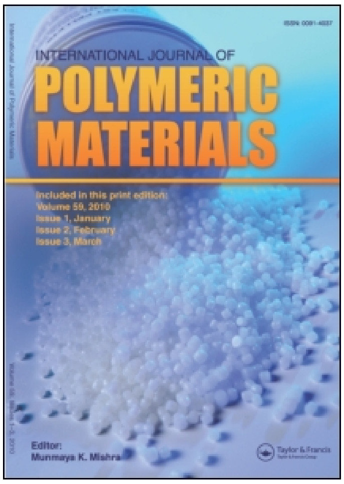

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Yu. A. Shlyapnikov[a]; N. K. Tyuleneva[a]
[a] United Institute of Chemical Physics, Moscow, Russia

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Inhibited Oxidation of Polyethylene: Anatomy of Induction Period

At the Occasion of the 100-th Anniversary of Hans L. J. Bäckström*

YU. A. SHLYAPNIKOV and N. K. TYULENEVA

United Institute of Chemical Physics, 117334, Moscow, Russia

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Oxidation of high-density polyethylene containing strong phenolic antioxidant 2,2′-methylene-bis(4-methyl-6-tertbutyl-phenol) has been studied. During the induction period the antioxidant is consumed according to first kinetical order with the rate constant depending on the initial antioxidant concentration. During the induction period about three moles of O_2 are consumed per one mole of antioxidant. The formation of hydrogen peroxide in induction period of oxidation has been established.

The mechanism of inhibited oxidation is discussed.

Keywords: High-density polyethylene; oxidation; antioxidants; oxidation kinetics; phenols

INTRODUCTION

The antioxidants are more reactive compounds than the polymer to which they are added. Therefore, they participate in many processes taking place in the polymer. Although the most important of these processes is chain termination, a large portion of the antioxidant is usually consumed in direct reaction with oxygen and in termination of secondary chains initiated by its oxidation [4,5]. In this work the authors studied some regularities of consumption of strong antioxidant

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*In the middle of 20-th Dr. Hans L. J. Bäckström first studied antioxidant consumption during induction period of inhibited oxidation in the liquid phase (Ref. [1–3]).

2,2′-methylene-bis(4-methyl-6 tertbutyl-phenol) (MBP) in oxidation of high-density polyethylene.

EXPERIMENTAL

High-density polyethylene, molecular weight $M_w = 224\,000$, $M_w/M_n = 38$. has been washed with boiling alcohol and heated in vacuum (100°, 13 hours) for decomposition of possible peroxides. Antioxidant 2,2′-methylene-bis(4-methyl-6-tertbutyl-phenol) was purified by vacuum distillation and mixed with the polymer powder with addition of alcohol with subsequent drying at room temperature. The samples were 0.1 cm films prepared by pressing polyethylene powder containing antioxidant in nitrogen atmosphere and oxidized at 200°C and oxygen pressure 300 mm Hg, volatile products were either removed by freezing with solid CO_2 or absorbed by KOH. To study oxygen consumption, the decrease of its pressure was registered by differential oil-filled manometer. Non-consumed antioxidant was extracted from samples by evaporation in vacuum and its concentration determined spectrophotometrically [6]. To determine hydrogen peroxide formed in the induction period iodometric analysis has been used [7].

RESULTS AND DISCUSSION

Figures 1 and 2 show the variations of antioxidant concentration, oxygen consumption and formation of hydrogen peroxide during induction period of oxidation of polyethylene containing antioxidant 2,2′-methylene-bis(4-methyl-6-tertbutyl-phenol) at initial concentrations 0.02 (Fig. 1) and 0.04 mol/kg (Fig. 2). As seen from these figures, antioxidant at the most part of induction period is consumed according to the first kinetical order ($-d[\mathrm{MBP}]/dt = k_a[\mathrm{MBP}]$, where k_a is apparent rate constant), that is the kinetical curves of antioxidant consumption may be transformed into straight lines in coordinates $\log[\mathrm{MBP}]_0/[\mathrm{MBP}]$ vs time characteristic for this kinetical order [5], but rate constants, calculated from these lines, differ for different antioxidant concentrations, and equal to $k_a = 2.0 \times 10^{-4}\ \mathrm{s}^{-1}$ at $[\mathrm{MBP}]_0 = 0.02$ mol/kg, and $k_a = 1.5 \times 10^{-4}\ \mathrm{s}^{-1}$ at $[\mathrm{MBP}]_0 = 0.04$ mol/kg.

Oxygen consumption in the induction period is directly proportional to the rate of consumption of antioxidant, the ratio $\Delta[N_{O_2}]/d[\mathrm{MBP}]$ where N_{O_2} (mol/kg) is the amount of oxygen consumed per

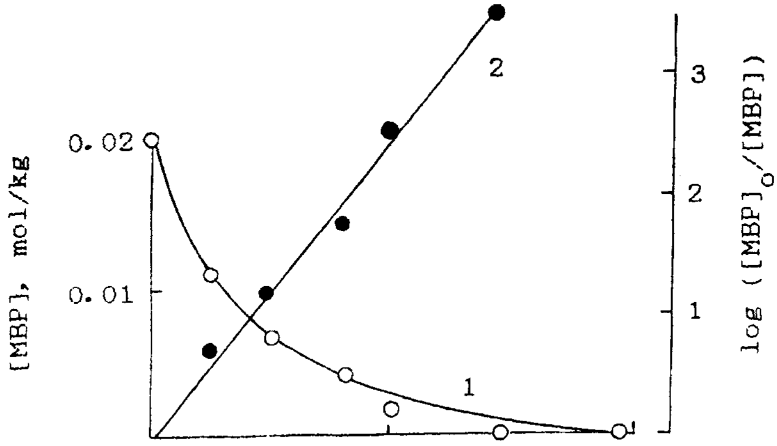

FIGURE 1 Variation of antioxidant concentration [MBP] in polyethylene during induction period of its oxidation at 200°C, oxygen pressure 300 mm Hg (1); 2-the same in coordinates log[MBP] vs time, 3-oxygen consumption, and 4-hydrogen peroxide formation in induction period. $[\mathrm{MBP}]_0 = 0.02$ mol/kg.

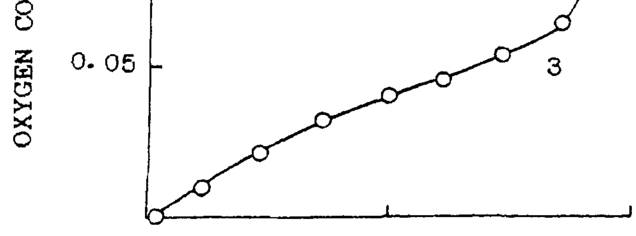

FIGURE 1b (Contd.)

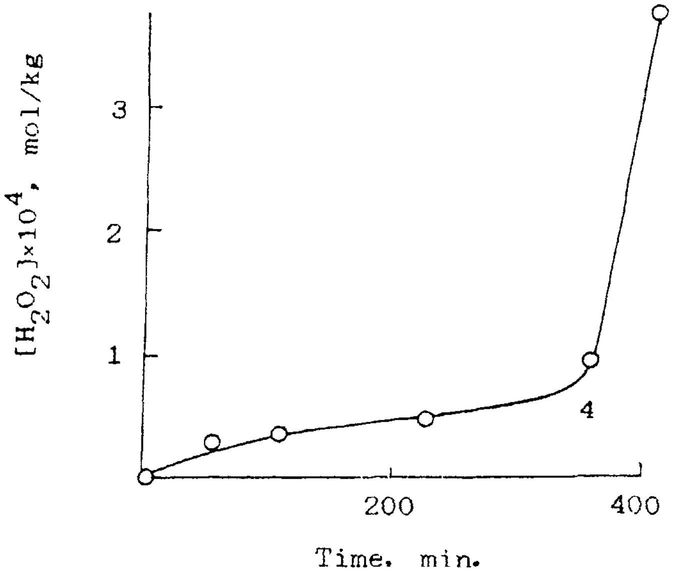

FIGURE 1c (Contd.)

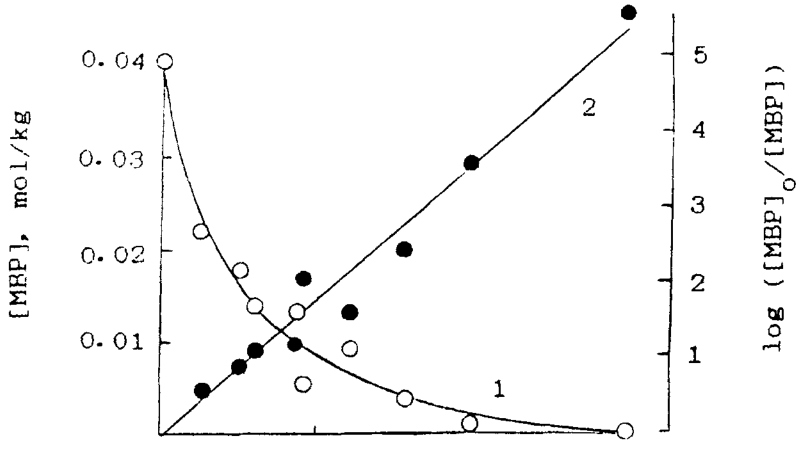

FIGURE 2 Variation of antioxidant concentration [MBP] in polyethylene during induction period of its oxidation at 200°C, oxygen pressure 300 mm Hg (1); 2-the same in coordinates log[MBP] vs time, 3-oxygen consumption, and 4-hydrogen peroxide formation in induction period. $[MBP]_0 = 0.04$ mol/kg.

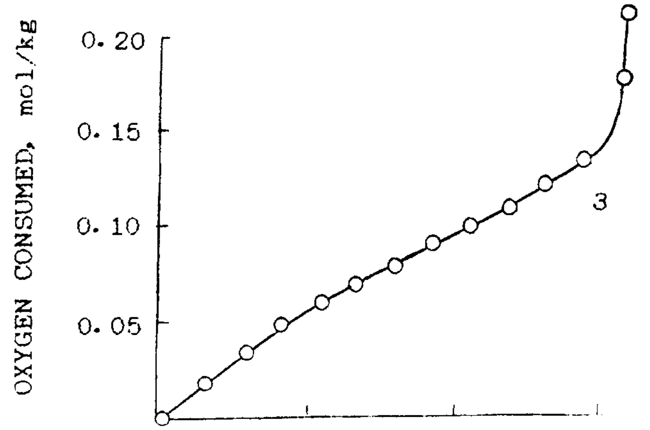

FIGURE 2b (Contd.)

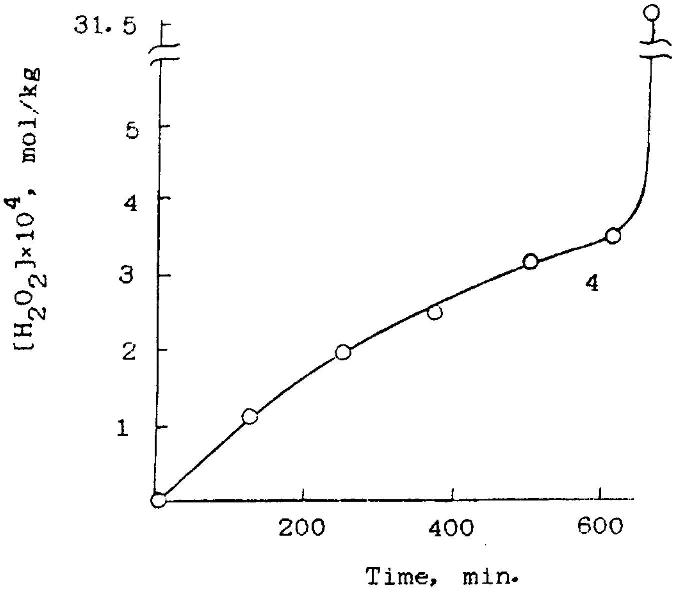

FIGURE 2c (Contd.)

mass unit of the polymer, being close to 3. The rate of hydrogen peroxide formation is small (1–2% of oxygen consumed) and changes approximately as $[MBP]^2$.

To explain the dependencies found consider the scheme of inhibited polyolefin oxidation [5, 8] (RH-the monomeric unit, and IH-antioxidant):

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot} \tag{1}$$

$$IH + O_2 \longrightarrow I^{\cdot} + HO_2^{\cdot} \tag{2}$$

$$HO_2^{\cdot} + RH \longrightarrow H_2O_2 + R^{\cdot} \tag{3}$$

$$HO_2^{\cdot} + IH \longrightarrow H_2O_2 + I^{\cdot} \tag{4}$$

$$I^{\cdot} + RH \longrightarrow IH + R^{\cdot} \tag{5}$$

$$HO_2^{\cdot} + R^{\cdot} \longrightarrow ROOH \tag{6}$$

$$HO_2^{\cdot} + I^{\cdot} \longrightarrow IOOH \tag{7}$$

Reactions (3) to (7) proceed mainly in cages formed by surrounding monomeric units and their rates are proportional to the number (i.e. concentrations) of the corresponding pairs, it means that the yields of free radicals (σ_r in reactions (1) and (3) and σ_{ri} in (2), (4) and (5)) as the yields of other products must be independent on the rates of corresponding reactions. The chain propagation proceeds according to the standard scheme:

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \tag{8}$$

$$RO_2^{\cdot} + RH \xrightarrow{k_2} \boxed{ROOH + R^{\cdot}; RH} \longrightarrow$$

$$\longrightarrow \chi ROOH + R^{\cdot} + \text{products} \tag{9}$$

In the absence of antioxidants the chain termination proceeds at recombination of two radicals, mainly of $RO_2^{\cdot}$:

$$RO^{\cdot} + RO^{\cdot} \xrightarrow{k_{t2}} ROOR + O_2 \tag{10}$$

when in the presence of antioxidant in reactions:

$$RO_2^{\cdot} + IH \xrightarrow{k_{t1}} ROOH + I^{\cdot} \tag{11}$$

$$ROOH + RH \xrightarrow{k_{db}} \boxed{RO^{\cdot} + R^{\cdot} + H_2O; RH}$$

$$\longrightarrow \sigma_{db}R^{\cdot} + \text{products} \tag{12}$$

The results of reactions (1–6) may be written as:

$$RH + O_2 \xrightarrow{k_o} R^{\cdot} + \boxed{HO_2^{\cdot}; RH}$$

$$\longrightarrow \sigma_r R^{\cdot} + \sigma_{hp} H_2O_2 + \text{inactive products} \tag{13}$$

and

$$IH + O_2 \xrightarrow{k_{oi}} I^{\cdot} + \boxed{HO_2^{\cdot}; RH}$$

$$\longrightarrow \sigma_{ri} R^{\cdot} + \sigma_{hpi} H_2O_2 + \text{inactive products} \tag{14}$$

where rectangles denote cages containing along with radicals the monomeric units RH, σ_{hp} and σ_{hpi} are the yields of hydrogen peroxide in both groups of reactions. At elevated temperatures, when the lifetimes of peroxide or hydroperoxide groups is much less than the reaction time, the steps (10) or (11) will result in chain termination only if the yields of free radicals in these groups decomposition is markedly less than the number of free radicals entering the reactions, i.e. less than 1.

It must be specially noted that because of extremely low mobility of polymeric compounds the yields of hydroperoxide groups and, especially, of free radicals from the cages are very low [9]: $\sigma_{ro} < 1, \sigma_{ri} < 1, \sigma_{hp} < 1$, and $\sigma_{db} \ll 1$.

According to theory of chain reactions, the chain branching rate is directly proportional to the active centers concentration and increases the number of free radicals participating in reaction, i.e. the chain branching proceeds in decomposition of hydroperoxide groups formed in the chain propagation reaction (9), when decomposition of peroxides ROOR and hydroperoxide groups formed in chain termination step (11) only decrease effectivity of chain termination [10].

To find the formulas describing the regularities of inhibited oxidation in the form convenient for comparing with experiment we must make some assumptions. Assuming that the oxygen concentration in the oxidizing polymer is high enough that we may neglect the concentration of radicals $R^{\cdot}$ compared to that of $RO_2^{\cdot}$, that because of high antioxidant concentration the oxidation chain terminate in reactions with antioxidant (11), and that the process is stationary, i.e. we may assume $d([R^{\cdot}]+[RO_2^{\cdot}])=0$ and $d[ROOH]/dt=0$ and, applying the method of Bodenstein [11] we get the expression for concentration of free (non-caged) radicals $RO_2^{\cdot}$ in reaction of inhibited oxidation:

$$[RO_2^{\cdot}]=\frac{(\sigma_r k_o[RH]+\sigma_{ri}k_{oi}[IH])[O_2]}{\sigma_{db}^{-1}(\alpha k_2[RH]+k_{t1}[IH])-k_{t1}[IH]} \tag{15}$$

It follows from (15) that a certain "critical" antioxidant concentration $[IH]_{cr}$ at and below which stationary radical concentration becomes infinitely large or negative, i.e. does not exist. This concentration may be found from condition that denominator of (15) is zero, and is equal to:

$$[IH]_{cr}=\frac{\alpha k_2[RH]}{(1-\sigma_{db})k_{t1}} \tag{16}$$

at $[IH]\gg[IH]_{cr}$ we may neglect the term $\alpha k_2[RH]$ compared to $k_{t1}[IH]$ in denominator of (15). Assuming also $\sigma_r k_o[RH]\ll\sigma_{ri}k_{oi}[IH]$, we get:

$$[RO_2^{\cdot}]=\frac{\sigma_{ri}\alpha k_{oi}[O_2]}{k_{t1}(1-\sigma_{db})} \tag{17}$$

and the rate of antioxidant consumption will be:

$$-\frac{d[IH]}{dt}=k_{oi}[IH][O_2]+k_{t1}[RO_2^{\cdot}][IH]$$

$$= k_{\text{oi}}[\text{IH}][\text{O}_2]\left\{1 + \frac{\sigma_{\text{ri}}\alpha k_{\text{oi}}}{(1-\sigma_{\text{db}})}\right\} = k_a[\text{IH}] \tag{18}$$

i.e. the antioxidant consumption will be first order in its concentration. If assumptions we made above are incorrect, which may take place at low antioxidant concentrations when [IH] is close to $[\text{IH}]_{\text{cr}}$ and $k_o\sigma_r[\text{RH}]$ is close to $(1+\sigma_{\text{ri}})[\text{IH}]$ marked deviations from this order will become noticeable.

If the antioxidant is consumed according to the first kinetical order $(-d[\text{IH}]/dt = k_a[\text{IH}])$ until its concentration becomes equal to critical one, and then with increased rate till the end of induction period, integrating the first order equation from initial concentration $[\text{IH}]_o$ till $[\text{IH}]_{\text{cr}}$, we find the formula describing dependence of induction period τ on initial concentration of effective antioxidant [4, 5]:

$$\tau = \tau_{\text{cr}} + \frac{1}{k_a}\ln\frac{[\text{IH}]_o}{[\text{IH}]_{\text{cr}}} \tag{19}$$

where $[\text{IH}]_{\text{cr}}$ is induction period at $[\text{IH}]_o = [\text{IH}]_{\text{cr}}$, which usually is close to induction period of oxidation of the same polymer in the absence of antioxidants.

As we saw from Figures 1 and 2, antioxidant MBP is consumed according to the first kinetical law, variations of apparent rate constant with initial antioxidant concentrations may be explained by incorrectness of assumptions made.

According to (18), the dependence of induction period on initial MBP concentration must follow the law (18). Accordingly, as seen from Figure 3, the curve 'induction period vs antioxidant concentration' for oxidation of polyethylene in the presence of MBP can be transformed into straight line in semilogarithmic coordinates (τ vs $\log[\text{IH}]$), but the rate constant k_a calculated from this curve is $k_a = 0.95 \times 10^{-5}\ \text{s}^{-1}$, that markedly (up to two times) differs from those calculated from antioxidant consumption.

Two reasons of this difference are possible: incorrectness of assumption we made deriving the expression (17), and effect of products of antioxidant transformation on critical concentration of the main antioxidant observed first in [12].

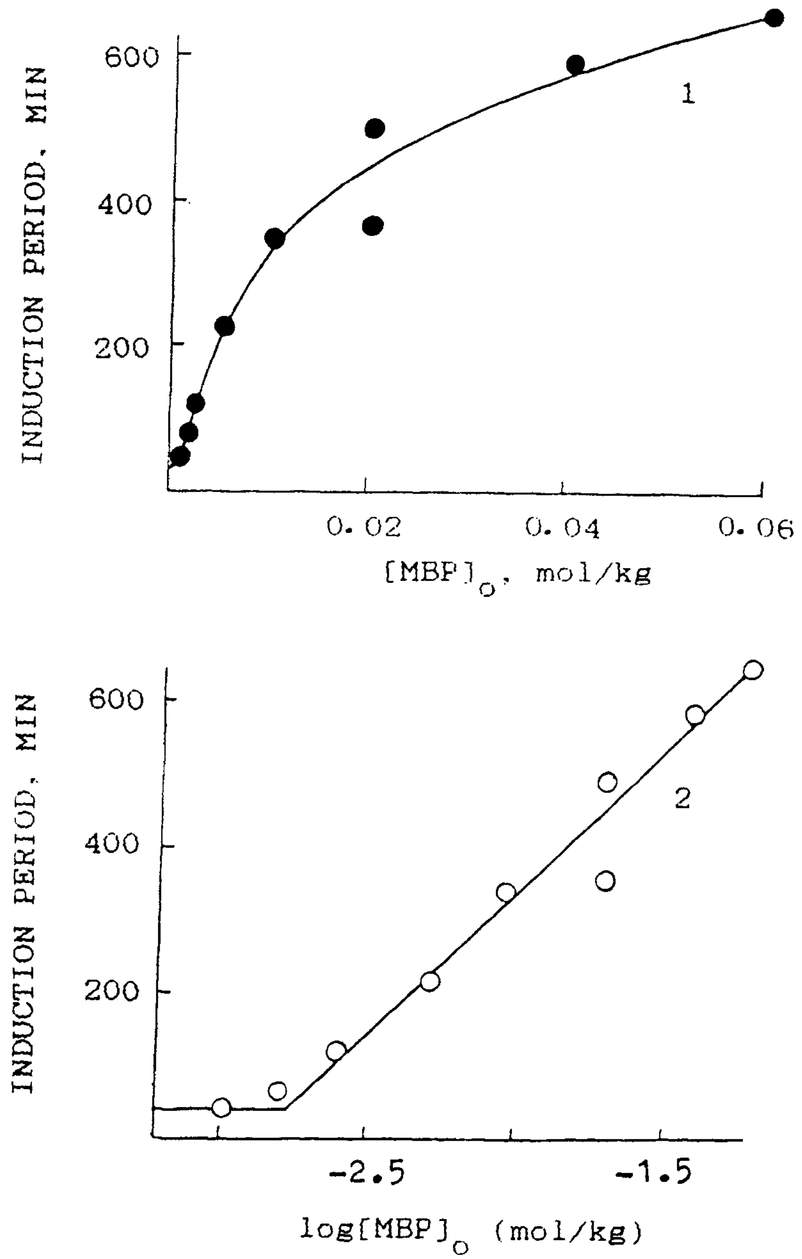

FIGURE 3 Induction period of polyethylene oxidation as function of *initial* antioxidant concentration $[MBP]_0$ (1), and of logarithm of antioxidant concentration (2). 200 C, oxygen, 300 mm Hg.

The slope of line "induction period vs logarithm of antioxidant concentration" if the dependence of τ on $\ln[\mathrm{IH}]_o$ is described by formula (19) is:

$$\frac{d\tau}{d(\ln[\mathrm{IH}]_o)} = \frac{1}{k_a}\left\{1 - \frac{d(\ln[\mathrm{IH}]_{\mathrm{cr}})}{d(\ln[\mathrm{IH}]_o)}\right\} \tag{20}$$

The products of initial antioxidant transformation participate in chain termination and thus decreases its critical concentration, i.e. $d(\ln[\mathrm{IH}]_{\mathrm{cr}})/d(\ln[\mathrm{IH}]_o) < 0$, $1/k_a$ found from this slope assuming $[\mathrm{IH}]_{\mathrm{cr}} = \mathrm{const.}$ will be greater, and correspondingly k_a smaller than the real rate constant of antioxidant consumption, as we found in our experiments.

Thus to find the quantitative regularities of antioxidant action even in the simplest polymers it is necessary to take into account not only the initial antioxidant and its reactions, but also the products of its transformation.

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