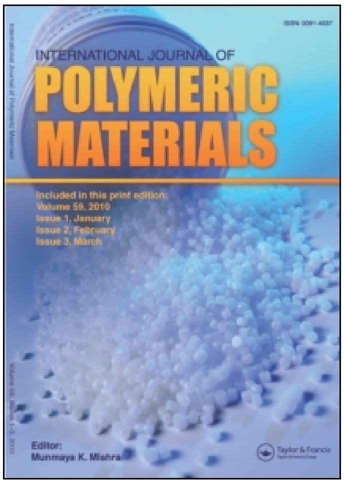

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A. A. Popov[a]; V. M. Parfenov[a]; S. K. Rakovski[b]; D. M. Shopov[b]
[a] Institute of Chemical Physics, Moscow, USSR [b] Institute of Kinetics and Catalysis, Sofia, Bulgaria

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Efficiency of Antiozonants under the Conditions of Static Deformation of Elastomers

A. A. POPOV and V. M. PARFENOV
Institute of Chemical Physics, Moscow, USSR

S. K. RAKOVSKI and D. M. SHOPOV
Institute of Kinetics and Catalysis, Sofia, Bulgaria

Influence of the chemical nature of an elastomer and antiozonants (AO) on the efficiency of antiozonants has been studied. The experimental data can be explained by different mechanism of their protective action in rubbers of different chemical nature of macrochains. There is superposition of the different factors: the interaction of AO with ozone and the formation of a protective film on the polymer surface, whereas in the presence of butadiene units the broken-down fragments can be cross-linked by the antiozonant.

KEYWORDS: Antiozonants, ozonolis, static deformation, elastomers, stabilization, mechanical properties

The object of the work was to study the influence of different factors on the efficiency of antiozonants (AO) under the conditions of static deformation of diene elastomers. These factors are as follows:

- chemical nature of the elastomer monomeric unit;
- chemical nature of the AO;
- degree of deformation;
- AO content in the sample;
- ozone concentration;
- nature of the elastomer cross-linking.

The mechanism of the action of antiozonants has been the subject of numerous investigations.[1,2,5,9] At present, however, there is no generally accepted view on this problem, which stands in the way of explaining the experimentally observed data, predicting the variation of the service properties of manufactured articles under different conditions and creating an effective protection of elastomers from ozone-induced degradation.

Ozone oxidation of unstretched vulcanizates has practically no effect on the strength properties of manufactured articles, as ozone interacts only with C=C double bonds in the surface layer. But even slight tensile deformations result in the appearance of cracks and a loss of service properties of the manufactured article.

We believe that studying the ozone-induced degradation of vulcanization in a broad range of deformations makes it possible to understand the role of each of the above factors in the crack-formation process and to provide important information on the mechanism of antiozonant action. Most of the data from literature, however, cover the range of only small deformations, mainly up to 20%, because in practice elastomers are most offten used in this very range of ε. This artificial limitation appears to us to be unjustified both from the scientific and the practical point of view.

Incomplete information on the corrosion process is also provided, in our opinion, by the most widely used method of investigation: visual study of the appearance and propagation of cracks. More accurate data can be obtained by using the method of stress relaxation.

INVESTIGATED MATERIALS

Elastomers: natural and synthetic cis-1,4-polyisoprene (NR and PI), polybutadiene (PB) and butadiene-styrene rubber (BSR). The cross-linking was accomplished using the sulfur and the radiation techniques. The sulfur vulcanization was conducted at 433 K for 15 min. The vulcanized mixture had the following composition (wt. pts): rubber—100, ZnO—3.0, stearin—1.0, sulfenamide C—1.0, sulfur—1.8, stabilizer—3.0.

The radiation cross-linking of rubbers was performed using the procedure described in Ref. 3. The rubbers were pre-purified as follows: dissolution in CCl_4 (1% solution) and precipitation by adding a three-fold volume of methyl alcohol, followed by drying. The stabilizer was added to the concentrated rubber solution before preparing the films for it to be uniformly distributed over the whole sample volume. The films containing the stabilizer were subjected to cross-linking. After cross-linking the presence of the stabilizer in the sample was verified by means of extraction and UV spectral analysis.

Ozone was generated and measured with the help of a double bond analyzer (ADS-4). Ozone concentration was varied in the range from $5 \cdot 10^{-5}$ to $6.4 \cdot 10^{-2}\,\text{mol/m}^3$. During the experiment the $[O_3]$ value was kept constant.

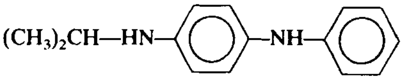
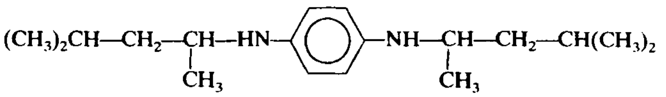
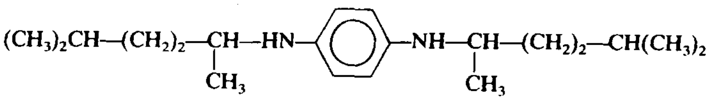
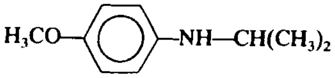
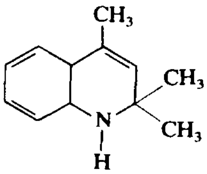
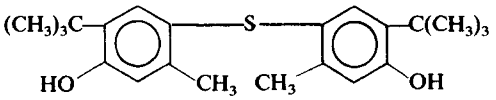
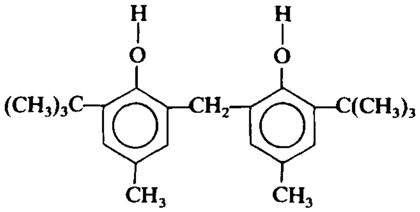
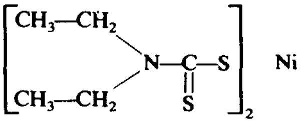
Stabilizers. Antiozonants belonging to the class of paraphenylene diamines (PPDA) were tested as stabilizers. For comparison, stabilizers of other classes were also used (Table I).

METHODS OF INVESTIGATION

The stress relaxation method was used to measure the stress decay kinetics in vulcanizates pre-stretched by the assigned value of ε. Stress relaxation in

TABLE I

Designations and structural formulae of the stabilizers used

No. of sample	Stabilizer	Formula
1.	control sample without a stabilizer	
2.	*N*-isopropyl-*N*′-phenyl PPDA (IPPD, 4010 NA)	
3.	*NN*′-di(1,3-dimethylbutyl)-PPDA (DHKPD, 4020)	
4.	*NN*′-di(1,4-dimethylpentyl) PPDA (DHPPD, 4030)	
5.	*N*-isopropyl-n-anisidine	
6.	2,2,4-trimethyl-1,2-dihydroquinoline (oligomer) (Flectol H, ASMHS)	
7.	di(4-oxy-2-methyl-5-tert-butylphenyl) sulfide (Santowhite Crystal) SANC	
8.	di(2-oxy-5-methyl-3-tert-butylphenyl) methane (2246, Vulkkanox BKF)	
9.	nickel diethyldithiocarbamate (Ni DEDTC)	

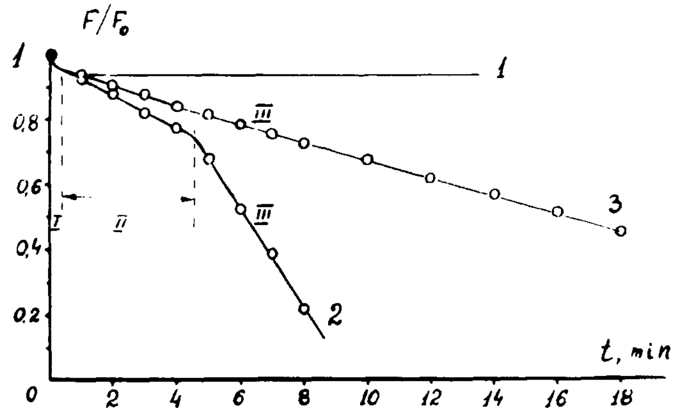


FIGURE 1 Stress relaxation in PI vulcanizates without a stabilizer in the atmosphere of oxygen (1) and ozone–oxygen mixture under the conditions of tensile deformation $\varepsilon = 10\%$ (2) and $\varepsilon = 100\%$ (3). $[O_3] = 9 \cdot 10^{-4}$ mol/m^3, 293 K.

vulcanizates with a thickness of the order of 200 μkm in the atmosphere of ozone–oxygen mixture was measured on an IChP-2 relaxometer at a temperature of 293 K in the 10–160% deformatin range. With PI taken as an example Figure 1 shows the typical curves of stress decay in strained unstabilized samples in the atmosphere of pure oxygen (curve 1) and in the presence of ozone (curves 2 and 3). In the atmosphere of oxygen a fast physical relaxation process is observed, taking place within several seconds. The initial stress σ_0 in this case varies insignificantly, reaching the value of σ_∞ (curve 1). In the presence of ozone the pattern changes radically: instead of coming out on the plateau the stress declines with time. Moreover, on some curves one clearly observes three regions differing in the nature of decay, designated as I, II and III.

Fast physical relaxation (region I) is followed by a portion of a relatively slow decay of stress (region II). It is bounded by the inflection point after which the stress drops more sharply (region III). The time after which this inflection appears can be equated to the time up to the appearance of visible cracks (τ_c), the visual parameter that is widely used in practice. Undoubtedly, cracks appear even before τ_c, which is observed with the help of the stress relaxation method that is more sensitive than visual observations. Indeed, it is already in portion II that one observes the decay of stress, i.e., apart from the origination of cracks on the sample surface, they begin to propagate. After this stage we already see an increase in the size of cracks, which leads to a change in the nature of the ozone corrosion process and an increase in the rate of stress decay (portion III). Therefore, region II characterizes the process of crack formation, while region III an active penetration of cracks into the sample up to its destruction.

It should be noted that the inflection point, corresponding to a change in the nature of the process, is clearly manifested at small deformations only (approximately up to 40%) and is not revealed at higher ones. This is seen from curve 3 in Figure 1, which corresponds to a sample stretched by 100%. Immediately after the region I portions where the cracks grow at a constant rate (III) is observed,

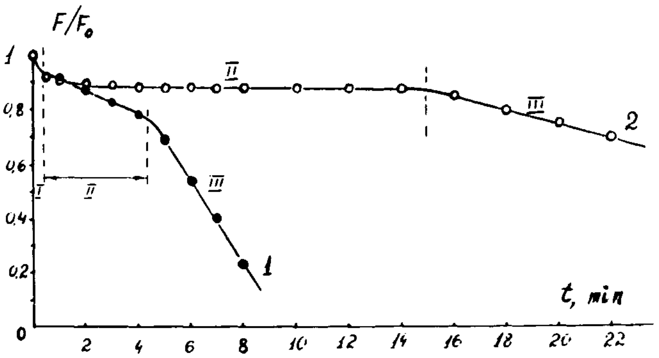


FIGURE 2 Stress relaxation in PI samples without a stabilizer (1) and with IPPD addition (5 wt. pts per 100 wt. pts of elastomer) (2). $[O_3] = 9 \cdot 10^{-4}$ mol/m^3, 293 K.

without the region II, which is indicative of an active crack growth from the very beginning of the experiment. This is in agreement with the data from literature, indicating that the time to the appearance of visible cracks, τ_c, sharply decreases with the growth of ε even in the range of small deformations.[5,6]

Another peculiarity of curve 3 (Figure 1) is its smaller slope in comparison with curve 2, i.e. the stress decay rate decreases with the growing deformation, which is caused by the appearance of the critical deformation ε_{cr}.

Let us now look at the peculiarities appearing in the presence of AO. In Figure 2 are compared the kinetic curves for the samples strained by 10% without additions and with IPPD added. Qualitatively the nature of the dependence does not change: in curve 2, as in curve 1, three different portions can be identified. In quantitative respect, however, the difference is quite tangible: the region II has markedly expanded, i.e. the time to the appearance of visible cracks has increased, and the rate of their growth has decreased (a smaller slope of the portion III with a constant growth rate). The region I has not undergone any changes, which is natural for physical relaxation.

The expression for the growth rate of cracks V_g can be written proceeding from the following considerations. The stress applied to the sample (F) is equal to the product of the true stress (σ) and the sample cross-section (S):

$$\frac{F_t}{F_0} = \frac{\sigma_t S_t}{\sigma_0 S_0} \tag{1}$$

where the subscripts 0 and t correspond to the initial and the current values. The physical relaxation proceeding sufficiently fast and having no effect on the course of chemical relaxation curves, it will be correct to say that $\sigma_t = \sigma_\infty$. Then, for the reduced rate of crack growth it can be written that

$$V_g = -\frac{\partial(S/S_0)}{\partial t} = -\frac{\sigma_0}{\sigma_\infty}\frac{\partial(F/F_0)}{\partial t} \tag{2}$$

i.e. the growth rate of cracks is determined by the derivative of the function of F/F_0 with respect to t in the portion III.

The decay of stress can be also quantitatively described with the help of the parameter τ, which is inversely proportional to the crack growth rate ($\tau = -1/V_g$). For the portion where the stress decay rate is constant the value of τ is constant and has the same meaning as the relaxation time τ' in Tobolski's formula:[7]

$$\sigma = \sigma_0 \cdot e^{-t/\tau'} \tag{3}$$

The existence of critical deformation in the ozone-induced ageing of vulcanizates and cross-linked rubbers has been known for a long time. This phenomenon is manifested in a maximal crack propagation rate and a minimal longevity being observed in a certain range of tensile deformations. Usually ε_{cr} lies in the region of small deformations (approximately from 5 to 50%). Diperent points of view are put forward with respect to the nature of ε_{cr} existence. For instance, Newton[4] tried to explain this anomalous phenomenon by the mutual effect of cracks: at small deformations a few cracks are formed and they grow independently of each other, with an increase in ε the number of cracks grows and they, in Newton's opinion, begin to influence each other, thereby slowing down their mutual growth. But this view was not confirmed by direct experiments[5] on the ozonization of strained samples with a differing number of initial cracks. "Critical" deformation proved to the unaffected by their number.

Other points of view are also put forward in the literature as regards the reason for the existence of ε_{cr}. This is dealt with in greater detail in the review.[7]

The method of infrared spectroscopy was used to study the degree of the ozone oxidation of sample surfaces with the help of an attachment of multiple attenuated total reflection (MATR) with the KRS-5 crystal. The number of reflections was 20, the angle of incidence of the beam 45°, the depth of beam penetration into the sample close to 1 μkm, the tests were conducted on a Specord 71 IR spectrophotometer (GDR). The sensitivity of measuring the oxidation was raised by analyzing the ratio between the optical densities of the absorption bands of the formed C=O carbonyl groups (D1720) and the C=C double bonds (D1650) entering into the reaction.

EXPERIMENTAL RESULTS AND DISCUSSION

The dependence of the rate of crack growth on deformation, $V_g = f(\varepsilon)$, in unstabilized PI samples (curves 1, 3 and 5 in Figure 3) was compared with this dependence in similar samples with a stabilizer (curves 2, 4, 6). The comparison was made in three different series, where the testing conditions differed substantially: 1. the content of stabilizer varied (1, 3 and 5 wt. pts of the anti-ozonant correspond to curves 2, 4 and 6); 2. the manner of cross-linking varied (curves 3 and 4 refer to PI sulfur vulcanizates); 3. the ozone concentration varied.

The control PI samples containing no stablizer have a similar $V_g = f(\varepsilon)$ dependence, irrespective of ozone concentration and the manner of cross-linking. With the growing deformation there is in all cases a decrease in the rate of crack growth, i.e. one observes a pattern characteristic for the region exceeding ε_{cr}.

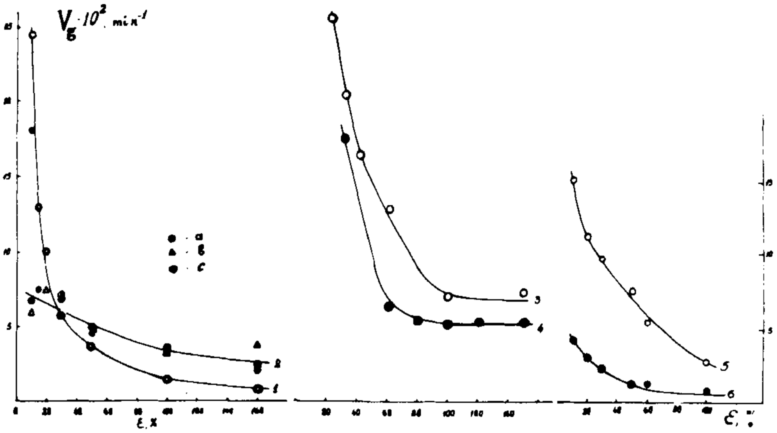


FIGURE 3 Crack growth rate V_g vs. deformation in PI samples without a stabilizer (1, 3, 5) and with a stabilizer present in the amount of 1, 3 and 5 wt. pts (2, 4 and 6). $[O_3] = 5 \cdot 10^{-4}$ (1, 2), $6.4 \cdot 10^{-2}$ (3, 4) and $9 \cdot 10^{-4}$ mol/m^3 (5, 6), 293 K. Stabilizer: IPPD (a), DHPPD (b) and N-isopropyl-n-anisidine (c).

The presence of AO in the amount of 1 wt. pt. raises the stability of samples only in the region of small deformations (up to ~25%). At higher ε the presence of a stabilizer does not raise the sample stability. On the contrary, their presence in the amount of 1 wt. pt. even increases somewhat the rate of crack growth at $\varepsilon > 25\%$ (curve 2 lies above curve 1). Moreover, this effect is observed for three different stabilizers denoted in Table I as No. 2, No. 3 and No. 5.

The IPPD stabilizer (No. 2) taken in a larger amount (3 wt. pts) raises the stability of PI in the whole range of deformations (Figure 3, curve 4 lies below curve 3). The stabilizing effect in this case is manifested in an approximately one and a half-twofold decrease in the rate of crack growth. A further increase in IPPD content (up to 5 wt. pts) results in a more pronounced and stable effect. Under all deformations a four-fold decrease in V_g is observed (cf. curves 6 and 5).

In agreement with the above data are the results of the IR spectral studies. Figure 4 shows the dependence of PI oxidation level on deformation in the presence of a stablizer (1 wt. pt. IPPD) and without it. It is seen from the figure that the stabilizer reduces the oxidation level of the sample surface layer only at small deformations (up to ~25%).

All these data are indicative of the important role of the amount of stabilizer introduced into a sample. It so happens that at large deformations a small amount of AO can even speed up the crack-formation process. And only its relatively high content allows reaching a steady stabilizing effect at any deformation.

One does not succeed in presenting an unambiguous interpretation of the observed pattern. On the one hand, intensification of the stabilizing effect with the growing AO content in polyisoprene is in good agreement with the widespread concept of the competition between the two reactions of ozone: with the double bonds of the polymer and with the stabilizer. The latter, having a higher reactivity with respect to ozone is capable of protecting the —C=C—

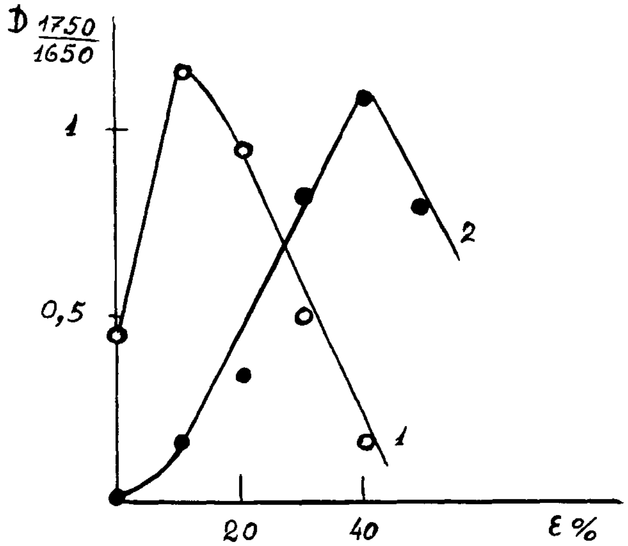


FIGURE 4 Oxidation level of PI surface without a stabilizer (1) and with IPPD (1 wt. pt.) as the stabilizer (2) vs. deformation. $[O_3] = 5 \cdot 10^{-4}$ mol/m^3, 293 K.

bonds of the rubber. Proceeding from this standpoint, however, one proves to be unable to understand the corrosion process acceleration in this presence of small AO additions under tensile deformations exceeding a certain value of ε (Figure 3, curves 1 and 2). Another widely accepted approach seems to be more appropriate in this case. One can try to explain this fact from the standpoint of the appearance of a protective surface film. Different opinions regarding the nature of this protective layer are expressed in the literature. No one doubts, however, that it is the stabilizer that plays the principal role in its formation. It should then be quite natural to assume that a small amount of AO may simply be not enough to form a sufficiently stable protective film capable of remaining intact at large deformations. But a partial protection of the surface will cause a local destruction, leading to an accelerated growth of defects on the unprotected sites of the surface.

The most probable, in our opinion, is a combined nature of the action of the antiozonant entering into the reactions with ozone both as a competitor with respect to the —C=C— bond of the polymer and a component taking part in the formation of the surface film. Moreover, only the inhibiting contribution is possible in accordance with the first mechanism, whereas the second can provide both a positive and a negative effect of AO action, depending on the particular conditions of the test. And the experimentally observed stabilizer effect will be determined by the result of the superposition of these two mechanisms.

Comparison of the results obtained at different ozone concentrations presupposes the knowledge of the quantitative V_g vs. $[O_3]$ dependence. From the literature it is known[5] that in the experimental dependences of the type of

$$y = A[O_3]^n \tag{4}$$

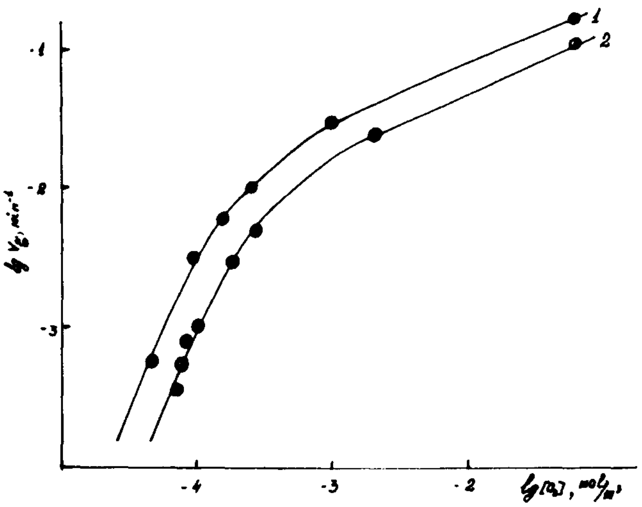


FIGURE 5 Crack growth rate in PI samples without a stabilizer (1) and with a stabilizer (3 wt. pts IPPD) (2) vs. ozone concentration. $\varepsilon = 40\%$, 293 K.

($y = \tau_c$, V_g, or duarability τ_a; A and n are coefficients) the exponent n can vary with the variation of [O_3].

The dependence of the rate of crack growth on ozone concentration is shown in Figure 5. Compared with each other are two curves, 1 and 2, obtained for the unstabilized and the stabilized PI sulfur vulcanizate (3 wt. pts IPPD). Figure 5 gives the pattern obtained with $\varepsilon = 40\%$. Of similar nature are the curves obtained with other deformations. The presence of the stabilizer is seen not to change the shape of the curve but only to displace it in a parallel direction towards smaller V_g values and larger [O_3], which the stabilizing effect actually consists in.

The dependence in question can be subdivided into three parts. The lg V_g function of lg [O_3] is linear at small ([O_3] $< 10^{-4}$ mol/m^3) and large ([O_3] $5 \cdot 10^{-4}$ mol/m^3) ozone concentration and follows the well known dependence (4). It should be noted that the sensitivity of V_g to [O_3] variation is much higher at small ozone concentrations, as compared with large ones, which tells on the value of n (3 and 0.5, respectively). The two linear portions are separated by a transition zone.

The dependence obtained in Figure 5 allows making two conclusions. Firstly, a qualitative comparison of AO efficiency can only be made in certain ranges of concentrations: either at [O_3] $< 10^{-4}$ or at [O_3] $> 5 \cdot 10^{-4}$ mol/m^3. Secondly, the stabilzing effect of the inhibitor is stronger at lower ozone concentrations than at higher ones. Thus, at $\varepsilon = 40\%$ the rate of crack growth in the stabilized sample decreases about four-fold, as compared wtih the control sample, at [O_3] $<$ 10^{-4} mole/m^3, whereas at high ozone concentrations V_g decreases only 1.7-fold (Figure 5). A similar picture was also observed with $\varepsilon = 60\%$.

Let us examine the role played by the chemical structure of rubbers in the efficiency of antiozonants. Figure 6 shows the dependence of the value of ln τ on

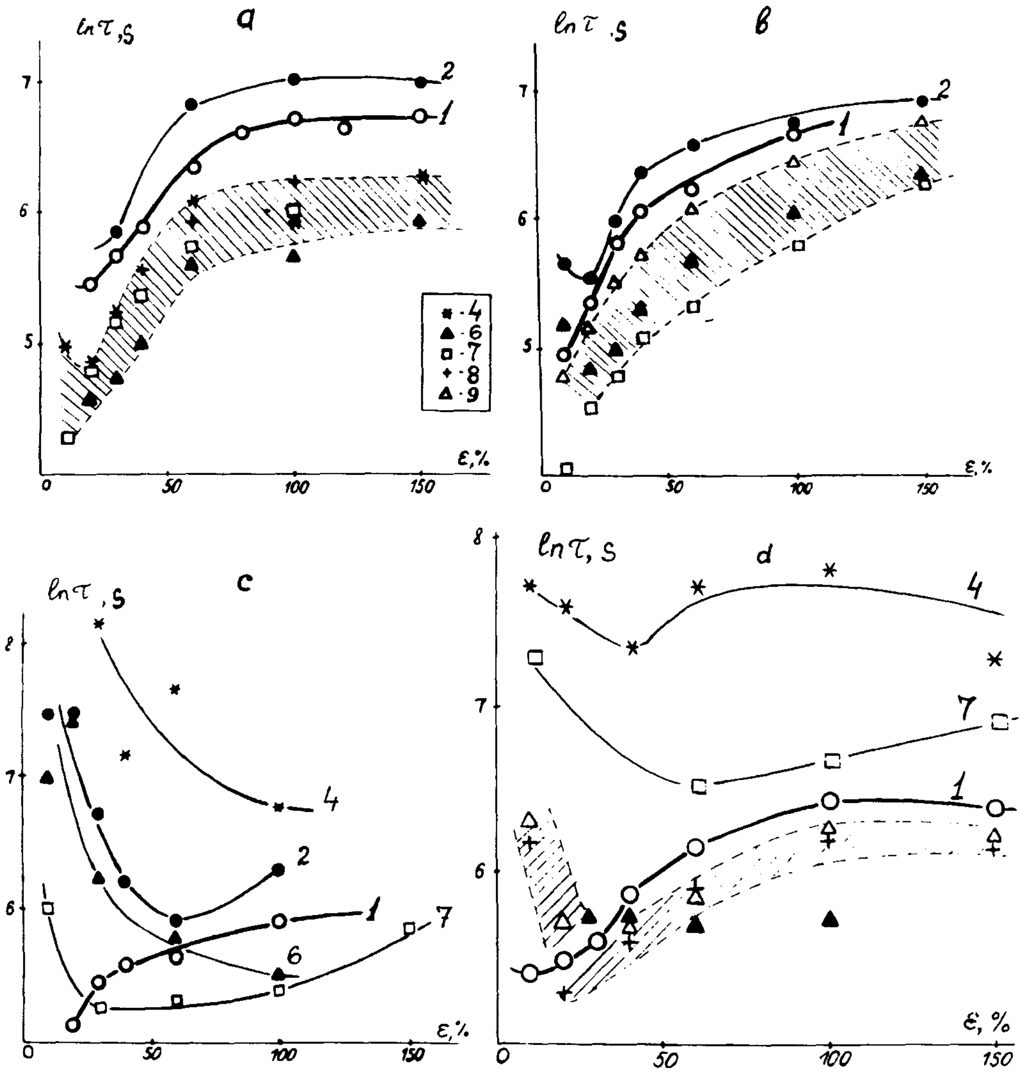


FIGURE 6 The value of ln τ vs. deformation in sulfur vulcanizates of PI (a), NR (b), PB (c) and BSR (d) without a stabilizer (curves 1) and with 3 wt. pts of stabilizer (the number of the curve corresponds to the number of the stabilizer in Table I). $[O_3] = 6.4 \cdot 10^{-2}\,\mathrm{mol/m^3}$, 293 K.

the degree of tensile deformation in this vulcanizates of PI (Figure 6a), NR (Figure 6b), PB (Figure 6c) and BSR (Figure 6). A similar pattern is observed only in two cases: PI and NR. This similarity is not only qualitative but also quantitative both for the control (curves 1) and the protected samples. The shape of all the curves, irrespective of the presence of the stabilizer, is also quite similar: the lowest stability (the highest growth rate of cracks) is observed in the range of critical deformations $\varepsilon \approx 10$–20%. But with an increase in the degree of stretching the stability increases (the parameter τ rises).

The nature of stability increase can be explained by a decrease in the reactivity accompanying the extension of cis-C—C═C—C— fragment in all the reactions accompanied by the rearrangement of two carbon atoms at the double bond from the Sp^2 into the Sp^3 state.[8] But ozone is known to attack the double bond with the formation of a primary addition product—molozonode.

There also exists another interpretation of the "critical deformation" phenomenon, based on the mechanism of orientation strengthening.[5] However, as shown by ESR spectral studies performed with the use of a probe radical,[8,10] at least up to 200% the tensile deformation of such elastomers as PI, NR and PB does not change the polymeric matrix rigidity (the segmental mobility of macrochains remains constant). That is why in these cases orientation strengthening cannot, in our opinion play any tangible role.

A different situation is taking place in the case of BSR co-polymer. The stretching of its vulcanizate raises substantially the rigidity of its polymeric matrix.[10] It is with the structural-physical changes that a rise in the value of τ with the growing ε, observed in Figure 6a, seems to be associated.

An efficient stabilizer for PI and NR under the chosen testing conditions is a quite widely used antiozonant—IPPD. In the whole range of deformations this stabilizer slows down the growth of cracks, which follows from the comparison of curves No. 1 and No. 2 in Figures 6a and 6b (curves No. 2 lie above curves No. 1). This slowing down, however, is not very great: in PI the V_g value decreases by a factor of approximately 1.6, in NR—1.3. Compositions containing other stabilizers are less resistant under these conditions to the ozone effect, as compared with the control samples, which is indicated in Figures 6a and 6b by a cross-hatched area within which the experimental points lie.

Similarity of the results obtained for PI and NR is caused by the identity of their monomer unit. A significant role of the chemical nature of the macrochain is confirmed by the difference in the results obtained for elastomers with other monomeric units. A relatively small difference in the structure of cis-1,4-polyisoprene monomer unit (the presence of a —CH_3 substituent) leads to a quite significant difference in the efficiency of stabilizers. Thus, from Figure 6c it is seen that PB vulcanizate is stabilized much better than PI and NR. Apart from IPPD, other stabilizers also prove it to be efficient in the whole deformation range: DDPPD (curve 4 in Figure 6c) and nickel DEDTC (the curve is not given because it is identical to curve 1 and lies above it), in the region of not very high deformations the stabilizing effect is manifested by Flectol H (up to 60%, curve 6) and SAN-C (up to 20%, curve 7).

It should be emphasized that for PB especially characteristic is a decrease in the efficiency of stabilizers with the growth of ε. The only exception is nickel DEDTC. Table II illustrates the stabilizing effect, expressed as the degree of a decrease in the crack growth rate with a differing deformation of samples, as compared with the samples that contain no stabilizers.

Azotization efficiency was earlier found to decrease with an increase in the degree of cis-1,4-polyisoprene deformation.[10–12] The present work confirms this. Thus, in Figure 6b the highest stabilizing effect of IPPD (curve 2) is seen for $\varepsilon = 10\%$ (a two-fold decrease in V_g); at larger deformations the effect decreases.

TABLE II

Degree of a decrease in the crack growth rate in PB samples in the presence of a stabilizer, compared with samples containing no stabilizers, at different deformations

Stabilizer		ε, %			
No.	Designation	20	30	60	100
4	DHPPD	—	14.7	5.0	2.4
2	IPPD	10.0	3.6	1.4	1.5
6	Flectol H	8.1	2.2	1.1	0.7
9	Ni DEDTC	1.4	1.6	1.6	1.6

But, as it follows from the above data, in the case of PB this situation is expressed to a much greater extent. Therefore, one can speak of a different nature of $\ln \tau = f(\varepsilon)$ dependences obtained for protected vulcanizates of the butadiene and the isoprene rubbers (cf. Figure 6c with Figures 6a and 6b).

For BSR vulcanizate one can note the following peculiarities. This elastomer, as well as PB, is stabilized with sufficient efficiency by DHPPD within the whole range of ε (Figure 6d, curve 4). The inhibiting effect is also exerted by SAN-C at all deformations (curve 7), although to a smaller extent than DHPPD. No data have been obtained for IPPD. All the other stabilizers slow down ozone destruction only at small ε (up to 20–30%), and at large deformations their presence causes the opposite effect—acceleration of crack growth.

Another similarity of BSR with PB manifests itself in a decrease in the efficiency of stabilizers with the growth of ε, although it is not as substantial as in PB. This is seen from the data on a decrease in V_g in strained BSR samples in the presence of a stabilizer (Table III).

In our opinion, the results presented in Figure 6 cannot be explained from the standpoint of the interception of ozone molecules by the stabilizer, i.e. with the help of a mechanism based on a higher AO reactivity with respect to ozone in comparison with the polymer C=C double bond. This follows from the obtained data regarding the influence of the chemical structure of macromolecules on the efficiency of stabilizers. Most clearly this is manifested for IPPD and DHPPD. The rate constants of their reactions with ozone are practically the same and equal to $1.2 \cdot 10^7$ and $1.3 \cdot 10^7\, \mathrm{dm}^3/\mathrm{mol} \cdot \mathrm{s}$, respectively. Their protective effect, however, differs considerably and depends on the type of the polymer. Indeed,

TABLE III

Degree of a decrease in the crack growth rate in BSR-30 samples in the presence of a stabilizer, compared with samples containing no stabilizer, at different deformations.

Stabilizer		ε, %				
No.	Designation	10	20	60	100	150
4	DHPPD	10.0	8.0	5.0	4.0	3.0
7	SAN-C	6.7	—	1.4	1.3	1.7
9	Ni DEDTC	2.3	1.2	0.8	0.8	0.8
8	Vulkanox BKF	2.3	0.8	0.8	0.8	0.8

IPPD raises and DHPPD lowers the stability of PI and NR samples, whereas for PB and BSR the DHPPD antiozonant is a very efficient stabilizer.

The facts of this kind can only be explained taking into account the active role played by the polymeric matrix itself. It should be noted that this role is hardly caused by the intermolecular interaction of the polymer with the stabilizer, as it has been assumed in the literature,[13] since the elastomers in question are by their nature of low polarity. From the standpoint of intermolecular interaction it is difficult to explain the considerable difference between PI and NR, on the one hand, and PB and BSR, on the other. More probably, the stabilizer enters into a chemical reaction with the products of the polymer oxidative degradation (cross-linking of the cut-off fragments). In this case the nature of the monomer unit can predetermine the course or the rate of such a reaction, thereby influencing the AO efficiency. From this point of view it proves possible to explain the DHPPD efficiency in the two cases of PB and BSR, because they have the same chemical fragments resulting from butadiene polymerization. And, possibly, it is with the products of the ozone oxidation of these very fragments, i.e. the aldehyde groups, that the given stabilizer interacts effectively. In polyisoprene chains a similar chemical process seems not to be taking place at all or to be going at an appreciably lower rate. This interpretation is in agreement with the data from the literature on the interaction of paraphenylenediamines with ozonized olefins.[2,14] It thus seems that, as noted above, two factors are being superimposed: the interaction of AO with ozone and the formation of a protective film on the polymer surface, whereas in the presence of butadiene units another means of protection appears—the cross-linking of the broken-down aldehyde fragments by the antiozonant. The latter, though more effective, is quite sensitive to deformation. Indeed, stretching must facilitate the drawing apart of the cut-off ends of the molecule and thereby impede their cross-linking.

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