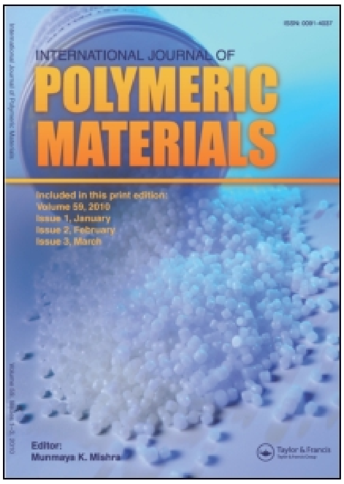

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Critical Concentrations of Some Phenolic Antioxidants in Butyl Rubber*

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Induction period of oxidation of butyl rubber non-linearly increases with concentrations of antioxidants: slowly below a certain threshold or "critical" concentration, and rapidly above that concentration. Three industrial antioxidants have been studied, the most effective from those appeared to be Agidol 2: 2,2′-methylene-bis(4-methyl-6-tert.butyl-phenol) otherwise known as "Antioxidant 22-46". The theory of the effect is considered.

Keywords: Antioxidants; phenolic; butyl rubber

INTRODUCTION

Butyl rubber containing 98,4% of isobutylene and 1.6% of isoprene links possess the greater stability to oxidation than polybutadiene and polyisoprene rubbers. Nevertheless this rubber and its vulcanizates need stabilization towards oxidation at elevated temperatures.

Oxidation of this rubber proceeds analogously to other hydrocarbon polymers by chain mechanism involving alternating free

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radicals R° and RO_2° [1, 2]:

$$RH(R'H, IH, \text{admixtures}) + O_2 \longrightarrow \cdots \longrightarrow fR^\circ \tag{0}$$

$$R^\circ + O_2 \longrightarrow RO_2^\circ \tag{1}$$

$$\begin{aligned} RO_2 + RH &\longrightarrow \boxed{ROOH + R^\circ} \longrightarrow \\ &\longrightarrow \alpha ROOH + R^\circ + \text{inactive products} \end{aligned} \tag{2}$$

Here RH denote isobutylene links, R′H – those butadiene, IH – antioxidant molecules, R° and RO_2° macroradicals.

Rectangle denotes the cage containing low-mobile radical and hydroperoxide group, the most part of which interact immediately after step 2:

$$ROOH + R^\circ \longrightarrow RO^\circ + ROH; \tag{2*}$$

$$RO^\circ + RH \longrightarrow ROH + R^\circ \tag{2**}$$

and α denotes the yield of groups —ROOH which did not decompose in the intercage reactions.

Following steps 0–2 are chain branching which proceeds at reactions of hydroperoxide groups with surrounding monomeric units:

$$ROOH + RH \longrightarrow \boxed{RO^\circ + R^\circ + RH} + H_2O \longrightarrow \sigma R^\circ + \text{products} \tag{3}$$

Hydroperoxide groups are formed in reaction of RO_2° with monomeric unit RH and decomposes in reactions with the same groups. In the stationary case the rates of hydroperoxide formation and decomposition are equal to one another, and the rate of chain branching is directly proportional to free radical concentration: $W_3 = \alpha\sigma W_2$.

Several steps of chain termination are possible without antioxidants:

$$R^\circ + RO_2^\circ \longrightarrow ROOR \tag{4}$$

$$RO_2^\circ + RO_2^\circ \longrightarrow ROOR + O_2 \tag{5}$$

In the presence of antioxidant (IH) we must add its reaction with RO_2°:

$$RO_2^\circ + IH \longrightarrow ROOH + I^\circ \tag{6}$$

followed by reactions of low-active radical I°, for example $I^\circ + I^\circ \rightarrow I{-}I$ or $I^\circ + R^\circ \rightarrow I{-}R$ in which free valences disappear or $I^\circ + RH \rightarrow IH + R^\circ$ leading to regeneration of both active radical and antioxidant molecule.

The reaction between two alkyl radicals R° is very improbable because of low concentration of these radicals. The rates of reactions 4 and 5 are proportional to the second power of total free radical concentration. In the beginning of the process when the radical concentrations are low these reactions are negligible compared to steps 2, 3 and in the presence of antioxidant with reaction 6.

At greater temperatures, when hydroperoxide groups are unstable, two different cases may take place: if the rate of chain branching is greater than that of chain termination, the process is self-accelerated, and if these rates are equal the process is stationary. Two types of stationarity exist: stationarity at low radical concentrations when the rate of chain termination in step 6 is equal to chain branching in step 3 ($W_6 = W_3 = \alpha\sigma W_2$), and stationarity at high radical concentration, when the most radicals terminate in steps 4 and 5, the rates of which are proportional to the second power of $[RO_2^\circ]$ or $[R^\circ]$. This type of stationarity corresponds to developed reaction in the absence of antioxidants.

Antioxidant concentration corresponding to the borderline between non-stationary process and the first type of stationarity is called "critical antioxidant concentration" $[IH]_{cr}$. On the curves "induction period *vs.* initial antioxidant concentration" to this critical concentration corresponds the sharp bend over which, at $[IH]_o > [IH]_{cr}$, induction period rapidly increases with increasing $[IH]_o$ [1, 3]. The smaller is critical concentration, the more effective is the antioxidant.

In this study the authors investigated oxidation of butyl-rubber in the presence of antioxidants.

EXPERIMENTAL

Two types of butyl rubber containing 1.6% (molecular) of isoprene units were studied: prepared by polymerization in solution (BR-1) and in suspension (BR-2). Antioxidants were: Agidol 2 (2,2′-methylene-bis(4-methyl-6-tert.butylphenol) known also as antioxidant 22–46), Wingstay L (butylated product of interaction of *p*-cresol and dicyclopentadiene with average molecular mass 600–700, containing two or more phenolic hydroxyls), and Irganox 1010 (the ester of 4-hydroxy-3,5-di-tert.butylpropyonic acid and pentaerithrol, containing four hydroxyls). BR-1 has been mixed with antioxidants by mixing two solutions, when BR-2-particles of 3 mm in size, has been mixed with antioxidant powder (suspension) with subsequent removal of water by filtration. The samples were oxidized in special device [1, 4] either without any treatment (BR-1 and some samples of BR-2) or after heating in evacuated sealed tubes at 180°C, 1 hour (BR-2).

Because one of the antioxidants studied, namely Wingstay L, is the mixture of several compounds, the concentration of all antioxidants is expressed in weight percents.

RESULTS AND DISCUSSION

Figure 1 shows the curves of oxygen consumption during oxidation of non-stabilized and stabilized with Agidol 2 samples of butyl rubber BR-2 at 180°C. As seen from this figure, oxidation is self-accelerated process, 0.1% of this antioxidant markedly prolong the induction period, calculated as time from beginning of reaction till the moment when samples absorb 0.25 mole of oxygen per 1 kg of rubber. The induction period of oxidation of BR-2 samples containing antioxidant if they were heated before oxidation are much greater than those of non-heated samples. This difference is due to non-regular antioxidant distribution in samples [5]. Heating the samples we gain the more regular distribution because of increase of both antioxidant solubility and coefficient of its diffusion. The same process taking place during oxidation results in temporary retardation of reaction seen in curve 2.

Figure 2 shows the dependencies of induction period of oxidation of BR-2 samples on initial concentration of Agidol 2: non-heated and heated at 180°C. The figure shows that heating before oxidation markedly increases the effectivity of antioxidant due to more regular distribution in the rubber. In the same time heating changes the shape of the curve "induction period *vs.* initial antioxidant concentrations."

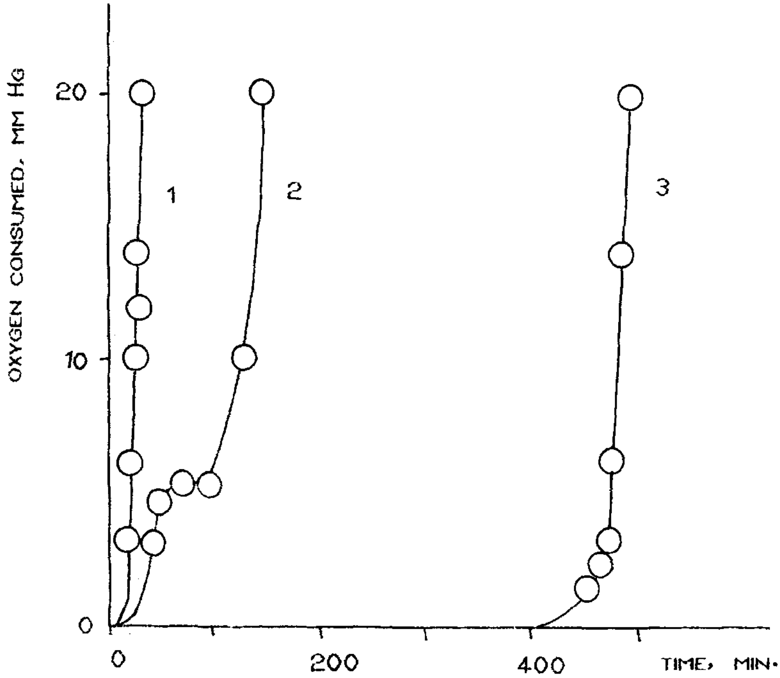


FIGURE 1 Oxygen consumption during oxidation of butyl rubber at 180°C and oxygen pressure 300 mm Hg: 1 – without antioxidant, 2,3-with Agidol 2, 0.1%, 2 – without pre-heating and 3 – pre-heated at 180°, 1 hour.

As seen from Figure 3, in pre-heated samples of BR-2 Agidol 2 at 190°C behaves as effective antioxidant, when both Wingstay L and Irganox-1010 only slightly increase the induction period, Wingstay L being slightly more effective than Irganox 1010.

Figures 4 and 5 show dependencies of induction period of oxidation of BR-1 on initial concentrations of Agidol 2 and Irganox 1010. At oxidation in the presence of Agidol 2 the sharp "critical" bend is observed near concentration of 0.07% at 180° and less distinct at 0.12–0.2% at 190° (Fig. 4), but on the corresponding curves for Irganox 1010 the marked bend is seen at 170°C and 180°C, both at about 0.02% by weight, when at 190° the bends are absent. (Fig. 5), *i.e.*, in the reaction conditions Irganox 1010 is less effective antioxidant compared to Agidol 2.

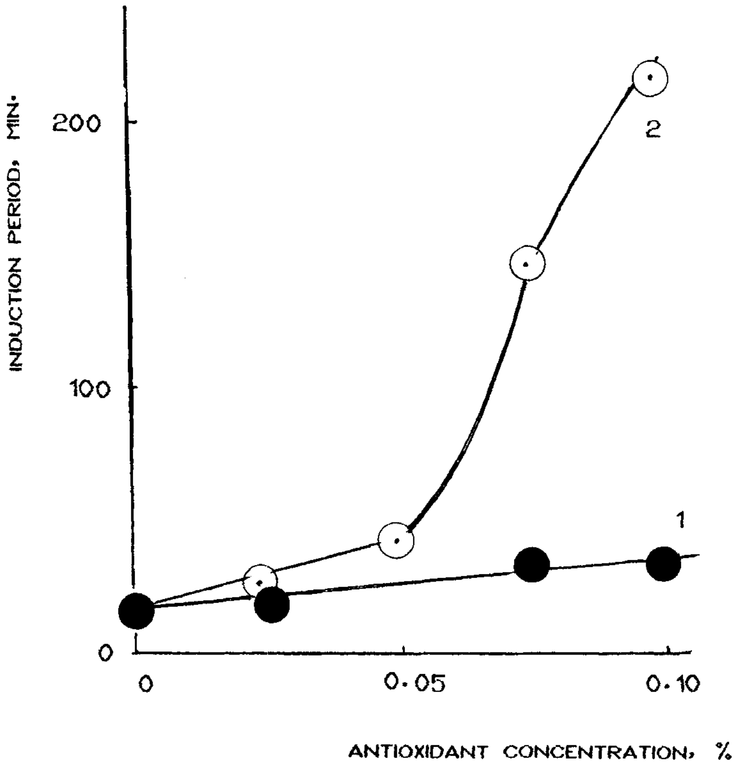


FIGURE 2 Induction period of oxidation of BR-2 samples as function of initial antioxidant concentration. Antioxidant Agidol 2, 190°C, oxygen, 300 m Hg: 1 – initial mixtures, 2 – the mixtures pre-heated before oxidation.

Comparing Figures 3, 4 and 5 shows that in pre-heated BR-2 samples Agidol 2 is more effective, but Irganox 1010 markedly less effective than in BR-1. This difference may be attributed to the lesser mobility of Irganox due to greater molecular mass of the latter.

Antioxidant Wingstay L also possess the critical concentrations as shown in Figure 6. In pre-heated BR-2 samples its critical concentrations at 170 and 180°C are close to 0.12%.

Comparing the figures we see that the more effective is the antioxidant, the more noticeable is existence of a certain threshold below which these antioxidants either do not affect or only slightly increase the induction period, when above markedly prolongs it. To

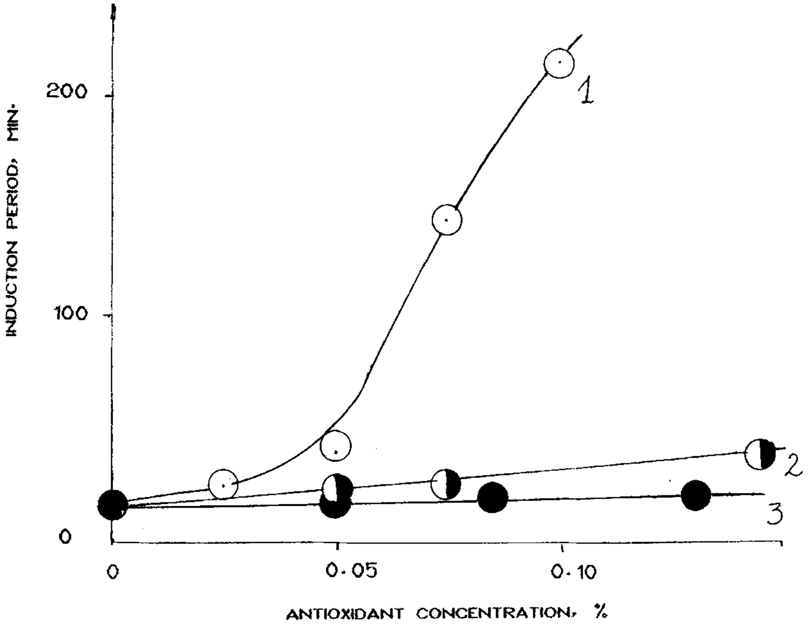


FIGURE 3 Induction period of oxidation of pre-heated BR-2 samples on initial concentrations of Agidol 2 (1), Wingstay L (92) and Irganox 1010 (3), 190°, oxygen, 300 mm Hg.

explain such effect it is necessary to consider the theory of critical antioxidant concentration [6].

This theory is based on assumption that the rates of the processes in which the number of active species, *i.e.*, of free peroxide radicals increase (in chemical kinetics the sum of these processes is called "chain branching") are directly proportional to concentration of these radicals x:

$$W_b = fx$$

where f is chain branching probability. On the other side, the rate of these radical decay, *i.e.*, the rate of chain termination is proportional to the product of antioxidant and radical concentrations:

$$W_t = k_t ix$$

(we write antioxidant concentration as "i" because some antioxidant do not contain mobile hydrogen atom).

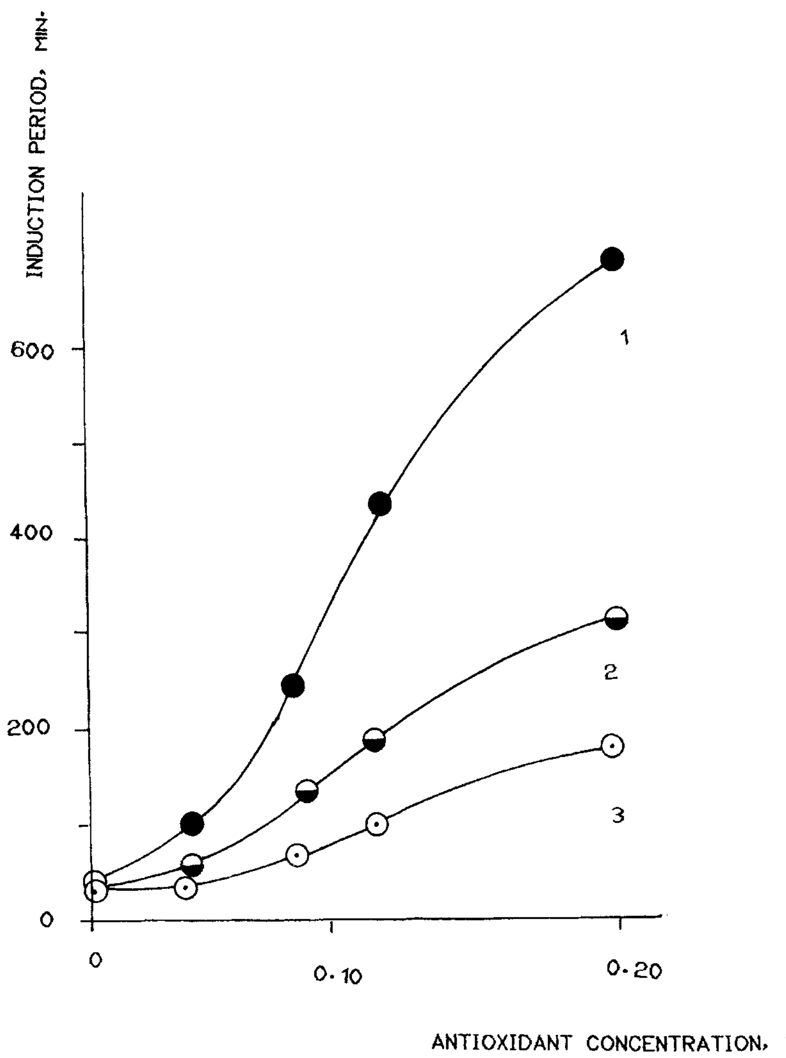


FIGURE 4 Induction period of oxidation of BR-1 samples as function of initial antioxidant concentration. Antioxidant Agidol 2, 180° (1), 190° (2) and 200°C (3), oxygen, 300 mm Hg.

The value of $(W_b - W_t)/x = (f - k_t i) = \varphi$ is called the factor of self-acceleration. If $\varphi > 0$, the number of free radicals formed is greater than those terminated and the process is self-accelerated, but if $\varphi < 0$

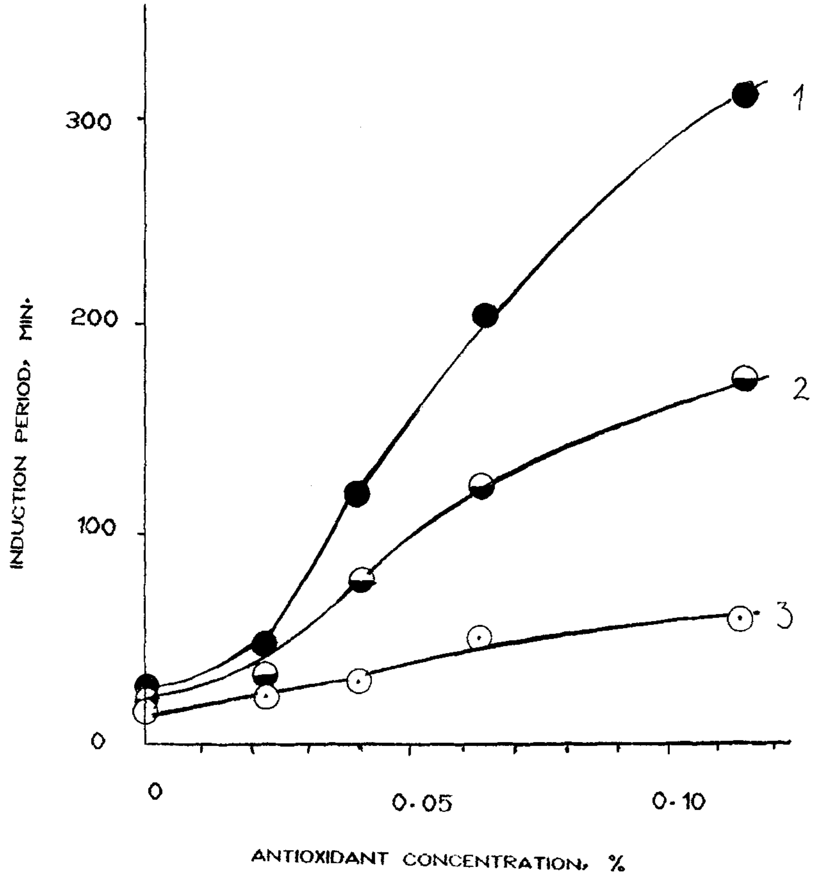
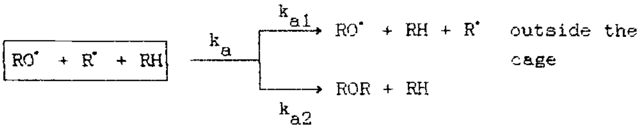


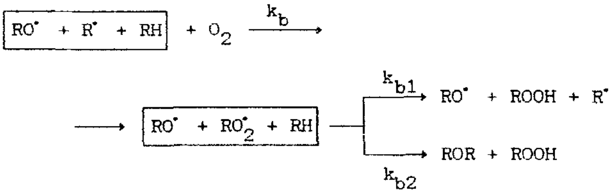
FIGURE 5 Induction period of oxidation of BR-1 samples as function of initial antioxidant concentration. Antioxidant Irganox 1010, 170° (1), 180° (2) and 190°C (3), oxygen, 300 mm Hg.

the rate decreases to the certain limit – to the stationary reaction rate. The critical antioxidant concentration corresponds to the intermediate case $\varphi = 0$. Differences between various antioxidants may be due to either differences between rate constants of chain termination k_t or to the factors non-considered in the scheme: to participation of the antioxidant in the step 3 (in the hydroperoxide group decomposition): $ROOH + RH \rightarrow \boxed{RO^\circ + R^\circ + H_2O} \rightarrow \sigma R^\circ$ + products. Consider the reactions taking place in the cage:

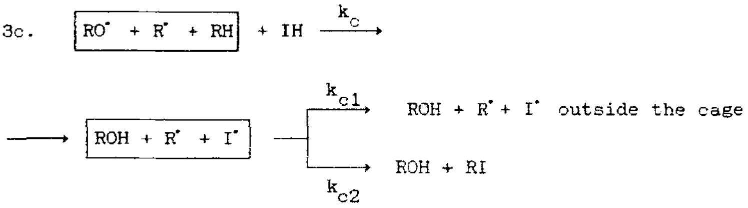
3a.



3b.



3c.



The yield of free (non-caged) radicals σ_{hp} will be:

$$\sigma_{hp} = \frac{2k_{a1} + 2k_{b1}[\mathrm{O_2}] + k_{c1}[\mathrm{IH}]}{k_a + k_b[\mathrm{O_2}] + k_c[\mathrm{IH}]}$$

or, if the most cages recombine in the absence of both O_2 and IH:

$$\begin{aligned}\sigma_{hp} &= \frac{2k_{a1} + 2k_{b1}[\mathrm{O_2}] + k_{c1}[\mathrm{IH}]}{k_a} \\ &= 2k_{a1}k_a^{-1} + 2k_{b1}k_a^{-1}k[\mathrm{O_2}] + k_{c1}k_a^{-1}[\mathrm{IH}] \\ &= \sigma_O + \sigma_1[\mathrm{O_2}] + \sigma_i[\mathrm{IH}]\end{aligned}$$

If the molecule of antioxidant entering the cage can destroy only one radical in it, the yield of free radicals from the cage will increase, if it can destroy both radicals in the same time the yield may be either smaller or slightly greater than those in the absence of it, but definitely smaller than in the presence of that destroying one radical [1, 5]. For this reason the effective antioxidant must possess at least two active groups in its molecule and both groups must either simultaneously

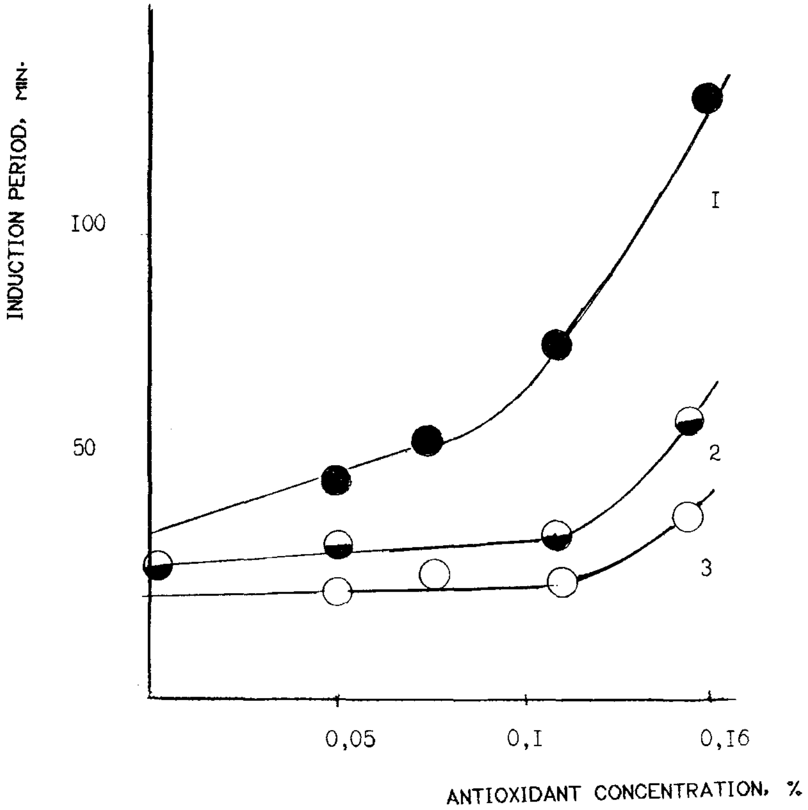


FIGURE 6 Induction period of oxidation of pre-heated BR-2 samples as function of initial antioxidant concentration. Antioxidant Wingstay L. 170° (1), 180° (2) and 190° (3), Oxygen, 300 mm Hg.

enter into the cage or be absent from it. Apparently phenolic hydroxyls of Agidol 2 are closer to one another than those of Irganox 1010, and the possibility that only one of them will enter the cage will for Irganox 1010 be much greater than for Agidol 2. This difference in structures explain the greater effectivity of the latter.

The molecular structure of butyl rubber is very similar to that of polyisobutylene. As shown earlier, the critical concentration of 2,2′-methylene-bis(4-methyl-6-tert.butylphenol) in this polymer is 3–4 times less than in isotactic polypropylene, and even monophenol – the methyl ester of 4-hydroxy-3,5-di-tert.butylphenylpropionic acid possesses critical concentration in polyisobutylene at 200°C [7] though not distinct.

Another problem connected with use of antioxidant is formation of intensively colored products of its transformation. The main role in this process play methyl groups in para-position to phenolic hydroxyl, which are present in Agidol 2 but absent in Irganox 1010 which does not stain polymers. For some of colored products of transformation of initial antioxidant possess the antioxidant properties, non-staining antioxidants may be less effective ones than their staining analogs.

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