

PRO-OXIDANT AND ANTIOXIDANT MECHANISMS IN POLYMER TECHNOLOGY*

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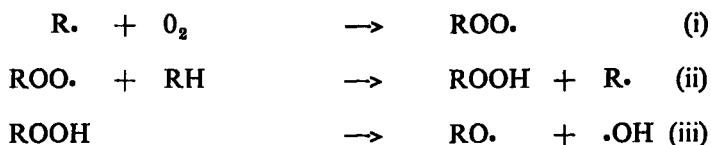
GERALD SCOTT†

It is one of the ironies of polymer science that although vulcanized rubber is one of the oldest technologically important polymers and has been studied systematically by chemists for many years, we know less about its chemistry than we do about most of the synthetic polymers. This arises from the extreme complexity of the sulphidic structures which result from the reaction of sulphur with rubber and although vulcanization was the making of rubber from one point of view, it has brought in its train complex problems of stabilisation. The nature of the degradation process is difficult to understand. On the one hand unvulcanized rubbers, whether natural or synthetic, always oxidize autocatalytically just as do pure hydrocarbons. NR is more stable than cis-polyisoprene because of the presence of natural antioxidants which increase the induction period. Sulphur-vulcanized rubbers on the other hand oxidize much more rapidly than raw or peroxide-vulcanized rubbers; never show an induction period but do show an initial rapid rate of oxidation followed generally by an auto-retarding stage (Stafford, 1954). See Fig. 1. The effect of phenolic or amine antioxidants is to reduce the slope of the curve whilst maintaining their general shape.

SULPHIDES IN AUTOXIDATION

Some light was thrown on this by the work of Bateman and his co-workers at N.R.P.R.A. who showed that certain allylic sulphides closely related to crosslinked rubber oxidized in the same sort of way (see Fig. 2) when initiated by a radical generator (AZBN) which disappeared quickly from the system (Bateman & Cunneen, 1955).

The significance of this finding was not fully appreciated at the time, since, what it implies is that the normal chain branching process (i) and (ii) associated with the formation of hydroperoxide in autoxidation is not occurring, so that hydroperoxides, if they are being formed, are not maintaining the chain reaction by reaction (iii).

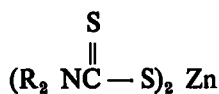


Later work at N.R.P.R.A. showed by Bateman *et al.* (1962) that in fact these sulphides themselves and the sulphoxides derived from them are powerful antioxidants in hydrocarbons. Moreover the antioxidant activity was shown to be associated with the ease of breakdown of sulphoxide. But this only serves to make the observation that we started with, namely the increased sensitivity of vulcanized rubber to oxygen, more difficult to understand.

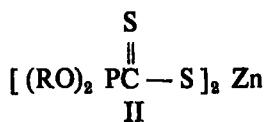
* Text of a lecture delivered to the Ceylon Association for the Advancement of Science.

† Professor of Chemistry, University of Aston in Birmingham, U.K.

At this stage we must for the moment leave the chemistry of rubber and discuss discoveries which were going on in parallel in other technological media. The discovery of polypropylene had led to very difficult problems in stabilisation since, as a result of its high processing temperature and its branched structure, it oxidized much more rapidly than polyethylene. Rubber antioxidants were found to be quite effective as stabilisers but were very powerfully synergised by a number of sulphur compounds of which the most important are shown below (I - IV).



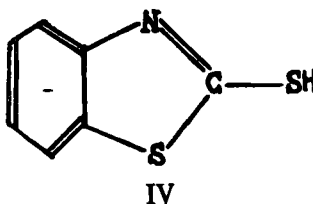
I



II



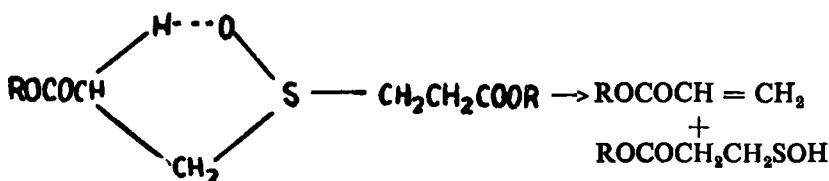
III



IV

I want to pick out the thiodipropionate ester class for special comment since this proved to be relatively ineffective when used alone (particularly when used as a stabiliser during the processing of the polymer) but synergised powerfully with phenolic antioxidants. Recent research by Scott and Shearn (1969) has shown that the reason for this apparently low activity of the sulphide when used alone is associated with an initial pro-oxidant effect which *increases* with the concentration of the antioxidant. This results in a concentration optimum above which the sulphide *destabilises* the polymer. The presence of a phenolic antioxidant in the system reduces the initial pro-oxidant effect without substantially altering the shape of the curve (Fig. 4).

The nature of this pro-oxidant effect has been studied in some detail in model systems. Following up the earlier observation that sulphides appear to inhibit the formation of chain branching hydroperoxide, it was found that thiodipropionate esters have the ability to bring about a catalytic decomposition of typical hydroperoxides, for example tetralin hydroperoxide. Moreover this decomposition process is associated with gas evolution which is also observable in the kinetics of tetralin autoxidation in the presence of thiodipropionate ester catalyzed by tetralin hydroperoxide (Scott, 1969 a). At a stoichiometric ratio of sulphide to hydroperoxide the pro-oxidant effect of the sulphide is evident (Fig. 5). A similar study of the sulphinyldipropionate esters (Scott, 1969 a) which are the next stage oxidation products, postulated by Bateman and his co-workers (Bateman *et al.*, 1962) to be the effective antioxidants formed by oxidation of sulphides, shows them (Fig. 6) to be even more pro-oxidant initially than the sulphides, although they are very rapidly auto-retarding again with the evolution of a gas (identified as SO_2) as a consequence of the breakdown of sulphoxides. This has led to the concept of two series of reactions proceeding in parallel. The first product formed is the appropriate acrylic ester and the corresponding sulphenic acid.



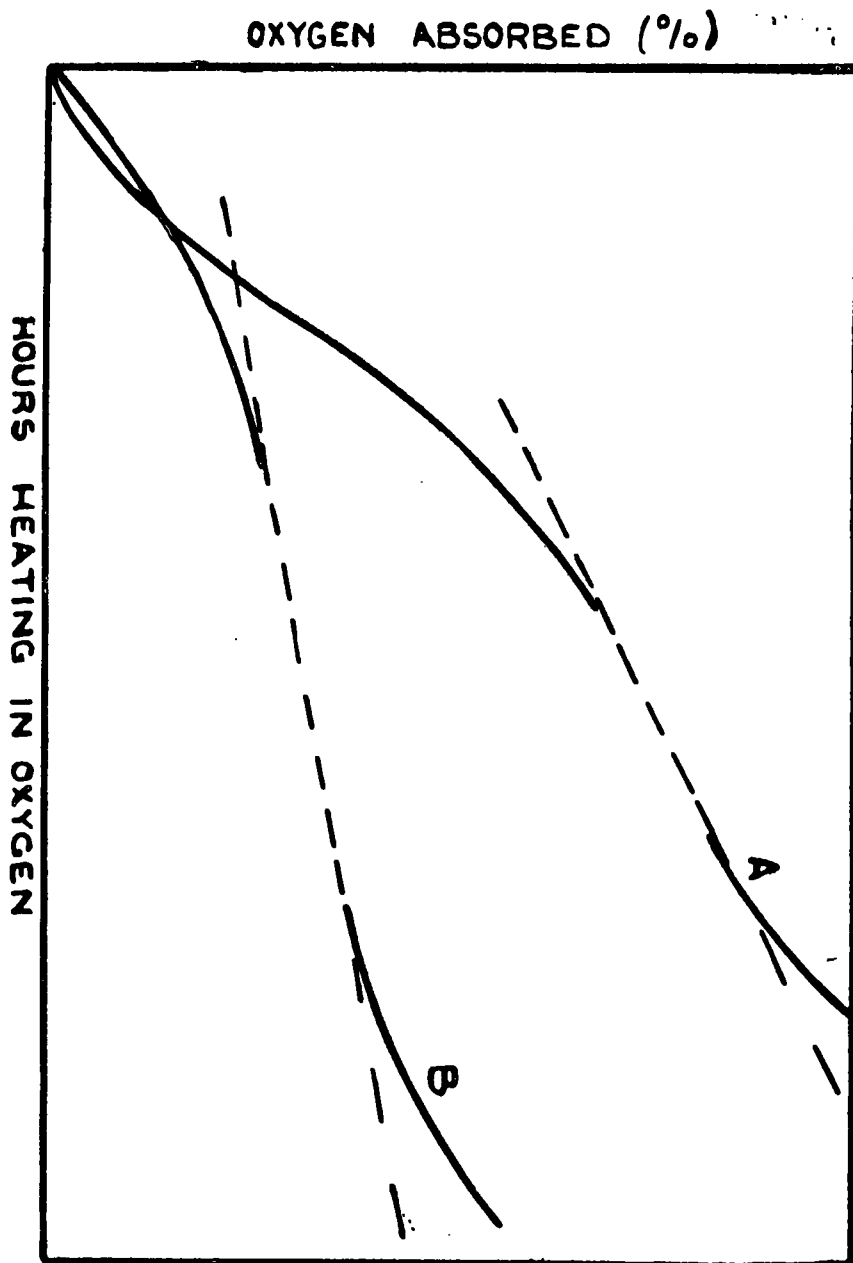


Fig. 1. Typical oxygen absorption curves for vulcanized rubber.

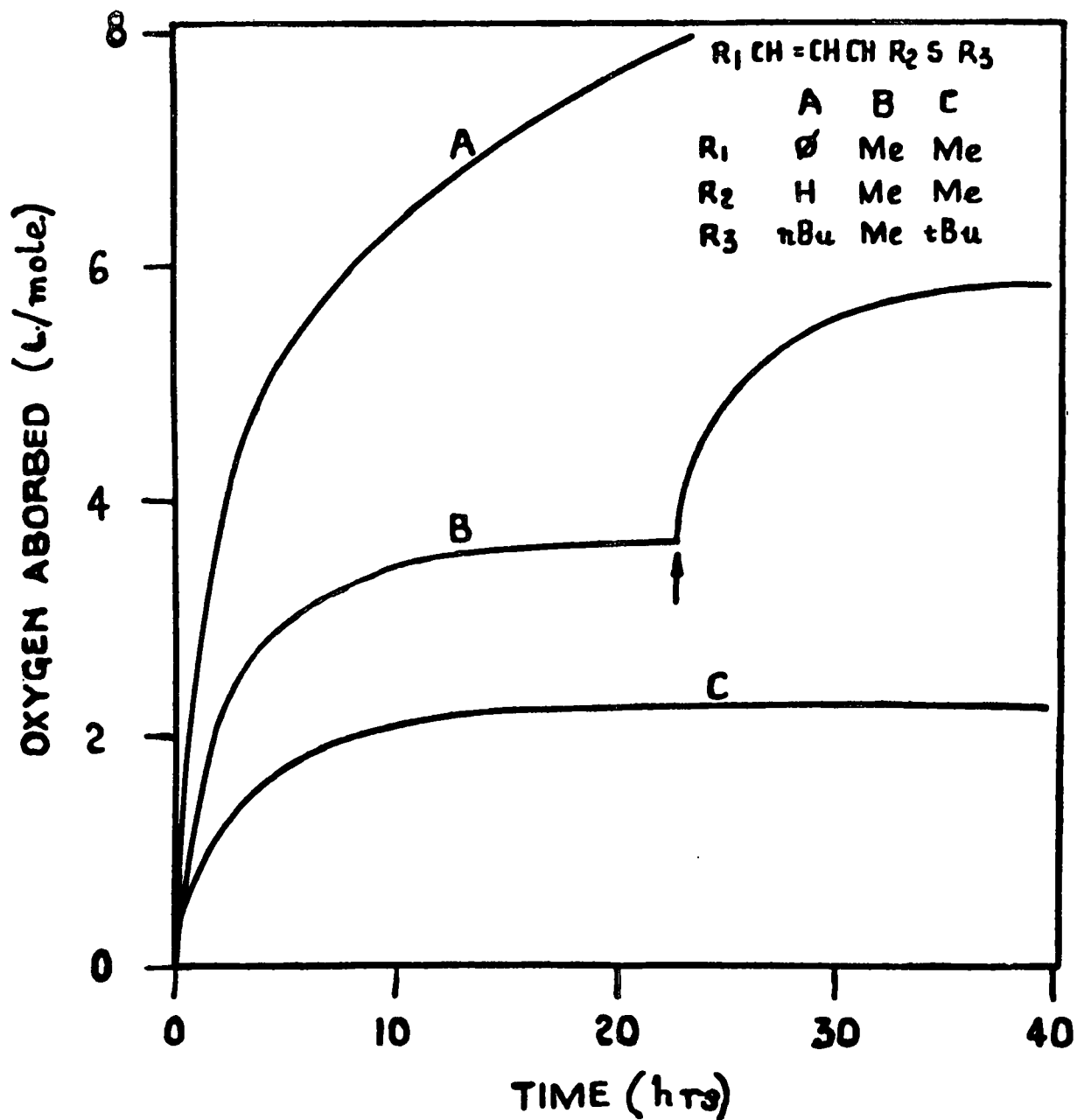


Fig. 2. Autoxidation of allylic sulphides in the presence of AZBN. (The discontinuity of curve B occurred on the further addition of initiator).

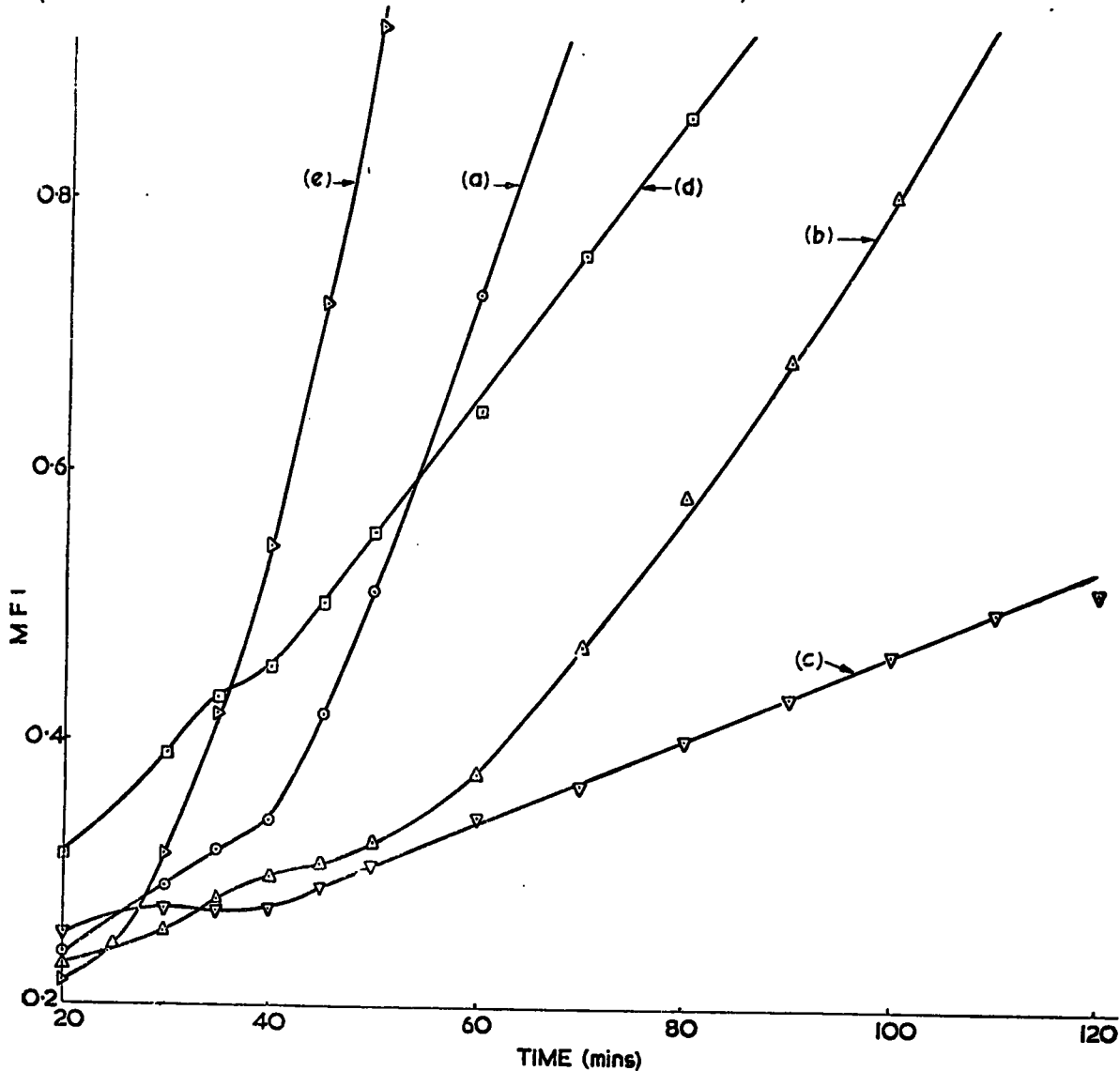


Fig. 3. Effect of DLTP concentration on the melt stability of otherwise unstabilised polypropylene. (a) 0.001 moles/100 g; (b) 0.002 moles/100 g; (c) 0.004 moles/100 g; (d) 0.006 moles/100 g; (e) 0.002 moles/100 g of dialkylsulphonyldipropionate.

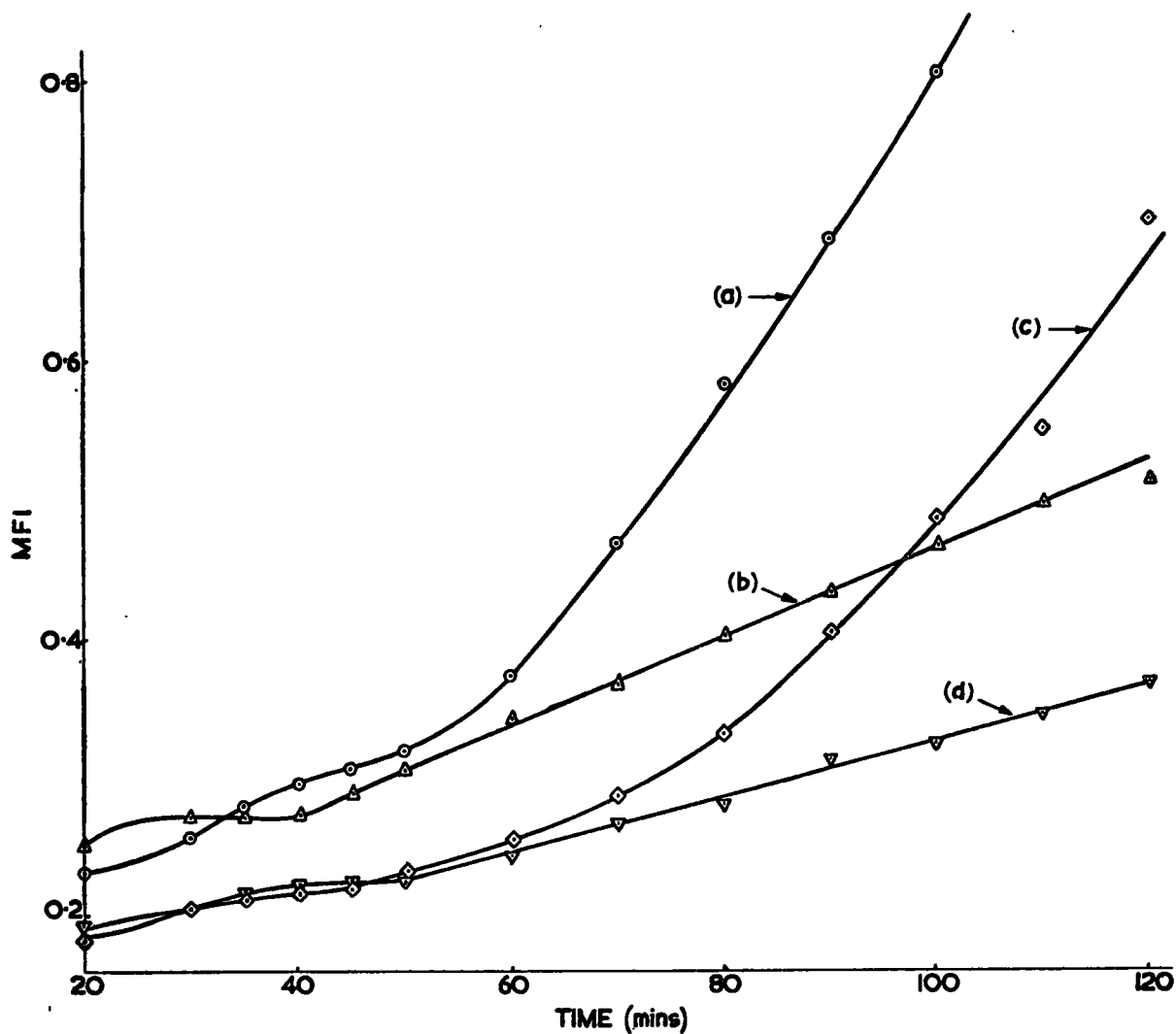
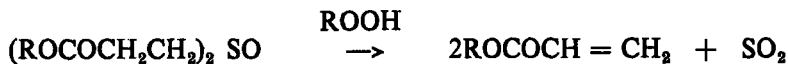


Fig. 4. Effect of 2, 6-di-tert-butyl-p-cresol (TBC) (0.001 moles/100 g) on the radical generating activity of DLTP. (a) no TBC, 0.002 moles/100 g DLTP; (b) no TBC, 0.004 moles/100 g DLTP; (c) with TBC, 0.002 moles/100 g DLTP; (d) with TBC, 0.004 moles/100 g DLTP.

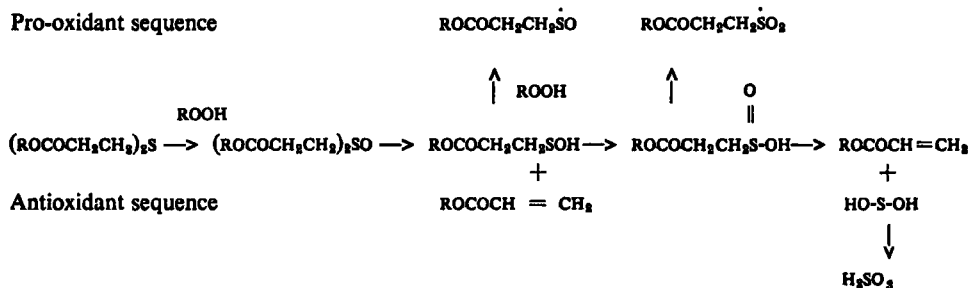
The sulphenic acid can then undergo two series of reactions in parallel — the first by a non-radical mechanism leads to the ultimate elimination of sulphur dioxide, an effective antioxidant.



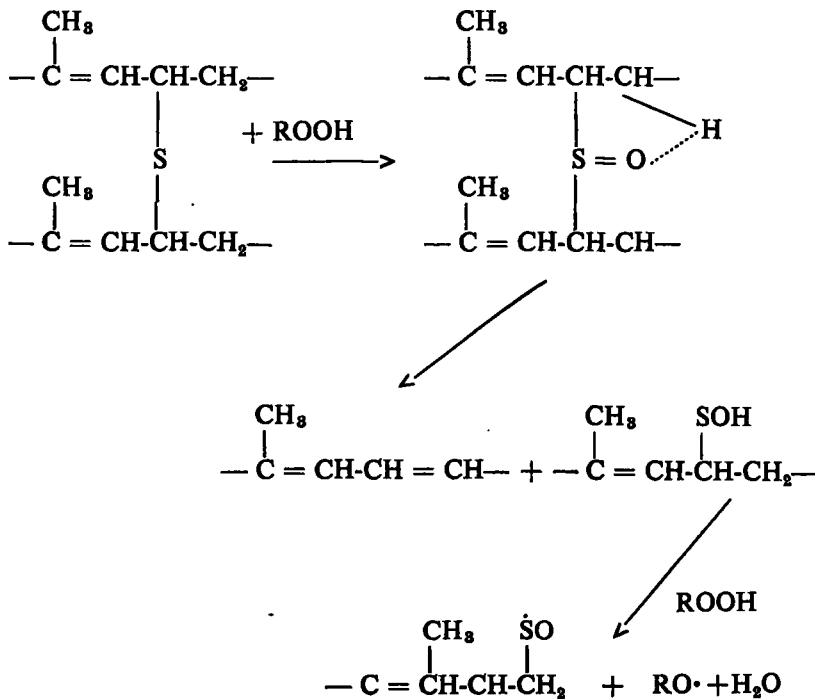
The second by redox reaction with hydroperoxide gives rise to free radical products which can initiate autoxidation.



The series of consecutive reactions shown below explain the pro-oxidant and auto-retarding nature of autoxidation in the presence of monosulphides.

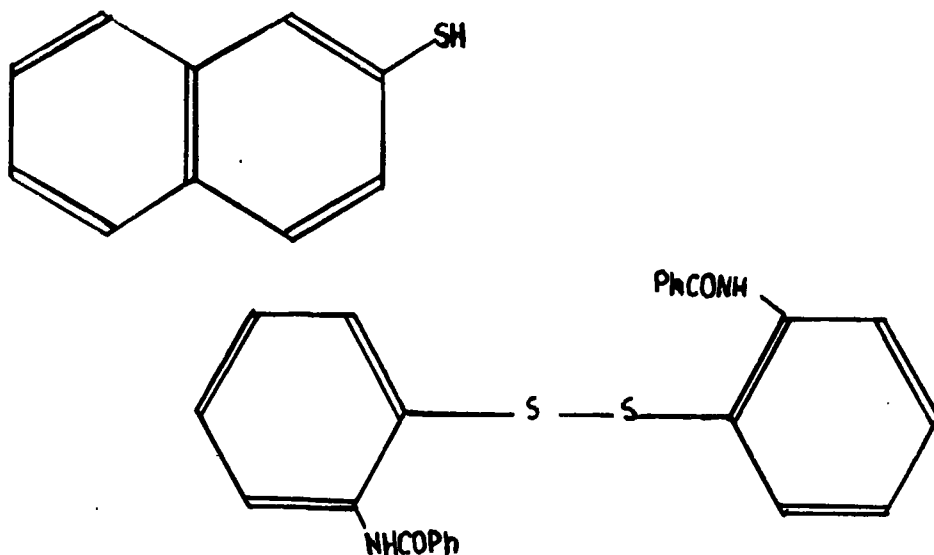


The reactions of a number of other monosulphides related to the crosslink in rubber have been shown to follow a similar course due to an entirely analogous breakdown (Colclough *et al.*, 1968). This results not only in crosslink scission but in an initial pro-oxidant effect.

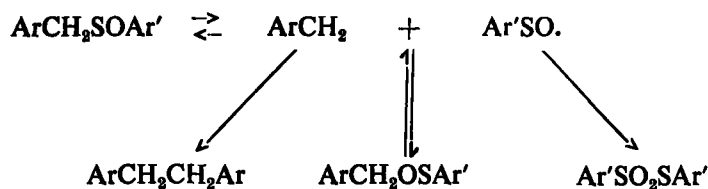


DISULPHIDES

This, however, is only part of the story of the dual role of sulphur compounds in rubber and in other polymers. Sulphur compounds such as thio- β -naphthol and o-benzoylamidodiphenyl disulphide have been used for many years to catalyse the breakdown of rubber under oxidative conditions and related disulphides (e.g. xylydisulphide) have been used in a similar way as rubber processing aids and even as reclaiming agent for *vulcanized* rubber. Disulphides and polysulphides are also present in vulcanized rubber and must be at least partly responsible for their poor ageing performance.



More recently, however, these same compounds have been shown to be effective stabilisers, particularly when used in combination with conventional phenolic antioxidants for polyolefins. A particularly interesting example of this is in the use of dibenzylmonosulphide, which has also been used as a chemical plasticiser for rubber (Mikhailov *et al.*, 1963), as a stabiliser for polypropylene (Fig. 7). Again, there is an initial rapid stage of oxidation followed by a very much longer induction period than is normally given by a conventional antioxidant. This reaction is obviously closely related to the homolytic behaviour of benzylic sulphides discussed by other workers (Abbott & Stirling, 1968; Miller *et al.*, 1968). It has been found that when there is no β -hydrogen to participate in five-centre elimination reactions, radical reactions are favoured leading to the formation of disproportionation products via radical intermediates:



Initial pro-degradant effects have been put to good use by polypropylene fibre manufacturers who require an initial reduction in molecular weight of the polymer to improve the properties of the fibre (Roberts *et al.*, 1964). Table 1 shows the effect of dibenzoylamidodiphenyl disulphide on polypropylene both during spinning and on ageing at 140°C.

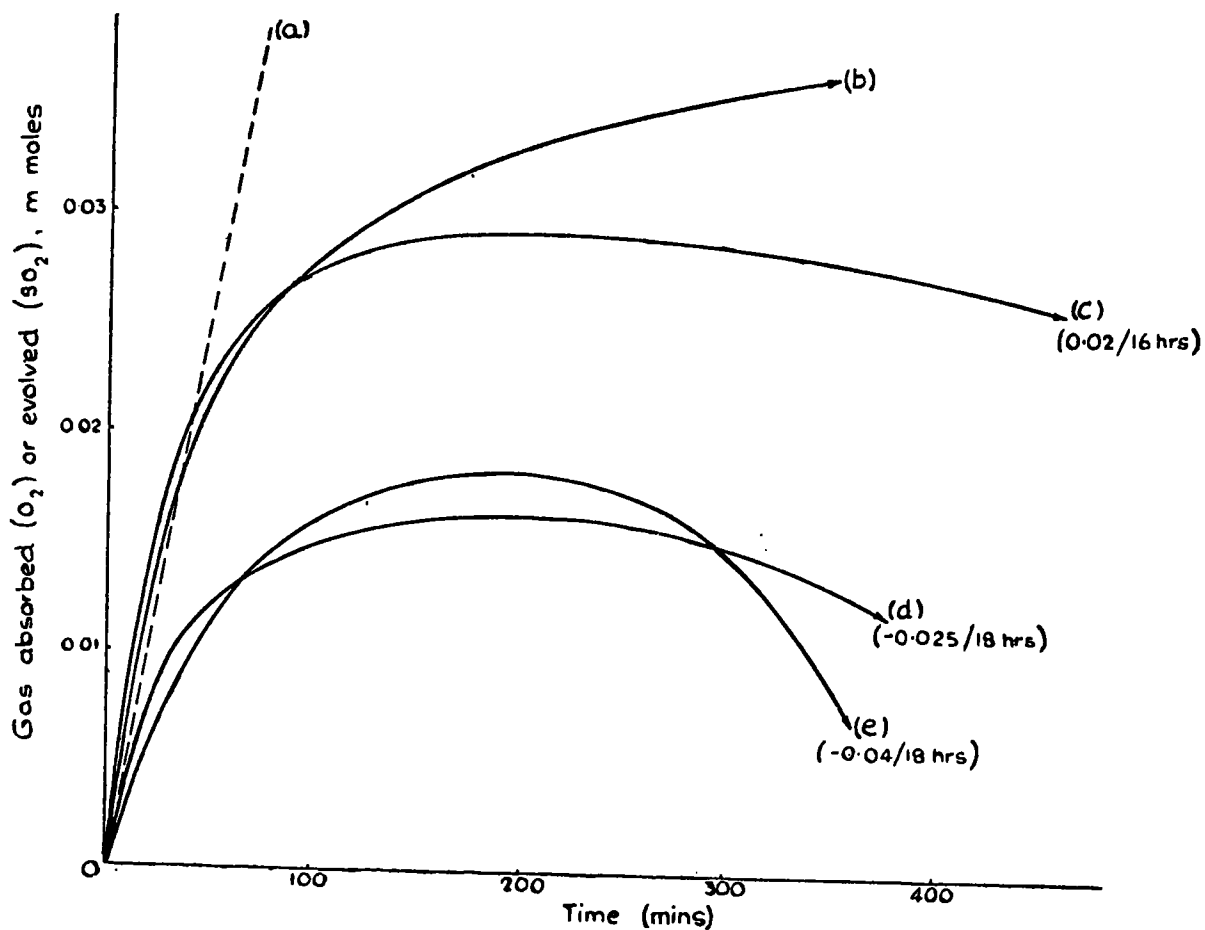


Fig. 5. Effect of DLTP on the oxidation of tetralin containing 1 m moles of tetralin hydroperoxide (in 4 cc) at 50°C. (a) No DLTP; (b) 2 m moles DLTP; (c) 1 m moles DLTP; (d) 0.5 m moles DLTP; (e) 0.05 m moles DLTP.

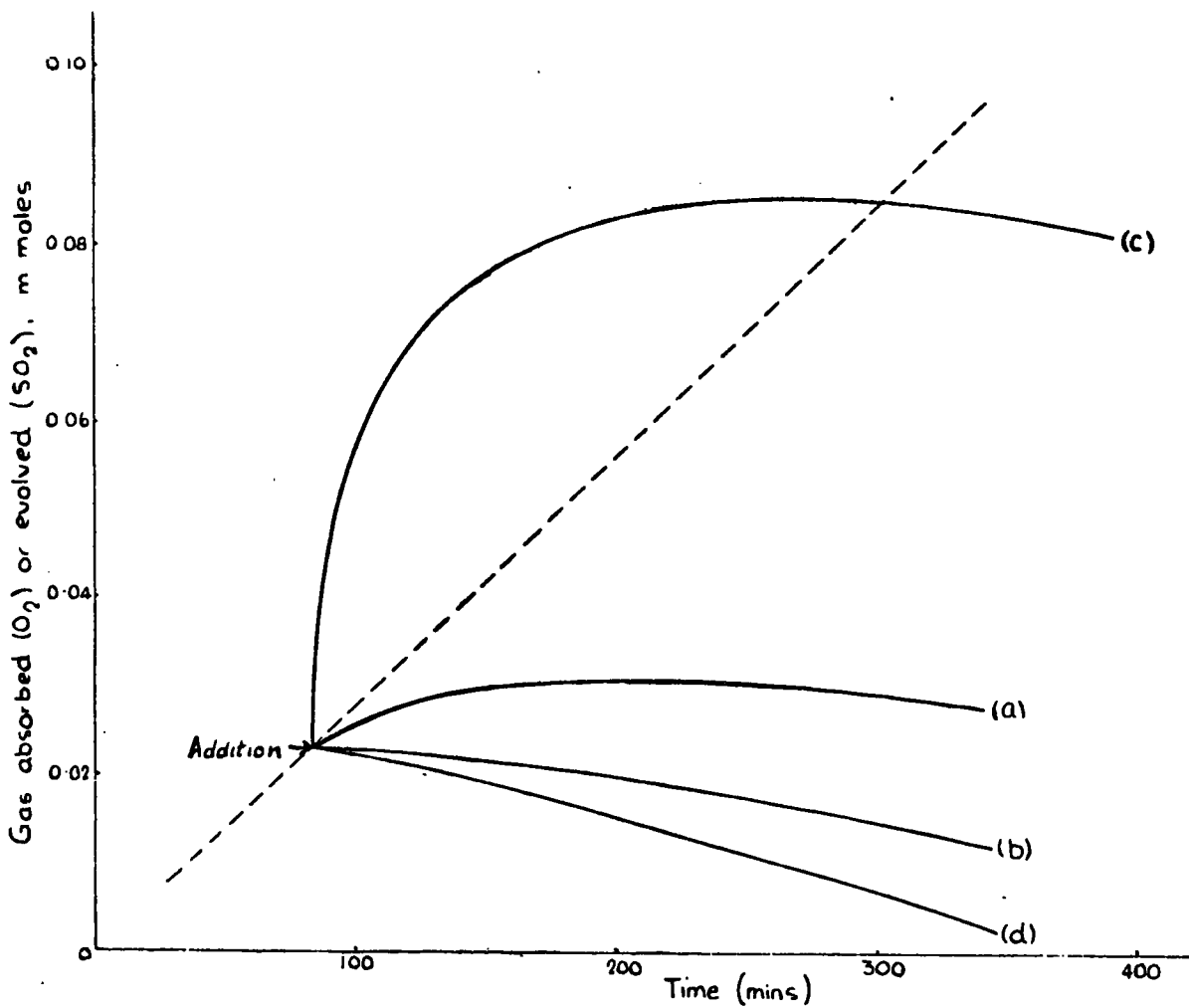


Fig. 6. Effects of antioxidants in tetralin at 50°C; 0.25 m moles of antioxidants in 4 cc tetralin containing 0.5 m moles of tetralin hydroperoxide. (a) DLTP in oxygen; (b) DLTP in nitrogen; (c) DLSP (dilaurylsulphonyldipropionate) in oxygen, (d) DLSP in nitrogen.

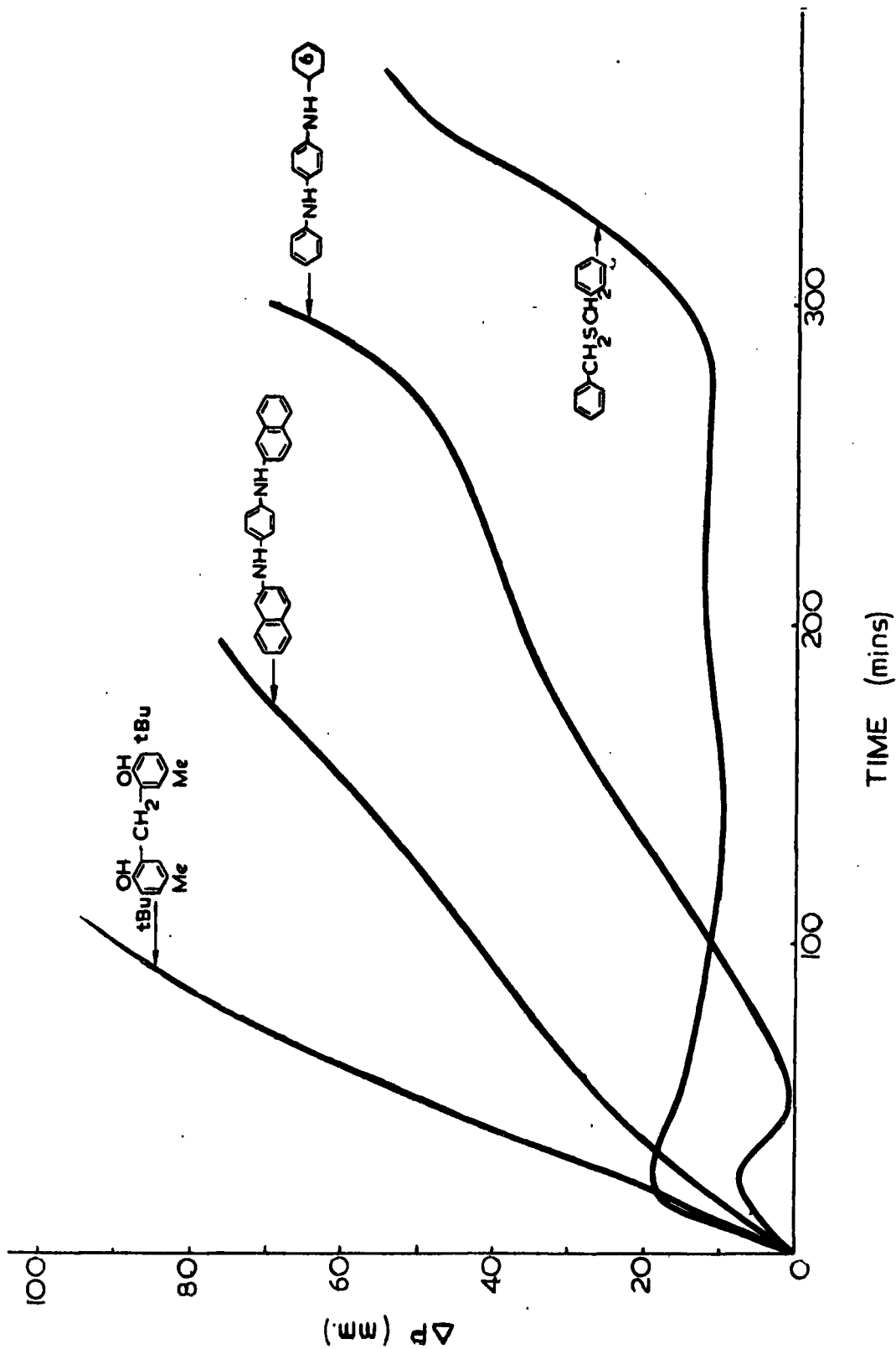


Fig. 7. Oxidation of polypropylene at 250°C in the presence of antioxidants (0.003 moles/100 g).

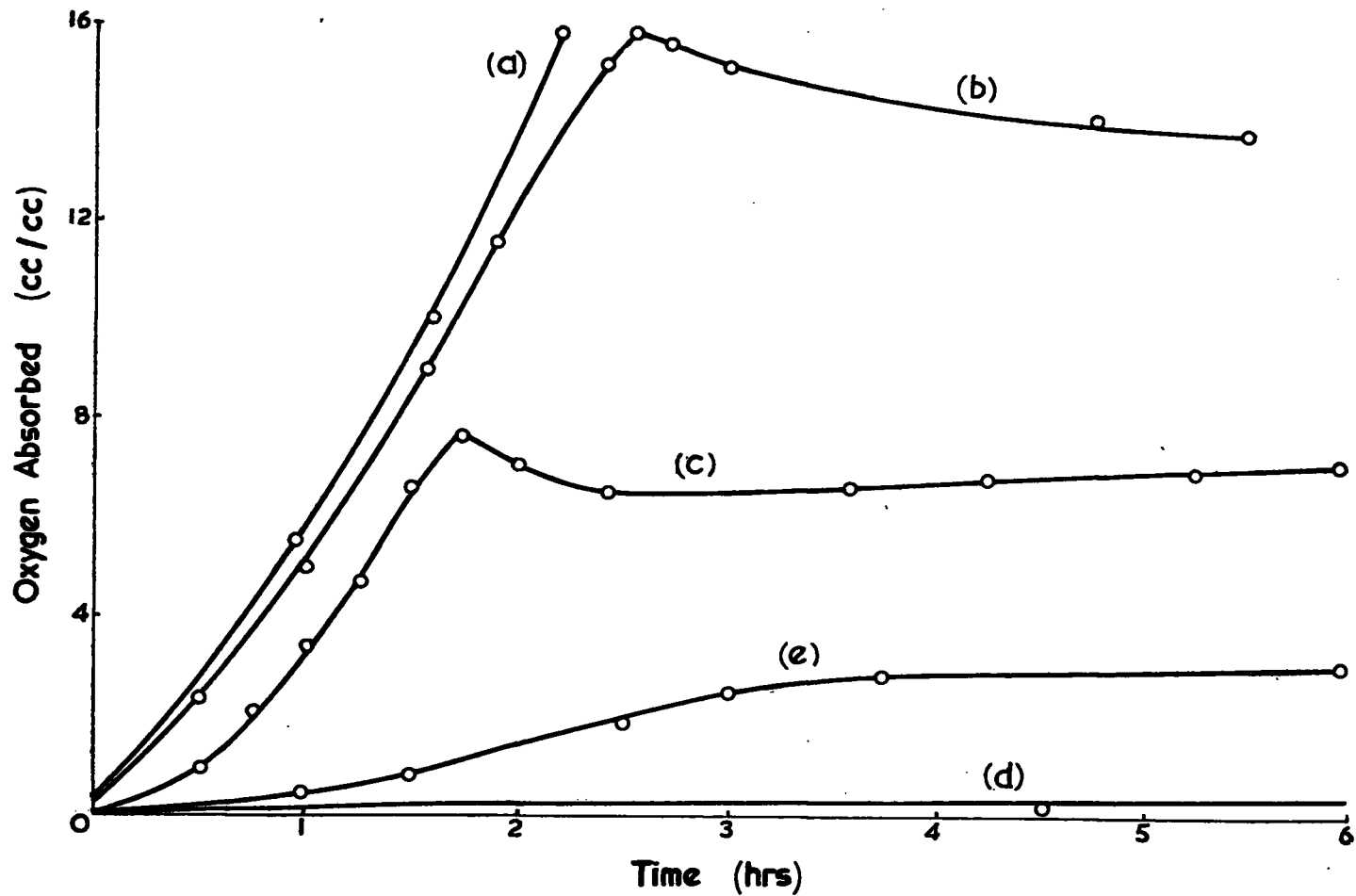
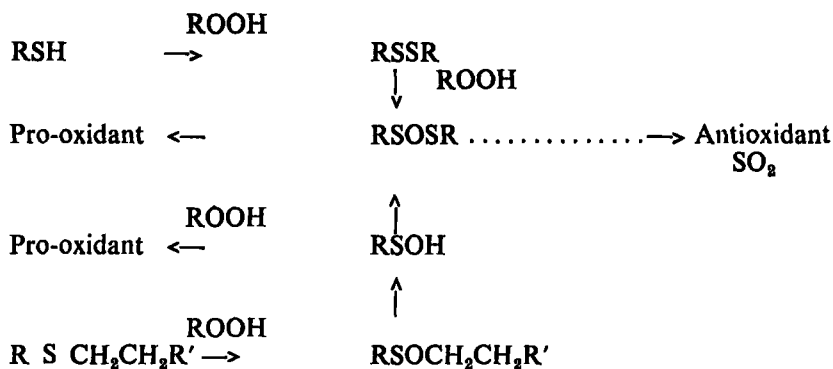


Fig. 8. Inhibition of cumene oxidation at 120°C by sulphur compound (at 0.1% concentration) and sulphur (at 0.02% concentration). (a) no antioxidant; (b) phenylbenzenethiolsulphonate; (c) phenyldisulphide; (d) phenylbenzenethiolsulphinate; (e) sulphur.

TABLE I
EFFECT OF 2, 2' - DIBENZOLYLAMIDODIPHENYL DISULPHIDE (PEPTON 22)
ON THE I. V OF SPUN POLYPROPYLENE FIBRE (INITIAL I.V = 3.5)

	Temperature °C	Spun yarn I. V	
		Before ageing	After ageing (100 hr at 140°C)
No additive	290	2.6	} < 0.1
"	280	2.9	
"	270	3.3	
Pepton 22	250	1.1	1.0

It can be seen that this compound, although a very powerful pro-degradant at 250°C, has a subsequent protective effect on the polymer. Hawkins and his co-workers have also observed the antioxidant activity of diaryl disulphides in polyolefins. By studies in model systems (cumene) they have found that, as in the case of the dialkylmonosulphides, there is an initial period of low activity before the disulphide (Fig. 8, curve C) is converted to a powerful antioxidant. There is evidence again of gas evolution as the onset of the retardation stage and again SO₂ was identified among the gaseous products. Of the derived oxidation products the thiol-sulphinates was found to be active immediately (curve D) and the thiolsulphanate was very much less active. The pattern, therefore, seems to be very similar to that found with the dialkylmonosulphides and the pro-oxidant and antioxidant function of thiols, disulphides, monosulphides, thiolsulphinates and sulphoxides can all be inter-related by their inter-conversion in the presence of peroxides.

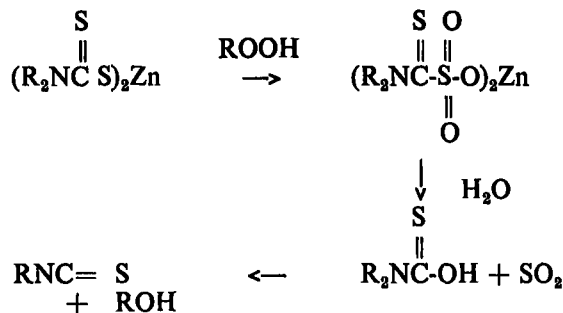


DITHIOCARBAMATES AND RELATED COMPOUNDS

One final example of the way in which fundamental studies of anti-oxidant mechanisms has thrown light on practical stabilising systems for both rubbers and plastics is the case of the so-called non-sulphur-cured rubbers. These vulcanisates, unlike the conventional sulphur-cured vulcanisates are extremely resistant to oxidation and it was shown by N.R.P.R.A. workers, Fletcher & Fogg (1958) and Dunn & Scanlon (1958) that extraction of the vulcanisate destroyed its good ageing behaviour. Zinc dialkyldithiocarbamates were identified as the major products of the extract and swelling metal dithiocarbamates back into rubber restored the good ageing behaviour.

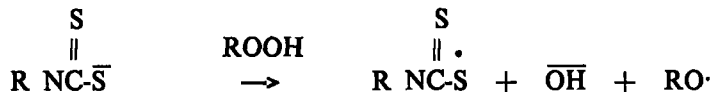
Quite independently it had been found that metal dithiocarbamates were powerful stabilisers for lubricating oils (Thomas *et al.*, 1956) and polyolefins, (Baum & Perrun, 1962) and studies in tetralin by Holdsworth *et al.* (1964) showed that zinc diethyl-dithiocarbamate was only effective in a hydroperoxide-initiated system (Figs. 9 and 10).

Once again the initial pro-oxidant effect followed by gas evolution (again identified as SO_2) should be noted. It was found again that the dithiocarbamates as a class were very powerful catalysts for the non-radical decomposition of hydroperoxides and the overall course of the removal of the zinc salt could be represented as follows :—



Evidence for the heterolytic decomposition of the hydroperoxide was that cumene hydroperoxide gives only phenol and acetone (Scott, 1969 b), the products expected in the basis of an acid decomposition and not acetophenone and cumyl-alcohol the products which would be formed in a homolytic breakdown.

Sulphur dioxide functions as an acid catalyst in this system and the pro-oxidant effect which appears to be common to most of the sulphur antioxidant systems is probably due to redox reactions between the metal complex and hydroperoxide.



SYNERGISM

It was mentioned earlier that a mixture of dilaurylthiodipropionate and a phenol gives a synergistic effect due to the removal of free radicals by the phenol during the pro-oxidant stage. It is found that in practice only a small proportion of phenol is necessary to give optimum synergism.

Other sulphur compounds are less efficient as antioxidants since they appear to give rise to more free radicals. Thus when polypropylene is processed at 165°C in the presence of a small proportion of phenolic antioxidant and added sulphur compounds (see Fig. 11), DLTP becomes a powerful antioxidant, MBI is less effective and MBT is less effective still. Pepton 22 is actually a pro-oxidant under these conditions. As a consequence it is found that, whereas a 5 to 1 molar ratio of sulphur compound to antioxidant is adequate to give optimum performance in the case of MBI, 1 to 9 ratio is necessary in the case of MBT (see Fig. 12).

I have probably said enough to have made the point that an understanding of the detailed chemical processes involved in stabilisation of polymers pays dividends in the design of new and improved stabilising systems. This kind of basic research has both scientific interest and yet makes a major contribution to improving the technological behaviour of important materials.

Finally, I would like to express my indebtedness to my co-workers who have contributed to the work described — in particular, to Mr. C. Armstrong and Mr. P. A. Shearn.

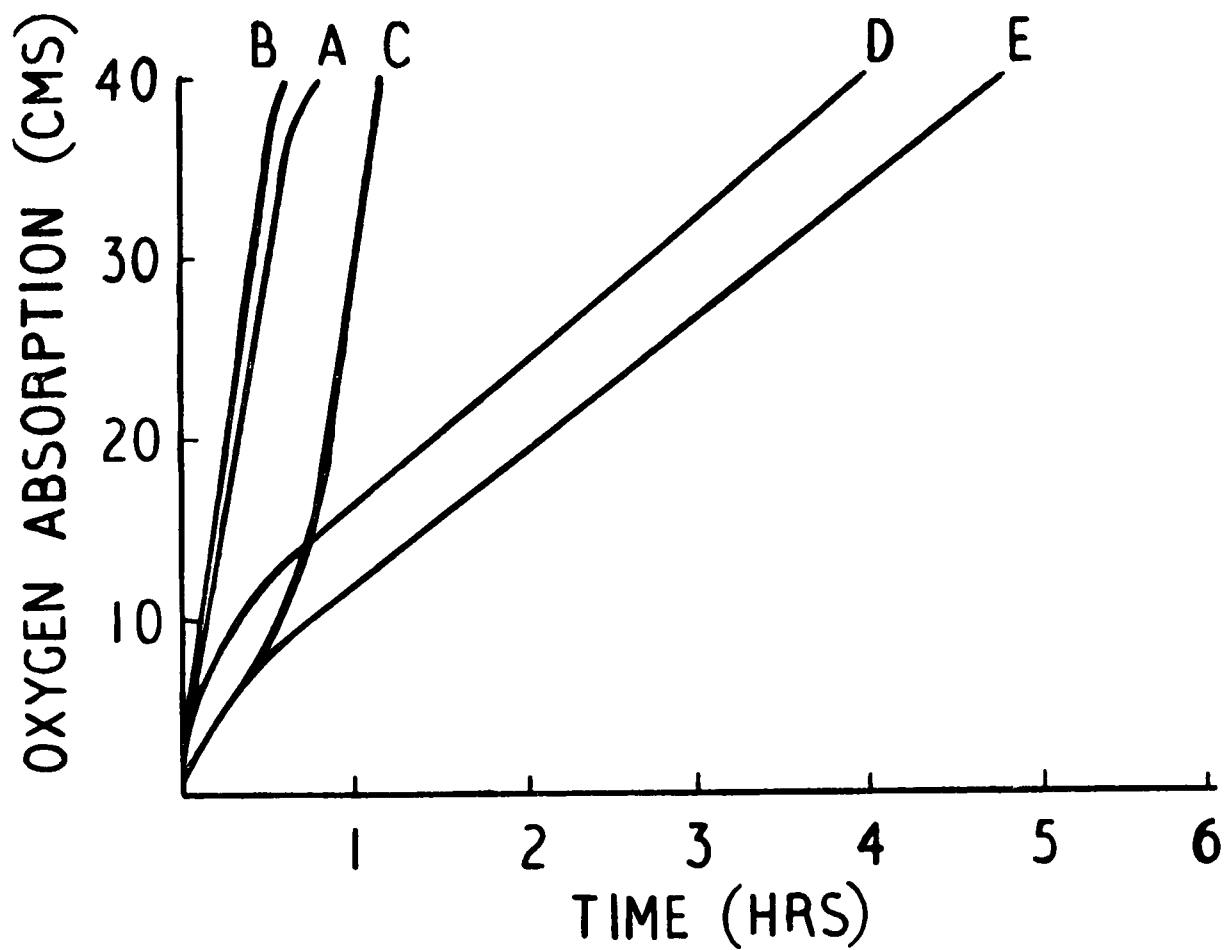


Fig. 9. Effect of zinc diethyldithiocarbamate (ZDC) on the oxidation; of tetralin at 50°C in the presence of aoz-di-isobutyronitrile (3%). (a) no antioxidant; (b) 0.00001 g/2 cc ZDC; (c) 0.0004 g/2 cc ZDC; (d) 0.005 g/2 cc ZDC; (e) 0.01 g/2 cc ZDC.

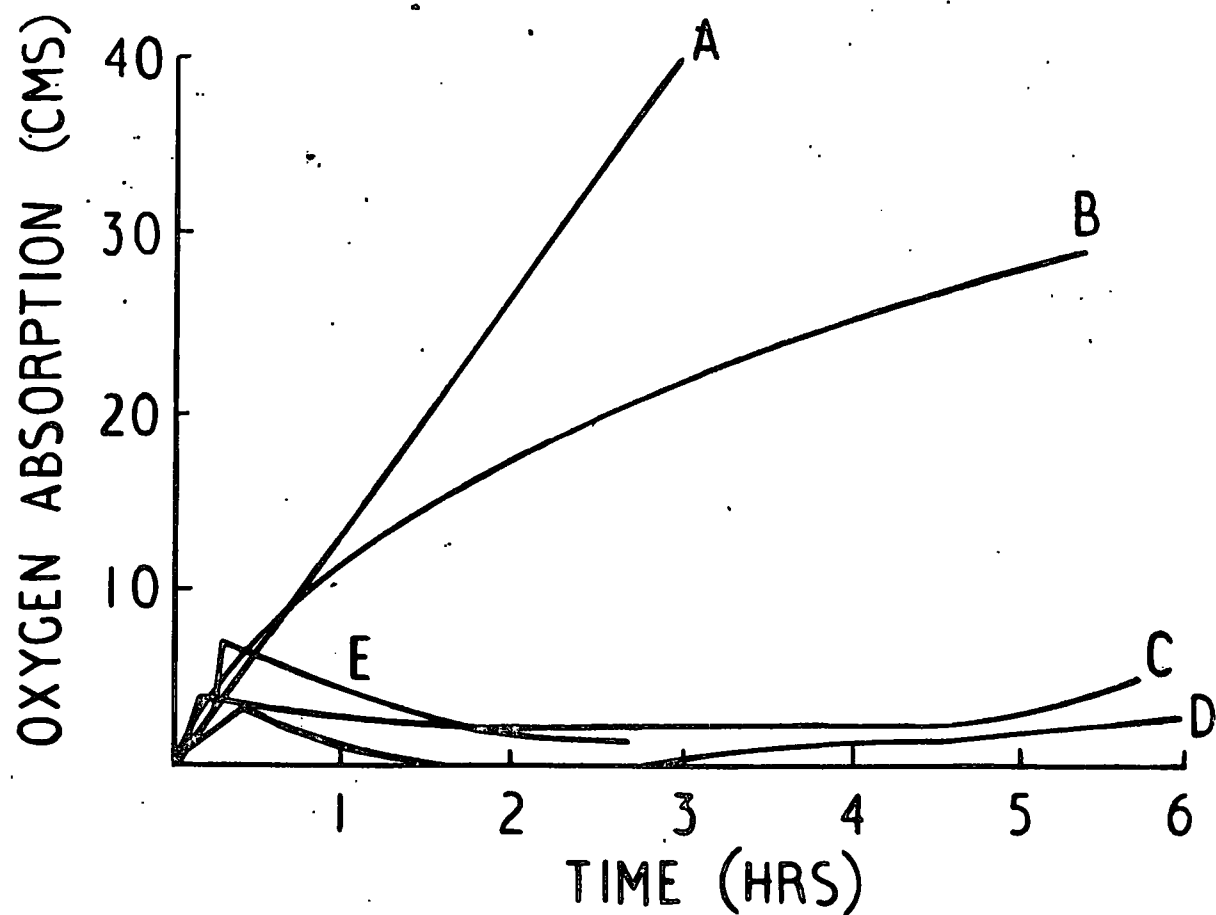


Fig. 10. Effect of zinc diethyldithiocarbamate on the oxidation of tetralin at 50°C in the presence of tetralin hydroperoxide (3%). (a) no antioxidant; (b) 0.00004 g/2 cc ZDC; (c) 0.0001 g/2 cc ZDC; (d) 0.0004 g/2 cc ZDC; (e) 0.001 g/2 cc ZDC.

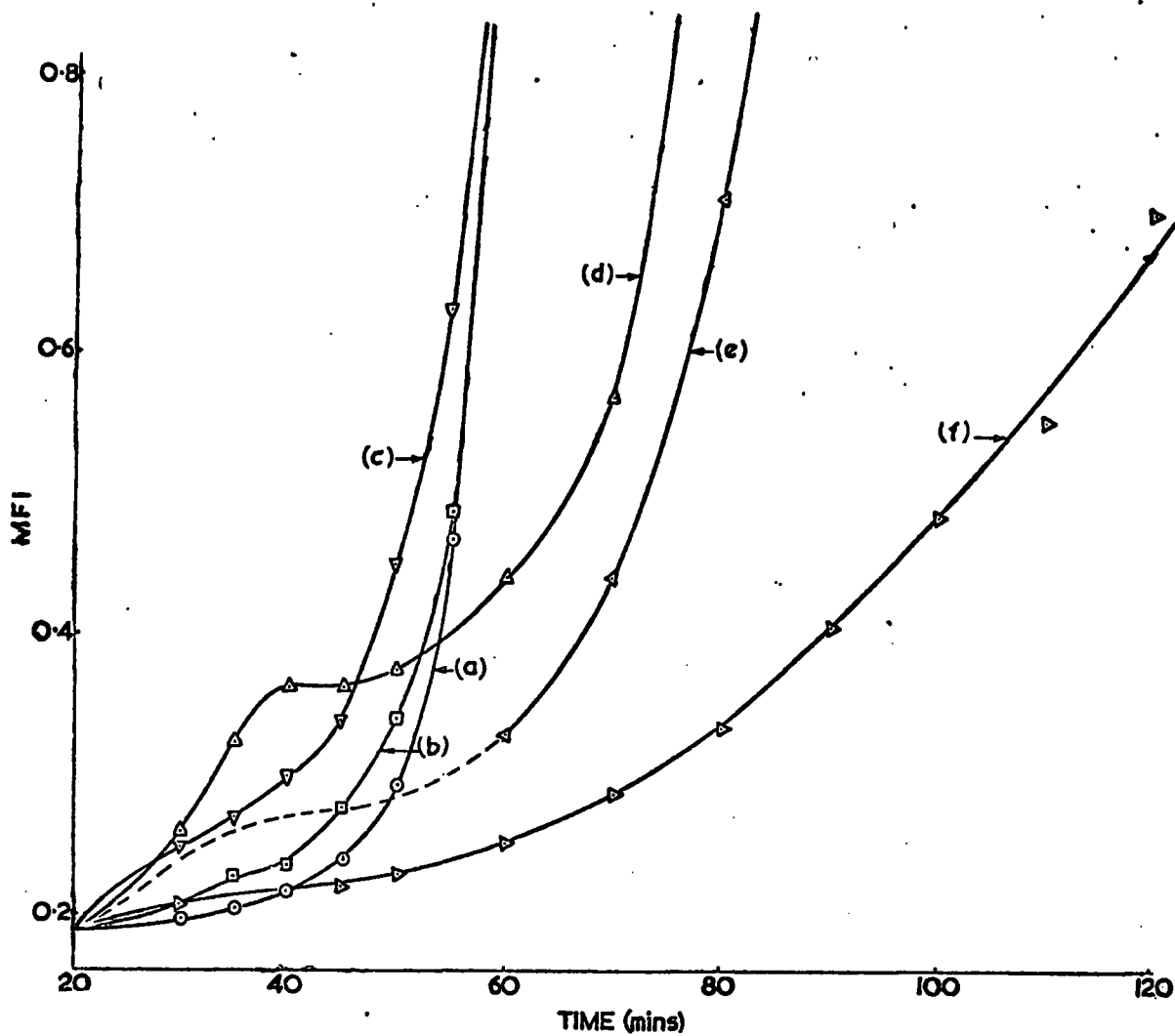


Fig. 14. Effect of milling at 165°C on polypropylene containing 0.001 moles/100 g of TBC and the following additives at 0.002 moles/100 g. (a) no additive; (b) dioctyl sebacate; (c) 2, 2'-dibenzoylaminodiphenyldisulphide (Pepton 22); (d) mercaptobenzthiazole (MBT); (e) mercaptobenzimidazole (MBI); (f) dilaurylthiodipropionate (DLTP).

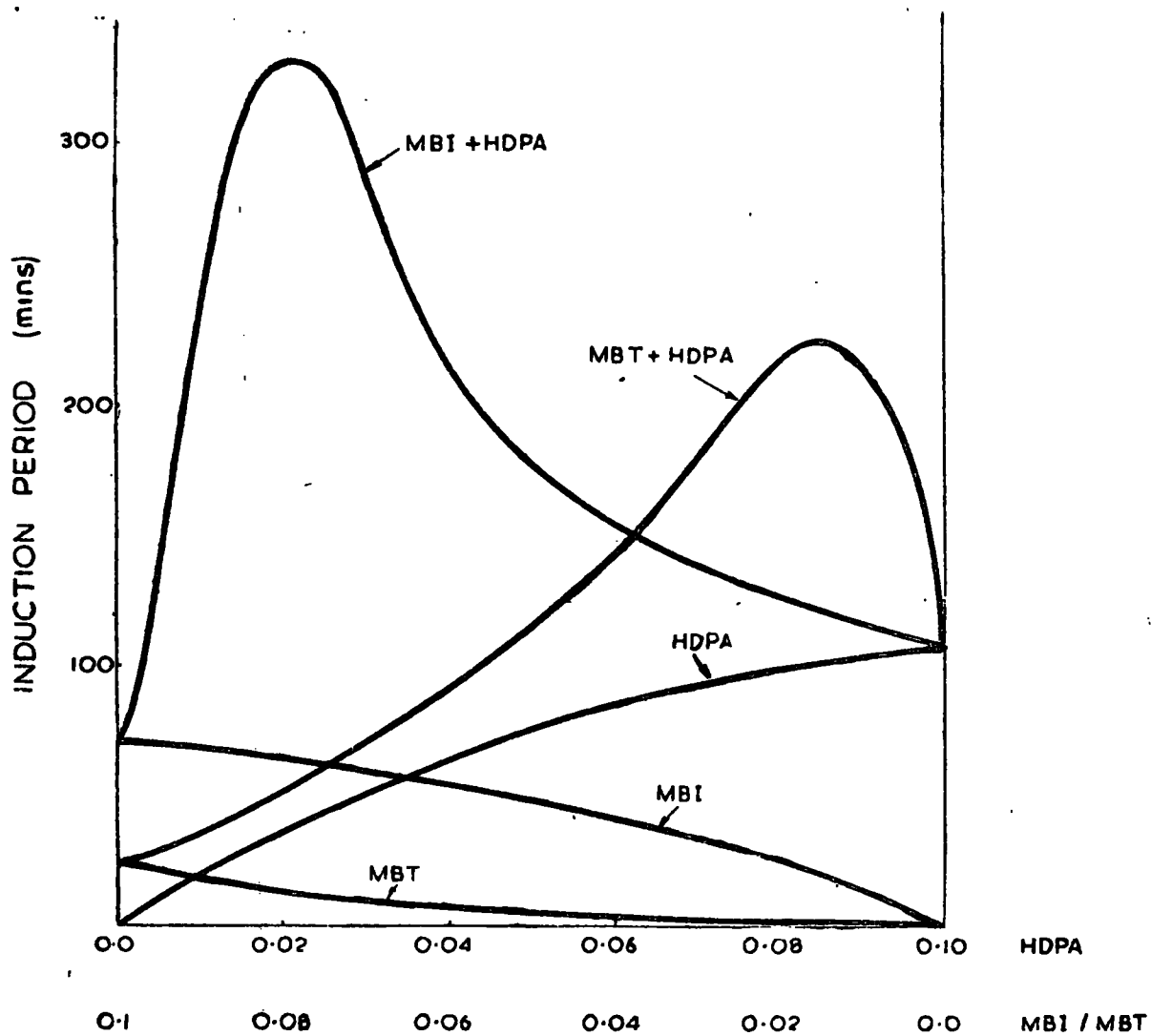


Fig. 12. Synergism between p-hydroxydiphenylamine (HDBA) and mercaptobenzimidazole (MBI) and mercaptobenzthiazole (MBT) at constant total concentration at 200°C.

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