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MODIFICATION OF SYNTHETIC RUBBERS TO IMPROVE THE ELASTIC AND STRENGTH PROPERTIES OF THE ELASTOMERIC COMPOSITIONS

The effect of carbon black P803 different manufacturers on the complex properties of rubber for the manufacture of molded rubber products. Pick up objects and methods. As objects of study chosen rubber mixture based on a combination of rubber SKI-3 and SKD, and rubber compounds based on natural rubber. Found that the use of carbon black P803 from different manufacturers have different effects on the viscosity index, resistance to aging under static compressive strain on the kinetics of vulcanization of rubber mixtures in which it was determined that the most extensive period of induction are rubber compounds using carbon black products P803 JSC "Tuymazytechcarbon" and rubber mixture with its addition have low curing rate due to a low pH aqueous suspensions. The studies show that the carbon black producer JSC "Ivanovo techcarbon and rubber" having a high pH value of an aqueous suspension, the rate of vulcanization of the rubber composition is quite high, as well as an increase in pH increases the activity of the carbon black at the time of mixing and causes premature vulcanization of rubber mixtures. The results obtained allowed to propose a rubber composition based on a combination of rubber SKI-3 and SKD with the addition of carbon black P803 producer of JSC "Tuymazytechcarbon" for the production of shock absorbers, which can be manufactured by JSC "Belarus'rezinotekhnika" without changing the production scheme of molded rubber products.

Key words: carbon black, rubber, rubber compound, physical and mechanical properties.

Introduction. The development of science and technology has led to the fact that due to the unique combination of properties rubber goods (RG) became, in many cases, irreplaceable materials [1]. Rubber goods are classified according to operational purposes, conditions of use (temperature, environment, pressure, etc.), structure (rubber, rubber-metal, rubber-fabric, solid, hollow, spongy), manufacturing technique, and so on.

In foreign industry rubber goods are developed and implemented in advanced technological processes and equipment. New materials that improve product durability are mastered. New technological processes developed and used in rubber goods industry are aimed at the intensification of production, reduction of material costs, reduced energy costs, and improved product quality. The use of the active compounds as ingredients of elastomeric compositions allows to effectively control the characteristics of rubber mixtures and their vulcanizates, which leads to improving the quality of various rubber products. Different fillers have a great influence on the properties of rubber compounds and finished products, so the correct selection of a filler with the desired characteristics is relevant.

Main part. The aim of this study is to develop formulations of rubber compounds for the manufacture on their basis of molded rubber goods, workable at ambient temperatures from –60 to 55°C. Table 1 presents a rubber compound formulation based on the combination of isoprene and butadiene rubber.

Table 1

Rubber compound formulation based on the combination of butadiene and isoprene rubber

Names of ingredients and parameters	Dosage, pts. wt
Butadiene rubber	75.0
Isoprene rubber	25.0
Technical sulfur	3.0
Sulfenamide	0.8
Zink white	20.0
Diafen	2.0
Protective wax	1.0
Carbon black P803	60.0
Carbon black P234	20.0
Stearinic acid	2.0
Total	208.8

Table 2 presents a rubber compound formulation based on natural rubber.

Isoprene rubber is similar in its properties with NR, but has lower cohesive strength and adhesion of rubber compounds. At the same time it has higher fluidity, which facilitates the processing by moulding or injection moulding [2].

Stereoregular butadiene rubber has a high frost and abrasion resistance. Butadiene rubber compounds are poorly processed by extrusion and calendering. To improve these properties, isoprene rubber add NR are added [2]. The combination of isoprene and butadiene rubbers in a ratio of 75 : 25 provides a rubber with a higher set of properties: wear resistance, resistance to multiple defor-

mations, elasticity [3]. Natural rubber is well combined with the ingredients and the obtained rubber compounds are characterized by high technological properties: they have good calendering and extrusion properties, they have low shrinkage and good framing. All these properties are determined by high cohesive strength and high adhesion of NR. As to adhesion, NR surpasses all synthetic rubbers [3]. NR rubbers have high abrasion resistance.

Table 2

Rubber compound formulation based on natural rubber (NR)

Names of ingredients and parameters	Dosage, pts. wt, and indicators value
Natural rubber	100.0
Technical sulfur	2.0
Sulfenamide	0.8
Zink white	5.0
Diafen	2.0
Protective wax	1.0
Carbon black P803	30.0
Bitumen	3.0
Stearinic acid	1.0
Total	144.8

Rubber reinforcing materials (carbon black P234 and P803) are added into the rubber compound. These materials increase the rate of vulcanization, impart rubbers a high wear resistance, strength and tear resistance, improve mixture processing and reduce shrinkage. Carbon black P803 is also introduced to reduce the formulation cost [4]. Introduction of the carbon black P803 improves the technical properties of the mixtures, increases the viscosity of the rubber compounds, reduces shrinkage and improves the quality of parts [2]. One of the ways to modify the properties of polymeric materials is their filling, i.e. introduction of solid, liquid and gaseous fillers, which are uniformly distributed in the volume of the resulting composition, and form a distinct interface with the polymer medium [5].

The effect of the carbon black P 803 (the main manufacturers are the towns of Stakhanov, Ivanovo, Tuymazy) on the complex of rubber properties for the manufacture of rubber products, workable at ambient temperatures from –60 to 55°C has been studied. Test samples of elastomeric compositions were milled at a constant rolls cooling using LM 320 160/160; vulcanization was carried out in a hydraulic press at a temperature (143 ± 3)°C. Vulcanization parameters with reference to the rheological curves (obtained on rheometer "Alpha Technologies") have been determined to evaluate the properties of rubber. Determination of the viscosity of rubber compounds and their tendency to pre-vulcanization on the rotating viscosimeter was carried out on the Mooney viscosimeter MV 2000 according to GOST 10722–76. Physical and mechanical sample characteristics were determined using GOST techniques, corresponding to these characteristics: nominal tensile strength, nominal elongation at break, nominal residual elongation after break (GOST 270–75); tear resistance (GOST 262–93); Shore A hardness (GOST 363–75). Determination of rubber resistance to heat ageing was carried out in accordance with GOST 9.024–74. Determination of rubber resistance to light-and-ozone ageing was carried out according to rubber standards. Ozone resistance was estimated by the ageing time before the appearance of the first cracks visible to the naked eye, as well as by the ageing time before the destruction of the sample, temperature limit of rubber brittleness being determined according to GOST 7912–74.

In the development of rubber compounds for various purposes RG an important task is to find the balance between the processing properties of the compositions, that meet certain processing requirements, and physical and mechanical properties of rubber, affecting the performance properties of goods and the production efficiency [6].

Test results of rubber compounds on the Mooney viscosimeter MV 2000 are presented in Table 3.

Table 3

Test results of rubber compounds on the viscosimeter Mooney MV

Producer	Mooney viscosity, conv. u.	Scorching, min					
		t_5		t_{35}		Δt	
Isoprene and butadiene rubber compounds							
JSC "Tuymazytechcarbon"	72	36		42		6	
JSC "Ivanovo techcarbon and rubber"	80	11		15		4	
PJSC "Stakhanov Carbon Black Plant"	69–79	24		30	40	6	Non-vulcanized
Rubber compound based on natural rubber (NR)							
JSC "Tuymazytechcarbon"	52	25		30		5	
JSC "Ivanovo techcarbon and rubber"	47	17		21		4	
PJSC "Stakhanov Carbon Black Plant"	45–58	20	26	25	33	5	7

The use of the carbon black P803 by different producers affects the viscosity index in different ways. The data presented in Table 3 shows that the addition of the carbon black P803 (manufacturer – JSC "Tuymazytechcarbon") to the butadiene and isoprene rubber compounds results in the lower rubber compound viscosity than that of the rubber compound with the addition of carbon black produced by JSC "Ivanovo techcarbon and rubber". But the viscosity of the rubber compound is higher than that of the rubber compound with the addition of the carbon black manufactured by PJSC "Stakhanov Carbon Black Plant". And when adding the carbon black P803 (manufacturer – the town of Ivanovo) to the NR rubber compound, the rubber compound viscosity index is lower than that of the rubber compound added with carbon black manufactured by JSC "Tuymazytechcarbon" and PJSC "Stakhanov Carbon Black Plant".

This is probably due to the fact that the carbon black P803 produced by JSC "Tuymazytechcarbon", JSC "Ivanovo techcarbon and rubber", and PJSC "Stakhanov Carbon Black Plant" has different bulk density. At low values of the carbon black bulk density, the rubber compound is inclined to pre-vulcanization. And as can be seen from Fig. 1, the viscosity index of the rubber compound using carbon black P803 (manufacturer – the town of Stakhanov) has significant variations, probably due to the variance index of the carbon black bulk density both within the batch and among the batches (Fig. 2).

Fig. 3 shows hardness dependence on the carbon black type.

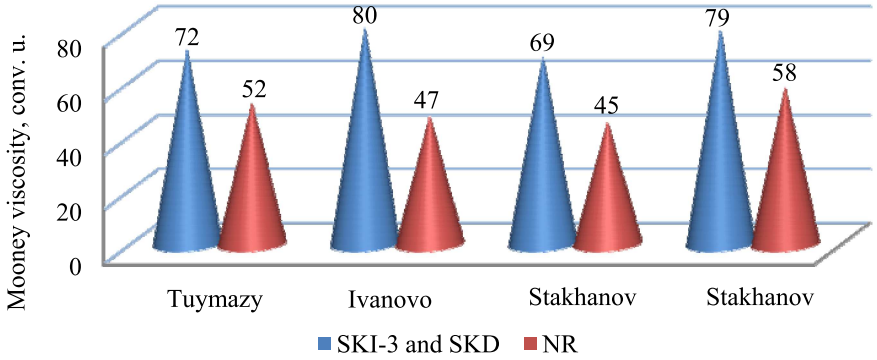

Fig. 1. Change of the isoprene, butadiene and NR rubber compound viscosity as a function of the applied carbon black

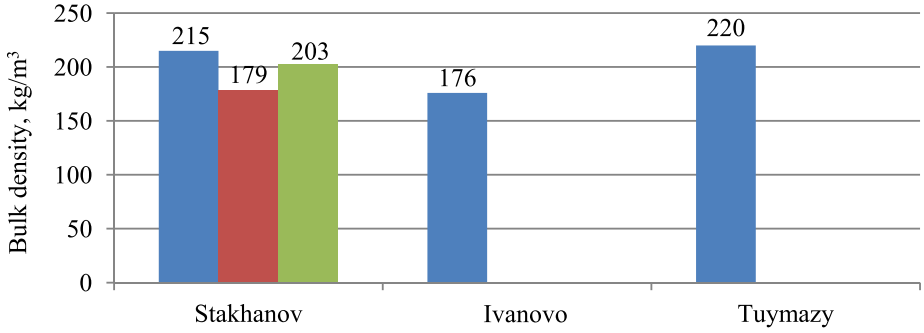

Fig. 2. The values of the carbon black bulk density by different producers

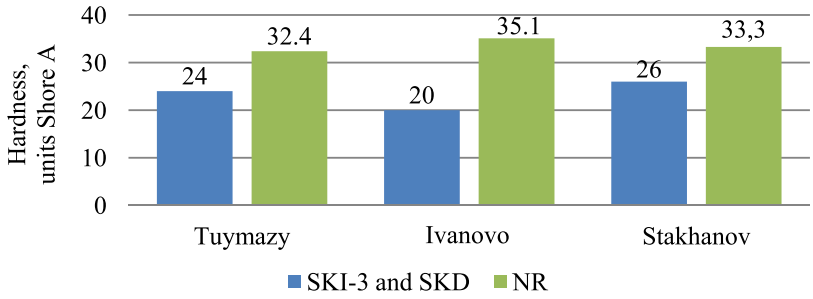

Fig. 3. Hardness dependence on the carbon black type

Rubber resistance to a destructive effect of mechanical stress characterizes its strength.

Stretching strains causing rubber rupture are the most dangerous. Therefore, determination of the strength properties of rubbers is carried out under tension exercised at a constant speed. The research results of physical and mechanical properties of the rubber compounds vulcanizates are shown in Table 4.

The introduction of carbon black should not have a significant impact on the change in strength characteristics and moreover to deteriorate them. As can be seen from Table 4, physical and mechanical properties of rubber compounds using carbon black P803 of different manufacturers have small differences that are associated with hardness indexes. The higher the hardness index, the higher is the value of the nominal and true strength (stress at break) and the lower is the elongation.

Rubber goods more often operate at high temperatures, so an integral part of our research was to study the effect of carbon black on the ageing resistance under static compressive strain.

With the introduction of the carbon black P803 (manufacturer – the town of Ivanovo) into a rubber compound based on the combination of isoprene and butadiene rubbers there is a decrease in the NCD index. While the use of the carbon black manufactured by the towns of Tuymazy and Stakhanov leads to an increase in this index (Fig. 4). At the same time rubber compound based on natural rubber with the carbon black manufactured by the town of Ivanovo has the highest NCD index, which in its turn highly depends on the hardness index. With the increase in hardness the NCD index value decreases.

Table 5 shows the results of investigation of the composition hardness.

Table 4

Physical and mechanical properties of rubber compounds vulcanizates

Manufacturer	Nominal tensile strength, MPa	Nominal elongation at break, %	Tear resistance, H/mm	Nominal compression set at 70°C during 24 h, %
Isoprene and butadiene rubber compound				
Tuymazy	14.8	440.0	59.0	24.0
Ivanovo	15.4	380.0	62.0	20.0
Stakhanov	15.0	400.0	60.0	26.0
NR rubber compound				
Tuymazy	25.5	620.0	54.0	32.4
Ivanovo	23.3	670.0	47.0	35.1
Stakhanov	24.3	640.0	48.0	33.3

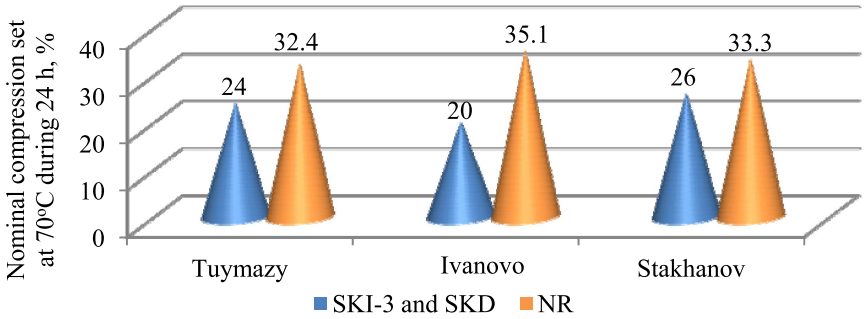

Fig. 4. Nominal compressive deformation change of the isoprene, butadiene and NR vulcanizate depending on the applied carbon black

Table 5

Hardness dependence on the applied carbon black

Parameters	Manufacturers		
	Tuymazy	Ivanovo	Stakhanov
Isoprene and butadiene rubber compound			
Hardness, units Shore A	71	74	58–70
Hardness in international units, units IRHD	70	72	59–72
NR rubber compound			
Hardness, units Shore A	50	45	42–51
Hardness in international units, units IRHD	49	44	40–49

Table 6

Carbon black P803 parameters

Parameter	GOST 7885–86 norm	Carbon black P803 actual parameters depending on the manufacturer		
		JSC "Tuymazytech-carbon"	JSC "Ivanovo-techcarbon and rubber"	PJSC "Stakhanov Carbon Black Plant"
Nominal specific surface area, m^2/g	14–18	19	17	18
Aqueous slurry	7.5–9.5	7.5	8.6	8.1
Bulk density, kg/m^3	Not rated	215	176	182–220
Mass fraction of losses (105°C), %	Not above than 0.50	0.17	0.21	0.26
Mass fraction of residue on the sieve, %	Not above than 0.01	Absent	Absent	Absent

Addition of the carbon black produced by different manufacturers into elastomeric compositions has virtually no effect on their hardness (Table 5). However, the addition of the carbon black produced in Stahanov leads to the hardness index variance in the range of 58 to 70 units, probably due to the heterogeneity of the carbon black. Carbon black parameters such as the specific geometrical surface area (m^2/g), or dispersion, estimated by the average particle diameter; structural properties, estimated by the butyric number (ml/100 g of carbon black); pH and the energy surface activity – all this has a significant impact on the technology of manufacturing and processing of rubber compounds as well as on a number of technical properties of vulcanizates [5]. With the increase of the carbon black dispersion, the content of oxygen compounds on the particle surface grows, and pH decreases. With the decrease of dispersion – pH increases. The pH greatly influences the vulcanization parameters of rubber compounds and the rubber ageing. Decreasing pH lowers the rate of vulcanization and increases the rate of rubber ageing. On the other hand, the increase of pH enhances the carbon black activity already at the mixing stage and causes pre-vulcanization and scorching of rubber compounds.

To explain the carbon black impact on the technological processes of rubber production as well as on rubber compounds properties, the following parameters are used:

– rubber compound viscosity;

– rubber compounds scorching;

– the possibility of processing on the technological equipment;

– carbon black impact on the kinetics of rubber compounds [5].

Carbon black P803 characteristics are presented in Table 6.

Vulcanization characteristics and kinetic curves were obtained using a vibratory rheometer. Rheometric curves analysis has shown that rubber compounds added with the P803 carbon black (producer – the town of Tuymazy) have the widest induction period. At the same time they have a low vulcanization rate due to a low pH of aqueous slurry. It is seen that the vulcanization rate of a rubber compound is rather high at a high carbon black pH produced in the town of Ivanovo. The pH increase enhances the carbon black activity already at the mixing stage and causes pre-vulcanization of rubber compounds.

Having studied the rheometric curves we can note that the rubber compounds added with the carbon black (producer – the town of Stakhanov) have a significant parameters variance, probably due to its heterogeneity, which largely affects the technological process.

Based on the data obtained we can conclude that the combination of isoprene and butadiene rubber compound added with the P803 carbon black (producer – JSC "Tuymazytechcarbon") is the most suitable for the production of vibration insulators. Due to their properties these rubber compounds are considered to be the most suited for vibration insulation production.

Conclusion. Carbon black P803 (manufacturer – JSC "Tuymazytechcarbon") has a more stable complex of physical and chemical characteristics. Therefore, it is recommended to use this filler in an amount of 60.0 pts. wt for the manufacture of molded rubber goods on the basis of synthetic isoprene and butadiene rubber blend in the ratio 75 : 25.

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