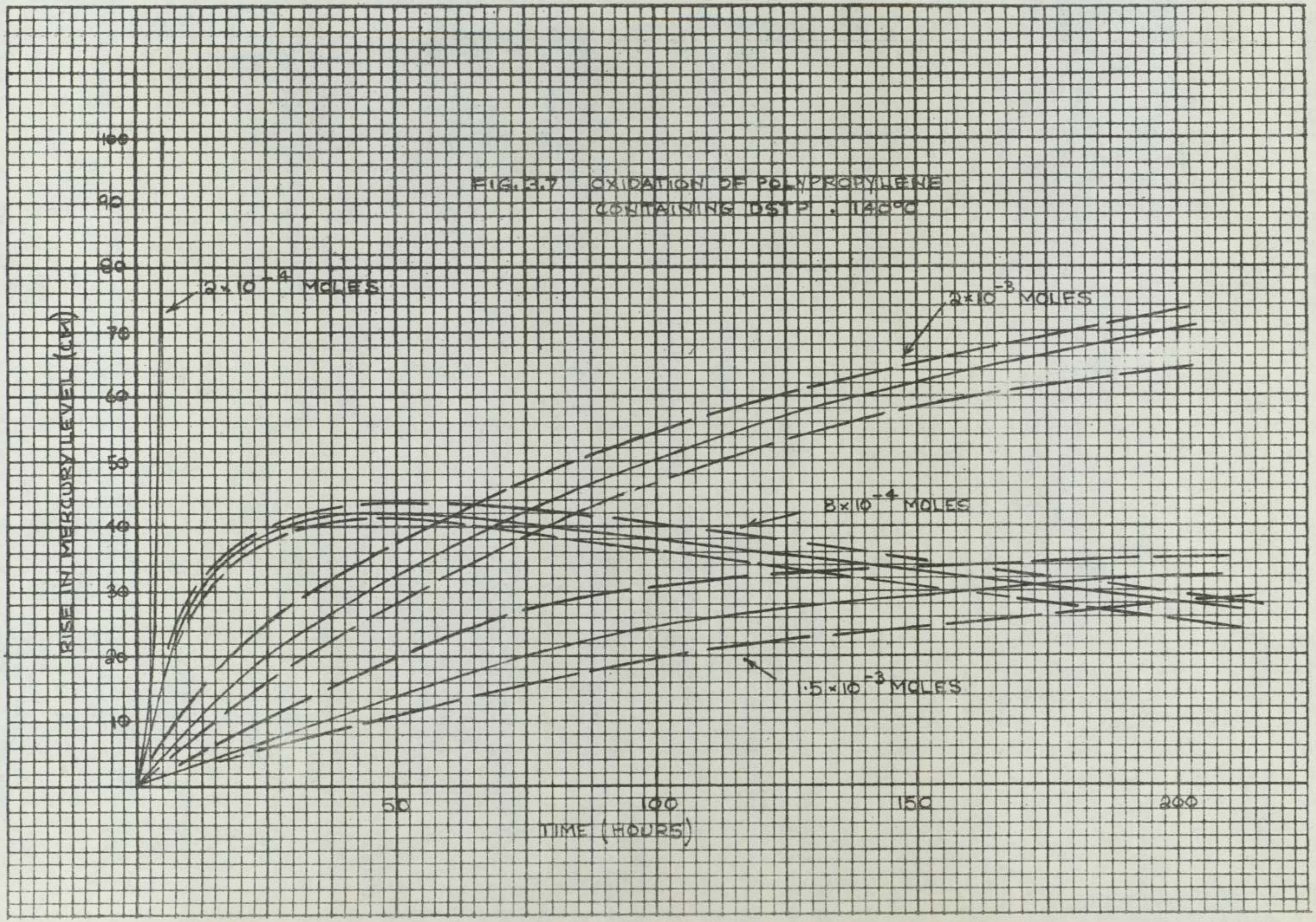


FIG. 3.7 OXIDATION OF POLYPROPYLENE CONTAINING DSTP, 140°C

curves shown in Figure 3.7 were produced by plotting all the information from the separate samples and drawing the best curve; the hatched lines indicate the area that would include the absorption curves from all samples at the given antioxidant concentration.

It is not altogether clear why these variations are observed. Samples cut from the same sheet and different sheets of polymer seemed to exhibit the same variations in behaviour and it is doubtful, therefore, that differences in the initial antioxidant concentration are responsible. Any inadequacies in the technique of dispersing the antioxidants would have presumably appeared in the investigations of the phenolic antioxidants. It is considered more likely that minor variations in the prior heat ageing that samples received during pressing have produced this experimental variability. Scott and Shearn (148) have demonstrated that thiodipropionates undergo oxidative reactions during processing which, in the extreme, can produce pro-oxidant effects and which lead to the formation of the active antioxidant species referred to earlier (149-152). During the pressing of the samples (at 200°C) the ageing history received, not only by different sheets of polymer but also within each sheet, may have varied slightly and thus may be producing the subsequent differences in antioxidant behaviour which were noticed.

Although DSTP did not produce a satisfactory pattern of stabilisation, without any absorption of oxygen over extended periods of time, Figure 3.7 demonstrates that a definite redirection of the oxidative reactions of the polymer occurred.

Unstabilised polypropylene was previously found to oxidise rapidly, the limit of the detection system (100 cm, 9.2 ml) being reached within four hours. At all the concentrations which were examined, DSTP appeared to reduce the rate of oxygen absorption. However, the curve for the concentration 8×10^{-4} moles/100 gm polymer clearly indicates that the observed 'absorption' is a combination of a real oxygen absorption and an evolution of volatile oxidation products. Thus the sulphur antioxidant appears to be limiting the oxidation reaction, but the extent to which this conclusion is influenced by the evolution of oxidation products cannot be estimated. It is significant perhaps that an increase in the concentration of DLTP in the range 2×10^{-4} moles to 1.5×10^{-3} moles/100 gm polymer results in an apparent decrease in the rate of oxidation during the early stages of reaction, when any evolution of oxidation products could be expected to have a less significant effect. A deviation from this trend is noticed, however, at an antioxidant concentration of 2×10^{-3} moles/100 g polymer.

Again, the differing pattern of behaviour between the oxidations at the lowest antioxidant concentration (2×10^{-4} moles/100 g polymer) and those at the three higher concentrations may indicate a change in the mechanism of action of the sulphur antioxidant at different concentrations. Thus, in the concentration range 2×10^{-4} moles to 8×10^{-4} moles/100 gm polymer a dramatic change in the oxidative pattern seems to occur and this may well be similar in nature to the marked alteration in behaviour that occurred in decalin between the 6.5×10^{-5} molar and 8×10^{-5} molar concentrations.

Although the 2×10^{-4} molar oxidation appears to show a behaviour similar to that observed with the phenolic additives, in fact no true antioxidant induction period was observed, the absorption of oxygen commencing immediately (Figure 3.8). However, the progress of the oxidation was inhibited to some extent. Unstabilised polypropylene gave a 50 cm rise in the mercury level (4.6 ml) after 110 minutes whereas the polymer containing antioxidant did not produce this absorption until nearly four hours had elapsed. The inhibiting effect did not appear immediately, however, as both series of oxidations followed the same pattern for about 50-60 minutes.

Again, it would appear that this phenomenon is related to the formation of active antioxidant species from the sulphur compound. However, it should be mentioned that the evolution of volatiles from the oxidising polymer samples cannot be accounted for by the evolution of sulphur dioxide that has been described by Scott (151) in studies of sulphur antioxidants in liquid hydrocarbons. At the highest concentration of DSTP, less than 0.05 ml of sulphur dioxide would be formed if all the antioxidant were oxidised to this gas.

A comparison of the effects of the antioxidants in the thiodipropionate series, at a concentration of 2×10^{-3}

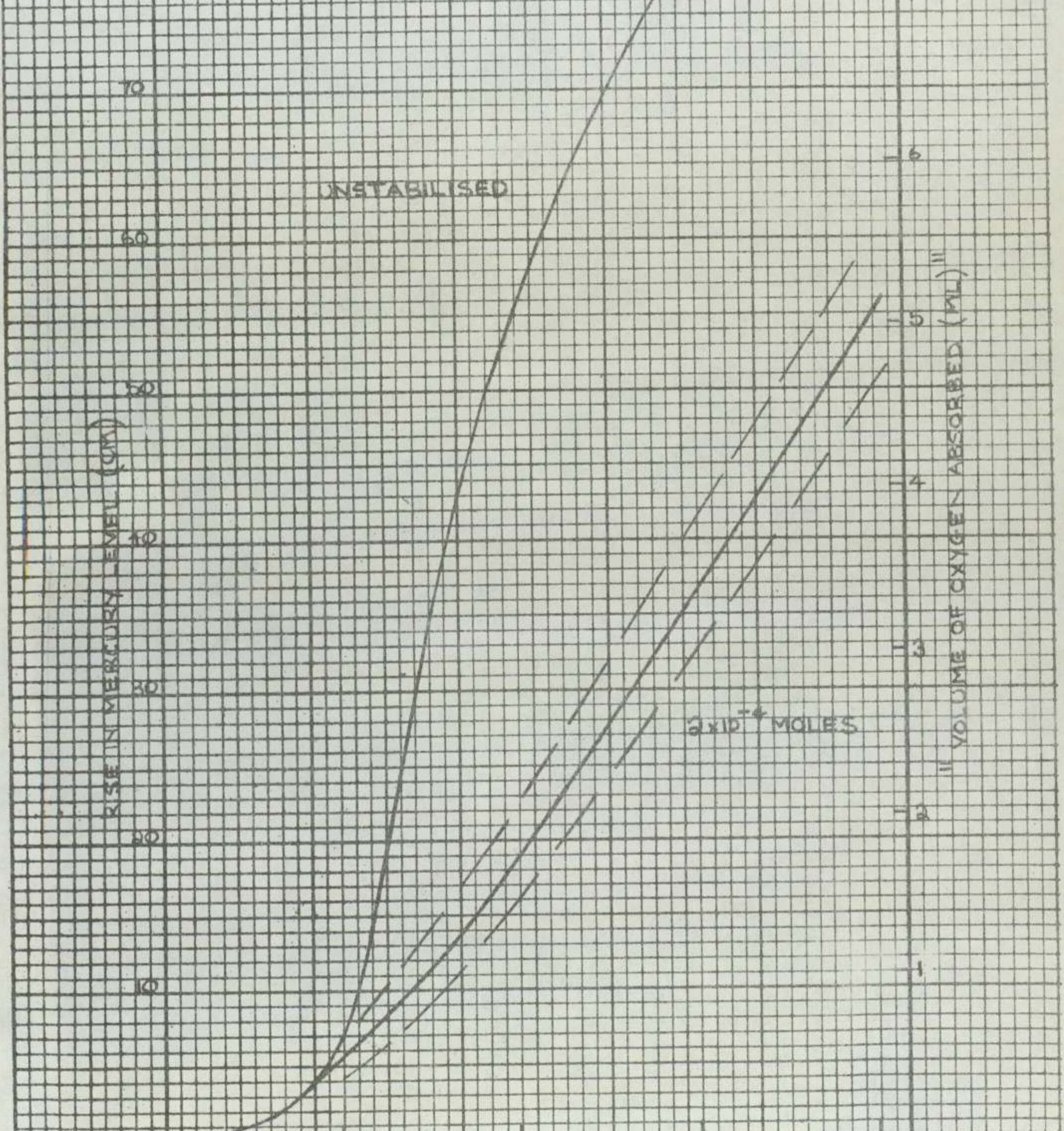


FIG. 3.8 OXIDATION OF POLYPROPYLENE CONTAINING DSTP, 140°C

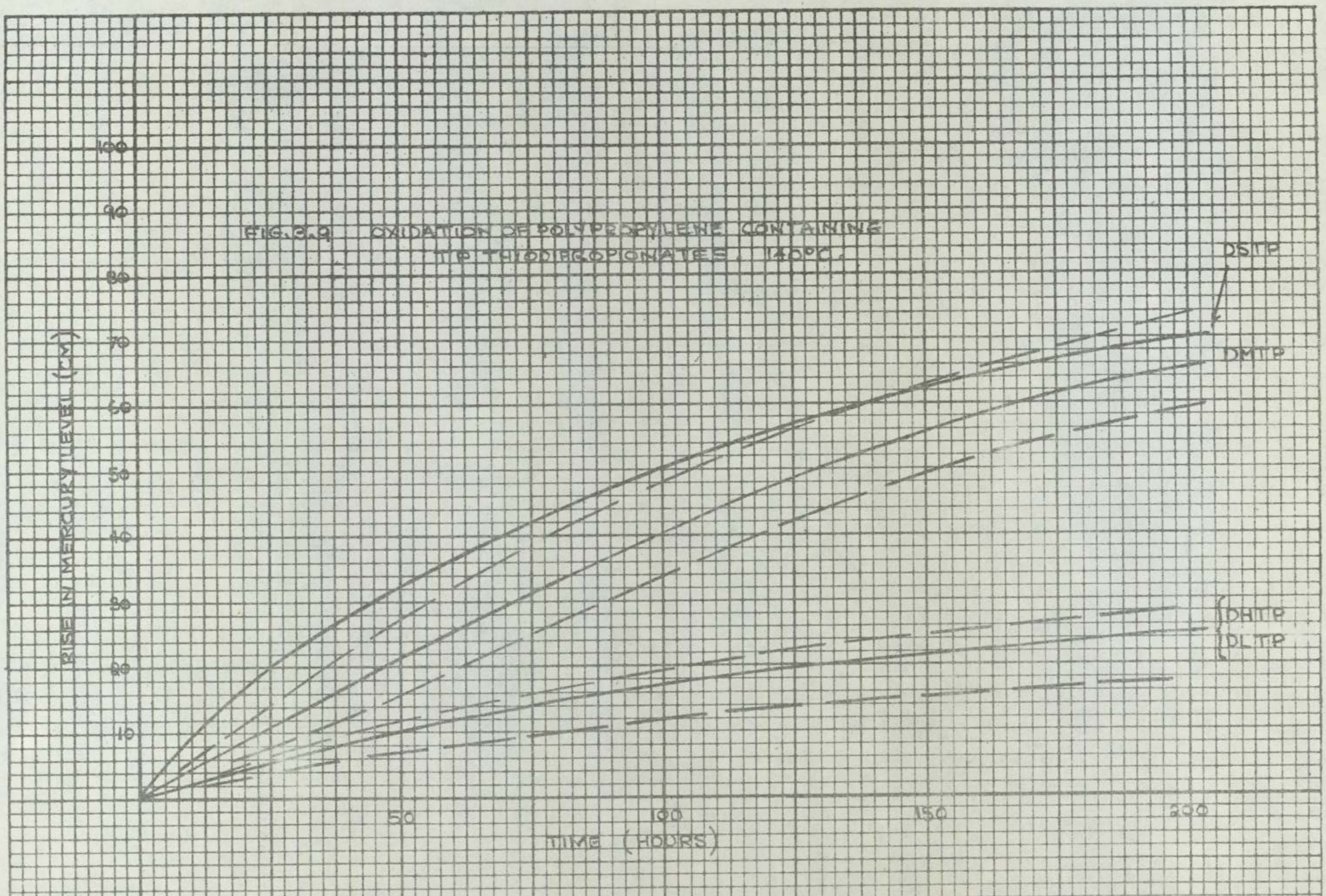


FIG. 3.9 OXIDATION OF POLYPROPYLENE CONTAINING ββ THIODIPROPIONATES, 140°C.

moles/100 gm polymer, are given in Figure 3.9. Within the limits of the experimental scatter, between different samples, it was not possible to distinguish between the behaviour of DHTP and DLTP.

A further difference in the behaviour of the phenolic and sulphur antioxidants should perhaps be mentioned. An examination of the oxidised polymer samples, at the end of each experiment revealed a difference in the appearance of the samples containing the two types of antioxidant. The polymer to which any of the phenolic antioxidants had been added were quite generally found to be opaque, yellow or orange-yellow in colour and crumbling; severely degraded unstabilised polymer also exhibited these characteristics. However, samples containing the thiodipropionates were brittle but did not crumble, coffee-brown in colour and almost transparent. The latter samples exhibited a considerably greater transparency than the original polymer and although no further evidence is available this may be an indication of differences in the mode of action of the two types of antioxidant in the crystalline regions of the polymer.

4. ANTIOXIDANT ACTIVITY IN POLYPROPYLENE. OXIDATION IN A FLOWING ATMOSPHERE.

4.1 Introduction

Following the previous studies of antioxidant activity in a restricted and static atmosphere, where it was hoped to produce activity data without the confusing influences of volatility, the present evaluation attempted to assess the importance of volatility upon antioxidant activity. Again however, the influences of other physical factors, such as mobility and compatibility, were expected to be maintained.

4.2 Experimental approach

The results which were detailed in the previous chapter indicated that the reproducibility of assessments based upon the ageing of moulded plaques is not particularly good. In particular it was noticed that the tests involving the sulphur antioxidants appeared to give a not insignificant scatter of results. The reproducibility of the evaluations of the phenolic antioxidants was somewhat better; however, in all these evaluations considerable efforts were made to ensure that the techniques which were used for the preparation and ageing of the samples were as nearly identical as was possible for each experiment. The literature abounds with comments about the poor reproducibility of evaluations involving antioxidants of all types in polymeric substrates. Some of the reasons for irreproducibility between different types of test will be apparent from the first chapter, however, the results that were detailed in the previous chapter indicate that the presence of oxygen during the preparation of samples appears to emphasise irreproducibility problems.

One of the major traditional technological techniques, which are used for assessing antioxidant activity, involves the ageing of polymer specimens in an oven. Apart from the general comments in the literature concerning poor reproducibility in antioxidant evaluations, the oven ageing technique has received particular criticism (see, for example, 76, 178). As it was intended that the "flowing atmosphere" tests described in this chapter should, of necessity, be based upon an oven ageing technique, it was considered worthwhile to attempt to develop an improved method of assessing antioxidant activity involving this technique.

In the last chapter oxygen absorption was used to monitor the progress of the oxidation of polypropylene, this being an extremely convenient method of approach, within the confines of the requirement for a closed environment. However, various other methods for following the oxidative degradation of polymers are used (180), based upon chemical and physico-chemical changes. Variations in the mechanical properties of polymers during oxidation are important for obvious reasons and have received considerable attention (180). Unfortunately, because the oxidation of stabilised polyolefins usually exhibits the typical induction period which is characteristic of saturated hydrocarbons (159-163), the changes in mechanical properties are generally insignificant until the onset of the calamitous oxidation at the end of this period.

The peculiar behaviour shown by the sulphur antioxidants in the oxygen absorption work on polypropylene suggested that some changes in mechanical properties might perhaps be detectable during the induction period of oven ageing. Destructive mechanical testing (tensile, impact) was considered to be too insensitive and is notoriously irreproducible ; it was therefore decided to follow the torsional properties of the polymer.

Gillham and coworkers (181-186) developed torsional braid analysis for studying the cross-linking reactions of thermosetting polymers and this technique appeared to offer high sensitivity and good reproducibility, if experimental care was taken, in three essential areas - the preparation of samples in the absence of oxygen, the ageing procedure and the assessment of physico-chemical changes. In essence the method is based upon the measurement of the torsional rigidity of a glass fibre/polymer composite braid by the assessment of the torsional period of an oscillating pendulum.

4.3 Torsional braid analysis; apparatus and technique.

The equipment consisted of two separate pieces of apparatus (Figures 4.1 and 4.2) which were used for the preparation and testing of the composite braid samples. The procedure described below is the finalised technique which was used in the antioxidant evaluations; various comments about details of the procedure will be made later.

4.3.1 Preparation of braids.

Glass fibre yarn (Turner Brothers Co Ltd, Grade 225-$\frac{1}{3}$) was cut into 27 cm lengths and heat cleaned at 400°C in air for 2 hours to remove the coating of size. Three lengths

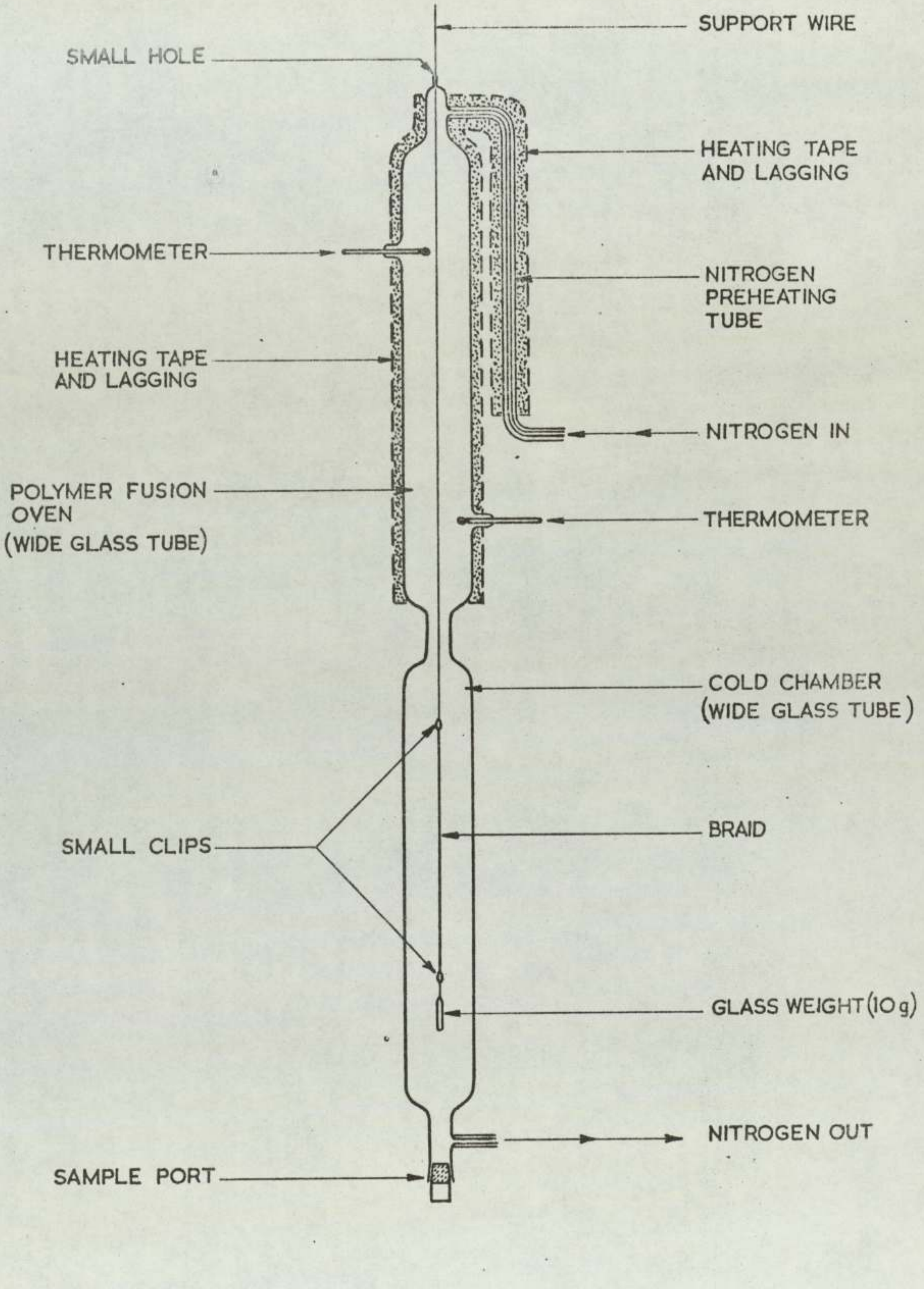


FIG. 4.1. APPARATUS FOR BRAID PREPARATION

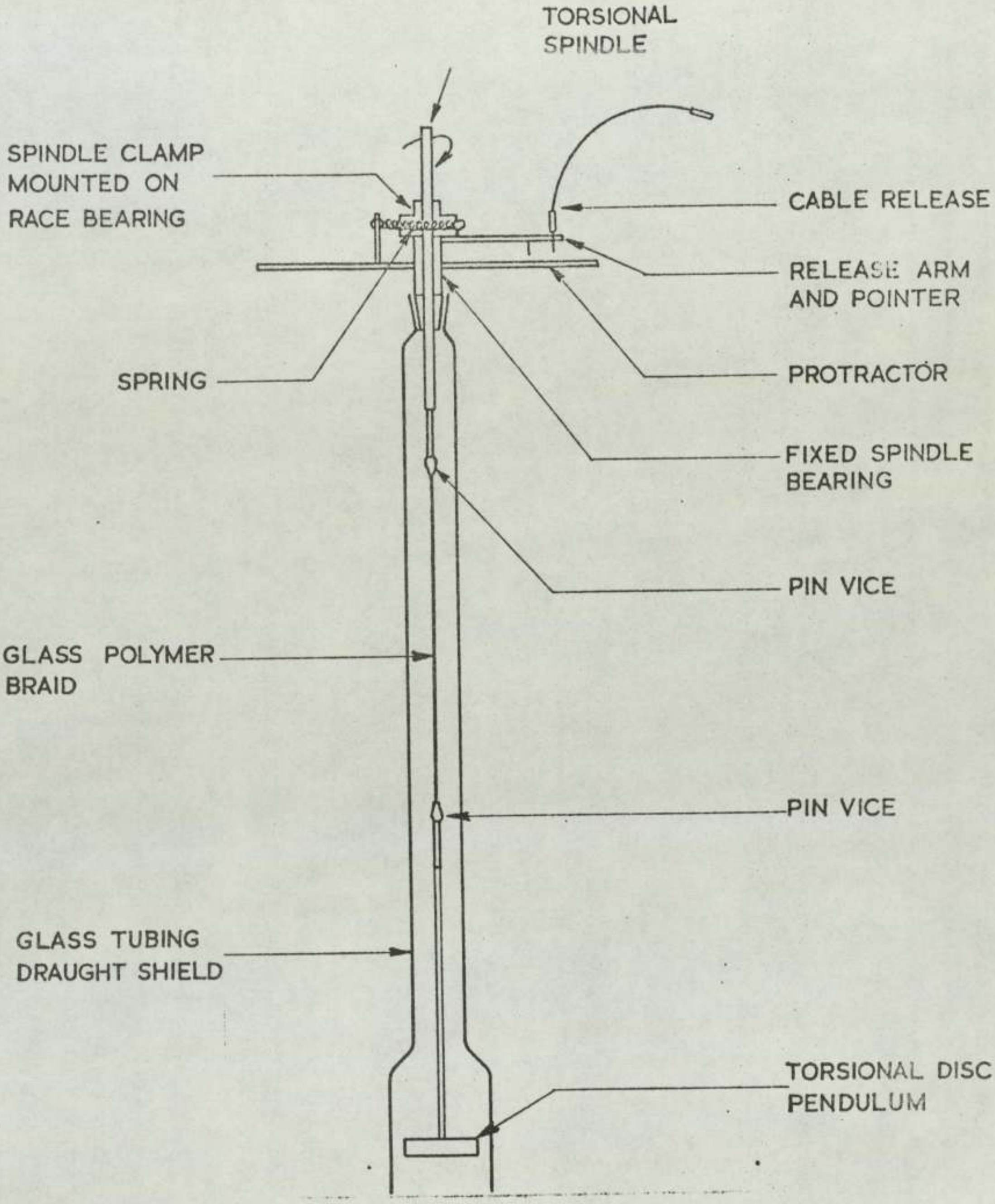


FIG 4.2 APPARATUS FOR DETERMINATION OF TORSIONAL PERIOD OF BRAIDS

of yarn were loosely twisted together and the ends cemented into 1 cm lengths of fine glass tubing (melting point tubing) with epoxy adhesive ; this was cured overnight at 120°C. The length of glass braid available for subsequent coating with polypropylene was therefore 25 cm.

The glass strands were dipped into distilled water, shaken to remove excess water and carefully drawn through polypropylene powder. Stabilised samples of polypropylene powder were prepared using the solvent dispersion technique described previously.

The powdered braid was then hoisted into the cold chamber of the preparation oven (Figure 4.1) through which nitrogen was passing (50 ml/minute; any oxygen had been removed by copper filings at 600°C-700°C); it was kept under slight tension by clipping a length of glass rod (10 gm) to its lower end. The braid was suspended in the cold chamber for 10 minutes to allow the removal of any air which had been trapped in the polymer powder.

The sample was then hoisted into the fusion oven, allowed to remain at 200°C for 10 minutes and was then lowered into the cold chamber where it was cooled for 5 minutes before removal.

This preparation technique gave a braid with a polypropylene content of 52 ± 2% and a radius of 0.30 ± 0.03 mm.

4.3.2 Measurement of torsional period.

The apparatus (Figure 4.2) was a simplified modification of that originally devised by Gillham (181) in which the torsional swing was induced by a spring rather than a falling weight. This latter system was foresaken for convenience, as the detailed quantitative evaluation of mechanical properties, that Gillham was seeking, was not considered essential in the present studies.

The braid sample under test was clamped in the torsional spindle and the pendulum, using pin vices, and the upper spindle was then hoisted into the torsion head and clamped.

The torsion head and release arm were rotated against the tension of the spring and held by a camera cable release whilst the pendulum was steadied. On disengaging the cable release, the torsion head and arm flicked round to a stop and set the pendulum into torsional vibration.

The cable release and stops were arranged so that the same angular twist could be applied in both clockwise and anticlockwise directions; torsional periods were always checked in both directions of applied torque although no differences in the periods of oscillation were found.

Using braids of the dimensions mentioned above, a pendulum weighing 59 gm and 3.5 cm in diameter (brass, 0.7 cm thick) was found to give conveniently measurable periods if the torsional head was rotated 40°. The total weight of the pendulum and pin vice was 92 gm; neither a pendulum of this total weight nor the torsional deformations of the magnitude which were used, were found to have any deleterious effects on the braids during testing.

With the above system, it was found that five complete periodic oscillations of the pendulum could be timed satisfactorily.

4.3.3 Ageing procedure.

In general, three or five braids were prepared from each stabilised polymer sample and after the initial torsional period of each had been measured, they were suspended vertically, by clips at one end, in the isolated cells of a Wallace oven, maintained at the required temperature. The requirements for reproducibility in this type of ageing procedure (178) were adhered to strictly; to prevent the cross contamination of the antioxidants by volatilisation, only one stabilised formulation was aged in a single cell ; the rate of flow of oxygen was kept constant throughout all the evaluations. The seven cells of the oven were supplied from a common source flowing at 28.3 litres/hour (1 ft^3/hour). The temperature control of the Wallace oven was better than ± 0.2°C at the operating temperatures which were used. Each time the braids were removed for testing, they were inverted on replacing in the oven, in an attempt to eliminate the effects of any minor temperature variations within each ageing cell. The braids were always allowed to cool to room temperature (20 ± 2°C) before their torsional periods were measured.

4.4 Determination of antioxidant activity - Results of initial studies.

Early in the evaluation it became apparent that the antioxidants within each series were showing activities which differed by several orders of magnitude. Thus, in order to conveniently compare the widely differing activities, the antioxidants were tested at two temperatures, 100°C and 140°C.

Initial assessments of the torsional braid technique were carried out using polypropylene stabilised with one antioxidant from the PP series of phenols and one of the thiodipropionates. The lauryl homologue of the phenols(LPP) and distearylthiodipropionate were chosen, as these antioxidants were both found to give conveniently measurable induction periods (100°C) at concentrations of 2×10^{-4} moles/100 gm polypropylene. The polyphenolic (MB) antioxidants were not available at this time and were not included.

Figure 4.3 shows the results of this initial evaluation and demonstrates two important points. Firstly, in this "flowing atmosphere" test the sulphur antioxidant produced an induction period in the oxidation of the polypropylene and secondly, a difference in behaviour between the phenolic and sulphur antioxidants is apparent during the induction period.

The presence of an induction period in the oxidation of the polypropylene stabilised with all the thiodipropionates was subsequently demonstrated at 100°C and 140°C. Comparing

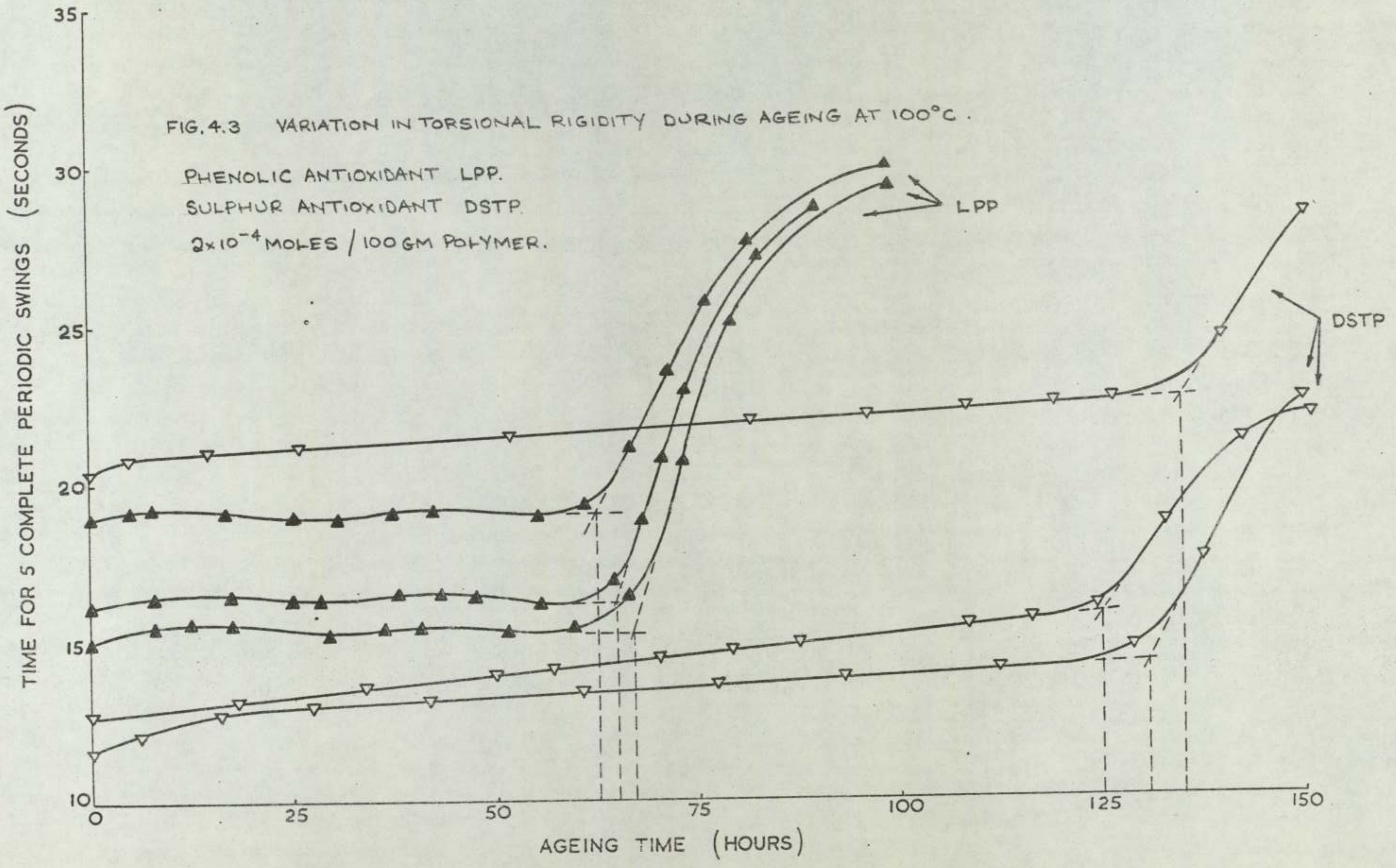


FIG. 4.3 VARIATION IN TORSIONAL RIGIDITY DURING AGEING AT 100°C.

PHENOLIC ANTIOXIDANT LPP.
SULPHUR ANTIOXIDANT DSTP.
2×10^{-4} MOLES / 100 GM POLYMER.

the behaviour in the previous oxygen absorption experiments and in the present evaluation, it would appear that the differing behaviour of the thiodipropionates is definitely dependent upon the extent to which oxidation products, formed from the sulphur antioxidant, are held in contact with the oxidising polymer. An extension of this approach involves the possibility that the sulphur antioxidant and/or its subsequent breakdown products redirect the oxidative pathways of the polymer to form species which can influence the further oxidation of the polymer. That the accumulation of polypropylene oxidation products can influence the further oxidative behaviour is acknowledged in the literature, however, as previously mentioned, there is disagreement as to whether a catalysis (76) or a retardation (168) occurs. In the oxygen absorption evaluation of the thiodipropionates in polypropylene it was apparent that the oxidation reaction commenced immediately; it would thus appear that the accumulation of oxidation products in polypropylene stabilised with thiodipropionates can have distinctly deleterious effects.

However, although in the present work the thiodipropionate stabilised polymer did exhibit an induction period, changes in the mechanical properties of the torsional braid specimens were observed during this period. In particular, an initial increase in the torsional period was noted at the start of the ageing cycle, followed by an upward trend in torsional period before the onset of the rapid autoxidative failure. This latter stage was found to exhibit a brief linear phase before the complete mechanical breakdown of the polymer occurred.

It will be noted that one of the braids examined in this series did not show the initial increase in torsional period. Although during the early experimental work and the following evaluations this phenomenon was observed occasionally, it did appear to be an exception. It is thought that the disappearance of this initial change may have been associated with the occurrence of a limited amount of oxidation during the preparation of the braid. A small amount of residual oxygen trapped in the polymer powder may have caused sufficient oxidation of the polymer to obliterate this initial phase and bring the torsional behaviour onto the smooth section of the upward curve.

These phenomena lend weight to the findings (148, 150) that thiodipropionate esters can cause an actual pro-oxidant effect in tetralin (150) and during the milling of polypropylene (148). Again, this pro-oxidant effect is attributable to the formation of free radical species, capable of initiating oxidative reactions in the substrate, before the formation of active antioxidant entities from the original antioxidant.

The initial loss of mechanical properties of the thiodipropionate stabilised braids, although in no way approaching the severity of a pro-oxidant effect, does indicate that some measure of oxidative deterioration had occurred before these reactions were brought under better control. The subsequent slow increase in torsional period indicates that a small amount of oxidative degradation is continuing throughout the time preceding the onset of catastrophic degradation. Denison and Condit (187-189) have reported that some absorption of oxygen is associated with the inhibition period produced by a variety of sulphur antioxidants in a hydrocarbon oil and Hawkins (190) has reported similar behaviour together with an initial more rapid phase of the oxidation.

The absorption of small amounts of oxygen is also known to be associated with the inhibited autoxidation of a wide variety of monomeric and polymeric hydrocarbons in the presence of phenolic compounds (191). The absorption techniques described previously were designed primarily to detect the major oxidative processes associated with the measurement of induction periods and they revealed no absorption of oxygen during the periods of inhibition of the phenolic antioxidants. Although it must be assumed that some absorption of oxygen occurred during the induction period in the present evaluation of the phenolic antioxidant, the concomitant changes in the mechanical properties of the polymer braid differed significantly from the behaviour associated with the thiodipropionate.

Rather than the general upward trend of torsional period that was observed with the thiodipropionate stabilised specimens, the induction period of the phenol stabilised samples was characterised by the presence of two shallow maxima and two minima. Again, during subsequent work this behaviour was noted with all the phenolic antioxidants in the experiments where the induction period was sufficiently long to be conveniently measurable. Antioxidants in both the propionate phenol (PP) series and the polyphenol (MB) series were found to exhibit this behaviour.

The differing phenomena that were observed with the antioxidants acting by peroxide decomposing and radical trapping mechanisms, indicate that these changes, although of relatively low magnitude, are primarily functions of the stabiliser rather than of the torsional braid technique.

The behaviour of the phenol stabilised systems may be associated with fluctuations in the crystalline structure of the polymer (52, 53, 192, 193) or possibly with variations in oxidative cross-linking reactions (194, 195) as the oxidation progresses. The adhesion of the polymer to the glass fibre support may have varied,thereby influencing the overall torsional properties of the composite, however, the fact still remains that the sulphur and phenolic antioxidants endowed the polymer composites with dissimilar torsional behaviour.

The torsional braid technique and the carefully controlled oven ageing process appeared to offer very reasonable reproducibility both in the measurement of induction period and in the detection of the more minor changes during the induction period. Throughout the torsional braid evaluations the limits of error in the induction period measurement were consistently better than ± 10%. It is interesting that differences in the original torsional periods of the braids did not appear to affect the induction period measurements (Figure 4.3). As experience was gained in the preparation of the braids it was found that variations in the initial torsional periods were reduced, again to within limits of ± 10%. Although it was possible to select samples with similar torsional properties, this was not considered necessary unless an obviously malformed sample was prepared.

A brief evaluation was carried out to determine whether the induction period measurements were being influenced by the factors associated with the accumulation of oxidation products and the diffusion of oxygen in the polymer which were mentioned earlier. Braid samples were prepared using only one strand of glass yarn to give a composite of radius 0.12 ± 0.02 mm (triple strand, 0.30 ± 0.03 mm) and these samples were aged and tested as before. Figure 4.4 shows that polypropylene stabilised with the LPP phenolic antioxidant (again 2×10^{-4} molar concentration) exhibited the same induction period in this and the previous test within the limits of experimental error. It would appear that the accumulation of oxidation products (and oxygen diffusion phenomena) were not having the marked affects that were noticed during the oxidation of polypropylene in a restricted atmosphere. However, in order to avoid any possible confusion the present evaluations were again carried out using samples of the same dimensions throughout.

An interesting feature of the work using thinner specimens was a rather more marked fluctuation of torsional properties during the induction period. The torsional rigidity of these thin samples was considerably lower than was found with the triple stranded samples and it would appear that the considerably longer torsional periods provided greater sensitivity. Unfortunately the single strand samples were rather delicate and, after some experimentation with several different sizes of specimen, it was decided to concentrate upon composities containing three strands of glass yarn.

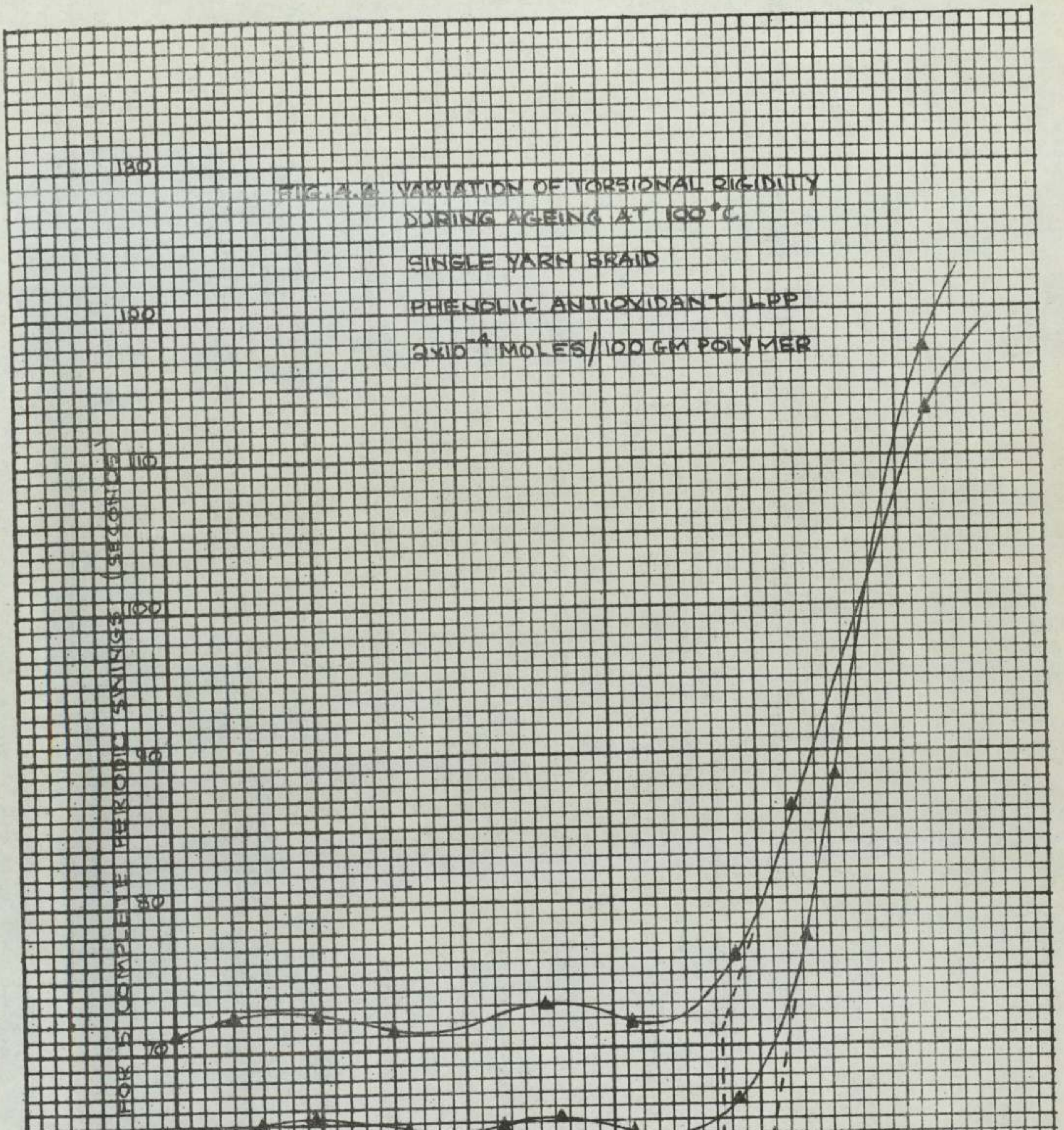


FIG. 4.6 VARIATION OF TORSIONAL RIGIDITY DURING AGEING AT 100°C

SINGLE YARN BRAID

PHENOLIC ANTIOXIDANT LPP

2×10^{-4} MOLES/100 GM POLYMER

4.5 Determination of antioxidant activity - Results.

4.5.1 Propionate substituted phenols and BHT.

The induction periods at 100°C and 140°C of polypropylene stabilised with the propionated phenol (PP) antioxidants, at concentrations of $2x10^{-4}$ moles (ØOH) and $2x10^{-3}$ moles (ØOH)/100 gm polymer, are shown in Figures 4.5 and 4.6.

The samples containing BHT and the lower homologues of the PP series gave induction periods of less than five hours at 140°C. With these extremely short periods of stabilisation, the time for the thermal equilibration of the oven, following the removal of samples for testing, became significant. (It would be possible to measure short induction periods meaningfully if the samples were aged in the actual torsional pendulum device, however).

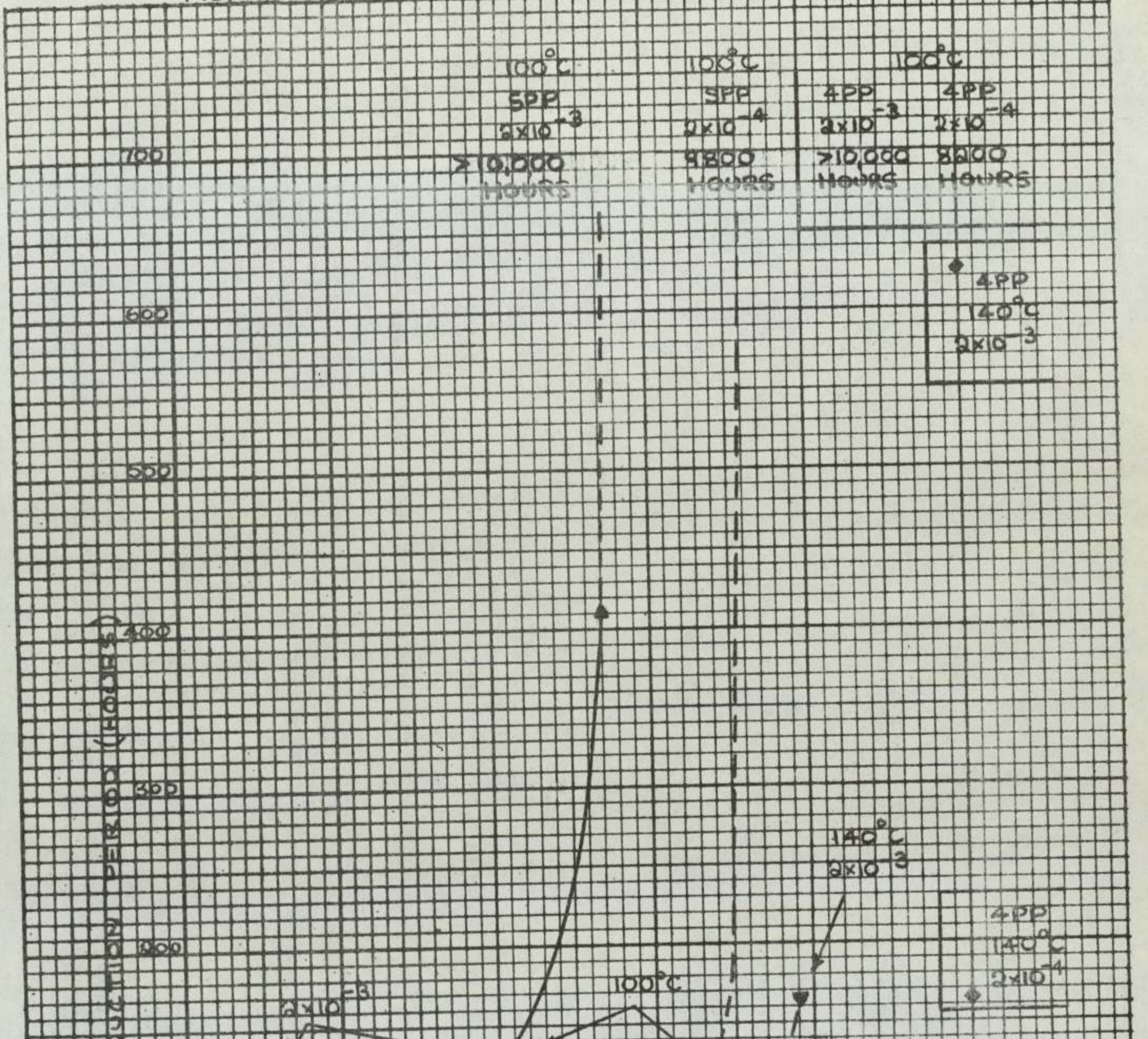
Comparisons of the activities of the antioxidants in the open oven torsional braid test and in the previous tests in decalin and polypropylene using a restricted environment reveal enormous differences in the relative behaviour of the stabilisers. The higher molecular weight homologues exhibited vastly greater relative activities in comparison with their counterparts with the shorter pendant carbon chains. These effects are certainly due to the differing contribution made by the loss of the antioxidants by volatilisation in the differing ageing environments.

The 4PP tetraphenol exhibits a different activity relative to the stearyl substituted phenol (SPP) at the two ageing temperatures; at $2x10^{-4}$ molar (ØOH) concentration, SPP gave a longer induction at 100°C (9800 hours) than the 4PP

Fig. 4.5 ACTIVITY OF PP PHENOLIC ANTIOXIDANTS. POLYPROPYLENE

Antioxidant	2×10^{-4} moles (ØOH)/100 gm polymer		2×10^{-3} moles (ØOH)/100 gm polymer		
	Induction period (hours)	**Average (hours)**	**Induction period (hours)**	**Average (hours)**	
BHT	22; 23; 26.	24	38; 42; 43; 41.	41	100°C
MPP	33; 31; 30; 29.	31	46; 46; 43; 49.	46	
HPP	45; 39; 41.	42	76; 79; 85.	80	
LPP	63; 67; 65; 70; 70.	67	385; 415; 440.	410	
SPP	9350; 9700; 9950; 10,300; 9800.	9800	>10,000	>10,000	
4PP	8150; 7650; 8400; 8600.	8200	>10,000	>10,000	
SPP	115; 105; 117; 115	113	156; 166; 172	165	140°C
4PP	118; 126; 130; 130	126	585; 610; 675	625	

FIG. 4.6 ACTIVITY OF PP PHENOLIC ANTIOXIDANTS. POLYPROPYLENE.



tetraphenol (8200 hours) at the same molar phenolic concentration; the reverse was found at 140°C (SPP, 113 hours; 4PP, 126 hours). It is felt that these results may be an indication of the effects of the relative mobilities and compatibilities of the two antioxidants, superimposed upon the volatility phenomena.

The results will be discussed further when information on the volatility and compatibility of the antioxidants has been presented.

4.5.2 Thiodipropionates.

Figures 4.7 and 4.8 show that the activities (100°C) of the sulphur antioxidants also exhibit a distinct dependence upon molecular weight, however, this dependence differs markedly at the two concentrations.

The evaluations in decalin and polypropylene by oxygen absorption demonstrated a marked change in antioxidant behaviour at different concentrations and in polypropylene this occurred between the concentrations $2x10^{-4}$ and $8x10^{-4}$ moles/100 gm. Further, in decalin the activity of distearyl thiodipropionate was shown to increase dramatically with increasing concentration.

It would appear that a similar pattern of behaviour is being observed in the present work; however, the effect is only noticeable with the higher homologues of the antioxidant series. The volatilisation of the lower molecular weight homologues appears to be so dominating that

Fig. 4.7 ACTIVITY OF TP THIODIPROPIONATE ANTIOXIDANTS. POLYPROPYLENE

Antioxidant	$2x10^{-4}$ moles/100 gm polymer		$2x10^{-3}$ moles/100 gm polymer		
	Induction period (hours)	Average (hours)	Induction period (hours)	Average (hours)	
DMTP	21; 23; 24; 27.	24	42; 44; 48.	45	100°C
DHTP	26; 25; 29; 28.	27	46; 46; 43; 44.	45	
DLTP	64; 59; 66; 66; 65.	64	875; 810; 795.	820	
DSTP	126; 133; 129; 131.	130	4450; 4250; 4050; 4400.	4300	

FIG. 4.8 ACTIVITY OF TP THIODIPROPIONATE ANTIOXIDANTS. POLYPROPYLENE.

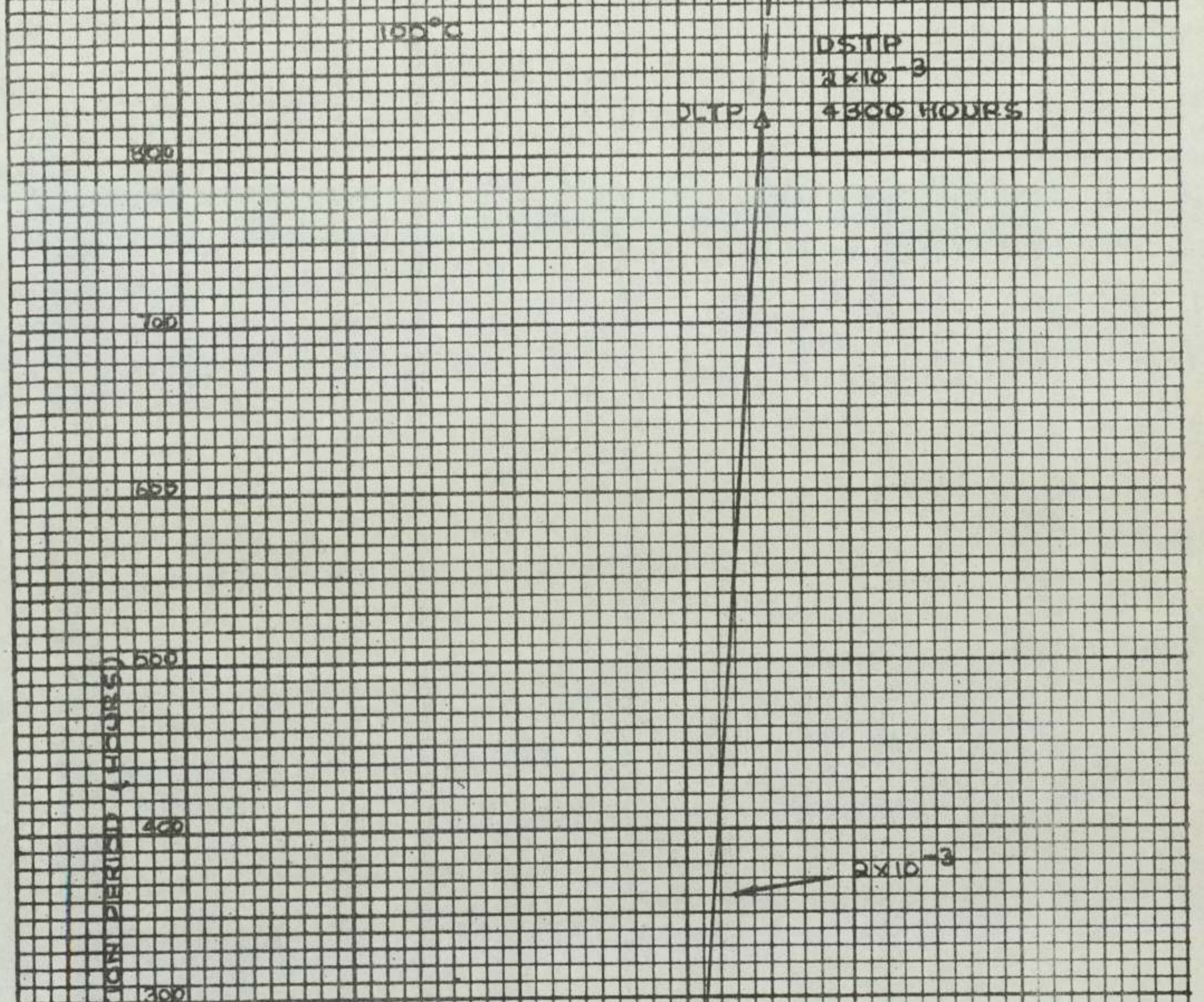
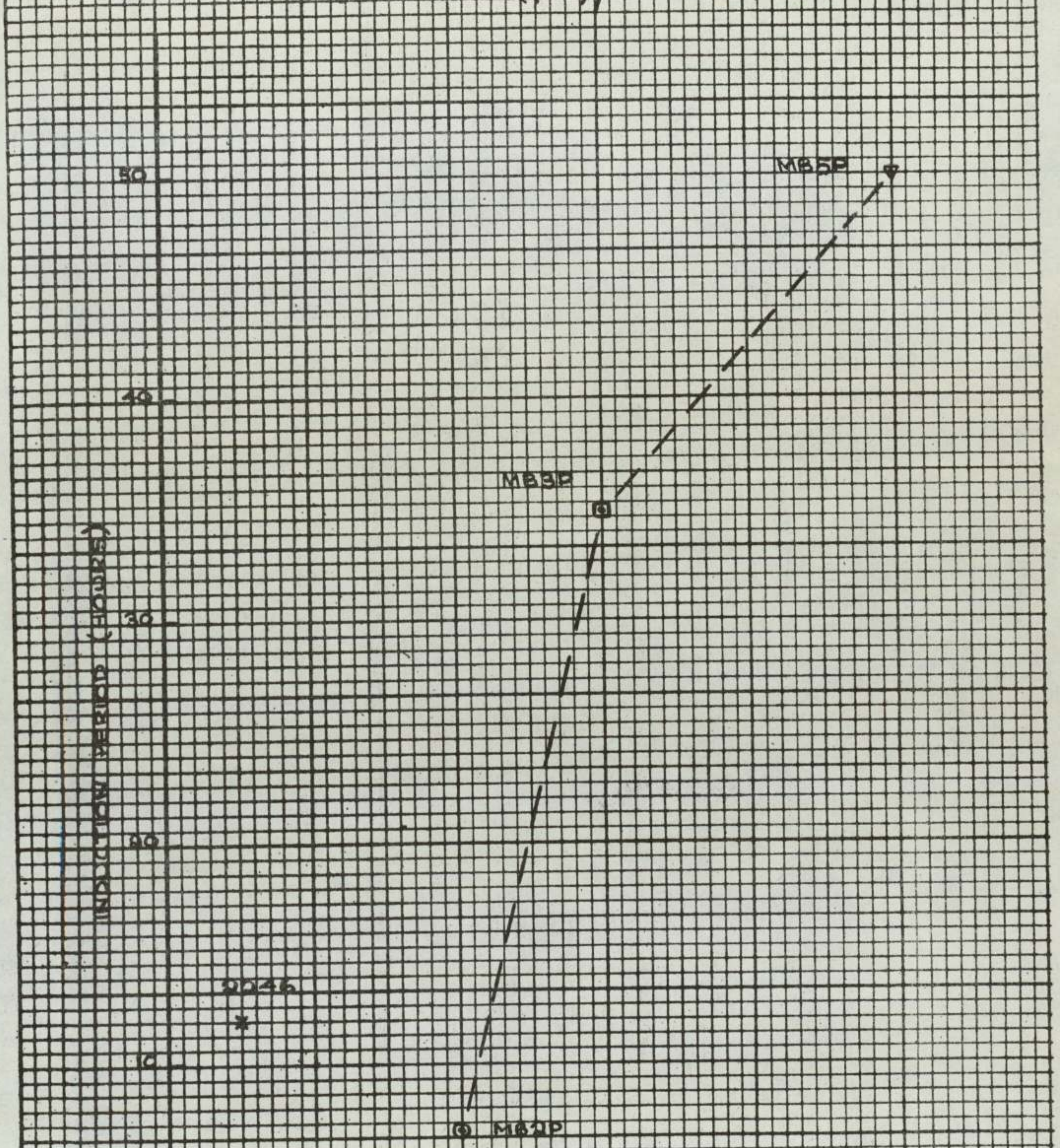


Fig. 4.9 ACTIVITY OF MB POLYPHENOLIC ANTIOXIDANTS. POLYPROPYLENE

Antioxidant	$2x10^{-3}$ moles (ØOH)/100 gm polymer		
	Induction period (hours)	Average (hours)	
2246	11.2; 11.9; 12.6; 12.2	12	140°C
MB2P	6.9; 7.4; 6.8.	7	
MB3P	37; 36; 36; 32; 36.	35	
MB5P	44; 52; 53; 48; 51.	50	

FIG. 4.10 ACTIVITY OF MB POLYPHENOLIC ANTIOXIDANTS, POLYPROPYLENE.

2×10^{-3} MOLES (ΦOH)/100 GM POLYMER. 140°C



their concentration (or the concentration of their active breakdown products) falls rapidly below the critical concentration for high activity, during the early stages of ageing.

The induction periods at 140°C were all extremely short and only the induction period for DSTP was measured satisfactorily using the torsional pendulum (29 hours).

4.5.3 Polyphenols.

Figures 4.9 and 4.10 show the activities of the polyphenolic antioxidants at 140°C.

The activities of the antioxidants in this series exhibited a general upward trend as the number of phenolic rings in the compounds increased. This behaviour contrasts markedly with that observed in decalin and polypropylene in a restricted atmospheric environment. The upward trend in activity is not completely regular, however, and it would appear that the effects of inherent antioxidant activity, volatility, compatibility and mobility are exerting varying degrees of influence through the antioxidant series; these effects will be discussed later.

5. VOLATILITY AND COMPATIBILITY

5.1 Volatility.

In order to assess the contributions made by the volatilities and compatibilities of the antioxidants to their activities in the preceding evaluations, these parameters were measured in isolation.

The former were measured in two ways; the volatilisation of the pure antioxidants was assessed by a simple weight loss technique and the volatilisation from polypropylene film was assessed by spectrophotometry. It was hoped that a comparison of the results obtained from the two methods would give some indications of the rate of diffusion of the antioxidants in the polymer.

5.2.1 Volatilities of the pure antioxidants. Method.

In the first chapter it was seen that various techniques have been developed to estimate the effect of antioxidant volatility during both accelerated ageing tests and the processing and service life of polymers. These included the measurement of the vapour pressure of pure antioxidant (74, 196); the estimation of antioxidant efficiency after storing stabilised polymer, at elevated temperatures, in an inert atmosphere (67); the direct measurement of weight loss from a sample of pure antioxidant stored at elevated temperatures (70, 71).

In the present work a simple weight loss method using pure antioxidant was adopted, but, rather than storing in air at elevated temperatures, a closed cell system,using a static nitrogen atmosphere,was devised, in an attmpt to avoid any direct oxidative reactions of the antioxidants.

The volatility cell is shown in Figure 5.1. 5gm antioxidant was placed in a 20 ml low-form beaker of internal diameter 3.5 cm. The open surface area of antioxidant was therefore 9.6 cm^2.

The beaker was placed in the chamber of the volatility cell, which was immersed in an oil bath at the required temperature ($\pm$ 0.2°C.). The top of the cell was closed by a cold finger through which cooling water (15°C - 18°C) was passed. The cell was quickly purged with nitrogen through the capillary tubes in the cold finger and, after two minutes had elapsed for gas expansion, the purging tubes were sealed with serum caps.

The beaker was periodically weighed to determine the amount of antioxidant which had volatilised and condensed on the cold finger.

The gas purging procedure was repeated and the cold finger was cleaned each time the beaker was replaced in the cell.

5.2.2 Volatilities of the pure antioxidants. Results.

The differences in the volatilities of the antioxidants

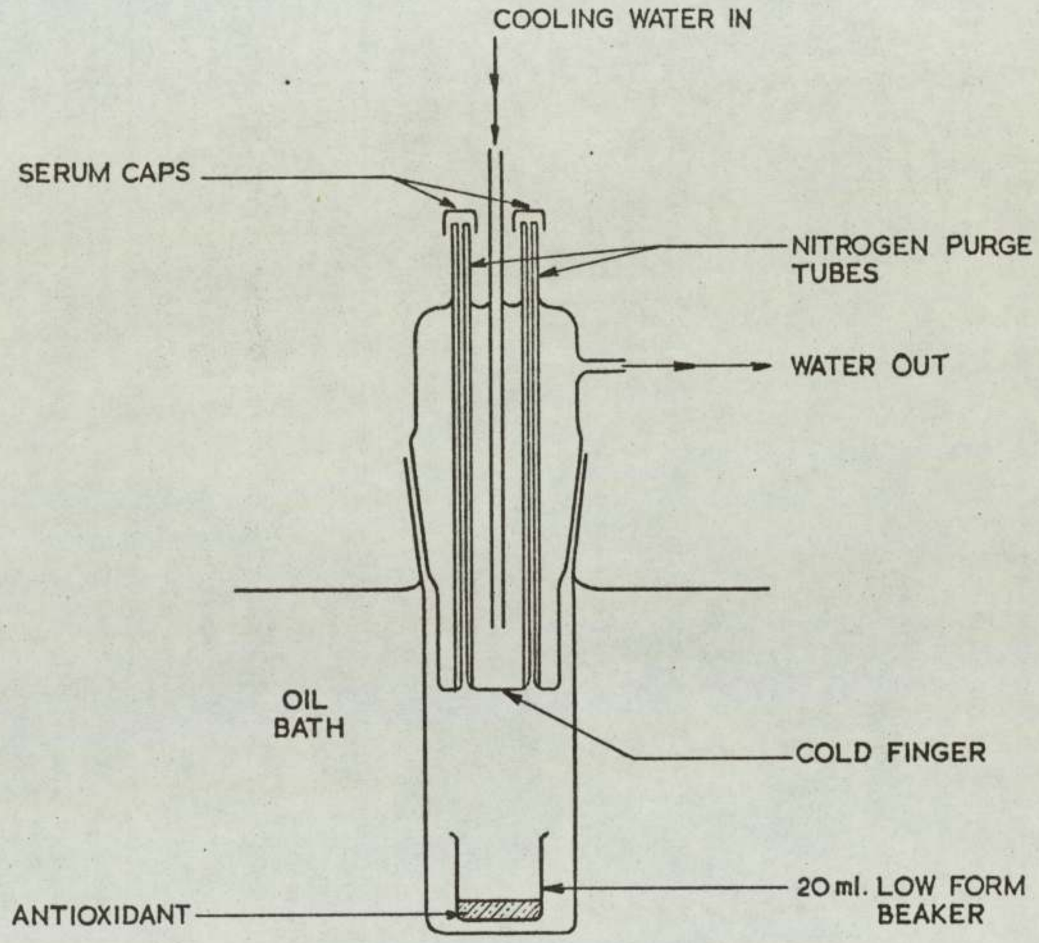


FIG. 5.1 APPARATUS FOR MEASUREMENT OF ANTIOXIDANT VOLATILITY.

were found to be extremely large and in order to obtain conveniently measurable weight losses on all the antioxidants, temperatures of 100°C, 140°C, 180°C and 220°C were used.

The procedure for the determination of volatility was found to be very reproducible; typical weight loss measurements, at 140°C, for four of the antioxidants, are given in Figure 5.2. The plot of weight loss by volatilisation against time is a straight line, but in most cases it does not pass through zero due to the initial volatilisation of small amounts of solvent or other volatile impurities (70). The strict linearity of the plots after this initial period confirms that the antioxidants were probably not undergoing reaction at the test temperature.

The volatilities of all the propionated phenol (PP) and thiodipropionate (TP) antioxidants are shown in Figure 5.3. (Unfortunately, only very small quantities of the polyphenolic (MB) antioxidants could be provided by the Royal Aircraft Establishment and these materials were not evaluated).

Semi-log plots of evaporation loss against temperature (Figure 5.4) exhibit straight line relationships with similar slopes for both series of stabilisers. An examination of previous workers' results (74) reveals the same type of behaviour, with various amine stabilisers, in that, although the vapour pressures obeyed an Arrhenius relationship, weight loss techniques produced curves on a semi-log/reciprocal temperature plot and linear relationships on semi-log/temperature plots.

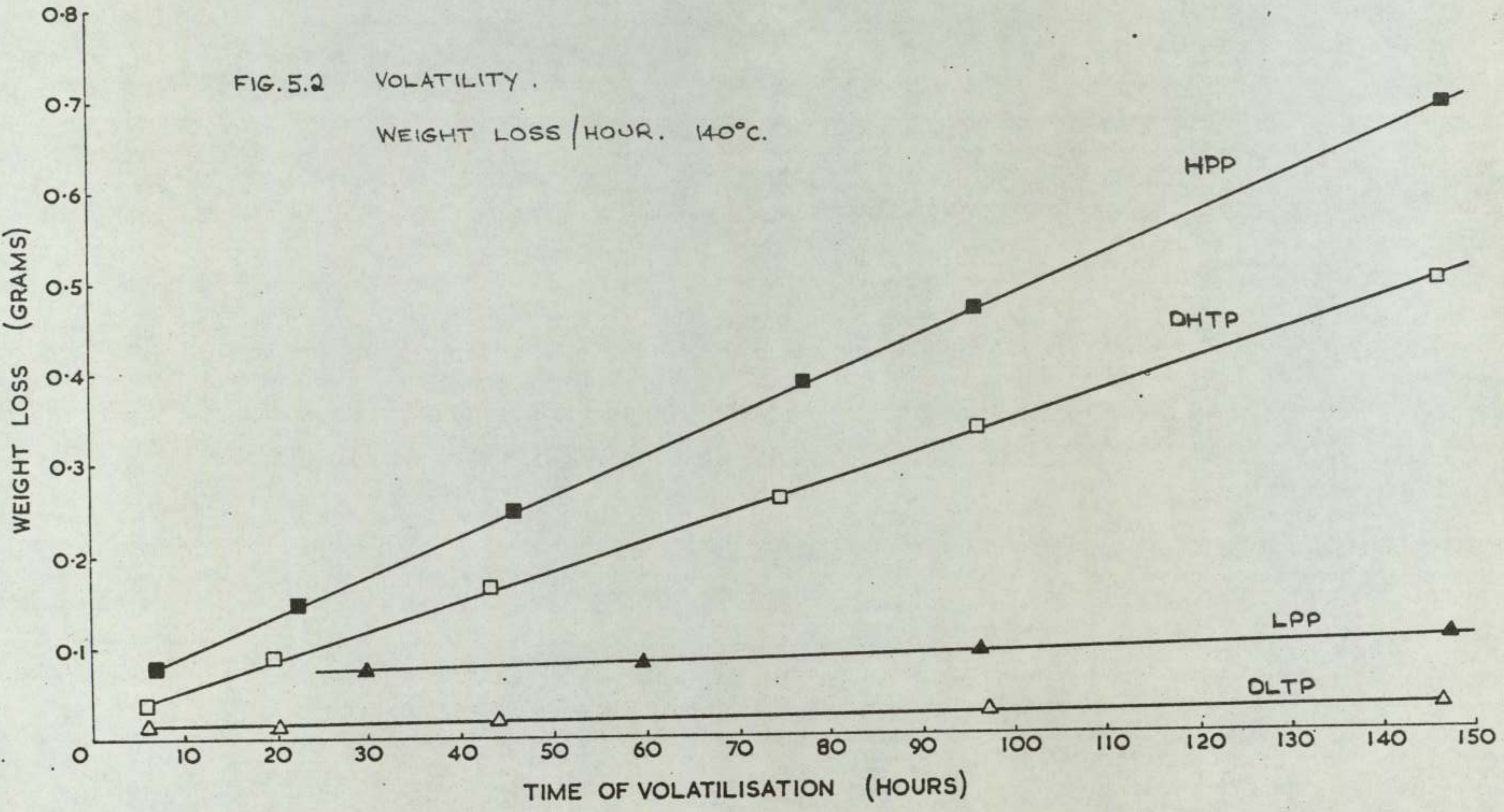


FIG. 5.2 VOLATILITY.

WEIGHT LOSS/HOUR. 140°C.

Fig. 5.3

Antioxidant	Volatility; weight loss/hour (gm/hour)				
	100°C	140°C	180°C	220°C	
BHT	1050				x 10^{-4}
MPP	37.5	480			
HPP	4.55	43.7	510		
LPP		2.27	36.3	312	
SPP		0.392	5.56	72	
4PP			1.16	13.32	
DMTP	350	2910			
DHTP	2.78	32.7	340		
DLTP		0.297	4.16	53.3	
DSTP		0.136	1.66	19.55	

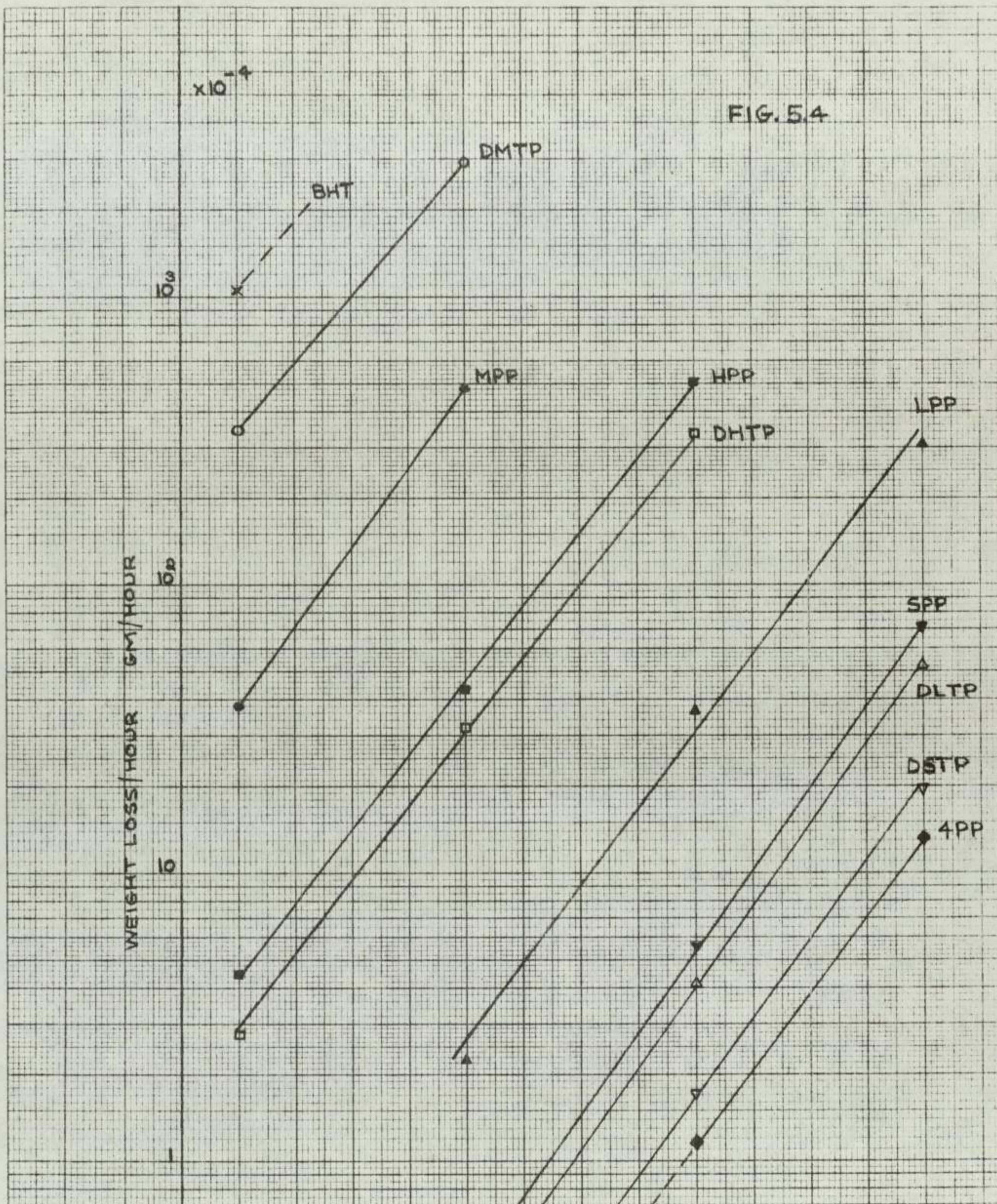

$\times 10^{-4}$
DMTP
BHT
10^3
MPP
HPP
DHTP
LPP
10^2
SPP
DLTP
DSTP
4PP
10
1
0·1
WEIGHT LOSS/HOUR GM/HOUR
100
120
140
160
180
200
220
TEMPERATURE OF VOLATILISATION °C

FIG. 5.4

The enormous differences in the volatilities of the antioxidants are self-evident. The relationships between the molecular weights and the volatilties of the antioxidants are shown in Figures 5.5 and 5.6. Comparing anti-oxidants of the same molecular weight from the PP and TP series, the thiodipropionate compounds are noticeably less volatile, presumably due to the increased molecular interaction associated with the two ester groups (71). However, the differences in volatility between the phenol and sulphur series decrease, and volatility becomes more dependent solely upon molecular weight, as the length of the less polar aliphatic side chain is increased.

The semi-log plots of volatility/length of pendant carbon chain and volatility/molecular weight (Figures 5.5 and 5.6) show a linear relationship up to a molecular weight of approximately 500 for both series of antioxidants. An increase in molecular weight above this level does not bring a concomitant equivalent reduction in volatility. At a molecular weight in the region of 1200 (e.g. antioxidant 4PP), a considerable further increase in molecular weight would be required to significantly reduce volatility.

5.2.3 Volatilities of antioxidants from polypropylene films.

Method.

The volatilisation of the antioxidants from polypropylene film was followed spectrophotometrically using UV spectroscopy for the phenolic antioxidants and IR spectroscopy for the thiodipropionates. Sheets of polypropylene ($10 \pm 0.5 \times 10^{-3}$ **inches**;

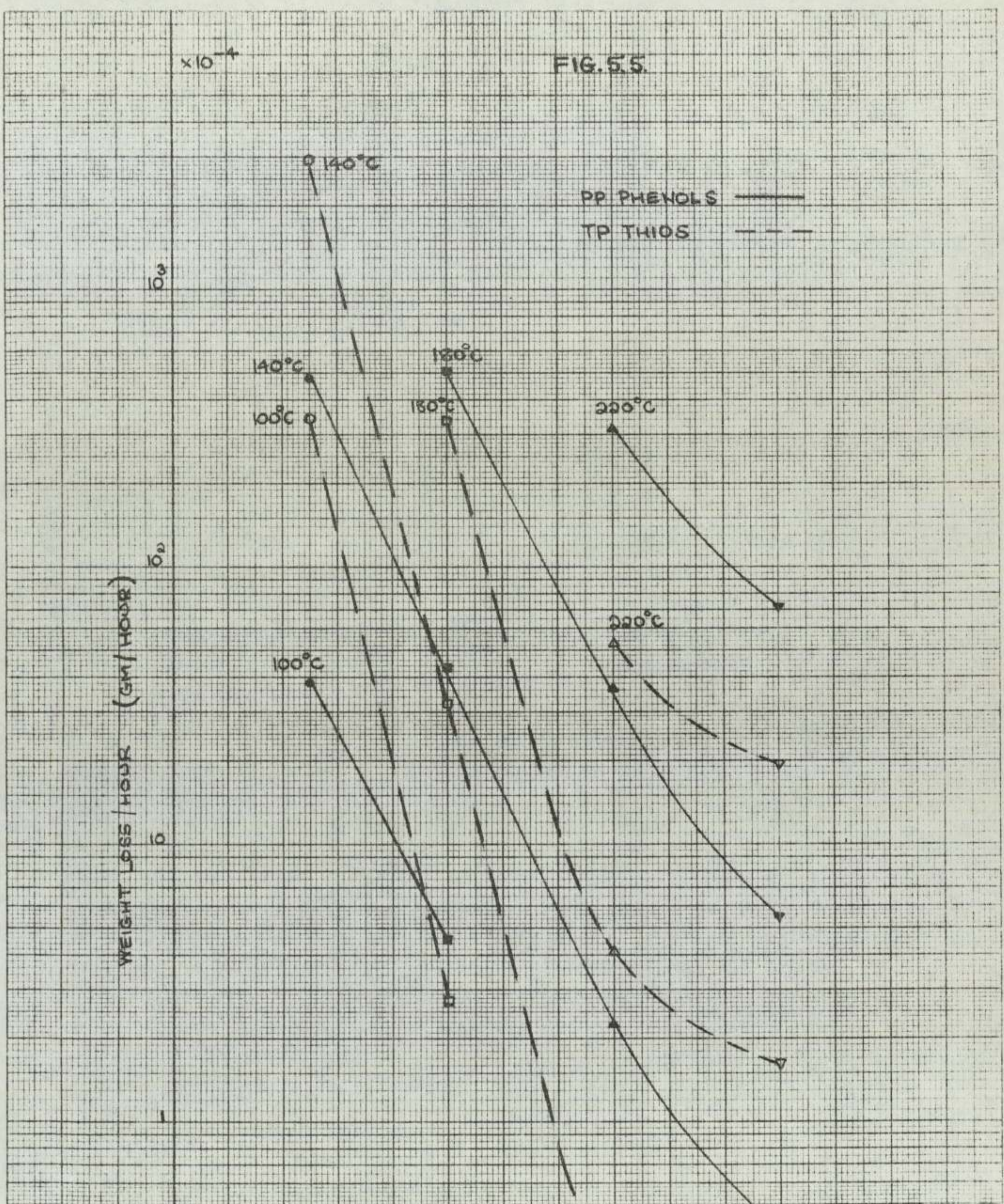

×10⁻⁴
140°C
PP PHENOLS
TP THIOS
10³
140°C
180°C
100°C
180°C
220°C
10²
WEIGHT LOSS / HOUR (GM/HOUR)
220°C
100°C
10
1
0·1
0 2 4 6 8 10 12 14 16 18 PP SERIES
0 4 8 12 16 20 24 28 32 36 TP SERIES
NUMBER OF CARBON ATOMS IN PENDANT SIDE CHAINS

FIG. 5.5.

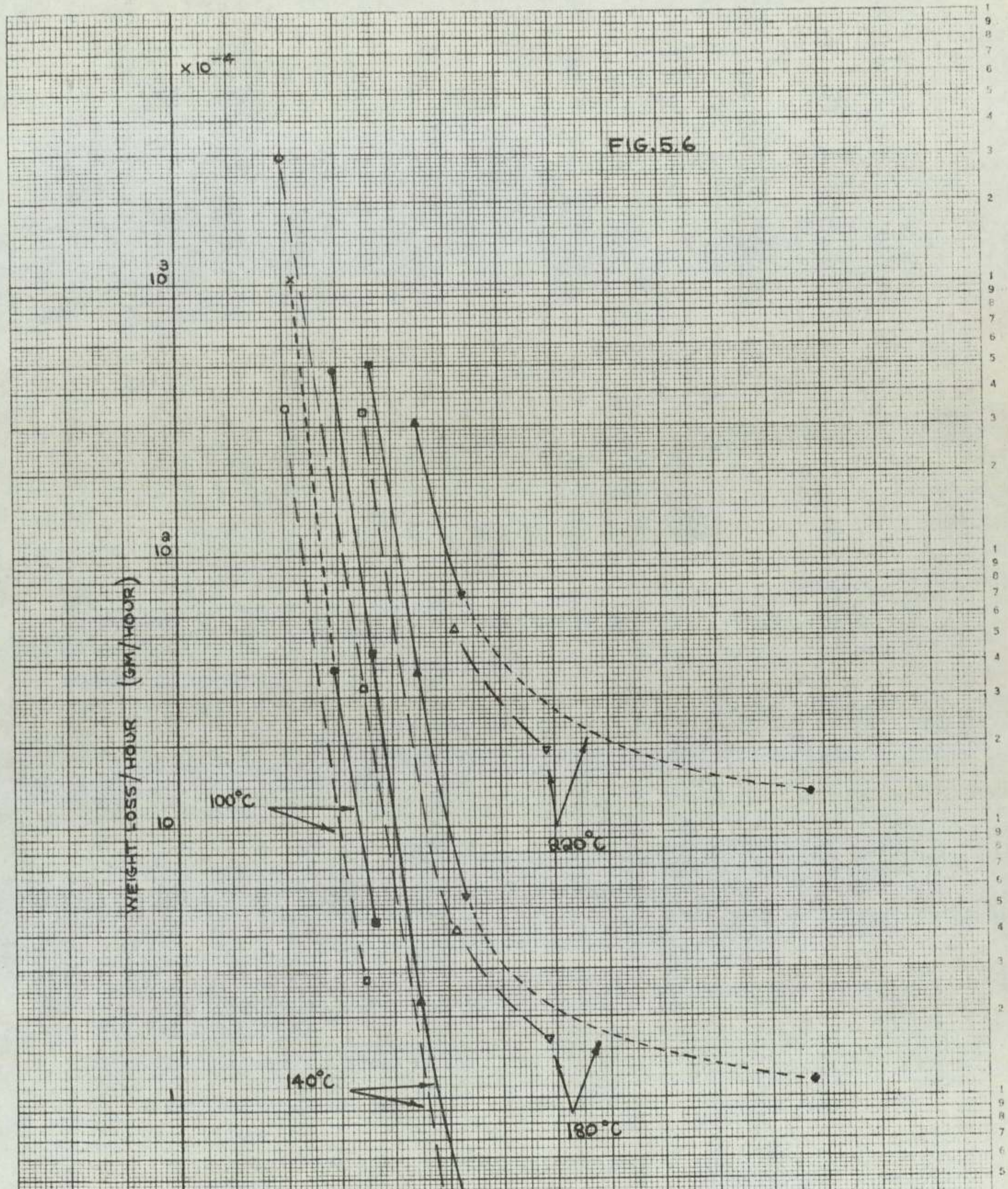


FIG. 5.6
×10⁻⁴
WEIGHT LOSS/HOUR (GM/HOUR)
10³
10²
10
1
0.1
100°C
140°C
180°C
220°C
DMTP
BHT
MPP
DHTP
HPP
LPP
DLTP
SPP
DSTP
4PP
100
200
300
400
500
600
700
800
900
1000
1100
1200
MOLECULAR WEIGHT

0.254 ± 0.012 mm thick) were pressed from stabilised polymer using exactly the same technique that was described previously (Chapter 3). The concentration of the antioxidants was 2×10^{-3} moles /100gm polymer and, as before, the phenolic antioxidants were added on a molar (ϕ OH) basis. Square samples (2.5 cm) were cut from the pressed sheets to fit directly into the sample slots of the spectrophotometers.

An exactly similar sample of unstabilised polypropylene was prepared, to be used as the blank in the spectrophotometry.

The stabilised samples were evaporated in the cells of the Wallace oven at 140°C, under nitrogen. All the precautions that were adopted for the torsional braid evaluation (Chapter 4) were carefully followed, in an attempt to improve the reproducibility and eliminate any cross-contamination of the antioxidants. The seven cells of the oven were again supplied from a common nitrogen source flowing at 28.3 litre/hour (1 ft.^{3}/hour), the same as the oxygen flow rate in the torsional braid evaluation.

The UV absorbances of the samples stabilised with the PP phenolic antioxidants were determined using a Unicam SP800 spectrophotometer in the conventional fashion. The absorbance of the phenolic B band (near 282 mμ) was measured directly from the spectral scan of the whole peak. The absorbance measurements were always carried out against the same reference sample of unstablilised polypropylene. However, it was found that slight variations in the thickness of the experimental samples produced small variations in the zero absorbance readings. To eliminate these variations, the absorbance was always adjusted to zero at 304 mμ, at the base of the phenolic B band peak, before the spectral scan was commenced.

The IR absorbances of the samples stabilised with the TP thiodipropionate antioxidants were determined using a Unicam SP 200 spectrophotometer. The absorbance of the ester frequency near 5.8μ (1720 cm $^{-1}$) was measured and a zero adjustment was made at 5.62μ (1780 cm $^{-1}$) in an analogous manner to that used in the UV work.

In general two samples of polypropylene film were evaporated under nitrogen for each antioxidant under examination.

It was found impossible to follow the evaporation of the MB polyphenol antioxidants using either UV or IR spectroscopy. Although the phenolic B band peak appeared at approximately 286 mμ, the extremely strong K band peak extended to longer wave lengths than was observed in the PP phenols and partly obscured the peak under examination. Repeated attempts were made to obtain reproducible results but unfortunately minor fluctuations in the shape and size of the K band peak obscured the reproducible measurement of variations in the size of the B band. Similar problems were encountered in IR spectrometry where it was found impossible to identify an unconfused peak which could be monitored during the volatilisation process.

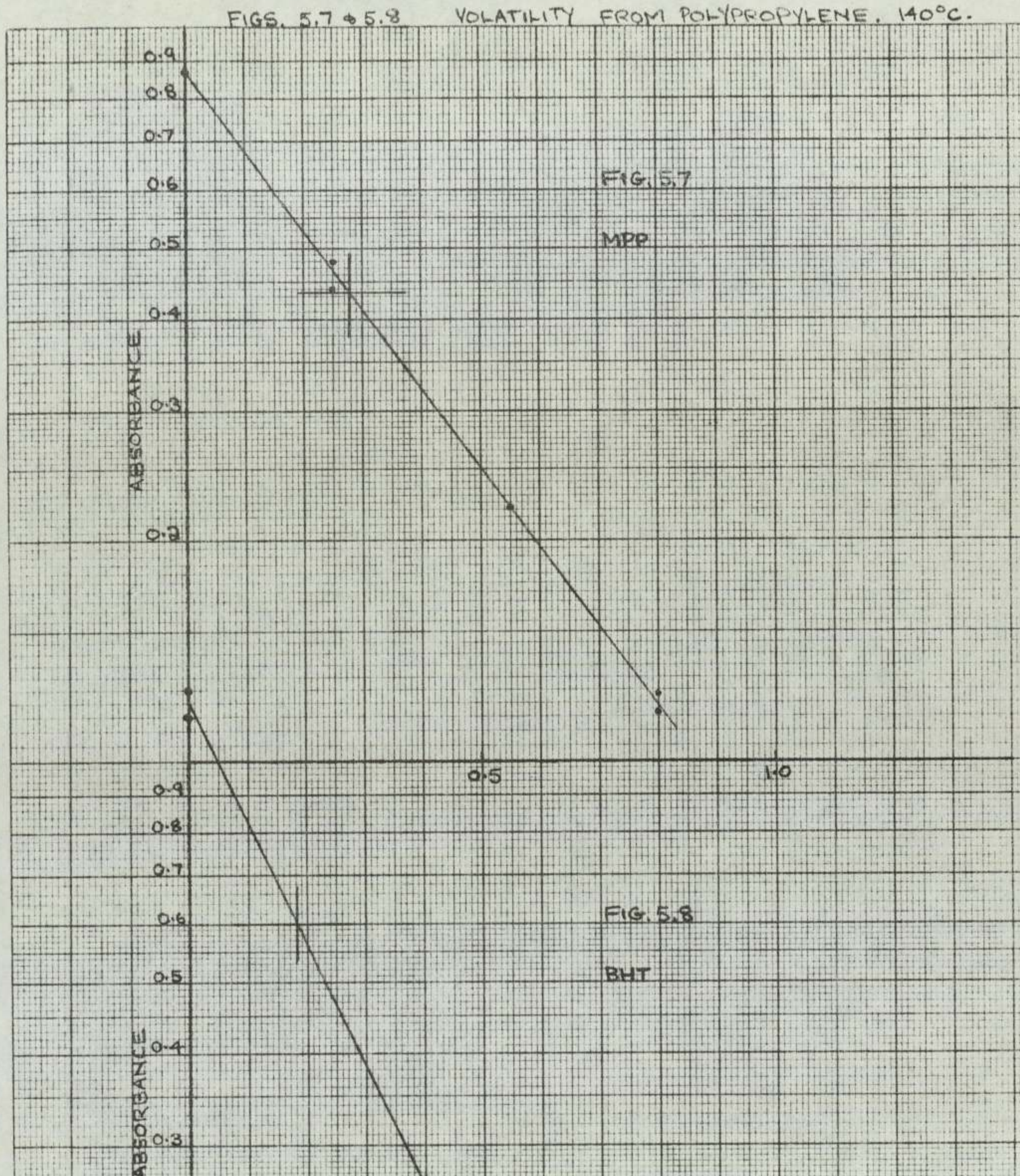
The loss of the antioxidants from the polypropylene films by volatilisation (140°C) is demonstrated in Figures 5.7 to 5.16 and the half-life of volatilisation is indicated for each antioxidant. The direct use of absorbance measurements in determining these half-lives depends upon the linearity of the absorbance/ concentration relationship for the antioxidants in polypropylene. The extinction coefficients for all the antioxidants were not determined; however, linearity of this relationship was demonstrated for the SPP phenolic antioxidant and the DSTP thiodipropionate antioxidant.

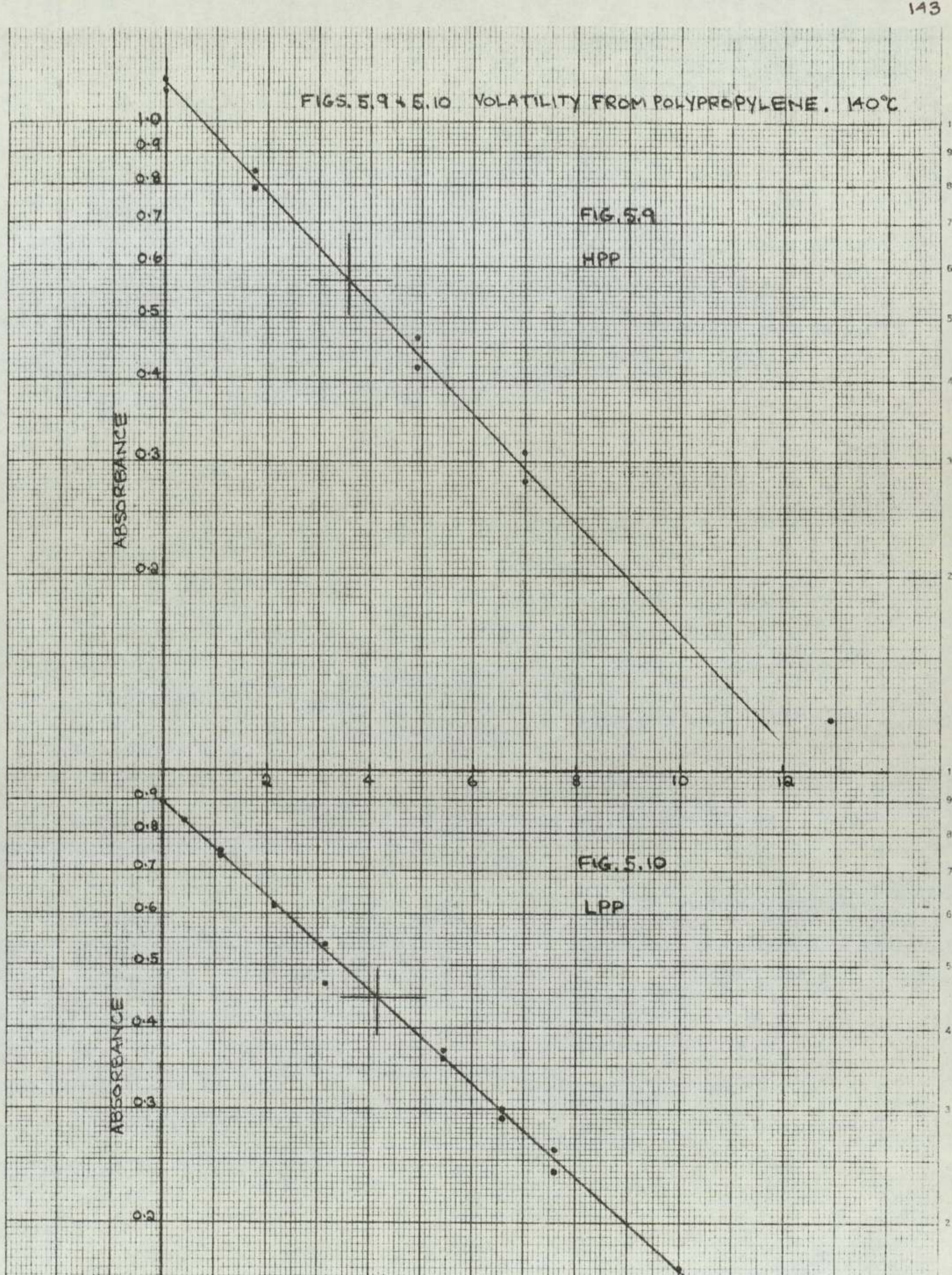
Where the two samples that were examined for each antioxidant gave very similar absorbance plots,a single line has been drawn through the accumulated points in Figures 5.7 to 5.14. If slightly greater variations are apparent between the two samples each has been treated individually and the average half-life quoted (Figures 5.15 and 5.16). Any variations appear to be due to slight differences in the initial antioxidant concentration and are probably associated with the techniques of sample preparation.

The half-lives of all the antioxidants are tabulated in Figure 5.17,together with their reciprocals,which give a direct means of comparison of the volatilities of the antioxidants from polypropylene and in the pure state.

This comparison is given in Figure 5.18,where it will be seen that a very close correlation exists between the two methods of determination. The comparison is taken further in Figure 5.19 where a log/log plot of the results of the two investigations is seen to show an amazingly linear

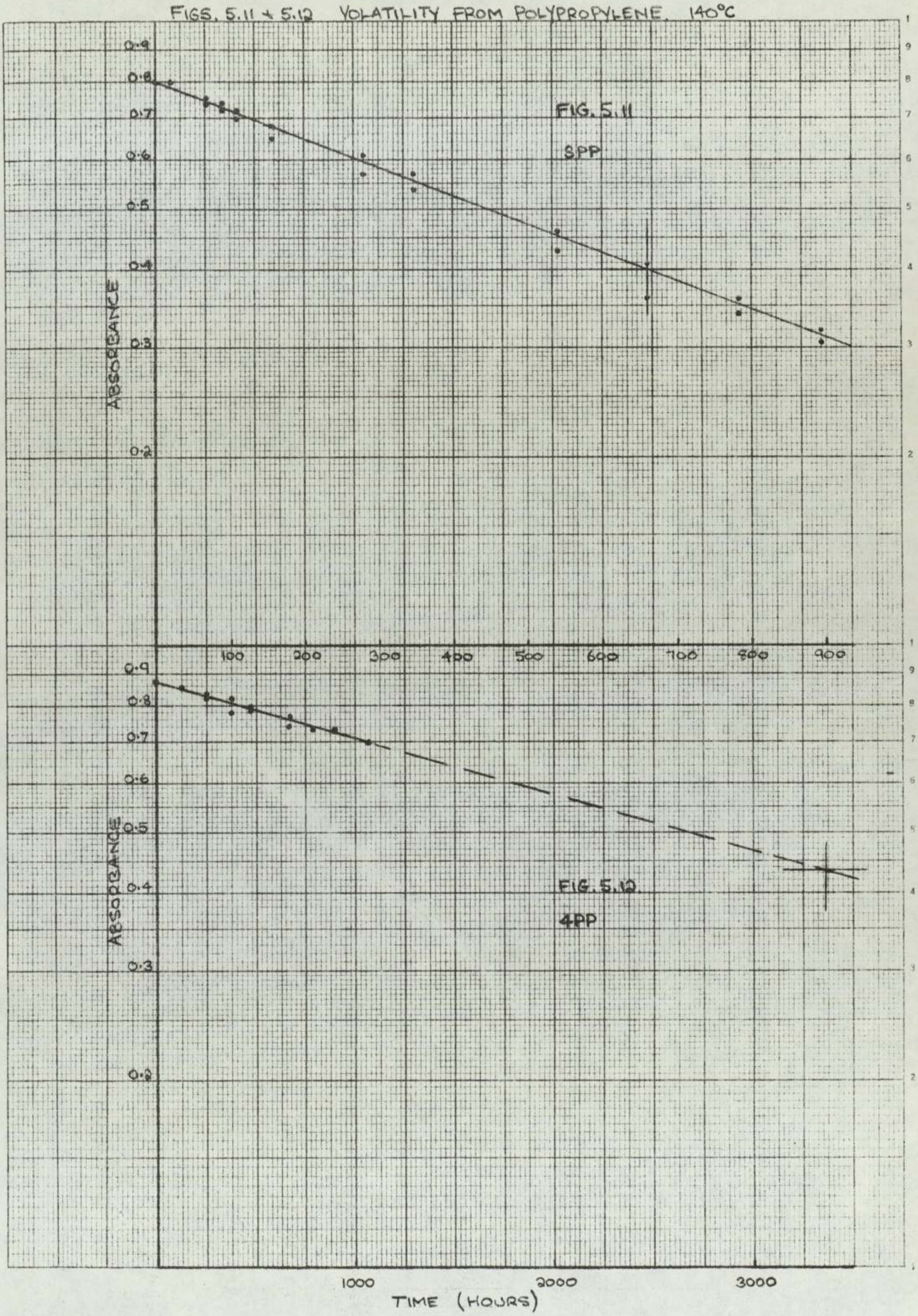
FIGS. 5.7 & 5.8 VOLATILITY FROM POLYPROPYLENE. 140°C.



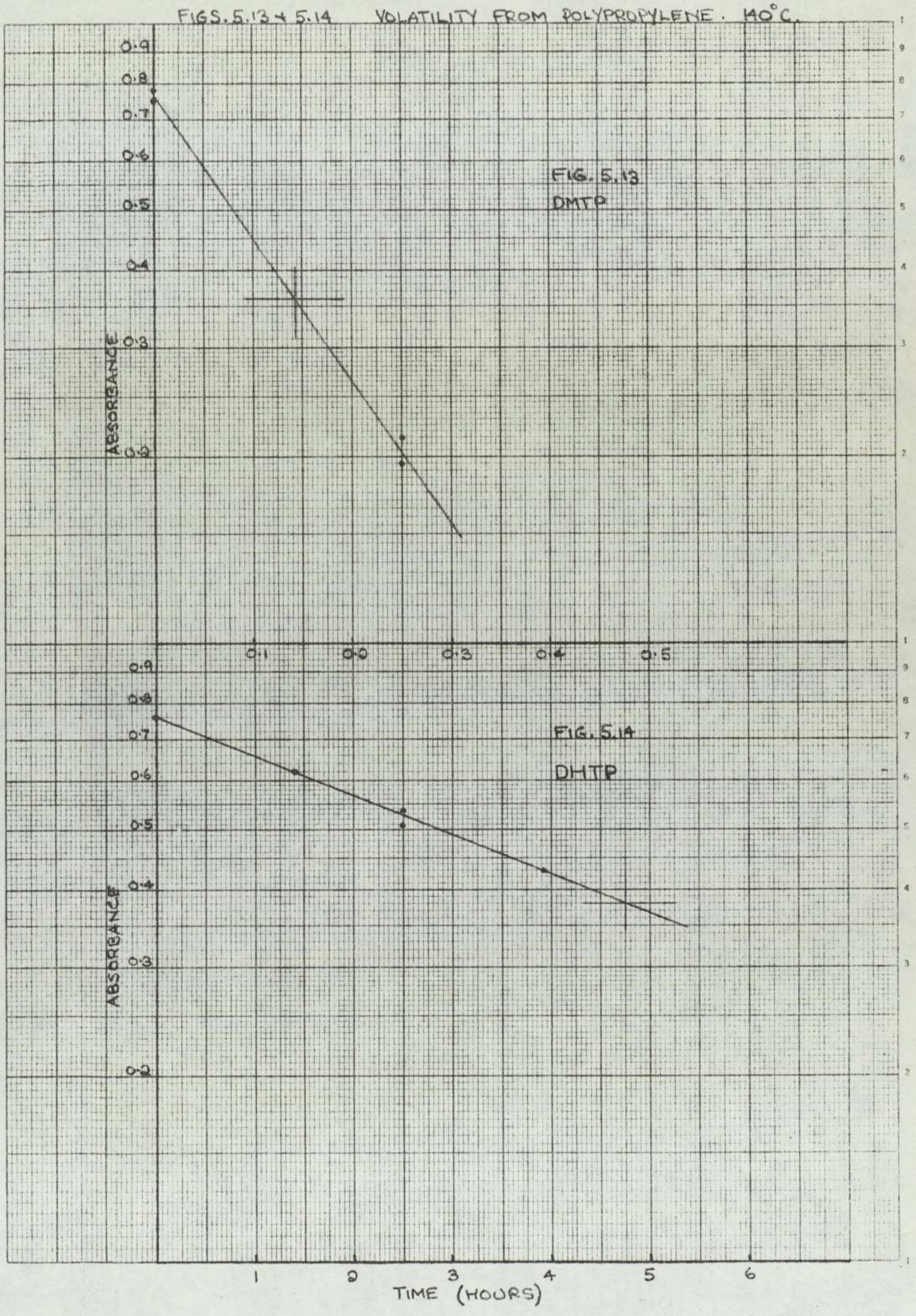


FIGS. 5.9 & 5.10 VOLATILITY FROM POLYPROPYLENE. 140°C

FIGS. 5.11 + 5.12 VOLATILITY FROM POLYPROPYLENE. 140°C



FIGS. 5.13 + 5.14 VOLATILITY FROM POLYPROPYLENE. 140°C.



FIGS. 5.15 + 5.16 VOLATILITY FROM POLYPROPYLENE, 140°C

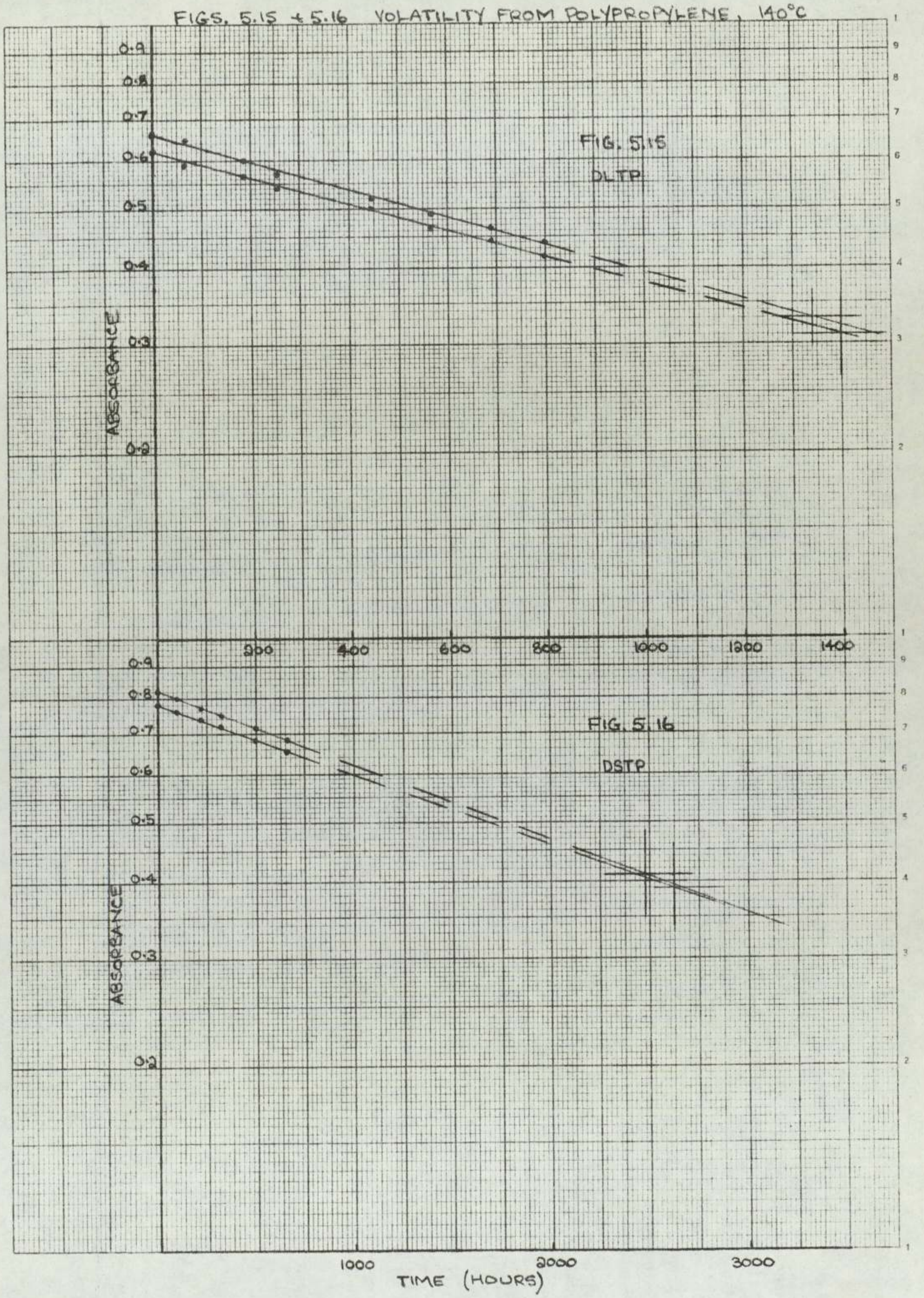


Fig. 5.17. Volatility from polypropylene. 140°C. Half-life.

Antioxidant	Half-life of volatilisation (hours).	Reciprocal half-life (hours^{-1}).	
BHT	0.09	11,100	x 10^{-3}
MPP	0.28	3,570	
HPP	3.6	278	
LPP	83	12.0	
SPP	660	1.52	
4PP	3360	0.298	
DMTP	0.14	7,150	
DHTP	4.7	213	
DLTP	1370	0.730	
DSTP	2550	0.392	

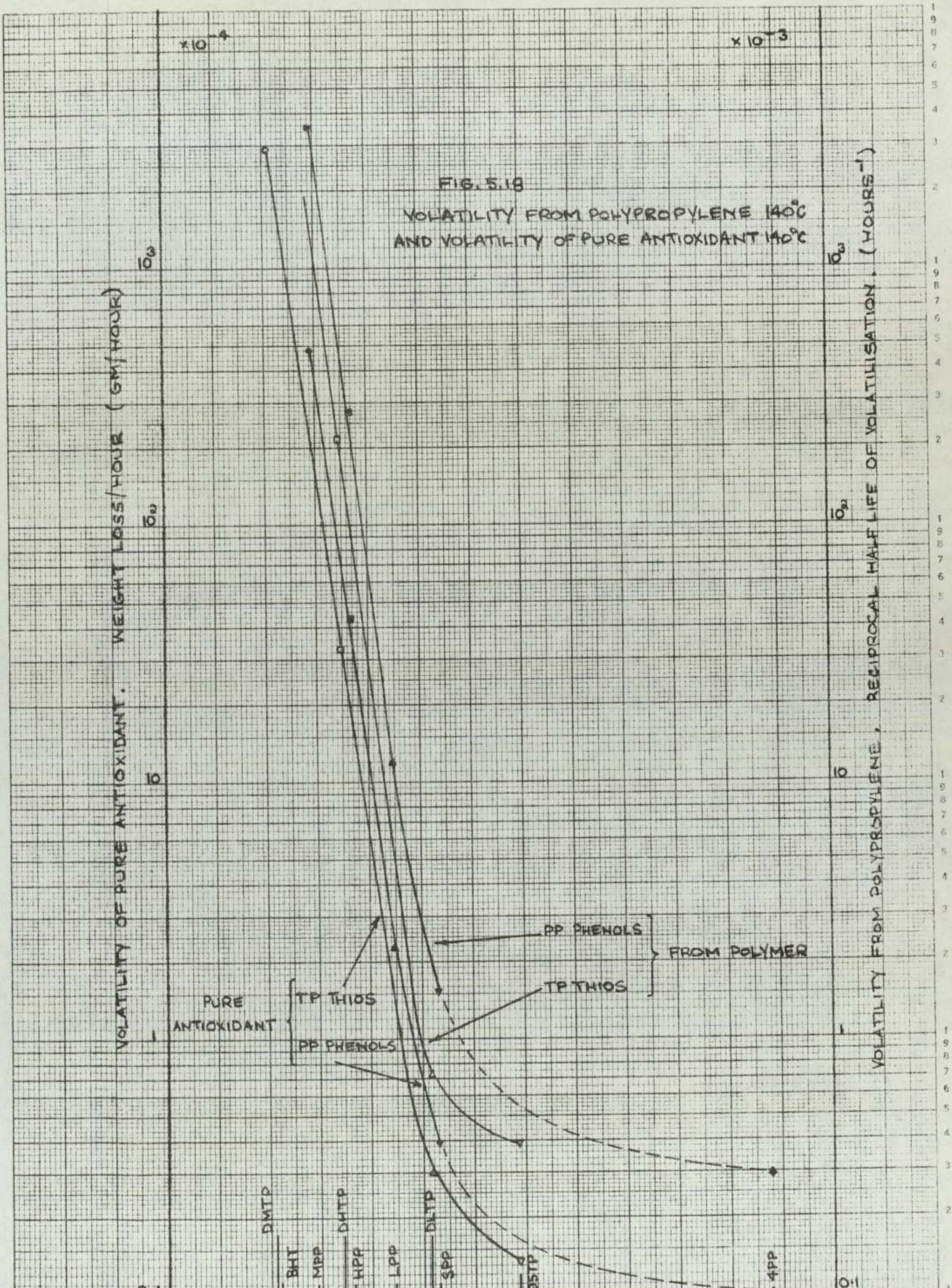


FIG. 5.18
VOLATILITY FROM POLYPROPYLENE 140°C
AND VOLATILITY OF PURE ANTIOXIDANT 140°C

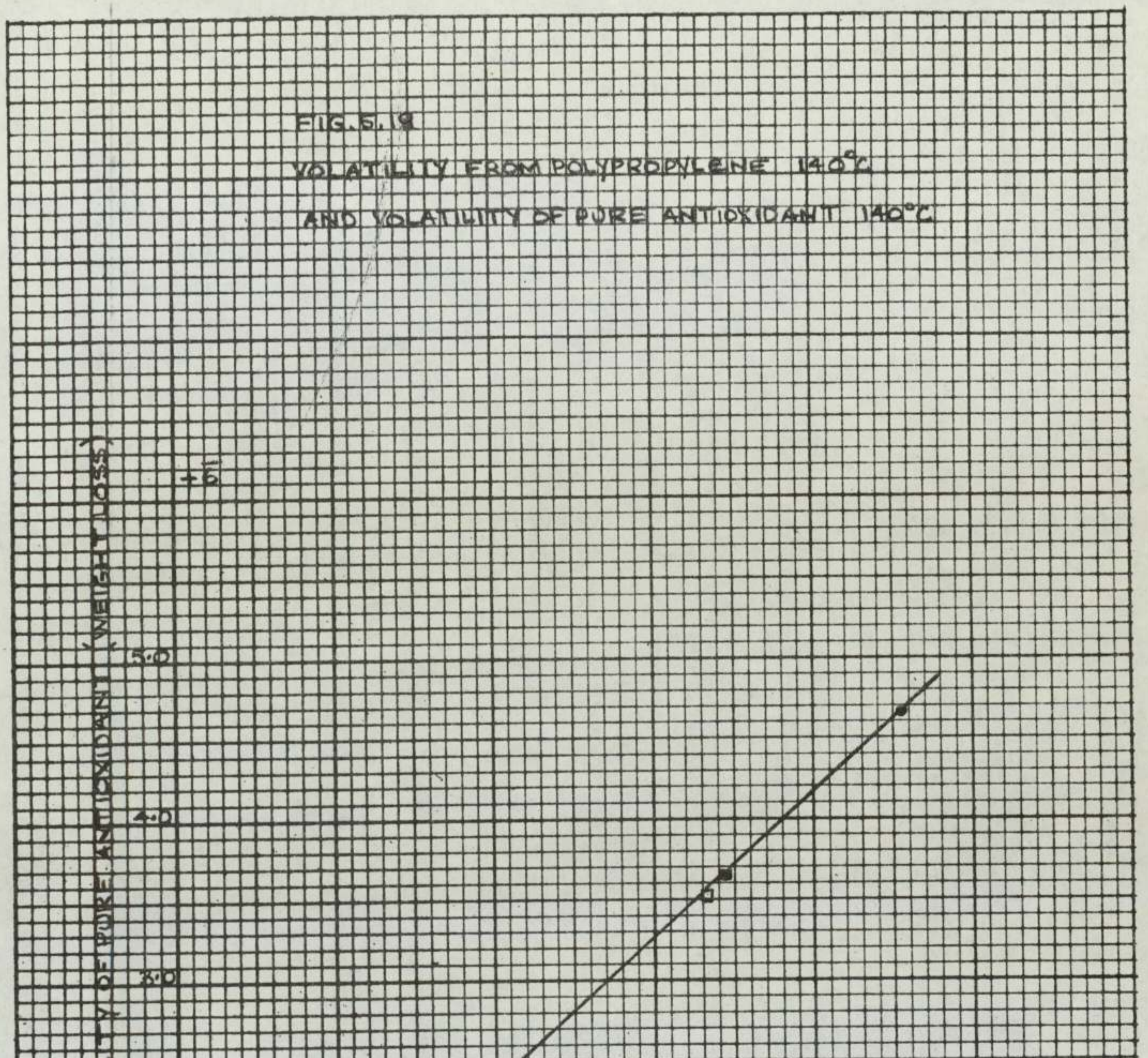


FIG. 5.19

VOLATILITY FROM POLYPROPYLENE 140°C AND VOLATILITY OF PURE ANTIOXIDANT 140°C relationship. Furthermore, this linear relationship forces the surprising conclusion that the volatilisation of the antioxidants from polypropylene does not appear to be controlled by any compatilibility or diffusion phenomena which are related to the molecular weight or molecular shape of the antioxidants. Spacht and co-workers (74) demonstrated that the rate of volatilisation of various amine and phenolic antioxidants from natural rubber was inversely related to the thickness of the polymer sample, and these workers pointed out that the volatility of the antioxidants from thin specimens approached the volatility of the pure compounds. It would appear that a similar situation exists in the present evaluations, in that the polypropylene samples (10×10^{-3} inches thick) had a sufficiently large surface/volume ratio to allow the antioxidants to evaporate without the constraints of compatibility and mobility effects becoming apparent.

The relationship between antioxidant volatility and activity will be discussed in the next chapter; however, an interim comment must be made in order to explain the motivation behind the next investigation. It will be noticed that although the half-life for the disappearance of the SPP stearyl substituted phenol is 660 hours at 140°C, the induction period of stabilisation which this antioxidant produced in polypropylene (torsional braid evaluation, 140°C) was only 165 hours. In order to obtain further information on the relationship between these two parameters, the volatility of the SPP antioxidant from polypropylene was determined in an oxygen atmosphere. The experimental procedure was exactly the same as that used in the investigations involving the inert atmosphere.

The absorbances were measured by both UV and IR spectroscopy. The UV evaluation was again based upon the phenolic B band and fortunately the generation of chromophores in the oxidising polymer did not appear to interfere with the determination. However, in order to confirm that no other interferences, due to the oxidation or other reactions of the phenolic nucleus, were confusing the evaluation, the volatilisation process was also monitored by IR spectroscopy. In this evaluation the absorption near 5.8 μ (1720 cm^{-1}) of the propionate ester side chain was monitored, using the technique which was employed for the evaluation of the thiodipropionate in an inert atmosphere. The zero absorbance adjustment was again made at 5.62 μ (1780 cm^{-1}). It was found that the majority of the antioxidant evaporation could be accomplished before the generation of carbonyl chromophores, in the oxidising polymer, began to interfere with the assessment of the antioxidant concentration.

Two samples of stabilised film were examined; the results are shown in Figures 5.20 and 5.21. The disappearance of the antioxidants in the inert atmosphere studies followed a characteristic logarithmic curve with time (straight lines on the semi-log plots); however, in an oxygen atmosphere this disappearance became directly linear with time, within the limits of experimental error. Furthermore, the process was considerably accelerated in the oxidising conditions. From the IR evaluations the antioxidant was estimated to

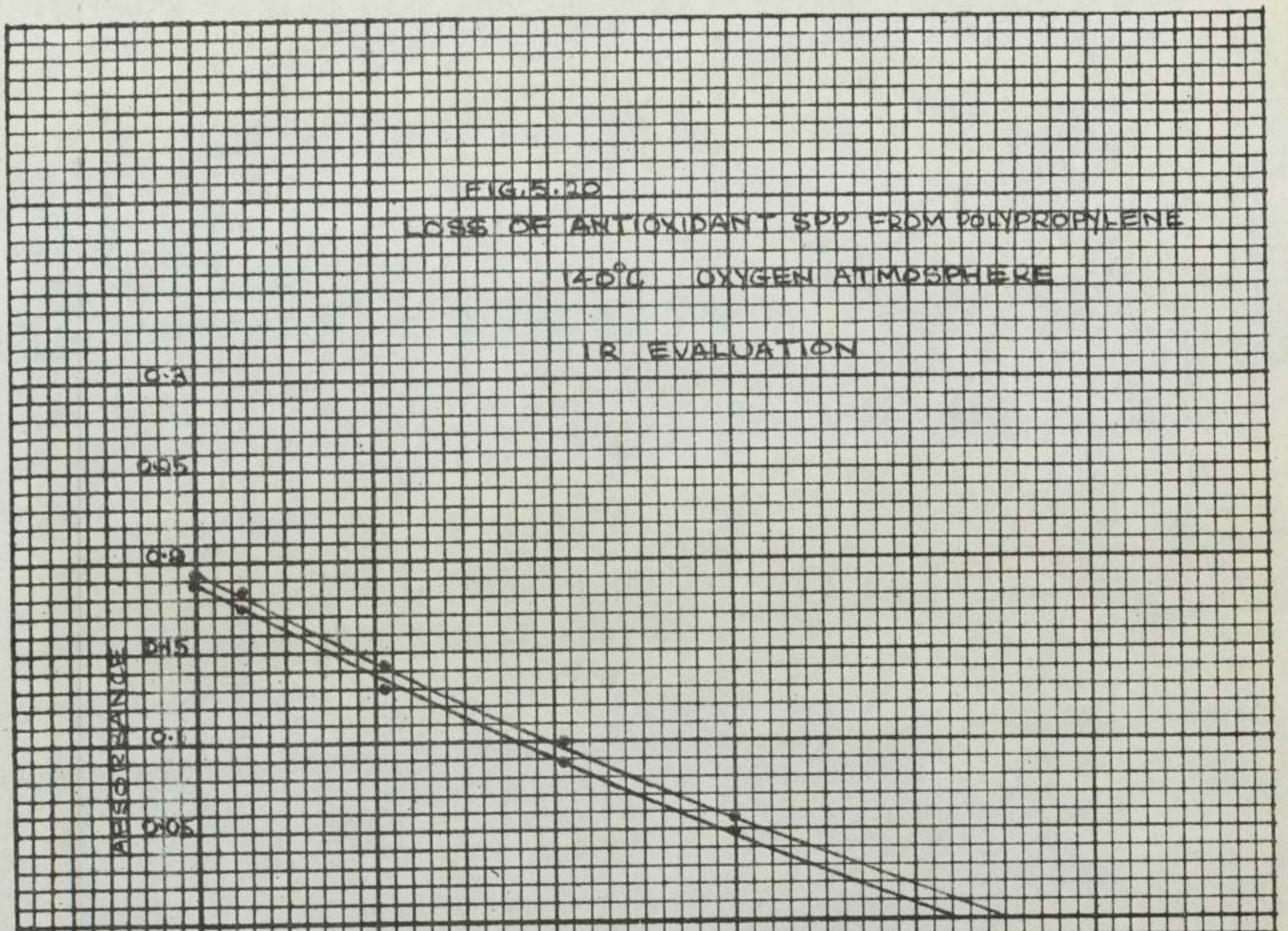


FIG. 5.20
LOSS OF ANTIOXIDANT SPP FROM POLYPROPYLENE
140°C OXYGEN ATMOSPHERE
IR EVALUATION

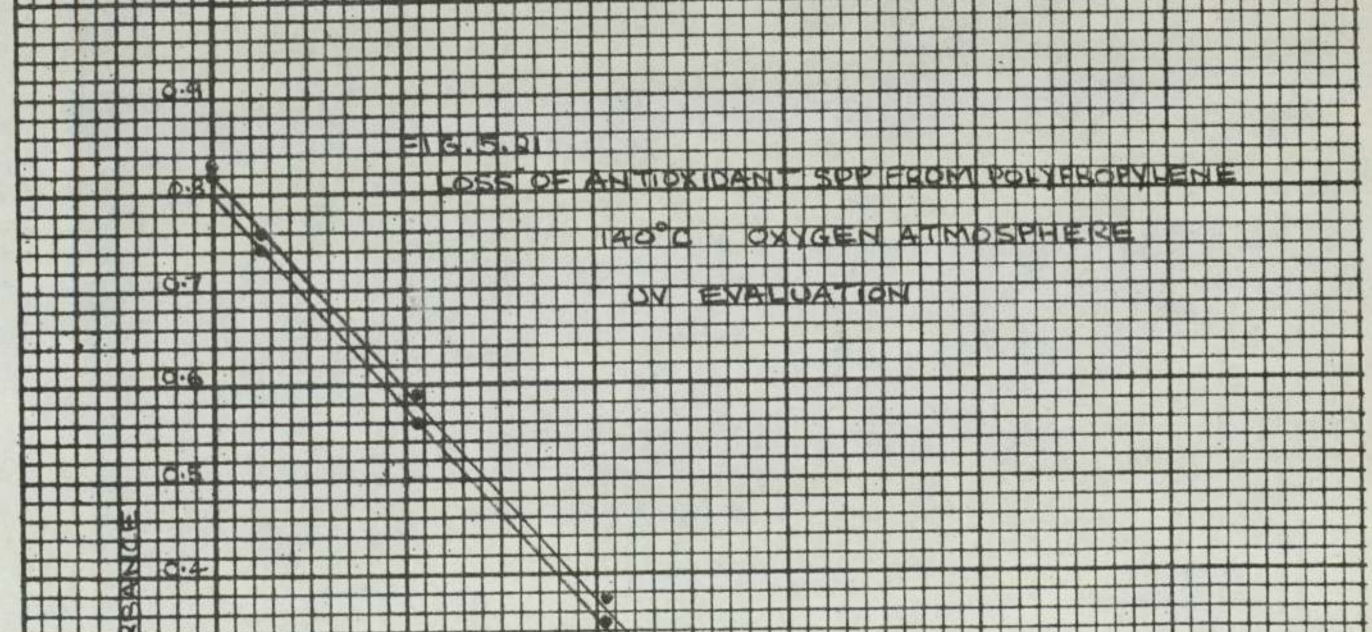


FIG. 5.21
LOSS OF ANTIOXIDANT SPP FROM POLYPROPYLENE
140°C OXYGEN ATMOSPHERE
UV EVALUATION

have volatilised completely after about 175 hours, the UV evaluation gave a figure of 145 hours. It appears very significant that these results straddle the induction period determination (165 hours) at the same temperature. The samples used in the spectroscopic evaluation also began to develop signs of opaque crazing and embrittlement in the period 150 - 180 hours.

The considerably higher loss of antioxidant in oxygen is considered to be due to the oxidation of the stabiliser to lower molecular weight products. The reasonably close correlation between the assessments of the losses of the phenolic nucleus (UV) and ester side chain (IR) may indicate that these functionalities remain on the same fragment of the oxidation products. Thus, it would appear that the oxidation reaction is occurring on the aliphatic side chain to produce products of markedly higher volatility. There would seem to be some relationship between this finding and the results of the evaluation of antioxidant activity in decalin. The PP series of phenolic antioxidants (and the TP thiodipropionates) exhibited a decrease in antioxidant activity as the length of the pendant side chain increased and, even in the absence of volatilisation phenomena, it would appear that oxidation reactions on the side chain were contributing detrimentally to the efficiency of the longer chain antioxidants.

A similar investigation of the DLTP and DSTP thiodipropionate antioxidants was attempted in an oxygen atmosphere at 140°C. The ester frequency was monitored by IR spectroscopy but unfortunately the development of carbonyl chromophores in the oxidising polypropylene was so rapid that their absorption frequencies completely obliterated the peak under examination. The oxidation of the polymer had reached an advanced stage after only 10 hours and this observation corresponds to the extremely short induction periods that were noted with these antioxidants in the torsional braid evaluation at 140°C (DLTP, less than 15 hours; DSTP, 29 hours at 2×10^{-3} moles/100gm. polymer).

The half-lives of volatilisation of DLTP and DSTP were found to be 1370 hours and 2550 hours respectively in nitrogen at 140°C; thus if it is assumed that the cessation of stabilisation is associated with the disappearance of the thiodipropionates or their active derivatives (discussed previously) then these antioxidant species must be considerably more volatile than the parent antioxidant. The sulphinic and sulphenic acids and sulphur dioxide, which have been suggested as breakdown products contributing to antioxidant activity (149 - 152) and which are formed by the oxidative cleavage of the thiodipropionates at the sulphur atom, would clearly have considerably higher volatilities than the parent antioxidant.

5.3 Compatibility.

Indications of the compatibilities of the antioxidants were obtained using two methods; the effects of the antioxidants on the crystallisation phenomena of the polymer were examined by differential thermal analysis and the and the solubilities of the antioxidants in hexane were determined.

5.3.1 D.T.A. on unstabilised and stabilised polypropylene. Method.

The melting exotherms and crystallisation endotherms were recorded on a Dupont Differential Thermal Analyser. The stabilisers were dispersed onto the polypropylene powder using the solvent dispersion technique, from dichloromethane, which has been described previously.

Approximately 18 mg polymer was placed in the sample cavity of the analyser and an empty zinc sample holder was used in the reference cavity. The analysis was carried out using a four cycle programme; the temperature was raised from ambient at 5°C/minute and the initial melting endotherm was recorded; the crystallisation exotherm was then recorded using a cooling cycle, at the same rate; the cooling cycle was stopped at 80°C and the melting and crystallisation programmes were repeated.

Prior to each analysis the cavity housing on the Analyser was flushed with nitrogen and a slight positive pressure of nitrogen was maintained throughout the recording cycles, to prevent any oxidation of the polymer samples occurring.

5.3.2 Solubility of antioxidants in hexane. Method.

A saturated solution of each antioxidant in n-hexane was prepared by maintaining an excess of additive under a small quantity of hexane, at 25± 0.1°C, in a sealed phial. Equilibration was allowed to take place over four days and the solutions were were shaken occasionally.

A portion of the supernatant saturated solution was removed from the bulk with a warm syringe (30°C), placed on an aluminium planchette and rapidly weighed. Two determinations were carried out.

The solvent was allowed to evaporate at room temperature and the samples were then stored in a dessicator over paraffin wax for 48 hours and re-weighed. No weight change was noted after applying a low vacuum for a further 24 hours.

5.3.3 Compatibility and Solubility. Results.

The D.T.A. melting endotherms and crystallisation exotherms of unstabilised polypropylene are shown in Figure 5.22. During the initial fusion cycle only one peak was detected, with a maximum at 165.5°C, however, after cooling, the second melting cycle produced twin endotherms, A and B, peaking at 161°C and 167°C respectively. The crystallisation exotherms during both the first and second cooling cycles peaked at the same temperature, 116°C.

The four-cycle programme was repeated several times on new samples of unstabilised polypropylene and subsequently on various stabilised formulations; reproducibility was generally good, the limiting factor being the accuracy with which the Analyser chart could be read, probably ± 0.2°C;

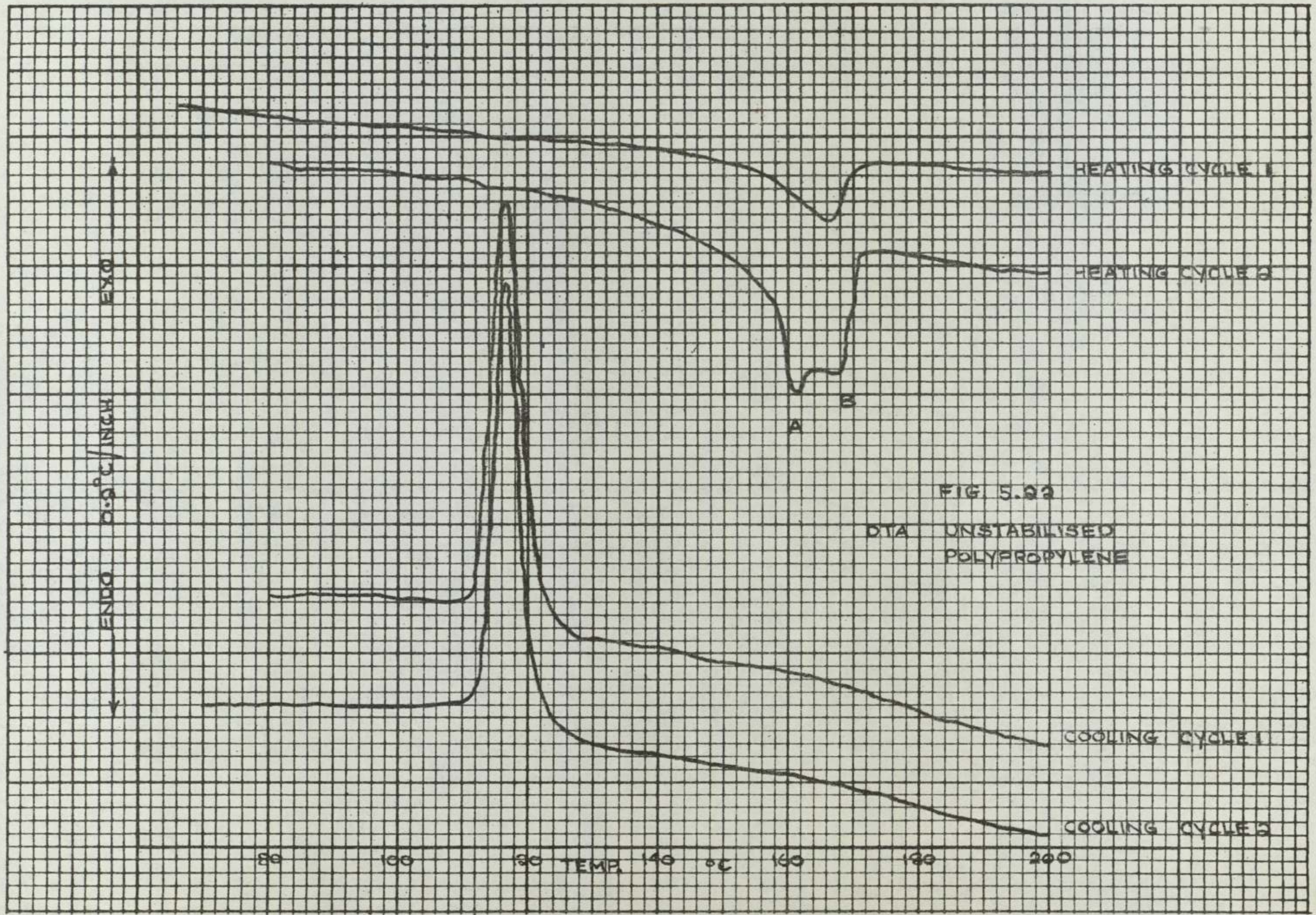


FIG 5.22

DTA UNSTABILISED POLYPROPYLENE

variations in the melting and crystallisation temperatures of 0.5°C between different polymer/stabiliser systems were considered to be of definite significance.

The twin endothermic peaks which were recorded during the second melting-cycle indicate that the initial fusion and crystallisation cycles had introduced a distinct structuring of the polymer into regions of low and high molecular order (197), peak A being associated with the lower melting, less ordered regions of the polymer and peak B with the more crystalline phase. It was found that if the melting and crystallisation cycles were repeated on the same sample, no further change occurred in the shape or position of the endothermic curve. Presumably after the first fusion and crystallisation cycles the orientation process had progressed as far as the heating and cooling programme would allow.

In the examination of the effects of the antioxidants on the melting and crystallisation characteristics of polypropylene, the additives were incorporated at a level of 2 x 10^{-2} moles, based on the active functionality, i.e. moles (ØOH) or gram atoms (S). Although these high concentrations (10% at molecular weight 500 for a monofunctional additive) unfortunately introduced the possibility of the excessive disturbance of the crystalline structure of the polymer, it was found impossible to obtain any reproducibly detectable changes in the melting and crystallisation characteristics of the polymer at lower additive concentrations.

Figures 5.23 to 5.29 show the temperatures of the maximum

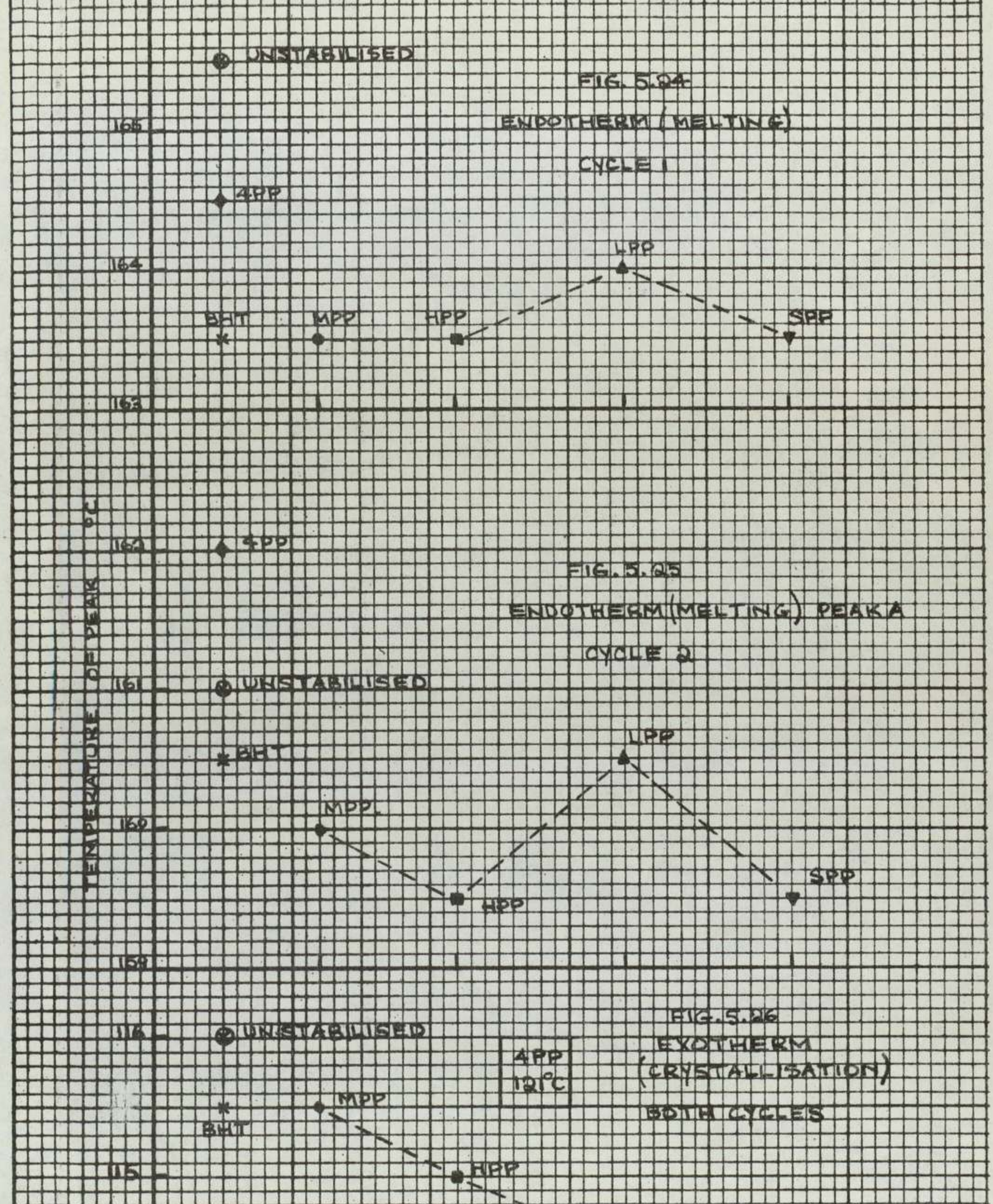
Fig. 5.23 D.T.A. on stabilised polypropylene.

Antioxidant concentration, 2×10^{-2} moles (ØOH) or (S).

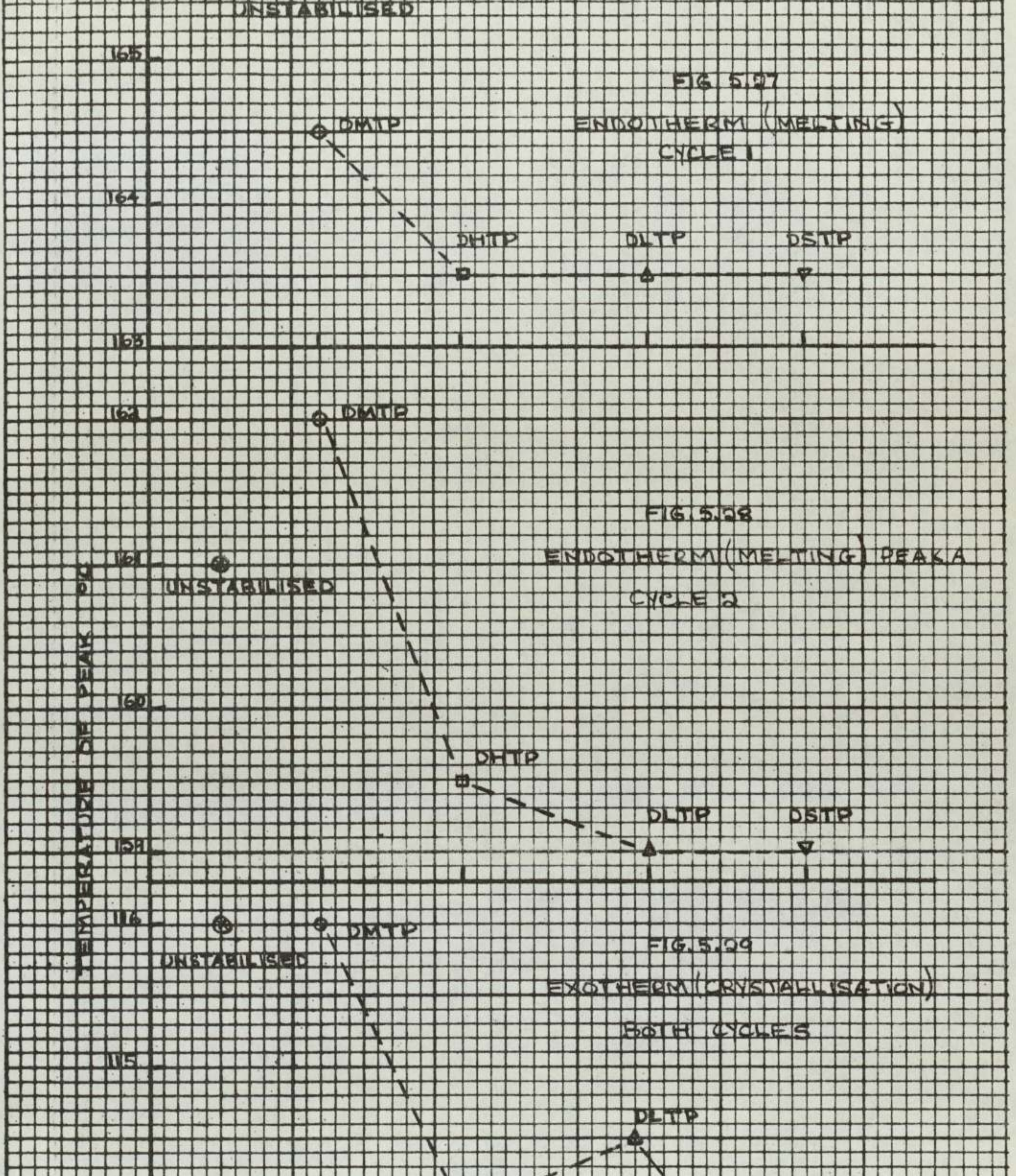
Antioxidant	Temperature of endothermic peak (melting)			Temperature of exothermic peak (crystallisation)	
	Cycle 1	Cycle 2		Cycle 1	Cycle 2
		Peak A	Peak B		
None	165.5	161	167	116	116
BHT	163.5	160.5	*	115.5	115.5
MPP	163.5	160	*	115.5	115.5
HPP	163.5	159.5	165	115	115
LPP	164	160.5	165	114.5	114.5
SPP	163.5	159.5	165	114	114
4PP	164.5	162		121	121
DMTP	164.5	162	*	116	116
DHTP	163.5	159.5	165.5	114	114
DLTP	163.5	159	165	114.5	114.5
DSTP	163.5	159	165.5	113.5	113.5

* Shoulder only.

FIGS. 5.24, 5.25, 5.26 DTA. POLYPROPYLENE/PP PHENOLS



FIGS. 5.27, 5.28, 5.29 DTA. POLYPROPYLENE/TP THIOS



exotherms and endotherms that were recorded for polypropylene containing the PP phenolic antioxidants and the TP thiodipropionates.

The traces of the first cycle endotherm (melting) and both exotherm cycles (crystallisations) had similar shapes to those exhibited by the polymer alone. However, the traces of the second endotherm cycle varied in shape between the various stabilised systems; these traces are shown in Figures 5.30 and 5.31.

All the linear chain phenolic antioxidants in the PP series caused a reduction in the crystallisation temperature of polypropylene (Figure 5.26) and, if the assuptions of Ambrovic and Mikovic (29) are correct, this indicates that these compounds are exhibiting some compatibility with the substrate. Furthermore, the depression of the crystallisation temperature increased with the increasing length of the pendant carbon chain; the long chain phenols appear to be more compatible than the shorter chain compounds. On this basis BHT appears to exhibit about the same compatibility as the methyl PP antioxidant.

However, the 4PP tetraphenol not only failed to depress the crystallisation point but in fact increased this temperature by 5°C. This antioxidant would appear to be acting as a liquid nucleating agent (M.p. 121 - 122°C) and exhibits no compatibility with the polymer as estimated by the present technique.

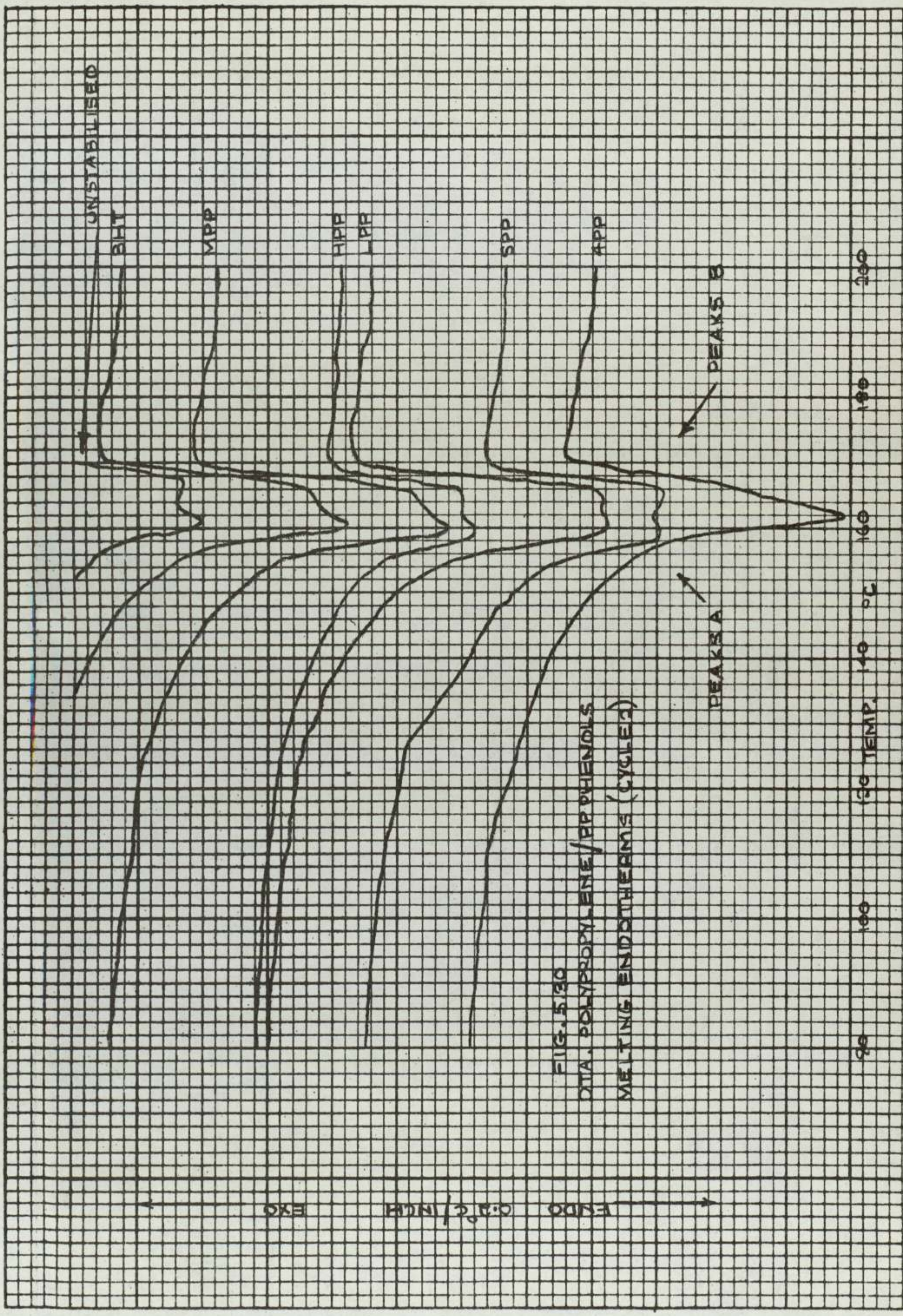


FIG. 5.30
DTA. POLYPROPYLENE/PP PHENOLS
MELTING ENDOTHERMS (CYCLE 2)

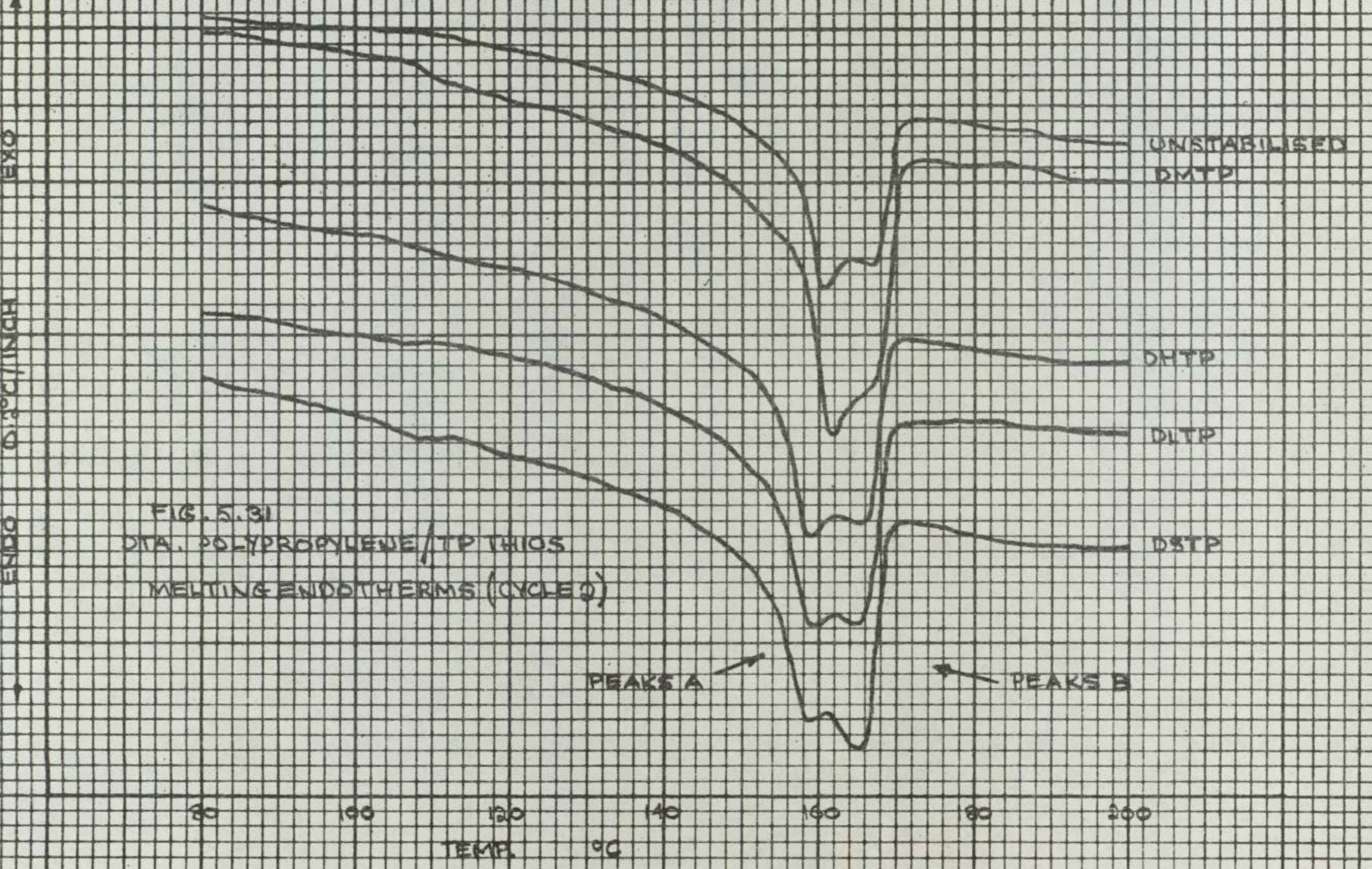


FIG. 5.31
DTA. POLYPROPYLENE/TP THIOS
MELTING ENDOTHERMS (CYCLE 2)

Some measure of support is gained for these conclusions from an examination of the melting endotherms of these compositions (Figure 5.30). Antioxidant 4PP almost completely destroyed the twin peak effect noticed in unstabilised polypropylene and produced a single endotherm in the peak A position (in fact a very slight shoulder appeared in the peak B position). As peak A is associated with a less ordered structure of the polymer it would appear that antioxidant 4PP produced such a rapid nucleating effect that the phase structuring process was not allowed to procede significantly during the crystallisation process and the growth of crystalline formations was severely repressed.

The melting curves associated with BHT and the linear chain PP antioxidants exhibit a decrease in peak A and an increase in peak B as the length of the pendant carbon chain increases. In fact in the cases of BHT and MPP, peaks A are more predominant and peaks B less predominant (shoulders) than those exhibited by unstabilised polypropylene. This trend continues with increasing pendant chain length until the reverse phenomena are noticed with antioxidant SPP.

The reasons for these effects are not completely clear, however, the interplay of two effects could be involved. The tendency of the stabilisers to disrupt the formation of crystalline structures in the polymer, simply as impurities, would reduce the crystallisation capabilities of the polymer matrix. Opposing this effect, the longer chain 'compatible' antioxidants would tend to reduce the bulk viscosity of the polymer/stabiliser system during crystallisation from the melt (38, 116). Thus, with the low chain length antioxidants the former phenomenon may prevail resulting in high endotherm peaks (A) associated with a less ordered structure; the longer chain antioxidants would tend to facilitate crystallisation and thereby bring peaks B into dominance.

If these postulates are correct, they agree, in some measure, with the conclusions of Nechitailo and Sanin (26) that antioxidants of low molecular volume can 'penetrate' the crystalline regions of the polymer. However, the present interpretation would be that the low molecular weight antioxidants do interact with the crystalline structure during crystallisation but, in so doing, reduce the order of these regions, thereby producing an increase in the dominance of the endotherm peak associated with the less ordered phase (peak A). Thus the low molecular weight antioxidants, rather than being compatible with the crystalline phase as Nechitailo and Sanin suggested, appear to generate areas of lower order in their crystalline surrounds.

The higher antioxidant homologues, while enhancing crystallisation by reducing the bulk viscosity of the system, would appear to be rejected by the forming crystalline structures and concentrate in the lower order phase of the polymer. Peak A, associated with the low order structures would thus be smaller than peak A of the unstabilised polymer and peak B correspondingly more dominant.

Figures 5.24 and 5.25 correlate the melting point endotherms (peak A) associated with the PP antioxidants . The cycle 2 results are considered to be more significant than the cycle 1 endotherms; at the start of cycle 1 the antioxidants were simply in a dispersed state on the surface of the particles of the polymer, however the cycle 1 and cycle 2 results do mirror each other to some extent.

The alternating behaviour of the melting points which are associated with the less ordered structure (peak A) is not understood. It would be expected from the above discussions that the depression of the melting point of the less ordered structures would become more marked with the longer chain antioxidants; this trend appears to hold for BHT, MPP,HPP and possibly SPP, however, the lauryl derivative exhibits anomalous behaviour.

The temperature at which melting peak A appeared for polypropylene containing antioxidant 4PP was higher than the equivalent peak for unstabilised polypropylene. This is not unexpected in that the rapid nucleation of crystallisation appears to have resulted in a total morpholgy intermediate between the low and high order structure found elsewhere.

A survey of the present evidence suggests that the antioxidants in the PP series which are substituted with longer pendant chains are probably more intimately associated with the polymer than their lower homologues. The compatibility of antioxidant 4PP appears to be very low.

The traces (Figure 5.31) of the cycle 2 melting endotherms for the thiodipropionate (TP) stabilised compositions show a similar pattern to those associated with the PP phenolic antioxidants; the transition from peak A predominance to peak B predominance, with the increasing length of the pendant side chain, is rather more marked, however.

In contrast to the phenolic antioxidants, the thiodipropionates DHTP, DLTP and DSTP depressed the melting point of the less ordered phase in a regular sequence (Figure 5.28). DMTP raised the melting point, possibly for reasons similar to those suggested in the discussion of antioxidant 4PP. Figure 5.29 shows that the crystallisation temperatures associated with the TP antioxidants did not show a regular behaviour, however. Although DHTP, DLTP and DSTP all depressed the crystallisation temperature, DLTP did not produce the degree of depression which could be expected from the melting phenomena.

Without further evidence it is difficult to explain these variations in the pattern of behaviour which were observed with the PP phenolic antioxidants (melting results) and with the thiodipropionates (crystallisation results). However, the results do perhaps give some insight into why Nechitailo and Sanin (26, melting studies) and Ambrovic and Mikovic (29, crystallisation studies) arrived at different conclusions on the compatibility of mono- and bisphenolic antioxidants.

The summation of the evidence on the TP antioxidants suggests that the longer chain derivatives are more 'compatible' with the substrate than their lower homologues. DMTP would

Fig. 5.32. Solubility of antioxidants in n-hexane. 25°C.

Antioxidant	Solubility at 25°C. gm antioxidant/100gm n-hexane
BHT	99.7
MPP	31.9
HPP	Fully miscible
LPP	Fully miscible
SPP	63.5
4PP	0.45
DMTP	6.92
DHTP	Fully miscible
DLTP	103.2
DSTP	5.13
2246	9.95
MB2P	0.25
MB3P	1.93
MB5P	0.22

appear to be incompatible.

The compatibilities of the MB polyphenolic antioxidants were not examined using DTA.

The solubilities of all the antioxidants in n-hexane are given in Figure 5.32. There appears to be little or no relationship between the solubilities of the highly soluble linear PP and TP antioxidants and their behaviour in the DTA evaluation. Antioxidant 4PP appears to be an exception, however; very low solubility in n-hexane is associated with DTA phenomena which can probably be related to low compatibility in polypropylene. Thus, it may be possible to extrapolate low hexane solubility characteristics of antioxidants to their behaviour in polypropylene.

6. DISCUSSION

Figure 6.1 shows a comparison of the activities of the PP phenolic antioxidants at 140^{o}C in polypropylene,under open and closed atmospheric conditions,and also in decalin.

Although the PP antioxidants exhibit very similar activities in the liquid hydrocarbon, a markedly different pattern of behaviour is apparent in the polymer in both the flowing and closed atmospheric environments.

In the restricted atmosphere, the activities of the monophenolic PP antioxidants with linear pendant side chains increase in the series MPP, HPP and LPP and then fall to SPP. As the volatisation of these antioxidants will be markedly curtailed in the restricted atmosphere, it would appear that these effects are linked with either compatibility or mobility phenomena. The behaviour of BHT lends some weight to these conclusions,for although this antioxidant exhibits a considerably higher activity than any of the PP antioxidants in decalin, its activity in polypropylene is relatively much lower.

Figure 6.2 compares the activities of BHT and the PP phenols with the melting points of these compounds and their solubilities in hexane. There would appear to be a definite relationship between low melting point, high solubility in hexane and high antioxidant activity. Low melting point and high hexane solubility can possibly be associated with low intermolecular polar bonding and high affinity for hydrocarbon substrates. If this is the case, the extension of the concept to polymeric

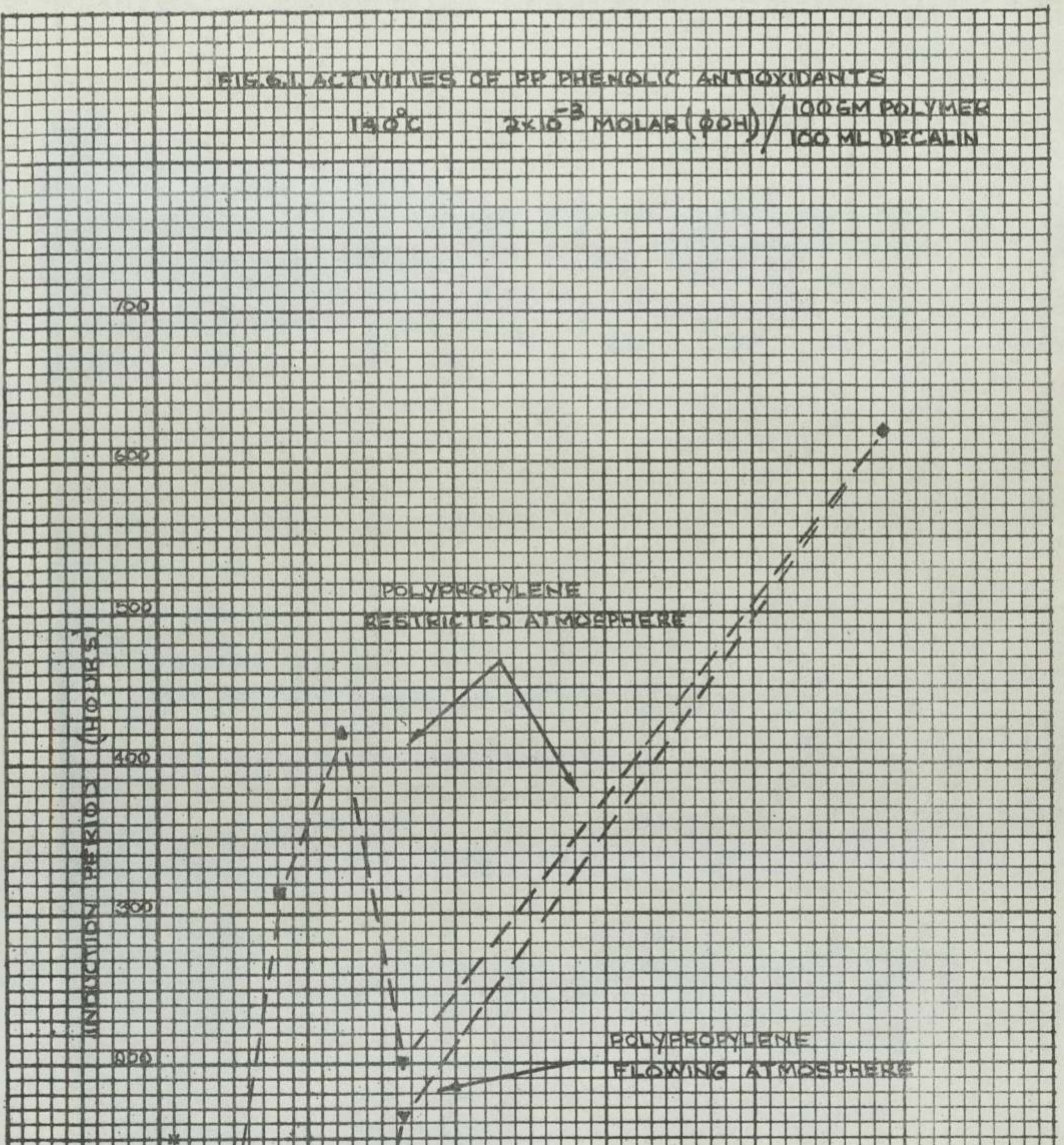


FIG.6.1 ACTIVITIES OF PP PHENOLIC ANTIOXIDANTS

140°C 2×10^{-3} MOLAR (ϕOH) / 100 GM POLYMER / 100 ML DECALIN

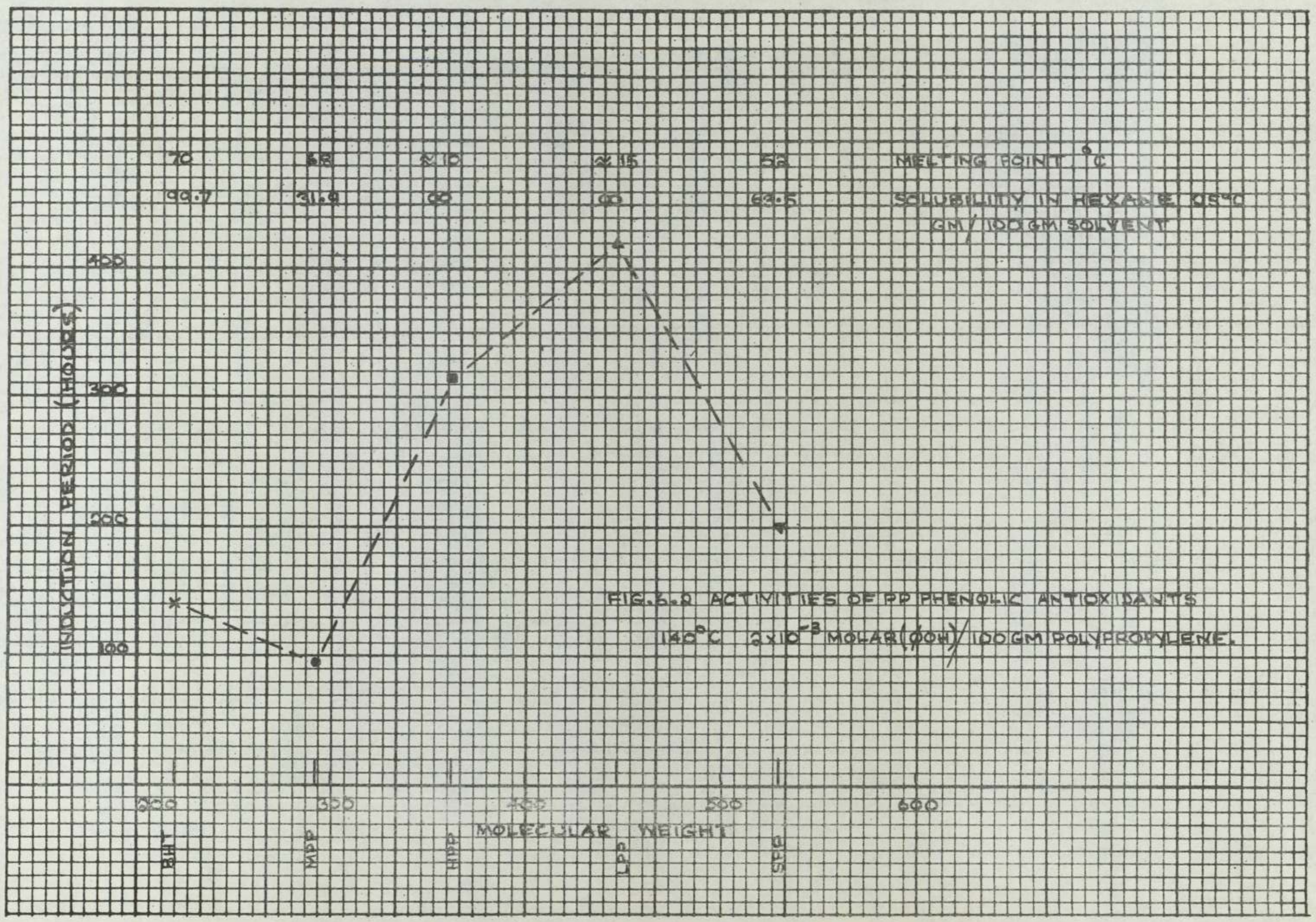


FIG.5.2 ACTIVITIES OF PP PHENOLIC ANTIOXIDANTS
140°C 2x10^{-3} MOLAR(ØOH)/100GM POLYPROPYLENE.

substrates conflicts with the compatibility data which have been obtained in this and other investigations (29,38,42) based upon the examination of first order transition phenomena. In these investigations phenolic compounds substituted with linear pendant chains were considered to exhibit increased compatibility as the length of the pendant chain increased.

Although the use of data on solubility in hydrocarbon solvents to assess compatibility phenomena in polymers was criticised earlier, it would appear that solubility information has produced correlations with the antioxidant activities of the PP phenols. However, these relationships may be fortuitous.

The activity of the 4PP tetraphenol is anomalous on the basis of the melting point (122°C) and the hexane solubility (0.45 gm/ 100 gm solvent) information; furthermore the DTA evaluation also indicated extremely limited compatibility. Hawkins (51) has suggested that antioxidants with extremely low compatibility can exhibit high activity because they tend to accumulate in the less ordered phase of the polymer.

The DTA evaluation indicated that the linear chain PP antioxidants were entrained to some extent in the more highly crystalline regions of the polymer. Hawkins' points out that any fraction of the total added antioxidant that resides in the more highly ordered regions of the polymer will tend to be wasted on two counts; the more crystalline regions of the polymer are inherently more stable to oxidation and furthermore, by residing in these regions, the antioxidants are depleting the concentration of stabiliser in the oxidatively sensitive areas of the substrate.

Ambrovic and Mikovic (29) suggested that stabilisers could be divided into two classes, those which resided primarily in the amorphous regions of the polymer and those which were also entrained in the more highly ordered regions. Although this picture of compatibility phenomena is probably a considerable over-simplification, thereare indications that an antioxidant which would traditionally be considered as 'incompatible', in that it had little effect upon the first order transitions of the crystalline polymer, may exhibit markedly higher stabilising activity than its 'compatible' analogues. Thus, it appears that antioxidant 4PP exhibits high antioxidant activity due to its rejection by the highly ordered regions of the polymer and its accumulation in the oxidatively sensitive amorphous phase. However, it will be seen later that low compatibility with these regions of lower molecular order may be limiting to some extent the full development of the activity of the tetraphenolic stabiliser.

Thus, the activities of the PP antioxidants may be associated with two conflicting compatibility phenomena. Incompatibility with the crystalline regions of the polymer would seem to be beneficial, however, if incompatibility is extremely marked and the stabiliser has only very limited solubility in the amorphous phase of the polymer, the full development of its activity may be curtailed.

The variations in the activities of the linear chain PP antioxidants may be produced by a combination of these effects. The DTA evaluation indicated that the lower PP homologues were entrained in the more highly ordered regions of the polymer to a greater extent than the long chain phenols and thus the lower homologues might be expected to show low activity. The long chain phenols exhibited some interaction with the crystalline phase of the polymer but were probabaly extruded into the amorphous phase, during crystallisation, to a greater extent than the lower homologues. However, the solubility of antioxidant SPP in hexane would indicate that the compatibility of this antioxidant with the amorphous phase of the polymer is not particularly high and the overall effect appears to limit the activity of this stabiliser. Antioxidant LPP seems to exhibit the best combination of low compatibility with the crystalline phase and high compatibility with the amorphous phase.

From the present work it is only possible to draw conclusions of a negative nature on the effects of the mobility of antioxidants on their activity. Boss and Chien (117, 118) have demonstrated that the mobility of a trisphenolic antioxidant is severely restricted in polypropylene and it would be expected that the mobility of antioxidant 4PP was similarly curtailed. However, this lack of mobility has not precluded high activity in the 4PP antioxidant and this suggests that the thermo-oxidative chain reactions continue until the site of oxidation (peroxy radical) meets a stabiliser molecule. Heller (96) has pointed out that the low activity of antioxidant 4PP against UV initiated oxidation (in comparison with BHT) may be connected with the low mobility of this antioxidant. The length of the oxidative kinetic chains associated with photo-initiated degradation are markedly shorter than is found in thermo-oxidative attack (198) and it would appear that in photo-catalysed degradation considerable oxidative damage is suffered by the polymer before the site of oxidation is eventually scavenged.

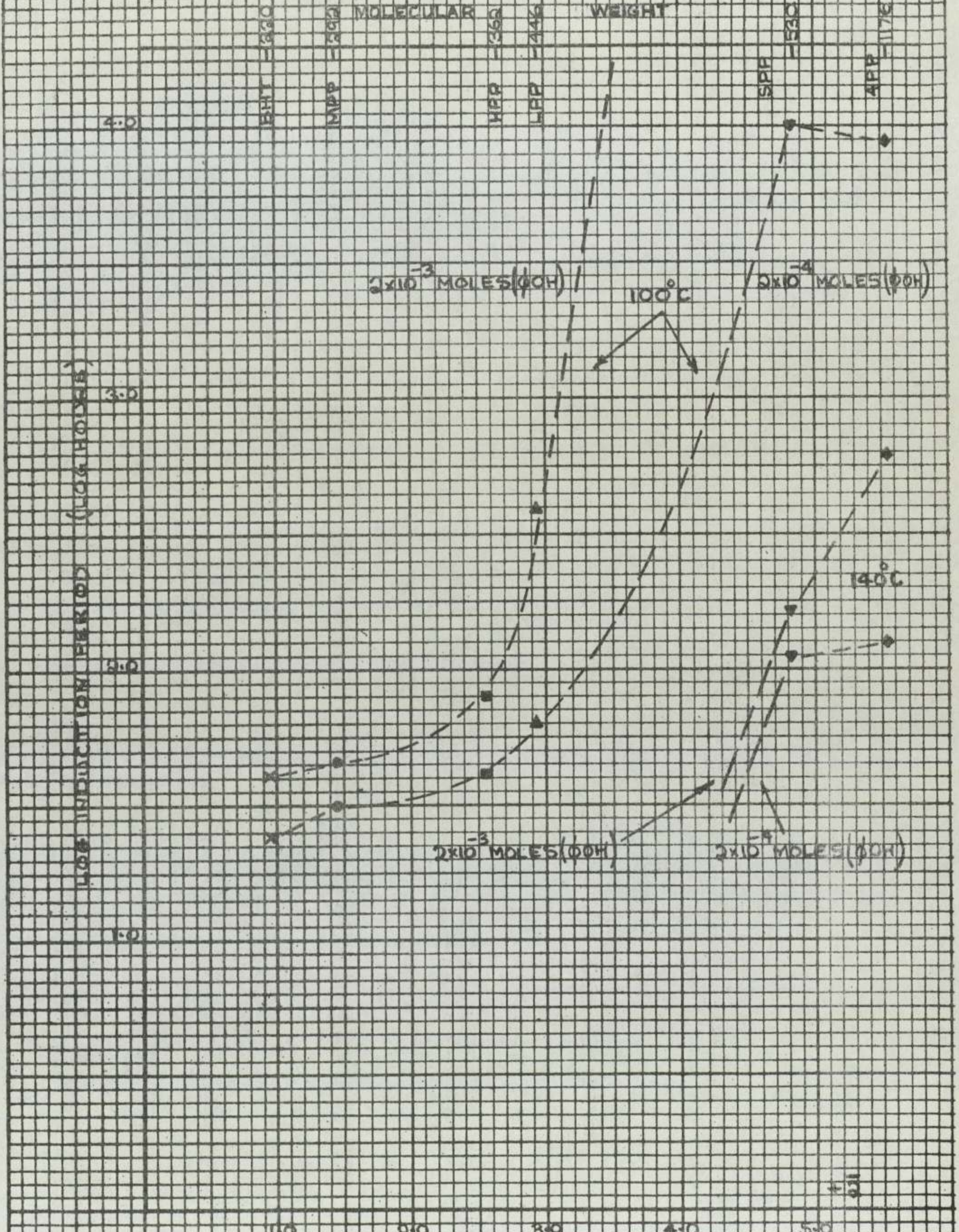
A comparison of the activities of the antioxidants in polypropylene in the restricted atmosphere and flowing atmosphere environments demonstrates the overwhelming importance of the effects of the volatilisation of the stabilisers.

Although antioxidants BHT, MPP, HPP and LPP exhibit considerable activity under conditions where their volatilisation is severely curtailed, their efficiency in the flowing atmosphere test is reduced to an insignificant level (induction periods, less than five hours) in comparison with the higher molecular weight SPP and 4PP antioxidants. The efficiencies of the latter antioxidants in a flowing atmosphere approach their efficiencies in the absence of volatility effects (induction periods; SPP, 165 hours, 200 hours; 4PP, 620 hours, 625 hours; respectively). Antioxidant 4PP exhibits almost the same activity in both tests and it would appear that volatilisation plays little part in determining the efficiency of this antioxidant at 140°C.

The examination of the effects of the volatilisation of the antioxidants on their efficiency is taken further in Figure 6.3 which forceably demonstrates the very marked increase in the activity of the antioxidants in the flowing atmosphere test as volatility decreases. The activity of antioxidant 4PP does not completely coincide with the trend to higher activity with decreasing volatility; it was suggested earlier that this effect may be due to the low compatibility of this antioxidant with the less ordered regions of the polymer.

It was shown in Section 5.2.3 that oxidative reactions on the backbone of the linear chain PP antioxidants could cause a breakdown of the higher molecular weight antioxidants to more volatile

FIG.6.3. VOLATILITY AND ACTIVITY. PP PHENOLS. POLYPROPYLENE.



species. Thus it appears that the volatilisation effects associated with these antioxidants are a combination of the volatilisation of the parent compounds and their oxidative breakdown products. It was demonstrated that the oxidative attack on the antioxidant occurred on the pendant alcohol moiety rather than between the aromatic ring and the ester group. That antioxidant 4PP would not suffer from this type of oxidative attack argues further for the involvement of mobility or compatibility effects in determining the activity of this antioxidant.

The importance of the effects of the direct oxidation of the linear chain PP antioxidants will depend upon the volatility of the parent compounds and their rate of oxidation to species of lower molecular weight. At high temperatures the volatility of the lower molecular weight antioxidants is probably so dominant that the oxidation of the parent compounds to more volatile species makes little contribution to the overall loss of these stabilisers. However, it has been shown that the less volatile antioxidant SPP does suffer from considerable oxidative breakdown and that this effect seriously reduces the activity of this stabiliser. The effects of the direct oxidation of the antioxidants to more volatile products will become relatively more important at lower temperatures; whereas the volatility of the antioxidants exhibited a direct proportionality with temperature, the oxidative processes could be expected to follow an approximately Arrhenius relationship.

The relationships between the volatility and activity of the TP thiodipropionates in the flowing atmosphere test are shown in Figures 6.4 and 6.5. As with the PP phenolic antioxidants a marked increase in activity is exhibited with increasing molecular weight and decreasing volatility. However, a comparison of the

FIG. 6.4. ACTIVITIES OF TP THIODIPROPIONATES

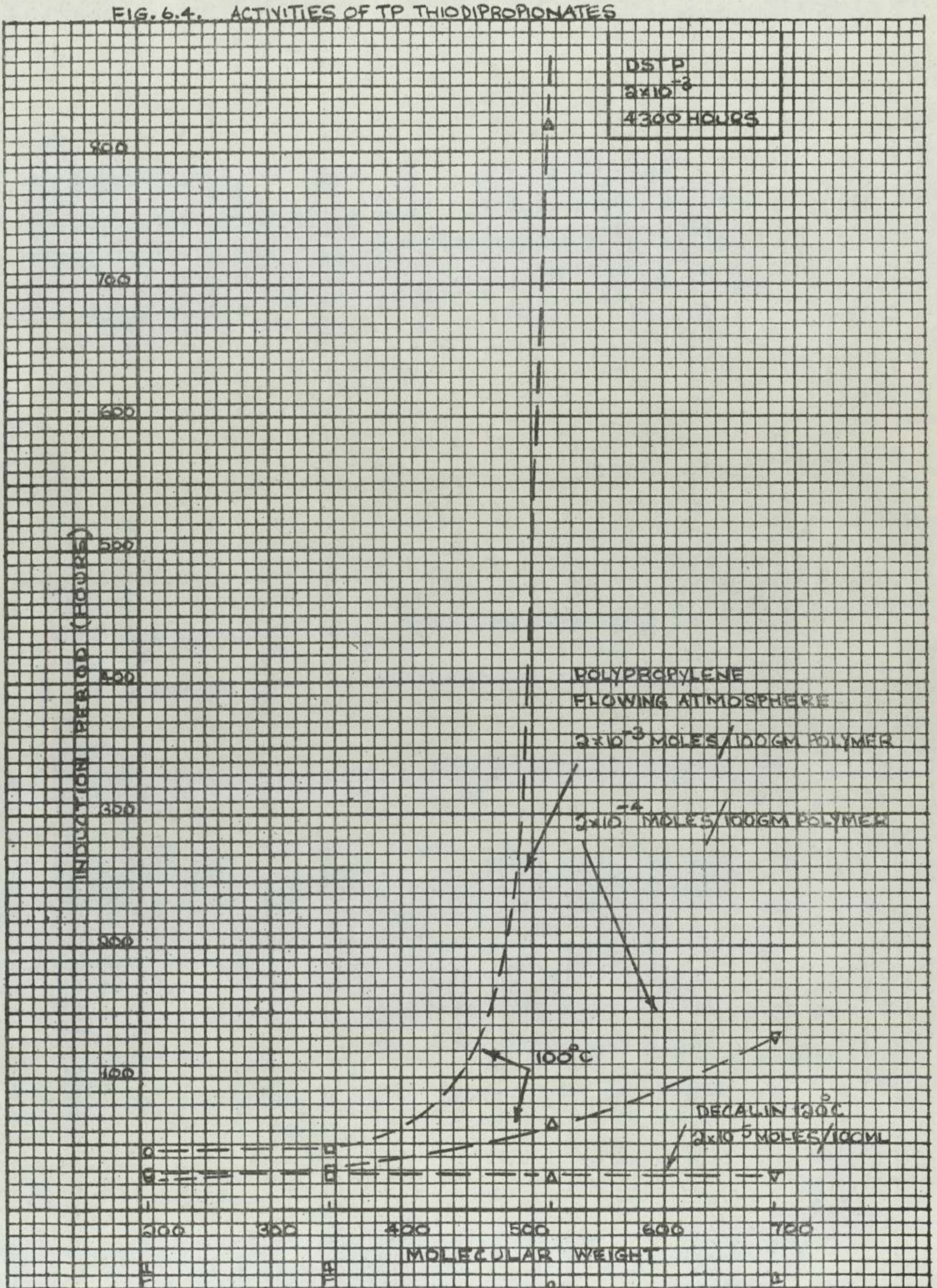
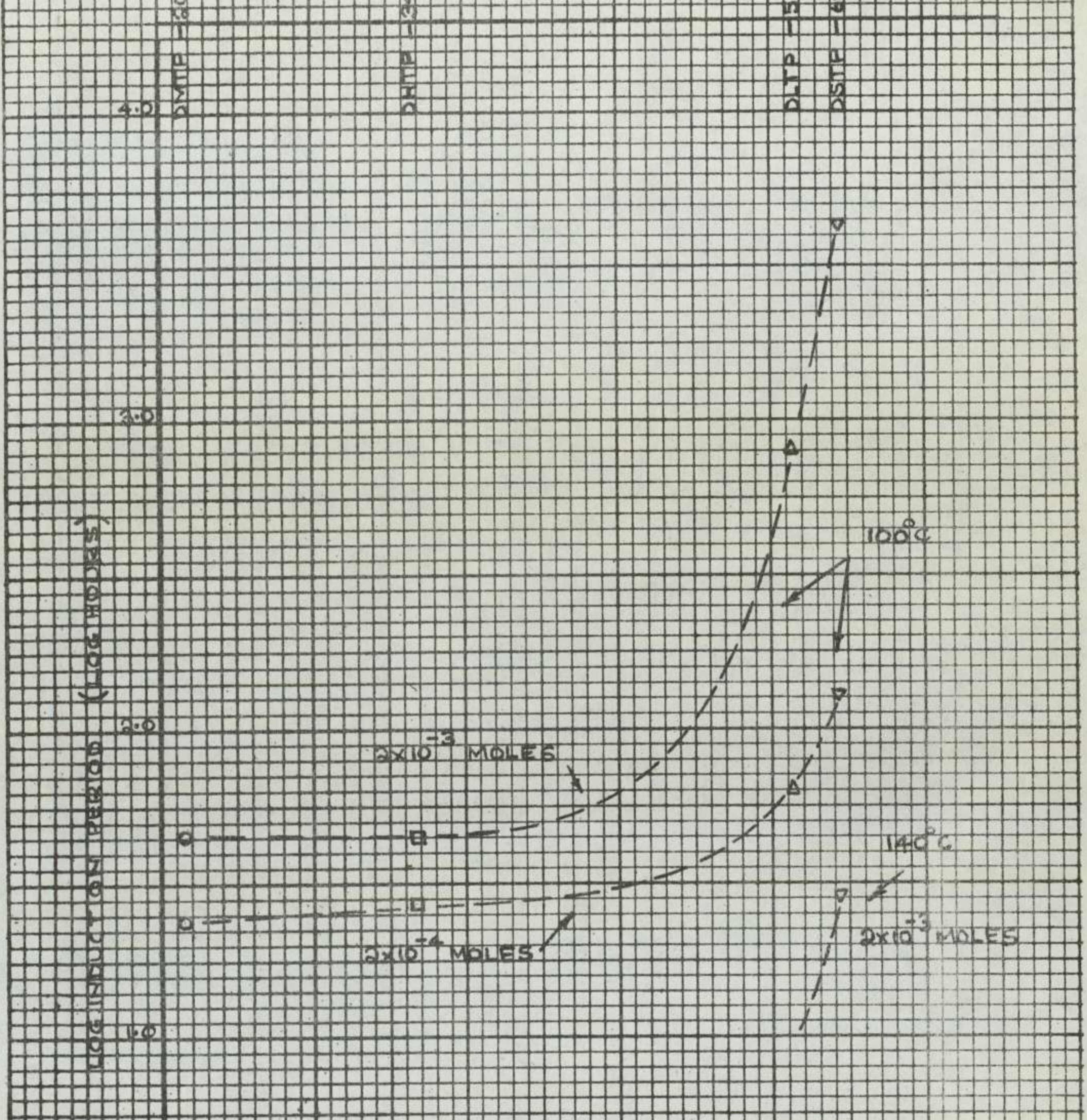


FIG.6.5. VOLATILITY AND ACTIVITY. TP THIODIPROPIONATES.



behaviour of the phenolic and thiodipropionate antioxidants (Figures 6.6 and 6.7) demonstrates a distinct difference in the dependence of stabilising activity on volatility, between the two types of antioxidant. The higher molecular weight sulphur antioxidants DLTP and DSTP exhibit considerably lower volatilities than the highest molecular weight linear chain phenol (SPP). From the relative efficiencies of the lower phenol and thiodipropionate homologues it would be expected that the higher thiodipropionates would exhibit considerably higher activity. This anomaly is almost certainly associated with the mechanism of action of the sulphur antioxidants in that the activity of these stabilisers is dependent upon their oxidative cleavage, at the sulphur atom, to active antioxidant species (149-152). These active breakdown products will clearly have considerably higher volatilities than the parent compound and thus are rapidly lost from the polymer.

In the examination of the sulphur antioxidants in polypropylene in a restricted atmosphere and in decalin (Sections 2.8.2 and 3.6.3), evidence appeared that indicated a change in the mechanism of action of the sulphur antioxidants as the concentration of the additives was increased. In polypropylene this mechanistic change occurred at concentrations between 2×10^{-4} moles and 8×10^{-4} moles/100 gm polymer. There is some evidence that a similar mechanistic change occurs in the flowing atmosphere tests. Figures 6.4 and 6.5 show that at a concentration of 2×10^{-3} moles/100 gm polymer, the higher molecular weight thiodipropionates develop activities well over an order of magnitude greater than their activities at 2×10^{-4} moles/100 gm polymer. Presumably the lower homologues cannot develop the activity which is associated with the higher concentration because volatilisation rapidly reduces their concentration to very low levels.

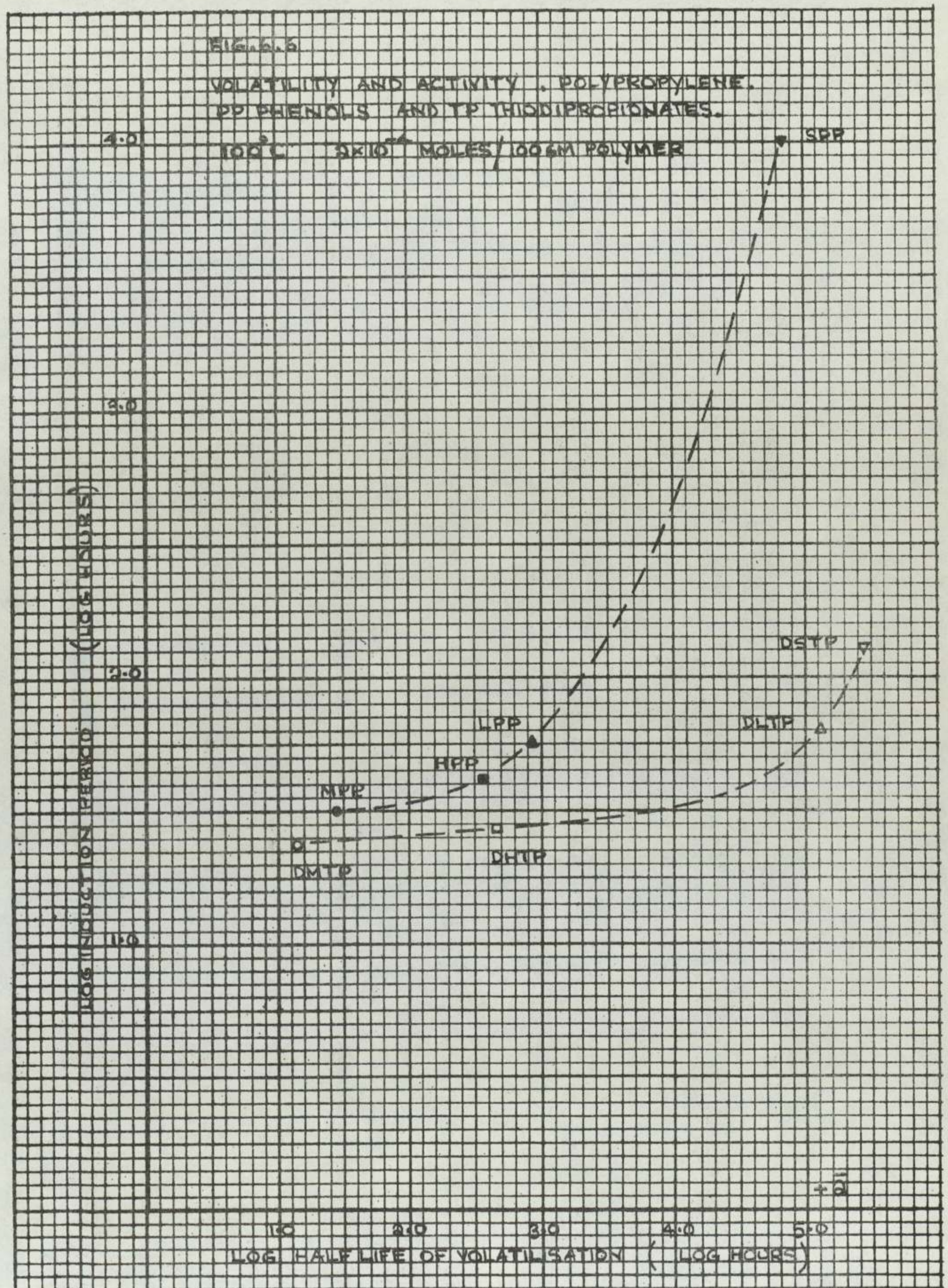


FIG. 6.6

VOLATILITY AND ACTIVITY . POLYPROPYLENE.
PP PHENOLS AND TP THIODIPROPIONATES.
100°C 2×10^{-4} MOLES/100GM POLYMER

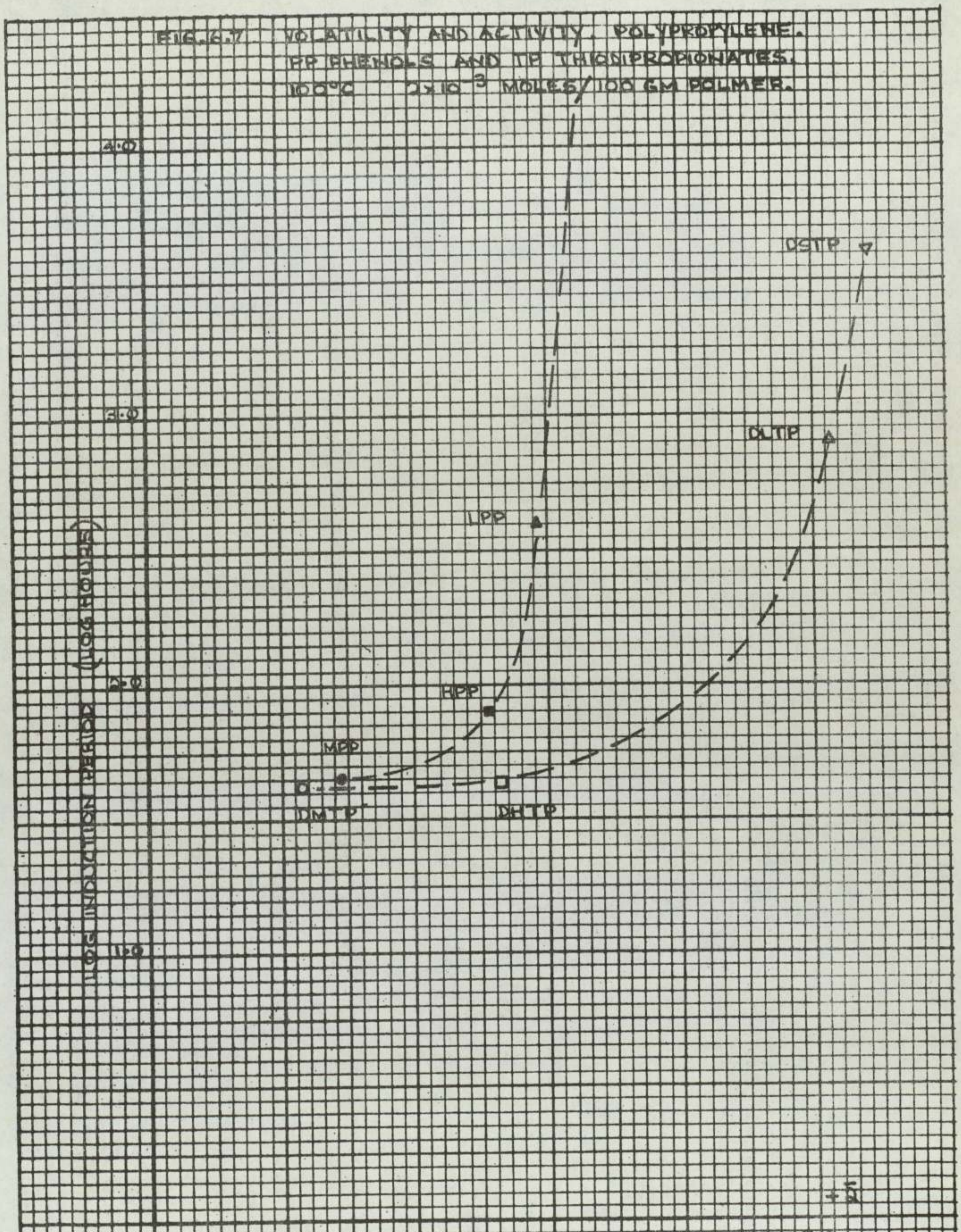


FIG. 6.7 VOLATILITY AND ACTIVITY. POLYPROPYLENE. PP PHENOLS AND TP THIODIPROPIONATES. 100°C 2×10^{-3} MOLES/100 GM POLMER.

Unfortunately it is not possible to draw any conclusions on the possible effects of mobility and compatibility phenomena on the activities of the thiodipropionates as the closed environment tests on these antioxidants did not provide induction period measurements and thus no basis for the assessment of activity in the absence of volatility effects could be obtained. However, volatility effects completely obliterated the more subtle variations in activity which were ascribed to differences in the compatibilities of the linear chain PP phenols. It is considered that a similar situation would exist with the thiodipropionate antioxidants and thus the differences in the activities of these stabilisers, in the flowing atmosphere test, are almost certainly associated primarily with the volatilities of the antioxidants and their breakdown products.

The above findings may explain why the network bound sulphur antioxidants (natural rubber) developed by Cain and Lee (121) did not exhibit the expected superior properties which were associated with network bound radical scavenging antioxidants (119). Although Bateman (122) suggested that the low mobility of these antioxidants was probably controlling their activity,it seems more likely that the predominating factor is the breakdown of the sulphur stabiliser and thus the detachment of the various active antioxidant species from the rubber network and their subsequent loss.

Figure 6.8 shows a comparison of the activities of the MB phenolic antioxidants in decalin and polypropylene at 140°C. A comparison of the activities of antioxidants MB3P and MB5P in decalin and in polypropylene, in a closed atmosphere (no volatility effects), reveals that an increase in the number of phenolic rings

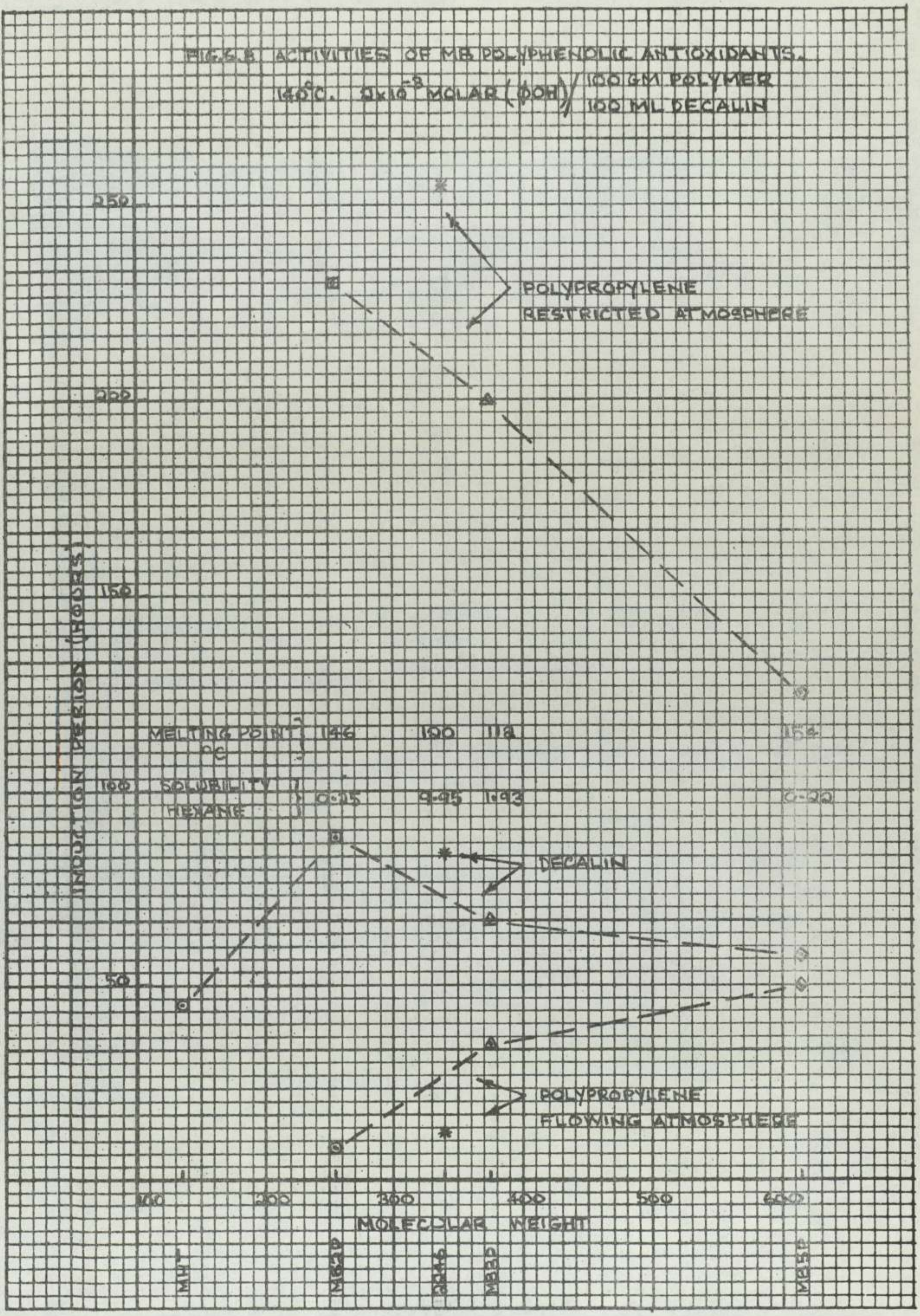


FIG.6.8 ACTIVITIES OF MB POLYPHENOLIC ANTIOXIDANTS.
140°C. 2x10^{-3} MOLAR (ϕOH)/ 100 GM POLYMER / 100 ML DECALIN

in the antioxidants produces approximately the same decrease in activity in the liquid hydrocarbon and the polymeric substrate. However, antioxidant MB3P shows a significantly higher relative activity in polypropylene than in decalin. The possible influences of intra and intermolecular bonding interactions in determining the activities of the MB antioxidants in decalin have already been mentioned and it would appear that these effects function in opposing directions in the liquid hydrocarbon and the polymeric substrates. In particular, compatibility and mobility effects may well be influencing the activities of the antioxidants in polypropylene and thus,although in decalin the inherent activity of the more soluble antioxidant MB2P is relatively low, the higher activity of this stabiliser in polypropylene is probably associated with enhanced compatibility.

However, a comparison of the activity of antioxidant 2246 in decalin and in polypropylene (again in the closed environment) indicates that the efficiencies of all the MB antioxidants in polypropylene are limited to some extent by low compatibility. Thus, although antioxidant 2246 exhibits inferior activity to MB2P in decalin, the more hexane soluble dibutylated antioxidant shows a higher relative efficiency in polypropylene.

The extremely low solubilities and the bulky molecular configurations of the MB antioxidants would indicate that the compatibilities of these antioxidants can probably be considered primarily in terms of their interaction with the less ordered regions of the polymer. Although antioxidant 2246 has a higher hexane solubility, Nechitails and Sanin (26) suggested that the bulky configuration of this antioxidant also precluded its entrainment in the crystalline regions of polypropylene.

It is likely that data on the solubility of antioxidants in liquid hydrocarbons bears a greater relationship to their environment in a crystalline polymer when the confusion caused by the entrainment of the stabilisers in the crystalline regions is not encountered.

The activities of the antioxidants in polypropylene in the flowing atmosphere are markedly lower than their performance in the restricted atmosphere and clearly volatilisation is again having profound effects. As before, antioxidant MB3P exhibits a higher relative efficiency in the polymeric substrate and,although compatibility effects may be involved,it is more likely that the overwhelming volatility phenomena are responsible. Thus the high relative activity of antioxidant MB3P would indicate that this stabiliser is exhibiting an enhanced inter molecular hydrogen bonding which is reducing its volatility. The behaviour of antioxidant 2246 lends some weight to this conclusion; although this antioxidant exhibits higher activity than stabiliser MB3P in decalin and in polypropylene under a closed atmosphere, its activity under conditions where volatility effects are important is remarkably poor. It appears that although the butylated structure of 2246 endows this antioxidant with a superior intrinsic activity, this configuration also reduces intermolecular hydrogen bonding and thus increases the volatility of the stabiliser.

The experimental techniques which have been used to assess the activity of the antioxidants in a closed atmosphere, with the aim of eliminating the effects of the volatilisation of the additives, require discussion.

In the present investigation the initiation of the oxidation of decalin could occur both in the liquid and vapour phases, although, following the end of the inhibited period of oxidation, the large volumes of oxygen which were absorbed indicate that the liquid phase reaction was predominating. It was pointed out previously that the products which have been identified in the advanced oxidation of decalin are long chain carboxylic acids (126). These products would not be expected to volatilise at the reaction temperature which was used. It is possible that minor oxidation products of higher volatility were not identified in previous product analyses, also the inhibited oxidations which have been studied in the present work could have generated other decalin oxidation products of lower boiling point; in these circumstances the measurements of the final rates of oxygen absorption, which were observed at the end of the induction period, would be affected by the volume of the volatile products in the vapour phase.

However, different final oxidation rates have been noted with different antioxidants in the same series of additives; as antioxidants within each series could be expected to operate by an essentially similar mechanism, it is considered that the different oxidation rates have significance. Thus, the general conclusion which has been drawn, remains valid, namely that in the evaluations of both the phenol and the sulphur antioxidants, there are residual antioxidant effects following the end of the induction period.

In the inhibited oxidation experiments, considerations of the molar volumes of the vaporised additives indicate that the amount of antioxidant present in the stabilised decalin could totally volatilise into the available oxygen atmosphere. However, the results which were obtained provide strong indications that very little volatilisation of the parent antioxidants occurred in practice.

In comparison with the tests in polypropylene, in which volatilisation could readily occur (torsional braid tests), the evaluations in decalin gave results which indicated that the antioxidants in each series (PP series etc) were exhibiting very similar stabilising activity at the same functional molar concentration. The differences between the volatilities of the antioxidants within each series have been shown to be very large and their similar activities would not be expected if varying contributions to antioxidant activity were being made from volatilised antioxidant in the gas phase oxidation of decalin and dissolved antioxidant in the liquid phase oxidation.

Antioxidants MPP and DMTP have similarly large volatility characteristics and these antioxidants showed almost the same antioxidant activity as the highest members of the series of stabilisers to which they belong; thus there does not appear to be any indication that the volatilisation of the parent antioxidants is involved in the determination of the 'inherent' activity of any of the antioxidants in decalin. The distribution of the parent antioxidants between the solution and vapour phases appears to favour the former.

However, the possibility does exist, in both series of phenols and with the thiodipropionates, that any oxidative breakdown products of the antioxidants may be volatilising. Oxidation of the phenols is unlikely to result in the formation of products which would exhibit volatilities markedly greater than those of BHT and MPP; however, the discussion of the mode of action of the thiodipropionates has shown that these antioxidants break down to lower molecular weight species in the course of their antioxidant action. Scott (149) has suggested that the final active products are sulphur oxides and it might be expected that, although the parent antioxidants are concentrated in the liquid phase, these volatile products and the intermediates in their formation could volatilise and act primarily in the vapour phase. Scott points out that the sulphur oxides are produced as hydrated species during the decomposition of hydroperoxide; these products would probably have a higher affinity for the hydroperoxidic and other polar species of low volatility, in the liquid phase, than would the sulphur oxides themselves. The intermediate sulphinic and sulphenic species would show a similar pattern of lower volatility in comparison with the parent thioether. The precise distribution of the various active antioxidant species between the vapour and liquid phases is not readily elucidated, therefore; however, the fact remains that all the thiodipropionate antioxidants and sulphur dioxide itself, exhibited similar activities (at the same molar concentration) in the oxidation of decalin, when the determinations were carried out in a closed system from which the antioxidant species could not escape.

The oxidation of unstabilised polypropylene in a closed atmosphere was monitored as a vigorous absorption of oxygen following a rapid rise to the maximum rate of oxidation. The major effect of the volatilisation of oxidation products, in over-riding the detection of the absorption reaction, was not noticed until the oxidation had progressed to an advanced stage. In the evaluations (phenolic antioxidants) in which an induction period was detected, there was no indication of either the absorption or the evolution of gas before the start of the catastrophic oxidation reaction. Thus, it is considered that the commencement of the vigourous absorption of oxygen correctly reflects the cessation of stabilising activity by the added antioxidants.

As with the decalin experiments discussed above, molar volume considerations indicate that the amount of antioxidant contained in the polypropylene samples in this evaluation, could totally volatilise into the available atmosphere in the monitoring apparatus. The excessive volatilisation of antioxidant, or breakdown products, would result in the early oxidation of the polymer depleted of stabiliser; however, as outlined above, such an oxidation would be detected by the measuring device.

Although no calamitous loss of antioxidant is occurring, it is possible that more subtle losses of the parent stabilisers or their breakdown products could be limiting the true efficiency of the stabilisers in the closed atmosphere tests. A comparative examination (Figure 6.9) of the volatilities of the PP phenolic antioxidants and their stabilising activities in polypropylene, under restricted and flowing atmospheres, is informative.

Antioxidant 4PP is particularly involatile, having a half-life of volatilisation of 3360 hours under nitrogen; this involatility is reflected by the open and closed oxidation tests which, within the limits of experimental error, give the same induction periods. It has been argued that, because the backbone of antioxidant 4PP is resistant to oxidation, this result indicates that little volatilisation of this stabiliser or its oxidative breakdown products is occurring. The induction period is markedly lower

FIG. 6.9 VOLATILITY AND ACTIVITY OF PP PHENOLIC ANTIOXIDANTS. POLYPROPYLENE.

ANTIOXIDANT	VOLATILITY HALF-LIFE AT 140^{o}C (hours) FLOWING N_2 ATMOSPHERE	INDUCTION PERIOD AT 140^{o}C (hours) 2×10^{-3} MOLES (Ø OH)/100 gm POLYMER	
		FLOWING O_2 ATMOSPHERE (torsional braid)	CLOSED O_2 ATMOSPHERE (O_2 absorption)
BHT	0.09	<5	140
MPP	0.28	<5	95
HPP	3.6	<5	315
LPP	83	<5	420
SPP	660	165	200
4PP	3360	625	620

than the half-life of volatilisation and it is considered that this measurement of activity reflects the inherent activity of the antioxidant in polypropylene.

The half-lives of volatilisation of the more volatile antioxidants, BHT, MPP, HPP and LPP, vary between 0.09 hours (BHT) and 83 hours (LPP). There are no indications in the literature that BHT oxidises to products which would be expected to have higher volatility than the parent antioxidant and thus the extremoly poor performance of this antioxidant in polypropylene, under a flowing atmosphere (< 5hours), reflects the high rate of loss of the parent antioxidant. However, in a restricted atmosphere, antioxidant BHT endowed a stability of 140 hours. Similar phenomena were noted with antioxidants MPP, HPP and LPP and it is considered that this indicates that the closed atmosphere, oxygen absorption, tests are therefore primarily reflecting the stabilising activity of the antioxidants, rather than their volatility. As the active phenolic products which may remain following the oxidative cleavage of the alkyl side chains of antioxidants HPP and LPP are highly unlikely to exhibit higher volatility than antioxidants BHT and MPP, the above conclusion is not affected by the observation that cleavage of this type does occur. Thus, although antioxidant LPP exhibits a half-life of volatilisation of 83 hours under nitrogen and would therefore show a considerably higher volatility under oxidising conditions, this antioxidant generates an induction period of 420 hours in the restricted atmosphere test.

Further weight is lent to the proposition that volatility is of only minor importance, under the restricted atmosphere conditions, by the irregularity of the activities of the antioxidants within the homologous series. Thus, although antioxidant SPP would be expected to show considerably higher activity than antioxidant LPP, if the effects volatility were of importance in the oxygen absorption tests, in practice this was not found to be the case.

As the volatilities of the MB polyphenolic antioxidants are all lower than those of the more volatile PP phenols, it is highly unlikely that volatility is having any significant effect upon the assessment of the activities of the MB antioxidants.

The oxidation of polypropylene containing the thioester antioxidants, in a closed environment, followed a dramatically different pattern to that observed with unstabilised polypropylene, and polymer containing the phenolic antioxidants. An examination of the half-lives of volatilisation of the thiodipropionates in comparison with those of the phenols, shows that the parent antioxidants should remain primarily in the polymer substrate. Furthermore, the thiodipropionate systems provided a conventional induction period when aged in a flowing atmosphere. It has therefore been suggested that the oxidative breakdown products of the thioesters are responsible for the redirection of the oxidation reactions of the polymer. Alongside the chemical effects of the breakdown of the thioesters within the polymer sample, the loss of volatile products, such as sulphur dioxide, to the vapour phase, is almost certainly making a contribution to the reaction sequences. However, the major differences between the results of the flowing and restricted atmosphere tests indicate that the redirection of the oxidative reactions of the polymer are due to the oxidation products of the thiodipropionates being constrained either within or in close proximity to the polypropylene sample. Because of the appearance of these phenomena, it was not possible to utilise the results which were obtained from the closed atmosphere tests, in the discussion of volatilisation effects.

7. CONCLUSIONS AND IMPLICATIONS.

In high temperature environments the loss of antioxidants by volatilisation is of primary importance in determining their activity.

The assessment of the activity of antioxidants at high temperatures, using accelerated oven ageing tests, can only be related to performance at lower temperatures when volatility effects are taken into account.

The initial requirement for an antioxidant to exhibit high activity in polymers in aggressive environments is that the antioxidant should remain in the polymer. Effects which are associated with the chemical efficiency of the antioxidant are of only minor significance compared with the effects of the persistence of the stabiliser in the polymeric substrate.

Two phenomena contribute to the volatilisation of radical trapping antioxidants, the loss of the parent compound and the oxidative cleavage of the backbone of the antioxidant to more volatile species. The present work indicates that when the latter phenomenon is reduced to a minimum, an antioxidant with a bulky molecular structure and with a molecular weight in excess of 1000-1200 has a sufficiently low volatility for this effect to be of minor importance in determining its activity at 140°C. However, considerably greater persistence would be required in more aggressive environments and it is doubtful if the above criteria would apply under conditions of water extraction at high temperature,for example. The volatilisation of antioxidants is of foremost importance in polymeric substrates of thin section and it appears that in these circumstances the loss of antioxidant can be considered solely in terms of the volatility of the pure antioxidant.

The mechanism of action of sulphur antioxidants precludes the dramatic improvements in performance that are associated with higher persistence in the radical trapping antioxidants. It is likely that a similar situation will exist in the case of peroxide decomposing phosphorus antioxidants, where again antioxidant action is associated with a breakdown of the parent stabiliser.

However, higher persistence of the parent sulphur antioxidant is distinctly beneficial and these effects could be expected to become more important in highly aggressive environments.

It would appear that attempts to improve the persistence of peroxide decomposing antioxidants, by increasing their molecular weight, should centre on two areas. By analogy with the phenolic stabilisers, improvements in the general oxidative stability of the backbone of the sulphur antioxidants could be expected to improve the persistence of these antioxidants. However, a more important requirement is the avoidance of polymeric or network-bound structures in which the sulphur atom is in the main backbone of the antioxidant; of necessity, peroxide decomposing action in structures of this type will involve the cleavage of the parent antioxidant to species of half the molecular weight (statistically) of the original stabiliser.

The present work has provided some indications that highest antioxidant activity is exhibited by stabilisers which tend to concentrate in the amorphous phase of polypropylene during crystallisation. Antioxidants of this type would be considered to be incompatible with polypropylene from assessments based upon the first order transition phenomena of the polymer and upon the solubility of the stabilisers in liquid hydrocarbons. However, there are indications that extremely low compatibility with the less ordered regions of the polymer can curtail activity. It should be noted that the grafting of antioxidants or their copolymerisation with the backbone of crystalline polymers may result in the antioxidants being unable to accumulate in the amorphous phase of the polymer during crystallisation.

The immobility or the restricted diffusion of an antioxidant in polypropylene does not necessarily preclude stabilising activity. However, the effects of diffusion phenomena upon the kinetic control of antioxidant reactions are difficult to isolate and identify and it remains unclear whether any reduction in the efficiency of thermo-oxidative stabilisers is associated with low mobility.

APPENDIX 1

Patents. Polymeric and Network Bound Stabilisers.

Allied Chemical	US 3,345,326	(1967)
American Cyanamid	US 3,200,068	(1965)
	Fr 2,002,152	(1969)
	Ger 1,908,027	(1969)
Atlas Powder	US 2,802,820	(1957)
Bayer	Ger 1,056,366	(1959)
Carlisle Chemical	US 3,396,185	(1968)
Compagnie de Signaux	Fr 1,376,649	(1964)
Dow	Ger 1,942,697	(1970)
Du Pont	US 3,457,328	(1969)
	US 3,438,910	(1969)
Eastman Kodak	US 3,1571517	(1964)
	Fr 1,407,630	(1965)
	UK 1,106,213	(1968)
Esso	US 3,477,991	(1966)

Ethyl	Fr 2.002,528	(1969)
Geigy	UK 1,105,699	(1968)
	Ger 1,931,452	(1970)
General Aniline	UK 1,105,935	(1968)
	US 3,361,709	(1968)
Goodrich	UK 948,549	(1964)
Goodyear	US 3,338,866	(1967)
	US 3,317,459	(1967)
Hercules	US 3,351,678	(1968)
	US 3,392,141	(1968)
	UK 1,165,231	(1969)
Hoechst	Fr 1,545,354	(1968)
Humble Oil	US 3,510,507	(1970)
I.C.I.	UK 1,052,702	(1968)
	UK 1,094,532	(1968)
	Belg 688,743	(1968)
	Ger 1,918,342	(1969)
Min.Tech/N.R.D.C.	UK 1,161,909	(1969)
	UK 1,144,641	(1969)

Mitsubishi Rayon	Jap 68 16392	
	Jap 68 16393	
	Jap 68 16395	
	Jap 68 16396	
	Jap 68 16397	
	Jap 68 21964	
	Jap 68 21965	
	Jap 68 21966	
	Jap 68 21967	
	Jap 68 21968	
	Jap 69 32,053	
	Jap 69 32,054	
	Jap 69 30,738	
	Jap 69 30,983	
	Jap 69 30,984	
	Jap 69 30,986	
	Jap 69 32,422	
	Jap 69 30,981	
	Jap 69 31,809	
	Jap 70 03,787	
Mitsui Chemical	Ger 1,947,590	(1970)
Monsanto	UK 971,753	(1964)
	UK 1,106,117	(1968)
	UK 1,128,388	(1968)
Montecatini	Ital 640,616	(1962)

Nalco Chemical	US 3,065,206	(1962)
N.R.P.R.A.	UK 1,185,896	(1970)
Pure Chemicals	Fr 1,321,898	(1963)
	UK 1,166,276	(1969)
Raychem	Fr 1,576,215	(1969)
Rohm & Hass	US 2,825,714	(1958)
Sun Oil	US 3,350,347	(1968)
Universal Oil	US 3,364,173	(1968)

APPENDIX 2

ATTEMPTS TO SYNTHESISE AND CHARACTERISE HIGH MOLECULAR WEIGHT ANTIOXIDANTS

A2.1 Background

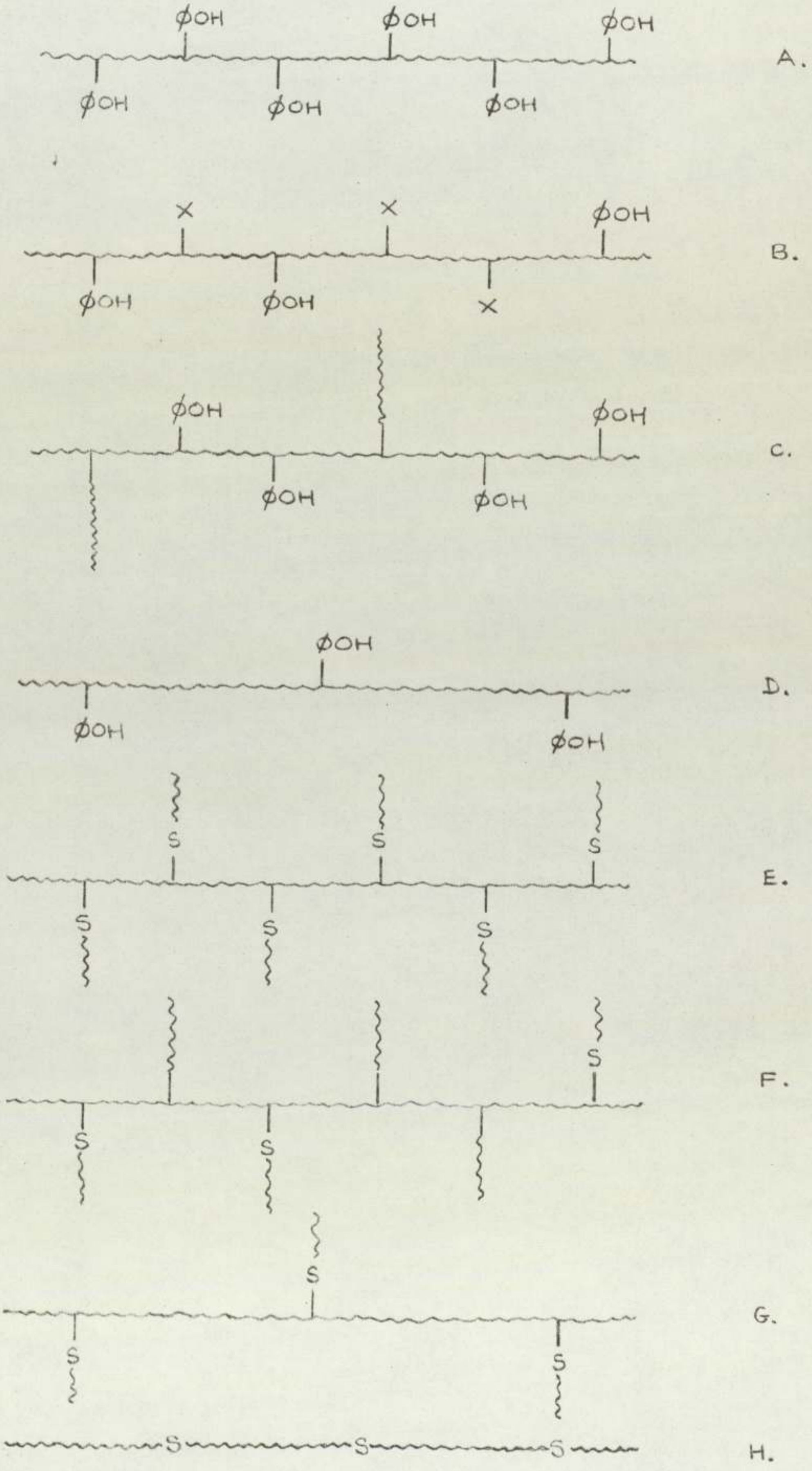
The highest molecular weight antioxidant examined in the work which has been described was the tetraphenolic stabiliser 4PP (Irganox 1010; Ciba-Geigy Ltd; molecular weight 1176); at the start of the present evaluations it was thought to be of interest to examine the antioxidant properties of materials of considerably higher molecular weight, in order that the effects which are associated with molecular size (and shape) would become fully developed.

Unfortunately, none of the preparative routes which were examined led to the isolation of characterisable high molecular weight stabilisers; the attempted preparations are outlined here as possible guide for further work.

It had been hoped that both phenolic and sulphur antioxidants could be produced, by well characterised routes giving oligomeric and polymeric materials. The types of structure which were considered to be of interest are shown in Figure A2.1.

Two potential routes appeared to be open; firstly, the polymerisation of a simple monomer, giving a polymeric backbone with pendant reactive side chains, which could

FIG. A2.1. REQUIRED STRUCTURES OF HIGH MOLECULAR WEIGHT ANTIOXIDANTS.



then be utilised for reaction with antioxidants containing suitable reactive sites; secondly, the formation of a polymerisable antioxidant species and its subsequent polymerisation under controlled conditions.

The former procedure appeared to have some advantages in that the initial polymeric backbone could first be characterised without the possible complications produced by bulky pendant antioxidant species. Subsequently, the antioxidant functionality could be introduced and a further characterisation could be undertaken in cross-reference. The method had the disadvantage that the complete saturation of pendant sites with antioxidant species might prove difficult with backbones of higher molecular weight; for this reason the method was thought to be applicable primarily to lower molecular weight oligomeric materials. The second technique, although providing a potentially cleaner route to polymeric backbones fully saturated with antioxidant species, held the disadvantage that it may be more difficult to fractionate and characterise polymeric materials consisting primarily of bulky and complex antioxidant side chains.

Both free radical and condensation polymerisations appeared to offer suitable syntheses; however, the free radical polymerisation of convenient monomers did not offer as much flexibility for the preparation of antioxidants with varying polymeric structures.

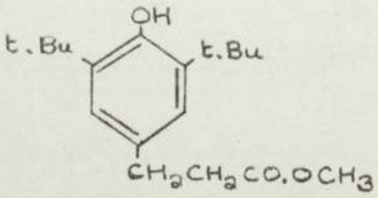
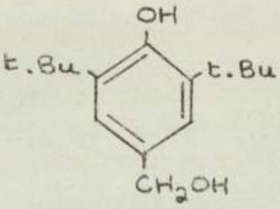
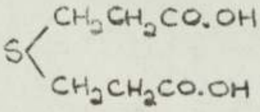
It was considered that the phenolic antioxidants should be based upon the 2,6-ditertiarybutyl-phenol structure, this being the basis of several commercial mono, bis, tris and tetra phenolic antioxidants which are widely used in polymers (see Introduction). This structure is acknowledged as having high antioxidant activity and few unwanted side effects (no discolouration in the presence of transition metal catalysts, no gas-fume fading etc).

The sulphur species which was thought worthy of examination was the thiodipropionate structure; sulphur antioxidants of this type are the major synergistic stabilisers in commercial use in polypropylene.

Within these limits there were several useful precursors to the required antioxidants, which were available from industry as development samples (Figure A2.2). The structures outlined in Figure A2.1 have been based upon these precursors.

Structures A and E show diagrammatically the basic high molecular weight antioxidants; by controlling the polymerisation reaction to produce polymers of varying molecular weights (possibly followed by fractionation), the effects of this parameter on antioxidant efficiency could be examined.

FIG. A2.2. PRECURSORS TO POLYMERIC ANTIOXIDANTS.

		CODE
	GEIGY	MPP
	SHELL	HMP
 $S\left\langle\begin{matrix}CH_2CH_2CO.OH\\CH_2CH_2CO.OH\end{matrix}\right.$	ROBINSON BROS.	TP

Structures B and F represent an attempt to determine the influence of the density of reactive antioxidant sites in the backbone, whilst maintaining a format as close as possible to those investigated in structures A and E. Thus, it was considered that the substitution of the phenolic hydrogen by a methyl group (in substituent X) would remove antioxidant activity from these nuclei whilst maintaining a similar molecular weight and structure. Similarly, with the sulphur antioxidants, the substitution of a long chain aliphatic acid (eg suberic acid) for thiodipropionic acid would give analogous comparisons with the sulphur antioxidants of structure E.

Structures C, D and G (and also F) represent attempts to examine the effects of compatibility on antioxidant activity, for stabilisers of similar molecular weight to those represented by A and E.

Finally, it was hoped that structure H would give some indication of the effects of incorporating sulphur functionalities in the antioxidant backbone rather than in side chains; comparisons of this type would allow the effects of the oxidative cleavage of sulphur antioxidants to be examined.

The preparations which were undertaken are outlined in the following sections.

A2.2 Syntheses based on oligomers of poly(vinyl alcohol) and Geigy's phenylpropionate ester.

The projected syntheses are shown in Figure A2.3.

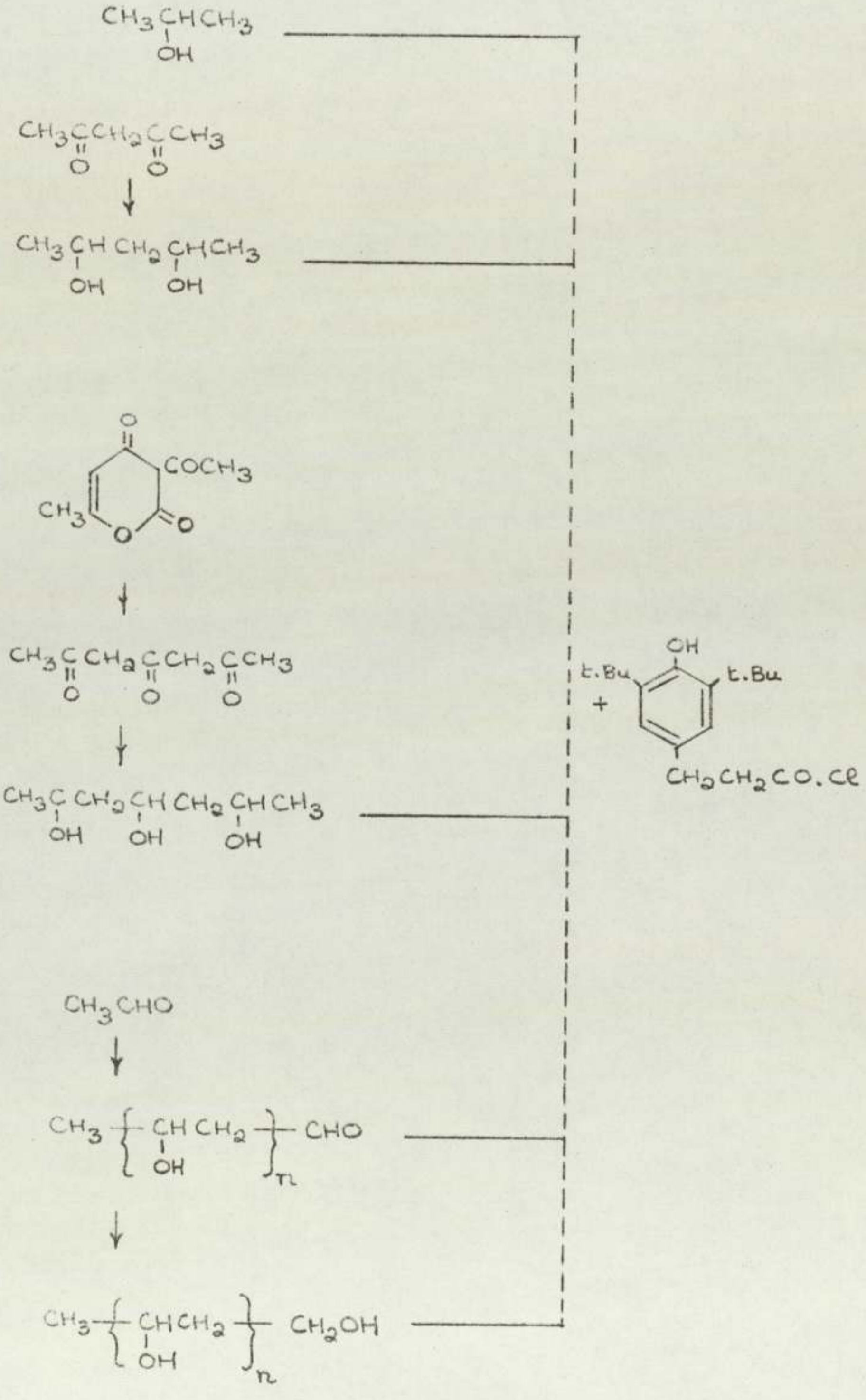
The preparation of low molecular weight vinyl alcohol polymers together with independent preparations of the model compounds have been detailed in the literature. The esterification or transesterification of these polyhydroxylic materials with antioxidant MPP or its acid derivatives appeared to offer a useful synthetic route; the use of the acid chloride derivative of MPP was chosen as being the most positive esterification technique and the least prone to side reactions.

Preparation of the parent acid and its acid chloride from ester MPP.

The hydrolysis of MPP was accomplished simply, by treatment with dilute sodium hydroxide solution under reflux. After pouring the reactants into excess dilute hydrochloric acid, the filtered product was recrystallised as white needles from ethanol (Mp 174°C; literature (199) 174°C).

The acid chloride was prepared by the dropwise addition of a solution of the parent acid in benzene to a three molar excess of thionyl chloride; the temperature was maintained below 20°C during the addition and the reaction was completed by heating to 60°C for one hour. After evaporation

FIG.A2.3. PROJECTED ROUTES TO POLYMERIC ANTIOXIDANTS BASED ON MPP AND OLIGOMERS OF POLY(VINYL ALCOHOL) TYPE STRUCTURES.



of the excess thionyl chloride, recrystallisation from dry petroleum ether (40°-60°C) yielded the acid chloride as white needles (Mp 72-73°C; literature (199) 73°C).

Preparation of 2,4-pentanediol

Acetylacetone was reduced to 2,4-pentanediol using sodium borohydride as described by Pritchard and Vollmer (200).

A solution of acetylacetone (250 gm) in methanol (750 gm) was added slowly to a stirred solution of sodium borohydride (62.5 gm) and sodium hydroxide (pellets, 1.25 gm) in water (625 gm), maintained below 20°C. The solvents were then removed rapidly under reduced pressure (20 mm Hg) and glycerol was added to the solid residue to liberate the diol from its borate complex. The product was distilled under reduced pressure, through a short fractionating column, yielding the colourless and rather viscous diol in 85% yield (Bp 73-74°C, 3 mm Hg, n_D^{20} 1.4345; literature (200) Bp 73-74°C, 3 mm Hg, n_D^{20} 1.434).

Preparation of 2,4,6-heptanetriol

Diacetylacetone was prepared from dehydracetic acid and then reduced to the triol. The first stage of the preparation was carried out according to the method of Bethell and Maitland (201).

Dehydracetic acid (200 gm) and concentrated hydrochloric acid (1000 ml) were refluxed until the evolution of carbon dioxide ceased (45 minutes). After evaporation under reduced pressure (20 mm Hg) to give a semi-solid mass, the reactants were dissolved in 10% sodium hydroxide solution. Barium hydroxide (480 gm), in boiling aqueous solution, was added and a yellow precipitate of barium dimethylpyrrone was collected; this was immediately dissolved in excess dilute hydrochloric acid (15%). Extraction of the acid solution with ether, followed by evaporation of the solvent, yielded a colourless oil. Distillation under reduced pressure gave diacetylacetone, in 55% yield, as an oil which crystallised to white platelets on cooling (Bp 96-97°C, 8 mm Hg, Mp 49-50°C; literature (201) Bp 96-97°C 7 mm Hg, Mp 49°C). Subsequent preparations revealed that purification of the product could also be achieved by recrystallisation from a minimum volume of ethanol.

The reduction of diacetylacetone to the triol has been carried out by Miyake and Kominami (202) using catalytic hydrogenation under pressure. However, the clean reduction of acetylacetone provided by sodium borohydride prompted an investigation of this route.

The reduction was carried out in an exactly similar way to that described above; however, the decomposition of the triol borate complex was accomplished by adding sorbitol (5 gm/gm triketone) rather than glycerol. Distillation of the liberated triol gave a colourless, viscous oil in 56% yield (Bp 134°C, 4 mm Hg, n^{20}_D 1.4627; literature (202) Bp 137°C, 4 mm Hg, n^{20}_D 1.4624).

Polymerisation of acetaldehyde to poly(vinyl alcohol)

The polymerisation of acetaldehyde, under pressure, has been shown by several workers to result in polymers based upon a polyether structure; Imoto (203) has reviewed this work. However, Imoto (203) has also shown that the polymerisation of acetaldehyde under pressure,using triethylamine as catalyst, can result in successive aldol condensation reactions giving a poly(vinyl alcohol) structure. It was found that a considerable amount of dehydration also occurred during polymerisation, leading to the introduction of unsaturation into the backbone of the polymer; the products were, in fact, quite highly coloured.

Imoto subsequently described (204-206) a polymerisation technique whereby poly(vinyl alcohol) structures could be produced which contained little or no unsaturation. This was accomplished by using sodium or lithium/mercury amalgams as catalysts and by carrying out the acetaldehyde polymerisations at low temperatures and at atmospheric pressure.

Imoto was able to obtain polymers with a range of average molecular weights up to approximately 950 (22 monomer units, approximately); an examination was carried out of the relationships between the molecular weights of the products and the catalyst composition and concentration, the temperature and duration of reaction and the type of solvent.

In the present work, several initial polymerisations were undertaken to determine the suitability of the polymers as precursors of high molecular weight antioxidants. The two preparations which are outlined below illustrate the basic polymerisation technique at low temperature and also the use of a subsequent treatment at higher temperature to obtain polymers of higher molecular weight.

Acetaldehyde (193 gm) was added to n-hexane (132 gm) in a flask which was continuously, yet slowly, purged with dry nitrogen. This solution was cooled to -50°C in acetone/dry ice and lithium/mercury amalgam (2.0 gm containing 5.6% lithium) was added with stirring. The temperature was allowed to rise to 0°C and was then maintained for 20 hours.

The reaction mixture was poured into water and, after the hexane solvent had been separated, the aqueous solution was decanted from the mercury residue. The alkali metal was then removed by passing the solution through an ion exchange column (20 cm x 4 cm, Permutit Zeocarb H228, hydrogen-form).

The solution was concentrated at 70°C under reduced pressure (10 mm Hg), giving a colourless and highly viscous liquid.

In the study of the two-stage polymerisation technique, a preparation exactly similar to detailed above was first carried out; however, following the low temperature polymerisation schedule, the reactants were heated to 70°C for one hour without removing the catalyst. The isolation of the polymer then followed the previous method, again giving a highly viscous colourless liquid.

The molecular weights of the products were determined by cryoscopy using benzene as the solvent; these are compared below with Imoto's results, which were obtained using the same technique:

Polymerisation	Found		Literature (205)	
	Yield	MW	Yield	MW
Single stage	49%	537	54%	572
Double stage	78%	943	81%	960

An initial examination of both samples by IR spectroscopy indicated the absence of ether stretching frequencies in the range 1110 cm^{-1} – 1140 cm^{-1} and a typical broad hydroxyl band, peaking at approximately 3300 cm^{-1}. It was not possible to conclusively identify any bands attributable to unsaturation; however the presence of aldehydic species (chain terminating) was indicated by a weak band at 1730 cm^{-1}. Unfortunately the presence of this carbonyl group preculuded the detection of unsaturation by UV spectroscopy; it had been intended to carry out a reduction of the aldehydic end groups before the polymers were used as intermediates and this would have enabled UV spectroscopy to be used for scanning any unsaturation. However, following the failure of the antioxidant preparations involving the diol and triol model compounds (see below), the investigation was concluded.

Preparation of the iso-propyl ester of MPP acid

A solution of MPP acid chloride in benzene was added with stirring to an equimolar quantity of isopropanol, in excess pyridine, at 0°C. The reactants were then heated to 40°C for one hour and allowed to cool overnight. After the removal of pyridine hydrochloride by filtration and the evaporation of the solvents under reduced pressure, the residue was recrystallised from ethanol giving the iso-propyl ester as white plates in almost quantitative yield (Mp 58°C; C 75.1%, H 10.2%, calculated C 75.0%, H 10.0%).

Reaction of MPP acid chloride with 2,4-pentanediol and 2,4,6-pentanetriol

A series of unsuccessful attempts were made to prepare the fully esterified derivatives of the diol and triol model compounds of poly(vinyl alcohol).

An initial examination of the solubility characteristics of the MPP acid revealed that it had very low solubility in aqueous alkaline media; thus the use of excess acid chloride in the esterification reaction posed potential difficulties in the separation of unreacted acid from the expected liquid ester products. Molar ratios of the reactants were therefore used in the attempted preparations of the di and tri esters.

The reactions were again carried out in pyridine and on completion pyridine hydrochloride was removed by filtration. Benzene was then added to the pyridine solution and the excess pyridine was removed by washing with dilute hydrochloric acid. After further washings with dilute sodium bicarbonate solution and water, the benzene solution was dried and the solvent was removed under reduced pressure yielding pale yellow oils from both the diol and triol.

A first series of preparations were carried out using a reaction schedule of one hour at 70°C and these appeared initially to have been partially successful in that the IR spectra of the products contained an ester carbonyl frequency at 1730 cm^{-1}. However, a shoulder on this peak, at 1700 cm^{-1}, indicated that some unreacted acid was present in the products from both the diol and triol esterifications.

Thin layer chromatography on the reaction products from the esterification of the diol revealed three spots which could be assigned to MPP acid. Chromatographic examination of the products from the triol esterification revealed five spots (at least) which could be attributed to esterification products and again an MPP acid spot appeared.

As partially esterified products could not be responsible for such complex chromatographic displays, it was considered possible that isomers of these optically asymmetric esters might be involved.

Thin layer chromatography had revealed that column chromatography (Camag alumina) would enable MPP acid to be removed from the products and this was carried out on both the diol and triol reaction products. Determinations of the molecular weights of these products using vapour phase osmometry demonstrated that nothing more than mono-esterification had been achieved in either preparation.

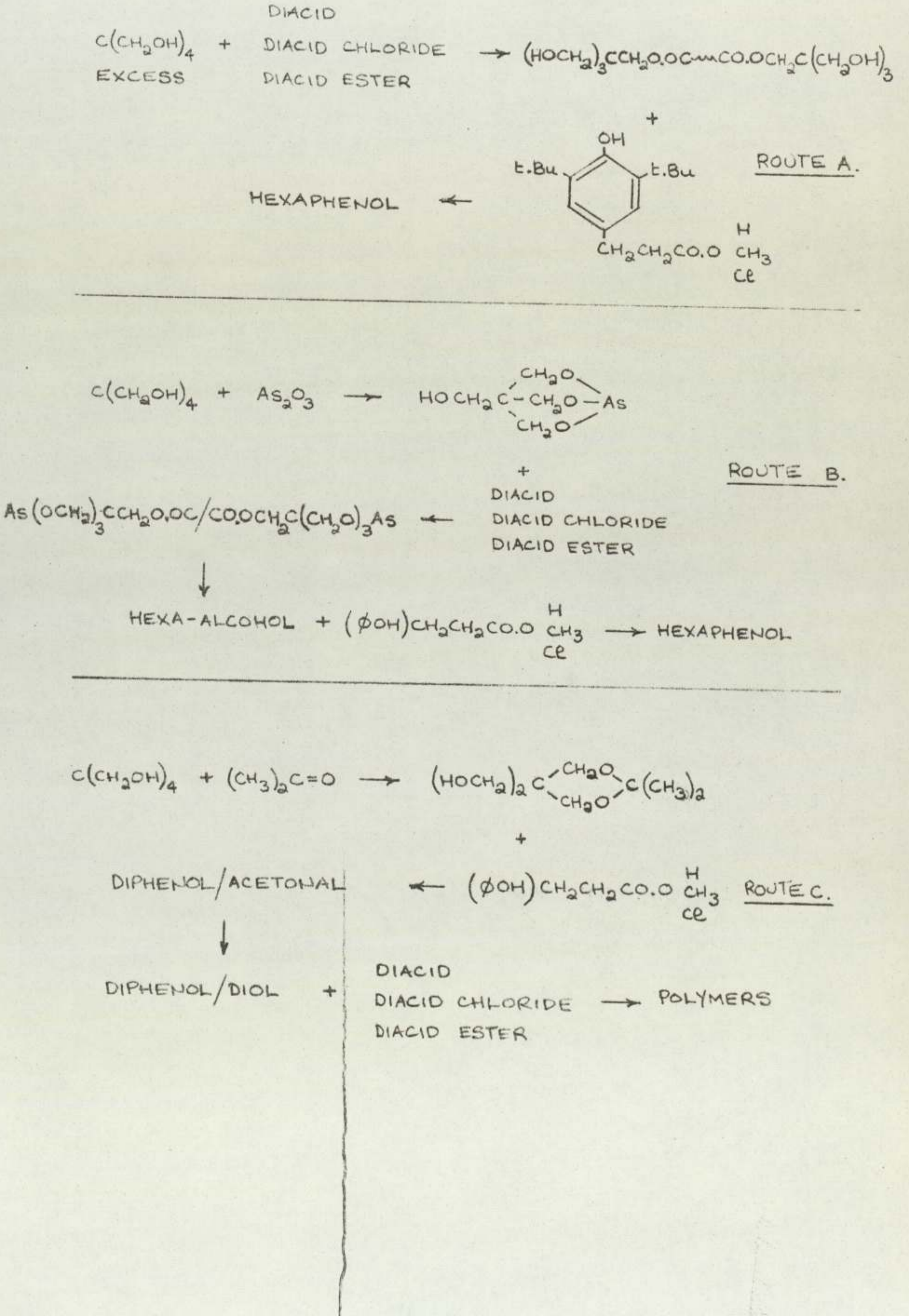
It was concluded that the complex thin layer chromatographic patterns must be due to the presence of products resulting from the dehydration of the diol and triol backbone. It was not, however, possible to identify bands in the IR spectra of the products which could be definitely attributed to unsaturated species, due to the complex nature of these traces.

A further series of preparations were attempted in which efforts were made to prevent dehydration reactions occurring alongside the esterification process. The preparations were carried out by the same method as described previously, using pyridine as solvent, but the severity of the reaction conditions were reduced by using lower reaction temperatures. Dehydration was still found to be occurring at 20°C; below this temperature the esterification reaction became slow and the analyses, which were outlined above, indicated that the amount of unreacted acid in the products was increasing whilst dehydration was still occurring.

A2.3 Syntheses based on polyesters of pentaerithritol and Geigy's phenylpropionate ester

The synthetic routes which were considered are shown in Figure A2.4. This approach is based upon the route used by Ciba-Geigy for the preparation of Irganox 1010 (antioxidant 4PP). However, whereas in this antioxidant, pentaerithritol is substituted with four antioxidant units, the preparation of bis or tris substituted derivatives offered the possibility of the controlled condensation of the unsubstituted hydroxyl groups with diacids, to produce characterisable polymers.

FIG. A2.4 PROJECTED ROUTES TO POLYMERIC ANTIOXIDANTS BASED ON MPP AND PENTAERITHRITOL.



A2.3.1 Route A

Although dangers of polyesterification exist in the reaction of excess diacid with pentaerithritol, this route was considered to be worth a brief examination as a method of preparing the first member of the series of oligomeric and polymeric antioxidants. Throughout this and subsequent work on pentaerithritol polyesters, adipic acid was used as the esterifying linkage. This acid was chosen in an attempt to introduce a polyolefin-compatible backbone into the final antioxidants; furthermore, it was hoped that the wide molecular spacing of the hydroxyl esterification sites in pentaerithritol adipate polyester would reduce the steric hindrance of antioxidant grafting or polymerisation reactions.

Direct di-esterification of adipic acid with pentaerithritol

Adipic acid was heated, in the absence of a solvent with a 5 molar excess of pentaerithritol (based on di-esterification); in a parallel experiment a 10 molar excess of the polyol was used. The reactants melted and stirring was commenced when the temperature reached 160°C. The temperature was increased to 190°C and after 3 hours an almost theoretical quantity of water had been evolved from the clear mobile liquids. The products solidified on cooling; their IR spectra revealed the required ester carbonyl absorption at 1730 cm^{-1}.

Although little polymerisation appeared to have occurred, considerable difficulty was encountered in the separation of the diester from the excess pentaerithritol, due to the intractable solubility characteristics of both materials. Attempted triturations, extractions and recrystallisations from a wide range of solvents met with no success; the products always had wide melting ranges.

A2.3.2 Route B

Preparation of pentaerithritol arsenite

Pentaerithritol arsenite was prepared by the method described by Englund (207) and Stevens (208).

Pentaerithritol (163 gm) and arsenic trioxide (119 gm) were heated slowly; the mixture began to melt at 80°C and water started to distil at 120°C, from a side arm condenser. Heating was continued rapidly to 230°C and the product was then cooled; approximately 31 ml of water was collected during the reaction (theoretical 32.5 ml).

The product was then vacuum distilled giving 230 gm (93%) of pentaerithritol arsenite (Bp 140°C, 0.7 mm Hg, Mp 105°-106°C; literature (208) Bp 140°C, 1 mm Hg, Mp 106°-107°C; (207) Mp 102°-103°C).

An examination of the IR spectrum of the arsenite revealed that the broad hydroxyl stretching frequency, at approximately 3300 cm^{-1} in pentaerithritol, had decreased considerably in intensity and had shifted to approximately 3450 cm^{-1}.

The isolated and intense absorption at 1130 cm^{-1} (C-O stretching) in pentaerithritol was found to be replaced by a multiple system ranging from 1140 cm^{-1} to 1180 cm^{-1}. The isolated absorption at 870 cm^{-1} (origin unknown) was replaced by a pair of peaks of similar intensity at 835 cm^{-1} and 905 cm^{-1}.

Reaction of pentaerithritol arsenite with adipyl chloride

The method used by Stevens (208) for the preparation of esters of pentaerithritol arsenite and monobasic acids was adopted. Adipyl chloride (18.3 gm; BDH, redistilled, 110°C 10 mm Hg) was added dropwise to a stirred solution of the arsenite (41.6 gm) in dry pyridine (150 ml) at 10°C. A precipitate of pyridine hydrochloride began to form almost immediately and a mildly exothermic reaction ensued; the reactants were then maintained at 50°C for 3 hours. The excess pyridine was then removed under reduced pressure leaving a light brown solid.

Two methods of isolating the esterified arsenite were examined in a series of preparations

(a) The crude product was triturated with 2 x 100 ml portions of absolute methanol at 0°C to dissolve pyridine hydrochloride. After filtration and drying (vacuum oven, ambient temperature) 40.5 gm of solid product remained (79%).

(b) The crude product was refluxed twice with 250 ml portions of petroleum ether (100°-120°C) for 15 minutes; the supernatant liquor was decanted hot and, on chilling in dry ice, yielded a white solid (36.8 gm, 70%).

The IR spectroscopic examination of these crude products indicated that esterification had been accomplished, absorptions being noted at 1730 cm^{-1}, 1195 cm^{-1}, 1175 cm^{-1} and 1150 cm^{-1}. However, the presence of a moderately strong, broad hydroxyl stretching frequency at approximately 3400 cm^{-1} and the appearance of an acidic carbonyl frequency, at 1720 cm^{-1}, as a weak shoulder on the ester carbonyl absorption, indicated that some hydrolysis of the acid chloride had occurred. Although the twin peaks at 835 cm^{-1} and 905 cm^{-1}, which appeared in the original arsenite spectrum, were again present, it was also considered possible that some hydrolysis of the arsenite functionality could have occurred.

Although several preparations were carried out using carefully dried solvents, it was found impossible to avoid these indications of minor hydrolysis. Whereas previous workers (207, 208) had found it possible to readily isolate, by distillation, the derivatives based upon monobasic acids, the separation of the present compound was found to be difficult. Distillation under reduced pressure lead to discolouration and decomposition; recrystallisation from a variety of carefully dried, solvents always resulted in products with hydroxylic species present.

Hydrolysis of the diarsenite of dipentaerithrityl adipate

Due to the difficulties encountered in isolating the arsenite derivative, attempts were made to procede directly to the hexa-alcohol.

Two methods of hydrolysis were investigated; the first was carried out heterogeneously on a silica gel column, the second using acid in the liquid phase.

(a) The crude arsenite (1.5 gm) was dissolved in methylene chloride and placed on a silica gel column (2 cm x 15 cm) packed with methylene chloride. The column was first eluted with methylene chloride (200 ml) and then with methylene chloride/methanol (6/1, 500 ml). Evaporation of the last elutant yielded a colourless and rather viscous oil (0.5 gm, 45% approximately).

(b) To a solution of the crude arsenite (5.25 gm) in acetone (30 ml) were added 2 ml water and a few drops of dilute hydrochloric acid. Arsenic sulphide was then precipitated by blowing hydrogen sulphide gas through the solution and the precipitate was filtered. Evaporation of the solvent produced a rather viscous colourless oil (3.2 gm, 84% approximately).

The IR spectra of the crude products exhibited the characteristic ester carbonyl frequency at 1730 cm^{-1}; the hydroxyl stretching frequency peaked at approximately

3300 cm^{-1}, as originally found in pentaerithritol. The twin peaks at 835 cm^{-1} and 905 cm^{-1}, associated with the arsenite structure, were seen to have been replaced by the single sharp absorption at 870 cm^{-1} which was noted in the spectrum of pentaerithritol.

Although IR analysis had indicated that the required diester was probably present in the crude products in significant concentrations, it was found difficult to isolate a characterisable derivative. Prolonged storage or the trituration of the oils themselves or their concentrated solutions in a variety of solvents, under ambient and refrigerated conditions did not result the crystallisation of the hexa-alcohol; pentaerithritol itself was deposited slowly in some cases, however, and this was attributed to the disproportionation of the partially esterified pentaerithritol structure (209).

Recrystallisation also met with little success; - it was however found that crystalline white solids could be isolated from alcoholic media; these products were always found to have a wide melting range (commonly in the region 140°-185°C).

Column chromatrography was not attempted in these isolations; it was considered that the isolation of sufficient starting material for subsequent preparations would be excessively time consuming.

Reaction of pentaerithritol arsenite with terephthalyl chloride

In an effort to obtain a product which could be more readily isolated, attempts were made to prepare the dipentaerithrityl terephthalate ester.

Terephthalyl chloride was prepared in the usual way by treating terephthalic acid with phosphorus pentachloride. After the evaporation of phosphorus oxychloride under reduced pressure, the crude product was recrystallised as yellow needles from a small quantity of dry benzene (Mp 78°C).

A solution of terephthalyl chloride (20.3 gm) in dry benzene (70 ml) was added dropwise to a stirred solution of pentaerithritol arsenite (41.6 gm) in dry pyridine (150 ml) at 10°C. A white precipitate began to form immediately and a mildly exothermic reaction ensued. The reactants were then heated at 50°C for 2 hours.

The solvents were removed under reduced pressure and the remaining near-white crude product was triturated with absolute methanol (2 x 50 ml) at 0°C, to remove pyridine hydrochloride; after drying a white residue remained (39.5 gm, 78% approximately).

The IR spectrum of this product again revealed that some hydrolysis had taken place; a broad absorption peaking at 3400 cm^{-1} was seen together with an absorption at 1040 cm^{-1} of medium intensity. However, a strong ester carbonyl absorption at 1715 cm^{-1} indicated that the esterification reaction had progressed to a considerable extent; a weak shoulder at 1680^{-1} argued the presence of unreacted acid species.

The difficulties which were encountered in isolating the arsenite/adipate derivative prompted the direct hydrolysis of the phthalate derivative without purification.

In successive experiments hydrolysis was carried out using the techniques described previously (silica gel column and acid hydrolysis) and a white solid was isolated using both procedures. Recrystallisation of this solid from aqueous ethanol yielded fine white needles (Mp. 186°C; C 55.2% H 3.7%, theoretical C 55.4% H 3.6%). In several experiments, hydrolysis on a silica column provided 40%-50% yields and acid hydrolysis provided 65%-75% yields, based on the crude starting material.

IR analysis revealed a broad hydroxyl stretching absorption at 3300 cm^{-1} and a strong carbonyl peak at 1715 cm^{-1}. A sharp peak at 815 cm^{-1} characterised a 1,4 disubstituted aromatic species. Two single carbon/hydrogen stretching frequencies appeared at 3120 cm^{-1} (aromatic) and 2960 cm^{-1} (aliphatic).

NMR spectroscopy (in TMS) revealed signals at 1.8 τ, 5.3 τ and 5.9 τ with intensities in the ratios 1/1/3 respectively. All were unsplit and were attributed to the aromatic, ester linkage and alcoholic methylene protons, respectively.

Reaction of dipentaerithrityl terephthalate with MPP acid chloride

A series of unsuccessful attempts were made to prepare the hexaphenol derivative of the above intermediate. In the preparations which were undertaken, it proved impossible to fully esterify the six available hydroxyl sites. The esterifications were carried out by adding a solution of MPP acid chloride to a suspension of the pentaerithritol derivative in excess pyridine at 10°C. The reactants were then heated to accelerate the esterification; it was found that even after treatment at 80°C for six hours,complete esterification had not been accomplished.

Preparations were carried out using both the required molar quantity of acid chloride for full esterification and double molar quantities. The unreacted acid was separated from the partially esterified products in the latter experiments by column chromatography with Camag alumina, a technique which allowed the recovery of a sufficientamount of the mixed esters for spectroscopic examination.

It was not clear why the hexa-functional intermediate was resistant to complete esterification; however, steric effects may well have been involved.

A2.3.3 Route C

Preparation of pentaerithritol mono-acetonal

After attempting the preparations suggested by Boeseken (201) and Orthner and Freyss (211), both of which gave poor yields, the method developed by Bonner, Bourne and Saville (209) was employed.

Concentrated hydrochloric acid (100 ml) was added to a mixture of acetone (4040 ml) and water (1060 ml). Pentaerithritol (200 gm) was added to the stirred solution and the reactants were heated to reflux, during which process the liquor cleared. Reflux was maintained for 30 minutes and the reactants were then allowed to cool overnight.

After neutralisation with sodium hydroxide solution (25%), the product was evaporated to dryness under reduced pressure (30 mm Hg). The resulting white solid was extracted for 6 hours with petroleum ether (40°-60°C), using a Soxhlet apparatus, to remove any diacetonal derivative; the solvent was then changed to ether and the monoacetonal was extracted (24 hours). After evaporation of the solvent, the monoacetonal was obtained as white platelets (65 gm, 25%;

Mp 126°-127°C; literature (209), Mp 126.5°-127.5°C).

Reaction of pentaerithritol diacetonal with MPP acid chloride and hydrolysis of the acetonal

The esterification procedure was similar to that used by Orthner and Freyss (211).

A solution of MPP acid chloride (27.8 gm) in dry benzene (30 ml) was added to a stirred suspension of pentaerithritol diacetonal (8.8 gm) in dry pyridine (60 ml) at 10°C; a slightly exothermic reaction occurred; the reactants were then heated at 50°C for three hours.

After filtration, to remove pyridine hydrochloride, the solvents were evaporated under reduced pressure (30 mm Hg), giving a pale yellow and rather viscous oil. This product was then extracted with petroleum ether (40°-60°C) to ensure a complete separation from residual pyridine salt. After filtration and evaporation the viscous oil was recovered (37.8 gm, 87%).

The IR spectrum of this crude product gave no indication that hydrogen bonded hydroxyl species were present (the hindered phenolic hydroxyl of the antioxidant moiety giving a sharp unbonded absorption at 2640 cm^{-1}). It appeared therefore that di-esterification had neared completion; an ester carbonyl absorption was apparent at 1730 cm^{-1} and no indications of unreacted acid species were seen.

It was found impossible to crystallise or recrystallise a solid product from the crude oil. Unfortunately time constraints precluded a more detailed examination of purification techniques. It was considered that column chromatographic separation would be well worthwhile.

Hydrolysis of the esterified acetonal

In the hope that the pentaerithritol diester would be a more easily purifiable product, the hydrolysis of the acetonal was examined. A solution of the acetonal was shaken with dilute hydrochloric acid (N/20) for two hours. After washing with water and drying, evaporation of the solvent yielded a white oil in almost quantitative amounts.

The IR spectrum of this crude product indicated that satisfactory hydrolysis had been accomplished; a broad hydroxyl absorption was apparent, peaking at approximately 3300 cm^{-1}, together with an ester carbonyl peak at 1730 cm^{-1}; again no evidence of acid species was noticeable.

Unfortunately, it again proved impossible to isolate a pure product by simple means; however, this route to higher molecular weight antioxidant offered promise and may be worth further investigation.

A2.4 Syntheses based upon thiodipropionic acid and glycols or polyesters of pentaerithritol

Alongside the syntheses based upon pentaerithritol and phenol antioxidant MPP, a restricted number of preparations were attempted based on thiodipropionic acid, in an effort to obtain polymeric sulphur antioxidants. The projected syntheses are shown in Figure A2.5.

Preparation of thiodipropionyl chloride

The acid chloride was prepared in the normal way using thionyl chloride, in three molar excess based upon dichlorination.

After evaporation of the excess thionyl chloride, the acid chloride was distilled under reduced pressure to give a very pale yellow liquid (Bp 120°C, 0.5 mm Hg; n_D^{20} 1.5185). Hydrolysis gave the parent acid (Mp 129°-130°C) in quantitative yield.

Monostearyl ester of thiodipropionic acid

Stearyl substitution of the thiodipropionate structure was considered to be worth examination as this side chain contributes both compatibility (with polyolefins) and molecular bulk. In fact, distearylthiodipropionate is a

FIG. A2.5 PROJECTED ROUTES TO POLYMERIC ANTIOXIDANTS BASED ON THIODIPROPIONIC ACID AND POLYOLS.

$$\left.\begin{array}{c} S(CH_2CH_2CO.OH)_2 \\ \text{OR} \\ S(CH_2CH_2CO.C\ell)_2 \\ \text{EXCESS} \end{array}\right| + CH_3(CH_2)_{17}OH \longrightarrow \text{MONO ESTER}$$

$$\text{MONO ESTER} + \left|\begin{array}{l} C(CH_2OH)_4 \longrightarrow \\ (HOCH_2)_3CCH_2O.OC \sim\sim CO.OCH_2C(CH_2OH)_3 \dashrightarrow \\ \text{ETC.} \end{array}\right.$$

$$\left.\begin{array}{c} S(CH_2CH_2CO.OH)_2 \\ \text{OR} \\ S(CH_2CH_2CO.C\ell)_2 \end{array}\right| + HOCH_2 \sim\sim CH_2OH \longrightarrow \begin{array}{c} \text{POLYMERS} \\ \downarrow \\ \text{FRACTIONATION} \end{array}$$

widely used synergistic sulphur antioxidant, in the industrial stabilisation of polyolefins.

Two methods of preparation were examined, Fischer esterification and the acid chloride route; it is worth noting that transesterification using alkaline catalysts leads to the decomposition of the thiodipropionate structure.

Fischer esterifications were carried out using 5 and 8 molar excesses of thiodipropionic acid with toluene as solvent. Concentrated sulphuric acid was used as catalyst and the reactions were carried out under a Dien and Stark apparatus to recover the water of reaction.

Although esterification took place it was found impossible to isolate the pure monoester. Unreacted acid was removed to a large extent by aqueous alkali washes, however, due to the similar solubility characteristics of the mono and diesters a preparative separation could not be readily found. Furthermore, considerable darkening of the reactants occurred during the esterification.

Analogous reactions using the acid chloride resulted in a much cleaner esterification. The preparations were carried out, using normal reaction conditions, by adding stearyl alcohol (solution in benzene) to the excess acid chloride, dissolved in pyridine. Again, however, it was found impossible to unequivocally separate the monoester.

At this time, the difficulties in achieving complete esterification of the pentaerithritol based oligomers was becoming apparent and work on the above routes ceased.

Reaction of thiodipropionyl chloride with 1,10-decanediol

Some initial attempts were made to prepare linear chain polyesters of thiodipropionic acid, with the sulphur functionality occurring in the backbone.

The acid chloride and diol were reacted in equimolar proportions in excess pyridine solvent; the acid chloride was added dropwise to a suspension of the diol, whilst the temperature of reaction was maintained below 10°C. The reactants were then heated to 35°C for one hour.

After cooling, acetyl chloride was added and the reactants were heated to 50°C. After further cooling, a sufficient excess of methanol was added to react with both the residual acetyl chloride and any remaining acid chloride end groups on the polymer. Reaction was again carried out at 50°C.

After cooling, ether was added to the reactants and pyridine hydrochloride was removed by filtration (this was decomposed in aqueous alkali to ensure no polymer had been removed). The filtered solution was then washed with dilute hydrochloric acid, dilute sodium carbonate solution and finally water. After drying, evaporation of the ether yielded a waxy and rather sticky white solid.

IR analysis indicated that no acidic or alcoholic hydroxyl species were present. A strong ester carbonyl frequency was apparent at 1735 cm^{-1}.

The product was examined by gel permeation chromatography (Dunlop Ltd). Unfortunately, this analysis revealed that the product had a molecular weight distribution which peaked sharply at a value equivalent to the combination of two molecules of thiodipropionic acid and two molecules of decane diol, approximately.

It had been intended to obtain molecular weight fractions from this polymer; this was not undertaken, however, as no higher fractions were available.

This synthetic route clearly offers promise and, although weaknesses exist with this type of structure in sulphur antioxidants (see main text, Conclusions and Implications), stabilisers of this type should be examined further.

A2.5 Syntheses based on Shell's hydroxymethyl substituted phenol and acrylic polymers

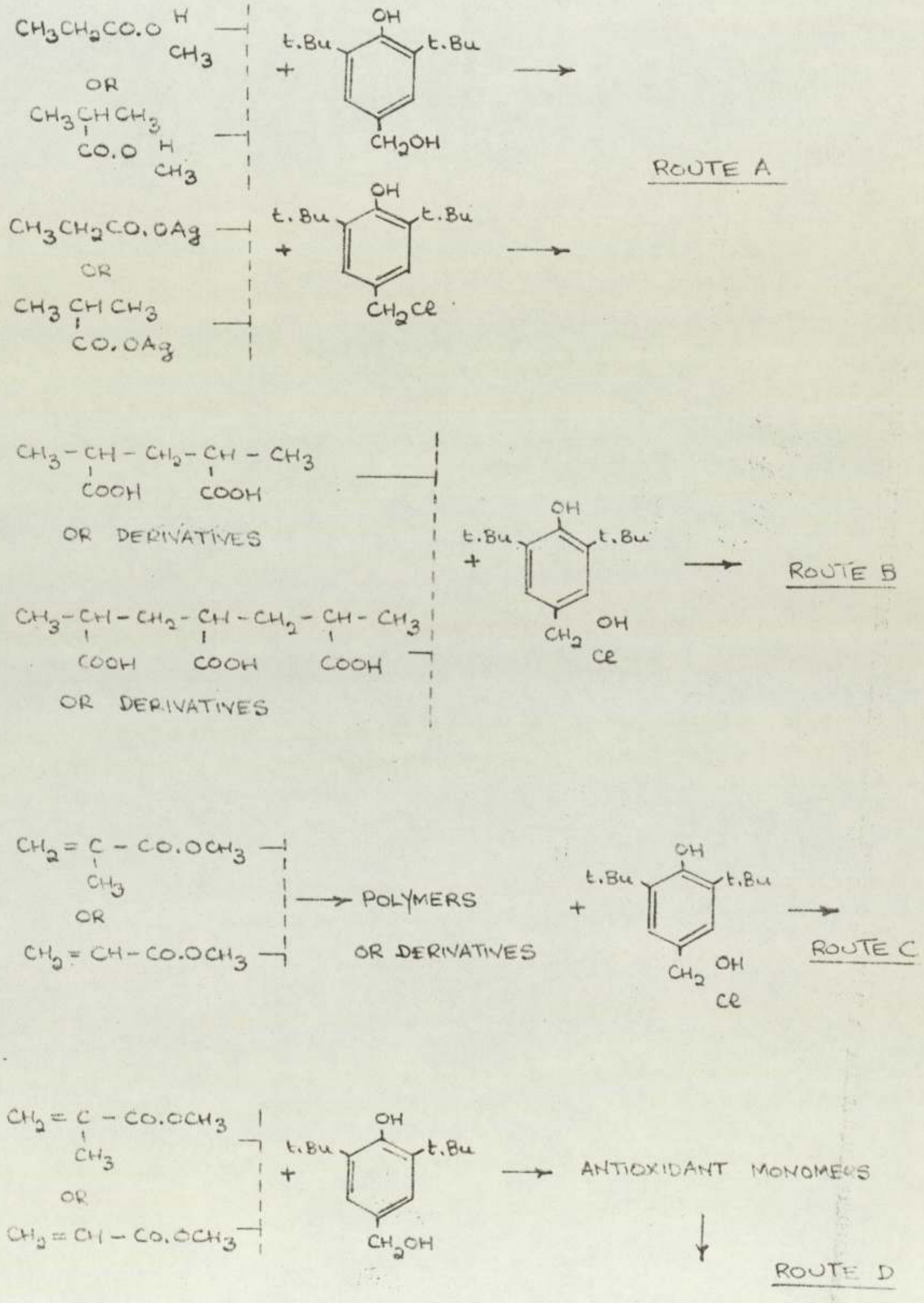
The synthetic routes which were considered, are shown in Figure A2.6. Routes A, B and C involve a grafting technique using acrylic polymers and model compounds; route D involves the preparation and polymerisation of an unsaturated antioxidant monomer.

Preparation of heptane-2,4,6-tricarboxylic acid

Pentane-2,4-dicarboxylic acid and the dimethyl ester are available from fine chemical suppliers. The heptane tricarboxylic acid is not available, however, and was prepared according to the method of Lim and Wichterle (212), via methyl β-bromo-isobutyrate. This latter starting material was prepared using the method of Price and Coyner (213).

A solution of methyl methacrylate (150 gm) in petroleum ether (40°-60°C, 1000 ml) was saturated with hydrogen bromide gas, whilst the temperature was maintained below 20°C (approximately 1 hour). Five 200 gm portions of ester were then added successively and the solution was saturated with hydrogen bromide after each addition. The reactants were allowed to stand overnight and the petroleum ether was then evaporated; distillation under reduced pressure gave

FIG. A2.6 PROJECTED ROUTES TO POLYMERIC ANTIOXIDANTS BASED ON HMP AND OLIGOMERS OF POLYACRYLATES



the bromo-ester, as a colourless liquid, in almost quantitative yield (Bp 57°C, 12 mm Hg; n_D^{20} 1.4553; literature (213) Bp 67°C, 17 mm Hg n_D^{20}1.4551; (212) Bp 57°C, 12 mm Hg).

A solution of sodium metal (16 gm) in absolute ethanol (500 ml) was prepared and ethyl cyano-acetate (58 gm) was added, in several small portions, with stirring. Methyl β-bromo-isobutyrate (155 gm) was added dropwise, whilst the temperature was maintained below 20°C. The reactants were then allowed to warm to ambient temperature and reaction was continued for 4 hours. Finally, the temperature was raised to 70°C for 3 hours. Sodium bromide was filtered from the solution and, after evaporation of the solvent, the product was distilled under reduced pressure (57 gm, 66%; Bp 168°C, 0.2 mm Hg; literature (212), Bp 165°C, 0.2 mm Hg).

The ester was hydrolysed by boiling for 20 hours with concentrated hydrochloric acid (200 ml). The tricarboxylic acid crystallised on cooling and, after filtration, was isolated in almost quantitative yield by recrystallisation from benzene (Mp 142°C; literature (212) 142°C).

It had been intended to prepare the trimethyl ester of this acid, again using the method of Lim and Wichterle; however, the lack of success in carrying out transesterification reactions with the phenolic intermediate (HMP; see below) brought work to a halt.

Esterification of benzyl alcohol derivative HMP

The direct Fischer esterification of HMP with the acrylic model compounds and the unsaturated acrylic monomers was not attempted due to the possibility of the adventitious debutylation of the hindered phenol occurring in the presence of acids.

In order to determine if the transesterification of HMP was feasible, without the possible interference of acrylic polymerisation reactions, the reaction between HMP and methyl propionate was examined. Two catalysts were studied, aluminium isopropoxide and sodium ethoxide.

In the examination of the isopropoxide catalyst, a series or preparations were attempted in which three and five molar excesses of methyl propionate were employed. Catalyst additions of 1% (based on the weight of methyl propionate) were used in both preparations; an additional preparation was carried out using 5% catalyst (based on the ester) and a five molar excess of methyl propionate.

The reactions were carried out at 70°C-75°C in a flask fitted with a fractionating column; the reaction temperature was above both the boiling point of methanol and its azeotrope with methyl propionate (62°C) but below the boiling point of the pure ester.

When it became evident that no reaction was occurring in any of the preparations, the reaction temperature was increased until methyl propionate started to distil. The distillate was examined by GLC and no methanol could be detected. Unreacted HMP phenol was present in the reaction media.

Exactly analogous experiments were carried out using sodium ethoxide as catalyst at the same concentrations. The alkali metal catalyst produced an intense orange discolouration when added to the phenol solution; this was attributed to the formation of the sodium phenate, quinones (quinone methides) or para-coupled species.

However, the preparations were progressed, but again, no transesterification could be monitored. The reaction products were highly coloured and contained resinous materials.

Reactions using aluminium isopropoxide as catalyst were attempted with methyl isobutyrate and methyl methacrylate (5 molar excess; 5% catalyst based on ester). Reaction temperatures up to 85°C were employed but again no transesterification occurred. The reaction involving the unsaturated ester was carried out under nitrogen with pyrocatechol (1%) present as a polymerisation inhibitor.

It was thought that the silver salt esterification technique might provide a more successful approach. However, attempts to prepare the chloro derivative of the HMP benzyl alcohol moiety met with no success. Chlorination using both thionyl chloride and phosphorus pentachloride at temperatures down to 0°C resulted in intensely coloured and resinified products.

The route was discontinued.

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