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RECYCLING OF WASTES OF PETROLEUM REFINING INDUSTRY BY USING THEM IN THE MANUFACTURE OF TIRE RUBBERS

Abstract: The important scientific direction of petrochemistry is manufacture of plasticizers, softeners, vulcanizing agents, fillers on the basis of industrial wastes.This allows expand the raw-material base, use heavy stocks of refinery wastes, reduce technogenic influence on the environmentand solve the problem of manufacture of import-substituting softeners for the rubber-processing industry of Kazakhstan. The feature of Kazakhstan petroleum is high concentration of sulfur compounds, in consequence of which much sulfuric wastes are formed, which are environmentally hazardous in open storage. Optimization of a receipt for developed rubber compounds for manufacture of a filler strip for passenger car tire beads was carried out in our work by serial analysis of influence of content of each of the components separately (sulfur and oil sludge) at the fixed amount of other ingredients on the rubber properties. In order to identify optimal amount of organic share of the oil sludge in the content of rubber compounds, rubber compounds with different content of organic share of the oil sludge were gained. Plasticizers and softeners were substituted to the organic share of the oil sludge. Also polymeric and colloidal sulfur mixture of Tengiz field was used as a vulcanizing agent in the receipts of rubber compounds. The results of comprehensive tests showed replaceability of traditionally used in the rubber compounds softeners to the organic share of the oil sludge and use of Tengiz sulfur as a vulcanizing agent.

Key words:organicshareofoilsludge, oilsludge, softeners, vulcanizingagent, Tengizsulfur, vulcanizing system, rubber compound, filler strip, bead.

Introduction

The rubber industry in Kazakhstan has very limited assortment of ingredients for rubber compounds. The important scientific direction of petrochemistry is manufacture of plasticizers, softeners, vulcanizing agents, fillers on the basis of industrial wastes. This allows expand the raw-material base, use heavy stocks of refinery wastes, reduce anthropogenic stress on the environment and solve the problem of manufacture of import-substituting softeners and vulcanizing agents for the rubber-processing industry of Kazakhstan. The feature of Kazakhstan petroleum is high concentration of sulfur compounds, in consequence of which much sulfuric wastes are formed [3-6].

Vulcanization plays an important role on rubber industry by offering the rubber products containing three-dimensional net work of rubber molecules. By this mean, the significant improvement innumerous properties including tensile and tear properties, set, resilience and abrasion of rubber vulcanizates is resulted. The vulcanization could generally be divided into 3 main systems, i.e., sulfur, peroxide, and metal oxide systems. The sulfur vulcanization system is generally preferential because of its superiority in mechanical properties and ease of cure behavior adjustment [5, 6]. Typically, the sulfur used in rubber industry originates from 2 main resources, i.e., natural resource and petroleum refinery. Basically, the

sulfur from natural resource is more prefer able because of its certain chemical structure in conjunction with its high sulfur content (99 %)[7].

The generally accepted is application of organic and inorganic low-molecular compounds in the receipts of rubber compounds. By theefficacy, polymers and products of low-molecular compounds are divided into softeners and plasticizers. The softeners are low-molecular compounds, which reduce yield temperature and not influence on vitrification temperature of rubber substances. The plasticizers are low-molecular compounds, which reduce vitrification temperature and yield temperature of the rubber substances.The important requirement to the plasticizers and softeners is their low cost. The great significance is also given to the availability of initial raw material used for their manufacture. Different other requirements to the plasticizers and softeners (absence of leachability by water, oils, etc.) are set by specific conditions, in which a manufactured product, containing the plasticizer and softener, will operate.

Experimental part. Sulfur is used in the rubber compounds as the vulcanizing agent, therefore in our work we offer to use refined Tengiz sulfur, gained from the wastes of oil production and refinery wastes, in the vulcanizing system.

Earlier we carried out experiments of the organic share of the oil sludge, gained from the oil sludge of "PetroKazakhstanOilProducts" LLP in the receipts of the rubber compounds on the basis of rubber substances of general assignment as the softeners, with substantiation of traditionally used softeners – oil PN-6SH and softener ASMG. The results of measurement of processing properties established -that the organic share of the oil sludge causes the plasticizing effect [8-11].

Optimization of the rubber compounds receipts. Optimization of the developed rubber compounds for manufacture of a filler strip for passenger car tire beads wascarried out by serial analysis of influence of content of each of the components separately (sulfur and oil sludge) at the fixed amount of other ingredients on the rubber properties.

In order to identify optimal amount of the organic share of the oil sludge in the content of rubber compounds, the rubber compounds with different content of the organic share of the oil sludge were gained. The plasticizers and softeners were substituted to the organic share of the oil sludge. Also polymeric and colloidal sulfur mixture of Tengiz field was used as the vulcanizing agent in the receipts of the rubber compounds.The rubber compounds' receipts used at the manufacture of the chafer strip are given in Table 1.

Fine mineral fraction of the oil sludge (1-5 mcm) was used in the receipt of the rubber compound for rubberizing of thefiller strip for passenger car tire beads.

Table 1 – Receipt of the optimal rubber compound for the rubberizing of thefiller strip for passenger car tire beads

Ingredients	Per 100 mass shares of the rubber substance					
	Control variant	Studied variant				
1	2	3	4	5	6	7
SKI-3	40,0	40,0	40,0	40,0	40,0	40,0
Butyl	60,0	60,0	60,0	60,0	60,0	60,0
Technical sulfur	2,4	-	-	-	-	-
Tengizsulfur	-	1,2	1,6	2,0	2,2	2,4
Sulfonamide "Ts"	1,2	1,2	1,2	1,2	1,2	1,2
Santogard PVI	0,4	0,4	0,4	0,4	0,4	0,4
Zinc oxide	5,0	5,0	5,0	5,0	5,0	5,0
Stearinic commercial acid	2,0	2,0	2,0	2,0	2,0	2,0
Softener ASMG	4,0	4,0	4,0	4,0	4,0	4,0
Organic share of the oil sludge	-	4,0	5,0	6,0	6,5	7,0
Oil PN-6SH	4,0	-	-	-	-	-
Acetone anil R	2,0	2,0	2,0	2,0	2,0	2,0
Diaphene FP	2,0	2,0	2,0	2,0	2,0	2,0
Technical carbon	70,0	60,0	55,0	50,0	45,0	40,0
Mineral share of the oil sludge	-	10,0	15,0	20,0	25,0	30,0

Methods. Vulcanizing features of the rubber compounds, gained on "Monsanto" rheometer, proved the fact that different dosages of the organic share of the oil sludge and sulfur have direct influence on the rubber compounds' vulcanizing kinetics. Addition of the organic share of the oil sludge into the rubber compounds results in reduction of minimal viscosity and stiffness of the elastomeric matrix system. This reduction is directly proportional to the percentage composition of the organic share of the oil sludge.Application of Tengizsulfur allows preserve duration of the plateau effect, hence preventing over-vulcanization of the filler striprubber.

Results and their discussion. Optimal ratio of the components, resulting in reduction of the minimal viscosity and increase in the beginning of vulcanizing, characterizing the best processing properties of the rubber compounds, is observed at 7 and 8 mass shares of the organic share of the oil sludge for the rubber compounds, meant for the filler strip. Analysis of the rubber compounds' vulcanometric curves shows that the optimal time for attaining the vulcanizing of the rubber compound for the rubber compound of the filler strip consists 23 minutes.

Physical-mechanical tests of the experimental rubbers have led to the conclusion about the highest appropriateness of using the organic share of the oil sludge in the receipts of the rubber compounds for the filler strip of the boardside panels, as when substituting traditionally used softeners to the organic share of the oil sludge, the rubber properties meet the rates of inspection. The best results are observed at the dosage of 8-10 mass shares of the organic share of the oil sludge for the rubber compounds, meant for the filler strip. Dependencies of the main physical-mechanical indicators of thevulcanized rubbers of the filler strip on the dosage of the organic share of the oil sludge and Tengizsulfurare given in Table 2.

Table 2 – Properties of the vulcanizates on the basis of rubber substances of general assignment for the filler strip with additives of the organic share of the oil sludge and Tengiz sulfur

Indicators	Inspection rates	1-v	2-v	3-v	4-v	5-v
Nominal tensile strength, kgf/cm^2, at least	92	107	104	109	111	111
Relative tensile elongation, %, at least	270	270	300	310	310	295
Shorehardness, c.u.	70	75	77	77	78	75

Conclusions

Insignificant reduction in the tensile indicators and increase in the elastic properties of the rubbers when increasing the organic share of the oil sludge dosage can be explained by plasticization effect mechanism of the organic share of the oil sludge low-molecular compounds, which permeate between macromoleculesby the same token reducing the rubber substance macromolecules' intermolecular interaction. Insignificantreductioninthestrengthpropertiesofthesidepanelrubbersis not fundamental, as the main strength for the board side panel structure is given by bead rings from a brass plated wire. Application of Tengiz sulfur allowed preserve the vulcanizing kinetics, which could be reduced when using the organic share of the oil sludge.AlsoapplicationofTengiz sulfur allowed increase hardness of the rubbers which is necessary to increase stiffness of the tire bead.

Thus, the results of the comprehensive tests showed the possibility of substitution of traditionally used in the rubber compounds softeners to the organic share of the oil sludge and use of Tengiz sulfur as the vulcanizing agent. The fillers in the receipts of the rubber compounds for formation of the filler strip can be partially substituted to the mineral share of the oil sludge.

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МҰНАЙ ӨНДІРУ МЕН МҰНАЙ ӨҢДЕУ ҚАЛДЫҚТАРЫН ШИНАЛЫҚ РЕЗИНАЛАР ӨНДІРІСІНДЕ ҰТЫМДЫ ПАЙДАЛАНУ МҮМКІНДІГІ

Аннотация.Тенгиз кен орнының мұнайын өндіру және өңдеу кезінде ашық алаңдарда сақталатын күкірттің көп қалдықтары түзіледі. Атмосфераның әсерінен, яғни жоғары температура (жазда 45-50^{0}С дейін) мен басқа да факторлардың әсерінен, адам денсаулығы мен қоршаған ортаға зиянды әсерін тигізетін күкірттің көп қоспалары түзіледі. Жұмыста күкіртті резина қоспасын вулкандаушы аген ретінде қолдану мүмкіндігі көрсетілген.

Компонент құрамының әрқайсысына бөлек (күкірт және мұнай шламы) резина қоспасына әсерін жүйелі түрде зерттеу арқылы, жеңіл шина бортының толықтырғыш бауын дайындау кезінде өңделген резина қоспасына, тіркелген басқа да ингредиенттер санына оңтайландыру жүргізілді.

Тенгиз күкіртін қолдану, ОЧН қолдану кезінде кемуге мүмкіндік беретін вулкандау кинетикасын сақтауға мүмкіндік берді. тенгиз күкіртін қолдану, Сонымен қатар дөңгелектің сыртқы бортының Кермектіктің арттыру үшін қажет резинаның қаттылығын жоғарылатады.

Кеңейтілген сынақтардың нәтижелері, резина қоспасында қолданылатын дәстүрлі жұмсартқыштарды мұнай шламы мен вулкандаушы агент ретінде қолданылатын тенгиз күкірті не алмастыру мүмкіндігін көрсетті

Толықтырғыш бауды дайындауға арналған резина қоспасының рецептіндегі толықтырғыштар мұнайшламының минералды бөлігіне ішінара ауыстырылуы мүмкін.

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

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УТИЛИЗАЦИЯ ОТХОДОВ НЕФТЕПЕРЕРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ ПУТЕМ ИСПОЛЬЗОВАНИЯ ИХ В ПРОИЗВОДСТВЕ ШИННЫХ РЕЗИН.

Аннотация. Важным научным направлением нефтехимии является производство пластификаторов, мягчителей, вулканизующих агентов, наполнителей на основе техногенных отходов. Это позволяет расширить сырьевую базу, использовать большие запасы отходов нефтепереработки, уменьшить техногенное воздействие на окружающую среду и решить проблему производства импортозамещающих мягчителей для резиновой промышленности Казахстана. Особенностью казахстанскихнефтей является повышенной содержание соединений серы, вследствие чего образуется много серных отходов, являющимися экологически опасными при открытом хранении. В нашей работе путем последовательного изучения влияния на свойства резин содержания каждого из компонентов в отдельности (серы и нефтешлама) при фиксированных количествах других ингредиентов была проведена оптимизация рецептур разработанных резиновых смесей для изготовления наполнительного шнура борталегковых шин. С целью выявления оптимального количества органической части нефтешлама(ОЧН) в составе резиновых смесей были получены резиновые смеси с различным содержанием ОЧН. Пластификаторы и мягчители были заменены на ОЧН. Также в рецептурах резиновых смесей в качестве вулканизующего агента была использована смесь

полимерной и коллоидной серы тенгизского месторождения. Результаты расширенных испытаний показали возможность замены традиционно используемых в резиновых смесях мягчителей на органическую часть нефтешлама и использования тенгизской серы в виде вулканизующего агента.

Ключевые слова: органическая часть нефтешлама (ОЧН), нефтешламы, мягчители, вулканизующий агент, тенгизская сера, вулканизующая система, резиновая смесь, наполнительный шнур, борт.

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