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PROPERTIES OF ELASTOMERIC COMPOSITIONS WITH PLASTICIZERS BASED ON SECONDARY RAW MATERIALS

Currently, as plasticizers in the rubber industry are widely used petroleum oils, the most common of which are: PO-6 and I-20. Due to lack of oil, much attention is paid to the recycling of waste oils. The aim of the recycling is further use of the products in the industry. In this context, the influence of the products of recycling waste engine oil (DVCH-1 and DVCH-2) in comparison with industrial oils on the technological properties of unfilled elastomeric compositions was investigate. The elastomeric compositions were based on poly isoprene, oil-filled styrene-butadiene and ethylene-propylene rubbers. The plasticizers were manufactured by IOOO "DVCH-Menedzhment". They were a mixture of hydrocarbons, C_{16}–C_{20} and differ from each other in the content of linear and branched paraffins.

Plastic-elastic and vulcanization properties of rubber compounds with different plasticizers were defined. Plastic-elastic properties of rubber compounds on the shear disk viscometer MV2000 in accordance with GOST 10722–76 was carried out. Kinetics of vulcanization on the rheometer ODR2000 according to GOST 12535–84 was defined. The correlation of the investigated properties of rubber compounds with the type and quantitative content of the used plasticizer was given.

Key words: the rubber, the plasticizer, the Mooney viscosity, the kinetics of vulcanization, the rubber mixture, relaxation voltage.

Introduction. One of the polymers modification methods is plasticization. Its essence is to change the properties of polymers by introducing admixtures of low molecular weight substances – plasticizers changing the viscosity of the system, the flexibility of the molecules, the mobility of supramolecular structures. Plasticizers are introduced into polymers to improve their elasticity or flexibility in the processing and operation [1–2].

At present petroleum oils are widely used as plasticizers in the rubber industry, the most common of which are PN-6 and I-20. However, due to lack of petrochemicals, much attention is paid to waste oil processing for further use in industry products based on it.

Car oil plays an important role for vehicle motor and it must be replaced regularly. However, waste oil as a product of the chemical industry has a huge potential to pollute the environment [3]. During operation, there is an accumulation of oxidation products and admixtures in the oil as well as impurities, pollution reducing the quality of the lubricant. As oil is a valuable raw material, waste oil is collected and subjected to regeneration for its preservation and future use. [4] The company IOOO "DFS-Management", which mainly focuses on machine oil collection and recycling operates in the Republic of Belarus. Features of the system of waste and sub-standard oil products collection and storage allow ensuring the stable quality of the final product. First of all, at the stage of raw material collecting from suppliers oil is divided into groups depending on the origin and transported to a production base "DFS-Menedzhment" in tank trucks with separate compartments. Oils arrived at the base are analyzed on the basic properties and divided into categories as to test results Intermediate storage is carried out in tanks of 60 m^3. After establishing of oil properties in the filled reservoirs, the raw material is transferred to 1000 m^3 tanks, where its properties are finally leveled. The stock is then sent to the main processing plant for oil physical and chemical cleaning. The technology of cleaning is to remove the vast majority of metals, water and volatile hydrocarbons contained in the waste oil. Thus, the bulk of the products make base oils, which differ depending on the type of feedstock. This technology allows obtaining a product which is characterized by high stability of properties.

Main part. The aim of this work was to study the effect of products obtained from waste machine oil (DFS-1, DFS-2) compared with industrial oils (I-20 and PN-6) on the elastomeric composition technological properties based on synthetic polyisoprene (SKI-3) oil-extended butadiene-styrene (SKMS 30ARKM-15) and ethylene-propylene (EPDM) rubbers. The plasticizers being investigated produced by the IOOO "DFS-Management" are a mixture of hydrocarbons C_{16}–C_{20} (TU BY 690656219.003-2014). The cleaning oil process includes several stages: the additives removal by physical-chemical treatment, separation of the main part of the emulsified water; complete removal of water and volatile fractions; filtering product. The regenerated mixture of hydrocarbons, supplied as a plasticizer, has physico-chemical characteristics presented in Table 1.

Table 1

Physical and chemical characteristics of researched plasticizer

Properties	Indicators
Flash temperature, °C	Not less 190
Content of mechanical impurities with particle size less than 1 micron, %	0.02
Water content, ppm	Not more 250
Sulfur content, %	Not more 0.6
Pour point temperature, °C	Not higher –21
Kinematic viscosity at 40°C, cSt	25–40
Density at 20°C, g/cm^3	0.85–0.90

Plasticizers RF-1 and DFS-2 under test differ in the content of linear and branched paraffins. All additives were introduced into the elastomeric matrix at a dosage of 2.5; 5.0; 7.5 and 10.0 pts. wt at 100.0 pts. wt of rubber. A comparative sample was rubber compound without plasticizers.

Determination of reservoir elastic properties of rubber compounds was carried out on shear disc viscometer MV2000 in compliance with GOST 10722–76 [4], and the study of the vulcanization kinetics – on rheometer according to GOST 12535–84 ODR2000 [5]. Indexes of rubber mixture viscosity is one of the most important characteristics of the rheological properties, as well as determines the dynamics of the working process, serves as a measure of the force that must be applied to the material for its course at a given speed at a particular stage of the process [6]. Fig. 1–3 shows the dependence of the Mooney viscosity of rubber compounds on the dosage of plasticizers.

Determination Mooney viscosity of rubber mixtures based on SRS-3 and EPDM showed that introducing of the test plasticizer DFS-1 has a more significant effect on Mooney viscosity, as compared to elastomeric compositions not containing plasticizers. Thus, the Mooney viscosity of rubber compounds based on SRS-3 and EPDM containing no plasticizer is and 15.7 75.0 conv. u Mooney, and when introduced 2.5 pts. wt DFS-1 is 7.6 and 61.6 conv. u. Mooney respectively.

The study of rubber mixtures based on SKMS 30 ARKM-15 showed, that the use of DFS 1DFS-2 as plasticizers contributes to a significant reduction in the Mooney viscosity elastomeric compositions as compared to rubber mixtures containing widely used industrial plasticizers-oils PN-6 and I-20.

The introduction of plasticizers contributes to a more even distribution of the ingredients in the rubber compound, reducing warming by mixing, thereby preventing in a certain extent premature mixture vulcanization, reduces power consumption for the production and further processing of rubber compounds.

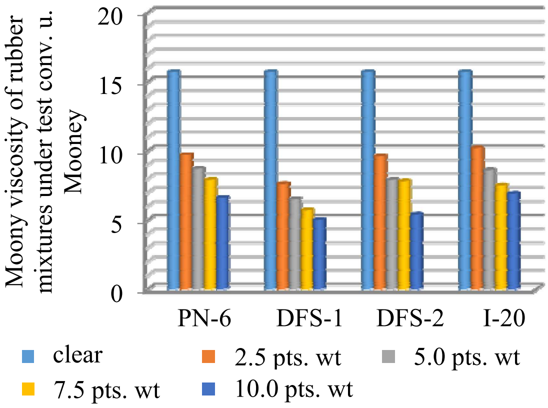

Fig. 1. Moony viscosity of rubber mixtures based on SRS-3

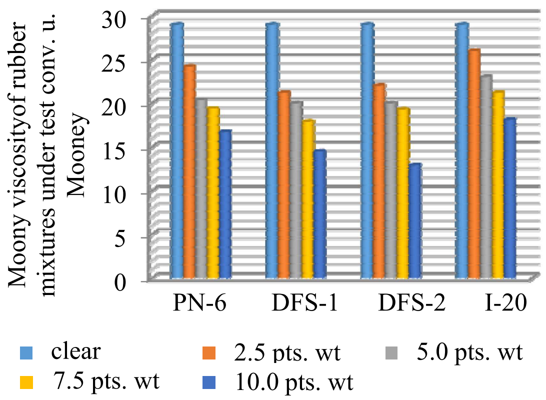

Fig. 2. The Mooney viscosity of rubber mixtures SKMS-based 30ARKM-15

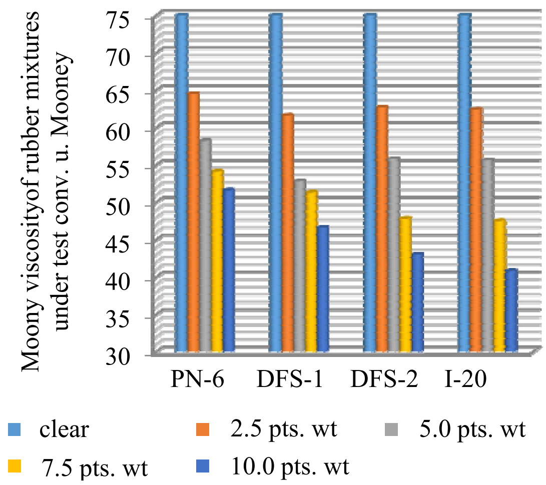

Fig. 3. The Mooney viscosity of rubber mixtures based on EPDM

Determination of Mooney viscosity of rubber compounds is not always sufficient to establish all the features of the elastomeric composition processing, so extra relaxation parameters are used. Specificity of rubber and rubber compounds processing is determined by their viscoelastic properties, manifested in the development of high elasticity deformation, rising to a maximum and implementing structural relaxation of tensions [7].

Dependencies of stress relaxation change of the elastomeric compositions under study on the dosage of entered plasticizers were established with viscometer MV2000, which within a minute after the rotor stopping recorded residual torque moment at frequent intervals. Based on the obtained data the relaxation factor (Kd), was calculated. It is one of the criteria for evaluating the processability of rubber and rubber compounds (Table 2).

The slope angle tangent to the graph of relaxation in 1 second after the rotor stopping (tgα'), or the slope of the relaxation curve in logarithmic coordinates (α), is a measure of the relaxation rate. The slope relaxation curve can be influenced by the polymerization process, molecular weight distribution, branching, the average molecular weight, microstructure, filler content, their particle size, the plasticizers content , additives, mixing method, and others [7].

As can be seen from the presented data, the plasticizers introduction in the elastomeric matrix based on SKI-3 contributes to significant relief of relaxation processes (after introduction of 2.5 pts. wt plasticizers the relaxation coefficient increases by 51–68%).

The use of oil PN-6 and researched plasticizer DFS-1 makes the greatest influence on this characteristic Thus, relaxation ratio of rubber mixture containing no additives, is 48.41%, while introducing of 2.5 pts. wt PN-6 and DFS-1 increases it to 81.54 and 77.63% respectively. The introduction of plasticizers not only reliefs relaxation processes but also significantly reduces the stress relaxation rate.

The Study of rubber mixtures based on SKMS 30 ARKM-15 and EPDM showed that administration of the test plasticizers DFS-1 and DFS-2 in the elastomeric matrix results in a significant increase in the stress relaxation coefficient compared to mixtures containing industrial plasticizers – PN-6 and I-20. Thus, relaxation ratio of rubber compounds based on SKMS 30 ARKM-15 containing 2.5 pts. wt oil PN-6 and I-20 is 53.18 and 55.37%, while introducing 2.5 pts. wt DFS-1 and DFS-2 increases it to 56.13 and 57.73% respectively. The changes in the slope angle tangent of the relaxation curve indicate increasing the stress relaxation rate. Thus, tgα' of rubber mixture based on EPDM containing no additives is –0.640, and when administered 2.5 pts. wt plasticizers DFS-1 and DFS-2, it increases to 0.645 and –0.660, respectively.

Such behavior of the rubber compounds properties is probably connected with differences in elastomeric matrix structure and, as a consequence, in the difference of their interaction with plasticizes.

Vulcanization is a complex of physical and chemical processes occurring in the rubber compound, the main of which is joining (cross-linking) of rubber macromolecules with various chemical bonds of different energy and nature into spatial vulcanization grid.

Table 2

Indicators of stress relaxation of rubber compounds being studied

Name of introduced ingredient	Amount of introduced ingredient, pts. wt	Rubber mixture based / indicators of rubber mixture relaxation					
		SRS-3		SKMS 30 ARKM-15		EPDM	
		tgα′	K_p, %	tgα′	K_p, %	tgα′	K_p, %
Without additive (Clear)	–	–1.581	48.41	–0.522	52.07	–0.640	48.00
Oil PN-6	2.5	–0.428	81.54	–0.608	53.18	–0.618	53.18
	5.0	–0.480	82.76	–0.591	53.48	–0.646	53.44
	7.5	–0.769	83.75	–0.575	54.27	–0.645	55.27
	10.0	–0.863	85.30	–0.566	60.22	–0.638	55.33
Plasticizers under study DFS-1	2.5	–0.987	77.63	–0.575	56.13	–0.645	53.90
	5.0	–0.987	79.85	–0.555	56.50	–0.635	57.20
	7.5	–0.835	81.93	–0.485	60.89	–0.628	57.32
	10.0	–0.850	83.60	–0.489	64.14	–0.623	58.80
Plasticizers under study DFS-2	2.5	–0.907	72.29	–0.543	57.73	–0.660	53.59
	5.0	–0.949	76.22	–0.535	59.00	–0.620	55.73
	7.5	–0.949	77.92	–0.529	59.03	–0.652	57.95
	10.0	–0.935	81.48	–0.480	66.67	–0.640	59.77
Oil I-20	2.5	–0.937	72.55	–0.550	55.37	–0.651	51.76
	5.0	–0.966	75.58	–0.559	56.86	–0.645	51.82
	7.5	–0.875	76.00	–0.557	56.90	–0.634	57.26
	10.0	–0.962	77.91	–0.547	59.28	–0.626	58.09

The properties of such grids are largely dependent on the distribution and concentration of chemical bonds of the average molecular weight and rubber molecular weight distribution [8]. Fig. 5–7 presents the time dependence for reaching the optimum vulcanization degree on the dosage of administrated plasticizes.

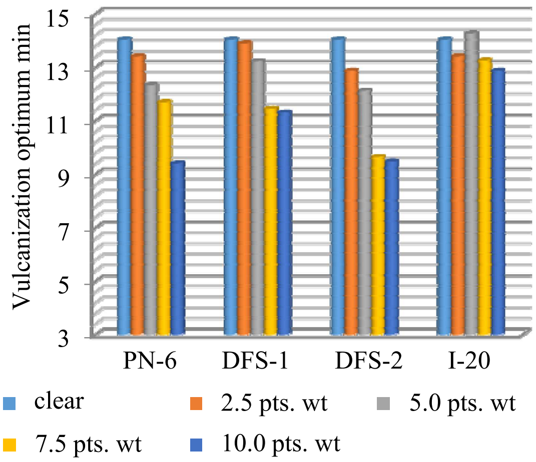

Fig. 4. Vulcanization optimum of rubber mixtures based on SKI-3

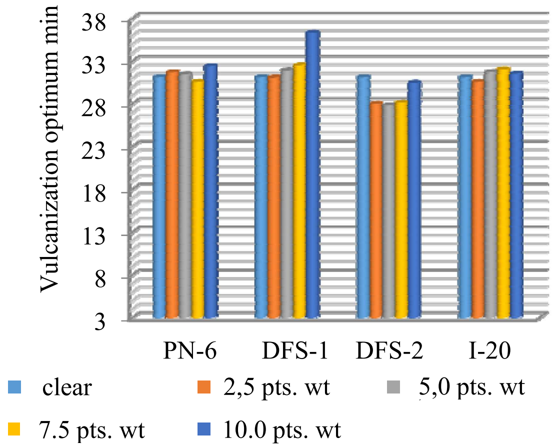

Fig. 5. Vulcanization optimum of rubber mixtures based on SKMS 30 ARKM-15

It was found that in rubber compositions based on SKI-3 and EPDM, administering oils PN-6 and investigated plasticizers DFS-1 and DFS-2 greatly reduces the time to reach an optimal degree of vulcanization compared with the rubber composition containing no additives, whereas the introduction of oil I-20 has virtually no effect on this indicator.

Studies of rubber mixtures based on SKMS 30 ARKM-15 have shown that when administered oils PN-6, I-20, as well as test plasticizer DFS-1, there were no significant changes in the time to reach an optimal degree of vulcanization compared with the rubber composition containing no additives.

At the same time the introduction of the test plasticizer DFS-2, there is some reduction in the vulcanization optimum. Thus, the time to reach an optimal degree of vulcanization of rubber mixture containing no additives is 5.66 m, and when administered 2.5 pts. wt DFS-2 it is 3.95 min.

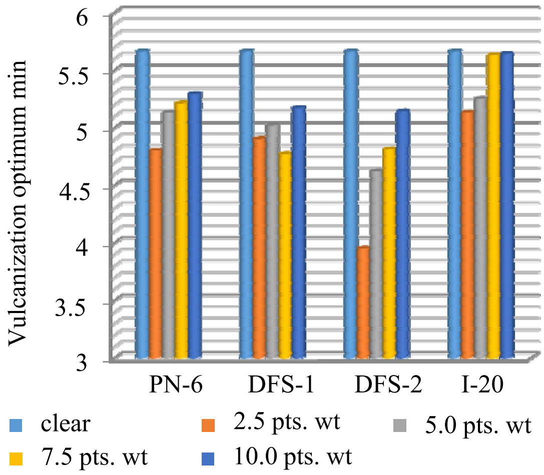

Fig. 6. Vulcanization optimum of rubber mixtures based on EPDM

Conclusion. Thus, the investigation results of plastoelastic properties of the filled elastomeric compositions based on a synthetic polyisoprene, the oil-extended butadiene-styrene and ethylene-propylene rubbers showed, that when administered investigated plasticizers RF-1 and DFS-2 in all of the elastomeric composition, the nature of change in the Mooney viscosity of rubber compounds is substantially similar to mixtures containing industrial plasticizers.

It is found that the use of test plasticizers RF-1 and DFS-2 results in a considerable relief of relaxation processes occurring in the volume of the elastomeric matrix, as compared to elastomeric compositions containing industrial plasticizers. It should be noted that the use of DVS-2 in the test unfilled rubber compounds causes a slight time reduction (10%) to reach an optimal degree of vulcanization.

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