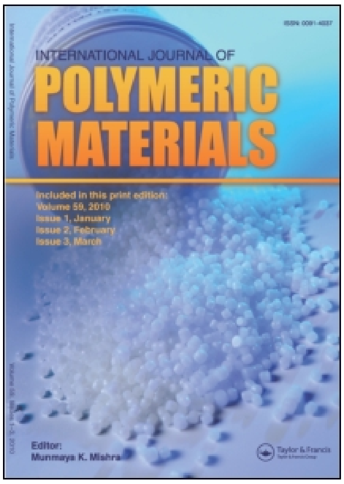

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The Processes Running during the Induction Period of Inhibiting Oxidation of Polyethylene

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Oxygen absorption in the induction period of polyethylene oxidation inhibited by a strong amine antioxidant *N*-phenyl-*N*′-cyclohexyl-*p*-phenylenediamine (PCHA) in the temperature range of from 200°C to 230°C is investigated.

It is found that the rate of O_2 absorption during the induction period in the presence of antioxidant varies in the range of from 2×10^{-6} to 2×10^{-5} mol/kg (210°C).

It is also stated that the main method of antioxidant consumption during the induction period consists of its direct oxidizing by molecular oxygen. The rapid oxidation of the polymer is shown to begin after the current antioxidant concentration reduction to the critical value.

Kinetic parameters of the oxidation reaction in a wide range of initial antioxidant concentration are determined.

KEY WORDS Oxidation, polyethylene

INTRODUCTION

The process of inhibited oxidation is complex because chain termination is not the only mechanism of inhibitor action. The actual compounds used as inhibitors can take part in all steps of the oxidation reaction: in chain initiation, propagation, branching and termination. In this paper we study the processes in the induction period of oxidation of polyethylene, the simplest hydrocarbon polymer.

The vapor pressures of hydrocarbons used in the study of inhibited oxidation at the temperatures of their oxidation amounts to several hundred millimeters of mercury, that is, it is comparable with the oxygen pressure above the oxidizing compound. In the reaction volume the gradients of oxygen and vapor gradients appear: the slight variations of temperature of different parts of the reaction system result in variations of pressures in it. This makes it extremely difficult to obtain reliable data of oxygen consumption rates during the slow inhibited oxidation. To solve this difficulty we study the oxidation of the high molecular weight hydrocarbon polyethylene ($\sim CH_2 \sim$), with viscosity average molecular weight ($M_w/M_w = 15.4$).

Polymeric compounds with such molecular weights do not evaporate. This property allows us not to make corrections for their vapor pressures.

EXPERIMENTAL

Polyethylene (PE) is purified by reprecipitation from m-xylene followed by washing with n-heptane, ethyl alcohol and further drying in a vacuum; *N*-phenil-*N'*-cyclohexyl-*p*-phenylenediamine, melting temperature 119°C, is purified by crystallization from *n*-heptane, followed by sublimation in a vacuum at a temperature of 200°C. The samples of polyethylene mixture with the inhibitor are prepared in a form of 0.1-cm thick plates having a mass of 0.2 g at 150°C in a nitrogen atmosphere. The samples are oxidized inside a closed system of approximate volume ~ 6 cm^3 provided by a differential oil manometer. The experiments are conducted at a temperature range of from 200°C to 230°C. To absorb the volatile product solid, KOH is placed in the cool part of the reaction volume. The oxygen pressure is kept within the range of from 294 to 300 mm Hg. The sensitivity of the system is 2×10^{-8} mole O_2 per 1 mm of the scale.

RESULTS AND DISCUSSION

Figure 1 represents the oxygen absorption curves during the polyethylene oxidation period at 210°C and various inhibitor concentrations (1×10^{-3}–8×10^{-2} mol/kg). The small concentrations of *N*-phenyl-*N'*-cyclohexyl-*p*-phenylenediamine (PCHA) ($\leq 1 \times 10^{-3}$ mol/kg) substantially decrease the oxygen absorption rate, but from $i_0 \geq 2.5 \times 10^{-3}$ mol/kg the initial oxygen absorption rate $(W_{02})_0$ noticeably decreases with increasing antioxidant concentration. However, within the entire investigated inhibitor concentration range, the oxygen absorption rate during the induction period always remains in the range of from 2×10^{-6} to 2×10^{-5} mol/kg sec., which is 1.5 to 2 orders lower than the polymer oxidation rate without antioxidant ($\sim 5 \times 10^{-4}$ mol/kg sec at 210°C). Figure 1 also shows that at concentrations of $i_0 \geq 2.5 \times 10^{-3}$ mol/kg the rate of O_2 absorption, being maximum at the beginning of the induction period, slowly decreases during the middle of the induction period and increases relatively rapidly at the end of it. The initial O_2 absorption rate increases with increasing inhibitor concentrations.

Dependence of the initial rate of oxygen absorption on initial inhibitor concentration is the curve with minimum and linear asymptote (Figure 2, curve 1).

Regardless of the relatively great sample thickness (0.1 cm) the oxidation process in the presence of inhibitor proceeds in kinetics-controlled regime, the increase of the sample thickness from 0.05 to 0.2 cm does not change the initial O_2 absorption rate calculated per mass unit. At initial PCHA concentration $i_0 = 0.04$ mol/kg and oxygen pressure $Po_2 = 300$ mm Hg, the initial oxygen absorption rate in the induction period of polyethylene oxidation is 1.07×10^{-5}, 1.10×10^{-5}, and 1.14×10^{-5} mol/kg sec at sample thickness 0.05, 0.10, and 0.20 cm, respectively. A slight decrease of the initial rate of O_2 absorption due to the reduction of the sample thickness may be explained by the greater role of the inhibitor evaporation from thinner samples. After the end of the introduction period, the process is proceeding in the diffusion-controlled regime. Though the polyethylene in the reaction is in a liquid state (melting point is 130°C), there is no oxygen transfer by convection due to great viscosity of the melt.

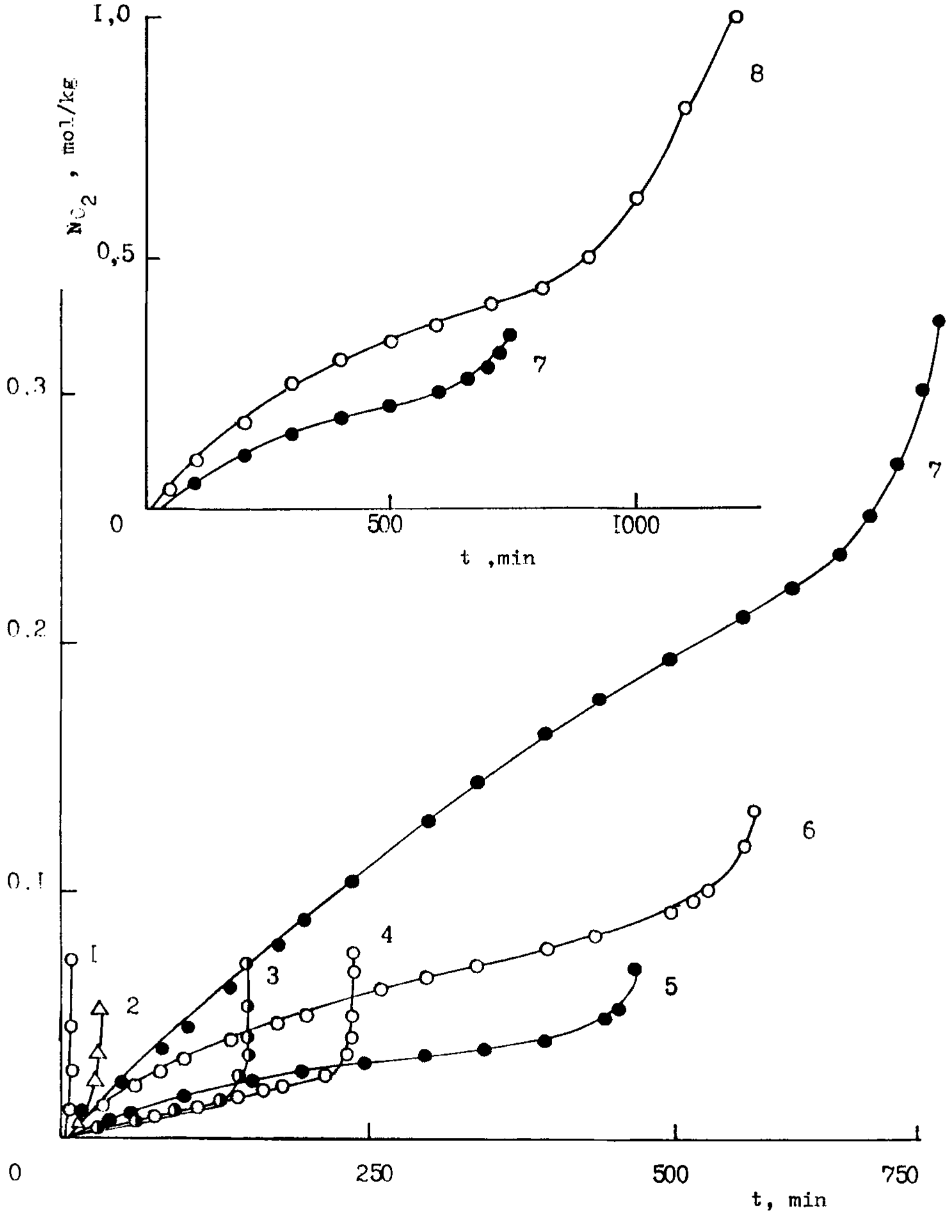


FIGURE 1 Oxygen consumption during polyethylene oxidation at 210°C; oxygen pressure 300 mm Hg; antioxidant concentrations (mol/kg): (1) i_0 = 0; (2) 0.001; (3) 0.0025; (4) 0.005; (5) 0.01; (6) 0.02; (7) 0.04; (8) 0.08.

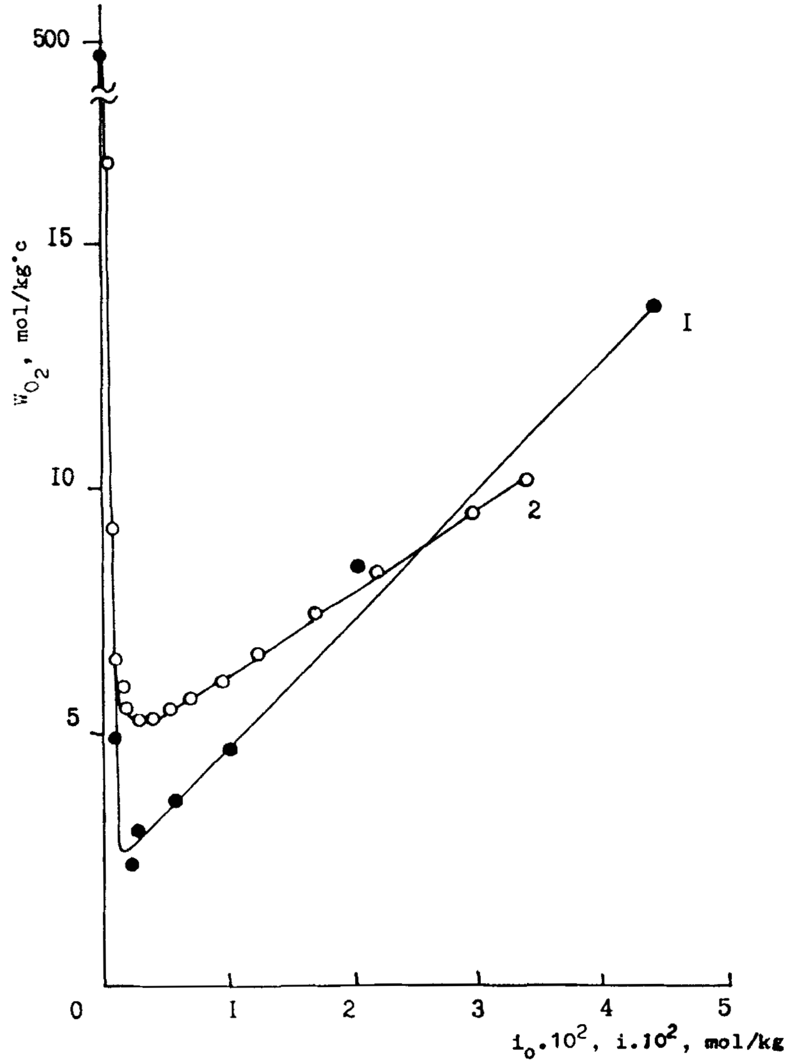


FIGURE 2 (1) Initial rate of oxygen consumption as a function of initial antioxidant concentration i_0. (2) Current rate as a function of current concentration i. Both at 210°C; oxygen pressure 300 mm Hg; i_0 = 0.04 mol/kg.

It is shown that the amount of oxygen absorbed to the end of the reduction period, calculated per one mole of inhibitor, is always the same (6 moles per mole of PCHA) (Figure 3).

Figure 4 represents the oxygen absorption curves during the polyethylene oxidation at oxygen pressure 300 mm Hg, the same initial concentrations of PCHA 0.04 mol/kg and various temperatures (200°–230°C). The curves have a similar shape but the length of the induction period is decreasing with increasing temper-

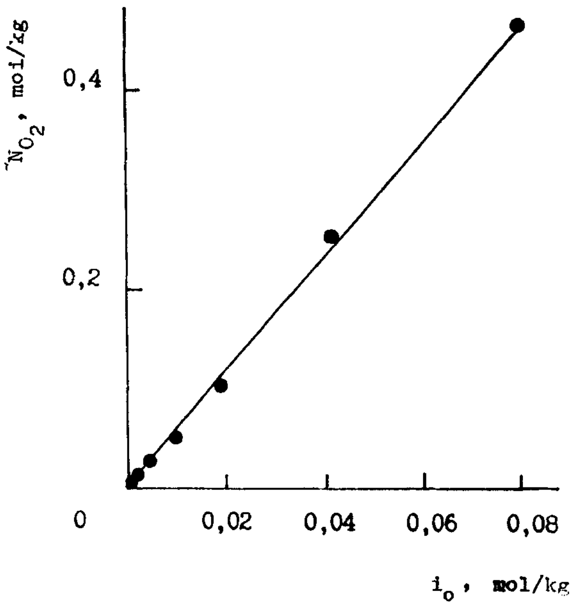


FIGURE 3 The amount of oxygen consumed (mol/kg) during the induction period as a function of initial antioxidant concentration (i_0) at 210°C; oxygen pressure 300 mm Hg.

ature. With a constant inhibitor concentration (i_0 = 0.04 mol/kg) the quantity of O_2 absorbed during the induction period is practically independent of the temperature and is equal to 0.24 mol/kg, that is, the same 6 moles of O_2 per one mole of inhibitor.

In order to study PCHA consumption during the induction period, the polyethylene samples with the inhibitor, previously oxidized for a necessary time, are cooled, then PCHA is extracted by vacuum evaporation (200°C, 60 min) and analyzed by spectrophotometry (1). The curves of PCHA concentration variation in the induction period (Figure 5) may be transformed into straight lines in the coordinates of the first order (Ln i_0/i versus time). Calculated from the straight line slope (Figure 5), the rate constants of PCHA consumption at 210°C and pressure of 300 mm Hg is equal to 1.0×10^{-4} sec^{-1} and changes with the temperature, with effective activation energy equal to 22.7 Kcal/mol (95 KJ/mol).

Comparing the oxygen absorption rate with the change of PCHA current concentration measured in a separate experiment, we find the curve of the dependence of the O_2 absorption rate on the current inhibitor concentration, which closely resembles in shape the similar dependence of the initial rate on the initial concentration (Figure 2, curve 2).

The dependence of the duration of the induction period τ on the initial PCHA concentration is a curve with a marked bend at certain PCHA concentrations (Figure 6) which coincides, according to 2, with the inhibitor critical concentration at which the chain termination rate is equal to the chain branching rate. This

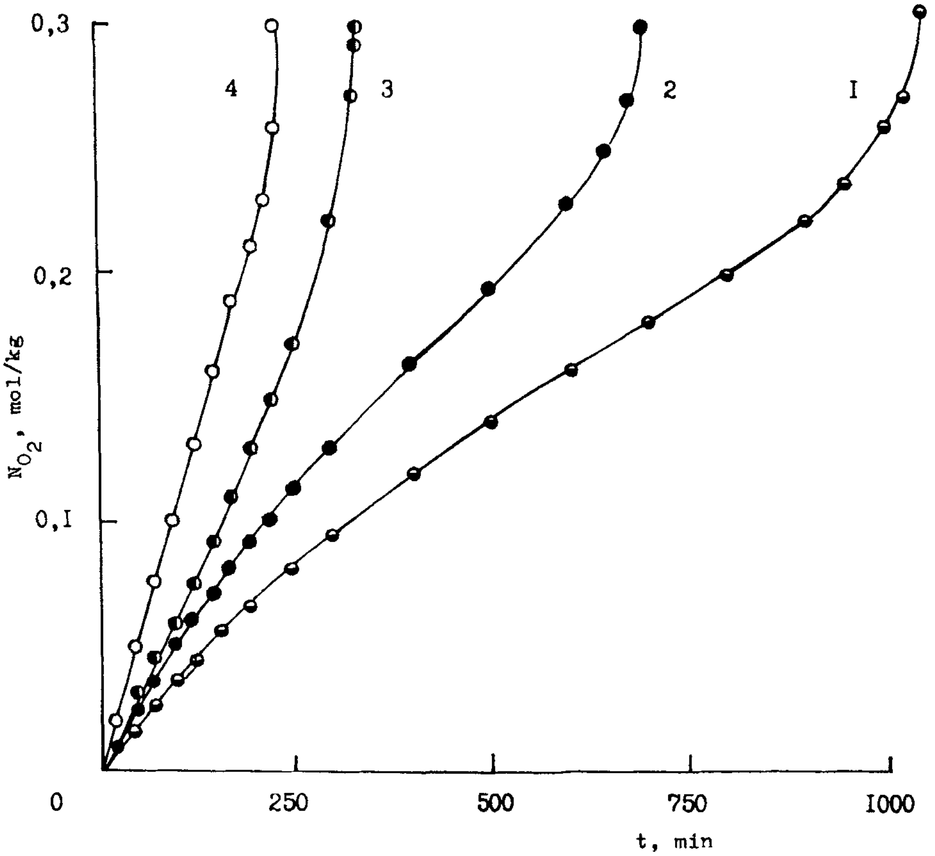


FIGURE 4 Oxygen consumption during polyethylene inhibited oxidation at various temperatures: (1) 200°C; (2) 210°C; (3) 220°C; (4) 230°C. i_0 = 0.04 mol/kg; oxygen pressure 300 mm Hg.

dependence transforms into a straight line in coordinates $\tau - \text{Ln}\, i_0$, that is, it may be expressed by the equation derived in [2]:

$$\tau = \tau_{cr} + \frac{1}{k_{eff}} \text{Ln}\frac{i_0}{i_{cr}} \tag{1}$$

where k_{eff} is the effective constant of the inhibitor consumption rate and τ_{cr} is the induction period at the critical value of PCHA concentration.

The first order of the inhibitor consumption, approximate stability of the relation N_{O_2}/i_0 at the end of the induction period and the O_2 consumption rate increase at high concentrations of the inhibitor may be explained on assumption that the main method of inhibitor consumption during the hydrocarbon oxidizing processes is its oxidation by molecular O_2 (see also references 2–4).

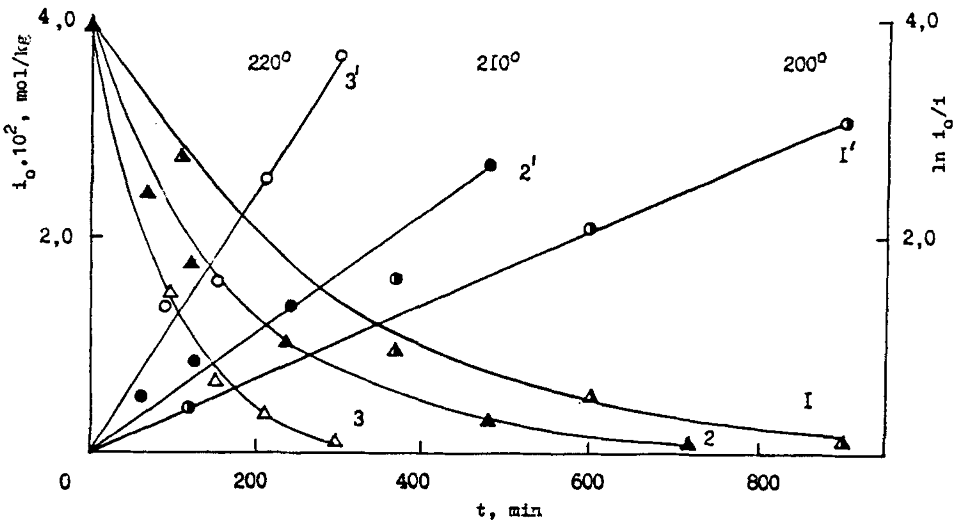


FIGURE 5 Antioxidant consumption during the induction period of polyethylene inhibited oxidation at various temperatures: 200°C (1 and 1'); 210°C (2 and 2'); 220°C (3 and 3'); in coordinates $i - t$ (1, 2, 3) and in coordinates $\ln i_0/i - t$ (1', 2', 3'); $i_0 = 0.04$ mol/kg; oxygen pressure 300 mm Hg.

Consider the oxidation scheme in detail ($\sim CH_2\sim$ is the fragment polyethylene molecule):

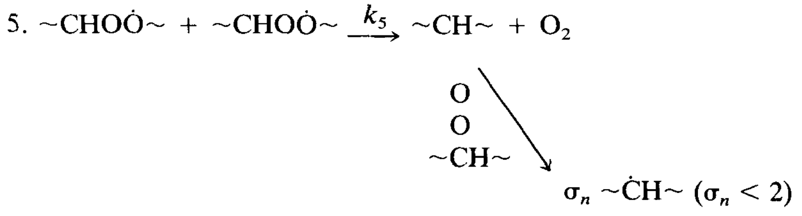
0. $\sim CH_2\sim + O_2 \xrightarrow{k_0} \ldots\ldots\ldots f_0 \sim\dot{C}H\sim$ + products

1. $\sim\dot{C}H\sim + O_2 \xrightarrow{k_1} \ldots \sim CHO{-}\dot{O}\sim$

2. $\sim CHO\dot{O}\sim + \sim CH_2\sim \xrightarrow{k_2} \alpha \sim CHOOH\sim + \sim\dot{C}H\sim$ + products

3. $\sim CHO\dot{O}\sim + IH \xrightarrow{k_3}$ products (opening) (2)

4. $\sim CHOOH\sim + \sim CH\sim \xrightarrow{k_4} \ldots\ldots\ldots \sigma \sim\dot{C}H\sim$ + products (breaking)



5. $\sim CHO\dot{O}\sim + \sim CHO\dot{O}\sim \xrightarrow{k_5} \sim CH\sim + O_2$

$$\begin{array}{l} O \\ O \\ \sim CH\sim \end{array} \searrow \sigma_n \sim\dot{C}H\sim \ (\sigma_n < 2)$$

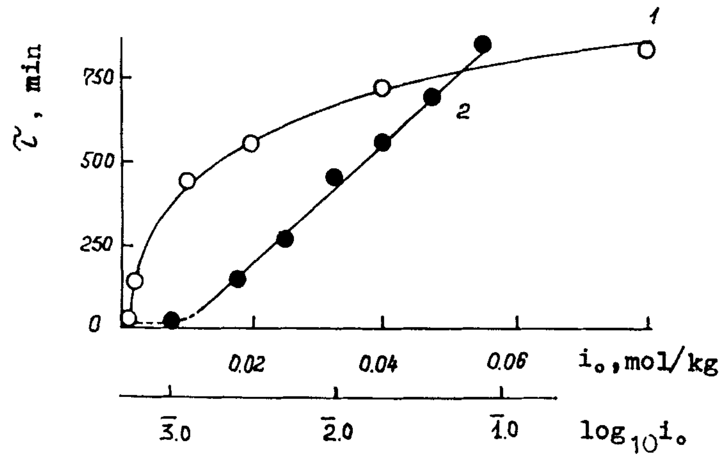


FIGURE 6 Induction period (τ_{ind}) of polyethylene oxidation as a function of initial diamine concentration in general (Figure 6a) and logarithmic (Figure 6b) coordinates at 210°C; oxygen pressure 300 mm Hg.

where f_0, f_1, α, σ, σ_n is the yield of free radicals in corresponding reactions.

To explain the first order of PCHA consumption on the inhibitor concentration, as well as the increase of the oxygen consumption rate with inhibitor concentration, the process should be complemented by the stage of interaction between the inhibitor and oxygen:

$$0.^{*}\ \mathrm{IH} + \mathrm{O}_2 \xrightarrow{k_0^*} \ldots \rightarrow f_i \sim\dot{\mathrm{C}}\mathrm{H}\sim + \text{ products} \qquad (3)$$

Denoting the radical concentrations as $\sim\dot{\mathrm{C}}\mathrm{H}\sim$ $-[\dot{\mathrm{R}}]$, $\sim\mathrm{CH}_2\sim$ $-$ [RH], $\sim$CHOOH$\sim$ $-$ [ROOH], and $\sim\mathrm{CHO}\dot{\mathrm{O}}\sim$ $-$ $[\mathrm{R}\dot{\mathrm{O}}_2]$, and assuming that $[\mathrm{R}\cdot] << [\mathrm{R}\dot{\mathrm{O}}_2]$, we obtain the balance equation of $\sim\mathrm{CHO}\dot{\mathrm{O}}\sim$ and $\sim$CHOOH$\sim$:

$$\frac{d\,[\mathrm{R}\dot{\mathrm{O}}_2]}{dt} = f_0k_0[\mathrm{RH}][\mathrm{O}_2] + f_ik_0^*[\mathrm{IH}][\mathrm{O}_2] + \sigma k_4[\mathrm{ROOH}][\mathrm{RH}]$$

$$- k_3[\mathrm{R}\dot{\mathrm{O}}_2][\mathrm{IH}] - k_5[\mathrm{R}\dot{\mathrm{O}}_2]^2 \qquad (4)$$

and

$$\frac{d[\mathrm{ROOH}]}{dt} = \alpha k_2[\mathrm{R}\dot{\mathrm{O}}_2][\mathrm{RH}] + k_3[\mathrm{R}\dot{\mathrm{O}}_2][\mathrm{IH}] - k_4[\mathrm{ROOH}][\mathrm{RH}]. \qquad (5)$$

At temperatures above 200°C, the average lifetime of hydroperoxides is approximately 10^1 sec and the induction period is 10^4 sec. We can consider that the hydroperoxide is a Bodenstein product, that is, we assume that not only does $d[R\dot{O}_2]dt = 0$, but also $d[ROOH]/dt = 0$. From this we can obtain

$$f_0k_0[RH][O_2] + f_ik_i^*[IH][O_2] + d\sigma k_2[RH][R\dot{O}_2] + \sigma k_3[IH][R\dot{O}_2] - k_5[R\dot{O}_2]^2 = 0. \quad (6)$$

Having neglected $k_5[R\dot{O}_2]^2$ in Equation (6), which is possible because of low concentrations of $[R\dot{O}_2]$, we obtain the meaning of the stationary concentration of $[R\dot{O}_2]$:

$$[R\dot{O}_2]_{st} = \frac{f_0k_0[RH][O_2] + f_ik_0^*[IH][O_2]}{(1 - \sigma)k_3[IH] - \alpha\sigma k_2[RH]}. \quad (7)$$

Expression (7) is of definite sense, that is, the stationary concentration of $[R\dot{O}_2]$ exists only in the case where $[IH] > [IH]_{cr}$. According to (5), (6),

$$[IH]_{cr} = \frac{\alpha\sigma k_2[RH]}{(1 - \sigma)k_3}$$

The inhibitor consumption will follow the first-order law in inhibitor concentrations, if $[IH] >> [IH]_{cr}$ and $k_0[RH] << k_0^*[IH]$.

With a sufficiently great chain length, when the reaction rates (1) and (2) in accordance with Scheme (2) are comparable, that is, $k_1[R\cdot][O_2] = k_2[R\dot{O}_2][RH]$ and the rate of radical formation in reaction (0.) is negligibly small compared to the rate at reaction (0.*), the expression of the oxygen consumption by the oxidizing polymer $(W_{O_2})_p$ is

$$(W_{O_2})_p = \frac{f_ik_0^*k_2[RH][IH][O_2]}{(1 - \sigma)k_3[IH] - \alpha\sigma k_2[RH]} = \frac{f_ik_0^*k_2[RH][O_2][IH]}{(1 - \sigma)([IH] - [IH]_{cr})k_3}. \quad (8)$$

The oxygen consumption rate in the inhibitor oxidation process (reaction 0.*) is

$$(W_{O_2})_i = \varepsilon k_0^*[O_2][IH] \quad (9)$$

where ε is number of oxygen molecules which oxidize one inhibitor molecule.

The overall oxygen consumption rate W_{O_2} is the sum of the rates at polymer oxidation and oxygen consumption by inhibitor and can be presented in the following form:

$$W_{O_2} = (W_{O_2})_p + (W_{O_2})_i = \frac{f_ik_0^*k_2[RH][O_2][IH]}{(1 - \sigma)([IH] - [IH]_{cr})k_3} + \varepsilon k_0^*[O_2][IH] \quad (10)$$

where the first term describes the oxygen consumption by oxidizing the polymer, and the second by oxidizing the inhibitor. With increasing concentration of the inhibitor, the first term of equation (10) tends to the limit equal to $f_i k_0^* k_2[\mathrm{RH}][\mathrm{O_2}]/(1 - \sigma)k_3$, and the second term grows linearly. From Equation (10), which satisfactorily governs curve 2 (see Figure 2), it follows that the minimum rate of the oxygen consumption by the polymer is equal to the length on the part of the ordinate axis that is cut by the asymptote at curve 1 (Figure 2), which is 2.3×10^{-6} mol/kg sec, and the asymptote slope for the inhibitor is $3.04 \times 10^{-1} = \varepsilon k_0^*[\mathrm{O_2}]$.

Thus, the polyethylene inhibited oxidation process in the presence of an aromatic diamine has been investigated. The antioxidant direct oxidation has been shown to be the main way of oxygen consumption and of overall process initiation.

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