# PROBLEMS INCURRED IN STABILIZING POLYMERS AGAINST OXIDATIVE DEGRADATION. MODEL STUDIES ON ACTIVE FUNCTIONAL GROUPS IN THE POLYMER SUBSTRATE AND NEW INHIBITORS

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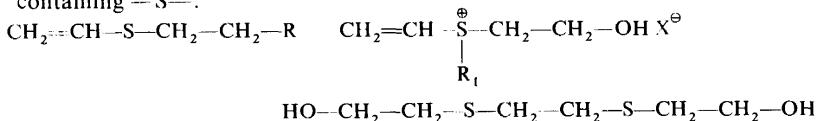
ABSTRACT

An investigation was made into the formation of functional groups that occur in unstabilized polyethylene during oxidation under the conditions of the induction test. Model substances were synthesized in which the nature and amount of functional groups, e.g. peroxide, carbonyl, hydroxyl, vinyl, etc., differed. The behaviour of these specimens was studied under the conditions of the oxidation test. The relationship of the induction time to the type of functional group allowed a sequence of reactivity to be drawn up, i.e.

$$—OOH > CO > —CH_2CH=CH_2 > —O—CH=CH_2 > —C=C—$$

$$> —\underset{\underset{CH_3}{|}}{C}—H > CHOH > CH—OR$$
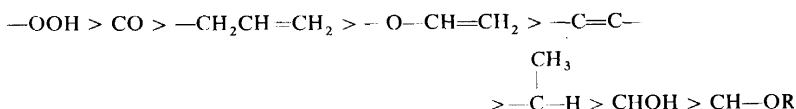
Here the damaging effect of the peroxide group on the alkyl ether group decreases from left to right. Comparison was made with a specimen stabilized with substituted phenols and a polymethylene produced by the decomposition of diazomethane.

The second part of the paper presents substances of the following structures containing —S—:

$$CH_2=CH—S—CH_2—CH_2—R \qquad CH_2=CH—\overset{\oplus}{\underset{\underset{R_1}{|}}{S}}—CH_2—CH_2—OH \ X^{\ominus}$$

$$HO—CH_2—CH_2—S—CH_2—CH_2—S—CH_2—CH_2—OH$$

The functional groups of these compounds compensate the injurious effect of the groups in the substrate, with the result that the compounds act as inhibitors. For example, the thioether bridges are converted to $>SO$ and $>SO_2$ derivatives. The sulphurous substances that also contain a vinyl double bond allow capture by disproportionation and addition reactions.

Although much work has been devoted to it, the problem of stabilizing polymers against oxidative degradation is still widely discussed. It retains its importance for the following reasons. (1) Increasing demands are being imposed by plastics processors and end users. (2) There are no technically

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perfect products available, i.e. most products display some defects, have fluctuations in their molar weights and morphology, and contain some impurities. Improvements in manufacturing processes and changes in the specifications for the raw materials may appear to be insignificant microscopically but, when regarded in detail, are often the reason for troublesome secondary effects. The need for developing even more effective inhibitors has not lost its urgency.

Because of this, oxidative reactions in polymers assume great practical importance. Much work has been carried out in this field. It is assumed that the first stage of oxidation is the formation of radicals and of hydroperoxides, which have been detected in all polyolefin oxidation processes.

We have tried to establish a relationship between oxidative degradation and the chemical structure of products with a defined amount of functional groups in the light of the many hypotheses that have been put forward and the analytical data available. Polyethylene was taken as a model.

Table 1

Character	Low-density polyethylene	High-density polyethylene
Density (g/cm^3)	0.918–0.920	0.925–0.950
Melt flow index MFI 190/2/16 g/10 min	1.2–1.7	0.1–0.6
CH$_3$/1000C	30–36	1
Crystallinity	34–40	75–80
Vinyl	0.05–0.2	1.0–0.3
$-CH=CH_2$		
Vinylidene	0.5–0.8	0.05–0.2
$>C=CH_2$		
1,4-*trans*	—	—
$-C=C-$		
$>CO$	0.01	0.01
$-OH$	+	+

It is generally realized that conventional polyethylenes are not uniform polymers consisting of nCH_2—CH_2 sequences (cf. *Table 1*). Strictly speaking, they must be considered as statistical copolymers with CH$_3$, vinyl, vinylidene and hydroxyl side groups and with carbonyl groups and double bonds in the chain. If the specimens have aged, hydroperoxide groups can also be detected, although they are only present in traces.

The induction period method was adopted to measure the oxidative degradation of the polymers. The polethylene specimens were flushed at 180°C with preheated pure oxygen, and the oxygen uptake was measured as a function of time (cf. *Figure 1*).

From *Figure 2*, it can be seen that the induction time for low-pressure polyethylene is different to that for high-pressure polyethylene. Hence, the decided differences in oxidation stability must be due to the structure.
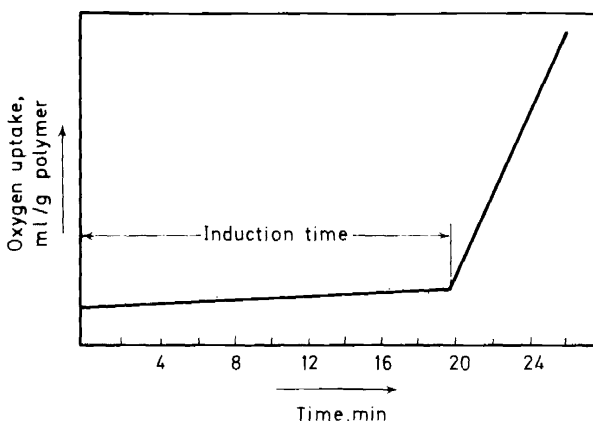
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Figure 1. Oxygen uptake at 180°C as a function of time. The flat portion represents the induction time.
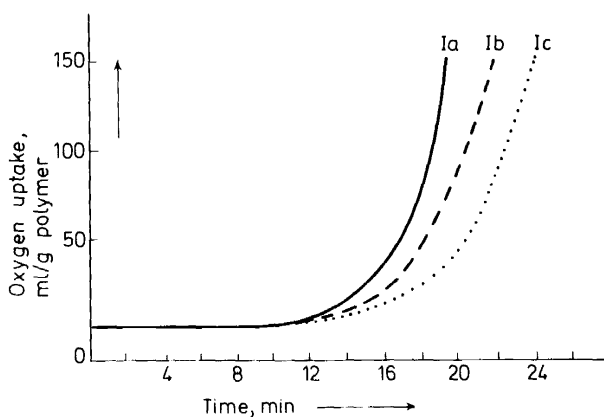

Figure 2. Induction times measured at 180°C for low-pressure and high-pressure polyethylene. I ――― high pressure polyethylene; Ib ――― low-pressure polyethylene; Ic ⋯ Ib reprecipitated.

In the case of the low-pressure type, it appears that traces of heavy metals arising from the polymerization process may also be of some significance: a decidedly higher stability is observed after precipitating in the presence of complexing agents (cf. *Figure 2*, curve Ic).

In order to determine which functional group is responsible for the degradation mechanism model compounds with the structures listed in *Table 2* were synthesized and tested.

The effect on the oxidation stability of increasing the proportion of the functional group is shown in *Figure 3*.

A good idea of which functional groups are responsible for oxidative degradation under the test conditions can be obtained from *Figure 4*. Each carbon skeleton was allotted the same amount of functional groups in

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Table 2. Synthesized model compounds. Structure, melt flow index, method of synthesis, and details of functional group

No.	Structure	MFI	Method of synthesis	Functional group type	%
Ia	$(CH_2—CH_2)_n$	3.8	Decomp. of diazomethane	—	
II	$(CH_2—CH_2)_{90}CO—$	1.8	Copolym. $CH_2=CH_2/CO$	CO	1.1
III	$—(CH_2—CH_2)_{10}—CO—$	4.0	Copolym. $CH_2=CH_2/CO$	CO	8.5
IV	$—(CH_2—CH_2)_{90}—CH—$ with OH	1.6	Reduction of II with $NaBH_4$	$—CH—$	~0.6
V	$—(CH_2—CH_2)_{10}—CH—$ OH	3.2	Reduction of III with $NaBH_4$	$—OH$ $—CH—$	~5.5
VI	$—(CH_2—CH_2)_{10}—C—$ $HOOH$	*	Reaction of III with H_2O_2 50°C, H^+	$—OH$ $—C—$ O $HOOH$ OH	~9
VIa	$—(CH_2—CH_2)_{90}—C—$ O $HOOH$	*	Reaction of II with H_2O_2 50°C, H^+	$—C—$ O OOH	~1.2
VII	$(—CH_2—CH_2)_{10}—CH—$ CH_3 $HOOH$	2.1	Ullmann reaction with CH_3Cl	$HOOH$ $—CH—$ CH_3	~5.0
VIII	$(—CH_2—CH_2)_{12}—C—$ CH_3 OOH	*	Ullmann reaction with CH_3Cl followed by (a) Admission of air (b) Reaction with H_2O_2	OOH $—C—$ CH_3	~8.0

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| No.	Structure	MFI	Method of synthesis	Functional group type	%
IX	$(CH_2-CH_2)_{10}-CH-$ $O-CH_3$	2.9	Reaction of V with diazomethane	$-O-CH_3$	~9
IXa	$(CH_2-CH_2)_{90}-CH-$ $O-CH_3$	1.2	Reaction of IV with diazomethane	$-O-CH_3$	~1
X	$(CH_2-CH_2)_{10}-CH-$ $O-CH=CH_2$	†	Vinylation of V with $HC\equiv CH$	$-O-CH=CH_2$	~12
Xa	$(-CH_2-CH_2)_{90}-CH-$ $O-CH=CH_2$ OH	1.5	Vinylation of IV with $HC\equiv CH$	$-O-CH=CH_2$	~1.5
XI	$-(CH_2-CH_2-)_{10}-C-$ $CH=CH_2$ OH	†	Ethynylation of III with $HC\equiv CH$, and following reduction	OH $-C-$ $CH=CH_2$	~8
XIa	$-(CH_2-CH_2-)_{90}-C-$ $CH=CH_2$ OH	1.6	Ethynylation of II with $HC\equiv CH$ and following reduction	OH $-C-$ $CH=CH_2$	~1
XII	$-(CH_2-CH_2)_9-C\equiv C-$	†	Dehydration of V	$-C\equiv C-$	~7
XIIa	$(-CH_2-CH_2)_{89}-C\equiv C-$	1.4	Dehydration of IV	$-C\equiv C-$	~0.8

* Decomposes
† Crosslinks
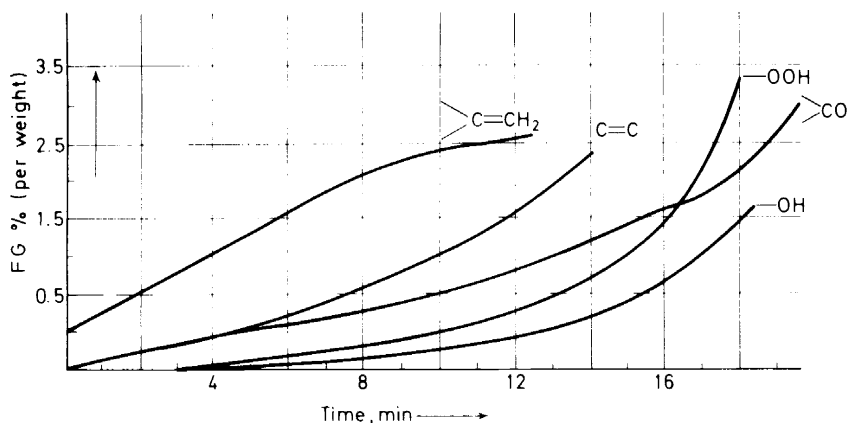
Figure 3. Proportion of the functional groups in polyethylene I (unstabilized) as a function of time at 180°C in the induction period test.
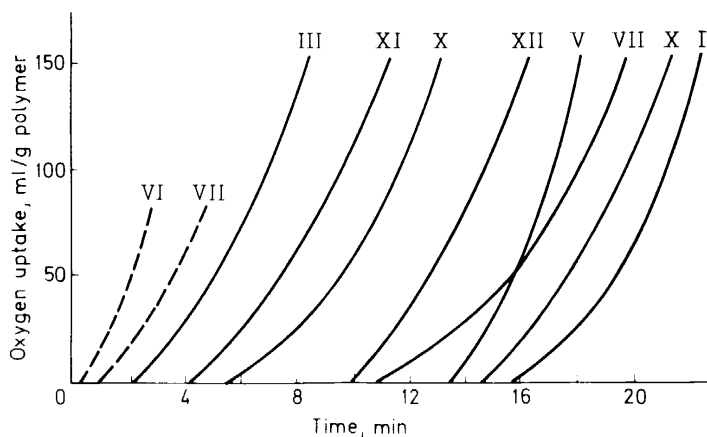

Figure 4. Relationship of induction time to the polymer structure.

order to facilitate comparison; in this case, one functional group on an average was allotted to each ten CH_2—CH_2 groups. The following conclusions can be derived by studying the relationships thus obtained between structure, i.e. functional groups, and induction time.

(1) The induction time is directly proportional to the stability of the product concerned.

(2) Peroxide groups are the most active and are primarily responsible for oxidative degradation (cf. *Figures 4* and 5). The degradation is so rapid that the specimen commences to decompose when it is being heated up. From about 80°C onwards, i.e. about 100°C below standard, measurement is no longer possible.

(3) Vinyl groups in the sidechain induce degradation more strongly than —C=C— groups in the chain.
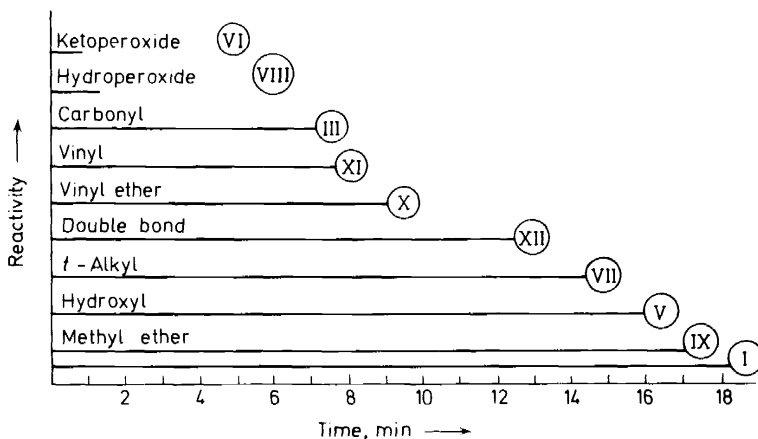
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Figure 5. Relationship between chemical structure and induction time. The Roman figures in the circles are the serial numbers of the products listed in *Table 2*. I denotes a general-purpose low-density polyethylene

(4) Methylated hydroxyl groups have practically no effect.

(5) An ideal $-CH_2-CH_2-$ polymer (Type Ia) without any side groups whatsoever is much superior to the general-purpose polymer I (high-pressure polyethylene), cf. *Table 3*.

The behaviour of this 'ideal polymer' will be considered later in the section dealing with the effect of antioxidants and in the part where their behaviour is compared to that of general-purpose polyolefins stabilized with conventional additives.

The relationship between the concentration of the functional groups and their efficiency is explained below.

In *Table 3*, the induction times for products with one functional group distributed over ten CH_2-CH_2 units are compared to those for one functional group distributed over ninety CH_2-CH_2 units. (The ratios in each case are statistical means.) The concentration of the functional groups concerned can be derived from *Table 2*. It can be seen that differences in

Table 3. The relationship of induction time to the concentration of the functional groups (FG)
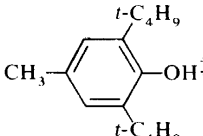
Type and No.	Ratio 1 FG to 10 $-CH_2-CH_2-$ Induction time, min	No.	Ratio 1 FG to 90 $-CH_2-CH_2-$ Induction time, min
Ketoperoxide VI	1	VIa	*ca.* 1
Hydroperoxide	2	—	—
Carbonyl III	5	II	11.5
Vinyl + hydroxyl VI	7.5	XIa	10
Vinyl ether X	9	Xa	12
C=C in the chain XII	13	XIIa	15
t-Alkyl VII	14.5	—	—
Hydroxyl V	16	IV	18
Methyl ether IX	17	IXa	19

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concentration of carbonyl groups exert a decided effect but that differences in concentration of the other functional groups are only slightly gradated.

The behaviour of specimen Ia is quite interesting. The induction time fluctuates in relationship to the time of storage and the ageing of the specimen. Freshly prepared polymethylene (Ia) has an induction time of about 65, whereas a one-week-old specimen kept under air with exclusion of light has a value of 40, although only traces of —CO or —OH could be detected in the specimen by the spectrometer.

Specimens for comparison purposes:

High-pressure polyethylene I   15–20
Ideal polymethylene Ia $(—CH_2—)_n$ 40–65

$$t\text{-}C_4H_9$$

I + 0.1 % wt CH_3—⟨ ⟩—OH‡   45–50

$$t\text{-}C_4H_9$$

The data submitted for comparison purposes in *Figure 4* and *Table 3* are the induction times in which 100 ml of oxygen were consumed for each gramme of resin. A clear gradation is evident on comparing the efficiency.

The results of the oxidation stability tests shown in *Figure 4* arrange the functional groups in a sequence ranging from —OO— groups to the general-purpose type I (high-pressure) polyethylene.

It is surprising to note that CO groups favour oxidative degradation much more than do —C≡C— groups. A tertiary hydroxy group combined with a vinyl group corresponding to that in compound XI is more active than a vinyl ether group (that in compound X) or a double bond in the chain (compound XII). This fact can be ascribed to the preference of hydroperoxide formation in compound XI.

The results presented in *Figures 4* and *5* allow the compound to be arranged in the sequence of oxidative degradation. The question thus arises whether other factors, such as contamination of the specimens by traces of heavy metals or other substances, may activate or inactivate oxidative degradation. It was already demonstrated in *Figure 2* that a precipitated specimen of low-pressure polyethylene (Ic) had a higher induction time than the original material (Ib).

In none of the cases investigated, could any change in the reactivity sequence presented in *Figure 4* be observed by varying the test conditions for the determination of induction time, i.e. by exposing the specimens to temperatures of 150°C and 100°C instead of to the temperature laid down, viz. 180°C.

The gradation in reactivity and the effect of the functional groups concerned, as determined on the model substances, can be exploited in practice.

(1) The injurious functional groups in polymers may be eliminated or converted into others that are less reactive.

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‡ 2,6-Di-*t*-butyl-4-methyl-phenol.

(2) The functional groups can be rendered ineffective by the introduction of competitive free radicals to inhibit oxidation of the polymer.

In all radical-induced autoxidation processes, substitution reactions take place, some of which are self-catalysing, and the dioxygen reacts as a di-radical with two unpaired electrons $\cdot O - O \cdot$. Consequently, another means of capturing less reactive radicals is the addition or formation of other radicals.

Radicals are formed by mechanochemical reactions occurring during the processing of polymers, e.g. during calandering or extrusion, but this is beyond the scope of the present paper.

MEASURES FOR PREVENTING OXIDATIVE DEGRADATION

(1) Chemical reactions with the polymers.
(2) The use of additives.

Tests on the model substances have demonstrated that peroxy groups are responsible for the most severe degradation. Therefore the following measures are required:

(a) The formation of —OO— groups should be prevented from the very beginning (but this is not possible in practice).
(b) Existing —OO— groups should be removed.

Peroxide decomposition

The stability of peroxides depends on their structure, and on the ambient conditions including temperature.

Much work has been done in relating differences in peroxy group stability to the structure[1]. Materials have to be found which will decompose all kinds of —OO— groups that have formed in the polymer.

Radical-induced decomposition

Morse[2] found that alkyl radicals derived from a solvent induce the decomposition of hydroperoxides in the presence of oxygen. The oxygen and the hydroperoxide compete for solvent radicals.

Thermally-induced decomposition

This also involves radical-induced decomposition. Kharasch et al.[3] studied some model reactions and proposed that, in fact, reduction takes place.

Solvent effects

Thomas et al.[4] studied decomposition in a range of solvents and suggested that the effect observed was induced decomposition of the peroxide by the solvent.

Metal ion effect

Metals or their ions, e.g. copper, manganese and cobalt, may act as catalysts and speed up decomposition. They are highly efficient autoxidation

catalysts. Dean[5] postulated reversible formation of a metal–peroxide coordination complex following an electron transfer. Kharasch *et al.*[3] proposed that the relative oxidation of alkylperoxy radicals is the source of oxygen.

Reduction methods
Peroxides can be reduced according to equation 1.

$$R'H + ROOH \rightarrow \begin{bmatrix} RO^{\cdot} \\ {}^{\cdot}R' \end{bmatrix} + H_2O \qquad (1)$$
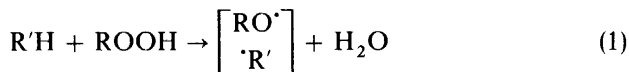
Examples of reducing agents (R'H) that can be used for this purpose are –S– compounds, P(III) derivatives, amines, sugars and all compounds with an unstable hydrogen atom[6]. In all cases free radicals are formed.

Non-radical-induced decomposition
The anionic mechanisms responsible for non-radical-induced decomposition are classified into the following three groups[7].

Catalysis by acids
Solvents with a high dielectric constant favour the decomposition reaction. The stronger the acid, the greater the rate of decomposition[8].

Catalysis by bases
Even weak bases or dinitriles, e.g. phthalonitrile, are powerful reagents for promoting decomposition[3, 9].

Intermolecular rearrangement
In this case, the end products are formed via an intermediate without the formation of radicals.

Stoichiometric reactions
This important type of reaction closely resembles the addition of reducing agents. Examples are the reaction between hydroperoxides and olefins yielding epoxides[10] and the reactions between hydroperoxides and sulphides[11].

MODEL REACTION TO ELIMINATE ACTIVE FUNCTIONAL GROUPS

The induction time of model compounds I and II can be lengthened by reducing them with a highly reactive agent[6].
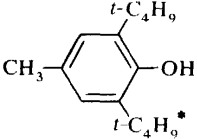
Another means of lengthening the induction time is to add sulphur or carbon black.

We tried to exploit the knowledge we had gained from our model experiments in finding highly reactive material that would either block the functional groups or would compete with them for oxygen.

The inhibitors commonly used are phenols and aromatic amines, which terminate the kinetic chain. The concentration of inhibitor undergoing oxidation is normally about one per cent or, in some cases, less.

Table 4. Induction times of polyethylene containing reducing agents

No.	Type	Specification	Induction time, min
I	High-pressure polyethylene	*Table 1*	15–20
Ib	Low-pressure polyethylene	*Table 1*	~20
Ia	Polymethylene	No funct. groups	~60
XIII	I reduced by SO_2 ⎫	Peroxides	~25
XIV	I reduced by H_2 ⎪	or CO	~35
XV	I reduced by H_2S ⎬	undetectable	~40
XVI	I reduced by $NaBH_4$ ⎭	by i.r.	~45
I	stabilized with 0.1 % wt of		45–50

$$t\text{-}C_4H_9$$

$$CH_3 \text{—} \underset{t\text{-}C_4H_9^{*}}{\overset{}{\bigcirc}} \text{—OH}$$
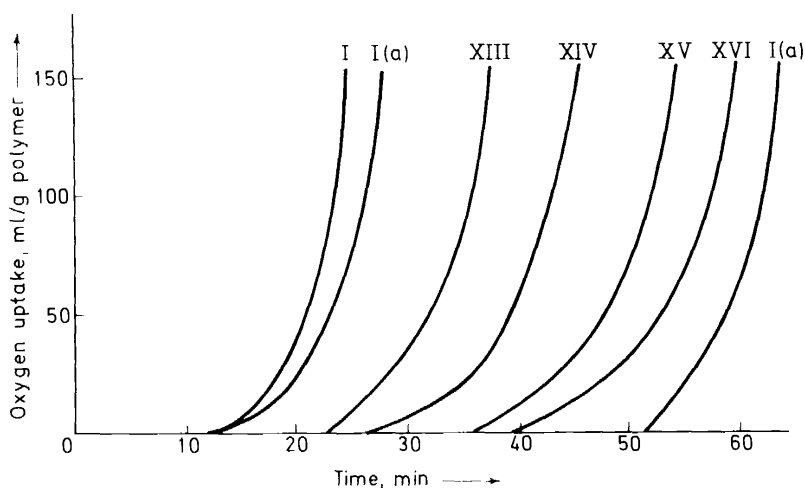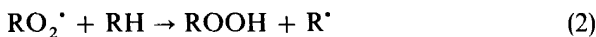
*2,6-Di-*t*-butyl-4-methyl-phenol.

Figure 6. Induction times of modified samples compared to that of the basic products.

Should the chain terminating reaction compete successfully with the propagation reaction,

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (2)$$

where RH represents a segment of the polymer, then the inhibitor must have one or more labile H atoms. As a result of the H atoms in the molecule, the inhibitor reacts more readily with the oxygen than the functional groups in the polymer.
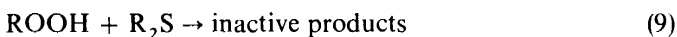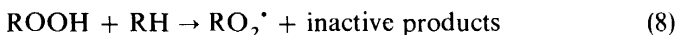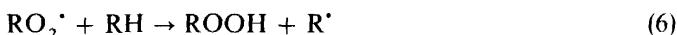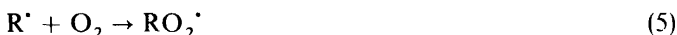
$$IH + O_2 \rightarrow I^{\cdot} + HOO^{\cdot} \qquad (3)$$

where IH represents the inhibitor. This reaction leads to an active free radical.

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$$HOO^{\cdot} + RH \rightarrow HOOH + R^{\cdot} \qquad (4)$$
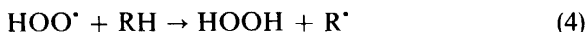
(A) If the number of free radicals formed during the oxidative degradation of one ROOH is greater than unity, each chain scission will be accompanied by the formation of more than one active free radical. Thus at any inhibitor concentration, oxidation will proceed autocatalytically during the induction period.

(B) If the number of kinetic chains formed by the decomposition of one ROOH is less than unity, the inhibitor is oxidized directly, and the reaction proceeds by the mechanism shown below, which has been proposed by Shlyapnikov and Miller[14].

$$IH + O_2 \rightarrow I^{\cdot} + HOO^{\cdot} \qquad (3)$$

$$I^{\cdot} + HOO^{\cdot} + RH \rightarrow R^{\cdot} + \text{inactive products} \qquad (4)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \qquad (5)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (6)$$

$$RO_2^{\cdot} + IH \rightarrow ROOH + I^{\cdot} \qquad (7)$$

$$ROOH + RH \rightarrow RO_2^{\cdot} + \text{inactive products} \qquad (8)$$

$$ROOH + R_2S \rightarrow \text{inactive products} \qquad (9)$$

Equation 8 applies when the oxidized material contains inhibitors that decompose hydroperoxides. Examples of these are organic sulphur compounds.

Features of an efficient inhibitor are:

(a) It should decompose peroxides without re-initiating autoxidation or a chain of radical formation;
(b) It should scavenge radicals without discolouration of the polymer;
(c) It should have an active double bond to react with ROOH to give unreactive epoxides;
(d) It should be compatible with the polymers; and
(e) It should be non-volatile.

All the compounds listed in *Table 5* can:
(a) Decompose hydroperoxides;
(b) React with ROOH via vinyl groups forming epoxides†;
(c) React with oxygen; and
(d) Scavenge radicals

$$\underset{A}{CH_2{=}CH}{-}\underset{B}{S}{-}\underset{C}{CH_2{-}CH_2{-}R}$$
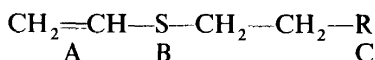
All these model compounds have three different units.
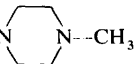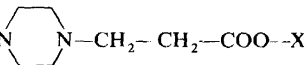
(A) $CH_2{=}CH{-}$ (a) radical absorbing, polymerization
(b) O_2 reaction $\rightarrow$ epoxides (hydroperoxide)
(c) $-OH$ addition $\rightarrow$ ethers

†Berlin[15] studied the effect of double bond systems as inhibitors in thermo-oxidative processes.

Table 5. Model compounds for stabilization

First series

No.	CH$_2$=CH—S—CH$_2$—CH$_2$—R	B. pt, °C
XVII	X—OOC—CH$_2$—CH$_2$—N⟨ ⟩O	160 mm Hg
XVIII	X—OOC—CH$_2$—CH$_2$—N⟨ ⟩N—CH$_3$	184–186 mm Hg
XIX	X—OOC—CH$_2$—CH$_2$—N⟨ ⟩N—CH$_2$—CH$_2$—COO—X	F. pt 35–40
XX	X—OOC—CH$_2$—CH$_2$—NH—(CH$_2$)$_3$—N⟨H⟩	195 mm Hg
XXI	X—O—CH$_2$—CH$_2$—CN	120–124 mm Hg
XXII	(X—O)$_3$—P	112–115/0·2 mm Hg

X   CH$_2$=CH—S—CH$_2$—CH$_2$

(B)   —S—

(a) O$_2$ reaction → —S— sulphoxides
‖
O

⇒SO$_2$ sulphones
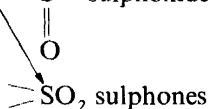
In the latter case, this entailed that about 20 litres of oxygen are absorbed by 1 mol of compound XVII, XVIII, XX, XXI
by $\frac{1}{2}$ mol of compound XIX
by $\frac{1}{3}$ mol of compound XXII (if only S reacts) and
by $\frac{1}{4}$ mol of compound XXII (if S and P react).

(b) radical scavenging—chain transfer.

(C)   R—

(a) Contains reducing and radical-scavenging groups (except XXI). XXI decomposes hydroperoxides in a base-catalysed reaction via the —CN groups.

Bolland[13] studied the autoxidation and autoinhibition of saturated thioethers and allylic sulphides in the presence of radical generators. He observed that the addition of a fresh quantity of a radical generator restored the rate of oxidation. This phenomenon indicates that efficient inhibitors are formed during the autoxidation process. These compounds are taken as monomers in various copolymerization reactions, in which case they act as chain transfer agents, i.e. they avoid crosslinkage during polymerization, an important function in the polymerization of dienes.

The efficiency of compounds XVII to XXII was investigated by adding them to general-purpose polyethylenes I and Ib and to the model polymers VI, VIa and VIII, which contain —O—O— groups.

In all cases, polyethylene I was inhibited with 0.1% wt of compounds XVII to XXII. The induction time curve for the uninhibited sample (I) is shown on the left of Figure 7, and the corresponding curves for the six inhibited samples on the right. The improvement in stability achieved by
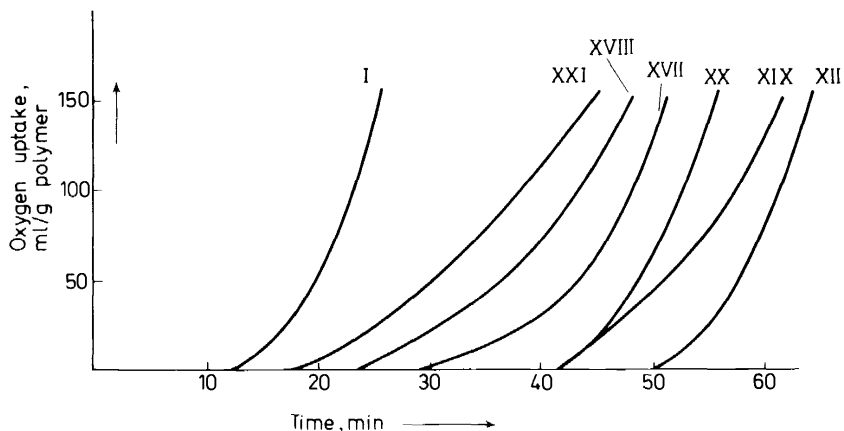
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Figure 7. Induction times for general-purpose unstabilized polyethylene and for polyethylene stabilized with inhibitors Nos. XVII to XXII.

Table 6. Correlation between induction time and sample VI, which contains —OOH groups, after stabilization

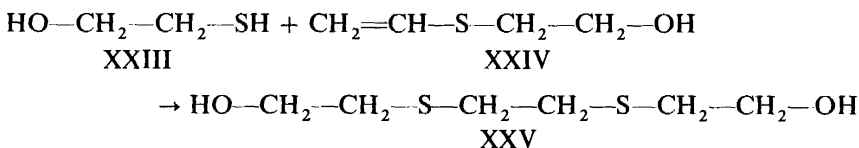| No.			Induction time, min
VI Ketoperoxide	$$\text{content of} -\overset{O}{\overset{\|}{C}}-$$ $$\text{HOOH}$$	9%	1
+ XVII 0.1% wt			6
XVIII 0.1% wt			5
XIX 0.1% wt			8
XX 0.1% wt			8
XXI 0.1% wt			3
XXII 0.1% wt			10
VIa Ketoperoxide	$$\text{content of} -\overset{O}{\overset{\|}{C}}-$$ $$\text{HOOH}$$	1.2%	1
XVII 0.1% wt			6
XVIII 0.1% wt			8
XIX 0.1% wt			8
XX 0.1% wt			10
XXII 0.1% wt			15
VIII Hydroperoxide	$$\text{content of} -\overset{CH_3}{\overset{\|}{\underset{\|}{C}}}-$$ $$\text{OOH}$$	~8%	2
XVII 0.1% wt			5
XVIII 0.1% wt			6
XIX 0.1% wt			8
XX 0.1% wt			8
XXI 0.1% wt			5
XXII 0.1% wt			12

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the inhibitors containing sulphur, i.e. XVII to XXII, can be seen clearly from *Figure 7*. It now remains to be clarified whether these inhibitors are still efficient if they are added direct to polymers containing —OOH groups, e.g. the model substances VI, VIa and VIII.

From *Table 6* it can be seen that the induction time can be increased by a factor of between three and ten.

The stabilizing agents in the second series have the formula

$$\underbrace{HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-OH}_{R_1}$$
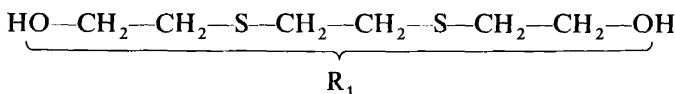
These compounds were synthesized by adding mercaptoethanol (XXIII) to vinyl hydroxyethyl ether (XXIV).

$$\underset{\text{XXIII}}{HO-CH_2-CH_2-SH} + \underset{\text{XXIV}}{CH_2{=}CH-S-CH_2-CH_2-OH}$$

$$\underset{\text{XXV}}{\rightarrow HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-OH}$$

Compound XXV is monoesterified with H_3PO_3 to give compound XXVI or diesterified with H_3PO_3 to give compound XXVII. Likewise, compounds XXVIII and XXIX are obtained by monocyanoethylation and dicyanoethylation of compound XXV.

Table 7

No.		Melting point, °C
XXV	$HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-OH$	122
XXVI	$(HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-O)_3P$	79–82
XXVII	$(O-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-O)_6P_2$	116–120
XXVIII	$HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-O-CH_2-$ CH_2-CH_2-CN	118
XXIX	$NC-CH_2-CH_2-O-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-$ $CH_2-O-CH_2-CH_2-CN$	110-112

The stabilizing agents in the third series are represented by

$$CH_2{=}CH-\overset{\oplus}{\underset{R}{S}}-CH_2-CH_2-OH\ X^{\ominus}$$
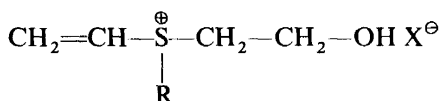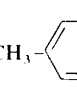
This class of compounds is synthesized by the alkylation of compound XXIV with a substance RX, where R may be an aliphatic, aromatic, or cycloaliphatic group and X^- is generally an anionic group to compensate the positive charge on the sulphonium bridge. Details of R and X^- are given in *Table 8*.

Compounds XXV to XXIX listed in *Table 7* and compounds XXX to XXXVIII listed in *Table 8* were also tested. The results of the induction time test are presented in *Figures 7* and *8*.

Table 8

No.	R	X⁻	Solid point, °C
XXX	—CH$_2$—CH$_2$—OH	HCOO⁻	
XXXI	—CH$_2$—CH$_2$—OH	$\frac{1}{2}$COO⁻ COO⁻	35
XXXII	—CH$_2$—CH$_2$—OH	$\frac{1}{3}$PO$_4^{3-}$	
XXXIII	—CH$_2$—CH$_2$—OH	$\frac{1}{2}$SO$_3^{2-}$	40
XXXIV	—CH$_2$—CH$_2$—OH	$\frac{1}{2}$H$_2$N—CH (SO$_3^-$, SO$_3^-$)	Decomp. at 70
XXXV	—CH$_2$—CH$_2$—OH	⟨benzene⟩—O⁻	30–35
XXXVI	—CH$_2$—CH$_2$—OH	X-substituted ⟨benzene⟩-O⁻, X = t-butyl	40–45
XXXVII	—CH$_2$—CH$_2$—OH	CH$_3$-⟨benzene, X⟩-O⁻	45
XXXVIII	—CH$_2$—CH$_2$—OH	Citric acid	65

Figure 8. Induction times for general-purpose unstabilized polyethylene (I) and for polyethylene stabilized with inhibitors Nos. XXV to XXIX.

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In *Figure 8*, the polyethylene (I) was stabilized with 0.1 % wt of compounds XXV to XXIX. The most efficient compounds are XXVI and XXVII, the mono-acid diesters of compound XXV, i.e.

$$HO-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-OH,$$

with phosphorous acid.

In *Figure 9*, the polyethylene (I) was again stabilized with 0.1 % wt of compounds XXX to XXXVIII. All the compounds are extremely efficient with the exception of XXX and XXXV, i.e. the formic and phenolic compounds.

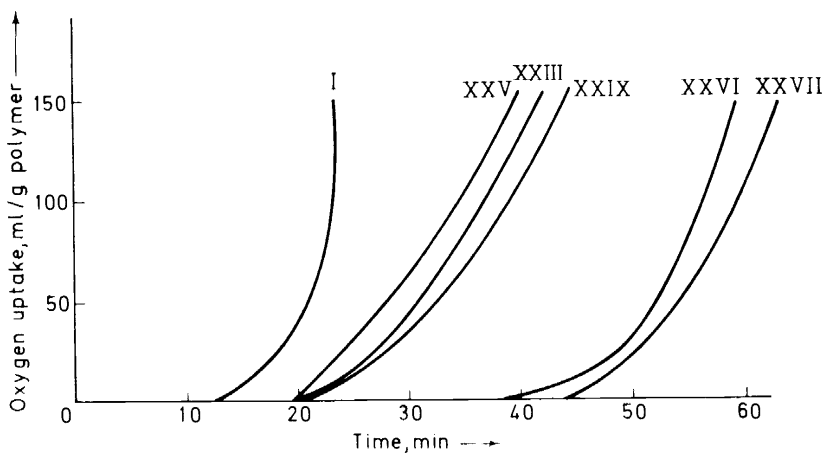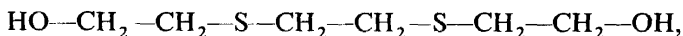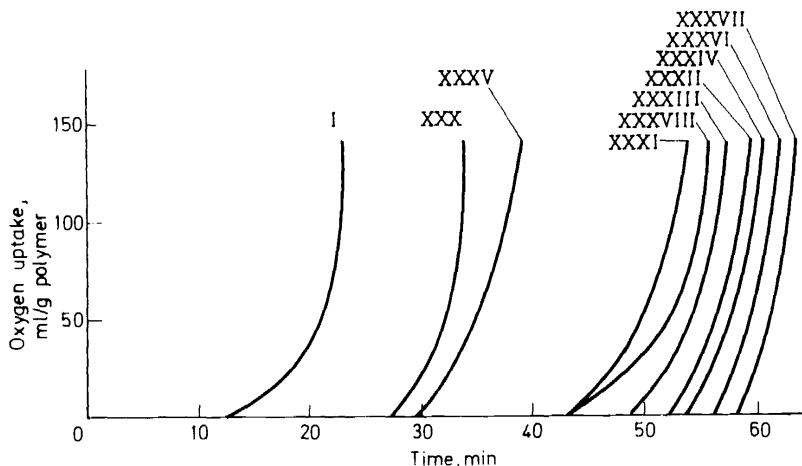The relationship of the proportion of functional group to time is presented in *Figure 10*.

Figure 9. Induction times for general-purpose unstabilized polyethylene (I) and for polyethylene stabilized with inhibitors Nos. XXX to XXXVII.
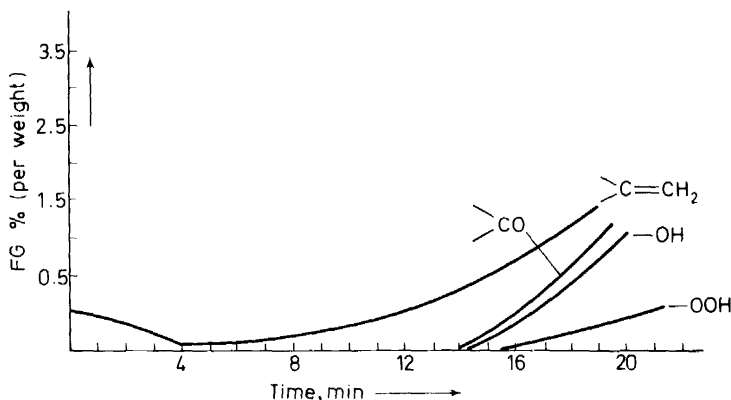

Figure 10. Proportion of the functional groups in polyethylene I stabilized with 0.1 % wt of XVII as a function of time at 180°C in the induction period test.

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Table 9. Relationship between the type of stabilizer and functional group in oxidized polyethylene (I) (after ten minutes)

Type of stabilizer	$>CO$	—OOH	$>C=CH_2$	—C=C—	—OH (% wt)
None	1.0	0.5	2.5	1.5	0.2
XVII	—	—	0.2	—	—
XVIII	—	—	—	—	—
XIX	—	—	—	—	0.1
XX	—	—	0.1	—	0.1
XXI	*ca.* 0.1	—	0.1	—	0.1
XXII	—	—	—	—	—
XXV	—	—	0.1	—	—
XXVI	—	—	0.1	—	0.1
XXVII	—	—	—	—	0.1
XXVIII	*ca.* 0.1	—	—	—	—
XXIX	—	—	—	—	—
XXX	—	—	—	—	0.1
XXXI	—	—	0.2	—	—
XXXII	—	—	0.1	—	—
XXXIII	—	—	0.2	0.1	0.1
XXXIV	—	—	—	—	0.1
XXXV	0.1	—	—	—	—
XXXVI	—	—	—	—	—
XXXVII	—	—	—	—	—
XXXVIII	—	—	0.3	—	—

The effect on the induction time of adding 0.1 % wt of the various inhibitors to the polyethylene (I) is presented in *Table 9*.

In order to determine the changes undergone by the inhibitors themselves during the induction test, compounds XVII to XXII (*Table 5*), XXV to XXIX (*Table 7*), and XXX to XXXVIII (*Table 8*), were oxidized at 180°C for ten minutes and twenty minutes. The results are listed in *Table 10*.

Table 10(a). Products of oxidation of the inhibitors in the induction time test (180°C in pure oxygen)

Compound No.	After 10 min	After 20 min
$CH_2=CH—S—CH_2—CH_2—R$ XVII	~40% XVII	~20% XVII
	~30% $>SO^*$	~35 $>SO$
	~10% $>SO_2^*$	~30 $>SO_2$
XVIII ⎫ XIX ⎬ similar to XVII XX ⎭		
XXI similar to XVII	~5% dimer cyclobutane derivatives $CH_2—CH—S—CH_2—CH_2—R$ ┃ ┃ $CH_2—CH—S—CH_2—CH_2—R$	~2%

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Table 10(a).—*Continued*

XXII	$\sim 35\%$ XXII	$\sim 10\%$ XII
	$\sim 10\% \diagup\!\!\!>\!\!SO$, P^{III}	$\sim 10\% \diagup\!\!\!>\!\!SO$, P^{III}
	$\sim 10\% \diagup\!\!\!>\!\!SO_2$, P^{III}	$\sim 25\% \diagup\!\!\!>\!\!SO_2$, P^{III}
	$\sim 20\%$ P^V $-S-$	$\sim 30\%$ P^V, $-S-$
	$\sim 10\%$ $P^V \diagup\!\!\!>\!\!SO$	$\sim 20\%$ P^V, $\diagup\!\!\!>\!\!SO$
	$\sim 10\%$ $P^V \diagup\!\!\!>\!\!SO_2$	$\sim 5\%$ P^V, $\diagup\!\!\!>\!\!SO_2$

* $\diagup\!\!\!>\!\!SO$ groups or $\diagup\!\!\!>\!\!SO_2$ groups instead of S in the basic inhibitor.

Table 10(b). Products of oxidation of the inhibitors in the induction time test (180°C in pure oxygen)

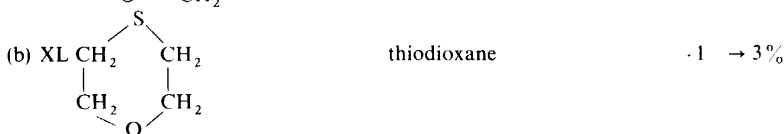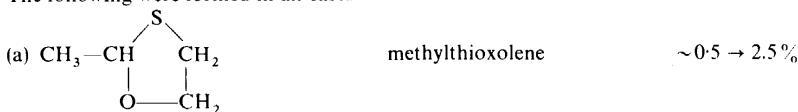| Compound No.	After 10 min	After 20 min
XXV	20% XXV	15% XXV
	15% $\diagup\!\!\!>\!\!SO$	35% $\diagup\!\!\!>\!\!SO$
	10% $\diagup\!\!\!>\!\!SO_2$	20% $\diagup\!\!\!>\!\!SO_2$
	50% condensed polymers linear and cyclic $(-CH_2-CH_2-S-)_n$	30% condensed polymers
XXVI	30% XXVI	20% XXVI
	10% $\diagup\!\!\!>\!\!SO$, P^{III}	5% $\diagup\!\!\!>\!\!SO$, P^{III}
	5% $\diagup\!\!\!>\!\!SO_2$, P^{III}	10% $\diagup\!\!\!>\!\!SO_2$, P^{III}
	10% $\diagup\!\!\!>\!\!SO$, P^V	20% $\diagup\!\!\!>\!\!SO$, P^V
	20% $\diagup\!\!\!>\!\!SO_2$, P^V	35% $\diagup\!\!\!>\!\!SO_2$, P^V
XXVII	25% XXVI	20% XXVI
	20% $\diagup\!\!\!>\!\!SO$, P^{III}	20% $\diagup\!\!\!>\!\!SO$, P^{III}
	10% $\diagup\!\!\!>\!\!SO_2$, P^{III}	20% $\diagup\!\!\!>\!\!SO_2$, P^{III}
	20% $-S-$, P^V	25% $-S-$, P^V
	20% $\diagup\!\!\!>\!\!SO$, P^V	15% $\diagup\!\!\!>\!\!SO$, P^V
	5% $\diagup\!\!\!>\!\!SO_2$, P^V	10% $\diagup\!\!\!>\!\!SO_2$, P^V

XXVII ⎫
XXIX ⎬ not examined

Table 10(c). Products of oxidation of the inhibitors in the induction time test (180°C in pure oxygen)
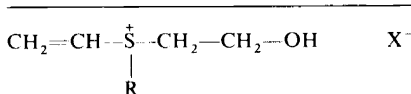
$$CH_2\!=\!CH\!-\!\overset{+}{S}\!-\!CH_2\!-\!CH_2\!-\!OH \qquad X^-$$
$$\overset{|}{R}$$

The following were formed in all cases

(a) $CH_3\!-\!\underset{|}{CH}\overset{/S\backslash}{}\underset{|}{CH_2}$ methylthioxolene $\sim\!0.5 \rightarrow 2.5\%$
$O\!-\!\!-\!CH_2$

(b) XL $\underset{|}{CH_2}\overset{/S\backslash}{}\underset{|}{CH_2}$ thiodioxane $\cdot 1 \rightarrow 3\%$
$\underset{\backslash O /}{CH_2 CH_2}$

(c) XLI oligomers formed by intramolecular OH-addition to the vinyl double bond
$$|\!-\!O\!-\!CH_2\!-\!CH_2\!-\!S\!-\!CH_2\!-\!CH_2\!-\!|_{5-15} \sim 10\%$$
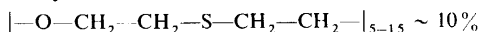
(d) Split compounds: from 2-mercaptoethanol ($HS\!-\!CH_2\!-\!CH_2\!-\!OH$), which was oxidized to $HO_3S\!-\!CH_2\!-\!CH_2\!-\!OH$, CO_2, SO_2 and lower carboxylic acids, and from $HO\!-\!CH_2\!-\!CH_2\!-\!S\!-\!CH_2\!-\!CH_2\!-\!S\!-\!CH_2\cdot CH_2\!-\!OH$ (XXV) about 3%, and from XXV itself, which was oxidized to $\diagdown SO$ and $\diagdown SO_2$ compounds 2.5 to 5%.
XXV was formed by the addition of 2-mercaptoethanol (ME) to XXIV
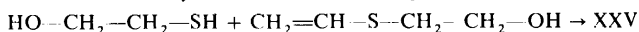
$$HO\!-\!CH_2\!-\!CH_2\!-\!SH + CH_2\!=\!CH\!-\!S\!-\!CH_2\!-\!CH_2\!-\!OH \rightarrow XXV$$
$$ME XXIV$$

X^- decomposes as follows

No.	After 10 min	
XXX	CO, CO_2	30%, 30%
XXXI	CO_2	50%
XXXII	P^V	40%
XXXIII	SO_2	50%
XXXIV	NH_3, CO_2, SO_2	10%, 10%, 20%
XXXV	oligomeric phenols	10%
	alkylated phenols	10%
XXXVI $\}$ XXXVII	similar to XXXV	
XXXVIII	CO_2	20%
	aconitic acid	20%

CALCULATION OF ELECTRON DISTRIBUTION BY THE HMO MODEL†

Electron distributions that are interesting for the reactivity are presented as $\Delta\rho$ values for αC, βC and acceptor R in *Figure 11*. The $\Delta\rho$ values are the differences between the individual nuclear charges and the π-electron densities.

†The electron distribution was calculated by Dr Feichtmayr, BASF.
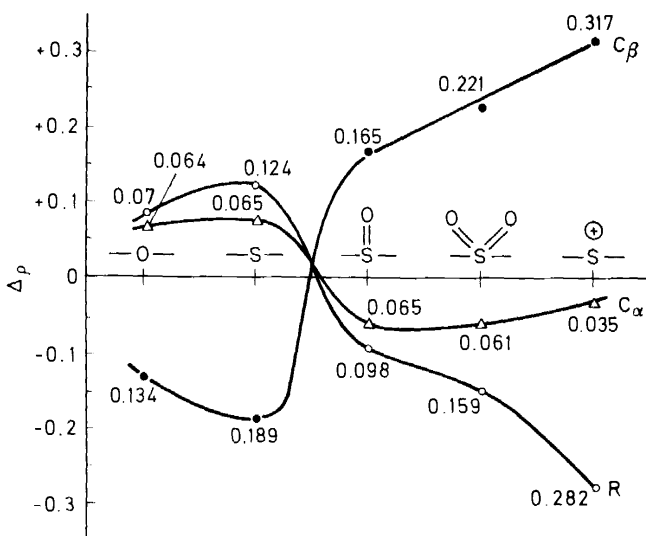
Figure 11. Electron distribution in the system
$$CH_2{=}CH{-}R - CH_2 - CH_2 - OH.$$

1 (βC)	1.13404	$\Delta\rho = -0.134$
2 (αC)	0.93643	$\Delta\rho = +0.064$
3 (Acceptor R)	1.92955	$\Delta\rho = +0.070$

The $\Delta\rho$ values for the other systems were calculated in the same way. The calculation confirms differences in behaviour of the various substituted sulphur derivatives in the experiment.

CONCLUSION

An approach combining analysis and synthesis of both the substrate—in this case polyethylene—and the additive has been adopted to obtain an insight into oxidative degradation by means of data that can be obtained by analysis. New inhibitor systems containing sulphur have been developed. These enter into competitive reactions and are themselves oxidized to inactive products, blocking chain reactions and decomposing peroxide groups.

Stabilization and the decomposition of polymers under defined conditions are problems that will remain topical as long as polymers are ingredients of articles that come into contact with food, etc. For this reason, optimum stabilization is always important.

In order to clarify the relationships between structure and active functional groups, a start has been made on the following studies:

(a) Checking the results obtained to see if they are valid for other systems too, e.g. polypropylene, polyisobutylene and polydienes;

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(b) The development of new test methods that closely simulate practical conditions and give more realistic information on the value of the polymers in end use. This study also includes mechanochemical reactions.

ACKNOWLEDGEMENTS

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