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M. B. NEIMAN, V. B. MILLER, Yu. A. SHLYAPNIKOV, and E. S. TORGUYEVA

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Abstract

Full Text

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DEPENDENCE OF THE INDUCTION PERIOD OF OXIDATION ON THE CONCENTRATION OF ANTIOXIDANT

(Presented by Academician V. N. Kondrat︠ʹ︡ev, 29 VII 1960)

In the 45 years that have elapsed since the discovery of antioxidants by Moureu and Dufraisse, numerous works have appeared devoted to the study of the mechanism of their action (the principal works on oxidation inhibitors have been systematized and summarized in the review ([1])).

However, the question of the dependence of the induction period of oxidation on the concentration of antioxidant has not been sufficiently investigated. In works on polymerization ([2]) it was assumed that between the rate of initiation w_i, the induction period τ, and the concentration of inhibitor x there exists the relation

$$\tau = x/w_i. \qquad (1)$$

Formula (1) implies a linear increase of the induction period with the concentration of inhibitor. The formula given is also often used to determine the rate of initiation in the oxidation of hydrocarbons in the liquid phase.

Fig. 1. Increase in the concentration of active centers with time in the oxidation reaction in the presence of various antioxidant additions. 0—without addition; 1—addition x_0; 2—$2x_0$; 3—$3x_0$; 4—$4x_0$; 5—$5x_0$.

Only recently a paper appeared ([3]) in which it was shown that, in the oxidation of rubber, the induction period increases linearly as a function of the antioxidant

Figure 2

Figure 2: Figure 2

concentration only up to certain, not very high concentrations of the latter. With further increase in the concentration of inhibitor, the linear relation ceases to hold, since the inhibitor itself is appreciably oxidized and begins to play the role of an initiator.

The question of the effect of very small concentrations of antioxidant on the induction period of oxidation has not yet been investigated.

As is known, oxidation reactions in the gas, liquid, and solid phases proceed in accordance with the chain theory of degenerate branching, developed by N. N. Semenov (^{4}). The concentration of active centers n increases with time according to the law

$$\frac{dn}{dt} = w_i + \varphi n, \tag{2}$$

where φ is the autoacceleration factor.

If an antioxidant that terminates chains is added to the oxidizing substance in concentration x, then the reaction will be described by the system of equations

$$\frac{dn}{dt} = w_i + \varphi n - kxn, \tag{3}$$

$$-\frac{dx}{dt} = kxn. \tag{4}$$

Here k is the rate constant of the reaction of the inhibitor with active centers. It is assumed here that, as a result of chain termination, a stable radical is obtained, which has practically no effect on the course of the oxidation reaction.

Fig. 2. Increase in the induction period as a function of the initial concentration of antioxidant

Let us introduce dimensionless variables: the concentration of active centers $v = n/w_i\tau_0$, the concentration of antioxidant $x = x/w_i\tau_0$, and the time $\theta = t/\tau_0$. Then equations (3), (4) are reduced to the form

$$\frac{dv}{d\theta} = 1 + av - bxv, \tag{5}$$

$$-\frac{dx}{d\theta} = bxv. \tag{6}$$

Figure 3

Figure 3: Figure 3

Here $a = \varphi\tau_0, \quad b = kw_i\tau_0^2$.

For values $x_0 < a/b$, the dimensionless concentration of active centers (and the oxidation rate) increase exponentially with time, as is shown by curves 0-2 in Fig. 1.

If $x_0 > a/b$, then a small, approximately stationary reaction rate is soon established, and the concentration of active centers is

$$v \simeq 1/(bx_0 - a). \tag{7}$$

Only when, as a result of consumption of the antioxidant, the value bx_0 approaches the value a, does the induction period end, and the reaction rate begins to increase, as is shown by curves 3-5 in Fig. 1.

Usually the end of the induction period is taken to be the time when an appreciable amount of reaction products accumulates in the system, which corresponds to some value $v = v_1$. This value v_1 is shown in Fig. 1 by a dashed line; the abscissas of the points of its intersection with the curves $v = f(\theta)$ determine the magnitudes of the induction periods at different additions x_0 of antioxidant.

It is clear that at small values of x_0 the induction period changes comparatively slowly, while at larger values it changes much more rapidly, as is shown in Fig. 2. Here the segment AB corresponds to values $x_0 < a/b$, and the segment BC to values $x_0 > a/b$. In reality there is a smooth transition of the straight line AB into the straight line BC, as is shown in the figure by the dashed line.

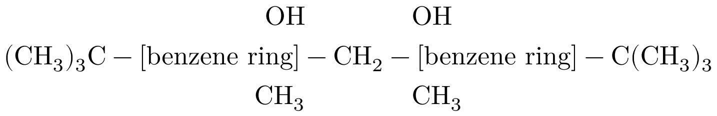
Fig. 3. Dependence of the induction period during thermo-oxidative destruction of polypropylene on the addition of antioxidant. In all experiments $p_{\mathrm{O2}} = 300$ mm

To verify the conclusions presented, we carried out a number of series of experiments to determine induction periods during the thermo-oxidative destruction of polypropylene in the presence of different concentrations of a series of antioxidants—derivatives of phenol and aromatic amines.

In all the cases investigated, in agreement with the considerations given above, at very small concentrations x the derivative $d\tau/dx$ had a small value, increasing sharply at higher concentrations x.

As an example, Fig. 3 gives the results of our experiments on the deter-

of the induction periods for the oxidation of molten polypropylene in the presence of various additions of antioxidant A:



$$(CH_3)_3C - \underset{CH_3}{\overset{OH}{\text{[benzene ring]}}} - CH_2 - \underset{CH_3}{\overset{OH}{\text{[benzene ring]}}} - C(CH_3)_3$$

The experiments were carried out in a static apparatus at an oxygen pressure $p = 300$ mm. The experimental procedure is described in work (^{5}). When the antioxidant concentration was varied from zero to 10^{-3} mole/kg, the induction period τ increased very slowly. With a further increase in inhibitor concentration, the slope of the curve $\tau = f(x)$ increases sharply; moreover, as the temperature is raised, the point of inflection shifts into the region of higher antioxidant concentrations.

The slopes $d\tau/dx$ in the region of small antioxidant concentrations at 190, 200, and 210° were, respectively, 10^6, $3 \cdot 10^5$, and $2 \cdot 10^5$ sec • kg/mole. The limiting values of these slopes can be derived in an elementary way from equation (3). When x_0 is small, setting $x_0 = \text{const}$ and integrating this equation, we obtain

$$n \simeq \frac{w_i}{\varphi - kx_0} e^{(\varphi - kx_0)t}. \tag{8}$$

As was done by one of us in work (^{6}), it may be assumed that at the end of the induction period τ, $n = \text{const}$, which leads to the approximate condition

$$(\varphi - kx_0)\tau = \text{const}. \tag{9}$$

When $x_0 = 0$, $\tau = \tau_0$, and we obtain:

$$\tau = \frac{\tau_0}{1 - \frac{k}{\varphi}x_0} \simeq \tau_0\left(1 + \frac{k}{\varphi}x_0\right) = \tau_0 + \frac{k\tau_0}{\varphi}x_0. \tag{10}$$

Thus, the limiting slopes of the curves in Fig. 3 at small values of x_0 have the value $k\tau_0/\varphi$. At the temperatures of our experiments, 190, 200, and 210°, τ_0 has the values 720, 600, and 480 sec, and φ has the values 0.015, 0.027, and 0.037 sec^{-1}. Using the above limiting values of the slopes, we find that the values of k at the indicated temperatures are, respectively, 21, 14, and 15 kg/mole • sec. This means that the activation energy and the steric factor of the reaction of the antioxidant with the active center are very small.

Let us also consider the slopes of the curves $\tau = f(x)$ in Fig. 3 at large values of x. These slopes at 190, 200, and 210° are, respectively, $6 \cdot 10^6$, $2 \cdot 10^6$, and 10^6 sec • kg/mole. The limiting value of the slope under these conditions, as follows from formula (1), is equal to $1/w_i$. Hence it is seen that, at the temperatures investigated by us, w_i varies from $1.6 \cdot 10^{-7}$ to $10 \cdot 10^{-7}$ mole/kg • sec. This corresponds to an activation-energy value of about 40,000 kcal/mole.

The usually accepted initiation reaction in the oxidation of hydrocarbons

$$\mathrm{RH} + \mathrm{O_2} = \mathrm{R}\cdot + \mathrm{HOO}\cdot$$

is characterized precisely by an activation energy of 40,000–50,000 cal/mole ([7]).

In studying various inhibitors, their effectiveness can be compared by the values of the rate constants k, determined as indicated above. By this method we have shown that, at small concentrations

N, N′-phenylcyclohexyl-*p*-phenylenediamine, as an antioxidant for polypropylene, is approximately 2 times more effective than oxidation inhibitor A.

Institute of Chemical Physics
Academy of Sciences of the USSR

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