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The following substances were used as additives: maleated rosin modified with oleic acid, containing maleopimaric acid ( $\approx 50\%$ ) which did not react with maleic anhydride rosin acids; rosin-itaconic acid adduct, containing up to  $\approx 50\%$  of citraconopimaric acid as a mixture of two isomers; octylimide of rosin-itaconic acid adduct; imide of maleated rosin and aniline, containing up to  $\approx 50\%$  of N-phenylimide of maleopimaric acid; imidoamide of maleated rosin and aniline, containing maleopimaric acid anilide N-phenylimide; imidoamide of maleated rosin and *p*-anisidine, containing maleopimaric acid *p*-methoxyphenylamide N-(*p*-methoxyphenyl)imide. Their uses as processing aids in rubber compounds based on synthetic isoprene rubber are considered. Processing parameters, such as Mooney viscosity, scorch resistance, kinetic characteristics of vulcanization of the rubber mixtures with nitrogen adducts of rosin are investigated.

**Key words:** rosin-maleic acid adduct, rosin-itaconic acid adduct, processing aid, Mooney viscosity, cure kinetics, adhesion, stickiness confection.

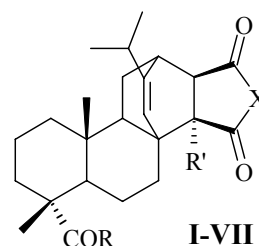
**Introduction.** Rosin is now being widely applied; it is used by about 70 industries: modifying additives in the production of polymer composite materials, pulp and paper industry, production of synthetic rubber, in the paint and printing industries, etc.

However, some consumers do not totally accept such properties of rosin as a comparatively low softening temperature, high acid value, insufficient moisture resistance, brittleness, a tendency to crystallize, the ability to be readily oxidized by atmospheric oxygen and others. Therefore, rosin used in the form of its derivatives, such as esters, amides, resinates (rosins salts of rosin acids), etc. which are mainly used as modifying agents.

From the literature it is known that very valuable products, such as insecticides, fungicides, algacides, flotation agents, and even steroids analogues and other physiologically active substances can be prepared from the individual rosin, especially from various modified rosins and rosin acids. At present, many foreign companies, such as Hercules, DuPont, Hest, Hensel etc, produce more than 500 kinds of derivatives of rosin and turpentine, which are widely used in the production of biologically active substances, plasticizers, adhesives, stabilizers, and others. In order to improve rubber quality the use of the rubber mixtures of nitrogen-containing derivatives of a diene adducts of rosin is very promising [1].

To stabilize the assortment of raw rubber and ingredients, to create rubber with new properties or increased quality is very promising to introduce special processing aids to the formulation. It leads to improving and stabilizing the technological properties of the rubber compounds, but at the same time does not affect the properties of rubber products.

**Main part.** In the process of synthesis on the basis of maleic and itaconic adducts a number of nitrogen-containing products were obtained: maleated rosin modified with oleic acid (ORMA), containing maleopimaric acid I ( $\approx 50\%$ ) which did not react with maleic anhydride rosin acids [1, 2]; rosin-itaconic acid adduct (RIA), containing up to  $\approx 50\%$  of citraconopimaric acid II as a mixture of two isomers [3]; octylimide of rosin-maleic acid adduct (OORMA) (a mixture of N-octylimide of maleopimaric acid III ( $\approx 50\%$ ) [4] and unreacted rosin acids); octylimide of rosin-itaconic acid adduct (ORIA) (a mixture of N-octylimide citraconopimaric acid IV ( $\approx 50\%$ ) and unreacted rosin acids); imide of maleated rosin and aniline (AORMA), containing up to  $\approx 50\%$  of N-phenylimide of maleopimaric acid V; imidoamide of maleated rosin and aniline (ARMA), containing N-phenylimide maleopimaric acid anilide VI; imidoamide of maleated rosin and *n*-anisidine (AnRMA), containing maleopimaric acid N-(*n*-methoxyphenyl)-amide *n*-methoxyphenyl imide VII:



R' = H:

R = OH, X = O (I), N(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> (III), NC<sub>6</sub>H<sub>5</sub> (V)R = NHC<sub>6</sub>H<sub>5</sub>, X = NC<sub>6</sub>H<sub>5</sub> (VI),R = NH(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>), X = N(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>) (VII)R' = CH<sub>3</sub>: X = O (II), N(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> (IV)

Softening temperature of the synthesized terpenoid products was determined with OptiMelt Stanford Research Systems MPA 100, thermal properties were studied with derivatograph MOM Q-1500D under nitrogen at a linear rate of temperature rise of 5°C/min [5]. The acid number was determined according to GOST 178231-72.

Preparation of adducts OORMA, ORIA, AORMA, ARMA, AnRMA was carried out in a three-necked round bottom flask of 500 ml, ORMA, KIA and maleic adduct – 2,000 ml equipped with a stirrer, a thermometer and a nozzle Wurtz with reflux condenser and heated on an oil bath.

*Modified maleic rosin adduct (ORMA)* [2]. 230 g of maleic anhydride was added to the melt pine gum rosin (1,000 g) for 1 h, at 170°C, the reaction temperature was raised to 195°C and kept under stirring for 5 hours. 125 g oleic acid was added to the mixture, it was stirred for 2 hours at 195°C. The obtained ORMA has a softening point at 100–110°C, an acid number of 262 mg KOH/g, unbound maleic anhydride content 0.49%, the initial decomposition temperature ( $T_{d,i}$ ) 250°C.

*Itaconic rosin adduct (RIA)* [3]. The mixture of 800 g pine gum rosin, 320 g itaconic acid were heated for 1 hour to 200°C and maintained at that temperature with stirring for 8 hours. Water is released from the mixture during heating resulting from the dehydration of itaconic acid. We received 1,072 g of product having a softening temperature of 102–112°C and an acid number of 268 mg KOH/g,  $T_{d,i} = 230^\circ\text{C}$ .

*Octylimide of rosin-maleic acid adduct (OORMA)*. To 150 g of the melt ORMA for 1 hour was added dropwise 48 ml of *n*-octylamine at 140 °C, the reaction temperature was raised to 190 °C and kept under stirring for 6 hours. OORMA received 175 g, softening point 35–45°C, an acid number of 115 mg KOH/g,  $T_{d,i} = 267^\circ\text{C}$ .

*Octylimide of rosin-itaconic acid adduct (ORIA)*. 45 ml of *n*-octylamine was added dropwise to 150g of RIA for 1 hour at 120°C, then the reaction mixture was kept under stirring at 180°C for 4 h at 200°C – 4 hours. It was obtained 180 g OKIA, softening point 62–72°C, an acid number 128 mg KOH/g,  $T_{d,i} = 262^\circ\text{C}$ .

*Imide of maleated rosin and aniline (AORMA)*. 14 ml of aniline was added dropwise to 100 g the melt ORMA for 3 h. During the addition of aniline the temperature of the reaction mixture was gradually raised from 150 to 190°C. At this time, the mixture should not foam and solidify. After the aniline addition, it was stirred for 5 h at 200°C. It was obtained 109 g AORMA, a softening temperature 110–120°C, an acid number 145 mg KOH/g.

*Imidoamide of maleated rosin and aniline (ARMA)*. This adduct was obtained by reacting pine gum rosin (1,000 g) and maleic anhydride (200 g)

in argon atmosphere at 180–200°C for 8 h 40 ml aniline was added dropwise to the melt of ARMA (100 g) for 2 h. During the addition of aniline the reaction temperature was gradually raised from 170 to 220°C. At this time, the mixture should not foam and solidify. After addition of aniline, the mixture was kept under stirring at 220°C for 6 h. It was obtained 136 g ARMA, a softening temperature 128–135°C, an acid number 80 mg KOH/g.

Product of *imidoamide of maleated rosin and n-anisidine* interaction (AnRMA). 52 g of *p*-anisidine was added to 100 g the molten adduct for 1 h. During the addition of *p*-anisidine reaction temperature was gradually raised from 160 to 190°C. At this time, the mixture should not foam and solidify. After the addition of *p*-anisidine mixture was kept under stirring at 200°C for 8 h. It was obtained 145 g AnRMA, a softening temperature 120–125°C, an acid number 58 mg KOH/g.

Since industrial rubber mixtures contain large amounts of ingredients that can affect the interaction between additives and the polymer, at the initial phase of the research the additives were introduced into the model rubber compounds that do not contain fillers and plasticizers [6].

At this stage the research was carried out to determine the effect of nitrogen containing adducts of rosin on the processing properties of industrial filled mixtures. The products which have shown their effectiveness in model rubber compounds: ORIA, AnRMA, AORMA, ARMA were used as additives. The mixtures of synthetic polyisoprene rubber (SKI-3) and its combination with a synthetic oil-filled styrene-butadiene rubber (SKMS-30 ARKM-15) were used as elastomer matrix.

Rubber compound should provide rubber with specified performance characteristics and still be technological at processing. Plasto-elastic properties of rubber compounds characterize their behavior at molding before vulcanization. They affect the process efficiency and product quality. To determine the rheological properties of polymers by rotational viscometry, the material sample is subjected to shear at a constant speed in a thin circular layer. In these devices, the shear deformation of the test material under pressure in a closed cylindrical chamber (form), is caused by rotation of the cylindrical disk (rotor), placed in the center of the sample.

The most common device of this type used in the rubber industry for testing raw rubber and rubber compounds is Mooney viscometer. Test results are expressed in Mooney viscosity units. The torsion moment  $M$  equal to 0.083 N·m is accepted as Mooney viscosity unit. The shear rate of the material under these conditions is about 1.5 s<sup>-1</sup>. On the surfaces and side surfaces of the mold halves and a cylindrical head disc rotor there are notches to eliminate slippage. Test results on a Mooney viscometer are presented in Fig. 1.

The results showed that addition of rosin adducts lead to a decrease in the Mooney viscosity (in comparison with the mixture without nitrogenous products). So, for mixtures containing AORMA ARMA and ORIA additions Mooney viscosity index was within 39.4–41.0 Mooney units. Value of the index for the mixture without additives was 52.8 Mooney units.

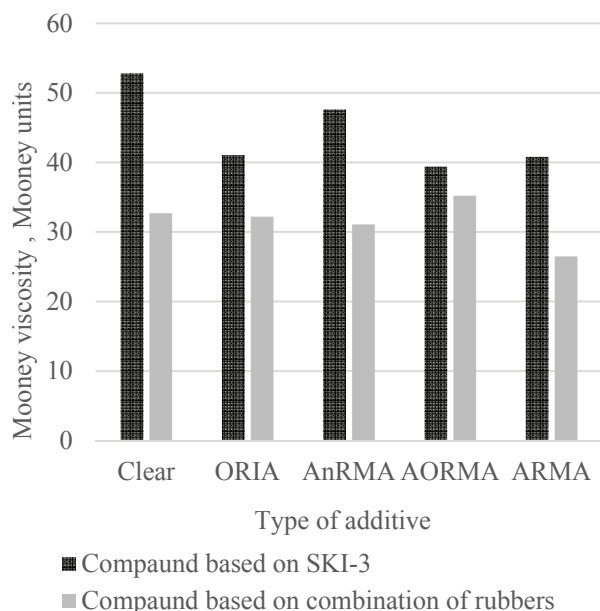


Fig. 1. Mooney viscosity indices of the investigated elastomeric compositions

The mixture based on a combination of rubbers SKI-3 and SK(M)C-30 ARKM-15 additive effect is manifested to a less degree. Increase of the viscosity of the elastomeric composition was observed only in the case of introducing additive AORMA (35.2 Mooney units in comparison with 32.7 Mooney units mixture containing no additives). Viscosity reduction up to 18% was observed only when using ARMA additives. The elastomeric compositions with additives and ORIA AnRMA almost do not differ from the sample without additives (viscosity of rubber mixtures is in the range of 31–32 Mooney units).

Thus, the introduction of additives allows viscosity reducing stresses caused by moving macromolecules, which may be due to their plasticizing effect. Increase of the viscosity in the case of using AnRMA is, apparently, due to physical interactions between the functional groups and an additive or elastomeric matrix components.

The next important technological characteristics are the kinetics parameters of rubber compounds vulcanization.

Curing is a complex of physical and chemical processes that occur in the rubber compound, the main of them is the linking rubber macromolecules

of different chemical bonds energy and nature in a single spatial grid vulcanization. During vulcanization of rubber mixtures ductility decreases and gradually increases the elasticity of the vulcanizate, its improved mechanical properties, greatly increased tensile strength, elongation, cold resistance, heat resistance, electrical resistance.

Introduction the active additive can affect the formation of the three-dimensional network, which will require changes in the conditions of vulcanization of products and processing parameters of elastomeric compositions. So the kinetics of rubber compounds vulcanization with nitrogen-containing products is of considerable interest. The results of the tests of the rubber compositions with vibrometre ODR-2000 are shown in the Table.

#### The kinetics of the rubber compounds vulcanization with nitrogen-containing products based on rosin

Type of the additive	The time required to increase the minimum torque at 2 units, min	The time to reach an optimal degree of vulcanization, min	The cure rate, $dH \cdot m/min$
Mixture based on SKI-3			
Additives free	6.36	10.67	12.39
ORIA	6.72	11.16	9.88
AnRMA	6.50	10.17	10.82
AORMA	6.79	10.76	9.77
ARMA	6.46	11.36	11.04
Mixture based on rosin compositions			
Additives free	8.40	22.48	2.03
ORIA	9.05	23.44	1.89
AnRMA	7.77	22.10	2.16
AORMA	9.47	23.84	1.79
ARMA	9.16	23.16	1.95

Analysis of the data showed that the introduction of the additives into the mixture based on SKI-3 allows reducing the speed of the vulcanization process, if compared with the mixture without additives up to 21% (mixtures with ORIA and AORMA showed the greatest effect). At the same time nitrogen containing adducts of rosin derivatives have a less affect on curing start time, and the time to reach the optimum vulcanization (index value in the rubber composition without additive was 10.67 min, and the index values of the mixtures with the additives is in the range from 10.17 min (AnRMA additive) to 11.36 m (ARMA additive).

Changing the time to reach an optimal degree of vulcanization of the rubber mixtures on the basis of a combination of SKI-3 and SK(M)C-30 ARKM-15 was within 8%. The greatest effect was observed with ORIA and AORMA additives. Thus, it

is seen that the optimum time change is associated with earlier start of the curing process. In the case of introduction these additives the time required to increase the minimum torque at 2 units increased 5-10% (this parameter indicates the beginning of the crosslinking process, and is confirmed in the increase of torque). Furthermore, additives ORIA and AORMA decreased the cure rate. The value of this indicator in mixtures with the additives was respectively 1.89 and 1.79 dN · m/min, in a mixture without additives – 2.03 dN · m/min.

Automobile tire is one of the major parts of the car and composition product. Its manufacturing technology is more difficult and much different from other rubber products manufacture. Tire has a complex configuration and is composed of several components. To provide a qualitative assembly and safe operation, all the elements (layers of the tires) should have the necessary autohesive properties.

Determination of the bond strength between the layers under layer separation was carried out according to GOST 6768-75. To test the samples a rectangular parallelepiped form (width  $(25 \pm 0.5)$  mm and not thicker than 12 mm) was used, and the layer separation was in the area at least 100 mm long.

The samples were kept for at least 24 hours at a temperature  $(23 \pm 2)^\circ\text{C}$ , relative humidity  $(50 \pm 5)\%$ . The force required to separate layers was determined from the graphics “load – time of layer separation” as the average of ten lowest peaks.

The bond strength between the layers under layer separation ( $R$ ), in Newtons per meter, was calculated by the formula:

$$R = \frac{P}{b},$$

where  $P$  is layer separation load, H;  $b$  – width of the sample, m.

Autohesion is linkage between homogeneous materials. Bonding strength between layers under layer separation is the force required to separate a multilayer sample under specified test conditions, related to the sample width.

The results of the tests investigating autohesion (stickiness) of the rubber compounds are shown in Fig. 2.

Analysis of the results showed that the introduction of all investigated additives leads to the increase of the strength between layers under layer separation.

The case of the rubber mixture based on SKI-3 shows that the use of additives leads to

increase of strength between layers under layer separation. Thus, if compared with the value of this parameter to the mixture without additives equal 100.30 N/m, the parameter values range from 120.75 N/m (ORIA additive) to 242.94 N/m (AORMA additive).

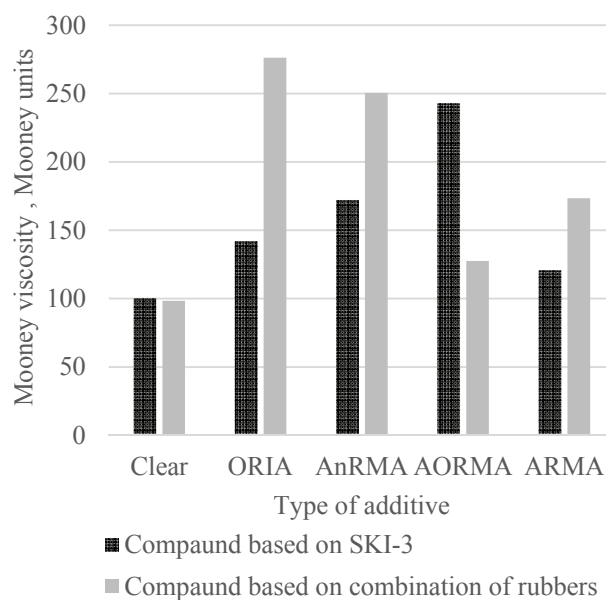


Fig. 2. Bond strength between the layers under layer separation

Introducing the additives into the rubber mixture based both on a combination of rubbers and on SKI-3 allows to increase the bond strength between the layers under layer separation. However, the highest bond strength between the layers were observed in the mixtures containing ORIA and AnRMA and reached 250.44 and 276.27 N/m respectively (the value of the index for the mixture without additives – 98.37 N/m)

Various character of influence of the additives on the rubber composition based both on SKI-3 and on a combination of rubber, is possibly due to differences in the structure of the additives, as well as using different adhesion promoters in blends.

**Conclusion.** Thus, the results of the research suggest that the synthesized nitrogen-based additives formed on the itaconic and maleic rosin adduct can be applied in the rubber compounds based on general-purpose rubbers as processing aids. Application of the products allows reducing viscosity of the compositions, it improves their adhesiveness and resistance to scorch, with virtually no impact on the kinetics of vulcanization of rubber mixtures.

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