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INFLUENCE OF MINERAL CARRIER TYPE IN THE STRUCTURE OF COMPOSITE VULCANIZATION ACTIVATOR ON THE PROPERTIES OF MOLDED RUBBER

Properties of the rubber mixtures and vulcanizates based on styrene-butadiene rubber composition in the presence of composite vulcanization activator were studied. Activators include zinc oxide, fatty acids and derivatives thereof, mineral fillers and organic fillers. It has been established that the use of new activator provides the desired cure rate. By the level of elastic and strength properties of prototypes to meet or exceed the standards of control. The possibility of reducing the dosage of vulcanization activators while maintaining the required level of vulcanization and physical-mechanical properties of molded rubber. Advantage of advanced products is the ability to reduce the content of environmentally hazardous zinc oxide formulations rubber goods and improved manufacturing techniques of rubber compounds through the use of non-dusting forms of ingredients.

Introduction. In modern elastomers technology conventional vulcanization activators are increasingly being replaced by composite ones which exhibit multifunctional action. They improve not only the cure characteristics of the compositions and elastic – strength properties of the vulcanizates, but facilitate the rubber compounds processing on the process equipment [1–2].

Vulcanization activators [3–5] in the form of mixed compositions including: zinc stearate and zinc oxide – Dispaktol-C; zinc stearate, zinc oxide, and fatty oxyethylated acids Dispaktol-MC were developed. Tekhnol CM a composite vulcanization activator was developed to replace the zinc oxide (white zinc). Its test in the hard rubber mixture based on styrene butadiene rubber has shown that it has the similar to zinc oxide following properties: equal kinetics of vulcanization, the degree of structuring, elastic strength properties under standard conditions, the resistance to thermal ageing and vulcanization reversion. We have analyzed the possibility of reducing the vulcanization cycle at using new dispersant activator – Dispraktol I, which is a complex salt of zinc, obtained in the eutectic melt of substances, and provides lower activation energy of rubber than conventional vulcanizing ingredients. Dispraktol I activating effect of results in increased cure rates and maximum torque, decrease in the viscosity of the rubber composition at its processing temperature (130°C) and at a temperature of vulcanization (155°C) and significantly reduces the chance of premature vulcanization.

At the same time enhancing the environmental safety requirements for rubber products both during the manufacturing process, and their operation has caused the widespread use in rubber compounding the ingredients based on natural raw materials [6–7]. The possibility of the creation of the activator-dispersion agent of rubber compositions based on a co-product of cotton seed oil production has been shown. Mixtures of higher fatty acids from various plants (rape, cotton and sunflower oils, and byproducts of fat and oil industries) were obtained as an alternative for technical stearin.

Main part. In the presence of accelerators and activators sulfur vulcanization is characterized by the occurrence of a number of consecutive and parallel reactions. Already in the production of rubber compounds sulfur accelerators and the fatty acid sorb on the surface of the activator (zinc oxide) and (or) a filler. As a result of these reactions there emerge actual curing agents which are gradually dispersing in the bulk rubber, and on the surface of dispersed particles there occurs adsorption of elastomeric rubber loops followed by formation of the spatial grid (dimensional grid) of the vulcanizate. Therefore, to achieve the desired duration and the degree of cure it is necessary to have in the rubber composition a sufficient amount of the zinc oxide particles capable of entering the effective interaction [8–9].

There are some ways to increase the effectiveness of the activator (zinc oxide) without increasing its dosage and under the conditions of providing interactions between components of sulfuric vulcanizing system and zinc oxide prior to their introduction into the rubber mixture [10]. We think that those methods obtaining composite vulcanization activators which have already considered the individual stages of formation of real vulcanization agents will be more effective.

Activating systems with different composition, method of preparation and the degree of component conversion comprising zinc oxide, fatty acids and their derivatives in various proportions, mineral component (diatomite, bentonite, shungite white soot, fine-disperse ash of sunflower husk) or an organic one (micro-cellulose, technical carbon) were used as the test objects.

The properties of silica used in the rubber industry, white soot BS-120 (GOST 18307–78), diatomite (content in wt.%: SiO_2 – 70–90; $A1_2O_3$ – 2.5–14.0; Fe_2O_3 – to 4; CaO – 0.4–0.6; MgO – 0.5–1.1); bentonite (content in wt %: SiO2 – 60.5; TiO_2 – 0.11; $A1_2O_3$ – 16.25; Fe2O3 – 1.70; FeO – 0.75; MgO – 2.38; MnO – 0.03; CaO – 1.75; Na_2O – 0.77) were studied when choosing a mineral carrier of composite vulcanization activators.

For comparison, spent sorbents of oil-fat production based on diatomite, bentonite, microcellulose, activated bentonite Tonsil were used as a carrier. Experienced vulcanization activators differed in outlet forms depending on the carrier used: paste, powder, agglomerated mass. The fundamental structure of the composite vulcanization activators is as follows: 18–20% of ZnO, 35–47% of fatty acids and their derivatives, 33–47% of fillers.

In the first step experienced activators of vulcanization were tested in a standard rubber mixture based on rubber SCS 30 ARC. In making the compositions we have noticed the improvement of their machinability when using experienced vulcanization activators, especially products based on microcellulose and bentonite. Analysis of technological and curing properties of rubber compounds and vulcanizates has shown that type of filler has little effect on the viscosity of the rubber compounds (Figure a), which is in the range of 68–70 conv. u, except for sample number 5, containing a vulcanization activator, based on bentonite.

It has been revealed that all investigated samples provide high speed of compositions vulcanization estimated by time of optimum achievement (Fig. b).

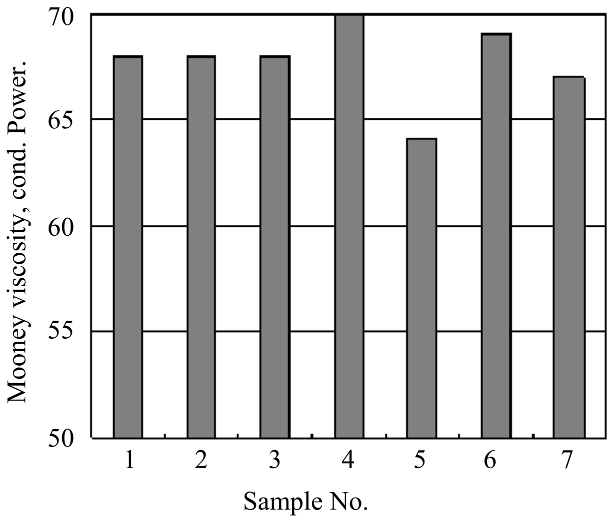
Activator of vulcanization using ash from sunflower husk as filler provides compositions with minimum time to achieve cure optimum that can be explained by the presence of alkali metal oxides (Ca, Mg) in filler, which activate the curing process additionally.

It should be noted that the rubber mixtures with this vulcanization activator may have an increased tendency to scorching.

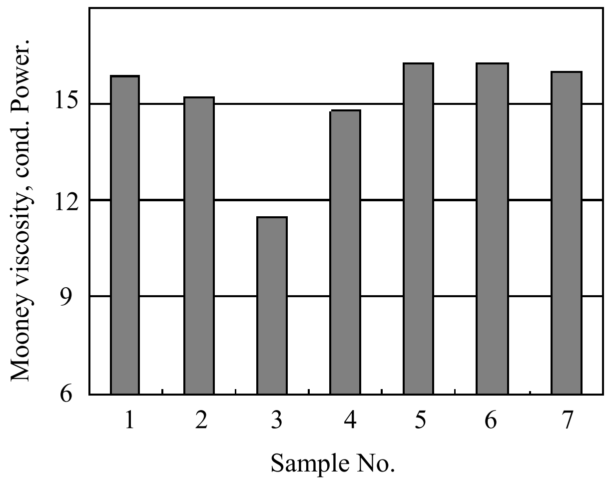
While studying the elastic and strength properties of rubbers with various vulcanization activators we have found that all samples meet the standards of control.

The improvement of strength parameters in the experimental rubbers compared with the norms of the standard: by 10–20% of conv. tensile strength, by 15–50% in tensile modulus has been noted.

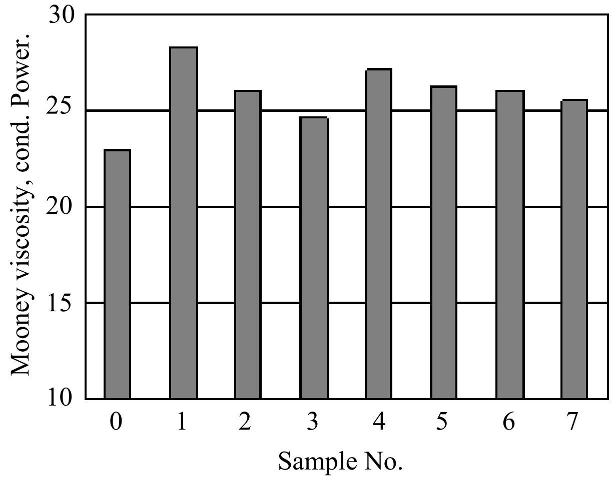
At the same time, the samples with vulcanization activators No. 3 and 4 showed reduced (400 vs. 420% according to standards) elongation at break that may be explained by some overvulcatization of compositions in the presence of these activators of vulcanization.



a



b



c

Rubber mixture viscosity (*a*), vulcanization optimum (*b*), conv. Tensile strength (*c*) of samples containing vulcanization activators based on different fillers: *1* – shungite; *2* – micro-cellulose; *3* – ash of burnt sun flower husk ; *4* – technical carbon; *5* – bentonite; *6* – white soot; *7* – diatomite; *0* – control standards (ac.to ASTM D 3185)

Sample No. 1 on the basis of shungite is of particular interest.

According to the data [11] the use in the formulation of rubber of a fine dispersed shungite powder in the amount up to 10 wt. h. activates the vulcanization process.

At the same time there is a decrease of strength properties of vulcanizates and an increase in relative elongation at break due to increased sorption on the developed shungite surface of rubber compounds ingredients and vulcanizing agents. This prevents the formation of a sufficiently thick and strong vulcanite network and, as a consequence, lowers the strength characteristics. In our case application of shungite powder as a synthesis carrier of the activating complex on its surface provides high strength characteristics of the rubber at stable high speed of vulcanization. This provides a convenient outlet shape of vulcanization activator as non-dusting powder or easily destroyed agglomerates depending on shungite dosage.

Data obtained by using waste sorbents of fat and oil production as the basis of experimental vulcanization activators (Table 1) indicated the possibility and feasibility of their use for these purposes. Rubber compounds based on activators had satisfactory technological properties, showed a high rate of vulcanization and rubbers were characterized by a high level of physical and mechanical properties.

Experienced vulcanization activators were tested in the formulation of molded rubber goods on the basis of the rubber SCS-30ARKM-15. The effect of activators on rubber properties at full and partial replacement of zinc oxide and stearic acids, including a decrease in the proportion of the activator of vulcanization of the rubber composition formulation was studied. The data obtained in the study of the kinetics of rubber vulcanization and elastic and strength properties are listed in Table 2.

The test results of composite curing activators in serial rubbers of molded rubber goods based on butadiene-styrene rubber showed improved technological properties and vulcanization characteristics of rubber compounds, high resistance to scorch, improved elastic-strength and dynamic properties.

Table 1

The influence of waste sorbent type in the activator composition on the properties of rubber mixtures and vulcanizates based on SCS-30ARKM

The name of parameters		Standard (ASTM D 3185)	Sample number, sorbent type		
			No 8 Microcellulose	No 9 Bentonite	No 10 Tonsil
Mooney viscosity MB (1 + 4) 100ºC, conv. unit.		–	64.0	69.0	70.0
Monsanto Rheometry, 100ºC	M_L, dH · m	–	9.00	9.00	9.00
	M_n, dH · m	–	35.50	37.00	36.00
	$t_{s, min}$	–	1.88	1.93	1.88
	$t_{90, min}$	–	14.50	16.25	15.25
	v, min^{-1}	–	7.92	6.98	7.48
Conv. stress at 300%-elongation, MPa		Not less 13.3	16.1	17.0	15.5
Conv. Tensile strength, MPa		Not less 23.0	25.1	25.4	26.0
Relative elongation at break, %		Not less 420	465	447	504
Relative residual elongation, %		–	12	10	16

Table 2

***Test results of vulcanization activator based on spent bentonite (sample No. 9) in the formulations of molded RTP**

Parameters name		Sample numbers			
		Serial	Zinc oxide and stearine replacement by experimental vulcanization activator		
			50%	75%	100%
viscosity ML (1 + 4) 100^{o}C, conv. unit		46	51	53	55
Monsanto Rheometry, 155ºC	M_{min}, dH · м	7.5	7.0	7.5	8.0
	M_{max}, dH · м	23.5	21.0	20.0	20.5
	M_{90}, dH · м	21.9	19.5	18.8	19.3
	τ_s, min	7.0	10.5	7.5	8.0
	τ_{90},min	16.3	19.3	14.8	15.0
	$\Delta\tau$, min^{-1}	10.7	10.8	14.7	14.3
Conv. Tensile strength, MPa		4.10	5.40	5.68	4.54
Relative elongation %		425	470	445	340
residual elongation, %		12	14	14	12

*Composition of vulcanizing group, mass h.: sulfur – 2.0; sulfonamide C – 1.5;zinc white – 5.0;technical stearine – 2.0.

Generalization of experimental data on the research of experimental products in the serial rubber mixtures of molded rubber goods allowed to optimize the manufacturing process and dosage of vulcanization activators.

Conclusion. It is shown that the utilization of the new composite vulcanization activator provides the desired cure rate. The elastic strength properties of experimental samples meet the standards of control.

The possibility of reducing the dosage of vulcanization activators from 6.5 to 3.5 mass per hour maintaining the required level of vulcanization and physical-mechanical parameters of molded rubbers has been found.

Advantage of advanced products is the ability to reduce the content of environmentally hazardous zinc oxide in the formulations of molded rubber goods by replacing traditionally used zinc oxide with experimental products.

The positive effect is also the improved manufacturing techniques due to the use of non-dusting forms of ingredients.

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