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G. Z. Turebekova[1], Sh. K. Shapalov [2], G. A. Takibayeva[2], A. Zh. Dayrabayeva[2], Zh. S. Sihinbayeva[2], S. Meziani[3], P. M. Zharylkasyn[2], M. Zh. Makhambetov [4]

[1]South Kazakhstan state pedagogical university, Shymkent, Kazakhstan,
[2] M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan,
[3]University de Lorraine, Nancy, France,
[4]Kh. Dosmuhamedov Atyrau state university, Atyrau, Kazakhstan.
E-mail: g.ture@mail.ru

APPLICATIONS OF SULPHUR OBTAINED WHEN OIL PRODUCTION IN THE COMPOUNDING OF RUBBER MIXES

Abstract. The results of research on the possibility of using by-product of oil production – sulfur vulcanizing system are given in work for production of technical rubbers.

Results of experiments on the possibility of using the purified polymeric sulfur are presented. It is shown that polymeric sulfur allows reducing amount of sulfur in a mix compounding, without reducing at the same time curing speed that leads, eventually, to improvement of quality of rubbers. Application of polymeric sulfur also gives a possibility of regulation the elastic properties of the received rubber mixes.

Sulfur polymeric was entered into rubber mixes for partial or full replacement of usual sulfur. Physical and mechanical properties and recipes tire-tread and the belt of rubber mixes are given. Substantial increase of the strong properties characterized by conditional durability at stretching and communication durability between rubber and a textile cord of belt rubber is revealed.

Results of researches have shown that use of Tengiz sulfur led to increase of strength properties by the belt and tire-tread rubbers due to increase of number of intermolecular communications in an elastomeric matrix, so all sulfur used in a compounding, enters chemical reaction.

Keywords: sulfur, oil production products, tire rubbers, rubber mix, vulcanized rubber, the vulcanizing agent, the vulcanizing system.

Introduction. In size of the established stocks, geological and thermobaric conditions of a bedding of the oil-bearing horizons and technical and economic features of development, Tengiz is unique not only among fields of Kazakhstan, but also the world. In 1998 "Tengizshevroil" (TShO) has conducted three-dimensional seismic researches then explored reserves of oil have been estimated by the enterprise at 1.3 billion t. The productive horizons of the field Tengiz lie at a depth over 5000 m, this oil-bearing collector occupies a site 19.3 km wide and 21 km long. Features of the field: the high intra reservoir pressure and high concentration of hydrogen sulfide – require the solution of the most difficult technical and technological tasks, and also environmental problems of utilization of sulfur [1].

In the processes of purification of crude oil of TShO hydrogen sulfide makes elementary sulfur which is the result of processing of the "sour" oil and gas designating content of hydrogen sulfide in them in Tengiz. It should be noted that Tengiz oil is paraffinic, easy, it makes density of 789-851 kg/m^3, the content of sulfur – from 0.5 to 0.8%. Commodity brands are gray: scaly, granulated and lump.

From year to year artificial "mountains" of sulfuric massifs turn out, about 69 kg are gray on 1 ton of the extracted oil. Use of this sulfur in the production technology of rubber mixes is represented perspective for a number of reasons. Massifs of sulfur are located in the sanitary protection zone of Tengiz gas-processing plant, a gas-polluted zone which is under the influence of the departing torch gases containing carbon, hydrogen various metals and many other things. Thus, use of the sulfur received on this field is a

topical problem from the point of view of its processing for the purpose of receiving high-quality rubber mixes for the tire industry [2].

A lot of elementary sulfur is consumed by rubber industry – for curing of rubbers. Sulfur entering into the vulcanizing group provides curing, i.e. transformation of plastic and viscoelastic rubber mix into highly elastic rubber as a result of formation of a uniform spatial grid with atoms of the sulfur connecting chemical bonds separate macromolecules of rubber [3].

Materials and methonds. Sulfur is the main agent of curing for the majority of rubber products, including buses. Special requirements which first of all treat a high level of purity of a product (minimum content of harmful impurity – metals of variable valence) and a high level of dispersibility are imposed to its quality and chemical composition. These characteristics define the vulcanizing activity of sulfur, its dispersancy in rubber, technological and technical properties of rubber mixes and rubbers. Constantly increasing quality requirements of car tires cause the need of creation of effective components of rubber mixes. Especially much attention is paid to development of the vulcanizing agents. Still in the early eighties of the last century there was polymeric sulfur which quickly began to be applied at the entities issuing tires and rubber products [4].

In this work we have conducted researches and results of experiments whenever possible of use of the purified polymeric sulfur are presented. Polymeric sulfur allows to reduce amount of sulfur in a compounding of rubber mixes, without reducing at the same time curing speed that brings, as a result to improvement of quality of rubbers. Use of polymeric sulfur are allows to regulate elastic properties of the received rubbers also.

Sulfur polymeric was entered into rubber mixes for partial or full replacement of usual sulfur.

Recipes belt and tread rubber compositions are shown in Table 1.

Table 1 – Recipes of rubber mixes

Name	Mass. n .to 100 mass. n. of rubber	
	Tread compound	The belt mixture
SKI-3	50	100
SKD	50	–
Sulfur	1,8-0	1,6-0
Sulphur polymer	0-1,5	0-1,3
sulfenamide M	1,5	1,4
Phthalic anhydride	0,3	0,3
Whitewash zinc	3,0	2,5
Stearic acid	2,0	2,0
Atsetonanil P	1,0	1,2
Oktofor NN	2,0	2,0
hydrocarbon resins	4,0	4,0
Wax CAR	1,0	–
Oil PN-6SH	4,0	4,0
Diaphene OP	1,5	1,5
Carbon P 245	55,0	50,0

Polymeric sulfur was entered on laboratory rollers at the end of mixture, at the second stage, for prevention of premature curing. The made experiments have shown that technology of mixture, processing of rubber mixes and curing practically does not differ from the standard mode applied in usual practice. Curing of samples was carried out at a temperature of 155^0C within 15 minutes. Test of samples for aging was carried out in the autoclave at a temperature of 3930K in the environment of saturated water vapor with a pressure of 0,2 MPas within 40 hours, and also in similar conditions at a constant irrigation by 5% water solution of chloride of sodium within 8 hours.

The received results show that use of the polymeric sulfur received at oil production on the field Tengiz allows to improve physical and mechanical properties of tire rubbers: tension when lengthening; conditional durability at stretching; relative to lengthening at a gap; an abradability and hardness by Shors.

Table 2 – Physical and mechanical properties of tire-tread rubbers

Indicators	Content of polymeric sulfur mass. n .to 100 mass. n. of rubber			
	Standard	0,5	1,0	1,5
Tension during the lengthening at 300% e MPa	8,9	8,9	8,7	8,5
Conditional tensile strength, MPa	19,8	19,9	20,8	21,2
Relative elongation at break%	650	650	644	645
Tear resistance kN/m	71	72	68	75
Resistance to repeated stretching at an elongation of 200%, thousand cycles	3,01	3,05	5,6	4,8
Abrasion, kJ/m^3	48	48	45,7	44,5
Shore hardness, standard units	53	53	53	55

Table 3 – Physical and mechanical properties of the belt rubber

Indicators	Content of polymeric sulfur mass. n .to 100 mass. n. of rubber				
	Standard	0,3	0,6	1,0	1,3
Tension during the lengthening at 300% e MPa	10,1	9,7	9,8	10,2	10,0
Conditional tensile strength, MPa	21,1	20,2	20,6	21,3	21,0
Relative elongation at break%	525	520	521	525	525
Tear resistance kN/m	63	60	60	64	62
Resistance to repeated stretching at an elongation of 200%, thousand cycles	6,1	5,2	5,5	6,2	5,6
Communication durability by the N-method, N	443	430	431	443	440

This technology allows resolving a complex of issues, including problems of utilization of the by-products which are formed in case of production of sulphurous oil.

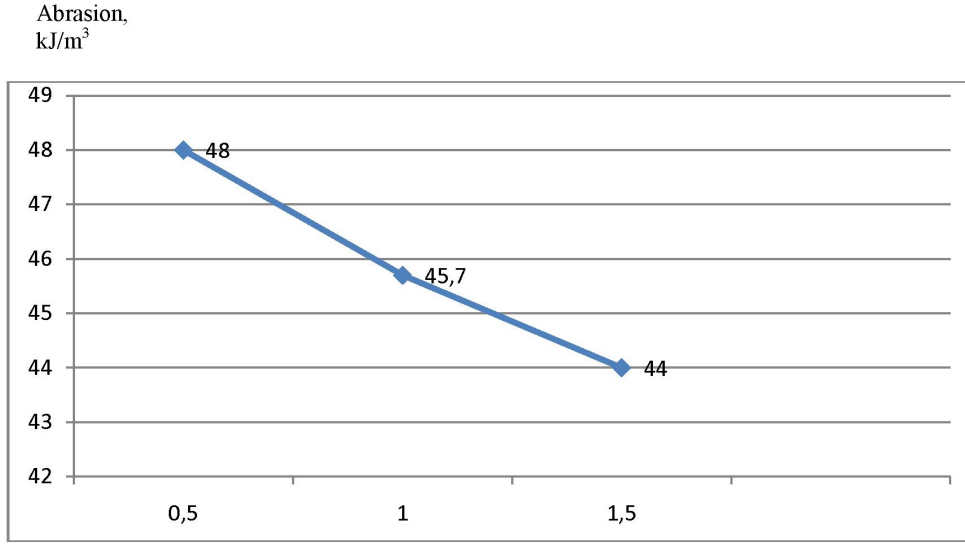

Figure 1 – Influence of sulfur content on the physical and chemical properties of the tread rubber

As shown in Figure 1 when using Tengiz purified sulfur, increase in conventional tensile strength and reduced abrasion of tread rubber that demonstrates improved strength properties is observed.

From the experimental data given in Figure 2 at addition of polymeric sulfur in a compounding of mix substantial increase of the strong properties characterized by conditional durability at stretching and communication durability between rubber and a textile cord of belt rubber is observed.

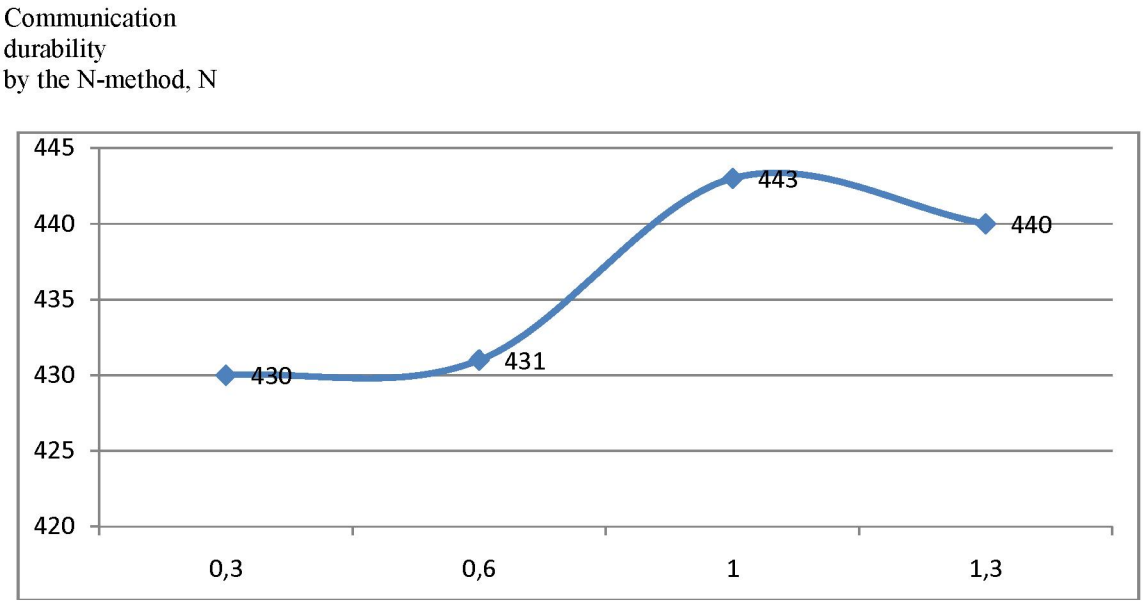

Figure 2 – Influence of sulfur content on the physical and chemical properties of the belt rubber

Conclusion. Thus, results of researches have shown that use of polymeric sulfur led to increase of strength properties by the belt and tire-tread rubbers due to increase of number of intermolecular communications in an elastic matrix as all sulfur used in a compounding of rubber mix reacts that in general improves physical and mechanical properties and quality of tire rubbers.

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Г. З. Туребекова[1], Ш. К. Шапалов[2], Г. А. Такибаева[2], А. Ж. Дайрабаева[2], Ж. С. Сыхинбаева[2], С. Мезиани[3], П. М. Жарылкасын[2], М. Ж. Махамбетов[4]

[1]Оңтүстік Қазақстан мемлекеттік педагогикалық институті, Шымкент, Қазақстан,
[2]М. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан
[3]Университе де Лоррейн, Нанси, Франция,
[4]Х. Досмухамедов атындағы Атырау мемлекеттік университеті, Казахстан

РЕЗИНА ҚОСПАЛАРДА МҰНАЙ ӨНЕРКӘСІБІНДЕ АЛЫНҒАН КҮКІРТПЕН ҚОЛДАНУ ЖОЛДАРЫ

Аннотация. Осы жұмыста мұнай өндеу өнеркәсібінде алынған - күкірттің- вулкандық жүйе үшін техникалық резеңке өндірісінде игеру мүмкіншілігін зерттеу нәтижелері келтірілген. Мұнайлы Солтүстік - Каспий аймағында, Қазақстан шетел компанияларымен бірге бірнеше перспективалық және ауқымды жобаларды жүзеге асырады. Тенгиз және аталмыш аймақтың басқа кен орындарының шикі мұнайы жоғары күкіртті болып табылады, яғни осындағы мұнайдың маңызды өзгешелігі ілеспе газда күкіртті сутектің зор мөлшері бар болып табылады. Шикі мұнайды тауар калпына келтіру үшін, ол тазаланады және нәтижеде элементарлық күкірт пайда болады. Мұнайды шығарудың артуымен күкірттің жинақталуы да өседі. Қазақстандық мұнайдан шығатын элементарлық күкірт - химиялық өнеркәсіптің индустриялық кәсіпорындары үшін құнды шикізат болып табылады. Алайда шынайы ақиқатқа сүйенер болсақ осы химиялық заттың негізгі көлемі әлі мұнай шығару нысандарының жанында тапталып тасталады. Күкірт, шиналық резеңке бұйымының көпшілігі үшін вулканизацияның негізгі агенті болып табылады. Оның сапасы мен химиялық құрамына айрықша талап көрсетіледі, оның ішінде ең маңыздысы шикізаттың адалдығының (зарарлы қоспаның, айнымалы валенттіктің, металдардың ең төмен мөлшері) және дисперсиялық биік дәрежесі жатады. Осы мінездемелер күкірттің вулканизациялық белсенділігін, оның каучукта дисперсиялануы, резеңке қоспаның және резеңкелердің технологиялық және техникалық қасиеттерін анықтайды. Полимерлік күкірт рецептурадағы вулканизацияның жылдамдығын төмендетпей күкірттің санын төмендетуге мүмкіндік береді, ақыр соңында протекторлы және брекерлы резеңке сапасының көтерілуіне алып келеді. Полимерлік күкірттің қолданысы, өндіріліп алынатын резеңкелердің икемділік қасиеттерін реттеуге мүмкіндік береді. Мұнай өнеркәсібінде шығатын күкірттің қолданатын кезінде дөңгелек резеңкелерінің физикалық-механикалық касиеттерін жақсартады.

Түйін сөздер: күкірт, полимерлі күкірт, өнеркәсібінде алынған заттар, шиналық, резеңке, резеңке қоспалар, вулканизаттар, вулканизациялау агенті, вулкандау жүйесі, протекторлық резеңке қоспалар, брекерлық резеңке қоспалар.

Г. З. Туребекова[1], Ш. К. Шапалов[2], Г. А. Такибаева[2], А. Ж. Дайрабаева[2], Ж. С. Сихынбаева[2], С. Мезиани[3], П. М. Жарылкасын[2], М. Ж. Махамбетов[4]

[1]Южно-Казахстанский государственный педагогический институт, Шымкент, Казахстан,
[2]Южно-Казахстанский государственный университет им. М. Ауэзова, Шымкент, Казахстан,
[3]Университет де Лоррейн, Нанси, Франция,
[4]Атырауский государственный университет им. Х. Досмухамедодова, Казахстан

ВОЗМОЖНОСТИ ПРИМЕНЕНИЯ СЕРЫ, ПОЛУЧАЕМОЙ ПРИ НЕФТЕДОБЫЧЕ В РЕЦЕПТУРАХ РЕЗИНОВЫХ СМЕСЕЙ

Аннотация. В работе приведены результаты исследований по возможности использования побочного продукта нефтедобычи – серы для вулканизующей системы при производстве технических резин. Представлены результаты экспериментов по возможности применения полимерной серы, синтезированной из тенгизской серы. Показано, что полимерная сера позволяет снизить количество серы в рецептуре смеси, не снижая при этом скорость вулканизации, что приводит, в конечном счете, к повышению качества резин. Применение полимерной серы позволяет также возможность регулирования эластических свойств получаемых резиновых смесей.

В резиновые смеси сера полимерная вводилась для частичной или полной замены обычной технической серы. Приведены физико-механические свойства и рецепты протекторных и брекерных резиновых смесей. Выявлено значительное повышение прочных свойств, характеризуемых условной прочностью при растяжении и прочностью связи между резиной и текстильным кордом брекерной резины.

Результаты исследований показали, что применение тенгизкой полимерной серы приводит к повышению прочностных свойств брекерных и протекторных резин за счет повышения количества межмолекулярных связей в эластмерной матрице, так как вся используемая в рецептуре сера вступает в химическую реакцию с макромолекулами каучука, образуя равномерную сетчатую структуру.

Ключевые слова: сера, полимерная сера, продукты нефтедобычи, шинные резины, резиновая смесь, вулканизат, вулканизующий агент, вулканизующая система, брекерная резиновая смесь, протекторная резиновая смесь.