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Antioxidant Stabilisation of Polymers

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Physicochemical aspects of the stabilisation of polymers are discussed. Attention is paid mainly to the aging and stabilisation of polymers under processing conditions. Topics considered are the kinetics and mechanism of the high-temperature oxidation of polymers, critical phenomena in the inhibited oxidation of polymers, the theory of synergism and antagonism among antioxidants, the reasons for differences in efficiency of antioxidants, and certain aspects of the relation between the efficiency of antioxidants and their molecular structure. A list of 132 references is included.

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I. INTRODUCTION

Physical and chemical processes, combined under the general term *aging*, begin immediately after formation of a polymer or a polymeric material. Oxygen and other components of the environment—ozone, water, etc.—are involved. Aging is accelerated by rise in temperature by light, by strong ionising radiations, and by mechanical stresses, being especially rapid under processing conditions for thermoplastic polymers.

We shall disregard the aging of polymers by light, one of the chief reasons for their deterioration under operating conditions, and also those types of aging that are specific to solid polymers. We shall concentrate on chemical processes occurring in polymer melts at high temperatures in the absence and in the presence of oxygen, frequently termed thermal and thermo-oxidative degradation†.

II. THERMO-OXIDATIVE DEGRADATION OF POLYMERS

If the polymer is processed in air, or if it has been stored in air before processing and contains dissolved oxygen, it will undergo thermo-oxidative degradation during processing. This type of polymer degradation has been studied the most thoroughly.

Many references have been made[1,2] to the great similarity in mechanism between the oxidation of polymers and the liquid-phase oxidation of hydrocarbons. On the other hand, little attention has been paid until recently to the differences between the oxidation of substances of low and of high molecular weight. Liquid-phase oxidation of the former is usually investigated at relatively low temperatures, not exceeding 130–150 °C, owing to their high partial vapour pressures at the experimental temperature, whereas the processing temperature of a polymer may exceed 200 °C. No information has appeared on the liquid-phase oxidation of lower hydrocarbons at such high temperatures.

† The term *degradation* frequently denotes only those processes that are accompanied by a decrease in molecular weight or degree of polymerisation.

We shall first consider those stages of oxidation that are common to compounds of low and high molecular weight. Oxidation of a hydrocarbon RH is regarded as a complicated radical chain reaction with degenerate chain branching involving the main states outlined below[3,4].

(*a*) Chain generation has been represented as either a uni-, bi-, or ter-molecular reaction:

$$RH \xrightarrow{k_0} R^{\cdot} + H^{\cdot} \qquad (1)$$

$$RH + O_2 \xrightarrow{k_0'} R^{\cdot} + HO_2^{\cdot} \qquad (2)$$

$$2RH + O_2 \xrightarrow{k_0''} 2R^{\cdot} + H_2O_2 . \qquad (3)$$

(*b*) Chain propagation (growth) occurs as follows:

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \qquad (4)$$

$$RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} . \qquad (5)$$

(*c*) Chain branching results from unimolecular breakdown of a hydroperoxide, reaction of a hydroperoxide with the hydrocarbon (polymer), or interaction of two hydroperoxy-groups:

$$ROOH \xrightarrow{k_4} RO^{\cdot} + {}^{\cdot}OH \qquad (6)$$

$$ROOH + RH \xrightarrow{k_4'} RO^{\cdot} + R^{\cdot} + H_2O \qquad (7)$$

$$2ROOH \xrightarrow{k_4''} RO_2^{\cdot} + RO^{\cdot} + H_2O . \qquad (8)$$

The radicals RO$^{\cdot}$ and HO$^{\cdot}$ are assumed to react rapidly with the surrounding material to form alkyl radicals R$^{\cdot}$:

$$RO^{\cdot}\,({}^{\cdot}OH) + RH \rightarrow ROH\,(H_2O) + R^{\cdot} . \qquad (9)$$

Breakdown of the radical RO$^{\cdot}$ may yield alkyl radicals of lower molecular weight: for example[5]

$$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O^{\cdot} \rightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + {}^{\cdot}CH_3 . \qquad (9a)$$

(*d*) Chain termination results from the recombination or disproportionation of any two free radicals involved in the

oxidation:

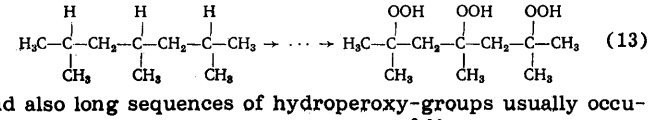
$$2R^{\cdot} \xrightarrow{k_6} R_2 \qquad (10)$$

$$R^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6'} ROOR \qquad (11)$$

$$2RO_2^{\cdot} \xrightarrow{k_6''} ROOR + O_2 . \qquad (12)$$

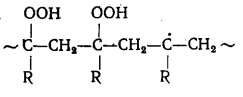
Considering the individual stages in greater detail, we note that chain generation has hitherto been the last studied. It probably occurs by reaction (2), but in real polymers chains may be generated also by reactions of various impurities[6], in particular metals of variable valency (primarily iron), peroxides, and other compounds.

As to the chain-propagating reactions (4) and (5), the majority of authors hold completely identical views. In compounds of fairly high molecular weight and in polymers, however, reaction (5) can take place in two ways: the radical $RO_2^{\cdot}$ can detach a hydrogen atom either from a neighbouring molecule or from an adjacent carbon atom in its own molecule. The latter path gives di- and even tri-hydroperoxides in yields comparable with that of the monohydroperoxide[7,8]

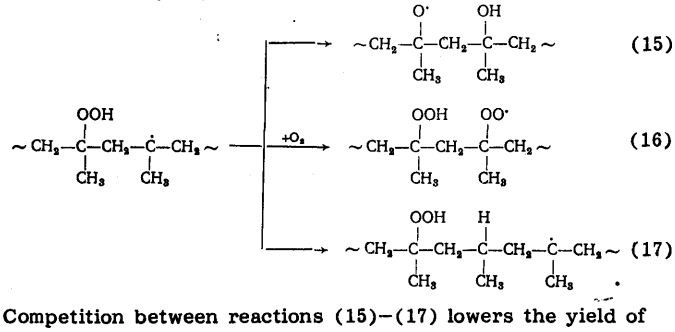

(13)

and also long sequences of hydroperoxy-groups usually occupying β positions in polyolefin molecules[9,10].

Propagation of the kinetic oxidation chain involves the formation of peroxyalkyl radicals


(14)

within an individual macromolecule. In such radicals an unstable hydroperoxy-group is always located near the free valency. Interaction of this valency with a hydroperoxy-group that has just been formed leads to loss of the latter. Other possible conversion paths for the peroxyalkyl radical—addition of an oxygen molecule and detachment of a hydrogen atom from the next monomer unit—result in removal of the reaction centre away from the hydroperoxy-group and stabilisation of the group[11]:

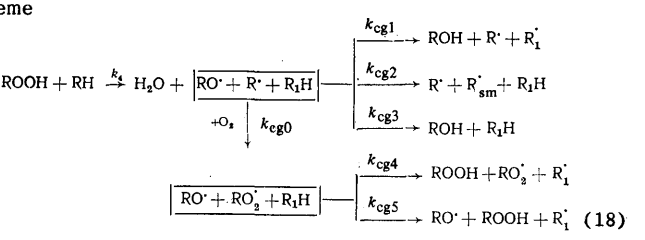

(15) (16) (17)

Competition between reactions (15)–(17) lowers the yield of hydroperoxide in the oxidation of polymers below that observed with analogues of low molecular weight, and the yield becomes dependent on the oxygen pressure. Whereas the oxidation of lower compounds gives hydroperoxide yields close to 100%,[4] only 5–40% is obtained in the oxidation of polyolefins[11–15].

Breakdown of a hydroperoxy-group into $RO^{\cdot}$ and $HO^{\cdot}$ radicals requires the consumption of large quantities of energy (~170 kJ mole^{-1} [16]) and apparently occurs only in the gas phase. In the liquid phase and especially in the molten polymer reactions (7) and (8) are more probable[3,17].

Considering reaction (7) for definiteness, we note that interaction of a hydroperoxy-group in a polymer with a monomer unit in the same or a neighbouring macromolecule produces a pair of free valencies (usually in the form of the radicals $R^{\cdot}$ and $RO^{\cdot}$) located either on neighbouring macromolecules or on a small segment of the same molecule. In a polymer the low translational mobility of a macromolecule is combined with the relatively high vibrational mobility of its segments necessary for the recombination of radicals. For this reason the major proportion of the radicals formed from a hydroperoxide will disappear immediately after formation. In order that breakdown of the hydroperoxy-group should lead to formation of two new kinetic chains (such secondary chain generation as a result of chemical transformation of reaction products is termed *degenerate chain branching*) the free valencies should move sufficiently far apart—should escape from the "cage" formed by molecules of the surrounding material.

In a polymer direct diffusion of primary radicals plays no appreciable part in the escape of radicals from the cage. Three other possibilities remain: one of the radicals of a pair may interact with a neighbouring monomer unit in the same or another macromolecule R_1H, it may react with an oxygen molecule, or the radical $RO^{\cdot}$ may break down with formation of a mobile small radical $R_{sm}^{\cdot}$. The main stages in the breakdown of a hydroperoxide can be represented by the scheme


(18)

in which a cage containing a pair of radicals together with segments of macromolecules R_1H is enclosed in a frame. Each reaction of one of the radicals increases the distance between the free valencies, and the probability of recombination diminishes rapidly. Neglecting for simplicity the probability of recombination of the secondary radicals $R_1^{\cdot}$ and $R_{sm}^{\cdot}$, we find for the mean yield of free radicals formed on the breakdown of ROOH the formula

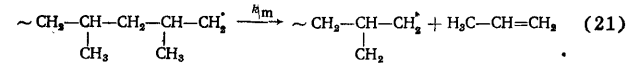
$$\delta = \frac{w_r}{k_4[ROOH][RH]} = \frac{2(k_{cg0}[O_2] + k_{cg1} + k_{cg2})}{k_{cg0}[O_2] + k_{cg1} + k_{cg2} + k_{cg3}}, \qquad (19)$$

This expression can be expanded as a series of powers of $[O_2]$. If the oxygen concentration is not too high ($[O_2] \ll k_3/k_{cg0}$) only two terms need be retained, so that[18]

$$\delta = \delta_0 + \delta_1[O_2]. \qquad (20)$$

Existence of such a relation at oxygen pressures over the polymer up to 1 atm has been established experimentally[18–20]. One of the experimental proofs will be examined below.

Radicals $R^{\cdot}$ in a polymer may be either terminal or central depending on whether the free valency is located at or remote from the end of a macromolecule. Radicals with a free valency at the end of the chain $R_e^{\cdot}$ are able to eliminate a monomer:


(21)

Reaction (21) involves no change in the number of terminal radicals, and therefore is disregarded in their balance. Radicals $R_e^{\cdot}$ are consumed mainly by reaction with oxygen (4), and the resulting radicals $ReOO^{\cdot}$ detach hydrogen from the

next monomer unit to form not terminal but central radicals $R_c^{\cdot}$.

From the balance equation for R_e

$$d[R_e^{\cdot}]/dt = \delta k_4 [ROOH][RH] - k_1 [R_e^{\cdot}][O_2], \quad (22)$$

we find, putting $\delta = \delta_e + \delta_1[O_2]$, that the dependence on the oxygen pressure of the rate of depolymerisation accompanying decomposition of a polymer hydroperoxide is

$$w_m = \frac{k_4 k_m}{k_1}[RH][ROOH]\{\delta_1 + \delta_0/[O_2]\}. \quad (23)$$

If $\delta_1 = 0$, i.e. if the yield of free radicals on decomposition of the polymer hydroperoxide is independent of the oxygen pressure, it follows from (23) that the rate of formation of monomer will tend to zero with rise in oxygen pressure; if $\delta_1 > 0$, however, it will tend to a limit other than zero.

The initial rate of formation of propene has been measured[20] in the decomposition of two types of polypropylene hydroperoxide: the usual hydroperoxide was obtained by oxidising polypropylene with molecular oxygen at 130 °C, and a postirradation sample was formed by heating to room temperature a specimen of the polymer first saturated with oxygen and exposed to a small dose of γ-rays. The postirradiation hydroperoxide contained isolated hydroperoxy-groups surrounded by unoxidised material. Fig.1 shows that the rate of formation of propene from both hydroperoxides tended to a finite limit or remained constant: i.e. in both cases the yield of free radicals increased under the influence of oxygen.

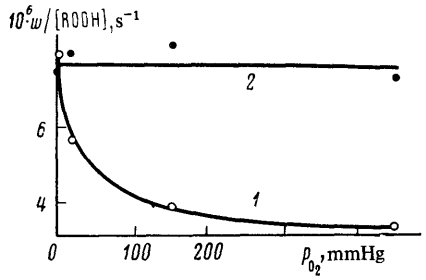


Figure 1. Dependence[20] on oxygen pressure at 130 °C of rate of formation of propene by the decomposition of polypropylene hydroperoxide prepared by: *1*) oxidation of polypropylene at 130 °C; *2*) postirradiation oxidation at room temperature.

Because of the competition between reactions (15)–(17) the sequence of hydroperoxy-groups includes unoxidised units and other functional groups, e.g. hydroxy, the proportions of which depend on the conditions of oxidation. During decomposition some of the hydroperoxy-groups break down, and new functional groups will appear on the polymer chain, not necessarily identical with those formed in the primary reactions. All this makes the concept of "polymer hydroperoxide" extraordinarily indefinite, and is the reason for the disagreement in published values of constants for "the same" hydroperoxide.

Termination of the oxidation chain can occur on the interaction of any two free radicals involved in the reaction. Not only macroradicals can take part in chain termination but also "light" radicals[21] formed by the breakdown of RO$^{\cdot}$ radicals, as in reaction (9a). The recombination of two macroradicals may lead to their cross-linking, which is accompanied by increase in the molecular weight of the linear polymer and even by formation in it of three-dimensional structures, often termed the "gel fraction" as a consequence of insolubility in substances that dissolve the unoxidised polymer[22].

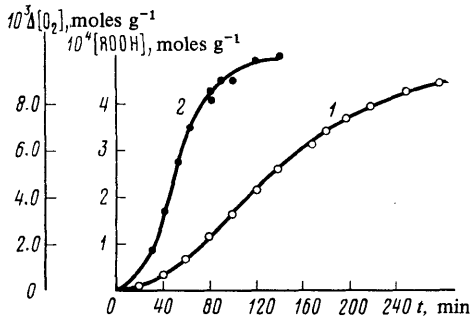


Figure 2. Oxidation of solid isotactic polypropylene[18] under an oxygen pressure of 400 mmHg at 130 °C: *1*) absorption of oxygen; *2*) accumulation of hydroperoxides.

The oxidation of polymers at not very high temperatures is autocatalytic[15–17]. This is explained by the increase rate of formation of free radicals with increase in hydroperoxide concentration, but the time of autocatalysis is of the same order of magnitude as the lifetime of the hydroperoxide, i.e. the reciprocal of its decomposition rate constant. Fig.2 shows a typical curve for the absorption of oxygen during the oxidation of a polymer (polypropylene). The curve has the sigmoid form characteristic of autocatalytic processes. Fig.2 shows that the times for attaining maximum rate of absorption of oxygen and maximum concentration of hydroperoxide are approximately the same.

The initial rate of absorption of oxygen in the oxidation is often too small to be measured, and only after some time, termed the *induction period*, does it increase sufficiently to begin to affect instruments used to observe the reaction. The dependence on the oxygen pressure p of the induction period τ in the oxidation of polymers is described in several cases by the formula[23,24]

$$\tau = a + bp^{-1}, \quad (24)$$

in which a and b are constants depending in particular on the sensitivity of the instrument recording the absorption of oxygen. The coefficients a and b vary with temperature according to the Arrhenius law, with effective activation energies calculated from their variation that are negative and usually differ from each other.

III. HIGH-TEMPERATURE OXIDATION OF POLYMERS

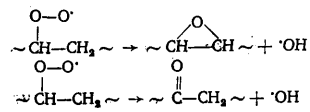
Long induction periods—from tens of minutes to several years—are usually observed in the oxidation of polymers (in the absence of stabilisers) at their working temperatures. With rise in temperature the induction period rapidly becomes shorter, and in the vicinity of 200 °C is already measured in

tens of seconds. At higher temperatures any induction period in oxidation becomes completely imperceptible.

The mechanism of the oxidation of polymers changes at 280–300 °C. The main stage of the chain propagation reaction (5) is replaced by breakdown of the peroxy-radical:

$$RO_2^{\cdot} \xrightarrow{k_{7a}} {}^{\cdot}OH + \text{Inactive products} \qquad RO_2^{\cdot} \xrightarrow{k_{7b}} R_1^{\cdot} + \text{Inactive products} \quad . \tag{25}$$

Such a reaction was first suggested by Enikolopyan[25] to explain the negative temperature coefficient of oxidation in the gas phase; he estimated its activation energy as ~85 kJ mole^{-1}. The isomerisation of $RO_2^{\cdot}$ radicals in polyethylene has been assumed[25] to involve the reactions



(26)

(27)

The occurrence of (26) is indicated by the formation of α-oxide groups in polyethylene that has been oxidised at temperatures above 300 °C. The carbonyl groups formed by several mechanisms are observed in polyethylene oxidised at any temperature; their content is greatest when oxidation has occurred at 300 °C. We can also complete the scheme by the reactions of $HO^{\cdot}$ radicals—chain transfer

$$RH + {}^{\cdot}OH \xrightarrow{k_8} R^{\cdot} + H_2O \tag{28}$$

and chain termination

$$R^{\cdot} + {}^{\cdot}OH \xrightarrow{k_9} ROH \quad . \tag{29}$$

If we write a set of balanced equations for the radicals $R^{\cdot}$, $RO_2^{\cdot}$, and $HO^{\cdot}$ and the hydroperoxide, and solve them by Bodenstein's method[27] on the assumption that the kinetic chains are long, i.e. that the rate of reaction (28) exceeds substantially that of (29), we obtain for the rate of high-temperature oxidation of a polymer containing aliphatic groups (RH) the formula[26]

$$w = \delta k_1 k_2 k_8 [RH]^2 [O_2] / 2 k_{7a} k_9. \tag{30}$$

According to (30) the rate of oxidation of a polymer, which varies little with oxygen pressure at low temperatures, becomes proportional to the concentration and hence pressure of oxygen at high temperatures. This conclusion is extremely important, since it shows that a polymer might be protected from oxidation by brief heating (e.g. during processing), by restricting the access of oxygen, or by introducing into the polymer absorbents for oxygen[28]. The last method can be used only for the short-term protection of a polymer from oxidation at high temperatures, being unsuitable for its protection under conditions of prolonged storage or operation in air. This question will be discussed in greater detail below.

In Fig.3 rate curves for the absorption of oxygen during the oxidation of polyethylene at 360 °C [? see Fig.3] under various oxygen pressures are plotted as $\lg(p_0/p)$ against time. The initial segments of these curves are straight lines. We shall show that this indicates proportionality between rate and oxygen pressure.

In a closed volume V the change in the quantity of oxygen N_{O_2} (in moles per kilogram of polymer) is related to the change in its pressure $-\Delta p$ by the formula

$$N_{O_2} = V(-\Delta p)/RTm, \tag{31}$$

in which m is the mass of the oxidisable specimen. If the rate of absorption of oxygen during the reaction is proportional to its concentration in the polymer $dN_{O_2}/dt = k_{exp}[O_2]$, while the concentration of oxygen in the polymer depends on its pressure above the polymer in conformity with Henry's law $[O_2] = \gamma p$, we can write

$$\frac{d}{dt}\left\{\frac{V(-\Delta p)}{RTm}\right\} = k_{exp}\gamma p. \tag{32}$$

Transferring p to the left-hand side, and dt to the right-hand side, and integrating the resulting equation from 0 to t and from p_0 to p, we finally obtain

$$\ln(p_0/p) = RTm\gamma k_{exp} t/V \quad . \tag{33}$$

Thus if the reaction velocity is proportional to the oxygen concentration, the kinetic curve becomes a straight line in the above coordinates, the slope of which is independent of the oxygen pressure, as is observed experimentally (Fig.3).

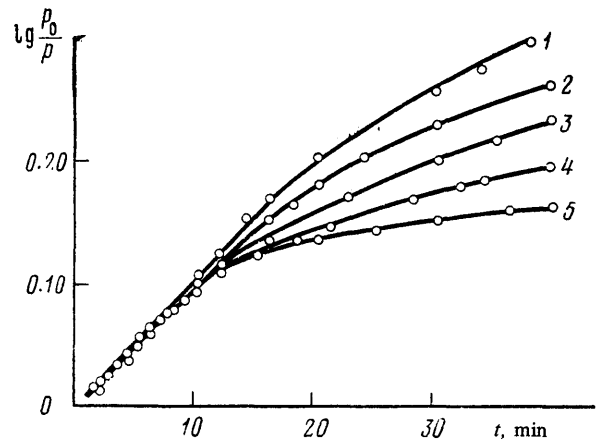


Figure 3. Absorption of oxygen in the high-temperature oxidation of polyethylene (melt)[26] at 300 °C [? see text] under different pressures (mmHg): *1*) 20; *2*) 40; *3*) 60; *4*) 80; *5*) 100.

The demoninator of formula (30) contains the quantity k_{7a}, whose temperature variation corresponds to an activation energy of ~85 kJ mole^{-1}. Rapid increase in the denominator with temperature should slow down the increase in rate (under otherwise similar conditions). Indeed, the rate of oxidation of polyethylene increases slightly with temperature above 300 °C, at which δ in the numerator of (30) reaches its stoichiometric limit ($0 \leq \delta_{max} \leq 2$). In the temperature range intermediate between low- and high-temperature oxidation a more complicated pattern is observed: the rate of absorption of oxygen diminishes with rise in temperature at low pressures (up to 60 mmHg), but at higher pressures it increases. The dependence on the oxygen pressure of the maximum rate of absorption of oxygen in the oxidation of high-density polyethylene is shown in Fig.4.

The monomer units of many thermostable polymers contain small aliphatic groups, mostly methylene or dimethylmethylene together with large aromatic or heterocyclic groups. When oxygen acts on such polymers, these aliphatic groups are the first to be oxidised. The rate is described by formula (30):

i.e. it is proportional to the oxygen pressure, and its temperature variation corresponds to low activation energies, in the range 20–80 kJ mole^{-1}. In some cases the rate of oxidation, decreasing as the aliphatic fragments are consumed, remains proportional to the square of the concentration of remaining methylene groups, as also follows from formula (30).

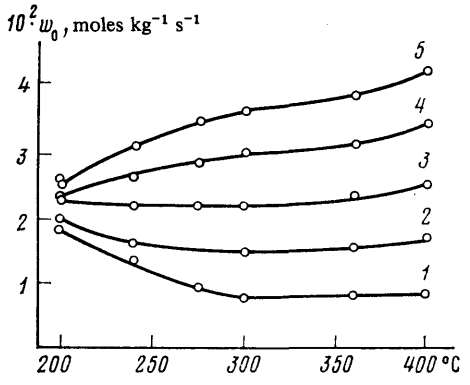


Figure 4. Temperature dependence of maximum rate of absorption of oxygen in the oxidation of polyethylene[26] under different oxygen pressures: *1*)–*5*) as in Fig. 3.

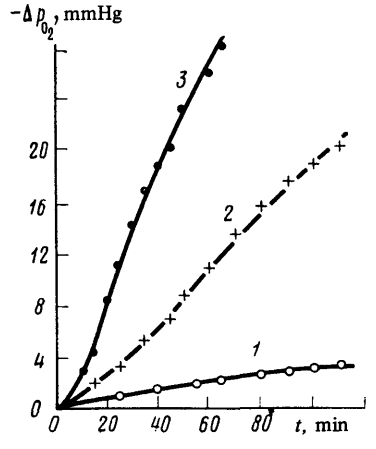


Figure 5. Absorption of oxygen during the oxidation of a polysulphone containing isopropylidene groups ~C(CH$_3$)$_2$~ in the chain[29] under an oxygen pressure of 150 mmHg at different temperatures (°C): *1*) 300; *2*) 350; *3*) 400.

The oxidation of aliphatic groups in a macromolecule may initiate oxidative degradation of aromatic groups, which in the absence of methylene groups takes place at temperatures up to 350–400 °C with considerably smaller velocities[29]. A sharp decrease in rate is observed[30] after the exhaustion of methylene groups, and it was suggested that high-temperature oxidation converted the latter mainly into ketone groups, without degradation of the macromolecules (polybenzoxazole[30]).

Oxidation of a polymer (a polysulphone containing phenylene and isopropylidene groups) at temperatures up to 400 °C was observed[29] to follow an autocatalytic course lasting tens of minutes (Fig. 5). Such long times of autocatalysis cannot be attributed to accumulation of hydroperoxides, since the lifetimes of the latter at such high temperatures are measured in fractions of a second, whereas the period of autocatalytic progress has the same order of magnitude as the lifetime of the product Pr responsible for autocatalysis. In order to show the existence of such a relation we examine the balance equation for this product.

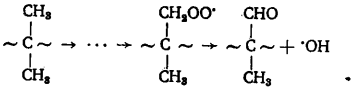
$$d[Pr]/dt = \varkappa w_{O_2} - k_{Pr}[Pr], \qquad (34)$$

in which w_{O_2} is the rate of absorption of oxygen and $\varkappa$ the yield of the product per mole of oxygen absorbed. Assuming to a first approximation that the rate w_{O_2} is constant, we find that

$$[Pr] = \frac{\varkappa w_{O_2}}{k_{Pr}}(1 - e^{-k_{Pr}t}). \qquad (35)$$

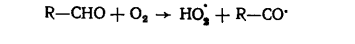
According to this formula the concentration of the product will differ from its maximum value of $\varkappa w_{O_2} k_{Pr}^{-1}$, by 10% when $\exp(-k_{Pr}t) = 0.1$ or at $t = 2.3\, k_{Pr}^{-1}$ and by 1% at $t = 4.6 k_{Pr}^{-1}$, whereas the lifetime of the product is k_{Pr}^{-1}.[27]

Autocatalysis in the high-temperature oxidation of polymers may be due to the formation of aldehyde groups[29]:

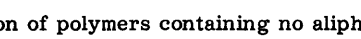


(36)

Oxidation of such groups may provide an additional source of free radicals[31]:

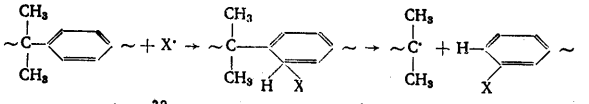


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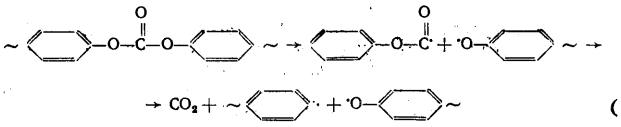
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The oxidation of polymers containing no aliphatic groups is far slower. The mechanism of their interaction with oxygen has not been reliably established. Besides detachment of hydrogen atoms from aromatic systems followed by addition of oxygen to the resulting macroradicals and small radicals reactions of the type



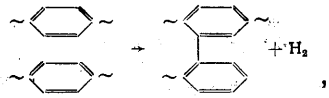
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are also possible[32]. Other suggestions have been rupture of the main chain into two macroradicals[33]



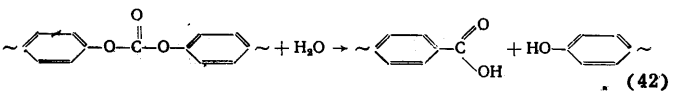
(40)

and direct combination of two aromatic systems with elimination of a hydrogen molecule[34]



(41)

Water formed at various stages in the high-temperature oxidation of heterochain polymers may be involved in reactions leading to rupture of the polymer chain[35]:



(42)

Not only HO· radicals but also other simple radicals—$CH_3^·$, $CH_3OO^·$, $C_6H_5^·$, etc.,—may be involved in the oxidation of polymers at high temperatures. The more reactive radicals take part mainly in chain-transfer reactions, and the less reactive in chain termination.

IV. CHEMICAL REACTIONS UNDERLYING THE STABILISATION OF POLYMERS

The properties of a polymeric material can be stabilised during thermo-oxidative degradation by two fundamentally different methods—by lowering the overall rate of oxidation or by eliminating individual undesirable consequences of the reaction, e.g. discoloration resulting from the accumulation of particular chromophoric groups in the polymer.

As already mentioned, the oxidation of organic compounds by molecular oxygen is a free-radical chain reaction with degenerate chain branching, i.e. with branching caused by reactions of intermediate products formed in the main chain reaction. The overall rate of the chain reaction can be diminished either by increasing the rate of chain termination or by decomposing the intermediate products involved in branching.

In 1947 Bolland and ten Have[36,37] suggested and substantiated a mechanism of chain termination in the oxidation of phenolic antioxidants in which a phenol molecule reacts with a peroxy-radical, donating to the latter a hydrogen atom and forming a hydroperoxide molecule and a relatively inactive free radical incapable of propagating the chain:

$$RO_2^· + ArOH \rightarrow ROOH + ArO^· . \qquad (43)$$

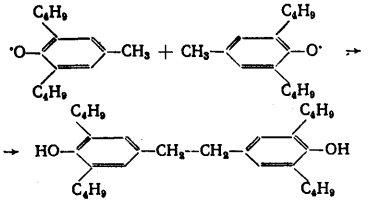
The subsequent fate of the inactive phenoxyl radical has been the subject of many investigations[36-46]. Among conversion products of the antioxidant have been found various compounds formed by dimerisation of phenoxy-radicals and also compounds of quinoid structure, which may result from oxidation and disproportionation of these radicals. Thus the antioxidant quinol is converted into the quinone, probably by interaction of the primary ArO· radical with a second peroxy-radical[37]:



(44)

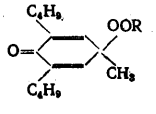
Formation of a quinone may result from disproportionation of two hydroxyphenoxy-radicals[38] or their reaction with an oxygen molecule.

The widely used antioxidant 2,6-di-t-butyl-4-methylphenol (Ionol) is known to yield dimerisation products of the primary radical[39-41]



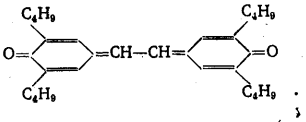
(45)

products of interaction of peroxy- and phenoxy-radicals[39]



(46)

and products of further conversion of compounds formed by dimerisation of ArO· [39,41]



(47)

However, the majority of phenoxy-radicals formed from this inhibitor under the usual conditions (non-sensitised) of the oxidation of polypropylene interacted to form intensely coloured products of high molecular weight. On further oxidation these products disappeared[42]. The radicals can also take part in chain transfer[43,44]:

$$ArO^· + RH \rightarrow ArOH + R^· . \qquad (48)$$

A scheme analogous to (43) was suggested[43,47] for chain termination by aromatic amines:

$$RO_2^· + R_1R_2NH \rightarrow ROOH + R_1R_2N^· . \qquad (49)$$

In 1954 Boozer and Hammond[48,49] proposed a different mechanism of chain termination, in which the antioxidant molecule initially adds a peroxy-radical reversibly to form a complex, which reacts with a second peroxy-radical to give an inactive product:

$$RO_2^· + A \rightleftharpoons ARO_2^· \qquad (50)$$

$$ARO_2^· + RO_2^· \rightarrow \text{Products} . \qquad (51)$$

This suggested mechanism has been criticised by many workers[46,50,51]. It was shown that "ordinary" oxidation inhibitors—phenols and aromatic amines—terminate oxidation chains in conformity with Eqn.(43) or (49). However, certain relatively ineffective antioxidants, such as anthracene and carbon black, were later shown to retard the oxidation of polyalkenes by the Boozer–Hammond mechanism of chain termination[48], i.e. by catalysing quadratic (involving the interaction of two active centres) termination of the oxidation chain[52,53].

It is interesting that phenols and amines, which react rapidly with peroxy-radicals, hardly interact if at all with alkyl radicals R·. Thus Dolgoplosk et al.[54] showed that, in the absence of oxygen, phenols and secondary aromatic amines do not retard the polymerisation of styrene and several other monomers, and only slightly retard that of allyl and vinyl acetates; in the presence of oxygen the same phenols and amines effectively inhibit the polymerisation of all these monomers. Similar observations were reported by other workers[55]. Vasil'ev showed[56] that, in the absence of oxygen, the antioxidant 2,6-di-t-butylphenol remains unconsumed in ethylbenzene containing an initiator.

According to Eqns.(43) and (49) interaction of a phenol or an amine molecule with a peroxy-radical gives a hydroperoxide molecule or a hydroperoxy-group, capable of breaking down subsequently into two free radicals. It was suggested[57] that relatively inactive free radicals could be used as antioxidants in order to eliminate this side-effect. In practice, however, such radicals proved to be relatively inactive antioxidants, since the concentration of alkyl radicals in the compound undergoing oxidation was extremely low in comparison with that of peroxy-radicals, while the "inactive" nitroxyl radicals at the high concentrations necessary for stabilisation played an appreciable part in the initiation of oxidation[58]. In those cases in which such radicals nevertheless retarded oxidation effectively it was found[59] that

they were first reduced to the corresponding aromatic amines:

$$2Ar_2NO^{\cdot} + x\,RH \rightarrow Ar_2NH + \text{Products} \ . \qquad (52)$$

In this process one amine molecule formed from two "stable" radicals; furthermore, it is accompanied by degradation of the polymer, so that it is more advantageous to introduce into the latter not the radical $Ar_2NO^{\cdot}$ but the corresponding aromatic amine.

Quinones behave similarly to "stable" radicals. Thus benzoquinone when heated in a hydrocarbon is slowly converted into a mixture of quinol and its mono- and di-ethers, which are actual inhibitors[60]. The view was also expressed[61] that quinones retard oxidation by reacting with $R^{\cdot}$ radicals.

Aromatic phosphites are also capable of terminating oxidation chains. The mechanism is apparently extremely complicated: these compounds can be hydrolysed to phenols, and can reduce peroxides and interact directly with peroxy-radicals. It was suggested[62,63] that this last reaction is represented by the equation

$$RO_2^{\cdot} + (ArO)_3P \rightarrow RO(ArO)_2PO + ArO^{\cdot} \ . \qquad (53)$$

Organic sulphides and phosphites (phosphorous esters) slow down oxidation by a mechanism involving decomposition of intermediate products. The first reports[64,65] of increase in the rate of decomposition of hydroperoxides in the presence of organic sulphides showed that purely aliphatic sulphides react most rapidly with hydroperoxides, mixed sulphides react more slowly, and aromatic sulphides hardly react at all. The antioxidant properties of these sulphides in the oxidation of white oil vary in the same sequence. Both during oxidation and on interaction with hydroperoxides the sulphides first pass into sulphoxides and then into sulphones:

$$ROOH + R_1{-}S{-}R_1 \rightarrow ROH + R_1{-}\overset{\overset{O}{\|}}{S}{-}R_1 \qquad (54)$$

$$ROOH + R_1{-}\overset{\overset{O}{\|}}{S}{-}R_1 \rightarrow ROH + R_1{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R_1 \ . \qquad (55)$$

These observations have been confirmed many times by other workers[66,67]. The yield of free radicals in reactions between hydroperoxides and sulphides is extraordinarily low, not exceeding one radical per thousand hydroperoxide molecules that have reacted[68].

Organic phosphites react with hydroperoxides by a similar mechanism[63]:

$$ROOH + P(OR_1)_3 \rightarrow ROH + O{=}P(OR_1)_3 \ . \qquad (56)$$

Several phosphites, e.g. iso-octyl diphenyl phosphite, are considerably more efficient than organic sulphides in reducing hydroperoxides[69].

V. KINETICS OF THE INHIBITED OXIDATION OF POLYMERS

Reductants of hydroperoxides are seldom used as individual antioxidants for polymer materials[70], but are usually employed mixed with substances that terminate oxidation chains, i.e. oxidation inhibitors in the narrow sense. The latter, however, are used both as individual antioxidants and as the main components of mixed antioxidants. Both cases will be discussed below.

As mentioned above, the chief substances used as oxidation inhibitors are phenols and secondary aromatic amines, of general formula IH. Because of their great reactivity such inhibitors, when introduced into a polymer undergoing oxidation, take part in all stages of the oxidation chain—generation, propagation, branching, and termination—and react with all types of free radicals formed in the polymer. The primary products formed from the inhibitors may undergo further reactions. All this makes the mechanism of inhibited oxidation extremely complicated. Below we shall take the mechanism of inhibited oxidation to mean the minimum set of main stages necessary for a quantitative description of the observed regularities.

The main stage at which oxidation is inhibited is chain termination

$$RO_2^{\cdot} + IH \rightarrow ROOH + I^{\cdot} \ . \qquad (57)$$

The resulting $I^{\cdot}$ radicals may be involved in chain transfer by interacting with the oxidisable material:

$$I^{\cdot} + RH \rightarrow IH + R^{\cdot} \ . \qquad (58)$$

If reaction (58) were the sole means of consumption of the relatively inactive radicals $I^{\cdot}$, they would sooner or later accumulate in sufficient concentration for the rate of reaction (58) to become comparable with that of (57). For every chain terminated there would then be a chain initiated by an $I^{\cdot}$ radical: i.e. the inhibitor would cease to influence the reaction velocity.

The situation is unaffected by taking into account the reaction of $I^{\cdot}$ radicals with alkyl radicals $R^{\cdot}$, for the concentration of the latter in the polymer is negligible in comparison with that of $RO_2^{\cdot}$. Because of the great viscosity of the medium and the near immobility of the macroradicals $R^{\cdot}$ and $RO_2^{\cdot}$ the rates of their reactions with IH molecules and $I^{\cdot}$ radicals will be determined by the frequency with which the reactant species meet, so that the difference in the reactivity of different substances towards the polymer radicals becomes insignificant. For example, the rate constants of the reactions of macroradicals with inhibitor molecules and inactive radicals in polystyrene differ by the factors of at most 10–15.[71]

Let us suppose for definiteness that the rate constant of reaction (57) amounts to 10% of that of the process

$$I^{\cdot} + R^{\cdot} \rightarrow RI \qquad (59)$$

while the concentration of $R^{\cdot}$ radicals is 1% of that of $RO_2^{\cdot}$ radicals. Then the rate of consumption of inhibitor radicals $I^{\cdot}$ will become equal to the rate of their formation only when $[I^{\cdot}]/[IH] = 10$, i.e. after almost all the inhibitor has been converted into radicals. Thus reaction (59) cannot effectively remove $I^{\cdot}$ radicals from the polymer.

With the same relative rate constants and radical concentrations the reaction

$$I^{\cdot} + RO_2^{\cdot} \rightarrow ROOI \qquad (60)$$

will occur at the same rate as the formation of $I^{\cdot}$ provided that $[I^{\cdot}]/[IH] \geq 0.1$. In a medium of low molecular weight reaction (60) converts an inactive $I^{\cdot}$ radical and an active $RO_2^{\cdot}$ radical into the quinolide peroxide(46),[39,72] but in a polymer it produces a peroxy-group "grafted" to the polymer chain. Breakdown of such a peroxy-group will yield two new radicals, apparently more active than their precursors. At the fairly high temperatures at which polymers are processed the peroxy-groups will break down almost instantaneously: i.e. reaction (60) may lead to conversion of an inactive $I^{\cdot}$ radical into an active $RO^{\cdot}$ radical.

Thus for a given substance effectively to inhibit the oxidation of a polymer it is necessary not only that the chain-termination (57) rate constant should be sufficiently high but also that termination should yield an inactive radical $I^{\cdot}$ that should be sufficiently rapidly consumed in reactions not

involving the polymer, e.g. recombination—such as (45)—or disproportionation

$$2I^{\cdot} \xrightarrow{k_6} \text{Products}, \qquad (61)$$

In fact the concentrations of inhibitor radicals formed in the oxidation of polypropylene with initial inhibitor concentrations of $(7-9)\times10^{-2}$ mole kg^{-1} do not exceed 10^{16} $g^{-1} = 1.7\times10^{-5}$ mole kg^{-1}: i.e. they are <1% of the inhibitor concentration[73]. Thus such reactions do indeed play an important part in the consumption of inhibitor radicals. The concentration of the latter (measured accurate to an unknown factor) has been shown[74] to be proportional to the square root of the rate of consumption of the inhibitor:

$$[I^{\cdot}] = \text{const}\left(-\frac{d[IH]}{dt}\right)^{1/2}, \qquad (62)$$

This is consistent with a mechanism of consumption of $I^{\cdot}$ radicals by recombination or disproportionation, when

$$d[I^{\cdot}]/dt = -d[IH]/dt - k_6[I^{\cdot}]^2. \qquad (63)$$

With $d[I^{\cdot}]/dt = 0$ when a steady concentration of the radicals is reached, we obtain for $[I^{\cdot}]$ an expression of the form (62).

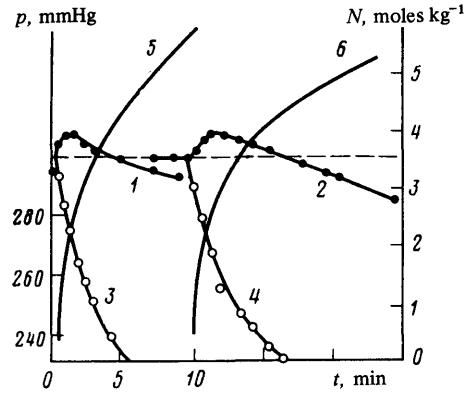


Figure 6. Effect of the inhibitor methylene-2,2′-bis-(4-methyl-6-t-butylphenol)—Antioxidant 22–46 (0.1 mole kg^{-1})—on the oxidation of polyethylene[75] under an initial pressure of 300 mmHg (broken line) at 260 °C: *1*) variation in total pressure in absence of inhibitor; *2*) as (1) in presence of inhibitor; *3*) partial oxygen pressure without inhibitor; *4*) partial oxygen pressure with inhibitor; *5*) formation of volatile products (*N*) without inhibitor; *6*) as (5) with inhibitor.

Fig. 6 illustrates the absorption of oxygen during the oxidation of polypropylene at 260 °C in the absence and in the presence of an inhibitor, the variation in total presssure in the reaction vessel, and the quantity of volatile degradation products evolved from the polymer during oxidation. It is evident that the inhibitor—in this case methylene-2,2′-bis-(4-methyl-6-t-butylphenol), known also as *Antioxidant 22–46*—merely delayed for some time the start of a rapid process characterised by a high rate of absorption of oxygen together with a high rate of formation of volatile degradation products[75]. The induction period from the start of the reaction to the rapid stage is short in the absence of an inhibitor, being measured at high temperatures in fractions of a second, but is lengthened by an inhibitor, sometimes by factors of 10^2–10^4. When oxidation passes into the rapid stage, the molecular weight and consequent properties of the polymer change rapidly, "disastrously", the material becomes unsuitable for practical use, and articles made from it disintegrate. Henceforward, therefore, we shall be interested only in processes occurring during the induction period.

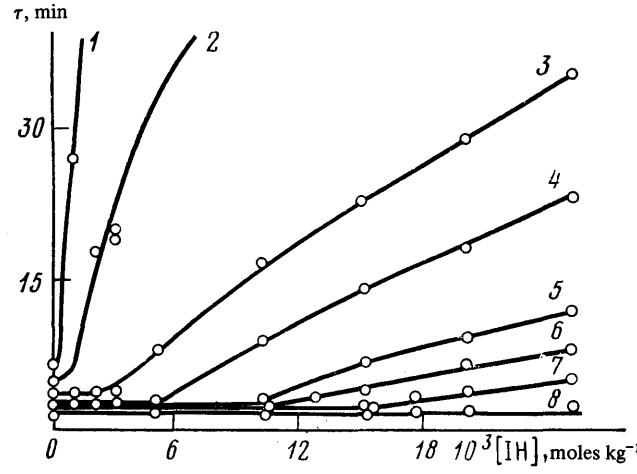


Figure 7. Dependence of induction period in the oxidation of polyethylene on concentration of Antioxidant 22–46 under 300 mmHg [76] at different temperatures (°C): *1*) 200; *2*) 220; *3*) 230; *4*) 240; *5*) 250; *6*) 260; *7*) 265; *8*) 270.

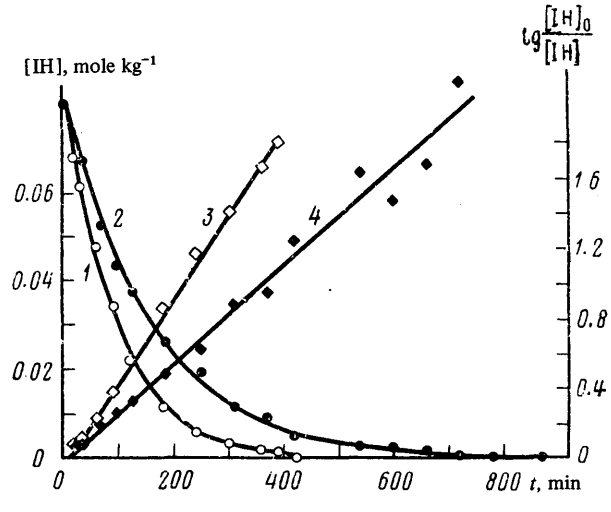


Figure 8. Effect of didecyl sulphide (0.08 mole kg^{-1}) on variation in concentration of Antioxidant 22–46 during induction period in the oxidation of polypropylene[80] under an oxygen pressure of 300 mmHg at 200 °C: *1*) sulphide absent; *2*) sulphide present; *3*) as (*1*) plotted for a first-order reaction; *4*) as (*3*) in the presence of sulphide.

Fig.7 illustrates the dependence of induction period on inhibitor concentration at various temperatures. Up to a certain critical concentration the inhibitor has hardly any effect, but beyond it the induction period increases with concentration. The critical concentration increases rapidly with temperature, while the slope of the curves diminishes. Around 280–290 °C, i.e. at temperatures at which the mechanism of oxidation changes, the "usual" antioxidants cease to retard oxidation, and their critical concentrations increase to several tenths of a mole per kilogram, i.e. 3–10 mass % and even above. Use of such high antioxidant concentrations is obviously inadmissible for the most diverse reasons, beginning with cost and ending with their marked effect on the properties of the polymer material.

The polymer does not remain unchanged during the induction period. Firstly the antioxidant (inhibitor) it contains is consumed. The corresponding curve can be linearised by plotting $\lg([IH]/[IH]_0]$ against time (Fig.8). Kinetic curves for a first-order reaction, described by formulae such as

$$-d[IH]/dt = k[IH], \quad (64)$$

$$[IH] = [IH]_0 e^{-kt} \quad (65)$$

become straight lines in such coordinates[27].

Increasing the vertical scale in Fig.8 would reveal that the slow consumption of inhibitor, which up to a certain time obeys a first-order law, accelerates sharply at the end of the induction period. This is immediately followed by a marked increase in the rate of absorption of oxygen: i.e. the induction period is complete. Consumption of the inhibitor accelerates immediately its concentration falls below this critical concentration. Denoting by τ_{cr} the portion of the induction period from attainment of the critical concentration to the start of the rapid reaction, assuming that the inhibitor concentration falls from $[IH]_0$ to $[IH]_{cr}$ during the time interval $\tau - \tau_{cr}$, substituting these values in Eqn.(65), and taking logarithms, we obtain the formula

$$\tau = \tau_{cr} + \frac{1}{k} \ln \frac{[IH]_0}{[IH]_{cr}} \quad (66)$$

relating the induction period with the concentration of inhibitor in the initial polymer[77,78]. This provides a good description of the experimental dependence of the induction period in the oxidation of polymers on the initial inhibitor concentration in all cases in which conversion products of the inhibitor have little effect on the rate of oxidation. A logarithmic dependence of induction period on inhibitor concentration was established empirically by Rosenwald[79], who studied the oxidation of petrol.

Fig.8 shows that, if a substance that reduces hydroperoxy-groups [didecyl sulphide $(C_{10}H_{21})_2S$] is introduced into a polymer containing an oxidation inhibitor, the first-order consumption of inhibitor is maintained, but the absolute value of the rate constant is lower[80].

During the induction period the molecular weight of the polymer decreases. At sufficiently high inhibitor concentrations—several times the critical value—an approximately linear relation exists between the rate of degradation of polymer chains and the inhibitor concentration, which breaks down only when the latter has fallen to roughly double the critical concentration, after which the rate of degradation increases sharply[81] (Fig.9). With few exceptions[69] reductants of hydroperoxy-groups do not lower the rate of polymer degradation. The rate of absorption of oxygen shows a similar dependence on the inhibitor concentration[82].

Volatile products, in particular monomers[74,83], are formed during the induction period in the inhibited oxidation of polyethylene and polypropylene, but their rates of formation are low ($\sim 10^{-9}$ mole kg^{-1} s^{-1} at 200 °C), and at sufficiently high inhibitor concentrations are independent both of such concentrations[74,83] and of the oxygen pressure[74].

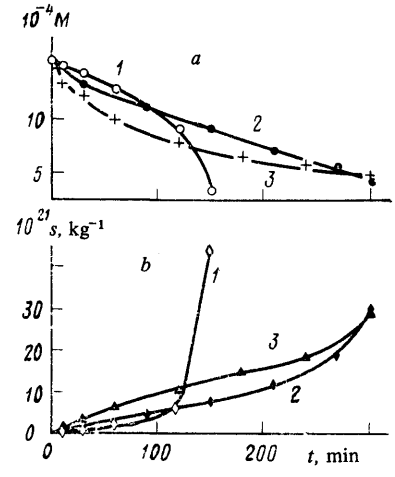


Figure 9. Variation in (*a*) molecular weight and (*b*) number of breaks in polymer chain during induction period in the inhibited oxidation of polypropylene under 300 mmHg at 200 °C in the presence of Antioxidant 22-46 at different initial concentrations (mole kg^{-1}): *1*) 0.004; *2*) 0.025; *3*) 0.0625.

Thus, as had been pointed out in the early work on inhibited oxidation[84], antioxidants do not arrest polymer oxidation and the accompanying degradative processes but merely lower their rates considerably.

According to the original theory an inhibitor terminates the kinetic oxidation chain and is itself thereby consumed[85] at a rate

$$-d[IH]/dt = \frac{1}{j} w_n, \quad (67)$$

where w_n is the rate of chain generation and j the stoichiometric inhibition coefficient, i.e. the number of free radicals destroyed by one inhibitor molecule. Comparison of Eqns. (66) and (67) clearly reveals agreement between experiment and theory if $w_n = k[IH]$, i.e. if the rate of chain generation is proportional to the inhibitor concentration, which can be explained only by involvement of the inhibitor in chain generation[86,87].

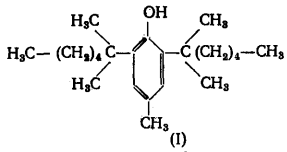
The aromatic amines and alkylated phenols used as inhibitors are considerably more reactive than the polymers they protect, not only towards peroxy-radicals but also towards molecular oxygen. For this reason, even at low (subcritical) inhibitor concentrations, the reaction

$$IH + O_2 \xrightarrow{k_8} I^{\cdot} + HO_2^{\cdot} \xrightarrow{(RH)} \cdots \rightarrow R^{\cdot} \quad (68)$$

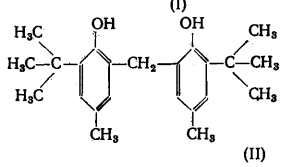
occurs at rates exceeding the rate of chain generation in the absence of an inhibitor, i.e. reactions (1)–(3),[77,78,80]

One reason for the difference in antioxidant efficiency between inhibitors belonging to the same class of compounds may be a difference in the rate constants of reaction (68). However, even compounds that are very similar in chemical

nature may differ very greatly in antioxidant efficiency. Thus the alkylphenols (I) and (II)


(69)

(I)


(70)

(II)

at equal concentrations of the phenolic hydroxyls give induction periods in the oxidation of polypropylene differing by factors of ten in length[77]. It might have been supposed that this was due to a difference in reactivity between the hydroxyls in (I) and (II), but experiment showed that the difference was qualitative in character: the introduction of variable concentrations of (I) into a polymer containing a constant concentration of (II) produced a greater shortening of the induction period the higher the concentration of (I), although such introduction of a second inhibitor increased the total inhibitor concentration (Fig.10). When a reductant for hydroperoxide (didecyl sulphide) was introduced into the polymer together with the inhibitors, the qualitative difference between (I) and (II) disappeared: just as in the case illustrated in Fig.7, the sulphide produced inflexions in the concentration dependence of the induction period, above which the length of the latter increased rapidly (Fig.11),[80] and the consumption of the inhibitor followed a first-order curve (Fig.12).

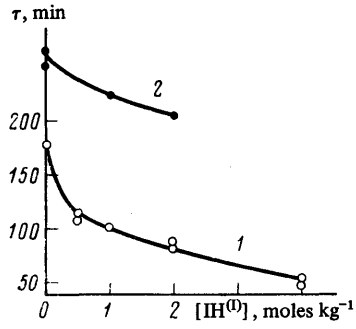
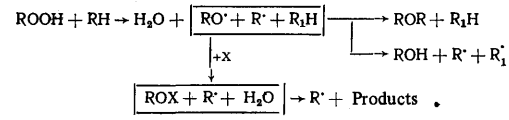


Figure 10. Dependence of induction period in the oxidation of polypropylene[77] under 300 mmHg of oxygen at 200 °C on concentration of inhibitor (I) for different contents of (II) (mole kg^{-1}): *1*) 0.01; *2*) 0.02.

In view of such behaviour of inhibitor (I) the difference could not be explained even on the assumption of a considerably greater rate of direct oxidation (68) of (I) than of (II). It was suggested that the difference between the monohydric (I) and dihydric (II) phenols was due to this difference in the number of active functional groups involved in chain termination[77,80,88].

In a substance undergoing oxidation free radicals appear and disappear in pairs. The pair formed on breakdown of a hydroperoxy-group most probably recombine, so that the yield of free radicals in this reaction is small (scheme 18). A hypothetical species X that might have destroyed only one of the radicals would have made recombination impossible for the other radical:


(71)

If in the absence of X the yield of radicals from the cage exceeds unity, the introduction of X will lower the yield of free radicals formed by decomposition of the hydroperoxy-group (and of any source of radicals in general). If, however, this yield is less than unity, X will increase the yield of free radicals.

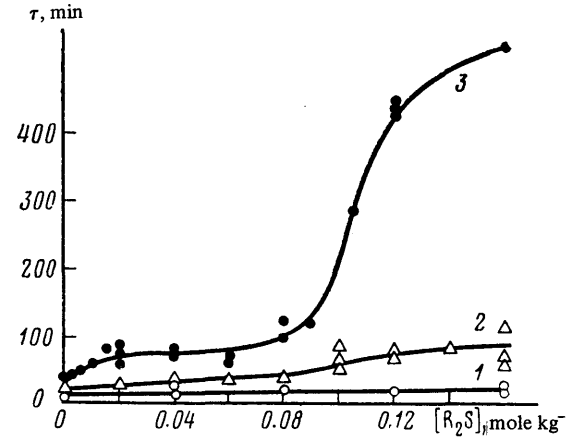


Figure 11. Dependence of induction period in the oxidation of polypropylene[80] under 300 mmHg of oxygen at 200 °C on the concentation of inhibitor (I) in the presence of different contents (mole kg^{-1}) or didecyl sulphide (R_2S): *1*) 0; *2*) 0.04; *3*) 0.08.

In order to estimate the possible effect we assume that recombination in a cage is so rapid that it can involve those X molecules that were present on formation of the cage. If the volume of the cage is taken to be $(10\ \text{Å})^3 = 10^{-24}$ litre, one litre of the polymer will contain 10^{24} cages. On introduction into the polymer of X at a concentration $0.01\ M = 6 \times 10^{21}$ litre^{-1} only 0.6% of the cages will contain X and, if in all these cages the yield of radicals changes from the original value δ_0 to unity, the observed yield of radicals in the presence of X will be $\delta_0 + 0.006(1-\delta_0)$, which will differ appreciably from the original value δ_0 only if the latter does not exceed 0.01.

Real inhibitors will obviously differ from the above substance X. Reaction between an inhibitor and an active radical forms a relatively inactive radical I$^\cdot$ capable of recombination with the other radical of the pair; but the lower activity of I$^\cdot$ than of RO$^\cdot$ or R$^\cdot$, and also the increase in

mean distance between the radicals after each step in the reaction, will lead to a change in the yield of radicals from the cage if an inhibitor molecule enters it. Increase in the number of active functional groups in the inhibitor molecule will obviously increase the probability that the molecule will interact simultaneously with the two radicals of the pair: i.e. a phenolic diol should not increase the yield of radicals from the cage, or should increase it far less than would a monophenol.

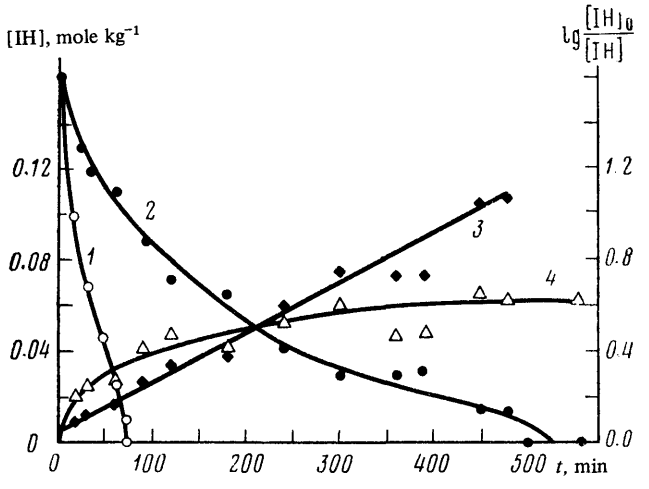


Figure 12. Consumption of inhibitor (I) during induction period in the oxidation of polypropylene[60] under 300 mmHg of oxygen at 200 °C: *1*) in absence of sulphide; *2*) in presence of didecyl sulphide (0.08 mole kg^{-1}); *3*) as (*2*) plotted as lg ($[IH]_0/[IH]$) against time; *4*) inhibitor vaporised from specimen containing sulphide.

Pudov[89,90] observed that inhibitors increased the yield of free radicals formed by the breakdown of hydroperoxy-groups in polypropylene. He showed that in the absence of an inhibitor the yield per hydroperoxy-group decomposed was ~10^{-2} radical, and the appreciable effect of the introduction of inhibitors into the polymer is consistent with the above estimates. In contrast, the yield of free radicals on the decomposition of lower peroxides or azo-compounds is 0.2–1.0, so that attempts to change this yield by means of inhibitors were unsuccessful[91].

Mono- and di-amines differ in effectiveness similarly to mono- and di-phenols: under comparable conditions diamines considerably surpass monoamines in antioxidant efficiency[92].

The presence of two hydroxy-groups in a phenol molecule is a necessary but not sufficient condition for the simultaneous entry of two phenolic hydroxyls into a cage containing a pair of radicals: it is necessary also that these groups should be located side by side in the most probable conformations of the diphenol molecule. Infrared spectra have been used[93] to determine the relative arrangement of hydroxy-groups. The close approach of two such groups leads to formation of a hydrogen bond O–H...O–H, corresponding in dilute solutions of the diphenol to an absorption band at 3440–3460 cm^{-1}. A hydrogen bond between a hydroxy-group and the π-electron system of an adjacent aromatic ring corresponds to a band at 3520–3550 cm^{-1}, and a free hydroxyl gives a band at 3630–3660 cm^{-1}.[94] The experiments show[93] that only those diphenols are effective antioxidants in whose molecules the hydroxy-groups are linked by a hydrogen bond, bond, i.e. are situated close together in the main conformation. The inhibitor 3,3',5,5'-tetra-t-butylbiphenyl-2,2'-diol, which differs from (II) in the absence of a methylene group between rings, has a unique conformation with OH...π hydrogen bonds, in which the hydroxy-groups are far apart, and is therefore an ineffective antioxidant. The effectiveness of (II) is greatly diminished also when one of its hydroxyls is replaced by an ester group[95].

Another possible mechanism by which an inhibitor can affect the yield of free radicals formed from a hydroperoxy-group is direct interaction between this group and the inhibitor molecule[96,97]:

$$ROOH + IH \rightarrow RO^{\cdot} + I^{\cdot} + H_2O \rightarrow \cdots \rightarrow \delta R^{\cdot}. \qquad (72)$$

The dependence of the yield of free radicals on the hydroperoxide concentration can be written (independently of the mechanism) as the series

$$\delta = \delta_0 + \delta_t [IH] + \delta_{tt} [IH]^2 + \ldots \qquad (73)$$

or at low inhibitor concentrations

$$\delta = \delta_0 + \delta_t [IH]. \qquad (74)$$

Thus with sufficiently high inhibitor concentratons, when the stages of chain generation (1)–(3) and quadratic chain termination (10)–(12) can be neglected, oxidation can be represented by the stages[88]

$$\begin{gathered} IH + O_2 \xrightarrow{k_0} I^{\cdot} + HO_2^{\cdot} \xrightarrow{(RH)} \cdots \rightarrow \alpha R^{\cdot} \\ R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \\ RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \\ RO_2^{\cdot} + IH \xrightarrow{k_3} ROOH + I^{\cdot} \\ ROOH + RH \xrightarrow{k_4(IH,O_2)} \delta R^{\cdot} + \text{Products} \\ ROOH + R_2S \xrightarrow{k_5} \text{Products} \end{gathered} \qquad (75)$$

which give rise to the balance equations

$$d[R^{\cdot}]/\alpha\, t = d\, k_0 [IH]\,[O_2] + k_2 [RO_2^{\cdot}]\,[RH] + \delta k_4 [ROOH]\,[RH] - k_1 [R^{\cdot}]\,[O_2], \qquad (76)$$

$$d[RO_2^{\cdot}]/d\,t = k_1 [R^{\cdot}]\,[O_2] - k_2 [RO_2^{\cdot}]\,[RH] - k_3 [RO_2^{\cdot}]\,[IH], \qquad (77)$$

$$[OH]/d\,t = k_2 [RO_2^{\cdot}]\,[RH] + k_3 [RO_2^{\cdot}]\,[IH] - k_4 [ROOH]\,[RH] - k_5 [ROOH]\,[R_2S] \qquad (78)$$

for $R^{\cdot}$, $RO_2^{\cdot}$, and ROOH.

If the process takes place at a sufficiently high temperature, at which the lifetime of hydroperoxy-groups is short compared with the duration of the reaction, we can attempt to solve Eqns.(76)–(78) by Bodenstein's method[98], i.e. by neglecting rates of change of the instantaneous radical and hydroperoxide concentrations in comparison with their rates of formation and consumption, equating $d[R^{\cdot}]/dt$, $d[RO_2^{\cdot}]/dt$, and d[ROOH]/dt to zero. The set of differential equations (76)–(78) then becomes a set of algebraic equations, which can readily be solved by the usual methods. It then follows from Eqn.(78) that the steady-state concentrations of peroxy-radicals and hydroperoxy-groups are related by the formula

$$[ROOH] = \frac{k_2 [RH] + k_3 [IH]}{k_4 [RH] + k_5 [R_2S]} [RO_2^{\cdot}]. \qquad (79)$$

Substituting for [ROOH] in (76) and solving simultaneously the resulting equation and (77), we find for the steady-state

concentration of peroxy-radicals

$$[RO_2^{\cdot}]_{st} = \alpha k_0 [IH] [O_2] \cdot \left[k_3 [IH] - \frac{\delta k_4 [RH] (k_2 [RH] + k_3 [IH])}{k_4 [RH] + k_5 [R_2S]} \right]^{-1}. \quad (80)$$

This will be finite (i.e. inhibited oxidation of a polymer will be a steady-state process) only if the antioxidant concentration exceeds some critical value

$$[IH]_{cr} = \delta k_2 k_4 [RH]^2 \cdot \{(1-\delta) k_3 k_4 [RH] + k_3 k_5 [R_2S]\}^{-1}, \quad (81)$$

i.e. the critical inhibitor concentration. When $[IH] < [IH]_{cr}$, the rate $d[RO_2^{\cdot}]/dt$ will increase without limit: i.e. Bodenstein's method will be inapplicable[99].

The physical significance of the critical concentration is that below it the oxidation will be autocatalytic (non-stationary) until the rate is limited by quadratic chain termination (12), but above this concentration the process will be stationary and occur at a very low rate. On the curves representing the dependence of the oxidation induction period on inhibitor concentration the critical concentration corresponds to a sharp inflexion, after which the induction period begins to increase with concentration[100] (Fig.6).

Substituting in (81) for δ from (74) and putting $[R_2S] = 0$, we obtain the quadratic equation

$$\delta_i k_3 [IH]^2_{cr} + (\delta_i k_2 [RH] - (1-\delta_0) k_3) [IH]_{cr} + \delta_0 k_2 [RH] = 0 \quad (82)$$

for the critical concentration of an inhibitor that increases the probability of degenerate chain branching. When

$$0 \leqslant \delta_i < (1-\delta_0^{1/2})^2 k_3 / k_2 [RH]$$

the quadratic equation has two positive real roots: i.e. an inhibitor that branches kinetic chains has two critical concentrations, and oxidation is a steady-state process only when the inhibitor concentration lies between them. An inhibitor for which the above relation exists between the constants δ_0, δ_i, k_2, and k_3 is an antioxidant of moderate strength[101].

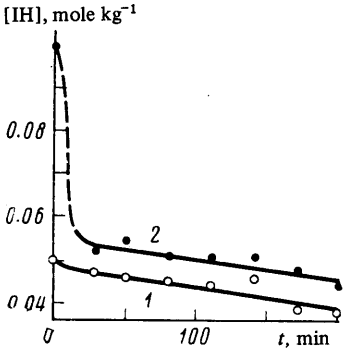


Figure 13. Variation in concentration of phenyl-2-naphthylamine in the initial stage of the induction period in the oxidation of polypropylene[104] under 300 mmHg of oxygen at 200 °C for different initial concentrations (mole kg^{-1}): *1*) 0.05; *2*) 0.10.

The lower (usual) critical concentration has been observed many times in the oxidation of simple compounds[102,103] and polymers[77,78,80,100]. The upper critical concentration appears as a sharp increase in rate of consumption of inhibitor above some concentration (Fig.13), which sometimes (not necessarily) slows down abruptly after the excess of inhibitor above the upper critical concentration has been consumed, or as a sharp "ceiling" (Fig.14) or maximum (Fig.15) in the dependence of induction period on inhibitor concentration. Whereas the rate of degradation of the polymer initially decreases and then smoothly increases with inhibitor concentrations in the range between lower and upper critical values, above the latter this rate increases sharply[104-106].

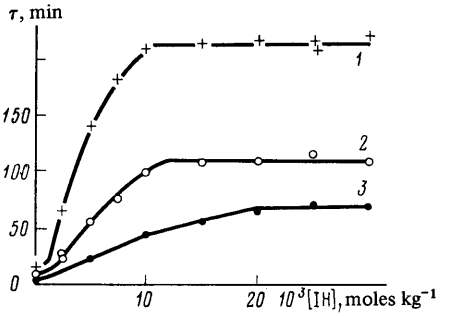


Figure 14. Dependence of induction period in the oxidation of polypropylene[105] under 300 mmHg of oxygen on concentration of methylene-2-2'-bis-(4-chloro-6-t-butylphenol) at different temperatures (°C): *1*) 180; *2*) 190; *3*) 200.

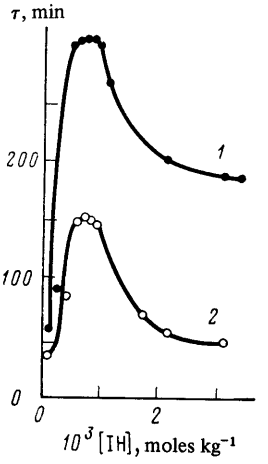


Figure 15. Dependence of induction period in the oxidation of an indene–coumaric resin[106] under 300 mmHg of oxygen on concentration of methylene-2,2'-bis-(4-methyl-6-t-butylphenol) at different temperatures (°C): *1*) 150; *2*) 180.

If in (82) we put $k_3[IH] \ll k_2[RH]$, i.e. confine our attention to low inhibitor concentrations, we find for the lower critical concentration of a moderately strong antioxidant the approximate formula[101]

$$[IH]_{cr} = \delta_0 k_2 [RH] \cdot (k_3 - \delta_i k_2 [RH])^{-1}. \quad (83)$$

The rate of consumption of the inhibitor can be written as the sum of the rates of its direct oxidation by molecular oxygen and its reaction with $RO_2^{\cdot}$ radicals:

$$-\frac{d[IH]}{dt} = k_0[IH][O_2] + \alpha k_0 k_3 [IH]^2 [O_2] \times$$
$$\times \left[k_3[IH] - \frac{\delta k_4 [RH](k_2[RH] + k_3[IH])}{k_4[RH] + k_5[R_2S]}\right]^{-1}. \quad (84)$$

When $[IH] \gg [IH]_{cr}$, the second term in the demoninator is small in comparison with $k_3[IH]$, and Eqn.(84) represents first-order consumption of the inhibitor. An inhibitor in whose presence δ remains approximately constant, and whose first-order rate of consumption is maintained even in the absence of R_2S, has been termed a *strong antioxidant*[80].

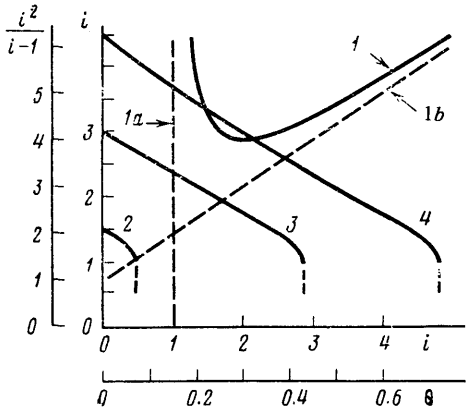


Figure 16. Calculation from Ref.101 of: *1*) dependence of dimensionless rate of consumption of an antioxidant of medium strength $w = i^2/(i-1)$ on its instantaneous concentration i; *1a,b*) asymptotes corresponding to (1); *2*)–*4*) variation in dimensionless concentration of the antioxidant with the dimensionless time θ during the oxidation induction period for different initial concentrations.

The law governing consumption of a moderately strong antioxidant can be found by substituting for δ from (74) in (84). Assuming also that $[R_2S] = 0$ with $k_3[IH] \ll k_2[RH]$ and $\delta_0 \ll 1$, we obtain

$$-\frac{d[IH]}{dt} = \left[1 + \frac{\alpha k_3}{k_6 - \delta k_2 [RH] - \delta_0 k_2 [RH]/[IH]}\right] k_0 [IH][O_2]. \quad (85)$$

This formula can be transformed into

$$-\frac{di}{d\theta} = \frac{i^2}{i-1} + \frac{k_3 - \delta_i k_2 [RH]}{k_3}, \quad (86)$$

where

$$i = [IH]/[IH]_{cr} \text{ и } \theta = \alpha k_0 k_3 [O_2] t/(k_3 - \delta_i k_2 [RH])$$

are dimensionless coordinates (of inhibitor concentration and time). If α is large, while the difference $k_3 - \delta_i k_2[RH]$ is small, the last term in (86) can be neglected, and the concentration dependence of the rate of inhibitor consumption becomes

$$-di/d\theta = i^2(i-1)^{-1}. \quad (86a)$$

Fig.16 shows that, despite the complicated concentration dependence of the rate of inhibitor consumption indicated by formula (86a), the minimum lies high above the abscissae axis, so that the rate departs little from its mean value, by not more than 20% over the range $i = 1.3$–4.7, and even 5.6% in the range 1.5–3. In conformity with this the variation in the concentration of antioxidant of moderate strength is nearly linear in the region of the critical concentration. Experimental curves for the consumption of many inhibitors, e.g. phenyl-2-naphthylamine[101] (Fig.17), are similar in form to the calculated curves in Fig.16.

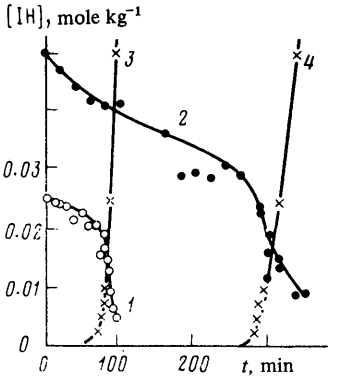


Figure 17. Inhibited oxidation of polypropylene[101] under 300 mmHg of oxygen at 200 °C: *1*) variation in concentration of phenyl-2-naphthylamine (initial concentration 0.025 mole kg^{-1}); *2*) as (*1*) but initially 0.05 mole kg^{-1}; *3*) absorption of oxygen (0.025); *4*) absorption of oxygen (0.05).

Equation (82) has no real roots, i.e. the inhibitor has no critical concentration, when

$$\delta_i > (1 - \delta_0^{1/2})^2 k_3/k_2[RH]$$

such an inhibitor cannot make oxidation a stationary process whatever its concentration: i.e. it is a weak antioxidant. Equations (75) cannot then be solved by Bodenstein's method. The autocatalysis factor for oxidation of a polymer in the presence of a weak antioxidant can be determined by means of Semenov's formula[107]

$$\varphi = (\nu\delta - 1)/\theta, \quad (87)$$

in which ν is the length of the unbranched chain, in the present case

$$\nu = 1 + k_2[RH]/k_3[IH], \quad (88)$$

and θ the lifetime of the branching product, i.e. $\theta = (k_4[RH])^{-1}$ when $[R_2S] = 0$. Substituting in (87) for δ from (74) and for ν from (88), we find that

$$\varphi = \frac{k_4[RH]}{k_3}\left\{\delta_i k_2[RH] - (1-\delta_0)k_3 + \delta_i k_3[IH] + \frac{\delta_0 k_2[RH]}{[IH]}\right\}. \quad (89)$$

The expression in braces is the left-hand side of (82) divided by [IH], and with

$$\delta_i > (1 - \delta_0^{1/2})^2 k_3/k_2[RH]$$

is positive at all values of [IH]. For certain mean values of [IH] both terms containing it in the brackets in Eqn.(89) can be neglected. Over this concentration range the rate of absorption of oxygen and of other stages in oxidation of a

polymer containing a weak antioxidant will be described by the exponential law $w = w_0 \exp(\phi t)$ with ϕ constant.

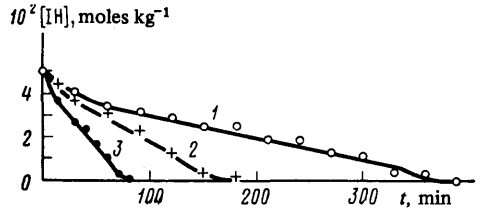


Figure 18. Variation in concentration of the weak antioxidant 2,6-di-t-butyl-4-phenylphenol during induction period in the oxidation of polypropylene under 300 mmHg of oxygen at (°C): *1*) 180; *2*) 190; *3*) 200.

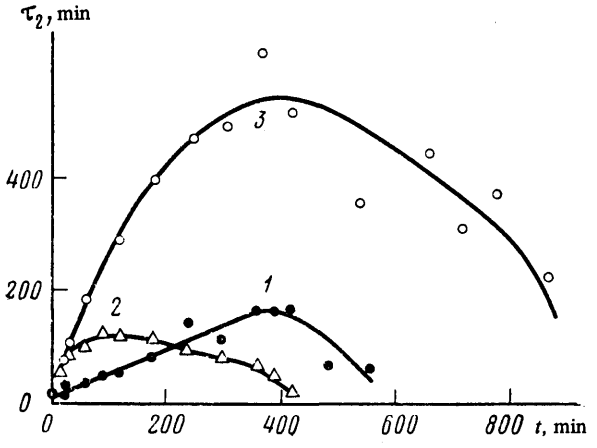


Figure 19. Dependence of induction period in the oxidation of polypropylene containing conversion products of antioxidants (unconsumed antioxidants removed by vaccum distillation at 200 °C) on duration of oxidation of initial specimens[80] under 300 mmHg of oxygen at 200 °C for additions of a mixture of inhibitor (I) (0.16 mole kg^{-1}) with: *1*) didecyl sulphide; *2*) inhibitor (II) (0.08 mole kg^{-1}); *3*) a mixture of (II) and didecyl sulphide (each 0.08 mole kg^{-1}).

The rate of consumption of inhibitors that are weak antioxidants considerably exceeds that of strong antioxidants. The proportion of direct oxidation of the inhibitor is then insignificant in comparison with its consumption in chain termination, the rate of which is given approximately by the product of the instantaneous inhibitor concentration and a quantity proportional to $\exp \phi t$. The curves described by this law are sometimes fairly complicated, but sometimes they approximate to straight lines[108,109] (Fig.18).

So far we have been considering only the action of the initial inhibitor. However, conversion products of inhibitors are usually involved in oxidation of a polymer, and are quite often fairly effective antioxidants. The conversion products remaining in a polymer after unconsumed inhibitor has been removed from it may ensure long induction periods (Fig.19).[80] Formula (81) shows that a weak inhibitor, in whose presence the critical concentration increases right up to $\delta = 1$, may behave as a strong antioxidant in the presence of a sufficient concentration of a reductant for hydroperoxide.

When a polymer contains both a weak or moderate antioxidant and a hydroperoxide reductant at a constant total concentration $[A] = [IH] + [R_2S]$, substitution in (81) of $\delta = \delta_0 + \delta_i[IH]$ and $[R_2S] = [A] - [IH]$, with neglect of $k_3[IH]$ in comparison with $k_2[RH]$, yields for the critical inhibitor concentration

$$[IH]_{cr}^2 - \left\{\frac{k_4[RH]}{k_3 k_5}(k_3 - \delta_i k_2 [RH]) + [A]\right\}[IH]_{cr} + \frac{\delta_0 k_2 k_4}{k_3 k_5}[RH]^2 = 0. \quad (90)$$

This quadratic equation has two positive real roots provided that [A] exceeds some critical value

$$[A]_{cr} = \frac{k_4[RH]}{k_3 k_5}(\delta k_2 [RH] - k_3) + 2[RH](\delta_0 k_2 k_4 / k_3 k_5)^{1/2}. \quad (91)$$

Thus for every concentration $[A] > [A]_{cr}$ there exist two critical mixture compositions such that only between them is oxidation a stationary process, but outside this range it is autocatalytic. On plots of induction period against composition short induction periods correspond to an autocatalytic process, but long induction periods to a steady-state process. If one of the mixture components is an antioxidant of medium strength, having a critical concentration even in the absence of a reductant, the region of a steady-state process will adjoin the edge of the diagram provided that $[A] > [IH]_{cr}$.

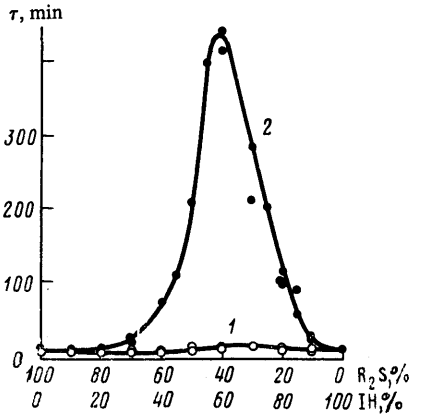


Figure 20. Dependence of induction period τ in the oxidation of polypropylene under 300 mmHg of oxygen at 200 °C on composition of a mixture of phenyl-2-naphthylamine (IH) and didodecyl thiodipropionate (R_2S) [97] at total concentrations (mole kg^{-1}): *1*) 0.005; *2*) 0.010.

Fig.20 shows such plots for two mixture concentrations lying below and above the critical total $[A]_{cr}$. It is evident that doubling the total concentration produces a sharp change in the character of the diagram, with appearance of a narrow maximum[97]. Many similar diagrams have been published[80,109,110].

The above phenomenon, consisting in the longer or more effective inhibition of oxidation by a mixture of two antioxidants than by each component at a specified total concentration, is termed *antioxidant synergism*. The only rigorous criterion of synergism may be the presence of a maximum in the composition dependence of induction period or of a minimum in that of rate of degradation. From a practical point of view it is advantageous to replace an individual antioxidant by a mixture only if the mixture at a constant total concentration (or a constant total cost) retards oxidation longer or more effectively than does each component, whence follows the above definition of synergism.

In some cases a mixture of two antioxidants is less effective than the more effective component at the same partial concentration, a phenomenon that is termed *antioxidant antagonism*. An example of such antagonism was illustrated in Fig. 10. We shall examine another example in greater detail.

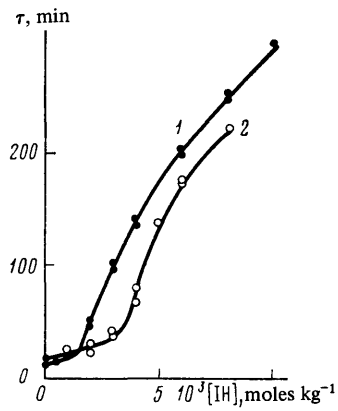


Figure 21. Effect of 2,4,6-tri-t-butylphenol (0.01 mole kg^{-1}) on dependence of induction period in the oxidation of polypropylene under 300 mmHg at 200 °C on the concentration of methylene-2,2′-bis-(4-methyl-6-t-butylphenol)[108]: *1*) second inhibitor absent; *2*) second inhibitor present.

In Fig. 21 the curve representing the dependence of the induction period in the oxidation of polypropylene, containing the weak antioxidant 2,4,6-tri-t-butylphenol at a constant concentration of 0.01 mole kg^{-1}, on the concentration of a second antioxidant (II) lies below the corresponding curve for pure polypropylene almost throughout its length[108], and the partial critical concentration of the strong antioxidant (II) is increased in the presence of weak 2,4,6-tri-t-butylphenol. Assuming that both antioxidants (IH′ and IH″) terminate chains, replacing $k_3[IH]$ in (81) by $k_{31}[IH'] + k_{32}[IH'']$, and rearranging ($[R_2S] = 0$), we obtain

$$[IH']_{cr} = \frac{\delta k_2 [RH]}{(1-\delta) k_{31}} - \frac{k_{32}}{k_{31}} [IH''] . \qquad (92)$$

Differentiating (92) with respect to [IH″], we then find that

$$\frac{\partial [IH']_{cr}}{\partial [IH'']} = \frac{k_2 [RH]}{(1-\delta)^2 k_3} \cdot \frac{\partial \delta}{\partial [IH'']} - \frac{k_{32}}{k_{31}} \qquad (93)$$

will be positive (i.e. the critical concentration of IH′ will increase in the presence of IH″) only if the second antioxidant increases the probability of degenerate chain branching sufficiently strongly, so that

$$\frac{\partial \delta}{\partial [IH'']} \cdot \frac{k_{32} (1-\delta)^2}{k_2 [RH]} > 0. \qquad (94)$$

Hence in this case the antagonism is explained by a marked increase in the probability of chain branching under the influence of the second antioxidant: mixtures of two inhibitors—one strong and the other a weak antioxidant—may in some cases be less effective than one of the components (the strong antioxidant) used separately at the same concentration as in the mixture.

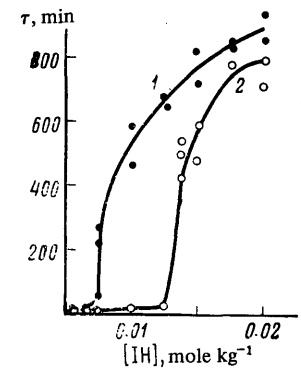


Figure 22. Effect of mixing of inhibitor with polymer on dependence of induction period in the oxidation of polypropylene under 300 mmHg at 200 °C on concentration of dimethylbis-*p*-aminophenylphenoxysilane[111]: *1*) non-uniform; *2*) uniform.

Diminished efficiency of an antioxidant may be due to insufficiently uniform admixture with the polymer. Thus a threefold increase in the "inoperative" concentration of the antioxidant dimethylbis-*p*-phenylaminophenoxysilane was observed[111] on passing from a uniform to a non-uniform distribution (polypropylene powder consisting of spherical particles of mean diameter 0.03 mm moistened with a benzene solution of the antioxidant and dried at room temperature) (Fig. 22).

A theory has been developed for the oxidation of a non-uniformly inhibited polymer[112]. Calculations were based on a simplified scheme for the progress of a branched chain reaction involving active centres of a single type. The variation in concentrations of active centres and inhibitor n and i during such reaction can be described by the equations[100]

$$dn/dt = w_0 + \varphi n - kin, \qquad (95)$$

$$-di/dt = kin, \qquad (96)$$

in which ϕ is the autocatalytic factor, w_0 the rate of chain generation, and k the rate constant of chain termination by the inhibitor. The critical inhibitor concentration in the reaction is $i_{cr} = \phi/k$. Progress of the reaction is autocatalytic or stationary according as $i < i_{cr}$ or $i > i_{cr}$.

For an extended non-uniformly inhibited specimen we must take into account the redistribution of inhibitor and active centres resulting from diffusion, for which purpose we introduce appropriate terms[113] into Eqns.(95) and (96):

$$\partial n/\partial t = D\partial^2 n/\partial x^2 + w_0 + \varphi n - kin, \qquad (95a)$$

$$\partial i/\partial t = D_i\partial^2 i/\partial x^2 - kin, \qquad (96a)$$

where D and D_i are the diffusion coefficients of active centres and of inhibitor, while x is the coordinate. In the oxidation of a long unidimensional specimen[112] part of which ($0 \leq x < x_1$) is devoid of inhibitor, while the remainder contains inhibitor at a constant concentration i_2, the initial concentration of active centres throughout the specimen equals their steady-state concentration in the inhibited portion:

$$n_0 = w_0/(ki_2 - \varphi).$$

The set of equations was integrated on a computer after transformation into

$$\partial N/\partial\tau = \gamma\partial^2 N/\partial z^2 + N(1-I) + (I_2 - 1), \qquad (97)$$

$$\partial I/\partial\tau = \partial^2 I/\partial z^2 - AIN. \qquad (98)$$

Here N and I are dimensionless concentrations corresponding to n and i, while z and τ are the dimensionless coordinate and time:

$$dz = (\varphi/D_i)^{1/2}dx;\ d\tau = \varphi dt;\ N = n/n_0;\ I = ki/\varphi = i/i_{cr}.$$

The coefficients are given by $A = kn_0/\phi$ and $\gamma = D/D_i$. Calculations were based on $A = 10^{-3}$, $\gamma = 1$, a uniform initial distribution of active centres ($N = 1$), and a non-uniform distribution of inhibitor ($I = 0$ for $0 \leq z < z_1$, and $I = I_2$ for $z \geq z_1$). Solutions of Eqns.(97) and (98) are illustrated in Fig.23.

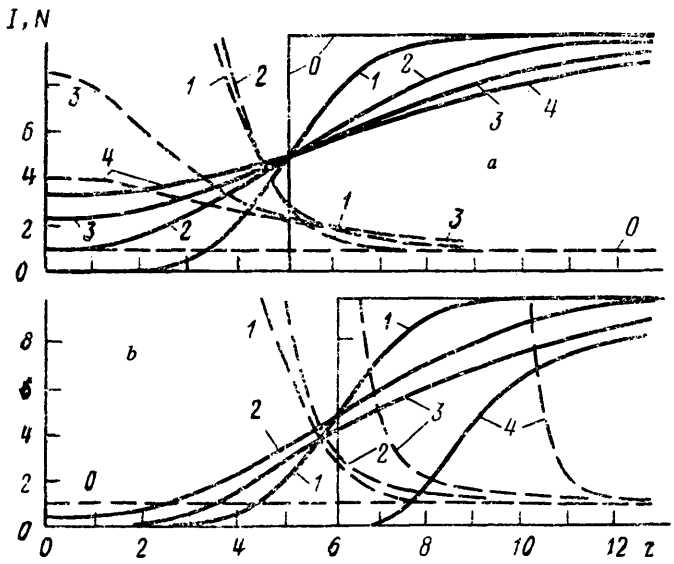


Figure 23. Distributions of dimensionless concentrations of inhibitor and active centres I and N in a unidimensional specimen[112] ($\gamma = 1$; $I_2 = 10$) for different values of z_1: *a*) 5.125; *b*) 6.15 at different times θ during the process: *0*) 0; *1*) 1; *2*) 5; *3a*) 10; *3b*) 12.5; *4a*) 15; *4b*) 17.5.

Fig.23 shows the distributions of dimensionless concentrations of inhibitor and active centres in specimens differing in the size of the initially uninhibited portion z_1. At first the process develops similarly in the two cases: both N and I increase in the originally uninhibited segment. After some time, however, a difference appears: if $z_1 = 5.125$ the concentration I increases monotonically throughout the range $0 \leq z < z_1$, but N begins to decrease: i.e. the process that began in the uninhibited portion of the specimen dies away. With $z_1 = 6.15$, on the other hand, I begins to decrease after some time, whereas N continues to increase. A reaction front appears: within a relatively narrow range of change in z the concentration I changes from approximately zero on the left to more than unity on the right, while N drops sharply in the same interval. The reaction front gradually moves to the right, towards larger z. There thus exists a limiting size of the originally uninhibited region such that, if the actual size is smaller, the process therein dies out; but if the portion free from inhibitor is larger than the critical size, a stable region of rapid oxidation arises, which spreads throughout the specimen.

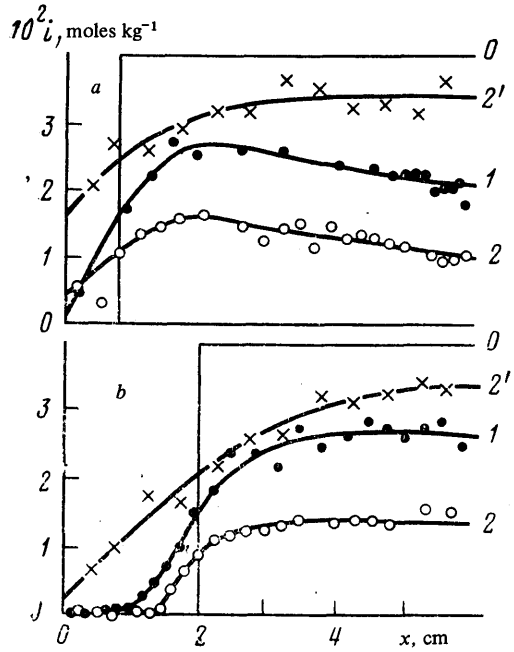


Figure 24. Concentration distribution of inhibitor methylene-2,2′-bis-(4-methyl-6-t-butylphenol) along specimen of atactic polypropylene[114] under an oxygen partial pressure of 150 mmHg (air) at 190 °C for different lengths x_1 (cm) of initially uninhibited region: *a*) 0.8; *b*) 2.0 after different periods of oxidation (min): *0*) 0; *1*) 150; *2*) 300; *2′*) 300, distribution of radioactive inhibitor and conversion products when labelled inhibitor used.

Fig.24 shows the concentration distribution of the inhibitor methylene-2,2′-bis-(4-methyl-6-t-butylphenol) (II) 150 and 300 min after the start of oxidation (in air at 190 °C) of specimens of atactic polypropylene having the non-uniform

initial inhibitor distribution shown by the broken lines 0. If the section devoid of inhibitor is 0.8 cm long, after some time inhibitor penetrates the left-hand (uninhibited) portion, suppressing oxidation. If the uninhibited portion is 2.0 cm long, inhibitor is not detected in the left-hand section, although in both cases conversion products of the inhibitor penetrate the specimen to the very edge ($z = 0$). After oxidation for 300 min the inhibitor-free portion becomes larger than it had been at 150 min. Apart from certain details, such as the maximum in the inhibitor distribution curves in Fig. 24*a* due to enhancement of its solubility in the slightly oxidised polymer and the greater rate of consumption of inhibitor in the right-hand portion (Figs. 23 and 24), calculation and experiment almost coincide[114,115].

Almost all the above experimental results relate to the oxidation of polypropylene, since systematic data have not appeared for other polymers. Passing from one polymer to another involves changes primarily in ease of detachment of the hydrogen atom from the monomer unit RH, in the distances between them, and in the solubility of oxygen: i.e. the rate constants k_0, k_1, k_2, and k_4, those of quadratic chain termination, and also the yields of hydroperoxide α and those of radicals on its breakdown δ are affected. Changes in these parameters entail changes in the rates both of uninhibited and of inhibited oxidation.

As mentioned above, inhibitors retard oxidation by interacting with peroxy-radicals $RO_2^{\cdot}$. The reactivity of such radicals is little dependent on the structure of the residue R, which is remote from the reaction centre. The rate of chain termination, i.e. the rate of interaction of $RO_2^{\cdot}$ radicals with inhibitor molecules, depends not only on the reactivity of the reactant species but also on the number of collisions between them, i.e. on concentrations and diffusion coefficients.

If a polymer contains functional groups capable of forming complexes with inhibitor molecules

$$IH + X{-}R \rightleftharpoons IH \cdot X{-}R, \qquad (99)$$

the concentration of mobile inhibitor molecules not bound in complexes will form only part its total concentration in the polymer [IH]. In the simplest case, when $[IH] \ll [IH]_p$ and $[IH]_p \ll [X{-}R]$, we obtain

$$[IH] \text{ moles kg}^{-1} = \frac{[IH \cdot XR]}{k[X{-}R]} = \frac{m[IH]_p}{1000kn}, \qquad (100)$$

where m is the equivalent weight of a monomer unit and n the number of functional groups in a unit that are involved in complex formation. Under otherwise similar conditions the effective rate constant of chain termination by an inhibitor that forms complexes with particular functional groups in the polymer will be smaller than the corresponding rate constant for an inhibitor that is incapable of complex formation. This apparently explains the relative ineffectiveness of phenolic inhibitors in polyamides[116].

Inhibitor molecules can be retained not only by polar groups but also by sites of disorder in the relative arrangement of macromolecules[117]. The sorption capacity of a polyalkene, i.e. the number of sites capable of retaining simple substances, can be increased by special treatment of the melt[118–120]. Enhancement of sorption capacity leads to some increase in the critical concentration of the inhibitor accompanied by decrease in the rate of its consumption, which at high inhibitor concentrations may lengthen the time during which it operates.

With a given polymer in the solid state the parameters k and i_{cr} in formula (66) for a particular inhibitor depend on the temperature–time conditions of preparation of the specimen[121,122]. Good compatibility of inhibitor with polymer diminishes the effectiveness of the former[123]. Compatibility was measured[123] by the rate of vaporisation of the inhibitor from the polymer, a quantity proportional to the concentration of mobile (not sorbed at any centres) inhibitor molecules.

The rate of inhibited oxidation increases[124,125] on passing from a homopolymer of ethylene to copolymers with propylene and with vinyl chloride. Both parameters in Eqn. (66), k and i_{cr}, increase, passing through maxima at certain contents of the foreign units. These parameters increase also with the γ-ray dosage of polyethylene[126]. Any breakdown in order of arrangement of macromolecules probably diminishes the stability of the polymer.

VI. SOME SPECIAL METHODS FOR THE STABILISATION OF POLYMERS

All known antioxidants rapidly become less effective with rise in temperature, and all the usual antioxidants cease to retard the oxidation of polymers between 270 and 300 °C. However, oxidation can be slowed down even at high temperatures.

A polymer can be protected from oxidation under processing conditions by conducting the operation in an inert atmosphere (nitrogen, carbon dioxide). In small-scale production an inert atmosphere can be produced in a closed space by the use of absorbents for oxygen, but these cannot protect the polymer from oxidation during storage and use[127]. To estimate the time during which such an absorbent acts we take the diffusion coefficient of molecular oxygen in the polymer at room temperature to be 10^{-6} cm^2 s^{-1},[128] and the solubility coefficient to be 0.02 mole kg^{-1} atm^{-1}. In air ($p_{O_2} = 0.2$ atm) the concentration of oxygen at the polymer surface will be 4 mmoles kg^{-1} or 4 μmoles cm^{-3}. If all the oxygen is absorbed in a layer 0.1 cm thick, its flow through 1 cm^2 of surface will be at least 40 pmoles cm^{-2} s^{-1}; and if the absorbent concentration is 0.1 mole kg^{-1} or 10 μmoles cm^{-2} in the 0.1-cm layer, the absorbent will be exhausted in 2.5×10^5 s or 3 days. This time will become shorter with rise in temperature.

One consequence of thermo-oxidative degradation is the formation of volatile products, some of which may be toxic[129]. Special absorbents are introduced into polymers to eliminate this effect. Thus barium, lead, or other salts of weak organic acids are added to absorb hydrogen chloride formed on the degradation of poly(vinyl chloride)[130]; polyamides are added to absorb formaldehyde formed in the oxidative degradation of polyoxymethylene; etc.

Discoloration during the oxidation of polymers is due to formation of a system of conjugated bonds. Substances capable of adding to such bonds will weaken the effect[130].

Every new component introduced into a polymer, either by chance or deliberately, influences the resistance of the latter to thermo-oxidative degradation. Thus metals of variable valency increase the yield of free radicals formed by the breakdown of hydroperoxides. This effect can be lessened by introducing into the polymer complexing agents, in particular ethylenediaminetetra-acetic acid and its derivatives[130].

The widely used colorant, filler, and photostabiliser—carbon black—protects a polymer from thermal oxidation at not very high temperatures, but catalyses the oxidation of many stabilisers at processing temperatures[131,132]. Polymers containing carbon black are protected by the use of thiophenols[131,132] and other sulphur derivatives[130].

At present no general methods are available for combating the harmful effects of impurities.

Thus intense research on the ageing and stabilisation of polymers has not yet eliminated the empirical selection of

stabilisers for specific polymer materials. However, from the time of the first investigations in this field the range of compounds among which effective stabilisers must be sought has been continually narrowed down, and the synthesis of novel stabilisers has become increasingly selective. In some cases the concept of critical concentrations has permitted prediction of the effects of mixing two antioxidants differing in structure. Among problems that remain unsolved in the stabilisation of polymers the first task is to develop methods for retarding oxidation at temperatures above 300 °C.

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