Inhibition effect of phenothiazine on the oxidation of natural rubber

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The effect of phenothiazine concentration on the inhibited oxidation of natural rubber which was freed of natural antioxidants and contained varying level of thermally generated radicals was studied. The inhibition effect of phenothiazine was compared with that of phenyl-β-naphthylamine. A scheme was proposed for the processes taking place in the presence of phenothiazine during inhibited oxidation of natural rubber which was either previously enriched or was not enriched with free radicals.

It was *Murphy*, *Ravner*, and *Smith* [1] who were concerned with the study of phenothiazine (PTA) and some its derivatives functioning as antioxidants. Phenothiazine as antioxidant became important for the stabilization of oxidized liquid and solid hydrocarbons because of its higher temperature limit (100—175°C) involving the inhibition without thermal decomposition of inhibitor itself. The above-mentioned authors tried to put forward the reaction mechanism of inhibition by phenothiazine. They assumed the existence of free radicals stabilized by resonance which were able to react with the peroxides accumulating in oxidized hydrocarbon and the possibility of partial regeneration of the radicals of antioxidant. *Tarasova* and *Eitingon* [2] examined the efficiency of phenothiazine and some other thioamine inhibitors for suppressing the oxidation of rubber and its vulcanizates.

This study is aimed at the investigation of the inhibition effect of phenothiazine on the oxidation of natural rubber freed of natural antioxidants and involves its comparison with the effect obtained in the oxidation of equal polymer which was previously enriched with the free radicals generated in an inert atmosphere.

Experimental

The hydrocarbon under investigation was natural rubber freed of natural antioxidants by acetone extraction. The method of sample extraction, the preparation of rubber solutions and films for kinetic tests, the pressure apparatus for thermal treatment of samples before subsequent oxidation and the manipulation with this apparatus are thoroughly described in preceding papers [3, 4].

Phenothiazine was purified by threefold recrystallization from ethanol solution. Its melting point was 182°C. First of all, the benzene solution of phenothiazine was prepared. Then the necessary amount of natural extracted rubber was added into the solution, which was shaken under formation of rubber sol.

Half of the rubber films underwent oxidation directly in air at 130°C while the second half of equal rubber films freed of the traces of sorbed oxygen were subjected before subsequent oxidation to the generation of free radicals for 1000 minutes in an inert atmosphere at 130°C.

The infrared spectroscopy was used for the indication of structural changes during the oxidation of rubber. The increase in absorbance of the band corresponding to carbonyl groups $\Delta A_{C=O}$ with the wavelength of 1720 cm^{-1} was recorded. The kinetic curves with a marked induction period were constructed according to the time dependence of the increase in the amount of carbonyl groups. The length of induction period was conventionally characterized by the period of time, in which $\Delta A_{C=O}$ reached the value of 0.025. The scattering of points along the axis of induction periods was ± 25 minutes.

Results

The dependence of the length of induction period of oxidation on the concentration of antioxidant is presented in Fig. 1. The curve *1* expresses the experimentally found effect of phenothiazine in the case of extracted natural rubber which was previously enriched with free radicals in an inert atmosphere and subsequently oxidized in air while the curve *2* shows the effect of the same antioxidant without any preliminary generation of radicals.

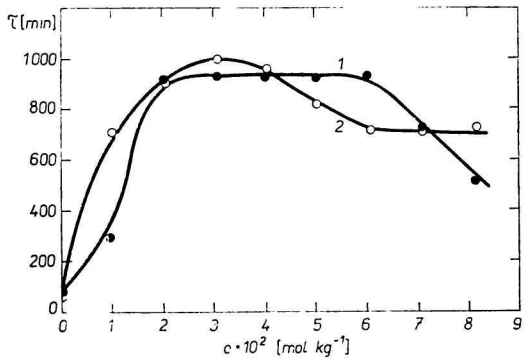

Fig. 1. Oxidation of extracted natural rubber. Dependence of the length of induction period (τ) on the concentration of antioxidant phenothiazine (mol kg^{-1}).
1. rubber previously enriched with free radicals in an inert atmosphere; *2.* rubber without any previous enrichment with free radicals.

As obvious, the inhibition effect of phenothiazine on the oxidation of rubber previously enriched with free radicals increases with concentration up to 2×10^{-2} mol kg^{-1} what results in a tenfold extension of induction period from 90 to 900 minutes and subsequently it remains constant in the concentration region from 2×10^{-2} to 6×10^{-2} mol kg^{-1} what corresponds to the composition of mixture from 0.4 to 1.2 weight %. Above the concentration of 6×10^{-2} mol kg^{-1} the effect of phenothiazine decreases. As evident, a higher concentration of antioxidant is not desirable for an equal initial level of generated radicals.

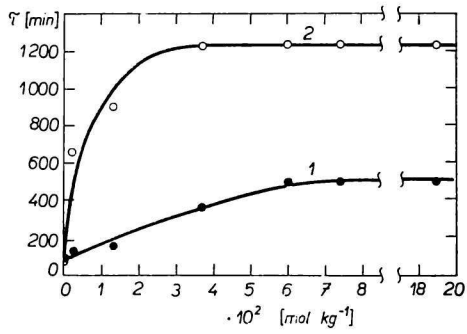

Fig. 2. Oxidation of extracted natural rubber. Dependence of the length of induction period (τ) on the concentration of antioxidant phenyl-β-naphthylamine (mol kg^{-1}).
1. rubber previously enriched with free radicals in an inert atmosphere; *2.* rubber without any previous enrichment with free radicals.

For extracted rubber, which was not thermally treated in an inert atmosphere before oxidation (Fig. 1, curve *2*), the induction period of oxidation increases more markedly with the concentration of antioxidant and it goes through a flat maximum in the concentration region of about 3×10^{-2} mol kg^{-1}. A slight decrease in the length of induction period of about 250 minutes can be observed in the concentration range from 4×10^{-2} to 6×10^{-2} mol kg^{-1}. At higher concentrations of phenothiazine (above 6×10^{-2} mol kg^{-1}) the length of the induction period of oxidation does not change and is equal to the length of induction period obtained with non-extracted rubber which was oxidized at equal temperature (700 minutes) [3].

As evident from the dependence of the length of induction period on the concentration of antioxidant, the inhibition effect of phenothiazine is different in the whole concentration interval.

In order to compare the inhibition effect of the antioxidants of secondary aromatic amine type to our results, Fig. 2 presents the dependence of the length of induction period on the concentration of phenyl-β-naphthylamine for the oxidation of extracted natural rubber which was either previously thermally treated or not treated [4].

It is obvious from Figs. 1 and 2 (curves *1*) that, in comparison with phenyl-β-naphthylamine (PBNA), PTA is a more efficient antioxidant provided equal conditions of preliminary thermal treatment have been observed. Without a previous generation of free radicals the oxidation of extracted natural rubber is suppressed more effectively by PBNA than by PTA (curves *2* in Figs. 1 and 2).

Discussion

In general, most oxidation reactions are assumed to follow a chain mechanism which involves the accumulation of hydroperoxides in the propagation stage of oxidation process. The decay of hydroperoxides results in an origination of new radicals which may initiate other chains. The presence of inhibitor in the reaction system brings about the termination of kinetic chains and raises simultaneously the probability of degenerated branching of chain but on the other hand a possible initiation and branching of kinetic chain by the effect of inhibitor cannot be excluded.

There are several mechanisms on the basis of which the effect of inhibitor on oxidation is interpreted. According to one of the suggested mechanisms of inhibition a successive disappearance of inhibitor from the reaction system during the process and its consumption are responsible for the retardation or temporary suppression of oxidation. The operative antioxidation effect of such inhibitor is relatively of short duration and requires

higher concentrations of antioxidant. Thus this type of inhibition is not desirable for many substrates undergoing oxidation.

A more effective inhibitor influences the oxidative chain reaction even if it is present in a relatively low concentration. This property is characteristic especially of the inhibitors of primary or secondary amine type, which inhibit the propagation of chain by transforming themselves into stable iminoxyl radicals. The most effective inhibition appears if the chain is interrupted in the rate-determining step.

The problem of the mechanism of the effect of antioxidants also involves some data referring to their effect on the process of thermoxidation due to initiation [5]. *Berlin et al.* [6] deduced different kinetic schemes for various mechanisms of the effect of antioxidants by using a conventionally chosen period of time for oxygen absorption. By integrating the theoretical differential equations of oxidation rate they found some relationships between the time of oxygen absorption and the initial concentration of inhibitor. For the antioxidants which possess a mobile hydrogen atom they deduced three kinetic schemes. In the first scheme the effect of initiation by inhibitor is assumed, in the second this effect is not assumed, and in the third the inhibitor is subjected to oxidation but it does not afford any reactive radicals.

The above-mentioned authors express the effect of the initiation by antioxidants by the following equation

$$\mathrm{AH} + \mathrm{O_2} \xrightarrow{\mathrm{RH}} \mathrm{R}\bullet$$

and from the kinetic scheme they deduce the relationship

$$t_a^{-1} \simeq c + b[\mathrm{AH}]_0 ,$$

where t_a, $[\mathrm{AH}]_0$, and c, b are the time of oxygen absorption, initial concentration of inhibitor, and constants, respectively. Provided the processes proceed during the induction period of hydrocarbon oxidation according to the scheme assumed, then the function $t_a^{-1} = f([\mathrm{AH}]_0)$ is linear.

The plot in Fig. 1 corresponding to extracted natural rubber, which was previously thermally treated in an inert atmosphere, shows an anomalous course at initial concentrations of inhibitor ranging from 6×10^{-2} to 8×10^{-2} mol kg^{-1} while the second

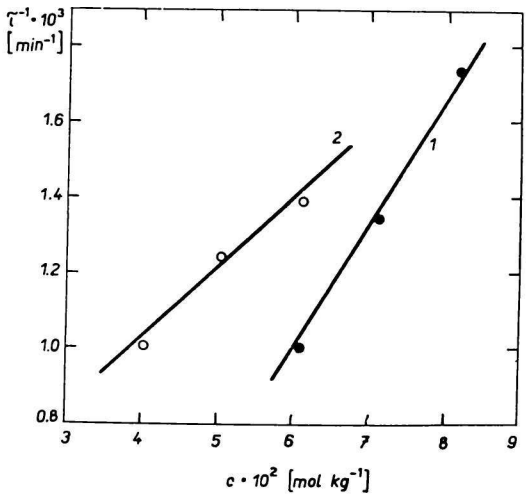

Fig. 3. Oxidation of extracted natural rubber. Dependence of the reciprocal value of the length of induction period (τ^{-1}) on the initial concentration of antioxidant phenothiazine (mol kg^{-1}). *1.* rubber previously enriched with free radicals in an inert atmosphere; *2.* rubber without any previous enrichment with free radicals.

plot referring to rubber, which was not enriched with free radicals, shows an anomalous course in the concentration range from 4×10^{-2} to 6×10^{-2} mol kg^{-1}. We tried to explain this phenomenon by assuming the effect of initiation by phenothiazine on thermoxidation in agreement with [6]. Fig. 3 gives the dependence of the reciprocal value of induction period on the initial concentration of PTA. The linear relations give evidence for the initiation of kinetic chains by the effect of inhibitor in the investigated concentration region.

The inhibitor itself may undergo several types of transformations:

a) The inhibitor is oxidized under formation of a compound which is not able to exhibit any additional antioxidative effect (the weak inhibitor).

b) The inhibitor is oxidized under formation of a compound which shows an antioxidative effect but the degree of inhibition is decreased. Further oxidation may produce an inactive compound.

c) The inhibitor forms a stable free radical which is able to regenerate during the reaction. This type of inhibitor is desirable supposing that the rate and the degree of regeneration are high. The effective inhibition time ought to be a function of the overall efficiency of inhibitor regeneration.

According to our experimental results, phenothiazine appears as an inhibitor, which is during oxidation subjected to changes characteristic of the inhibitors of the type b) and c).

The qualitative interpretation of the stabilizing effect of phenothiazine is as follows.

The proton on nitrogen bond is in connection with a special type of resonance which is responsible for the stability of the free radical of phenothiazine. It is possible that the *S* bond in the molecule of PTA also raises the probability of its stabilizing effect. The antioxidative effect of phenothiazine due to the formation of free radicals stabilized by resonance has been described by *Lewis* and *Michaelis* and their co-workers [7, 8].

In order to elucidate the reaction mechanism of peroxides and hydroperoxides with amines and thioamines, *Buchachenko* and *Kavun* [9] studied the elementary reactions of formation and transformation of radicals. They found that the reactions between amines and hydroperoxides studied brought about the origination of radicals even at laboratory temperature (the bond energies O—O in peroxides and hydroperoxides differ very little). Using the e.p.r. method for the investigation of the reaction between phenothiazine and hydroperoxide they revealed a spectrum with hyperfine structure which they attributed to the so-called "primary" radicals of diarylnitrogen. In the presence of excess hydroperoxide and at increased temperature they observed a change in the e.p.r. spectrum, which was due to the successive transformation of "primary" radicals into "secondary" iminoxyl radicals with marked antioxidative properties. The generation of the stable iminoxyl radical of phenothiazine was revealed earlier by *Tarasova* and *Eitingon* [2].

On the basis of experimental results and data available in literature it is possible to propose the probable pathway of the reactions characterizing the inhibition effect of phenothiazine in oxidation process.

The reactions, which produce different radicals from phenothiazine, may be summarized as follows

$$Ar_2NH + ROO\bullet \rightarrow ROOH + Ar_2N\bullet\,, \qquad (A)$$

$$Ar_2N\bullet + ROOH \rightarrow Ar_2NOH + RO\bullet\,, \qquad (B)$$

$$Ar_2NH + ROOH \rightarrow Ar_2N\bullet + ROH(H_2O)\,, \qquad (C)$$

$$Ar_2NOH + ROOH \rightarrow Ar_2NO\bullet + ROH(H_2O)\,. \qquad (D)$$

At lower concentrations of PTA, the products of amine oxidation react with the radicals of R• and ROO• type and thus continue to take part in the process of inhibition. But they do not bring about any branching of kinetic chain because hydroperoxides originate only to a small extent in their presence.

$$Ar_2N\bullet + ROO\bullet \rightarrow ROOAr_2N\,, \qquad (E)$$

$$ROOAr_2N + H\bullet \rightarrow RH + Ar_2NOO\bullet\,, \qquad (F)$$

$$Ar_2N\bullet + O_2 \rightarrow Ar_2NOO\bullet\,, \qquad (G)$$

$$Ar_2NOO\bullet \rightarrow Ar_2N\bullet + O_2\,, \qquad (H)$$

$$Ar_2NOO\bullet \rightarrow \text{oxidation products.} \qquad (J)$$

The subsequent reaction may also be included among termination reactions

$$Ar_2N\bullet + Ar_2N\bullet \rightleftarrows (Ar_2N)_2\,. \qquad (K)$$

The product originating in direct reaction (K) was proved experimentally [7].

The partial regeneration of inhibitor may be explained by the reaction (H). The total regeneration is not possible because the reactions reducing the concentration of $Ar_2N\bullet$ are operative and as many experiments have shown, the inhibitor is consumed finally. Reaction (H), in which the peroxy compound dissociates thermally under formation of the original compound and molecular oxygen is well known [10]. Reaction (J) involves the formation of oxidation products, which in the case of phenothiazine may function as effective inhibitors [11] because of the presence of sulfur bond.

The effect of PTA on the inhibition of the oxidation of natural rubber by molecular oxygen in the region of its higher concentrations may be explained by the idea that the inhibitor takes part in the initiation reaction as stated by *Berlin et al.* [6].

The experimental results obtained confirm the proposed reaction pathway for the inhibition by phenothiazine in the investigated concentration region, the effect being markedly smaller at higher concentrations of antioxidant and higher level of radicals.

It may, however, be supposed that phenothiazine is not operative only in the above mechanism. Because of its structure and the possibility of subsequent oxidative transformations some oxidation intermediates are formed which are able to take part in the following process of inhibition. The efficiency of phenothiazine may be enhanced by the regeneration of the portion which has been oxidized. It cannot be excluded that PTA present in higher concentrations might influence the initiation in the process of thermoxidation of natural rubber.

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