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MECHANISM OF THE OXIDATIVE THERMAL DEGRADATION AND OF THE STABILISATION OF POLYMERS

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1. OXIDATION IN GAS AND LIQUID PHASES

After Bakh[1] and Engler[2] had formulated the peroxide theory of oxidation, many papers appeared on the oxidation of hydrocarbons and other organic compounds. Many oxidations were found to be autocatalytic and characterised by well-defined induction periods. Work in this field entered a new phase of development with the theory of chain branching[3], and especially the theory of degenerate explosions[4]. The principal results obtained on oxidation were generalised on the basis of the theory of chain reactions[5]. Under the influence of the work done by the Semenov and Hinshelwood schools, a great deal of research effort was devoted to the mechanism of the oxidation of organic compounds in the gas and liquid phases.

Shortly afterwards it was suggested that the main task of research in this field was to determine the rate constants of the elementary reactions in a complicated radical-chain

process of oxidation, so that the rate of oxidation could be calculated from its hypothetical mechanism. Comparison of the experimental results with theoretical calculation would enable the correctness of the proposed mechanism to be assessed. Recent monographs by Semenov[6] and by Kondrat'ev[7] have summarised the progress achieved on these lines.

The most important results were obtained in investigations of gas-phase oxidations. Nalbandyan and Voevodskii based a radical–chain scheme for the oxidation of hydrogen on published data and their own results, and showed that all deductions made from this scheme agreed well with experiment[8]. Values of many of the constants adopted in this work have now been verified and refined[9].

The development of the electron paramagnetic resonance (EPR) method has permitted the experimental detection of several free radicals and atoms formed in the course of oxidation, and has thus yet again confirmed the correctness of the accepted schemes for the oxidation of hydrogen and of several other substances. It has been demonstrated that hydrogen atoms[10,11], oxygen atoms[12], and $HO_2^{\cdot}$ radicals[13] are formed in the oxidation of hydrogen.

Semenov and his coworkers, having set up a scheme for the oxidation of methane, used published values for the rate constants of the elementary reactions to calculate the maximum concentration of formaldehyde formed in this process[6]. The result differed from the experimental value by less than an order of magnitude, which must be regarded as good agreement, since only rough values were known for many of the rate constants used in the calculations.

Matters are considerably worse than in the gas phase for research on the mechanism of oxidation in the liquid phase. In spite of the large amount of work done in this field, the results of which have been surveyed in several reviews[14-18], it has not yet proved possible to solve the problem of constructing from elementary reactions a mechanism for even the simplest liquid-phase oxidations of organic compounds. Therefore work on the elementary processes occurring in the liquid phase and on determining their rate constants becomes of great importance[19,20].

The development of work in this field has been considerably accelerated by the application of new methods of investigation. Much new information has been obtained, for example, by the use of labelled atoms, especially by the kinetic tracer method[21]. This method has yielded the sequence in which various intermediate products are formed in the oxidation of cyclohexane and other hydrocarbons, and has also yielded the rates of formation and consumption of the intermediate products[22,23]. The relative rates of several liquid-phase radical reactions have been determined by means of labelled atoms[24-27].

Chemiluminescence provides a promising method[28] of investigating the rates of several radical reactions in the liquid phase, and has recently been successfully employed to prove that R$^{\cdot}$ and $RO_2^{\cdot}$ radicals are involved in the liquid-phase oxidation of hydrocarbons[29]. It has made possible assessment of the competition between the reactions

$$R^{\cdot}+O_2 \xrightarrow{k_1} RO_2^{\cdot},$$

and

$$R^{\cdot}+R^{\cdot} \xrightarrow{k_3} RR,$$

and evaluation of the ratio $k_1/\sqrt{k_2}$ for the oxidation of ethylbenzene at 60°, for which 2.7×10^4 litre$^{1/2}$ mole$^{-1/2}$ sec$^{-1/2}$ has been obtained.

By means of the chemiluminescence method it has been possible to measure the absolute rates of several oxidations, the efficiencies of various initiators, and rate constants for reactions between radicals and several antioxidants. The immense prospects of developing this method for the investigation of oxidation mechanisms in liquid and solid phases are easily visualised.

Among other methods, polarography was first employed to determine peroxides and aldehydes formed in the oxidation of hydrocarbons[30]; while chromatography has been widely used for kinetic investigations in gas, liquid, and solid phases[31].

Rates of initiation and chain branching in liquid-phase oxidations are often determined by the so-called inhibitor method, in which the rate of consumption of an inhibitor is measured[32]. The weak points in this method have been discussed[33,34].

The mechanism of the radical–chain oxidation of n-decane has been investigated in very great detail[35-39]. On the basis of this and the work of other investigators it can now be assumed that the most probable scheme for the oxidation of a hydrocarbon RH in the liquid phase is as follows:

$$RH+O_2 \xrightarrow{w_i} R^{\cdot}+HO_2^{\cdot}.$$

A termolecular initiation reaction[40] is also possible, since it is less endothermic:

$$2RH+O_2 \longrightarrow 2R^{\cdot}+H_2O_2.$$

The chain reaction is then propagated as follows:

$$R^{\cdot}+O_2 \xrightarrow{k_1} RO_2^{\cdot},$$

$$RO_2^{\cdot}+RH \xrightarrow{k_2} ROOH+R^{\cdot}.$$

Chain termination takes place by the recombination of radicals:

$$\left.\begin{aligned} RO_2^{\cdot}+RO_2^{\cdot} &\xrightarrow{k_3} \\ R^{\cdot}+R^{\cdot} &\xrightarrow{k_3'} \\ R^{\cdot}+RO_2^{\cdot} &\xrightarrow{k_3''} \end{aligned}\right\} \text{inactive products}.$$

Degenerate branching occurs as a result of breakdown of the hydroperoxide:

$$ROOH \xrightarrow{k_4} RO^{\cdot}+OH.$$

The sector method[41] has yielded values of the rate constants k_1-k_4 and the rate of initiation w, which has made it possible to calculate the rate of the complicated reaction in the early stages of oxidation, when no products other than the hydroperoxide play a significant part.

Since the values of the constants depend on the structure of the radical R$^{\cdot}$, and the mechanism of the process changes as active reaction products accumulate, it is clear what a large amount of work must first be done before it is possible to solve the problem of determining the mechanism of a liquid-phase oxidation from the elementary reactions.

2. OXIDATION IN THE SOLID PHASE

Investigations of the mechanism of oxidation in the solid phase, in particular of the oxidation of polymers, are in a still worse situation. Work in this field has begun comparatively recently.

Since polymers are obtained from monomers belonging to different classes of organic compounds, they differ among themselves not only in the fine mechanisms of oxidation but even in the character of the overall processes. In the oxidation of poly(vinyl chloride), for example, an important part is played by the elimination of HCl molecules and the formation of double bonds. The oxidation of polyamides takes place without an appreciable induction period, and differs markedly in character from the oxidation of hydrocarbons. The oxidative thermal degradation of polysiloxanes is also distinctive. Condensation polymers — epoxide resins, polyarylates, and polycarbonates — begin to oxidise at comparatively high temperatures. The oxidation of unvulcanised and vulcanised rubbers is also very characteristic.

Let us consider results obtained for the oxidation of polypropylene, since the process has been investigated in the greatest detail for this polymer, and its mechanism is very close to that of the liquid-phase oxidation of hydrocarbons.

The EPR method has shown the formation of two types of radicals — alkyl $RCH_2\dot{C}HCH_2R$ and allyl $RCH_2\dot{C}HCH{:}{:}CHCH_2R$ — in polyolefins on exposure to γ-rays or fast electrons. It may be assumed that radicals of the allyl type are formed by the reaction of alkyl radicals with macromolecules containing double bonds[42]. The EPR method has also shown that radicals R in polymers can add on oxygen to form peroxy-radicals $RO_2^{\cdot}$.[43]

The sector method has been used[44,45] to study the oxidation of 2,4,6-trimethylheptane, a model compound for a segment of the polypropylene molecule. The light-initiated oxidation took place by the radical–chain mechanism

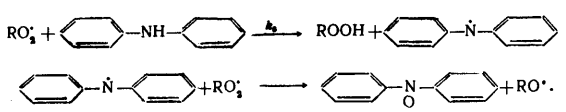
$$RH+h\nu \xrightarrow{w_i} R^{\cdot},$$

$$R^{\cdot}+O_2 \xrightarrow{k_2} RO_2^{\cdot},$$

$$RO_2^{\cdot}+RH \xrightarrow{k_3} ROOH+R^{\cdot},$$

$$RO_2^{\cdot}+RO_2^{\cdot} \xrightarrow{k_4} \text{inactive products}.$$

Chain termination on the addition of diphenylamine is represented by



Values of all the elementary reaction constants were determined over the temperature range 6–80°. Application of the EPR method showed the formation of a stable diphenylnitric oxide radical.

The EPR method has shown the formation of a peroxide radical in the oxidation of ethylbenzene[46], and the rate constants of recombination of the radical have been determined.

3. OXIDATION OF POLYPROPYLENE

Isotactic polypropylene and other polyolefins oxidise by a radical–chain mechanism with degenerate branching. This is indicated by the presence of a well-defined induction period and the autocatalytic character of the reaction, which obeys the law $w = Ae^{\varphi t}$. Branching takes place at hydroperoxides[47]. Addition of a peroxide to the polymer shortens the induction period in proportion to the square root of its concentration, which indicates the occurrence of quadratic chain termination.

The accumulation of peroxides in the oxidation of atactic polypropylene has been studied, and the effective activation energy of formation of several of its oxidation products has been determined[48,49].

In a more detailed investigation of the kinetics of the oxidation of isotactic polypropylene[50] volatile degradation products were frozen out in traps cooled in solid carbon dioxide, and among them were detected water, formaldehyde, acetaldehyde, acetone, methanol, hydrogen peroxide, carbon dioxide, and hydrogen. The aldehydes and the hydrogen peroxide were determined polarographically, and other products by gas and gas–liquid chromatography. Fig. 1 shows one of the chromatograms obtained. The hydroperoxide formed in polypropylene was determined iodometrically. The accumulation of C : O and OH groups was followed by means of the infrared absorption spectra.

Fig. 2 shows the oxygen absorption curve obtained in an experiment at 130° and an oxygen pressure of 400 mm. The maximum rate of absorption of oxygen corresponds to the oxidation of 15% of the monomer units in the polymer. At the same instant the peroxide concentration also reaches a maximum. During the first 50 min of oxidation almost the whole of the absorbed oxygen is present as hydroperoxides.

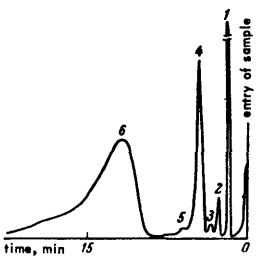


Fig. 1. Chromatogram of volatile products obtained in the oxidation of isotactic polypropylene:
1) H_2 + CO; 2) CH_3CHO; 3) unidentified; 4) CH_3COCH_3; 5) unidentified; 6) H_2O.

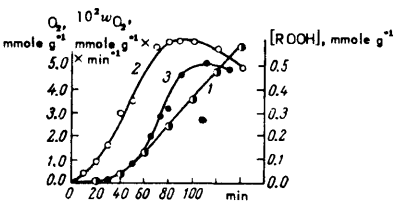


Fig. 2. Oxidation of polypropylene at 130° and p_{O_2} = 440 mm:
1) absorption of oxygen; 2) rate of absorption of oxygen; 3) accumulation of peroxides.

Calculation based on the results of several series of experiments showed that the rate of absorption of oxygen was proportional to $[RH]^{3/2} \times [ROOH]^{1/2}$. This conclusion is confirmed by Fig. 3, in which the experimental results are plotted as $w_{O_2}/([RH] \times [ROOH])$ against $([RH]/[ROOH])^{1/2}$. The concentration [RH] was taken to mean the number of unoxidised tertiary carbon atoms in 1 g of polymer. It was assumed that not more than one molecule of oxygen added on to each monomer unit.

Determinations were also made of the rates of formation of water, acetone, aldehydes, hydrogen peroxide, and methanol. Fig. 4 shows the rate curves for the formation of water and acetone, those for the other products being of the same form. The curves for acetone, aldehydes, and hydrogen peroxide can be compared with that for water by changing the velocity (vertical) scale, as shown in Fig. 5. In this way the relation between the rates of formation of the various products during the process is unaffected.

It may be supposed that all secondary products are formed by breakdown of the primary oxidation products, which are the hydroperoxides. The experiments showed that the rate w of formation of water and the other substances was proportional to the product [ROOH] × [RH], as is evident from Fig. 6. This confirms the suggestion that all the substances formed result from decomposition of a hydroperoxide. The proportionality of the rate to the

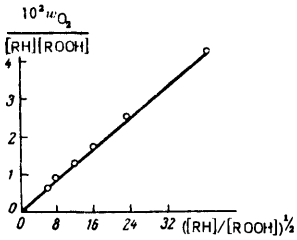


Fig. 3. Dependence of rate of absorption of oxygen on the concentrations [RH] and [ROOH].

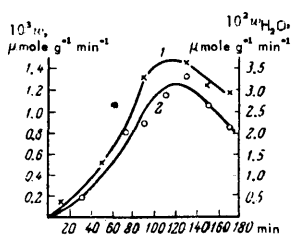


Fig. 4. Variation, during the oxidation of polypropylene at 130° and p_{O_2} = 400 mm, in rate of formation of: 1) water; 2) acetone.

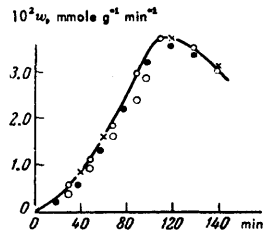


Fig. 5. Comparison of curves for the rate of formation of oxidation products of polypropylene with the rate curve for the formation of water, made by plotting the rates on different scales: ○) acetone; ●) acetaldehyde; ×) hydrogen peroxide.

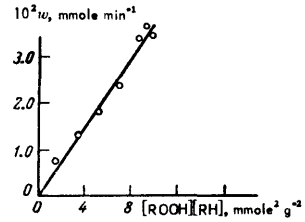


Fig. 6. Dependence of rate of formation of oxidation products of polypropylene on peroxide concentration.

above concentration product also shows that the hydroperoxide breaks down as a result of reaction with the polymer, according to the equation

$$ROOH + RH \longrightarrow RO^{\cdot} + H_2O + R^{\cdot},$$

i.e. by a bimolecular mechanism, not by a unimolecular mechanism as suggested above.

The possibility of such a mechanism for the decomposition of peroxides had been mentioned earlier[51-53], as the heat absorbed in this reaction (15 kcal mole^{-1}) was less by 25 kcal mole^{-1} than the quantity absorbed in the unimolecular decomposition. Breakdown of a hydroperoxide would be still more rapid if it reacted with a compound in which the bond energy of the hydrogen atom were less than in RH.

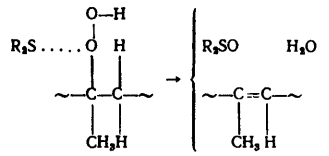
The energy of the N–H bond in antioxidants is considerably lower than that of the C–H bond in hydrocarbons. Rates of decomposition of the hydroperoxide formed in the oxidation of isotactic polypropylene have been compared[54,55] in the absence and in the presence of antioxidants. The rate of decomposition of the hydroperoxide in the presence of polypropylene at temperatures between 90° and 130° was found to be considerably lower than the rate of breakdown

of the same hydroperoxide when *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (0.38 mmole g^{-1}) was added to the polypropylene (Fig. 7).

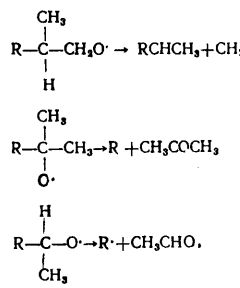
The activation energy of the decomposition of polypropylene hydroperoxide in polypropylene was found to be 25 kcal $mole^{-1}$, and in the presence of the above antioxidant 13 kcal $mole^{-1}$.

Ingold has recently shown that several antioxidants belonging to the substituted phenol and aromatic amine class also accelerate the breakdown of the hydroperoxides formed in the oxidation of a white mineral oil[56].

Dialkyl sulphides accelerate the decomposition of polypropylene hydroperoxide by a different mechanism. Data on the effect of added dihexadecyl sulphide on the decomposition[55] at 110° show (Fig. 8) that the hydroperoxide concentration falls extremely slowly in the absence of the sulphide, but considerably more rapidly at the start of the reaction in its presence. The rate of formation of water during decomposition of the hydroperoxide in the presence of the sulphide is characterised by a well-defined maximum. Such reaction kinetics can be explained by the formation of an addition product between the sulphide and the hydroperoxide, which breaks down into a sulphoxide, water, and an olefin as follows:

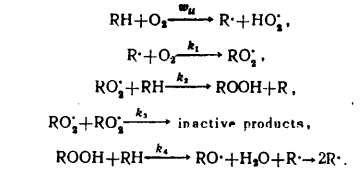


The bimolecular decomposition of hydroperoxides always involves the formation of water, alkyl radicals, and alkoxy-radicals. Breakdown of the latter radicals can yield, depending on their structure, formaldehyde, acetone, acetaldehyde, and other volatile products:



as well as non-volatile alcohols, ketones, and aldehydes, the presence of which in the oxidised polymer is shown by the infrared spectra. The non-volatile products contain about 70% of absorbed oxygen.

The observed facts are well explained by the following scheme for the oxidation of polypropylene:



From this scheme we derive the following differential equations representing the variation in concentration of the radicals R$^{\bullet}$ and $RO_2^{\bullet}$

$$\frac{d[R^{\bullet}]}{dt} = w_u + k_2[RH][RO_2^{\bullet}] + 2k_4[RH][ROOH] - k_1[R^{\bullet}][O_2]. \quad (1)$$

$$\frac{d[RO_2^{\bullet}]}{dt} = k_1[R^{\bullet}][O_2] - k_2[RH][RO_2^{\bullet}] - k_3[RO_2^{\bullet}]^2. \quad (2)$$

Applying the Bodenstein–Semenov method and combining these equations, we obtain

$$w_u + 2k_4[RH][ROOH] - k_3[RO_2^{\bullet}]^2 = 0. \quad (3)$$

Hence for the concentration of $RO_2^{\bullet}$ radicals we find the expression

$$[RO_2^{\bullet}] = \sqrt{\{w_u + 2k_4[RH][ROOH]\}/k_3}. \quad (4)$$

Bearing in mind that $k_1[R^{\bullet}][O_2]$ is equal to the rate of absorption of oxygen w_{O_2}, substituting for $[RO_2^{\bullet}]$ in Eqn. (1), and neglecting w_u, we obtain

$$w_{O_2} = k_2\sqrt{2k_4/k_3}\,[RH]^{1/2}[ROOH]^{1/2} + 2k_4[RH][ROOH]. \quad (5)$$

Division of both sides of Eqn. (5) by [RH][ROOH] converts it into

$$\frac{w_{O_2}}{[RH][ROOH]} = 2k_4 + k_2\sqrt{\frac{2k_4}{k_3}\,\frac{[RH]}{[ROOH]}}. \quad (6)$$

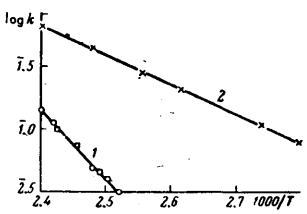


Fig. 7. Temperature dependence of rate of decomposition of polypropylene hydroperoxide: 1) in the presence of *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine; 2) in the absence of this antioxidant; □) results obtained by iodometric titration; ×) results obtained from the rate of formation of the products.

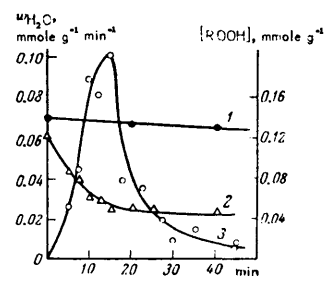


Fig. 8. Kinetics of the decomposition of polypropylene hydroperoxide at 110°: 1) alone; 2) in the presence of dihexadecyl sulphide (0.29 mmole g^{-1}); 3) rate of formation of water in the presence of the sulphide (left-hand scale).

If the above mechanism corresponds to the oxidation of polypropylene, the dependence of rate of absorption of oxygen on hydroperoxide concentration should give a linear relation between

$$\frac{w_{O_2}}{[RH]\,[ROOH]} \text{ and } \sqrt{\frac{[RH]}{[ROOH]}}.$$

Fig. 6 shows that the experimental results agree well with Eqn. (6).

If water and other volatile products are formed by the breakdown of hydroperoxides, the rates of formation w of volatile products in the thermal decomposition of hydroperoxides should decrease with time in proportion to the diminution in the concentration of peroxides. Experimental results for the rates of formation of water, acetone, and aldehydes can be made to fit well on a single curve by appropriate choice of scale (Fig. 9), the equation of this curve representing the variation in concentration of the hydroperoxide undergoing decomposition. In Fig. 9 the scales on which rates of formation of water, acetone, formaldehyde, and acetaldehyde are plotted are in the ratios 1 : 40 : 72 : 138.

It is significant that the relative rates of formation of volatile products in the oxidation of polypropylene and in the decomposition of hydroperoxides are practically the same (see Table).

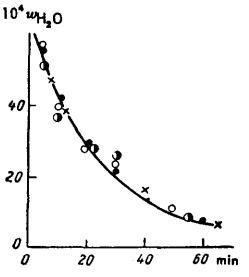


Fig. 9. Variation in rates w of formation of volatile products in the decomposition of polypropylene hydroperoxide at 130°: ○) acetone; ◑) water; ×) acetaldehyde; ●) formaldehyde.

TABLE. Relative rates of formation of volatile products in the oxidation of polypropylene and in the decomposition of hydroperoxides.

Product	Oxidation of polypropylene	Decomposition of hydroperoxides
H_2O	1	1
CH_3COCH_3	0.025	0.025
CH_2O	0.017	0.014
CH_3CHO	0.008	0.007

The results cited above show that hydroperoxides constitute the primary oxidation product of polypropylene, and their decomposition yields several volatile and non-volatile secondary products.

4. CRITICAL ANTIOXIDANT CONCENTRATION

About forty years ago Christiansen[57] and Bäckstrom[58] explained the inhibition of oxidation by small amounts of impurities on the assumption that oxidation is a chain process and that the impurities terminate the reaction chains. This theory was developed by Semenov[5].

It is generally accepted that carbon-chain polymers are oxidised by a chain mechanism involving degenerate branching[3]. Initiation results from the attack of oxygen on the RH molecule according to the equation

$$RH+O_2 \xrightarrow{w_u} R^{\cdot}+HO_2^{\cdot}.$$

The chain reaction is propagated *via* the radicals R$^{\cdot}$ and $RO_2^{\cdot}$:

$$ROO^{\cdot}+RH \xrightarrow{k_2} ROOH+R^{\cdot},$$

$$R^{\cdot}+O_2 \xrightarrow{k_3} RO_2^{\cdot},$$

hydroperoxide molecules being formed as the primary reaction product, which can then decompose, giving rise to branching:

$$ROOH \xrightarrow{k_4} RO^{\cdot}+H\dot{O}.$$

It is assumed that antioxidants JH react with active $RO_2^{\cdot}$ radicals to form inactive products:

$$RO_2^{\cdot}+JH \xrightarrow{k_5} \text{inactive products}.$$

Semenov showed that a consequence of the above mechanism, described by the differential equations

$$\frac{d[RO_2^{\cdot}]}{dt} = w_u - k_5[JH][RO_2^{\cdot}] + k_4[ROOH], \quad (7)$$

$$\frac{d[ROOH]}{dt} = k_2[RH]\,[RO_2^{\cdot}] - k_4[ROOH], \quad (8)$$

is the presence of a "critical" antioxidant concentration[6]. In fact, a solution of these linear equations can be written

$$[RO_2^{\cdot}] = \Sigma A_i e^{\lambda_i t} + B_i, \quad (9)$$

where the λ_i are the roots of the secular determinant

$$\begin{vmatrix} -k_5[JH]-\lambda & k_4 \\ k_2[RH] & -k_4-\lambda \end{vmatrix} = 0. \quad (10)$$

This yields the quadratic equation

$$\lambda^2 + \{k_4 + k_5[JH]\}\lambda + k_4k_5[JH] - k_2k_3[RH] = 0. \quad (11)$$

Since the coefficient of λ is positive, the sum of the roots of the equation is negative. This means either that both roots are negative or that one root is positive while the other is negative but larger in absolute magnitude. If both roots are negative, the values of $[RO_2^{\cdot}]$ and [ROOH] do not increase to infinity but tend to a constant value: *i.e.* we are dealing with a stationary slow reaction. If one root is positive, the radical concentration increases all the time, and we are dealing with a non-stationary accelerating process.

Whether a process is stationary or non-stationary can be determined by finding the sign of the independent term in Eqn. (11). If

$$[JH] > \frac{k_2}{k_5}[RH], \quad (12)$$

the independent term is positive, and hence both roots of Eqn. (11) are negative. Thus if the inequality (12) is observed, the oxidation process is stationary, and consequently the antioxidant is preventing acceleration of the oxidation. If

$$[JH] < \frac{k_2}{k_5}[RH], \qquad (13)$$

the independent term in Eqn. (11) is negative, and hence one root of this equation is positive. Hence the radical concentration will increase to high values in conformity with Eqn. (9), and oxidation will be accelerated, *i.e.* will be non-stationary.

The antioxidant concentration defined by the equation

$$[JH]_{cr} = \frac{k_2}{k_5}[RH], \qquad (14)$$

is termed the "critical" concentration. At lower antioxidant concentrations the oxidation is a non-stationary process, and at higher concentrations it is stationary.

A similar result has been obtained by a somewhat different method[59]. If the number of radicals is n, the rate of initiation w_u, the autocatalytic factor φ, and the concentration of antioxidant x,

$$\frac{dn}{dt} = w_u + \varphi n - knx, \qquad (15)$$

$$-\frac{dx}{dt} = knx, \qquad (16)$$

where k is the velocity constant for reaction of the radicals with the antioxidant. Clearly, when

$$kx < \varphi, \qquad (17)$$

the reaction will be autocatalytic; but when

$$kx > \varphi, \qquad (18)$$

it will be a stationary reaction. Thus the critical antioxidant concentration is given by the equation

$$x_{cr} = \varphi/k. \qquad (19)$$

If condition (18) holds at the start of the reaction, the radical concentration will soon reach a stationary value, which will be maintained for a period of time between 0 and τ, during which the concentration x will fall comparatively slowly to the value x_{cr}, as shown in Fig. 10. The reaction will then begin to accelerate, with the radical concentration increasing rapidly, while the antioxidant concentration will drop rapidly to zero.

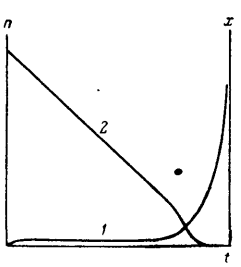


Fig. 10. Variation in concentration during a chain oxidation: 1) radicals n; 2) antioxidant x.

Several workers have shown[47,59-62] that a critical concentration is in fact observed in the inhibition of the oxidation of liquid hydrocarbons and polymers by various antioxidants (Fig. 11).

In the book by Emanuel' and Lyaskovskaya[63] the mechanism of the inhibition of oxidation is corrected by replacing the equation

$$RO_2^{\cdot} + JH \rightarrow \text{inactive products},$$

with

$$RO_2^{\cdot} + JH \rightarrow ROOH + J^{\cdot}.$$

However, the whole of Semenov's derivation is repeated unchanged, the secular equation (10) and the formula for the critical inhibitor concentration (14) being given without change. Nevertheless, if the reasonable correction of Emanuel' is accepted, Eqn. (8) must be replaced by

$$\frac{d[ROOH]}{dt} = k_2[RH][RO_2^{\cdot}] + k_5[JH][RO_2^{\cdot}] - k_4[ROOH], \qquad (20)$$

when the secular equation will become

$$\begin{vmatrix} k_5[JH] - \lambda & k_1 \\ k_2[RH] + k_5[JH] & -k_3 - \lambda \end{vmatrix} = 0. \qquad (21)$$

Under these conditions the independent term in the quadratic equation for λ will be independent of [JH] and always negative. This means that one root of the quadratic equation will be positive, and the oxidation will be non-stationary at all antioxidant concentrations. Thus the scheme which has been adopted provides no explanation of the occurrence of a critical antioxidant concentration.

The generally accepted mechanism of the inhibition of oxidation is based on the following hypotheses: (1) the inhibitor terminates reaction chains, but does not affect the initiation of chains; (2) the hydroperoxide decomposes with formation of two active radicals. It follows from these postulates that the inhibitor is consumed according to a linear law if its concentration exceeds a critical value. The rate of consumption of the inhibitor is then equal to the rate of initiation, and the induction period increases in proportion to the inhibitor concentration.

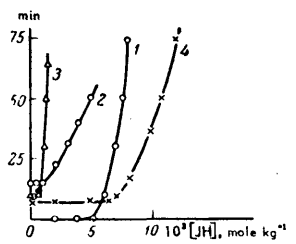


Fig. 11. Dependence of induction period in oxidation on antioxidant concentration: 1) poly(ethylene oxide) and Stabiliser 22-46 at 145° and (p_{O_2}) 340 mm; 2) tetralin and tri-t-butylphenol at 140° and 300 mm; 3) pentane and diphenylamine at 170° and 300 mm; 4) polypropylene and phenyl-2-naphthylamine at 200° and 300 mm.

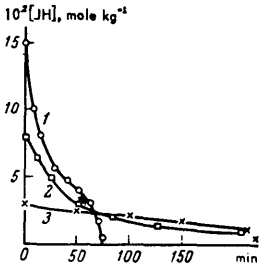


Fig. 12. Consumption of antioxidants in polypropylene at 200° and p_{O_2} = 300 mm: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) methylenebis-2,2′-(4-methyl-6-t-butylphenol); 3) phenyl-1-naphthylamine.

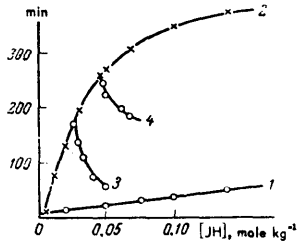


Fig. 13. Induction period in the oxidation of polypropylene at 200° and p_{O_2} = = 300 mm in the presence of antioxidants: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) methylenebis-2,2′-(4-methyl-6-t-butylphenol); 3) and 4) mixtures of these two antioxidants.

Experimental work has shown that the above assumptions are not in fact justified. Antioxidants are not usually consumed according to a linear law[64]. Thus 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol, on addition to polypropylene, at first disappears rapidly, then more slowly, and after that again more rapidly. The antioxidant methylenebis-2,2′-(4-methyl-6-t-butylphenol) in polypropylene is used up according to a first-order law until its concentration falls to a critical value, after which it vanishes rapidly. If polypropylene is stabilised with phenyl-1-naphthylamine, the latter is consumed during oxidation, at first slowly and then considerably more rapidly. Curves representing the consumption of these antioxidants are illustrated in Fig. 12. Similar results have been obtained by Likhtenshtein[65], who has investigated the kinetics of the consumption of diphenylamine in the inhibition of the oxidation of polypropylene, hexadecane, and other hydrocarbons.

5. INITIATION OF OXIDATION BY ANTIOXIDANTS

The above results indicate the complexity of the action of antioxidants. It may be thought that they not only terminate reaction chains but also are able to initiate oxidation. If an antioxidant only terminates chains, its introduction into a polymer cannot shorten the induction period, but this can occur under certain conditions if it is able also to initiate chains.

In order to realise such conditions, methylenebis-2,2′-(4-methyl-6-t-butylphenol) was added (0.02 mole kg^{-1}) to polypropylene, when the induction period at 200° and an oxygen pressure of 300 mm was increased to 180 min. If another antioxidant, 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol, was added to the polypropylene stabilised in this way, the induction period fell from 180 to 50 min[64], as shown in Fig. 13. Ingold observed a similar effect, which he termed "antagonistic", on the addition to a hydrocarbon fuel of two antioxidants, 2,4,6-trimethylphenol and *N*-phenyl-1-naphthylamine, or methylenebis-2,2′-(4-methyl-6-t-butylphenol) and *NN′*-di-s-butyl-*p*-phenylenediamine[56]. An antagonistic effect of this kind was observed in the inhibition of polypropylene oxidation by several antioxidant mixtures.

The ability of antioxidants to initiate oxidation also provides an explanation of the fact that, with increase in the inhibitor concentration, the induction period increases more slowly than linearly, as shown by the typical curve in Fig. 14.

The efficiency of an antioxidant will clearly depend on the relative rates of chain termination and initiation. Since the latter process is characterised by the higher activation energy, a rise in temperature produces a more rapid increase in the rate of initiation than in the rate of chain termination. Therefore the efficiency of an antioxidant should diminish with rise in temperature, as is actually observed experimentally.

Initiation by antioxidants has not yet been subjected to detailed investigation, but three probable mechanisms can be suggested for this process. Firstly, initiation may result from oxidation of the inhibitor by the reaction

$$JH + O_2 \rightarrow HO_2^{\cdot} + J\,.$$

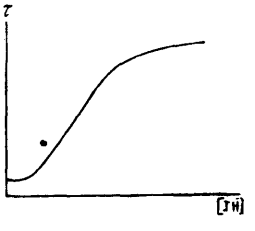


Fig. 14. Typical curve for variation of induction period with antioxidant concentration.

with formation of the comparatively active radical $HO_2^{\cdot}$, whose presence during oxidation has recently been proved by the EPR method[13]. Secondly, relatively inactive inhibitor radicals J$^{\cdot}$ can sometimes react with polymer molecules:

$$J^{\cdot} + RH \rightarrow JH + R^{\cdot},$$

active radicals being formed. The possibility of such a reaction has been demonstrated by the EPR method[66]. Finally, antioxidants may initiate oxidation by reacting with hydroperoxides[55,67]:

$$ROOH + JH = RO^{\cdot} + H_2O + J^{\cdot}.$$

A significant fact indicating initiation of a reaction which consumes the antioxidant is the fall in molecular weight of the polymer during the induction period, when the number of ruptured bonds is proportional to such consumption[68].

This phenomenon is seen especially well in the oxidative thermal degradation of polypropylene to which has been added di-t-butylcresyl disulphide†, investigated by Lukovnikov *et al.*[69] Fig. 15 shows that the induction period is greatly increased, but the molecular weight of the polymer drops rapidly.

Thus the assembly of known facts leads to the conclusion that the first assumption, that antioxidants do not influence initiation, is incorrect. The second assumption, that two active radicals are formed on the breakdown of a hydroperoxide, is probably also of doubtful validity. Several papers have shown[70,71] that hydroperoxides can decompose in solution without forming radicals and without initiating chains.

The conditions under which a "critical" antioxidant concentration is possible can be determined, as Shlyapnikov has shown[72], if the hypothesis, that breakdown of a hydroperoxide ultimately yields δ active $RO_2^{\cdot}$ radicals, is introduced into the scheme of polymer oxidation.

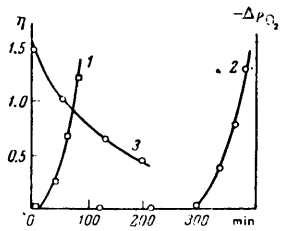


Fig. 15. Oxidation of polypropylene: 1) absorption of oxygen by unstabilised polymer; 2) absorption of oxygen by polymer stabilised with di-t-butyl-*p*-cresyl disulphide† and catechol naphthol phosphite; 3) fall in viscosity in latter case.

† The Russian nomenclature is obscure: perhaps di-(2-hydroxy-5-methyl-3-t-butyl) disulphide is meant (Ed. of Translation).

The mechanism of the oxidation of a polymer RH containing an antioxidant JH can be represented by the following scheme:

$$JH + O_2 \xrightarrow{w_u} J^{\cdot} + HO_2^{\cdot} \rightarrow RO_2^{\cdot},$$
$$RO_2^{\cdot} + RH \xrightarrow{k_3} ROOH + R^{\cdot},$$
$$ROOH + RH \xrightarrow{k_4} \delta RO_2^{\cdot},$$
$$RO_2^{\cdot} + JH \xrightarrow{k_5} ROOH + J^{\cdot}.$$

If a sulphide R_2S, capable of breaking down the hydroperoxide without forming active products[73], is added to the polymer, the equation

$$ROOH + R_2S \xrightarrow{k_6} \text{inactive products},$$

must be added to the above scheme. In this case Eqns. (7) and (8) become

$$\frac{d[ROOH]}{dt} = k_3[RH][RO_2^{\cdot}] + k_5[JH][RO_2^{\cdot}] - k_4[RH][ROOH] - k_6[R_2S][ROOH]. \quad (22)$$

$$\frac{d[RO_2^{\cdot}]}{dt} = w_u - k_5[JH][RO_2^{\cdot}] + k_4[RH][ROOH]. \quad (23)$$

The secular determinant may be written

$$\begin{vmatrix} -k_4[RH] - k_6[R_2S] - \lambda & k_3[RH] + k_5[JH] \\ k_4[RH] & -k_5[JH] - \lambda \end{vmatrix} = 0, \quad (24)$$

or in expanded form

$$\lambda^2 + \{k_4[RH] + k_5[JH] + k_6[R_2S]\}\lambda + k_4k_5[RH][JH] + k_5k_6[JH][R_2S] - k_3k_4[RH]^2 - k_4k_5[RH][JH] = 0. \quad (25)$$

An analysis similar to that of Eqn. (11) enables us to calculate the critical antioxidant concentration as

$$[JH]_{cr} = \frac{\delta k_3k_4[RH]^2}{(1-\delta)k_4k_5[RH] + k_5k_6[R_2S]}. \quad (26)$$

In the particular case in which the concentration $[R_2S]$ is zero, we obtain

$$[JH]_{cr} = \frac{\delta}{1-\delta} \times \frac{k_3}{k_5} \times [RH]. \quad (27)$$

From Eqn. (27) it is evident that a stationary reaction and a critical antioxidant concentration can occur only if $\delta < 1$, *i.e.* when decomposition of the hydroperoxide yields on the average less than one active radical. If $\delta \geq 1$, the reaction is non-stationary at all antioxidant concentrations, and no critical concentration of antioxidant exists.

6. THEORY OF SYNERGISM

Even if $\delta > 1$, addition to the polymer of the sulphide R_2S in sufficient concentration may make the denominator on the right-hand side of Eqn. (26) positive, which will allow a critical antioxidant concentration to be realised. The correctness of this conclusion has been confirmed experimentally[72].

When the antioxidant 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol is added in various concentrations to polypropylene, the induction period at 200° and p_{O_2} = 300 mm increases linearly from 8 min to 65 min: *i.e.* no critical concentration of the antioxidant is observed. If didecyl sulphide is added as well as the above phenol, a critical concentration is clearly evident, which in conformity with Eqn. (26) diminishes with increasing concentration of the sulphide (Fig. 16).

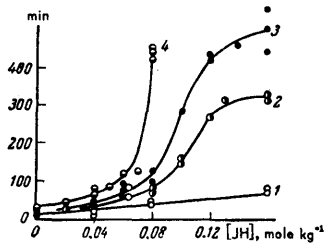


Fig. 16. Dependence of induction period in the oxidation of polypropylene on concentration of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol at 200° and p_{O_2} = 300 mm in the presence of different concentration (mole kg^{-1}) of didecyl sulphide: 1) 0; 2) 0.04; 3) 0.08; 4) 0.12.

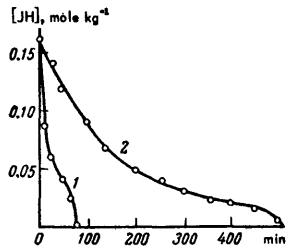


Fig. 18. Consumption of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm: 1) alone; 2) in the presence of didecyl sulphide.

Didecyl sulphide itself is an inefficient antioxidant, its addition to polypropylene lengthening the induction period only very slightly. However, addition to the polymer of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol as well as the sulphide produces a sharp increase in the induction period with the appearance of a critical concentration (Fig. 17).

Addition of didecyl sulphide to polypropylene greatly diminishes the rate of consumption of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol (Fig. 18). Similarly, but to a smaller extent, the rate of consumption of the antioxidant methylenebis-2,2'-(4-methyl-6-t-butylphenol) in polypropylene is decreased by the addition of didecyl sulphide, as is evident from the curves in Fig. 19. These facts are fully consistent with the theory developed in Ref. 72.

The mutual strengthening of effectiveness observed in mixtures of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol and didecyl sulphide is due to breakdown of the hydroperoxide and the slowing down in the consumption of antioxidant. Either of these oxidation inhibitors alone lengthens the induction period only slightly. When mixed, however, they are able to extend the induction period in the oxidation of polypropylene to 450 min at 200° and p_{O_2} = 300 mm, as shown in Fig. 20.

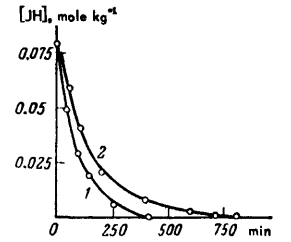


Fig. 19. Consumption of methylenebis-2,2'-(4-methyl-6-t-butylphenol) in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm: 1) alone; 2) in the presence of didecyl sulphide.

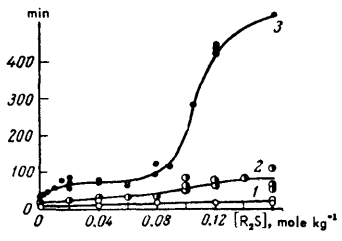


Fig. 17. Dependence of induction period on concentration of didecyl sulphide at 200° and p_{O_2} = 300 mm in the presence of different concentrations (mole kg^{-1}) of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol: 1) 0; 2) 0.04; 3) 0.08.

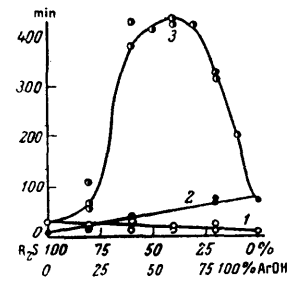


Fig. 20. Dependence of induction period in oxidation of propylene at 200° and p_{O_2} = = 300 mm on: 1) concentration of didecyl sulphide; 2) concentration of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 3) mole fractions of these stabilisers when their total concentration is 0.2 mole kg^{-1}.

There can be no doubt that many cases of the mutual strengthening of effectiveness observed when mixtures of antioxidants and sulphides are added to polymers [66,74] are explained by the above theory. The most efficient of the mixtures investigated to date contains catechol 4-methyl--2,6-di-t-butylphenol phosphite and bis-2-hydroxy-4-t--butyl-*m*-tolyl sulphide (SAO-6). At a total concentration of 0.015 mole kg^{-1} this mixture lengthens the induction period in the oxidation of polypropylene at 200° and p_{O_2} = = 200 mm to 400 min (Fig. 21).

When an antioxidant radical J$^{\cdot}$ causes the initiation of oxidation, the effectiveness of the antioxidant can be increased by adding a second substance which captures the J$^{\cdot}$ radicals. Likhtenshtein has shown [75] that such a case occurs in the stabilisation of polypropylene with diphenylamine if polyphenylene or diphenylpicrylhydrazyl is added to the polymer as a second substance.

Fig. 22 illustrates the results obtained in this paper. With increase in the diphenylamine concentration the induction period τ slowly increases (curve *1*). If both diphenylamine and polyphenylene are added to the polypropylene,

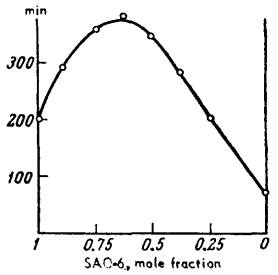


Fig. 21. Induction period in the oxidative thermal degradation, at 200° and p_{O_2} = = 200 mm, of polypropylene, stabilised with mixtures of SAO-6 and the phosphite of catechol and 4-methyl-2,6-di-t-butylphenol (total stabiliser concentration 0.015 mole kg^{-1}).

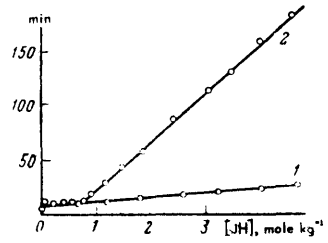


Fig. 22. Dependence of induction period, in the oxidative thermal degradation of stabilised polypropylene at 172° and p_{O_2} = = 200 mm, on the concentration of diphenylamine: 1) in the absence of polyphenylene; 2) in the presence of 3% of polyphenylene.

the variation of τ with the diphenylamine concentration (curve *2*) shows a well developed mutual strengthening effect, and the appearance of a critical antioxidant concentration is clearly evident.

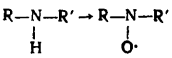
The phenomenon of the mutual strengthening of the action of antioxidants, often termed "synergism", has been discussed in detail in several monographs and reviews [63,67,76,77].

The results discussed above clearly show how disadvantageous is the fact that antioxidants are involved in the initiation of oxidation as well as the termination of chains. The most important part here is played by the formation of hydroperoxides in the reaction of peroxide radicals $RO_2^{\cdot}$ with antioxidants containing loosely combined hydrogen. Among such antioxidants are the widely employed derivatives of phenols and aromatic amines.

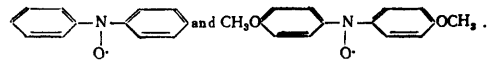
It seems to the Reviewer that one of the most important problems in the inhibition of oxidation is the search for new classes of antioxidants, not containing weakly bound hydrogen. In this respect, triesters of phosphorus acid [78] and also polyphenylenes, polyphenylacetylenes, and polyazophenylenes [79] are undoubtedly of interest.

7. FREE RADICALS AS STABILISERS

In connection with the above problem, an attempt has been made to use as antioxidants, instead of amine derivatives, radicals obtained by replacing the active amino--hydrogen by an oxygen atom:



The following radicals have been synthesised [80]:

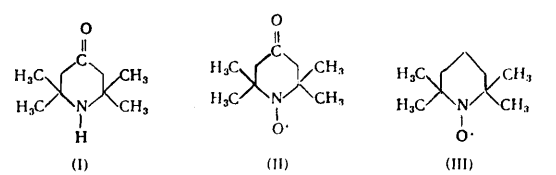


These comparatively stable radicals are good antioxidants for polypropylene and several liquid hydrocarbons.

The fact that the nitric oxide radical obtained by oxidising diphenylamine is itself an antioxidant was noted by Thomas, who compared the inhibition of the oxidation of white mineral oil by small additions of diphenylamine and of diphenyl nitric oxide [81].

Likhtenshtein's experiments have shown [65] that diphenyl nitric oxide is consumed very slowly during the induction period in the oxidation of hexadecane at 150°, probably at the same rate as initiation. The rate of consumption of diphenyl nitric oxide does not increase until the end of the induction period (Fig. 23).

Aliphatic nitric oxides have also been synthesised [82] from 2,2,6,6-tetramethyl-4-oxopiperidine (I), their formulae being given below



The radical (II) is a far better antioxidant for polypropylene [62] than is (I), as can be seen from Fig. 24. This is probably

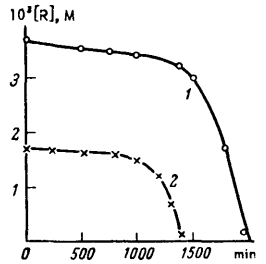


Fig. 23. Consumption of diphenylnitric oxide in the oxidation of hexadecane at 150° and p_{O_2} = 500 mm with different initial concentrations of the radical: 1) 0.0038 M; 2) 0.0018 M.

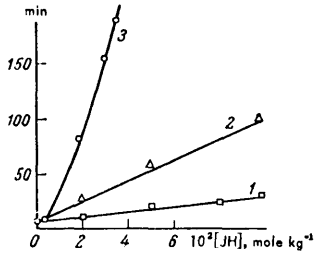
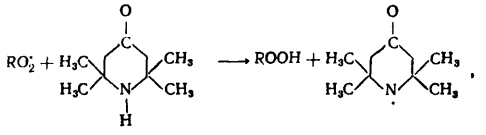
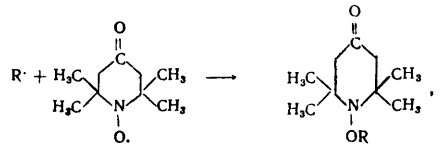


Fig. 24. Dependence of induction period in oxidation of polypropylene at 170° on concentration of: 1) 2,2,6,6-tetramethyl-4-oxopiperidine (I); 2) diphenylamine; 3) nitric oxide radical (II) of (I).

associated with the fact that the latter reacts with $RO_2^{\cdot}$ radicals as follows:



whereas (II) adds on R· radicals according to the equation



without the formation of peroxide molecules.

The great stability of the radicals (II) and (III) is probably due to effective screening of the NO by the methyl groups.

The radical (II) is a good antioxidant, inhibiting the oxidative thermal degradation of polyamides. Whereas capron [brand of 6-polyamide fibre produced in the Soviet Union (Ed. of Translation)] absorbs oxygen at 180° without an appreciable induction period, whether it is unstabilised or has been stabilised with the usual antioxidants, addition of small amounts of the radical (II) delays by many minutes the start of appreciable absorption of oxygen.

The consumption of the radical (II) during the induction period has been measured by the EPR method. It is only after the EPR signal has vanished, *i.e.* after all the radical has been used up, that autocatalytic oxidation of the capron begins, as can be seen from the curves in Fig. 25.

The induction period in the oxidation of capron at 200° and an oxygen pressure of 200 mm becomes longer with increase in the concentration of radical (II) (Fig. 26). A critical antioxidant concentration is observed in this case, probably indicating the occurrence of a stationary reaction which is the result of chain termination without simultaneous formation of hydroperoxides and initiation of oxidation. All known stabilisers for capron diminish the rate of absorption of oxygen, as is observed when the radical (II) is employed as antioxidant.

Since the radical (II) has demonstrated its universality as antioxidant in the oxidation of several hydrocarbons, polypropylene, and polyamides, it has been tried as an inhibitor of the oxidative thermal degradation of polyformaldehyde, which is rapid[83,84] at 200°. Enikolopyan[85] has shown that degradation of polyformaldehyde begins at the

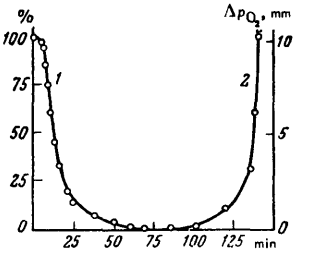


Fig. 25. Induction period in the oxidation of 6,8-polyamide: 1) consumption of (II); 2) absorption of oxygen (right-hand scale).

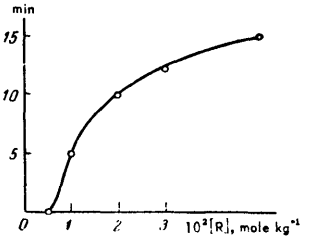


Fig. 26. Dependence of induction period in oxidation of 6,8-polyamide at 200° and p_{O_2} = = 200 mm on concentration of (II).

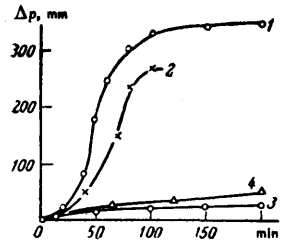


Fig. 27. Increase in pressure accompanying the oxidation of acetylated polyformaldehyde at 200° and p_{O_2} = 600 mm: 1) alone; 2) in the presence of 2% of polyamide; 3) in the presence of 1.2% of polyamide + 0.8% of (II); 4) oxidation of Delrin.

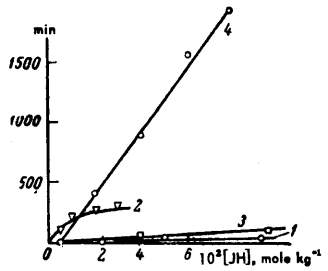


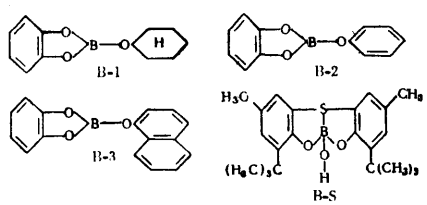
Fig. 28. Dependence of induction period in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm on concentration of: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) Stabiliser 22-46; 3) Polygard; 4) ester of SAO-6 and boric acid.

ends of the molecule, with the liberation of formaldehyde, which reacts with oxygen to give formic acid. In order to stabilise polyformaldehyde, a polyamide must be added to it to combine with the formaldehyde, and also a substance to bind the formic acid. Addition to an acetylated polyformaldehyde of 1.2% of a polyamide resin and 0.8% of radical (II) provides excellent stabilisation, the resulting product being more stable than Delrin (see Fig. 27). It can be supposed that some radicals are formed by the oxidative thermal degradation of polyformaldehyde, and these are captured by the radical (II).

Work on radical inhibitors has started only recently, and the progress achieved in a short time suggests that it is a promising line of research.

8. BORATE STABILISERS

Another line of work in the search for new stabilisers for polymers is the use as antioxidants of orthoboric esters containing no weakly bound hydrogen. Several such esters have been described[86], and the structural formulae of some of the most effective antioxidants among the esters which have been tested are given below:



The antioxidants B-1, B-2, and B-3 are esters formed by catecholboric acid with cyclohexanol, phenol, and 1-naphthol respectively. They are all good antioxidants, inhibiting the oxidative thermal degradation of polypropylene at 200°. B-2 and B-3 have well marked critical concentrations. B-3 is a strong antioxidant, while B-2 and B-1 are considerably weaker.

It is interesting that the ester of boric acid and the bis-hydroxyphenyl sulphide SAO-6, which has been labelled B-S above, has proved the most effective antioxidant among all the boric esters which we have investigated, in spite of the presence of a hydroxy-hydrogen in its molecule.

Fig. 28 illustrates experimental induction periods for the oxidation of polypropylene, stabilised with various antioxidants, at 200° and p_{O_2} = 200 mm. It is evident that B-S is a far more efficient stabiliser than 2,6-bis(1,1-dimethylhexyl)-4-methylphenol, Stabiliser 22-46, or Polygard. At a concentration of 0.04 mole kg^{-1} it inhibits oxidation for 840 min, whereas Polygard delays oxidation by only 50 min, and Stabiliser 22-46 by about 300 min.

It can be hoped that the search for new antioxidants may be the starting point for the development of research in this important field for polymer chemistry.

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1,3-DICHLOROBUT-2-ENE AND NEW PREPARATIONS BASED ON IT

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I. INTRODUCTION

Soon after its discovery, 1,3-dichlorobut-2-ene, one of the side-products of the manufacture of chloroprene rubber [1-5], attracted the attention of chemists who attempted to find applications for it. There are several reviews dealing with the reactions of 1,3-dichlorobut-2-ene and its applications [6-9], the last (published in 1954) covering only certain aspects of this problem. Since in recent years many papers have appeared, describing various interesting syntheses based on this compound, we have attempted an assessment of the importance of the investigations which have been made.

In the manufacture of chloroprene rubber 1,3-dichlorobut-2-ene is formed as a result of the addition of a second molecule of hydrogen chloride to vinylacetylene in the presence of a copper catalyst [1,2]:

$$HC\equiv C-CH=CH_2 \xrightarrow[CuCl]{HCl} [CH_2=C=CH-CH_2Cl] \rightarrow$$
$$\rightarrow CH_2=CCl-CH=CH_2 \xrightarrow[CuCl]{HCl} CH_2CCl=CH-CH_2Cl.$$

Under the usual conditions of chloroprene synthesis the yield of 1,3-dichlorobut-2-ene does not exceed 3%, but it can clearly be increased by using an excess of hydrochloric acid [2]. Carothers, who first described 1,3-dichlorobut-2-ene, quotes the following physical constants for this compound: b.p. 127-129°/756 mm and 53-54°/50 mm; d_4^{20} 1.1591; n_D^{20} 1.4724. [2] Distilled 1,3-dichlorobut-2-ene is a colourless liquid with a sharp smell and lachrymatory action.

Later it was found that the 1,3-dichlorobut-2-ene obtained by dehydrochlorination of monovinylacetylene consists of two stereosiomers (*cis* and *trans*). Hatch and coworkers separated the geometrical isomers of 1,3-dichlorobut-2-ene by fractional distillation and investigated their properties [10-13]. According to their data, the mobility of the allyl chlorine in the high-boiling β-isomer (b.p. 131°/748 mm) is higher than in the low-boiling α-isomer (b.p. 127.8°/745 mm), while the latter is higher than in allyl chloride [11-13]. Heating favours the conversion of the β-isomer to the α-isomer [10,11].

The configuration of the stereoisomers was convincingly demonstrated by reduction of the α and β forms with $LiAlH_4$ to the *trans*- and *cis*-2-chlorobut-2-enes respectively [13]:

$$ClCH_2-\underset{\|}{C}(Cl)-CH_3 \rightarrow CH_3-\underset{\|}{C}(Cl)-H \qquad H-\underset{\|}{C}(Cl)-CH_2Cl \rightarrow H-\underset{\|}{C}(Cl)-CH_3.$$

The high reactivity of 1,3-dichlorobut-2-ene depends primarily on the mobility of the allyl chlorine atom. Thus 1,3-dichlorobut-2-ene is readily hydrolysed and reacts with aromatic hydrocarbons, malonic and acetoacetic esters, ammonia and amines, sodium cyanide, thiocyanate salts, thiourea, etc.

The double bond in 1,3-dichlorobut-2-ene readily undergoes addition reactions and is ruptured by the action of oxidants. As was to be expected, the chlorine atom at the double bond cannot be substituted: both in 1,3-dichlorobut-2-ene itself and in its derivatives it can be removed as HCl by the action of alkali and sulphuric acid. In the first case an acetylenic compound or its isomerisation product is formed, and in the second a carbonyl compound (sulphuric acid hydrolysis):

$$-\underset{|}{C}(Cl)=\underset{|}{C}(H)- \rightarrow -\overset{\|}{C}(=O)-CH_2- + HCl.$$

Thus the possibilities of syntheses starting from 1,3-dichlorobut-2-ene are inexhaustable. The compounds formed (ethers, esters, amines, etc.) by the substitution of the