## MACROMOLECULAR COMPOUNDS
## AND POLYMERIC MATERIALS

# Influence of Chemically Inert Fillers on the Efficiency of Polyethylene Inhibition by Antioxidants

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**Abstract**—The influence of chemically inert dispersed fillers ($Al_2O_3$, $SiO_2$) on the efficiency of the polyethylene oxidation inhibition by commercial antioxidants (Irganox 1010, Neozon D) was studied. Introduction of chemically inert fillers into inhibited polymers alters the inhibitor distribution in the sample volume. The first fraction of the additive remains conventionally dissolved in the polymer (occurs in the dissolved state and in sorption sites), the second fraction is localized at the filler–polymer interface (separates out in the interfacial zone and accumulates in microcavities and voids of this zone), and the third fraction is adsorbed on the filler (forms an adsorption layer on the particle surface). As a result, the heat resistance of the filled polymer changes.

Filling of polymers by introducing solid filler particles and protection of polymers against thermal oxidation using inhibiting additives, antioxidants, are the main methods for controlling the properties of composite materials [1]. Unfortunately, both methods are used without taking into account the mutual effect of the mixture components on their performance in composites. The effects of fillers and antioxidants are usually studied separately, i.e., without the second additive. However, if additives are introduced into a polymer jointly, their effect can differ significantly from the effects of the same additives introduced separately. The results of studies reported in [2] can serve as example.

Many inert mineral fillers exerting reinforcing effect in polymeric composites exhibit high ability to adsorb low-molecular-mass substances, including antioxidants. Combination of fillers and antioxidants in polymeric composites should lead to inevitable loss of a fraction (possibly significant) of the inhibitor due to its adsorption on the filler surface. As a result, the polymer becomes less heat-resistant. This reasoning does not refer to reversible adsorption of antioxidants, because in this case they are gradually released into the bulk of the polymer being oxidized and act in accordance with destination.

The antioxidant performance in polymers depends not only on their reactivity but also on the diffusion mobility. Specifically the diffusion ensures the uniform distribution of the additive throughout the sample volume and its transport to the zone of the initiation of oxidation reactions. Fillers can both decrease and increase the diffusion coefficient. A decrease in the diffusion coefficient is usually attributed to an increase in the diffusant path distance [3], and an increase in the diffusion coefficient is attributed to poor wetting of the filler with the polymer, when the diffusing substance can penetrate through a layer of the gas separating the polymer and filler particles [4, 5].

Formation of new interfaces, microcavities, and voids in polymers upon filling opens new possibilities for enhancing the antioxidant effect. If the concentration of an antioxidant introduced into a polymer exceeds the solubility limit (saturation concentration), the mixture undergoes phase segregation with exudation of the additive on the sample surface. Confirming data on the exudation of antioxidant additives from thin polyethylene films are given in numerous papers, in particular, in [6]. The antioxidant released from the bulk of the sample on its external surface is then either evaporated into the atmosphere or washed out with the working medium

with which the sample contacts in the course of operation. Therefore, the formation of additional interfaces, microcavities, and voids upon polymer filling actually opens new possibilities for reservation or accumulation of the antioxidant fraction that was lost without filler. Thus, in filled polymers, the antioxidant can be distributed between three fractions: The first fraction is uniformly dissolved in the bulk of the polymer [7], the second is adsorbed on the surface of filler particles (if such adsorption is possible), and the third separates out on interfaces and in microcavities and voids formed upon polymer filling.

In the course of oxidation of a filled inhibited polymer, the antioxidant dissolved in the bulk of the polymer and located in sorption sites is consumed first. Its loss is gradually replenished by the diffusion transport of the additive present on polymer–filler interfaces. Thus, owing to reduction of the antioxidant loss via exudation from the film, the filled polymer can surpass in the heat resistance the unfilled polymer. The present study was aimed at checking this assumption.

In this study we examined the possibility of enhancing the thermal oxidation resistance of polyethylene inhibited by commercial phenolic and amine antioxidants via additional introduction of chemically inert mineral fillers into the polymer.

## EXPERIMENTAL

Experiments were performed with powdered nonstabilized high-density polyethylene [GOST (State Standard) 16338–85, grade 20308-005), into which phenolic [Irganox 1010, 3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionic acid pentaerythritol ester] and amine (Neozon D, 2-phenylnaphthylamine) antioxidants were introduced. These antioxidants are widely used for thermal stabilization of polyolefins, and their properties have been described in sufficient detail [8, 9]. Aluminum oxide $Al_2O_3$ (GOST 8136–85) and silicon oxide $SiO_2$ [Kovelos, TU (Technical Specification) 2168-002-14344269–09] were used as dispersed fillers. The specific surface areas of $Al_2O_3$ and $SiO_2$ were 200 and 300 $m^2 g^{-1}$, respectively.

When preparing the composites, unless otherwise indicated, the polymer powder was first treated with the solution of an antioxidant in acetone. After complete evaporation of the solvent, the filler powder was introduced into the inhibited polymer by mechanical mixing. Then, the resulting mixture was again wetted with acetone and stirred on a magnetic stirrer for 3 min. The mixtures
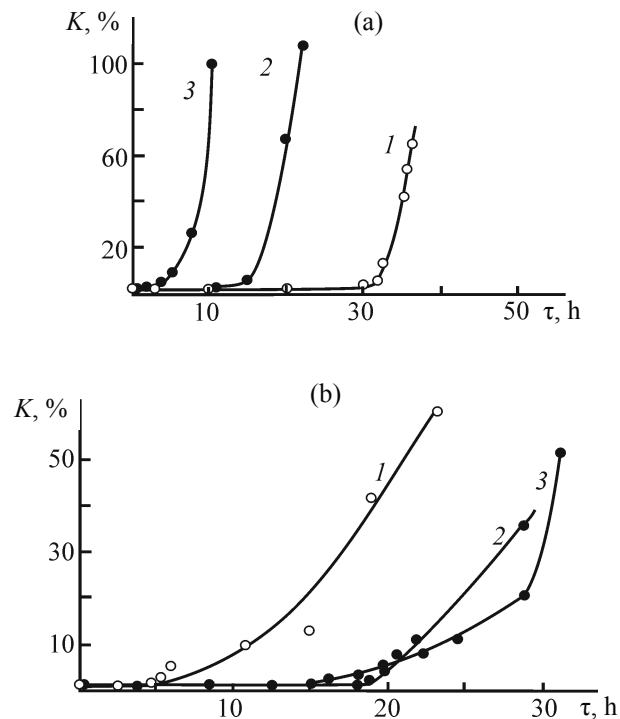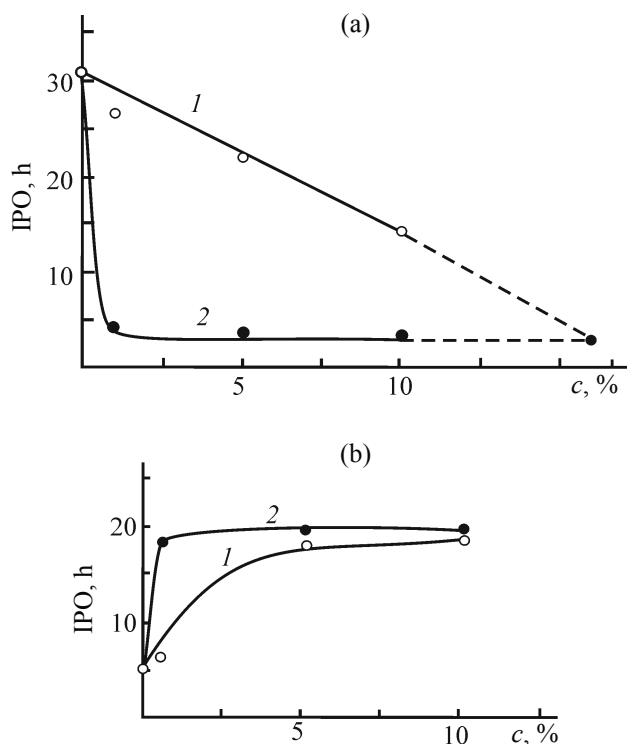


**Fig. 1.** Extinction parameter $K$ of the absorption band at 1720 $cm^{-1}$ in the IR spectra of polyethylene films containing 0.1 wt % inhibitor as a function of oxidation time $\tau$. Inhibitor: (a) Irganox 1010 and (b) Neozon D; filler: (*1*) none, (*2*) 10 wt % $Al_2O_3$, and (*3*) 10 wt % $SiO_2$; oxidation temperature, °C: (a) 150 and (b) 140; KBr support.

obtained were dried in air at room temperature to completely remove the solvent and then stirred finally. From the resulting mixtures, 100-μm-thick films for the experiments were prepared by hot pressing (150°C, 30–90 s).

Then, the films were applied by fusion onto supports inactive in polyethylene oxidation (KBr plates were used), after which the samples obtained were transferred into ovens for oxidation at a constant temperature in air.

The extent of the polymer oxidation was evaluated by IR spectroscopy from the content of carbonyl groups. In the course of tests, the oxidation process was interrupted, the samples were cooled to room temperature, and their IR spectra were recorded, after which the samples were placed again into the oven to continue the oxidation. The extent of oxidation of the polymer films was quantitatively characterized by the extinction parameter $K$ of the absorption band of carbonyl groups. This parameter was calculated as the percent ratio of the area of the absorption band in the range 1840–1670 $cm^{-1}$ to the area of the reference absorption band in the range 1500–1390 $cm^{-1}$.

**Fig. 2.** IPO of 100-μm-thick polyethylene films containing 0.1 wt % inhibitor as a function of filler concentration c. Inhibitor: (a) Irganox 1010 and (b) Neozon D; filler: (*1*) aluminum oxide and (*2*) silicon oxide; oxidation temperature, °C: (a) 150 and (b) 140; KBr support.

The induction period of oxidation (IPO) was determined from the kinetic dependences of the accumulation of carbonyl groups. The oxidation time required for reaching the extinction parameter equal to 3–4% was considered as IPO. The IR spectra were recorded with a Vertex 70 Fourier spectrometer (Bruker, Germany, 2004).

## RESULTS AND DISCUSSION

Figure 1 shows data on accumulation of carbonyl-containing groups in samples of inhibited polyethylene containing fillers: aluminum oxide (curves *2*) and silicon oxide (curves *3*). The amounts of the filler (10 wt %) and antioxidant (0.1 wt %) in the samples are equal. As can be seen, introduction of fillers exerts opposite effect on the heat resistance of the polymer inhibited by two different antioxidants. With a phenolic antioxidant, Irganox 1010, introduction of fillers into polyethylene makes IPO shorter, whereas filling of the polymer inhibited by an amine antioxidant, Neozon D, on the contrary, makes IPO longer. For the unfilled polyethylene inhibited by Irganox

1010, IPO is 31 h; upon introduction of 10 wt % silicon oxide or aluminum oxide, it decreases to 3.5 and 15 h, respectively. For the unfilled polyethylene inhibited by Neozon D, IPO is as short as 5 h; introduction of 10 wt % aluminum oxide or silicon oxide into the inhibited polymer increases IPO to 18 h.

Figure 2 shows how the concentration of each filler affects IPO of the inhibited polyethylene (antioxidant concentration in the polymer 0.1 wt %). As can be seen, with antioxidants of different nature, the effect of fillers on the heat resistance of the polymer is opposite. With phenolic antioxidant, IPO decreases as the filler concentration is increased, becoming close to IPO of the uninhibited polymer. In other words, introduction of any of the chemically inert fillers can virtually fully suppress the inhibiting effect of the phenolic antioxidant. Silicon oxide exerts a stronger suppressing effect: Already at a filler concentration of 1 wt %, IPO decreases to 4 h, whereas for the unfilled polymer IPO is 31 h (Fig. 2a, curve *2*). With aluminum oxide used instead of silicon oxide, IPO decreases to 4 h only on introducing approximately 20 wt % filler (Fig. 2a, curve *1*).

The stronger effect of silicon oxide on IPO is also manifested in the case of using the amine antioxidant. However, IPO in this case, on the contrary, increases (Fig. 2b). Introduction of only 1 wt % silicon oxide into polyethylene inhibited by Neozon D increases IPO from 5 to 18 h (Fig. 2b, curve *2*). To obtain the same result with aluminum oxide, the filler dosage should be increased to 10 wt % (Fig. 2b, curve *1*). Thus, chemically inert mineral fillers affect the performance of commercial antioxidants in polyethylene inhibition. With the amine antioxidant, Neozon D, introduction of fillers increases IPO, whereas with the phenolic antioxidant, Irganox 1010, the filler weakens the inhibiting effect, and IPO of the composite decreases. The extent to which the fillers affect IPO depends on their concentration and nature. Silicon oxide exerts on IPO a stronger effect than aluminum oxide does. These differences are probably associated with the ability of fillers to adsorb antioxidants.

To evaluate the adsorption properties of fillers, we performed the following experiment. A portion of fillers of constant weight (500 mg) was wetted with a solution of an antioxidant in acetone, and the mixture was kept at room temperature for 24 h. After that, the liquid phase was separated from the filler, and the filler coated with an adsorbed antioxidant layer was washed with pure acetone. Then, the filler was dried in air to fully remove the solvent,
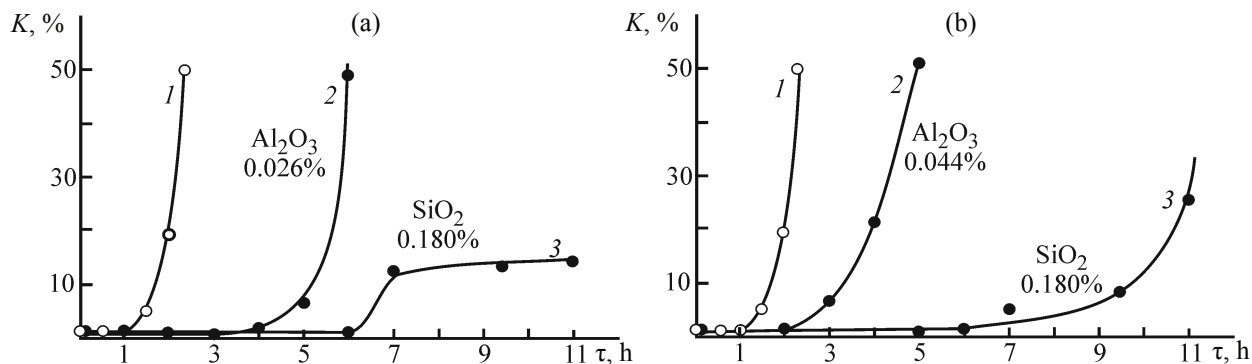
**Fig. 3.** Extinction parameter $K$ of the absorption band at 1720 cm$^{-1}$ in the IR spectra of (*1*) unfilled uninhibited and (*2*) filled inhibited polyethylene films as a function of oxidation time $\tau$. Inhibitor (adsorbed on the filler surface): (a) Irganox 1010 and (b) Neozon D; filler (1 wt %): (*2*) Al$_2$O$_3$ and (*3*) SiO$_2$; oxidation temperature 150°C; KBr supports. The antioxidant concentration relative to the polymer is indicated at the curves.

after which the amount of the antioxidant adsorbed on the surface of filler particles was determined by weighing. Data on the fraction of the antioxidant adsorbed on the filler (in percents relative to the whole amount of the antioxidant taken into the experiment) are given in the table in the numerator. In the course of the experiment, we collected the antioxidant solution separated from the filler. For this purpose, the acetone solution after washing the filler particle surface was collected in a separate vessel, left to fully evaporate acetone, and weighed to determine the amount of the antioxidant as dry residue. From these data, we calculated the fraction of the antioxidant remaining in the vessel after performing the experiment (also expressed in percents relative to the initial antioxidant amount). The data obtained allowed us to construct the antioxidant balance: The first fraction was adsorbed on the surface of filler particles, the second fraction remained in the vessel as dry residue, and the third fraction volatilized in the course of the experiment. The amounts of the third, volatilized, fraction of the antioxidant are also given in the table (denominator).

Weight fractions m of the antioxidant adsorbed on the surface of filler particles (numerator) and volatilized into the atmosphere in the course of the experiment (denominator)

| Filler | $m$, %, relative to initial antioxidant weight | |
|---|---|---|
| | Irganox 1010 | Neozon D |
| Al$_2$O$_3$ | $\dfrac{4\text{–}9}{\approx 0}$ | $\dfrac{8.5\text{–}13.5}{7.0}$ |
| SiO$_2$ | $\dfrac{42.5\text{–}46.5}{\approx 0}$ | $\dfrac{44.0\text{–}48.0}{14.5}$ |

As seen from the table, silicon oxide considerably surpasses aluminum oxide in the ability to adsorb both antioxidants. On the average, about 45% of the antioxidant used (200 mg was taken) was deposited on the silicon oxide surface, whereas on the aluminum oxide surface only 5–15% was deposited.
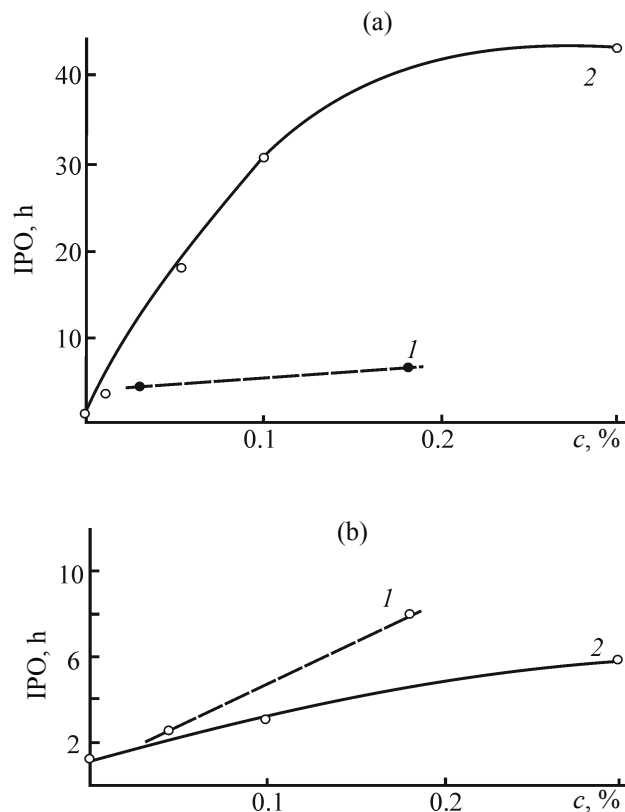


**Fig. 4.** IPO of inhibited polyethylene films as a function of inhibitor concentration c. Inhibitor: (a) Irganox 1010 and (b) Neozon D. Antioxidant introduction procedure: (*1*) I and (*2*) II; oxidation temperature 150°C.
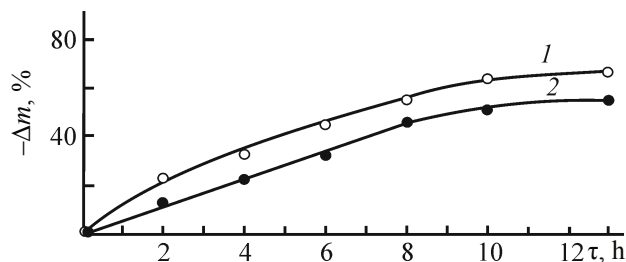
**Fig. 5.** Kinetic curves of Neozon D volatilization at 100°C from (*1*) a polyethylene film containing 10 wt % antioxidant and (*2*) the same film with additionally introduced 1 wt % SiO₂. (Δ*m*) Weight loss relative to the initially introduced antioxidant amount and (τ) time.

The fillers with the antioxidant layer deposited from a solution of the antioxidant in acetone can be subsequently used as additives enhancing the heat resistance of the polymer. Data in Fig. 3 confirm this statement.

In this case, particles of the filler (concentration 1 wt %) with the antioxidant layer deposited from a solution in acetone were introduced into uninhibited polyethylene. The films obtained from these mixtures were oxidized in air at 150°C. Along with the kinetic curves of accumulation of carbonyl groups in the filled films, the corresponding curve for the uninhibited unfilled polyethylene is given for comparison (Figs. 3a and 3b, curves *1*).

As can be seen, introduction of the antioxidant as a layer deposited on the filler surface enhances the resistance of the polymer to thermal oxidation, evaluated by IPO. This means that, irrespective of the kind of the filler, the antioxidant undergoes desorption from the particle surface and transfer into the bulk of the polymer, suppressing oxidation reactions. The higher the concentration of the antioxidant introduced into the polymer, the stronger is the antioxidant effect (the antioxidant concentration relative to the polymer is indicated at curves in Figs. 3a and 3b).

It was interesting to compare the effect of polyethylene inhibition at two procedures for antioxidant introduction. In both cases, antioxidant was introduced as acetone solution. In the first, already considered, case (procedure I), the filler powder was wetted with the antioxidant solution, and in the second case (procedure II), the polymer powder was treated with the antioxidant solution and, after the solvent evaporation, taken for preparing films, without introducing the filler. Apparently, the second procedure for preparing inhibited films was characterized by more uniform distribution of the antioxidant in the bulk of

the polymer, and a stronger antioxidant effect could be expected in this case.

The efficiency of the polyethylene inhibition with the two procedures for antioxidant introduction is compared in Fig. 4. Here, the dependence of IPO on the concentration of the antioxidant additive introduced into the polymer is given. As can be seen, IPO increases with increasing concentration, and the efficiency of one or another procedure for antioxidant introduction can be judged from the steepness of the IPO increase and from the IPO level reached. Introduction of Irganox 1010 into the polymer by procedure II appears to be more efficient than its introduction by procedure I, when the additive is localized only in sites of location of the filler particles (Fig. 4a, curves *1*, *2*). The more uniformly is the antioxidant distributed in the sample film, the stronger is its antioxidant effect. With Neozon D, the trend is opposite. More uniform introduction of Neozon D into the bulk of polyethylene by application of the modifier onto each polymer particle (procedure II) can be less efficient than the nonuniform introduction (procedure I), when it is introduced in the form of adsorbed layer on the surface of filler particles (Fig. 4b, curves *1*, *2*).

We believe that this anomaly is due to high volatility of Neozon D, compared to Irganox 1010, from the sample film. When studying the adsorption of the antioxidants on the fillers, we already noted relatively large loss of Neozon D due to its volatilization from the solution into the atmosphere. For example, in the experiment with the deposition of Neozon D on silicon oxide, the antioxidant loss was about 14% (see table). Under these conditions, Irganox 1010 underwent virtually no volatilization, i.e., its loss did not exceed the experiment uncertainty. Such a difference between the antioxidants was also observed in experiments of other kind. For example, when a thin layer of Neozon D on a support is heated in air at 150°C, approximately 20% of the initial antioxidant amount volatilizes in 5 h. Under the same conditions, virtually no sublimation of Irganox 1010 is detected. In another experiment, a polyethylene film containing uniformly distributed Neozon D was heat-treated at 100°C. In this experiment, 45.3% of the antioxidant introduced into the polymer volatilized in 6 h. In the film containing Irganox 1010, the antioxidant loss did not exceed 0.8%.

Apparently, high volatility of Neozon D is the main cause of its low performance. A considerable fraction of the antioxidant volatilizes from the samples in the course

of storage and operation instead of exerting the protecting effect against thermal oxidation. The antioxidant is not consumed in radical deactivation reactions and is merely removed from the reaction zone.

A question remains: To what extent does the introduction of fillers exhibiting high adsorption ability into the inhibited polyethylene affect the kinetics of Neozon D volatilization? The following tests were performed for this purpose. We tested in parallel the inhibited polyethylene films containing the filler and free of it. The Neozon D volatilization in these tests was monitored by the weight loss in the course of the heat treatment.

Figure 5 shows the kinetic curves of the Neozon D volatilization from the unfilled polyethylene film (curve *1*). As can be seen, more than a half of the antioxidant volatilizes from the film upon heat treatment at 100°C for 8 h. Introduction of the filler reduces the volatilization. Apparently, if the filler were taken in an amount larger than 1 wt %, the suppressing effect on the antioxidant volatilization would be stronger.

## CONCLUSIONS

The data obtained account for the difference in the mechanisms of the filler effect on the induction period of oxidation of polyethylene inhibited by Irganox 1010 and Neozon D. With Neozon D inhibitor, the fillers impede the antioxidant volatilization from the film and thus increase the induction period of oxidation. The higher the adsorption ability of the filler, the stronger is its enhancing effect on the efficiency of using the antioxidant. With Irganox 1010, the antioxidant volatilization from the film is extremely low. In this case, more uniform distribution of the antioxidant in the bulk of the polymer is a more important factor. Introduction of the filler makes the antioxidant distribution nonuniform; as a result, the induction period of the composite oxidation becomes shorter. The higher the adsorption ability of the filler, the more pronounced is the decrease in the induction period of oxidation.

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