Inhibitory effect of a mixture of phenyl-β-naphthylamine, phenothiazine, and α,α-diphenyl-β-picrylhydrazyl on the oxidation of natural rubber

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The effect of concentration of a ternary mixture of antioxidants DPPH—PBN—PT on the oxidation of extracted natural rubber was investigated. At the equimolar ratio, a strengthened inhibitory effect of the mixture was observed with respect to the additivity of individual components or binary mixtures of the antioxidants DPPH—PBN and DPPH—PT. The course of the observed induction periods as a function of concentration of the original mixture is similar to that of additive induction periods. It was confirmed that DPPH is a synergistic component of the ternary inhibitory system.

Изучалось влияние концентрации трехкомпонентной смеси ДФПГ—ФБН—ФТ на окисление экстрагированного натурального каучука. Нашли, что смесь при эквимолярном отношении обладает повышенным ингибиционным воздействием по сравнению с аддитивностью отдельных компонентов, а также с двухкомпонентной смесью антиокислителей ДФПГ—ФБН и ФДПГ—ФТ. Ход зависимости наблюдаемых индукционных периодов от концентрации исходной смеси аналогичен ходу зависимости аддитивных индукционных периодов. Подтвердилось, что ДФПГ является синергическим компонентом в трехкомпонентной ингибиционной системе.

The effect of phenyl-β-naphthylamine (PBN) and phenothiazine (PT) on the oxidation of natural rubber in the presence of α,α-diphenyl-β-picrylhydrazyl (DPPH) was followed in [1, 2]. In both cases, the binary antioxidative mixture at certain molar ratios showed a synergistic effect when used with the extracted natural rubber thermally treated and subsequently oxidized as well as with rubber directly oxidized in air. The mixture of antioxidants PBN and PT exhibited a weakened effect in the whole range of molar ratios. The effect of individual antioxidants on the oxidation of natural rubber has been reported in [4, 5].

The aim of this work was to determine the effect of a ternary mixture of antioxidants PBN—PT—DPPH on the oxidation of natural rubber.

Experimental

The hydrocarbon studied was natural rubber deprived of natural antioxidants by the acetone extraction in nitrogen at room temperature. The experimental technique and procedure were described in previous papers [2—4, 6]. Structural changes of the natural rubber in the course of oxidation were indicated by i.r. spectroscopy, in the form of the absorbance changes of carbonyl groups. The induction period of oxidation was read off from kinetic curves representing the time dependence of $\Delta A_{C=O}$ as the time corresponding to $\Delta A_{C=O} = 0.025$.

Results and discussion

The effect of a mixture of PBN and PT in the presence of DPPH on the oxidation of the extracted natural rubber was investigated at a molar ratio of the components 1 1 1. The effect of the equimolar mixture was followed in two series of samples, as in the previous works. In the first series the mixture of antioxidants and of the substrate was thermally treated in an inert atmosphere at 130°C for 1000 minutes and exposed to a subsequent oxidation. In the second series the same samples were subjected to a direct oxidation in air at 130°C.

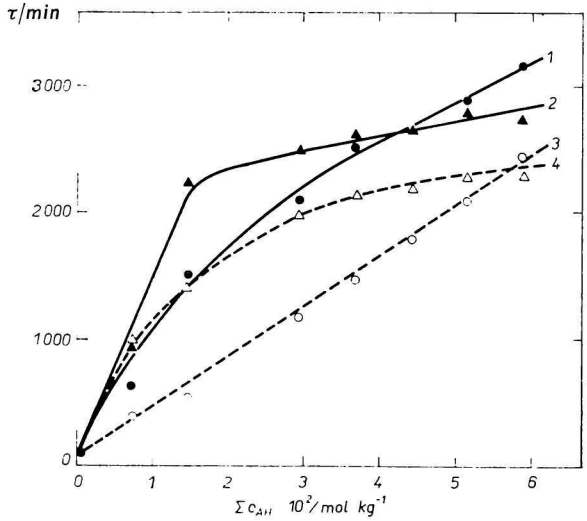

Fig. 1. Dependence of the induction period of oxidation τ (min) on the starting total concentration (mol kg^{-1}) of a mixture of antioxidants at an equimolar ratio 1 1 1. *1.* Extracted natural rubber preliminary enriched by free radicals in an inert atmosphere (130°C, 1000 minutes, N_2) and subsequently oxidized in air at 130°C; *2.* extracted natural rubber oxidized in air at 130°C; *3*, *4.* calculated additive effect of a mixture of the antioxidants corresponding to the curves *1* and *2*, respectively.

The dependence of the induction period of oxidation on the total starting concentration of the antioxidative mixture is shown in Fig. 1 for both series of samples.

The course of the curves in Fig. 1 indicates that also in this case the value of the induction periods depends on the condition whether the extracted rubber was thermally treated prior to the oxidation in air. The value of the induction period of oxidation at the concentration of the antioxidants up to 4.2×10^{-2} mol kg^{-1} is lower for the extracted natural rubber preliminary treated than for a directly oxidized rubber. At higher concentrations, the induction periods are practically invariable. Calculated additive curves *3* and *4* follow very closely the course of the observed curves, however, the induction periods do not reach the values determined experimentally. The induction periods for the additive curves were read off from diagrams of the concentration dependences of induction periods for the individual antioxidants [4, 5].

Curves *1* and *2* in Fig. 1 shows a strengthened inhibitory effect of the investigated ternary mixture of antioxidants. This strengthened effect follows also from a comparison of the values of the induction period of oxidation with corresponding values for the binary mixture DPPH—PBN and DPPH—PT at the same molar fraction of DPPH, $x_{\mathrm{DPPH}} = 0.33$, and the total starting concentration of the antioxidants equal to 3.9×10^{-2} mol kg^{-1}. The values are given in Table 1.

The difference between the course of the dependences determined for the ternary antioxidative mixture of DPPH—PBN—PT on one hand and for binary mixtures DPPH—PBN [1] and DPPH—PT [2] on the other is due mainly to a different reaction rate of DPPH with PBN and PT, and to the action of the formed >N• radicals

$$\mathrm{DPPH} + \mathrm{PT} \xrightarrow{k_1} \mathrm{DPPH\text{-}H} + \mathrm{PT}(>\mathrm{N}\bullet), \qquad (1)$$

$$\mathrm{DPPH} + \mathrm{PBN} \xrightarrow{k_1'} \mathrm{DPPH\text{-}H} + \mathrm{PBN}\bullet . \qquad (1')$$

From the literature data [7—10] as well as from our own experiments [1, 2, 4, 6] it follows that $k_1 > k_{1'}$. Compared with the original mixture, the inhibitory system thus contains also DPPH-H and the PBN• radical while phenothiazine changes

Table 1

Induction periods of oxidation for various mixtures of antioxidants at constant molar fraction of DPPH ($x_{\mathrm{DPPH}} = 0.33$) and constant starting total concentration of antioxidants ($\Sigma\, c_{\mathrm{AH}} = 3.9 \times 10^{-2}$ mol kg^{-1})

Equimolar mixture of antioxidants	Induction period of oxidation	
	radicalized (min)	non-radicalized (min)
DPPH : PBN : PT 1 1 1	2600	2600
DPPH : PBN[a] 1 1	2200	2000
DPPH : PT[b] 1 1	1800	2200

a) and *b*) — values from [1, 2].

into products, probably dimers, which may also influence the value of the induction period of oxidation. Reactions (*1*) and (*1'*) are not responsible for the whole course of the function $\tau = f(\Sigma c_{AH})$ for ternary mixture, since other very complicated reactions may occur during the thermal treatment as well as during the direct oxidation. The strengthened effect of a ternary mixture of the studied antioxidants seems to be affected also by a superposition of some other factors which cannot be deduced from the reported experimental results. DPPH comports himself as a synergistic component also in this system since a mixture of PBN—PT is antagonistic in the whole range of molar concentrations.

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