

Inhibition Effect of Phenyl- β -naphthylamine on the Oxidation of Natural Rubber in the Presence of α,α -Diphenyl- β -picrylhydrazyl

J. HRIVÍKOVÁ and V. KELLÖ

*Department of Physical Chemistry, Slovak Technical University,
Bratislava 1*

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The inhibition effect of a mixture consisting of phenyl- β -naphthylamine and α,α -diphenyl- β -picrylhydrazyl on the oxidation of natural rubber deprived of natural antioxidants was studied under conditions allowing the thermal generation of different amounts of rubber macroradicals. With increasing amount of radicals and at equimolar ratio of both substances, an outstanding synergism was observed. The function of both components in the course of the oxidation process is discussed.

As shown in previous papers [1–4], the heat treatment of natural rubber from which natural antioxidants have been removed in oxygen-free medium may produce higher concentrations of free radicals. The effect of inhibitors and free radical scavengers on the termination reactions influencing the concentration of macroradicals was discussed. A possible stimulated antioxidation effect of phenyl- β -naphthylamine (PBN) inhibitor in combination with α,α -diphenyl- β -picrylhydrazyl (DPPH) functioning as free radical scavenger was suggested. The changes in the free radical amounts were investigated on the basis of their reactivity with oxygen indicated by the oxidation rate which was followed by the method of infrared spectroscopy.

It has been found [1, 2, 4] that the synthetic antioxidant PBN added to the extracted rubber reduces the reactivity of generated radicals with respect to their recombination, most likely owing to the formation of an intermediate stable radical complex, on the one hand, and enhances the reactivity with respect to oxygen, on the other hand. It has been ascertained that a limiting concentration of PBN (1.5 weight %) exists above which the induction period of subsequent oxidation does not shorten but remains constant.

The effect of DPPH on the generation of free radicals by heat treatment of rubber as well as on oxidation depends on its concentration. There are two waves which appear on the kinetic oxidation curves. The induction period shortens with increasing concentration of DPPH while the stationary part of the second wave lowers. The catalytic effect of DPPH on the decomposition of hydroperoxides may be responsible for the first wave whereas the second wave corresponds to the usual oxidation mechanism with degenerate branching. The induction period of this wave increases with the concentration of DPPH what is likely due to the exhaustion of the scavenger.

Experimental and Results

The specimens of natural rubber were freed from natural antioxidants in a modified extractor [7] by using 40 hours' acetone extraction in nitrogen atmosphere at laboratory temperature.

The purification method, purity of samples used, preparation of films for kinetic tests, pressure apparatus for the heat treatment prior to subsequent oxidation and pertinent manipulation were described in detail in previous papers [1, 3]. A half of the rubber films of about 30 μm thickness were subjected to oxidation directly in air at $130.0 \pm 0.5^\circ\text{C}$ in a thermostat while the second half of the equal rubber films rid of the traces of sorbed oxygen by repeated evacuation (10^{-4} Torr) and blowing through purified nitrogen of 2 atm pressure during the period of two weeks was kept at 130°C for 1000 minutes in the oxygen-free atmosphere prior to the subsequent oxidation performed in the presence of air.

The structural changes occurring in the course of the oxidation of rubber were investigated by the method of infrared spectroscopy [5] by measuring the increase of absorbance of the band corresponding to carbonyl groups $\Delta A_{\text{C=O}}$ (wave number 1720 cm^{-1}). The single-beam Perkin—Elmer 12B infrared spectrometer was used. The kinetic curves having a distinct induction period were constructed on the basis of time dependence of the increase in the amount of carbonyl groups. This induction period gives information on the probable mechanism of radical processes in solid polydiene in the presence of admixtures. The length of induction period was conventionally characterized by the period of time in which the quantity $\Delta A_{\text{C=O}}$ reached the value of 0.025.

A. The effect of the mixture containing PBN and DPPH on the ageing of extracted natural rubber enriched with free radicals prior to oxidation

DPPH as a free radical scavenger essentially lengthens the induction period of subsequent oxidation of the extracted rubber enriched with free radicals prior to oxidation by means of heat treatment in an inert atmosphere. On the other hand, PBN functioning as antioxidant enhances the reactivity of generated rubber radicals with respect to oxygen [3]. Thus, it was convenient to follow the cumulative effect of these substances and the influence of DPPH as a decomposer of the peroxides by non-radical mechanism on the inhibition effect of PBN during oxidation.

Varying molar ratios of DPPH to PBN (1 : 4, 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1, and 4 : 1) as well as different overall concentrations of both components (0.4, 0.8, 1.2, and 1.6 weight %) were chosen.

The relationship between the induction period of oxidation and the molar composition for various overall concentrations is presented in Figs. 1–4. The curve 1 expresses the experimentally established influence of synergistic mixture while the curves 2 and 3 express the direct influence of the components DPPH and PBN. The curve 2 in Fig. 1 expresses the calculated additive effect of both components for a given composition.

A synergistic effect with a maximum at the molar ratio 1 : 1 is to be observed at the overall concentration of components of 0.4 weight % and all molar ratios. As evident from Fig. 1, a marked maximum of induction period belongs to the above ratio. This maximum grows rapidly with increasing overall concentration of the components (Figs. 5–8). Two waves with induction periods at 2,400 min. and 7,250 min., respectively, appear on the kinetic curve of oxidation at the overall concentration of 1.6 weight % (Fig. 7). The existence of two waves was observed only at that overall concentration

of the admixtures and their molar ratio 1 : 1. This phenomenon has already been described [3] for the overall concentration of 1.5 weight % and molar ratio 1 : 1 while the formation of two waves does not occur at lower concentrations. The boundary concentration corresponding to the beginning double-wave formation on kinetic curves may thus be found in the overall concentration interval from 1.2 to 1.5 weight %.

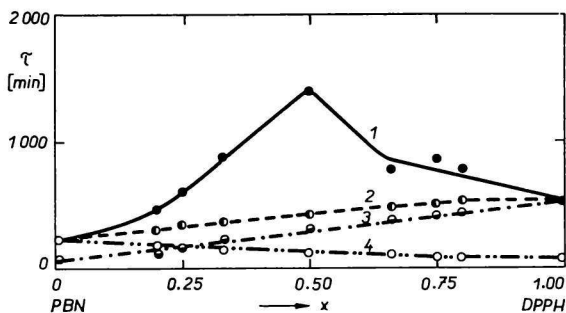


Fig. 1. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.

1. curve of the mixture, $\Sigma c = 0.4$ weight %; 2. additive curve obtained by addition of τ for corresponding concentrations of DPPH and PBN; 3. dependence of τ on the concentration of pure component DPPH; 4. dependence of τ on the concentration of pure component PBN.

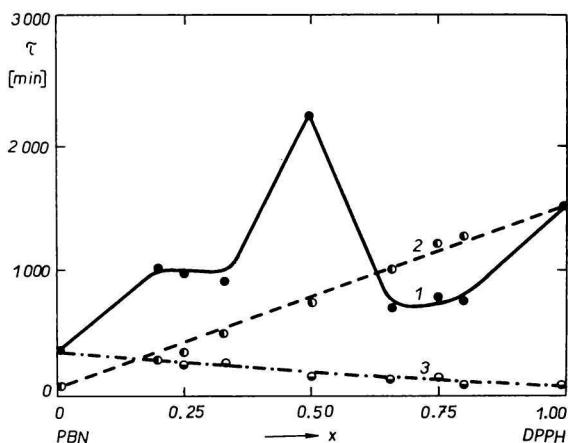


Fig. 2. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.

1. curve of the mixture, $\Sigma c = 0.8$ weight %; 2. dependence of τ on the concentration of pure component DPPH; 3. dependence of τ on the concentration of pure component PBN.

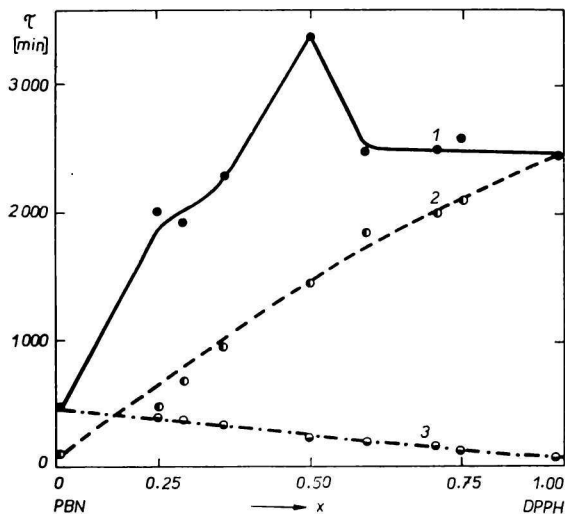


Fig. 3. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.

1. curve of the mixture; $\Sigma c = 1.2$ weight %; 2. dependence of τ on the concentration of pure component DPPH; 3. dependence of τ on the concentration of pure component PBN.

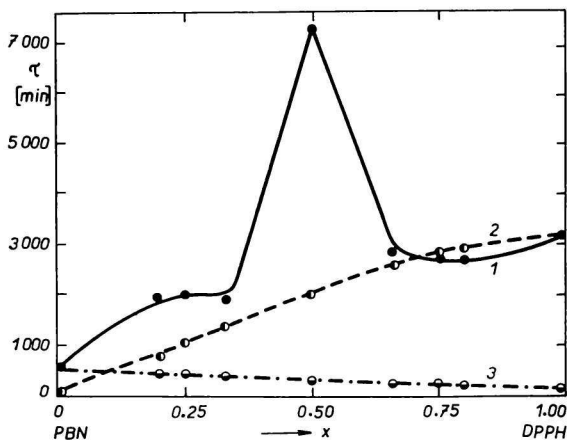


Fig. 4. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.

1. curve of the mixture, $\Sigma c = 1.6$ weight %; 2. dependence of τ on the concentration of pure component DPPH; 3. dependence of τ on the concentration of pure component PBN.

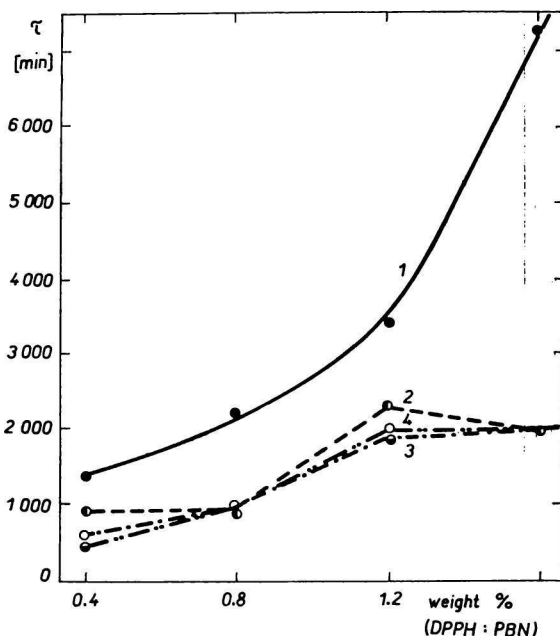


Fig. 5. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in weight %. 1. molar ratio of DPPH to PBN equals 1 : 1; 2. molar ratio of DPPH to PBN equals 1 : 2; 3. molar ratio of DPPH to PBN equals 1 : 3; 4. molar ratio of DPPH to PBN equals 1 : 4.

The relationship between the induction period of oxidation and concentration for the overall concentrations of admixtures of 0.8, 1.2, and 1.6 weight % (Figs. 2–4) is similar to that found for 0.4 weight %. However, the maxima of this relationship are gradually getting more marked. Figs. 5 and 6 (curves 2–4) present the dependence of induction period on overall concentration for other molar ratios. Provided the content of DPPH prevails (ratios of DPPH to PBN 2 : 1, 3 : 1, and 4 : 1), an essential lengthening of induction period appears in the concentration region from 0.8 to 1.2 weight % (Fig. 6). Above the concentration of 1.2 weight % the induction period does not practically change or increases very slightly. The curves 2–4 in Fig. 5 refer to the prevailing content of PBN (ratio of DPPH to PBN 1 : 2, 1 : 3, and 1 : 4). As evident, the increase in the content of PBN has only a slight effect on the lengthening of induction period.

The synergistic efficiency has been evaluated by means of the so-called "index of relative synergistic effect" I_{rs} [8]

$$I_{rs} = \frac{\tau_{(AH+S)} - \tau}{\tau_{AH} + \tau_S - \tau}$$

τ , τ_{AH} , τ_S , and $\tau_{(AH+S)}$ being the induction period of non-stabilized polymer, the induction period of the polymer stabilized by an antioxidant having a certain concentration c_{AH} , the induction period of the polymer stabilized by a synergistic compound

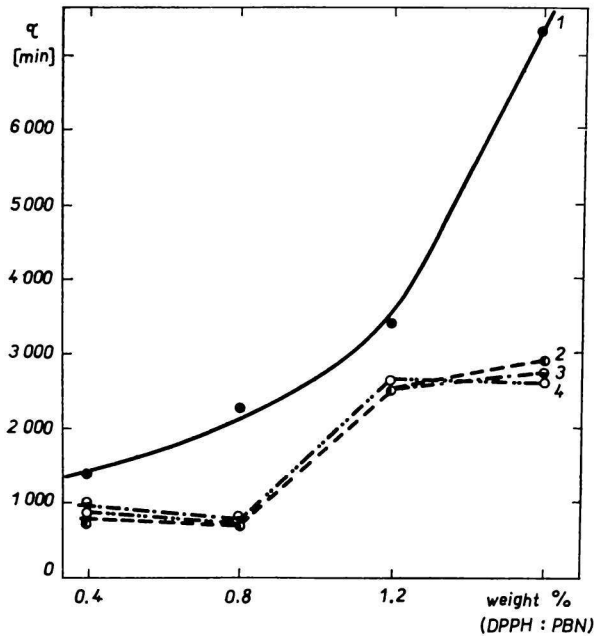


Fig. 6. Relationship between the length of induction period of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in weight %. 1. molar ratio of DPPH to PBN equals 1 : 1; 2. molar ratio of DPPH to PBN equals 2 : 1; 3. molar ratio of DPPH to PBN equals 3 : 1; 4. molar ratio of DPPH to PBN equals 4 : 1.

having the concentration c_s , and the induction period of the polymer stabilized by a mixture of synergistic compound and antioxidant having the concentration c_{AH} and c_s , respectively. The values of I_{rs} for different molar ratios are given in Table 1. The dependence of I_{rs} on overall concentration for the molar ratio of DPPH to PBN 1 : 1 is presented in Fig. 9 (curve 1). This curve shows a minimum at the overall concentration of compounds of 1.2 weight %. Besides the observed synergism, an antagonism with the values of $I_{rs} < 1$ also appears at an excess of DPPH (molar ratios 4 : 1, 3 : 1, and 2 : 1) for the overall concentration of 0.8 and 1.6 weight %. For the concentration of 1.6 weight %, it is more correct to consider only the additive effect because the value of I_{rs} is little different from 1. The observed phenomenon is demonstrated in Figs. 2, 4 and 8.

B. The effect of the mixture containing PBN and DPPH on the ageing of extracted natural rubber

A series of parallel experiments without a heat treatment of samples, *i.e.* without previous enrichment with free radicals gives the following results.

The dependence of the induction period of oxidation on molar ratios of the components and their overall concentration is presented in Figs. 10–12. The numbering of curves is identical with that in Figs. 1–4.

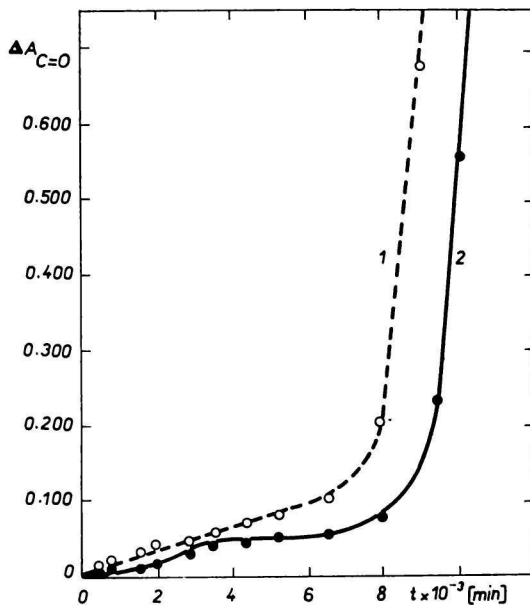


Fig. 7. Dependence of absorbance difference $\Delta A_{C=O}$ on the time of the subsequent oxidation of extracted natural rubber enriched with free radicals prior to oxidation, the overall concentration of DPPH and PBN present in the system being 1.6 weight %. The temperature of oxidation 130°C.

1. molar ratio of DPPH to PBN equals 4 : 1; 2. molar ratio of DPPH to PBN equals 1 : 1.

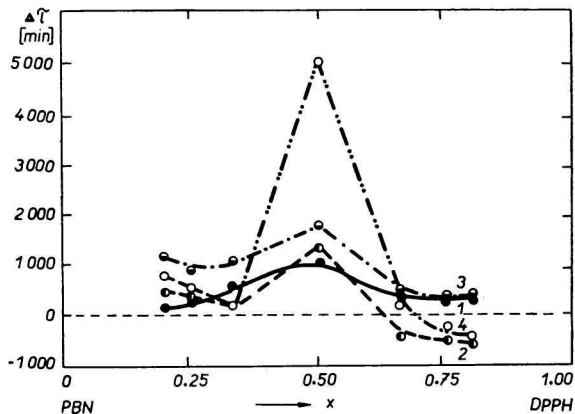


Fig. 8. Relationship between the lengthening of induction period $\Delta \tau$ and the composition of admixture consisting of DPPH and PBN present in different molar ratios for the subsequent oxidation of extracted natural rubber subjected to heat treatment.

$\Delta \tau = \tau_{\text{syn.}} - \tau_{\text{ad.}}$; $\tau_{\text{syn.}}$ — induction period found experimentally, $\tau_{\text{ad.}}$ — induction period calculated on the assumption of additive effect of both components.

1. overall concentration of 0.4 weight %; 2. overall concentration of 0.8 weight %; 3. overall concentration of 1.2 weight %; 4. overall concentration of 1.6 weight %.

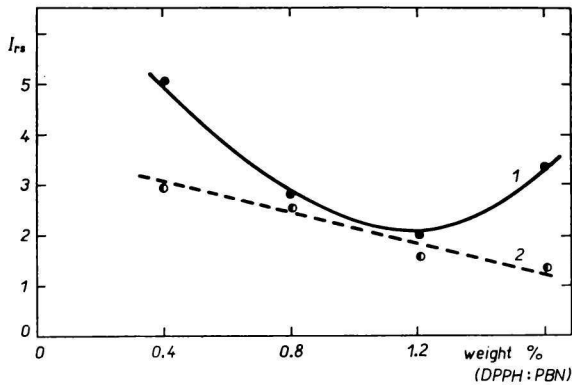


Fig. 9. Variation of the index of relative synergistic effect I_{rs} with the overall concentration of antioxidant mixture for the molar ratio of DPPH to PBN 1 : 1.
 1. extracted natural rubber subjected to previous heat treatment (1,000 minutes, 130°C, N₂); 2. extracted natural rubber without previous heat treatment, oxidation at 130°C.

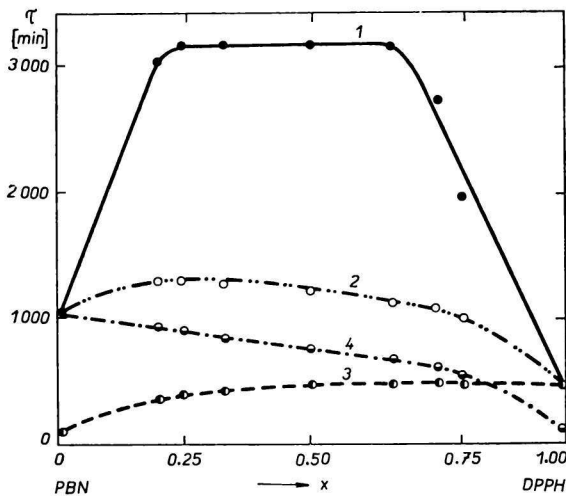


Fig. 10. Relationship between the length of induction period of extracted natural rubber non-enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.
 1. curve of the mixture, $\Sigma c = 0.4$ weight %; 2. additive curve obtained by addition τ for the corresponding concentrations of DPPH and PBN; 3. dependence of τ on the concentration of pure component DPPH; 4. dependence of τ on the concentration of pure component PBN.

From the character of curves it may be concluded that the synergistic effect manifests itself in a wider region of molar ratios, in particular, if the content of DPPH exceeds that of PBN (molar ratios of DPPH to PBN 2 : 1, 3 : 1, and 4 : 1). In contrast to the samples enriched with free radicals prior to oxidation, no distinct maximum occurs at the molar ratio 1 : 1. If the content of PBN exceeds that of DPPH an additive effect

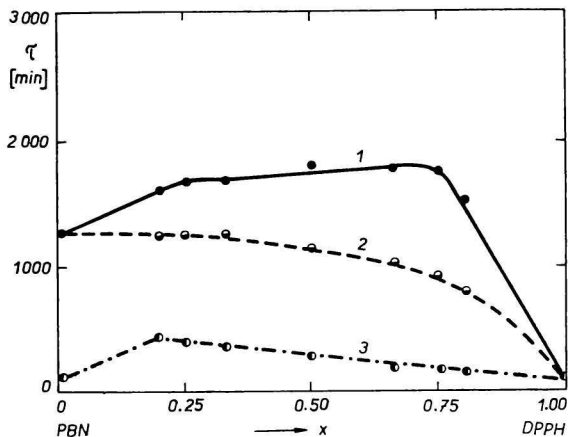


Fig. 11. Relationship between the length of induction period of extracted natural rubber non-enriched with free radicals prior to oxidation (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in molar ratios.

1. curve of the mixture; $\Sigma c = 1.6$ weight %; 2. dependence of τ on the concentration of pure component DPPH; 3. dependence of τ on the concentration of pure component PBN.

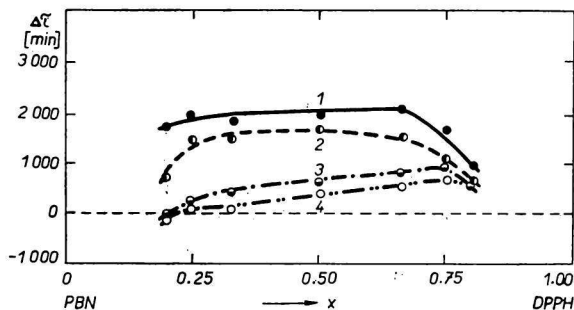


Fig. 12. Relationship between the lengthening of induction period $\Delta\tau$ for the extracted natural rubber non-treated thermally and the composition of DPPH and PBN mixture expressed in various molar ratios.

$\Delta\tau = \tau_{\text{syn.}} - \tau_{\text{ad.}}$; $\tau_{\text{syn.}}$ — induction period found experimentally, $\tau_{\text{ad.}}$ — induction period calculated on the assumption of additive effect of both components.

1. overall concentration of 0.4 weight %; 2. overall concentration of 0.8 weight %; 3. overall concentration of 1.2 weight %; 4. overall concentration of 1.6 weight %.

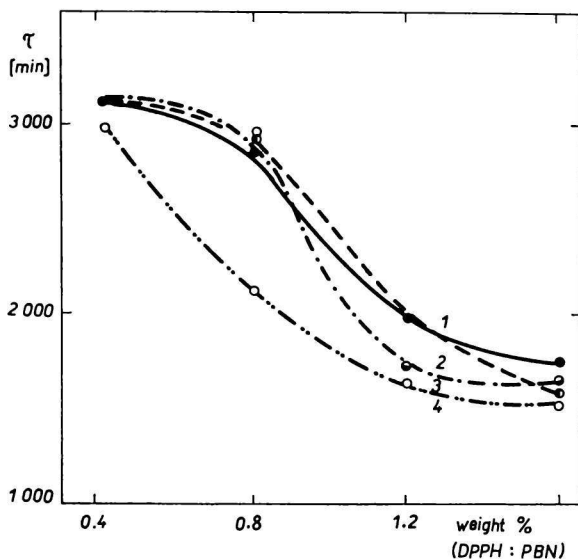


Fig. 13. Relationship between the length of induction period for the oxidation of extracted natural rubber non-enriched with free radicals (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in weight %.

1. molar ratio of DPPH to PBN equals 1 : 1; 2. molar ratio of DPPH to PBN equals 1 : 2; 3. molar ratio of DPPH to PBN equals 1 : 3; 4. molar ratio of DPPH to PBN equals 1 : 4.

of components on oxidation is more likely to be observed (Fig. 12, curves 3 and 4). The kinetic oxidation curves show a single wave at all molar ratios and all concentrations. The relationships between the length of induction period and overall concentration of components for different molar ratios are presented in Figs. 13 and 14. With increasing concentration, the curves tend to fall at all molar ratios. The greatest synergistic effect has been observed at the lowest overall concentration of components (0.4 weight %) for all molar ratios what is in contrast to the samples treated thermally prior to oxidation. Fig. 15 shows this effect for both cases at the molar ratio of DPPH to PBN 1 : 1.

The values of I_{rs} belonging to this series of samples are given in Table 1, too. The dependence of I_{rs} on overall concentration for the molar ratio of DPPH to PBN 1 : 1 is presented in Fig. 9 (curve 2). In general, the values of I_{rs} are lower than those established with the thermally treated samples.

Discussion

Let us analyze the effect of particular components on the course of rubber oxidation in thermally treated samples from the point of view of reaction mechanism.

a) *Equimolar ratio of components.* The effect of the antioxidant PBN on the oxidation of a polymer of polydiene type is largely affected by the presence of DPPH which plays an important part as a synergistic component. A marked synergism

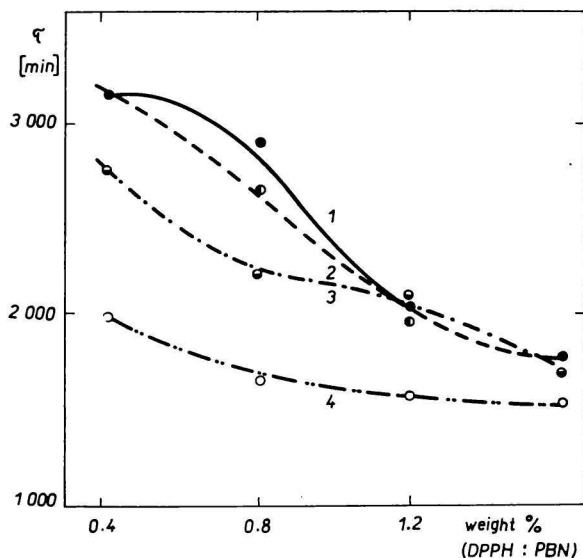


Fig. 14. Relationship between the length of induction period for the oxidation of extracted natural rubber non-enriched with free radicals (τ) and the composition of binary mixture of the antioxidants DPPH and PBN expressed in weight %.

1. molar ratio of DPPH to PBN equals 1 : 1; 2. molar ratio of DPPH to PBN equals 2 : 1; 3. molar ratio of DPPH to PBN equals 3 : 1; 4. molar ratio of DPPH to PBN equals 4 : 1.

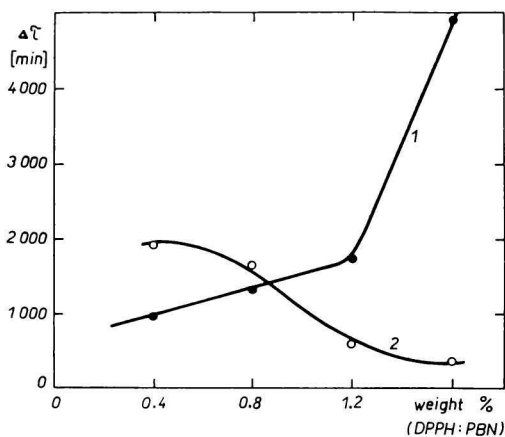
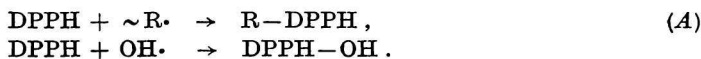


Fig. 15. Synergistic inhibition effect of the admixture containing DPPH and PBN in molar ratio 1 : 1 on the subsequent oxidation.

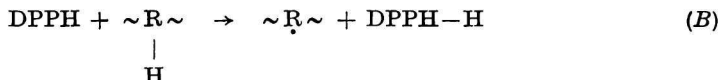
1. thermally treated extracted natural rubber; 2. thermally non-treated extracted natural rubber.

observed at the molar ratio 1 : 1 may be due to various properties of DPPH which can be effective during the oxidation process. We shall attempt to propose the probable mechanism for this oxidation.

First of all, the scavenger character may be effective in reactions



Neither the termination reactions resulting in branching and cross-linking nor the transfer reaction



may be excluded. In the latter reaction, α,α -diphenyl- β -picrylhydrazine is formed. This substance is likely a more efficient antioxidant under given conditions than PBN. This reaction, however, does not take place to such a large extent since the synergistic effect coming into existence in systems containing more PBN than DPPH (Table 1), is smaller, the average value of I_{rs} being about 2. The antioxidant DPPH-H can also be formed in a reaction of DPPH with PBN [6]:



At the overall concentration of 1.6 weight % involving a higher content of DPPH, too, when two waves appear on kinetic curve, DPPH has a catalytic effect on the decomposition of hydroperoxides according to radical mechanism



This reaction proceeds only to a small extent what is indicated by the low stationary part of the first wave on the curve 2 in Fig. 7.

DPPH as a synergistic component in the couple of antioxidants decomposes hydroperoxides by non-radical mechanism



This ability of DPPH is probably most operative at the given molar ratio 1:1. DPPH thus protects the free radical inhibitor from its rapid consumption whereas the inhibitor retards the formation of hydroperoxides and so prevents the consumption of DPPH. The molar ratio 1:1 seems to suggest this idea.

DPPH consumed can be partially regenerated according to the reaction



b) A content of DPPH exceeding that of PBN is undesirable because the catalytic effect of DPPH on the radical decomposition of hydroperoxides according to the reaction (D) is effective to a higher degree. This circumstance is confirmed by the antagonism observed (Figs. 1-4) and by the additive effect of both components on subsequent oxidation.

c) A content of PBN exceeding that of DPPH also results in a synergism which is, however, not so distinct as in the case of molar ratio 1:1. Besides the protection of PBN from its rapid exhaustion by the effect of DPPH, the inhibitor is able to react according to following equations:

in an inert medium

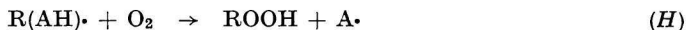


Table 1

Values of I_{rs} for varying molar ratios of DPPH to PBN and various overall concentrations of antioxidants in extracted natural rubber containing different amounts of free radicals

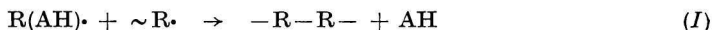
	Molar ratio DPPH : PBN							Concentration of mixture [weight %]
	4 : 1	3 : 1	2 : 1	1 : 1	1 : 2	1 : 3	1 : 4	
I_{rs}	1.93	2.49	2.08	5.05	3.76	2.81	2.62	0.4
Samples enriched	0.56	0.60	0.64	2.87	1.44	2.02	2.30	0.8
with free radicals	1.23	1.23	1.31	2.09	2.00	2.07	2.82	1.2
	0.87	0.92	1.09	3.36	1.15	1.49	1.78	1.6
I_{rs}	2.25	2.93	2.89	2.93	2.78	2.70	2.59	0.4
Samples non-enriched	1.85	2.30	2.56	2.56	2.22	2.08	1.44	0.8
with free radicals	1.85	2.19	1.82	1.55	1.36	1.12	1.06	1.2
	1.84	2.03	1.65	1.36	1.16	1.08	0.99	1.6

during subsequent oxidation

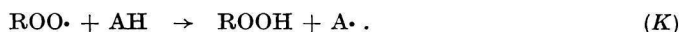


under formation of less reactive radicals $\text{A}\cdot$.

The formed radical complexes may decay in the inert medium under regeneration of AH which reacts in the subsequent oxidation in air according to reactions



during subsequent oxidation



In the thermally non-treated samples containing small amounts of DPPH (overall concentration of 0.4 weight %) the radicals probably decay in the reactions (A) and (B) what protects PBN from its rapid exhaustion. At higher concentrations of DPPH its catalytic effect on the decomposition rate of hydroperoxides according to the reaction (D) starts to be effective. The observed shortening of induction period with increasing overall concentration of mixture may serve as a proof of this fact.

The function of DPPH as a synergist (reaction E) is effective not only at the molar ratio of DPPH to PBN 1 : 1 but also at a content of DPPH exceeding that of PBN (molar ratios 2 : 1, and 3 : 1).

If the content of PBN largely exceeds that of DPPH (molar ratio of DPPH to PBN 1 : 4), the induction period does not so change (Fig. 12, curve 4) because the content of PBN in samples exceeds the limiting concentration above which the efficiency becomes constant.

Conclusion

The cumulative effect of the synthetic antioxidant phenyl- β -naphthylamine (PBN) and of the free radicals scavenger α,α -diphenyl- β -picrylhydrazyl (DPPH) on the oxidation of the natural rubber samples either freed from natural antioxidants or subjected to previous heat treatment was studied. This effect was estimated by the length of the induction period of oxidation and by means of the so-called index of relative synergistic effect I_{rs} . A very marked synergism was to be observed in thermally treated specimens provided the molar ratio of the above components was 1 : 1. This synergism increased with overall concentration of that mixture. A moderate synergistic effect of these components in the specimens non-enriched with free radicals was observed over a wide range of concentrations and it was established that this effect decreased with increasing molar content of DPPH. The synergistic effect, however, decreased with increasing concentration of the mixture. It has been found that the stable free radicals of DPPH enhance the termination processes at low concentration whereas they may catalyze the decomposition of hydroperoxides in the course of polymer oxidation at higher concentrations.

The synergistic action of DPPH — *i.e.* the decomposition of hydroperoxides by non-radical processes — was clearly marked at its equimolar ratio to PBN if rubber was thermally treated in an inert atmosphere prior to subsequent oxidation.

In the present paper, an attempt has been made to clear up the synergistic, antagonistic and additive effect of the synthetic antioxidant and stable free radical present in different molar ratios by using a reaction mechanism assumed for the thermal decomposition of natural rubber either in an inert atmosphere or in the presence of atmospheric oxygen.

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