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FEATURES OF RUBBER CROSSLINKING IN THE PRESENCE OF COMPOSITE VULCANIZATION ACTIVATORS

The features of curing polydienes by vulcanizing system based on composite curing activators was studied. Based on analysis of the investigating results of cure and elastic-strength properties rubbers was found that the modification of zinc oxide as a basis of the formation of actual curing agents increases of the active sites of vulcanization and as a consequence, increases the rate of vulcanization and improving physical and mechanical properties of rubbers.

Introduction. Many years of experience studying the vulcanization [1–4] as a process of crosslinking macromolecules cross bonds prove that it is impossible to create a single curing agent. This is due to differences in molecular structure of the rubbers, and extreme diversity of exploitation requirements to the products. Recently, the study of this issue requires special attention because of the need in fast response to changing resource base and involvement in the production the ingredients which are economically more beneficial, including energetical and (or) environmental reasons.

Investigation of different ways of sulfur vulcanization systems modification and especially their components that can affect the course of the curing process and rubber quality, acquires and practical significance. It includes the improvement of production forms of powdered ingredients, but especially introduced in the mixture in small doses, as well as directional control duration of the induction period, the cure rate of the compositions, and the quality indicators of products.

Regarding this problem, the study in the field of structure and properties of rubbers, obtained with different composition and properties of the activating systems, is one of the opportunities to learn and clarify the mechanism of formation of products of the interaction of the components in the vulcanization, it is a current issue from theoretical and practical points of view. Existing ideas about the nature of the action of activating systems in vulcanization are based on different points of view [3–4]. In addition to the lack of overall concept many private matters have not been clarified yet, for example, there are no clear data on the role of metal oxides in different action mechanism and different curing systems on the nature of the elastomers.

Main part. Taking into account [1, 3] that the diffusion is the transfer of matter at the molecular level, and the molecule in the zinc oxide is only hypothetical, its diffusion in the rubber composition is improbable. Low solubility of zinc oxide in combination with diffusion of the main components of vulcanizing system in rubbers assume the formation of heterophase vulcanization centers [3–6], which significantly differ by systems with different amounts of zinc oxide. Considering these facts, we studied zinc white with a various content of beneficial agent zinc oxide, ranged from 86.0 to 99.8 %. Physical-chemical characteristics of zinc white brands from different manufacturers are shown in Table 1.

Table 1

Physical-chemical characteristics of zinc white of various grades

Cipher sample	ZnO*, %	Admixture contents (CaO, MgO, FeO, PbO), %	Sieve residue, sieve membrane No 014, %	Δ, %	*S*, mkm
1	99.8	0.172	–	0.02	30
2	99.8	0.148	–	0.03	30
3	97.5	0.169	–	0.13	40
4	94.7	0.310	0.15	1.8	50
5	89.0	1.210	1.04	4.7	80
6	86.0	4.258	1.21	7.2	90

* Content of the basic substance based on ZnO; Δ – mass losses during ignition; S – degree of dispersion.

Analysis of the data in table 1 showed that the coposition of zinc white in addition to zinc oxide comprises various admixtures in the form of metal oxides (mostly calcium and magnesium oxides), and a small proportion of organic compounds. That is why it was interesting to examine the individual effects of these oxides on the kinetics of vulcanization, vulcanization grid structure, and rubber indices.

Table 2 summarizes the results of metal oxides use as vulcanization activators having amphoteric (zinc, iron) and alkaline (calcium, magnesium) properties. It was found that at similar levels of binding sulfur, zinc oxide provides the optimum combination of length, types and variants of stereo addition of crosslinking sulfur bonds.

Table 2

Influence of the nature and vulcanization activators ratio on the properties of rubber mixtures and stress-strain rubbers indices based on SKI-3

Vulcanization activator	M_V, conv. unit	τ_{90}, min (155°C)	M_{300}, MPa	f_p, MPa	ε, %	*B*, kN/m	*N*, thousand cycles	$S_{fr} \times 10^2$, %
ZnO	38	7.7	11.5	18.0	403	68	167	18
MgO	27	5.5	4.7	8.9	443	20	143	25
CaO	46	5.0	6.4	8.7	367	26	192	25
ZnO:MgO(1 : 1)	40	7.0	7.8	11.2	373	24	190	32
ZnO:MgO(1 : 2)	40	7.0	9.4	14.6	410	31	158	25
ZnO:CaO (1 : 1)	42	6.0	7.6	11.9	393	32	126	20
ZnO:CaO (1 : 2)	42	7.3	10.3	12.6	346	28	144	20
MgO:CaO(1 : 1)	29	4.5	6.7	9.8	383	21	190	20
MgO:CaO (1 : 4)	32	10.0	5.8	9.9	406	22	65	32
ZnO:MgO:CaO (1 : 1 : 2)	42	7.4	9.2	11.5	345	25	101	20
ZnO:Fe_2O_3 (10 : 1)	27	9.4	12.1	17.6	397	39	154	28
ZnO:Fe_2O_3 (1 : 1)	36	8.0	11.7	18.5	406	63	170	20

Note: M_V – Mooney viscosity; τ_{90} – optimum vulcanization time; M_{300} – conventional stress at 300% elongation; f_p, – conventional tensile strength; ε – relative elongation at break; *B* – break resistance; *N* – dynamic endurance; S_{fr} – free sulfur content.

The addition of even small amounts of calcium or magnesium oxide to zinc white leads to reduction of strength properties of the rubber. Theoretically, this means that at close levels of sulfur crosslinking zinc white provides the optimum combination of length, types, and variants of stereo addition of crosslinking sulfur bonds. Changes of the physical-mechanical rubbers indices are due to differences in the structure of the spatial grid of vulcanizates, obtained using different metal oxides, namely zinc white ensures formation of the optimal vulcanization structure during vulcanization.

Table 3 shows test results of rubber mixtures and vulcanizates containing zinc white of varying quality.

Table 3

Influence of the basic material on the properties of rubber compounds and rubber based on SKI -3

Indices	Basic material contens ZnO, %					
	99.8	99.7	97.5	94.7	89.0	86.0
M_v, c. units	50.4	52.5	56.7	52.5	54.6	56.7
τ_{90}, minn (190°C)	1.7	1.7	1.9	1.9	2.0	2.1
M_{300}, MPa	13.9	13.7	13.3	13.0	12.8	9.5
f_p, MPa	22.0	21.1	18.8	18.2	18.1	14.7
ε, %	460	470	440	440	425	395
B, kN/m	66.7	59.9	45.1	38.5	35.6	27.1
H_A, c. units	37	39	37	37	36	36
E, %	61	58	58	59	60	57
N, thousand cycles	9.4	9.5	9.3	9.2	70	6.2
S_{fr}, %	0.24	0.28	0.41	0.30	0.34	0.38
$n_{ef} \cdot 10^{-19}$, sm^{-3}	7.4	7.4	7.3	7.1	6.3	6.0

During the testing of rubber compounds and rubbers, manufactured on the basis of six grades of zinc white, it was found the cure rate decreasing with a decrease in the content of a beneficial agent in zinc white, which influences the spatial grid structure and physical-mechanical properties of the vulcanizates. In the rubbers with effective activation system (99.7–99.8 % of zinc oxide in zinc white), the areas of strong physical or chemical interactions alternate, probably, with weakened areas of intermolecular interactions [1, 5–6]. This causes micro-unequal distribution of crosslinking bonds in elastomer medium.

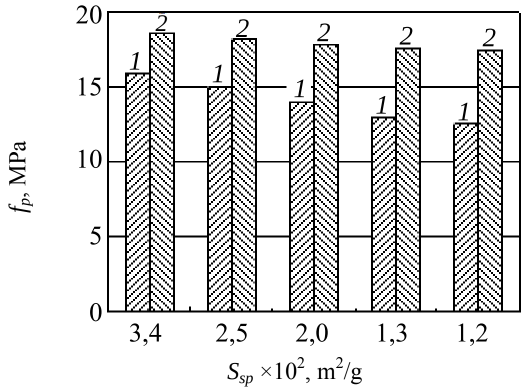
As a result of activated crosslinking in these systems, more dense and stable grid structure is formed [1, 5], the amount of free sulfur is reduced, thereby providing the improved vulcanizate properties (Table 3).

Authors [1–2] note that the shortage of zinc oxide causes the reactions, aimed mainly at formation of intra- cyclic sulfides and fewer polysulfide crosslinking bonds.

This is consistent with the data in table 3: at sufficiently high content of zinc oxide (6 pht according to the prescription), but in insufficient quantity (as chemically pure substance), which is able to enter an effective interaction, the properties of the compositions deteriorate.

Reduced rubber resistance to the action of multiple stretching is proportional to decrease of zinc oxide in zinc white, which is associated with the increase in the number of defects in vulcanizates grid that may arise because of the presence of mineral non-dissolving particles of impurities, and because of the increase of particle size of zinc white.

From the literature [6–8], and production techniques we have learned several physical-chemical methods of modification of sulfur vulcanizing systems of different compositions. This affects both problems at the same time, namely, improving the dispersibility of ingredients in rubber compounds [6, 9], components interactivation, formation of active complexes and new chemical compounds [5, 8], and the issues of improving the final forms of the particulate components and improving the environmental situation in a preparatory workshops [6–8]. Create activating complexes by modifying zinc white with different content of zinc oxide that can provide new properties of compositions on their basis. Modification of zinc white by mechanical grinding followed by determining the degree of dispersion has led to improved quality of rubber (figure), probably due to formation of a great number of ACV particles.



The dependence of the conditional strength of coating rubber at break on the specific surface area of zinc white S_{sp}: *1* – initial zinc white; *2* – after disintegration.

Investigation of the protector properties of cushion and rubber conveyor belts showed that changes in the dispersion degree of zinc white do not affect the rate of compositions vulcanization, i.e. the rate of formation ACV reactions. Disintegration of less than 30 microns led to a reduction of physical and mechanical indices of the rubbers being investigated that is likely to explain qualitative shift of ACV reactions from heterogeneous to homogeneous type. Considering that zinc oxide is not a molecular crystal, and it can not form with the sulfur and accelerators eutectic mixtures and solid solutions of [1, 6], and in the process of preparing the rubber composition is reacts first with fatty acid, it was studied the mechanism of ACV formation and space network rubber structure in the modification of zinc white when fusing zinc oxide with stearic acid at 70–100° in 24–72 hrs.

Features of changes in the compositions structure and their components, caused by differences in the modification conditions containing zinc white, were evaluated quantitatively and qualitatively in the study of the properties of mixtures and physical-mechanical properties of the vulcanizates. Properties of the compositions containing vulcanization activators in the form of alloys are shown in Table 4.

Table 4

Properties of rubber mixtures and rubbers based on SKI-3 with zinc white of "BCOM" grade

Indices	Mixture of ZnO and stearin	Alloy, 70°C		Alloy, 110°C	
		24 hrs	72 hrs	24 hrs	72 hrs
M_v, conv. units.	50.4	54.6	42.0	50.4	44.1
M_{min}, H dm	5.2	7.5	3.5	7.8	3.2
M_{max}, H dm	29.2	28.0	20.6	29.3	20.1
M_{90}, H dm	26.8	26.0	18.9	27.2	18.4
τ_{90}, min	1.7	1.7	1.7	1.7	1.9
$S_{fr.}$, %	0.24	0.25	0.17	0.24	0.10
n_{ef}· 10^{-19}, sm^{-3}	7.4	7.1	5.1	7.2	5.9
M_{300}, MPa	13.9	13.5	7.4	13.0	8.1
f_p,MPa	22.0	21.0	13.5	17.1	14.0
ε, %	460	445	437	460	423
B, kN/m	66.6	31.0	12.1	46.8	15.8
E, %	37	36	32	34	30
H_A, conv. units.	61	59	61	61	65
N, thousands of cycles	9.4	10.6	13.2	8.9	10.7

Analysis showed that the viscosity of the rubber mixtures based on rubber SKI-3 has tendency to decrease with fusion time increasing irrespective of the temperature of the process. An increase of vulcanization activity of zinc white with a reduced content of the basic substance when using the latter in alloys and improvement of the vulcanizates quality were defined.

The established fact of improving rubber strength indicators is associated with the formation (during preparation of the alloy, and the vulcanization process beginning) of intermediate complexes of optimum structure and activity, resulting in further (at the latter stages of vulcanization) effective use of sulfur.

General analysis of the experimental data allowed us to determine the time of mechanical action on the system, providing controlled modification of zinc white. The found similarities in the nature of changes in the basic properties of the compositions with modified in various ways zinc white allowed us to hypothesize the existence of ACV "precursors", representing complexes with one or more fragments of the fatty acid. The number of fragments of fatty acid is determined by the pretreatment time of the system "zinc oxide: stearic acid" and, respectively, the degree of chemical transformations of the components in them.

As a result of crosslinking in these systems, the optimal network structure is formed providing the best technical properties of the vulcanizates.

Conclusion. These experiments allow clarifying the interaction mechanism of the vulcanizing group components in the presence of various activators and systems, in the course of ACV formation, and assess the possibility of using modified zinc white with a reduced content of useful substance.

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