Introduction To protect unsaturated rubbers against ozone-induced degradation, they are blended with saturated thermoplastics and rubbers. There are different ideas on the mechanism of antiozonant protection: the surface protection of an ozone-unstable rubber though enrichment of the vulcanizate surface with an ozone-resistant component [1] and the bulk protection mechanism associated with the phase structure and the structure of the interphase layers [2-9]. The bulk protection mechanism was studied using systems based on butadiene–acrylonitrile rubbers (BNRs) with poly(vinil chloride) (PVC) as an example and ethylene–propylene-diene elastomers (EPDM) [2, 3, 6-9]. This mechanism is supported by the data obtained by Zateev [10], who found, in an electron microscopy study, that an ozone-resistant component does not prevent the formation, on the vulcanizate surface, of primary ozone-induced microcraks by which ozone penetrates into the sample. In [2] the ozone resistance, phase structure, and the structure of interphase layer in vulcanized blends of butadiene–acrylonitrile rubbers with poly(vinil chloride) was studied by measuring mechanical stress relaxation in an inert and ozone-containing atmosphere, EPR and frustrated multiple internal reflectance IR spectra. The ozone-protective action of PVC in the blends with NBR begins at a PVC content corresponding to the formation of a continuous spatial framework, while the efficiency of protection is determined by strength of the transition layer. The PVC component hinders the growth and coalescence of microcracks on the vulcanizate surface. The ozone resistance, surface layer structure, and composition of covulcanizates of butadiene–acrylonitrile rubbers containing different amounts of acrylonitrile units with ethylene–propylene terpolymers were stadied using the stress relaxation and ESR and FMIR IR spectroscopy techniques. The ozone resistance of the materials was chown to depend on the compatibility of the components, the development of the interphase layer that determines the degree of covulcanization of the rubbers, and the EPDM network density [3]. In order to obtain insight into the mechanism of the antiozonant action of a low unsaturation component (the ethylene–propylene–diene elastomer) in crosslinked blends with butadiene–nitrile rubbers. We studied the dependence of the rate of ozone-induced degradation of the diene matrix on the phase structure of blends, volume and the structure of the interphase layer, the amount of crosslinks formed in it, and the strength of the ethylene–propylene–diene elastomer network. It was of interest to relate the specific features of the structure of the interphase interaction region and its volume to the efficiency of inhibition of ozone degradation of the diene elastomer in cured heterophasic blends of NBR copolymers of different polarities with ethylene–propylene–diene elastomers manufactured by Uniroyal, DSM and domestic EPDM which differ in the comonomer ratio and in the stereoregularity of propylene sequences [11-13]. Experimental A heterophase crosslinked blend of BNR and EPDM with a ratio of 85:15 (by weight) having a dispersed EPDM structure and 70:30, which represented a system of interpenetrating crosslinked networks, was studied. Commercial nitrile–butadiene rubbers (trademarks BNKS-18, BNKS-28, and BNKS-40) were used. The AN-unit contents were 18, 28, and 40 wt %, respectively, and the values of the Mooney viscosity (at 100°C) were 40–50, 45–65, and 45–70 rel. units, respectively. The content of trans-1,4-, 1,2-, and cis-1,4-units of butadiene was estimated via IR spectroscopy (bands at 967, 911, and 730 cm–1) [14] with the use of extinction coefficients from [15] (Table 1). EPDM of the Royalen brand (Uniroyal, USA), the DSM 778, 714, and 712 brands (DSM N.V., Netherlands) and domestic EPDMs having different relative amounts of ethylene, propylene, and ethylidene norbornene (ENB) units and different degrees of microtacticities of the propylene sequences respectively, were used. The composition, the molecular-mass characteristics, the Mooney viscosity, the isotacticity of EPDM propylene units according to IR data [14, 16, 17] are given in Table 2. For domestic EPDMs the data on the Mooney viscosity; the content of ethylene, propylene, and ethylidenenorbornene units according to the manufacturer’s data. Table 1 - Isomeric composition of butadiene units in different butadiene–AN copolymers Copolymer Content of units, % trans-1,4- 1,2- cis-1,4- BNKS -18 BNKS -28 BNKS -40 82.0 76.4 93.0 8.2 14.4 4.4 9.8 9.2 2.6 A vulcanizing system for NBRs had the following composition, phr: stearic acid, 2.0; Sulfenamide Ts (N-cyclohexylbenzothiazole-2-sulfenamide), 1.5; zinc oxide, 5.0; and sulfur, 0.75. EPDM of the Royalen brand, the DSM and domestic EPDM was vulcanized with supported Peroximon F-40 taken in an amount of 5.5 phr. Each rubber was mixed with its vulcanizing system by roll milling at 40–60°C for 15 min. Then, a rubber blend was prepared under the same conditions. The blends were vulcanized at 170°C within 15 min. The ozone resistance of the blends was studied via the method of stress relaxation at an ozone concentration of 8.5×10–5 mol/l, 30°C and at a tensile strain of 30-150% on an IKhF-2 relaxometer [2]. Relaxation rate vr in the ozone-containing medium in the steady-state region next to the region of the fast physical relaxation reflects the kinetics of accumulation of chain ruptures in the diene matrix (Fig. 1). The efficacy of retardation of degradation during the introduction of EPDM, vrrel, corresponds to the intensity of the decrease in the rate in the presence of the ozone-resistant component relative to that in the presence of the BNR vulcanizate. Fig. 1 - Decay curves of force F in drawn specimens of NBR covulcanizates containing (1) 15 and (2) 30 phr EPDM Table 2 - Composition and basic characteristics of ethylene–propylene–diene elastomers EPDM brand Ethylene : propylene, wt % Isotacticity, % ENB content, wt % Mooney viscosity R 512 R 505 R 521 778 714 712 EPDM-40 Elastokam 6305 EPDM-60(I) EPDM-60(II) Elastokam 7505 68/32 57/43 52/48 65/35 50/50 52/48 70/30 74/26 60/40 60/40 60/40 20 24 22 13 12 11 29 9,5 13 13 9,5 4 8 5 4.5 8 4,5 4 5,4 4 6,7 5,1 57 55 29 63 63 63 36-45 67 60 62 83 The region of a low relaxation rate with quasiequilibrium stress σ* reflects the strength of the EPDM network because it represents the superposition of stresses in the network and in the matrix connected through interfacial layers [6-8]. The absence of the continuous structure of EPDM or its breakdown during tensile drawing is accompanied by a stress drop to zero due to propagation and merging of ozone microcracks. The method of swelling in a selective solvent, n-heptane, (Zappa's method [6, 18, 19]) was used for studying the formation of the interfacial layer in the crosslinked heterophase blends of BNR with different contents of polar acrylonitrile units and EPDM which are characterized by different comonomer compositions and stereoregularities of propylene units. The density of the interfacial layer and the number of crosslinks in this layer were characterized by a difference between the equilibrium degree of swelling and the additive values in a nonpolar solvent n-heptane [18, 19]. When the above parameters were higher, this tendency suggested the occurrence of a weak interfacial interaction between thermodynamically incompatible polymer components, one of which contained polar units. In such systems, only local mutual solubility of segments of nonpolar chain fragments is possible [20–27]. A lower chain packing density in the interfacial layer and a lower number of crosslinks are provided not only by a lower compatibility between polybutadiene and polyolefin copolymers but also by chemical bonding between butadiene units and polar acrylonitrile fragments that are randomly distributed in BNKS-18 or exist as microblocks in BNKS-40 [28, 29]. The friability of the interfacial layer is associated with a reduced number of crosslinks [22]. Difference $-\alpha$ (between the equilibrium degree of swelling Qeq of covulcanizate and the additive value Qad (deviation of the equilibrium degree of swelling from the additive value) as calculated from the equilibrium values of each of homovulcanizates can be estimated through the following equation [19]: $-\alpha = [(Qad-Qeq)/(Qad-Q2)]$ 100%, where Q2 is the degree of swelling of the second elastomer (BNR). The Flory–Huggins interaction parameter χ for polybutadienes and EPDM with n-heptane and solubility parameters δ or cis-PB, EPDM, and BNKS were reported in [30, 31]. Results And Discussion Formation of a strong interfacial layer is the key factor of the mechanism describing retardation of ozone degradation of a diene rubber by elastomer additives with a low degree of unsaturation. In [6] specific features of interfacial interaction in such systems were established Zappa's method. The formation of the interfacial layer in the crosslinked heterophase blends of BNR with different contents of polar acrylonitrile units (Table 1) and EPDM which are characterized by different comonomer compositions and stereoregularities of propylene units (Table 2) was studying. The density of the interfacial layer and the content of the formed crosslinks for EPDM influence on the kinetics of ozone degradation of the diene matrix and the efficacy of protective action of EPDM. The density of the interfacial layer and the number of crosslinks in this layer were characterized by a difference between the equilibrium degree of swelling and the additive values in a nonpolar solvent n-heptane [20, 21]. It was proposed that the interfacial layer in the crosslinked blend of copolymers with different polarities may develop via diffusion penetration of EPDM units into the nonpolar regions of BNR [20-27]. The objects of research in this study were heterophase crosslinked BNR–EPDM (70 : 30) blends. At this content of the nonpolar component, a system of interpenetrating crosslinked networks appears. Both isolated EPDM particles and their conglomerates are distributed in the BNR matrix. The size of EPDM particles in the blend depends on compatibility of the components and increases with the polarity of BNR. The value of –α depends on the amount of crosslinks in the interfacial layer and its volume. Let us assume that the major fraction of polar units of BNR is uninvolved in its formation and the value of –α was recalculated to the 100% content of butadiene units –α100% (Fig. 2) and used to characterize the structure of the interfacial interaction zone and the amount of crosslinks contained in it. In such a manner, the effect of the interfacial layer volume could be minimized. As will be shown below, this situation may not be attained in all cases (Fig. 2 and 3). It is seen that a linear decrease in the value of –α100% with an increase in the total content of 1,4-cis and 1,2 units is observed for the crosslinked blends of BNR with all DSM EPDM samples and EPDM-60(I) characterized by a low isotacticity of propylene (Table 2). The fact that the value of –α100% decreases in proportion to the amount of 1,4-cis and 1,2 isomers of butadiene units for EPDM-based blends provides evidence that the density of the transition layer increases. This circumstance implies that the mutual solubility of EPDM comonomers and butadiene units that occur for the most part in the 1,4-trans configuration in the neighborhood of these isomers is improved. For DSM and EPDM-60(I) the region of interfacial interaction is bounded by nonpolar BNR units. The compatibility of chain portions of these EPDM samples with the polar acrylonitrile groups is ruled out. As the proportion of propylene units in EPDM is increased, the compatibility of the components, the density of the interfacial layer, and the amount of crosslinks in it drop sharply (the absolute value of –α100% increases). Thus, the higher the content of atactic propylene units in EPDM, the lower the adhesion interaction of the components and the worse its compatibility with BNR. 1,4-Trans units (Table 1), which show the tendency toward ordering at the low content of acrylonitrile and other isomers [28, 29]. Ordered structures worsen compatibility of polymers even to a higher extent [20-29]. Fig. 2 - The plots the value of –α 100% for covulcanizates EPDM with DSM (1) 778, (2) 714, (3) 712, (4) EPDM-60(I); –α (5) for R 521; –αcis+1,2 for (6) R 505 and (7) Elastokam 6305 as a function of the total content of 1,4-cis- and 1,2-butadiene isomers in BNR For BNR covulcanizates with EPDM R 512 containing a large proportion of ethylene units and distinguished by the presence of stereoregular propylene sequences, the value of –α100% linearly decreases with the content of butadiene units by a factor of 2.6 (Fig. 3). This fact leads us to infer that, firstly, ethylene units adjoining predominantly short isotactic propylene sequences are well compatible with all isomers of butadiene units. Secondly, an increase in the density of the interfacial layer and in the amount of crosslinks in it (a decrease in –α100%) with a rise in the proportion of nonpolar units in BNR implies that EPDM molecular fragments may penetrate into BNR regions that apparently contain single polar acrylonitrile groups. EPDM-40 with a higher degree of isotacticity of propylene units (as compared with EPDM R 512) is characterized by a far more intensive penetration of propylene chain fragments in their rigid isotactic configuration into BNR regions containing single polar groups. An increased volume of the interfacial layer and its local density reduction are confirmed by the fact that the value of (–α) for blends with EPDM-40 is higher than that for the EPDM R 512-based blends. For the covulcanizates of R 521 EDPM, which contains a large amount of isotactic propylene sequences [11, 12], the proportional decrease in the value of –α by a factor of 1.85 is observed in the –α–Σ(1,4-cis and 1,2 units) coordinates (Fig. 1). Fig. 3 - (2) (–α) and (1, 3, 4) (–α 100%) vs. overall content of butadiene units c for (1) EPDM R 512, (2) EPDM-40, (3) EPDM-60 (II), (4) Elastokam 7505, in their covulcanizates with BNR Consequently, at a high content of isotactic propylene units, EPDM shows better compatibility with BNR if the butadiene comonomer is enriched with 1,4-cis and 1,2 units (a reduction in the value of –α). The values of –α do not take into consideration restrictions related to the mutual interpenetration of segments of dissimilar chains associated with the presence of polar groups in BNR. As a result, it is not improbable that BNR portions containing polar groups may be involved in the interfacial interaction region. This circumstance is related to the specific features of BNR interaction with EPDM containing a large proportion of isotactic propylene chain fragments. This observation may be attributed to the rigidity of isotactic propylene sequences arising from hindered conformational transitions. The potential barrier to transitions between rotational isomers of monomer units for the isotactic PP is 21 kJ/mol, while for PE, the potential barriers of T–G and G–G transitions are 2.5 and 8.8−10 kJ/mol, respectively [32]. For blends with EPDM R 505, which contains a large amount of ENB, the linear dependence is attained when the values of –α100% are recalculated to the 1% of the sum of 1,4-cis and 1,2 units in BNR (−αcis + 1,2) (Fig. 2) [6]. An analysis of the –αcis + 1,2 versus Σ(1,4-cis and 1,2 units) curves demonstrates that −αcis + 1,2 decreases by a factor of 5.3 with an increase in the total amount of these butadiene unit isomers. The data presented above suggest that the chain fragments of this EPDM are well compatible only with those portions of butadiene chains that contain 1,4-cis and 1,2 isomers, while in the case of 1,4-trans units, compatibility is much worse. It appears that the bulky diene group, as in EPDM 714, significantly hinders the incorporation of EPDM chain portions into butadiene regions of BNR. For Elastokam 6305 with a high content of ethylene units (74%), with a higher amount of ENB (5,4%) and a very low degree of isotacticity of propylene sequences (9.5%) (Table 2), as follows from Fig. 1, the dependence on the overall content of cis-1,4- and 1,2-butadiene units in BNR also is linear if –αcis-1,4 + 1,2 This copolymer is compatible only with butadiene chain fragments of BNR containing preferably cis-1,4- and 1,2-isomers. Hence, when propylene units are characterized by a very low microtacticity (9.5%), compatibility between the components decreases. As was shown in [6], the high content of ethylene units, whatever the configuration of propylene sequences, provides a better compatibility with butadiene copolymer BNKS. However, as atactic configuration in the blend dominates, the depth of penetration of EPDM segments is limited by the butadiene part of the copolymer. Because, in EPDM-60 (I), half of all propylene units exist in the isotactic configuration and the content of diene groups is lower, its segments are able to diffuse into nonpolar SKN regions to a greater depth than segments of Elastokam 6305. EPDM-60 (II) with a higher content of ENB (6.7%) is compatibilized only with butadiene units (Fig. 3, curve 3) and (−α100%) increases by a factor of 1.8 as their content grows. This tendency suggests that this interfacial layer is characterized by an increased friability and the number of crosslinks in this layer is low. The higher the volume of this layer (the lower the polarity of BNR), the higher the (–α100%) values. The ratio between ethylene and propylene units in Elastokam 7505 is similar to that in EPDM-60 (II), but the degree of isotacticity of propylene units is lower (9.5%) and the Mooney viscosity is very high (Table 3). Elastokam 7505 is characterized by the minimum compatibility with all BNR samples. As follows from Fig. 3 (curve 4), the friability of the interfacial layer of this EPDM is maximum; as a result, (–α100%) markedly increases with a decrease in the polarity of SKN (by a factor of ~3). The worst results were observed for EPDM-60 (II) with an increased content of diene units and for Elastokam 7505 with a high Mooney viscosity. Thus, the structure of interfacial interaction zone depends on the comonomer composition of EPDM, the stereoregularity of propylene units, and the isomerism of butadiene units. The amount of interphase crosslinks grows with an increase in the total content of 1,4-cis and 1,2-butadiene units in BNR except EPDM with a high content of ethylene units and a low content of predominantly isotactic propylene units. A high compatibility of BNR with this EPDM may be provided by interaction with butadiene units regardless of their isomeric composition. Owing to conformational restrictions, stereoregular propylene units can penetrate into BNR regions that apparently contain single polar acrylonitrile units. As a result, the volume of the interfacial zone increases but its density and the amount of crosslinks contained in it decrease locally. The compatibility of propylene fragments of EPDM chains that predominantly occur in the atactic configuration with butadiene units is much worse. The interfacial layer is looser, and the region of diffusion penetration of phases is confined by the presence of nonpolar units. The proportional growth of the density of interfacial layer and the amount of crosslinks with an increase in the total amount of isomers of butadiene units contained in BNR in a smaller amount is explained by disordering of 1,4-trans units. As a result, their compatibility with portions of EPDM molecules is facilitated. The ability of EPDM that contains a large amount of diene units and stereoregular propylene units to compatibilize with butadiene units of BNR is close to that of EPDM with a low degree of isotacticity of the propylene comonomer and is determined by steric hindrances related to the presence of the bulky diene. However, a higher content of diene groups ensures better crosslinking of EPDM with the matrix. As a result, the total amount of crosslinks between phases is higher than that for blends with EPDM having the same ratio of ethylene and propylene units but a smaller amount of diene (cf. EPDM R 505 and R 521, EPDM 714 and EPDM 712). The largest amount of crosslinks in the interfacial layer forms when EPDM with a high content of ethylene units is used despite the moderate amount of diene contained in it. Data on the efficiency of retardation of the ozone induced degradation of diene rubber in the absence (85:15 blend) and presence of the EPDM network (70:30 blend) at different strains are given in Table 3 (EPDM of the Royalen brand and the DSM). In the case of the continuous EPDM network, the degradation rate for the BNKS-18 or BKNS-28 matrix reaches a minimum (value vdrel is maximum) [7]. The efficiency of retardation of the ozone degradation of BNKS-18 in the presence of the Royalen EPDMs, which except R 505 have a high stereoregularity of propylene units, is much higher than that in the case of DSM EPDMs of the same composition with a low degree of isotacticity of propylene sequences. The degradation inhibition efficiency vdrel in the BNKS-18 blend with EPDM 778 is five times below that in the blend with EPDM R512. In blends of highly polar NBRs, vdrel sharply decreases and the differences between the blends level out. This leveling is due to a decrease in the length of the interphase interaction zone as a result of an increase in the amount of polar acrylonitrile units in NBR. The breaking of adhesion contacts facilitates microphase separation during the deformation of a specimen and considerably increases the rate of growth of ozone microcracks and their coalescence (Table 3). There is no difference in vdrel between BKNS-40 covulcanizates with DSM EPDMs at amounts of the ozone-resistant components of 15 and 30 phr. This indifference is explained by the low compatibility of the components, an increase in the particle size of the dispersed copolymer, and an extremely low strength of its network or its absence as such (Fig. 2). Whenever the network is formed in the covulcanizates, its degradation takes place at strains of 30–50%, unlike in the case of Uniroyal EPDMs of the same compositions [7]. The amount of crosslinks between the phases in the blend of EPDM R521 is considerably greater, unlike the case of EPDM 712 of the same monomer composition with a low microtacticity of propylene units [7, 13]. As follows from the data presented in Table 3, for the BNKS-18 blend with EPDM R521 is three times that of the blend with EPDM 712. A reduction in the compatibility of components is responsible for the formation of a dispersion structure with coarser particles of the dispersed phase and weak bonding between these particles. The topological structure of a blend is characterized by a large distance between neighboring elements of the EPDM network [4]. The growth and coalescence of microcracks stop when a microcrack propagates to the interphase. The crack formation rate decreases as the distance between neighboring network elements becomes shorter. This decrease is responsible for the considerable difference in the efficiency of retardation of BNKS-18 degradation between the blends containing EPDM 778 and EPDM 712, EPDM R512, and EPDM R521, which is due to the specifics of interphase interaction in heterophasic blends. Table 3 - Efficiency of retardation of ozone degradation vdrel of acrylonitrile–butadiene rubber by ethylene–propylene–diene elastomers at component ratios of 85 : 15 and 70 : 30 and values for –α NBR covul-canizates with EPDM vdrel (85:15) at ε=30% vdrel (70:30) at different strains, % –α,% 30 50 70 90 BNKS -18 778 714 712 R 512 R 505 R 521 1.5 1.8

1.7 1.7 0.9 1.3 5.1 5.1 6.8 26.0 4.5 20.4 4.2 3.1 5.7 7.9 2.6 7.5 3.8 3.1 3.6 4.0 2.9 4.9 4.2 2.9 5.6 3.4 2.0 4.5 12.6 48.9 79.8 8.1 52.5 27.1 BNKS -28 778 714 712 R 512 R 505 R 521 1.6 1.5 2.3 1.2 1.0 3.0 2.3 2.5 3.2 3.8 1.5 4.4 1.7 2.0 2.9 2.5 1.4 3.6 2.2 1.9 3.0 2.2 1.5 2.3 1.9 - 1.8 1.6 1.5 1.7 7.4 36.0 63.4 14.5 25.3 20.9 BNKS -40 778 714 712 R 512 R 505 R 521 1.9 2.2 2.1 1.8 1.5 1.9 1.9 2.1 2.1 3.1 1.3 2.7 0.6 1.7 1.8 2.4 1.1 1.6 - - - 1.3 1.1 1.5 - - - 0.7 1.7 1.0 12.4 42.6 69.9 15.4 32.6 38.6 An increase in polarity during the use of BNKS-28 does not lead to a decrease in the interphase density in the blends with both EPDM brands, a result that is due to the influence of the isomer composition of butadiene units on the compatibility of NBR with EPDM. It was shown that the interphase density and the amount of crosslinks in the interlayer increase with an increase in the total content of cis-1,4- and 1,2-butadiene units in BNKS (Table 1). Despite this circumstance, a considerable decrease in vdrel takes place, a result that is due to the decrease in the interphase volume with an increase in the amount of polar units in NBR. Correspondingly, has a minimal value vdrel in the blends with BNKS-40. An increased amount of ENB units in EPDM R505 and EPDM 714 at the same ratio of ethylene to propylene units as in EPDM 521 and EPDM 712, respectively (Table 2), facilitates a decrease in the number of crosslinks between the phases if the propylene units have the isotactic configuration (R505) or an increase if the configuration is atactic. Nonetheless, a decrease in the efficiency of retardation of ozone degradation and, as will be shown below, in the EPDM network strength takes place in all cases. A large amount of the bulky diene impedes the formation of a dense bulk interlayer. A doubled amount of diene groups in R505 as compared to R521 leads to a twofold decrease in the amount of interphase ligaments in the BNKS-18 blend and to a drop in vdrel by a factor of 4.5. In the blends of all NBRs with EPDM 714, the amount of crosslinks increases by a factor of 1.6–1.8, and falls in the BNKS-18 and BNKS-28 blends by a factor of 1.3. Thus, even an increase in the amount of crosslinks primarily along the interface decreases the ozone protection effect. This result is due to a small depth of interpenetration of copolymer chain segments, a situation that leads to a reduction in the strength of interphase contacts. The most effective protection is provided by the compatibility of NBR with EPDM having a large proportion of ethylene units at a high isotacticity of propylene sequences and a moderate amount of diene groups. The character of the dependence of the quasi-equilibrium stress σ* on strain in accordance with the specifics of adhesive interaction of phases reflects the ability of the EPDM network to withstand deformation [7]. Owing to the fact the EPDM phase is bonded to the matrix through interlayers containing chemical links between the components, the value of σ* is the superposition of stresses in the matrix and the EPDM phase. Nonetheless, this quantity gives an insight into stresses that emerge in the EPDM vulcanization network during deformation of the specimen. The network strength is affected by the degree of development of the interlayer, its length, the amount of chemical links between the phases, and the degree of crosslinking in the EPDM phase [6-8]. At a low compatibility of components (blends based on BKNS-40), the dependence of σ* on the presence of microcrystalline domains of ethylene and isotactic propylene sequences in the copolymer manifests itself also [11-13, 33,34]. All DSM EPDMs with propylene units of low stereoregularity form a less strong network in their cured blends with NBR as compared to Uniroyal EPDMs (Fig. 4). The networked structures of EPDMs in the blends with less polar BNKS-18 show the highest strength. In the covulcanizates with BKNS-28 the degradation of the EPDM 712 network with a high content of atactic propylene units occurs at ε = 110% and that of the EPDM 714 network with a higher proportion (8%) of diene groups takes place at ε = 50% [7]. At the same time, the values of σ* for the Royalen EPDM blends of the same composition (R505 and R521) are retained at a sufficiently high level (0.10–0.15 MPa) [7]. The EPDMs of both brands with a large amount of ethylene units form the strongest three dimensional framework. EPDM R512 and EPDM R521 with a high proportion of ethylene or isotactic propylene units form networks that vary in strength; however, a decrease in the quasi-equilibrium stress σ* on passing from NBR blends having a lower amount of acrylonitrile units to the blends with a higher amount of acrylonitrile units (e.g., from BNKS-18 to BNKS-28) is proportional to the increase in the amount of polar units in NBRs. Thus, the strength of the EPDM network depends on the interlayer length. The breaking of interphase interaction by polar units leads to a drop in the EPDM network strength [7]. Fig. 4 - Quasi-equilibrium stress σ* as a function of the departure of equilibrium swelling from the additive value, –α: BNKS-18 (I,IV), BNKS-28 (II-V), and BNKS-40 (III-VI) covulcanizates with (1–3) EPDM R512, EPDM R505, and EPDM R521 and (4−6) EPDM 778, EPDM 714, and EPDM 712 In the case of blends of DSM EPDMs, a proportional decrease in the stress σ* with a growth in the proportion of acrylonitrile units is observed only for EPDM 778 covulcanizates with BNKS-18 and BNKS-28. Consequently, such a decrease in these materials is also the basic reason for the drop in the strength of the EPDM network structure. However, in the blend of BNKS-40 with EPDM 778, a decline in the EPDM network strength is nonproportionally strong at a rather high density and a large amount of crosslinks in the interlayer (Table 3). This behavior is explained in terms of a decrease in the volume of the interphase owing to its length and the depth of the interpenetration region of unlike chains. When the atactic fraction prevails in EPDM with a high ethylene content, the compatibility with highly polar NBR is limited by the amount of butadiene units in the latter. Figure 3 depicts the plots of the quasi-equilibrium stress versus –α100% for NBR covulcanizates with EPDMs manufactured by different companies. As the interphase density and the amount of crosslinks between the components increase (–α100% decreases), the EPDM network strength in the blends with the most developed interlayer proportionally increases. The slope of the linear plot characterizes the relative contribution of the interphase length and the depth of interdiffusion of unlike chains in an interlayer to the network strength. At the hypothetical maximal interphase density corresponding to –α100% = 0, the network strengths of Royalen and Keltan EPDMs in these blends will be 4.3 and 3.1 MPa, respectively. The lower EPDM network strength in the latter case is due to a smaller interphase volume along the depth of the interphase interaction zone as well as to a lower concentration of microcrystalline domains (amount of gel fraction in Table 1) [11-13, 31]. In this study, we investigated olso the effect of the very low stereoregularity of propylene units, the content of diene groups, and the Mooney viscosity (Table. 2) on the structure of interfacial region and the efficacy of protective action of EPDM (Table. 4) [8]. The influence of the above parameters on the kinetics of ozone degradation of the diene matrix and the efficacy of protective action of EPDM was investigated [7]. Figure 3 presents the (–α) value plotted against the content of butadiene units in BNKS for the crosslinked blends with EPDM-40 (curve 2). As compared with other commercial EPDMs, EPDM-40 is characterized by a very high degree of isotacticity (29%) of propylene chain fragments (about 90% of the isotactic fraction) (Table. 2). In the case of EPDM-40, an increase in the number of crosslinks in the interfacial layer, as defined by the (−α) parameter, is proportional to an increase in the content of butadiene fragments. However, in this case, limitations on the region of segmental interdiffusion, as provided by the nonpolar fragments of SKN, do not contribute to the value of (–α) (Fig. 3). Therefore, EPDM-40 with a higher degree of isotacticity of propylene units (as compared with EPDM R 512) is characterized by a far more intensive penetration of propylene chain fragments in their rigid isotactic configuration into BNKS regions containing single polar groups. Table 4 - Efficacy of ozone degradation retardation of BNKS (vdrel) by ethylene–propylene–diene elastomers (30 phr) and σ* at different tensile strains e,% EPDM -40 Elastokam 6305 EPDM -60 (1) EPDM -60 (2) Elastokam 7505 vd 103 min-1 BNKS vdrel sx, MPa vdrel sx, MPa vdrel sx, MPa vdrel sx, MPa vdrel sx, MPa BNKS-18 30 50 70 90 110 130 150 48,0 43,0 3,5 3,0 2,2 0,27 0,30 0,23 0,23 0,19 0,17 0,17 11,6 7,4 2,9 4,1 2,4 0,34 0,43 0,35 0,34 0,34 0,36 0,31 12,1 5,7 4,0 4,0 2,8 0,30 0,31 0,25 0,30 0,26 0,26 4,5 3,4 2,1 0,24 0,25 0 1,8 2,7 0 0 240 256 200 190 122 BNKS -28 30 50 70 90 110 130 1,8 3,0 1,4 1,3 1,2 0,09 0,21 0,17 0,17 0,18 2,2 2,0 1,6 1,3 1,0 0,11 0,15 0,11 0,16 0 2,8 4,0 3,2 1,8 1,5 0,16 0,22 0,23 0,15 0,13 0,14 1,8 2,4 1,7 0,13 0,12 0 1,9 2,5 2,3 0,10 0,13 0 165 192 163 134 100 BNKS -40 30 50 70 90 110 2,9 1,4 1,2 1,3 2,1 0,15 0,13 0,10 0,08 0 2,0 1,2 0 0 3,2 1,6 1,7 2,0 0,08 0,09 0,07 0 1,3 0,8 1,0 1,3 0,08 0,04 0,07 0 2,2 1,3 2,2 0 0 0 115 94 99 117 130 An increased volume of the interfacial layer and its local density reduction are confirmed by the fact that the value of (–α) for blends with EPDM-40 is higher than that for the EPDM R 512-based blends (Fig. 4) [7, 8]. This increase comes to 1.3-, 1.5-, and 1.7-folds for BNKS-18, BNKS-28, and BNKS-40, respectively. Hence, a difference in the number of crosslinks increases with the increasing polarity of BNKS. As the region of adhesion interaction of elastomers is increased, the efficacy of reduction in the rate of ozone degradation vdrel of the diene matrix dramatically increases in the blends with the less polar BNKS-18 (Table 4). The efficacy of degradation retardation vdrel is much higher for the blends of EPDM-40 and crosslinked BNKS-18 as compared with the blends containing EPDM R 512 (by a factor of 48 and 26, respectively) (Tabl. 3 and 4). This behavior can be explained by reduced dimensions of EPDM-40 particles and a small distance between network elements that are the consequences of high compatibility. In the blends with BNKS-40 with the increasing strain, the interfacial layer partially breaks down owing to its discontinuous structure; as a result, vdrel decreases dramatically (Table 4). For the blend containing EPDM-40, this breakdown is observed at ε = 110%, while for the EPDM R 512-containing blend, this effect occurs at ε = 70% [7, 8]. Therefore, in the case of the blends based on EPDM-40, the interfacial microseparation takes place at higher strains. With the increasing polarity of BNKS, vdrel abruptly decreases owing to decreased length, depth, and density of the interfacial layer and crosslinks between phases. Comparing the efficacy of degradation retardation in BNKS -18 containing EPDM-40 or Elastokam 6305 with a high content of ethylene units (74%) and a very low degree of isotacticity of propylene sequences (9.5%) (Table 2), one can conclude that the properties of the latter blend appear to be much worse (Table 4). As follows from Fig. 2, for Elastokam 6305, the dependence on the overall content of cis-1,4- and 1,2-butadiene units in BNKS is linear if the (–α) value is normalized to the 100% content of nonpolar units and 1% content of cis-1,4-and 1,2-isomers (–αcis+1,2). Therefore, one can conclude that this copolymer is compatible only with butadiene chain fragments of BNKS containing preferably cis-1,4- and 1,2-isomers. Hence, when propylene units (9.5%) are characterized by a very low microtacticity, compatibility between the components decreases. Even in the blends containing BNKS-18, vdrel is not high, despite a very high content of ethylene units in EPDM. As was shown in [6-8], the high content of ethylene units, whatever the configuration of propylene sequences, provides a better compatibility with butadiene copolymer BNKS. However, as atactic configuration in the blend dominates, the depth of penetration of EPDM segments is limited by the butadiene part of the copolymer; hence, vdrel is lower. The volume of the formed interfacial layer is smaller. This blend is characterized by a high strength of the EPDM network. High values of the quasi-equilibrium stress are preserved up to a strain of 150% [8]. The dependence of σ* on the presence of microcrystalline domains of ethylene and isotactic propylene sequences [11, 12, 33, 34] in the copolymer manifests itself also. EPDM-60 (I) (ENB 4%) is characterized by a lower content of ethylene units and a somewhat higher degree of isotacticity of propylene chain fragments (13%). In the blends containing EPDM-60(I), the dependence of the number of crosslinks in the interfacial layer is similar to that as observed for the blends containing DSM 778 of close comonomer composition and stereoregularity of propylene units [7] (Fig. 2). Because, in EPDM-60 (I), half of all propylene units exist in the isotactic configuration and the content of diene groups is lower, its segments are able to diffuse into nonpolar SKN regions to a greater depth than segments of Elastokam 6305. As a result, with an increase in tensile strain, the protection efficacy of EPDM-60 (I) in the blends with BNKS -28 and BNKS -40 decreases to a lesser extent and the strength σ* of EPDM-60 (I) network is higher than the strength of the Elastokam 6305 network (Table 4) [8]. EPDM-60 (II) with a higher content of ENB

(6.7%) is compatibilized only with butadiene units (Fig. 8, curve 2) and (−α100%) increases by a factor of 1.8 as their content grows. This tendency suggests that this interfacial layer is characterized by an increased friability and the number of crosslinks in this layer is low. The higher the volume of this layer (the lower the polarity of BNKS), the higher the (–α100%) values. Therefore, the efficacy of ozone degradation retardation is low even for the blends based on BNKS -18 containing EPDM-60 (II) and the strength of the EPDM network is small (Table 4). The ratio between ethylene and propylene units in Elastokam 7505 is similar to that in EPDM -60 (II), but the degree of isotacticity of propylene units is lower (9.5%) and the Mooney viscosity is very high (Table 3). Elastokam 7505 is characterized by the minimum compatibility with all SKN samples. As follows from Fig. 3 (curve 3), the friability of the interfacial layer of this EPDM is maximum; as a result, (–α100%) markedly increases with a decrease in the polarity of BNKS (by a factor of ~3). Evidently, the efficacy of ozone degradation retardation of the diene matrix in the presence of Elastokam 7505 is low and the quasi-equilibrium stress σ* in the crosslinked blends of BNKS-18 and BNKS-40 is zero at the minimum strain (30%) [8]. In the above blends, compatibility between components is so small that, as can be judged by the σ* value, the copolymer exists in the dispersed state and does not form any continuous three-dimensional structure (Table 4). The fact that the strength of the EPDM network decreases to zero at low strains indicates the development of a coarse dispersed structure with weak bonds between particles; this behavior is likewise observed for the blends based on BNKS-40 and Elastokam 6305. Conclusion Thus, the reduction of the rate of ozone degradation of the diene elastomer is explained in terms of compatibility of the components, the volume and density of the interphase, and the amount of crosslinks in the interlayer, the EPDM network strength depending on the amount of chemical crosslinks between the phases and on the degree of crosslinking of the EPDM phase or on the presence of microcrystalline domains of ethylene and isotactic propylene sequences. It has been found that not only the comonomer ratio in EPDM but also the stereoregularity of propylene sequences determines the specifics of formation of the interphase and its volume in crosslinked heterophasic blends with NBRs of different polarities. The most dense and voluminous interlayer with the largest amount of crosslinks provides the most effective protection against ozone degradation to the diene matrix.