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PROPERTIES OF MODEL RUBBER COMPOUNDS WITH DIFFERENT VULCANIZATION ACTIVATORS

Influence of various vulcanization activators on properties of unfilled elastomeric compositions based on synthetic polyisoprene and oil-extended butadiene-styrene rubbers is investigated. Plasto-elastic and relaxation properties, and also scorching resistance and kinetics of curing of rubber mixes with traditional and composite vulcanization activators are defined. As the composite vulcanization activator “Vulkativ-FC” was used. Its feature is the lowered content of zinc oxide and presence in the composition saturated fatty acids. The correlation of elastic and strength properties of vulcanizates with type and containing of the applied activator is established.

Introduction. Vulcanization of rubber compounds based on unsaturated rubbers by sulfur and accelerators without activators makes it impossible to obtain the rubber with necessary complex of technical properties. The use of activators with accelerators allows to influence not only technological process of vulcanization, but also the structure of the rubber. In addition to a significant increase in the rate of cross-linking in the main period with maintaining or increasing of the induction period, an increase in the crosslinking density of the vulcanizate is observed, a decrease of sulphidity of crosslinks increases the resistance of rubber to elevated temperatures [1].

Activators are both inorganic and organic compounds that are used to activate fully effective and organic accelerators. Among the inorganic activators most commonly zinc oxide is used, (lead oxides and magnesium are also used, but much less frequently), and among organic activators – stearic acid [2–3].

Just while manufacturing sulfur compounds, accelerators, and fatty acids are adsorbed on the surface of dispersed zinc oxide particles. In the result of the interaction of these components of the mixture with each other, on the one hand the actual vulcanizing agents (AVA) are formed, and the other – the salts of fatty acids, which are surface-active compounds (SAC) for the system. Dispersed particles, formed on the surface of zinc oxide, acquire kinetic stability, adsorbing molecules of SAC, and gradually dispersed (solubilized) in the mass of rubber. The surface layer of surfactant improves the compatibility of the actual vulcanizing agent with the rubber and promotes adsorption of rubber on the surface of particles dispersed AVA [4].

In this regard, an actual problem is the use of composites in the structure of rubber mixtures activators containing both a combination of primary and secondary activator. At the same time, deficiency of the zinc oxide and some of its negative impact on the environment requires the development of formulations of rubber mixtures containing a lower dose of the primary vulcanization activator.

Main part. The purpose of this work – to determine the effect of the composite vulcanization activator “Vulcativ-FC” with partial or complete replacement of zinc oxide on the technological and technical properties of model rubber compounds based on SKI-3 and SK(M)S-15 30 ARKM. Objects of the study were unfilled elastomeric composition comprising zinc oxide in pure form and in a ratio of 3 : 1, 1 : 1 и 1 : 3. The total dosage of vulcanization activators was 5,0 wt. h. 100 wt. h. of the rubber. The characteristic feature of the composite activator “Vulcativ-FC” is the reduced content of zinc oxide in the presence of saturated fatty acids, which enhance the effect of dispersing and activating (TU 2294 001–31273447–2010).

One of the most important methods for evaluation of technological properties of rubber compounds is to determine their Mooney viscosity [5].

Table 1 shows the results of a study of unfilled rubber mixtures on viscometer MV 2000.

Table 1

The Mooney viscosity of the unfilled rubber compounds

Activators of vulcanization	Rubber mixture based on / Mooney viscosity, Mooney cond. u.	
	SKI-3	SK(M)S-30 ARKM-15
Zinc oxide	8.1	28.2
Zinc oxide: “Vulcativ-FC” (3 : 1)	9.2	29.9
Zinc oxide: “Vulcativ-FC” (1 : 1)	8.7	30.8
Zinc oxide: “Vulcativ-FC” (1 : 3)	8.4	30.9
“Vulcativ-FC”	10.0	29.5

These data show that the replacement of zinc oxide by activator of vulcanization results in an increase of Mooney viscosity of rubber mixtures based on investigated rubbers. Thus, for the mixture based on the SRS-3, containing only zinc oxide, the viscosity index is 8.1 cond. u Mooney and for mixtures with predominant content of the new activator viscosity value in the Mooney is 10.0 conv. u Mooney. A similar relationship was revealed for the elastomeric compositions based on styrene butadiene rubber IC (M) 30-C-15 ARKM.

Determination of viscosity of rubber compounds on Mooney is not always sufficient to establish all the features of the processing of elastomeric compositions, so additional relaxation rates are applied. Specificity of rubber processing and rubber compounds are determined by their viscoelastic properties manifested in the development of highly elastic deformation, rising to a maximum and implementing structural stress relaxation [6].

Establishing of dependencies changes stress relaxation study elasto-dimensional on compositions of the composition of activators was held by viscometer MV 2000, which for a minute after stopping the rotor recorded evidence of residual torque at frequent intervals. On the base of these data, relaxation ratio (K_p) is calculated, which is a criterion for evaluating the processability of rubber and rubber compounds (Table 2).

Slope of the tangent to the graph of relaxation 1 second after stopping the rotor (tg α') or the slope of the relaxation in logarithmic coordinates (α), is a measure of the rate of relaxation. Particular synthesis, molecular weight distribution, branching, the average molecular weight, the microstructure of the polymer, filler content, size of particles, the additive content, the method mixing et al. may influence the slope of the relaxation curve [3, 6, 7].

From the table it is clear that at increase in the maintenance of the new activator in elastomeric compounds on the basis of SK(M)S-30 ARKM-15 relaxation coefficient practically doesn't change (distinction for the compositions containing oxide of zinc and “Vulcativ-FC” makes about 1%). At the same time for rubber mixes on the basis of SKI-3 it is revealed that application in an individual type of the composite activator promotes simplification of the relaxation processes proceeding in an elastomeric matrix. So, value of coefficient of a relaxation for the rubber mix containing the industrial activator of curing makes 79.0%, and for mix with the studied activator Kr = 84.0%. Change of a tangent of angle of an inclination of a curve relaxation also testifies to increase in speed of a relaxation of tension. In this case for composition with tg zinc oxide α′ = –1.158, and for mix with the composite activator – 1.217.

The analysis of the obtained data allows to assume that the insignificant increase in viscosity according to Mooney doesn't lead rubber mixes on the basis of SKI-3 and SK(M)S-30 ARKM-15 at introduction of the Vulcativ-FC activator to deterioration of a processability of elastomeric compositions as it isn't observed considerable change of the relaxation indicators characterizing specific features of technological properties of rubbers and rubber mixes.

When processing elastomeric compositions the important characteristic is resistance of rubber mixes to premature vulcanization or a skorching. The size of the induction period depends on composition of mix and the vulcanizing system, temperature parameters of technological processes, and also the modes of mechanical loading. For a quantitative assessment of tendency of rubber mixes to semivulcanization indicators of the beginning (t5) and speed of semivulcanization (Δt) are used [8]. Results of researches of tendency to premature semivulcanization of the elastomeric compositions containing various activators of curing are given in Table 3. On the basis of the received results it is revealed that use of the composite activator of curing as a part of elastomeric compositions promotes increase of resistance to semivulcanization of rubber mixes. It should be noted that for the rubber mixes on the basis of SKI-3 containing various combinations of activators, change of speed of semivulcanization is insignificant in comparison with composition on the basis of SK(M)S-30 ARKM-15. In this case the major factor reducing resistance of rubber mixes to semivulcanization is the polymer nature. Synthetic isoprene rubbers of the SKI-3 type have big not limitation in comparison with butadiene–styrene rubbers that, in the turn, promotes increase in speed of sewing together of macromolecules of rubber. At the same time results of researches showed that with increase in the maintenance of the “Vulcativ-FC” activator as a part of rubber mixes on the basis of SK(M)S-30 ARKM-15 the speed of semivulcanization decreases by 1.2–1.5 times.

Such nature of change of properties of compositions probably is connected with processes of education of the valid agent of curing in which accelerators and activators of curing participate the vulcanizing agent. Because the content of zinc in the composite activator is less, than when using only than zinc oxide, and also in view of difficult composition of the studied ingredient, it is possible that at a temperature of carrying out test the speed of interaction of all components of the vulcanizing system is less, than in case of use of traditional activators of vulcanization.

Table 2

Indicators of a relaxation of tension of the studied rubber mixes

Activators of vulcanization	Rubber mix on a basis / Indicators of a relaxation of rubber mixes			
	SKI-3		SK(M)S-30 ARKM-15	
	tg α´	K_r, %	tg α´	K_r, %
Zinc oxid	–1.158	79.0	–0.754	55.3
Zinc oxide: “Vulcativ-FC” (3 : 1)	–1.182	79.1	–0.688	54.8
Zinc oxide: “Vulcativ-FC” (1 : 1)	–1.206	80.1	–0.644	54.7
Zinc oxide: “Vulcativ-FC” (1 : 3)	–1.201	79.6	–0.667	54.4
“Vulcativ-FC”	–1.217	84.0	–0.657	54.3

Table 3

Tendency to semivulcanization of the studied rubber mixes

Vulcanization activators	Rubber mix on a basis / Indicators of a relaxation of rubber mixes			
	SKI-3		SK(M)S-30 ARKM-15	
	tg α´	K_r, %	tg α´	K_r, %
Zinc oxide	–1.158	79.0	–0.754	55.3
Zinc oxide: “Vulcativ-FC” (3 : 1)	–1.182	79.1	–0.688	54.8
Zinc oxide: “Vulcativ-FC” (1 : 1)	–1.206	80.1	–0.644	54.7
Zinc oxide: “Vulcativ-FC” (1 : 3)	–1.201	79.6	–0.667	54.4
“Vulcativ-FC”	–1.217	84.0	–0.657	54.3

Together with the main process of formation of cross connections as a result of interactions of polymer with the vulcanizing agent the other collateral processes occured cyclizations and modifications of polymeric chains, regroupings of the communications of the formed vulcanization connections, thermal and oxidizing destruction of chains of polymer and the vulcanization connection [2].

Vulcanization is the finishing process of production of rubber products in many respects defining their behavior at operation [6]. Determination of kinetic parameters of curing allows to estimate influence of various ingredients on change of properties of elastomeric compositions in the course of formation of a spatial grid of a vulcanizate.

Results of research of kinetics of vulcanization of rubber mixes are given in Table 4.

Results of researches showed that at introduction of the composite activator to rubber mixes on the basis of SKI-3 in the ratio zinc oxide: “Vulcativ-FC” 3 : 1 and 1: 1 it is practically not observed changes of kinetics of curing. When using the new activator in an individual look as a part of elastomeric compositions optimum timecuring it is reduced in comparison with the rubber mix containing zinc oxide by 1.17 times. It is known [3] that oxide of zinc shows the greatest activity of interaction with components of the vulcanizing system, being in a soluble form, in the form of salts of fatty acids. Because in composite the curing activator oxide of zinc is together with fatty saturated acids, probably it and promotes transition at a zinc oxide curing temperature to the soluble form providing higher speed of process of structuring.

For mixes on the basis of SK(M)S-30 ARKM-15 similar dependence of change of kinetic parameters of curing, as for mixes on the basis of polyisoprenes is observed at introduction of a combination of activators in the same ratios. However at further increase in the maintenance of “Vulcativ-FC” in rubber mix optimum time of curing increases (by 1.04–1.07 times) a little and decrease in speed of curing is observed. In this case reduction of the content of oxide of zinc as a part of elastomeric composition leads to structuring process delay that is perhaps connected, first of all, with low-fullness of rubber and features of interaction of the components which are a part of the vulcanizing system, namely accelerators and activators of curing.

Activators of curing have impact not only on kinetics of curing of rubber mixes, but also on elastic and strength properties of rubbers due to change of density of a stitching of a vulcanizate and sulfidity of cross communications [1]. The main elastic and strength indicators of the studied rubbers are given in Table 5.

From the table it is visible that the increase in the contents as a part of rubber mixes on the basis of the studied rubbers of the new composite activator leads to decrease in conditional durability at stretching of rubbers. Thus it should be noted that in case of introduction of a combination zinc oxide: “Vulcativ-FC” in ratios 3 : 1 and 1 : 1 value of this indicator is in limits of an error of admissible GOST 270–75 [9]. For vulcanizate on the basis of SKI-3 improvement of elastic properties is revealed at application of “Vulcativ-FC” So, for rubbers with zinc oxide the indicator of relative lengthening at a gap is equal 890%, and for rubber with the studied activator – 980%.

Table 4

Optimum time of vulcanization (t_{90}) and speed of vulcanization (*tRh*) the studied rubber mixes

Activators of vulcanization	Rubber mix on a basis			
	SKI-3		SK(M)S-30 ARKM-15	
	t_{90}, min	tRh, min^{-1}	t_{90}, min	tRh, min^{-1}
Zinc oxide	14.50	1.48	45.15	0.70
Zinc oxide: “Vulcativ-FC” (3 : 1)	14.53	1.49	43.23	0.73
Zinc oxide: “Vulcativ-FC” (1 : 1)	14.54	1.47	44.83	0.65
Zinc oxide: “Vulcativ-FC” (1 : 3)	13.98	1.52	47.11	0.45
“Vulcativ-FC”	12.39	1.43	48.18	0.43

Table 5

Conditional durability at stretching (f_r) and relative lengthening at a gap (ε_p) the studied rubbers

Activators of vulcanization	Rubber mix on a basis			
	SKI-3		SK(M)S-30 ARKM-15	
	ε_r,%	f_r, MPa	ε_r,%	f_r, MPa
Zinc oxide	890	18.6	530	1.9
Zinc oxide: “Vulcativ-FC” (3 : 1)	900	17.9	490	1.8
OZinc oxide: “Vulcativ-FC” (1 : 1)	950	17.6	480	1.8
Zinc oxide: “Vulcativ-FC” (1 : 3)	965	16.5	480	1.5
“Vulcativ-FC”	980	14.5	500	1.5

At the same time for vulcanizate on the basis of SK(M)S-30 ARKM-15 it isn't established to accurate dependence of change of relative lengthening at a gap from the maintenance of the composite activator as a part of elastomeric composition. Such nature of change of properties of rubbers on a basis the used rubbers at introduction of “Vulcativ-FC” it is possibly caused not only features of a structure of an elastomeric matrix, but also distinctions of structure of the received vulcanizate, namely density of a cross stitching and energy of the formed communications between rubber macromolecules.

Conclusion. Thus, on the basis of the received results it is established that introduction of the composite activator of curing of “Vulcativ-FC” to rubber mixes on the basis of SKI-3 and SK(M)S-30 ARKM-15 in combinations with zinc oxide in the ratio 1 : 1 and 1 : 3 allows to receive the rubber mixes and vulcanizate which aren't conceding on properties to the elastomeric compositions containing the traditional activator – zinc oxide. Decrease in the maintenance of an expensive and ecologically not safe component as a part of rubber mixes can promote increase of profitability of production and reduction of environmental pollution.

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