

УДК 678.675

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### THE INFLUENCE OF RECIPE INGREDIENTS OF ELASTOMERIC COMPOSITION ON THE ELASTIC-DEFORMATION PROPERTIES OF TIRE

The results of researches of elastomeric compositions on the basis of the natural rubber, containing a Vulcuren VPKA-9188 are given in this paper. This ingredient use as substitute of the accelerator of sulfuric curing of DFG. The addition of the component allows to lower aniline allocation at rubber usage, to carry out vulcanization with high speed and practically without reversion. It is established that addition of various vulcanization systems to rubber mixes influences technical properties of vulcanizates. The parameters of the crack growth resistance to the repeated flexing differ in 1.1–1.4 times. Such distinction probably is connected with the nature and density of the cross-linking bonds which are forming in volume of elastomeric composition in the course of curing. Application of studied ingredient in serial elastomeric composition of tire rubbers demands correction of composition and dosage of vulcanizing system.

**Introduction.** Rubber is a complex multi-component system consisting of a polymeric base and a variety of chemical additives (ingredients). The ingredients are necessary both for performing chemical transformations of rubber during their processing (increasing of plasticity and cross-linking, etc.), and giving rubber articles certain properties [1]. Depending on the purpose of the rubber composition and manufacturing technology of it product, both the composition and contents of ingredients varies considerably. The properties of rubber, on the basis of each particular rubber can be improved by the recipe techniques only to a certain level, i.e., the ingredients of the rubber composition contribute only to a more complete realization of the properties of rubber. Rubber and ingredients unequally affect various properties of rubber and rubber mixtures. Since in each particular case not all, but only specific characteristics of rubber and rubber mixtures are essential, then when preparing the mixture recipe primarily those ingredients are chosen, on which the values of these characteristics mainly depend [2].

The reasons for changes in the properties of the polymer composition caused by mechanical forces that determine weariness and fatigue, can be divided into three types:

- 1) the emergence of free macro-radicals due to a mechanical deformation at impact;
- 2) the mechanical activation of chemical interactions with macromolecules with the components of rubber mixture;
- 3) reorientation, repackaging of chain segments and elements of supramolecular structures of elastomer and agglomerates particles of a filler under the influence of external forces.

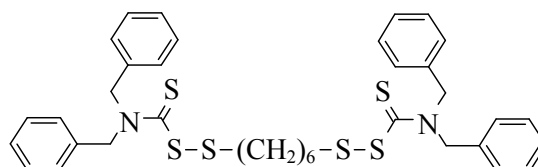
Each of these components of fatigue plays a principal or secondary role depending on specific

properties of the ingredients of the elastomeric composition, nature and chemical reactivity of the rubber components contained in the matrix, mode of mechanical impacts, etc. [3].

**Main part.** The expansion of assortment of ingredients for rubber compounds for improving the properties of elastomeric compositions to increase the quality of the finished product is an urgent task. In this paper, the elastomer compositions containing Vulcuren VPKA-9188 were the objects of investigation.

Vulcuren VPKA-9188 is used as a substitute for sulfur vulcanization accelerator, diphenylguanidine (DPG). The advantage of using this ingredient, is primarily, the environmental aspect. The introduction of this material provides an extremely low level of aniline compared with DFG. Therefore Vulcuren VPKA-9188 can be used as a vulcanization accelerator for "green" tires. Besides, the rubber composition containing the investigated vulcanization accelerator exhibits a lower Mooney viscosity as compared with the rubber composition containing DPG, the vulcanization process occurs at a high speed and without reversion vulcanizates exhibit high hardness according to A. Shore. The use of Vulcuren VPKA-9188 as a secondary accelerator in rubber mixtures with silicon dioxide provides faster vulcanization, better scorch resistance, similar processing in combination with zinc soaps, similar mechanical properties, lower loss factor.

Vulcuren VPKA-9188 (1,6-bis (N, N-dibenzyltiokarbamoilditio) hexane) has the following chemical structure:



The nature of rheometric curve of vulcanization of rubber mixtures shows that in the presence of the substance the vulcanization reversion is not observed. Tensile strength of the samples is high enough, heat generation is less in comparison with samples Vulcuren VPKA-9188.

The research on the impact of the new accelerator on elastic-deformation properties of rubber was carried out in the elastomeric compositions on the basis of natural rubber (NR) containing carbon black N330, dosage 43.0 phr.

An essential feature of the reactions occurring during fatigue of vulcanizates under elevated temperature conditions is a mechanical activation of thermal dissociation of weak bonds in the grid revealed when comparing the rate constants of static and dynamic creep in vacuum. The clarification of the nature of this phenomenon has led to the conclusion that mechanical activation is associated with hysteresis losses in rubber and is due to the contribution of the energy component of deformation of weak structures of the grid such as crosslinking. The influence of hysteresis at elevated temperatures is inverse to that which occurs at ordinary temperatures of fatigue. Mechanically activated destruction is considered as an alternative to physical non-equilibrium relaxation of deformed fragments of vulcanate grid. The growth of vulcanizates mechanical losses lead to higher stresses due to the large instant deviations from the equilibrium of highly elastic deformations, which in their turn causes an increase of the coefficients of destruction of mechanical activation. The growth rate and the strain amplitude cause the same influence [4].

The results of studies on rubber tear propagation resistance at bending at higher temperatures are shown in Table 1. Tests were carried out at a temperature of 110°C.

Table 1

**Results of the study of resistance of rubbers to formation and growth of cracks at flexing**

Principal distinction	Resistance to cracks growth at bending, th. cycle
<i>Option 1:</i> About 1.0 phr sulfur 1,1 phr Santocure TBBS 1,2 phr DTDM	6.00
<i>Option 2:</i> 0.75 phr sulfur 0.6 phr Santocure TBBS 2,0 phrVulkuren PKA-9188	5.50

The fatigue failure at higher temperatures is regarded as the summation of of acts of thermo-mechanical and thermo-oxidative destruction at the

mouth of the most dangerous defect, which is converted into a hotbed of destruction [4].

The studies revealed that changes in the composition of the vulcanizing system, namely replacing ditiodimorfalin (DTDM) by Vulcuren VPKA-9188, reducing the dosage, and the main curing agent accelerator Santocure TBBS, crack growth resistance index is slightly reduced (less than 10%). So, rubber floor with inefficient vulcanizing system (option 1) the number of cycles until a crack length of 12 mm [5] is 6,000 cycles, and for the vulcanizate containing accelerator Vulcuren VPKA-9188, this figure is 5,500 cycles.

In sulfur vulcanizates due to the acceleration of thermal decomposition of acts of weak crosslinks under dynamic loading the oxidative degradation, initiated by these acts, is also accelerating. In the defective areas of vulcanizates the appearance of nonequilibrium stretched chains and crosslinks are more likely than on the average in terms of volume, therefore the growth of defects, determining the fatigue endurance, is due to mechanically activated grid breaks in estuaries. The overgrowth of defects caused only by mechanically activated local destruction rate is higher than the average in terms of the elastomer composition [4].

At equal thermal oxidative stability rubber has poorer fatigue properties at higher temperatures with higher hysteresis losses even while maintaining a constant and uniform temperature of tests. The inverse relationship is set for normal temperatures [3, 4].

To determine the effect of the new accelerator on the vulcanization grid structure, the study of rubber was carried out before and after exposure to cyclic strain and temperature. The results of studies of the structure of vulcanizates are shown in Table 2.

Table 2

**Results of the research to determine the concentration of cross-links in vulcanizates**

Index	Option 1	Option 2
Before test		
$M_c$	4,245	4,092
$n \cdot 10^{-20}, \text{cm}^{-3}$	1.305	1.357
$v \cdot 10^4, \text{mole/cm}^3$	2.17	2.25
After test		
$M_c$	4,184	4,136
$n \cdot 10^{-20}, \text{cm}^{-3}$	1.324	1.339
$v \cdot 10^4, \text{mole/cm}^3$	2.20	2.22

*Note.*  $M_c$  - the average molecular weight of the interval of the molecular chain, concluded between the two crosslinked;  $n$  - the number of cross-links contained in 1 cm<sup>3</sup> of the vulcanizate;  $v$  - crosslink density.

The data obtained show that the crosslink density of elastomeric compositions based on NC containing less effective curing system and the system of the studied accelerator is almost the same.

On the basis of structure of the ingredients it can be assumed that the structure of the vulcanizate comprises cross-links similar in nature. It is known [1], that the reducing the sulfur content and increasing the dosage of curing accelerators leads to a decrease in cross-link sulphidity and enhances heat resistance of the rubber. Poly-sulfide bonds prone to disintegration and rearrangement under the influence of temperature, thus deteriorating heat resistance of the vulcanizates.

The results of studies of rubber before and after exposure to cyclic strain and temperature showed that the structure of vulcanizates varies slightly. However, it should be noted that in the case of rubber, comprising a half-effective curing system under the influence of temperature and repeated cyclic deformations, structuring processes, leading to a decrease in the average molecular weight of the molecular chain segment confined between two cross-links, and increase crosslink density are predominant. In the case of rubber containing Vulcuren VPKA-9188, reverse tendency is observed, indicating that, under the influence of temperature and mechanical stresses in the bulk of the vulcanizate destruction processes are predominant. Perhaps this change in the structure at high temperatures is explained by minor differences in terms of resistance to crack growth at flex.

The next group of objects of study was different by composition of the vulcanizing system, as well as the dosage and the mark of the used filler: N330, Ecorax 1670, Vulcan 1380.

The results of rubber investigation on its resistance to cracks growth at repeated bending at higher temperatures are shown in Table 3. The tests were carried out at a temperature of 110°C.

When studying the effects of different types of carbon black and curatives on crack propagation resistance at a bend, it was found that the best results are observed for the rubber containing Vulcan 1380 and the combination of Vulkuren VPKA-9188 + Santokur TBBS.

The results of the study for determining the density of cross-linking of vulcanizates before and after the multiple exposure to cyclic strain are presented in Table 4.

The obtained data revealed that the vulcanizates containing an effective curing system (option 3); vulcanizates containing the analyzed vulcanization accelerator and new brands of black carbon characterized by almost the same values of cross-link density and the number of cross-links contained in 1 cm<sup>3</sup> of the vulcanizate, have the highest cross-link density. This dependence is also

observed in the study of the samples after tests on multiple longitudinal bend. It should be noted that for all the investigated rubbers after exposure to temperature and cyclic strain, the reduction of the average molecular weight of the molecular chain segment confined between two cross-linked is observed, as well as the increasing of cross-link density, which indicates the occurrence of structuring processes.

Table 3

**Resistance to cracks growth  
of investigated rubbers at repeated bending**

Principal distinction	Resistance to cracks growth at bending, th. cycle
<i>Option 3:</i> 43.0 phr N330 1.2 phr DTDM 1.0 phr Santocure TBBS 0.2 phr Santogard PVI	7.65
<i>Option 4:</i> 38.0 phr Ecorax 1670 0.8 phr Vulkuren VPKA-9188 1.0 phr including sulfur	8.85
<i>Option 5:</i> 38.0 phr Vulcan 1380 0.8 phr Vulkuren VPKA-9188 1.0 phr Santocure TBBS 0.2 phr Santogard PVI	10.50

The analysis of results obtained for rubber containing the analyzed accelerator showed that the structure of vulcanizates does not differ, and the indicators on the crack growth resistance at flex differ by 1.2 times. Probably, this difference is due to the nature of the cross-link bonds, since at high temperatures the cross-links with lower sulphidity possess greater thermal stability.

Table 4

**Results of the research to determine  
the concentration of cross-links**

Index	Option 3	Option 4	Option 5
Before test			
$M_c$	3,924	4,655	4,557
$n \cdot 10^{-20}, \text{cm}^{-3}$	1.412	1,190	1.216
$v \cdot 10^4, \text{mole/cm}^3$	2.34	1,98	2.02
After test			
$M_c$	3,615	4,211	4,181
$n \cdot 10^{-20}, \text{cm}^{-3}$	1.555	1.316	1.326
$v \cdot 10^4, \text{mole/cm}^3$	2.58	2.19	2.20

**Conclusion.** Thus, it was determined that the use of Vulcuren VPKA-9188 (1,6-bis (N,N-dibenziltio-carbamolditio) hexane) in the composition of the vulcanizing system sufficiently contributes to the formation of strong cross-links. The application of a new vulcanization accelerator will significantly improve the environmental problems resulting from the curing process. However, the use of this substance in the serial tire rubber recipes making corrections of the vulcanizing group composition is necessary.

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*Received 05.03.2013*