Inhibitory effect of phenothiazine and phenyl-β-naphthylamine on the oxidation of natural rubber

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The effect of a mixture of antioxidants, phenyl-β-naphthylamine (PBN) and phenothiazine (PT) on the oxidation of natural rubber was studied. The inhibitory effect of this mixture on the oxidation of the preliminary thermally treated and subsequently oxidized rubber was found to be smaller than in the case of a direct oxidation. The investigated mixture showed a weakened effect, *i.e.* antagonism, in the whole range of molar ratios and total starting concentrations. Magnitude of the antagonistic effect of the mixture of antioxidants was expressed by negative values of the index of the relative inhibitory efficiency.

Изучалось влияние смеси антиокислителей фенил-β-нафтиламина (ФБН) и фенотиазина (ФТ) на окисление экстрагированного натурального каучука. Нашли, что в случае каучука, предварительно термически обработанного и потом окисленного на воздухе, ингибиционное воздействие смеси антиокислителей меньше, чем в случае прямого окисления. Приведенная смесь во всей области мольных отношений компонентов и во всем интервале общих исходных концентраций проявляет ослабленное воздействие — антагонизм. Величина антагонистического воздействия смеси антиокислителей выражается отрицательными значениями показателя относительного ингибиционного воздействия.

The antioxidative effect of phenothiazine on the oxidation of hydrocarbons was described in [1—4] and that of phenyl-β-naphthylamine on the oxidation of natural rubber in [5—8]. It was already pointed out in [4] that, in comparison with PBN, phenothiazine is a more efficient antioxidant in oxidation of the preliminary thermally treated natural rubber. However, the oxidation of extracted natural rubber without the preliminary generation of free radicals is better suppressed by PBN than PT. *Tarasova et al.* [3] studied a mixture of PT and PBN and found a synergism of this mixture at the molar ratio 1 1. In previous works the influence of mixtures of PBN—DPPH [8] and PT—DPPH [9] on the oxidation of natural rubber was investigated and a synergistic effect was found. For the sake of evaluation of the reactivity of PBN and PT as amine antioxidants, it was interesting to re-examine the effect of their mixture on the oxidation of natural rubber.

Experimental

The experimental technique and procedures are comprehensively described in previous papers [5, 6, 9]. Structural changes in the process of the oxidation of natural rubber were detected by means of i.r. spectroscopy. An increased absorbance of the band with wavenumber 1720 cm^{-1} corresponding to carbonyl groups was recorded. The induction period was determined from the course of the increase of $\Delta A_{C=O}$ of films with a thickness of 30 nm. The time interval in which $\Delta A_{C=O}$ reached a value 0.025 was considered to be the induction period. The inhibitory effect of a mixture of the antioxidants was expressed by means of the index of the relative inhibitory efficiency, I_{re}, defined in [9].

Results and discussion

Fig. 1 shows dependences of the induction period on the molar composition of a mixture of antioxidants PBN—PT at various total concentrations in the extracted natural rubber, preliminary enriched by free radicals in an inert medium and subsequently oxidized in air.

The same dependence found for the natural rubber oxidized in air, without a preliminary radical-enrichment, is shown in Fig. 2.

As evident from Figs. 1 and 2, the total efficiency of a mixture of antioxidants PBN and PT is lower with the thermally treated rubber than with the rubber directly oxidized.

An undistinctive maximum (Fig. 2) is observed on the curves corresponding to a direct oxidation of the rubber in the presence of the antioxidative mixture PBN—PT, however, the efficiency of the mixture never exceeds the induction period of oxidation at the same concentration of PBN alone.

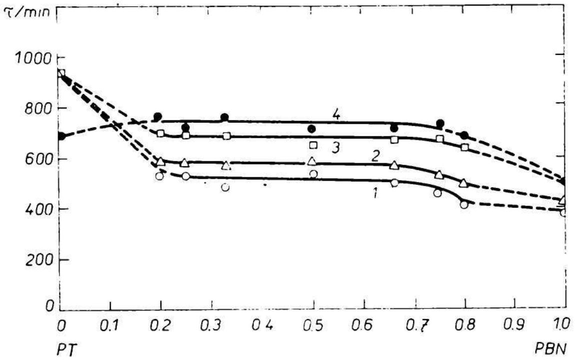

Fig. 1. Dependence of the induction period of oxidation τ (min) on the molar ratio of PBN (x_{PBN}) in the mixture PBN—PT, for extracted natural rubber preliminary enriched by free radicals in an inert medium (130°C, 1000 minutes) and subsequently oxidized in air (130°C).

Concentrations of the mixture (mol kg^{-1} × 10^{2}): *1.* 3.3; *2.* 4.0; *3.* 5.6; *4.* 7.3.

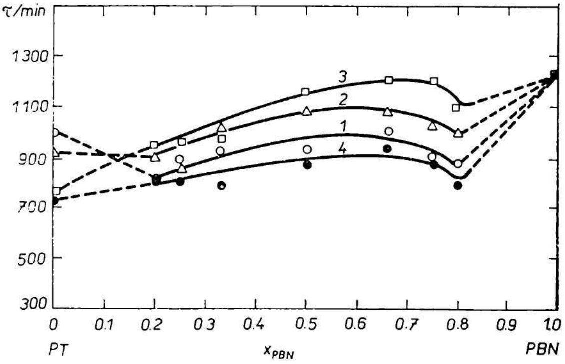

Fig. 2. Dependence of the induction period of oxidation τ (min) on the molar fraction of PBN (x_{PBN}) in the mixture PBN—PT, for extracted natural rubber oxidized in air (130°C).
Concentrations of the mixture (mol kg^{-1} × 10^2): *1.* 3.3; *2.* 4.0; *3.* 5.6; *4.* 7.3.

The course of the dependence of the induction period of oxidation upon the total concentration of the mixture at a constant molar ratio of components for boundary cases $c_{\mathrm{PBN}} > c_{\mathrm{PT}}$, $c_{\mathrm{PBN}} = c_{\mathrm{PT}}$, and $c_{\mathrm{PBN}} < c_{\mathrm{PT}}$ is shown in Figs. 3 and 4.

Figs. 3 and 4 show that no strengthened effect of a mixture of the antioxidants was observed in the whole investigated concentration range. For a thermally treated rubber, the efficiency of the inhibitory effect of mixture lies between the efficiencies of pure components (Fig. 3), while for the non-radicalized rubber in the concentration range 0.0—3.5 × 10^{-2} mol kg^{-1}, it is below the efficiencies of pure antioxidants. The evaluation of the antioxidative effect for both cases by means of the

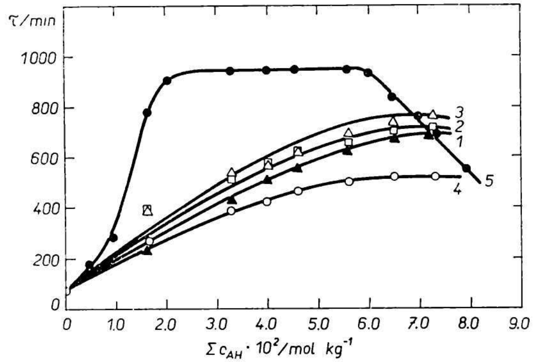

Fig. 3. Dependence of the induction period of oxidation τ (min) on the total concentration c_{AH} (mol kg^{-1}) of the mixture of antioxidants PBN—PT at a constant molar fraction of PBN (x_{PBN}).
Extracted natural rubber preliminary enriched by free radicals in an inert atmosphere (130°C, 1000 minutes) and subsequently oxidized in air (130°C), values of x_{PBN}: *1.* 8.8; *2.* 0.5; *3.* 0.2; *4.* pure PBN; *5.* pure PT.

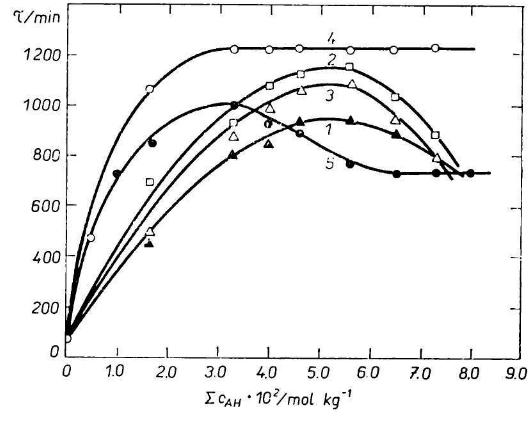

Fig. 4. Dependence of the induction period of oxidation τ (min) on the total concentration c_{AH} (mol kg^{-1}) of the mixture of antioxidants PBN—PT at a constant molar fraction of PBN (x_{PBN}).

Extracted natural rubber oxidized in air, values of x_{PBN}: *1.* 0.8; *2.* 0.5; *3.* 0.2; *4.* pure PBN; *5.* pure PT.

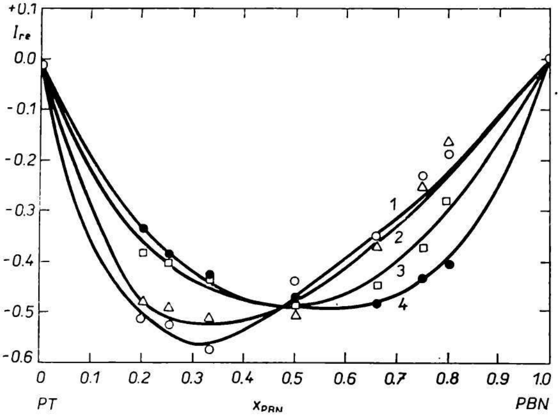

Fig. 5. Dependence of the index of the relative inhibitory efficiency (I_{re}) of the antioxidative mixture PBN—PT on the molar fraction of PBN (x_{PBN}).

The oxidation of extracted natural rubber preliminary thermally treated in an inert atmosphere (130°C, 1000 minutes) and subsequently oxidized in air (130°C), with various starting concentrations of the mixture (mol kg^{-1} × 10^2): *1.* 3.3; *2.* 4.0; *3.* 5.6; *4.* 7.3.

index of the relative inhibitory efficiency I_{re} (Figs. 5 and 6) confirmed a weakened inhibitory effect of the mixture.

The observed induction period of oxidation of the thermally treated extracted natural rubber in the presence of the antioxidative mixture of PBN and PT (Fig. 1) is shortened, in comparison with the direct oxidation (Fig. 2). This is caused by a decrease of antioxidants during the thermal treatment owing to a chemical re-

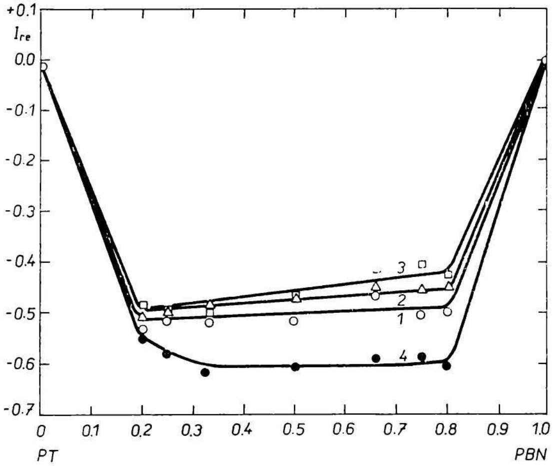

Fig. 6. Dependence of the index of the relative inhibitory efficiency (I_{re}) of the antioxidative mixture PBN—PT on the molar fraction of PBN (x_{PBN}).
The oxidation of extracted natural rubber in air (130°C), with various starting concentrations of the mixture (mol kg^{-1} × 10^2): *1.* 3.3; *2.* 4.0; *3.* 5.6; *4.* 7.3.

action of the generated free radicals of the substrate with the present antioxidants, especially with PBN [4, 5]. Fig. 3 also shows that the course of the dependence $\tau = f(c_{AH})$ resembles the dependence of the induction period of oxidation upon the concentration of pure PBN.

In the case of a direct oxidation of the extracted natural rubber (Fig. 4), the dependence $\tau = f(c_{AH})$ resembles more the course characteristic for the presence of pure PT.

So far the explanation for the antagonism has been only qualitative, *e.g.* the formation of a complex inactive towards peroxyradicals, between two antioxidants [10], a different reactivity of the radicals of antioxidants $A_1^{\cdot}$ and $A_2^{\cdot}$ towards $RO_2^{\cdot}$ causing the formation of recombination products $A_1—A_2$ [11], or the explanation involving hydrocarbon participation [12, 13]. Similar explanation may be used for the anomalous behaviour of a mixture of the antioxidants PBN and PT in the process of oxidation of the extracted natural rubber, both in the oxidation after the preliminary thermal treatment in an inert atmosphere and in the direct oxidation in air.

However, the results achieved with PBN and PT indicate that the efficiency of a mixture of antioxidants depends not only on the presence of mobile hydrogen atoms, but also on other factors which were so far investigated only scarcely or not at all. They are *e.g.* the state of the electron pair on the nitrogen atom, the participation of a stable radical A• in the process of inhibition, a possible inhibition through the complex formation between the antioxidant and peroxyradical or some other radicals.

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