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PHYSICO-MECHANICAL PROPERTIES OF VULCANIZATES CONTAINING WASTE FROM THE FAT AND OIL INDUSTRY

Annotation: *For the first time, the possibility of replacing carbon black and stearic acid with waste from the fat and oil industry (diatomite, bleached clay) is investigated. The value of the conditional tensile strength for vulcanizates containing stearic acid is 8,26 MPa, and for the studied vulcanizates containing selected clay, it is in the range of 7,88-8,39 MPa, for those containing diatomite is 7,88-8,43 MPa. The elongation at break for the studied vulcanizates containing selected clay increases from 280% to 300%, for those containing diatomite is from 280 to 297%. A hardness according Shore is found for the studied ones containing selected clay and diatomite in the range of 64-71 conv.units, for the reference rubber of 63 conv.units.*

The conducted studies show that the conditional strength and tear resistance decrease when carbon black is replaced with selected clay, as well as diatomite, but the indicators remain within the permissible limits for this rubber. The main role in enhancing the regenerate is played by caoutchouc. Therefore, carbon black and stearic acid can be replaced with less active, but cheaper and environmentally friendly ingredients. Extended physico-mechanical tests of experimental rubbers led to the conclusion that is most expedient to use waste from the fat-and-oil industry in the formulation of rubber mixtures for the manufacture of under-rail laying of railway tracks, since when using waste from the fat-and-oil industry, the properties of rubbers practically do not change, comply with control standards.

Key words**:** *waste from the oil production, ingredients, regenerate, bleached clay, diatomite, under-rail gasket.*

Introduction. Nowadays, the amount of polymer waste has reached about one and a half million tons per year. At the same time, the used amount of polymer waste is very small. Therefore, the problem of polymer waste recycling is in urgent importance currently. It is known that worn tires can be used as a cheap polymer raw material in the production of regenerate from them. Issues related to the regeneration and further use of used tires and rubber products are important [1-4].

In previous studies, we received a tire regenerate and a sub-rail gasket [1, 5-7].

The purpose of this work was to compare the physical and mechanical parameters of vulcanizes.

Research materials and methods.

The objects of the study were considered:

– Diatomite – waste from the fat and oil industry, «Arai» LLP, Shymkent

– Bleach clay – waste of the fat and oil industry, «Aray» LLP, Shymkent

– A recipe for a rubber compound for a sub-rail gasket OP 356, CP328 of «ECO-Tire» LLP;

The research method:

– IR spectral analysis on the device of the INFRARED Fourier spectrometer ShimadzuIRPrestige-21 with the prefix of the disturbed total internal reflection (DTIR) Miracle of PikeTechnologie (Figure 1,2).

Experimental rubber mixtures were obtained on rollers (GOST 14333-79E Rubber-processing rollers).

Results and their discussion.

During vulcanization in the presence of sulfur, when heated, double bonds break –CH=CH- and polymer chains are «cross–linked» by sulfide bridges -C-S-C-. Due to the formation of a three-dimensional spatial structure, the thermoplastic polymer passes into a thermosetting state. The vulcanization scheme is shown below:

$$(-CH_2-CH=CH-CH_2-)_n \quad\quad (-CH_2-CH-CH-CH_2-)_n$$

$$+nS \quad \rightarrow \quad S$$

$$(-CH_2-CH=CH-CH_2-)_n \quad\quad (-CH_2-CH-CH-CH_2-)_n$$

The change in the IR spectra of tire regenerate and vulcanizate was determined on the IR spectrum. IR spectroscopic analysis was performed on the ShimadzuIRPrestige-21 infrared Fourier spectrometer device. Chemical changes and the reaction mechanism during the interaction of rubber and sulfur were studied using IR spectroscopy.

The IR spectroscopy method makes it possible to monitor changes in the spectral parameters of functional groups under the influence of temperature, irradiation, and during the storage of polymer materials.

As is known, the presence of unsaturated compounds confirms the appearance of absorption bands above 3000 cm-1. However, provided a stronger main band below 3000cm-1, does not overlap these bands. A double bond can also be confirmed by the appearance of a band of valence vibrations C = C in the area of 1650cm-1, and the nature of substitution can be determined by the bands of non-planar deformation vibrations C-N. Overtones and bands of C-H plane deformation vibrations can also be useful in this case [8].

In the spectra (Fig. 1), intense bands in the range from 450 to 3000 cm-1 are visible. According to the IR spectrum of the tire regenerate (Fig. 1), the absorption peak in the area of 2954.95, 2912.51, 2846.93 cm-1 of this spectrum belongs to the oscillation of C-H3 bonds in alkanes 2954.95 cm-1 is overlapped by the absorption of alkanes.

In the spectra (Fig. 2) of the vulcanizate, intense bands are visible in the range from 450 to 3000 cm-1 – bands of valence vibrations of the C-H, 2951.09, 2908.65, 2846.93cm-1 groups are caused by mixing vibrations of the C-H and C-C groups. 2951.09 cm-1 is overlapped by the absorption of alkanes -C-H2- it also has bands of true and torsional vibrations of about 1300 [8]. In our studies, the bands of fan and torsional vibrations are -1307.74 cm-1. The position of the band 1180.44 is more constant. The absorption peak in the area of 698.23 709.80, 798.53cm-1 contains sulfur-containing functional groups -C-S- sulfoxides. Group S-CH2 band ~ 1415.75cm-1 corresponding to the band C-CH2.

Vulcanizates based on regenerate from tires change slightly with aging. This can be judged by the absorption bands at 991.41, 960.55, 910.40 cm-1 (deformation and valence vibrations of C-H bonds in the structures R1CH=CHR2 and R1R2C=CHR3). Since the intensity of the absorption band at 1643.35cm-1 (Fig.1), which is characteristic of valence vibrations of the C-C double bond, increases markedly and therefore at the same time its expansion into the lower frequency range is observed. The intensity of valence vibrations has a strong dependence on the molecular environment. It is obvious that when the polymer chain interacts, the symmetry of the molecule decreases relative to the double bonds, which gives an absorption band of greater intensity [9,10].

Figure 3,4 shows the tire regenerate and the under-rail gasket.

We compared the results of technological and physico-mechanical parameters of rubber compounds and vulcanizates. Comparative analyses of different formulations are given in Tables 1,2 and in Figures 5-16.

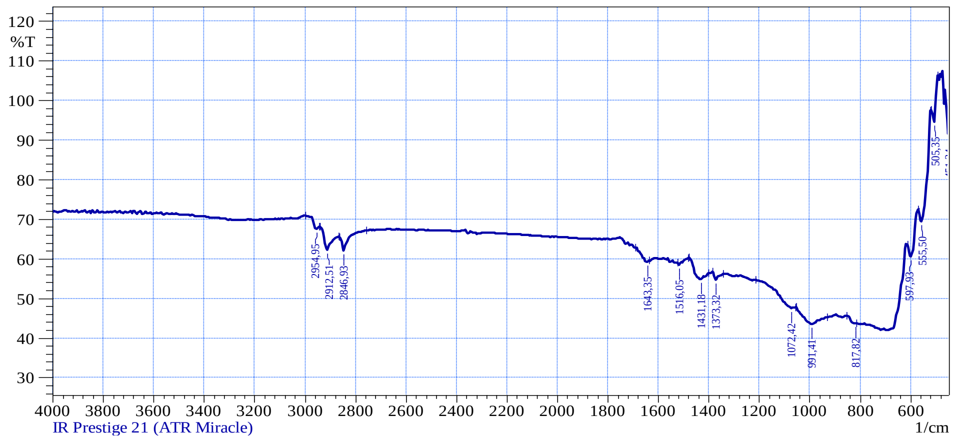

Figure 1 – The spectrogram of the tire regenerate

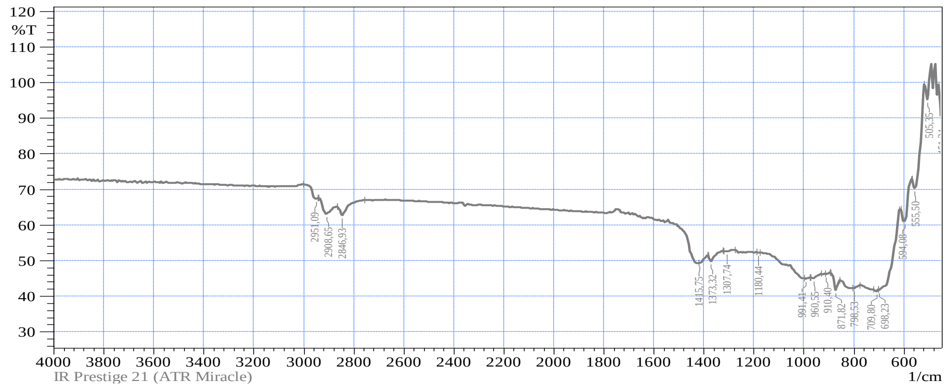

Figure 2 – Spectrogram of the under-rail laying

Figure 3 - Tire regenerate

Figure 4 - Under-rail gasket

Table 1 – Comparative test results of samples with the replacement of carbon black with diatomite and selected clay

Name of indicators	The norm according to GOST R 56291-2014	Sample number						
		The standard	1	2	3	1¹	2¹	3¹
The content of carbon black, m.p.		*10*	*5*	*3*	*0*	*5*	*3*	*0*
The content of diatomite, m.p.		*0*	*5*	*7*	*10*	*0*	*0*	*0*
The content of the selected clay, m.p.		*0*	*0*	*0*	*0*	*5*	*7*	*10*
The change in elongation at break after complex climatic aging in terms of the actual values determined before climatic aging, %	± 30%	-24%	-26%	-27%	-27%	-24%	-24%	-26%

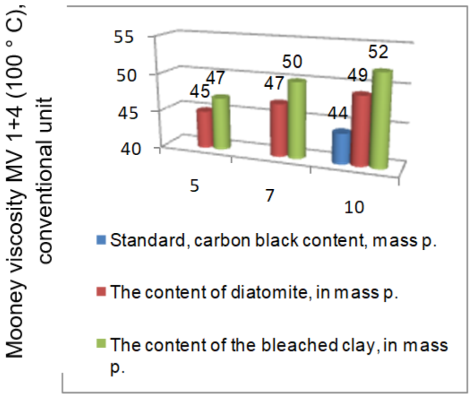

Figure 5 – Diagram of the dependence of the viscosity of the rubber compound for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

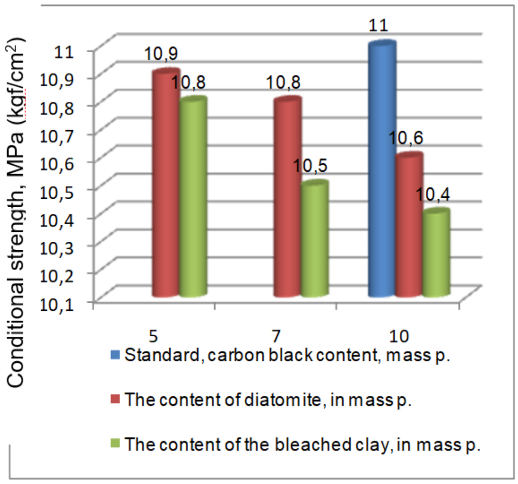

Figure 6 – Diagram of the dependence of the conditional strength of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

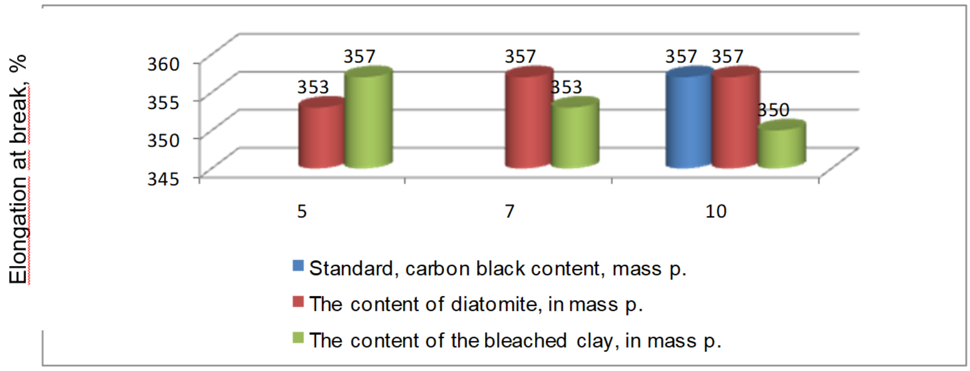

Figure 7 – Diagram of the dependence of the elongation at rupture of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

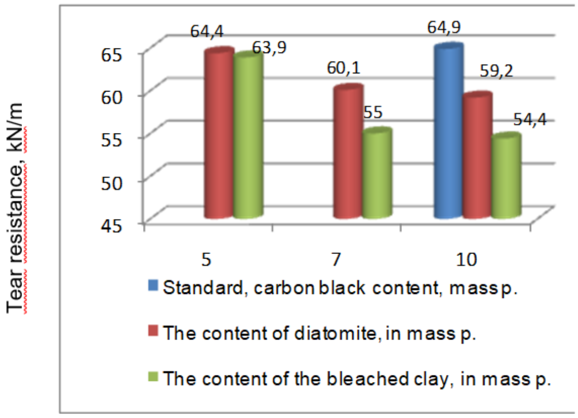

Figure 8 – Diagram of the dependence of the tear resistance of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

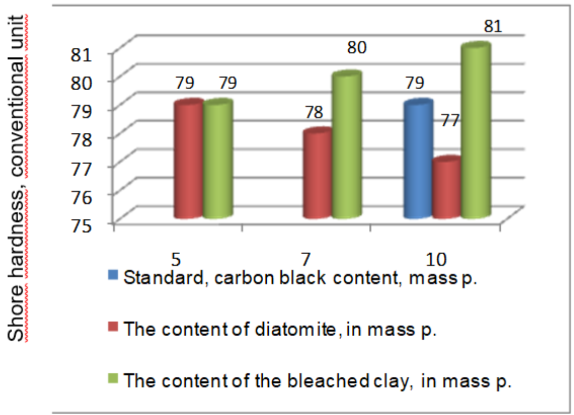

Figure 9 – Diagram of the dependence of the Shore hardness of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

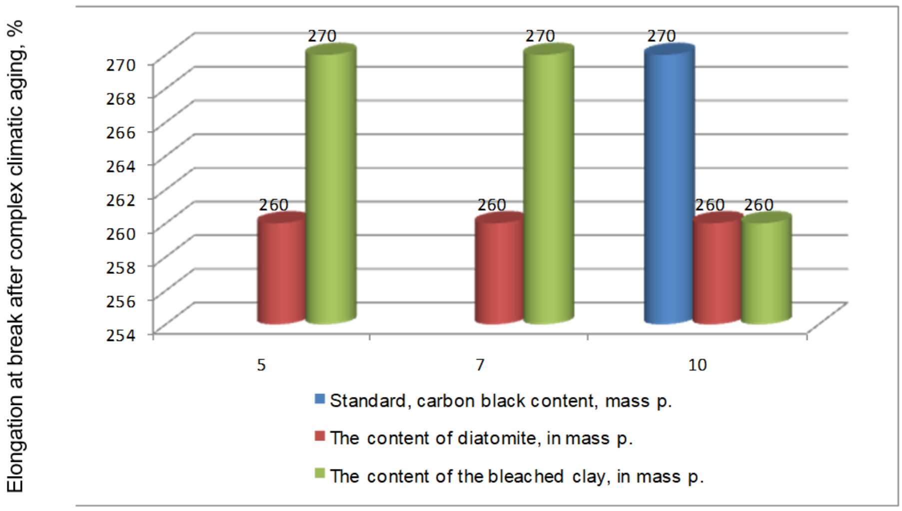

Figure 10 – Diagram of the dependence of the elongation at break after complex climatic aging of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

Table 2 – Comparative test results of samples with replacement of diatomite and bleached clay with stearic acid

Name of indicators	Standard	Sample number						
		The standard	4	5	6	4^1	5^1	6^1
The content of stearic acid, in mass parts		0,6						
The content of Diatomite, in mass parts			0,3	0,6	0,9			
Content of Bleached clay, mass parts						0,3	0,6	0,9
Change in conditional strength after thermal aging in air at a temperature of 90 ° C for 72 hours, %, not less	minus 25%	-20,9	-21,5	-21,8	-20,9	-21,8	-20,9	-21,2
Change in elongation at break after thermal aging in air at a temperature of 90 ° C for 72 hours, %, not less	minus 30%	-20,9	-21,5	-21,2	-21,4	-21,2	-21,4	-21,0

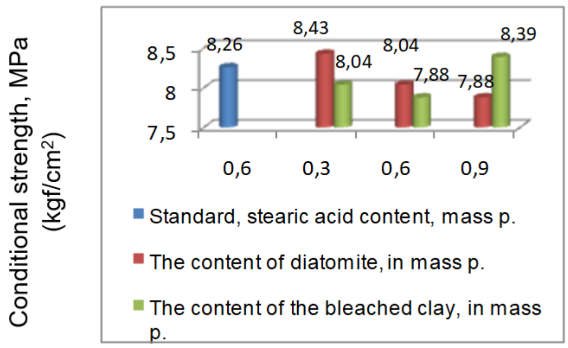

Figure 11 – Diagram of the dependence of the conditional strength of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

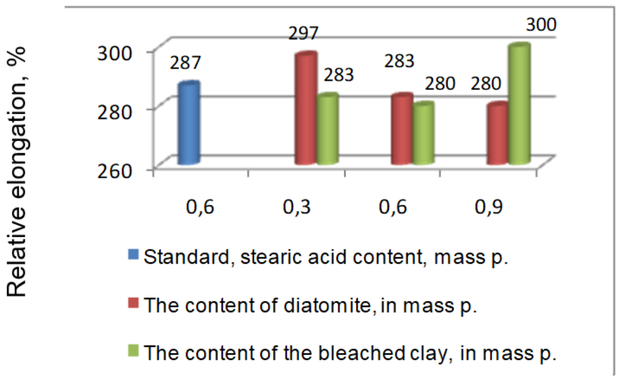

Figure 12 – Diagram of the dependence of the relative elongation of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

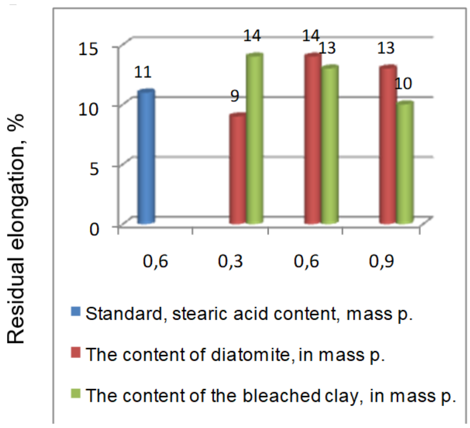

Figure 13 – Diagram of the dependence of the residual elongation of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

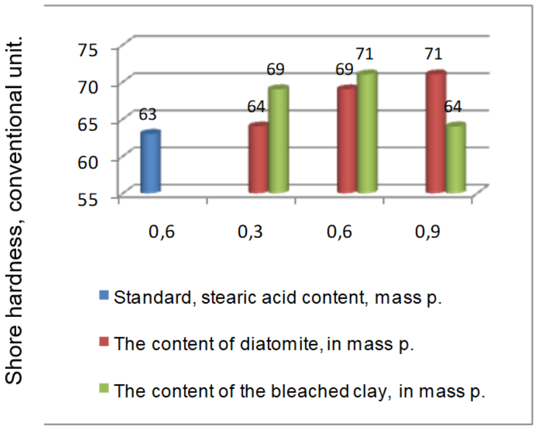

Figure 14 – Diagram of the dependence of the Shore hardness of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

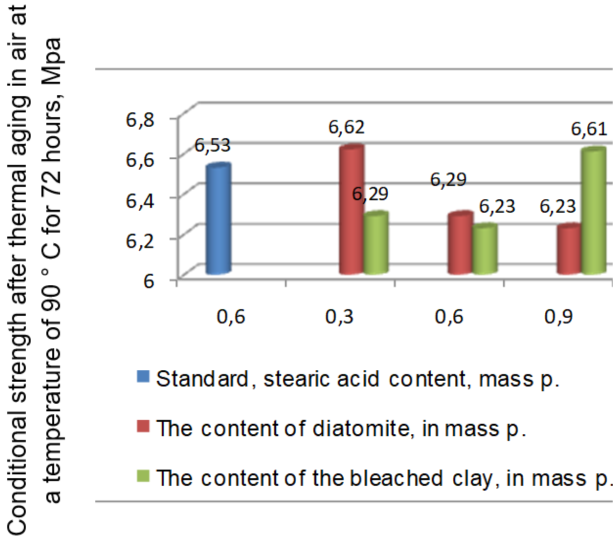

Figure 15 – Diagram of the dependence of the conditional strength of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

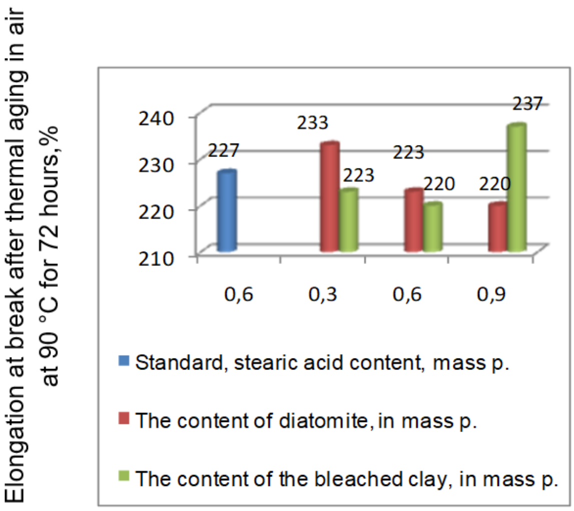

Figure 16 – Diagram of the dependence of the elongation at rupture of rubber for the manufacture of a sub-rail gasket on the content of diatomite and bleached clay

For the first time, the possibility of replacing carbon black and stearic acid with waste from the fat and oil industry (diatomite, bleached clay) was investigated. As can be seen from the analysis of the diagrams, the Mooney viscosity value for a rubber compound containing carbon black is 44.0 conv.units, and for the studied rubber mixtures containing selected clay, is in the range of 47-52 cont.units, and containing diatomite is in the range of 45-49 conv.units (Figure 5). The value of the conditional strength for vulcanizates containing carbon black is 11.0 MPa, and for the studied vulcanizates containing selected clay, it is in the range of 10.4-10.8 MPa, for rubbers containing diatomite it is in the range of 10.6-10.9 MPa (Figure 6). The elongation at break for the studied vulcanizates containing chipped clay increases from 350% to 357%, for vulcanizates containing diatomite from 353% to 357% compared with the reference rubber compound equal to 357% (Figure 7). The tear resistance of the reference rubber is 64.9kN/m, for those containing chipped clay it increases from 54.4 to 63.99kN/m, for those containing diatomite it increases from 59.2 to 64.4 kN/m (Figure 8).

A hardness according Shore is found for the studied rubbers containing selected clay in the range of 79-81 conv.units, for that containing diatomite is 77-79 conv.units, and for the reference rubber is 79 conv.units (Figure 9). The rubber compound for the overhead rail gaskets is prepared based on the resulting regenerate. Due to the addition of 10 m.p. of rubber and 10 m.p. of carbon black (standard), the performance of rubbers is significantly higher than that of the control from pure regenerate. The possibility of replacing carbon black with selected clay, as well as diatomite, was investigated.

The conducted studies show that the conditional strength and tear resistance (Figure 6, 8) decrease when carbon black is replaced with chipped clay, as well as diatomite, but the indicators remain within the permissible limits for this rubber. The main role in enhancing the regenerate is played by rubber.

The value of the conditional tensile strength for vulcanizates containing stearic acid is 8.26 MPa, and for the studied vulcanizates containing chipped clay is in the range of 7.88-8.39 MPa, for those containing diatomite is 7.88-8.43 MPa (Figure 11). The elongation at break for the studied vulcanizates containing selected clay increases from 280% to 300%, for those containing diatomite from 280 to 297% (Figure 12). A hardness according Shore is found for the studied ones containing selected clay and diatomite in the range of 64-71 conv.units, for the reference rubber is 63 conv.units (Figure 14), which corresponds to the indicators of the control norm. The effect of carbon black and stearic acid is less noticeable, so it can be replaced with less active, but cheaper and environmentally friendly ingredients.

According to Table 1, 2 and Figures 5-16, it can be said that the conducted studies show that the indicators remain within the permissible limits for this rubber. Therefore, carbon black and stearic acid can be replaced with less active, but cheaper and environmentally friendly ingredients.

Conclusion. Extended physic-mechanical tests of experimental rubbers led to the conclusion that is most expedient to use waste from the fat-and-oil industry in the formulation of rubber mixtures for the manufacture of under-rail laying of railway tracks, since when using waste from the fat-and-oil industry, the properties of rubbers practically do not change, and comply with control standards.

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МАЙ ӨНЕРКӘСІБІНІҢ ҚАЛДЫҚТАРЫ БАР ВУЛКАНИЗАТТАРДЫҢ ФИЗИКА-МЕХАНИКАЛЫҚ ҚАСИЕТТЕРІ

Техникалық көміртегі мен стеарин қышқылын май өнеркәсібінің қалдықтарымен (диатомит, ағартқыш саз) ауыстыру мүмкіндігі алғаш рет зерттелуде. Құрамында стеарин қышқылы бар вулканизаттар үшін шартты созылу беріктігінің мәні 8,26 МПа, ал құрамында ағартқыш саз бар зерттелетін вулканизаттар үшін 7,88-8,39 МПа, құрамында диатомит бар 7,88-8,43 МПа. Құрамында ағартқыш саз бар зерттелетін вулканизаттар үшін үзілудің салыстырмалы ұзаруы 280%-дан 300%-ға дейін, құрамында диатомит 280%-дан 297%-ға дейін артады. Ағартқыш саз және диатомиті бар зерттеушілерге арналған резина үшін шора А бойынша қаттылығы 64-71 ш.б. аралығында, эталонды резина үшін 63 ш.б.

Зерттеулер көрсеткендей, техникалық көміртекті ағартқыш сазға, сондай-ақ диатомитке ауыстырған кезде шартты беріктік пен сынуға төзімділік төмендейді, бірақ көрсеткіштер берілген резина үшін рұқсат етілген шектерде қалады. Регенератты күшейтуде басты рөлді резина атқарады. Сондықтан көміртегі мен стеарин қышқылын аз белсенді, бірақ арзан және экологиялық таза ингредиенттермен алмастыруға болады. Тәжірибелі резиналардың кеңейтілген физика-механикалық сынақтары темір жолдардың рельс асты төсемін жасау үшін резина қоспаларының рецептінде май өнеркәсібінің қалдықтарын пайдаланудың ең үлкен орындылығы туралы қорытындыға әкелді, өйткені май өнеркәсібінің қалдықтарын пайдаланған кезде резиналардың қасиеттерінің көрсеткіштері іс жүзінде өзгермейді, бақылау нормаларына сәйкес келеді.

Түйін сөздер: *өсімдік майы өндірісінің қалдықтары, ингредиенттер, регенерат, ағартқыш саз, диатомит, рельс астындағы төсем.*

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ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА ВУЛКАНИЗАТОВ, СОДЕРЖАЩИХ ОТХОДЫ МАСЛОЖИРОВОЙ ПРОМЫШЛЕННОСТИ

Впервые исследуется возможность замены технического углерода и стеариновой кислоты на отходы масложировой промышленности (диатомит, отбельная глина). Значение условной прочности при растяжении для вулканизатов, содержащих стеариновую кислоту равна 8,26 МПа, а для исследуемых вулканизатов, содержащих отбельную глину, находится в интервале 7,88-8,39МПа, для содержащих диатомит 7,88-8,43 МПа. Относительное удлинение при разрыве для исследуемых вулканизатов, содержащих отбельную глину возрастает с 280 % до 300%, для содержащих диатомит с 280 до 297%. Твердость по ШоруА находится для исследуемых, содержащих отбельную глину и диатомит в интервале 64-71 усл. ед., для эталонной резины 63 усл. ед.

Проведенные исследования показывают, что условная прочность и сопротивление раздиру снижаются при замене технического углерода на отбельную глину, а также на диатомит, но показатели остаются в пределе допустимых для данной резины. Основную роль в усилении регенерата играет каучук. Поэтому технический углерод и стеариновую кислоту можно заменить на менее активные, но более дешевые и экологически чистые ингредиенты. Расширенные физико-механические испытания опытных резин привели к выводу о наибольшей целесообразности использования отходов масложировой промышленности в рецептуре резиновых смесей для изготовления подрельсовой прокладки железнодорожных путей, так как при использовании отходов масложировой промышленности показатели свойств резин практически не изменяются, соответствует нормам контроля.

Ключевые слова: *отход производства растительного масла, ингредиенты, регенерат, отбельная глина, диатомит, подрельсовая прокладка.*

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