Inhibitory effect of phenothiazine on the oxidation of natural rubber in the presence of α,α-diphenyl-β-picrylhydrazyl

[a]J. HRIVÍKOVÁ, [b]A. HRIVÍK, and [a]V. KELLÖ

[a]*Department of Physical Chemistry, Slovak Technical University, 880 37 Bratislava*

[b]*Department of Technology of Plastics and Fibres, Slovak Technical University, 880 37 Bratislava*

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The effect of phenothiazine (PT) on the oxidation of natural rubber in the presence of α,α-diphenyl-β-picrylhydrazyl (DPPH) was studied. Their inhibitory effect was expressed by means of the length of the induction period of oxidation and the index of the relative inhibitory efficiency I_{re}. The synergistic effect on the subsequent oxidation of natural rubber thermally treated in an inert medium could be observed only at higher concentrations of phenothiazine and it decreased with increasing total concentration of the antioxidative mixture. Antagonism was observed at high concentrations of DPPH in the presence of PT. At the oxidation of natural rubber without thermal treatment the mixture of DPPH and PT appeared to be synergistic and the synergistic effect increased with the molar fraction of DPPH. The course of the reaction between DPPH and PT, accompanied by the formation of DPPH-H and phenothiazinyl radicals PT (>N•), was confirmed and the radicals were detected by the e.p.r. method. Furthermore, basic reactions between DPPH and PT in the presence of a thermally treated and subsequently oxidized rubber as well as the rubber oxidized without a preliminary thermal treatment are described.

Изучалось влияние фенотиазина (ФТ) на окисление натурального каучука в присутствии α,α-дифенил-β-пикрилгидразила (ДФПГ). Их ингибиционное воздействие было выражено с помощью длины индукционного периода окисления и показателя относительного ингибиционного воздействия $I_{ов}$. Нашли, что синергический эффект при термической обработке каучука в инертной среде и далее окисленного можно наблюдать только в области повышенных концентраций фенотиазина, который с повышением общей концентрации смеси антиокислителей понижается. При высоких концентрациях ДФПГ в присутствии ФТ наблюдается антагонизм. При окислении натурального каучука без термической обработки смесь ДФПГ и ФТ проявляется как синергическая, причем синергический эффект с повышением мольной доли ДФПГ углубляется. Подтвердился механизм реакции между ДФПГ и ФТ с возникновением ДФПГ-Г и фенотиазиниловых радикалов, присутствие которых доказалось методом ЭПР В статье далее описываются основные реакции между ДФПГ и ФТ в присутствии термически обработанного и потом окисленного каучука, а также каучука окисленного без предварительной термической обработки.

Several authors dealt with the inhibitory effect of phenothiazine as an antioxidant. *Murphy et al.* [1] used phenothiazine for stabilization of liquid and solid hydrocarbons. They explained the inhibitory reaction mechanism of phenothiazine by the formation of free radicals stabilized owing to the resonance. These radicals can react with peroxides and their partial regeneration is assumed. *Colclough* [2] found that phenothiazine acts as a retardant of the uninitiated oxidation of squalene while a marked inhibitory period was observed at the initiated oxidation with AIBN. *Tarasova et al.* [3] obtained similar results; they observed a marked inhibitory period at the initiated oxidation of rubber SKI-3 at 130°C. In the study of the inhibitory effect of phenothiazine on the oxidation of natural rubber, *Hriviková* and *Kellö* [4] found that an appreciable inhibitory effect appears only at a low concentration of phenothiazine (up to 0.6% w/w) and a different level of free radicals. A difference in the efficiency of the antioxidant depending on the amount of the radicals generated before the subsequent oxidation in air was observed only in the range of higher concentrations of the inhibitor (over 1% w/w).

A number of works found in literature describes phenothiazine as a decomposer of hydroperoxides and peroxides [2, 3, 5—7], which is a possible explanation for its antioxidative effect. The inhibitory effect of DPPH on the oxidation of rubber is described in [8—10].

So far, only few authors have studied the effect of phenothiazine in the presence of other inhibitors. *Tarasova et al.* [3] found that the mixture of PT and phenyl-β-naphthylamine with the molar ratio 1 1 shows the synergism at the oxidation of rubber SKI-3 at 130°C. The authors explained this effect as a consequence of the influence of thio derivatives on the decomposition of hydroperoxides.

The synergistic effect of phenothiazine in the presence of chloranile [7] on the oxidation of paraffine oil is explained by the formation of π complex with a higher inhibitory influence.

The aim of this work was to examine the effect of a mixture of PT and DPPH on the oxidation of extracted natural rubber. The physical and chemical changes of antioxidants in the course of and after the oxidation were not examined.

Experimental

The studied hydrocarbon was a natural rubber deprived of natural antioxidants by the acetone extraction in nitrogen atmosphere at room temperature for 40 hrs. The extraction of samples, the preparation of rubber solutions and films for kinetic tests, the pressure apparatus for thermal treatment of the samples prior to the subsequent oxidation together with the necessary manipulation are described elsewhere [8, 9].

DPPH and PT were purified by a recrystallization from benzene (m.p. 144°C) and from ethanol (m.p. 182°C), respectively. The benzene solution of DPPH and PT was prepared at first, then the required amount of extracted natural rubber was added, and a rubber sol was prepared by shaking.

Half of the rubber films (thickness 30 nm) was exposed to the oxidation in air at 130°C. The second half of the same films was freed of the traces of sorbed oxygen and subjected to generation of free radicals at 130°C for 1000 minutes in an inert atmosphere before the subsequent oxidation.

The i.r. spectroscopy method was employed to indicate structural changes of rubber in the process of the oxidation. An increasing absorbance $\Delta A_{C=O}$ of the band corresponding to carbonyl groups (1720 cm^{-1}) was observed. From the time dependence of the increasing amount of carbonyl groups, kinetic curves with a marked induction period were determined. The length of the induction period was conventionally characterized by the time interval in which $\Delta A_{C=O}$ reached a value of 0.025.

The efficiency of the inhibitory mixture of antioxidants was evaluated by means of an index of the relative inhibitory efficiency I_{re}, expressed by the relationship

$$I_{re} = \frac{\tau_0 - \tau_{ad} + \tau_s}{\tau_{ad} - 2\tau_s},$$

where τ_0 is the observed induction period of oxidation of substrate in the presence of antioxidants, τ_{ad} the additive induction period of the individual antioxidants, τ_s the induction period od substrate.

The case for $I_{re} > 0$ is denominated as synergism while for $I_{re} < 0$ it is called antagonism.

Results and discussion

The effect of a mixture of PT and DPPH on the oxidation of extracted natural rubber

The effect of a mixture of PT and DPPH on the oxidation of extracted natural rubber was examined with samples thermally treated (130°C, 1000 minutes) and subsequently oxidized at 130°C as well as with samples not subjected to the thermal treatment. The resulting effect of these antioxidants was evaluated from the length of the induction period.

In Fig. 1 the dependence of the induction period on the molar ratio of the mixture DPPH : PT (4 1, 3 1, 2 1, 1 1, 1 : 2, 1 3, and 1 4) for natural rubber thermally treated and subsequently oxidized in air is shown. An analogous series of experiments, carried out without the preliminary thermal treatment is shown in Fig. 2.

Figs. 3 and 4 illustrate the evaluation of the index of the relative inhibitory efficiency of the mixture of DPPH and PT in a dependence on the molar fraction of DPPH (x), for the individual total initial concentrations given in Figs. 1 and 2. Values of τ_{ad} and τ_s were taken from Fig. 5.

The results shown in Figs. 1—4 point at a different effect of the mixture of antioxidants.

The overall course of the oxidation of a thermally treated and subsequently oxidized natural rubber in the presence of a mixture of antioxidants depends both on the molar ratio and the amount of the individual antioxidants (Fig. 1). At the molar ratio DPPH PT ranging from 1 4 to 1 1, the influence of phenothiazine is manifested and the inhibitory effect of mixture decreases with increasing total starting concentration. At the molar ratio 1 4—4 1 the influence of DPPH prevails and the inhibitory effect of mixture increases with its starting concentration.

The induction period of the oxidation of extracted natural rubber in the presence of the mixture of DPPH and PT (Fig. 2) is independent both of the molar ratio

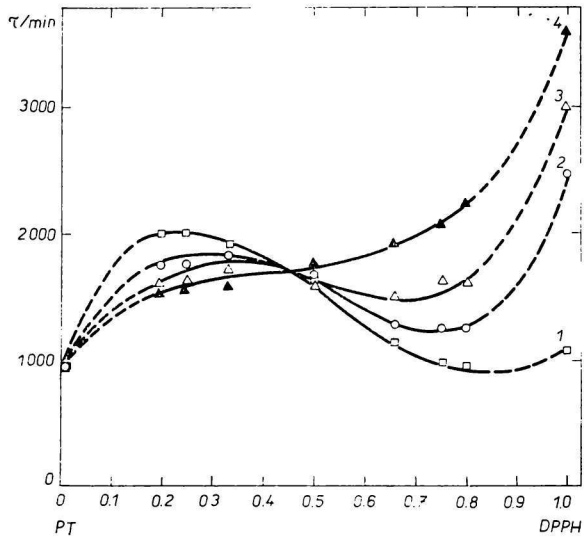

Fig. 1. Dependence of the induction period of the oxidation τ (min) on the molar ratio of the mixture of DPPH and PT for extracted natural rubber preliminary thermally treated and oxidized in air (130°C).
Starting total concentrations of the mixture ($\Sigma c_{AH} \times 10^2$ mol kg^{-1}): *1.* 1.65; *2.* 3.3; *3.* 5.0; *4.* 6.6.

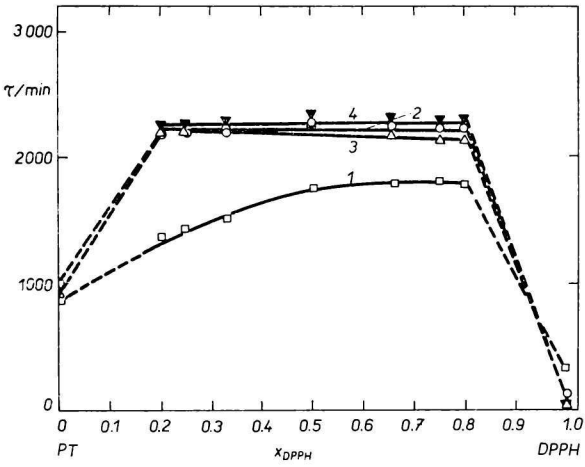

Fig. 2. Dependence of the induction period τ (min) on the molar ratio DPPH : PT for extracted natural rubber oxidized in air (130°C).
Starting total concentrations ($\Sigma c_{AH} \times 10^2$ mol kg^{-1}): *1.* 1.65; *2.* 3.3; *3.* 5.0; *4.* 6.6.

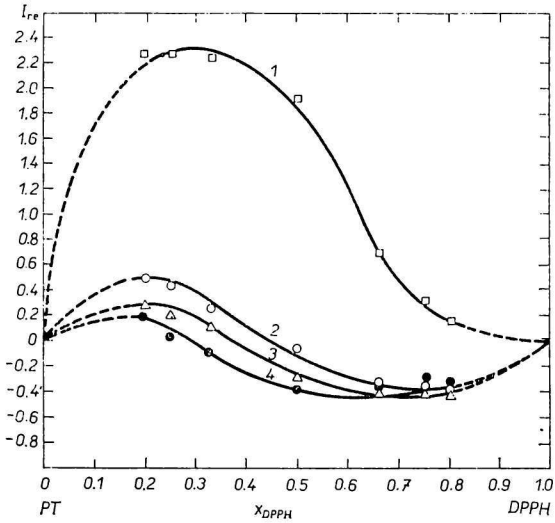

Fig. 3. Dependence of the index of the relative inhibitory efficiency (I_{re}) on the molar fraction of DPPH in the mixture of DPPH with PT for extracted natural rubber preliminary thermally treated and oxidized in air (130°C).
For starting total concentrations $\Sigma\, c_{AH}$ see Fig. 1.

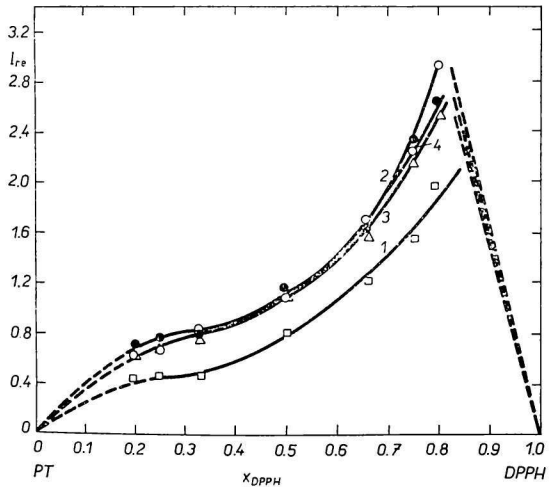

Fig. 4. Dependence of the index of the relative inhibitory efficiency (I_{re}) on the molar fraction of DPPH in the mixture of DPPH and PT for extracted natural rubber oxidized in air (130°C).
For starting total concentrations $\Sigma\, c_{AH}$ see Fig. 1.

of the components and of the starting concentration of the mixture ranging from 3.3×10^{-2} to 6.6×10^{-2} mol kg^{-1}. Only for the concentration 1.65×10^{-2} mol kg^{-1}, a variation of the induction period is observed, depending on the molar fraction of DPPH in the mixture of DPPH and PT.

The effect of a mixture of antioxidants DPPH and PT on the oxidation of the used substrate is shown in Figs. 3 and 4, as a dependence of the index of the relative inhibitory efficiency on the molar fraction of DPPH at various concentrations of the binary antioxidative mixture.

At the subsequent oxidation of thermally treated rubber in the presence of mixture of DPPH and PT, a "practical" synergism is observed in the whole range of molar fractions only at the lowest concentration of the mixture (1.65×10^{-2} mol kg^{-1}, see Fig. 3, curve *1*). The calculated index of the relative inhibitory efficiency decreases with increasing concentration of the mixture, in the further course only a "strengthened" effect of the mixture is observed at $x_{DPPH} < 0.5$, then it changes through additive into an antagonistic effect (Fig. 3, curves *2*—*4*).

At the oxidation of the natural rubber without a thermal treatment, the practical synergism is observed in the whole range of molar ratios and the examined starting concentrations.

The observed anomalies cannot be sufficiently explained by the achieved results. Therefore we attempted to examine basic reactions between DPPH and PT in benzene before the addition of natural rubber.

Spectrophotometric study of the reaction of DPPH with phenothiazine

The reaction of DPPH with secondary amines was studied by several authors mainly from the aspect of reactivity of the mobile hydrogen atom [11—14] as

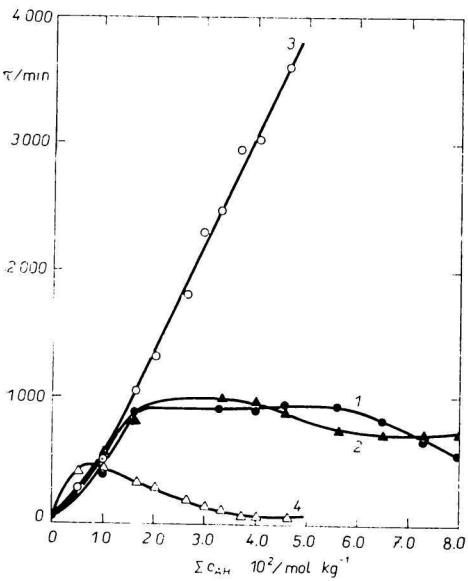

Fig. 5. Dependence of the induction period τ (min) of the oxidation of extracted natural rubber on starting total concentrations of the antioxidant (mol kg^{-1}).
1. Oxidation of extracted natural rubber preliminary thermally treated (130°C, 1000 minutes) in nitrogen and subsequently oxidized in air at the presence of PT; *2.* oxidation (130°C) without a preliminary thermal treatment in the presence of PT; *3.* conditions as for curve *1*, in the presence of DPPH; *4.* conditions as for curve *2* in the presence of DPPH.

well as of the reactions of the formed products. α,α-Diphenyl-β-picrylhydrazine was found to be formed by the reaction of DPPH with all the studied amines, the reaction rate depending on the nature of the used substrate, this being a secondary amine. The reaction of DPPH with PT has been studied mainly in the recent years [15, 16]. *Jackson* and *Patel* [15] described the e.p.r. spectrum of the phenothiazinyl radical and *Constantinescu et al.* [16] identified some of the reaction products. Since the samples of extracted natural rubber were prepared for the oxidative tests from benzene solutions at the presence of a mixture of antioxidants, the effect of the individual components on their mutual reaction was to be examined.

A spectrophotometric method was used for the study of this reaction, which made it possible to follow the decrease of DPPH in the visible region ($\lambda_{max} = 520$ nm). The reactions were carried out at 25°C in benzene solution at a constant concentration of DPPH (3×10^{-5} mol l^{-1}). It was impossible to follow the decrease of PT in the u.v. region because of the absorption of DPPH in the same region. Measurements were performed using a spectral photocolorimeter Specol (Zeiss, Jena). The experimental results are shown in Fig. 6.

These kinetic measurements are characterized by a fast reaction in the initial reaction stage (1 min) corresponding to the time which is needed for carrying out a measurement. Afterwards, the reaction rate varies very little. Similar reaction course was not observed with any of the secondary amines as yet studied.

Absorbance (A) of the solution measured after 100 minutes of the mutual reaction is shown in Fig. 7; the molar ratios DPPH : PT were 1.6 1 for sample *4*, 1 1.25 for sample *5*, and 1 : 2.53 for sample *6*.

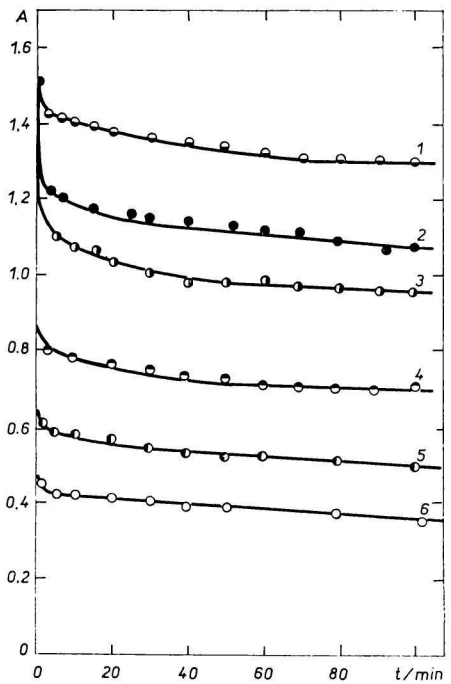

Fig. 6. Kinetics of the reaction of DPPH with PT at its various concentrations determined from the time-dependence (min) of the absorbance (A). Concentrations of PT (10^5 mol l^{-1}): *1.* 0.2; *2.* 0.5; *3.* 0.9; *4.* 2.0; *5.* 3.8; *6.* 7.6.

From Fig. 7 it is evident that the reaction between DPPH and PT was not quantitative under given conditions since the presence of DPPH was observed even at the excess of PT. When the reaction was carried out at 80°C, the maximum at $\lambda = 520$ nm did not appear.

The dependence of the rate of the decrease of DPPH in the initial stage of the reaction upon the PT concentration is shown in Fig. 8.

The partial reaction order with respect to PT in the presence of a large excess of DPPH was graphically evaluated as unitary. At an excess of PT, a deviation from the straight line was observed, this being caused probably by a superposition of the bands of DPPH and those of the formed products of PT or the bands of adducts.

The reaction of DPPH with PT resulted in the formation of DPPH-H and phenothiazinyl radical PT(>N•).

The presence of DPPH-H was detected by a reaction with PbO_2 which restored the original violet colour characteristic for DPPH. Intensity and duration of this colouring depended on the molar ratio DPPH PT.

The spectrophotometric results were also confirmed by the e.p.r. method by which a measurable level of the free phenothiazinyl radicals was detected.

Reactivity of the PT(>N•) radical is affected by the molecular structure itself. From the results of several authors [1, 6, 15, 16], namely those of *Constantinescu et al.* [16], it may be assumed that the phenothiazinyl radicals can take part in further reactions. From these radicals phenothiazine and phenothiazinesulfoxide but also dimers and other products till now unidentified were found to be formed. Dimers are formed especially by the C—N 3,10′ or 1,10′ bond, however, the formation of the N—N dimer is also admitted. In absence of oxygen the phenothiazinyl

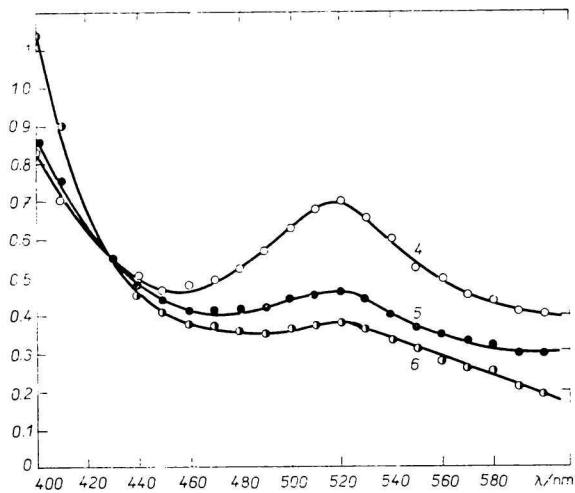

Fig. 7. Dependence of the absorbance (A) on λ (nm) at various molar ratios of DPPH : PT. *4*. 1.6 : 1; *5*. 1 1.25; *6*. 1 2.53.
Temperature 25°C, reaction time 100 minutes, total concentration of the mixture (10^5 mol l^{-1}): *4*. 2.0; *5*. 3.8; *6*. 7.6.

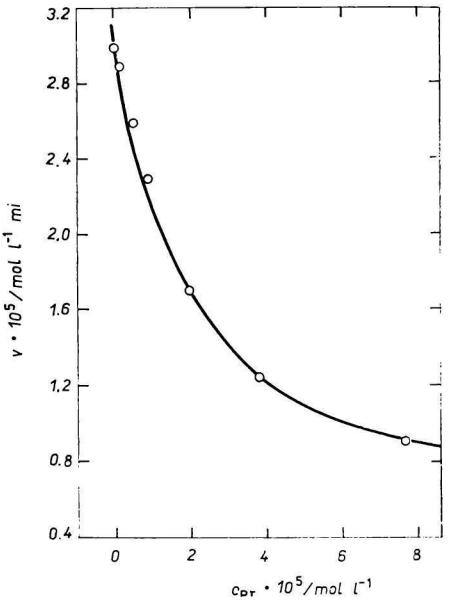

Fig. 8. Dependence of the rate of the decrease of DPPH (mol l^{-1} min^{-1}) on the amount of PT (mol l^{-1}) at 25°C.

radicals act as inhibitors in radical reactions, while in oxidative reactions they form stable iminoxyl radicals NO•. The mechanism of the formation of iminoxyl radicals was described by *Wieland* [17] and several authors [3, 15, 18—21] detected them experimentally by the e.p.r. method. The chemism of the effect of DPPH on the oxidation of rubber is described in other works [8, 10].

Study of the reaction of DPPH with phenothiazine by the e.p.r. method

The e.p.r. method provides sufficient information on the structure of free radicals and a direct proof of the detachment of the mobile hydrogen atom from the phenothiazine molecule by the effect of DPPH, *i.e.* the formation of PT(>N•) radical.

In the last decade, several authors published e.p.r. spectra of free radicals derived from phenothiazine. *Gagnaire et al.* [22] first obtained a resolved e.p.r. spectrum of free phenothiazinyl radicals with a hyperfine structure corresponding to the interaction of the unpaired electron with protons of the adjacent aromatic rings. The analysis of the contributions of all protons was realized by *Billon et al.* [23], *Odiot* and *Tonnard* [24] and later by *Gilbert et al.* [25] and by *Lhoste* and *Tonnard* [26].

Especially important appears to be the work of *Gilbert et al.* [25] who analyzed the experimental spectrum ($g = 2.0053$) with respect to MO calculations and determined interaction constants for the PT(>N•) radical. They achieved a good agreement of the experiment with a theory using a computer simulated spectrum based on interaction constants with the line width 0.33 G. *Shine* and *Mach* [27] obtained analogously the e.p.r. spectrum of the phenothiazinyl radical by irradiation of PT in ethanol. These authors also achieved a good agreement of the experiment with the theory and determined $g = 2.0053$.

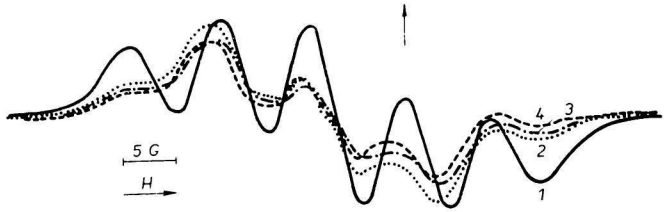

Fig. 9. The e.p.r. spectrum of DPPH and of the PT(>N•) radical in benzene solution at a molar rate of components 1 1 in various time-intervals after their mixing. Total concentration of the mixture 4.0×10^{-4} mol l^{-1}, 23°C. *1.* DPPH; *2.* 4 min; *3.* 15 min; *4.* 45 min reaction time.

Jackson and *Patel* [15] detected the PT(>N•) radicals and phenothiazineiminoxyl radicals PT(>NO·) in the series of oxidative tests with PT in liquid phase, using various oxidizing agents. The authors demonstrated a dependence of the spectrum shape, the line width and the changes of interaction constants upon the nature of the solvent.

Jackson and *Patel* [15] obtained the PT(>N•) radicals by a reaction of PT with DPPH in benzene and they reported the following interaction constants

$$a^{N} = 7.05 \text{ G}, \quad a^{H}_{3,7} = 3.66 \text{ G}, \quad a^{H}_{1,9} = 2.85 \text{ G}, \quad a^{H}_{2,5} = 0.95 \text{ G}, \quad a^{H}_{4,6} = 0.95 \text{ G}.$$

The authors mentioned that incomplete splitting made it impossible to determine more subtle differences in the interaction constants of hydrogens in the positions 2 and 4.

Our experiments were aimed to the proof of a radical reaction of DPPH with PT in benzene at room temperature when DPPH-H and PT(>N•) radicals are formed, prior to the addition of the extracted natural rubber to oxidative tests.

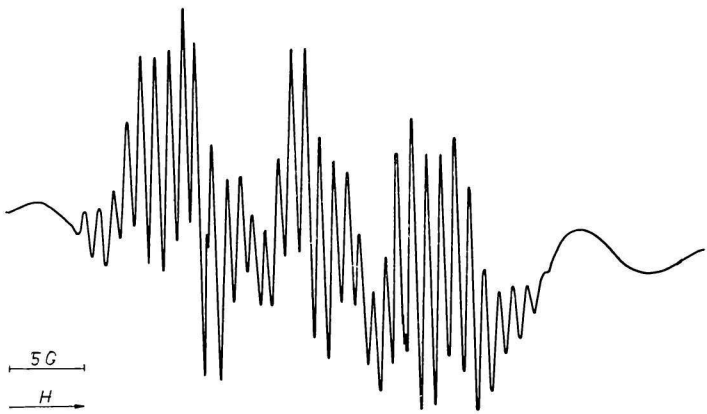

Fig. 10. The e.p.r. spectrum of a mixture of DPPH and PT(>N•) radicals in benzene. Molar ratio DPPH : PT = 1 1, total concentration of the mixture 4.0×10^{-4} mol l^{-1}.

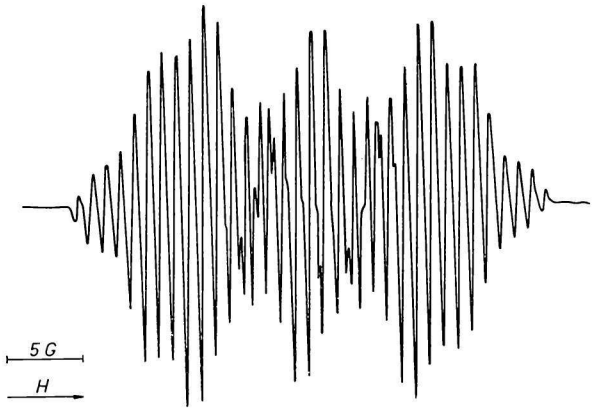

Fig. 11. The e.p.r. spectrum of the phenothiazinyl radical in benzene. The mixture DPPH PT = 1 : 4, $c_{mix} = 4.0 \times 10^{-4}$ mol l^{-1}.

The e.p.r. spectra were measured at room temperature using a spectrometer Varian, Model E-3, with the field modulation 100 kHz, the simulated spectra with Varian SS-100 electron optics.

The stable DPPH radical in benzene exhibits a quintet, while the PT(>N•) radical a triplet. Fig. 9 shows the e.p.r. spectrum of the DPPH radical in benzene at 4.0×10^{-4} mol l^{-1} (curve *1*) and after the addition of PT at the molar ratio 1 1 in various times after mixing the components (curves *2*, *3*, *4*). The triplet of the PT(>N•) radicals is obviously superimposed on the quintet of the DPPH radical. A convenient adjustment of the instrumental constants enabled us to achieve a hyperfine spectral structure of this system including line splitting of the triplet part of the spectrum. The spectrum of the equimolar mixture of DPPH and PT with a hyperfine structure is shown in Fig. 10.

As mentioned above, at the excess of PT with respect to DPPH ($c_{PT} > c_{DPPH}$), the DPPH-H and PT(>N•) radicals and others products with a non-radical character are present in the reaction mixture. The spectrum should show the triplet corresponding to the PT(>N•) radical. This presumption was verified using the mixture of DPPH and PT with a molar ratio 1 4 and the total concentration of the mixture 4.0×10^{-4} mol l^{-1}. The obtained spectrum with a hyperfine structure is shown in Fig. 11. The value of the g factor was determined to be $g = 2.0047$.

Using the interaction constants of *Jackson* and *Patel* [15], the spectrum with the line width 0.3 G was computed. The calculated spectrum of the phenothiazinyl radical is shown in Fig. 12. A good agreement of both spectra follows from a comparison of Figs. 11 and 12.

The experimental results achieved in the course of the examination of the inhibitory effect of PT in the presence of DPPH on the oxidation of extracted natural rubber under the condition of the thermal treatment demonstrated a very complicated nature of this inhibitory system which does not enable an univocal interpretation of the results.

The results of the spectrophotometric as well as the e.p.r. measurements of the samples of both kinds, the first thermally treated at 130°C for 1000 minutes and subsequently oxidized — the series *A* of experiments, the second only oxidized

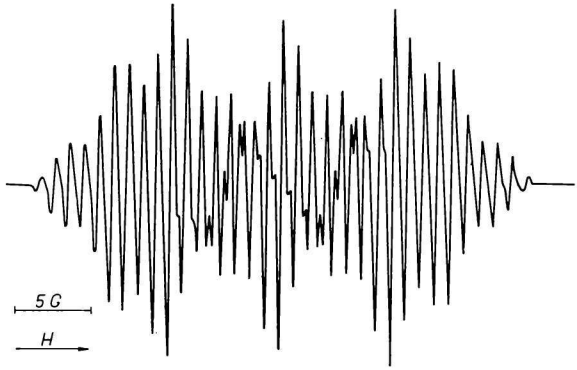

Fig. 12. Calculated spectrum of the phenothiazinyl radical.

at 130°C — series *B*, point out the following basic reactions which probably take place from the samples preparation

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

$$2\text{PT}(>\text{N}\bullet) \xrightarrow{k_2} \text{D-PT (dimers of PT)}, \qquad (2)$$

$$\text{DPPH} + \text{PT}(>\text{N}\bullet) \xrightarrow{k_2'} \text{products}. \qquad (2')$$

Brook et al. [12] admitted also the formation of a complex between DPPH and amines.

It was found for the reaction (*1*) that when $c_{PT} > c_{DPPH}$, the inhibitory mixture contains PT, DPPH-H and reaction products, however, if $c_{PT} < c_{DPPH}$, the inhibitory mixture contains DPPH-H, DPPH, and reaction products.

When $c_{PT} > c_{DPPH}$ and substrate R-H is present, then, besides the reaction (*1*), (*2*), (*2'*), the following reactions may also occur

$$\text{DPPH} + \text{RH} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \text{DPPH-H} + \text{R}\bullet, \qquad (3), (3')$$

$$\text{R}\bullet + \text{PT} \xrightarrow{k_4} \text{RH} + \text{PT}(>\text{N}\bullet), \qquad (4)$$

$$\text{R}\bullet + \text{PT}(>\text{N}\bullet) \xrightarrow{k_5} \text{products}, \qquad (5)$$

$$\text{R}\bullet + \text{DPPH} \xrightarrow{k_6} \text{products}. \qquad (6)$$

It follows from the experimental results that if $k_1 \gg k_3$, the reactions (*3*) to (*6*) occur in a smaller extent in comparison with the reaction (*1*).

If $c_{PT} < c_{DPPH}$ and the substrate R-H is present, the reaction (*3*) as well as reactions (*4*) to (*6*) cannot be neglected with respect to the excess of DPPH even when $k_1 \gg k_3$.

These reactions take place already during the sample preparation and they are identical for both the experimental series *A* and *B*.

The course of the dependence of the induction period of oxidation upon the molar ratio of the components at various concentrations of the mixture of DPPH and PT (Figs. 1 and 2) as well as the resulting inhibitory effect of the mixture of antioxidants, expressed by means of the index of the relative inhibitory efficiency of the antioxidative mixture (Figs. 3 and 4) are different for the series *A* and *B* of experiments. The difference is caused by the reactions (*1*) to (*6*) occurring during the thermal treatment of the substrate RH as well as the products of the reaction of DPPH with PT.

The analysis of the results of the series *A* of experiments in the step of the thermal treatment in an inert atmosphere indicates that, besides the reactions (*1*) to (*6*), radicals R• must be formed by the reaction

$$\mathrm{RH} \xrightarrow{k_7} \mathrm{R\bullet} + \mathrm{H\bullet}, \qquad (7)$$

and even the presence of radicals formed by a decomposition of hydroperoxides cannot be excluded

$$\mathrm{ROOH} \xrightarrow{k_8} \mathrm{RO\bullet} + \mathrm{OH\bullet}. \qquad (8)$$

At the presence of antioxidants AH (PT and DPPH), hydroperoxides may also decompose in a non-radical way

$$\mathrm{ROOH} + \mathrm{AH} \xrightarrow{k_9} \text{products}. \qquad (9)$$

In the step of the thermal treatment in the series *A* of experiments, where $c_{\mathrm{PT}} > c_{\mathrm{DPPH}}$, the inhibitory mixture contains PT, DPPH-H, D-PT, and some non-reacting products. The induction period of the immediate oxidation at the presence of the same inhibitory system in the series *B* (Fig. 2) is independent both of the molar fraction and of the total concentration of the mixture. Thus in the series *A*, the variation of the induction period of oxidation depending on the molar fraction and the total concentration of antioxidants may be explained, in the region of $c_{\mathrm{PT}} > c_{\mathrm{DPPH}}$, by reactions occurring in the step of the thermal treatment. The free radicals formed by the reaction (*7*) or by other transfer reactions, may disappear owing to the reactions (*3'*), (*4—6*) and possibly (*10*) and (*11*) while the inhibitory mixture probably decreases by the reactions (*5*), (*6*), and (*10*). Several authors, especially *Constantinescu et al.* [16] found that phenothiazine dimers (D-PT) exert inhibitory properties and therefore they can take part in the inhibitory reactions

$$\mathrm{R\bullet} + \text{D-PT} \xrightarrow{k_{10}} \text{products}, \qquad (10)$$

$$\mathrm{R\bullet} + \mathrm{R\bullet} \xrightarrow{k_{11}} \text{products}. \qquad (11)$$

In the series *A*, the observed different course of the dependence $\tau = \mathrm{f}(x_{\mathrm{DPPH}})$ on the total concentration of the mixture in the region of $c_{\mathrm{PT}} < c_{\mathrm{DPPH}}$ is determined mainly by the presence of free DPPH. As mentioned above, the original mixture of the antioxidants PT and DPPH becomes, in fact, a mixture of DPPH, DPPH-H, and D-PT formed by the reactions (*1*), (*2*), and (*2'*). The free DPPH reacts with the substrate R-H by the reaction (*3*) while its decrease in the step of the thermal treatment is realized by the reaction (*6*).

For the oxidation of the substrate RH in the presence of the antioxidants PT,

DPPH-H, DPPH, and D-PT the induction period of the oxidation (τ) was found to be independent both of the molar composition and the total concentration of the mixture.

The basic reactions taking place in the oxidative step were described for individual antioxidants in another works [4, 8—10, 28]. Those works pointed out that the inhibitory mixture acts as a scavenger of free radicals, a decomposer of hydroperoxides, a source of iminoxyl radicals >NO• and, in the case of phenothiazine, as a source of complexes and oxidation products derived from phenothiazine (phenothiazone, phenothiazinesulfoxide). The function of the last products in the oxidative step is not yet known.

Considering the index of the relative inhibitory efficiency for the series *A* and *B* of experiments (Figs. 3 and 4) it is evident that these products also take part in the reactions during the thermal treatment as well as in the oxidative step.

In the series *A*, the observed antagonism at higher starting total concentrations of antioxidants (Fig. 3) may be also ascribed to a reaction of the DPPH radical with the isomeric phenothiazinyl radical with increased electron density at carbon atoms in positions 3,7 and, to a minor extent, in positions 1,9. A recombination of the DPPH radical with the PT(>N•) radical is little probable, owing to steric hindrances.

References

1. Murphy, C. M., Ravner, H., and Smith, N. L., *Ind. Eng. Chem.* ***42***, 2479 (1950).
2. Colclough, J., *J. Chem. Soc.* ***1964***, 4790.
3. Tarasova, Z. N., Eitingon, I. I., Senatorskaya, L. G., Fedorova, T. V., Snisarenko, A. N., Andronova, G. I., and Dogadkin, D. A., *Vysokomol. Soedin.* ***5***, 892 (1963).
4. Hrivíková, J. and Kellö, V., *Chem. Zvesti* ***27***, 249 (1973).
5. Cavanaugh, J., *J. Amer. Chem. Soc.* ***81***, 2507 (1959).
6. Bodea, C. and Silberg, I., *Recent Advances in the Chemistry of Phenothiazines*, in *Advances in Heterocyclic Chemistry*, Vol. 9. Academic Press, New York, 1968.
7. Kikkawa, S., Hayashi, T., and Fujita, K., *J. Chem. Soc. Jap.* ***1972***, 402.
8. Hrivíková, J., *Thesis*. Slovak Technical University, Bratislava, 1964.
9. Tkáč, A. and Hrivíková, J., *Collect. Czech. Chem. Commun.* ***30***, 3861 (1965).
10. Tkáč, A., Kellö, V., and Hrivíková, J., *Collect. Czech. Chem. Commun.* ***31***, 551 (1966).
11. Kuzminskii, A. S. and Angert, L. G., *Dokl. Akad. Nauk SSSR* ***96***, 1187 (1954).
12. Brook, A. G., Anderson, R. J., and Tissot van Patot, J., *Can. J. Chem.* ***36***, 159 (1958).
13. Hazell, J. E. and Russel, K. E., *Can. J. Chem.* ***36***, 1729 (1958).
14. McCowan, J. C., Powell, T., and Raw, R., *J. Chem. Soc.* ***1959***, 3103.
15. Jackson, C. and Patel, N. K. D., *Tetrahedron Lett.* ***1967***, 2255.
16. Constantinescu, T. and Enache, S., *Farmacia* (Bucharest) ***19***, 731 (1971).
17. Wieland, H., *Ber.* ***1***, 494 (1912).
18. Buchachenko, A. L., *Stabil'nye radikaly*. (Stable Radicals.) P. 113. Izd. Akad. Nauk SSSR, Moscow, 1963.
19. Beniska, J., Kavun, S. M., Tarasova, Z. N., and Dogadkin, D. A., *Vysokomol. Soedin.* ***8***, 893 (1966).
20. Baird, J. C. and Thomas, J. R., *J. Chem. Phys.* ***35***, 1507 (1961).
21. Shine, H. S., Veneziani, C., and Mach, E. E., *J. Org. Chem.* ***31***, 3395 (1966).

22. Gagnaire, D., Lemaire, H., Rassat, A., and Servoz-Gavin, P., *C. R. Acad. Sci.* (Paris) ***255***, 1441 (1962).
23. Billon, J. P., Cauquis, C., and Combrisson, J., *J. Chim. Phys.* ***61***, 374 (1964).
24. Odiot, S. and Tonnard, F., *J. Chim. Phys.* ***61***, 382 (1964).
25. Gilbert, B. C., Hanson, P., Norman, R. O. C., and Sutcliffe, B. T., *Chem. Commun.* ***1966***, 161.
26. Lhoste, J. M. and Tonnard, F., *J. Chim. Phys.* ***63***, 678 (1966).
27. Shine, H. S. and Mach, E. E., *J. Org. Chem.* ***30***, 2130 (1965).
28. Hrivíková, J. and Kellö, V., *Chem. Zvesti* ***25***, 17 (1971).

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