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THE SYNTHESIZED COBALT- AND NICKEL-CONTAINING ADHESION PROMOTERS IN MODEL ELASTOMER COMPOSITIONS

The influence of new modifiers of adhesion on the technological properties of the unfilled elastomer compositions based on synthetic isoprene rubber SKI-3 is investigated. Synthesized adhesion promoters constitute silica acid fillers modified with cobalt, nickel, and a combination of cobalt and nickel. This fillers contain a reduced number (compared with industrial cobalt stearate) of ions of metals of variable valence on the surface. The samples were investigated by roentgenofluorescscence analysis on wave x-ray fluorescence spectrometer Axios (PANalytical, Netherlands) to establish the quantitative composition of the adhesion modifiers. Tests are carried out to determine the dependency of the change of Mooney viscosity of rubber mixtures, relaxation processes, occurring in volume of an elastomer matrix, and the time to reach the optimal degree of vulcanization of the investigated dosages of the adhesion promoters and amounts of metal ions on their surface.

The type and dosage of the synthesized promoters of adhesion of rubber to the brass plated steel cord are established that improve the technological properties of the unfilled elastomer compositions. It is revealed that the introduction of rubber mixtures based on SKI-3 cobalt-containing modified silica acid fillers with 7.3 and 9.3 wt % allows obtaining elastomeric compositions with similar properties to the compositions containing industrial cobalt stearate.

Key words: promoter adhesion, rubber, steel cord, viscosity, relaxation, kinetics of vulcanization.

Introduction. Rubber-bitumen systems structurally are complicated materials. The functionality of such materials is also very difficult: they provide safe operation of tires and rubber products under heavy static and dynamic loadings, at high temperatures, different environments and other corrosive influences [1].

The operational reliability of the rubber products greatly depends on the bond strength between the reinforcing elements and the degree of conservation of this indicator after the influence of aggressive factors [2]. It is known [3] that for increasing the adhesion strength of the composition of the elastomeric compositions, injected adhesion promoters are added, among which the most widespread system based on organic salts of metals of variable valency, primarily of cobalt [4]. The role of modifier, however, is not reduced to functions only of the adhesion promoter, as its presence usually changes the whole complex of properties of rubber mixtures and their vulcanizates [5].

Main part. The aim of this work was to study the effect of new synthesized adhesion promoters on the basis of silica filler in comparison with industrial cobalt stearate on the technological properties of the elastomer compositions.

The investigated adhesion promoters are characterized by low content of metals. This fact increases the interest to these substances, taking into account environmental and technological risk of salts of metals of variable valency, which may contribute to the oxidation of rubbers and rubber compounds during processing and operation [6].

The synthesized adhesion promoters, representing a modified by cobalt, nickel, and cobalt together with nickel silica acid filler (MSAF), was received in the Department of technology of petrochemical synthesis and polymer materials processing, of the Belarusian State Technological University. Characteristics of these promoters of adhesion for the quantitative content of metal on their surface are given in Table 1.

Table 1

Characteristics of adhesion promoters

Identification	Metal	Content, wt %
Cobalt stearate	Co	10.5
SAF	–	–
MSAF1 Co	Co	4.6
MSAF2 Co	Co	7.3
MSAF3 Co	Co	9.3
MSAF1 Ni	Ni	2.4
MSAF2 Ni	Ni	4.2
MSAF3 Ni	Ni	6.1
MSAF1 Co-Ni	Co Ni	1.8 0.7
MSAF2 Co-Ni	Co Ni	3.7 0.8
MSAF3 Co-Ni	Co Ni	5.8 1.2

As the object of research unfilled elastomeric composition based on synthetic isoprene rubber SKI-3 was used. Promoters of adhesion, and silica acid filler (SAF) was introduced into rubber compounds at dosages of 0.5, 1.0 and 1.5 phr. A reference sample was elastomeric composition comprising used in the industry cobalt stearate.

Determination of the viscosity according to Mooney rubber mixtures was carried out on a rotational shear viscometer MV2000 in accordance with GOST 10722-76. A study of stress relaxation elastomeric compositions containing the adhesion promoters was carried out on the viscometer MV2000, which within minutes after stopping the rotor fixed dependency of torque from time [7]. On the basis of the obtained data the relaxation factor (Kr) was calculated which is the criterion for evaluating processing AIDS rubber and rubber compounds. The kinetics of the curing was determined on the rheometer ODR2000 according to GOST 12535-84.

Plastoelastic properties of rubbers and rubber compounds, characterize their behavior in processing, i.e. their technological properties [8]. One of the methods of assessing and predicting the technological behaviour of elastomers and elastomer compositions based on them is rotary viscosimetry. Table 2 shows the results of determining the viscosity according to Mooney and the coefficients of the relaxation of the unfilled rubber compounds containing the analyzed promoters of adhesion.

The data obtained show that increasing dosages of cobalt stearate, the SAF, as well as nickel and cobalt and nickel adhesion promoters leads to increased Mooney viscosity in rubber mixes. The highest value of this indicator (24.8 conv. units) identified in elastomeric compositions containing 1.5 phr of cobalt stearate. The increase in the viscosity of rubber compounds may be due to the agglomeration of particles of polar promoters of adhesion due to stronger interaction with each other than with the elastomeric matrix [9].

The introduction of the modified cobalt-silica fillers leads to the decrease of viscosity according to Mooney elastomer compositions with increasing doses of the tested components and number of metal ions on their surface. So, with the introduction of 0.5 phr cobalt MSAF with the minimum (4.6 wt %) number of metal Mooney viscosity of rubber compound is 27.7 conv. units, and when using 0.5 phr promoter from 9.3 wt % Co – 20.3 conv. units Mooney. Such character of change of properties can be related to the fact that modifications of the SAF by cobalt reduces the number of groups –OH on its surface, and therefore weakens the interaction between the silica filler particles, which leads to improving the interaction between non-polar polymer with a polar additive.

Rubber mixtures are multicomponent systems consisting of multiple ingredients for various purposes. This leads to a large variety of forms of molecular mobility and the corresponding relaxation processes occurring in the volume of elastomeric matrix [10].

Table 2

The Mooney viscosity and the coefficients of relaxation of the unfilled rubber compounds

The name of the adhesion promoter	The dosage of the adhesion promoter, phr	Mooney viscosity, conv. Muni units.	The coefficient of relaxation of rubber compounds Kr, %
Cobalt stearate	0.5	19.7	63.4
	1.0	21.3	52.8
	1.5	24.8	48.8
SAF	0.5	16.0	65.0
	1.0	21.5	60.0
	1.5	23.1	55.4
MSAF1 Co	0.5	27.7	45.9
	1.0	17.1	59.1
	1.5	15.8	66.4
MSAF2 Co	0.5	20.9	53.6
	1.0	16.8	61.3
	1.5	15.2	70.1
MSAF3 Co	0.5	20.3	55.2
	1.0	16.3	68.9
	1.5	15.1	73.4
MSAF1 Ni	0.5	15.4	70.6
	1.0	16.8	67.1
	1.5	18.7	65.5
MSAF2 Ni	0.5	17.9	66.4
	1.0	19.3	65.9
	1.5	20.1	64.8
MSAF3 Ni	0.5	21.1	62.2
	1.0	21.6	61.1
	1.5	22.8	58.0
MSAF1 Co-Ni	0.5	19.4	65.8
	1.0	19.6	64.7
	1.5	19.7	63.4
MSAF2 Co-Ni	0.5	20.1	62.3
	1.0	21.9	60.0
	1.5	23.5	57.9
MSAF3 Co-Ni	0.5	21.6	60.2
	1.0	22.8	58.5
	1.5	24.3	56.0

An analysis of the estimated coefficients of the relaxation of rubber compounds showed that the increased content of nickel and cobalt and nickel promoters of adhesion leads to a slight decrease in the rate of the relaxation processes occurring in the volume of the elastomeric matrix. Similar changes in relaxation properties are observed in elastomeric compositions with cobalt stearate and SAF. The use of cobalt-containing promoters adhesion increases the flow rate of the relaxation processes. So, with the introduction of 1.5 phr modified cobalt-silica fillers, containing a 4.6, 7.3 and 9.3 wt % Co values of Kr are, respectively, of 66.4, 70.1 and 73,4% (in samples with cobalt stearate Kr varies from 48.8 to 63.4%). The ambiguous character of changes in the relaxation properties can be associated with the polarity of the surface of the promoters of adhesion and their interaction with the surface of the rubber ingredients of the rubber mixture. Increase of the coefficients of the relaxation of rubber compounds when using modified cobalt-silica fillers indirectly indicates their uniformity and compatibility with the elastomeric matrix.

Rubber products represent the products of vulcanization of rubber mixtures. The nature of the curing process is the connection of the macromolecules of the rubber cross-links of different nature and energy in to break up the spatial grid [8]. This process is influenced by all the ingredients of the elastomer composition.

The study of adhesion promoters can participate in the curing process with the formation of chemical and physical relationships at various stages of the process, and interact with the components of the curing system. The results of the study of the influence of adhesion promoters on the time to reach the optimum degree of vulcanization is shown in Fig. 1 and 2.

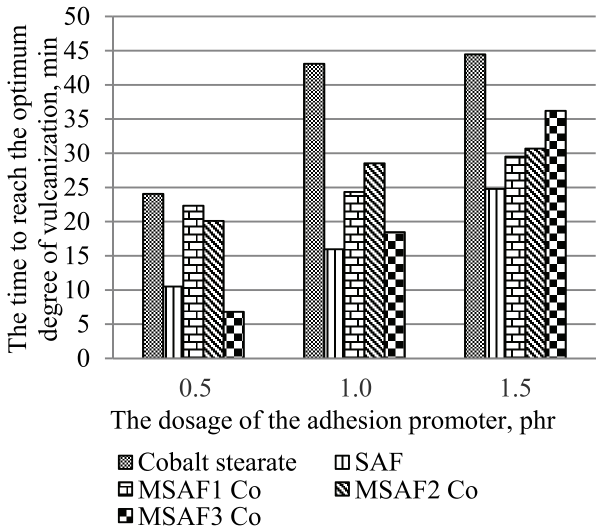

Fig. 1. The time to reach the optimum degree of vulcanization of the elastomeric compositions with cobalt stearate, SAF and cobalt-containing promoters of adhesion

The results showed that the increase in the content of industrial cobalt stearate, 0.5 to 1.5 phr leads to an increase in time of achievement of the optimum degree of vulcanization (t90) from 24.06 min before 44.47 respectively. At the same time, the introduction in the rubber mixture of the silica filler and cobalt-containing promoters adhesion in the same dosage leads to a reduction of the optimum of vulcanization in comparison with the samples containing cobalt stearate. The greatest change in the kinetics of vulcanization is observed when using 0.5 phr the synthesized promoter from 9.3 wt % Co. So, the t90 of elastomer composition is 6.80 min, which is 72% lower than when using cobalt stearate in the same dosage.

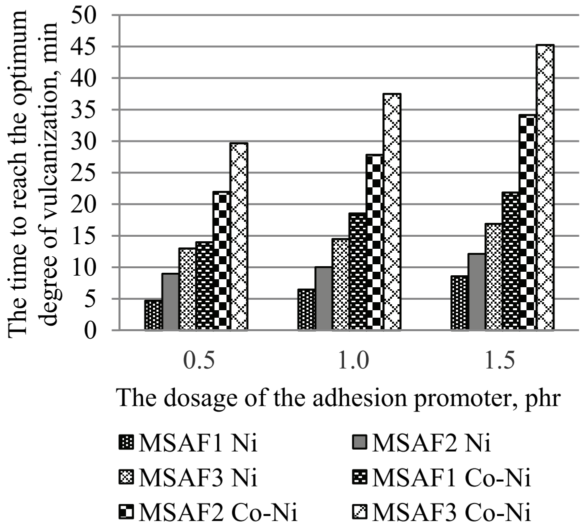

Fig. 2. Time of the optimal degree of vulcanization of the elastomer composition with nickel- and cobalt-nickel promoters of adhesion

It should be noted that with increasing the content of modified cobalt-silica fillers whilst achieving the optimum degree of vulcanization increases. The maximum value of t90 = 36.2 min is detected by using a 1.5 phr cobalt-containing promoter from 9.3 wt % Co.

In the case of modified cobalt-silica fillers the strict regularities of changes in the kinetics of vulcanization of quantitative content of cobalt ions on the surface of synthesized adhesion promoters is not observed.

Comparative analysis of kinetic parameters of vulcanization showed that, as in the case of modified cobalt-silica fillers, the use of nickel- and cobalt-nickel promoters of adhesion leads to a reduction in the optimum vulcanization compared to the cobalt stearate (the exception is the promoter from 5.8 wt % Co and 1.2 wt % Ni at doses of 0.5 and 1.5 phr). The highest value of t90 = min of 16.88 is detected by using a 1.5 phr -containing adhesion promoter from 6.1 wt % Ni, 2.63 times less than that of the elastomeric compositions containing 1.5 phr stearate and cobalt.

It should be noted that the increase in dosages in elastomer composition modified with Nickel, and a combination of cobalt and nickel silica fillers, and the quantity of metals on their surface leads to an increase in time of achievement of the optimum degree of vulcanization. Thus, the change from 0.5 to 1.5 phr dosage nickel-containing adhesion promoter of from 2.4 wt % Ni leads to an increase of t90 from 4.69 to 8.57 min, and in the case of using a promoter from 6.1 wt % Ni from 12.99 to 16.88 min respectively.

Conclusion. It is established that the introduction to the elastomeric composition of modified silica fillers with 7.3 and 9.3 wt % Co at the dosage of 0.5 phr, from 4.2 wt % Ni at dosage of 1.0 and 1.5 phr and from 6.1 wt % Ni and cobalt-nickel promoter adhesion in all the dosages allows to store the value of the viscosity according to Mooney rubber mixtures at the level of compositions containing industrial adhesion promoter.

Introduction to the elastomeric composition of cobalt MSAF in dosages of 1.0 and 1.5 phr, modified by nickel, and a combination of cobalt and nickel silica fillers in all the dosages can accelerate the relaxation processes, occurring in volume of the elastomeric matrix. It is revealed that the maximum values of the relaxation coefficients are rubber mixtures containing 1.5 phr MSAF with 7.3 and 9.3 wt % Co and 0.5 phr MSAF with 2.4 wt % Ni.

Analysis of kinetic parameters of vulcanization process showed that the use in elastomer compositions of synthesized adhesion promoters in almost all cases leads to a shorter time to achieve an optimal degree of vulcanization. The greatest changes of this indicator are observed in the case of using nickel-containing silica fillers (t90 decreases 1.85–times of 6.65). Cobalt- and cobalt-nickel MSAF, to a lesser extent influence the curing process: the time to reach the optimum degree of vulcanization is reduced to 1.08–3.54. Such character of change of properties can be associated with acceleration of the processes of crosslinking of rubber chains in the presence of synthesized adhesion promoters.

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