Pure & Appl. Chem., Vol.52, pp.337-348.
Pergamon Press Ltd. 1980. Printed in Great Britain.

THE CRITICAL PHENOMENA IN THE INHIBITED OXIDATION OF POLYOLEFINS

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The theory of the critical phenomena in the inhibited oxidation of polymers is considered. This theory deals with the lower and the upper critical concentrations of inhibitors, the critical values of the mixed antioxidant composition, etc. The theory is illustrated by experiments on inhibited oxidation of polyolefins.

Critical phenomena which consist in a sharp change of reaction kinetics under certain "critical" values of reaction conditions are characteristic of branched chain reactions.

To understand the nature of critical phenomena consider a mechanism of the branched chain reaction in the presence of an inhibitor. In the most simple case, the change in active centers concentration n in the course of such a reaction is expressed by equation

$$\frac{dn}{dt} = W_o + fn - gn = W_o + \varphi n \qquad (1)$$

where f denotes the probability of chain branching, i.e. the mean number of new chains formed by one center per unit of time, and g is the probability of chain termination during that time. The value

$$\varphi = f - g \qquad (2)$$

is called the factor of autoacceleration. If $f > g$, i.e. $\varphi > 0$, the number of active centers increases according to expression

$$n = n_o e^{\varphi t} \qquad (3)$$

where n_o is the value of n when $t = 0$.

If $f < g$, i.e. $\varphi < 0$, the reaction is stationary, i.e. its rate is not an explicit function of the reaction time. The rate of such a process is

$$W = k_p n = k_p \frac{W_o}{f - g} \qquad (4)$$

where k_p is the propagation rate constant. The values of reaction conditions at which φ becomes 0 are called critical (Ref.1).

The solution to the system

$$\frac{dn}{dt} = W_o + fn - k_t n \qquad (5)$$

and

$$-\frac{di}{dt} = k_t i n \qquad (6)$$

where i is the inhibitor concentration, and k_t the chain termination rate constant ($g = k_t i$), is the series of curves $n(t)$ (Fig. 1). The curves corresponding to $i_o < fk_t^{-1}$ differ from that for $i_o > fk_t^{-1}$ so that when $i_o > fk_t^{-1}$ there is a certain delay in the active center concentration increase. The concentration of inhibitor

$$i_{cr} = \frac{f}{k_t} \qquad (7)$$

is called the critical one.

It may be seen from Fig.2 that the time necessary to achieve a certain value of n known as the induction period (τ) increases with the initial concentration of inhibitor so that there is a sharp bend in the curve $\tau(i_o)$ at the point $i_o = i_{cr}$ (Ref.2). Such a dependence permits easy estimation of the critical inhibitor concentration, namely the lower one.

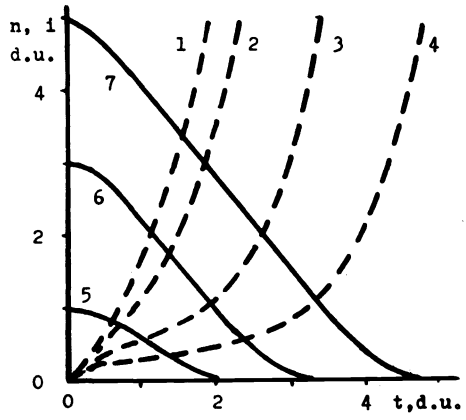


Fig.1. Dimensionless concentrations of active centers (1 - 4) and of inhibitor (5 - 7) as function of dimensionless time in the course of branched chain reaction described by system (5)-(6). $W_o = f = k_t = 1$, initial concentrations of inhibitor: 0 (1), 1 (2;5), 3 (3;6), and 5 (4;7) dimensionless units.

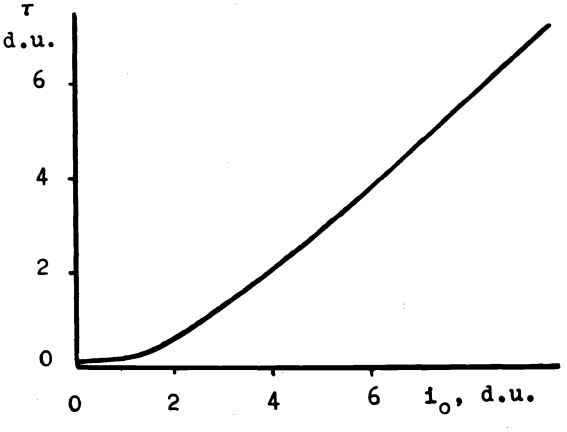


Fig.2. Induction period as a function of the initial inhibitor concentration (calculated from equations (5) and (6)).

Fig.3 shows as example the dependence of induction period for high density polyethylene oxidation on the concentration of the inhibitor 2,2′-methylene-bis(4-methyl-6-tert.butylphenol). A certain difference in the peculiarities of calculated and theoretical curves is due to the difference between the complex mechanism of polymer oxidation and simplified mechanism used for calculations.

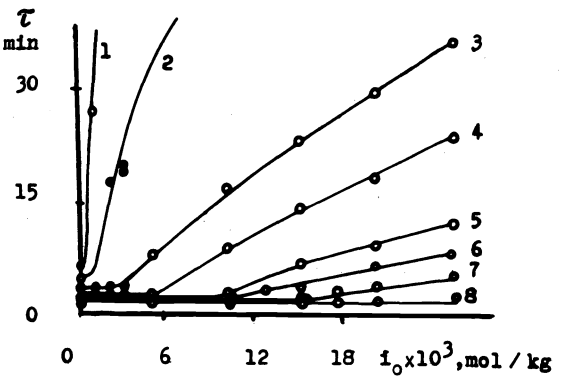


Fig.3. Induction period of polyethylene oxidation as a function of the initial concentration of 2,2′-methylene-bis(4-methyl-6-tert.butylphenol). Oxygen, 300 torr; temperatures: 200 (1), 220 (2), 230 (3), 240 (4), 250 (5), 260 (6), 265 (7) and 270°C (8).

Free radicals of $R^\bullet$, $RO_2^\bullet$, and some other types are the active centers in the polymer oxidation. Direct chain branching, i.e. a reaction of type

$$R^\bullet\ (RO_2^\bullet) + nRH \longrightarrow 3R^\bullet(RO_2^\bullet) + \text{products} \qquad (8)$$

where RH denotes the monomeric unit of polyolefin, cannot proceed because the free radicals in polymer oxidation reactions do not possess the energy needed for such a branching. Formed as a result of reaction (8) the combination of three free radicals surrounded by a thick fence of neighbouring segments of macromolecules would recombine with probability close to unity. For this reason only degenerate chain branching is possible in a polymeric substance (and in the liquid phase hydrocarbon oxidation), i.e. additional chain generation proceeds as a result of decomposition of relatively stable intermediates, the hydroperoxide groups, or of oxidation of aldehyde groups formed at high extents of polymer oxidation.
According to Semenov (Ref.3), the factor of autoacceleration of a degenerate branched chain reaction is

$$\varphi = \frac{\nu\delta - 1}{\Theta} \qquad (9)$$

where ν is the unbranched chain length, δ is the probability of degenerate chain branching at one step of chain propagation, and Θ is the mean lifetime of the chain branching product.
The result of substituting the chain length value (Ref.3) $\nu = 1 + k_p/k_t i$ into Eq.9 is

$$\varphi = k_d\left(\delta + \frac{\delta k_p}{k_t i} - 1\right) \qquad (10)$$

where $k_d = 1/\Theta$ is the rate constant of hydroperoxide group decomposition. Assuming that $\varphi = 0$, we find the value of the inhibitor critical concentration

$$i_{cr} = \frac{\delta k_p}{k_t(1 - \delta)} \qquad (11)$$

It results from Eq.11 that the first condition for the critical concentra-

tion existence is

$$\delta < 1 \qquad (12)$$

Following are some experimental data on the critical inhibitor concentrations in polyolefin oxidation.

Fig.4 shows the experimental dependence of the induction period of polyethylene oxidation on the logarithm of inhibitor concentration. In these coordinates the dependence of induction period on i_o at $i_o > i_{cr}$ transforms into straight line. It may be seen also from Fig.3 and Fig.4 that the critical concentration which corresponds to the bend in the curve $\tau(i_o)$ increases with the oxidation temperature. The effective activation energies calculated from such dependences are 28 kcal/mol in polyethylene and 33 kcal/mol in polypropylene and practically do not depend on the nature of effective inhibitors.

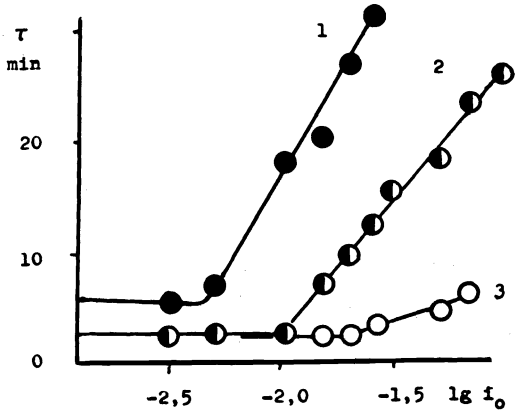


Fig.4.
Induction period of polyethylene oxidation as a function of the logarithm of inhibitor concentration. Oxygen, 300 torr; 230 (1), 240 (2) and 250°C (3).

It follows from linearisation of curves $\tau(i_o)$ in semilogarithmical coordinates that above the critical concentration the inhibitor consumption is first order in inhibitor concentration. In Ref.4 an expression is proposed which connects the induction period with the critical concentration and the effective rate constant, k_{eff}, of inhibitor consumption in the given polymer

$$\tau = \tau_{cr} + \frac{1}{k_{eff}} \ln \frac{i_o}{i_{cr}} \qquad (13)$$

This expression satisfactorily describes the experimental dependences which are shown in Fig.3 and Fig.4.

If the initial inhibitor concentration is constant, τ decreases with the oxidation temperature until i_{cr} becomes equal to i_o. Above this limiting temperature, which depends on i_o, the inhibitor does not retard oxidation. The lower critical concentration of inhibitor depends upon the structure and composition of the oxidizing polymer. It rapidly increases with any disturbance of macromolecule structure caused by replacing the homopolymer by a copolymer (Fig.5), by γ-irradiation of polymer (Fig.6), and depends on method of the sample preparation. In polyolefin samples prepared by fast cooling of the polymer melt the critical concentrations of the same inhibitor are ever higher that in samples prepared by slow cooling (Refs. 5-7).

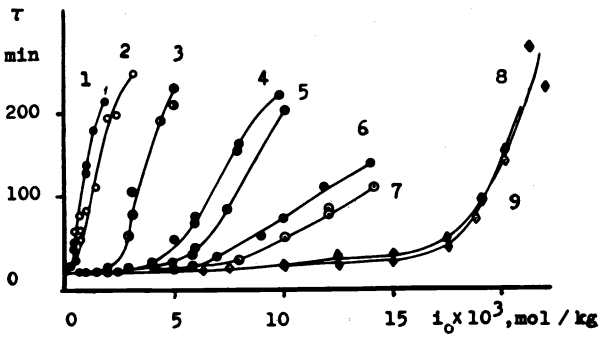


Fig.5. Induction period of oxidation of ethylene-propylene copolymers as a function of concentration of phenyl-β-naphtylamine. 180°C, 300 torr, propylene units content (mol.%): 0 (1), 0.6 (2), 1.5 (3), 4.4 (4), 5.1 (5), 12 (6), 24 (7), and 100 (8 - isotactic, and 9 - atactic polypropylenes).

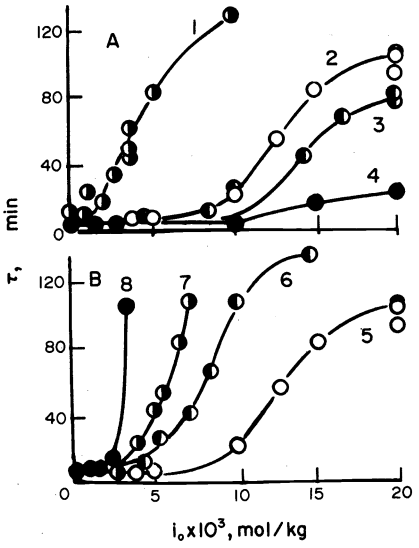


Fig.6. Induction period of polyethylene oxidation as a function of concentration of 2,2'-methylene-bis(4-methyl-6-tert.butylphenol), 200°C, oxygen, 300 torr. Polyethylene irradiated with γ-rays at a dose: 0 (1), 50 (2;5 - 8): A - without a third component, B - with dilaurylthiodipropionate, 0 (5), 0.0125 (6), 0.025 (7), and 0.050 mol/kg.

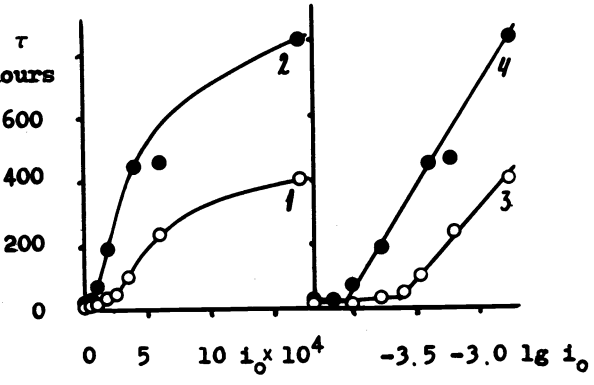
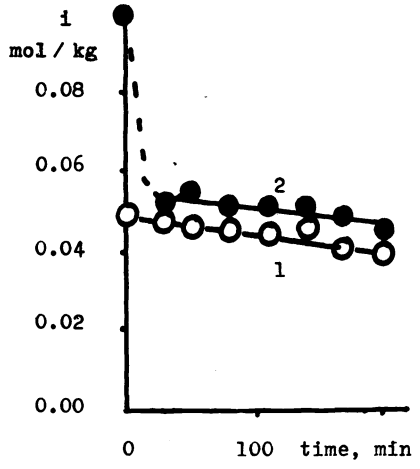


Fig.7. Induction period of polypropylene oxidation as a function of concentration of the methyl ester of 3,5-di-tert.butyl-4-hydroxyphenyl-β-propyonic acid. 100°C, 300 torr, rapidly cooled (1) and slowly cooled (2) samples. 3 and 4 - the same curves in coordinates τ - lg i_0.

Besides the lower critical concentration considered here an upper critical concentration of inhibitor can be observed in certain cases.
It can be seen from Fig.8 that the phenyl-β-naphtylamine inhibitor added to polymer in a concentration i_0=0.05 mol/kg (200°C, 300 torr) is slowly consumed for a prolonged period. If one increases the initial concentration of this inhibitor to 0.10 mol/kg a part of it quickly (in some minutes) disappeares until the concentration becomes 0.052 mol/kg , after which moment the rate of consumption rapidly decreases. In the period of rapid con-

sumption the molecular mass of polymer also sharply decreases. In some cases above the upper critical concentration the induction period of polymer oxidation stops rising with the initial inhibitor concentration (Fig.9).



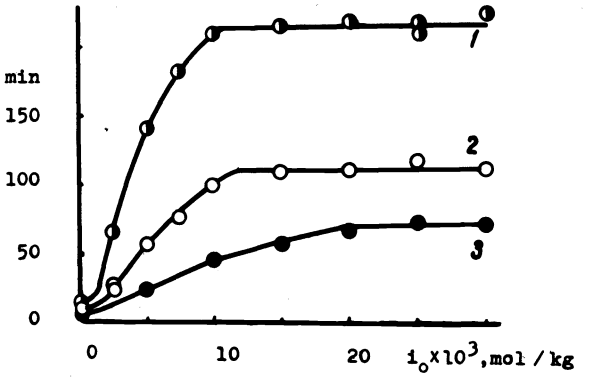


Fig.8.(left) Consumption of phenyl-β-naphtylamine during the induction period of polypropylene oxidation when the initial inhibitor concentrations are under (1) and above (2) the critical one.Oxygen, 300 torr, 200°C.

Fig.9.(right) Induction period of polypropylene oxidation as a function of concentration of 2,2'-methylene-bis(4-chloro-6-tert.butylphenol) at 180 (1), 190 (2), and 200°C (3); oxygen, 300 torr.

To explain the existence of the upper critical concentration it is necessary to accept the idea that the degenerate chain branching probability increases with concentrations of some inhibitors (Ref.8):

$$\delta = \delta_0 + \delta_i i + \delta_{ii} i^2 + \ldots \qquad (14)$$

or to retain only two first terms of the expression

$$\delta = \delta_0 + \delta_i i \qquad (15)$$

Substituting the above expression into Eq.10 and putting $\varphi = 0$, we obtain the quadratic equation for determination of i_{cr}

$$\delta_i i_{cr}^2 + \frac{\delta_i k_2 [RH]}{k_t} - (1 - \delta_0)\, i_{cr} + \frac{\delta_i k_2 [RH]}{k_t} = 0 \qquad (16)$$

When

$$\delta_i k_2 [RH] < (1 + \delta_0 - 2\sqrt{\delta_0}) k_t \qquad (17)$$

this equation has two real positive roots, i_{1cr} and i_{2cr}. The oxidation is stationary and its rate is low only when $\varphi < 0$, that is in the range between i_{1cr} and i_{2cr}.The former is the lower and the latter is the upper critical concentrations.

If

$$\delta_i k_2 [RH] > (1 + \delta_0 = 2\sqrt{\delta_0}) k_t \qquad (18)$$

The equation 16 has no real roots, i.e. there will be no stationary reaction range in the presence of such an inhibitor. The inhibitor for which Eq. 16 is true cannot effectively retard the polymer oxidation.

Of certain interest is the case when a mixture of two inhibitors is added to the polymer. We shall consider only the lower critical concentration. Substituting $k_{1t}i_1 + k_{2t}i_2$ for $k_t i$ in Eq.10, we find the expression for the critical concentration of the first inhibitor i_{1cr} in the presence of the second one

$$i_{1cr} = \frac{\delta k_2[RH]}{k_{1t}(1 - \delta)} - \frac{k_{2t}}{k_{1t}} i_2 \qquad (19)$$

According to Eq.19, when δ = const. the partial critical concentration of the first inhibitor must decrease in the presence of the second one. However, as one may see from Fig.10, the critical concentration of the inhibitor 2,2'-methylene-bis(4-methyl-6-tert.butylphenol) in the presence of another phenolic inhibitor, 2,4,6-tri-tert.butylphenol, not only does not decrease but even increases, that is $\partial i_{1cr}/\partial i_2 > 0$. It follows from Eq.19 that this requires

$$\frac{\partial \delta}{\partial i_2} > \frac{k_{2t}(1 - \delta_o)^2}{k_2[RH]} \qquad (20)$$

or, assuming that δ does not depend on i_1 and the dependence of δ on i_2 is described by expression 15 ($\delta = \delta_o + \delta_i i_2$)

$$\delta_i k_2[RH] > (1 - \delta_o)^2 k_{2t} \qquad (21)$$

If $\delta_o < 1$, so $\sqrt{\delta_o} > \delta_o$, and $(1 - \delta_o)^2 > (1 - \sqrt{\delta_o})^2 = 1 + \delta_o - 2\sqrt{\delta_o}$, i.e. all the inhibitors which increase the lower critical concentrations of ones possessing such concentrations must be deprived of critical concentrations. In Ref.9 a classification has been proposed according to which the inhibitor deprived of the critical concentration is a weak antioxidant.

Consider another case when a mixture of two antioxidants of different action is added to the polymer, i.e. the mixture of the chain terminating inhibitor and a compound decomposing the hydroperoxide with practically no radical yield. Such compounds are the aliphatic sulfides (Ref.10):

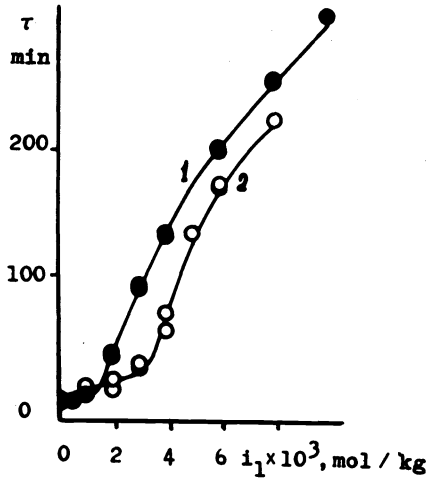
$$ROOH + R_2S \xrightarrow{k_s} ROH + R_2SO \qquad (22)$$

Substituting $1/\theta_1 = k_2[RH] + k_s[R_2S]$ for $1/\theta = k_d = k_4[RH]$ in Eq.9 and assuming that only a part of the hydroperoxide $k_4[RH]/(k_4[RH] + k_s[R_2S])$ decomposes producing free radicals, we obtain the expression for φ in the polymer, containing the mixture of two antioxidants

$$\varphi = \left\{ \frac{\nu \delta k_4[RH]}{k_4[RH] + k_s[R_2S]} - 1 \right\} (k_4[RH] + k_s[R_2S]) = \varphi_o - k_s[R_2S] \qquad (23)$$

According to Eq.23, if $k_s[R_2S]$ is high enough, the factor of autoaccelera-

tion φ may become 0 and even negative when Eq.20 is true for given system polymer - inhibitor i.e. when in the absence of the hydroperoxide decomposer the inhibitor cannot effectively retard the oxidation. If Eq.17 is true for the given inhibitor and the latter has two critical concentrations, the added hydroperoxide decomposer can widen the range over which oxidation is stationary, that is to diminish the lower critical concentration and rise the upper one.



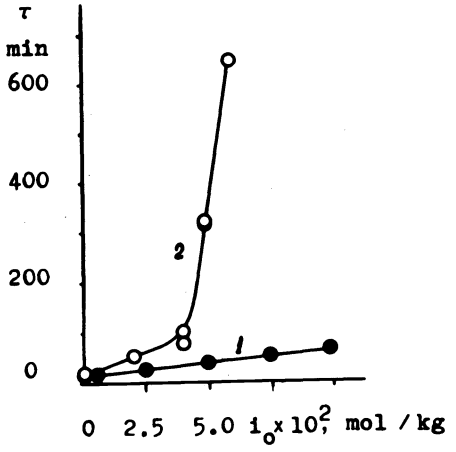


Fig.10.(left) Induction period of polypropylene oxidation as a function of concentration of 2,2'-methylene-bis(4-methyl-6-tert.butylphenol) in the absence (1) and in the presence of weak antioxidant 2,4,6-tri-tert.butylphenol. 200°C, oxygen, 300 torr, i_2 = 0.1 mol/kg.

Fig.11.(right) Induction period of polypropylene oxidation as a function of 2,4,6-tri-tert.butylphenol concentration in the absence (1) and in the presence of dilaurylthiodipropionate (R_2S), 0.08 mol/kg; 200°C, 300 torr.

Fig.11 shows that in the presence of dilaurylthiodipropionate the inhibitor 2,4,6-tri-tert.butylphenol has a critical concentration, while in the absence of sulfide it has no critical concentration and increases that of the effective inhibitor (see also Fig.10).

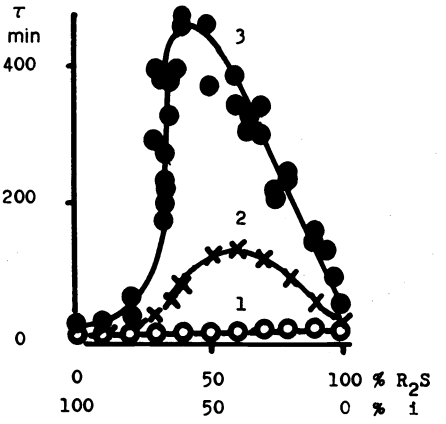
If over the whole set of experiments the sum of initial concentrations of inhibitor and hydroperoxide decomposer is kept constant

$$i_0 + [R_2S]_0 = [A] = \text{const.} \qquad (24)$$

i_0 will be the function of R_2S concentration. On the other hand, it follows from Eq.23 that the critical concentration of inhibitor diminishes with increasing concentration of sulfide, i.e. the lower is i_0 the higher must be $k_s[R_2S]$ for φ to become zero. If Eq.18 is true, the inhibitor cannot effectively retard the oxidation in the absence of R_2S. The hydroperoxide decomposer cannot terminate chains and so cannot effectively retard oxidation in the absence of inhibitor. If $[A]$ is sufficiently high, the curves $i_{cr}=f([R_2S])$ and $i_0=f'([R_2S])$ intersect in two points, i.e. two critical values of the mixed antioxidant composition exist and within these values the oxidation will be stationary and slow. Long induction pe-

riods will correspond to this range of stationary reaction while outside the oxidation will proceed with short induction periods.
It may be seen from Fig.12 that within a certain composition range the mixture of a weak antioxidants 2,6-di-tert.butyl-4-phenylphenol and dilaurylthiodipropionate effectively retards the polypropylene oxidation while outside this range the induction periods are short. At 200°C the maximum in the curve "composition - induction period" appears only if the overall concentration $[A]$ exceeds 0.01 mol/kg. Thus the experimental results support the theory.

Fig.12.
Induction period of polypropylene oxidation as a function of the composition of mixture of 2,6-di-tert.butyl-4-phenylphenol and dilaurylthiodipropionate. 200°C, 300 torr, total concentrations of antioxidants A : 0.005 (1), 0.010 (2), and 0.030 mol/kg .



A polymer sample oxidation in the presence of an inhibitor, a strong antioxidant, unevenly distributed over the sample was considered in Ref.11. Taking into account the diffusion of active centers and of the inhibitor, the system of Eq.6&7 will become

$$\frac{\partial n}{\partial t} = W_o + fn - k_t in + D_n \frac{\partial^2 n}{\partial x^2} \qquad (25)$$

$$\frac{\partial i}{\partial t} = - k_t in + D_i \frac{\partial^2 i}{\partial x^2} \qquad (26)$$

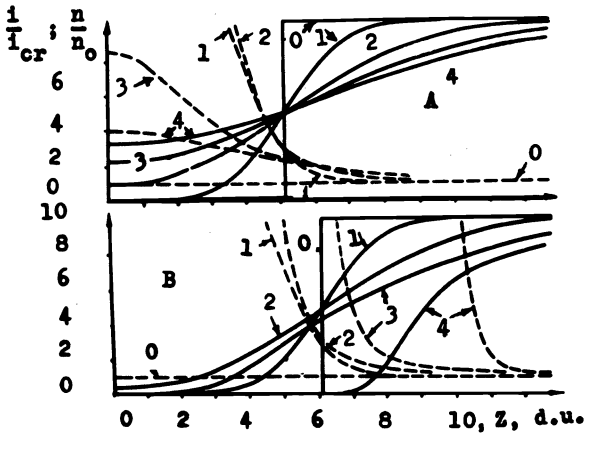
where D_n and D_i are the diffusion coefficients of the active centers and of the inhibitor. The system has been integrated numerically. For convenience the variables in Eq.25&26 were substituted by dimensionless ones:

$dz = (f/D_i)dx$; $d\tau = fdt$; $N = n/n_o$; $\gamma = D_n/D_i$; $I = (k_t/f)i = i/i_{cr}$,

$A = (k_t/f)n_o = k_t W_o (f^2(I_2 - 1))^{-1}$.

The initial conditions were: $N = 1$ over the whole sample length $0 \leqslant z < \infty$, $I = 0$ at $0 \leqslant z < z_1$ and $I = I_2 > I_{cr}$ at $z_1 \leqslant z < \infty$.
The dimensionless concentrations of active centers and of inhibitor calculated for various sizes of the initially uninhibited part of the sample ($z_1 = 5.125$ and $z_1 = 6.15$ dimensionless units) are shown in Fig.13. Two different sizes of uninhibited part correspond to two different paths of the process. If $z_1 = 5.125$, the inhibitor, diffusing through the uninhibited part of the sample suppresses an arising autoaccelerated reaction, whi-

le if $z_1 = 6.15$ a fast reaction zone is retained at the edge of the uninhibited part, and further on it extends. Calculations show that there is a certain limiting (i.e. critical) size of the uninhibited part of the sample. If the real size of the uninhibited part is larger than the limiting one, the fast reaction zone is retained in this part, but if it is smaller than the limiting size, the inhibitor suppresses the reaction. The limiting size of the uninhibited part of the sample must depend on the oxidation conditions and on the inhibitor concentration outside that part.
Experiments support the possibility of two process paths in the unevenly inhibited sample and the existence of a limiting size of the uninhibited part of it (Ref.12 & 13). Unevenly inhibited samples were prepared from amorphous atactic polypropylene by means of uniting plates of the uninhibited and inhibited polymer. After heating the sample in air during a certain time, it was cut into little fragments in which the inhibitor concentration was determined. It is seen from Fig.14 that when the length of the uninhibited part was 0.8 cm (190°C, inhibitor 2,2'-methylene-bis(4-methyl-6-tert.-butylphenol), $i_0 = 0.04$ mol/kg) the reaction proceeded by the first path : the inhibitor suppressed the reaction, whereas when the size of that part was 2.0 cm the second path was observed : there arose a spreading fast reaction zone.



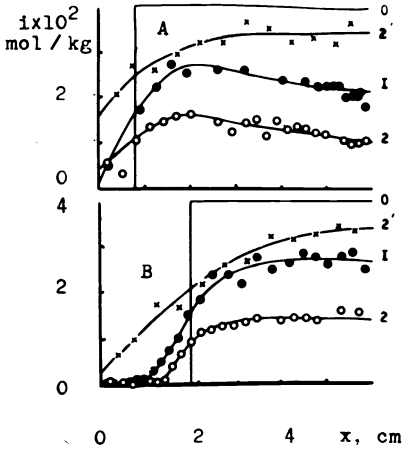


Fig.13.(left) Distribution of dimensionless concentrations of inhibitor i/i_{cr} (———) and of active centers n/n_0 (- - -) over the sample length (calculated by Eqs.25 & 26). The lengths of uninhibited parts are 5.125 (A) and 6.15 (B), the reaction time : (A) 0 (0), 1 (1), 5 (2), 10 (3), and 15 (4); (B) 0 (0), 5 (2), 12.5 (3), and 17.5 (4) dimensionless time units.

Fig.14.(right) Distribution of inhibitor concentration (1; 2) and the sum of inhibitor and the products of its conversion concentrations (2') over the length of atactic polypropylene sample. 190°C, air, inhibitor 2,2'-methylene-bis(4-methyl-6-tert.butylphenol), $i_0 = 0.04$ mol/kg . Lengths of the uninhibited part of sample : 0.8 cm (A) and 2.0 cm (B), the oxidation times : 0 (0), 150 min (1), and 300 min (2; 2').

It was found by varying the sizes of sample parts that in the case shown in

the critical size of the uninhibited part was 1.4 ± 0.05 cm. The critical size rose with the inhibitor concentration and decreased with oxidation temperature. Some quantitative differences between the calculation and experiment were due to no allowance for side reactions of the inhibitor in the simplified calculations.

The idea of a critical size of the uninhibited part of the sample makes possible an unbiassed estimate of the admissible degree of evenness in the mixing of the polymer and inhibitor. The value of the lower critical concentration is the measure of the inhibitor efficiency in the given polymer. Besides their practical value, the critical phenomena may serve as a tool for study of the chain branching and chain termination reactions in polyolefin oxidation. The facts of inhibitor and oxygen participation in degenerate chain branching were found by means of critical phenomena. It will be stressed, however, that the hydroperoxide decomposition reaction is not only step of polyolefin oxidation responsible for degenerate chain branching probability. Unlike the oxidation of low-molecular hydrocarbons, the hydroperoxide yield of polyolefin oxidation is substantially lower than 100 % and depends on the oxidation conditions (Refs. 14 & 15), i.e. the same effect of oxygen or inhibitor on degenerate chain branching can be caused in different ways.

Study of critical phenomena permits understanding the phenomenon of synergism and many other regularities of polyolefin inhibited oxidation.

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